Degradation of Amoxicillin Trihydrate (AMT) with suspended/immobilized TiO_2 catalyst and Parabolic Trough Collector

A Dissertation

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Masters in Technology

in

Environmental Science and Technology

Submitted

By

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CERTIFICATE

This is to certify that thesis entitled, "**Degradation of Amoxicillin Trihydrate (AMT) with suspended/immobilized TiO_2 catalyst and Parabolic Trough Collector**" submitted by **Ms. Divya Dixit** 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.

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DECLARATION

I, the undersigned, hereby declare that the research work presented in the M.Tech project entitled "**Degradation of Amoxicillin Trihydrate (AMT) with suspended/immobilized TiO_2 catalyst and Parabolic Trough Collector**" has been carried out by me under the supervision and guidance of ***Dr. Anoop Verma, School of Energy and Environment & Dr. Madhup Kumar Mittal, Departmemt of Mechanical Engineering, 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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Thank you for making this a reality.

Divya Dixit

ABSTRACT

Heterogeneous photocatalytic degradation of AMT using TiO_2 in suspension form as well as immobilized form was investigated in the present study. The degradation rate was observed to follow first-order kinetics. TiO_2 loading 0.5 g L^{-1}, pH 5.8, C_0 100 mg L^{-1} were the optimized conditions for obtaining the better degradation rates. Cement beads and alginate balls were used for the immobilization of TiO_2 for the degradation of AMT. 87%, 69% and 52% degradation was observed under shallow pond slurry reactor, coated cemented beads, immobilized sodium alginate ball using solar irradiation. Reduction in COD and TOC values along with the generation of ammonium further indicated the mineralization of the AMT. The effect of initial concentration, catalyst recycling as well as area/volume was also studied for the practical applications. Experiments conducted on Parabolic Trough Collector (PTC) with TiO_2 immobilized cement beads at the flow rate of 0.1Lmin^{-1} in the presence of oxidant (0.12 gL^{-1}) yielded 92% degradation within 4 h of irradiation as confirmed by LC-MS technique. Durability studies were conducted and the structure of TiO_2 was found to be intact after fourth recycle. XRD and solid spectra analysis of TiO_2 confirmed that no deformities occurred in the structure of the catalyst after use. Thus, use of renewable energy along with a durable catalyst can be a promising technique for degrading bio recalcitrant compounds from commercial point of view.

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1. INTRODUCTION

India is one of the leading producers of pharmaceutical products and occupies 4th rank in terms of volume and 13th in terms of value. Analysts estimate tremendous growth in production and consumption of pharmaceutical products in India as compared to other countries. The term "pharmaceutical" covers a wide-ranging class of compounds with substantial variability in behavior, structures, function, and activity. Pharmaceutically active compounds (PhACs) such as antibiotics like penicillin, anti-convulsants, antidepressants, anti-inflammatories, hormones, and analgesics are meant to reduce symptoms and cure diseases in humans and animals **(Bila and Dezotti, 2003)**. However, they are not metabolized completely within the body and 90% of the drug is excreted which can enter municipal and natural water systems via residential or commercial discharges, including hospital effluent **(Raloff et al., 1998).** The Associated Press reported that concentrations of pharmaceuticals in Indian plants are 150 times the highest levels detected in the U.S.

The potential impact of pharmaceutical compounds like Amoxicillin Trihydrate (AMT) in the aquatic environment on public health is a matter of great concern. AMT is an antibiotic useful for the treatment of a number of bacterial infections commonly prescribed for children. It is on the World Health Organization's List of Essential Medicines, a list of the most important medication needed in a basic health system (**Huong and Hoang, 2009**).

Figure 1.1 shows various source pathways through which pharmaceutical compounds enters life cycle of human beings and animals. Endocrine disruption, aquatic toxicity, development of resistance in pathogenic bacteria and genotoxicity are some of the health hazards caused by pharmaceutical compounds.

Not much is known about the chronic effects of these compounds in drinking water, long-term ingestion of mixtures in drinking water is a public health concern **(Boyd et al., 2003).**

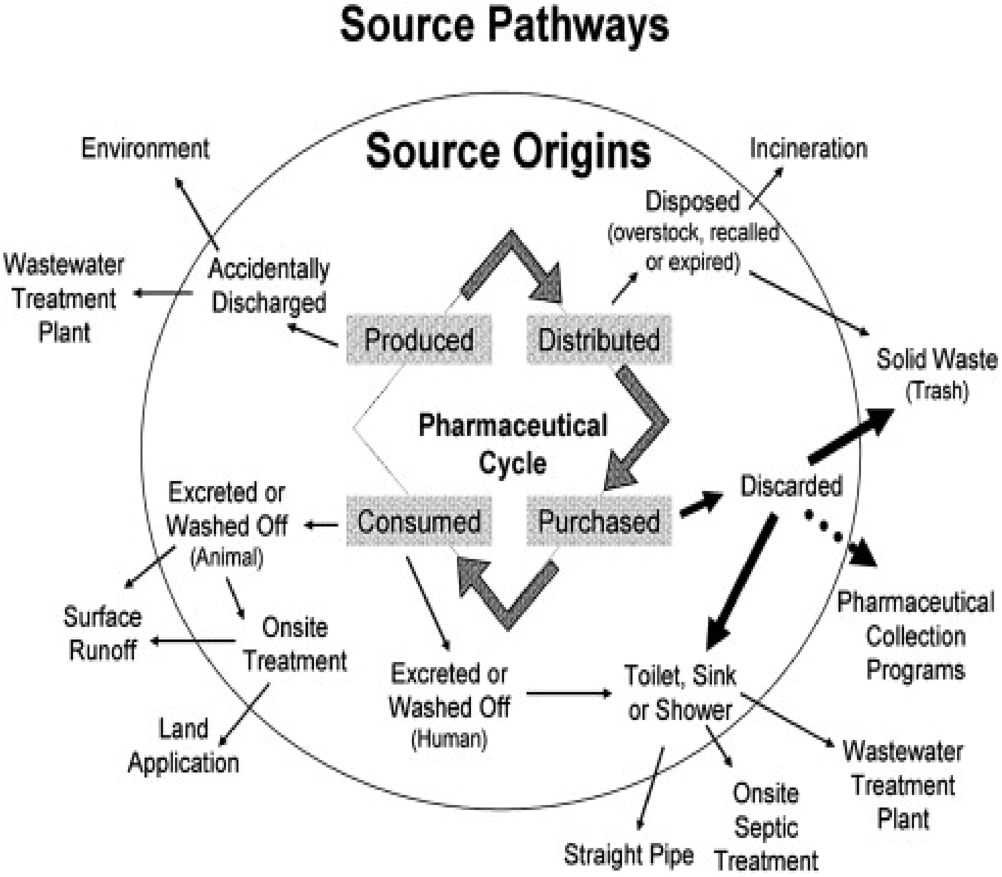


Figure 1.1: Various source pathways of pharmaceutical waste entering the environment (source: USGS).

These alarming levels draw attention towards the need of proper treatment technology to degrade pharmaceutical industry wastewater. However, all these compounds are resistant to conventional chemical treatment methods (shown in figure 1.2), such as coagulation, activated carbon adsorption, etc. Also, the biological treatment is considered as the typical process for natural decontamination **(Marco et al., 1997)**. Unfortunately, all organic pollutants are not biodegradable and there is a class of products noted as bio-recalcitrant organic compounds. As a result, the use of alternative treatment technologies that aim to transform them into their biodegraded form is a matter of great concern. The search for effective means of removing these compounds is of interest to regulate authorities everywhere **(Kositzi et al., 2004)**. Figure 1.2 shows the conventional wastewater treatment technology generally applied to all types of contaminants. However, treatment plants designed for a particular class of contaminants are not into practice.

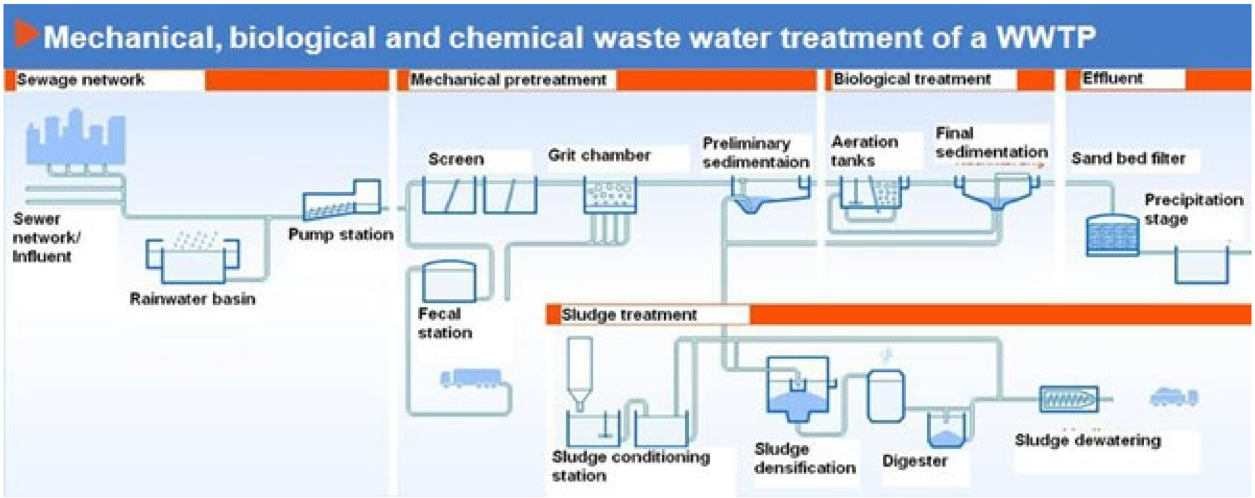


Figure 1.2: Conventional wastewater treatment plant.

Thus, implementation of advanced treatment technologies is required to achieve the degradation of priority pollutants **(Radjenovic, 2009)**. Among these emerging technologies, Advanced Oxidation Processes (AOPs) have already been used for treatment of waste-water containing recalcitrant compounds such as antibiotics. Advanced oxidation processes (AOPs) are very promising methods for the remediation of contaminated wastewaters containing non-biodegradable organic pollutants (Fig.1.3). The main mechanism of AOPs is the generation of highly reactive free radicals like hydroxyl radicals ($OH^{\bullet}$) which are effective in destroying organic chemicals because of their high reactive electrophilic behavior (figure 1.4).

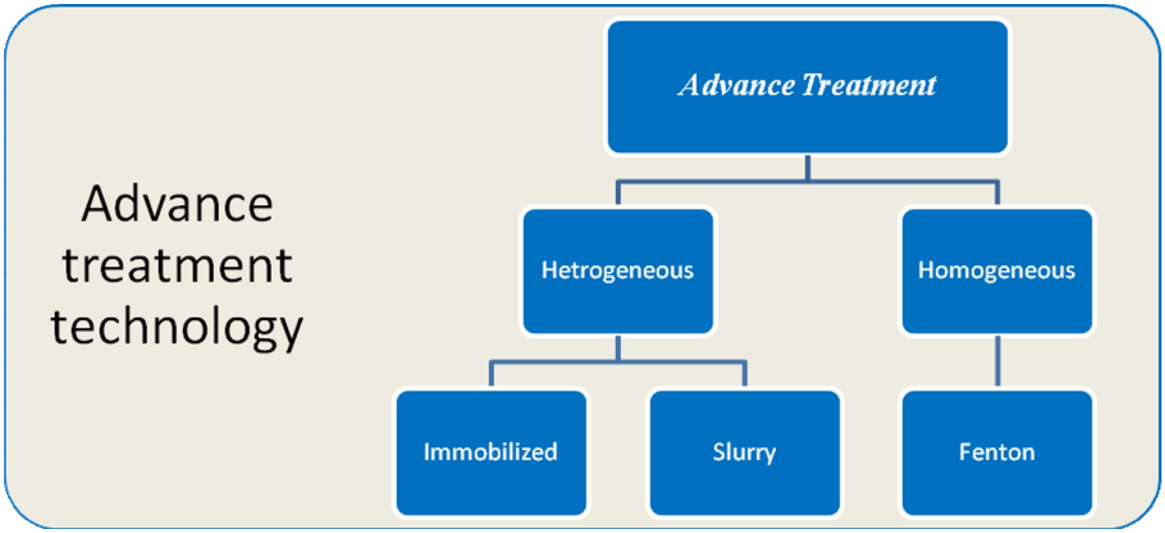


Figure 1.3: Types of advanced oxidation processes.

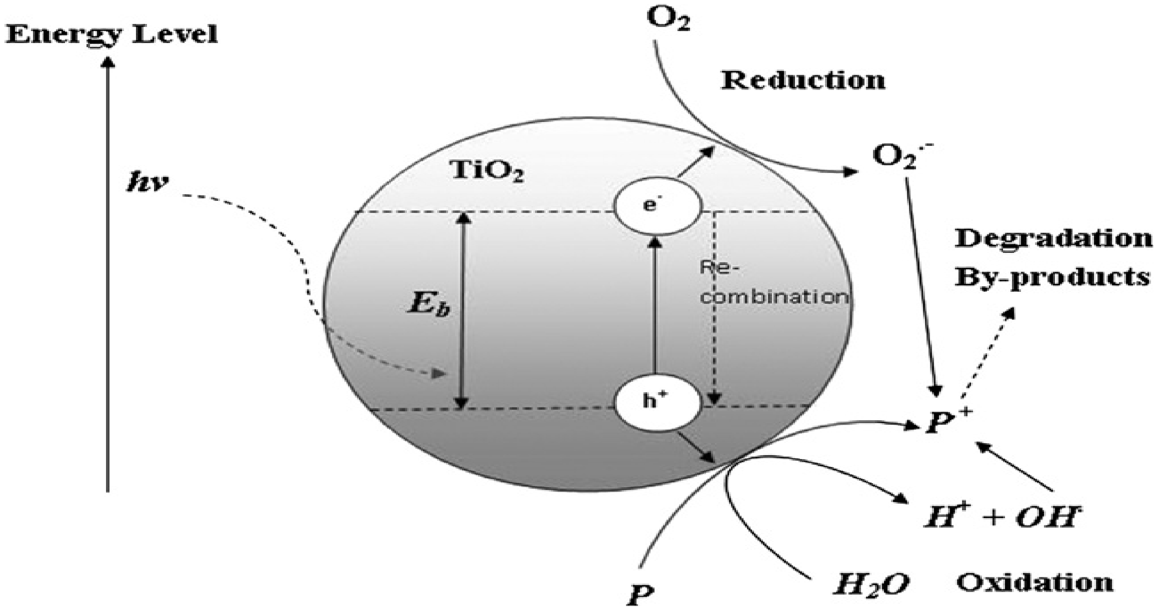


Figure 1.4: Photo-induced formation mechanism of electron hole pair in a semiconductor TiO_2 particle with the presence of water pollutant (Fujishima et al., 2000).

Recent studies have demonstrated that heterogeneous photocatalysis using semiconductors such as titanium dioxide (TiO_2) and UV light irradiation can be used to destroy a wide range of organic pollutants dissolved in water **(Hoffman et al., 1995; Fujshima et al., 2000; Gaya and Abdullah, 2008; Akpan and Hameed, 2009; Rauf and Ashraf, 2009).**While potentially effective, most of the UV based AOPs have drawbacks in terms of high operational cost, which is mainly a result of high energy consumption. This drawback can be overcome by applying solar irradiation (sunlight) instead of artificial UV irradiation (UV lamps) **(Malato et al., 2002)**. The use of solar irradiation for the photo catalytic oxidation of organic contaminants in wastewater is a fast developing application **(Zhang et al., 2000)**. The combination of solar light and catalysts has proven to be a promising alternative **(Bauer et al., 1999)**. The energy needed to activate the semiconductor catalyst recommended for the solar detoxification process corresponds to UV component of the solar radiation. Selection of catalyst must be in such a way that it uses maximum fraction of solar energy **(Balasaraswathy, 2004)**. There are two types of solar reactor designs generally used for photo catalytic degradation: concentrating and non-concentrating solar reactors. Matthews **(1986)** reported the use of suspended TiO_2 in a solar illuminated tubular reactor equipped with a parabolic trough concentrator (PTC) for the degradation of a variety of organic compounds. However, the need for a catalyst recovery system led to the conclusion that scaling up of such a design may be complex. Light-concentrating reactors require reflectors and solar tracking devices, which are expensive and difficult to maintain. Further, they can only concentrate the direct component of the solar radiation. Non-concentrating solar reactors make use of both direct and diffuse components of solar ultraviolet radiation and have the potential for low cost development and greater efficiency **(Nogueria and Jardim, 1996)**. In terms of wastewater treatment designs based on non- concentrating category are more mature having flexible working conditions, controlled concentration ratio (ratio of collector aperture area to the absorber area) and temperature. Designs of non-concentrating solar reactors (one sun) include tubular **(Malato et al.,2002)**, double-skin **(Nogueria and Jardim, 1996)**, shallow pond **(Wyness et al.,1994)**, falling film **(Nogueria and Jardim, 1996)**, coated mesh **(Feitz et al.,2000)** , cascade **(Xi et al.,2001;Chan et al.,2003;Guillard et al.,2003)** and fountain **(Puma and Yue, 2001)**.

