"IN-SITU DUAL EFFECT STUDIES FOR THE DEGRADATION OF PHENAZONE USING SLURRY AND FIXED BED APPROACH"

Submitted in the fulfilment of the partial requirements for the award of degree of

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Chemistry
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Submitted by

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CERTIFICATE

This is to certify that this Thesis entitled **"In-situ dual effect studies for degradation of Phenazone using slurry and fixed bed approach"** submitted by **Ms. Charu** (Roll. No. 301502009) in partial of the fulfilment requirement for the award of **Master in Science** Degree in Chemistry from **School of Chemistry and Biochemistry, Thapar University, Patiala (Punjab),** India. It is an exclusive record of candidate's own research under the supervision of **Dr. Anoop Verma and Dr. Soumen Basu**. This Thesis in part or full has not been submitted in any other institute for award of such kind of degree.

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DECLARATION

I, the undersigned, hereby declare that the research work presented in M.Sc. project entitled **"In-situ dual effect studies for the degradation of Phenazone using slurry and Fixed bed approach"** has been carried out by me under the supervision and guidance of **Dr. Anoop Verma (School of Energy and Environment) and Dr. Soumen Basu (School of Chemistry and Biochemistry) Thapar University 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 **SUDARSHAN KUMAR** and **SANTOSH KUMARI** and all my family members. 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.

Charu

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ABSTRACT

The present study deals with heterogeneous photocatalytic, photo-Fenton and in-situ dual process for the degradation of Phenazone in slurry and fixed-bed using TiO_2 and waste foundry sand. The degradation rate followed the first order rate kinetics with optimized condition for the photocatalytic degradation of Phenazone TiO_2 0.375g/L, H_2O_2 0.075g/L, C_0

50mg/L at pH 5 with the wavelength 244 nm. Approximately 94% reduction in the concentration of compound was observed after 3 hours. Present study focuses on use of foundry sand as an iron source for the photo-Fenton treatment of Phenazone. Experiment was performed in UV light to check the efficiency of the process. The degradation rate was observed to follow first-order kinetics Foundary sand 1.0g/L, pH 3, H_2O_2 0.450g/L were optimized conditions for obtaining the better degradation rates. Approximately 93% reduction in the concentration of Phenazone was observed after 180 min. In-situ dual treatment for the degradation of Phenazone was also carried out at optimized conditions for slurry mode in sunlight TiO_2 0.375g/L, H_2O_2 0.450g/L at pH 3. The percentage degradation of Phenazone in natural sunlight as 95% was achieved in 90 min. The dual treatment is also carried out in Fixed-bed reactor at optimised conditions H_2O_2 1.350g/L at pH 3 with 96% reduction in the concentration of Phenazone was observed after 4 hours. The COD reduction (75%) along with the generation of nitrite, nitrate confirmed the complete mineralization of the selected compound. Fixed-bed studies were also carried out with TiO_2 on Clay/F.S. disc which eliminates the implication of slurry mode photocatalysis. The recyclability of catalyst was confirmed by recycling the disc for at least 10 cycles and characterized by the SEM/EDAX. Therefore, the technique visualized in this study by employing renewable energy and durable catalyst can provide a viable solution to the industries for treating bio-recalcitrant compounds.

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Chapter 1

INTRODUCTION

India is one of the largest producers of pharmaceutical products and occupies 5^{th} rank in terms of volume. According to the literature, there is a rapid increase in growth of production and consumption of pharmaceutical products in India as compared to other countries **(Oulton, 2009).** The pharmaceutical products include a variety of compounds with substantial variability like antibiotics, anti-depressants, anti-inflammatory, analgesics, etc. India is reportedly breeding ground for most of the multi-drug resistant microbes due to extensive usage and improper disposal of pharmaceuticals into the environment **(Yang et al., 2017)**. Most of these drugs are not metabolized completely in the body as in many cases, 90% of it is excreted out as such which ultimately enter and pollute the aquatic environment. The existence of pharmaceutical compounds in environment occur through diverse routes such as discharge of treated wastewater, seepage from landfills sites, sewer lines, runoff from animal wastes etc. as shown in fig. 1.1**(Klavarioti et al., 2009).**

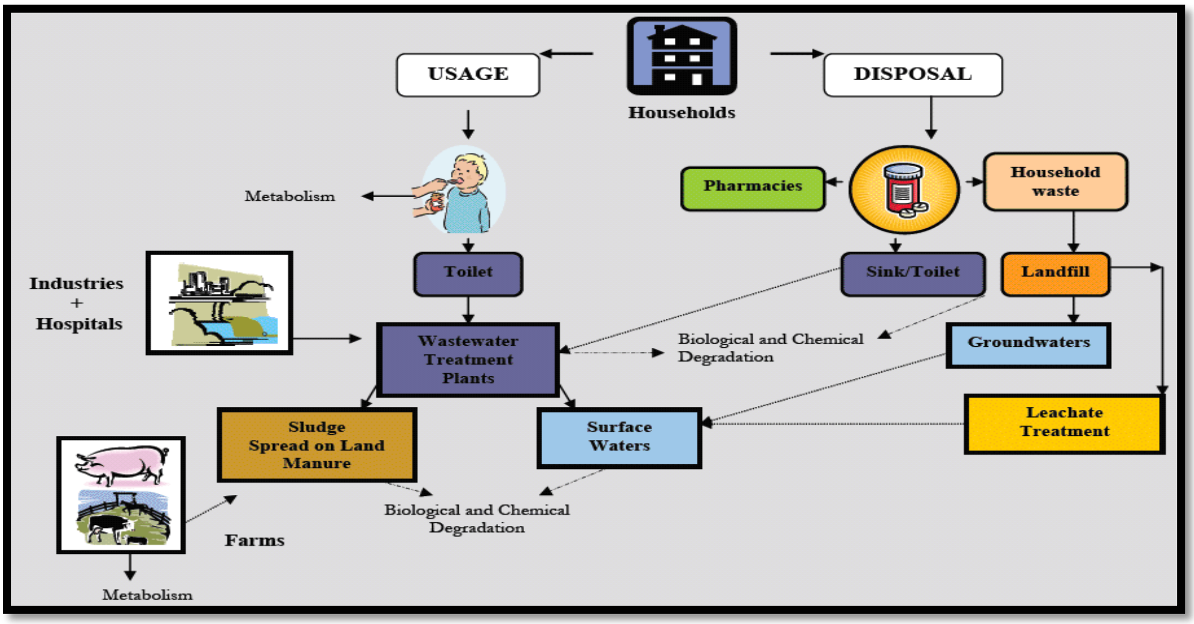

Fig. 1.1: Fates of pharmaceutical in environment

Pharmaceutical pollution in water rushed to an international notice in 2007 when a research team from Sweden found high levels of pharmaceutical compounds in water downstream of a wastewater treatment plant in Patancheru, Andhra Pradesh **(Ryu,**

2013). Poor waste management, storage, transfers and improper disposal of liquid, solid and semi-solid waste mainly contributes to the organic pollutant load to surface and ground water. According to World Health Organization (WHO), micro-pollutants including pharmaceuticals present in water even in traces are harmful for humans as well as aquatic life **(Huong and Hoang, 2009).**

Many recent studies have reported the occurrence of human and veterinary drugs as well as their metabolites in trace concentrations in various water bodies all over the world **(Chau, 2010).** Amongst a large variety of pharmaceuticals, Phenazone, an antipyretic, analgesic and anti-inflammatory drug has been frequently detected in aquatic systems **(Favier et al., 2015).** The persistent nature and non-biodegradability of Phenazone has already been confirmed by various studies **(Ekowati et al., 2016).** Phenazone is mainly used to treat acute migraine problems and to relieve general pain and fever. Few studies have indicated the presence of these types of recalcitrant organic pollutants at low concentration even in drinking water thus proving the ineffectiveness of traditional biological and physical treatment units **(Gulkowska et al., 2008; Loos et al., 2013)**. These frequent reports drew the attention of researchers towards the urgent need of some alternative and effective wastewater treatment technologies.

Advanced oxidation processes (AOPs) are considered to be efficient wastewater treatment processes for the degradation of pollutants which are known to be non-biodegradable or have low biodegradability. AOPs can be classified according to the presence and absence of light source as shown in fig.1.2. The high cost of water treatment via AOPs always limits its applications at field-scale level. Current research in the field of AOPs is being focused mainly towards reducing the treatment time along with cost minimization.

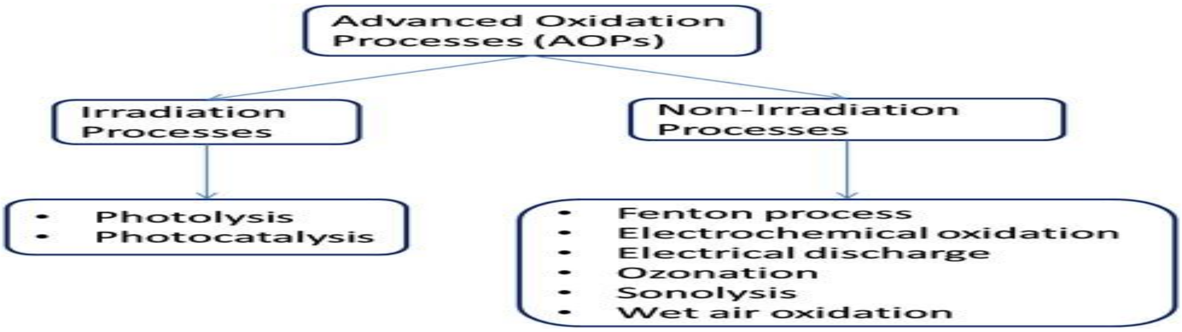

Fig. 1.2: Classification of AOPs

The current study deals with the degradation of an antipyretic drug, Phenazone through heterogeneous photocatalysis, photo-Fenton and dual process incorporating photo-Fenton and photocatalysis in the same treatment unit. Waste foundary sand (FS) has been used as an alternative iron source in photo-Fenton process. To best of our knowledge, this is first reported study for the degradation of antipyretic drugincorporating in-situ dual effect. Further, more studies on heterogeneous processes of dual process are required to be carried out to optimize the operating parameters to achieve maximum degradation of various pharmaceuticals present in wastewater under realistic conditions as well as on an field scale.

Chapter 2

OVERVIEW OF INDIAN PHARMACEUTICAL INDUSTRIES AND ADVANCED TREATMENT TECHNOLOGIES

The pharmaceutical industries are growing day by day and produce a large variety of products including drugs, chemicals, etc. for use as medication. India is the third largest producer of pharmaceuticals in the world. These pharmaceuticals industries are associated with land, air and water pollution. The most commonly detected pharmaceutical in aquatic environment including antipyretic, cholesterol (plant and animal steroids), antibiotics, caffeine (stimulant), and coprostanol (fecal steroid), triclosan (antimicrobial disinfectant) and so on **(Kolpin et al., 2002).** The existence of these pharmaceutical compounds in water has raised serious health concerns worldwide. Their presence even in small traces can affect the aquatic and terrestrial ecosystem **(Schwartz et al., 2003; Alexy et al., 2005).** Major health issues due to pharmaceutical pollution in water including gentoxicity, aquatic toxicity endocrine disruption. Concerns about their prospective risk firstly across in 1999 with the complication of feminization of living in the downstream of wastewater treatment plant (WWTP) owing to the presence of pharmaceutical compounds in river **(Yang et al., 2017).**

Till now, conventional biological and chemical water treatment methods are being used for the removal of recalcitrant organic pollutant from waste water **(Gobel et al., 2007;Stackelberget al., 2007).** Due to their persistent and non-biodegradable nature, these methods they are not able to remove the pollutant completely from water. Instead, convert the pollutant from one form to another form. The other complications associated with these methods are: (a) higher energy consumption, (b) production of large amount of sludge, (c) operational problems like foaming and bulking in secondary clarifiers **(Sreekanth et al., 2009;Kositzi et al., 2005; Oz et al., 2005).** Thus there is an urgent requirement of some alternative method which can degrade the recalcitrant organic pollutant like pharmaceutical completely shown in fig 2.1.

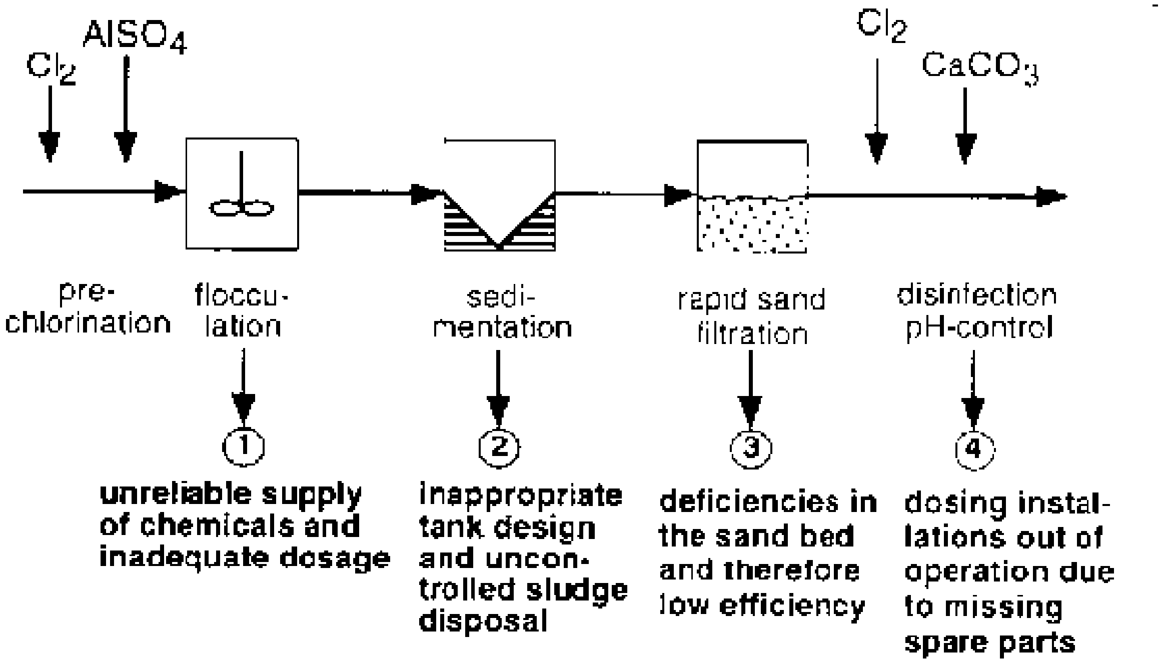

Fig. 2.1: Problems related to conventional treatment methods.

Advanced Oxidation Processes (AOPs) have been demonstrated as the most promises technologies for the treatment of waste water containing recalcitrant compounds **(Radenovic, 2009).** The main mechanism of AOPs is the generation of highly reactive free radicals like hydroxyl radicals ($OH^{\bullet}$) which can effective in degrading natural chemicals due to their high reactive electrophilic behavior. Among various AOPs, heterogeneous processes like photocatalysis and photo-Fenton have shown high potential for degradation of wide range of organic pollutants in water (**Konstantinou and Albanis, 2005; Glaze et al., 2000).**

TiO_2 is the most commonly used catalyst in heterogeneous photocatalytic processes due to its low cost, easily available, non-toxic and photocatalytically stable nature **(Pekakis et al., 2006).**TiO_2photocatalysis involve both photo-oxidation and photo-reduction (redox) reactions for the generation of hydroxyl radicals ($^{\bullet}OH$) as shown in fig. 2.2.There are numerous of studied reported in literature **(Sadik et al., 2007)** for the photocatalytic degradation of majority of organic pollutants using suspended TiO_2. The catalyst separation from aqueous solution post-treatment is the main implication that limits its practical applications. Though fixed-bed photocatalysis has also been practiced in various studies **(Daneshver et al., 2005; Verma et al., 2015; Bansal and Verma, 2017)** durability and stability of immobilized catalyst is always the major concern. The other problem that is faced in photocatalytic processes is the recombination of electrons and holes which slow down the degradation process.

