Studies on Advanced Oxidation Processes for the Removal of Acetamiprid from Wastewater

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Certificate

This is to certify that the thesis entitled **“Studies on Advanced Oxidation Processes for the Removal of Acetamiprid from Wastewater”** is an authentic original work done by **Fasnabi P.A.** under my supervision and guidance in School of Engineering, Cochin University of Science and Technology. No part of this thesis has been presented for any other degree from any other institution. All the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the doctoral committee have been incorporated in the thesis.

Dr. G. Madhu
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Declaration

I hereby declare that the work presented in the thesis entitled **“Studies on Advanced Oxidation Processes for the Removal of Acetamiprid from Wastewater”** is based on the original work done by me under the supervision of **Prof. (Dr.) G. Madhu,** Division of Safety and Fire Engineering, School of Engineering, Cochin University of Science and Technology. No part of this thesis has been presented for any other degree from any other institution.

Kochi -22
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Fasnabi P.A.

Dedicated to

My Loving Parents

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Abstract

Pollution of water with pesticides has become a threat to the man, material and environment. The pesticides released to the environment reach the water bodies through run off. Industrial wastewater from pesticide manufacturing industries contains pesticides at higher concentration and hence a major source of water pollution.

Pesticides create a lot of health and environmental hazards which include diseases like cancer, liver and kidney disorders, reproductive disorders, fatal death, birth defects etc.

Conventional wastewater treatment plants based on biological treatment are not efficient to remove these compounds to the desired level. Most of the pesticides are phyto-toxic i.e., they kill the microorganism responsible for the degradation and are recalcitrant in nature. Advanced oxidation process (AOP) is a class of oxidation techniques where hydroxyl radicals are employed for oxidation of pollutants. AOPs have the ability to totally mineralise the organic pollutants to CO_2 and water. Different methods are employed for the generation of hydroxyl radicals in AOP systems.

Acetamiprid is a neonicotinoid insecticide widely used to control sucking type insects on crops such as leafy vegetables, citrus fruits, pome fruits, grapes, cotton, ornamental flowers. It is now recommended as a substitute for organophosphorous pesticides. Since its use is increasing, its presence is increasingly found in the environment. It has high water solubility and is not easily biodegradable. It has the potential to pollute surface and ground waters.

Here, the use of AOPs for the removal of acetamiprid from wastewater has been investigated. Five methods were selected for the study based on literature survey and preliminary experiments conducted. Fenton process, UV treatment, UV/ H_2O_2 process, photo-Fenton and photocatalysis using TiO_2 were

selected for study. Undoped TiO_2 and TiO_2 doped with Cu and Fe were prepared by sol-gel method. Characterisation of the prepared catalysts was done by X-ray diffraction, scanning electron microscope, differential thermal analysis and thermogravimetric analysis. Influence of major operating parameters on the removal of acetamiprid has been investigated. All the experiments were designed using central compoiste design (CCD) of response surface methodology (RSM). Model equations were developed for Fenton, UV/ H_2O_2, photo-Fenton and photocatalysis for predicting acetamiprid removal and total organic carbon (TOC) removal for different operating conditions. Quality of the models were analysed by statistical methods. Experimental validations were also done to confirm the quality of the models. Optimum conditions obtained by experiment were verified with that obtained using response optimiser.

Fenton Process is the simplest and oldest AOP where hydrogen peroxide and iron are employed for the generation of hydroxyl radicals. Influence of H_2O_2 and Fe^{2+} on the acetamiprid removal and TOC removal by Fenton process were investigated and it was found that removal increases with increase in H_2O_2 and Fe^{2+} concentration. At an initial concentration of 50 mg/L acetamiprid, 200 mg/L H_2O_2 and 20 mg/L Fe^{2+} at pH 3 was found to be optimum for acetamiprid removal. For UV treatment effect of pH was studied and it was found that pH has not much effect on the removal rate. Addition of H_2O_2 to UV process increased the removal rate because of the hydroxyl radical formation due to photolyis of H_2O_2. An H_2O_2 concentration of 110 mg/L at pH 6 was found to be optimum for acetamiprid removal. With photo-Fenton drastic reduction in the treatment time was observed with 10 times reduction in the amount of reagents required. H_2O_2 concentration of 20 mg/L and Fe^{2+} concentration of 2 mg/L was found to be optimum at pH 3.

With TiO_2 photocatalysis improvement in the removal rate was noticed compared to UV treatment. Effect of Cu and Fe doping on the photocatalytic

activity under UV light was studied and it was observed that Cu doping enhanced the removal rate slightly while Fe doping has decreased the removal rate. Maximum acetamiprid removal was observed for an optimum catalyst loading of 1000 mg/L and Cu concentration of 1 wt%.

It was noticed that mineralisation efficiency of the processes is low compared to acetamiprid removal efficiency. This may be due to the presence of stable intermediate compounds formed during degradation

Kinetic studies were conducted for all the treatment processes and it was found that all processes follow pseudo-first order kinetics. Kinetic constants were found out from the experimental data for all the processes and half lives were calculated. The rate of reaction was in the order, photo-Fenton>UV/ H_2O_2>Fenton> TiO_2 photocatalysis>UV. Operating cost was calculated for the processes and it was found that photo-Fenton removes the acetamiprid at lowest operating cost in lesser time.

A kinetic model was developed for photo-Fenton process using the elementary reaction data and mass balance equations for the species involved in the process. Variation of acetamiprid concentration with time for different H_2O_2 and Fe^{2+} concentration at pH 3 can be found out using this model. The model was validated by comparing the simulated concentration profiles with that obtained from experiments.

This study established the viability of the selected AOPs for the removal of acetamiprid from wastewater. Of the studied AOPs photo-Fenton gives the highest removal efficiency with lowest operating cost within shortest time.