The parabolic trough collector is one of the most proven and commercial concentrating solar power technologies. Their potential to concentrate sunlight can be used for harnessing UV radiations for the wastewater treatment processes. The solar parabolic trough systems use cylindrical parabolic collectors. The parabolic trough collector (PTC) requires single axis tracking to concentrate solar radiation on the focal line receiver. The transparent receiver tube absorbs concentrated solar radiation which leads to generation of hydroxyl radicals in the presence of catalyst and transforms complex compounds into simple molecules like water and carbon dioxide. The efficiency is the measurement of the performance of a collector, defined as the ratio of energy achieved to incident solar energy for the same period of time **(Duffie and Beckman, 2006)**. The possibility of integrating photocatalysis and solar technologies **(Clark and Allen, 1978; Jannot and Coulibaly, 1997; Hegazy, 1999)** has triggered further attention because of lower treatment costs due to the use of renewable solar energy.

In these configurations the TiO_2 catalyst is either suspended in the liquid or supported on the walls of the reactor. The reactor configurations utilizing slurry suspensions of TiO_2 in general outperform those using supported photocatalysts but a catalyst recovery system is needed which may increase treatment costs. In contrast, if the catalyst is supported directly on the reactor wall it makes replacement of the catalyst unpractical should this deactivate over time. Therefore, it is desirable to have a supported photocatalyst that can be easily replaced, economical and easy to produce.

2. OBJECTIVES

This study focuses on the performance of a slurry batch, immobilized batch reactor along with solar parabolic trough collector for the degradation of Amoxicillin Trihydrate (AMT), a pharmaceutical compound.

- **SHALLOW POND SLURRY REACTOR STUDIES**

To perform degradation studies of AMT using TiO_2 in suspension form and to measure the effects of various parameters like effect of pH, effect of H_2O_2, effect of Area/volume ratio etc. on degradation rate of AMT.

- **TiO_2 IMMOBILIZATION**

Efforts would be done for selecting the low cost support material for immobilizing the catalyst TiO_2. Efficacy would be checked in terms of AMT photodegradation along with recycling studies.

- **DEGRADATION STUDIES USING PARABOLIC TROUGH COLLECTOR**

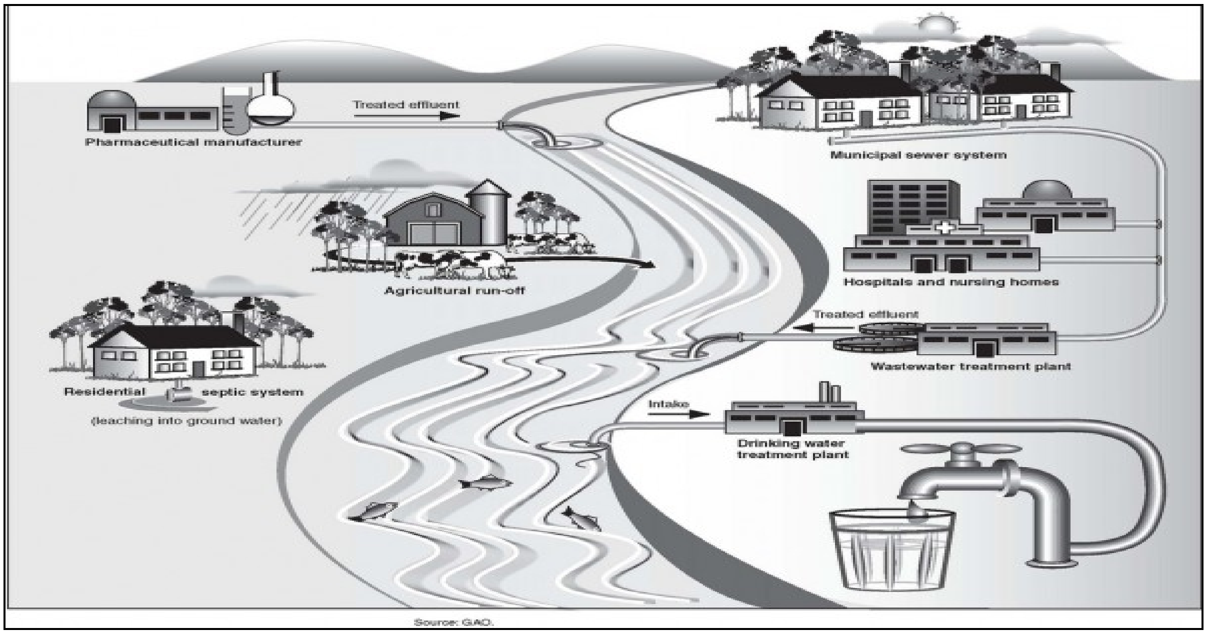
After the lab-scale, photocatalytic degradation studies would be performed on solar collectors (concentrating) using best immobilized catalyst at lab scale. Effect of flow rate along with durability of the catalyst on support material would also be studied.

3. REVIEW OF LITERATURE

The concern for pharmaceuticals and personal care products (PPCPs) as toxic substances in the environment and the need to assess their environmental risk have greatly increased since the 21st century. Most if not all urban wastewater is contaminated with medicinal compounds, differing only in the type and abundance of the substances present. The existence of drugs in surface waters **(Boud et al., 2003),** groundwater **(Ahel et al., 1998; Clara et al., 2004)**, and even marine systems **(Buser et al., 1998)** has also been confirmed. This may be due to excretion of a significant amount of pharma compound in its original form. Several reviews dealing with the exposition and effect of pharmaceuticals have been published **(Halling-Sorensen et al., 1998; Daughton and Ternes, 1999; Jones et al., 2004; Zuccato et al., 2006).** Propranolol, diclofenac , ibuprofen, amoxicillin and fluoxetine are other examples of pharmaceuticals reported to affect aquatic organisms at or around environmentally relevant levels in laboratory experiments. Compounds having relatively short half-lives would likely survive in only the freshest of sewage sludge samples, but it is important to understand the fate and behavior of these compounds during wastewater treatment in order to assess the likely concentration of contaminants in sludges and effluents, and hence their potential contribution to the pollution of the environment.

3.1. Environmental impacts of Pharmaceuticals Effluent

Several categories of pharmaceuticals raise particular concerns: those produced and consumed in especially large quantities, those highly potent at low concentrations, and those particularly persistent and bio-accumulative in the environment. Within these categories, two types of pharmaceuticals – antimicrobials and endocrine disrupting chemicals (EDCs) – can be appropriately singled out as priorities. There is a great possibility of release of these pharmaceutical compounds into water cycle. Figure 3.1 shows various routes of transmission of pharmaceutical wastewater into aquatic streams. Effluent from pharmaceutical industry, sewage treatment plants, hospitals and homes is dumped into surface and ground water sources causing contamination of drinking water.



Source: GAO.

Figure 3.1: Various pathways of entering pharmaceutical compounds in water cycle (Source: USEPA).

Indians are one of the leading consumers of antibiotics as human medicine, which have showed an increasing trend of prescription over the last decade. Among all antibiotics, penicillin occupies an important place due to their high consumption rates in all places of the country. Amoxicillin trihydrate (table 3.1), is one such semi synthetic betalactam penicillin that acts by inhibiting the synthesis of bacterial cell walls **(Kaur et al., 2009).**

Table 3.1: Chemical characteristics of AMT (Mohammadi et al., 2012).

Characteristics	
IUPAC name	(2S,5R,6R)-6-[(R)-(-)-2-amino-2-(p-hydroxyphenyl)acetamido]-3,3-dimethyl-7-oxo-4thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid trihydrate
Molecular formula	$C_{16}H_{19}N_3O_5S_3H_2O$
Molecular weight	419.45
Appearance	White or almost white powder

It is widely used to treat certain infections caused by bacteria such as pneumonia, bronchitis, nausea and infections of ear, throat, skin and urinary tract. It is also used in the standard eradication treatment of gastric H. pylori infection combined with a second antibiotic and an acid-suppressing agent (**Venkateswaramurthy et al., 2010**). However, some other reports and clinical trials indicate that the therapies cannot bring out complete eradication of H. pylori and suggest that the therapeutic effect needs more investigation. Pharmacopoeias have reported liquid chromatography **(US Pharmacopoeia, 2007; Indian Pharmacopoeia, 2007; British Pharmacopoeia, 2009)** and potentiometric methods **(Sutherland et., 1972)** for the analysis of amoxicillin in pure form and in pharmaceutical formulations (Figure 3. 2).

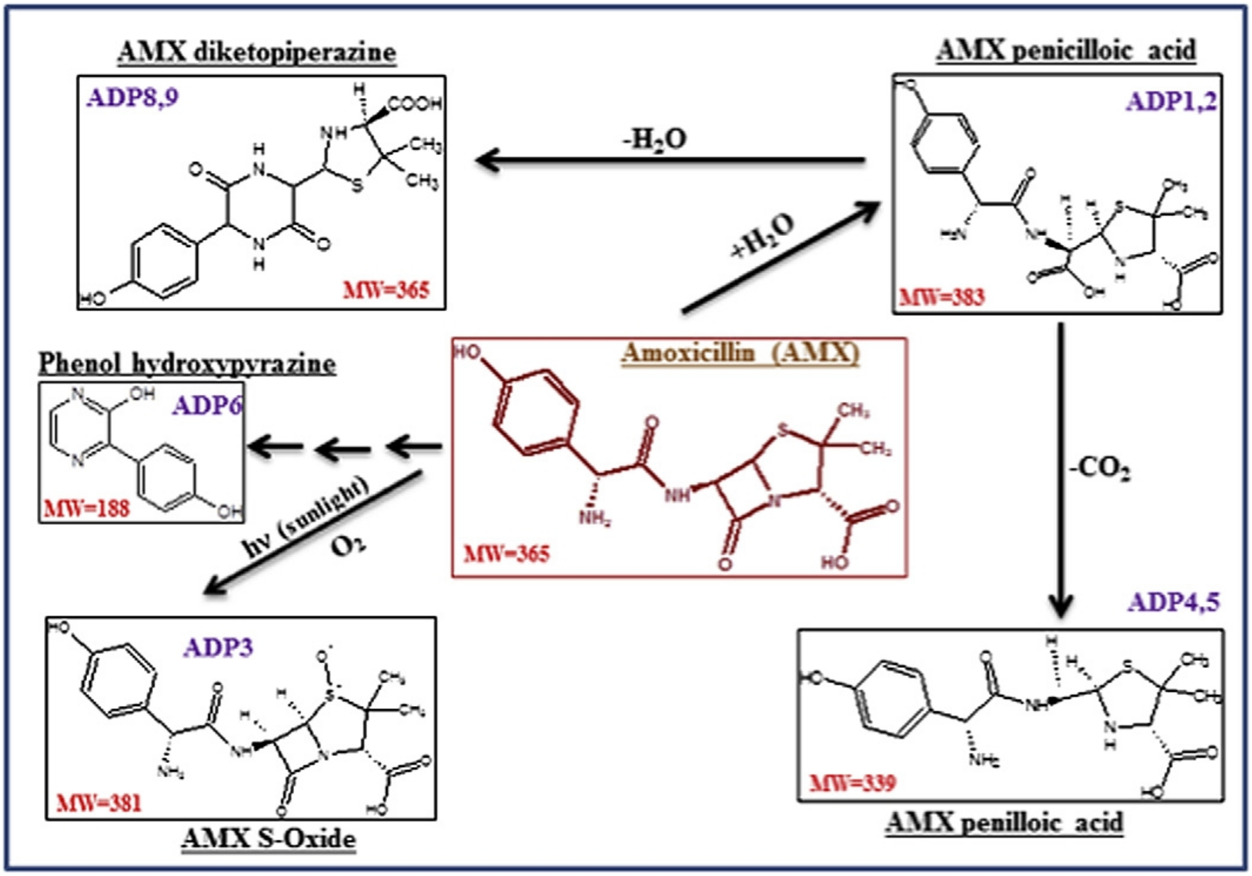


Figure 3.2: Suggested degradation pathway of amoxicillin in aqueous medium (Gozlan et al., 2010).

3.2. Conventional Technologies

Conventional technologies including biological (**Eddy and Metcalf, 2005)**, thermal, and physicochemical treatments (**Chaung and Cheng, 1992)** have been used to remove the aqueous pollutants. Treatment of pharmaceutical wastewater has always been troublesome to reach the desired effluent standards due to the wide variety of the products produced in a drug manufacturing plant, thus, there is variable wastewater composition and fluctuations in pollutant concentrations.

3.3. Advanced Oxidation Technology

Advanced oxidation processes (AOPs) with the capability of exploiting the high reactivity of hydroxyl radicals in driving oxidation have emerged a promising technology for the treatment of wastewaters containing refractory organic compounds. Several technologies like Fenton, photo-Fenton, cavitation, ozonation, photocatalysis, etc. are included in the AOPs and their main difference is the source of radicals **(Kim and Ihm, 2010).**

AOPs can be broadly defined as aqueous phase oxidation methods based on the intermediacy of highly reactive species such as (primarily but not exclusively) hydroxyl radicals in the mechanisms leading to the destruction of the target pollutant. The main mechanism of AOPs function is the generation of highly reactive free radicals. Hydroxyl radicals (HO•) are effective in destroying organic chemicals because they are reactive electrophiles (electron preferring) that react rapidly and non-selectively with nearly all electron-rich organic compounds **(Stasinakis, 2008).**

3.3.1. Heterogeneous Catalysis

Heterogeneous photocatalysis can be defined as catalytic process during which one or more reaction steps occur by means of generation of electron-hole pair by suitable light on the surface of the solid semiconductor materials. The distribution and utilization of light energy due to the presence of solid catalyst material in liquid or gaseous mixtures makes this process more complex compared with homogeneous process **(Kositzi et al., 2004; Verma et al., 2013).**

3.3.2. Optimum operating conditions

3.3.2.1. Operating pH

The generation of the hydroxyl radicals in AOP’s is effected by pH of the solution which is a powerful oxidizing agent. The effect of the solution pH on the degradation rate can be explained mainly by adsorption of compound on TiO_2 surface. TiO_2 shows an amphoteric character so that either a positive or a negative charge can be developed on its surface. The point of zero charge of the used TiO_2 (Degussa P-25) is widely reported at pH≈6 **(Zhang et al., 2000; Verma et al., 2013)**.

3.3.2.2. Catalyst concentration

Degradation rate of insecticide increases with increased catalyst concentration and becomes constant above a certain level and then decreases after one particular optimum dose. This is because with the increasing concentration of TiO_2, the number of photons absorbed in UV light and the number of pollutant molecules absorbed on the surface of catalyst are increased owing to an increase in rate of photocatalytic reaction. Above a certain level, the pollutant molecules available are not sufficient for the adsorption by the increased number of TiO_2 particles. The other reason for this is clustering of catalyst particles at higher concentrations and thus causing a decrease in the number of active sites on its free surface **(Malato, 2003; Verma et al.,2012)**.

3.3.2.3. Concentration of hydrogen peroxide

Concentration of hydrogen peroxide plays a more crucial role in deciding the overall efficacy of the degradation process. Usually percentage degradation of the pollutant increases with an increase in the dosage of hydrogen peroxide. The residual hydrogen peroxide contributes to COD and hence excess amount is not recommended. Also, the presence of hydrogen peroxide is harmful to many of the microorganisms and will affect the overall degradation efficiency significantly. One more negative effect of hydrogen peroxide, if present in large quantities is that it acts as a scavenger for the generated hydroxyl radicals. Thus, the loading of hydrogen peroxide should be adjusted in such a way that the entire amount is utilized **(Kim and Ihm, 2010; Verma et al., 2013)**.

3.4. Various Materials for TiO_2 immobilization

3.4.1. TiO_2-treated wet wood board

Antifungal activity of TiO_2-film against A. niger on wood under UVA (365 nm) irradiation was investigated experimentally. TiO_2 #1 and #2 were respectively suspended in deionized water for 30 min of pre-sonication to disperse the particles uniformly. Paulownia (size 25*25 mm, 2 mm thick) was used as the test substrate to be coated with the TiO_2 photocatalyst film. Another kind of paulownia surface that is coated with Alkyd paint was used for investigating the inhibition effect on different substrates **(Fenga et al., 2009)**. The coated films were printed by the dip-coating method. The volume of the TiO_2 coating applied to each wood board was approximately 1.5 mg/cm^2. Photographs of TiO_2 #1 and #2 surfaces are shown in Figure 3.3.