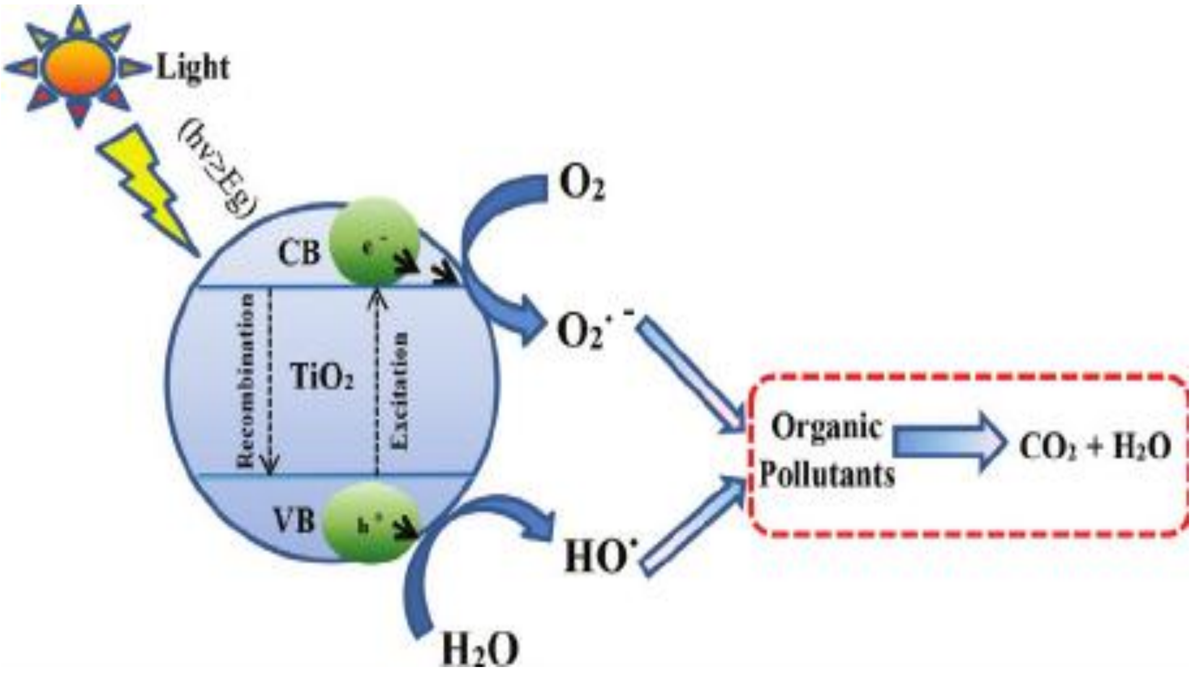

Fig. 2.2: Mechanism of TiO_2photocatalysis.

Among AOPs another treatment technology that has been extensively used is photo-Fenton process for the degradation of recalcitrant pollutants **(Titus et al., 2005).** Fenton reagent (Fe^{2+} +H_2O_2) leads to the generation of hydroxyl radicals at acidic pH as shown in reaction. However, the study main drawbacks of this process are the formation of iron sludge along with incomplete mineralization of pollutant.

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$

$Fe_2^{+} + H_2O_2 \rightarrow Fe^{3+} + {}^{-}OH + OH^{\bullet}$

Many efforts have been reported **(Neyens and Baeyens, 2003; Machulek et al., 2007)** to overcome the limitation of photocatalysis and photo-Fenton process. There are recent studies where integration of two processes like photocatalysis and photo-Fenton in the same unit have been highlighted attaining higher degradation efficiency. The dual process leads to the production of hydroxyl radical in abundance. These active radical are generated not only through TiO_2photocatalysis but also from photo-Fenton and iron oxide catalysis

(Bacardit et al., 2007). Moreover, dual process prevents frequent recombination of electrons and holes by engaging the photo excited electron from surface of TiO_2 in the production of Fe^{2+} ions which contribute to simultaneous photo-Fenton reaction. Though better degradation efficiencies have been achieved in literature practical applicability of process is still debatable. There are very rare studies which deal with complete immobilization of both catalysts (iron and TiO_2) for the degradation of pollutant.

Taking into account the above discussed flaws of individual processes, the current study has introduced the concept of dual process (photocatalysis and photo-Fenton) in the same treatment unit both in slurry and fixed form for the degradation of persistent drug, Phenazone. This is the first reported study where detailed degradation and mineralization of Phenazone has been discussed through individual processes (photocatalysis and photo-Fenton) as well as through coupling of these processes.

Chapter 3

REVIEW OF LITREATURE

Since 21^{st}centuary,the problem of pharmaceuticals and personal care of products as toxic substances in the environment arises which increases the need to assess their environmental risk. The existence of drugs in surface water **(Boud et al., 2003),** groundwater **(Ahel et al., 1998; Clara et al., 2005)** isdue to excretion of durgs in original form. Amoxicillin, fluoxetine, ibuprofen are widely used pharmaceutical durgs which are reported to affect aquatic systsm.

3.1 Environmental impacts of Pharmaceuticals Effluent

A severe concern is raised by large number of pharmaceutical industries which produce and consume large quantities of drugs.Within these categories, two types of pharmaceuticals are there, one is antimicrobials and the other is endocrine disrupting chemicals (EDCs). There is a large amount of these drugs released into the environment. Effluent from pharmaceutical industry, sewage treatment plants, hospitals and homes, several drugs are dumped into surface and ground water which causes contamination in drinking water as shown in fig. 3.1.

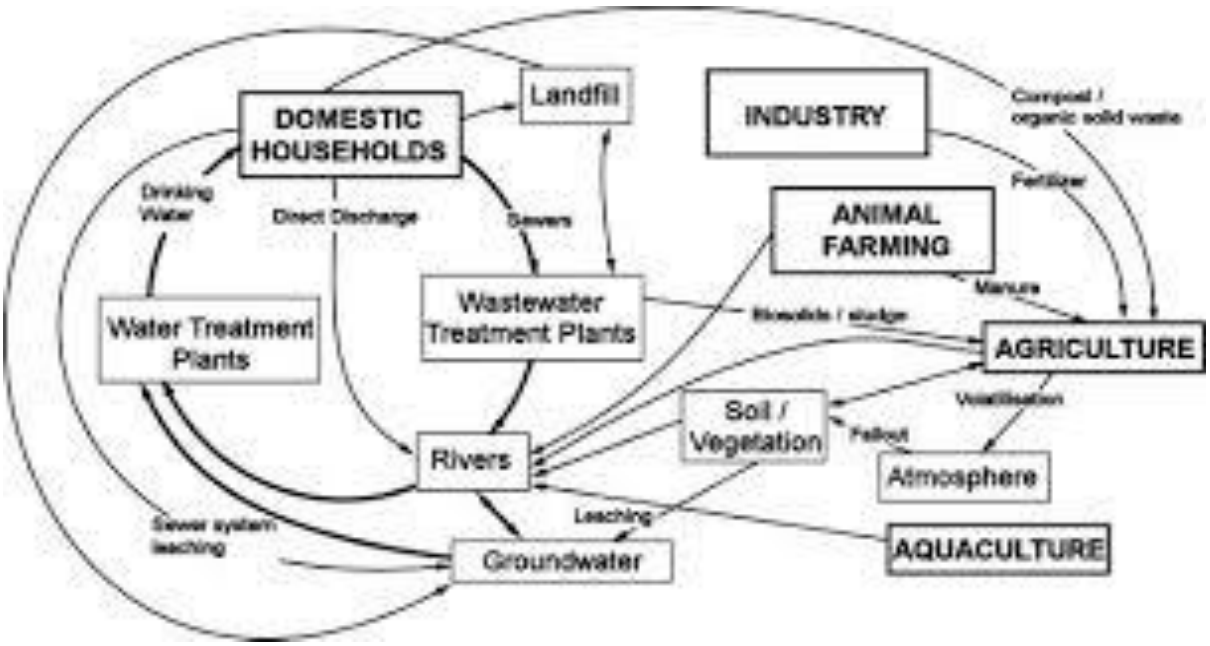

Fig 3.1:Various routes through which pharmaceutical compounds enter the water cycle.

Antibiotics, as medicines are largely consumed by Indians. Among all antibiotics, penicillin occupies an important place due to its high consumption rates in all places of the country. Phenazone is synthesized by the condensation of phenyl hydrazine and ethyl acetoacetate, is a non-steroidal antipyretic and anti-inflammatory drug.

Table 3.1: Chemical characteristics of Phenazone

IUPAC name	1, 5-Dimethyl-2-phenylpyrazol-3-one
Molecular formula	$C_{11}H_{12}N_2O$
Molecular weight	188.225g/mol
Appearance	White crystalline solid

It is widely used to treat diseases such as fever, body pain and infections of ear, skin. The presence of antibiotics have been confirmed in hospital, municipal wastewater **(Brown et al., 2006)**, surface water **(Anderson et al., 2005; Cahill et al., 2005)**, groundwater (**Cahill et al., 2005)** and even in drinking water **(Jones et al., 2005)**. Generally, methods used for the treatment of wastewater containing pharmaceuticals include physio-chemical and biological treatment methods. A physico-chemical technique, conventional method includes chemical removal, activated carbon and chlorination **(Deegan et al., 2011; Eddy and Metcalf, 2005)**. These methods do not easily remove the pollutants completely. There are several drawbacks which lead to the emergence of new alternative techniques.

3.2 Advanced Oxidation Processes (AOPs)

AOPs are oxidative methods which involves the formation of intermediate radicals or the hydroxyl radicals (OH•). Its standard oxidation potential being greater than the conventional oxidants makes them highly effective in the oxidation of a number of organic compounds **(Hernandez et al., 2002; Bautitz and Nogueira, 2007)**. These radicals are generated from oxidizing agents such as ozone or hydrogen peroxide, which are generally combined with metallic or semiconductor catalysts and UV radiation. Various techniques comes under AOPs like Fenton, photo-Fenton, cavitation, ozonation and photocatalysis may vary with the source of radicals **(Kim and Ihm, 2010)**.

3.2.1 Heterogeneous photocatalysis

Photocatalysis is defined as ‘‘change in the rate of a chemical reaction or its initiation on exposure to ultraviolet, visible or infrared radiation in the presence of the photocatalyst which absorbs light quanta”**(Braslavsky, 2007).** In 1972, Fujishima and Honda discovered the possibility of water splitting by means of a photo electrochemical cell consisting of a rutile TiO_2 photo anode and a Pt counter electrode, **(Fujishima et al.,2008).** This discovery prompted new applications such as air purification, self-cleaning surfaces, organic synthesis, disinfection, and anti-cancer therapy. An interesting application of this discovery is in water purification. Degradation of various organic target compounds such as dyes, pesticides and pharmaceuticals has been demonstrated.

Most common heterogeneous photocatalysts are transition metal oxides and semiconductors, which have their unique characteristics. When a photon with energy equal to or more than the materials band gap is absorbed by the semiconductor, an electron is excited from the valence band to the conduction band, generating a positive hole in the valence band**(Lhomme et al.,2008).** The excited electrons and holes combine and release energy which is gained during the excitation of the electron as heat. Excitation recombination sometimes leads to an inefficient photocatalyst. Due to this reason efforts are being done to develop functional photocatalysts for extending exciton lifetime and improving electron-hole separation by using some approaches.

Verma et al.,2011 investigated the photocatalytic degradation of malathion using TiO_2 in aqueous phase under artificial UV-A and solar light .The optimum operating condition for better degradation was 0.3 g/L TiO_2, pH 6 and 2.5 mL H_2O_2 at which 65% degradation was achieved in artificial UV –A. It was observed that better results were obtained in natural solar light irradiation (80%) than the artificial UV-A light.

Many pharmaceutical compounds have been found in the environment in which ibuprofen (IBF), is one of the most consumed medicine. The degradation efficiency of IBF was investigated under TiO_2/UV radiation. At optimum condition, degradation of IBF using 20 mg/L of TiO2, pH 7.8 and 5 mg/L was achieved in less than 60 min of irradiation. **(Braz et al., 2015).**

3.2.2 Fenton and photo-Fenton

The reaction between addition of H_2O_2 and iron was first described by the Fenton in 1895. Fenton and photo-reaction depends not only on the amount of H_2O_2 and iron added but also depends upon the operating pH value. A homogeneous photo-catalytic degradation of H acid was done using Advanced Oxidation Processes (AOPs) such as UV, UV/H_2O_2, UV/H_2O_2/Fe^{2+} (photo-Fenton process). The experimental results showed degradation of dyes under UV light at pH= 3 after 90 min**(Kumar et al.,2011).**The degradation of the pharmaceuticals was done by using very low concentrations of reagents (Fe (III) and H_2O_2). The Fluoxetine degradation was strongly favoured with iron citrate. Ciproflaxin degradation was only little bit increased with iron citrate degrading to 86 % with Fe cit and 75 % with Fe $(NO_3)_3$, after 20 min. However, during photo-Fenton process the redox iron cycle was not influenced by the HE content**(Joao et al., 2017).**

Advanced Oxidation Processes like photo-Fenton represents promising strategies for pathogen inactivation in wastewater effluents. The use of Fe(II) salts, under any combination of H_2O_2concentration, sunlight irradiance or starting pH (6–8), induced a faster inactivation compared to their Fe(III) counterparts. Moreover, ICP-MS analyses revealed that starting with Fe(II) which has higher amount of iron in solution than Fe(III), which led to higher inactivation kinetics. Even so, a 5-log MS2 inactivation was achieved upon exposure to 600 W/m^2 for 30 min in presence of Fe(III) and H_2O_2(1:1 ratio). Furthermore, the inactivation of MS2 was only slightly decreased in presence of the bacterial host, suggesting a low competition for the oxidants in the bulk. The enhancement of iron solubilisation through its complexation by organic matter present in wastewater was also investigated, observing an efficient viral inactivation despite the presence of reactive oxygen species (ROS) scavengers. The present data propose a simple model for describing MS2 photo-Fenton inactivation in wastewater. Finally, the pathway describing the photo-Fenton-induced MS2 inactivation in wastewater was proposed, in presence or absence of bacteria.

3.2.3 Fixed-bed photo catalysis

UV/TiO_2 systems are mostly used in suspension. The main problem that arises in slurry mode is the filtration of catalyst. TiO_2 is the most efficient widely used catalyst in heterogeneous photo catalysis, it can be fixed on various supports like clay, polythene film, pumice stone, and stainless steel, silica. Several studies are described in literature using TiO_2 in the fixed-bed mode for treating the waste water **(Madani et al., 2006).**

The purpose of this work was to examine the treatment of wastewater coming from pharmaceutical industries through a continuous heterogeneous catalytic wet peroxide oxidation (CWPO) process using Fe_2O_3/SBA-15 Nano composite catalysts. To elucidate the influence of significant variables on the oxidation system such as temperature, pH and oxidant concentration effect on the degradation of pharmaceutical compound was observed from wastewater **(Melero et al., 2009)**.

The fixed band photocatalytic degradation of fungicide utilizing catalyst coated spherical cement beads has been examined. The reduction in TOC and COD along with the production of nitrate and nitrite under the optimized conditions confirm the mineralization **(Singh et al., 2017)**.

Various supports of TiO_2

TiO_2 coating was done on stainless steel coupons and on glass beads using sol-gel technique and Degussa P-25 powder enriched method. Both these techniques were in comparison. Stainless-steel coupons coated with TiO_2 were used in the quartz reactor for the removal of organic pollutants found in water **(Balasubramanian et al., 2005).** During experiments, the agglomeration of particles might also block the lively websites of the catalyst, which is believed to make a contribution to its instability. Recently, titanium oxide (TiO_2) became an alternative support for heterogeneous catalyst. TiO_2 supported steel catalysts have attracted interest due to TiO_2 nanoparticles excessive hobby for numerousdiscount and oxidation reactions at low pressures and temperatures. The aforementioned residences make heterogeneous TiO_2 supported catalysts, shows as an excessive capability in photocatalyst-related packages, electrodes for moist sun cells, synthesis of quality chemical compounds, and others. This assessment focuses on TiO_2 as a fabric for heterogeneous catalysts and its ability packages. **(Samira Bagheri et al., 2015).**

Dual effect

Bansal et al., 2016 investigated to reduce the treatment time for degradation of pentoxifylline (PEN) using novel $FeTiO_2$ complex by dual effect (photo catalysis and photo-Fenton). Waste Foundary sand (FS) and fly ash (FA) was used as alternative iron source along with TiO_2. Initially, dual effect was executed in slurry mode where 59% synergy was obtained for degrading PEN and also caused the reduction in treatment time from 90 to 30 min. In the subsequent experiments, FA/FS was entrapped in small pockets made of fine cotton cloth keeping TiO_2 either in suspension or immobilized on clay beads. Significant improvements over the first order rate constant (k) were achieved for the dual process along with reduction in treatment time. Even two to three fold increases in ‘k’ was observed using novel Fe-TiO_2 complex for the degradation of PEN confirming in-situ dual effect. The existence of TiO_2 as well as iron on the complex surface even after 55 recycles was confirmed through SEM/EDS, XRD and diffuse reflectance spectroscopy. The mineralization of PEN was validated by reduction in COD and TOC along with the production of several anions. While intermediates formed during the degradation of PEN were identified through GC–MS analysis.