Keywords: - Advanced oxidation processes, Acetamiprid, Fenton Process, UV treatment, UV/ H_2O_2 process, photo-Fenton process, TiO_2 photocatalysis, Response surface methodology

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Abbreviations

AARE	Arithmetic Average Relative Error
AOP	Advanced Oxidation Process
BOD	Biochemical Oxygen Demand
CCD	Central Composite Design
CIBRC	Central Insecticides Board and Registration Committee
COD	Chemical Oxygen Demand
DTA	Differential Thermal Analysis
EE/O	Electrical Energy per Order
EPA	Environmental Protection Agency
HPLC	High Performance Liquid Chromatograph
POP	Persistent Organic Pollutants
RMSE	Root Mean Square Error
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
SI	Scatter Index
TGA	Thermogravimetric Analysis
TOC	Total Organic Carbon
US	Ultra-Sound
UV	Ultra-Violet
WAO	Wet Air Oxidation
XRD	X-ray Diffraction

Notations

A_0	Constant term in the model equation
A_1, A_2	Regression coefficient for linear effects
A_{11}, A_{12}	Regression coefficients for quadratic effects
A_{12}	Interaction coefficient
C	Acetamiprid concentration at time t
C_0	Initial acetamiprid concentration
D	cystalline size
P	Rated power of UV lamp, kW
R	Correlation Coefficient
t	Time taken for treatment, minutes
V	Volume of the reaction mixture, Litres
X_1	H_2O_2 concentration in Fenton process, mg/L
X_2	Fe^{2+} concentration in Fenton process, mg/L
X_3	pH in UV/ H_2O_2 process
X_4	H_2O_2 concentration in UV/ H_2O_2 process, mg/L
X_5	H_2O_2 concentration in photo-Fenton process, mg/L
X_6	Fe^{2+} concentration in photo- Fenton process, mg/L
X_7	Catalyst loading in TiO_2 photocatalysis, mg/L
X_8	Cu concentration in Cu doped TiO_2, wt %
β	Width at half maximum height of peak in XRD pattern
θ	X-ray diffraction angle
λ	Wavelength of X-ray diffraction

* * *

Chapter 1

Introduction

1.1 Introduction

Pollution of ground and surface water with pesticides has great impact on human health and environment. Green revolution was made possible with the use of fertilisers and pesticides. The first invented insecticide, DDT was considered as a boon to the mankind when it was discovered. Now it is banned in most of the countries because of its adverse effects on man, materials and environment. The residues of DDT were identified even in human breast milk. This happens because most of the pesticides are non-biodegradable and due to biomagnification it accumulates in the food chain. As the population is increasing and the availability of cropland is limited, it is necessary to increase the food production to ensure food safety. It is also a prerequisite to improve the standard of living of the people (Zhang et al., 2007;

Zhang, 2008). Most of the countries could achieve the target with the help of fertilisers and pesticides. Researchers pointed out that if the consumption of pesticides is prohibited, the food production would drop sharply and the food prices would soar (Guo et al., 2007).

Industrial wastewater is a major source of pollution of water bodies because of high concentration of pollutants contained in it. Pesticides pose great threat to the conventional wastewater treatment plants as most of the pesticides are toxic to the microorganisms employed for biological treatment of wastewater. Moreover, they have high stability and/or low biodegradability.

1.2 Pollution Due to Pesticides and its Health Effects

Pesticides are designed to control pests, but they can also be toxic to the desired species including humans. At present India is major consumer and producer of pesticides in Asia. Majority of Indian population is engaged in agriculture and hence they are exposed to these pollutants (Gupta, 2004). These pesticides are finally discharged to the environment and reach the human beings directly and indirectly.

Pesticides can cause adverse health effects on humans and other living species. Health effects can be acute, chronic or mild depending on the type of pesticide, concentration and frequency of exposure. The adverse health effects of pesticides range from mild effects such as irritation to skin and eye to severe health effects such as affecting the nervous system, mimicking hormones causing reproductive problems, and cancer (Lederman, 1996; Gilden et al., 2010).

A systematic review found that occurrence of some types of cancers particularly brain, prostate, kidney, non- Hodgkin lymphoma and leukemia has positive associations with pesticide exposure (Bassil et al., 2007). Strong evidence also exists for other negative outcomes from pesticide exposure including neurological, birth defects, fatal death, and neuro developmental disorder (Jeyaratnam,1985). The American Medical Association recommends limiting exposure to pesticides and using safer alternatives. It is estimated by World Health Organization and the UN Environment Programme that each year 3 million workers in agriculture in the developing world experience severe poisoning from pesticides (Miller, 2004).

Pesticides have become the inevitable part of modern life style and the solution for the pollution due to these materials is either go for biodegradable, non-toxic pesticides or reduce the use of pesticides and treat the wastewater effectively before discharging to the environment.

1.3 Acetamiprid

Acetamiprid ((E)-N_1-[6-chloro-3- pyridyl) methyl]- N_2-cyano-N_1-methylacetamidine) belongs to the class of the new effective nicotinic insecticides, the fastest growing class of insecticides. It has been widely used for the control of Hemiptera (mainly aphids), Thyasnoptera and Lepidoptera on various crops, vegetables, fruits and tea along with fleas infesting animal live stock and pets. It is systemic insecticide with translaminar action which has a contact and stomach action (Singh et al., 2012). It is intended to control sucking insects on crops such as leafy vegetables, citrus fruits, pome fruits, grapes, cotton, cole crops, and ornamental plants. It is also a key pesticide in commercial cherry farming due to its effectiveness against the larvae of the cherry fruit fly. It acts on the central nervous system of pests. Acetamiprid is an insecticide recommended as a substitute for some world - wide used organophosphorous pesticides (Guohong et al., 2009).

Being highly soluble in water, acetamiprid has the potential to reach the surface and ground waters. It is not easily biodegradable and has low photolytic reaction rate under solar radiation (US Environmental Protection Agency (EPA), 2002). Acetamiprid is classified as toxicity category rating II in acute oral studies with rats, toxicity category III in acute dermal and inhalation studies with rats, and toxicity category IV in primary eye and skin irritation studies with rabbits (European commission-2004). The EPA considers it as only moderately toxic to bees; however, some media sources and the recent documentary *Vanishing of the Bees* have blamed neonicotinoids like acetamiprid for colony collapse disorder (Wells, 2007).