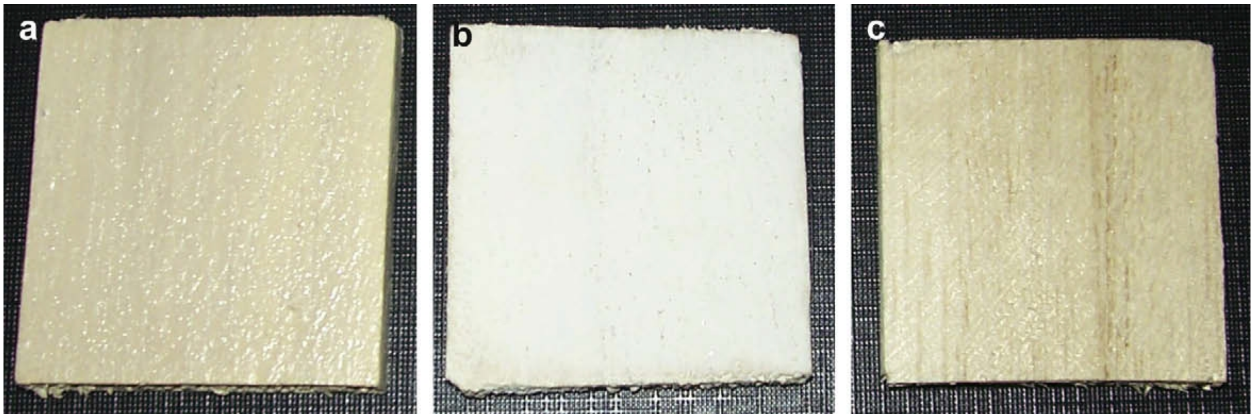


Figure 3.3: Photograph of TiO_2 thin film on wood surface (a) TiO_2 #1, (b) TiO_2 #2, (c) Absence of TiO_2.

3.4.2. TiO_2 coating on stainless steel and glass beads

Optimization of method of preparing TiO_2 films to increase the porosity of the coatings on the glass beads, as well as on stainless steel was done. The activity of TiO_2 films obtained on stainless steel substrates via a conventional alkoxide sol–gel method and via a Degussa P-25 powder enriched (PE) variation of the conventional alkoxide method was compared. Stainless steel coupons were coated with TiO_2 by conventional alkoxide sol gel and the powder enriched (PE) sol gel method. These coated coupons were used as the immobilized TiO_2 catalyst in the quartz batch reactor. Figure 3.4 shows the thick layer of TiO_2 present on a stainless steel substrate after just three coating/heat treatment cycles.SEM micrographs of the surface of the PE alkoxide sol–gel coated glass beads (Figure 3.5) show a relatively continuous surface. The surface is free of macrocracks that expose the substrate surface or significant depths to previous layers **(Balasubramanian et al., 2004)**.

The depth of the cracks is smaller than even the thickness of a single coating layer leading us to characterize them as microcracks when compared to the thickness of the coatings.

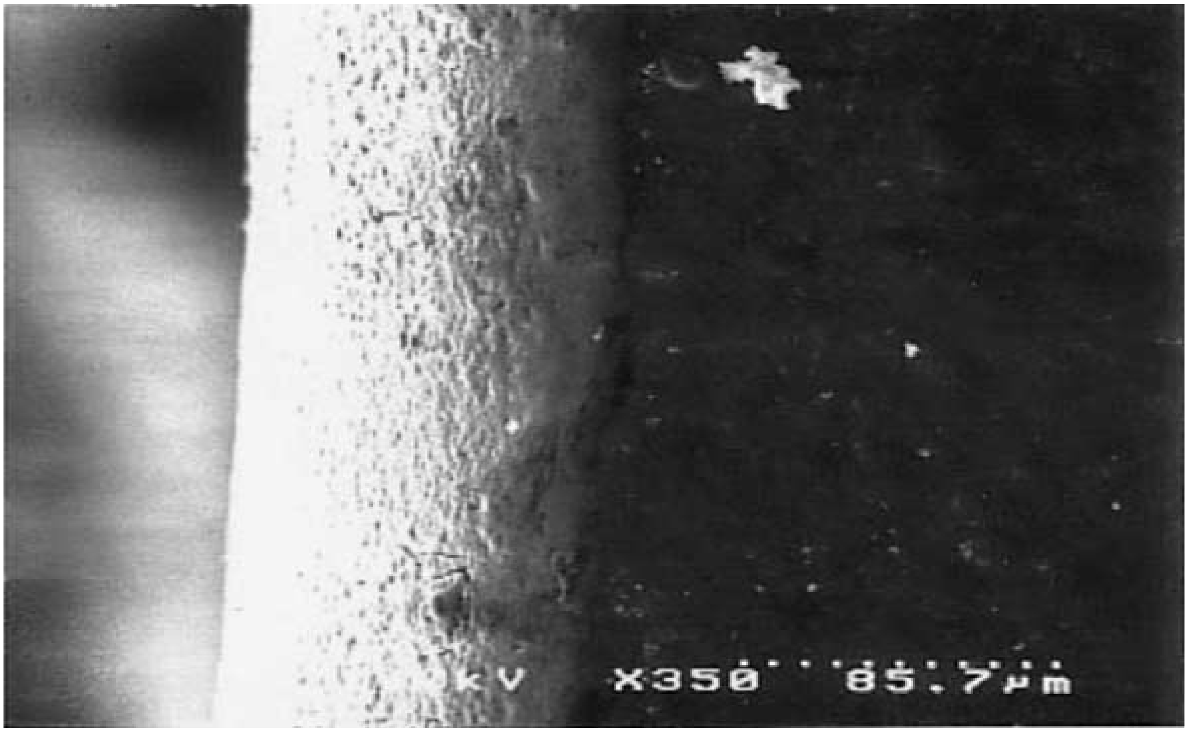


Figure 3.4: SEM micrograph of stainless steel coupon coated with PE alkoxidesol–gel after 3 dip coating/heat treatment cycles at 600 °C.

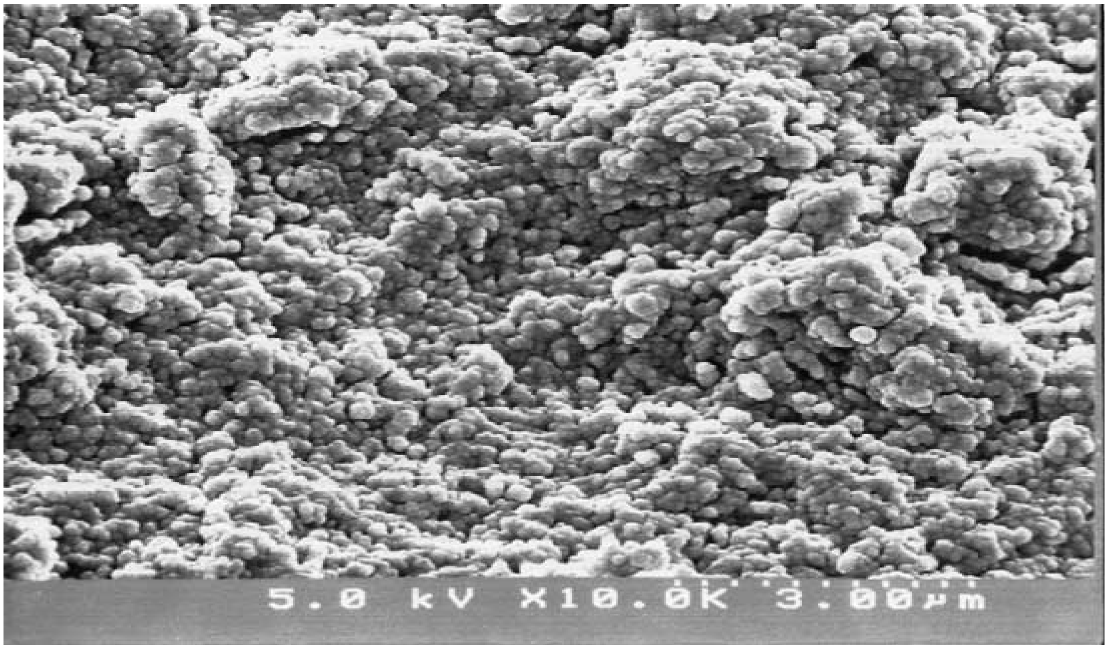


Figure 3.5: SEM micrograph of TiO_2 film on glass bead after 8 coating/heat treatment cycles showing the lack of any micro cracks.

3.4.3. TiO_2 immobilization on stone

The method adopted for the immobilization involves the preformed TiO_2 and does not require expensive precursors. A reactor was made of Cuddapah stone.It is an inert solid support for the immobilization of TiO_2. The TiO_2 was suspended in minimum amount of water (4 g of TiO_2in 100 ml of water) and 5 ml of acrylic emulsion was added under stirring. After cleaning the stone, the TiO_2+acrylic emulsion mixture was spread with a laboratory spray gun. The coated TiO_2 film was left for air-drying (Figure 3.6). Coating was repeated twice to get a uniform film without pin holes. TiO_2 photocatalyst in such an immobilized form is economical and efficient process for the treatment of effluents at larger scale that may be adopted for diluted wastewaters containing H-acid **(Noorjahan et al., 2003)**.

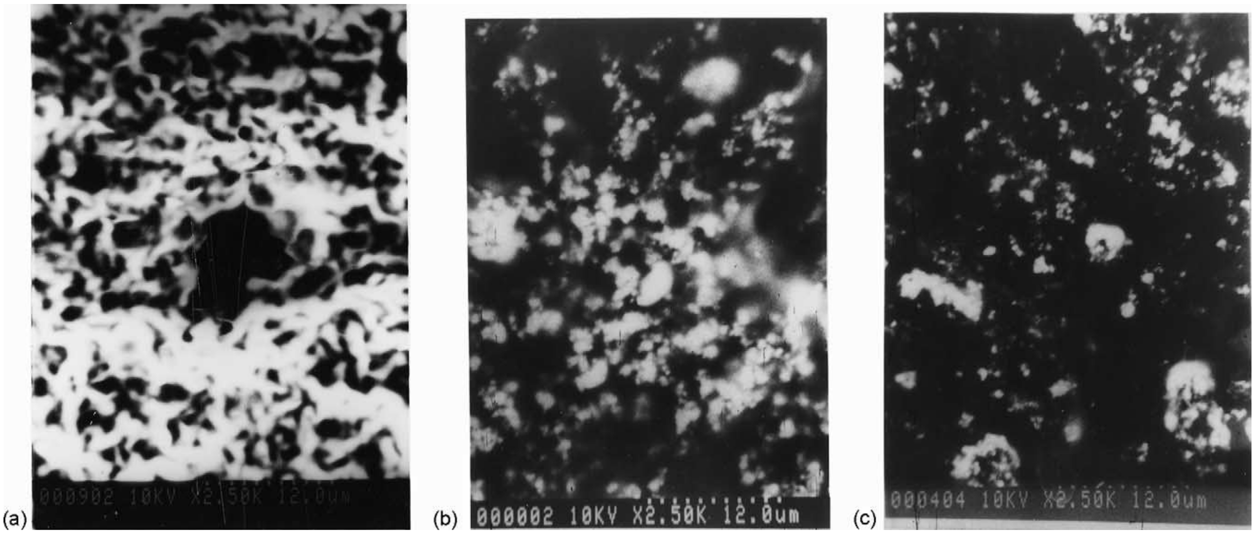


Figure 3.6: SEM images of TiO_2 thin films supported on Cuddapah stone: (a) emulsion film (without TiO_2); (b) TiO_2+ emulsion film (before treatment); (c) TiO_2+ emulsion film (after 30 days treatment).

3.4.4. TiO_2 fixing using pumice stones

Impregnation on pumice stone pellets fixed either on cement or on polycarbonate sheet. On cement, pellets were added before hardening of cement and on polycarbonate they were pasted using chloroform to dissolve the superficial layer of the polymer. Then, the pellets were impregnated with a sonicated suspension of TiO_2 (6 g/60 ml) dried, washed to eliminate the excess of titania and let to dry again before use. The weight of TiO_2 retained was 50–60 gm^{-2}.

Micrographs of bare and impregnated pellets of pumice stone are given in Figure 3.7. It clearly appears that the rough and porous surface of pumice stone is covered with TiO_2 with small cracks as dry clay.

Pumice stone is a soft material and its fixing over the pellets on a hard slanting plank surface is with cement or polycarbonate .In another study, TiO_2 was impregnated on pumice stone pellets by simply brushing with TiO_2 milk or impregnating TiO_2 milk with conventional soaking, drying and heat treatment methods **(Subramanium et al., 2003)**.

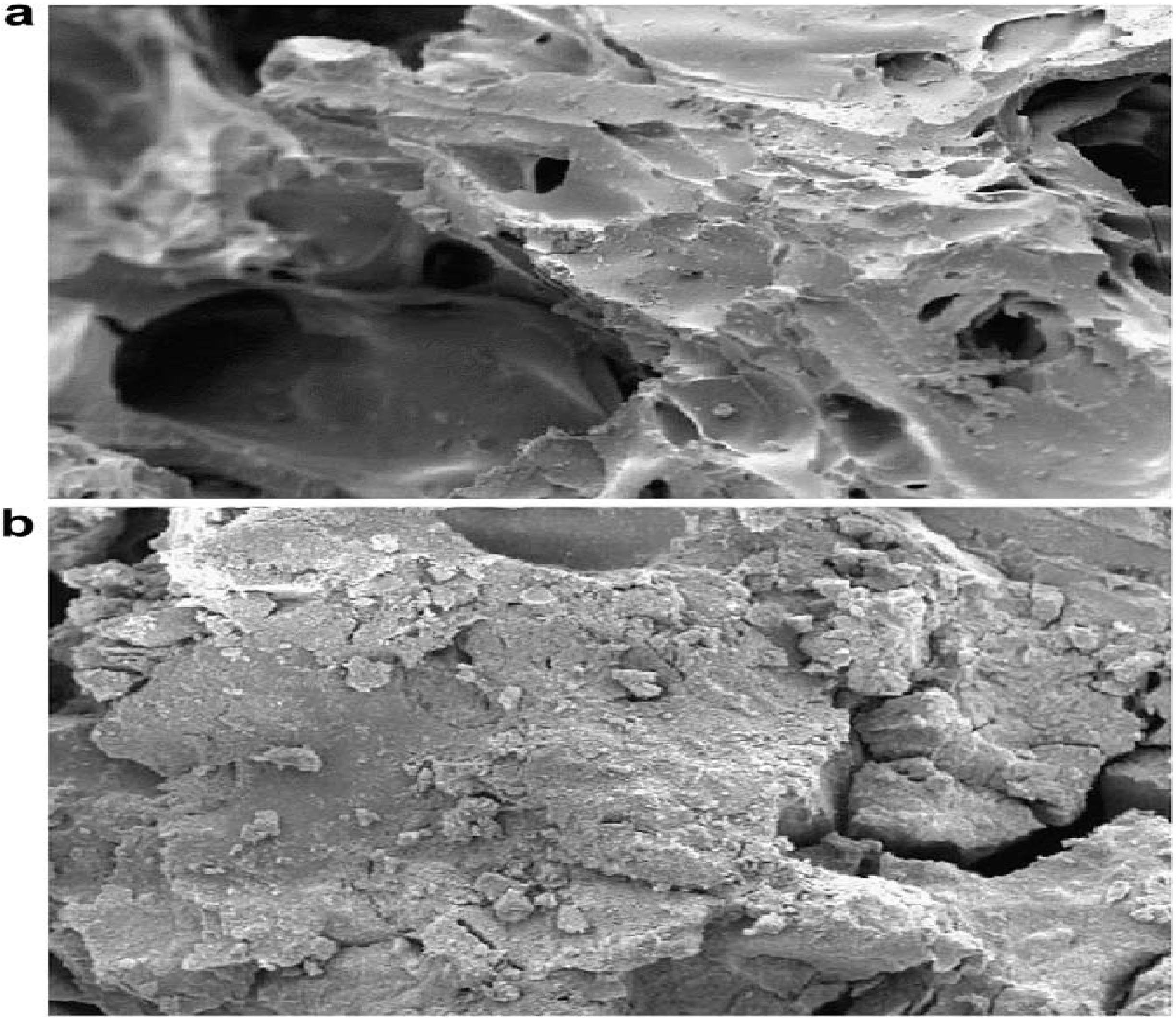


Figure 3.7: A photograph of pellets of pumice stone (magnification 250); (a) pumice stone (b) pumice impregnated with TiO_2 P25.

3.4.5. TiO_2 coating inside the quartz tube

The reactor was built of seven quartz tubes having the following dimensions: length, 300 mm; inner diameter, 16 mm; and outer diameter, 20 mm. The inner surface of the tubes was partly covered with TiO_2 particles, i.e. the catalyst was fixed only to the bottom part of the horizontally positioned tube. The total area covered with catalyst, determined for one tube, amounted to 6030 mm^2 **(Malato et al., 2002)**.

3.4.6. TiO_2 coating on pebbles

Rao and Chaturvedi, (2012) investigated the decoloration and mineralization of textile wastewater using pebble coated with catalyst in the direct sunlight (figure 3.8).