The photocatalytic degradation of non-biodegrable azo dye acid orange was performed through a heterogeneous Fenton-like process utilizing (Fe-TiO_2 NIAs) as a photocatalysts in the presence of H_2O_2 under UV light **(Yufeng et al., 2015)**.Various other similar studies are also reported in literature **(Mazille et al., 2009, 2010; Sakhtivel et al., 2003)** using the concept of dual effect in slurry mode for the degradation of various organic pollutants. These all studies have reported the synergistic effect of dual process for the degradation of pollutants. None of these studies reports on the complete immobilized system for dual effect studies thus limiting their field-scale applications.

Though there are numerous of studies reported in literature for the treatment of pharmaceuticals through advanced oxidation processes, there are very less studies using the concept of dual effect for treating recalcitrant pollutants. There is need to undergo extensive research in this area to explore its field-scale applications.

Research gap

There are limited studies on the degradation of compounds like Phenazone through photocatalysis and photo-Fenton.

There is still scope of research in selecting the suitable technique for the reduction in treatment time of recalcitrant compounds.

The concept of dual effect (photocatalysis and photo-Fenton) in fixed mode has not been discussed yet.

The loss in activity of photocatalyst has been observed after few recycles of the catalyst immobilized support materials in most of the reported studies.

Chapter 4

OBJECTIVES

Based upon the literature study following objective have also been studied.

1. Photocatalytic degradation of Phenazone with process optimized by varying pH, oxidant dose and catalyst dose.
2. Heterogeneous photo-Fenton degradation studies for Phenazone using waste foundary sand.
3. In-situ dual effect degradation studies of Phenazone using both slurry and fixed-bed approach.

Chapter 5

MATERIALS AND METHODS

This study includes a number of analytical techniques required for the study of the compound and to follow its degradation pathway. Standard methods have been used throughout the study and all equipment's were calibrated before use.

5.1.Pharmaceutical compound

Phenazone ($C_{11}H_{12}N_2O$) as show in fig. 5.1, having molecular weight 188.23 and density 1.07 g/cm was purchased from Loba Chemicals (India). Stock solutions of 50ppm were prepared in distilled water stored in the volumetric glass flask. Phenazone widely used as a pain reliever. Due to its high stability and low biodegradability it is difficult to remove it from wastewater through conventional techniques.

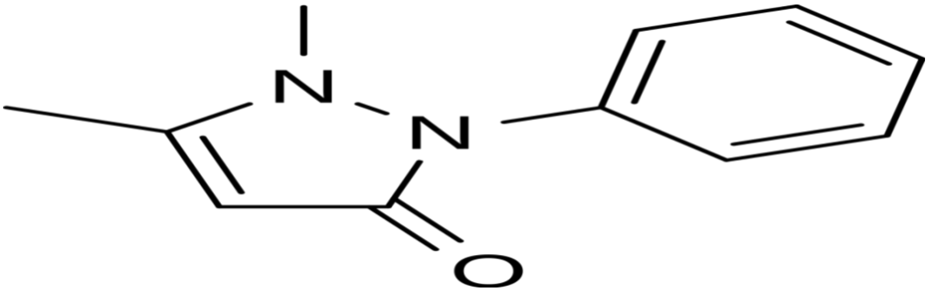

Fig. 5.1: Chemical structure of Phenazone

5.2 Reagents and chemicals

Degussa P25 TiO_2, purchased from Evonik industries, India, was used as a catalyst. Hydrogen peroxide (H_2O_2), 30%w/v, was used as an oxidant which is obtained from Ranbaxy, India. Waste Foundary sand (FS) were collected from industry, Gurgaon, India. Clay used for making plates was obtained from local vendor, Patiala, India. Sodium acetate (98.5% purity) and acetic acid (99.5% purity) used for the preparation of acetate buffer were procured from TCI Chemicals, India. The concentrated solutions of HCl and NaOH is used for maintaining the pH. The double distilled water was used for preparation of all solutions.

5.3 Instrument used

5.3.1 pH meter

The pH of the soution was adjusted by the help of pH meter purchased from Eutech Instrument was calibrated with freshly prepared buffer solutions (pH 5 and 9) from time to time throughout study.

5.3.2 UV-Vis Spectrophotometer

UV-Vis (Hi tachi V- 500 UV/VIS, Japan) spectrophotometer was used for Phenazone photo degradation analysis .

5.3.3 Branson bath sonicator

Ultrasonic bath Tank model no. EN 60 US) with frequency of 33 KHz was used for homogenization of catalyst suspension in the process of catalyst coating on different supports.

5.3.5 Solid spectra and XRD pattern

For the determination of deformity in the structure of catalyst before or after subsequent treatment cycles, UV Spectrophotometer(Shimadzu UV 2550, Japan) and XRD Model X Pert PRO from PANanalytical,Netherland has been used through the analysis of fresh and recycled TiO_2.These techniques were applied to study the recycling feasibilities.

5.3.5 GC-MS analysis

The scan mass range varied from 70 to 400. Heleium gas having flow rate of 1.0ml/min utilized as a carrier gas. The temperature was set at 280^0C.The temperature program for GC oven was balanced in the range of 40^0C to 260^0C with 10^0 heighting in temperature. The volume of test utilizing for infusion was 1.0 micro litre and 1-10 GC split proportion was utilized. For the confirmation of intermediate products during the photocatalytic degradation of Phenazone, the GC-MS was performed.

5.5 Experimental setup and procedure

5.5.1 Lab scale reactor setup

UV (photo-Fenton and photocatalysis) treatment of Phenazone was carried out in wooden chamber. Roof of reactor was equipped with seven UV tubes (36W) and maximum wavelength at 365nm. Temperature of 25^0C was maintained inside the reactor through an exhaust fan.

Glass bowl (1200mL capacity, 17cm diameter and 5cm height) as batch reactor was used. The solution was magnetically stirred throughout the reaction. Phenazone working solution was made by dissolving a 50 mg of Phenazone in 1000mL double distilled water . The solution was prepared weekly and stored at room temperature. For the photocatalytic experiments, 200 mL of the stock aqueous solution was taken in a reactor with required amount of TiO_2 and was magnetically stirred under UV irradiation. While for the heterogeneous photo-Fenton experiments, 200 mL of the stock aqueous solution was taken in a reactor with required amount of FS and was magnetically stirred under UV irradiation. An aliquot of 3-5 mL sample was collected from reaction vessel at regular time intervals using a syringe and filtered through a Millipore filter (0.55 µm). Fig.shows the pictures of the slurry batch reactor setup in artificial UV light. The process was optimized by varying the parameters like catalyst concentration, amount ofH_2O_2, pH, UV intensity, depth of the reactor based on which reaction kinetics was studied. All experiments were performed at three times for best accuracy of results.

Fig5.1: Lab scale setup of reactor in UV light

5.5.2 TiO_2 immobilization

Clay/FS disc was prepared manually using the mixture of clay and foundrysand (FS) followed by firing at high temperature (900-1000°C) for 2 h. These discs were then used for

TiO_2 coating (clay/FS/TiO_2). Standard dip coating method was employed by dipping the clay/FS discs in TiO_2 slurry (2%).Two coatings were sufficient for a uniform layer of catalyst on disc. The catalyst was coated on the disc in the form of film with average thickness of 50µm as confirmed from SEM-EDAX. Fig. 5.2 shows the image of TiO_2 coated Disc.

Fig, 5.2: The image of TiO2 coated Disc

5.5.3 Experimental procedure

Fixed-bed studies were performed using same batch reactor containing clay/FS/TiO_2 discand 200 mL of Phenazone solution and was irradiated by UV light. Aeration was provided by means of spargers and mixing was done using magnetic bead at a time. The samples were collected by means of a syringe at regular intervals.

Fig. 5.3: Fixed bed studies at Lab Scale in UV light.

Chapter 6

RESULT AND DISCUSSION

The degradation of target pollutant, Phenazone studied through different AOP's like heterogeneous photocatalysis, photo- Fenton and the combination of both processes in this chapter. The process has been optimized by varying certain operating parameters like concentration of H_2O_2, catalyst dose, pH.

6.1 Standard calibration curve of Phenazone

Standard calibration curve was prepared employing known concentration of Phenazone. A graph of absorbance versus concentration of Phenazone solution was plotted as shown in fig. 6.1. The concentration of Phenazone solution was varied from10 mgL^{-1} to 60 mgL^{-1}at 255 nm. The regression coefficient of curve was 0.995 and slope of curve 0.0533.

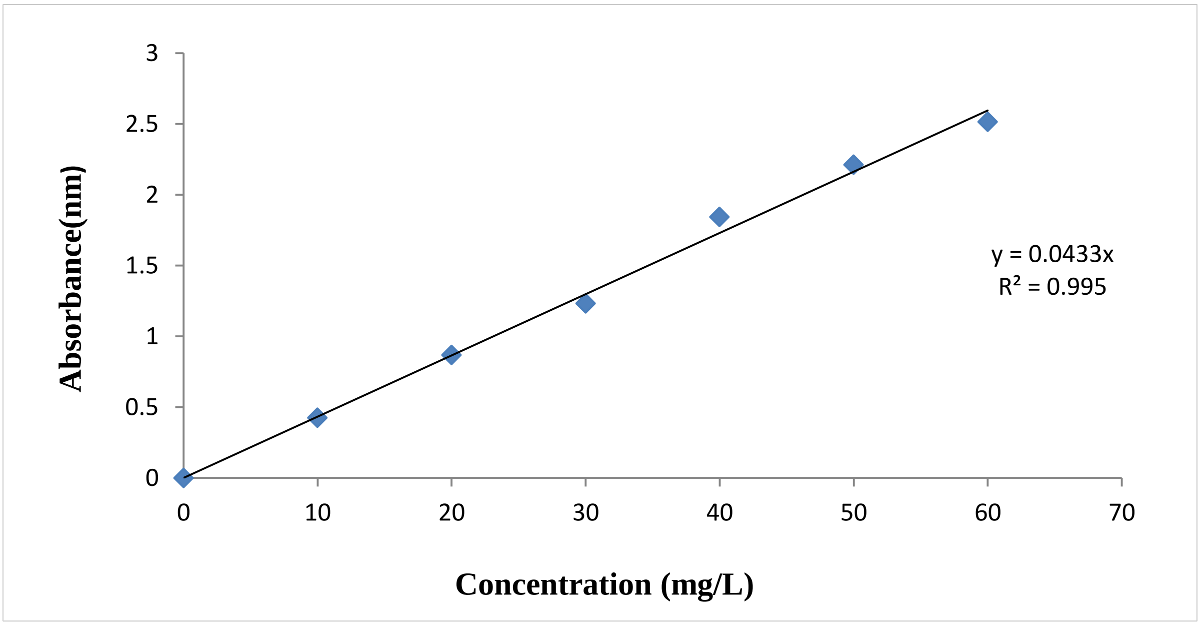

Fig. 6.1: Standard calibration curve of Phenazone.

6.2 Degradation of Phenazone through TiO_2 photocatalysis

6.2.1 Preliminary studies

Preliminary experiments were performed to check the impact of individual parameters on the degradation of Phenazone. A negligible amount of photo degradation (2-3%) was as certained when Phenazone solution was exposed to only Ultraviolet light (photolysis). Whereas surface adsorption studies (TiO_2 only) showed 93% reduction in concentration of the compound. The decrease in concentration of the compound is mainly due to adsorption on the surface of catalyst() Moreover, once H_2O_2 alone was used, degradation (1-2%) was achieved which can be follow due to the production of insufficient quantity of hydroxyl radicals. The photocatalytic treatment (UV + TiO_2 + H_2O_2) of Phenazone showed significant amount of degradation i.e. 93% after 180min (Fig. 6.2) because of the substantial increase in the generation of OH radicals. Thus, it leads to a proposition that adsorption-desorption of Phenazone and reaction intermediates is relatively slower than the formation of electron/hole pairs.

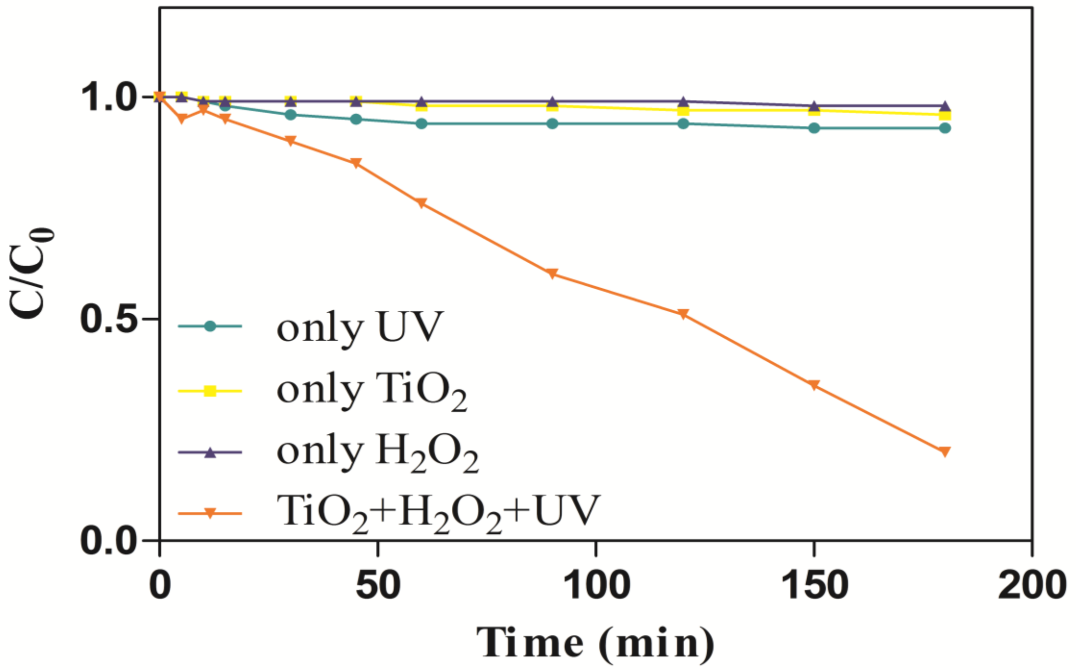

Fig. 6.2: Photocatalytic degradation of Phenazone in the absence and presence of TiO_2, UV and H_2O_2 .

6.2.2: Photodegradation Kinetics

Various kinetic models are outlined for the photocatalytic degradation of various organic pollutants. (Verma et al., 2013) Langmuir-Hinshelwood (L-H) mechanics model is the most acceptable model for nearly all photocatalytic reactions. In accordance with L-H model, the speed of degradation of organic pollutants is declared by equation

$-dC/dt = k_r KC/(1 + K C)$

Whereas,

k_r =the reaction rate constant,

K = the equilibrium adsorption constant,

C = substrate concentration at any time t.

Most of the photo catalytic experiments describe pseudo-first order kinetic expression which agree with L-H model for finding out the degradation rates of assorted organic pollutant over TiO_2equation , i.e.,

$-dC/dt = kC$

or $\ln C_0/C = kt$

The first order rate constant k was calculated from the slope of graph between $\ln C_0/C$ and time.Where

C_0 = initial concentration and

C = final concentration

6.2.3 Effect of TiO_2 dose

Optimum dose of TiO_2 is needed for the photocatalytic experiments to achieve best degradation efficiency. However, high concentration of catalyst isn't suggested because it becomes tough to separate the catalyst from suspension at higher concentration and furthermore, it makes the method additional expensive**(Killicet al., 2007).**Photocatalytic experiments were run for 3 hours with 0.050g/L of Phenazone at its natural pH i.e.5.In our study, the concentration of TiO_2 was varied from 0.125-1.5gL^{-1}. The graph between $\ln C_0/C$ vs time for varying dose of TiO_2 is shown in (fig. 6.3a)that represents nearly a straight line atall concentrations of TiO_2. The degradation rate constant , k is calculated for each TiO_2conentration(Fig. 6.3b). Fig. 6.3 b clearly indicate the photocatalytic rate constant of degradation initially increased from 0.035 to 0.077 min^{-1} with increasing dose of TiO_2upto0.375 gL^{-1} .There after the value of k decreases with increases in TiO_2 dose. This may be due to the decrease in penetration of light , rise in scattering of light and formation of aggregate of TiO_2 particles. Moreover, it leads to decrease in generation of OH radical. The best dose of photocatalyst was selected 0.375g/L at which (85%) degradation was attained after irradiation of 3 hours. The optimized dose (0.375g/L) was practically observed.

