

Photocatalytic degradation of pharmaceutical compounds using fixed-bed reactors

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In

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by

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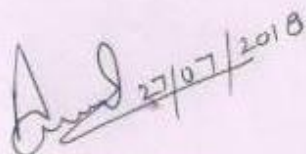
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(Deemed to be University)

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CERTIFICATE

This is to certify that the thesis entitled '**Photocatalytic degradation of pharmaceutical compounds using fixed-bed reactors**' which has been submitted by Ms. Palak Bansal in the partial fulfilment of the requirements for the award of the degree of 'Doctor of Philosophy' in School of Energy and Environment, Thapar Institute of Engineering and Technology, Patiala, India, is a record of the candidate's own independent and original research work carried out by her under my supervision and guidance. The matter embodied in this thesis has not been submitted, in part or full, to any other institute for the award of any degree in other University or Institute.



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DECLARATION

This is to declare that the research work which is being presented in this thesis entitled '**Photocatalytic degradation of pharmaceutical compounds using fixed-bed reactors**' in partial fulfilment of requirement of the degree of 'Doctor of Philosophy' in School of Energy and Environment, Thapar Institute of Engineering and Technology, Patiala, India, is an authentic record of my own research work carried out under the supervision of Dr. Anoop Verma (Associate Professor, School of Energy and Environment, TIET, Patiala, India). Documents, embodied in this thesis, from other researchers' works are duly listed in the reference section.

The matter presented in this thesis has not been submitted, in part or full, to any other institute for the award of any degree.

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ABSTRACT

Pharmaceutical compounds lie within the category of emerging contaminants that have been extensively detected in the aquatic systems over the past few years. Advanced oxidation processes (AOPs) including TiO_2 photocatalysis and photo-Fenton have achieved promising applications in context to the treatment of wastewater containing these types of emerging contaminants. However, each of these techniques possesses few drawbacks (frequent electron-hole recombination, increased treatment time, catalyst separation post-treatment, generation of iron sludge, high dosages of H_2O_2) which have restricted their successful implementation at field-scale.

Thus, best efforts have been devoted in the present study to seek the commercial applications of AOPs by overcoming most of the concerns raised by these individual processes (photocatalysis or photo-Fenton). Attempts were made to integrate these two processes i.e. photocatalysis and photo-Fenton within the same treatment unit for the enhanced degradation of target recalcitrant pharmaceutical compounds i.e. Cephalexin (CEX) and Pentoxifylline (PEN). Most of the individual drawbacks of photocatalysis and photo-Fenton were effectively covered by this dual process (photocatalysis and photo-Fenton) owing to the production of hydroxyl radicals in abundance.

Waste materials like foundry sand (FS) and fly ash (FA) were employed as alternative sources of iron which further defined the economic viability of our process. The systematic approach was followed in the present study to shift the dual process from slurry to fixed-bed mode for the degradation of CEX and PEN. After confirming the prominence of dual effect in slurry mode (**Section 4.6**), FS/FA was entrapped in small pockets made of fine cotton cloth while keeping TiO_2 in suspensions. In the subsequent experiments, TiO_2 was immobilized on clay beads which were used along with FS/FA pockets to bring the treatment unit completely in fixed-mode. Through these studies, significant improvement in the degradation efficiency of each compound was obtained in case of in-situ dual process resulting into the significant reduction in treatment time to almost half. Though, reasonably good amount of degradation was achieved even in fixed-bed studies incorporating dual effect, durability of the catalyst support always remains a concern. In either case, recyclability of fine cotton cloth pockets

(entrapment material for iron source) was not up to the mark as they were recycled for only 8 times with significant reduction in the degradation efficiency of PEN (**Section 4.7.1**).

Trials were executed to further improve the practicability of dual process by enhancing the durability and efficiency of support materials. Efforts were made to incorporate FS along with clay in order to prepare different supports for catalyst immobilization (**Section 4.7.2**). The support materials of different shapes (hollow circular discs, rectangular slabs and spherical beads) were prepared from clay and waste FS for TiO₂ immobilization. Now both catalysts i.e. iron and TiO₂ required for the dual effect study were incorporated within the same support material. Among these varying shaped catalyst immobilized supports, spherical beads depicted the best results in terms of degradation efficiency of CEX (80%) as well as catalyst recyclability (10 cycles). However, degradation efficiency continued to decrease with subsequent recycling tests. Actually, addition of FS along with clay reduced the binding efficiency of support.

In the subsequent trials, the spherical beads were modified by adding FA along with FS in conjunction with clay (**Section 4.7.6**). Addition of FA provided sufficient compressive strength to the beads. These TiO₂ immobilized beads containing FS and FA were optimized for the present study and were named as Fe-TiO₂ composite beads. These Fe-TiO₂ composite beads were used for carrying out the proper optimization of in-situ dual process for the degradation of CEX and PEN. The effect of several operating parameters including size of composite beads, catalyst dose, oxidant concentration, calcinations temperature and number of TiO₂ coatings on the degradation efficiency of process was studied using Fe-TiO₂ composite beads. This in-situ dual process using Fe-TiO₂ composite beads revealed 93% degradation of CEX after 210 min and 85% degradation of PEN after 120 min of natural solar irradiations. The treatment time was reduced to less than half in case of in-situ dual process as compared to that of individual processes for the degradation of CEX and PEN. There was almost two to three fold increase in the value of rate constant, 'k' in case of in-situ dual process as compared to individual processes for the degradation of each compound. Moreover, overall synergy of in-situ dual process over individual processes was found to be more than 20% in case of both compounds. Fe-TiO₂ composite beads were recycled for maximum number of times (> 45 recycles) as discussed in **Section 4.7.9**. The recyclability efficiency of composite beads was counter confirmed through different characterization techniques like SEM/EDS, XRD and DRS.

The complete mineralization studies of each compound (CEX and PEN) were also conducted in terms of reduction in COD and TOC along with the generation of various anions like nitrite, nitrate and sulfate ions (**Section 4.7.11**). The intermediates formed during the degradation process of each compound were carefully identified through GC-MS analysis based on which degradation pathways were proposed in each case. Finally, the quality of the treated water in case of CEX and PEN was checked in terms of cyto-toxicity and acute toxicity analysis (**Section 4.7.12**).

The photo-response efficiency of in-situ dual process using Fe-TiO₂ composite beads was further enhanced by modifying the composite beads by replacing TiO₂-P25 with doped TiO₂. The coating of TiO₂-P25 over the surface of beads was replaced with Ag-TiO₂, N-TiO₂ and N-Ag-TiO₂ (**Section 4.8** and **Section 4.9**). These modified catalysts were first comprehensively characterized through various techniques like SEM/EDS, XRD, DRS, FTIR, XPS, TGA and Raman spectroscopy before immobilizing them on the surface of beads. While after doped catalyst immobilization, the presence of iron along with catalysts and dopants was confirmed through SEM/EDS, XRD and DRS analysis. The in-situ dual process in conjunction with modified catalysts further enhanced the degradation efficiency of process resulting into the significant reduction in treatment time. The complete mechanism for this modified in-situ dual process using doped catalysts was also proposed for the degradation of pollutants.

Scale-up studies were also conducted for the degradation of CEX and PEN through in-situ dual process using Fe-TiO₂ composite beads (**Section 4.10** and **Section 4.11**). Pilot-scale solar reactors like re-circulation type fixed-bed glass reactor and once-through fixed-bed cascade reactor incorporating in-situ dual effect were fabricated and comprehensively optimized for the degradation of target pollutants (CEX and PEN). The Fe-TiO₂ composite beads demonstrated extended recyclability efficiency (> 70 cycles) even under flow conditions thus, highlighting the practical feasibility of in-situ dual process. The detailed cost of treatment process using these pilot-scale reactors was evaluated in each case to envisage the economic viability of technique.

Finally, real effluent from a pharmaceutical industry was treated successfully through in-situ dual process using highly durable and inexpensive composite beads further highlights the field-scale applications of presented technique (**Section 4.12**). The process was optimized using Response surface methodology (RSM) based Box-Behnken design (BBD) model. An

almost 80% reduction in COD was achieved when the effluent was treated under solar irradiations at pilot-scale in a once-through cascade reactor at optimized conditions using Fe-TiO₂ composite beads. The treated wastewater was completely non-toxic as confirmed through cyto-toxicity and acute toxicity analysis.

To the best of our knowledge, this is the first reported study dealing with fixed-bed in-situ dual process using waste materials along with successful scale-up trails for the treatment of pharmaceutical wastewater.

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Chapter 1

INTRODUCTION

1.1 Fate of pharmaceuticals in environment

During the recent years, developing countries like India has emerged as one of the fastest progressing economies in the world (Rehman et al., 2015). Although India has made a remarkable progress during these years, half of its population still lacks ingress to the basic requirements of life owing to the prevalence of poverty in many parts of the country. Consequently, policy makers are pressurized to provide basic facilities including education, food, health, and living at economical prices (PricewaterhouseCoopers, 2013). Therefore, the concerned authorities continuously encouraged the investment from foreign to improve their economy in order to ensure the basic facilities (Kuntluru et al., 2012). In view of this scenario, most of the global manufacturers of pharmaceuticals have relocated their production units from west to Asian countries including India (Rehman et al., 2015).

As a result, India has become one of the most prominent pharmaceuticals manufacturing countries in the world which now offers potential benefits like low production cost, easy clinical trials, etc. It is expected that India would be among the top 10 pharmaceutical manufacturers in the whole world by 2020 (PricewaterhouseCoopers, 2013). Yet, this rapid progression in the industrial sector or rising incomes has not brought any kind of improvements in water, public health and sanitation (Laxminarayan and Heymann, 2012). Only 36% of the entire population in India has access to improved sanitation provisions. This population fraction is much lower than that of Brazil (81.3%), Indonesia (58.8%) and China (65.3%) (World bank, 2015). Among these countries, India faces the greatest concerns for a range of infectious diseases like tuberculosis, typhoid, diarrhea, dengue, swine flu, malaria, hepatitis, etc. Thus, multi-millions of drugs or antibiotics are being prescribed or sold daily to cure these types of diseases.

Consequently, combination of certain factors including poor public health, high rate of infectious diseases, poor hygiene facilities, inexpensive antibiotics and rising incomes altogether have led to the sudden change in consumption pattern of pharmaceuticals in India (Mathew and

Unnikrishnan, 2012). An almost 36% increase in the consumption of antibiotics has been reported between 2000 and 2010 (Van Boeckel et al., 2014). In 2010, India has been reported as the world's largest consumer of antibiotics to cure human health (Laxminarayan and Chaudhury, 2016).

After administration, these pharmaceutical drugs or antibiotics are not completely metabolized within the body and most of them are excreted out without getting transformed. After getting released from the body, these pharmaceuticals follow a complex and interconnected route (Figure 1.1) towards the aquatic environment. Pharmaceuticals may also enter water when patients, hospitals or pharmaceutical companies dispose of unused pharmaceutical compounds. These contaminants after entering the aquatic environment ultimately reach the drinking water (Huerta-Fontela et al., 2011), posing a threat to human health. These organic compounds are persistent and thus cannot be completely removed by conventional treatment plants (Fatta-Kassinos et al., 2011; Sires and Brillas, 2012). However, these pollutants are transmuted through these conventional treatment processes resulting into the formation of transformation products (Huhnerfuss et al., 2010; Fatta-Kassinos et al., 2011). The concentration of individual pharmaceutical pollutants or their transformed products in the environment is generally very low ranging from ngL^{-1} to mgL^{-1} . Nevertheless, total concentration of these contaminants and transformed products may become a major source of public concern (Lopez-Serna et al., 2012) as these contaminants can give rise to chronic toxicity (Klavarioti et al., 2009; Christen et al., 2010). Moreover, these contaminants along with their metabolites ultimately result into the development of drug resistant micro-organisms (Munir and Xagorarakis, 2011; Kristiansson et al., 2011) which has been evolved as a serious global problem (Hersher, 2012; WHO, 2012).

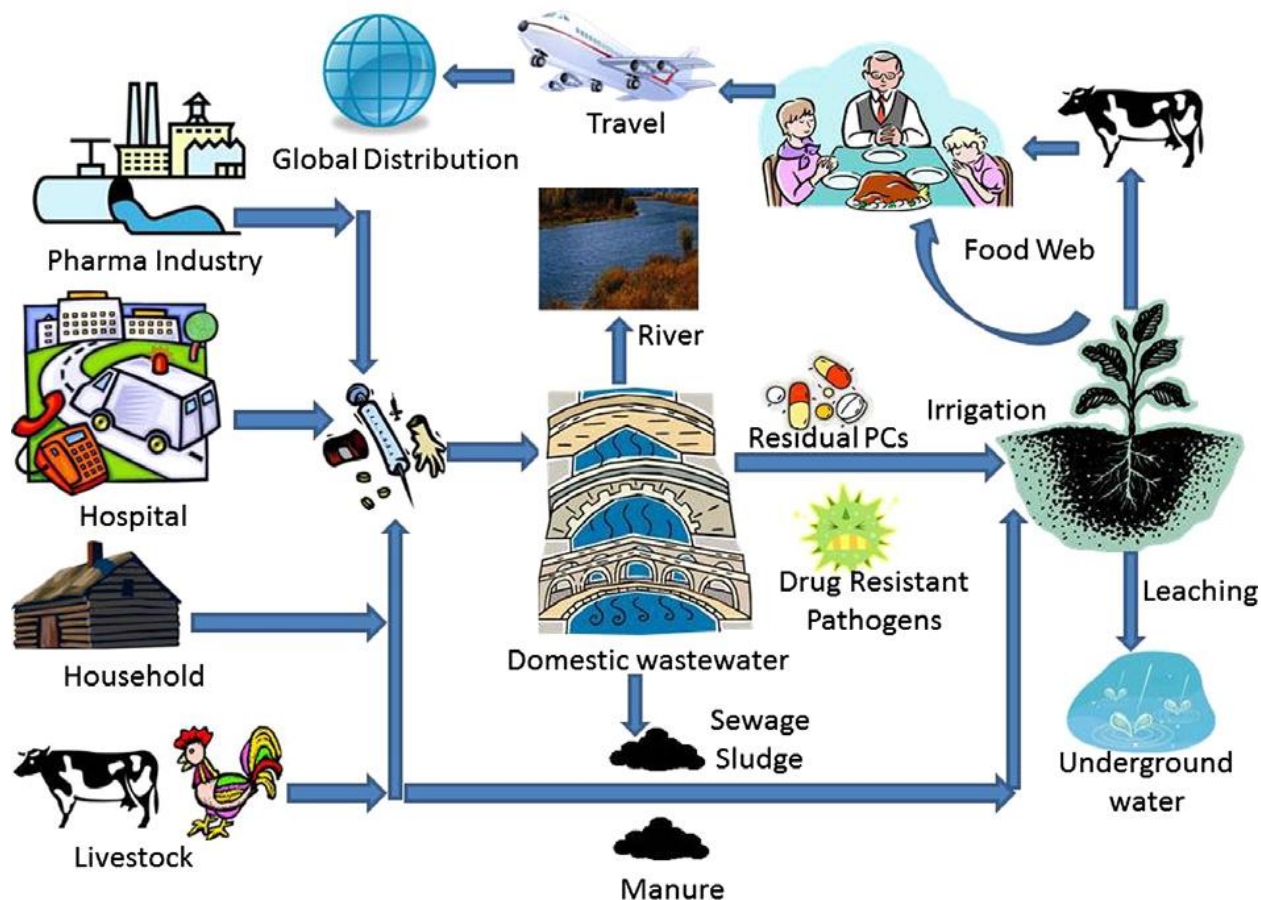


Figure 1.1: Fate of pharmaceuticals in environment (Rehman et al., 2015).

The prevalence of antibiotic or drug resistance problem all over the world owing to the excessive intake of these pharmaceutical compounds has emerged serious concerns among research and development (R & D) sector of the pharmaceutical industries. As a result, new advanced drugs are being launched annually. Manufacturing units related to these advanced drugs rely on conventional treatment methods for the treatment of pharmaceutical wastewater. Most of these drugs find their routes to the environment in the absence of any advanced treatment. Over and above, most of the pharmaceutical industries do not follow environmental regulations and dispose off their highly contaminated effluent into the water bodies without undergoing any effective treatment (Barbieri et al., 2012; Safiullah et al., 2012). This wastewater generally comprises of a diverse range of organic and inorganic precursors, intermediates and finished products (Altaf and Ali, 2010; Imran, 2005) thus causing serious health issues to the whole ecosystem (Aziz et al., 2012; Rehman et al., 2011). A case study on wastewater quality of

Patancheru industrial area (Hyderabad, India) which is comprised of more than 90 pharmaceutical manufacturing units has been reported by few researchers (Fick et al., 2009; Larsson et al., 2007). The concentration of pharmaceutical compounds in water was observed to be very high (up to 31 mgL^{-1}) even after undergoing through wastewater treatment plant (Fick et al., 2009; Larsson et al., 2007). Similar findings have been reported in China as well where relatively high concentrations of pharmaceutical compounds were detected in the treated effluent of manufacturing unit (Li et al., 2008). These investigations revealed the inappropriateness and inefficiency of traditional wastewater treatment technologies suggesting that these methods cannot remove the pharmaceuticals completely from water. In the conventional wastewater treatment units, these pollutants are subjected to a succession of different reactions resulting into the formation of more complex intermediates (Figure 1.2) that could adversely affect the aquatic life (Bound and Voulvoulis, 2004; Diwan et al., 2010).

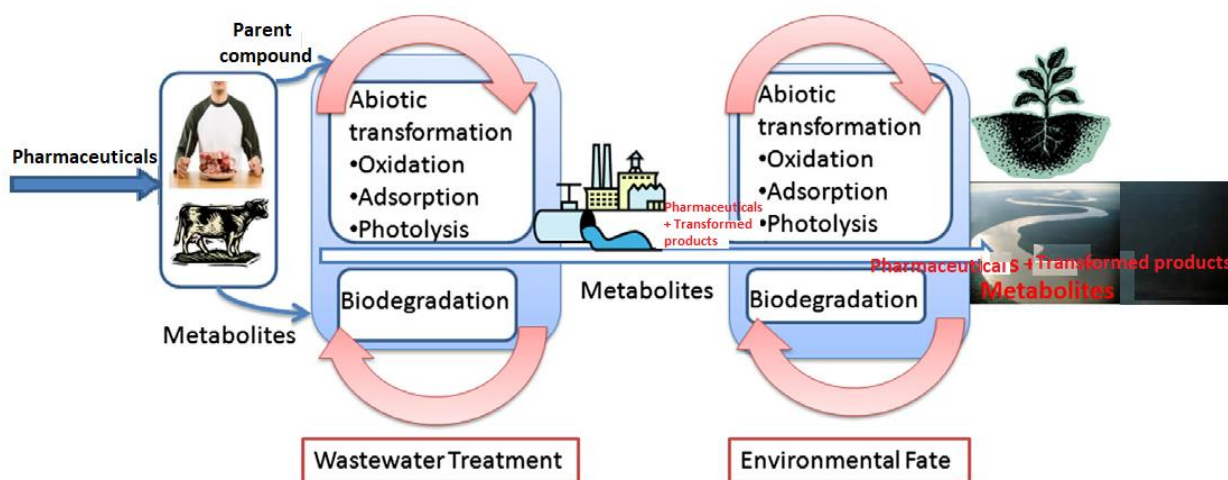


Figure 1.2: Transformation of pharmaceuticals in environment.

As a result, it may be concluded that traditional water treatment methods including adsorption, coagulation, air stripping, aerobic or anaerobic treatment, etc possesses inefficacies in one and another form. Most of these methods simply transform the pollutants from one phase to the other rather than removing them completely from the water bodies. Thus, in-capabilities of the conventional treatment methods (Adams et al., 2002; Stackelberg et al., 2007) have prompted the scientists to work in an area of advanced treatment technologies like microfiltration, ozonation, advanced oxidation processes (AOPs), reverse osmosis, electro-dialysis, etc for the

degradation and mineralization of bio-recalcitrant compounds present in wastewater. Among all these advanced treatment technologies, AOPs have proven their credentials since last two decades in the field of wastewater treatment.

1.2 Overview of advanced oxidation processes

Advanced oxidation processes (AOPs) or technologies have put their strong bet in the field of wastewater treatment targeting bio-recalcitrant pollutants. AOPs are the oxidation methods based on the generation of reactive species including hydroxyl radicals for the destruction of organic pollutants (Comninellis et al., 2008; Esplugas et al., 2002). Almost all processes falling under the category of AOPs rely on the strong oxidation potential of hydroxyl radicals which ultimately oxidizes and mineralizes the recalcitrant pollutants.

The proven credentials of AOPs can be viewed from numerous of publications related to the advanced oxidation based removal of a wide range of pollutants like dyes, phenols, pesticides, pharmaceuticals, polymers, chlorophenols (Oller et al., 2011; Stasinakis, 2008; Yuan et al., 2011). AOPs have even shown potential in the treatment of real wastewater from various sources like pharmaceutical industry, textile industry, pulp and paper mill, etc (Agulló-Barceló et al., 2013). For all these applications, there is always a concern i.e. whether to use AOPs as a single process or in combination with other conventional methods. For real time applications, it is always suggested to use AOPs as a pre-treatment to biological process or as a tertiary treatment (Oller et al., 2008).

AOPs can be classified as photochemical oxidation processes which include photo-ozonation (UV/O₃), semiconductor based photocatalysis (metal-oxide/UV), photo-Fenton (UV/H₂O₂/Fe²⁺), and chemical oxidation processes including ozonation (O₃, O₃/H₂O₂), Fenton (H₂O₂/Fe²⁺) as shown in figure 1.3. Among these AOPs, semiconductor such as metal oxide based photocatalysis has gained a significant attention in the past 20 years due to the following reasons: (a) cost-effectiveness; (b) low-toxicity; (c) environment-friendly; (d) easily modified by doping; and (e) capability to extend its use without any significant reduction in its photocatalytic activity (Chan et al., 2011; Chatterjee and Dasgupta, 2005). Various metal oxides like titanium dioxide (TiO₂), tungstate (WO₃), zinc oxide (ZnO), molybdate (MoO₄), vanadate (VO₄) exhibit good photocatalytic properties (Chakrabarti and Dutta, 2004; Guo et al., 2010). Out of these,

TiO₂ is the most extensively investigated photocatalyst due to its high catalytic activity, inexpensiveness, chemical stability, non-toxicity (Saïen et al., 2009).

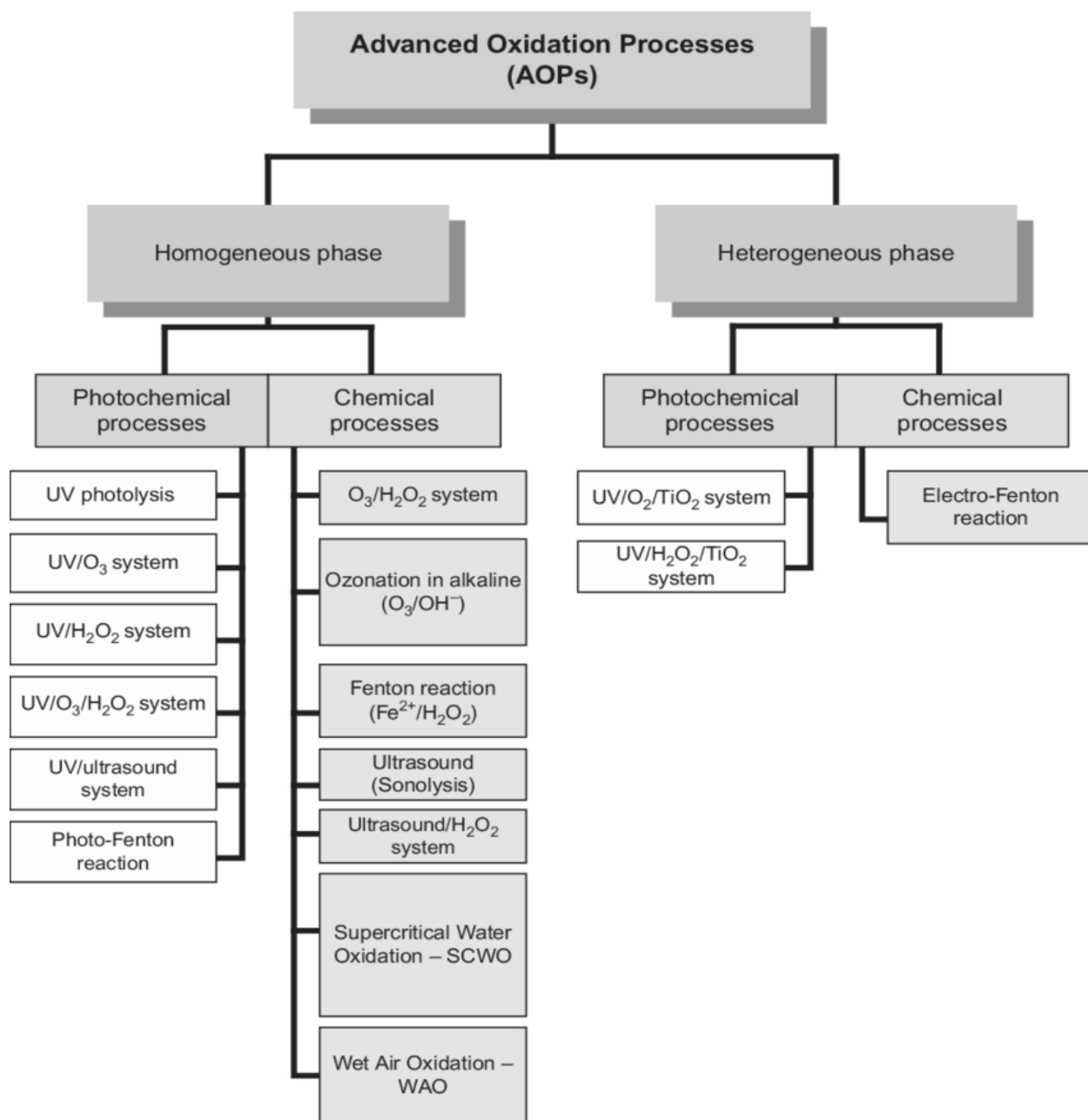


Figure 1.3: Classification of AOPs.

1.3 Applications of heterogeneous photocatalysis for wastewater treatment

Heterogeneous photocatalysis i.e. TiO₂ photocatalysis is the most widely studied technique in the field of AOPs. The technique has depicted its great potential for the tertiary

treatment of municipal wastewater (Al-Bastaki et al., 2004; Arana et al., 2002), removal of endocrine disrupting chemicals (Dimitroula et al., 2012; Likodimos et al., 2010; Miranda-García et al., 2011), water disinfection (Agulló-Barceló et al., 2013; Dominguez-Espindola et al., 2013), effluents containing pathogens that are resistant to chlorination (Ede et al., 2012; Gamage and Zhang, 2010), hospital effluents (Chong and Jin, 2012; Rizzo et al., 2014), real effluents from various industries including pulp and paper mills (Ghaly et al., 2011; Kansal et al., 2008; Rodrigues et al., 2008), dairy (Banu et al., 2008), textile (Luo et al., 2009; Pekakis et al., 2006; Toor et al., 2006), distilleries and agricultural oil mills (Gernjak et al., 2004; Nogueira et al., 2016), pharmaceuticals (Deegan et al., 2011; Talwar et al., 2017), synthetic wastewaters containing organic pollutants like phenols (Torbina et al., 2015; Tshuto et al., 2017; Zulfakar et al., 2011), chlorophenols (Sivlim et al., 2012), herbicides (Seck et al., 2013) and pesticides (Vela et al., 2017), ammonia (Shavisi et al., 2014), plasticizers (Singla et al., 2016) and surfactants (Czech and Curie-Sklodowska, 2012). The work related to heterogeneous photocatalysis has been represented in literature using slurry as well as immobilized/fixed approach.

The photocatalytic characteristics of TiO₂ are acquired from the generation of charge carriers upon absorption of UV light equivalent to the band gap (Fujishima et al., 2008). The detailed mechanism of TiO₂ photocatalysis is now well established and has been presented in figure 1.4. The mechanism can be further understood from the following equations (1.1-1.6):



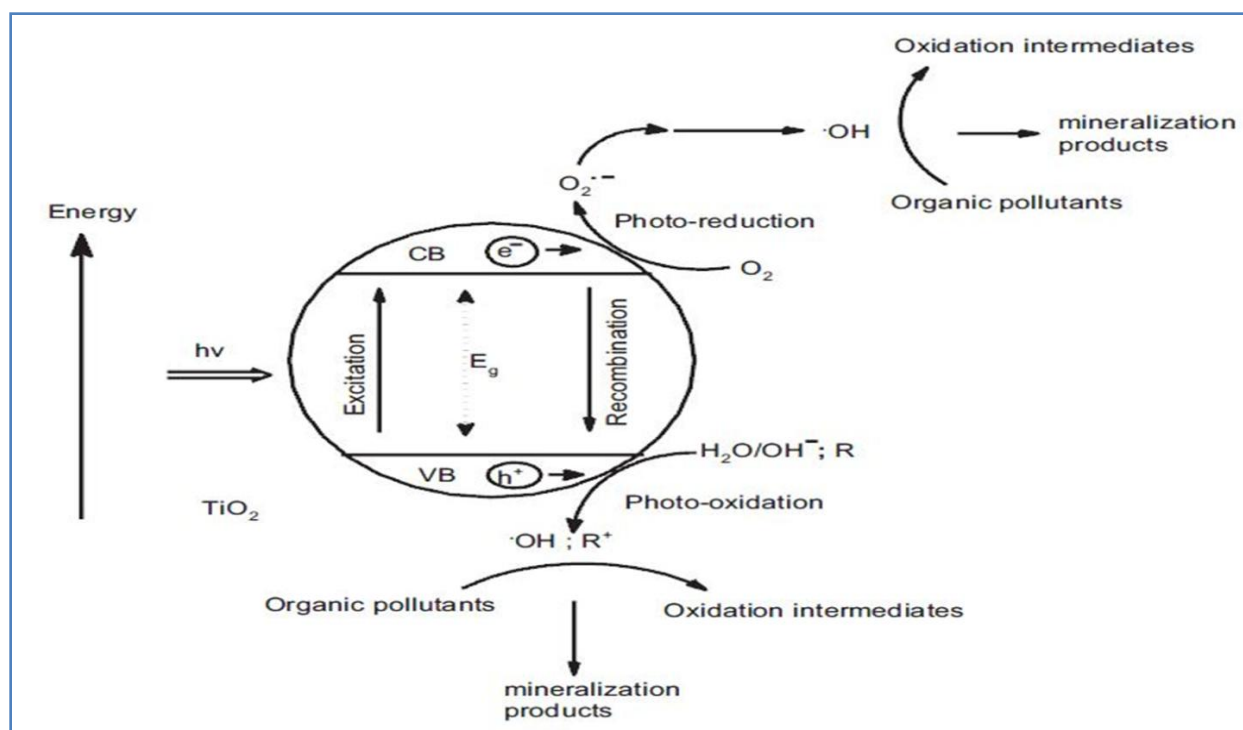


Figure 1.4: Mechanism of TiO₂ photocatalysis.

The use of TiO₂ in suspended form has gained an immense attention owing to its excellent degradation efficiency. Actually, finely powdered catalyst particles suspended in solution provide sufficient surface area and do not involve any mass transfer implications. However, poor light absorption capacity, frequent recombination of charge carriers along with low specific surface area of the catalyst always remain a concern with conventional TiO₂.

New avenues are being constantly explored in order to improve the efficiency of heterogeneous photocatalysis by repressing the concerns raised by this process. The performance of any photocatalyst generally depends upon certain factors which include size, shape, specific surface area, pore structure, exposed surface area and crystalline phase (Nakata and Fujishima, 2012). Various studies have reported the nano-structures and micro-structures of TiO₂ with varying morphologies and characteristics (Chen and Mao, 2006). Different shapes of TiO₂ nano-structures have been synthesized and are reported in literature which include spheres (Kondo et al., 2008; Liu et al., 2010), nanorods (Huang et al., 2016; Sun et al., 2016), fibers (Reddy et al., 2014), tubes (Podporska-Carroll et al., 2015), sheets (Diak et al., 2015) and interconnected architectures (Hasegawa et al., 2010). These nano-structured TiO₂ have established their applications not only in photocatalysis but also in lithium-ion batteries (Ding et al., 2011), dye-

sensitized solar cells (Ahn et al., 2010) and electro-chromic displays (Periyat et al., 2010). These micro or nano-structured catalysts possess higher specific surface area in comparison to conventional photocatalysts. Moreover, most of these catalysts have the tendency to prevent electron-hole recombination to some extent thus, exhibiting better photocatalytic activity.

Numerous of other studies have reported that doping or deposition of TiO_2 with metals/non-metals (Chen et al., 2015; Phattalung et al., 2017; Zielińska-Jurek et al., 2017) can open up new channels for the development of catalyst with significantly improved photo-response efficiency. The mechanism of doped TiO_2 photocatalysis is more or less same as compared to un-doped TiO_2 photocatalysis. The only difference in case of doped TiO_2 photocatalysis is the generation of new energy level in the structure of TiO_2 owing to the presence of dopant. Figure 1.5 depicts the mechanism of doped and un-doped TiO_2 photocatalysis.

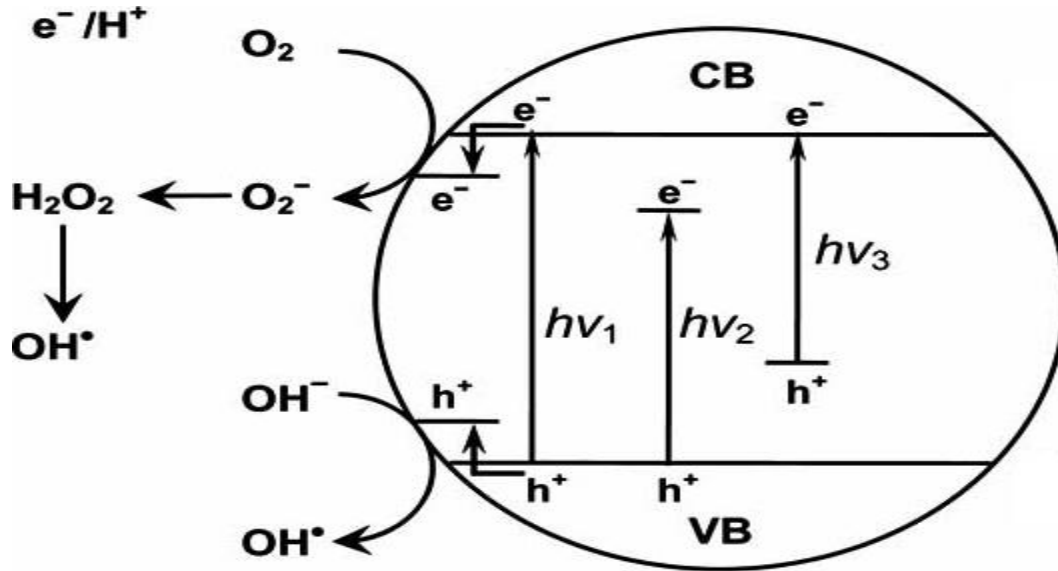


Figure 1.5: Mechanism of TiO_2 photocatalysis: $h\nu_1$ = un-doped TiO_2 ; $h\nu_2$ = metal-doped TiO_2 and $h\nu_3$ = non-metal-doped TiO_2 (Zaleska, 2008).

The photo-activity of metal-doped TiO_2 can be elucidated on the basis of the generation of a new energy level below the conduction band of TiO_2 owing to the dissipation of metal nanoparticles within the matrix of TiO_2 (Melcher et al., 2017). As clear from figure, photon of light possessing energy equivalent to $h\nu_2$ can excite the electron from the defect state to the conduction band of TiO_2 . Additional advantage of metal-doping is the inhibition of electron-hole

recombination due to the trapping of electrons by metals during irradiation. On the other hand, non-metal doped TiO_2 results into the following inferences: (a) Narrowing of the band gap due to the introduction of a new energy level above the valence band of TiO_2 , (b) Formation of oxygen deficient sites in TiO_2 thus enhancing the visible activity of catalyst (Matějová et al., 2018).

Though promising results in terms of high photocatalytic activity even under visible spectrum of light have been obtained through modification of TiO_2 , field-scale applications of these modified catalysts are yet to be explored. Actually most of the studies related to these modified catalysts are being reported in suspension mode thus facing the major complication of expensive catalyst separation post-treatment. Moreover, poor catalyst recyclability efficiency in slurry photocatalysis makes the process cost-intensive. Therefore, these processes have limited accessibility for successful scale-up.

1.4 Pilot-scale reactors with prominence of fixed-bed photocatalysis

Different configurations of pilot-scale photo-reactors including parabolic trough collectors (PTCs) (Adesina, 2004), concentrating falling film reactors (Pacheco et al., 1990), compound parabolic collectors (CPCs) (Martinez et al., 2014; Navntoft et al., 2007), tubular reactors (Vargas and Núñez, 2010), shallow pond reactors (Mozia et al., 2012), double-skin sheet reactor (Dillert et al., 1999), flat plate reactor (Plantard et al., 2012), falling film photo-reactor (Zayani et al., 2009), thin film cascade reactor (Chan et al., 2003), step reactor (Thu et al., 2005), slurry bubble column reactor (Kamble et al., 2004) and flat packed-bed reactor (Hanaor and Sorrell, 2014) have been reported for the photocatalytic degradation of a wide range of pollutants. Each type of reactor has certain advantages as well as disadvantages. PTCs and concentrating falling film reactors are expensive due to existence of water cooling provisions, moving parts and even solar tracking devices. Thus, they are not competent enough for scale-up or commercialization. On the other hand, double-skin sheet reactors require continuous purging of solution with air which may cause filming problems while, using suspended TiO_2 again made them incompetent for commercialization. Flat plate reactors also possess scale-up implications since they operate under laminar flow conditions and need purging with air or addition of oxidants. Falling film reactors using supported TiO_2 face film diffusion resistance resulting into limited degradation efficiency. CPCs are the most widely used reactor configurations but they generally suffer from optical losses as well as glass tubes aging. In case of packed CPCs,

complications regarding clogging of reactor, catalyst fouling and high cost of pumping exist which further made them unsuitable for field-scale applications (Abdel-Maksoud et al., 2016).

Applications of TiO₂ photocatalysis are always preferred in its fixed mode (Blanco et al., 2015; Pronina et al., 2015). To seek the commercial applications of heterogeneous photocatalysis, a robust and affordable technique for immobilizing TiO₂ on inert supports (having high exposed surface area) needs to be developed. Such TiO₂ immobilized supports must not offer catalyst attrition or stripping off the catalyst particles from the surface for prolonged period.

Different supports for TiO₂ immobilization have been reported which include polystyrene beads (Fabiya and Skelton, 2000), concrete surface (Delnavaz et al., 2012), pebbles (Rao and Chaturvedi, 2012), silica gel beads (Li et al., 2015), glass spheres (Borges et al., 2015), glass plate (Miyawaki et al., 2016), zeolite (Montañez et al., 2015), etc. Although, numerous of studies related to supported catalyst are reported in literature, successful implementation of the technique at field-scale has not been attained till now. The stability or durability of supported catalyst has not been discussed thoroughly in any of the reported studies. Even though the technique is more efficient and successful in terms of its commercial viability, the selection of inert, efficient and robust materials for catalyst immobilization always remain a challenge for AOP scientists. Further, mass transfer implications and the treatment time in fixed-mode catalysis also remain a liability towards its commercial applications. As the process consumes more time, hence more energy is required for the treatment of pollutants.

1.5 Applications of homogeneous photocatalysis

Some of the flaws of TiO₂ photocatalysis like mass transfer implications have been covered by homogeneous photocatalysis i.e. photo-Fenton. Photo-Fenton process produces hydroxyl radicals through the catalytic activity of Fe²⁺/H₂O₂ in the presence of light (Carra et al., 2015; Papoutsakis et al., 2015; Torrades et al., 2014). The mechanism of photo-Fenton reaction can be understood from equations (1.7-1.9) (Chamarro et al., 2001; Will et al., 2004).





Scientists have undergone a vast investigation in this area as there are fair chances for reduction in treatment time because the process offers negligible mass transfer implications. There are few studies available in literature (Gernjak et al., 2004; Lofrano et al., 2009), that have experienced a significant reduction in treatment time in comparison to heterogeneous photocatalysis for the removal of pollutants. The photo-Fenton based treatment has been applied widely for the removal of a variety of non-biodegradable pollutants present in water (Lan et al., 2015; Serna-Galvis et al., 2016; Tamimi et al., 2008). Few studies related to photo-Fenton process have even reported the scale-up trials for the treatment of wastewater (Duran et al., 2011; Michael et al., 2012). Yet, field-scale applications of this process are still questionable. Actually, the generation of huge quantity of iron sludge and high dose of H_2O_2 are the major drawbacks of this process (Babuponnusami and Muthukumar, 2014). Further, lower efficiency of photon utilization restricts its industrial applications (Ramirez et al., 2007).

1.6 Dual concept of photocatalysis and photo-Fenton

Coupling of two processes i.e. photocatalysis and photo-Fenton can reasonably solve the implications offered by these processes when operated separately as discussed in previous sections. The major challenge of this dual process is that both mechanisms (photocatalysis and photo-Fenton) work in a controlled manner.

The dual process drastically improves the degradation efficiency of the pollutants resulting in the reduction of treatment time. The improved degradation efficiency by the introduction of Fenton reagent in the TiO_2 photocatalytic system can be attributed to the production of hydroxyl radicals in abundance. Actually, hydroxyl radicals are generated not only through a single process but simultaneously by both ongoing processes i.e. photocatalysis and photo-Fenton. Moreover, presence of iron in the system suppresses the recombination of electron and holes in TiO_2 thereby enhancing the overall catalytic activity. Actually, ferric iron adsorbed on the surface of TiO_2 gets reduced to ferrous iron using the photon excited electron from the conduction band of TiO_2 (Equation 1.10). This results into the promotion of photo-Fenton reaction from ferrous iron along with the separation of charge carriers on the surface of TiO_2 .



The concept of dual effect was propounded by few studies for enhancing the degradation efficiency of photocatalytic system (Mazille et al., 2009a, b; Su et al., 2015). However, the technique has not been explored thoroughly to seek its practical applications. Moreover, most of the studies reported in this area deal with catalysts suspensions which further restricts the implementation of technique at large-scale.

The present study is somehow a step closer for visualizing the commercial applications of this dual process. A novel concept of in-situ dual effect (coupling of photocatalysis and photo-Fenton) within the same treatment system has been introduced in the present research work. This novel concept takes over the advantages of both processes i.e. photocatalysis or photo-Fenton while minimizing the drawbacks of each process at the same time. Furthermore, the present study has been reported in completely fixed form thereby further increasing the chances to get the technique commercialized.

Efforts have been made in the current research work to develop unique support systems for merging source of iron and TiO₂ together in one composite that can be recycled efficiently for numerous of times. In addition to this, waste materials like foundry sand (FS) and fly-ash (FA) have been used as alternative sources of iron in the present study which further makes the process economical. In fact, this is the first reported study till date where all parameters are being incorporated into one composite for the degradation of organic pollutants especially using waste FA and FS. Actually, FS and FA possess the characteristics of leaching iron species under acidic conditions. Thus, this unique property of these waste materials has been used to execute photo-Fenton reaction simultaneously along with TiO₂ photocatalysis. The mechanism of this proposed in-situ dual process has been presented in figure 1.6.

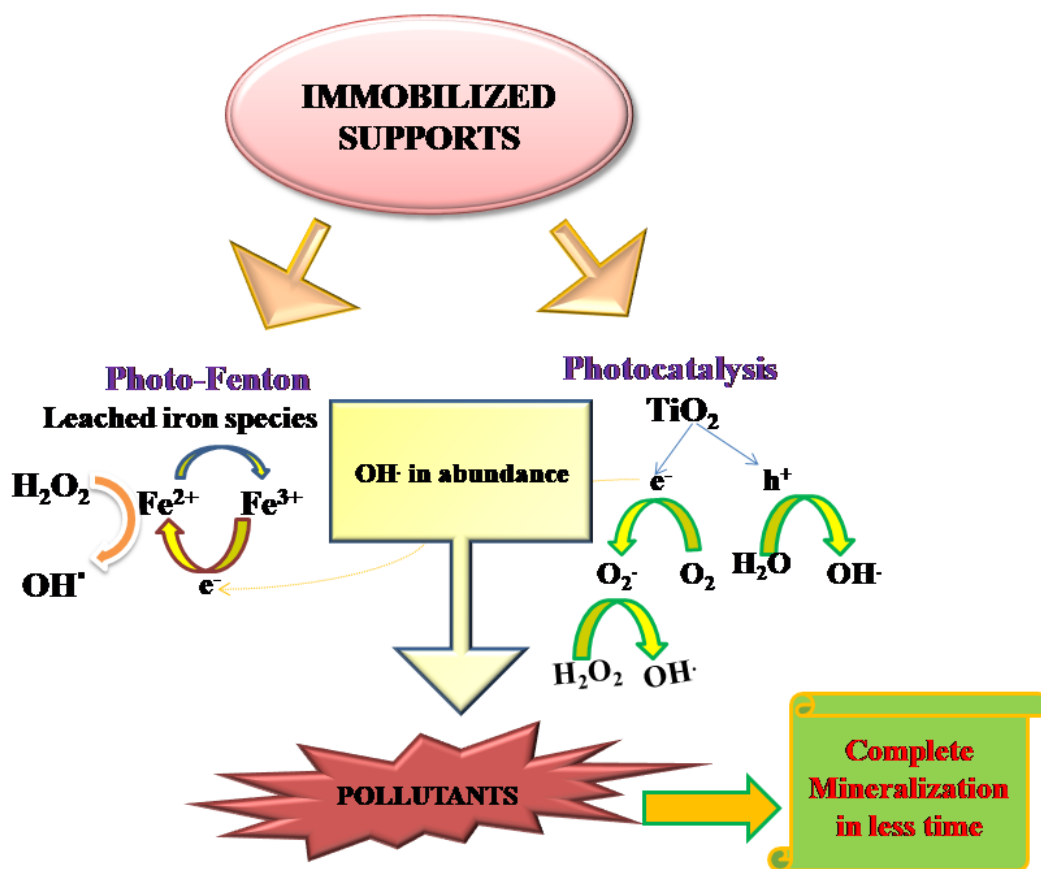


Figure 1.6: Mechanism of in-situ dual effect.

1.7 Target pharmaceutical compounds

After an intensive survey, pharmaceuticals like Pentoxifylline (PEN) and Cephalexin (CEX) have been selected as target pollutants in the present study. PEN is a vasodilator drug intended for the treatment of muscle pain arising from peripheral artery disease (Magureanu et al., 2010). PEN has been frequently detected at various concentrations in effluents resulting from different sources like Canadian sewage treatment plants (Metcalf et al., 2003), hospitals in Taiwan (Lin et al., 2008), river in Romania (Moldovan, 2006) and in Germany (Sacher et al., 2008). The persistence and non-biodegradable nature of PEN has been confirmed in various reported studies (Kang, 2012; Lin et al., 2015; Mone and Chandrasekhar, 2010).

CEX is a cephalosporin β -lactamic antibiotic, which is most commonly used to treat several urinary and respiratory tract infections. CEX exhibits only 10% biotransformation rate leading to the fact that rest 90% is excreted out in urine unchanged (Comninellis et al., 2008). The evidence of non-biodegradability of CEX can be revealed from its ubiquitous presence in various aquatic environments such as coastal water (Gulkowska et al., 2007), municipal wastewater (Li et al., 2009) and treated effluent from industry (Saravanane and Sundararaman, 2009).

1.8 Aim of the proposed study

The proposed research work was conducted to study the photo-degradation of recalcitrant pharmaceuticals i.e. CEX and PEN. Best efforts were devoted to reduce the treatment time for the degradation of these pollutants by incorporating the concept of in-situ dual process within the treatment unit. The process was executed at lab-scale as well as at pilot-scale with proper optimization of process by selecting the most appropriate catalyst supports that could exhibit the extended recyclability efficiency. Complete mineralization studies were conducted through stoichiometric calculations with estimation of anions and carbon-dioxide along with identification of intermediates through GC-MS analysis. The field-scale applications of the proposed technique were validated by treating the real wastewater of a pharmaceutical industry via in-situ dual process.

Through this study, authors claim certain novel findings which include in-situ dual process especially in fixed-mode, extended durability of the catalyst immobilized support, pilot-scale demonstration incorporating fixed-bed in-situ dual effect for the treatment of pharmaceutical wastewater along-with significant reduction in treatment time.

Chapter 2

REVIEW OF LITERATURE

2.1 Overview

During the last few decades, the existence and fate of pharmaceuticals and personal care products (PPCPs) in the aquatic environment has received substantial attention by the scientific group. The occurrence of these types of emerging contaminants was first detected in surface waters in U.S.A and Europe during 1960s (Stumm-Zollinger and Fair, 1965). These contaminants reach the surface waters via domestic, hospital or industrial effluents and through the effluents from conventional wastewater treatment plants (WWTPs), where these recalcitrant pharmaceuticals are not removed completely. Indeed, research reveals that even up to 90% of the pharmaceutical residues can be obtained from the effluent of treatment plant (Cooper et al., 2008). Generally, physico-chemical methods like membrane separation, activated carbon, chemical removal, chlorination and biological methods involving activated sludge, trickling filters, rotating biological contactors are used as the conventional wastewater treatment technologies (Deegan et al., 2011; Gupta et al., 2006). All these methods cause transformation of pollutants rather than destroying them completely (Adams et al., 2002; Gobel et al., 2007; Stackelberg et al., 2007).

Therefore, continual discharge of the incompletely treated pharmaceutical wastewater (through conventional WWTPs) to the aquatic environment results into the unreliable ecological effects. Actually, this inefficiently treated wastewater might act unforeseeably when combined with other chemicals already present in the environment, which could further lead to the formation of more toxic products (Li, 2014). Several studies have even reported the occurrence of few pharmaceuticals in drinking water as well (Jelic et al., 2011; Jones et al., 2005; WHO, 2012). The exposure of pharmaceuticals via drinking water has risen several health risks to the humans thus leading to the onset of major issues among governmental as well as non-governmental water suppliers, water regulators and among the public (Jelic et al., 2012). The presence of pharmaceuticals in the aquatic environment induces chronic toxicity (Crane et al.,

2006). Figure 2.1 demonstrates the exposure, fate and the consequences of pharmaceutical compounds in the environment.

Exposure

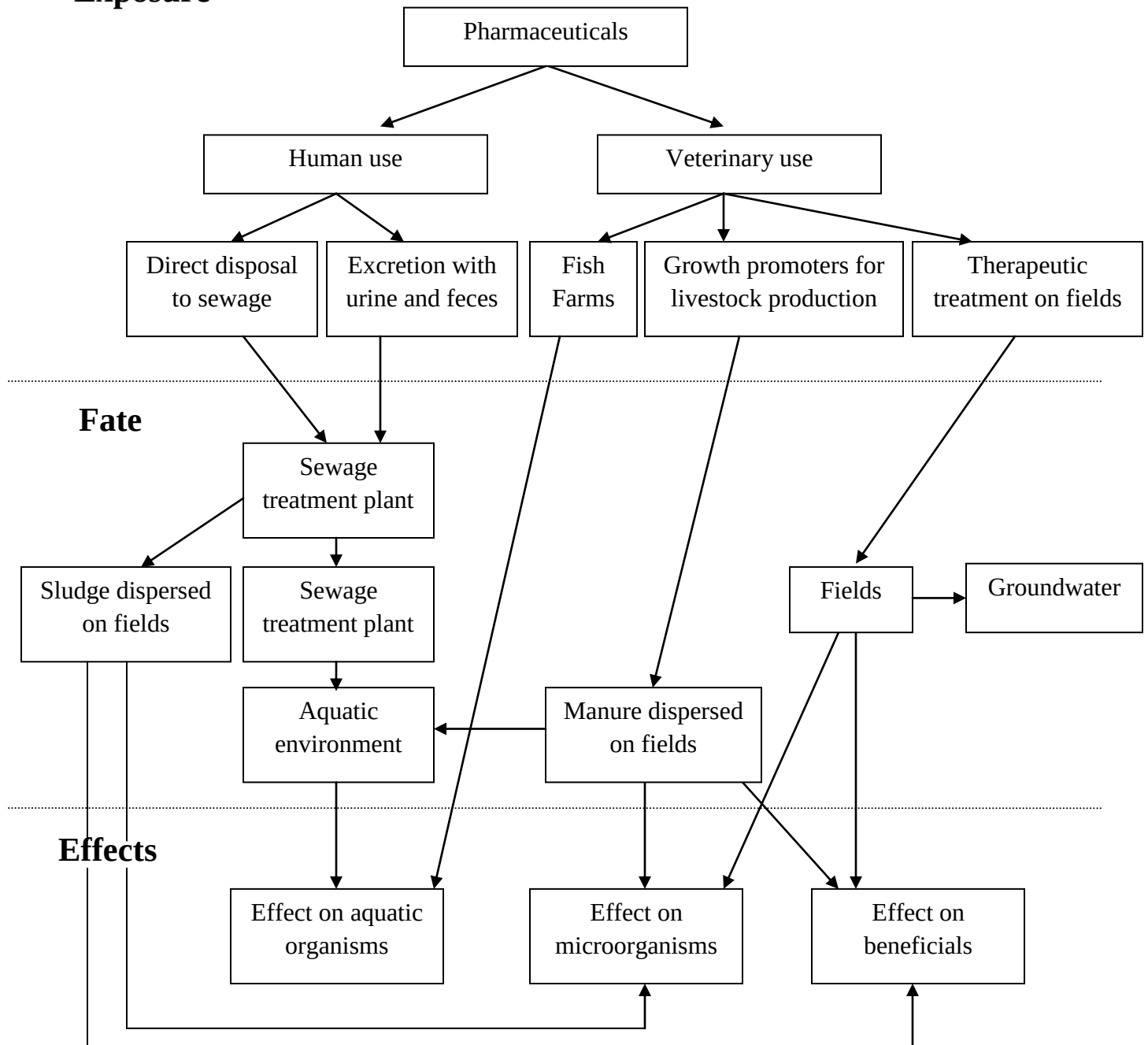


Figure 2.1: Exposure, fate and effect of pharmaceuticals in environment (Halling-Sørensen et al., 1998).

The in-capabilities of conventional treatment technologies in efficiently treating the wastewater containing recalcitrant pollutants like pharmaceuticals have led to the development of advanced treatment methods like advanced oxidation processes (AOPs). The literature was thoroughly reviewed to examine the latest progression in the field of wastewater treatment through AOPs. This review clearly addresses the drawbacks and advantages of AOPs (specifically homogeneous and heterogeneous photocatalysis) in context to their commercial applications for the treatment of wastewater. Various possibilities have been glanced to overcome the pitfalls of each individual process. The feasibility of coupling of two different processes within the treatment unit has also been discussed along with its potentiality towards the commercialization of process. This review substantially aims at the degradation of recalcitrant organic pollutants present in water through AOPs.

2.2 Assets and liabilities of advanced oxidation processes (AOPs)

AOPs are the oxidative technologies involving the formation of highly reactive hydroxyl radicals ($\text{OH}^\bullet$) which possess comparatively greater oxidation potential in comparison to other oxidants (Bautitz and Nogueira, 2010; Hernandez et al., 2002). AOPs present an effective technological solution to the conventional water treatment related problems. Such solutions are necessary for supporting and increasing the competitiveness of discrete industrial sectors involving water technology sector worldwide (Comninellis et al., 2008).

The emerging interest of industrial as well as academic communities in the field of AOPs can be reflected from the expanding list of publications in various scientific journals devoted to the environment related applications (Comninellis et al., 2008). Most of the published articles are either dedicated to TiO_2 photocatalysis or photo-Fenton (Hashimoto et al., 2005; Pouran et al., 2015). These techniques have demonstrated promising results in context to the degradation of a variety of recalcitrant pollutants present in water (Lima et al., 2017; Klammerth et al., 2010; Nakata and Fujishima, 2012). However, both techniques offer several implications that restrict their successful implementation at field-scale.

2.2.1 Applications of TiO_2 photocatalysis

The applications of TiO_2 photocatalysis lie in the photocatalytic oxidation (PCO) to induce partial or total mineralization of liquid phase pollutants to form benign substances

(Zeltner and Tompkin, 2005). There are thousands of publications related to the removal of micro-pollutants from water via photocatalysis using TiO_2 as a free standing particulate (Doll and Frimmel, 2005; Perez-Estrada et al., 2005). It has been reported that the efficiency of photocatalytic system depends upon certain operational parameters including loading of catalyst (Ji et al., 2013; Nomikos et al. 2014; Rammohan and Nadagouda, 2013) and its properties i.e. crystalline phase, porosity, specific surface area (Kozlova and Vorontsov, 2010), initial substrate concentration (Doll and Frimmel, 2004), light intensity (Dionysiou et al., 2008), presence of oxygen (Muzyka and Fox, 1991), solution's pH (Piscopo et al., 2001), and presence of organic (Yang et al., 2010) or inorganic content (Zhao et al. 2012) in solution.

Usually, photocatalytic degradation rate follows a linear trend with the concentration of catalyst up-to a certain dose beyond which effective penetration of light into the solution is not possible which subsequently affects the degradation efficiency (Gaya and Abdullah, 2008). Various studies (Karunakaran and Senthilvelan, 2005; Qamar et al., 2006) have revealed the linear trend of photocatalytic rate even with the intensity of light. The pH of solution affects ionization states of the organics, surface charge properties as well as rate of formation of hydroxyl radicals during the reaction (Haroune et al., 2014; Schwegmann et al., 2013). The PZC i.e. point of zero charge of TiO_2 lies between pH value of 4.5 and 7.0 (Chong et al., 2010). The acidic organic compounds experience an increased photocatalytic degradation rate at low pH owing to the intensified adsorption on the surface of TiO_2 (Gogniat et al., 2006). On the contrary, alkaline organic substances experience enhanced photocatalytic degradation rate at higher pH range (Haroune et al., 2014; Ji et al., 2013). Dissolved oxygen acts as an electron scavenger to form superoxide radicals which further reacts with H_2O_2 to produce additional hydroxyl radicals (Guo et al., 2011; Wang et al., 2011). Axelsson and Dunne (2001) reported that photocatalytic degradation of 3,4-dichlorophenol enhanced in the presence of dissolved oxygen due to the generation of additional hydroxyl radicals while degradation of pollutant occurred in the absence of oxygen. On the other hand, presence of dissolved organics retarded the photocatalytic reaction rate of the target pollutant owing to the prevalence of certain factors like radiation attenuation, surface fouling of catalyst and competition for catalyst active sites. Doll and Frimmel (2005) observed that during the photocatalytic oxidation of carbamazepine, value of rate constant reduced to an extent of around 40% in the presence of even very low concentration of dissolved organics i.e. 0.5 mgL^{-1} .

The applications of TiO₂ photocatalysis have been applied for the destruction of various classes of organic pollutants like aldehydes (Kim and Choi, 2007), carboxylic acids (Harada and Tanaka, 2006; Singh et al., 2007), chloroanilines (Chu et al., 2007), chlorophenols (Aggarwal et al., 2017; Guillard et al., 1999), dyes (Mrowetz et al., 2003; Qamar et al., 2005), herbicides (Haque and Muneer, 2003), insecticides (Verma et al., 2017), phenolics (Pelizzetti and Minero, 1993), pharmaceuticals (Bansal et al., 2016; Reyes et al., 2006) and polymers (Horikoshi et al., 2001) spiked in de-ionized water. Though a reasonably good amount of degradation efficiency has been achieved in all these reported studies, there are certain drawbacks falling in one or the other compartment which really restrict their visualization for field-scale applications. Some of the lacunae identified are as follows:

- Use of artificial UV lamps (costly) (Esplugas et al., 2002);
- Separation of catalyst (expensive filtration/centrifugation) (Pronina et al., 2015);
- Frequent recombination of electron/hole (Samarghandi et al., 2007); and
- Increased energy costs and scale-up implications (Blanco et al., 2015).

2.2.2 Applications of photo-Fenton process

Some of the aforementioned concerns raised in case of heterogeneous photocatalysis are being overcome by the other widely used technique among AOPs i.e. photo-Fenton. Fenton based oxidation process is the catalytic reaction between H₂O₂ and iron ions to produce hydroxyl radicals (Fenton, 1894). Extensive studies have been reported on the applications of photo-Fenton process for the degradation of recalcitrant pollutants like dyes (Punji et al., 2012; Tokumura et al., 2013), insecticides (Gonzalez-Olmos et al., 2012), pesticides (Ortega-Liévana et al., 2012), pharmaceuticals (Elmolla and Chaudhury, 2009; Gogate and Pandit, 2004), chlorophenols (Ghaly et al., 2001), etc.

Lofrano et al. (2009) evaluated the comparison between photo-Fenton and photocatalytic processes for the degradation of catechol. The treatment time was significantly reduced (30 min) in case of photo-Fenton process as compared to photocatalysis (240 min) thus saving the huge energy costs. Actually, homogeneous photo-Fenton reactions offer no mass-transfer implications owing to the existence of iron species in solution in the same phase as that of reactants thus resulting into the significant degradation efficiency of process (Pouran et al., 2015). The photo-

Fenton process depends upon certain operational parameters like substrate concentration, Fenton reagent, temperature and pH (Pouran et al., 2015). Ravina et al. (2002) have reported that increase in the concentration of target pollutant i.e. Diclofenac from 10-80 mgL⁻¹ decreased the removal efficiency of photo-Fenton process and thereby increased the mineralization time. Similar types of findings were reported in other studies (Ayodele et al., 2012; Tamimi et al., 2008) as well. Moreover, different studies have reported that existence of both reagents i.e. H₂O₂ along with iron in the presence of UV light is necessary to successfully conduct the photo-Fenton reaction (Chamarro et al., 2001). The absence of any of the reagents leads to an insignificant removal efficiency of the process (Ayodele et al., 2012; Ortega-Lie'bana et al., 2012). Furthermore, the optimum pH range for the photo-Fenton process has been observed to be 2.8-3.5 as investigated in several studies (Kavitha and Palanivelu, 2004; Silva et al., 2007). Actually, it has been found that species like Fe (OH)²⁺(H₂O)₅ possessing higher light absorption coefficient are generated at pH close to 3 (Michael et al., 2012). Most of the studies dealing with photo-Fenton process have been performed at room temperature (Monteagudo et al., 2011; Primo et al., 2008) owing to the decomposition of H₂O₂ at high temperature (>50 °C) (Muthukumari et al., 2009; Yip et al., 2005).

Though homogeneous photo-Fenton process has been observed to be a feasible solution for the treatment of bio-recalcitrant pollutants, it offers certain liabilities as stated below:

- Increased cost of the process (De Torres-Soci'as et al., 2015);
- Poor regeneration of catalyst (Pouran et al., 2015);
- High dose of H₂O₂ (Jorda et al., 2011); and
- Generation of huge amount of iron sludge (Hermosilla et al., 2009).

The above mentioned issues have to be resolved before actually implementing the photo-Fenton process at large scale. These implications can be suppressed to some extent in heterogeneous photo-Fenton process by stabilizing the iron within the structure of catalyst as depicted in several studies (Garrido-Ramírez et al., 2010; Herney-Ramirez et al., 2010). Numerous of catalysts have been applied in heterogeneous photo-Fenton reaction which include zeolite (Kasiri et al., 2008), clays (Feng et al., 2006; De Leon et al., 2008), ferrite (Liu et al., 2012), magnetite (Avetta et al., 2014) and minerals (Chen et al., 2010; Li et al., 2015; Sannino et al., 2012). The main asset of heterogeneous processes is that the problem of iron sludge

generation in case of homogeneous process gets nullified completely. However, these processes result into the slower oxidation rate as compared to homogeneous process (Punzi et al., 2012) owing to the existence of a smaller fraction of iron over the surface of catalyst.

2.2.3 Fixed-bed photocatalysis

While in case of heterogeneous photocatalysis, immobilized or entrapped catalyst configurations could eliminate the post-treatment filtration or centrifugation step completely. Reviews are available in the literature on supported TiO_2 for water decontamination (McCullagh et al., 2011). Manaserro et al. (2017) evaluated the comparison between photocatalytic efficiency of slurry and fixed-bed systems (using TiO_2 immobilized glass rings) in context to the degradation of clofibric acid present in water. The reaction rate obtained in case of slurry systems was almost thrice to that of fixed-bed systems. But the study concluded that the reaction rates in case of fixed-bed systems could be significantly increased by improving the absorption of photons of light inside the fixed-bed reactor. As a result, porosity, light absorption coefficient of immobilized catalyst and total exposed surface area are the major factors which significantly affect the photocatalytic efficiency of the fixed-bed photocatalytic system. A wide range of support materials have been used for catalyst immobilization to carry out the photocatalytic degradation of pollutants. Calcium alginate beads were used as catalyst entrapment material for the degradation of pharmaceutical compounds (Sarkar et al., 2015). TiO_2 was coated on granular expanded clay through sol-gel method employing dip coating process for the photocatalytic degradation of an antibiotic, doxycycline (Pronina et al., 2015). The coating was found to be mechanically stable and the porous nature of coated expanded clay improved the adsorption of pollutant. Vereb et al. (2014) investigated the photocatalytic degradation of phenol (100 ppm) using TiO_2 supported Al_2O_3 -based ceramic paper which was stable up to five 2-h cycles. Mukherjee et al. (2013) evaluated five distinct cross-linked polymer/ TiO_2 composites for the photocatalytic degradation of aspirin under artificial UV and natural solar light. The freeze dried films had porous structure and exhibited highest degradation capability but they were not strong enough to maintain their stability after seven hours. In another study, TiO_2 immobilized polystyrene beads were used for the mineralization of methylene blue and were found to be mechanically stable and possessed good photocatalytic activity which remained substantially higher up to 10 recycles (Fabiya et al., 2000).

A variety of other support materials have also been explored for catalyst immobilization and are reported in literature which include glass plates (Chekir et al., 2017; Miyawaki et al., 2016), soda lime glass (Hunoh et al., 2005), cement supports (Benhabiles et al., 2017), ceramic tiles (Kemmitt et al., 2004), aluminum (Chen et al., 2006), cellulose fibre cloth (Stephan et al., 2011), SBA-15 (Sharma et al., 2008), pebbles (Rao et al., 2012), silica gel beads (Li et al., 2014), glass spheres (Borges et al., 2015), cement slabs (Verma et al., 2015), glass rings (Manaserro et al., 2017; Parra et al., 2004), glass beads (Balasubramanian et al., 2004), organic fibres and pumice stone (Rao et al., 2004), steel coupons (Balasubramanian et al., 2004), cuddapah stone (Noorjahan et al., 2003), non-woven paper (Kernani et al., 2014), transparent raschig rings (Saien et al., 2009) and glass fibre (San You et al., 2001). The use of these types of TiO_2 immobilized support materials in photocatalytic degradation process nullified the expensive catalyst separation step after the treatment (Gaya and Abdullah, 2008). Thus, scale-up of the process could be visualized. Yet, the prolonged use of immobilized catalyst and the durability of support material to be used for longer period have not been observed in any of the reported studies.

Before visualizing the commercial-scale applications of fixed-bed photocatalysis, certain liabilities of the process need to be looked upon carefully as mentioned below:

- Durability of the supported photocatalyst;
- Inertness of the support material;
- Cost and ease of availability of the catalyst immobilized supports; and
- Film-diffusion resistance

In this context, Feitz et al. (2000) also reported that efficiency of the photocatalytic system reduces with substantial increase in treatment time using supported catalyst as compared to catalyst suspensions. An almost 60-70% reduction in the system performance has been reported in case of fixed-bed photocatalysis using immobilized TiO_2 in comparison to the suspended catalysts (Kabra et al., 2004). Thus, there are limited studies on the field-scale applications of this technique. Actually, film-diffusion resistance owing to the existence of low area to volume ratio in case of supported catalyst systems has really restricted the researchers to come up with the feasible solutions for large-scale applications in context to fixed-bed processes.

This disadvantage could be repressed with proper designing of reactor, which should allow maximum illumination of catalyst and restrain mass transfer implications (Vezzoli et al., 2013).

2.2.4 Extended photo-response efficiency of TiO₂

To explore the field-scale applications of AOPs, research is now focused towards the utilization of natural solar radiations. Using natural solar light instead of artificial UV lamps is an environmentally attractive and economical solution for photocatalysis or photo-Fenton like processes (Chan et al., 2003). The applications of solar-driven photocatalytic processes fit well for countries like India which receives immense solar light throughout the year.

In view of the solar induced applications of photocatalytic processes, the most challenging task is to look for an appropriate material/catalyst that could harvest solar radiations efficiently. In addition to this, catalyst should have an ability to resist electron-hole recombination (Park et al., 2016). Though TiO₂ has been extensively investigated for the photocatalytic degradation of a large variety of pollutants due to its low cost and photostability (Schneider et al., 2014), it is deficit in terms of high electron hole recombination and its restricted absorption only in UV region. In order to boost the photocatalytic efficiency of TiO₂, research is mainly oriented towards the suppression of electron-hole recombination and enrichment of properties related to light absorption. Selection of the appropriate physical characteristics of photocatalyst like particle size (Liu et al. 2014), crystallinity (Tanaka et al. 1991), morphology (Lakshminarasimhan et al. 2007) and crystal facets (Kiatkittipong et al. 2011) could augment the photocatalytic efficiency by the generation of photocurrent and photoluminescence. In addition to this, various effective modifications in the structure of TiO₂ either by doping with metals/non-metals or configuring nano-composites are reported in literature for developing highly efficient photocatalysts (Aba-Guevara et al., 2017; Huang et al., 2015; Lin et al., 2016; Nasir et al., 2014).

Modification of TiO₂ with metals/non-metals not only reduces the band gap of TiO₂ but also prevents frequent electron-hole recombination. Doping of TiO₂ with several noble metals like Ag (Suwanchawalit et al., 2012), Pt (Kim et al., 2005), Au (Primo et al., 2011), Pd (Ismail et al., 2010), transition metals like W (Ke et al., 2008), Fe (Yang et al., 2002), Cr (Zhang et al., 2008), Ni (Haque et al., 2013) and non-metals like N (Cheng et al., 2016), C (Ananpattarachai et

al., 2016; Markad et al., 2017), S (Ksibi et al., 2008), B (Li et al., 2013) are being reported in literature. In comparison to un-doped TiO_2 , modified TiO_2 possessing higher light absorption capacity has the ability to significantly improve the processes like enhancement of oxidation-reduction reactions, prevention of electron-hole recombination, increased organic adsorption, thereby enhancing the overall photocatalytic activity.

Numerous of studies confirmed that modification of TiO_2 with non-metals could successfully extend the photo-response efficiency of TiO_2 to such an extent that it becomes active even in visible light where as doping of TiO_2 with noble metals restrict the recombination of charge carriers on TiO_2 surface by transferring the photon excited electron to these metals (Devi et al., 2012; Kim et al., 2005). Tian et al. (2009) reported the synergistic effect of nitrogen doping followed by Au metallization in context to the enhanced visible light activity of TiO_2 for the degradation of organic pollutants. Doping of TiO_2 with nitrogen enhances the photo-response efficiency by extending its light absorption capacity whereas presence of noble metal hinders the electron-hole recombination thus, further improving the overall photocatalytic activity of the catalyst. Fang et al. (2011) also reported the extended light absorption capacity of Ag_2O modified TiON thin film but photocatalytic activity of the catalyst was not studied. However, a recent report by Gao et al. (2017) confirmed the enhanced photocatalytic activity of Ag loaded N- TiO_2 in context to methyl orange degradation.

Although miscellaneous of studies related to doped or co-doped photocatalysts as discussed above have been reported over the past few years, none of these studies has ever represented the field-scale applications of these modified catalysts. Actually, these studies possess the following liabilities which restrict their large-scale applications:

- Tedious methods have been followed using costly raw materials in almost all reported studies to prepare modified TiO_2 ; and
- Most of the studies have used modified TiO_2 in suspension mode which further adds expensive step of catalyst separation post-treatment.

To harness the advantages of doping or co-doping, the process must be economically scaled-up.

2.2.5 Pilot-scale applications of AOPs

To promote the applicability of AOPs at field-scale in near future, it is mandatory to execute the scale-up trails of lab-scale results. The successful implementation of a large-scale photocatalytic treatment process necessitates a multidisciplinary prospective between all the operational parameters which directly or indirectly affects the capture as well as subsequent utilization of the photons of light inside a reactor (Motegh et al., 2014). Photocatalytic reactors can be grouped as concentrating and non-concentrating types. Concentrating reactors are based on parabolic trough concentrators (PTC) using direct solar radiations. These reactors use only direct radiations and require solar tracking devices which are costly and difficult to maintain. These types of reactors receive large amount of photons of nearly all wavelengths. Moreover, the thermal energy from the concentrated radiation can simultaneously be employed for other applications (Al Momani et al., 2007; Parra et al., 2001). Non-concentrating reactors are simple, low cost reactors which use both direct and diffused solar radiations and are more efficient (Nogueira et al., 1996).

Photocatalytic reactors have really opened up new channels where one can visualize the field-scale applications with certain design modifications. Numerous renowned scientists have reported the detailed kinetic studies of reactors employing the basic principles of AOPs (Ola and Maroto-Valer, 2015). However in all these studies, it always remained unclear whether to follow the heterogeneous/homogeneous photo-Fenton approach or heterogeneous photocatalytic approach. Compound parabolic collector (CPC) has been discussed to the greatest extent in literature for the treatment of wastewater either through photocatalysis (Fernandez et al., 2005; Haranaka-Funai et al., 2017; Miranda-García et al., 2011; Sordo et al., 2008) or photo-Fenton (Fallmann et al., 1999a,b; Garcia Mantano et al., 2008; Michael et al., 2012; Oller et al., 2008). The reflector design of CPC with an ability to capture both (direct and diffuse) solar radiations has represented the excellent performance efficiency in context to solar photochemical as well as photocatalytic applications (Blanco et al., 1999; Funken et al., 2001). Nevertheless, use of expensive reflectors along with maintenance problems are some of the implications associated with these types of collectors. Gernjak et al. (2004) evaluated the comparison of homogeneous photo-Fenton process and heterogeneous photocatalytic process for the treatment of olive mill wastewater at pilot-scale using compound parabolic collector (CPC) and a falling-film reactor

(FFR). The photo-Fenton process proved to be more effective than photocatalysis in terms of degradation as well as mineralization efficiency. The results were almost comparable in case of each type of pilot-scale reactor i.e. CPC and FFR. Yet in all these pilot-scale reactors, industrial-scale applications of either homogeneous photo-Fenton process or heterogeneous slurry photocatalysis have not been attained owing to the prevalence of certain flaws offered by these techniques. As discussed earlier, generation of iron sludge, catalyst regeneration problems, high dose of oxidant are the major problems faced in case of photo-Fenton process while separation of catalyst and its recyclability are the concerns that are usually encountered in slurry photocatalysis which restrict their large-scale applications.

The applications of TiO_2 photocatalysis are always preferred in its fixed-form. A variety of different studies have also been reported employing fixed-bed photocatalysis for the treatment of wastewater at pilot-scale. The designing of reactor must incorporate a high ratio between activated immobilized catalyst and illuminated surface and should also ensure that sufficient density of catalyst is in contact with the aqueous solution that has to be treated so as to improve the degradation efficiency of the reactor. The effectiveness of five continuous stirred tank reactors (CSTRs) connected in series was evaluated for the photocatalytic degradation of 10 ppm of 2,4-dinitrophenol (DNP) in aqueous solution (Miyawaki et al., 2016). Square shaped container with TiO_2 immobilized glass plate served as a reactor and for the source of UV radiations, two blacklight blue fluorescent lamps of 4 W each were fixed in each reactor. The proposed system increased the degradation rate by overcoming the problem of film diffusion resistance in immobilized catalyst. The non-concentrating pebble bed photocatalytic reactor (PBPR) comprising of a horizontal or inclined trough was reported for the degradation and decolorization of reactive dye solutions (Rao et al., 2012). Decolorization and mineralization of the dyes occurred side by side with the total mineralization efficiency of 28%. Zayani et al. (2009) evaluated the photocatalytic degradation of commercial azo dye, Yellow Cibacron FN-2R (YC) in a pilot scale solar thin-film fixed-bed reactor (TFFBR). A falling film closed loop fixed bed step reactor was modeled and designed for the photocatalytic degradation of pesticides namely metolachlor and chlortoluron (Stephan et al., 2011). TiO_2 was immobilized on cellulose fibre cloth which was fixed on the steps. The reactor consisted of six similar sized regular steps and three UV-lamps and was designed to treat 5L of solution at a time. The photocatalytic degradation of emerging contaminants taking paracetamol (50 ppm) as a model contaminant

using supported TiO_2 over glass spheres was carried out in a packed bed photoreactor with continuous recirculation system using sodium vapour lamp as a light source resulting into 42% removal of paracetamol after 8 hour of photocatalytic treatment (Borges et al., 2015). Likewise, various other pilot-scale fixed-bed photocatalytic reactors including continuous flow packed-bed reactor (Pestana et al., 2014), thin film inclined step photo-reactor (Berkani et al., 2015), continuous annular reactor (Yurdakal et al., 2010), solar mesh reactor (Feitz et al., 2000) and solar cascade reactor (Chan et al., 2003) have also been reported for the degradation of organic pollutants present in water.

Though extensive literature exists in the area of fixed-bed photocatalytic reactors, the main implication that arises with almost all the configurations of reactors is the scale-up studies for commercial applications. The major pitfalls of the above discussed pilot-scale fixed-bed studies include:

- Increased treatment time;
- High energy costs;
- Poor recyclability efficiency of the immobilized catalyst;
- Film-diffusion resistance; and
- Frequent electron-hole recombination.

Thus, these drawbacks have to be nullified by one or the other way to visualize its commercial applications.

2.2.6 Integration of photocatalysis and photo-Fenton

The increasing emphasis on the development of environment friendly and effectual treatment methods to completely eliminate recalcitrant organic pollutants from wastewater has prompted the scientists to investigate new innovative modifications that can be implanted in the present advanced wastewater treatment technologies. Research in this particular area is always being focused towards the reduction in treatment time along with cost optimization of the process. To enhance the degradation efficiency and reduce the time of photocatalytic reaction, many efforts have been devoted and reported in literature for increasing the concentration of hydroxyl radicals prevailing in the photocatalytic process. Addition of oxidants like H_2O_2 , $\text{S}_2\text{O}_8^{2-}$, IO_4^- , ClO_4^- have already been proven effective for improving the reaction rate (Malato et al.,

2000). There are few other reports where coupling of the two processes (photocatalysis and photo-Fenton) have been practiced for achieving higher degradation efficiency of the treatment system (Mazille et al., 2009a,b; Sakhtivel et al., 2002; Su et al., 2015). Kumar et al. (2014) observed the synergistic effect of the combined treatment process i.e. photo-Fenton and photocatalysis over the individual processes in context to the treatment of hospital wastewater. The process efficiency was enhanced to a great extent with almost 99% removal efficiency of COD and subsequently resulting into the significant reduction in treatment time as well. The improved degradation efficiency by the introduction of Fenton reagent in the TiO_2 photocatalytic system can be attributed to the production of sufficient amount of hydroxyl radicals generated simultaneously by both ongoing processes i.e. photocatalysis and photo-Fenton at the same time. Moreover, presence of iron suppresses the recombination of electrons and holes in TiO_2 thereby enhancing its photocatalytic activity (Zhu et al., 2004).

In view of the above discussed studies, integrated process of photocatalysis and photo-Fenton has demonstrated an excellent degradation efficiency of the system by overcoming most of the concerns raised by the individual processes which include recombination of electrons and holes, increased treatment time and mass transfer implications. Nonetheless, viability of this integrated process for commercial or field-scale applications is still debatable due to the following reasons:

- Most of the reported studies deal with the cases where both the catalysts are in suspension form thus restricting the practical applicability of the technique due to the expensive separation of catalyst post-treatment; and
- None of the studies have been reported yet with complete immobilization of both catalysts (iron source and TiO_2) for the degradation of pollutants.

Fixed-bed studies using cost-effective and durable catalyst immobilized inert supports incorporating both photocatalysis and photo-Fenton at the same time can open up new channels in this particular field for the effective treatment of wastewater. Furthermore, these supports in conjunction with doped catalysts thus incorporating modified photocatalysis along-with photo-Fenton could present a ground-breaking step in the field of AOPs for the water treatment.

2.3 Summary

AOPs have proven their credentials over conventional water treatment technologies for the degradation and mineralization of a variety of recalcitrant organic pollutants present in wastewater. Nevertheless, field-scale applications of these processes are yet to be explored.

Even though heterogeneous photocatalysis using suspended TiO_2 revealed reasonably good degradation efficiency, certain operational implications like expensive separation of catalyst post-treatment, ineffective utilization of solar spectrum, recombination of charge carriers, inefficient recovery of catalyst, have restricted its applicability at industrial-scale. Homogeneous photo-Fenton process has even demonstrated much better degradation and mineralization efficiency of the organic pollutants in comparison to photocatalysis. However, generation of iron sludge, catalyst regeneration problems and high dose of H_2O_2 in case of homogeneous photo-Fenton process limits its large-scale applications. Heterogeneous photo-Fenton process nullified the problem of iron sludge generation but with dramatically reduced process efficiency.

Some of the pitfalls of heterogeneous photocatalysis like expensive separation of catalyst post-treatment have been resolved by immobilization of catalyst over inert supports. But at the same time, fixed-bed studies add further limitations to the process like increased treatment time, mass-transfer implications and poor recyclability efficiency of the immobilized catalyst, which remain unresolved. While, doping of the catalyst with metals/non-metals have reduced the complications like ineffective use of solar light and recombination of charge carriers but tedious catalyst synthesis procedures using expensive precursors remained their core problem. Moreover, studies related to immobilization of doped catalyst are scarce.

In literature, many pilot-scale reactors employing homogeneous photo-Fenton, heterogeneous slurry and fixed-bed photocatalysis have been discussed. Compound parabolic collector (CPC) has shown its great potential for the destruction of a wide range of pollutants but its higher capital cost have raised the economic issues of AOPs. Thus, non-concentrating solar fixed-bed reactors have been found to be more economical and feasible for wastewater treatment. However, none of the studies has demonstrated the prolonged use or activity of the immobilized catalyst under flow conditions. Hence, extensive investigation is still required in context to fixed-

bed photocatalytic reactors related to their proper design modifications and parametric optimization.

Very few studies are available in literature related to the concept of dual process by coupling of photocatalysis and photo-Fenton. The studies have demonstrated a significant improvement in the process efficiency by overcoming most of the concerns faced in discrete processes. Fixed-bed studies incorporating this dual effect have not discussed till now. Thus, commercial visualization of this process has not been attained yet.

2.4 Objectives of the study

As a result, efforts have been made in the present research work to suppress the pitfalls offered by individual AOPs i.e. photocatalysis or photo-Fenton by coupling these two processes together in the same treatment unit. The commercial applications of the technique were visualized by executing this dual process in fixed-mode. Sustainable low cost fixed catalysts made out of waste materials along with TiO_2 incorporating dual effect (photocatalysis and photo-Fenton) were used in dual effect studies. The dual process resulted into significant reduction in treatment time of targeted pharmaceutical compounds i.e. Cephalexin (CEX) and Pentoxifylline (PEN). The feasibility of the technique was confirmed by conducting the degradation studies in pilot-scale solar reactors. In this view, the doctoral research work was conducted with the following objectives:

- Selection and durability studies of novel inert support materials for (i) TiO_2 and (ii) doped TiO_2 immobilization for the degradation of selected compounds;
- To study the synergistic effect of photocatalysis and photo-Fenton with selected immobilized photocatalyst; and
- Development of pilot-scale solar reactors employing fixed-bed photocatalysis for degradation and testing of pharmaceutical compounds.

Chapter 3

MATERIALS AND METHODS

The current chapter includes all materials used along with the methodologies adopted for performing the degradation experiments, analysis and characterization of samples during the degradation studies of pharmaceuticals.

3.1 Collection of pharmaceutical compounds

Cephalexin (CEX) and Pentoxifylline (PEN) were used as model pharmaceutical compounds in the present study. CEX, (6R,7R)-7-[(2R)-2-amino-2-phenylacetamido]-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid was procured as a capsule under the brand name, 'Phexin' from local drugstore, Patiala, Punjab (India). CEX was used in the native form without any further purification/modification. The structure of CEX is shown in figure 3.1.

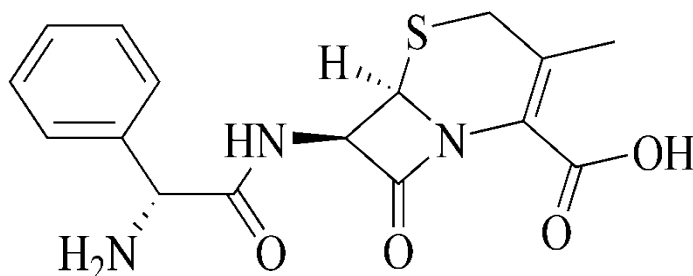


Figure 3.1: Chemical structure of Cephalexin.

CEX is a beta-lactum antibiotic, which is most commonly used to treat several urinary and respiratory tract infections. Cephalexin exhibits only 10% biotransformation rate leading to the fact that rest 90% is excreted out in urine unchanged (Comninellis et al., 2008). The evidence of non-biodegradability of CEX can be revealed from its ubiquitous presence in various aquatic environments such as coastal water (Gulkowska et al., 2007), municipal wastewater (Li et al., 2009) and treated effluent from industry (Saravanane and Sundararaman, 2009).

The other pharmaceutical compound, PEN, 3,7-dimethyl-1-(5-oxohexyl)-2,3,6,7-tetrahydro-1H-purine-2,6-dione, >98% purity, was purchased from TCI Chemicals Pvt. Ltd.

(India). PEN was employed as such without undergoing any further purification. The structure of PEN is shown in figure 3.2.

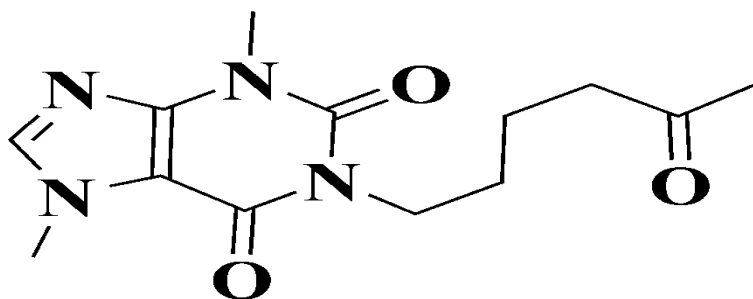


Figure 3.2: Chemical structure of Pentoxifylline.

PEN is a vasodilator drug which is intended for the treatment of muscle pain arising from peripheral artery disease. PEN has been frequently detected at various concentrations in effluents resulting from different sources like Canadian sewage treatment plants (Metcalf et al., 2003), hospitals in Taiwan (Lin et al., 2008), river in Romania (Moldovan et al., 2006) and in Germany (Sacher et al., 2008). The persistence and non-biodegradable nature of PEN has been confirmed in various reported studies (Kang et al., 2012; Lin et al., 2015; Mone et al., 2010).

3.2 Chemicals and reagents

Degussa TiO₂-P25, containing anatase and rutile in the ratio 70:30, having 50 m²g⁻¹ as BET surface area with particle size as 30 nm, procured from Evonik industries (India), was used as a photocatalyst. Hydrogen peroxide (H₂O₂), 30% w/v, (AR grade) was used as an oxidant and was obtained from Ranbaxy (India). Waste fly ash (FA) and foundry sand (FS), used as alternative sources of iron, were collected from local industry, Patiala, Punjab (India). H₂SO₄ (0.1N) and NaOH (0.1N), procured from SD Fine Chemicals Ltd. (India), were used initially for pH adjustment. Fine cotton cloth for making pockets for entrapping FS and FA was procured from local market, Patiala, Punjab (India). Clay used for making spherical beads was obtained from local vendor, Patiala (India). Sodium acetate (>98.5% purity) and acetic acid (>99.5% purity) used for the preparation of acetate buffer were procured from TCI Chemicals pvt. Ltd. (India). Sodium carbonate (anhydrous), >98.5% purity, used to remove H₂O₂ interference prior to COD analysis was procured from Loba Chemicals (India). Silver nitrate, AgNO₃ (>99%

purity), urea, NH_2CONH_2 (>99% purity), and Potassium Bromate, KBrO_3 (AR) were obtained from Loba Chemicals (India). Potassium thiosulphate, $\text{K}_2\text{S}_2\text{O}_8$ (AR) was obtained from Merck (U.S.).

Silver sulphate (AgSO_4) and concentrated sulphuric acid (H_2SO_4) of analytical grade (AR), used during COD estimation were obtained from SD Fine Chemicals Ltd. (India). The reagents including phosphate buffer, calcium chloride (CaCl_2), ferric chloride (FeCl_3), magnesium sulphate (MgSO_4) and sodium hydroxide (NaOH) of AR grade were used during BOD determination and were also purchased from SD Fine Chemicals Ltd. (India).

For iron estimation, hydroxylamine hydrochloride, ammonium acetate, 1, 10-phenanthroline monohydrate, concentrated hydrochloric acid (HCl), ferrous ammonium sulphate and potassium permanganate were used. All these chemicals were of analytical grade (AR) and were procured from Loba Chemie pvt. Ltd. (India).

All other reagents used for the analysis of anions (nitrite, nitrate, sulfate and ammonical nitrogen) include phosphoric acid, sulfanilamide, N-(1 Naphthyl)-ethylene diamine dihydrochloride, Barium chloride, sodium tetra borate, boric acid, sodium thiosulfate, methylene blue and isopropyl alcohol. These all chemicals were also of analytical grade and were procured from Loba Chemie pvt. Ltd. (India). The double distilled water was used for preparing all aqueous solutions.

3.3 Entrapment for iron source

Small pockets (Length=5 cm, Breadth=3.5 cm) of fine cotton cloth (Figure 3.3) were made manually for the entrapment of iron source i.e. FS and FA. FS and FA were used as an alternative iron source in the present study. Characterization of FS and FA through EDS analysis for the presence of iron has already been reported in our earlier studies (Rajput et al., 2016). For reference, the data of EDS analysis has been shown in table 3.1 and 3.2. The material (fine cotton cloth) was selected for sustainable leaching of iron besides remaining inert. Pockets containing FS, FA and mixture of FA/FS were named as P1, P2 and P3 respectively. A known amount of FS and FA was weighed before entrapment in pockets. In this manner, each pocket was marked carefully based on the amount of FS/FA it contained. The pockets were not chosen

as an entrapment material for photocatalyst owing to the very fine particle size of TiO_2 (30 nm) that would easily drain away from the pockets after single use.

Table 3.1: Composition of foundry sand through EDS analysis

Element	Na K	Mg K	Al K	Si K	K K	Ca K	Ti K	Fe K	Cu K	Total
Weight %	1.93	1.21	7.85	58.1	1.77	1.49	1.36	23.16	3.13	100
Atomic %	2.73	1.62	9.48	67.43	1.48	1.21	0.93	13.52	1.6	

Table 3.2: Composition of fly ash through EDS analysis

Element	O K	Mg K	Al K	Si K	K K	Ca K	Ti K	Fe K	Cu K	Total
Weight %	55.87	0.42	17.66	21.85	0.67	0.5	1.33	1	0.7	100
Atomic %	69.45	0.35	13.02	15.47	0.34	0.25	0.55	0.35	0.22	

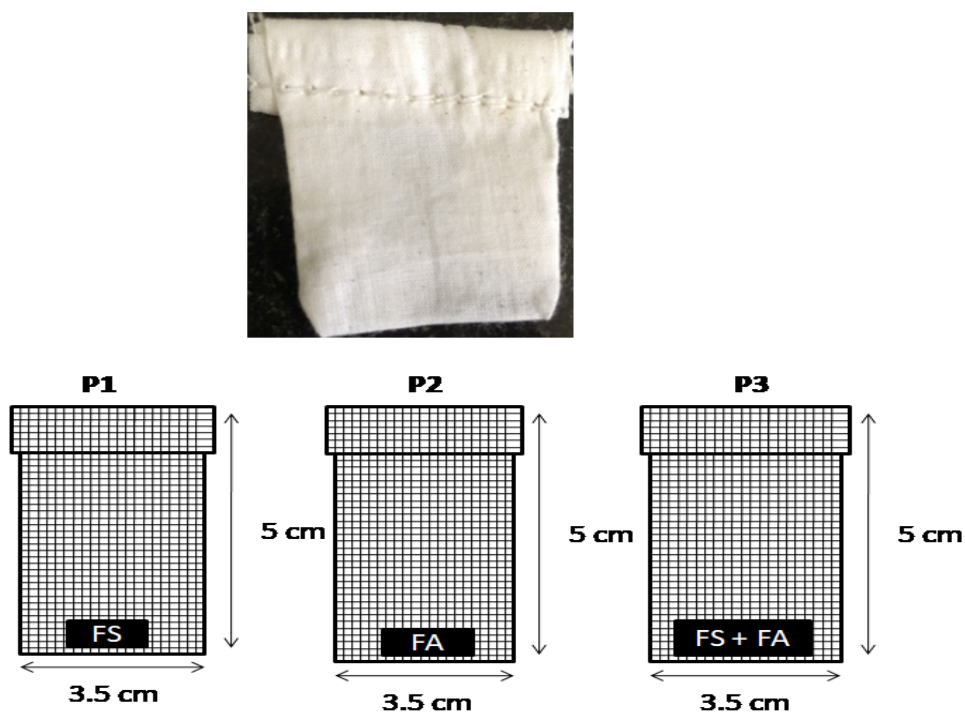


Figure 3.3: Actual photograph along with schematic diagram of pockets (P1, P2 and P3) made of fine cotton cloth containing desired amount of FA/FS.

3.4 TiO₂ immobilization

For TiO₂ immobilization, inert supports of various different shapes (Figure 3.4) including hollow circular disc (Outer diameter = 13.5 cm, Inner diameter = 5 cm), rectangular slabs (Length = 6.5 cm, Breadth = 2.5 cm) and spherical beads (Average diameter = 1.5 cm) were prepared manually using waste foundry sand (FS) with clay as binding material in the ratio (1:1). All supports were calcined in muffle furnace for almost 2 hr at high temperature ranging from 800-1000°C to become solid and gain strength. These supports without TiO₂ immobilization were named as 'blank' supports. Iron was leaching by-default from these supports under acidic conditions owing to the presence of FS and thus, these blank supports were used in the photo-Fenton experiments. While for TiO₂ immobilization, standard dip coating method was followed. Briefly, 2% slurry of TiO₂ was prepared using double distilled water and was sonicated for nearly 30 min for proper dispersion and mixing of TiO₂ particles. The blank supports were dipped in the sonicated solution of TiO₂ for almost 24 h with constant shaking. The supports were then calcined for an hour in a muffle furnace at 400 °C for the effective binding of catalyst particles over the surface of supports. After bringing the supports to room temperature, each support was washed with water to remove the loosely bound particles of TiO₂. Two cycles of catalyst coatings were sufficient for the formation of uniform layer of TiO₂ on each support. After TiO₂ immobilization, the supports were given the prefix 'composite' as it contained both catalysts i.e. iron (FS) as well as TiO₂. For the control experiments, all supports (disc, slabs and beads) were prepared using only clay without adding any iron source i.e. FS. These supports after TiO₂ immobilization were given the prefix 'control' and were used for conducting photocatalytic experiments as it contained only TiO₂.

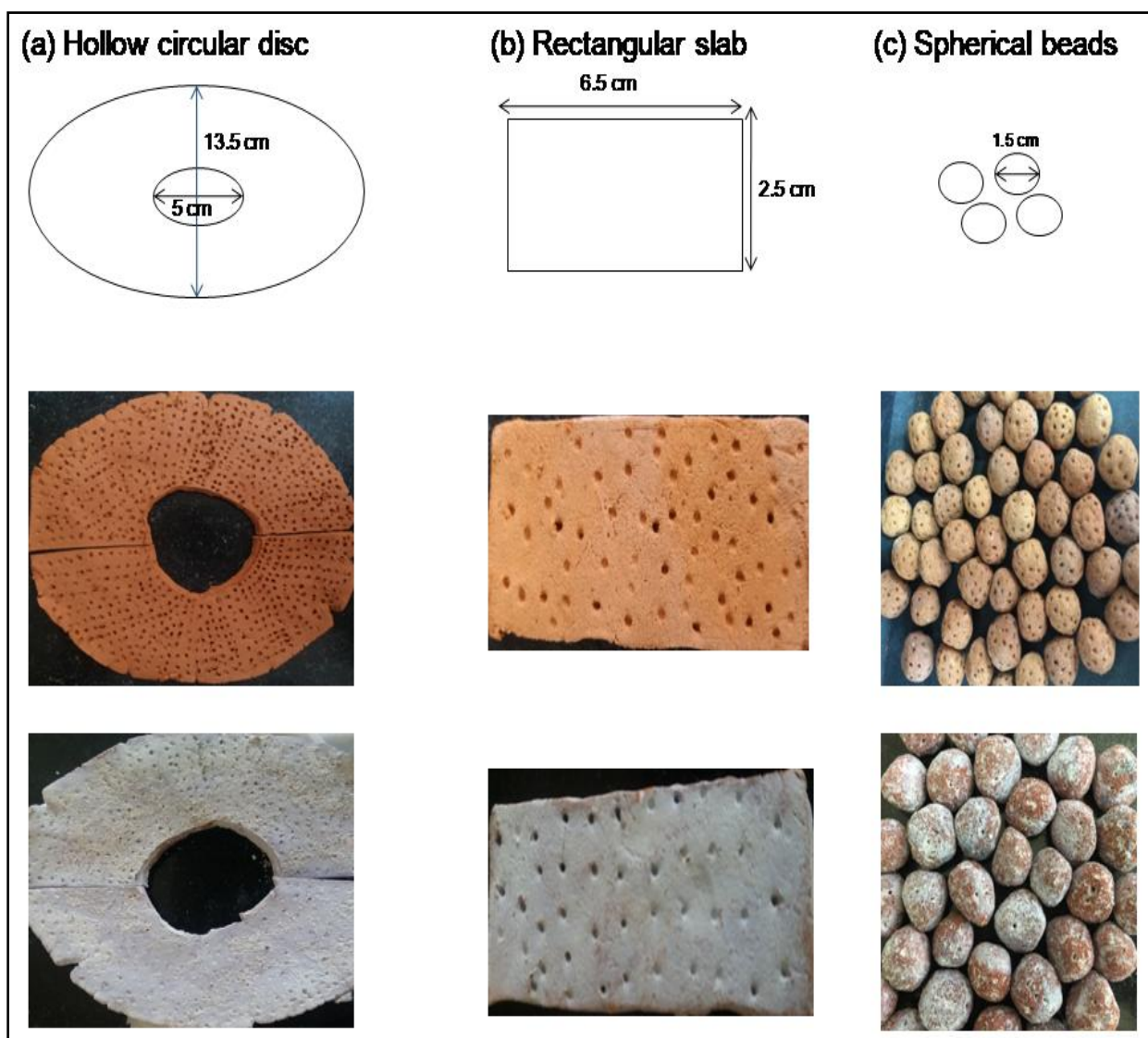


Figure 3.4: Line diagram along with actual photographs of blank and TiO_2 immobilized different shaped composite supports (a) hollow circular disc, (b) rectangular slab and (c) spherical beads.

For further enhancing the durability and stability of supports, various other combinations of materials using FS, FA and clay were used to prepare spherical composite beads (Diameter = 1.5 cm). Two other types of composite beads i.e. (i) FA + clay (1:1), and (ii) FS + FA + clay (1:1:2) were prepared for TiO_2 immobilization. The actual photographs of blank and TiO_2 immobilized composite beads are shown in figure 3.5. The diameter of beads was measured through vernier caliper. Beads were prepared manually of nearly the same size. From a lot,

nearly fifty beads were picked and their diameter was measured from different sides. The average value of diameter from all beads was considered. The coating of TiO_2 on beads was done using the same dip coating method as described earlier. TiO_2 load on each bead was approximately in the range 30-40 mg. The thickness of catalyst film on beads was about $40\mu\text{m}$ as confirmed by analysis through SEM/EDS. The clay/FA/FS/ TiO_2 composite beads were termed as Fe- TiO_2 composite in the present study.

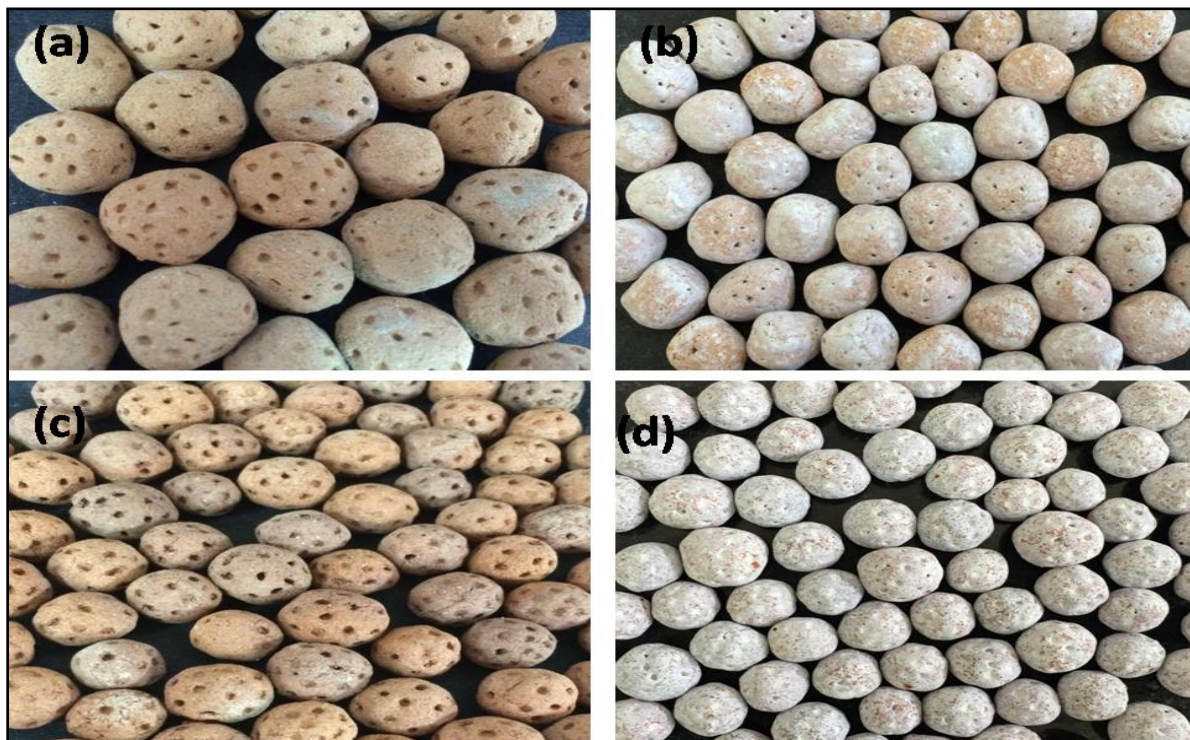


Figure 3.5: Actual photographs of (a) blank beads (clay/FA), (b) TiO_2 immobilized composite beads (clay/FA/ TiO_2), (c) blank beads (clay/FA/FS) and (d) TiO_2 immobilized composite beads (clay/FA/FS/ TiO_2).

3.5 Experimental set-up and procedure for dual effect studies at lab-scale

The photocatalytic experiments were conducted at laboratory-scale in a wooden UV chamber that contained seven UV tubes (Philips) of 36 W (365 nm) each attached underneath the roof of chamber (Figure 3.6). A 1000 mL borosilicate glass bowl (17 cm diameter and 5 cm height) was utilized as a batch reactor. All experiments were performed at an average UV intensity of $23 \pm 2 \text{ Wm}^{-2}$ as measured by means of an eppley radiometer (model no. 33013). For

getting the required intensity of UV irradiations throughout the reaction, the distance of reactor was varied from the tubes through lab jack. The stock solution (100 mgL^{-1}) of each pharmaceutical compound (CEX and PEN) was made using double distilled water. The working solution of 50 mg L^{-1} (200 mL) for each compound i.e. CEX and PEN was used for the photocatalytic experiments.

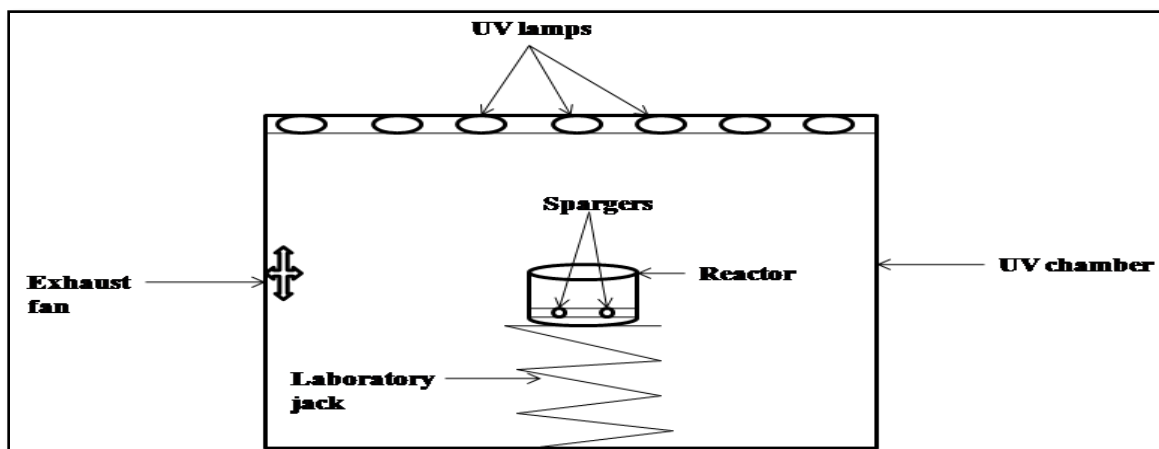


Figure 3.6: Experimental set-up at lab-scale

For dual effect studies in slurry mode, the aqueous solution of PEN or CEX was magnetically stirred with desired amount of TiO_2 and FA/FS under UV-A irradiations. The required aeration was provided by means of sparger. In the subsequent trails, experiments were performed in partial fixed-mode by using P1/P2/P3 along with TiO_2 suspension and solution was stirred magnetically with supply of proper aeration.

While for completely fixed-bed studies, same batch reactor was employed with P1 and appropriate number of TiO_2 coated clay beads for the treatment of target pharmaceuticals. For sustaining the homogeneity of reaction, two spargers were used to supply sufficient amount of aeration. The spargers were placed at equal distance from centre along the diameter of reactor thus visibly confirming the uniform aeration throughout the solution. The flow rate of the inlet air was 3.5 L min^{-1} . The same set-up was utilized for fixed-bed trials using appropriate number of rectangular slabs or spherical beads covering the entire bottom of the batch reactor with adequate supply of aeration by means of two spargers. Whereas, for fixed-bed studies using hollow circular disc, continuous stirred type conditions were maintained using a magnetic stirrer. Adequate amount of sample was collected through a syringe after uniform time intervals, filtered

in case of slurry processes through Millipore filter (0.45 μm) and was subsequently analyzed. The same average intensity was kept in artificial UV irradiations taking into consideration the average UV intensity of sunlight. After optimization of operating parameters under artificial UV light, the experiments were carried out in natural solar light. The total solar intensity was measured regularly during the experimental period by means of pyranometer. The average solar intensity during the experimental period was in the range of 800-900 Wm^{-2} . All experiments were performed thrice for reproducibility of results. Suitable statistics has been applied for proper validation of results. The mean value of results has been quoted in the study and standard deviation has been represented in the form of error bars in graphs wherever required.

3.6 Synthesis of doped TiO_2 (Ag- TiO_2 , N- TiO_2 and Ag-N- TiO_2)

In the present study, Ag doped TiO_2 , N doped TiO_2 and N, Ag doped TiO_2 were synthesized for enhancing the light absorption capacity of TiO_2 -P25. For the preparation of silver doped TiO_2 , silver ions were deposited on TiO_2 -P25 through surface impregnation method (Kaur et al., 2016). Briefly, 2g of TiO_2 -P25 powder was added to 15 mL of double distilled water which was then sonicated for nearly 30 minutes followed by stirring for an hour (Solution A). Then desired amount of dopant solution (Solution B) i.e. AgNO_3 in this case was added to TiO_2 -P25 suspension drop wise under continuous stirred conditions. The suspension was allowed to stir for about 8 h. Then it was left at room temperature overnight. The suspension was then dried in oven at 80 $^\circ\text{C}$ for around 12 h. The dried material was grounded into powder form using mortar and pestle followed by calcinations at 450 $^\circ\text{C}$ for 2h.

While for the synthesis of nitrogen doped TiO_2 , exactly the same procedure was followed using urea as a source of nitrogen. Nitrogen-silver co-doped TiO_2 was also prepared using the same method with fixed concentration of nitrogen solution (0.1 wt%). Firstly the adequate concentration of silver solution was added to the TiO_2 suspension followed by the addition of nitrogen solution (0.1 wt%). The schematic procedure for the synthesis of doped TiO_2 has been represented in figure 3.7.

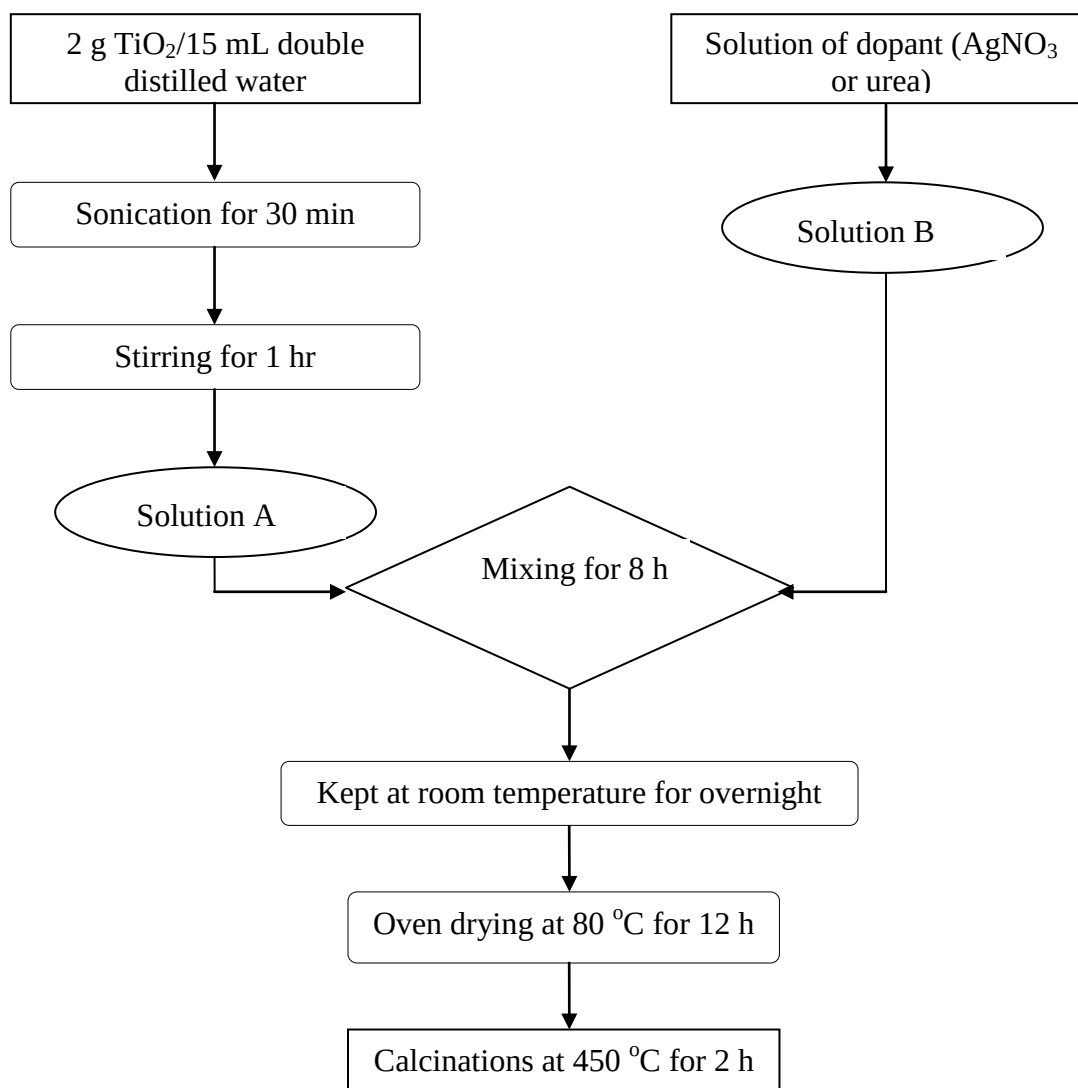


Figure 3.7: Schematic diagram for the overall synthesis of doped TiO₂.

3.7 Doped TiO₂ immobilization

For conducting the modified photocatalytic experiments in fixed-bed mode, doped TiO₂ (Ag-TiO₂ or N-TiO₂ or N-Ag-TiO₂) was immobilized on the same spherical clay beads (used for control experiments) as discussed in Section 3.4. The actual photograph of beads is shown in figure 3.8. The catalyst immobilization on beads was followed using the same dip coating method as described earlier. Here, the required number of beads was dipped in catalyst suspension (2% doped TiO₂ slurry in methanol) under continuous shaking conditions for around 1h. Two coatings were sufficient enough to obtain a uniform layer of catalyst on beads. The

beads were muffled at 300 °C after each coating. Then beads were washed with water to drain off the loosely bound catalyst particles.

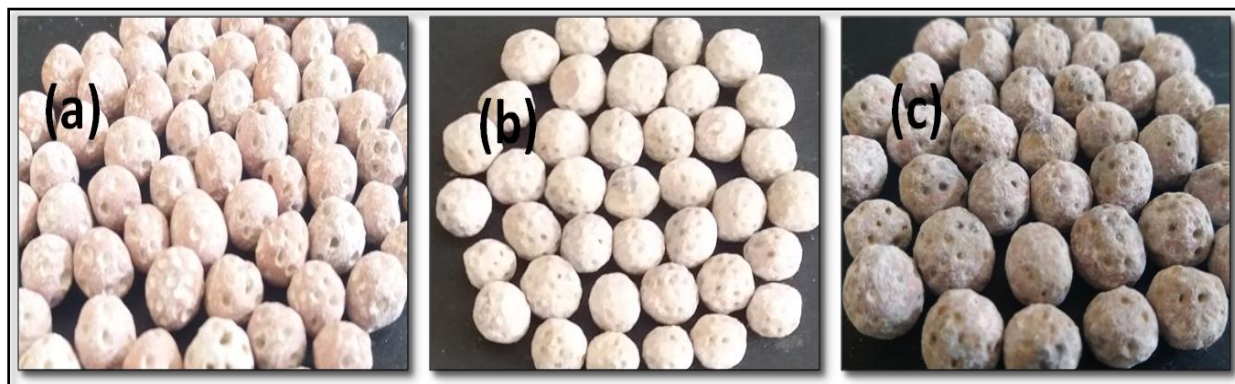


Figure 3.8: Actual photograph of (a) Ag-TiO₂, (b) N-TiO₂ and (c) N-Ag-TiO₂, immobilized clay beads.

While for performing the modified dual process in fixed-mode, blank composite beads (clay/FA/FS) described in section 3.4 were used for doped TiO₂ immobilization (Figure 3.9). The catalyst was immobilized in the same manner as described in case of clay beads. This immobilization system using composite beads is termed as Fe-Ag-TiO₂ composite owing to the existence of iron in composite (due to FA/FS). These Fe-Ag-TiO₂ composite contributed to dual effect studies (modified photocatalysis and photo-Fenton) as iron was leaching in-situ from beads owing to the presence of FA and FS.

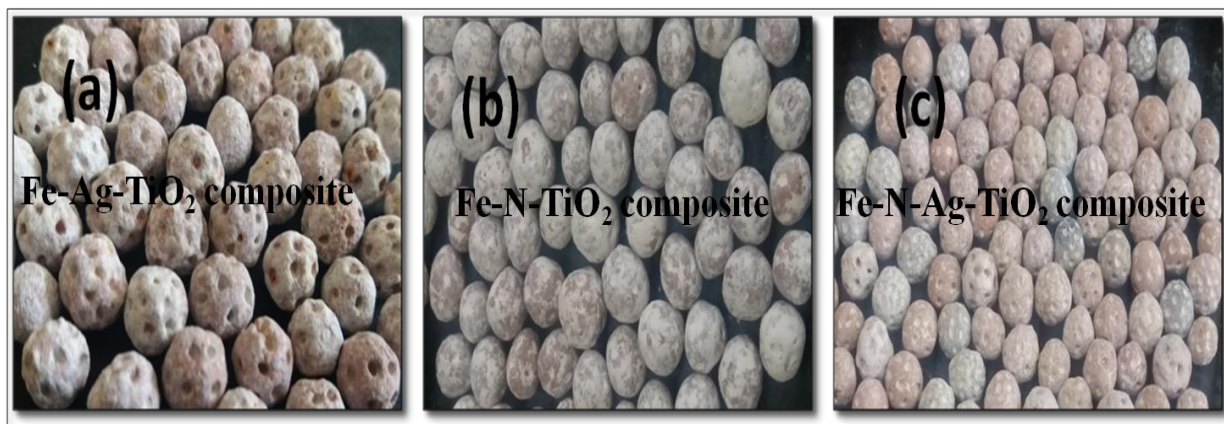


Figure 3.9: Actual photograph of (a) Fe-Ag-TiO₂ composite, (b) Fe-N-TiO₂ composite and (c) Fe-N-Ag-TiO₂ composite.

3.8 Experimental set-up and procedure for modified dual effect studies at lab-scale

The lab-scale photocatalytic experiments for the degradation of pharmaceuticals (PEN or CEX) were carried out in 100 mL glass beakers (batch reactor in this case) with 40 mL of pharmaceutical solution (50 mg L^{-1}) under natural solar irradiations. For each experiment, desired amount of doped catalyst was added to the pharmaceutical aqueous solution and was stirred for 30 min in dark. Adsorption studies were followed by exposing the pharmaceutical solution under continuous stirring in natural sunlight. The operating parameters including concentration of dopant, dose of catalyst, addition of oxidant, were optimized in slurry mode. For fixed-bed photocatalytic studies, adequate number of doped catalyst immobilized beads covering the entire bottom surface of batch reactor at optimized conditions was used for the degradation of pharmaceuticals under sunlight. While for modified dual process in fixed-mode, appropriate number of Fe-Ag-TiO₂ composite was used at optimized conditions for the degradation of pharmaceuticals under sunlight. Adequate amount of sample ($\sim 3 \text{ mL}$) was taken out at regular intervals of time, filtered in case of slurry photocatalysis through syringe filter and was subsequently analyzed.

3.9 Pilot-scale solar fixed-bed glass reactor

A solar non-concentrating flat-bed reactor ($40 \text{ cm} \times 20 \text{ cm} \times 2.5 \text{ cm}$) made up of glass was employed for the degradation of PEN and CEX under natural solar irradiations. The reactor was provided with two inlets and two outlets and also contained a provision of up to 5 detachable glass baffles (Length = 6 cm, Height = 2.5 cm, Thickness = 0.5 cm) as depicted in figure 3.10. The reactor was operated in re-circulation mode and was designed to treat a total volume of 5 L. Pharmaceutical aqueous solution (5 L) with adequate amount of H₂O₂ was pumped from the storage tank through the reactor bed where it came in contact with Fe-TiO₂ composite beads at optimum flow rate and then circulated again into the storage tank. The pH of the solution was stabilized to its natural pH i.e. 4 with addition of adequate amount of acetate buffer. Around 3-4 mL sample was collected at regular intervals of period and was subsequently analyzed. The reactor was shielded with transparent cling film to prevent any evaporation losses.

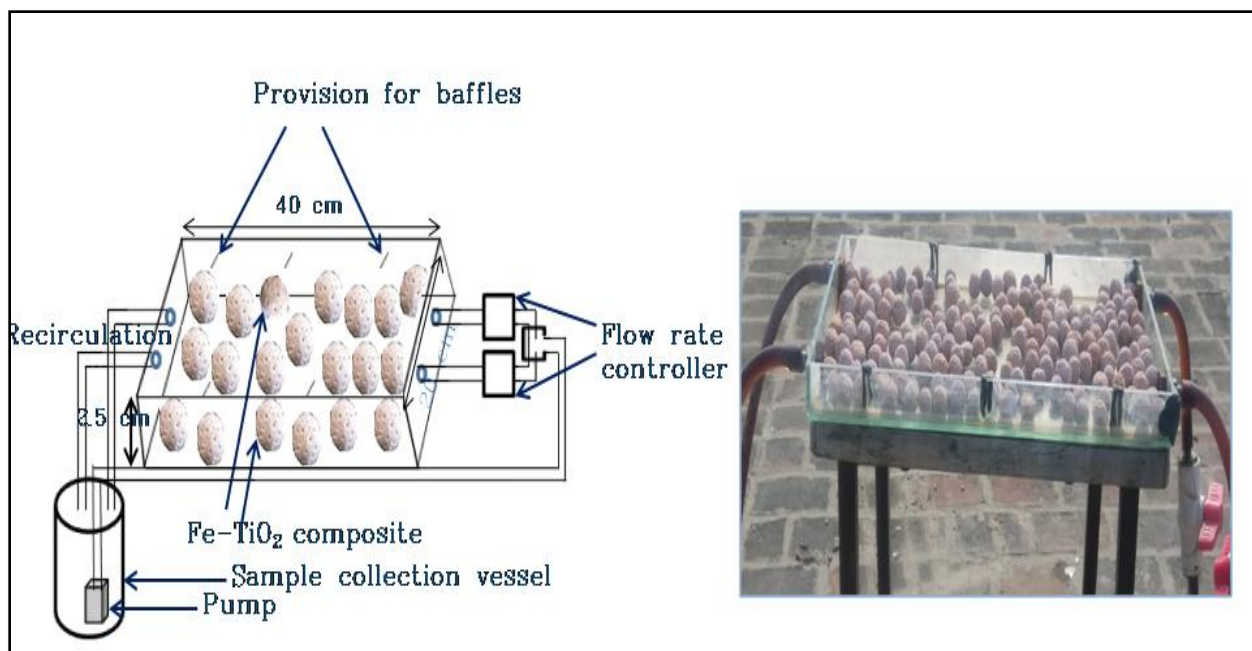


Figure 3.10: Line diagram along with actual photograph of pilot-scale glass reactor.

3.10 Pilot-scale solar fixed-bed once through cascade reactor

A packed-bed reactor (Length = 25 cm; Breadth = 16 cm; Depth = 3 cm) made up of aluminum was fabricated for studying the once-through fixed-bed system. Sufficient quantity of spherically shaped Fe-TiO₂ composite was placed inside the reactor covering its entire bottom surface. All experiments were conducted with 5 L of CEX or PEN solution (50 mgL⁻¹) under natural solar irradiations at acidic conditions adjusted with addition of adequate amount of acetate buffer. Acidic conditions were maintained in order to facilitate the photo-Fenton reaction along with photocatalysis. Aqueous solution of pharmaceutical (5 L) with appropriate concentration of H₂O₂ was pumped from the tank through the reactor where it came in contact with Fe-TiO₂ composite at fixed flow rate and was then collected in a collection tank. Approximately 3 mL of sample was collected for analysis at regular intervals of time period.

For a cascade reactor system, reactors having similar dimensions were connected in series and were placed on different steps maintained at equal heights as shown in figure 3.11. In case of preliminary studies, experiments were conducted in re-circulation mode to confirm the prominence of in-situ dual effect and evaluate the overall degradation efficiency of process as

well as treatment time. The parametric optimization was carried out in continuous mode of cascade reactor system.

The space time (τ) or retention time of a single reactor was calculated according to the following formula:

$$\tau = \frac{V}{v_o} \quad (3.1)$$

Where, τ = space time (min), V = volume of reaction mixture in a reactor (L), v_o = volumetric flow rate (Lmin^{-1})

Volume of reaction mixture in a reactor was calculated after subtracting the volume of reactor covered with spherical composite beads.

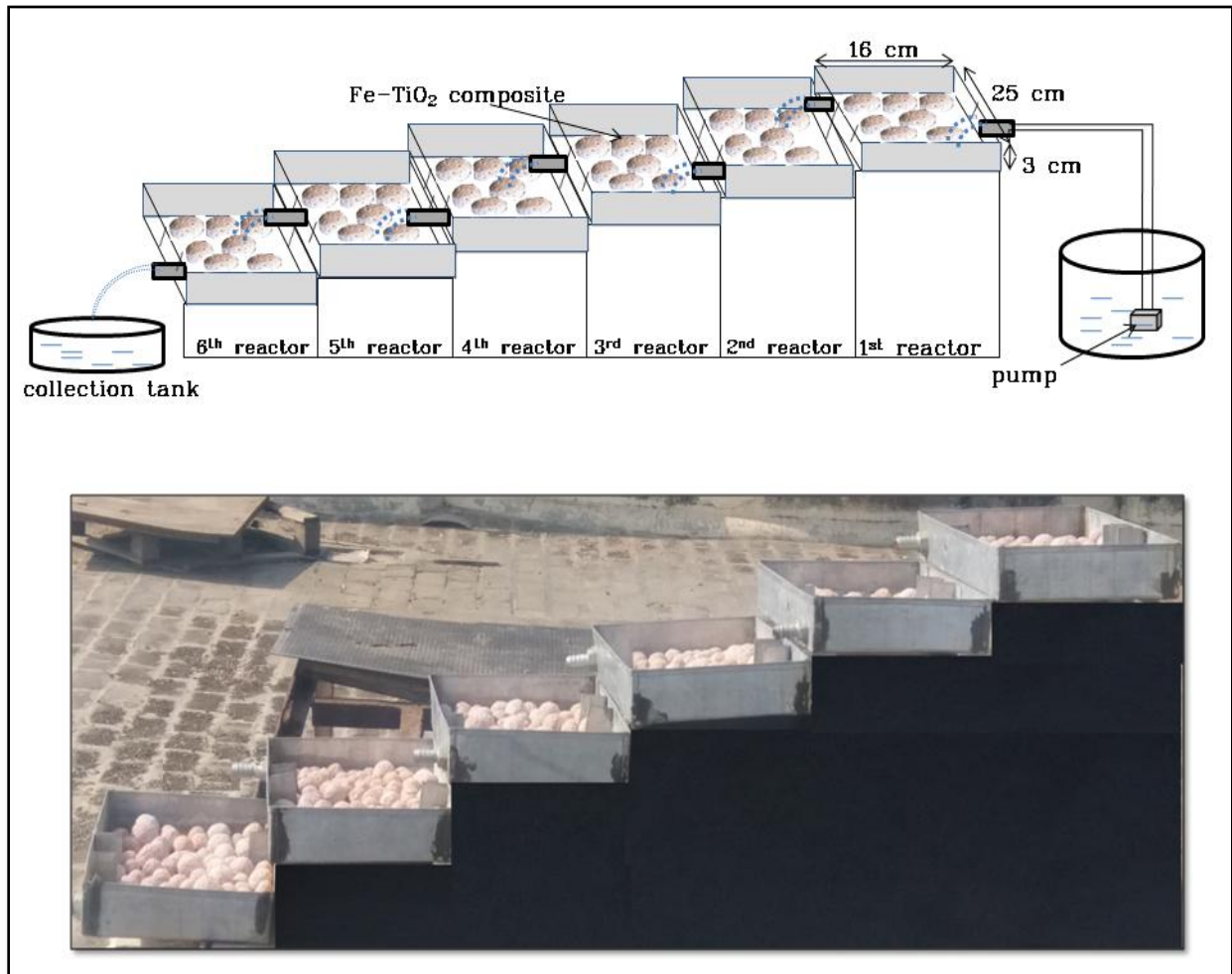


Figure 3.11: Line diagram along with actual photograph of pilot-scale cascade reactor.