1.4 Conventional Methods of Wastewater Treatment

Conventional wastewater treatment generally classified as 1) preliminary treatment 2) primary treatment 3) secondary treatment 4) Tertiary treatment or advanced treatment

In **preliminary treatment**, impurities such as coarse solids, grit are removed. The objective is to protect the downstream equipments and to enhance the efficiency of the subsequent stages.

Primary treatment removes settlable solids by sedimentation and floating materials such as oil and grease by techniques such as froth flotation.

Sedimentation removes a good percentage of organic and inorganic pollutants which can contribute a high reduction in COD. Some amount of heavy metals, organic nitrogen and phosphorous are also removed in this operation. The effluent from primary treatment containing colloidal particles and dissolved compounds are given to the secondary treatment system for further treatment.

Secondary treatment generally employs aerobic biological treatment techniques. The objective of the treatment is to remove the colloidal and dissolved organic matter present in the effluent to an acceptable limit. Different methods/ techniques are employed for biological treatment of waste water. It differs either in the way oxygen is supplied or in the way biological growth is maintained in the system. These techniques have a removal efficiency of 70-90% BOD. But this system may fail if contains non-biodegradable compounds. The non-biodegradable compounds are generally removed in the advanced treatment systems. But if these compounds have the ability to kill the microorganisms (phytotoxic), biological treatment systems will miserably fail.

In **tertiary/Advanced treatment** systems removal of specific compounds are targeted. It generally includes chemical oxidation, reverse osmosis, ion exchange, microfiltration, nanofiltration etc. In some cases these techniques are used in combination with primary and secondary treatment (eg: chemical addition in primary and secondary treatment).

1.5 Advanced Oxidation Processes (AOPs) - An Overview

The commonly used tertiary treatment techniques are not efficient enough to produce water that contains persistent pollutants within acceptable limit. AOPs can be employed for this purpose in which oxidation by hydroxyl radicals is employed. AOPs are recommended when the wastewater contains compounds of low biodegradability and/or high chemical stability. A chemical wastewater treatment system using AOPs can convert the pollutants completely to CO_2 and water. In some cases, the non-biodegradable initial compounds are converted to biodegradable compounds in which a combination of AOP and biological treatment can be made use of (Poyatos et al., 2010).

AOPs uses different mechanisms for the production of hydroxyl radicals, which include the simplest Fenton (Fe^{2+}/ H_2O_2) process, processes utilising ozone, ultraviolet (UV) light, ultrasound (US), high temperature and pressure cavitation etc. The hydroxyl radicals are very reactive and are not highly selective (Andreozzi et al., 1999). It has an oxidation potential of + 2.8 eV next only to fluorine in the list of known oxidants (Table 1.1).

Table 1.1 Oxidation power of oxidation species

Oxidation species	**Redox potential (eV)**
Flourine	3.03
Hydroxyl radical	2.80
Ozone	2.07
Hydrogen peroxide	1.78
Permanganate	1.69
Chlorine dioxide	1.56
Chlorine	1.36
Oxygen	1.23

(Source: Zhou H and Smith D.W., 2002)

A brief overview of the commonly used AOPs is presented in this section.

1.5.1 Fenton Process

Among the AOPs, the Fenton process is quite well known and has been successfully applied for the treatment various recalcitrant compounds. In the Fenton process the organic molecules are oxidized with hydroxyl radicals formed by the reaction between H_2O_2 and the iron (Walling and Goosen, 1973). It has been widely used for the removal COD, TOC, dyes, pigments, pesticides etc (Chamarro et al., 2001). Main mechanism of hydroxyl radical formation can be represented as

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \ldots\ldots\ldots\ldots \quad (1.1)$$

The hydroxyl radicals further oxidises the pollutants to CO_2 and water or to intermediate compounds.

1.5.2 UV/ H_2O_2 Process

UV/H_2O_2 process is very efficient with a wide range of applications mainly in the treatments of aqueous solutions. This process utilises the formation of hydroxyl radicals by the decomposition of H_2O_2 in the presence of UV light. The oxidation of organics can occur either by the direct photolysis or by the oxidation with hydroxyl radicals.

$$H_2O_2 + h\nu \rightarrow 2OH^{\cdot} \ldots\ldots\ldots\ldots \quad (1.2)$$

1.5.3 Photo-Fenton Process

The formation of iron sludge is the main disadvantage of the Fenton process. Photo-Fenton process uses UV light along with Fenton reagent

(H_2O_2 and Fe^{2+}). It reduces the formation of iron sludge by converting the Fe^{3+} formed back to Fe^{2+} (JianHui et al., 2012).

$$H_2O + Fe^{3+} + h\nu \rightarrow OH^{\bullet} + H^{+} + Fe^{2+} \quad \text{..} \quad (1.3)$$

The formation of additional hydroxyl radicals reduces the requirement of H_2O_2 and iron needed for the removals of pollutants.

1.5.4 Ozonation

Ozonation can be used for the degradation of organic pollutants in water. Ozone is a powerful oxidant (Electrochemical oxidation potential of 2.07V) which is generally produced by an electric discharge method in presence of air or oxygen. Two ways of oxidizing action is possible in the ozonation process. One way is the direct reaction between the ozone and the dissolved compounds and the other is the reaction between the generated radicals produced in the ozone decomposition and the dissolved compounds (Chiron S., 2002; Esplugas et al., 2002). Main reactions taking place are

$$O_3 + OH^{-} \rightarrow O_3^{\cdot -} + OH^{\bullet} \quad \text{..} \quad (1.4)$$

$$O_3^{\cdot -} \rightarrow O_2 + O^{\cdot -} \quad \text{..} (1.5)$$

$$O^{\cdot -} + H^{-} \rightarrow OH^{\bullet} \quad \text{..} \quad (1.6)$$

1.5.5 H_2O_2/O_3 Process

H_2O_2 can be combined with ozone to enhance the transformation of O_3 to $OH^{\cdot}$. In solution H_2O_2 is a weak acid, which partially dissociates into the hydroperoxide ion (HO_2^-) in water. H_2O_2 reacts slowly with O_3, whereas the HO_2^- ion can rapidly react with O_3 to form $OH^\cdot$ (Hoigne J., 1998).