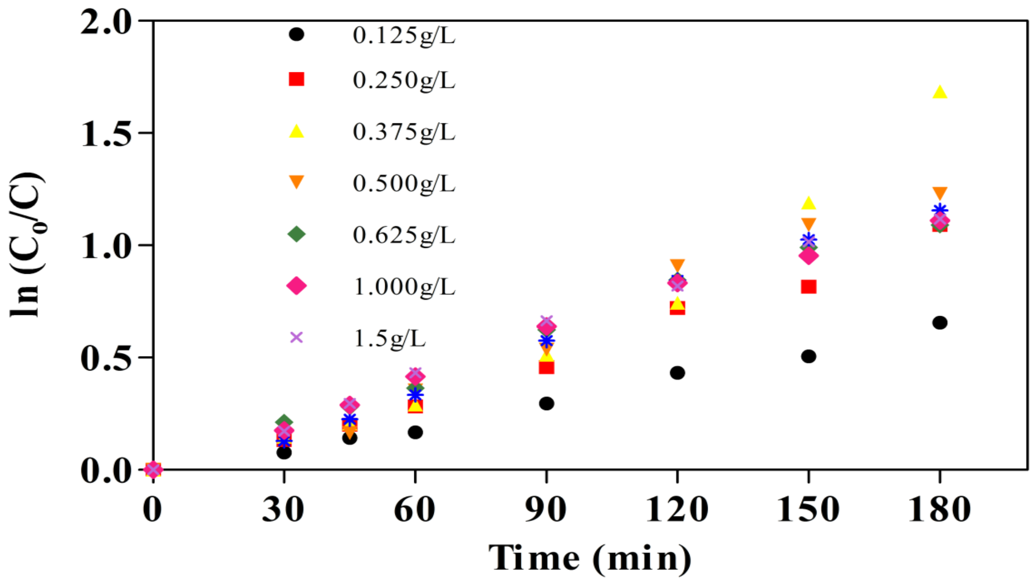

Fig. 6.3 (a) Plot of lnC_0/C vs time at different concentrations of TiO_2.

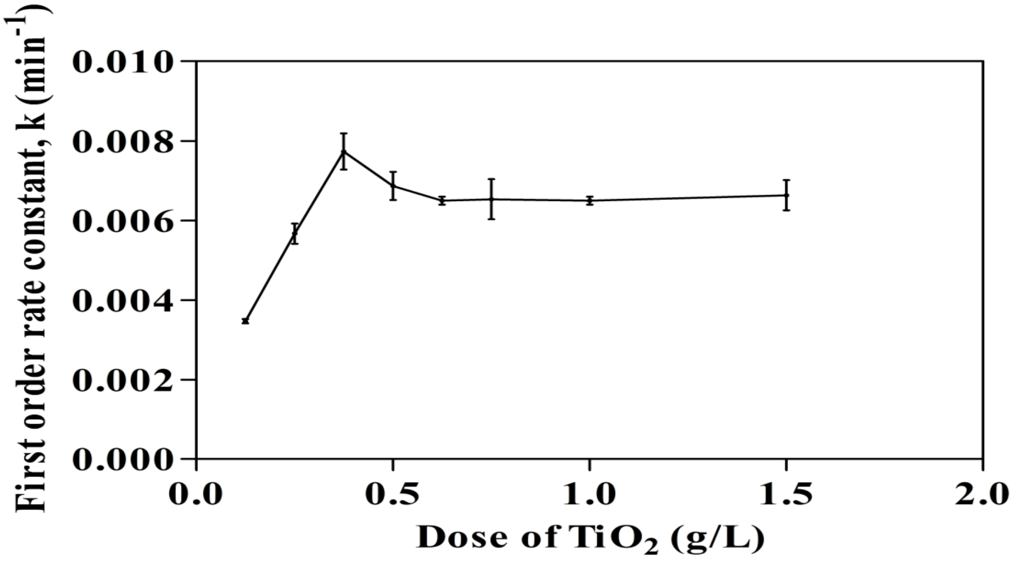

Fig. 6.3(b) Plot of first order rate constant, k vs variation in TiO_2 during photocatalytic degradation of Phenazone (C_0= 50 mg/L, V= 200 mL).

6.2.5 Effect of H_2O_2 dose

The addition of oxidant(H_2O_2) increase the range of photocatalytic degradation because its leads to the generation of OH radical after accepting photon excited electron from conduction band .It also generate OH radical according to the following reaction:

$H_2O_2 + {}^{\bullet}O_2^- \rightarrow {}^{\bullet}OH + OH^- + O_2$

The photocatalytic experiments were run by varying the concentration of H_2O_2 from 0.030 g/L to 0.3 g/L with optimized dose of TiO_2 which is 0.375g/L. The value of k is calculated from straight line of graph between ln (C_0/C) vs time (Fig. 6.5 a). The photo catalytic degradation rate constant increases from ($0.0095 min^{-1}$ $0.0127 min^{-1}$) with the increase in the dose of H_2O_2 in the range of 0.030 -0.075g/L (6.5 b). The percentage degradation of Phenazone increased from 85% to 95% at optimized dose of H_2O_2 i.e. 0.075g/L. The decrease in rate constant, k beyond 0.075g/L is due to the predominating scavenging of ${}^{\bullet}OH$ and hole which forms $HO_2^{\bullet}$ as shown in reactions at higher concentration of H_2O_2**(Zhao et al., 2005).**

${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$

$H_2O_2 + h^+ \rightarrow H^+ + HO_2^{\bullet}$

Thus the best dose of oxidant, H_2O_2selected was 0.075g/L which resulted in 95% of degradation after 180 min of irradiation at 0.375 g/L of TiO_2 at its natural pH i.e. 5.

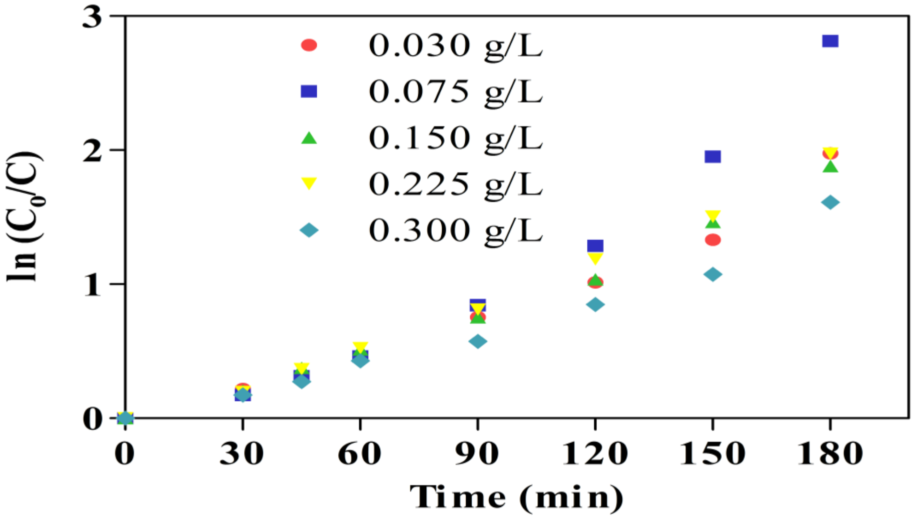

Fig. 6.5 (a) Plot of lnC_0/C vs time at different concentrations of H_2O_2.

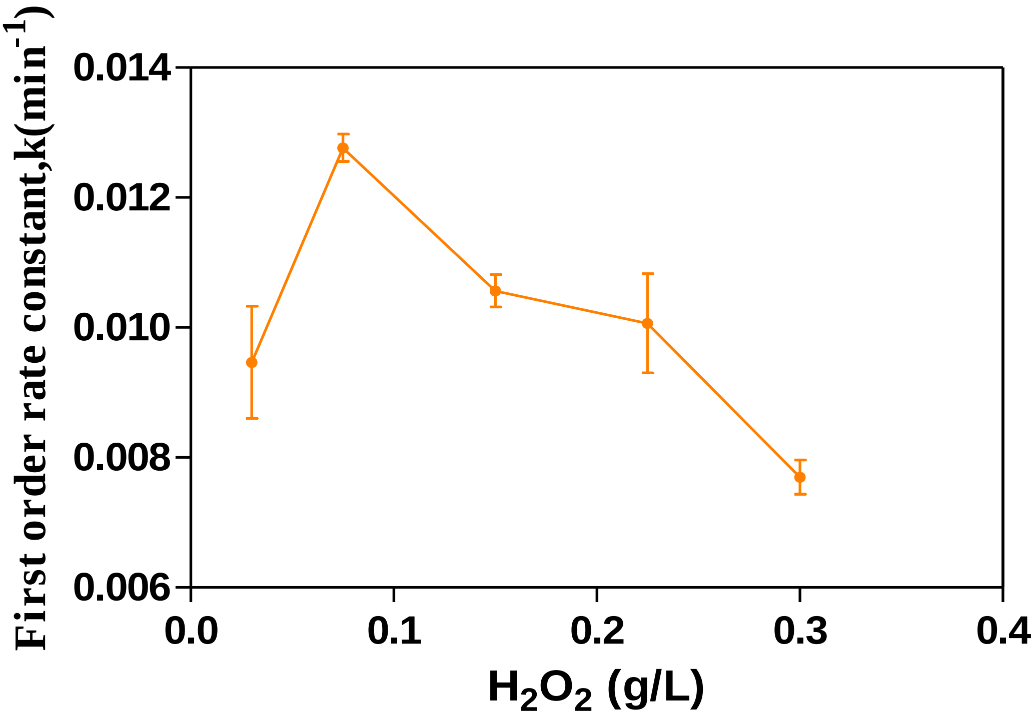

Fig. 6.5 (b) Plot of first order rate constant, k vs variation in H_2O_2 during photocatalytic degradation of Phenazone (C$_0$= 50 mg/L, V= 200 mL).

6.2.5 Effect of pH

To study the effect of pH on photocatalytic degradation rate ofPhenazone, pH was varied in the range 3-8 with optimized conditions i.e. TiO_2 0.375 g/L, 0.075 g/L of H_2O_2 with Co = 0.25g/L. The initial pH of the solution portrays the surface charge characteristics of catalyst and therefore adsorption of the compound can be depicted. The surface charge of TiO2 is positive at acidic pH and becomes negative at basic pH **(Toor et al., 2007)**. Thus, pH plays an important part in the adsorption/desorption characteristics of the photo catalyst.

A plot of ln C$_0$/C versus time at different pH values is shown in Fig. 6.5 (a). The rate of degradation was maximum at acidic pH i.e. 5. Thereafter, large decrease in the degradation rate was observed at alkaline pH as 'k' was significantly higher (0.0128min^{-1}) in acidic pH as compared to k value (0.0058min^{-1}) in basic pH as shown in fig. 6.5 (b). Decrease in degradation at higher pH may be due to the poor adsorption of pollutant on catalyst surface. All experiments were run at solution's natural pH i.e.5, at which approximately 95% degradation was attained under optimized conditions.

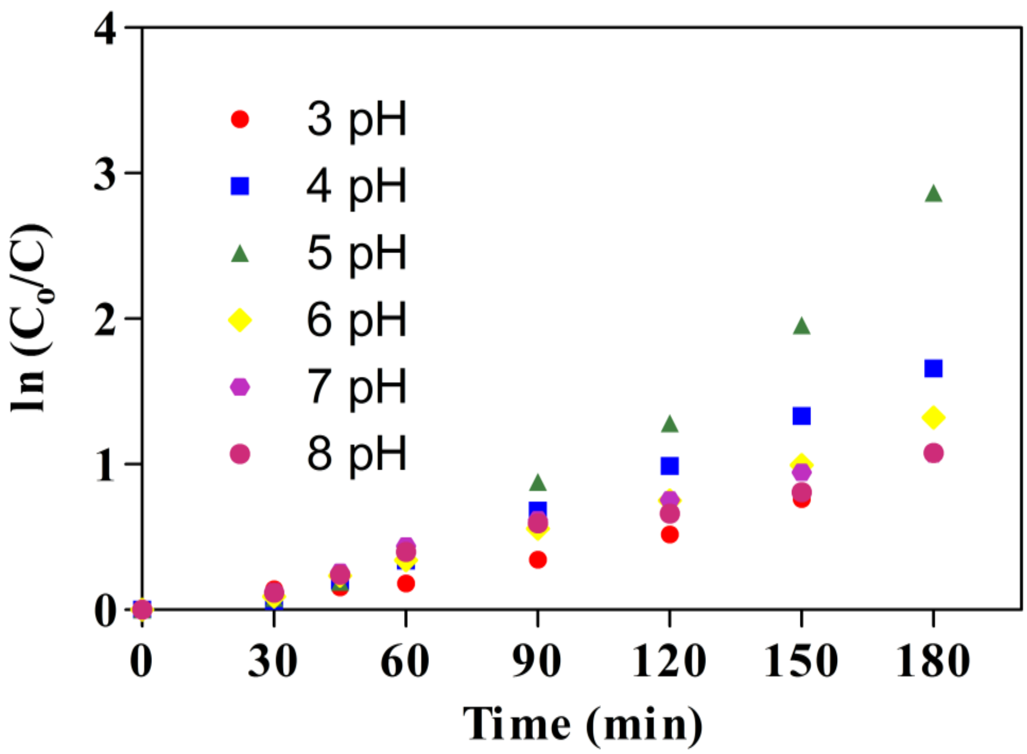

Fig. 6.5 (a) Plot of $\ln C_0/C$ vs time at different pH.

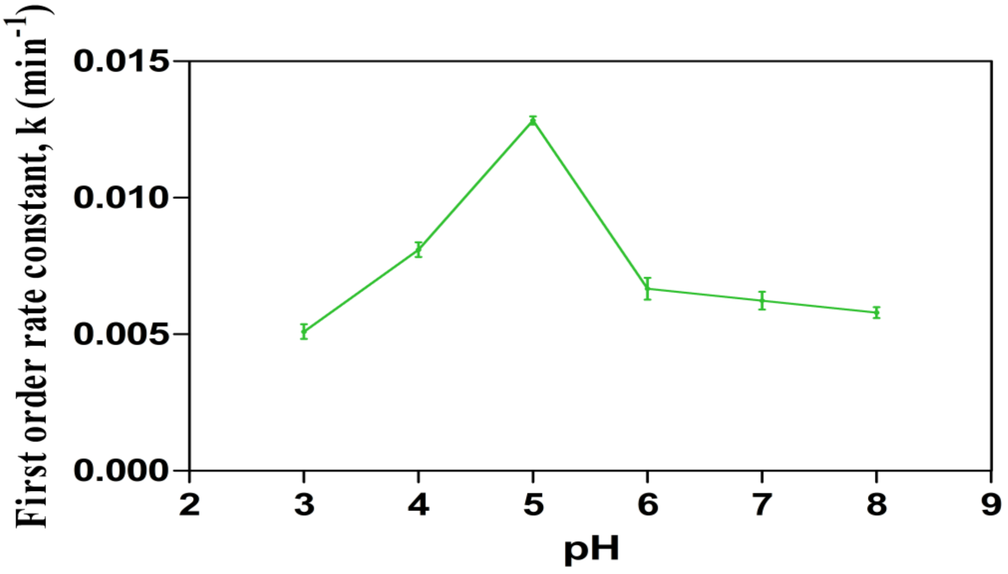

Fig. 6.5(b) Plot of first order rate constant, k vs variation in pH during photocatalytic degradation of Phenazone (C_0= 50 mgL-1, V= 200 mL).

6.3 Degradation of Phenazone through heterogeneous photo Fenton

6.3.1 Preliminary studies of photo-Fenton

Preliminary experiments were performed to check the effect of individual parameters on the degradationofPhenazone as shown in fig. 6.6. All experiments were conducted at acidic pH(pH=3) with 200 mL of Phenazone aqueous solution (50mg/L). Waste FS was used as a substitute for iron source in the present study. Adsorption studies were carried out in the presence of only FS which revealed 10% removal of Phenazone after 180 mins. Negligible amount of degradation was achieved in the presence of only H_2O_2(2-3%) and only UV light (5-5%). When all operating parameters were combined together significant amount of degradation (70%) was attained.

