Investigations on the degradation of an antibiotic Cephalexin using suspended and supported TiO_2: Mineralization and Durability studies

A Dissertation

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Masters of Technology
in
Environmental Science and Technology

Submitted
By

PALAK BANSAL
(Reg. No. 601301008)

Under Supervision of

Dr. Anoop Verma
School of Energy and Environment

School of Energy and Environment
Thapar University, Patiala
July 2015

CERTIFICATE

This is to certify that thesis entitled, "**Investigations on the degradation of an antibiotic Cephalexin using suspended and supported TiO_2: Mineralization and Durability studies**" submitted by **Ms. Palak Bansal** in partial fulfilment of the requirements for the award of **Masters in Technology** Degree in **Environmental Science & Technology** at **Thapar University**, **Patiala** is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied in this thesis has not been submitted to any other university/ institute for award of any Degree or Diploma.

Dr. Anoop Verma
Assistant Professor
School of Energy and Environment

Dr. A.S. Reddy
Head
School of Energy and Environment
Thapar University

Dr. S.S Bhatia
Dean
Academic Affairs
Thapar University, Patiala

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Palak Bansal

ABSTRACT

The rise in levels of antibiotics in treated wastewater poses a great threat to human health worldwide. The present study demonstrates the degradation studies of antibiotic Cephalexin using slurry and innovative fixed-bed photocatalysis under UVA (365 nm) irradiations. The decay of Cephalexin was monitored by UV-spectrophotometer/HPLC analysis. Studies showed that the variation in UV intensity, dose variation of TiO_2 and H_2O_2, area by volume (A/V), pH affects the degradation to a great extent. The degradation rate followed the pseudo-first order kinetics with optimized conditions for the degradation of antibiotic were TiO_2 1.0 g L^{-1}, H_2O_2 0.15 mL with UV intensity of 25 Wm^{-2}. Approximately 93% reduction in the concentration of compound was observed after 2 h of irradiations. The COD reduction (80%) along with the generation of nitrite, nitrate and sulphate ions as well as elimination of the parent compound peak in HPLC chromatograms confirmed the complete mineralization of the selected compound. Fixed-bed studies were also carried out with TiO_2 coated on spherical cement beads which eliminates the implications of slurry mode photocatalysis. The durability of catalyst was confirmed by recycling the beads for at-least fifty cycles and characterized by SEM-EDAX. An attempt was also made to study pilot-scale fixed-bed baffled solar reactor for the degradation of Cephalexin, which confirmed 70% degradation after 10 h of photocatalytic treatment. 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.

DECLARATION

I, the undersigned, hereby declare that the research work presented in the M.Tech project entitled "**Investigations on the degradation of an antibiotic Cephalexin using suspended and supported TiO_2: Mineralization and Durability studies**" has been carried out by me under the supervision and guidance of ***Dr. Anoop Verma, School of Energy and Environment, 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.

Palak Bansal

Palak Bansal
(Reg. No.601301008)
M.Tech Environmental Science and Technology
Thapar University
Patiala

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INTRODUCTION

Water pollution is a major global concern and it is a leading cause of diseases and deaths worldwide. Among various causes of water pollution, pollution due to the presence of pharmaceutical compounds rushed to an international notice in 2007, when a research team from Sweden found that the level of pharmaceuticals in water downstream of a wastewater treatment plant in Patancheru, Andhra Pradesh, India was 150 times higher than that in US **(Ryu, 2013)**.

Pharmaceutical compounds are the compounds used to treat, cure and prevent diseases in humans and animals **(Bila and Dezotti, 2003)**. Among all the categories of pharmaceuticals, antibiotics engross an important position due to their widespread use in human and veterinary medicine. The consumption of antibiotics has been increased by 36% from 2000 to 2010. The largest absolute increase in consumption was observed for cephalosporins, broad-spectrum penicillins, and fluoroquinolones **(Boeckel et al., 2014)**.

Pharmaceutical pollution in water is an emerging issue. Before the public health is more affected due to drug contamination, actions must be taken to ensure that our waterways are safer and cleaner. Pharmaceutical pollution is caused mainly by the improper disposal of drugs into the environment. The main contributors of pharmaceutical pollution involve the manufacturers, their distributors and finally the consumers. When pollutants enter the water bodies, not only humans are suffered but also the surrounding environment **(Chau, 2010)**.

Since pharmaceutical companies are mainly responsible for this tremendous pharmaceutical pollution, they must make efforts to counteract the environmental impacts. Many industries don’t have proper waste management systems and so they drain the waste directly into fresh water without proper treating the waste which poses serious threat to the water organisms. The treatment of industrial wastewater must be properly designed for the specific type of effluents produced. Therefore, there is a great need of developing proper cost-effective treatment methods to treat and degrade these pharmaceutical compounds emerging from industries and polluting the water bodies.

However, treatment methods that are suitable for municipal wastewaters should also work with some modifications for industrial wastewaters. There are numerous of prominent new treatment technologies including AOPs like oxidation, ozonation, perozonation, direct photolysis, TiO_2 photocatalysis, solar photocatalysis, Fenton reactions and ultrasonic irradiation for the degradation of micropollutants which are known to be persistant or have low biodegradability and possess high chemical stability. These technologies considerably improve the removal rate of pharmaceutical compounds from wastewaters. The consequent goal of AOPs is to mineralize the contaminants, with conversion to carbon dioxide, water and other minerals **(Deegan et al., 2011)**. Key AOPs comprise of homogenous and heterogeneous photocatalysis based on near ultraviolet (UV) or visible solar irradiation **(Ashfaq and Khatoon, 2014)**. Heterogeneous photocatalysis using TiO_2 as a catalyst has proven to be an effective treatment technique for the purification of wastewater. TiO_2 can be used either in suspended form or in supported form. The choice of catalyst is mostly restricted towards TiO_2 in photocatalysis due to its high photo-reactivity and it is chemically and biologically inert. In general, wavelengths between 300 and 400 nm (near UV range) play role in TiO_2 photocatalysis, which can be supplied either by artificial UV lamps or by a small part of the solar spectrum **(Kanakaraju et al., 2013)**.

Cephalexin is a semi-synthetic first generation cephalosporin bactericidal antibiotic that is intended for oral administration and used in human and veterinary medicine worldwide. It is authorized to treat several bacterial infections including respiratory tract infections, skin infections, urinary tract infections, bone infections and sinus infections. Various studies have confirmed the presence of Cephalexin in wastewater **(Lin et al., 2009; Watkinson et al., 2009)**.

Therefore, the current study deals with the degradation of an antibiotic Cephalexin using heterogeneous photocatalysis employing suspended and supported TiO_2 and efforts have also been made to scale up the prototype reactor. Thus, pilot-scale reactor has been designed to study the degradation of compound and significant amount of degradation has been achieved. Furthermore, more studies on heterogeneous photocatalysis 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 industrial scale.

CHAPTER 2

PHARMACEUTICAL INDUSTRIES AND ADVANCED TREATMENT TECHNOLOGIES

The pharmaceutical industry develops and produces biological products, drugs, chemicals, botanical products, and other pharmaceutical products for use as medication. India is the third largest manufacturer of pharmaceuticals. In the last few decades, industrialization has given rise to the continuous discharge of liquid, solid, and gaseous emissions into natural systems and thus degrading the environment **(Mehta et al., 1995).** The most commonly detected compounds were from pharmaceutical background, that is, coprostanol (fecal steroid), cholesterol (plant and animal steroids), caffeine (stimulant), and triclosan (antimicrobial disinfectant), and so on **(Kolpin et al., 2002)**.

However, antibiotics are not metabolized entirely within the body and 90% of the drug is excreted out which can enter municipal and natural water systems through residential or commercial discharges, including hospital effluent **(Raloff, 1998)**. The presence of pharmaceutical compounds within the water sources is a matter of great concern worldwide. These compounds possess some specific properties and can affect the aquatic and terrestrial ecosystem even at very low concentrations. The complication that may arise due to the existence of antibiotics in water resources is the evolution of antibiotic resistant bacteria **(Schwartz et al., 2003, Alexy et al., 2004)**, thus poses a great threat to the environment due to their persistence in water. Some of the health problems due to the persistence of pharmaceutical compounds in water include endocrine disruption, aquatic toxicity, and genotoxicity. Concerns about their prospective risk arose in 1999 with the issue of feminization of fish living in the downstream of wastewater treatment plant (WWTP) due to the existence of pharmaceuticals in river water **(Daughton and Ternes, 1999; Larsson et al., 1999)**.

There are various possible sources and routes by which pharmaceutical compounds enter and pollute the environment as shown in figure 2.1.

Figure 2.1: Fate of pharmaceuticals in environment.

The pharmaceutical industry uses wide array of wastewater treatment methods. Traditionally, biological treatment methods (both aerobic and anaerobic) have been employed for managing the pharmaceutical wastewater **(Suman and Anjaneyulu, 2005)**. Conventional methods like clarification, coagulation, flocculation, sedimentation and filtration **(Adams et al., 2002, Gobel et al., 2007, Stackelberg et al., 2007)** have shown either their incapabilities or lower efficiencies (fig. 2.2) in treating bio-recalcitrants. Various other techniques like activated carbon adsorption, reverse osmosis and air stripping are often used in conjunction with traditional methods to treat waste water containing pharmaceuticals. Most of these techniques don’t destroy the pollutants completely rather transfer them from one phase to the other phase. Some of the other problems associated with these techniques include high energy consumption, the production of large amounts of sludge **(Sreekanth et al., 2009)** and operational problems like colour, foaming and bulking in secondary clarifiers **(Oz et al., 2004)**. The presence of pharmaceutical compounds in drinking water shows the incapability of conventional treatment methods for removing these pollutants effectively.

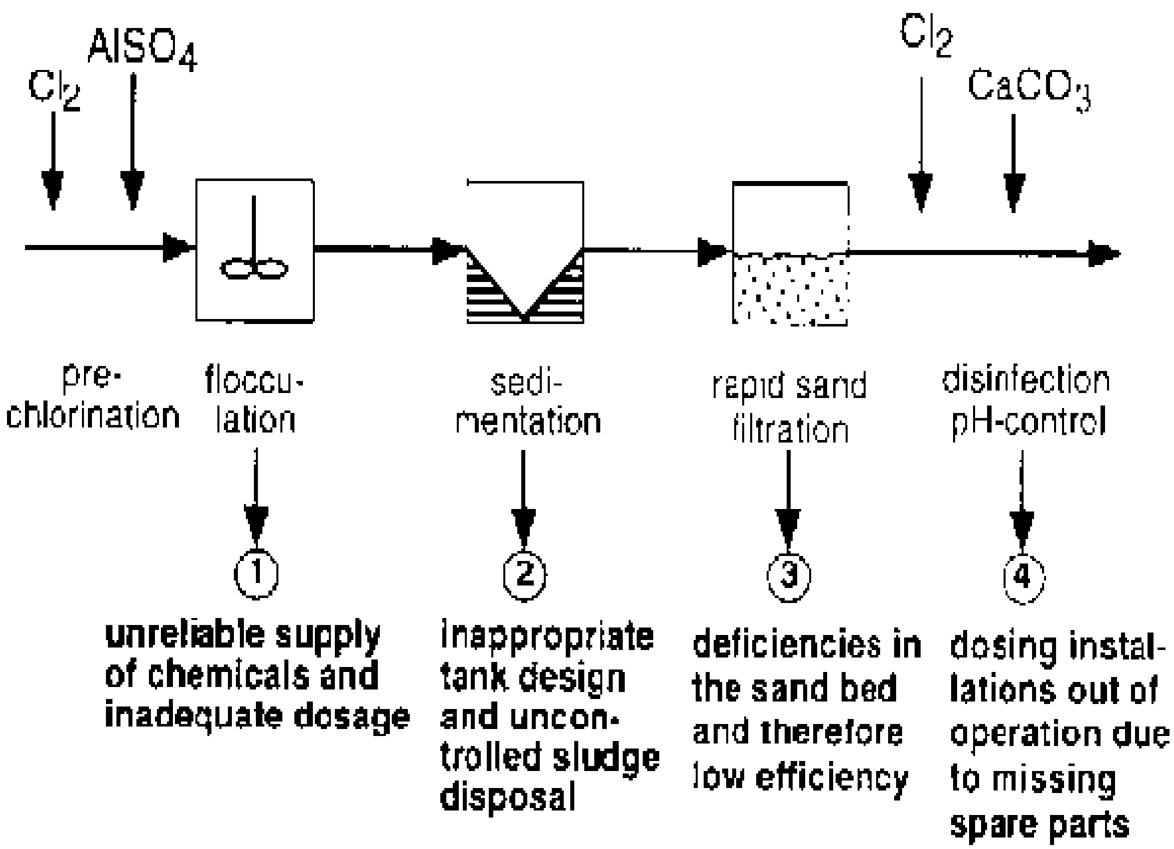

Figure 2.2: Problems associated with conventional treatment methods.

Advanced oxidation processes (AOPs) (fig. 2.3) have found their prominent place in literature worldwide for treating different kinds of wastewaters. AOPs may significantly improve the degradation and can be used as a pre-treatment to biological treatment or as a tertiary treatment **(Oller et al., 2007)**. AOPs can also handle the fluctuating flow rates easily. Cost of the chemical agent and the energy source can be a major issue for the implementation of AOPs on an industrial scale **(Legrini et al., 1993)**. However, by using solar irradiation can substantially reduce the capital cost of AOPs **(Trovo et al., 2008)**. Catalyst must be selected in such a manner that it uses maximum fraction of solar energy **(Balasaraswathy, 2004)**.

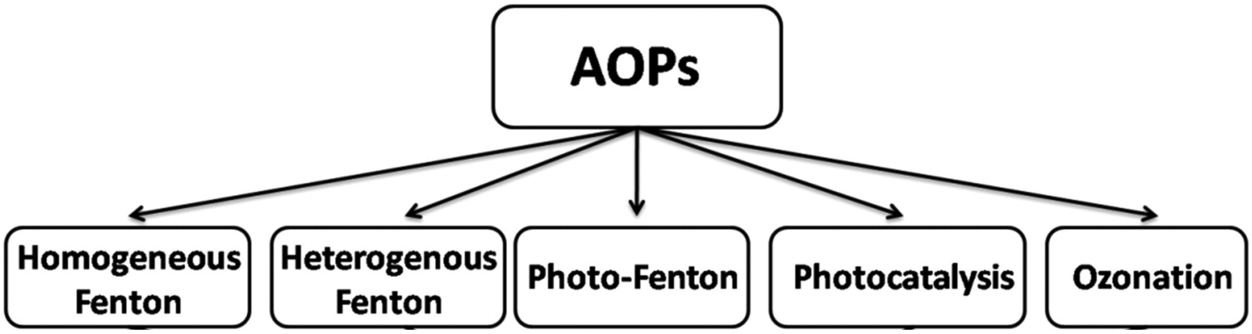

Figure 2.3: Types of advanced oxidation processes.

Among various AOPs, TiO_2 photocatalysis has emerged as a competent and promising tool for handling wastewaters containing bio-recalcitrant compounds. Moreover, TiO_2 is commercially available, inexpensive, non-toxic, versatile and photochemically stable **(Pekakis et al., 2006)**. The mechanism of TiO_2 photocatalysis (fig. 2.4) is well established where it characterizes the formation of hydroxyl radicals ($^{\bullet}OH$) which are capable enough to degrade wide variety of pollutants present in wastewater. Being non-selective, the hydroxyl radicals react readily with organic molecules adsorbed on surface, either by electron or hydrogen atom which leads to the degradation of compounds **(Sadik et al., 2007)**. The reactions 1-6 describe the complete mechanism of TiO_2 photocatalysis.

$$TiO_2 + h\nu \rightarrow TiO_2\,(e^- + h^+) \quad (1)$$

$$h^+ + H_2O \rightarrow H^+ + {}^{\bullet}OH \quad (2)$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH \quad (3)$$

$$\text{Organics} + {}^{\bullet}OH \rightarrow \text{Degradation products} \quad (4)$$

$$e^- + O_2 \rightarrow {}^{\bullet}O_2 \quad (5)$$

$$H_2O_2 + e^- \rightarrow {}^{\bullet}OH + OH^- \quad (6)$$

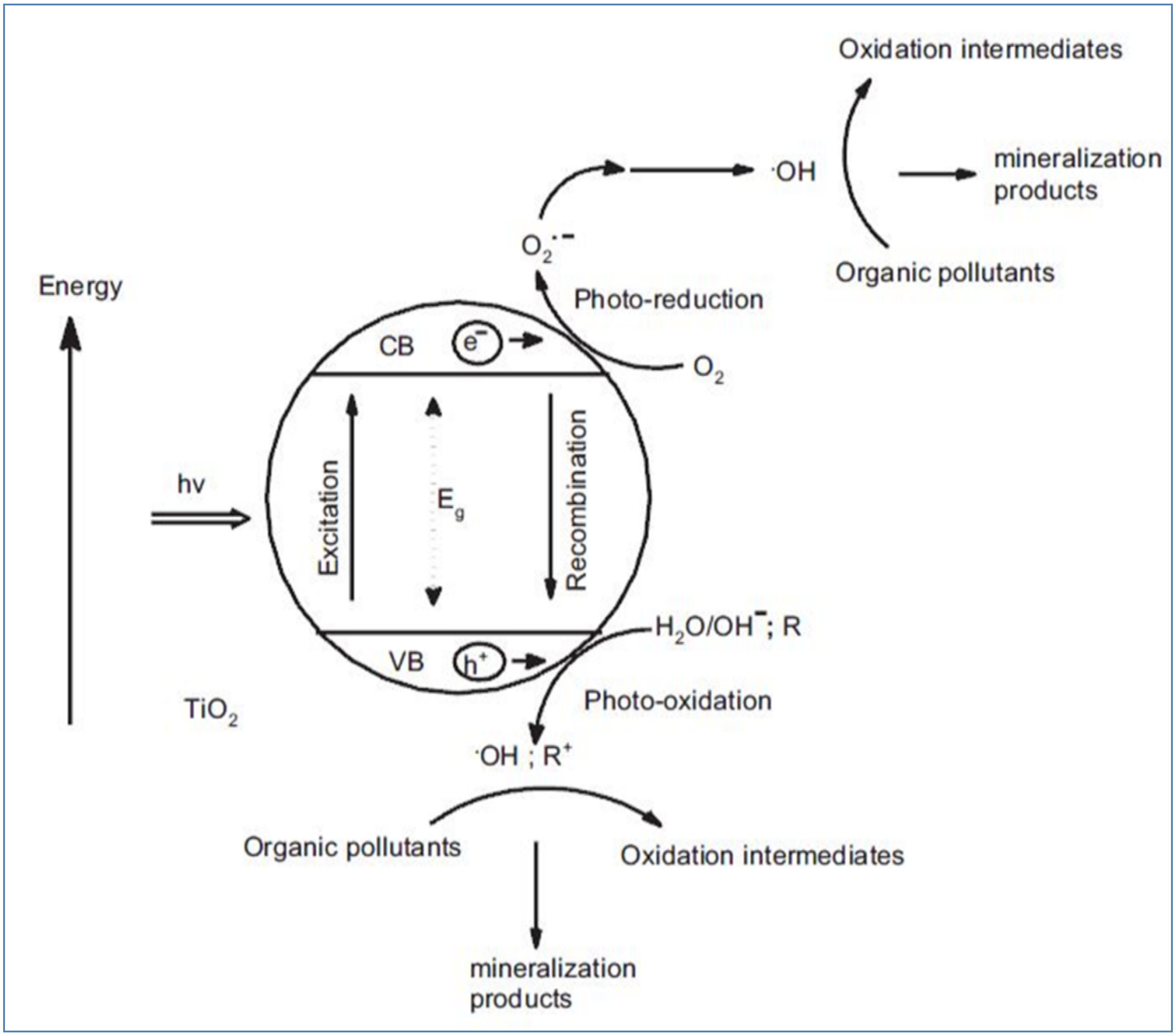

Figure 2.4: Mechanism of TiO_2 photocatalysis.

Although slurry photocatalysis is gaining importance in AOP, the separation of catalyst from slurry is always a technical hindrance towards its commercial applications. Immobilization or catalyst fixing on inert support can technically remove this hindrance. Studies related to catalyst fixing on supports are cited in literature **(Daneshvar et al., 2005, Verma et al., 2014)** but durability, recyclability of the support has not been covered effectively. The present study covers these concerns by coating TiO_2 on inert cement beads and using them for studying the degradation of selected compound.

Solar reactors for photocatalytic treatment can be grouped as concentrating reactors and non-concentrating reactors. Concentrating reactors are based on parabolic trough concentrators (PTC) using direct solar radiations. These reactors use only direct radiations and require solar tracking devices which are costly and difficult to maintain. Non-concentrating reactors are simple, low cost reactors which use both direct and diffused solar radiations and are more efficient **(Nogueira and Jardim, 1996)**. Non-concentrating solar reactors can be made in different designs like tubular **(Malato et al.,2002)**, falling film **(Nogueria and Jardim, 1996)**, shallow pond **(Wyness et al.,1994)** and fountain **(Puma and Yue,2001)**. Shallow pond non-concentrating solar reactor can be constructed onsite and can be used at pilot scale **(Toor et al., 2005)**. Therefore, these reactors can be best commercialized for treatment of wastewater in industries.