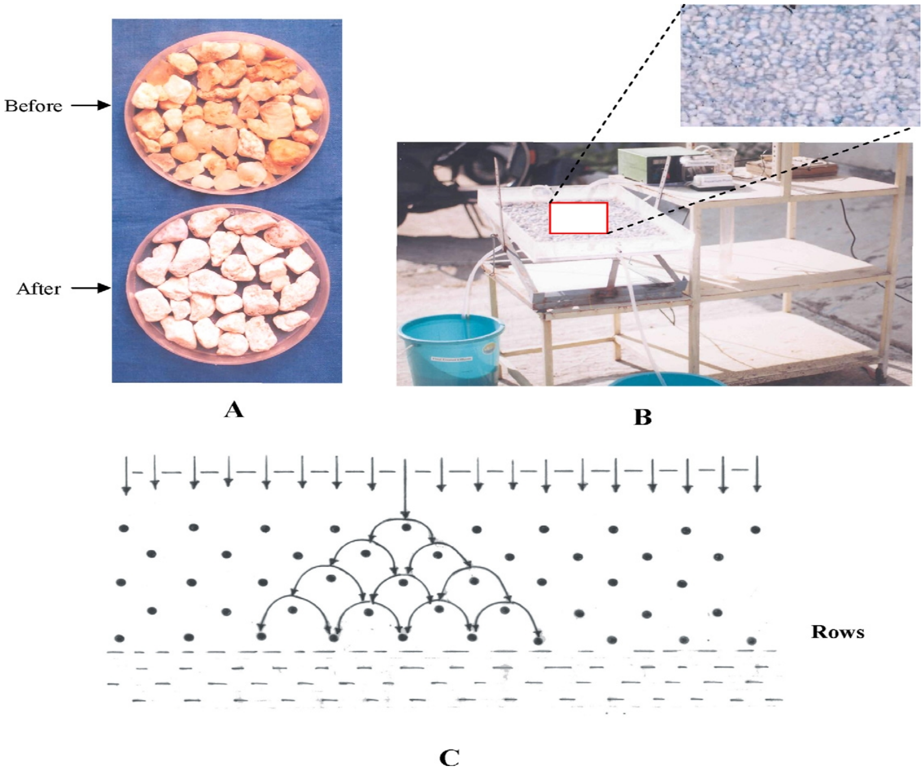


Figure 3.8:(A) Pebbles before and after TiO_2 coating, (B) solar photocatalytic pebble bed reactor and the close-up of pebbles, (C) arrangement of pebbles in a pebble-bed reactor and expected water distribution pattern (arrows indicate the direction of flow of water).

The trough (inner length, 52 cm; inner width, 45 cm; height, 0.8 cm) was fabricated using a transparent Perspex sheet. The pebbles position in an ordered configuration forming equilateral triangles allows the optimal distribution of the liquid over the pebbles to avoid preferential channeling.

3.5. Solar collectors

Solar photocatalytic technology may be defined as that which efficiently collects solar photons and enters them in a suitable reactor to promote specific catalytic reactions. The equipment that does this is called a solar collector. Traditionally, solar collector systems have been classified in two broad groups depending on the degree of concentration reached in them. The concentration factor (C) of a solar collector is defined as the relationship between collector aperture area and absorber area. The aperture area is the area that intercepts the radiation and the absorber area is the area of the component that receives the solar radiation.

Solar collectors are of following types:

3.5.1. Non-concentrating collectors

Solar collectors without concentrators are static and have no solar tracking. They are usually flat plates facing the equator, with a specific inclination, depending on the geographic location, and/or strategy of use. They can also have very low concentration factors (typically below 1.5X) and are most commonly of the CPC type given that these are ideal. Their main advantages are their simplicity and low cost.

3.5.1.1. Flat Plate Reactor

The collector under consideration is a flat plate solar air collector consisting of a transparent cover, a blackened metal sheet (absorber) and an insulated base that delimitates an air duct. The insulation at the front consists of a layer of air trapped between the transparent cover and the absorber (Figure 3.9). Its dimensions are defined by the following design variables: length L and width l (i.e. capture surface) and height of channel d **(Luna et al., 2010)**.

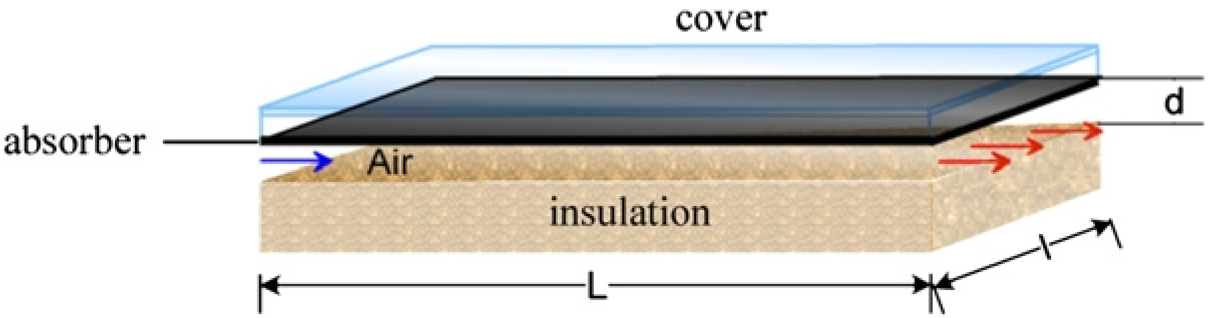


Figure 3.9: Flat Plate collector design.

3.5.1.2. Compound Parabolic Collectors

Non-tracking CPCs were originally developed for solar thermal energy applications and the same principle has been employed for disinfection purposes during this research. CPC collectors are interesting cross between trough concentrators and non-concentrating, one-sun systems. They are static collectors with a reflective surface following involutes around a cylindrical reactor tube.

When designed with a concentration ratio of one they have both the advantages of parabolic trough collectors and one-sun designs. Due to the reflector design, both the direct and diffuse UV radiation arriving at the aperture area can be collected and available for the detoxification process in the reactor (Figure 3.10). Any UV radiation reflected by the CPC is distributed around the back of the photoreactor and as a result most of the reactor tube circumference is illuminated. Hence, its performance has been shown to be very close to that of the simple tubular photoreactor, whilst only requiring about one third of the reactor tube material **(Blanco and Malato, 1999)**.

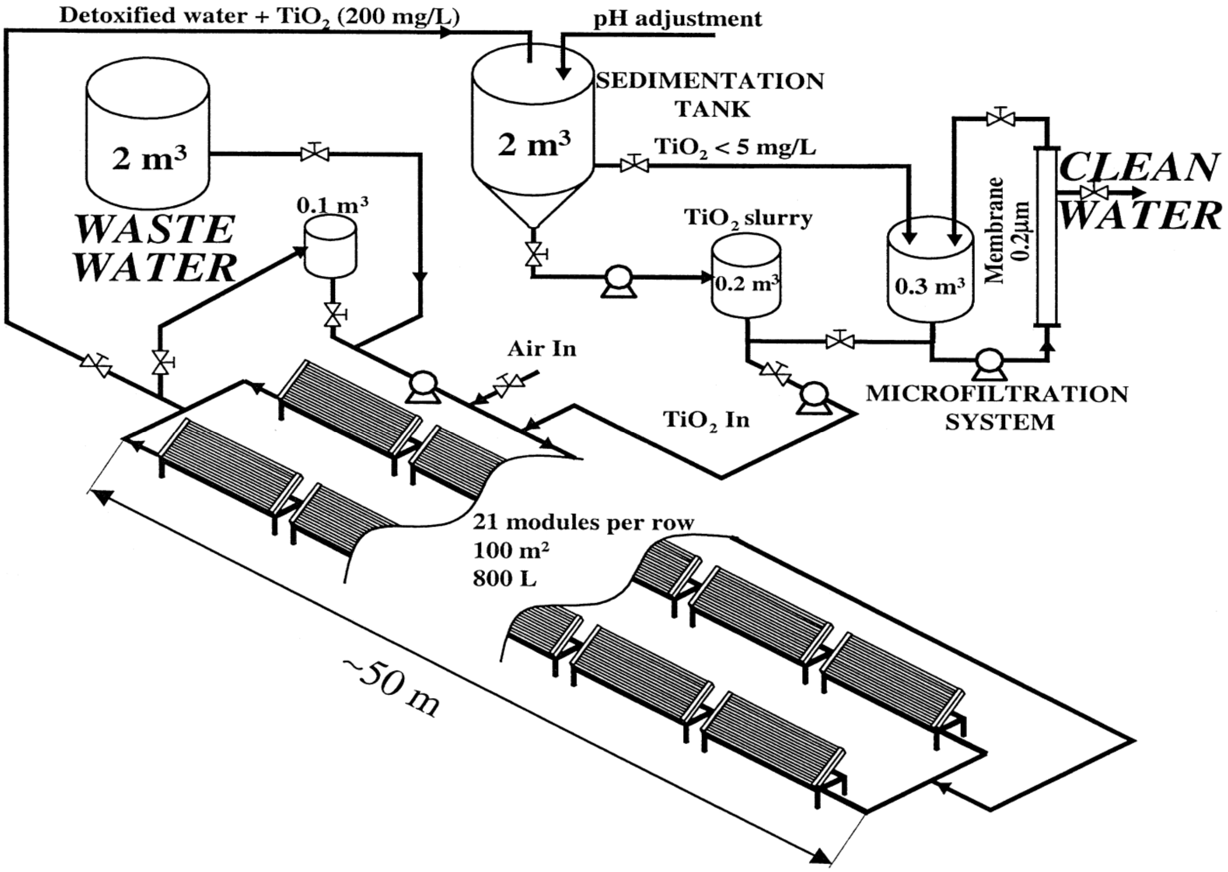


Figure 3.10: Isometric drawing of solar detoxification demonstration plant.

Sarria (2003) combined the solar-biological system (figure 3.11) at field pilot scale for the treatment of a model biorecalcitrant compound 5-amino-6-methyl-2-benzimidazolone (AMBI) and the mineralization observed was in the range of 80%-90%.

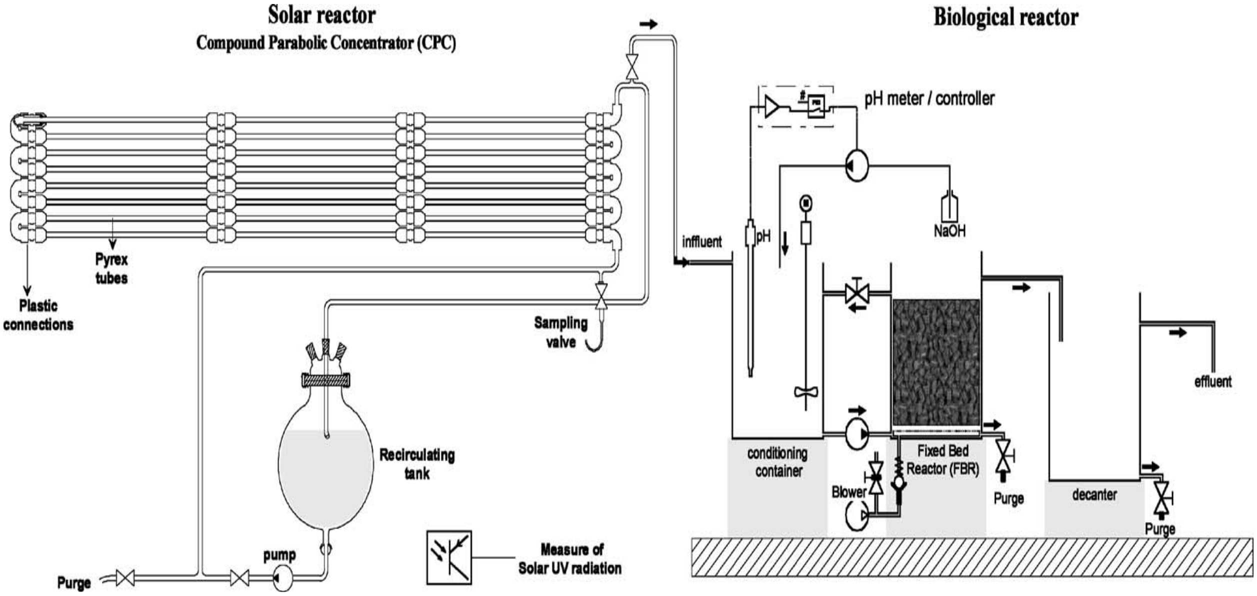


Figure 3.11: Schematic representation of the coupled solar-biological flow reactor.

The coupled bioreactor consists of Compound Parabolic Solar Collector (CPC) and a bioreactor. CPC is a static collector with a reflective surface describing an in-volute around a cylindrical reactor tube. Due to the reflector design as shown almost all the UV radiation arriving at the CPC aperture area (not only direct, but also diffuse) can be collected and so be available for the process in the reactor. The UV light reflected by the CPC is distributed around the back of the tubular photoreactor and as a result, most of the reactor tube circumference is illuminated.

The CPC has three modules (collector surface 3.08 m^2, photoreactor volume 24 l, and total reactor volume 60 l) whereas one module consists of eight tubes and mounted on a fixed platform 46° tilted (local latitude). The three modules are connected in series with water directly flowing through them at 30 l min^{-1}, leading finally to a recirculation tank connected to a centrifugal pump.

3.5.2. High-concentrating collectors

3.5.2.1. Parabolic Trough Collectors (PTC)

The first photoreactors for solar photocatalytic applications designed at the end of the eighties were based on concentrating solar reactors. Parabolic-trough collectors (PTCs) are most promising type of concentrating solar reactors which is proved to be effective for waste water treatment .PTCs consists of a structure that supports a reflective concentrating parabolic surface.

This structure has one or two motors controlled by a solar tracking system on one or two axes that keeps the collector aperture plane always perpendicular to the solar rays (Figure 3.12). In this situation, all solar radiation available on the aperture plane is reflected and concentrated on the absorber tube that is located in the geometric focus of the parabola. The size and length of the collector is small, which can translate into a reactor that is able to support higher pressures and a large amount of energy per unit volume **(Arasu and Somakumar, 2007)**. PTC technology was relatively mature and existing hardware could be easily modified for the photochemical processes. The first outdoors engineering-scale reactor developed (in USA) was a converted solar thermal parabolic-trough collector in which the absorber/glazing-tube combination had been replaced by a simple pyrex glass tube through which contaminated water could flow.

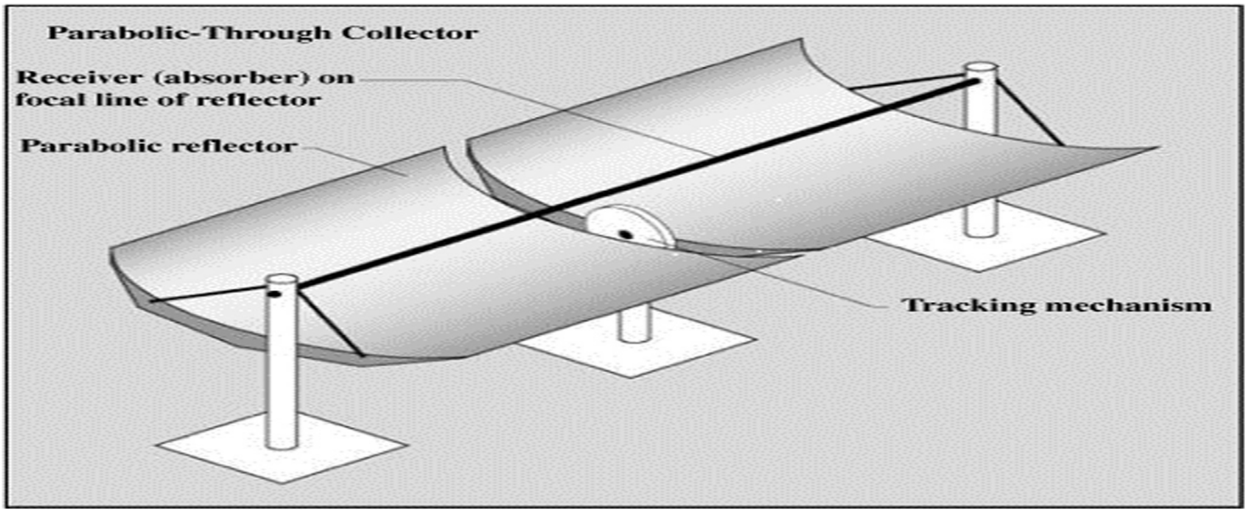


Figure 3.12: Schematic figure of PTC.

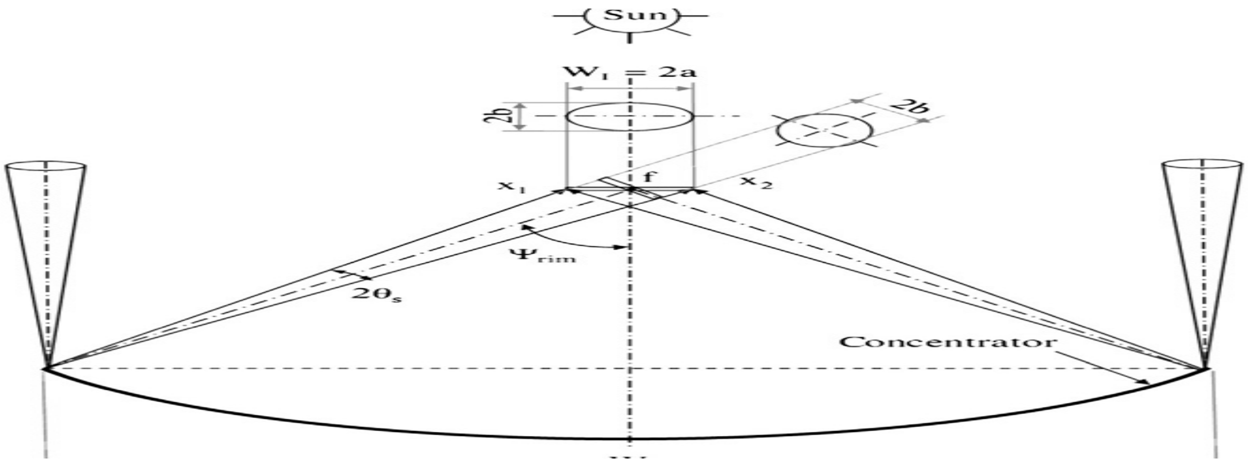


Figure 3.13: Design considerations for parabolic collectors (Mcloughlin et al., 2004).

