FENTON AND PHOTO-FENTON OXIDATION OF SELECTED PHARMACEUTICAL COMPOUNDS IN WATER

Thesis

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

By

MAHAMOOD

DEPARTMENT OF CIVIL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY KARNATAKA,

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May, 2013

D E C L A R A T I O N

by the Ph.D. Research Scholar

I hereby *declare* that the Research Thesis entitled **"Fenton and Photo-Fenton Oxidation of Selected Pharmaceutical Compounds in Water"** Which is being submitted to the **National Institute of Technology Karnataka, Surathkal** in partial fulfillment of the requirements for the award of the Degree of **Doctor of Philosophy** in **Civil Engineering** is a *bonafide report of the research work carried out by me*. The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

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C E R T I F I C A T E

This is to *certify* that the Research Thesis entitled **"Fenton and Photo-Fenton Oxidation of Selected Pharmaceutical Compounds in Water"** submitted by **Mahamood** (Register Number: **090682CV09F02**) as the record of the research work carried out by *him, is accepted as the Research Thesis submission* in partial fulfillment of the requirements for the award of degree of **Doctor of Philosophy**.

Dr. B. Manu
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Prof. Katta Venkataramana
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Dedicated

To my affectionate wife M. Riazunnisa and my beloved teachers ...

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ABSTRACT

In the present study, the degradation of three selected pharmaceuticals viz. paracetamol (PCM), amoxicillin (AMX) and diclofenac (DCF) is carried out using Fenton and UVC assisted photo-Fenton oxidation processes in batch mode at ambient temperature (27 ± 3^{o} C). In addition to Fe^{2+}, iron extracted from laterite soil (Fe (LS)) is also studied as an alternate catalyst in Fenton reagent. The experimental conditions like pH, $[H_2O_2]_0$, $[Fe^{2+}]_0$, $[Fe\ (LS)]_0$, are optimized by Fenton process for the initial concentration of 0.066 mM for PCM, 0.027 mM for AMX and 0.031 mM for DCF. For the optimization of the initial experimental conditions, drug degradation and chemical oxygen demand (COD) removal are measured as the objective parameters. The optimum pH for the degradation of PCM and AMX is 3.0 but for DCF and mixture of the drugs it is 3.5. The H_2O_2 is varied in the range 0 to 2.94 mM, Fe^{2+} is varied from 0 to 0.036 mM and Fe (LS) is varied from 0.004 to 0.036 mM for their optimization in Fenton oxidation. The optimum molar ratio of $[H_2O_2]_0$: $[Fe^{2+}]_0$ is observed to be 98.55 : 1 for PCM, 98.55 : 1 for AMX and 57.49 : 1 for DCF. However, the $[H_2O_2]_0$: $[Fe\ (LS)]_0$ molar ratios are observed as 65.70 : 1 for PCM, 76.65 : 1 for AMX and 76.65 : 1 for DCF. Then, the Fenton and photo-Fenton oxidations are carried out at the optimal conditions for the initial drug concentration in the range of 0.066 – 0.331 mM for PCM, 0.027 – 0.137 mM for AMX and 0.031 – 0.157 mM for DCF.

The degradation of PCM and AMX is 100 % but the degradation of the DCF is only 79.29 % with Fe^{2+} and 74.29 % with Fe (LS) in Fenton oxidation for 240 min of reaction time. However, in 120 minutes UV irradiation time, the photo – Fenton oxidation has demonstrated 100 % degradation of PCM and AMX for both the catalysts but DCF degradation is 98.57 % (with Fe^{2+}) and 85.71 % (with Fe (LS)). It is also observed that the degradation and mineralization is more with Fe^{2+} than Fe (LS) for both PCM and DCF; but it is more with Fe (LS) than Fe^{2+} for AMX. In Fenton oxidation of mixture of drugs using Fe^{2+}, the percent drug degradation is 68.55 (PCM), 70.77 (AMX), 62.56 (DCF) and percent COD removal is 64.80 in 240 min. Similarly, when Fe (LS) is used in Fenton oxidation, the percent drug degradation is 57.22 (PCM), 76.71 (AMX), 55.75 (DCF) and percent COD removal is 60.00 in 240 min. However, in photo-Fenton oxidation of mixture of drugs using Fe^{2+}, the percent drug degradation is 70.01 (PCM), 75.70 (AMX), 64.79 (DCF) and percent COD removal is 74.40 in 120 min. On the other hand, using Fe (LS), the percent drug degradation is 59.98 (PCM), 77.87 (AMX), 59.29 (DCF) and percent COD removal is 58.40 in 120 min. The value of the pseudo second-order rate constants for DCF > PCM > AMX when they are treated individually. The complete degradation of model drugs is observed with Fe^{2+} as well as Fe (LS) as catalysts in both the *AOPs*. Therefore, Fe (LS) may be effectively used as an alternate catalyst in Fenton's reagent to degrade the selected drugs in water. The operating cost for the treatment of drugs in mixture is less by about 49 % with Fe^{2+} and 40 % with Fe (LS) in Fenton process and about 59 % with Fe^{2+} and 57 % with Fe (LS) in photo-Fenton process when compared to the costs for the treatment of the drugs individually. Furthermore, Fenton and photo-Fenton oxidation using Fe (LS) as catalyst appears to be a very promising technology for the oxidation of PCM, AMX and DCF in aqueous solutions.

Keywords: AOPs; COD removal; degradation of pharmaceuticals; Fenton oxidation; Laterite soil; UVC assisted photo-Fenton oxidation

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NOMENCLATURE

$R^{\bullet}$	Organic Radical
$[AMX]_0$	Initial concentration of amoxicillin
$[DCF]_0$	Initial concentration of diclofenac
$[Drug]_0$	Initial Drug concentration
$[Fe\ (LS)]_0$	Initial concentration of Iron extracted from laterite soil
$[Fe^{2+}]_0$	Initial concentration of Ferrous ion
$[H_2O_2]_0$	Initial concentration of Hydrogen Peroxide
$[PCM]_0$	Initial concentration of paracetamol
µg	Micro gram
AC	Activated Carbon
AMX	Amoxicillin
AOPs	Advanced Oxidation Processes
API	Active Pharmaceutical Ingredient
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DCF	Diclofenac
DOC	Dissolved Organic Content
EDR	Electro Dialysis Reversal
EPA	Environmental Protection Agency
EROD	Ethyoxyresorufin O-deethylase
Fe (LS)	Iron extracted from laterite soil
Fe^{2+}	Ferrus ion
Fe^{3+}	Ferric ion
FO	Fenton Oxidation
GAC	Granular Activated Carbon
H_2O_2	Hydrogen Peroxide
K_{ow}	Octanol–water partition coefficient
MBR	Membrane Bio-Reactor
MF	Microfiltration
mM	milli molar concentration

MSW	Municipal Solid Waste
NF	Nanofiltration
ng	Nano gram
NSAID	Non - Steroidal Anti - Inflammatory Drug
PAC	Powdered Activated Carbon
PCM	Paracetamol
PFO	Photo-Fenton Oxidation
PhACs	Pharmaceutically Active Compounds
PPCPs	Pharmaceuticals and Personal Care Products
RO	Reverse Osmosis
R-X or RH	Organic compound or substance
STP	Sewage Treatment Plant
UF	Ultra filtration
Us	Ultra Sound
UV	Ultra Violet radiation
UV-C	Ultra Violet radiation – C band
WTW	Wastewater Treatment Works
WWTP	Waste Water Treatment Plant
λ_{max}	Characteristic wavelength of drug at maximum light absorbance

CHAPTER 1

I N T R O D U C T I O N

Chapter 1

INTRODUCTION

1.1. Background and Motivation

The galloping population, ever increasing industrialization, rapid urbanization and the struggle for the better existence and living standards have increased the stress on the limited water supplies. Consequently the use and reuse / recycle of water have become inevitable. Day after day, millions of tons of untreated sewage and industrial and agricultural wastes are introduced into the water systems and pure water has become scarce. In addition, there has been a rise in the use of various kinds of agrochemicals like pesticides, industrial chemicals, pharmaceuticals, fragrances, cosmetics, sunscreens, and dietary supplements. The pharmaceuticals are a class of emerging environmental chemical pollutants widely used in both the human and veterinary medicine; these are produced in large amounts throughout the world and the quantities of many are on par with agrochemicals. The wide use of new pharmaceuticals, with distinct modes of biochemical action, has been adding to the large array of chemical classes already present. Further the mode of action of many of these new pharmaceuticals has not been fully understood. Most of the products are disposed into the environment on a continual basis via domestic and industrial sewage systems. It is evident from the literature that many of these pharmaceutical compounds and their metabolites are ubiquitous and display persistence (Daughton and Ternes 1999).

The presence of the pharmaceutical compounds is observed in surface water (Daughton and Ternes 1999; Kolpin et al. 2002; Erickson 2002; Pedersen et al. 2005; Jasim et al. 2006; Bester et al. 2007; Vieno et al. 2007), ground water, sewage effluents (Morse and Jackson 2004, Ternes et al. 2004; Khanal et al. 2006; Zhou et al. 2009), drinking water (Westerhoff et al. 2005; Zwiener 2007), and also in solid waste (Musson and Townsend 2009). The drug concentrations detected in the environment were generally in the ng/L to µg/L range (Daughton and Ternes 1999; Kolpin et al.

2002). However, pharmaceuticals retain their chemical structure long enough to do their therapeutic work and remain in the environment for a long time; this is considered dangerous both at low and high concentrations (Klavarioti et al. 2009). Consequently, the presence of these pharmaceuticals may have adverse effects on aquatic life and the human. Different types of organisms have varying level of sensitivity and are affected differently, depending on the class of pharmaceutical and its modes of action etc., (Eissen and Backhaus 2011). It is also reported in the literature that there is effect of toxicity on the aquatic life and the effect of toxicity on human is still unknown (Daughton and Ternes 1999; Musson and Townsend 2009). The effects like feminization in fish, inhibition of growth in microbes and plants, toxicity and endocrine disruption in fish were reported (Boxall 2004; Bolong et al. 2009). Low concentrations of pharmaceuticals in water may not pose much risk to adult humans, but fetuses, infants or children and other organisms may be affected. Children may have an eight fold greater risk of adverse effects of pharmaceutical exposure (Collier 2007). As the pharmaceuticals are bioactive and also when they have been continuously introduced into the environment, they would certainly affect the man and the ecosystems; hence there should be some regulations for these compounds to discharge into environment.

There are currently, no statutory maximum contaminant levels for pharmaceutical compounds in drinking water and no regulatory requirement to monitor them (Zwiener 2007). The U.S. Environmental Protection Agency (EPA) is assigned with regulating the chemicals that negatively affect human and the ecosystems, but pharmaceuticals are not included in its regulatory scheme. In spite of years of stimulation by environmental scientists, the EPA has evinced very little interest to the dangers posed by widespread pharmaceutical contamination (Adams 2010). However, the European Union (EU) has a tendency to use more precaution than United States with regard to environmental risk assessment. In 2001, the European Agency for the Evaluation of Medicinal Products proposes that an environmental risk assessment be required for human use medicinal products if the predicted concentration in surface water is grater than 0.01 μg / L but in U.S., environmental risk assessments are

required for new human use drugs if the predicted concentration at the point of entry into the aquatic environment is greater than or equal to 1 μg / L (Erickson 2002).

The silence of unclearness of the toxicity of the pharmaceutical compounds in low concentration may lead to the irrecoverable damage. Hence, as a precautionary measure, considering the potential adverse effects of pharmaceuticals, they should be removed from the aqueous solutions. The conventional biological treatment methods are economical but not efficient in removing the pharmaceutical compounds. The physical methods are uneconomical and may not remove the pharmaceutical pollutants completely. A number of chemical treatment techniques have emerged in the last few decades to degrade non-biodegradable organic pollutants. Among these treatment techniques, the advanced oxidation processes (AOPs) appear to be promising and have proved capable of completely degrading the pharmaceuticals from aqueous solutions (Klavarioti et al. 2009). These processes are based on the generation of hydroxyl radical ($OH^{\bullet}$), which is a more powerful oxidant (E^o 2.8V) than the other chemical oxidants like ozone (E^o 2.0V) or H_2O_2 (E^o 1.8V) (Zazo et al., 2005).

Among AOPs, Fenton and photo-Fenton oxidation processes have emerged as the most promising methods for effective degradation of organic non-biodegradable pollutants. In a comprehensive review, Neyens and Baeyens (2003) have indicated that the Fenton's oxidation is very effective in the removal of many hazardous organic pollutants from water and wastewaters. Fenton oxidation process is cost effective, clean, easy to operate, can degrade and mineralize most of the organic compounds, has more pharmaceutical removal efficiencies. Photo-Fenton oxidation is most economical; degradation of organics is very fast, complete removal of organic is possible within minutes. The photo-Fenton reaction involves irradiation with solar or UV light which significantly increases the rate of contaminant degradation by photo reduction of Fe^{3+} to Fe^{2+}. Fenton's reaction generates hydroxyl radicals and photo-Fenton reactions reduce the Fe^{3+} to Fe^{2+}, thus leading to production of additional OH radicals and continuous regeneration of Fe^{2+} in a catalytic way (Sun and Pignatello 1993). It is also observed that the additional amounts of OH radicals are also produced from the direct photolysis of H_2O_2 (Laat et al. 1999).

The ultraviolet “C”-band (UVC) is highly energetic form of radiation that can cause separation or degradation of bonds in many of the organic molecules (Legrini et al., 1993). Any organic pollutant is able to undergo a direct photolysis if its absorbance spectrum overlaps the spectral range of the available radiation (Rizzo et al. 2009). But the effectiveness of direct photolysis due to UVA and UVB may be less than UVC. The efficacy of Fenton and photo-Fenton process may also depend up on the type of catalyst used in Fenton reagent. The catalyst like Fe^{2+} has been extensively used in Fenton reagent for several years. But, the use of iron extracted from laterite soil, hereby referred to as Fe (LS), as catalyst in Fenton reagent has not yet been reported. The Fe (LS) is eco-friendly when compared to Fe^{2+} and is naturally available in most of the land area between the tropics of Cancer and Capricorn. In India, laterite soil is spread in the western coastal region, the edge of the plateau in the east, covering parts of Karnataka, Tamil Nadu and Orissa and a small part of Chota Nagpur Plateau in the north and Meghalaya in north-east. The laterite soil contains 16 - 67 % of the ferric oxide and is easily available.

Thus, the Fenton and photo-Fenton treatment processes seems to be appropriate technologies for the treatment of pharmaceuticals. Paracetamol (PCM), amoxicillin (AMX) and diclofenac (DCF) are selected as model pharmaceutical compounds for the present study as they are being produced in large quantities all over the world. Tones of these chemicals are used and consumed every year, so their traces are frequently found in environment, further the ecological effects due to its presence are examined and reported. Hence, the present study focuses on oxidation of selected pharmaceutical compounds viz. PCM, AMX and DCF by Fenton and photo-Fenton processes. The evaluation of Fe (LS) as alternate catalyst in Fenton reagent is worthwhile effort for the treatment of these selected pharmaceuticals.

1.2. Objectives of the Present Research

The main objective of this study is to evaluate Fenton and Photo-Fenton oxidation processes for possible degradation and mineralization of the model pharmaceutical compounds selected for the study.

The scope of this study includes:

The evaluation of the effect of

- pH for the drug degradation at a particular initial concentration of Fe^{2+}, H_2O_2, and drug concentration
- $[Fe^{2+}]_0$ and $[H_2O_2]_0$ on the drug degradation at the optimum pH and for a particular drug concentration by varying $[Fe^{2+}]_0$, $[H_2O_2]_0$ simultaneously.
- $[Fe\ (LS)]_0$ and $[H_2O_2]_0$ on the drug degradation at the optimum pH and for a particular drug concentration by varying $[Fe\ (LS)]_0$, $[H_2O_2]_0$ simultaneously.
- Kinetic studies on drug degradation at the optimum ratios of $[Drug]_0$ / $[H_2O_2]_0$, $[Fe^{2+}]_0$ / $[H_2O_2]_0$, $[Fe\ (LS)]_0$ / $[H_2O_2]_0$ by varying initial concentration of drug and determination of kinetic rate constants for the drug degradation
- pH for the drug mineralization at a particular initial concentration of Fe^{2+}, H_2O_2, and concentration each drug in equal weight proportions in the mixture of PCM, AMX and DCF
- $[Fe^{2+}]_0$ and $[H_2O_2]_0$ on the drug mineralization at the optimum pH and for a particular drug concentration in mixture of drugs by varying $[Fe^{2+}]_0$, $[H_2O_2]_0$ simultaneously.
- $[Fe\ (LS)]_0$ and $[H_2O_2]_0$ on the drug mineralization at the optimum pH and for a particular drug concentration in mixture of drugs by varying $[Fe\ (LS)]_0$, $[H_2O_2]_0$ simultaneously.
- Initial concentration on drug mineralization when PCM, AMX and DCF are in the mixture.

1.3. Organization of the thesis

The thesis is presented in five chapters. **Chapter 1** briefly describes the topic and states the objectives of the present research work. **Chapter 2** examines the current literature on the subject of pharmaceutical compounds, their occurrence, effects and presents an overview of the treatment technologies available. A summary of literature review is provided. **Chapter 3** describes the materials used**,** experimental procedures adopted and analytical techniques applied in the present study. **Chapter 4** furnishes the results obtained during this study. **Chapter 5** briefly summarizes the research work and presents the conclusions. **Appendix I** provides the procedure for simultaneous determination of paracetamol, amoxicillin and diclofenac in water using double beam UV – VIS spectrophotometer. **Appendix II** briefly explains about the operating costs for the treatment of paracetamol, amoxicillin, diclofenac and the mixture of the drugs by Fenton and photo-Fenton processes. The Appendix II is followed by **references, list of publications** based on the present study and a brief **curriculum vitae** of the researcher.

CHAPTER 2

L I T E R A T U R E R E V I E W

Chapter 2

LITERATURE REVIEW

This chapter presents an overview on pharmaceutical compounds, the pharmaceutical industry in India, sources, occurrence, and fate of the drugs in environment, detrimental effects of disposal of unused / unwanted pharmaceutical compounds by the human and treated and untreated pharmaceutical wastewater on aquatic life and the human. Finally an overview of some of the promising treatment technologies for the removal of pharmaceutical compounds- especially advanced oxidation processes (AOPs) for the treatment of water and wastewater containing pharmaceutical active compounds (PhACs) with the emphasis on Fenton and photo-Fenton oxidation processes is presented.

Pharmaceutical and personal care products (PPCPs) are the chemicals used for the humans, domestic animals, or agricultural crops that treat disease; alter or improve physiological, cosmetic or emotional function, appearance or status; prevent disease; help in the diagnosis or monitoring of health or disease; or serve to formulate the active ingredient into a commercial product (Daughton 2007). PPCPs can be broadly classified into (1) *Pharmaceutical compounds;* both human and veterinary *(2) Protective Care Products* include cosmetics, fragrances, soaps, detergents, insect repellants, sun-screen agents, skin anti-aging preparations, and disinfectants. (3) *Nutriceuticals* are bioactive chemicals contained in nutritional supplements (Motzer 2006). Pharmaceuticals are biologically active and they are purposefully designed to have a biological effect at therapeutic concentrations (Pontius 2002). Pollution from pharmaceutical compounds is a widespread and under-regulated source of environmental contamination (Cuevas 2011).

The pharmaceutical industry in India plays a vital role in Indian economy and is estimated to be worth $ 4.5 billion, growing at about 8 to 9 percent annually. Indian pharma industry is ranked 3rd in production and 14th in terms of value in the world. Indian pharmaceutical industry meets 70 % of the country's demand for bulk drugs,

drug intermediates, pharmaceutical formulations, chemicals, tablets, capsules, orals and vaccines. There are 250 large and about 8000 small scale pharmaceutical units in India. The Indian pharmaceuticals market is expected to reach $ 55 billion in 2020 from $ 12.6 billion in 2009 and it has potential to reach $ 70 billion by 2020 in an aggressive manner (http://www.cci.in/pdf/surveys_reports/indian-pharmaceuticals-industry.pdf). With the current scenario of pharmaceutical industry in India, it is evident that the increasing amounts of liquid and solid wastes that contain pharmaceuticals are entering in to aquatic environment.

2.1. Sources, Occurrence and Fate of PPCPs in the Environment

Partially metabolized human and veterinary pharmaceuticals in urine and feces, underground leakage of septic systems, manufacturing and research facilities, pharmacies, physicians, humanitarian drug surplus, unused or expired PPCPs, landfill leachate, aquaculture, agriculture, and pest control also convey PPCPs to the environment (Daughton 2007). The PPCPs have been continually discharged as a complex mixture to the aquatic environment through various paths but primarily by both untreated and treated domestic and industrial sewage (Daughton and Ternes 1999). However, the release of drugs into the environment is a function of the quantity of drugs manufactured, the dosage frequency and amount, the excretion efficiency of the parent compound and metabolites, tendency of the drug to sorb to solids, and the metabolic transformation capability of subsequent sewage treatment (Daughton and Ternes 1999). Many of the studies have showed that both pharmaceuticals and their active metabolites neither efficiently removed by wastewater treatment nor biodegraded; and thus, the unchanged compounds are often discharged from sewage treatment plants into receiving waters (Herberer 2002; Halling-Sørensen et al. 1998; Daughton and Ternes 1999, Zwiener 2007). Many of the pharmaceuticals are found to be present in wastewater influent, effluent, sludge solid phase and sludge liquid phase in West Texas (Karnjanapiboonwong et al. 2011). The Fig. 2.1 presents an overview of the pathways by which pharmaceutical compounds enter the environment.

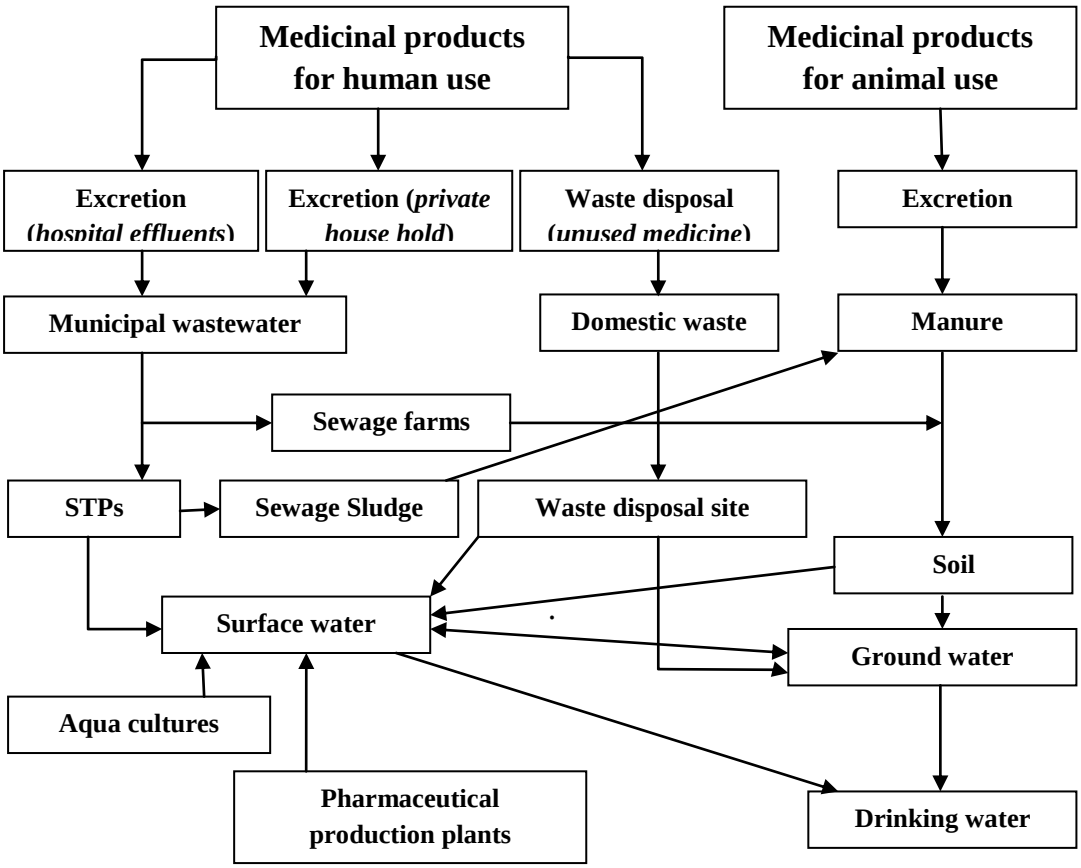


Fig. 2.1 Overview of the pathways by which the pharmaceutical compounds enter the environment

The U.S. Geological Survey (USGS) studied in 139 U.S. streams for 95 contaminants from industrial, human, and agricultural wastewater sources during 1999-2000 and noticed one or more compounds in 80 percent of the streams with more than 10 chemicals in one-third of the streams (Erickson 2002). Ternes et al. (2004) reported that 32 pharmaceuticals, 4 hormones, 5 metabolites and 5 biocides were detected in the WWTP outflows in Germany during 1996-1998. In another study, 41 kinds of pharmaceuticals including 12 antibiotics and 10 analgesics were detected in the secondary effluent of WWTP in Japan (Kim et al. 2009). An investigation of water supply systems found the occurrence of 26 PhACs; seven of which were present in drinking water, 16 in groundwater and post-treatment effluent, and three PhACs were observed in both (Collier 2007). Thus, PhACs travel from administration to excretion,

entering municipal sewage treatment plants, then surface and groundwater recharge, and returning back to humans via drinking water.

The widely used paracetamol (acetaminophen) has been identified as one of the most frequently detected pharmaceutical compounds in the survey of 139 streams in the U.S. by the USGS (Kolpin et al. 2002). In their assessment, acetaminophen is detected in as many as 24% of the samples with a median concentration of 0.11 µg/L, but concentration as high as 10 µg/L is also reported (Kolpin et al. 2002). Also, paracetamol is found to be present in STP effluents up to a concentration of 6 µg/L (Ternes 1998) and more than 65 µg/L in the Tyne River, UK (Roberts and Thomas 2006). Hartmann and co-workers measured 2-83 µg/L of ciprofloxacin in the effluent of a large Swiss hospital (Hartmann et al., 1998). Concentrations measured for beta-lactams in hospital effluents are 20-80 µg/L in hospital effluents (Kummerer, 2001). Andreozzi et al., (2004) reported presence of amoxicillin in Italian WWTP effluents at concentrations up to 0.12 µg/L. In the UK, amoxicillin is detected in aquatic environment up to 245 ng/L concentration (Kasprzyk-Horden et al., 2007). In Australia, Watkinson et al. (2007) detected amoxicillin concentration up to 0.28 µg/L in WWTP effluents. Though it has been proven that diclofenac is rapidly degraded by direct photolysis under normal environmental conditions (Buser et al. 1998; Tixier et al. 2003; Aguera et al. 2005), it is still one of the most frequently detected compounds in the water environment. The presence of diclofenac in wastewater treatment plant effluent and surface water has been reported to be in the range of 0.14 - 1.48 µg/L (Zhang et al. 2008). Sacher et al. (2001) reported the presence of diclofenac in groundwater at concentrations up to 0.59µg/L. Jux et al. (2002) reported the presence of diclofenac in surface water at concentrations up to 15µg/L and Metcalfe et al. (2004) reported a maximum concentration of 28.4µg/L diclofenac in aquatic environment. Some studies documenting the occurrence of PPCPs in aquatic environment is given in Table 2.1.

The PPCPs undergo various phases of metabolism or degradative actions or sequencing actions in environment and the conjugates formed by the parent compounds can act as storage reservoirs from which the free drugs can later be released into the environment (Daughton and Ternes 1999). Some PPCPs in the

environment may undergo structural changes under the influence of sunlight, oxygen, microorganisms, and other environmental conditions, leading to metabolites with significantly differing properties (Knutson et al. 2010).

Table 2.1 Some of the PPCPs occurrence in aquatic environment reported in literature

PPCP	Use	Reference
Acebutolol	Beta blocker	Vieno et al. 2007
Atenolol	Beta blocker	Vieno et al. 2007
Acetaminophen (paracetamol)	*Antipyretic*	*Ternes 1998; Kolpin et al. 2002; Roberts and Thomas 2006*
Amoxicillin	*Antibiotic*	*Kummerer 2001; Kasprzyk-Horden et al. 2007; Andreozzi et al.2004; Watkinson et al, 2007*
Benzafibrate	Lipid regulator	Vieno et al. 2007
Butalyted hydroxyanisol	Antioxidant	Pedersen et al. 2005
Caffeine	Stimulant	Pedersen et al. 2005; Godfrey et al. 2007;
Carbamazepine	Anticonvulsant, Anti-manic, antidepressant	Heberer et al. 2002; Pedersen et al. 2005; Godfrey et al. 2007; Vieno et al. 2007; Zhou et al. 2009
Cetirizine	H1-receptor antagonist	Larsson et al. 2007
Cimetidine	Antiasthmatic	Kolpin et al. 2002
Ciprofloxacin	Fluroquinolone-Antibiotic	Vieno et al. 2007; Larsson et al. 2007
Codeine	Analgesic	Kolpin et al. 2002
Cotinine	Nicotine metabolite	Kolpin et al. 2002; Godfrey et al. 2007
Clofibric	Acid Lipid regulator	Heberer et al. 2002
Diclofenac	*Non-steroidal anti-inflammatory (NSAID)*	*Zhang et al. 2008; Sacher et al. (2001) ; Jux et al. (2002) ; Metcalfe et al. (2004)*
Diazepam	Anti-anxiety	Heberer et al. 2002
Diltiazem	Blood pressure control	Kolpin et al. 2002
Erythromycin-18	Antibiotic	Kolpin et al. 2002
Fluoxetine	Antidepressant	Kolpin et al. 2002
Fenofibrate	Lipid regulator	Heberer et al. 2002; Pedersen et al. 2005
Gemfibrozil	Lipid-regulator	Heberer et al. 2002
Ibuprofen	NSAID	Heberer et al. 2002; Pedersen et al. 2005; Vieno et al. 2007
Iopromide	Contrast agent	Heberer et al. 2002
Ketoprofen	Antiplogistic	Vieno et al. 2007
Sulfamethoxazole	Antibiotic	Godfrey et al. 2007; Heberer et al. 2002
Warfarin	Anticoagulant	Kolpin et al. 2002

2.2. Effects of PPCPs on the Human and the Environment

The PPCPs present in the environment, biochemically interact with the living organisms and may adversely affect them (Daughton and Ternes 1999). The physiological, toxicological, and dose-response properties of many of the bioactive chemicals in

specific pharmaceuticals are well known (Knutson et al. 2010) and pharmaceuticals are designated to target specific metabolic pathways in humans and domestic animals but can have numerous other unknown effects on metabolic systems of non target organisms (Daughton and Ternes 1999). The actual effects of long-term exposures to small concentrations over time are unknown but the cumulative adverse impacts of low concentrations of PPCPs, individually or in combination, over time cannot be overlooked (Knutson et al. 2010).

The concentrations of PhACs in aquatic environment have been observed in the ng/L to μg/L range; and this level of exposure may not pose much risk to the adult humans, but fetuses, infants or children and other organisms may be affected. Children may have an eight fold greater risk of adverse effects of pharmaceutical exposure (Collier 2007). The developing infants in pregnant women are also susceptible to low PhAC exposures and post-natal exposure to PhACs during breast-feeding is also a reason for the concern (Collier 2007). The subclinical doses of the drugs are known to cause effects at the cellular and organ system levels; and thus, developing fetuses and children subjected to chronic exposure may experience long-term alterations in organ systems (Collier 2007). Therefore, the concentrations may appear low in aquatic environment but chronic exposure to these low levels may harm the human and ecosystems that are unable to mineralize PPCPs (Collier 2007).

The negative impacts on aquatic life from pharmaceutical contaminants are under investigation. The preliminary results indicate that the PPCPs have negative impact on aquatic life (Enick et al. 2007). The potential impacts to aquatic life depend on the extent to which aquatic life is exposed to the PPCPs and the persistence and concentration level of the PPCPs. A mixture of PhACs usually occurs in the environment and the study with aquatic organisms indicates that low concentrations of PhACs have increased toxicity when present in a mixture with other PhACs. The toxicity of the mixture follows the concept of concentration addition, with compounds acting in an additive fashion (Triebskorn et al. 2007). Cleuvers (2004) supported such findings, indicating that diclofenac, ibuprofen, acetylsalicylic acid and naproxen show greater toxicities as a mixture than as individual compounds. Bolong et al. (2008) observed the disorganized reproductive tissues and abnormal ratios of estrogen and

testosterone in aquatic organism, *juvenile alligators* in Lake Apopka, Florida due to the presence of PhACs. Fish eating birds and mammals may contain concentrations of PhACs many times higher than those found in fish on which they feed (Bolong et al. 2008).

Estrogenic hormones are the most endocrine disrupting chemicals as their disrupting potency can be several thousand times higher than other chemicals and are biologically active even at low concentration (Bolong et al. 2008). 17α-ethenylestradiol shows high estrogenic activity in the lower ng/L range, and the photo-transformation products of diclofenac are toxic and pro-inflammatory in low concentrations (Musolff 2009). Subtle effects of some PPCPs on aquatic and terrestrial life are shown in the Table 2.2.

In India and Pakistan, a catastrophic decline of *Gyps* vultures is reported due to an analgesic and anti-inflammatory drug, *diclofenac* (Taggart et al. 2007). The drug is regularly used for veterinary medication and residues entered the vultures as they fed on dead domestic livestock, causing renal failure and resulting in an over 95 % decline in some populations since early 1990s(Oaks et al. 2004). Another study finds the diclofenac to cause vitellogenin induction in male *Japanese medaka* (a variety of fish) at environmentally relevant concentrations of just 1 µg/L (Hong et al. 2007). It is also observed that Cytopathology occurs in livers, kidneys and gills of rainbow trout at 1 µg/L (Triebskorn et al. 2004; Hartmann et al. 2008).

Little is known about the risks associated with waters containing trace pollutants such as antibiotics, though research in this area is developing. Oetken et al. (2005) demonstrated that the antiepileptic carbamazepine had a significant and specific chronic effect against the oligochaete *Chiromus* at environmentally relevant concentrations. Antibiotics at sub-inhibitory concentrations can have an effect on cell functions and change the genetic expression of virulence factors or the transfer of antibiotic resistance (Kummerer 2009). As pharmaceutical contaminants have become more and more endemic and more concentrated in both the environment and human drinking water, it has become necessary to abate their impacts (Cuevas 2011).

Considering the potential adverse effects of the PPCPs, they should be removed from the environment.

Table 2.2 Reported subtle effects of certain PPCPs on aquatic and terrestrial organisms.

Compound	Effects	Reference
17β-estrodioal (synthetic steroid)	Feminization in fish and causes mimicking estrogen/hormone effect to non-target	Bolong et al. 2008
	Endocrine disrupting effects on fish, reptiles and invertebrates	Boxall 2004
Butalyted hydroxyanisol	Estrogenic to breast cancer cells, stimulates human estrogen receptor	Bolong et al. 2008
Estrone	Feminization in fish and causes mimicking estrogen/hormone effect to non-target	Bolong et al. 2008
Tricosan	Toxic, kill microorganism (biocide) and also cause bacteria resistance development towards triclosan	Bolong et al. 2008
Nitro and amino-nitro musks	Very high acute aquatic toxicity	Daughton and Ternes 1999
Fenfluramine (synthetic steroid)	Enhances release of serotonin (5-HT) in crayfish which in turn activate the release of ovary stimulating hormone resulting in larger ooxytes with enhances amounts of vitellin.	Daughton and Ternes 1999
Methyltestosterone (synthetic steroid)	Impersex, reduced fecundity, oogenesis, spermatogenesis in snails	Boxall 2004
Ibuprofen (Anti inflammatory)	Stimulation of growth of cyanobacteria and inhibition of growth of aquatic plants	Boxall 2004
Erythromycin (Antibacterial)	Inhibition of growth of cyanobacteria and aquatic plants	Boxall 2004
Carbamazepine (Analgesic)	Inhibition of basal EROD activity in cultures of rainbow trout hepatocytes	Boxall 2004
Diclofenac (Analgesic)	Inhibition of basal EROD activity in cultures of rainbow trout hepatocytes	Boxall 2004

2.3. Overview of the Treatment Technologies Adopted for the removal of PPCPs

Although, the PPCPs are currently not regulated in drinking water directives worldwide, precautionary measures should be taken to remove pharmaceuticals as high as possible through existing or improved treatment techniques (Ternes et al. 2002). A number of chemical methods, physical methods, and biological methods are available for treating wastewaters. If it is made to work successfully, biological treatment is more economical than any other type of treatment (Woodard 2001). Physical treatment methods consist of sedimentation, flotation, filtering, stripping, ion exchange, adsorption, and other processes that remove dissolved and undissolved substances without changing their chemical structures. Chemical methods include chemical precipitation, chemical oxidation or reduction including Advanced Oxidation Processes (AOPs) (Woodard 2001). The Table 2.3 gives an overview of treatment technologies available for treating waters containing PPCPs.

Table 2.3 Overview of the treatment technologies for the treatment of Water/Wastewater containing PPCPs

	Biological processes	**Physical processes**	**Chemical/Advanced oxidation processes**
Process	Pure and Mixed cultures (Bio-sorption, Bio-augmentation, Biodegradation) Aerobic and Anaerobic, MBRs,	sedimentation, flotation, filtering, stripping, ion exchange, adsorption	Chemical precipitation, chemical oxidation/ reduction including Advanced Oxidation Processes (AOPs), other chemical reactions that involve exchanging or sharing electrons between atoms
Remarks	Biological treatment is more economical but not effective in complete removal of PPCPs.	Effective in physical separation of PPCPs but not the complete removal	Effective and complete removal is possible with AOPs.

2.3.1. Biological Treatment Methods

Biological processes are a good option for wastewater treatment as they are relatively economical and the end products of complete degradation are harmless. However, due to the refractory nature of some elements in the effluents, the biological treatment is sometimes quite complicated. Since many PPCPs are detected in significant amounts

in STP effluents and surface water, it can be said that the conventional biological treatments are inefficient in removal of PPCPs (Castiglioni et al. 2006).

Various mechanisms like as sorption, biodegradation, volatilization, chemical and bio-transformations are possible removal mechanisms for PPCPs in STPs (Suarez et al. 2008). Although in many cases, the differences between them cannot be easily distinguished, recent works have concluded that only two of them, microbial degradation and sorption to suspended solids, are really relevant (Carballa et al. 2005). The effectiveness of these removal mechanisms greatly depends on the physicochemical properties and the chemical structure of each substance. According to their physico-chemical properties, PPCPs can be divided into three main groups: lipophilic (with high K_{ow} values), neutral (non-ionic) and acidic (hydrophilic and ionic) compounds (Carballa et al. 2005).

Volatilization: The PPCPs like fragrances can be removed easily by volatilization in the aeration depending up on the flow of air, type of aeration and Henry coefficient (Suarez et al. 2008).

Sorption: The ratio between the concentrations in the solid and liquid phases at equilibrium conditions is called the solid - water distribution coefficient (K_d, in L/Kg), which determines the fraction of PPCPs sorbed onto sludge (Suarez et al. 2008).

Absorption: Polycyclic musk fragrances are the most lipophilic compounds which can be easily absorbed by cell membrane of microorganism and the lipid fractions of the sludge and the lipophilicity is characterized by the octanol-water partition coefficient (K_{ow}) (Suarez et al. 2008).

Adsorption: The surface of the microorganisms is negatively charged, anionic species of acidic compounds (e.g. naproxen) are also negatively charged, and cationic species of other PPCPs (e.g. trimethoprim) are positively charged and hence the cationic species are easily removed by adsorption. The removal by adsorption depends upon dissociation constant (K_a), lipophilic character (K_{ow}) and acidity (pK_a) (Suarez et al. 2008).

Biological Transformation: Generally, conventional STPs contains high amount of organic content and hence the high concentration of carbon is available as nutrient to microbes, which initiates copiotrophic metabolism. The very low concentrations of most PPCPs limit their biodegradation in STPs and PPCPs are present at enzyme-subsaturating levels, which necessitate an oligotrophic metabolism (Daughton and Ternes 1999). Moreover, the chemical structure of some PPCPs is made very complex and strong to remain unaltered during its application and so the PPCPs are excreted unchanged (Suarez et al. 2008).

Many of the PPCPs are attempted for removal from water / wastewater with conventional biological methods and percentage removal of some of the PPCPs in conventional wastewater treatment plants reported in literature is shown in the Table 2.4.

Table.2.4 Percentage removal of some PPCPs in conventional STP

S.No.	PPCP	% Removal	Mechanism of removal	Reference
1	Carbamazepine	Nil	No mechanism in STP removes it.	Castiglioni et al. 2006
2	Clofibric acid	34-51	Adsorption	Castiglioni et al. 2006
3	Bezafibrate	50-83	Adsorption	Castiglioni et al 2006
4	Ibuprofen	>90	Adsorption	Castiglioni et al. 2006, Suarez et al. 2008
5	17β-estradiol	85-99	Sorption & biotransformation	Khanal et al. 2006
6	Estrone	25-80	Sorption & biotransformation	Khanal et al. 2006
7	Musks	50-75	Volatilization, sorption	Suarez et al. 2008
8	Amoxicillin	75-100	Sorption	Castiglioni et al. 2006

The removal rate of pharmaceuticals in STPs can vary and is potentially affected by the nature of the pharmaceutical, the treatment process employed, the age of the activated sludge, temperature, the light intensity, and the characteristics of the influent (Castiglioni et al. 2006).

A study by Wang et al. (2008) demonstrated that the pharmaceuticals Clofibric acid has no effect on microbial growth in wastewater with high organic loading, but there is a possibility that carbamazepine, in concentrations of more than 10 μg/l, can affect microbes in STPs with low organic loading. So, the inhibition of microbial growth by some pharmaceuticals may be a reason for the incomplete removal of these compounds in STPs. Also, Wang et al. (2008) pointed out that effects on microbial

growth possibly occur at lower concentrations. Some of the attempts, reported in literature, to degrade pharmaceuticals with higher efficiency are dealt in the following sections.

Carballa et al. (2005) tried to remove diclofenac, carbamazepine and ibuprofen by coagulation-flocculation and flotation from the treated sewage effluent. Because lipophilic trace pollutants are likely to be found adsorbed on colloids, coagulation-flocculation technique may be an option to remove certain non-polar pharmaceuticals from the wastewater (Carballa et al. 2005). On the other hand, the non-polar pharmaceuticals, sorbed onto the fine solid particles or lipophilic phases that are adhered to the up streaming bubbles of air can be removed by floatation technique (Carballa et al. 2005). Carballa et al. (2005) reported diclofenac, carbamazepine and ibuprofen removal up to 45 %, 35 % and 25 % respectively in floatation technique.

Sewage sludge contaminated with pharmaceuticals can be subjected to additional anaerobic treatment in order to remove pharmaceuticals (Carballa et al. 2007). The methanogenisis process of the anaerobic treatment is reported to be not affected with carbamazepine and sulfamethoxazole in concentrations up to 400 mg/L, but diclofenac inhibited methanogenisis at high concentrations (Carballa et al. 2007). Sulfamethoxazole – 99 %, diclofenac – 69 %, ibuprofen – 41 %, iopromide – 25 % are removed to some extent by the anaerobic digestion. However, carbamazepine is not removed by the process (Carballa et al. 2007).

So as to remove pharmaceuticals from STP effluents membrane bioreactors (MBRs) are adopted in laboratory scale and for some compounds in pilot scale (Clara et al. 2005; Radjenovic et al. 2007). Clara et al. (2005) found that diclofenac is not removed by size exclusion, but a partial removal can be obtained by increasing the sludge retention time. On the other hand, Ibuprofen is removed to a high amount (> 90%) and Carbamazepine is not removed. Clara et al. (2005) concluded that membrane bioreactors show no additional pharmaceutical removal compared to conventional treatment, especially size exclusion seemed to be ineffective for the purpose. In contrast to Clara et al. (2005), a study by Radjenovic et al. (2007) showed a greater pharmaceutical removal in case of diclofenac, metoprolol, Clofibric acid removal

compared to conventional treatment. But, ibuprofen removal is similar to conventional treatment and carbamazepine is not degraded in both MBR and conventional treatment.

2.3.2. Physical Treatment Methods

Nanofiltration (NF) and reverse osmosis (RO) are effective physical methods of pharmaceutical removal, though trace levels of compounds are detectable in membrane permeates (Snyder et al. 2007; Zwiener 2007). As the rejection efficiency depends on the concentration of the pharmaceutical compounds, more effort at lower concentrations is required. But rejection efficiencies are higher for negatively charged compounds than neutral compounds (Zwiener 2007). In spite of several advantages with nanofiltration, there are some unresolved troubles like membrane fouling and remediation, further treatment of concentrates, chemical resistance and short lifetime of membranes, inadequate rejection of pollutants, and the need for modeling and simulation tools and are necessary to be resolved (Van der Bruggen et al. 2008).

Activated carbon (AC) is a powerful process to remove PPCPs and only a few of PPCPs like iodinated contrast media and the antibiotic sulfamethoxazole show inadequate affinity to activated carbon (Ternes et al. 2004). Adsorption on activated carbon depends on the non-polar nature of uncharged compounds which do not have functional groups or N-heterocyclic structural groups and so the octanol–water partition coefficient (K_{ow}) is helpful for predicting removal efficiency (Zwiener 2007). The adsorption technologies are limited to the amount of flow produced since high flow rates for these techniques are not feasible due to rapid saturation of the adsorbents, leading to its regeneration. This technology is essentially limited to the contaminants phase transfer and does not allow the ultimate elimination of the PPCPs.

2.3.3. Chemical Treatment Methods

Chemical processes are destructive alternatives when biological treatments are not capable to completely remove PPCPs from water and wastewater and physical processes are limited to simply phase-transfer. Chemical methods of wastewater treatment depends upon (1) the tendency of the pollutants to react or interact with treatment chemicals, and (2) the chemical characteristics of the products of reaction,

their solubilities, volatilities, or the inability of the product to remain in water (Woodard 2001). Among the various chemical treatment technologies, Advanced Oxidation Processes (AOPs) are reported to be the most effective in the removal of non biodegradable substances.

Advanced Oxidation Processes (AOPs) : These are defined by Glaze et al. (1987) as the near ambient temperature and pressure water treatment processes, which involve the generation of highly reactive hydroxyl radicals ($OH^{\bullet}$) in sufficient quantity to influence water purification. $OH^{\bullet}$ radicals are extremely reactive species that attack most of the organic molecules.

The AOPs are used to destroy the complex refractory organic constituents individually or with conventional treatment methods. These processes are the most efficient to treat either high or low concentrations of pollutants. The final intention of the oxidation process is to mineralize the organic contaminants present in aqueous solution in to carbon dioxide, water and inorganic ions through degradation reactions involving species strongly oxidizing. It can be seen from Table 2.5 that hydroxyl radicals are more powerful oxidants than many chemical species used in conventional chemical processes.

Table 2.5 Oxidation potential against Standard Hydrogen Electrode of some oxidants

Oxidant	Oxidation potential E^o (V)
Fluorine	3.03
Hydroxyl radical	2.80
Singlet oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permanganate	1.68
Hypobromous acid	1.59
Chlordioxide	1.57
Hypochlorous acid	1.49
Hypochloric acid	1.45
Chlorine	1.36
Bromine	1.09
Iodine	0.54

Source: Legrini et al. 1993

The mechanism of reaction in AOPs usually involves the abstraction of a hydrogen atom or the addition to unsaturated carbon-carbon links and starting a sequence of oxidative reactions that can lead to complete mineralization of organic contaminant (Lucas 2009). The AOPs effectiveness depends on the 1) pH of the solution 2) presence of catalyst 3) presence of radical scavengers 4) photochemical processes that inhibit UV light penetration 4) reagent concentration 5) structure of the organics etc (Metcalfe et al. 2006; Neyens and Baeyens 2003).