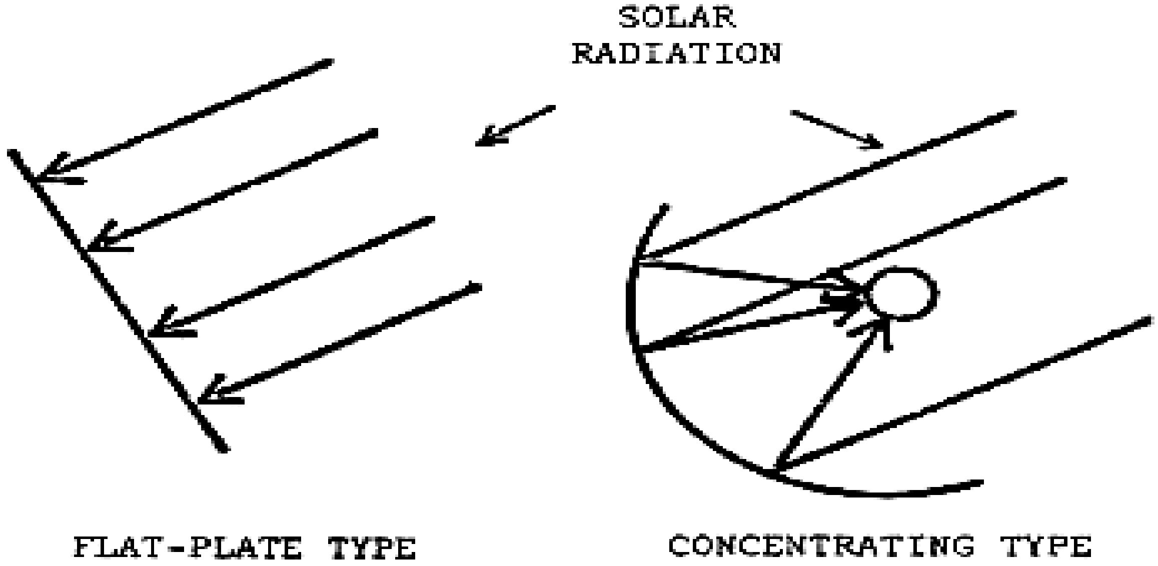

Figure 2.5: Types of solar reactors.

Thus, these kinds of solar reactors can be fabricated with some modifications and can be useful in obtaining a viable solution for treating the wastewater containing different types of recalcitrant compounds in various industries.

CHAPTER 3

REVIEW OF LITERATURE

3.1 Overview

During the last two decades, the presence and fate of pharmaceuticals in the environment and in the water sources have received substantial awareness by the scientific community. The occurrence of pharmaceutical compounds and personal care products (PPCPs) were first observed in surface waters in U.S. and Europe in 1960s **(Stumm-Zollinger and Fair, 1965)**. Although pharmaceuticals and PPCPs are found to be present in the environment in traces, their chemical subsistence, microbial resistance and synergistic effects are yet to be known **(Ankley et al., 2007; Madukasi et al., 2010)**, which is a matter of concern. Furthermore, even low concentrations can pose serious threat to aquatic life **(Miege et al., 2008; 2009)**. Pharmaceutical pollution of water directly threatens the health of humans who utilize the polluted water for drinking and washing and indirectly harms health by devastating livelihoods—dramatically reducing the agricultural productivity of the land, harming agricultural infrastructure, and which leads to the massive death of livestock and fish **(Dhara et al., 2010)**.

There are a number of routes through which pharmaceuticals enter the water bodies (figure 3.1). Pharmaceuticals can enter the water bodies through human and animal excretion as compounds in human excretion are passed to sewage treatment plants (STPs) from where they reach the surface water. Whereas, compounds in animal excretion can enter surface water through agricultural runoff, or may enter groundwater by seeping through the soil. Pharmaceuticals may also enter water when patients, hospitals or pharmaceutical companies dispose of unused pharmaceutical compounds and when pharmaceutical companies discard toxic wastes produced during manufacturing **(Ryu, 2013)**.

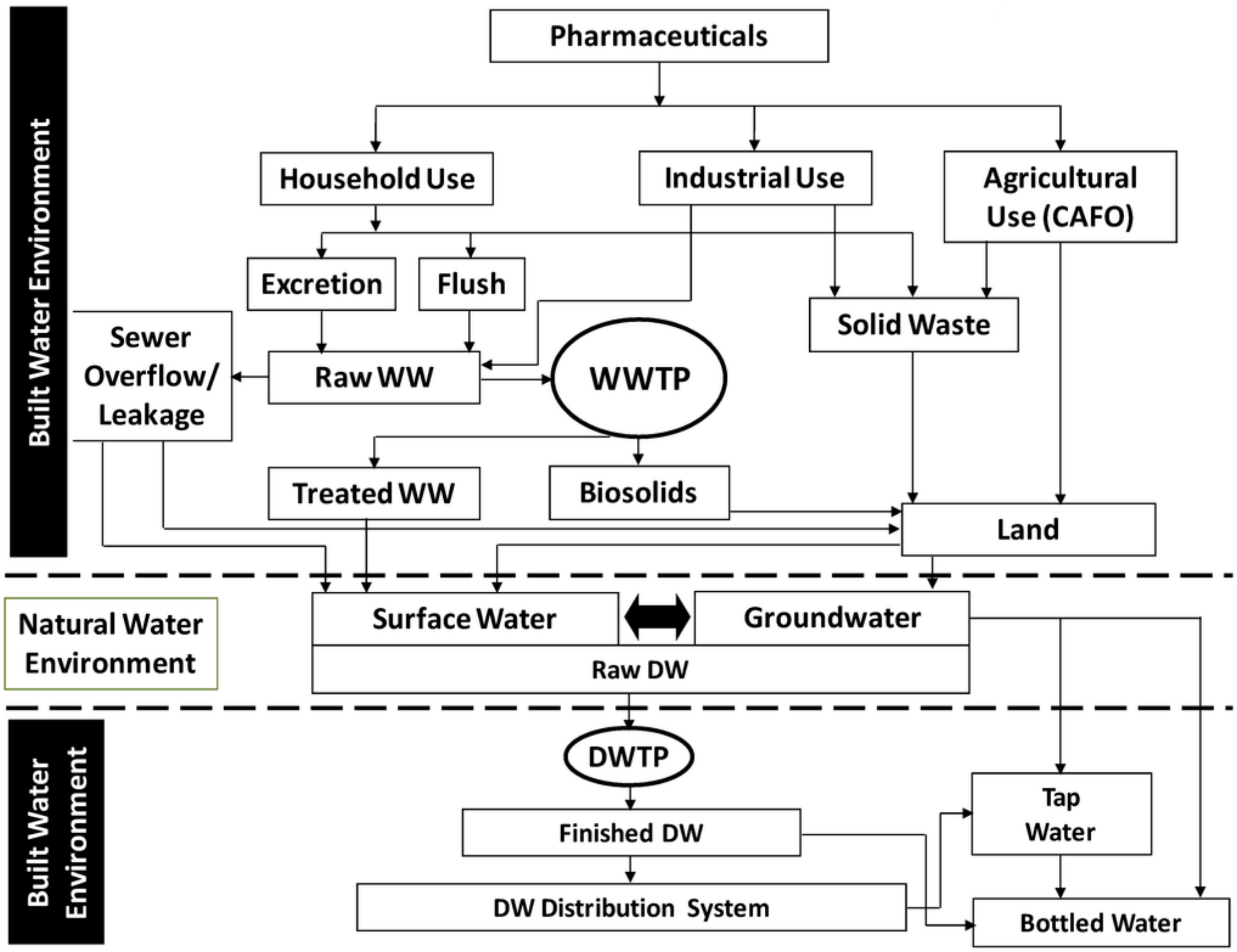

Figure 3.1: Sources and pathways of pharmaceuticals entry into water cycle.

Multi-millions of antibiotics are prescribed daily as the consumption of antibiotics in India has increased to a great extent due to the wide spread of diseases. Among various antibiotics, Cephalexin is one of the widely used semi-synthetic cephalosporin antibiotic having maximum absorption at 263 nm and a half life of 50-80 min. It is widely used in human and veterinary medicine and produced in large quantities **(Guo et al., 2010)**. It acts in the same manner as penicillin by inhibiting the bacterial cell wall synthesis. It is used to treat several bacterial infections.

The presence of antibiotics have been confirmed in hospital, municipal wastewater **(Brown et al., 2006)**, surface water **(Anderson et al., 2004, Cahill et al., 2004)**, groundwater

(Cahill et al., 2004) and even in drinking water **(Jones et al., 2005)**. Generally, methods employed for the treatment of wastewater containing pharmaceuticals include physico-chemical and biological treatment methods. Physico-chemical techniques include membrane separation, chemical removal, activated carbon and chlorination **(Deegan et al., 2011)**. Biological treatment technologies involve both aerobic and anaerobic treatment methods. Traditionally, aerobic treatment methods like activated sludge, extended aeration, trickling filters or rotating biological contactors are used for the treatment of wastewater containing pharmaceuticals **(Gupta et al., 2006)**. These conventional methods have shown either their incapabilities or lower efficiencies in treating the wastewater containing bio-recalcitrant compounds **(Adams et al., 2002; Gobel et al., 2007; Stackelberg et al., 2007)**. These techniques don't destroy the pollutants completely rather transfer them from one phase to the other phase. These drawbacks led to the emergence of new alternative techniques.

3.2 Advanced Oxidation Processes (AOPs)

AOPs are oxidative methods that involve the formation of intermediate radicals, the hydroxyl radicals ($OH^{\bullet}$), which are highly reactive and less selective compared to other oxidants (e.g. chlorine, molecular ozone). 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 like ozone or hydrogen peroxide, that are generally combined with metallic or semiconductor catalysts and UV radiation. Various techniques like Fenton, photo-Fenton, cavitation, ozonation, photocatalysis, etc. comes under AOPs and they vary only with the source of radicals **(Kim and Ihm, 2010)**.

3.2.1 Heterogeneous Photocatalysis

Photocatalysis is the advancement of a photochemical transformation using a catalyst such as TiO_2 or Fenton's reagent (**Chatterjee and Dasgupta, 2005; Herrmann, 2005; Dalrymple et al., 2007**). Most of the photocatalysts are semiconductor metal oxides which usually possess a narrow band gap. Radicals that are generated react with impurities in the wastewater and degrade them unselectively (**Lhomme et al., 2008**). Titania is the most widely used heterogeneous photocatalyst which is mainly because of its cost effectiveness, inertness and photostable nature (**Gaya and Abdullah, 2008**). TiO_2 can either be used in slurry form or supported form. The degradation of bipenyls and chlorobiphenyls using TiO_2 photocatalysis in aqueous mode is the first reported study (**Carey et al., 1976**). Since then, the number of publications has grown considerably regarding the removal of micropollutants through TiO_2 photocatalysis in slurry form (**Doll and Frimmel, 2005a, b, c; Perez-Estrada et al., 2005a**).

Toor et al., 2013 carried out research for the photocatalytic degradation of a herbicide, Isoproturon in aqueous solution using TiO_2. The optimum conditions obtained for the better degradation of compound were TiO_2 dose of 0.5 gL^{-1}, pH 5.0, and C_0 25 mgL^{-1}. The mineralization studies were also performed which were confirmed by the reduction in COD (96 %) and TOC (90 %) along with the generation of ammonium ions whereas various intermediates formed were confirmed by the data of HPLC and LC-MS study.

The degradation of herbicide, Paraquat using UV/TiO_2 photocatalysis was investigated by **Leyva et al., 1998**. According to the experimental results, direct photolysis showed slower degradation of Paraquat in the presence of dissolved oxygen. While addition of TiO_2 showed a substantial increase in the initial rate of reaction. Complete photocatalytic degradation occurred after three hours of irradiation at high pH.

Verma et al., 2012 investigated the photocatalytic degradation of an insecticide, Chlorpyrifos using TiO_2 in aqueous phase under artificial UV-A and solar light. The optimum operating conditions for better degradation were determined which were obtained as TiO_2 dose 4 gL^{-1}, pH 6.5 and H_2O_2 3 gL^{-1} at which 90 % degradation was achieved. It was observed that better results were obtained under sunlight as compared to artificial UV light. The effect of sonication on TiO_2 slurry for better dispersion of the catalyst particles was also studied.

Ying-ping et al., 2006 carried out the photocatalytic degradation of dye sulforhodamine-B (SRB) in aqueous solution using titanium dioxide in the presence of three types of light sources namely : UV light, natural solar light, and visible light at pH=2.5. The experimental results showed a higher degradation of SRB under artificial UV and natural solar light when compared to that of visible light as confirmed by COD and TOC analysis. The degradation rate constants for UV-A, sunlight and visible light obtained were 0.197 min^{-1}, 0.152 min^{-1}, 0.027

min^{-1}, respectively. The mineralization study was confirmed by the formatioin of amine products as indicated by infrared spectrophotometry.

The degradation of three textile dyes namely Reactive Yellow 17 (RY 17), Reactive Red 2 (RR 2) and Reactive Blue 4 (RB 4) in aqueous solution was carried out by TiO_2 (**Choi et al., 2002).** Different catalysts like TiO_2 (Degussa P25), TiO_2 (Merck), ZnO, ZrO_2, WO_3 and CdS were tested for the efficient degradation of all the dyes. TiO_2 (Degussa P25) showed the best degradation among all the catalysts used. The best degradation results were obtained for Reactive Yellow 17 (RY 17) followed by Reactive Red 2 (RR 2) and Reactive Blue 4 (RB 4). The degradation was confirmed by COD analysis.

The sonolytic, sonophotocatalytic as well as photocatalytic degradation of 4-chloro-2-nitrophenol was investigated using TiO_2 in slurry mode. Experiments were performed using artificial UV light coupled with ultrasound for the purpose of sonicating the slurry. The optimum conditions for better degradation of the compound were determined as catalyst dose at 1.5 gL^{-1}, pH 7 and oxidant dose at 1.5 gL^{-1} at which 80 % degradation was obtained after 120 min of irradiation. Sonication imparted synergistic effect as degradation was improved to 96 % increase after 90 min of treatment in sonophotocatalysis (**Verma et al., 2013**).

Apart from the removal of above discussed organic pollutants, TiO_2 photocatalysis has also emerged as a promising technique in the removal of active pharmaceutical ingredients (APIs) including non-steroidal anti-inflammatory drugs, analgesics and antibiotics.

3.2.1.1 Removal of antibiotics

The four main classes of antibiotics include beta lactam antibiotics, quinolones, sulfonamides and tetracyclines. Some of the beta lactum antibiotics include amoxicillin, ampicillin, cloxacillin and Cephalexin.

Dimitrakopoulou et al., 2012 investigated the photocatalytic degradation of amoxicillin (AMX) using TiO_2 with ultrapure water and secondary effluent water employing different TiO_2 materials. TiO_2 Degussa P25 (250 mgL^{-1}), among various catalysts tested appeared to be the most efficient photocatalyst, which showed complete degradation after 25 min and 93 % mineralization was achieved after 90 min of reaction for 10 mgL^{-1} of AMX. Using TiO_2

(Anatase) under the same conditions, it took at least 45 min to attain complete degradation. Moreover, not more than 75% mineralization was achieved after 90 min of photocatalytic treatment. Secondary effluent water restrained the degradation of AMX due to the existence of organic matter, bicarbonates, and chlorides.

Elmolla and Chaudhuri, 2009 studied the photocatalytic degradation of three antibiotics including amoxicillin, ampicillin and cloxacillin in aqueous solution using TiO_2 under UVA (365 nm) radiation. The degradation rate constants (k) obtained were 0.007, 0.003 and 0.029 min^{-1} for amoxicillin, ampicillin and cloxacillin, respectively. Addition of H_2O_2 at ambient pH 5 and TiO_2 dose of 1.0 gL^{-1} resulted in complete degradation of amoxicillin, ampicillin and cloxacillin after 30 min of irradiations. The removal of Dissolved organic carbon (DOC) along with the generation of nitrate (NO_3^-), ammonia (NH_3) and sulphate (SO_4^{2-}) ions during the degradation confirmed the mineralization of organic carbon, nitrogen and sulphur. $UV/H_2O_2/TiO_2$ photocatalysis was found to be effective for the degradation of amoxicillin, ampicillin and cloxacillin in aqueous solution.

Another study by **Elmolla and Chaudhuri, 2010** compared the efficiency of different AOPs like fenton, photo-Fenton, TiO_2 photocatalysis and ZnO photocatalysis on AMX, ampicillin and cloxacillin under UV-A irradiation. Under optimum experimental conditions, depending upon the pseudo-first order rate constants, the highest value of rate constant (0.029 min^{-1}) was attained in photo-Fenton followed by Fenton (0.0144 min^{-1}). Almost similar results of $UV/TiO_2/H_2O_2$ and UV/ZnO were obtained with values of rate constants 0.0005 and 0.00056 min^{-1}, respectively. BOD_5/COD appeared to be improved for all the methods except for UV/ZnO treatment.

Hospital wastewater containing AMX was treated by TiO_2 photocatalysis as well as with photo-Fenton process. The study showed that complete degradation occurred with TiO_2 photocatalysis after 30 min of irradiation while, only 85% degradation occurred using photo-Fenton process after 60 min of reaction. Whereas, the percentage removal of COD was higher in case of photo-Fenton (64.6%) as compared to photocatalysis (44%). Moreover, toxicity inhibition studies with Artemia salina proved that both treatments were effective in reducing toxicity and hence, 43.5 and 46.3 % of reductions were achieved in the photo-Fenton and photocatalysis, respectively (**Martins et al., 2009)**.

Klauson et al., 2010 studied the photocatalytic degradation of AMX and compared the efficiency of the process with using doped and undoped titania with artificial UV radiation and sunlight. It was observed that using sunlight degraded the compound three times more fast than artificial UV-A irradiation. Doped catalysts with Fe and C also indicated comparable efficiencies as that of TiO_2-Degussa P25. The different degradation products were identified at different AMX concentrations (10, 25 and 100 mgL^{-1}). Only small amounts of nitrate, ammonia and sulfate were detected and the common degradation product found at all photocatalytic conditions was p-Hydroxybenzoic acid.

It can therefore be concluded that photocatalysis with TiO_2 under artificial UV-A and natural solar light promote efficient degradation of beta-lactum antibiotics.

3.3 Fixed-bed photocatalysis

UV/TiO_2 systems are mostly used in suspension but the main problem that arises in slurry mode is the filtration of catalyst that limits its use at industrial scale. As TiO_2 is the most favorable and widely used catalyst in heterogeneous photocatalysis, it can be fixed on various supports like glass, stainless steel, pumice stone, polythene film and silica. Various studies are reported in literature using TiO_2 in the fixed-bed mode for treating the wastewater (**Pozzo et al., 1997; Madani et al., 2006**).

3.3.1 Various supports for TiO_2 immobilization

Stainless steel

TiO_2 coating was done on stainless steel coupons and glass beads. The method followed for coating was conventional alkoxide sol-gel method and Degussa P-25 powder enriched method. Both these methods were compared. Stainless steel coupons coated with TiO_2 were used in the quartz reactor for the removal of organic pollutants present in water. Figure 3.2 depicts the SEM micrograph of stainless steel coupons immobilized with TiO_2 through powder enriched alkoxide sol-gel after three coating cycles **(Balasubramanian et al., 2004)**.

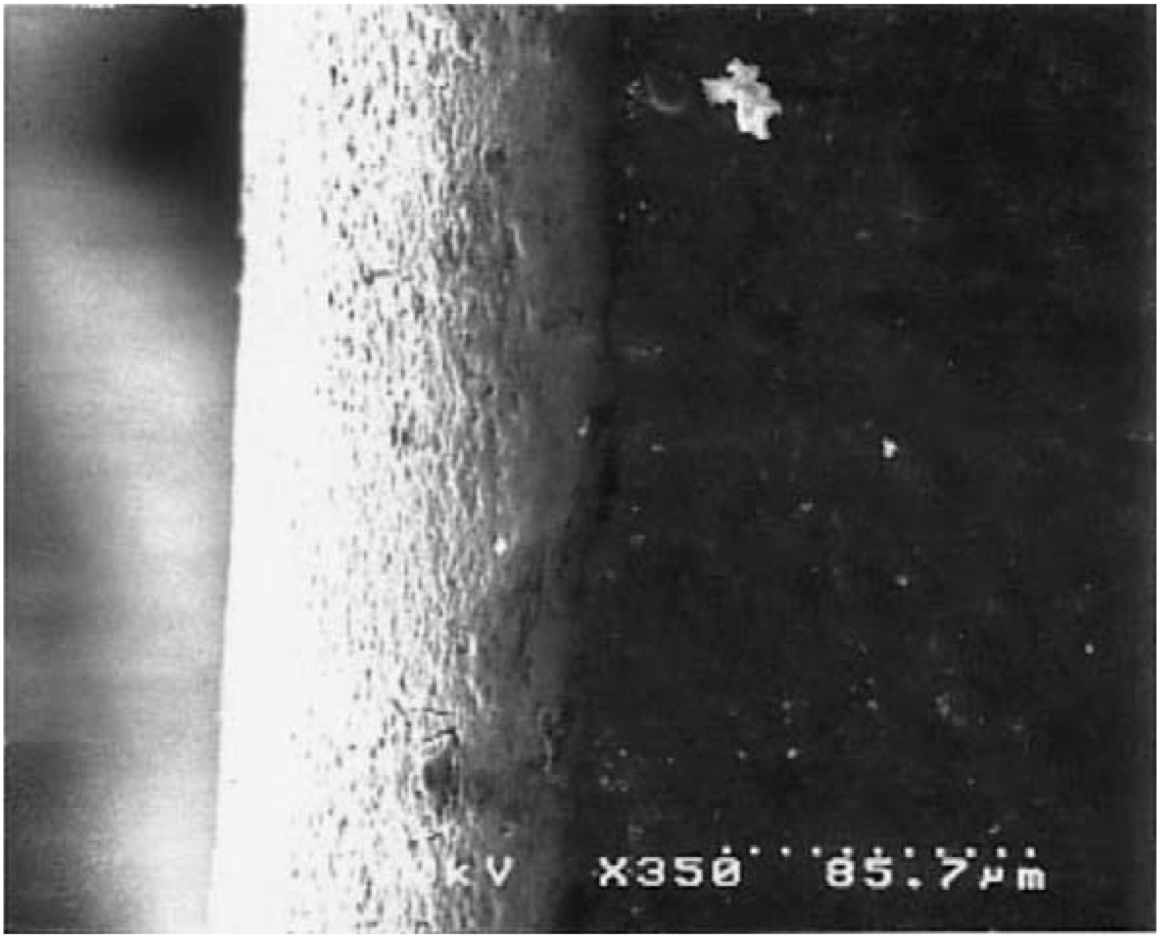

Figure 3.2: SEM micrograph of TiO_2 coated stainless steel coupons after 3 coating cycles.

