A Novel concept of in-situ dual effect (photocatalysis and photo-Fenton) in fixed mode for the degradation of pharmaceutical compounds

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Masters of Sciences

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Submitted

By

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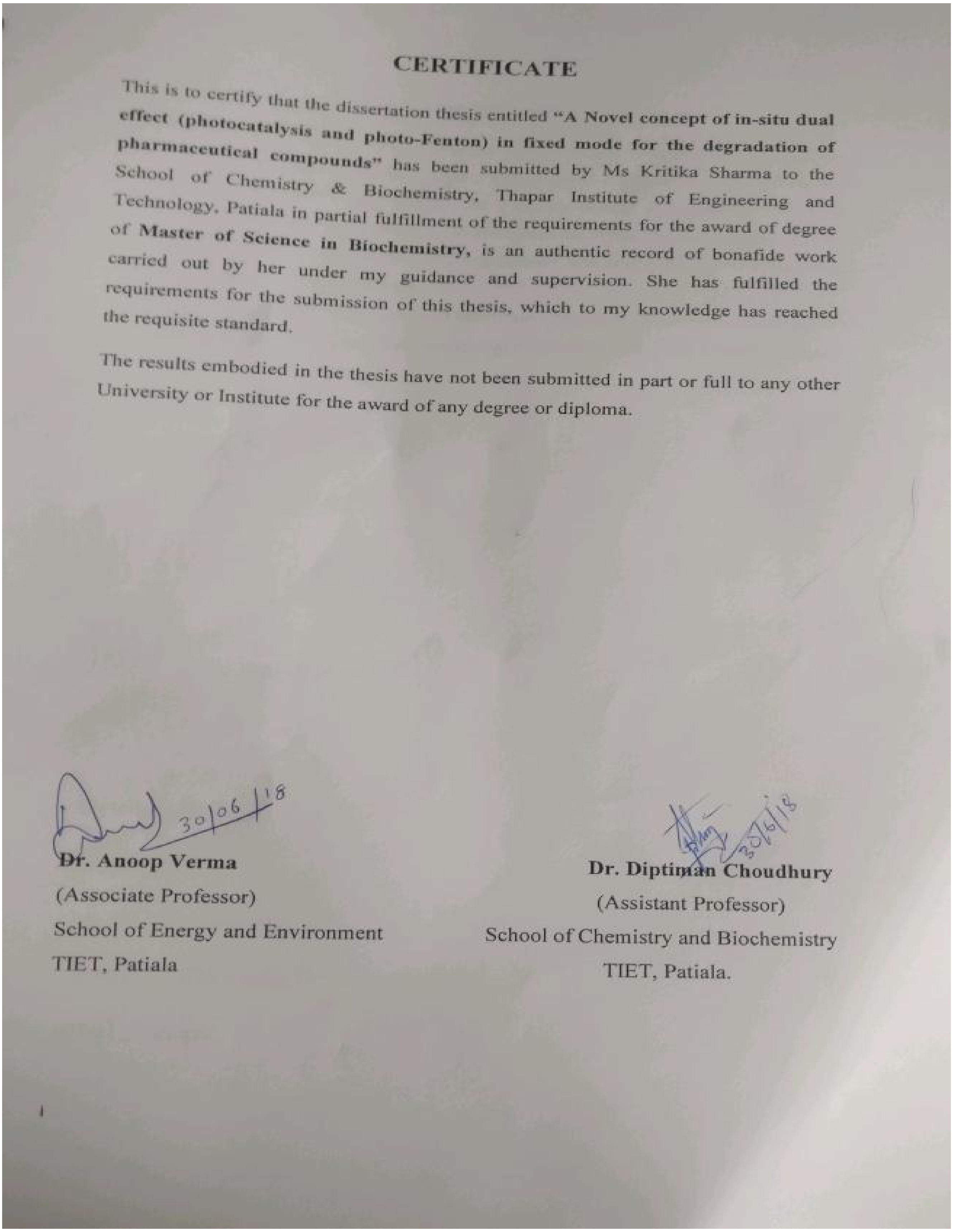

CERTIFICATE

This is to certify that the dissertation thesis entitled **"A Novel concept of in-situ dual effect (photocatalysis and photo-Fenton) in fixed mode for the degradation of pharmaceutical compounds"** has been submitted by Ms Kritika Sharma to the School of Chemistry & Biochemistry, Thapar Institute of Engineering and Technology, Patiala in partial fulfillment of the requirements for the award of degree of **Master of Science in Biochemistry,** is an authentic record of bonafide work carried out by her under my guidance and supervision. She has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results embodied in the thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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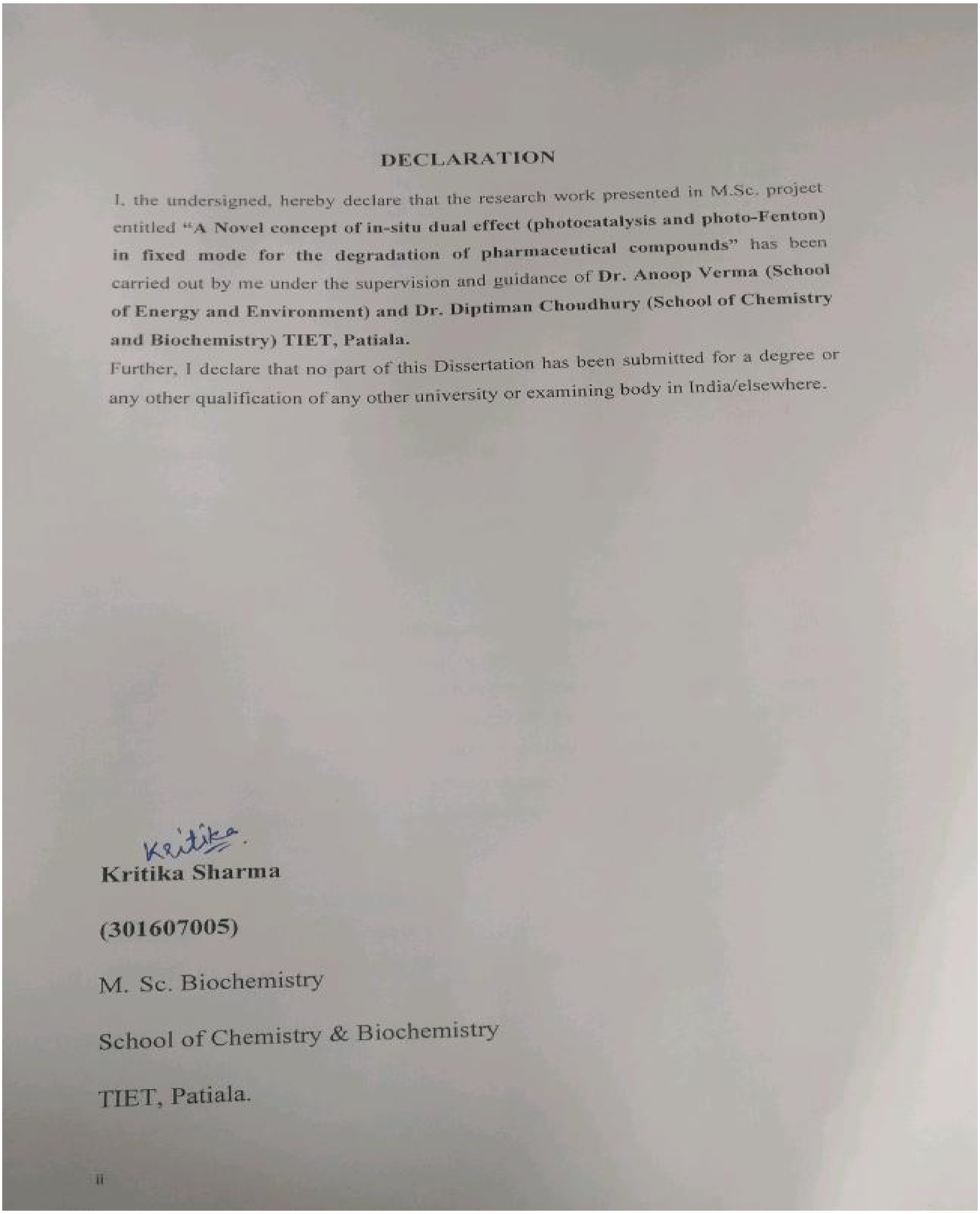

DECLARATION

I, the undersigned, hereby declare that the research work presented in M.Sc. project entitled **"A Novel concept of in-situ dual effect (photocatalysis and photo-Fenton) in fixed mode for the degradation of pharmaceutical compounds"** has been carried out by me under the supervision and guidance of **Dr. Anoop Verma (School of Energy and Environment) and Dr. Diptiman Choudhury (School of Chemistry and Biochemistry) TIET, Patiala.**

Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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I dedicate this thesis to my parents and my brother. I am really thankful for providing me the best education and inspiring me so that i can accomplish my dreams. And above all, I pay my regards to the Almighty for his blessings.

Kritika

Kritika Sharma

ABSTRACT

Novel composite clay beads combined with foundry sand (FS)/fly-ash (FA) were taken as the support materials for fixing the TiO_2 and have been subsequently used as iron source. The in-situ generation of iron in case of beads that are composed of either FS/FA or both induced dual effect (photocatalysis and photo-Fenton) in the same degradation unit thus produces synergistic effect for the reduction in the concentration of antibiotic Ofloxacin. Composite beads (FS/FA/TiO_2) showed relatively best results (92% degradation) at optimized conditions with 300mgL^{-1} H_2O_2 dose, 3.8 pH and 25Wm^{-2} UV intensity in the batch reactor experiments. The enhancements over the first order rate constant (k) were accomplished for the dual effect along with decrease in treatment time. Indeed, even a few overlay increments in ‘k' value was observed by utilizing novel Fe-TiO_2 complex for the ofloxacin reduction affirming in-situ double impact.

The stability of the catalyst after 40 recycles was observed through SEM/EDAX and FT-IR analysis which further justified its use in the field-scale applications. Further, mineralization of ofloxacin was validated by estimation of nitrate, nitrite and ammonia as its by products and along with generation of various anions i.e., total iron, ferric and ferrous ion determination, the intermediate products were also identified through GC–MS analysis.

With these results, subsequently the concept has been introduced for the treatment of real pharmaceutical effluent. The COD of the real effluent from a local pharmaceutical industry was reduced from 1076 mgL^{-1} to 279 mgL^{-1} using novel composite beads.

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Chapter 1

Introduction

General

Since many years, the biggest environmental havoc humans have been facing is the water pollution and its scarcity. Water bodies are being polluted by various means such as floods, landslides, soil erosion, volcanic eruptions and most importantly by human abuse which is not only deteriorating the aquatic life but human life as well. Many land and water animals have been killed by the scarcity of pure water for years. Many parts of the world do not have sufficient supply of fresh water for the survival of living being. Water is the most essential requirement of all domestic, commercial and industrial activities. The industrial operations constitutes primarily pesticides, pharmaceutical, textile and other chemical industries generate wastewater with many pharmaceutical drugs and their metabolites or intermediates. Humans have understood this issue, but neglect it by discarding waste directly into rivers, streams, oceans and lakes. These days the solid waste and water waste management is a major concern for healthy human existence. Traces of active pharmaceutical ingredients which are toxic to human and have lead to the microorganism resistance have also been reported in the water cycle and have increased concerns among regulators, water suppliers and the citizens regarding the potential risks to human health **(Deschamps et al., 2012)**. Antibiotics were as of late positioned as a noteworthy hazardous group on the grounds that of their high poisonous quality to bacteria and algae, even at small amounts. Such dangers incorporate expansion in the advent of lethal instances of hospital-borne diseases with such microorganicms that have gained resistance against anti-infection agents **(Hernando et al., 2006; Watkinson et al., 2009).**

Almost all of the surface water reserves and ground water are contaminated by microorganisms (pathogenic), suspended solids, biodegradable organics, heavy metals, domestic waste and industrial waste like cosmetics, dyes and pharmaceuticals. Many industries discard their remains into the rivers and streams directly without any prior treatment. **Kolpin et al.(2002)** executed the first nationwide reconnaissance of the presence of pharmaceuticals, hormones, and other organic wastewater contaminants (OWCs) in water samples from a network of 139 streams across 30 states during 1999 and 2000 in USA **(Andreozzi et al.,2003)** .The most common contaminants in the sewage water were anti-inflammatory drugs and analgesics **(Radjenovic et al.,2008)** acetaminophen (7.1–11.4 mg/L) and ibuprofen (14.6–31.3 mg/L), beta-blocker atenolol (0.84–2.8 mg/L),bezafibrate (1.9–29.8 mg/L) and lipid regulators gemfibrozil (2.0–5.9 mg/L),hypoglycaemic agent glibenclamide (0.12–15.9 mg/L), antibiotic ofloxacin (0.89–31.7 mg/L) and a diuretic hydrochlorothiazide (2.3–4.8 mg/L).

Pharmaceuticals that possess active pharmaceutical ingredients (APIs) which were basically designed to treat human ailments have now started causing negative impact on the environment due to their excessive use and releasing their toxic intermediate compounds directly into water bodies. An enormous amount of such pharmaceutical wastes can be found in ground water-table, surface water and in direct water supply for public and domestic use as well. Among various APIs, antibiotics, anti-inflammatory drugs, beta blockers (β-blockers), antidepressants, antiepileptics, hormones,etc. are some of the most important groups of drugs in creating the environment pollution **(Collins et al.,2007)**.There is a severe necessity to control their progressive concentration in the environment.

Traditional wastewater treatment technologies include preliminary, primary, secondary and tertiary treatments, based on the physical, chemical and biological processes **(Petra et al., 2015)**. The treatment of wastewater with the active sludge is the most popular biological process. A lot of pharmaceuticals, few poly-cyclic scents and some endocrine desrupting synthetics were investigated in a few waste water treatment plants (WWTPs) **(Clara et al., 2005)**. These treatment techniques consists AC (activated carbon) and membrane processes. Various sorts of layer and applications were surveyed for the elimination of APIs, including distinctive strategies of filtration, for example, electro dialysis inversion, ultra filtration, microfiltration, nano filtration, blends of various layers in arrangement, reverse osmosis and membrane bioreactors **(Bellona and Drewes, 2007)**. Activated carbon is fundamentally utilized as granular shape in fixed bed channels or in type of powdered feed **(Singh et al., 2011)**. In conventional channels, Granular activated carbon (GAC) utilized as a substitution of anthracite media, giving both filtration and adsorption. Somehow, transfer and carbon recovery are natural contemplations.

Hence, Physico-chemical treatment strategies are not favoured for the expulsion of such sort of medications because of expensive adsorbents, films cleaning, concoction coagulants and development of vast measure of sludge. The basic procedures related with hydrolysis, sewage treatment, biodegradation and sorption are worthless for the deterioration of numerous pharmaceuticals **(Gartiser etal., 2007)**. Hence, Conventional methods are not sufficient to eradicate inorganic industrial wastes so far. Numerous other techniques have been employed for industrial waste treatment like advanced oxidation process (AOP).

AOP has been widely used for the treatment of dyes, textiles, pharmaceuticals and other industrial effluents. AOPs include homogeneous (Ozonation, photolysis, photo-Fenton, UV/H_2O_2,) and heterogeneous (fixed-bed photocatalysis, dual effect) photocatalysis. Among these heterogeneous photocatalysis is much more effective as the catalyst is immobilized over the fixed-bed surface which helps in overcoming the limitation of homogeneous photocatalysis. Also in dual effect, along with the catalyst fixation, there is continuous leaching of iron which raises the degradation quotient many times.

In the current study, the dual effect degradation studies of pharmaceutical compound, ofloxacin have been discussed. This in-situ dual effect study is quite efficient than other advance oxidation processes in terms of cost efficiency, less time consuming and is applicable at industrial scale as well. The success of this process at industrial scale was determined by treating a real pharmaceutical effluent from a pharmaceutical industry.

Chapter 2

Pharmaceutical Industry: Wastewater Treatment

2.1 Overview

Indian pharmaceutical segment is assessed to represent 3.1 – 3.6% of the worldwide pharmaceutical industry in terms of value and 10% in terms of volume. It is required to develop to US$100 billion by 2025. The market is required to develop to US$ 55 billion by 2020, rising as the 6th biggest pharmaceutical market all around by total size.

The concern here arises is that in pharmaceutical and textile manufacturing industries, as the water streams through system, it carries chemicals and by-products along with it. Therefore, this wastewater requires prior treatment to remove bacteria, waste solids, regulated chemicals, oils and grease before its discharge into the environment.

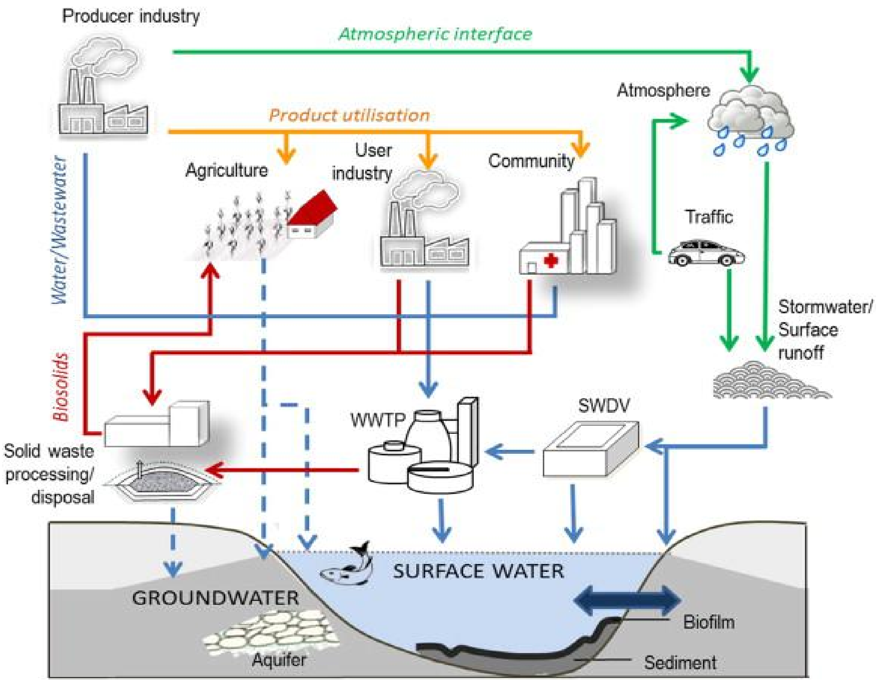


Figure2.1: Exposure pathways of various contaminants into the aquatic environment (WWTP: Wastewater treatment Plant; SWDV: Stormwater Detention Vault)(Source: Gerbersdorf et al.,2015)

In figure 2.1, it has been featured that the advancement in the sensitivity of the chemical testing and difficulties in testing conventions as well as strategies, and additionally the requirement for ATC (Anthropogenic Trace Compounds) pointer substances to empower cross-national legitimate observing schedule. Also, a pattern in ecotoxicology is depicted to advocate for a superior execution of haul tests, to refer the lethality on the population and biosphere and in addition on human-well being, and to adjust different test levels and endpoints. Moreover, the potential sources of ATCs and the flow evacuation proficiency of wastewater treatment plants (WWTPs) to show the best places and end systems have been examined. Knowledge gaps in confinement as well as transport of ATCs with their section in surface waters and groundwaters are additionally underscored in connection to their physical and chemical properties, biological interactions and non-living conditions keeping in mind the end goal to featured research requirements. At last, the significance and remaining difficulties of a proper ATC hazard assessment as this will significantly help with distinguishing the most important calls for activity, in choosing the most encouraging measures, and in assessing the achievement of executed administration techniques **(Gerbersdorf et al., 2015)**.