The design of parabolic collector geometric parameter includes rim angle and collector aperture. The rim angle plays major role in focal distance and focal image (receiver) size. The size of focal image may be determined based on the parabolic geometry (Figure 3.13).

The image at focal line on horizontal surface is in the form of ellipse. The focal image size of parabolic trough collector is evaluated by estimating ellipse major and minor axis dimensions. The concentration ratio of parabolic trough collector is calculated for different rim angles varied from 5° to 85° insteps of 5°. The concentrator requires lengthy and stronger receiver support which shifts the center of gravity of the collector away from its axis **(Bahnemann, 2004)**. Therefore, the system requires higher torque for tracking and stronger receiver support to avoid bending.

Lacunae:

- A very few studies have been done on design modifications of solar collectors to harness solar energy instead of UV radiations for the degradation of bio recalcitrant compounds by advanced oxidation processes.
- According to literature search in solar photo catalysis, the concept of recycling is being ignored generally and the studies in which the recycling was done, the stability of the catalyst was very low after few recycle.

4. MATERIALS AND METHODS

This study includes various analytical techniques required for the assessment of the compound and to follow its degradation pathway. Standard methods have been used all through the study and all equipments were calibrated before use.

4.1. Pharmaceutical compound

AMT (figure 4.1) is a semi synthetic beta lactam antibiotic that acts by inhibiting the synthesis of bacterial cell walls. It is a congener of ampicillin (a semi-synthetic aminopenicillin) differing from the parent drug only by hydroxylation of the phenyl side chain **(Kaur et al., 2011).** It is most widely used group of antibiotics in human medicine, which have showed an increasing trend of prescription over the last decade. Due to its high stability and low biodegradability it is difficult to remove it from wastewater through conventional techniques **(Sutherland et al., 1972)**.

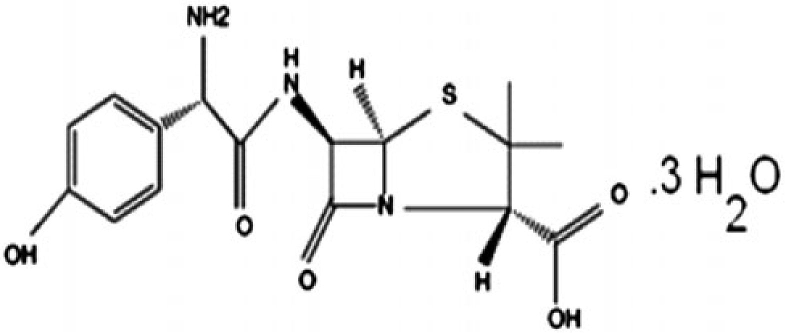


Figure 4.1: Chemical structure of Amoxicillin Trihydrate (AMT).

Compound was scanned over a range of 190 nm to 400 nm with the help of UV- Vis spectrophotometer and maximum absorbance was observed at 230 nm.

4.2. Reagents and chemicals

The photo catalyst was TiO_2 P-25 (a mixture of Anatase and Rutile form of titanium dioxide in the ratio of 70:30, procured from Degussa Company, India branch, Bombay). 30 % (w/v) Hydrogen Peroxide (Ranbaxy laboratories) was used as an electron acceptor. COD **(APHA, 1992: Sec. 5220C)**, TOC **(Harp, 2002)** and NH_4^+ ions **(APHA, 1992: Sec. 4550C)** concentration of raw compound was determined by standard methods. In all experiments double distilled water was used.

4.3. Instruments used

4.3.1. pH meter

The pH of the solution was adjusted by 0.1N HCl and 0.1N NaOH measured with the help of pH meter (purchased from Eutech instrumentation, figure). Instrument was calibrated with freshly prepared buffur solutions (pH 4 and 9) from time to time throughout study.

4.3.2. UV-Vis Spectrophotometer

UV-Vis (Hitachi V- 500 UV/VIS, Japan) spectrophotometer was used for AMT photo degradation analysis (fig).

4.3.3. Radiometer

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

4.3.4. 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 different supports.

4.3.5. Muffle Furnace

Rate controlled muffle furnace (temperature range 200 to 800 ^{0}C) was used for the fixation of catalyst coating on cement beads. It was operated at a temperature of 300 ^{0}C for this purpose.

4.4. Solid spectra and XRD pattern

UV spectrophotometer (Shemadzu UV 2450, Japan) and XRD Model X' Pert PRO from PANalytical, Netherland has been used for the analysis of used and unused TiO_2 to determine the deformity, if any in the structure of the catalyst before or after the subsequent treatment cycles. Thus, these techniques were applied to study the recycling feasibilities.

4.5. LC-MS Technique

For the confirmation of intermediates products during the photocatalytic degradation of AMT, the LC-MS was performed. The details of LC-MS are as under:

Instrument: Waters, Micromass Q-TOF micro U.K
Separation Module: Waters Alliance 2795
LC Column: Waters X-Terra C18(2.1*100mm, 5um)
Ionization: Electro spray Positive (ES+)
Acquisition: MRM, unit resolution

Injection Volume: 20 micro liters
Flow rate: 0.3 ml/min

For Mass spectrometer following parameters were used

Desolvation Gas: 500Lts/Hr
Cone Gas: 45 Lts/Hr
Desolvation Temperature: 200C
Source Temperature: 800C
Capillary Voltage: 3000V
Cone Voltage: 30V
Collision energy: 10v
Gases used : Argon,N2

4.6. Solar-photo-reactors and methodology

4.6.1. Shallow pond slurry type reactor

A shallow pond of capacity 1200 mL was used for the solar photocatalytic studies (figure 4.2). The catalyst was used in the form of aqueous slurry with the AMT solution. Continuous stirring at the rate of 150 rpm and aeration at 4.5 L/h was provided so that TiO_2 molecules remain in suspension. Samples were withdrawn at regular intervals with the help of syringe and filtered with 0.45 micron filters followed by analysis with UV Vis spectrophotometer.

Figure4.2: Shallow pond slurry type reactor

4.6.1.1. TiO_2 entrapped alginate balls

Catalyst entrapment

2 % Sodium Alginate gel and 2% homogenized catalyst were mixed together to form alginate balls with the help of auto pipette. Small (3 mm) TiO_2 entrapped alginate balls were developed using Calcium chloride; for the formation and storage of coated alginate balls. The balls were kept in refrigerator for complete binding of catalyst, at the temperature of 3^0C for an hour.

Experimental Procedure

Around 40 TiO_2 entrapped alginate balls were placed in a shallow pond with 200 mL of AMT solution under sunlight. Sample was aerated continuously at 4.5 L/h without re-circulation. The samples were collected for analysis from pond at regular interval. Figure 4.3 shows TiO_2 entrapped alginate balls after the treatment of compound.

Figure 4.3: TiO_2 entrapped Alginate balls.

4.6.1.2. TiO_2 immobilized cement beads

Catalyst coating

Cement beads of 1.0 to 2.5 cm diameter were prepared with sand and cement. They were dispersed with required amount of homogenized TiO_2 slurry until uniform deposition was achieved. Beads were given appropriate heat treatment at suitable temperature in oven to remove excess water. The same cycle was repeated for two times for getting uniform and stable film of the catalyst. The coated beads were washed with water after each cycle to remove the loosely bound catalyst particles.

Experimental Procedure

25 cement beads were kept in a shallow pond of 200 mL capacity for photo degradation under solar irradiation. AMT solution was aerated at 4.5 L/h and samples were withdrawn for analysis at regular interval. Figure 4.4 shows the cemented beads after coating of the catalyst.

Figure 4.4: TiO_2 immobilized cement beads.

4.7. Parabolic Trough Collector

A solar parabolic concentrator was designed by Ecosense Sustainable Solutions Private Limited which continuously reflects the radiation onto the receiver which carries the AMT solution to be degraded. The solar receiver was made of a transparent borosil glass with rubber cork at both ends of the glass tube. An automatic tracking system was installed in the collector to concentrate maximum solar radiation at the focal tube (figure 4.4 & 4.5). All specifications of the collector are listed in table 4.1. The receiver tube was packed with 100 TiO_2 coated cement beads. AMT solution (5 L) with optimum amount of oxidant from the storage tank was pumped through the receiver tube, where it was passed through cement beads at the flow rate of 1 L/min and then flows back into the storage tank. Solution temperature was recorded by temperature sensors. UV intensity was also measured by radiometer. Samples were taken at regular intervals and analyzed for degradation using spectrophotometer and subsequent mineralization through LC-MS.

Table4.4.1: Specifications of parabolic trough collector.

Items	**Value**
Collector aperture	0.8 m
Collector length	1.25 m
Rim angle	90^0
Focal distance	0.2 m
Receiver diameter	12.8 mm
Concentration ratio	19.89
Water flow rate	0.5-2 L/min
Storage tank capacity	5 L
Tank material	Stainless steel
Water pump	367.65 W

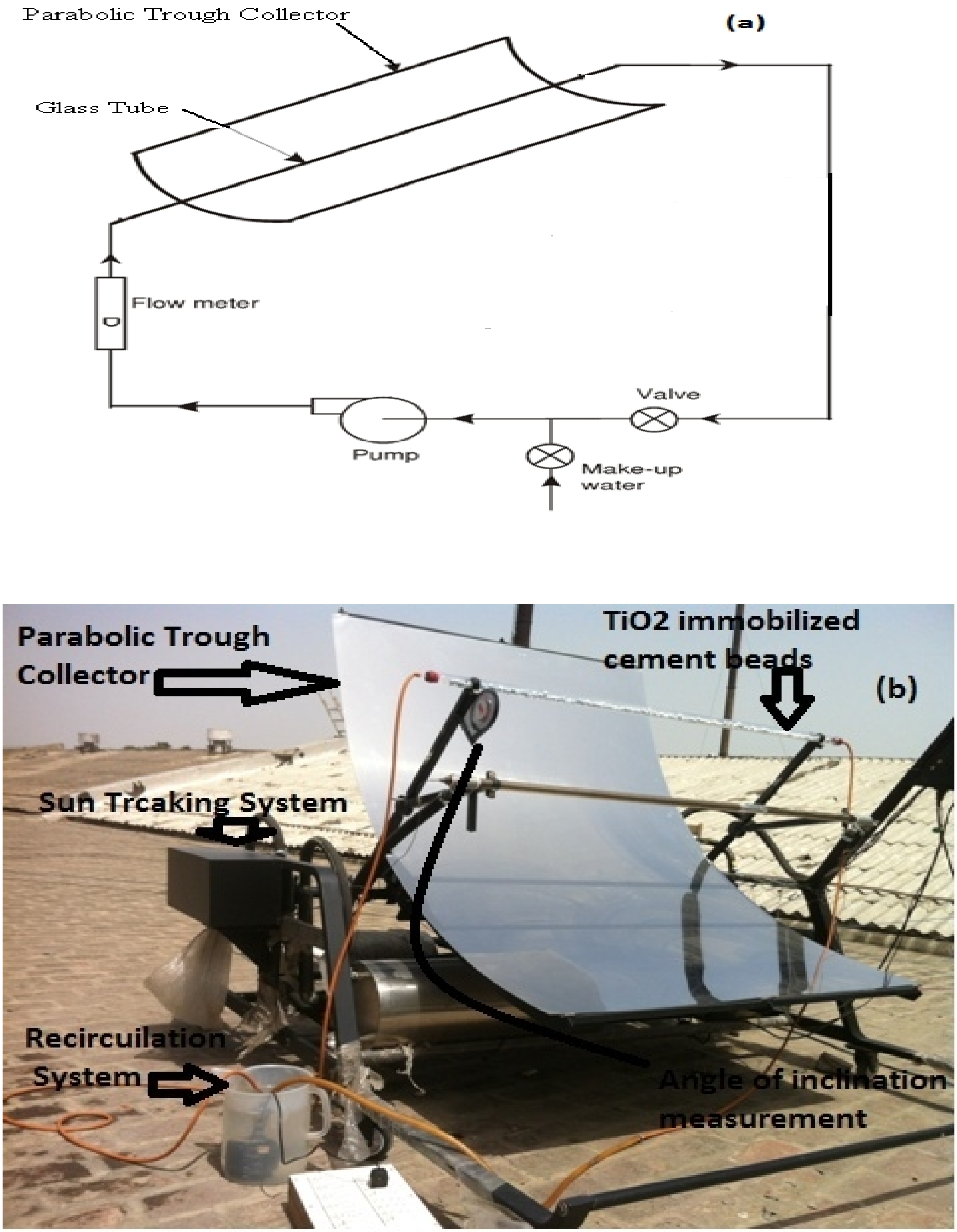


Figure 4.5: (a) Schematic diagram of parabolic trough collector (b) Actual site photograph of Parabolic Trough collector.

5. RESULTS AND DISCUSSION

This section elaborates all the inferences that correspond to the photocatalytic degradation of AMT by using suspended as well as immobilized TiO_2 as catalyst. These observations were then subjected to pilot scale solar parabolic trough collector to analyse its degradation capacity and its viability to be used for field scale applications. All experiments were conducted in triplicates for reproducibility of the results.

5.1. Pharmaceutical Compound Characteristics:

Technical grade (98% pure) Amoxicillin Trihydrate (AMT) was purchased from Fluka, India (CAS 26787-78-0) and was analyzed for various characteristics.

5.1.1. Standard curve of Amoxicillin Trihydrate

A graph plot of absorbance vs. concentration of AMT solution was prepared by varying known concentration of AMT solution (figure 5.1). AMT concentration was varied from 50 mgL^{-1} to 150 mgL^{-1} at 230 nm. From this graph we can calculate unknown concentration for AMT solution. Regression coefficient was found to be 0.998 and slope was 0.023.

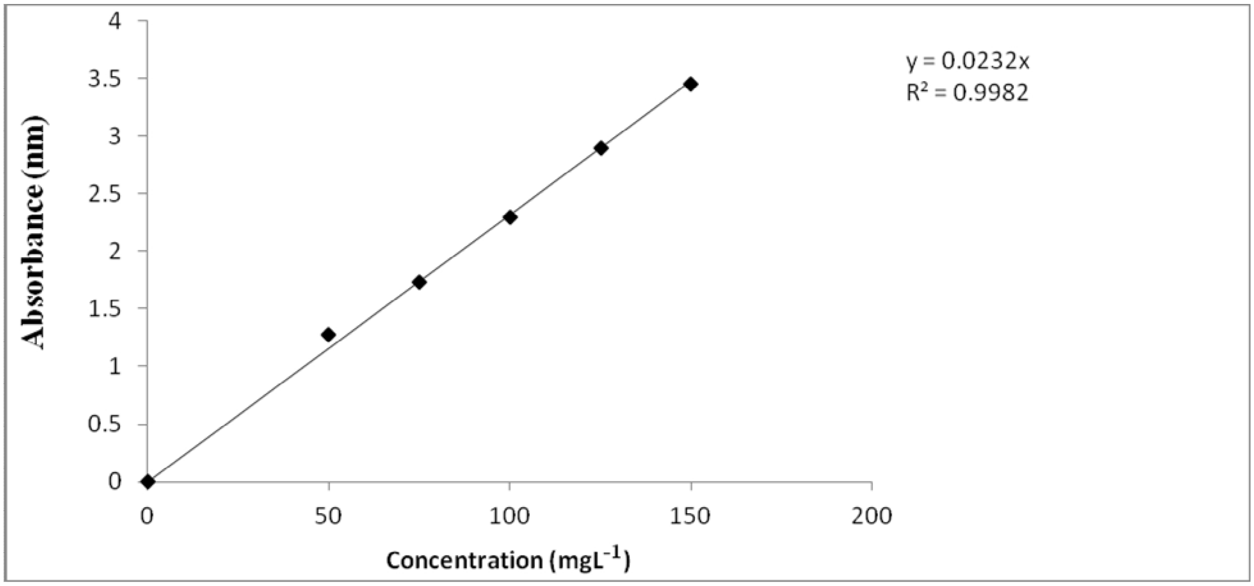


Figure 5.1: Standard curve of Amoxicillin Trihydrate

5.2. Photocatalytic treatment and process optimization

Photocatalytic treatment is influenced by various factors like concentration of the catalyst, operating pH of the process, concentration of the electron acceptor, initial concentration etc. It is evident from literature (**Verma et al., 2013**) that photocatalytic reactions can usually be described by a pseudo-first order kinetic expression i.e.