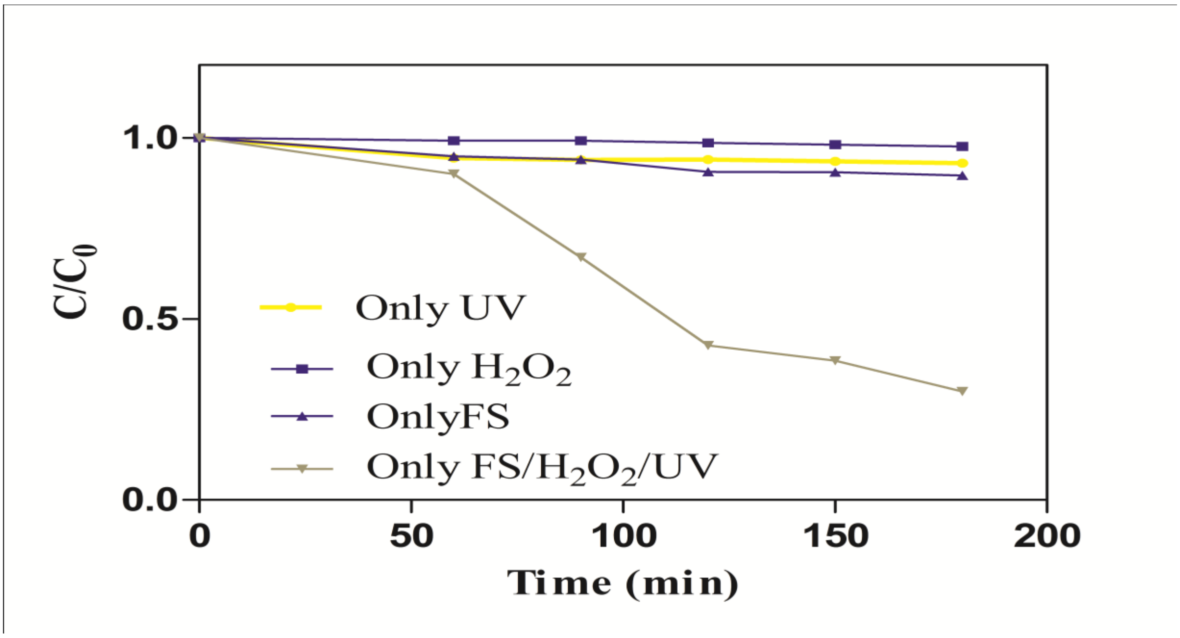

Fig. 6.6: photo-Fenton degradation of Phenazone in absence and presence of FS, UV and TiO_2.

6.3.2 Effect of Foundary sand dose

For degradation of Phenazone by photo-Fenton process ,the concentration of FS was varied from 0.250g/L to 1.0g/L.The removal efficiency of Phenazone was increased initially with increase the dose of FS upto 1g/L as shown in fig 6.7 a and 6.7 b. The possible justification for this intiailly increase in removal of Phenazone is the utilization of H_2O_2 by ferrous ions leading to the generation of hydroxyl radicals. While further increasing the dose of FS

(>1g/L) did not improve the degradation of Phenazone. It may be due to the prevailing scavenging effect of hydroxide radical there by reducing the removal efficiency. Thus , 1g/L of FS concentration was selected as optimized dose in our study at which almost 70% degradation of Phenazone was achieved after 180 mins. of Photo-Fenton treatment.

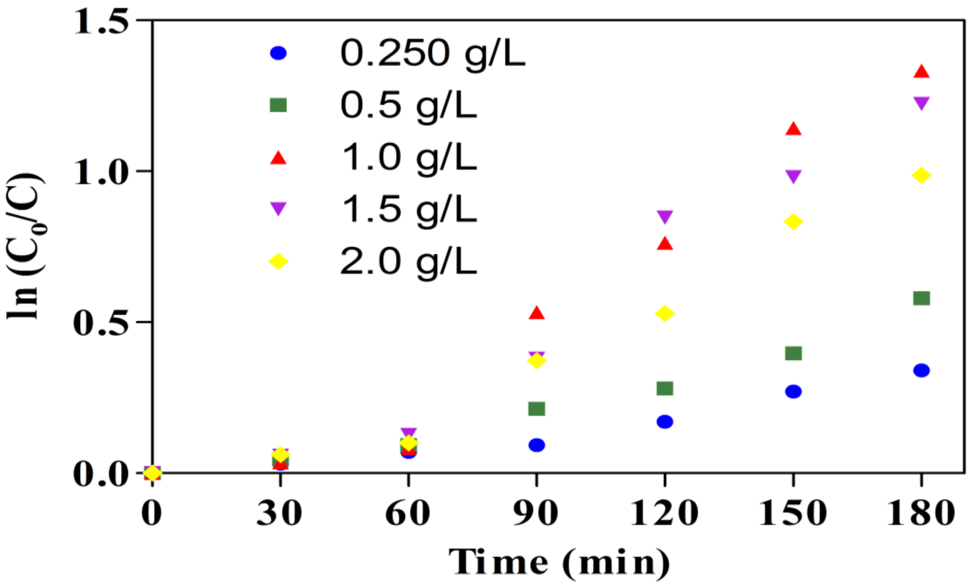

Fig. 6.6 (a) Plot of lnC_0/C vstime at different concentration of Foundary sand at pH3

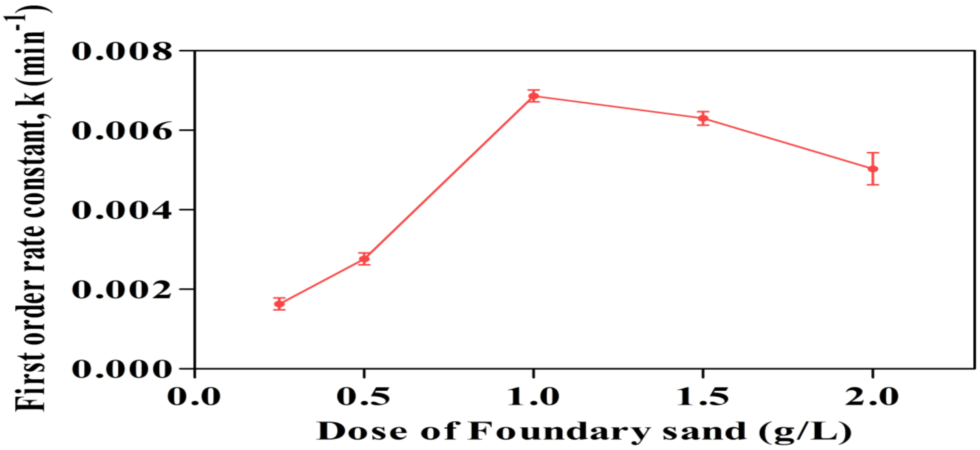

Fig. 6.6(b) Plot of first order rate constant, k vs variation in Foundary sand during photo-Fenton degradation of Phenazone (C_0= 50 mgL^{-1}, V= 200 mL,pH3).

6.3.3 Effect of H_2O_2

Fig. 6.7 (a) shows the degradation of Phenazone at various concentration of H_2O_2. The concentration of H_2O_2 varied in range from 0.075 g/L - 0.525 g/L. A plot of ln (C_0/C) for the effect of H_2O_2 variation is depicted in fig.(6.7a). It is now well established that the degradation increases on increasing the concentration of H_2O_2. In the present study optimum value at $H_2O_2$is obtained 0.550g/L. The maximum degradation of 93% was attained at 0.450 g/L dose of H_2O_2 within reaction time of 180 min. Suitable explanation for increase in degradation of Phenazone with initially increase in concentration of H_2O_2upto 0.450g/L is that more H_2O_2 molecules will be available to react with Fe^{2+} ions which further increase the number of hydroxyl radicals. The degradation rate constant increased from 0.0067min^{-1}to 0.0139as shown in Fig. 6.7b, with the addition of H_2O_2 in the range of 0.030 -0.450g/L. After that degradation rate constant started decrease with further increase in the concentration of H_2O_2.This is due to the consumption of all OH radicals by the H_2O_2 and there are very less OH radicals available which ultimately slow down the degradation process.

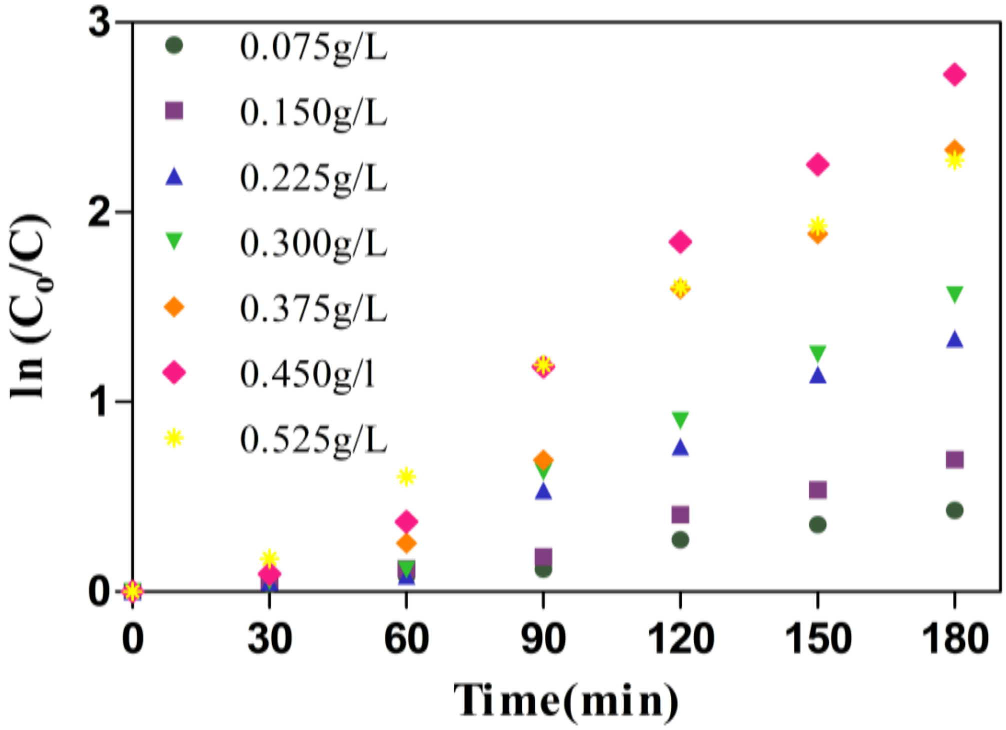

Fig. 6.7 (a) Plot of $\ln C_0/C$ vs time at different concentration of H_2O_2 at pH3 .

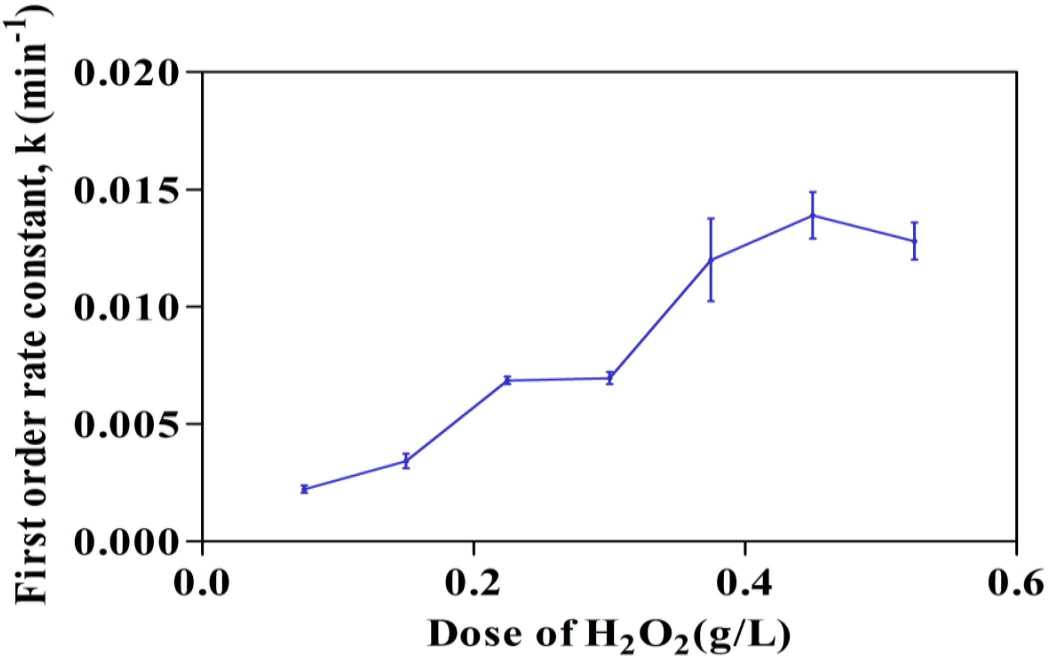

Fig. 6.7(b) Plot of first order rate constant, k vs variation in Foundary sand during photo-Fenton degradation of Phenazone (C_0= 50 mg/L, V= 200 mL,pH3).

6.5 In-situ dual effect studies for the degradation of Phenazone

6.5.1 Slurry mode

To further enhance the degradation of Phenazone trials were executed by conducting the experiments incorporating both photocatalysis and photo-Fenton in the same treatment. The experiments were performed with 50 mg/L of Phenazone aqueous solution in a batch reactor under UV light. The optimized dose of TiO_2(0.375g/L)in photocatalysis and Foundary sand (1.0g/L) in photo-Fenton with H_2O_2(0.550g/L) at pH 3 were taken for dual process . The dual effect studies accelerated the speed of the reaction with enhanced degradation rate constant i.e. 0.0305 min^{-1}.The treatment time was reduced from 3 hrs to 105 min. The rate constant was increased to 0.0310 min^{-1} from 0.0128 min^{-1}(photocatalysis) and 0.0139min^{-1}(photo-Fenton).The overall synergy of dual process for degradation of Phenazone was observed to be 13.87% as calculated from the following formula

% synergy = $100*\{(k_{\text{dual process}})-(k_{\text{photo-Fenton}} + k_{\text{photocatalysis}})\}/ (k_{\text{dual process}})$

= 100*{(0.0310)-(0.0128 + 0.0139)}/0.0310 =13.87%

In view of the practical applications the dual process was performed under natural sunlight as well at optimized conditions. The degradation was further enhanced in natural sunlight as 95% was achieved in 90 min instead of 105 min (artificial UV)as shown in fig. 6.9 which highlights the effectiveness of studied technique.

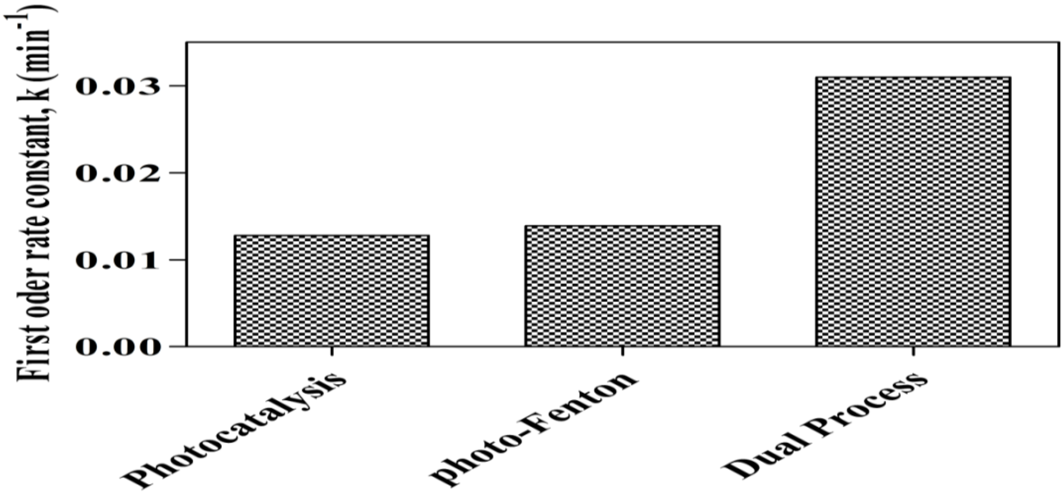

Fig. 6.8 (a): First order rate constant for the degradation of Phenazone through different processes in slurry mode.