Furthermore, wastewater treatment plants are not much effective in complete degradation and removal of by-products formed after the conventional treatment processes of the wastewater.

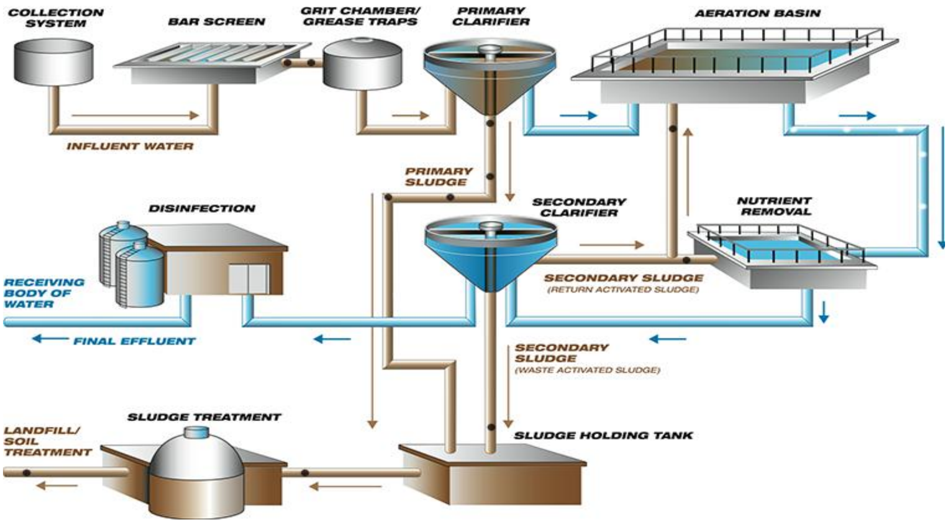


Figure 2.2: Pharmaceutical wastewater treatment plant (Source: Hach)

Most of the pharmaceutical substances are, by nature, hydrophilic and biologically active, all together that the human body can metabolize them effectively, and prevent from excreting out before their required action for the treatment of a disease. As discussed in figure 2.2, influent water upon entering the collection system will be discharged as a blend of metabolites, as unaltered substance, or conjugated with an inactivating compound appended to the particle **(Kanakaraju et al., 2014)**. When they enter a wastewater-treatment plant, pharmaceuticals are not more often than not totally mineralized. They are either incompletely held in the slop, or processed to a more hydrophilic yet at the same time constant shape and, along with this, go through the wastewater-treatment plant (WWTP) and wind up in the collecting water systems. Their expulsion in WWTPs is variable and relies upon the characteristics of the substance and conditions of the process (e.g. Sludge Retention time (SRT), Hydraulic retention time (HRT), temperature **(Clara et al., 2005;Vieno et al., 2005)**. Numerous pharmaceutically dynamic mixes (PhACs) are scarcely decreased and they are, in this manner, identified in WWTP effluents.

2.2. Application of Advance Treatment Technologies

When the conventional biological methods of organic compound degradation became inefficient, the researchers started exploiting the use of advance oxidation processes (AOPs). Advance oxidation process involves the generation of free hydroxyl radicals which basically account for the reduction of organic and inorganic compounds **(Esplugas et al., 2007)**. Hydroxyl radicals could be produced with the help of oxidants like ozone, hydrogen peroxide, oxygen, ultraviolet sunlight, catalysts (titanium dioxide, Zinc Oxide, Silicon dioxide etc). Electrooxidation and photocatalysis are two major methods in AOP. In electrooxidation techniques, various kind of electrodes are used with an electrolyte which causes the production of $OH^{\bullet}$ radicals and participate in the degradation process. While in photocatalysis, in the presence of light (UV/UV-Vis) and H_2O_2, hydroxyl radicals are generated.

AOPs generally involve three basic steps in the treatment. First, the production of hydroxyl radicals; secondly, attack of hydroxyl radicals on the organic compound converting it into small inorganic fragments and third is the mineralization of the compound.

The mechanism of hydroxyl radical production relies on various AOP techniques involves the homolytic cleavage of the O-O bond of H_2O_2 leads to generation of $2^{\cdot}OH$ radicals **(Audenaert et al., 2011)**. Various advance oxidation treatment processes have been given in the table 2.1 some of them have been consistently worked upon by many researchers **(Gultekin and Ince, 2007)** and some are recently cited and not much studied(dual effect)**(Verma et al., 2014).**

Table 2.1: AOT processes for water and wastewater treatment

Photochemical processes
Photocatalysis
Dual effect
UV/ H_2O_2 /O_3
Ozonation
Photolysis
Microwave
Photo-Fenton
Vacuum UV (VUV)
Sono photocatalysis
UV/Ultrasound

Source: Gultekin and Ince, 2007

2.2.1 Homogeneous photocatalysis

Ozonation (O_3) is the most widely recognized advance oxidation treatment as of now utilized in wastewater treatment in spite of the fact that it is more typical in the sterilization of drinking water. Ozone is for the mostly utilized in wastewater treatment to aid the mineralisation of natural compounds. Ozone has been appeared to proficiently debase natural aggravates that have activated aromatics **(Khetan et al., 2007)**, amines for example, phenols, alkyl aromatics and olefinic moieties **(Westerhoff et al., 2005)**. It has likewise been appeared to degrade antiepileptics (carbamazepine), anti-phlogisitcs (diclofenac), antibotics (ciprofloxacin) ,sedatives (diazepam) and oral contraceptives (17 Rethinylestradiol) **(Witte et al.,2009; McDowell et al.,2005; Lee et al.,2008;Huber et al.,2008).**

Mechanism for Ozone based AOP involves reaction between Ozone and a hydroxyl ion leads to the formation of H_2O_2 (in charged form) (as shown in equation 2.1-2.2). Then, a second Ozone molecule reacts with the HO_2^- to produce the ozonide radical (equation 2.2-2.4). This radical gives to ·OH upon protonation**(Benitez et al.,2002)**

$O_3 + HO^- \rightarrow HO_2^- + O_2$ (2.1)

$O_3 + HO_2^- \rightarrow HO_2\cdot + O_3^-\cdot$ (2.2)

$O_3^-\cdot + H^+ \rightarrow HO_3\cdot$ (2.3)

$HO_3\cdot \rightarrow \cdot OH + O_2$ (2.4)

The characteristic drawbacks of Ozonation includes, more cumbersome technology than UV disinfection, chlorination needs more efficient contacting systems and highly complex equipment. Ozone being reactive and corrosive in nature requires corrosion resistant materials (**Lee et al., 2008)**. It is extremely toxic and inflamatory if it comes in direct contact to the human body. Ozonation economically is not feasible as it cannot treat wastewater with large amounts of suspended solids, COD, BOD and TOC (**Huber et al., 2008)**.

In Photolysis process, UV light is likewise classified as photochemical degradation / homogeneous degradation / direct photolysis. The studies which utilize UV alongside different AOPs, UV alone is constantly inspected to decide its commitment to debasement **(Rivas et al., 2009)**. In the greater part of cases, it has been observed to be second rate compared to combinatory procedures in spite of the fact that this can be substrate dependant and furthermore relies upon the light source utilized e.g. UV/A, UV/C etc.**(Rivas et al.,2009; Haque et al.,2007; Yang et al.,2008).** Organic compound C when receives a photon from light it gets forms an excited state C* which further degrades the compound.

$C + h\nu \rightarrow C^* \rightarrow \text{Degradation products}$ (2.5)

$H_2O_2 + h\nu \rightarrow 2\ HO^\cdot$ (2.6)

Major drawbacks are absence of any residual effect, deposition of scales on the sleeves of lamps the lamps gradually reduces the transmittance.

In UV/H_2O_2, since**,** hydrogen peroxide is a poor oxidant for some natural pollutants so it cannot be employed as such. UV light below 400 nm must be utilized in order for hydrogen peroxide for effective photolysis. UV/H_2O_2 has been contemplated in the degradation of phenazone, ibuprofen, phenytoin diphenylhydramine, with elimination of < 40 % in all cases at generally higher amounts of H_2O_2 and low conce3ntrations of pharmaceuticals (5 μM) **(Yuan et al., 2009)**. A comparative study about with naproxen, carbamazepine and clofibric corrosive accomplished expulsion efficiencies between 20-50 % with medium pressure lights at 100mJ/cm^3 **(Pereira et al., 2007)** It would give the idea that disintegration of pharmaceuticals with this procedure is substrate-dependant, and it can be believed to be second rate when contrasted with different AOPs, for example, Ozonation **(Vogna et al., 2004)**.

In Fenton Process with Hydrogen Peroxide, ferrous salts are utilized along with hydrogen peroxide to produce $^{\bullet}OH$ radicals. The preferred standpoint here is that it is exceptionally powerful and just little centralizations of reagents are required. It has effectively reduced pharmaceutical compounds including Gemfibrozil (lipid-controller), Metronidazole (antimicrobial operator), Penicillin and numerous compounds **(Arslan-Alaton et al.,2004; Shemer et al.,2006; Molinari et al.,2007)**However, its productivity is reliably contrasted with the Photo-Fenton process which is more proficient once more, creating both a higher level of degradation and mineralization.

Photo-Fenton Process, photoactive iron (III) salts are incorporated along with the light. $FeCl_3$, $Fe(NO_3)_2$ and $FeSO_4.7H_2O$ are typical iron complexes that are being utilized. Various pharmaceuticals have been decomposed utilizing this procedure with extremely encouraging mineralisation productivity with dipyrone, diclofenac, amoxicillin, ofloxacin and gemfibrozil **(Ravina et al.,2002;Perez-Estrada et al.,2007;Bautitz et al.,2007;Arslan-Alaton et al., 2007; Molinari et al.,2007)**. This procedure has awesome potential with respect to sunlight based applications since the ferric-oxalate complex $[Fe(C_2O_4)_3]^{3-}$ permits more visible light prompted photocatalysis. In the dominant part of studies where sunlight based light has been brought under control, oxalate compounds are used. Likewise with the Fenton, significant obstructions exist to its application in full scale water treatment including, controlled pH to solubilise the iron salts , the cost of required oxidant (H_2O_2), and furthermore, for this situation, light is required **(Beltran-Heredia et al.,2001).** Along with these disadvantages, the photocatalyst can't be preserved. Despite what might be expected, little sums of iron salts (at times as low as 2 mgL^{-1}) can be utilized to accomplish the whole mineralization **(Perez-Estrada et al., 2007)**.

$$Fe_{aq}^{2+} + H_2O_2 \rightarrow \mathrm{Fe_{aq}^{3+}} + \mathrm{OH^-} + \mathrm{OH^{\cdot}} \qquad (2.7)$$

$$Fe_{aq}^{3+} + H_2O_2 + H_2O \rightarrow \mathrm{Fe_{aq}^{2+}} + \mathrm{H_3O^+} + \mathrm{HO_2^-} \qquad (2.8)$$

$$Fe_{aq}^{3+} + H_2O \overset{\mathrm{hv}}{\rightarrow} \mathrm{Fe_{aq}^{2+}} + \mathrm{H^+} + \mathrm{OH^{\cdot}} \qquad (2.9)$$

These examinations generally encounters issue in keeping up high concentrations of H_2O_2, the production of a high amount of anions in the treated wastewater and a lot of ferrous iron sludge**(Nidheesh, 2015).**

2.2.2 Heterogeneous Photocatalysis

The heterogeneous photocatalysis is a veritable process, which is used to oxidize the organic compounds in suspension. Complete mineralization of organic compounds to carbon dioxide, inorganic anions and water can be attained by photocatalytic process. The vital materials in the process of photocatalysis are the semiconductors in which titanium dioxide takes a role model among others **(Diebold et al., 2003)**. Even though titanium dioxide is a very good photocatalyst, it possesses a huge drawback, that is, its lesser activity in visible region. Pure titanium is active only in UV region of the solar spectrum based on its band gap energy(3.2eV for anatase). This rationally abandons the use of of sunlight as a source of energy since the sunlight constitutes around 5-8% of UV light.

Hydroxyl radical production mechanism for photocatalytic oxidation with TiO_2 involves, irradiation of the photocatalytic surface leads to an excited electron (e^-) and electron gap (h^+) (equation 2.10)while the water gets adsorbs onto the catalyst surface (equation 2.11-2.13) and the highly reactive electron gap will react with water**(Benitez et al.,2002)**

$$TiO_2 \overset{hv}{\rightarrow} e^- + h^+ \qquad (2.10)$$

$$TiO_2 + H_2O \rightarrow Ti\,OH^- + OH^{\cdot} \qquad (2.11)$$

$$Ti\,OH^- + h^+ \rightarrow Ti\,OH^{\cdot} \qquad (2.12)$$

$$TiO_2 + O_2 + e^- \rightarrow TiO_2 + O_2^- \qquad (2.13)$$

The most important semiconductor photocatalyst in water purification studies is TiO_2. Portions of other metal compounds, for example, ZnO, CdS and ZnS have been utilized as a part of relative examinations along with TiO_2. In some cases, these semiconductors are less dynamic under comparative conditions and at times can be less steady under illumination **(Murphy et al.,2014).**

The specific wavelengths that can be employed with TiO_2 photocatalysis have been mentioned in the table2.1.

Table 2.2: UV categories and corresponding energies in eV

Spectral Sub Category	Wavelength Range (nm)	E (in eV)
UV-A	400-350	3.09-3.93
UV-B	315-280	3.93-4.42
UV-C	280-100	4.42-12.39

At the point when a semiconducting metal oxide retains a photon of vitality equivalent to or higher than its bandgap (hʋ≥Eg), an electron is excited from its valence band to its conduction band, in a femto second timescale **(Hu and Wang**

2017). The photonic excitation abandons an exciton with a purge valence band opening and a filled conduction band (electron-hole pair). The fate of the isolated electron and opening can take after various pathways as depicted in the figure 2.3 **(Jing et al.,2017).** One probability is relocation of the electron and hole to the surface of the semiconductor. Whereas at the surface, the photocatalyst is capable to give the electron to an electron acceptor (A) which is normally molecular oxygen. Thus, a given species (D) can be oxidized by a valence band hole. These charge exchange forms are subject to the situation of the valence and the conduction band edges individually and furthermore on the redox capability of the adsorbed species **(Chen et al.,2017)**. As this response way brings about a delayed lifetime of the electron-hole pair, a higher amount of reactive oxygen species is delivered bringing about more productive degradation of contaminants in water. Recombination can happen either in the semiconductor mass or at the surface, thereby, releasing the heat (or light) and can hinder the photocatalytic action as the redox properties of the semiconductor are extinguished.

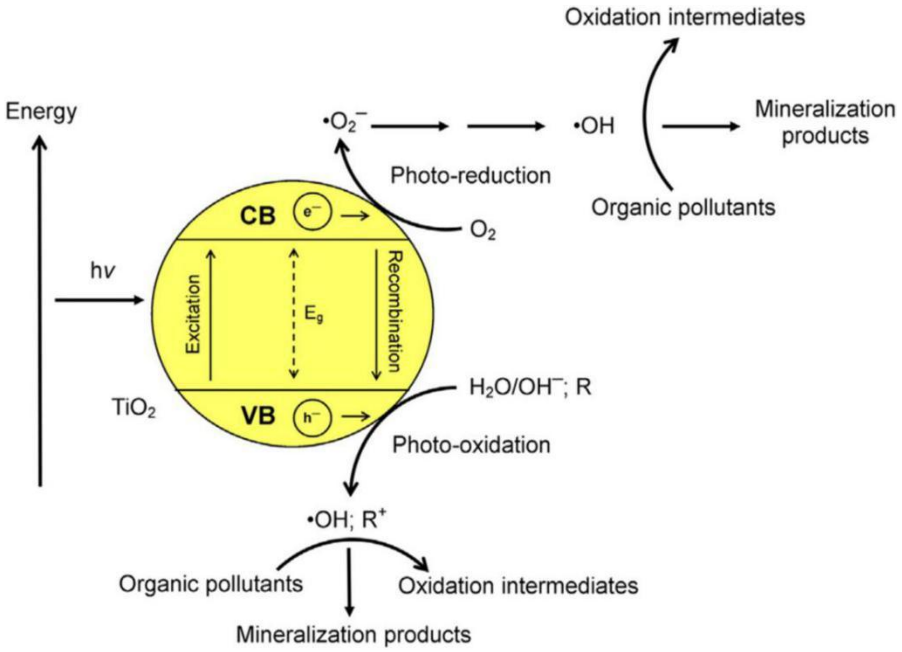


Figure 2.3: Heterogenous photocatalytic mechanism

(Source: Jing et al.,2017)

2.2.3 Dual effect of photocatalysis and photo-Fenton

The vast majority of the pilot-scale examinations revealed till-date are fundamentally established on the homogeneous photo-Fenton process **(Sirtori et al., 2009)**. Research in this specific zone have been continually engaged towards decreasing the treatment time with cost effectiveness of the process. In this investigation, novel idea of inducing dual impact (photocatalysis and photo-Fenton) proposed in context of decrease in treatment time for the objective contaminant. The dual technique has tremendous degradation effectiveness however not much applied well yet. The cost of technique and high amount of these synthetic compounds can be considerably decreased if the two distinct procedures (photo-Fenton and photocatalysis) are coupled together in one framework which would thus build the degradation rate also. The idea of dual impact has been recently proposed by few examinations for improving the degradation effectiveness **(Kumar et al., 2014; Bansal and Verma, 2017).**

The enhanced debasement effectiveness by the presenting dual impact can be ascribed to the creation of adequate measure of hydroxyl radicals produced at the same time by both continuous procedures(figure2.4). Additionally, iron decreases the coupling of electron-holes in TiO_2 and hence, upgrading its photocatalytic action **(Su et al., 2015).**

The capability of waste materials that could be reused and utilized as cost effective iron source in the process has been proposed which is a new process. In-situ dual impact has been as of late found which has prompt synergistic impact of both the procedures at once **(Bansal and Verma, 2017).** In any case, the investigation concentrates generally combined with strength of the catalyst examined upto many recycles.