All solar experiments were conducted from 9 a.m to 4 p.m at Thapar University, Patiala (30.3398° N, 76.3869° E), Punjab, India. The solar intensity was measured regularly by means of pyranometer during the experimental period. All experiments (lab-scale or pilot-scale) were performed at-least three times for reproducibility of results and suitable statistics has been applied for evaluation of results. The mean value of results has been quoted in the study and standard deviation has been presented in the form of error bars in graphs wherever required.

3.11 Treatment of real pharmaceutical effluent through in-situ dual process

Real effluent was procured from a formulation unit of a pharmaceutical industry located in Ambala, Haryana (India). Coagulation–flocculation was carried out using FeCl_3 as a coagulant. The experiments were conducted in a jar test apparatus with a wastewater volume of 1000 mL stirred at 120 rpm for initially 30 s followed by slow agitation for 15 min. The flocs were allowed to settle for 1 h and the supernatant was collected. The process was optimized using various concentrations of FeCl_3 . Coagulation–flocculation was used as a pre-treatment step prior to the execution of all photo-experiments.

The batch experiments for the photo-treatment of effluent were carried out at laboratory-scale in a wooden UV chamber using the same borosilicate glass bowl as a batch reactor as discussed in section 3.5. The pre-treated real pharmaceutical wastewater (200 mL) was used for all photo-experiments with adequate number of catalyst immobilized Fe-TiO_2 composite beads. For maintaining the homogeneity of reaction and sufficient aeration into the treatment system, two air spargers with inlet flow rate of 3.5 L min^{-1} were used. For the time-dependent analysis, adequate quantity of sample from the batch reactor was collected by means of syringe after regular time intervals. After conducting parametric optimization under artificial UV irradiations, the experiments were performed in natural sunlight.

The statistical tool, response surface methodology (RSM) on the basis of Box-Behnken design (BBD) has been used in the present study for parametric optimization in context to the treatment of real pharmaceutical wastewater via in-situ dual process in fixed-mode. Regression analysis along-with process optimization was conducted by employing Design Expert v.6.0.8 software. The experimental data was analyzed and fitted through a second order polynomial equation, Equation 3.2.

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + e \quad (3.2)$$

Where, Y is the response, β is a constant (intercept), β_i , β_{ii} , β_{ij} are linear, quadratic as well as interaction coefficients, X_i , X_i^2 , X_j are the independent variables and e is the residual term. There are three responses (Y_1 : COD, Y_2 : Nitrate ion concentration and Y_3 : Nitrite ion concentration). Thus, multi-response along with desirability functional approach was used for the process optimization involving different responses simultaneously. The value of desirability resides between 0 and 1 rendering the closeness of response towards its ideal value (Hiwarkar et al., 2017).

Preliminary trials were executed for the treatment of real wastewater at various experimental conditions to determine the appropriate working range of operating parameters. The working range of variables or operating parameters derived from BBD model is listed in Table 3.3. The independent variables used in the study were: treatment time (A), H_2O_2 dose (B), number of beads (C). These variables were coded as follows: low (-1), center (0) and high (+1) levels. ANOVA (Analysis of variance) and coefficient of determination, R^2 were employed for assessing the significance of each operating parameter residing in the polynomial equation.

Table 3.3: The original and coded levels of operating variables

Original variables	Factors	Coded levels		
		-1	0	+1
Treatment time (t), h	A	1	3.5	6
H_2O_2 concentration, $mg\ L^{-1}$	B	150	450	1200
Catalyst dose, % area of reactor bed covered with beads	C	50	100	150

3.12 Characterization of samples

The catalysts (immobilized and doped TiO_2) were characterized through various techniques. The band gap of catalyst was analyzed through diffuse reflectance spectroscopy (DRS) with UV-2600, Shimadzu (Asia Pacific) in the range 200-800 nm. The surface morphology as well as elemental composition of the catalyst was observed through SEM-EDS

analysis (Scanning electron microscopy [model-JSM-6510LV, JEOL (Japan)] - Electron dispersive spectroscopy [model-INCA-act, Oxford instruments (U.K)]. The crystalline structure of the catalyst was analyzed through XRD (X-ray diffraction) using X'Pert pro diffractometer from $2\theta = 20-80^\circ$. The band gap energy of the catalyst was observed through UV-visible diffuse reflectance spectrophotometer (DRS), UV-2600, Shimadzu (Asia Pacific). Fourier transform infrared spectrum (FTIR) of the catalyst was recorded on FT-IR Perkin Elmer spectrometer from $4000-200\text{ cm}^{-1}$ using KBr pellets. The Raman spectroscopy was carried out employing confocal micro Raman spectrometer (STR 500, Airix Corporation, Japan) coupled with a diode green laser at 532 nm. The XPS (X-ray photoelectron spectroscopy) analysis was performed with XPS, Omicron Nanotechnology, Oxford Instruments. Thermo-gravimetric analysis (TGA) was performed with SDT Q600 TGA/DTA (TA Company, USA). Around 30 mg of sample was utilized for analysis and the sample was scanned between 30°C and 980°C under nitrogen atmosphere. In case of supported catalysts, the catalyst powder was extracted by scraping off gently from the surface of beads in order to carry out the analysis through each technique except SEM/EDS. The beads were directly used for analysis via SEM/EDS.

3.13 Analytical determinations

The analysis of the samples was carried out at regular intervals of time through UV-visible absorption spectroscopy (LABINDIA, T60 U) with $\lambda_{\text{max}}=273\text{ nm}$ and 263 nm for PEN and CEX respectively. The analysis of samples was carried out using high performance liquid chromatography, HPLC, (Shimadzu, Japan) also. The HPLC unit had a communication module (CBM-20A) with diode array detector (SPD-M20A) and with pump (LC-20 CE). The system was operated with flow rate of 1.0 mL min^{-1} in binary mode using formic acid, 0.05% in water and acetonitrile as mobile phase in case of PEN with C-18 column and having particle size of $5\text{ }\mu\text{m}$. UV detector was set at 273 nm for PEN. Ammonium acetate (0.01M) and acetonitrile (10 %) were employed as mobile phase in case of CEX with UV detector set at 263 nm . $20\text{ }\mu\text{L}$ of sample was injected each time and each analysis lasted for 20 min. The intermediates formed during the degradation of PEN and CEX were identified through gas chromatography-mass spectrometry (GC-MS) analysis. The gas chromatograph, 45x-GC (Bruker, United States) was integrated with mass detector, MS-SCION-45P (Bruker) connected with wax column of MS (length 30 m and diameter 0.25 m). The m/z was scanned in the range from 50–410. Helium was

utilized as a carrier gas with flow rate equal to 1.0 mL min^{-1} . The injection temperature was adjusted to 280°C while the temperature for GC oven was adjusted in the range $40\text{--}260^\circ\text{C}$ with every 10° increment in temperature. $1 \mu\text{L}$ of sample was injected and 1:10 split ratio was employed for GC. Standard APHA methods (1989) were followed for the monitoring and evaluation of nitrite ions (APHA, 1989: Sec. 4500- NO_2 (B)), nitrate ions ((APHA, 1989: Sec. 4500- NO_3 (E)), sulfate ions (APHA, 1989: Sec. 4500- SO_4^{2-} (E)), COD ((APHA, 1989: Sec. 5220 (C)) and for iron estimation ((APHA 2012: Sec. 3111(B)). The evolution of CO_2 was determined through gas chromatograph (NUCON-5765) employing Propak-Q column. Nitrogen was used as a carrier gas with a flow rate of 30 mL/min using thermal conductivity detector. The injection volume for gaseous sample used was 1 mL . The total organic carbon (TOC) content was monitored through TOC analyzer, model- Multi N/C 2100 BU, Analytic Jena AG Corporation (Germany). H_2O_2 interference was removed prior to COD and TOC determination by adding adequate amount of concentrated solution of sodium carbonate followed by heating at 90°C for 1 h as reported in literature (Wu and Englehardt, 2012). The generation of hydroxyl radicals was validated by monitoring the fluorescent signal through fluorescence spectrophotometer (LS-45, Perkin Elmer) at 425 nm owing to the production of 2-hydroxy terephthalic acid (fluorescent compound) resulting from the reaction between hydroxyl radicals and sodium salt of terephthalic acid.

3.14 Nomenclature for catalyst supports

Table 3.4 shows the complete list of different supports along with their naming used in different sections throughout the study.

Table 3.4: Terms defined for catalyst support materials throughout the study

Section 4.7.1	
P1, P2, P3	P1 – pocket containing FS P2 – pocket containing FA P3 – pocket containing FA + FS
Blank clay beads	Clay beads without TiO_2 coating
Control beads	(Clay + TiO_2) beads
Section 4.7.2	
Blank disc	(Clay + FS) disc without TiO_2 coating

Blank slab	(Clay + FS) slab without TiO ₂ coating
Blank beads	(Clay + FS) beads without TiO ₂ coating
Control disc	(Clay + TiO ₂) disc
Control slab	(Clay + TiO ₂) slab
Control beads	(Clay + TiO ₂) beads
Composite disc	(Clay + FS + TiO ₂) disc
Composite slab	(Clay + FS + TiO ₂) slab
Composite beads	(Clay + FS + TiO ₂) beads
Section 4.7.6	
Blank composite beads	(Clay + FA) beads or (Clay + FA + FS) beads
Control beads	(Clay + TiO ₂) beads
Composite beads	(Clay + FA + TiO ₂) beads or (Clay + FA + FS + TiO ₂) beads
Section 4.7.6 – Section 4.7.12, Section 4.10 – Section 4.12	
Fe-TiO ₂ composite	(Clay + FA + FS + TiO ₂) beads
Blank composite	(Clay + FA + FS) beads
Control beads	(Clay + TiO ₂) beads
Section 4.8	
Fe-Ag-TiO ₂ composite	(Clay + FA + FS + Ag-TiO ₂) beads
Fe-TiO ₂ composite	(Clay + FA + FS + TiO ₂) beads
Blank composite	(Clay + FA + FS) beads
Control beads	(Clay + TiO ₂) beads
Section 4.9	
Fe-N-Ag-TiO ₂ composite	(Clay + FA + FS + N-Ag-TiO ₂) beads
Fe-Ag-TiO ₂ composite	(Clay + FA + FS + Ag-TiO ₂) beads
Fe-N-TiO ₂ composite	(Clay + FA + FS + N-TiO ₂) beads
Fe-TiO ₂ composite	(Clay + FA + FS + TiO ₂) beads
Blank composite	(Clay + FA + FS) beads
Control beads	(Clay + TiO ₂) beads

Chapter-4

RESULTS AND DISCUSSION

Overview

For the first time, a novel concept of in-situ dual effect by coupling photocatalysis and photo-Fenton within the same treatment unit has been discussed completely in fixed form for the degradation of recalcitrant pharmaceutical compounds i.e. Cephalexin (CEX) and Pentoxifylline (PEN) under artificial UV irradiations as well as under natural solar light. Attempts have been made in the present study to introduce the effect of photocatalysis and photo-Fenton at the same time and at the same place in the system. The individual drawbacks of photocatalysis and photo-Fenton (electron-hole recombination, iron sludge generation, increased treatment time) have been effectively covered by this in-situ dual process. The in-situ dual process resulted into the production of hydroxyl radicals in abundance. In this context, results confirmed the drastic reduction in treatment time with in-situ dual process as compared to individual processes (photo-Fenton or photocatalysis). Moreover, using waste materials like fly ash (FA) and foundry sand (FS) as substitute for iron really define the economic viability of process along with reduction in treatment time.

Preliminary experiments were carried out with catalysts (iron and TiO_2) suspensions to confirm the synergistic effect of dual process over discrete processes (photocatalysis or photo-Fenton). For fixed-bed studies, various materials like fine cotton cloth for catalyst entrapment and clay in conjunction with FA and FS for catalyst immobilization were used. Comprehensive study was carried out to investigate the effect of several operating parameters including size/shape of support material, catalyst dose, and oxidant concentration. The selected support material was also used for doped TiO_2 immobilization to study the modified photocatalysis along with photo-Fenton (modified in-situ dual process) for the degradation of selected pharmaceuticals (CEX and PEN). Durability studies for the immobilized catalyst system were undertaken to study the economic feasibility of the reported technique. Mineralization of the target pollutants was confirmed through the production and monitoring of various anions,

evolution of CO₂ along-with reduction in TOC and COD. The intermediates formed during the degradation of parent compounds were analyzed through GC-MS. Based on the identified intermediates, tentative pathways for the degradation of respective compounds were proposed.

Degradation studies for both compounds (CEX and PEN) were carried out systematically. The process optimization was carried out using one compound by varying operational parameters and subsequently, viability of this process was counter-checked by carrying out the degradation of other compound at similar optimized conditions.

Scale-up of the novel in-situ dual process was also carried out with the development of pilot-scale non-concentrating fixed-bed reactors. Pilot-scale reactors like solar fixed-bed glass reactor and once-through cascade reactor incorporating in-situ dual effect were fabricated and studied in detail for the degradation of target pollutants to highlight the practical applicability of technique. Finally, successful treatment of real pharmaceutical effluent through in-situ dual process in reduced treatment time using highly durable and inexpensive composite beads further highlights the field-scale applications of presented technique.

The flow of the experimental work has been presented in the form of a flow chart (Figure 4.1) to have a clear vision of what and how the work has been covered in subsequent sections.

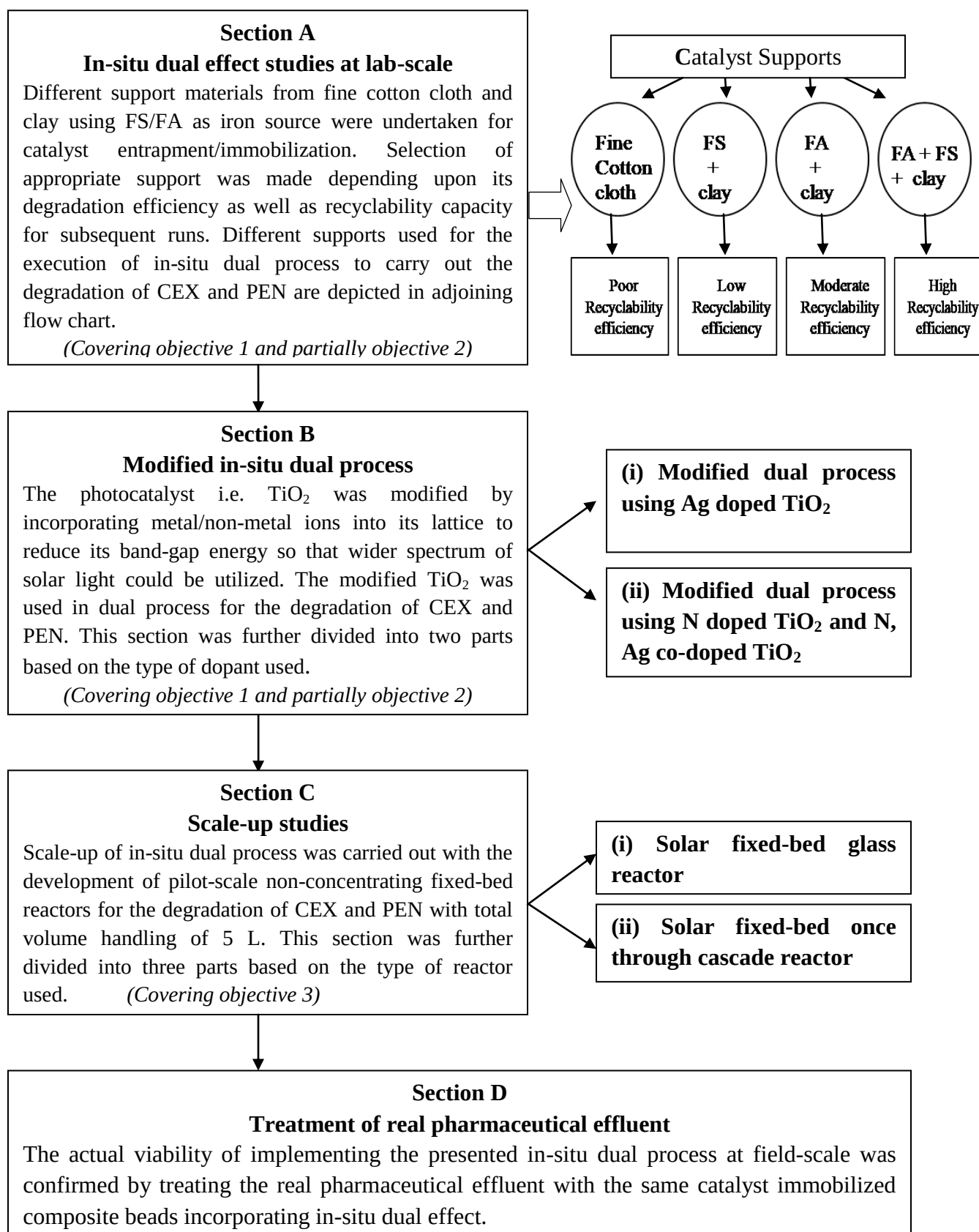


Figure 4.1: The structure of results and discussion

4.1 Photo-degradation kinetics

For photo-degradation experiments, the rate relies upon various operating parameters including catalyst dose, addition of oxidant, pH, etc. Certain different models were proposed for the decomposition of organic pollutants via photocatalytic treatment but L-H (Langmuir-Hinshelwood) kinetic model validated the best fitting for most of the photo-degradation experiments. The rate of decomposition of organics based on the L-H model is defined as follows:

$$-\frac{dC}{dt} = k_r \frac{KC}{1 + KC} \quad (4.1)$$

Where, k_r = reaction rate constant, K = equilibrium adsorption constant, C = bulk substrate concentration (mgL^{-1}) at any time, t . For low substrate concentrations, factor KC is negligible and can be ignored. Thus, according to L-H model, photocatalytic degradation rate can be generally defined through pseudo-first order kinetics as follows:

$$-dC/dt = k_r KC = kC \quad (4.2)$$

Or

$$\ln C_0/C = kt \quad (4.3)$$

where, C_0 and C are the initial and final concentration of substrate (mgL^{-1}) respectively, k is the apparent first order rate constant (time^{-1}). The value of 'k' can be obtained from the slope of a plot between $\ln C_0/C$ and time.

4.2 Synergy calculations

In the present research work, synergistic effect of in-situ dual process by integrating photocatalysis and photo-Fenton within the same treatment unit was observed over individual processes (photocatalysis or photo-Fenton) for the degradation of recalcitrant pharmaceuticals i.e. Cephalexin (CEX) and Pentoxifylline (PEN). Synergistic effects are meant to be the phenomenon when the degradation efficiency of integrated system is more than the sum of individual processes (Mazille et al., 2009a). The synergy of one process over the other for dual effect in the present work was calculated and quantified using the value of first order rate

constant, 'k' in each case as per the following equations 4-6 (Madhavan et al., 2010; Verma et al., 2013):

Synergy of dual process over photocatalysis:

$$\% Synergy = 100 \times \frac{\{(k_{dual} - k_{photocatalysis})\}}{k_{dual}} \quad (4.4)$$

Synergy of dual process over photo-Fenton:

$$\% Synergy = 100 \times \frac{\{(k_{dual} - k_{photo-Fenton})\}}{k_{dual}} \quad (4.5)$$

Overall synergy:

$$\% Synergy = 100 \times \frac{\{(k_{dual} - (k_{photocatalysis} + k_{photo-Fenton}))\}}{k_{dual}} \quad (4.6)$$

Where, k_{dual} = first order rate constant in case of dual process (time^{-1}), $k_{photocatalysis}$ = first order rate constant in case of photocatalysis (time^{-1}) and $k_{photo-Fenton}$ = first order rate constant in case of photo-Fenton (time^{-1}).

4.3 Statistical analysis

The comparison between the efficiency of different processes was evaluated on Graph pad prism software 5.0 using Tukey's multiple comparison test under 1-way ANOVA. The difference between two processes was considered to be significant if value of probability (P-value) was found to be less than 0.05 otherwise considered to be as insignificant. All experiments were performed at least thrice and results were expressed as mean values while error bars were also included in all graphs wherever applicable to denote the standard deviation.

4.4 Standard calibration curve of CEX and PEN

The wavelength scan of CEX and PEN solution was studied in the range from 200 to 800 nm. Maximum absorbance i.e. λ_{max} was obtained at 263 nm in case of CEX and 273 nm in case of PEN. Accordingly, the standard concentrations of CEX and PEN were varied from 10 mg L⁻¹ to 80 mg L⁻¹ and their absorbance at 263 nm and 273 nm respectively were measured. The

calibration curve was obtained by plotting a curve between absorbance and standard concentrations (Figure 4.2a, b). Coefficient of determination, R^2 was found to be 0.999 with value of slope to be 0.021 in case of CEX where as in case of PEN, R^2 was 0.994 with value of slope to be 0.039. The unknown concentrations of CEX and PEN can be determined from their respective calibration curves.

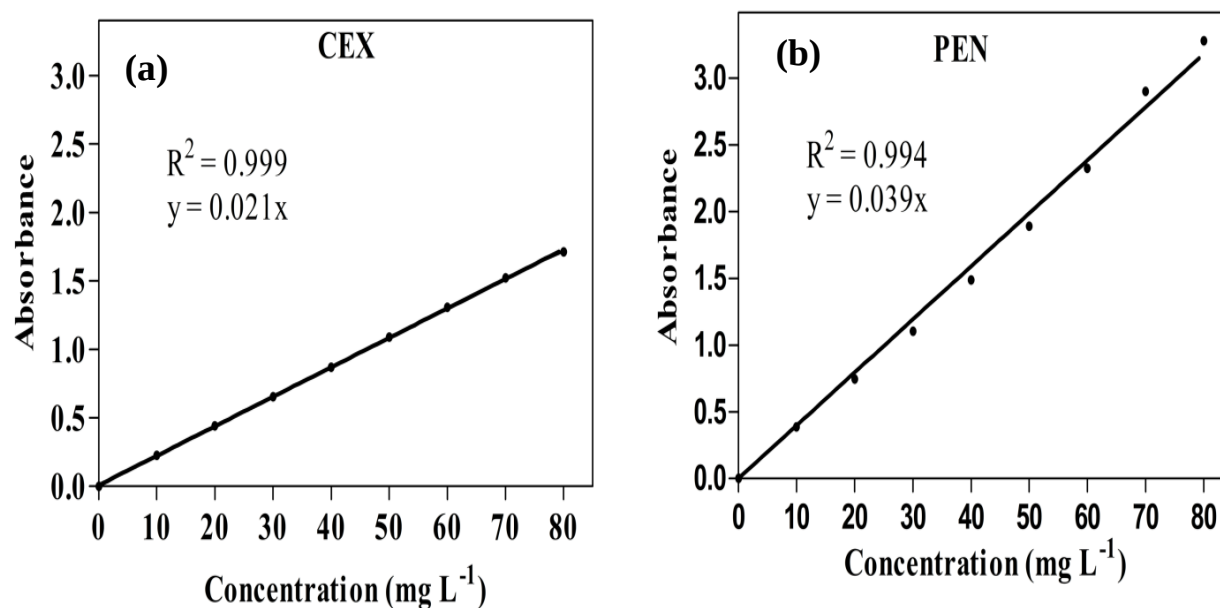


Figure 4.2: Calibration curve of (a) CEX and (b) PEN.

Section A

In-situ dual effect studies for the degradation of CEX and PEN at lab-scale

Degradation of CEX and PEN was carried out at lab-scale under artificial UV irradiations/natural sunlight using waste FS or FA as an alternative iron source. To confirm the prominence of dual effect concept for the degradation of CEX, experiments were initially executed in slurry mode using suspensions of TiO₂ and FS/FA. Further, the main emphasis of this research was to study the degradation of CEX and PEN in fixed mode for which various different supports like catalyst entrapment material using fine cotton cloth and catalyst immobilization materials using clay, FA and FS were prepared. The degradation efficiency of CEX and PEN was evaluated simultaneously with execution of detailed experimental study on

either compound while optimized conditions were applied for the degradation of other compound as well to check the viability of process.

4.5 Blank studies

Initially, control experiments were performed separately with CEX (50 mgL^{-1}) as well as PEN (50 mgL^{-1}) using catalyst suspensions in the presence or absence of UV irradiations. Three different adsorption experiments were carried out in dark for each compound using suspensions of TiO_2 (250 mgL^{-1}), FA (500 mgL^{-1}) and FS (500 mgL^{-1}) separately. Negligible amount of reduction in the concentration of CEX (5-7%) and PEN (4-6%) was observed with each adsorption experiment. The slight reduction in the concentration of CEX or PEN was mainly due to the development of pollutant film on the catalyst surface which might have blocked most of the active sites of catalyst thus ceasing further degradation of pollutant (Toor et al., 2007). Likewise, the presence of only H_2O_2 (150 mgL^{-1}) also revealed negligible removal of CEX (4-6%) and PEN (3-5%) due to the inadequate production of OH radicals. Photolytic experiments in the presence of only UV light also led to 3-5% and 6-8% removal of CEX and PEN respectively. This leads to a fact that degradation occurred in the presence of catalyst under UV irradiations was due to the activity of catalyst. The effect of individual parameters on the degradation of CEX and PEN is depicted in figure 4.3a and 4.3b, respectively.

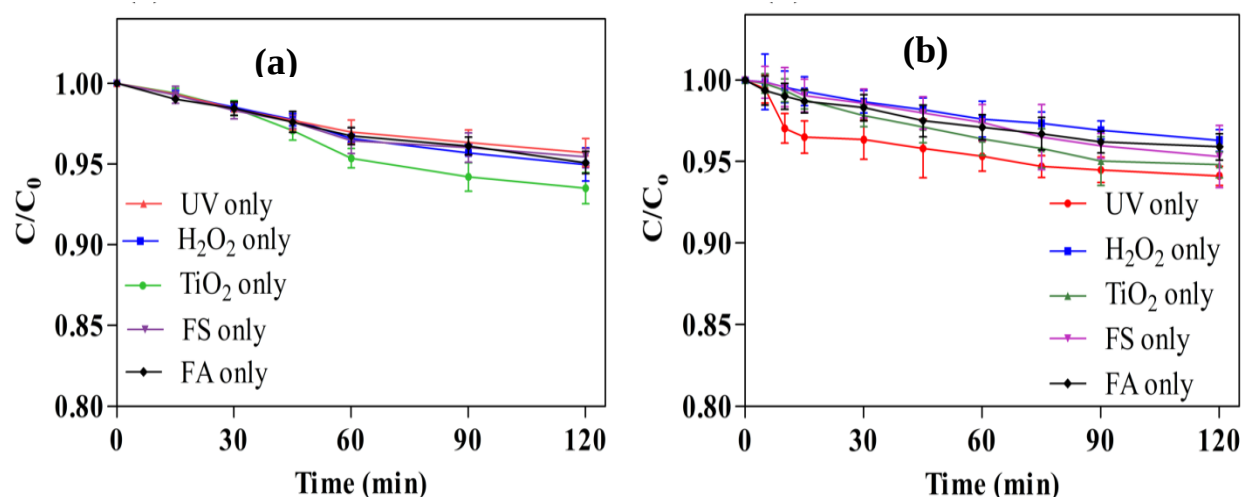


Figure 4.3: Effect of individual parameters in the presence and absence of UV irradiations for the removal of (a) CEX and (b) PEN.

4.6 Establishment of dual effect in slurry mode

To evaluate the prominence of dual effect for the degradation of CEX and PEN, experiments were initially conducted in slurry mode using FS/FA as an iron source and TiO_2 as a photocatalyst using fixed amount of H_2O_2 . The experiments were carried out invariably in artificial UV and natural solar radiations to establish the validation of dual effect in both the cases. All experiments for the degradation of CEX were conducted under acidic conditions ($\text{pH} = 3.5$). The photo-Fenton studies with either FS (500 mgL^{-1}) or FA (500 mgL^{-1}) as an iron source in the presence of $150 \text{ mgL}^{-1} \text{ H}_2\text{O}_2$ led to almost 45% degradation of CEX after 120 min of UV irradiations. Photocatalytic treatment using 250 mgL^{-1} of TiO_2 and $150 \text{ mgL}^{-1} \text{ H}_2\text{O}_2$ revealed around 83% degradation of CEX after 120 min of reaction. Photocatalytic degradation was significantly higher ($P < 0.05$) than photo-Fenton. Interestingly when these two individual processes (photo-Fenton and photocatalysis) were combined together by using either 500 mgL^{-1} FS and $250 \text{ mgL}^{-1} \text{ TiO}_2$ or 500 mgL^{-1} FA and $250 \text{ mgL}^{-1} \text{ TiO}_2$ in the same treatment unit with an addition of $150 \text{ mgL}^{-1} \text{ H}_2\text{O}_2$, reduction in treatment time was observed as almost 85% degradation of CEX was obtained within 90 min of reaction.

The dual process yielded much higher degradation ($P < 0.05$) as compared to individual processes. The first order rate constant, 'k' in case of dual process (0.021 min^{-1}) was increased almost five times as compared to photo-Fenton (0.004 min^{-1}) and two times in comparison to photocatalysis (0.013 min^{-1}). The overall synergy of dual process over individual processes (photo-Fenton and photocatalysis) for the degradation of CEX was observed to be 19%. The effect of different processes on the degradation of CEX can be visualized from figure 4.4a.

Likewise, figure 4.4b indicates the effect of individual processes along with dual process on the degradation of PEN. Similar pattern as that for CEX was observed in case of PEN as well. All experiments for the degradation of PEN were carried out at its natural pH i.e. 4. The experiments were conducted at pH 3 also but there was no drastic increase in degradation efficiency as compared to pH 4. In view of the practical applications, pH was not varied and experiments were carried out at natural pH i.e. 4. Photocatalytic treatment of PEN revealed almost 93% degradation which was significantly higher ($P < 0.05$) as compared to 80% in case of photo-Fenton treatment after 90 min of UV irradiations (solar light). The dual process yielded

much higher degradation ($P < 0.05$) in comparison to individual processes. The treatment time was reduced to 30 min for achieving an almost 92% degradation of PEN. The drastic increase in first order rate constant in case of dual process (0.096 min^{-1}) i.e. seven folds as compared to photo-Fenton (0.014 min^{-1}) and three folds as compared to photocatalysis (0.031 min^{-1}) confirms the viability of dual process. The overall synergy of dual process over individual processes (photo-Fenton and photocatalysis) for the degradation of PEN was observed to be 48%.

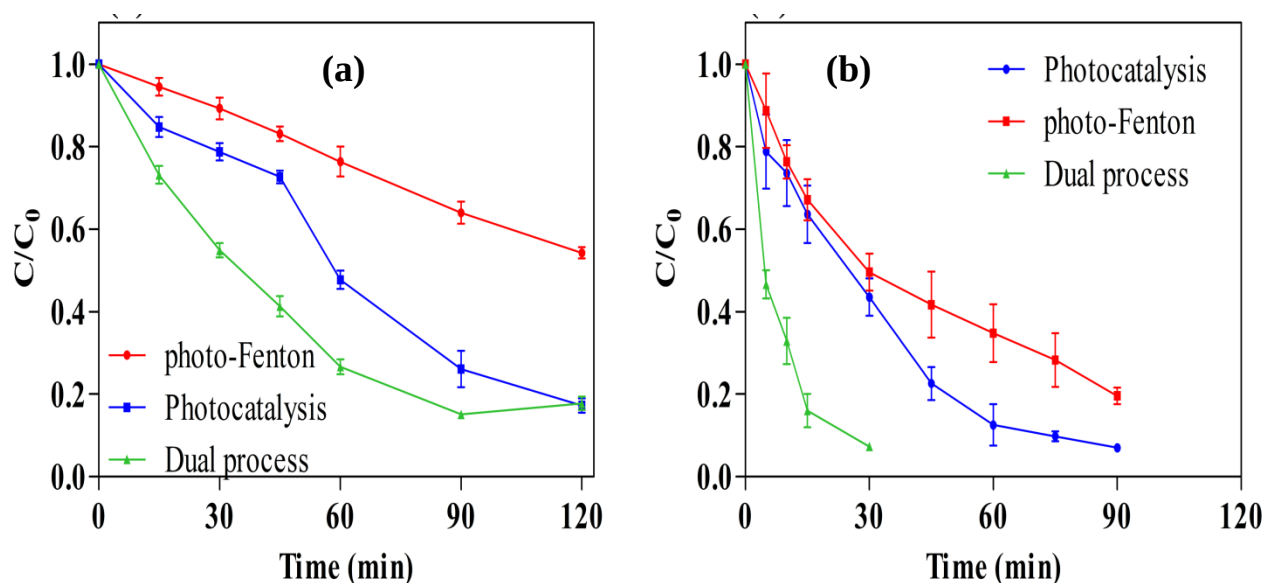
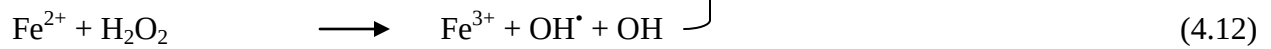
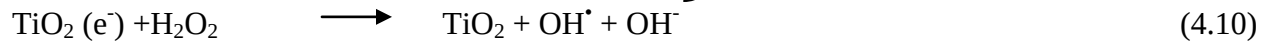
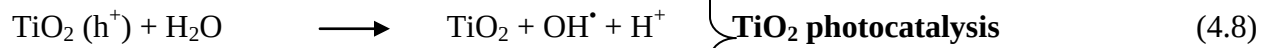


Figure 4.4: Comparison between different processes for the degradation of (a) CEX and (b) PEN (Experimental conditions: CEX = 50 mgL^{-1} , PEN = 50 mgL^{-1} , V = 200 mL).

Thus, prominence of dual process over distinct processes was proved in case of both target pollutants. The possible reason for the improved degradation efficiency in case of dual process was the generation of hydroxyl radicals in abundance from both processes i.e. photocatalysis and photo-Fenton going on simultaneously within the same treatment unit. Moreover, photo-excited electron over the surface of TiO_2 might get involved in the regeneration of ferrous ions from ferric ions thus facilitating the photo-Fenton reaction. This further prevents the frequent recombination of charge carriers on TiO_2 thereby enhancing the process efficiency. Equations 4.7-4.12 explains the generation of hydroxyl radicals via dual process.



This plausible mechanism of dual process can be more clearly understood from figure 4.5.

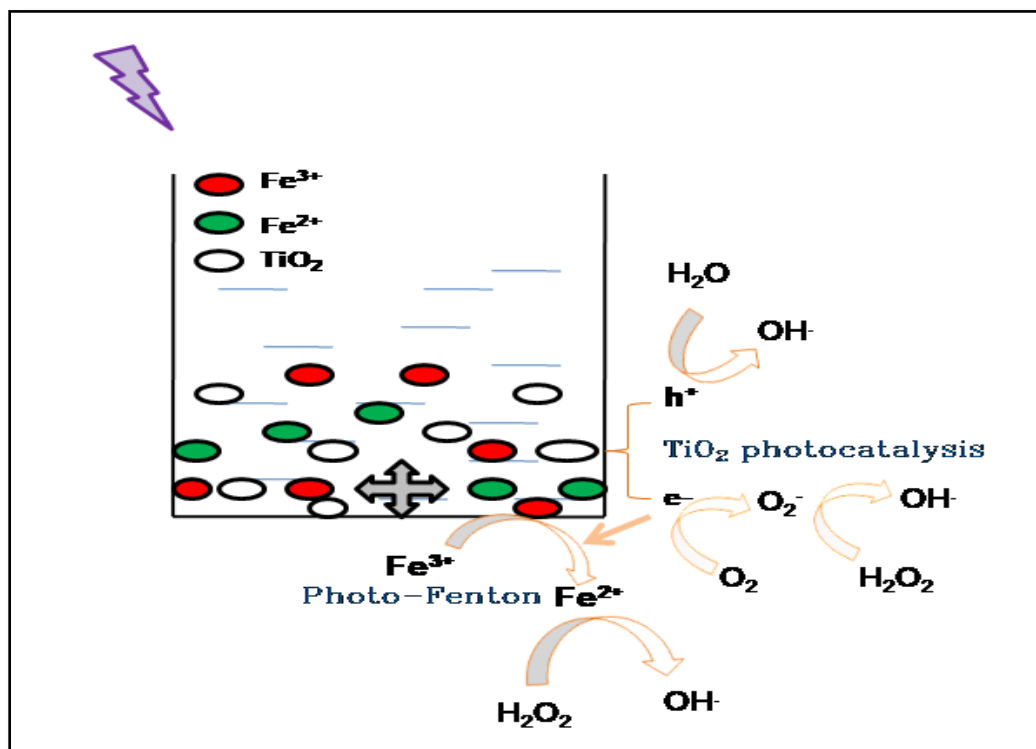


Figure 4.5: Plausible mechanism of dual effect.

4.7 Dual effect studies in fixed-mode

Reactions with catalyst suspension always have complications regarding its separation from aqueous solution after the treatment process thus limiting its practical applications. In this context, the present study attempts to shift the dual process from slurry to fixed-bed mode step-wise for the degradation of CEX and PEN. After confirming the prominence of dual effect in slurry mode, FS/FA was entrapped in small pockets made of fine cotton cloth while keeping TiO_2 in suspensions. Fine cotton cloth was selected on the basis of fine size of FS and FA so that they do not drain out from the pockets. In the subsequent experiments, TiO_2 was immobilized on clay beads which were used along with FS/FA pockets to bring the treatment unit completely in fixed-mode. Selection of the support material for catalyst immobilization plays a vital role in designing the fixed-bed photocatalytic systems. The support material must acquire certain characteristics including excellent stability with subsequent cycles of photocatalytic experiments, must be capable enough to adsorb the pollutant on its surface for an efficient photocatalytic reaction and most importantly, it should provide sufficient exposed surface area (Srikanth et al., 2017). Again, the target pollutants (CEX and PEN) were selected invariably in the present study as detailed experimental variations were carried out on any one of the compounds while degradation of the second compound was performed only at optimum conditions to view the viability of process. Different supports for catalyst entrapment/immobilization used in the present research are discussed below:

4.7.1 Fine cotton cloth for catalyst entrapment

To compensate the loss of either FA or FS with subsequent cycles, small pockets (Figure 3.3) were prepared from fine cotton cloth for the entrapment of FS/FA. The main purpose of using pockets besides its recyclability with subsequent runs was to examine the leaching trend of iron from pocket. Based on the composition, pockets were named as P1, P2 and P3. P1 contained known amount of FS and P2 contained known amount of FA while P3 contained mixture of FA and FS. The pockets were used along with suspensions of TiO_2 as depicted in figure 4.6.

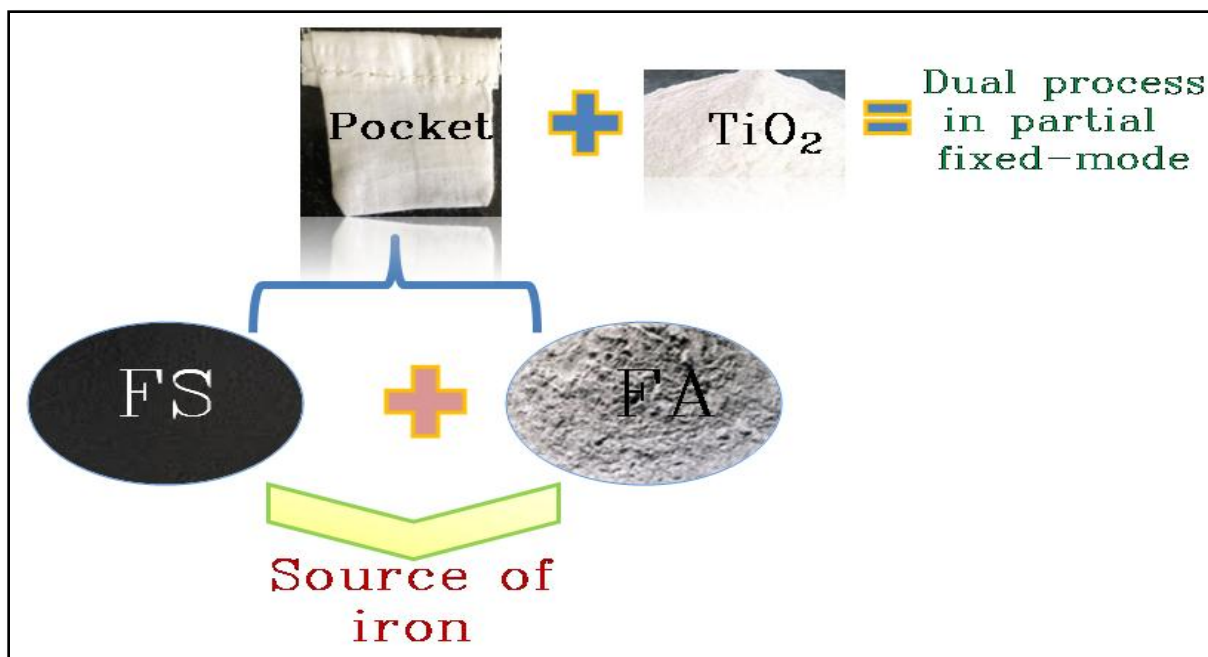


Figure 4.6: Pictorial presentation of dual process in partial fixed-mode using pockets.

To investigate the efficiency of P1, P2 and P3 in dual process, PEN was used as a target pollutant for carrying out the degradation experiments. All experiments were performed in a batch reactor with 50 mgL⁻¹ of PEN solution by adding 250 mgL⁻¹ of TiO₂ and 150 mgL⁻¹ of H₂O₂ along with pockets (P1, P2, P3) containing FS/FA at natural pH of PEN i.e. 4. Each pocket (P1 or P2 or P3) contained an equal quantity of either FS or FA or both i.e. 125 mg. A reasonably good amount of degradation i.e. nearly 90% was achieved via dual process after 45 min of treatment time when either of the pockets (P1, P2 or P3) was used along with TiO₂. No significant difference ($P > 0.05$) was observed in the degradation efficiency of dual process with different pockets. The concentration of iron content leached into the solution during the dual process has been presented in table 4.1. Subsequently, individual processes like photo-Fenton using 125 mg P1 and 150 mgL⁻¹ of H₂O₂ and photocatalysis using 250 mgL⁻¹ of TiO₂ along with 150 mgL⁻¹ of H₂O₂, were also performed separately to establish the prominence of dual process. The first order rate constant in case of dual process (0.069 min⁻¹) was increased two fold in comparison to photocatalysis (0.031 min⁻¹) while it increased to almost four times as compared to photo-Fenton (0.017 min⁻¹) thus confirming the synergistic effect of dual process. Results were confirmed by reusing the pockets again and again for subsequent cycles. The weight of pockets was checked after each cycle for determining the loss of FS/FA from the pockets. The

major problem that occurred with P2 and P3 was the significant reduction in their weights after each cycle as compared to P1. It might be due to the smaller particle size of FA that drained out easily from pockets so these pockets were not suitable to be used for subsequent cycles. Table 4.1 shows the weight of pockets along with the iron content leached into the solution for successive cycles.

Table 4.1: The weight of pockets P1, P2 and P3 after each cycle along with iron content leached into the solution for successive cycles.

Number of cycles	P1			P2			P3		
	Initial weight (mg)	Final weight (mg)	Iron content (mgL ⁻¹)	Initial weight (mg)	Final weight (mg)	Iron content (mgL ⁻¹)	Initial weight (mg)	Final weight (mg)	Iron content (mgL ⁻¹)
1	641	638	0.707	538	488	0.669	506	478	0.829
2	638	634	0.569	488	434	0.377	478	442	0.489
3	634	634	0.50	434	386	0.301	442	420	0.411
4	634	632	0.45	386	302	0.198	420	403	0.313
5	632	635	0.39	302	245	0.102	403	388	0.234
6	635	633	0.322	245	221	0.068	388	351	0.169
7	633	628	0.212	221	201	0.044	351	308	0.112
8	628	625	0.19	201	184	0.021	308	279	0.076

To bring the treatment unit completely in fixed-bed mode, TiO₂ immobilized clay beads (control beads) instead of TiO₂ suspensions were used along with P1 containing 125 mg FS (Figure 4.7). Accordingly, adsorption experiments in dark using blank clay beads (without TiO₂ coating) revealed only 5–6% reduction in pollutant concentration. Appropriate number of TiO₂ coated clay beads (control beads) covering the entire bottom surface of a batch reactor along with P1 and oxidant (150 mgL⁻¹ H₂O₂) were used to carry out the degradation of PEN.



Figure 4.7: Pictorial representation of dual process in fixed-mode.

The major problem that was faced with clay beads was the rising pH of solution after few minutes of reaction which lowered down the efficiency of dual process. Actually at higher pH, the efficiency of photo-Fenton process was dramatically reduced which subsequently lowered down the overall efficacy of dual process. This problem was best resolved by stabilizing the pH of PEN solution to its natural pH i.e. 4 with addition of appropriate amount of acetate buffer. As a result, significant amount of degradation of PEN i.e. around 88% was achieved via dual process in fixed-mode after 120 min of treatment time. In addition to this, control beads (TiO_2 immobilized clay beads) showed excellent recyclability efficiency as beads were successfully reused for 40 numbers of cycles without any significant decrease in the degradation efficiency using fresh P1 for each cycle (Figure 4.8a).

While, recyclability of P1 was not up to the mark as the same pocket (P1-125 mg) was recycled 8 times in dual process with notable decrease in the % degradation of PEN after each cycle (Figure 4.8b). The reduction in concentration of the leached iron from pocket was also observed after each cycle as indicated in table 4.1. This reduction in concentration of leached iron species from pocket decreased the efficiency of photo-Fenton reaction which further leads to the overall reduction in % degradation of PEN. To check the viability of dual process in fixed-mode using P1 along with TiO_2 immobilized clay beads, experiments were performed with CEX as well which revealed an almost 80% degradation of CEX after 120 min of treatment time.

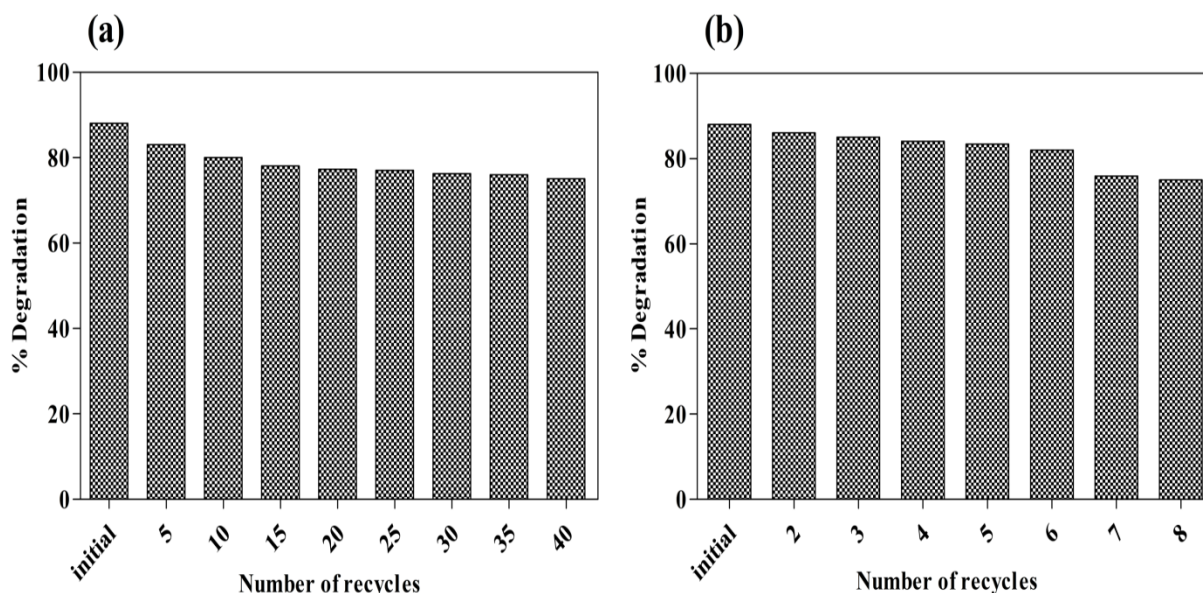


Figure 4.8: Recyclability studies of (a) TiO_2 immobilized clay beads and (b) P1-125 mg.

The results clearly indicated that TiO_2 immobilized clay beads (control beads) with high durability could be successfully used at large-scale. But in order to visualize the concept of dual effect at field-scale, equally stable and durable support for entrapping or immobilizing the iron source is also required. Therefore, further studies are required to look for some highly durable and stable modified supports incorporating dual effect (photocatalysis and photo-Fenton) that could be successfully recycled for subsequent runs.

4.7.2 Clay in conjunction with FS

Trials were executed to further improve the practicability of dual process by enhancing the durability and efficiency of support materials. The systematic leaching of iron from FS (in case of pockets) has already been confirmed in previous section. Moreover, clay as a raw material for catalyst supports has also proven its great potential in terms of its durability and strength. Thus, these two factors were taken into consideration while preparing different supports to be used for dual process. Efforts were made to incorporate FS along with clay in order to prepare different supports for catalyst immobilization. The size and shape of the immobilizing agent or support material is a crucial parameter to be considered in case of fixed-bed reactors as exposed surface area of the immobilized catalyst always remains a major issue.

In this context, support materials of different shapes (hollow circular discs, rectangular slabs and spherical beads) were prepared from clay and waste FS for TiO_2 immobilization as discussed in section 3.4. All fixed-bed experiments were performed at acidic pH i.e. 3.5 (stabilized with acetate buffer) with fixed amount of H_2O_2 i.e. 150 mgL^{-1} under artificial UV irradiations. This section discusses the detailed degradation of CEX using differently shaped supports for the execution of dual process while degradation of PEN was carried out with optimized support to confirm the effectiveness of dual process via selected catalyst support. The degradation of CEX using various support materials has been discussed in following section:

Degradation of CEX with TiO_2 immobilized disc

The hollow circular disc with outer diameter = 13.5 cm and inner diameter = 5 cm (Figure 3.4a) was designed so as to facilitate better mixing of the particles as disc was used under continuous stirred type conditions (Section 3.5). The experiments were conducted under artificial

UV irradiations with control disc (clay/TiO₂), blank disc (clay/FS) and composite disc (clay/FS/TiO₂) to study the synergistic effect of in-situ dual process over individual processes (photo-Fenton or photocatalysis) for the degradation of CEX. The experiments executed with control disc represented solely TiO₂ photocatalysis which revealed 55% degradation and photo-Fenton reactions with blank disc yielded 33% degradation whereas dual process with composite disc resulted into 73% degradation of CEX after 240 min of treatment as indicated in figure 4.9a. Thus, degradation of CEX via in-situ dual process was significantly higher ($P < 0.05$) in comparison to individual processes.

The rate of degradation was accelerated through in-situ dual process as it took lesser time (almost 150 min) to achieve 55% degradation of CEX as compared to 240 min via photocatalysis. Moreover, value of rate constant, 'k' was improved to 0.0053 min⁻¹ in case of integrated process compared to 0.0013 min⁻¹ (photo-Fenton) and 0.0036 min⁻¹ (photocatalysis) as shown in figure 4.9b. In addition to this, overall synergy of dual process over individual processes was quantified to be 7.6%. Composite disc led to the in-situ leaching of iron which contributed to photo-Fenton reaction along with on-going photocatalysis owing to the presence of TiO₂ on its surface. The amount of leached iron from composite disc during the dual process at regular time intervals was quantified as listed in table 4.2.

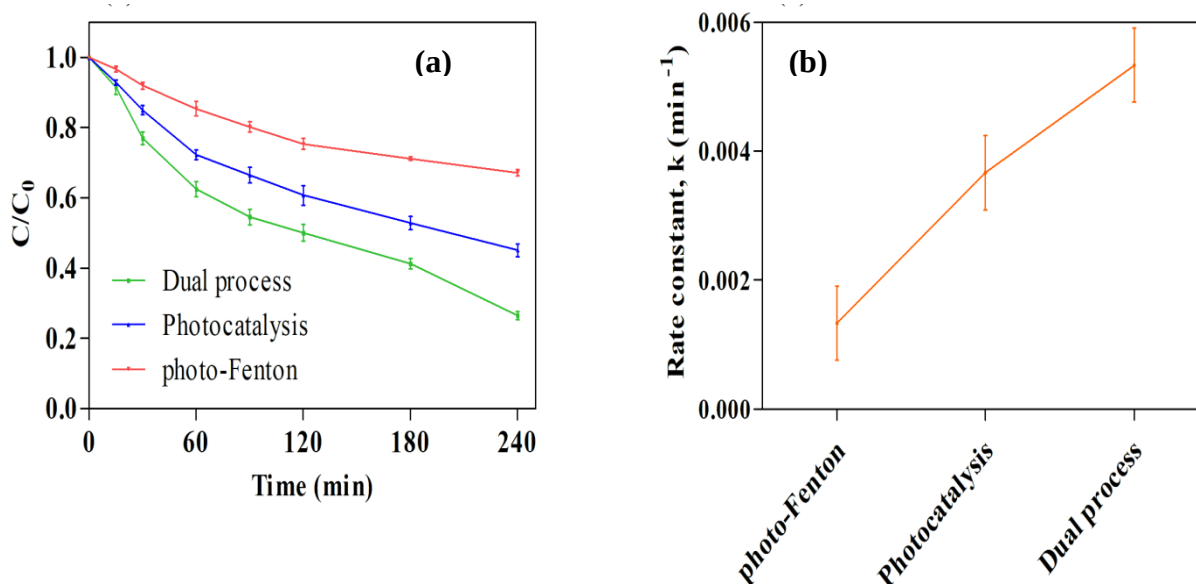


Figure 4.9: (a) Plot of C/C_0 vs time, and (b) Values of rate constant for the degradation of CEX via different processes using hollow circular disc.

Table 4.2: Concentration of total iron including ferrous and ferric iron leached out from composite disc during the degradation of CEX.

Time (min)	Total iron (mgL⁻¹)	Ferrous iron (mgL⁻¹)	Ferric iron (mgL⁻¹)
30	1.289	0.763	0.526
60	0.676	0.514	0.161
120	0.491	0.231	0.26
180	0.387	0.196	0.19
240	0.317	0.121	0.196

The decrease in concentration of leached iron content during the course of reaction as depicted in table 4.2 confirmed the utilization of iron species in photo-Fenton reaction occurring simultaneously along with photocatalysis.

Though satisfiable results were obtained using composite disc, its reusability was not up to the mark. The photocatalyst was not strongly immobilized over the disc as TiO₂ particles started draining off after the first cycle. The disc was recycled five times with significant reduction ($P < 0.05$) i.e. almost 20% in the degradation efficiency of CEX. While with further recycling tests, TiO₂ particles continued to drain out from the surface of disc which resulted into continuous decrease in the degradation efficiency of CEX. Actually, binding of the catalyst to any support depends upon the surface area of support. Greater the surface area of support, less firmly is the catalyst bound to it. In the present case, TiO₂ particles were not firmly bound to the surface owing to the larger surface area of disc (123 cm²). Moreover, continuous stirring of the solution could also be responsible for detachment of catalyst particles from the surface of disc with time. Therefore, it may be presumed that in the recycling tests, degradation of CEX took place mainly due to the existence of leached iron species in solution contributing to photo-Fenton reaction. Actually, there was systematic leaching of iron in solution from the composite supports (containing FS) as iron was detected in solution in each and every recycling test.

Degradation of CEX with TiO₂ immobilized slabs

Likewise, experiments were performed with catalyst immobilized rectangular slabs having length = 6.5 cm and breadth = 2.5 cm (Figure 3.4b) for the degradation of CEX. The

major disadvantage of these types of immobilized systems is the improper mixing of particles as continuous stirring of the solution is not possible using such catalyst support materials. Thus, two air spargers were used in place of stirrer to acquire the desired mixing in the treatment system. Different processes i.e. photocatalysis, photo-Fenton and in-situ dual process were performed using control, blank and composite slabs for the degradation of CEX under UV irradiations in the same pattern as discussed in earlier section. The synergistic effect of dual process over individual processes was observed for the degradation of CEX in the same manner as studied in case of composite disc. Expectedly, composite slabs exhibiting dual process yielded significantly higher ($P < 005$) decomposition of CEX (67%) in contrast to photocatalysis (47%) and photo-Fenton (29%) after 240 min of UV irradiations (Figure 4.10a). The value of rate constant, 'k' was highest i.e. 0.004 min^{-1} in case of dual process as compared to photo-Fenton i.e. 0.0012 min^{-1} and photocatalysis i.e. 0.0026 min^{-1} (Figure 4.10b). In this case, overall synergy of dual process over individual processes came out to be 5%. Table 4.3 depicts the concentration of leached iron species including ferrous and ferric ions from the composite slabs during the degradation process.

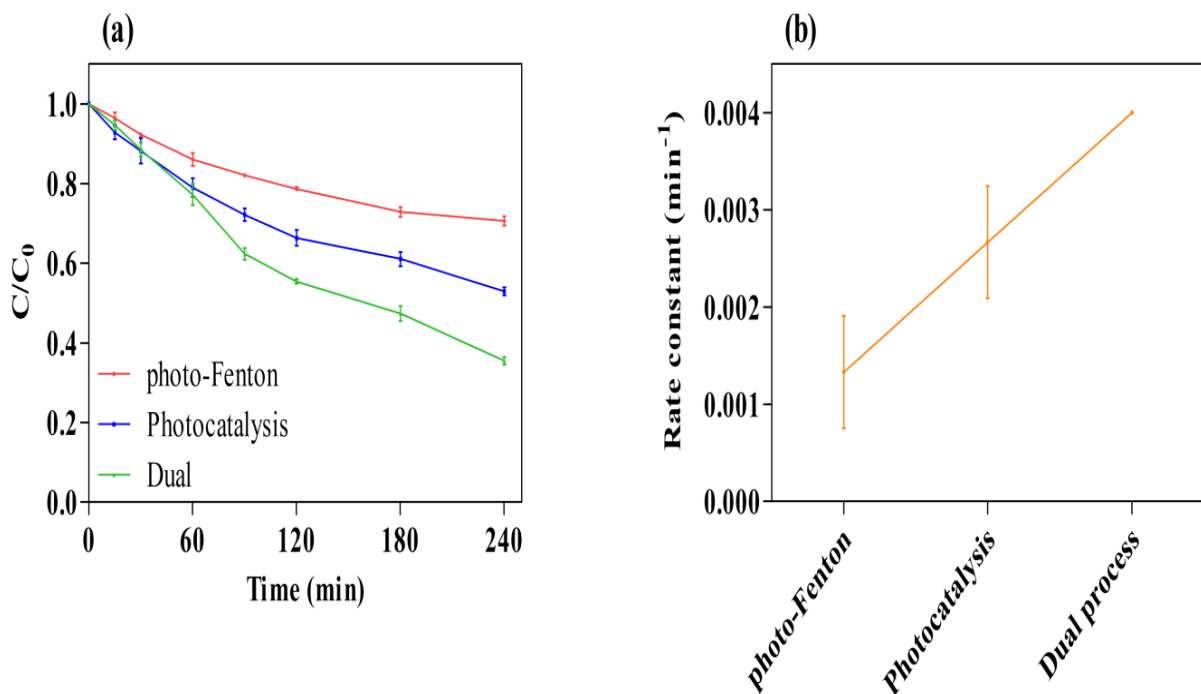


Figure 4.10: (a) Plot of C/C_0 vs time, and (b) Values of rate constant for the degradation of CEX via different processes using rectangular slabs.

Table 4.3: Concentration of total iron including ferrous and ferric iron leached out from composite slabs during the degradation of CEX.

Time (min)	Total iron (mgL⁻¹)	Ferrous iron (mgL⁻¹)	Ferric iron (mgL⁻¹)
30	0.953	0.52	0.433
60	0.757	0.317	0.439
120	0.682	0.266	0.415
180	0.439	0.176	0.263
240	0.213	0.152	0.06

Though degradation of CEX was more promising in case of composite disc (owing to the presence of desirable mixing conditions) in contrast to slabs, durability and stability of immobilized catalyst was much better in case of slabs. Owing to the lesser surface area of each slab (16.3 cm²) as compared to disc (123 cm²), binding of catalyst to the surface of slabs was better. An almost 20% reduction in degradation efficiency was observed after reusing the slabs subsequently for 10 runs as compared to 5 times in case of disc. However with further recycling tests, degradation of CEX continued to decrease with continual draining off the photocatalyst particles from the surface of slabs. To provide insight into the commercial applications of the studied technique, the immobilized catalyst must represent high durability i.e. at-least 50 recycles without any significant reduction in degradation efficiency. Thus, efforts are still required to look for some other support materials that could display high durability and can be successfully used for field-scale applications.

Degradation of CEX with TiO₂ immobilized beads

In spite of the improper mixing of particles in this case as well, spherical composite beads with diameter 1.5 cm (Figure 3.4c) revealed the best results in terms of degradation efficiency as well as durability/recyclability of immobilized catalyst as compared to the other catalyst supports (circular discs, rectangular slabs) discussed in previous sections. Actually, the overall exposed surface area of immobilized catalyst was significantly enhanced using spherical shaped beads as catalyst immobilized support which led to a remarkable increase in the efficiency of treatment process. Though overall exposed surface area of immobilized catalyst was highest in case of beads, specific surface area of single bead was very low (0.071 cm²) which favored the firm

binding of catalyst over the surface of beads. The composite beads were successfully reused for more than 10 cycles with almost 15% diminution in the degradation efficiency of CEX. However, using the same beads subsequently for further experiments resulted in continual decrease in degradation of CEX either due to the fouling of catalyst or weathering off some of the catalyst particles from the surface with prolonged use. The catalyst was re-activated by either exposing the catalyst immobilized beads to natural sunlight for an hour or were calcined in muffle furnace at 200 °C for 30 min.

Composite beads resulted into 80% degradation of CEX with highest value of rate constant i.e. 0.006 min^{-1} after 240 min of UV irradiations (Figure 4.11a). Synergistic effect was confirmed when photocatalytic experiments were conducted using control beads revealing 0.004 min^{-1} as rate constant and photo-Fenton process yielded 0.0014 min^{-1} as rate constant using blank beads (Figure 4.11b). Overall synergy of dual process over discrete processes was observed to be around 10%. Thus, degradation of CEX was significantly higher ($P < 0.05$) in case of in-situ dual process as compared to distinct processes. Table 4.4 demonstrates the concentration of leached iron species into the solution from composite beads during the degradation process.

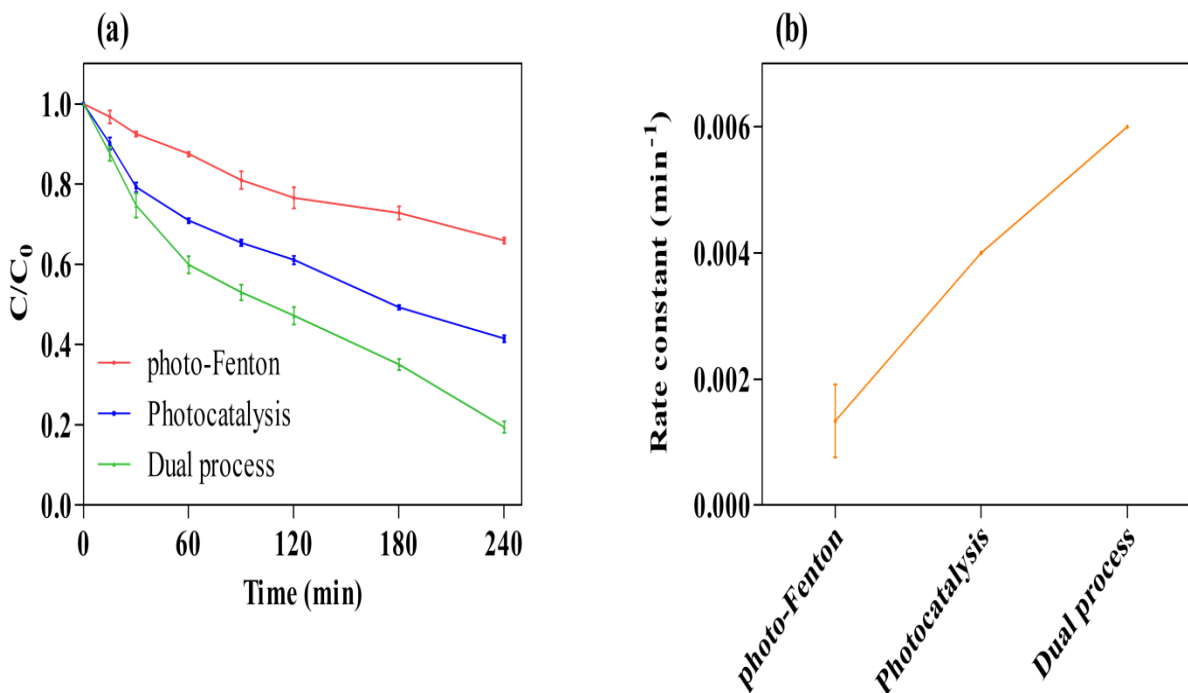


Figure 4.11: (a) Plot of C/C_0 vs time, and (b) Values of rate constant for the degradation of CEX via different processes using spherical beads.

Table 4.4: Concentration of total iron including ferrous and ferric iron leached out from composite disc during the degradation of CEX.

Time (min)	Total iron (mgL⁻¹)	Ferrous iron (mgL⁻¹)	Ferric iron (mgL⁻¹)
30	1.26	0.63	0.624
60	0.479	0.306	0.173
120	0.369	0.219	0.15
180	0.317	0.161	0.156
240	0.225	0.132	0.092

Comparison between studied TiO₂ immobilized supports

Catalyst immobilized support materials (FS + clay) of varying shapes (hollow circular discs, rectangular slabs and spherical beads) were used to study the in-situ dual effect for the degradation of CEX. It was observed that shape of the support material plays a significant role in fixed-bed studies. In the present study, degradation rate of CEX with different shaped supports was attained in the following trend: spherical beads (0.006 min⁻¹) > hollow circular disc (0.0053 min⁻¹) > rectangular slabs (0.004 min⁻¹) as shown in figure 4.12a. This trend is typically in support of the fact that more the overall exposed surface area of the immobilized catalyst more is the degradation efficiency. The overall exposed surface area of the immobilized catalyst was drastically increased to almost 0.0265 m² when spherical beads were used as supports where as exposed surface area remained quite low in case of slabs (0.0113 m²) and disc (0.0123 m²) for the same batch reactor. In spite of the significant variation in the exposed surface area of beads and disc, there was no significant variation ($P > 0.05$) in the degradation rate constants. The reason for the improved degradation rate in case of disc was the availability of better mixing conditions in the system. Actually in case of disc, better mixing conditions were attained using stirrer. In addition to the enhanced degradation efficiency of CEX, spherical beads also displayed maximum stability/durability of immobilized catalyst as compared to disc and slabs. The durability of catalyst immobilized supports acquired the following trend: spherical beads > rectangular slabs > circular disc. The beads were recycled for 10 runs with almost 15% reduction in the degradation efficiency as demonstrated in figure 4.12b. Thus, best results with respect to

the degradation efficiency and recyclability of the immobilized catalyst among differently shaped supports were obtained with spherical composite beads.

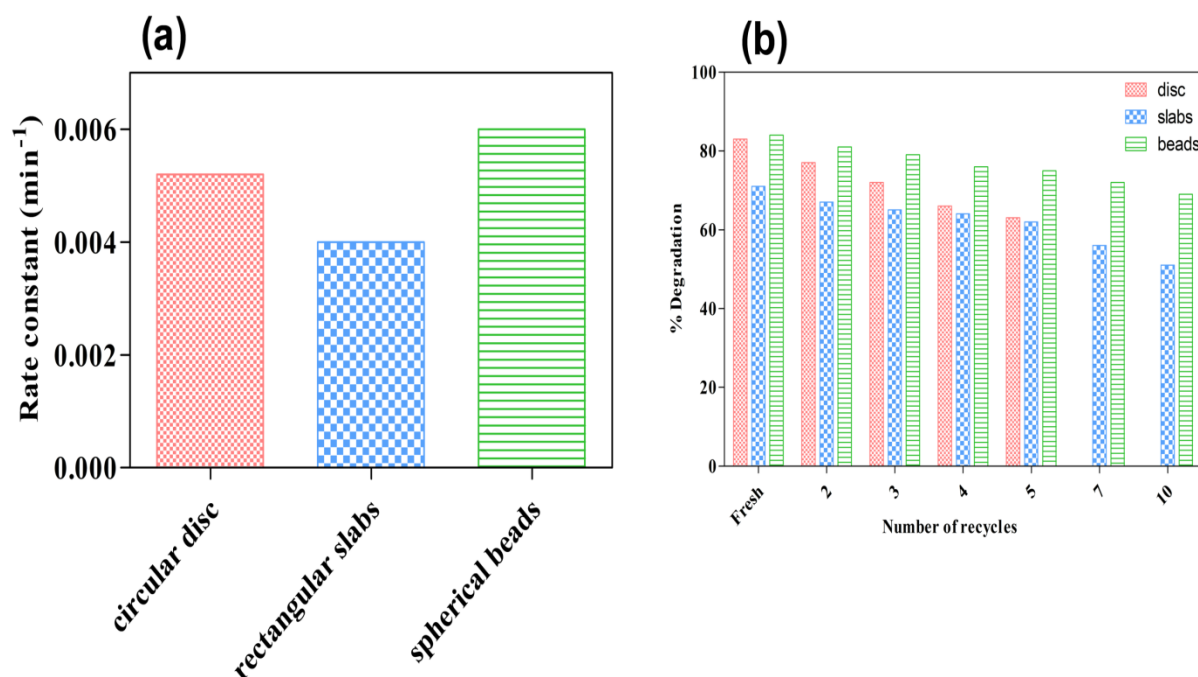


Figure 4.12: (a) Plot of First order rate constant vs different supports for the degradation of CEX (b) Recyclability studies of different supports for the degradation of CEX.

However, some variations or modifications in the support material are still required to further enhance their recyclability efficiency so that technique can be successfully implemented at field-scale. The studied catalyst immobilized supports were not capable of recycling for more than 10 runs as the catalyst was not strongly intact to the support and was continuously draining off from the surface.

Thus, it can be concluded that clay beads in conjunction with FS were not showing enough compressive strength or durability for subsequent cycles. This means that either some other alternative source of iron could be used instead of FS or some other material could be added along with FS and clay to enhance the binding capacity of support. For example, use of FA along with FS provides the compressive strength to the material (Naik et al., 2011). Moreover, FA is also a source of iron as discussed in section 3.3. In this regard, FA was added along with FS to prepare composite beads for TiO₂ immobilization as discussed in section 4.7.6. Highly durable and stable catalyst immobilized supports (most likely to be spherically shaped)

with sufficient exposed surface area incorporating in-situ dual effect are required that could easily meet the field-scale applications.

To the best of our knowledge, this is the first reported study detailing with fixed-bed approach incorporating in-situ dual process (photocatalysis and photo-Fenton) for the degradation of CEX with reduced treatment time.

4.7.3 Proposed mechanism of dual effect in fixed-mode

From the results, it is evident that dual process in all respects (slurry or fixed mode) has yielded much better degradation of CEX than individual processes (photocatalysis or photo-Fenton). In dual process, abundant of hydroxyl radicals (Section 4.11.1, Figure 4.62) are generated through TiO₂, iron oxide and dissolved iron ions thus leading to the enhancement of degradation efficiency and confirming the synergistic effect. Hydroxyl radicals are generated not only through photo-Fenton reaction and TiO₂ photocatalytic reaction but also from iron oxide catalysis (Mazille et al., 2009). Some of these forms of iron oxide (iron dititanium oxide, diiron titanium oxide and iron titanium oxide) are somewhat confirmed in our study as depicted in XRD analysis of composite beads (Section 4.7.4). The photo-generated electron from the conduction band of TiO₂ got trapped by iron oxide and could possibly participate in the regeneration of Fe²⁺ ions (Equation 4.17) promoting the photo-Fenton reaction and simultaneously restraining the recombination of electrons and holes on TiO₂ (Mazille et al., 2009). This proposed mechanism of dual effect is depicted in figure 4.13 though further experimental analysis is required for solid confirmation of mechanism owing to the involvement of several active species.

It is now quite obvious that abundant of hydroxyl radicals are generated through several processes in the same treatment unit that are mainly involved in the degradation of pollutant. Therefore, the presence of profuse amount of these radicals are responsible for accelerating the degradation of CEX and subsequently reducing the treatment time in case of dual process in the present study. Generation of hydroxyl radicals in abundance can be understood from Equations 4.13-4.20.



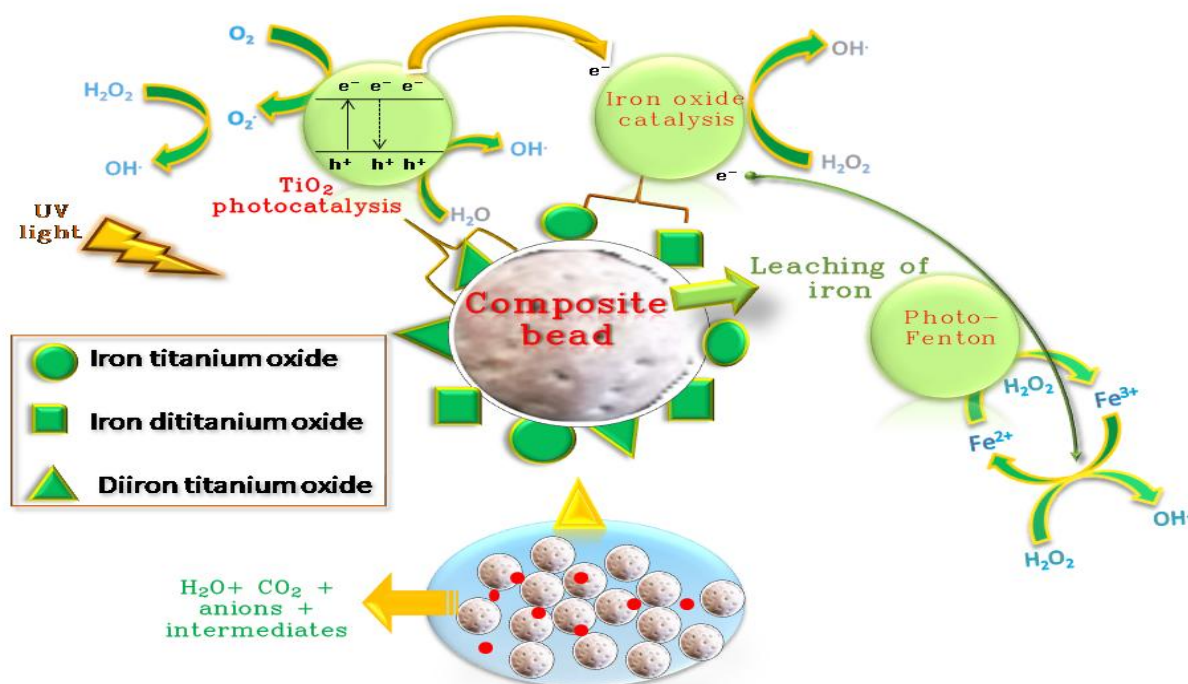
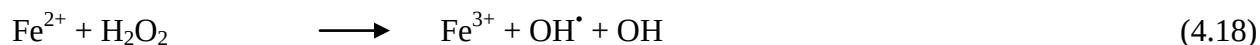
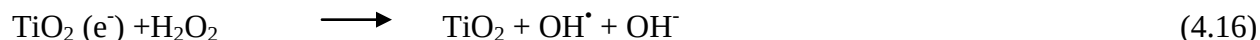
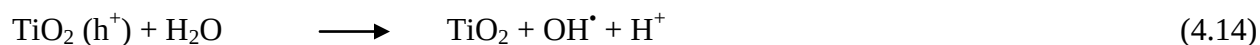


Figure 4.13: Proposed mechanism of in-situ dual process.

4.7.4 Characterization of TiO₂ immobilized composite beads

The spherical composite beads were characterized through several techniques for the presence of TiO₂ as well as iron on its surface to further confirm our claim for the existence of in-situ dual process (photocatalysis and photo-Fenton) within the same treatment unit.

SEM/EDS analysis

The morphological characteristics and elemental composition of composite beads were analyzed through scanning electron microscopy (SEM) and electron-dispersive spectroscopy (EDS), respectively as shown in figure 4.14a. The prominent peaks of 'Ti' and 'Fe' in the EDS image of fresh composite bead (Figure 4.14a (i)) strongly affirm our claim for the utilization of composite beads for integrated process. The smooth surface in the SEM image clearly indicates the uniform coating of TiO_2 on the surface of beads. To confirm the presence of immobilized catalyst along with iron even after 10 recycles, SEM/EDS analysis of recycled composite beads was also performed which is depicted in figure 4.14a (ii). Irregular surface was observed in the SEM image owing to the weathering off some of the catalyst particles with subsequent recycles. However, discrete peaks of 'Ti' and 'Fe' in EDS image depicts the existence of both catalysts even in recycled beads.

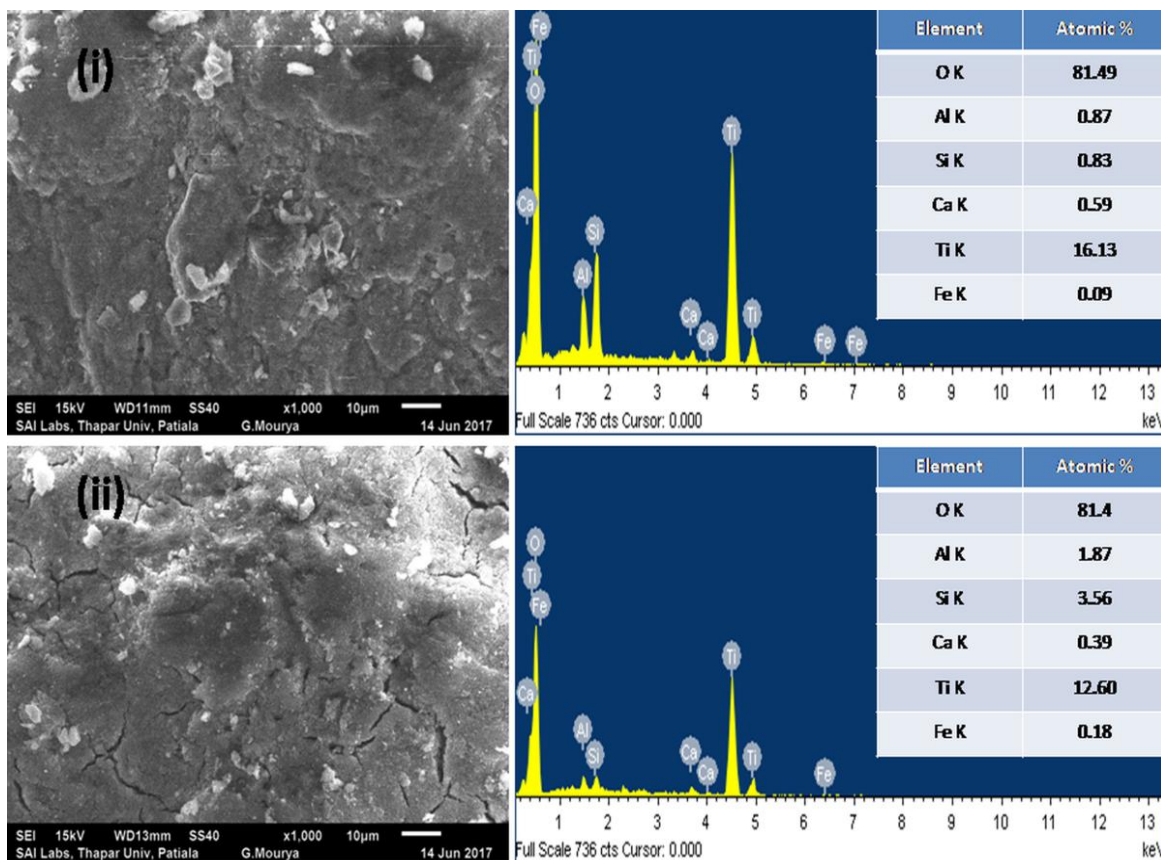


Figure 4.14a: SEM/EDS image of composite beads (i) freshly coated beads and (ii) after 10 recycles.

XRD analysis

X-ray diffraction (XRD) analysis of the composite beads was performed to examine whether any defect or change had occurred in TiO_2 due to the existence of iron. XRD pattern of composite beads was compared with fresh TiO_2 to confirm the activity of catalyst over composite beads as shown in figure 4.14b. The presence of both anatase and rutile phase of TiO_2 (marked as 'A' and 'R' respectively) in the XRD pattern of composite beads proved that no surface defect occurred in TiO_2 and thus its activity was retained. Along-with anatase and rutile peaks, few other peaks also appeared in the XRD pattern. These additional peaks indicated the presence of several forms of iron-oxide over the surface of composite beads. Iron Titanium oxide (Reference code: 00-043-1011) marked as 'ITO', Diiron (III) Titanium oxide (Reference code: 01-073-1631) marked as 'DTO' and iron (II) dititanium oxide (Reference code: 01-089-8065) marked as 'IDO' were identified through diffraction peaks along-with TiO_2 . The presence of these forms of iron oxides along with TiO_2 over composite beads further validated the effective utilization of beads for binary processes. The detailed mechanism of dual process using these forms of iron oxide along-with TiO_2 has already been discussed in section 4.7.3.

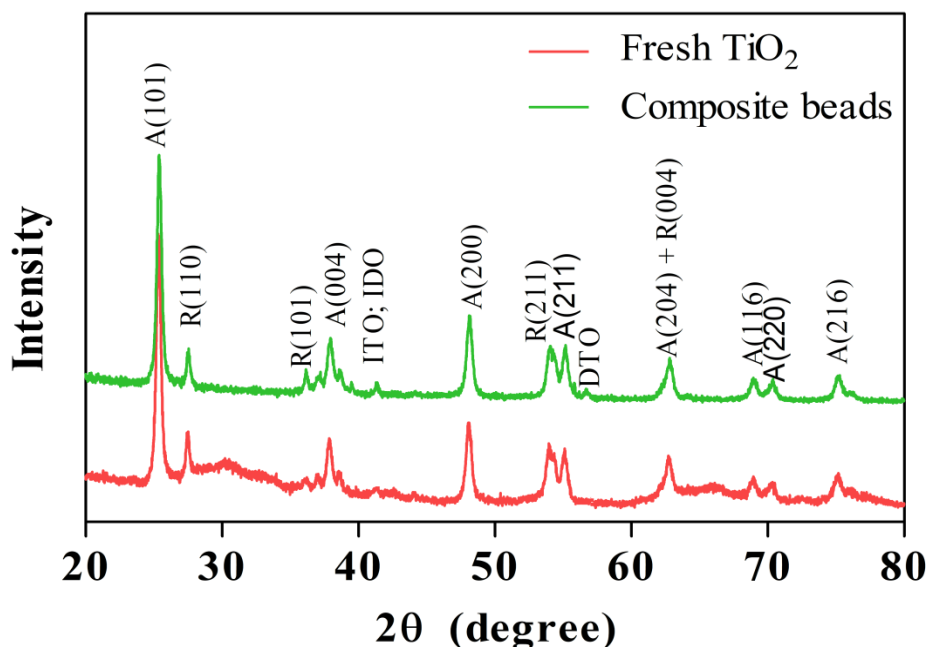


Figure 4.14b: XRD pattern of (a) fresh TiO_2 and (b) composite beads.

UV-visible diffuse reflectance spectroscopy (DRS) analysis

Diffuse reflectance spectrums of composite beads and fresh TiO_2 are demonstrated in figure 4.14c. The analysis of samples was carried out in the UV-visible range from 200-800 nm. The UV-visible spectrum of composite beads displayed its capacity for absorbing the light even in visible spectra (owing to the presence of iron) as compared to TiO_2 which is capable to absorb only UV light. The band gap of TiO_2 and composite beads was quantified using following equation:

$$E_g = h\nu = \frac{hc}{\lambda} \quad (4.21)$$

E_g = band gap energy (eV), c = speed of light, h = Planck's constant and λ = absorption wavelength

Consequently, absorption edge in case of composite beads was extended to 422 nm resulting into the narrowing of band gap ($E_g = 2.94$ eV) in contrast to TiO_2 ($E_g = 3.14$ eV).

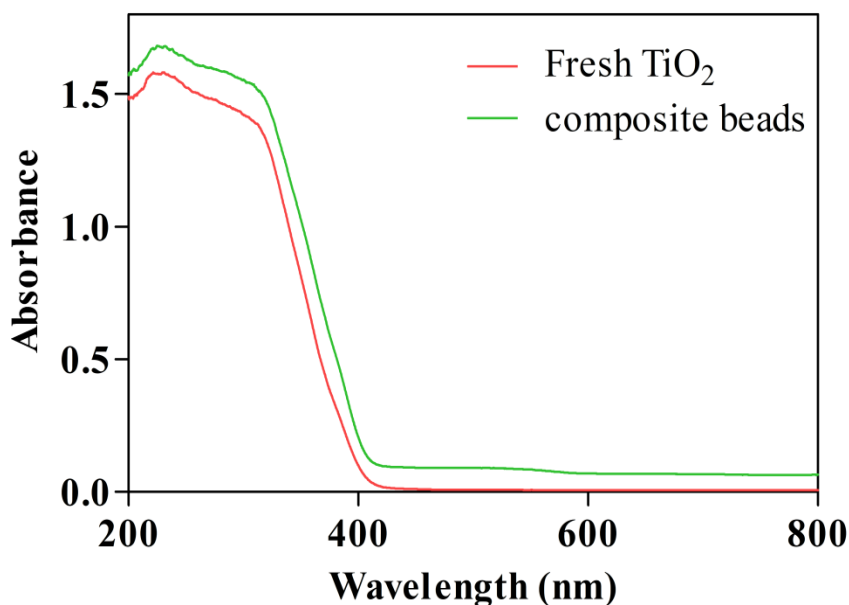


Figure 4.14c: UV-visible DRS of (a) fresh TiO_2 and (b) composite beads.

FTIR analysis

The morphological features of composite beads in comparison to fresh TiO_2 were also analyzed through FTIR spectroscopy. The infrared spectra of TiO_2 and composite beads are shown in figure 4.14d. The appearance of peaks corresponding to wave number ranging from 400-1200 cm^{-1} in both spectrums confirms the occurrence of Ti-O-Ti bonds in both samples thus proving the retention of TiO_2 lattice. The peak occurring at 503.73 cm^{-1} and 430.39 cm^{-1} in TiO_2 and composite beads, respectively represent the anatase phase (Ganesh et al., 2012). The broad peak appearing at 2078.19 cm^{-1} in the spectra of composite beads corresponds to the formation of Fe-O-Ti bond (Sayyar et al., 2015). Thus, results are in a good correlation with XRD pattern which already confirmed the existence of several forms of iron oxide i.e. 'ITO', 'DTO' and 'IDO'. The transmittance bands appearing at 1632.63 cm^{-1} and 1627.02 cm^{-1} in case of TiO_2 and composite beads respectively represent the Ti-OH groups. The occurrence of transmittance band at 3407.91 cm^{-1} and 3410.82 cm^{-1} in case of TiO_2 and composite beads can be correlated with the presence of O-H groups stretching vibrations (Ganesh et al., 2012; Sayyar et al., 2015).

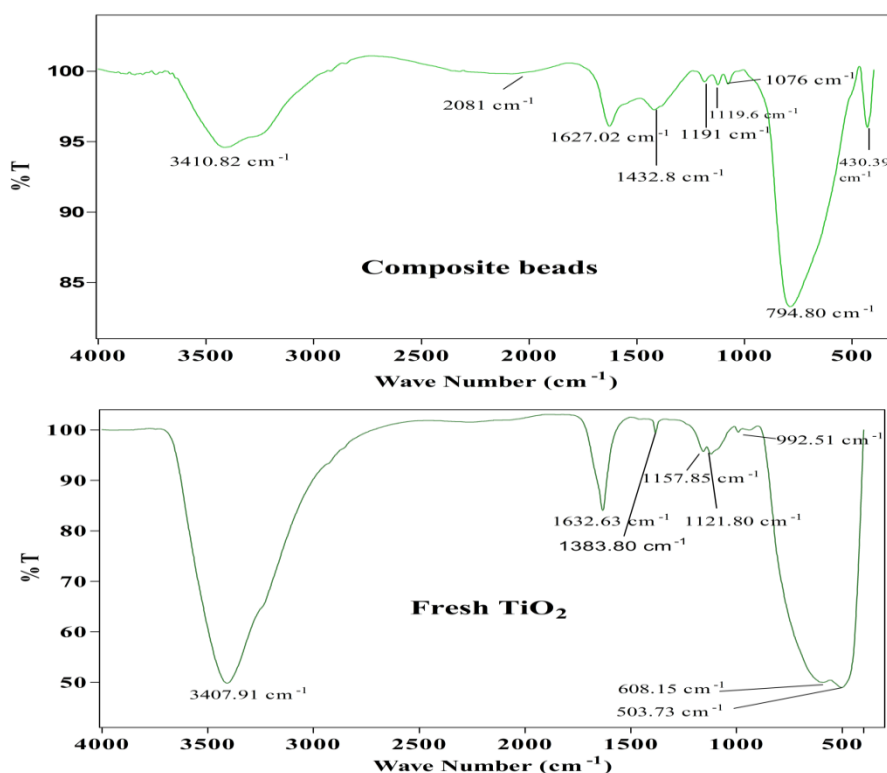


Figure 4.14d: FT-IR spectra of (a) fresh TiO_2 and (b) composite beads.

Thermo-gravimetric analysis (TGA)

The thermo-gravimetric (TG) curves of TiO_2 as well as composite beads are depicted in figure 4.14e. No remarkable variation in weights of the catalysts was observed in the temperature ranging from 30-980 $^{\circ}\text{C}$. An almost 97% weight of immobilized catalyst was retained after undergoing through high temperature (980 $^{\circ}\text{C}$) as compared to 98.6% in case of TiO_2 . Thus, it can be concluded that composite beads displayed an excellent thermal stability as compared to TiO_2 depending upon its inorganic structure.

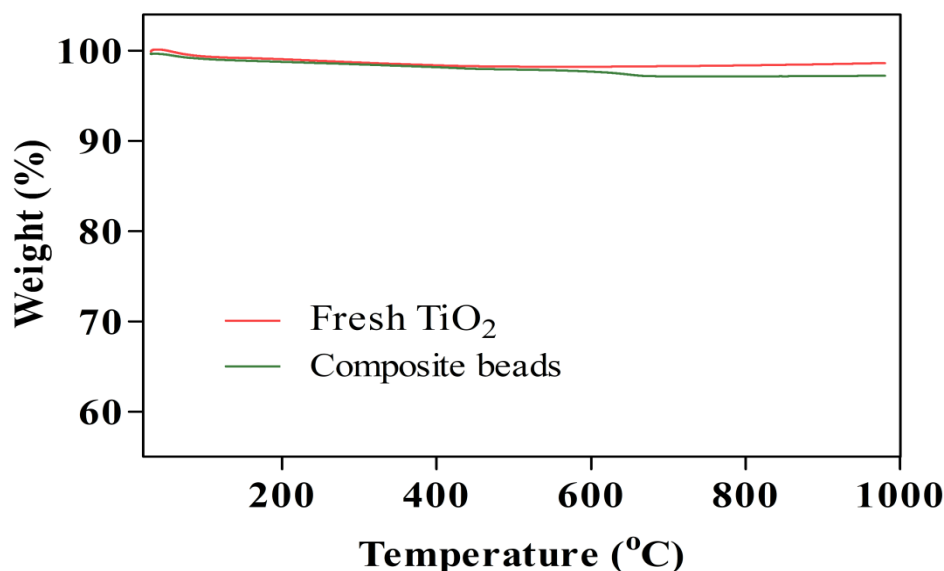


Figure 4.14e: TGA analysis of (a) fresh TiO_2 and (b) composite beads.

4.7.5 Mineralization studies

The mineralization of CEX was confirmed with generation of anions including nitrite, nitrate and sulfate ions along with reduction in COD during the treatment process as shown in table 4.5. The concentration of nitrite and sulfate ions followed an increasing trend throughout the reaction while concentration of nitrate ions followed a declining trend with the possibility of getting converted into nitrite ions (Doudrick et al., 2011). There was almost 80% reduction in COD after 120 min of treatment time. The intermediates (1-11) formed during the degradation process were identified through GC-MS analysis. The GC chromatograms indicating identified intermediates are shown in figure 4.15a. Based on these identified intermediates, a tentative pathway for the decomposition of CEX has been proposed as displayed in figure 4.15b. The fragmentation of CEX led to the formation of byproducts **(1)** and **(2)**. Reduction of **(1)** could lead

to the formation of (7) which on fragmentation could produce (8) and (9). By-product (8) could undergo benzene ring cleavage to form (10) which on successive demethylation and hydroxylation could yield the final product (11). On the other hand, consecutive dehydroxylation and reduction of (2) could lead to the formation of (3). Further reduction of (3) could possibly yield (4). The opening of cyclic ring of (4) with breakage of C-N bonds led to the production of (5). The by-product (5) could form (6) after undergoing through deamination followed by demethylation. The removal of thioether group from (6) followed by hydroxylation could finally yield the end product (7). To the best of our knowledge, this is the first reported study till date depicting the degradation pathway for CEX.

Table 4.5: Concentration of anions formed during the degradation of CEX.

Time (min)	Concentration		
	Nitrate (mgL ⁻¹)	Nitrite (µgL ⁻¹)	Sulfate (mgL ⁻¹)
30	5.09	1.33	15.6
60	4.53	1.67	22.4
90	4.07	2.3	36.3
120	3.2	2.83	44.2
150	2.8	6.33	51.3

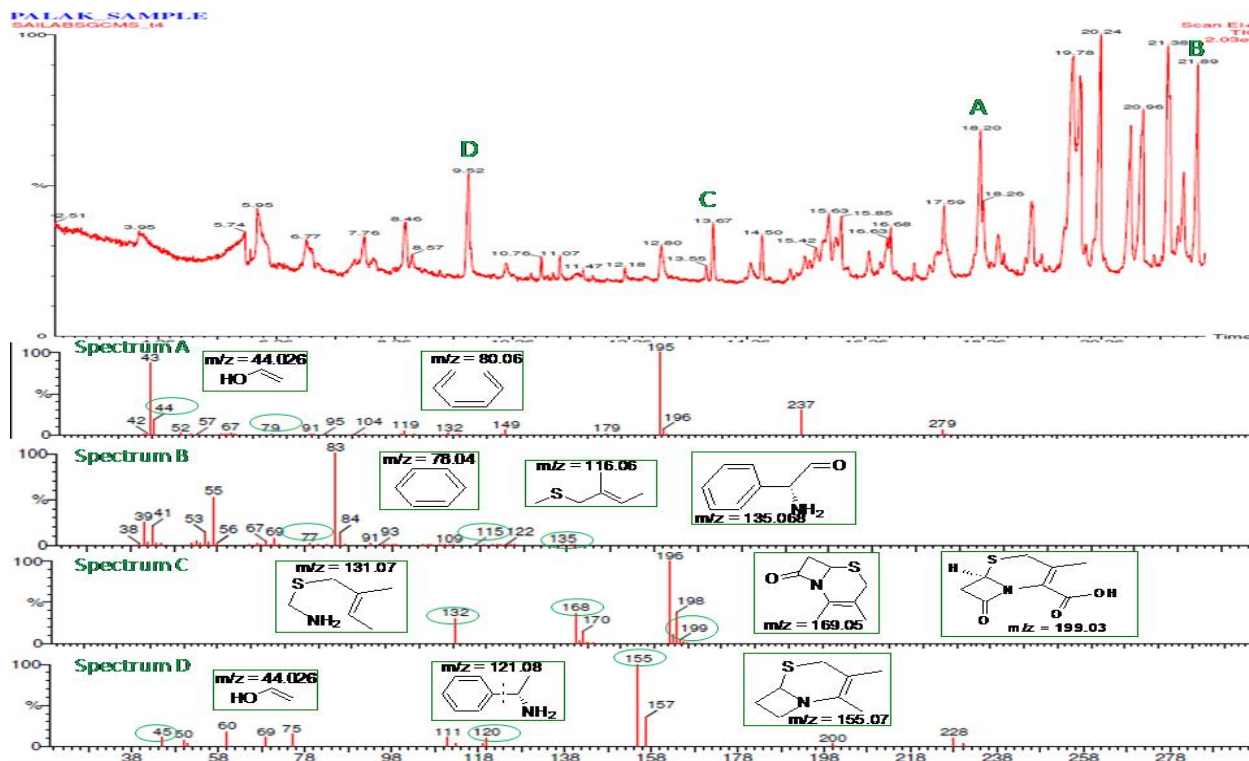


Figure 4.15a: GC chromatograms for the identification of intermediates during the degradation of CEX.

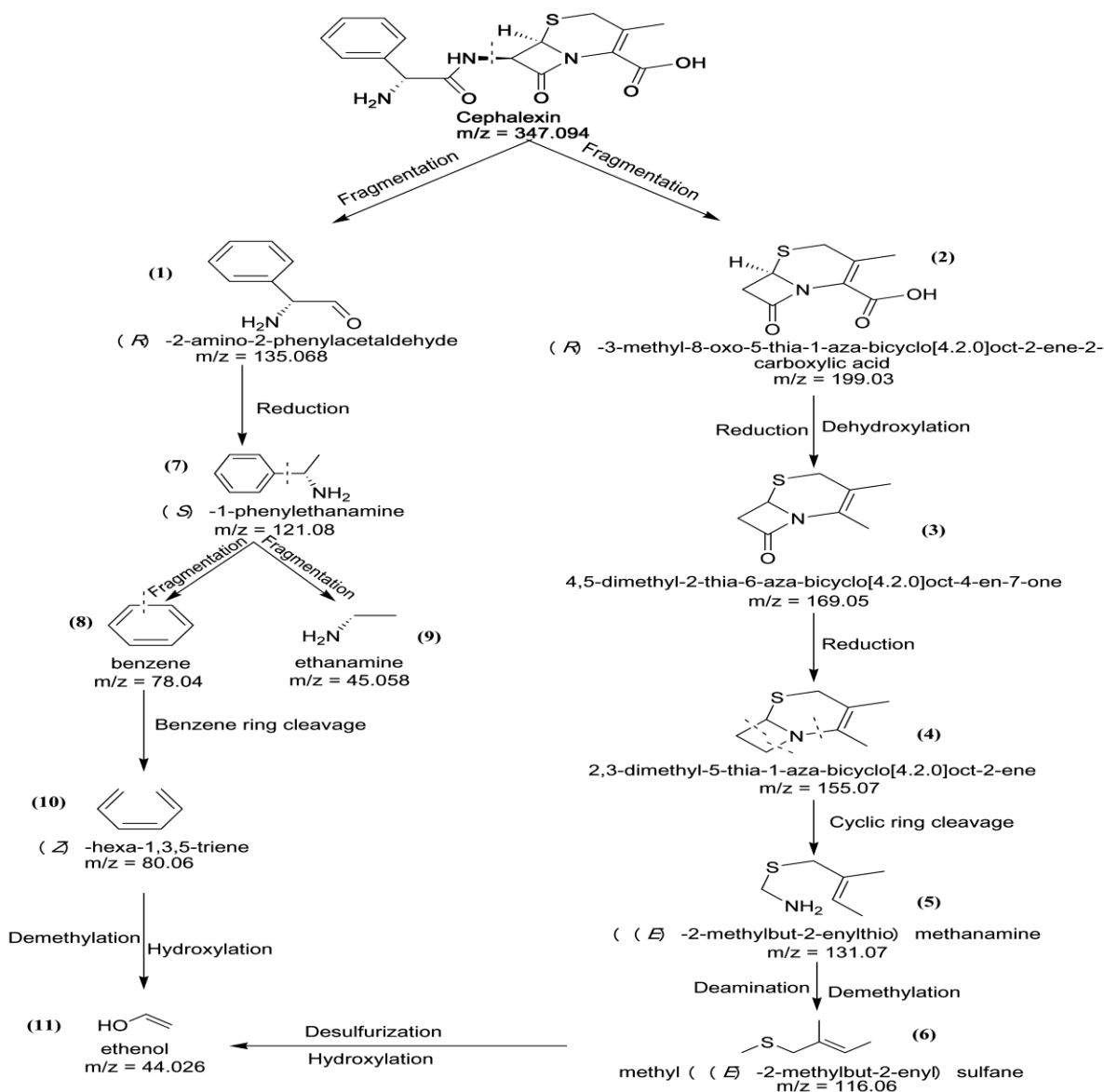


Fig. 4.15b: Tentative pathway for the degradation of CEX.

The generation of several anions along with significant reduction in COD and reasonably good degradation efficiency of CEX proved the effectiveness of in-situ dual process towards the mineralization of recalcitrant pollutants. Various shapes of supports along with their durability were discussed leading to a conclusion that spherical beads as support material could provide maximum exposed surface area to the immobilized catalyst. Though, it was observed that spherical beads (FS + clay) did not display high durability or stability of immobilized catalyst. For successful implementation of the in-situ dual effect concept at field-scale, high recyclability

efficiency of immobilized catalyst (more than 50 runs) without any significant reduction in degradation efficiency with subsequent cycles is required.

4.7.6 Clay in conjunction with FS and FA

Thus to survey the enhanced durability of the supports, various combinations of different materials (FS, FA and clay) were used to prepare spherical composite and control beads. Two different types of beads i.e. (i) FA + clay, and (ii) FS + FA + clay were prepared for TiO_2 immobilization. These beads were checked and assessed for their efficacy as well as enhanced durability for the decomposition of CEX. Beads exhibiting best results in terms of the degradation efficiency along with increased recyclability were used for process optimization taking into consideration the various parameters like number of catalyst immobilized beads, size of beads, oxidant dose, Area/Volume ratio of batch reactor, calcinations temperature and number of catalyst coatings. However, same control beads (clay/ TiO_2) as discussed in section 4.7.1 were used to conduct the photocatalytic experiments. The degradation of PEN was also carried out at optimized conditions in order to evaluate the viability of studied technique. Mineralization studies were also undertaken by monitoring the reduction in COD and TOC along with production of various anions like sulfate, nitrite and nitrate ions. Toxicity of the treated water was also checked by means of Kirby Bauer test and bio-assay test.

Effect of oxidant addition

Though prominence of dual process over individual processes has already been proved in context to the degradation of CEX and PEN, major contribution of H_2O_2 whether in photocatalysis or in photo-Fenton is unknown. The enhancement in photocatalytic degradation efficiency of organic pollutants in aqueous suspensions by adding oxidants like H_2O_2 is now a well known fact and has been reported in literature (Poulios et al., 2003). Generally, addition of H_2O_2 increases the production of hydroxyl radicals thereby enhancing the degradation rate. Thus to study the contribution of H_2O_2 towards the enhancement of degradation efficiency of CEX via photocatalysis, experiments were conducted at natural pH of CEX i.e. 5.5 with varying doses of H_2O_2 . In the present work, H_2O_2 was varied in the range 75-375 mgL^{-1} . An inappreciable increase in the degradation efficiency of CEX (only 3-5%) was noticed as dose of H_2O_2 was increased up to 150 mgL^{-1} in case of all catalyst immobilized beads. Approximately 70%

degradation of CEX was achieved with 150 mgL^{-1} of H_2O_2 in each case. When H_2O_2 dose was increased beyond 150 mgL^{-1} , scavenging effect was predominant as there was no reduction/significant change in the degradation of CEX as depicted in figure 4.16. This leads to the fact that H_2O_2 did not contribute significantly ($P > 0.05$) to the photocatalytic process but same amount of H_2O_2 (150 mgL^{-1}) when used in dual effect studies (next section) at acidic pH revealed significantly higher ($P < 0.05$) degradation of CEX thus proving the predominance of photo-Fenton. Therefore, it can be concluded that H_2O_2 contributed majorly to photo-Fenton reaction rather than photocatalysis for the degradation of CEX.

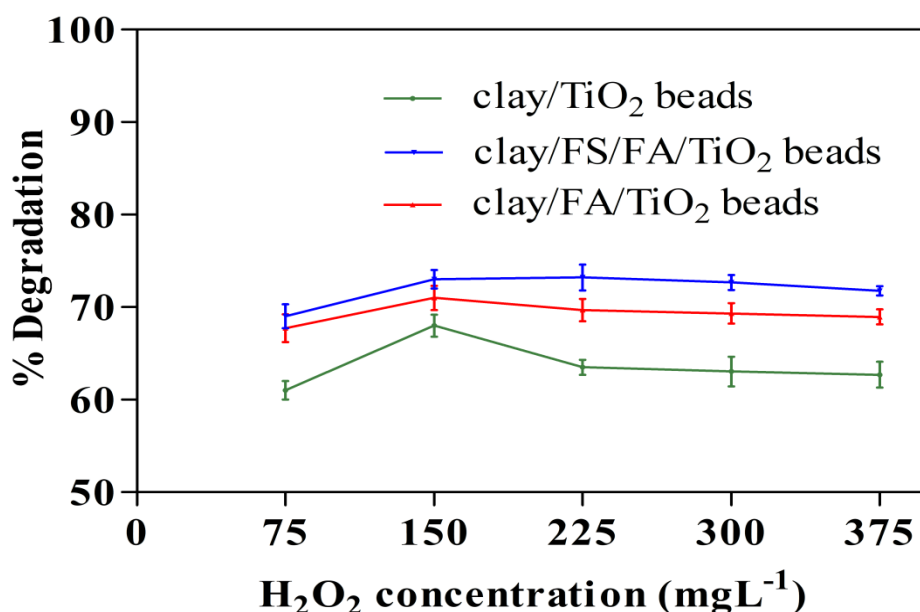


Figure 4.16: Effect of H_2O_2 concentration on the photocatalytic degradation of CEX through TiO_2 immobilized beads (CEX: 50 mgL^{-1} , $V = 200 \text{ mL}$, $\text{pH} = 5.5$).

Dual effect studies with different TiO_2 immobilized composite beads

To conduct the dual effect studies with different TiO_2 immobilized composite beads (clay/FA/ TiO_2 and clay/FA/FS/ TiO_2), degradation of CEX (50 mgL^{-1}) was carried out at acidic pH i.e. 3.5 with addition of 150 mgL^{-1} H_2O_2 . The pH was stabilized using appropriate amount of acetate buffer. Accordingly, blank studies were executed in dark with composite beads (clay/FA/ TiO_2 and clay/FA/FS/ TiO_2) which revealed an insignificant amount of reduction (5-7%) in the concentration of CEX after 240 min. To confirm the occurrence of photo-Fenton reaction (owing to the leaching of iron species), experiments were conducted under UV irradiations with blank beads (clay, clay/FA, clay/FA/FS). An almost 35% degradation was

attained in case of blank composite beads (clay/FA, clay/FA/FS) after 240 min of UV irradiations. On the other hand, negligible amount of CEX removal (3-4%) occurred in case of blank clay beads within the same treatment time thus, further confirming the occurrence of photo-Fenton reaction in case of blank composite beads. It was therefore proved that iron was leaching in case of only blank composite beads due to the presence of FA and FS.

To confirm the prominence of dual process over individual processes, photocatalytic experiments were conducted under similar conditions using control beads i.e. TiO_2 immobilized clay beads (without containing any FA/FS) which revealed an almost 75% degradation of CEX after 240 min of treatment. Expectedly, degradation of CEX was significantly higher ($P < 0.05$) with composite beads (clay/FA/ TiO_2 , clay/FS/FA/ TiO_2) exhibiting in-situ dual process as compared to that of blank and control beads imparting individual processes i.e. photo-Fenton and photocatalysis respectively. The % removal of CEX was augmented to almost 81% and 89% with clay/FA/ TiO_2 and clay/FA/FS/ TiO_2 respectively after 240 min of treatment (Figure 4.17a). The highest value of first order rate constant, k , under dual effect studies for the photo-degradation of CEX came out to be 0.011 min^{-1} using clay/FA/FS/ TiO_2 beads (Figure 4.17b).

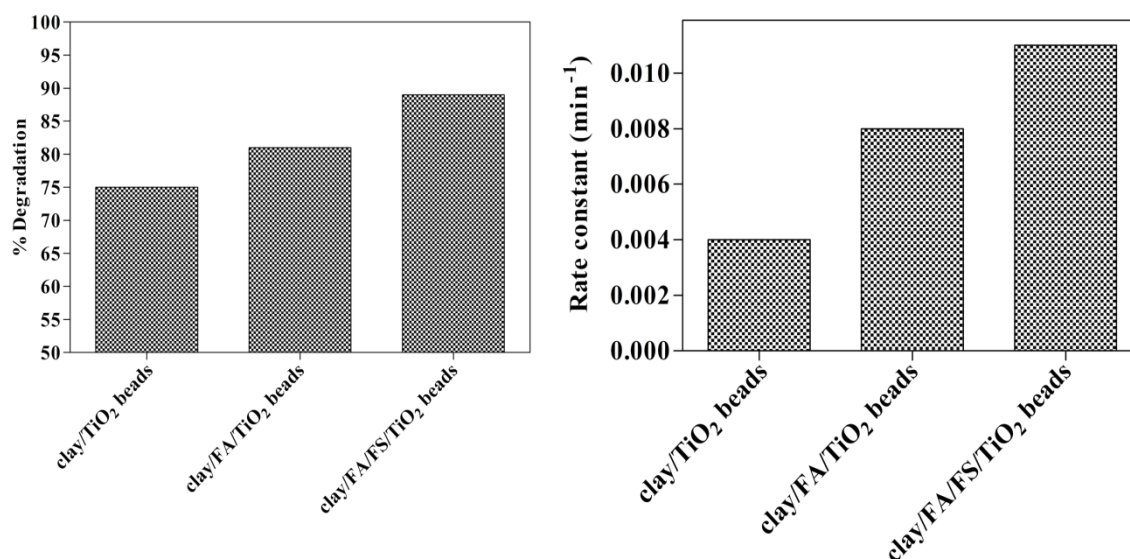


Figure 4.17: Degradation of CEX using different TiO_2 immobilized composite beads under acidic conditions (CEX: 50 mgL^{-1} , $V = 200 \text{ mL}$, $\text{pH} = 3.5$).

Furthermore, the half-life of CEX was found to be 60 min in case of clay/FA/FS/ TiO_2 beads which was considerably lower in comparison to 90 min in case of clay/FA/ TiO_2 beads and

180 min in case of control beads (clay/TiO₂) as shown in table 4.6. In spite of the uniform coating of TiO₂ on each bead, degradation was comparatively lower in case of clay/FA/TiO₂ beads as compared to clay/FA/FS/TiO₂. This might be due to the presence of lower iron content in case of clay/FA/TiO₂ beads in contrast to clay/FA/FS/TiO₂ beads. The concentration of leached iron species in case of composite beads during the course of reaction is depicted in table 4.7. Thus, it can be said that photo-Fenton reaction was more prominent in case of clay/FA/FS/TiO₂ beads. An overall synergy of dual process with composite beads (clay/FS/FA/TiO₂) over individual processes (photocatalysis or photo-Fenton) was observed to be nearly 28%.

Table 4.6: Concentration of total iron including ferrous and ferric iron leached out from different composite beads during the degradation of CEX.

Time (min)	clay/FA/TiO ₂			clay/FA/FS/TiO ₂		
	Total iron (mgL ⁻¹)	Ferrous iron (mgL ⁻¹)	Ferric iron (mgL ⁻¹)	Total iron (mgL ⁻¹)	Ferrous iron (mgL ⁻¹)	Ferric iron (mgL ⁻¹)
30	0.331	0.201	0.13	0.612	0.332	0.28
60	0.174	0.098	0.076	0.376	0.233	0.143
120	0.131	0.076	0.055	0.211	0.108	0.103
180	0.108	0.054	0.054	0.165	0.065	0.1
240	0.098	0.031	0.067	0.112	0.055	0.057

Table 4.7: Kinetic parameters for the degradation of CEX using different catalyst immobilized beads for dual effect studies.

Types of beads	t _{1/2} (min)	k (min ⁻¹)
Clay/TiO ₂	180	0.004
Clay/FA/TiO ₂	90	0.008
Clay/FA/FS/TiO ₂	60	0.011

Apart from the degradation efficiency, selection of the appropriate composite beads was evaluated on the basis of durability and stability of immobilized catalyst with subsequent cycles without displaying any loss in its activity. The order of stability of catalyst immobilization system in terms of catalyst intactness over the surface of different composite beads followed the trend: clay/FA/FS/TiO₂ > clay/FA/TiO₂. Accordingly, composite beads with composition

clay/FS/FA/TiO₂ were employed for maximum number of recycles without any significant loss in its degradation efficiency as discussed in subsequent sections. Actually use of FS along with FA increases the overall iron content which is the major facilitator of photo-Fenton process. On the other hand, incorporation of FA with FS increases the compressive strength or binding capacity of support thereby enhancing the durability of beads (Naik et al., 2011). As overall best results in terms of the degradation of CEX and durability of immobilized catalyst were observed with composite beads with composition clay/FA/FS/TiO₂, these beads were further used for optimization of all operating parameters. To remove any ambiguity regarding the composition and naming of composite beads, these selected beads having composition clay/FA/FS/TiO₂ are termed as Fe-TiO₂ composite in the subsequent sections.

With this dual effect concept, the treatment time was significantly reduced to 4 h in comparison to 5 h reported in literature (Ajoudanian et al., 2015) for the degradation of CEX. Moreover, this particular study in literature has reported 76% degradation of CEX under mercury lamp irradiation via heterogeneous photocatalysis using NiO incorporated into clinoptilolite nanoparticles in slurry mode. Whereas the present study incorporating in-situ dual process has confirmed 89% degradation of CEX in completely fixed form, thus authenticating the practical applicability of studied technique.

Effect of number of TiO₂ coatings

The influence of number of catalyst coatings on the surface of selected composite beads i.e. Fe-TiO₂ composite was studied for the photo-degradation of CEX. The degradation of CEX became steady as number of TiO₂ coatings was incremented from 2 to 4. There was no significant improvement in the degradation till 4th coating. An almost 89% degradation of CEX was achieved after 4 h of treatment in each case. However, degradation was comparatively low (68%) with only single coating of TiO₂. With each coating, a uniform layer of TiO₂ of certain thickness was developed on the surface of beads. Beyond a particular thickness of catalyst film, with further coatings of TiO₂, catalyst particles were not strongly intact to the surface of beads and were susceptible to detach from the surface (Verma et al., 2014). This would additionally increase the turbidity of solution thereby hindering the effective penetration of light due to the

increasing concentration of catalyst in solution. Thus two coatings of TiO_2 on the surface of beads were sufficient in our case.

Effect of calcinations temperature

The effect of different calcinations temperatures (200-500°C) on the photocatalytic activity of the catalyst immobilized composite beads i.e. Fe- TiO_2 composite was studied for the degradation of CEX. The catalyst immobilized beads were calcined for two hours at different temperatures. Better degradation efficiency was achieved at 400°C as compared to lower temperatures. Beyond 400°C, no improvement in the degradation efficiency of CEX was achieved. Stability of the catalyst also remains a concern at high temperature. Moreover, transformation of phases could also occur at high temperature in case of TiO_2 . It has been reported in various studies that anatase to rutile transformation occurs in the temperature ranging from 400-1200 °C (Hirano et al., 2003; Kim et al., 2001). Thus, all beads in the present study were subjected to calcinations at 400°C after TiO_2 coating.

Effect of bead size and number of beads

The size of catalyst immobilized supports affects the exposed surface area of the catalyst to make better contact with the target pollutant. Thus, size of catalyst immobilizing system/support is considered as a vital parameter especially in fixed-bed photocatalytic systems. This is particularly important when field-scale applications are to be considered. Actually, size of the catalyst support materials really helps in designing of the pilot-scale reactors where exposure of the catalyst surface area always remains a concern. In the current research work, the surface area of selected composite beads (Fe- TiO_2 composite) was altered by varying the diameter of beads for studying the degradation of CEX. Beads of three different average diameters i.e. 10 mm, 15 mm and 20 mm (Figure 4.18), measured by means of vernier caliper (as detailed in section 3.4), were compared for the degradation of CEX.



Figure 4.18: Actual photograph of different sized Fe- TiO_2 composite beads.

The maximum degradation efficiency was attained with smaller sized beads (Figure 4.19a). It was observed that value of the first order rate constant, 'k' was increased to almost 0.012 min^{-1} with decrease in the diameter of beads from 20 mm to 10 mm (Figure 4.19b). Actually available surface area of catalyst was more with smaller diameter beads (10 mm) which enhanced the degradation efficiency of CEX. However, the catalyst coating was not found to be stable on 10 mm size bead as it was drained away after few recycles. Therefore, 15 mm sized bead was optimized for all the experiments as it was found to be stable in terms of strength as well as catalyst activity.

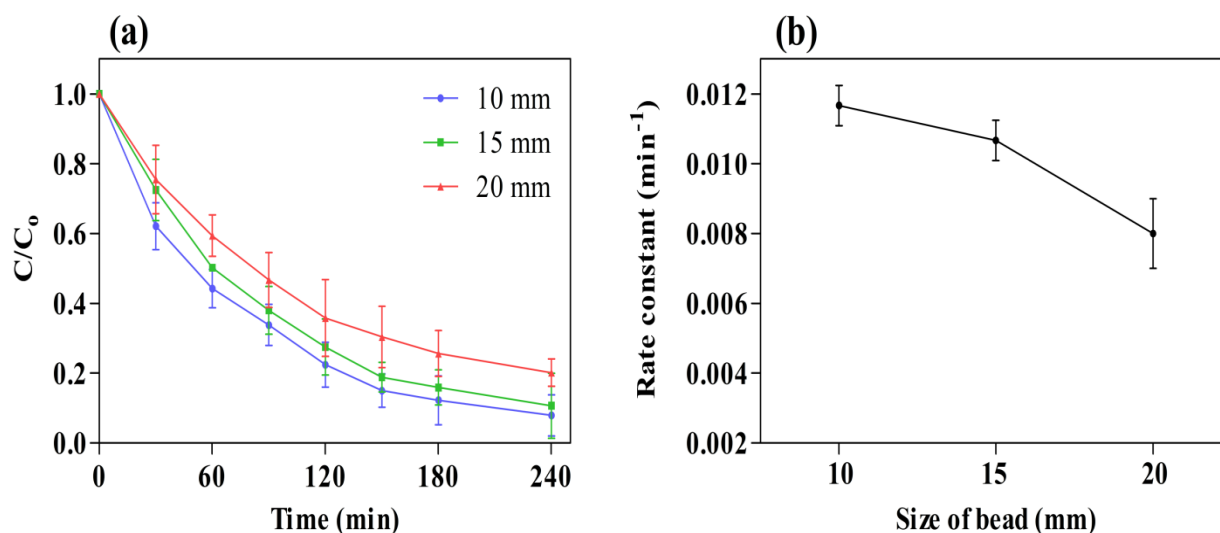


Figure 4.19: (a) Plot of C/C_0 vs time, and (b) Values of rate constant to study the effect of bead size for the degradation of CEX via in-situ dual process.

For a particular reactor design, the number of catalyst beads required for achieving the desired degradation rate is an important parameter. In our study for a batch reactor, beads (Fe-TiO₂ composite) were varied from 30 to 70 in number for the degradation of CEX.

Actually, number of catalyst beads in our study can indirectly correlate with the dose of catalyst. An increasing trend in the degradation efficiency was observed as the number of beads was increased from 30 to 50. Actually, both concentrations of TiO₂ and iron increases (simultaneously contributing to both photocatalysis and photo-Fenton) which further enhances the generation of OH radicals. The best degradation (89%) of CEX was attained with 50 beads (Figure 4.20a) covering the whole bottom surface area of the batch reactor (without any overlap of beads) as almost all active sites of the catalyst were exposed and freely available for the

pollutant binding which led to its efficient degradation. The value of rate constant, 'k' was maximum (0.011 min^{-1}) with 50 number of beads (Figure 4.20b). When number of beads was reduced to 30, degradation rate also decreased (57.35%) as number of available active sites of the catalyst gets reduced. Beads were overlapped one over the other as their number was increased to 70 leading to reduction in degradation rate. The reason for this may be the reduction in effective surface area leading to an ineffective binding of pollutant with the catalyst and moreover, it is possible that antibiotic solution got trapped in the void spaces.

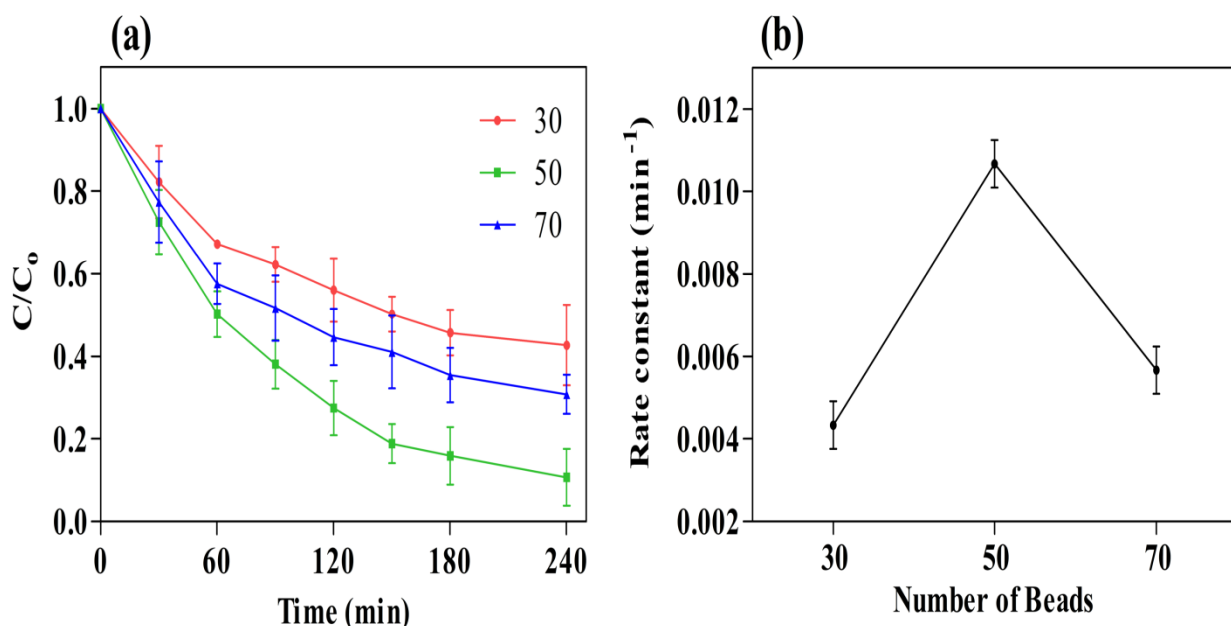


Figure 4.20: (a) Plot of C/C_0 vs time, and (b) Values of rate constant to study the effect of number of beads for the degradation of CEX via in-situ dual process.

4.7.7 Degradation studies under natural solar radiations

After parametric optimization under artificial UV irradiations, the experiments were conducted under natural solar light during March-April, 2016. The average solar intensity during the experimental period was nearly 865 Wm^{-2} as determined through pyranometer. To cross-confirm the effectiveness of in-situ dual process, photocatalysis and photo-Fenton were also carried out under sunlight at all optimized conditions as shown in figure 4.21. Solar induced degradation of CEX was comparatively better than artificial UV irradiations for all the processes. Significant increase ($P < 0.05$) in the degradation of CEX ($\sim 15\%$) was observed in case of photo-Fenton reaction as degradation was enhanced to 50% from 35% with an established fact that photo-Fenton reactions cover comparatively wider spectrum of radiations (UV + visible). No

significant increase ($P > 0.05$) in degradation of CEX was achieved in case of photocatalysis (78%). As a result, significant improvement ($P < 0.05$) in the degradation efficiency of CEX occurred via dual process under natural solar light using Fe-TiO₂ composite. The degradation of CEX was enhanced to almost 94% from 89% with reduction in treatment time to almost 3.5 h in case of dual process. Thus, promising results under natural solar irradiations further highlights the efficacy and practical feasibility of the studied in-situ dual effect with highly active and low cost composite beads (Fe-TiO₂ composite).

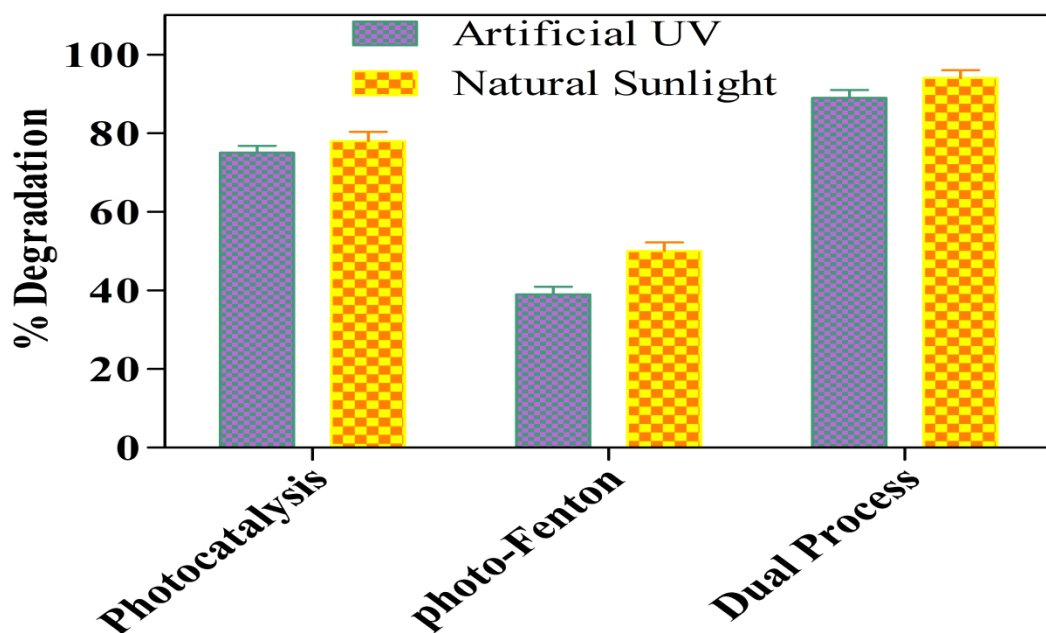


Figure 4.21: Effect of natural solar radiations on the degradation of CEX ($C_0 = 50 \text{ mgL}^{-1}$, $V = 200 \text{ mL}$, $\text{H}_2\text{O}_2 = 150 \text{ mgL}^{-1}$, $\text{pH} = 3.5$, average bead diameter = 15 mm).