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+ \quad \text{...}(1.7)$$

$$O_3 + HO_2^- \rightarrow OH^\bullet + O_2^- + O_2 \quad \text{...}(1.8)$$

$$H_2O_2 + 2O_3 \rightarrow 2OH^\bullet + 3O_2 \quad \text{...}(1.9)$$

1.5.6 O_3/UV Process

Hydroxyl radicals can be produced by using UV light to the ozonated water. Photolysis of ozone generates hydrogen peroxide and thus O_3/UV involves all of the organic destruction mechanisms present in H_2O_2/O_3 and H_2O_2/UV processes. The generation of H_2O_2 in this method is much less efficient than the electrochemical method used in the industry. Hence the O_3/UV process would be expected to be more expensive than O_3/H_2O_2 process (Zhou and Smith, 2002).

1.5.7 H_2O_2/ O_3/UV Process

If H_2O_2 is used in the O_3/UV process, the decomposition of ozone is accelerated and production of hydroxyl radicals is increased. It is a combination of two systems H_2O_2/O_3 and UV/O_3. The rate of removal of pollutants will generally be increased but of course at the expense of additional cost. This process uses both O_3 and UV and hence it is one of the costlier AOP (Shu and Chang, 2005). The reaction taking place is

$$2O_3 + H_2O_2 + h\nu \rightarrow 2OH^\bullet + 3O_2 \quad \text{..}(1.10)$$

1.5.8 O_3/US Process

Sonochemical degradation which combines destruction of the target compounds by free radical reaction and thermal cleavage is proven to be effective for removing low concentration organic pollutants from aqueous streams. The chemical effect of ultrasound is produced through the phenomenon of cavitation. Cavitation is the formation of microbubbles in solution that implode violently after reaching a critical resonance size (Ray et al., 2004). When a liquid is irradiated with ultrasound, the ultrasound waves pass through the medium in a series of alternate compression and expansion cycles. When the acoustic amplitude is large enough to stretch the molecules during its negative pressure (rarefaction) cycle to a distance that is greater than the critical molecular distance to hold the liquid intact, microbubbles are created, then collapse in the subsequent compression cycle, giving rise to extremes of temperature and pressure (Lesko et al., 2006). Sonochemical effect takes place either due to the pyrolytic decomposition inside the bubbles or by the reduction and oxidation due to the generation of $H^{\cdot}$ and $OH^{\cdot}$ radicals at the gas–liquid interface, and to lesser extent in bulk solution.

The production of hydroxyl radicals through cavitation can be increased by addition of ozone. The major reactions taking place are

$$O_3 + H_2O \rightarrow O_2 + 2OH^{\cdot} \quad \text{..........} (1.11)$$

$$O_3 + OH^{\cdot} \rightarrow HO_2^{\cdot} + O_2 \quad \text{..........} (1.12)$$

$$O_3 + HO_2^{\cdot} \rightarrow 2O_2 + OH^{\cdot} \quad \text{..........} (1.13)$$

$$HO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + O_2 \quad \text{..........} (1.14)$$

1.5.9 H_2O_2/US Process

Combined use of H_2O_2 and ultrasound results in the formation of free radicals in gaseous phase of the cavitation bubbles which is formed during ultrasound sonication. The following are the major reactions taking place in the presence ultrasound radiation

$$H_2O_2 +))) \rightarrow 2OH^{\bullet} \tag{1.15}$$

$$H_2O_2 + O_2 +))) \rightarrow 2HO_2^{\bullet} \tag{1.16}$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \tag{1.17}$$

Addition of UV along with this process enhances the formation of free radicals.

1.5.10 Electrochemical Oxidation

In this process electrical energy is acting as a vector for the degradation of pollutants. The reactions taking place are

Anode reactions

$$H_2O \rightarrow H^+ + OH^{\bullet} + e^- \tag{1.18}$$

$$OH^{\bullet} \rightarrow O + H^+ + e^- \tag{1.19}$$

$$O + O_2 \rightarrow O_3 \tag{1.20}$$

Cathode reactions

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1.21}$$

The efficiency of this process depends on many factors. But the choice of electrode plays a major role (Chen et al., 2007).

1.5.11 Electro-Fenton Process

This process has the combined advantage of electrochemical and Fenton processes. The disadvantages of Fe^{3+} formation can be decreased by cathodical reduction of Fe^{3+} to Fe^{2+}. The fast generation of Fe^{2+} accelerates the production of hydroxyl radical (Priambodo et al., 2011).

In the electro-Fenton process, H_2O_2 is formed by the reduction of the dissolved oxygen on the cathode surface. H_2O_2 can then react with Fe^{2+} to produce OH· (Fenton's reaction)

Cathode reactions

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad \text{.........}(1.22)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^- \quad \text{.........}(1.23)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad \text{.........}(1.24)$$

Overall reaction is

$$O_2 + 3H^+ + 3e^- \rightarrow H_2O + OH^{\cdot} \quad \text{.........}(1.25)$$

In the anodic compartment, the reaction that takes place is simply the oxidation of water

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \quad \text{.........}(1.26)$$

1.5.12 E-Beam, Gamma and Other Ionising Radiations

E-beam utilises the ionising radiations from an electron beam to initiate the chemical changes in the pollutants in aqueous solutions. The energy of the electron beam is so high to make chemical changes but is too low to create radioactivity. The energy emitted by the electron beam is absorbed almost completely by the target compound's orbit electrons which will result in increasing the energy level of the electrons. The electrons from an electron accelerator react with water molecules to form reactive intermediates, such as hydroxyl radicals, hydrated electrons, and hydrogen atoms.

The net reaction is shown below:

H_2O + ^^^ ® 2.7 •OH + 0.6 •H + 2.6 e_{aq}- + 0.45 H_2 + 0.7 H_2O_2 + 2.6 H_3O^+ ..(1.27)

The combination of products that result from this reaction creates a unique environment where oxidizing and reducing reactions occur simultaneously (Nickelson et al., 1992; Allen, 1996).