Various examinations are centered around the scaling procedure utilizing TiO_2 particularly in suspension phase incorporates annular photoreactor **(Autin et al., 2013)**, fixed-bed photoreactor **(Borges et al., 2015)**, photocatalytic Taylor vortex reactor **(Jia et al., 2011)**, fluidized bed reactor **(Kang et al., 2011)**, covered fiber optic link reactor, falling film reactor **(Luna et al., 2014)**, thin film settled bed sloping plate reactor **(Khan et al., 2012)**, ridged plate reactor **(Passalía et al., 2011)**.

Albeit effective as far as accomplishing complete degradation still there are numerous operational and also plan suggestions those renders their field scale perception. Complicated mass exchange confinements, solidness of the support, additional time utilization and so on are the factors of concern for scale examinations. Far beyond most scale up contemplates have been operated in distribution mode **(Marugán et al., 2009; McCullagh et al., 2011)** subsequently offers greater treatment time for a given plot. Subsequently keeping in consideration the above factors and also field scale uses of this innovation, endeavors would be made to think about the in-situ dual technique. In this method, the batch will be dealt with in consistent mode so it could be encouraged to the organic reactor as well.The proposed idea would lead to decrease in treatment time by presenting in-situ dual method with reduction in mass exchange limitations.

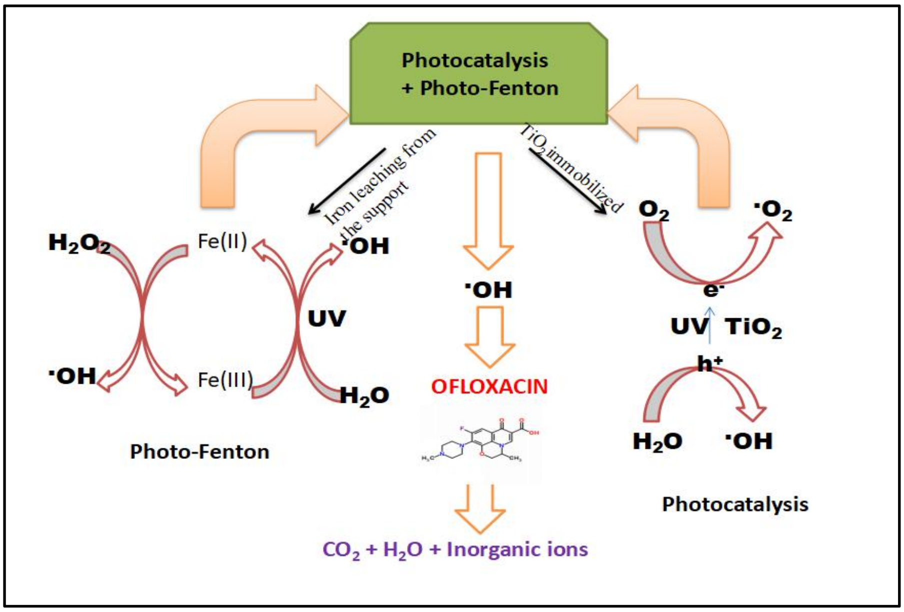


Figure 2.4 Ofloxacin reduction by dual effect.

Chapter 3

Literature review

3.1 Brief Overview

Pharmaceuticals constitute a large group of medicinal services items customized for human and veterinary utilization. Reports demonstrate that the generation and utilization market of pharmaceuticals has been consistently expanding as of late both internationally and in the European Union (EU). In 2007, for example, the manufacturing market of pharmaceuticals in the EU was roughly € 163 billion (at ex-production line costs) with a yearly normal development of 3.5% since 2003. Then again, the utilization market in the region expanded by yearly normal rate of 7.3% in the vicinity of 2003 and 2007 measuring, at ex-manufacturing plant costs, an expected € 141 billion out of 2007 (CBI, 2010). In spite of the advantages of pharmaceuticals to humanity, a developing concern about their potential unfavorable effects on biota **(Kostich and Lazorchak, 2008)** and human well being has risen because of their consistent contribution to nature **(Baran et al., 2011)**. Since pharmaceuticals are available at extremely low levels (ng/L–µg/L) in wastewater **(Daneshvar et al., 2010),** traditional STPs (Sewage Treatement Plants) are not sufficient to eradicate them **(Bendz et al., 2005; Cooper et al., 2008)**. In addition, some pharmaceutical branches being stubborn escape through STPs and sum up in surface water **(Sim et al., 2010)**, soil **(Martin et al., 2012)** and groundwater **(Fram and Belitz, 2011)**, For example, literature findings demonstrated the wide occurence of pharmaceuticals in surface waters few ng/L to g/L in nations like USA **(Gibs et al., 2013)**, Belgium **(Van De Steene et al., 2010),** Portugal **(Madureira et al., 2010)**, Germany **(Scheurer et al., 2012)** and Spain **(de Garcia et al., 2013).**

The primary sources of pharmaceuticals to STPs incorporates sewage from local areas (i.e. houses, private and public organizations, hotels, dormitories and so forth.), animal culturing, and sludge from hospitals and pharmaceutical ventures **(Kümmerer et al., 2009)** and are mainly from the discharge of unmetabolized buildups by means of urination and defecation **(Brown et al., 2006; Heberer et al, 2002).** Moreover, the bio-transformed metabolites of pharmaceuticals may hold the fundamental structure of their parent compound **(Ibanez et al., 2017).** Hence, they can show some type of organic action and may add up to the surroundings as general ecological hazard. This recommends in the assessment of natural hazard, the role of pharmaceutical metabolites to the general hazard ought to be considered since they can be available in significant amounts with respect to the parent compound. Additionally, direct flush of expired and unused pharmaceuticals to sewers from at least one of these sources can't be neglected **(Heberer et al., 2002)**. Incomplete digestion of manufacturing effluent containing pharmaceutical deposits puts pressure of pharmaceuticals to STPs **(Kummerer, 2009)**

Isolation and Antibiotic Susceptibility Pattern of *Escherichia coli* from Urinary Tract Infections in a Tertiary Care Hospital of north eastern Karnataka showed that of the total 1000 samples, 395 cases were culture-positive for *E.coli*. These isolates were tested for antibiotic susceptibility by disk diffusion method.As shown in figure 3.1,of the total 395 *E. coli* isolates, 170 (43%) were multi-drug resistant (MDR). The isolates showed high level of sensitivity to Imipenem (89.53%), Ciprofloxacin (82%),Nitrfurantion (79.95%) Gentamaycin (75.90%), and Cefixim (70.47%) while high resistance to cephalexin (60%) , Cotrimoxasol (51.05%) but very low sensitivity.Henceforth, it was concluded that a substantial count of the urinary tract infections in the subjects were caused due to multiple drug resistance to *E. coli.* The sensitivity pattern displayed a consistent decline from 2012 to 2015 with Imipenem and ciprofloxacin as they were currently the most effective antibiotics **(kulkarni et al., 2017).**

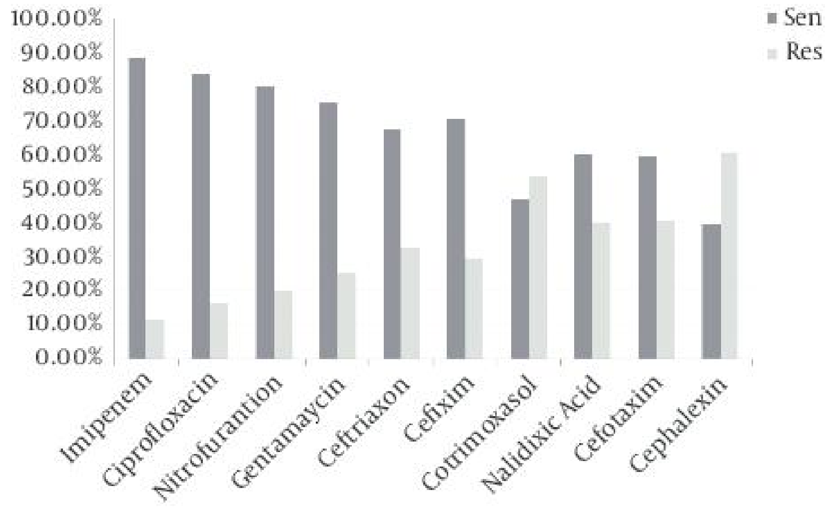


Figure 3.1 Antibiotic Sensitivity Pattern of *Escherichia coli* Isolated From Urine Specimens (Source: kulkarni et al., 2017)

3.2 Fate of pharmaceuticals in Wastewater treatment:

Numerous pharmaceuticals to a great extent are being evacuated in wastewater treatment plants by adsorption to sludge by means of electrostatic or hydrophobic forces, contingent upon the nature of pharmaceutical and the predominant pH condition in the wastewater **(Jia et al., 2012; Yamamoto et al., 2009)**. Sorption to sludge has been accounted for as a significant expulsion pathway for flouroquinolones (40-100%) from wastewater **(Conkle et al., 2010; Jia et al., 2012**). In spite of the generous evacuation of fluoroquinolones in wastewater treatment plants(principally by adsorption to sludge), consideration ought to be given due their presence in soil and surface water because of effluent evacuation and land use of sludge as a biosolid **(Heberer, 2002; Hu et al., 2010)**.

Biological treatment in Sewage treatment plants (STPs) is influenced by the structural abilities and the antibacterial impact of pharmaceuticals. In this manner, the part of STPs in evacuating numerous pharmaceuticals is constrained **(Heidler and Halden, 2007; Jia et al., 2012; Lajeunesse et al., 2012).**

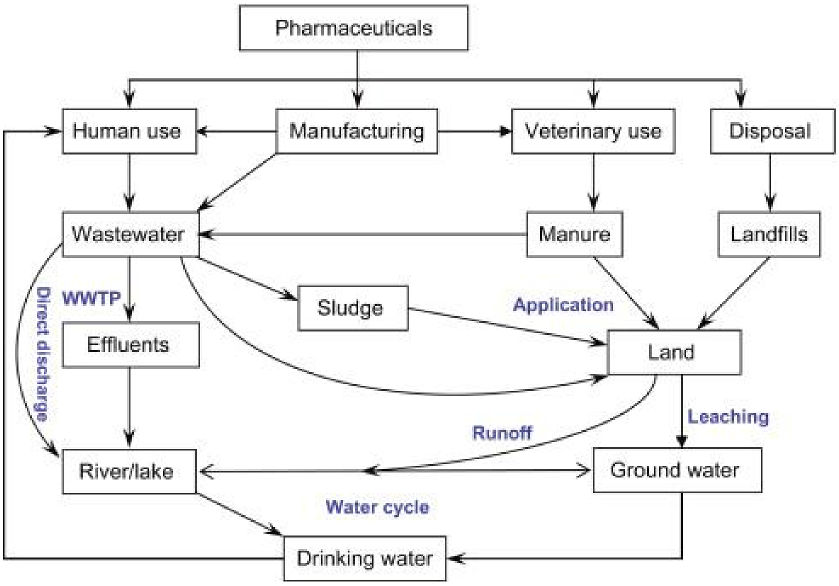


Figure 3.2: Fate and occurence of pharmaceuticals in environment

(Source: Ying et al., 2013)

Pharmaceuticals production occurs via batch processes which consist of various steps and at each step different kinds of intermediary products are formed which are released out as wastes but could be harmful to the surroundings (figure 3.2). When these compounds gets discharged from pharmaceutical industries, hospitals, households, they might enter the wastewater treatment plants (WWTPs) **(Kanakaraju et al., 2014)**. Due to variation in physical and chemical properties of pharmaceutical compounds and wastewater treatment plants (WWTPs) installations, the efficiency of treatments can deviate drastically, requiring a wide range of techniques and methods for removal of the waste. The conventional methods of treatment become ineffective on APIs due to their non-biodegradable nature and high solubility, thereby rendering an increased concentration of parent compound and its metabolites to the terrestrial as well as aquatic environment.

3.3 Concerns related to the release of pharmaceuticals into the environment

Walters et al. (2010) observed in their mesocosms experiments that among the at first recognized 15 pharmaceuticals, five of them in particular ciprofloxacin, azithromycin, norfloxacin and carbamazepine had half-life time between 1–3 years in the mud sewage sludge blend showing high protection from biotic and abiotic treatments. Likewise, studies have demonstrated the incapability of sunlight based photolysis in deteriorating psychiatric drugs, for example,alprazolam, diazepam, and oxazepam in the aquatic condition **(Calisto et al., 2011)**. Additionally, **Yamamoto et al. (2009)** revealed that 8 pharmaceuticals considering carbamazepine, atenolol and ibuprofen indicated resistance from sun based photodegradation when illuminated for 50–70 h. The biodegradability of pharmaceuticals in coastal surface water tests was additionally examined by **Benotti and Brownawell (2009)**. In this examination, they found that pharmaceuticals for example, carbamazepine, antipyrine and trimethoprim were observed to be non-biodegradable with halflife times between 35 to >100 days. Pharmaceuticals, for example, carbamazepine (140 ng/L) and sulfathiazole (10 ng/L) were likewise identified in completed the process of drinking water (n=12) after traditional drinking water treatment (i.e., flocculation-sedimentation-activated carbon filtration) showing that a few drugs can escape such medications **(Stackelberg et al., 2004; Stackelberg et al., 2007).**

The insufficiencies of STPs in degradation of various classes of pharmaceuticals gave the opportunity to many researchers to concentrate on the application of advanced oxidation processes (AOPs) for the eradication of pharmaceuticals from water and wastewater matrices to control their negative impacts.

3.4. Advanced oxidation processes (AOPs)

AOPs, including ozonation, sonolysis, photo-Fenton photocatalysis, photolysis, and heterogeneous photocatalysis for the removal of drugs, are the techniques that are mainly dependent on the production and utilization of highly reactive species such as hydroxyl radicals ($HO^{\bullet}$) to oxidize particular targeted compound. Since, hydroxyl radicals are quite unstable and reactive ($E_o = +2.59$ V; pH <12), therefore, their reactions with target organic compounds are extremely rapid and nonspecific **(Asghar et al., 2015)**.

3.5. Photocatalytic reactors

Photocatalytic reactors can be arranged in light of the conveyed condition of the photocatalyst, i.e., in suspension or fixed form. Photocatalytic reactors can utilize either UV or sunlight. Solar photocatalytic reactors are very effective for the photoxodation of organic pollutants in water. Such sort of reactors can distinguish into concentrating or nonconcentrating reactors **(de Lasa et al.2005)** Both type of reactors possess specific advantages and disadvantages. For instance, non-concentrating reactors can utilize direct and diffuse solar radiation, however are bigger in size in contrast with the concentrating reactors and possess losses of high frictional pressure **(de Lasa et al.2005)**. However, the applications of solar photocatalytic reactors have been restricted because of the inalienable nature of TiO_2.

Slurry reactors

The most popular type of reactors for the wastewater treatment are basically the slurry reactors. As compared to the fixed bed photocatalytic reactors, they have been proved to be much more efficient and provide a greater surface area to volume ratio contributing to the most important factor in the photocatalytic degradation **(Chong et al., 2010)**. However, the complication of these reactors is that they are unable to separate the TiO_2 particles from the treated water. Although, various post- treatment procedures such as settling tanks **(Chong et al., 2010)** have been employed to overcome this issue but none of them was cost effective.

Fixed bed TiO_2 reactors

The catalyst in TiO_2 fixed bed reactors are immobilized to the surface via physical forces and chemical bonding. These techniques allow the continuous use of the catalyst with no losses or issues of catalyst separation from the treated water sample.

Dual photocatalytic layer reactors have been created to establish the downstream removal of photocatalyst. The photocatalytic layer reactors can be generalized in two classes (1) irradiation of the membrane module and (2) irradiation of feed tank containing photocatalyst in suspension **(Molinari et al.,2002)**. Different layers, for example, ultra-filtration, micro-filtration, and nanofiltration layers might be utilized for this reason depending on the necessities of the treated water quality **(Chong et al. 2010)**. Photocatalytic layer reactors have been effectively utilized for the debasement of 4-nitrophenol and tricholoroethylene **(Tsuru et al.,2003).**However , these reactors have disadvantages, for example, low surface area to volume ratio, significant pressure drop and catalyst fouling **(de Lasa et al.,2005)**. Another issue related with the membrane photocatalytic reactors is the dispersion of organic compounds to the surface of the catalyst which is slow especially when the concentration of the organic compound is low **(Augugliaro et al.2006)**. To cumbersome the issue of slow diffusion, nano sized pores should be used to allow the catalyst to execute selective permeation and generating the oxidized permeation stream. It can be concluded that the photocatalytic reactors can be either immobilized or slurry systems and each have certain favorable circumstances and drawbacks identified with their outline and efficiency. Additional investigation on the plan and vital productivity of photocatalytic reactors could make reduction process more achievable for further applications in water treatment. Membrane photo-reactors have all the earmarks of being a promising contrasting option to traditional photo-reactors and more research here can help conquer a portion of the issues looked with the utilization of ordinary reactors.

The most vital objective in photocatalytic water treatment is the designing of photocatalytic reactors. According to the earlier reviews the photocatalytic reactors have been said to be of two main categories, (i)lab-scale reactors, where the volume of the reactor solution is <1 L, and (ii)pilot-scale reactors, where the volume is >5 **(Lazar et al.,2012).** Furthermore, numerous manipulations have been done in these reactors also like use of LEDs as light source, the fabrication of NTO-immobilized catalytic beds and post -separation/reuse of NTO powder catalysts **(Lazar et al.,2012)**.