Glass rings, plate and glass beads

Coating of the catalyst on glass rings as well as glass beads was tested for the degradation of pesticide atrazine. Two types of TiO_2 namely TiO_2 P25 and TiO_2 in colloidal form containing only anatase were used and compared for their efficiencies over degradation of pesticide. The coating of catalyst over rings and beads was done following the dip coating method. The photocatalytic degradation of atrazine with supported TiO_2 P25 over glass rings was as effective as TiO_2 in slurry mode. No significant decrease in the catalytic activity of immobilized TiO_2 over rings was observed after using the same batch for seven experiments **(Parra et al., 2004)**.

TiO_2 was coated on glass plate **(Verma et al., 2013)**. The glass plate was first made rough by means of sand paper and then degreased by immersing in HNO_3 solution. The coating of TiO2 was done following the dip coating method. The coated glass plate was calcined at 300

^{0}C in muffle furnace for one hour. This coated glass plate was used vertically at an inclination of 20 ^{0}C and 45 ^{0}C in a reactor for the degradation of 2-chloro-4-nitrophenol as shown in figure 3.3. the whole setup comprising of angle variation plate and coated glass plate was kept on a movable trolley for the maximum penetration of sunlight. 72% degradation of the compound was achieved after 8 h of irradiation. The surface area using this immobilized support for photocatalytic treatment has been found to increase thus improving the degradation.

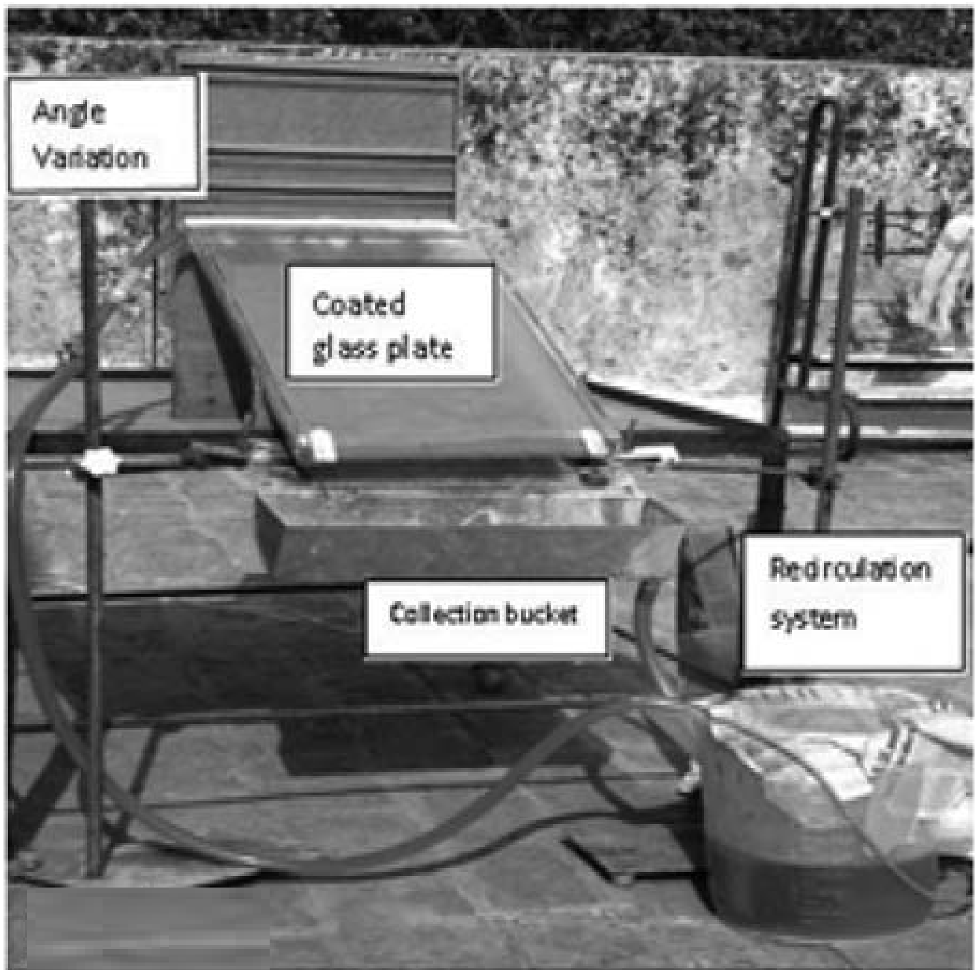

Figure 3.3: TiO_2 coated glass plate reactor for the degradation of 2-chloro-4-nitrophenol.

Balasubramanian et al., 2004 also used glass beads for the photocatalytic degradation of organic pollutants and coating of the glass beads with catalyst was done using the same method as described above in case of stainless steel. SEM micrographs of TiO_2 coated glass beads after eight coatings are shown in figure 3.4 which demonstrates a continuous surface.

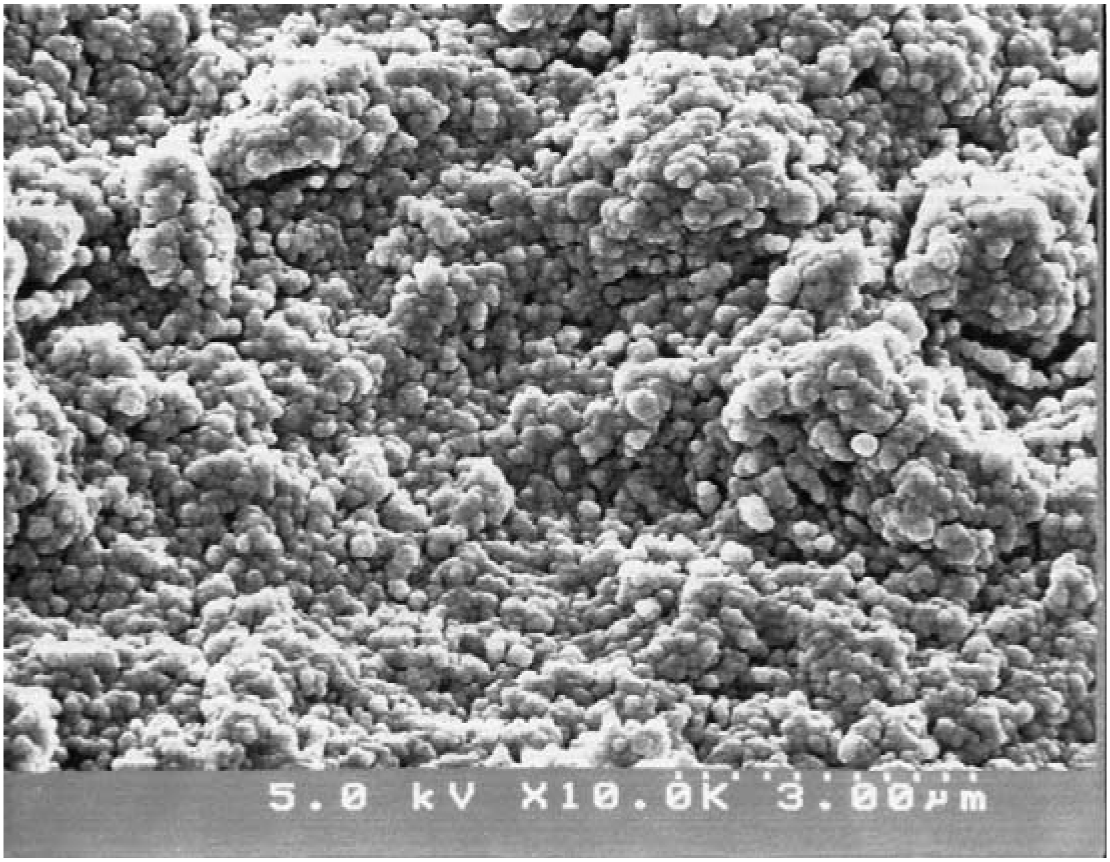

Figure 3.4: SEM micrograph of TiO_2 coated glass beads after 8 coating cycles.

Stones

TiO_2 was immobilized on an inert support like cuddapah stone. The coating was done twice with a laboratory spray gun using the mixture of TiO_2 and acrylic emulsion. This immobilized system was used for the photocatalytic degradation of H-acid. The thin film of TiO_2 was found to be stable even after 30 days of experiments. The use of acrylic emulsion in coating improved the adherence of TiO_2 particles without bringing any change in its Photocatalytic activity. A thin film fluidized bed reactor (TFFBR) (Figure 3.5) made up of cuddapah stone having dimensions: length=144 cm, breadth=52 cm and height=10 cm. the aqueous solution of H-acid was made to flow in a reactor at a flow rate of 750 mL min^{-1} using a circulation pump. Thus, TFFBR proved to be an efficient system for the degradation of recalcitrant compounds like H-acid since it prevents post-treatment filtration **(Noorjahan et al., 2003)**.

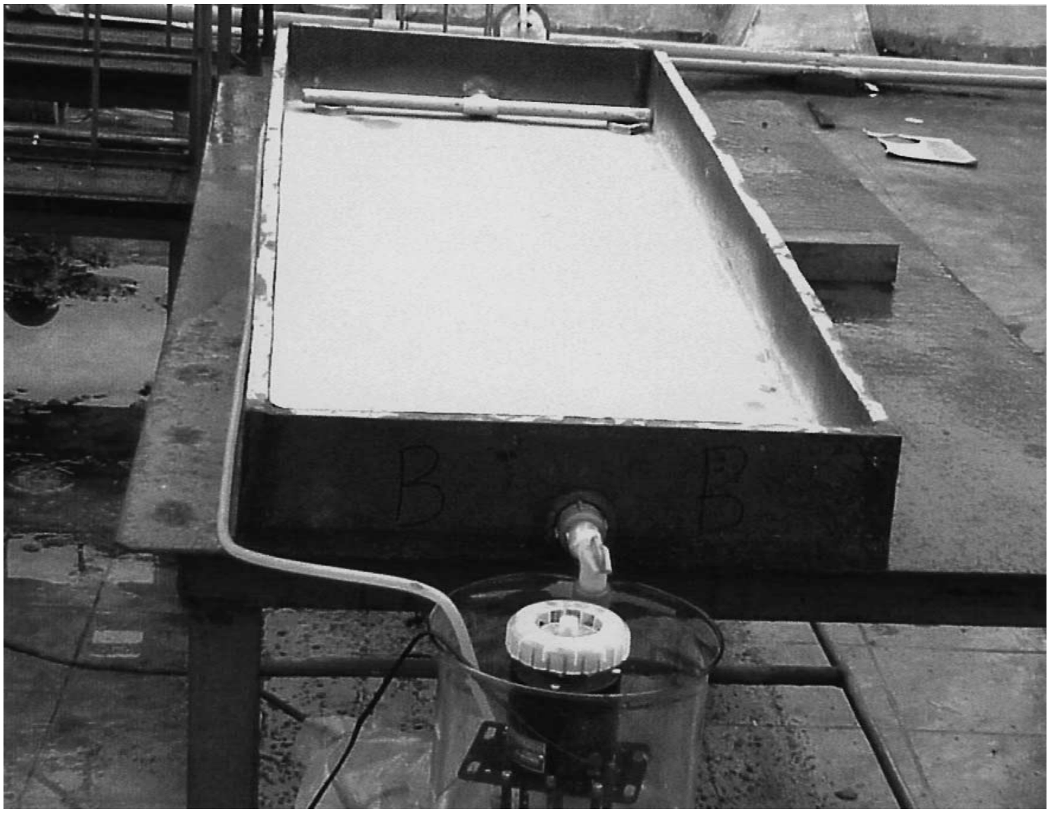

Figure 3.5: Thin film fluidized bed reactor (TFFR) for the degradation of H-acid.

Subrahmanyam et al., 2003 carried out an investigation for the degradation of dyes and dye industry pollutants through heterogeneous photocatalysis using supported TiO_2 over pumice stones. Soaking, drying and heat treatment methods were followed for the immobilization of catalyst over pumice stone pellets. As pumice stone is a soft material, its pellets are fixed either on cement or polycarbonate. The same method of heterogeneous photocatalysis using supported TiO_2 over pumice stone was also used for the removal of pathogens from drinking water as well as for the removal of recalcitrants present in wastewater. Two reactors were designed using pumice stone pellets. One is the thin film fixed bed photocatalytic reactor. The other is the multi-tube reactor as shown in figure 3.6. A total volume of 8 L of solution was used in a reactor at a time having flow rate of 2 L min^{-1} under solar irradiation. Time required by such reactors for the E. Coli deactivation was 20-40 min under solar irradiation thus ensuring its technical feasibility **(Subrahmanyam et al., 2008)**.

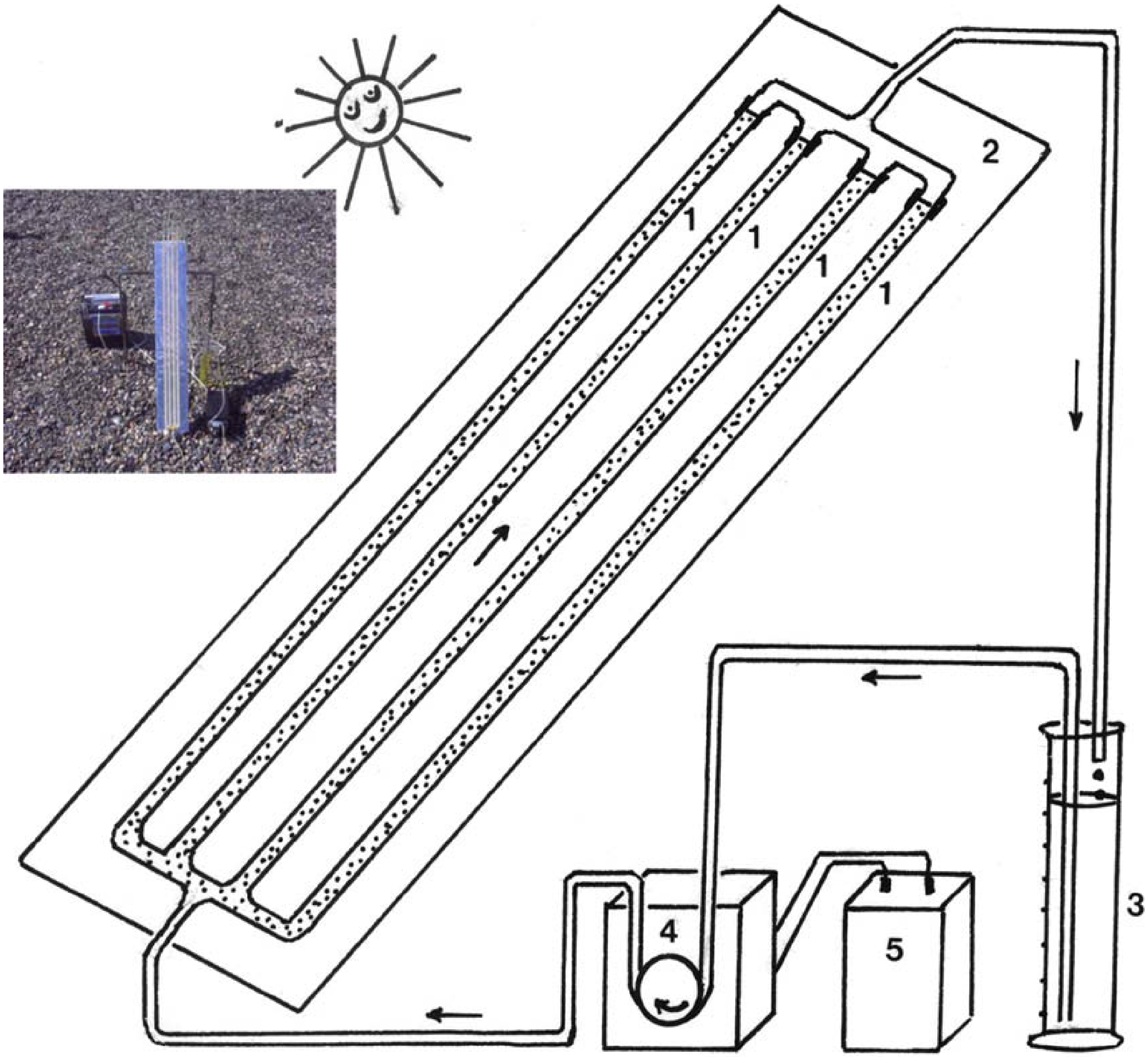

Figure 3.6: Multi-tube photocatalytic reactor with pumice stone immobilized with TiO_2, (1) tubes filled with catalyst (L) = 750 mm, diameter 5 mm; (2) reflecting surface; (3) volumetric jar with solution (4) peristaltic pump; (5) battery.

Rao and Chaturvedi, 2012 studied the decoloration and mineralization of wastewater from textile industries using fixed-bed photocatalysis. For the fixed-bed, they coated pebbles with TiO_2 under direct sunlight as shown in figure 3.7. The trough (inner length, 52 cm; inner width, 45 cm; height, 0.8 cm) was made up of transparent Perspex sheet. The pebbles were placed uniformly forming equilateral triangles which leads to the optimal distribution of liquid over the pebbles thus avoiding preferential channeling.

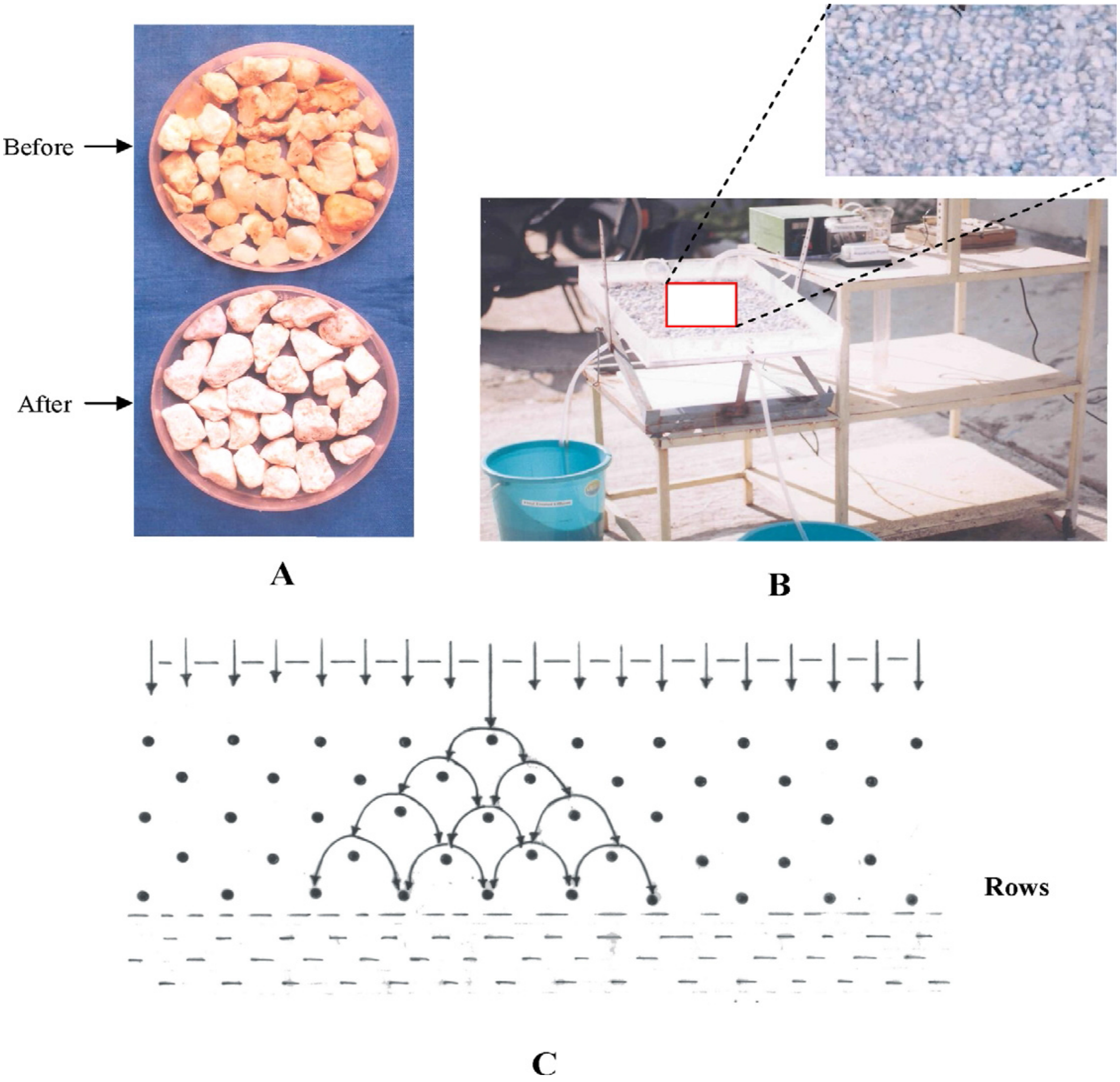

Figure 3.7: (A) Pebbles before and after TiO_2 coating, (B) solar photocatalytic fixed bed reactor (C) arrangement of pebbles in a pebble-bed reactor and expected pattern of water distribution (arrows indicate the direction of flow of water).