Gamma radiation can split water to generate hydroxyl radical and other radicals such as peroxide radicals ($HO_2^{\cdot}$), ions such as hydronium ion (H_3O^+), hydrogen ion (H^+) etc. Gamma radiation is very-high-energy ionising radiation originating in the nucleus of the atom and produced following spontaneous decay of radioactive materials, such as cobalt-60 and cesium-137 (Emmi et al., 2008).

1.5.13 Microwaves

Microwaves can be used to decompose non-degradable materials from wastes. It was found that the significant enhancement of thermally driven chemical reactions is possible by use of microwave irradiation. The essential features of microwave effects have yet to be clarified and fully understood. Hence, additional investigations are necessary to clarify how microwaves interact with reacting substrates as they may be relevant in applications to environmental remediation processes (Serpone et al., 2010).

1.5.14 Heterogeneous Photocatalysis

Photocatalysis has been widely used for the removal of pollutants from aqueous solutions. It is based on semiconductor photochemistry. Titanium dioxide is the commonly used effective catalyst for this purpose. It is non-toxic, relatively inexpensive, chemically stable and widely available. When Titania is irradiated by UV light having sufficient energy to displace the electrons in valence band to conduction band, a electron-hole pair results.

Different mechanisms are suggested for the photocatalytic oxidation of organic compounds. The adsorption of the pollutant on the surface of the catalyst is considered to be the initial step of the process which is followed by direct subtraction of the pollutant's electrons by positively charged holes. Oxidation of pollutants by hydroxyl generated from water of the aqueous environment is another way of pollutant removal. Both reactions may proceed simultaneously and which mechanism dominates depends on the chemical and adsorption properties of the pollutant (Fujishima at al., 2000). The reaction mechanism can be represented as

$$TiO_2 + h\nu \rightarrow TiO_2(h^+ + e^{-)} \quad \text{...} (1.28)$$

$$TiO_2h^+ + (OH^-) \rightarrow TiO_2 + OH^\bullet \quad \text{..} (1.29)$$

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^- \quad \text{..} (1.30)$$

1.5.15 Photocatalytic Ozonation

Titanium oxide is used in presence of ozone under UV light. The mechanism suggested by Tanaka et al. (1996) is as follows

$$TiO_2 + h\nu \rightarrow TiO_2(h^+ + e^-) \qquad (1.31)$$

$$e^- + O_3 \rightarrow O_3^- \qquad (1.32)$$

$$O_3^- \rightarrow O_2 + O^- \qquad (1.33)$$

$$O^- + H_2O \rightarrow OH^- + OH^\bullet \qquad (1.34)$$

$$OH^- + h^+ \rightarrow OH^\bullet \qquad (1.35)$$

1.5.16 Wet Air Oxidation

In wet air oxidation (WAO), oxidation by dissolved oxygen is utilized for removing soluble and suspended organic materials from water. It is a liquid phase reaction in which water plays an important role. Water provides a medium for dissolved oxygen to react and also take part in the removal of pollutants by hydrolyzing it. The oxidation is considered to be a free radical reaction and can be catalyzed using homogeneous or heterogeneous catalysts. The reactions take place at temperatures of 150° to 320°C and pressures of 150 to 3200 psia (Lin et al., 1996).

The WAO process can be used to convert organic compounds containing carbon, hydrogen, and oxygen into carbon dioxide, water, and short-chain biodegradable compounds such as acetic acid and formaldehyde. But the mineralisation efficiency is not as high. For complete mineralization high temperature or catalytic converters are to be employed.

1.6 Scope of the Study

The pollution of ground and surface waters by wastewater containing pesticides and other persistent organic pollutants (POPs) is becoming a threat to the man, material and environment. It cannot be treated effectively with biological treatment systems. Treatment scheme utilising AOPs can handle these pollutants effectively by converting them to CO_2 and water or to biodegradable compounds.

Acetamiprid, a neonicotinoid insecticide is a widely used insecticide for controlling pests on vegetables, fruits, pet animals etc. Its use is increasing widely because of its ability to attack the pests selectively. It has high water solubility and hence has potential to pollute water bodies. Despite its extended use its removal from wastewater has been less frequently studied. Even though some reports are available on the removal of this compound from aqueous solution at a low concentration (5 mg/L or less) using Fenton and photocatalysis, removal at higher concentrations are seldom investigated. This study investigates in detail the suited AOPs for the removal of this compound from wastewater (as high as 50 mg/L) and the optimisation of the processes by Response Surface Methodology (RSM).

1.7 Objectives of the Study

The main objective of this study was to identify and optimise the suited AOPs for the removal of acetamiprid from wastewater. All experiments were aimed at the complete removal of acetamiprid and degree of mineralisation of these processes were also analysed. AOPs processes viz.: - Fenton process, UV treatment, UV /H_2O_2 process, photo-Fenton process and photocatalysis using TiO_2 are selected for the study based on the literature survey (Badawy et al., 2006; Cao et al., 2008; Khan et al., 2010) and the preliminary experiments conducted. Following investigations were carried out in order to achieve the objective. All the experiments were designed according to Central Composite design (CCD) of Response Surface Methodology (RSM).

- Determination of the effect of operating parameters such as H_2O_2 dosage, Fe^{2+} dosage on the removal of acetamiprid by Fenton oxidation
- Determination of the effect of pH on the removal of acetamiprid by UV treatment
- Determination of the effect of pH, H_2O_2 dosage on the removal of acetamiprid by UV/H_2O_2 process.
- Determination of the effect of operating parameters such as H_2O_2 dosage, Fe^{2+} dosage on the removal of acetamiprid by photo-Fenton process
- Synthesis of undoped, Cu doped and Fe doped TiO_2 by sol gel method
- Determination of the effect of operating parameters such catalyst loading on the removal of acetamiprid by TiO_2 photocatalysis
- Determination of the effect of Cu and Fe doping on the activity of TiO_2 for removal of acetamiprid from wastewater
- Development of regression models for predicting acetamiprid removal and TOC removal by the selected AOPs

- Optimisation of the operating parameters for the above processes by Response optimiser
- Determination of kinetic parameters such as rate constant and half life period for the selected processes.
- Comparison of the selected processes based on rate of removal and operating cost.
- Development of a kinetic model for photo-Fenton process using batch reactor data and kinetic data available in literature

1.8 Organisation of the Thesis

The thesis is divided into five Chapters. In chapter 1 statement of research problem and objectives are introduced. Chapter 2 gives an up-to-date literature review in the areas related to the research in the thesis. Methodology of the experiments and the details of various methods of analysis are given in Chapter 3. The results of the experiments are reported in chapter 4. A detailed discussion of the results and kinetic modeling details of the photo-Fenton process are included in the chapter 4. Chapter 5 summarises the study and gives the concluding remarks. List of references is given at the end.