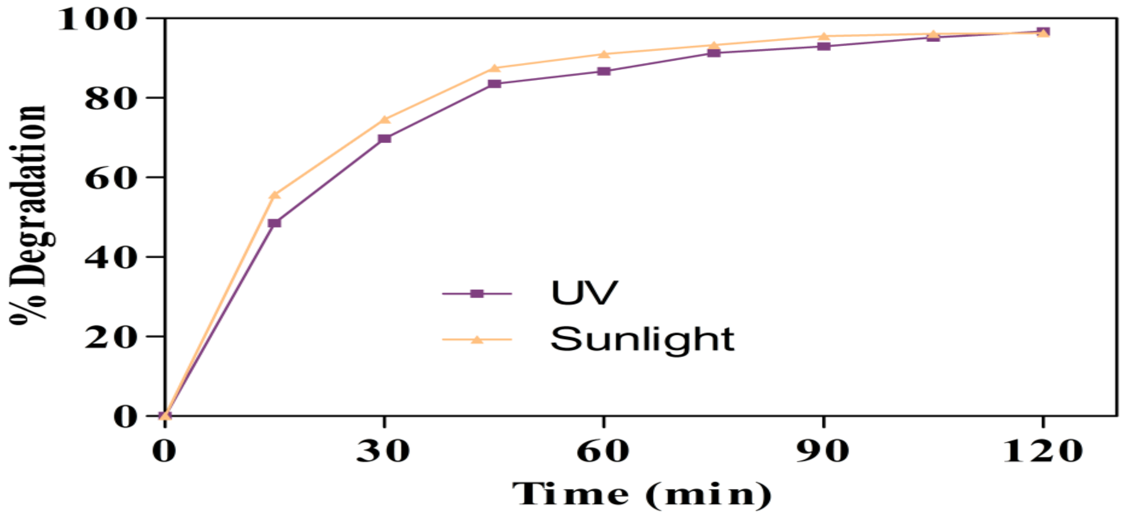

Fig. 6.8(b): Effect of artificial UV and natural solar irradiation on dual-effect degradation of Phenazone.

6.5.2 Fixed-bed Studies

To further increase the practical applicability of studied dual process, low cost fixed bed was designed. TiO_2 immobilized circular FS disc was utilized for fixed bed dual process in the present study (as discussed in section 5.5.2) .

The experiments were conducted with blank disc (clay/FS disc) at optimized condition to confirm the occurrence of photo–Fenton reaction, which revealed (63%) degradation of Phenazone after 5 hours. 67% degradation occurred when clay/TiO_2 disc was used which depicted photocatalytic process. While when clay/FS/TiO_2disc was used (95.88%) degradation occurred after 5 hours. Thus synergistic effect of in-situ dual process was proved as rate constant was also proved as rate constant was also increased from 0.005min^{-1} (photocatalysis, photo-Fenton) to 0.005min^{-1} in case of dual effect. There was no need to add any iron source separately as iron was found to leach out from disc in situ. The concentration of iron leached out in the solution at different time periods during the reaction was estimated as shown in table 2.

Table 2: The concentration of total iron leached out in solution from clay/FS/TiO_2 disc.

Time (min)	Concentration of Iron (mg/L)
30	0.776
60	1.36
120	2.27
180	1.55
250	0.69

To further optimize the fixed-bed dual process, H_2O_2 was varied from 0.550g/L to 1.500g/L. As H_2O_2 was increased from 0.1053min^{-1} to0.3159min^{-1}, degradation increased. Thereafter, degradation rate started declining due to the prevailing scavenging effect. A plot of$\ln C_0/C$ vstime for varying H_2O_2 dose is shown in fig.6.9(b). Conclusively, 1.350g/L was selected as optimal dose in our study.

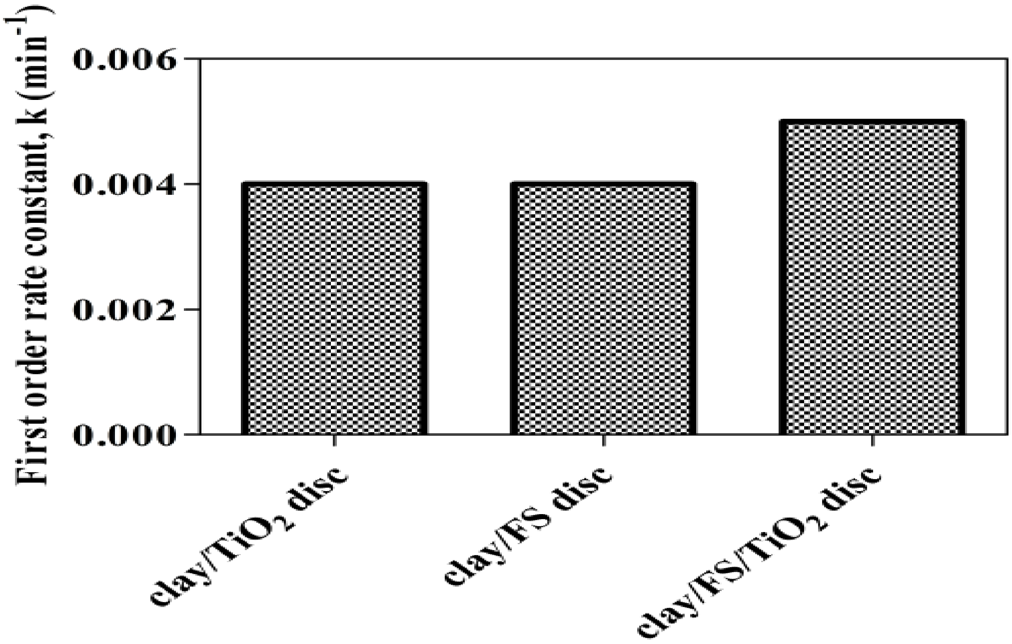

Fig.6.9(a): First order rate constant for the degradation of Phenazone through different processes in fixed bed.

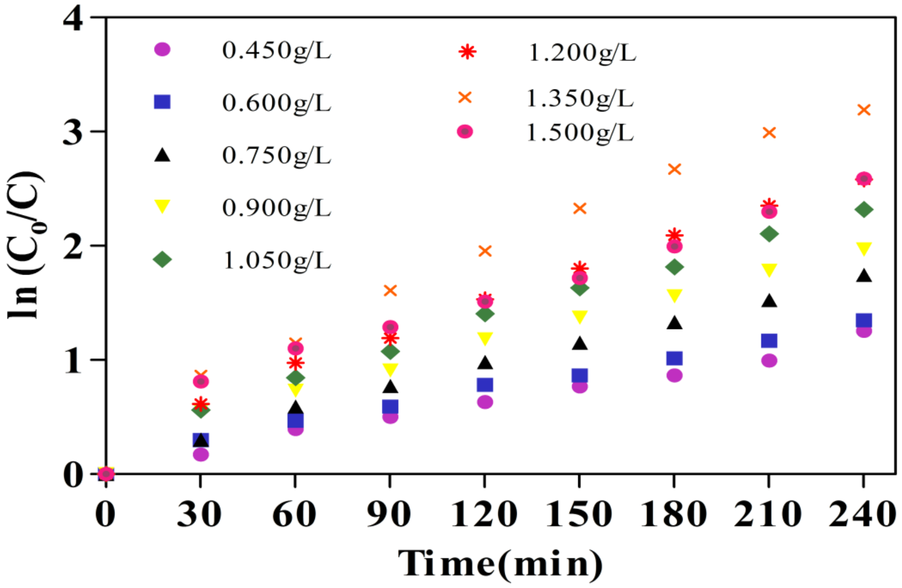

Fig. 6.9 (b) Plot of lnC_0/C vs time at different concentration of H_2O_2 at pH3

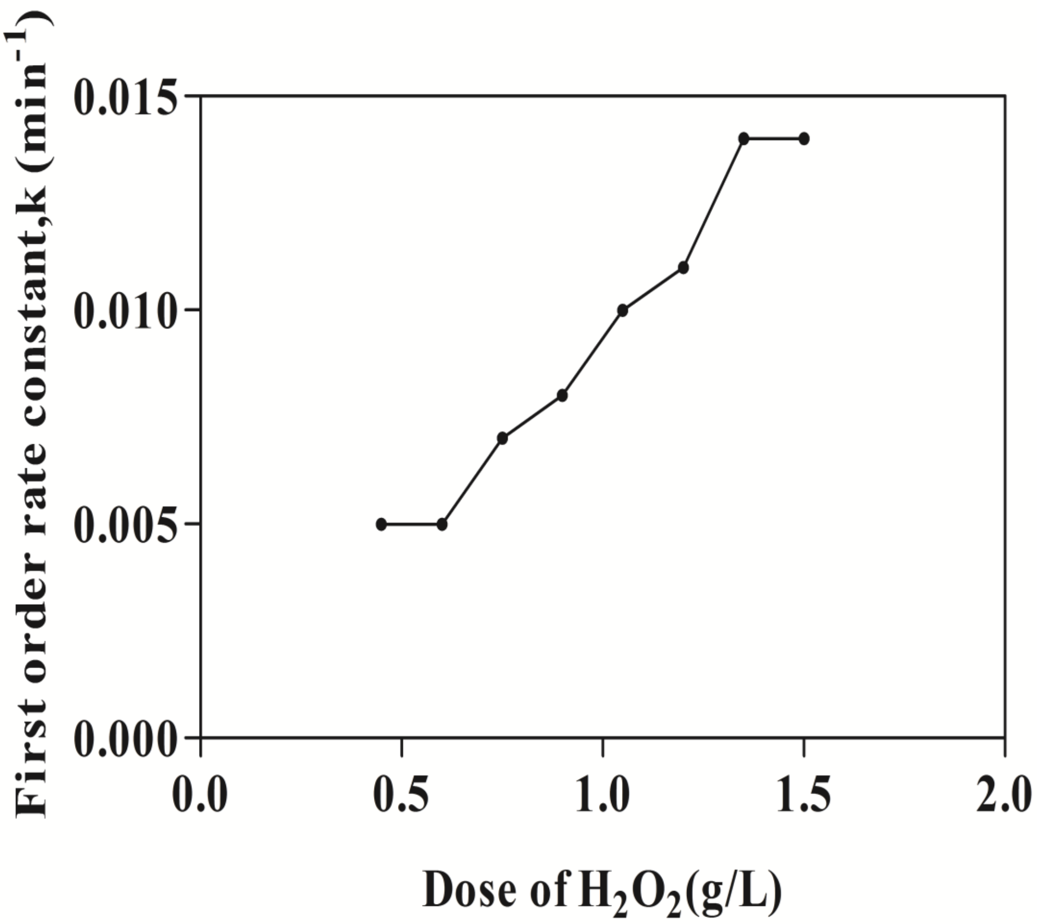

Fig. 6.9 (c): Plot of first order rate constant for the degradation of Phenazone through different concentrations of H_2O_2 using dual process infixed bed.

6.5.2.1Durability studies

Fig.6.10 shows the durability and stability of immobilized catalyst is considered to be the most significant parameter as far as practical applications are concerned. Generally the removal efficiency of catalyst decreases after few recycles due to the attrition of catalyst layer from support **(Parra et al., 2005).** Durability of clay/FS/TiO_2 disc has been checked in the present study in terms of the degradation efficiency for Phenazone. The clay/FS/TiO_2disc was recycled for more than 10 runs with almost 20% reduction in degradation efficiency after 10 recycles as shown in the fig.. The reduction in degradation efficiency may be due to the instability of TiO_2 layer on disc as well as attrition problem. The discs were given heat treatment for about 1hr at 100^0 C in over after each cycle.

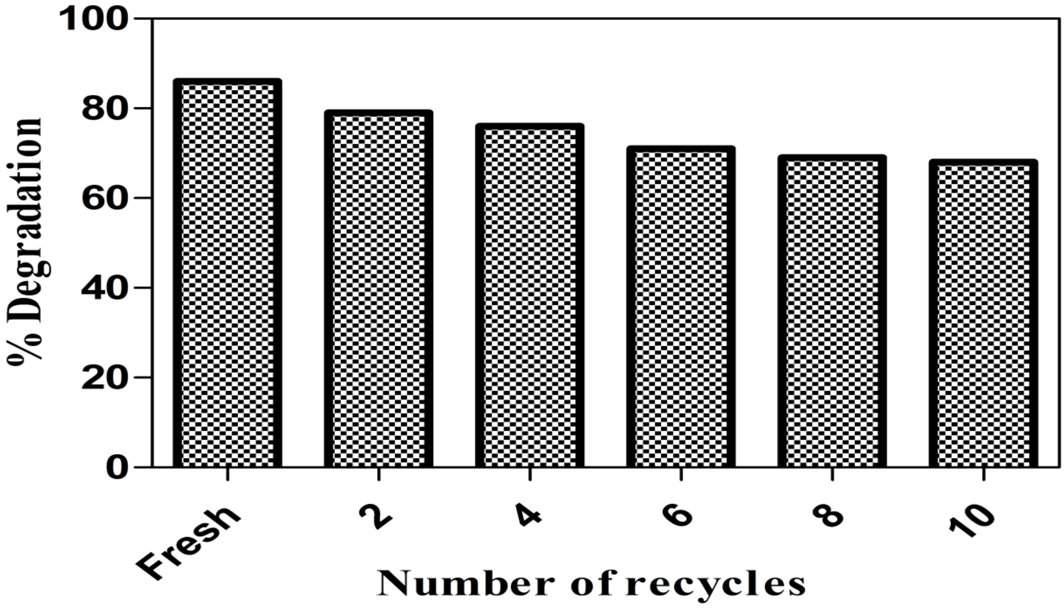

Fig. 6.10: Recyclability studies of clay/FS/TiO_2 disc for the dual effect studies.

6.5 Characterization clay/FS/TiO_2 disc

6.5.1 SEM/EDS

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) of clay/FS, fresh clay/FS/TiO_2 and recycled clay/FS/TiO_2 were performed to analyze the morphological characteristics as well as their elemental composition. The smooth surface in SEM image of fresh Clay/FS/TiO_2 disc indicates the presence of uniform layer ofTiO_2 on the disc as shown in fig.6.11 (a). While, some irregularities in case of recycled clay/FS/TiO_2 disc were due to the instability of TiO_2 on disc as some of the TiO_2 particles drained away after 10 recycles.The strong peaks of ‘Fe’, ‘Ti’ and ‘O’ in case of fresh clay/FS/TiO_2, recycled clay/FS/TiO_2 in EDS images cross confirm our claim for the utilization of clay/FS/TiO_2 disc for dual effect studies.

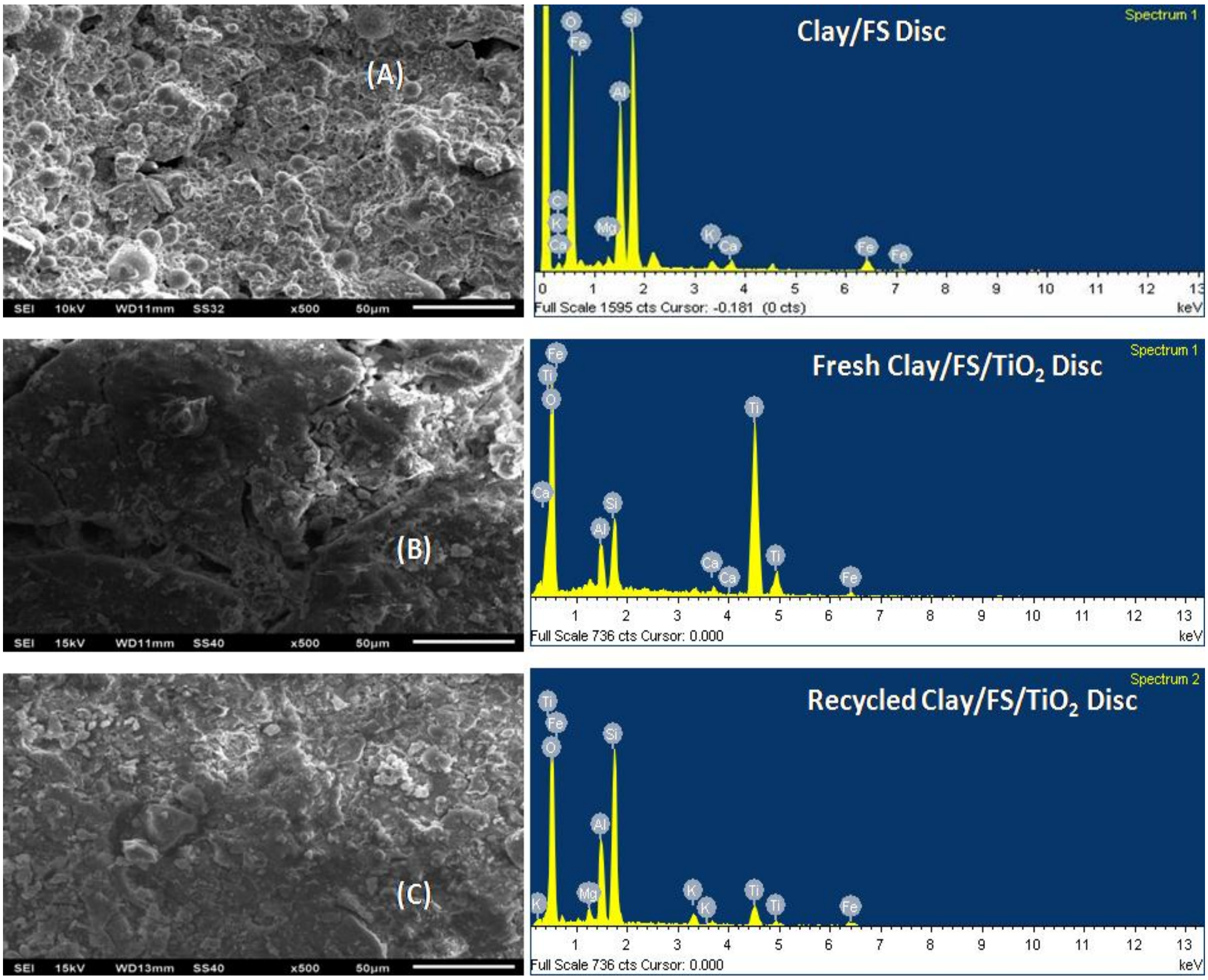

Fig. 6.11(a): Images of SEM/EDS (a) Clay/FS, (b) Fresh Clay/FS/TiO_2 Disc, (c) Recycled Clay/FS/TiO_2 Disc

6.5.2 XRD and UV-visible spectroscopy

X-ray diffraction(XRD) investigation of fresh TiO_2-P25, fresh clay/FS/TiO_2 disc and recycled clay/FS/TiO_2 disc was to check any change had occurred in photocatalytic activity of recycled clay after 10 cycles. The presence of anatase and rutile phase of TiO_2 marked by 'A' and 'R' in fig. 6.10(b) even in recycled disc proves the retention of TiO_2 activity after 10 runs.Moreover some other diffraction peaks were also observed in XRD pattern of fresh clay/FS/TiO_2 disc and recycled clay/FS/TiO_2 disc which further proves the existences of iron oxides along with TiO_2. The iron oxide peaks are referred to as 'ITO' i.e. iron titanium dioxide and 'IDO' i.e. iron di-titanium oxide and 'DTO' i.e. diiron(III) titanium oxide. Therefore it can be concluded thatclay/FS/TiO_2 disc can be successfully utilized for dual effect studies for more than 10 runs.