4.7.8 Degradation studies of PEN at optimized conditions

Finally, viability of the in-situ dual process using selected composite beads (Fe-TiO₂ composite) was confirmed by conducting the experiments at all optimized conditions ($V = 200 \text{ mL}$, $\text{H}_2\text{O}_2 = 150 \text{ mgL}^{-1}$, average bead diameter = 15 mm) for the degradation of PEN (50 mgL^{-1}) under natural solar irradiations. Preliminary experiments were carried out to check the adsorption of PEN on blank composite beads which resulted into negligible reduction of pollutant (4-5%) after 120 min. All reactions were carried out in a similar manner with optimized number of composite beads i.e. 50 covering the entire bottom surface of reactor. As initial pH of the PEN solution ($\text{pH} = 4$) was already acidic, all reactions were carried out at this pH.

To study the effect of photo-Fenton reaction on the degradation of PEN, initially reactions were performed with blank composite beads (without TiO_2 immobilization) in the presence of 150 mgL^{-1} of H_2O_2 under natural solar irradiations. The photo-Fenton reaction resulted into an almost 72% reduction in the concentration of PEN after 150 min of solar irradiations whereas, photocatalytic treatment of PEN using control beads (clay/ TiO_2) led to an almost 75% degradation after 150 min of solar irradiations. While, in-situ dual process using composite beads (Fe-TiO_2 composite) took almost half time (75 min) to achieve 75% degradation of PEN thereby confirming the prominence of in-situ dual effect. The degradation was however increased to around 85% after 120 min of reaction using the composite beads. Figure 4.22a depicts the plot of C/C_0 Vs time to visualize the effect of different processes on the solar induced degradation of PEN. From the analysis of kinetic data, it was noticed that value of rate constant (0.034 min^{-1}) in case of in-situ dual effect was almost two fold as compared to 0.015 min^{-1} (photocatalysis) and three fold as compared to 0.012 min^{-1} (photo-Fenton) as depicted in figure 4.22b. From the statistical analysis also, it was confirmed that degradation of PEN via in-situ dual process was significantly higher ($P < 0.05$) than photocatalysis or photo-Fenton. An overall synergy of in-situ dual process over the individual processes was observed to be around 20%.

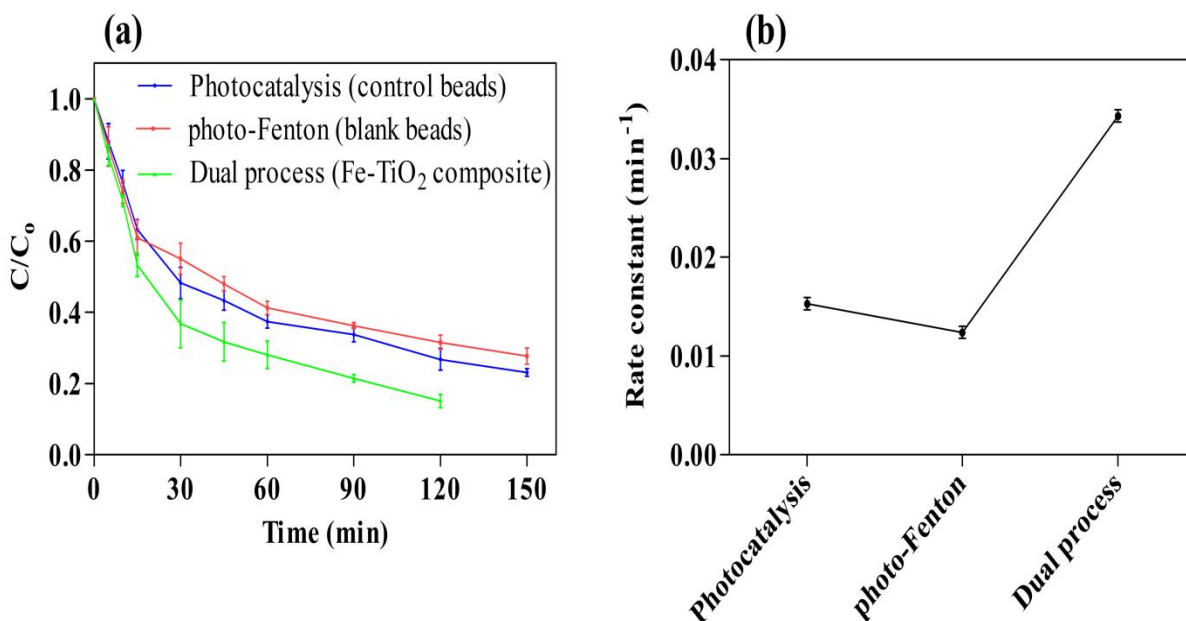


Figure 4.22: (a) Plot of C/C_0 vs time, and (b) Values of rate constant to study the effect of different processes on the degradation of PEN ($C_0 = 50 \text{ mgL}^{-1}$, $V = 200 \text{ mL}$, $\text{H}_2\text{O}_2 = 150 \text{ mgL}^{-1}$, average bead diameter = 15 mm).

As already mentioned, composite beads (Fe-TiO₂ composite) used in the present study consisted of FA and FS. Therefore, there might be concerns regarding the leaching of various toxic metals (present in FA/FS) along with iron from the composite beads (Fe-TiO₂ composite) during the course of reaction. To confirm this, treated solution of PEN (leachate) was analyzed through AAS. No simultaneous leaching of heavy metals such as lead, chromium and nickel was detected as shown in table 4.8.

Table 4.8: Characterization of leachate (treated solution) through AAS.

S. No.	Parameter	FA/FS (mgL ⁻¹)	Leachate (mgL ⁻¹)
1	Lead as Pb	0.53	<0.06
2	Nickel as Ni	<0.10	<0.10
3	Chromium as Cr	0.29	<0.05

4.7.9 Durability studies

The recyclability of immobilized catalyst with its retained activity is generally a major concern towards field scale applications of fixed-bed photocatalysis. The main motive of the present research work was to study the in-situ dual effect for the degradation of target pharmaceuticals i.e. CEX and PEN. Thus, the reported study needs to confirm both sustainable leaching of iron as well as stability of TiO₂ coating over the composite beads (Fe-TiO₂ composite) with subsequent recycling tests. In this view, durability of the composite beads was checked in terms of the intactness of both catalysts (i.e. iron as well as TiO₂).

In the current research work, durability as well as activity of catalyst immobilized composite beads (Fe-TiO₂ composite) were evaluated separately in terms of number of recycling tests for the photo-degradation of CEX as well as PEN. The beads were successfully used for at-least 35 runs without any significant loss in its activity in terms of degradation of CEX. While, the recycling tests were extended to 45 runs to further visualize the recycling capacity of composite beads in terms of the degradation efficiency of PEN (Figure 4.23). After 5 numbers of recycles, there was no significant difference ($P > 0.05$) in the degradation efficiency of both compounds between subsequent runs. The catalyst was intact to the surface and was active enough to exhibit a significant amount of degradation even after recycling for more than 35-45

cycles. Significant amount of degradation via in-situ dual process using recycled composite beads also confirms the systematic leaching of iron even from recycled beads thus contributing to photo-Fenton reaction going on simultaneously along with photocatalysis. The presence of iron along with TiO_2 even in recycled composite beads can be further confirmed from characterization of composite beads as discussed in following sections.

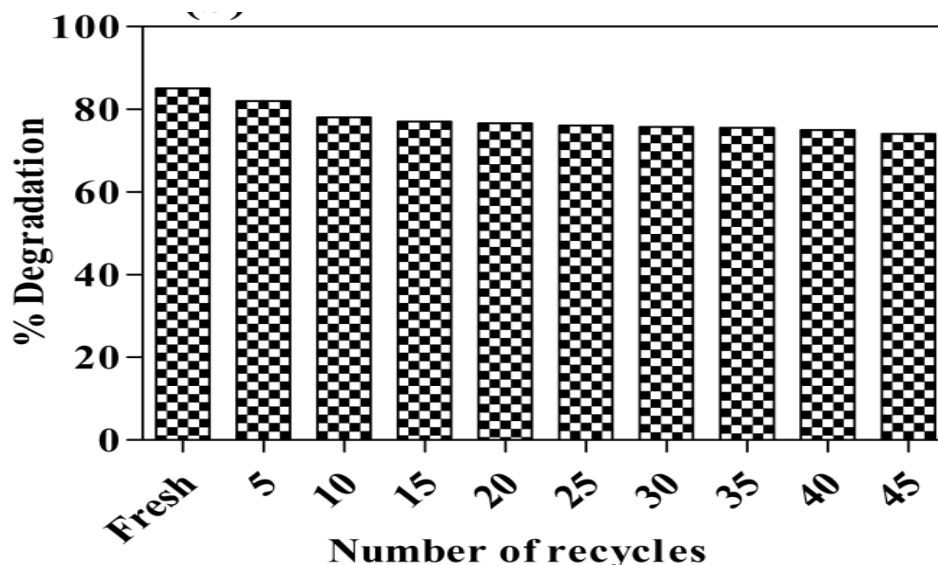


Figure 4.23: Recyclability studies of Fe-TiO₂ composite in terms of number of recycles for the degradation of PEN.

It has been reported in literature that the immobilized catalyst loses some of its activity after five or six recycles of experiment (Parra et al., 2004). The catalyst has to undergo some kind of heat treatment to regain its activity which is totally undesirable from economic point of view. Generally, supported catalyst has to undergo heat treatment at high temperature after every experiment to regain its activity.

Trials were executed in the present study to use the catalyst immobilized beads as such without undergoing any kind of heat treatment after the reaction. It was observed that immobilized catalyst was quite active as only a slight reduction in degradation efficiency of CEX was observed thus confirming the stability and efficacy of catalyst immobilized composite beads (Figure 4.24). The stability of catalyst film in case of composite beads (Fe-TiO₂ composite) with subsequent cycles without any re-activation opens up new channels in the field of waste water treatment with fixed-bed photocatalysis.

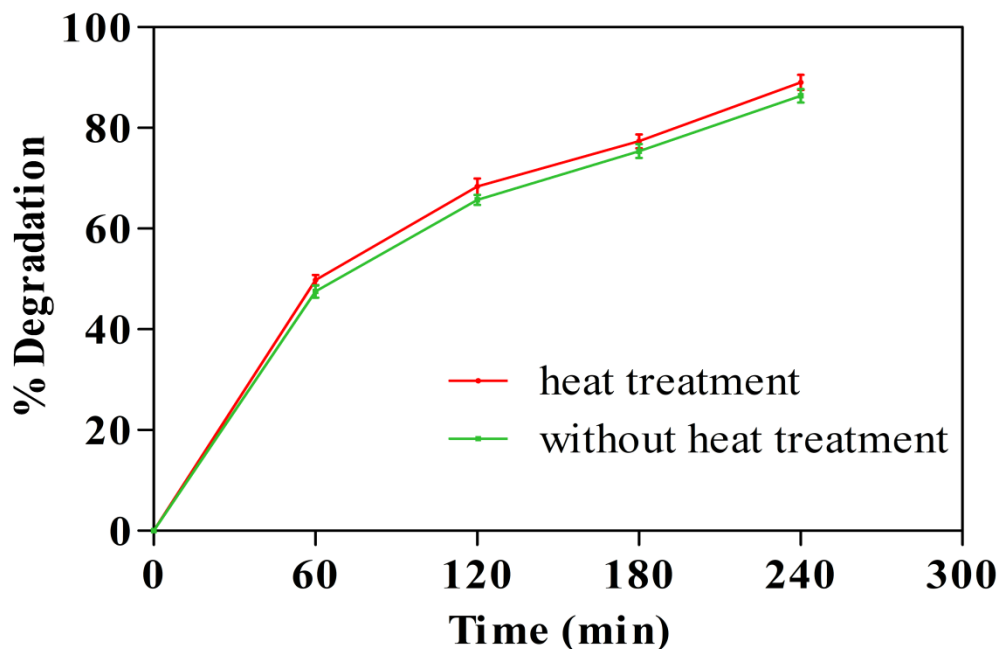


Figure 4.24: Effect of heat treatment on the beads for the degradation of CEX.

4.7.10 Characterization of composite beads (Fe-TiO₂ composite)

The optimized composite beads (Fe-TiO₂ composite) were characterized through several techniques to ensure the presence of TiO₂ along with iron even in recycled beads to confirm our claim of their effective utilization in dual effect studies even after 45 recycles.

SEM/EDS analysis

Scanning electron micrographs (SEM) were used to indicate the morphological characteristics of immobilized catalyst over the surface of composite beads (Fe-TiO₂ composite). The SEM images of freshly coated and recycled Fe-TiO₂ composite (45 runs) are shown in figure 4.25a (i and ii). Both SEM images were almost identical in terms of the surface morphologies of Fe-TiO₂ composites clearly confirming the durability of composite to be used even after 45 recycles. The electron dispersion spectra (EDS) in figure 4.25a (i and ii) of fresh and recycled (45 times) Fe-TiO₂ composites respectively indicated the elemental composition of composites. The EDS results confirmed the presence of iron in composite along with TiO₂. The existence of iron was attributed to the FA/FS used along with clay during the preparation of composite as no additional iron source was added in the composite. The prominent peaks of ‘Ti’,

‘O’ and ‘Fe’ even in recycled composite proves the intactness of TiO_2 as a film over composite along with the presence of iron even after 45 cycles. Thus, it can be concluded that Fe- TiO_2 composites can be effectively utilized in in-situ dual processes for field-scale applications.

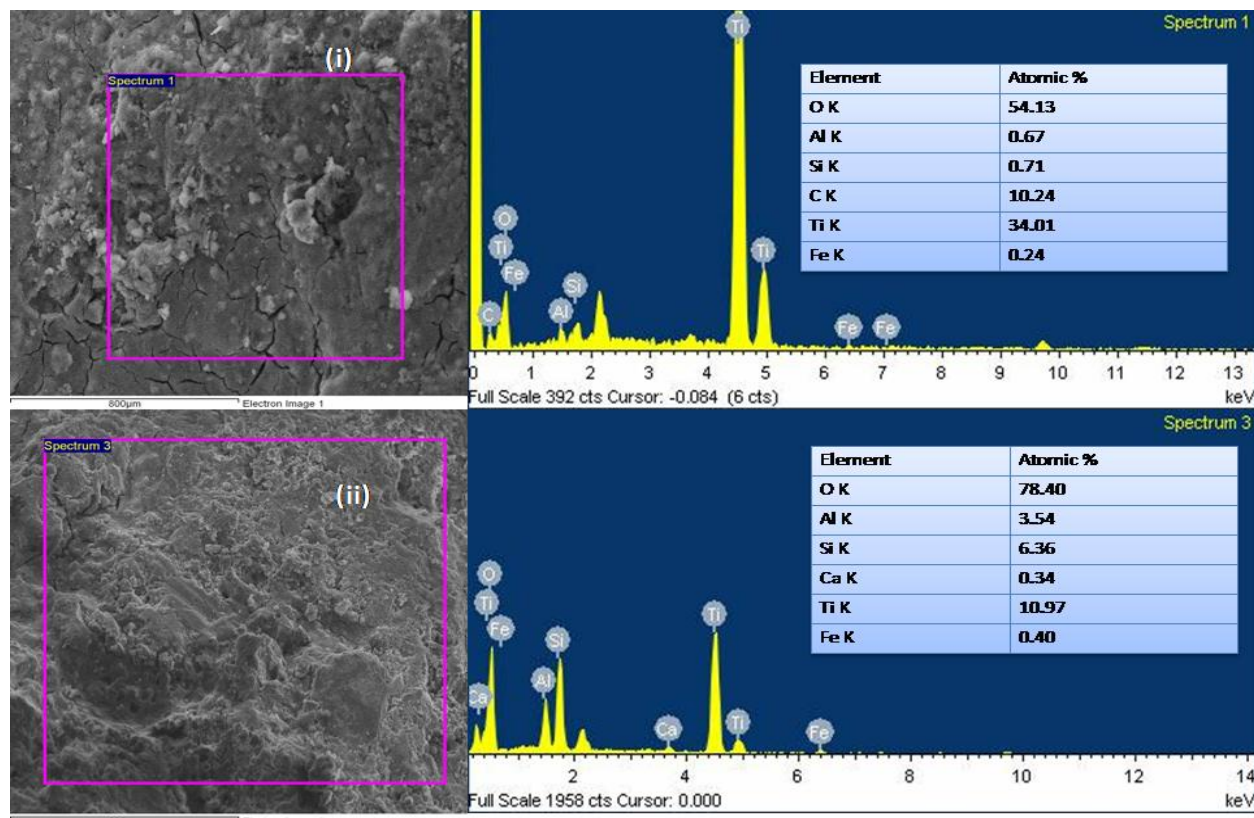


Figure 4.25a: SEM along with EDS images of (i) freshly coated Fe- TiO_2 composite and (ii) recycled Fe- TiO_2 composite (45 recycles).

XRD analysis

X-Ray Diffraction (XRD) of fresh TiO_2 -P25 and recycled Fe- TiO_2 composite was performed to verify whether any change in the photocatalytic activity of immobilized TiO_2 over composite occurred after 45 recycles. XRD pattern of TiO_2 -P25 and immobilized catalyst extracted from the surface of Fe- TiO_2 composite is shown in figure 4.25b. The strong diffraction peaks at $2\theta=25.4^\circ$, 37.8° , 48° , 54.8° , 62.5° and 70° corresponding well to 101, 004, 200, 211, 204, 220 planes showed the presence of anatase phase of TiO_2 -P25 in Fe- TiO_2 composite and is indicated by ‘A’ in figure. While, the diffraction peaks at $2\theta=27.4^\circ$, 36.2° , 53.8° and 62.5° corresponding to 110, 101, 211 and 004 planes depicted the presence of rutile phase of TiO_2 -P25 in composite and is indicated by ‘R’ in figure. The existence of anatase (reference code: 01-075-

2546) and rutile (reference code: 01-089-8304) phase of TiO₂-P25 confirmed the retention of catalyst activity over composite even after 45 recycles. In addition to the anatase and rutile peaks of TiO₂, few more diffraction peaks were observed in XRD pattern of immobilized catalyst over composite which confirmed the presence of iron dititanium oxide (reference code: 01-076-2372) and iron titanium oxide (reference code: 01-070-0143) along with TiO₂. The diffraction peaks at $2\theta=20.7^\circ$, 26.7° , 33.2° , 40.3° , 41° , 50.16° , 60° , 64.9° , 73.19° and 78.6° ensured the presence of iron titanium oxide marked as 'ITO' in graph whereas peaks at $2\theta=20.7^\circ$, 26.7° , 40.3° , 41° , 42.4° , 60° , 64.9° , 73.19° and 78.6° assured the existence of iron dititanium oxide marked as 'IDO' in graph. The presence of ITO and IDO validated the existence of iron oxides on the surface of composite beads along with TiO₂. The use of these iron oxides in in-situ dual process can be clearly understood from the dual effect mechanism (Figure 4.13) that was discussed in case of clay/FS/TiO₂ beads. Therefore, Fe-TiO₂ composite can be suitably used for dual effect studies for numerous cycles without losing the catalyst activity.

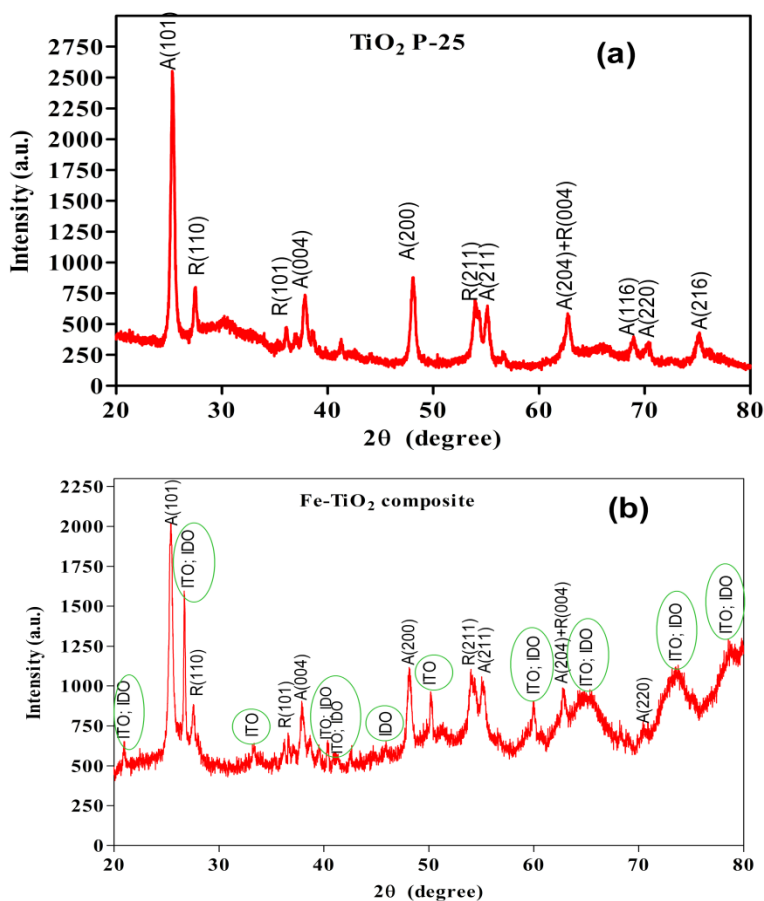


Figure 4.25b: XRD pattern of (a) fresh TiO₂-P25 and (b) recycled Fe-TiO₂ composite.

UV-visible diffuse reflectance spectroscopy (DRS) of Fe-TiO₂ composite

Accordingly, the band gap energy of fresh TiO₂-P25 and immobilized catalyst from Fe-TiO₂ composite was analyzed from diffuse reflectance spectrometer (DRS). The analysis of the samples was carried out in the range 200-800 nm as shown in figure 4.25c. The absorption edge in case of Fe-TiO₂ composite was extended to 431 nm. The band gap was quantified according to equation 4.21 as already discussed before. The band gap was comparatively lower ($E_g = 2.87$ eV) in case of Fe-TiO₂ composite as compared to TiO₂ ($E_g = 3.14$ eV). The reduction in band gap in case of Fe-TiO₂ composite cross-confirms the formation of 'ITO' and 'IDO' (as discussed in XRD), thus facilitating the absorption of light comparatively at lower levels of energy thereby making the absorption feasible even in visible spectrum. The spectral shift might be due to the formation of an energy level within the band gap of TiO₂.

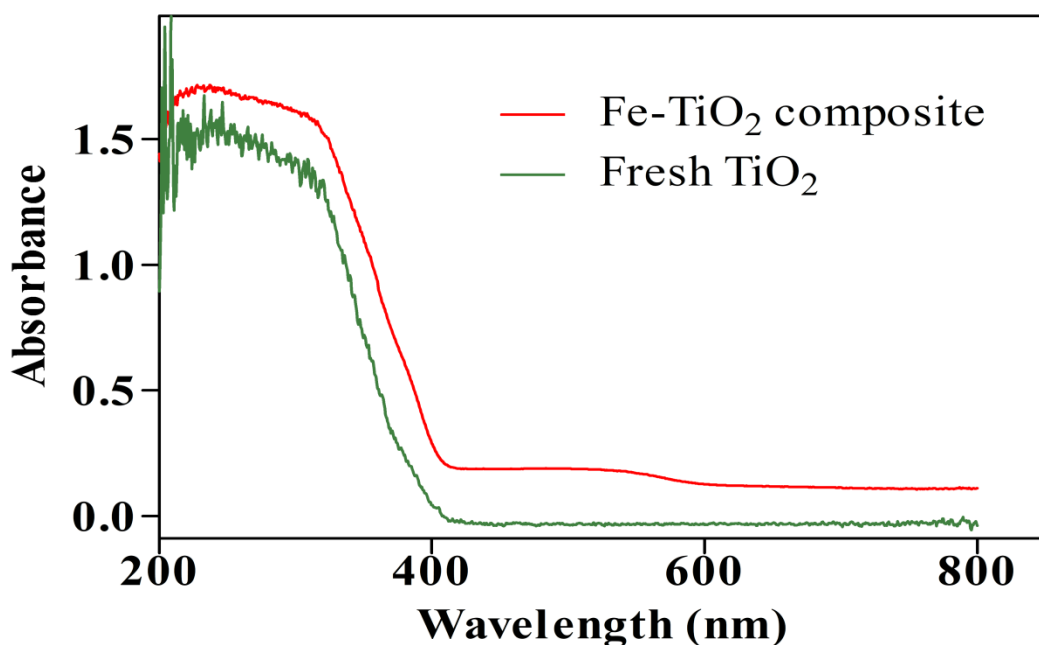


Figure 4.25c: UV-visible DRS of fresh TiO₂ and Fe-TiO₂ composite.

4.7.11 Mineralization studies

Since the catalyst immobilized support has now been optimized as Fe-TiO₂ composite (clay + FA + FS + TiO₂), the mineralization studies were carried out again for both compounds i.e. CEX and PEN. The mineralization of each compound was validated by evaluating the

reduction in TOC and COD along with quantification of various anions. The intermediates formed during the degradation process were also identified through GC-MS analysis.

In case of CEX, production of various anions including nitrite, nitrate and sulfate ions was observed during the degradation process. Maximum production of anions was observed during the first hour of reaction. Table 4.9 shows the concentration of anions formed during the treatment of CEX. Along with the generation of anions, an almost 82% and 73% reduction in COD and TOC respectively was observed after 4 h of photo-treatment of CEX thus confirming the mineralization of CEX. The mass spectra analysis for the identification of intermediates during the photo-degradation of CEX via in-situ dual process using Fe-TiO₂ composite is shown in figure 4.26. Table 4.10 depicts the complete list of intermediates identified during the degradation of CEX through GC-MS analysis. Few intermediates including (R)-2-amino-2-phenylacetaldehyde and (R)-3-methyl-8-oxo-5-thia-1-aza-bicyclo [4.2.0] oct-2-ene-2-carboxylic acid were found to be same as detected earlier for the degradation of CEX via in-situ dual process using composite beads with composition clay/FS/TiO₂ as discussed in section 4.7.5.

Table 4.9: Concentration of anions formed during the degradation of CEX.

Time (min)	Concentration (mgL ⁻¹)		
	Nitrate	Nitrite	Sulfate
60	1.09	0.37	1.42
120	1.25	0.49	1.79
180	1.67	0.55	2.21
240	1.96	0.68	2.72

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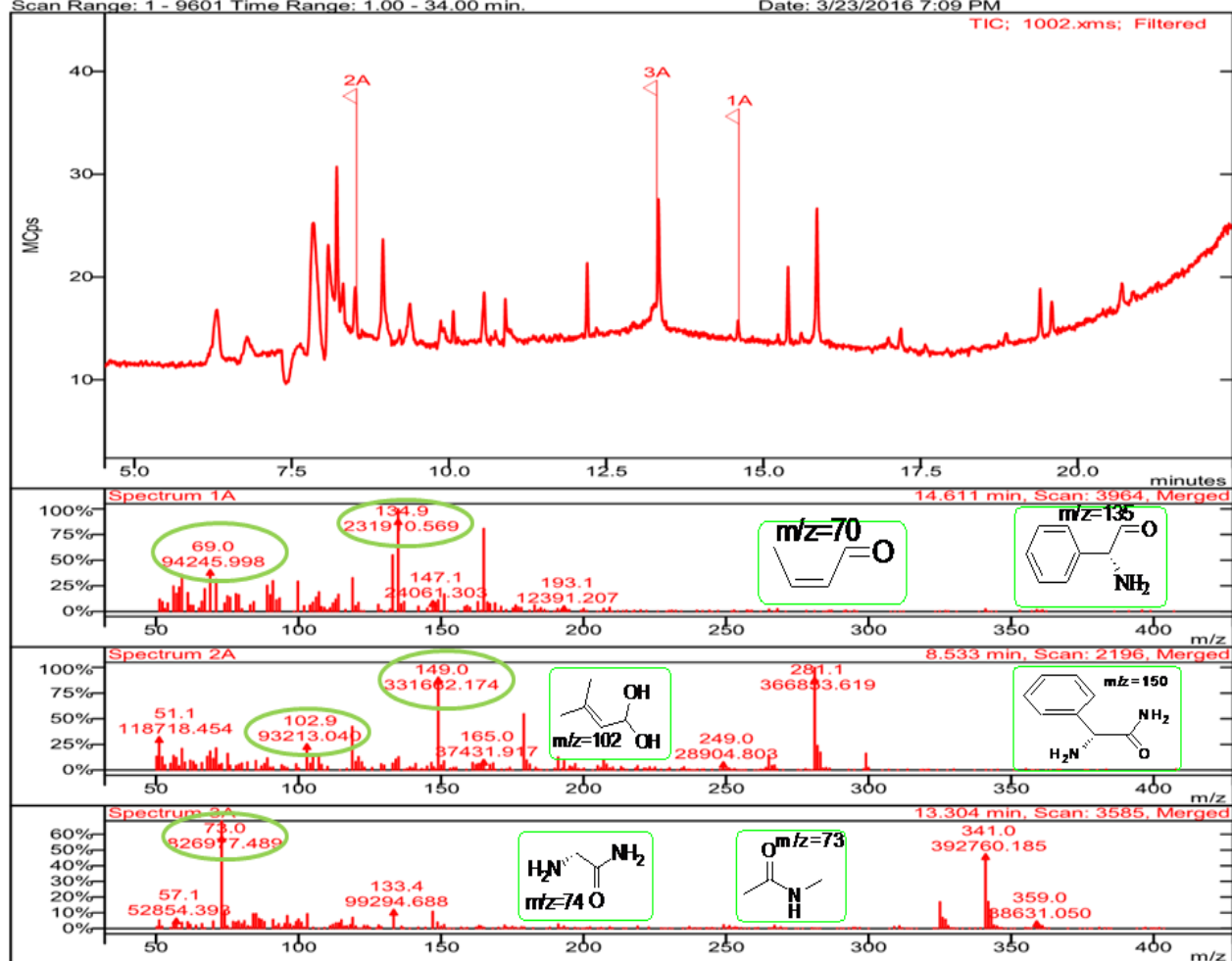
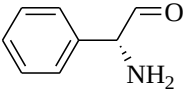
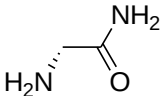
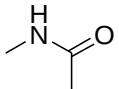
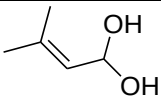
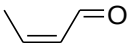


Figure 4.26: Mass spectra analysis for the identification of intermediates during the photo-degradation of CEX.

Table 4.10: List of intermediates identified during the degradation of CEX.

S.No.	Name of the compound	m/z ratio	Chemical structure
1	(R)-2-amino-2-phenylacetamide	150.079	<chem>NC(=O)[C@H](c1ccccc1)N</chem>
2	(R)-3-methyl-8-oxo-5-thia-1-aza-bicyclo[4.2.0]oct-2-ene-2-carboxylic acid	199.03	<chem>CC1=C(C(=O)O)N2C(=O)SC12</chem>

3	(R)-2-amino-2-phenylacetaldehyde	135.068	
4	2-aminoacetamide	74.048	
5	N-methylacetamide	73.053	
6	3-methylbut-2-ene-1,1-diol	102.068	
7	(Z)-but-2-enal	70.042	

Similarly, the mineralization studies for PEN were conducted by monitoring the reduction in TOC and COD along with the production of nitrite and nitrate ions. The production of nitrite and nitrate ions was maximum during the first 30 min of reaction as depicted in table 4.11. After 1 hr, there was a steady increase in the concentration of nitrite ions while nitrate ions concentration started decreasing with the possibility of conversion from nitrate to nitrite and some part of nitrate could also result in the formation of ammonium ions. The accumulated electrons could possibly reduce nitrate to nitrite according to chemical equation 4.22 (Kudo et al., 1992). Actually the acetic acid (from acetate buffer used in our treatment) could serve as hole scavenger thereby enhancing the reduction of nitrates (Prairie et al., 1993). 94.7% and 90% reduction in COD and TOC respectively occurred after 120 min of reaction thus confirming the mineralization of PEN.



The degradation by-products of PEN (I₁-I₇) were identified through GC-MS analysis as depicted in figure 4.27a. Based on these identified by-products, a tentative degradation pathway for PEN has been proposed (Figure 4.27b). The demethylation of PEN in route A led to the formation of 3-methyl-1-(5-oxohexyl)-1H-purine-2,6(3H,7H)-dione from which 1-(4-hydroxy-5-oxohexyl)-3,7-dimethyl-1H-purine-2,6(3H,7H)-dione was formed by successive hydroxylation and methylation. The fragmentation of this compound led to the generation of intermediate I₁. The subsequent oxidation of I₁ produced I₂. The reduction followed by demethylation and oxidation of I₂ ultimately led to the production of I₃. On the other hand, the oxidation of PEN in route B could lead to the formation of 3,7-dimethyl-1-(5-oxohexyl)-1H-purine-2,6,8(3H,7H,9H)-

trione which on fragmentation could give rise to the intermediates I₄ and I₅. I₄ was further oxidized to I₆. The removal of carbonyl group (ketone) from I₆ followed by oxidation led to the generation of I₇.

Table 4.11: Concentration of anions formed during the degradation of PEN.

Time (min)	Concentration	
	Nitrate (mgL ⁻¹)	Nitrite (µgL ⁻¹)
30	5.34	9
60	4.01	9.69
90	2.87	10.59
120	1.66	11.66

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Sample: p1

Scan Range: 1 - 6250 Time Range: 3.00 - 60.01 min

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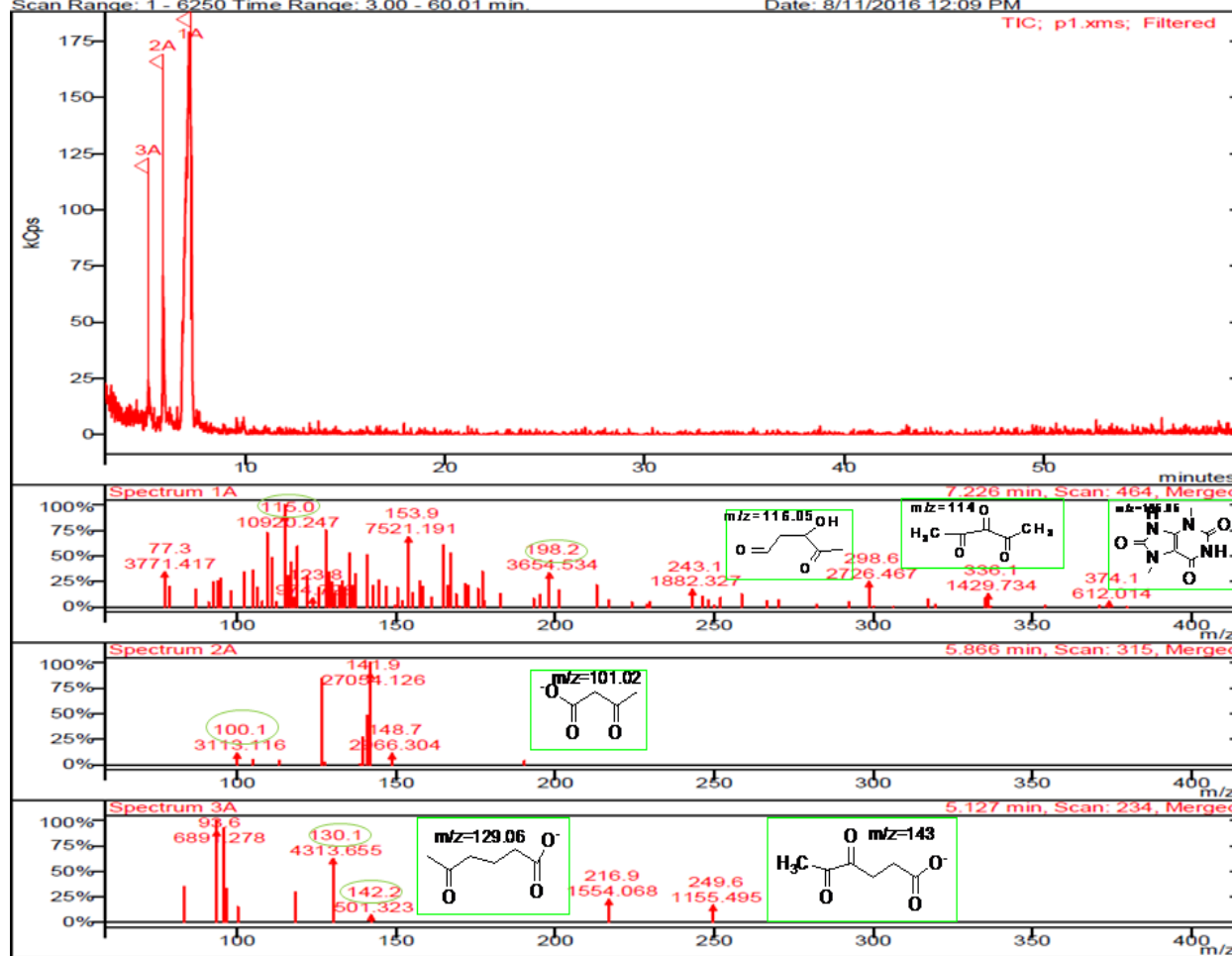


Figure 4.27a: Mass spectra analysis for the identification of intermediates during the degradation of PEN.

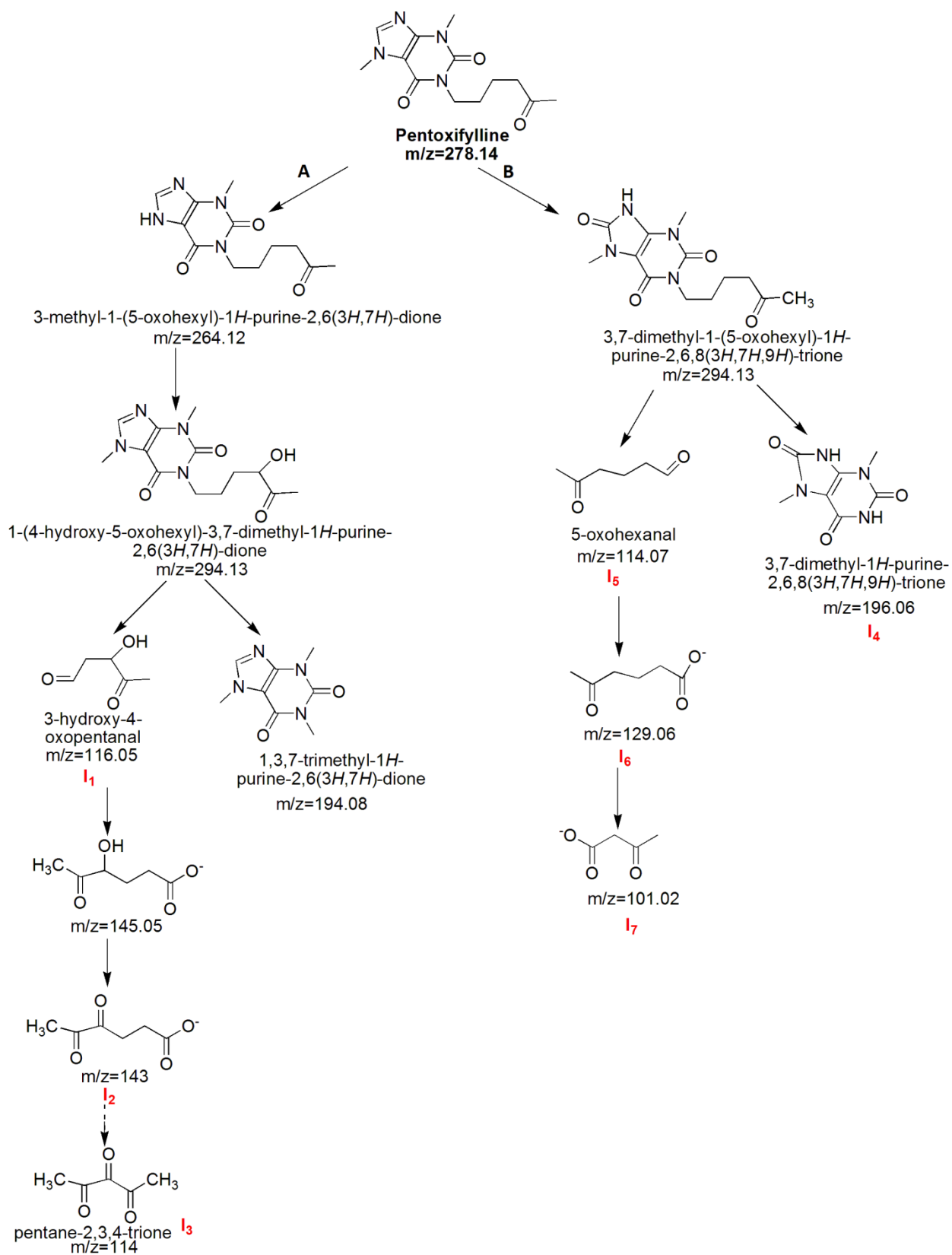


Figure 4.27b: Tentative pathway for the degradation of PEN.

4.7.12 Toxicity analysis

The effectiveness of in-situ dual process via Fe-TiO₂ composite was further confirmed by assessing the quality of treated solutions of PEN and CEX. The quality of treated solutions of each compound was checked by performing the cyto-toxicity and acute toxicity tests. Cyto-toxicity of the treated samples was carried out through Kirby-Bauer method (agar well diffusion) taking pure working solutions of respective parent compound as control while acute toxicity was conducted through bio-assay method of the treated samples.

For Kirby-Bauer test, 5 mm wells were punched in Muller Hinton agar plates using a sterile cork borer. Subsequently, 30 µl of samples taken at different intervals (15 min, 60 min and 120 min) during the treatment process of PEN was dispensed in each well and allowed to diffuse at 37 °C for 20 minutes. The wells were sealed with molten MHA and allowed to solidify. Further, the plates were swabbed with 18–24 h old 0.5 McFarland adjusted culture of *E.coli*. The plates were then incubated at 37 °C for overnight. Cyto-toxic activity was determined by measuring the zone of inhibition formation around the well. No zone of inhibition was observed in any sample thus indicating that samples did not acquire any toxicity during or after treatment as shown in figure 4.28a. Likewise, cyto-toxicity was determined in case of CEX as well adjusted culture of *B. Subtilis*. It was observed that pure working solution of CEX (control) exhibited a clear zone of inhibition which dramatically disappeared after the treatment process as shown in figure 4.28b. Thus, it can be concluded that samples lose their toxicity after treatment through in-situ dual process.

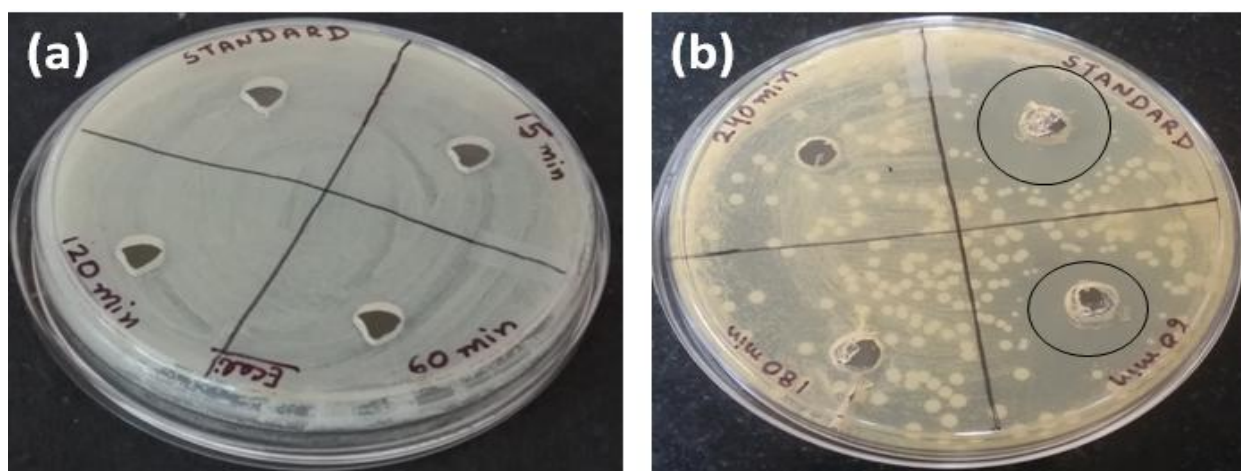


Figure 4.28: Toxicity analysis through agar well diffusion assay during the degradation of (a) PEN and (b) CEX.

Further, acute toxicity potential of the treated samples of both CEX and PEN was checked using bio-assay method (acceptable by Central Pollution Control Board, India) based on toxicity factor i.e. minimum amount of dilution of wastewater required for achieving no mortality for zebra fish. According to the results from toxicity test, 100% survival was obtained after 96 h of test in case of both CEX and PEN (Figure A1, A2 (Appendix)). Therefore, it can be concluded that the treated water in case of CEX and PEN was non-toxic in all respects leading to a proposition that in-situ dual process using Fe-TiO₂ composite can be successfully adopted for field-scale applications.

Section B

Modified in-situ dual process

4.8 Modified in-situ dual process for the degradation of CEX and PEN using Ag doped TiO₂

The effectiveness of in-situ dual effect using Fe-TiO₂ composite for the degradation and mineralization of CEX and PEN has already been established in Section A. In this particular section, efforts have been made to further widen the solar applications of Fe-TiO₂ composite. For this, photo-response efficiency of Fe-TiO₂ composite was enhanced by replacing TiO₂-P25 with Ag doped TiO₂ in composite. The Ag modified TiO₂ (synthesis procedure has already been briefed in Section 3.6) was characterized through several techniques to confirm the distribution of Ag on TiO₂ surface. To confirm the enhanced activity of doped TiO₂, initially photocatalytic experiments were conducted in slurry mode with process optimization for the degradation of PEN. For fixed-bed studies, Ag modified Fe-TiO₂ composite (now termed as Fe-Ag-TiO₂ composite) was used incorporating in-situ dual effect (modified photocatalysis and photo-Fenton) for the degradation of PEN under natural solar irradiations. The mineralization studies were also carried out by monitoring the generation of various anions along with reduction of COD and TOC whereas intermediates were identified through GC-MS analysis. To confirm the viability of Fe-Ag-TiO₂ composite, modified in-situ dual process was carried out at optimized conditions for the degradation of CEX as well. To the best of our knowledge, this is the first ever reported study introducing the concept of in-situ dual effect using immobilized doped TiO₂.

4.8.1 Characterization of Ag-TiO₂-P25

The Ag doped TiO₂ (1.5 wt. %) was characterized through various techniques and was compared with TiO₂-P25 to confirm the presence of Ag onto the surface of TiO₂.

UV-visible diffuse reflectance spectroscopy (DRS) analysis

The band gap energy of the catalysts was identified through UV-visible diffuse reflectance spectroscopy. The diffuse reflectance spectra of TiO₂-P25 and Ag-TiO₂-P25 are shown in figure 4.29a. The spectra of Ag-TiO₂-P25 displayed a new broad band between 400 and 800 nm which can be ascribed to the presence of Ag particles. Therefore the broad band in doped catalyst clearly depicted the capability of absorption of light even in visible spectrum which is directly in correlation with previously reported studies for Ag doped catalysts (Ko et al., 2011). The band gap of catalysts was calculated using equation 4.21. In the present case, absorption edge was increased to 432 nm and thus, band gap narrowing was resulted in case of doped catalyst ($E_g = 2.87$ eV) as compared to TiO₂-P25 ($E_g = 3.14$ eV). Suwanchawalit et al. (2012) has demonstrated similar kind of results indicating reduction in band gap energy of TiO₂ owing to the existence of silver particles.

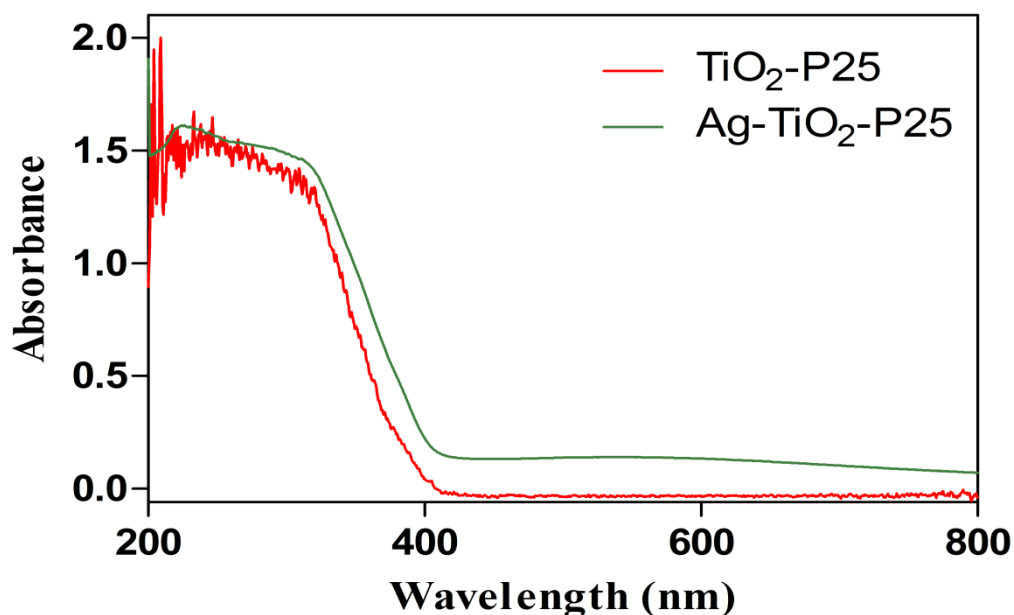


Figure 4.29a: UV-visible DRS of TiO₂-P25 and Ag-TiO₂-P25.

SEM/EDS analysis

The surface morphological structures of synthesized Ag-TiO₂-P25 along with TiO₂-P25 were investigated through SEM analysis (Figure 4.29b (i)). The SEM image demonstrated high extent of aggregation of some crystalline particles. Similar kinds of results were observed earlier by Suwanchawalit et al. (2012). The Ag particles were not perceived through SEM image owing to its either smaller size or its low quantity impregnated onto the surface of TiO₂.

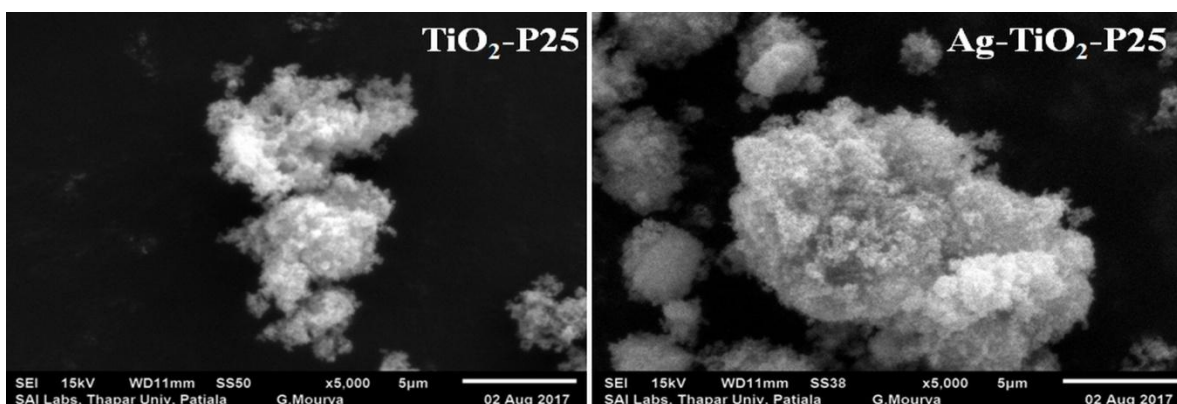


Figure 4.29b (i): SEM images of TiO₂-P25 and Ag-TiO₂-P25.

However, the occurrence of Ag particles onto TiO₂ surface was confirmed through EDS analysis (Figure 4.29b (ii)). The distinguished peak of Ag along with Ti and O peaks assured the impregnation of Ag particles onto TiO₂ surface.

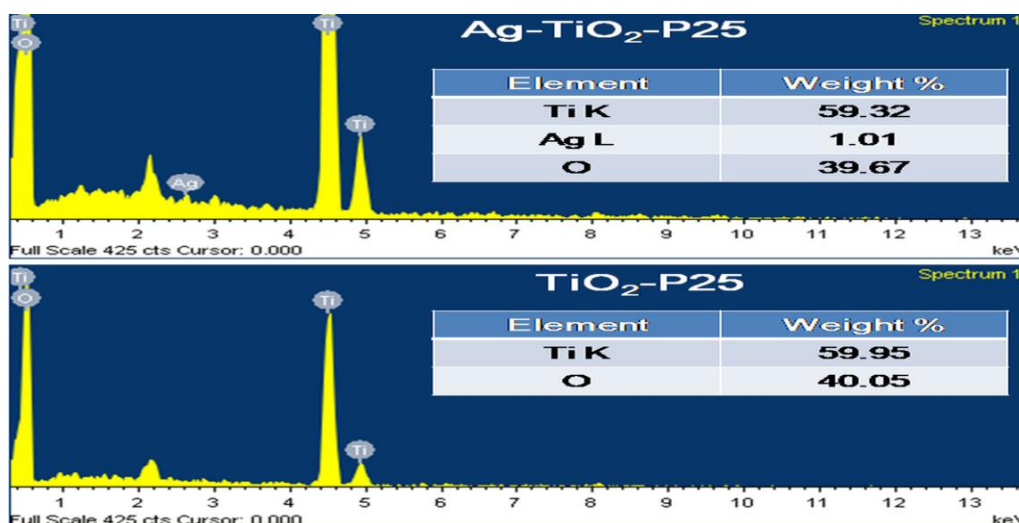


Figure 4.29b (ii): EDS images of TiO₂-P25 and Ag-TiO₂-P25.

XRD analysis

The XRD patterns of TiO_2 -P25 and Ag-TiO_2 -P25 are shown in figure 4.29c. The bicrystalline structure was observed for TiO_2 -P25 containing anatase and rutile phases marked as 'A' and 'R' in figure. For Ag-TiO_2 -P25, the characteristic peaks corresponding to anatase and rutile phase for TiO_2 were retained. This means that presence of silver did not change the crystalline structure of TiO_2 . No other dominant peaks corresponding to Ag were observed in the XRD pattern thus depicting that Ag particles were either dispersed well onto the surface of TiO_2 or were too low in amount to be analyzed through XRD peaks (Nainani et al., 2012). However, the reference codes (01-071-4613; 01-076-1489; 00-043-1038) corresponding to silver obtained from XRD data confirms the presence of Ag particles on the surface of TiO_2 .

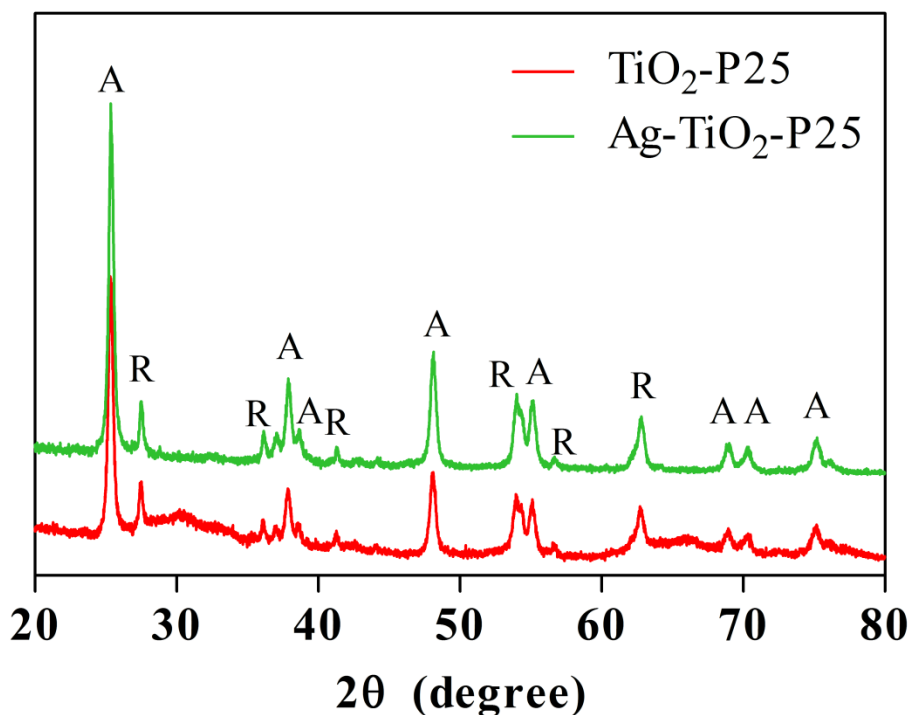


Figure 4.29c: XRD pattern of TiO_2 -P25 and Ag-TiO_2 -P25.

Raman spectroscopy

Figure 4.29d illustrates the Raman spectra of TiO_2 -P25 and Ag-TiO_2 -P25. The Raman peaks identified at 139.6, 394, 513 and 637 cm^{-1} indicated the presence of anatase phase of TiO_2 (Prakash et al., 2015; Yang et al., 2008). It was observed that the Raman peaks corresponding to

TiO₂-P25 shifted towards higher wave numbers i.e. 139.6 to 140.5, 394 to 396, 513 to 515 and 637 to 639 cm⁻¹ in case of Ag doped TiO₂. This clearly indicated that doping of Ag led to several lattice defects in TiO₂ nanoparticles (Yang et al., 2008). However, no distinguished peak relating to Ag was observed which may be due to the existence of lower concentration of Ag ions. A weak broad band in the region between 300 and 350 cm⁻¹ could possibly correlate with the presence of rutile phase of TiO₂ in both catalysts (Balachandran and Eror, 1982; Porto et al., 1967). Thus, it may be concluded from results that activity of TiO₂ was retained in both catalysts as confirmed from the prominent peaks of anatase and rutile phase in each case.

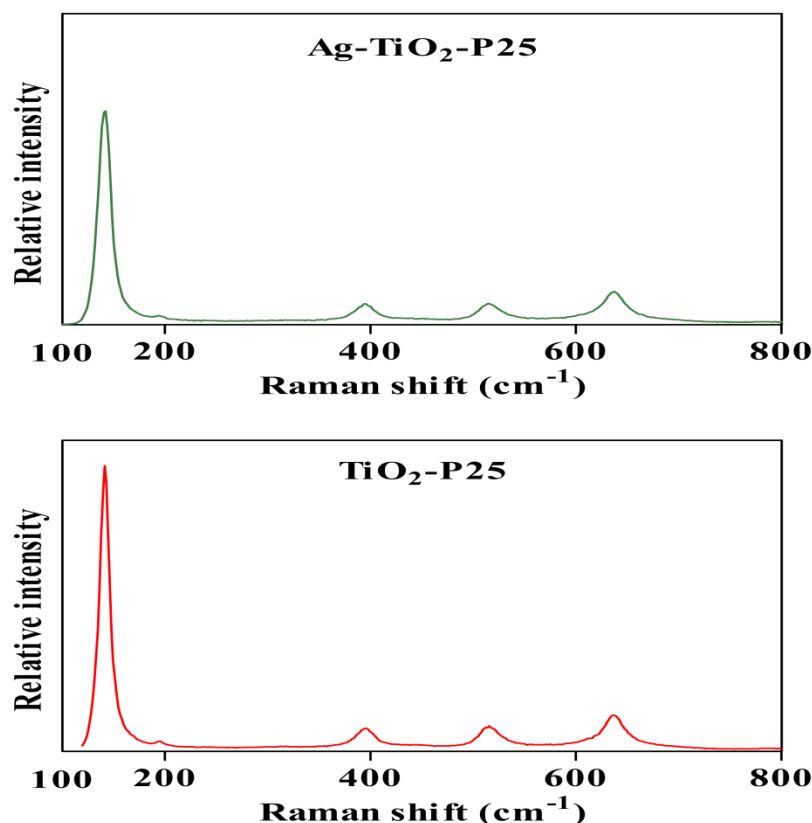


Figure 4.29d: Raman spectra of TiO₂-P25 and Ag-TiO₂-P25.

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of TiO₂-P25 and Ag-TiO₂-P25 are presented in figure 4.29e. The bands below 700 cm⁻¹ depicted the occurrence of metal oxide vibrations like Ag-O or Ti-O or Ag-Ti-O (Yuan et al., 2010). The weak band at 442 cm⁻¹ in case of Ag-TiO₂-P25 corresponded to Ag-Ti-O vibrations (Ivanova et al., 2013). The existence of peaks at 503 cm⁻¹ and 501 cm⁻¹ in TiO₂-P25

and Ag-TiO₂-P25 respectively indicated the presence of anatase phase of TiO₂ (Ganesh et al., 2012). The peaks occurring at 603 cm⁻¹ and 607 cm⁻¹ in case of Ag-TiO₂-P25 and TiO₂-P25 respectively could possibly belong to the rutile phase of TiO₂ (Shukla et al., 2010). The peaks at 1623 cm⁻¹ and 1640 cm⁻¹ in both cases could be assigned to H-O-H vibrations (Yuan et al., 2010). Large number of hydroxyl groups is favorable for photocatalytic process as it can produce more hydroxyl radicals thus improving the oxidation of pollutants. The strong peak at 3421 cm⁻¹ in each case could be correlated with the chemically adsorbed water (Zhang et al., 2013). Thus, presence of Ag ions along with anatase and rutile phase in Ag-TiO₂-P25 confirms the retention of catalyst activity after doping.

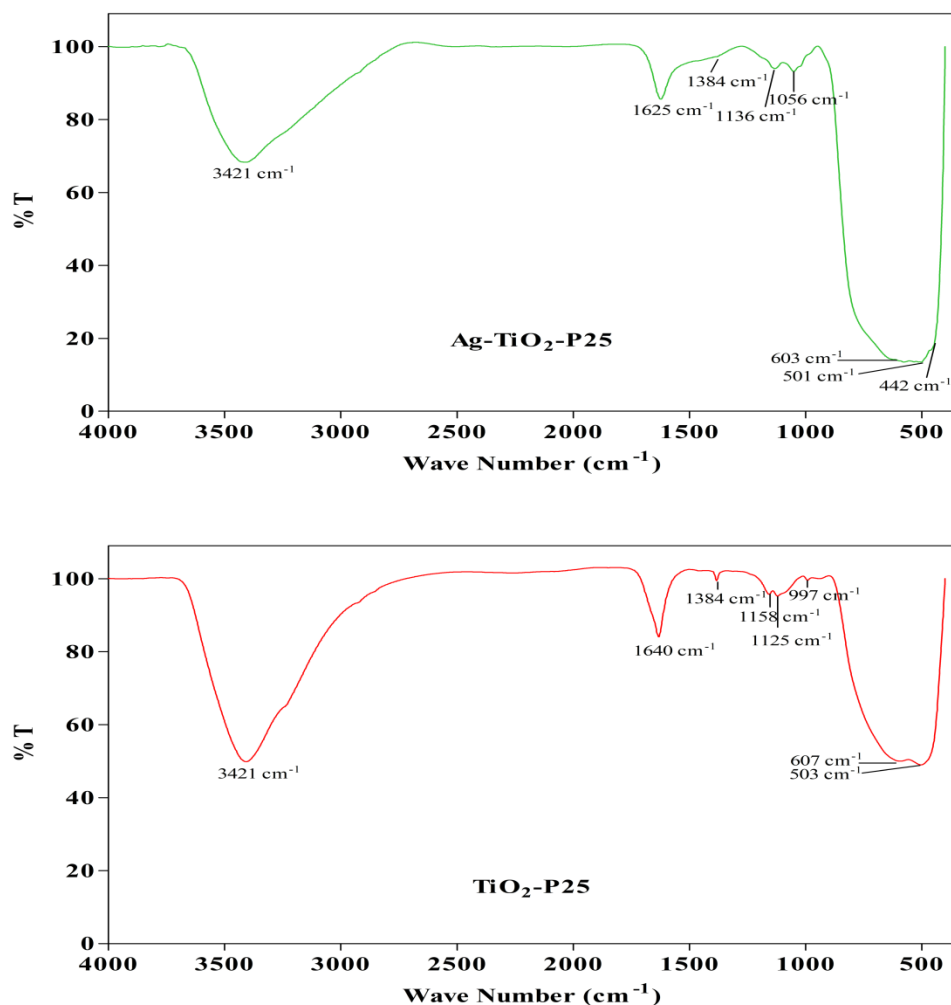


Figure 4.29e: FT-IR spectra of TiO₂-P25 and Ag-TiO₂-P25.

X-ray photo-electron spectroscopy (XPS)

The existence of Ag onto TiO_2 surface was also verified through XPS analysis. The survey scan results of TiO_2 -P25 and Ag- TiO_2 -P25 are depicted in figure 4.29f. The results clearly indicated that TiO_2 -P25 consisted of only two elements i.e. Ti and O in major proportions while additional peak corresponding to Ag was observed in Ag- TiO_2 -P25. It is therefore evident that Ag was successfully impregnated onto TiO_2 surface. The occurrence of C 1s peak in both the cases could be ascribed to adventitious carbon employed for correcting binding energy shifts generated by samples (Ko et al., 2011).

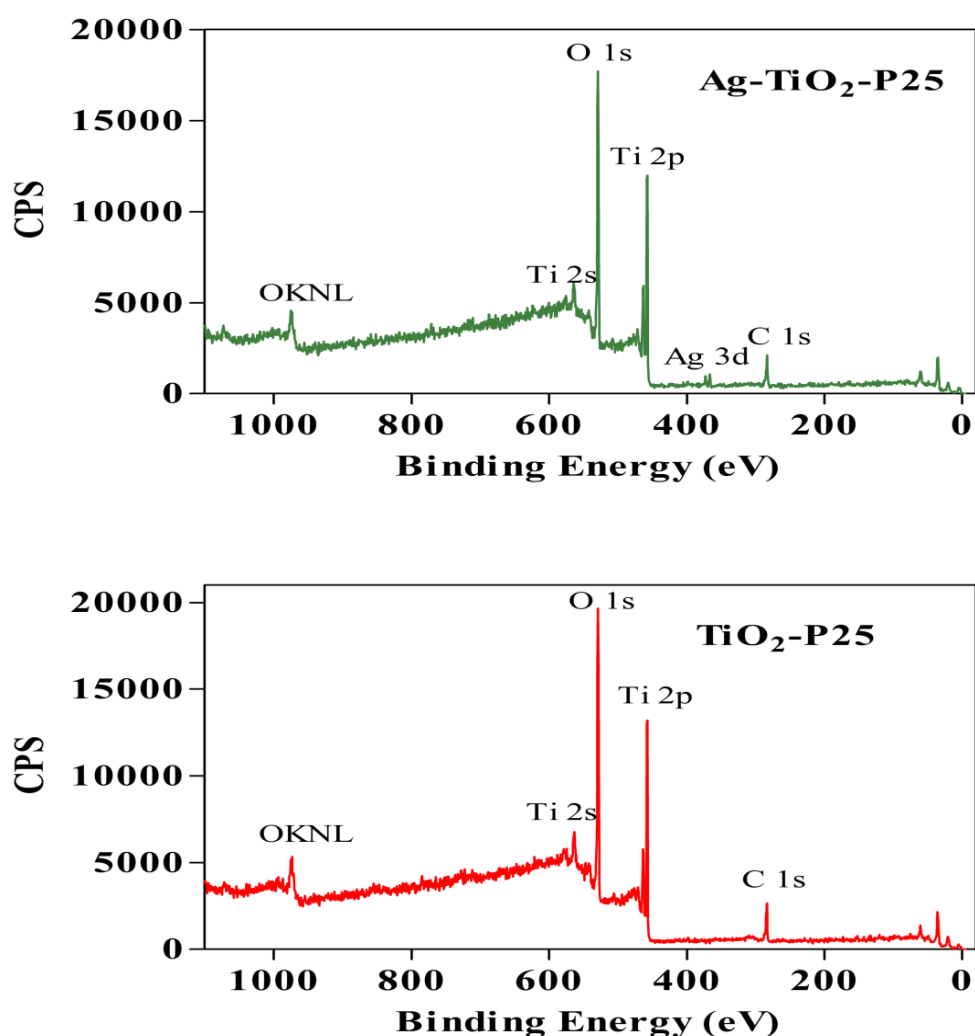


Figure 4.29f: XPS analysis of TiO_2 -P25 and Ag- TiO_2 -P25.

Thermo-gravimetric analysis (TGA)

The thermo-gravimetric (TG) curves of TiO_2 -P25 and Ag-TiO_2 -P25 are shown in figure 4.29g. No prominent change in weights was observed with respect to both catalysts in the temperature range from 30-980 °C. Thus, Ag-TiO_2 -P25 also displayed an outstanding thermal stability in contrast to TiO_2 -P25 depending upon its inorganic structure. Liu et al. (2016) has also reported similar kind of results in case of TG analysis for Ag-TiO_2 .

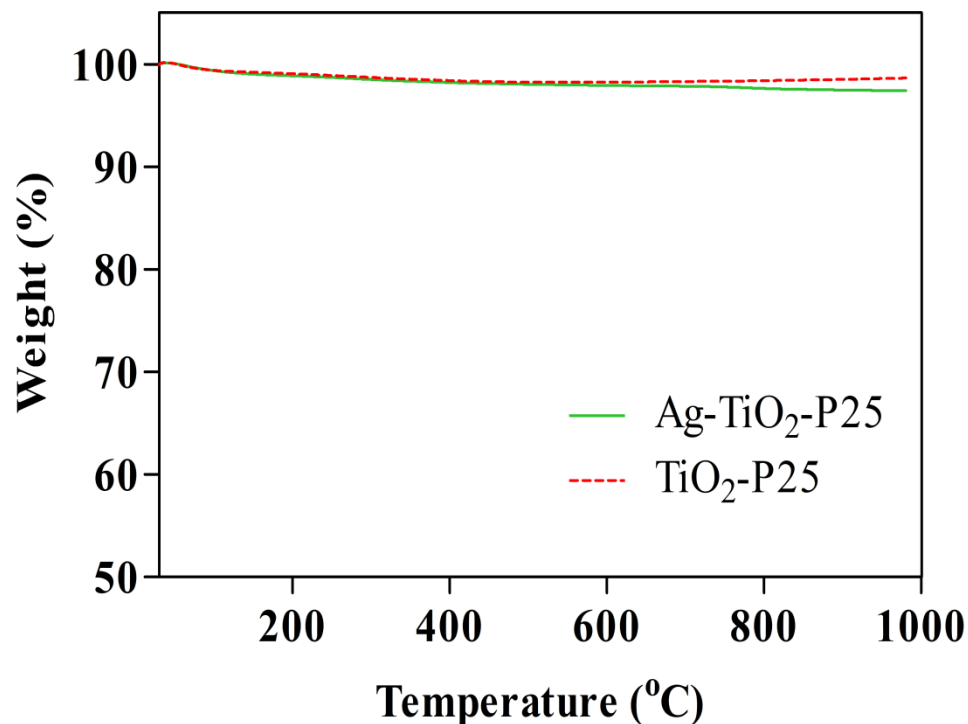


Figure 4.29g: TGA analysis TiO_2 -P25 and Ag-TiO_2 -P25.

From the characterization results, it can be concluded that Ag-TiO_2 was successfully synthesized following the surface impregnation technique. The presence of silver along with TiO_2 was confirmed through each technique leading to proposition that silver particles were uniformly distributed over the surface of TiO_2 . Moreover, the resultant catalyst Ag-TiO_2 depicted significant absorption in the visible spectrum due to the narrowing of band gap as confirmed through DRS analysis. As a result, photocatalytic activity of doped catalyst was checked under natural solar irradiations as discussed in subsequent sections.

4.8.2 Photocatalytic activity of Ag-TiO₂-P25

Initially, blank experiments were conducted with aqueous solution of PEN (50 mg L⁻¹) to study the removal of pollutant through adsorption on catalyst surface as well as through photolysis. Negligible amount of removal (3-5%) in the concentration of PEN was observed in either case. The solar irradiated PEN solution in the presence of doped and undoped catalysts resulted in significant degradation. Therefore, the photocatalytic process was further intensified with proper optimization of operating parameters for better degradation efficiency. Figure 4.30a shows the normalized concentration of PEN in the presence of un-doped and doped TiO₂ with varying dopant amounts as a function of treatment time. The dopant concentration was varied in the range 0.25-2.0 wt. %. The maximum degradation efficiency (91.7%) was achieved with 1.5 wt. % of dopant after 45 min of reaction. Further increasing the dopant concentration resulted in reduced degradation efficiency owing to the increase in recombination of electrons and holes (Jaiswal et al., 2012). It might be ascribed that dopants at low concentration trap the photon excited electrons and prevent frequent recombination of electrons and holes thereby improving the photocatalytic activity. The first order rate constant, 'k' in case of Ag-TiO₂-P25 was significantly higher ($P < 0.05$) as compared to TiO₂-P25. It was observed that value of 'k' was increased to 0.055 min⁻¹ with 1.5 wt. % Ag-TiO₂-P25 in comparison to 0.037 min⁻¹ in case of TiO₂-P25.

To determine the optimum dose of doped catalyst, the concentration of Ag-TiO₂-P25 (1.5 wt. %) was varied from 250 mgL⁻¹ to 1500 mgL⁻¹. The degradation of PEN initially increased with increase in the catalyst dose up-to 750 mgL⁻¹ (Figure 4.30b). Thereafter, it either became almost constant or started declining due to the increasing turbidity of solution or obstruction in penetration of light at higher catalyst dose (Bansal et al., 2016). The values of rate constants obtained in each case were statistically analyzed. The rate constant in case of 750 mgL⁻¹ of catalyst dose was 0.055 min⁻¹ which was significantly higher ($P < 0.05$) than at any other dose. Thus, 750 mgL⁻¹ of catalyst dose was selected as optimum concentration for carrying out further degradation studies.

The effect of different oxidants like K₂S₂O₈, KBrO₃ and H₂O₂ (6 mM each) on the photocatalytic degradation of PEN is illustrated in figure 4.30c. The addition of oxidants further enhanced the efficiency of sunlight/Ag-TiO₂-P25 system by further promoting the separation of

electrons and holes (Fang et al., 2004). The value of rate constant obtained in case of $K_2S_2O_8$ (0.148 min^{-1}) was found to be significantly higher ($P < 0.05$) than $KBrO_3$ (0.075 min^{-1}) and H_2O_2 (0.061 min^{-1}). Thus, the most effective oxidant for the degradation of PEN was found to be $K_2S_2O_8$. Almost 90% degradation was achieved within 15 min of reaction using $K_2S_2O_8$. The effect of oxidants on the degradation of PEN in the current study was in the order: $K_2S_2O_8 > KBrO_3 > H_2O_2$. The formation of hydroxyl radicals through $S_2O_8^{2-}$ takes place according to the following equations (Zhang et al., 2006):



Therefore, the dose of $K_2S_2O_8$ was altered from 2 mM to 12 mM to decide the optimum concentration of oxidant for attaining the best possible degradation efficiency of the system. 10 mM of $K_2S_2O_8$ was selected as the optimum concentration in the present case at which 91.7 % degradation was achieved within 10 min of treatment (Figure 4.30d). The value of rate constant, 'k' was drastically increased to 0.248 min^{-1} at optimum dose of $K_2S_2O_8$ i.e. 10 mM. Increasing the oxidant concentration beyond 10 mM reduced the efficiency of system which might be possible due to the prevailing scavenging effect of hydroxyl radicals. Although numerous studies have been reported in literature (Behnajady and Eskandarloo, 2013; Ko et al., 2011; Mehrabad et al., 2016) in context to Ag-TiO₂-P25 for the degradation of wide variety of pollutants. Our study has a novel content of using this Ag-TiO₂-P25 in conjunction with iron (from waste materials) to incorporate in-situ dual effect in fixed-mode. The first order rate constant, 'k' and photonic efficiency of the catalyst along with treatment time in different cases for the present study has been calculated and presented in table 4.12. The detailed calculations of photonic efficiency have been provided in text A1 (Appendix).

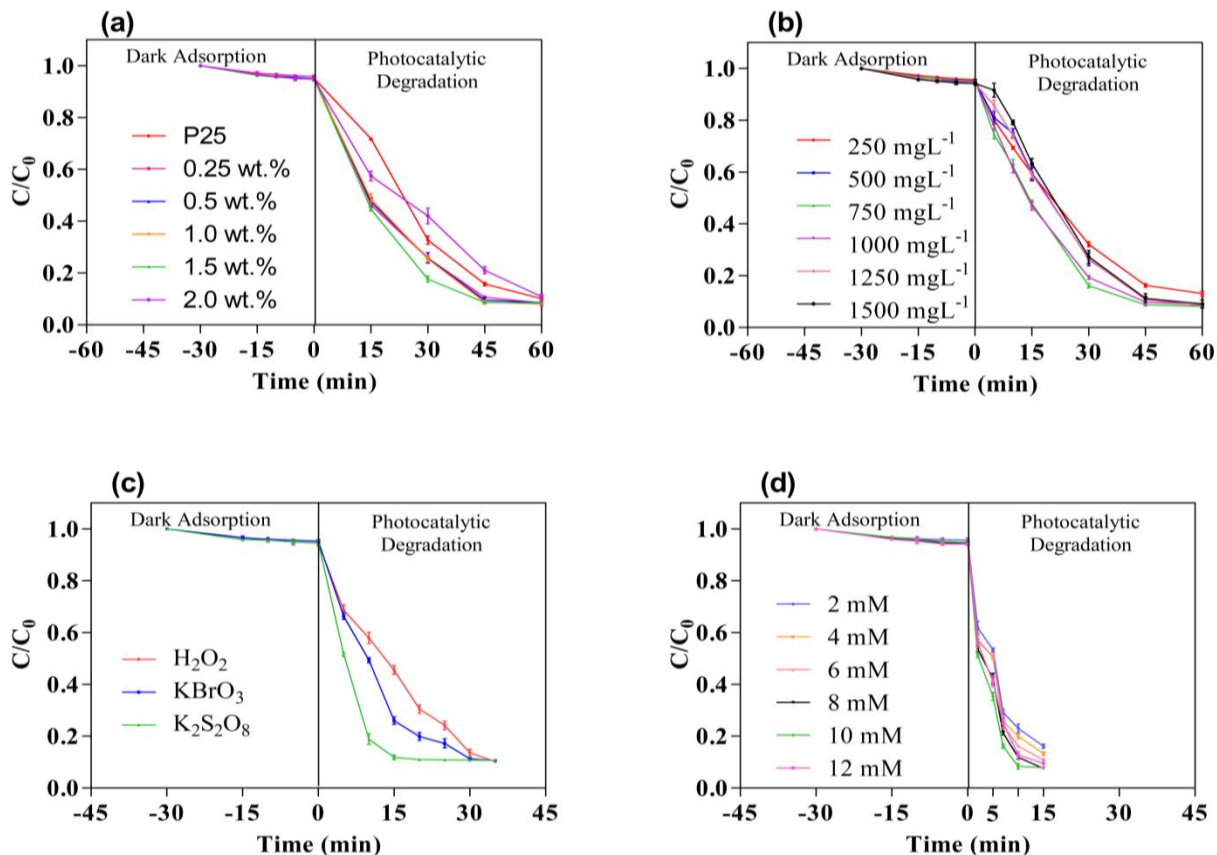


Figure 4.30: Normalised concentration of PEN with (a) varying dopant concentration, (b) dose of Ag-TiO₂-P25, (c) types of oxidants and (d) dose of K₂S₂O₈.

Table 4.12: Values of rate constant and photonic efficiency under different operating conditions.

Optimum conditions	First order rate constant, k (min ⁻¹)	R (mol L ⁻¹ s ⁻¹) × 10 ⁻⁸	I ₀ (Einstein L ⁻¹ s ⁻¹) × 10 ⁻⁶	Photonic efficiency, ζ (%) (R/I ₀)*100	Treatment time (min)
(A) CATALYST SUSPENSIONS					
<i>Effect of doping</i>					
TiO ₂ -P25	0.037	11.03	2.309	4.77	60
Ag- TiO ₂ -P25 (1.5 wt. %)	0.055	16.4	2.309	7.1	45
<i>Types of oxidants</i>					
H ₂ O ₂	0.061	17.6	2.309	7.88	35
KBrO ₃	0.075	22.375	2.309	9.69	30

$K_2S_2O_8$	0.148	44.15	2.309	19.12	15
<i>Dose of oxidant ($K_2S_2O_8$)</i>					
10 mM	0.245	73.1	2.309	31.6	10
(B) FIXED BED STUDIES					
TiO ₂ -P25 immobilized clay beads	0.065	19.39	2.309	8.39	45
Ag- TiO ₂ -P25 immobilized clay beads	0.088	25.3	2.309	10.9	30
Ag- TiO ₂ -P25 immobilized clay beads (5 mm)	0.099	29.2	2.309	12.6	30
Fe-Ag-TiO ₂ composite	0.132	39.38	2.309	17.05	15
Blank composite	0.024	7.16	2.309	3.1	45
Fe-TiO ₂ composite	0.073	21.77	2.309	9.43	30

4.8.3 Fixed-bed studies

This section pertains to the fixed-bed applications of Ag doped TiO₂ in context to the degradation of target pharmaceutical i.e. PEN. Fixed-bed studies were carried out under sunlight using highly durable spherical clay beads as inert support materials for doped catalyst immobilization. Best efforts have been devoted in the present study to reduce the treatment time and enhance the degradation of PEN using Ag doped catalyst even in fixed mode. Different types of spherical beads i.e. clay and clay based composite (Fe-TiO₂ composite) were used for doped catalyst immobilization. The fixed-bed experiments were carried out in the same batch reactor at natural pH of PEN solution i.e. 4, using optimized dose of K₂S₂O₈ (10 mM) with adequate number of Ag-TiO₂-P25 (1.5 wt. %) immobilized spherical beads under natural solar irradiations. The major problem that was faced with fixed-bed studies using catalyst immobilized beads was the rising pH of solution after few minutes of reaction. As discussed in earlier sections, pH of the solution was stabilized to its natural pH by adding suitable amount of acetate buffer. Thereafter, pH of the solution remained almost constant throughout the reaction. None of the research articles in literature have ever reported the detailed studies on the immobilization of doped catalysts especially in context to in-situ dual effect.

Ag-TiO₂-P25 immobilized clay beads

To affirm the activity and efficacy of immobilized doped catalyst, degradation of PEN was carried out with TiO₂-P25 immobilized clay beads as well as with doped TiO₂ immobilized clay beads. The degradation was significantly higher ($P < 0.05$) in case of doped TiO₂ as compared to undoped TiO₂. Significant reduction in treatment time was observed in case of immobilized doped TiO₂ which revealed an almost 90% removal of PEN within 30 min of treatment as compared to immobilized TiO₂-P25 which took 45 min to attain the same amount of degradation (Figure 4.31).

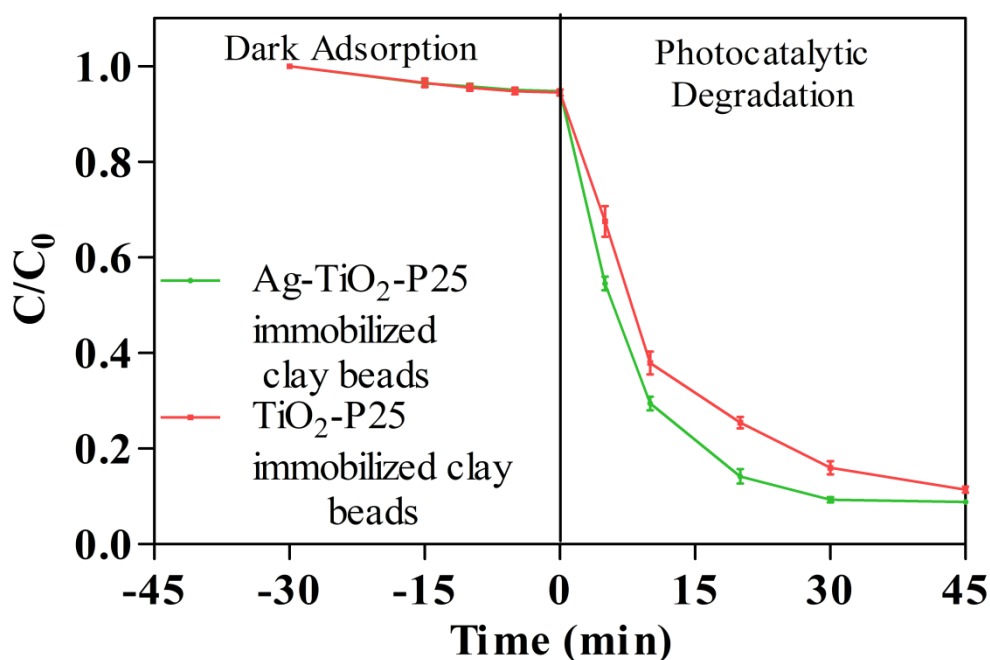


Figure 4.31: Effect of doped and undoped TiO₂ immobilized clay beads on the photo-degradation of PEN.

Figure 4.32 depicts the SEM-EDS along with elemental mapping of doped TiO₂ immobilized clay bead. It is clear from SEM image that catalyst formed a uniform layer on the surface of beads. The significant peaks of 'Ti', 'O' and 'Ag' were observed in the EDS spectra suggesting that Ag doped TiO₂ was successfully immobilized on clay beads. From elemental mapping, it was proved that Ag particles were invariably dispersed onto TiO₂ surface.

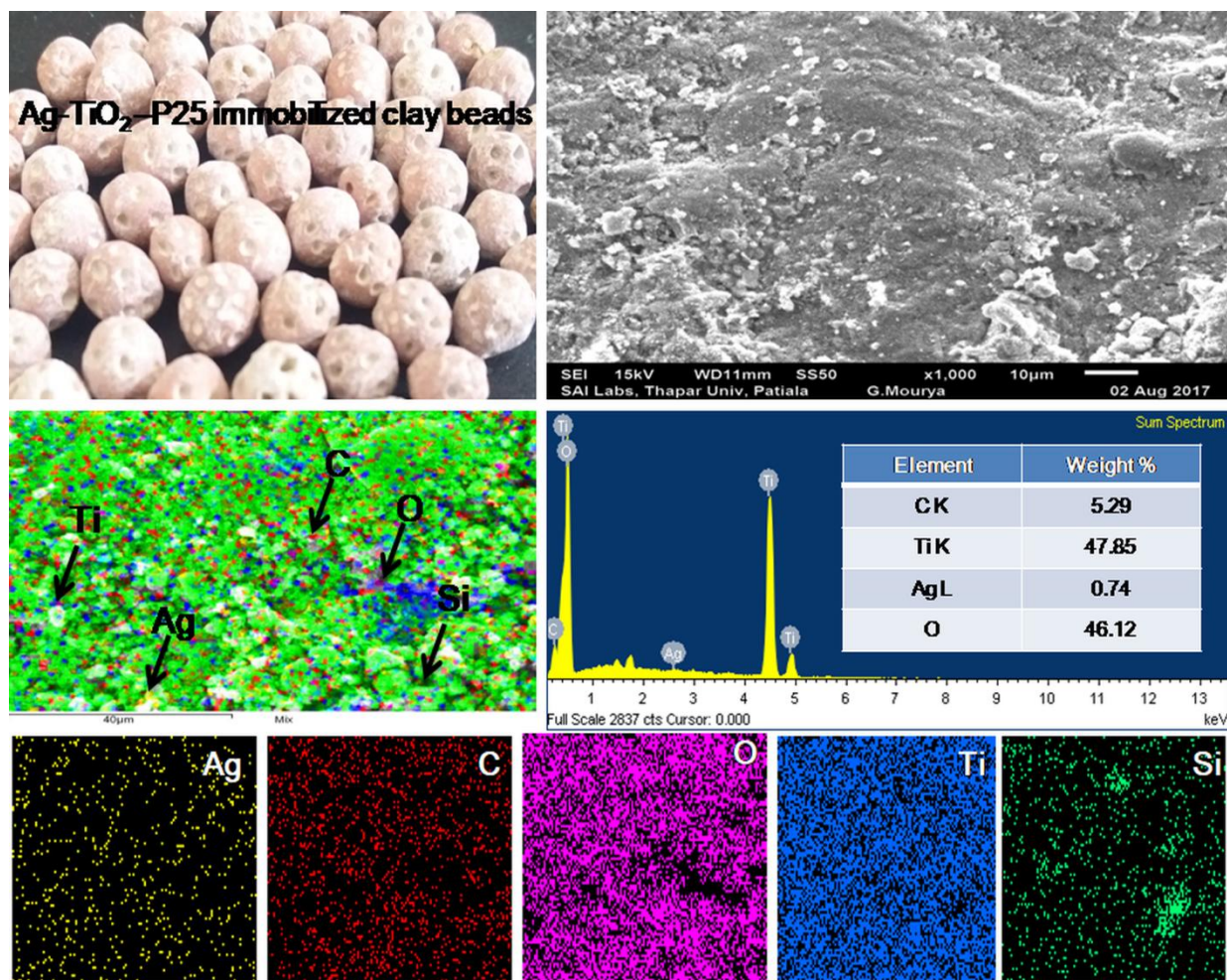


Figure 4.32: Actual photographs along with SEM/EDS/mapping images of Ag-TiO₂-P25 immobilized clay beads.

Fe-Ag-TiO₂ composite

This section defines the novel part of the study where in-situ dual effect with modified catalysis has been attempted. Best efforts have been made to approach the efficiency of the system as close as that of slurry mode. For this, experiments were performed in the same manner as described above using Ag modified Fe-TiO₂ composite (now termed as Fe-Ag-TiO₂ composite). Figure 4.33a illustrates the SEM-EDS along with elemental mapping of Fe-Ag-TiO₂ composite. The SEM image depicted the morphological structure of the composite thus displaying a uniform layer of catalyst on its surface. The EDS spectra clearly portrayed the presence of silver and iron along with titanium and oxygen as can be seen through their

significant peaks in the spectrum. Their presence can be further confirmed through elemental mapping which proved that ‘Ag’ and ‘Fe’ particles were uniformly dispersed onto TiO_2 surface.

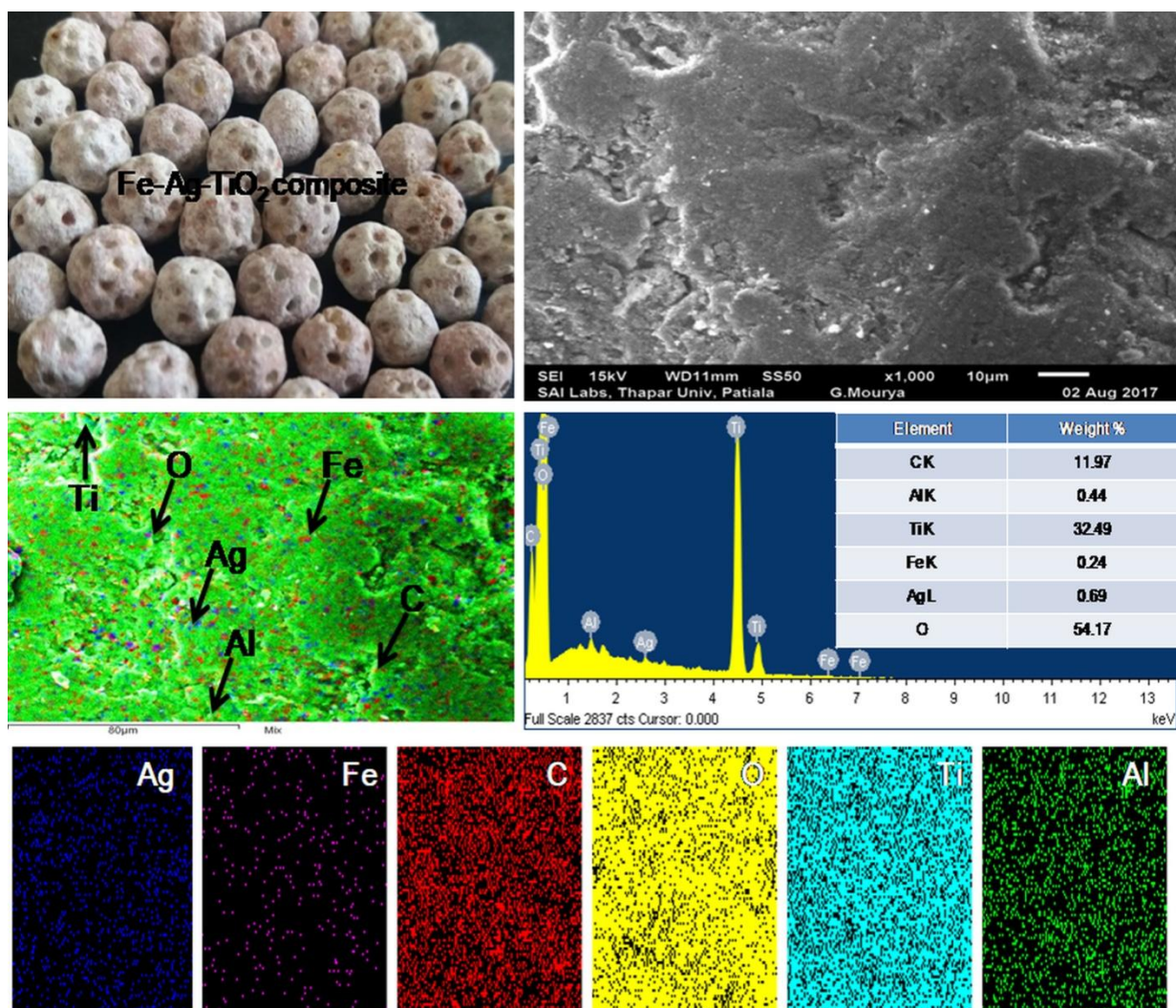


Figure 4.33a: Actual photographs along with SEM/EDS/mapping images of Fe- Ag-TiO₂ composite.

The band-gap energy was also calculated for Fe-Ag-TiO₂ composite through UV visible DRS analysis (Figure 4.33b) according to equation 4.21. The absorption edge was extended to 447 nm and band gap was further narrowed down with $E_g = 2.77$ eV in comparison to Ag-TiO₂ (2.87 eV) and TiO₂-P25 (3.14 eV). The narrowing down of band gap in case of Fe-Ag-TiO₂ composite can be possibly due to the presence of iron along with silver in composite.

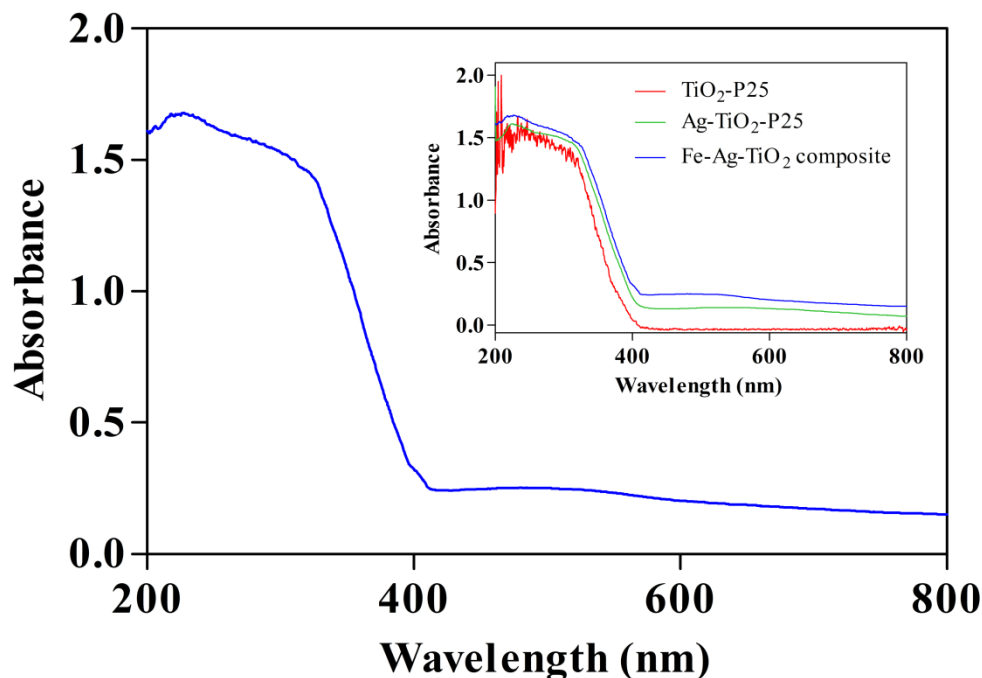


Figure 4.33b: UV-visible DRS of Fe- Ag-TiO₂ composite.

It was perceived in the present study that iron was leaching from the composite by default (Table 4.13) which contributed to photo-Fenton reaction occurring simultaneously with modified photocatalysis. The existence of this dual effect with doped TiO₂ accelerated the degradation of PEN as treatment time was reduced to almost 15 min for achieving 88% degradation (Figure 4.34). To confirm the occurrence of photo-Fenton reaction, blank composite beads (without any coating of catalyst) were used for the reaction and 60% degradation of PEN was achieved after 30 min of irradiations. The reactions were performed with Fe-TiO₂ composite (TiO₂-P25 immobilized composite) as well to confirm that Fe-Ag-TiO₂ composite exhibited best results among all immobilized catalysts. Synergistic effect of modified dual process over doped TiO₂ photocatalysis and photo-Fenton was observed. The synergy of modified dual process came out to be 25% and 80% over doped TiO₂ photocatalysis and photo-Fenton respectively. However, overall synergy of the modified dual process came out to be approximately 7%.

Table 4.13: Concentration of iron leached out in solution through Fe-Ag-TiO₂ composite during the degradation of PEN.

Time (min)	Concentration (mg L ⁻¹)		
	Total iron	Ferrous iron	Ferric iron
5	0.93	0.21	0.72
10	0.82	0.71	0.11
15	0.65	0.52	0.13

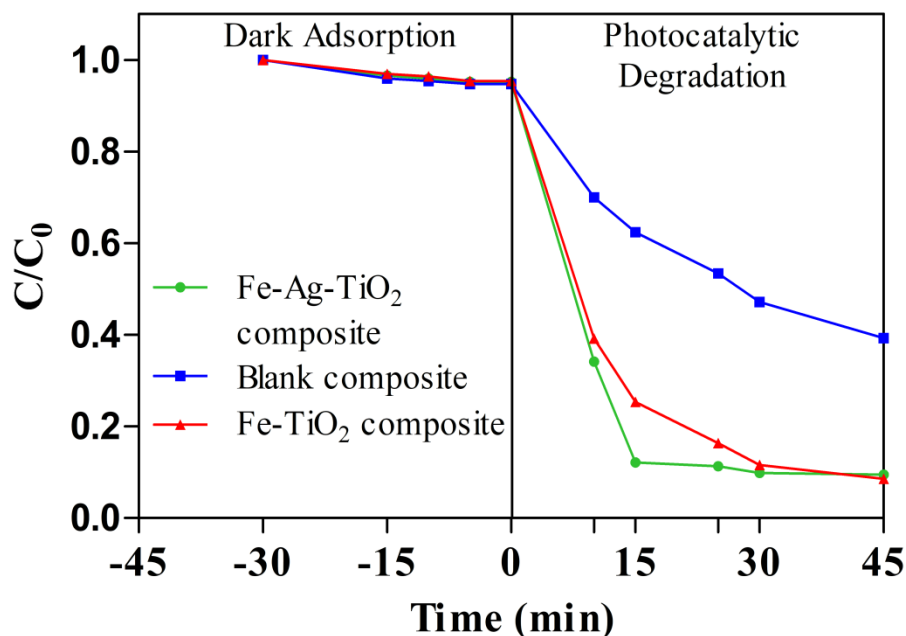


Figure 4.34: Degradation of PEN using Fe-Ag-TiO₂ composite (modified dual process), blank composite (photo-Fenton), Fe-TiO₂ composite (dual process).

The reason for the increased degradation of PEN due to this dual effect is two-fold. The first reason is the generation of hydroxyl radicals in abundance (Figure 4.35). The hydroxyl radicals were formed not only through one process but due to the coupling of different processes like doped TiO₂ photocatalysis, photo-Fenton and iron oxide catalysis. Secondly, the recombination of electrons and holes became infrequent due to two factors. The photo-excited electron from TiO₂ might get entrapped by iron-oxide and involved in the formation of Fe²⁺ ions thus facilitating the photo-Fenton reaction. The other factor is that impregnated Ag particles onto TiO₂ could also behave as electron traps thus promoting electron-hole separation and thereby boosting the oxidation process.

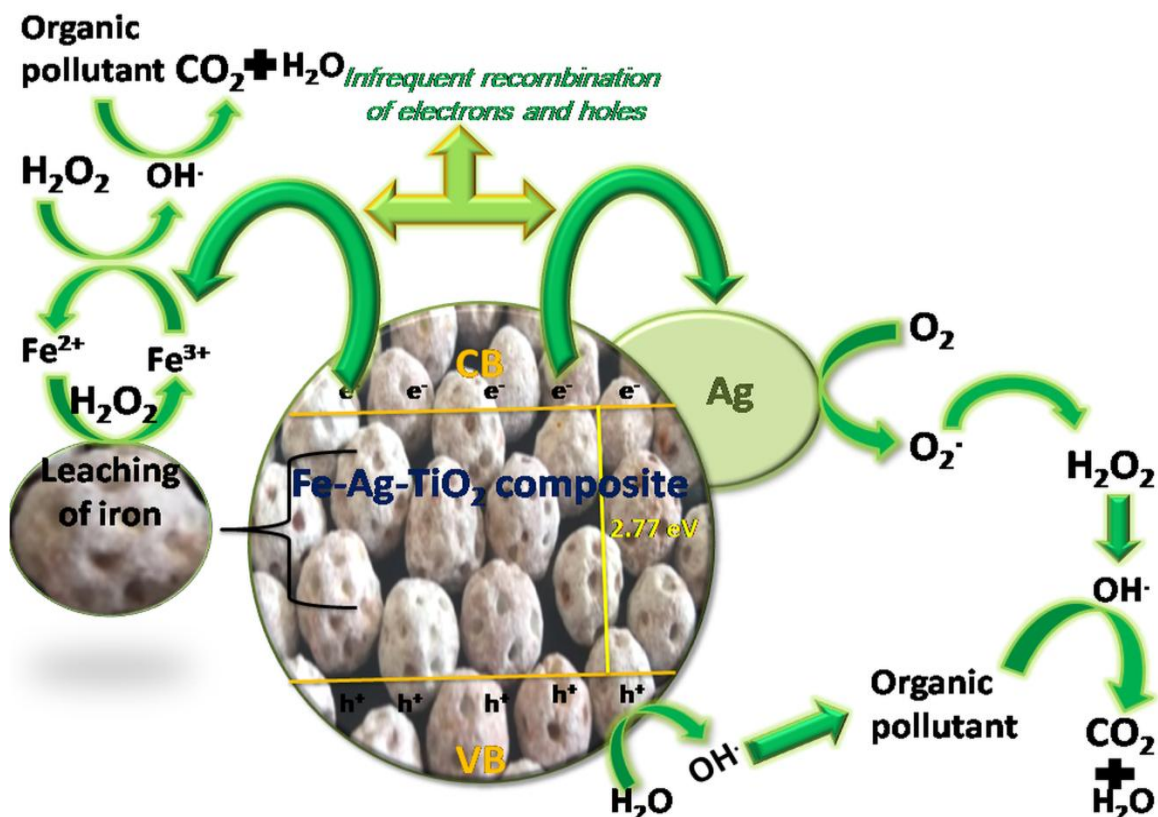


Figure 4.35: Proposed mechanism of modified in-situ dual process using Ag-TiO₂.

The viability of this modified dual process was counter checked by carrying out the degradation of CEX with Fe-Ag-TiO₂ composite. An almost 80% degradation of CEX was achieved after 30 min of reaction via modified dual process which was significantly higher ($P < 0.05$) as compared to 70% using Ag-TiO₂ immobilized clay beads and 55% using TiO₂-P25 immobilized clay beads. Thus, with certain modifications, Fe-Ag-TiO₂ composite can be represented as an economical and viable solution to various industries for solar induced degradation of recalcitrant organic pollutants.

4.8.4 Mineralization studies

The mineralization of PEN through modified dual process was also validated through the production of various anions like nitrite, nitrate and ammonium ions along with reduction in COD and TOC. It may be presumed that nitrogen atoms of PEN were dissipated into ammonium, nitrite and nitrate ions (Figure 4.36). The declining trend of nitrate ion concentration suggests that some of the nitrate ions might get converted into nitrite and ammonium ions (Kudo et al.,

1992). Almost 75% and 68% reduction in COD and TOC respectively were obtained after 15 min of reaction.

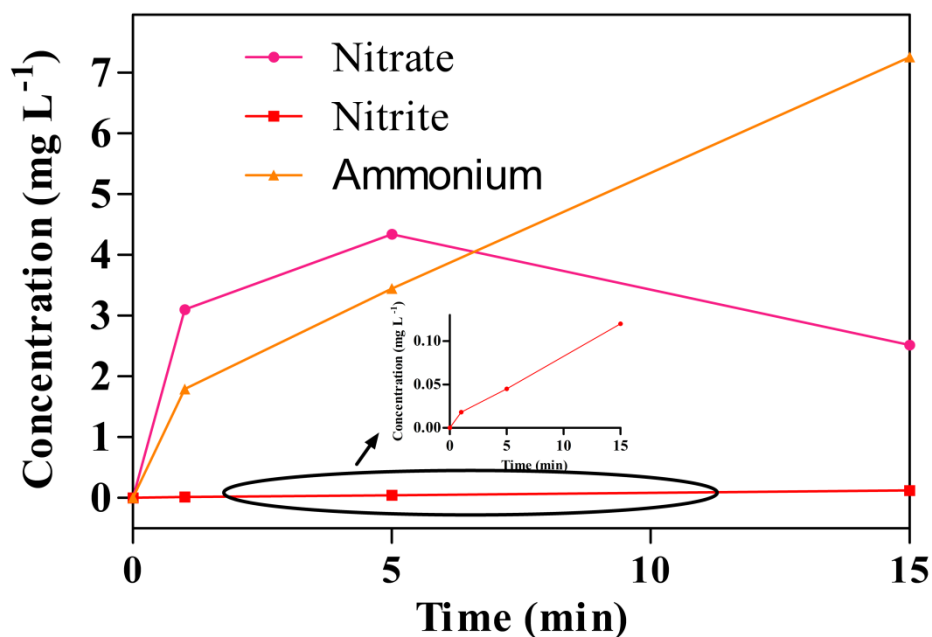
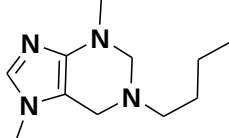
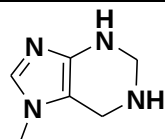
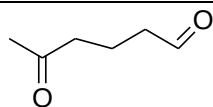
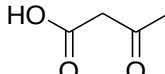
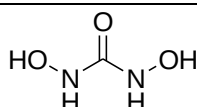


Figure 4.36: Concentration of various anions generated during the degradation of PEN via modified dual process.

Table 4.14 shows the intermediates or by-products formed during the decomposition of PEN as determined through GC-MS analysis. From the analysis, it is clear that complex chain molecules have been decomposed into linear chain molecules thus supporting the hypothesis for complete mineralization of PEN. The chromatograms of GC-MS analysis have been provided in Appendix (Figure A3).

Table 4.14: Intermediates formed during the degradation of PEN via modified dual process.

S.No.	Name of the compound	m/z	Structure
1	1-hexyl-1,6-dihydro-3,7-dimethyl-3H-purin-2(7H)-one	250.179	
2	1-butyl-3,7-dimethyl-1H-purine-2,6(3H,7H)-dione	236.127	

3	1-butyl-2,3,6,7-tetrahydro-3,7-dimethyl-1 <i>H</i> -purine	208.169	
4	2,3,6,7-tetrahydro-7-methyl-1 <i>H</i> -purine	138.091	
5	5-oxohexanal	114.07	
6	3-oxobutanoic acid	102.032	
7	1,3-dihydroxyurea	92.02	
8	propan-2-one	58.042	
9	acetaldehyde	44.026	

Modified in-situ dual process with Ag-TiO₂ employing different oxidants has revealed promising results in terms of the degradation efficiency of PEN. The use of oxidant i.e. K₂S₂O₈ has shown its greater potential in dual effect studies as compared to other oxidants. However, it was not used in further experiments in view of the economy of process. Actually, main focus of the study was to visualize its commercial-scale applications. Thus, taking into consideration the overall cost of the technique in addition to the process efficiency, H₂O₂ was used in all further experiments along with scale-up trails.

4.9 Modified in-situ dual process for the degradation of CEX and PEN using N doped TiO₂ and N, Ag co-doped TiO₂

The applications of modified in-situ dual process using TiO₂ doped with noble metals like Ag have already been studied in Section 4.8. In addition to the doping with noble metals, numerous of studies in literature confirmed that modification of TiO₂ with certain non-metals including N (Asahi et al., 2014), C (Ananpattarachai et al., 2016), S (Ksibi et al., 2008), B (Li et al., 2013) but specifically N could extend the photo-response efficiency of TiO₂ to a great extent. Moreover, Tian et al. (2009) reported the synergistic effect of nitrogen doping followed by metallization with noble metals in context to the enhanced visible light activity of TiO₂ for the degradation of organic pollutants. Doping of TiO₂ with nitrogen enhances the photo-response efficiency by extending its light absorption capacity whereas presence of noble metal hinders the electron-hole recombination thus, further improving the overall photocatalytic activity of the catalyst. In this context, N-Ag co-doped TiO₂ was also synthesized in the present study to seek its practical applications especially in combination with in-situ dual process. Fe-TiO₂ composite was modified by replacing TiO₂-P25 with N-Ag co-doped TiO₂ thus termed as now Fe-N-Ag-TiO₂ composite (procedure for synthesis has been briefed in section 3.6 and 3.7) which was then used for the execution of modified in-situ dual process. CEX was chosen as a target pollutant in this study to check the efficacy of Fe-N-Ag-TiO₂ composite mediated modified in-situ dual process. To confirm the viability of Fe-N-Ag-TiO₂ composite, modified in-situ dual process was carried out at optimized conditions for the degradation of PEN as well. To the best of our knowledge, this is the first reported study in context to the in-situ dual effect using N-Ag-TiO₂ especially in fixed-mode.

4.9.1. Characterization of prepared photocatalysts

The prepared photocatalysts i.e. N-TiO₂ and N-Ag-TiO₂ were characterized through several techniques to confirm their activity and distribution of N or Ag particles onto the surface of TiO₂.

UV-visible diffuse reflectance spectroscopy (DRS) analysis

The band gap energy of prepared photocatalysts was calculated through UV-visible diffuse reflectance spectroscopy (DRS). The diffuse reflectance spectra of the catalysts were compared with that of un-doped TiO_2 -P25 as shown in figure 4.37a. The spectra of both catalysts i.e. N-TiO_2 and N-Ag-TiO_2 depicted a strong visible light response with a minor red-shift (Gao et al., 2017; Song and Gao, 2007) as compared to TiO_2 -P25. N-Ag-TiO_2 even displayed a new broad absorption peak in the visible range i.e. between 400 and 800 nm which can be attributed to the synergistic effect of N, Ag and TiO_2 (Yang et al., 2016). The band gap energy of all catalysts was calculated using the equation 4.21 as discussed before.

In the present research work, absorption edge was extended to 428 nm in case of N-TiO_2 and 444 nm in case of N-Ag-TiO_2 whereas it was nearly 403 nm in case of TiO_2 -P25. Similar kind of results were reported earlier in which absorption edge was extended to 450 nm in case of Ag and N co-doped TiO_2 depicting high bactericidal activity against *E. Coli* (Wu et al., 2010). The band gap energy in the present case was observed to be 2.89 eV in case of N-TiO_2 and 2.79 eV in case of N-Ag-TiO_2 whereas E_g in case of TiO_2 -P25 was 3.07 eV.

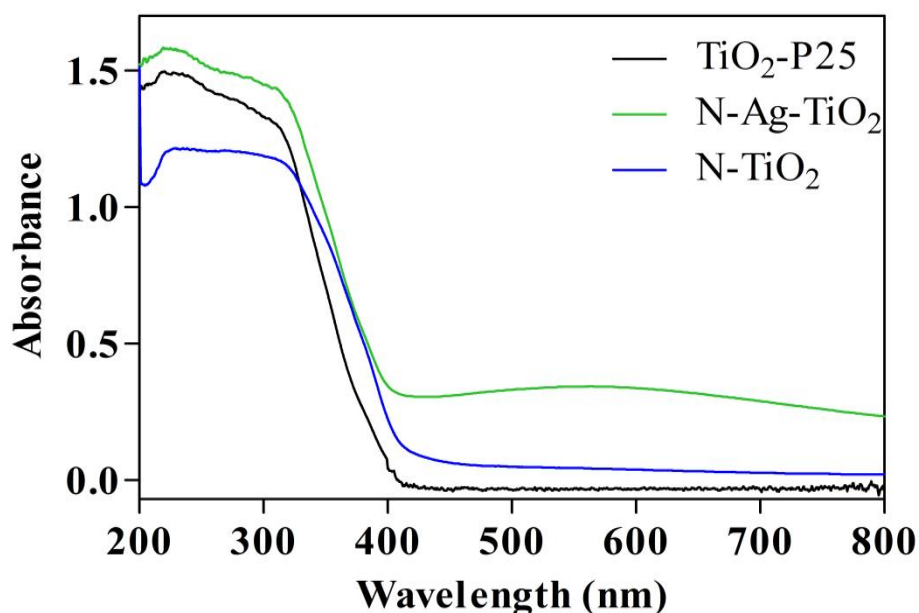


Fig. 4.37a: UV-visible DRS of TiO_2 -P25, N-TiO_2 and N-Ag-TiO_2 .

SEM/EDS analysis

The morphological characteristics of synthesized N-TiO₂, N-Ag-TiO₂ were identified and compared with that of TiO₂-P25 through SEM analysis as shown in figure 4.37b. The SEM images of N-TiO₂ and N-Ag-TiO₂ (Figure 4.37b (i)) demonstrated high magnitude of aggregation of particles as compared to TiO₂-P25 which might be due to the interaction of additional particles like Ag or N with crystalline particles of TiO₂ (Suwanchawalit et al., 2012). The EDS spectra along with SEM images in figure 4.37b (ii) showed the elemental composition of each catalyst. Owing to the presence of N particles in very low concentration (0.1 wt. %), its occurrence either in N-TiO₂ or in N-Ag-TiO₂ was not perceived through EDS analysis. However, a significant peak of 'Ag' was identified in EDS spectra of N-Ag-TiO₂ whereas prominent peaks of 'Ti' and 'O' were present in case of each catalyst. The other characterization techniques were carried out to cross-confirm the uniform distribution of respective dopants in prepared catalysts.

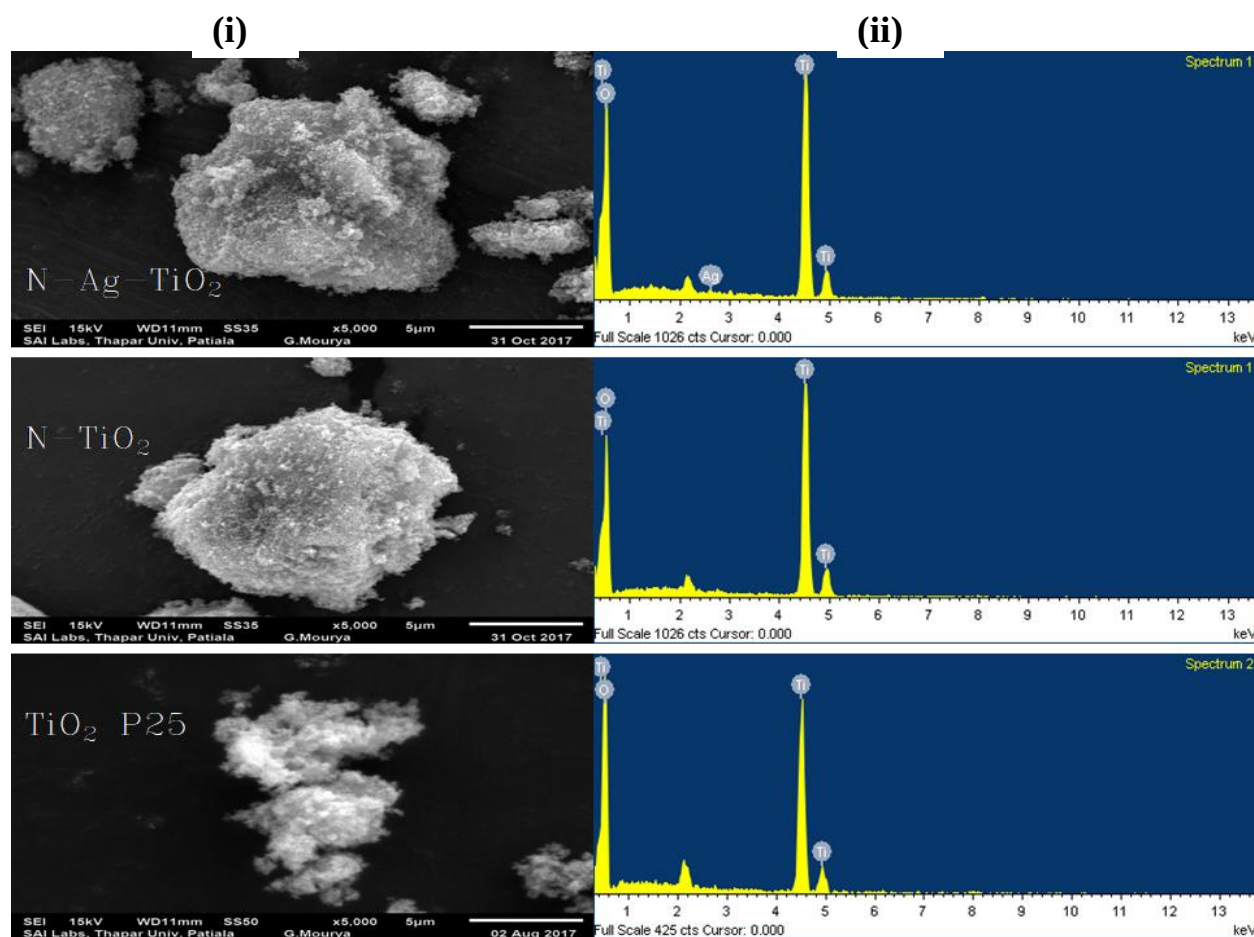


Fig. 4.37b: (i) SEM and (ii) EDS images of TiO₂-P25, N-TiO₂ and N-Ag-TiO₂.

XRD analysis

The x-ray diffraction patterns of N-TiO₂, N-Ag-TiO₂ and TiO₂-P25 are shown in figure 4.37c. The bicrystalline structure of TiO₂-P25 containing both anatase and rutile phases, was retained in case of prepared doped catalysts i.e. N-TiO₂ and N-Ag-TiO₂. The anatase and rutile phases were indicated as 'A' and 'R' respectively in figure. No other significant and sharp diffraction peaks corresponding to either 'N' or 'Ag' were identified in the XRD patterns of N-TiO₂ or N-Ag-TiO₂ thus suggesting that concentration of silver or nitrogen were too low to be examined through XRD peaks (Nainani et al., 2012). However, reference codes 01-072-0157, 01-089-2775, 01-073-2332 referring to dinitrogen (N₂) and reference codes 01-074-1901, 03-065-5307 referring to dinitrogen oxide (N₂O₂) and nitrogen oxide (N₂O₄) were obtained through XRD data of N-TiO₂ which confirmed the uniform distribution of nitrogen particles over the surface of TiO₂. On the other hand, reference codes 00-041-1104 and 03-065-3958 corresponding to silver oxide (Ag₂O) and Titanium nitride (Ti₄N_{2.33}) obtained through XRD data of N-Ag-TiO₂ further confirmed the deposition of silver and nitrogen particles both on the surface of TiO₂.

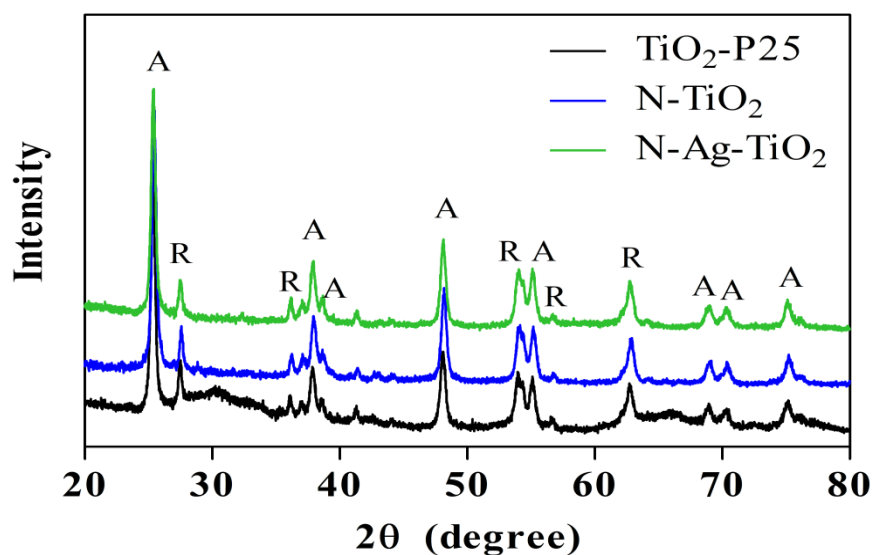


Fig. 4.37c: XRD pattern of TiO₂-P25, N-TiO₂ and N-Ag-TiO₂.

Raman spectroscopy

Figure 4.37d demonstrates the Raman spectra of N-Ag-TiO₂, N-TiO₂ and TiO₂-P25. The prominent peaks in the range of 140, 398, 511, and 640 cm⁻¹ in case of all catalysts corresponded

to the anatase phase of TiO_2 (Prado et al., 2009; Prakash et al., 2015). Therefore, the results clearly revealed that doping with either N or N/Ag did not change the phase of TiO_2 . No characteristic peak related to rutile phase was observed in raman spectrum. However, weak broad bands ranging from 300 to 350 cm^{-1} could be correlated with rutile phase of TiO_2 in each catalyst (Balachandran et al., 1982; Porto et al., 1967).

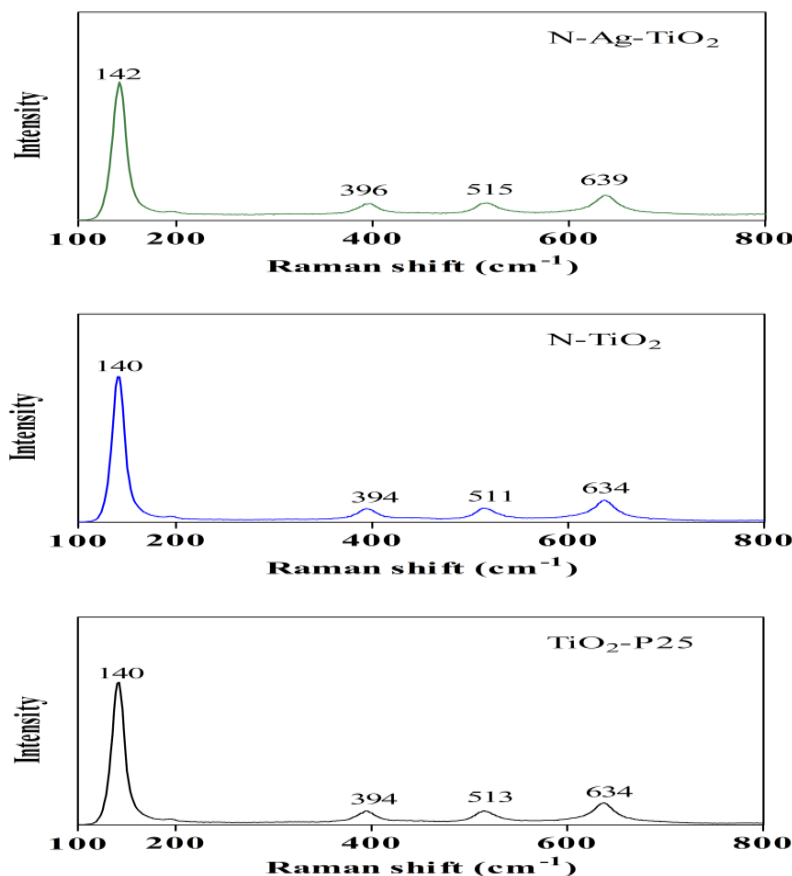


Fig. 4.37d: Raman spectra of TiO_2 -P25, N- TiO_2 and N-Ag- TiO_2 .

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of N-Ag- TiO_2 , N- TiO_2 and TiO_2 -P25 are shown in figure 4.37e. The structures of all three spectra were observed to be characteristically different thus signifying the incorporation of different elements i.e. Ag or N into the TiO_2 sample. Various peaks of TiO_2 between 400 and 1200 cm^{-1} could be correlated with Ti-O vibrations thus indicating the generation of Ti-O-Ti bonds in each case (Sayyar et al., 2015). The presence of weak band at 439 cm^{-1} in case of N-Ag- TiO_2 belonged to Ag-Ti-O vibrations (Ivanova et al., 2013). The peaks

in the vicinity of 2800 to 3500 cm^{-1} in each case could be attributed to Ti-OH bonds (Bae et al., 2003). The peaks at 1624.59 and 1629 cm^{-1} in case of N-TiO₂ and N-Ag-TiO₂ respectively could be assigned to N-H bending vibrations. The peak at 1640 cm^{-1} in case of TiO₂-P25 could be correlated with H-O-H vibrations (Yuan et al., 2010). Hence, the presence of N or Ag was confirmed in case of doped samples along with the retention of TiO₂ peaks.

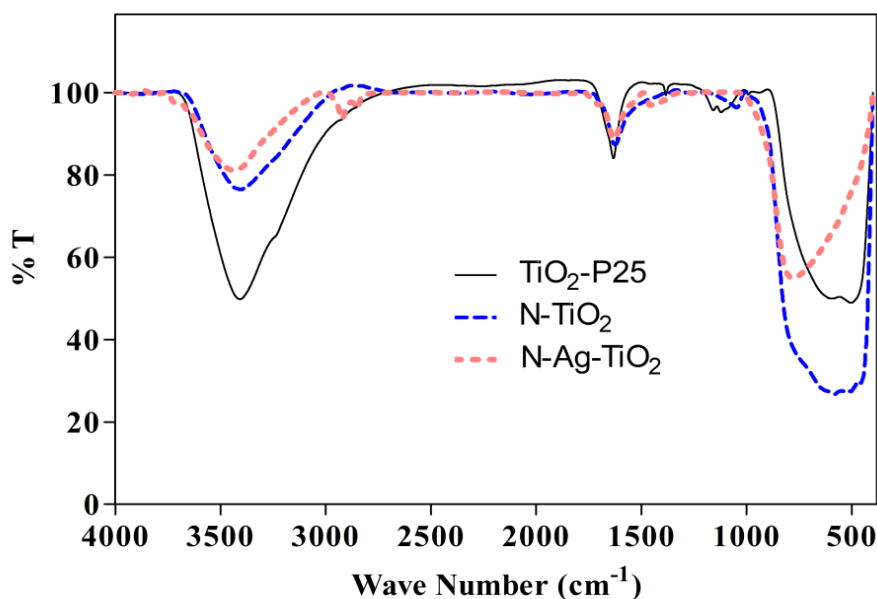


Fig. 4.37e: FT-IR spectra of TiO₂-P25, N-TiO₂ and N-Ag-TiO₂.