Fibers

Studies have been conducted for coating quartz sand with TiO_2 P25 **(Heinzle et al., 1996)**. Coating was carried out in 2-propanol thus making a suspension of TiO_2 and quartz sand which was air-dried after filtering and washing with 2-propanol. The coated quartz sand was then heated at 400 ^{0}C for 1 h. This coated quartz sand was loaded in fluidized bed photoreactor and the degradation of 4-chlorophenol and p-toluenesulfonic acid was investigated.

Studies are reported regarding coating of TiO_2 on fiber **(Stephan et al., 2011)**. Coated fiber was deposited on the steps in the falling film closed loop step reactor. These studies were conducted for the degradation of pesticide chlortoluron. Satisfactory results were obtained regarding the degradation of compound but still some improvements are required in case of commercial applications.

A hydrosol dip coating method was used for coating quartz optical fibers and quartz rods **(Hoffmann et al., 1995)**. Three coatings were found to be sufficient for efficient coating. These coated fibers and rods were fired at high temperature ranging from 200 ^{0}C and 500 ^{0}C in a muffle furnace. An optical fibre reactor (figure 3.8) bundled with these coated fibers was employed for the photocatalytic degradation of 4-chlorophenol.

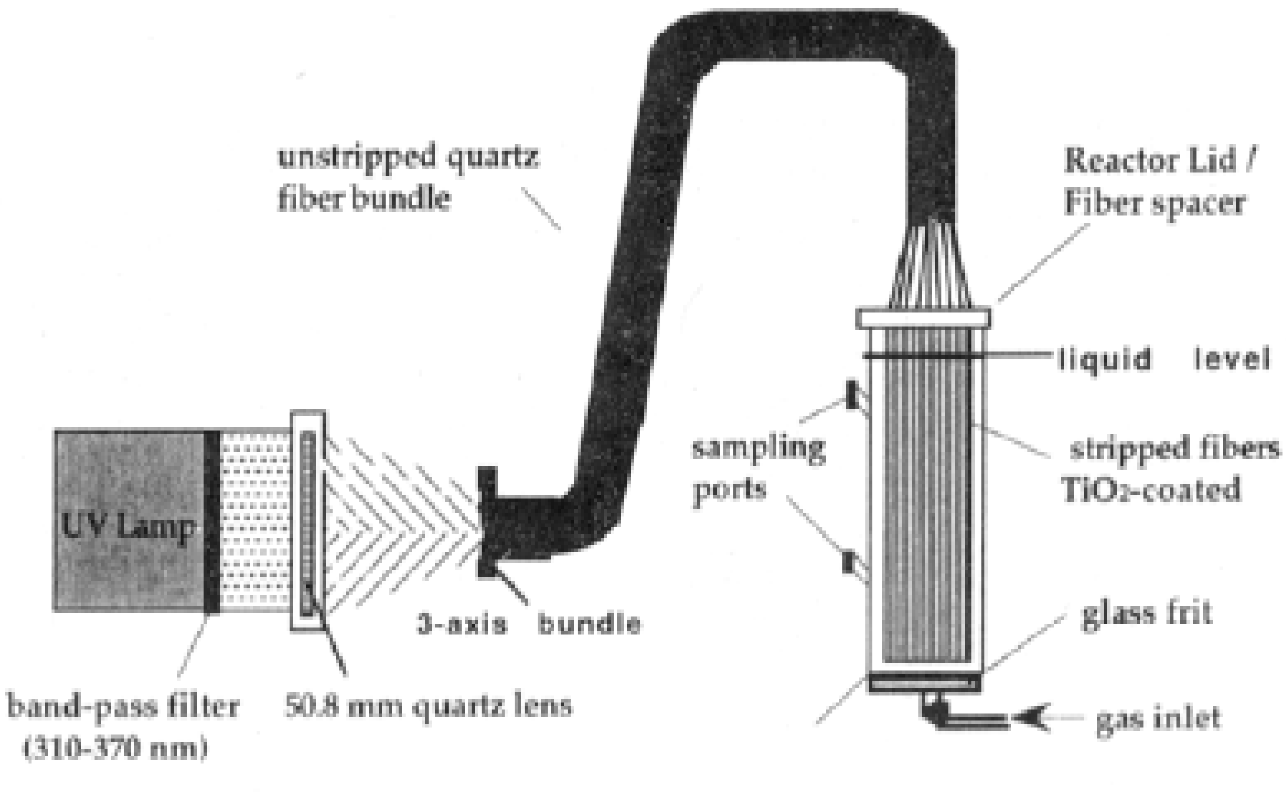

Figure 3.8: Optical fibre reactor for the degradation of 4-chlorophenol.

Concrete slabs and beads

Thin film coating of the catalyst is a widely used method for the photocatalytic degradation of organic pollutants. **Zayani et al., 2009** made use of a thin film fixed-bed reactor for the photocatalytic degradation of commercial textile azo dyes. After proper stirring, TiO_2 suspension was applied to the outer surface of the concrete plate using a painting roller which was then left under solar radiations for one day.

Cemented slabs were coated with TiO_2 and were used in photocatalytic experiments to study the degradation of 2-chloro-4-nitrophenol. Coating was done following the dip coating method. 75 % degradation was achieved using this support material. Catalyst was found to be stable after reuse. The same slabs were used for at least ten experiments and were found to be durable enough **(Verma et al., 2014)**.

TiO_2 was immobilized on cement beads of different diameters and their efficacy was checked for the degradation of herbicide isoproturon. Coating of TiO_2 on beads was carried out using standard dip coating method. Two cycles of coating were repeated using the same method and after every cycle, beads were calcined at 400 ^{0}C for two hours in muffle furnace. The same coated beads were used in solar baffled reactor to study the degradation of the compound and significant degradation was achieved using the immobilized beads **(Verma et al., 2014)**.

CHAPTER 4

OBJECTIVES

The present study is focused on the photocatalytic degradation of antibiotic Cephalexin using slurry and fixed-bed photocatalysis at batch scale along with the fixed-bed solar baffled pilot scale reactor.

The study is undertaken with the following objectives:

- To study the degradation of Cephalexin using slurry photocatalysis.
- To study the influence of operating parameters like catalyst dose, oxidant addition, UV intensity, depth of reactor on the degradation of compound.
- To study the degradation of compound using cement beads as inert support in fixed bed photocatalysis.
- To study the degradation of compound using fixed bed solar baffled reactor.

CHAPTER 5

MATERIALS AND METHODS

This section discusses about the various analytical methods used for the treatment of compound. Standard methods have been employed throughout the study.

5.1 Pharmaceutical compound

Cephalexin hydrate (Figure 5.1), (6R,7R)-7-[(2R)-2-amino-2-phenylacetamido]-3-methyl-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid, CAS No. 15686-71-2, was purchased from local market, Patiala (India) and was employed as received without any further purification. Cephalexin is a semi-synthetic beta lactum antibiotic which acts in the same manner as penicillin by inhibiting the synthesis of bacterial cell walls. It is widely used in human and veterinary medicine to prevent bacterial infections. It is being detected in wastewater at low concentrations and being highly stable and low biodegradability, it is difficult to remove through conventional techniques.

Maximum absorbance of the compound was obtained at 263 nm after scanning it through UV- Vis spectrophotometer over a range of 190 to 450 nm.

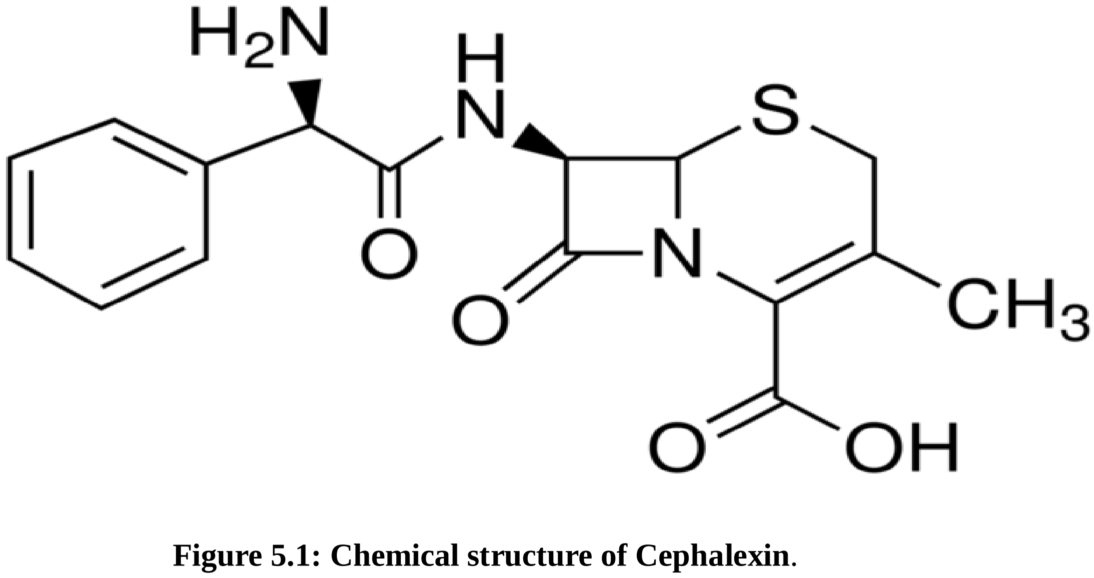

Figure 5.1: Chemical structure of Cephalexin.

5.2 Reagents and chemicals

TiO_2 P-25 (a mixture of anatase and rutile form of titanium dioxide in the ratio of 70:30) was used as a photocatalyst and procured from Evonik Industries, India. Hydrogen Peroxide, H_2O_2, procured from Ranbaxy, India was used as an oxidant. The concentrated solutions of HCl and NaOH were obtained from Merck and were used for adjusting the pH. The double distilled water was used for preparation of all solutions. Standard methods as per American Public Health Association (APHA) were employed for calculating NO_2^- **(APHA, 1989: Sec. 4500-NO_2 (B))**, NO_3^- **(APHA, 1989: Sec. 4500-NO_3 (E))**, SO_4^{2-} **(APHA, 1989: Sec. 4500-SO_4^{2-}(E))** and COD **(APHA, 1989: Sec. 5220 (C))**.

5.3 Instruments used

5.3.1 pH meter

The pH meter (purchased from Eutech instrumentation) was used to adjust the pH of the solution using 0.1N HCl and 0.1N NaOH. Instrument was calibrated weekly with freshly prepared buffer solutions (pH 4 and 9).

5.3.2 UV-Vis Spectrophotometer

UV-Vis spectrophotometer (LABINDIA, model no. T60 U) was used for photo degradation analysis of Cephalexin at 263 nm.

5.3.3 Radiometer

Eppley (model no. 33013) radiometer was used to measure solar UV Intensity hourly during experimental days.

5.3.4 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 cement beads.

5.3.5 Muffle Furnace

Rate controlled muffle furnace (temperature range 200 to 1200 ^{0}C) was used for the fixation of catalyst coating on cement beads. It was operated at a temperature of 250 ^{0}C for this purpose.

5.3.6 COD Digester

COD Digester was used for the digestion of samples in the process of COD determination.

5.4 HPLC analysis

The samples were also analysed using HPLC [Shimazdu, communication module (CBM-20A), diode array detector (SPD-M20A), pump (LC-20AD)] for the confirmation of Cephalexin degradation. HPLC was performed on binary HPLC system with C-18 column (250 mm x 4.60 mm), particle size 5 µm using ammonium acetate (0.01M) and acetonitirile as mobile phase with UV detector at 263 nm for Cephalexin. Flow rate was maintained at 1.0 mL min^{-1} with 10% acetonitrile. Each analysis lasted 20 min and the injection volume was 20µL.

5.5 SEM-EDAX analysis

The morphology of freshly coated cement bead and recycled bead was studied using SEM (JSM-6510LV, JEOL, Japan) and EDS (INCAX-act, Oxford instruments, United Kingdom).

5.6 Experimental setup and procedure

5.6.1 Lab scale reactor setup

The rectangular wooden UV chamber was used for performing the photocatalytic experiments described in our previous studies **(Verma et al., 2014)**. The batch reactor used was made up of borosil glass, 17.4 cm in diameter and 5.2 cm in height having a capacity of 1200 mL. The reactor was placed on a laboratory jack in a rectangular wooden UV chamber having dimensions 1.37 m × 0.9 m × 1.0 m. The chamber contained 36 W UV tubes having wavelength of 365 nm and were installed on the underneath of the chamber. The required UV intensity could be achieved by varying the distance of reactor from UV tubes **(Toor et al., 2006)**. The average UV intensity was varied from 10 to 24 Wm^{-2} which is equivalent to the average intensity of UV radiation in sunlight. An exhaust fan was installed for controlling the proper temperature inside the chamber. The reaction was carried out in natural solar light as well. Antibiotic aqueous solution was made by dissolving specific amount of Cephalexin in double distilled water and magnetically stirring it at 30-40°C for 30 minutes. The solution was prepared weekly and stored at room temperature.

For the photocatalytic experiments, the antibiotic aqueous solution was maintained in dark for 1 h to attain the complete adsorption equilibrium. A 200 mL of the antibiotic aqueous solution was taken in a batch reactor with required amount of TiO_2 and was magnetically stirred under UV irradiation. The aeration was provided by means of a sparger. An aliquot of 3-4 mL was collected from reaction vessel at regular time intervals using a syringe and filtered through a Millipore filter (0.45 µm). Figure 5.2 (a) and 5.2 (b) shows the pictures of the slurry batch reactor setup in artificial UV light and natural sunlight respectively.

The process was optimized by varying the parameters like catalyst concentration, amount of oxidant, pH, UV intensity, depth of the reactor based on which reaction kinetics was studied. All experiments were carried out in triplicate for reproducibility of results. The standard deviation for all the experiments was in the range of 1-5%.

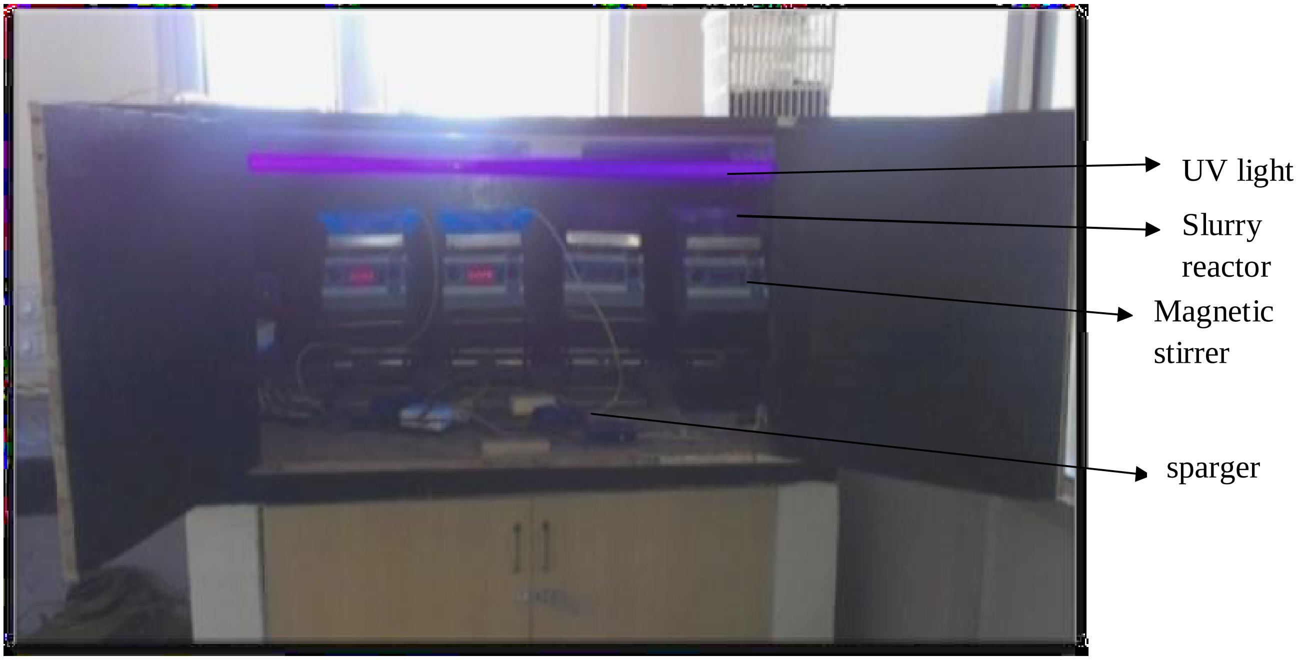

Figure 5.2a: Lab-scale setup of slurry reactor in UV light.

Figure 5.2b: Lab-scale slurry reactor in sunlight.

5.6.2 TiO_2 coated cement beads

5.6.2.1 TiO_2 immobilization

Around 200 cement beads of different size were prepared manually by mixing sand and cement. From these beads, almost 50 beads of uniform size were selected and used for TiO_2 coating. TiO_2 was coated on cement beads using method described in previous studies **(Verma et al., 2014)**. Even the previously coated beads of earlier study were also used for checking their efficacy in degrading the Cephalexin. The catalyst was coated on the beads in the form of film with average thickness of 40µm as confirmed from SEM-EDAX. Figure 5.3 shows the image of TiO_2 coated cement beads.

Figure 5.3: TiO_2 coated cement beads.

5.6.2.2 Experimental procedure

Fixed-bed photocatalytic studies were performed using same batch reactor containing required number of catalyst coated cement beads and 200 mL of antibiotic solution and was irradiated by UV light. Aeration was provided by means of two spargers at a time. The samples were collected by means of a syringe at regular intervals. The lab-scale setup is shown in figure 5.4.

Figure 5.4: Lab-scale setup of fixed-bed reactor.

5.7 Fixed-bed baffled solar reactor

The pilot scale set-up comprised of a concrete baffled reactor having dimensions of 30 cm x 20 cm as shown in line diagram (Figure 5.5a). The reactor consisted of four baffles arranged uniformly. The catalyst coated cement beads were placed in every chamber of the baffled reactor in a manner that they are efficiently immersed in the solution to be treated. The flow rate of the antibiotic solution was maintained for achieving the desired retention time. The reactor was shielded with a transparent film for effective penetration of sunlight and for preventing the evaporation losses (Figure 5.5b).

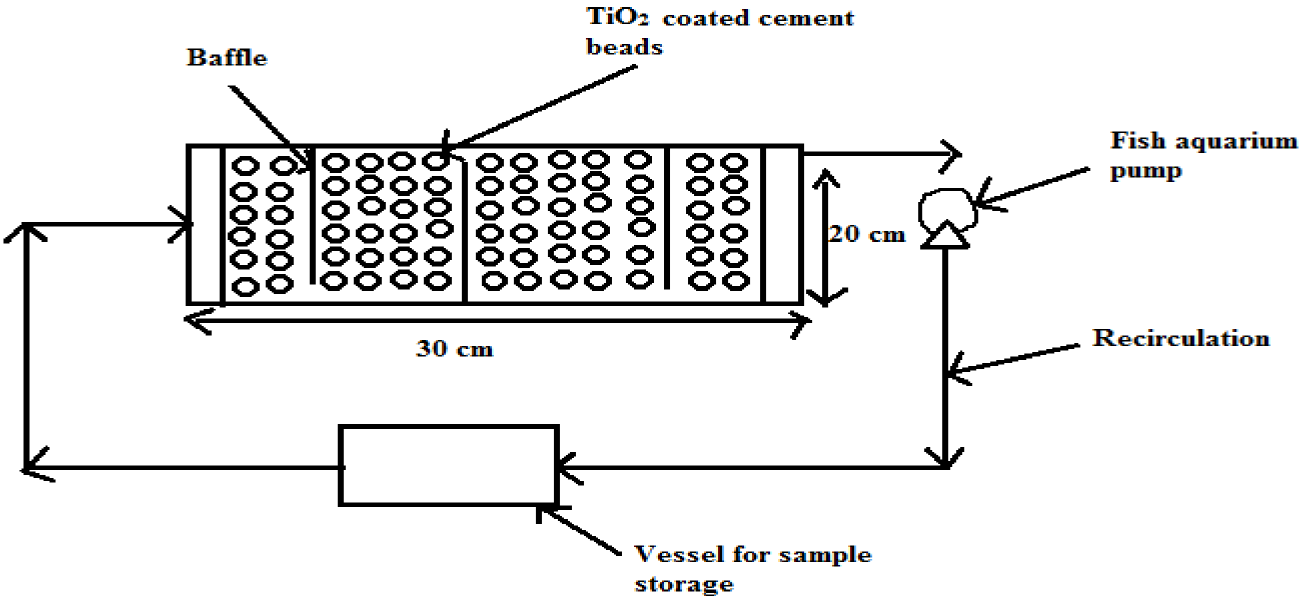

Figure 5.5a: Line diagram of solar fixed-bed baffled reactor.