AOPs can be classified as homogeneous or heterogeneous processes with further subdivisions with or without the energy requirements (Fig. 2.2). AOPs include Fenton type oxidation, which uses hydrogen peroxide and Fe^{2+}, ozonization, photo-catalysis, UV (ultraviolet)-H_2O_2, UV-H_2O_2-Fe (II, III), electro-coagulation, and electro-decomposition that oxidizes the non-degradable organic compounds with the OH radicals, which are produced during the reactions (Woodard 2001). Another mineralization process considered as wet air oxidation (WAO), where the organics are oxidized in an aqueous medium by way of oxygen from air at elevated temperature (250 – 300^oC) and high pressure (100 -150 bar) with catalysts like Cu^{2+} present.

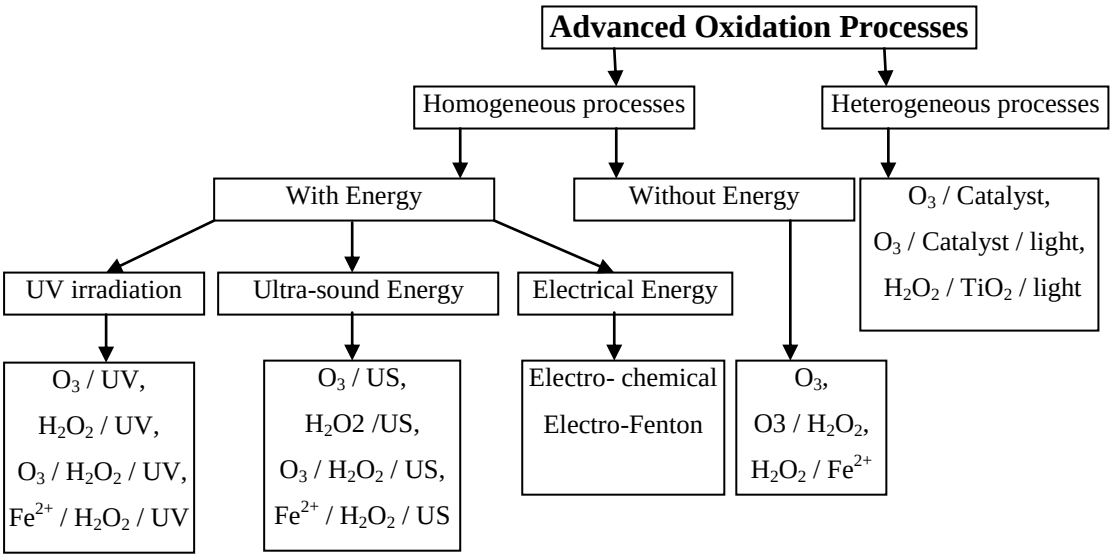


Fig. 2.2 AOPs to treat recalcitrant organic materials in aqueous solution

Fenton oxidation process: Fenton Oxidation (FO) is very effective in the removal of many hazardous organic pollutants from water as it can completely convert the contaminants to harmless compounds like CO_2, water and inorganic salts (Neyens and

Baeyens 2003). The Fenton's reagent is a mixture of H_2O_2 and ferrous iron, which dissociate the oxidant (H_2O_2) and form the highly reactive hydroxyl radicals capable of destroying the organic pollutants in a homogeneous catalytic oxidation process. The Fenton reaction is discovered by H. J. Fenton (Fenton 1894), when oxidizing polycarboxylic acids (malic acid and tartaric acid) with H_2O_2 and observed that there is a high increase in the presence of ferrous ions (Fe^{2+}). Forty years later, the Haber-Weiss (1934) mechanism is suggested, revealing that the effective oxidative agent in the Fenton reaction is the hydroxyl radical (HO•). The hydroxyl radicals are generally referred to as the primary oxidizing chemical species generated in accordance with the fundamental Eq. (2.1) (Walling, 1975). The FO of organics involves a complex reaction sequence in an aqueous solution (Neyens and Baeyens 2003).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^- \quad \textit{(chain initiation)}\ k_1 \approx 70\ M^{-1}\ s^{-1} \qquad (2.1)$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{–}OOH^{2+} + H^+ \qquad k_2 = 0.001\text{–}0.01\ M^{-1}\ s^{-1} \qquad (2.2)$$

$$Fe\text{–}OOH^{2+} \rightarrow HO_2\bullet + Fe^{2+} \qquad (2.3)$$

$$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO_2^- \quad \textit{(at pH = 3)}\ k_3 = 1.3 \times 10^6\ M^{-1}\ s^{-1} \qquad (2.4)$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+ \quad \textit{(at pH = 3).}\quad k_4 = 1.2 \times 10^6\ M^{-1}\ s^{-1} \qquad (2.5)$$

$$RH + OH\bullet \rightarrow H_2O + R\bullet \textit{ (Chain propagation)} \qquad (2.6)$$

$$R\bullet + H_2O_2 \rightarrow ROH + OH\bullet \qquad (2.7)$$

$$R\bullet + O_2 \rightarrow ROO\bullet \qquad (2.8)$$

$$R\bullet + Fe^{3+} \quad \text{oxidation} \rightarrow R^+ + Fe^{2+} \qquad (2.9)$$

$$R\bullet + Fe^{2+} \quad \text{reduction} \rightarrow R^- + Fe^{3+} \qquad (2.10)$$

$$2R\bullet \quad \text{dimerization} \rightarrow R\text{–}R \qquad (2.11)$$

$$OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet \qquad K_5 = 3.3 \times 10^7\ M^{-1}\ s^{-1} \qquad (2.12)$$

$$OH\bullet + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad \textit{(chain termination)}\ K_6 = 3.2 \times 10^8\ M^{-1}\ s^{-1} \qquad (2.13)$$

$$Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2\ Fe^{3+} + 2H_2O \qquad (2.14)$$

The ferrous ion (Fe^{2+}) initiates the reactions and catalyses the decomposition of H_2O_2 to generate hydroxyl radicals [Eq. 2.1]. The newly formed ferric ions may catalyses the decomposition of H_2O_2 to water and oxygen [Eq. 2.1 to 2.5]. As the rate of reaction (Eq. 2.1) is much more than the rate of reactions (Eq. 2.2) to (Eq. 2.5), the rate of formation of ferric ions is more than the formation of ferrous ions. Hence, sufficient initial [Fe^{2+}] is required to accelerate the oxidation of organic matter. The presence of more Fe^{2+} also act as OH• scavenger [Eq. 2.13] and OH• scavenging rate of Fe^{2+} is ten times more than that of H_2O_2. H_2O_2 with Fe^{2+} is required to produce OH• radical [Eq. 2.1]; H_2O_2 is consumed to convert ferric ions to ferrous ions [Eq. 2.3 and 2.4], which are useful in reaction (1) and also H_2O_2 is consumed to oxidize the organic matter and produce hydroxyl radicals [Eq. 2.7]. Hence, sufficient concentration of H_2O_2 is needed to meet all the demands. H_2O_2 can act as an OH• scavenger [Eq. 2.12] as well as an initiator [Eq. 2.1]. Since $k_5 > k_1$ -the scavenging rate is more than reaction initiation rate-the concentration of H_2O_2 should be optimized to produce maximum hydroxyl radicals. Hydroxyl radical can oxidize the organics (RH) to produce Organic radicals (R•) [Eq. 2.6], which are highly reactive and cab be further oxidized. It is further observed that the OH• required are proportional to the concentration of the organics.

Reaction (Eq. 2.9) competes with both the chain termination reaction [Eq. 2.13] and with the propagation reaction (2.6) of Fenton chemistry. This competition for hydroxyl radical between Fe^{2+}, RH and Fe^{3+} leads to the non-productive decomposition of hydrogen peroxide and limits the yield of hydroxylated (oxidized) organic compounds. Therefore, the Stoichiometric relationship between Fe^{2+}, RH and Fe^{3+} has to be established to maximize the efficiency of the degradation process. Reagent conditions- [Fe^{2+}], [H_2O_2] and reaction conditions- pH, temperature, [organic] determine the overall Fenton's oxidation efficiency.

The equation (2.14) suggests that the presence of H^+ is required in the decomposition of H_2O_2, indicating the need for an acid environment to produce the maximum amount of hydroxyl radicals. Literature on Fenton studies reported that acidic pH levels near 3 are usually optimum for Fenton oxidations (Neyens and Baeyens 2003). In the presence of organic substrates (RH), excess ferrous ion, and at low pH,

hydroxyl radicals can add to the aromatic or heterocyclic rings as well as to the unsaturated bonds of alkenes or alkynes.

The Fenton oxidation process has been successfully applied in the degradation of several compounds like chlorophenols (Kwon et al. 1999), pharmaceutical waste (Tekin et al. 2006), wastewater from amoxicillin manufacture (Zhang et al. 2008) and pentachlorophenol (Zimbron et al. 2009). Advanced oxidation of amoxicillin by Fenton's reagent degraded the amoxicillin completely but mineralization is not complete due to formation of refractory intermediates (Ay and Kargi 2010). Khan et al. (2009) examined the effects of iron type Fe^{2+}, Fe^{3+}, and Fe^{0} in Fenton reaction and it is observed that Fenton reagent using Fe^{2+} is more effective in the DOC reduction compared to Fe^{3+} and Fe^{0}.

Photo-Fenton process: Fenton reaction rates are strongly enhanced by irradiation with UV or visible light (Ruppert et al. 1993; Sun and Pignatello 1993). The photo-Fenton reaction involves irradiation with solar or UV light which significantly increases the rate of contaminant degradation by photo reduction of Fe^{3+} to Fe^{2+}. Fenton's reaction generates hydroxyl radicals (Eq. 2.15) and photo-Fenton reactions reduce the Fe^{3+} to Fe^{2+} (Eq. 2.16) (Faust and Hoigné 1990), thus leading to production of additional OH radicals and continuous regeneration of Fe^{2+} in a catalytic way (Sun and Pignatello 1993).

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + HO\cdot \quad \text{(Fenton reaction)} \qquad (2.15)$$

$$Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + HO\cdot \qquad (2.16)$$

The hydroxylated ferric ion, $Fe(OH)^{2+}$, the predominant complex of Fe^{2+} in acidic conditions in aqueous solution, can be reduced to Fe^{2+} by ultraviolet or visible radiation. It is also observed that the additional amounts of OH radicals are also produced from the direct photolysis of H_2O_2 (Laat et al. 1999) (Eqn. 2.17). However, in the presence of iron complexes of strongly absorbing radiation, this reaction (Eqn.2.17) will contribute only in small scale for the photo-degradation of organic contaminants (Safarzadeh-Amiri et al. 1997).

$$H_2O_2 + h\upsilon \rightarrow 2HO\bullet \qquad (2.17)$$

At pH = 3.0, the hydroxy-Fe^{3+} complexes are more soluble and the species $Fe(OH)^{2+}$ are more photoactive, which is the predominant form of these complexes (Kim and Vogelpohl 1998). Therefore, the optimum performance of the photo-Fenton process is considered to be at pH 3.0.

UV irradiation has been used for the degradation of a large array of organic contaminants for the past several years. The efficiency of direct photolysis depends upon the energy of the UV light. The ultraviolet "C"-band (UVC) consists of short wavelengths between 200 to 280 nm and it is highly energetic form of radiation that can cause separation or degradation of bonds in many of the organic molecules (Legrini et al. 1993). Any organic pollutant (e.g. PCM, λ_{max}=243 nm) is able to undergo a direct photolysis if its absorbance spectrum overlaps the spectral range of the available radiation (Rizzo et al. 2009). But the effectiveness of direct photolysis due to UVA (320-400 nm) and UVB (280-320 nm), which are also naturally available near the Earth's surface, may be less than UVC. Yang et al. (2008) demonstrated that UVA (365nm) radiation has degraded negligible amount of PCM, whereas UVC degraded substantial concentration of PCM. UVC alone can degrade organic compounds to some level with negligible mineralization whereas UVC with Fenton reagent mineralizes the organics to a larger extent (Catalkaya et al. 2003). The efficacy of photo-Fenton process may also depend up on the type of catalyst used in Fenton reagent.

The published research shows that the photo-Fenton process presents an efficient performance in the degradation of organic pollutants such as 4-chlorophenol (Bauer and Fallmann 1997), nitrobenzene and anisole (Zepp et al. 1992), herbicides (Sun and Pignatello 1993). In a photo-Fenton's Oxidation of hospital wastewater, the biodegradability in terms of BOD_5 / COD ratio, increased from 0.3 to 0.52 at a dosage ratio of COD: H_2O_2: Fe^{2+} = 1: 4: 0.1, pH 3 (Kajitvichyanukul et al. 2006). Diagne et al. (2008) reported that methyl parathion (MP) is very quickly destroyed after 4 min following a pseudo-first-order kinetics and overall mineralization was achieved at 120 min .in the photo-Fenton Oxidation for the treatment of 0.2 mM MP aqueous solutions at 20 mM H_2O_2 and 0.5 mM Fe^{3+}, corresponding to a [H_2O_2] / [Fe^{3+}] ratio of 40. Bauer and Fallmann (1997) compared various AOPs like Photo-Fenton, UV /

O_3 / Fe^{2+} and UV / O_2 / Fe^{2+} methods and found that the photo-Fenton method is the cheapest available process for the treatment of refractory wastewaters.

Oxidation with Hydrogen Peroxide (H_2O_2): The oxygen - oxygen single bond in H_2O_2 is relatively weak and is subject to break-up to yield •OH free radicals: (Woodard 2001).

H - O - O - H ⟶ •OH + •OH or, peroxide ⟶ Rad• (2.18)

The two •OH free radicals can attack a molecule of organic matter and produce another free radical. This is called a chain-initiating step:

•OH + RH → H_2O + R• Chain-initiating step (2.19)

This process continues till the organics are broken down to carbon dioxide and water.

R• + R - C → R + R• + C• Chain propagation steps (2.20)

RH + R• + O → CO_2 + H_2O (2.21)

RH + C• + O → CO_2 + H_2O Chain termination step (2.22)

Hydrogen Peroxide plus UV Light (UV/H_2O_2): •OH free radicals are formed at a faster rate when H_2O_2 is added to an aqueous solution along with irradiation with ultraviolet light (UV) (Woodard 2001).

$$H_2O_2 \xrightarrow{UV} 2OH^{\bullet} \quad (2.23)$$

or to obtain an electron from the target organic compounds and dissociate into one hydroxide ion (nine protons and ten electrons (OH^-)) and one hydroxyl free radical (nine protons and nine electrons (•OH)),

$$H_2O_2 + e^- \longrightarrow \bullet OH + OH^- \quad (2.24)$$

The hydroxyl free radicals then go on to bring about a chain reaction.

This technology for treatment various pollutants is reported in the literature. 39 pharmaceuticals including 12 antibiotics and 10 analgesics are treated with UV/H_2O_2 process at UV dose of 923 mJ / cm^2 with 90 % removal efficiency (Kim et al. 2009). For H_2O_2 / UV process at pH 5.5, paracetamol in aqueous solution is completely

removed with mineralization up to 40% and it formed number of intermediates (Andreozzi et al. 2003). Diclofenac in water is completely degraded and mineralized up to 39% by H_2O_2 / UV at pH 5-6 after 90 min. (Vogna et al. 2004). Amoxicillin, ampicillin and cloxacilllin antibiotics in aqueous solution completely degraded and mineralized by UV / H_2O_2 / TiO_2 photocatalysis at pH 5, H_2O_2 100 mg/L and TiO_2 1.0 g/L with in 30 min. (Elmolla and Choudhuri 2010a). Park and Lee (2009) conducted the decomposition of acetic acid with several advanced oxidation processes such as TiO_2-UV-H_2O_2, Fe^{2+}-H_2O_2-UV, UV-H_2O_2 and TiO_2-UV system and identified that the acetic acid is efficiently decomposed within 120 minutes of UV radiation under the initial concentration of 500 ppm and UV- H_2O_2 process is most effective in COD removal rate and the decomposition efficiency. Achilleos et al. (2010) demonstrated the diclofenac decomposition by UV – A / TiO2 photocatalysis and concluded that the method is an efficient method for the destruction and mineralization of diclofenac in aqueous systems.

Oxidation with Ozone: Ozone reacts with organic compounds and oxidizes alcohols, aldehydes, and ketones to acids. Ozone requires less assistance from heat, catalysts, enzymes, or direct microbial action (Woodard 2001).

Ozonation contributed substantially to overall removal of naproxen, ketoprofen, triclosan, crotamiton, sulfa pyridine, macrolide antibiotics, and Estrone; compounds with a C = C double bond or an aromatic structure with electron donors (e.g., phenol, alkyl, methoxy, or non- protonated amine) are susceptible to ozonation; compounds with amide structures are resistant (Nakada et al. 2007; Zwiener 2007). Ozonation removed ≥ 80% of the phenolic antiseptics, crotamiton, sulfonamide and macrolide antibiotics, and 17β-estradiol (Nakada et al. 2007). Paracetamol in aqueous solution completely removed with mineralization up to 30% for ozonation at pH 5.5 (Andreozzi et al. 2003). Diclofenac in water is completely degraded and mineralized up to 32% by ozonation at pH 5-6 after 90 min. (Vogna et al. 2004). Despite the advantages associated with ozonation, the effectiveness of ozone may be limited by; a) its relatively low solubility and stability in solution, b) the fact that ozonation often does not lead to complete oxidation and c) relatively slow reaction rates with some

organic compounds. However, the overall oxidative effectiveness with O_3 can be increased with the addition of TiO_2 / H_2O_2 / UV-light (Metcalfe 2006).

Ozone plus Hydrogen Peroxide: When both ozone and hydrogen peroxide are present in water containing organics two •OH radicals are formed from one hydrogen peroxide and two ozone molecules: (Woodard 2001).

$$O_3 + H_2O_2 \rightarrow OH\bullet + O_2 + HO_2\bullet \quad (2.25)$$

O_3 / H_2O_2 degraded the pharmaceuticals with efficiencies of more than 90% in most of the cases (Rosal et al. 2008).

Electro-chemical Oxidation: Electrochemical advanced oxidation processes are environmentally friendly methods based on the destruction of organic pollutants in wastewaters with in situ electro-generated hydroxyl radical. Electro-chemical oxidation utilizes energy from spontaneous chemical reactions in the form of electricity to supply energy in order to get non spontaneous chemical reactions running (Muff 2010). Electrochemistry is redox chemistry, where electrons are transferred from one species to another. A species is in this terminology said to be oxidized when it loose electrons and reduced when it gains electrons. The mineralization rate is independent of pH, increases with increase in applied current and temperature (Brillas et al. 2005). Paracetamol can be destroyed to a larger extent by electrochemical oxidation (Waterston et al. 2005; Sires et al. 2006; Skoumal et al. 2006 and Garrido et al. 2007).

Other AOPs: Sonolysis and Gamma ray irradiation is also used to mineralize non-biodegradable organic contaminants. Guyer and Ince (2011) studied the degradation of diclofenac in water by homogenous and heterogeneous sonolysis and found that the efficiency of non-reactive iron superoxide nano-particles than that of reactive divalent iron. Gamma ray irradiation is also an effective method to degrade diclofenac and the degradation efficiency of diclofenac increased significantly with the increase in radiation dose (Liu et al. 2011).

2.4. Summary of the Literature Review

The literature review can be summarized as follows:

1. Pharmaceutical and Personal Care Products are continuously conveyed into the aquatic environment as a complex mixture via number of routes.
2. The pharmaceuticals are bioactive and designated to target specific pathway in humans. Pharmaceuticals retain their chemical structure long enough to do their therapeutic work and remain in the environment for a long time. This is considered dangerous both at low and high concentrations.
3. Though the concentrations present in aquatic environment are very low in the range of ng/L to µg/L, the cumulative adverse impacts of low concentrations of PPCPs, individually or in combination, over time, cannot be ignored.
4. This level of exposure may not pose much risk to adult humans, but same may not be true in case of fetuses, infants or children and other organisms. Children may have an eight fold greater risk of adverse effects of pharmaceutical exposure. The effects like feminization in fish, inhibition of growth in microbes and plants, toxicity and Endocrine disruption in fish are reported. As a precautionary measure, considering the potential adverse effects of pharmaceuticals, they should be removed from the aqueous solutions.
5. Biological processes are reported to be cost effective and have many advantages over physical and chemical methods if it works. But, for majority of PPCPs biological processes are inefficient since the PPCPs are found in significant amounts in STP effluents. Physical treatment methods can be efficient in physically separating some of the PPCPs from water but are inefficient in complete removal of it from the environment.
6. Advanced Oxidation Processes (AOPs) are reported to be the most effective in the removal of non biodegradable substances like PPCPs.

Among the AOPs employed, heterogeneous photocatalysis, ozonation and Fenton reactions are the most popular ones.

7. Fenton oxidation process is cost effective, easy to operate, can degrade and mineralize most of the organic compounds and has more pharmaceutical removal efficiencies. Photo-Fenton oxidation is the most economical; degradation of organics is very fast, complete removal of organic is possible within minutes.
8. The use of iron extracted from laterite soil as catalyst in Fenton reagent has not yet been reported for the treatment of organics. The Fe (LS) is naturally available in the west coast of India and other parts of the world between the tropics of Cancer and Capricorn. Therefore, it is valuable to conduct studies on Fe (LS) in Fenton reagent for the treatment of pharmaceuticals.
9. The Fenton and photo-Fenton processes appear to be more effective treatment methods for the removal of pharmaceutical compounds from water and hence its evaluation can be a worthwhile effort.

CHAPTER 3

MATERIALS AND METHODS

Chapter 3

MATERIALS AND METHODS

This chapter is about the materials used, instruments used, experimental procedure and methods adopted during the studies. Preparation of synthetic sample, operation of reactor, analytical procedures adopted for determining concentration of the selected drug, COD, pH, H_2O_2, iron in both influent & effluent and HPLC analysis of drug degradation are also described.

3.1 Materials

3.1.1 Model Pharmaceutical Compounds

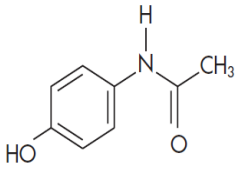
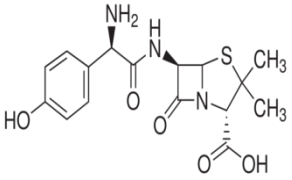
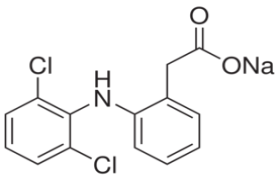
The pharmaceutical compounds used in the present study viz. paracetamol (PCM), amoxicillin (AMX) and diclofenac (DCF) are selected on basis of their use, production in large quantities, occurrence in aquatic systems, and their aquatic environmental problems.

Paracetamol (PCM): Paracetamol (4-hydroxyacetanilide or 4- acetamidephenol or acetaminophen or Tylenol) is extensively used over-the-counter analgesic (pain reliever) and antipyretic (fever reducer) drug (Botting 2000). It is also used as intermediate for pharmaceuticals and azo dyes, stabilizer for hydrogen peroxide, photographic chemicals and control of brown tree snake population (Hiremath et al. 2006). The recommended therapeutic dose for adults is 4 g (Farrell 1986) and PCM induced liver damage is normally seen only with daily doses greater than 10 g.. Pregnant women and infants are susceptible to even low concentrations of the drug. The wide use and potentially nefarious chemistry exhibited by PCM render it an important pharmaceutical compound to investigate in the environment. The physicochemical properties of paracetamol are listed in the Table 3.1.

A saturated aqueous solution has a pH of about 6 and is stable (half-life over 20 years) but stability decreases in acid or alkaline conditions, the paracetamol being slowly broken down into acetic acid and p-aminophenol. This toxicity is due to the chemical

structure of the compound and the way our bodies break it down. It is metabolized to a reactive intermediate at high dose.

Table 3.1 Physicochemical Characteristics of the Selected Pharmaceutical Compounds

Properties	Pharmaceuticals		
	Paracetamol	**Amoxicillin**	**Diclofenac Sodium**
Synonym	Acetaminophen, N-Acetyl-p-aminophenol	(2S,5R,6R)-6-[[(2R)-2-amino-2-(4-hydroxyphenyl)acetyl]amino]-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid	(o-(2,6-dichloroanilino)phenyl) aceticacidmonosodiumsalt
Structure			
Use	Analgesic and antipyretic drug	Antibiotic	NSAID
Appearance	white crystalline powder	yellow crystalline	White crystalline powder
Formula	$C_8H_9NO_2$	$C_{16}H_{19}N_3O_5S$	$C_{14}H_{11}Cl_2NO_2$ Na
Mol. Wt (g)	151.20	365.40	318.13
Solubility	11 g/L	3.43 g/L	50 mg/mL
Stability	Stable	-	Stable, Hygroscopic
M.P / B.P	168 / 172 ^{0}C	169 / 172 ^{0}C	275 / 277 ^{0}C
pK_a	9.5	2.4 – 9.6	4.2
λ_{max}	243	226	276

Solubility in water is at 25^o C; $pK_{a,}$ = dissociation constant (Suarez et al. 2008; Prankerd 2007); λmax = Wave length of the compound in nm for maximum absorbance

Table 3.2 List of Chemicals Used in the Present Study

Compound	Formula	Make	Purity
Paracetamol	$C_8H_9NO_2$	SD Fine Chem. Ltd. ,India	98.0%
Amoxicillin	$C_{16}H_{19}N_3O_5S$	Merck ,India	98.0%
Diclofenac Sodium	$C_{14}H_{11}Cl_2NO_2$ Na	Sigma ,India	99.9%
Hydrogen peroxide	H_2O_2	Merck, India	50% (w/v)
Iron (II) Sulphate heptahydrate	$FeSO_4$. $7H_20$	Merck, India	98.0%
Hydrochloric acid	HCl	Merck, India	35.0%
Sulphuric acid	H_2SO_4	Merck, India	98.0%
Sodium hydroxide	NaOH	Merck, India	98.0%
Sodium Thiosulphate	$Na_2S_2O_3$. $5H_2O$	Merck, India	99.5%
Potassium dichromate	$K_2Cr_2O_7$	Merck, India	99.0%
Ammonium molybdate	$(NH_4)_5Mo_7O_{24}$. H_2O	Merck ,India	99.0%
Acetonitrile	C_2H_3N	Merck, India	99.8%
Ammonium hydroxide	NH_4OH	NICE ,India	25% NH_3
Ammonium nitrate	NH_4NO_3	Merck, India	99.0%
Potassium iodide	KI	Merck, India	99.8%
Starch as indicator	$(C_6H_{10}O_5)n$	Merck, India	Pure
potassium Thiocynate	KSCN	Merck, India	98.0%
Mercuric Sulfate	$HgSO_4$	Merck, India	99.0%
Silver Sulfate	Ag_2SO_4	Merck, India	99.8%
1, 10-phenanthrolline monohydrate	$C_{12}H_8N_2$. H_2O	Merck, India	99.8%
Ammonium iron (II) sulphate hexahydrate	$(NH_4)_2$ Fe $(SO_4)_2$. $6H_2O$	Merck ,India	99.0%
Methanol (HPLC)	CH_3OH	Merck ,India	99.9%
Methanol (AR)	CH_3OH	Merck ,India	99.8%
Sodium Petanesulphonate	$C_5H_{11}O_3SNa$	Merck ,India	95.0%
Formic acid	HCOOH	Merck ,India	96.0%
Monobasic potassium phosphate	KH_2PO_4	Merck ,India	AR
Potassium hydroxide	KOH	Merck ,India	99.99%
Glacial acetic acid	CH_3CO_2H	Merck ,India	99.99%

Amoxicillin (AMX): Amoxicillin is semi-synthetic penicillin with a beta-lactam ring inhibiting synthesis of bacterial cell wall. It is widely used human and veterinary medicine of environmental concern. Presence of low concentrations of antibiotics in environment developed antibiotic resistant bacteria.

Diclofenac (DCF): Diclofenac is a Non-steroidal Anti-inflammatory Drug (NSAID) used as analgesic, antiarthritic and antirhumatic. It is used worldwide and has been produced in hundreds of tons annually. About 15% is excreted unchanged after human consumption (Landsdrop et al. 1990). It seems to be rapidly degraded by direct photolysis under environmental conditions (Buser et al. 1998). It is the most frequently detected drug at concentrations up to 510 µg/L. It affects kidneys and alterations of gills in rainbow trout at 5 µg/L concentrations (Schwaiger et al. 2004). Catastrophic decline of *Gyps* vultures in North India due to DCF is also reported (Taggart et al. 2007).

PCM is purchased from SD Fine Chemicals Ltd., AMX is purchased from Merck, India and DCF is purchased from Sigma, India. All the other chemicals used in the experimentation are AR grade or HPLC grade. The chemicals that are used in the experiments are listed in Table 3.2. The chemicals are used as received. All experiments are performed in Millipore Elix-3 deionized water (Electrical conductivity $\leq$ 0.065 µS/cm). All the reagents required are prepared with the same deionized water.

3.1.2 Instruments or equipments used in the present study

The instruments or the equipment used for experimentation and analysis in the present study are listed in the Table 3.3.

3.1.3 Preparation of Synthetic Wastewater of Selected Drugs

The simulated paracetamol aqueous stock, amoxicillin aqueous stock and diclofenac aqueous stock solutions of each 1000 mg / L concentration are prepared every week with Millipore Elix-3 deionized water (conductivity $\leq$ 0.065 µS / cm) and stored in the dark at 4^{o} C in an air-tight amber glass bottle for a maximum time of 7 days.

Table 3.3 List of instruments used in the present study

Sl. No.	Required Instruments	Make	Purpose
1	UV-VIS double beam spectrometer 2201	Systronics, India	Measurement of absorbance, characteristic wave length and concentration of the drug
2	HPLC system – LC-10AT	Shimadzu, Japan	Analysis of the drugs and their reaction intermediates
3	COD digester – ET 125	Lovibond, Germany	COD determination
4	Spectrocolorimeter – PC Spectro	Lovibond, Germany	Iron measurements
5	Digital pH meter	Lovibond, Germany	pH adjustments and measurement
6	Magnetic Stirrers KEMI – 450	KEMI, India	Uniform mixing of the drugs and the reagents in Fenton and photo-Fenton process
7	Semi micro balance	Shimadzu, Japan	Weighing drugs and chemicals
8	UVC lamp: Diameter -10 mm, Length - 330 mm, Power- 8 watts, Light Intensity- 30 mWs/cm^2, Life of lamp- 9000 hrs	Philips, Germany	Photo-Fenton process

3.2 Experimental Methodologies

3.2.1 Spectral and Chemical Characterization of the Model Pharmaceutical compounds

UV-VIS spectrum is recorded for (PCM), (AMX) and (DCF) using UV-VIS double beam spectrophotometer and the absorbance peak is observed to be at wavelength 243 nm (PCM), 226 nm (AMX) and 276 nm (DCF). For the range of concentrations considered for each drug, a linear relationship (calibration curves) between absorbance and concentration are established. These calibration curves are used to measure the dug concentration, before and after treatment.

COD calibration curves between the drug concentration and COD are established for concentrations ranging from 5 to 50 mg / L (0.033 to 0.331 mM) for PCM, 5 to 50 mg / L (0.014 to 0.137 mM) for AMX and 10 to 50 mg / L (0.031 to 0.157 mM) for DCF. The COD is about 1.55 mg / L per mg of PCM, 1.64 mg / L per mg of AMX concentration, 1.5 mg / L per mg of DCF and these values are used in calculating the corresponding initial COD of the drug samples. The initial COD values are calculated in the subsequent experiments with the use of these calibration curves.

3.2.2 Fenton and Photo-Fenton oxidation processes

(a) Fenton-reactor and degradation procedure

Fig. 3.1 Experimental Setup for Fenton's Oxidation of the Selected Pharmaceuticals

The Fenton oxidation experimental setup as shown in Fig. 3.1 consists of a 2-L capacity batch reactor over a magnetic stirrer with AC power supply connection. The experiments are conducted at ambient temperature (27 ± 3^{o} C) in batch reactors. A 1000 mL solution of required drug concentration is prepared from the stock drug solution and is taken in a 2-L reactor. The intrinsic pH of the wastewater is 6.32 (PCM), 6.2 (AMX), 5.6 (DCF), 6 (Mixture of the three drugs) but the initial pH of 3 (PCM and AMX), 3.5 (DCF and the Mixture of the drugs) of the solution is maintained using 0.1 N H_2S0_4 and 0.1N NaOH. Appropriate amount of Fe^{2+} concentration from the 1000 mg / L stock solution, freshly prepared from $FeSO_4.7H_2O$, is added to the reactor bath and stirred with magnetic stirrer. Required amount of H_2O_2 is added to the reactor bath to initiate the reaction. As the pH of the solution drops down to about 1.2 – 1.3 with addition of the iron extract from laterite

soil; for the experiments with iron extracted from laterite soil (Fe (LS)), the pH of 3 or 3.5 is adjusted after adding appropriate iron solution, stirred with magnetic stirrer and then H_2O_2 is added. The mixture of the drugs solution and Fenton's reagent is stirred with magnetic stirrer during treatment. The aliquot of drug solutions are taken out for analysis at pre-defined time intervals and filtered through 0.45 µm Millipore filter membrane for COD analysis and for determination of PCM and AMX concentration by using UV-VIS Spectrophotometer and High Performance Liquid Chromatography (HPLC). But for the DCF, acetonitrile is added to the sample and mixed thoroughly and then the sample is filtered to determine the concentration of DCF as to take care of the diclofenac precipitation at pH lower than 3.5. However, for COD measurement in DCF treatment, acetonitrile is not added as it contributes to the COD.

(b) Photo-reactor and Photo-Fenton degradation procedure

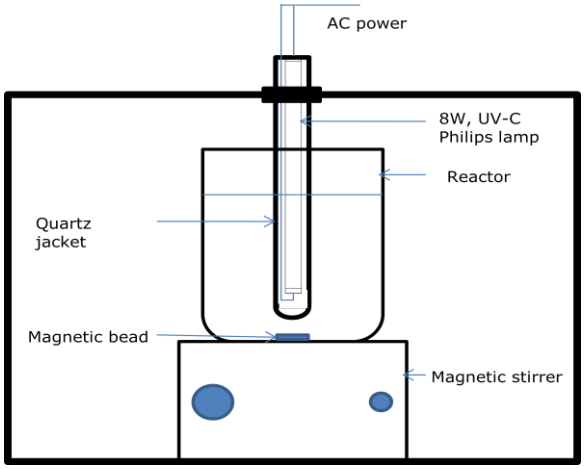


Fig. 3.2 Schematic Representation of the Photochemical Reactor

The photo-reactor setup as shown in Fig. 3.2 consists of an enclosed chamber comprising a reactor (2L volume), 8W UV-C Philips lamp covered with a quartz jacket; connected to AC power and a magnetic stirrer. All photo-Fenton experiments are carried out at ambient temperature (27 ± 3^{o} C) in batch mode. A 1000 mL solution of required drug concentration is prepared from the stock drug solution and is taken in the 2-litre reactor. The initial pH of 3 or 3.5 of the solutions is adjusted using 0.1 N H_2SO_4 and 0.1N NaOH. Appropriate amount of Fe^{2+} concentration from the 1000 mg / L stock solution, which has been freshly prepared from $FeSO_4.7H_2O$, is added to the reactor bath and stirred with magnetic stirrer. The solution is kept in dark for 20

minutes for the maximum absorbance of light. Required amount of H_2O_2 is added to the reactor bath to initiate the reaction and simultaneously the UVC lamp is switched on. As the pH of the solution drops down to about 1.2 - 1.3 with addition of the iron extract from laterite soil; for the experiments with Fe (LS), pH is adjusted after adding appropriate iron solution, stirred with magnetic stirrer and then H_2O_2 is added. The mixture of drug solution and Fenton's reagent is stirred with magnetic stirrer during treatment. The aliquot of drug solution samples are taken out for analysis at pre-defined time intervals; filtered through 0.45-µm Millipore filter membrane for COD analysis and for determination of drug concentration by using UV-VIS spectrophotometer and also by High Performance Liquid Chromatography (HPLC). However, for the DCF, acetonitrile is added to the sample and mixed thoroughly and then the sample is filtered through 0.45-µm filter to determine the concentration of DCF as to take care of the diclofenac precipitation at pH lower than 3.5. On the other hand, for COD measurement in DCF treatment, acetonitrile is not added as it contributes to the COD.

The key features of Fenton and photo-Fenton oxidation are its reagent conditions i.e. $[Fe^{2+}]$, $[H_2O_2]$ and the reaction characteristics i.e. pH, temperature and the quantity and chemical structure of organic and inorganic constituents. Hence, the optimization of pH, $[H_2O_2]_0$, $[Fe^{2+}]_0$, $[Fe\ (LS)]_0$, $[Drug]_0$ is carried out at room temperature for the selected drugs.

3.2.3 Effect of pH

Table 3.4 Experimental conditions for the optimization of pH in degradation of the selected drug by Fenton oxidation process

Selected Drug for treatment	Initial experimental conditions					
	$[PCM]_0$	$[AMX]_0$	$[DCF]_0$	$[Fe^{2+}]_0$	$[H_2O_2]_0$	Initial pH
	mM	mM	mM	mM	mM	Varied in the range at the rate of 0.5
PCM	0.066	-	-	0.036	0.59	2.0 - 5.5
AMX	-	0.027	-	0.018	0.59	2.0 - 5.5
DCF	-	-	0.031	0.018	0.59	2.5 - 4.5
Mixture of drugs PCM + AMX + DCF	0.066	0.027	0.031	0.036	2.35	2.0 - 4.0

The pH of the solution is an important parameter for Fenton and photo-Fenton oxidation processes, which controls the production rate of hydroxyl radical and the concentration of Fe^{2+}. It is also an important operational variable in actual wastewater treatment. Generally, the optimal pH of the solution in Fenton and photo-Fenton processes is in the range of 2 – 4 (Neyens and Baeyens 2003). In order to find the accurate optimal pH of reaction mixture for the efficient degradation of PCM, AMX, DCF and the mixture of these three drugs in Fenton oxidation; the experimental conditions shown in Table 3.4 are adopted.

Procedure: The pH optimization for the treatment of the selected drug is carried out with H_2O_2 and Fe^{2+} as catalyst in Fenton oxidation. The same experimental procedure, which is outlined in Fenton oxidation for the degradation of the selected drug, is followed to know the effect of pH and to optimize the pH for the maximum removal of the drug (degradation) and the corresponding COD (mineralization). During the treatment the mixture of drug and Fenton reagent is continuously stirred with magnetic stirring for 3 h, while the concentration are measured and COD values are determined after 24 h of reaction time. Similar procedure is adopted for the optimization of pH in the oxidation of all the drugs in water by Fenton oxidation. The same optimal pH obtained in Fenton oxidation with Fe^{2+} catalyst is considered for all the experiments with Fe (LS) as well as photo-Fenton process for the treatment of selected drugs in water.

3.2.4 Effect of H_2O_2 and Iron Catalyst Concentration

Hydrogen peroxide is the basis for the radical generation in Fenton's Oxidation. Hence, an investigation of H_2O_2 consumption and optimization in Fenton's oxidation is vital for using H_2O_2 efficiently and also for the other best possible conditions that were to be found in aforesaid process. The addition of iron catalysts significantly improves the degradation of organic compounds. In order to find the optimal initial H_2O_2 dosage and initial Iron catalyst (Fe^{2+} or Fe (LS)) of for the degradation of PCM, AMX, DCF and the mixture of these three drugs in Fenton oxidation; the experimental conditions shown in Table 3.5 are adopted.

Table 3.5 Experimental conditions for the optimization of initial H_2O_2 dosage and initial Iron catalyst (Fe^{2+} or Fe (LS)) in degradation of the selected drug by Fenton oxidation process

Selected Drug for treatment	Initial experimental conditions						
	$[PCM]_0$	$[AMX]_0$	$[DCF]_0$	Initial pH	$[Fe^{2+}]_0$ Range	$[Fe\ (LS)]_0$ Range	$[H_2O_2]_0$ Range
	mM	mM	mM	Optimum value	mM	mM	mM
PCM	0.066	-	-	3.0	0.000 – 0.022	-	0.15 – 1.47
	0.066	-	-	3.0	-	0.004 – 0.022	0.29 – 1.47
AMX	-	0.027	-	3.0	0.004 – 0.018	-	0.29 – 1.62
		0.027		3.0	-	0.009 – 0.022	0.29 – 1.32
DCF	-	-	0.031	3.5	0.009 – 0.022	-	0.00 – 1.62
			0.031	3.5	-	0.009 – 0.022	0.00 – 1.62
Mixture of drugs PCM	0.066	0.027	0.031	3.5	0.009 – 0.036	-	1.62 – 2.65
+ AMX + DCF	0.066	0.027	0.031	3.5	-	0.009 – 0.036	1.76 – 2.94

Procedure: The investigation for optimization of initial H_2O_2 concentration and initial Iron catalyst (Fe^{2+} or Fe (LS)) concentration is carried out at the experimental conditions shown in the Table 3.5. The similar experimental procedure, which is outlined in Fenton oxidation for the degradation of the selected drug, is followed to know the effect of initial H_2O_2 concentration and initial Iron catalyst (Fe^{2+} or Fe (LS)) concentration and to optimize the same for the maximum removal of the drug (Degradation) and the corresponding COD (Mineralization). During the oxidation process, the mixture of drug and Fenton reagent is continuously stirred with magnetic stirring for 3 h, while the treated sample concentrations are measured and corresponding sample COD values are determined after 24 of reaction time. From the results obtained, the optimum ratio of $[H_2O_2]_0$ / $[Fe^{2+}]_0$ and the optimum ratio of $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ are calculated. Similar procedure is adopted for the optimization of initial H_2O_2 concentration and initial Iron catalyst (Fe^{2+} or Fe (LS)) concentration in the oxidation of all the drugs in water by Fenton oxidation. The optimized values of initial H_2O_2 concentration, initial Iron catalyst (Fe^{2+} or Fe (LS)) concentration, ratio of $[H_2O_2]_0$ / $[Fe^{2+}]_0$ and the ratio of $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ obtained in Fenton oxidation are

considered for the investigation on effect of initial concentration, kinetic studies as well as photo-Fenton process for the treatment of selected drugs in water.

3.2.5 Effect of Initial Concentration of the Selected Drug

From the literature it is evident that the concentrations of the selected pharmaceutical in the aquatic environment are in the range of ng/L to µg/L. An initial concentration of the selected pharmaceutical from 10 mg / L to 50 mg / L is adopted keeping in view the analytical instruments available in our laboratory. The oxidation experiments are carried out at the optimum conditions for 24 hours; however, the drug degradation and COD removal are very slow and not appreciable after 240 minutes of reaction time in Fenton oxidation. Hence, further experiments are carried out for a reaction time of 240 minutes in Fenton oxidation. Similarly, the experiments in photo-Fenton process are carried out at the optimum conditions for 9 hours; but the drug removal and COD removal are significant within 120 minutes of reaction time. Therefore, the further experiments are conducted in photo-Fenton process for 120 minutes.

Table 3.6 Experimental conditions for the study of effect of initial concentration of the selected drug in degradation by Fenton oxidation and photo-Fenton oxidation

Selected Drug for treatment	Initial experimental conditions						
	$[PCM]_0$ Range	$[AMX]_0$ Range	$[DCF]_0$ Range	Optimum pH	Optimum $[Fe^{2+}]_0$	Optimum $[Fe(LS)]_0$	Optimum $[H_2O_2]_0$
	mM	mM	mM		mM	mM	mM
PCM	0.066 – 0.331	-	-	3.0	0.009	-	0.88
	0.066 – 0.331	-	-	3.0	-	0.013	0.88
AMX	-	0.027 – 0.137	-	3.0	0.009	-	0.88
		0.027 – 0.137		3.0	-	0.013	1.03
DCF	-	-	0.031 - 0.157	3.5	0.018	-	1.03
			0.031 - 0.157	3.5	-	0.013	1.03
Mixture of drugs PCM + AMX + DCF	0.066 – 0.331	0.027 – 0.137	0.031 - 0.157	3.5	0.018	-	2.06
	0.066 – 0.331	0.027 – 0.137	0.031 - 0.157	3.5	-	0.018	2.35

In order to find the in order to find the effect of initial concentration of the drug in degradation of PCM, AMX, DCF and the mixture of these three drugs in Fenton

oxidation and photo-Fenton oxidation; the experimental conditions shown in Table 3.5 are adopted.

Procedure: The similar experimental procedure, which is outlined in Fenton oxidation or photo-Fenton oxidation for the degradation of the selected drug, is followed to know the effect of initial drug concentration at the optimal conditions of pH, H_2O_2 and iron catalyst optimize the same for the maximum removal of the drug (Degradation) and the corresponding COD (Mineralization). The optimum ratios of $[Drug]_0$ / $[H_2O_2]_0$, $[H_2O_2]_0$ / $[Fe^{2+}]_0$ and $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ are maintained for all the concentrations of the selected drug. The drug concentration and corresponding COD removals are analyzed after a reaction time of 0, 1, 3, 5, 10, 15, 30, 45, 60, 120, 180 and 240 minutes in Fenton process. Similarly, the drug concentration and corresponding COD removals are analyzed after a UVC irradiation time of 0, 1, 3, 5, 10, 15, 30, 45, 60, 90 and 120 minutes in Fenton process.

3.2.6 Kinetic Studies on the Selected Drug Degradation

The kinetic models illustrated in literature (Chen and Pignatello 1997; Rivas et al. 2002; Kang et al. 2002) are comparatively complex involving a large number of reactions to illustrate the interactions among the chemical species involved in the oxidation process. Yet, the oxidation reactions of organic species may be described with a pseudo-second order kinetic models (Zazo and Cases 2005).

A number of chemical species are involved in the reaction scheme of Fenton oxidation, but, at given experimental conditions, OH radical is the primary oxidizing species in the overall process (Zazo and Cases 2005, Kang et al. 2002). In this study, the degradation rates of drug are described with pseudo-second order kinetics equation (Eq. 3.1).

$$-r_2 = kC_d{}^2 C_{OH}. = k' C_d{}^2 \quad \text{.....(3.1)}$$

In the present investigation, kinetic studies are conducted at the optimum conditions for 240 minutes of reaction time in Fenton oxidation and 120 minutes of UV irradiation time in photo-Fenton oxidation. The oxidation is fast in the beginning for

reaction time up to 5 minutes and therefore, the second-order kinetic equation has been fit up to the reaction time of 5 minutes (Zazo and Cases 2005).

3.2.7 Extraction of Iron from Laterite Soil by Leaching with HCl

Fig. 3.3 Schematic representation of Iron extraction from laterite soil

Iron is extracted from laterite soil as per the procedure explained by Olanipekun (2000). Laterite soil for the extraction of iron is procured from the earth crust in the local area. The dried laterite soil is crushed to powder and is passed through a 150µ sieve. 0.5g of this sieved soil is taken in a glass beaker and 20mL of 1: 1 HCl is added. This solution is mixed and grinded till the entire sample is dissolved. Then this beaker with sample is kept for heating on a sand bath for maximum evaporation till a residue is formed at the bottom of the beaker. The residue left is baked in an oven for 1 h. Again to this baked residue, 20mL of 1: 1 HCl is added and it is heated for 1 min, after heating 20mL of hot distilled water is added. This solution is filtered through a Whitman- 42 filter paper and the filtrate obtained is transferred to a Nessler's cylinder and is diluted up to 100mL. The resulting solution obtained after dilution is the iron extract from the laterite soil. The iron extraction from laterite is schematically represented in the Fig. 3.3.

3.2.8 Simultaneous Determination of PCM, AMX and DCF in Water using UV – VIS Spectrophotometer

A simple, rapid, economic, sensitive and accurate spectrometric method is developed for quantitative estimation of paracetamol (PCM), amoxicillin (AMX) and diclofenac (DCF) in water. Simultaneous determination of PCM, AMX and DCF in water by UV – Vis spectrophotometer is based on the additivity of absorbance of the three

drugs. The absorption maxima of the drugs are found be at 243 nm for PCM, 226 nm for AMX and 276 nm for DCF in demineralized water and these wavelengths are selected for the analysis. The drugs obeyed Beer – Lambert's Law in the concentration range of 0 - 25 mg/L at their respective wavelengths. Calibration curves of each drug at the selected wavelengths are established. Three simultaneous equations are formed with absorptivity coefficients, unknown concentration of the drugs in mixture and total absorbance of the mixture at all the three wavelengths. The standard absorptivity values are calculated at each wavelength and the quantity of drugs in water are calculated by solving matrix using Cramer's rule. This method can be applied successfully for the determination PCM, AMX and DCF, when they are in mixture. The calibration curves and the analytical validation parameters are given in the Appendix I.