XPS analysis

Figure 4.37f depicts the XPS spectra of TiO₂-P25, N-TiO₂ and N-Ag-TiO₂ along with spectra of Ti 2p, O 1s, N 1s and Ag 3d from synthesized N-Ag-TiO₂. Figure 4.37f (i) indicates the Ti 2p spectrum of N-Ag-TiO₂ in which peaks corresponding to binding energies of Ti 2p_{3/2} and Ti 2p_{1/2} levels were observed at 458.07 and 463.86 eV, respectively. The results in the present study are in a good correlation with a reported study in literature (Tseng et al., 2014). Figure 4.37f (ii) demonstrates the O 1s spectrum in which peaks were observed around 529.3 and 531.6 eV. The peak at 529.3 eV could be assigned to Ti-O bonds (Gorska et al., 2008) whereas peak at 531.6 eV corresponded to H-O bonds (oxygen atom involved in hydroxyl groups) or in oxynitrides (Chen et al., 2005; Zhao et al., 2010). Figure 4.37f (iii) shows the N 1s spectrum which confirmed the presence of N possessing a binding energy of 398.9 eV, further proposing the interstitial formation of either Ti-N-O or Ti-O-N oxy-nitride bonds (Tseng et al., 2014).

Figure 4.37f (iv) demonstrates the Ag 3d spectrum in which two individual peaks were observed at 367.46 and 373.43 eV that were respectively correlated with Ag 3d_{5/2} and Ag 3d_{3/2} thus suggesting the presence of Ag⁰ (Chen et al., 2011).

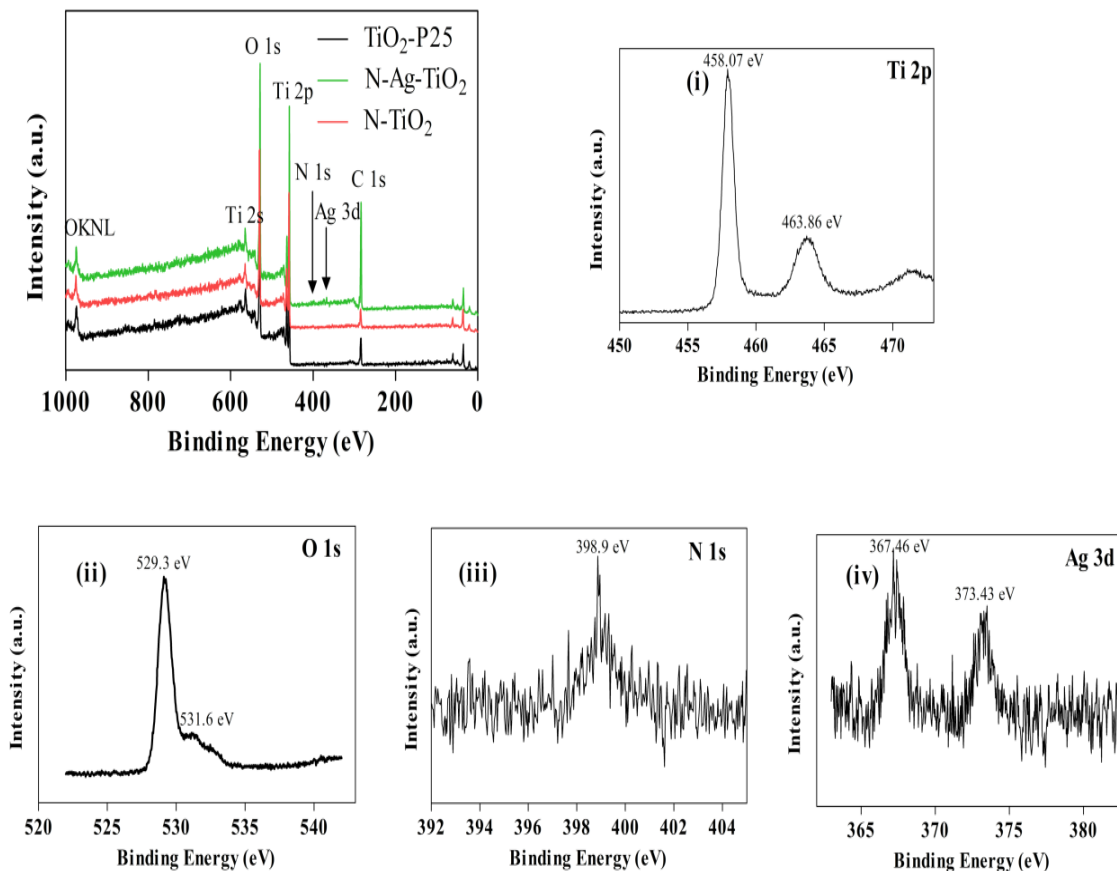


Figure 4.37f: XPS analysis of TiO₂-P25, N-TiO₂ and N-Ag-TiO₂ along with (i) Ti 2p spectrum, (ii) O 1s spectrum, (iii) N 1s spectrum and (iv) Ag 3d spectrum.

TGA analysis

The thermo-gravimetric (TG) curves of TiO₂-P25 along with N-TiO₂ and N-Ag-TiO₂ are shown in Figure 4.37g. No prominent change in weights was observed in any catalyst with temperature ranging from 30 to 650 °C. Thus, doped catalysts also displayed an outstanding thermal stability in contrast to undoped TiO₂-P25 depending upon its inorganic structure.

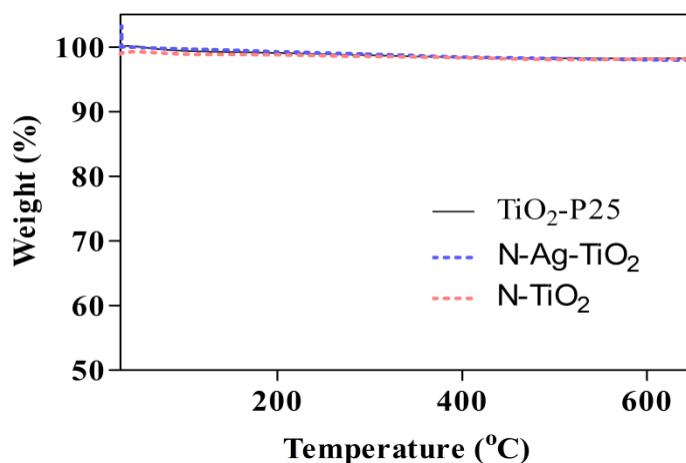


Figure 4.37g: TGA analysis of TiO₂-P25, N-TiO₂ and N-Ag-TiO₂.

As a result, N-TiO₂ and N-Ag-TiO₂ were successfully synthesized following the surface impregnation technique. Though presence of nitrogen was not detected via EDS analysis, its presence was confirmed through other techniques like SEM, XRD, FTIR and XPS. Moreover, the resultant catalysts i.e. N-TiO₂ and N-Ag-TiO₂ depicted significant absorption in the visible light due to the narrowing of band gap as confirmed through DRS analysis. Thus, photocatalytic activity of each catalyst was checked under natural solar irradiations as discussed in subsequent sections.

4.9.2 Photocatalytic activity of N-TiO₂

Before conducting the photocatalytic experiments, blank studies were carried out with aqueous solution of CEX (50 mgL⁻¹) to study its removal either through adsorption (dark studies) on the surface of catalyst or through direct photolysis (only solar light). Only 5-6% reduction in the concentration of CEX was achieved in each case. The solar induced photocatalytic experiments using TiO₂-P25 and N-TiO₂ resulted in significant degradation of CEX. However, modified photocatalytic process (using N-TiO₂) yielded better degradation of CEX than conventional photocatalysis (using TiO₂-P25). The modified photocatalytic process was further intensified with proper optimization of N concentration.

The concentration of N in case of N-TiO₂ was varied from 0.05-1.0 wt. %. All experiments were carried out under natural solar irradiations with 200 mgL⁻¹ of catalyst dose. It

is clear from figure 4.38a that the photocatalytic degradation of CEX first followed an increasing trend and then decreased with maximum degradation (82%) achieved using the photocatalyst containing 0.1 wt. % N. There was a drastic increase in the degradation rate constant of CEX as concentration of N was increased to 0.1 wt. %. Beyond 0.1 wt. %, no improvement in the degradation efficiency of CEX was observed owing to the blocking of active sites of catalyst as well as frequent recombination of charge carriers at high dopant concentrations (Jaiswal et al., 2012). It might be ascribed that dopants at low concentration trap the photon excited electrons and prevent frequent recombination of electrons and holes thereby improving the photocatalytic activity. The value of rate constant in case of N-TiO₂ was significantly higher ($P < 0.05$) in comparison to un-doped TiO₂. There was almost 29% increase in the degradation rate constant of CEX (0.035 min⁻¹) with N-TiO₂ (0.1 wt. %) as compared to that of undoped TiO₂ (0.025 min⁻¹). The reason for the enhanced photocatalytic activity of N-TiO₂ is probably the increased light absorption capacity of catalyst due to N-doping thus leading to the generation of more charge carriers which participate in surface redox reactions. In addition to this, it has been reported in literature that N-doping leads to the generation of oxygen vacancies on the surface which further favors the water molecules adsorption thereby enhancing the production of hydroxyl radicals (Gurkan et al., 2012; Valentin et al., 2005).

The optimum dose of N-TiO₂ was determined by varying the concentration of N-TiO₂ (0.1 wt. %) from 0.25 gL⁻¹ to 1.5 gL⁻¹. The degradation of CEX initially increased with an increase in the catalyst dose up to 1.25 gL⁻¹ (Figure 4.38b). Thereafter, the degradation of CEX started declining either due to the increase in turbidity of aqueous solution or obstruction in penetration of light at higher catalyst dose which ultimately affects the generation of hydroxyl radicals (Bansal et al., 2016). Thus, 1.25 gL⁻¹ of doped catalyst was selected as an optimum concentration at which the value of rate constant was increased to 0.038 min⁻¹ after 45 min of solar irradiations. The values of rate constant along with photonic efficiency under different conditions have been listed in Table 4.15.

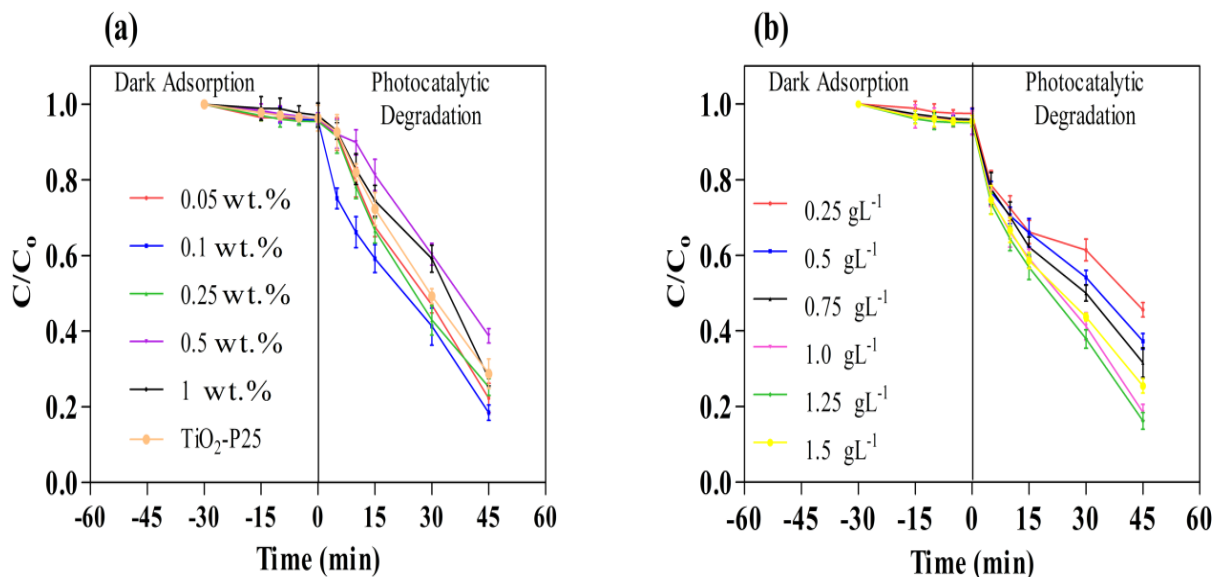


Figure 4.38: Normalized concentration of CEX with (a) varying N concentration, (b) dose of N-TiO₂.

Table 4.15: Values of rate constant and photonic efficiency under different operating conditions.

Optimum conditions	First order rate constant, k (min ⁻¹)	R (mol L ⁻¹ s ⁻¹) × 10 ⁻⁸	I ₀ (Einstein L ⁻¹ s ⁻¹) × 10 ⁻⁶	Photonic efficiency, ζ (%) (R/I ₀)*100
(A) CATALYST SUSPENSIONS				
N Doping				
TiO ₂ -P25	0.025	5.99	2.56	2.33
N- TiO ₂ (0.1 wt. %)	0.035	8.4	2.56	3.28
Catalyst dose				
1.25 gL ⁻¹ N- TiO ₂ (0.1 wt. %)	0.038	9.12	2.56	3.56
N, Ag Co-doping				
N (0.1 wt. %) – Ag (1.5 wt. %) TiO ₂	0.044	10.56	2.56	4.12
(B) FIXED BED STUDIES				
TiO ₂ -P25	0.009	2.16	2.56	0.84

immobilized clay beads				
N- TiO ₂ immobilized clay beads	0.011	2.64	2.56	1.031
N-Ag- TiO ₂ immobilized clay beads	0.014	3.36	2.56	1.31
(C) IN-SITU DUAL EFFECT STUDIES				
Fe-N-Ag-TiO ₂ composite	0.025	6.00	2.56	2.34
Fe-N-TiO ₂ composite	0.018	4.32	2.56	1.68
Fe-Ag-TiO ₂ composite	0.020	4.80	2.56	1.87
Fe-TiO ₂ composite	0.016	3.84	2.56	1.5
Blank composite	0.005	1.20	2.56	0.46

4.9.3. Photocatalytic activity of N-Ag-TiO₂

Though reasonably good photocatalytic efficiency of N modified TiO₂ was achieved for the degradation of CEX, efforts were made in the present study to further enhance the photo-response efficiency of N-TiO₂ by incorporating Ag particles along with N onto the surface of TiO₂. The photocatalytic activity of N-Ag-TiO₂ was examined by conducting the degradation experiments under natural solar irradiations using 250 mgL⁻¹ of doped catalyst. Interestingly, degradation rate was significantly enhanced with N-Ag-TiO₂ as compared to that of N-TiO₂.

Similarly, here also, Ag concentration was varied from 0.1-2.0 wt. %. The degradation of CEX was incremented with increase in the concentration of Ag particles from 0.1-1.5 wt. % (Figure 4.39). Thereafter, degradation of CEX started decreasing due to the formation of aggregates thus reducing the specific surface area of catalyst at higher dopant concentration. The photocatalyst (N-Ag-TiO₂) containing 1.5 wt. % Ag and 0.1 wt. % N was optimized in the present study. The value of rate constant was significantly higher ($P < 0.05$) in case of N (0.1 wt. %)-Ag (1.5 wt. %)-TiO₂ as compared to other compositions of N-Ag-TiO₂. The degradation rate

constant of CEX was enhanced to 0.044 min^{-1} using N-Ag-TiO₂ at which 88% degradation of CEX was achieved after 45 min of solar irradiations. This might be due to the better light absorption capacity of N-Ag-TiO₂ compared to N-TiO₂ (as discussed in Section 4.9.1) which ultimately led to the generation of more hydroxyl radicals. To counter-check the photocatalytic efficiency of N-Ag-TiO₂, adsorption studies were also conducted in dark which revealed negligible amount of CEX removal (4-5%). Thus, it can be concluded that Ag and N co-doped TiO₂ proved to be the most efficient photocatalyst for the degradation of CEX.

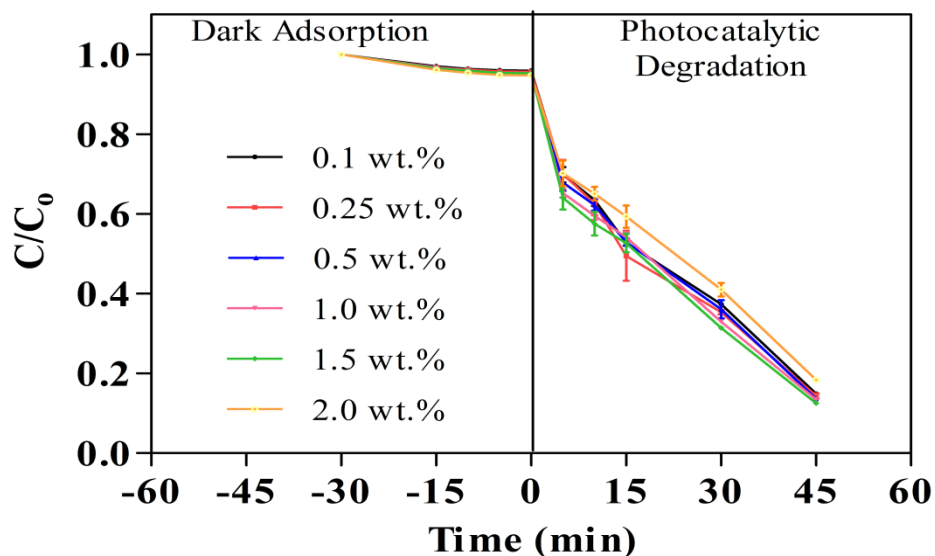


Figure 4.39: Effect of N, Ag co-doping on the degradation of CEX with varying concentration of Ag.

4.9.4 Fixed-bed studies

This section particularly deals with the fixed-bed photocatalytic studies for the degradation of CEX using supported Ag, N co-doped TiO₂ to seek the practical applications of modified catalyst. For this, the doped catalyst was immobilized on spherical clay beads and was examined for its catalytic activity in context to the degradation of CEX. The fixed-bed experiments were carried out with CEX aqueous solution using appropriate number of co-doped catalyst immobilized clay beads under natural solar irradiations.

The photo-response efficiency of the already established in-situ dual process (using Fe-TiO₂ composite beads as discussed in Section 4.7.6) was further enhanced by using co-doped

TiO₂ instead of TiO₂-P25 for coating the composite beads (detailed in section 3.7). Actually, these composite beads possessed the tendency to leach out iron species in solution under acidic conditions. The leached iron species could easily be used simultaneously for photo-Fenton process along-with ongoing modified TiO₂ photocatalysis. Owing to the leaching of iron from these materials under acidic conditions, experiments with composite beads were conducted at low pH i.e. 3.5 (adjusted with buffer). As Fe²⁺/H₂O₂ acts as a catalyst in photo-Fenton reaction, H₂O₂ was added in the system to study the modified dual process for the degradation of CEX.

Doped catalyst immobilized clay beads

To seek the commercial-scale applications of modified catalysts, the photocatalytic activity of N-TiO₂ and N-Ag-TiO₂ was assessed in fixed-mode using spherical clay beads as inert supports for catalyst immobilization. For drawing out the comparison between different photocatalysts in fixed form, TiO₂-P25 immobilized clay beads (control beads) were also used. Before conducting the photocatalytic experiments under solar irradiations, adsorption studies were carried out in dark with appropriate number of catalyst immobilized beads. Adsorption experiments resulted in insignificant removal (4-6%) of CEX from aqueous solution with each type of catalyst coated beads. Dark studies were followed by irradiating the CEX solution containing catalyst immobilized beads under natural solar light. In case of fixed-bed studies also, N-Ag-TiO₂ depicted significantly higher ($P < 0.05$) photocatalytic efficiency compared to N-TiO₂ and TiO₂-P25 (Figure 4.40). The photocatalytic degradation rate constant of CEX with different catalysts in fixed form followed the successive trend: N-Ag-TiO₂ (0.014 min⁻¹) > N-TiO₂ (0.011 min⁻¹) > TiO₂-P25 (0.009 min⁻¹). A maximum of 55% degradation of CEX was achieved after 60 min of solar irradiations using N-Ag-TiO₂ immobilized clay beads.

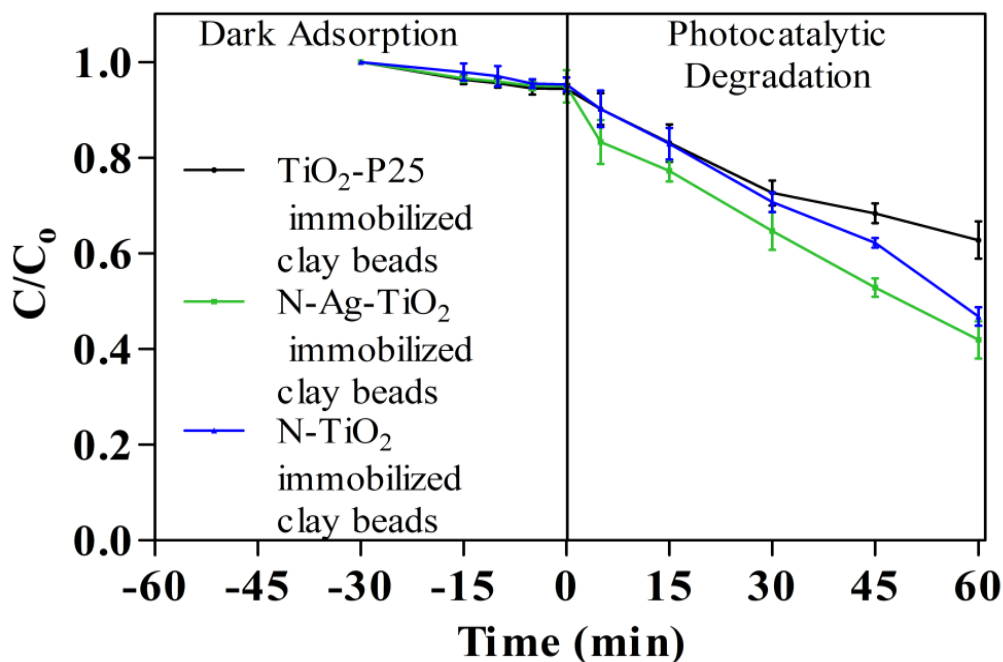


Figure 4.40: Effect of doped and un-doped TiO₂ immobilized clay beads on the degradation of CEX.

Modified in-situ dual process

In continuation with the earlier studies, the efficacy of in-situ dual effect in conjunction with N, Ag co-doped TiO₂ was also evaluated for the degradation of CEX. All fixed-bed experiments incorporating in-situ dual effect were carried out under natural solar irradiations using appropriate number of N-Ag-TiO₂ immobilized composite beads with addition of adequate amount of H₂O₂ at acidic pH i.e. 3.5. Owing to the presence of iron in composite beads, this modified TiO₂ immobilization system was termed as Fe-N-Ag-TiO₂ composite.

The presence of 'Fe' along with 'Ag', 'N', 'Ti', 'O' on the surface of composite beads was confirmed through several characterization techniques. Figure 4.41a depicts the SEM along with EDS image of Fe-N-Ag-TiO₂ composite. SEM image depicted the surface morphology of the composite beads. From the SEM image, it can be presumed that a uniform layer of catalyst was present on the surface of composite beads. On the other hand, the EDS image demonstrated the elemental composition of Fe-N-Ag-TiO₂ composite. The significant peaks of 'Fe', 'Ag', 'Ti' and 'O' were observed in through EDS analysis thus depicting their presence in the composite. As in case of N-Ag-TiO₂ (Section 4.9.1), no specific peak corresponding to 'N' appeared owing

to the presence of 'N' in very low concentration. However, the presence of 'N' along with all other elements was confirmed through XRD analysis (Figure 4.41b). Reference numbers 01-083-0875, 01-072-5182 and 01-072-6226, corresponding to Fe_4N , AgTi_3 and Fe_2O_3 respectively were obtained through XRD data which confirmed the presence of all expected elements in composite. Moreover, it was confirmed that 'anatase' (Reference number: 01-072-7058) and 'rutile' (Reference number: 01-083-2242) phase of TiO_2 were also retained thus indicating that doping as well as immobilization did not affect the activity of TiO_2 . The band gap energy of Fe-N-Ag- TiO_2 composite was also calculated through UV-visible diffuse reflectance spectroscopy (DRS). The diffuse reflectance spectrum of composite is shown in figure 4.41c. It was observed that the absorption edge in case of Fe-N-Ag- TiO_2 composite was extended to 453 nm. The band gap energy in the present case was observed to be 2.73 eV. Therefore, it can be concluded that Fe-N-Ag- TiO_2 composite exhibited a higher visible light response than any other catalyst under study.

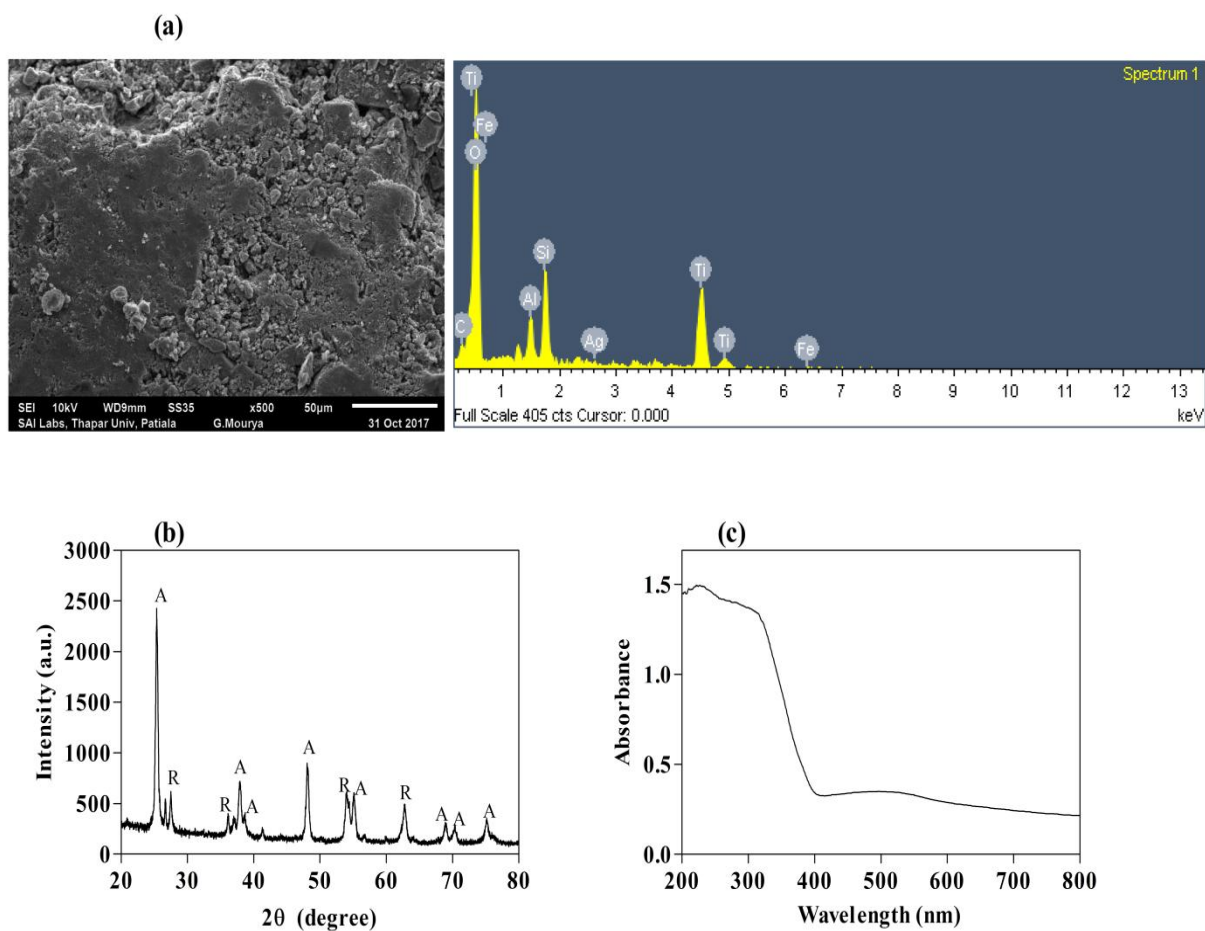


Figure 4.41: (a) SEM/EDS image, (b) XRD and (c) DRS of Fe-N-Ag- TiO_2 composite.

To carry out the modified in-situ dual process using Fe-N-Ag-TiO₂ composite beads, concentration of H₂O₂ was varied in the range (0.2-1.6 gL⁻¹) to determine its optimum dose for achieving the best possible degradation of CEX. The degradation of CEX via modified in-situ dual process initially followed an increasing trend with an increase in the dose of H₂O₂ up to 0.4 gL⁻¹ owing to the increase in production of hydroxyl radicals. In case of modified dual process, H₂O₂ was not utilized in a single process but in three different processes (i.e. modified photocatalysis, photo-Fenton and iron-oxide catalysis) which ultimately leads to the generation of hydroxyl radicals in abundance. However, with further increase in the dose of H₂O₂ beyond 0.4 gL⁻¹, degradation of CEX either became constant or started decreasing (Figure 4.42) which might be due to the predominance of scavenging effect of over produced hydroxyl radicals at higher concentration of H₂O₂. Thus, 0.4 gL⁻¹ of H₂O₂ was optimized in the current study at which degradation of CEX was incremented to 77% via modified in-situ dual process after 60 min of solar irradiations. On the other hand, 82% degradation of PEN was achieved via modified in-situ dual process under similar conditions after 30 min of solar irradiations. The concentrations of leached iron species from Fe-N-Ag-TiO₂ composite beads during the course of reaction are depicted in Table 4.16. The value of rate constant ('k') for the degradation of CEX in case of modified in-situ dual process (0.025 min⁻¹) was found to be significantly higher ($P < 0.05$) as compared to modified photocatalysis (0.014 min⁻¹) and photo-Fenton (0.005 min⁻¹). Thus, synergistic effect of in-situ dual process over individual processes i.e. modified photocatalysis and photo-Fenton was observed. To quantify the overall synergy, modified photocatalytic and photo-Fenton experiments were conducted separately using N-Ag-TiO₂ immobilized clay beads (without containing FA/FS) and blank composite beads (without TiO₂ coating), respectively at optimized dose of H₂O₂ i.e. 0.4 gL⁻¹ and at pH = 3.5 under natural solar irradiations. An overall synergy of dual process over individual processes for the degradation of CEX was found to be 24% as quantified from equation 4.6.

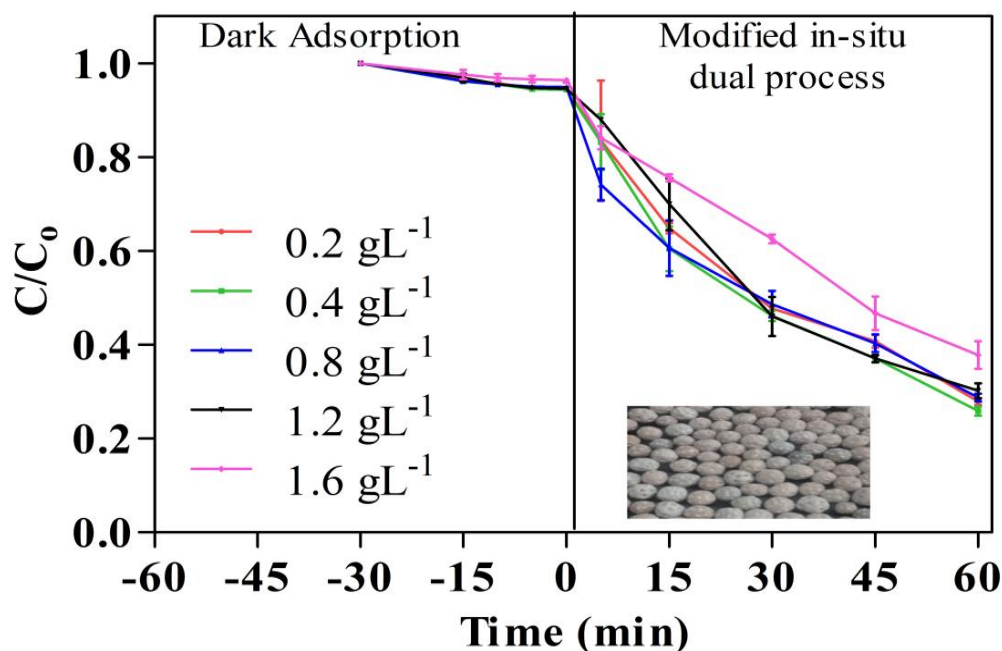


Figure 4.42: Modified in-situ dual process using Fe-N-Ag-TiO₂ composite with varying H₂O₂ dose for the degradation of CEX.

Table 4.16: Concentration of leached iron species from Fe-Ag-N-TiO₂ composite beads during the degradation of CEX

Time (min)	Concentration (mgL ⁻¹)		
	Total iron	Ferrous	Ferric
15	0.21	0.079	0.131
30	0.25	0.11	0.14
45	0.32	0.19	0.13
60	0.22	0.11	0.11

Comparison among different composite beads

To further confirm the effectiveness of Fe-N-Ag-TiO₂ composite for the degradation of CEX, additional experiments were conducted using different kinds of catalyst immobilized composite beads (Figure 4.43) at optimized dose of H₂O₂ i.e. 0.4 gL⁻¹ and at pH = 3.5 under natural solar irradiations. It was found that degradation of CEX was significantly higher ($P < 0.05$) in case of Fe-N-Ag-TiO₂ composite as compared to other composites. The degradation rate constant followed the successive trend for the degradation of CEX: Fe-N-Ag-TiO₂ composite

(0.025 min^{-1}) > Fe-Ag-TiO₂ composite (0.020 min^{-1}) > Fe-N-TiO₂ composite (0.018 min^{-1}) > Fe-TiO₂ composite (0.016 min^{-1}) > blank composite (0.005 min^{-1}).

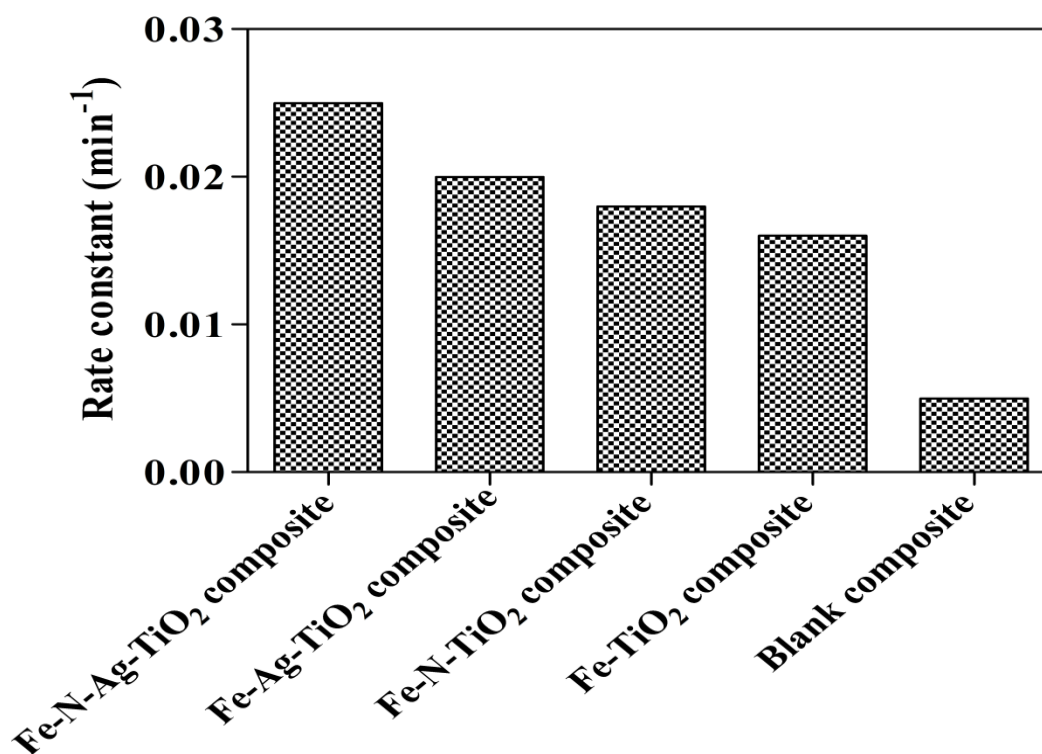


Figure 4.43: Comparison of in-situ dual processes using different composite beads.

For drawing out the comparison of degradation efficiency of CEX via modified in-situ dual process (using Fe-N-Ag-TiO₂ composite) with in-situ dual process (using Fe-TiO₂ composite), experiments were conducted with 200 mL of CEX solution using Fe-N-Ag-TiO₂ composite under solar irradiations. It took almost 150 min to attain 90% degradation of CEX using Fe-N-Ag-TiO₂ composite as compared to 210 min using Fe-TiO₂ composite as reported in section 4.7.7. Thus, Fe-N-Ag-TiO₂ composite demonstrated the highest performance efficiency in terms of the degradation of CEX.

To seek the practical applications of modified in-situ dual process, recyclability efficiency of Fe-N-Ag-TiO₂ composite was monitored by reusing the composite for subsequent cycles and was evaluated in terms of the degradation efficiency of CEX. Fe-N-Ag-TiO₂ composite was successfully recycled for 15 runs for the degradation of CEX. It was observed that there was almost 5-10% loss in the degradation efficiency of CEX during the first five recycles owing to the draining off the loosely bound catalyst particles from the surface of beads.

After 5 runs, there was an insignificant reduction in the degradation efficiency of CEX as shown in figure 4.44, thus further highlighting the commercial viability of this novel technique. This is the first ever reported study in context to the modified in-situ dual process depicting practical applications of co-doped TiO_2 especially in fixed-form along with its reasonably good recyclability efficiency.

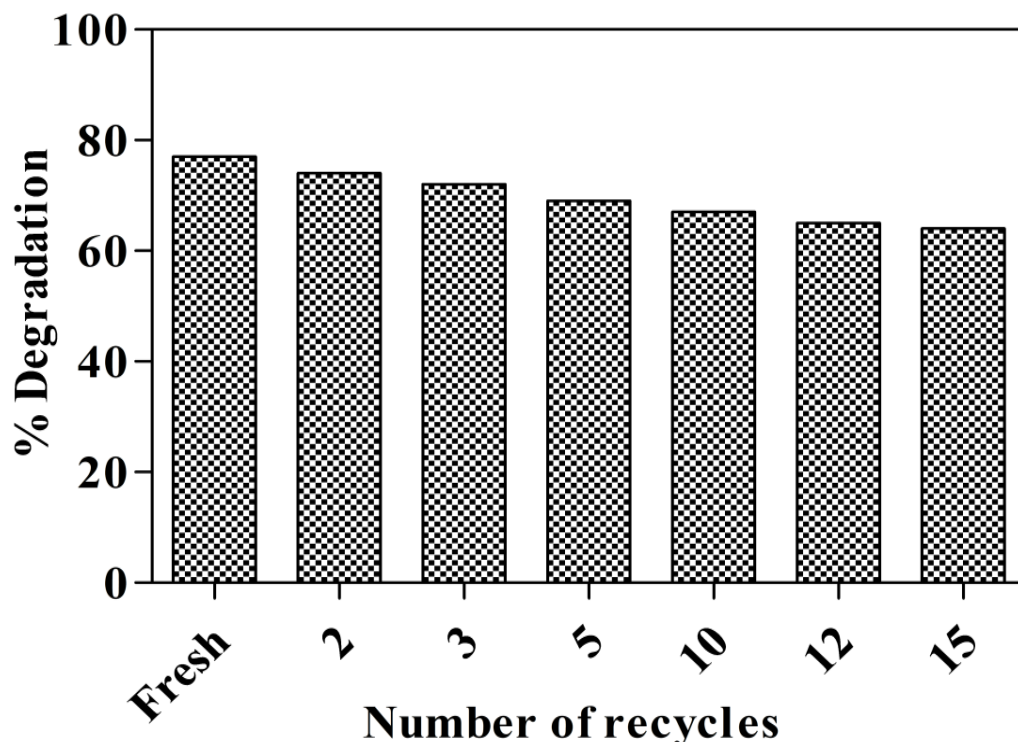


Figure 4.44: Recyclability studies of Fe-N-Ag- TiO_2 composite.

4.9.5 Proposed mechanism of modified in-situ dual process

The enhanced degradation efficiency of CEX via modified in-situ dual process can be explained on the basis of electron-hole pair formation as well as separation. Actually, the catalytic activity depends upon the number of charge carriers involved during a photocatalytic reaction. In the present work, reduction in band-gap energy of Fe-N-Ag- TiO_2 composite has already been proven which clearly indicated that both visible and UV spectrum of solar irradiations were involved during the photo-reaction (Section 4.9.1). Thus, more electron-hole pairs were produced during the reaction. At the same time, Ag particles distributed on the surface of TiO_2 trapped the photon excited electron from conduction band of TiO_2 and favored the

separation of electron-hole pair thereby enhancing the catalytic activity of TiO_2 . In addition to this, presence of iron-oxides (confirmed from XRD analysis, Section 4.9.1) on the surface of composite also facilitated the electron-hole separation as iron-oxide also trapped the excited electron from TiO_2 . This trapped electron got involved in the regeneration of ferrous ions from ferric ions thus promoting the photo-Fenton reaction going on simultaneously along with photocatalysis. Thus, profuse amount of hydroxyl radicals were generated through different processes including modified TiO_2 photocatalysis, photo-Fenton and iron-oxide catalysis (Figure 4.45).

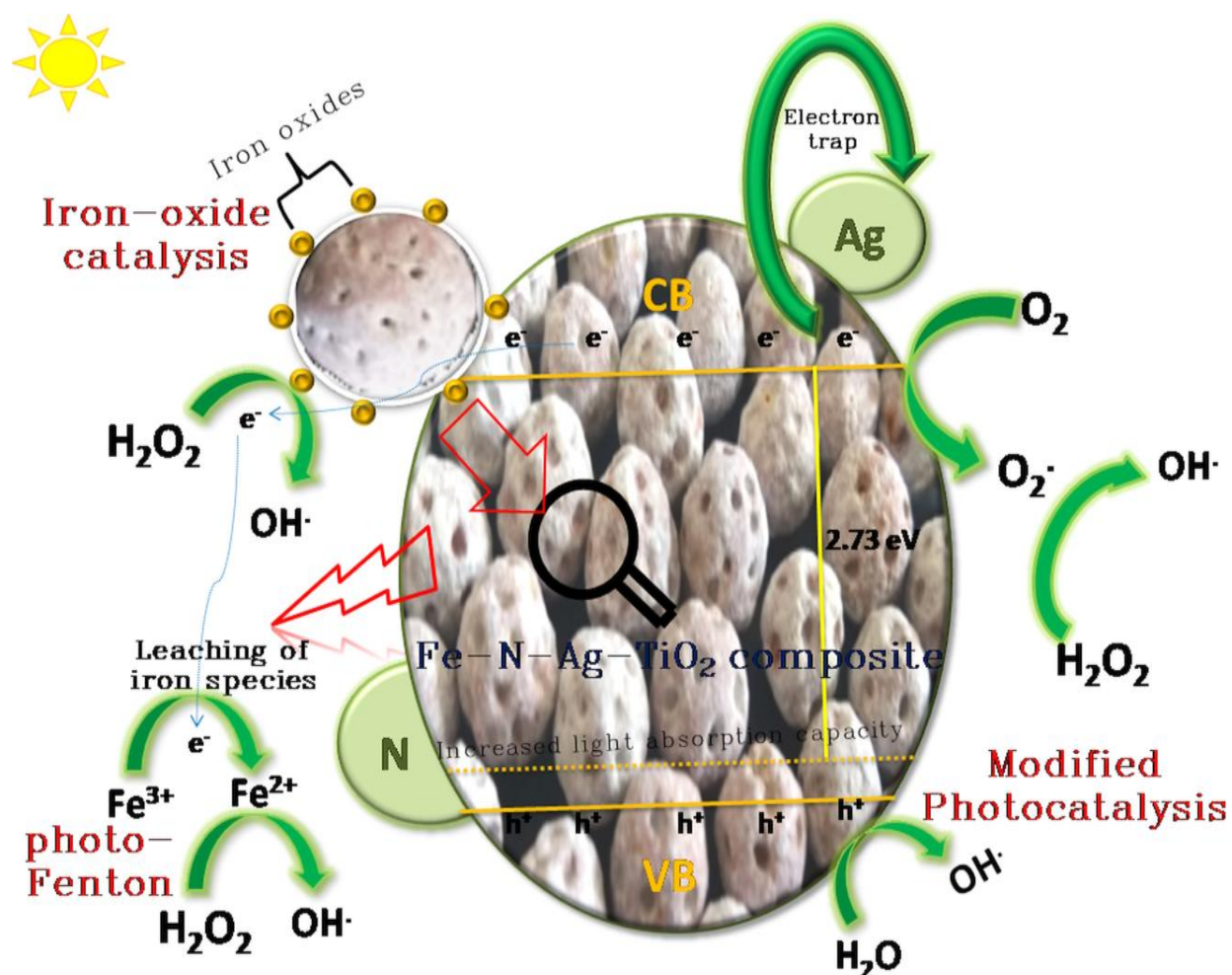


Figure 4.45: Proposed mechanism of modified in-situ dual process.

4.9.6 Mineralization studies

The mineralization of CEX through modified in-situ dual process was validated through generation of various anions like sulfate, nitrite and nitrate ions along with reduction in COD and TOC during the treatment process. There was almost 74% reduction in COD and 71% reduction in TOC after 60 min of treatment under solar irradiations. The production of nitrate ions was maximum during the initial 15 minutes. Thereafter, concentration of nitrate ions started decreasing with the possibility of conversion from nitrate to nitrite ions. The sulfate and nitrite ions followed an increasing trend throughout the reaction as can be depicted from Table 4.17. The intermediates formed during the degradation of CEX were identified through GC-MS analysis. The intermediates formed during the degradation process via modified in-situ dual process were some-what different from those that were identified in Section 4.7.11. Based on these intermediates, a tentative pathway for the degradation of CEX was proposed again as shown in figure 4.46. The GC chromatograms have been provided in Appendix (Figure A4). Thus, it was clear from the pathway that complex structure of parent compound (CEX) was decomposed completely into linear chain molecules.

Table 4.17: Concentration of anions produced during the degradation of CEX via modified in-situ dual process

Time (min)	Nitrite (μgL^{-1})	Nitrate (mgL^{-1})	Sulfate (mgL^{-1})
15	0.27	1.13	0.44
30	0.56	1.92	0.93
45	1.66	0.76	1.23
60	2.9	0.54	1.6

Section C

Scale-up studies using Fe-TiO₂ composite beads

To promote the applicability of AOPs at field-scale in near future, it is mandatory to execute the scale-up trails of lab-scale results. The established in-situ dual effect in the present study using Fe-TiO₂ composite beads (Section 4.7.6) was scaled up for the degradation of CEX and PEN with the development of pilot-scale solar reactors. Fe-TiO₂ composite beads were selected for the scale-up studies especially in view of their extended recyclability efficiency (> 45 recycles) which has not been achieved with any other type of beads. Moreover, inexpensive nature of these Fe-TiO₂ composite beads would expectedly make the process cost-effective. The pilot-scale solar reactors taken into consideration for the present study were re-circulation type fixed-bed glass reactor and once through cascade reactor with total volume handling of 5 L. The detailed cost of the process has been evaluated using each type of reactor.

4.10 Pilot-scale fixed-bed glass reactor

The feasibility of in-situ dual process employing Fe-TiO₂ composite beads was checked in a pilot-scale solar non-concentrating flat-bed reactor (Figure 3.10) made up of glass with volume handling of 5 L. The pilot-scale in-situ dual process was intensified with proper optimization of operating parameters taking PEN as a target pollutant while viability of process was confirmed by executing the degradation of CEX under optimized conditions.

4.10.1 In-situ dual effect studies at pilot-scale

Initially experiments were conducted to study the effect of individual operating parameter on the removal of target pollutant i.e. PEN. Each experiment was performed for 4h with 5 L of PEN solution (50 mgL⁻¹) in a pilot-scale reactor with flow rate of 0.4 Lmin⁻¹ under natural solar light. Adsorption experiments were carried out under dark in the presence of only Fe-TiO₂ composite which resulted in only negligible amount of PEN removal (6-8%) owing to the blocking of active sites of catalyst due to the formation of pollutant layer on catalyst surface (Toor et al., 2007). Photolytic studies were carried out with PEN solution in the presence of only solar light which revealed just 3-5% removal of PEN. In the presence of only H₂O₂ also, similar type of results were obtained as only 2-3% removal of PEN was achieved. Photocatalytic

experiments with Fe-TiO₂ composite and control beads (TiO₂ immobilized clay beads (without FS/FA)) in the presence of sunlight yielded around 30% degradation of PEN in both cases. Photo-Fenton experiments with blank composite beads (without TiO₂ coating) under sunlight in the presence of 0.3 gL⁻¹ H₂O₂ revealed approximately 35% degradation of PEN. Addition of H₂O₂ in photocatalytic experiments improved the degradation to around 45% in case of control beads and to around 70% in case of Fe-TiO₂ composite. Fe-TiO₂ composite took almost half time (2 h) in comparison to that of control beads (photocatalysis) to achieve 45% degradation and around 1.5 h in comparison to blank composite beads (photo-Fenton) to attain 35% degradation of PEN. This drastic increment in the degradation of PEN in case of Fe-TiO₂ composite can be attributed to the in-situ dual effect (photocatalysis and photo-Fenton) owing to the systematic leaching of iron in solution through composite thereby contributing to the occurrence of photo-Fenton along with photocatalysis. The results are represented graphically in figure 4.47a and figure 4.47b. The photonic efficiency of the system in case of dual process was increased to 0.71 % from 0.3 % (photocatalysis) and 0.25 % (photo-Fenton). The synergistic effect of dual process over photocatalysis was observed to be 68.24% and over photo-Fenton was 64.189%. The overall synergy of dual process came out to be 32.4%. The first order rate constant in case of dual process (0.296 h⁻¹) was significantly higher ($P < 0.05$) as compared to that of photo-Fenton (0.106 h⁻¹) and photocatalysis (0.0946 h⁻¹) as shown in figure 4.47b.

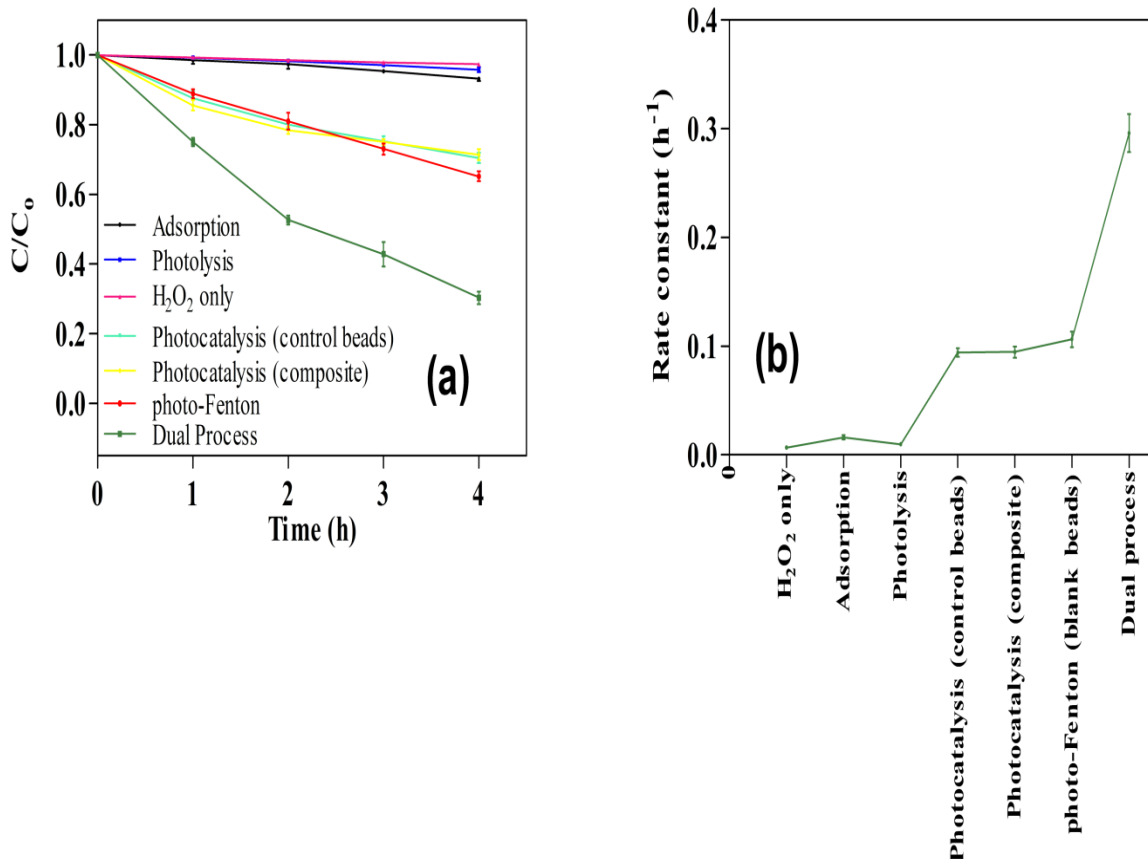


Figure 4.47: Plot of (a) C/C_0 vs time (b) First order rate constant for the degradation of PEN through different processes ($C_0=50 \text{ mgL}^{-1}$, $V = 5 \text{ L}$).

The reason for the escalated degradation process is the abundant generation of hydroxyl radicals (Section 4.11.1, Figure 4.62) through different processes occurring in the same treatment unit as already discussed before.

The trend of iron leaching was studied by determining the total iron concentration along with ferrous and ferric ion estimation at regular intervals of period during the reaction as depicted in figure 4.48. It is clear from figure that total iron concentration initially increased up to 2 h and thereafter it started decreasing thus manifesting its contribution in photo-Fenton reaction.

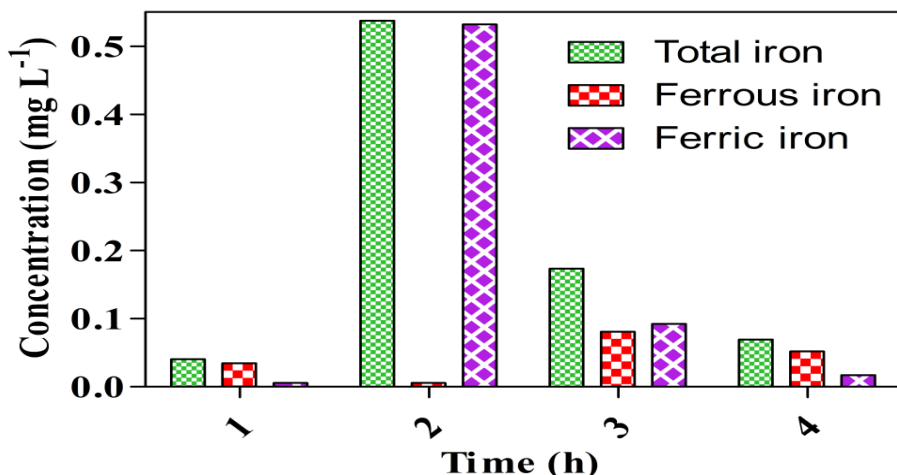


Figure 4.48: Determination of the total iron concentration along with ferrous and ferric ion estimation during the degradation of PEN through dual process.

All further experiments were conducted with Fe-TiO₂ composite in order to optimize the operating parameters for dual process at pilot-scale.

Effect of oxidant dose

As our study incorporates the concept of in-situ dual effect with Fe-TiO₂ composite, studying the effect of variation of H₂O₂ thus becomes extremely prominent as its addition accelerates the dual effect. Optimal concentration of H₂O₂ escalates the generation of hydroxyl radicals increasing the degradation efficiency. Actually hydroxyl radicals were not produced solely through TiO₂ photocatalysis but also through photo-Fenton and iron oxide catalysis going on simultaneously. However overdose of H₂O₂ can also cause scavenging effect thus lowering down the degradation rate (Zhao et al., 2004). In the present study, H₂O₂ was varied in the range 0.3-1.5 gL⁻¹ with 5 L of PEN solution (50 mg L⁻¹) at a flow rate of 0.4 L min⁻¹. The degradation of PEN increased initially with increase in the dose of H₂O₂ up to 0.9 gL⁻¹. Thereafter, degradation either became almost constant or started declining due to the prevalence of scavenging effect. The optimum dose of H₂O₂ selected for the present study was 0.9 gL⁻¹ which revealed almost 83% degradation of PEN with maximum value of first order rate constant i.e. 0.469 h⁻¹ (Figure 4.49a and Figure 4.49b). The photonic efficiency of the system was further increased to 1.09 % with optimized dose of oxidant. To observe the synergistic effect of dual process, photocatalysis with control beads and photo-Fenton with blank beads were also carried out at optimum dose of oxidant which revealed 67% and 60% degradation respectively. The

degradation was significantly higher ($P < 0.05$) in case of dual process in comparison to individual processes. An almost 50% degradation of PEN was achieved within 1 h of treatment in case of dual process whereas it took almost 3 h to reach the same amount of degradation with photocatalysis and more than 3 h with photo-Fenton. The synergy of dual process over photocatalysis was almost 48% and over photo-Fenton was 58%. However, overall synergy of dual process was 6%.

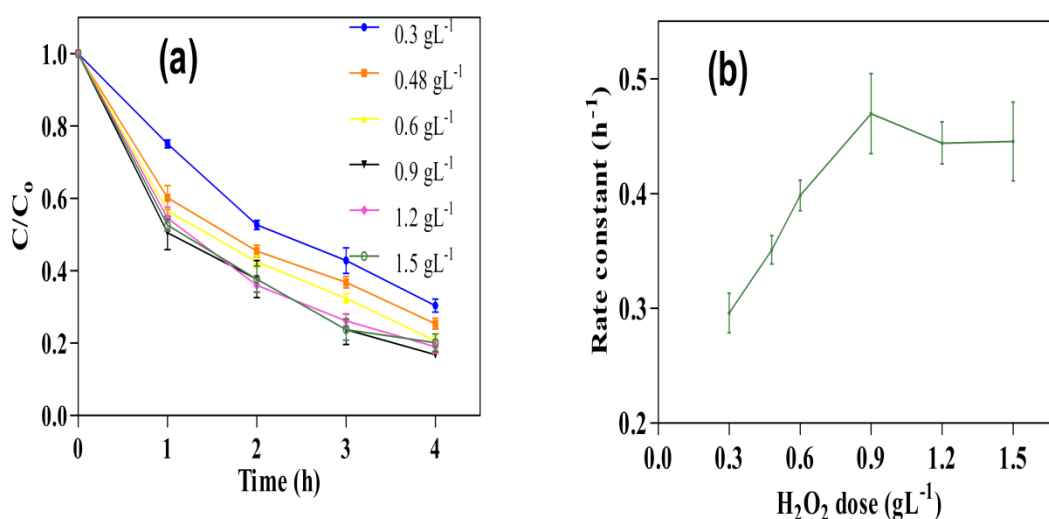


Figure 4.49: Plot of (a) C/C_0 vs time and (b) First order rate constant for the effect of H_2O_2 dose on the degradation of PEN through dual process ($C_0=50 \text{ mg/L}^{-1}$, $V = 5 \text{ L}$).

Effect of flow rate

The amount of turbulence and dissolved oxygen plays an important role in the photocatalytic reaction systems which can be controlled with optimum recycle flow rate. In the present research work, the recycle flow rate was varied from 0.2-2.0 L/min at optimized dose of H_2O_2 (0.9 g/L). It was observed that initially the degradation also increased with increase in flow rate from 0.2-0.8 L/min . The possible justification for this kind of behavior is that increasing the recycle flow rate increases the dissolved oxygen molecules which act as electron scavenger and prevents recombination of electron and holes thus promoting the redox reaction to take place at the catalyst surface. Similar kind of results were reported for the degradation of phenol when recycle flow rate was increased from 0.250-0.50 L/min (Adishkumar et al., 2016). Chan et al. (2001) also reported that turbulence created due to recycle flow rate stimulates the

effectual mass transfer during photocatalytic reactions. When flow rate was further increased from 0.8-2.0 Lmin⁻¹, degradation of PEN started declining. With increased flow rate, pollutant contact time with catalyst particles decreases. It exits without making an efficient contact with catalyst particles thus reducing the degradation efficiency. After verifying the results statistically, 0.8 Lmin⁻¹ was adopted as an optimum flow rate at which degradation was increased to around 89% (Figure 4.50a) with maximum value of first order rate constant i.e. 0.578 h⁻¹ as shown in figure 4.50b after 4h of treatment. In this case, photonic efficiency of the system was incremented to 1.34%.

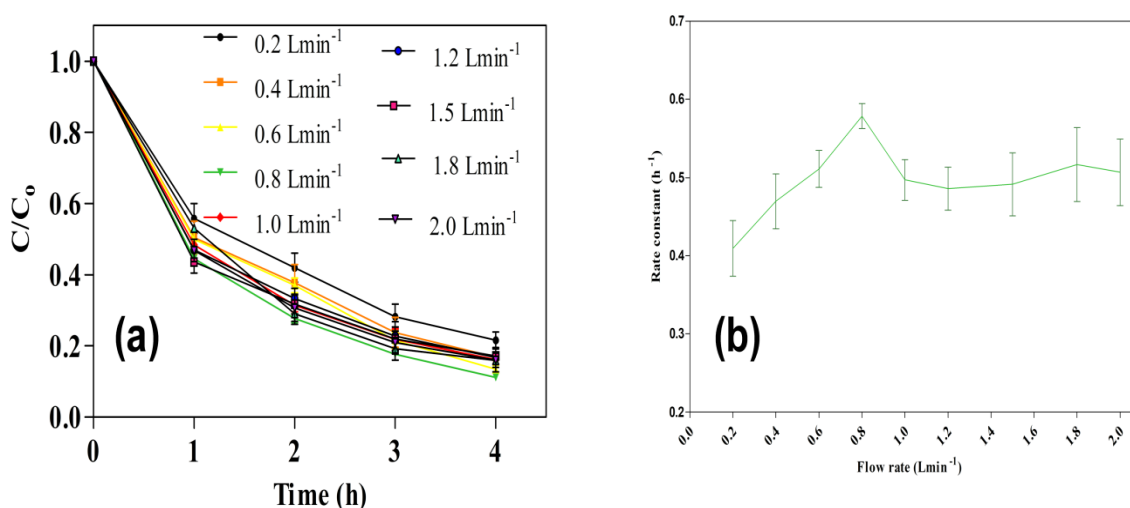


Figure 4.50: Plot of (a) C/C_0 vs time and (b) First order rate constant for the effect of flow rate on the degradation of PEN through dual process ($C_0=50 \text{ mgL}^{-1}$, $V = 5 \text{ L}$, $\text{H}_2\text{O}_2 = 0.9 \text{ gL}^{-1}$).

Effect of catalyst dose (Iron/TiO₂) and composite size

The catalyst in the present dual effect study comprised of both iron and TiO₂ content. Both must be present in optimum concentrations in order to get best degradation rate. It is somewhat difficult to optimize the catalyst dose in completely fixed-bed studies. Best efforts have been made in the current research to optimize the catalyst dose by varying the catalyst amount (iron and TiO₂) in various ways. The amount of catalyst was varied by varying the number of Fe-TiO₂ composite i.e. altering the concentration of both iron and TiO₂ simultaneously. The number of Fe-TiO₂ composite was expressed in terms of the percentage area

of the available reactor bed (under study) covered with composite. When number of Fe-TiO₂ composite was increased from 25% to 75% of reactor bed area, degradation of PEN also increased. As with less number of composite (25%), available active sites of the catalyst were reduced for the reaction to take place. When number of composite was further increased from 75% to 150% of reactor bed area, degradation efficiency of the process started decreasing (Figure 4.51a) along with significant reduction in the value of rate constant (Figure 4.51b). This might be due to the prevailing shadowing effect which further enhances problem of proper catalyst illumination thus reducing the effective available surface area for catalyst binding with pollutant. Therefore, composite covering 75% of reactor bed area was selected to be optimum for present study.

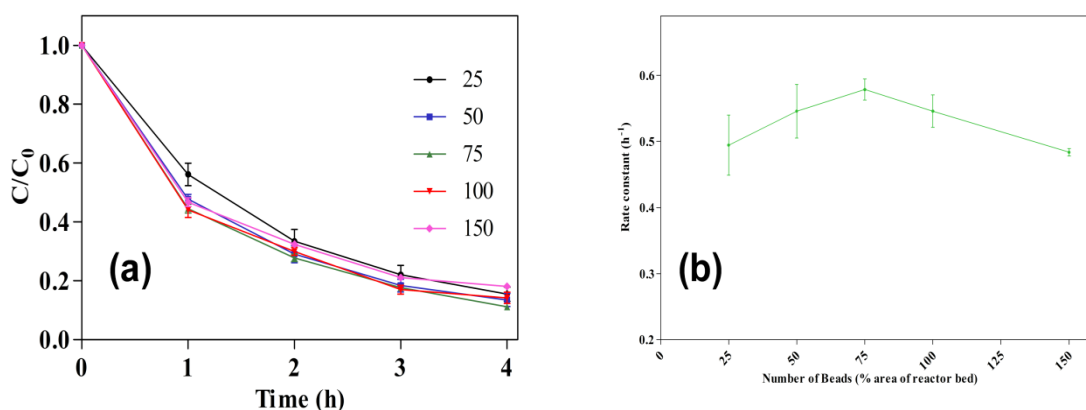


Figure 4.51: Plot of (a) C/C_0 vs time and (b) First order rate constant for the effect of catalyst dose (number of composite beads) on the degradation of PEN through dual process ($C_0=50 \text{ mgL}^{-1}$, $V = 5 \text{ L}$, $\text{H}_2\text{O}_2 = 0.9 \text{ gL}^{-1}$, Flow rate = 0.8 Lmin^{-1}).

Alternatively catalyst dose was varied by reducing the amount of iron by replacing 50% of Fe-TiO₂ composite with control beads. The degradation was reduced to 75% which might be due to the lowering efficiency of photo-Fenton reaction. Similar trend was followed when amount of iron was increased by replacing 50% of Fe-TiO₂ composite with blank beads as degradation was reduced in this case also. As a result, composite covering 75% of reactor bed area without any addition of control or blank beads gave the best degradation (89%) with significantly higher ($P < 0.05$) value of rate constant being 0.578 h^{-1} in comparison to other dosages after 4 h of treatment. Under these conditions, the optimum concentration of leached

iron species was observed to be 0.79 mgL^{-1} at which significant increase in % removal of PEN was observed. The concentration of leached iron during the course of reaction at optimized catalyst dose has been provided in table 4.18.

Table 4.18: Concentration of leached iron species at optimized catalyst dose

Time (h)	Ferrous iron (mg L^{-1})	Ferric iron (mg L^{-1})	Total iron (mg L^{-1})
0.5	0.028	0.15	0.178
1	0.60	0.18	0.78
2	0.05	0.54	0.59
3	0.13	0.14	0.27
4	0.092	0.15	0.242

Attempts have also been made to study the effect of surface area available for reaction by varying the diameter of composite in the range 10-20 mm as measured through vernier caliper. Best degradation (89%) and maximum rate constant (0.578 h^{-1}) was attained with 15 mm sized composite (Figure 4.52). Degradation decreased significantly ($P < 0.05$) with small sized composite (10 mm) as compared to that of 15 mm sized beads due to the ineffective activation of the catalyst by photons as photons of light had to traverse a longer path to reach the catalyst surface. For larger sized composite (20 mm) also, the degradation decreased significantly ($P < 0.05$) compared to 15 mm beads which might be due to the ineffective availability of the surface area for reaction to take place as composite were not effectively getting wet in the solution. This is the first ever reported study using Fe-TiO₂ composite to study the dual effect at pilot-scale level.

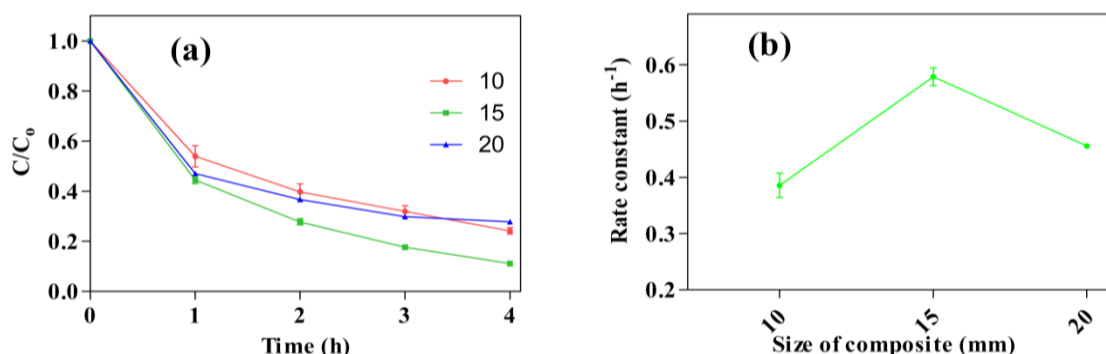


Figure 4.52: Plot of (a) C/C_0 vs time and (b) First order rate constant for the effect of size of composite on the degradation of PEN through dual process ($C_0=50 \text{ mgL}^{-1}$, $V = 5 \text{ L}$, $\text{H}_2\text{O}_2 = 0.9 \text{ gL}^{-1}$, Flow rate = 0.8 Lmin^{-1}).

Effect of number of baffles

The addition of baffles to the reactor is supposed to increase the retention time thereby increasing the degradation efficiency. The number of baffles was varied from 0 to 5. The % degradation of PEN was increased to 93% (with increased rate constant i.e. 0.697 h^{-1}) as number of baffles increased from 0 to 3 as shown in figure 4.53a and figure 4.53b. Thereafter, degradation started declining which may be due to the occurrence of shading effect caused by baffles. The degradation of PEN was decreased significantly ($P < 0.05$) as the number of baffles was increased to 5 from 3. The prevalence of shading effect of baffles caused an ineffective absorption of photons of solar light by catalyst. Similar trend was observed in a study by Adishkumar et al. (2015) where degradation of phenol was reduced with three baffles due to the shading effect.

The viability of the pilot-scale fixed-bed glass reactor incorporating in-situ dual effect was confirmed when significant amount of degradation of CEX i.e. 89% was achieved after 5 h of solar irradiations at all optimized conditions.

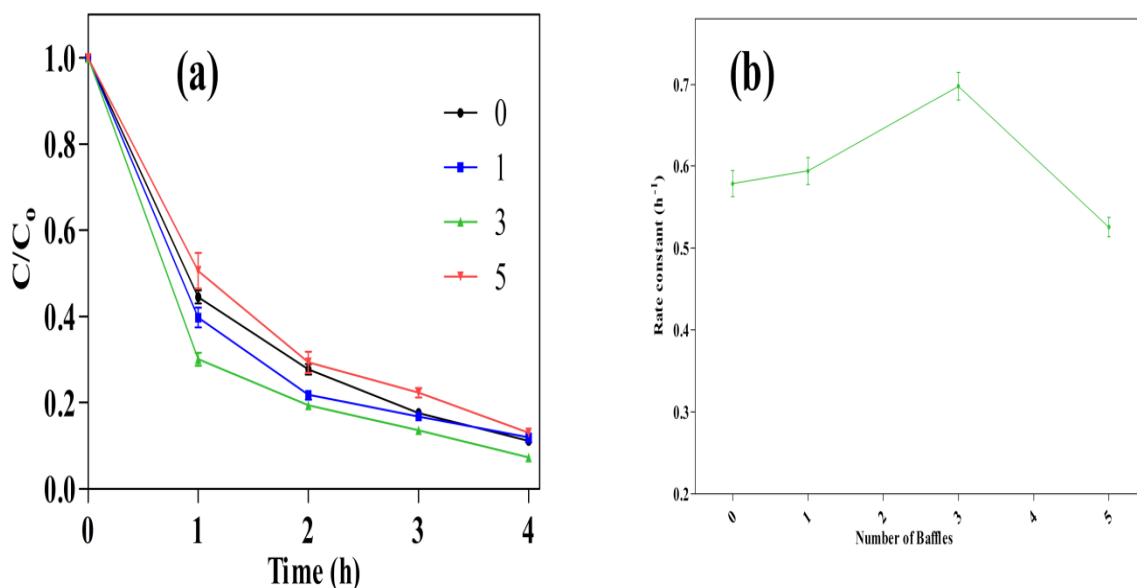


Figure 4.53: Plot of (a) C/C_0 vs time and (b) First order rate constant for the effect of number of baffles on the degradation of PEN through dual process ($C_0=50 \text{ mgL}^{-1}$, $V = 5 \text{ L}$, $\text{H}_2\text{O}_2 = 0.9 \text{ gL}^{-1}$, Flow rate = 0.8 Lmin^{-1} , number of composite = 75% of reactor bed area).

4.10.2 Catalyst recyclability studies

The main strength of this study basically reports the durability of Fe-TiO₂ composite even under flow conditions along with sustainable leaching of iron from the composite. The durability of Fe-TiO₂ composite was studied by recycling it for subsequent runs and was analyzed in terms of degradation efficiency for PEN. For the first time, this kind of innovative study has been presented where the composite once prepared were used for optimization of all operating parameters. In other words, the Fe-TiO₂ composite beads prepared on the very first day were used for all the parametric optimization till last results have been withdrawn. To the best of our knowledge, no such report has ever been cited in literature.

The composite beads were successfully recycled for 35 cycles without any significant reduction in the degradation efficiency (Figure 4.54). The composite beads were not given any kind of heat treatment for catalyst re-activation as discussed in section 4.7.9. The various characterization techniques also proved the durability and stability of composite even after 35 recycles as discussed in section 4.10.3. To further strengthen our claim of this novelty, composite previously used for at-least fifty cycles (old composite) were used as such for the degradation of compound under study. Even these composite were able to demonstrate a reasonable amount of degradation efficiency (83%) after 4 h of treatment. The slight loss in degradation efficiency (~10%) might be attributed to the weathering-off catalyst particles from composite (Singh et al., 2017) along with restricted leaching of iron. The amount of catalyst loss from the surface of composite was determined by weighing the composite bead before and after the recycling tests. There was almost 7-8% loss in the concentration of coated catalyst after recycling the bead for 50 runs thus signifying the presence of sufficient quantity of catalyst even in recycled composite which could contribute further in the photocatalytic experiments.

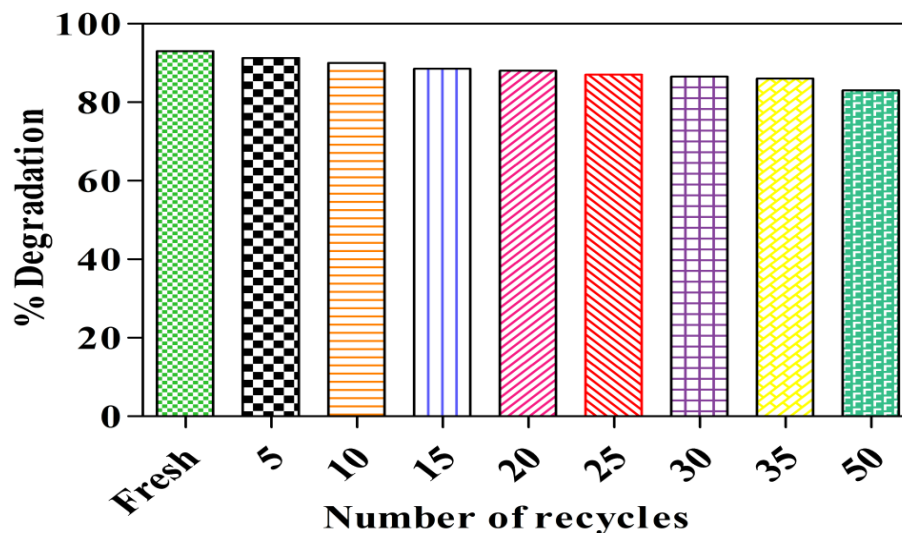


Figure 4.54: Recyclability studies of Fe-TiO₂ composite for the degradation of PEN.

4.10.3 Characterization of catalyst

SEM/EDS analysis

The SEM-EDS images of recycled composite (35 cycles) and old composite (50 cycles) are illustrated in figure 4.55a. The surface morphology of both the composite were almost same as that of freshly coated composite beads thus indicating that surface characteristics did not change even after 50 recycles. The sharp peaks of iron, Titanium and Oxygen in electron dispersive spectrum in both cases substantiate the stability and intactness of both catalysts (iron and TiO₂) even after 50 recycles. Thus, it can be concluded from SEM-EDS results that Fe-TiO₂ composite can be used even for further studies.

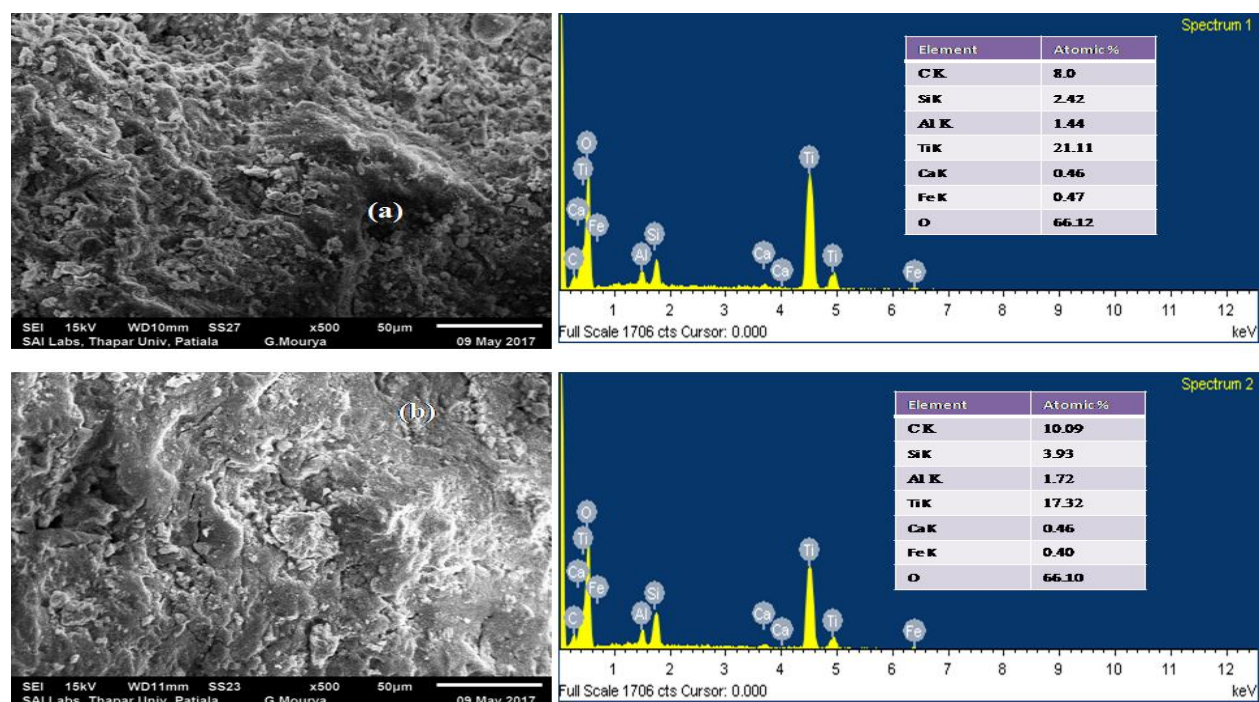


Figure 4.55a: SEM/EDS image of Fe-TiO₂ composite (a) after 35 recycles and (ii) after 50 recycles.

XRD analysis

The X-ray diffraction patterns of recycled Fe-TiO₂ composite along with TiO₂-P25 are shown in figure 4.55b. The occurrence of crystalline planes corresponding to anatase (reference code: 01-072-7058), marked as 'A' and rutile (reference code: 01-072-4814), marked as 'R' in the XRD pattern of Fe-TiO₂ composite clearly indicated that photocatalytic activity of TiO₂-P25 in composite beads was still retained even after 35 recycles. Diffraction peaks corresponding to Iron Titanium oxide (reference code: 01-070-0143), indicated as 'ITO' and Iron(II) dititanium oxide (reference code: 01-089-8065), indicated as 'IDO', also occurred along with anatase and rutile peaks thus confirming the presence of both iron and TiO₂ in recycled composite. The role of these forms of iron oxides has already been discussed before.

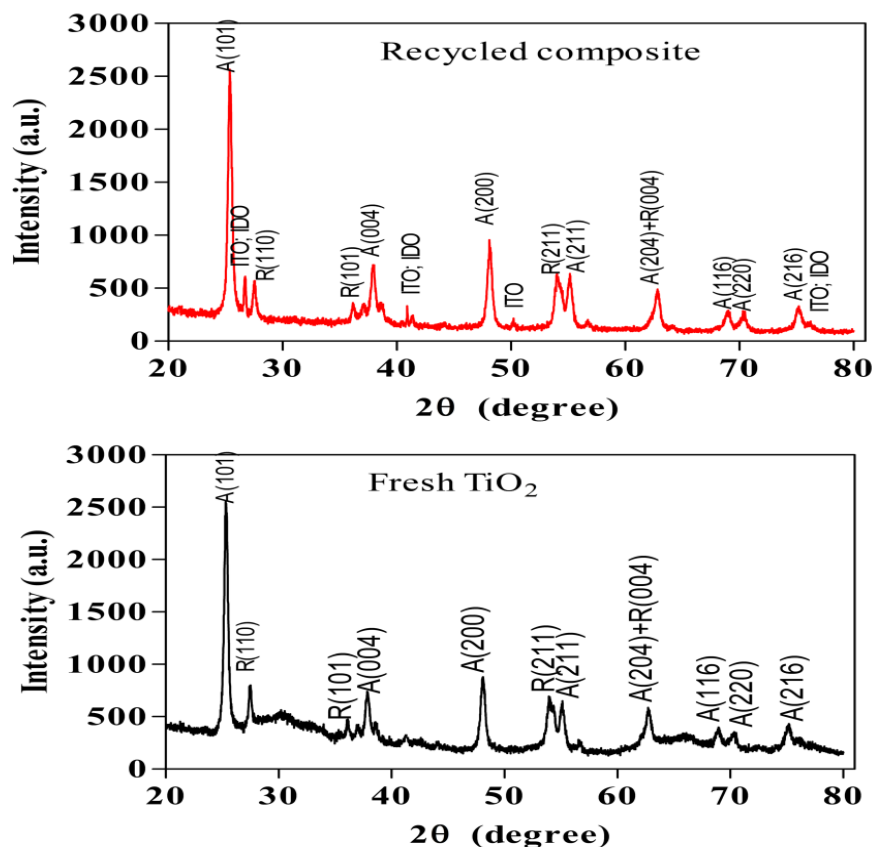


Figure 4.55b: XRD pattern of (a) fresh TiO₂ and (b) recycled Fe-TiO₂ composite (35 recycles).

UV-visible DRS analysis

UV-Vis diffuse reflectance spectra (DRS) of recycled Fe-TiO₂ composite and TiO₂-P25 are presented in figure 4.55c. The samples were analyzed in the range 200-800 nm. The spectra of Fe-TiO₂ composite displayed the capability of absorption of light even in the visible region which clearly reflects the presence of iron in composite. The absorption edge was extended to 440 nm and band gap narrowing was observed in case of composite ($E_g = 2.9$ eV) in comparison to TiO₂-P25 ($E_g = 3.14$ eV).

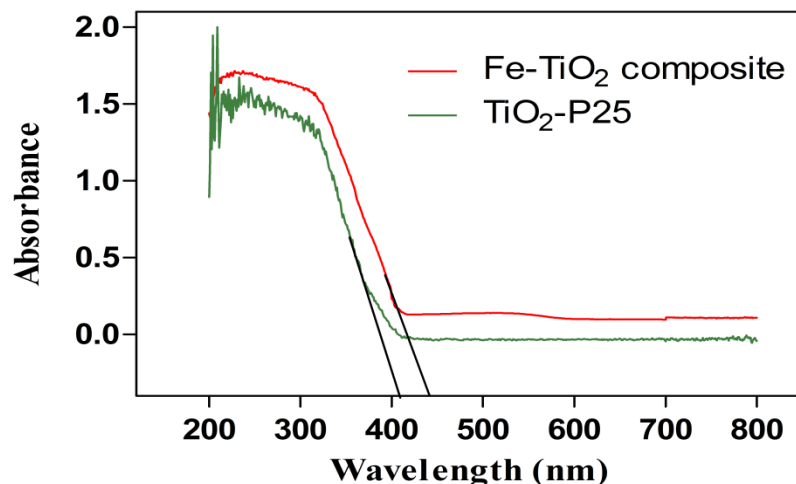


Figure 4.55c: UV-visible DRS of (a) fresh TiO_2 and (b) recycled Fe-TiO_2 composite (35 recycles).

FTIR analysis

The surface characteristics of recycled Fe-TiO_2 composite and $\text{TiO}_2\text{-P25}$ were also identified through FTIR spectroscopic studies. The infrared spectrum of $\text{TiO}_2\text{-P25}$ and composite is depicted in figure 4.55d. The generation of Ti-O-Ti bonds in both the spectrums can be indicated by the Ti-O vibrations as observed by several peaks occurring between 400 and 1200 cm^{-1} wave number thus proving the existence of TiO_2 lattice. The anatase phase in case of $\text{TiO}_2\text{-P25}$ and Fe-TiO_2 composite in the spectrum occurred at 503.73 cm^{-1} and 471.03 cm^{-1} respectively. The results are in accordance with an earlier reported study (Ganesh et al., 2012) which suggested the occurrence of Ti-O-Ti vibrations especially for anatase phase between 400 and 640 cm^{-1} . Stoyanova et al. (2013) reported that bonds occurring in the range 510-590 cm^{-1} could represent vibrations between FeO_6 units. The bond at 513.93 cm^{-1} could possibly represent similar vibrations in the present study in case of composite. The peak at 2078.19 cm^{-1} in Fe-TiO_2 composite spectra corresponds to the generation of Fe-O-Ti bond which further confirms our claim for the presence of iron in composite. Almost similar peak for the presence of Fe-O-Ti bond in Fe/TiO_2 powder has been reported in literature (Serpone et al., 1993). The results are in a good agreement with XRD pattern which confirmed the presence of ‘ITO’ and ‘IDO’. The bonds appearing at 1632.63 cm^{-1} and 1631.16 cm^{-1} in case of $\text{TiO}_2\text{-P25}$ and Fe-TiO_2 composite respectively correspond to the Ti-OH groups. The presence of transmittance band at 3407.91 cm^{-1} in case of $\text{TiO}_2\text{-P25}$ and at 3409.40 cm^{-1} in case of Fe-TiO_2 composite correspond to the O-H

groups stretching vibrations as indicated in various studies (Ganesh et al., 2012; Sayyar et al., 2015).

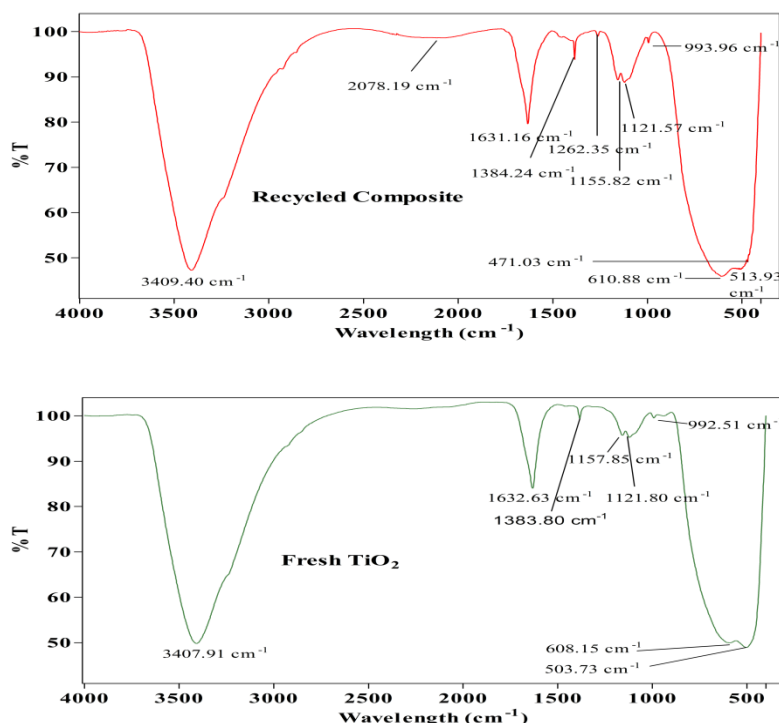


Figure 4.55d: FT-IR spectra of (a) fresh TiO₂ and (b) recycled Fe-TiO₂ composite (35 recycles).

Raman spectroscopy

The Raman spectrums of recycled Fe-TiO₂ composite and TiO₂-P25 are shown in figure 4.55e. The prominent peaks at 140-142 (E_g), 188-192 (E_g), 389-390 (B_{1g}), 509-510 (E_g) and 632-634 (E_g) cm⁻¹ in the spectra of both samples correspond to the anatase phase of TiO₂. The Raman peaks reported in literature for anatase TiO₂ are at 108-188, 198, 205, 320, 387-448, 512-543, 625-670 cm⁻¹ (Ganesh et al., 2012; Singh et al., 2008). The anatase peak at 140-142 cm⁻¹ in both the spectrums is the strongest of all observed peaks thus indicating the predominance of anatase nanoparticles. The results are in accordance with previously reported studies (Balachandran and Eror, 1982). An additional weak broad band (not marked in figure) was also observed in the region from 350-360 cm⁻¹ corresponding to the rutile phase of TiO₂. The similar band for rutile phase has been reported earlier (Balachandran and Eror, 1982; Porto et al., 1967). Small weak and broad bands in the region from 300-350 cm⁻¹ were also observed in the spectra of recycled

composite. These bands do not belong either to anatase or rutile phase of TiO_2 so existence of these bands could be correlated with presence of iron or oxides of iron. No other additional prominent peaks of iron oxides were observed in the Raman spectra thus proving the retention of TiO_2 structure even in recycled composite. The presence of iron in composite did not exhibit any negative effect in the activity of TiO_2 . None of the studies in literature have reported such comprehensive characterization of composites that have been especially used in fixed mode and contributing to in-situ dual effect.

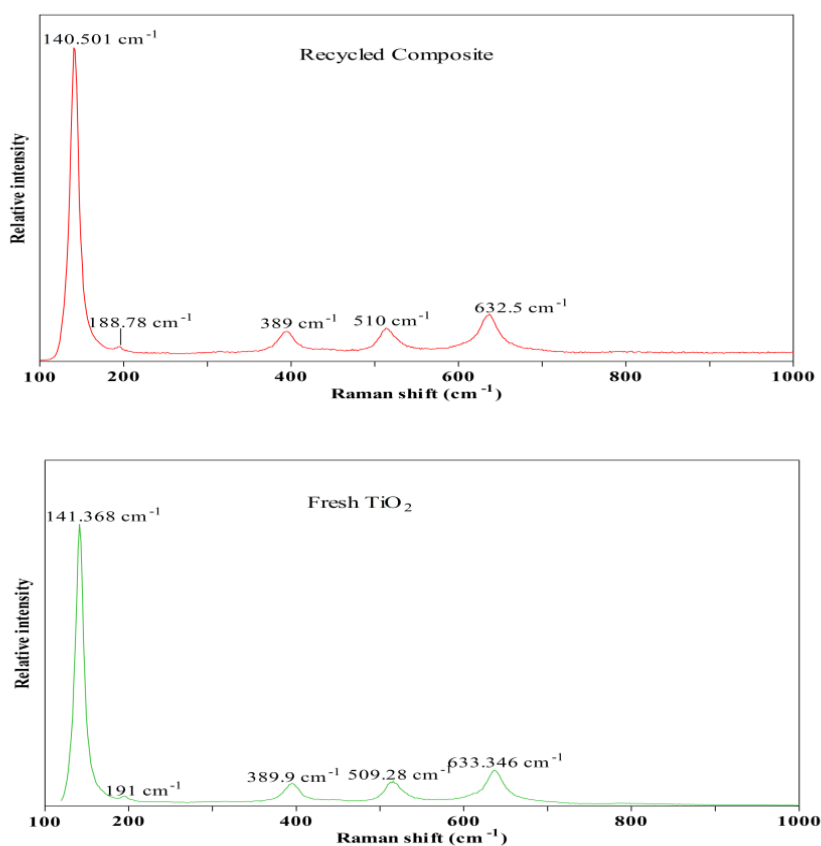
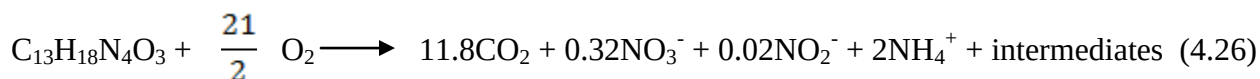
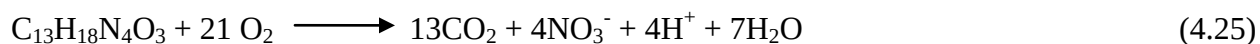


Figure 4.55e: Raman spectra of (a) fresh TiO_2 and (b) recycled Fe- TiO_2 composite (35 recycles).

Thus, presence of iron along with TiO_2 even in recycled composite beads (35 recycles) has been confirmed through several characterization techniques. This further justifies our claim for the extended recyclability efficiency of the composite beads even under flow conditions. From the results, it is clear that composite beads could be successfully used in dual effect studies even after 35 recycles.

4.10.4 Mineralization studies

The mineralization studies of PEN were carried out again to evaluate the effectiveness of in-situ dual process at pilot-scale. The mineralization of PEN was confirmed through reduction in COD and TOC along with the generation of anions like nitrite, nitrate, ammonium ions and evolution of CO₂ as shown in figure 4.56. The nitrogen atoms in PEN were found to be converted into nitrite, nitrate and ammonium ions. Similar types of results were presented by Grover et al. (2014) where nitrogen atoms of imidacloprid were dissipated into nitrite and nitrate ions. In the present work, the concentration of nitrate ions followed a decreasing trend after 1 h of reaction whereas nitrite and ammonium ions followed an increasing trend in their concentration with the probability of conversion of nitrate into nitrite and ammonium ions (Kudo et al., 1992). There was almost 94% and 91% reduction in COD and TOC respectively after 4 h of treatment. The stoichiometrically balanced chemical equation for complete mineralization of PEN is indicated in equation 4.25. The chemical equation 4.26 obtained through quantification of nitrite, nitrate, ammonium ions and CO₂ evolution deviates from equation 4.25 thus indicating partial mineralization of PEN. The calculations for CO₂ mass balance have been provided in Appendix (text A2). The partial mineralization of PEN might be due to the formation of several intermediate products during the degradation of PEN. The intermediates formed during the degradation of PEN in a pilot-scale reactor incorporating in-situ dual effect were identified through GC-MS analysis. Few additional intermediates were detected during the degradation process at pilot-scale in comparison to that of lab-scale as discussed in section 4.7.11. Thus, degradation pathway was proposed again based on these intermediates as depicted in figure 4.57.



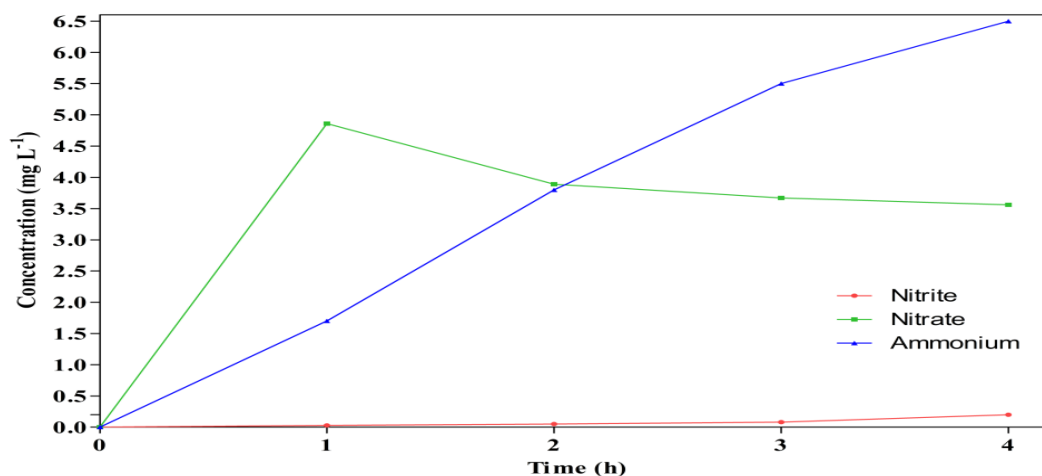


Figure 4.56: Generation of nitrite, nitrate and ammonium ions during the photodegradation of PEN.

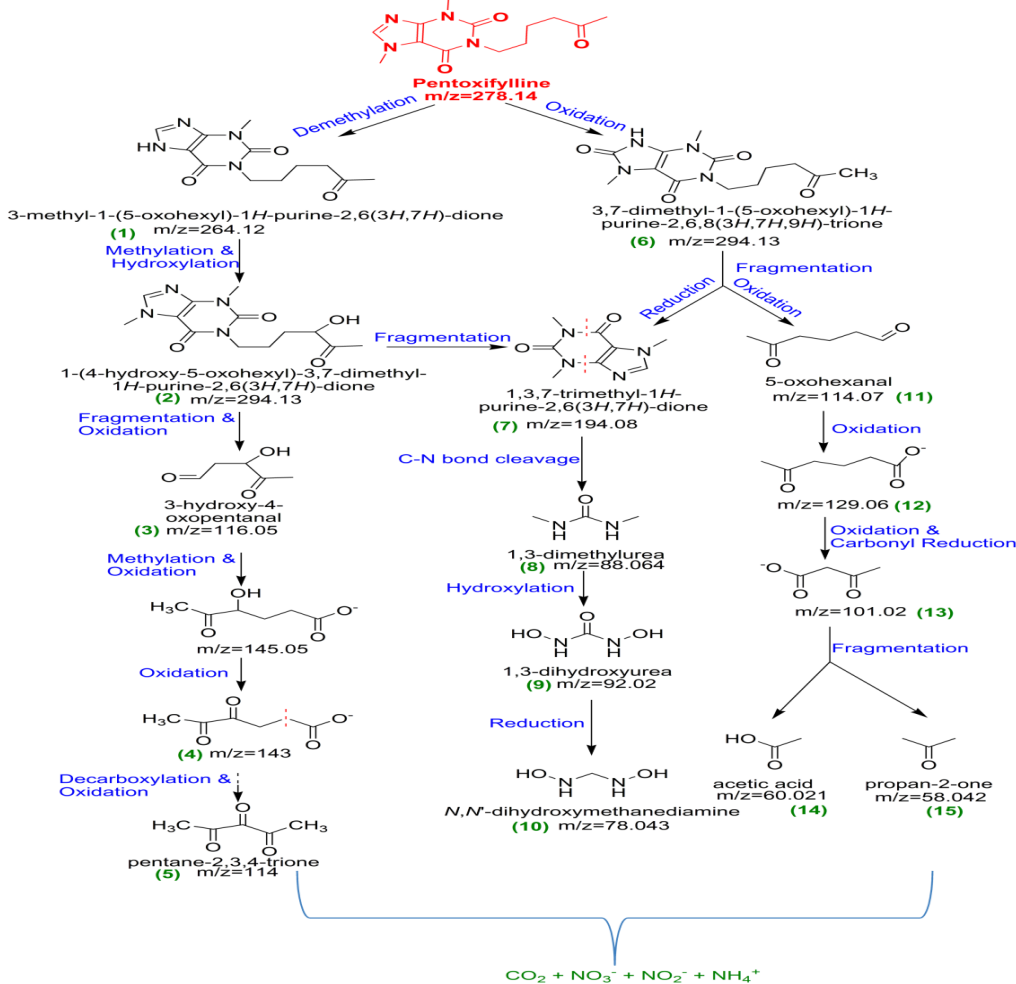


Figure 4.57: Tentative pathway for the degradation of PEN in a pilot-scale fixed-bed glass reactor incorporating in-situ dual effect.

4.10.5 Evaluation of cost of treatment process

Cost has always been a major topic of discussion when new and innovative technologies are taken into consideration. For successful commercialization of a process, new technology must provide significant reduction in overall treatment costs over competent techniques. In case of photocatalytic treatment unit installation, the overall cost must comprise of design, fabrication, light source, start-up of process, electricity cost, cost of catalyst used with an assumption that land is available free of cost. Most of the studies in literature have reported either the cost of only energy consumption (Haranaka-Funai et al., 2017) or operating cost (Alalm et al., 2015) excluding the fabrication and design cost of reactor. The overall cost of the treatment process has been evaluated in the present study taking into consideration the complete cost of Fe-TiO₂ composite, oxidant used, light source, operating cost of process including electricity cost and fabrication cost of the reactor as discussed in table 4.19.

Table 4.19: Evaluation of cost of treatment process

<i>(A) Preparation of Fe-TiO₂ composite</i>
Cost of raw materials (clay, FA, FS) = 0.0 \$
Electricity consumption during firing of support at high temperature = 0.75 kWh
Electricity price in India = 0.0699 \$/kWh
Cost of electricity consumption = $0.0699 \times 0.75 = 0.0524$ \$/kWh
Cost of TiO ₂ used (16 g) = 0.048 \$
Total cost of Fe-TiO₂ composite = $0.0524 + 0.048 = 0.1004$ \$
<i>(B) Oxidant (H₂O₂)</i>
Cost of total oxidant (750 mL) used (for 50 runs) = 10.374 \$
<i>(C) Operating cost of treatment process</i>
Cost of light source (sunlight) = 0.0 \$
Number of runs = 50
Total volume of water treated = $5\text{L} \times 50 = 250\text{ L}$ (0.25 m^3)
Cost per $\text{m}^3 = (A+B)/0.25 = 41.89$ \$/m ³
With 93% degradation ($C_o = 50\text{ mgL}^{-1}$), concentration of PEN removed = 46.5 mgL^{-1} (0.0465 kgm^{-3})
Cost per kg of concentration removal = $(A+B)/0.0465 = 225.25$ \$/kg of concentration removal
Energy consumption during operation of process (pumping of solution treatment) = $18 \times 4 \times 50 = 3600\text{ Wh}$
Energy consumed per kg of concentration removal = $3600/0.0465 = 7.741$ kWh per kg of concentration removal
Cost for energy consumption = $0.0699 \times 7.741 = 0.541$ \$/kWh
Overall operating cost = $225.25 + 0.541 = 225.79$ \$
<i>(D) Fabrication of reactor</i>
Total cost including pump, baffles, pipe = 15.548 \$

Total cost of treatment process = $C + D = 241.33$ \$
Total cost of above treatment process comes out to be 241.33 \$ for 50 runs
Cost of treatment process for single run (5 L) would be 4.826 \$. This cost could be further minimized by effective designing of solar collectors for large-scale applications.

The overall cost of the treatment process has been evaluated for 50 runs. In view of the catalyst recyclability studies which clearly prove the stability and efficacy of catalyst even after 50 runs, the overall cost of process can be further reduced when applied for additional cycles. As a result, the studied pilot-scale reactor using highly efficient low cost catalyst can present an economic solution to various field-scale applications.

4.11 Once-through fixed-bed cascade reactor (Plug-flow approach)

In the recent studies, development of continuous photocatalytic systems either continuous stirred type reactor (CSTR) or plug-flow reactor (PFR) has been discussed in view of its field-scale applications related to wastewater treatment (Vaiano et al., 2015; Miyawaki et al., 2016). However, PFR, where there is no axial mixing of reaction mixture, is always desired as a continuous flow system owing to its high productivity and selectivity (Prokopová and Prokop, 2009). But the concept of PFR visualization in case of photocatalytic systems has not been investigated widely. Thus, attempts have been made in the present study to approach PFR in a continuous photocatalytic system incorporating in-situ dual effect for the degradation of CEX. To the best of our knowledge, this is the first ever reported study till date in which pilot-scale once-through cascade reactor system incorporating in-situ dual effect has been visualized to approach a PFR.

4.11.1 Prominence of dual effect in a cascade reactor

As in all earlier cases, here also, the prominence of dual effect was established at pilot-scale using a cascade reactor. For this, the cascade reactor system (comprising of 3 packed-bed reactors in series) was operated in re-circulation mode with a total working volume of 5 L at a fixed flow rate. All experiments were performed under solar irradiations at acidic pH (pH = 3.5) with addition of fixed amount of H_2O_2 i.e. 300 mgL^{-1} . Under these conditions, photocatalytic experiments using control beads (TiO_2 immobilized clay beads (without FS/FA)) led to almost 56% degradation of CEX after 5 h of solar irradiations. Where as, photo-Fenton experiments

using blank composite beads (without TiO₂ coating) yielded an almost 41% degradation of CEX after 5 h of treatment.

Interestingly, the treatment time for the degradation of CEX through in-situ dual process using Fe-TiO₂ composite beads was drastically reduced as it took almost 3 h to achieve 55% degradation of CEX as compared to 5 h in case of photocatalysis. Furthermore, it took almost 1.5 h to attain 40% degradation of CEX as compared to 5 h in case of photo-Fenton. Thus, the precedence of in-situ dual effect among individual processes (photocatalysis or photo-Fenton) was confirmed using Fe-TiO₂ composite beads. Actually iron species were leaching from the composite beads by-default which facilitated the occurrence of photo-Fenton reaction along with photocatalysis. Moreover, rate constant, 'k' was significantly higher ($P < 0.05$) in case of dual process (0.004 min^{-1}) as compared to photocatalysis (0.0026 min^{-1}) and photo-Fenton (0.001 min^{-1}). Therefore, 35% and 75% synergy of in-situ dual process was observed over photocatalysis and photo-Fenton respectively. However, overall synergy of dual process over individual processes was observed to be 10%.

All the preliminary experiments (photolysis, adsorption or oxidant addition) were carried out to evaluate the effect of individual parameters on the degradation of model compound i.e. CEX (Figure 4.58). Each experiment revealed negligible removal of CEX (3-8%) due to the inadequate production of OH radicals.

Thus, the performance of pilot-scale cascade reactor system was intensified by executing the in-situ dual process and operating the reactor in once-through mode to seek its practical feasibility.

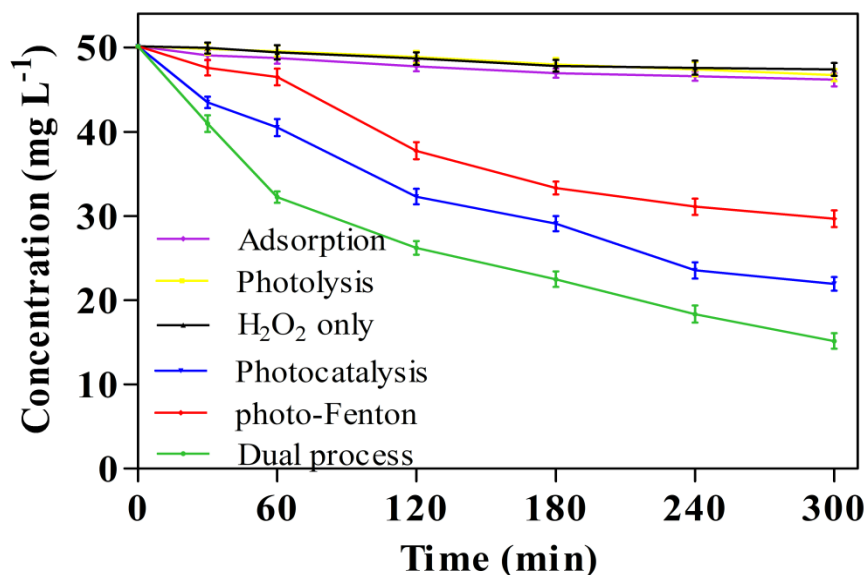


Figure 4.58: Concentration profile of CEX during its treatment through different processes ($C_0=50 \text{ mgL}^{-1}$, Number of reactors = 3, $V = 5 \text{ L}$).

Synergistic effect of oxidant addition

Generally, the optimum use of oxidant addition is always recommended due to the predominance of scavenging effect of hydroxyl radicals at higher dose of oxidant besides its expensive nature (Chan et al., 2003). In the present study, owing to the occurrence of in-situ dual process, H_2O_2 was not utilized solely in photocatalysis but also in photo-Fenton and iron oxide catalysis for the generation of hydroxyl radicals. Thus, studying the effect of H_2O_2 dose for the degradation of CEX via in-situ dual process becomes extremely significant as its addition affects the efficiency of all processes occurring simultaneously. In this context, experiments for the degradation of CEX were carried out using Fe-TiO₂ composite at acidic conditions ($\text{pH} = 3.5$) in a once through cascade reactor (3 reactors in series) under natural solar irradiations at a flow rate of 0.1 Lmin^{-1} with varying doses of H_2O_2 . At this particular flow rate, space time in each reactor was nearly 6 min as calculated from equation 3.1 (discussed in Section 3.10).

In the current research work, the amount of H_2O_2 was varied from 300-1500 mgL^{-1} for the degradation of CEX. Figure 4.59 shows the concentration profile of CEX in each reactor at different doses of H_2O_2 . The degradation of CEX increased with an increase in the concentration of H_2O_2 up to 600 mgL^{-1} . Thereafter, degradation of CEX either became constant or started

decreasing owing to the existence of scavenging effect at high dose of H_2O_2 (Ioannou et al., 2011; Velegraki et al., 2015). Thus, 600 mgL^{-1} of H_2O_2 was chosen as an optimum dose in the present study at which maximum reduction in the concentration of CEX ($\sim 24\%$) was achieved at the exit of 3rd reactor. It took almost 50 min to pass the total volume of CEX solution (5 L) by this reactor system in once through mode. Further efforts would be made in subsequent sections to increase the degradation of CEX using this optimized dose of H_2O_2 in minimum possible time.

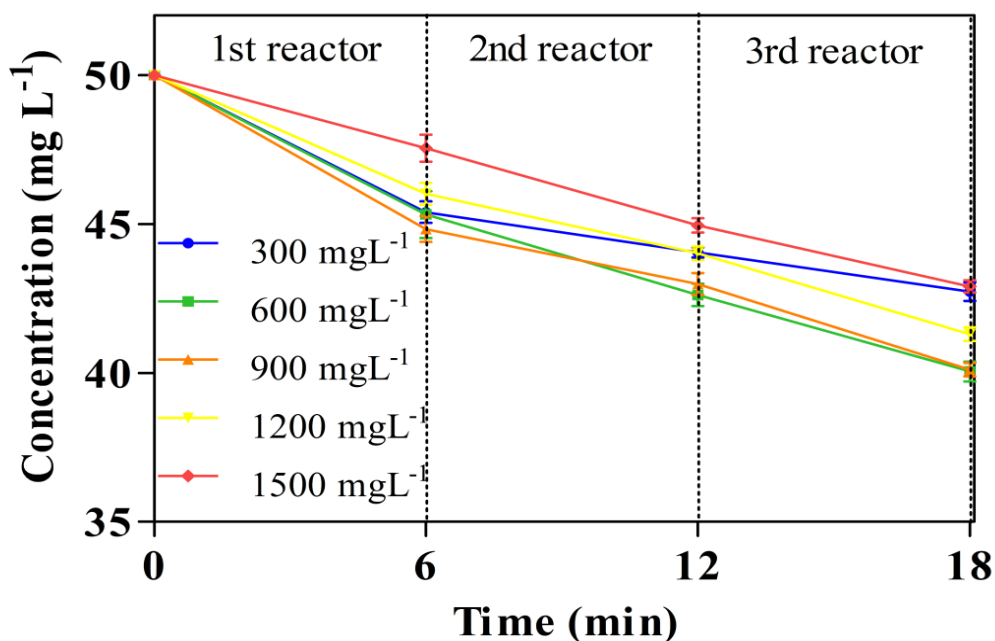


Figure 4.59: Effect of H_2O_2 dose on the concentration profile of CEX during its treatment through in-situ dual process ($C_0=50 \text{ mgL}^{-1}$, Number of reactors = 3, $V = 5 \text{ L}$).

Effect of number of reactors

The effect of number of reactors on the degradation efficiency of CEX via once through dual process was evaluated by varying the number of reactors from one to six in a cascade reactor system with total volume handling of 5 L. All experiments were conducted at optimized dose of H_2O_2 i.e. 600 mgL^{-1} under natural solar irradiations at a flow rate of 0.1 Lmin^{-1} . It is evident from figure 4.60 that maximum amount of reduction in the concentration of CEX ($\sim 13\%$) occurred at the end of first reactor with a space time of 6 min. With further increase in the number of reactors from two to six, conversion of CEX was lower ($\sim 5\text{-}6\%$) in each successive reactor as compared to the 1st reactor. It might be due to the fragmentation of parent compound

during its treatment in the first reactor resulting into the formation of some relatively stable intermediates which took comparatively more time to decompose. However, degradation of CEX was incremented to almost 44% at the end of sixth reactor with a space time of nearly 6 min for each reactor. It took almost 50 min to treat the total volume i.e. 5 L of CEX using once-through process.

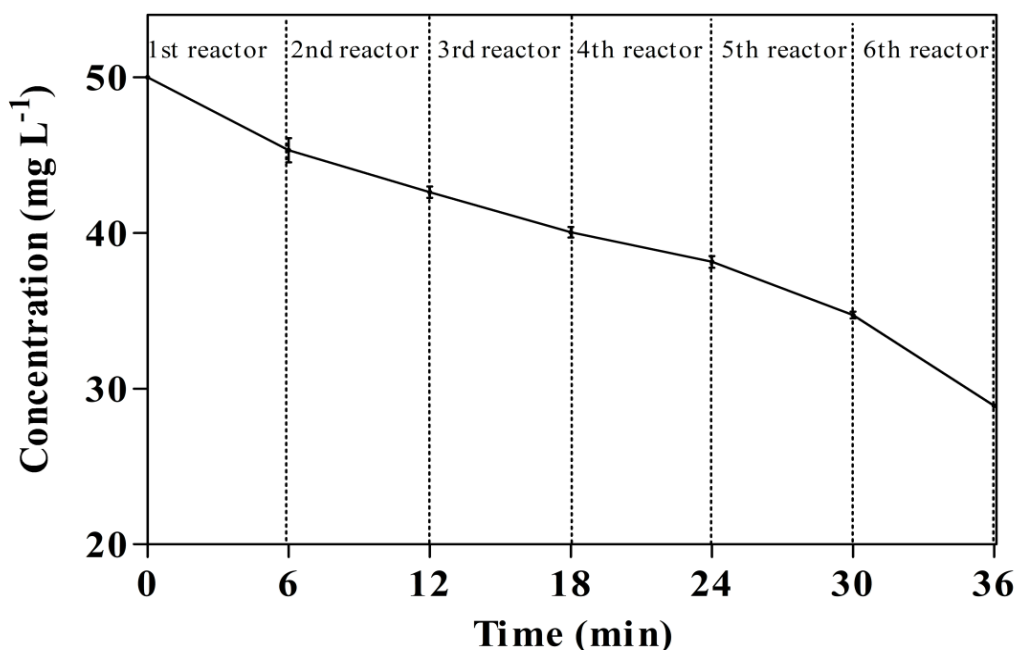


Figure 4.60: Effect of number of reactors on the concentration profile of CEX during its treatment through in-situ dual process ($C_0=50 \text{ mgL}^{-1}$, $\text{H}_2\text{O}_2 = 600 \text{ mgL}^{-1}$, $V = 5 \text{ L}$).

The optimum number of reactors is basically determined on the basis of maintenance and control of the reactor system which further depends upon the configuration of reactors, conversion factor and nature of pollutant (Miyawaki et al., 2016). Motegh et al. (2014) theoretically investigated the degradation of cyanide in bubble column slurry reactors connected in series and concluded that eight numbers of reactors would be the best for attaining 99% conversion. Visualizing practical approach in these types of reactors is not feasible as there may be huge energy losses owing to slurry photocatalysis. In the present study although additional number of reactors (> 6) would further increase the degradation efficiency of CEX, this would make the maintenance and control of system difficult. In this context, number of reactors was not increased further as per the available conditions while efforts were made to increase the

degradation efficiency of CEX by optimizing further operating parameters taking six as optimum number of reactors.

Effect of flow rate

The flow rate of aqueous solution affects the dissolved oxygen as well as turbulence in the system which plays a significant role in photocatalytic reactions. Moreover, flow rate of the aqueous solution decides the space time of pollutant (Equation 3.1). Thus, lower flow rate with high retention time is always desirable for maximum degradation efficiency. In the present study, experiments were performed with varying flow rate of CEX solution ranging from 0.025 Lmin^{-1} – 0.4 Lmin^{-1} at optimized dose of H_2O_2 i.e. 600 mgL^{-1} under natural solar irradiations in a cascade reactor (6 reactors in series). It is clear from figure 4.61 that amount of reduction in the concentration of CEX was lowered down with an increase in the flow rate of solution. The most probable reason for the decreased degradation efficiency of CEX is the reduction in retention time of pollutant at higher flow rates as the pollutant leaves without making proper contact with the catalyst. Although degradation of CEX was better at lower flow rates, overall treatment time was also significantly increased which is commercially not desirable. In this regard, 0.05 Lmin^{-1} with retention time of nearly 12 min in each reactor was selected as an optimum flow rate for the degradation of CEX in a cascade reactor system.

The degradation of CEX was more or less same at 0.025 Lmin^{-1} . However, overall treatment time of CEX (5L) was almost twice ($\sim 200 \text{ min}$) in this case as compared to 100 min in case of 0.05 Lmin^{-1} . Although optimized flow rate i.e. 0.05 Lmin^{-1} is less from its commercial point of view, it is still 10 times higher than the reported value i.e. 0.006 Lmin^{-1} in literature (Miyawaki et al., 2016) in context to 2,4-dinitrophenol removal from water. Actually, low flow rate (0.05 Lmin^{-1}) was optimized in the present case according to the available reactor volume which was quite low in comparison to the large-scale reactors. The process can be intensified further with even high flow rates for the large-scale reactors having high reaction volume which are capable of incorporating in-situ dual effect.

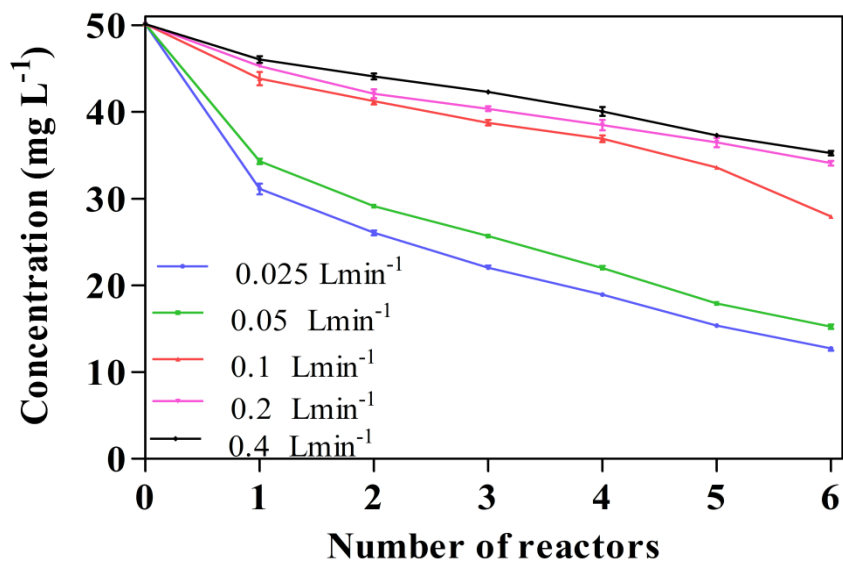


Figure 4.61: Effect of flow rate on the concentration profile of CEX during its treatment through in-situ dual process ($C_0=50 \text{ mgL}^{-1}$, $\text{H}_2\text{O}_2 = 600 \text{ mgL}^{-1}$, number of reactors = 6, $V = 5 \text{ L}$).

The prominence of in-situ dual effect was confirmed again at all optimized conditions by carrying out the degradation of CEX separately through photocatalysis and photo-Fenton in a cascade reactor system in continuous mode. An almost 54% and 28% degradation of CEX was achieved at the end of sixth reactor in case of photocatalysis and photo-Fenton respectively. The degradation was significantly higher ($P < 0.05$) in case of in-situ dual process i.e. 70% in contrast to these individual processes. Moreover in case of dual process, nearly 55% degradation of CEX was attained at the end of fourth reactor as compared to sixth reactor in case of photocatalysis. The precedence of in-situ dual effect can also be visualized in terms of the generation of hydroxyl radicals. Figure 4.62 clearly depicts that the generation of hydroxyl radicals was significantly higher in case of dual process as compared to the individual processes. The leaching of iron from the composite during the treatment process was also confirmed by estimating the concentration of total iron in each reactor as depicted in table 4.20.

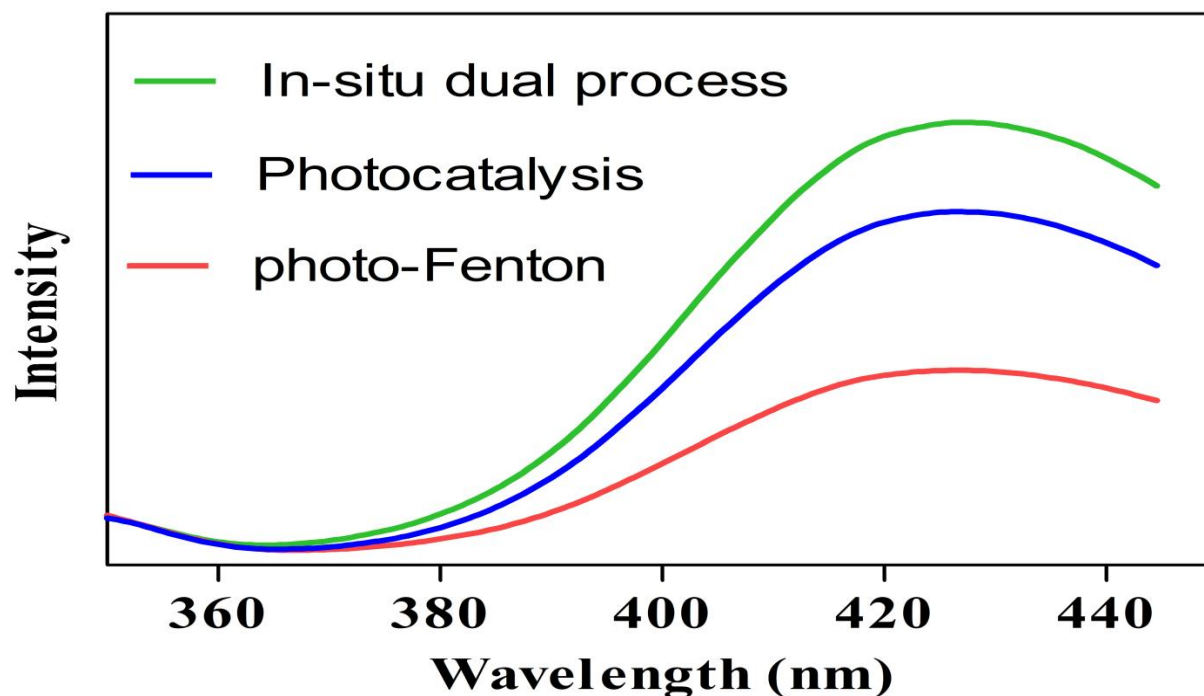


Figure 4.62: Generation of hydroxyl radicals through different processes in a cascade reactor system at optimized conditions.

Table 4.20: Concentration of leached iron species from Fe-TiO₂ composite beads during the treatment of CEX.

Reactors	Concentration (mgL ⁻¹)		
	Total iron	Ferrous iron	Ferric iron
1	0.11	0.069	0.041
2	0.25	0.11	0.14
3	0.36	0.19	0.17
4	0.32	0.069	0.25
5	0.39	0.12	0.27
6	0.3	0.086	0.21

An almost 70% degradation of CEX occurred at the exit of sixth reactor in a fixed-bed pilot-scale cascade reactor system incorporating in-situ dual effect at all optimized conditions after 100 min of treatment time. The concentration profile of CEX at the exit of each reactor connected in series at optimized conditions has been shown in figure 4.63. The treatment time was significantly lower in contrast to the reported studies for the degradation of CEX. Almasi et al. (2017) investigated the degradation of CEX via sono-photocatalytic treatment in slurry mode

in a photo-reactor with total volume handling of 1 L and observed a maximum of 78.6% degradation after 120 min. Ajoudanian and Nezamzadeh-Ejhieh (2015) reported 76% degradation of CEX at lab-scale after 300 min of treatment time with volume handling of 20 mL via heterogeneous catalysis using suspensions of NiO supported on clinoptilolite nanoparticles.

Therefore, in contrast to these reported studies, the current investigation has presented a unique and viable solution for the treatment of recalcitrant pollutants like CEX at pilot-scale (5 L) in minimized time by incorporating the novel concept of in-situ dual effect using Fe-TiO₂ composite in completely fixed-form. The viability of the process was further confirmed when significant amount of degradation (75%) was attained in case of PEN as well under the same optimized conditions.

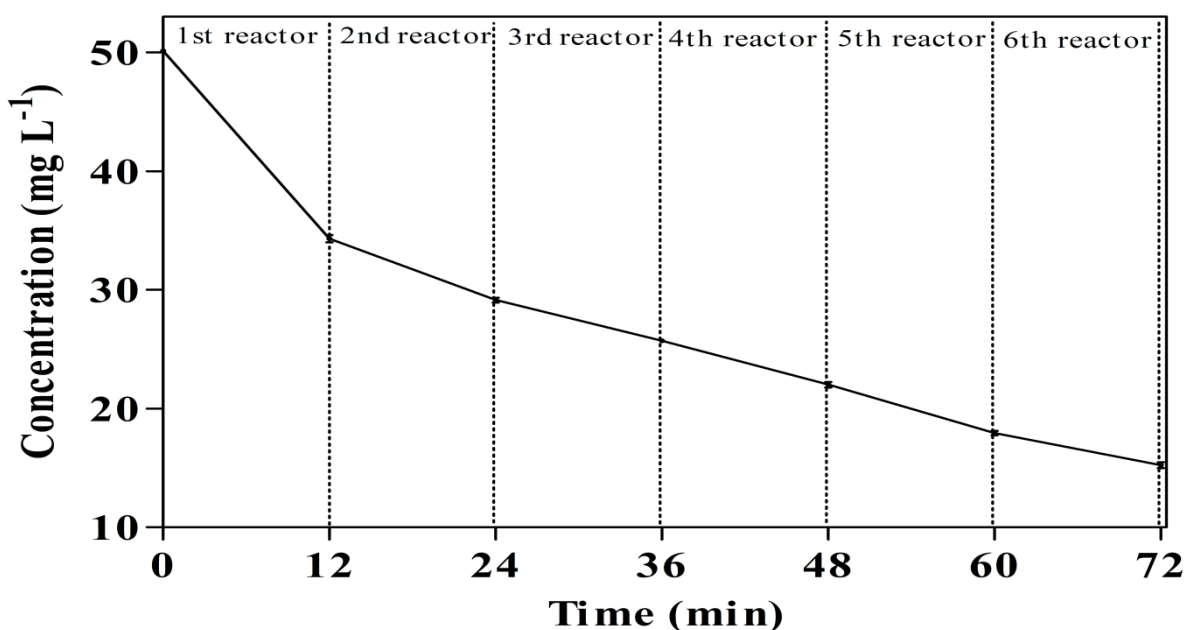


Figure 4.63: Concentration profile of CEX at the exit of each reactor in a cascade reactor system at all optimized conditions.