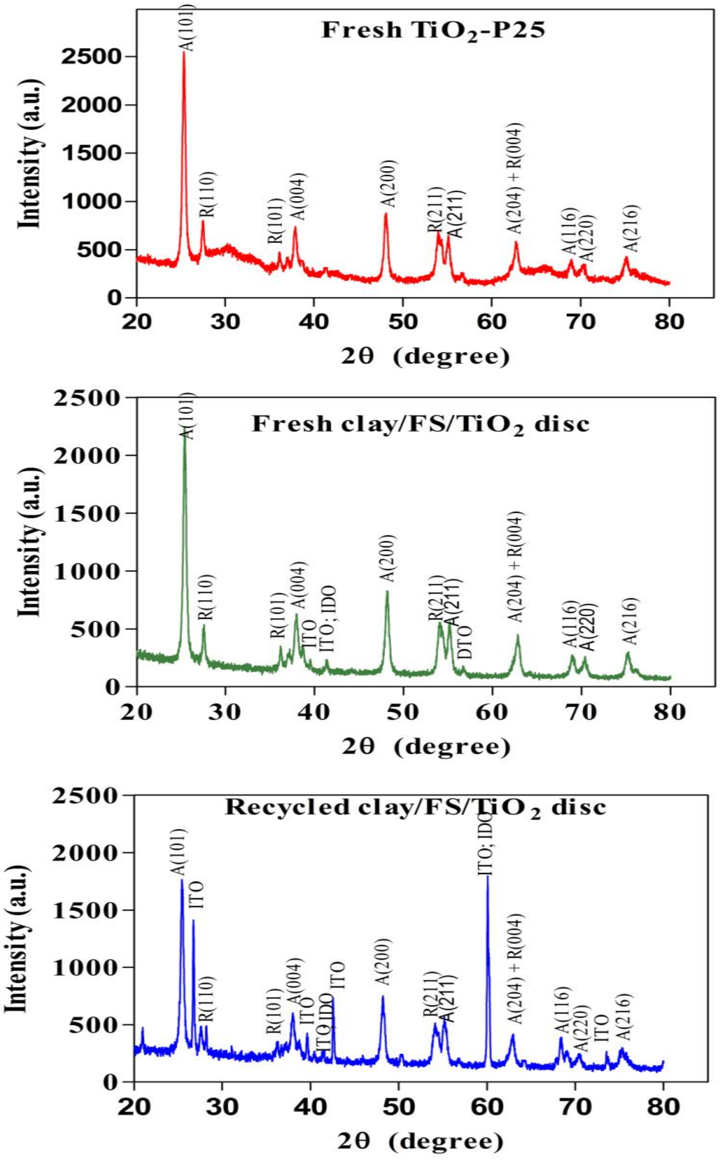

Fig. 6.11 (b): XRD pattern of TiO_2-P25, fresh clay/FS/TiO_2 disc and recycled clay/FS/TiO_2 disc

The band gap of fresh TiO_2- P25, fresh clay/FS/TiO_2 disc and recycled clay/FS/TiO_2 disc was also analyzed through UV-visible diffuse reflectance spectroscopy (DRS) from 200-800nm as depicted. It was observed that band gap was reduced in case of fresh clay/FS/TiO_2 disc and recycled clay/FS/TiO_2 disc. The results are in a good correlation with XRD and SEM/EDS further confirming the presence of iron along with TiO_2 in clay/FS/TiO_2 disc.

Thus, it can be concluded that absorption of light in case of clay/FS/TiO_2 disc is possible even in visible light as shown in fig. 6.11(c).

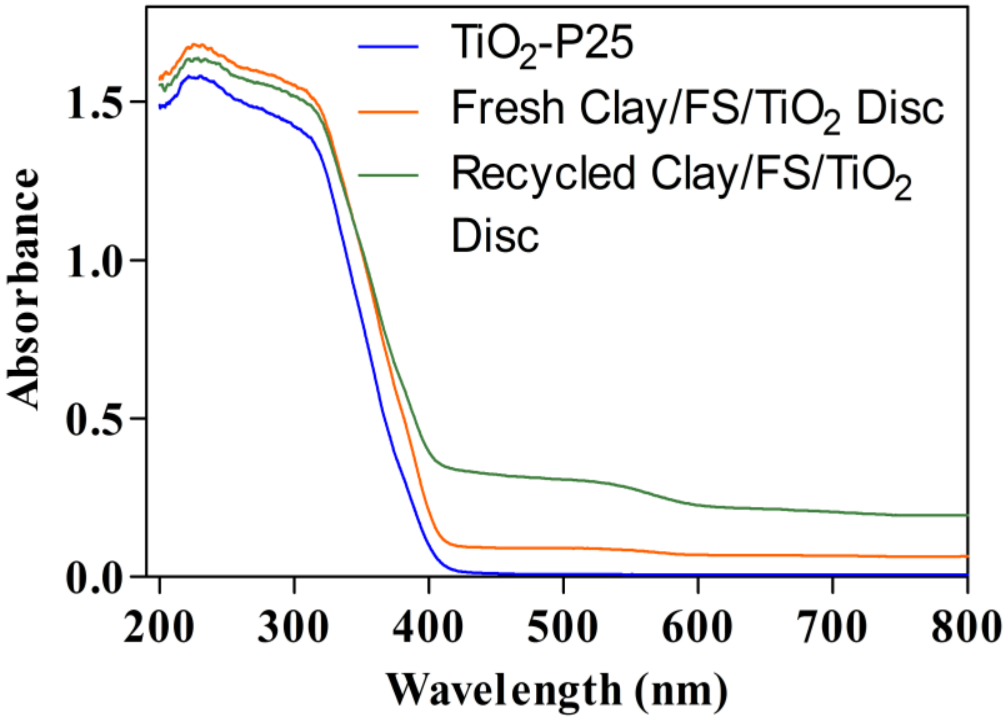

Fig. 6.11(c): UV-visible DRS (a) TiO_2-P25, (b)Fresh Clay/FS/TiO_2 Disc (c) Recycled Clay/FS/TiO_2 Disc

6.6 Mineralization studies

The generation of ions as well as Chemical oxygen demand (COD) is expressed in the form of their percentage removal as shown in fig.. It was observed that nitrate ions followed a decreasing trend with time possibilities of conversion of nitrate to nitrite ions (20%). However 75% reduction in COD occurred after 2 hours of the treatment as in fig 6.12(a).

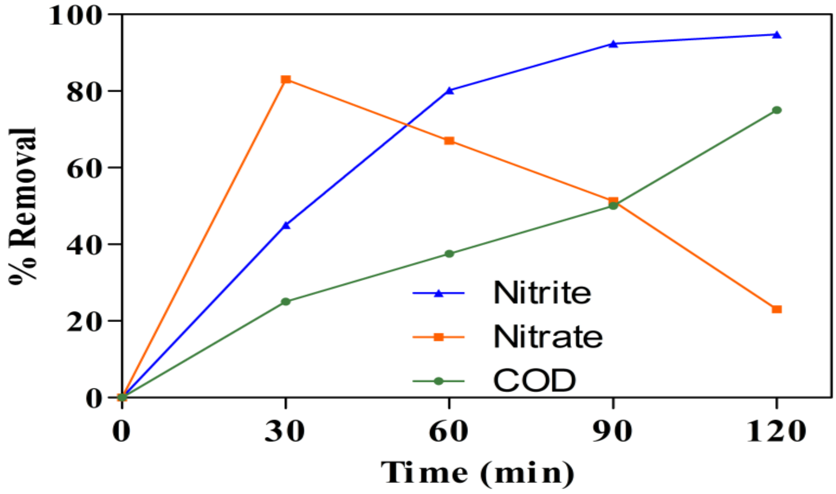

Fig. 6.12 (a): The nitrite and nitrate ions and COD during the degradation of Phenazone by dual process.

The intermediates formed during the degradation of Phenazone were carefully identified there GC-MS analysis as shown in fig 6.12(b). Based on these intermediates a degradation pathway for Phenazone has been proposed tentatively as shown in fig.6.12(c).

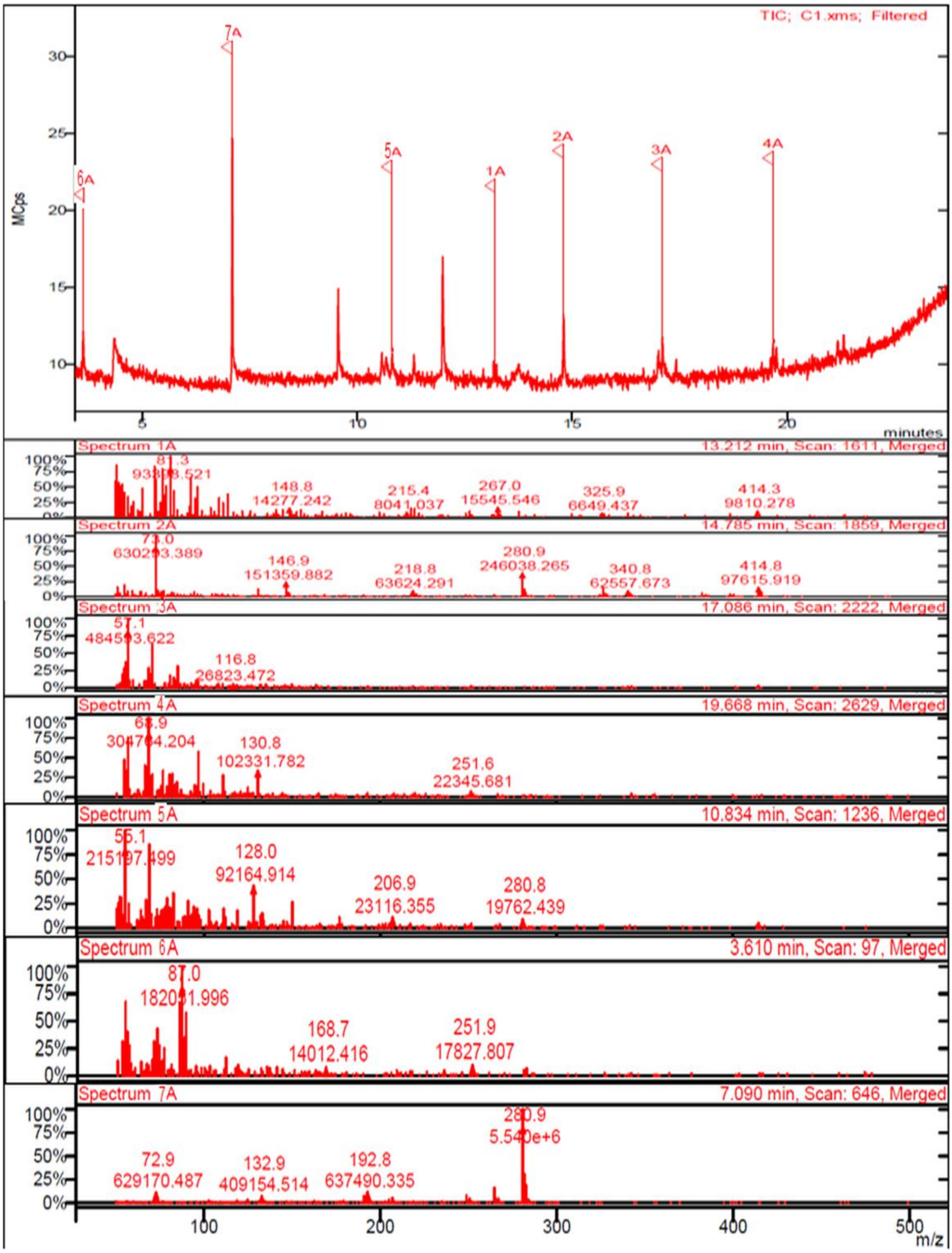

Fig. 6.12 (b) GC-MS analysis for the identification of intermediates.

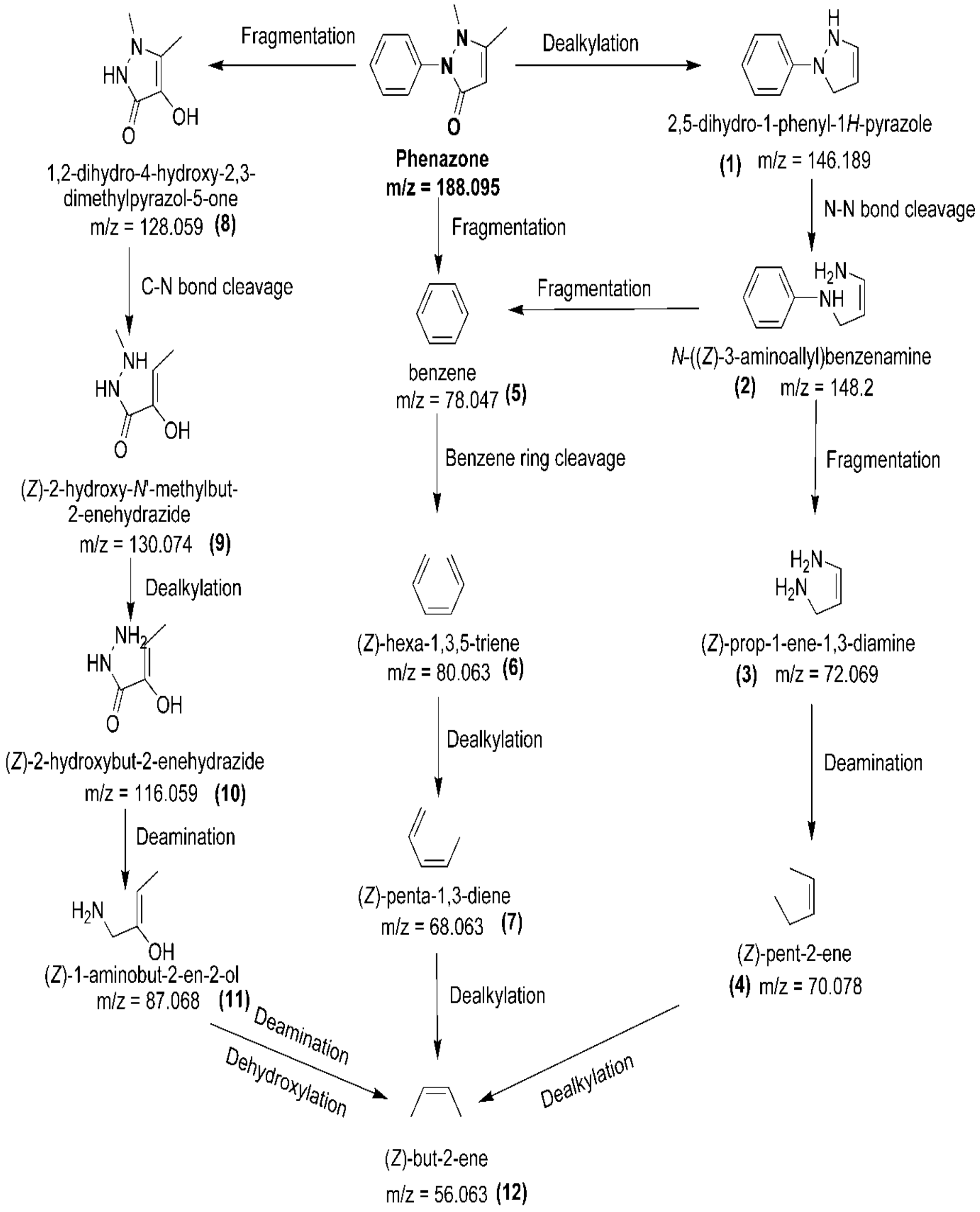

Fig. 6.12(c):Proposed degradation pathway for Phenazone.