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Chapter 2

Literature Review

Contents

2.1 Introduction

Pollution of water resources by pollutants such as pesticides is a threat to the modern life practice. Effluents from pesticide manufacturing industries contain pesticides at higher concentration. They pose problems because of their toxicity, recalcitrant nature, acute and chronic health effects. The common choice of biological treatment plant is less effective in handling these persistent pollutants.

2.2 Pesticides: - Uses and Impacts

Pesticides are substances or a mixture of substances intended to kill the pests. The target pests can include weeds, insects, microbes, fish, mammals etc. Pesticides are generally classified into four categories depending on the use; insecticides, herbicides, fungicides and bactericides. The use of it includes killing mosquitoes, invasive weeds, illness causing parasites and fleas, controlling algae and weeds, managing rodents and insects in grocery shops and houses. Agricultural workers have been using synthetic pesticides widely because of its wide availability, simplicity in application and economic returns. Pesticides are targeting the pests, but about 98% of the pesticides reach a destination other than the target species in addition to reaching the water, air and soil resulting in undesired effects (Hurley et al., 1998). Pesticides reach the people which do not use it directly, when large amount of pesticides are washed into streams, lakes, rivers etc. The intensive use of pesticides raises a serious environmental concern. The development of pesticide resistance was observed in important pests due to excessive and indiscriminate use of pesticides (Jayaraj, 1989)

Most of the pesticides belong to the class of persistent organic pollutants (POPs). They have long life span, do not biodegrade easily and accumulate in the tissues of living organisms.

The extent of biomagnification and their transport in food chain is again proved by the presence of residues of DDT and benzene-hexachloride, suspected carcinogens, in the breast milk samples collected from mothers in Punjab. The amount of residue was very high and babies were ingesting 21 times the amount of these chemicals considered acceptable through their mother’s milk (Jumanah, 1994). One study conducted by Centre for Environment and Science, New Delhi revealed alarming levels of pesticides in the blood samples collected from villagers of Punjab (Mathur, 2010).

2.2.1 Health Effects of Pesticides

The effects of pesticides on man and environment have been a topic of discussion in the last decades. Studies revealed a positive association of pesticide use for different types of cancers found in human (Jeyaretnam, 1990). Neurological, reproductive and genotoxic effects of pesticides are also been reported (Sanborn et al., 2007). Immunosuppressive nature of pesticides is a threat to the population exposed to infectious diseases (Xavier et al., 2004).

Prolonged exposure to pesticides can cause kidney and liver disorders (Azmi et al., 2006). Mimicking or blocking of hormones by certain pesticides are also been identified. Some pesticides can trigger inappropriate hormone activity. Endocrine disrupting activity of a large number of pesticides is also reported (McKinlay et al., 2008). A study conducted by Grace Chitra et al. (2005) among farmers revealed that chronic diseases like hypertension, diabetes, asthma, ophthalmic disorders are common in those who are exposed to pesticides.

2.2.2 Effects on Ecosystem

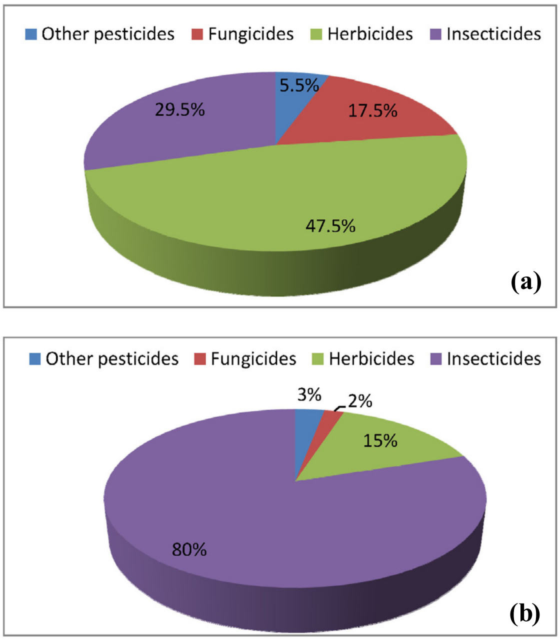
Adverse effects of pesticides on the aquatic as well as terrestrial ecosystems are a matter of concern. Pesticides destroy the habitats of birds in addition to causing health effects. The famous book “The silent spring” by Rachel Carson depicts the effect of accumulation of DDT in the bird’s tissue. Reduction of population of insect eating birds such as pheasants, grouse and partridges are reported due to reduction of their food because of insecticide use. Palmer et al. (2007) reported the reduction of earthworms due to the pesticide use which will result in the reduction of birds and mammals that feed on them.

Aquatic lives are susceptible to pesticide pollution very badly since the pesticides residues in soil and air finally reaches the water bodies through runoff. Pesticide use is one of the main reasons of disappearance of many rare species of fish and other aquatic species. Many of them kills fishes, turtles, frogs, water birds and other wildlife.

Pesticides reduce nitrogen fixation reducing crop yield which is essential for the growth of higher plants. Pesticides also kill pollinator bees which may also result in colony collapse disorders (Wells, 2007).

2.3 Pesticide Consumption in India and World Wide

The world wide consumption of pesticides is about 2 million tonnes per year: Europe contributes 45 %, 25% by USA and 25 % by rest of the world. India’s share is 3.75%. DDT and malathion are still continuing as the top most consuming pesticides despite development of new pesticides. Of the total consumption herbicides share is 47.5%, insecticides 29.5%, fungicides 17.5% and other pesticides contributes 5.5% (Fig 2.1).