3.3 Analytical Methods

With any research, one of the most important aspects is ensuring that sampling, analysis and system operations are performed consistently and properly throughout the experimental process. To achieve the most accurate and reliable results possible, extreme care is taken to ensure all lab and sampling equipment are as clean as possible. This is achieved by adhering to the methods and procedures described in Standard Methods for the Examination of Water and Wastewater (APHA 2005). All glassware used is thoroughly washed with soap and water immediately after use. To remove the organic matter (e.g. COD vials) chromic acid is used to clean the glassware. The glassware is rinsed with reagent water before use. In this study, pH, drug concentrations, COD, H_2O_2 concentration, iron concentrations are measured/ determined in every experiment and HPLC analysis is done for some experiments.

3.3.1 Drug Concentration with Spectrophotometer

The selected drug concentrations before and after treatments are measured to evaluate the degree of degradation of the contaminants during the selected AOP process. For this purpose a UV-VIS double beam spectrophotometer with a photomultiplier tube detector and controlled through PC, model Systronics 2201 is used. The system offers wavelength range from 190 to 999.9 nm, wavelength setting resolution 0.1 nm

(max.), and a variable spectral bandwidth from 0.5 nm to 6.0 nm. Fig. 3.4 shows the photo of spectrophotometer.

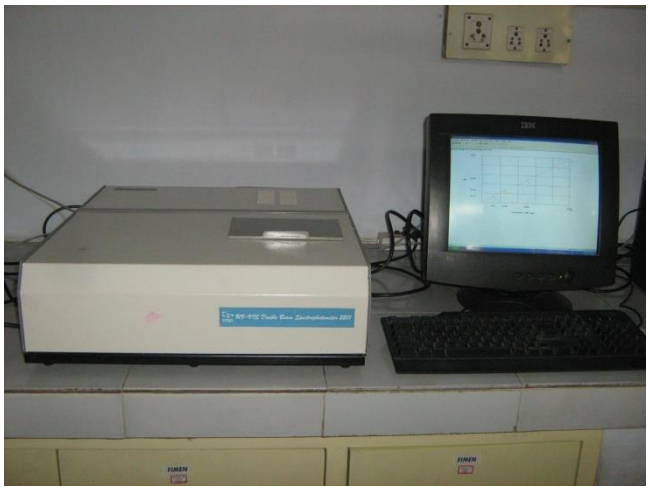


Fig. 3.4 Spectrophotometer used in the study

The principle of the spectrophotometer is based on the Beer Lamberts' law which states that the absorbance of light is proportional to the path length of the sample (cuvette) and concentration of the compound in the solution. The principle is based on the fact that the number of photons absorbed is directly proportional to the number or concentration of atoms, ions or molecules. But at higher concentrations the law does not holds good. The presence of other chemicals also interferes with the absorbance and concentration measurements.

Sampling: The supernatant is taken and filtered through 0.45-µm Millipore filter and sample is collected from filtered solution for the measurement of concentration with spectrophotometer. In case of DCF measurement, a sample collected from treated sample is added with acetonitrile and mixed thoroughly in order to take care of the precipitation and redissolution of DCF for pH less than 3.5 and then the sample is filtered through the 0.45-µm Millipore filter for the measurement of concentration with spectrophotometer.

Procedure: The concentration of the selected drug is found by 'Concentration by Standard Method'. The calibration curve already established for the selected drug is opened. The Millipore deionized water which is used to prepare the solutions is taken in the reference cuvette, the sample is taken in sample cuvette and placed in its

positions. The sample measurement is carried out by selecting the single wavelength & sample. The cell where the sample is kept is selected and name of the sample is entered in the corresponding cell. The readings for the absorbance and the concentration of the drug sample at the corresponding wavelength are displayed on single wavelength analysis. Similar procedure is adopted for all the drugs selected to measure the initial drug concentration as well as the concentration after treatment for a specified reaction time.

When the concentration of the drug is high, the sample is diluted and the concentration is measured. To get the corresponding concentration of the sample, the above reading is multiplied by the dilution factor. In order to make correction for the interference of the H_2O_2 present in the solution, standards of the H_2O_2 at different concentrations are prepared and the standard calibration curve of the concerned selected drug is used to measure the interference of the H_2O_2. A curve is plotted with H_2O_2 concentration vs. interference and slope of it gives the interference of H_2O_2 per mg of H_2O_2. This value is used to make correction corresponding to the H_2O_2 present in the solution of the drug after treatment by the selected AOP. In case of treatment for the mixture of the PCM, AMX and DCF, the interference on the measurement of one drug by the other two has also been observed. To make correction for this, the solutions of the mixture of drugs with different concentrations, but the concentration of each drug is equal in each solution, are prepared. The above procedure is adopted to determine the correction per mg of each drug on the other one and is used in finding the final concentration of the concerned selected drug. The interference of pH on the measurement of concentration is very less and negligible. The filtration of sample is taken care of the settled iron in the reactor. The above mentioned procedure is adopted to make correction for the dissolved iron in the solution.

3.3.2 Chemical Oxygen Demand (COD)

The COD is determined to evaluate the degree of mineralization of the selected drugs during the AOP process. For the digestion of sample in COD determination, COD digester – ET125 (Lovibond, Germany) is used. To improve the accuracy of the COD determination, the FAS titrant is prepared with Molarity of 0.025M instead of 0.1M. FAS solution is prepared weakly but it is standardized daily against standard $K_2Cr_2O_7$

digestion solution. The COD is analyzed in duplicate for each sample to yield the most reliable data. Fig. 3.5 shows the photo of COD digester used in the present study.

Fig. 3.5 COD digester used in the study

Sampling: The supernatant is taken and filtered through 0.45-µm Millipore filter and the sample is collected from filtered solution for the measurement of COD. In case of DCF measurement, a sample collected from treated sample is not added with acetonitrile as it impart high COD to the sample but the solution is mixed thoroughly and the sample is collected for COD determination.

Procedure: The COD of the samples is determined by Closed Reflux, Titrimetric Method (5220 C) as per the procedure outlined in the Standard Methods (APHA 2005).

$$COD\ as\ mgO2/\ L = \frac{(A-B)xMx8000}{mL\ sample} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots\ldots\ldots\ldots\ldots (3.1)$$

Where: A = mL FAS used for blank

B = mL FAS used for sample

M = Molarity of FAS, and

8000 = milliequivalent weight of oxygen x 1000 mL/L

Final COD obtained using Eq. 3.1 is quantitatively corrected for hydrogen peroxide interference according to the correlation equation (Eq. 3.2) given by Kang et al. (1999).

$$COD(mg/L) = COD_m - (0.4706 - 4.06\times10^{-5}\times[H_2O_2])\times[H_2O_2] \quad \text{.....(3.2)}$$

.Where:

COD_m = the measured chemical oxygen demand values in mg / L as per Eq. 3.1

$[H_2O_2]$ = Hydrogen peroxide concentration present in solution after treatment in mg / L

3.3.3 Hydrogen peroxide (H_2O_2)

H_2O_2 concentration in the sample is determined by Iodometric Titration Method (Kolthoff 1920). Iodometry can be applied to measure many oxidizing agents. The principle is that an excess of iodide is added to the sample in acidic solution. Then, the oxidizing agent reacts quantitatively with the iodide to form a stoichiometrically equivalent amount of triiodide anion, Eq. (3.3). By titration the amount of triiodide anion formed is determined by addition of thiosulphate, which reacts quantitatively to tetrathionate, Eq. (3.4). Starch, forms a blue-grey complex with the triiodide ion. Consequently, in the presence of starch as an indicator the complete disappearance of the triiodide ion can be visually observed, because the assay's colour changes from dark blue-grey to transparent.

$$H_2O_2 + 3I^- + 2H^+ \leftrightarrow I_3^- + 2H_2O \quad \text{.....(3.3)}$$
$$I_3^- + 2S_2O_3^{2-} \leftrightarrow 3I^- + S_4O_6^{2-} \quad \text{.....(3.4)}$$

The method is somewhat less accurate than the permanganate titration, but is less susceptible to interference by organics and is more suitable for measuring mg / L levels of H_2O_2. The other oxidizing agents will also produce iodine but the reducing agents will react with the liberated iodine. The contribution from these oxidizing agents can be omitted by acid and molybdate catalyst.

Procedure: Typically 25 mL of sample is taken in conical flask. 10 mL H_2SO_4 (20%) and 10 - 15 mL KI (1% w/v) solution and then 2 drops of ammonium molybdate are

added to the sample. Upon addition of iodide solution in the presence of an oxidant the solution becomes dark yellow. The solution is left standing for 20 - 30 min at room temperature in a closed bottle protected from light. The sample mixture is titrated with 0.1 N sodium thiosulphate till colour changes to straw yellow colour. Then, 2 – 5 drops of starch solution are added as an indicator. The solution becomes dark blue upon the addition of the starch solution. Subsequently, titration is continued with 0.1 N $Na_2S_2O_3$ solutions. The hydrogen peroxide concentration can be calculated with Eq. (3.5) assuming that all oxidation of iodide to triiodide ion is due to its presence.

$$C_{H_2O_2} = \frac{V_{Na_2S_2O_3}}{V_{Sample}}.x1700 mg/L \quad \text{.....(3.5)}$$

The sodium thiosulphate is standardized periodically to evaluate its strength and then used in the experiments.

3.3.4 Iron concentration (Fe^{2+}, Fe^{3+} and total iron)

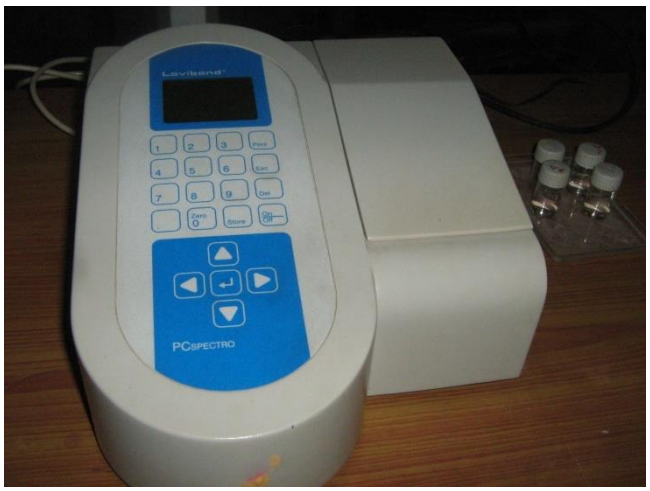


Fig. 3.6 Spectrocolorimeter used in the study

The iron may exist in both ferrous and ferric forms. The form of iron may be altered as result of oxidation or reduction. Normally ferrous iron is dissolved in water, and ferric iron is readily settles. Oxidizing agents (such as hydrogen peroxide) interfere with the test because they oxidize ferrous iron to ferric iron, which does not form

complexes with the reagent. The ferric iron combines with Thiocynate ions to form a red coloured ferric Thiocynate that can be measured colorimetrically at 510nm.

The dissolved iron, considered to be that passing through a 0.45-µm membrane filter, may include colloidal iron. The value of the determination depends greatly on the care taken to obtain a representative sample. When taking a sample portion for determining iron in suspension, shake the sample container often and vigorously to obtain a uniform suspension of precipitated iron. For precise determination of total iron, use a separate container for sample collection. Treat with acid to place iron in solution and prevent adsorption or deposition on the walls of the sample container. The Iron concentration is measured with Spectrocolorimeter (PC Spectroll, Lovibond, Germany). Fig. 3.6 shows the photo of Spectrocolorimeter used in the study.

Procedure: Series of standards iron standards ranging from 0.5 to 2.5 mg / L are prepared using ferrous ammonium sulphate. Each iron standard is mixed with 4 mL of 4N HCl, 5 mL 5% KSCN and made to 100mL with DI water in a Nessler's tube. The spectrometer is calibrated using these standards by setting the wavelength at 510 nm and the method is stored in it. AOP treated solution is thoroughly mixed and some sample is taken in the Nessler's tube. To this, 4 mL of 4N HCl, 5 mL 5% KSCN and made to 100mL with the same sample. The mixture is thoroughly mixed and kept for 15 minutes to develop a stable orange colour. Then, sample is taken in 10 mm path length cuvette and iron concentration in the sample is measured using the calibrated method stored in the spectrophotometer.

3.3.5 pH

The pH value is by definition the negative common logarithm of the activity of the positively charged hydrogen ions in aqueous solution. Whenever the pH value of a solution is reported this data should be accompanied by the temperature at which it was measured. For the measurement of pH, a SensoDirect pH 100 meter (Lovibond, Germany) is used. The 'SensoDirect pH 100' is a portable, battery-powered pH meter with a pH range of 0 – 14. The unit has an automatic check on the battery level. The gel electrode to the device can be used anywhere over the pH range 0 – 14 with a resolution of 0.01 pH and is resistant to temperature from 0 – 80^{o} C.

The pH of the solutions is measure at room temperature (27 ± 3^{o} C) but the solution temperature is around 26 ± 2 ^{o} C. This measurement was performed with temperature compensation carried out manually in the pH meter.

Procedure: Measurement of pH is carried out by submersing the electrode and waiting until the instrument reached equilibrium. A correct calibration of the pH meter is essential for correct measurement. To this end, the pH meter is calibrated with two point calibration with two standard buffer solutions at pH 4.00 and pH 7.00 obtained from Lovibond. The calibration of pH meter is performed weekly but to achieve greater accuracy it is re-calibrated before each new series of measurements. The electrode connector is never held by hand to avoid false readings. The electrode is always kept fit with cap filled with 3M KCl solution.

3.3.6 HPLC Analysis

The HPLC analysis is carried out for 10 mg / L initial concentration of the model pharmaceutical compound to follow the degradation. The chromatographic system employed in this study is Shimadzu LC-10AT HPLC. The system consists of 2LC-10ATvp solvent delivery pump (sub-master / A pump and vice / B pump), Rheodyne 7725i manual injection valve, SPD-10Avp UV - Vis detector, SCL-10AVP system control device, a desktop computer and other components. The chromatographic column used for separation was a C18 reversed phase column (µBondapak 5 micron, 4.6 x 300 mm). The whole system control and the data evaluation are conducted via PC interface LC solution software.

Procedure: An appropriate volume of sample is drawn and filtered through 0.45 um pore size Millipore syringe-driven filters. Blank (one injection), standard drug solution (2 injections) and the drug sample (one injection) are separately injected into the HPLC system. The chromatograms are recorded and the response for major peaks is measured.

There is a linear relationship between the drug peak area and the drug concentration in the sample. Hence, the drug concentration in the sample can be calculated by using the peak area of the drug standard and its concentration.

Chromatographic Conditions: The chromatographic conditions used in the analysis of the selected drugs are shown in the Table 3.7.

Table 3.7 Chromatographic conditions used in the HPLC analysis of PCM, AMX, and DCF

Condition	Drug analyzed		
	PCM	AMX	DCF
Column	C-18, 5µm, 4x300 mm	C-18, 5µm, 4x300 mm	C-18, 5µm, 4x300 mm
Column Temperature	30^{o} C	30^{o} C	30^{o} C
Flow rate	1.5 mL / min	1.5 mL / min	1.0 mL / min
Wavelength	243 nm	226 nm	276 nm
Injection volume	20 µL	20 µL	20 µL
Gradient time	30 minute	10 minute	10 minute
Diluent	Methanol: Water = 10: 90 (v/v)	6.8g monobasic potassium phosphate in 1L water, pH = 5 ± 0.1	Methanol
Mobile phase	Methanol : water (0.01M Sodium petanesulphonate + formic acid (0.2%)) = 10: 90 (v/v)	Diluent: Acetonitrile = 96: 4 (v/v)	Methanol: Water = 70: 30 (v/v) + 1 mL Glacial acetic acid

CHAPTER 4

RESULTS AND DISCUSSION

Chapter 4

RESULTS AND DISCUSSION

A detailed study is carried out in order to optimize the reaction conditions like pH, H_2O_2 Fe^{2+} and Fe (LS) dosages for the maximum drug degradation and the maximum COD removal (mineralization). Then, the effect of initial drug concentration on the degradation and mineralization of drug is evaluated. Further, the kinetic study of drug degradation is conducted and the corresponding chemical reaction kinetic constants are calculated. The Fenton and photo-Fenton oxidation processes for the possible degradation and mineralization of PCM, AMX and DCF are evaluated.

4.1. Fenton and Photo-Fenton Oxidation of Paracetamol in Water

4.1.1 Spectral and Chemical Characterization of Paracetamol

The UV-VIS spectrum of PCM is recorded from 190 to 500 nm using UV-VIS spectrophotometer and the absorbance peak for PCM is observed to be at wavelength 243 nm (Fig.4.1 (a)). A calibration curve between sample absorbance and concentration is established with 4 different PCM concentrations in the range of 6.25 to 50 mg/L (41.34 x 10^{-3} to 330.69 x 10^{-3} mM). For the range of concentrations considered; a linear relationship between absorbance and concentration is established (Fig. 4.1 (b)). A COD calibration curve (Fig. 4.1 (c)) between PCM concentration and COD is established for PCM concentrations ranging from 5 mg/L to 50 mg/L (33.07 x 10^{-3} to 330.69 x 10^{-3} mM). The COD is about 1.55 mg/L per mg (6.61 x 10^{-3} mM) of PCM concentration, and this value is used in calculating the corresponding initial COD of the PCM samples. The PCM sample concentration, before and after treatment, is measured and the initial COD values are calculated in the subsequent experiments with the use of calibration curves.

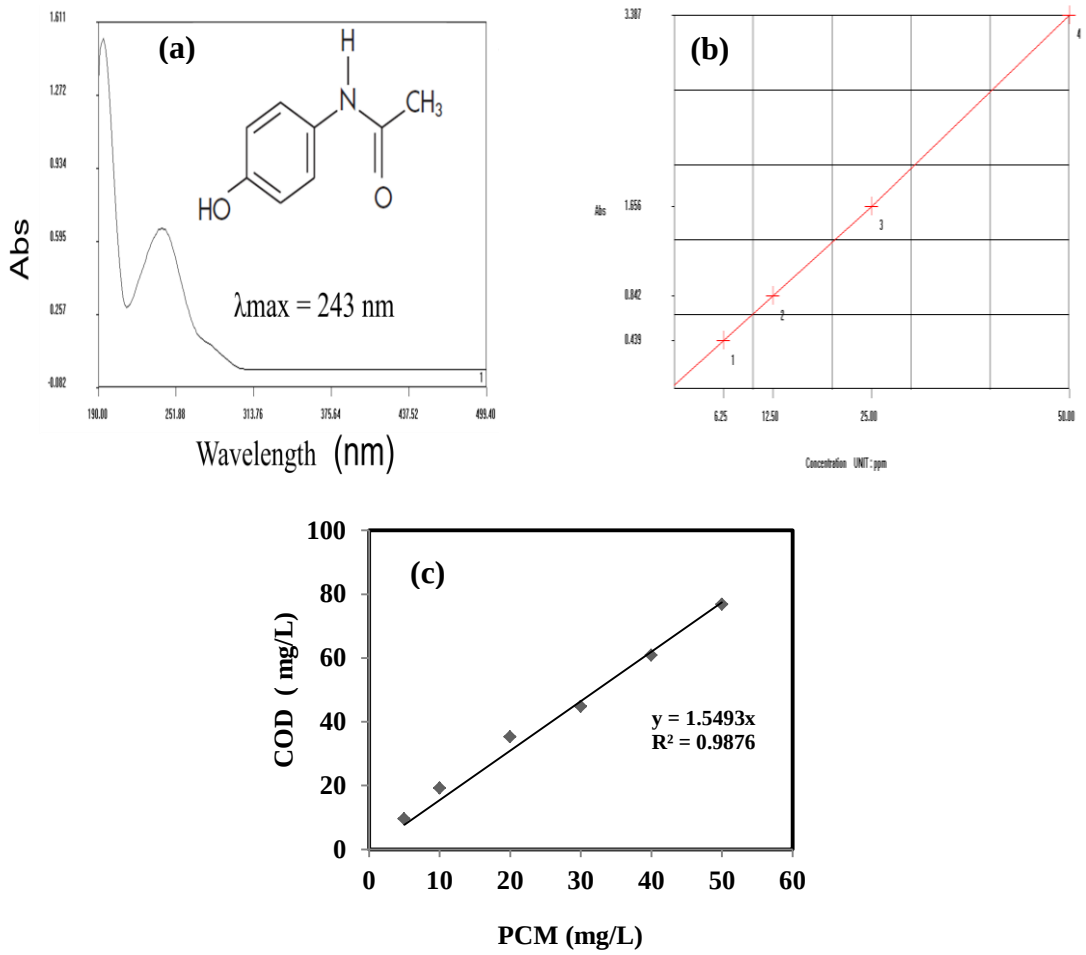


Fig. 4.1 (a) UV-VIS Spectrum of PCM with Chemical Structure (b) Calibration Curve for PCM (Standard data from UV-VIS double beam spectrophotometer) (c) Calibration Curve for COD of PCM.

4.1.2 Fenton Oxidation of Paracetamol Using Fe^{2+} as Iron Catalyst

This part deals with the investigation of effect of various parameters like pH on degradation and mineralization of PCM and chemical kinetic studies on PCM degradation.

Effect of pH

The oxidation experiments are conducted at different pH values varying from 2.0 to 5.5 with initial PCM concentration of 66.14 x 10^{-3} mM, $[H_2O_2]_0$ = 0.59 mM and $[Fe^{2+}]_0$ = 35.81 x 10^{-3} mM. The maximum percent PCM degradation and percent COD removal are observed to be 77.83 and 75.00 respectively at pH 3 (Fig. 4.2). The Fig. 4.2 shows percent paracetamol degradation and COD removal at different pH,

$[PCM]_0$ = 66.14 x 10^{-3} mM, $[H_2O_2]_0$ = 0.59 mM and $[Fe^{2+}]_o$ = 35.81 x 10^{-3} mM. From the Fig. 4.2 it is clearly visible that the PCM removal is less for the other values of pH.

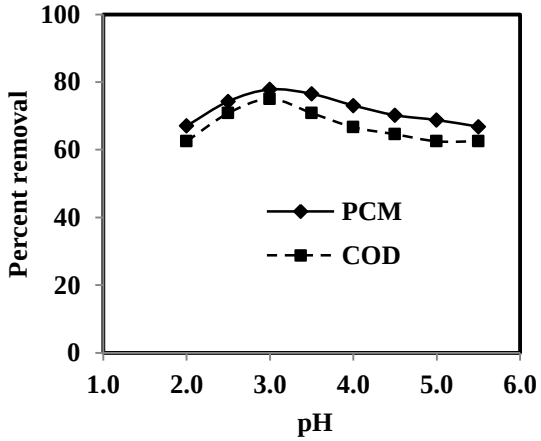


Fig. 4.2 Percent PCM degradation and percent COD removal at different pH; [Reaction conditions; Fenton oxidation, $[PCM]_0$ = 66.14 x 10^{-3} mM, $[H_2O_2]_0$= 0.59 mM and $[Fe^{2+}]_0$ = 35.81 x 10^{-3} mM, reaction time 24 hours].

At pH 3, PCM removal is maximum and it may be due to the formation of more $Fe(OH)^+$ which has much higher activity than Fe^{2+} in Fenton's oxidation (Badawy and Ali 2006). When pH is greater than 3, oxidation efficiency rapidly decreases due to auto-decomposition of H_2O_2 affecting the production of OH radicals (Badawy and Ali 2006) and deactivation of ferrous catalyst with the formation of ferric hydroxide precipitates (Luis et al. 2009). Also there is a decrease in oxidation potential of hydroxyl radical with increase in the pH value (Lucas and Peres 2006). When pH is less than 3, the reaction of H_2O_2 with Fe^{2+} is seriously affected that leads to reduction in hydroxyl radical production and water is formed by the reaction of OH radicals with H^+ ions (Lucas and Peres 2006).

The COD removal is maximum at pH 3 but on either side of the pH 3 the COD removal is less. The COD removals is observed to be less than the PCM degradation and it indicates the formation of oxidation intermdiates. The optimum pH value of 3, where the maximum degradation and mineralization has occurred is maintained in all the susequent experiments on degradation of PCM.

Effect of H_2O_2 and Fe^{2+} Concentration

Hydrogen peroxide is the basis for the radical generation in Fenton's Oxidation. The hydroxyl radicals either oxidize the pollutant and other intermediates or react with the oxidant itself to cause reduction in pollutant removal efficiency. Hence, an investigation of H_2O_2 consumption and optimization in Fenton's oxidation is vital for using H_2O_2 efficiently and also for the other best possible conditions that are to be found in aforesaid process.

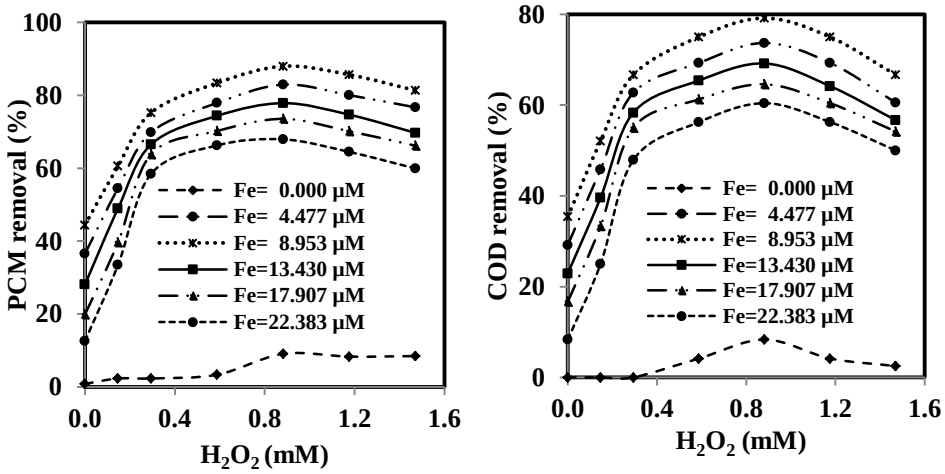


Fig. 4.3 Variations in (a) percent PCM degradation, (b) percent COD removal [Reaction conditions; Fenton oxidation, pH= 3, $[PCM]_0$ = 66.1 x 10^{-3} mM, $[H_2O_2]_0$ = 0 – 1.47 mM, $[Fe^{2+}]_0$ = 0 – 22.4 x 10^{-3} mM, reaction time = 24 hours].

The investigation for optimization of hydrogen peroxide concentration is carried out by varying H_2O_2 concentration from 0 to 1.47 mM, varying the iron concentrations in the range of 0 – 22.4 x 10^{-3} mM for $[PCM]_0$ 66.1 x 10^{-3} mM at solution pH 3. The maximum paracetamol degradation is 88.0 % and the corresponding COD removal is 79.2% at H_2O_2 concentration of 0.88 mM and $[Fe^{2+}]_o$ of 8.95 x 10^{-3} mM after a reaction time of 24 hours. The reaction equation 4.1 describes the reaction of complete mineralization of PCM in the Fenton Oxidation process.

$$C_8H_9NO_2 + 21H_2O_2 + Fe(II) \rightarrow 8CO_2 + 25H_2O + HNO_3 + Fe(II) \ldots\ldots\ldots\ldots (4.1)$$

The quantity of hydrogen peroxide required, based on stoichiometric calculation (Eq. 4.1), for the complete mineralization of paracetamol is 4.72 mg (0.13 mM) of H_2O_2 per mg (6.61 x 10^{-3} mM) of paracetamol. However, in the present study, the

maximum percent PCM degradation is observed to be 88.0 and the corresponding percent COD removal is 79.2 at H_2O_2 concentration of 0.88 mM after a reaction time of 24 hours (Fig. 4.3). Initially, the drug and COD removal efficiency is increased with increase in H_2O_2 concentration and further increase in the H_2O_2 concentration decreased the removal efficiencies. The maximum PCM degradation and COD removal is observed at 0.88 mM of H_2O_2. When $[H_2O_2]_0$ is less than 0.88 mM, the degradation and mineralization are less, which is due to less production of OH radicals. When $[H_2O_2]_0$ is greater than 0.88 mM, the degradation and mineralization are less because of the scavenging effect of OH radicals with increase in the H_2O_2 concentration. This can be explained by the fact that the very reactive OH radicals are consumed by the increased H_2O_2 that results in the generation of less reactive OOH radical (Eq. 4.2) (Hsueh et al. 2005) and the hydroxyl radical is scavenged according to the reactions (Eqs. 4.3 and 4.4) (Chen and Pignatello 1997).

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \quad \text{(4.2)}$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad \text{(4.3)}$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad \text{(4.4)}$$

The results obtained for the removal efficiencies can be related to the incomplete mineralization and the presence of intermediates in the aqueous solution as can be seen in Fig. 4.3.

Both the Paracetamol degradation and COD removal from the aqueous solution are significantly improved even with the addition of very low concentrations of Fe^{2+} to H_2O_2. The variations in percent PCM degradation and COD removal under the different concentrations of the Fe^{2+} and H_2O_2 maintaining pH of 3, reaction time of 24 hours can be observed in Fig. 4.3. The maximum paracetamol degradation and COD removal are observed to be 9.10% and 8.33% respectively with oxidation by H_2O_2 alone. But the paracetamol degradation and COD removal increased up to 88.0% and 79.2% respectively with the addition of Fe^{2+} to the solution. The max paracetamol degradation and COD removal are observed to be 88.0% and 79.2% respectively at

8.95 x 10^{-3} mM Fe^{2+} concentration. The degradation and mineralization increased with increase in Fe^{2+} concentration due to increase in OH radical production (Rivas et al. 2002; Yilmaz et al. 2010). At higher Fe^{2+} concentrations the paracetamol and COD removals are less due to the ferrous ion inhibition that occurs when high concentration of Fe^{2+} is present in the system and Fe^{2+} itself can react with OH radicals resulting in the scavenging of OH radical (Hsueh et al. 2005). The observed ratios, $[PCM]_0$ / $[H_2O_2]_0$ = 1 : 13.3 (molar) and $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 98.6 : 1 (molar) at which degradation and mineralization is the maximum, are maintained in the further experiments for studying the effect of initial PCM concentration.

Effect of Initial PCM Concentration

The oxidation experiments are carried out at the optimum conditions for 24 hours; however, the PCM degradation and COD removal are very slow and not appreciable after 240 minutes of reaction time. Hence, further experiments are carried out for a reaction time of 240 minutes. The variations in percent PCM degradation and percent COD removals at optimum conditions for 240 minutes of reaction time are shown in Fig. 4.4.

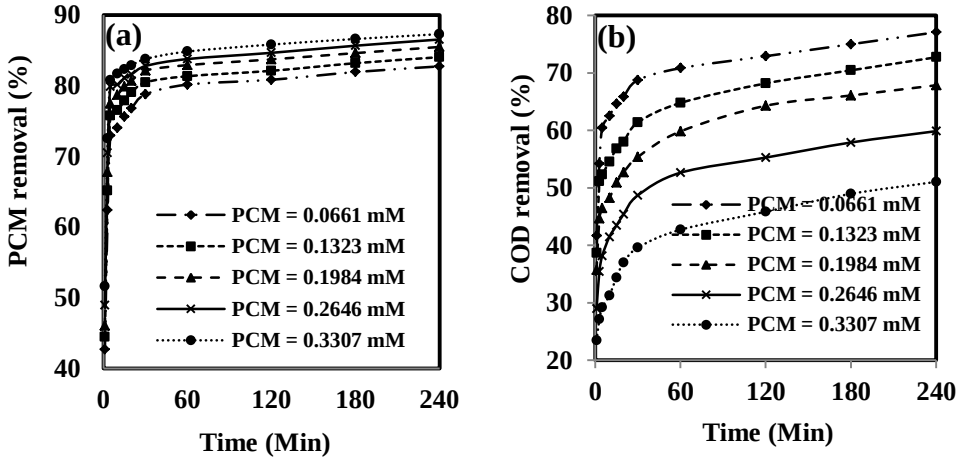


Fig. 4.4 Variations in (a) percent PCM degradation and (b) percent COD removal; [Reaction conditions; Fenton oxidation, pH 3, $[PCM]_0$ / $[H_2O_2]_0$ = 1 : 13.3 (molar) and $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 98.6 : 1 (molar), reaction time 240 min].

The percent PCM degradation and percent COD removal are observed as 73.0 and 60.4 respectively in 5 minutes, whereas 83.0 percent PCM degradation and 77.1 of percent COD removal are observed in 240 minutes for 66.1 x 10^{-3} mM initial

concentration of PCM. With the increase in PCM concentration from 66.1 x 10^{-3} to 330.7 x 10^{-3} mM, the percent drug removal increased from 82.7 to 87.3 and the percent COD removal decreased to 51.0 from 77.1. The degradation of PCM increases and the mineralization decreases with increase in initial PCM concentration.

The degradation of PCM can be well supported by comparing the UV-VIS spectrum of the sample before and after treatment. The UV-VIS spectrum, before treatment, has a peak at 243 nm in the UV region as seen in the Fig. 4.5. But, in the UV-VIS spectrum of treated sample, peak at 243 nm is disappeared, indicating the degradation of PCM in Fenton oxidation.

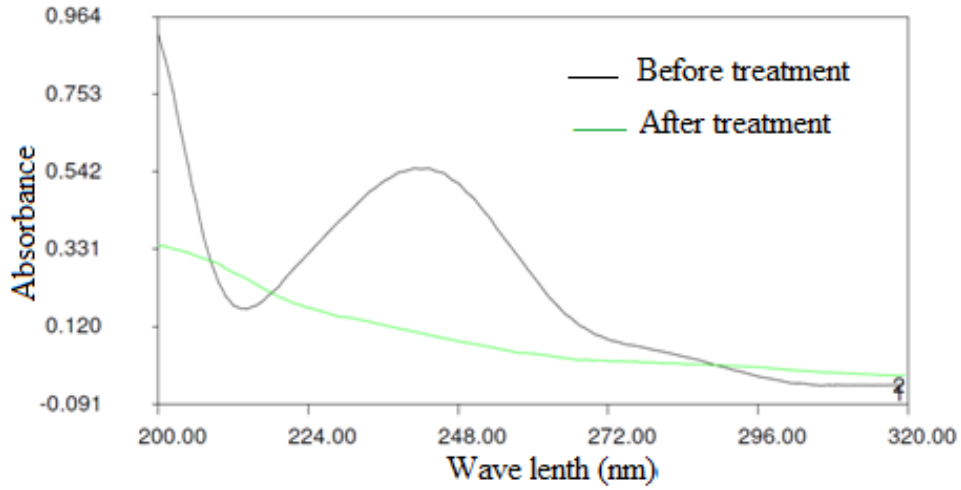


Fig. 4.5 UV – VIS absorbance spectra for PCM [Reaction condition: Fenton oxidation, pH = 3, $[PCM]_0$ = 66.1 x 10^{-3} mM, $[H_2O_2]_0$ = 0.88 mM, $[Fe^{2+}]_0$ = 8.95 x 10^{-3} mM, reaction time 240 min]

At the optimum $[H_2O_2]_0$ / $[Fe^{2+}]_0$ ratio of 98.6: 1 (molar), degradation of the drug increases with increase in its initial concentration. The fact that the disappearance of PCM increases with the substrate concentration clearly means that a competitive reactions are occurring. This probably due to synergetic effect of OH radicals along with the drug radicals formed in the Fenton oxidation wherein both the kinds of the radicals may degrade the substrate molecule. On the other hand, the formation of intermediates also may increase with increase in substrate concentration and hence COD removal decreased with increase in DCF concentration. This result is comparable with the literature, where COD removal of pharmaceutical wastewater by

Fenton's oxidation is more for the lower initial concentrations of drugs (Tekin et al. 2006; Yilmaz et al. 2010).

Kinetic Studies on PCM Degradation

In the present investigation, kinetic studies are conducted at the optimum conditions for 240 minutes of reaction time. The oxidation is fast in the beginning for reaction time up to 5 minutes and therefore, the second-order kinetic equation has been fit up to the reaction time of 5 minutes (Zazo et al. 2005). The Fig.4.6 shows the trend of a pseudo second-order reaction kinetic model (Eq. 3.1) for initial PCM concentrations from 10 - 50 mg/L at optimum conditions in the 5 minutes.

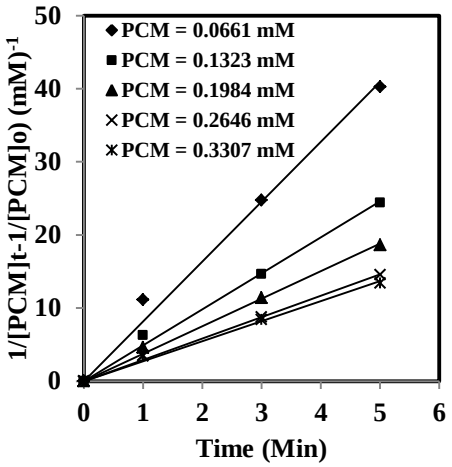


Fig. 4.6 Trend of pseudo-second order reaction kinetics for degradation of PCM in 5 min; [Reaction conditions; Fenton oxidation, pH 3, $[PCM]_0$ / $[H_2O_2]_0$ = 1 : 13.3 (molar), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 98.6 : 1 (molar) and $[PCM]_0$ = 66.1 x 10^{-3} to 330.7 x 10^{-3} mM].

The values obtained for the pseudo second-order kinetic constants at ambient temperature (27 ± 3^o C) are summarized in Table 4.1. When other conditions like nature of the reactants, temperature, light, catalysts and solvent used etc are constant; the reaction rate depends up on the concentration of the drug, concentration of OH radicals for all reaction rates (Arnaut et al. 2007). It is observed from the results that the rate of degradation decreased with the increase in initial PCM concentration. The rate constant decreased with increase in concentration of PCM and it is because the rate constant in a second-order reaction is inversely proportional to the initial concentration of the reactant.

Table 4.1 Pseudo Second order kinetic rate constants for degradation of PCM by Fenton oxidation using Fe^{2+} as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[PCM]_0$ mM	$[Fe^{2+}]_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}s^{-1}$	R^2
66.1×10^{-3}	8.95×10^{-3}	0.88	136.4	0.990
132.3×10^{-3}	17.9×10^{-3}	1.76	81.9	0.994
198.4×10^{-3}	26.7×10^{-3}	2.65	62.7	0.996
264.6×10^{-3}	35.8×10^{-3}	3.53	48.8	0.997
330.7×10^{-3}	44.8×10^{-3}	4.41	45.6	0.995

Similar kinetic studies are carried out for Fe (LS) in Fenton's reagent in the subsequent studies.

4.1.3 Fenton Oxidation of Paracetamol Using Fe (LS) as Iron Catalyst

The optimum pH value of 3 obtained during the investigation of PCM degradation using Fe^{2+} is maintained for the Fenton experiments with Fe (LS). The effect of various parameters like $[H_2O_2]_0$, [Fe (LS)] and $[PCM]_0$ on Fenton oxidation of PCM using Fe (LS) as iron catalyst are elaborated below.

Effect of H_2O_2 and Fe (LS) Concentration

The Fenton oxidation experiments are conducted to investigate optimum hydrogen peroxide concentration with Fe (LS) in Fenton's reagent. The hydrogen peroxide concentration is varied from 0.294 to 1.47 mM and Fe (LS) concentration is changed from 4.48×10^{-3} to 22.4×10^{-3} mg/L for initial PCM concentration of 66.1×10^{-3} mM at initial solution pH of 3. Fig. 4.7 shows the variations in percent PCM degradation and COD removal under the different dosages of Fe (LS) and H_2O_2 for 66.1×10^{-3} mM initial concentration of PCM at pH of 3, reaction time of 24 hours. It is observed that the maximum percent PCM degradation is 80.1 and the corresponding percent COD removal is 75.0 at initial H_2O_2 concentration of 0.88 mM and initial Fe (LS) concentration of 13.3×10^{-3} mM after a reaction time of 24 hours.

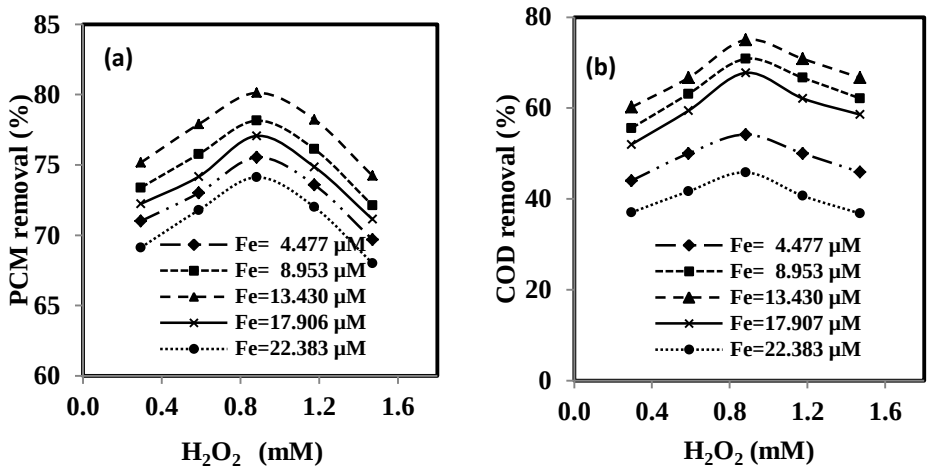


Fig. 4.7 Variations in (a) percent PCM degradation (b) percent COD removal; [Reaction conditions; Fenton oxidation, pH = 3, $[PCM]_0$ = 66.1 x 10^{-3} mM, $[H_2O_2]_0$ = 0.29 - 1.47 mM, $[Fe\ (LS)]_0$ = 4.48 x 10^{-3} to 22.4 x 10^{-3} mM].

The removal efficiency increased up to a maximum level with increase in H_2O_2 concentration and further increase in the H_2O_2 concentration decreased the removal efficiency. Both the PCM degradation and COD removal increased with addition of Fe (LS). This is because sufficient catalyst is required to produce more amounts of OH radicals. It has also been observed that at higher Fe (LS) concentrations the PCM and COD removals are reduced. This is due to the scavenging of OH radicals by higher catalyst concentrations. As per the results obtained, the optimum $[PCM]_0$ / $[H_2O_2]_0$ molar ratio 1 : 13.3 and molar ratio of $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ = 65.7 : 1 are maintained in the subsequent experiments conducted to investigate the effect of initial PCM concentration.

Effect of initial PCM concentration

The initial PCM concentration is varied from 66.1 x 10^{-3} to 330.7 x10^{-3} mM with the optimum $[PCM]_0$ / $[H_2O_2]_0$ molar ratio 1 : 13.3 and the optimum $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ molar ratio 65.7 : 1 constant for all the concentrations of PCM. Fig. 4.8 shows the variations in percent PCM degradation and percent COD removal at the optimum conditions in 240 minutes of reaction time.

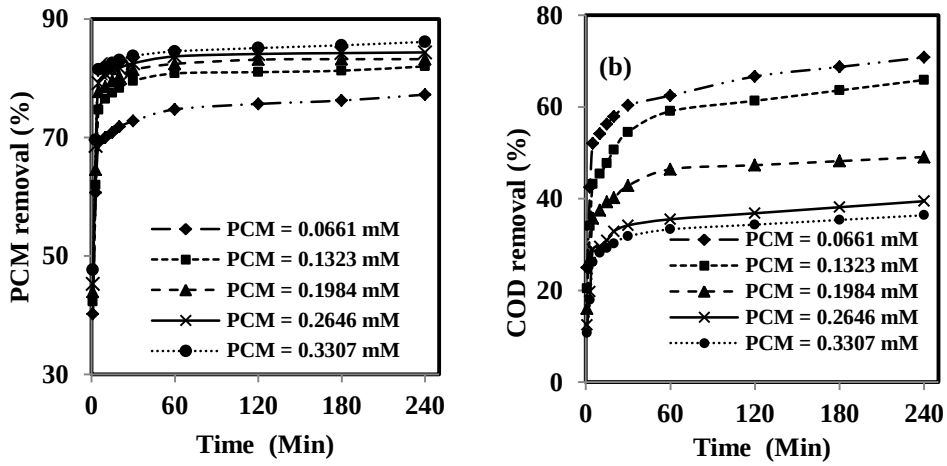


Fig. 4.8 Variations in (a) percent PCM degradation and (b) percent COD removal; [Reaction conditions; Fenton oxidation, pH 3, $[PCM]_0$ / $[H_2O_2]_0$ = 1 : 13.3 (molar) and $[H_2O_2]_0$ / [Fe (LS)]$_0$ = 65.7 : 1 (molar), reaction time = 240 min].

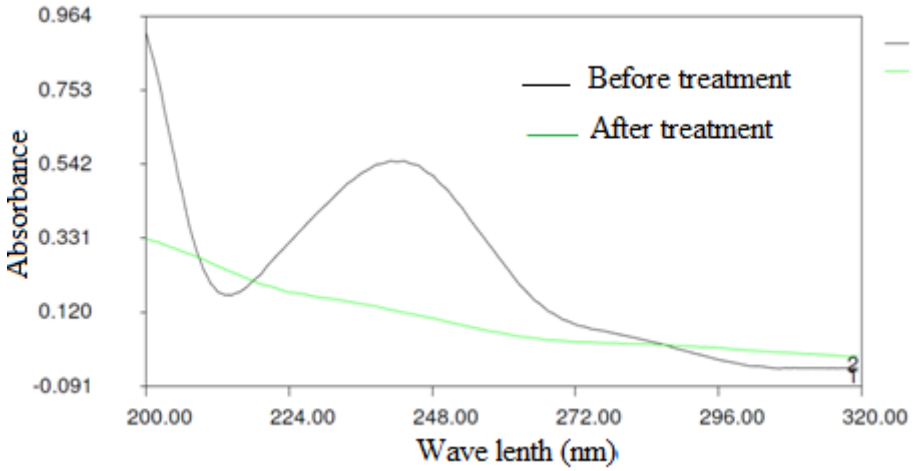


Fig. 4.9 UV – VIS absorbance spectra for PCM [Reaction condition: Fenton oxidation, pH = 3, $[PCM]_0$ = 66.1 x 10^{-3} mM, $[H_2O_2]_0$ = 0.88 mM, [Fe (LS)]$_0$ = 13.3 x 10^{-3} mM, reaction time 240 min]

The percent PCM degradation and the percent COD removal are 69.2 and 52.1 respectively in 5 minutes where as 77.2 percent PCM degradation and 70.8 percent COD removal is observed in 240 minutes for 10 mg/L initial PCM concentration. The percent drug removal increased from 77.2 to 86.1 and the percent COD removal decreased from 70.8 to 36.4 with the increase in drug concentration from 66.1 x 10^{-3} to 330.7 x10^{-3} mM. The use of Fe (LS) in Fenton reagent also followed the similar PCM degradation trend as that of Fe^{2+}. At the optimum $[H_2O_2]_0$ / [Fe (LS)]$_0$ ratio,

degradation of the drug increases with increase in its initial concentration is due to higher probability of availability of the drug molecules to the OH radicals for the oxidation. The reduction in COD removal at high pollutant concentrations is due to the formation of intermediate oxidation products. The degradation of PCM can also be observed by comparing the spectrum of the sample before and after treatment. The spectrum, before treatment, has a peak at 243 nm is disappeared in the spectrum of the sample after treatment as seen in the Fig. 4.9.

Kinetic Studies on PCM Degradation

Kinetic studies are carried out at the optimum conditions for 240 minutes of reaction time. The oxidation is fast in the beginning for reaction time up to 5 minutes and therefore, the second-order kinetic equation has been fit up to the reaction time of 5 minutes (Zazo and Cases 2005). The Fig.4.10 shows the trend of a pseudo second-order reaction kinetic model (Eq. 3.1) for initial PCM concentrations from 66.1 $x10^{-3}$ to 330.7 $x10^{-3}$ mM at optimum conditions in the 5 minutes.