It has been cited in many papers that fixed-bed photocatalytic reactors have advantages over the ones that are based on slurry method. In slurry photocatalysis, there are maximum chances of catalyst toxicity and carcinogenicity due to accumulation of crystallized nanostructures of the catalyst used such a TiO_2. In the fixed-bed reactor the catalyst is immobilized and cannot be solubilized in the reaction mixture, thereby reducing the possible toxicity. Along with the use of oxidants like H_2O_2, fenton reagent is also added sometimes to the photocatalytic system in order to elevate the rate of degradation which then increases the production of more OH radicals.

The researchers have also synthesized nano structured photocatalytic TiO_2 particles which were fixed on the surface of transparent Raschig ring packings **(Saien et al., 2011).** It was found that suspensions with initial concentration of dye 30mg/L, within the range of typical concentration in textile waste suspensions, were processed under the mild operating conditions of natural pH of 6.75 and temperature of 25 degrees celsius **(Saien et al., 2012).**

In recent studies, there are evidences of synthesis of ammonia-modified graphene (AG) sheets organized with Fe_3O_4 nanoparticles as a magnetically recoverable photocatalyst by a general in situ solution chemical approach **(Boruah et al., 2017)**. These AG/Fe_3O_4 nano composite represented enormous photocatalytic activity for the degradation of phenol (92.43%), 2-nitrophenol(98%) and 2-chlorophenol (97.15%) within 70-120 min. As a result, it also showed its efficiency in photo-Fenton process, 93.56% phenol, 98.76% 2-nitrophenol and 98.06% of 2-chlorophenol degradation was accomplished within 50-80 min under solar radiation **(Boruah et al., 2017).**

The discharge of ammonia-rich effluents in waste water treatment plants have also been discussed in some papers. It has been evidently said that nitrate can be in-vivo reduced to nitrite, that can perform nitration reactions in the stomach with amines and amides to form a variety of N-nitroso compounds, which are highly carcinogenic. Various processes like reverse osmosis, electrotype-dialysis, activated carbon adsorption have been implied to eliminate nitrate but these processes have been proved to be quite expensive and difficult to manage. The biological processes involved in denitrification have been proved to be the most efficient in this. Hence, biological organisms can also be applied on fixed bed reactors to remove organic pollutants and their intermediates.

3.6. Concerned pharmaceutical target: Ofloxacin

Ofloxacin (OFX) is an antimicrobial compound of the fluoroquinolone family. Fluoroquinolones are not completely processed by the human body. From 20 to 80% of fluoroquinolones that are consumed gets discharged in a pharmacologically dynamic form **(Gerding et al., 1996)**. Due to this reason fluoroquinolones affect residential sewage wastewater. Remaining amounts of antibiotics and fluoroquinolones obtained in wastewater can be dangerous to life forms in the water that encounter them **(Wilson et al., 2003)**. Bacteria presented to antimicrobial deposits introduce in natural lattices may experience mutations in their genetic makeup, bringing about microorganisms that are impervious to the compound. All the more intense medications must be utilized as a part of the treatment of infections due to antibiotic resistant microbes. In this way, it is critical to utilize treatment advancements that are fit for expelling the leftover antimicrobial movement of these compounds. Ofloxacin have been investigated to be widely found in surface water (10–535 ng L^{-1}), hospital wastewater (25 000–35 000 ng L^{-1}) and municipal WWTP effluent (53–1800 ng L^{-1}) **(Rodrigues et al.,2014;Hapeshi et al.,2010).**

Ofloxacin is known for its broad spectrum of activity in response to most of the gram negative and gram positive bacteria such as *Staphylococcus aureus* (methicillin-resistant) and *Pseudomonas aeruginosa* (Enterobacteriacae). In addition, ofloxacin has tremendous activity against *Mycobacterium tuberculosis*, *Chlamydia trachomatis* and *Neisseria gonorrhoeae*. Clinical trials till date have illustrated the efficacy of this flouroquinolone drug ofloxacin in the treatment of urinary tract infections, lower respiratory tract infections and sexually transmitted diseases. Adverse side-effects to ofloxacin are generally mild and include central nervous system, gastrointestinal, and hypersensitivity reactions. However, significant pharmaceutical compound interactions with ofloxacin have not been so far reported. Many infection causing bacteria such as *Mycobacterium tuberculosis* have attained multiple drug resistance. New compounds that are actively working against these bacteria include grepafloxacin which is a C5 flouroquinolone. A board of 130 detaches of *Mycobacteria* including 33 M. tuberculosis secludes and 97 segregates of various types of atypical *Mycobacteria* were investigated for susceptibility to ofloxacin, grepafloxacin, and ciprofloxacin. Preliminary investigation results of macrophage tests demonstrated that grepafloxacin was more dynamic than ciprofloxacin and ofloxacin, especially against *Mycobacterium kansasii* and, to a less extent, against *Mycobacterium marinum* and *Mycobacterium avium* complex and Be that as it may, the three fluoroquinolones had tantamount exercises against *M. tuberculosis*. Therefore, to prevent the bacteria and other microbes to attain resistance against these anti-microbial agents also, we need to degrade and eradicate these compounds from the wastewater efficiently and in lesser time which is greatly successful by applying dual effect of AOPs.

Table3.1: Photocatalytic treatments for pharmaceuticals cited in the literature

Target Compound	Mode of treatment	Matrix used	Experimental set-up	Results	References
Ornidazole	PC	Double distilled water	Halogen tungsten lamp as visible light source (500W)	Degradation efficiency reached about 90.5%. COD values reduced with increase in illumination time from the initial value.	Zhao et al. (2012)
Paracetamol	DP and PC	Milli-Q water	Black light blue UV-A (8W) & UV-C (15W)	Under UV-C illumination the degradation and mineralization of the drug occurred rapidly in the presence of catalyst TiO2.	Yang et al. (2008)
Amoxicillin	PC	Distilled water	UV lamp (365nm, 6W)	TiO_2 dose of $0.1 gL^{-1}$ with addition of H_2O_2 at low pH gives complete degradation of almost all antibiotics	Elmolla & Chaudhury (2010)
Propanolol &Metoprolo Beta blockers	PC	Milli-Q water	Solar simulator (1kW, Xe-OP lamp)	$0.4 gL^{-1}$ of TiO_2 P25 was enough to reach maximum removal of both the drugs.	Romero et al. (2014)
Ibuprofen & carbamazepine	PC	MQ water & Wastewater from WWTP	UV-A lamp (9W); solar simulator(1000W, Phillip Xe lamp)	UV-A and solar photocatalysis much effective for degradation of carbamazepine and degaradtion under UV illumination seened to be sensitive to TiO_2 catalyst loading.	Achilleos et al. (2010)
Cephalexin	Dual process	Double distilled water	Clay beads mixed with fly ash & foundary sand (UV	Dual effect showed 89% degradation and COD reduced to 82% with formation of various anions.	Bansal et al. (2017)

			irradiation $25Wm^{-2}$)		
Ofloxacin	PC & DP	Milli-Q water	Mercury lamp (15W)	Degradation efficiency during DP was 89.3% and addition of more of H2O2 raised it to 97.8%	Peres et al. (2014)

*PC- Photocatalysis

*DP- Direct photolysis

Research gaps

On the basis of the work cited in the literature, following gaps have been identified:

1. Photocatalytic studies using new inert materials those with high durability have not been yet studied by many researchers.

2. Studies on dual effect are least cited in the literature yet and their subsequent applications for the degradation have not been reported.

3. In fact, dual effect in fixed form has not been studied much and there is no consistency in repeated number of operations.

Chapter 4

Objectives

Based on the research gaps, following objectives have been identified:

1. Selection of inert support material for catalyst immobilization along with suitable iron source.
2. Application of selected support material in application of in-situ dual effect for the degradation of ofloxacin.
3. Process optimization and durability studies.

Chapter 5

Methods and Materials

In this section, the techniques and materials used in the reduction of pharmaceutical compound Ofloxacin by dual process has been discussed. The specificity and properties of pharmaceutical compound adopted has been explained in the materials section. The instruments used to execute the photocatalytic degradation of the compound have been discussed in detail in the methodology section.

5.1 Materials

5.1.1 Pharmaceutical compound

(a) Ofloxacin is a synthetic broad-spectrum antibacterial drug administered orally obtained from nearby pharmaceutical industry in Patiala, Punjab. (±)-9-fluoro-2,3-dihydro-3-methyl-10-(4-methyl-1-piperazinyl)-7oxo-7H-pyrido[1,2,3 -de]-1,4-benzoxazine-6-carboxylic acid is the chemical name of the compound and is a fluorinated carboxyquinolone. The chemical structure has been represented in figure5.1.

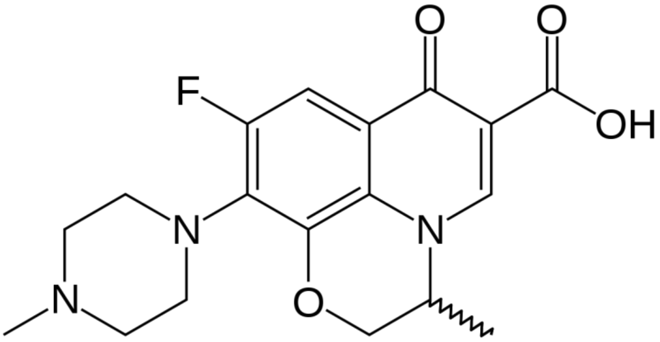


Figure 5.1 structure of ofloxacin

The empirical formula of Ofloxacin is $C_{18}H_{20}FN_3O_4$, and has a molecular mass 361.4 g/mol. It is a crystalline off-white to pale yellow colored powder. Ofloxacin is known to inhibit the bacterial replication by blocking the enzyme DNA gyrase, and therefore halts its growth and reproduction. This drug is active against many gram positive and gram negative bacteria and is better than other flouroquinolones like ciprofloxacin and norfloxacin and hence is widely used. Also, there have been no studies reported on the degradation of ofloxacin using dual effect of photocatalysis and photo-Fenton.

(b) Real pharmaceutical effluent was obtained form a pharmaceutical industry in Ludhiana, Punjab.

5.1.2 Catalyst and reagents used

Degussa P25 TiO_2 was purchased from Evonik Industries (India) and used as a photocatalyst. Hydrogen peroxide (H_2O_2),30% w/v used as an oxidant was obtained from Ranbaxy, India. Clay was bought from a local vendor while a waste foundry sand (FS) and fly ash (FA) were accepted as gift samples from local industry, Patiala (India) for the preparation of inert fixed-bed materials and were utilized without any further purification. NaOH and concentrated H_2SO_4, bought from Merck, were taken as reagents for pH maintenance. Acetic acid (>99.5%) and sodium acetate (>98.5%) for the acetate buffer were obtained from TCI Chemicals (India) Pvt. Ltd. Milli-Q water was used for the preparation of all the medias.

5.2 Instruments used

5.2.1 UV-Vis Spectrophotometer

UV-Vis spectrophotometer (LABINDA, model no. T60 U) was used for the analysis of degradation of ofloxacin at 288nm. The calibration curve was obtained for different concentrations of ofloxacin and a particular absorbance value was identified for 20ppm concentration at 288nm.

5.2.2 pH meter

The pH of the initial sample solution of the pharmaceutical drug was maintained by addition of acetate buffer as per requirement and was measured by a pH meter of Thermo Scientific Orion Star Series.

5.2.3 Branson bath sonicator

Ultrasonic bath tank (MODEL NO. EN 60 US) was used having frequency of 33kHz for the homogenization of suspended catalyst during the catalyst coating on the clay beads.

5.2.4 Muffle Furnace

A muffle furnace (temperature range 200-1200 °C) was used for fixing the catalyst coated on the clay beads. It was run at a temperature of 250 °C for the same.

5.2.5 UV Chamber and batch reactor

A lab scale rectangular wooden chamber was fabricated with UV tubes inside it for carrying out dual effect operations **(Verma et al.,2014)**. A borosil glass batch reactor was used for lab scale experiments which measured a diameter of 17.4 cm and height of 5.2 cm and had a capacity of 1200mL. A laboratory jack was used to place the batch reactor in the UV chamber which had dimensions 1.37m x 0.9 x 1.0 m. 36W UV tubes with wavelength of 365nm were installed on the underneath of the UV chamber. Inside the UV chamber aeration was provided by using spargers. An exhaust fan was also installed to maintain the temperature of the UV chamber(figure 5.2)

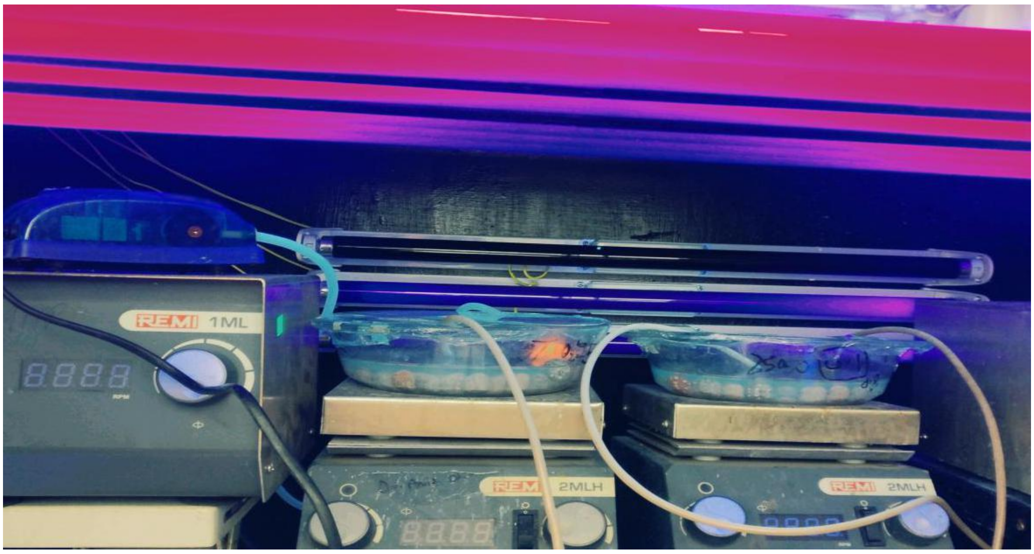


Figure 5.2 Actual image of batch reactors placed inside a UV chamber

5.2.6 COD digester

Chemical oxygen demand is the amount of oxygen required for the oxidative degradation of the particulate and soluble organic matter in water. It is an important water quality testing parameter as it provides an estimation of the harmful effect of the wastewater on the surrounding environment. Higher COD depicts that the amount of waste organic matter is more in the water which will eventually reduce the dissolved oxygen content in that particular water body. The COD digestion method involves the use of a strong oxidizing compound, potassium dichromate ($K_2Cr_2O_7^{2-}$) which oxidizes organic matter in the solution into water and carbon dioxide at low pH conditions. The sample in a COD digester is oxidized for 2 hours at 150 °C.

5.2.7 SEM-EDAX

SEM-EDAX analysis is done for the identification of the TiO_2 on the beads (both freshly coated and recycled). The model used for SEM was JSM-6510LV, JEOL, Japan while that of EDAX was INCAX-act, Oxford instruments, UK.

5.2.8 FT-IR

Fourier-transform infrared spectroscopy is a vibrational spectroscopic technique, that is, it takes advantage of the asymmetric molecular stretching, vibration, and rotation of chemical bonds when they are exposed to designated wavelengths of light. Range of group frequency is 4000-1500cm^{-1} while that of finger print region is 1500-400cm^{-1}. The model used for FT-IR analysis was Spectrum-two FT-IR spectrophotometer, L160000F.

5.2.9 UV-DRS

UV-Vis diffuse reflectance spectra was used for the evaluation of band gap energy of freshly TiO_2 coated and recycled composite beads in the UV-Vis region ranging from 200-800nm.. The model used for this was UV-2600 shimadzu (Asia pacific).

5.3 TiO_2 immobilization

Industrial waste products Foundry sand (FS) and fly ash (FA) were utilized as elective iron source with TiO2. For the immobilization of TiO_2, clay beads were prepared manually with mixture of materials which were clay + FA + FS (2:1:1). The characterization of FS and FA was done to confirm the presence of iron as cited in previous studies **(Rajput at al., 2016;Verma et al.,2015)**. The binding material used in all the studies was Clay. Spherical shaped beads were formulated manually by taking accurate proportions of the FS and FS materials. The beads were cured by muffling at 1000 °C for 1 h and then they were drenched in water to make them hard and for gaining the proper strength. The beads of equal sizes were chosen for catalyst immobilization. TiO_2 coating done the on beads by using the standard dip-coating method as cited in the literature **(Verma et al., 2014)**. Uniform film of TiO_2 was then acquired on the beads surface. This thin film of catalyst on the surface of beads was confirmed by SEM/EDS analysis. For the catalyst immobilized beads, notations used is FS/FA/TiO_2 beads. Figure 5.3 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 has been discussed in the section 6.4.3.

Figure 5.3 a) Uncoated beads b) TiO_2 coated beads

5.4 Experimental protocol and Set-up

5.4.1 Dual process using artificial UV source

1. The 20ppm (20mgL^{-1}) stock solution of ofloxacin was freshly prepared everyday using distilled water to carry the experiments.
2. A batch reactor was covered with the beads to its surface.
3. The desired volume was taken from the stock solution into a bowl.
4. The pH of the solution was adjusted to 3.5 by using acetate buffer.
5. The optimum concentration of the oxidant H_2O_2 was added to the suspension.

6. The batch reactor was then placed on a magnetic stirrer inside the UV temperature at optimum distance from the UV lights so that the required intensity of UV lights will fall on the suspension to carry out photocatalysis reaction.
7. The aeration was provided by means of the spargers.
8. The sample was collected in a syringe (5ml) at regular intervals and using a filter it was poured into the test tubes. Filter of 4.5μm size was used to separate out the particles if present.
9. The reaction was kept under process for 120 minutes.
10. The %degradation of the collected samples was estimated by taking absorbance at 288nm in a UV-Spectrophotometer.