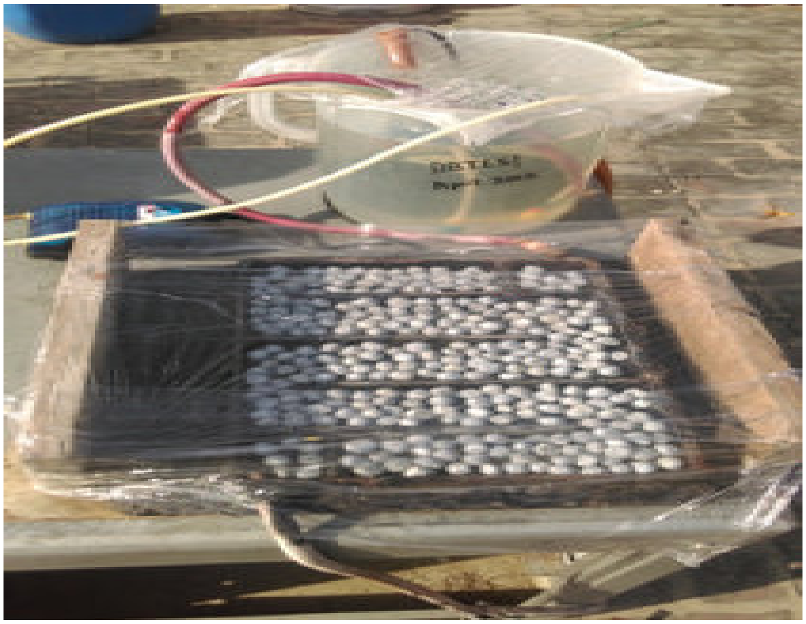

Figure 5.5: Pilot-scale solar fixed-bed baffled reactor.

The above reactor was designed to treat a maximum solution of 5 L. With certain design modifications, the reactor can be devised to treat a large volume of solution with a desired retention time for better results at industrial scale.

CHAPTER 6

RESULTS AND DISCUSSION

The photocatalytic degradation of Cephalexin using slurry and fixed-bed photocatalysis employing TiO_2 has been discussed in this chapter. Process has been optimized by varying certain operating parameters like concentration of oxidant, catalyst dose, pH, A/V ratio and intensity of UV. Pilot-scale studies were also conducted using a baffled solar reactor to see its viability for commercial applications.

6.1 Standard calibration curve of Cephalexin

Standard calibration curve was plotted using known concentration of Cephalexin. A graph of absorbance versus concentration of Cephalexin solution was plotted by varying the known concentration of the solution as shown in figure 6.1. The concentration of Cephalexin solution was varied from 10 mgL^{-1} to 80 mgL^{-1} at 263 nm. The regression coefficient and slope of the curve were found to be 0.9998 and 0.0217 respectively.

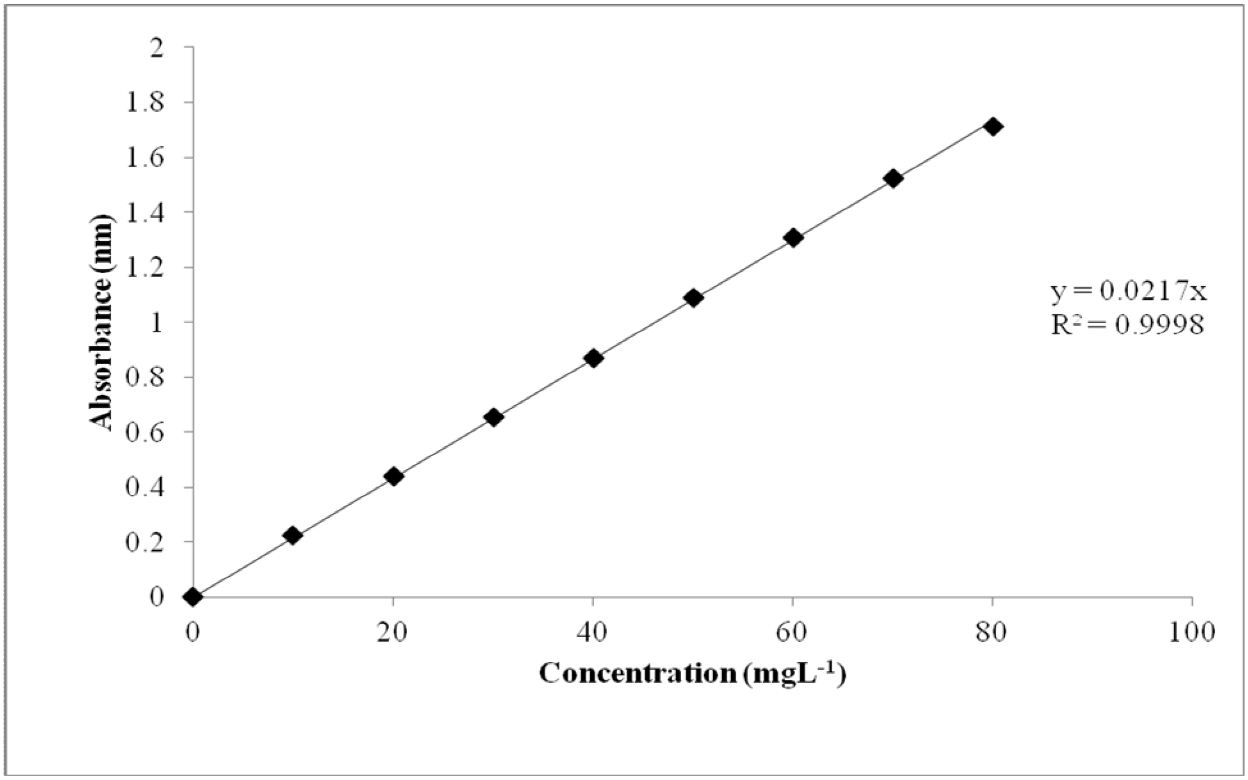

Figure 6.1: Standard calibration curve of Cephalexin.

6.2 Degradation studies using slurry photocatalysis

6.2.1 Preliminary studies

Preliminary experiments were performed to study the effect of individual parameters on the degradation of Cephalexin. A negligible amount of photodegradation (8.73%) was observed when only Cephalexin solution was exposed to UV light in a batch reactor. While adsorption studies (TiO_2 only) showed 10.75% reduction in concentration of the compound. The reduction in concentration of the compound is mainly due to its adsorption on the surface of catalyst. Moreover, when H_2O_2 alone was used, 7.17% degradation was achieved which may be due to the production of very less amount of OH radicals. The photocatalytic treatment (UV + TiO_2 + H_2O_2) of Cephalexin showed significant degradation i.e. 93.47% after 2 h (Figure 6.2) due to the substantial increase in the generation of hydroxyl radicals. Thus, it leads to an assumption that adsorption-desorption of Cephalexin and reaction intermediates are comparatively slower than the formation of electron/hole pairs.

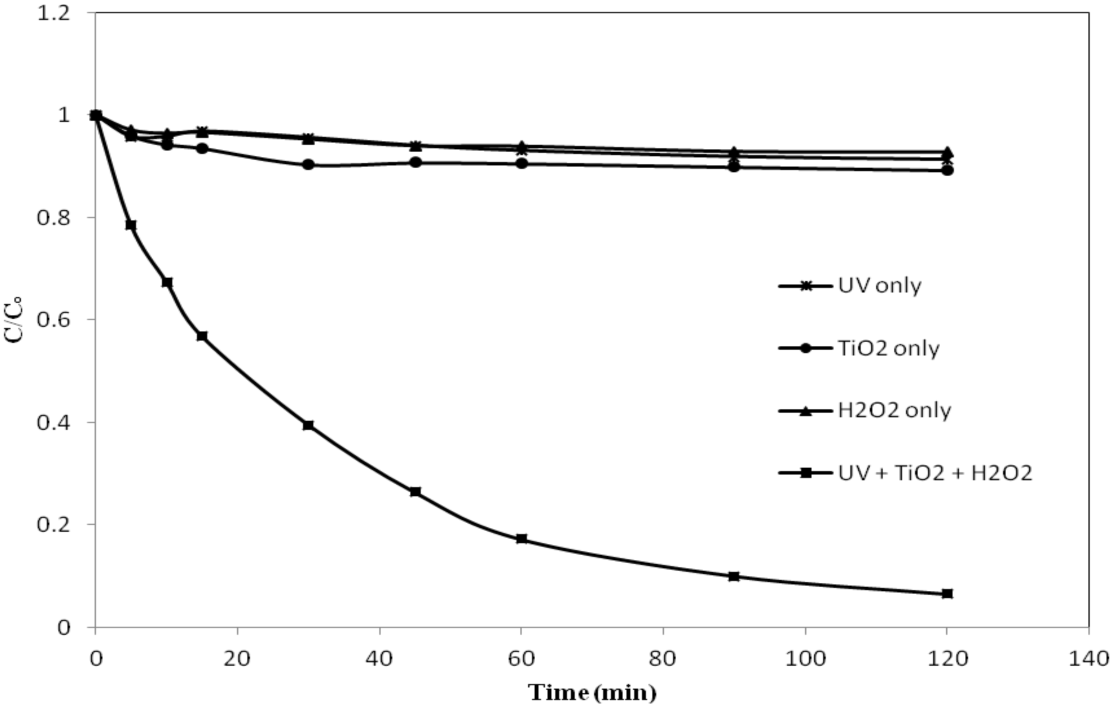

Figure 6.2: Photocatalytic degradation of Cephalexin in the presence and absence of TiO_2, H_2O_2 and UV. Experimental conditions: C_0=50 mgL^{-1}, V = 200 mL, UV intensity = 25 Wm^{-2}.

6.2.2 Photodegradation Kinetics

Various kinetic models have been defined for the photocatalytic degradation of different organics. Langmuir-Hinshelwood (L-H) kinetics model is the most acceptable model for almost all photocatalytic reactions. According to L-H model, the rate of degradation of organic pollutants is stated by equation 1.

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

Where, k_r is the reaction rate constant, K is the equilibrium adsorption constant, C is the substrate concentration at any time t. The factor KC being very small at low substrate concentrations can be neglected. Almost all the photocatalytic experiments describe pseudo-first order kinetic expression according to L-H model for studying the degradation rates of various organic compounds over TiO_2 (equation 2), i.e., $-dC/dt = kC$

$$\text{or } \ln C_0/C = kt \qquad (2)$$

Thus a plot of $\ln C_0/C$ versus time represents a straight line and slope of which gives k, an apparent first-order reaction rate constant. C_0 and C are initial and final concentration of the reactant, respectively.

6.2.3 Effect of TiO_2 concentration

An appropriate concentration of TiO_2 is required for the photocatalytic experiments. However, high concentration of catalyst is not recommended as it becomes difficult to separate the catalyst from slurry at higher concentration and moreover, it makes the process more expensive. In our study, initial concentration of TiO_2 was varied from 0.25-1.75 gL^{-1}. Photocatalysis was carried out for two hours with 50 mgL^{-1} of Cephalexin at its natural pH i.e. 5.5. A plot of $\ln C_0/C$ vs time is shown in figure 6.3 (a) which represents almost a straight line at all concentrations of TiO_2. The slope of straight line is used to calculate degradation rate constant, k. Figure 6.3 (b) demonstrates that the photocatalytic degradation rate constant (k) initially increased from .011 to .0206 min^{-1} by increasing the TiO_2 concentration up to 1.0 gL^{-1}

and then decreased with further increase in photocatalyst concentration. The reasons for this may be the reduction in the penetration of light, increase in the scattering of light **(Kansal et al., 2007)**, formation of aggregates and settling of TiO_2 under high concentration of catalyst **(Kilic et al., 2007)**. The decrease in photocatalytic reaction rate owed to reduction of OH radicals due to above cited factors. The best suitable amount of catalyst selected was 1.0 gL^{-1} of TiO_2 at which approximately 80% degradation was achieved after irradiation of 2 hrs. The optimized dose (1.0 gL^{-1}) was reasonably lower for field-scale applications in case of photocatalytic degradation of Cephalexin.

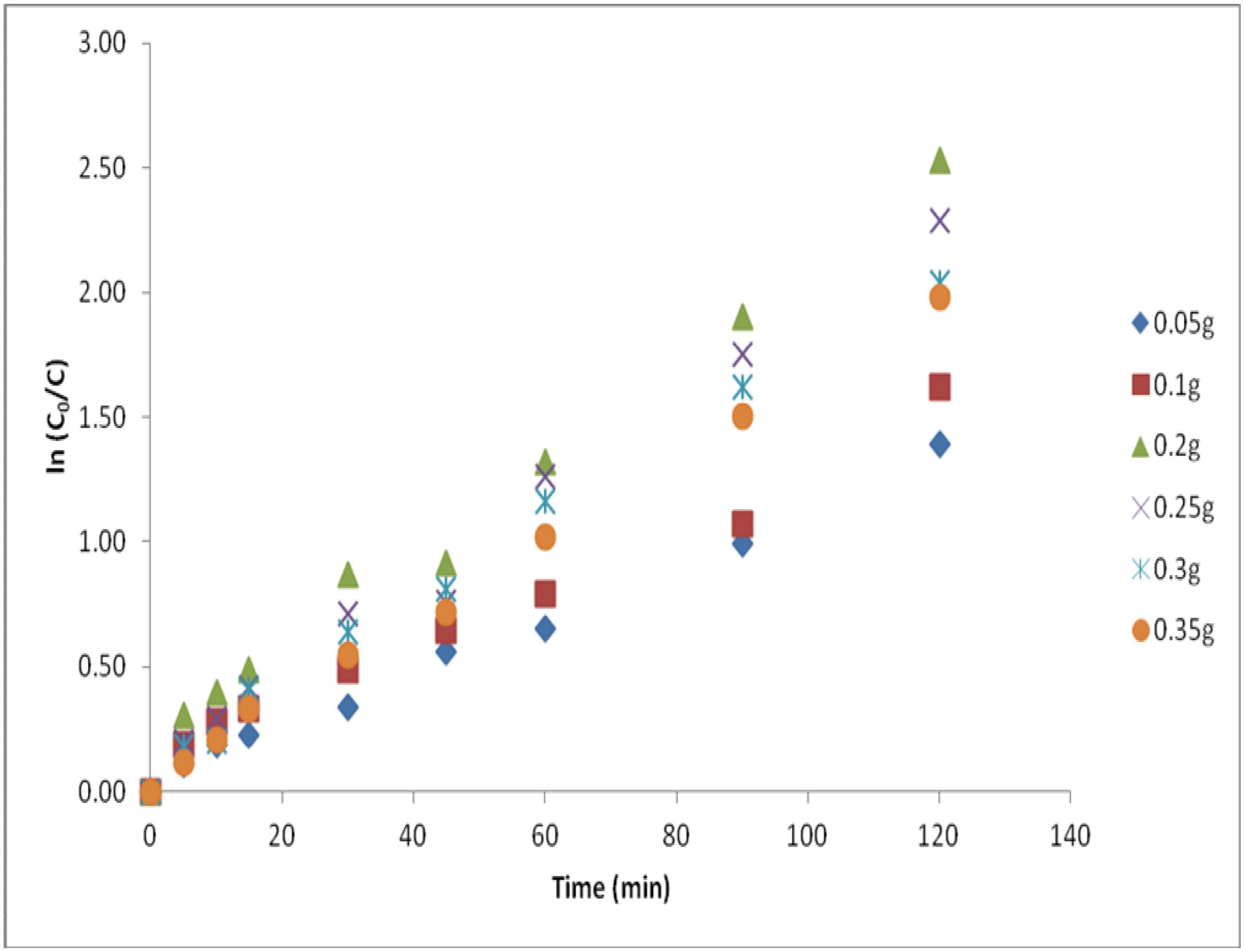

Figure 6.3 (a): Plot of ln C_0/C vs time at different concentrations of TiO_2.

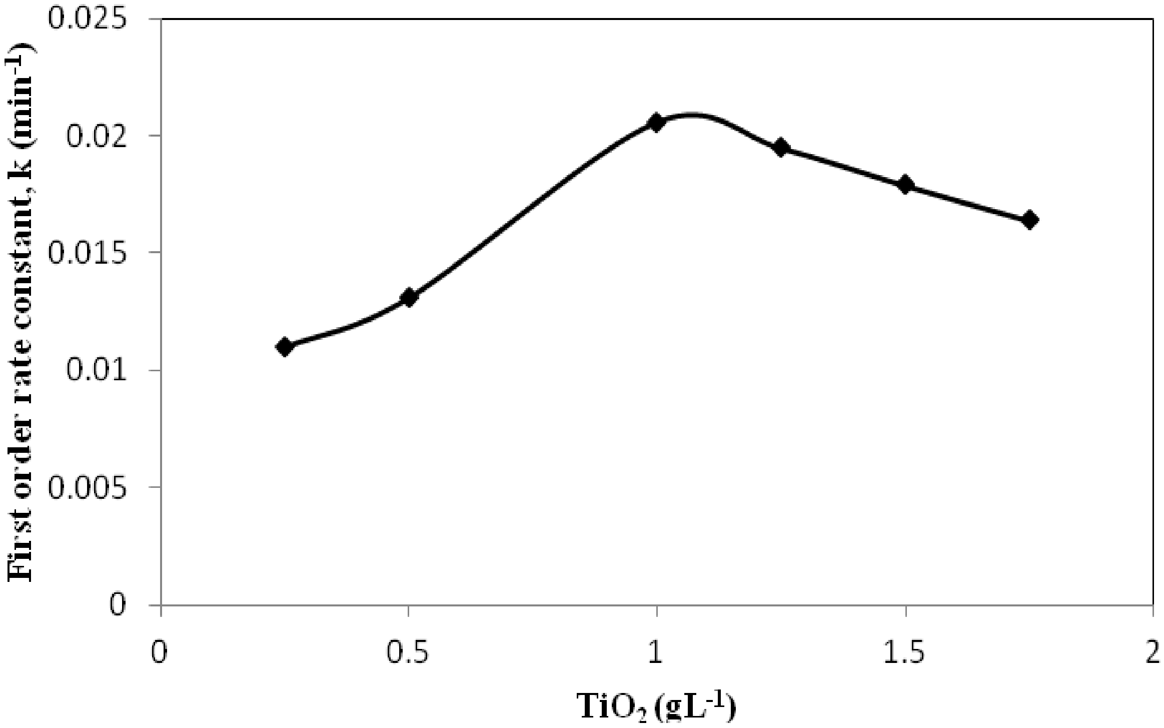

Figure 6.3 (b): Plot of first order rate constant, k vs variation in TiO_2 concentration during photocatalytic degradation of Cephalexin (C_0= 50 mgL^{-1}, V= 200 mL).

6.2.4. Effect of H_2O_2 addition

The role of oxidant (H_2O_2) addition to enhance the rate of photodegradation is now evident and well established in literature **(Malato et al., 2000; Poulios et al., 2003)**. Actually, H_2O_2 forms the $^{\cdot}OH$ radical after accepting the photon excited electron from the conduction band. It also forms $^{\cdot}OH$ radicals according to reaction (1) **(Kositzi et al., 2004)**.

$$H_2O_2 + {}^{\cdot}O_2^- \rightarrow {}^{\cdot}OH + OH^- + O_2 \qquad (1)$$

In order to calculate the optimum concentration of H_2O_2, the experiments were carried out by varying the initial concentration of H_2O_2 from 0.025-0.35 mL/200 mL with optimum TiO_2 concentration of 0.2 gL^{-1}. A plot of ln C_0/C is depicted in figure 6.4 (a) which represents a straight line from which k is calculated. Photocatalytic degradation rate constant (k) increased from 0.0212 min^{-1} to 0.0252 min^{-1} with the increase in addition of H_2O_2 in the range of 0.025-0.15 mL (Figure 6.4 (b)). The degradation increased from 80% to 93% with the addition of 0.15

mL of H_2O_2. The degradation rate constant (k) started decreasing after 0.15 mL of H_2O_2. This may be due to the scavenging of $^{\cdot}OH$ and hole which forms HO_2 as shown in reactions (2) and (3) **(Zhao et al., 2004; Behnajady et al., 2006)** at high concentrations of H_2O_2.

$$^{\cdot}OH + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \tag{2}$$

$$H_2O_2 + h^+ \rightarrow H^+ + HO_2^{\cdot} \tag{3}$$

Therefore, the best suitable amount of oxidant selected was 0.15 mL of H_2O_2 which resulted in 93% of degradation after 2 hrs of irradiation at 1 gL^{-1} of TiO_2 at its natural pH i.e. 5.5. These optimized conditions were employed for further experiments.