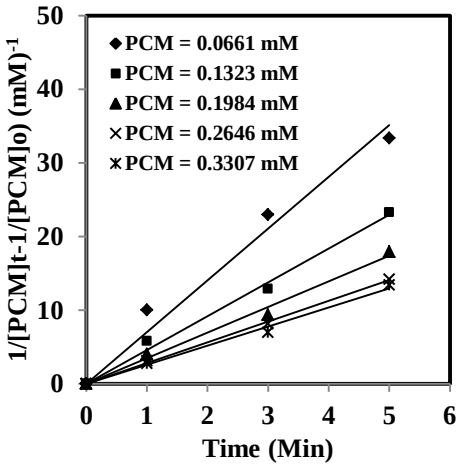


Fig. 4.10 Trend of pseudo-second order reaction kinetics for degradation of PCM in 5 min; [Reaction conditions; Fenton oxidation, pH 3, $[PCM]_0$ / $[H_2O_2]_0$ = 1 : 13.3 (molar), $[H_2O_2]_0$ / [Fe (LS)]$_0$ = 65.7 : 1 (molar), and $[PCM]_0$ = 66.1 $x10^{-3}$ to 330.7 x 10^{-3} mM].

The values obtained for the pseudo second-order kinetic constants at ambient temperature (27 ± 3^o C) are summarized in Table 4.2. It is observed that the rate of degradation decreased with the increase in initial PCM concentration. This can be

supported by the fact that the rate constant in a second-order reaction is inversely proportional to the initial concentration of the reactant.

Table 4.2 Pseudo Second order kinetic rate constants for degradation of PCM by Fenton oxidation using Fe (LS) as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[PCM]_0$ mM	$[Fe\ (LS)]_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}s^{-1}$	R^2
66.1 x 10^{-3}	13.4 x 10^{-3}	0.88	117.0	0.976
132.3 x 10^{-3}	26.9 x 10^{-3}	1.76	76.6	0.992
198.4 x 10^{-3}	40.3 x 10^{-3}	2.65	58.0	0.990
264.6 x 10^{-3}	53.8 x 10^{-3}	3.53	47.0	0.998
330.7x 10^{-3}	67.2 x 10^{-3}	4.41	43.2	0.991

The PCM samples are also analyzed by HPLC to determine the extent of degradation and formation of intermediates.

HPLC Analysis

HPLC analysis is carried out for the PCM samples of 66.1 x10^{-3} mM concentration treated at the optimum conditions for a reaction time of 240 minutes. The chromatogram of PCM before and after Fenton oxidation using Fe^{2+} and Fe (LS) is shown in Fig. 4.11.

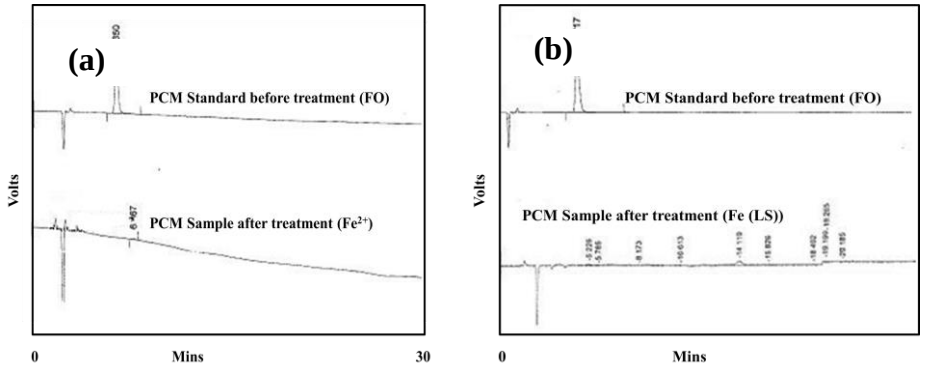


Fig. 4.11 HPLC chromatogram of (a) PCM standard before treatment and PCM sample after treatment with Fe^{2+} (b) PCM standard before treatment and PCM sample after treatment with Fe (LS); [Reaction conditions; Fenton oxidation, pH 3.5, $[PCM]_0$ = 66.1 x10^{-3} mM, $[H_2O_2]_0$ = 0.88 mM, $[Fe^{2+}]$ = 8.95 x 10^{-3} mM, [Fe (LS)] = 13.4 x 10^{-3} mM, reaction time = 240 min].

PCM peak before treatment is observed at 5.350 minutes of elution time (Fig. 4.11 (a)) and PCM peak is absent after treatment with Fe^{2+}. 100% PCM degradation and a small peak corresponding to an intermediate are observed at 6.167 minutes for Fenton oxidation of PCM with Fe^{2+} (Fig. 4.11 (a)). However, for the Fenton oxidation of PCM with Fe (LS), the PCM peak for standard before treatment is observed at 4.717 minutes elution time (Fig. 4.11 (b)). After treatment of PCM by Fenton oxidation for 240 minutes reaction time, 100% degradation is observed, but 10 intermediates in small quantities between 5 and 20 minutes are observed (Fig. 4.11 (b)).

4.1.4 Photo-Fenton Oxidation of Paracetamol Using Fe^{2+} as Iron Catalyst

The efficacy of the Fenton oxidation process can be strongly enhanced by irradiation with UV or visible light (Sun and Pignatello, 1993). This part of study deals with the effect of initial concentration of PCM and a kinetic study on degradation and mineralization of PCM by photo-Fenton oxidation process. UVC assisted photo-Fenton process is carried out at the optimum conditions that are obtained during the Fenton oxidation of PCM.

Effect of Initial PCM Concentration

Initially, oxidation experiments are carried out at the optimum conditions for 12 hours. However, the PCM degradation and COD removal are very slow and not appreciable after 120 minutes of UV irradiation time. Hence, further photo-Fenton experiments are carried out for a reaction time of 120 minutes.

The percent PCM degradation and the percent COD removal are 80.6 and 72.9 respectively in 5 minutes but 90.0 percent PCM degradation and 89.6 percent COD removal are observed in 120 minutes for 66.1 x 10^{-3} mM initial PCM concentration as can be seen in Fig. 4.12. The percent drug removal increased from 90.0 to 94.6 and the percent COD removal decreased from 89.6 to 56.3 with the increase in drug concentration from 66.1 x 10^{-3} to 330.7 x 10^{-3} mM.

At the optimum $[H_2O_2]_0$ / $[Fe^{2+}]_0$ molar ratio of 65.7 : 1, degradation of the drug increases with increase in its initial concentration. This may be due to the synergetic effect of OH radicals and the drug radicals formed in photo-Fenton oxidation in which

both the kinds of radicals may involve in the degradation of the substrate. On the other hand, the formation of the intermediates also may increase with increase in the substrate concentration and hence COD removal decreased with increase in the concentration of substrate. This result is in accordance with the literature, where COD removal of pharmaceutical wastewater by UV-Fenton Oxidation is more for the lower initial concentrations of the pollutant (Devi et al. 2009). This phenomenon of decrease in COD removal with increase in initial paracetamol concentration is also associated with the characteristics of UV visible absorption spectrum of the PCM (λ_{max}=243 nm) that is significant near 254 nm (UV-C light is used) and hence the solution with higher drug concentration absorbs a more significant fraction of the emitted UV light at 254 nm than that of a lower initial concentration, consequently, the number of available photons decreases leading to a decrease in the formation of OH radicals (Feng et al. 2003) to degrade the intermediates formed in the reaction. The kinetic studies carried out explain the chemical reactions further.

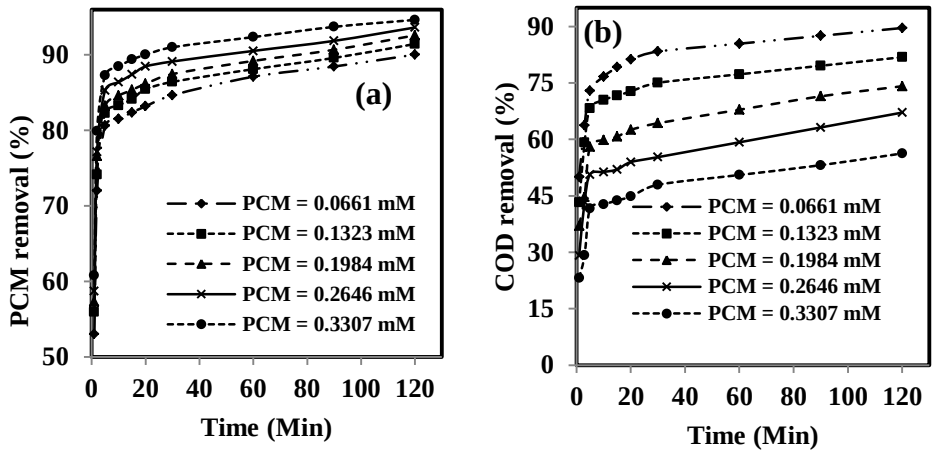


Fig. 4.12 Variations in (a) percent PCM degradation and (b) percent COD removal; [Reaction conditions; Photo-Fenton oxidation, pH 3, $[PCM]_0$ / $[H_2O_2]_0$ = 1 : 13.3 (molar), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 98.6: 1 (molar) and UVC irradiation time = 120 min].

The photo-Fenton degradation of the PCM can well be supported by the comparison of the absorbance spectrum of sample before and after treatment. The absorbance peak a 243 nm in the spectrum that is present before treatment is absent after treatment and it can be observed in the Fig. 4.13.

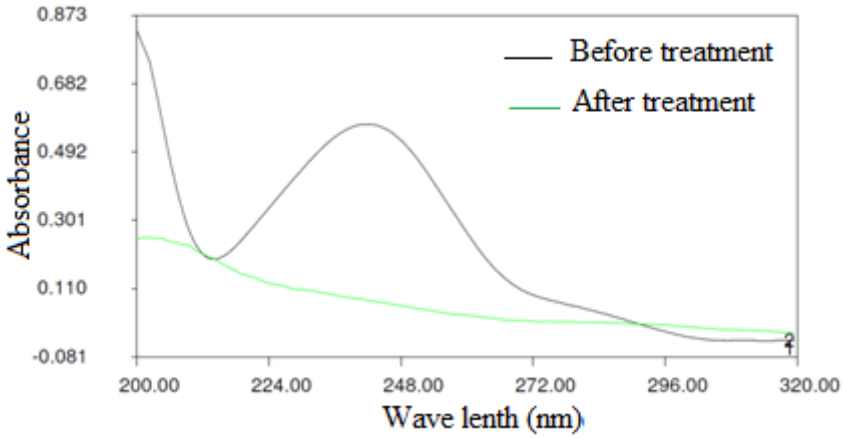


Fig. 4.13 UV – VIS absorbance spectra for PCM [Reaction conditions; Photo-Fenton oxidation, pH = 3, $[PCM]_0$ = 66.1 x 10^{-3} mM, $[H_2O_2]_0$ = 0.88 mM, $[Fe^{2+}]_0$ = 8.95 x 10^{-3} mM, reaction time 120 min]

Kinetic Studies on PCM Degradation

Kinetic studies are carried out at the optimum conditions for 120 minutes of reaction time. The oxidation is fast in the beginning for reaction time up to 5 minutes and therefore, the second-order kinetic equation (Eq. 3.1) has been fit up to the reaction time of 5 minutes (Zazo et al. 2005).

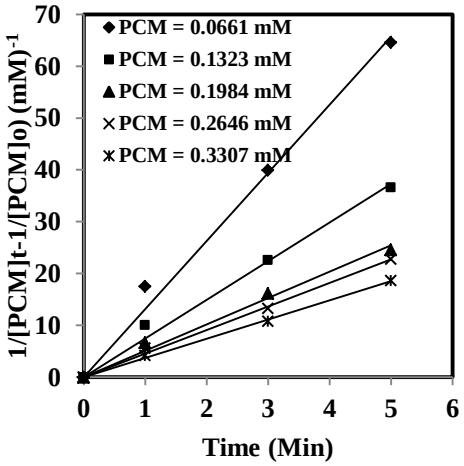


Fig. 4.14 Trend of pseudo-second order reaction kinetics for degradation of PCM in 5 min; [Reaction conditions; Photo-Fenton oxidation, pH 3, $[PCM]_0$ / $[H_2O_2]_0$ = 1: 13.3 (molar), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 98.6: 1 (molar), and $[PCM]_0$ = 66.1 x10^{-3} to 330.7 x10^{-3} mM].

The Fig.4.14 shows the trend of a pseudo second-order reaction kinetic model (Eq. 3.1) for initial PCM concentrations from 66.1 x 10^{-3} to 330.7 x10^{-3} mM at optimum conditions in the 5 minutes UV irradiation time. The values obtained for the pseudo second-order kinetic constants at ambient temperature (27 ± 3^{o} C) are summarized in Table 4.3. It is observed that the rate of degradation decreased with the increase in initial PCM concentration.

Table 4.1.3 Pseudo Second order kinetic rate constants for degradation of PCM by photo-Fenton oxidation using Fe^{2+} as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[PCM]_0$ mM	$[Fe^{2+}]_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}S^{-1}$	R^2
66.1 x 10^{-3}	8.95 x 10^{-3}	0.88	219.1	0.991
132.3 x 10^{-3}	17.9 x 10^{-3}	1.76	124.3	0.991
198.4 x 10^{-3}	26.9 x 10^{-3}	2.65	84.8	0.989
264.6 x 10^{-3}	35.8 x 10^{-3}	3.53	75.8	0.996
330.7 x 10^{-3}	44.8 x 10^{-3}	4.41	61.9	0.998

4.1.5 Photo-Fenton Oxidation of Paracetamol Using Fe (LS) as Iron Catalyst

Effect of initial PCM concentration

The variations in percent PCM degradation and percent COD removal at the optimum conditions within 120 minutes of reaction time is shown in Fig. 4.15. The percent PCM degradation and the percent COD removal are 72.8 and 58.3 respectively in 5 minutes where as 79.0 percent PCM degradation and 77.1 percent COD removal are observed in 120 minutes for 66.1 x10^{-3} mM initial PCM concentration. The percent drug removal increased from 79.0 to 89.5 and the percent COD removal decreased from 77.1 to 41.5 with the increase in drug concentration from 66.1 x10^{-3} to 330.7 x10^{-3} mM. The use of Fe (LS) in Fenton reagent also followed the similar PCM degradation trend as that of Fe^{2+} in UVC assisted photo-Fenton process.

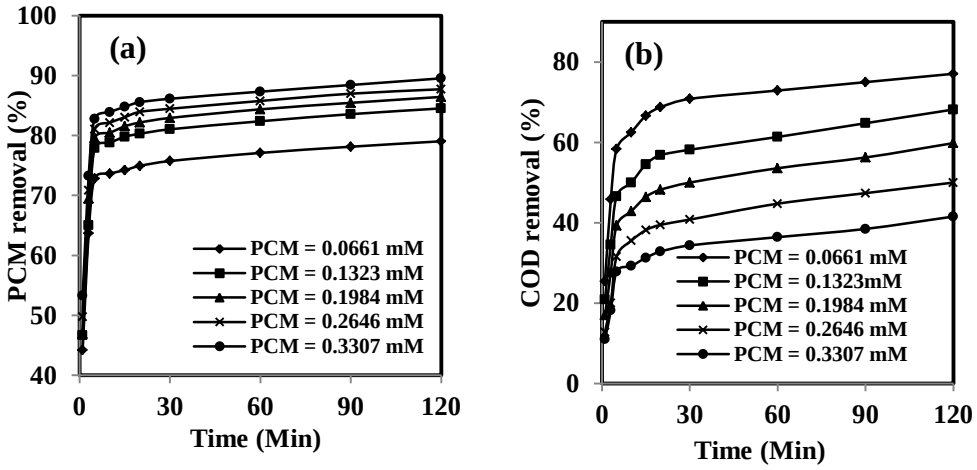


Fig. 4.15 Variations in (a) percent PCM degradation and (b) percent COD removal; [Reaction conditions; Photo-Fenton oxidation, pH 3, $[PCM]_0$ / $[H_2O_2]_0$ = 1: 13.3 (molar), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 65.7: 1 (molar), and $[PCM]_0$ = 66.1 $x10^{-3}$ to 330.7 $x10^{-3}$ mM, UVC irradiation time = 120 min].

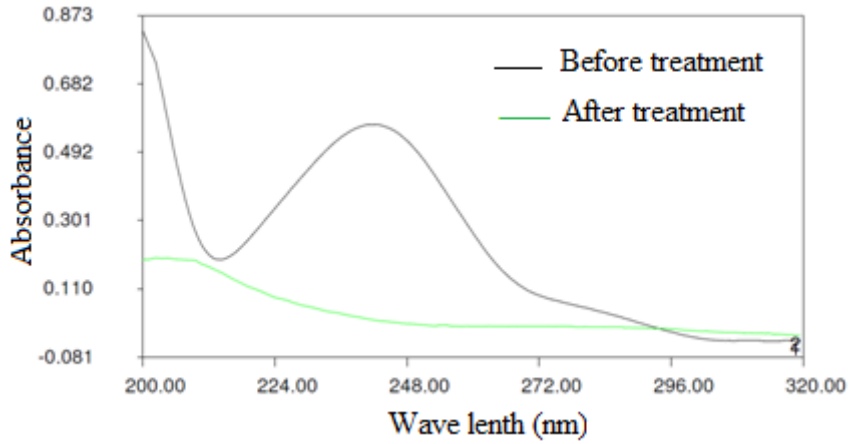


Fig. 4.16 UV – VIS absorbance spectra for PCM [Reaction conditions; Photo-Fenton oxidation, pH = 3, $[PCM]_0$ = 66.1 x 10^{-3} mM, $[H_2O_2]_0$ = 0.88 mM, [Fe (LS)]$_0$ = 13.3 x 10^{-3} mM, reaction time 120 min]

The degradation of PCM increased and the mineralization of PCM decreased with the increase in initial PCM concentration (Fig. 4.15). This may be due to the synergetic effect of OH radicals and the drug radicals formed in photo-Fenton oxidation in which both the kinds of radicals may involve in the degradation of the substrate. On the other hand, the formation of the intermediates may also increase with increase in the substrate concentration and hence COD removal decreased with increase in the concentration of substrate. This result is in accordance with the findings of Devi et al.

(2009), where COD removal of pharmaceutical wastewater by UV-Fenton Oxidation is more for the lower initial concentrations of the pollutant.

The Fig. 4.16 shows that the absorbance peak which is present before treatment is disappeared after treatment. This supports the photo-Fenton degradation of PCM using Fe (LS) as catalyst in the Fenton reagent. The kinetic studies are carried out further to analyze the reaction in the photo-Fenton oxidation process.

Kinetic Studies on PCM Oxidation

Kinetic studies are carried out at the optimum conditions for 120 minutes of reaction time. The oxidation is fast in the beginning for a reaction time up to 5 minutes and therefore, the second-order kinetic equation (Eq. 3.1) has been fit up to the reaction time of 5 minutes (Zazo et al. 2005). The Fig.4.17 shows the trend of a pseudo second-order reaction kinetic model (Eq. 3.1) for initial PCM concentrations from 66.1 x 10^{-3} to 330.7 x10^{-3} mM at optimum conditions in the 5 minutes UV irradiation time.

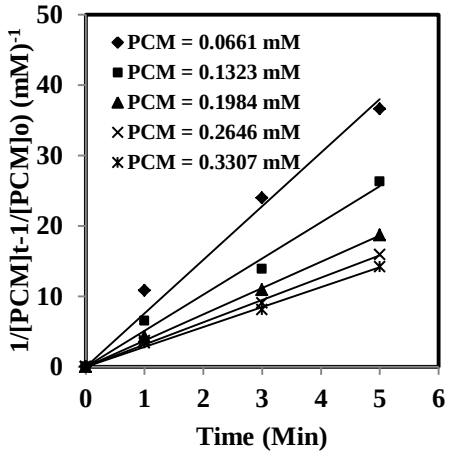


Fig. 4.17 Trend of pseudo-second order reaction kinetics for degradation of PCM in 5 min; [Reaction conditions; Photo-Fenton oxidation, pH 3, $[PCM]_0$ / $[H_2O_2]_0$ = 1: 13.3 (molar), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 65.7: 1(molar), and $[PCM]_0$ = 66.1 x10^{-3} to 330.7 x10^{-3} mM].

The values obtained for the pseudo second-order kinetic constants at ambient temperature (27 ± 3^o C) are summarized in Table 4.4. It is observed that the rate of degradation has decreased with the increase in initial PCM concentration. As the rate

constant is inversely proportional to initial concentrations in second-order reactions, the rate of degradation has decreased with the increase in initial PCM concentration. The results obtained in photo-Fenton process using Fe^{2+} and Fe (LS) are compared and analyzed.

Table 4.4 Pseudo Second order kinetic rate constants for degradation of PCM by photo-Fenton oxidation using Fe (LS) as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[PCM]_0$ mM	$[Fe\ (LS)]_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}s^{-1}$	R^2
66.1×10^{-3}	13.4×10^{-3}	0.88	126.7	0.982
132.3×10^{-3}	26.9×10^{-3}	1.76	85.5	0.988
198.4×10^{-3}	40.3×10^{-3}	2.65	62.2	0.998
264.6×10^{-3}	53.8×10^{-3}	3.53	52.7	0.997
330.7×10^{-3}	67.2×10^{-3}	4.41	47.0	0.996

HPLC Analysis

HPLC analysis is carried out for the PCM samples of 66.1×10^{-3} mM concentration treated at optimum conditions. The chromatogram of PCM before and after treatment using Fe^{2+} and Fe (LS) are shown in Fig. 4.18. The PCM peak before treatment is observed at 4.717 minutes of elution time (Fig. 4.18 (a)). When Fe^{2+} is used, for the sample after treatment for 120 minutes, no peaks in chromatogram are observed as seen in Fig. 4.18 (b). When Fe (LS) is used, for the sample after treatment for 120 minutes, two minor peaks in chromatogram (Fig. 4.18 (c)), one at 5.975 min and the other peak at 7.200 min corresponding to reaction intermediates, are observed. Hence, there is complete PCM degradation after the treatment for 120 minutes in both the cases of Fe^{2+} and Fe (LS). That is, 100 % of PCM is degraded with Fe^{2+} and Fe (LS). The intermediates formed have contributed to COD. The HPLC analysis showed the better and accurate results over the spectrophotometer analysis. The results obtained in Fenton and photo-Fenton processes for degradation of PCM are compared and analyzed.

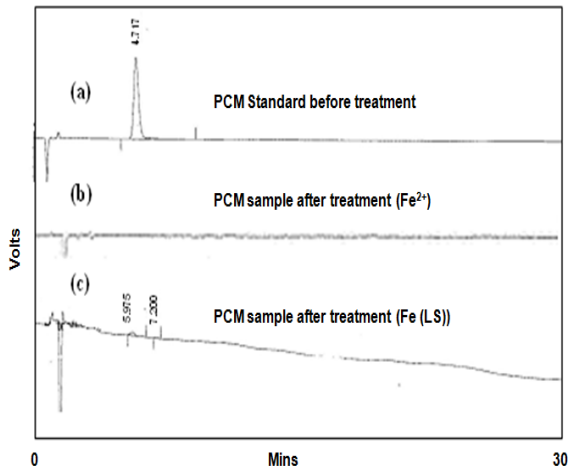


Fig. 4.18 HPLC chromatogram of (a) PCM standard before treatment (b) PCM sample with $[Fe^{2+}]_o$ = 8.95 x 10^{-3} mM after treatment (c) PCM sample with $[Fe\ (LS)]_o$ = 13.4 x 10^{-3} mM; [Reaction conditions; Photo-Fenton oxidation, pH = 3, $[PCM]_0$ = 66.1 x 10^{-3} mM, $[H_2O_2]_0$ = 0.88 mM and UVC irradiation time = 120 min.].

4.1.6 Comparison of Results in Fenton and Photo-Fenton Oxidation of Paracetamol

The Fenton and photo-Fenton process for degradation of PCM are carried out at the same optimum experimental conditions. The Fenton process is carried out for 240 minutes and the photo-Fenton process is carried out for 120 minutes till the significant results of degradation are obtained for the oxidation of PCM in water. Fig. 4.19 shows the comparison of percent PCM degradation and percent COD removal between Fenton oxidation and UVC assisted photo-Fenton oxidation.

At the optimum conditions, 5.71 % more PCM degradation and 6.25 % more COD removal for 66.1 x 10^{-3} mM of $[PCM]_0$ whereas 1.16 % more PCM degradation and 14.6 % more COD removal for 330.7 x 10^{-3} mM of $[PCM]_0$ are observed for Fe^{2+} than that of Fe (LS) in Fenton oxidation. On the other hand, in photo-Fenton oxidation, 11.0 % more PCM degradation and 12.5 % more COD removal for 66.1 x 10^{-3} mM of $[PCM]_0$ whereas 5.10 % more PCM degradation and 14.7 % more COD removal for 330.7 x10^{-3} mM of $[PCM]_0$ are observed for Fe^{2+} compared to Fe (LS) in 120 minutes of UVC irradiation time.

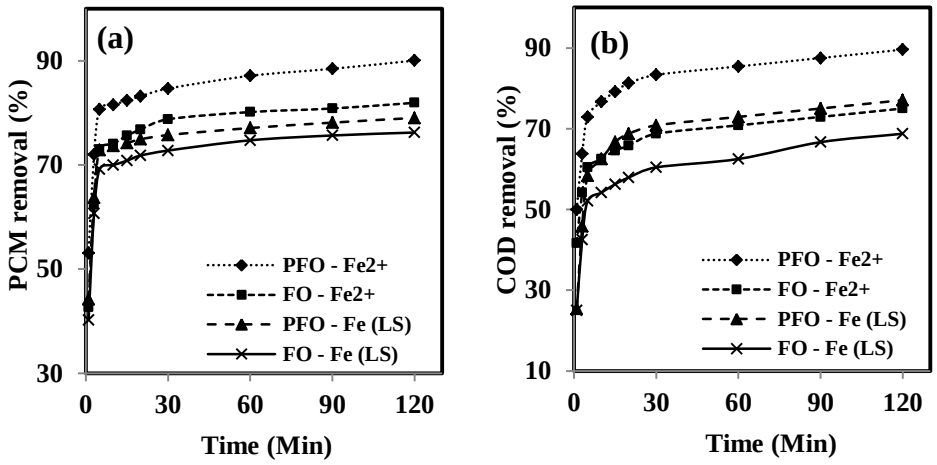


Fig. 4.19 Comparison for (a) percent PCM removal and (b) percent COD removal between Fenton and photo-Fenton processes; [Reaction conditions; UVC 8W light source, pH 3, $[PCM]_0 / [H_2O_2]_0$ = 1 : 13.3 (molar), $[H_2O_2]_0 / [Fe^{2+}]_0$ = 98.6 : 1 (molar), $[H_2O_2]_0$ / [Fe (LS)]$_0$ = 65.7 : 1 (molar), and $[PCM]_0$ = 66.1 x 10^{-3} mM].

In Fenton and photo-Fenton oxidation, the PCM degradation and COD removals are less for the Fe (LS) when compared to Fe^{2+} (Fig. 4.19). Also, the second-order kinetic rate constants are higher for Fe^{2+} than Fe (LS) in oxidation of PCM. When Fe (LS) is used, chloride ions are present in the system that may form chloro-Fe (III) complexes that leads to decrease in the rates of generation of Fe^{2+} and this inhibit the formation of OH radicals and also the OH radicals present in the system may be scavenged by chloride to form less reactive dichloride anion radicals ($Cl_2^{\bullet -}$) (Laat et al. 2004). Thus, the Fenton reaction mechanism in presence of chlorides may be via less reactive dichloride anion radicals ($Cl_2^{\bullet -}$) (E^o =2.09 V) (Ledakowiez et al. 2000). Conversely, in the presence of Fe^{2+}, the mechanism of Fenton reaction is through formation of highly reactive hydroxyl radicals (E^o = 2.8V) (Troung et al. 2004). The degradation of PCM through less reactive dichloride ion radical mechanism is the cause for the low degradation and mineralization when Fe (LS) is used in Fenton reagent. The PCM samples are also analyzed by HPLC to determine the extent of degradation and formation of intermediates.

The PCM degradation and mineralization efficiencies are more for UVC assisted photo-Fenton oxidation over the Fenton oxidation process. This is because of the

production of more number of highly reactive oxidizing OH radicals in direct and indirect photolysis with UV irradiation. PCM degradation of 8.11 % more with Fe^{2+} and 2.81 % more with Fe (LS) and COD removal of 14.6 % more with Fe^{2+} and 8.33 % more with Fe (LS) are observed for UV-C photo-Fenton over Fenton oxidation at the optimum experimental conditions within 120 minutes reaction time. It is observed that the rate of the degradation reactions in photo-Fenton process is higher than that in Fenton process. When Fe^{2+} is used, the kinetic constants for degradation is about 1.36 to 1.61 times more as can be observed from Tables 4.1 and 4.3 and when Fe (LS) is used, it is about 1.07 to 1.12 times more as can be observed from Tables 4.2 and 4.4 in photo-Fenton process over Fenton process at optimum conditions for PCM concentrations ranging from 66.1 x 10^{-3} to 330.7 x 10^{-3} mM. Over all, both the Fenton and photo-Fenton processes, when Fe^{2+} and Fe (LS) are used as catalysts, may be the most effective in removing the PCM from aqueous solutions.

4.1.7 Comparison of Results of the Present Study with the Literature

The comparison of present study with some important results in literature is shown in Table 4.5. In the present study, PCM degradation of 100 % with both Fe^{2+} and Fe (LS), COD removal of 77.1 % with Fe^{2+} and 70.8 % with Fe (LS) within 240 minutes of reaction time by Fenton process are observed. Moreover, PCM degradation of 100% with both Fe^{2+} and Fe (LS), COD removal of 89.6 % with Fe^{2+} and 77.1 % with Fe (LS) within 120 minutes of reaction time by UV-C assisted photo-Fenton process are observed. As compared with the literature, the extent of the degradation and mineralization obtained in the present study are greater than the most of the reported works.

Table 4.5 Comparison of results in the present study with the Literature on advanced oxidation of PCM in aqueous solution

Reference	Method	Results		
		Degradation (%)	Mineralization (%)	Reaction time in min
Andreozzi *et al*. (2003)	Ozonation		30	120
	H_2O_2/UV		40	120
Skoumal *et al*. (2006)	O_3/UVA		96	240
Waterston *et al*. (2006)		26		300
Sires *et al*. (2006)	Electrochemical		98	360
Garrido et al. (2007)			96	240
Dalmazio *et al*. (2008)	TiO_2/UV	90		160
Yang, *et al*. (2008)		95		80
Isariebel *et al*.(2009)	Sonolysis	100	39	480
Present study	H_2O_2/Fe^{2+}	100	77.1	240
		73.0	60.4	5
	H_2O_2/Fe (LS)	100	70.8	240
		69.2	52.1	5
	H_2O_2/Fe^{2+}/UV-C	100	89.6	120
		80.6	72.9	5
	H_2O_2/Fe (LS) / UV-C	100	77.1	120
		72.8	58.3	5

4.2 Fenton and Photo-Fenton Oxidation of Amoxicillin in Water

4.2.1 Spectral and Chemical Characterization of Amoxicillin

The UV-VIS absorbance spectrum of AMX is recorded from 190 to 350 nm using UV-VIS spectrophotometer and the absorbance peak for AMX is observed to be at wavelength 226 nm as seen in Fig.4.20 (a). A calibration curve between sample absorbance and concentration is established with 4 different AMX concentrations in the range of 5 to 40 mg/L (13.7×10^{-3} to 109.5×10^{-3} mM). For the range of concentrations considered, a linear relationship between absorbance and concentration is established as shown in Fig. 4.20 (b).

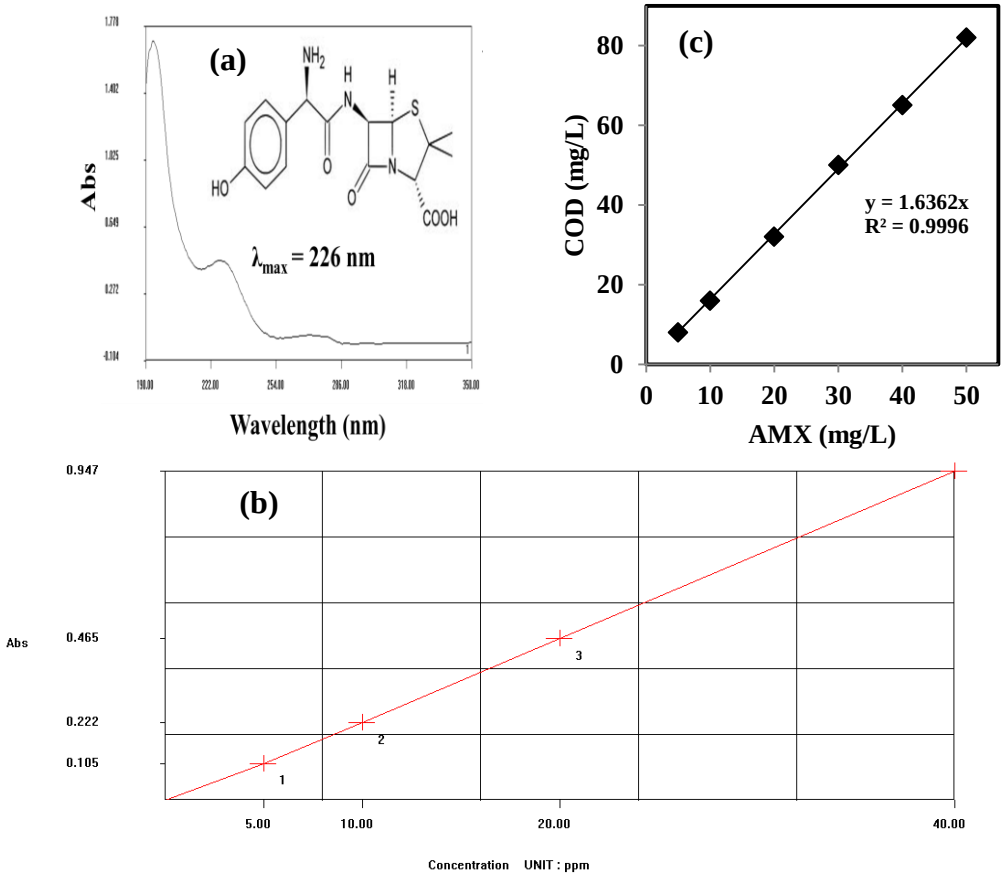


Fig. 4.20 (a) UV-VIS Spectrum of AMX with Chemical Structure (b) Calibration Curve for AMX (Standard data from UV-VIS double beam spectrophotometer) (c) Calibration Curve for COD of AMX.

A COD calibration curve (Fig. 4.20 (c)) between AMX concentration and COD is established for AMX concentrations ranging from 5 to 50 mg/L (13.7 x 10^{-3} to 136.8 x 10^{-3} mM). The COD is about 1.64 mg/L per mg of AMX concentration. This value is used in calculating the corresponding initial COD of the AMX samples.

4.2.2 Fenton Oxidation of Amoxicillin Using Fe^{2+} as Iron Catalyst

This part deals with the study of effect of various parameters like pH, $[H_2O_2]_0$, $[Fe^{2+}]_0$, $[Fe\ (LS)]_0$ on degradation and mineralization of AMX and chemical kinetic studies on AMX degradation.

Effect of pH

The oxidation experiments are conducted at different pH values varying from 2 to 5.5 with initial AMX concentration of 27.4 x 10^{-3} mM, $[H_2O_2]_0$ 0.59 mM and $[Fe^{2+}]_0$ 17.9 x 10^{-3} mM. The maximum percent AMX degradation and percent COD removal are observed to be 58.9 and 48.9 respectively at pH 3 (Fig. 4.21). From the Fig. 4.21, it is clearly visible that the AMX removal is less for the other values of pH.

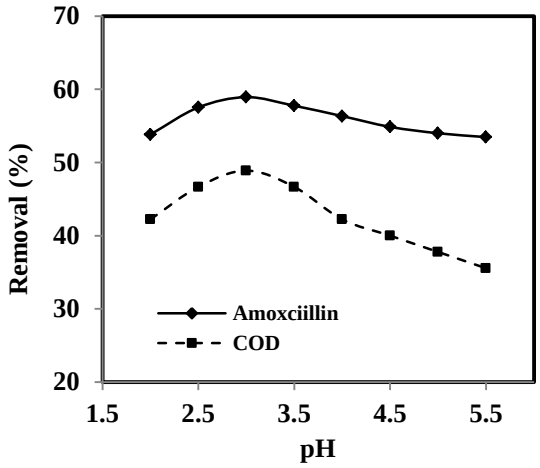


Fig. 4.21 Percent AMX degradation and percent COD removal at different pH; [Reaction conditions; Fenton oxidation, $[AMX]_0$ = 27.4 x 10^{-3} mM, $[H_2O_2]_0$= 0.59 mM and $[Fe^{2+}]_0$ = 17.9 x 10^{-3} mM, reaction time = 24 h].

At pH 3, AMX removal is maximum and it may be due to the formation of more $Fe(OH)^+$ which has much higher activity than Fe^{2+} in Fenton's oxidation (Badawy and Ali 2006). When pH is greater than 3, oxidation efficiency rapidly decreases due to auto-decomposition of H_2O_2 affecting the production of OH radicals (Badawy and Ali 2006) and deactivation of ferrous catalyst with the formation of ferric hydroxide precipitates (Luis et al. 2009). When pH is less than 3, the reaction of H_2O_2 with Fe^{2+} is seriously affected that leads to reduction in hydroxyl radical production and water is formed by the reaction of OH radicals with H^+ ions (Lucas and Peres 2006). Similarly, the COD removal is maximum at pH 3 but for other values of pH 3 the COD removal is less. However, the COD removal is observed to be less than the AMX degradation and it may be due to the formation of oxidation intermdiates. The optimum pH value of 3, where the maximum degradation and mineralization has taken place is maintained in all the susequent experiments on degradation of amoxicillin.

Effect of H_2O_2 and Fe^{2+} Concentration

The investigation for optimization of hydrogen peroxide concentration is carried out by varying H_2O_2 concentration from 0.29 to 1.47 mM, keeping the iron concentrations from 4.48 x 10^{-3} to 17.9 x 10^{-3} mM for initial amoxicillin concentration 27.4 x 10^{-3} mM at the optimum solution pH 3. The reaction equation 4.5 describes the reaction for complete mineralization of AMX in the Fenton Oxidation.

$$C_{16}H_{19}N_3O_5S + 47H_2O_2 + Fe(II) \rightarrow 16CO_2 + 54H_2O + 3HNO_3 + H_2SO_4 + Fe(II) \quad .....(4.5)$$

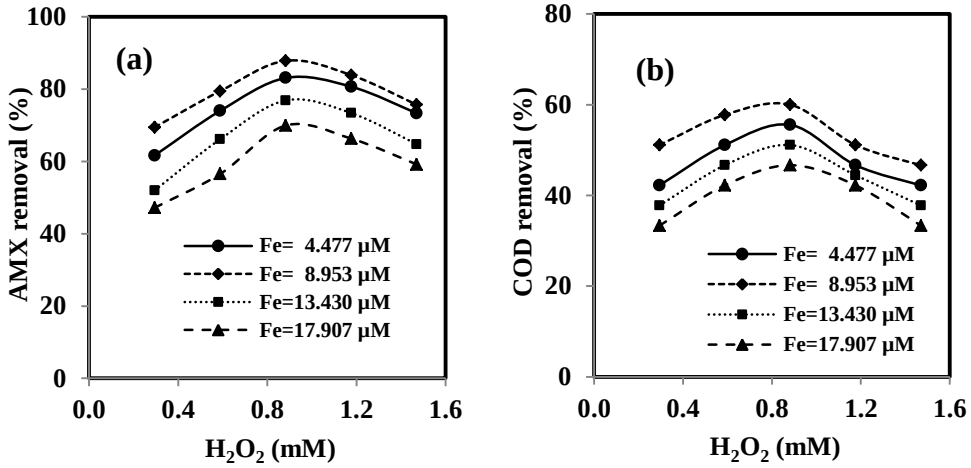


Fig. 4.22 Variations in (a) percent AMX degradation, (b) percent COD removal [Reaction conditions; Fenton oxidation, $[AMX]_0$ = 27.4 x 10^{-3} mM, pH= 3, $[H_2O_2]_0$ = 0.29 to 1.47 mM, $[Fe^{2+}]_0$ = 4.48 x 10^{-3} to 17.9 x 10^{-3} mM, reaction time = 24 h].

The quantity of hydrogen peroxide required, based on Stoichiometric calculation (Eq. 4.5), for the complete mineralization of AMX is 4.37 mg per mg of AMX (47 moles of H_2O_2 per mole of AMX). However, in the present study, the maximum percent AMX degradation is observed to be 87.9 and the corresponding percent COD removal is 60.00 for 27.4 x 10^{-3} mM initial concentration of AMX at H_2O_2 concentration of 0.88 mM after a reaction time of 24 hours (Fig. 4.22). In the beginning, the drug and COD removal increased up to a maximum value with increase in H_2O_2 concentration and further increase in the H_2O_2 concentration decreased the removal efficiencies. The maximum AMX degradation and COD removal is observed at 0.88 mM of H_2O_2. This may be due to production of less number of OH radicals when $[H_2O_2]_0$ is less than 0.88 mM. On the other hand, when $[H_2O_2]_0$ is greater than 0.88 mM, the

degradation and mineralization are less because of the scavenging effect of OH radicals with increase in the H_2O_2 concentration. This can be explained by the fact that the very reactive OH radicals are scavenged by the increased H_2O_2 that results finally into water (Hsueh et al. 2005).

Both the AMX degradation and COD removal are significantly improved with the addition of Fe^{2+} to the solution. The maximum percent AMX degradation is 87.88 and the corresponding percent COD removal is 60.00 at 8.95 x 10^{-3} mM Fe^{2+} concentration and the same can be seen in Fig. 4.22. The degradation and mineralization increased with increase in Fe^{2+} concentration up to 8.95 x 10^{-3} mM due to increase in OH radical production (Yilmaz et al. 2010). After that, with the increase in Fe^{2+} concentrations, the AMX and COD removals are less. This may be due to the reaction of Fe^{2+} with OH radicals that results in the scavenging of OH radical (Hsueh et al. 2005). It is also observed that there is incomplete degradation even at the optimum dosages of H_2O_2 and Fe^{2+}. This may be due to refractory intermediates formed during the treatment. Consequently, the observed molar ratios, $[AMX]_0$ / $[H_2O_2]_0$ = 1 : 32.2 and $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 98.6 : 1 at which degradation and mineralization is the maximum, are considered as optimum. These values are maintained in the subsequent experiments for studying the effect of initial AMX concentration.

Effect of Initial AMX Concentration

The variations in percent AMX degradation and percent COD removals at optimum conditions for 240 minutes of reaction time are shown in Fig. 4.23. The percent AMX degradation and percent COD removal are observed as 33.9 and 25.5 respectively in 5 minutes, whereas 80.0 percent AMX degradation and 72.5 of percent COD removal are observed in 240 minutes for 27.4 x 10^{-3} mM initial concentration of AMX. With the increase in AMX concentration from 27.4 x 10^{-3} to 136.8 x 10^{-3} mM, the percent drug removal increased from 80.0 to 90.5 and the percent COD removal decreased to 72.5 from 59.0.

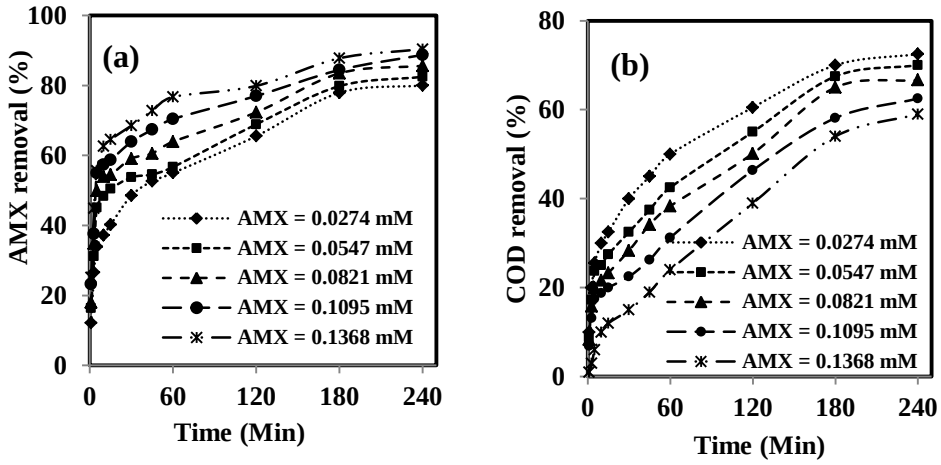


Fig. 4.23 Variations in (a) percent AMX degradation and (b) percent COD removal; [Reaction conditions; Fenton oxidation, pH 3, $[AMX]_0$ / $[H_2O_2]_0$ = 1 : 32.2 (molar) and $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 98.6: 1 (molar), reaction time = 240 min]

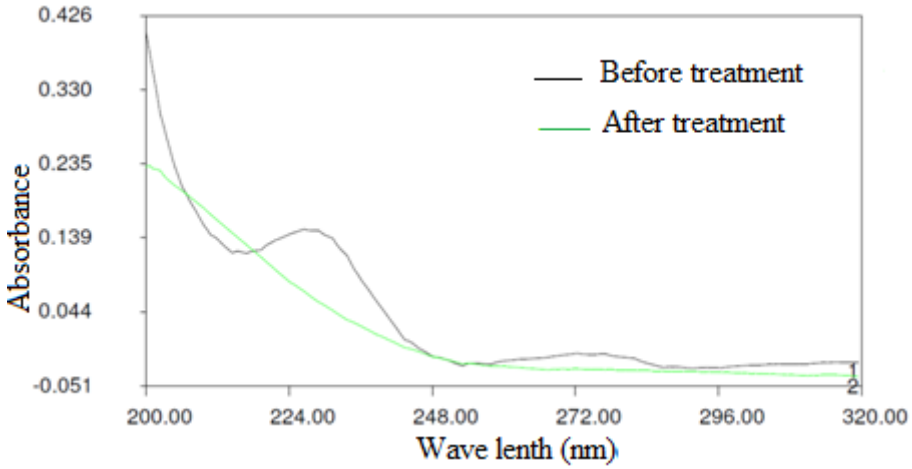


Fig. 4.24 UV – VIS absorbance spectra for AMX [Reaction condition; Fenton oxidation, pH = 3, $[AMX]_0$ = 27.4 x 10^{-3} mM, $[H_2O_2]_0$ = 0.88 mM, $[Fe^{2+}]_0$ = 8.95 x 10^{-3} mM, reaction time = 240 min]

The degradation of AMX increased and the mineralization decreased with increase in initial AMX concentration. This may be due to the synergetic effect of OH radicals and the drug radicals formed in Fenton oxidation in which both the radicals may involve in the degradation of the substrate. On the other hand, the formation of the intermediates also may increase with increase in substrate concentration and hence COD removal decreased with increase in the concentration of substrate. This result is comparable with the literature, where COD removal of pharmaceutical wastewater by

Fenton's oxidation is more for the lower initial concentrations of drugs (Yilmaz et al. 2010). The degradation of AMX is also supported by the UV-VIS absorbance spectrum of AMX before and after treatment. The UV-VIS absorbance peak is observed at 226 nm before treatment and is disappeared after treatment (Fig. 4.24) indicating the degradation of AMX.

Kinetic Studies on AMX Degradation

The kinetic studies on AMX degradation are conducted at the optimum conditions for 240 minutes of reaction time. The oxidation is fast in the beginning for reaction time up to 5 minutes and therefore, the second-order kinetic equation has been fit up to the reaction time of 5 minutes (Zazo et al. 2005) and the trend is plotted as shown in Fig.4.25

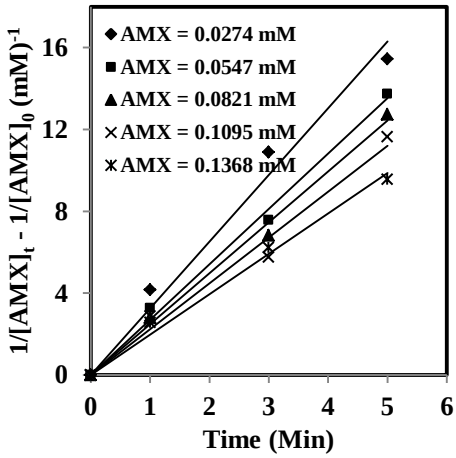


Fig. 4.25 Trend of pseudo-second order reaction kinetics for degradation of AMX in 5 min; [Reaction conditions; Fenton oxidation, pH 3, $[AMX]_0$ / $[H_2O_2]_0$ = 1 : 32.2 (molar), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 98.6 : 1 (molar) and $[AMX]_0$ = 27.4 x 10^{-3} to 136.8 x 10^{-3} mM].