(Source: De et al., 2014)

Fig. 2.1 a) Worldwide consumption of pesticide
b) Pesticide consumption in India

India ranks second in the manufacture of pesticides in Asia and ranks twelfth globally (Mathur, 2010). The production capacity of pesticides in India is more than 1,39,000 metric tons annually with more than 219 technical grade/ manufacturing units and over 4000 formulation units (Directorate of plant protection, quarantine and storage –Government of India, 2014). However the usage of pesticides in India is only 0.5 kg/ha compared to 6.6 kg/ha in Korea and 12 kg/ha in Japan. In India cotton cultivation is the major consumer of pesticides and contributes 37% followed by rice at 20%.

Even though the pesticide consumption in India is low compared to the developed countries, the reports on environmental pollution due to pesticides are alarming.

2.4 Treatment Options for Pesticide Removal from Wastewater

The methods employed for any wastewater treatment depends on the type and concentration of the compound present and the level of pollutants allowed in the discharge. The methods can be destructive such as chemical oxidation, incineration or non-destructive such as coagulation, adsorption. The choice also depends on the cost of the treatment and the volume of wastewater to be treated. Basic treatment techniques such as flocculation/ coagulation, chemical precipitation biological oxidation are also used for the removal of certain pesticides.

Removal of fine particles and colloids by flocculation and coagulation is often practiced in the conventional waste water treatment plants. They remove inorganic as well as organic matter. They can also be used to remove pesticides to certain extent.

Misra et al. (2013) reported the use of coagulation using alum, $FeSO_4$ and polyaluminium chloride for the treatment of pesticide in wastewater. Removal using adsorbents such as activated carbon prepared from different sources (Erol et al., 2005; Ourania et al., 2010; Gupta et al., 2011) and modified polymeric materials (Kyriakopoulosa et al., 2005) are also been reported. Removal of methyl parathion using water melon peel was reported by Zuhra et al. (2008).

The above methods produces large amount of wastes and results only in recuperation of the pollutants. The methods like incineration are effective only at very high concentrations and have high capital and operating costs.

AOPs are commonly used for the removal of pesticides as complete mineralisation could be achieved.

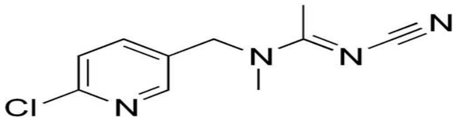
2.5 Acetamiprid- Uses and Impacts

Acetamiprid is a member of neonicotinoid insecticide family. Neonicotinoids are relatively new class of insecticide. They represent a class of fastest growing insecticide covering 17% of global pesticide market (Jeschke et al., 2008). Acetamiprid is highly efficient in controlling insects such as aphids, whiteflies, moth, leafhopper etc. (Mateu-Sanchez et al., 2003; Tomizawa et al., 2003). It is widely used against insects on leafy vegetables, fruiting vegetables, cole crops, citrus fruits, pome fruits, grapes, cotton and ornamental plants and flowers. They have unique selective nervous attacking mechanism and because of their efficacy they are recommended as an alternative to highly hazardous organophosphorous pesticides which are being banned in many countries (US Environmental Protection Agency, 2002).

In India, Central Insecticides Board and Registration Committee (CIBRC) recommends the use of acetamiprid on cotton. It is now being used on vegetables, fruits and ornamental flowers also. Its demand increased from 33 MT in 2006 to 65 MT in 2010.

Acetamiprid is not readily biodegradable and it is soluble in most organic solvents. Its water solubility is fairly high (2.95 g/L at pH 7, 25^0C) and hence has the potential to pollute ground and surface water. Its solubility is more in acidic and alkaline conditions. It shows no photodegradation in the dark and very low photolytic rate in sunlight (European commission-2004). Because of its widespread use it is increasingly present in the environment (Guzsvány et al., 2009). Acetamiprid is classified as toxicity category rating II in acute oral studies with rats. Structure and important physical properties of acteamiprid is given in table 2.1.

Table 2.1 Properties of acetamiprid

Common Name	Acetamiprid
Name (IUPAC):	(E)-N-[(6-chloro-3-pyridyl)methyl]-N-cyano-N-methyl acetamidine
Molecular Formula	$C_{10}H_{11}ClN_4$
Structure	
Molecular Weight	222.68
CAS	135410-20-7
Pesticide Type	Insecticide
Chemical Family	Neonicotinoid insecticide
Application Sites	Control of sucking-type insects on leafy vegetables, fruiting vegetables, cole crops, citrus fruits, pome fruits, grapes, cotton, and ornamental plants and flowers
Method of Application	Ground and aerial application using standard commercial sprayers
Application Rates	Application rates a maximum of 0.55 pounds active ingredient per acre per season.
Carrier	Water
Physical characteristics	
Physical State	Solid, Powder
Color	white powder
Odor	Odorless
Melting Point	98.9 $^{\circ}$C
Solubility in Water	2.95 x 10^{+3} mg/L at pH 7, $25^{\circ C}$
Vapor Pressure	1 x 10^{-8} mm Hg
pKa	0.7 @25^{0}C

2.6 Advanced Oxidation Processes

Advanced Oxidation Processes (AOPs) are a class of oxidation techniques in which hydroxyl radicals are produced by different methods and utilised for pollutant removal. AOPs are recommended when wastewater contains compounds of high chemical stability and/or low biodegradability. AOPs are considered to be efficient enough to mineralise the pollutants completely to CO_2 and water. But in practice 100% mineralisation is rarely achieved. The mechanism of AOPs selected for study and their applications reported in the literature are given below

2.6.1 Fenton Process

Fenton is one of the oldest and simplest AOPs used so far. It does not require any sophisticated set up and can be applied at room temperature. It uses hydrogen peroxide as oxidant and iron as catalyst.

The reaction, famously known as Fenton reaction after it's inventor J.H Fenton in 1894 is

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.1)$$

Fe^{3+} formed by the reaction 2.1 will react with H_2O_2 again known as Fenton like reaction

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.2)$$

It is reported in the literature that the Fenton-like reaction is much slower than the Fenton reaction.