$-dC/dt = k\ C_t$.

i.e. In $C_0/C_t = kt$

Where C_0 and C_t are the concentration of AMT at times 0 and t, and k is an apparent reaction rate constant. Plot of $\ln C_0/C_t$ vs. time was plotted and slope of graph was taken as apparent reaction rate constant (k). Dark, photolytic and catalytic experiments were performed to see their effect on AMT removal.

5.2.1. Preliminary studies

Blank experiments were conducted to see the effect of AMT degradation with or without catalyst in presence or absence of solar radiations. Role of oxidant on degradation of AMT was also studied individually or in combination with sunlight and catalyst. As shown in figure 5.2 it was evident that there was a small decrease (8 %) in concentration of AMT due to its adsorption on the surface of the catalyst. Also, presence of only H_2O_2 could not trigger the degradation at high rate as the generation of some OH radicals cannot create a big difference in degradation. However, when TiO_2, H_2O_2 and sunlight were used in combination with each other the degradation rate increased substantially due to the generation of more hydroxyl radicals **(Verma et al., 2012)**.

The relative efficiencies of the above combinations are in following order:

TiO_2 + H_2O_2 +Sunlight > TiO_2+ Sunlight > TiO_2+ H_2O_2 > H_2O_2 +Sunlight >Sunlight only > H_2O_2 only > TiO_2 only

Simultaneous presence of TiO_2+H_2O_2 +Sunlight yielded maximum degradation of 87% after optimization of catalyst concentration, oxidant concentration and pH value as shown in next section. This experiment showed that heterogeneous photo catalysis is an effective method to treat AMT. Therefore, it formed the basis of all experiments conducted in case of immobilization of catalyst and Parabolic Trough Collector.

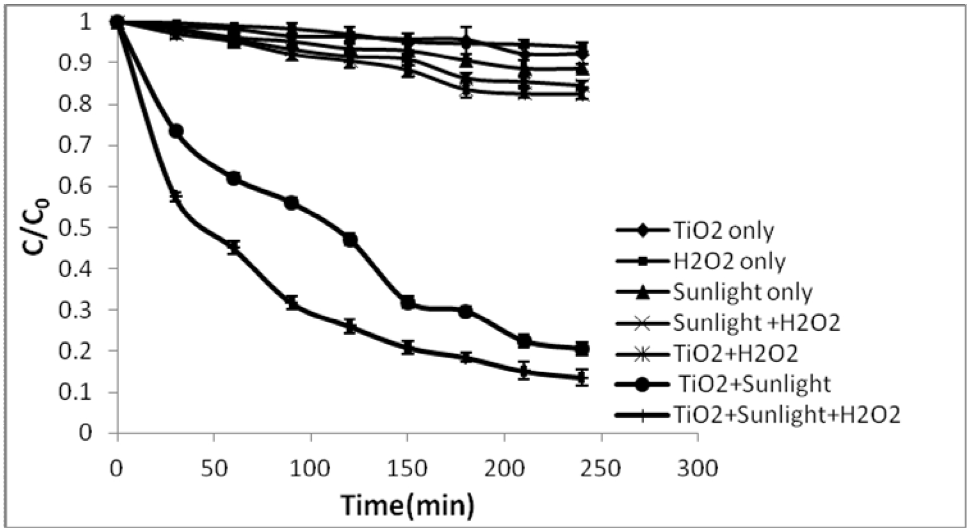


Figure 5.2: Photolysis, photocatalytic reduction of AMT in the presence and absence of TiO_2 along with adsorption and slurry TiO_2 (C_0=100 mg L^{-1}, V = 200 mL).

5.2.2. Catalyst optimization studies

Amount of catalyst to be used for heterogeneous catalysis have always been a point of concern. High catalyst concentration makes it difficult to remove the catalyst from the slurry as well as it increases the cost of the process. Thus, efforts have been done to minimize the concentration of the catalyst used without compromising the efficacy of the process. TiO_2 was varied in the concentrations ranging from 0.25 gL^{-1} to 2.5 gL^{-1} in the presence of sunlight for 4 hours (figure 5.3). The photo catalytic activity of suspended TiO_2 was found to be directly proportional to the total surface exposed. Figure 5.4 demonstrate that the reaction rate increases with the increase of the catalyst concentration up to 0.5 gL^{-1} and was almost constant till 1.0 gL^{-1} which corresponds to the optimum of light absorption. The reaction rates from 0.5 gL^{-1} to 1.0 gL^{-1} were comparable and not much difference was noted in reaction rate up to 1.0 gL^{-1} , therefore 0.5 gL^{-1} TiO_2 concentration was selected as best suitable catalyst amount. The AMT degradation efficiency of 80% was achieved at this concentration after the irradiation of 4 hours. However, on further increasing catalyst concentration beyond 1.0 gL^{-1} the increase in turbidity of the solution reduces the light transmission through the solution due to clustering of catalyst particles at higher concentration and thus causing a decrease in the number of active sites on its free surface. Moreover, decrease in opacity and increase in scattering of solar UV light by TiO_2 particles at higher concentration leads to interruption in the passage of radiation through the AMT solution

(Akpan and Hameed, 2009). Also, high catalyst concentration may not be useful due to possible aggregation resulting in a loss of surface area available for light capturing **(Okamoto et al., 1985)**.

So an amount of 0.5 gL^{-1} of TiO_2 has been taken for the subsequent experiments for the optimization of the operating pH and concentration of oxidant to be added.

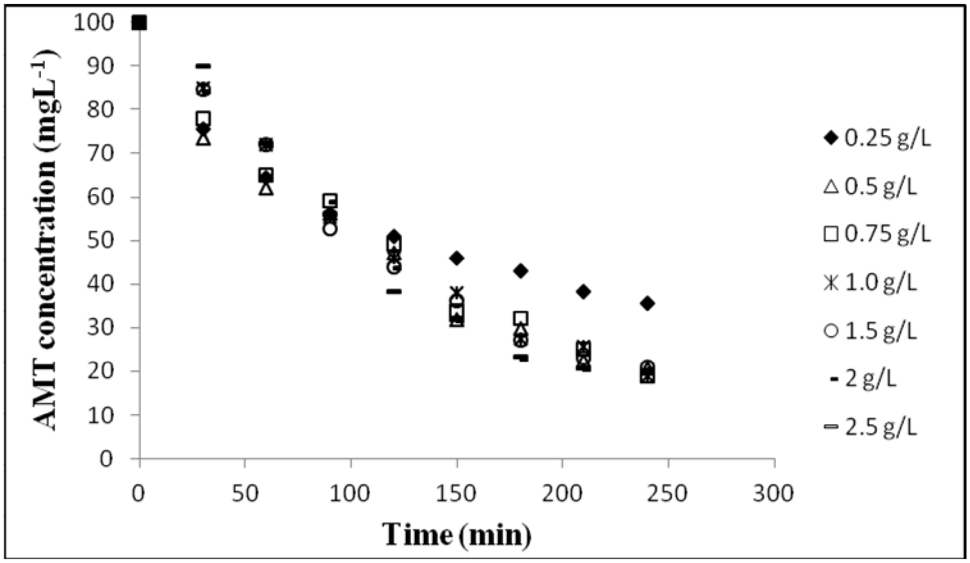


Figure 5.3: Concentration profiles of AMT at different TiO_2 concentrations (C_0=100 mg L^{-1}, V = 200 mL, initial pH=5.8)

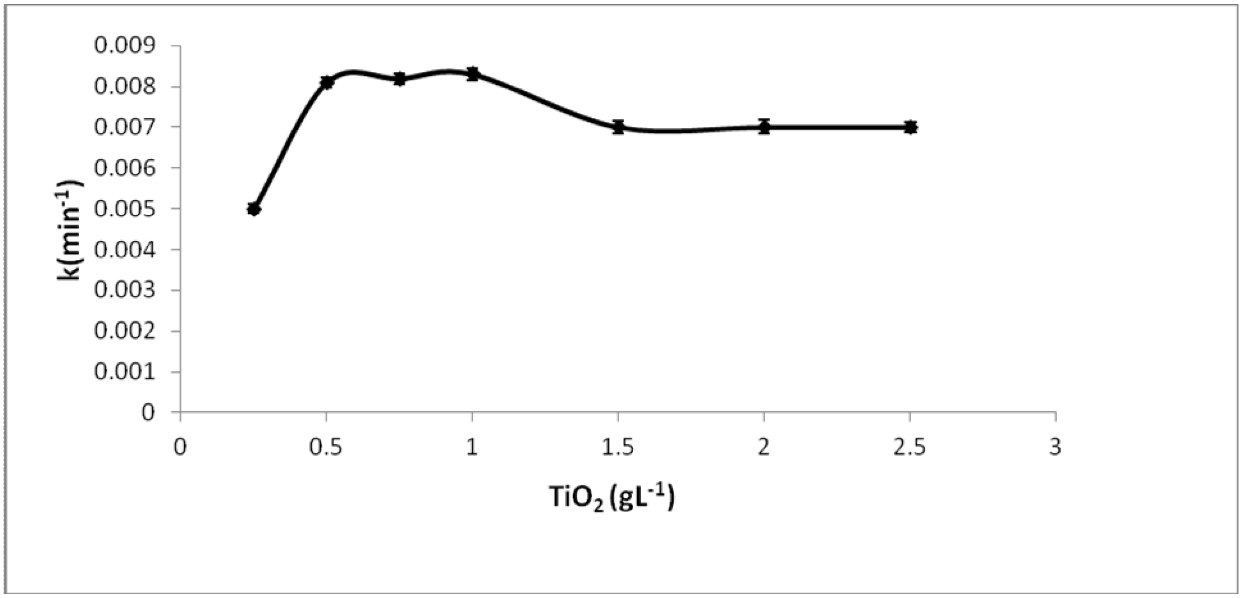


Figure 5.4: Plot of first order rate constant vs. TiO_2 concentration for photocatalytic degradation of AMT (V = 200 mL, C_0=100 mgL^{-1}, initial pH=5.8)

5.2.3. Influence of pH

The effect of the pH on the degradation rate can be explained mainly by adsorption of AMT on TiO_2 surface. The effect of pH on the rate of photocatalytic degradation of AMT was studied in range of pH between 2 and 9 (figure 5.5). Also figure 5.6 shows kinetic rate constant for AMT removal as a function of reaction pH. The rate of disappearance of AMT from the suspension was found to be increased from 2 pH to 4 pH and then became stable between 4 pH to 7 pH and then decreased thereafter up to 9 pH. In slightly acidic suspensions, the adsorption of a pollutant on the TiO_2 particles increased significantly comparing to the extent of adsorption in alkaline suspensions. This is attributed to the fact that TiO_2 shows an amphoteric character so that either a positive or a negative charge can be developed on its surface **(Malato et al., 2002)**.The point of zero charge (pzc) of the used TiO_2 (Degussa P-25) is widely reported at pH≈6.5. The TiO_2 surface is positively charged in acidic solution and negatively charged in basic solution. Therefore, pH value has a significant role in adsorption/desorption properties of the catalyst surface **(Hoffman et al., 1995)**. However, maximum degradation rate was observed to be at pH 5 and pH 6; which is close to the AMT's initial pH i.e. 5.8. To minimize the cost of the process and to avoid the use of reagents, further studies were performed at initial pH of AMT solution.

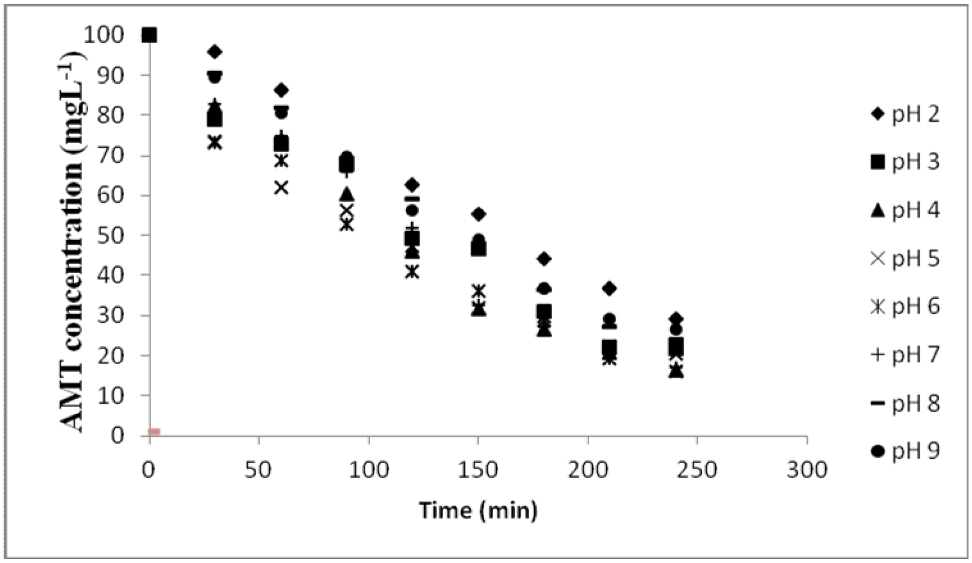


Figure5.5: Concentration profiles of AMT at different pH values (C_0=100 mg L^{-1}, TiO_2=0.5 gL^{-1}, V = 200 mL)

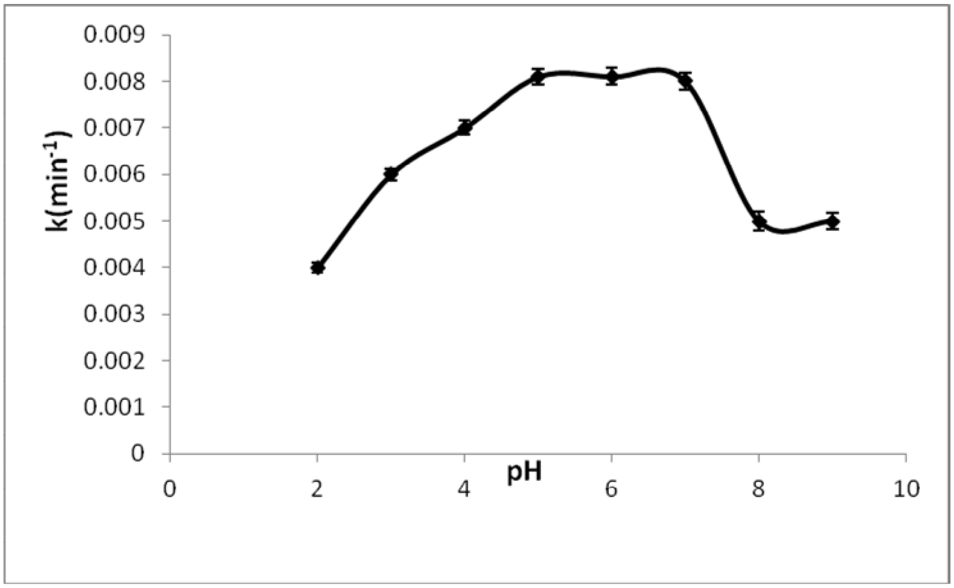


Figure 5.6: Plot of first order rate constant vs. pH values for photocatalytic degradation of AMT (TiO_2=0.5 gL^{-1}, C_0=100 mgL^{-1}, V = 200 mL)

Therefore, the formation of OH free radicals was supplied by the reaction of positive holes with water and OH on the surface of titanium dioxide at its initial pH. Thus, AMT solution was kept at its initial pH i.e. 5.8 for subsequent reactions.

5.2.4. Addition of Electron acceptor

The effect of adding oxidant on the photodegradation efficiency of AMT was investigated by varying the amount of H_2O_2 from 0.03 gL^{-1} to 0.21 gL^{-1} (figure 5.7). From figure 5.8 it can be noted that degradation efficiency of AMT increased from 80% to 87 % by adding H_2O_2 up to 0.12 gL^{-1}, but further increasing the oxidant concentration up to 0.21 gL^{-1}, degradation rate of AMT decreased again. The rate improvement at lower H_2O_2 dosages is probably due to generation of OH radicals by direct photolysis of H_2O_2 in sunlight. Also, it facilitates the electron-hole recombination, according to the following equation **(Malato, 2003)**:

$TiO_2 (e-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH^{\cdot}$

H_2O_2 accepts the photo generated electron from the conduction band and thus promotes the charge separation, and thereby forming OH radicals.

However, at a high concentration of H_2O_2, it also acts as a scavenger as shown in the following equations **(Verma et al., 2013)**

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

$H_2O_2 + OH^{\cdot} \rightarrow H_2O + O_2$

In addition, the high dose of H_2O_2 might absorb and attenuate the incident UV light available for the photocatalysis process. Thus, 0.12 gL^{-1} H_2O_2 was taken as the best suitable amount which yields maximum degradation i.e. 87% in 4 hour at 0.5 gL^{-1} catalyst concentration and at 5.8 pH. These optimized conditions were used in all subsequent experiments.