The values obtained for the pseudo second-order kinetic constants at ambient temperature (27 ± 3^o C) are summarized in Table 4.6. It is observed from the results that the rate of degradation decreased with the increase in initial concentration of AMX. This may be supported by the fact that the rate constant in a second-order reaction is inversely proportional to the initial concentration of the reactant.

Table 4.6 Pseudo Second order kinetic rate constants for degradation of AMX by Fenton oxidation using Fe^{2+} as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[AMX]_0$ mM	$[Fe^{2+}]_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}s^{-1}$	R^2
27.4×10^{-3}	8.95×10^{-3}	0.88	54.3	0.981
54.7×10^{-3}	17.9×10^{-3}	1.76	45.2	0.994
82.1×10^{-3}	26.7×10^{-3}	2.65	41.5	0.993
109.5×10^{-3}	35.8×10^{-3}	3.53	37.3	0.979
136.8×10^{-3}	44.8×10^{-3}	4.41	33.0	0.990

Similar kinetic studies are carried out for Fe (LS) in Fenton's reagent in the subsequent oxidation experiments.

4.2.2 Fenton Oxidation of Amoxicillin Using Fe (LS) as Iron Catalyst

The optimum pH value of 3 obtained during the investigation of AMX degradation using Fe^{2+} is maintained for the Fenton experiments with Fe (LS). The assessment of effect of various parameters like $[H_2O_2]_0$, [Fe (LS)] and $[AMX]_0$ on Fenton oxidation of AMX using Fe (LS) as iron catalyst are elaborated below.

Effect of H_2O_2 and Fe^{2+} Concentration

The Fenton oxidation experiments are conducted to investigate optimum hydrogen peroxide concentration with Fe (LS) in Fenton's reagent. The hydrogen peroxide concentration is varied from 0.44 to 1.32 mM and Fe (LS) concentration is changed from 8.95×10^{-3} to 22.4×10^{-3} mM for initial AMX concentration of 27.4×10^{-3} mM at initial solution pH of 3. The variations in percent AMX degradation and COD removal under the different dosages of Fe (LS) and H_2O_2 for 27.4×10^{-3} mM initial concentration of AMX at pH of 3 are shown in Fig. 4.26. It is observed that the maximum percent AMX degradation is 90.7 and the corresponding percent COD removal is 75.6 at initial H_2O_2 concentration of 1.03 mM and initial Fe (LS) concentration of 13.4×10^{-3} mM after a reaction time of 24 hours.

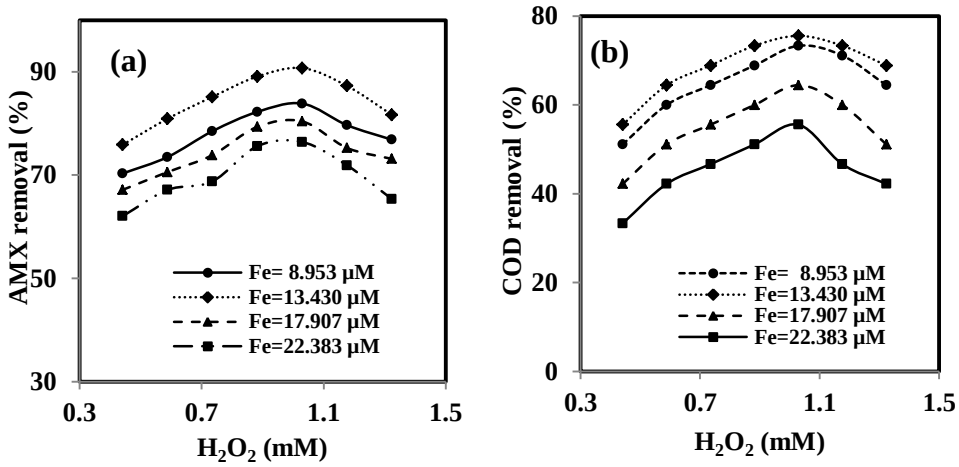


Fig. 4.26 Variations in (a) percent AMX degradation (b) percent COD removal; [Reaction conditions; Fenton oxidation, $[AMX]_0$ = 27.4 x 10-3 mM, pH 3, $[H_2O_2]_0$ = 0.44 to 1.32 mM, $[Fe\ (LS)]_0$ = 8.95 x 10^{-3} to 22.4 x 10^{-3} mM].

The removal efficiency increased up to a maximum level with increase in H_2O_2 concentration due to formation of higher amount of OH radicals and further increase in the H_2O_2 concentration decreased the removal efficiency due to the scavenging of OH radicals with increase in the H_2O_2 concentration. The maximum percent degradation of AMX and COD are observed to be at H_2O_2 concentration of 1.03 mM. This may due to presence of maximum number of OH radicals at that concentration of H_2O_2.

In the same way, both the AMX degradation and COD removal increased with addition of Fe (LS). This is because sufficient catalyst is required to produce more amounts of OH radicals. The degradation and COD removals are the maximum at Fe (LS) concentration of 13.4 x 10^{-3} mM. It may be due to presence of maximum amount of OH radicals in the treatment system. However, the AMX and COD removals are less at Fe (LS) concentrations higher than 13.4 x 10^{-3} mM. This is due to the scavenging of OH radicals by higher catalyst concentrations. As per the results obtained, the optimum molar ratios are $[AMX]_0 / [H_2O_2]_0$ = 1 : 37.6 and $[H_2O_2]_0 / [Fe\ (LS)]_0$ = 76.6 : 1. These values are considered in the subsequent experiments that are conducted to investigate the effect of initial AMX concentration.

Effect of initial AMX concentration

The initial AMX concentration is varied from 27.4 x 10^{-3} to 136.8 x 10^{-3} mM and the optimum molar ratio of $[AMX]_0$ / $[H_2O_2]_0$ = 1 : 37.6 and the optimum $[H_2O_2]_0$ / [Fe (LS)]$_0$ ratio 76.6 : 1 are kept constant for all the concentrations of AMX. The Fig. 4.27 shows the variations in percent AMX degradation and percent COD removal at the optimum conditions in 240 minutes of reaction time.

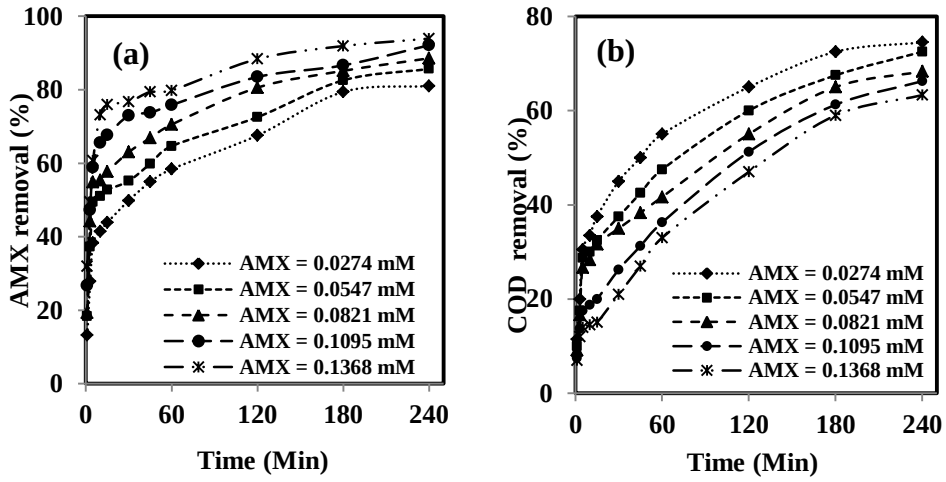


Fig. 4.27 Variations in (a) percent AMX degradation and (b) percent COD removal; [Reaction conditions; Fenton oxidation, pH 3, $[AMX]_0$ / $[H_2O_2]_0$ = 1 : 37.6 (molar) and $[H_2O_2]_0$ / [Fe (LS)]$_0$ = 76.6: 1 (molar), reaction time = 240 min].

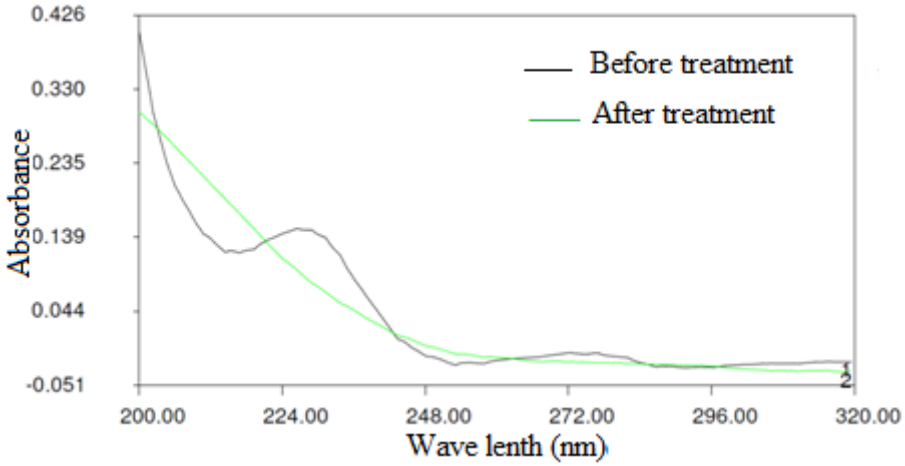


Fig. 4.28 UV – VIS absorbance spectra for AMX [Reaction conditions; Fenton oxidation, pH = 3, $[AMX]_0$ = 27.4 x 10^{-3} mM, $[H_2O_2]_0$ = 1.03 mM, [Fe (LS)]$_0$ = 13.4 x 10^{-3} mM, reaction time = 240 min]

The percent AMX degradation and the percent COD removal are 38.3 and 30.5 respectively in 5 minutes where as 81.0 percent AMX degradation and 74.5 percent

COD removal is observed in 240 minutes for 27.4 x 10^{-3} mM initial AMX concentration. The percent drug removal increased from 81.0 to 93.9 and the percent COD removal decreased from 74.5 to 63.3 with the increase in drug concentration from 27.4 x 10^{-3} to 136.8 x 10^{-3} mM in 240 minutes of reaction time. The degradation of AMX increased and the mineralization decreased with increase in initial AMX concentration. This may be due to the synergetic effect of OH radicals and the drug radicals formed in Fenton oxidation in which both the kinds of radicals may involve in the degradation of the substrate. On the other hand, the formation of the intermediates also may increase with increase in substrate concentration and hence COD removal decreased with increase in the concentration of substrate. This result is comparable with the literature, where COD removal of pharmaceutical wastewater by Fenton's oxidation is more for the lower initial concentrations of drugs (Yilmaz et al. 2010). The absorbance spectrum of AMX (Fig. 4.28) also supported the degradation of the drug using Fe (LS) in Fenton oxidation.

Kinetic Studies on AMX Degradation

Kinetic studies on AMX degradation are carried out at the optimum conditions for 240 minutes of reaction time. The oxidation is fast in the beginning for reaction time up to 5 minutes and therefore, the second-order kinetic equation has been fit up to the reaction time of 5 minutes (Zazo et al. 2005).

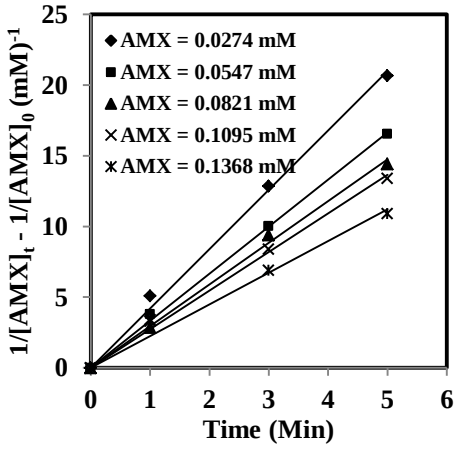


Fig. 4.29 Trend of pseudo-second order reaction kinetics for degradation of AMX in 5 min; [Reaction conditions; Fenton oxidation, pH 3, $[AMX]_0$ / $[H_2O_2]_0$ = 1 : 37.6 (molar), $[H_2O_2]_0$ / [Fe (LS)]$_0$ = 76.6 : 1 (molar), and $[AMX]_0$ = 27.4 x 10^{-3} to 136.8 x10^{-3} mM].

The trend of a pseudo second-order reaction kinetic model (Eq. 3.1) for initial AMX concentrations from 66.1 x 10^{-3} to 330.7 x10^{-3} mM at optimum conditions in the 5 minutes is shown in Fig. 4.29. The values obtained for the pseudo second-order kinetic constants at ambient temperature (27 ± 3^{o} C) are summarized in Table 4.7. It is observed that the rate of degradation decreased with the increase in initial AMX concentration. This can be supported by the fact that the rate constant is inversely proportional to the concentration of substrate.

Table 4.7 Pseudo Second order kinetic rate constants for degradation of AMX by Fenton oxidation using Fe (LS) as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[AMX]_0$ mM	$[Fe (LS)]_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}s^{-1}$	R^2
27.4 x 10^{-3}	13.4 x 10^{-3}	1.03	70.00	0.996
54.7 x 10^{-3}	26.9 x 10^{-3}	2.06	55.50	0.999
82.1 x 10^{-3}	40.3 x 10^{-3}	3.09	49.17	0.999
109.5 x 10^{-3}	53.7 x 10^{-3}	4.12	45.50	0.994
136.8 x 10^{-3}	67.2 x 10^{-3}	5.15	37.33	0.981

HPLC Analysis

AMX samples of 27.4 x 10^{-3} mM concentration treated by Fenton oxidation at the optimum conditions for a reaction time of 240 minutes are analyzed with HPLC. The Fig. 4.30 shows the chromatogram of AMX samples before and after treatment using Fe^{2+} and Fe (LS). AMX peak before treatment is observed at 3.492 minutes of elution time (Fig. 4.30 (a)) and no other compounds are identified. After treatment in Fenton oxidation with Fe^{2+}, the peak corresponding to AMX is disappeared and five peaks at different elution times are noticed that means AMX is degraded completely and five intermediate compounds are formed which may contribute COD (Fig. 4.30 (b)). Similarly, after Fenton oxidation of AMX with Fe (LS), the peak corresponding to AMX is disappeared indicating complete degradation of AMX and five other peaks indicating reaction intermediates at various elution times are noticed (Fig. 4.30 (c)).

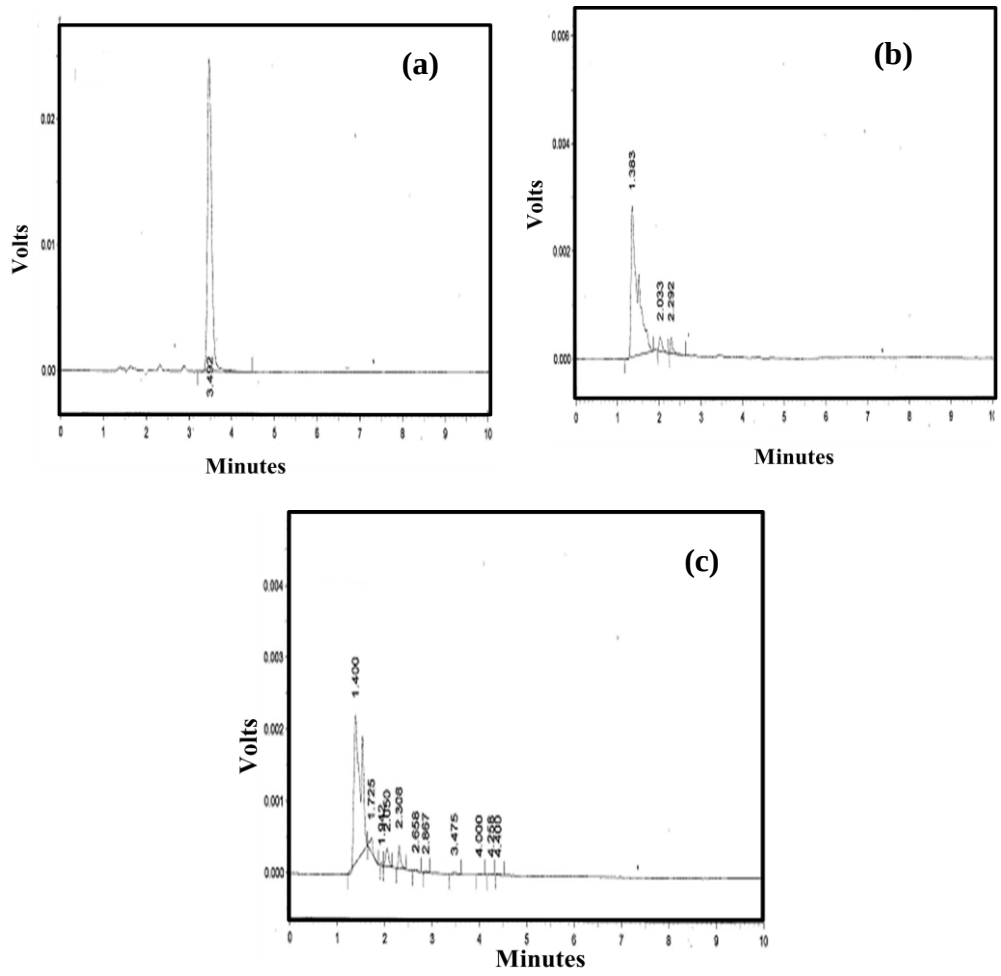


Fig. 4.30 HPLC chromatogram of (a) AMX standard before treatment (b) AMX sample after treatment at $[Fe^{2+}]_0$ = 8.95 x 10^{-3} mM, $[H_2O_2]_0$ = 0.88 mM (c) AMX sample after treatment at [Fe (LS)]$_0$ = 13.4 x 10^{-3} mM, $[H_2O_2]_0$ = 1.03 mM; [Reaction conditions; Fenton oxidation, $[AMX]_0$ = 27.4 x 10^{-3} mM, pH 3, reaction time = 240 min].

At optimum conditions, complete degradation and incomplete mineralization of AMX is recognized with both the Fe^{2+} and Fe (LS) as catalysts in Fenton oxidation within 240 minutes as can be seen in Fig. 4.30.

4.2.4 Photo-Fenton Oxidation of Amoxicillin Using Fe^{2+} as Iron Catalyst

This part of study deals with the effect of initial concentration of AMX and a kinetic study on degradation of and mineralization of AMX by photo-Fenton oxidation process. UVC assisted photo-Fenton process is carried out at the optimum conditions that are obtained during the Fenton oxidation of AMX.

Effect of Initial AMX Concentration

The photo-Fenton oxidation experiments are carried out for a reaction time of 120 minutes. The percent AMX degradation and the percent COD removal are 41.9 and 35.0 respectively in 5 minutes but 79.0 percent AMX degradation and 75.0 percent COD removal are observed in 120 minutes for 27.4 x 10^{-3} mM initial AMX concentration as can be seen in Fig. 4.31. The percent drug removal increased from 79.0 to 92.6 and the percent COD removal decreased from 75.0 to 65.0 with the increase in drug concentration from 27.4 x 10^{-3} to 136.8 x 10^{-3} mM.

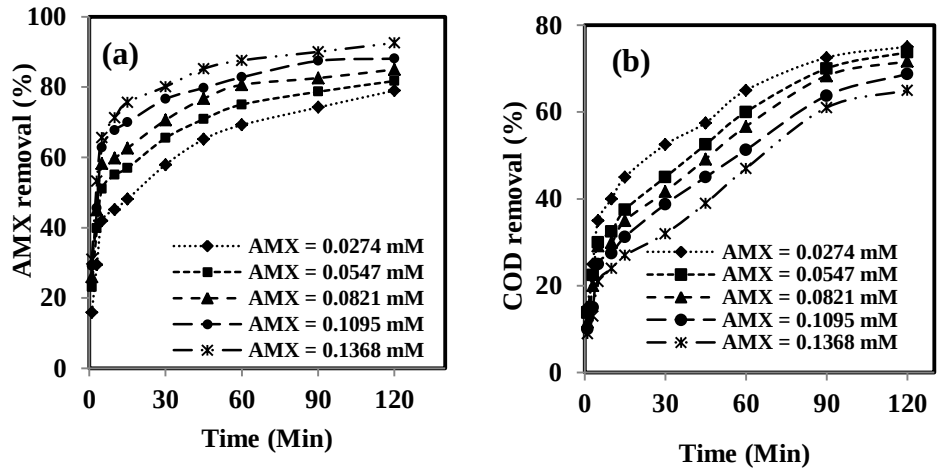


Fig. 4.31 Variations in (a) percent AMX degradation and (b) percent COD removal; [Reaction conditions; Photo-Fenton oxidation, pH 3, $[AMX]_0$ / $[H_2O_2]_0$ = 1 : 32.2 (molar), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 98.6 : 1 (molar) and UVC irradiation time = 120 min].

At the optimum $[H_2O_2]_0$ / $[Fe^{2+}]_0$ molar ratio of 98.6 : 1, the degradation of AMX increased and the mineralization decreased with increase in initial AMX concentration. This may be due to the synergetic effect of OH radicals and the drug radicals formed in photo-Fenton oxidation in which both the kinds of radicals may involve in the degradation of the substrate. On the other hand, the formation of the intermediates also may increase with increase in substrate concentration and hence COD removal decreased with increase in the concentration of substrate. This result is in agreement with the literature, where COD removal of pharmaceutical wastewater by UV-Fenton Oxidation is more for the lower initial concentrations of the pollutant (Devi et al. 2009). This phenomenon of decrease in COD removal with increase in initial amoxicillin concentration is also associated with the characteristics of UV

visible absorption spectrum of the AMX (λ_{max}=226 nm) and hence the solution with higher drug concentration absorbs a more significant fraction of the emitted UVC light than that of a lower initial concentration; consequently, the number of available photons decreases leading to a decrease in the formation of OH radicals (Feng et al. 2003) to degrade the intermediates formed in the reaction.

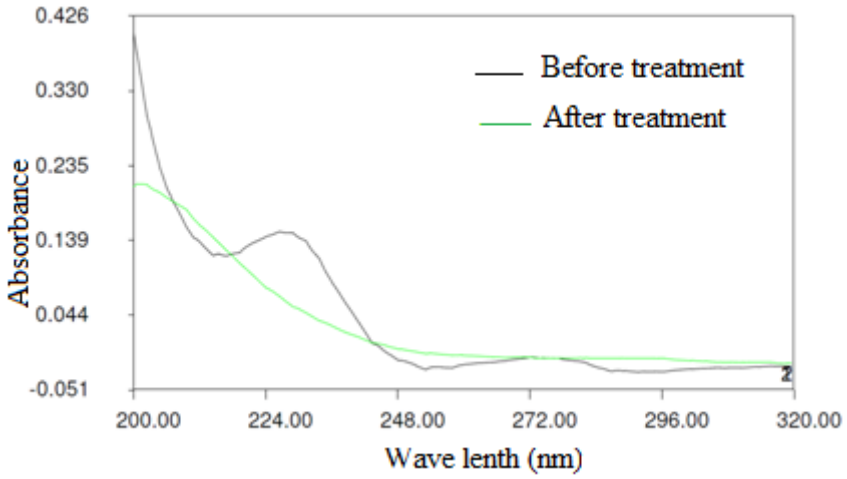


Fig. 4.32 UV – VIS absorbance spectra for AMX [Reaction condition; Photo-Fenton oxidation, pH = 3, $[AMX]_0$ = 27.4 x 10^{-3} mM, $[H_2O_2]_0$ = 0.88 mM, $[Fe^{2+}]_0$ = 8.95 x 10^{-3} mM, reaction time 240 min.]

The degradation of the AMX can well be supported by the absorbance spectra of AMX sample before and after treatment (Fig. 4.32). The kinetic studies are carried out in the subsequent experiments.

Kinetic Studies on AMX Degradation

Kinetic studies are carried out at the optimum conditions for 120 minutes of reaction time. The oxidation is fast in the beginning for reaction time up to 5 minutes and therefore, the second-order kinetic equation (Eq. 3.1) has been fit up to the reaction time of 5 minutes (Zazo et al. 2005).

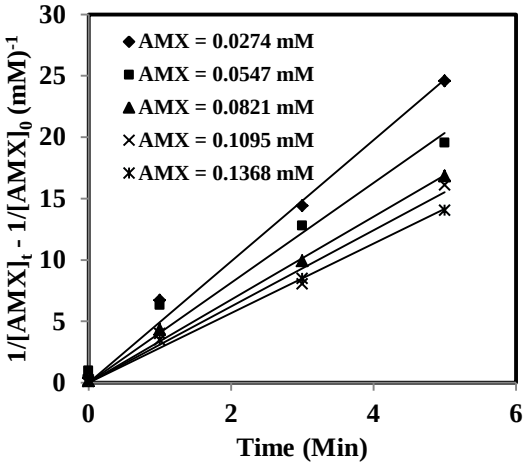


Fig. 4.33 Trend of pseudo-second order reaction kinetics for degradation of AMX in 5 min; [Reaction conditions; Photo-Fenton oxidation, pH 3, $[AMX]_0$ / $[H_2O_2]_0$ = 1: 32.2 (molar), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 98.6: 1 (molar), and $[AMX]_0$ = 27.4 x 10^{-3} to 136.8 x 10^{-3} mM].

Table 4.8 Pseudo Second order kinetic rate constants for degradation of AMX by photo-Fenton oxidation using Fe^{2+} as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[AMX]_0$ mM	$[Fe^{2+}]_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}s^{-1}$	R^2
27.4 x 10^{-3}	8.95 x 10^{-3}	0.88	82.3	0.989
54.7 x 10^{-3}	17.9 x 10^{-3}	1.76	67.8	0.964
82.1 x 10^{-3}	26.9 x 10^{-3}	2.65	56.3	0.994
109.5 x 10^{-3}	35.8 x 10^{-3}	3.53	51.8	0.980
136.8 x 10^{-3}	44.8 x 10^{-3}	4.41	47.2	0.996

The Fig.4.33 shows the trend of a pseudo second-order reaction kinetic model (Eq. 3.1) for initial AMX concentrations from 27.4 x 10^{-3} to 136.8 x 10^{-3} mM at optimum conditions in the 5 minutes UV irradiation time. The values obtained for the pseudo second-order kinetic constants at ambient temperature (27 ± 3^o C) are summarized in Table 4.8. It is observed that the rate of degradation decreased with the increase in initial AMX concentration. This may due to the verity that the rate constant is inversely proportional to the substrate concentration in pseudo second-order kinetic reactions.

4.2.5 Photo-Fenton oxidation of Amoxicillin Using Fe (LS) as Iron Catalyst

Effect of initial AMX concentration

Fig. 4.34 briefs the variations in percent AMX degradation and percent COD removal at the optimum conditions within 120 minutes of reaction time. The percent AMX degradation and the percent COD removal are 44.7 and 42.5 respectively in 5 minutes where as 81.6 percent AMX degradation and 80.0 percent COD removal are observed in 120 minutes for 27.4 x 10^{-3} mM initial AMX concentration. The percent drug removal increased from 81.6 to 97.6 and the percent COD removal decreased from 80.0 to 68.0 with the increase in drug concentration from 27.4 x 10^{-3} to 136.8 x 10^{-3} mM.

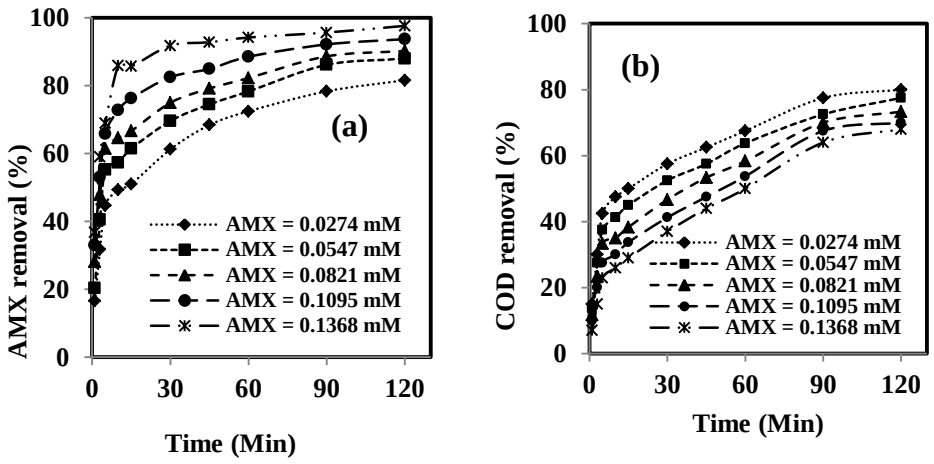


Fig. 4.34 Variations in (a) percent AMX degradation and (b) percent COD removal; [Reaction conditions; Photo-Fenton oxidation, pH 3, $[AMX]_0$ / $[H_2O_2]_0$ = 1 : 37.6 (molar), $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ = 76.7 : 1 (molar), UVC irradiation time = 120 min].

The use of Fe (LS) in Fenton reagent also followed the similar AMX degradation trend as that of Fe^{2+} in UVC assisted photo-Fenton process. The degradation of AMX increased and the mineralization decreased with increase in initial AMX concentration. This may be due to the synergetic effect of OH radicals and the drug radicals formed in photo-Fenton oxidation in which both the kinds of radicals may involve in the degradation of the substrate. On the other hand, the reduction in COD removal at high AMX concentrations is due to the formation of intermediate oxidation products and reduction in availability of total number of photons with increase in AMX concentration.

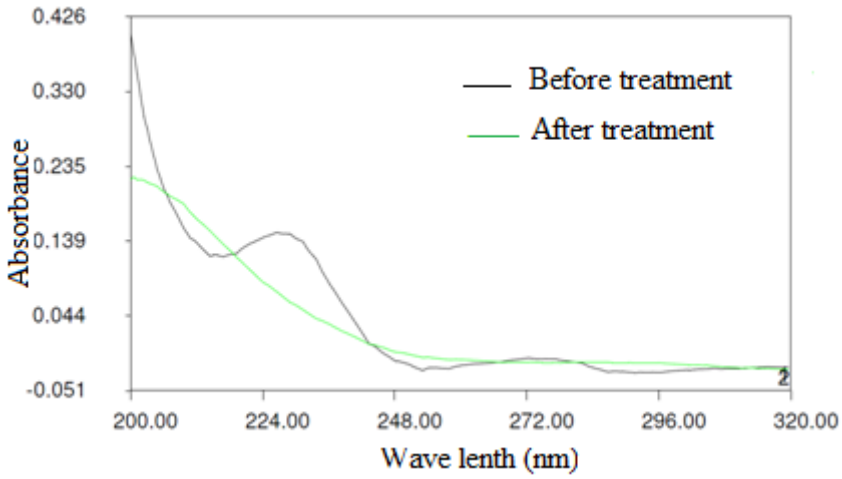


Fig. 4.35 UV – VIS absorbance spectra for AMX [Reaction condition; Photo-Fenton oxidation, pH = 3, $[AMX]_0$ = 27.4 x 10^{-3} mM, $[H_2O_2]_0$ = 1.03 mM, $[Fe\ (LS)]_0$ = 13.4 x 10^{-3} mM, reaction time = 240 min]

Fig. 4.35 shows the absorbance spectra of AMX before and after treatment. It can be observed that the peak at 226 nm before treatment is disappeared after treatment indicating the degradation of the drug in photo-Fenton oxidation of AMX using Fe (LS) as catalyst. The kinetic studies are carried out further to analyze the reaction in the photo-Fenton oxidation process.

Kinetic Studies on AMX Degradation

Kinetic studies on AMX degradation are carried out at the optimum conditions for 120 minutes of reaction time. The oxidation is fast in the beginning for a reaction time up to 5 minutes and therefore, the second-order kinetic equation (Eq. 3.1) has been fit up to the reaction time of 5 minutes (Zazo et al. 2005). The Fig.4.36 shows the trend of a pseudo second-order reaction kinetic model (Eq. 3.1) for initial AMX concentrations from 27.4 x 10^{-3} to 136.8 x 10^{-3} mM at optimum conditions in the 5 minutes UV irradiation time.

The values obtained for the pseudo second-order kinetic constants at ambient temperature (27 ± 3^o C) are summarized in Table 4.9. It is observed that the rate of degradation decreased with the increase in initial AMX concentration. As the rate constant is inversely proportional to initial concentrations in second-order reactions, the rate of degradation has decreased with the increase in initial AMX concentration.

The AMX samples are also analyzed by HPLC to determine the extent of degradation and formation of intermediates.

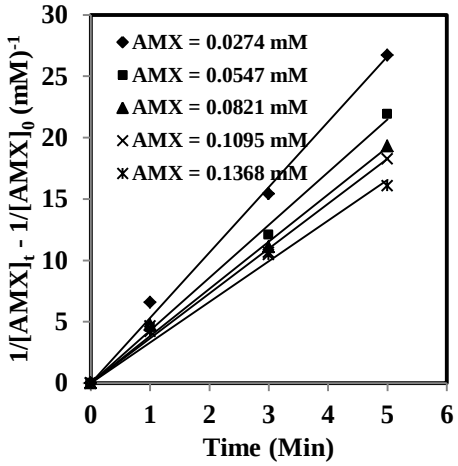


Fig. 4.36 Trend of pseudo-second order reaction kinetics for degradation of AMX in 5 min; [Reaction conditions; Photo-Fenton oxidation, pH 3, $[AMX]_0$ / $[H_2O_2]_0$ = 1 : 37.6 (molar), $[H_2O_2]_0$ / [Fe (LS)]$_0$ = 76.7 : 1(molar), and $[AMX]_0$ = 27.4 x 10^{-3} to 136.8 x 10^{-3} mM].

Table 4.9 Pseudo Second order kinetic rate constants for degradation of AMX by photo-Fenton oxidation using Fe (LS) as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[AMX]_0$ mM	[Fe (LS)]$_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}s^{-1}$	R^2
27.4 x 10^{-3}	13.4 x 10^{-3}	1.03	88.8	0.996
54.7 x 10^{-3}	26.9 x 10^{-3}	2.06	71.7	0.999
82.1 x 10^{-3}	40.3 x 10^{-3}	3.09	64.2	0.999
109.5 x 10^{-3}	53.8 x 10^{-3}	4.12	60.8	0.994
136.8 x 10^{-3}	67.2 x 10^{-3}	5.15	55.2	0.981

HPLC Analysis

HPLC analysis is carried out for the AMX samples of 27.4 x 10^{-3} mM concentration treated photo-Fenton oxidation at optimum conditions. The Fig. 4.37 shows the chromatogram of AMX before and after treatment using Fe^{2+} and Fe (LS). AMX peak before treatment is observed at 3.492 minutes of elution time (Fig. 4.37 (a)).

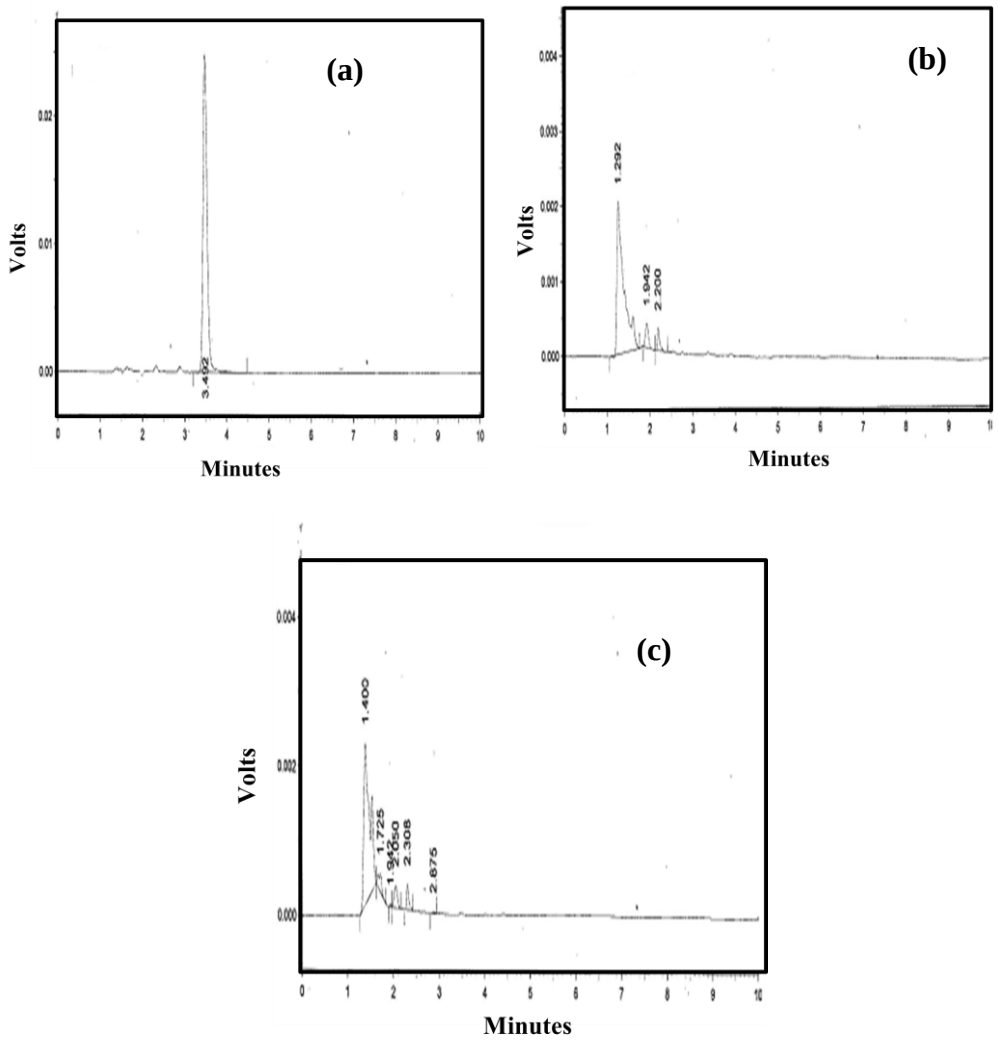


Fig. 4.37 HPLC chromatogram for (a) AMX standard before treatment (b) AMX sample after treatment at $[Fe^{2+}]_0$ = 8.95 x 10^{-3} mM, $[H_2O_2]_0$ = 0.88 mM (c) AMX sample with [Fe (LS)]$_0$ = 13.4 x 10^{-3} mM, $[H_2O_2]_0$ = 1.03 mM; [Reaction conditions; Photo-Fenton oxidation, $[AMX]_0$ = 27.4 x 10^{-3} mM, pH = 3, and UVC irradiation time = 120 min].

After treatment in Fenton oxidation with Fe^{2+}, the peak corresponding to AMX is absent but six peaks at different elution times are noticed in the chromatogram that means complete AMX is degraded and six intermediate compounds are formed to contribute COD (Fig. 4.37 (b)). Similarly, after Fenton oxidation of AMX with Fe (LS), the peak corresponding to AMX is absent but some other peaks at various elution times are noticed. This indicates the complete AMX degradation and formation of intermediates compounds which contribute to COD (Fig. 4.37 (c)). At

optimum conditions, complete degradation and incomplete mineralization of AMX is recognized with both the Fe^{2+} and Fe (LS) used in Fenton oxidation in 120 minutes. The HPLC analysis showed the better and accurate results over the spectrophotometer analysis. The results obtained in Fenton and photo-Fenton processes for degradation of AMX are compared and analyzed.

4.2.6 Comparison of Results in Fenton and Photo-Fenton Oxidation of Amoxicillin

The Fenton and photo-Fenton process for degradation of AMX are carried out at the same optimum experimental conditions. The Fenton process is carried out for 240 minutes and the photo-Fenton process is carried out for 120 minutes. The AMX degradation and mineralization efficiencies are more for UVC assisted photo-Fenton oxidation over the Fenton oxidation process. This is because of the production of more number of highly reactive oxidizing OH radicals in direct and indirect photolysis with UV irradiation. Fig. 4.38 shows the comparison of percent AMX degradation and percent COD removal between Fenton oxidation and UVC assisted photo-Fenton oxidation.

At the optimum conditions, 1.03 % more AMX degradation and 2.00 % more COD removal for 27.4 x 10^{-3} mM concentration of $[AMX]_0$ whereas 3.54 % more AMX degradation and 4.30 % more COD removal for 136.8 x 10^{-3} mM of $[AMX]_0$ are observed for Fe (LS) than that of Fe^{2+} in 240 minutes of reaction time. In Fenton oxidation, the AMX degradation and COD removals are more for the Fe (LS) when compared to that of Fe^{2+}. Also, the second order kinetic rate constants for Fe (LS) are about 1.21 times higher than that of Fe^{2+} in the Fenton oxidation of AMX. In photo-Fenton oxidation, at the optimum conditions, 2.59 % more AMX degradation and 5.00 % more COD removal for 27.4 x 10^{-3} mM of $[AMX]_0$ whereas 5.04 % more AMX degradation and 3.00 % more COD removal for 136.8 x 10^{-3} mM of $[AMX]_0$ are observed for Fe (LS) than that of Fe^{2+} in 120 minutes of UVC irradiation time (Fig. 4.38).

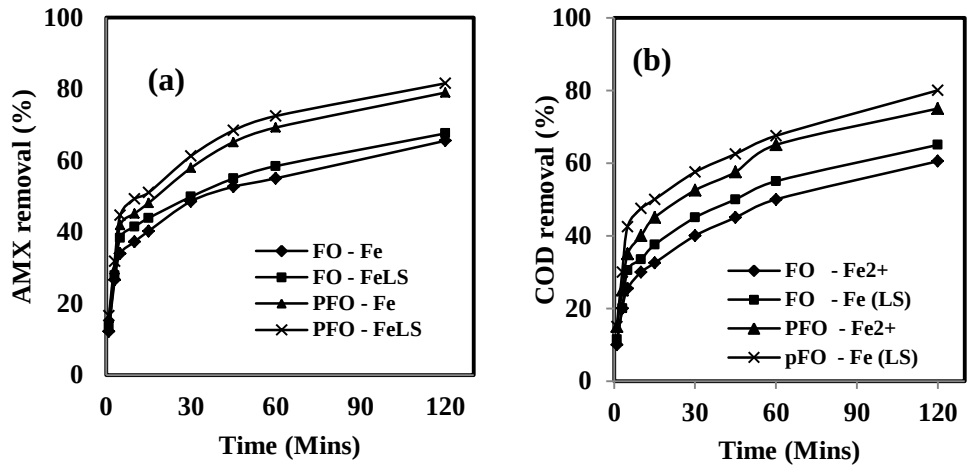


Fig. 4.38 Comparison of results between Fenton and photo-Fenton processes (a) percent AMX removal and (b) percent COD removal [Reaction conditions; UVC 8W light source, $[AMX]_0 = 27.4 \times 10^{-3}$ mM, pH 3, $[AMX]_0 / [H_2O_2]_0 = 1 : 32.2$ (molar) for Fe^{2+}, $[AMX]_0 / [H_2O_2]_0 = 1 : 37.6$ (molar) for Fe (LS), $[H_2O_2]_0 / [Fe^{2+}]_0 = 98.6 : 1$ (molar), $[H_2O_2]_0 / [Fe\ (LS)]_0 = 76.7 : 1$ (molar)].

When Fe (LS) is used, chloride ions are present in the oxidation system that may react with amine group in amoxicillin to form ammonium chloride due to greater affinity between them and hence the availability of chloride is less to form chloro-Fe (III) complexes and to scavenge the OH radicals present in the system. The acid in extract of iron from laterite soil acts as catalyst to break open the more highly strained four-membered β - lactam ring of AMX. The carbonyl group in the beta-lactam ring is highly susceptible to nuecleophiles and as such does not behave like a normal tertiary amide which is usually quite resistant to nucleophilic attack. Because of the above reasons the degradation and mineralization of AMX is more for Fe (LS) than Fe^{2+}.

AMX degradation of 13.5 % more with Fe^{2+} and 14.0 % more with Fe (LS) and COD removal of 14.5 % more with Fe^{2+} and 15.0 % more with Fe (LS) are observed for UV-C photo-Fenton over Fenton oxidation at the optimum experimental conditions within 120 minutes reaction time. It is observed that the second order kinetic rate constants are higher in photo-Fenton oxidation process than Fenton oxidation process. When Fe^{2+} is used, the second order degradation rate constants are about 1.44 times more for photo-Fenton oxidation than Fenton oxidation can be observed from Tables

4.6 and 4.8. Similarly, when Fe (LS) is used, the second order degradation rate constants are about 1.34 times more for photo-Fenton oxidation than Fenton oxidation can be observed from Tables 4.7 and 4.8. Over all, both the Fenton and photo-Fenton processes, when Fe^{2+} and Fe (LS) are used as catalysts, are the most effective in removing the AMX from aqueous solutions.

4.2.7 Comparison of Results of the Present Study with the Literature

Table 4.10 Comparison of results in the present study with the Literature on advanced oxidation of AMX in aqueous solution

Reference	Method	Experimental conditions			Results	
		$[AMX]_o$ mg/L	pH	Reaction time (min)	Degradation (%)	Mineralization (%)
Andrezoi et al. (2005)	O_3	5x10-4 M	5.5	4 20	100% -	- 18.2%
Elmolla and Chaudari (2010a)	UVA/H_2O_2/ TiO_2	104	5.0	30	100%	-
Elmolla and Chaudari (2009)	UVA/H_2O_2/ Fe^{2+}	500	3	75 1	- 100%	89.2%
Elmolla and Chaudari (2010b)	UVA/H_2O_2/ TiO_2 UVA/TiO_2 UVA/ZnO	104	5.0 3 5	300	100% 61% 100%	26% 12% 25%
Ghauch et al., (2009)	Fe^0	20		150	90%	
Zhang et al., (2006)	Extraction/FO/ RO/RO		3			99.7%
Ay and Kargi (2010)	H_2O_2/Fe^{2+}	105	3.5	2.5	100%	37%
Ay and Kargi (2011)	UVC/H_2O_2/ Fe^{2+}	10-200	3.5	60	100%	53%
Present study	**H_2O_2/Fe^{2+}** **H_2O_2/Fe (LS)** **UVC / H_2O_2/ Fe^{2+}** **UVC /H_2O_2/ Fe (LS)**	**10**	**3**	**240** **240** **120** **120**	**100%**	**72.5** **74.5** **75.0** **80.0**

The Table 4.2.5 consists of the comparison of results of the present study with some important results in the literature. In the present study, AMX degradation of 100 % with both Fe^{2+} and Fe (LS) by the both Fenton process and UV-C assisted photo-Fenton process are observed. COD removal of 72.5 % with Fe^{2+} and 74.5 % with Fe (LS) within 240 minutes of reaction time are observed by Fenton process. However, the COD removal of 75.0 % with Fe^{2+} and 80.0 % with Fe (LS) within 120 minutes of reaction time by UV-C assisted photo-Fenton process are observed.