5.4.2 Dual process using natural solar irradiation

1. The pilot scale experimental set-up consists of a glass reactor having dimensions of 30cm x 20cm(figure5.4)
2. The reaction comprises of 5 baffles fitted uniformly.
3. The catalyst coated beads were uniformly spread in every portion of the baffled reactor in a way that they would be immersed in the solution appropriately for their treatment.
4. The flow rate of the solution was maintained for acquiring the optimum desired retention time.
5. The reactor was designed in a manner that it could treat a maximum of 5L solution.
6. This proved an evidence that the dual process could be applied at industrial scale and great success in the treatment of wastewater at a large scale could be achieved.

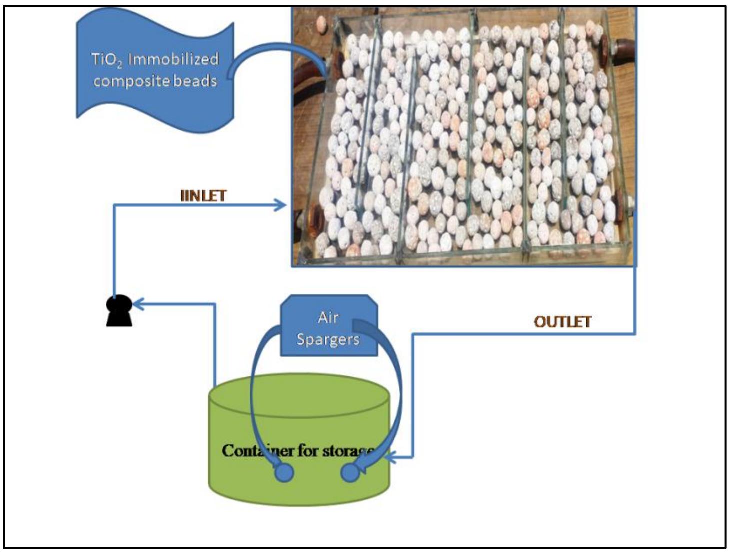


Figure 5.4 solar glass baffled reactor.

5.4.3 Experimental procedure for the real wastewater treatment using dual effect

1. Desired volume of the pharmaceutical compound was taken from the stock solution in the batch reactor.

2. Dual effect TiO_2 coated beads were spread in the batch reactor covering the entire surface of the reactor.

3. The pH was checked and then set at 3.8 which is the optimized pH value in our studies.

4. After the addition of H_2O_2 ($300 mgL^{-1}$) and covering the reactor with a thin film , it was placed over the jack in the UV chamber, provided the aeration and Uv lights were switched on.

5. After every 30 minutes, 5ml sample was collected with a syringe.

6. For the analysis of COD value, the procedure that was followed is mentioned below:

   a) 3ml of sample was poured in the COD vials.

   b) To all the vials 1.5ml potassium dichromate was added.

   c) 3.5ml of sulfuric acid and silver nitrate solution was added slowly.

   d) Now, COD digestion of these vials containing the solution was done for 2 hours at 150 °C.

   e) COD was measured after the digestion.

Chapter 6

Results and discussions

In this chapter, the degradation of ofloxacin by using fixed-bed dual effect of photo-Fenton and photocatalysis has been discussed. Specific operating parameters like catalyst dose, oxidant concentration, pH, area/volume ratio and ultra-voilet light intensity have been varied to set particular optimized conditions for efficient execution of the process. For the commercial applications of our technique, pilot scale studies using baffled solar reactors were also conducted.

6.1 Standard calibration curve of ofloxacin

Absorbance versus concentration graph for the known concentrations of ofloxacin was plotted giving a standard calibration curve of the solution. The concentration of ofloxacin solution was varied from 10mgL^{-1} to 50mgL^{-1} at 288nm wavelength. The values of slope and the regression luoride ed were found to be 0.0672 and 0.9933 respectively.

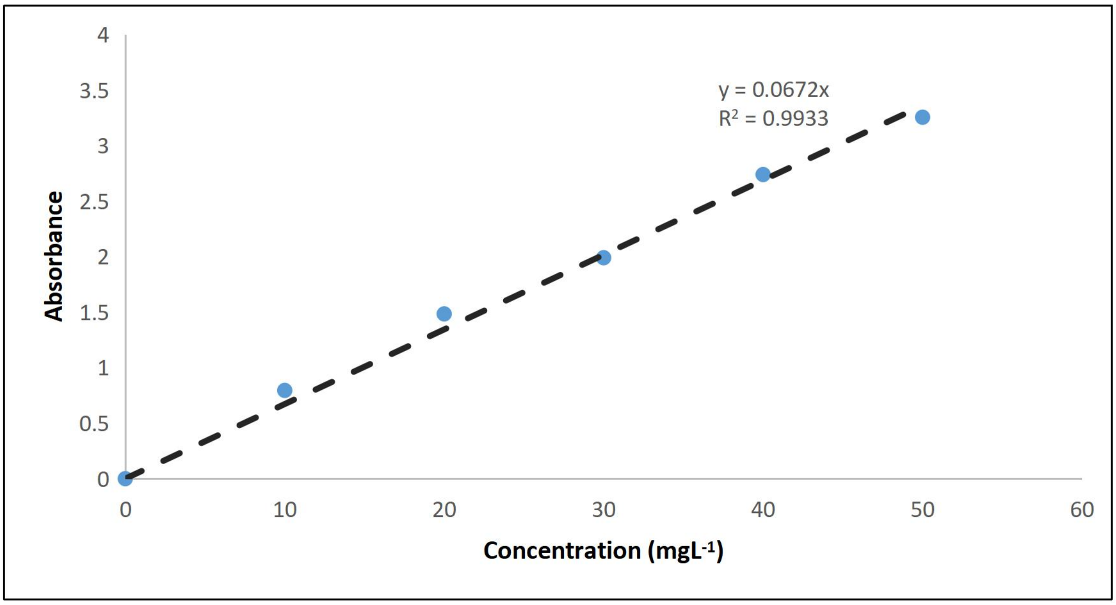


Figure6.1: standard calibration curve for Ofloxacin

6.2. Degradation studies using dual effect

6.2.1. Preliminary studies

In order to study the effect of individual parameters on the degradation of the concerned pharmaceutical compound ofloxacin various preliminary reactions/experiments were performed. When the ofloxacin solution was exposed to UV light, only 16% of degradation was observed after 1 hour reaction in a batch reactor. The adsorption studies by photocatalysis, only 10% degradation was seen which was only due to the adsorption of the compound on the catalyst surface and little amount of free radical generation. When H_2O_2 alone was used, 19% of the degradation was achieved which might have be due to the production hydroxyl radicals. While 45% degradation was observed using photo-Fenton technique in which only the iron and hydroxyl radical production by H_2O_2 were responsible for the reduction in the concentration of the compound. The degradation of the compound by photocatalytic process was 25%. Significant reduction in the concentration of ofloxacin was observed when dual process (photocatalysis+photo-Fenton) was employed and it showed about 80% degradation in only 1 hour. Hence, from these studies it can be assumed that, dual process is quite effective in the degradation of ofloxacin. When the reaction time was preceded further, it showed 92% degradation in 2hours.

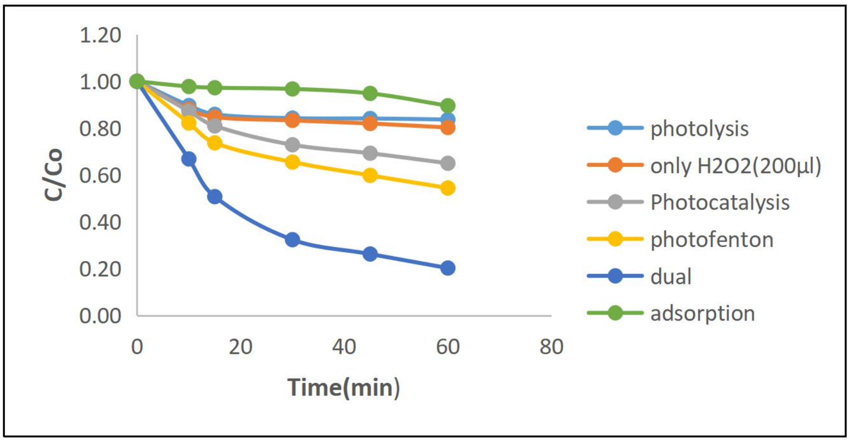


Figure 6.2: Photocatalytic degradation of ofloxacin in the presence and absence of TiO_2, H_2O_2 and UV. Experimental conditions: C_o =20mgL^{-1}, V = 200mL

6.2.2 Kinetic studies of dual effect in ofloxacin degradation

The kinetic study of photocatalytic degradation of ofloxacin has been described using the Langmuir-Hinshelwood (L-H) kinetic model. This model indicates that the rate of reaction is directly proportional to the fraction of the surface of photocatalyst that is covered by the substrate (θ).

Therefore,

$$\text{Rate, r} = -\frac{dC}{dt} = k\,\theta \tag{6.1}$$

$$\theta = \frac{KC}{(1+KC)} \tag{6.2}$$

Here, k is the rate constant of the reaction and K is the reactant adsorption constant. By substituting Eq. (6.1) in Eq. (6.2)

$$r = -\frac{dC}{dt} = k\,\frac{KC}{(1+KC)} \tag{6.3}$$

Upon Integrating Eq. (6.3):

$$\ln\frac{C}{Co} + K(Co - C) = kKt \tag{6.4}$$

Where, t is the time of irradiation. Equation (6.3) represents zero order for time when the concentration C (mol L^{-1}) is higher. The solution was then diluted, and the reaction rate became an apparent first-order reaction:

$$r = -\frac{dC}{dt} = k\,KC = k_{ap}\,C \tag{6.5}$$

Where k_{ap} depicts the apparent constant of the pseudo first order rate of the reaction. By Integrating Eq. (6.5)

$$\ln\frac{C}{Co} = k_{ap}t \tag{6.6}$$

A graph of ln (Co/C) vs t was plotted and the apparent kinetic rate constant (k_{ap}) was determined.

6.2.3 Prominence of dual process over individual processes

Dual effect has showed tremendous degradation efficiency over the individual processes, that is, photocatalysis and photo-Fenton. During the degradation studies of pharmaceutical compound Ofloxacin, it was observed that the synergistic effect of dual process over the photo-Fenton was 61.41% while that on photocatalysis was

72.48%. The overall synergy of dual process over both the processes was found to be 34%.

Synergy of dual over photocatalysis process:

$$\%\,Synergy = 100\ \times \{(k_{dual} - k_{photocatalysis})\}/k_{dual} \qquad (6.7)$$

$$\%\ Synergy = 100\,x\,\{(0.0298\text{-}0.082)\}/0.0298$$

$$\%Synergy = 72.48\%$$

Synergy of dual over photo-Fenton process:

$$\%\,Synergy = 100\ \times \{(k_{dual} - k_{photoFenton})\}/k_{dual} \qquad (6.8)$$

$$\%\ Synergy = 100\,x\,\{(0.0298\text{-}0.0115)\}/0.0298$$

$$\%Synergy = 61.41\%$$

Synergy of dual over both photocatalysis and photo-Fenton process i.e overall synergy:

$$\%\,Synergy = 100\ \times \{(k_{dual} - (k_{photocatalysis} + k_{photoFenton}))\}/k_{dual} \qquad (6.9)$$

$$\%\ Synergy = 100\,x\,\{(0.0298\text{-}\ (0.0082+0.0115))\}/0.0298$$

$$\%Synergy = 34\%$$

Hence, the synergistic effects of dual technique over both the individual processes lead to the tremendous increase in rate of the reaction. Therefore, it confirms that our process is feasible.

6.3 Parametric optimization

6.3.1 Effect of H_2O_2

The oxidant (H_2O_2) addition raises the scope of photocatalytic degradation since it prompts the production of OH radical as soon as the electron gets excited by a photon of light to a higher energy state. It additionally produce $^\bullet$OH radical as per the following response:

$$H_2O_2 + {}^\bullet O_2 \longrightarrow {}^\bullet OH + OH^- + O_2 \qquad (6.10)$$

The effect of different H_2O_2 concentrations was varied in the range of 75mgL^{-1} to 750mgL^{-1} keeping the volume (200ml) and pH(3.8) of the solution constant. A great increment was observed in the degradation of ofloxacin when the concentration of the oxidant was increased. But after a particular increase in the H_2O_2 concentration the degradation rate become slower. After using a maximum concentration of the oxidant, it was seen that the optimum amount of the oxidant will be $300mgL^{-1}$ which further indicated that higher dose of the oxidant might have declined the degradation rate due to scavenging effect.

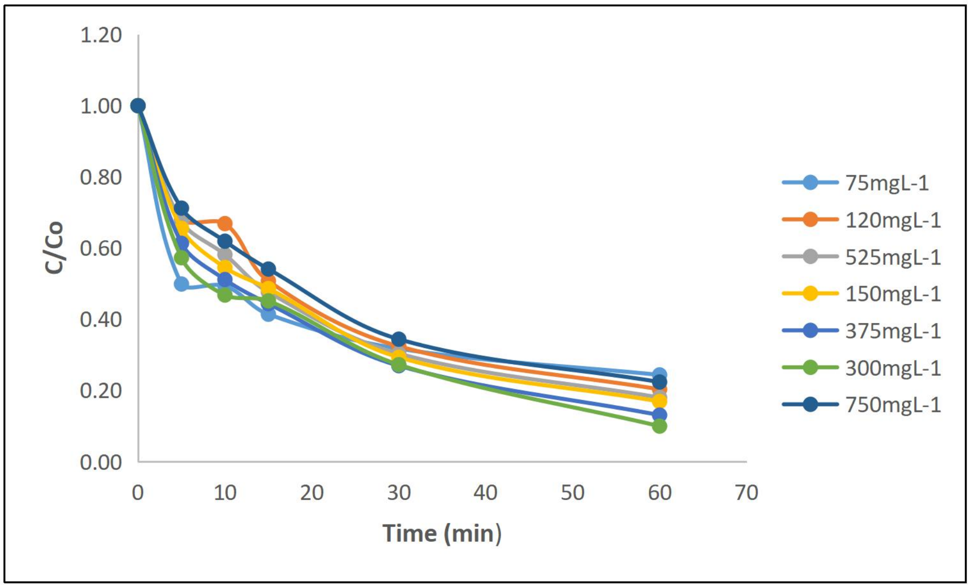


Figure 6.3.1(a): Plot of C/Co versus time at different concentrations of H_2O_2

Furthermore when the first order rate constant (k) was plotted against the changing H_2O_2 dose, it was observed that initially the rate constant increased upto $0.04min^{-1}$ at $300mgl^{-1}$ but further addition of the oxidant eventually decreased the k value which showed the scavenging effect of higher dose of H_2O_2.

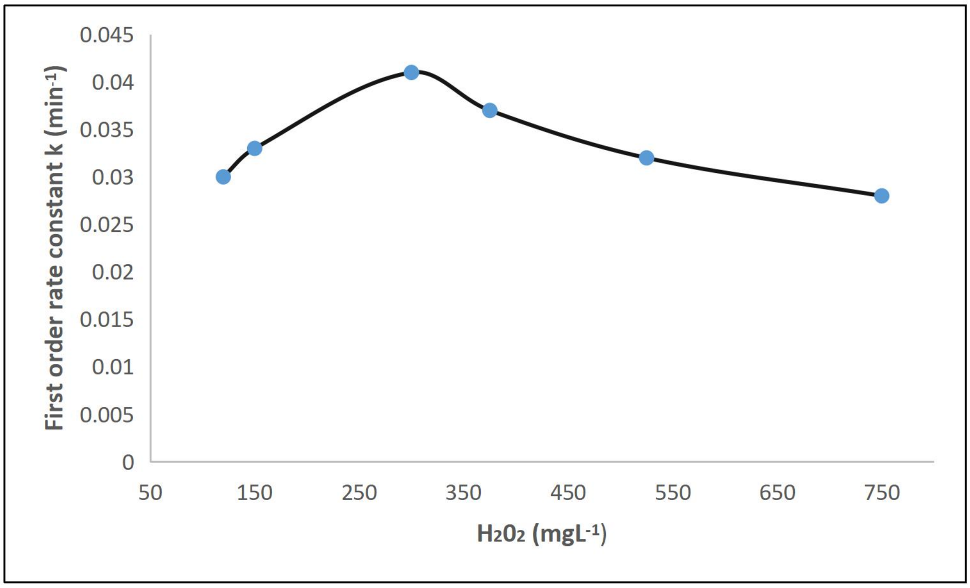


Figure 6.3.1(b) : Plot of first order rate constant, k vs varying H_2O_2 dose during dual effect on the degradation of Ofloxacin (Co=20mgL^{-1}, V= 200mL).

6.3.2 Effect of UV intensity

The most important parameter in the photocatalytic degradation is the use of UV light (artificial/natural solar irradiation). The studies performed at UV intensities from 10Wm^{-2}, 17Wm^{-2} and 25Wm^{-2} showed that the optimized UV light irradiation which showed the maximum degradation of Ofloxacin was at 25Wm^{-2}. These studies provided the evidence for the degradation at the optimized UV intensity. The fact that when the batch reactor was placed at a distance of 21cm (25Wm^{-2}) from the UV irradiating tubes the degradation rate was found to be maximum. As the distance from the UV irradiation was decreased, the light scattered and less amount of light was able to reach the solution and hence the degradation slowed down. Similarly, when the batch reactor was placed at a distance of 28cm (10Wm^{-2}) from the UV tubes the light reaching the solution was insufficient and therefore, no significant degradation was seen.