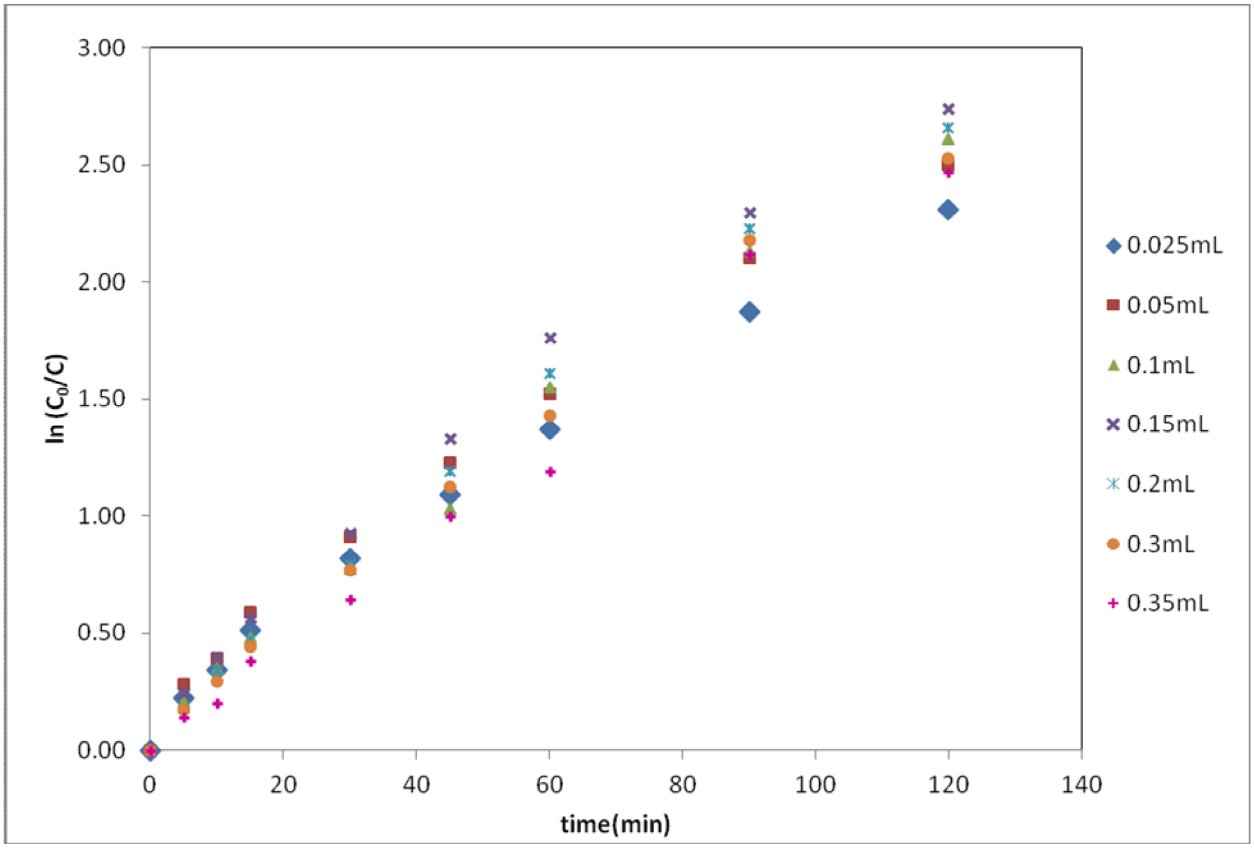

Figure 6.4 (a): Plot of ln C_0/C versus time at different concentrations of H_2O_2.

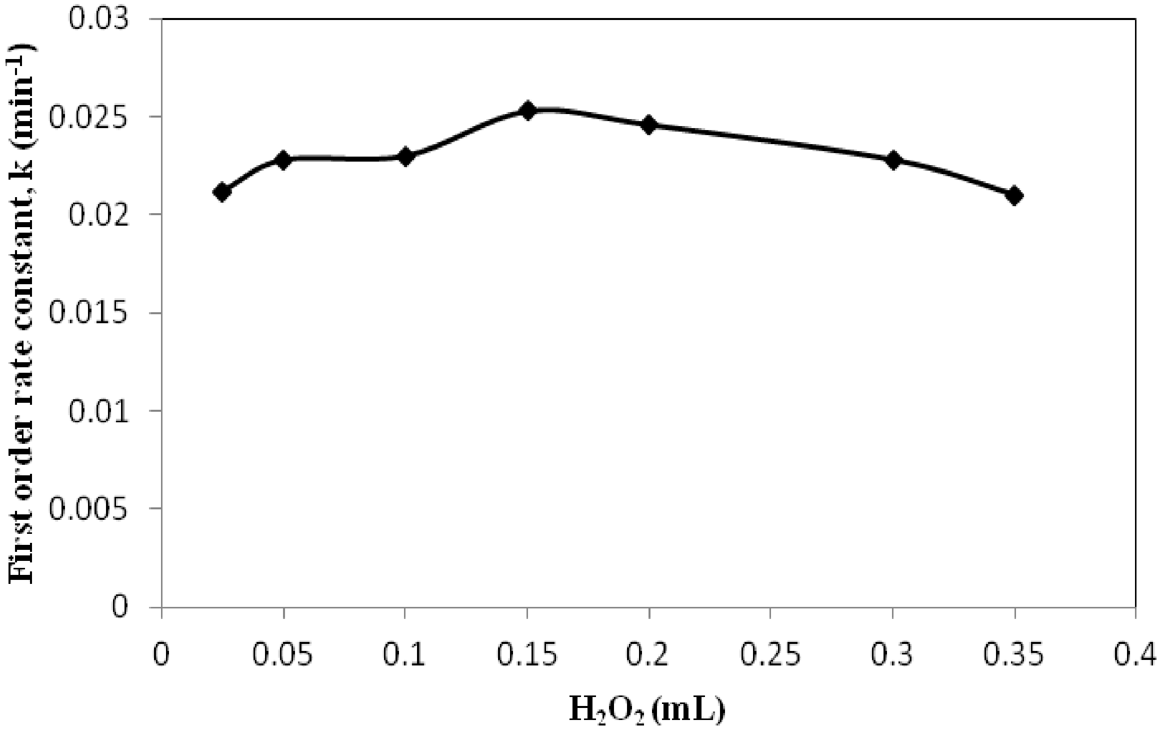

Figure 6.4 (b): Plot of first order rate constant, k vs varying H_2O_2 dose during photocatalytic degradation of Cephalexin (C_0= 50 mgL^{-1}, V= 200 mL).

6.2.5. Effect of UV intensity

The most fascinating application of AOP is use of solar radiations for the degradation of contaminants. As the solar UV radiation intensity is not constant throughout the year **(Dubey et al., 2009)**, the aqueous solution of Cephalexin (50 mgL^{-1}) containing optimum concentration of TiO_2 and H_2O_2 was irradiated at different UV intensities keeping the A/V constant at 1.19 cm^{2}mL^{-1}. Figure 6.5 (a) depicts the plot of ln C_0/C versus time that represents a straight line at different UV intensities. The degradation rate constant increased from 0.0161 to 0.0252 min^{-1} with the increasing UV intensity from 10 to 25 Wm^{-2} (Figure 6.5 (b)). This is due to the release of more OH radicals with increase in the intensity of UV radiations which subsequently leads to the higher rate of degradation.

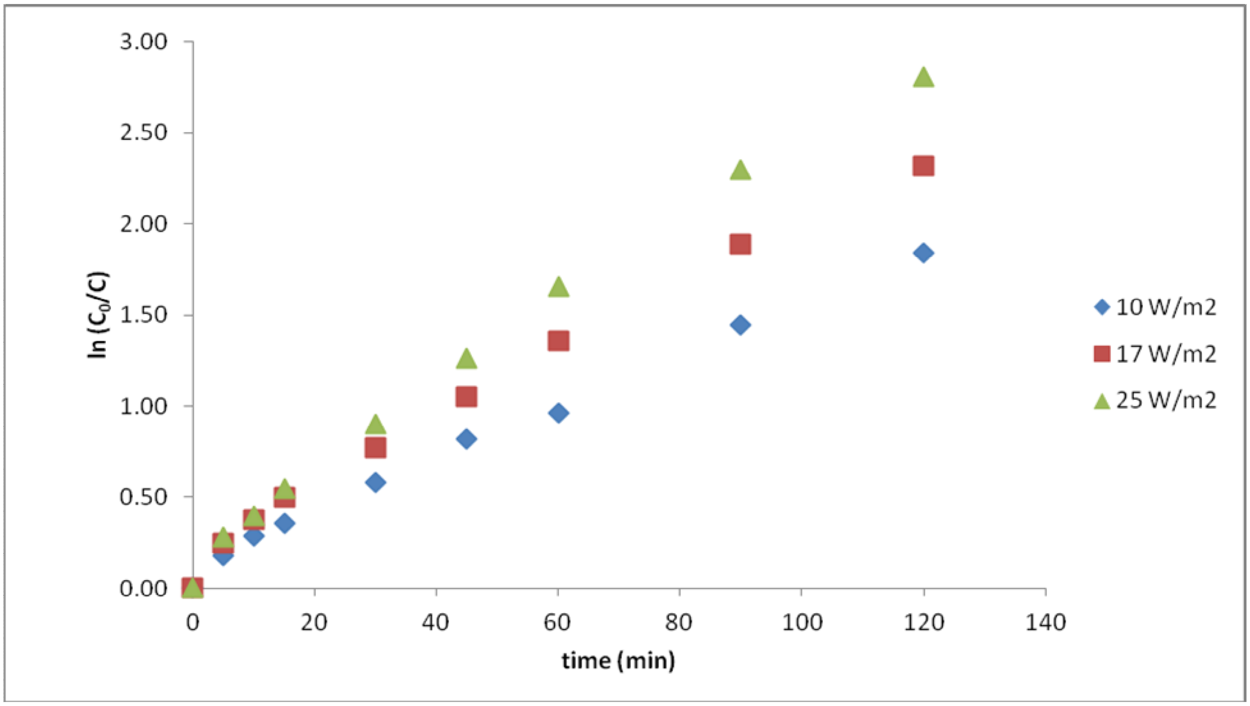

Figure 6.5 (a): A plot of ln C_0/C vs time at different UV intensities.

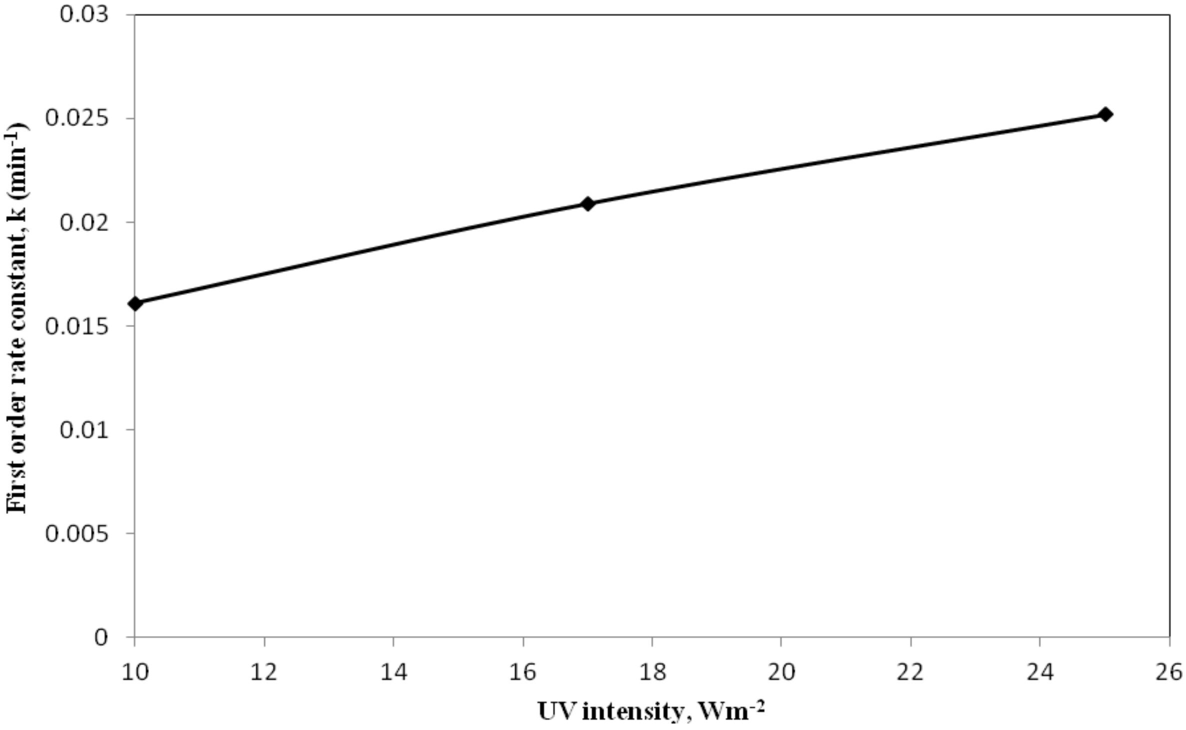

Figure 6.5 (b): Plot of first order rate constant, k vs variation in UV intensity during photocatalytic degradation of Cephalexin (C_0= 50 mgL^{-1}, V= 200 mL).

6.2.6. Effect of pH

To observe the effect of initial pH on photocatalytic degradation of Cephalexin, pH was varied in the range 3-8.5 with optimized conditions i.e. TiO_2 0.2 gL^{-1} and 0.15 mL of H_2O_2 with C_o = 50 mgL^{-1}. The initial pH of the solution portrays the surface charge characteristics of the catalyst and therefore adsorption of the compound can be depicted. The surface charge of TiO_2 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 catalyst **(Hoffman et al., 1995)**. Figure 6.6 (a) demonstrates a plot of ln C_0/C versus time at different pH values. The rate of degradation in our study was maximum at acidic pH i.e. 3, then insignificantly decrease up to pH 5.5 and thereafter a considerable decrease in the degradation rate was observed at alkaline pH as 'k' was significantly higher (0.0311 min^{-1}) in acidic pH as compared to k value (0.0130 min^{-1}) in basic pH as depicted in Figure 6.6 (b). All studies were conducted at solution's natural pH i.e. 5.5 at which approximately 93% degradation was attained under optimized conditions.

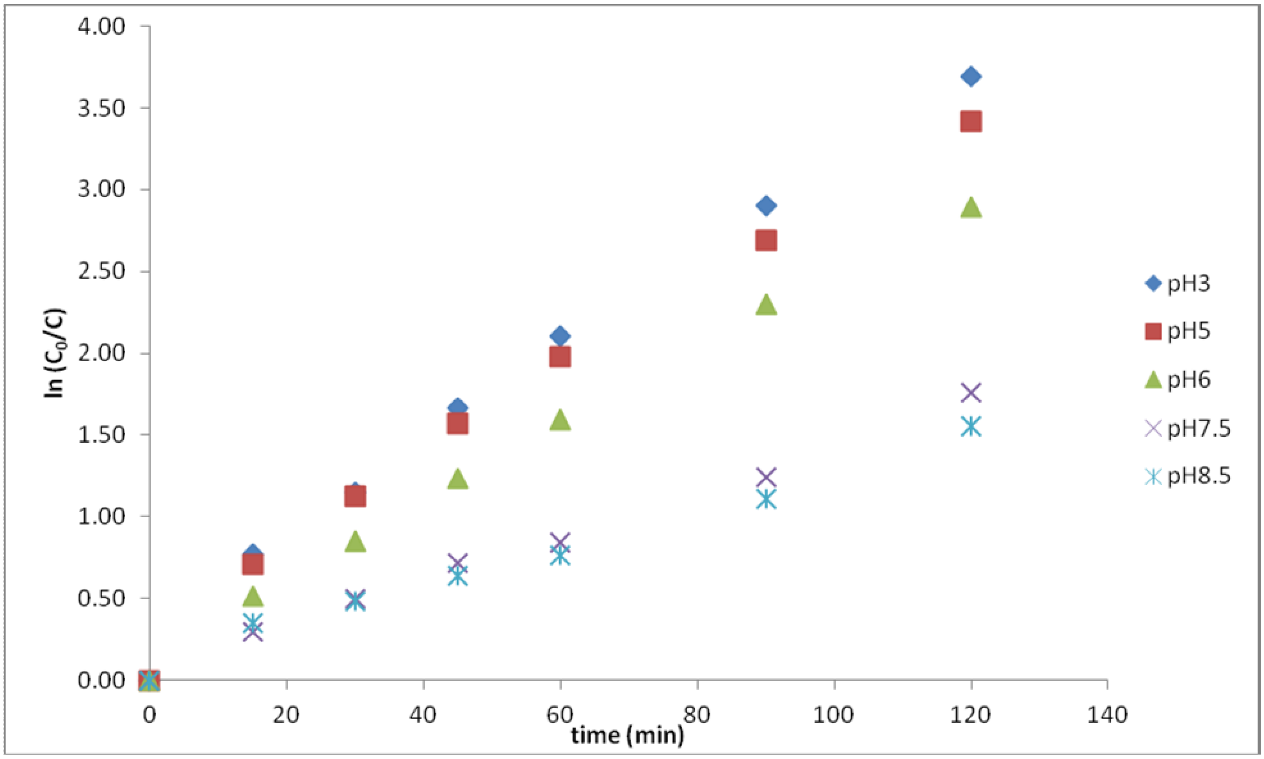

Figure 6.6 (a): Plot of ln C_0/C versus time at different pH values.

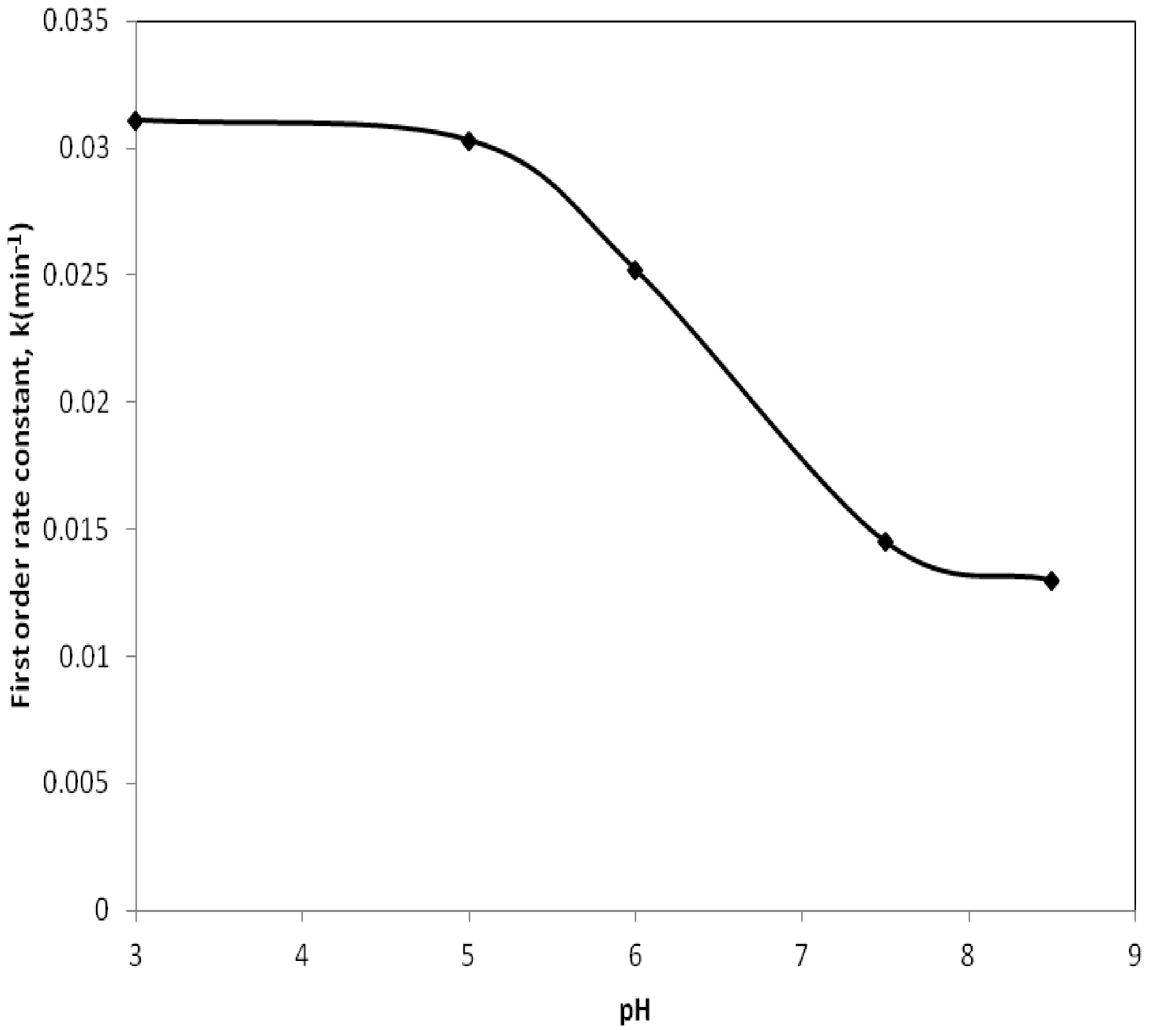

Figure 6.6 (b) Plot of first order rate constant, k vs variation in pH during photocatalytic degradation of Cephalexin (C_0= 50 mgL^{-1}, V= 200 mL).