4.3 Fenton and Photo-Fenton Oxidation of Diclofenac in Water

4.3.1 Spectral and Chemical Characterization of Diclofenac

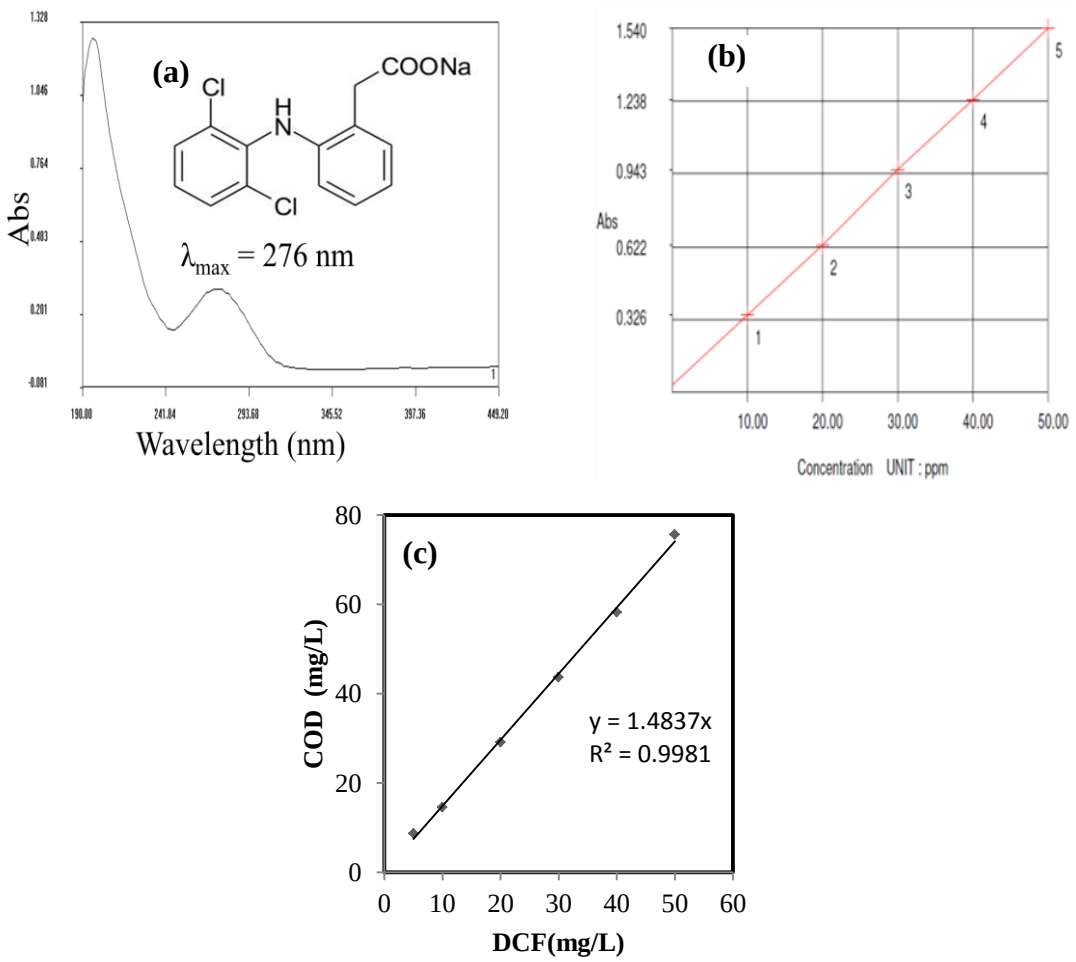


Fig. 4.39 (a) UV-VIS absorbance Spectrum of DCF with Chemical Structure (b) Calibration Curve for DCF (Standard data from UV-VIS double beam spectrophotometer) (c) Calibration Curve for COD of DCF

The UV-VIS absorbance spectrum of DCF is recorded from 190 to 450 nm using UV-VIS spectrophotometer and the absorbance peak for DCF is observed to be at wavelength 276 nm as shown in Fig.4.39 (a). A calibration curve between sample absorbance and concentration is established with 5 different DCF concentrations in the range of 31.4 x 10^{-3} to 157.2 x 10^{-3} mM. For the range of concentrations considered, a linear relationship between absorbance and concentration is established (Fig. 4.39 (b)). A COD calibration curve (Fig. 4.39 (c)) between DCF concentration and COD is established for DCF concentrations ranging from 15.7 x 10^{-3} to 157.2 x 10^{-3} mM. The COD is about 1.5 mg/L per mg of DCF concentration and this value is used in calculating the corresponding initial COD of the DCF samples. The DCF sample concentration, before and after treatment, is measured and the initial COD values are calculated in the subsequent experiments with the use of calibration curves.

4.3.2 Fenton Oxidation of Diclofenac Using Fe^{2+} as Iron Catalyst

This part deals with the evaluation of effect of various parameters like pH, $[H_2O_2]_0$, $[Fe^{2+}]_0$ and [Fe (LS)]$_0$ on degradation and mineralization of DCF and chemical kinetic studies on DCF degradation.

Effect of pH

The oxidation experiments are conducted at different pH values varying from 2.5 to 4.5 with initial DCF concentration of 31.4 x 10^{-3} mM, $[H_2O_2]_0$ 1.03 mM and $[Fe^{2+}]_0$ 17.9 x10^{-3} mM. The maximum percent DCF degradation and percent COD removal are observed to be 94.2 and 89.3 respectively at pH 3.5 (Fig. 4.40). From the Fig. 4.3.2 it is clearly evident that the DCF removal is less for the other values of pH.

At pH 3.5, DCF removal is maximum and it may be due to the formation of more $Fe(OH)^+$ which has much higher activity than Fe^{2+} in Fenton's oxidation (Badawy and Ali 2006). When pH is greater than 3.5, oxidation efficiency rapidly decreases due to auto-decomposition of H_2O_2 affecting the production of OH radicals (Badawy and Ali 2006) and deactivation of ferrous catalyst with the formation of ferric hydroxide precipitates (Luis et al. 2009). Also there is a decrease in oxidation potential of hydroxyl radical with increase in the pH value (Lucas and Peres 2006). When pH is less than 3.5, the reaction of H_2O_2 with Fe^{2+} is seriously affected that leads to

reduction in hydroxyl radical production and water is formed by the reaction of OH radicals with H^+ ions (Lucas and Peres 2006).

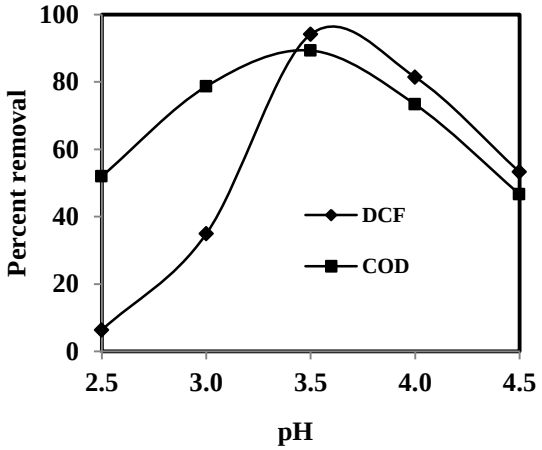


Fig. 4.40 Percent DCF degradation and percent COD removal at different pH; [Reaction conditions; Fenton oxidation, $[DCF]_0$ = 31.4 x 10^{-3} mM, $[H_2O_2]_0$ = 1.03 mM and $[Fe^{2+}]_0$ = 17.9 x10^{-3} mM, reaction time = 24 h].

During this study, an important observation has been noticed when the pH of the reaction mixture falls below 3.5. When pH is less than 3.5, precipitation of diclofenac is observed and hence it can be stated that under these acidic conditions DCF precipitates and settle down at the bottom of the reactor making DCF absent from the aqueous solution. A similar observation is reported by Perez-Estrada et al. (2005) in photo-Fenton degradation of diclofenac. This critical observation is considered in the subsequent experiments to avoid the confusion between 'precipitation' and 'degradation' and to obtain reliable results of expereiments (Perez-Estrada et al. 2005) when the pH falls below 3. Importantly, it should be noted that the DCF precipitation takes place at initial stage and then the degradation process is governed by the continuous redissollution of DCF (Perez-Estrada et al. 2005).

The COD removal is maximum at pH 3.5 but on either side of the pH 3.5 the COD removal is less. When pH is less than 3.5, the addition of acetonitirle for redissolution of DCF leads to higher COD values of the sample and therfore acetonitrile is not added to the sample for COD analysis. Therefore, the COD removal at pH less than 3.5 is not only due to oxidation of DCF alone but also due to removal of some precipitated DCF during the filtration of the sample. For this reason, the COD

removals at pH less than 3.5 are relatively more than the degradation of DCF. The COD removal at pH greater than 3.5 is observed to be less than the DCF degradation indicating the formation of oxidation intermdiates. Though, the maximum DCF removal is observed to be at a pH of 3.6 as seen in the Fig. 4.3.2, the optimum pH is considered as 3.5 in view of the maximum removals of both COD and DCF. The optimum pH value of 3.5, where the maximum degradation and mineralization has occurred is maintained in all the susequent experiments on degradation of diclofenac.

Effect of H_2O_2 and Fe^{2+} Concentration

The study for optimization of hydrogen peroxide concentration is carried out by varying H_2O_2 concentration from 0.15 to 1.62 mM, changing the iron concentrations from 8.95 x 10^{-3} to 22.4 x 10^{-3} mM for initial diclofenac concentration 31.4 x 10^{-3} mM at the optimum solution pH 3.5. The reaction equation 4.6 describes the reaction for complete mineralization of DCF in the Fenton Oxidation process.

$$C_{14}H_{10}Cl_2NO_2.Na + 33H_2O_2 + Fe(II) \rightarrow 14CO_2 + 37H_2O + HNO_3 + HCl + NaCl + Fe(II) \quad ...(4.6)$$

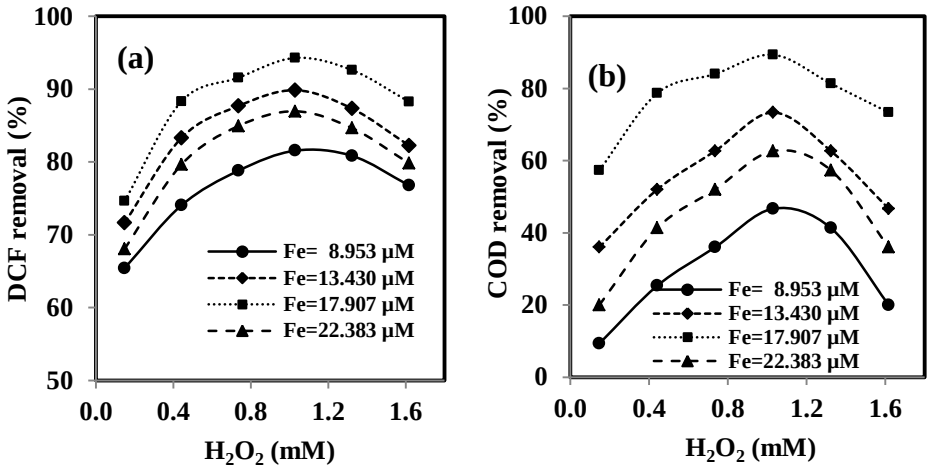


Fig. 4.41 Variations in (a) percent DCF degradation, (b) percent COD removal [Reaction conditions; Fenton oxidation, $[DCF]_0$ = 31.4 x10^{-3} mM, pH= 3.5, $[H_2O_2]_0$ = 0.15 to 1.62 mM, $[Fe^{2+}]_0$ = 8.95 x 10^{-3} to 22.4 x 10^{-3} mM, reaction time = 24 h].

The quantity of hydrogen peroxide required, based on Stoichiometric calculation (Eq. 4.1), for the complete mineralization of DCF is 3.53 mg per mg of DCF (33 moles of H_2O_2 per mole of DCF). However, in the present study, the maximum percent DCF

degradation is 94.3 and the corresponding percent COD removal is 89.3 at H_2O_2 concentration of 1.03 mM after a reaction time of 24 hours (Fig. 4.41). At the outset, the removal efficiency is increased with increase in H_2O_2 concentration up to 1.03 mM but further increase in the H_2O_2 concentration results in the decrease of the degradation and mineralization. The maximum DCF degradation and COD removal is observed at 1.03 mM of H_2O_2. When $[H_2O_2]_0$ is less than 1.03 mM, the degradation and mineralization are less, which is due to less production of OH radicals. On the other hand, when $[H_2O_2]_0$ is greater than 1.03 mM, the degradation and mineralization are less because of the scavenging effect of OH radicals with increase in the H_2O_2 concentration. This can be explained by the fact that the very reactive OH radicals are consumed by the increased H_2O_2 that results finally into water (Hsueh et al. 2005). The results obtained for the removal efficiencies indicate the incomplete mineralization and the presence of intermediates in the aqueous solution as can be seen in Fig. 4.41.

Along with the disappearance of DCF, COD removal from the aqueous solution is significantly affected by the addition of Fe^{2+} to the reaction mixture. The maximum percent DCF degradation of 94.3 and the corresponding percent COD removal of 89.33 are observed at 17.9 x 10^{-3} mM Fe^{2+} concentration. The variations in percent DCF degradation and COD removal can be observed in Fig. 4.41. The degradation and mineralization increased with increase in Fe^{2+} concentration up to 17.9 x 10^{-3} mM due to increase in OH radical production (Yilmaz et al. 2010). Contrary to this, at Fe^{2+} concentrations higher than 17.9 x 10^{-3} mM, the DCF and COD removals are less. This may be due to the reaction of Fe^{2+} with OH radicals that results in the scavenging of OH radical (Hsueh et al. 2005). The observed ratios, $[DCF]_0$ / $[H_2O_2]_0$ = 1 : 32.8 (molar) and $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 57.5 : 1 (molar) at which degradation and mineralization is the maximum, are maintained in the subsequent experiments for studying the effect of initial DCF concentration.

Effect of Initial DCF Concentration

Initially, the oxidation experiments are carried out at the optimum conditions for 24 hours; however, the DCF degradation and COD removal are not substantial after 240 minutes of reaction time. Hence, subsequent experiments are carried out for a

reaction time of 240 minutes. The variations in percent DCF degradation and percent COD removals at optimum conditions are shown in Fig. 4.42. The percent DCF degradation and percent COD removal are observed as 66.4 and 52.0 respectively in 5 minutes, while 74.3 percent DCF degradation and 72.8 of percent COD removal are observed in 240 minutes for 31.4 x 10^{-3} mM (10 mg/L) initial concentration of DCF. With the increase in DCF concentration from 31.4 x 10^{-3} mM to 157.2 x 10^{-3} mM (10 to 50 mg/L), the percent drug removal increased from 74.3 to 82.3 and the percent COD removal decreased to 50.9 from 72.8.

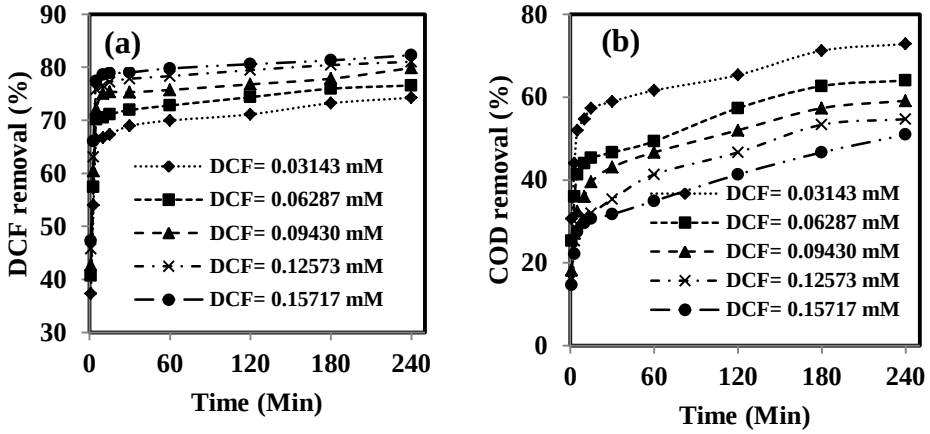


Fig. 4.42 Variations in (a) percent DCF degradation and (b) percent COD removal; [Reaction conditions; Fenton oxidation, pH 3.5, $[DCF]_0 / [H_2O_2]_0$ = 1 : 32.8 (molar) and $[H_2O_2]_0 / [Fe^{2+}]_0$ = 57.5 : 1 (molar), reaction time = 240 min].

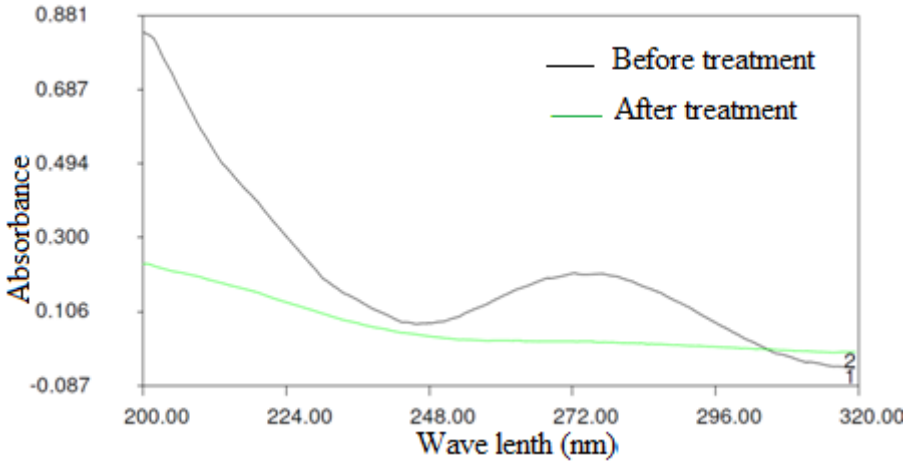


Fig. 4.43 UV – VIS absorbance spectra for DCF [Reaction condition; Fenton oxidation, pH = 3.5, $[DCF]_0$ = 31.4 x 10^{-3} mM, $[H_2O_2]_0$ = 1.03 mM, $[Fe^{2+}]_0$ = 17.9 x 10^{-3} mM, reaction time = 240 min]

The fact that the disappearance of DCF increases with the substrate concentration clearly means that a competitive reactions are occurring. This probably due to synergetic effect of OH radicals along with the drug radicals formed in the Fenton oxidation wherein both the kinds of the radicals may degrade the substrate molecule. On the other hand, the formation of intermediates also may increase with increase in substrate concentration and hence COD removal decreased with increase in DCF concentration. This can be supported by the literature, where COD removal of pharmaceutical wastewater by Fenton oxidation is more for the lower initial concentrations of drugs (Yilmaz et al. 2010).

The degradation of DCF can be supported by UV-VIS absorbance spectra of DCF sample before and after treatment. By comparing the UV-VIS spectra as shown in the Fig. 4.43, it is evident that the absorbance peak of DCF at 276 nm is disappeared in the spectra of DCF sample after treatment indicating the degradation of DCF.

Kinetic Studies on DCF Degradation

The kinetic studies on DCF degradation are conducted at the optimum conditions for 240 minutes of reaction time. The oxidation is fast in the beginning for reaction time up to 5 minutes and therefore, the second-order kinetic equation has been fit up to the reaction time of 5 minutes (Zazo et al. 2005).

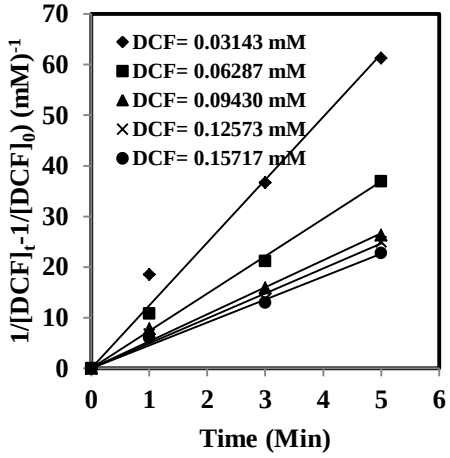


Fig. 4.44 Trend of pseudo-second order reaction kinetics for degradation of DCF in 5 min; [Reaction conditions; Fenton oxidation, pH 3, $[DCF]_0$ / $[H_2O_2]_0$ = 1 : 32.8 (molar), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 57.5 : 1 (molar) and $[DCF]_0$ = 31.4 x 10^{-3} to 157.2 x 10^{-3} mM].

The trend of a second-order reaction kinetic model [Eq. 3.1] for initial DCF concentrations varying from 31.4 x 10^{-3} to 157.2 x 10^{-3} mM treated at the optimum conditions is shown in Fig. 4.44. The values obtained for the pseudo second-order kinetic constants at ambient temperature (27 ± 3^{o} C) are tabulated in Table 4.11. It is observed from the results that the rate of degradation decreased with the increase in initial DCF concentration. This can be supported by the fact that the rate constant in a second-order reaction is inversely proportional to the initial concentration of the reactant.

Table 4.11 Pseudo Second order kinetic rate constants for degradation of DCF by Fenton oxidation using Fe^{2+} as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[DCF]_0$ mM	$[Fe^{2+}]_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}s^{-1}$	R^2
31.4 x 10^{-3}	17.9 x 10^{-3}	1.03	207.0	0.981
62.9 x 10^{-3}	35.8 x 10^{-3}	2.06	123.1	0.983
94.3 x 10^{-3}	53.7 x 10^{-3}	3.09	88.9	0.985
125.7 x 10^{-3}	71.6 x 10^{-3}	4.12	82.1	0.986
157.2 x 10^{-3}	89.6 x 10^{-3}	5.15	75.6	0.991

The subsequent experiments are carried out to evaluate the Fe (LS) in the Fenton oxidation of DCF. Similar kinetic studies are carried out for Fe (LS) in Fenton's reagent in the succeeding oxidation experiments.

4.3.3 Fenton Oxidation of Diclofenac Using Fe (LS) as Iron Catalyst

The optimum pH value of 3.5 obtained during the investigation of DCF degradation using Fe^{2+} is maintained for the Fenton experiments with Fe (LS). The effect of various parameters like $[H_2O_2]_0$, [Fe (LS)] and $[DCF]_0$ on Fenton oxidation of DCF using Fe (LS) as iron catalyst are elaborated below.

Effect of H_2O_2 and Fe (LS) Concentration

In this study, the hydrogen peroxide concentration is varied from 0 to 1.62 mM and Fe (LS) concentration is varied from 8.95 x 10^{-3} to 22.4 x 10^{-3} mM for initial DCF concentration of 31.4 x 10^{-3} mM at initial solution pH of 3.5. Fig. 4.45 shows the

variations in percent DCF degradation and COD removal at the different dosages of Fe (LS) and H_2O_2 for 31.4 x 10^{-3} mM initial concentration of DCF at pH of 3.5, reaction time of 24 hours. The maximum percent DCF degradation is observed to be 68.1 and the corresponding percent COD removal is observed to be 60.0 at initial H_2O_2 concentration of 1.03 mM and initial Fe (LS) concentration of 13.4 x 10^{-3} mM after a reaction time of 24 hours. The percent degradation of DCF and COD removal increased with increase in H_2O_2 concentration up to 1.03 mM. This may be due to increase in OH radicals with the increase in H_2O_2 concentration up to 1.03 mM. Further increase in the H_2O_2 concentration decreased the degradation and mineralization. This is because of the scavenging of OH radicals with increase in the H_2O_2 concentration.

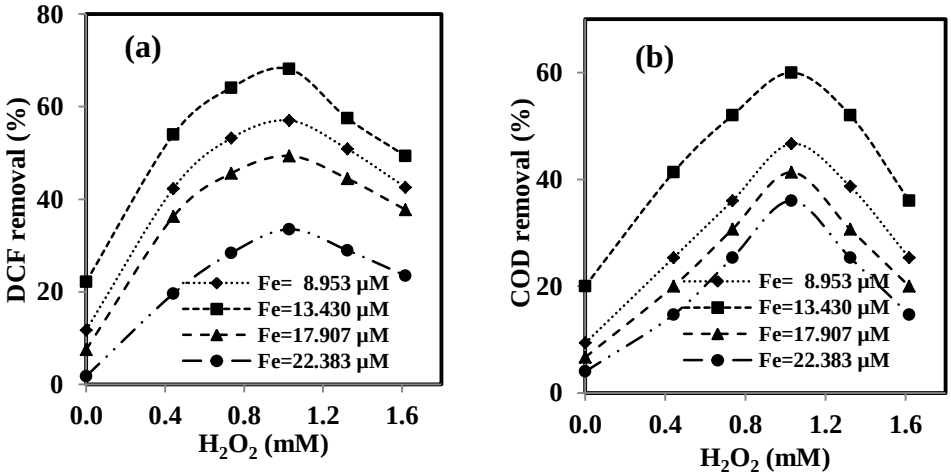


Fig. 4.45 Variations in (a) percent DCF degradation (b) percent COD removal; [Reaction conditions; Fenton oxidation, $[DCF]_0$ = 31.4 x 10^{-3} mM, pH 3.5, $[H_2O_2]_0$ = 0 – 1.62 mM, $[Fe\ (LS)]_0$ = 8.95 x10^{-3} to 22.4 x 10^{-3} mM, reaction time = 24 h].

Moreover, both the DCF degradation and COD removal increased with addition of Fe (LS) as shown in Fig. 4.45. This is because sufficient catalyst is required to produce more amounts of OH radicals. The degradation and COD removals are the maximum at Fe (LS) concentration of 13.4 x 10^{-3} mM. It may be due to presence of maximum amount of OH radicals in the treatment system. However, the DCF and COD removals are less at Fe (LS) concentrations higher than 13.4 x 10^{-3} mM. This is due to the scavenging of OH radicals by higher catalyst concentrations. As per the results obtained, the optimum molar ratios are $[DCF]_0$ / $[H_2O_2]_0$ = 1 : 32.8 and $[H_2O_2]_0$ / [Fe

$(LS)]_0$ = 76.7 : 1. These values are considered in the subsequent experiments that are conducted to investigate the effect of initial AMX concentration.

Effect of initial DCF concentration

The initial DCF concentration is varied from 31.4 x 10^{-3} to 157.2 x 10^{-3} mM and the optimum $[DCF]_0$ / $[H_2O_2]_0$ molar ratio 1 : 32.8 and the optimum $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ molar ratio 76.7 : 1 are kept constant for all the concentrations of DCF. Fig. 4.46 shows the variations in percent DCF degradation and percent COD removal at the optimum conditions in 240 minutes of reaction time.

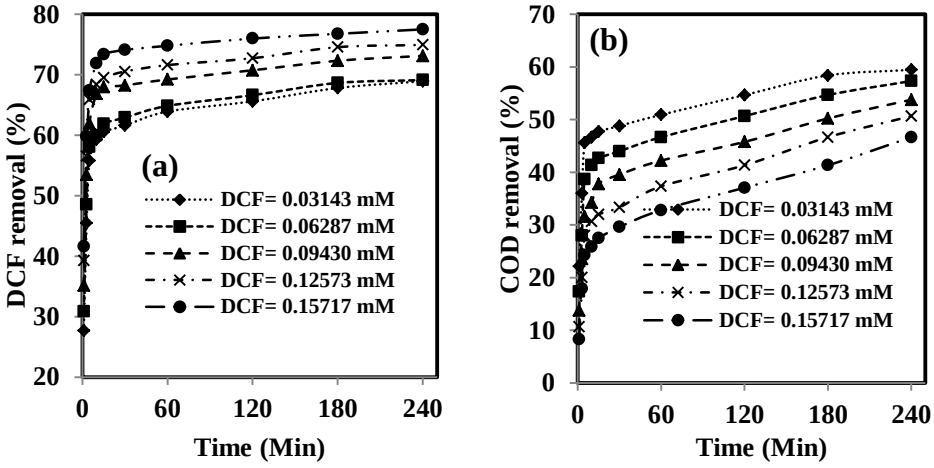


Fig. 4.46 Variations in (a) percent DCF degradation and (b) percent COD removal; [Reaction conditions; Fenton oxidation, pH 3.5, $[DCF]_0$ / $[H_2O_2]_0$ = 1 : 32.8 (molar) and $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ = 76.7 : 1 (molar), reaction time = 240 min].

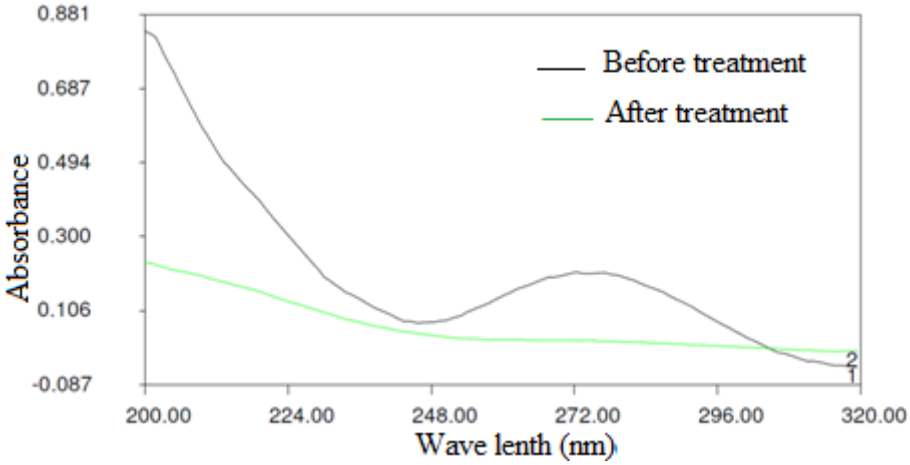


Fig. 4.47 UV – VIS absorbance spectra for DCF [Reaction condition: Fenton oxidation, pH = 3.5, $[DCF]_0$ = 31.4 x 10^{-3} mM, $[H_2O_2]_0$ = 1.03 mM, $[Fe\ (LS)]_0$ = 13.4 x 10^{-3} mM, reaction time = 240 min].

The percent DCF degradation and the percent COD removal are 55.8 and 45.6 respectively in 5 minutes while 68.9 percent DCF degradation and 59.5 percent COD removal is observed in 240 minutes for 31.4 x 10^{-3} mM initial DCF concentration. The percent drug removal increased from 68.9 to 77.5 and the percent COD removal decreased from 59.5 to 46.7 with the increase in drug concentration from 31.4 x 10^{-3} to 157.2 x 10^{-3} mM. The use of Fe (LS) in Fenton reagent also followed the similar DCF degradation trend as that of Fe^{2+}. The degradation of DCF increased and the mineralization decreased with increase in initial DCF concentration. This may be due to the synergetic effect of OH radicals and the drug radicals formed in Fenton oxidation in which both the kinds of radicals may involve in the degradation of the substrate. On the other hand, the formation of the intermediates also may increase with increase in substrate concentration and hence COD removal decreased with increase in the concentration of substrate. This result is in agreement with the result of Yilmaz et al. 2010, who reported the COD removal of pharmaceutical wastewater by Fenton's oxidation is more for the lower initial concentrations of drugs. The UV-VIS absorbance spectrum of DCF (Fig. 4.47) also supports the degradation of the drug using Fe (LS) in Fenton oxidation.

Kinetic Studies on DCF Degradation

Kinetic studies on DCF degradation are carried out at the optimum conditions for 240 minutes of reaction time. The oxidation is fast in the beginning of reaction and therefore, the second-order kinetic equation is used to fit the data obtained up to the reaction time of 5 minutes.

The Fig. 4.48 shows the trend of a pseudo second-order reaction kinetic model [Eq. 3.1] for initial DCF concentrations ranging from 31.4 x 10^{-3} to 157.2 x10^{-3} mM at the optimum conditions within the 5 minutes. The values obtained for the pseudo second-order kinetic constants obtained at ambient temperature (27 ± 3^{o} C) are summarized in Table 4.12. The rate of degradation decreased with the increase in initial DCF concentration. This can be supported by the fact that the rate constant is inversely proportional to the concentration of substrate.

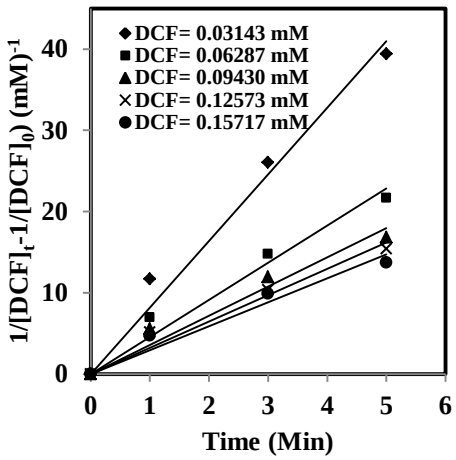


Fig. 4.48 Trend of pseudo-second order reaction kinetics for degradation of DCF in 5 min; [Reaction conditions; Fenton oxidation, pH 3, $[DCF]_0$ / $[H_2O_2]_0$ = 1 : 32.8 (molar), $[H_2O_2]_0$ / [Fe (LS)]$_0$ = 76.7 : 1 (molar), and $[DCF]_0$ = 31.4 x10^{-3} to 157.2 x 10^{-3} mM].

Table 4.12 Pseudo Second order kinetic rate constants for degradation of DCF by Fenton oxidation using Fe (LS) as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[AMX]_0$ mM	$[Fe (LS)]_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}s^{-1}$	R^2
31.4 x 10^{-3}	13.4 x 10^{-3}	1.03	136.7	0.981
62.9 x 10^{-3}	26.9 x 10^{-3}	2.06	76.1	0.968
94.3 x 10^{-3}	40.3 x 10^{-3}	3.09	59.8	0.960
125.7 x 10^{-3}	53.7 x 10^{-3}	4.12	53.9	0.964
157.2 x 10^{-3}	67.2 x 10^{-3}	5.15	49.1	0.950

HPLC Analysis

HPLC analysis is carried out for the DCF samples of 31.4 x 10^{-3} mM concentration treated at the optimum conditions for a reaction time of 240 minutes. The Fig. 4.49 shows the chromatogram of DCF before and after treatment using Fe^{2+} and Fe (LS). DCF peak before treatment is observed at 5.167 minutes of elution time (Fig. 4.49 (a)). About 79.3 % of DCF is degraded and four intermediates are formed to contribute COD when Fe^{2+} is used (Fig. 4.49 (b)). However, when Fe (LS) is used, about 74.3 % of DCF is removed and also intermediates formed that contribute to

COD (Fig. 4.49 (c)). At optimum conditions, incomplete degradation and mineralization of DCF is observed with both Fe^{2+} and Fe (LS) used in Fenton oxidation in 240 minutes as can be seen in Fig. 4.49.

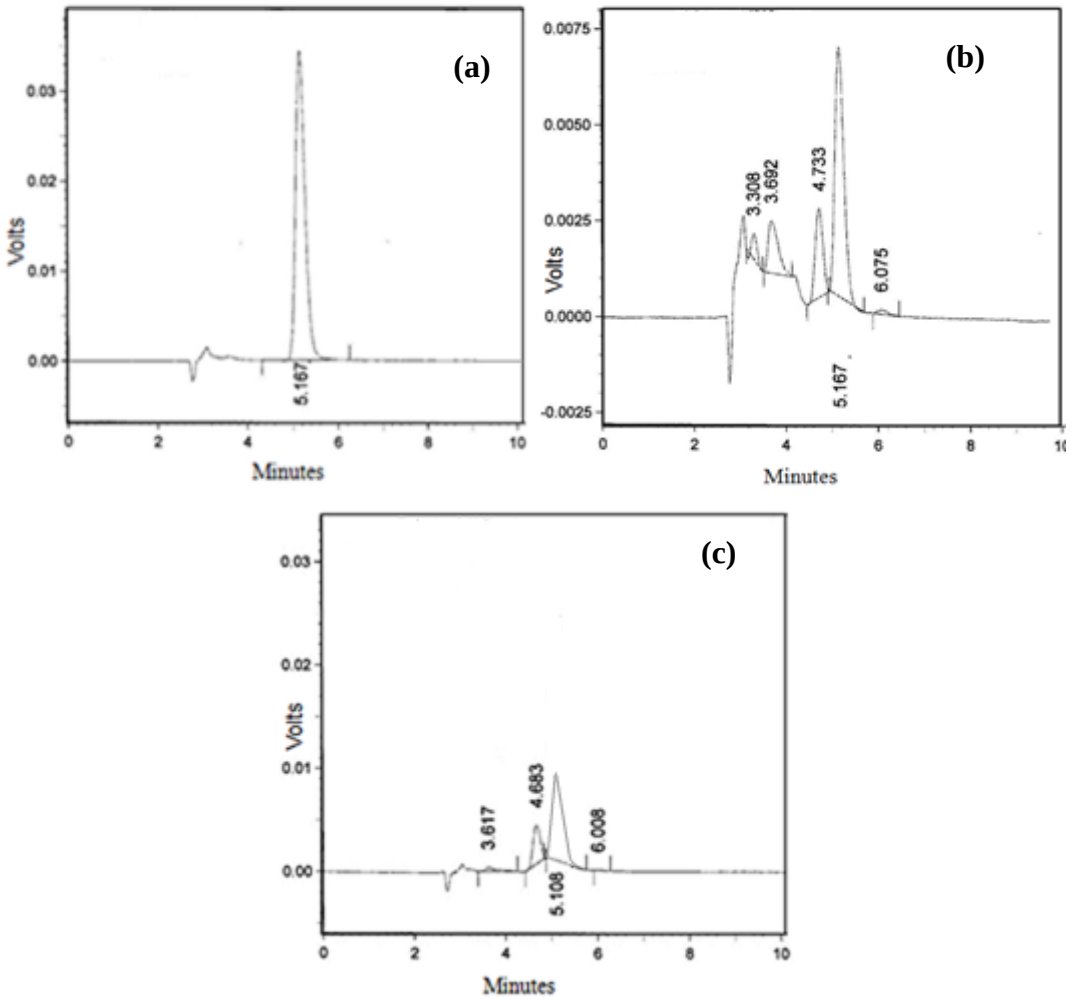


Fig. 4.49 HPLC chromatogram of (a) DCF standard before treatment (b) DCF sample after treatment with $[Fe^{2+}]_0$ = 17.9 x 10^{-3} mM (c) DCF sample after treatment with [Fe (LS)]$_0$ = 13.4 x 10^{-3} mM; [Reaction conditions; Fenton oxidation, pH 3.5, $[DCF]_0$ = 31.4 x 10^{-3} mM, $[H_2O_2]_0$ = 1.03 mM, reaction time = 240 min].

4.3.4 Photo-Fenton Oxidation of Diclofenac Using Fe^{2+} as Iron Catalyst

The efficacy of the Fenton oxidation process can be strongly enhanced by irradiation with UV or visible light (Sun and Pignatello, 1993). This part of study deals with the effect of initial concentration of DCF and a kinetic study on degradation of and mineralization of DCF by photo-Fenton oxidation process. UVC assisted photo-

Fenton process is carried out at the optimum conditions that are obtained during the Fenton oxidation of DCF.

Effect of Initial DCF Concentration

Initially, the oxidation experiments are carried out at the optimum conditions for 12 hours; however, the DCF degradation and COD removal are very slow and not appreciable after 120 minutes of UV irradiation time. Subsequently, photo-Fenton experiments are carried out for a reaction time of 120 minutes. The percent DCF degradation and the percent COD removal are 81.2 and 62.7 respectively in 5 minutes but 85.9 percent DCF degradation and 74.9 percent COD removal are observed in 120 minutes for 31.4 x 10^{-3} mM initial DCF concentration as can be seen in Fig. 4.50. The percent drug removal increased from 85.9 to 89.7 and the percent COD removal decreased from 74.9 to 57.9 with the increase in drug concentration from 31.4 x 10^{-3} to 157.2 x 10^{-3} mM.

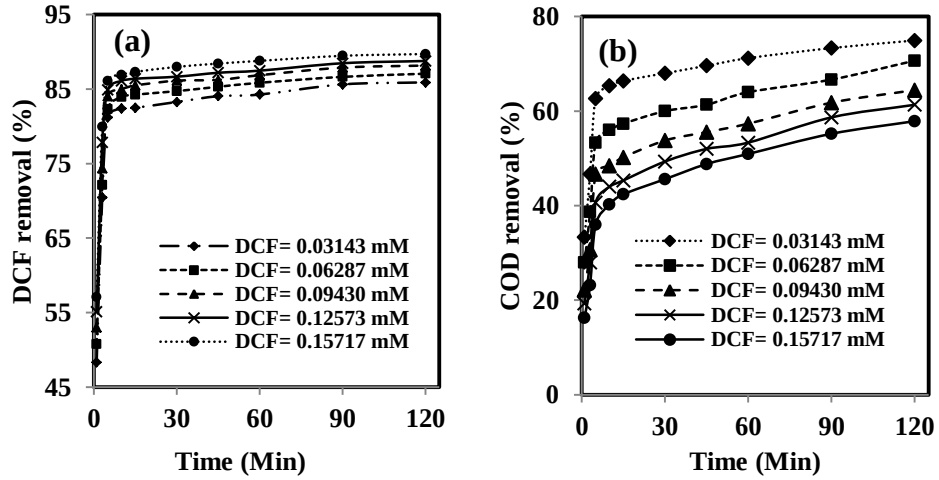


Fig. 4.50 Variations in (a) percent DCF degradation and (b) percent COD removal; [Reaction conditions; Photo-Fenton oxidation, pH 3.5, $[DCF]_0$ / $[H_2O_2]_0$ = 1 : 32.8 (w/w), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 57.5 : 1 (molar) and UVC irradiation time = 120 min].

At the optimum $[H_2O_2]_0$ / $[Fe^{2+}]_0$ ratio of 57.5 : 1 (molar), degradation of the drug increased with increase in its initial concentration. This may be due to the synergetic effect of OH radicals and the drug radicals formed in photo-Fenton oxidation in which both the kinds of radicals may involve in the degradation of the substrate. On the other hand, the formation of the intermediates may also increase with increase in the substrate concentration and hence COD removal decreased with increase in the

concentration of substrate. This result is in accordance with the literature, where COD removal of pharmaceutical wastewater by UV-Fenton Oxidation is more for the lower initial concentrations of the pollutant (Devi et al. 2009). This phenomenon of decrease in COD removal with increase in initial diclofenac concentration is also associated with the characteristics of UV visible absorption spectrum of the DCF (λ_{max}=276 nm) that is significant near 254 nm (UV-C light is used) and hence the solution with higher drug concentration absorbs a more significant fraction of the emitted UV light at 254 nm than that of a lower initial concentration, consequently, the number of available photons decreases leading to a decrease in the formation of OH radicals (Feng et al. 2003) to degrade the intermediates formed in the reaction.

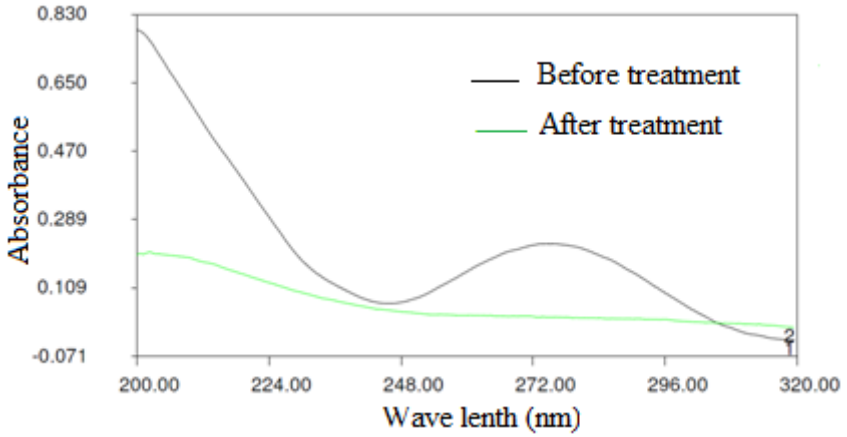


Fig. 4.51 UV – VIS absorbance spectra for DCF [Reaction condition; Photo-Fenton oxidation, pH = 3.5, $[DCF]_0$ = 31.4 x 10^{-3} mM, $[H_2O_2]_0$ = 1.03 mM, $[Fe^{2+}]_0$ = 17.9 x 10^{-3} mM, reaction time = 120 min]

The degradation of the DCF can well be supported by the absorbance spectra of DCF sample before and after treatment (Fig. 4.51). The kinetic studies are carried out in the following experiments.

Kinetic Studies on DCF Degradation

A number of chemical species are involved in the reaction scheme of photo-Fenton oxidation, but, at given experimental conditions, OH radical is the primary oxidizing species in the overall process (Zazo et al. 2005). Aromatic intermediates of the oxidation may reduce Fe^{3+} to Fe^{2+} (Chen and pignatello 1997) that increase significantly the OH radical generation, which in turn enhances the oxidation rate. Due to the ability of regeneration of OH radicals in the oxidation system, the

concentration of OH radicals can be considered constant at different operating conditions (Zazo et al. 2005). In this study, both degradation and mineralization rates of DCF are described with pseudo-second order kinetics equation (3.1).

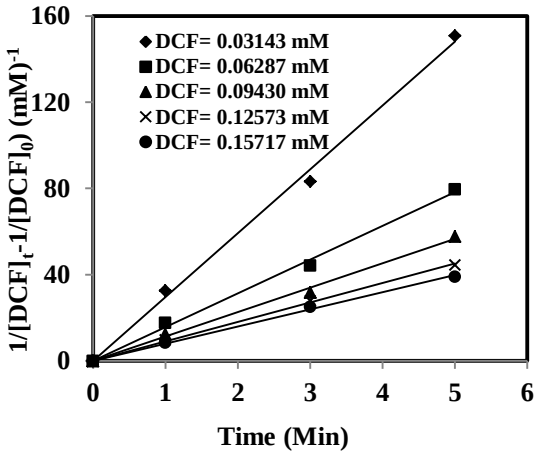


Fig. 4.52 Trend of pseudo-second order reaction kinetics for degradation of DCF in 5 min; [Reaction conditions; Photo-Fenton oxidation, pH 3.5, $[DCF]_0$ / $[H_2O_2]_0$ = 1: 32.8 (molar), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 57.5 : 1 (molar), and $[DCF]_0$ = 31.4 x 10^{-3} to 157.2 x 10^{-3} mM].

Table 4.13 Pseudo Second order kinetic rate constants for degradation of DCF by photo-Fenton oxidation using Fe^{2+} as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[DCF]_0$ mM	$[Fe^{2+}]_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}s^{-1}$	R^2
31.4 x 10^{-3}	17.9 x 10^{-3}	1.03	493.1	0.996
62.9 x 10^{-3}	35.8 x 10^{-3}	2.06	259.7	0.996
94.3 x 10^{-3}	53.7 x 10^{-3}	3.09	188.6	0.996
125.7 x 10^{-3}	71.6 x 10^{-3}	4.12	148.3	0.998
157.2 x 10^{-3}	89.6 x 10^{-3}	5.15	130.5	0.998

The oxidation is observed to be fast in the beginning of reaction and therefore, the second-order kinetic equation has been fit up to the reaction time of 5 minutes. The Fig.4.52 shows the trend of a second-order reaction kinetic model [Eq. (3.1)] in the 5 minutes for degradation of DCF at optimum conditions. The rate of degradation and mineralization decreased with the increase in initial DCF concentration (Table 4.13)

as the rate constant of the second order reaction is inversely proportional to the initial concentration. Hence, it is observed that with the increase in initial concentration, the rate constants decreased. The similar experimentation is carried out with Fe (LS) as catalyst.

4.3.5 Photo-Fenton Oxidation of Diclofenac Using Fe (LS) as Iron Catalyst

Effect of initial DCF concentration

The variations in percent DCF degradation and percent COD removal at the optimum conditions within 120 minutes of reaction time are shown in Fig. 4.53. The percent DCF degradation and the percent COD removal are 61.4 and 45.6 respectively in 5 minutes where as 71.9 percent DCF degradation and 65.3 percent COD removal are observed in 120 minutes for 31.4 x 10^{-3} mM initial DCF concentration. The percent drug removal increased from 71.9 to 80.5 and the percent COD removal decreased from 65.3 to 52.0 with the increase in drug concentration from 31.4 x 10^{-3} to 157.2 x 10^{-3} mM.

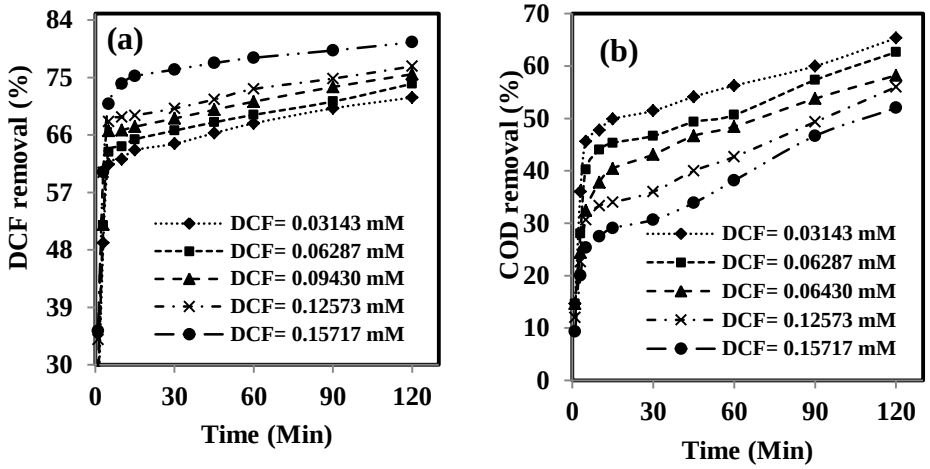


Fig. 4.53 Variations in (a) percent DCF degradation and (b) percent COD removal; [Reaction conditions; Photo-Fenton oxidation, pH 3.5, $[DCF]_0$ / $[H_2O_2]_0$ = 1 : 32.8 (molar), $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ = 76.7 : 1 (molar), UVC irradiation time = 120 min].