4.11.2 UV spectral analysis

Figure 4.64 depicts the reactor dependent change in absorption spectra for the degradation of CEX through in-situ dual process in a fixed-bed cascade reactor at all optimized conditions. The absorption spectrum was attained by carrying out the scan in the range 200-450 nm. The spectrum of CEX exhibits the main prominent band in the UV region with maximum at 263 nm. The continuous decrease in the intensity of absorption peaks of CEX at $\lambda_{\text{max}} = 263$ nm at

the exit of each reactor indicated the gradual decomposition of CEX. Maximum degradation of CEX was observed at the end of sixth reactor.

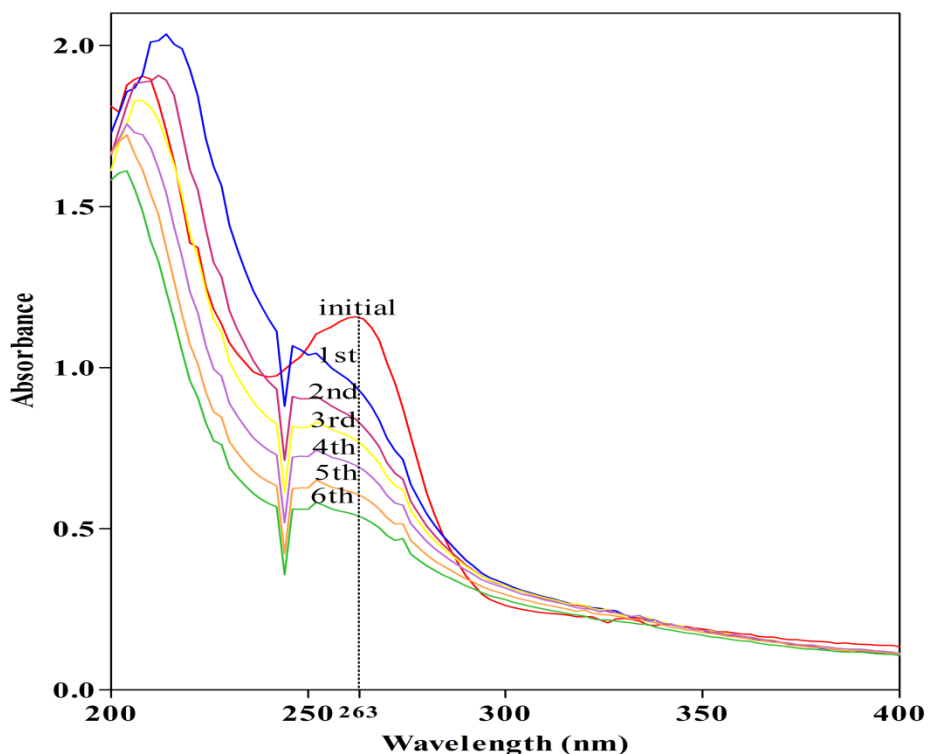


Figure 4.64: UV-spectral analysis for the degradation of CEX in a cascade reactor system at optimized conditions ($C_0=50 \text{ mgL}^{-1}$, $\text{H}_2\text{O}_2 = 600 \text{ mgL}^{-1}$, number of reactors = 6, flow rate = 0.05 Lmin^{-1} , $V = 5 \text{ L}$).

4.11.3 Plug-Flow approach

The reaction efficiency of plug-flow reactor systems is always high compared to that of continuous stirred tank reactors (CSTRs). But in case of plug-flow reactors with immobilized catalyst, film diffusion resistance or mass transfer implications predominates which substantially reduces the reaction efficiency of system. However theoretically, these systems are predicted to yield high efficiency in the absence of above stated implications. As a result, for the present study, conversion efficiency in the plug-flow reactor has been set as a target value for multiple fixed-bed reactors in series.

The design equation of a plug-flow reactor can be expressed as follows:

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{-r_A} \quad (4.27)$$

Or

$$\frac{V}{v_0} = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A} \quad (4.28)$$

Or

$$\frac{V}{v_0} = \frac{1}{k} \int_0^{X_A} \frac{dX_A}{1-X_A} \quad (4.29)$$

Where, $-r_A = kC_A$, and

$$X_A = 1 - \frac{C_A}{C_{A0}}$$

V = volume of reaction mixture (L), F_{A0} = molar flow rate (moles min^{-1}), v_0 = volumetric flow rate (L min^{-1}), C_A = final concentration (mg L^{-1}), C_{A0} = initial concentration (mg L^{-1}), X_A = conversion, r_A = reaction rate ($\text{mg L}^{-1} \text{ min}^{-1}$), k = rate constant (min^{-1})

The main emphasis of the present research work was to bring the reaction performance of fixed-bed cascade reactor system (incorporating in-situ dual effect) in PFR range. Though there are few studies in literature that had approached the concept of plug-flow in their photocatalytic reactor system, commercial viability of these reported systems was questionable due to high treatment time (Miyawaki et al., 2016). Moreover, recyclability and stability of the catalyst for subsequent cycles in these types of systems were either very low or had not been discussed. Other implications that are usually encountered in these systems include mass-transfer implications or film diffusion resistance or low exposed surface area of the immobilized catalyst.

Thus, the present study aimed at achieving approximately the same conversion efficiency as that of plug-flow systems after overcoming most of the aforementioned limitations (Figure 4.65). The ‘waterfall’ effect observed in the present cascade reactor system reduced the film diffusion resistance where as the spherical shaped support for catalyst immobilization provided the maximum overall exposed surface area of TiO_2 . The mass transfer implications were further reduced by the occurrence of photo-Fenton along with photocatalysis in the present reactor system thereby reducing the treatment time and enhancing the overall reaction efficiency of system. In addition to this, excellent recyclability efficiency (> 70 cycles) of immobilized catalyst (Section 4.11.4) in comparison to reported studies really highlights the commercial

viability of the present reactor system. In the present study, the number of fixed-bed reactors (with Fe-TiO₂ composite) connected in series was increased till the conversion efficiency approached to that of plug-flow reactor.

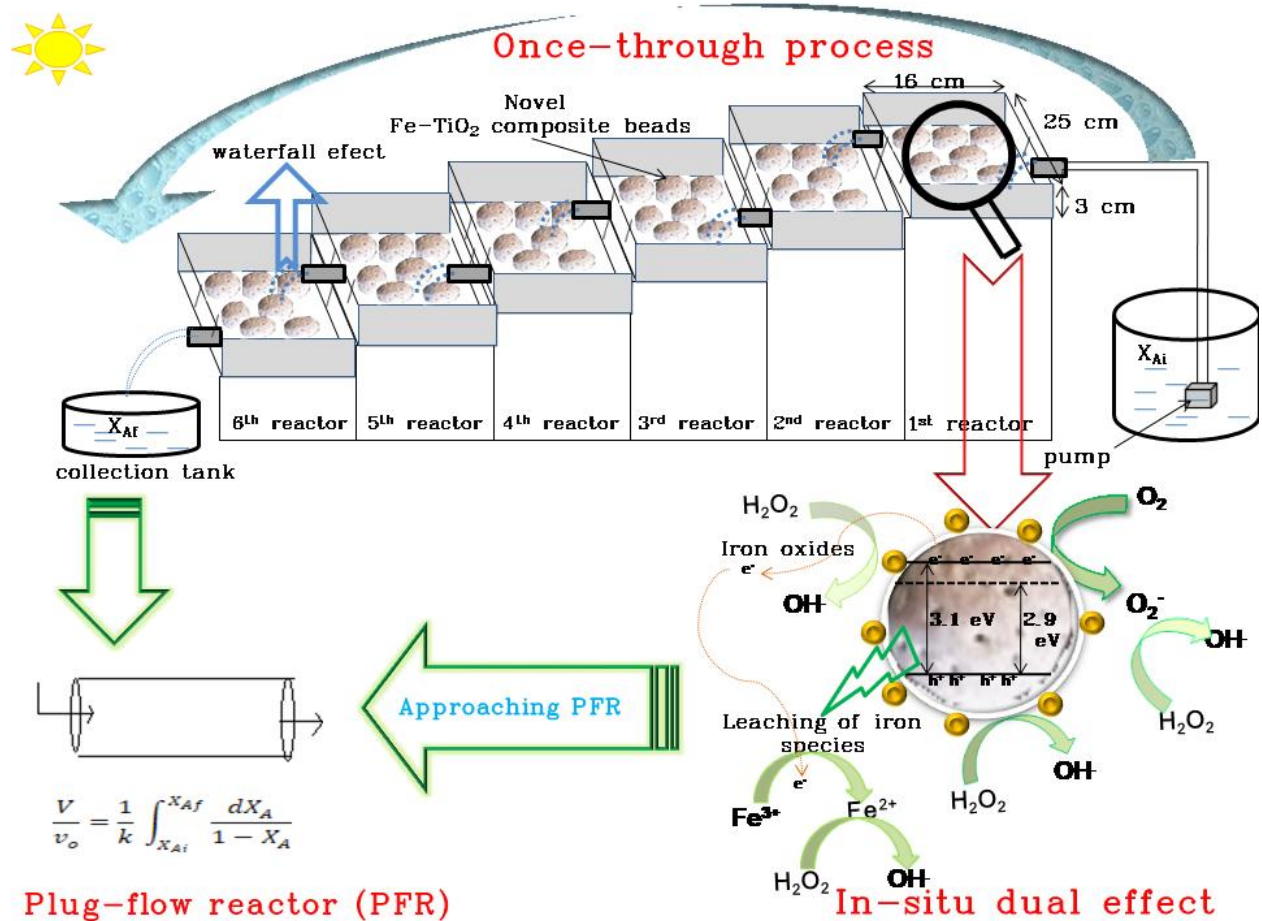


Figure 4.65: Once-through reactor incorporating in-situ dual process to approach the performance efficiency equal to PFR.

The theoretical conversion efficiency of CEX in a plug-flow reactor using the equations (1-3) was obtained as 73.4% with exit concentration of CEX as 13.3 mgL⁻¹. While, experimental value of CEX concentration calculated at the end of sixth reactor in a cascade reactor system using Fe-TiO₂ composite was 14.8 mgL⁻¹ which is close to the theoretical value (~10% deviation) obtained in case of plug-flow reactor. Thus, it leads to a fact that when six fixed-bed reactors (with Fe-TiO₂ composite) incorporating in-situ dual effect are connected in series, it is feasible to operate the reactor system with performance roughly similar to that of plug-flow reactor.

Therefore, agreement of experimental results with theoretical prediction of plug-flow approach clearly indicated that studied cascade reactor system incorporating in-situ dual effect can be successfully used to attain a higher conversion of pollutant in comparatively lesser space time. Furthermore, the concept of in-situ dual effect using highly durable and economical Fe-TiO₂ composite in a cascade fixed-bed reactor system (six reactors in series) can be implemented at field-scale with certain modifications. To the best of our knowledge, this is the first reported study in which a pilot-scale fixed-bed reactor system incorporating in-situ dual effect has been visualized to approach a plug-flow reactor.

4.11.4 Extended durability studies

One of the novel findings of this study is the extended durability of reported Fe-TiO₂ composite beads in terms of exhibiting in-situ dual effect. Thus to confirm our claim, the parametric optimization studies were performed with Fe-TiO₂ composite beads previously used for at-least 45 recycles. In the recycling tests, our reported approach needs to confirm both sustainable leaching of iron as well as stability of TiO₂ coating over the composite. The recyclability efficiency of Fe-TiO₂ composite beads was evaluated in terms of the degradation efficiency of CEX with subsequent recycles.

To counter-check the efficiency of used composite beads, experiments were executed simultaneously with freshly prepared Fe-TiO₂ composite beads as well. There was 7-8% reduction in the degradation efficiency of CEX during the initial few recycling tests (5-6 cycles) owing to the weathering off loosely bound catalyst particles from the surface of composite beads. Thereafter, degradation efficiency was observed to be more or less same. Fe-TiO₂ composite were successfully recycled for 70 runs without any major reduction in the degradation efficiency of CEX as shown in figure 4.66. This confirms that sufficient quantity of catalyst particles were intact to the surface even in the recycled composite beads. None of the studies related to fixed-bed photocatalysis in literature have ever reported such high recyclability efficiency of catalyst. The recycled Fe-TiO₂ composite in the present study was characterized through various techniques (Section 4.11.5) which further confirmed the presence of Fe along with TiO₂ even after 70 recycles.

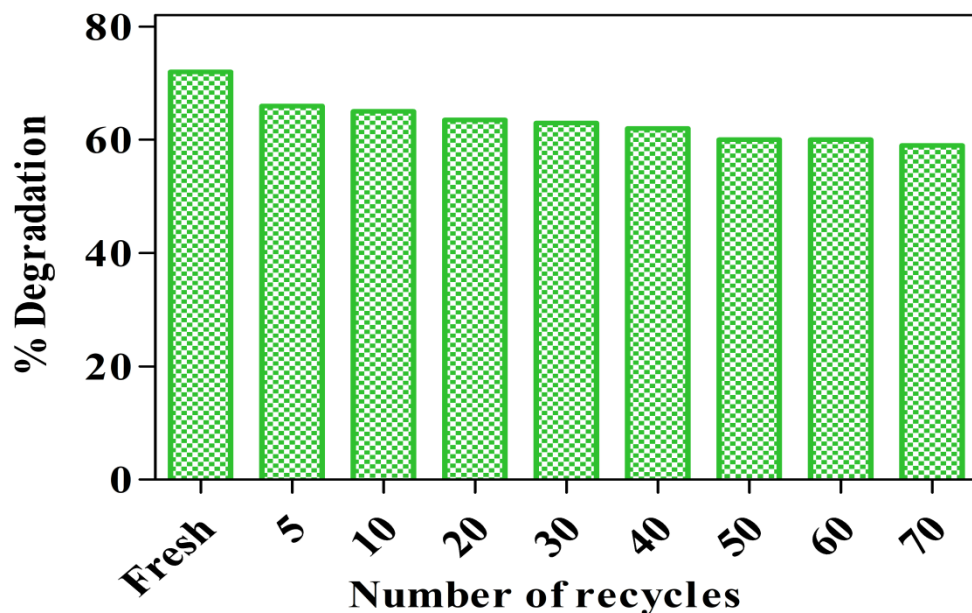


Figure 4.66: Recyclability studies of Fe-TiO₂ composite beads for the degradation of CEX.

4.11.5 Characterization of immobilized catalyst

The intactness of catalyst particles (TiO₂ and iron) in recycled composite beads (70 recycles) as compared to fresh composite beads was checked through several characterization techniques as discussed below:

SEM/EDS

Figure 4.67a demonstrates the SEM and EDS images of freshly prepared and recycled (70 cycles) Fe-TiO₂ composite. The surface morphology of fresh and recycled composite is almost same indicating a uniform coating of TiO₂ over the surface which remained intact even after 70 recycles as depicted in figure. The sharp and prominent peaks of 'Fe', 'O' and 'Ti' in EDS spectra of both fresh and recycled composite justified the presence of both iron and TiO₂ even in recycled composite. It leads to a fact that Fe-TiO₂ composite with high recyclability efficiency can be successfully used in dual effect studies.

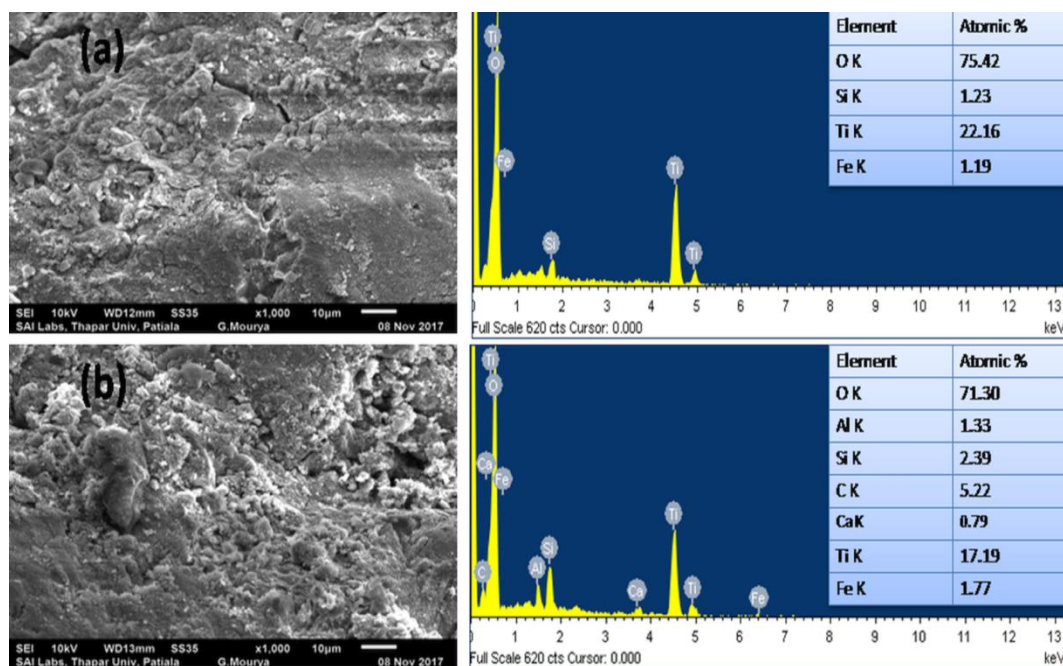


Figure 4.67a: SEM/EDS analysis of Fe-TiO₂ composite beads (a) Fresh composite beads and (ii) after 70 recycles.

XRD analysis

The retention of activity of immobilized TiO₂ over composite beads after recycling tests (70 cycles) was confirmed through XRD analysis. The diffraction patterns of recycled immobilized TiO₂ as well as fresh TiO₂ are depicted in figure 4.67b. Both phases of TiO₂ i.e. anatase (A) and rutile (R) were retained even after recycling the composite for 70 cycles. The reference codes for anatase and rutile phase obtained through XRD data were 01-084-1286 and 01-089-0552 respectively. Along with anatase and rutile peaks of TiO₂, some other peaks corresponding to several forms of iron oxide also existed in the diffraction pattern. These additional peaks were correlated with iron (III) oxide indicated as 'IO' (01-073-0603), iron diiron (III) oxide marked as 'IDO' (01-079-0416), iron titanium oxide marked as 'ITO' (01-070-0143) and diiron (III) titanium oxide symbolized as 'DTO' (01-089-8066). The presence of iron oxides along with TiO₂ onto the surface of composite enhances the efficiency of in-situ dual process. As already been discussed, the photo-excited electron during the photocatalytic process is entrapped by iron oxide and helps in the regeneration of ferrous ions which further facilitates the simultaneously ongoing photo-Fenton reaction.

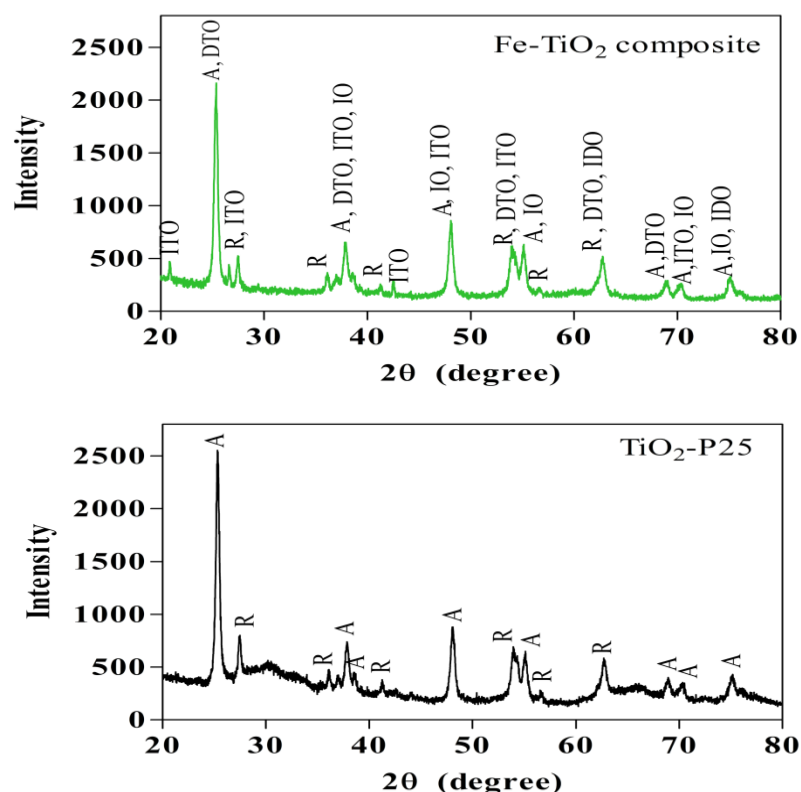


Figure 4.67b: XRD pattern of (a) fresh TiO₂-P25 and (b) recycled Fe-TiO₂ composite beads (70 recycles).

UV-visible Diffuse reflectance spectroscopy

The band gap energy of immobilized catalyst was also calculated and compared with that of fresh TiO₂. The UV-visible scan was carried out in the range 200-800 nm. The spectra of both samples (immobilized and fresh TiO₂) have been presented in figure 4.67c. A slight red shift was observed in the spectra of immobilized catalyst over composite which might be due to the presence of iron. Therefore, Fe-TiO₂ composite demonstrated the capability of absorbing the light even in visible spectrum. The band gap of catalyst was quantified using equation 4.21.

Absorption edge in case of immobilized catalyst was extended to 425 nm with calculated band gap energy, $E_g = 2.9$ eV which was much lower in comparison to fresh TiO₂ with $E_g = 3.14$ eV.

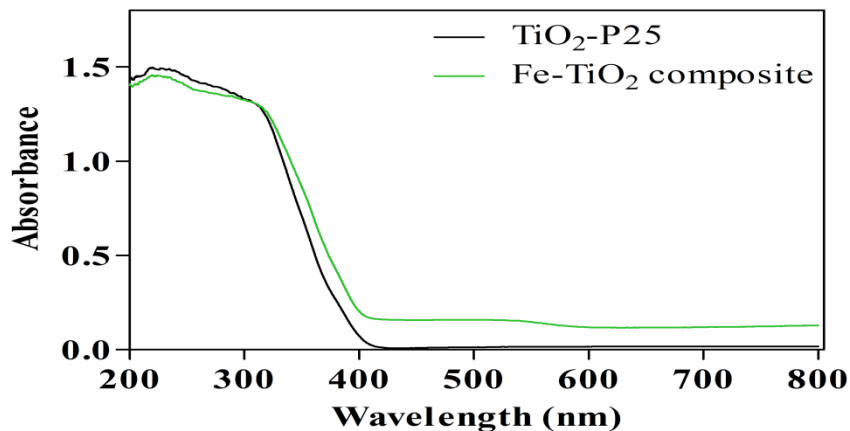


Figure 4.67c: UV-visible DRS of (a) fresh TiO₂-P25 and (b) recycled Fe-TiO₂ composite beads (70 recycles).

XPS analysis

The surface composition of recycled Fe-TiO₂ composite was also verified through XPS analysis and compared with fresh TiO₂. The surface survey scan of immobilized catalyst and fresh TiO₂ is depicted in figure 4.67d. The scan of TiO₂ clearly indicated the prominent peaks of 'Ti' and 'O' without any other additional peak whereas scan of immobilized catalyst portrayed other weak peaks as well in addition to 'Ti' and 'O'. The additional weak peak in case of immobilized catalyst corresponded to 'Fe'. The presence of iron along with TiO₂ in composite was confirmed by each characterization technique leading to a proposition that highly durable and stable Fe-TiO₂ composite could be efficiently used for dual effect studies.

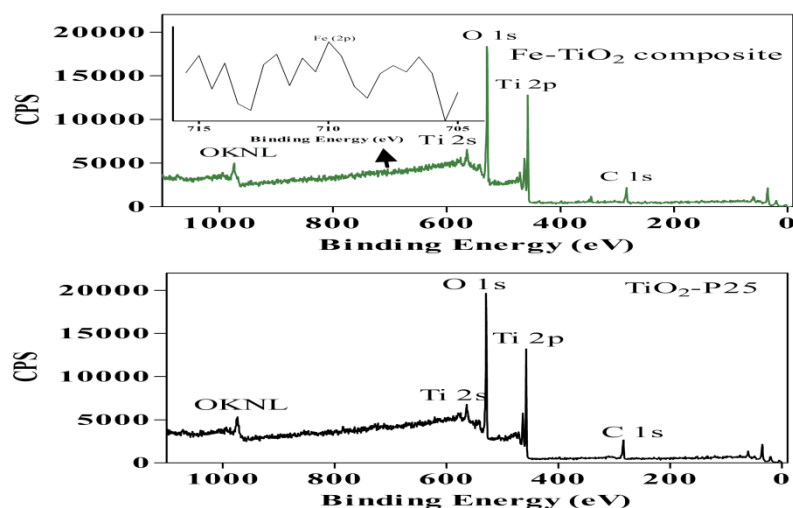


Figure 4.67d: XPS analysis of (a) fresh TiO₂-P25 and (b) recycled Fe-TiO₂ composite beads (70 recycles).

TGA analysis

The thermal analysis was also carried out to determine whether any change occurred in the thermal stability of catalyst due to the presence of iron. The thermo-gravimetric curves of immobilized catalyst over composite and fresh TiO_2 are shown in figure 4.67e. There was no significant variation in the mass of both samples with change in the temperature from 30-980 $^\circ\text{C}$. Thus, Fe-TiO_2 composite demonstrated an excellent thermal stability as well in contrast to TiO_2 .

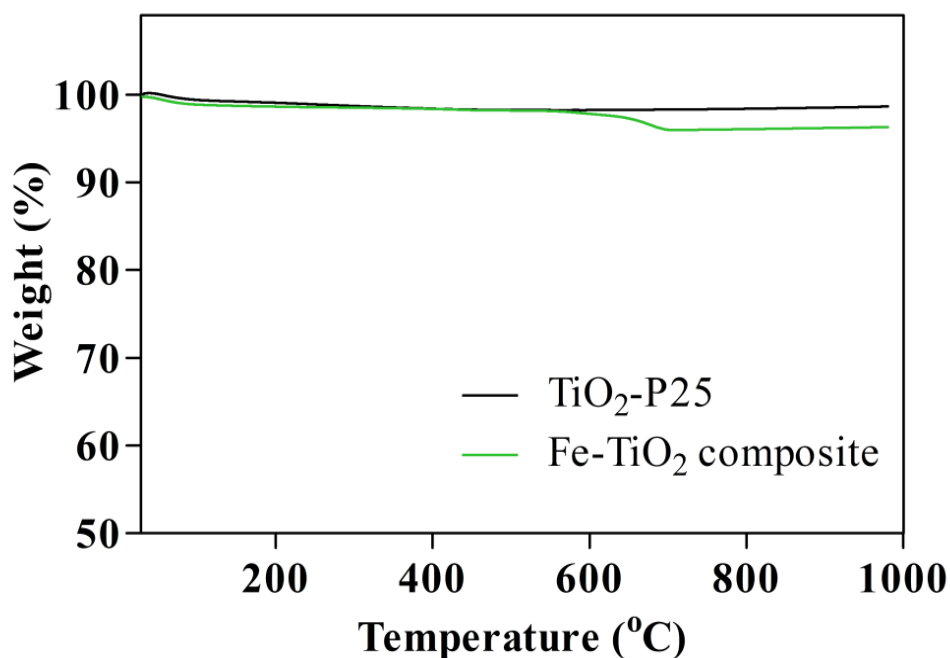


Figure 4.67e: TGA analysis of (a) fresh TiO_2 -P25 and (b) recycled Fe-TiO_2 composite beads (70 recycles).

Several characterization techniques as discussed above claimed the stability and activity of Fe-TiO_2 composite beads even after 70 recycles. Both catalysts i.e. iron and TiO_2 were found to be intact even in recycled beads thus suggesting that beads could be successfully used even in further dual effect experiments. Thus, it leads to a conclusion that Fe-TiO_2 composite beads incorporating in-situ dual effect have the capability to be used for field-scale applications.

4.11.6 Intermediates and pathway prediction for the degradation of CEX

FTIR analysis

The degradation of CEX was further analyzed through FTIR spectra. The infrared spectrum of untreated parent compound i.e. CEX and treated solution of different reactors (1 to 6) in a cascade reactor system is presented in figure 4.68. It is clear from figure that untreated CEX consisted of numerous peaks corresponding to several different bonds present in its complex structure. The peaks between 600 cm^{-1} and 1000 cm^{-1} represented the bending vibrations of alkene ($=\text{C-H}$) while peaks between 1080 cm^{-1} and 1360 cm^{-1} corresponded to the stretching vibrations of C-N group. The weak bands between 1400 cm^{-1} and 1600 cm^{-1} represent the aromatic nature of compound while a small peak at 1464 cm^{-1} could be correlated with CH_3 bending vibrations. Strong peaks between 1500 cm^{-1} and 1700 cm^{-1} corresponded to amide group. The broad transmittance band at 3400 cm^{-1} symbolized the stretching vibrations of O-H group. The peak at 3000 cm^{-1} represented the stretching vibrations of amine (N-H). Most of these peaks present in CEX got disappeared after undergoing treatment through in-situ dual process thus suggesting an almost complete decomposition of CEX. Strong peaks between 3300 cm^{-1} and 3500 cm^{-1} in case of treated solution in each reactor corresponded to the O-H stretching vibrations. These peaks were comparatively more sharp and prominent as compared to the peak in untreated CEX which might be due the generation of OH radicals during the treatment process. The weak transmittance band between 1600 cm^{-1} and 1680 cm^{-1} represented the stretching vibrations of alkene ($\text{C}=\text{C}$) group whereas band between 600 cm^{-1} and 700 cm^{-1} could be correlated with the bending vibrations of alkene ($=\text{C-H}$) in the treated solution in each reactor. The high intensity of transmittance in the treated solution towards the end reactor could be accounted for the complete oxidation of CEX via in-situ dual process. Thus, it was confirmed from FTIR analysis that complex structure of CEX was transformed into the simpler and linear molecules after the treatment process as detailed in GC-MS analysis.

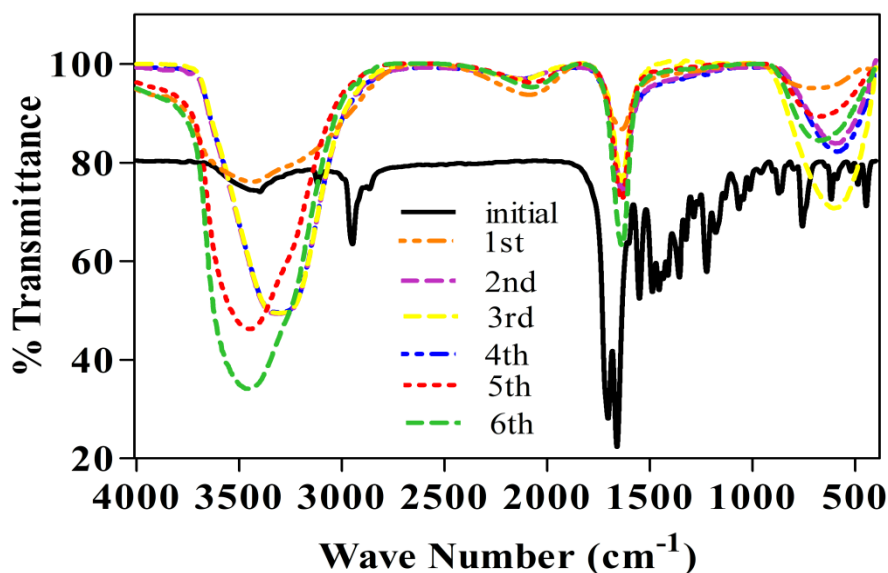


Figure 4.68: FTIR analysis to confirm the degradation of CEX in a cascade reactor system at optimized conditions.

GC-MS analysis

To check the efficacy of pilot-scale once through cascade reactor system, the intermediates formed during the treatment of CEX were once again identified through GC-MS analysis. The chromatograms are provided in Appendix (Figure A5). Based on these intermediates (1-14), a tentative pathway for the degradation of CEX has been proposed (Figure 4.69). The fragmentation of CEX could lead to the formation of (R)-2-amino-2-phenylacetamide **(1)** and (R)-3-methyl-8-oxo-5-thia-1-aza-bicyclo[4.2.0]oct-2-ene-2-carboxylic acid. The by-product **(1)** could further be fragmented into **(2)** and **(3)**. The deamination of **(3)** could produce **(4)** which might get reduced into **(5)**. The cleavage of benzene ring of **(5)** could yield **(6)**. Successive fragmentation of **(6)** could finally result into linear chain molecules **(7)** and **(8)**. On the other hand, (R)-3-methyl-8-oxo-5-thia-1-aza-bicyclo[4.2.0]oct-2-ene-2-carboxylic acid might get reduced to form by-product **(9)**. The breakdown of cyclic ring of **(9)** could yield **(10)** which further resulted into the formation of **(11)** after undergoing decarboxylation. The cleavage of cyclic ring of **(11)** could produce **(12)**. The by-product **(12)** could possibly undergo fragmentation to yield other linear chain molecules **(13)** and **(14)**. It can therefore be concluded

that complex molecule of CEX has been broken down into simpler and linear chain molecules suggesting a complete decomposition of CEX through in-situ dual process in minimized time.

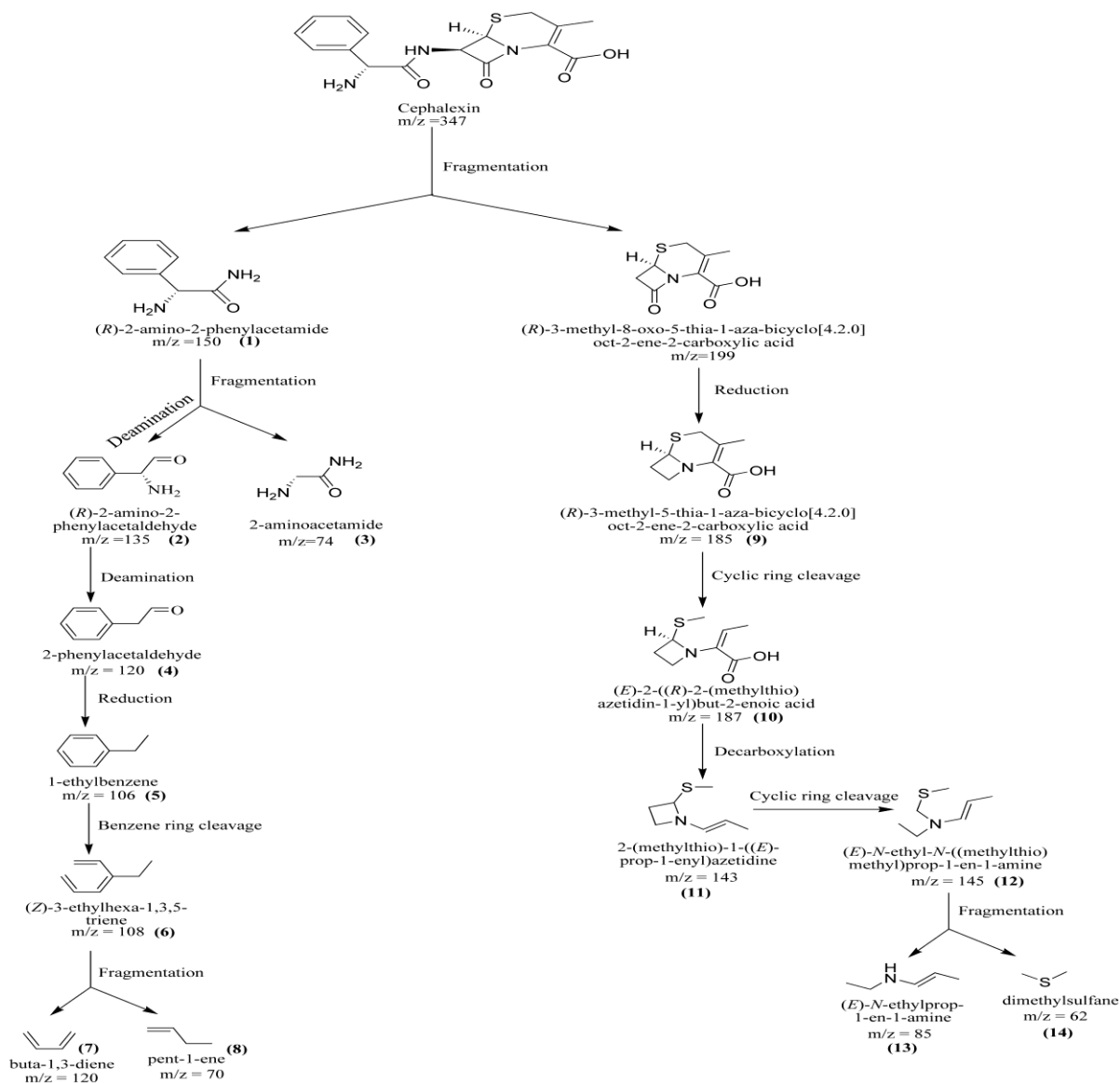


Figure 4.69: Tentative pathway for the degradation of CEX.

4.11.7 Mineralization studies

The mineralization of CEX was evaluated at all optimized conditions in terms of the generation of anions including nitrate, nitrite and sulfate ions along with depletion in COD and TOC values. There was almost 70% and 63% reduction in COD and TOC respectively at the exit

of sixth reactor of a cascade reactor system. It can be presumed that nitrogen atoms of CEX were converted into nitrate and nitrite ions (Grover et al., 2014). It was observed that concentration of nitrate ions were maximum during the treatment of CEX in first two reactors of a cascade reactor system. Thereafter, concentration of nitrate ions started decreasing (from reactor 3-6) with a probability of transformation of nitrate ions into nitrite ions. While, concentration of nitrite and sulfate ions followed an increasing trend throughout the treatment process (from reactor 1-6) as shown in table 4.21. The calculations for CO₂ mass balance have been provided in Appendix (Text A3). The stoichiometrically balanced theoretical chemical equation for the complete mineralization of CEX is indicated in equation 4.30. The experimental chemical equation 4.31 obtained through the quantification of anions including nitrite, nitrate, sulfate ions and CO₂ evolution at the exit of reactor 6 partially deviates from equation 4.30, thus indicating an incomplete mineralization of CEX owing to the formation of intermediates as discussed in previous section.

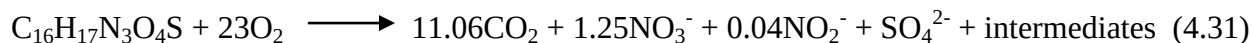
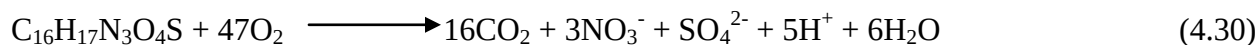


Table 4.21: Concentration of anions produced during the degradation of CEX

Reactors	Nitrite (µg L ⁻¹)	Nitrate (mg L ⁻¹)	Sulfate (mg L ⁻¹)
1	0.33	1.73	0.7
2	0.66	2.0	1.1
3	2.66	0.80	1.4
4	3.0	0.61	2.2
5	4.33	0.23	2.7
6	6.0	0.18	3.3

4.11.8 Cost evaluation

Most of the studies in literature associated with AOPs deal with the degradation of various organic pollutants without considering the cost of treatment. Actually, there are different

expenses involved in the whole treatment process that should be considered while deciding the economy of process. Real costs of the process must include the fabrication of reactor, reagents, catalysts, operating cost and electricity consumption. Therefore, efforts have been made in the present study to evaluate the overall cost of the process at pilot-scale with an assumption that land was available free of cost. The estimation of cost at pilot-scale can provide a rough idea to consider the real applications of photocatalytic reactor at field-scale. The overall cost of treatment process in the current research work has been presented in detail in table 4.22. The overall cost has been evaluated for 70 numbers of runs which came out to be 299.52 \$. More precisely for a single operation of a process to treat 5 L of solution, the overall cost would be 4.27 \$ which came out to be 0.85 \$ per litre. The costs evaluated in this study are significantly lower than other reported studies related to AOPs (Ozkal et al., 2016; Vishnuganth et al., 2016). Most of the studies in literature have evaluated only the cost of electricity consumption during the operation of process or analysis cost without considering the cost of reactor fabrication or catalyst used (Haranaka-Funai et al., 2017; Mehrjouei et al., 2014).

Table 4.22: Evaluation of cost of treatment process.

(A) Fe-TiO₂ composite
Cost of raw materials (clay, FA, FS) = 0.0 \$
Electricity consumption during firing of blank composite at high temperature = 0.75 kWh
Electricity price in India = 0.0699 \$/kWh
Cost of electricity consumption = $0.0699 \times 0.75 = 0.0524$ \$/kWh
Cost of TiO ₂ used (20 g) = 0.06 \$
Total cost of Fe-TiO₂ composite = $0.0524 + 0.06 = 0.1124$ \$
(B) Oxidant (H₂O₂) addition
Cost of total oxidant (700 mL) used (for 70 runs) = 9.6824 \$
(C) Operating cost of treatment process
Cost of light source (sunlight) = 0.0 \$
Number of runs = 70
Total volume of water treated = $5\text{L} \times 70 = 350\text{ L}$ (0.35 m^3)
Cost per $\text{m}^3 = (A+B)/0.35 = 27.98$ \$/m ³
With 70% degradation ($C_o = 50\text{ mgL}^{-1}$), concentration of CEX removed = 35 mgL^{-1} (0.035 kgm^{-3})
Cost per kg of concentration removal = $(A+B)/0.035 = 279.85$ \$/kg of concentration removal
Energy consumption during operation of process (pumping of solution during treatment) = $18 \times 1.7 \times 70 = 2142\text{ Wh}$
Energy consumed per kg of concentration removal = $2142/0.035 = 61.2$ kWh per kg of concentration removal
Cost for energy consumption = $0.0699 \times 61.2 = 4.277$ \$/kWh
Overall operating cost = $279.85 + 4.277 = 284.12$ \$

(D) Fabrication of cascade reactor system
Total cost including pump, reactors, pipe, valves = 15.40 \$
Total cost of treatment process = C + D = 299.52 \$
Total cost of above treatment process comes out to be 299.52 \$ for 70 runs
Total cost of treatment process for single run (5 L) would be 4.27 \$.

To the best of our knowledge, this is the first reported study that has evaluated the detailed cost of treatment process in context to pilot-scale fixed-bed reactor using AOPs. In view of the excellent recyclability efficiency of Fe-TiO₂ composite beads, overall cost of the process in the present study can be further reduced when used for more cycles. Therefore, a cascade reactor system with highly durable and stable Fe-TiO₂ composite beads can provide a low cost solution to various industries for the treatment of wastewater in minimized treatment time.

Section D

Treatment of real pharmaceutical effluent

4.12: Applications of in-situ dual process for the treatment of real effluent from pharmaceutical industry

After the establishment of in-situ dual effect and extended durability of Fe-TiO₂ composite beads, the applications of the process were extended to the treatment of real pharmaceutical effluent. The real pharmaceutical effluent was subjected to primary treatment i.e. coagulation using FeCl₃ as a coagulating agent, prior to in-situ dual process. The parametric optimization in case of in-situ dual process was carried out under artificial UV-A irradiations using Box-Behnken design model (BBD) and response surface methodology (RSM). The degradation as well as mineralization of the real wastewater was evaluated in terms of reduction in COD along with generation of anions. The main emphasis of the study was to increase the biodegradability of real pharmaceutical wastewater in reduced treatment time so that in-situ dual process could be successfully employed as a primary treatment option prior to biological methods.

The real pharmaceutical effluent was initially characterized for the parameters including COD, BOD, TDS, TSS, nitrate, nitrite, chloride, turbidity and pH as listed in table 4.28.

4.12.1 Coagulation-flocculation

Before directly proceeding into the photocatalytic treatment of real pharmaceutical effluent, coagulation-flocculation studies were carried out to reduce the turbidity of solution so that photocatalytic treatment can be applied effectively. The coagulation was conducted at natural pH of effluent i.e. pH = 5.1 using FeCl_3 as a coagulating agent. This particular pH i.e. 5.1 was in the vicinity of optimized pH values (i.e. 5.5-6) reported in literature (Jorfi et al., 2016; Rodrigues et al., 2008) in context to coagulation studies. Thus, pH of effluent was not varied to conduct the coagulation studies.

The influence of coagulant dose on the reduction in COD was investigated at natural pH of effluent by varying the concentration of FeCl_3 from 100 to 1000 mgL^{-1} . The COD of effluent decreased from 4800 to 3680 mgL^{-1} with an increase in the concentration of coagulant up to 200 mgL^{-1} . Beyond 200 mgL^{-1} , COD either became constant or started increasing as shown in figure 4.70. Thus, 200 mgL^{-1} of FeCl_3 was selected as an optimum coagulant concentration for the present study. At this optimized dose of coagulant, an almost 90% reduction in turbidity of solution was observed (Table 4.28). Thus, coagulation served as a pre-treatment step in the present study before conducting any photo-treatment.

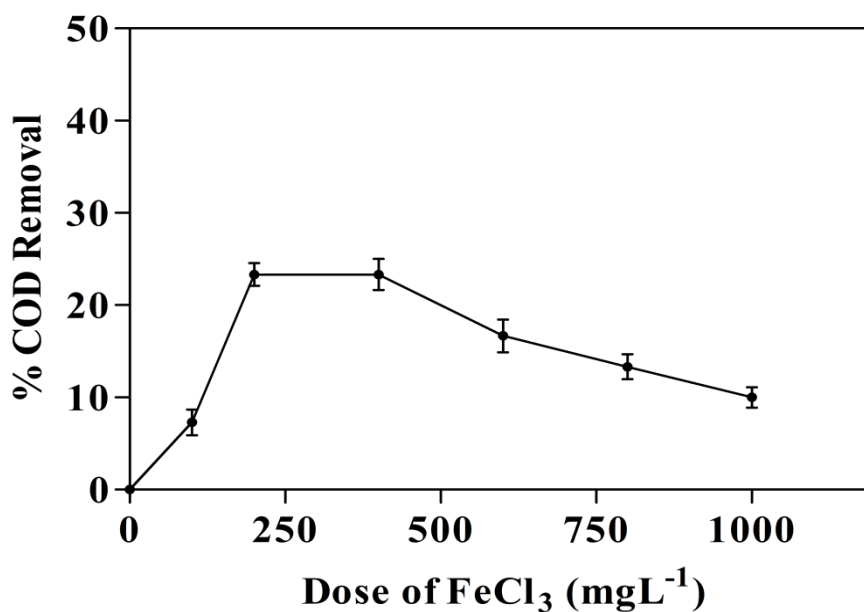


Figure 4.70: Effect of coagulant dose on the COD removal efficiency of real effluent.

4.12.2 Prominence of dual effect

The pre-treated pharmaceutical effluent was subjected to different photo-treatment processes before actually conducting the dual effect experiments (coupling of photocatalysis and photo-Fenton). All experiments were initially performed in suspension mode at acidic conditions ($\text{pH} = 3.5$) under artificial UV-A irradiations with initial COD of 3680 mgL^{-1} obtained after pre-treatment step. Dark studies (i.e. adsorption) were carried out separately in the presence of TiO_2 as well as FS/FA which revealed insignificant reduction in COD (8-10%) in each case. Photolytic studies in the presence of UV light revealed an almost 12-15% reduction in COD after 5 h. Thus, it was confirmed that adsorption and photolysis did not impart any significant contribution towards the treatment of effluent.

TiO_2 photocatalysis using 1.0 gL^{-1} of TiO_2 and 300 mgL^{-1} of H_2O_2 revealed an almost 75% removal in COD with final value of COD to be 940 mgL^{-1} after 5 h of UV irradiations. Photo-Fenton studies with 1.0 gL^{-1} of FS/FA and 300 mgL^{-1} of H_2O_2 reduced the concentration to around 1860 mgL^{-1} i.e. ~50% removal of COD after 5 h. On the other hand, dual process by integrating photocatalysis and photo-Fenton took almost 4 h to achieve nearly 75% removal in COD as compared to 5 h in photocatalysis while it took almost 3 h to attain 50% reduction of COD as compared to 5 h via photo-Fenton. Thus, dual process drastically enhanced the degradation process resulting into an almost 91% removal in COD with final value of COD to be 320 mgL^{-1} after 5 h of treatment (Figure 4.71). Therefore, the prominence of dual effect was established in suspension mode. Now, this concept was further used in fixed-mode throughout the study for the treatment of real wastewater.

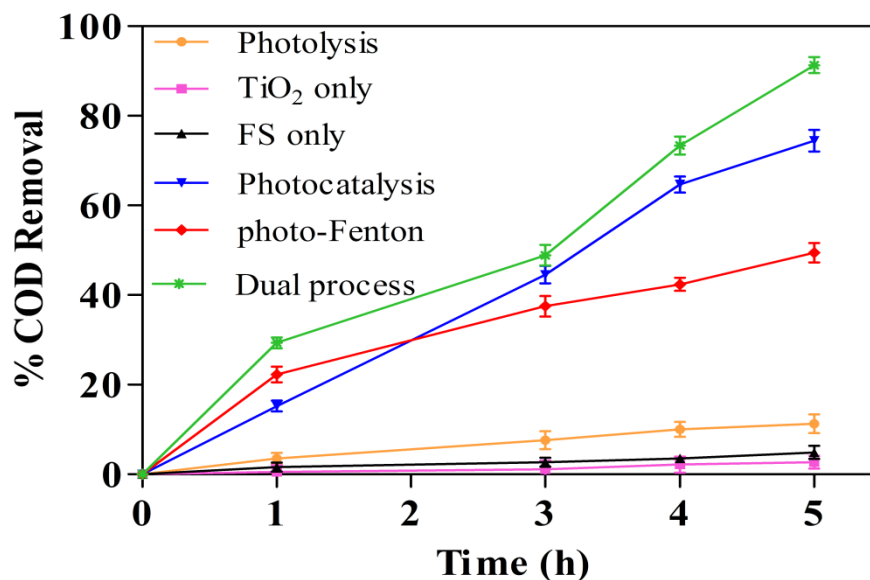


Figure 4.71: Effect of different treatment processes in slurry mode on the treatment of real effluent.

4.12.3 In-situ dual effect studies in fixed-mode

This section reports the real time applications of in-situ dual process using Fe-TiO₂ composite beads for the treatment of real effluent from a pharmaceutical industry. These unique composite beads had the tendency to leach out iron species in solution under acidic conditions (as already discussed in previous sections) thus, participating in photo-Fenton reaction along with TiO₂ photocatalysis. The in-situ dual process using Fe-TiO₂ composite beads was optimized through response surface methodology (RSM) to obtain the best operating conditions for the effective treatment of real wastewater. All experiments were carried out under acidic conditions i.e. pH = 3.5.

Statistical analysis

For the in-situ dual process (photocatalysis + photo-Fenton) under artificial UV irradiations, concentrations of COD along with nitrite and nitrate ions were considered as responses under various operating conditions. B-B design matrix and concentrations of COD, nitrite and nitrate ions are depicted in Table 4.23. The dose of catalyst i.e. Fe/TiO₂ was varied in terms of the number of composite beads (expressed in the form of %age bottom surface area of

batch reactor covered with beads) from 50-125%, H₂O₂ from 150-1200 mgL⁻¹ while treatment time was varied from 1 to 6 h.

Table 4.23: BBD design matrix and response for the treatment of effluent.

Run	Time (h)	H ₂ O ₂ (mgL ⁻¹)	Number of beads (% area of reactor bed covered)	COD (mgL ⁻¹) Y ₁	Nitrate (mgL ⁻¹) Y ₂	Nitrite (µgL ⁻¹) Y ₃
1	3.50	150.00	150.00	1600	2.1	113.33
2	1.00	675.00	150.00	2550	3.09	76.66
3	3.50	675.00	100.00	1420	2.9	195
4	6.00	150.00	100.00	805	1.87	456.66
5	3.50	675.00	100.00	1280	3.2	166.6
6	3.50	1200.00	50.00	1800	4.064	145.4
7	1.00	675.00	50.00	2800	2.54	233.33
8	3.50	675.00	100.00	1300	3.29	211.11
9	3.50	150.00	50.00	2000	2.05	213.33
10	6.00	675.00	50.00	550	2.36	373.33
11	6.00	1200.00	100.00	304	3.8	423.33
12	3.50	675.00	100.00	1260	3.4	211
13	1.00	1200.00	100.00	2400	4.47	176.66
14	6.00	675.00	150.00	520	1.45	468
15	3.50	675.00	100.00	1380	3.29	176.66
16	1.00	150.00	100.00	2640	2.68	57.77
17	3.50	1200.00	150.00	1580	3.56	240

For selecting the best model for the treatment of real wastewater through in-situ dual process, sequential F-test in combination with other measures was utilized. Quadratic model was propounded for the present study as value of P for each response (Y₁, Y₂ and Y₃) came out to be less than 0.0001. Second order polynomial equations obtained from ANOVA Table for each response have been depicted in Equations 4.32-4.34.

$$\% \text{ COD removal (Y}_1\text{)} = +1328 - 1038.87A - 132.62B - 112.50C + 22.12A^2 + 162.12B^2 + 254.88C^2 - 90.25 AB + 55AC + 45BC \quad (4.32)$$

$$\text{Nitrate concentration (Y}_2\text{)} = +3.22 - 0.41A + 0.90B - 0.10C - 0.30A^2 + 0.29B^2 - 0.56C^2 + 0.035AB - 0.37AC - 0.14BC \quad (4.33)$$

$$\text{Nitrite concentration (Y}_3\text{)} = +192.07 + 147.11A + 18.04B - 8.43C + 98.17A^2 - 11.64B^2 - 2.42C^2 - 38.06AB + 62.84AC + 48.65BC \quad (4.34)$$

Where A, B and C are the coded values of treatment time, H₂O₂ dose and number of beads respectively. A positive or negative sign before each term in the equation corresponds to either synergistic or antagonistic effect of factors on the process efficiency, respectively (Sheydaei et al., 2014).

The significance of each operating parameter was determined on the basis of P-values and F-values. F-value > 5 and P-value < 0.05 depicted the significance of operating variables on the process efficiency for the treatment of effluent (Appavoo et al., 2014). The P-values and F-values obtained in the present study from ANOVA table for each response are presented in tables 4.24-4.26. The Model F-values of 81.37, 48.76 and 51.65 corresponding to responses Y₁, Y₂ and Y₃ respectively implied the significance of model in case of each response. The significant model terms for response Y₁ (COD) came out to be A (treatment time), B (H₂O₂ dose), C (number of beads), B² (quadratic term of H₂O₂ concentration) and C² (quadratic term of number of beads). The significant model terms for response Y₂ (Nitrate ion concentration) came out to be A (treatment time), B (H₂O₂ dose), A² (quadratic term of treatment time), B² (quadratic term of H₂O₂ concentration), C² (quadratic term of number of beads) and AC (interaction between treatment time and number of beads). The significant model terms for response Y₃ (nitrite ion concentration) came out to be A (treatment time), A² (quadratic term of treatment time), AB (interaction between treatment time and H₂O₂ dose), BC (interaction between H₂O₂ dose and number of beads) and AC (interaction between treatment time and number of beads). The values of determination coefficient i.e. R² for responses Y₁, Y₂ and Y₃ were observed to be 0.8774, 0.9443 and 0.8552, respectively which validated the model fitting and demonstrated a good correlation between predicted experimental and observed actual results. Figure 4.72 states a correlation between predicted and actual values for the treatment of effluent. Figure clearly represented a good fit for regression. Adequate precision ratios for the treatment of effluent were found to be 29.565, 25.254 and 23.695 in case of Y₁, Y₂ and Y₃ respectively. Precision ratio > 4

is preferable which further confirms the adequate model fitting (Rajkumar and Muthukumar, 2012).

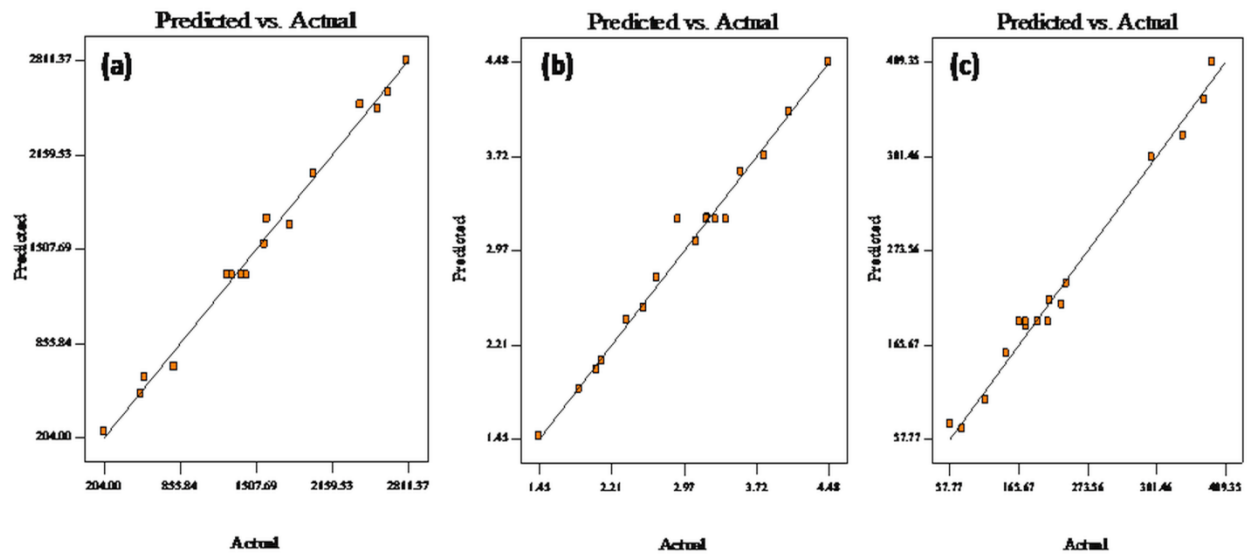


Figure 4.72: The regression plot of predicted vs actual for (a) COD removal, (b) Nitrate ion concentration and (c) Nitrite ion concentration.

Table 4.24: ANOVA analysis obtained from response Y_1 (COD).

Source		Sum of Square	DF	Mean SQUARE	F Value	Prob > F	Source
Model		9.341×10^6	9	1.038×10^6	81.37	< 0.0001	significant
	A	8.634×10^6	1	8.634×10^6	676.92	< 0.0001	
	B	1.407×10^5	1	1.407×10^5	11.03	0.0127	
	C	1.013×10^5	1	1.013×10^5	7.94	0.0259	
	A^2	2061.12	1	2061.12	0.16	0.6997	
	B^2	1.107×10^5	1	1.107×10^5	8.68	0.0215	
	C^2	2.735×10^5	1	2.735×10^5	21.44	0.0024	
	AB	32580.25	1	32580.25	2.55	0.1540	
	AC	12100.00	1	12100.00	0.95	0.3625	
	BC	8100.00	1	8100.00	0.64	0.4517	
Residual		89285.25	7	12755.04			
Lack of Fit		70405.25	3	23468.42	4.97	0.0777	not significant
Pure Error		18880.00	4	4720.00			
Cor Total		9.430×10^6	16				

Table 4.25: ANOVA analysis obtained from response Y₂ (Nitrate ion concentration).

Source		Sum of Square	DF	Mean SQUARE	F Value	Prob > F	Source
Model		10.53	9	1.17	48.76	< 0.0001	significant
	A	1.36	1	1.36	56.71	0.0001	
	B	6.47	1	6.47	269.49	<0.0001	
	C	0.083	1	0.083	3.45	0.1056	
	A ²	0.37	1	0.37	15.50	0.0056	
	B ²	0.35	1	0.35	14.37	0.0068	
	C ²	1.31	1	1.31	54.76	0.0001	
	AB	4.900×10 ³	1	4.900×10 ³	0.20	0.6651	
	AC	0.53	1	0.53	22.20	0.0022	
	BC	0.077	1	0.077	3.20	0.1170	
Residual		0.17	7	0.024			
Lack of Fit		0.023	3	7.706×10 ³	0.21	0.8830	Not significant
Pure Error		0.14	4	0.036			
Cor Total		10.70	16				

Table 4.26: ANOVA analysis obtained from response Y₃ (Nitrite ion concentration).

Source		Sum of Square	DF	Mean SQUARE	F Value	Prob > F	Source
Model		2.481×10 ⁵	9	27571.37	51.65	< 0.0001	significant
	A	1.731×10 ⁵	1	1.731×10 ⁵	324.33	< 0.0001	
	B	2602.81	1	2602.81	4.88	0.0630	
	C	567.85	1	567.85	1.06	0.3367	
	A ²	40580.79	1	40580.79	76.02	< 0.0001	
	B ²	570.68	1	570.68	1.07	0.3356	
	C ²	24.60	1	24.60	0.046	0.8362	
	AB	5792.73	1	5792.73	10.85	0.0132	
	AC	15792.95	1	15792.95	29.58	0.0010	
	BC	9467.29	1	9467.29	17.73	0.0040	
Residual		3736.78	7	533.83			
Lack of Fit		2121.14	3	707.05	1.75	0.2950	not

						significant
Pure Error	1615.64	4	403.91			
Cor Total	2.519×10 ⁵	16				

Response surface methodology and optimization

The relationship between output (COD, nitrite and nitrate ions concentrations) and the operating parameters (catalyst dose (number of beads), oxidant dose (H₂O₂) and treatment time) is shown in response surface plots (Figure 4.73). The influence of catalyst dose (expressed as % area of reactor bed covered with beads) and dose of H₂O₂ on the COD reduction keeping time to be constant at 6 hr can be interpreted from the contour graph (Figure 4.73a). It was observed that value of COD decreased with an increase in the concentration of H₂O₂ from 150 to 1200 mgL⁻¹ due to the increase in the production of OH radicals. In the present study, OH radicals were not produced from a single process but through combination of three different processes i.e. photocatalysis, photo-Fenton and iron-oxide catalysis (as discussed in previous sections). From the analysis (Figure 4.73a), it can be concluded that with increase in the number of composite beads (catalyst dose) up to 100% and H₂O₂ dose (1200 mgL⁻¹), % removal of COD increased. Significant reduction in COD was attributed to the leached iron species promoting photo-Fenton reaction along with the intact layer of TiO₂ simultaneously, contributing to photocatalysis. Moreover, exposed active sites of catalyst were maximum and were freely available for effective binding with the pollutant when entire bottom surface area of the batch reactor was covered with 100% beads thus resulting into the maximum removal of COD. With further increase in the number of composite beads, no further reduction in COD was observed. Actually, beads were overlapping one above the other thus, reducing the exposed surface area of the immobilized catalyst and preventing the effective binding of pollutant with the catalyst. Thus, it was observed that maximum COD removal was observed with number of beads covering nearly 100% of the reactor bed area with H₂O₂ dosage of ~1200 mgL⁻¹. Furthermore, it was observed that value COD continued to decrease with increase in the treatment time from 1 to 6 h. No further reduction in COD was attained when treatment time was extended beyond 6 h.

Similarly, the influence of catalyst dose (expressed as % area of reactor bed covered with beads) and treatment time on the concentration of nitrate ions keeping H₂O₂ dose to be constant

(1200 mgL⁻¹) can be visualized from figure 4.73b. The results indicated that nitrate ions production was found to be maximum during the initial 1 hr of treatment process. Thereafter, concentration of nitrate ions followed a declining trend with the probability of transformation of nitrate ions into nitrite ions. Figure 4.73c demonstrates the effect of H₂O₂ dose and treatment time keeping catalyst dose to be constant (beads covering 100% of reactor bed area) on the concentration of nitrite ions. The influence of H₂O₂ on nitrite ion production was observed to be same as in case of COD removal. The concentration of nitrite ions followed an increasing trend throughout the reaction. Furthermore, it was observed that nitrite ions production reached to a maximum value with number of beads covering the reactor bed area in the range from 100-110% (Figure 4.73d). With further increase in the number of beads, production of nitrite ions decreased due to the decrease in process efficiency. Maximum concentration of nitrite ions was produced at the end of 6h.

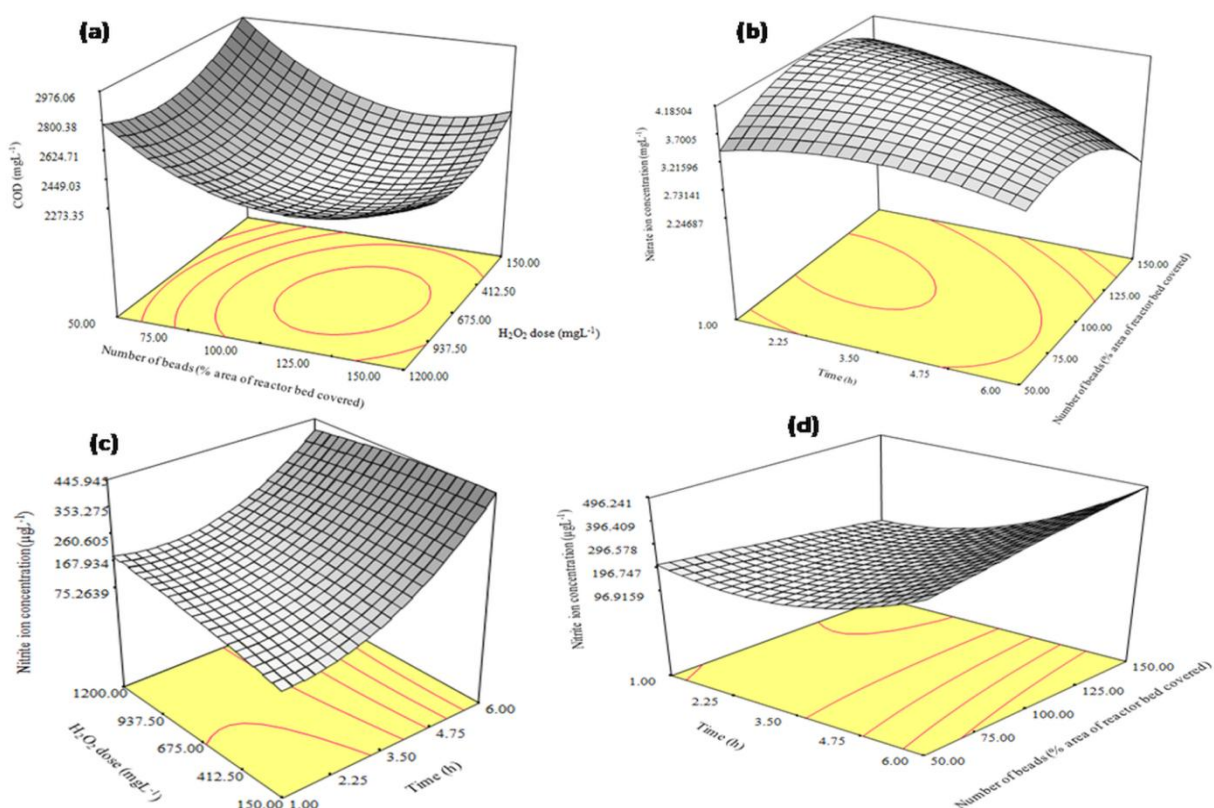


Figure 4.73: 3-D response graphs for the treatment of effluent (a) COD vs number of beads and H₂O₂, (b) Nitrate ion concentration vs number of beads and time, (c) Nitrite ion concentration vs H₂O₂ and time and (d) Nitrite ion concentration vs time and number of beads.

Thus, generation of anions (nitrite and nitrate) along with significant reduction in COD clearly indicated the breakdown as well as mineralization of organic pollutants present in pharmaceutical effluent.

Confirmation of in-situ dual effect at optimized conditions

The optimized conditions obtained through RSM were time = 6 h, H_2O_2 dose = 1155 mgL^{-1} and catalyst dose equivalent to 102% area of reactor bed covered with Fe-TiO₂ composite beads. The precedence of in-situ dual effect was confirmed again in fixed-mode at these optimized conditions by carrying out the treatment of effluent separately through photocatalysis as well as photo-Fenton. Expectedly, in-situ dual process was found to be the most efficient treatment method among different processes as maximum reduction in COD (~90%) was achieved via in-situ dual process. On the other side, an almost 75% and 55% reduction in COD was achieved through photocatalysis and photo-Fenton respectively after 6 h of treatment. In case of in-situ dual process, it took almost 4 h to achieve 75% COD reduction of effluent as compared to 6 h with photocatalysis whereas it took almost 3 h to achieve 55% COD reduction as compared to 6 h with photo-Fenton. Thus, the efficiency of treatment process in terms of COD reduction after 6 h of treatment time was observed in the successive trend: in-situ dual process (89.1%) > photocatalysis (74.5%) > photo-Fenton (54.8%) as depicted in figure 4.74. It was observed that when the reaction was extended further beyond 6 h, the value of COD became almost constant i.e. no further reduction in COD occurred. The concentration of leached iron species during the course of in-situ dual process was estimated and listed in Table 4.27.

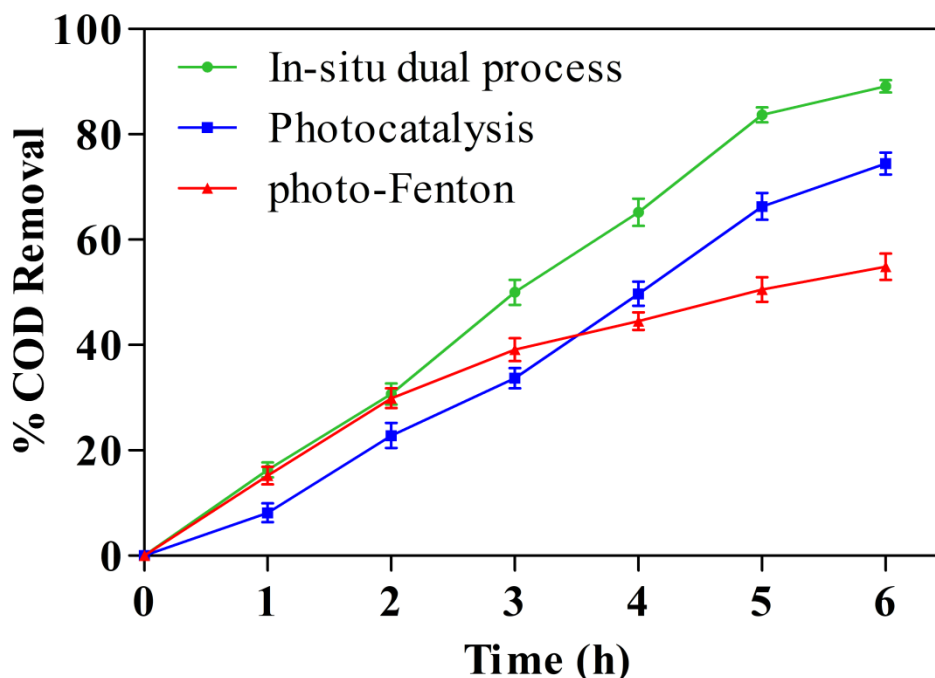


Figure 4.74: Comparison of different processes for the treatment of effluent at optimized conditions.

Table 4.27: Concentration of leached iron species from composite beads during the treatment of effluent via in-situ dual process.

Time (h)	Concentration (mgL ⁻¹)		
	Total iron	Ferrous iron	Ferric iron
1	0.164	0.072	0.092
2	0.25	0.15	0.1
3	0.29	0.18	0.11
4	0.33	0.078	0.252
5	0.24	0.098	0.142
6	0.22	0.11	0.11

Now after getting significant reduction in COD, emphasis would be on the checking of biodegradability of wastewater so that the established dual effect could be successfully used as a pre-treatment step prior to biological treatment. In the present study, even though the maximum COD reduction occurred after 6 h of in-situ dual process, the reaction could also be stopped even after 5 h of treatment based on its BOD₅/COD ratio which became 0.71 after 5 h of treatment whereas it was 0.8 after 6 h of treatment. On the other hand, BOD₅/COD ratio remained below

0.5 in case of photocatalysis and photo-Fenton even after 6 h of treatment. The characterization of effluent before and after the treatment process (in-situ dual process) has been shown in Table 4.28.

Table 4.28: Characterization of effluent before and after the treatment process.

Parameter	Before treatment	After Coagulation	After treatment (In-situ dual process)
COD (mgL ⁻¹)	4800	3680	400
BOD (mgL ⁻¹)	830	Not measured	320
BOD/COD	0.172	n/a	0.8
Total Dissolved solids (TDS) (mgL ⁻¹)	1320	1180	880
Total Suspended solids (TSS) (mgL ⁻¹)	620	130	55
Nitrate (mgL ⁻¹)	20	Not measured	3.6
Nitrite (µgL ⁻¹)	125	Not measured	540
Chloride (mgL ⁻¹)	25	Not measured	120
Turbidity (NTU)	742	70	35
pH	5.07	Not measured	4.88

Although photocatalysis depicted better COD removal efficiency in contrast to photo-Fenton, better decolorization efficiency was observed in case of photo-Fenton process as clearly visualized from figure 4.75. However, best decolorization efficiency was observed in case of in-situ dual process. Therefore, it can be further hypothesized that photo-Fenton was predominant during the early stages of in-situ dual process as it contributed mainly towards the decolorization of wastewater besides generating hydroxyl radicals. Hence, it can be proposed that after removal of color from the solution, TiO₂ photocatalysis became more effective and prominent due to the efficient penetration of light in the solution. Thus, in-situ dual process proved to be the most efficient process in each respect i.e. in terms of COD removal, generation of anions as well as decolorization of sample. This is for the first time when this novel concept of in-situ dual process especially in fixed-mode has been discussed in detail for the treatment of real effluent.

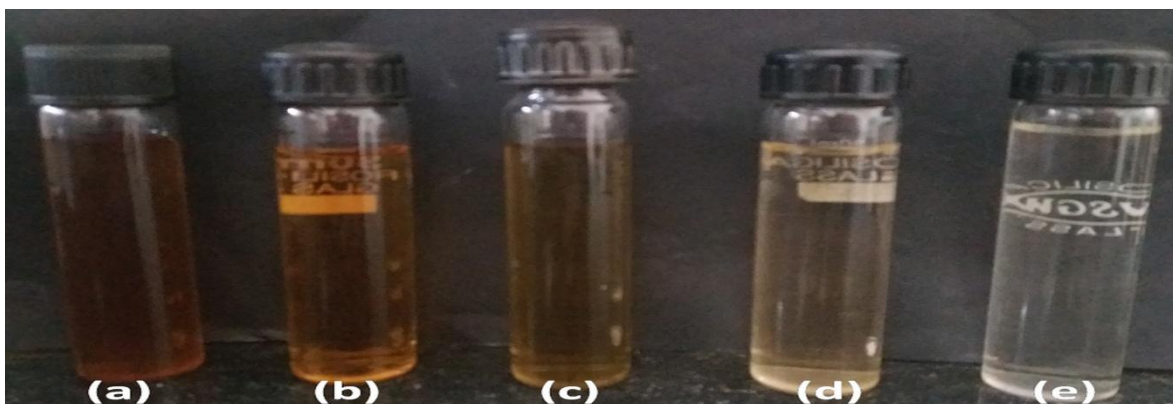


Figure 4.75: Actual photograph of samples representing the effect of different processes on the color removal of effluent (a) raw effluent, (b) after coagulation, (c) after photocatalysis, (d) after photo-Fenton and (e) after in-situ dual process.

4.12.4 Practical feasibility of in-situ dual effect under natural solar irradiations

Ultimately, the feasibility of any wastewater treatment technology at field-scale depends upon its efficiency under natural solar irradiations instead of artificial sources of light. In this view, scale-up studies using in-situ dual process were conducted under natural solar irradiations to check the practical viability of technique. The optimized parameters from the above lab-scale trails were used to execute the scale-up studies under natural solar irradiations.

The scale-up trails using in-situ dual process for the treatment of real wastewater were executed in a pilot-scale solar once-through cascade reactor system (Section 4.11) with total volume handling of 5 L. The reactor was operated at a fixed flow rate of 0.05 Lmin^{-1} (having a space time of 12 min for each reactor) with addition of optimized dose of H_2O_2 i.e. 1155 mgL^{-1} and catalyst dose equivalent to 102% area of each reactor bed covered with Fe-TiO₂ composite beads. The flow rate i.e. 0.05 Lmin^{-1} was chosen based on the optimization studies conducted previously as detailed in Section 4.11. This reactor system using Fe-TiO₂ composite beads incorporating in-situ dual effect gave promising results in context to the treatment of effluent as well. The reduction in COD was observed to be rapid in case of this once-through reactor system. Actually, the solution after retaining for almost 12 min in a reactor came into contact with fresh batch of composite beads in the successive reactor. All active sites of catalyst were freely available to make contact with the pollutant in case of fresh batch of composite beads

which intensified the process efficiency. While in case of lab-scale batch reactor, the solution remained in contact with the same composite beads during the whole reaction period with a possibility of blocking of some of the active sites of catalyst during the reaction. In the present case, maximum reduction in COD (~80%) was observed at the end of 4th reactor in a cascade reactor system (Figure 4.76). Thereafter, COD value became almost constant without any significant reduction in its value. It took almost 100-120 min to pass the total operational volume of 5L of wastewater through the reactor.

The initial reactors mainly helped in the reduction of turbidity and color of the real wastewater due to the predominance of photo-Fenton in the dual process. The efficacy of subsequent cascade reactors became more prominent towards the reduction of COD of wastewater. Moreover, simultaneous occurrence of both effects within the same system accelerate the degradation process in subsequent cascades which is prominent in our results as 5 L of solution of real pharmaceutical waste was treated in less than 120 min.

Thus, promising results even at pilot-scale for the effective treatment of real pharmaceutical effluent under natural solar irradiations further confirmed the field-scale applications of fixed-bed in-situ dual process using Fe-TiO₂ composite beads. None of the reported studies in literature has ever reported such applications of fixed-bed processes especially in context to real wastewater from industries.

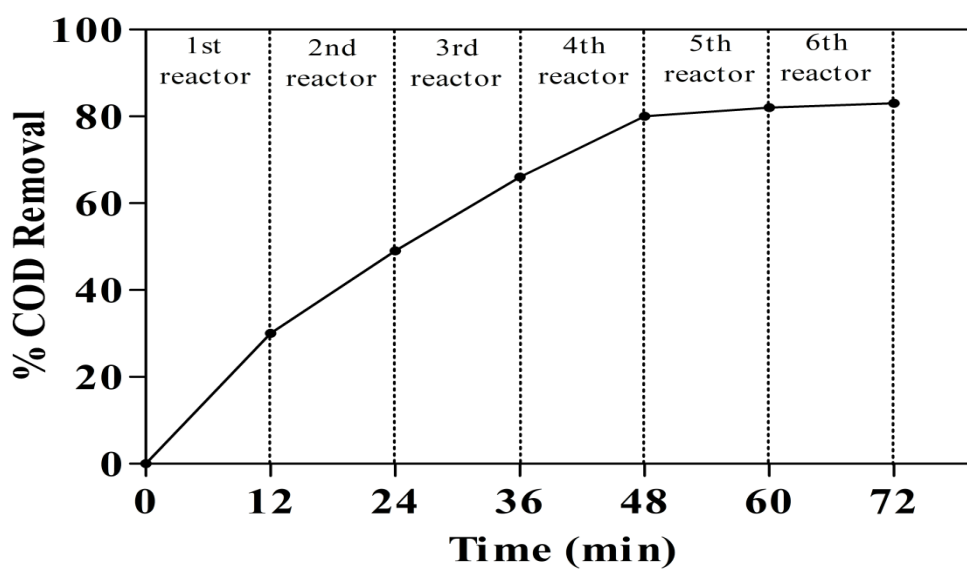


Figure 4.76: Treatment of effluent at pilot-scale in a once-through cascade reactor.

4.12.5 Extended recyclability efficiency of Fe-TiO₂ composite beads

The recyclability efficiency of Fe-TiO₂ composite beads was evaluated again during the treatment of effluent to seek its real time applications. Fe-TiO₂ composite beads were successfully recycled for at-least 35 runs without depicting any significant reduction in their activity. The recyclability efficiency of Fe-TiO₂ composite beads was evaluated in terms of COD removal efficiency of effluent with subsequent recycling tests as shown in figure 4.77. There was almost 8-12% reduction in the removal of COD using the same composite beads for more than 35 runs. The stability and activity of immobilized catalyst along with the presence of iron even in recycled composite beads (35 recycles) was further confirmed through several characterization techniques as discussed in subsequent sections (Section 4.12.6).

To further rationalize our claim in context to the commercial applications of in-situ dual process, experiments related to effluent treatment were conducted with Fe-TiO₂ composite beads that were prepared earlier and had been previously used for at-least 70 recycles. The efficacy of these old composite beads was also checked in terms of % COD removal of effluent at all optimized conditions. Nearly 78% reduction in COD of effluent was attained after 6 h of treatment via in-situ dual process using these old composite beads. Significant amount of reduction in COD even after 70 recycles postulated that the studied technique can be successfully implemented at field-scale using these highly durable and economical Fe-TiO₂ composite beads. Till date, there have been no studies in literature reporting such high rate of catalyst recyclability especially in context to the treatment of real industrial effluent.

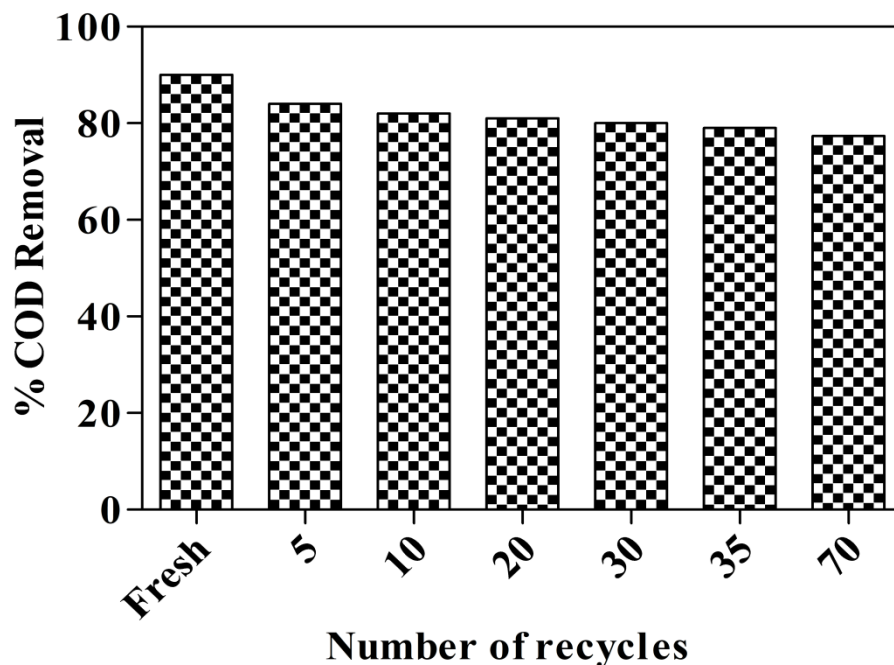


Figure 4.77: Recyclability studies of Fe-TiO₂ composite beads

4.12.6 Characterization of Fe-TiO₂ composite beads

SEM/EDS analysis

Figure 4.78a demonstrates the SEM along with EDS images of fresh as well as recycled Fe-TiO₂ composite beads (35 recycles). The SEM images depicted almost similar morphology in each case thus suggesting that surface characteristics of composite beads did not change even after 35 recycles. Furthermore, the existence of sharp peaks corresponding to ‘Ti’, ‘O’ and ‘Fe’ in EDS spectra in each case authenticated the intactness of TiO₂ layer on the surface along with the existence of iron even in recycled composite beads. Thus, these results from SEM/EDS analysis clearly demonstrated that recycled composite beads could be effectively utilized for dual effect studies owing to the presence of TiO₂ and Fe even after 35 recycles.

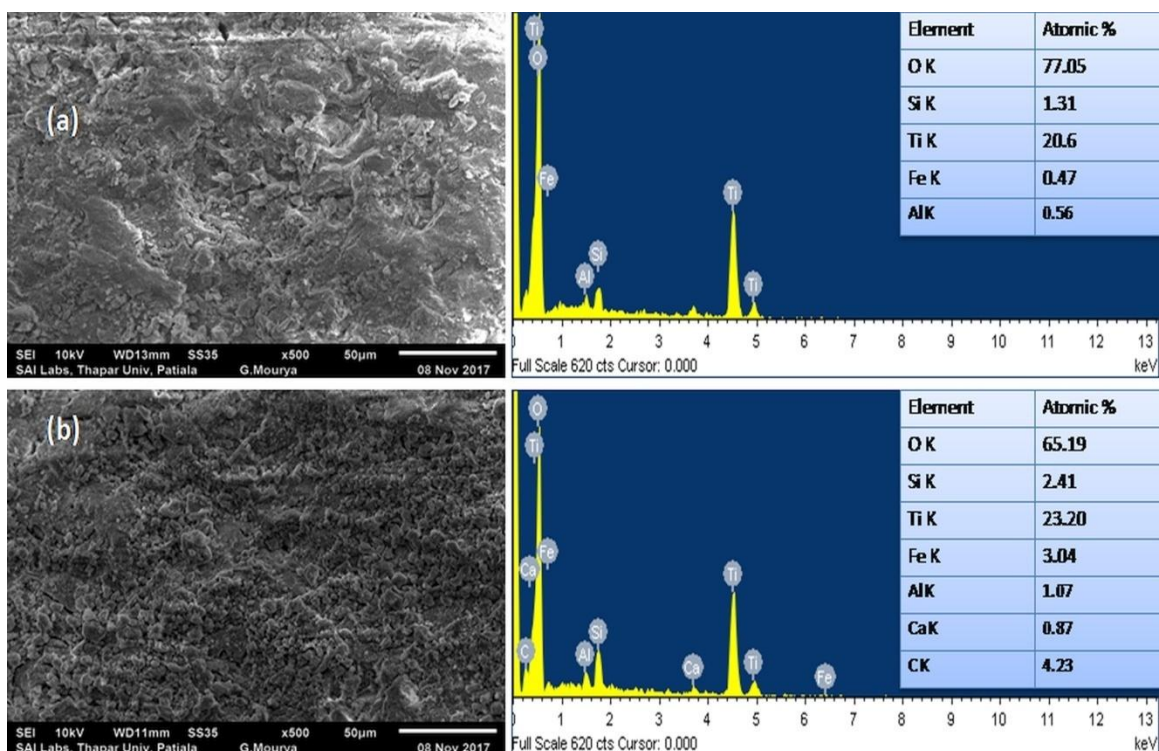


Figure 4.78a: SEM and EDS images of fresh as well as recycled Fe-TiO₂ composite beads.

XRD analysis

The X-ray diffraction patterns of fresh and recycled Fe-TiO₂ composite beads are shown in figure 4.78b. It was observed that biphasic nature of TiO₂-P25 was retained in each case as prominent peaks corresponding to anatase (marked as 'A') as well as rutile (marked as 'R') appeared in the diffraction pattern. In addition to this, some other diffraction peaks indicating the presence of iron in composite beads were observed in each case. These peaks confirmed the presence of few forms of iron oxides on the surface of composite beads. The forms of iron oxides detected in each case were iron (III) oxide (IO), iron diiron (III) oxide (IDO), iron titanate (IT), wustite (W) and iron titanium oxide (ITO). The role of these iron oxides in the in-situ dual process has already been established in the previous sections. Hence, XRD studies further confirmed our claim of extended durability of Fe-TiO₂ composite beads.

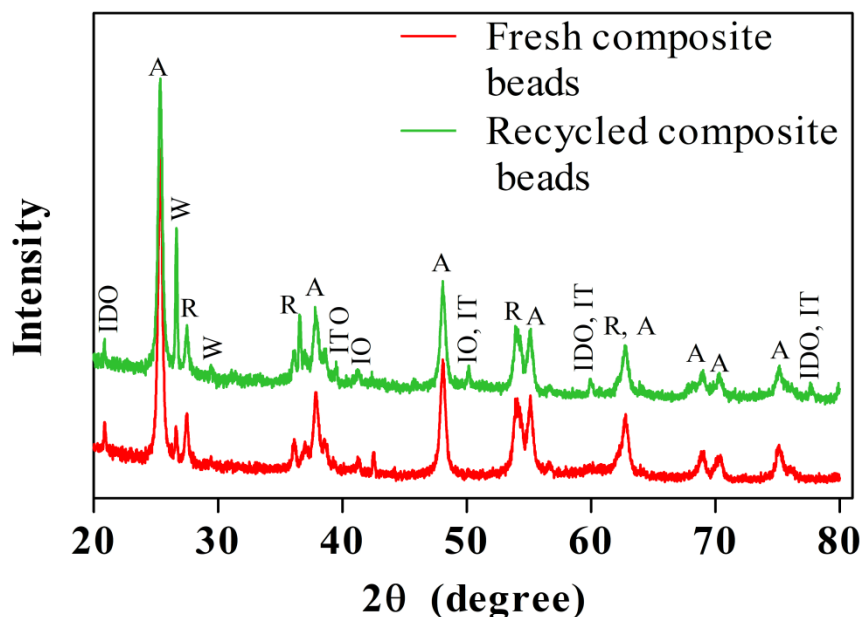


Figure 4.78b: XRD patterns of fresh and recycled Fe-TiO₂ composite beads.

DRS analysis

The UV-visible light absorption patterns of fresh and recycled Fe-TiO₂ composite beads are shown in figure 4.78c. An almost similar light absorption patterns in each case depicted that the activity of immobilized catalyst was retained even after 35 recycles thereby highlighting the efficiency of Fe-TiO₂ composite beads.

Moreover, the band gap energy of Fe-TiO₂ composite beads was also calculated in contrast to TiO₂-P25 using the equation 4.21. The band gap energies (E_g) calculated for fresh and recycled Fe-TiO₂ composites were nearly same i.e. 2.92 eV and 2.87 eV while band gap energy (E_g) in case of TiO₂-P25 was observed to be 3.1 eV. Therefore, the band gap energy was observed to be significantly lower in case of composite beads as compared to TiO₂-P25 which might be due to the existence of iron in composite beads. Thus, it leads to a proposition that apart from extended durability efficiency, Fe-TiO₂ composite beads also exhibited high photo-response efficiency thereby increasing their light absorption capacity as compared to conventional TiO₂-P25.

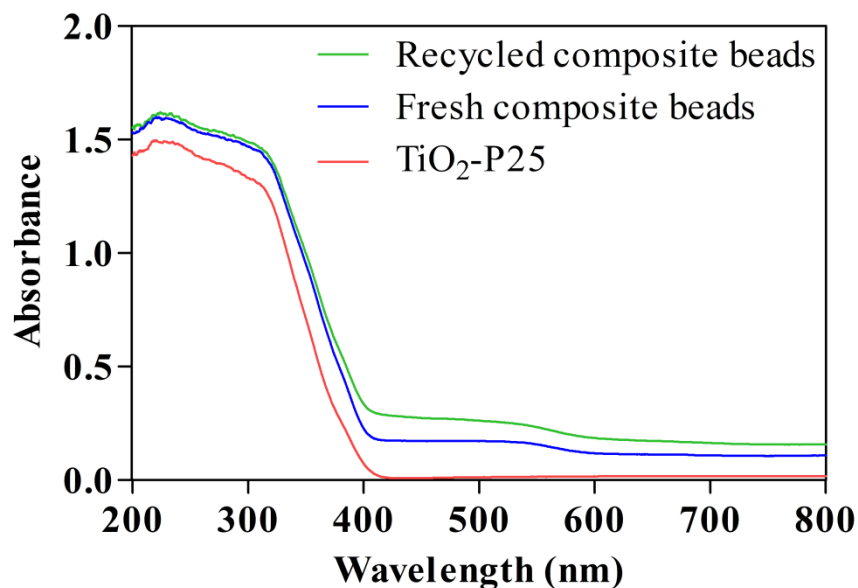


Figure 4.78c: UV-visible DRS of TiO₂-P25, fresh Fe-TiO₂ composite beads and recycled Fe-TiO₂ composite beads.

4.12.7 Identification of intermediates or by-products

UV-spectral analysis

Figure 4.79a depicts the change in absorption spectra before and after the treatment of real pharmaceutical effluent via in-situ dual process using highly efficient and durable Fe-TiO₂ composite beads at all optimized conditions. The absorption spectra were obtained by carrying out the scan in the wavelength ranging from 190 to 800 nm. Many prominent peaks were present especially in the UV region in case of untreated effluent sample which got almost disappeared after undergoing treatment for 6 h through in-situ dual process. The disappearance of these peaks further indicated the effectiveness of in-situ dual process towards the treatment of industrial wastewater.

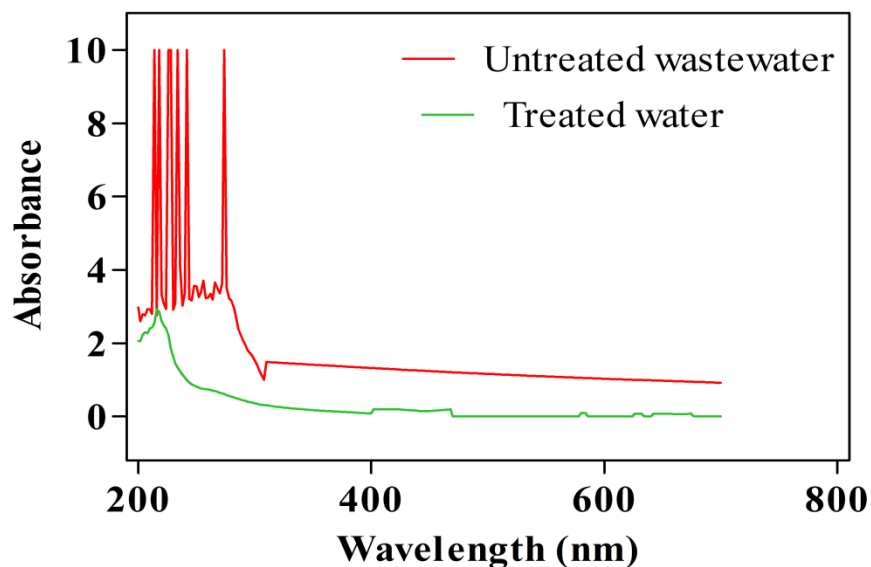


Figure 4.79a: UV-spectral analysis of treated and untreated effluent.

GC-MS analysis

The organic pollutants present in the effluent before and after the treatment process (in-situ dual process) were identified through GC-MS analysis. The untreated effluent mainly comprised of precursors (meant for the synthesis of mainly drugs, antibiotics or anti-inflammatory agents) and chemicals used for encapsulation. Few drugs including ibuprofen and butibufen intended for various disorders were also identified in the untreated sample. These identified organics were mostly hazardous and were mainly toxic to aquatic life as well as humans. After the treatment process, most of these identified products were eliminated from the solution. The treated solution consisted of chemicals intended for encapsulation in major proportions while few other compounds were also identified in minor proportions. However, these detected organics in treated effluent were non-toxic as compared to that of untreated solution (as confirmed through toxicity analysis). It could be therefore proposed that most of the organic pollutants present in raw effluent were mineralized into anions after undergoing treatment through in-situ dual process. Based on this analysis, a tentative mechanism for the destruction of organic pollutants has also been proposed as shown in figure 4.79b.

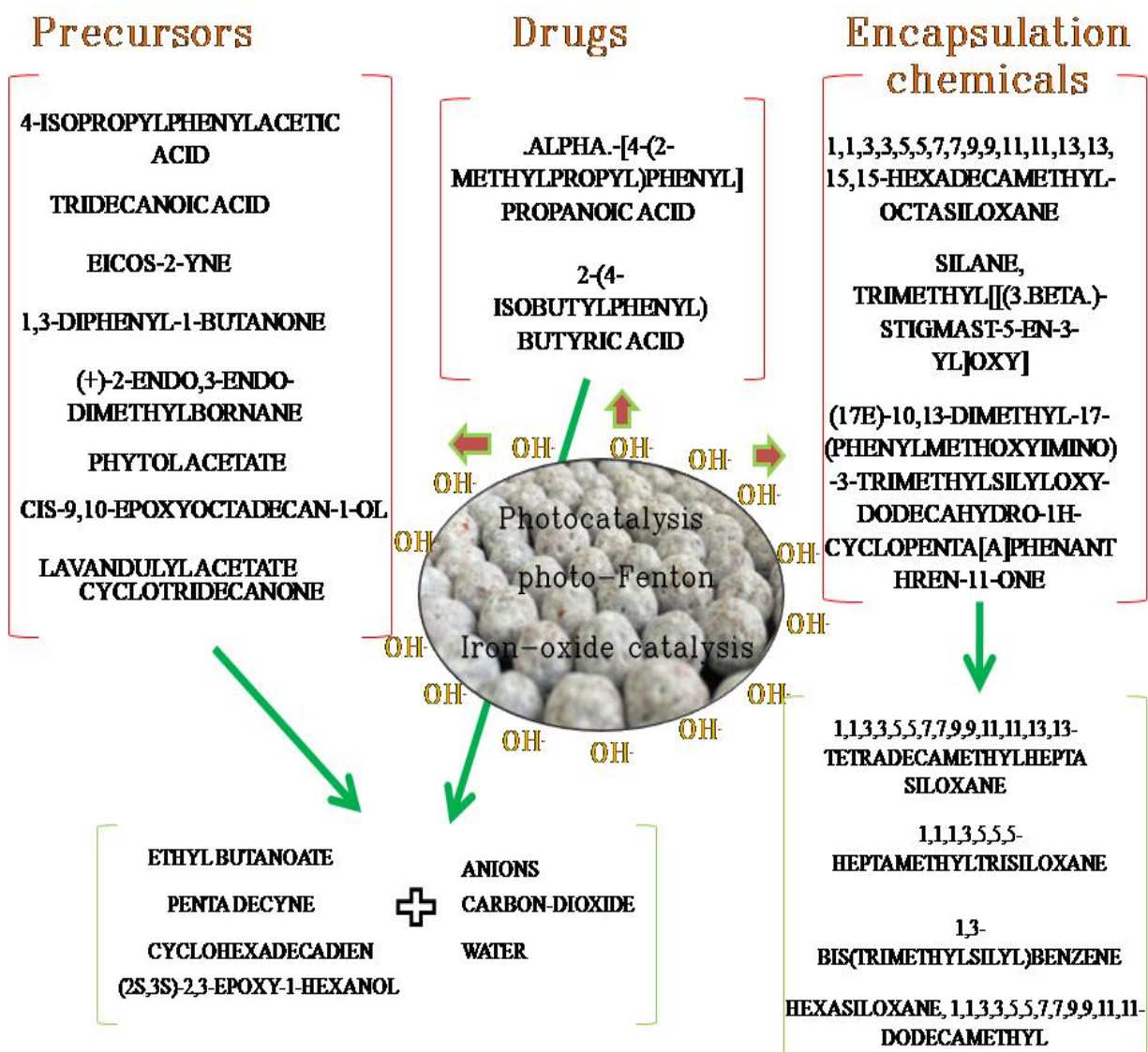


Figure 4.79b: Tentative mechanism for the destruction of pollutants present in real pharmaceutical effluent through in-situ dual process.

4.12.8 Toxicity analysis

To check the quality of treated effluent via in-situ dual process using Fe-TiO₂ composite, toxicity analysis was performed through agar well diffusion assay (Kirby-Bauer test) against *E. Coli* taking untreated effluent as control. Concisely, 0.5 cm well was punched in Muller Hinton agar (MHA) plates using a sterile cork borer. Subsequently, approximately 30 µl of samples i.e. control, coagulated along with treated samples at different time intervals i.e. 1 h, 3 h, 5 h and 6 h were poured in well of different plates and were allowed to diffuse at 37 °C for about 20

minutes. The plates were swabbed with culture of *E. Coli*. Thereafter, plates were kept in an incubator at a temperature of 37 °C for overnight. The cytotoxic activity of the samples was analyzed through the occurrence of zone of inhibition around the well. The biggest zone of inhibition was observed in case of control (untreated effluent sample). The size of zone was observed to follow a declining trend during the treatment process. The zone finally disappeared after 5 h of treatment thus indicating the non-toxicity of treated sample. The decreasing size of zone during the treatment was in a complete agreement with the decolorization trend of effluent at the same time as shown in figure 4.80. It could be proposed that color of the sample was directly proportional to its toxicity behavior.

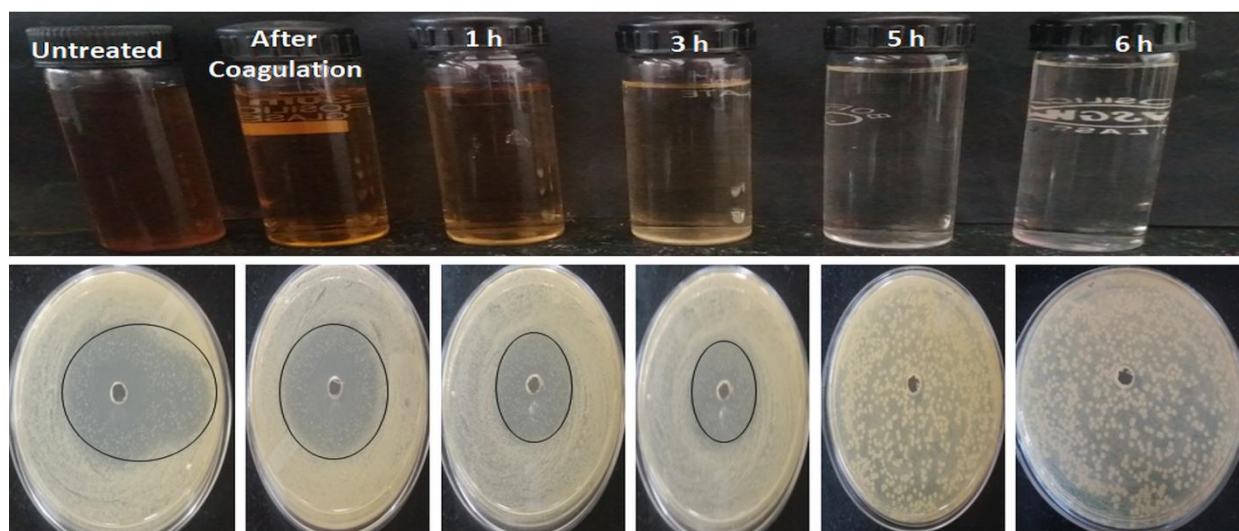


Figure 4.80: Color of the samples along with their toxicity analysis at different time intervals during the treatment of effluent via in-situ dual process.

In addition to the cyto-toxicity analysis, acute toxicity of the treated effluent (after 6 h of treatment) via in-situ dual process was also assessed through bio-assay method (acceptable by Central Pollution Control Board, CPCB) which is based upon the toxicity factor. Toxicity factor is actually the minimum amount of dilution of sample required for achieving no mortality for the zebra fish. In the present investigation, 100% survival of fish was attained after 96 h of bio-assay test (Figure A6, Appendix). It can be therefore deduced that the treated pharmaceutical effluent via in-situ dual process was completely non-toxic in each respect. Thus, in-situ dual process using highly durable and efficient Fe-TiO₂ composite beads can be effectively used for field-scale applications.

Chapter-5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The potential applications of waste materials like foundry sand (FS) and fly-ash (FA) as alternative sources of iron have been visualized in the present study for the treatment of wastewater. For the first time, the study presented the novel in-situ dual effect (coupling of photocatalysis and photo-Fenton) for the degradation and mineralization of pharmaceuticals i.e. Cephalexin (CEX) and Pentoxifylline (PEN) in fixed-mode. The degradation process followed the first-order kinetics. Before proceeding directly to the fixed-bed studies, the prominence of dual effect over individual processes (photocatalysis or photo-Fenton) was first established in slurry mode. An overall synergy of dual process over individual processes was obtained as 19% and 48% in case of CEX and PEN, respectively.

After establishment of dual effect in slurry mode, fixed-bed studies were conducted for the degradation of CEX and PEN using various catalyst support materials. The fixed-bed study was carried out systematically in order to select the most appropriate catalyst support material capable of incorporating in-situ dual effect for the enhanced degradation of target pharmaceuticals. The selection of the catalyst support material was made on the basis of certain factors which include: maximum available exposed surface area of the catalyst, intactness of both catalysts i.e. iron and TiO_2 on the support material for prolonged period and extended durability of the support. The durability of the supported catalyst was found to be strongly dependent upon material and shape of the support. Results showed that recyclability of fine cotton cloth pockets (entrapment material for iron source) used along with either suspended TiO_2 or TiO_2 immobilized clay beads for dual effect studies, was not up to the mark. The pockets were recycled for a maximum number of 8 times with notable reduction in the degradation efficiency of PEN due to the continuous draining off the FS/FA particles from the pores of pockets. Therefore, owing to the poor recyclability efficiency, pockets were not used further.

Thus to seek the better durability and degradation efficiency of supports, clay in conjunction with FS was used to prepare TiO₂ immobilized supports thus, incorporating both the catalysts (iron + TiO₂) within the same support. Using these raw materials (FS and clay), TiO₂ immobilized supports of varying shapes including hollow circular disc, rectangular slabs and spherical beads were prepared. The prominence of dual effect over individual processes was confirmed in each case. However, among these varying shaped catalyst immobilized supports, spherical beads depicted the best degradation efficiency of CEX (80%) owing to the availability of maximum exposed surface area of catalyst (0.0265 m²). The beads were recycled for almost 10 runs with almost 15% reduction in the degradation efficiency of CEX. Hence, some variations or modifications in the support material were still required to further enhance their recyclability efficiency. Actually, addition of FS along with clay reduced the binding efficiency of support.

As a result, addition of FA along with FS in conjunction with clay provided sufficient compressive strength to the beads. These TiO₂ immobilized beads containing FS and FA were recycled for maximum number of times (> 45 recycles) and were named as Fe-TiO₂ composite beads. The recyclability efficiency of composite beads was counter confirmed through different characterization techniques like SEM/EDS, XRD and DRS. These Fe-TiO₂ composite beads were used for carrying out the proper optimization of in-situ dual process for the degradation of CEX and PEN. The optimized conditions obtained for the degradation of CEX and PEN using Fe-TiO₂ composite beads were V = 200 mL, H₂O₂ = 150 mgL⁻¹, average bead diameter = 15 mm, number of TiO₂ coatings = 2 and calcinations temperature = 400 °C. At these optimized conditions, 94% degradation of CEX after 210 min and 85% degradation of PEN after 120 min were achieved under natural solar irradiations. With in-situ dual process, the treatment time was reduced to less than half as compared to individual processes in case of both compounds i.e. CEX and PEN. In addition to this, more than 20% synergy of in-situ dual process over individual processes was confirmed in each case.

Further, an almost complete mineralization of CEX and PEN via in-situ dual process using Fe-TiO₂ composite beads was validated through significant reduction in COD (> 80%) and TOC (> 70%) along with generation of anions like nitrite, nitrate and sulfate in each case. The intermediates formed during the degradation process of each compound were also identified through GC-MS analysis which further validated the decomposition of CEX and PEN. The non-

toxic nature of the treated solutions of CEX and PEN was confirmed through cyto-toxicity and acute toxicity analysis.

The applications of doped TiO_2 (Ag-TiO_2 , N-TiO_2 and N-Ag-TiO_2) were also visualized in fixed-mode especially in conjunction with in-situ dual effect concept. This fixed-bed modified in-situ dual process has not been discussed before in any of the reported studies till date. The light absorption capacity of modified Fe-TiO_2 composite beads was significantly enhanced resulting in narrowing of the band gap energy (up to 2.73 eV in case of Fe-N-Ag-TiO_2 composite) as confirmed through DRS analysis. The degradation rate constant followed the successive trend for the degradation of CEX via modified in-situ dual process: Fe-N-Ag-TiO_2 composite (0.025 min^{-1}) > Fe-Ag-TiO_2 composite (0.020 min^{-1}) > Fe-N-TiO_2 composite (0.018 min^{-1}) > Fe-TiO_2 composite (0.016 min^{-1}) > blank composite (0.005 min^{-1}). These modified composite beads were recycled 10 times with almost 10% reduction in the degradation efficiency of CEX.

Scale-up studies were also conducted with the development of pilot-scale solar fixed-bed reactors using novel Fe-TiO_2 composite beads incorporating in-situ dual effect. Recirculation type fixed-bed glass reactor with volume handling of 5 L was employed for the degradation of PEN using Fe-TiO_2 composite beads under natural solar irradiations. Around 93% degradation of PEN was achieved after 4 h of solar irradiations at optimized conditions i.e. oxidant dose of 0.9 gL^{-1} with adequate number of composite (composite covering 75% of reactor bed area) and 3 baffles at recycle flow rate of 0.8 Lmin^{-1} . On the other hand, once-through fixed-bed cascade reactor with volume handling of 5 L was employed for the degradation of CEX using Fe-TiO_2 composite beads under natural solar irradiations. The reaction performance of the once-through cascade reactor system (comprising of six packed-bed reactors in series) with a space time (τ) of 12 min and incorporating in-situ dual effect approached to that of plug-flow reactor (PFR). An almost 70 % degradation of CEX was achieved at the exit of 6th reactor of cascade system operated at an optimized flow rate of 0.05 Lmin^{-1} . In addition to this, Fe-TiO_2 composite beads depicted an excellent recyclability efficiency (> 70 cycles) even under continuous flow conditions as confirmed through SEM/EDS, DRS, XRD, XPS and TGA analysis. The detailed evaluation of overall cost of the treatment process using each type of pilot-scale reactor further

visualized the practical feasibility of the presented in-situ dual process using highly durable Fe-TiO₂ composite beads.

The real-time applications of in-situ dual process using Fe-TiO₂ composite beads were demonstrated in context to the treatment of real effluent from a pharmaceutical industry. The combination of coagulation and in-situ dual process (using Fe-TiO₂ composite beads) efficiently removed the recalcitrant and toxic chemicals from real wastewater resulting into significant reduction in COD (90%) after 6 h of treatment at optimized conditions. The optimized conditions obtained through RSM for the treatment of real wastewater via in-situ dual process were time = 6 h, H₂O₂ dose = 1155 mgL⁻¹ and catalyst dose equivalent to 102% area of reactor bed covered with Fe-TiO₂ composite beads. The biodegradability index (BOD₅/COD) of wastewater reached to 0.8 from 0.172 at these optimized conditions. The treatment time was significantly reduced to less than 120 min when treatment of wastewater was carried out in a pilot-scale once through fixed-bed cascade reactor at a flow rate of 0.05 Lmin⁻¹ using the same Fe-TiO₂ composite beads under natural solar irradiations. The recalcitrant and toxic chemicals present in the raw effluent were either completely removed or transformed into non-toxic intermediates after the treatment process as confirmed through GC-MS analysis. The non-toxic nature of treated solution (confirmed through cyto-toxicity and acute toxicity analysis) further validated the efficacy of presented in-situ dual process towards the treatment of industrial effluents.

Applications of novel Fe-TiO₂ composite beads capable of incorporating in-situ dual effect in the treatment of real pharmaceutical effluent have claimed our novelty for real time applications of the proposed technology. The extended durability and stability of composite beads further highlights its commercial applications.

5.2 Recommendations

Fixed-bed in-situ dual process using Fe-TiO₂ composite beads has shown its great potential for the treatment of water/wastewater containing recalcitrant compounds such as pharmaceuticals. The use of waste materials like foundry sand and fly ash as alternative sources or iron has represented a good recycling/reuse option for minimizing such hazardous waste from the environment. Thus, future research would aim towards the utilization of more waste

materials from the environment as either alternative sources of iron or as effective binding materials that can be used to prepare more durable catalyst immobilized supports.

Furthermore, the future investigations would emphasize on the more techno-economic analysis for the establishment of large-scale applications of in-situ dual process in context to wastewater treatment using more durable and efficient composite materials.

The enhanced degradation as well as photo-response efficiency of the doped catalysts has been visualized especially in conjunction with in-situ dual effect in fixed-mode. Thus, advanced techniques for catalyst synthesis using low cost sources of dopant could provide a better and sustainable solution in research and development of photocatalysis. Moreover, studies related to in-situ dual process in conjunction with modified catalysts could be extended to large scale.

The use of same composite beads with more efficient reactor design capable of handling large volumes can open up new channels in the field of wastewater treatment with applications of advanced oxidation technology.

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APPENDIX



**Sophisticated Analytical Instruments Laboratories
Society** *(Registered as Society with Registrar of Firms & Societies, Punjab, Chandigarh)*
Thapar Technology Campus, Bhadson Road, Patiala-147 004 (India)

TEST REPORT

Test Report No.:	NN/17-18/201	Date:	25.09.2017
Service No.	NN/17-18/201 (01)	Customer's Ref.	Sample submitted by Ms. Palak on dtd 20.09.2017
Customer's name and address:			
To School of Energy and Environment Thapar University Patiala Kind attn: Dr. Anoop Verma			
Sample Description		Effluent Samples (Research Samples)	
Condition of the sample received		O.K.	
Customer's sample identification No. (if any)		--	
Quantity/number of samples		One	
Sampling Procedure (if any)		--	
Test parameters		Toxicity	
Standard/Specification/Method followed		IS:6582-2001	
Deviations (if any)		--	
Documents constituting this report (if any)		--	
Date of Receipt of Job		Date of Completion of Job	Total Number of Pages
20.09.2017		25.09.2017	1

TEST RESULTS

S. No.	Parameters	Test Method	Unit	Result
1	Toxicity	IS:6582-2001	--	100% survival in as such sample after 96 hours.

.....end of report.....


S.Chandra
 Head, SAI Labs
 (Authorized Signatory)

**Figure A1: Acute toxicity analysis of the treated sample of CEX via in-situ dual process
(Section 4.7.12).**



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Thapar Technology Campus, Bhadson Road, Patiala-147 004 (India)

TEST REPORT

Test Report No.:	NN/15-16/272	Date:	11.03.2017
Service No.	NN/15-16/272 (01)	Customer's Ref.	Sample submitted by Ms. Palak dtd 07.03.2017
Customer's name and address:			
To School of Energy & Environment Thapar University Patiala Kind attn: Dr. Anoop Verma			
Sample Description		Waste Water	
Condition of the sample received		O.K.	
Customer's sample identification No. (if any)		--	
Quantity/number of samples		One	
Sampling Procedure (if any)		--	
Test parameters		Toxicity	
Standard/Specification/Method followed		IS:6582-2001	
Deviations (if any)		--	
Documents constituting this report (if any)		--	
Date of Receipt of Job		Date of Completion of Job	Total Number of Pages
07.03.2017		11.03.2017	1

TEST RESULTS

S. No.	Parameters	Test Method	Unit	Results
1	Toxicity	IS:6582-2001	--	100% survival in as such sample after 96 hours

.....end of report.....

S.Chandra
Head, SAI Labs
(Authorized Signatory)

- Note:
1. The results listed refer only to the tested samples and applicable parameters. Endorsement of products is neither inferred nor implied.
 2. Samples will be destroyed after one month from the date of issue of the test report unless otherwise specified
 3. This report is not to be reproduced wholly or in part and cannot be used as an evidence in the products is neither inferred nor implied. court of law and should not be used in any advertising media without special permission in writing.
 4. In case any reconfirmation of contents of the test report is required, please contact the authorized signatory of the test report within 15 days of the issue of test report

Figure A2: Acute toxicity analysis of the treated sample of PEN via in-situ dual process (Section 4.7.12).

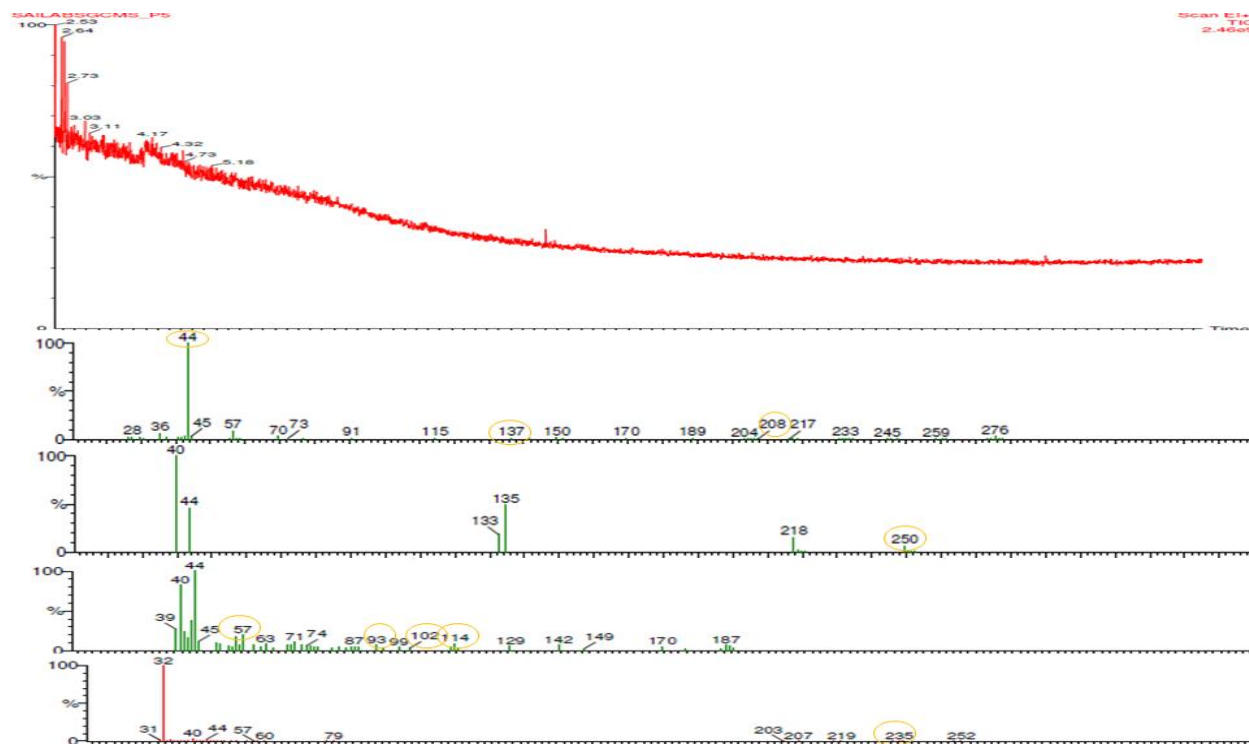


Figure A3: GC-MS chromatograms for the identification of intermediates during the degradation of PEN via modified in-situ dual process (Section 4.8.4).

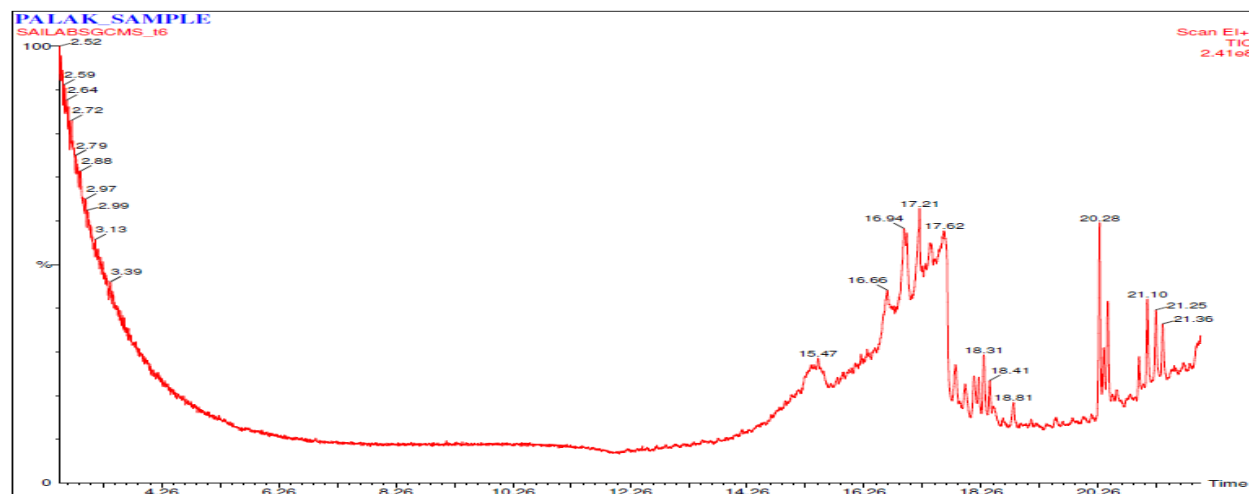


Figure A4: GC-MS chromatograms for the identification of intermediates during the degradation of CEX via modified in-situ dual process (Section 4.9.6).

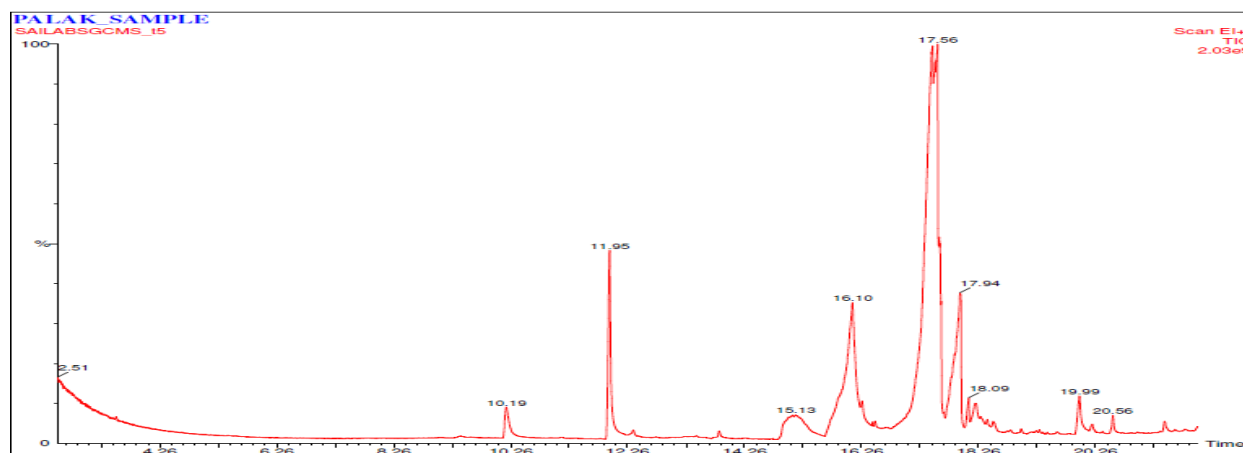


Figure A5: GC chromatograms for the identification of intermediates during the degradation of CEX (Section 4.11.6).

Text A1: Calculation of photonic efficiency (Section 4.8 - 4.10)

The photonic efficiency of the photocatalytic system in each case was quantified as the ratio of photocatalytic degradation rate and the incident photon flux, as depicted in the following equation:

$$\zeta = \frac{R}{I} \times 100$$

Where, ζ is the photonic efficiency (%), R is the photodegradation rate of PEN ($\text{mol L}^{-1} \text{s}^{-1}$) and I is the incident photon flux ($\text{E L}^{-1} \text{s}^{-1}$).

Few approximations have been adopted for the calculation of incident photon flux as discussed below. The average solar intensity reaching the ground surface during the experimental period was 835 Wm^{-2} as measured through pyranometer. Around 3% of the total average solar intensity corresponds to ultraviolet radiations in the range of wavelength from 200-400 nm while, 44% of the total solar intensity corresponds to visible region from 400-800 nm. The values of incident light intensity were obtained through certain approximations in the present study.

Incident photon flux (I_0) ($\text{Einstein L}^{-1} \text{s}^{-1}$) was calculated using the following equation:

$$I_0 = \left[I \times \lambda \times \left(\frac{A}{V} \right) \right] \div [h \times c \times N_A]$$

I = incident light intensity (Wm^{-2}), λ = wavelength (m), A = area of photo-reactor (m^2),

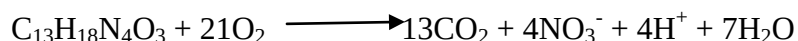
V = volume of solution to be treated (L), h = Planck's constant (6.626×10^{-34} Js), speed of light (3×10^8 ms⁻¹) and N_A = Avogadro number (6.022×10^{23}).

Text A2: Calculation for mass balance of CO₂ formation in case of PEN (Section 4.10.4)

Initial concentration of PEN applied = 50 ppm (0.179 mM)

Amount of PEN in 5 L = 0.898 mM

Complete mineralization of PEN can proceed according to the following equation:



13 molecules of CO₂ could be produced by 1 molecule of PEN

Highest amount of CO₂ that could be produced = $13 \times 0.898 = 11.67$ mM

Amount of CO ₂ produced (ppm)	Amount of CO ₂ produced in 5 L (mM)	Percentage of CO ₂ formed
93.96	$\frac{93.96 \times 5000 \times 1000}{1000 \times 1000 \times 44} = 10.66$	$\frac{10.66}{11.67} \times 100 = 91.3\%$

Text A3: Calculation for mass balance of CO₂ formation in case of CEX (Section 4.11.7)

Initial concentration of CEX applied = 50 ppm

Amount of CEX in 5 L = 0.72 mM

Complete mineralization of CEX can proceed according to the following equation:



16 molecules of CO₂ could be produced by 1 molecule of CEX.

Highest amount of CO₂ that could be produced = $16 \times 0.72 = 11.52$ mM

Amount of CO ₂ produced (ppm)	Amount of CO ₂ produced in 5 L (mM)	Percentage of CO ₂ formed
70.18	$\frac{70.18 \times 5000 \times 1000}{1000 \times 1000 \times 44} = 7.97$	$\frac{7.97}{11.52} \times 100 = 69.2\%$



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TEST REPORT

Test Report No.:	NN/17-18/241	Date:	25.11.2017
Service No.	NN/17-18/241 (01)	Customer's Ref.	Sample submitted by Ms. Palak on dtd 21.11.2017
Customer's name and address:			
To School of Energy and Environment Thapar University Patiala Kind attn: Dr. Anoop Verma			
Sample Description		Effluent Samples (Research Samples)	
Condition of the sample received		O.K.	
Customer's sample identification No. (if any)		--	
Quantity/number of samples		One	
Sampling Procedure (if any)		--	
Test parameters		Toxicity	
Standard/Specification/Method followed		IS:6582-2001	
Deviations (if any)		--	
Documents constituting this report (if any)		--	
Date of Receipt of Job		Date of Completion of Job	Total Number of Pages
21.11.2017		25.11.2017	1

TEST RESULTS

S. No.	Parameters	Test Method	Unit	Result
1	Toxicity	IS:6582-2001	--	100% survival in as such sample after 96 hours.

.....end of report.....