6.7 Statistical Analysis

The experiments were executed three times to obtain reproduction results. One way ANOVA has been applied on all experiment data as shown in tables 1-6. It is clear from results that F-values in all cases are greater than 5 thus providing its significance. While, p-values are less than 0.01 in all cases **(Rushing et al., 2015)**.

Anova: Single Factor

SUMMARY

Dose of TiO_2(g/L)	*Count*	*Sum*	*Average*	*Variance*
0.125	3	0.0104	0.003467	3.33E-09
0.25	3	0.017	0.005667	6.33E-08
0.375	3	0.0232	0.007733	2.03E-07
0.5	3	0.0206	0.006867	1.23E-07
0.625	3	0.0195	0.0065	1E-08
0.75	3	0.0196	0.006533	2.53E-07
1	3	0.0195	0.0065	1E-08
1.5	3	0.0199	0.006633	1.43E-07

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3.31E-05	7	4.72E-06	46.64021	1.81E-09	2.657197
Within Groups	1.62E-06	16	1.01E-07			
Total	3.47E-05	23				

Table 3: Statistical analysis for the effect of TiO_2 dose on the degradation of Phenazone through photocatalysis.

Anova: Single Factor

SUMMARY

Dose of H_2O_2(g/L)	*Count*	*Sum*	*Average*	*Variance*
0.03	3	0.0284	0.009467	7.43E-07
0.075	3	0.0383	0.012767	4.33E-08
0.15	3	0.0317	0.010567	6.33E-08
0.225	3	0.0302	0.010067	5.83E-07

0.3	3	0.0231	0.0077	7E-08

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.05E-05	4	1.01E-05	33.65078	8.94E-06	3.47805
Within Groups	3.01E-06	10	3.01E-07			
Total	4.35E-05	14				

Table4: Statistical analysis for the effect of H_2O_2 dose on the degradation of Phenazone through photocatalysis.

Anova: Single Factor

SUMMARY

pH	*Count*	*Sum*	*Average*	*Variance*
3	3	0.0153	0.0051	7E-08
4	3	0.0243	0.0081	7E-08
5	3	0.0385	0.012833	2.33E-08
6	3	0.02	0.006667	1.63E-07
7	3	0.0187	0.006233	1.03E-07
8	3	0.0174	0.0058	4E-08

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.000119	5	2.38E-05	304.4028	3.33E-12	3.105875
Within Groups	9.4E-07	12	7.83E-08			
Total	0.00012	17				

Table5: Statistical analysis for the effect of pH on the degradation of Phenazone through photocatalysis.

Anova: Single Factor

SUMMARY

Dose of FS(g/L)	*Count*	*Sum*	*Average*	*Variance*
0.25	3	0.0049	0.001633	2.33E-08
0.5	3	0.0083	0.002767	2.33E-08

1	3	0.0206	0.006867	2.33E-08
1.5	3	0.0189	0.0063	3E-08
2	3	0.0151	0.005033	1.63E-07

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6.1E-05	4	1.53E-05	289.7342	2.73E-10	3.47805
Within Groups	5.27E-07	10	5.27E-08			
Total	6.16E-05	14				

Table 6: Statistical analysis for the effect of foundary sand (g/L) on the degradation of Phenazone through heterogeneous photo-Fenton.

Anova: Single Factor

SUMMARY

Dose of H_2O_2(g/L)	*Count*	*Sum*	*Average*	*Variance*
0.075	3	0.0067	0.002233	2.33E-08
0.15	3	0.0103	0.003433	9.33E-08
0.225	3	0.0206	0.006867	2.33E-08
0.3	3	0.0209	0.006967	6.33E-08
0.375	3	0.036	0.012	3.07E-06
0.45	3	0.0417	0.0139	9.7E-07
0.525	3	0.0384	0.0128	6.3E-07

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.000389	6	6.48E-05	93.09211	1.8E-10	2.847726
Within Groups	9.75E-06	14	6.96E-07			
Total	0.000399	20				

Table 7: Statistical analysis for the effect of H_2O_2 (g/L) on the degradation of Phenazone through heterogeneous photo-Fenton.

Anova: Single Factor

SUMMARY

Dose of H_2O_2 (g/L)	*Count*	*Sum*	*Average*	*Variance*
0.45	3	0.015	0.005	0
0.6	3	0.015	0.005	0
0.75	3	0.021	0.007	0
0.9	3	0.024	0.008	0
1.05	3	0.03	0.01	0
1.2	3	0.033	0.011	4.51E-36
1.35	3	0.042	0.014	0

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.000197	6	3.29E-05	5.1E+31	1.5E-218	2.847726
Within Groups	9.03E-36	14	6.45E-37			
Total	0.000197	20				

Table 8: Statistical analysis for the effect of H_2O_2 (g/L) on the degradation of Phenazone through dual effect.

CONCLUSION

The present study was undertaken with the concept of introducing in-situ dual effect (photocatalysis + photo-Fenton) for the degradation of Phenazone using TiO_2 and Foundry sand in both slurry and fixed-bed mode. Parameters like concentration of catalyst, oxidant, pH play a significant role in the degradation of antibiotic. The optimized conditions obtained for better degradation of Phenazone are TiO_2 0.375g /L, H_2O_2 0.075g/L and C_0 50 mg/LUV/H_2O_2/TiO_2 photocatalysis resulted in 93% degradation of Phenazone in aqueous solution. The optimized conditions obtained for better degradation of Phenazone are FS 1.0g/L, H_2O_2 0.550 g/L. UV/H_2O_2/TiO_2 photo-Fenton resulted in 95% degradation of Phenazone in aqueous solution. Degradation observed was 97%, under slurry mode at optimized conditions TiO_2 0.375g/L, $H_2O_2$0.550g/L, FS 1.0g/L.The mineralization of antibiotic Phenazone was confirmed by reduction in COD (75%) along with the generation of nitrite ions (98%), nitrate ions (20%) after 120 min of irradiation. For fixed-bed studies, TiO_2 coated on Clay/FS disc yielded 95%degradation after 250 min using batch reactor. The durability of disc is usually a major concern for commercial applications and in our study, durability of disc was confirmed by SEM-EDAX analysis which provedthe stability of catalyst even after 10 recycle for degrading Phenazone. The intermediates formed during the degradation of Phenazone were carefully identified there GC-MS analysis. No study has been carried out so far for the degradation of Phenazone through, Photo-Fenton and dual process in slurry and fixed-bed photocatalysis. Although attempts have been made for the degradation of compound at lab scale and modifications are still required to make the process economical and viable. Durability of the supported material to be used for longer period and the choice of supported material are the major concerns to be looked carefully for field scale applications.

Hence, in the proposed study, efforts have been made to obtain a viable solution to treat wastewater containing these types of bio-recalcitrant compounds using photocatalysis.

REFERENCES

1. Adams C., Wang Y., Loftin K., Meyer M., Removal of antibiotics from surface and distilled water in conventional water treatment processes, *Journal of Environmental Engineering*, 128(2002) 253-260.
2. Ahel, M., Mikac, N., Cosovic, B., Prohic, E., Soukup, V.(1998).The impact of contamination from a municipal solid waste landfill (Zagreb, Croatia) on underlying soil. Water Sci.Technol.37, 203-210.
3. Alexy R., Kumpel T., Kummerer K., Assessment of degradation of 18 antibiotics in the Closed Bottle Test, *Chemosphere*, 57(2002) 505-512.
4. Andreson P. D., D'Aco V.J., Shanahan P., Chapra S.C., Buzby M.E., Cunningham V.L., Duplessie B.M., Hayes E.P., Mastrocco F.J., Pranke N.J., Rader J.C., Samuelian J.H., Schwab B.W., Screening Analysis of of human pharmaceutical compounds in U.S. surface waters, *Environmental Science and Technology*, 38 (2004) 839–849.
5. Balasubramanian G., Dionysiou D.D. and Markam T., Evaluating the activities sofimmobilized TiO2 power firms for the photo catalytic degradation of organic contaminations in water, of human pharmaceutical compounds in U.S. surface
6. Bansal, Palak., Verma, Anoop(2017) Novel Fe-TiO_2 composite driven dual effect for reduction in treatment time of pentoxyxilline: Slurry to immobilized approach.125,135-145.
7. Bautitz I.R., Nogueira R.F.P., Photodegradation of lincomycin and diazepam in sewage treatment plant effluent by photo-Fenton process, *Catalysis Today*, 151 (2010) 94-99.
8. Bila D.M., Dezotti M., Pharmaceutical drugs in the environment, *Quimica Nova*, 26 (2003) 523–530.
9. Boeckel T.P.V., Gandra S., Ashok A., Caudron Q., Grenfell B.T., Levin S.A., Laxminarayan R., Global antibiotic consumption 2000 to 2010: an analysis of national pharmaceutical sales data, *The Lancet Infectious Diseases*, 14 (2014) 742-750.
10. Boyd,G.R., Reemtsma, H., Grimm, D.A., Mitra, S.(2003). Pharmaceuticals and personal care products(PPCPs) in surface and treated waters of Louisiana, USA and Ontario. Canada, Sci. Tot. Environ. 311, 135-149.

11. Brown K.D., Kulis J., Thomson B., Chapman T.H., Mawhinney D.B., Occurrence of antibiotic in hospital, residential, and daily effluent, municipal waste water, and the Rio Grande in New Mexico, , *Science of the Total Environment*, 366 (2006) 772-783.
12. Cahill J.D., Furlong E.T., Burkhardt M.R., Kolpin D., Andreson L.G., Determination of pharmaceutical compounds in surface and ground water samples by solid-phase extraction and high performance liquid chromatography- electrospray ionization mass spectrometry, *Journal of Chromatography A*, 1041 (2004) 171–180.
13. Chau G., Pharmaceutical pollution in water, *Hohonu*, 8 (2010) 75-77.
14. Clara, M., Strenn, B., Kreuzinger, N. (2004). Carbamazepiene as a possible anthropogenic marker in the aquatic environment: Investigations on the behaviour of carbamazepine in wastewater treatment and during groundwater infilteration. Water Res. 38, 947-954.
15. Daneshvar N., Salari D., Niaei A., Rosoulifard M.H., Khataee A.R., Immobilization of TiO2 nano power on glass beads for photocatalytic decolorization of an azo dye C.I. Red23, , *Journal of Environmental Science and Health Part-A*, 40 (2005) 1605–1617.
16. Deegan A.M., Shaik B., Nolan K., Urell K., Oelemoller M., Tobin J., Morissey A., Treatment options for wastewater effluents from pharmaceutical companies, *Internationaljournal of Environmental Science and Technology*, 8 (2011) 649-666.
17. Gobel A., McArdell C.S., Joss A., Seigrist H., Giger W., Fate of sulphonamides, macrolides and trimethoprim in different waste water treatment technologies, *Science of the Total Environment*, 372 (2007) 361-371.
18. Hernandiz R., Zappi M., Colucci J., Comparing the performance of various advanced oxidation processes for treatment of acetone contaminated water, *Journal of Hazardous Materials*, 92 (2002) 33-50.
19. Houng V.T., Houng , V.D.(2009). Simulation determination of Amoxicillin and Clavulanate in combined tablets by non derivable and derivable UV spectrophotometric techniques. Int. J. Pharm. Tech. Res.1(4), 1173-1181
20. Jones O.A., Lester J.N., Voulvoulis N., Pharmaceuticals: a threat to drinking water, *Trends Biotechnology,* 23 (2005) 163-167.
21. Jones, A.H., Vouloulis, N., Lester, J.N.(2004). Potential ecological and human health risks associated with the presence of pharmaceutically active compounds in the aquatic environment. Cri. Rev. Toxicol. 34, 335-350.
22. Kim, H.K., Ihm, K.S. (2010). Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial waste waters. J. Hazard. Mater. 37(1), 1-12
23. Kolpin D.W., Furlong E.T., Meyer M.T., Thurman E.M., Zaugg S.D., Barber L.B., Buxton H.T., Pharmaceuticals, hormones and other organic waste water contaminations in U.S. streams, 1999-2000: A national reconnaissance, *Environmental Science and Technology*, 36 (2002) 1202–1211.

24. Kositzi M., Antoniadis A., Poulios I., Kirdis I., Malato S., Solarphotocatalytic treatment of simulated dye stuff effluents, Solar Energy, 77(2004)591-600.
25. Lhomme L., Brosillon S., Wolbert D., Photocatalytic degradation of pesticides in pure water and a commercial agricultural solution on TiO2 coated media, Chemosphere, 70 (2008) 381-386.
26. Madani M.E., Guillard C., Pe'rol N., Chovelon J.M., Azzouzi M.E., Zrineh A., and Hermann J.M., photocataltiv degradation of diuron in aqueous solution in presence of two industrial titania catalysts, either as suspended powders or deposited on flexible industrialphotoresistant papers, *Applied Catalysis B: Environmental*, 65 (2006) 70–76.
27. Malato S., Blanco J., Vidal A., Richter C., Photocatalysis with solar energy at a pilot plant scale: An overview, *Applied Catalysis*, 37 (2002) 1–15.
28. Noorjahan, M., Pratap Reddy, M., DurgaKumari, V., Lavedrine, B., Boule, P.m Subhramanyam, M.(2003). Photocatalytic degradation of H-acid over novel TiO2 thin film fixed bed reactor and in aqueous suspensions, J. Photochem.. Photobiol. A.: Chemistry, 156, 179-187
29. Oller I., Malato S., Sanchez-Perez J., Maldonado M., Gernjak W., Munoz J., Trovo A., Melo S., Nogueira R., Photodegradation of the pharmaceuticals omoxicillin, bezafibrate and paracetamol by the Photo-Fenton process- Application to sewage treatment plant effluent, *Journal of Photochemistry and Photobiology A*, 198 (2008) 215–220.
30. Oz N., Ince O., Ince B., Effect of wastewater composition on methanogenic activity in an anaerobic reactor, *Journal of Environmental Science and Health Part-A*, 39 (2004) 2029-2042.
31. Parra S, Stanca SE, Guasaquillo I, et al. Photocatalytic degradatine of atrazine using suspended and supported TiO_2. Appl Catal B. 2004;51:107-116.
32. Pekakis P.A., Xekoukoulotakis N.P., Mantzavinos D., Treatment of textile dye house waste water, *Water Research*, 40 (2006) 1276–1286.
33. R. L. Oulton, T Kohn, D.M. Cwiertny , J. Environment Monitor. 12(11), 2010, 1956-1978.
34. Rao, N.N., Chaturvedi V., Li., G. (2012). Novel pebble bed photocatalytic reactor for solar treatment of textile waste water, Chem. Engg. J. 184, 90-97
35. Rushing H, Andrew K, James W. Design and analysis of experiment by Douglas Montgomery: a supplement for using JMP.Cary (NC):SAS Institute; 2014.
36. Ryu A., Pharmaceutical pollution of water in India: International market failure, *Harvard Health Policy Review*, 14 (2013) 25-28.
37. Sadik W.A., Nashed A.W., El-Dermerdash A.M., Photodecolourization of ponceau 4R by heterogeneous photocatalysis, *Journal of Photochemistry and Photobiology A: Chemistry*, 189 (2007) 135–140.

38. Toor A.P., Verma A., Singh V., Jotshi C. K., & Bajpai P. K., Treatment of bleaching effluents from the pulp and paper industry by photocatalytic oxidation, *Tappi Journal*, 6 (2007) 9–13.
39. Y. Su, Z. Wu, Y. Wu, J. L. Sun, C. Lin, Acid orange Ⅱ degradation through a heterogeneous Fenton-like reaction using Fe-TiO_2 nanotube arrays as a photocatalyst, J. Mater Chem. A 3 (2015)8543-8544.