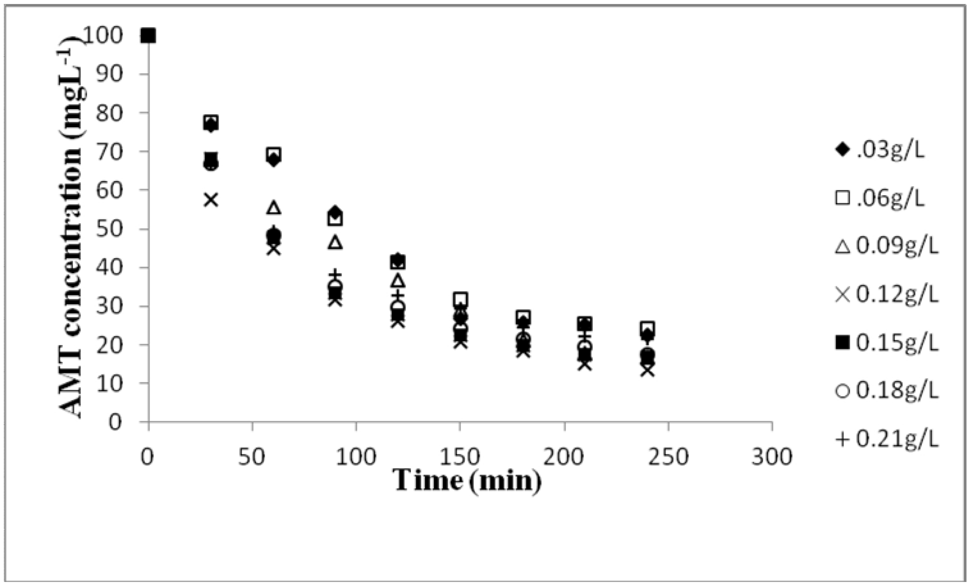


Figure 5.7: Concentration profiles of AMT at different H_2O_2 concentrations (C_0=100 mg L^{-1}, TiO_2=0.5 gL^{-1}, pH=5.8, V = 200 mL)

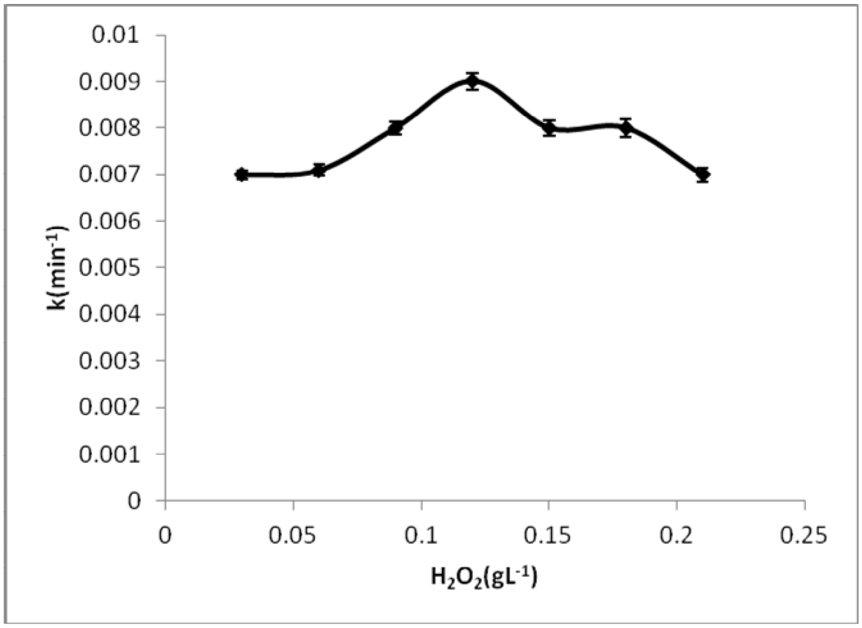


Figure 5.8: Plot of first order rate constant vs. H_2O_2 concentration for photocatalytic degradation of AMT (C_0=100 mg L^{-1}, TiO_2=0.5 gL^{-1}, pH=5.8, V = 200 mL)

5.2.5. Effect of Area/Volume Ratio

Depth of the reactor plays a crucial role in the photocatalytic degradation of the compound for field scale applications. It determines the extent of effective solar light penetration for degradation of the compound. Generally less depth and more area is required for more solar light penetration. This can be achieved by either keeping the volume constant and varying the area or by keeping area constant and varying the volume. In our studies, we have varied the volume by keeping the aperture constant. Thus, experiments were conducted with all the optimum conditions in the shallow slurry pond reactor under sunlight at different A/V ratios ranging from 0.76 to 5.35 cm^2mL^{-1}. The degradation efficiency increased with the reduction in the volume of the sample to be treated i.e. less depth (figure 5.9). Actually, reducing the volume, increases A/V ratio thus enhancing surface area of solution leading to increase in path length of photons resulting in more OH radicals **(Verma et al., 2014a)**. Similar studies were done by Bahnemann **(1999)** with three different dyes which show that, at the higher penetration of light irradiation, the enhancement was considerably higher because that the electron–hole formation is predominant and, hence, electron–hole recombination is negligible. However, at lower light penetration rate, electron–hole pair separation competes with recombination which in turn decreases the formation of free radicals, thereby, causing less effect on the percentage degradation of the dyes.

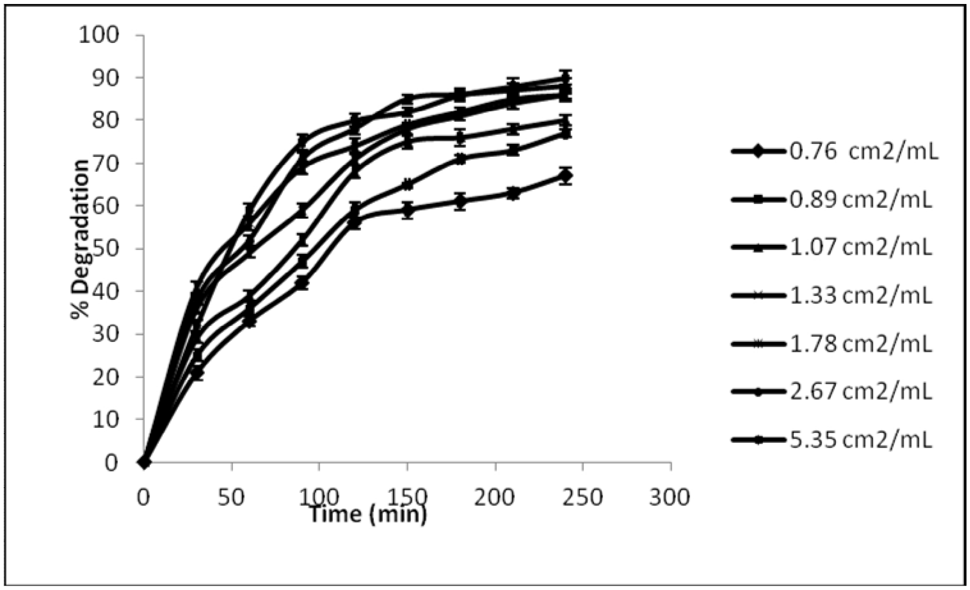


Figure 5.9: Effect of A/V ratio on degradation of AMT (C_0=100 mg L^{-1}, TiO_2=0.5 gL^{-1}, pH=5.8, H_2O_2=0.12 gL^{-1})

5.2.6. Effect of initial AMT concentration

To study the effect of substrate concentration on the degradation rate, the AMT concentration was varied from 50 to 200 mgL^{-1} with all the optimum conditions. It was observed that the degradation rate increased up to 100 mgL^{-1} of AMT solution and decreased thereafter (figure 5.10). The other reason may be due to insufficient production of OH radicals by the catalyst for the higher concentration of the substrate. According to **Evgenidou E. et al., (2005)** it is obvious that the rate increases with the increase of the initial concentration of pollutant until it reaches a saturation value at high concentration of the insecticide. Also, it was reported that thr recombination of photogenerated electrons and holes at the surface of TiO_2 can complete within 10^{-9} s,which suggests that polllutant can be degraded only if it is adsorbed on catalyst surface. Thus surface adsorption is of utmost importance in controlling the AMT degradtion rate. At fixed concentration of TiO_2 and consequently constant total sites available for adsorption, the degradation efficiency tends to decrease with further increase (beyond 100 mgL^{-1}) in the initial concentration of AMT.

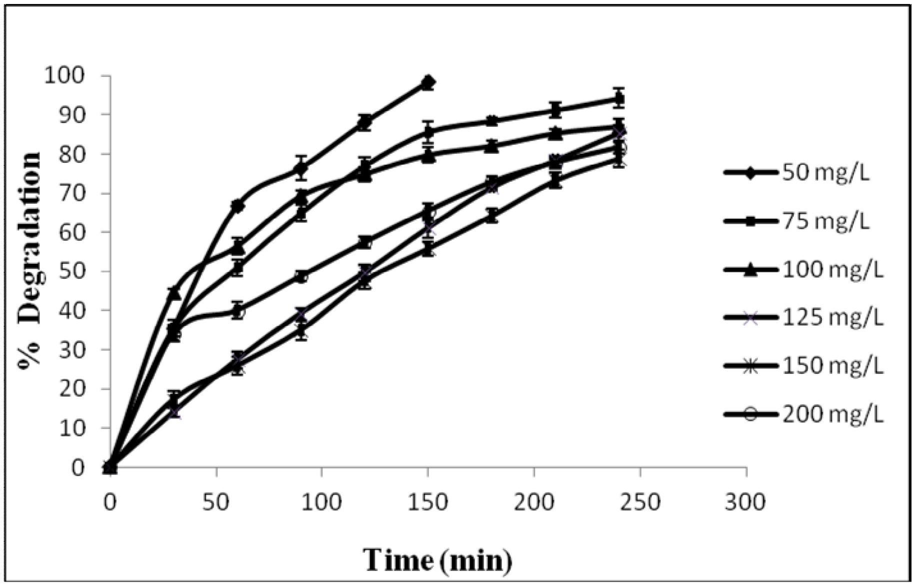


Figure 5.10: Effect of substrate concentration at photo-catalytic degradation of AMT (TiO_2=0.5 gL^{-1}, pH=5.8, H_2O_2=0.12 gL^{-1}, V = 200 mL).

5.3. Catalyst immobilization studies

Due to prolonged exposure and free contact of TiO_2 suspensions with solar radiation in a photo-reactor, slurry mode photo-catalysis yields better efficiency then the immobilized TiO_2 catalyst. However, it is rather difficult to separate and reuse this catalyst powder from treated water which often limits its practical applications. Use of immobilized TiO_2 as photocatalyst decreases the efficiency of the process as compared to slurry mode photocatalysis due to less contact of catalyst with the organic pollutants. Moreover flow velocity also influences the rate of reaction; it should not be too high or too low. Although reaction time increases for the same extent of degradation as in shallow pond slurry type reactor but it has no limitation like separation of the catalyst from the effluent with the help of filtration or any other method. This makes the process inexpensive and therefore increases the possibility of field scale applications. However, several studies have been reported quoting the significant loss in the contact area between the immobilized photocatalyst and the light source which limits its efficiency in the photocatalytic degradation of the organic substrates **(Subrahmanyam et al., 2008)**.

5.3.1. Degradation studies with catalyst coated cemented beads and entrapped sodium alginate balls

Experiments were conducted using TiO_2 immobilized cement beads as well as TiO_2 entrapped alginate balls for the degradation of AMT under solar radiation under all the optimum conditions achieved in shallow slurry pond reactor. As reported by **Ghanem et al., 2009**, various studies have been cited in the literature where cement bed has been used for catalyst fixing in degradation of pollutants. However, the degradation rate of AMT using TiO_2 immobilized cement beads has not been reported yet. Blank experiments with uncoated cement beads had little effect on AMT degradation as there was less than 10% degradation. Whereas, coated cement beads gave 69% degradation after 6 hours of irradiation in sunlight under optimized conditions as shown in Figure 5.11. These results were compared with the degradation rate of AMT by TiO_2 entrapped sodium alginate balls which physically entrap the catalyst in the gel. Blank alginate balls could not degrade the compound even at optimized conditions. The experiment was performed using sodium alginate balls in shallow slurry pond type reactor under sunlight with all the optimum conditions. After the irradiation of 6 hours only 52 % degradation could be achieved in case of catalyst entrapped alginate balls (figure 5.11).To the best of our knowledge, AMT degradation studies by this method have not been reported yet. As, alginate balls were not robust enough to withstand the process conditions, thus for further studies on solar parabolic trough collector, catalyst immobilized cement beads were used.

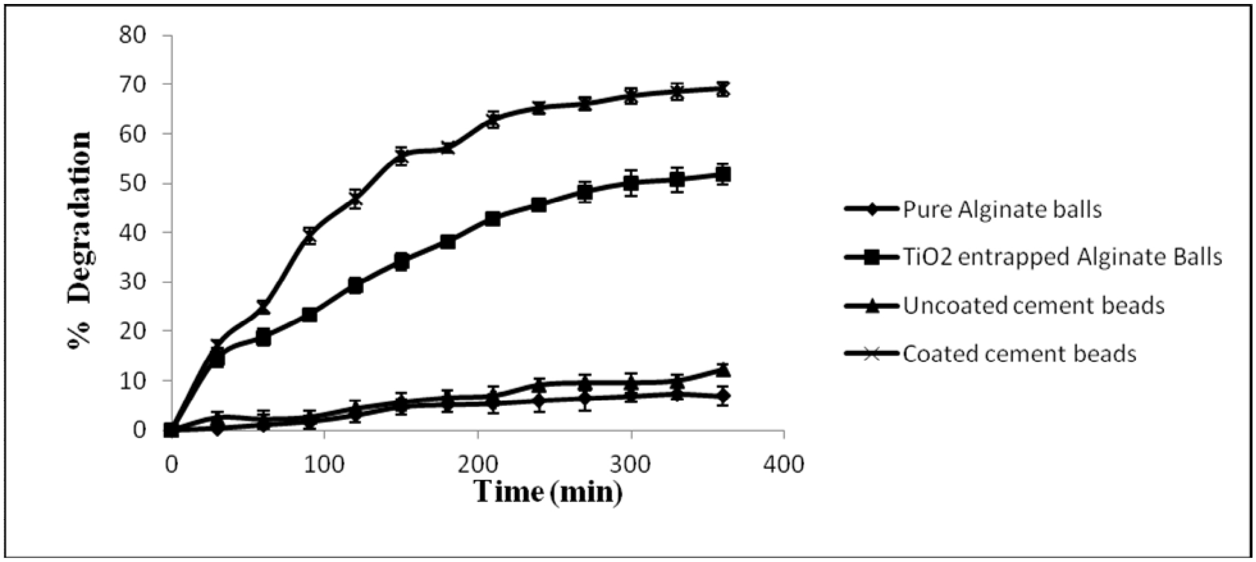


Figure 5.11: Comparative photocatalytic degradation studies of AMT solution using TiO_2 entrapped alginate balls and TiO_2 immobilized cement beads AMT (C_0=100 mgL^{-1}, pH=5.8, H_2O_2=0.12 gL^{-1}, V = 200 mL)

5.4. Solar parabolic collector

The parabolic trough concentrator (PTC) was designed by Ecosense Sustainable Solutions Private Limited, India. PTC was used for the degradation of AMT by using immobilized TiO_2 catalyst under concentrated sunlight. The receiver tube was packed with 100 immobilized TiO_2 cement balls and AMT solution with optimum amount of H_2O_2 was made to pass through the continuous circulation system. The temperature range was found to be between 50 and 100^0C depending upon position of collector and time of the day. Although the temperature increases by decreasing the diameter of the receiver tube as decrease in diameter reduces the surface area which results in energy losses **(Reddy and Ravikumar, 2012)**.

The receiver diameter was kept 2.54 cm to get required temperature and a relatively large area. **(Sano et al., 2004)**. All experimental days were not clear, clouds sometimes reduced sunlight, hence the UV irradiance and the temperature of receiver were constantly changing. Between 10 a.m. and 2 p.m., the UV irradiance was in the range of 35-50 Wm^{-2}, and the sunlight receiver maintained the temperatures above around 150 ^{0}C. AMT degradation studies were conducted with immobilized TiO_2 beads in PTC. The retention time of AMT solution was found to be 90 s. The AMT degradation observed was 30% and 92 % after 4 h under concentrated solar irradiation without TiO_2 and with immobilized TiO_2 respectively (Figure 5.13).

Figure 5.12: Representation of Solar Parabolic Collector at the angle of inclination of (a) -40^0 (b) 0^0 (c) 20^0 (d) 40^0 respectively.