The use of Fe (LS) in Fenton reagent also followed the similar DCF degradation trend as that of Fe^{2+} in UVC assisted photo-Fenton process. The degradation of DCF increased and the mineralization of DCF decreased with the increase in initial DCF concentration (Fig. 4.53). This may be due to the synergetic effect of OH radicals and

the drug radicals formed in photo-Fenton oxidation in which both the kinds of radicals may involve in the degradation of the substrate. Conversely, the reduction in COD removal at high DCF concentrations is due to the formation of intermediate oxidation products and reduction in availability of total number of photons with increase in DCF concentration.

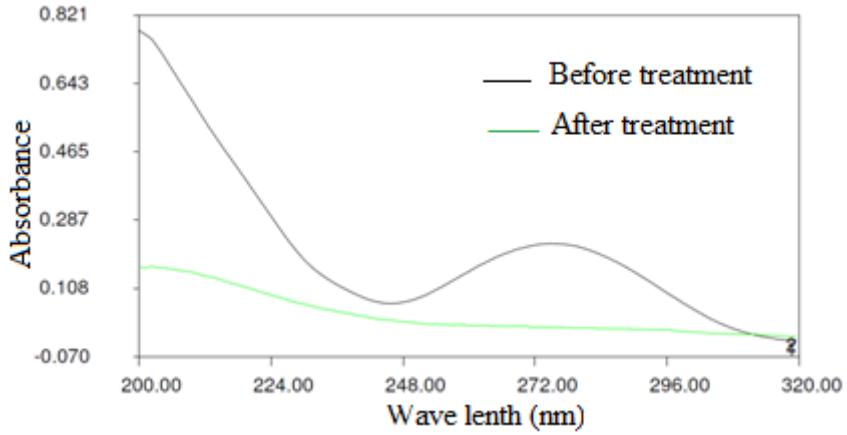


Fig. 4.54 UV – VIS absorbance spectra for DCF [Reaction condition; Photo-Fenton oxidation, pH = 3.5, $[DCF]_0$ = 31.4 X 10^{-3} mM, $[H_2O_2]_0$ = 1.03 mM, $[Fe\ (LS)]_0$ = 13.4 x 10^{-3} mM, reaction time = 120 min]

Fig. 4.54 shows the UV-VIS absorbance spectra of DCF before and after treatment. It can be observed that the peak at 276 nm before treatment is disappeared after treatment indicating the degradation of the drug in photo-Fenton oxidation of DCF using Fe (LS) as catalyst. The kinetic studies are carried out further to analyze the reaction in the photo-Fenton oxidation process.

Kinetic Studies on DCF Degradation

Kinetic studies on DCF degradation are carried out at the optimum conditions for 120 minutes of reaction time. The oxidation is faster in the beginning of reaction and therefore, the second-order kinetic equation is used up to the reaction time of 5 minutes. The Fig. 4.55 shows the trend of a second-order reaction kinetic model (Eq. 3.1) in the 5 minutes for initial DCF concentrations ranging from 31.4 x 10^{-3} to 157.2 x 10^{-3} mM at the optimum conditions. The values obtained for the second-order kinetic constants at ambient temperature (27 ± 3^{o} C), are summarized in Table 4.14. As the rate constant is inversely proportional to initial concentrations in second-order reactions, the rate of degradation has decreased with the increase in initial DCF

concentration. The results obtained in photo-Fenton process using Fe^{2+} and Fe (LS) are compared and analyzed. The DCF samples are also analyzed by HPLC to determine the extent of degradation and formation of intermediates.

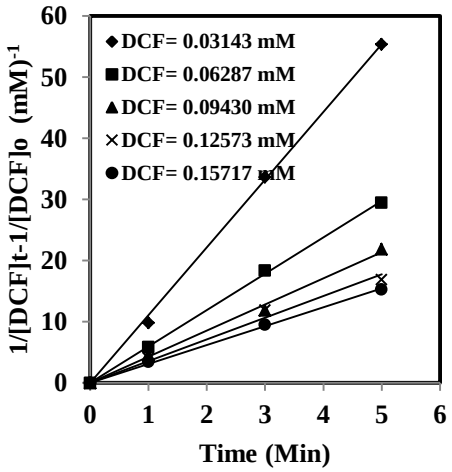


Fig. 4.55 Trend of pseudo-second order reaction kinetics for degradation of DCF in 5 min; [Reaction conditions; Photo-Fenton oxidation, pH 3.5, $[DCF]_0$ / $[H_2O_2]_0$ = 1 : 32.8 (molar), $[H_2O_2]_0$ / [Fe (LS)]$_0$ = 76.7 : 1(molar), and $[DCF]_0$ = 31.4 x 10^{-3} to 157.2 x 10^{-3} mM].

Table 4.14 Pseudo Second order kinetic rate constants for degradation of DCF by photo-Fenton oxidation using Fe (LS) as iron catalyst

Initial conditions			Pseudo Second order kinetic constants	
$[DCF]_0$ mM	[Fe (LS)]$_0$ mM	$[H_2O_2]_0$ mM	$M^{-1}s^{-1}$	R^2
31.4 x 10^{-3}	13.4 x 10^{-3}	1.03	184. 7	0.999
62.9 x 10^{-3}	26.9 x 10^{-3}	2.06	99.3	0.999
94.3 x 10^{-3}	40.3 x 10^{-3}	3.09	71.2	0.999
125.7 x 10^{-3}	53.8 x 10^{-3}	4.12	59.3	0.995
157.2 x 10^{-3}	67.2 x 10^{-3}	5.15	51.6	0.985

HPLC Analysis

HPLC analysis is carried out for the DCF samples of 31.4 x 10^{-3} mM concentration treated at optimum conditions. The Fig. 4.56 shows the chromatogram of DCF before and after treatment using Fe^{2+} and Fe (LS). DCF peak before treatment is observed at 5.167 minutes of elution time (Fig. 4.56 (a)). When Fe^{2+} is used, for the sample after treatment for 120 minutes, two minor peaks in chromatogram at 5.133 min

corresponding to diclofenac and at 4.658 min corresponding to an intermediate are observed as seen in Fig. 4.56 (b).

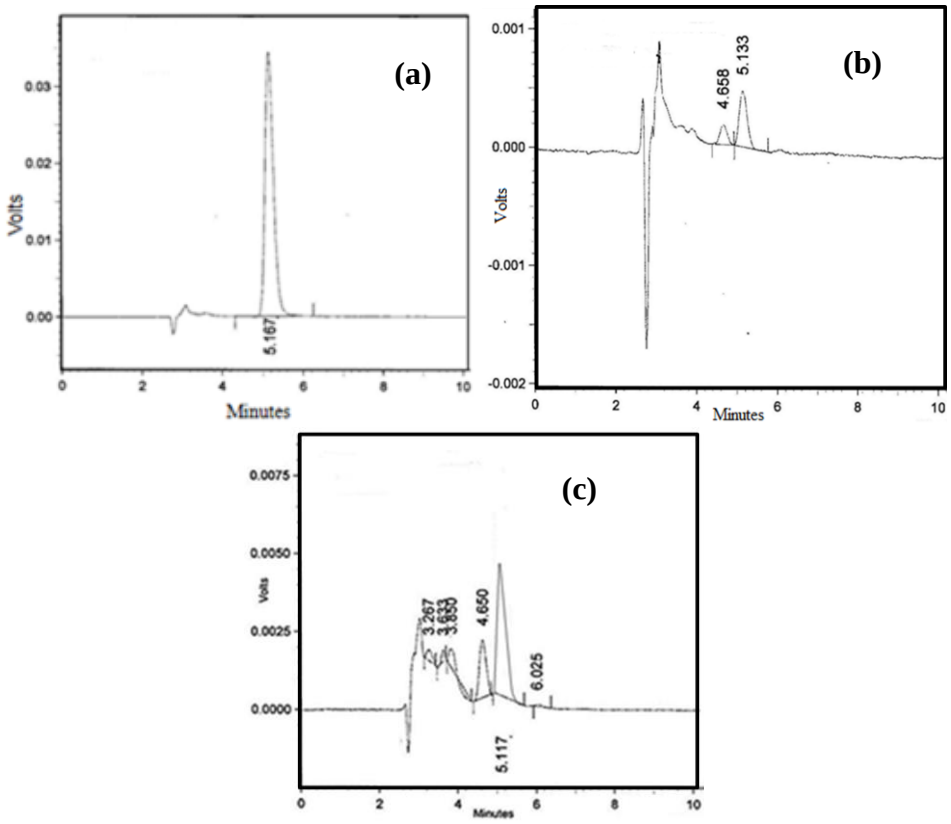


Fig. 4.56 HPLC chromatogram of (a) DCF standard before treatment (b) DCF sample after treatment with $[Fe^{2+}]_o$ = 17.9 x 10^{-3} mM (c) DCF sample with $[Fe\ (LS)]_o$ = 13.4 x 10^{-3} mM; [Reaction conditions; Photo-Fenton oxidation, $[DCF]_0$ = 31.4 x 10^{-3} mM , pH = 3.5, $[H_2O_2]_0$ = 1.03 mM and UVC irradiation time = 120 min].

When Fe (LS) is used, for the sample after treatment for 120 minutes, six peaks in chromatogram (Fig. 4.56 (c)), one at 5.177 min corresponding to DCF and the other 5 peaks corresponding to reaction intermediates are observed. Hence, there is no complete DCF degraded and mineralized even after the treatment for 120 minutes in both the cases of Fe^{2+} and Fe (LS). About 98.6 % of DCF is degraded with Fe^{2+} and only about 85.7 % of DCF is degraded with Fe (LS). The intermediates formed have contributed to COD. The results obtained in Fenton and photo-Fenton processes for degradation of DCF are compared and analyzed.

4.3.6 Comparison of Results in Fenton and Photo-Fenton Oxidation of Diclofenac

The Fenton and photo-Fenton oxidation for degradation of DCF are carried out at the same optimum experimental conditions. The Fenton process is carried out for 240 minutes and the photo-Fenton process is carried out for 120 minutes till the significant degradation results are obtained for the oxidation of DCF in water. The DCF degradation and mineralization efficiencies are more for UVC assisted photo-Fenton oxidation over the Fenton oxidation process. This is because of the production of more number of highly reactive oxidizing OH radicals in direct and indirect photolysis with UV irradiation. Fig. 4.57 shows the comparison of percent DCF degradation and percent COD removal between Fenton oxidation and UVC assisted photo-Fenton oxidation.

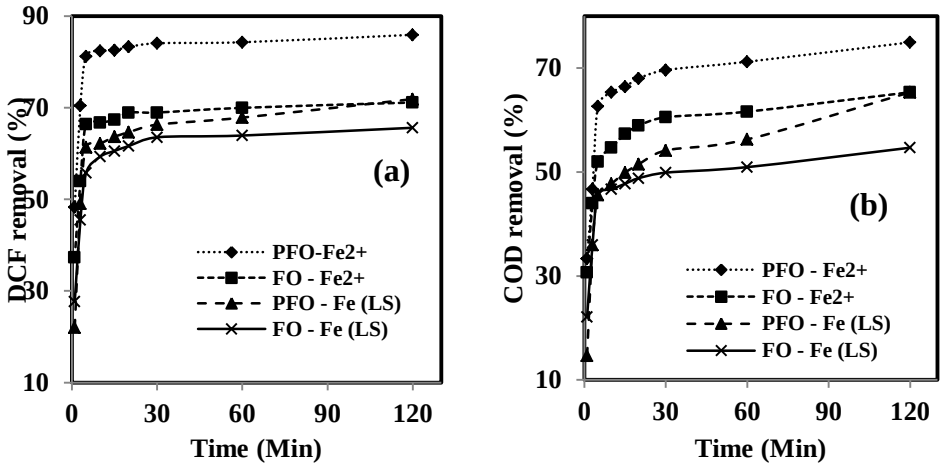


Fig. 4.57 Comparison of results between Fenton and photo-Fenton processes (a) percent DCF removal and (b) percent COD removal [Reaction conditions; UVC 8W light source, $[DCF]_0 = 31.4 \times 10^{-3}$ mM, pH = 3.5, $[DCF]_0 / [H_2O_2]_0 = 1 : 32.8$ (molar), $[H_2O_2]_0 / [Fe^{2+}]_0 = 57.5 : 1$ (molar), $[H_2O_2]_0 / [Fe\ (LS)]_0 = 76.7 : 1$ (molar)].

At the optimum conditions in the Fenton oxidation for 240 minutes, 5.30 % more DCF degradation and 13.3 % more COD removal for 31.4×10^{-3} mM of $[DCF]_0$ whereas 4.76 % more DCF degradation and 4.27 % more COD removal for 157.2×10^{-3} mM of $[DCF]_0$ are observed for Fe^{2+} than that of Fe (LS). In Fenton oxidation, the DCF degradation and COD removals are less for the Fe (LS) when compared to Fe^{2+} (Fig. 4.57). Also, the second-order kinetic rate constants for Fe^{2+} are 1.54 times higher than that of Fe (LS) in Fenton oxidation of DCF.

When Fe (LS) is used, chloride ions are present in the system that may form chloro-Fe (III) complexes that leads to decrease in the rates of generation of Fe^{2+} and this inhibit the formation of OH radicals and also the OH radicals present in the system may be scavenged by chloride to form less reactive dichloride anion radicals ($Cl_2^{\bullet -}$) (Laat et al. 2004). Thus, the Fenton reaction mechanism in presence of chlorides may be via less reactive dichloride anion radicals ($Cl_2^{\bullet -}$) (E^o =2.09 V) (Ledakowiez et al. 2000). Conversely, in the presence of Fe^{2+}, the mechanism of Fenton reaction is through formation of highly reactive hydroxyl radicals (E^o = 2.8V) (Troung et al. 2004). The degradation of DCF through less reactive dichloride ion radical mechanism is the cause for the low degradation and mineralization when Fe (LS) is used in Fenton reagent. The DCF samples are also analyzed by HPLC to determine the extent of degradation and formation of intermediates.

DCF degradation of 14.8 % more with Fe^{2+} and 6.26 % more with Fe (LS) and COD removal of 9.60 % more with Fe^{2+} and 10.7 % more with Fe (LS) are observed for UV-C photo-Fenton over Fenton oxidation at the optimum experimental conditions within 120 minutes reaction time. When Fe^{2+} is used, the kinetic constants for degradation is about 2.03 times more in photo-Fenton process over Fenton process at optimum conditions for DCF concentrations ranging from 31.4×10^{-3} to 157.2×10^{-3} mM and can be observed from Tables 4.11 and 4.13. Similarly, When Fe (LS) is used, the kinetic constants for degradation is about 1.20 times more in photo-Fenton process over Fenton process at optimum conditions for DCF concentrations ranging from 31.4×10^{-3} to 157.2×10^{-3} mM and can be observed from Tables 4.12 and 4.14. Over all, both the Fenton and photo-Fenton processes, when Fe^{2+} and Fe (LS) are used as catalysts, are the most effective in removing the DCF from aqueous solutions.

4.3.7 Comparison of Results of the Present Study with the Literature

There are several works reported on the advanced oxidation of DCF (Vogna et al. 2004; Naddeo et al. 2009; Vogna et al. 2004; Perez-Estrada et al. 2005; Calza et al. 2006; Rizzo et al. 2009; Naddeo et al. 2009; Zhao et al. 2009; Alahmad and Alawi 2010; Achilleos et al. 2010; Guyer and Ince 2011; Khayyat et al. 2011).

Table 4.15 Comparison of results in the present study with the literature on advanced oxidation of DCF in aqueous solution

Reference	Method	Experimental conditions			Results	
		$[DCF]_o$ mg/L	pH	Reaction time	Degradation (%)	Mineralization (%)
Vogna et al. (2004)	UV/H_2O_2		5-6	90 min		39
	O_3			90 min		32
Perez-Estrada et al. (2005)	Solar UV-Fenton		7	60 min	100	
				100 min		100
Calza et al. (2006)	Solar / TiO2	15		120 min		100
Rizzo et al. (2009)	UV/TiO_2	15		120 min		85
Naddeo et al. (2009)	Sonolysis	40		40 min		36
	O_3					22
	Sonolysis+O_3					39
Zhao et al. (2009)	Electro-oxidation	30	5.7	240 min	100	72
Alahmad and Alawi (2010)	Solar/TiO_2/SiO_2	100 µg/L		9 h	96.2	
Achilleos et al. (2010)	UV-A/TiO_2	10	6	240 min		71 (DW)* 42 (GW)* 47 (STPE)*
Guyer and Ince (2011)	Homogeneous/heterogeneous Sonolysis	30 µM	3	90 min		22
Khayyat et al. (2011)	MIP/UVC	44 mg/L		120 hours	100	
	MIP/HCl	50 mg/L			78	
Present study	**H_2O_2/Fe^{2+}**	**10**	**3.5**	**240 min**	**79.3**	**72.8**
				5 min	**66.4**	**52.0**
	H_2O_2/Fe (LS)			**240 min**	**74.3**	**59.5**
				5 min	**55.8**	**45.6**
	H_2O_2/Fe^{2+}/UV-C			**120 min**	**98.6**	**74.9**
				5 min	**81.2**	**62.7**
	H_2O_2/Fe (LS)/UV-C			**120 min**	**85.7**	**65.3**
				5 min	**61.4**	**49.9**

*DW= Distilled water; GW= Ground water; STPE= Sewage treatment plant effluent; MIP= Molecularly Imprinted Polymer

The Table 4.15 comprises the comparison of results of the present study with some important results in the literature. In the present study, DCF degradation of 79.3 % with Fe^{2+} and 74.3 % with Fe (LS), COD removal of 72.8 % with Fe^{2+} and 59.5 % with Fe (LS) within 240 minutes of reaction time by Fenton process, DCF degradation of 98.6 % with Fe^{2+} and 85.7 % with Fe (LS), COD removal of 74.9 % with Fe^{2+} and

65.3 % with Fe (LS) within 120 minutes of reaction time by UV-C assisted photo-Fenton process are observed. As compared with the literature, the extent of the degradation and mineralization obtained in the present study are greater than the most of the reported works due to optimized conditions of the processes and UV-C light effectiveness in photo-Fenton oxidation process.

4.4 Comparison of the Results Obtained for Oxidation of PCM, AMX and DCF by Fenton and Photo-Fenton Processes

The percent degradation and mineralization of PCM, AMX and DCF of 10 mg / L initial concentration of each drug treated by Fenton oxidation (Reaction time 240 min) and photo-Fenton oxidation (Reaction time 120 min) at optimal conditions are shown in Table 4.16.

Table 4.16 Percent degradation and mineralization of PCM, AMX and DCF treated by Fenton oxidation (Reaction time 240 min) and photo-Fenton oxidation (Reaction time 120 min) at optimal conditions ($[PCM]_0 = 66.1 \times 10^{-3}$ mM (10 mg / L), $[AMX]_0 = 27.4 \times 10^{-3}$ mM (10 mg / L), $[DCF]_0 = 31.4 \times 10^{-3}$ mM (10 mg / L).

Drug	$[Drug]_0$ mM	Optimal Conditions				Degradation (%)		Mineralization (%)	
		pH_0	$[H_2O_2]_0$ mM	$[Fe^{2+}]_0$ mM	$[Fe\ (LS)]_0$ mM	FO	PFO	FO	PFO
PCM	66.1×10^{-3}	3.0	0.88	8.95×10^{-3}	-	100	100	77.1	89.6
			0.88	-	13.4×10^{-3}	100	100	70.8	79.0
AMX	27.4×10^{-3}	3.0	0.88	8.95×10^{-3}	-	100	100	72.5	75.0
			1.03	-	13.4×10^{-3}	100	100	74.5	80.0
DCF	31.4×10^{-3}	3.5	1.03	17.9×10^{-3}	-	79.3	98.6	72.8	74.9
			1.03	-	13.4×10^{-3}	74.3	85.7	59.5	65.3

The degradation of PCM and AMX is 100 % but the degradation of the DCF is only 79.3 % (for Fe^{2+}) and 74.3 % (for Fe (LS)) in Fenton oxidation. However, during the photo – Fenton oxidation, 100 % degradation of PCM and AMX for both the catalysts but DCF degradation of 98.6 % (for Fe^{2+}) and 85.7 % (for Fe (LS)) are observed. The mineralization of the drugs is different for different drugs. The mineralization of PCM is the highest compared to AMX and DCF. On the other hand, the oxidant and

catalyst requirement is more for DCF when compared to that for PCM and AMX. For the treatment of PCM, the optimal requirement of H_2O_2 is 0.88 mM with both the iron catalysts, but the optimal iron requirement is 8.95 x 10^{-3} mM for Fe^{2+} and 13.4 x 10^{-3} mM for the Fe (LS). For the treatment of AMX, the optimal requirement of H_2O_2 is 0.88 mM for Fe^{2+} and 1.03 mM for the Fe (LS), and the optimal iron requirement is 8.95 x 10^{-3} mM for Fe^{2+} and 13.4 x 10^{-3} mM for the Fe (LS). For the treatment of PCM, the optimal requirement of H_2O_2 is 1.03 mM with both the iron catalysts, but the optimal iron requirement is 8.95 x 10^{-3} mM for Fe^{2+} and 13.4 x 10^{-3} mM for the Fe (LS). For the AOPs selected, H_2O_2 required for DCF > AMX = PCM with Fe^{2+} and H_2O_2 required for DCF = AMX > PCM with Fe (LS). Moreover, catalyst required for DCF > AMX = PCM with Fe^{2+} and DCF = AMX = PCM with Fe (LS). It is also observed that the degradation and mineralization is more with Fe^{2+} than Fe (LS) for both PCM and DCF. Conversely, the degradation and mineralization is more with Fe (LS) than Fe^{2+} for AMX.

Table 4.17 Pseudo-second order rate constants ($M^{-1}s^{-1}$) for the degradation of PCM, AMX and DCF treated by Fenton oxidation (Reaction time 240 min) and photo-Fenton oxidation (Reaction time 120 min) at optimal conditions

$[Drug]_0$ in mg / L	FO						PFO					
	PCM		AMX		DCF		PCM		AMX		DCF	
	Fe^{2+}	Fe (LS)	Fe^{2+}	Fe (LS)	Fe^{2+}	Fe (LS)	Fe^{2+}	Fe (LS)	Fe^{2+}	Fe (LS)	Fe^{2+}	Fe (LS)
10	136.4	117.0	54.3	70.0	206.9	136.7	219.1	126.7	82.3	88.8	493.1	184.7
20	81.9	76.6	45.2	55.5	123.1	76.1	124.3	85.5	67.8	71.7	259.7	99.3
30	62.7	58.0	41.5	49.2	88.9	59.8	84.8	62.2	56.3	64.2	188.6	71.2
40	48.8	47.0	37.3	45.5	82.1	53.9	75.8	52.7	51.8	60.8	148.3	59.3
50	45.6	43.2	33.0	37.3	75.6	49.1	61.9	47.0	47.2	55.2	130.5	51.6

The pseudo-second order rate constants in $M^{-1}s^{-1}$ for the degradation of PCM, AMX and DCF treated by Fenton and photo-Fenton processes at the optimal conditions are shown in Table 4.17. The value of the rate constants for the degradation of DCF > PCM > AMX as observed in the Table 4.4.2. In both Fenton and photo-Fenton oxidation for both Fe^{2+} and Fe (LS), the degradation rate constants for DCF are 1.30

to 3.76 times higher than the AMX and 1.2 to 2.13 times higher than PCM; the rate constants for the PCM degradation is about 1.06 to 1.76 times higher than AMX degradation. For all the drugs, the rate constants are very high for the photo-Fenton oxidation than the Fenton oxidation. This may be due to formation of additional amount of OH radicals, which can degrade additional amount of substrate within the same time, in the photo-Fenton oxidation. In both the oxidation processes, when Fe (LS) is used, the degradation rate constants are less for PCM and DCF compared to use of Fe^{2+}; but for AMX the rate constants are higher for Fe (LS) compared to Fe^{2+}.

The drug degradation may follow different pathways depending on the treatment applied (Perez-Estrada et al. 2005) and the structure of the molecule. The degradation also depends on number of benzene rings, other rings like β – lactam ring and thiazolidine ring, substituents on aromatic rings and the position of the substituents on benzene rings. The type of bonding (covalent, ionic or polar etc.) of constituents and its position on aromatic rings than the molecular weights may decide the bond dissociation energies and hence the degradation of the organic molecules (e.g. C - C bond joining the rings is very stable and C – F bond is more stable than C - H bond) (Johns et al. 1962).

Paracetamol is a simple molecule consists of a benzene ring core, substituted by one hydroxyl group and the nitrogen atom of an amide group in the para (1, 4) pattern. The presence of two activating groups also makes the benzene ring highly reactive toward electrophilic aromatic substitution. As the substituents are ortho, para-directing and para with respect to each other, all positions on the ring are more or less equally activated. A saturated aqueous solution has a pH of about 6.3 but stability decreases in acid, the paracetamol being slowly broken down into acetic acid and p-aminophenol. The constituents present are less in number and the molecular weight of the PCM is less than 50 % of the weight of AMX or DCF. Owing to the above reasons, the amount of H_2O_2 required is less in the Fenton and photo-Fenton processes for the 100 % degradation and higher mineralization when compared to the AMX and DCF.

Amoxicillin is a complex molecule consists of a benzene ring, beta-lactam ring fused to five membered thiazolidine ring, amine and amide groups between benzene and beta-lactam rings, acetic acid and methyl groups to thiazolidine ring. The higher degradation and mineralization of the AMX in Fenton and photo-Fenton process when compared to that of DCF can be attributed to the fact that the ring is very strained and the bond between the carbonyl and the nitrogen atom in the beta-lactam ring is very unstable to be broken down and hence make the AMX molecule reactive.

The mineralization of the diclofenac in terms of chlorine ions release is a quick process, while the amino moiety is mainly transformed into NH_4^+ and in a lesser extent into NO_3^- ions (Calza et al. 2006). The chlorine ions so released may form chloro-Fe (III) complexes that leads to decrease in the rates of generation of Fe^{2+} and this inhibit the formation of OH radicals and also the OH radicals present in the system may be scavenged by chloride to form less reactive dichloride anion radicals ($Cl_2^{\bullet -}$) (Laat et al. 2004). The two benzene rings are relatively more stable than other groups in the DCF. Due to the above reasons, the degradation and mineralization of the DCF may be less when compared to that of PCM and AMX by Fenton and photo-Fenton processes with both the Fe^{2+} and Fe (LS) as catalysts.

4.5 Fenton and Photo-Fenton Oxidation of the Mixture of Paracetamol, Amoxicillin and Diclofenac in Water

A mixture of PhACs usually occurs in the environment. A study indicates that low concentrations of individual PhACs have increased toxicity on aquatic organisms when present in a mixture (Triebskorn et al. 2007). The toxicity of the mixture follows the concept of concentration addition, with compounds acting in an additive fashion (Triebskorn et al. 2007). The studies by Cleuvers (2004) supported such findings, indicating that diclofenac, ibuprofen, acetylsalicylic acid and naproxen show greater toxicities as a mixture than as individual compounds. Consequently, the efficacy of the Fenton and photo-Fenton processes for the possible degradation of the mixture of the model compounds viz. PCM, AMX and DCF is evaluated and presented in this part of the study.

4.5.1 Fenton Oxidation of the Mixture of Drugs Using Fe^{2+} as Iron Catalyst

This part deals with the investigation of effect of various parameters like initial pH, $[H_2O_2]_0$ and $[Fe^{2+}]_0$ on degradation and mineralization of the mixture of selected drugs.

Effect of pH

The oxidation experiments are conducted at different pH values varying from 2.0 to 4.0 with $[PCM]_0 = 66.1 \times 10^{-3}$ mM (10 mg/L), $[AMX]_0 = 27.4 \times 10^{-3}$ mM (10 mg/L), $[DCF]_0 = 31.4 \times 10^{-3}$ mM (10 mg/L), $[H_2O_2]_0 = 2.35$ mM and $[Fe^{2+}]_0 = 35.8 \times 10^{-3}$ mM. The mineralization and degradation of each drug in the mixture increased up to a pH of 3.5 and then it is decreased with increase in pH as can be observed in Fig. 4.58. The maximum percent drug degradation is 67.9 (PCM), 70.5 (AMX), 64.5 (DCF) and the maximum percent COD removal is observed to be 52.8 at pH 3.5 as can be seen in Fig. 4.58.

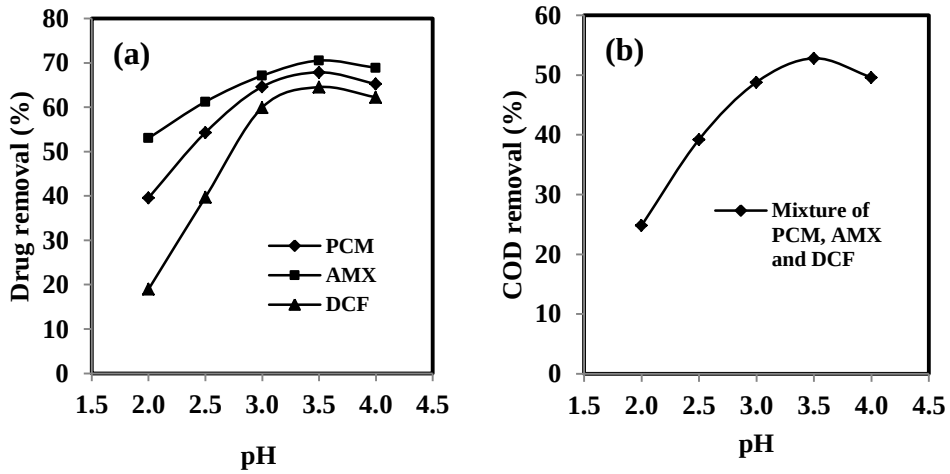


Fig. 4.58 (a) Percent PCM, AMX and DCF degradation and (b) percent COD removal at different pH; [Reaction conditions; Fenton oxidation; $[PCM]_0$ = 10 mg/L (66.1×10^{-3} mM), $[AMX]_0$ = 10 mg/L (27.4×10^{-3} mM), $[DCF]_0$ = 10 mg/L (31.4×10^{-3} mM), $[H_2O_2]_0 = 2.35$ mM and $[Fe^{2+}]_0 = 35.8 \times 10^{-3}$ mM, reaction time = 24 h].

At pH 3.5, the drugs removal is maximum and it may be due to the formation of more $Fe(OH)^+$ which has much higher activity than Fe^{2+} in Fenton's oxidation (Badawy and Ali 2006). When pH is greater than 3.5, oxidation efficiency rapidly decreased due to auto-decomposition of H_2O_2 affecting the production of OH radicals (Badawy and Ali 2006) and deactivation of ferrous catalyst with the formation of ferric hydroxide

precipitates (Luis et al. 2009) and hence the drug removals are less. When pH is less than 3.5, the reaction of H_2O_2 with Fe^{2+} is affected that leads to reduction in hydroxyl radicals and water is formed by the reaction of OH radicals with H^+ ions (Lucas and Peres 2006).

The drug removals for AMX > PCM > DCF for the pH values maintained in the experiments. This may be due to the inherent properties of the selected drugs such as chemical structure, mode of action with radicals and other an-ions if present and the presence of acid conditions in the oxidation system. Similar to degradation, the COD removal is maximum at pH 3.5 as can be seen in Fig. 4.58 (b). But for the other values of pH, the COD removal is less. The COD removal observed to be less than the drugs degradation is due to the formation of oxidation intermdiates. The critical pH value of 3.5 that gives maximum degradation and mineralization is maintained in all the susequent experiments on degradation of diclofenac.

Effect of H_2O_2 and Fe^{2+} Concentration

The experiments for optimization of hydrogen peroxide concentration is carried out by varying H_2O_2 concentration in the range 1.47 to 2.65 mM, iron concentrations in the range 8.95 x 10^{-3} to 35.8 x 10^{-3} mM for the mixture of the drugs taken as $[PCM]_0$ = 66.1 x 10^{-3} mM, $[AMX]_0$ = 27.4 x 10^{-3} mM, $[DCF]_0$ = 31.4 x 10^{-3} mM at solution pH 3.5.

In the present study, the maximum percent drug degradation is 82.9 (PCM), 93.4 (AMX), 76.4 (DCF) and the corresponding percent COD removal is 71.2 at H_2O_2 concentration of 2.06 mM after a reaction time of 24 hours and can be observed in Fig. 4.59. The quantity of hydrogen peroxide required, based on Stoichiometric calculation, for the complete mineralization of the mixture of the selected drugs is 0.37 mM for the mixture of one mg of each drug. However, maximum degradation and mineralization of the drugs in the mixture is achieved at 0.21 mM of H_2O_2 per mg of each drug. Initially, the degradation and mineralization increased with increase in H_2O_2 concentration up to 2.06 mM and then it is decreased with increase in H_2O_2 concentration. The maximum drug degradation and COD removal is observed at 2.06 mM of H_2O_2. When $[H_2O_2]_0$ is less than 2.06 mM, the degradation and mineralization

are less due to less production of OH radicals. When $[H_2O_2]_0$ is greater than 2.06 mM, the degradation and mineralization are again less because of the scavenging of OH radicals by H_2O_2. This can be explained by the fact that the very reactive OH radicals are scavenged by the increased H_2O_2 that results finally into water (Hsueh et al. 2005). The results obtained for the removal efficiencies indicate the incomplete mineralization and the presence of intermediates in the aqueous solution and can be observed in Fig. 4.59.

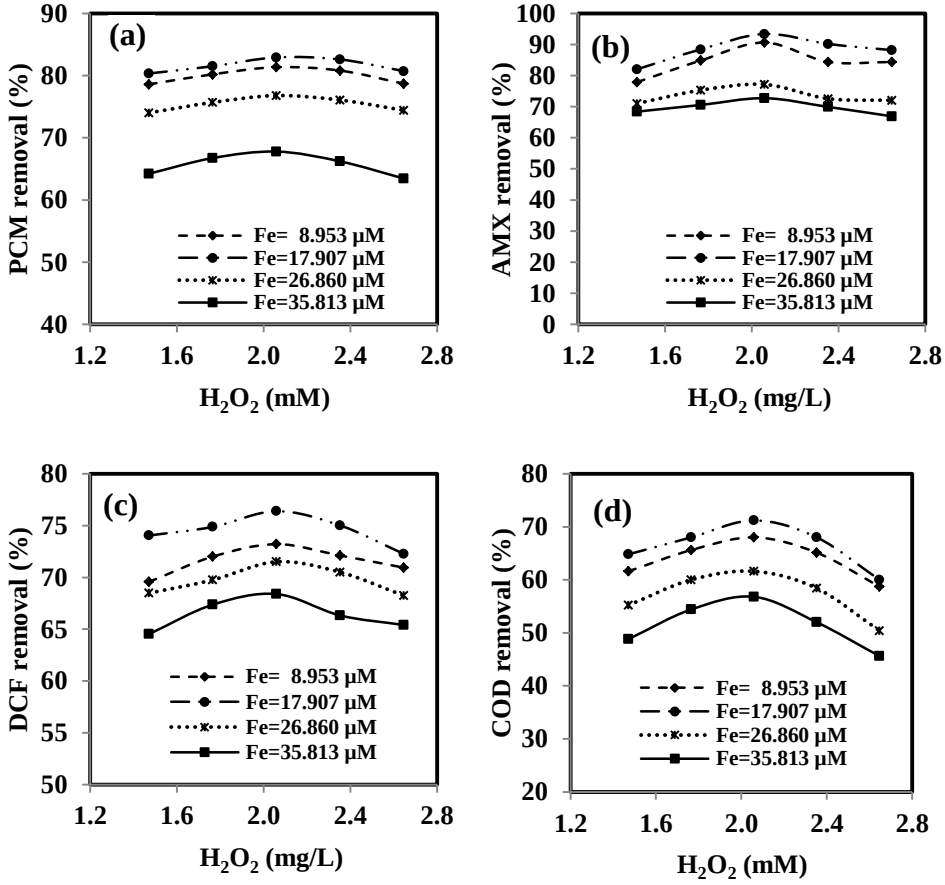


Fig. 4.59 Variations in (a) percent PCM degradation, (b) percent AMX degradation, (c) percent DCF degradation, (d) percent COD removal [Reaction conditions; Fenton oxidation; $[PCM]_0$ = 10 mg/L (66.1 x 10^{-3} mM), $[AMX]_0$ = 10 mg/L (27.4 x 10^{-3} mM), $[DCF]_0$ = 10 mg/L (31.4 x 10^{-3} mM), pH= 3.5, $[H_2O_2]_0$ = 1.47 to 2.65 mM, $[Fe^{2+}]_0$ = 8.95 x 10^{-3} to 35.8 x 10^{-3} mM, reaction time = 24 h].

The drug degradation and COD removal are significantly improved with the addition of Fe^{2+} to the solution. The variations in percent drug degradation and COD removal under the different concentrations of the Fe^{2+} and H_2O_2 at pH of 3.5, reaction time of

24 hours is elucidated in Fig. 4.5.2. The degradation and mineralization increased with increase in Fe^{2+} concentration up to 17.9 x 10^{-3} mM due to increase in OH radical production (Yilmaz et al. 2010). The degradation and mineralization are observed to be the maximum for 17.9 x 10^{-3} mM of Fe^{2+} concentration. At higher Fe^{2+} concentrations the drug and COD removals are less due to the reaction of Fe^{2+} with OH radicals that results in the scavenging of OH radical (Hsueh et al. 2005*)*. The maximum percent DCF degradation is 82.9 (PCM), 93.4 (AMX), 76.4 (DCF) and the corresponding percent COD removal is 71.2 at17.9 x 10^{-3} mM of Fe^{2+} concentration. The observed ratios, $[PCM + AMX + DCF]_0 / [H_2O_2]_0$ = 3 : 7 (w/w) and $[H_2O_2]_0 / [Fe^{2+}]_0$ = 115.0 : 1 (molar) at which degradation and mineralization is the maximum, are used in the subsequent experiments for studying the effect of initial DCF concentration.

Effect of Initial Concentration of Each Drug

The variations in percent drug degradation and percent COD removals at optimum conditions for 240 minutes of reaction time are shown in Fig. 4.60. The percent drug degradation is observed to be 13.2 (PCM), 39.0 (AMX), 8.33 (DCF) and percent COD removal is observed as 21.6 in 5 minutes, whereas 68.6 (PCM), 70.8 (AMX), 62.6 (DCF) percent drug degradation and 64.8 percent COD removal are observed in 240 minutes. With the increase in each drug concentration from 10 to 50 mg/L, the percent drug removal increased from 68.6 to 83.3 (PCM), 70.8 to 90.0 (AMX), 62.6 to 78.8 (DCF) and the percent COD removal decreased to 43.7 from 64.8.

The degradation of the drugs increases and the mineralization decreased with increase in initial concentration of drugs. At the optimum $[H_2O_2]_0 / [Fe^{2+}]_0$ molar ratio of 115.0: 1, degradation of the drug increased with increase in its initial concentration. This may be due to the synergetic effect of OH radicals and the drug radicals formed in Fenton oxidation in which both the radicals may involve in the degradation of the substrate. On the other hand, the formation of the intermediates also may increase with increase in substrate concentration and hence COD removal decreased with increase in the concentration of substrate. This result is comparable with the literature, where COD removal of pharmaceutical wastewater by Fenton's oxidation is more for the lower initial concentrations of drugs (Yilmaz et al. 2010).

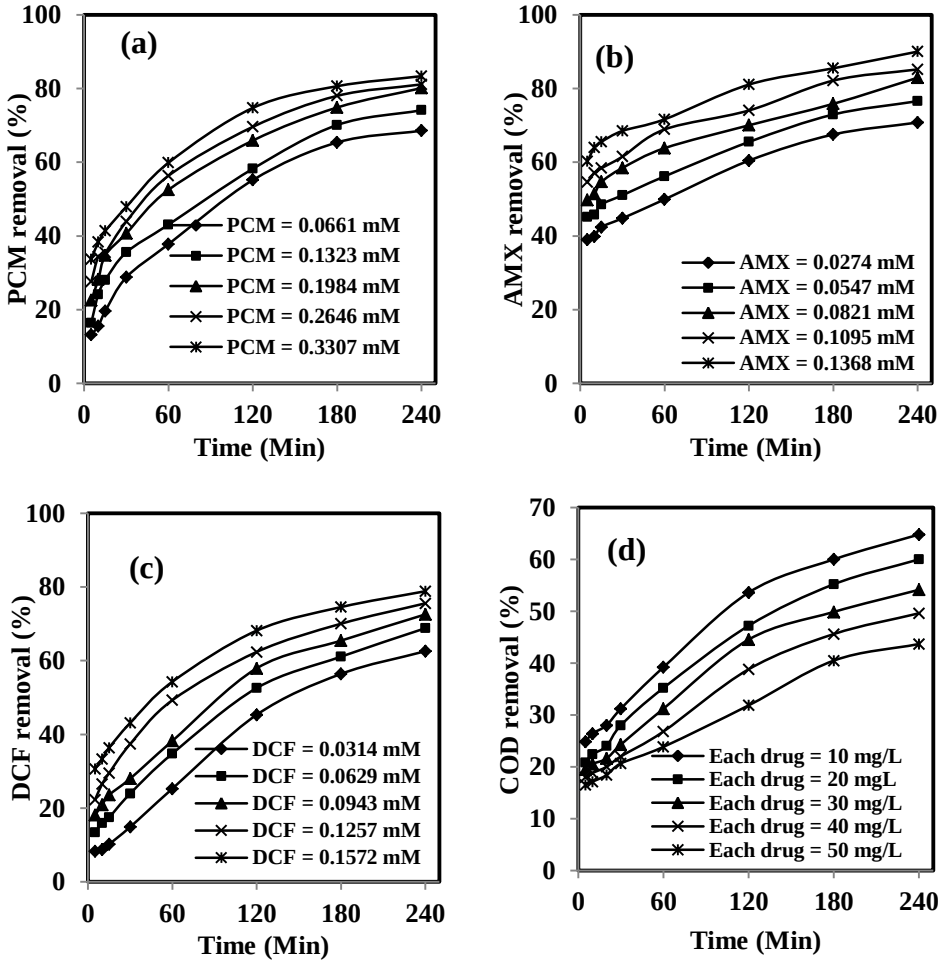


Fig. 4.60 Variations in (a) percent PCM degradation, (b) percent AMX degradation, (c) percent DCF degradation and (d) percent COD removal; [Reaction conditions; Fenton oxidation; pH 3.5, $[PCM + AMX + DCF]_0$ / $[H_2O_2]_0$ = 3 : 7 (w/w) and $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 115.0 : 1 (molar), reaction time = 240 min].

4.5.2 Fenton Oxidation of the Mixture of Drugs Using Fe (LS) as Iron Catalyst

The optimum pH value of 3.5 obtained using Fe^{2+} in Fenton reagent is used for the Fenton experiments using Fe (LS). The effect of various parameters like $[H_2O_2]_0$, [Fe (LS)]$_0$ and [Drug]$_0$ on Fenton oxidation using Fe (LS) as iron catalyst are discussed below.

Effect of H_2O_2 and Fe (LS) Concentration

The Fenton oxidation experiments are conducted to obtain optimum hydrogen peroxide concentration with Fe (LS) in Fenton's reagent.

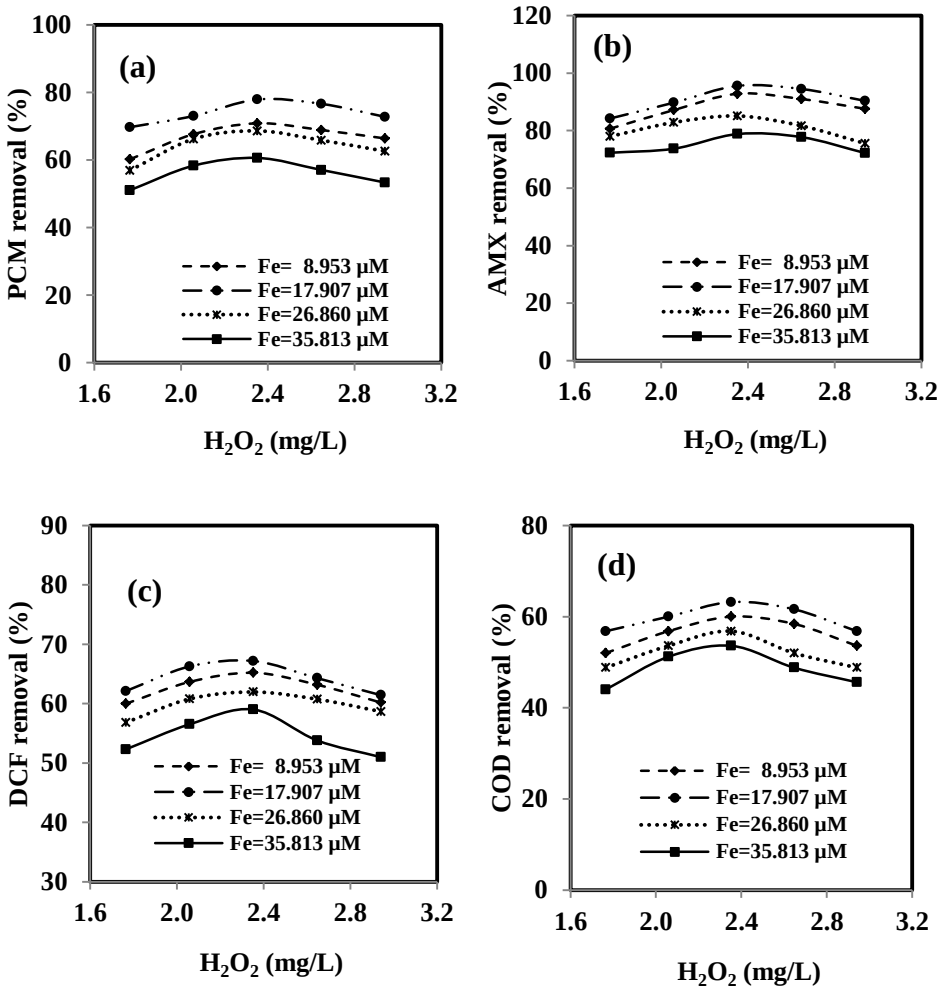


Fig. 4.61 Variations in (a) percent PCM degradation, (b) percent AMX degradation, (c) percent DCF degradation and (d) percent COD removal; [Reaction conditions; Fenton oxidation; $[PCM]_0$ = 10 mg/L (66.1 x 10^{-3} mM), $[AMX]_0$ = 10 mg/L (27.4 x 10^{-3} mM), $[DCF]_0$ = 10 mg/L (31.4 x 10^{-3} mM), pH= 3.5, $[H_2O_2]_0$ = 1.77 to 2.94 mM, $[Fe^{2+}]_0$ = 8.95 x 10^{-3} to 35.8 x 10^{-3} mM, reaction time = 24 h].

The hydrogen peroxide concentration is varied from 1.77 to 2.94 mM and Fe (LS) concentration is varied from 8.95 x 10^{-3} to 35.8 x 10^{-3} mM for initial concentration of 10 mg/L of each drug at initial solution pH of 3.5. Fig. 4.61 shows the variations in percent drug degradation and COD removal under the different dosages of Fe (LS) and H_2O_2 for 10 mg/L initial concentration of each drug at pH of 3.5, reaction time of 24 hours. The maximum percent drug degradation is observed to be 77.9 (PCM), 95.6 (AMX), 63.2 (DCF) and the corresponding percent COD removal is 63.2 at initial

H_2O_2 concentration of 2.35 mM and initial Fe (LS) concentration of 17.9 x 10^{-3} mM, reaction time of 24 hours.