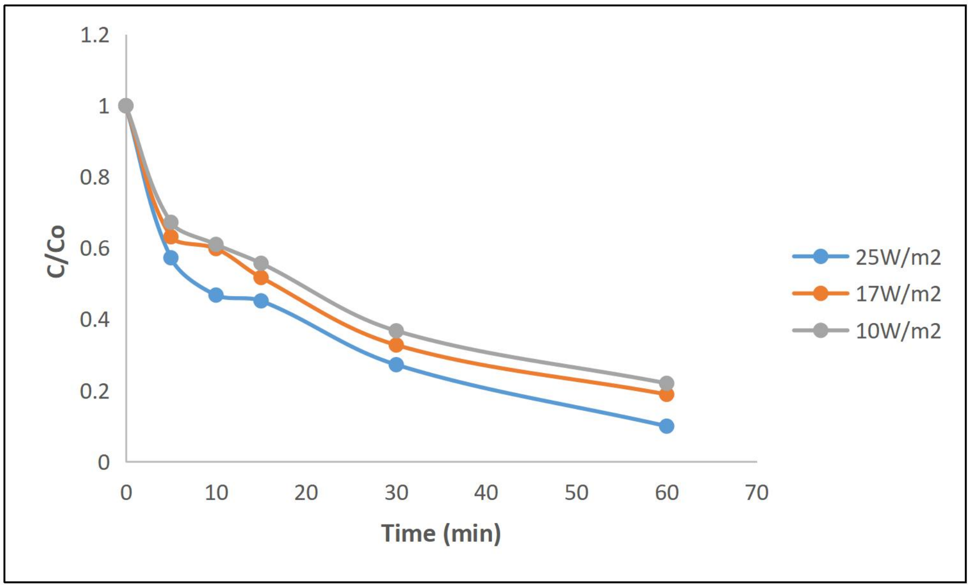


Figure6.3.2 (a): Plot of C/Co vs time at varying UV intensities

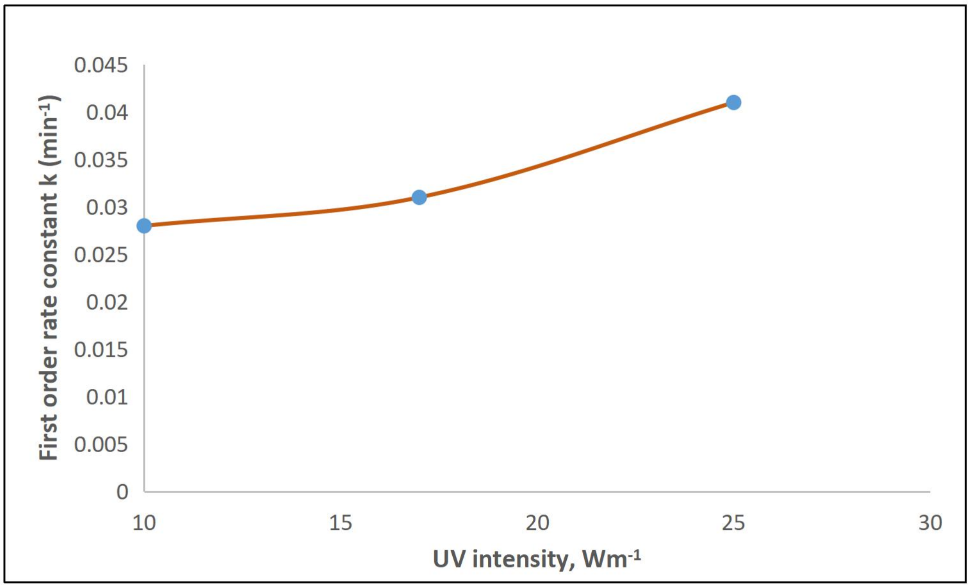


Figure6.3.2 (b): Plot of first order rate constant, k vs UV intensity variation for dual effect on Ofloxacin degradation (Co=20mgL^{-1}, V=200mL)

6.3.3 A/V ratio effect of the Batch reactor

The depth of the reactor forms a major limitation in the field-scale application of AOP as the penetration of solar radiations should be sufficient to reach the solution. Generally less depth and more exposed area is recommended for the better penetration of light **(Toor et al., 2006).** In our studies, this was achieved after varying the volume of the solution and keeping the area of the batch reactor constant. Area/Volume ratio of the batch reactor was varied in the range of 0.182 cm^2 ml^{-1} to 0.364 $cm^2 ml^{-1}$. A plot of C/Co vs time is shown in figure 6.3.3(a) at varying ratios of A/V. A tremendous increase in the reduction of ofloxacin was achieved by increasing the A/V ratio as the rate constant 'k' increased as demonstrated in the figure 6.3.3(b). As the A/V ratio increases (area kept constant), solution gets less deeper which leads to an increased path length of the photons of light entering the solution, therefore, resulting in the more OH radical production and hence, rate of photocatalytic degradation increased. The decreased degradation rate accompanied by the reduction in the volume was due to the reason that beads were not completely immersed in the solution and hence, the rate of reaction slows down as shown in figure 6.3.3(a). Therefore, the optimum value obtained for A/V ratio was 0.273 which showed the maximum degradation.

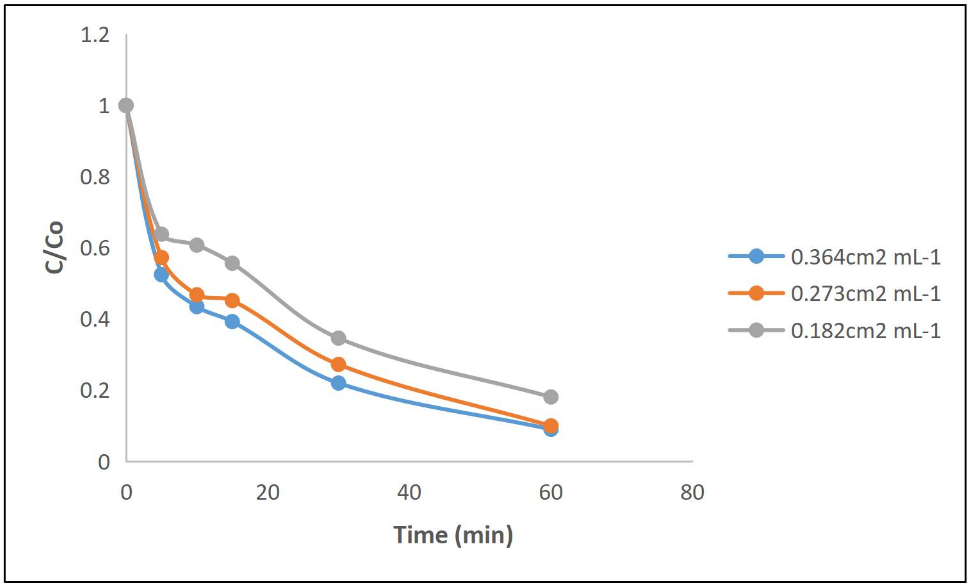


Figure 6.3.3(a) : C/Co vs time plot at different A/V ratio during Ofloxacin degradation by dual process.

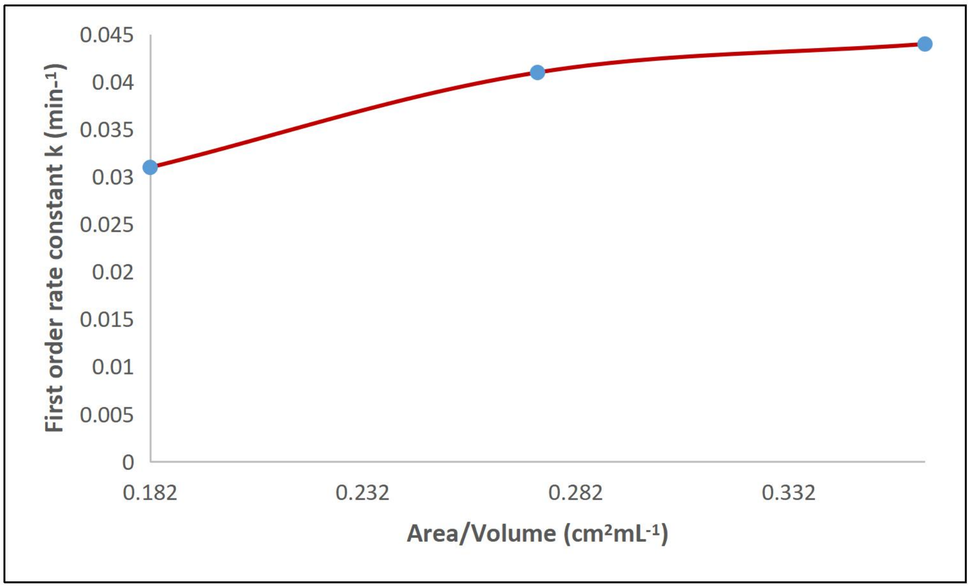


Figure 6.3.3(b): A plot of k vs effect of A/V ratio for the dual effect on the degradation of Ofloxacin (Co=20mgL^{-1})

6.3.4 Effect number of beads variation

The effect of variation of beads was studied by varying the covered surface area from 50 to150%. It was observed that when the surface of the reactor was fully covered i.e. 100% showed maximum degradation of 92%, but when the area covered was decreased to 50% the degradation was 71% this might be due to the less amount of TiO_2 dose and significantly less percentage of iron leaching from the beads . But when the beads were overlapped to 150%, the degradation was again decreased to 80% due to the shadow effect i.e. formation of dead zones and with the large increase in iron content, TiO_2 active sites were blocked.

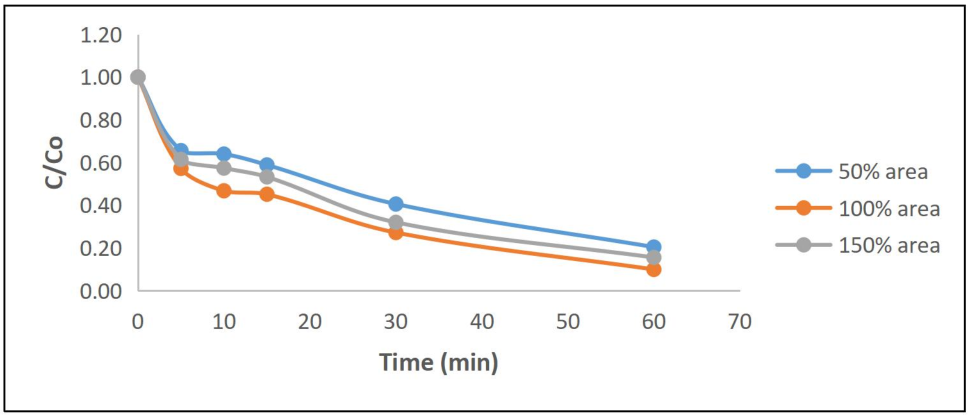


Figure 6.3.4(a) : C/Co vs time plot for the variation in number of beads during Ofloxacin degradation by dual process (Co=20mgL^{-1}, V=200mL)

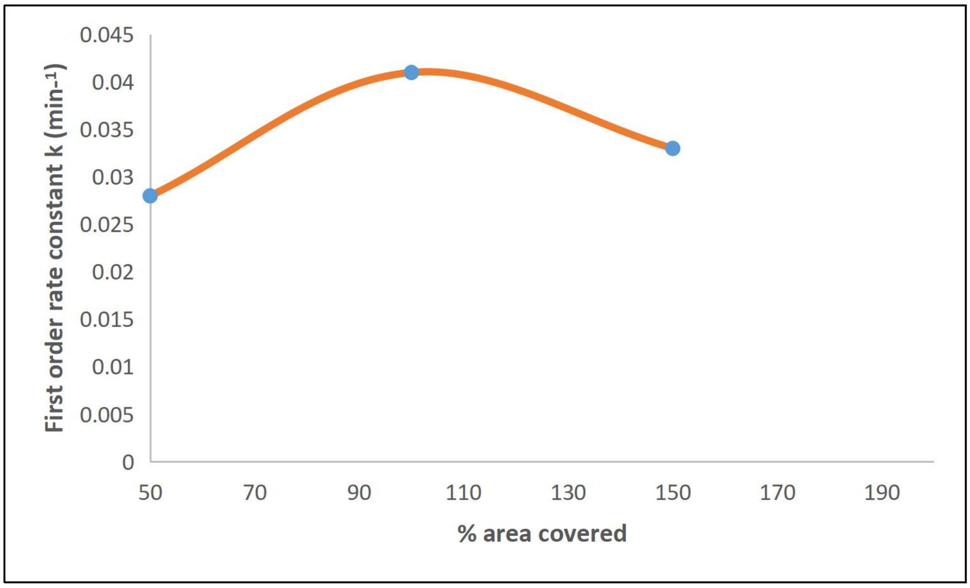


Figure 6.3.4(b): Plot of k versus %area covered in the degradation Ofloxacin by dual process (Co=20mgL^{-1}, V=200mL)

Optimization analysis

Through this study, % degradation of ofloxacin was maximized. The values of optimum parameters are defined in the given table 6.1. At this optimum condition, the final reduction of ofloxacin by dual effect was about 92% after a reaction of 60 minutes.

Table6.1: Optimized reaction conditions.

Parameters	**Optimum values**
A/V ratio	0.273 cm^{2}ml^{-1}
Time	60 minutes
H_2O_2 dose	300 mgL^{-1}
UV intensity	25Wm^{-2}
% area covered	100%

6.3.5 Comparative studies of solar irradiation and artificial UV light

The comparative analysis of the %degradation of ofloxacin in sunlight and artificial UV irradiation was done in a batch reactor at optimized conditions of pH, H_2O_2 concentration and volume of the solution. The experiments in sunlight were conducted in the months of May and June. The studies showed that the degradation in sunlight was more than that in the artificial UV light. In sunlight the %degradation of ofloxacin by dual effect was found to be 92% while that in artificial UV it was 88% after treatment of 1 hour. The reason behind this was that Fe is more active in the Visible region which was available in case of solar irradiation and not in the artificial UV chamber.

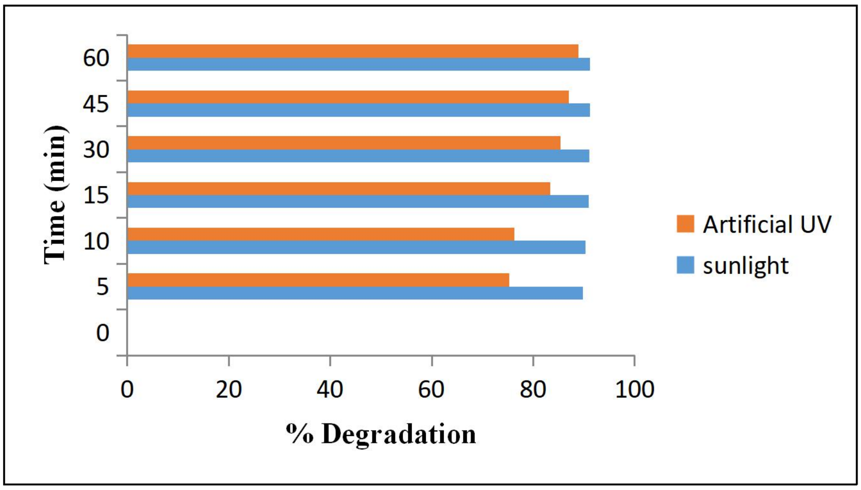


Figure6.3.5: Artificial UV and solar irradiation effect on the degradation of Ofloxacin by dual process (Co=20mgL^{-1}, V=200mL)

6.3.6 Durability of beads

The durability is the most important factor in the successful application of photocatalytic degradation by dual effect. The beads as a support material for the catalyst and iron source immobilization must have the potential to retain the catalyst on its surface and iron leaching into the solution for a longer duration so that they can be reused again and again. Although the activity of the coated catalyst decreases after few cycles but the catalyst can be activated again at high temperature (480 °C). However as cited in the literature, this re-activation of the supported catalyst is not economically feasible. In the current study, it was observed that the immobilization of the catalyst and iron into the clay beads was done in such a manner that even after thirty to forty cycles the degradation efficiency of ofloxacin did not reduced much as shown in the figure6.3.6. The gradual reduction in dual effect (92%-80%) after thirty cycles may be accounted to the loss of the catalyst and less amount of iron leaching into the solution during consecutive cycles of the reaction. The stability of the catalyst and iron presence in the beads was determined by SEM-EDAX of both the fresh beads and recycled beads and it was found that the catalyst was till intact as a film and iron was still actively leaching even after forty cycles.

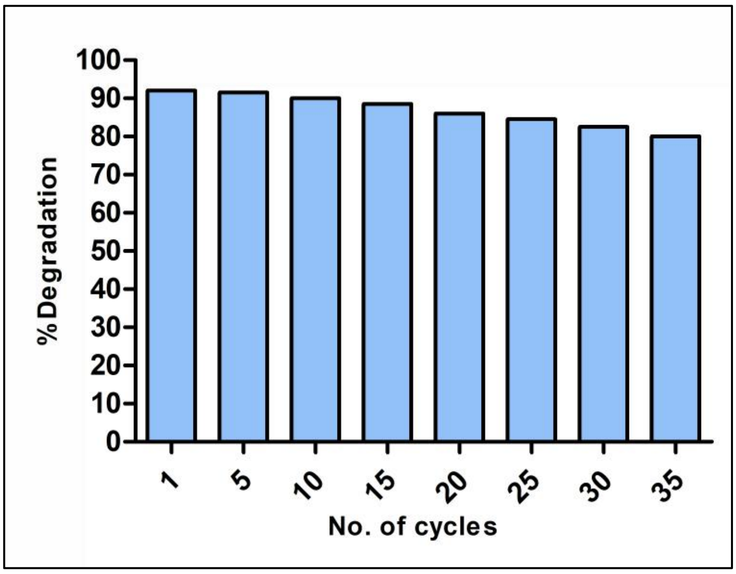


Figure6.3.6: A plot showing the durability of clay beads during the degradation of ofloxacin by dual effect (Co=20mgL^{-1} , V= 200ml).

6.4 Characterization analysis

6.4.1 FT-IR analysis

Fourier-transform infrared spectroscopy is a vibrational spectroscopic technique, that is, it takes advantage of the asymmetric molecular stretching, vibration, and rotation of chemical bonds when they are exposed to designated wavelengths of light. Range of group frequency is 4000-1500cm^{-1} while that of finger print region is 1500-400cm^{-1}. The graph below displays that the peaks in the range 800-1200 cm^{-1} for both the fresh and recycled spectrum, confirms the presence of Ti-O-Ti bonds in both the samples which claims the retention of TiO_2 lattice in the immobilized beads.

The peaks observed in the range 450 to 550cm^{-1} at 503.73 cm^{-1} and 430.39 cm^{-1} in TiO2 and composite beads, respectively describes the anatase phase. The broad 77 peak appearing at 2078.19 cm^{-1} in the spectra of composite beads corresponds to the formation of Fe-O-Ti bond. 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.