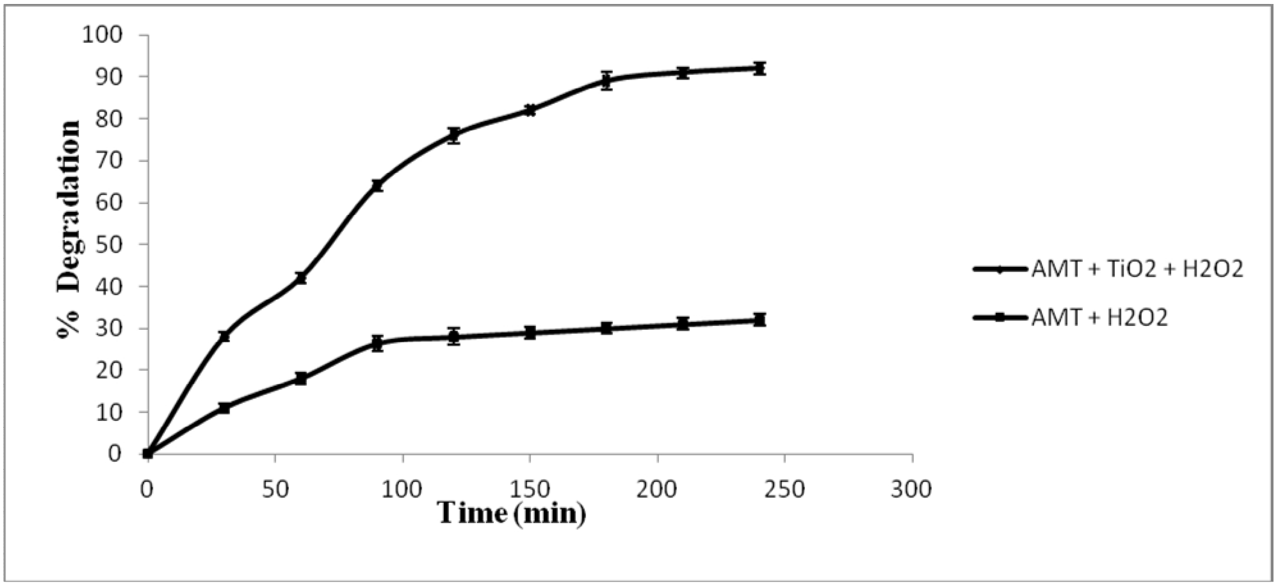


Figure 5.13: Photocatalytic degradation studies of AMT solution with and without catalyst using PTC (C_0=100 mg L^{-1}, pH=5.8, H_2O_2=0.12 gL^{-1})

5.4.1. Flow rate variation

PTC was operated at three different flow rates i.e. 0.05 $Lmin^{-1}$, 0.1 $Lmin^{-1}$ and 0.2 $Lmin^{-1}$ to determine the effect of flow rate on the degradation of AMT. 71, 92 and 79 % degradation rates were observed after photocatalytic treatment at the flow rates of 0.05 $Lmin^{-1}$, 0.1 $Lmin^{-1}$ and 0.2 $Lmin^{-1}$ respectively (figure 5.14). Better circulation rates yield more degradation but as the flow was increased beyond 0.1 $Lmin^{-1}$ the degradation rate decreased due to low residence time under turbulent conditions. Thus, residence time play an important role in determining the efficacy of the process.

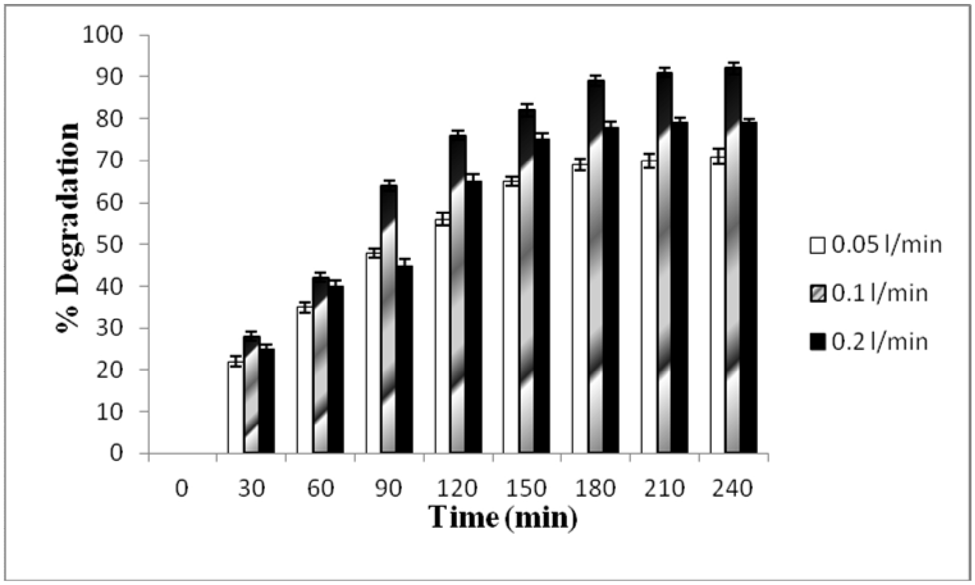


Figure 5.14: Flow rate variations for photocatalytic degradation studies of AMT solution using PTC (C_0=100 mg L^{-1}, pH=5.8, H_2O_2= 0.12 gL^{-1}).

5.5. Durability studies

The main implication in the studies and applications in immobilized catalysis is durability of the supported catalyst. The catalyst stability on the support is very important parameter for deciding the subsequent degradation cycles. In our study, the catalyst was recycled up to 4 cycles and catalytic efficiency was determined after each cycle (figure 5.15). The morphology of recycled catalyst was studied using UV-solid spectra and XRD technique. From XRD images and solid spectra analysis (figure 5.16 &5.17), it is clear that catalyst is intact even after fourth recycle confirming its stability. The reduction in efficiency of catalyst might be due to accumulation of intermediates formed during oxidation, surface deposition and loss of active phase leaching **(Verma et al., 2014b)**.

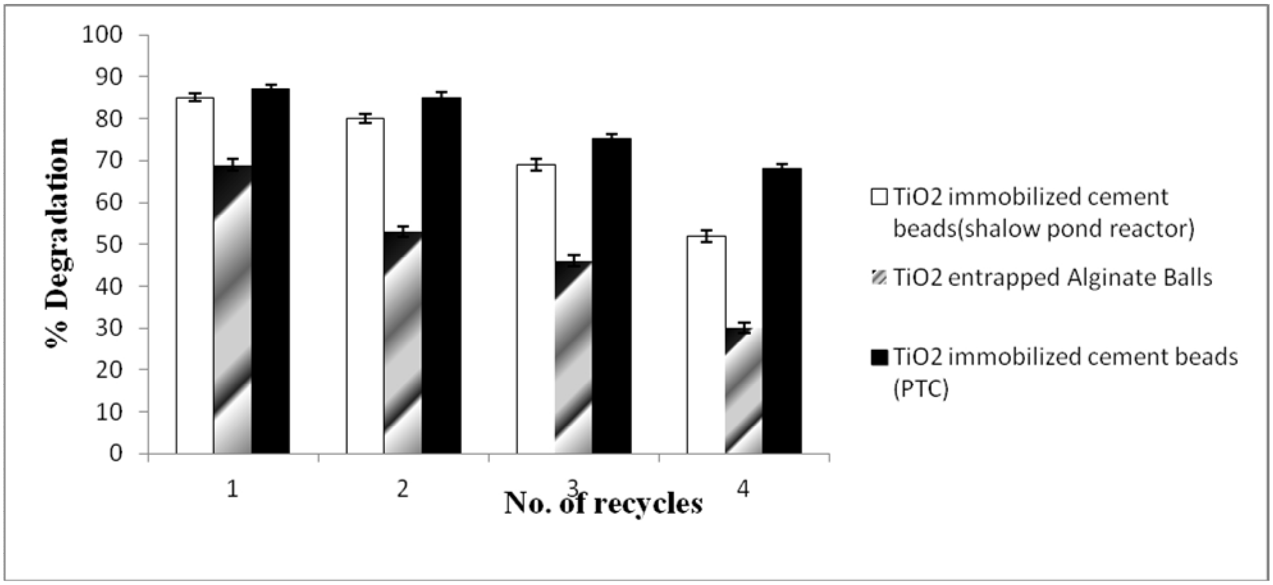


Figure 5.15: Durability studies of catalyst entrapped sodium alginate balls and immobilized TiO_2 cement beads in (i) shallow pond slurry reactor (ii) PTC at optimized conditions (C_0=100 mg L^{-1}, pH=5.8, H_2O_2=0.12 gL^{-1}, V = 200 mL).

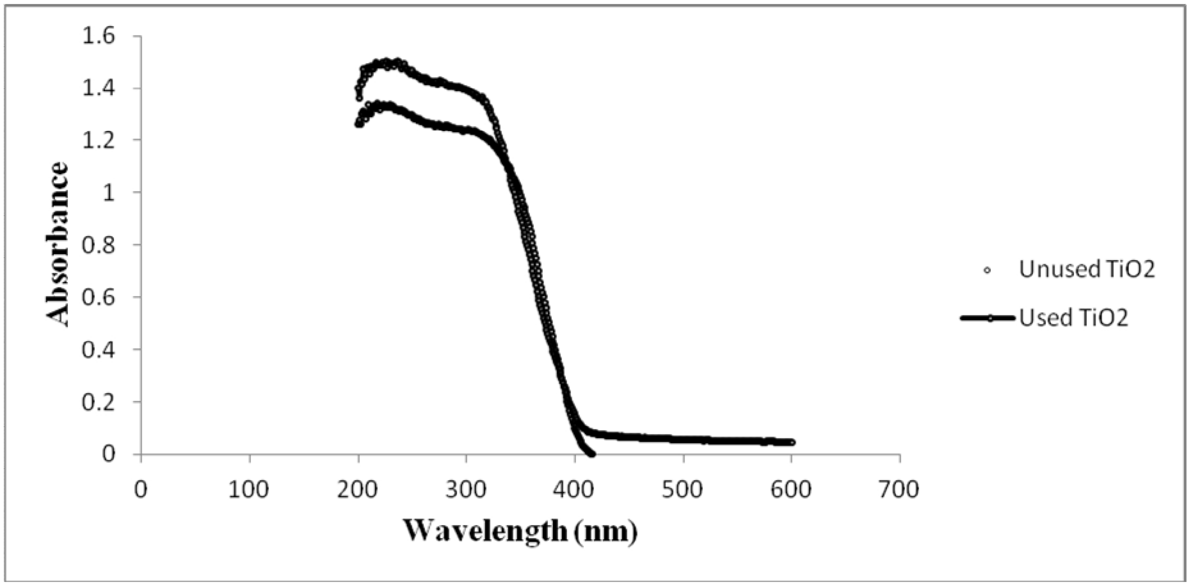


Figure 5.16: Solid spectra characterization of unused and used TiO_2.

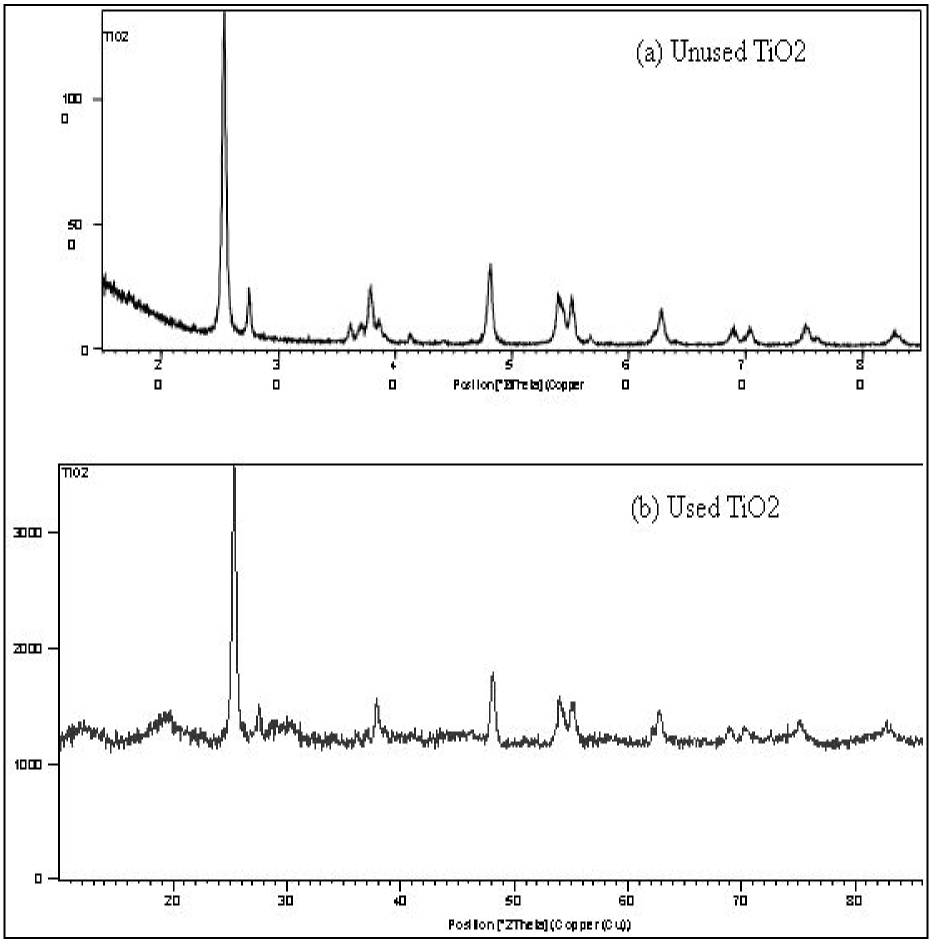


Figure 5.17: XRD pattern of (a) used TiO$_2$ (b) unused TiO$_2$.

5.6. Mineralization studies

To evaluate mineralization of the compound by photocatalysis, formation of CO$_2$ along with generation of anions and cations are preferred indicators **(Verma et al., 2014a)**. In this study, TOC and COD reduction along with formation of NH$_4^+$ ions was determined for confirming the degradation of AMT. TOC and COD reduction was observed to be 83 % and 86 % after 4 h of photocatalytic treatment (Figure 5.18). Increase in concentration of NH$_4^+$ions (69 %) in the first hour and 75% subsequently confirmed the mineralization of AMT.

For the confirmation of intermediates, the LC-MS analysis of the treated sample was performed. Analysis confirmed the formation of various intermediates, which subsequently degraded during photocatalytic treatment of AMT.

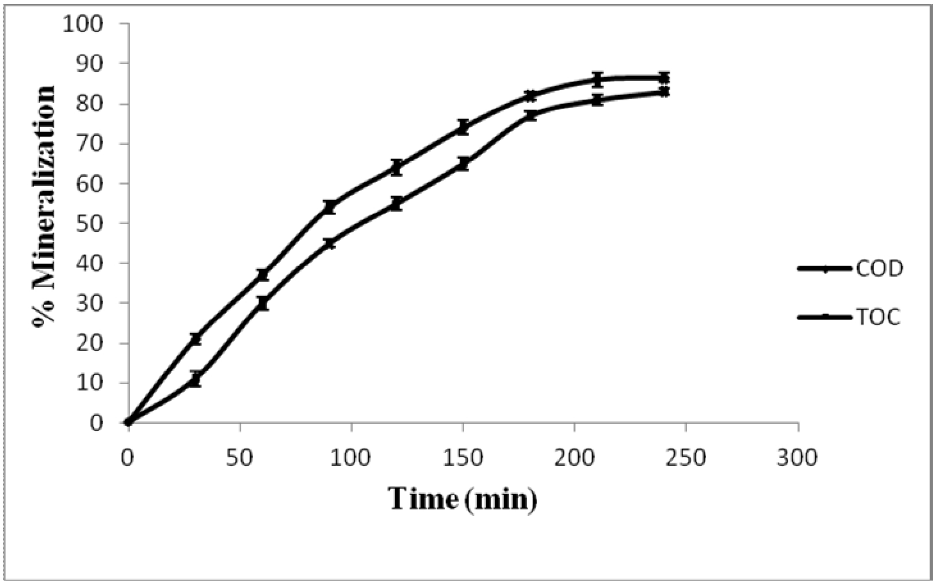


Figure 5.18: Mineralization studies of AMT at optimized conditions (C_0=100 mg L^{-1}, pH=5.8, H_2O_2=0.12 gL^{-1}, V = 200 mL).

6. CONCLUSIONS

- Photocatalytic degradation of AMT has been studied using TiO_2 as a catalyst in suspension as well as immobilized form in sunlight. TiO_2 was immobilized on cement beads and was also entrapped in alginate balls
- Degradation observed was 87%, 69%, 52% and 92% under shallow pond slurry reactor, coated cemented beads, immobilized sodium alginate ball and parabolic trough collector; respectively at optimized conditions i.e. 5.8 pH, TiO_2 0.5 gL^{-1} and H_2O_2 of 0.12 gL^{-1}.
- A/V ratio, initial concentration of AMT as well as flow rate plays an important role in the degradation process of AMT. The COD reduction (86%) and TOC reduction (83%) along with ammonium ion generation confirmed the mineralization of the AMT. Durability studies of each supporting material confirmed that the structure of TiO_2 was intact even after 4 recycles (analyzed through XRD and solid spectra).
- Parabolic trough collector has been proved as a promising technique for the degradation of bio recalcitrant compounds. To the best of our knowledge, PTC along with immobilized catalyst has not been used for the degradation of AMT so far.
- Although best efforts have been made to treat the compound at lab scale as well as pilot scale, lot of modification have to be done for making the process economically successful and viable. Parameters like retention time, durability studies for longer time, best supporting material are the concerns needed to be addressed carefully for commercial applications of the treatment process.

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1. Dixit D., Verma, A. (2014). Slurry and fixed bed photocatalysis for the degradation of Amoxicillin Trihydrate (AMT) using solar irradiations. Water Research (Communicated).
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