6.2.7. Effect of A/V Ratio of the Batch Reactor

One of the major limitations for field-scale application of AOP is restriction of depth of reactor for effective penetration of solar radiations. More exposed area and less depth is generally recommended for the effective penetration of light **(Toor et al., 2006)**. This can be achieved either by varying area of the reactor keeping the volume constant or volume of solution to be treated can be varied keeping the area constant. In our studies, the Area/Volume (A/V) of the batch reactor was varied in the range of 0.79 to 2.38 cm^2 mL^{-1} by varying the volume of solution keeping the aperture constant. A plot of ln C_0/C versus time is shown in figure 6.7 (a) at varying ratios of A/V. A significant increase in degradation was achieved by increasing the A/V ratio as 'k' increased from 0.0188 to 0.0351 min^{-1} as demonstrated in figure 6.7 (b). By increasing A/V (keeping area constant), depth of the solution becomes less which leads to an increase in path length of photons entering the solution resulting in higher OH radical yield thereby improving the photocatalytic degradation rate **(Verma et al., 2014)**. At lower penetration of light, electron-hole recombination is more which decreases the yield of hydroxyl radicals thereby reducing the degradation rate. However, A/V ratio of 1.19 cm^2mL^{-1} was used for further experiments.

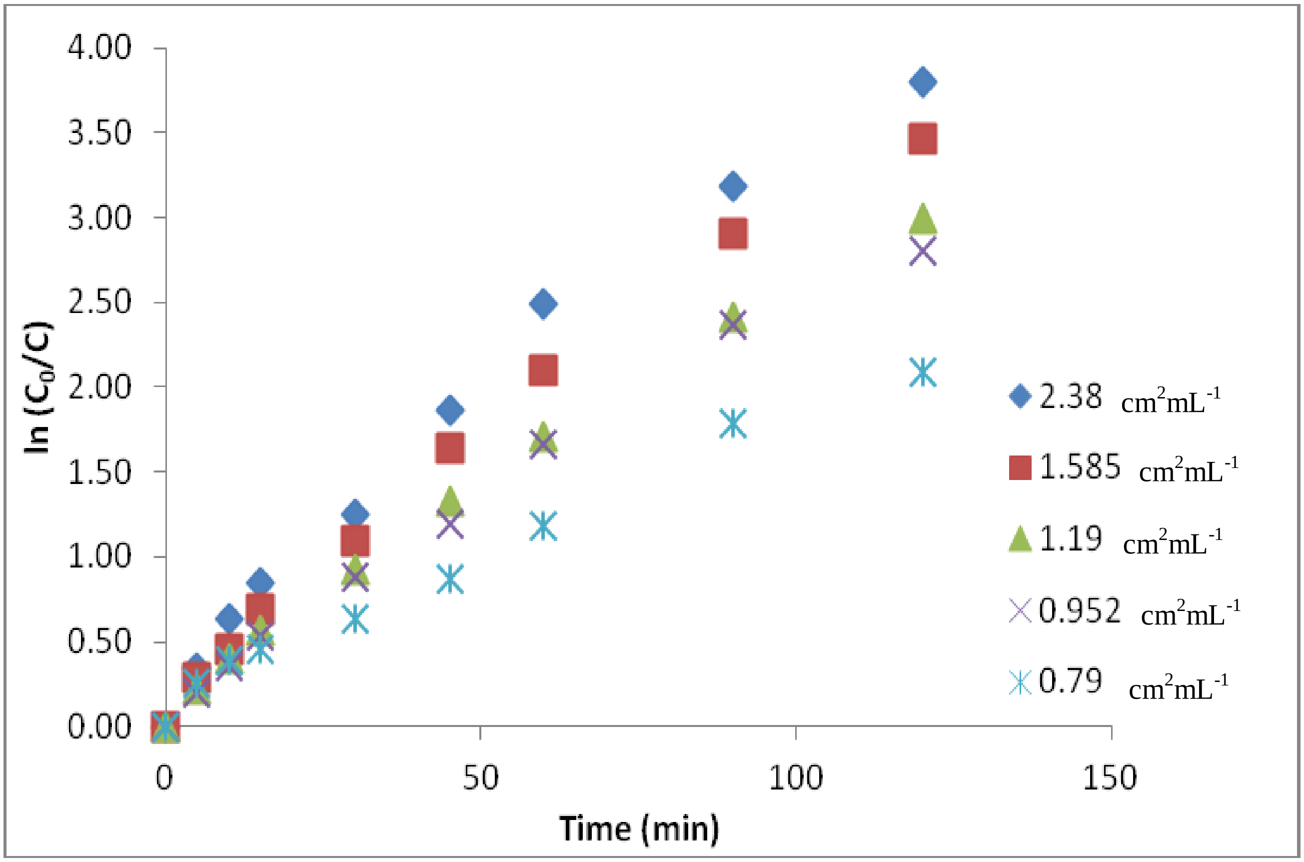

Figure 6.7 (a): Plot of ln C_0/C versus time at different A/V ratio.

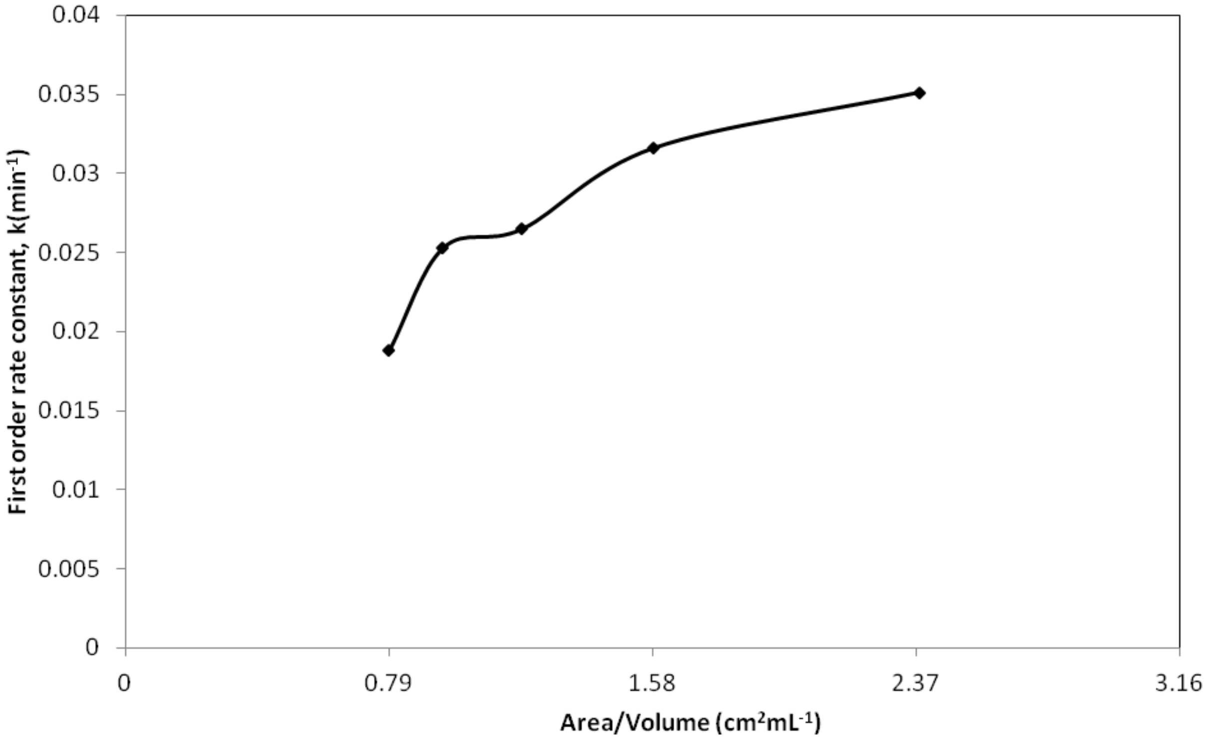

Figure 6.7 (b): Plot of first order rate constant, k vs effect of A/V ratio during photocatalytic degradation of Cephalexin (TiO_2 = 1gL^{-1}, C_0=50 mgL^{-1}).

6.2.8 Effect of initial substrate concentration

In order to study the effect of initial concentration of substrate on the percentage degradation of Cephalexin, the concentration of Cephalexin was varied from 10 mgL^{-1} to 80 mgL^{-1} at all optimized conditions. It was observed that degradation initially increased with the increase in the concentration of substrate up to 50 mgL^{-1} and thereafter became almost constant or decreased further (Figure 6.8). According to L-H model, it is quite obvious that the rate of degradation is first order at lower concentrations of substrate and then becomes zero order at higher concentrations **(Toor et al., 2005)**. The similar fashion has been followed in our studies too as the degradation rate became almost constant after 50 mgL^{-1}. The other reason for the saturation or decrease of degradation rate after a certain concentration of substrate may be the inadequate production of OH radicals at higher concentration of substrate. It is also reported that degradation of pollutant or contaminant occurs when it gets properly adsorbed on the surface of the catalyst. So the adsorption of pollutant on catalyst surface is of maximal importance. Therefore, at constant dose of TiO_2, the available active sites on TiO_2 surface for adsorption are also constant so the percentage degradation does not further improve rather remain constant or decrease (after 50 mgL^{-1}) with increase in the amount of substrate.

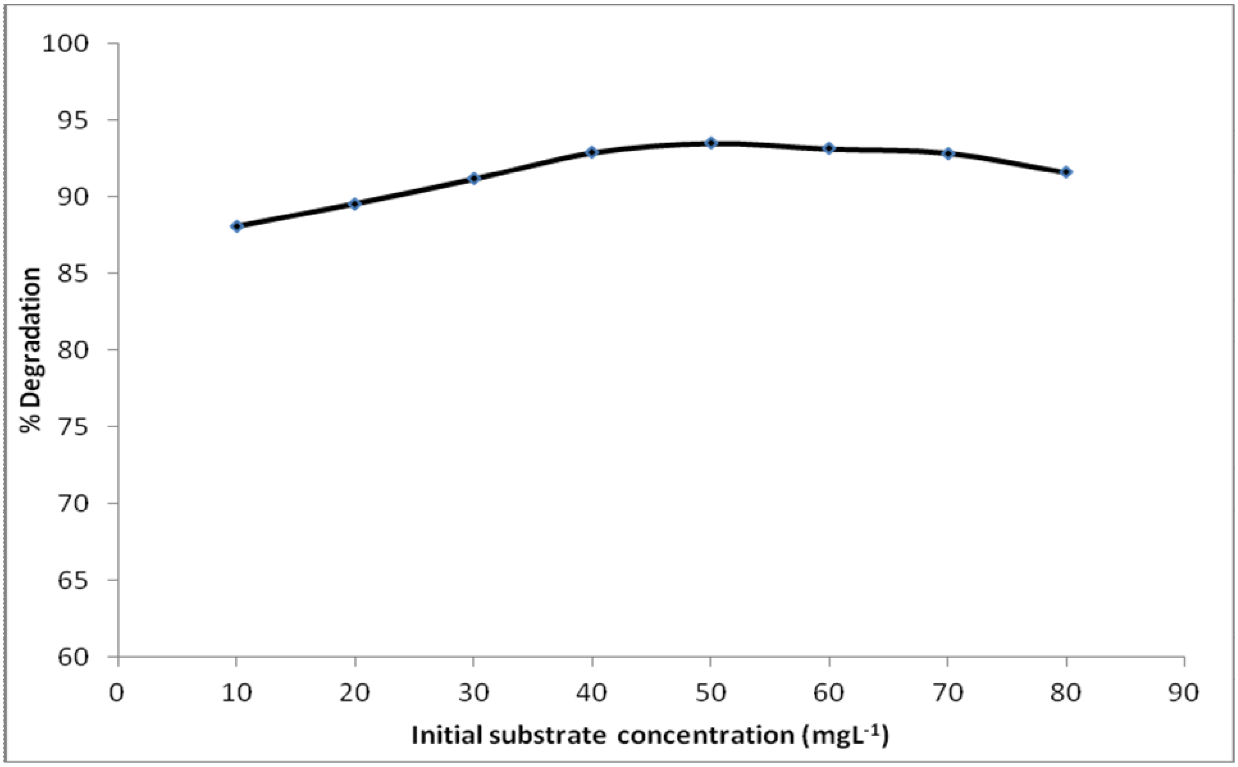

Figure 6.8: Effect of initial substrate concentration on the degradation of Cephalexin (TiO_2 = 1gL^{-1}, H_2O_2 = 0.15 mL).

6.2.9 Solar versus artificial UV irradiation

The cost of energy source is always a barrier for field-scale applications of advanced oxidation processes. The capital cost of the process can be minimized by the use of natural solar radiations instead of artificial UV light. In the current study, the photocatalytic experiments were carried out in sunlight also and the effect of both artificial UV and natural solar irradiation on the percentage degradation of Cephalexin was compared. The reaction conditions were optimized under simulated UV irradiations and these conditions were used for solar experiments. The percentage degradation was increased to 98% when photocatalysis was carried out in natural sunlight while 93% degradation occurred when irradiated in artificial UV light as demonstrated in figure 6.9. Hence, the technology used in the study is economically feasible and can also give a viable solution to the industries for treating recalcitrant compounds.

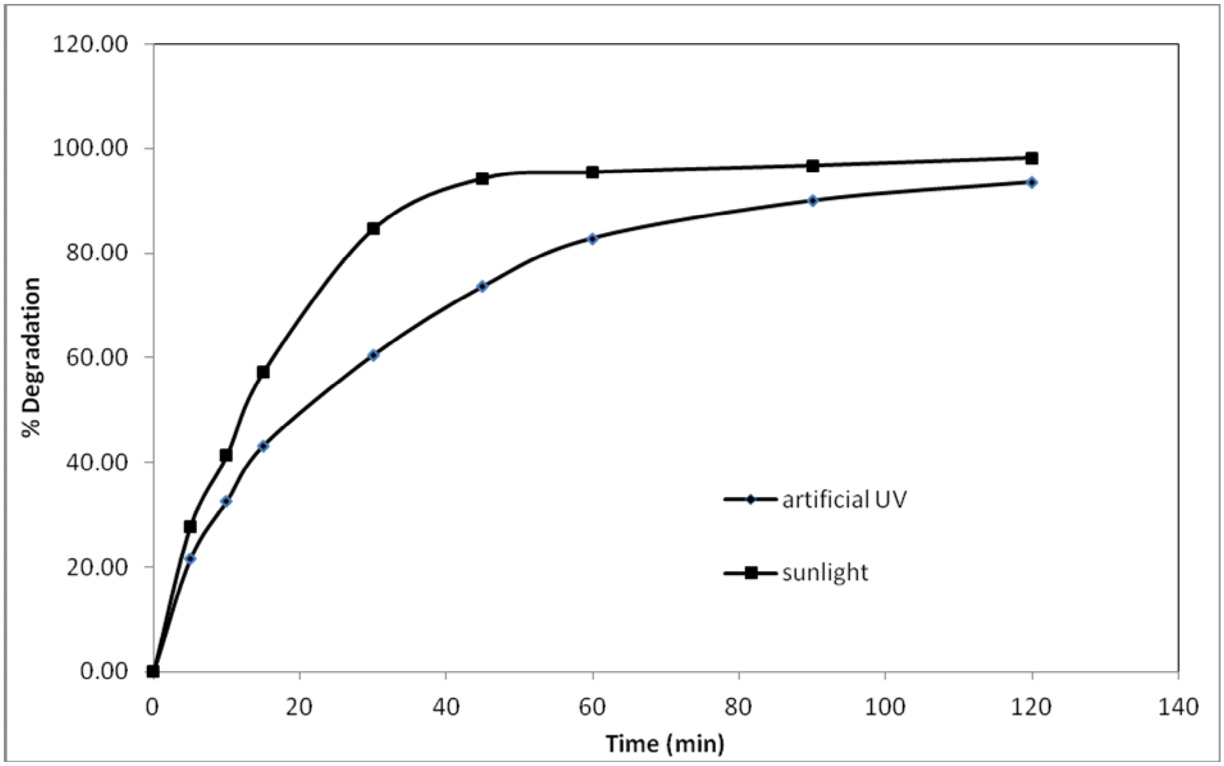

Figure 6.9: Effect of artificial UV and natural solar irradiation on degradation of Cephalexin.

6.3 Degradation studies using fixed-bed photocatalysis

The main implications for field-scale applications of slurry photocatalysis is separation of catalyst from the treated solution. Advantage of high mass transfer rates thus high degradation in slurry mode is always compensated in filtration cost involved for separating the catalyst. In this context, efforts have been made to study the degradation of Cephalexin using fixed-bed catalysis with TiO_2 coated cement beads reported in our previous studies **(Verma et al., 2014)**. The coating on the beads was so effective that the same beads from previous studies were used for the degradation of Cephalexin along with freshly coated beads. The 80.91% degradation of

Cephalexin was achieved using freshly coated beads, whereas old beads yielded 66.87% degradation after 5 h of irradiations (Figure 6.10). Blank runs using uncoated beads and TiO_2 coated beads + H_2O_2 didn't yield significant degradation confirming the activity of TiO_2 coated beads in solar UV radiations.

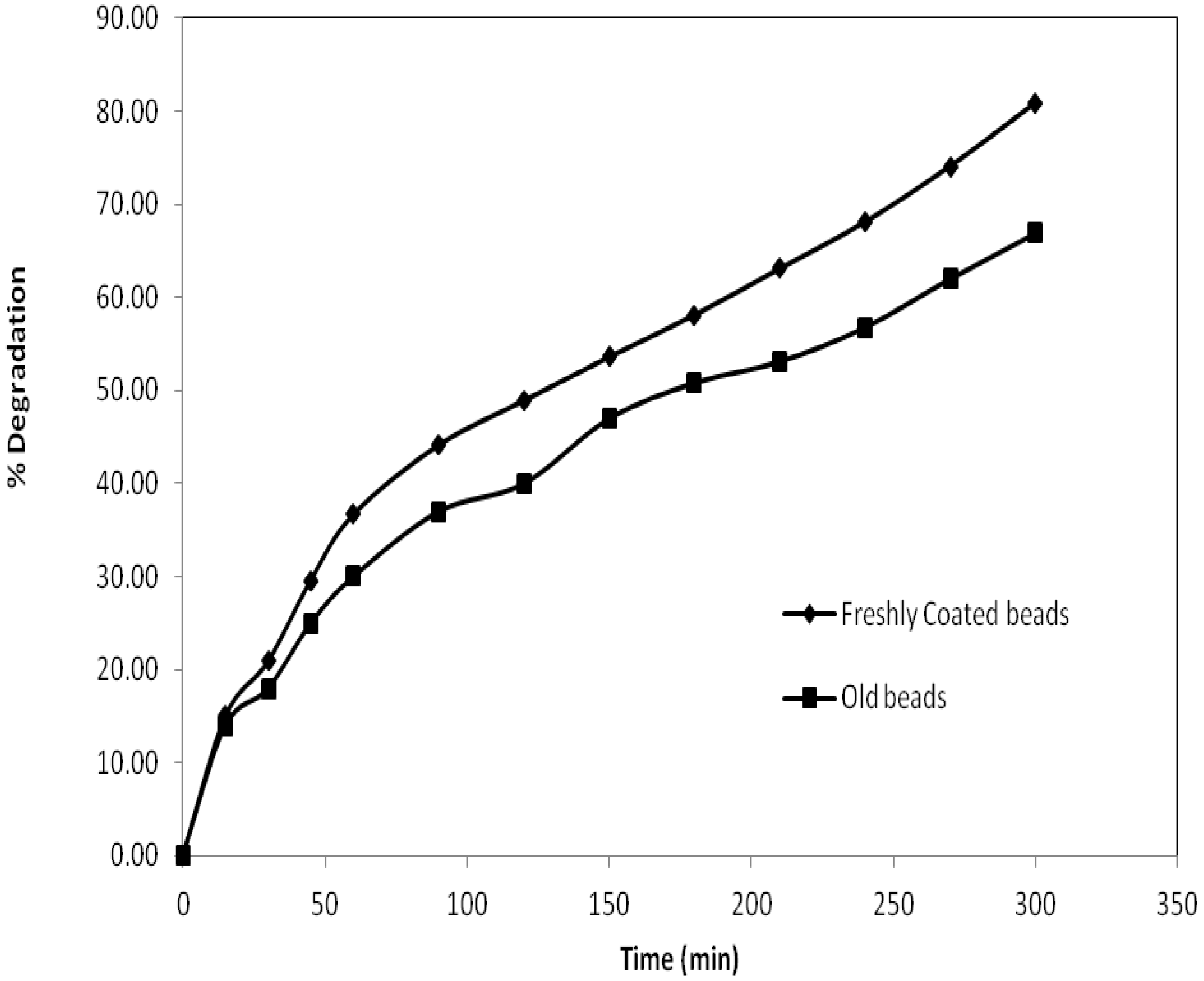

Figure 6.10: Effect of fresh and old catalyst coated cement beads on the degradation of Cephalexin in fixed-bed photocatalysis.