The removal efficiency increased up to a critical level with increase in H_2O_2 concentration and further increase in the H_2O_2 concentration decreased the removal efficiency. The maximum drug degradation and COD removal is observed at 2.35 mM of H_2O_2. This may be due to production of less number of OH radicals when $[H_2O_2]_0$ is less than 2.35 mM. On the other hand, when $[H_2O_2]_0$ is greater than 2.35 mM, the degradation and mineralization are less because of the scavenging of OH radicals with increase in the H_2O_2 concentration. This may be due to the fact that the very reactive OH radicals are scavenged by the increased H_2O_2 that results finally into water (Hsueh et al. 2005).

The drug degradation and COD removal increased with addition of Fe (LS). This is because sufficient catalyst is required to produce the most favorable amounts of OH radicals. The degradation and mineralization increased up to a critical dosage of Fe (LS) (17.9 x 10^{-3} mM) and then it decreased with increase in Fe (LS) concentration. The decrease in degradation and mineralization at higher Fe (LS) concentration is due to the scavenging of OH radicals by Fe (LS) itself. The maximum percent drug degradation is observed to be 77.9 (PCM), 95.6 (AMX), 63.2 (DCF) and the corresponding percent COD removal is 63.2 at initial Fe (LS) concentration of 17.9 x 10^{-3} mM and initial H_2O_2 concentration of 2.35 mM, reaction time of 24 hours. As per the results obtained, the optimum $[Drug]_0$ / $[H_2O_2]_0$ ratio 3 : 8 (w/w) and ratio of $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ 131.4 : 1 (molar) are considered in the subsequent experiments conducted to investigate the effect of initial DCF concentration.

Effect of Initial Concentration of Each Drug

The initial drug concentration of each selected drug is varied from 10 to 50 mg/L with the optimum $[Drug]_0$ / $[H_2O_2]_0$ ratio 3 : 8 (w/w) and the optimum $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ ratio 131.4 : 1 (molar) constant for all the concentrations of each drug. The variations in percent DCF degradation and percent COD removal at the optimum conditions in 240 minutes of reaction time are shown in Fig. 4.62. The percent drug degradation is observed to be 8.89 (PCM), 41.5 (AMX), 5.83 (DCF) and the corresponding percent

COD removal is 18.4 in 5 minutes where as 57.2 (PCM), 76.7 (AMX), 55.8 (DCF) percent drug degradation and 60.0 percent COD removal is observed in 240 minutes for 10 mg/L initial each drug concentration.

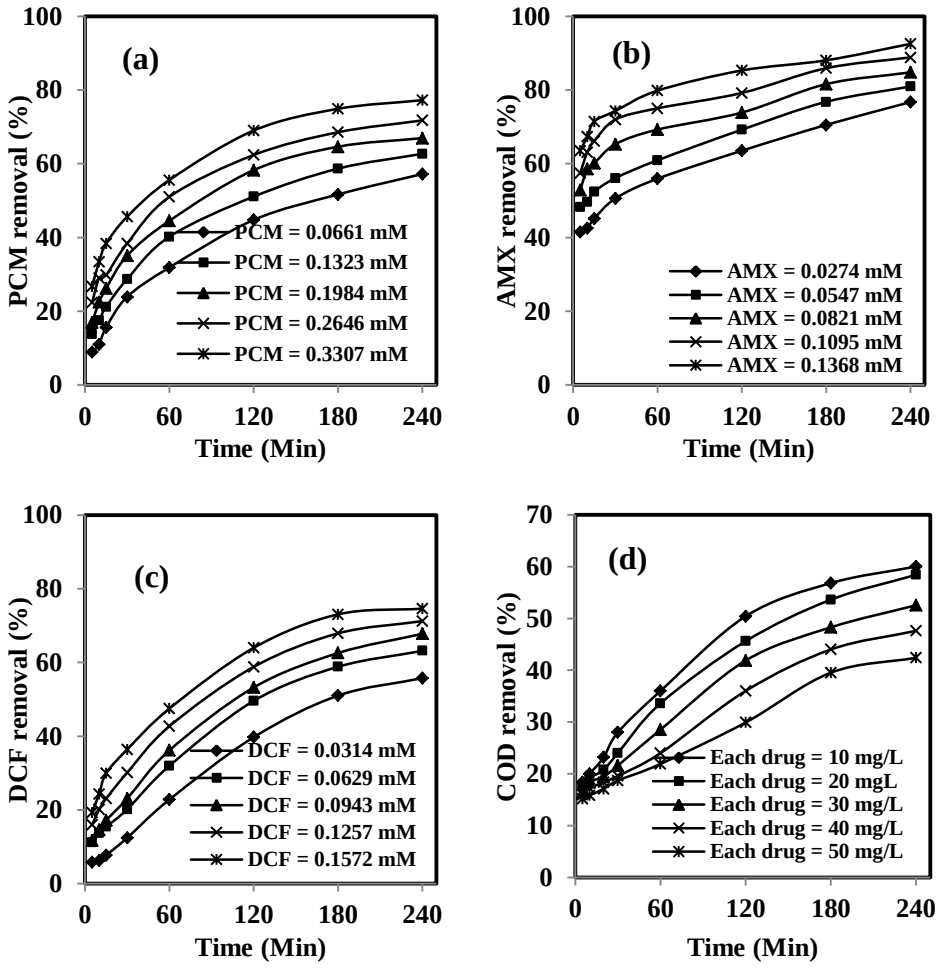


Fig. 4.62 Variations in (a) percent PCM degradation, (b) percent AMX degradation, (c) percent DCF degradation and (d) percent COD removal; [Reaction conditions; Fenton oxidation; pH 3.5, $[Drug]_0$ / $[H_2O_2]_0$ = 3 : 8 (w/w) and $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ = 131.4 : 1 (molar), reaction time = 240 min].

The percent drug removal increased from 57.2 to 77.2 (PCM), 76.7 to 92.5 (AMX), 55.8 to 74.6 (DCF) and the percent COD removal decreased from 60.0 to 42.4 with the increase in concentration of each drug from 10 to 50 mg/L. The use of Fe (LS) in Fenton reagent also followed the similar drug degradation trend as that of Fe^{2+}. At the optimum $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ molar ratio of 131.4 : 1, degradation of the drug increases with increase in its initial concentration due to the synergetic effect of OH

radicals and the drug radicals formed in Fenton oxidation in which both the radicals may involve in the degradation of the substrate. Conversely, the formation of the intermediates also may increase with increase in substrate concentration and hence COD removal decreased with increase in the concentration of substrate.

4.5.3 Photo- Fenton Oxidation of the Mixture of Selected Drugs Using Fe^{2+} as Iron Catalyst

This part of study deals with the effect of initial concentration of the selected drugs in degradation and mineralization of the drugs by photo-Fenton oxidation process. UVC assisted photo-Fenton process is carried out at the optimum conditions that are obtained in the Fenton oxidation of DCF.

Effect of Initial Concentration of Each Drug

The photo-Fenton oxidation experiments are carried out for a reaction time of 120 minutes. The variations in percent drugs degradation and percent COD removal at the optimum conditions in 120 minutes of UVC irradiation time are shown in Fig. 4.63. The percent drug degradation is 21.8 (PCM), 48.4 (AMX), 20.0 (DCF) and the percent COD removal is 39.2 in 5 minutes but 70.0 (PCM), 75.7 (AMX), 64.8 (DCF) percent of the selected drugs degradation and 74.4 percent COD removal are observed in 120 minutes for 10 mg/L initial DCF concentration. The percent drug removal increased from 70.0 to 89.3 (PCM), 75.7 to 92.8 (AMX), 64.8 to 79.9 (DCF) and the percent COD removal decreased from 74.4 to 50.1 with the increase in concentration of each drug from 10 to 50 mg/L in a reaction time of 120 minutes.

At the optimum $[H_2O_2]_0$ / $[Fe^{2+}]_0$ molar ratio of 115.0 : 1, degradation of the drugs increases with increase in its initial concentration. This may be due to the synergetic effect of OH radicals and the drug radicals formed in photo-Fenton oxidation in which both the kinds of radicals may involve in the degradation of the substrate. The reduction in COD removal with increase in drug concentrations may be due to increase in the formation of intermediate oxidation products with the increase in drug concentration. This result is in agreement with finding of Devi et al. 2009, where COD removal of pharmaceutical wastewater by UV-Fenton Oxidation is more for the lower initial concentrations of the pollutant. This phenomenon of decrease in COD

removal with increase in initial drug concentration is also associated with the absorbance of a more significant fraction of the emitted UV light at 254 nm than that of a lower initial concentration; consequently, the number of available photons decreases leading to a decrease in the formation of OH radicals (Feng et al. 2003) to degrade the residual drug if any and its intermediates formed in the reaction. Subsequent experiments are carried out to find the efficacy of the photo-Fenton oxidation with Fe (LS) as catalyst.

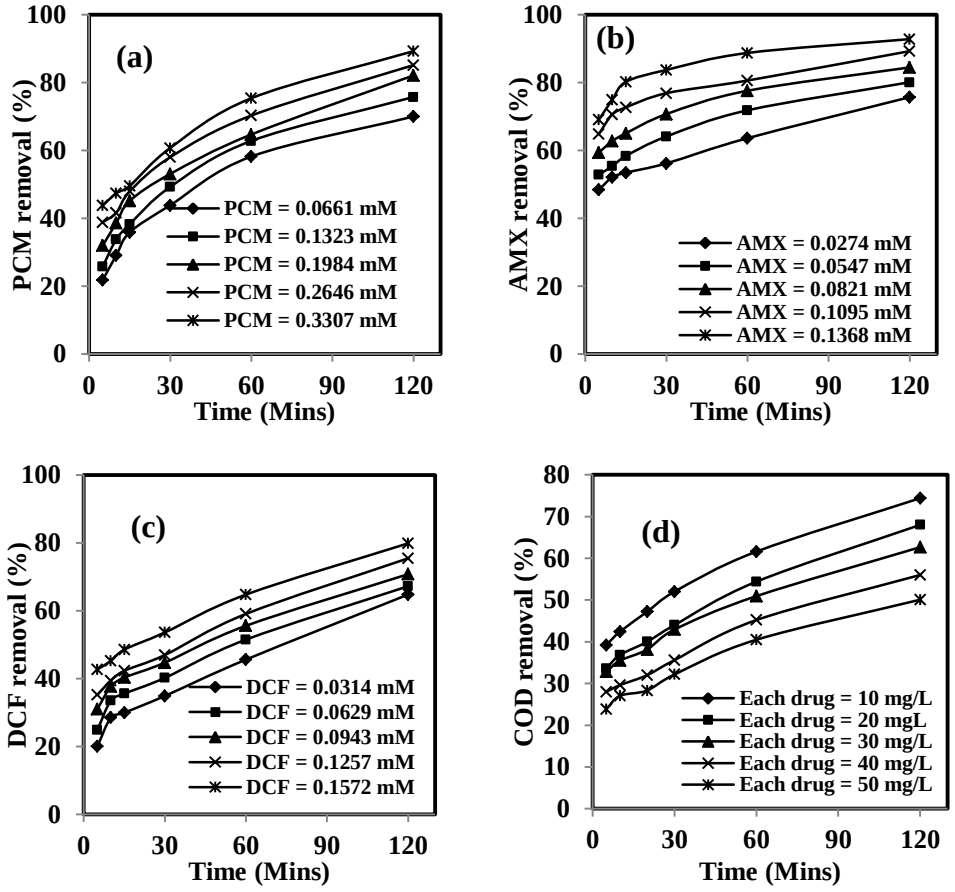


Fig. 4.63 Variations in (a) percent PCM degradation, (b) percent AMX degradation, (c) percent DCF degradation and (d) percent COD removal; [Reaction conditions; Photo-Fenton oxidation; pH 3.5, $[Drug]_0$ / $[H_2O_2]_0$ = 3 : 7 (w/w), $[H_2O_2]_0$ / $[Fe^{2+}]_0$ = 115.0 : 1 (molar) and UVC irradiation time = 120 min].

4.5.4 Photo- Fenton Oxidation of the Mixture of Selected Drugs Using Fe (LS) as Iron Catalyst

Effect of Initial Drug Concentration

The variations in percent drugs degradation and percent COD removal at the optimum conditions in 120 minutes of UV irradiation time are shown Fig. 4.64.

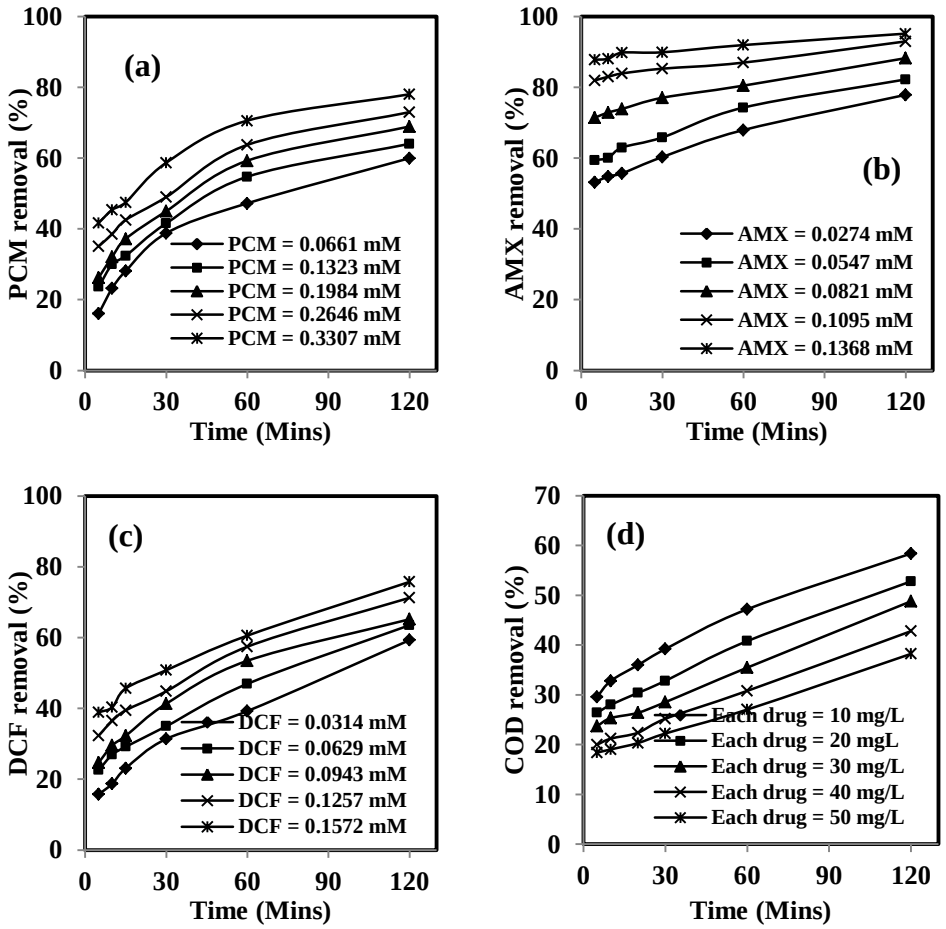


Fig. 4.64 Variations in (a) percent PCM degradation, (b) percent AMX degradation, (c) percent DCF degradation and (d) percent COD removal; [Reaction conditions; Photo-Fenton oxidation; pH 3.5, $[Drug]_0$ / $[H_2O_2]_0$ = 1 : 8 (w/w), $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ = 131.4 : 1 (molar), UVC irradiation time = 120 min].

The percent drug degradation is 16.1 (PCM), 53.2 (AMX), 15.7 (DCF) and the percent COD removal is 29.6 and in 5 minutes where as 60.0 (PCM), 77.9 (AMX), 59.3 (DCF) percent drugs degradation and 58.4 percent COD removal are observed in 120 minutes for 10 mg/L initial concentration of each drug. The percent drug removal

increased from 60.0 to 78.0 (PCM), 77.9 to 95.2 (AMX), 59.3 to 75.8 (DCF) and the percent COD removal decreased from 58.4 to 38.2 with the increase in concentration of each drug from 10 to 50 mg/L in reaction time of 120 minutes. The use of Fe (LS) in Fenton reagent also followed the similar drug degradation trend as that of Fe^{2+} in UVC assisted photo-Fenton process.

The degradation of the drug increased and the mineralization of DCF decreased with the increase in initial drug concentration (Fig. 4.64). When drug concentration is increased, comparative reactions may be occurring between the substrate molecules and other species in the oxidation system. For instance, there may also be synergetic effect due to OH radicals and drug radicals on degradation of substrate and hence the degradation increased with increase in drug concentration. On the other hand, the reduction in COD removal at high drug concentrations is due to the formation of intermediate oxidation products and reduction in availability of total number of photons with increase in drug concentration. The results of Fenton and photo-Fenton process are compared in the next section.

4.5.5 Comparison of Results in Fenton and Photo-Fenton Oxidation of Mixture of the Selected Drugs

The Fenton and photo-Fenton process for degradation of the mixture of selected drugs are carried out at the same optimum experimental conditions. The Fenton process is carried out for 240 minutes and the photo-Fenton process is carried out for 120 minutes. Fig. 4.65 shows the comparison of percent drug degradation and percent COD removal between Fenton oxidation and UVC assisted photo-Fenton oxidation. At the optimum conditions in Fenton oxidation, 11.3 % more PCM degradation, 6.81 % more DCF degradation and 4.80 % more COD removal for 10 mg/L of each drug whereas 6.11 % more PCM degradation, 4.23 % more DCF degradation and 1.28 % more COD removal for 50 mg/L of each drug are observed for Fe^{2+} compared to Fe (LS). However, the AMX degradation is 5.95 % more for 10 mg/L of each drug and 2.50 % more for 50 mg/L of each drug for Fe (LS) compared to Fe^{2+} in FO.

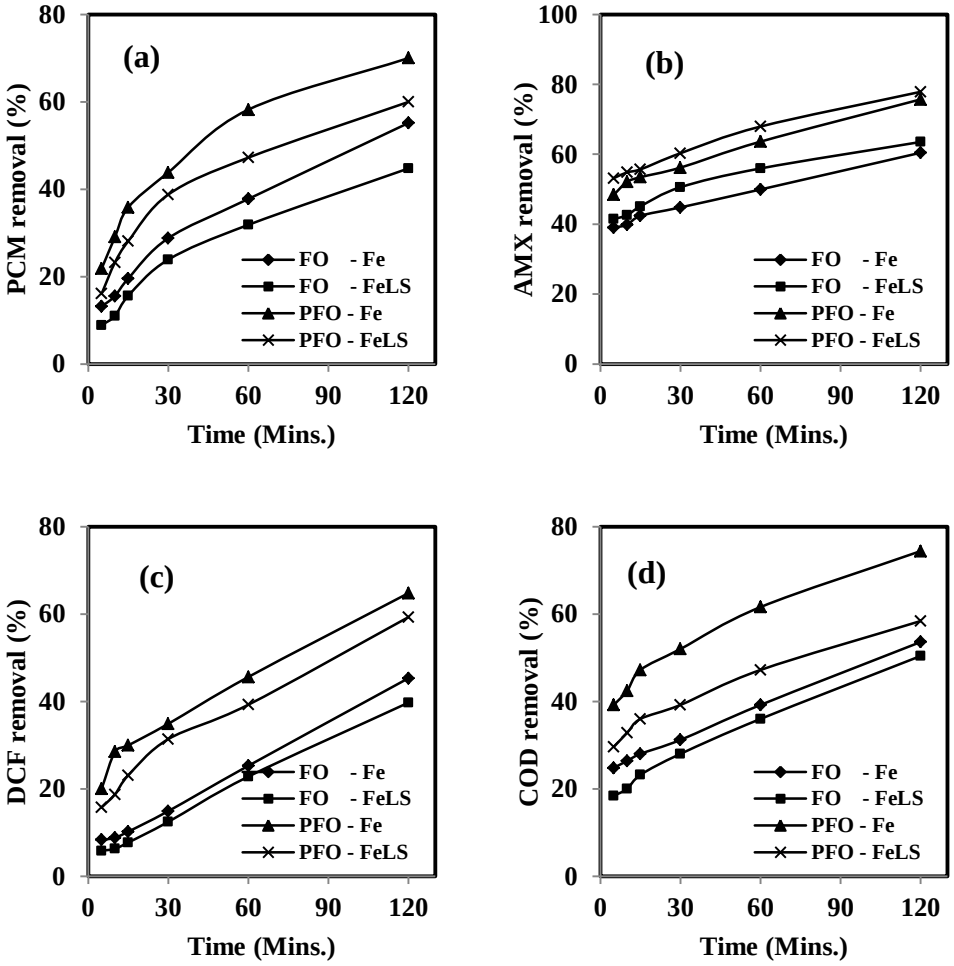


Fig. 4.65 Comparison between Fenton and photo-Fenton process of (a) percent PCM removal, (b) percent AMX removal, (c) percent DCF removal and (d) percent COD removal; [Reaction conditions; UVC 8W light source, $[PCM]_0$ = 10 mg/L, $[AMX]_0$ = 10 mg/L, $[DCF]_0$ = 10 mg/L, pH 3.5, $[Drug]_0 / [H_2O_2]_0$ = 3 : 7 (w/w) for Fe^{2+}, $[Drug]_0 / [H_2O_2]_0$ = 3 : 8 (w/w) for Fe (LS), $[H_2O_2]_0 / [Fe^{2+}]_0$ = 115.0 : 1 (molar), $[H_2O_2]_0 / [Fe (LS)]_0$ = 131.4 : 1 (molar)].

At the optimum conditions in photo-Fenton oxidation of the mixture of selected drugs, 10.03 % more PCM degradation, 5.49 % more DCF degradation and 16.0 % more COD removal for 10 mg/L of each drug as well as 11.2 % more PCM degradation, 4.12 % more DCF degradation and 11.8 % more COD removal for 50 mg/L of each drug are observed for Fe^{2+} than that of Fe (LS) in 120 minutes of UVC irradiation time. However, the AMX degradation is 2.17 % more for 10 mg/L of each

drug and 2.34 % more for 50 mg/L of each drug for Fe (LS) than that of Fe^{2+} in 120 minutes of UVC irradiation time.

The degradation and mineralization of the selected drugs are more for UVC assisted photo-Fenton oxidation over the Fenton oxidation process. This is because of the production of more number of highly reactive oxidizing OH radicals in direct and indirect photolysis with UV irradiation. DCF degradation of 12.7 % more with Fe^{2+} and 4.05 % more with Fe (LS) and COD removal of 3.73 % more with Fe^{2+} and 6.93 % more with Fe (LS) are observed for UV-C photo-Fenton over Fenton oxidation at the optimum experimental conditions within 120 minutes reaction time.

When Fe (LS) is used, chloride ions are present in the system that may form chloro-Fe (III) complexes that leads to decrease in the rates of generation of Fe^{2+} and this inhibit the formation of OH radicals and also the OH radicals present in the system may be scavenged by chloride to form less reactive dichloride anion radicals ($Cl_2^{\bullet -}$) (Laat et al. 2004). Thus, the Fenton reaction mechanism for PCM and DCF degradation in presence of chlorides may be via less reactive dichloride anion radicals ($Cl_2^{\bullet -}$) (E^o =2.09 V) (Ledakowiez et al. 2000). Conversely, in the presence of Fe^{2+}, the mechanism of Fenton reaction for degradation of PCM and DCF is through formation of highly reactive hydroxyl radicals (E^o = 2.8V) (Troung et al. 2004). The degradation of PCM and DCF through less reactive dichloride ion radical mechanism may be the cause for the low degradation and mineralization when Fe (LS) is used in Fenton reagent. On the other hand, the chloride ions present in the oxidation system may react with amine group in AMX. Also, the acid in iron extracts of laterite soil, acts as catalyst to break the more highly strained four-membered lactam ring. The carbonyl group in the β-lactam ring is highly susceptible to nucleophilic attack. Consequently, the degradation and mineralization of AMX is more for Fe (LS) than Fe^{2+}.

Hence, both the Fenton and photo-Fenton processes, when Fe^{2+} and Fe (LS) are used as catalysts, appear to be the most effective in removing the selected drugs from aqueous solutions.

There are a number of important factors in selecting a waste-treatment technology, together with: economics, regulations, effluent quality goals, operation. Even though, all these factors are essential, the dominant factor is often economics (Bolton et al. 2001). Since, electric energy can represent a major fraction of the operating costs; the adoption of the optimal treatment process in the industrial environment will depend on favourable process economics. Therefore, in the present study, the operational cost of Fenton and Photo-Fenton processes for treating one liter of water containing 10 mg/L concentration of each selected drug is estimated by considering chemicals used at the optimal conditions and power requirements.

The estimated operating cost per liter of waste for the treatment of PCM is Rs. 0.034 (INR) using Fe^{2+} and Rs. 0.027 (INR) using Fe (LS) in Fenton oxidation and Rs. 0.096 (INR) using Fe^{2+} and Rs. 0.089 (INR) using Fe (LS) in photo-Fenton oxidation. In the same way, the operating cost for the treatment of AMX and DCF is Rs. 0.036 (INR) using Fe^{2+} and Rs. 0.030 (INR) using Fe (LS) in Fenton oxidation and Rs. 0.098 (INR) using Fe^{2+} and Rs. 0.092 (INR) using Fe (LS) in photo-Fenton oxidation. However, the operating cost for the treatment of the mixture of three drugs is Rs. 0.055 (INR) using Fe^{2+} and Rs. 0.052 (INR) using Fe (LS) in Fenton oxidation and Rs. 0.121 (INR) using Fe^{2+} and Rs. 0.118 (INR) using Fe (LS) in photo-Fenton oxidation. It is observed that the operating cost for the treatment of drugs in mixture is less by about 49 % using Fe^{2+} and 40 % using Fe (LS) in Fenton process and about 59 % using Fe^{2+} and 57 % using Fe (LS) in photo-Fenton process when compared to the costs for the treatment of the drugs individually. It can also be noticed that the operational costs are less up to 20% for Fe (LS) when compared to Fe^{2+} in both Fenton and photo-Fenton oxidation of the selected drugs individually or in mixture. Moreover, the Fenton process is cost effective over the photo-Fenton and hence it may be applied to industry for treating the wastewater containing PCM, AMX or DCF.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Chapter 5

CONCLUSIONS

In this chapter, some of the important conclusions of the present study are presented. Also, some suggestions for further study are recommended.

5.1 Conclusions

The following points summarize the findings/conclusions that emerge from the results of the present research work.

1. The optimum pH for the maximum degradation and mineralization by the selected AOPs for PCM and AMX is 3.0; for DCF and mixture of drugs it is 3.5. The DCF precipitates when pH falls below 3.5 and therefore this observation is critical during the oxidation processes.

2. The $[Drug]_0$ / $[H_2O_2]_0$ molar ratios in Fenton oxidation using Fe^{2+} as catalyst are observed to be 1: 13.34 for PCM, 1 : 32.24 for AMX and 1 : 32.75 for DCF. But the $[Drug]_0$ / $[H_2O_2]_0$ molar ratios in Fenton oxidation using Fe (LS) as catalyst are observed to be 1: 13.34 for PCM, 1 : 37.62 for AMX and 1 : 32.75 for DCF. On the other hand, the $[H_2O_2]_0$ / $[Fe^{2+}]_0$ molar ratios in Fenton oxidation are observed as 98.55 : 1 for PCM, 98.55 : 1 for AMX and 57.49 : 1 for DCF. However, the $[H_2O_2]_0$ / $[Fe\ (LS)]_0$ molar ratios in Fenton oxidation are observed as 65.70 : 1 for PCM, 76.65 : 1 for AMX and 76.65 : 1 for DCF.

3. The PCM degradation of 100 % with both Fe^{2+} and Fe (LS), COD removal of 77.08 % with Fe^{2+} and 70.83 % with Fe (LS) within 240 min of reaction time by Fenton process are observed. Besides, PCM degradation of 100 % with both Fe^{2+} and Fe (LS), COD removal of 89.58 % with Fe^{2+} and 77.08 % with Fe (LS) within 120 min of reaction time during UV-C assisted photo-Fenton process are observed.

4. The AMX degradation of 100 % with both Fe^{2+} and Fe (LS) by the both Fenton process and UV-C assisted photo-Fenton process are observed. COD removal of 72.50 % with Fe^{2+} and 74.5 % with Fe (LS) within 240 min of reaction time are observed by Fenton process. However, the COD removal of 75.00 % with Fe^{2+} and 80.00 % with Fe (LS) within 120 min of reaction time by UV-C assisted photo-Fenton process are observed.

5. The DCF degradation of 79.29 % with Fe^{2+} and 74.29 % with Fe (LS), COD removal of 72.80 % with Fe^{2+} and 59.47 % with Fe (LS) within 240 min of reaction time by Fenton process, DCF degradation of 98.57 % with Fe^{2+} and 85.71 % with Fe (LS), COD removal of 74.93 % with Fe^{2+} and 65.33 % with Fe (LS) within 120 min of reaction time by UV-C assisted photo-Fenton process are observed.

6. Treatment for the Mixture of drugs: The optimal molar ratios are observed to be $[H_2O_2]_0 / [Fe^{2+}]_0$ = 114.98 : 1 and $[H_2O_2]_0$ / [Fe (LS)]$_0$ 131.4 : 1. In Fenton oxidation using Fe^{2+}, the percent drug degradation is 68.55 (PCM), 70.77 (AMX), 62.56 (DCF) and percent COD removal is 64.80 in 240 min. Similarly, when Fe (LS) is used in Fenton oxidation, the percent drug degradation is 57.22 (PCM), 76.71 (AMX), 55.75 (DCF) and percent COD removal is 60.00 in 240 min. However, in photo-Fenton oxidation using Fe^{2+}, the percent drug degradation is 70.01 (PCM), 75.70 (AMX), 64.79 (DCF) and percent COD removal is 74.40 in 120 min. On the other hand, using Fe (LS), the percent drug degradation is 59.98 (PCM), 77.87 (AMX), 59.29 (DCF) and percent COD removal is 58.40 in 120 min.

7. H_2O_2 consumption is 26.32 % less when Fe^{2+} is used and 20 % less when Fe (LS) is used for the treatment of mixture of drugs compared to the treatment of the drugs individually in Fenton and photo-Fenton oxidation of the selected pharmaceutical compounds.

8. Fe^{2+} consumption is 50 % less and Fe (LS) consumption is 55.56 % less for the treatment of mixture of drugs compared to the treatment of the drugs

individually in Fenton and photo-Fenton oxidation of the selected pharmaceutical compounds.

9. The degradation of PCM and DCF is marginally less for the Fe (LS) over Fe^{2+} catalysts in Fenton and photo-Fenton processes. Conversely, the degradation of AMX is more for the Fe (LS) over Fe^{2+} catalysts in both the Fenton and photo-Fenton processes.

10. When Fe^{2+} is used as catalyst, the PCM degradation kinetic constants are about 1.48 times more; AMX degradation kinetic constants are about 1.44 times more; DCF degradation kinetic constants are about 2.03 times more in photo-Fenton process compared to Fenton process.

11. Similarly, When Fe (LS) is used as catalyst, the PCM degradation kinetic constants are about 1.10 times more; AMX degradation kinetic constants are about 1.34 times more; DCF degradation kinetic constants are about 1.20 times more in photo-Fenton process compared to Fenton process.

12. In both Fenton and photo-Fenton oxidation for both Fe^{2+} and Fe (LS), the degradation rate constants for DCF are 1.30 to 3.76 times higher than the AMX and 1.2 to 2.13 times higher than PCM; the rate constants for the PCM degradation is about 1.06 to 1.76 times higher than AMX degradation.

13. The operating cost for the treatment of drugs in mixture is less by about 49 % with Fe^{2+} and 40 % with Fe (LS) by Fenton process and about 59 % with Fe^{2+} and 57 % with Fe (LS) by photo-Fenton process when compared to the costs for the treatment of the drugs individually.

14. The operational costs are less for Fe (LS) when compared to Fe^{2+} in both Fenton and photo-Fenton oxidation of the selected drugs individually or in mixture.

15. UVC assisted photo-Fenton process is more efficient over Fenton process in degradation and mineralization of PCM, AMX and DCF. But, the Fenton

process is cost effective over the photo-Fenton and can be applied to industry for treating the wastewater containing PCM, AMX and DCF.

16. The iron from laterite soil (Fe (LS)) as a catalyst in Fenton's reagent has demonstrated satisfactory degradation and mineralization of PCM, AMX and DCF and hence may be used as an alternate catalyst in the AOPs.

17. Fenton and photo-Fenton processes appear to effectively degrade the selected pharmaceutical compounds viz. paracetamol, amoxicillin, diclofenac in aqueous solutions.

18. Therefore, Fenton and photo-Fenton oxidation using Fe (LS) as catalyst appears to be an effective and economical for the oxidation of PCM, AMX and DCF in aqueous solutions.

5.2 Recommendations for Future Research Work

1. A two stage chemical-biological treatment can be evaluated. As the compounds are non-biodegradable, Fenton or photo-Fenton process can be used as pretreatment to increase the bio-degradability of the pollutants. Then, the effluent from these processes can be treated by biological methods to completely remove the pollutants in eco-friendly manner.

2. Toxicity tests can be carried out in order to determine the toxicity of the treated effluent, taking into account that toxicity test is a very important parameter in the general strategy proposed for wastewater treatment. Besides, the organic compounds responsible for the bio-recalcitrance can be identified.

3. Pilot scale studies can also be carried out and the extrapolation of the technology to full-scale applications will be a closer evaluation of the influence of water quality on treatment effectiveness to imitate the actual field conditions to determine the efficiency of the Fenton and photo-Fenton processes for the treatment of pharmaceutical compounds.

APPENDIX I

SIMULTANEOUS DETERMINATION OF PARACETAMOL, AMOXICILLIN AND DICLOFENAC IN WATER BY UV-VIS SPECTROPHOTOMETER

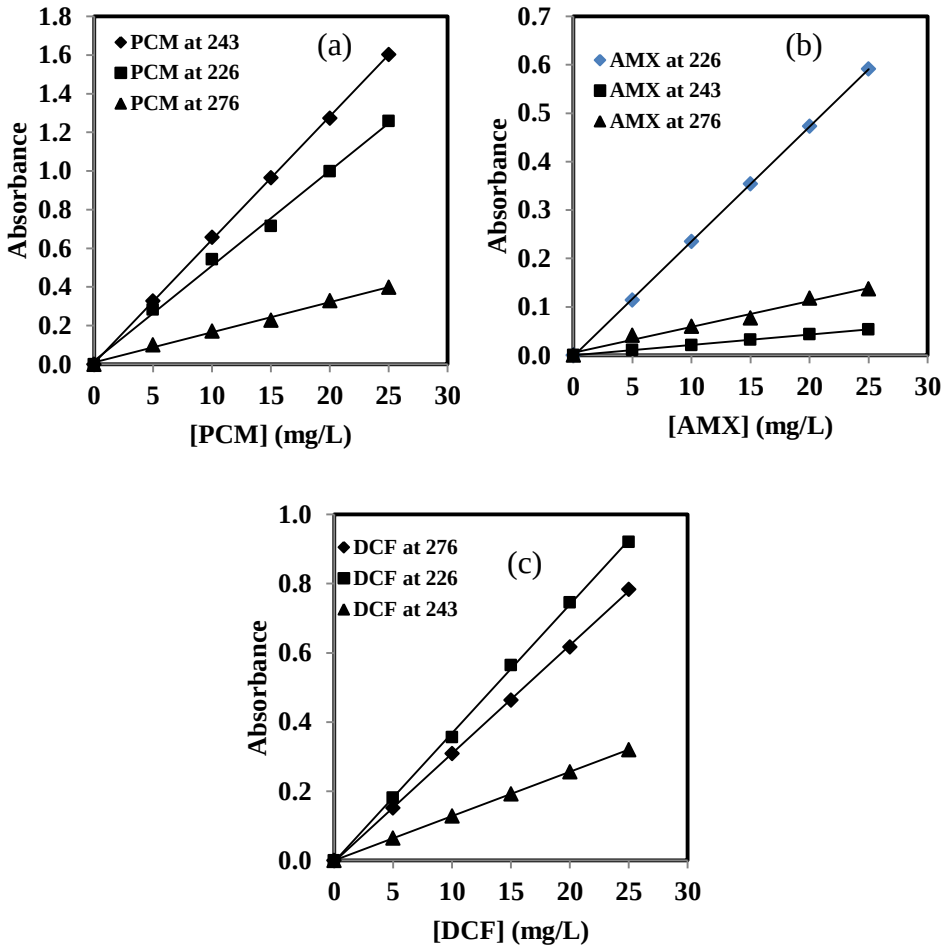


Fig. A.1 (a) Calibration Curve for PCM at 243, 226 and 276 nm (b) Calibration Curve for AMX at 226, 243 and 276 nm and (c) Calibration Curve for DCF at 276, 226 and 243 nm

A Systronics double beam UV – Vis spectrophotometer model 2201 with 1 cm matched quartz cells. The stock solutions of PCM, AMX and DCF are further diluted with the deionised water to get concentration of 10 mg/L. The solutions are scanned with spectrophotometer in the wavelength range of 200 to 500 nm. The wavelengths of maximum absorbance for PCM, AMX and DCF are found to be 243 nm, 226 nm and 276 nm respectively. The stock solutions are diluted with deionised water to

obtain concentration range of 5 – 25 mg/L of each drug and the absorbance of samples of each drug is measured at 243 nm, 226 nm and 276 nm. The calibration curves of PCM, AMX and DCF are drawn for Concentration vs. absorbance at 243 nm, 226 nm and 276 nm as seen in Fig. A.1. For the accuracy and repeatability of the method, each absorbance is measured for at least 3 times. The slope of the each line in the calibration curve gives the absorptivity or absorption coefficient of the selected drug at corresponding wavelength. The analytical validation parameters for the simultaneous determination of the concentrations of PCM, AMX and DCF are shown in Table A. 1.

Table A.1 Analytical validation parameters

Drug	**Parameter**	**Observations**		
PCM	Wavelengths (nm)	243	226	276
	Beer's law range (mg/L)	5 - 25	5 - 25	5 - 25
	Standard regression equations	0.0638x + 0.00069	0.0492x + 0.0177	0.0156x + 0.0094
	Correlation Coefficient	0.9998	0.9967	0.9941
AMX	Wavelengths (nm)	243	226	276
	Beer's law range (mg/L)	5 - 25	5 - 25	5 - 25
	Standard regression equations	0.0053x + 0.0055	0.0237x - 0.002	0.0021x + 0.0001
	Correlation Coefficient	0.9827	1	0.9998
DCF	Wavelengths (nm)	243	226	276
	Beer's law range (mg/L)	5 - 25	5 - 25	5 - 25
	Standard regression equations	0.0128x	0.0371x - 0.0033	0.0312x - 0.0033
	Correlation Coefficient	1	0.9995	0.9998

The absorbance of a mixture of drugs at 243nm, 226 nm and 276 nm are measured and the following method is used to find concentration of each drug.

In the mixture, all the three drugs absorb at each other's wavelength of maximum absorbance. The absorbance of the mixture of drugs at each wave length is the sum of absorbance of all the drugs.

By Beer Lambert's Law

Absorbance, $A = abC$

Where, a = absorptivity

b = path length = 1 cm

C = Concentration of drug

Therefore, A = aC

The accuracy of calculation of the concentration C depends on the accurate measurement of absorptivity 'a' and the absorbance 'A' of the mixture

The absorbance of mixture at each wavelength is derived as follows

$a_1C_1 + b_1C_2 + c_1C_3 = A_1$ at $\lambda_1 = 243$ nm.....(A1.1)

$a_2C_1 + b_2C_2 + c_2C_3 = A_2$ at $\lambda_2 = 226$ nm.....(A1.2)

$a_3C_1 + b_3C_2 + c_3C_3 = A_3$ at $\lambda_3 = 276$ nm.....(A1.3)

Where,

A_1, A_2 and A_3 = absorptions of the mixture of the drugs at 243 nm, 226 nm and 276 nm

C_1, C_2 and C_3 = Concentration of PCM, AMX and DCF

a_1, a_2 and a_3 = absorptivity of PCM at 243 nm, 226 nm and 276 nm respectively

b_1, b_2 and b_3 = absorptivity of AMX at 243 nm, 226 nm and 276 nm respectively

c_1, c_2 and c_3 = absorptivity of DCF at 243 nm, 226 nm and 276 nm respectively

Since the above equations have 3 unknowns, Matrix method is used to calculate concentration of PCM, AMX and DCF.

The above equations can be rearranged to a matrix form, where, all the coefficients on the left hand side will form a matrix say 'A', the unknown concentrations of the drugs can be arranged into a vector 'C' and the right hand side absorbance can also be arranged into another vector say 'R'.

$$A = \begin{bmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{bmatrix} \qquad C = \begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix} \qquad R = \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix}$$

Therefore, $AC = R \longrightarrow C = A^{-1}R$

$$\longrightarrow \begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix} = \begin{bmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{bmatrix}^{-1} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix}$$

By using the Cramer's, the unknown concentrations of the PCM, AMX and DCF are determined in MS excel.

APPENDIX II

OPERATING COSTS FOR THE TREATMENT OF PARACETAMOL, AMOXICILLIN, DICLOFENAC AND THE MIXTURE OF THE DRUGS BY FENTON AND PHOTO-FENTON PROCESSES

A full economic analysis of the net at hand cost (capital investment, installation and operating costs) of implementing a technology is a difficult task and it is both site and problem specific. Since, electric energy can represent a major fraction of the operating costs. Moreover, electric energy dose requirements also dictate the size of the principal equipment needed to generate the requisite dose (Bolton et al. 2001).

Most of the AOPs are generally electric-energy-driven for the pollutant removal. The photochemical processes are the most important commercially among all the AOPs. In the case of Fenton and photo-Fenton processes in the present study, the process economics are primarily dependent on the costs of electricity (power for mixing and power for UV-lamp) and the chemicals used. The estimated operational costs are represented as treatment costs per unit volume for a particular waste stream and technology.

The power requirements for the rapid dispersion of the selected drug and other chemicals in Fenton and photo-Fenton processes are calculated as per the method reported by Sincero and Sincero (2010). The electrical energy consumed by UV lamp is photo-Fenton process is calculated considering the rated power of the lamp, treatment time and volume of the wastewater treated. For the drug degradation, the Fenton oxidation process is carried out for 240 minutes reaction time and the photo-Fenton process is carried out for 120 minutes reaction time; hence the power requirement for 240 min and 120 min is estimated. The operating costs for the treatment of PCM, AMX, DCF and the Mixture of the drugs in water by Fenton and photo-Fenton oxidation processes are estimated and presented in Table B.1.

Table B. 1 The estimated operating costs per liter for the treatment of PCM, AMX and DCF and the mixture of drugs in water by Fenton and photo-Fenton oxidation processes for 10 mg / L concentration of each drug

Drug	Method	Catalyst	Amount in INR
PCM	Fenton Oxidation	Fe^{2+}	**0.034**
		Fe (LS)	**0.027**
	Photo-Fenton Oxidation	Fe^{2+}	**0.096**
		Fe (LS)	**0.089**
AMX	Fenton Oxidation	Fe^{2+}	**0.036**
		Fe (LS)	**0.030**
	Photo-Fenton Oxidation	Fe^{2+}	**0.098**
		Fe (LS)	**0.092**
DCF	Fenton Oxidation	Fe^{2+}	**0.036**
		Fe (LS)	**0.030**
	Photo-Fenton Oxidation	Fe^{2+}	**0.098**
		Fe (LS)	**0.092**
MIXTURE OF DRUGS	Fenton Oxidation	Fe^{2+}	**0.055**
		Fe (LS)	**0.052**
	Photo-Fenton Oxidation	Fe^{2+}	**0.121**
		Fe (LS)	**0.118**

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List of Publications based on PhD Research Work

Papers in Refereed International Journals

1. Manu, B., **Mahamood**, Vittal, H and Shrihari, S. (2011). "A novel catalytic route to degrade paracetamol by Fenton process." *Int. J. Res. Chem. Environ.,* 1 (1), 157-164.

2. Manu, B. and **Mahamood.** (2011)**.** "Enhanced degradation of paracetamol by UV-C supported photo-Fenton process over Fenton oxidation." *Water Sci. Technol*., 64 (12), 2433 - 2438**.**

3. MANU, B. and **MAHAMOOD.** (2011). **"**Degradation of Paracetamol in Aqueous Solution by Fenton Oxidation and Photo-Fenton Oxidation Processes Using Iron from Laterite Soil as Catalyst." *Int. J. Earth sci. Eng*., 4 (6), 1103 - 1110.

4. Manu, B. and **Mahamood**. (2012) "Degradation Kinetics of Diclofenac in Water by Fenton's Oxidation." *J. Sustan. Energy Environ*., 3 (4), 173 – 176.

NITK Research Bulletin

5. Manu, B. and **Mahamood**. (2012). "Fenton's Oxidation of Amoxicillin in Water" NITK Research Bulletin, 21 (2), 30 – 38.

Presentations in Conferences

6. Manu, B. and **Mahamood**. "Advanced Oxidation of Diclofenac in Aqueous Solution by Fenton Process: Use of Iron Extracted from Lateritic Soil as Catalyst." 27th Convention of Environmental Engineers on "Green Technology", Institution of Engineers (India), Mangalore, Karnataka State, India, 24 – 25 January, 2012, 1 – 9.

7. Manu, B. and **Mahamood**. "Fenton's Oxidation of Diclofenac in Water: A Kinetic Study." National Conference on Contemporary Civil Engineering Research & Practices (CCERP – 2012), Manipal Institute of Technology, Manipal, Karnataka State, India, 20 – 21 April, 2012, 508 – 517.

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Teaching Experience

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1	Government Polytechnic for Women, Hindupur, Anantapur Dist. A. P., India	09-03-1995	18-06-1997	2 Yrs - 3 mths	Lecturer
2	Government Polytechnic for Women, Palamaner, Chittoor Dist. A. P., India	19-06-1997	08-03-2000	2 Yrs - 9 mths	Lecturer
		09-03-2000	08-03-2005	5 Yrs - 0 mths	Senior Scale Lecturer
		09-03-2005	Till date	7 Yrs – 2 mths	Selection Grade Lecturer

Subjects Taught : Environmental Engineering, Environmental Studies, Engineering Mechanics, Reinforced Cement Concrete, Steel Structures, Surveying, Estimation and Costing

Consultancy Work :Design, Drawing, Estimation and construction of Buildings

Research Experience : 03 years of research Experience in water and wastewater Treatment

Publications

Books : Environmental Studies, V. G. S. Publishers, Vijayawada, Andhra Pradesh, India

Papers in Refereed International Journals

1. Manu, B., **Mahamood**, Vittal, H. and Shrihari, S. (2011). "A novel catalytic route to degrade paracetamol by Fenton process." *Int. J. Res. Chem. Environ.*, 1 (1), 157-164.
2. Manu, B. and **Mahamood.** (2011)**. "**Enhanced degradation of paracetamol by UV-C supported photo-Fenton process over Fenton oxidation. *Water Sci. Technol*., 64 (12), 2433 - 2438**.**
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7. Mohd Omair, **Mahamood** and B. Manu. (2011). "Biodegradation of selected pharmaceutical Chemicals using SBR." 3rd international Geography Congress, Centrefor Water Resources Development and Management (CWRDM), Kozhikode, Kerala, India, 6th May, 2011.
8. Manu, B. and **Mahamood**. (2012). "Advanced Oxidation of Diclofenac in Aqueous Solution by Fenton Process: Use of Iron Extracted from Lateritic Soil as Catalyst." 27th Convention of Environmental Engineers on "Green Technology", Institution of Engineers (India), Mangalore, Karnataka State, India, 24 – 25 January, 2012, 1 - 9.
9. Manu, B. and **Mahamood**. (2012). "Fenton's Oxidation of Diclofenac in Water: A Kinetic Study." National Conference on Contemporary Civil Engineering Research & Practices (CCERP – 2012), Manipal Institute of Technology, Manipal, Karnataka State, India, 20 – 21 April, 2012, 508 – 517.