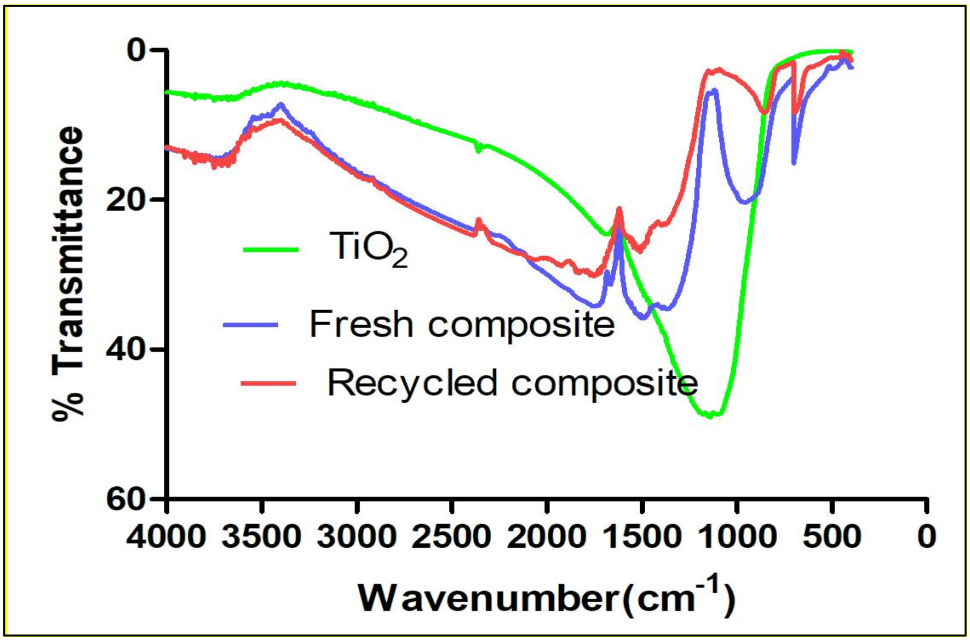


Figure 6.4.1 FT-IR graph of the catalyst (TiO_2), freshly composite and recycled composite beads.

6.4.2 UV-DRS

Evaluation of band gap energy was carried out using UV-Vis diffuse reluctance spectra. A comparison was made between recycled Fe-TiO_2 composite and fresh TiO_2 P25 powder samples and their the scan was taken in the range 200-800nm. The spectra obtained from Fe-TiO_2 composite sample displayed that due the presence of iron in composite, the light was able to absorb in the visible region also. The band gap of the prepared catalyst and TiO_2 P25 was estimated by the equation :

$$E_g = h\nu = hc/\lambda$$

Here, E_g is the band gap energy(eV) ; h is the Planck constant; c is the speed of light; and λ is the wavelength.

Utilizing the given equation the value of band gap energy was 3.2eV for P-25 TiO_2 , 3.15eV for fresh catalyst (beads) and 3.18 eV for recycled catalyst (beads), confirming the activity of the catalyst even after repeated use and not much reduction in the band gap energy after reuse.

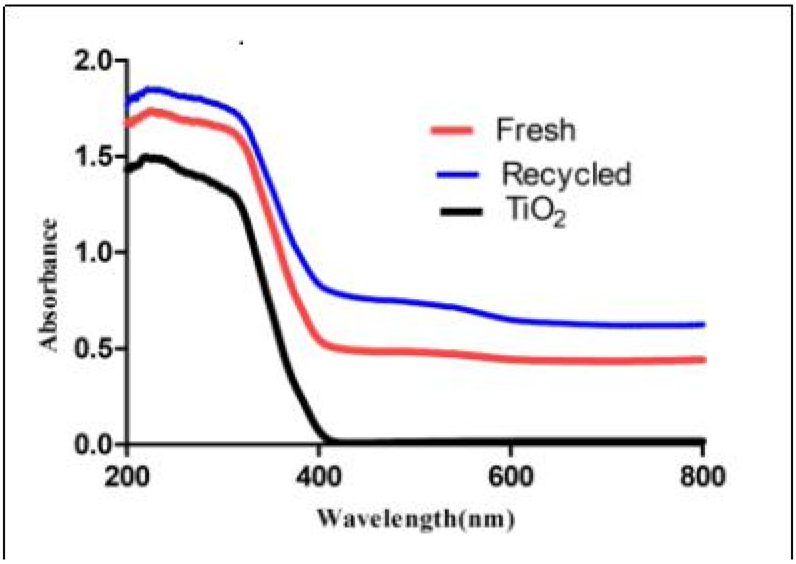
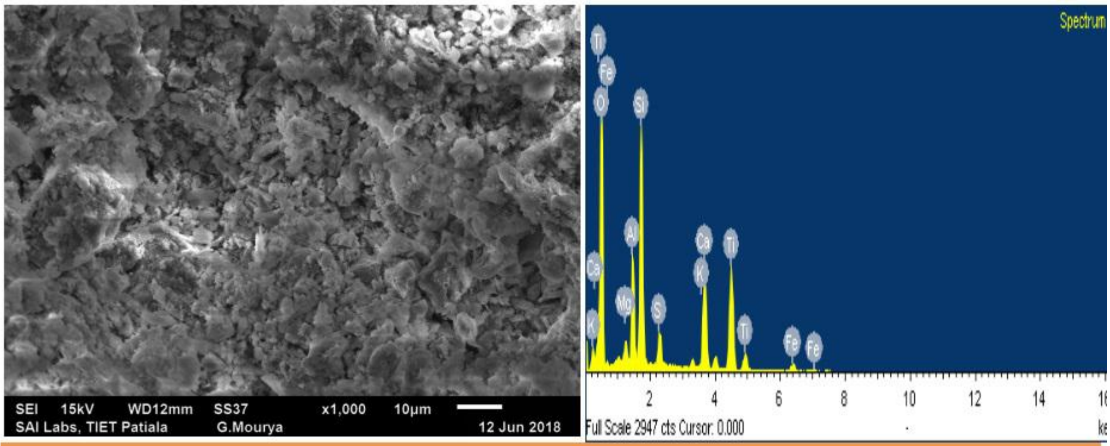


Figure6.4.2 A graph of UV-Vis DRS for the pure TiO_2 catalyst, fresh and recycled composite beads.

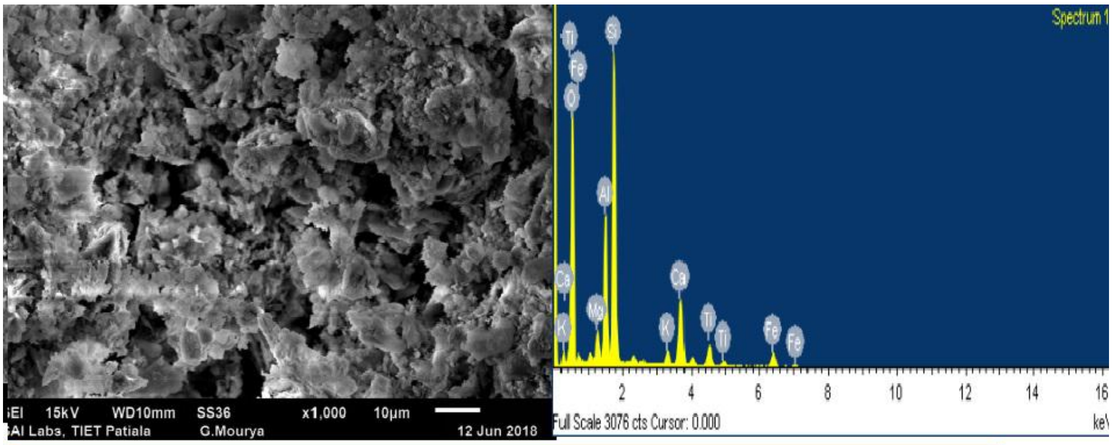
6.4.3 SEM-EDAX

The SEM-EDAX (Scanning Electron Microscopy –Energy Dispersive X-ray Analysis) images have been depicted in the Figures6.4.3(a)for the freshly coated FA+FS(unused) spherical beads, the recycled beads 6.4.3(b)which have been through 40 recycles shows that the uniform coating of the catalyst TiO_2 over the bead surface have been faded to a very less extent after repeated cycles. The presence of Fe, Ti, and O were confirmed by observing distinct peaks in EDAX.



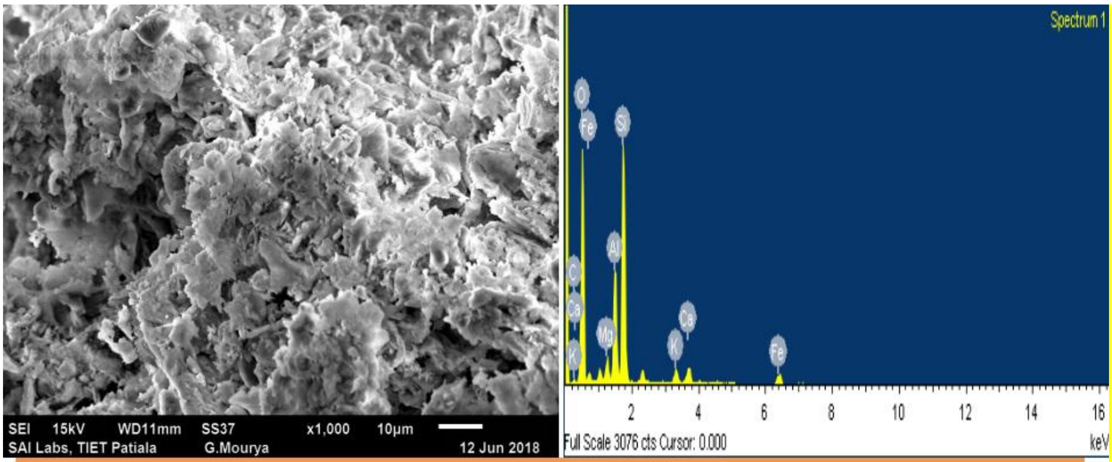
ELEMENTS	Mg K	Al K	Si K	S K	K K	Ca K	Ti K	Fe K	O	Total
WEIGHT	1.20	5.51	13.58	2.60	0.74	10.81	19.13	3.21	43.21	100

Figure 6.4.3(a) SEM-EDAX of fresh composite beads.



ELEMENTS	Mg K	Al K	Si K	K K	Ca K	Ti K	Fe K	O	Total
WEIGHT	1.88	9.33	22.68	1.63	9.81	4.41	6.64	44.23	100

Figure6.4.3(b) SEM-EDAX of composite recycled beads.



ELEMENTS	C K	Mg K	Al K	Si K	K K	Ca K	Fe K	O	Total
WEIGHT	1.83	2.20	9.96	24.80	2.42	3.35	7.93	47.52	100

Figure 6.4.3(c) SEM-EDAX of uncoated (FS/FA) beads.

6.5 Mineralization studies

The mineralization of the treated synthetic ofloxacin water was achieved by estimating the iron, nitrate, nitrite and ammonia concentrations. Also, the intermediate products formed during the ofloxacin reduction were confirmed by GC-MS analysis.

6.5.1 Nitrite and Nitrate estimation

Ofloxacin, in its structure has nitrogen atoms, and hence during its mineralization, nitrite and nitrate inorganic compounds were formed. Initially, the amount of nitrite production was less but as the reaction proceeded the nitrite formation increased with the reduction of ofloxacin as shown in figure 6.5.1(a). When nitrate concentration was estimated in the treated ofloxacin solution, it was seen that the nitrate concentration initially increased drastically but then gradually with the reduction of the ofloxacin compound in the solution, the concentration of nitrate began to decrease and after sometime it became constant shown in figure 6.5.1(b) and hence, it was concluded that the complete mineralization of the ofloxacin compound was achieved.

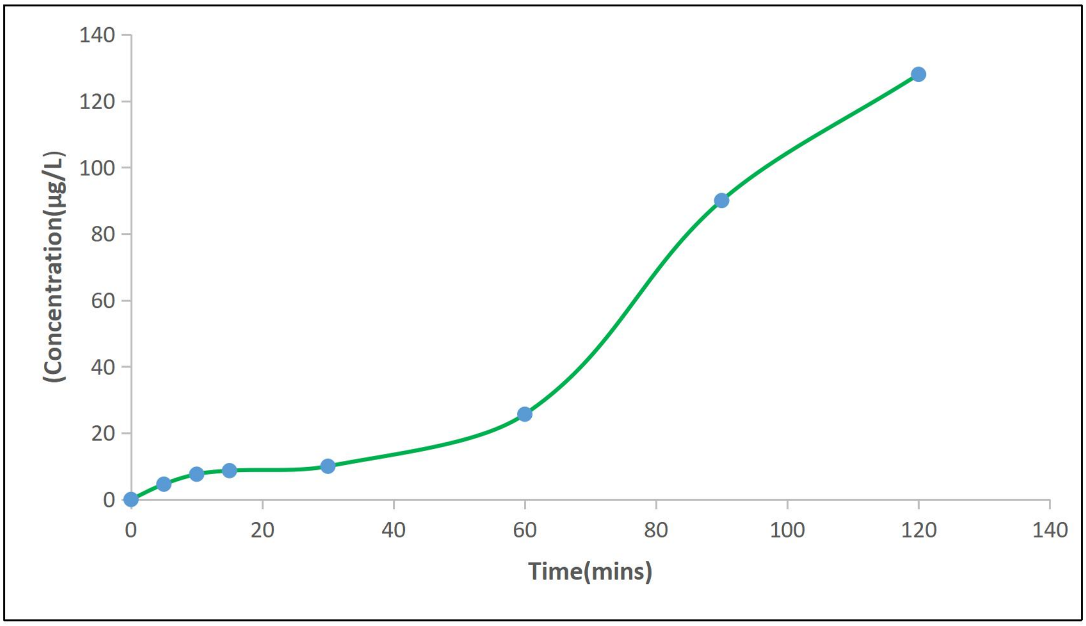


Figure 6.5.1 (a): Graph showing the nitrite concentration during the ofloxacin degradation by dual effect

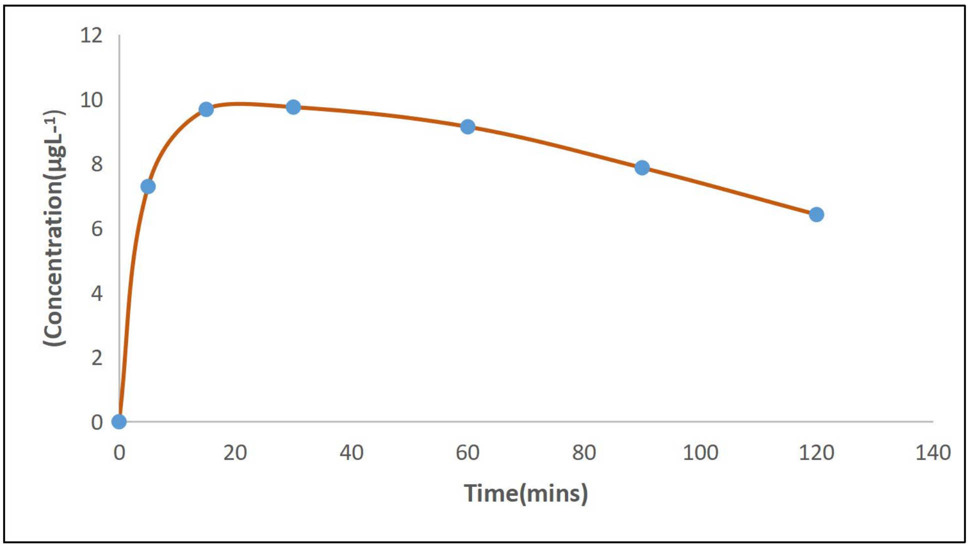


Figure 6.5.1 (b): Graphical representation of nitrate concentration during ofloxacin degradation by dual effect

6.5.2 Ammonia estimation

Ammonia estimation of the treated ofloxacin solution was done to confirm the mineralization of the compound as it forms ammonia as its end product as per GC-MS analysis. The figure 6.5.2 shows the concentration of ammonia estimated after a reaction of 5 hour in sunlight.

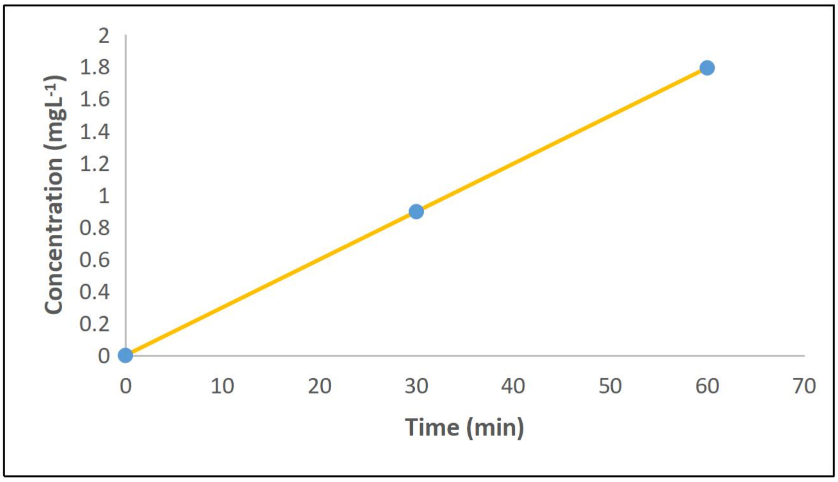


Figure 6.5.2 Plot of ammonia concentration vs time.

6.5.3 Iron Estimation

To confirm the iron leaching from the beads during the reduction of ofloxacin by dual effect, iron estimation was done(figure 6.5.3). In this study, the amount of Total iron, Ferrous and ferric ion concentration was obtained. It was observed that after a reaction of 60 minutes the concentration of the total iron in solution was 6.266 mgL^{-1} . The amount of ferrous ions was comparatively less. But the concentration of ferric ions was significantly much more. From this observation it was concluded that the ofloxacin mineralization gives more ferric ions.