S. Chandra
Head, SAI Labs
(Authorized Signatory)

- Note:
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SAI/FM/CSC-11

Figure A6: Acute toxicity analysis of the treated sample of real pharmaceutical effluent via in-situ dual process (Section 4.12.8).

LIST OF CONTRIBUTIONS

➤ Published Articles

- Bansal, P., & Verma, A. (2017). Synergistic effect of dual process (photocatalysis and photo-Fenton) for the degradation of Cephalexin using TiO₂ immobilized novel clay beads with waste fly ash/foundry sand. *Journal of Photochemistry and Photobiology A: Chemistry*, 342, 131-142.
- Bansal, P., & Verma, A. (2017). Novel Fe-TiO₂ composite driven dual effect for reduction in treatment time of pentoxifylline: Slurry to immobilized approach. *Materials & Design*, 125, 135-145.
- Bansal, P., & Verma, A. (2018). In-situ dual effect studies using novel Fe-TiO₂ composite for the pilot-plant degradation of pentoxifylline. *Chemical Engineering Journal*, 332, 682-694.
- Bansal, P., Verma, A., Mehta, C., Singla, J., & Toor, A.P. (2018). Assessment of integrated binary process by coupling photocatalysis and photo-Fenton for the removal of Cephalexin from aqueous solution. *Journal of Materials Science*, 53, 7326-7343.
- Bansal, P., & Verma, A. Pilot-scale single-step reactor combining photocatalysis and photo-Fenton aiming at faster removal of Cephalexin. *Journal of Cleaner Production*, 195, 540-551.
- Bansal, P., Verma, A., & Talwar, S. Detoxification of real pharmaceutical wastewater by integrating photocatalysis and photo-Fenton in fixed-mode. *Chemical Engineering Journal*, 349, 838-848.

➤ Articles Under Review

- Bansal, P., & Verma, A. Applications of sunlight responsive Fe-Ag-TiO₂ composite incorporating in-situ dual effect for the degradation of pentoxifylline. *Material Science and Engineering: B*

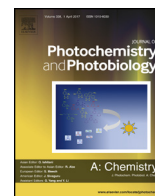
- Bansal, P., & Verma, A. Applications of Ag and N co-doped TiO₂ for the enhanced degradation of Cephalexin: In-situ dual effect studies. ***Chemosphere. (Revision sent)***

➤ **Conference Presentations**

- Poster Presentation on “Assessment of in-situ dual effect (photocatalysis and photo-Fenton) for the degradation of Cephalexin in fixed-bed mode” International Conference on Advanced Oxidation Processes, AOP-2016, BITS Goa. December 17-20, 2016.
- Oral Presentation on “Dual effect studies (photocatalysis and photo-Fenton) for the degradation of Cephalexin in fixed-bed mode” International Conference on Harnessing Engineering Technology & Innovation for Sustainable Growth, HETIS 2016, Punjab University, Chandigarh.

➤ **Workshops attended**

- Participated in International Workshop on “Heterogeneous Catalysis and Applications” delivered by Prof. Alex Ibadon, The University of Hull, UK organized by Global Initiative for Academic Networks (Gian) held at Panjab University, Chandigarh. August 01-05, 2016.



Invited paper

Synergistic effect of dual process (photocatalysis and photo-Fenton) for the degradation of Cephalexin using TiO₂ immobilized novel clay beads with waste fly ash/foundry sand

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ABSTRACT

Novel composite clay beads mixed with foundry sand (FS)/fly-ash (FA) were used as support materials for fixing the catalyst TiO₂ and subsequently used as iron source. The in-situ iron generation in case of beads that contained either FS/FA or both induced dual effect (photo-Fenton and photocatalysis) in the same treatment unit thus leading to synergistic effect for the degradation of antibiotic Cephalexin. Composite beads (FS/FA/TiO₂) showed relatively best results (89% degradation) as compared to FS/TiO₂ (79%) or FA/TiO₂ (81%) at optimized conditions. From the kinetics data, there was 30–45% increase in first order rate constant in case of FS/FA/TiO₂ beads pertaining to dual effect. The stability of the catalyst even after 35 recycles, as confirmed through SEM/EDS and XRD analysis; justified its claim for field-scale applications. Further, mineralization of pollutant was validated by reduction in COD (82%) along with generation of various anions whereas intermediate products were identified through GC–MS analysis.

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1. Introduction

There have been recent concerns related to the management and handling of industrial waste like foundry sand (FS) and fly-ash (FA) as they can pose serious threats to the society. With established environmental and health impacts of these kinds of waste, there is widespread demand of efficient handling of these waste. Worldwide generation of FA and FS is approximately 131 and 13 million tonnes per year, respectively [1,2]. Their effective management in terms of recycling/reuse is a need of the hour as large amounts of chemicals and manpower have been required to handle this kind of environmental concern. The studies pertaining to the utilization of such kind of waste as construction material [3] or as adsorbents for contaminants [4,5] have been reported. With known composition of iron, aluminium, FS/FA can be effectively used for wastewater treatment. Very few studies have demonstrated the efficacy of waste FA and FS to be recycled and used as low-cost alternative iron source in water treatment technologies [6,7]. However, the present study innovates the in-situ dual effect concept using FS and FA for treating the non-biodegradable waste with reduction in treatment time.

The increasing emphasis on the development of environment friendly and effectual treatment methods to completely eliminate recalcitrant organic pollutants from wastewater has prompted the scientists to investigate new innovative modifications that can be implanted in the present advanced wastewater treatment technologies. Among advanced oxidation processes, one of the economic alternative that has shown promising results in the field of wastewater treatment is the photo-Fenton process that produces hydroxyl radicals through the catalytic activity of Fe²⁺/Fe³⁺ in the presence of hydrogen peroxide [8–11]. However, the generation of iron sludge and incomplete mineralization of organic pollutants are the major drawbacks of this process [12]. Further, lower efficiency of photon utilization restricts its industrial applications [13].

Among advanced oxidation processes, another method that has been extensively explored is TiO₂ photocatalysis for the transformation of large variety of non-biodegradable pollutants into inorganic species [14–16]. The use of TiO₂ suspensions offers more desirable degradation efficiency due to better mass transfer applications and more effective illumination of the catalyst surface. The main pitfall of using suspended catalyst is its separation from the aqueous solution after treatment which becomes a hurdle towards its commercial applications [17]. Therefore, a viable solution to the preceding problem is immobilization of TiO₂ over some suitable inert support materials

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in a manner so as to avail sufficient amount of surface area to attain an effectual photodecomposition of the pollutants [18,19]. An extensive literature is available on the fixed-bed photocatalytic degradation of different organic pollutants using several types of support materials like cellulose fibre cloth [20], SBA-15 [21], cement beads [22], pebbles [23], silica gel beads [24], glass spheres [25], glass plate [26], cement slabs [27]. Although effective durability of the supports has been quoted in these studies but the increase in treatment time has always been a concern due to mass transfer limitations. Moreover, the successful implementation of photocatalytic systems has not been accomplished yet because of certain operational implications as well as high energy costs. These implications can be handled by modifying the process along with proper optimization of all the operating parameters which subsequently give way to their field-scale applications [28].

To enhance the degradation efficiency and reduce the time of photocatalytic reaction, many efforts have been devoted and reported in literature for increasing the concentration of hydroxyl radicals prevailing in the photocatalytic process. Addition of oxidants like H_2O_2 , $\text{S}_2\text{O}_8^{2-}$, IO_4^- , ClO_4^- have already been proven effective for improving the reaction rate [29,30]. There are recent reports where coupling of the two processes (photocatalysis and photo-Fenton) have been cited for achieving higher degradation efficiency [28]. Although successful yet the viability of the process for commercial or field-scale utilization is still debatable. Most of the reported studies [31,32] deal with the cases where both the catalyst are in suspension form thus restricting the practical applicability of the technique due to the separation of catalyst post-treatment. None of the studies have been reported with complete immobilization of both catalysts (iron source and TiO_2) for the degradation of pollutants. Moreover treatment time for the degradation of the target pollutant was on higher side in these reported studies.

An effective utilization of waste FS and FA in dual process (photo-Fenton and photocatalysis) has been done to incorporate the synergistic effects of both processes so as to boost the

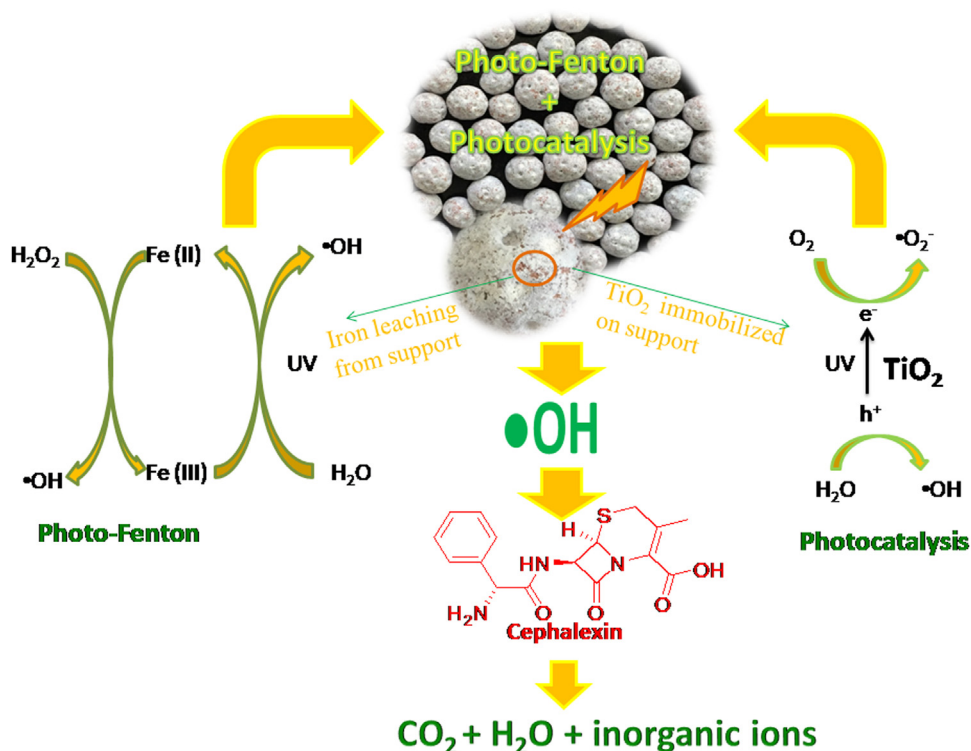
degradation efficiency with reduction in treatment time for the removal of organic pollutants from water (Scheme 1). This is the first reported study of the dual effect with in-situ iron leaching besides giving value addition to waste. The model pollutant selected for the current research work is a cephalosporin β -lactamic antibiotic, Cephalexin (CEX) which is most commonly used to treat several urinary and respiratory tract infections. Cephalexin exhibits only 10% biotransformation rate leading to the fact that rest 90% is excreted out in urine unchanged [33]. The evidence of non-biodegradability of CEX can be revealed from its ubiquitous presence in various aquatic environments such as coastal water [34], municipal wastewater [35] and treated effluent from industry [36].

In the present investigation, the degradation of CEX using supported TiO_2 incorporating the dual effect has been demonstrated in batch experiments. TiO_2 was immobilized on various types of spherical beads comprising of appropriate portions of clay, FS and FA. These beads were assessed and checked for their efficacy and durability for the degradation of CEX. The various operating parameters like number of beads, size of beads, addition of oxidant, buffer, Area/Volume of reactor were optimized for best degradation of the pollutant. Further, mineralization of the pollutant was confirmed by reduction in COD along with monitoring of sulphate, nitrate and nitrite ions generation while intermediates formed were analyzed through GC–MS. The tentative degradation pathway for CEX has also been proposed.

2. Experimental

2.1. Chemicals and reagents

Cephalexin (CEX), (6R,7R)-7-[(2R)-2-amino-2-phenylacetamido]-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid was procured as a capsule under brand name, 'Phexin' from local drugstore, Patiala (India). CEX was used as collected without any further modification. Degussa P25 TiO_2 , used



Scheme 1. Dual effect of photo-Fenton and photocatalysis for the degradation of CEX.

as a photocatalyst, was obtained from Evonik industries (India). The oxidant, hydrogen peroxide (H_2O_2), 30% w/v was purchased from Ranbaxy, India. For preparing inert support materials, clay was obtained from local vendor whereas waste foundry sand (FS) and fly ash (FA) were received as gift samples from local industry, Patiala (India) and were used without any additional purification. Concentrated H_2SO_4 and NaOH, procured from Merck, were used for pH adjustment. Sodium acetate (>98.5%) and acetic acid (>99.5%) for preparing acetate buffer were purchased from TCI Chemicals (India) Pvt. Ltd. The double distilled water was utilized for the preparation of all solutions.

2.2. TiO_2 immobilization

For TiO_2 immobilization, four kinds of beads of varying diameter were made manually with combinations of materials namely a) clay only, b) clay + FS (1:1), c) clay + FA (1:1) and d) clay + FA + FS (2:1:1). FA and FS were characterized for the presence of iron as reported in previous studies [6,11]. Clay was used just as a binding material in the last three cases. Small portion of the mixture containing appropriate amounts of FA, FS and clay was taken and spherical beads were prepared manually. The curing of beads was done by muffling at 1000°C for 1 h and subsequently drenched in water to become hard and for acquiring proper strength. From the lot, uniform sized beads were picked and their diameter was measured from all directions with vernier caliper. The similar sized beads were selected for catalyst immobilization. TiO_2 was coated on beads using the standard dip-coating method as detailed in our earlier studies [22]. Two coatings were enough for attaining the uniform catalyst film on the beads surface. TiO_2 load on each bead was approximately in the range 30–40 mg. The thin film of catalyst on the beads was confirmed through SEM/EDS analysis with approximate thickness of around $40\text{ }\mu\text{m}$ on each bead. For representing the results, the notations are used accordingly. For catalyst immobilized beads, notations are: a) clay/ TiO_2 beads, b) FS/ TiO_2 beads, c) FA/ TiO_2 beads and d) FS/FA/ TiO_2 beads. Whereas for bare beads (without catalyst immobilization), notations are a) clay beads, b) FS beads, c) FA beads and d) FS/FA beads. Fig. 1(i) depicts the actual photographs of TiO_2 immobilized clay beads and correspondingly SEM/EDS images of bare FS/FA beads and catalyst immobilized FS/FA/ TiO_2 beads is illustrated in Fig. 1(ii). While SEM/EDS images of bare and catalyst immobilized other clay beads are given in Supplementary files (Figs. S1–S3 in Supplementary material).

2.3. Experimental set-up and procedure

The photocatalytic experiments were conducted at laboratory-scale in a wooden UV chamber that contained seven UV tubes (Philips) of 36 W (365 nm) each attached underneath the roof of chamber (Supplementary information, Fig. S4) as detailed in our earlier studies [37]. A 1000 mL borosilicate glass bowl (17 cm diameter and 5 cm height) was utilized as a batch reactor. All experiments were performed at an average UV intensity of $23 \pm 2\text{ W m}^{-2}$ as measured by means of an eppley radiometer (model no. 33013) and can be altered by varying the distance of reactor from the tubes through lab jack. The antibiotic stock solution (100 mg L^{-1}) was made using double distilled water. The working solution of 50 mg L^{-1} (200 mL) was used for the photocatalytic experiments with appropriate number of catalyst immobilized beads. For sustaining the homogeneity of reaction, two spargers were used to supply sufficient amount of aeration. The spargers were placed at equal distance from center along the diameter of reactor thus visibly confirming the uniform aeration throughout the solution. The flow rate of the inlet air was

3.5 L min^{-1} . Adequate amount of sample was collected through syringe after uniform intervals and was subsequently analyzed. After optimization of operating parameters under artificial UV light, the experiments were carried out in natural solar light. All the experiments were performed thrice for reproducibility of results and the standard deviation observed was approximately 3–5%.

2.4. Chemical analysis

The analysis of samples was done through UV–vis spectrophotometer, LABINDIA, model-T60U and HPLC, Shimadzu, Japan (communication module (CBM-20A) with diode array detector (SPD-M20A), pump (LC-20AD)). Binary HPLC system with C-18 column, $250\text{ mm} \times 4.60\text{ mm}$ and particle size $5\text{ }\mu\text{m}$ was used for the performance of HPLC. Ammonium acetate (0.01 M) and acetonitrile (10%) were employed as mobile phase and UV detector was set at 263 nm for Cephalexin while flow rate was retained at 1.0 mL min^{-1} . $20\text{ }\mu\text{L}$ sample was injected and each analysis lasted for 20 min. Gas chromatograph (45×-GC, Bruker, U. S.A) incorporated with mass detector (MS-SCION-45P, Bruker) and equipped with MS wax column (length 30 m and diameter 0.25 mm) was used for the identification of intermediates. The range of scanning mass m/z was set from 50 to 410. Helium, carrier gas was employed at a flow rate of 1.0 mL min^{-1} . The temperature for injector was set at 280°C . The GC oven temperature program was adjusted from 40 to 260°C with 10° increment in temperature. The injection volume of sample was $1\text{ }\mu\text{L}$ and split ratio of GC used was 1:10.

Standard methods were used for the monitoring of nitrite ions [38], nitrate ions [39], sulphate ions [40], COD [41]. Iron was estimated through colorimetric method by determining the colored complex of Fe^{2+} and 1,10-phenanthroline spectrophotometrically at 510 nm [42]. The morphology of blank and TiO_2 immobilized beads was evaluated through SEM (JSM-6510LV, JEOL, Japan) and EDS (INCA-act, Oxford instruments, United Kingdom) analysis for the confirmation of catalyst stability. The structural characteristics of immobilized catalyst were also confirmed through XRD analysis of the catalyst powder extracted from the recycled bead.

3. Results and discussion

3.1. Preliminary studies

Blank experiments were conducted in a batch reactor with bare beads (without catalyst coating) in UV light (Photolytic studies) which revealed only slight degradation of CEX (6–7%) with all kinds of beads i.e. clay, FS, FA and FA/FS beads. While in the presence of catalyst coated beads only (Adsorption studies), 8–10% removal of compound was achieved. This is with respect to the pollutant monolayer formation on the catalyst surface which blocked all active sites due to which no further degradation of pollutant occurred [43]. The presence of H_2O_2 only showed 5% degradation because of negligible amount of hydroxyl radical production. TiO_2 coated beads + UV + H_2O_2 revealed 67–73% removal of CEX with different beads after 5 h of treatment (Fig. 2). However in acidic conditions (in the presence of buffer), the degradation of CEX was further improved to more than 80% after 4 h of treatment in all the cases as discussed in section 3.3. An imperceptible variation in results with all types of beads indicates the uniform distribution and coating of catalyst on each bead leading to dual processes.

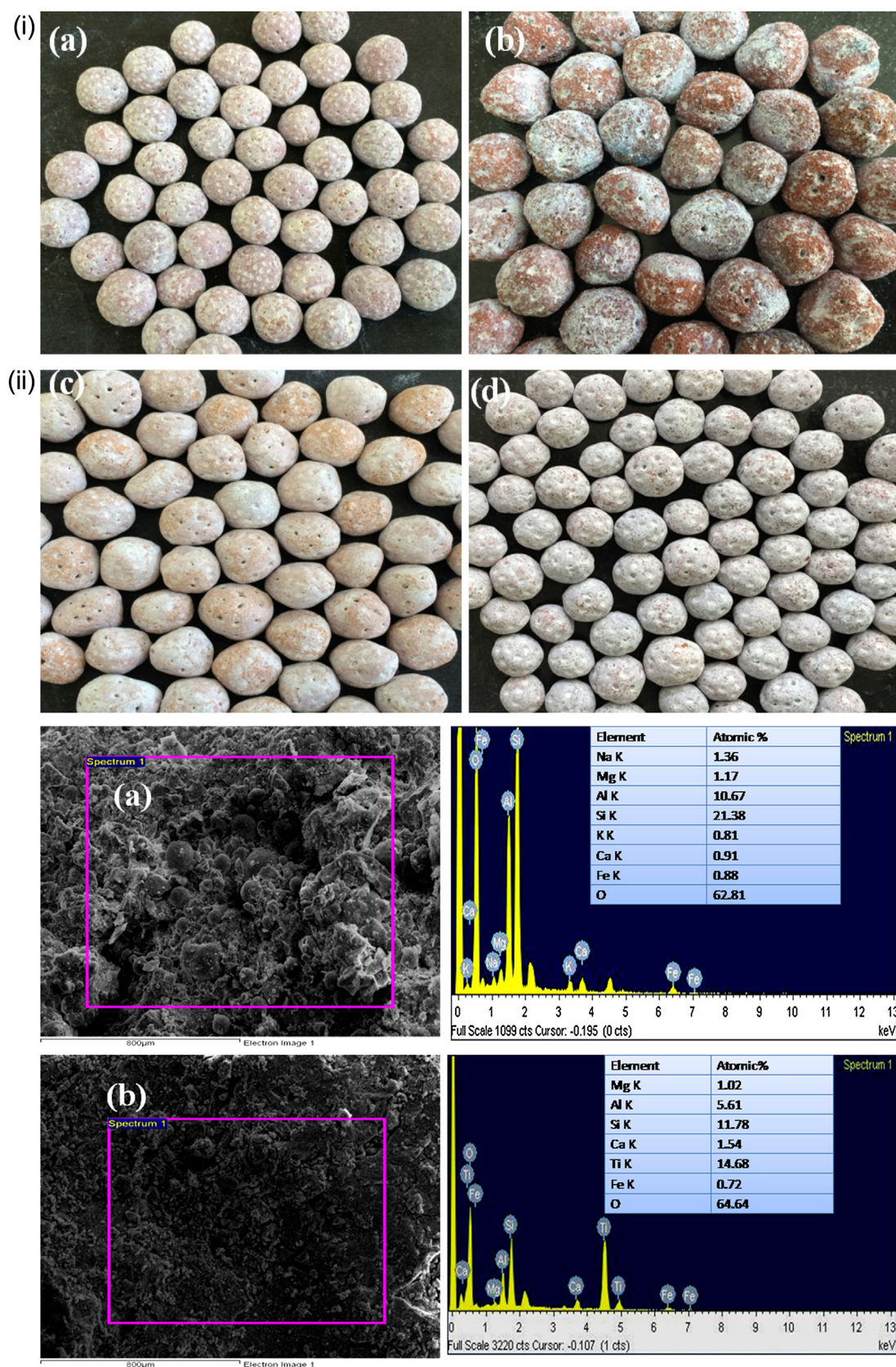


Fig. 1. (i). The actual photographs of TiO_2 immobilized (a) clay/ TiO_2 beads, (b) FS/ TiO_2 beads, (c) FA/ TiO_2 beads and (d) FS/FA/ TiO_2 beads. (ii). SEM/EDS images of (a) bare and (b) catalyst immobilized FS/FA/ TiO_2 beads while that of (i) clay/ TiO_2 beads, (ii) FS/ TiO_2 beads and (iii) FA/ TiO_2 beads are given in Supplementary files.

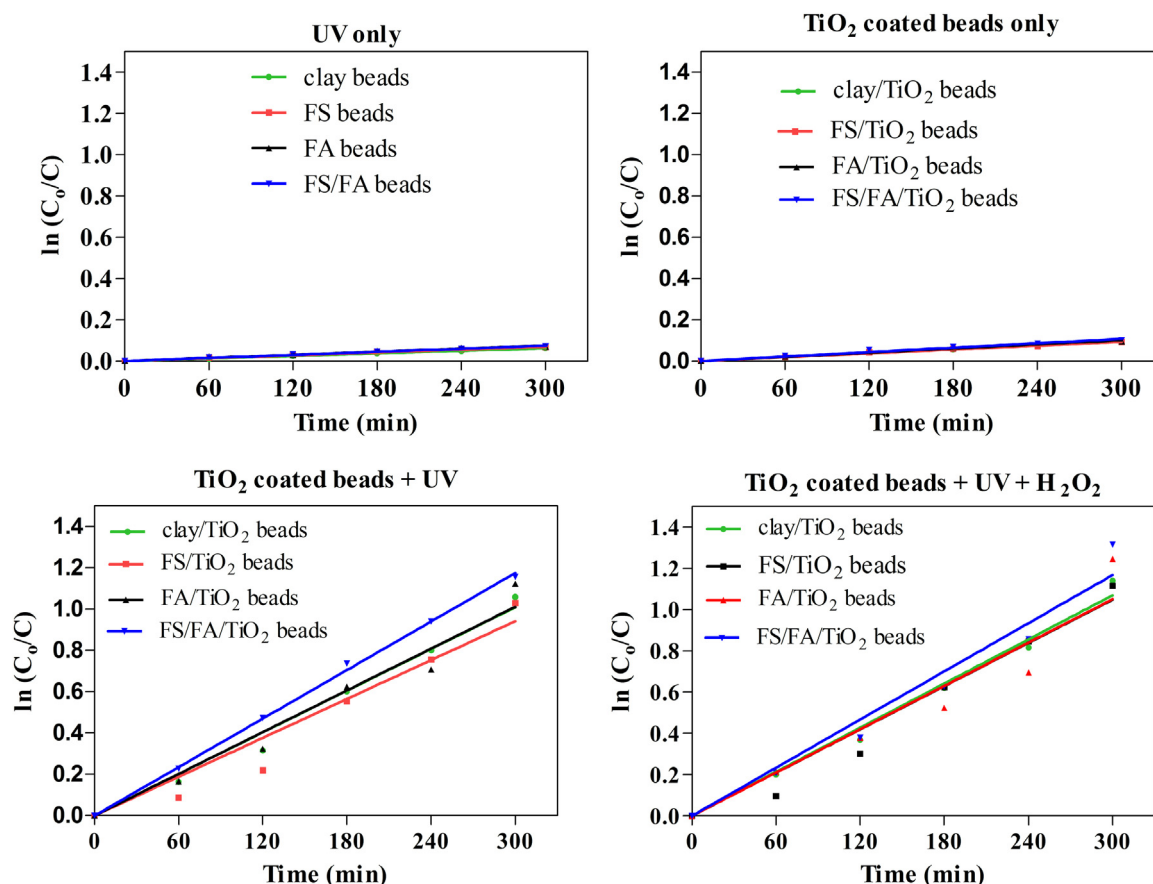


Fig. 2. Preliminary studies for the photocatalytic degradation of CEX in case of clay/TiO₂, FS/TiO₂, FA/TiO₂ and FS/FA/TiO₂ beads under different conditions: (a) UV only (b) TiO₂ coated beads only (c) TiO₂ coated beads + UV (d) TiO₂ coated beads + UV + H₂O₂ ($C_0 = 50 \text{ mg L}^{-1}$, $V = 200 \text{ mL}$).

3.2. Effect of oxidant addition

The improvement in photocatalytic degradation of organic pollutants in aqueous solution by the addition of oxidant like H₂O₂ is now well established and reported in literature [44] as it enhances the production of $\cdot\text{OH}$ radicals. However, overdose of oxidant shows the declining rate of degradation due to the scavenging effect at higher concentration of oxidant. In the present study, H₂O₂ was varied from 75 mg L^{-1} to 375 mg L^{-1} for the degradation of CEX. The addition of H₂O₂ (150 mg L^{-1}) showed an inappreciable increase (only 3–5%) in the degradation efficiency of CEX after 5 h of treatment in each case. This leads to the fact that H₂O₂ did not contribute significantly to the photocatalytic process but same amount of H₂O₂ when used in dual effect studies (Section 3.3) at lower pH revealed higher degradation of CEX thus proving the predominance of photo-Fenton. Moreover, if H₂O₂ was increased beyond 150 mg L^{-1} , scavenging effect prevailed as there was no reduction/significant change in the degradation of CEX as depicted in Fig. 3.

3.3. Dual effect studies

To confirm the prominence of dual effect in case of TiO₂ coated clay beads with FA/FS, efforts were made to study the degradation of CEX at acidic pH. All experiments were conducted under artificial UV-A irradiations with 50 mg L^{-1} of CEX at optimized dose of H₂O₂. The pH was adjusted with $0.1 \text{ N H}_2\text{SO}_4$. Initially experiments were performed using TiO₂ coated clay beads (without FA/FS) in lower pH range to affirm the photocatalytic degradation in

acidic range. As such there was no any sufficient reportable improvement in the degradation of CEX was noticed in lower pH range. In case of TiO₂ coated clay beads with FA/FS, higher degradation rate was observed at lower pH with maximum at pH 3.5 thus validating the dual effect. To further confirm this, separate experiments were carried out for the degradation of CEX with bare beads (without TiO₂ immobilization) containing FA and FS at pH 3.5 with suitable amount of H₂O₂. 35% degradation was achieved in case of FA/FS beads after 5 h of illumination (Fig. 4a). Actually at

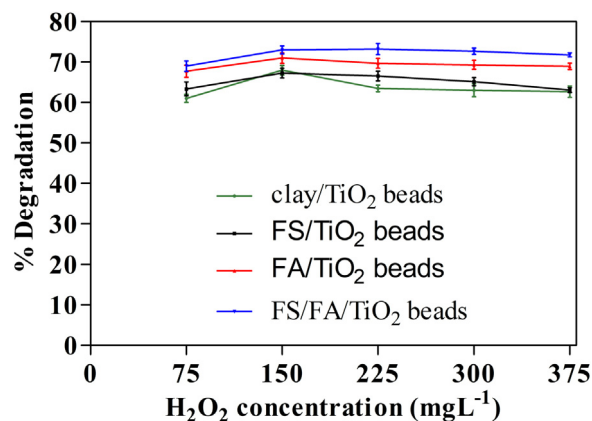


Fig. 3. Plot of % degradation vs variation in H₂O₂ concentration during photo-degradation of CEX in case of clay/TiO₂, FS/TiO₂, FA/TiO₂ and FS/FA/TiO₂ beads ($C_0 = 50 \text{ mg L}^{-1}$, $V = 200 \text{ mL}$).

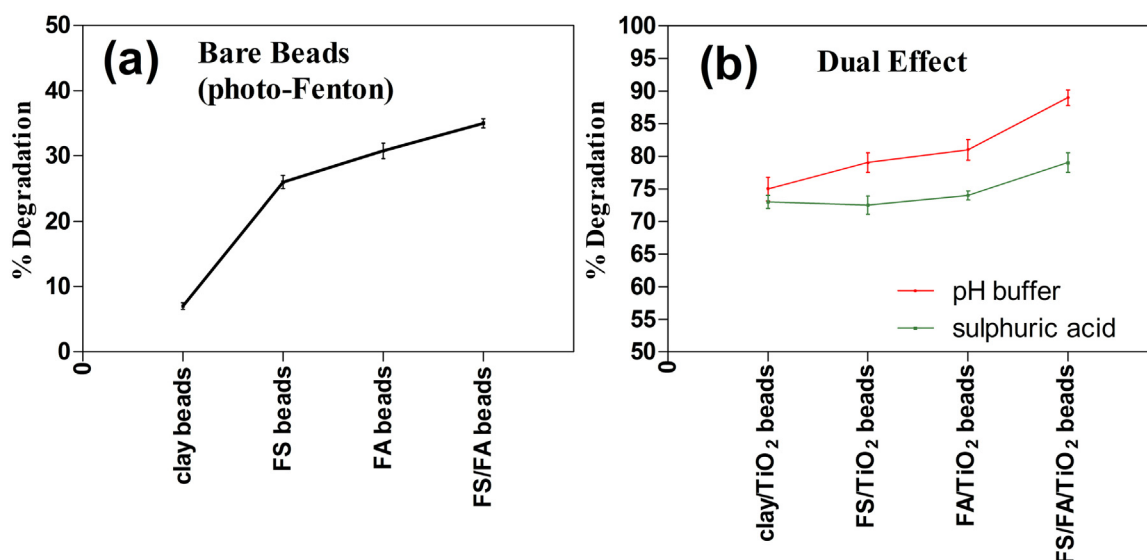


Fig. 4. (a) Degradation of CEX with bare beads (without catalyst immobilization) after 5 h of treatment, (b) Effect of acetate buffer on the degradation of CEX ($C_0 = 50 \text{ mgL}^{-1}$, $V = 200 \text{ mL}$, $\text{H}_2\text{O}_2 = 150 \text{ mgL}^{-1}$, $\text{pH} = 3.5$).

low pH, iron was leaching from the beads containing FA and FS (Table 1) thus confirming the simultaneous effect of photo-Fenton along with photocatalysis leading to the generation of more hydroxyl radicals. The other feasible explanation for better results at low pH is the synergistic effect of photo-Fenton for the degradation of CEX.

However, the main implication observed while studying the dual effect was the slow increase in degradation rate after 1 h of photo-treatment. This was attributed to the increase in pH of solution after few minutes of the reaction. The pH of CEX solution was checked after every 10 min and it increased to around 6.0 after 1 h of photo-treatment (Supplementary information, Table S1). This would lead to the poor adsorption of CEX on catalyst surface along with cessation of photo-Fenton radical reaction. The preceding complication was best resolved by adjusting the pH with acetate buffer as pH of the solution remained acidic throughout the treatment time of 4 h in this case thus accelerating the degradation rate. Therefore, the degradation of CEX was further augmented to more than 80% and reached to a maximum of 89% with beads containing FA and FS after 4 h of treatment instead of 5 h (Fig. 4b). The highest value of first order rate constant, k , under dual effect studies for the photo-degradation of CEX came out to be 0.011 min^{-1} whereas the half-life of CEX was found to be 60 min in case of FA/FS/TiO₂ beads which was considerably lower in comparison to clay/TiO₂ (180 min), FS/TiO₂ (120 min), FA/TiO₂ (90 min) (Table 2).

For the present study, the integrated effect of photocatalysis and photo-Fenton depicted synergistic results for the degradation of CEX as discussed in Section 3.7. Hydroxyl radicals were

generated in abundance (Eqs. (1)–(8)) through the dual processes (photocatalysis and photo-Fenton) occurring simultaneously which led to the improvement in degradation efficiency affirming synergistic effect. During this dual process, recombination of electron and hole pair on TiO₂ surface was inhibited by engaging the photo-excited electron from TiO₂ in regeneration of ferrous ions thereby favoring the photo-Fenton reaction [31] as depicted in Equation (5):

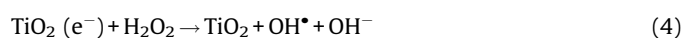
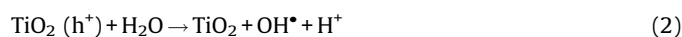


Table 1

Estimation of iron leached out in solution from bare and catalyst coated beads before reaction.

Type of Bead	Iron (mgL^{-1})
Bare beads before reaction	
FS beads	0.31
FA beads	0.43
FS/FA beads	0.75
TiO ₂ coated beads before reaction	
FS/TiO ₂ beads	0.26
FA/TiO ₂ beads	0.356
FS/FA/TiO ₂ beads	0.63

Table 2

Kinetic parameters for the degradation of CEX using different kinds of beads with the addition of acetate buffer for dual effect studies.

Types of beads	$t_{1/2}$ (min)	k (min^{-1})
Clay/TiO ₂	180	0.004
FS/TiO ₂	120	0.006
FA/TiO ₂	90	0.008
FS/FA/TiO ₂	60	0.011

Use of catalyst immobilized support system for subsequent cycles without any loss of its activity is always a concern. In present work the order of stability of immobilized catalyst in terms of catalyst particle intactness over surface of beads for the degradation of CEX was in the order of FA/FS/TiO₂ beads > FA/TiO₂ beads > FS/TiO₂ beads. Accordingly, FS/FA/TiO₂ beads were used for maximum number of cycles. Moreover, the observed rate constants during the dual process were in the following order: FA/FS/TiO₂ beads (0.011 min⁻¹) > FA/TiO₂ beads (0.008 min⁻¹) > FS/TiO₂ beads (0.006 min⁻¹) > clay/TiO₂ beads (0.004 min⁻¹). Actually with FA/FS/TiO₂ beads, iron content also increases which is the main facilitator of photo-Fenton reaction. Thus, it can be concluded that in dual effect studies using FA/FS/TiO₂ beads, the value of *k* increases to almost three fold in comparison to the value of *k* during photocatalysis using clay beads (Fig. 5). As overall best results for degradation of CEX were observed with FA/FS/TiO₂ beads, these beads were selected for conducting further experiments to optimize rest of the operating parameters. The treatment time was also reduced to 4 h with established dual effect in this study in comparison to 5 h as cited in literature [45]. Moreover, the studies reported 76% degradation in slurry mode whereas our studies confirmed 89% degradation in immobilized form, thus authenticating the prominence of dual effect. The outcome of this study would help in designing the dual effect pilot scale fixed-bed reactors (using waste FS, FA) for the treatment of industrial waste.

3.4. Effect of bead size and number of beads

The surface area of the catalyst available for better contact with the pollutant in photocatalytic phenomenon especially in fixed-bed mode is an important operating parameter. This is particularly important when field-scale applications are to be considered as size of the catalyst support materials really help in designing of the pilot-scale reactors where exposure of the catalyst surface area always remain a concern. In the current research work, the surface area of beads was altered by varying the diameter of beads for studying the degradation of CEX. Three different diameter beads of 10 mm, 15 mm and 20 mm, measured by means of vernier caliper, were assessed and compared for the better degradation of CEX. It was observed that degradation rate improved with smaller diameter beads (10 mm) due to the more availability of catalyst surface area (Fig. 6a). However, the catalyst coating was not found to be stable on 10 mm size bead as it was drained away after few recycles. Therefore, 15 mm sized bead was optimized for all the experiments as it was found to be stable in terms of strength and catalyst activity.

For a particular reactor design, the number of catalyst beads required for achieving the desired degradation rate is an important

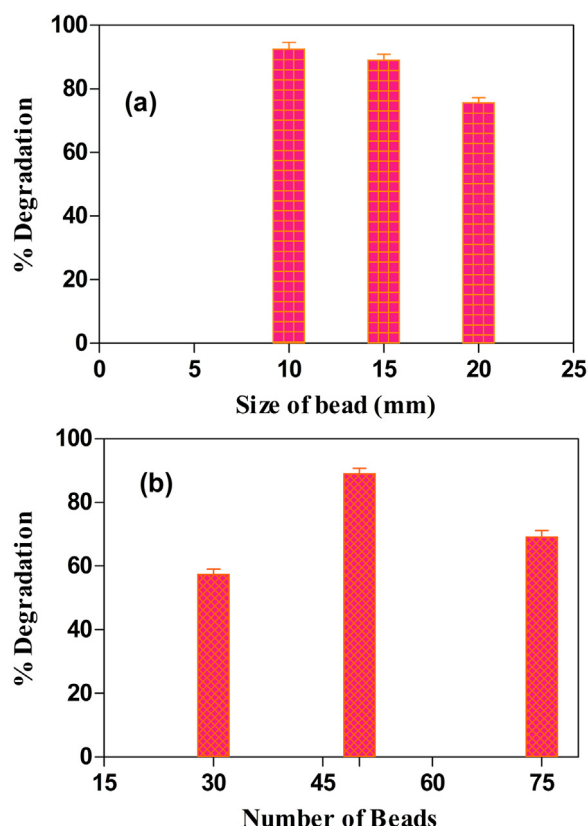


Fig. 6. Plot of % degradation of CEX vs (a) diameter of TiO₂ coated FS/FA/TiO₂ beads and (b) number of TiO₂ coated FS/FA/TiO₂ beads ($C_0 = 50 \text{ mg L}^{-1}$, $V = 200 \text{ mL}$, $\text{H}_2\text{O}_2 = 150 \text{ mg L}^{-1}$, $\text{pH} = 3.5$).

parameter. In our study for a batch reactor, beads were varied from 30 to 70 in number for the degradation of CEX. The best degradation (89%) of CEX was attained with 50 beads covering the whole bottom surface area of the batch reactor (without any overlap of beads) as almost all active sites of the catalyst were exposed and freely available for the pollutant binding which led to its efficient degradation. When number of beads was reduced to 30, degradation rate also decreased (57.35%) as number of available active sites of the catalyst gets reduced. Beads were overlapped one over the other as their number was increased to 70 leading to reduction in degradation rate (Fig. 6b). The reason for this may be the reduction in effective surface area leading to an ineffective binding of pollutant with the catalyst and moreover, it is possible that antibiotic solution got trapped in the void spaces. Moreover, as

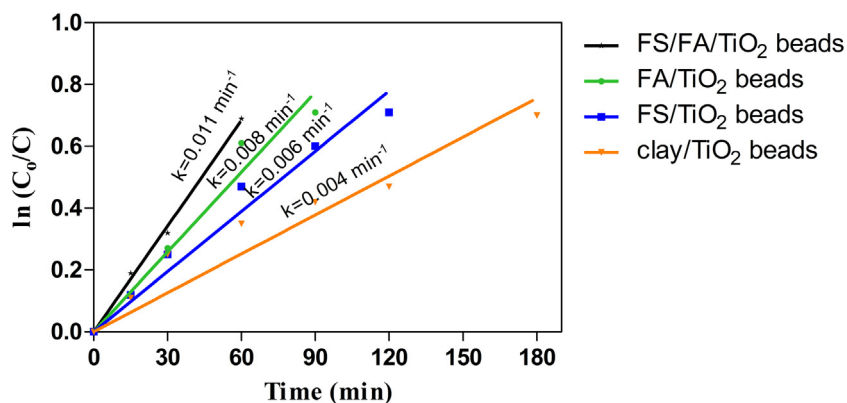


Fig. 5. Plot of first order rate constant vs TiO₂ coated beads during the dual effect studies for the degradation of CEX.

we increase the number of beads, both TiO_2 and iron concentration increases (contributing to both processes i.e. photo-Fenton and photocatalysis) further enhancing the formation of OH radicals. Thus scavenging effect predominates in that case [46,47].

3.5. Degradation studies under natural solar radiations

With established fact that photo-Fenton covers wider spectrum (UV + visible), degradation of CEX was carried out under natural sunlight for all the three processes namely photocatalysis, photo-Fenton and dual process using all the optimized parameters. The experiments were carried out under natural sunlight during the months of March–April from 10:00 a.m. to 2:00 p.m. at Patiala (30.3398°N, 76.3869°E), Punjab (India). The average intensity of solar UV radiations during the period was $24 \pm 3 \text{ W m}^{-2}$ which was measured by pyranometer. As expected, better results were obtained under natural solar radiations for all three processes namely: photo-Fenton 50%, photocatalysis 78% and dual process 94% (Fig. 7) along with reduction in their treatment time. Effect was more prominent in dual effect (as expected) where the treatment time was reduced to 3.5 h as compared to 4 h when reaction was carried out in artificial UV radiations with all optimized conditions.

3.6. Durability studies

The durability and stability of immobilized catalyst mostly depends upon the support material deciding the practical viability of process for field-scale applications. In this context, clay proved to be the excellent binding material for catalyst immobilization which has been checked in terms of number of recycles of catalyst coated beads for the degradation of CEX. The beads were successfully recycled for at-least thirty-five cycles without any significant reduction in their efficiency (Fig. 8i). The SEM/EDS image of recycled beads clearly depicts that catalyst was intact after thirty-five cycles (Fig. 8ii (a)). The peaks of Fe along with Ti and O in EDS data revealed the existence of iron along with TiO_2 even in recycled beads thereby proving the effectiveness of beads for dual effect studies. The activity of catalyst film after 35 recycles was also confirmed through XRD analysis of the immobilized catalyst extracted from the recycled bead (Fig. 8ii (b)). The XRD data revealed that crystalline plane of the immobilized catalyst did not change even after 35 recycles though the intensity of the peaks was lower as compared to the fresh catalyst. The diffraction peaks proved the presence of anatase and rutile phase of TiO_2 marked as

'A' and 'R' respectively in figure. Generally, the catalyst has to be re-activated by exposing it to high temperature after each cycle which is economically not feasible. In our previous study, supported catalyst was re-activated by exposing them either to sunlight or keeping in oven for one hour after every reaction [22]. In the present study, the beads were used as such without giving any heat treatment after reaction and only a slight decrease in percentage degradation of CEX was observed thus proving the stability and durability of immobilized catalyst (Fig. 8iii). The stability of catalyst film with subsequent cycles without any re-activation opens up new channels in the field of waste water treatment with fixed-bed photocatalysis.

3.7. Synergistic effect

Synergistic effects are meant to be the phenomenon when the degradation efficiency of integrated system is more than the sum of individual processes [48]. The synergy of one process over the other for dual effect in the present case was calculated and quantified as per the following Eqs. (9)–(11) [49,50].

Synergy of dual process over photocatalysis:

$$\begin{aligned} \% \text{ Synergy} &= 100 \times \{(k_{\text{dual}} - k_{\text{photocatalysis}}) / (k_{\text{dual}})\} \\ &= 100 \times \{0.007 - 0.004\} / 0.007 \\ &= 42.8\% \end{aligned} \quad (9)$$

Synergy of dual process over photo-Fenton:

$$\begin{aligned} \% \text{ Synergy} &= 100 \times \{(k_{\text{dual}} - k_{\text{photo-Fenton}}) / (k_{\text{dual}})\} \\ &= 100 \times \{0.007 - 0.001\} / 0.007 \\ &= 85.7\% \end{aligned} \quad (10)$$

Overall synergy:

$$\begin{aligned} \% \text{ Synergy} &= 100 \times \{(k_{\text{dual}} - (k_{\text{photocatalysis}} + k_{\text{photo-Fenton}})) / (k_{\text{dual}})\} \\ &= 100 \times \{0.007 - (0.004 + 0.001)\} / 0.007 \\ &= 28.5\% \end{aligned} \quad (11)$$

Thus, dual process with synergistic results prompts its applications at field-scale with drastic decrease in the treatment time besides giving value addition to waste.

3.8. Mineralization studies

The mineralization of CEX was evaluated in terms of COD reduction and generation of nitrite, nitrate and sulphate ions. Production of nitrite, nitrate and sulphate ions was more than 50%

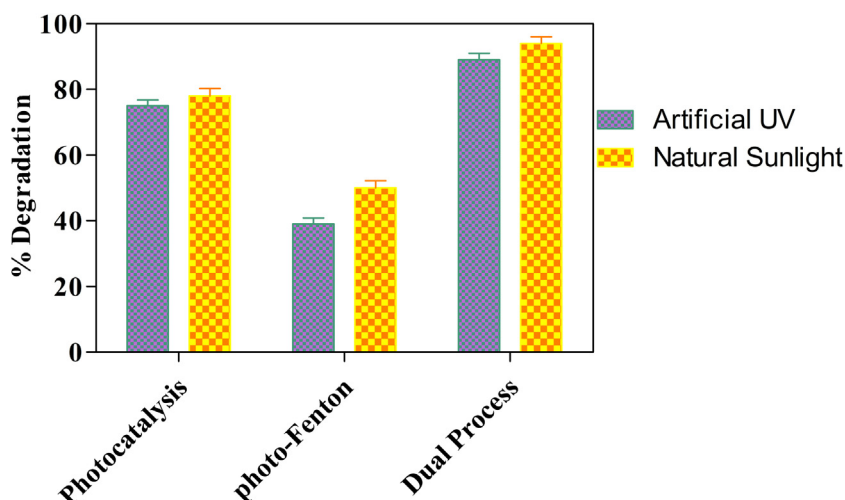


Fig. 7. Effect of natural solar radiations on the degradation of CEX ($C_0 = 50 \text{ mg L}^{-1}$, $V = 200 \text{ mL}$, $\text{H}_2\text{O}_2 = 150 \text{ mg L}^{-1}$, $\text{pH} = 3.5$, average bead diameter = 15 mm).

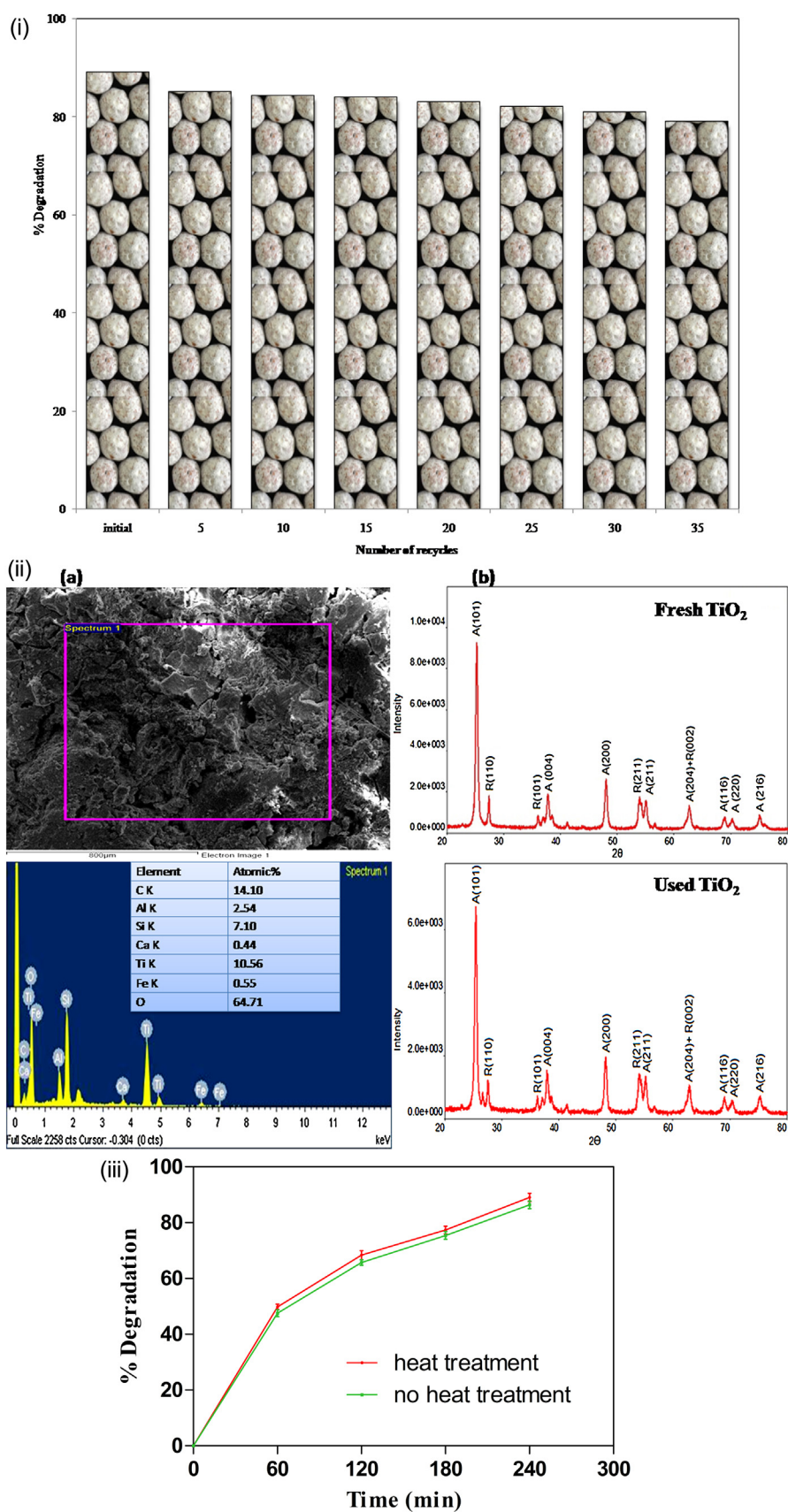


Fig. 8. (i) Durability studies of TiO_2 coated FS/FA/ TiO_2 beads for the photodegradation of CEX ($C_0 = 50 \text{ mg L}^{-1}$, $V = 200 \text{ mL}$, $\text{H}_2\text{O}_2 = 150 \text{ mg L}^{-1}$, $\text{pH} = 3.5$, average bead diameter = 15 mm). (ii) (a) SEM along with EDS image of TiO_2 coated FS/FA/ TiO_2 beads after 35 recycles, (b) XRD pattern of fresh (unused) TiO_2 and used TiO_2 extracted from recycled bead. (iii) Effect of heat treatment on the beads for the degradation of CEX ($C_0 = 50 \text{ mg L}^{-1}$, $V = 200 \text{ mL}$, $\text{H}_2\text{O}_2 = 150 \text{ mg L}^{-1}$, $\text{pH} = 3.5$, average bead diameter = 15 mm).

after the first hour of photo-treatment and reached to 80.7%, 85.6% and 88.17% respectively after 4 h (Fig. 9i). The concentration of ions produced is mentioned in the Supplementary information, Table S2. The actual as well as stoichiometrically balanced chemical equations are provided in the Supplementary information. The COD was reduced to around 82% after 5 h of treatment. The possible intermediates ((2)–(8)) that could be formed were identified through GC–MS analysis as depicted in Fig. 9ii. The probable pathway for the degradation of CEX has been proposed which is shown in Fig. 9iii. The fragmentation of CEX led to the formation of byproducts (2) and (3). While product (2) could either undergo deamination to yield (4) or fragmented into (5). The fragmentation of product (3) could yield intermediates (6) and (7). The successive deamination and demethylation of intermediate (7)

could further yield (8). The expected m/z fragments of CEX and its degradation products are depicted in Supplementary information (Fig. S5 in Supporting material). To the best of our knowledge, this is the first reported study till date depicting the degradation pathway for CEX.

4. Conclusions

The study demonstrated the applicability of novel inert clay beads for catalyst immobilization for the photodegradation of CEX by incorporating the in-situ dual effect. Out of four different kinds of beads, FA/FS/TiO₂ beads depicted the best results in terms of degradation efficiency and number of recycles. The dual effect of two different processes i.e. photo-Fenton and photocatalysis

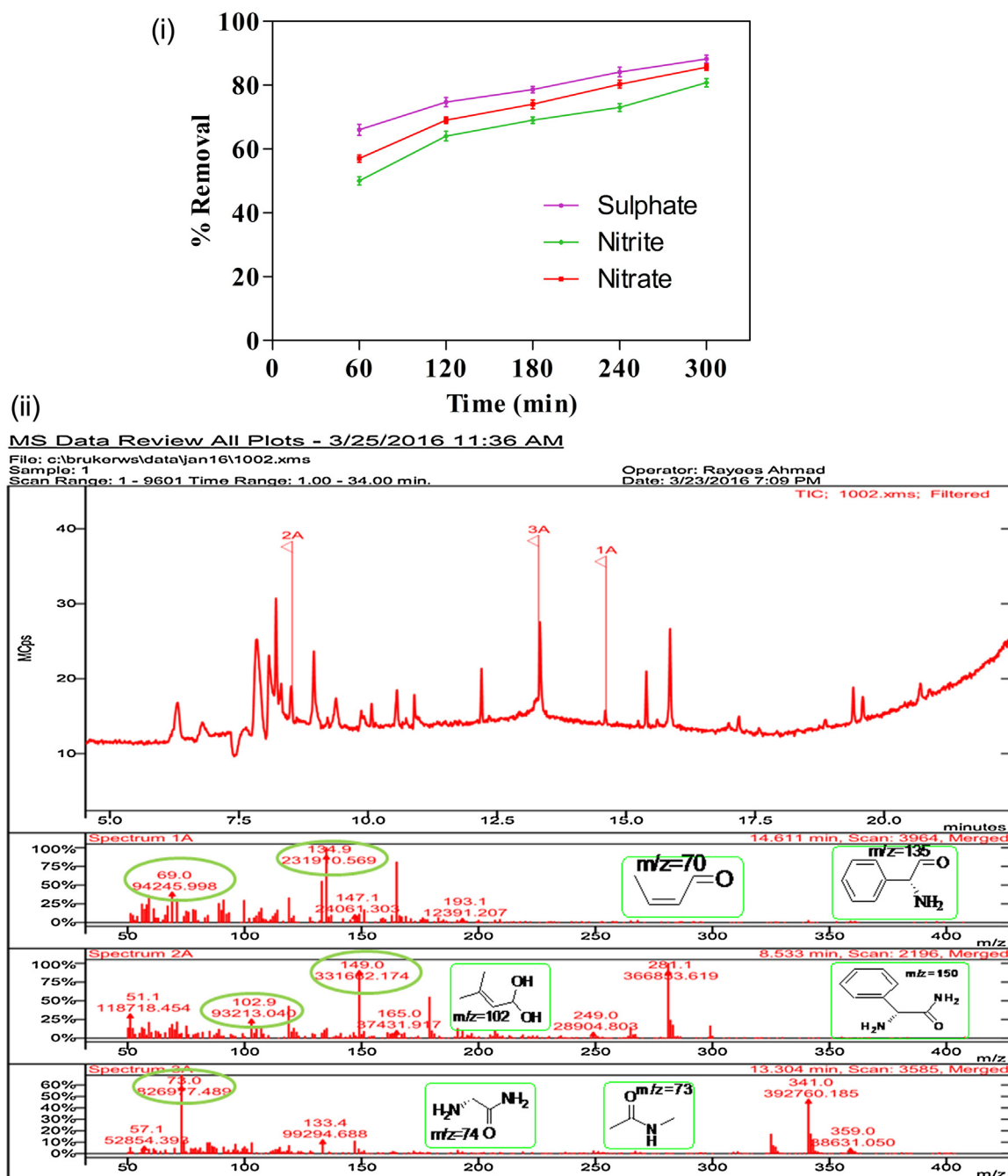


Fig. 9. (i) Generation of nitrite, nitrate and sulphate ions during the photodegradation of CEX. (ii) Mass spectra analysis for the identification of intermediates during the photo-degradation of CEX. (iii) Proposed degradation pathway for CEX.

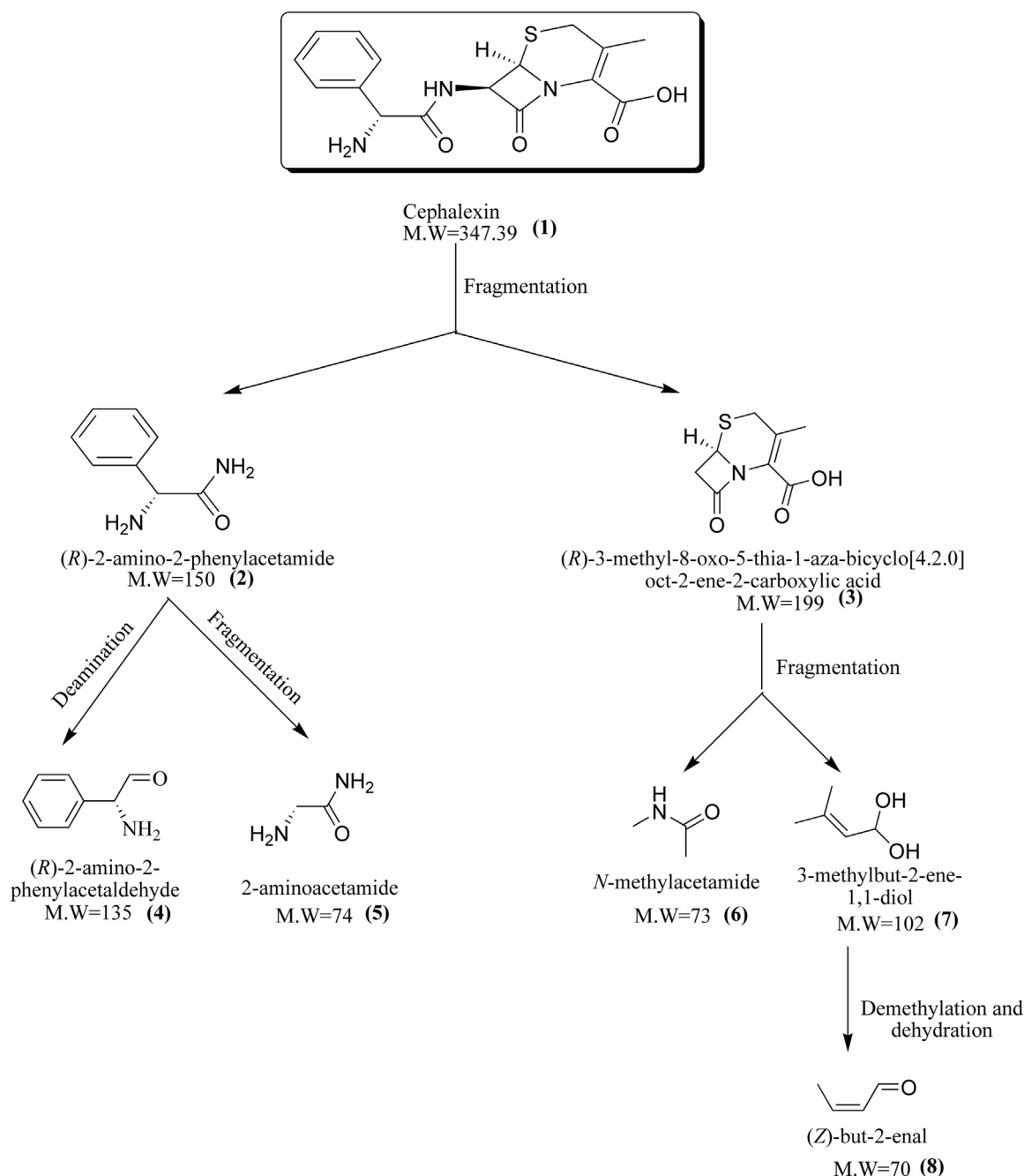


Fig. 9. (Continued)

showed a synergistic effect on the degradation of CEX as better degradation was achieved in lesser time. Around 89% degradation of CEX was achieved after 4 h of photo-treatment under simulated UV irradiations with catalyst immobilized FA/FS/TiO₂ beads under optimized conditions. The effect of different parameters like addition of oxidant, size of beads, number of beads, A/V ratio has been investigated for process intensification which would be helpful for designing of field-scale reactors. The mineralization of CEX was confirmed through COD reduction and generation of nitrite, nitrate and sulphate ions. The identification of intermediates through GC–MS analysis leads to the proposition of a degradation pathway for CEX. The beads selected for the present study proved to be very effective and durable for catalyst immobilization as beads were successfully recycled for at least

thirty five cycles without loss of catalyst activity as confirmed by SEM/EDS and XRD. Use of beads for subsequent cycles without reactivation at high temperature opens up new opportunities in the field of photocatalysis especially in field-scale applications. This will save a huge energy in terms of reactivation thus bringing down the cost of operation for any AOP with fixed-bed catalysis. These results along with the dual effect of photo-Fenton and photocatalysis drew up new challenges working in this area for designing field-scale reactors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jphotochem.2017.04.010>.

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Novel Fe-TiO₂ composite driven dual effect for reduction in treatment time of pentoxifylline: Slurry to immobilized approach

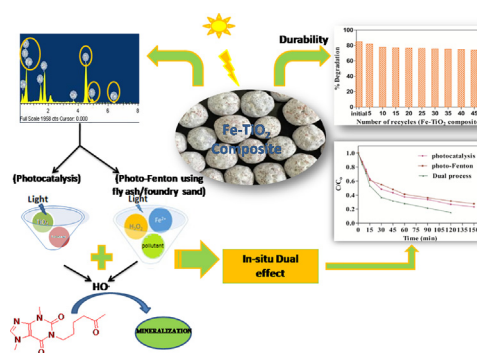
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HIGHLIGHTS

- Dual effect was studied for the degradation of Pentoxifylline in subsequent slurry/fixed mode.
- Fe-TiO₂ composite using waste fly ash/foundry sand was used to instigate the in-situ dual effect.
- Treatment time got reduced to almost half with dual process in each mode.
- Composite was successfully recycled 45 times without affecting the degradation efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

Attempts have been made to reduce the treatment time for degradation of pentoxifylline (PEN) using novel Fe-TiO₂ composite by incorporating dual effect (photocatalysis and photo-Fenton). Waste foundry sand (FS) and fly ash (FA) was used as alternative iron source along with TiO₂ either in suspended or supported form. Initially, dual effect was executed in slurry mode where 49% synergy was obtained for degrading PEN along with reduction in treatment time from 90 to 30 min. In the subsequent experiments, FA/FS was entrapped in small pockets made of fine cotton cloth keeping TiO₂ either in suspension or immobilized on clay beads. Significant improvements over the first order rate constant (*k*) were achieved for the dual process along with reduction in treatment time. Even two to threefold increase in '*k*' was observed using novel Fe-TiO₂ composite for the degradation of PEN confirming in-situ dual effect. The existence of TiO₂ as well as iron on the composite surface even after 45 recycles was confirmed through SEM/EDS, XRD and diffuse reflectance spectroscopy. The mineralization of PEN was validated by reduction in COD and TOC along with the production of several anions. While intermediates formed during the degradation of PEN were identified through GC-MS analysis.

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1. Introduction

Fly ash (FA) and foundry sand (FS), resulting in large quantities from the combustion of coal and from the foundry industry post casting,

respectively lie under the category of harmful wastes as they can induce adverse effects not only to the environment but also to the health of humans [1,2]. Their eventual disposal is a major concern for industries as the potential reuse of such kinds of waste is undergoing investigation to a great extent [3]. Few attempts have been reported in literature with regard to the recycling of foundry sand and fly ash for their use as building and construction material [4,5] and as low-cost adsorbent for various pollutants [6,7].

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Waste FA and FS represent a good blend of unburned carbon, silica and metal oxides including iron and aluminium leading to a proposition that these types of waste materials can be used for wastewater treatment [8]. Recent studies have concluded that FA and FS can be used in advanced wastewater treatment technologies like photo-Fenton as oxides of iron and aluminium can serve as in-situ Fenton system [9]. Photo-Fenton is one of the well established advanced oxidation processes that involve the intermediacy of hydroxyl radicals through the reactivity of ferrous and ferric ions in the presence of an oxidant like H_2O_2 for the degradation of pollutants [10]. However, successful implementation of the technique has not been achieved yet due to low utilization efficiency of photons [11].

TiO_2 photocatalysis, no doubt, has established its reputation in the field of advanced wastewater treatment [12–15] but recombination of electrons and holes always remain a point of concern while thinking for its commercial applications [16]. The applications of TiO_2 photocatalysis are always preferred in its fixed mode due to implications of nanoparticle separation from slurry [17–19]. Although the technique is more efficient and successful in terms of its commercial viability, the selection of inert, efficient and robust materials for catalyst immobilization will remain a challenge for advanced oxidation process (AOP) scientists. Moreover, the treatment time in fixed-mode catalysis always remains a big concern as it consumes more time, hence more energy for the treatment of pollutants.

Research in this particular area is always being focused towards reducing the treatment time along with cost optimization of the process. The present study has successfully demonstrated the reduction in treatment time for the target pollutant with the introduction of dual effect (photocatalysis and photo-Fenton) both in slurry and fixed-mode. The concept of dual effect has been recently suggested by few studies for enhancing the degradation efficiency [20–22]. The improved degradation efficiency by the introduction of Fenton reagent in the TiO_2 photocatalytic system can be attributed to the production of sufficient amount of hydroxyl radicals generated simultaneously by both ongoing processes i.e. photocatalysis and photo-Fenton. Moreover, presence of iron suppresses the recombination of electron and holes in TiO_2 thereby enhancing its photocatalytic activity [23]. The dual effect concept with certain innovations in slurry and fixed-bed mode has been incorporated in the present study utilizing waste FA/FS as alternative iron source. The current study was aimed at the development of unique support systems for either entrapping/immobilizing FS/FA/ TiO_2 separately or merging all in one composite that can be recycled efficiently numerous times. In fact, this is the first reported study where all parameters are being incorporated into one composite for the degradation of pharmaceutical drugs like Pentoxifylline especially using FA/FS.

The presence of various pharmaceutical drugs at high concentrations in effluents of wastewater treatment plant in Patancheru, Hyderabad (India) has been analyzed [24]. Pentoxifylline (PEN), a vasodilator drug intended for the treatment of muscle pain arising from peripheral artery disease [25], was chosen as a target pollutant in this study. PEN has been frequently detected at various concentrations in effluents resulting from different sources like Canadian sewage treatment plants [26], hospitals in Taiwan [27], river in Romania [28] and in Germany [29]. The persistence and non-biodegradable nature of PEN has been confirmed in various reported studies [30–32].

The present investigation was being formulated for the degradation of PEN using natural solar irradiations with the concept of dual effect from slurry to the fixed-bed in subsequent steps. Trials were executed in slurry mode (TiO_2 as well as FS/FA) to affirm the dual effect. In the successive attempts, FS/FA was entrapped in small pockets made of fine cotton cloth while keeping TiO_2 in suspensions. To bring the complete system in fixed-bed mode for overcoming the problem of filtration post treatment, TiO_2 was immobilized on clay beads which were used along with FS/FA pockets. Efforts were also made to create a novel Fe- TiO_2 clay based composite using FA/FS to instigate the in-situ dual effect for faster degradation of PEN. Durability of each system was checked in terms of the number of recycles and loss in degradation efficiency. The

mineralization of PEN was validated by reduction in chemical oxygen demand (COD) and total organic carbon (TOC) along with the generation of nitrite and nitrate ions. The intermediates formed during the photo-degradation of PEN were analyzed through gas chromatography–mass spectrometry (GC–MS).

2. Experimental

2.1. Chemicals and reagents

Pentoxifylline (PEN), >98% purity, was purchased from TCI Chemicals (India) Pvt. Ltd. PEN was employed as such without undergoing any further purification. Degussa P25 TiO_2 , procured from Evonik industries, India, was used as a photocatalyst. Hydrogen peroxide (H_2O_2), 30% w/v, was used as an oxidant and was obtained from Ranbaxy, India. Waste fly ash and foundry sand (FS) were collected from local industry, Patiala, India. Fine cotton cloth for making pockets for entrapping FS and FA was procured from local market, Patiala, India. Clay used for making spherical beads was obtained from local vendor, Patiala, India. Sodium acetate (>98.5% purity) and acetic acid (>99.5% purity) used for the preparation of acetate buffer were procured from TCI Chemicals, India. The double distilled water was used for preparing all aqueous solutions.

2.2. Catalyst immobilization/entrapment

Small pockets (Length = 5 cm, Breadth = 3.5 cm) of fine cotton cloth (Fig. 1a) were made manually for the entrapment of FS and FA. The material was selected for sustainable leaching of iron besides remaining inert. Pockets containing FS, FA and mixture of FA/FS (1:1) were named as P1, P2 and P3 respectively. FS and FA were weighed before entrapment in pockets. In this manner, each pocket was marked carefully based on the amount of FS/FA it contained.

While, for TiO_2 immobilization, spherical beads of diameter 15 mm (Fig. 1b) were made manually using clay. The beads were calcined at high temperature (1000 °C) for 1 h in order to gain strength. TiO_2 was immobilized on beads following the dip-coating method. Two coatings of catalyst were sufficient for the formation of uniform layer of TiO_2 on beads. The detailed explanation of method for TiO_2 coating on beads is quoted in our reported study [33]. The thickness of catalyst film on beads was about 40 μm as confirmed by analysis through SEM/EDS.

For making Fe- TiO_2 composite, clay was mixed with FA and FS in appropriate proportions (2:1:1) i.e. 2 portions of clay with 1 portion each of FS and FA. This mixture was used to make spherical beads in the same manner as normal clay beads were made as discussed above (Fig. 1c). TiO_2 was coated on beads using the similar method as followed for clay beads.

2.3. Experimental set-up and procedure

All photocatalytic experiments were carried out at laboratory-scale under natural solar irradiations. The schematic diagram of setup is shown in Fig. S1, Supplementary information. A borosilicate glass bowl (17 cm diameter and 5 cm height) having capacity of 1000 mL was employed as a batch reactor. The stock solution of PEN (100 mgL^{-1}) was made with double distilled water. The 200 mL working solution of PEN (50 mgL^{-1}) was used for all the slurry and fixed-bed experiments. For dual effect studies in slurry mode, the aqueous solution of PEN was magnetically stirred with 250 mgL^{-1} of TiO_2 and FA/FS (1:1) under sunlight. The required aeration was provided by means of sparger. In the subsequent trials, P1/P2/P3 was used along with TiO_2 suspension and solution was stirred magnetically with proper aeration. For fixed-bed studies, same batch reactor was employed with PEN solution and desired P1 along with appropriate number of TiO_2 coated clay beads. Sufficient aeration was supplied by means of two spargers with flow rate of 3.5 $L min^{-1}$. The fixed-bed studies were also performed with Fe- TiO_2 composite in the same

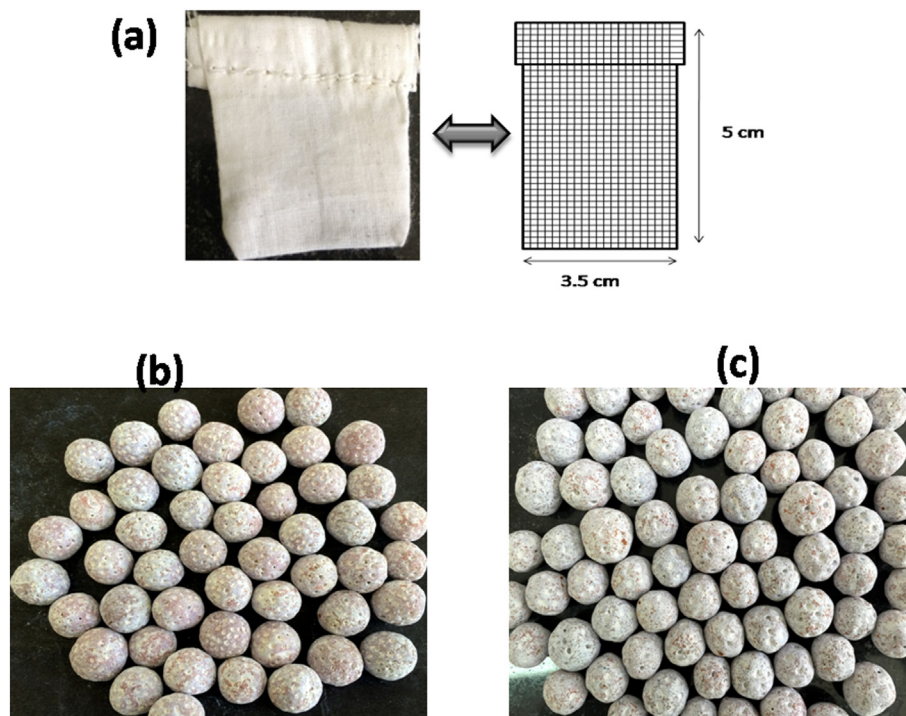


Fig. 1. (a): Actual photograph along with schematic diagram of pocket made of fine cotton cloth containing desired amount of FA/FS, (b) Actual photograph of TiO_2 immobilized clay beads and (c) Actual photograph of Fe- TiO_2 composite.

manner but there was no need to add any pocket. An aliquot of 3 mL sample was collected in each case through syringe after regular intervals, filtered through 0.45 μm millipore filter in case of slurry and partial slurry mode experiments and was successively analyzed. The composition of FA/FS and clay was analyzed and characterized through EDS and was cited as control in this study (Table S3–S5).

Photocatalytic reactions can be explained through pseudo-first order kinetics (eqns. 1 & 2):

$$-dC/dt = kC \quad (1)$$

or

$$\ln C_0/C = kt \quad (2)$$

where, k is a first-order rate constant, C_0 is the initial concentration of pollutant and C is the final concentration of pollutant. The slope of linear plot between natural logarithm of any change in concentration of PEN and irradiation time gave the value of first order rate constant which was further employed in kinetics studies.

The experiments were conducted under natural solar light in the months April to July from 10:00 a.m. to 4:00 p.m. at Thapar University, Patiala (30.3398° N, 76.3869° E), Punjab (India). The average solar intensity during this period was 26 W m^{-2} as measured through pyranometer. All experiments were carried out three times for consistency of results. The standard deviation was observed in the range of 3–5%.

2.4. Chemical analysis

The samples were analyzed using UV-vis spectrophotometer (LABINDIA, T60 U) and HPLC (Shimadzu, Japan), communication module, CBM-20A having diode array detector, SPD-M20A and pump, LC-20 CE. Binary HPLC system having C-18 column with particle size of 5 μm was employed for the execution of HPLC. Formic acid (0.05% in water) and acetonitrile were utilized as mobile phase and UV detector was adjusted at 273 nm for PEN while flow rate

was set at 1.0 mL min^{-1} . The injection volume of sample was 20 μL and each analysis proceeded for 20 min. GC-MS analysis with gas chromatograph of 45 $\times$ GC, Bruker, United States integrated with mass detector of MS-SCION-45P, Bruker and installed with MS wax column having length 30 m and diameter 0.25 mm was utilized for the determination of intermediates. The range of scanning m/z was set at 50–410. Helium as a carrier gas was used at a flow rate of 1.0 mL min^{-1} . The temperature of injection was set at 280 $^\circ\text{C}$. The temperature program for GC oven was set at 40–260 $^\circ\text{C}$ with 10 $^\circ$ rise in temperature. The injection volume of sample was 1 μL while split ratio of 1:10 was used for GC. AAS (Atomic absorption spectroscopy) model GBC 932 AA was used to characterize FA and leachate (solution left after treatment) using air-acetylene as a source of fuel for metals iron, lead, manganese and nickel and nitrous oxide-acetylene fuel is used for chromium. Sample was injected after digestion through capillary and hollow cathode lamp was used as light source. Standard methods [34] were employed for the monitoring of nitrite ions, nitrate ions, COD and for iron estimation. The reduction in (TOC) was measured through TOC analyzer, Multi N/C 2100 BU, Analytic Jena AG Corporation, (Germany). The morphology of TiO_2 immobilized clay beads as well as Fe- TiO_2 composite was evaluated through SEM, JSM-6510LV, JEOL (Japan) while their elemental composition was confirmed through EDS, INCA-X-act, Oxford instruments (United Kingdom). The activity of immobilized catalyst was also confirmed through XRD and UV-visible diffuse reflectance spectrometer. Standard Kirby-Bauer method (agar well diffusion assay) was used to analyze the cytotoxic potential of treated PEN solution against clinical isolates of *E. coli* (DH5-Alpha strain). The acute toxicity of treated water sample was also evaluated through Indian standard bio-assay method (IS:6582–2001).

3. Results and discussion

3.1. Dual effect studies in slurry mode

The effect of individual parameters on the degradation of PEN was evaluated in slurry mode in the presence and absence of light, catalyst

and oxidant. The experiments were performed with 50 mg L^{-1} of PEN aqueous solution in a batch reactor under sunlight. Adsorption experiments with TiO_2 and FS/FA only revealed negligible amount of pollutant reduction (4–5%) owing to the formation of pollutant layer on the surface of catalyst and blocking its active sites thus ceasing the further reduction of pollutant [35]. The addition of H_2O_2 only reduced 3–5% concentration of PEN due to an inconsiderable production of hydroxyl radicals. Similarly, photolytic studies also depicted a little amount of reduction (5–6%) in the concentration of PEN. Thus, the individual parameters had an insignificant contribution towards the degradation of PEN (Fig. 2a). Solar photo-Fenton using either FS/FA alone (varied from 250 to 625 mg L^{-1}) or their mixture with the addition of 150 mg L^{-1} H_2O_2 under acidic conditions ($\text{pH} = 4$) yielded almost 80% degradation of PEN in 90 min. On the other hand, photocatalytic reaction by adding 250 mg L^{-1} of TiO_2 in the presence of sunlight degraded 93% of PEN after 90 min. Whereas, the dual effect studies (photo-Fenton and photocatalysis) by combining all the parameters accelerated the rate of reaction as almost 92% degradation of PEN was achieved after 30 min of treatment. The drastic increase in first order rate constant in case of dual process (0.096 min^{-1}) i.e. seven folds as compared to photo-Fenton (0.014 min^{-1}) and three folds as compared to photocatalysis (0.031 min^{-1}) confirms the viability of our process (Fig. 2b). Therefore, the dual process demonstrated the synergistic effect for the decomposition of PEN in slurry mode as calculated from eq. 3 [36]:

$$\begin{aligned} \% \text{synergy} &= 100 \times \{ (k_{\text{dual process}}) - [(k_{\text{photo-Fenton}}) + (k_{\text{photocatalysis}})] \} \\ &/ (k_{\text{dual process}}) = 100 \times \{ (0.096) - [0.018 + 0.031] \} / 0.096 \quad (3) \\ &= 48.9\% \end{aligned}$$

3.2. Dual effect studies with entrapment of FS/FA in pockets along with TiO_2 suspensions

Reactions with catalyst suspension always have complications regarding its separation from aqueous solution after the treatment process thus limiting its practical applications. In this context, the present

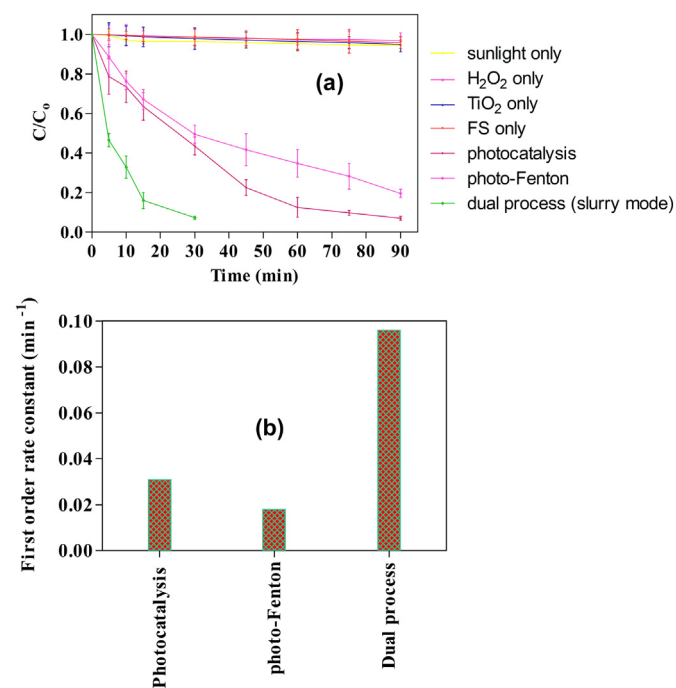


Fig. 2. (a) Degradation of PEN using different processes in slurry mode and (b) First order rate constant for the degradation of PEN through different processes in slurry mode ($C_0 = 50 \text{ mg L}^{-1}$, $V = 200 \text{ mL}$).

study attempts to shift the dual process from slurry to fixed-bed mode step-wise. To compensate the loss of either FA or FS with subsequent cycles, efforts were made to entrap the FA/FS in small pockets (P1, P2, P3) made of fine cotton cloth while TiO_2 was kept in suspensions. All experiments were performed in a batch reactor under natural solar light with 50 mg L^{-1} of PEN solution by adding 250 mg L^{-1} of TiO_2 and 150 mg L^{-1} H_2O_2 along with pockets containing FS/FA. The pH of solution was stabilized to its natural pH i.e. around 4 with the addition of appropriate amount of acetate buffer. Further, all the experiments were carried out at this pH i.e. 4 where photo-Fenton as well as photocatalysis were going on simultaneously. The experiments were conducted at pH 3 also but there was no drastic increase in degradation efficiency as compared to pH 4. In view of the practical applications, pH was not varied and experiments were carried out at natural pH i.e. 4. The pocket size was varied based on the amount of FA/FS it contained. In case of P1, the amount of FS was varied from 25 mg to 250 mg. It was observed that as the weight of FS in P1 increases initially up to 125 mg, the degradation rate also increases. Beyond 125 mg, the rate of degradation either became constant or it started decreasing as shown in Fig. 3a. For the same pollutant concentration, P1 with greater amount of FS was leaching excess amount of iron (inset of Fig. 3a). Excess iron could probably block the active sites of TiO_2 thereby, reducing the efficiency of dual process. Besides, unreasonably high amount of FS could also lead to the development of iron sludge. Accordingly, best results were obtained with 125 mg pocket size citing it to be optimum in context to iron/pollutant concentration. Almost 91% degradation was achieved after 45 min of treatment with dual process using 125 mg P1. Subsequently, photo-Fenton was also performed separately with 125 mg P1 and the process yielded 80% degradation of PEN after 150 min thus ensuring the synergistic effect of dual process (Fig. 3b). Results were confirmed

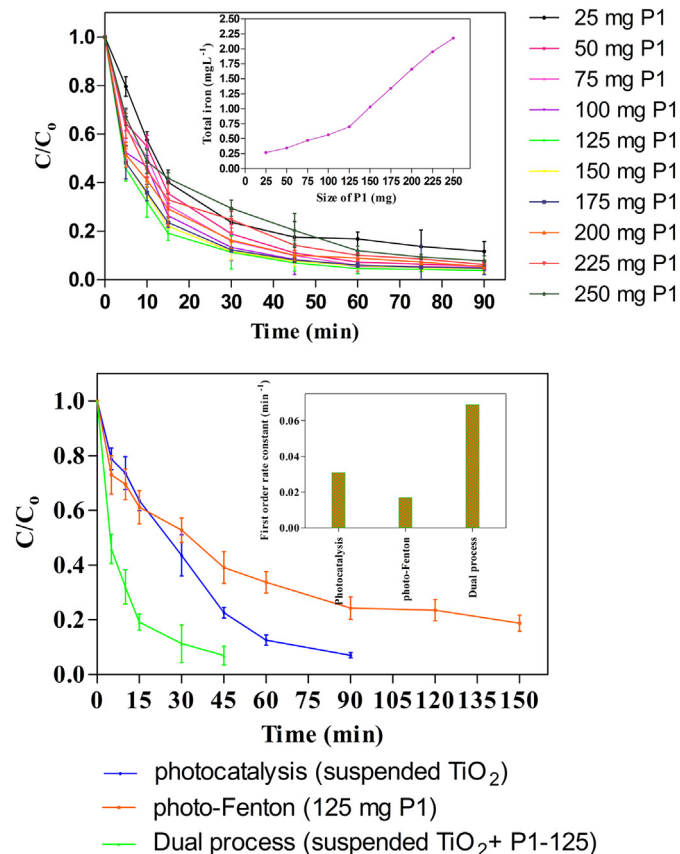


Fig. 3. (a) Effect of P1 size on the degradation of PEN in dual process and amount of iron leaching from different sized P1 (inset), (b) Comparison of photo-Fenton, photocatalysis and dual process for the degradation of PEN using P1–125 and suspended TiO_2 and first order rate constant of different processes (inset).

by reusing this pocket again and again for subsequent cycles. The weight of pocket was checked after each cycle for determining the loss of FS from the pocket. Table S1 (Supplementary information) shows the weight of pocket after each cycle along with the iron content leached into the solution for successive cycles. The first order rate constant in case of dual process (0.069 min^{-1}) for the degradation of PEN was increased two fold in comparison to photocatalysis (0.031 min^{-1}) while it increased to almost four times as compared to photo-Fenton (0.017 min^{-1}).

Similarly experiments were conducted with P2 and P3 also. Though significant amount of degradation was achieved using these pockets as well but the major problem that occurred was the reduction in their weights after each cycle (Table S2, Supplementary information). It may be due to the smaller particle size of FA that drained out easily from pockets so these pockets cannot be used for subsequent cycles.

3.3. Dual effect studies in fixed-bed mode

To bring the treatment unit completely in fixed-bed mode, TiO_2 immobilized clay beads were used along with P1 containing 125 mg FS. The experiments were conducted under sunlight at acidic conditions ($\text{pH} = 4$) with appropriate number of catalyst coated clay beads covering the entire bottom surface of a batch reactor along with P1 and oxidant ($150 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$). To confirm the synergistic effect of dual process for the degradation of PEN, photo-Fenton and photocatalytic reactions were performed separately by adding P1 along with H_2O_2 and catalyst coated beads respectively. Photo-Fenton reaction yielded 80% degradation of PEN after 150 min whereas photocatalysis using catalyst coated clay beads reduced the pollutant concentration to about 75% after 150 min of treatment. Accordingly, adsorption experiments in dark using blank clay beads (without TiO_2 coating) revealed only 5–6% reduction in pollutant. The combination of two processes degraded the pollutant to around 88% after 120 min of reaction thus proving the effectiveness of dual effect (Fig. 4). Similarly, the first order rate constant was also the highest in case of dual process (0.023 min^{-1}) as compared to photo-Fenton (0.017 min^{-1}) and photocatalysis (0.015 min^{-1}). The same pocket (P1–125 mg) was recycled 8 times in dual process with notable decrease in the % degradation of PEN after each cycle (Fig. 5). The reduction in iron leaching out in solution from pocket was also observed after each cycle as indicated in Fig. 4a. This loss of iron leaching from pocket could lead to the reduction in % degradation of PEN. Similarly, the durability and efficacy of immobilized TiO_2

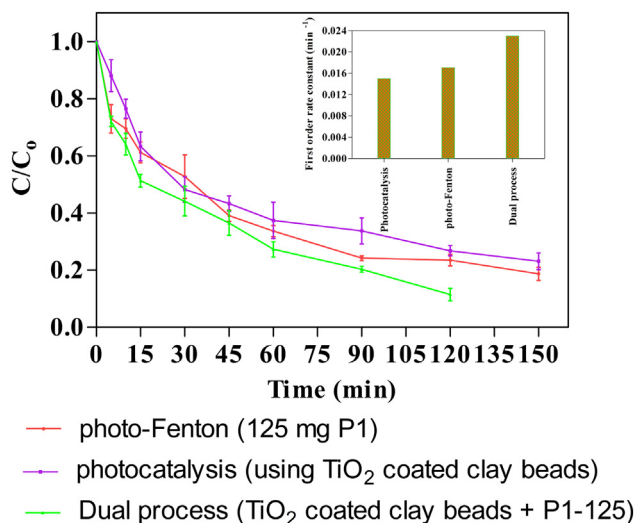


Fig. 4. Comparison of photo-Fenton, photocatalysis and dual process for the degradation of PEN using P1–125 and TiO_2 immobilized clay beads and inset figure shows the first order rate constant values of different processes ($C_0 = 50 \text{ mg L}^{-1}$, $V = 200 \text{ mL}$, $\text{H}_2\text{O}_2 = 150 \text{ mg L}^{-1}$, $P1 = 125 \text{ mg}$).

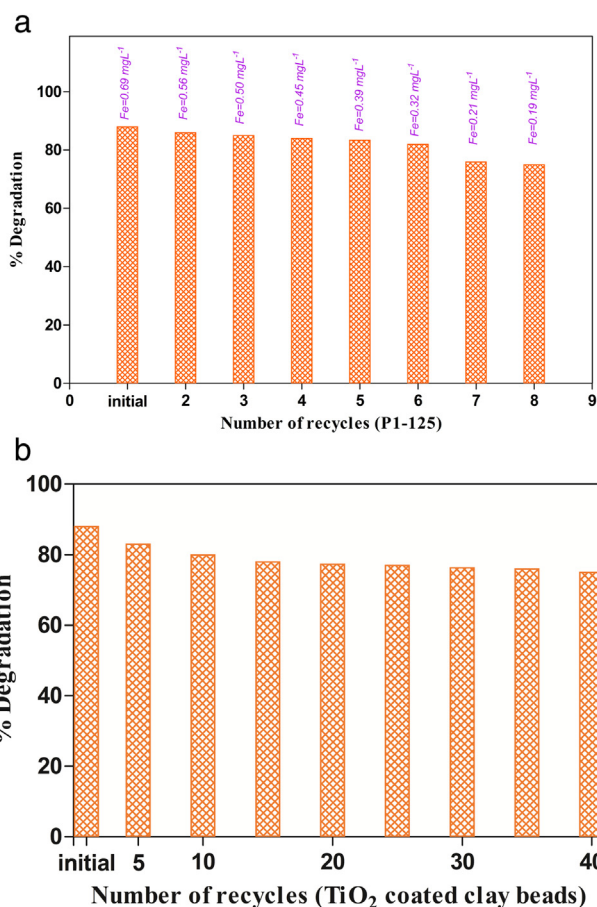


Fig. 5. a. Recyclability studies of P1–125 for the degradation of PEN in dual process along with amount of iron leached out from P1 after subsequent cycles. b. Recyclability studies of TiO_2 immobilized clay beads for the degradation of PEN in dual process (fixed mode).

was checked by recycling the beads for the degradation of PEN. The beads were successfully recycled for around 40 cycles without any prominent loss in catalyst activity along with new P1–125 each time (Fig. 5b).

3.4. In-situ dual effect studies

Trials were done to further improve the practicability of the technique by enhancing the durability and efficiency of support materials. Efforts were made to modify the clay beads by incorporating FA and FS along with clay during the preparation of beads. Composites were made using different combinations (FA + clay, FS + clay, FA + FS + clay). Composites containing FA + FS + clay were selected for this study based on the durability, stability of immobilized catalyst and degradation efficiency. The catalyst was immobilized on these beads as discussed in Section 2.2 thus forming Fe- TiO_2 composite. Reactions were performed in the same manner with relevant number of composites covering the whole bottom of reactor. In this case there was no need of adding any additional iron source as iron was leaching out from the composite in-situ. The reactions were carried out with PEN solution (50 mg L^{-1}) using blank beads containing iron only (without TiO_2 coating) in the presence of 150 mg L^{-1} of H_2O_2 under sunlight to confirm the leaching of iron from beads in solution at acidic conditions. 72% degradation of PEN occurred after 150 min confirming the occurrence of photo-Fenton reaction. Adsorption studies were also carried out using blank beads in dark and 4–5% removal of pollutant occurred after 120 min. As discussed in Section 3.3, 75% degradation of PEN occurred through photocatalysis using TiO_2 coated clay beads (without FA/FS) after 150 min. While using Fe- TiO_2 composite, 75% degradation of PEN

was attained in almost half of the time (75 min of reaction) thereby, confirming the synergistic effect of dual process (Fig. 6). Degradation of PEN reached to around 85% after 120 min of treatment using the composite. From the kinetic data, it was observed that value of first order rate constant in case of dual process (0.034 min^{-1}) was almost two fold that of photocatalysis (0.015 min^{-1}) and three fold that of photo-Fenton (0.012 min^{-1}) as depicted in inset of Fig. 6. Around 20% synergy of photo-Fenton over photocatalysis was obtained employing Fe-TiO₂ composite. The leachate (treated solution) was also analyzed and characterized through AAS concerning the leaching of various metals. No subsequent leaching of heavy metals like lead, nickel and chromium was detected as depicted in supplementary information (Table S6). Further experiments can be performed by varying the composition of Fe-TiO₂ composite using different amount of FS/FA. The durability of the composites was checked in terms of the number of recycles for the degradation of PEN. The composites were successfully recycled for approximately 45 times without any significant reduction in the degradation efficiency of PEN (Fig. 6b).

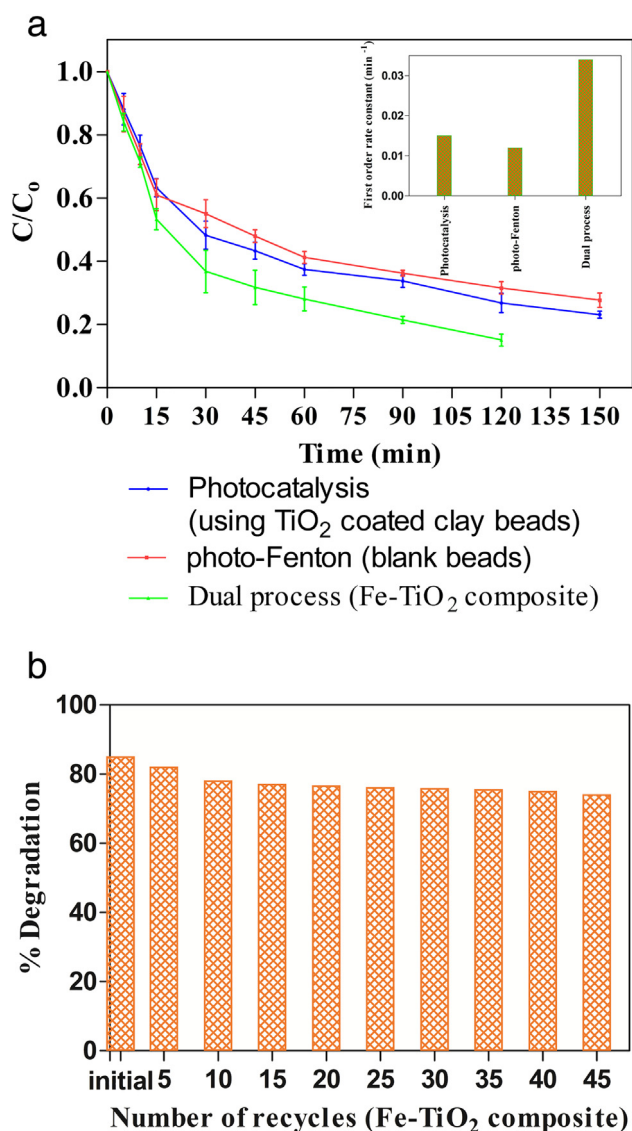


Fig. 6. a. Comparison of photo-Fenton, photocatalysis and dual process for the degradation of PEN using Fe-TiO₂ composite and inset figure shows the first order rate constant values of different processes ($C_0 = 50 \text{ mgL}^{-1}$, $V = 200 \text{ mL}$, $\text{H}_2\text{O}_2 = 150 \text{ mgL}^{-1}$). b. Recyclability studies of TiO₂ immobilized clay beads for the degradation of PEN.

3.5. Proposed mechanism of dual effect

From the results, it is evident that dual process in all respects (slurry or fixed mode) has yielded much better degradation of PEN than individual processes (photocatalysis or photo-Fenton). In dual process, abundant of active radicals are generated through TiO₂, iron oxide and dissolved iron ions thus leading to the enhancement of degradation efficiency and confirming the synergistic effect. Hydroxyl radicals are generated not only through photo-Fenton reaction and TiO₂ photocatalytic reaction but also from iron oxide catalysis. Some of these forms of iron oxide (iron dititanium oxide and iron titanium oxide) are somewhat also confirmed in our study as depicted in XRD analysis of Fe-TiO₂ composite (Section 3.6.2). The photo-generated electron from TiO₂ got trapped into iron oxide and could possibly participate in the regeneration of Fe^{2+} ions promoting the photo-Fenton reaction and simultaneously restraining the recombination of electrons and holes on TiO₂ [21]. This proposed mechanism of dual effect is depicted in Fig. 7 though further experimental analysis is required for solid confirmation of mechanism owing to the involvement of several active species.

It is now quite obvious that abundant of hydroxyl radicals are generated through several processes in the same treatment unit that are mainly involved in the degradation of pollutant. Therefore, the presence of profuse amount of these radicals are responsible for accelerating the degradation of PEN and subsequently reducing the treatment time in case of dual process in the present study. The half life of PEN was 5–6 times lower in case of dual process (5 min) as compared to photo-Fenton (30 min) and photocatalysis (25 min) in slurry mode as shown in Table 1. The degradation was undoubtedly faster in slurry mode in comparison to fixed-bed due to lesser mass-transfer implications. However, the half life of PEN was still at least two times lower in case of dual process (15 min) to that of photo-Fenton (35 min) and photocatalysis (30 min) in fixed mode. Thus, synergistic effects were confirmed between photocatalysis and photo-Fenton in dual process.

3.6. Characterization

3.6.1. SEM/EDS analysis

Scanning electron micrographs (SEM) were used to indicate the morphological characteristics of immobilized catalyst over the surface of clay beads as well as composite beads. The SEM images of freshly coated and recycled clay beads (40 times) are shown in Fig. 8 (i and ii). The morphologies of the immobilized catalyst in both cases were almost the same thus suggesting that no change occurred in the surface morphology of TiO₂ even after using the same beads for almost 40 times. The catalyst was intact as a layer on the surface of beads even after 40 recycles. Fig. 8 also depicts the electron dispersion spectra (EDS) of the catalyst immobilized clay beads. Strong peaks of Ti and O are present in both cases thereby proving the presence of significant amount of TiO₂ over clay beads even after 40 recycles.

Similarly, the SEM analysis of fresh and recycled (45 times) Fe-TiO₂ composites are shown in Fig. 8b (i and ii) respectively. Both SEM images were almost identical in terms of the surface morphologies of Fe-TiO₂ composites clearly confirming the durability of composite to be used even after 45 recycles. The electron dispersion spectra (EDS) in Fig. 8 (i and ii) of fresh and recycled (45 times) Fe-TiO₂ composites respectively indicated the elemental composition of composites. The EDS results confirmed the presence of iron in composite along with TiO₂. The existence of iron was attributed to the FA/FS used along with clay during the preparation of composite as no additional iron source was added in the composite. The peaks of Ti, O and Fe even in recycled composite prove the intactness of TiO₂ as a film over composite along with the presence of iron even after 45 cycles. Thus, it can be concluded that composites can be effectively utilized in dual processes for field-scale applications.

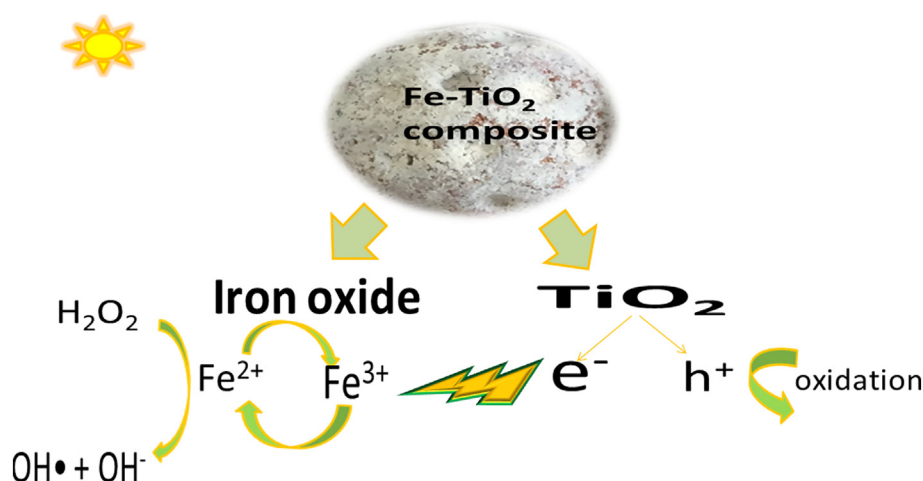


Fig. 7. Schematic diagram of possible synergistic effect in dual process under solar irradiation.

3.6.2. XRD and diffuse reflectance UV–visible spectroscopy of Fe-TiO₂ composite

X-Ray Diffraction (XRD) of fresh TiO₂-P25 and recycled Fe-TiO₂ composite was performed to verify whether any change in the photocatalytic activity of immobilized TiO₂ over composite occurred after 45 recycles. XRD pattern of TiO₂-P25 and immobilized catalyst extracted from the surface of Fe-TiO₂ composite is shown in Fig. 8c. The strong diffraction peaks at $2\theta = 25.4^\circ, 37.8^\circ, 48^\circ, 54.8^\circ, 62.5^\circ$ and 70° corresponding well to 101, 004, 200, 211, 204, 220 planes showed the presence of anatase phase of TiO₂-P25 in Fe-TiO₂ composite and is indicated by 'A' in figure. While, the diffraction peaks at $2\theta = 27.4^\circ, 36.2^\circ, 53.8^\circ$ and 62.5° corresponding to 110, 101, 211 and 004 planes depicted the presence of rutile phase of TiO₂-P25 in composite and is indicated by 'R' in figure. The existence of anatase (reference code: 01–075–2546) and rutile (reference code: 01–089–8304) phase of TiO₂-P25 confirmed the retention of catalyst activity over composite even after 45 recycles. In addition to the anatase and rutile peaks of TiO₂, few more diffraction peaks were observed in XRD pattern of immobilized catalyst over composite which confirmed the presence of iron dititanium oxide (reference code: 01–076–2372) and iron titanium oxide (reference code: 01–070–0143) along with TiO₂. The diffraction peaks at $2\theta = 20.7^\circ, 26.7^\circ, 33.2^\circ, 40.3^\circ, 41^\circ, 50.16^\circ, 60^\circ, 64.9^\circ, 73.19^\circ$ and 78.6° ensured the presence of iron titanium oxide marked as 'ITO' in graph whereas peaks at $2\theta = 20.7^\circ, 26.7^\circ, 40.3^\circ, 41^\circ, 42.4^\circ, 60^\circ, 64.9^\circ, 73.19^\circ$ and 78.6° assured the existence of iron dititanium oxide marked as 'IDO' in graph. The presence of

ITO and IDO validated the existence of iron along with TiO₂ leading to a proposition that the composite can be suitably used for dual effect studies for numerous cycles without losing the catalyst activity.

Accordingly, the band gap energy of fresh TiO₂-P25 and immobilized catalyst from Fe-TiO₂ composite was analyzed from diffuse reflectance spectrometer (DRS). The analysis of the samples was carried out in the range 200–800 nm as shown in Fig. 8d. The reduction in band gap in case of Fe-TiO₂ composite cross-confirms the formation of 'ITO' and 'IDO' (as discussed in XRD), thus facilitating the absorption of light comparatively at lower levels of energy thereby making the absorption feasible even in visible spectrum. The spectral shift might be due to the formation of an energy level within the band gap of TiO₂.

3.7. Mineralization studies

The mineralization studies were conducted by monitoring the reduction in TOC and COD along with the production of nitrite and nitrate ions (Fig. 9). The production of nitrite and nitrate ions was maximum (87% and 81% respectively) during the first 30 min of reaction. After 1 h, there was a steady increase in the concentration of nitrite ions while nitrate ions concentration started decreasing with the possibility of conversion from nitrate to nitrite and some part of nitrate could also result in the formation of ammonium ions. The accumulated electrons could possibly reduce nitrate to nitrite according to chemical eq. 5 [37]. Actually the acetic acid (from acetate buffer used in our treatment) could serve as hole scavenger thereby enhancing the reduction of nitrates [38]. 94.7% and 90% reduction in COD and TOC respectively occurred after 120 min of reaction. The TOC was reduced to 0.98 mg L^{-1} from 10.1 mg L^{-1} after 120 min. The degradation by-products of PEN (I₁–I₇) were identified through GC–MS analysis based on which a tentative degradation pathway has been proposed (Fig. 9b). The demethylation of PEN in route A led to the formation of 3-methyl-1-(5-oxohexyl)-1H-purine-2,6(3H,7H)-dione from which 1-(4-hydroxy-5-oxohexyl)-3,7-dimethyl-1H-purine-2,6(3H,7H)-dione was formed by successive hydroxylation and methylation. The fragmentation of this compound led to the generation of intermediate I₁. The subsequent oxidation of I₁ produced I₂. The reduction followed by demethylation and oxidation of I₂ ultimately led to the production of I₃. On the other hand, the oxidation of PEN in route B could lead to the formation of 3,7-dimethyl-1-(5-oxohexyl)-1H-purine-2,6,8(3H,7H,9H)-trione which on fragmentation could give rise to the intermediates I₄ and I₅. I₄ was further oxidized to I₆. The removal of carbonyl group (ketone) from I₆ followed by oxidation led to the generation of I₇.

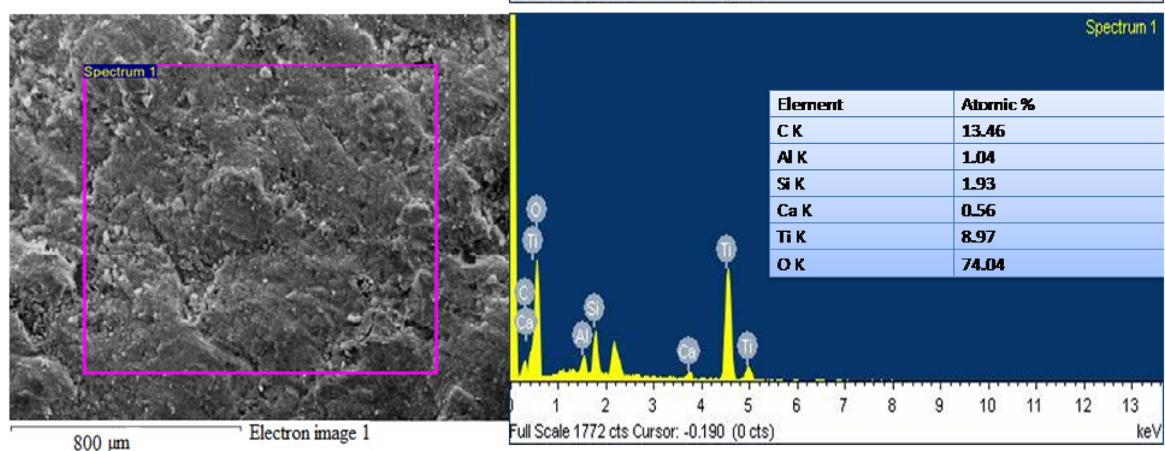
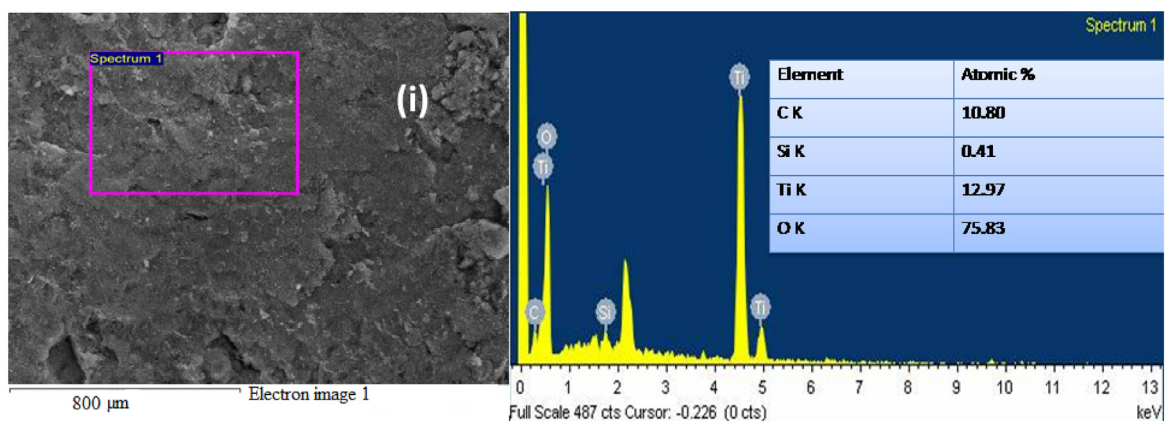


Table 1

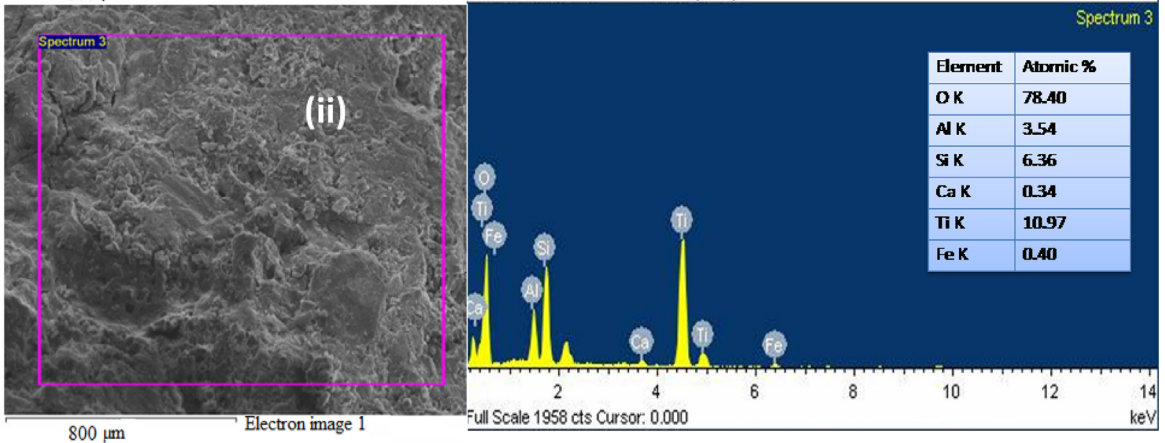
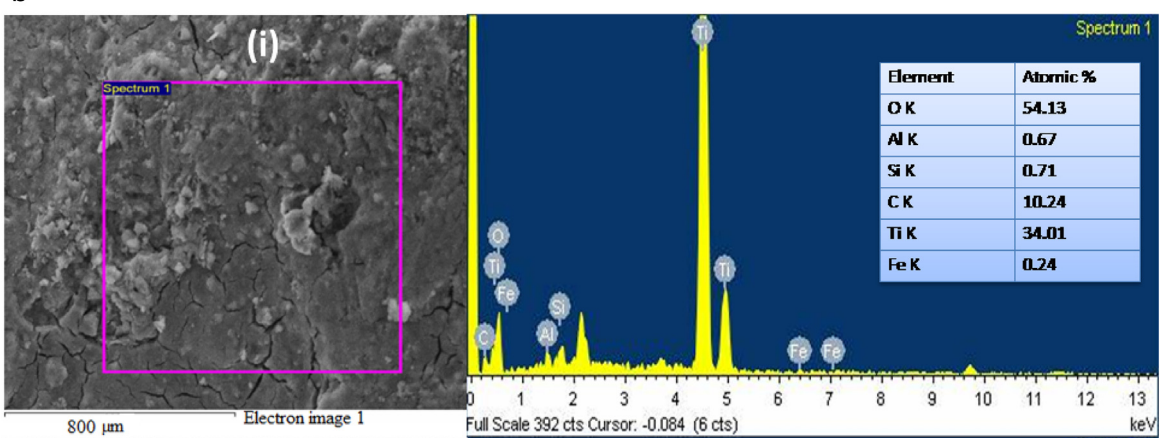
The half life of PEN in each treatment process.

Process	Half-life (min)
Slurry mode	
Photocatalysis	25
Photo-Fenton	30
Dual process	5
Entrapment of FS/FA in pockets along with TiO ₂ suspensions	
Photocatalysis	25
Photo-Fenton	35
Dual process	5
Fixed mode	
Photocatalysis	30
Photo-Fenton	35
Dual process	15
Fe-TiO ₂ composite	
Photocatalysis	30
Photo-Fenton	35
Dual process	15

a



b



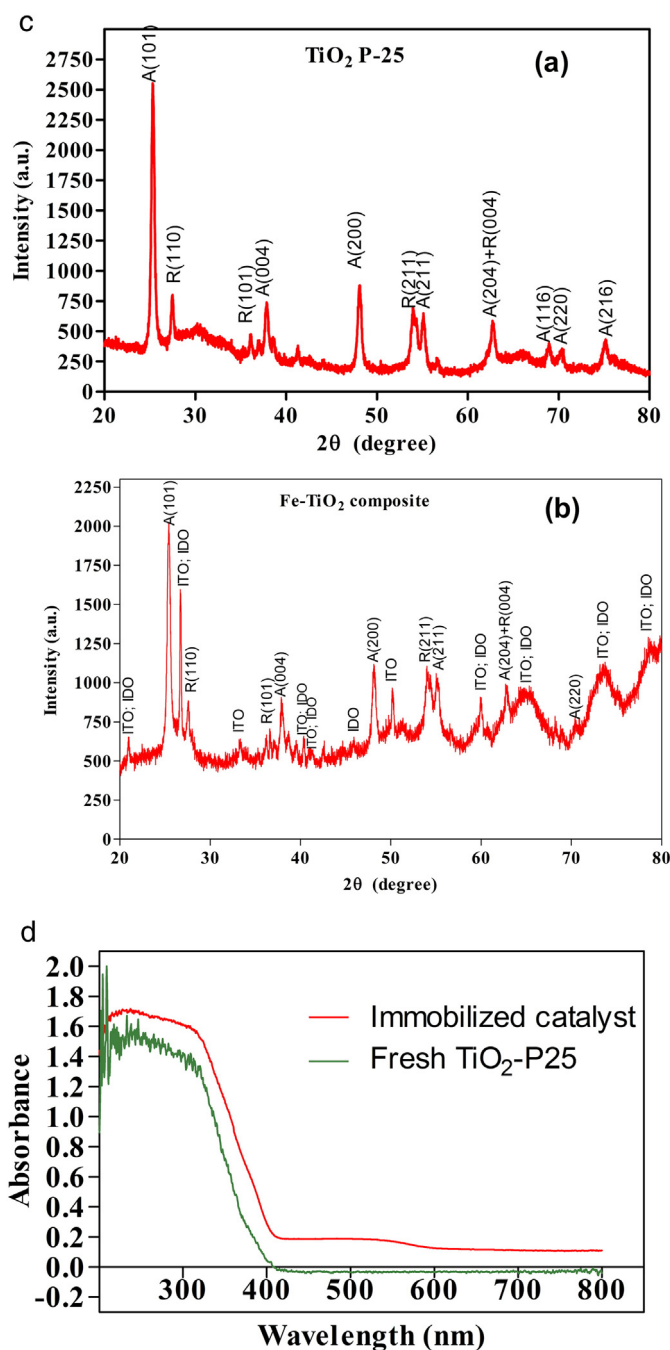


Fig. 8. a. SEM along with EDS image of TiO_2 coated clay beads (i) freshly coated and (ii) after 40 recycles b. SEM along with EDS image of Fe- TiO_2 composite (i) fresh and (ii) after 45 recycles. c. XRD pattern of (a) fresh TiO_2 -P25 and (b) recycled Fe- TiO_2 composite. d. UV-visible DRS of (a) fresh TiO_2 -P25 and (b) recycled Fe- TiO_2 composite.

3.8. Toxicity analysis

To cross-confirm whether the parent compound was completely mineralized (as discussed in Section 3.7) or transformed into toxic intermediates, toxicity analysis was performed through agar well diffusion assay against *E. coli* taking pure solution of PEN (50 ppm) as control. Briefly, 5 mm wells were punched in Muller Hinton agar plates using a sterile cork borer. Subsequently, 30 μl of samples taken at different intervals (15 min, 60 min and 120 min) during the treatment process was dispensed in each well and allowed to diffuse at 37 $^\circ\text{C}$ for 20 min. The wells were sealed with molten MHA and allowed to solidify. Further, the plates were swabbed with 18–24 h old 0.5 McFarland adjusted culture of *E. coli*. The plates were then incubated at 37 $^\circ\text{C}$ for overnight.

Cytotoxic activity was determined by measuring the zone of inhibition formation around the well. No zone of inhibition was observed in any sample thus indicating that samples did not acquire any toxicity during or after treatment as shown in Fig. S2 (Supplementary information).

Further, acute toxicity potential of the treated sample was checked using bio-assay method (acceptable by Central Pollution Control Board, India) based on toxicity factor i.e. minimum amount of dilution of wastewater required for achieving no mortality for zebra fish. According to the results from toxicity test, 100% survival was obtained after 96 h of test (analysis report is given in supplementary file). Therefore, it can be concluded that the treated water is non-toxic in all respects leading to a proposition that in-situ dual process using prepared composite can be successfully adopted for field-scale applications.

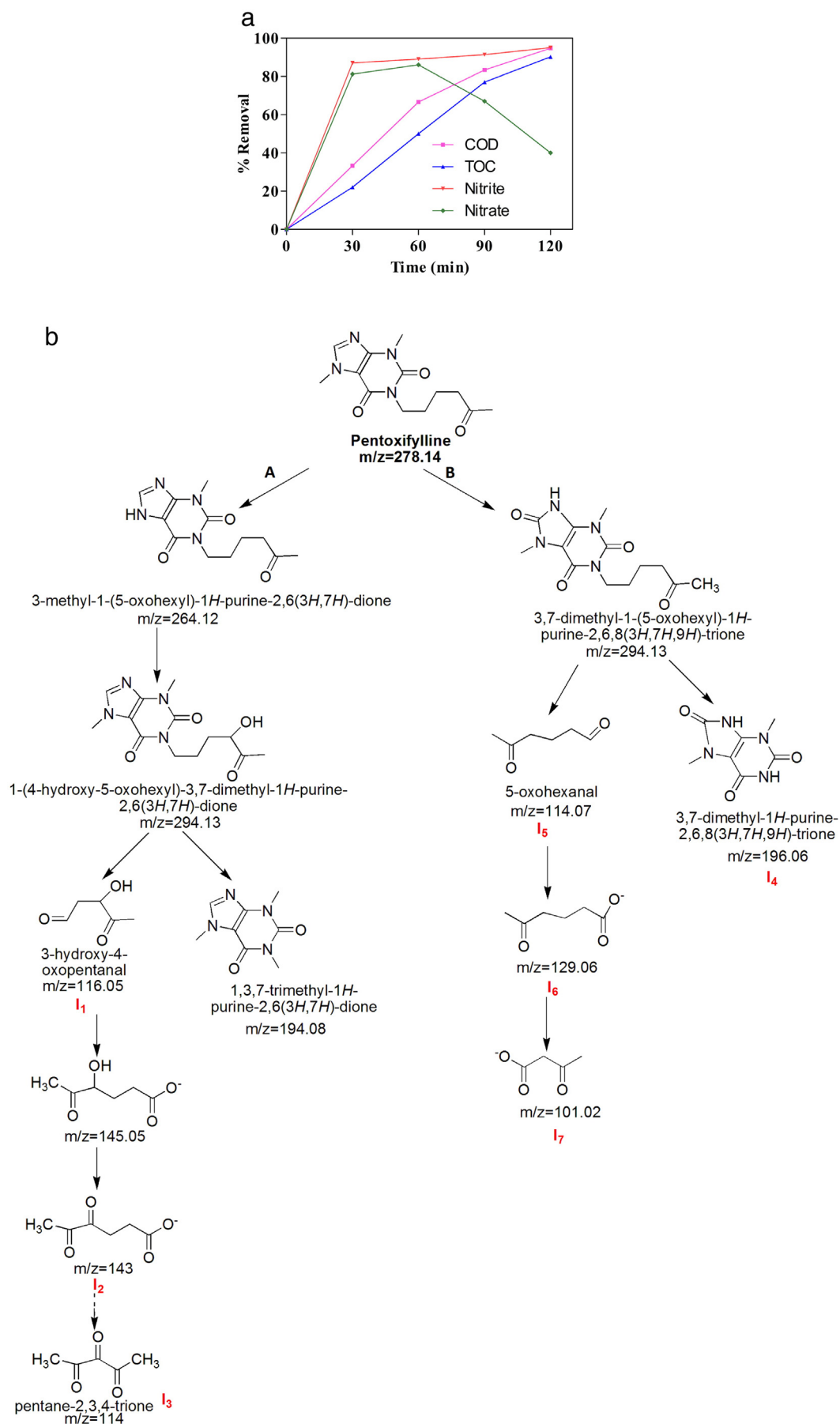


Fig. 9. a. Generation of nitrite, nitrate and sulphate ions along with reduction in COD and TOC during the photodegradation of PEN. b. Proposed degradation pathway for PEN.

4. Conclusion

A simple and economic method has been presented to prepare a highly active immobilized photocatalyst combined with iron (Fe-TiO₂ composite). The preparation of the composite was carried out using easily available and cheap material (clay) mixed with waste FA/FS followed by TiO₂ coating under ambient conditions without any addition of chemicals. Significant reduction in treatment time was achieved with dual effect studies in both slurry and fixed mode. Almost three times reduction in treatment time was achieved with dual process in slurry mode for the degradation of PEN. While, the treatment time was reduced to half in case of dual process in fixed-bed. A remarkable increase in first order rate constant 'k' was observed for the dual process during the degradation of PEN. The observed value of 'k' was as high as seven times in case of slurry mode and two to three times in case of fixed mode. Surface characterization of recycled immobilized catalyst on composite through SEM/EDS, UV-visible diffuse spectra and XRD analysis showed the presence of iron along with TiO₂ confirming the intactness, stability and activity of catalyst even after 45 recycles. Two to six folds decrease in half-life of PEN in case of dual process prompts its applications in wastewater treatment as a pre-treatment option subsequently followed by biological process.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.matdes.2017.03.083>.

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Assessment of integrated binary process by coupling photocatalysis and photo-Fenton for the removal of cephalixin from aqueous solution

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ABSTRACT

A novel concept of integrated process by coupling photocatalysis and photo-Fenton especially in fixed mode has been presented in the current study for the removal of recalcitrant pharmaceuticals like cephalixin (CEX) from aqueous solution in reduced treatment time. Waste materials like foundry sand (FS) was used as a substitute for iron along with TiO₂. The parametric optimization was carried out in slurry mode using Box–Behnken design model (BBD) and response surface methodology. For fixed-bed studies, support materials of varying shapes (hollow circular disk, rectangular slabs, spherical beads) were prepared using clay in conjunction with FS for TiO₂ immobilization. Different supports were compared on the basis of degradation efficiency, exposed surface area of catalyst as well as their recyclability capacity for the degradation of CEX. Iron was leaching by default from the supports during the degradation process which contributed simultaneously to photo-Fenton process along with photocatalysis. Spherical beads with 0.0265 m² exposed surface area of catalyst and better recyclability efficiency (10 cycles) yielded best degradation efficiency (80%) of CEX after 240 min of treatment time. The presence of iron along with TiO₂ on the surface of beads was confirmed through TGA, SEM/EDS, XRD, DRS and FTIR. The mineralization of CEX was validated through quantification of nitrite, nitrate and sulfate ions along with reduction in COD. A tentative pathway for the degradation of CEX was also proposed based on the identification of intermediates through GC–MS analysis.

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Introduction

Since treatment methodologies pertaining to traditional sewage treatment plants have been proved to be deficient for the removal of bio-recalcitrant organic pollutants including pharmaceuticals from wastewater, other effective alternative techniques are under constant investigation [1]. Under this perspective, various advanced oxidation processes (AOPs) have manifested their potential for the elimination of various recalcitrant pollutants from aqueous solution [2–4]. Among these advanced treatment technologies, heterogeneous photocatalysis as well as homogeneous photo-Fenton processes have been considered to be the most promising tools in context to pollutants abatement [5–7]. In spite of reasonably good degradation efficiency of these processes owing to the high oxidation potential of OH radicals, frequent recombination of electrons and holes, more treatment time, catalyst separation in case of photocatalysis and generation of iron sludge as well as incomplete mineralization of pollutants in case of photo-Fenton are some of the pitfalls that restrict their successful implementation at field scale [8–10].

The above-discussed flaws in individual processes (photocatalysis and photo-Fenton) can be resolved to some extent if these two processes are coupled together in the same treatment system. With this type of integrated system, hydroxyl radicals are produced in huge quantity from both the processes going on simultaneously in the same treatment unit, thus enhancing the degradation efficiency with the possibility of reduction in treatment time. Moreover, electron-hole recombination in photocatalysis also becomes infrequent with this coupled process which further increases the efficiency of degradation process. Actually, the excited electron gets trapped by the iron present in the system which blocks the recombination of electron and hole to some extent [11]. Few studies are reported in the literature which has attempted this type of coupled process for the degradation of organic pollutants with improved degradation efficiency [12, 13]. Though excellent degradation efficiency with reduced treatment time has been achieved in most of these studies, increased cost of the process due to an additional iron source along with photocatalyst and generation of iron sludge are still some of the complications which hinders its practical viability. Moreover, separation of

both catalysts post-treatment further makes the treatment process more complex. None of the studies in the literature has ever discussed about the practical feasibility of this technique at field scale as most of these studies deal with slurry systems.