6.3.1 Durability studies

The durability of supported catalyst is very important in fixed-bed photocatalysis. Generally, the activity of supported catalyst reduces after certain runs **(Parra et al., 2004)**. The supported catalyst can be re-activated at high temperature (480 °C) which is economically not feasible. In the present study, efforts have been made to check the durability of immobilized catalyst on cement beads for the degradation of Cephalexin. The cement beads were adequately recycled for at least fifty to sixty times without any significant decrease in efficiency in regard to the degradation of Cephalexin as shown in Figure 6.11 (a). For re-activation, the cement beads were heated in oven at 100 °C for one hour after every cycle or even sunlight exposure for 1-2 h was sufficient. The reduction in photocatalytic efficiency of coated beads may be attributed to the loss of catalyst from beads during subsequent cycles or blocking of certain catalytic sites. SEM-EDAX of the recycled coated beads confirmed the stability of the catalyst on beads which showed that the catalyst was intact in the form of film even after fifty cycles (Figure 6.11 (b)).

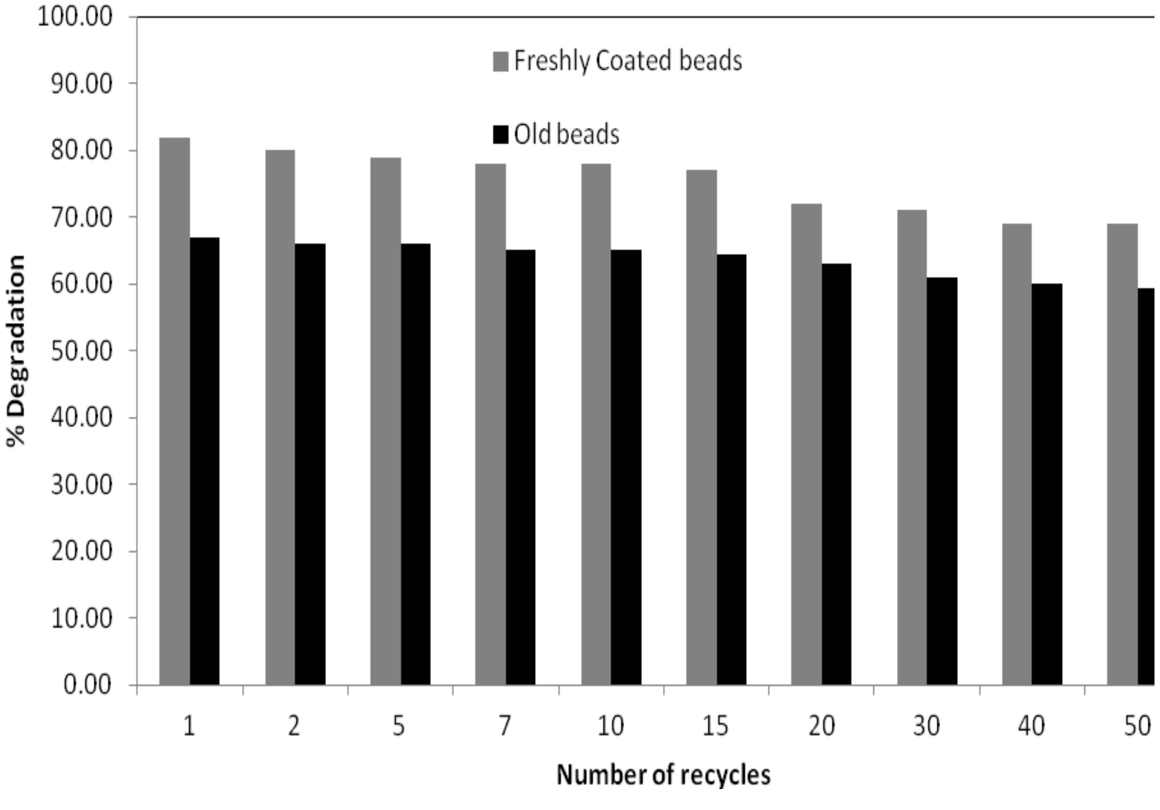

Figure 6.11 (a): Durability studies of catalyst coated cement beads (new and old) for the fixed-bed photocatalytic degradation of Cephalexin (C_0= 50 mgL^{-1}, TiO_2= 1 gL^{-1}, UV intensity= 25 Wm^{-2}).

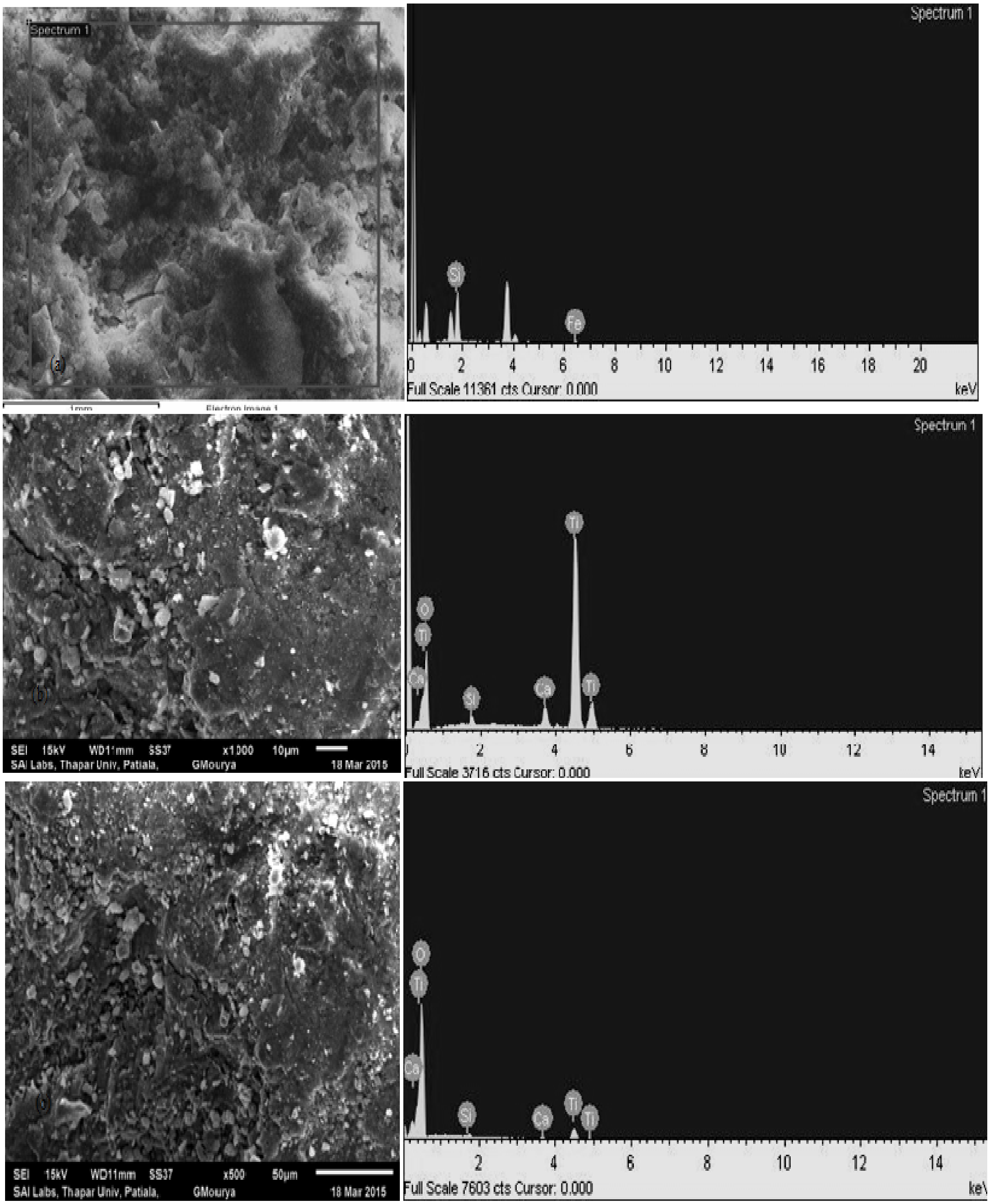

Figure 6.11 (b) : SEM photographs of (a) blank cement beads without any TiO_2 coating, (b) freshly coated TiO_2, (c) after 50th recycle along with EDAX data.

6.3.2. Degradation of Cephalexin using solar fixed-bed reactor (pilot-scale)

From commercial point of view, scale up of prototype reactors is very important for studying the degradation of selected compound. On the similar trends as in our previous studies **(Verma et al., 2014)**, the degradation of Cephalexin was studied using pilot-scale fixed-bed solar photocatalytic reactor (6.12 (b)). The experiments were performed in the month of March with average solar UV intensity to be 25-27 Wm^{-2} and surrounding temperature was 27 ± 3 ^oC. The total working volume was 5 L with flow rate sufficient enough to maintain good contact/retention time of Cephalexin in reactor. Four baffles were provided in reactor design to improve the retention time of solution for better degradation. The 70% degradation of Cephalexin was achieved after 10 h of solar photocatalytic treatment (6.12 (a)). The same reactor was used fifteen to twenty times for studying the degradation of Cephalexin using same TiO_2 coated beads. Actually, after each run the reactor with coated beads was left exposed to solar radiations for two-three hours for activation of catalyst or otherwise oven heated. Attrition of catalyst is one problem at high flow rates otherwise studied reactor can boost commercial applications of wastewater treatment with certain design modifications.

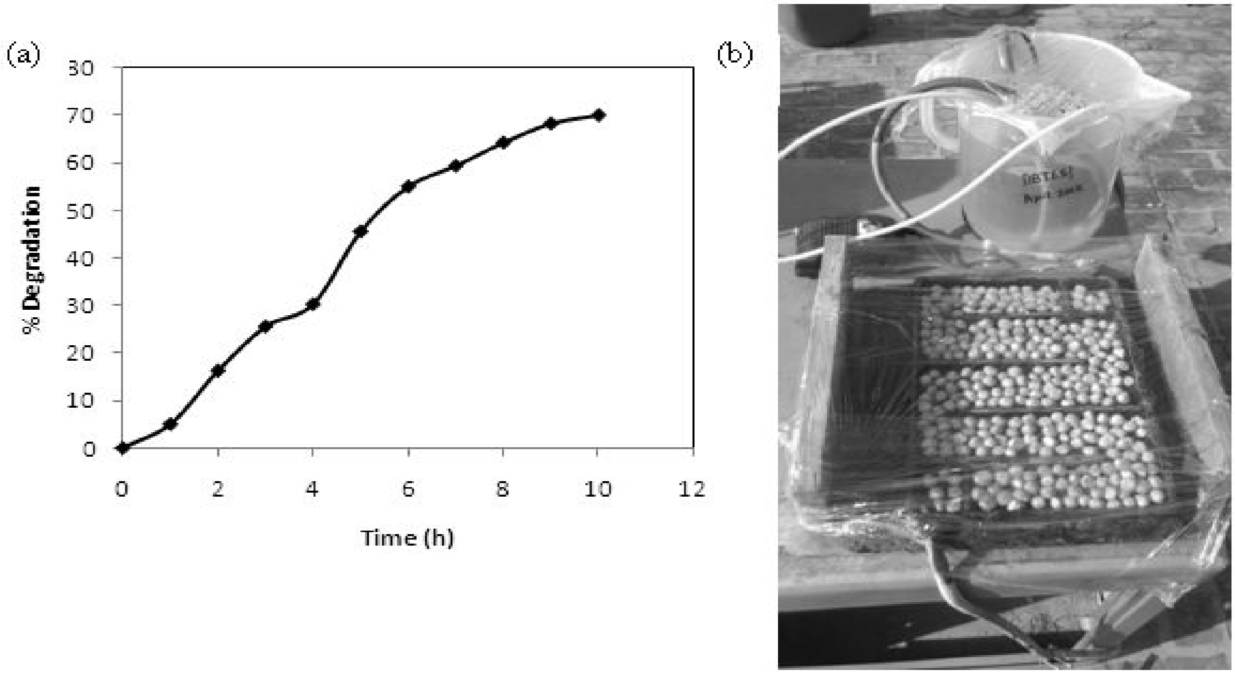

Figure 6.12(a). Degradation studies of Cephalexin using pilot-scale fixed-bed reactor with recirculation (b) Actual photo of pilot-scale solar fixed-bed reactor.

6.4. Mineralization studies

Formation of inorganic anions and cations along with the generation of CO_2 generally indicates complete mineralization of compound during photocatalytic treatment (**Evgenidou et al., 2005)**. In this context, COD reduction along with generation of nitrite, nitrate and sulphate ions were monitored for studying mineralization of Cephalexin. With optimized conditions, 80% reduction of COD was achieved after two hours at which generation of Nitrite (NO_2^-), Nitrate (NO_3^-) and Sulphate (SO_4^{2-}) ions were maximum. It was observed that nitrite, nitrate and sulphate ions were generated rapidly in the initial 30 minutes of irradiation and became almost constant after 2 hours of photocatalysis as depicted in figure 6.13 (a). Moreover, HPLC chromatograms (Figure 6.13 (b)) indicated the disappearance of peak for the parent compound at 263 nm. Absence of other peaks in chromatogram confirmed that either no intermediates were formed or they were completely mineralized.

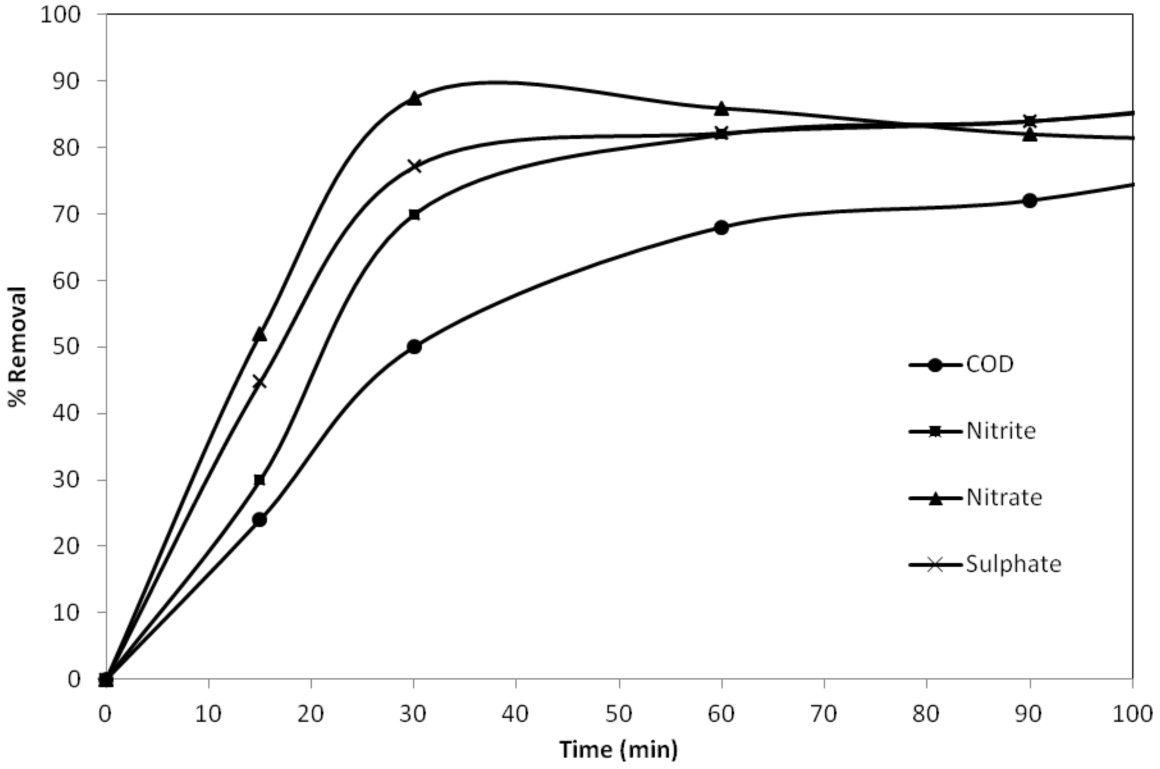

Figure 6.13(a): COD reduction and the generation of nitrite, nitrate and sulphate ions during the photocatalytic degradation of Cephalexin.

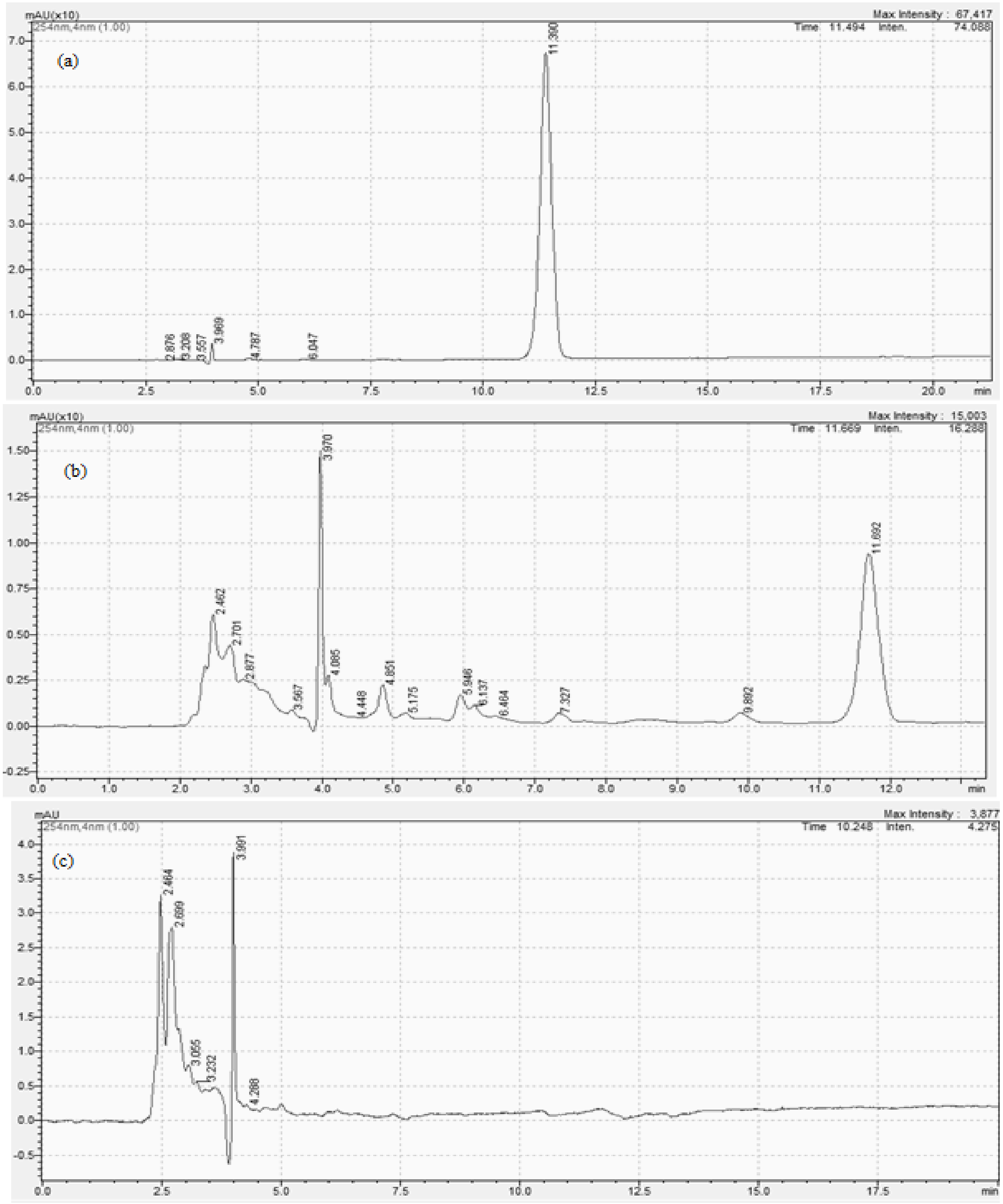

Figure 6.13(b): HPLC chromatogram of (a) initial standard, (b) after 30 min of photocatalytic treatment and (c) after 120 min of photocatalytic treatment.

CHAPTER 7

CONCLUSIONS

The present study was undertaken to show the photocatalytic degradation of Cephalexin using TiO_2 in slurry and fixed-bed mode. Parameters like concentration of catalyst, oxidant, pH, UV intensity, A/V ratio play a significant role in the degradation of antibiotic. The optimized conditions obtained for better degradation of Cephalexin are TiO_2 1.0 g L^{-1}, H_2O_2 0.15 mL and C_0 50 mg L^{-1}. UV/H_2O_2/TiO_2 photocatalysis resulted in 93.47% degradation of Cephalexin in aqueous solution. The mineralization of antibiotic Cephalexin was confirmed by reduction in COD (80%) along with the generation of nitrite ions (88%), nitrate ions (80.90%) and sulphate ions (88.57%) after 2 h of irradiation. For fixed-bed studies, TiO_2 coated on cement beads yielded 80.91% degradation after 5 h using batch reactor. The durability of beads is usually a major concern for commercial applications and in our study, durability of beads was confirmed by SEM-EDAX analysis which proved the stability of catalyst even after 50th recycle for degrading Cephalexin. Pilot-scale reactor confirmed 70% degradation of antibiotic after 10 h of solar irradiation, thus foreseeing field-scale applications of the technology. To the best our knowledge, no study has been carried out so far for the degradation of Cephalexin through slurry and fixed-bed photocatalysis. Although attempts have been made to its best for the degradation of compound at lab scale and pilot scale, 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.

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2. “A Study of Photocatalytic process involving the Degradation of Antibiotic Cephalexin using Slurry and Fixed-bed” National Seminar on Sustainable Renewable Energy Generation- Current Scenario. Energy research centre, Punjab University, Chandigarh. March 20-21, 2015.