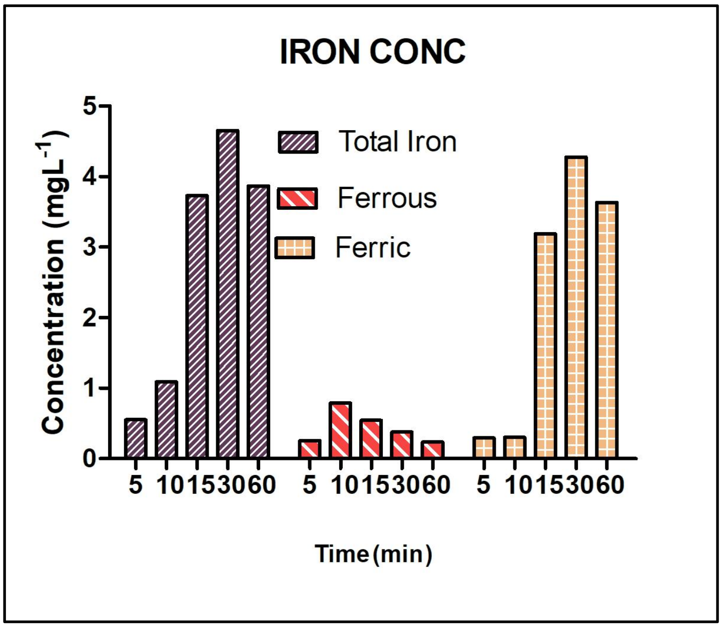


Figure 6.5.3: Bar graph showing the leaching of iron during the degradation of ofloxacin by dual effect

6.5.4 GC-MS analysis

The mineralization studies of ofloxacin were described through GC-MS (Gas chromatography-Mass spectroscopy) analysis for identification of compounds formed during degradation of ofloxacin as shown in figure6.5.4(a) and figure6.5.4(b) along with chromatograms. The degradation mechanism displayed in the figure first formed a compound 1-(3-fluoro-5-hydroxy-4-(4-methylpiperazin-1-yl)phenyl)ethanone by the C-N bond cleavage which further formed two different compounds by denitrogenation i.e., 1-(3-fluoro-5-hydroxyphenyl)ethanone and 1-methylpiperazine which further generated compounds acetophenone and N-ethyl-N-methylethanamine, respectively. The former compound by deacetylation formed a benzene ring which further might have reduced into some by-products. The other intermediate inorganic compounds formed included, nitrate, nitrite, Hydrogen fluoride, ammonia, carbon dioxide and water.

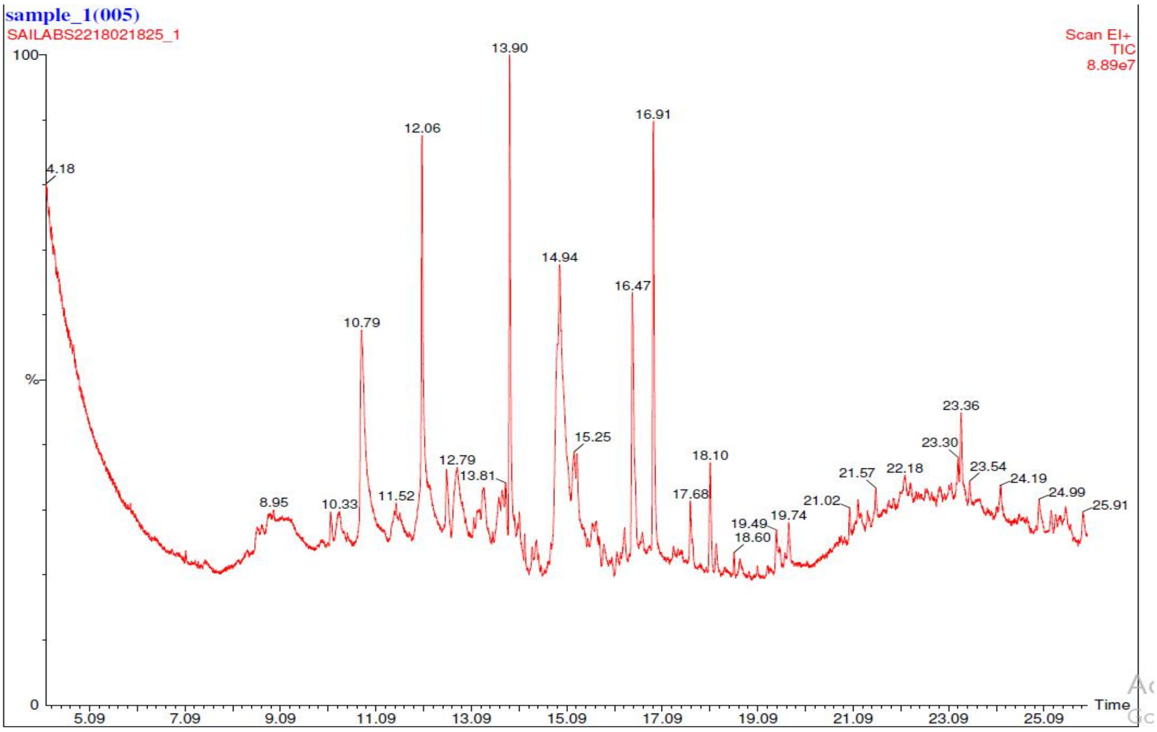


Figure6.5.4(a): Plot showing peaks for the intermediates formed in GC-MS analysis during the degradation of ofloxacin.

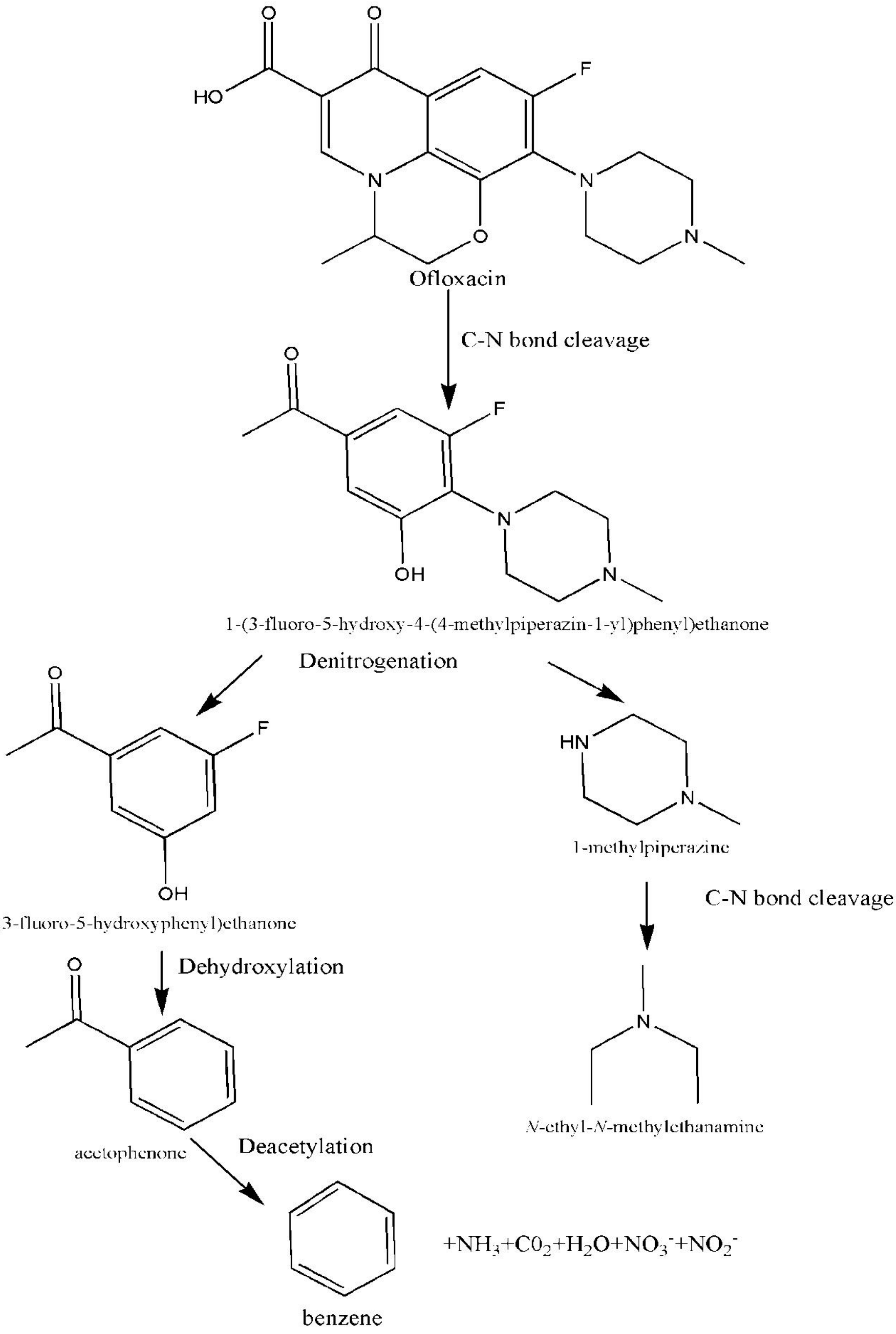


Figure 6.5.4(b) A mechanism proposed by GC-MS after the degradation of ofloxacin by dual effect.

6.6 Toxicity analysis

The bio-assay test for the untreated and treated ofloxacin solution was carried out by using *E.coli* DH-5α strain. The test was performed by zone inhibition method which is also termed as Kirby-Bauer method. The bacterial culture with various concentrations of ofloxacin in the agar plate was cultured for 24 hours in the incubator at 37 ^{0}C. After 24 hours it was observed that the zone of inhibition did not existed in 3 sections of the plate as per shown in Figure6.6. The *E.coli* DH-5α strain is a laboratory bacterial strain. It is a gram negative bacterial strain sensitive towards toxic compounds. Absence of zone of inhibition showed that the pharmaceutical compound had been completely mineralized. It was interpreted that the untreated ofloxacin solution was toxic to the bacterial strain as zone of inhibition was seen but after dual effect degradation, the zone of inhibition was gone and it was be concluded that the treated ofloxacin solution was non toxic in nature.

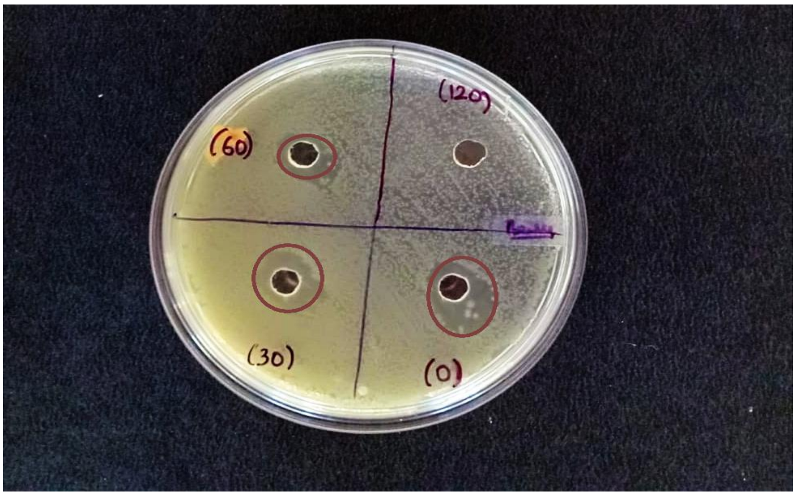


Figure 6.6: Toxicity test of ofloxacin showing zone of inhibition in the section labeled as (0); while the one labeled as (30), (60) and (120) shows the consecutive times of degradation increasing the bacterial growth.

Real pharmaceutical wastewater treatment

In- situ dual effect degradation of real pharmaceutical wastewater

Various experiments were executed to find the optimum conditions for the in- situ dual effect degradation of real wastewater under UV illumination with varying pH, H_2O_2 dose, UV intensity and the time of degradation etc. The optimized conditions for the effective degradation were pH 3.8, 300mgL^{-1} H_2O_2 dose, 25Wm^{-2} UV intensity.

Characterization of treated wastewater

The real pharmaceutical wastewater was investigated for its general characteristics such as TSS,TDS, pH, BOD and COD. The Table 6.2 shows the characterization of the untreated real pharmaceutical wastewater.

Table6.2: characterization of real pharmaceutical wastewater.

Parameter	**Concentration(mgL^{-1}) (Untreated)**	**Concentration(mgL^{-1}) (Treated)**
COD	1076	279
BOD	250	125
pH	4.8	4.0
TSS	780	90
TDS	5260	2010
Biodegradability Index (BOD_5/COD)	0.232	0.448

Real pharmaceutical wastewater was treated in the current study using batch and continuous reactor. Significant reduction in COD (74%) was observed along with the decrease in the treatment time by dual effect as compared to the individual processes of photocatalysis and photo-Fenton. Novel foundry sand and Fuller’s earth beads were used for the reactions. Optimization of various parameters were performed in the sunlight . After 5 hours of treatment COD reduction was from 1076 to 279 mgL^{-1} as shown in figure6.7(a). The in-situ dual effect also raised the biodegradability index from 0.232 to 0.448. For the scaling up of the process treatment of 5L of wastewater was performed in continuous mode with COD reduction of 80.9% in 6 hours. Various characterizations were performed to confirm the recyclability after 40 recycles confirming the activity and prominence of dual effect (figure 6.7(b)).

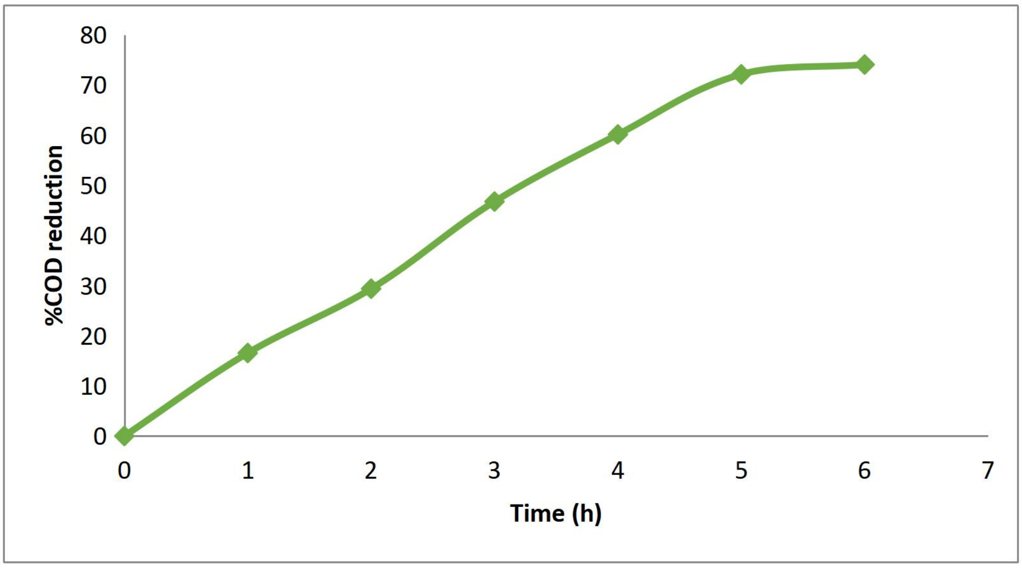


Figure 6.7(a): plot of %COD reduction vs time for the real wastewater treatment by dual effect.

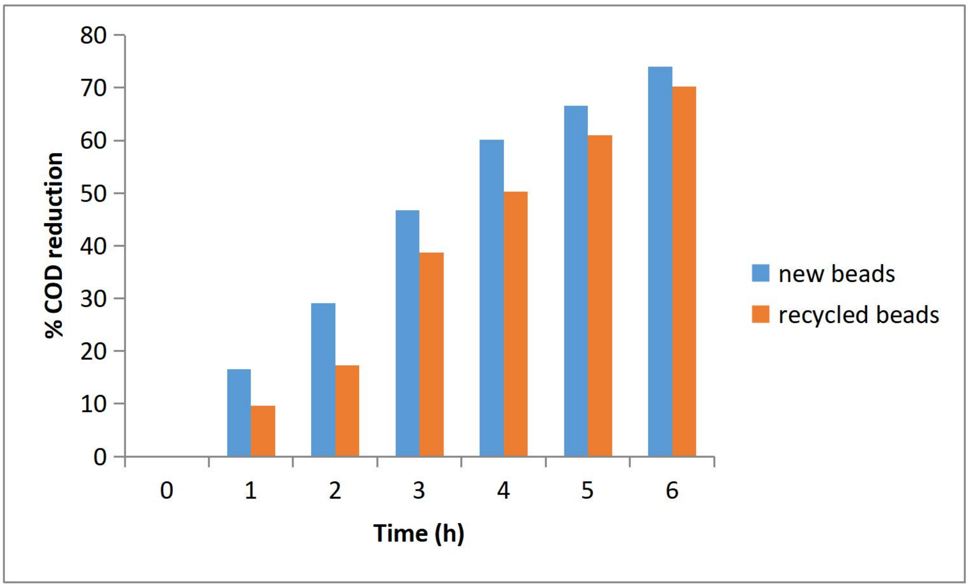


Figure 6.7(b): plot of % COD reduction vs time for the treatment of real effluent with new and recycled composite beads.

Chapter 7

CONCLUSION

In this study, Fe-TiO_2 composition was used in the photo-degradation of a pharmaceutical compound ofloxacin. The iron leaching from the composite along with TiO_2 displayed in-situ dual effect (photocatalysis and photo-Fenton). The reduction of ofloxacin was carried out at optimized conditions of pH(3.8), H_2O_2 dose (300mgL^{-1}), UV intensity(25Wm^{-2}), A/V ratio 0.273. The working solution concentration was set at 20ppm. To confirm the industrial scale applications of the dual effect, a simple non-concentrating reactor was used with the same Fe-TiO_2 composite spherical beads with a total working volume of 5L. The overall synergistic effect (34%) of dual effect over the individual processes strengthened our technique. The durability studies proved that Fe-TiO_2 composite was quite efficient to be effectively reused even after 40 cycles and that too with the same degradation proficiency as it was seen in the initial reactions. The reused composite retention of the TiO_2 nanoparticles along with leaching of iron was affirmed through different characterization studies like SEM/EDAX, UV-DRS, FTIR. The mineralization of the compound ofloxacin was studied through the intermediate formed during GC-MS analysis and the estimation of nitrate, nitrite, total iron concentrations. Along with reduction of the pharmaceutical compound ofloxacin in the synthetic wastewater, the real effluent from a local pharmaceutical industry was also treated with the same reaction conditions and it was observed that the technique successfully reduced the contamination of the real waste to 80% in a reaction of 6 hours. Hence, it was concluded that the dual effect technique was successful in the treatment of the pharmaceutical wastewater and its mineralization studies proved that with this treated water was free of toxic compounds.

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