Taking into account the aforementioned concerns, the present investigation has successfully integrated the two processes (photocatalysis and photo-Fenton) together in one unit for the enhanced degradation of an antibiotic, cephalexin (CEX). CEX is a beta-lactam antibiotic which is widely used for the treatment of several urinary as well as respiratory tract infections. Since CEX possesses nearly 10% biotransformation rate, 90% of it is excreted out as such in urine, thereby increasing the environmental concern of antibiotic resistance [14]. The persistence nature of CEX as well as its ubiquitous existence in aquatic environment has been confirmed in various studies [15, 16]. Thus, CEX was taken as a target pollutant in the current research work. The integrated system by coupling photocatalysis and photo-Fenton was operated in slurry as well as in fixed form with parametric optimization in suspended mode under artificial UV irradiations. Considering the overall economy of process, waste foundry sand (FS) has been utilized as a substitute for iron. The optimization of crucial operating parameters like dose of FS, TiO_2 , H_2O_2 and treatment time was done using Box–Behnken design model (BBD) and response surface methodology (RSM). The treatment time for CEX removal was significantly reduced as compared to the reported studies in the literature [17]. After getting optimized conditions in slurry mode, trials were executed in fixed mode by preparing TiO_2 immobilized supports of varying shapes from FS using clay as a binding material. Iron was leaching from these TiO_2 immobilized supports by default which led to the occurrence of photo-Fenton reaction along with photocatalysis without adding any extra iron supplement into the system. Different shaped TiO_2 immobilized supports were compared in terms of the degradation efficiency of CEX, recyclability and stability of immobilized catalyst and exposed surface area of catalyst. The selected TiO_2 immobilized support (spherical composite beads) was characterized through SEM/EDS, XRD, DRS, FTIR and TGA analysis for confirming the presence of both TiO_2 and iron on the surface of beads. To further foresee its field-scale applications, process was scaled up with the development of pilot-scale fixed-bed non-

concentrating solar reactor with total volume handling of 5 L. The mineralization studies were carried out by evaluating the generation of various anions (sulfate, nitrite and nitrate) along with reduction in COD. The intermediates formed during the degradation of CEX were identified using GC–MS analysis. To the best of our knowledge, this is the first reported study dealing with thorough investigation on coupled process in the same treatment unit especially at the same time for the degradation of CEX with parametric optimization using BBD and RSM.

Materials and methods

Chemicals and reagents

Cephalexin (CEX) was bought from local medical store, Patiala (India), under the brand name 'Phexin'. CEX was used in the native form without undergoing any modification. TiO_2 -P25 obtained from Evonik Industries, India, was utilized as a photocatalyst. Hydrogen peroxide, H_2O_2 (30% w/v), was procured from Loba Chemie Pvt Ltd (India). Waste foundry sand (FS) was collected from local industry, Patiala (India), and was used as such without any further purification. Clay was obtained from local vendor, Patiala (India). Sodium acetate (> 98.5%) as well as acetic acid (> 99.5%) purchased from Loba Chemie Pvt Ltd (India) were used for the preparation of acetate buffer. Double-distilled water was being employed throughout the experimental work.

TiO_2 immobilization

For TiO_2 immobilization, inert supports of different shapes (Fig. 1) including hollow circular disk (outer diameter = 13.5 cm, inner diameter = 5 cm), rectangular slabs (length = 6.5 cm, breadth = 2.5 cm) and

spherical beads (diameter = 1.5 cm) were prepared manually using waste foundry sand (FS) with clay as binding material in the ratio (1:1). FS was used as an alternative iron source in the present study. Characterization of foundry sand for the presence of iron has already been reported in the previous studies [18]. For reference, composition of foundry sand is provided in table S1 (Supplementary information). All supports were calcined in muffle furnace for almost 2 h at high temperature ranging from 900 to 1000 °C to become solid and gain strength. These supports without TiO_2 immobilization were named as blank supports and were used in the photo-Fenton experiments. While for TiO_2 immobilization, standard dip coating method was followed as reported in previous studies [5, 19]. After TiO_2 immobilization, the supports were given the prefix 'composite' as it contained both catalysts, i.e., iron as well as TiO_2 . For the control experiments, all supports were prepared using only clay without adding any FS. These supports after TiO_2 immobilization were given prefix 'control' and were used for conducting photocatalytic experiments as it contained only TiO_2 .

Characterization

The spherical composite beads (selected after optimization) were characterized for the existence of iron as well as TiO_2 through several techniques. The surface morphological characteristics of composite beads were studied through scanning electron microscopy (SEM), model no. JSM-6510LV, JEOL (Japan). The elemental composition of composite beads was identified through electron-dispersive spectroscopy (EDS), model no. INCAX-act, Oxford instruments (UK). X-ray diffraction (XRD) analysis was performed to determine the crystalline structure of catalyst over composite beads using X'Pert pro diffractometer ranging from $2\theta = 20$ – 80° . The band gap energy of catalyst over composite beads was calculated from analysis through UV–visible diffuse reflectance spectrometer (DRS), UV-2600, Shimadzu (Asia Pacific) in the UV–visible range from 200 to 800 nm. The surface characteristics of catalyst over composite beads were also investigated through Fourier transform infrared spectroscopy (FTIR). The FTIR spectrums were analyzed through FTIR PerkinElmer spectrometer ranging from 4000 to 200 cm^{-1} employing KBr pellets. Thermo-gravimetric analysis (TGA) was carried out using SDT Q600 TGA/DTA

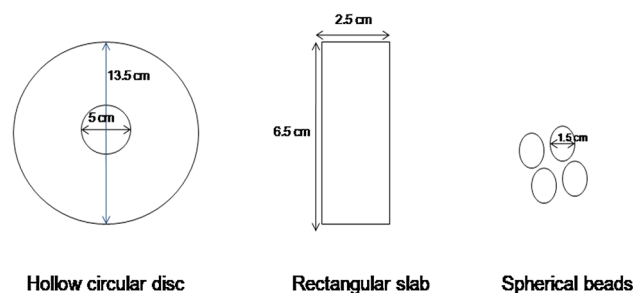


Figure 1 Line diagram of supports of different shapes.

Table 1 Original and coded levels of operating variables

Original variables	Factors	Coded levels		
		− 1	0	+ 1
Foundry sand (FS) concentration, mg L ^{−1}	A	500	1500	2500
TiO ₂ concentration, mg L ^{−1}	B	50	150	250
H ₂ O ₂ concentration, mg L ^{−1}	C	150	450	750
Treatment time (<i>t</i>), min	D	10	65	120

(TA Company, USA). Around 3 mg sample was taken for carrying out the analysis, and scanning of sample was performed in the range of 30–980 °C under inert nitrogen atmosphere. The generation of hydroxyl radicals was validated by monitoring the fluorescent signal through fluorescence spectrophotometer (LS-45, PerkinElmer) at 425 nm owing to the production of 2-hydroxy terephthalic acid (fluorescent compound) resulting from the reaction between hydroxyl radicals and sodium salt of terephthalic acid.

Experimental procedure

The experiments were carried out at laboratory scale in a wooden chamber containing seven UV tubes (Philips) of 36 W emitting UV-A radiations (365 nm). The complete details of laboratory-scale experimental setup have been supplied earlier in reported study [20]. A batch reactor (capacity 1000-mL glass bowl with 17 cm diameter and 5 cm height) of borosilicate containing 200 mL of working solution of CEX (50 mg L^{−1}) was kept over the laboratory jack under UV irradiations. An average UV intensity of $23 \pm 2 \text{ W m}^{-2}$ (measured through an Eppley radiometer (model no.-33013)) was maintained throughout the study. For slurry experiments and fixed-bed experiments using circular disk, continuous stirred-type conditions were maintained using a magnetic stirrer, while for fixed-bed experiments using adequate number rectangular slabs and spherical beads covering the entire base of the batch reactor, desired mixing was obtained by means of two air spargers with a flow rate of 3.5 L min^{-1} . All experiments were conducted under acidic conditions (pH = 3) maintained with an addition of appropriate amount of acetate buffer.

After definite intervals of time, adequate quantity of sample ($\sim 3 \text{ mL}$) was collected, filtered in case of slurry experiments and was successively analyzed.

Design of experiments

Response surface methodology (RSM) based upon Box–Behnken design (BBD) is an advantageous statistical tool used for modeling and parametric optimization [21]. This design was applicable for three level variables on response functions with minimum possible number of experiments [22, 23]. Total number of experiments (*N*) is defined by $N = 2K(K - 1) + C_0$, where *K* refers to the number of operational parameters and *C*₀ refers to the number of center points [24].

Therefore, in the current research work, RSM-based BBD was applied for the parametric optimization of CEX degradation via integrated process in slurry mode. Regression analysis as well as optimization was carried out using Design Expert v.6.0.8 software. The experimental data from design were examined and fitted through a second-order polynomial, Eq. (1).

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + e \quad (1)$$

where *Y* is the response, β is a constant (intercept), β_i , β_{ii} , β_{ij} are linear, quadratic and interaction coefficients, X_i , X_i^2 , X_j are the independent variables, and *e* refers to the residual term.

Preliminary experiments were carried out for the degradation of CEX at various operating conditions to decide the appropriate working range of parameters. The center of experiments was decided on the basis of preliminary experimental runs. The range of variables and operating parameters derived from BBD are listed in Table 1. The independent variables used were FS dose (A), TiO₂ dose (B), H₂O₂ concentration (C) and treatment time (D) and were coded for low (− 1), center (0) and high (+ 1) levels. ANOVA (analysis of variance) and coefficient of determination *R*² were employed for evaluating the significance of each parameter in the polynomial equation and fit the quality of experimental data.

Chemical analysis

The reduction in concentration of CEX after particular time intervals in each sample was measured through UV–visible spectrophotometer (LABINDIA, model–T60 U) at characteristic absorption wavelength of CEX (263 nm). The intermediates or by-products produced during the decomposition of CEX were determined through GC–MS (gas chromatography–mass spectrometry) analysis. The gas chromatograph, 45 × – GC, Bruker (USA), was connected with mass detector, MS–SCION-45P, Bruker, coupled with MS wax column (length = 30 m and diameter = 0.25 m). The m/z was scanned ranging from 30 to 350. Helium, a carrier gas, was employed at a flow rate of 1.0 mL min^{-1} . The temperature for injection was set at 280°C , while GC oven temperature was set in the range between 40 and 260°C with 10° increment in temperature. Approximately, $1 \mu\text{L}$ sample was used for injection, and split ratio of 1:10 was utilized for GC. Standard APHA methods [25] were used for the monitoring and quantification of nitrate, nitrite and sulfate ions, COD estimation and determination of total iron comprising of ferrous and ferric ions. H_2O_2 interference was omitted prior to COD determination by adding an adequate quantity of concentrated sodium carbonate solution and heating it at 90°C for about 1 h as described in the literature [26].

Synergy calculations

The synergy of binary process in the present study over discrete processes, i.e., photocatalysis and photo-Fenton, has been calculated by using the following equations:

Synergy over TiO_2 photocatalysis or photo-Fenton:

$$\% \text{ Synergy} = 100 \times \frac{\{k_{\text{binary}} - k(\text{photocatalysis or photoFenton})\}}{k_{\text{binary}}} \quad (2)$$

Overall synergy:

$$\% \text{ Synergy} = 100 \times \frac{\{[k_{\text{binary}} - (k_{\text{photocatalysis}} + k_{\text{photoFenton}})]\}}{k_{\text{binary}}} \quad (3)$$

where ' k ' is the first-order rate constant (min^{-1}) for each process.

Results and discussion

Preliminary studies

Initially, preliminary studies were carried out to analyze the influence of individual operating parameter on the degradation of CEX in the presence and absence of UV light as depicted in Fig. 2. Adsorption experiments in dark using TiO_2 and FS separately resulted into negligible amount of CEX removal (5–7%). The slight decrease in CEX concentration is generally due to the formation of pollutant (CEX) layer over the surface of TiO_2/FS , thus inhibiting almost all the active sites of catalyst which ceases further degradation of CEX [27]. Similarly, only 4–6% removal of CEX was obtained when experiment was performed in the presence of only H_2O_2 owing to the inadequate generation of OH radicals. Likewise, photolytic studies also led to only 3–5% removal of CEX. On the other side, photo-Fenton reaction using FS (0.5 g L^{-1}) as an alternative iron source along with addition of $300 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ under acidic conditions ($\text{pH} = 3$) revealed almost 45% degradation of CEX after 120 min of treatment time. Photocatalytic experiments with 0.25 g L^{-1} of TiO_2 and $300 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ yielded approximately 83% degradation of CEX after 120 min of UV irradiations. Interestingly, the integration of these two processes, i.e., photo-Fenton and photocatalysis by adding 0.5 g L^{-1} FS and $0.25 \text{ g L}^{-1} \text{ TiO}_2$ within the same unit in the presence of $300 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$ resulted in 85% degradation of CEX after 90 min of treatment. Thus, the degradation rate of CEX was accelerated using the integrated process resulting in

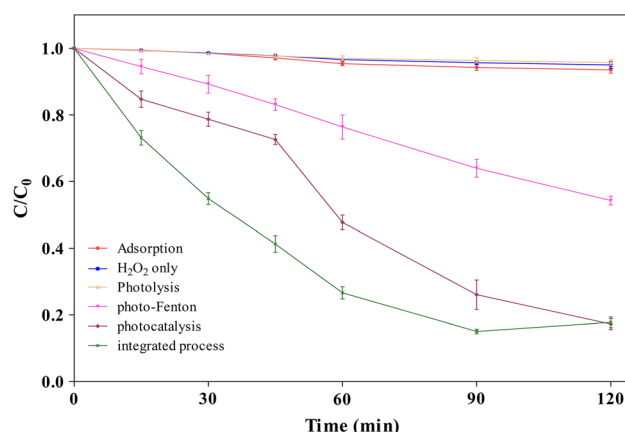


Figure 2 Plot of C/C_0 versus time for the degradation of CEX through preliminary processes.

significant reduction in treatment time from 120 to 90 min. The value of rate constant ' k ' in case of integrated process (0.021 min^{-1}) was increased five times as compared to photo-Fenton (0.004 min^{-1}) and almost twofold in contrast to photocatalysis (0.013 min^{-1}). Moreover, the overall synergy of integrated process over distinct processes (photo-Fenton and photocatalysis) was observed to be 19%. Therefore, in view of the best possible degradation of CEX in minimum time, integrated process by coupling photocatalysis and photo-Fenton within the same treatment unit has been investigated thoroughly in the present study.

Statistical analysis

For the integrated process (photocatalysis and photo-Fenton) under UV irradiations, photo-degradation of CEX was considered as a response under different operating conditions. B-B design matrix and % degradation of CEX are listed in Table 2. The dose of TiO_2 was varied from 50 to 250 mg L^{-1} , FS ranged from 500 to 2500 mg L^{-1} , H_2O_2 ranged from 150 to 750 mg L^{-1} , while treatment time ranged from 10 to 120 min. The dose of TiO_2 was varied in a narrow range in view of the economy of process.

For choosing the best model for the degradation of CEX through integrated process, sequential F-test along with other adequate measures were used as depicted in Table 3. Quadratic model was suggested in the present case as value of P for response was less

Table 2 BBD design matrix and responses for CEX degradation

Run	Foundry sand, FS (mg L^{-1})	TiO_2 (mg L^{-1})	H_2O_2 (mg L^{-1})	Treatment time, t (min)	% Degradation, Y
1	1500.00	250.00	750.00	65.00	77.3
2	1500.00	150.00	750.00	10.00	17.02
3	1500.00	250.00	150.00	65.00	78.8
4	1500.00	150.00	450.00	65.00	79.6
5	500.00	150.00	750.00	65.00	67.19
6	1500.00	150.00	150.00	120.00	87.68
7	500.00	50.00	450.00	65.00	60.29
8	2500.00	150.00	450.00	10.00	29.46
9	2500.00	250.00	450.00	65.00	77.66
10	1500.00	150.00	450.00	65.00	80.45
11	2500.00	150.00	150.00	65.00	83.3
12	500.00	150.00	150.00	65.00	79.1
13	1500.00	150.00	150.00	10.00	33.08
14	1500.00	50.00	150.00	65.00	60.875
15	500.00	250.00	450.00	65.00	77.38
16	500.00	150.00	450.00	10.00	24.13
17	1500.00	150.00	450.00	65.00	83.18
18	1500.00	250.00	450.00	10.00	29.13
19	1500.00	150.00	750.00	120.00	88
20	1500.00	150.00	450.00	65.00	82
21	2500.00	50.00	450.00	65.00	70.2
22	500.00	150.00	450.00	120.00	85.8
23	1500.00	50.00	450.00	120.00	87.01
24	1500.00	150.00	450.00	65.00	78.8
25	1500.00	50.00	450.00	10.00	22.8
26	1500.00	250.00	450.00	120.00	88.4
27	1500.00	50.00	750.00	65.00	62.79
28	2500.00	150.00	450.00	120.00	89.7
29	2500.00	150.00	750.00	65.00	73.89

Table 3 Selection of appropriate model for the degradation of CEX

Source	Sum of squares	DF	Mean square	F value	P	Remark
Sequential model sum of squares						
Mean	1.318E+005	1	1.318E+005			
Linear	12005.64	4	3001.41	25.09	< 0.0001	
2FI	101.35	6	16.89	0.11	0.9941	
Quadratic	2575.41	4	643.85	46.39	< 0.0001	Suggested
Cubic	145.45	8	18.18	2.23	0.1719	Aliased
Residual	48.88	6	8.15			
Total	1.467E+005	29	5057.68			
Lack of fit tests						
Linear	2858.42	20	142.92	45.13	0.0010	
2FI	2757.07	14	196.93	62.19	0.0006	
Quadratic	181.66	10	18.17	5.74	0.0534	Suggested
Cubic	36.21	2	18.11	5.72	0.0672	Aliased
Pure error	12.67	4	3.17			
Source	SD	R ²	Adjusted R ²	Predicted R ²	Press	Remark
Linear	10.94	0.8070	0.7748	0.7278	4049.50	
2FI	12.40	0.8138	0.7104	0.5193	7151.28	
Quadratic	3.73	0.9869	0.9739	0.9283	1066.15	Suggested
Cubic	2.85	0.9967	0.9847	0.6481	5234.56	Aliased

than 0.0001. A second-order polynomial equation obtained from ANOVA table has been depicted in Eq. (4), where A, B, C and D are the coded values of FS, TiO₂, H₂O₂ dosages and treatment time, respectively. A positive or negative sign before each factor in the equation represents synergistic or antagonistic effect of term on the degradation efficiency of CEX, respectively [21].

$$\begin{aligned} \% \text{ Degradation (Y)} = & +80.81 + 2.53A + 5.39B \\ & - 3.05C + 30.91D - 2.76A^2 \\ & - 5.95B^2 - 3.90C^2 - 19.75D^2 \\ & - 2.41AB + 0.62AC - 0.36AD \\ & - 0.85BC - 1.24BD + 4.09CD \end{aligned} \quad (4)$$

The *P* values as well as *F* values were used as the tools to determine the significance of each variable. High *F* value (greater than 5) and very low probability *P* value (less than 0.05) indicated the significance of variables on the degradation efficiency of CEX [28]. The Model *F* value of 75.56 implied that the model was significant. The *P* and *F* values obtained in the present study from ANOVA table are presented in Table 4. The significant model terms for the degradation of CEX were found to be A (FS dose), B (TiO₂ dose), C (H₂O₂ dose), D (treatment time), B² (quadratic term of TiO₂ concentration), C² (quadratic

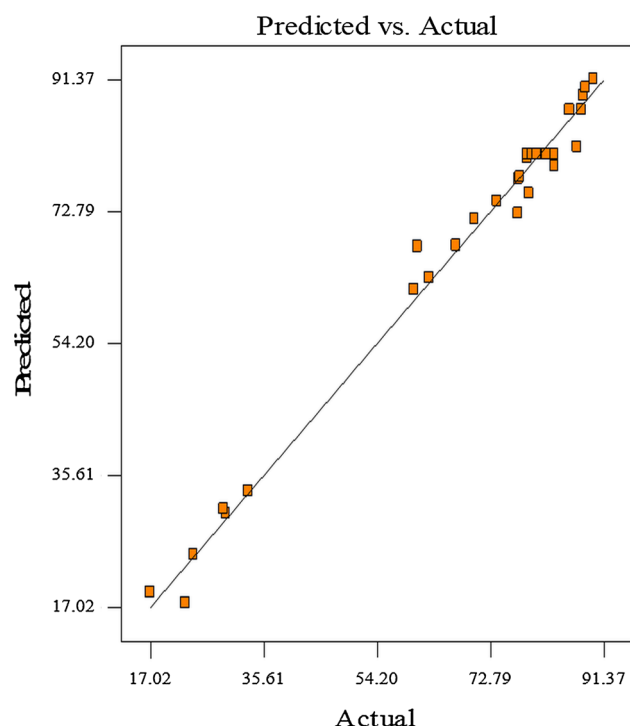
term of H₂O₂ concentration), D² (quadratic term of treatment time) and CD (interaction between H₂O₂ concentration and treatment time). The value of determination coefficient, i.e., *R*² = 0.9283, validated the model fitting and indicated a good correlation between predicted experimental and observed actual results. Figure 3 shows a correlation between predicted and actual values for CEX degradation. Figure clearly represents a good fit for regression. An adequate precision ratio for the degradation of CEX was found to be 27.546. Precision ratio above 4 is desirable which further confirms the adequate fitting of model [29].

Response surface methodology and optimization

Figure 4 shows the response surface plots along with contours representing the influence of each parameter on the degradation of CEX. The concentration of TiO₂ was varied in a narrow range from 50 to 250 mg L⁻¹, while waste FS was varied over a wider range from 500 to 2500 mg L⁻¹. Initially, with an increase in the concentration of both catalysts, i.e., TiO₂ and FS, the degradation of CEX also increased owing to the generation of OH radicals in abundance from both processes (photocatalysis and photo-

Table 4 ANOVA obtained from the response

Source	Sum of squares	DF	Mean square	F value	P value Prob > F
Model	14682.40	14	1048.74	75.56	< 0.0001
A	76.61	1	76.61	5.52	0.0340
B	348.89	1	348.89	25.14	0.0002
C	111.90	1	111.90	8.06	0.0131
D	11468.23	1	11468.23	826.22	< 0.0001
A ²	49.59	1	49.59	3.57	0.0796
B ²	229.48	1	229.48	16.53	0.0012
C ²	98.62	1	98.62	7.11	0.0185
D ²	2530.42	1	2530.42	182.30	< 0.0001
AB	23.18	1	23.18	1.67	0.2171
AC	1.56	1	1.56	0.11	0.7422
AD	0.51	1	0.51	0.037	0.8506
BC	2.92	1	2.92	0.21	0.6538
BD	6.10	1	6.10	0.44	0.5181
CD	67.08	1	67.08	4.83	0.0452

**Figure 3** Regression plot of predicted versus actual for % degradation of CEX.

Fenton) occurring simultaneously. Beyond certain dosages of both catalysts, the degradation of CEX started declining which may be due to the ineffective penetration of light in CEX solution at high concentration of catalysts, thus interfering with the production of OH radicals [5]. Overdose of iron, i.e., FS in the present study, generates iron sludge and may also cause scavenging effect of OH radicals. Likewise,

overdose of TiO_2 decreases the transparency of solution, thus inhibiting the effective penetration of light which affects the generation of OH radicals. Thus, optimum concentration of FS and TiO_2 for the degradation of CEX via coupled process was found to be 300 and 38.65 mg, respectively. The influence of H_2O_2 on the degradation of CEX with time at optimized dose of FS and TiO_2 is demonstrated in Fig. 4b. The amount of OH radicals generating from two simultaneously occurring processes, i.e., photocatalysis and photo-Fenton, within the same treatment unit increased with an increase in the concentration of H_2O_2 up to 241 mg L^{-1} . However, scavenging effect of OH radicals predominated at high dose of H_2O_2 .

Finally, the optimal conditions for the best possible degradation of CEX via integrated process were attained by a polynomial equation. The optimum values for FS dosage, TiO_2 concentration, H_2O_2 amount and treatment time were 1500, 193.25, 241 mg L^{-1} and 87 min, respectively. At optimum conditions, % degradation of CEX predicted by BBD was 90.428%. An almost 90% degradation of CEX was achieved at optimum conditions which is in close proximity to the predicted value.

None of the studies in the literature has reported the degradation of CEX within this duration. Ajoudanian and Nezamzadeh-Ejhieh [17] had reported approximately 76% degradation of CEX after 5 h of treatment time. Thus, studied integrated process using waste FS along with low concentration of photocatalyst in the current research work has

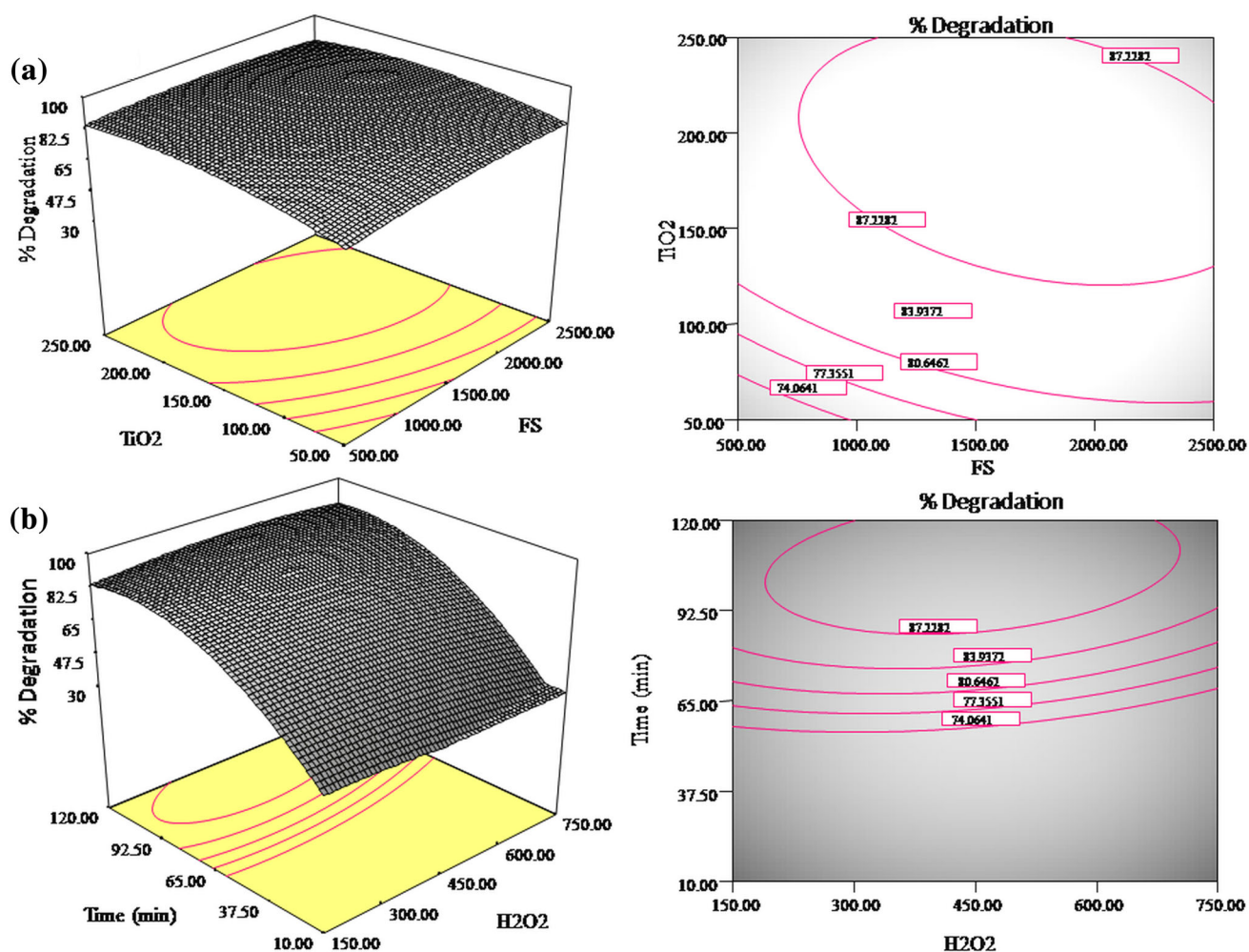


Figure 4 3-D response graph along with contours for the degradation of CEX **a** % degradation versus FS and TiO₂ and **b** % degradation versus H₂O₂ and time.

successfully reduced the treatment time to 90 min with significant degradation of CEX (90%).

Fixed-bed studies

Though excellent degradation efficiency of CEX was attained via integrated process in slurry mode, separation of catalysts post-treatment makes the overall process complex as well as expensive. Thus, in view of the field-scale applications, trials were executed to shift the whole treatment unit completely in fixed mode. Selection of the inert supports for catalyst immobilization plays a crucial role in designing and operation of fixed-bed photocatalytic reactors. The exposed surface area of immobilized catalyst totally depends upon the size/shape of immobilizing agent which is thus considered to be the most significant

parameter in case of fixed-bed reactors. In this regard, supports of different shapes (circular disks, rectangular slabs and spherical beads) were prepared using waste FS and clay for TiO₂ immobilization as detailed in Sect. 2.2. Iron was found to be leaching from the supports by default under acidic conditions which led to the occurrence of photo-Fenton process simultaneously along with photocatalysis. All fixed-bed reactions were carried out using optimized concentration of H₂O₂ (241 mg L⁻¹) under UV irradiations.

Degradation of CEX with TiO₂ immobilized disk

The hollow circular disk was designed so as to facilitate the continuous stirred-type conditions which led to desirable mixing of the particles. The

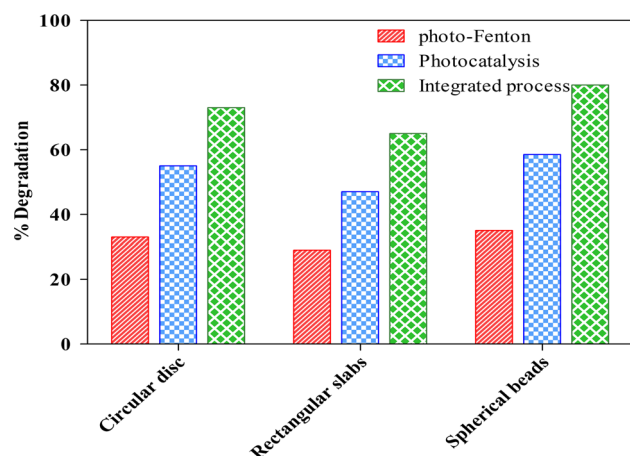


Figure 5 Effect of supports of various shapes (hollow circular disk, rectangular slabs, spherical beads) on the degradation of CEX through photocatalysis, photo-Fenton and integrated process.

experiments were performed with control disk (clay/ TiO_2) representing photocatalysis, blank disk (clay/FS) portraying photo-Fenton and composite disk (clay/FS/ TiO_2) displaying integrated process for the degradation of CEX. Photocatalytic experiments revealed 55% degradation, and photo-Fenton process yielded 33%, whereas integrated process resulted in 73% degradation of CEX after 240 min of treatment as indicated in Fig. 5. The rate of degradation was accelerated through integrated process as it took lesser time (almost 150 min) to achieve 55% degradation of CEX as compared to 240 min via photocatalysis. Moreover, value of rate constant ' k ' was improved to 0.0052 min^{-1} in case of integrated process compared to 0.0012 min^{-1} (photo-Fenton) and 0.0036 min^{-1} (photocatalysis). In addition to this, overall synergy of integrated process over individual processes was quantified to be 7.6%. Composite disk led to the in situ leaching of iron contributing to photo-Fenton along with occurrence of photocatalysis owing to the presence of TiO_2 on its surface. The amount of leached iron from composite disk during the integrated process was quantified as listed in Table S2 (Supplementary information).

Though satisfiable degradation efficiency of CEX was obtained using circular composite disk, its recyclability was not up to the mark. The catalyst was not firmly attached over the surface of disk as most of the TiO_2 particles drained off even after the first cycle. The same composite disk was reused five times with significant reduction ($\sim 20\%$) in the

degradation efficiency of CEX. It may be postulated that in the recycling experiments, degradation of CEX occurred mainly due to the simultaneously ongoing photo-Fenton reaction.

Degradation of CEX with TiO_2 immobilized slabs

Likewise, experiments were performed with catalyst immobilized rectangular slabs for the degradation of CEX. The major disadvantage of these types of immobilized systems is the improper mixing of particles as continuous stirring of the solution is not possible using such catalyst support materials. Thus, two air spargers were used in place of stirrer to acquire the desired mixing in the treatment system. Different processes, i.e., photocatalysis, photo-Fenton and integrated process, were performed using control, blank and composite slabs for the degradation of CEX under UV irradiations in the same pattern as discussed in earlier section. The synergistic effect of integrated process over individual processes was observed for the degradation of CEX in the same manner as studied in case of composite disk. Expectedly, composite slabs exhibiting integrated process yielded best results for the decomposition of CEX (65%) in contrast to photocatalysis (47%) and photo-Fenton (29%) after 240 min of UV irradiations (Fig. 5). The value of rate constant ' k ' was the highest, i.e., 0.004 min^{-1} , in case of integrated process as compared to photo-Fenton, i.e., 0.0012 min^{-1} and photocatalysis, i.e., 0.0026 min^{-1} . The overall synergy of integrated process over individual processes came out to be 5%.

Though degradation of CEX was more efficient in case of composite disk (owing to the presence of desirable mixing conditions) in contrast to slabs, durability and stability of immobilized catalyst was much better in case of slabs. An almost 20% reduction in degradation efficiency was observed after reusing the slabs subsequently for 10 runs as compared to 5 times in case of disk. Thus, efforts are still required to further enhance the efficiency of process with durable and stable immobilized catalysts so that technique can be implemented at field scale.

Degradation of CEX with TiO_2 immobilized beads

In spite of the improper mixing of particles in this case also, spherical composite beads revealed the best results in terms of degradation efficiency as well as

durability/recyclability of immobilized catalyst. Actually, the exposed surface area of immobilized catalyst was significantly improved using spherical shaped beads as catalyst support which led to a remarkable increase in the efficiency of treatment process. The composite beads were successfully reused for more than 10 cycles with almost 15% diminution in the degradation efficiency of CEX. However, using the same beads subsequently for further experiments, continual decrease in degradation of CEX was observed due to the weathering off photocatalyst particles from the surface of beads.

Composite beads resulted in 80% degradation of CEX with the highest value of rate constant, i.e., 0.006 min^{-1} after 240 min of UV irradiations (Fig. 5). Synergistic effect was confirmed when photocatalytic experiments were conducted using control beads revealing 0.004 min^{-1} as rate constant, and photo-Fenton process yielded 0.0014 min^{-1} as rate constant using blank beads. Overall synergy of integrated process over discrete processes was observed to be around 10%.

To bring into insight the commercial applicability of the studied integrated process, experiments were executed with composite beads under natural sunlight as well. Interestingly, treatment time was reduced from 240 min to 210 min to achieve almost 82% degradation of CEX when experiments were executed under natural solar radiations. Actually, photo-Fenton reaction covers wider range of spectrum (UV + visible) which might be the probable reason for enhancement of degradation efficiency of CEX with integrated process under sunlight. The solar experiments were carried out during the

months of April–May 2017 from 10:00 a.m. to 2:00 p.m. at Thapar University, Patiala (30.3398°N , 76.3869°E), Punjab (India). The average solar intensity during the experimental period was 865 W m^{-2} .

Though the degradation time was significantly increased with fixed-bed approach in comparison with slurry process incorporating integrated effect, the treatment time was still lower as compared to individual processes in fixed mode. In our previous study [5], 80% degradation of CEX took 300 min via fixed-bed photocatalysis using TiO_2 immobilized cement beads. Therefore, the treatment time was successfully reduced in the present study incorporating novel concept of integrated effect by coupling photocatalysis and photo-Fenton using novel composite beads.

Comparison between studied TiO_2 immobilized supports

TiO_2 -coated supports (FS + clay) of different shapes (hollow circular disks, rectangular slabs and spherical beads) were employed to study the degradation of CEX through integrated process. It was confirmed that shape of the immobilizing agent imparts a significant contribution in fixed-bed studies. In the current research work, the degradation rate of CEX with different shaped supports followed the successive order: spherical beads (0.006 min^{-1}) > circular disk (0.0052 min^{-1}) > rectangular slabs (0.004 min^{-1}) as shown in Fig. 6a. This order is with regard to the established fact that the more the exposed surface area of immobilized catalyst, the more the degradation efficiency. The exposed surface area of immobilized catalyst was significantly incremented to almost

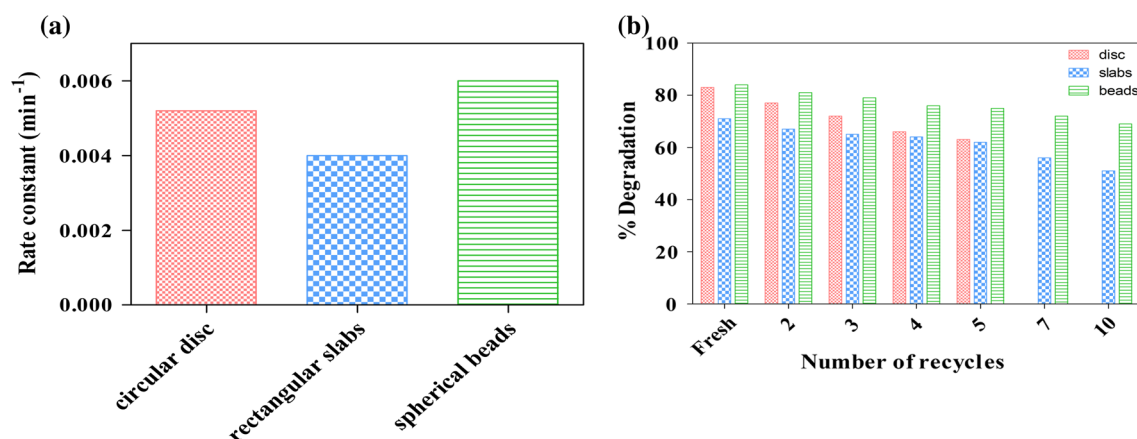


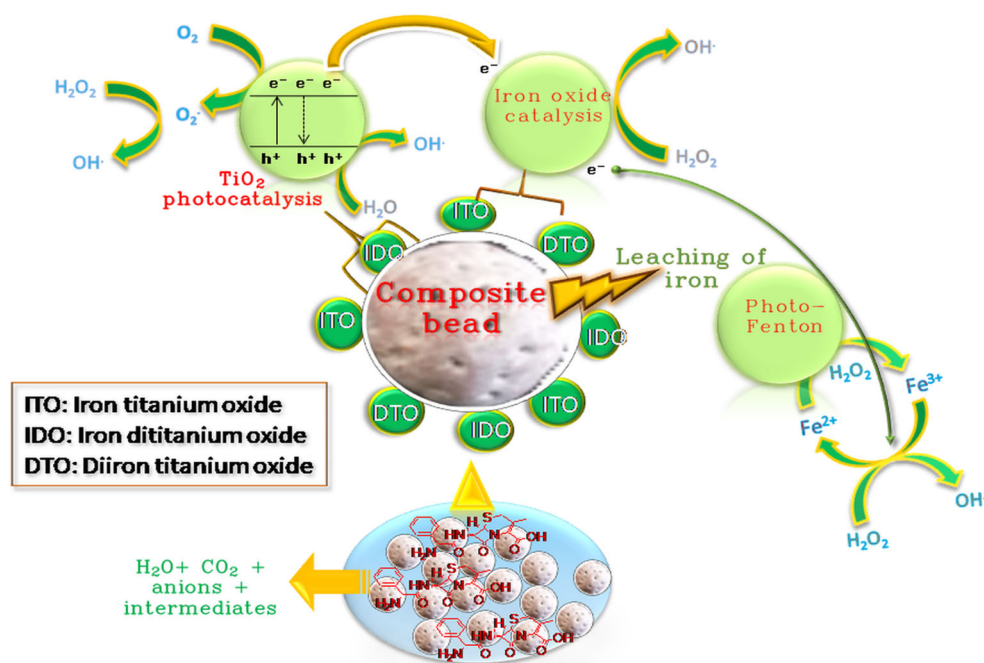
Figure 6 **a** Plot of first-order rate constant versus different supports for the degradation of CEX, **b** recyclability studies of different supports for the degradation of CEX.

0.0265 m² in case of spherical beads, whereas exposed surface area remained quite low in case of slabs (0.0113 m²) and circular disk (0.0123 m²). In spite of the significant variation in the exposed surface area of beads and disk, degradation rate constants in each case came out to be almost same. The reason for the improved degradation rate in case of disk was the availability of better mixing conditions in the system. In addition to the enhanced degradation efficiency of CEX, spherical beads also displayed maximum stability/durability of immobilized catalyst. The durability of catalyst immobilized supports acquired the following trend: spherical beads > rectangular slabs > circular disk. The beads were recycled for more than 10 runs with almost 15% reduction in the degradation efficiency as demonstrated in Fig. 6b. Thus, best results with respect to the degradation efficiency and recyclability of the catalyst were obtained with spherical composite beads. However, some variations or modifications in the support material are still required to further enhance their recyclability efficiency so that technique can be successfully implemented at field scale. To the best of our knowledge, this is the first reported study detailing fixed-bed approach incorporating binary process (photocatalysis and photo-Fenton) for the degradation of CEX with reduced treatment time.

Proposed mechanism of binary process

It is clear from results that binary process by coupling photocatalysis and photo-Fenton whether in slurry or in fixed mode has proven to be the most efficient technique in comparison with discrete processes (photocatalysis or photo-Fenton) for the degradation of CEX. In binary process, active radicals are produced not only from single process but from different processes like photocatalysis and photo-Fenton occurring simultaneously within the same unit. Thus, abundant of active radicals, i.e., hydroxyl radicals, are generated in the system, thereby enhancing the degradation efficiency. However, in the present case, hydroxyl radicals were produced not only through heterogeneous TiO₂ photocatalysis and homogeneous photo-Fenton process (leached iron species), but also through iron oxide catalysis as depicted in Scheme 1. Various forms of iron oxide present on the surface of composite were already confirmed through XRD analysis as discussed in Sect. 3.6.2. The presence of iron oxide on the surface of beads restrained the recombination of electrons and holes, thus ultimately enhancing the degradation efficiency of CEX. Actually, photon-excited electron from TiO₂ got entrapped by iron oxide and participated in the regeneration of Fe²⁺ ions from Fe³⁺ ions, thus facilitating the photo-Fenton reaction [11].

Scheme 1 Proposed mechanism of binary process.



Characterization of composite beads

The spherical composite beads were characterized through several techniques for the presence of TiO_2 as well as iron on its surface to further confirm our claim for the existence of coupled process (photo-catalysis and photo-Fenton) within the same treatment unit.

SEM/EDS analysis

The morphological characteristics and elemental composition of composite beads were analyzed through scanning electron microscopy (SEM) and electron-dispersive spectroscopy (EDS), respectively, as shown in Fig. 7a. The prominent peaks of 'Ti' and 'Fe' in the EDS image (Fig. 7a(ii)) strongly affirm our claim for the utilization of composite beads for integrated process. The smooth surface in the SEM image clearly indicates the uniform coating of TiO_2 on the surface of beads. To confirm the stability of immobilized catalyst even after 10 recycles, SEM/EDS analysis of recycled composite beads was also performed which is depicted in Fig. 7a(ii). Irregular surface was observed in the SEM image owing to the weathering off some of the catalyst particles with subsequent recycles. However, discrete peaks of 'Ti' and 'Fe' in EDS image depicts the existence of both catalysts even in recycled beads, thus suggesting that beads can be effectively used for binary process even after 10 recycles.

To further confirm our claim of effectively using the recycled beads (> 10 recycles) in binary process, their photocatalytic activity in comparison with fresh beads was evaluated on the basis of their capacity to generate hydroxyl radicals. Fluorescence spectrometric detection of hydroxyl radicals was performed using fresh and recycled composite beads. Significant amount of hydroxyl radicals were produced in case of recycled beads as well in comparison with fresh beads as shown in fig. S1 (Supplementary information). Thus, it can be concluded that the beads did not lose their photocatalytic activity and can be efficiently used for further experiments.

XRD analysis

X-ray diffraction (XRD) analysis of the composite beads was performed to examine whether any defect or change had occurred in TiO_2 due to the existence

of iron. XRD pattern of composite beads was compared with fresh TiO_2 to confirm the activity of catalyst over composite beads as shown in Fig. 7b. The presence of both anatase and rutile phase of TiO_2 (marked as 'A' and 'R', respectively) in the XRD pattern of composite beads proved that no surface defect occurred in TiO_2 , and thus, its activity was retained. Along with anatase and rutile peaks, few other peaks also appeared in the XRD pattern. These additional peaks indicated the presence of several forms of iron oxide over the surface of composite beads. Iron titanium oxide (reference code: 00-043-1011) marked as 'ITO', Diiron (III) titanium oxide (reference code: 01-073-1631) marked as 'DTO' and iron (II) dititanium oxide (reference code: 01-089-8065) marked as 'IDO' were identified through diffraction peaks along with TiO_2 . The presence of these forms of iron oxides along with TiO_2 over composite beads further validated the effective utilization of beads for binary processes. The detailed mechanism of binary process using these forms of iron oxide along with TiO_2 has been discussed in Sect. 3.5.

DRS analysis

Diffuse reflectance spectrums of composite beads and fresh TiO_2 are demonstrated in Fig. 7c. The analysis of samples was carried out in the UV-visible range from 200 to 800 nm. The UV-visible spectrum of composite beads displayed its capacity for absorbing the light even in visible spectra (owing to the presence of iron) as compared to TiO_2 which is capable of absorbing only UV light. The band gap of TiO_2 and composite beads was quantified using the following equation.

$$E_g = h\nu = \frac{hc}{\lambda} \quad (5)$$

E_g = band gap energy (eV), c = speed of light, h = Planck's constant, and λ = absorption wavelength.

Consequently, absorption edge in case of composite beads was extended to 422 nm resulting into the narrowing of band gap ($E_g = 2.94$ eV) in contrast to TiO_2 ($E_g = 3.14$ eV).

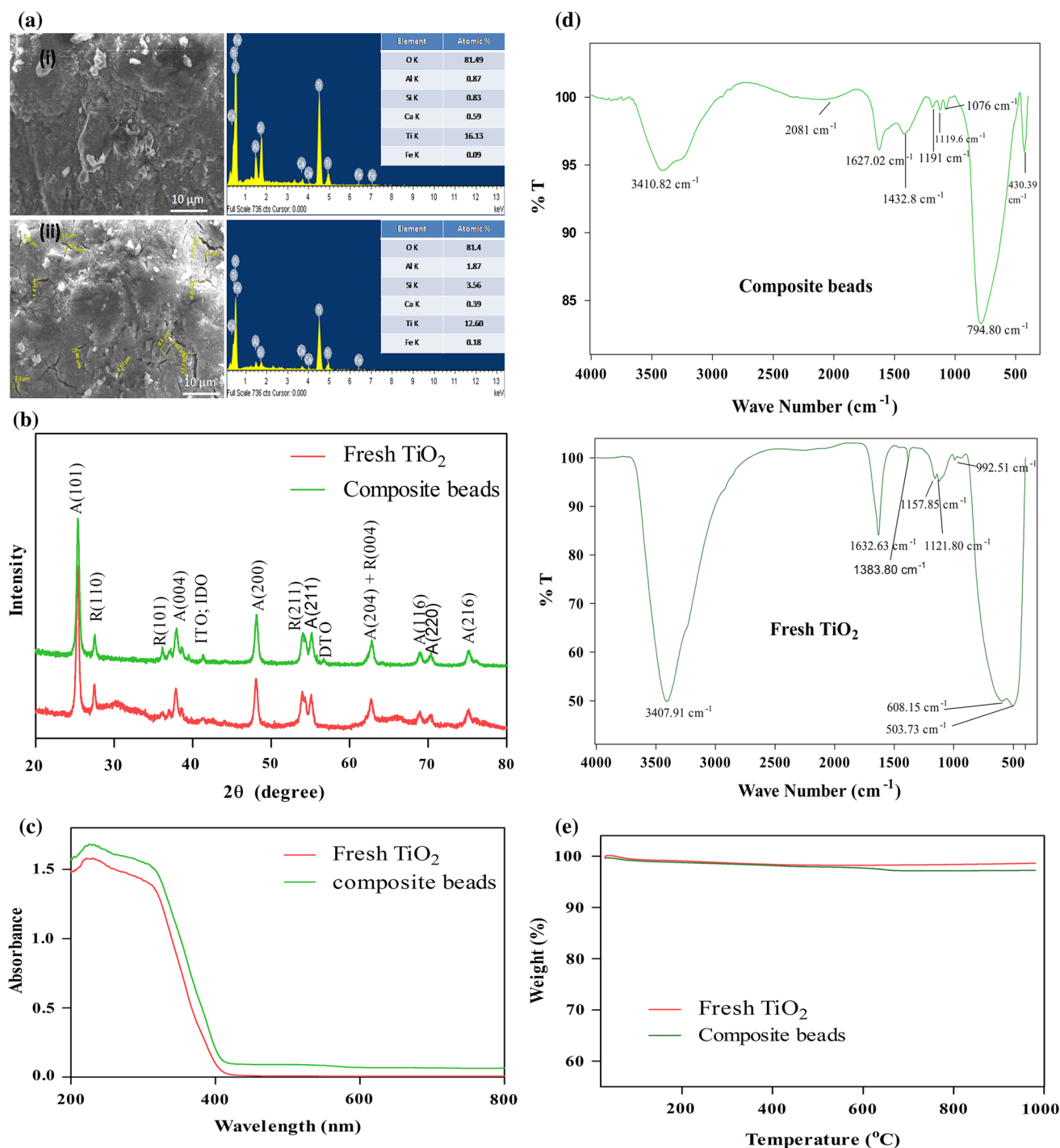


Figure 7 **a** SEM/EDS image of composite beads (i) freshly coated beads and (ii) after 10 recycles. **b** XRD pattern of **a** fresh TiO_2 and **b** composite beads. **c** UV-visible DRS of **a** fresh TiO_2 and **b** composite beads. **d** FTIR spectra of **a** fresh TiO_2 and **b** composite beads. **e** TGA analysis of **a** fresh TiO_2 and **b** composite beads.

FTIR analysis

The morphological features of composite beads in comparison with fresh TiO_2 were also analyzed through FTIR spectroscopy. The infrared spectra of

and **b** composite beads. **d** FTIR spectra of **a** fresh TiO_2 and **b** composite beads. **e** TGA analysis of **a** fresh TiO_2 and **b** composite beads.

TiO_2 and composite beads are shown in Fig. 7d. The appearance of peaks corresponding to wave number ranging from 400 to 1200 cm^{-1} in both spectrums confirms the occurrence of Ti–O–Ti bonds in both samples, thus proving the retention of TiO_2 lattice.

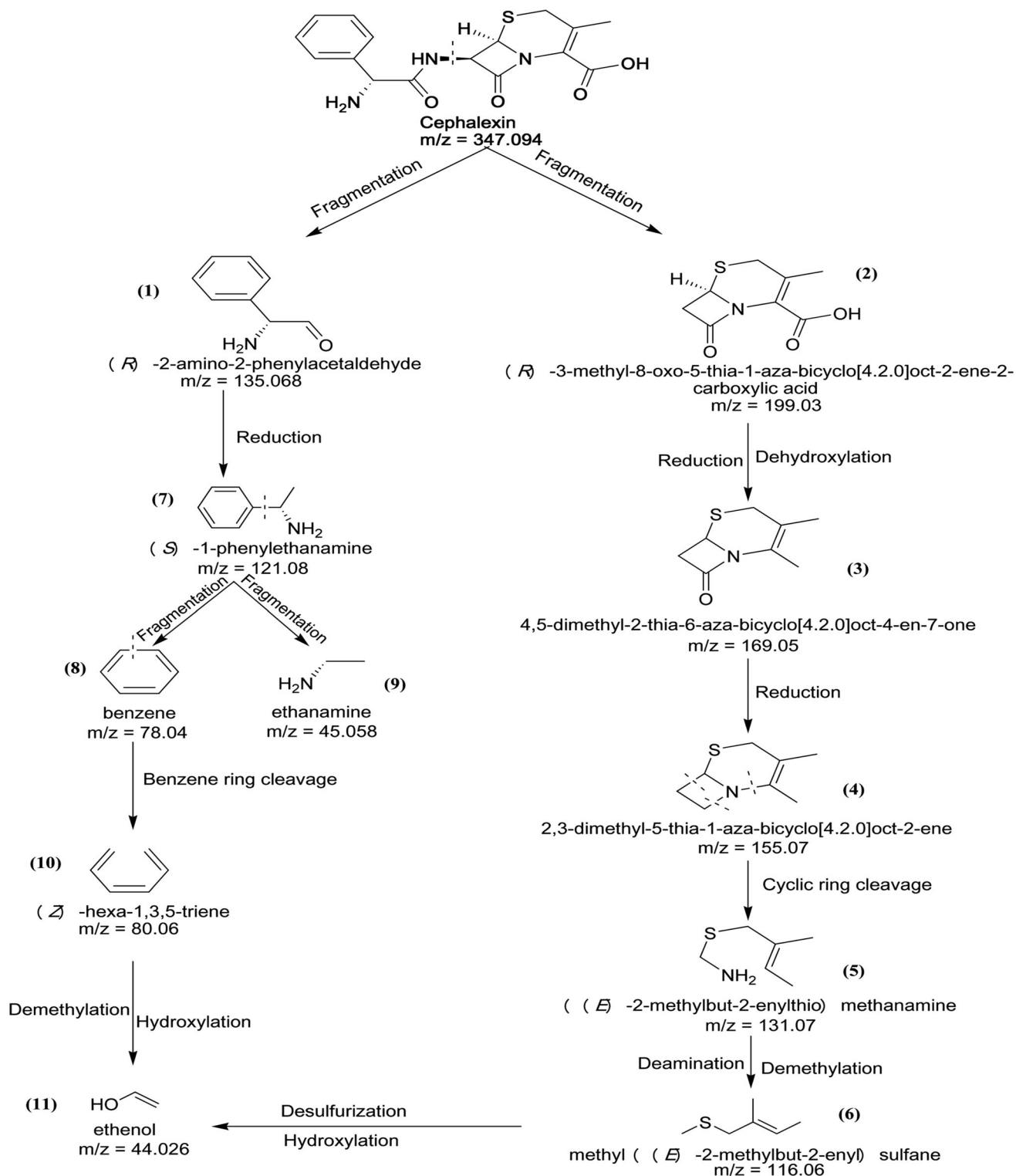


Figure 8 Tentative pathway for the degradation of CEX.

The peak occurring at 503.73 and 430.39 cm^{-1} in TiO_2 and composite beads, respectively, represents the anatase phase [30]. The broad peak appearing at

2078.19 cm^{-1} in the spectra of composite beads corresponds to the formation of Fe–O–Ti bond [31]. Thus, results are in a good correlation with XRD

pattern which already confirmed the existence of several forms of iron oxide, i.e., 'ITO', 'DTO' and 'IDO'. The transmittance bands appearing at 1632.63 and 1627.02 cm^{-1} in case of TiO_2 and composite beads, respectively, represent the Ti–OH groups. The occurrence of transmittance band at 3407.91 and 3410.82 cm^{-1} in case of TiO_2 and composite beads can be correlated with the presence of O–H groups stretching vibrations [30, 31].

TGA analysis

The thermo-gravimetric (TG) curves of TiO_2 as well as composite beads are depicted in Fig. 7e. No remarkable variation in weights of the catalysts was observed in the temperature ranging from 30 to 980 °C. Thus, it can be concluded that composite beads displayed an excellent thermal stability as compared to TiO_2 depending upon its inorganic structure.

Mineralization studies

The mineralization of CEX was confirmed with generation of anions including nitrite, nitrate and sulfate ions along with reduction in COD during the treatment process as shown in table S3. The concentration of nitrate ions in the current study followed a declining trend with the possibility of getting converted into nitrite ions [32]. There was almost 80% reduction in COD after 240 min of treatment time. The intermediates (1–11) formed during the degradation process were identified through GC–MS analysis. Based on these identified intermediates, a tentative pathway for the decomposition of CEX has been proposed as displayed in Fig. 8. The GC chromatograms indicating identified intermediates are shown in fig. S2 (Supplementary information).

Conclusion

A novel concept of binary process by integrating photocatalysis and photo-Fenton using waste materials like FS has been successfully demonstrated at laboratory scale in context of reduction in treatment time for the degradation of CEX. The treatment time was reduced to almost 90 min from 120 min for the degradation of CEX using integrated process. The optimized conditions in slurry mode obtained

through RSM based on BBD were FS: 1500 mg L^{-1} , TiO_2 : 193.25 mg L^{-1} , H_2O_2 : 241 mg L^{-1} and treatment time: 87 min. Experimental results were fitted to a second-order polynomial equation with value of determination coefficient R^2 to be 0.9283 obtained through statistical analysis which validated the model fitting. The practical applicability of studied integrated process was further confirmed by executing trials in fixed mode. Different supports with shapes like hollow circular disks, rectangular slabs and spherical beads were prepared using clay and FS for TiO_2 immobilization and were compared for their efficacy and durability for the degradation of CEX. TiO_2 immobilized spherical beads, i.e., composite beads exhibited best results in terms of degradation efficiency (80%) and recyclability (more than 10 cycles) as compared to other supports. Comprehensive characterization of composite beads through SEM/EDS, TGA, XRD, DRS and FTIR proved the presence of iron along with TiO_2 on the surface of beads which further confirmed our claim for their effective utility in integrated process. Mineralization of CEX was validated by production of various anions like nitrite, nitrate and sulfate along with reduction in COD (80%), and accordingly, suitable degradation mechanism was being proposed by analyzing intermediates through GC–MS analysis. The integrated process using composite beads with reduced treatment time can provide a better and economic solution to various industries for treating wastewater containing recalcitrant pollutants.

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Compliance with ethical standards

Conflict of interest There is no conflict of interest regarding any kind of content in the manuscript.

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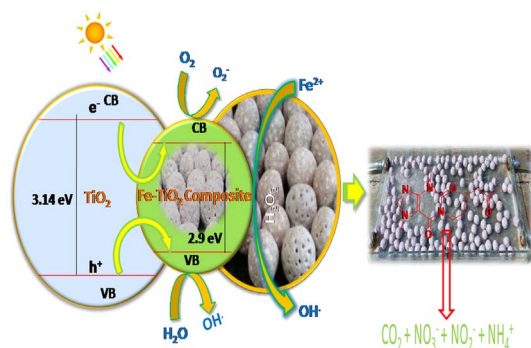
In-situ dual effect studies using novel Fe-TiO₂ composite for the pilot-plant degradation of pentoxifylline



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GRAPHICAL ABSTRACT



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ABSTRACT

An inexpensive sunlight responsive Fe-TiO₂ composite has been fabricated for the in-situ photo-degradation of an environmentally persistent pharmaceutical drug, pentoxifylline (PEN). There was sustainable leaching of iron into the solution through composite under acidic conditions thus exhibiting in-situ dual effect (photocatalysis and photo-Fenton) at the same time in the treatment unit. Scale-up studies were performed in a simple non-concentrating fixed-bed reactor using these Fe-TiO₂ composite with total volume handling of 5 L. The main strength of the study lies in the demonstration of reduction in treatment time to nearly half with overall synergy (32.4%) of dual process over individual processes. The process was intensified with proper optimization of all operating parameters like flow rate, number of baffles, catalyst and oxidant dose. The photonic efficiency of the system incorporating dual effect employing Fe-TiO₂ composite under all optimized conditions was increased to 1.62% with almost 93% removal of PEN after 4 h of treatment. The Fe-TiO₂ composite was durable enough to be successfully recycled for more than 35 runs without any significant reduction in degradation efficiency. The recycled composite retained the TiO₂ nanoparticles along with existence of iron as confirmed through various characterization techniques like SEM/EDS, XRD, DRS, FTIR and Raman spectroscopy. The generation of various anions, evolution of CO₂ and reduction in COD and TOC along-with formation of various intermediates (confirmed through GC-MS analysis) were studied to validate the mineralization of PEN. An approximate cost of the overall process has also been evaluated to envisage the commercial applications of the studied technique.

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1. Introduction

The increased intake of drugs or antibiotics in developing countries like India has evolved global problems of antibiotic resistance at alarming concentrations [1,2]. India has highest resistance rate to almost every drug or antibiotic to treat it [3]. This is mainly due to the lack of awareness programs related to dangers of overusing antibiotics. Situation gets intensified even more due to poverty, illiteracy especially when more than 60% population lives in rural areas. The subsequent effect attributed to the overuse of drugs is the ultimate occurrence of these drugs in surface waters either through secretion or disposal and thus included in category of emerging contaminants [4]. Most of these contaminants are persistent to environment and escalates the worldwide pollution of aquatic systems and has become one of the life threatening environmental problems that need to be addressed on immediate basis [5]. In spite of many published reports [6–8] regarding the presence of these micro-contaminants even in drinking water, conventional treatment methods are being relied in developing countries.

Replacement of traditional water treatment methods with efficient advanced water treatment technologies is need of the hour to improve the quality of treated effluents [9]. Various advanced oxidation processes (AOPs) including heterogeneous photocatalysis [10,11] and homogenous photo-Fenton processes [12,13] have proven their effectiveness for wastewater detoxification. However, the artificial source of UV radiation in these treatment processes causes majority of maintenance and operating cost of the treatment unit due to the consumption and regular replacement of UV lamps [14]. Therefore, using natural solar radiations instead of artificial lamps is an environmentally attractive and economical solution for photocatalysis or photo-Fenton like processes [15]. The applications of solar-driven photocatalytic reactors fit well for countries like India which receives immense solar light throughout the year.

The most challenging task is to look for an appropriate material/catalyst that could harvest solar radiations efficiently. In addition to this, catalyst should have an ability to resist electron-hole recombination [16]. Though TiO_2 has been extensively investigated for photocatalytic degradation of large variety of pollutants [17] due to its low cost and photostability, it is deficit in terms of high electron hole recombination and its absorption in UV region. Various effective modifications in the structure of TiO_2 either by doping with metals/non-metals or preparing nano-composites are reported in literature [18–21] to overcome the above discussed flaws. Tedious methods have been followed using costly raw materials in almost all reported studies to prepare modified TiO_2 . Moreover, these studies deal with catalyst suspensions thereby facing problem of catalyst separation after treatment.

The present study reports the synthesis of novel inexpensive support of Fe- TiO_2 composite using waste materials like foundry sand (FS) and fly ash (FA). Furthermore, none of the studies has reported scale-up of the process using modified TiO_2 for the degradation of pollutants as majority of studies have used small volume of aqueous solutions for treatment [22,23]. There are numerous of other studies that have focused on the scaling-up of process but with unmodified TiO_2 using non-concentrating photocatalytic reactors including flat-plate, tubular and shallow pond [24,25]. Though successful in terms of excellent degradation efficiency, practical feasibility of these reactors has not reached up to the mark due to more consumption of treatment time and costly separation of catalyst post-treatment. Fixing of catalyst particles on supports is the only solution left to pacify some of the concerns but reduced efficiency of the system with more treatment time are the questions to be answered yet. In this context, Feitz et al. (2000) [26] reported that efficiency of the system reduces with substantial increase in treatment time using supported catalyst as compared to catalyst suspensions. Efforts have been made in the present study to scale-up the process in fixed mode with total volume handling of 5 L using Fe- TiO_2 composite incorporating in-situ dual effect (photocatalysis and photo-

Fenton) with significant reduction in treatment time. In fact this is the first reported study using novel Fe- TiO_2 composite for pilot-scale studies.

Therefore, the main objective of current research work is to explore the feasible and low-cost solution for the removal of non-biodegradable pharmaceutical drug, pentoxifylline (PEN) in minimum possible time with development of simple solar non-concentrating reactor. PEN is a vasodilator drug mainly used for the treatment of atherosclerotic disease in periphery vascular system. The high stability and recalcitrant nature of PEN has already been proved [27] with concentration of PEN to be reported as high as 1370 ng L^{-1} in aquatic environment [28]. Degradation of PEN has been studied in literature through photo-Fenton [29], ozonation [27] and non-thermal plasma treatment [30]. The in-situ dual effect concept with Fe- TiO_2 composite has been used in the present study for scaling up of the process. The process has been intensified by studying the influence of various operating parameters like flow rate, number of baffles, dose of oxidant and catalyst to achieve the optimum conditions for best degradation efficiency. The durability and stability of the composite was evaluated by recycling it for subsequent runs along with its comprehensive characterization through various techniques like DRS, XRD, SEM/EDS, Raman spectroscopy and FTIR. The intermediates were identified through GC-MS analysis. Mineralization of the pollutant was studied through reduction in COD and TOC along with the formation of various anions and carbon-dioxide. This is the first reported study till date with scale-up of the process using Fe- TiO_2 composite in fixed-mode incorporating in-situ dual effect for the removal of organic pollutants from water. The overall cost of the process has also been evaluated for the first time to envisage the commercial applications of the presented technique.

2. Materials and methods

2.1. Chemicals and reagents

Pentoxifylline (PEN) (> 98% purity) procured from TCI Chemicals, India was used without undergoing any purification or modification. Degussa TiO_2 -P25 was obtained from Evonik (India) while Hydrogen Peroxide (H_2O_2) (30% w/v), an oxidant was purchased from Ranbaxy (India). Waste fly ash (FA) as well as waste foundry sand (FS) was collected as such from a local industry, Patiala (India). Clay was acquired from local vendor, Patiala (India). Sodium acetate, > 98.5% purity and acetic acid, > 99.5% purity, purchased from TCI Chemicals (India) were used for preparing acetate buffer. Sodium carbonate (anhydrous), > 98.5% purity was procured from Loba Chemie pvt Ltd (India). All aqueous solutions were prepared with double distilled water.

2.2. Fe- TiO_2 composite

Briefly, spherical beads of varying diameter (10–20 mm) were prepared manually using clay, FS and FA in the ratio 2:1:1 (Blank beads). Based upon the strength of composite as well as optimum iron content analysis, this particular ratio (2:1:1) was fixed and has been reported in this study. When ratio of FA or FS was increased, sufficient binding of the support was not obtained thus lowering down the durability of composite. Whereas when ratio of iron salt was decreased, sufficient amount of iron was not leached into the solution thereby reducing the efficiency of dual process. The blank beads were baked in muffle furnace at 1000°C for 1 h. Fe- TiO_2 composite was prepared by coating the blank beads with TiO_2 using standard dip-coating method as discussed in reported study [31]. Two coatings of catalyst were sufficient for the formation of uniform layer of TiO_2 on beads. FA and FS were already characterized earlier for the presence of iron in these waste materials [32]. The SEM-EDS images of blank beads and freshly coated composite are depicted in Fig. 1. The presence of iron along with TiO_2 can be clearly seen in EDS spectra of freshly coated composite. For confirming

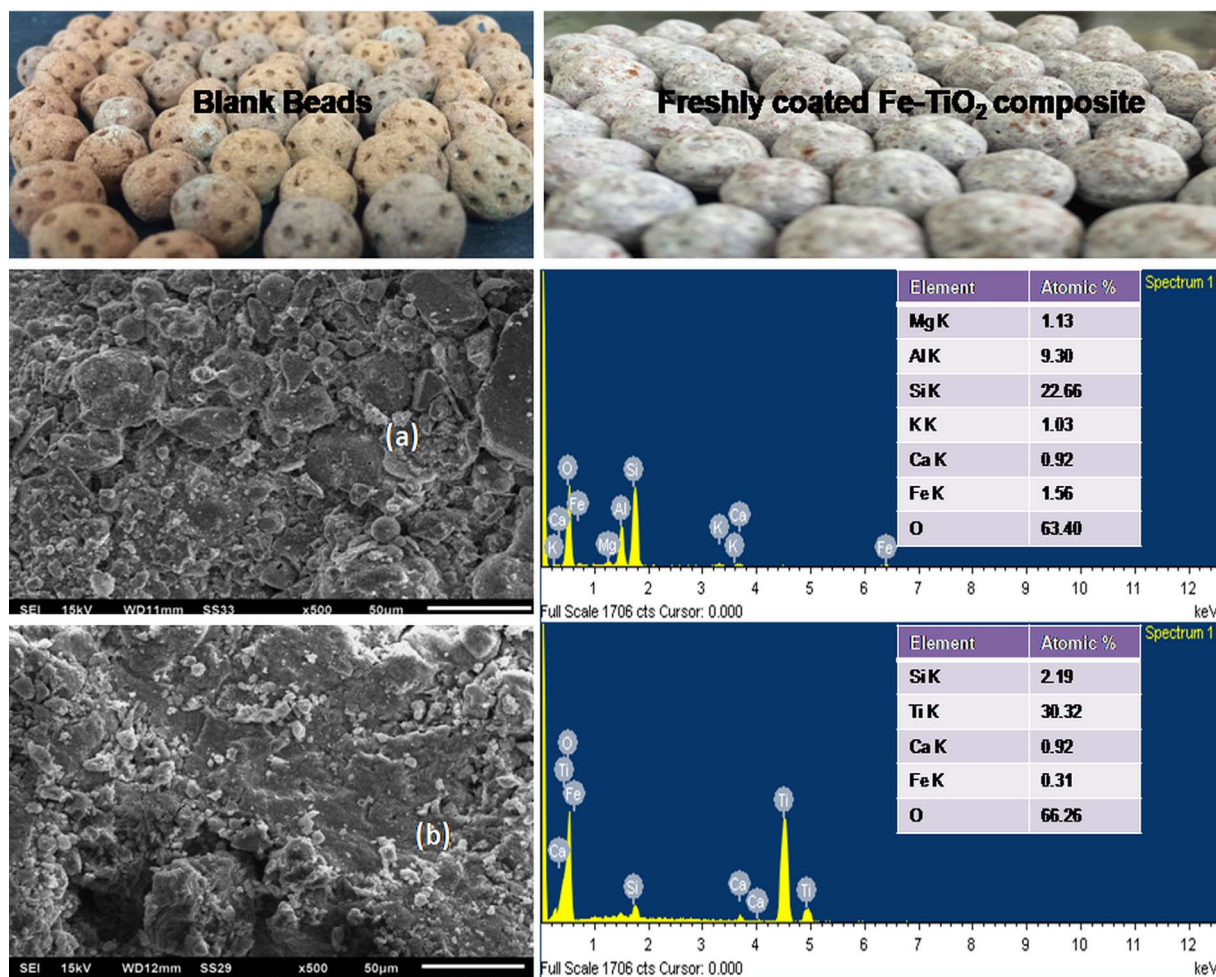


Fig. 1. Actual photographs along with SEM/EDS images of (a) blank and (b) Fe-TiO₂ composite.

the efficacy of Fe-TiO₂ composite, a comparative analysis was also carried out by preparing different TiO₂ immobilized supports using clay + FA and clay + FS. For conducting control studies, TiO₂ coated clay beads (Control beads) were prepared in the same manner as discussed for composite. The difference is that these beads did not contain any FA or FS.

2.3. Characterization techniques

The prepared immobilized catalyst (Fe-TiO₂ composite and control beads) was characterized through various techniques for the presence of iron along with TiO₂. The surface morphology of Fe-TiO₂ composite as well as control beads was assessed through scanning electron microscopy (SEM), model-JSM-6510LV, JEOL, Japan. The elemental composition of composite and control beads was evaluated through electron dispersion spectroscopy (EDS), model-INCA-X-act, Oxford instruments, United Kingdom. X-ray diffraction (XRD) studies were performed to analyze the crystalline structure of the prepared catalyst using X'Pert pro diffractometer in the range from 2θ = 20–80°. The band gap energy of the catalyst was observed through UV–visible diffuse reflectance spectrophotometer, UV-2600 (Shimadzu, Asia Pacific). The analysis was carried out in the range from 200 to 800 nm. The surface of the catalyst was also investigated through Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded on FT-IR Perkin Elmer spectrometer in the range of 4000–200 cm^{−1} employing

KBr pellets. The Raman spectra were recorded using confocal micro Raman spectrometer, STR 500, Airix Corporation (Japan) integrated with a diode green laser (532 nm).

2.4. Solar photocatalytic reactor

A solar non-concentrating flat-bed reactor (40 cm × 20 cm × 2.5 cm) made up of glass was employed for the degradation of PEN. The reactor was provided with two inlets and two outlets and also contained a provision of up to 5 detachable glass baffles (Length = 6 cm, Height = 2.5 cm, Thickness = 0.5 cm) as depicted in Fig. 2. The reactor was operated in recirculation mode and was designed to treat a total volume of 5 L. PEN aqueous solution (5 L) with adequate amount of H₂O₂ was pumped from the storage tank through the reactor bed where it was passed through Fe-TiO₂ composite at optimum flow rate and then circulated again into the storage tank. The experiments were conducted at natural pH of PEN solution i.e. 4. The major problem that occurred was the increase in pH of solution during the course of reaction which reduces the efficiency of simultaneously on-going photo-Fenton process. Thus, pH of the solution was stabilized to its natural pH with addition of adequate amount of acetate buffer. Around 3–4 mL sample was collected at regular intervals of period and was subsequently analyzed. The reactor was shielded with transparent cling film to prevent any evaporation losses.

All solar experiments were conducted in the months of February–May 2017 from 10 a.m to 4 p.m at Thapar University, Patiala (30.3398°

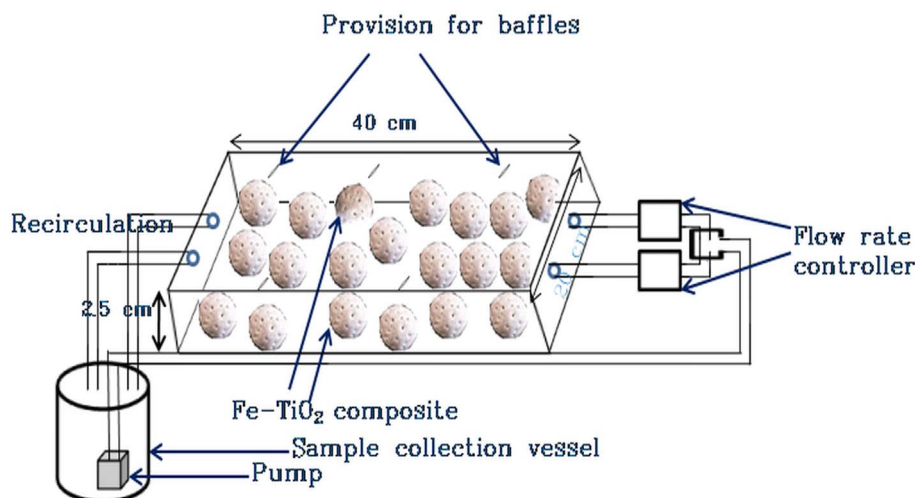


Fig. 2. Line diagram of pilot-scale non-concentrating solar photo-reactor.

N, 76.3869° E), Punjab, India. The solar intensity was measured regularly by means of pyranometer (Apogee: MP-100). The average solar intensity was 835 W m^{-2} during this period. All experiments were performed at-least three times for reproducibility of results and suitable statistics has been applied for evaluation of results.

2.5. Analytical determinations

The analysis of the samples was carried out at regular intervals of time through UV–visible absorption spectroscopy (LABINDIA, T60 U) with $\lambda_{\text{max}} = 273 \text{ nm}$ for PEN and high performance liquid chromatography, HPLC, Shimadzu (Japan). The HPLC unit had a communication module (CBM-20A) with diode array detector (SPD-M20A) and with pump (LC-20 CE). The system was operated with flow rate of 1.0 mL min^{-1} in binary mode using formic acid, 0.05% in water and acetonitrile as mobile phase with C-18 column and having particle size of $5 \mu\text{m}$. UV detector was set at 273 nm for PEN. $20 \mu\text{L}$ sample was injected each time and each analysis lasted for 20 min. The intermediates formed during the degradation of PEN were identified through gas chromatography–mass spectrometry (GC–MS) analysis. The gas chromatograph, $45 \times \text{GC}$ (Bruker, United States) was integrated with mass detector, MS-SCION-45P (Bruker) connected with wax column of MS (length 30 m and diameter 0.25 m). The m/z was scanned in the range from 50 to 410. Helium was utilized as a carrier gas with flow rate equal to 1.0 mL min^{-1} . The injection temperature was adjusted to 280°C while the temperature for GC oven was adjusted in the range $40\text{--}260^\circ\text{C}$ with every 10° increment in temperature. $1 \mu\text{L}$ of sample was injected and 1:10 split ratio was employed for GC. Standard APHA methods (1989) [33] were followed for the monitoring and evaluation of nitrite, nitrate and ammonium, total iron including ferrous and ferric ions and for COD estimation. The evolution of CO_2 was determined through gas chromatograph (NUCON-5765) employing Propak-Q column. Nitrogen was used as a carrier gas with a flow rate of 30 mL/min using thermal conductivity detector. The injection volume for gaseous sample used was 1 mL . The total organic carbon (TOC) content was monitored through TOC analyzer, model-Multi N/C 2100 BU, Analytic Jena AG Corporation (Germany). H_2O_2 interference was removed prior to COD and TOC determination by adding adequate amount of concentrated solution of sodium carbonate followed by heating at 90°C for 1 h as reported in literature [34].

2.6. Synergy calculations

The synergy of dual process in the current study over individual processes (photocatalysis and photo-Fenton) has been evaluated and quantified using the following equations [35]:

Synergy over photocatalysis or photo-Fenton:

$$\% \text{ Synergy} = 100 \times \frac{\{[k_{\text{dual}} - k(\text{photocatalysis or photoFenton})]\}}{k_{\text{dual}}} \quad (1)$$

Overall Synergy:

$$\% \text{ Synergy} = 100 \times \frac{\{[k_{\text{dual}} - (k_{\text{photocatalysis}} + k_{\text{photoFenton}})]\}}{k_{\text{dual}}} \quad (2)$$

where 'k' is the pseudo first-order rate constant in each process.

2.7. Calculation of photonic efficiency

The photonic efficiency of the photocatalytic system in each case was quantified as the ratio of photocatalytic degradation rate and the incident photon flux, as depicted in the following equation [36]:

$$\zeta = \frac{R}{I} \times 100 \quad (3)$$

where ζ is the photonic efficiency (%), R is the photodegradation rate of PEN ($\text{mol L}^{-1} \text{ s}^{-1}$) and I is the incident photon flux ($\text{E L}^{-1} \text{ s}^{-1}$). The other details for the calculation of photonic efficiency are provided in [Supporting information](#).

3. Results and discussion

3.1. Dual effect studies

Initially experiments were conducted to study the effect of individual operating parameter on the removal of target pollutant i.e. PEN. Each experiment was performed for 4 h with 5 L of PEN solution (50 mg L^{-1}) in pilot-scale reactor with flow rate of 0.4 L min^{-1} under natural solar light. Before conducting the fixed-bed studies, preliminary experiments were performed with catalyst suspensions to confirm the prominence of dual effect (photocatalysis and photo-Fenton). Adequate quantity of iron source i.e. FS and FA (0.25 g L^{-1} each) was used along with TiO_2 (0.25 g L^{-1}) and $0.3 \text{ g L}^{-1} \text{ H}_2\text{O}_2$ to conduct the dual process for the degradation of PEN. Excellent degradation efficiency (92%) of PEN was achieved with dual process after almost 1.5 h of reaction. While, it took almost 3 h to achieve this much of degradation by photocatalysis and almost 4 h through photo-Fenton process thus confirming the efficacy of dual process. However, slurry processes offer limitations in terms of expensive catalyst separation as well as complication of process post-treatment thus limiting its feasibility at field-scale. In view of these concerns, efforts have been made in the present study to visualize the practical applicability of dual process by using Fe- TiO_2 composite in completely fixed form.

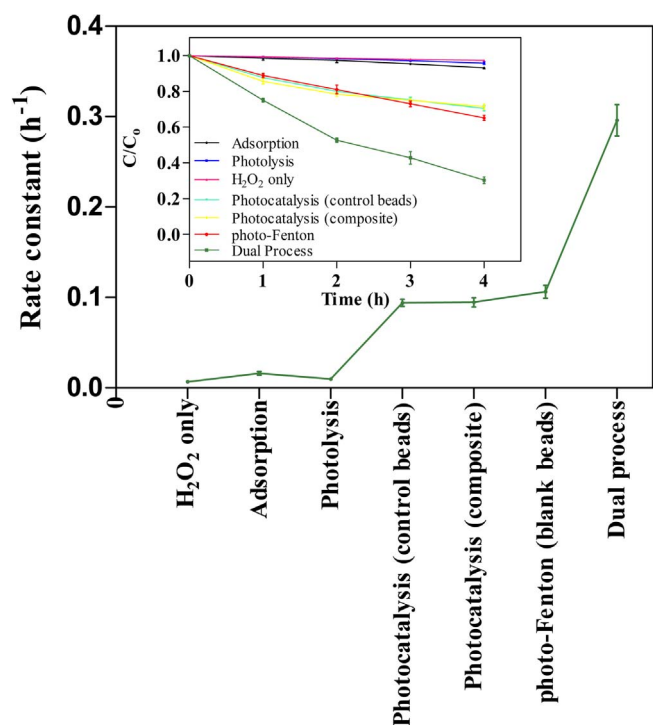
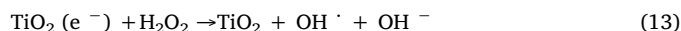
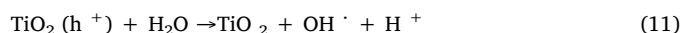
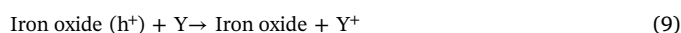
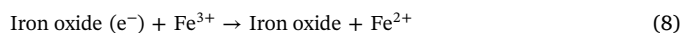
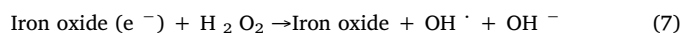
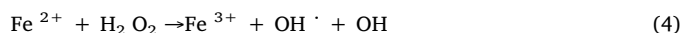


Fig. 3a. Plot of First order rate constant for the degradation of PEN through different processes, Plot of C/C_0 vs time for the degradation of PEN through different processes (inset). ($C_0 = 50 \text{ mg L}^{-1}$, $V = 5 \text{ L}$).

For fixed-bed studies, initially adsorption experiments were carried out under dark in the presence of only Fe-TiO₂ composite which resulted in only negligible amount of PEN removal (6–8%) owing to the blocking of active sites of catalyst due to the formation of pollutant layer on catalyst surface [37]. Photolytic studies were carried out with PEN solution in the presence of only solar light which revealed just 3–5% removal of PEN. In the presence of only H₂O₂ also, similar type of results were obtained as only 2–3% removal of PEN was achieved. Photocatalytic experiments with Fe-TiO₂ composite and control beads in the presence of sunlight yielded around 30% degradation of PEN in both cases. Photo-Fenton experiments with blank beads under sunlight in the presence of 0.3 g L⁻¹ H₂O₂ revealed approximately 35% degradation of PEN. Addition of H₂O₂ in photocatalytic experiments improved the degradation to around 45% in case of control beads and to around 70% in case of Fe-TiO₂ composite. Fe-TiO₂ composite took almost half time (2 h) to achieve 45% degradation and around 1.5 h to attain 35% degradation of PEN. This drastic increment in degradation of PEN in case of Fe-TiO₂ composite can be attributed to the in-situ dual effect (photocatalysis and photo-Fenton) owing to the systematic leaching of iron in solution through composite thereby contributing to the occurrence of photo-Fenton along with photocatalysis. The results are represented graphically in Fig. 3a. The photonic efficiency of the system in case of dual process was increased to 0.71% from 0.3% (photocatalysis) and 0.25% (photo-Fenton). The synergistic effect of dual process over photocatalysis was observed to be 68.24% and over photo-Fenton was 64.189% as calculated from Eq. (1). The overall synergy of dual process came out to be 32.4% as quantified through Eq. (2). The first order rate constant in case of dual process was almost twice as compared to that of photo-Fenton and photocatalysis. The reason of the escalated degradation process is the abundant generation of hydroxyl radicals through different processes occurring in the same treatment unit. Actually, hydroxyl radicals are produced not only from TiO₂ photocatalysis but also from homogeneous photo-Fenton (through leached iron species) and iron-oxide catalysis (through adsorbed iron species) as depicted in Scheme S1 (Supplementary information). Various forms of iron-oxide present on the surface of Fe-TiO₂ composite

have been detected through XRD analysis as discussed in Section 3.8. The probable mechanism of dual effect can be understood with the following reactions:



The trend of iron leaching was studied by determining the total iron concentration along with ferrous and ferric ion estimation at regular intervals of period during the reaction as depicted in Fig. 3b. It is clear from figure that total iron concentration initially increased up to 2 h and thereafter it started decreasing thus manifesting its contribution in photo-Fenton reaction. The role of ferrous and ferric ions formation during the reaction can be clearly understood from Eqs. (4)–(6).

All further experiments were conducted with Fe-TiO₂ composite in order to optimize the operating parameters for dual process at pilot-scale.

3.2. Effect of oxidant dose

As our study presents the novel concept of in-situ dual effect with Fe-TiO₂ composite, studying the effect of variation of H₂O₂ thus becomes extremely prominent as its addition accelerates the dual effect. Optimal concentration of H₂O₂ escalates the generation of hydroxyl radicals increasing the degradation efficiency. Actually hydroxyl radicals were not produced solely through TiO₂ photocatalysis but also through photo-Fenton or iron oxide catalysis going on simultaneously as clearly depicted in Eq. (4), (7) and (13). However overdose of H₂O₂ can also cause scavenging effect thus lowering down the degradation rate [38]. In the present study, H₂O₂ was varied in the range 0.3–1.5 g L⁻¹ with 5 L of PEN solution (50 mg L⁻¹) at a flow rate of

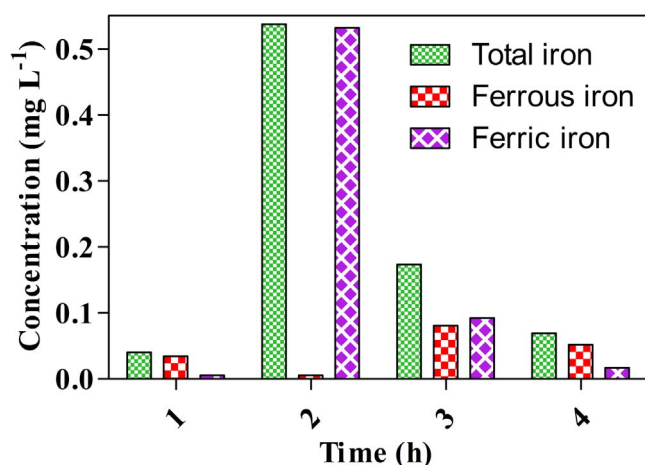


Fig. 3b. Determination of the total iron concentration along with ferrous and ferric ion estimation during the degradation of PEN through dual process.

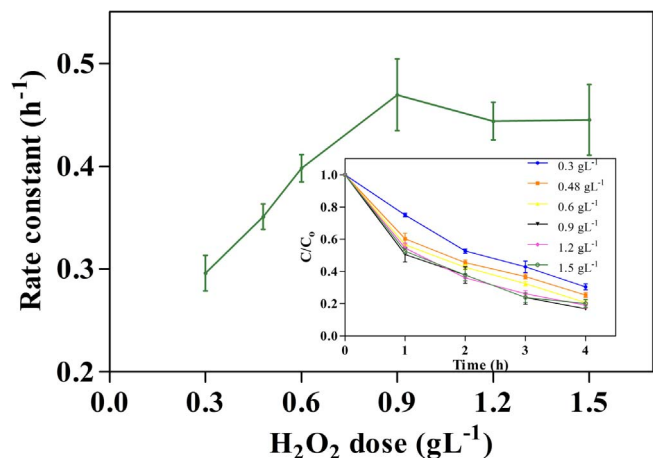


Fig. 4. Plot of First order rate constant for the effect of H_2O_2 dose on the degradation of PEN through dual process, Plot of C/C_0 vs time for the effect of H_2O_2 dose (inset). ($C_0 = 50 \text{ mg L}^{-1}$, $V = 5 \text{ L}$).

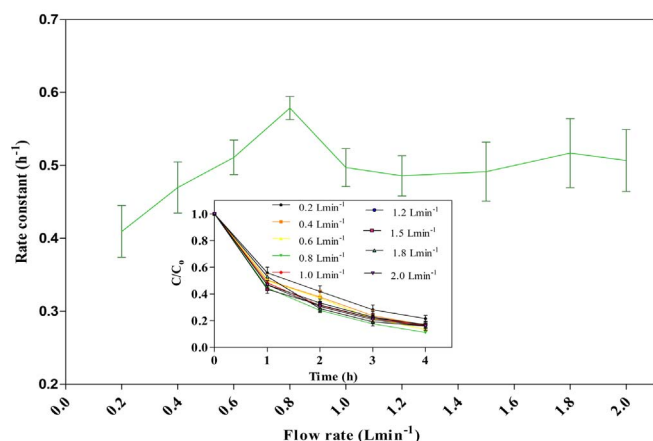


Fig. 5. Plot of First order rate constant for the effect of flow rate on the degradation of PEN through dual process, Plot of C/C_0 vs time for the effect of flow rate (inset). ($C_0 = 50 \text{ mg L}^{-1}$, $V = 5 \text{ L}$, $\text{H}_2\text{O}_2 = 0.9 \text{ g L}^{-1}$).

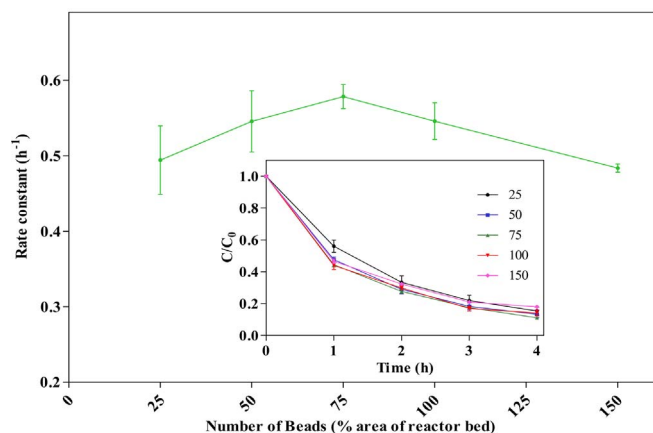


Fig. 6a. Plot of First order rate constant for the effect of catalyst dose (number of composite beads) on the degradation of PEN through dual process, Plot of C/C_0 vs time for the effect of catalyst dose (inset). ($C_0 = 50 \text{ mg L}^{-1}$, $V = 5 \text{ L}$, $\text{H}_2\text{O}_2 = 0.9 \text{ g L}^{-1}$, Flow rate = 0.8 L min^{-1}).

0.4 L min^{-1} . The degradation of PEN increased initially with increase in the dose of H_2O_2 up to 0.9 g L^{-1} . Thereafter, degradation either became almost constant or started declining due to the prevalence of scavenging effect. The optimum dose of H_2O_2 selected for the present

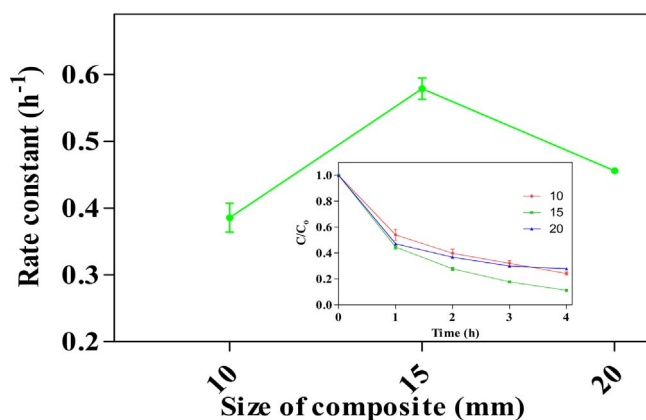


Fig. 6b. Plot of First order rate constant for the effect of size of composite on the degradation of PEN through dual process, Plot of C/C_0 vs time for the effect of composite size (inset). ($C_0 = 50 \text{ mg L}^{-1}$, $V = 5 \text{ L}$, $\text{H}_2\text{O}_2 = 0.9 \text{ g L}^{-1}$, Flow rate = 0.8 L min^{-1}).

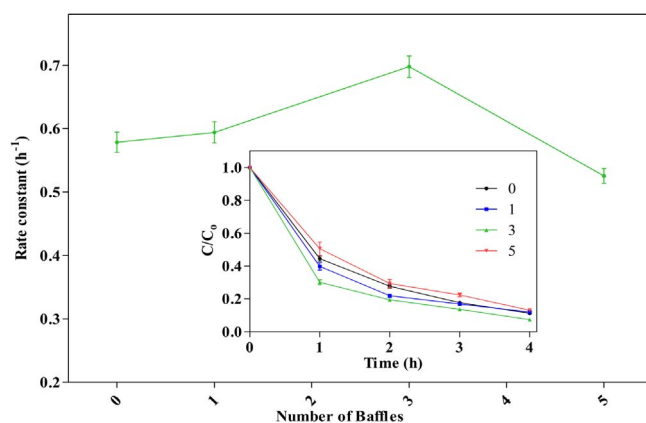


Fig. 7. Plot of First order rate constant for the effect of number of baffles on the degradation of PEN through dual process, Plot of C/C_0 vs time for the effect of number of baffles (inset). ($C_0 = 50 \text{ mg L}^{-1}$, $V = 5 \text{ L}$, $\text{H}_2\text{O}_2 = 0.9 \text{ g L}^{-1}$, Flow rate = 0.8 L min^{-1} , number of composite = 75% of reactor bed area).

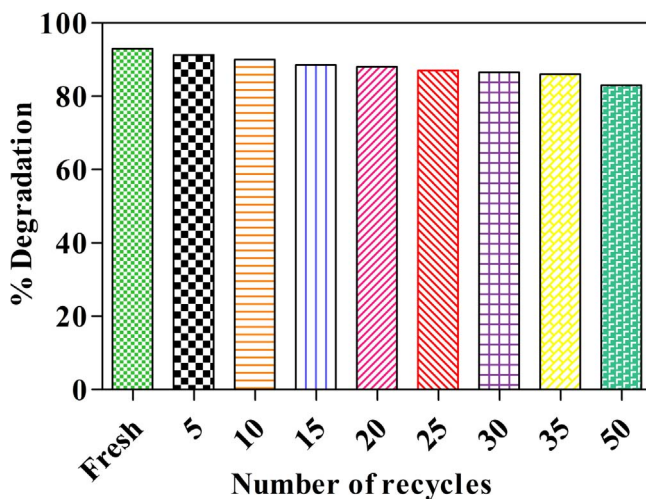


Fig. 8. Recyclability studies of Fe-TiO₂ composite for the degradation of PEN.

study was 0.9 g L^{-1} which revealed almost 83% degradation of PEN with maximum value of first order rate constant i.e. 0.469 h^{-1} (Fig. 4). The photonic efficiency of the system was further increased to 1.09% with optimized dose of oxidant. To observe the synergistic effect of dual process, photocatalysis with control beads and photo-Fenton with blank beads were also carried out at optimum dose of oxidant which revealed

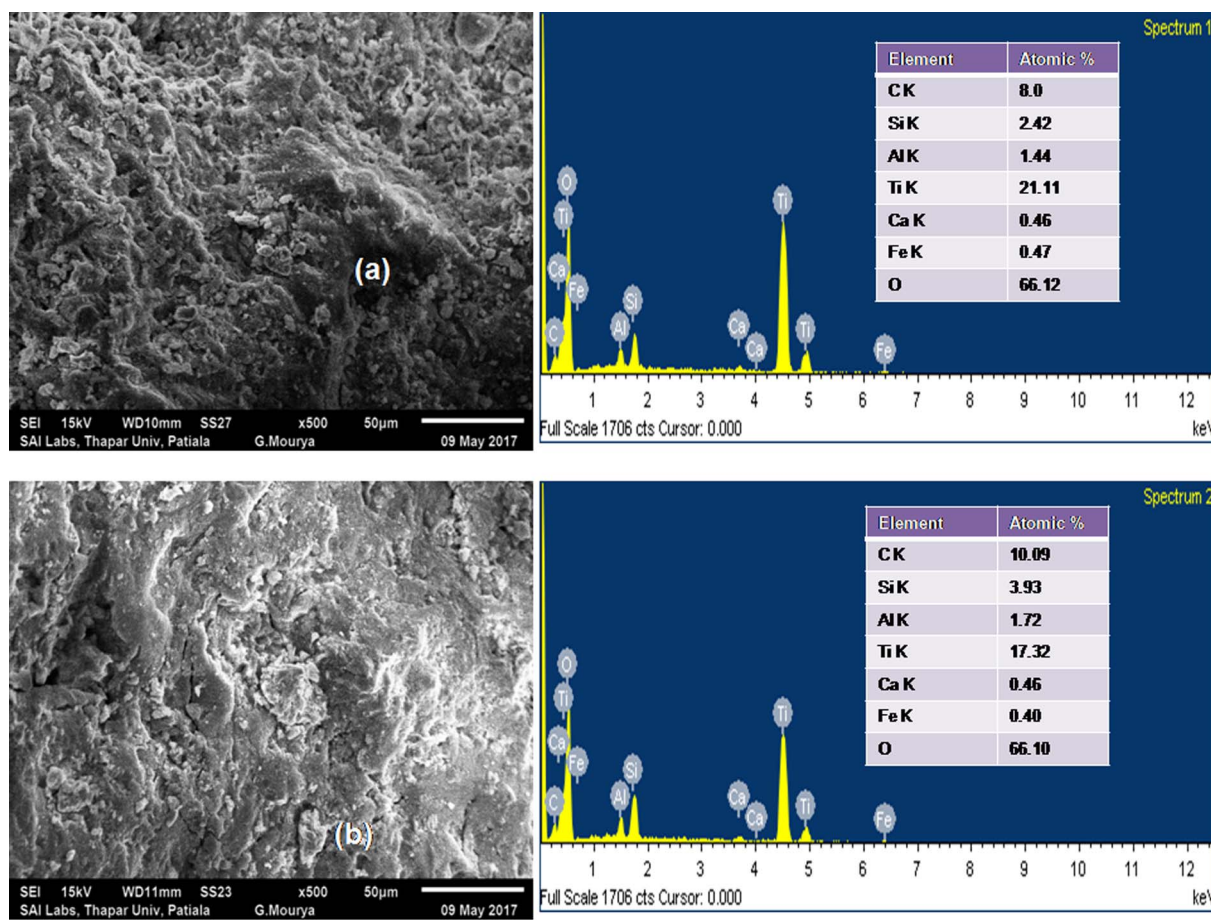


Fig. 9a. SEM/EDS image of Fe-TiO₂ composite (a) after 35 recycles and (ii) after 50 recycles.

67% and 60% degradation respectively. The degradation was faster in case of dual process as almost 50% degradation of PEN was achieved within 1 h of treatment whereas it took almost 3 h to reach same amount of degradation with photocatalysis and more than 3 h with photo-Fenton. The synergy of dual process over photocatalysis was 48% and over photo-Fenton was 58%. However, overall synergy of dual process was 6%.

3.3. Effect of flow rate

The amount of turbulence and dissolved oxygen plays an important role in the photocatalytic reaction systems which can be controlled with optimum recycle flow rate. In the present research work, the recycle flow rate was varied from 0.2 to 2.0 L min⁻¹ at optimized dose of H₂O₂ (0.9 g L⁻¹). It was observed that initially the degradation also increased with increase in flow rate from 0.2 to 0.8 L min⁻¹. The possible justification for this kind of behavior is that increasing the recycle flow rate increases the dissolved oxygen molecules which act as electron scavenger and prevents recombination of electron and holes thus promoting the redox reaction to take place at the catalyst surface. Similar kind of results were reported [14] for the degradation of phenol when recycle flow rate was increased from 0.250 to 0.50 L min⁻¹. Chan et al. (2001) [15] also reported that turbulence created due to recycle flow rate stimulates the effectual mass transfer during photocatalytic reactions. When flow rate was further increased from 0.8 to 2.0 L min⁻¹, degradation of PEN started declining. With increased flow rate, pollutant contact time with catalyst particles decreases. It exits without making an efficient contact with catalyst particles thus reducing the degradation efficiency. Therefore, 0.8 L min⁻¹ was adopted as an optimum flow rate at which degradation was increased to around 89%

with maximum value of first order rate constant i.e. 0.578 h⁻¹ as shown in Fig. 5 after 4 h of treatment. In this case, photonic efficiency of the system was incremented to 1.34%.

3.4. Effect of catalyst dose (Iron/TiO₂) and composite size

The catalyst in the present dual effect study comprised of both iron and TiO₂ content. Both must be present in optimum concentrations in order to get best degradation rate. It is somewhat difficult to optimize the catalyst dose in completely fixed-bed studies. Best efforts have been made in the current research to optimize the catalyst dose by varying the catalyst amount (iron and TiO₂) in various ways. The amount of catalyst was varied by varying the number of Fe-TiO₂ composite means altering the concentration of both iron and TiO₂ simultaneously. The number of Fe-TiO₂ composite was expressed in terms of percentage area of the reactor bed covered with composite. When number of Fe-TiO₂ composite was increased from 25% to 75% of reactor bed area, degradation of PEN also increased. As with less number of composite (25%), available active sites of the catalyst were reduced for the reaction to take place. When number of composite was further increased from 75% to 150% of reactor bed area, degradation rate started decreasing (Fig. 6a). This might be due to the prevailing shadowing effect which further enhances problem of proper catalyst illumination thus reducing the effective available surface area for catalyst binding with pollutant. Therefore, composite covering 75% of reactor bed area was selected to be optimum for present study.

Alternatively catalyst dose was varied by reducing the amount of iron by replacing 50% of Fe-TiO₂ composite with control beads. The degradation was reduced to 75% which might be due to the lowering efficiency of photo-Fenton reaction. Similar trend was followed when

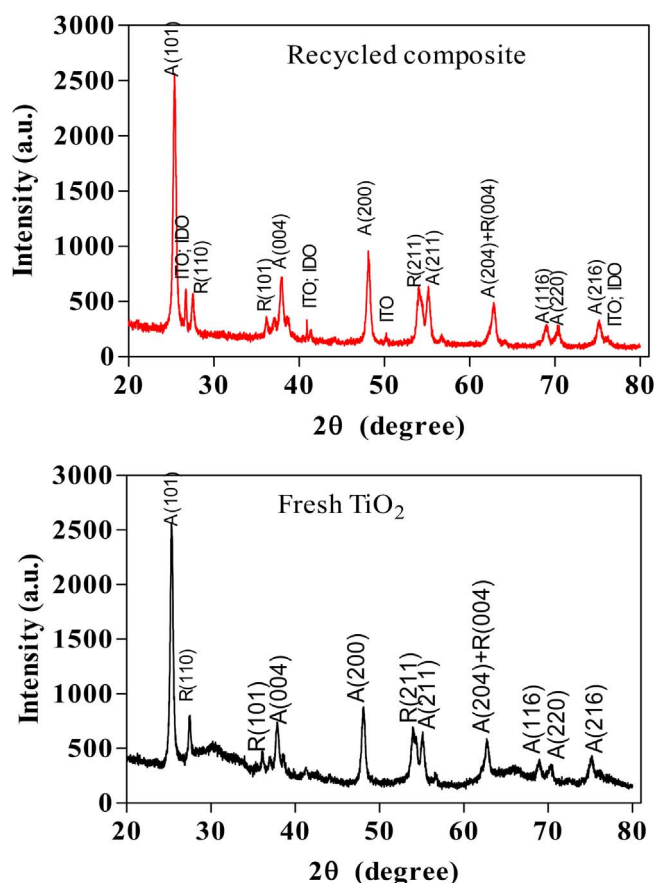


Fig. 9b. XRD pattern of (a) fresh TiO_2 and (b) recycled Fe- TiO_2 composite (35 recycles).

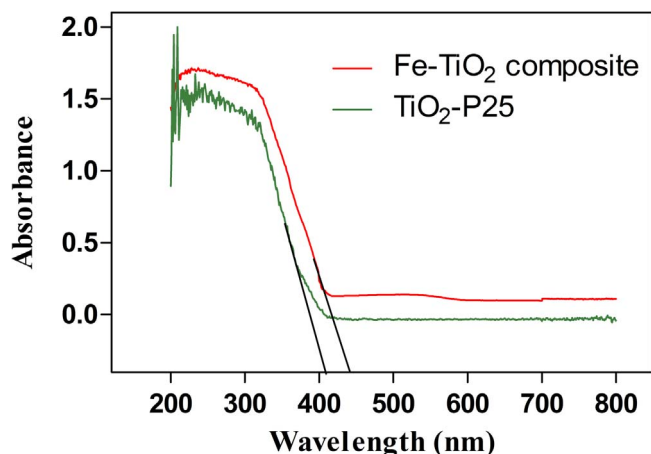


Fig. 9c. UV-visible DRS of (a) fresh TiO_2 and (b) recycled Fe- TiO_2 composite (35 recycles).

amount of iron was increased by replacing 50% of Fe- TiO_2 composite with blank beads as degradation was reduced in this case also. As a result, composite covering 75% of reactor bed area without any addition of control or blank beads gave the best degradation (89%) with highest rate constant being 0.578 h^{-1} after 4 h of treatment. With these optimized conditions, the optimum concentration of leached iron species was observed to be 0.79 mg L^{-1} at which significant increase in % removal of PEN was observed. The concentration of leached iron during the course of reaction at optimized catalyst dose has been provided in Table S7 (Supplementary information).

Attempts have also been made to study the effect of surface area available for reaction by varying the diameter of composite in the range

10–20 mm as measured through vernier caliper. Best degradation (89%) and maximum rate constant (0.578 h^{-1}) was attained with 15 mm sized composite having exposed surface area of around 0.08 m^2 (Fig. 6b). Degradation decreased with small sized composite (10 mm) due to the ineffective activation of the catalyst by photons as photons of light had to traverse a longer path to reach the catalyst surface. For larger sized composite (20 mm) also, the degradation decreased which might be due to the ineffective availability of the surface area for reaction to take place as composite were not effectively getting wet in the solution. This is the first ever reported study using Fe- TiO_2 composite to study the dual effect at pilot-scale level.

3.5. Effect of number of baffles

The addition of baffles to the reactor is supposed to increase the retention time thereby increasing the degradation efficiency. The number of baffles was varied from 0 to 5. The % degradation of PEN was increased to 93% (with increased rate constant i.e. 0.697 h^{-1}) as number of baffles increased from 0 to 3 as shown in Fig. 7. Thereafter degradation started declining which may be due to the occurrence of shading effect caused by baffles. The prevalence of shading effect of baffles caused an ineffective absorption of photons of solar light by catalyst. Similar trend was observed in a study by Adishkumar et al. (2015) [14] where degradation of phenol was reduced with three baffles due to shading effect. The photonic efficiency of system in the present study reached to a maximum value of 1.62% with three baffles. The results of photonic efficiency are also presented in tabulated form (Table S8, Supplementary information) for drawing out clear comparison between different operating conditions.

3.6. Catalyst recyclability studies

The main strength of this study basically reports the durability of Fe- TiO_2 composite along with sustainable leaching of iron from composite. The durability of Fe- TiO_2 composite was studied by recycling it for subsequent runs and was analyzed in terms of degradation efficiency for PEN. For the first time, this kind of innovative study has been presented where the composite once prepared were used for optimization of all operating parameters. In other words, the composite prepared on the very first day were used for all the parametric optimization till last results have been withdrawn. To the best of our knowledge, no such report has ever been cited in literature. The composite were successfully recycled for 35 cycles without any significant reduction in degradation efficiency (Fig. 8). The various characterization techniques also proved the durability and stability of composite even after 35 recycles as discussed in Section 3.7. The composite was exposed to sunlight for almost 1 h after each reaction cycle for re-activation of the catalyst. To further strengthen our claim of this novelty, composite previously used for at-least fifty cycles (old composite) in our earlier studies were used as such for the degradation of compound under study. Even these composite were able to demonstrate a reasonable amount of degradation efficiency (83%) after 4 h of treatment. The slight loss in degradation efficiency ($\sim 10\%$) might be attributed to weathering-off the catalyst from composite [39] along with restricted leaching of iron. The amount of catalyst loss from the surface of composite was determined by weighing the composite bead before and after recycling tests. There was almost 7–8% loss in the concentration of coated catalyst after recycling the bead for 50 runs thus signifying the presence of sufficient quantity of catalyst even in recycled composite which could contribute further in the photocatalytic experiments.

For further confirming the efficacy of Fe- TiO_2 composite among different types of supports, experiments were performed with catalyst immobilized clay + FA and clay + FS beads as well. Best degradation was observed in case of Fe- TiO_2 composite (Table S9, Supplementary information). Either FS or FA along with clay was not sufficiently providing compressive strength to the composite as confirmed through

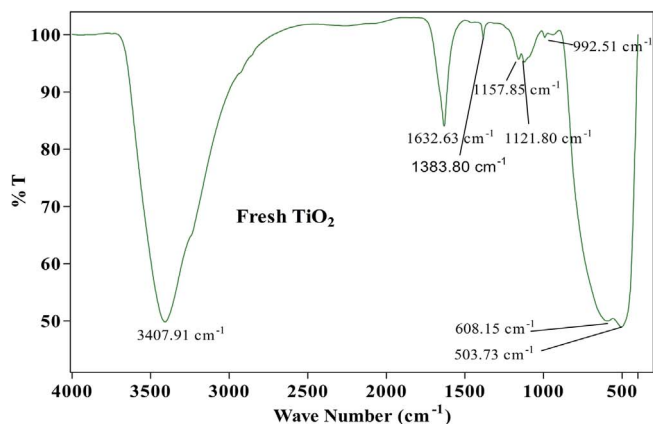
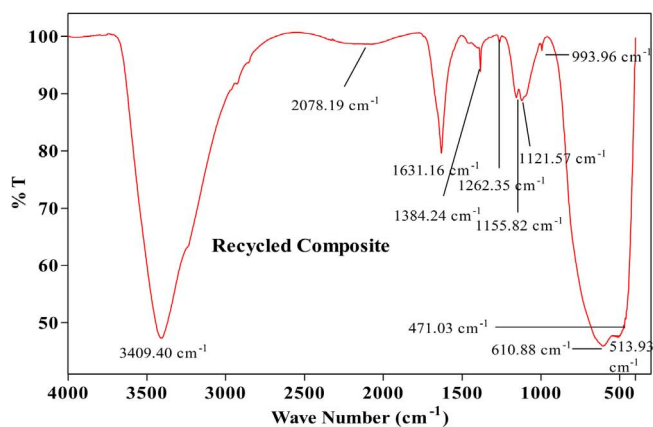


Fig. 9d. FT-IR spectra of (a) fresh TiO₂ and (b) recycled Fe-TiO₂ composite (35 recycles).

recyclability studies. Moreover, catalyst was not efficiently intact to the surface of beads in case of clay + FA and clay + FS beads. Actually, addition of FA in FS (in case of Fe-TiO₂ composite) provides compressive strength along with increasing the iron content. Thus, Fe-TiO₂ composite was used for maximum number of recycles. Therefore, it leads to a proposition that the presented technique can be successfully executed for real-time applications using these highly durable and economic composite.

3.7. Statistical analysis

Each experimental data was verified statistically for proper validation and confirmation of results. Analysis of variance (ANOVA) was applied in each case to test the degree of variation among first order rate constant, k in each case at different operating conditions. The statistical analysis of all the data has been provided in [Supplementary information \(Table S1–S6\)](#). Statistical results clearly indicated that F -values were greater than 5 in each case suggesting it to be significant [40]. Whereas, p -values were less than 0.01 in each case further defining a significant correlation of at least one term in regression equation with first order rate constant.

3.8. Characterization of catalyst

The SEM-EDS images of recycled composite (35 cycles) and old composite (50 cycles) are illustrated in [Fig. 9a](#). The surface morphology of both the composite were almost same as that of freshly coated thus indicating that surface characteristics did not change even after 50 recycles. The sharp peaks of iron, Titanium and Oxygen in electron dispersive spectrum in both cases substantiate the stability and intactness of catalyst even after

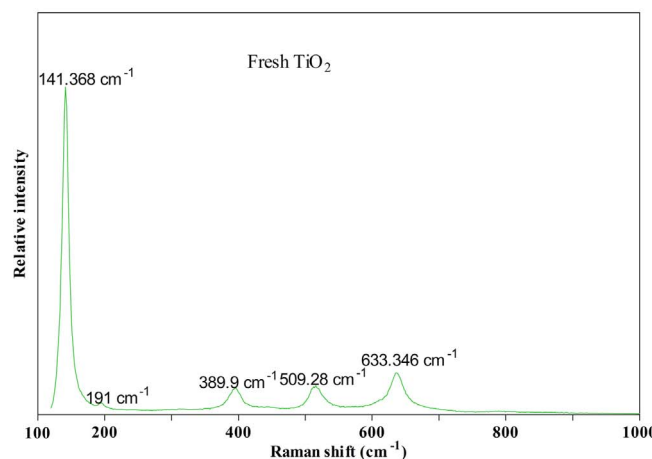
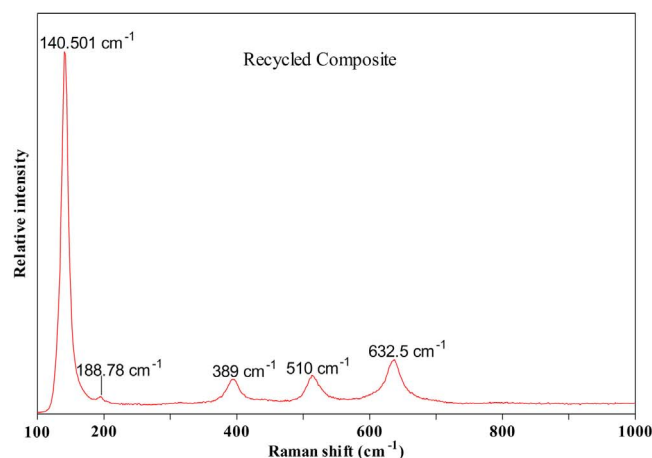


Fig. 9e. Raman spectra of (a) fresh TiO₂ and (b) recycled Fe-TiO₂ composite (35 recycles).

50 recycles. Thus it can be concluded from SEM-EDS results that Fe-TiO₂ composite can be used even for further studies.

The X-ray diffraction patterns of recycled Fe-TiO₂ composite along with TiO₂-P25 are shown in [Fig. 9b](#). The occurrence of crystalline planes corresponding to anatase (reference code: 01-072-7058), marked as 'A' and rutile (reference code: 01-072-4814), marked as 'R' in Fe-TiO₂ composite clearly indicated that photocatalytic activity of TiO₂-P25 in Fe-TiO₂ composite was still retained even after 35 recycles. Diffraction peaks corresponding to Iron Titanium oxide (reference code: 01-070-0143), indicated as 'ITO' and Iron(II) dititanium oxide (reference code: 01-089-8065), indicated as 'IDO', also occurred along with anatase and rutile peaks thus confirming the presence of both iron and TiO₂ in recycled composite. The role of these forms of iron oxides in dual effect can be inferred from Eqs. (7) to (9).

UV-Vis diffuse reflectance spectra of recycled Fe-TiO₂ composite and TiO₂-P25 are presented in [Fig. 9c](#). The samples were analyzed in the range 200–800 nm. The spectra of Fe-TiO₂ composite displayed the capability of absorption of light even in the visible region which clearly reflects the presence of iron in composite. The band gap of TiO₂-P25 and prepared catalyst was estimated using following eq.

$$E_g = h\nu = \frac{hc}{\lambda} \quad (14)$$

where E_g : band gap energy (eV), c : speed of light, h : Planck's constant and λ : absorption wavelength

As a result, absorption edge was extended to 440 nm and band gap narrowing was observed in case of composite ($E_g = 2.9$ eV) in comparison to TiO₂-P25 ($E_g = 3.14$ eV).

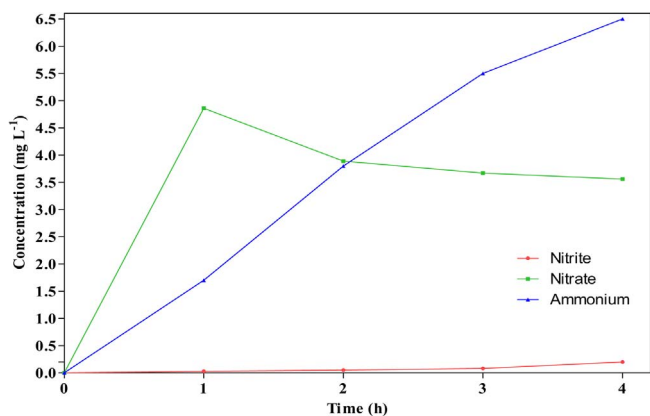


Fig. 10a. Generation of nitrite, nitrate and ammonium ions during the photodegradation of PEN.

The surface characteristics of recycled Fe-TiO₂ composite and TiO₂-P25 were also identified through FTIR spectroscopic studies. The infrared spectrum of TiO₂-P25 and composite is depicted in Fig. 9d. The generation of Ti-O-Ti bonds in both the spectrums can be indicated by the Ti-O vibrations as observed by several peaks occurring between 400 and 1200 cm⁻¹ wave number thus proving the existence of TiO₂ lattice. The anatase phase in case of TiO₂-P25 and Fe-TiO₂ composite in the spectrum occurred at 503.73 cm⁻¹ and 471.03 cm⁻¹ respectively. The results are in accordance with an earlier reported study [41] which suggested the occurrence of Ti-O-Ti vibrations especially for anatase phase between 400 and 640 cm⁻¹. Stoyanova et al. (2013) [42] reported that bonds occurring in the range 510–590 cm⁻¹ could represent vibrations between FeO₆ units. The bond at 513.93 cm⁻¹ could

possibly represent similar vibrations in the present study in case of composite. The peak at 2078.19 cm⁻¹ in Fe-TiO₂ composite spectra corresponds to the generation of Fe-O-Ti bond which further confirms our claim for the presence of iron in composite. Almost similar peak for the presence of Fe-O-Ti bond in Fe/TiO₂ powder has been reported in literature [36]. The results are in a good agreement with XRD pattern which confirmed the presence of 'ITO' and 'IDO'. The bonds appearing at 1632.63 cm⁻¹ and 1631.16 cm⁻¹ in case of TiO₂-P25 and Fe-TiO₂ composite respectively correspond to the Ti-OH groups. The presence of transmittance band at 3407.91 cm⁻¹ in case of TiO₂-P25 and at 3409.40 cm⁻¹ in case of Fe-TiO₂ composite correspond to the O-H groups stretching vibrations as indicated in various studies [41,43].

The Raman spectra of recycled Fe-TiO₂ composite and TiO₂-P25 are shown in Fig. 9e. The prominent peaks at 140–142 (E_g), 188–192 (E_g), 389–390 (B_{1g}), 509–510 (E_g) and 632–634 (E_g) cm⁻¹ in the spectra of both samples correspond to the anatase phase of TiO₂. The Raman peaks reported in literature for anatase TiO₂ are at 108–188, 198, 205, 320, 387–448, 512–543, 625–670 cm⁻¹ [41,44]. The anatase peak at 140–142 cm⁻¹ in both the spectrums is the strongest of all observed peaks thus indicating the predominance of anatase nanoparticles. The results are in accordance with previously reported studies [45]. An additional weak broad band (not marked in figure) was also observed in the region from 350 to 360 cm⁻¹ corresponding to the rutile phase of TiO₂. The similar band for rutile phase has been reported earlier [45,46]. Small weak and broad bands in the region from 300 to 350 cm⁻¹ were also observed in the spectra of recycled composite. These bands do not belong either to anatase or rutile phase of TiO₂ so existence of these bands could be correlated with presence of iron or oxides of iron. No other additional prominent peaks of iron oxides were observed in the Raman spectra thus proving the retention of TiO₂ structure even in recycled composite. The presence of iron in composite

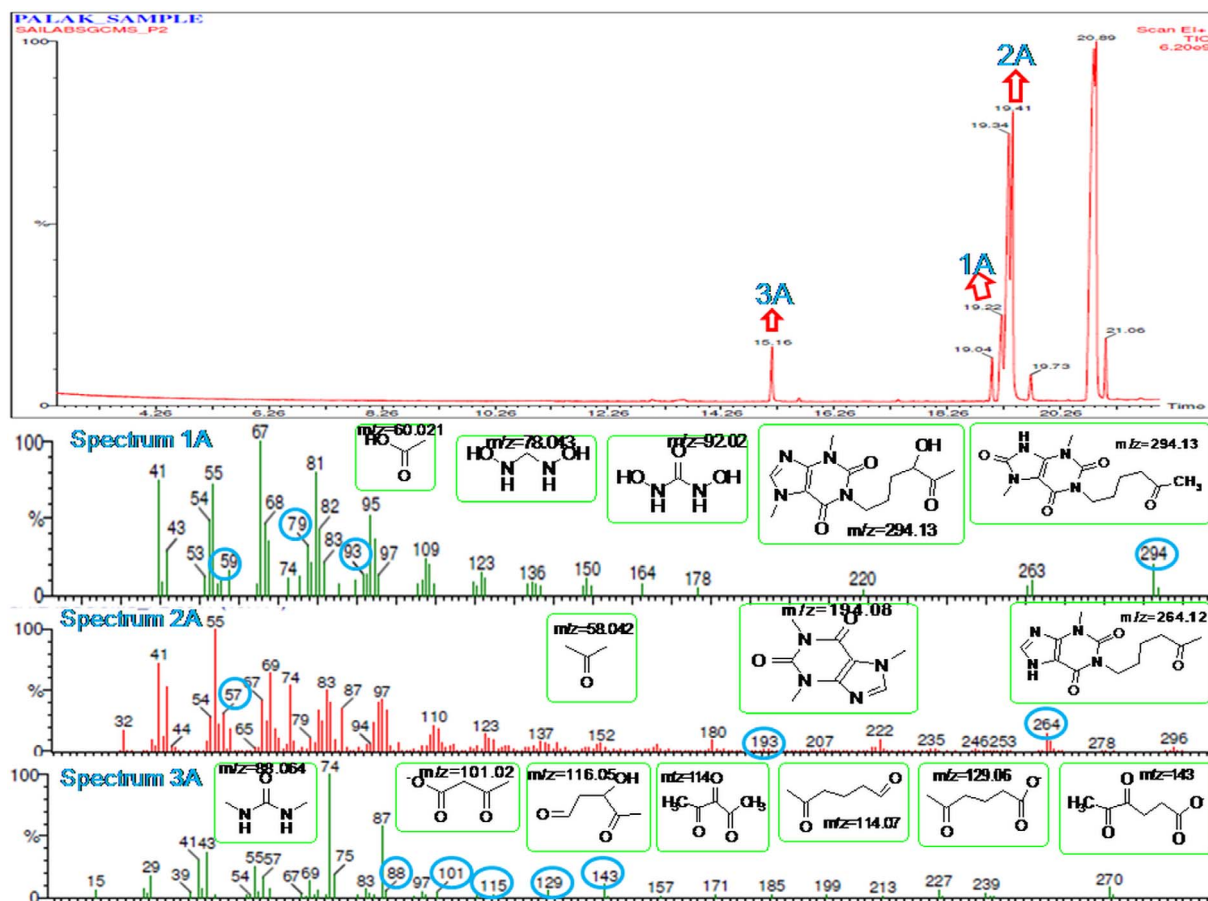


Fig. 10b. Identification of intermediates during the degradation of PEN through mass-spectra analysis.

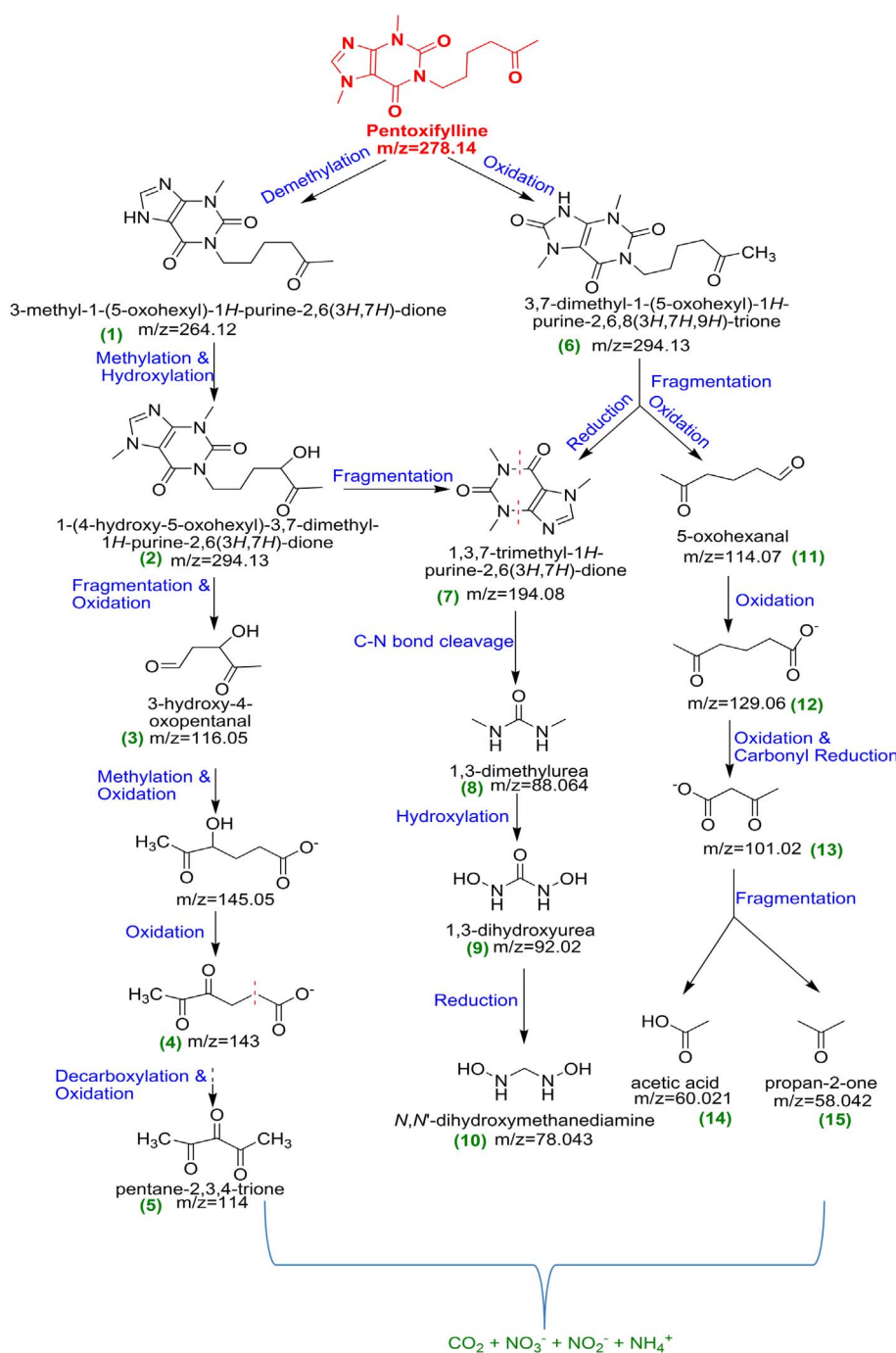


Fig. 10c. Tentative pathway for the degradation of PEN.

did not exhibit any negative effect in the activity of TiO₂. None of the studies in literature have reported such comprehensive characterization of composites that have been especially used in fixed mode and contributing to in-situ dual effect.

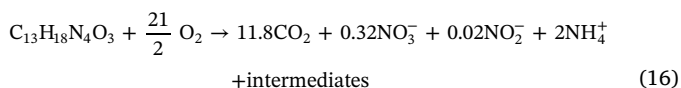
3.9. Mineralization studies

The mineralization studies of PEN were carried out through reduction in COD and TOC along with generation of anions like nitrite, nitrate, ammonium ions and evolution of CO₂ as shown in Fig. 10a. The nitrogen atoms in PEN were found to be converted into nitrite, nitrate and ammonium ions. Similar types of results were presented by Grover et al. (2014) [47] where nitrogen atoms of imidacloprid were dissipated into nitrite and nitrate ions. In the present study, the concentration of nitrate ions followed a decreasing trend after 1 h of reaction whereas

nitrite and ammonium ions followed an increasing trend in their concentration with the probability of conversion of nitrate into nitrite and ammonium ions [48]. There was almost 94% and 91% reduction in COD and TOC respectively after 4 h of treatment. The Stoichiometrically balanced chemical equation for complete mineralization of PEN is indicated in Eq. (15). The chemical equation (16) obtained through quantification of nitrite, nitrate, ammonium ions and CO₂ evolution deviates from Eq. (15) thus indicating partial mineralization of PEN. The calculations for CO₂ mass balance have been provided in Supporting information. The partial mineralization of PEN might be due to the formation of several intermediate products during the degradation of PEN. The intermediates identified through GC–MS analysis are depicted in Fig. 10b along with chromatograms. Based on these intermediates, a degradation pathway has been proposed as shown in Fig. 10c.

Table 1
Evaluation of cost of treatment process.

(A) Preparation of Fe-TiO₂ composite	
Cost of raw materials (clay, FA, FS) = 0.0 \$	
Electricity consumption during firing of support at high temperature = 0.75 kWh	
Electricity price in India = 0.0699 \$/kWh	
Cost of electricity consumption = 0.0699 × 0.75 = 0.0524 \$/kWh	
Cost of TiO ₂ used (16 g) = 0.048 \$	
Total cost of Fe-TiO ₂ composite = 0.0524 + 0.048 = 0.1004 \$	
(B) Oxidant (H₂O₂)	
Cost of total oxidant (750 mL) used (for 50 runs) = 10.374 \$	
(C) Operating cost of treatment process	
Cost of light source (sunlight) = 0.0 \$	
Number of runs = 50	
Total volume of water treated = 5 L × 50 = 250 L (0.25 m ³)	
Cost per m ³ = (A + B)/0.25 = 41.89 \$/m ³	
With 93% degradation (C ₀ = 50 mg L ⁻¹), concentration of PEN removed = 46.5 mg L ⁻¹ (0.0465 kg m ⁻³)	
Cost per kg of concentration removal = (A + B)/0.0465 = 225.25 \$/kg of concentration removal	
Energy consumption during operation of process (pumping of solution treatment) = 18 × 4 × 50 = 3600 Wh	
Energy consumed per kg of concentration removal = 3600/0.0465 = 7.741 kWh per kg of concentration removal	
Cost for energy consumption = 0.0699 × 7.741 = 0.541 \$/kWh	
Overall operating cost = 225.25 + 0.541 = 225.79 \$	
(D) Fabrication of reactor	
Total cost including pump, baffles, pipe = 15.548 \$	
Total cost of treatment process = C + D = 241.33 \$	
Total cost of above treatment process comes out to be 241.33 \$ for 50 runs	
Cost of treatment process for single run (5 L) would be 4.826 \$. This cost could be further minimized by effective designing of solar collectors for large-scale applications.	



4. Evaluation of cost of treatment process

Cost has always been a major topic of discussion when new and innovative technologies are taken into consideration. For successful commercialization of a process, new technology must provide significant reduction in overall treatment costs over competent techniques. In case of photocatalytic treatment unit installation, the overall cost must comprise of design, fabrication, light source, start-up of process, electricity cost, cost of catalyst used with an assumption that land is available free of cost. Most of the studies in literature have reported either the cost of only energy consumption [49] or operating cost [50] excluding the fabrication and design cost of reactor. The overall cost of the treatment process has been evaluated in the present study taking into consideration the complete cost of Fe-TiO₂ composite, oxidant used, light source, operating cost of process including electricity cost and fabrication cost of the reactor as discussed in Table 1.

The overall cost of the treatment process has been evaluated for 50 runs. In view of the catalyst recyclability studies which clearly prove the stability and efficacy of catalyst even after 50 runs, the overall cost of process can be further reduced when applied for additional cycles. As a result, the studied pilot-scale reactor using highly efficient low cost catalyst can present an economic solution to various field-scale applications.

5. Conclusion

For the first time, a novel approach has been followed to incorporate in-situ dual effect for the degradation of PEN using Fe-TiO₂ composite.

A simple non-concentrating fixed-bed reactor with total volume handling of 5 L was used for degradation studies. This owed to a significant reduction in treatment time in case of dual effect. The first order rate constant, *k* in case of dual process was observed to be thrice (0.296 h⁻¹) as compared to photocatalysis (0.094 h⁻¹) and photo-Fenton (0.099 h⁻¹). The optimized conditions obtained for best possible degradation (93%) of PEN were oxidant dose of 0.9 g L⁻¹ with adequate number of composite (composite covering 75% of reactor bed area) and 3 baffles at recycle flow rate of 0.8 L min⁻¹. The results were verified through suitable statistics which clearly indicate a significant correlation of at least one term in regression equation with first order rate constant. The comprehensive characterization of recycled Fe-TiO₂ composite through SEM/EDS, XRD, DRS, FTIR and Raman spectroscopy confirmed the photo-stability and durability of catalyst even after 35 recycles thus highlighting its commercial viability. Almost complete mineralization of PEN into various anions and CO₂ along with proven reduction in COD and TOC further leads to a proposition that studied pilot-scale reactor with certain modifications using economic Fe-TiO₂ composite can easily replace traditional water treatment methods in developing countries with reduced treatment time.

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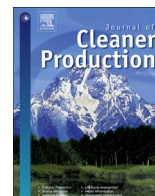
Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2017.09.121>.

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Pilot-scale single-step reactor combining photocatalysis and photo-Fenton aiming at faster removal of Cephalexin

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ABSTRACT

A solar pilot-scale cascade reactor system with novel Fe–TiO₂ composite beads possessing unusual characteristics of in-situ dual effect i.e. coupling of photocatalysis and photo-Fenton has been investigated in once-through mode. The cascade arrangement of packed-bed reactors maintained sufficient turbulence in the system besides eliminating the implications of film-diffusion resistance. The synergistic effect (10%) of in-situ dual process over individual processes has significantly reduced the treatment time of a recalcitrant antibiotic, Cephalexin (CEX). The reaction performance of the once-through cascade reactor system (comprising of six packed-bed reactors in series) incorporating in-situ dual effect at optimized conditions i.e. H₂O₂: 600 mgL^{−1}, flow rate: 50 mLmin^{−1}, with a space time (T) of 12 min approached to that of plug-flow reactor (PFR). The mineralization of CEX was evaluated through reduction in COD (70%) and TOC (63%) along with generation of anions and evolution of CO₂. The treated solution of CEX was completely non-toxic as confirmed through Kirby-Bauer test and bio-assay analysis based on toxicity factor. In addition to this, Fe–TiO₂ composite beads depicted an excellent recyclability efficiency (>70 recycles) even under continuous flow conditions as confirmed through SEM/EDS, DRS, XRD, XPS and TGA analysis. The overall cost of treatment process was evaluated in detail to visualize the practical feasibility of the presented high performance reactor system.

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1. Introduction

In the recent studies, development of continuous photocatalytic systems either continuous stirred type reactor (CSTR) or plug-flow reactor (PFR) has been discussed in view of its field-scale applications related to wastewater treatment (Miyawaki et al., 2016; Vaiano et al., 2015). However, PFR, where there is no axial mixing of reaction mixture, is always desired as a continuous flow system owing to its high productivity and selectivity (Prokopová and Prokop, 2009). Nonetheless, the concept of PFR visualization in case of photocatalytic systems has not been investigated widely. Thus, there is an urgent requirement to apply a real-time PFR approach in continuous photocatalytic system so that its scale-up for large-scale applications can be anticipated.

Though there are various reported studies related to the effective photocatalytic degradation of organic pollutants in continuous flow reactors employing suspensions of catalyst (Ehrampoosh et al., 2011; McCullagh et al., 2010; Zhou et al., 2018a; b), practical

feasibility of the process has not reached up to the mark. Actually, expensive filtration of the treated solution and low recyclability efficiency of the catalyst increases the overall cost of the process. Thus, it is always reasonable to reuse TiO₂ or any other photocatalyst supported on some material (Bansal et al., 2016; Miranda-García et al., 2011; Verma et al., 2014). In this context, most of the studies (Chan et al., 2003; Freudenhammer et al., 1997) have utilized thin films of TiO₂ that are simpler to prepare and most suitable for continuous operation of photocatalysis. The stability of catalyst film and its subsequent reuse along with increased time of treatment always remained a major concern in these types of reactors. The photocatalytic efficiency or conversion efficiency of the system can be enhanced if the continuous flow reactor is designed in such a manner that it approaches the plug-flow conditions. In this view, Miyawaki et al. (2016) have used five CSTRs in series approaching plug-flow conditions with a thin film of TiO₂ over glass plate for the degradation of 2,4-dinitrophenol. Though higher amount of conversion efficiency was achieved in this reactor system due to lower film diffusion resistance, practical feasibility of this process is low owing to the high treatment time and more energy consumption which increases the overall operating cost.

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In this view, the main emphasis of the present investigation was to develop a cost-effective photocatalytic reactor system possessing field-scale applications. A novel concept of in-situ dual effect (photocatalysis and photo-Fenton) in fixed-mode was introduced using Fe–TiO₂ composite beads. Fe–TiO₂ composite beads possessed unique characteristics of unusual in-situ dual effect as iron was leaching by-default from these beads during the reaction thus contributing to photo-Fenton reaction along with on-going TiO₂ photocatalysis. Actually, these composite beads were fabricated using waste materials like fly-ash (FA) and foundry sand (FS) as iron source with a layer of TiO₂ on its surface. Few forms of iron oxide were also present on the surface of composite beads which further enhanced the performance efficiency of the process by preventing the recombination of charge carriers (Scheme S1 and Text S1, Supplementary information). Six packed-bed reactors containing these high performance Fe–TiO₂ composite beads were arranged in a cascade manner. The ‘waterfall’ effect of this cascade system supplied enough aeration and turbulence in the system besides removing the film diffusion resistance thus enhancing the overall efficiency of process.

The main target of the current research work was to enhance the performance efficiency of the once through cascade reactor system to such an extent that it approaches a plug-flow reactor. Though it is difficult to approach plug-flow conditions especially in fixed-bed photocatalytic systems, introduction of novel in-situ dual effect in combination with the once through cascade reactor system successfully led to the accomplishment of plug-flow conditions with reduced treatment time. A beta-lactum cephalosporin antibiotic, Cephalexin (CEX) was chosen as a model pollutant in the present study. The recalcitrant nature as well as low transformation rate of CEX has already been proven in various studies (Comminellis et al., 2008; Gulkowska et al., 2007; Li et al., 2009).

Thus in the present research work, decomposition and mineralization of CEX along with its toxicity analysis has been carried out at pilot-scale in a cascade once-through reactor incorporating in-situ dual process. To the best of our knowledge, this is the first reported study claiming once through fixed-bed process approaching the efficiency of PFR using Fe–TiO₂ composite beads.

2. Materials and methods

2.1. Chemicals and reagents

The sources of chemicals have been provided in supplementary information (Text S2).

2.2. Fe–TiO₂ composite beads

Spherical beads of diameter 1.5 cm were prepared manually from FS and FA using clay as a binding material. Clay, FS and FA were used in the ratio of 2:1:1. This particular ratio was chosen in view of the high strength and durability of beads. These beads were treated at high temperature in muffle furnace (800–1000 °C) for 1 h in order to become solid and acquire strength. These beads before TiO₂ immobilization were termed as blank beads. Blank beads were used solely for photo-Fenton experiments. FS and FA were utilized as alternative source of iron in the study.

Fe–TiO₂ composite beads were prepared by immobilizing TiO₂ over blank beads following the standard dip-coating method discussed elsewhere (Verma et al., 2014). Iron was leaching by-default from these beads under acidic conditions. The systematic leaching of iron was observed from these beads during the course of reaction. For conducting the photocatalytic experiments solely (i.e. without involving any iron species), clay beads (without FS/FA) were prepared and were coated with TiO₂. These beads were

termed as control beads and were used for photocatalysis.

2.3. Characterization techniques

Various characterization techniques including SEM/EDS, XRD, DRS, TGA and XPS were performed to confirm the activity and stability of catalyst (iron and TiO₂) over composite beads even after recycling them. The details of all techniques have been supplied in Text S3 (Supplementary information).

2.4. Pilot-scale novel once through cascade reactor system

A packed-bed reactor (Length = 25 cm; Breadth = 16 cm; Depth = 3 cm) made up of aluminum was fabricated for studying the once-through fixed-bed system. Sufficient quantity of spherically shaped Fe–TiO₂ composite (Diameter = 1.5 cm) was used so as to cover the entire bottom surface of the reactor. All experiments were conducted with 5 L of CEX solution (50 mgL^{−1}) under natural solar irradiations at acidic conditions (pH = 3.5) adjusted with addition of adequate amount of acetate buffer. Acidic conditions were maintained in order to facilitate the photo-Fenton reaction along with photocatalysis. The aqueous solution of CEX (5 L) with appropriate concentration of H₂O₂ (ranging from 300 to 1500 mgL^{−1}) was pumped from the tank through the reactor where it came in contact with Fe–TiO₂ composite at fixed flow rate and was then collected in a collection tank. The reactions were carried out without recirculation i.e. once through mode. Approximately 3 mL of sample was collected for analysis at regular intervals of time.

For a cascade reactor system, reactors having similar dimensions were connected in series and were placed on different steps maintained at equal heights as shown in Fig. 1. The slope of the overall cascade reactor system was adjusted according to the latitude of Patiala (India). The cascade design of reactor supplied sufficient aeration into the system due to the ‘waterfall’ effect. In case of preliminary studies, experiments were conducted in recirculation mode to confirm the prominence of in-situ dual effect and evaluate the overall degradation efficiency of CEX as well as treatment time. The parametric optimization was carried out in once through mode of cascade reactor system.

The space time (T) or retention time of a single reactor was calculated according to the following formula:

$$\tau = \frac{V}{v_0} \quad (1)$$

Where, τ = space time (min), V = volume of reaction mixture in a reactor (L), v_0 = volumetric flow rate (Lmin^{−1}).

Volume of reaction mixture in a reactor was calculated after subtracting the volume of reactor covered with spherical composite beads.

All solar photocatalytic experiments were conducted during the months of August–October 2017 from 10 a.m. to 4 p.m. at Thapar University, Patiala (30.3398° N, 76.3869° E), India. The total solar intensity was measured regularly during the experimental period by means of a pyranometer. The average intensity of solar irradiations during this period was 806 Wm^{−2}. All experiments were conducted thrice to obtain reproducible results.

2.5. Analytical determinations

All details related to analytical techniques used in the study have been provided in Text S4 (Supplementary information).

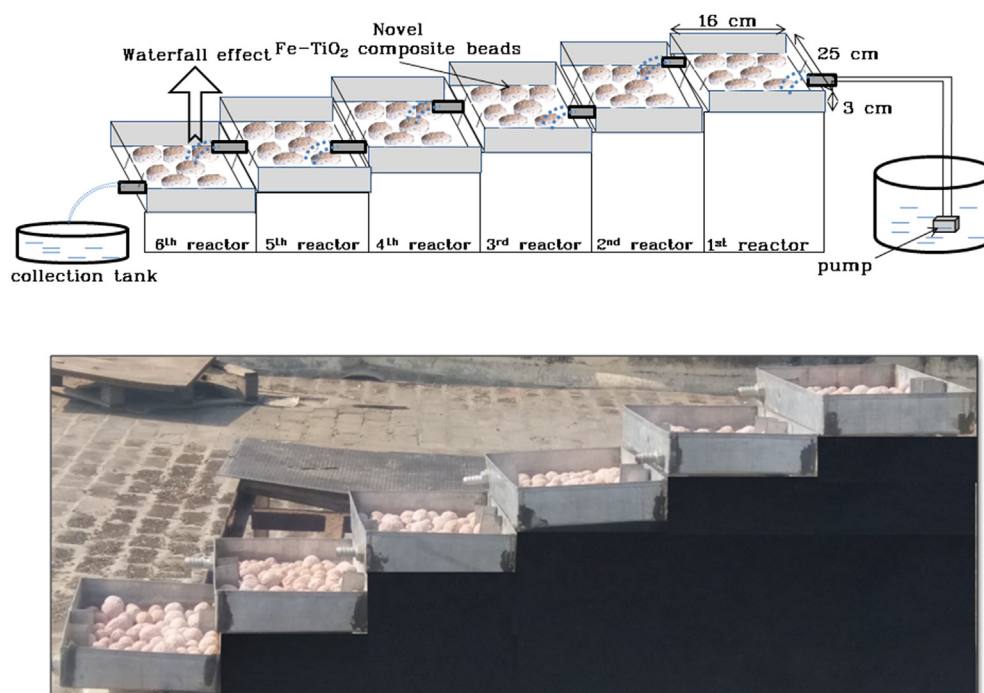


Fig. 1. Schematic diagram and actual photograph of once-through cascade reactor system with six packed-bed reactors connected in series.

2.6. Synergy calculations

In the preliminary experiments, synergy of in-situ dual process over discrete processes (photocatalysis or photo-Fenton) was quantified using the following equations:

Synergy over photocatalysis or photo-Fenton:

$$\% \text{ Synergy} = 100 \times \frac{\left[k_{\text{dual}} - k_{(\text{photocatalysis or photo-Fenton})} \right]}{k_{\text{dual}}} \quad (2)$$

Overall Synergy:

$$\% \text{ Synergy} = 100 \times \frac{\left[k_{\text{dual}} - (k_{\text{photocatalysis}} + k_{\text{photo-Fenton}}) \right]}{k_{\text{dual}}} \quad (3)$$

Where, 'k' is the pseudo first-order rate constant (min^{-1}) in each process.

3. Results and discussion

3.1. Prominence of dual effect

Before directly proceeding towards the details of plug-flow approach integrated with in-situ dual effect studies, the prominence of dual effect was established. For this, the cascade reactor system (comprising of 3 packed-bed reactors in series) was operated in re-circulation mode with a total working volume of 5 L at a fixed flow rate. All experiments were performed under solar irradiations at acidic pH ($\text{pH} = 3.5$) with addition of fixed amount of H_2O_2 i.e. 300 mgL^{-1} . Under these conditions, photocatalytic experiments using control beads led to almost 56% degradation of CEX after 5 h of solar irradiations. Where as, photo-Fenton experiments using blank beads (without TiO_2 coating) yielded an almost 41% degradation of CEX after 5 h of treatment. Actually, the

presence of iron in FA and FS has already been confirmed through EDS analysis as reported in our previous study (Rajput et al., 2016). Moreover, the addition of FA along-with FS increased the compressive strength as well as binding capacity of support material besides increasing the concentration of iron species (Naik et al., 2011).

Interestingly, the treatment time of CEX through in-situ dual process using Fe– TiO_2 composite beads was drastically reduced as it took almost 3 h to achieve 55% degradation of CEX as compared to 5 h in case of photocatalysis. Furthermore, it took almost 1.5 h to attain 40% degradation of CEX as compared to 5 h in case of photo-Fenton. Thus, the precedence of in-situ dual effect among individual processes (photocatalysis or photo-Fenton) was confirmed using Fe– TiO_2 composite beads. Actually iron species were leaching from the composite beads by-default which facilitated the occurrence of photo-Fenton reaction along with photocatalysis. Moreover, rate constant, 'k' was incremented to 0.004 min^{-1} in case of dual process as compared to 0.0026 min^{-1} (photocatalysis) and 0.001 min^{-1} (photo-Fenton). Therefore, 35% and 75% synergy of in-situ dual process was observed over photocatalysis and photo-Fenton respectively. However, overall synergy of dual process over individual processes was observed to be 10%.

All the preliminary experiments (photolysis, adsorption or oxidant addition) were carried out to evaluate the effect of individual parameters on the degradation of model compound i.e. CEX (Fig. 2). Each experiment revealed negligible removal of CEX (3–8%) due to the inadequate production of OH radicals.

3.2. Synergistic effect of oxidant addition

Generally, the optimum use of oxidant addition is always recommended due to the predominance of scavenging effect of hydroxyl radicals at higher dose of oxidant besides being costly (Chan et al., 2003). In the present study, owing to the occurrence of in-situ dual process, H_2O_2 was not utilized solely in photocatalysis but also in photo-Fenton and iron oxide catalysis for the generation of

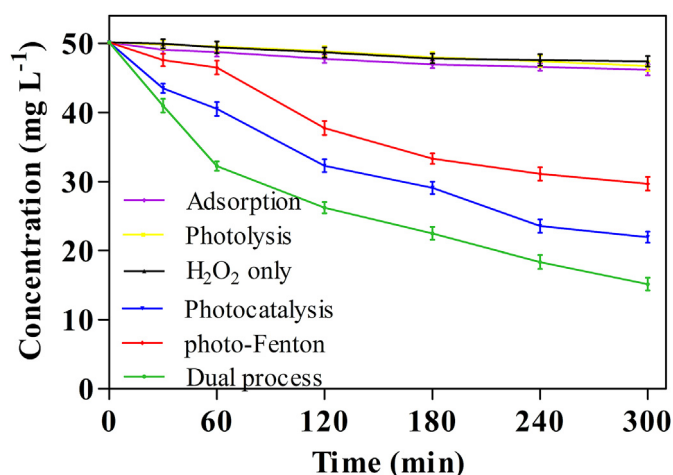


Fig. 2. Concentration profile of CEX during its treatment through different processes ($C_0 = 50 \text{ mgL}^{-1}$, Number of reactors = 3, $V = 5 \text{ L}$).

hydroxyl radicals. The complete mechanism of oxidation and reduction reactions via this in-situ dual process has been explained in Text S1 and Scheme S1 provided in Supplementary information. Thus, studying the effect of H_2O_2 dose for the degradation of CEX via in-situ dual process becomes extremely significant as its addition affects the efficiency of all processes occurring simultaneously. In this context, experiments for the degradation of CEX were carried out using Fe– TiO_2 composite at acidic conditions ($\text{pH} = 3.5$) in a once through cascade reactor (3 reactors in series) under natural solar irradiations at a flow rate of 100 mLmin^{-1} with varying doses of H_2O_2 . At this particular flow rate, space time in each reactor was nearly 6 min as calculated from eqn. (1) (Section 2.4).

In the current research work, the amount of H_2O_2 was varied from 300 to 1500 mgL^{-1} for the degradation of CEX. Fig. 3 shows the concentration profile of CEX in each reactor at different doses of H_2O_2 . The degradation of CEX increased with an increase in the concentration of H_2O_2 up to 600 mgL^{-1} . Thereafter, degradation of CEX either became constant or started decreasing owing to the existence of scavenging effect at high dose of H_2O_2 (Ioannou et al., 2011; Velagraki et al., 2015). Thus, 600 mgL^{-1} of H_2O_2 was chosen as an optimum dose in the present study at which maximum reduction in the concentration of CEX ($\sim 24\%$) was achieved at the

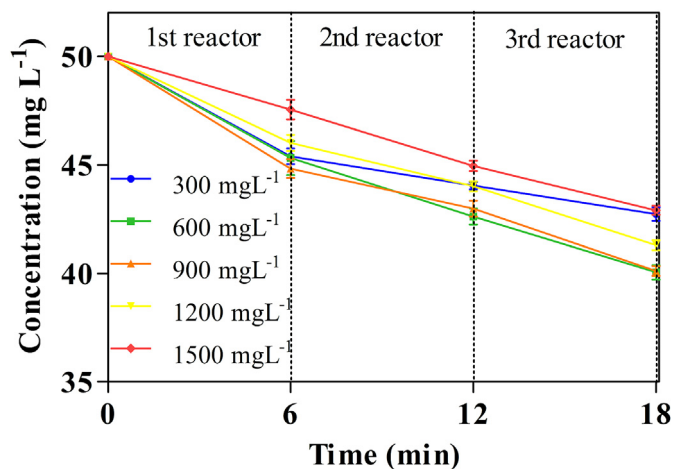


Fig. 3. Effect of H_2O_2 dose on the concentration profile of CEX during its treatment through in-situ dual process ($C_0 = 50 \text{ mgL}^{-1}$, Number of reactors = 3, $V = 5 \text{ L}$).

exit of 3rd reactor. It took almost 50 min to pass the total volume of CEX solution (5 L) by this reactor system in once through mode. Further efforts would be made in subsequent sections to increase the degradation of CEX using this optimized dose of H_2O_2 in minimum possible time.

3.3. Effect of number of reactors

The effect of number of reactors on the degradation efficiency of CEX via once through dual process was evaluated by varying the number of reactors from one to six in a cascade reactor system with total volume handling of 5 L. All experiments were conducted at optimized dose of H_2O_2 i.e. 600 mgL^{-1} under natural solar irradiations at a flow rate of 100 mLmin^{-1} . It is evident from Fig. 4 that maximum amount of reduction in the concentration of CEX ($\sim 13\%$) occurred at the end of first reactor with a space time of 6 min. With further increase in the number of reactors from two to six, conversion of CEX was lower ($\sim 5\text{--}6\%$) in each successive reactor as compared to the 1st reactor. It might be due to the fragmentation of parent compound during its treatment in the first reactor resulting into the formation of some relatively stable intermediates which took comparatively more time to decompose. However, degradation of CEX was incremented to almost 44% at the end of sixth reactor with a space time of nearly 6 min for each reactor. It took almost 50 min to treat the total volume i.e. 5 L of CEX using once-through process.

The optimum number of reactors is basically determined on the basis of maintenance and control of the reactor system which further depends upon the configuration of reactors, conversion factor and nature of pollutant (Miyawaki et al., 2016). Motegh et al. (2014) theoretically investigated the degradation of cyanide in bubble column slurry reactors connected in series and concluded that eight numbers of reactors would be the best for attaining 99% conversion. Visualizing practical approach in these types of reactors is not feasible as huge energy losses may occur owing to slurry photocatalysis. In the present study although additional number of reactors (>6) would further increase the degradation efficiency of CEX, this would make the maintenance and control of system difficult. In this context, number of reactors was not increased further while efforts were made to increase the degradation efficiency of CEX by optimizing further operating parameters taking six as optimum number of reactors.

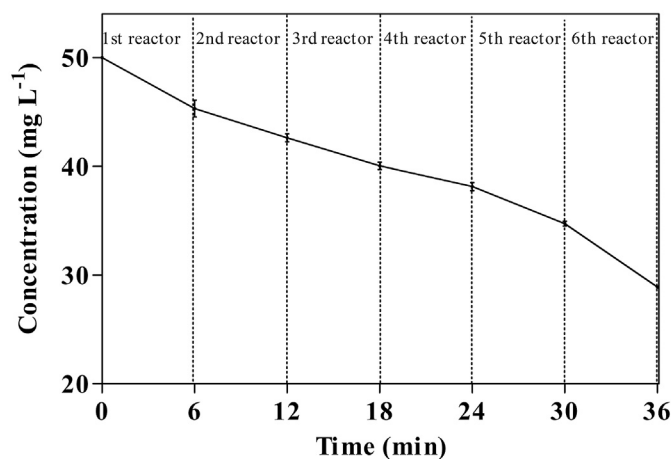


Fig. 4. Effect of number of reactors on the concentration profile of CEX during its treatment through in-situ dual process ($C_0 = 50 \text{ mgL}^{-1}$, $\text{H}_2\text{O}_2 = 600 \text{ mgL}^{-1}$, $V = 5 \text{ L}$).

3.4. Effect of flow rate

The flow rate of aqueous solution affects the dissolved oxygen as well as turbulence in the system which plays a significant role in photocatalytic reactions. Moreover, flow rate of the aqueous solution decides the space time of pollutant (Eqn. (1)). Thus, lower flow rate with high retention time is always desirable for maximum degradation efficiency. In the present study, experiments were performed with varying flow rate of CEX solution ranging from 25 mLmin⁻¹ to 400 mLmin⁻¹ at optimized dose of H₂O₂ i.e. 600 mgL⁻¹ under natural solar irradiations in a cascade reactor (6 reactors in series). It is clear from Fig. 5 that amount of reduction in the concentration of CEX was lowered down with an increase in the flow rate of solution. The most probable reason for the decreased degradation efficiency of CEX is the reduction in retention time of pollutant at higher flow rates as the pollutant leaves without making proper contact with the catalyst. Although degradation of CEX was better at lower flow rates, overall treatment time was also significantly increased which is commercially not desirable. In this regard, 50 mLmin⁻¹ with retention time of nearly 12 min in each reactor was selected as an optimum flow rate for the degradation of CEX in a cascade reactor system.

The degradation of CEX was more or less same at 25 mLmin⁻¹. However, overall treatment time of CEX (5 L) was almost twice (~200 min) in this case as compared to 100 min in case of 50 mLmin⁻¹. Although optimized flow rate i.e. 50 mLmin⁻¹ is less from its commercial point of view, it is still 10 times higher than the reported value i.e. 6 mLmin⁻¹ in literature (Miyawaki et al., 2016) in context to 2,4-dinitrophenol removal from water. The process can be intensified further with comparatively larger reaction volume having capacity of incorporating in-situ dual effect.

The prominence of in-situ dual effect was confirmed again at all optimized conditions by carrying out the degradation of CEX separately through photocatalysis and photo-Fenton in a cascade reactor system in continuous mode. An almost 54% and 28% degradation of CEX was achieved at the end of sixth reactor in case of photocatalysis and photo-Fenton respectively. The degradation was significantly higher (70%) in case of in-situ dual process in contrast to these individual processes. Moreover in case of dual process, nearly 55% degradation of CEX was attained at the end of fourth reactor as compared to sixth reactor in case of photocatalysis. The precedence of in-situ dual effect can also be visualized through the generation of hydroxyl radicals in abundance in

case of dual process as compared to the individual processes as depicted in Fig. S1 (Supplementary information). The leaching of iron from the composite during the treatment process was also confirmed by estimating the concentration of total iron in each reactor as depicted in Table S1 (Supplementary information).

An almost 70% degradation of CEX occurred at the exit of sixth reactor in a fixed-bed pilot-scale cascade reactor system incorporating in-situ dual effect at all optimized conditions after 100 min of treatment time. The concentration profile of CEX at the exit of each reactor connected in series at optimized conditions has been shown in Fig. S2 (Supplementary information). The treatment time was significantly lower in contrast to the reported studies for the degradation of CEX. Almasia et al. (2017) investigated the degradation of CEX via sono-photocatalytic treatment in slurry mode in a pilot-scale reactor with total volume handling of 1 L and observed a maximum of 78.6% degradation after 120 min (Almasia et al., 2017). Ajoudanian and Nezamzadeh-Ejhieh (2015) reported 76% degradation of CEX at lab-scale after 300 min of treatment time with volume handling of 20 mL via heterogeneous catalysis using suspensions of NiO supported on clinoptilolite nanoparticles (Ajoudanian and Nezamzadeh-Ejhieh, 2015). Therefore, in contrast to these reported studies, the current investigation has presented a unique and viable solution for the treatment of recalcitrant pollutants like CEX at pilot-scale (5 L) in minimized time by incorporating the novel concept of in-situ dual effect using Fe–TiO₂ composite in completely fixed-form.

3.5. UV spectral analysis

Fig. 6 depicts the reactor dependent change in absorption spectra for the degradation of CEX through in-situ dual process in a

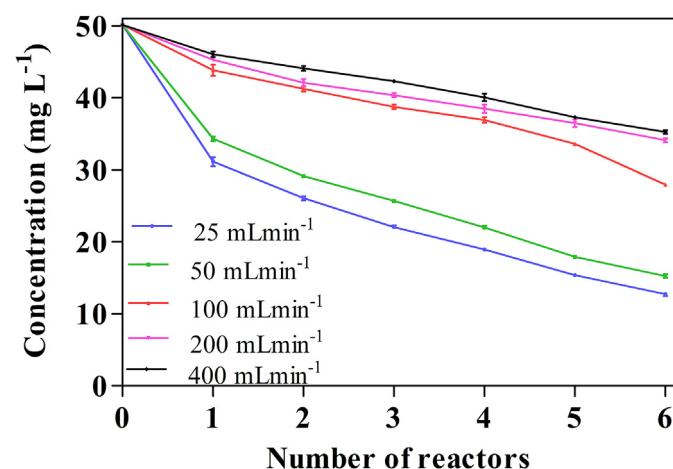


Fig. 5. Effect of flow rate on the concentration profile of CEX during its treatment through in-situ dual process ($C_0 = 50 \text{ mgL}^{-1}$, $\text{H}_2\text{O}_2 = 600 \text{ mgL}^{-1}$, number of reactors = 6, $V = 5 \text{ L}$).

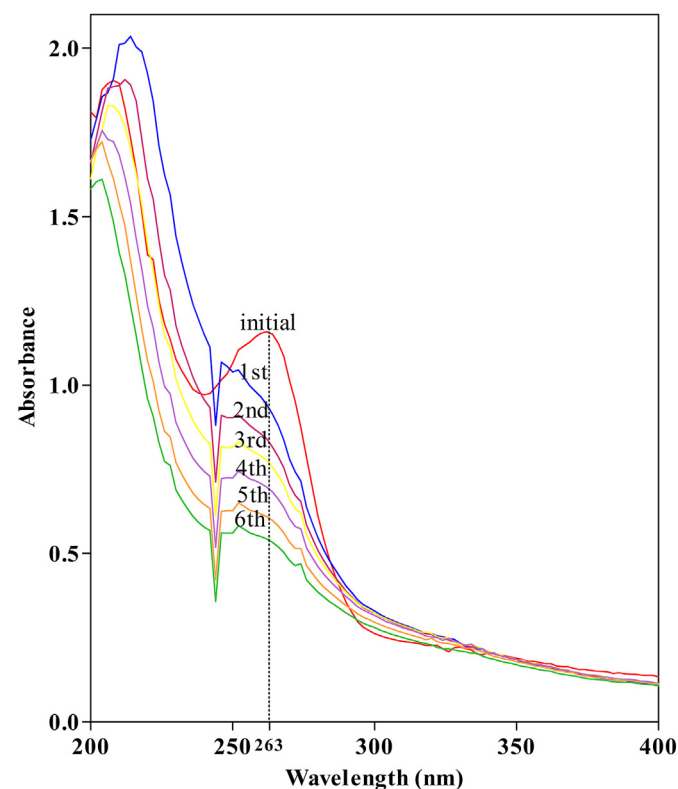


Fig. 6. UV-spectral analysis for the degradation of CEX in a cascade reactor system at optimized conditions ($C_0 = 50 \text{ mgL}^{-1}$, $\text{H}_2\text{O}_2 = 600 \text{ mgL}^{-1}$, number of reactors = 6, flow rate = 50 mLmin⁻¹, $V = 5 \text{ L}$).

fixed-bed cascade reactor at all optimized conditions. The absorption spectrum was attained by carrying out the scan in the range 200–450 nm. The spectrum of CEX exhibits the main prominent band in the UV region with maximum at 263 nm. The continuous decrease in the intensity of absorption peaks of CEX at $\lambda_{\max} = 263$ nm at the exit of each reactor indicated the gradual decomposition of CEX. Maximum degradation of CEX was observed at the end of sixth reactor.

3.6. Durability studies

One of the novel findings of this study is the extended durability of reported Fe–TiO₂ composite beads in terms of exhibiting in-situ dual effect. Thus to confirm our claim, the parametric optimization studies were performed with Fe–TiO₂ composite beads previously used for at-least 45 recycles. In the recycling tests, our reported approach needs to confirm both sustainable leaching of iron as well as stability of TiO₂ coating over the composite. The recyclability efficiency of Fe–TiO₂ composite beads was evaluated in terms of the degradation efficiency of CEX with subsequent recycles.

To counter-check the efficiency of used composite beads, experiments were executed simultaneously with freshly prepared Fe–TiO₂ composite beads as well. There was 7–8% reduction in the degradation efficiency of CEX during the initial few recycling tests (5–6 cycles) owing to the weathering off loosely bound catalyst particles from the surface of composite beads. Thereafter, degradation efficiency was observed to be more or less same. Fe–TiO₂ composite were successfully recycled for 70 runs without any major reduction in the degradation efficiency of CEX as shown in Fig. 7. This confirms that sufficient quantity of catalyst particles were intact to the surface even in the recycled composite beads. None of the studies related to fixed-bed photocatalysis in literature have ever reported such high recyclability efficiency of catalyst. The recycled Fe–TiO₂ composite in the present study was characterized through various techniques (Section 3.8) which further confirm the presence of Fe along with TiO₂ even after 70 recycles.

3.7. Plug-flow approach

The reaction efficiency of plug-flow reactor systems is always high compared to that of continuous stirred tank reactors (CSTRs). But in case of plug-flow reactors with immobilized catalyst, film diffusion resistance or mass transfer implications predominates which substantially reduces the reaction efficiency of system.

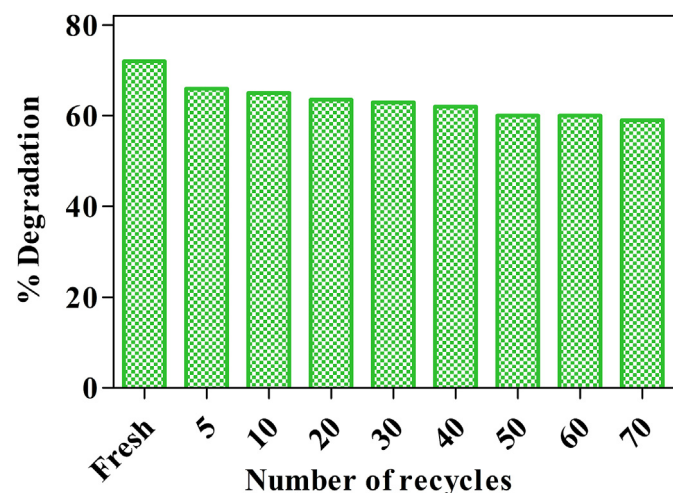


Fig. 7. Recyclability studies of Fe–TiO₂ composite beads for the degradation of CEX.

However theoretically, these systems are predicted to yield high efficiency in the absence of above stated implications. As a result, for the present study, conversion efficiency in the plug-flow reactor has been set as a target value for multiple fixed-bed reactors in series.

The design equation of a plug-flow reactor can be expressed as follows:

$$\frac{V}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} \quad (4)$$

Or

$$\frac{V}{v_0} = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A} \quad (5)$$

Or

$$\frac{V}{v_0} = \frac{1}{k} \int_0^{X_A} \frac{dX_A}{1 - X_A} \quad (6)$$

These conversions can be understood from the following equations:

$$-r_A = kC_A \quad (7)$$

$$X_A = 1 - \frac{C_A}{C_{A0}} \quad (8)$$

V = volume of reaction mixture (L), F_{A0} = molar flow rate (moles min^{-1}), v_0 = volumetric flow rate (L min^{-1}), C_A = final concentration (mgL $^{-1}$), C_{A0} = initial concentration (mgL $^{-1}$), X_A = conversion, r_A = reaction rate (mgL $^{-1}\text{min}^{-1}$), k = rate constant (min $^{-1}$).

The main emphasis of the present research work was to bring the reaction performance of fixed-bed cascade reactor system (incorporating in-situ dual effect) in PFR range. Though there are few studies in literature (Miyawaki et al., 2016) that had approached the concept of plug-flow in their photocatalytic reactor system, commercial viability of these reported systems was questionable due to high treatment time. Moreover, recyclability and stability of the catalyst for subsequent cycles in these types of systems were either very low or had not been discussed. Other implications that are usually encountered in these systems include mass-transfer implications or film diffusion resistance or low exposed surface area of the immobilized catalyst.

Thus, the main target of the present study was to achieve approximately the same conversion efficiency as that of plug-flow systems after overcoming most of the aforementioned limitations. The 'waterfall' effect observed in the present cascade reactor system reduced the film diffusion resistance where as the spherical shaped support for catalyst immobilization provided the maximum overall exposed surface area of TiO₂. The mass transfer implications were further reduced by the occurrence of photo-Fenton along with photocatalysis in the present reactor system thereby reducing the treatment time and enhancing the overall reaction efficiency of system. In addition to this, excellent recyclability efficiency (>70 recycles) of immobilized catalyst (Section 3.8) in comparison to reported studies really highlights the commercial viability of the present reactor system. In the present study, the number of fixed-bed reactors (with Fe–TiO₂ composite) connected in series was increased till the conversion efficiency approached to that of plug-flow reactor.

The theoretical conversion efficiency of CEX in a plug-flow

reactor using the equations (1)–(3) was obtained as 73.4% with exit concentration of CEX as 13.3 mgL^{-1} . While, experimental value of CEX concentration calculated at the end of sixth reactor in a cascade reactor system using Fe–TiO₂ composite was 14.8 mgL^{-1} which is close to the theoretical value (~10% deviation) obtained in case of plug-flow reactor. Thus, it leads to a fact that when six fixed-bed reactors (with Fe–TiO₂ composite) incorporating in-situ dual effect are connected in series, it is feasible to operate the reactor system with performance roughly similar to that of plug-flow reactor.

Therefore, agreement of experimental results with theoretical prediction of plug-flow approach clearly indicated that studied cascade reactor system incorporating in-situ dual effect can be successfully used to attain a higher conversion of pollutant in comparatively lesser space time. Furthermore, the concept of in-situ dual effect using highly durable and economical Fe–TiO₂ composite in a cascade fixed-bed reactor system (six reactors in series) can be implemented at field-scale with certain modifications. To the best of our knowledge, this is the first reported study in which pilot-scale fixed-bed reactor system incorporating in-situ dual effect has been visualized to approach a plug-flow reactor.

3.8. Characterization of immobilized catalyst

3.8.1. SEM/EDS

Fig. 8a demonstrates the SEM and EDS images of freshly prepared and recycled (70 cycles) Fe–TiO₂ composite. The surface morphology of fresh and recycled composite is almost same indicating a uniform coating of TiO₂ over the surface which remained intact even after 70 recycles as depicted in figure. The sharp and prominent peaks of 'Fe', 'O' and 'Ti' in EDS spectra of both fresh and recycled composite justified the presence of both iron and TiO₂ even in recycled composite. It leads to a fact that Fe–TiO₂ composite with high recyclability efficiency can be successfully used in dual effect studies.

3.8.2. XRD

The retention of activity of immobilized TiO₂ over composite beads after recycling tests (70 cycles) was confirmed through XRD analysis. The diffraction patterns of recycled immobilized TiO₂ as well as fresh TiO₂ are depicted in Fig. 8b. Both phases of TiO₂ i.e. anatase (A) and rutile (R) were retained even after recycling the composite for 70 cycles. The reference codes for anatase and rutile phase obtained through XRD data were 01-084-1286 and 01-089-0552 respectively. Along with anatase and rutile peaks of TiO₂, some other peaks corresponding to several forms of iron oxide also existed in the diffraction pattern. These additional peaks were correlated with iron (III) oxide (Fe₂O₃) indicated as 'IO' (01-073-0603), iron diiron (III) oxide (Fe₃O₄) marked as 'IDO' (01-079-0416), iron titanium oxide marked as 'ITO' (01-070-0143) and diiron (III) titanium oxide symbolized as 'DTO' (01-089-8066). The presence of iron oxides along with TiO₂ onto the surface of composite enhances the efficiency of in-situ dual process. Actually the photo-excited electron during the photocatalytic process is entrapped by iron oxide and helps in the regeneration of ferrous ions which further facilitates the simultaneously ongoing photo-Fenton reaction. This mechanism can be clearly understood from Scheme S1 and Text S1 (Supplementary information).

3.8.3. UV–visible diffuse reflectance spectroscopy

The band gap energy of immobilized catalyst was also calculated and compared with that of fresh TiO₂. The UV–visible scan was carried out in the range 200–800 nm. The spectra of both samples (immobilized and fresh TiO₂) have been presented in Fig. 8c. A slight red shift was observed in the spectra of immobilized catalyst

over composite which might be due to the presence of iron. Therefore, Fe–TiO₂ composite demonstrated the capability of absorbing the light even in visible spectrum. The band gap of catalyst was quantified using following eq. (9) (Zhou et al., 2018b):

$$\alpha h\nu = A(h\nu - E_g)^{\frac{n}{2}} \quad (9)$$

Where, α : absorption coefficient, h : Planck's constant ($6.62607004 \times 10^{-34} \text{ m}^2 \text{ kg}^{-1}$), ν : frequency, A : constant, E_g : the band gap energy in eV. Here $n=2$ for indirect band gap in case of semiconductor, $\alpha=0$, $A=1$ as reported in literature (Reddy et al., 2003). Thus eq. (9) can be rewritten as follows:

$$E_g = h\nu = \frac{hc}{\lambda} \quad (10)$$

Here, c : speed of light ($3 \times 10^8 \text{ ms}^{-1}$), and λ : absorption wavelength (m).

Absorption edge in case of immobilized catalyst was extended to 425 nm with calculated band gap energy, $E_g = 2.9 \text{ eV}$ which was much lower in comparison to fresh TiO₂ with $E_g = 3.1 \text{ eV}$.

3.8.4. XPS analysis

The surface composition of recycled Fe–TiO₂ composite was also verified through XPS analysis and compared with fresh TiO₂. The surface survey scan of immobilized catalyst and fresh TiO₂ is depicted in Fig. 8d. The scan of TiO₂ clearly indicated the prominent peaks of 'Ti' and 'O' without any other additional peak whereas scan of immobilized catalyst portrayed other weak peaks as well in addition to 'Ti' and 'O'. The additional weak peak (near 710 eV binding energy) in case of immobilized catalyst corresponded to 'Fe'. The graph has been separately shown in Fig. s3 (supplementary information). The presence of iron along with TiO₂ in composite was confirmed by each characterization technique leading to a proposition that highly durable and stable Fe–TiO₂ composite could be efficiently used for dual effect studies.

3.8.5. TGA analysis

The thermal analysis was also carried out to determine whether any change occurred in the thermal stability of catalyst due to the presence of iron. The thermo-gravimetric curves of immobilized catalyst over composite and fresh TiO₂ are shown in Fig. 8e. There was no significant variation in the mass of both samples with change in the temperature from 30 to 980 °C. Thus, Fe–TiO₂ composite demonstrated an excellent thermal stability as well in contrast to TiO₂.

3.9. Intermediates and pathway prediction for the degradation of CEX

3.9.1. FTIR analysis

The degradation of CEX was further analyzed through FTIR spectra. The infrared spectrum of untreated parent compound i.e. CEX and treated solution of different reactors (1–6) in a cascade reactor system is presented in Fig. 9a. It is clear from figure that untreated CEX consisted of numerous peaks corresponding to several different bonds present in its complex structure. The peaks between 600 cm^{-1} and 1000 cm^{-1} represented the bending vibrations of alkene ($=\text{C}-\text{H}$) while peaks between 1080 cm^{-1} and 1360 cm^{-1} corresponded to the stretching vibrations of C–N group. The weak bands between 1400 cm^{-1} and 1600 cm^{-1} represent the aromatic nature of compound while a small peak at 1464 cm^{-1} could be correlated with CH₃ bending vibrations. Strong peaks between 1500 cm^{-1} and 1700 cm^{-1} corresponded to amide group. The broad transmittance band at 3400 cm^{-1} symbolized the

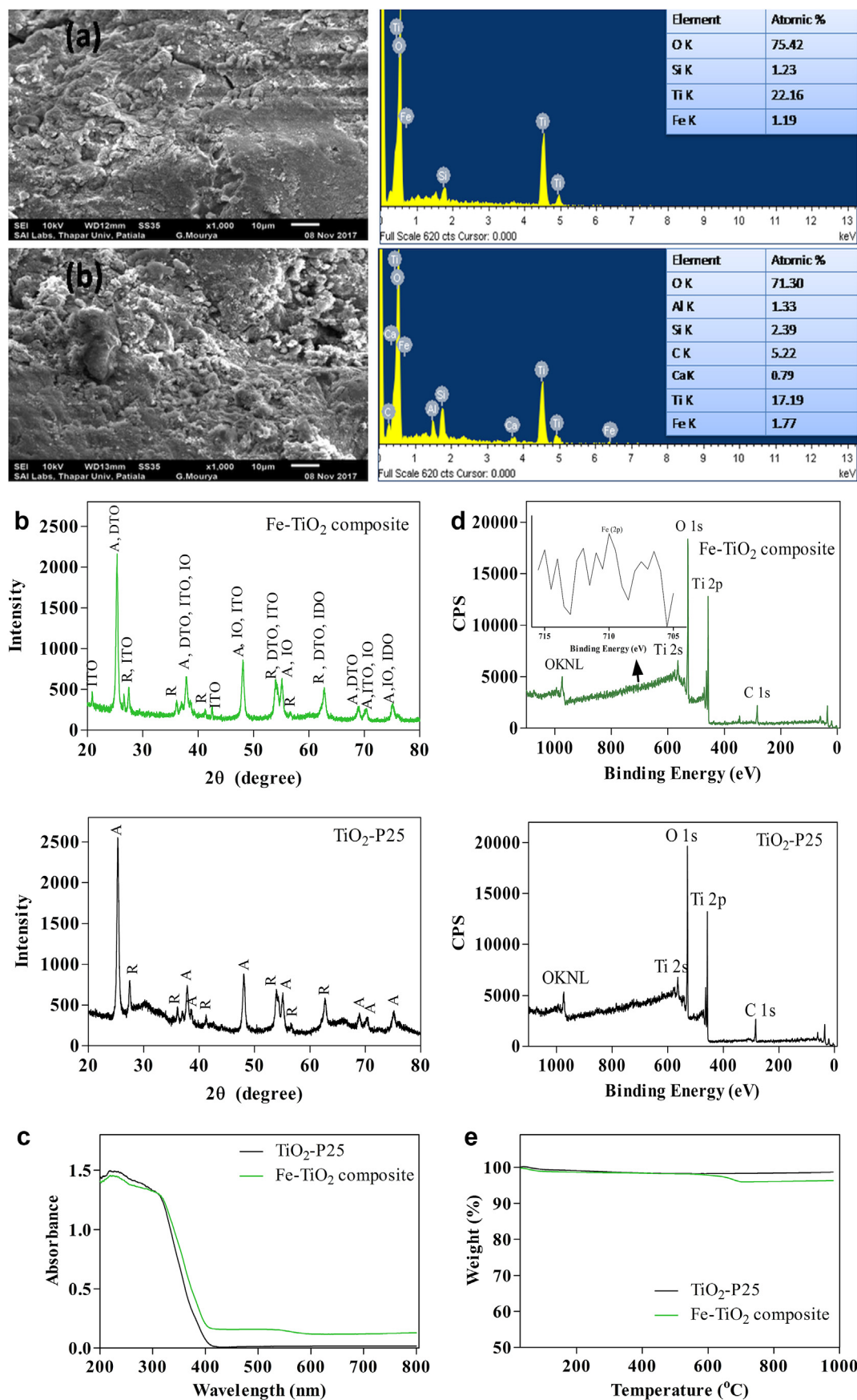


Fig. 8. a SEM/EDS analysis of Fe-TiO₂ composite beads (a) Fresh composite beads and (ii) after 70 recycles. Fig. 8b: XRD pattern of (a) fresh TiO₂-P25 and (b) recycled Fe-TiO₂ composite beads (70 recycles). Fig. 8c: UV-visible DRS of (a) fresh TiO₂-P25 and (b) recycled Fe-TiO₂ composite beads (70 recycles). Fig. 8d: XPS analysis of (a) fresh TiO₂-P25 and (b) recycled Fe-TiO₂ composite beads (70 recycles). Fig. 8e: TGA analysis of (a) fresh TiO₂-P25 and (b) recycled Fe-TiO₂ composite beads (70 recycles).

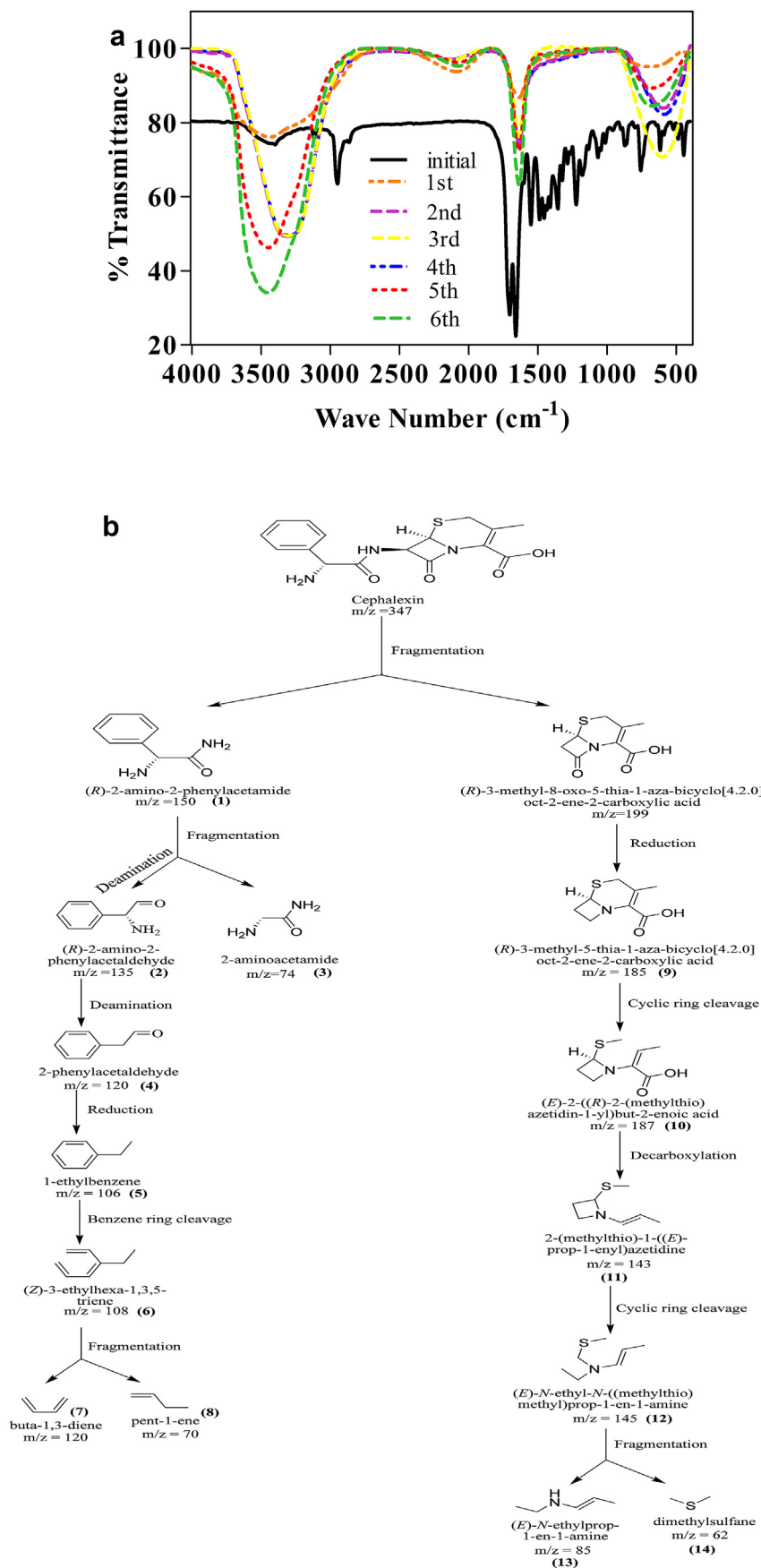


Fig. 9. aFT-IR spectra of treated and untreated solution to confirm the degradation of CEX in a cascade reactor system at optimized conditions. Fig. 9b: Tentative pathway for the degradation of CEX.

stretching vibrations of O–H group. The peak at 3000 cm^{-1} represented the stretching vibrations of amine (N–H). Most of these peaks present in CEX got disappeared after undergoing treatment through in-situ dual process thus suggesting an almost complete decomposition of CEX. Strong peaks between 3300 cm^{-1} and 3500 cm^{-1} in case of treated solution in each reactor corresponded to the O–H stretching vibrations. These peaks were comparatively more sharp and prominent as compared to the peak in untreated CEX which might be due the generation of OH radicals during the treatment process. The weak transmittance band between 1600 cm^{-1} and 1680 cm^{-1} represented the stretching vibrations of alkene (C=C) group whereas band between 600 cm^{-1} and 700 cm^{-1} could be correlated with the bending vibrations of alkene (=C–H) in the treated solution in each reactor. The high intensity of transmittance in the treated solution towards the end reactor could be accounted for the complete oxidation of CEX via in-situ dual process. Thus, it was confirmed from FTIR analysis that complex structure of CEX was transformed into the simpler and linear molecules after the treatment process as detailed in GC-MS analysis.

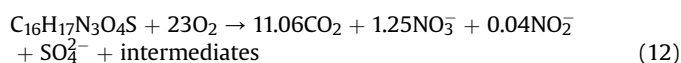
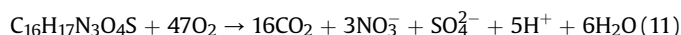
3.9.2. GC-MS analysis

The intermediates formed during the treatment of CEX in a cascade reactor were identified through GC-MS analysis. The GC chromatograms and mass spectra depicting the identified intermediates are shown in Figs. S4 and S5 (Supplementary information), respectively. Based on these intermediates (1–14), a tentative pathway for the degradation of CEX has been proposed (Fig. 9b). The fragmentation of CEX could lead to the formation of (R)-2-amino-2-phenylacetamide (**1**) and (R)-3-methyl-8-oxo-5-thia-1-aza-bicyclo[4.2.0]oct-2-ene-2-carboxylic acid. The by-product (**1**) could further be fragmented into (**2**) and (**3**). The deamination of (**3**) could produce (**4**) which might get reduced into (**5**). The cleavage of benzene ring of (**5**) could yield (**6**). Successive fragmentation of (**6**) could finally result into linear chain molecules (**7**) and (**8**). On the other hand, (R)-3-methyl-8-oxo-5-thia-1-aza-bicyclo[4.2.0]oct-2-ene-2-carboxylic acid might get reduced to form by-product (**9**). The breakdown of cyclic ring of (**9**) could yield (**10**) which further resulted into the formation of (**11**) after undergoing decarboxylation. The cleavage of cyclic ring of (**11**) could produce (**12**). The by-product (**12**) could possibly undergo fragmentation to yield other linear chain molecules (**13**) and (**14**). It can therefore be concluded that complex molecule of CEX has been broken down into simpler and linear chain molecules suggesting a complete decomposition of CEX through in-situ dual process in minimized time.

3.10. Mineralization studies

The mineralization of CEX was evaluated at all optimized conditions in terms of the generation of anions including nitrate, nitrite and sulfate ions along with depletion in COD and TOC values. There was almost 70% and 63% reduction in COD and TOC respectively at the exit of sixth reactor of a cascade reactor system. It can be presumed that nitrogen atoms of CEX were converted into nitrate and nitrite ions (Grover et al., 2014). It was observed that concentration of nitrate ions were maximum during the treatment of CEX in first two reactors of a cascade reactor system. Thereafter, concentration of nitrate ions started decreasing (from reactor 3–6) with a probability of transformation of nitrate ions into nitrite ions. While, concentration of nitrite and sulfate ions followed an increasing trend throughout the treatment process (from reactor 1–6) as shown in Table S2 (Supplementary information). The calculations for CO_2 mass balance have been provided in supplementary information (Text S5). The stoichiometrically balanced theoretical

chemical equation for the complete mineralization of CEX is indicated in eqn. (11). The experimental chemical equation (12) obtained through the quantification of anions including nitrite, nitrate, sulfate ions and CO_2 evolution at the exit of reactor 6 partially deviates from eqn. (3) thus indicating an incomplete mineralization of CEX owing to the formation of intermediates as discussed in previous section.



3.11. Toxicity analysis

To re-affirm whether the target pollutant i.e. CEX was sufficiently mineralized through in-situ dual process (as stated in Section 3.10) or converted into toxic intermediates or by-products, toxicity analysis was carried out by evaluating acute and cytotoxicity of samples (Hu et al., 2017). In the present study, cytotoxicity was evaluated through Kirby-Bauer test (agar well diffusion assay) against *B. subtilis* (MTCC441) taking working solution of CEX (50 mgL^{-1}) as control. Briefly, 0.5 cm wells were made in Muller Hinton agar (MHA) plates with a sterile cork borer. Subsequently, approximately $30\text{ }\mu\text{L}$ of samples from different reactors (1st, 4th and 6th) during the treatment was poured in each well and were diffused at 37°C for nearly 20 min. The plates were then swabbed with 18–24 h old culture of *B. subtilis*. The plates were kept in an incubator at 37°C for overnight. The cytotoxic activity was analyzed through the formation of zone of inhibition around the well. The biggest zone of inhibition was observed in case of control (untreated sample) while the size of zone was dramatically reduced in a treated sample after the first reactor. Moreover, zone of inhibition got completely disappeared in case of treated samples after the 3rd reactor (Fig. S6, supplementary information) thus indicating that sample became non-toxic after the treatment process.

Furthermore, acute toxicity of the treated sample (obtained at the exit of 6th reactor of a cascade system) was also evaluated through bio-assay method which is based on the toxicity factor. Toxicity factor can be defined as the minimum quantity of dilution of water sample required for attaining no mortality for the zebra fish. In the present study, 100% survival of zebra fish was attained after 96 h of toxicity test (analysis report has been supplied in supplementary information 2). It can be deduced that the treated aqueous solution of CEX was completely non-toxic thus suggesting that the presented cascade reactor system incorporating in-situ dual effect using Fe– TiO_2 composite can be implemented at field-scale.

4. Cost evaluation

Most of the studies in literature associated with AOPs deal with the degradation of various organic pollutants without considering the cost of treatment. Actually, there are different expenses involved in the whole treatment process that should be considered while deciding the economy of process. Real costs of the process must include the fabrication of reactor, reagents, catalysts, operating cost and electricity consumption. Therefore, efforts have been made in the present study to evaluate the overall cost of the process at pilot-scale with an assumption that land was available free of cost. The estimation of cost at pilot-scale can provide a rough idea to consider the real applications of photocatalytic reactor at field-

Table 1
Evaluation of cost of treatment process.

S. No.	Cost of different units of treatment process	
(A)	Fe–TiO₂ composite preparation	
	Cost of raw materials (clay, FA, FS)	0.0 \$
	Electricity consumption during firing of blank composite at high temperature	0.75 kWh
	Electricity price in India	0.0699 \$/kWh
	Cost of electricity consumption	$0.0699 \times 0.75 = 0.0524$ \$/kWh
	Cost of TiO ₂ used (20 g)	0.06 \$
	Total cost of Fe–TiO ₂ composite	$0.0524 + 0.06 = 0.1124$ \$
(B)	Oxidant (H₂O₂) addition	
	Cost of total oxidant (700 mL) used (for 70 runs)	9.6824 \$
(C)	Operating cost of treatment process	
	Cost of light source (sunlight)	0.0 \$
	Number of runs	70
	Total volume of water treated	$5 \text{ L} \times 70 = 350 \text{ L} (0.35 \text{ m}^3)$
	Cost per m ³	$(A + B)/0.35 = 27.98$ \$/m ³
	With 70% degradation ($C_0 = 50 \text{ mgL}^{-1}$), concentration of CEX removed	$35 \text{ mgL}^{-1} (0.035 \text{ kgm}^{-3})$
	Cost per kg of concentration removal	$(A + B)/0.035 = 279.85$ \$/kg of concentration removal
	Energy consumption during operation of process (pumping of solution during treatment)	$18 \times 1.7 \times 70 = 2142 \text{ W h}$
	Energy consumed per kg of concentration removal	$2142/0.035 = 61.2 \text{ kW h per kg of concentration removal}$
	Cost for energy consumption	$0.0699 \times 61.2 = 4.277$ \$/kWh
	Overall operating cost	$279.85 + 4.277 = 284.12$ \$
(D)	Fabrication of cascade reactor system	
	Total cost including pump, reactors, pipe, valves	15.40 \$
Total cost of treatment process (for 70 runs) = C + D = 299.52 \$		
Total cost of treatment process for single run (5 L) = 4.27 \$.		

scale. The overall cost of treatment process in the current research work has been presented in detail in Table 1. The overall cost has been evaluated for 70 numbers of runs which came out to be 299.52 \$. More precisely for a single operation of a process to treat 5 L of solution, the overall cost would be 4.27 \$ which came out to be 0.85 \$ per litre. The costs reported in this study are significantly lower than other reported studies related to AOPs (Ozkal et al., 2016; Vishnuganth et al., 2016). Most of the studies in literature have evaluated only the cost of electricity consumption during the operation of process or analysis cost without considering the cost of reactor fabrication or catalyst used (Haranaka-Funai et al., 2017; Mehrjouei et al., 2014).

To the best of our knowledge, this is the first reported study that has evaluated the detailed cost of treatment process in context to pilot-scale fixed-bed reactor using AOPs. In view of the excellent recyclability efficiency of Fe–TiO₂ composite beads, overall cost of the process in the present study can be further reduced when used for more cycles. Therefore, a cascade reactor system with highly durable and stable Fe–TiO₂ composite beads can provide a low cost solution to various industries for the treatment of wastewater in minimized treatment time.

5. Conclusions

The present research work has reported the prominent solution of problems encountered in conventional fixed-bed systems like mass transfer implications, durability of the immobilized catalyst and increased treatment time by incorporating novel in-situ dual effect. The treatment time was drastically reduced using novel Fe–TiO₂ composite beads capable of incorporating in-situ dual effect. Moreover, these composite beads exhibited remarkable durability (>70 recycles) which further claims our novelty. Study of cascade reactor system (six reactors in series) using Fe–TiO₂ composite beads approaches PFR through the introduction of in-situ dual effect. The cascade design of reactor system reduced the film diffusion resistance besides maintaining sufficient amount of aeration in the system. The mineralization studies as well as toxicity analysis of the treated solution clearly indicated the commercial viability of the presented reactor system. Furthermore, the

overall cost of the process evaluated in this study is significantly lower than other reported studies related to AOPs. The once-through cascade reactor system approaching PFR is viable at field-scale applications as compared to CSTR.

The presented fixed-bed cascade reactor system incorporating in-situ dual effect with proven validation of theoretical prediction can be effectively used at large-scale to treat the wastewater in minimized time.

Declarations of interest

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jclepro.2018.05.219>.

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Detoxification of real pharmaceutical wastewater by integrating photocatalysis and photo-Fenton in fixed-mode

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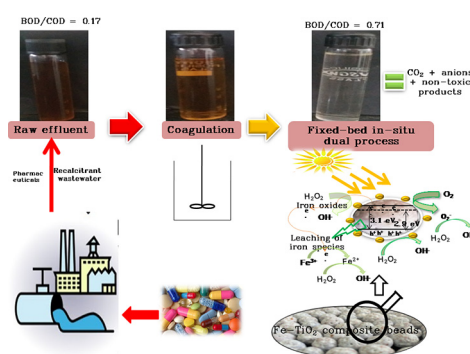
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HIGHLIGHTS

- Real pharmaceutical effluent was treated via fixed-bed in-situ dual process.
- Coagulation was used as a pre-treatment step prior to in-situ dual process.
- Fe-TiO₂ composite beads depicted excellent recyclability efficiency (> 70 recycles).
- The intermediates were identified through GC–MS analysis.
- The treated wastewater was analyzed through cyto-toxicity and acute toxicity tests.

GRAPHICAL ABSTRACT



ARTICLE INFO

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ABSTRACT

The applications of novel Fe-TiO₂ composite capable of incorporating in-situ dual effect (photocatalysis and photo-Fenton) have been studied for the treatment of real pharmaceutical effluent using batch and continuous reactors. The treatment time was reduced to a great extent using these novel composite beads along with significant reduction in COD (83%). Coagulation using FeCl₃ as a coagulating agent was used as a pre-treatment step prior to in-situ dual process. The parametric optimization in case of in-situ dual process was carried out in batch mode under artificial UV-A irradiations. The biodegradability index (BOD₅/COD) of wastewater became 0.71 from 0.172 after 5 h of treatment via in-situ dual process. The intermediates present in the real wastewater before and after the treatment process, were carefully identified through GC–MS analysis based on which a tentative degradation mechanism for the treatment of pharmaceutical wastewater has been proposed. The treated wastewater was found to be completely non-toxic as confirmed through cyto-toxicity as well as acute toxicity analysis. The field-scale applications of fixed-bed in-situ dual process using Fe-TiO₂ composite beads were validated from successful treatment (~80% COD reduction) of real wastewater (5 L) in less than 120 min in a pilot-scale once-through cascade reactor under natural solar irradiations. Moreover, Fe-TiO₂ composite beads represented an outstanding recyclability efficiency (> 70 recycles) without depicting any significant reduction in their activity as confirmed through various characterization techniques.

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1. Introduction

The advent of new pharmaceutical drugs or antibiotics in the medical sciences has resulted in the severe contamination of surface water [1], ultimately drinking water [2,3] due to the ineffectiveness of conventional treatment methods. The problem is more severe in developing countries like India where illness rate is high owing to the prevalence of poor hygienic conditions leading to the consumption of more drugs or antibiotics. The presence of these contaminants in aquatic environment even in low concentrations ($< 1\mu\text{g L}^{-1}$) can pose serious threats to humans as well as wildlife [4].

Emerging technologies like advanced oxidation processes (AOPs) i.e. hydroxyl radicals derived oxidation-reduction techniques, in the recent past have demonstrated their capabilities to treat a wide range of pollutants ranging from dyes, phenols, pesticides, pharmaceuticals, polymers, chlorophenols [5–8]. However, when it comes to the real wastewater applications, AOPs have shown their incapability in view of its commercial viability. The major hurdles that are being faced towards the field-scale applications of these technologies include increased treatment time, process approach, increased energy costs, catalyst separation and source of light [9–12].

Among AOPs, Fenton treatment has shown its credentials in the complete removal of trace-level pharmaceuticals from water [13]. However, high dose of H_2O_2 along with generation of huge quantities of iron sludge from these processes have restricted their successful implementation at large scale. Whereas in TiO_2 photocatalysis, but is always there between slurry and fixed-bed approach. The applications of TiO_2 photocatalysis are always preferred in fixed form owing to the additional step of costly catalyst separation post-treatment. Though there are numerous reports in literature that have used fixed photocatalysts, increased treatment time, frequent recombination of charge carriers, mass transfer implications and poor catalyst recyclability efficiency are some of the concerns that inhibited its application at field-scale. In this context, the proposed process (in-situ dual process) combining heterogeneous photo-Fenton and photocatalysis in the present study, has successfully removed most of these implications usually faced in conventional processes for the treatment of wastewater.

Furthermore, most of the reported studies related to either photocatalytic or photo-Fenton treatment have been performed using high concentrations of pharmaceuticals spiked in de-ionized water rather than treating real pharmaceutical effluent [14,15]. Thus, research is still oriented towards the establishment of real applications of advanced treatment technologies for the successful treatment of industrial wastewater.

As a result, best efforts were made to seek the commercial applications of AOPs for the treatment of industrial wastewater by overcoming most of the implications usually faced either in conventional photocatalysis or photo-Fenton. For this, a novel concept of in-situ dual effect i.e. integrating photocatalysis and photo-Fenton within the same treatment unit was applied for the first time especially in fixed-mode in context to the treatment of real pharmaceutical effluent. The main emphasis of the study was to represent the in-situ dual process as an effective pre-treatment option prior to biological treatment of industrial wastewater. Unique spherical Fe- TiO_2 composite beads from clay, foundry sand (FS) and fly-ash (FA) with a layer of TiO_2 on its surface were prepared to execute the in-situ dual process. Actually waste FA and FS were utilized as alternative sources of iron. These composite beads were susceptible to leach out iron species under acidic conditions thus contributing to photo-Fenton reaction along with on-going photocatalysis. Besides photo-Fenton and photocatalysis, these composite beads were contributing to iron-oxide catalysis as well owing to the presence of few forms of iron-oxides on their surface (confirmed through XRD). These iron-oxides had the capacity to capture photon excited electron from the conduction band of TiO_2 thus promoting electron-hole separation thereby enhancing the overall catalytic activity. At the same time, this captured electron had the tendency to

regenerate ferrous ions from ferric ions hence stimulating the photo-Fenton reaction (Scheme S1, Supplementary reaction). Consequently, abundance of hydroxyl radicals generated through different processes augmented the oxidative destruction of toxic pollutants present in effluent.

Through this study, authors claim certain novel findings which include in-situ dual process especially in fixed-mode, extended durability of catalyst supported composite beads, pilot-scale demonstration for the successful treatment of real pharmaceutical wastewater along-with significant reduction in treatment time.

2. Materials and methods

2.1. Wastewater, chemicals and reagents

Real effluent was procured from a formulation unit of a pharmaceutical industry located in Ambala, Haryana (India). TiO_2 -P25 (70% anatase, 30% rutile) was bought from Evonik industries, Mumbai (India) while hydrogen peroxide (H_2O_2) (30% w/v), used as an oxidant in the study, was bought from Ranbaxy industries, Gurgaon (India). Waste fly-ash (FA) as well as foundry sand (FS), used as alternative sources of iron were obtained from a local industry, Patiala (India). These waste materials were employed without undergoing any purification. Clay was collected from the local market, Patiala (India). Sodium acetate ($> 98.5\%$) and acetic acid ($> 99.5\%$), purchased from TCI Chemicals, Chennai (India) were utilized in the preparation of acetate buffer. Anhydrous sodium carbonate ($> 98.5\%$) and Ferric chloride (FeCl_3) was obtained from Loba Chemicals, Mumbai (India).

2.2. Fe- TiO_2 composite beads

Waste FS and FA were employed as alternative sources of iron in the present study. The presence of iron in these waste materials was already confirmed and reported in our earlier study [16]. Moreover, addition of FA along-with FS also increased the compressive strength and binding capacity of supports apart from augmenting the concentration of iron [17]. Thus, spherical beads with average diameter of 1.5 cm were prepared manually using FS, FA and clay (1:1:2). The diameter of beads was measured through vernier caliper. From a lot of nearly 100 beads, fifty beads were picked and their diameter was measured from different sides. The average value of diameter from all beads was considered. These beads were heated at high temperature (800–1000 °C) in muffle furnace for 1 h in order to acquire strength. The beads were denoted as blank beads before TiO_2 immobilization. Blank beads were merely used for photo-Fenton experiments. Actually, these beads possessed the characteristics of leaching iron species (owing to the presence of FA/FS) under acidic conditions.

Blank beads were coated with a layer of TiO_2 following the dip-coating method as detailed in our previous studies [18,19]. These TiO_2 coated beads were termed as Fe- TiO_2 composite beads. These composite beads were successfully used for in-situ dual process due to the systematic leaching of iron species in solution contributing to photo-Fenton along with the presence of TiO_2 layer over the surface of beads promoting photocatalysis within the same unit.

Control beads were also prepared from clay (without FS/FA) and were coated with a layer of TiO_2 in the same manner as discussed above. These beads were used solely for TiO_2 photocatalysis due to the absence of any iron species.

2.3. Characterization techniques

Fe- TiO_2 composite beads were characterized through different techniques to confirm its stability and activity after the recycling tests. The surface characteristics along with elemental composition of Fe- TiO_2 composite beads were assessed through scanning electron microscope (SEM) having model No. - JSM-6510LV (JEOL, Japan) and electron

dispersion spectrometer (EDS) having model No. - INCAX-act (Oxford instruments, United Kingdom). The crystalline planes of the catalyst were analyzed through X-ray diffraction (XRD) using X'Pert pro diffractometer by varying the values of 2θ from 20 to 80°. The band gap energy of immobilized catalyst was analyzed through UV–visible diffuse reflectance spectro-photometer (DRS) having model No. - UV-2600 (Shimadzu, Asia Pacific). The wavelength scan was performed in the UV–visible region from 200 to 800 nm. Atomic absorption spectroscopy, AAS (GBC 932 AA) was used to detect the presence of any heavy metals in the treated wastewater sample. Fuel source used for the detection of metals including lead and nickel was air-acetylene while for chromium, nitrous oxide-acetylene was employed. The sample was injected after digestion through capillary. Hollow cathode lamp was employed as a source of light.

2.4. Coagulation-flocculation

Coagulation–flocculation was carried out using FeCl_3 as a coagulant. The experiments were conducted in a jar test apparatus with a wastewater volume of 1000 mL stirred at 120 rpm for initially 30 s followed by slow agitation for 15 min. The flocs were allowed to settle for 1 h and the supernatant was collected. The process was optimized using various concentrations of FeCl_3 . Coagulation–flocculation was used as a pre-treatment step prior to the execution of all photo-experiments.

2.5. Batch experiments

The batch experiments for the photo-treatment of effluent were carried out at laboratory-scale in a wooden UV chamber comprising of seven UV-A (365 nm) tubes (36 W) of Philips ([Supplementary information, Fig. S1](#)). A borosilicate glass bowl (Diameter = 17 cm, Height = 5 cm, Capacity = 1000 mL) was employed as a batch reactor. The average intensity of UV-A irradiations i.e. $23 \pm 2 \text{ Wm}^{-2}$, measured through an eppley radiometer (model-33013) was maintained throughout the reaction. The intensity could be altered by varying the distance of batch reactor from the UV tubes by means of lab jack. The pre-treated real pharmaceutical wastewater (200 mL) was used for all photo-experiments with adequate number of catalyst immobilized composite beads. For maintaining the homogeneity of reaction and sufficient aeration into the treatment system, two air spargers with inlet flow rate of 3.5 Lmin^{-1} were used. For the time-dependent analysis, adequate quantity of sample from the batch reactor was collected by means of syringe after regular time intervals. After conducting parametric optimization under artificial UV-A irradiations, the experiments were performed in natural sunlight.

The experimental design for optimization has been detailed in [Supplementary information \(Text S1\)](#).

2.6. Pilot-scale fixed-bed once through cascade reactor

Six packed-bed aluminum reactors (Length = 25 cm; Breadth = 16 cm; Depth = 3 cm) were connected in series and were placed at equal heights ([Fig. S1, Supplementary information](#)). The slope of this cascade reactor system was maintained in view of the latitude of Patiala (India). The cascade design of system supplied sufficient aeration and turbulence into the reactor. Appropriate quantity of Fe-TiO_2 composite beads was placed in each packed-bed reactor to conduct the in-situ dual process. The reactor was designed to handle a total volume of 5 L of effluent. The coagulated sample of effluent (5 L) containing optimized concentration of H_2O_2 was pumped from the in-let tank through the reactor where it came in contact with Fe-TiO_2 composite beads at a fixed flow rate and was then collected in a collection tank. Acidic conditions (pH = 3–3.5) were maintained throughout the reaction by addition of acidic buffer in order to facilitate the photo-Fenton reaction along with photocatalysis. Approximately 3 mL of sample was

collected at the exit of each packed-bed reactor for analysis at regular intervals of time.

The space time (τ) of a single packed-bed reactor was calculated using following formula:

$$\tau = \frac{V}{v_0} \quad (1)$$

where, τ = space time (min), V = volume of reaction mixture in a reactor (L), v_0 = volumetric flow rate (Lmin^{-1})

Volume of reaction mixture in a reactor was calculated after subtracting the volume of reactor covered with spherical composite beads.

All solar photocatalytic experiments were conducted during the months of October–November 2017 from 10 A.M to 4 P.M at Thapar Institute of Engineering and Technology, Patiala (30.3398° N , 76.3869° E), India. The average intensity of solar irradiations (300–700 nm) during this period was 788 Wm^{-2} as measured through pyranometer. All experiments were conducted thrice to obtain reproducible results.

2.7. Analytical determinations

The samples of real pharmaceutical effluent during the treatment process were analyzed through monitoring the reduction in COD. %COD removal was calculated using the following formula:

$$\% \text{COD removal} = \left(\frac{C_0 - C}{C_0} \right) \times 100 \quad (2)$$

where, C_0 is the initial COD of raw pharmaceutical effluent and C is the final COD of treated water.

The synergy of dual process over discrete processes i.e. photocatalysis or photo-Fenton was calculated using the following equations:

Synergy of dual process over photocatalysis or photo-Fenton:

$$\% \text{Synergy} = 100 \times \frac{\{[k_{\text{dual}} - k(\text{photocatalysis or photoFenton})]\}}{k_{\text{dual}}} \quad (3)$$

Overall Synergy:

$$\% \text{Synergy} = 100 \times \frac{\{[k_{\text{dual}} - (k_{\text{photocatalysis}} + k_{\text{photoFenton}})]\}}{k_{\text{dual}}} \quad (4)$$

where, 'k' defines the first order rate constant (min^{-1}) with respect to each process.

Generation of anions including nitrite and nitrate ions was also quantified in order to confirm the mineralization of pollutants present in the real wastewater. Standard APHA methods (1989) were followed for the analysis of nitrite, nitrate ions, total iron concentration and also for estimating COD. The hydroxyl radicals generated during the in-situ dual process was quantified through fluorescence spectroscopy (model LS-45, Perkin Elmer) by examining the fluorescent signal at 425 nm. Actually a fluorescent compound namely 2-hydroxy terephthalic acid is produced at this wavelength owing to the occurrence of reaction between hydroxyl radicals ($\cdot\text{OH}$) and sodium salt of terephthalic acid. Total organic carbon (TOC) was estimated using TOC analyzer (Multi N/C 2100 BU, Analytic Jena AG Corporation (Germany)). The H_2O_2 interference was removed prior to COD and TOC determination by adding adequate quantity of concentrated solution of sodium carbonate followed by heating the solution at 90°C for 1 h as reported in literature [20]. Biological oxygen demand (BOD) was determined through manometric method using Oxi-Top Control (WTW, "Wissenschaftlich-technische-Werkstatten GmbH", Weilheim, (Germany)). The same operating instructions were followed for the measurement of BOD as supplied by the manufacturer.

The spectral analysis was carried out using UV–vis spectro-photometer (LABINDIA, Model No. T60-U) in the wavelength range from 200 to 800 nm. The organic pollutants present in the real pharmaceutical wastewater before and after the treatment process were analyzed through GC–MS (Gas chromatography–Mass spectrometry). The analysis was carried out on GC (45 × –GC, Bruker (U.S.A)) coupled

with a mass detector (MS-SCION-45P, Bruker (U.S.A)) with silica capillary column (Length: 30 m, Diameter: 0.25 mm) coated with a 5% diphenyl and 95% Dimethyl Polysiloxane. The injector temperature was adjusted at 300 °C. Helium was utilized as a carrier gas at a flow rate of 1.0 mLmin⁻¹. The temperatures relating to the inlet as well as ion source were 250 and 280 °C, respectively. The sample injection volume was 1.0 µL.

3. Results and discussion

3.1. Coagulation-flocculation

Before directly proceeding into the photocatalytic treatment of real pharmaceutical effluent, coagulation-flocculation studies were carried out to reduce the turbidity of solution so that photocatalytic treatment can be applied effectively. The coagulation was conducted at natural pH of effluent i.e. pH = 5.1 using FeCl₃ as a coagulating agent. This particular pH i.e. 5.1 was in the vicinity of optimized pH values (i.e. 5.5–6) reported in literature [21,22] in context to coagulation studies. Thus, pH of effluent was not varied to conduct the coagulation studies.

The influence of coagulant dose on the reduction in COD was investigated at natural pH of effluent by varying the concentration of FeCl₃ from 100 to 1000 mgL⁻¹. The COD of effluent decreased from 4800 to 3680 mgL⁻¹ with an increase in the concentration of coagulant up to 200 mgL⁻¹. Beyond 200 mgL⁻¹, COD either became constant or started increasing as shown in Fig. S2 (Supplementary information). Thus, 200 mgL⁻¹ of FeCl₃ was selected as an optimum coagulant concentration for the present study. At this optimized dose of coagulant, an almost 90% reduction in turbidity of solution was observed (Table 1). Thus, coagulation served as a pre-treatment step in the present study before conducting any photo-treatment.

3.2. Prominence of dual effect

The pre-treated pharmaceutical effluent was subjected to different photo-treatment processes before actually conducting the dual effect experiments (coupling of photocatalysis and photo-Fenton). All experiments were initially performed in suspension mode at acidic conditions (pH = 3.0–3.5) under artificial UV-A irradiations with initial COD of 3680 mgL⁻¹ obtained after pre-treatment step. Dark studies (i.e. adsorption) were carried out separately in the presence of TiO₂ as well as FS/FA which revealed insignificant reduction in COD (8–10%) in each case. Photolytic studies in the presence of UV light revealed an almost 12–15% reduction in COD after 5 h. Similarly, UV + H₂O₂ also depicted an insignificant reduction (16–18%) in COD due to insufficient production of hydroxyl radicals. Thus, it was confirmed that adsorption and photolysis did not impart any significant contribution towards the

treatment of effluent.

TiO₂ photocatalysis using 1.0 gL⁻¹ of TiO₂ and 300 mgL⁻¹ of H₂O₂ revealed an almost 75% removal in COD with final value of COD to be 940 mgL⁻¹ after 5 h of UV irradiations. Photo-Fenton studies with 1.0 gL⁻¹ of FS/FA and 300 mgL⁻¹ of H₂O₂ reduced the concentration to around 1860 mgL⁻¹ i.e. ~50% removal of COD after 5 h. On the other hand, dual process by integrating photocatalysis and photo-Fenton took almost 4 h to achieve nearly 75% removal in COD as compared to 5 h in photocatalysis while it took almost 3 h to attain 50% reduction of COD as compared to 5 h via photo-Fenton. Thus, dual process drastically enhanced the degradation process resulting into an almost 91% removal in COD with final value of COD to be 320 mgL⁻¹ after 5 h of treatment (Fig. S3, Supplementary information). Therefore, the prominence of dual effect was established in suspension mode. The synergy of dual process over photo-Fenton was found to be 65% while over photocatalysis, it came out to be 39%. However, overall synergy of dual process over individual processes was approximately 5%. Now, this concept of dual process was further used in fixed-mode throughout the study for the treatment of real wastewater.

3.3. In-situ dual effect studies in fixed-mode

The main emphasis of the present investigation was to seek practical applications of in-situ dual effect concept in completely fixed-mode for the treatment of real pharmaceutical effluent. For this, Fe-TiO₂ composite beads were used instead of catalysts suspensions for the treatment of wastewater. These unique composite beads had the tendency to leach out iron species in solution under acidic conditions thus participating in photo-Fenton reaction along with TiO₂ photocatalysis. The in-situ dual process using Fe-TiO₂ composite beads was optimized through response surface methodology (RSM) to obtain the best operating conditions for the effective treatment of real wastewater. All details of statistical analysis have been provided in text S2 (Supplementary information). All experiments were carried out under acidic conditions i.e. pH = 3.5.

3.3.1. Parametric optimization

The relationship between output (COD, nitrite and nitrate ions concentrations) and the operating parameters (catalyst dose (number of beads), oxidant dose (H₂O₂) and treatment time) is shown in response surface plots (Fig. 1). The influence of catalyst dose (expressed as % area of reactor bed covered with beads) and dose of H₂O₂ on the COD reduction keeping time to be constant at 6 h can be interpreted from the contour graph (Fig. 1a). It was observed that value of COD decreased with an increase in the concentration of H₂O₂ from 150 to 1200 mgL⁻¹ due to the increase in the production of OH radicals. In the present study, OH radicals were not produced from a single process but through combination of three different processes i.e. photocatalysis, photo-Fenton and iron-oxide catalysis (as discussed in previous sections). From the analysis (Fig. 1a), it can be concluded that with increase in the number of composite beads (catalyst dose) up to 100% and H₂O₂ dose (1200 mgL⁻¹), % removal of COD increased. Significant reduction in COD was attributed to the leached iron species promoting photo-Fenton reaction along with the intact layer of TiO₂ simultaneously, contributing to photocatalysis. Moreover, exposed active sites of catalyst were maximum and were freely available for effective binding with the pollutant when entire bottom surface area of the batch reactor was covered with 100% beads thus resulting into the maximum removal of COD. With further increase in the number of composite beads, no further reduction in COD was observed. Actually, beads were overlapping one above the other thus, reducing the exposed surface area of the immobilized catalyst and preventing the effective binding of pollutant with the catalyst. Thus, it was observed that maximum COD removal was observed with number of beads covering nearly 100% of the reactor bed area with H₂O₂ dosage of ~1200 mgL⁻¹. Furthermore, it was observed that value COD continued to decrease with increase in the

Table 1
Characterization of effluent before and after the treatment process.

Parameter	Before treatment	After Coagulation	After treatment (In-situ dual process)
COD (mgL ⁻¹)	4800	3680	400
BOD (mgL ⁻¹)	830	Not measured	320
BOD/COD	0.172	n/a	0.8
Total Dissolved solids (TDS) (mgL ⁻¹)	1320	1180	880
Total Suspended solids (TSS) (mgL ⁻¹)	620	130	55
Nitrate (mgL ⁻¹)	20	Not measured	3.6
Nitrite (µg ⁻¹)	125	Not measured	540
Chloride (mgL ⁻¹)	25	Not measured	120
Fluoride (mgL ⁻¹)	0.3	Not measured	—
Sulfate (mgL ⁻¹)	526	Not measured	284
Turbidity (NTU)	742	70	35
pH	5.07	Not measured	4.88

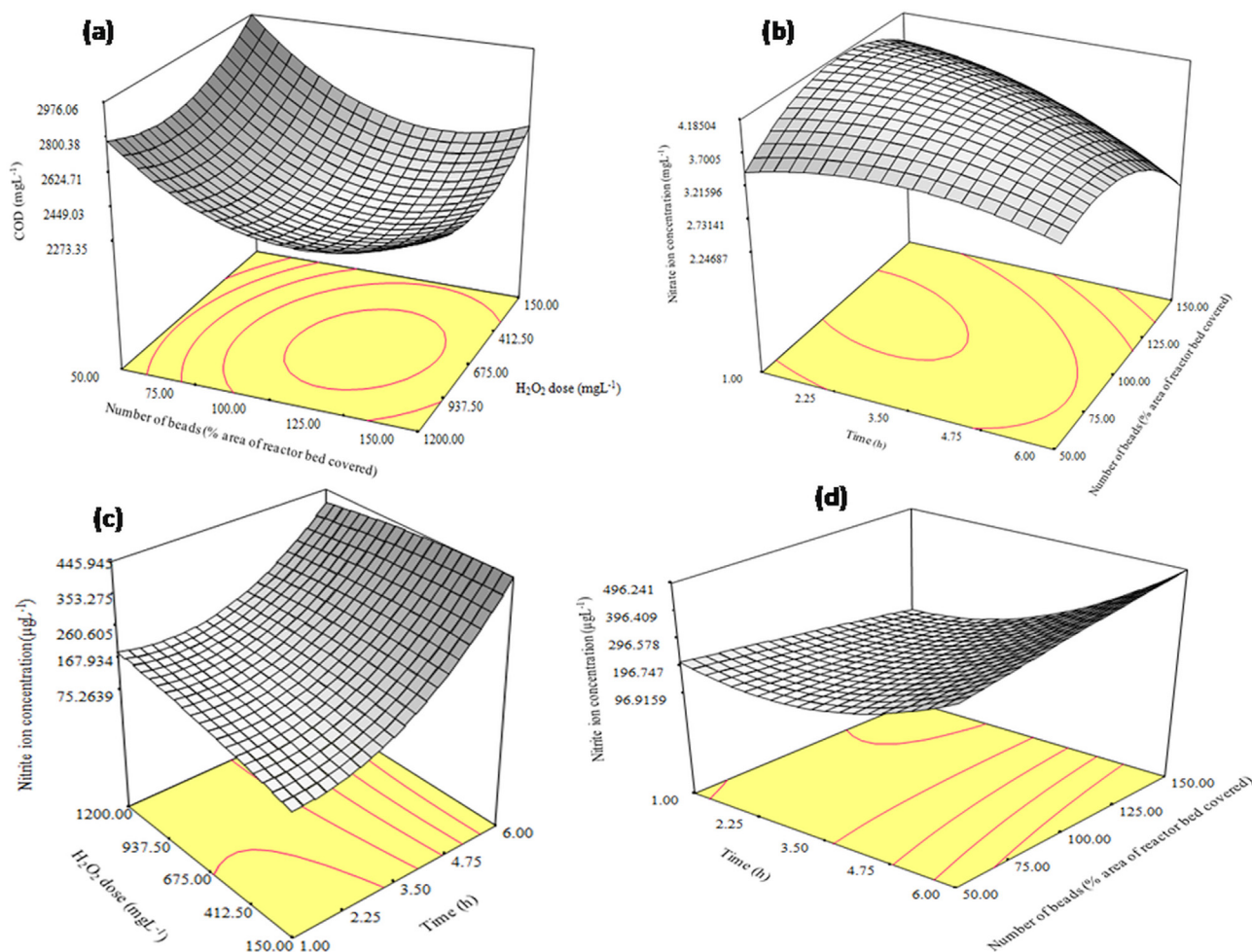


Fig. 1. 3-D response graphs for the treatment of effluent (a) COD vs number of beads and H_2O_2 , (b) Nitrate ion concentration vs number of beads and time, (c) Nitrite ion concentration vs H_2O_2 and time and (d) Nitrite ion concentration vs time and number of beads.

treatment time from 1 to 6 h. No further reduction in COD was attained when treatment time was extended beyond 6 h.

Similarly, the influence of catalyst dose (expressed as % area of reactor bed covered with beads) and treatment time on the concentration of nitrate ions keeping H_2O_2 dose to be constant (1200 mgL^{-1}) can be visualized from Fig. 1b. The results indicated that nitrate ions production was found to be maximum during the initial 1 h of treatment process. Thereafter, concentration of nitrate ions followed a declining trend with the probability of transformation of nitrate ions into nitrite ions. Fig. 1c demonstrates the effect of H_2O_2 dose and treatment time keeping catalyst dose to be constant (beads covering 100% of reactor bed area) on the concentration of nitrite ions. The influence of H_2O_2 on nitrite ion production was observed to be same as in case of COD removal. The concentration of nitrite ions followed an increasing trend throughout the reaction. Furthermore, it was observed that nitrite ions production reached to a maximum value with number of beads covering the reactor bed area in the range from 100 to 110% (Fig. 1d). With further increase in the number of beads, production of nitrite ions decreased due to the decrease in process efficiency. Maximum concentration of nitrite ions was produced at the end of 6 h.

Thus, generation of anions (nitrite and nitrate) along with significant reduction in COD clearly indicated the breakdown as well as mineralization of organic pollutants present in pharmaceutical effluent.

3.3.2. Confirmation of in-situ dual effect at optimized conditions

The optimized conditions obtained through RSM were time = 6 h, H_2O_2 dose = 1155 mgL^{-1} and catalyst dose equivalent to 102% area of

reactor bed covered with Fe-TiO₂ composite beads. The production of hydroxyl radicals using the optimized number of composite beads at an optimum dose of H_2O_2 was also confirmed through fluorescence spectrometric detection as shown in Fig. S4 (Supplementary information). The precedence of in-situ dual effect was confirmed again in fixed-mode at these optimized conditions by carrying out the treatment of effluent separately through photocatalysis as well as photo-Fenton. Expectedly, in-situ dual process was found to be the most efficient treatment method among different processes as maximum reduction in COD (~90%) was achieved via in-situ dual process. On the other side, an almost 75% and 55% reduction in COD was achieved through photocatalysis and photo-Fenton respectively after 6 h of treatment. In case of in-situ dual process, it took almost 4.5 h to achieve 75% COD reduction of effluent as compared to 6 h with photocatalysis whereas it took almost 3 h to achieve 55% COD reduction as compared to 6 h with photo-Fenton. Thus, the efficiency of treatment process in terms of COD reduction after 6 h of treatment time was observed in the successive trend: in-situ dual process (89.1%) > photocatalysis (74.5%) > photo-Fenton (54.8%) as depicted in Fig. 2. It was observed that when the reaction was extended further beyond 6 h, the value of COD became almost constant i.e. no further reduction in COD occurred. The concentration of leached iron species during the course of in-situ dual process was estimated and listed in Table S3 (Supplementary information). To check if any heavy metals were also eluted from FS and FA along with iron species, the treated solution was characterized through AAS. From the results, it was concluded that no such heavy metal was eluted from FS and FA as shown in Table S4 (Supplementary

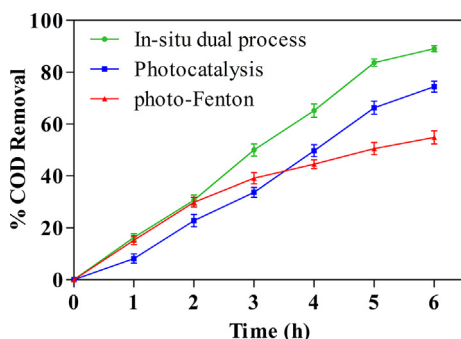


Fig. 2. Comparison of different processes for the treatment of effluent at optimized conditions.

information).

Now after getting significant reduction in COD, emphasis would be on the checking of biodegradability of wastewater so that the established dual effect could be successfully used as a pre-treatment step prior to biological treatment. In the present study, even though the maximum COD reduction occurred after 6 h of in-situ dual process, the reaction could also be stopped even after 5 h of treatment based on its BOD_5/COD ratio which became 0.71 after 5 h of treatment whereas it was 0.8 after 6 h of treatment. On the other hand, BOD_5/COD ratio remained below 0.5 in case of photocatalysis and photo-Fenton even after 6 h of treatment. The characterization of effluent before and after the treatment process (in-situ dual process) has been shown in Table 1.

Although photocatalysis depicted better COD removal efficiency in contrast to photo-Fenton, better decolorization efficiency was observed in case of photo-Fenton process as clearly visualized from Fig. S5 (Supplementary information). However, best decolorization efficiency was observed in case of in-situ dual process. Therefore, it can be further hypothesized that photo-Fenton was predominant during the early stages of in-situ dual process as it contributed mainly towards the decolorization of wastewater besides generating hydroxyl radicals. Hence, it can be proposed that after removal of color from the solution, TiO_2 photocatalysis became more effective and prominent due to the efficient penetration of light in the solution. Thus, in-situ dual process proved to be the most efficient process in each respect i.e. in terms of COD removal, generation of anions as well as decolorization of sample. This is for the first time when this novel concept of in-situ dual process especially in fixed-mode has been discussed in detail for the treatment of real effluent.

3.4. Practical feasibility of in-situ dual effect under natural solar irradiations

Ultimately, the feasibility of any water treatment technology at field-scale depends upon its efficiency under natural solar irradiations instead of artificial sources of light. In this view, scale-up studies using in-situ dual process were conducted under natural solar irradiations to check the practical viability of technique. The optimized parameters from the above lab-scale trails were used to execute the scale-up studies under natural solar irradiations.

The scale-up trails using in-situ dual process for the treatment of real wastewater were executed in a pilot-scale solar once-through cascade reactor system (comprising of six packed-bed reactors connected in series) with total volume handling of 5 L. The reactor was operated at a fixed flow rate of 0.05 L min^{-1} (having a space time of 12 min for each reactor) with addition of optimized dose of H_2O_2 i.e. 1155 mg L^{-1} and catalyst dose equivalent to 102% area of each reactor bed covered with $Fe-TiO_2$ composite beads. The flow rate i.e. 0.05 L min^{-1} was chosen based on the studies conducted previously in detail for the proper optimization of this particular reactor. This reactor system using $Fe-TiO_2$ composite beads incorporating in-situ dual effect gave promising results

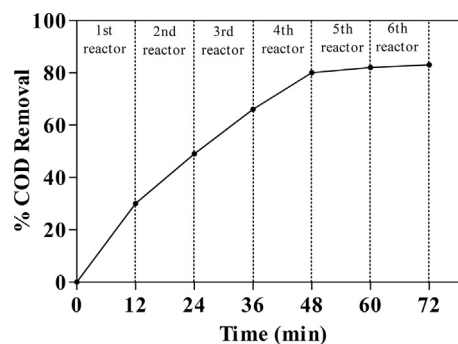


Fig. 3. Treatment of effluent at pilot-scale in a once-through cascade reactor.

in context to the treatment of effluent. The reduction in COD was observed to be rapid in case of this once-through reactor system. Actually, the solution after retaining for almost 12 min in a reactor came into contact with fresh batch of composite beads in the successive reactor. All active sites of catalyst were freely available to make contact with the pollutant in case of fresh batch of composite beads which intensified the process efficiency. While in case of lab-scale batch reactor, the solution remained in contact with the same composite beads during the whole reaction period with a possibility of blocking of some of the active sites of catalyst during the reaction. In the present case, maximum reduction in COD ($\sim 80\%$) was observed at the end of 4th reactor in a cascade reactor system (Fig. 3). Thereafter, COD value became almost constant without any significant reduction in its value. It took almost 100–120 min to pass the total operational volume of 5 L of wastewater through the reactor.

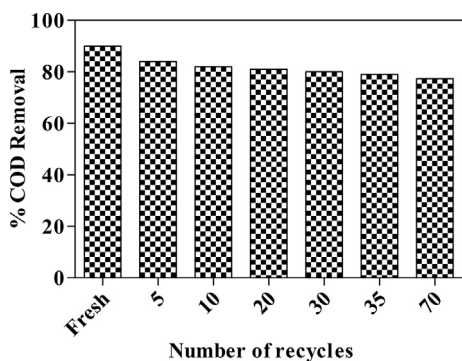
The initial reactors mainly helped in the reduction of turbidity and color of the real wastewater due to the predominance of photo-Fenton in the dual process. The efficacy of subsequent cascade reactors became more prominent towards the reduction of COD of wastewater. Moreover, simultaneous occurrence of both effects within the same system accelerate the degradation process in subsequent cascades which is prominent in our results as 5 L of solution of real pharmaceutical waste was treated in less than 120 min.

Thus, promising results even at pilot-scale for the effective treatment of real pharmaceutical effluent under natural solar irradiations further confirmed the field-scale applications of fixed-bed in-situ dual process using $Fe-TiO_2$ composite beads. None of the reported studies in literature has ever reported such applications of fixed-bed processes especially in context to real wastewater from industries.

3.5. Extended recyclability efficiency of $Fe-TiO_2$ composite beads

The other novel finding of the present research work was the outstanding efficacy of $Fe-TiO_2$ composite beads in terms of its prolonged recyclability besides its extended photo-response efficiency. $Fe-TiO_2$ composite beads were successfully recycled for at-least 35 runs without depicting any significant reduction in their activity. The recyclability efficiency of $Fe-TiO_2$ composite beads was evaluated in terms of COD removal efficiency of effluent with subsequent recycling tests as shown in Fig. 4. There was almost 8–12% reduction in the removal of COD using the same composite beads for more than 35 runs. The stability and activity of immobilized catalyst along with the presence of iron even in recycled composite beads (35 recycles) was further confirmed through several characterization techniques as discussed in subsequent sections (Section 3.6).

To further rationalize our claim in context to the commercial applications of in-situ dual process, experiments related to effluent treatment were conducted with $Fe-TiO_2$ composite beads that were prepared almost 6 months ago and had been previously used for at-least 70 recycles (old composite beads). The efficacy of these old composite beads was also checked in terms of % COD removal of effluent at all

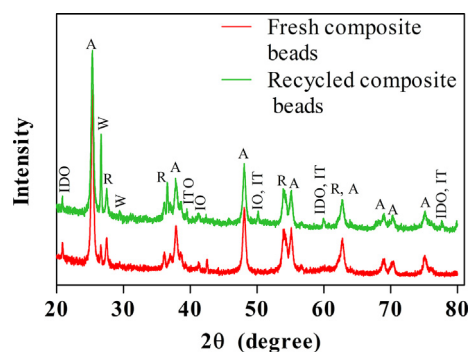
Fig. 4. Recyclability studies of Fe-TiO₂ composite beads.

optimized conditions (Fig. 4). Nearly 78% reduction in COD of effluent was attained after 6 h of treatment via in-situ dual process using these old composite beads. Significant amount of reduction in COD even after 70 recycles postulated that the studied technique can be successfully implemented at field-scale using these highly durable and economical Fe-TiO₂ composite beads. Till date, there have been no studies in literature reporting such high rate of catalyst recyclability especially in context to the treatment of real industrial effluent.

3.6. Characterization of Fe-TiO₂ composite beads

3.6.1. SEM/EDS analysis

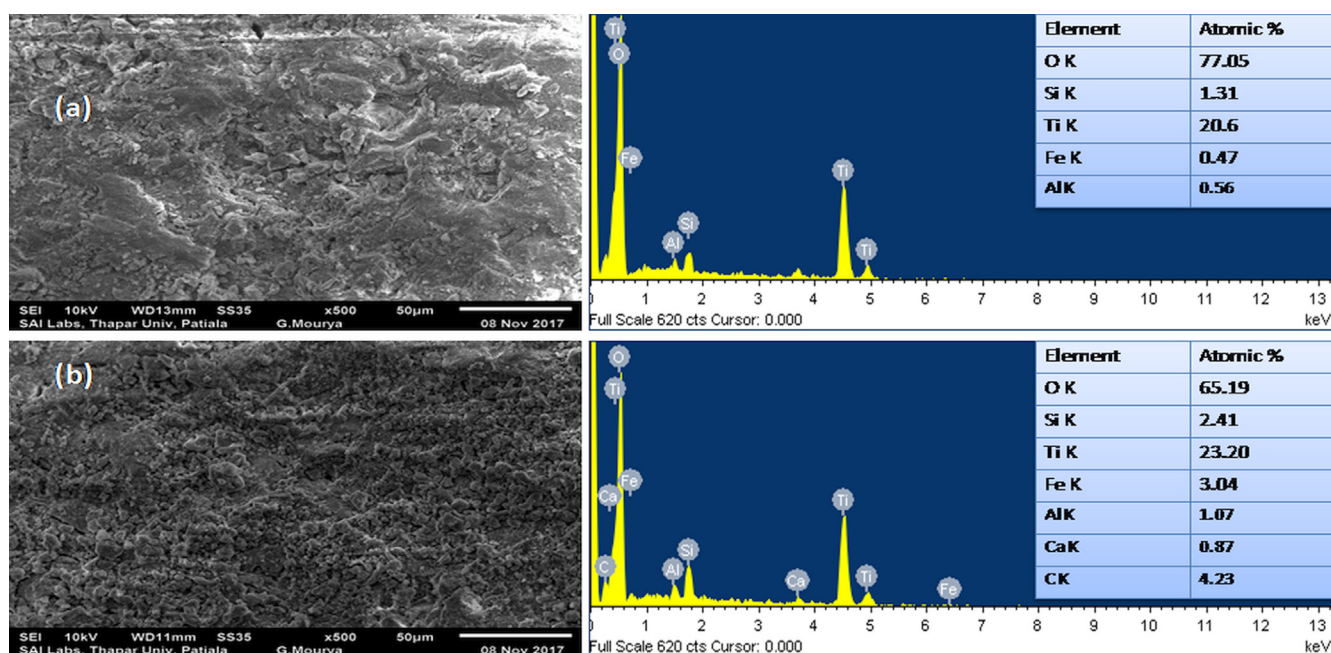
Fig. 5a demonstrates the SEM along with EDS images of fresh as well as recycled Fe-TiO₂ composite beads (35 recycles). The SEM images depicted almost similar morphology in each case thus suggesting that surface characteristics of composite beads did not change even after 35 recycles despite the elution of iron. Actually, the iron source i.e. FA/FS was embedded inside the beads whereas TiO₂ was coated over the surface. Iron was leaching out (in low concentration) systematically throughout the reaction as can be visualized from Table S3 (Supplementary information). Almost similar kind of surface characteristics even in recycled beads clearly indicates the stability and intactness of TiO₂ layer over the surface despite the leaching of iron. The loosely bound TiO₂ particles drained away during the initial cycles.

Fig. 5b. XRD patterns of fresh and recycled Fe-TiO₂ composite beads.

Thereafter TiO₂ remained intact to the surface stabilizing the surface characteristics. The existence of sharp peaks corresponding to 'Ti', 'O' and 'Fe' in EDS spectra in each case further authenticated the intactness of TiO₂ layer on the surface along with the existence of iron even in recycled composite beads. Thus, these results from SEM/EDS analysis clearly demonstrated that recycled composite beads could be effectively utilized for dual effect studies owing to the presence of TiO₂ and Fe even after 35 recycles.

3.6.2. XRD analysis

The X-ray diffraction patterns of fresh and recycled Fe-TiO₂ composite beads are shown in Fig. 5b. It was observed that biphasic nature of TiO₂-P25 was retained in each case as prominent peaks corresponding to anatase (marked as 'A') as well as rutile (marked as 'R') appeared in the diffraction pattern. In addition to this, some other diffraction peaks indicating the presence of iron in composite beads were observed in each case. These peaks confirmed the presence of few forms of iron oxides on the surface of composite beads. The forms of iron oxides detected in each case were iron (III) oxide, iron diiron (III) oxide, diiron (III) titanium oxide and iron titanium oxide. The role of these iron oxides in the in-situ dual process can be understood from Scheme S1 (Supplementary information). Hence, XRD studies further confirmed our claim of extended durability of Fe-TiO₂ composite beads.

Fig. 5a. SEM and EDS images of fresh as well as recycled Fe-TiO₂ composite beads.

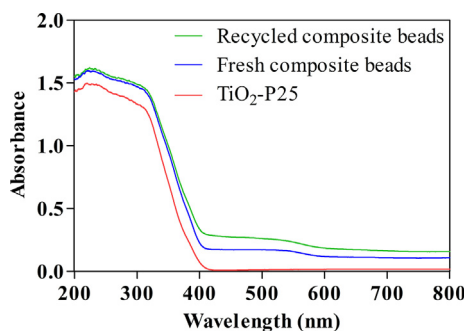


Fig. 5c. UV-visible DRS of $\text{TiO}_2\text{-P25}$, fresh Fe-TiO_2 composite beads and recycled Fe-TiO_2 composite beads.

3.6.3. DRS analysis

The UV-visible light absorption patterns of fresh and recycled Fe-TiO_2 composite beads are shown in Fig. 5c. An almost similar light absorption patterns in each case depicted that the activity of immobilized catalyst was retained even after 35 recycles thereby highlighting the efficiency of Fe-TiO_2 composite beads.

Moreover, the band gap energy of Fe-TiO_2 composite beads was also calculated in contrast to $\text{TiO}_2\text{-P25}$ using the following equation:

$$E_g = h\nu = \frac{hc}{\lambda} \quad (5)$$

where, E_g : the band gap energy in eV, c : speed of light ($3 \times 10^8 \text{ ms}^{-1}$), h : Planck's constant ($6.62607004 \times 10^{-34} \text{ m}^2 \text{ kgs}^{-1}$) and λ : absorption wavelength (m).

The band gap energies (E_g) calculated for fresh and recycled Fe-TiO_2 composites were nearly same i.e. 2.92 eV and 2.87 eV while band gap energy (E_g) in case of $\text{TiO}_2\text{-P25}$ was observed to be 3.1 eV. Therefore, the band gap energy was observed to be significantly lower in case of composite beads as compared to $\text{TiO}_2\text{-P25}$ which might be due to the existence of iron in composite beads. Thus, it leads to a proposition that apart from extended durability efficiency, Fe-TiO_2 composite beads also exhibited high photo-response efficiency thereby increasing their light absorption capacity as compared to conventional $\text{TiO}_2\text{-P25}$.

3.7. Identification of intermediates or by-products

3.7.1. UV-spectral analysis

Fig. 6a depicts the change in absorption spectra before and after the treatment of real pharmaceutical effluent via in-situ dual process using highly efficient and durable Fe-TiO_2 composite beads at all optimized conditions. The absorption spectra were obtained by carrying out the scan in the wavelength ranging from 190 to 800 nm. Many prominent peaks were present especially in the UV region in case of untreated effluent sample which got almost disappeared after undergoing treatment for 6 h through in-situ dual process. The disappearance of these

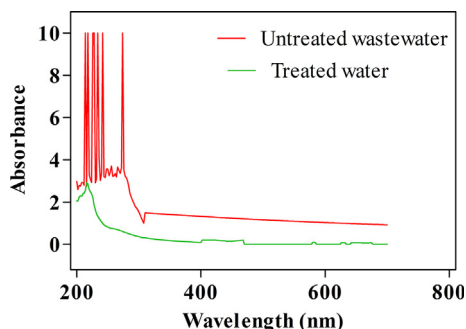


Fig. 6a. UV-spectral analysis of treated and untreated effluent.

peaks further indicated the effectiveness of in-situ dual process towards the treatment of industrial wastewater.

3.7.2. GC-MS analysis

The organic pollutants present in the effluent before and after the treatment process (in-situ dual process) were identified through GC-MS analysis as listed in Tables 2 and 3 respectively. The GC and m/z spectral data have been provided in Fig. S6 (Supplementary information). The untreated effluent mainly comprised of precursors (meant for the synthesis of mainly drugs, antibiotics or anti-inflammatory agents) and chemicals used for encapsulation. Few drugs including ibuprofen and butibufen intended for various disorders were also identified in the untreated sample. These identified organics were mostly hazardous and were mainly toxic to aquatic life as well as humans. After the treatment process, most of these identified products were eliminated from the solution. The treated solution consisted of chemicals intended for encapsulation in major proportions while few other compounds were also identified in minor proportions. However, these detected organics in treated effluent were non-toxic as compared to that of untreated solution (as confirmed through toxicity analysis). It could be therefore proposed that most of the organic pollutants present in raw effluent were mineralized into anions after undergoing treatment through in-situ dual process. Based on this analysis, a tentative mechanism for the destruction of organic pollutants has also been proposed as shown in Fig. 6b.

3.8. Toxicity analysis

To check the quality of treated effluent via in-situ dual process using Fe-TiO_2 composite, toxicity analysis was performed through agar well diffusion assay (Kirby-Bauer test) against *E. coli* taking untreated effluent as control. Concisely, 0.5 cm well was punched in Muller Hinton agar (MHA) plates using a sterile cork borer. Subsequently, approximately 30 μL of samples i.e. control, coagulated along with treated samples at different time intervals i.e. 1 h, 3 h, 5 h and 6 h were poured in well of different plates and were allowed to diffuse at 37 °C for about 20 min. The plates were swabbed with culture of *E. coli*. Thereafter, plates were kept in an incubator at a temperature of 37 °C for overnight. The cytotoxic activity of the samples was analyzed through the occurrence of zone of inhibition around the well. The biggest zone of inhibition was observed in case of control (untreated effluent sample). The size of zone was observed to follow a declining trend during the treatment process. The zone finally disappeared after 5 h of treatment thus indicating the non-toxicity of treated sample. The decreasing size of zone during treatment was in a complete agreement with the decolorization trend of effluent at the same time as shown in Fig. 7. It could be proposed color of the sample was directly proportional to its toxicity behavior.

In addition to the cyto-toxicity analysis, acute toxicity of the treated effluent (after 6 h of treatment) via in-situ dual process was also assessed through bio-assay method (acceptable by Central Pollution Control Board, CPCB) which is based upon the toxicity factor. Toxicity factor is actually the minimum amount of dilution of sample required for achieving no mortality for the zebra fish. In the present investigation, 100% survival of fish was attained after 96 h of bio-assay test (analysis report has been provided separately in Supplementary file). It can be therefore deduced that the treated pharmaceutical effluent via in-situ dual process was completely non-toxic in each respect. Thus, in-situ dual process using highly durable and efficient Fe-TiO_2 composite beads can be effectively used for field-scale applications.

3.9. Cost analysis

Cost analysis is considered to be one of the most significant factors in case of wastewater treatment. The major hurdle in the implementation of AOPs at large scale has always been the overall high

Table 2

List of various compounds identified through GC–MS analysis in untreated pharmaceutical effluent.

S. No.	Compound	Retention time	Molecular mass	Molecular formula	Matching%	Remark
1.	Ibuprofen	27.51	206	C ₁₃ H ₁₈ O ₂	95.1	Non-steroidal anti-inflammatory drug
2.	(Z)-1-(2,4,6-trimethylphenyl)-3-methyl-1-butene	9.17/12	188	C ₁₄ H ₂₀	76.2	Precursor for the manufacture of various drugs related to nervous system disorders.
3.	Benzeneethanol	27.51	224	C ₁₆ H ₁₆ O	85.4	Antiseptic and disinfectant.
4.	4-isopropylphenylacetic acid	27.51	178	C ₁₁ H ₁₄ O ₂	79	Flavoring agent.
5.	Hexadecanoic acid	34.49	256	C ₁₆ H ₃₂ O ₂	95.3	Used to produce personal care products.
6.	Butibufen	34.49	220	C ₁₄ H ₂₀ O ₂	89.7	Anti-inflammatory agent.
7.	Tridecanoic acid	34.49	214	C ₁₃ H ₂₆ O ₂	94.5	Flavoring or fragrance agent
8.	Nonanoic acid	34.49	158	C ₉ H ₁₈ O ₂	93.4	Used in the preparation of plasticizers.
9.	Dodecanoic acid	34.49	200	C ₁₂ H ₂₄ O ₂	91.2	Precursor for the manufacture of various pharmaceuticals.
10.	Tetradecanoic acid	34.49	228	C ₁₄ H ₂₈ O ₂	91.1	Used to synthesize flavor and as an ingredient in personal care products.
11.	(+)-2-endo,3-endo-dimethylbornane	51.29	166	C ₁₂ H ₂₂	93.2	Used in reduction reactions during the synthesis of chemicals.
12.	Eicos-2-yne	51.29	278	C ₂₀ H ₃₈	92.3	Used for synthesis of drugs for respiratory, sexual or dermatological disorders.
13.	Neophytadiene	51.29	278	C ₂₀ H ₃₈	92.2	Flavoring agent.
14.	2-hydroxytetraacosanolide	51.29	382	C ₂₄ H ₄₆ O ₃	91.2	Essential oil, used in synthesis of chemicals
15.	Phytol	51.29	296	C ₂₀ H ₄₀ O	90	Precursor for the manufacture of synthetic forms of vitamin E and vitamin K
16.	9-Eicosyne	51.29	278	C ₂₀ H ₃₈	87.5	Used for synthesis of drugs for respiratory, sexual or dermatological disorders.
17.	Phytol acetate	52.96	338	C ₂₂ H ₄₂ O ₂	98.8	Flavoring or fragrance agent
18.	2-decen-1-ol	52.96	156	C ₁₀ H ₂₀ O	95.2	Flavoring or fragrance agent
19.	Trans-tetrahydroionone	52.96	196	C ₁₃ H ₂₄ O	95.1	Used for encapsulation
20.	Lavandulyl acetate	52.96	196	C ₁₂ H ₂₀ O ₂	94.1	Flavoring or fragrance agent
21.	Silane	56.98	486	C ₃₂ H ₅₈ OSi	63.8	Used for encapsulation
22.	1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-octasiloxane	59.54	578	C ₁₆ H ₅₀ O ₇ Si ₈	80.2	Used for encapsulation
23.	1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethylheptasiloxane	60.34	504	C ₁₄ H ₄₄ O ₆ Si ₇	76.2	Used for encapsulation
24.	6-acetoxy-2,6,10,10-tetramethyl-1-oxa-spiro(4.5)dec-3-ene	60.34	252	C ₁₅ H ₂₄ O ₃	74	Flavoring or fragrance agent

Table 3

List of various compounds identified through GC–MS analysis in treated pharmaceutical effluent through in-situ dual process.

S. No.	Compound	Retention time	Molecular mass	Molecular formula	Matching%	Remark
1.	1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-octasiloxane	48.68/59.30/58.76	578	C ₁₆ H ₅₀ O ₇ Si ₈	79.4	Used for encapsulation.
2.	1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethylheptasiloxane	48.68/59.30	504	C ₁₄ H ₄₄ O ₆ Si ₇	74.4	Used for encapsulation.
3.	(-)-(2R,9S,10S)-2,5,5,9-tetramethyl-trans-1-decalone	50.39	208	C ₁₆ H ₁₆ O	87.4	Used in synthesis of steroids.
4.	(2S,3S)-2,3-epoxy-1-hexanol	50.39	116	C ₆ H ₁₂ O ₂	83.6	Flavoring agent.
5.	Santalane	50.39	208	C ₁₅ H ₂₈	76.1	Precursor for manufacture of pharmaceutical
6.	1,3-bis(trimethylsilyl)benzene	53.02/55.96	222	C ₁₂ H ₂₂ Si ₂	70.4	Used for encapsulation.

cost of the process. In this regard, best efforts have been made in the present study to explore an economic solution for the treatment of industrial wastewater using AOPs. Thus to highlight the commercial viability of the presented in-situ dual process using highly durable and economic Fe-TiO₂ composite beads, overall treatment cost of the process at pilot-scale using cascade reactor has been evaluated. For the evaluation of cost, all expenses involving fabrication of reactor, synthesis of composite beads, oxidant used, electricity cost have been included as shown in Table S5 (Supplementary information). The overall cost of the treatment process came out to be 25.047 \$ which has been calculated for 70 runs. However, for single run (i.e. for the treatment of 5 L of wastewater), the cost came out to be 0.357 \$. This cost can be further reduced when same recycled beads would be employed for more cycles. The calculated cost clearly demonstrates the commercial viability of the technique.

4. Conclusions

For the first time, field-scale applications of novel in-situ dual process in fixed-mode have been presented in the present study for the treatment of non-biodegradable effluent from a real pharmaceutical industry. The combination of coagulation and in-situ dual process (using Fe-TiO₂ composite beads) efficiently removed the recalcitrant and toxic chemicals from real wastewater resulting into significant reduction in COD (83%) after 5 h of treatment at optimized conditions. The optimized conditions obtained through RSM for the treatment of real wastewater via in-situ dual process were time = 6 h, H₂O₂ dose = 1155 mgL⁻¹ and catalyst dose equivalent to 102% area of reactor bed covered with Fe-TiO₂ composite beads. The biodegradability index (BOD₅/COD) of wastewater reached to 0.7 from 0.172 at these optimized conditions. The treatment time was significantly reduced to less than 120 min when treatment of wastewater was carried out in a pilot-scale once through fixed-bed reactor using the same Fe-TiO₂

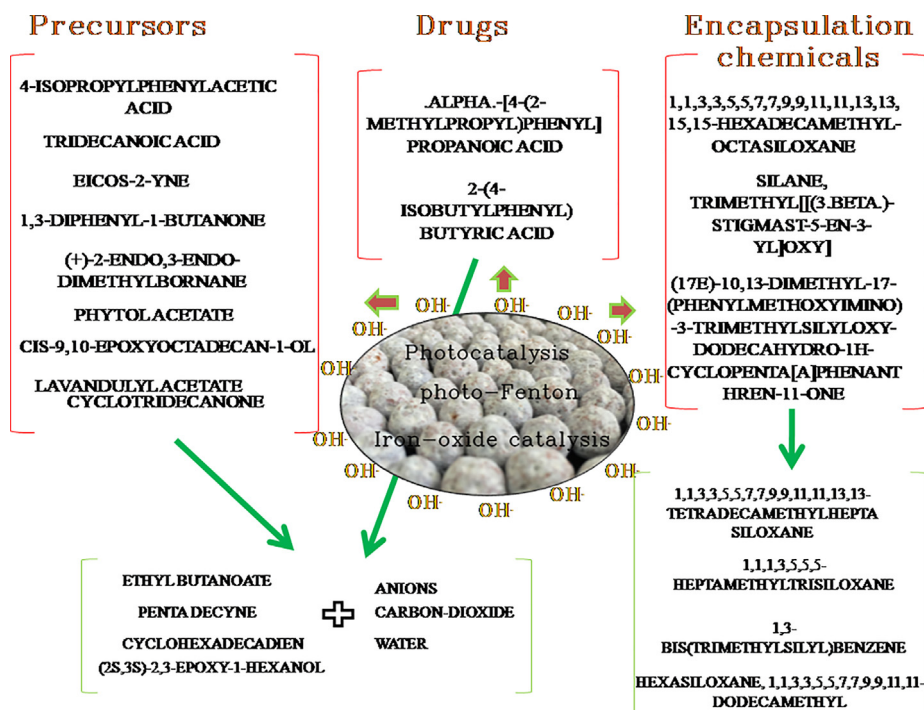


Fig. 6b. Tentative mechanism for the destruction of pollutants present in real pharmaceutical effluent through in-situ dual process.

composite beads under natural solar irradiations. The recalcitrant and toxic chemicals present in the raw effluent were either completely removed or transformed into non-toxic intermediates after the treatment process as confirmed through GC–MS analysis. The non-toxic nature of treated solution (confirmed through cyto-toxicity and acute toxicity analysis) further validated the efficacy of presented in-situ dual process towards the treatment of industrial effluents. The excellent recyclability efficiency of composite beads (> 70 recycles) as confirmed through SEM/EDS, DRS and XRD further envisaged the practical viability of technique. To the best of our knowledge, this is the first ever reported study till date towards the commercial scale applications of AOPs especially in fixed-mode using highly durable and inexpensive composite beads for the enhanced treatment of industrial wastewater.

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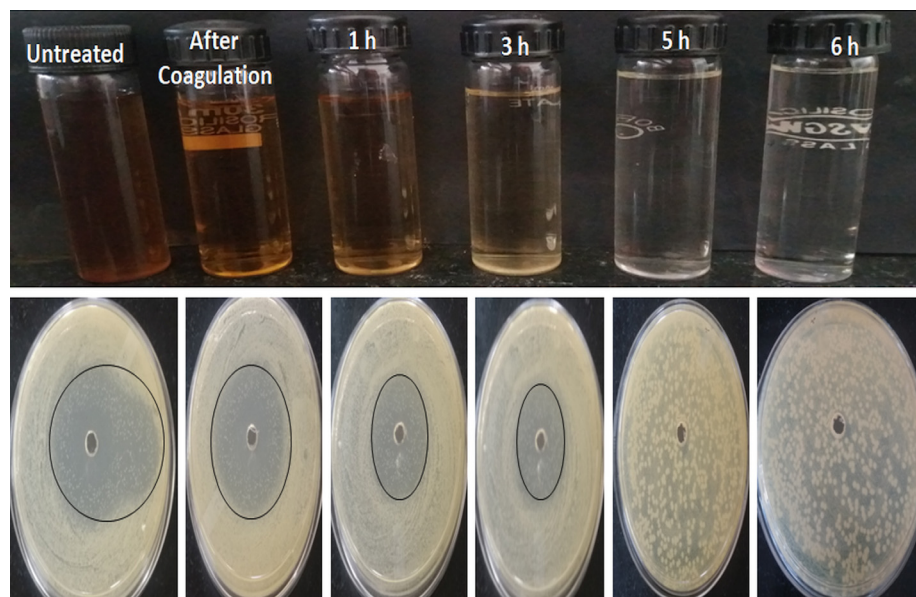


Fig. 7. Color of the samples along with their toxicity analysis at different time intervals during the treatment of effluent via in-situ dual process.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2018.05.140>.

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