The other possible reactions reported are (Chamarro et al., 2001; Neyens and Baeyens, 2003)

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{-} \quad \text{...}(2.3)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+} \quad \text{..}(2.4)$$

The hydroxyl radicals formed will react with organics (RH) by abstraction of protons producing organic radicals ($R^{\bullet}$) which are highly reactive and can be further oxidised. Hydroxyl radicals can also add to the aromatic or heterocyclic rings.

The requirement of acidic pH and formation of iron sludge are the two main drawbacks of this process. pH, H_2O_2 dosage and iron dosage are the main factors affecting the efficiency of the process (Gogate and Pandit, 2004; Stansinakis, 2008).

The optimum pH of the process is reported as 2.8-3 (Alaton et al., 2008; Chitra et al., 2012). At higher pH (>4) iron precipitates as iron hydroxide (Badawy et al., 2006), which lowers the concentration of free soluble iron for reacting with peroxide. At very low pH (<2), the peroxide gets solvated in the presence of high concentration of H^+ ions to form stable $[H_3O_2]^+$ ions. In addition to that less reactive $[Fe(H_2O)_6]^{2+}$ is also formed (Kavitha et al., 2005).

The optimum use of H_2O_2 and Fe^{2+} is very important since excess dosage can result in scavenging of the hydroxyl radicals formed, as per the following equations

$$H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad \text{.............................}(2.5)$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \quad \text{.............................}(2.6)$$

Walling (1975), simplified the overall Fenton chemistry as

$$2Fe^{2+} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{3+} + 2H_2O \quad \text{.....................}(2.7)$$

The above reaction accounts for the dissociation of water also. The equation suggests the need for acidic environment (H^+) for the reaction.

Fenton process has been extensively used for the removal of COD, TOC, dyes, pigments, phenolic compounds etc. (Walling and Goosen, 1973; Sheng and Cho, 1997; Kang and Hwang, 2000; Chamarro et al., 2001)

Conventional oxidation treatments have found difficulty to oxidise highly coloured effluents from textile industries containing dyestuffs and complex structure organic compounds at low concentration or if they are especially refractory to the oxidants. Fenton oxidation was effectively utilised for the treatment of these compounds (Dae-Hee et al., 1999; Ledakowicz et al., 2001; Al-Kdasi et al., 2004).

Utilisation of the process for the treatment of desizing wastewater containing less than 0.2% Poly vinyl alcohol (PVA) and blue G (a direct dye) or Black B (a reactive dye) was reported by Sheng and Cho (1997). An optimal pH of 3 and temperature of 30^0C was reported. Two step Fenton process intended for chemical coagulation followed oxidation was also investigated by them. Szpyrkowicz et al. (2001) used Fenton process for the oxidation of disperse dyes (disperse red 74, disperse blue 139, and disperse yellow 126). The best treatment results were obtained for Fenton process at optimal pH of 3 and hydrogen peroxide and ferrous sulphide dose of 600 and 550 mgdm-^{3}. 95% colour removal within 5 minutes for textile wastewater was obtained by Fenton process containing PVA and reactive dyestuff R9H under low dosage of hydrogen peroxide and ferrous iron (Kang et al., 2002a)

Effective utilisation of Fenton process was reported for the degradation of azodyes (Tantak and Chaudhari, 2006), azoic dyes (Faouzi et al., 2006), reactive orange 113 (Gutowska et al., 2007), acid dyes (Alaton et al., 2008). All these studies revealed that the dosage of H_2O_2 and Fe^{2+} depends on the target compound and the optimum pH is 3 irrespective of the target.

Application of Fenton process was also reported for a wide variety of wastewater such as oil recovery industry wastewater (Dincer et al., 2008), landfill leachate (Petruzzelli et al., 2007), natural gas plant wastewater (Omar et al., 2010), combined industrial wastewater containing phenolic compounds, cyanides and organics (Mandal et al., 2010).

The use of this process was also reported for the degradation of specific compounds such as phenols, cresols, EDTA, etc.

Destruction of cresols by Fenton oxidation was reported by Kavitha and Palanivelu (2005). The optimal reacting conditions were $[H_2O_2] = 31.64$ mM, $[Fe^{2+}] = 0.90$ mM for o- and p-cresol and 0.72 mM for m-cresol at pH 3.0. The degradation efficiency was as high as 82% within 120 min at optimal conditions. Phenol degradation in the presence of chlorides and sulphates by

Fenton oxidation was reported by Siedlecka et al. (2005). Fenton oxidation was used for the degradation of EDTA and novel complexing agents in paper mill process and waste water by Pirkanniemi et al. (2007). Over 90% degradation of EDTA within 3 min was reported when temperature was 60 ^{0}C, pH 4 and molecular ratio of H_2O_2:Fe^{2+}: EDTA of 70:2:1 or higher. Zoh and Senstrom (1999) investigated the Fenton oxidation of high explosive RDX and HMX in aqueous solution. They reported rapid degradation of RDX and HMX between 20 and 50 ^{0}C and 90% degradation of RDX in 70 min at 25 ^{0}C. Fenton's oxidation of 2,4,6 trichlorophenol (TCP) was reported by Farrokhi et al. (2004). More than 99% of TCP was degraded in 10 minutes with an initial concentration of TCP 0.60 mM, at pH=3, H_2O_2=1.8mM, Fe^{2+}=0.6 mM.

Removal by Fenton process has been reported for different class of pesticides. Removal of organophosphorous pesticides (fenitrothion, diazinone and profenfos) by Fenton oxidation was reported by Badawy et al. (2006). The optimum conditions obtained for the best degradation were pH=3, COD: H_2O_2=4.4:1, H_2O_2: Fe^{2+} ratio =100:1. Li et al. (2009) used the Fenton reagent for the removal of triazophos from wastewater. They could obtain a COD removal of 96.3 % at optimum conditions of pH -4, 2.5 g/L $FeSO_4.7H_2O$, 100 mL/L 30 % H_2O_2 and a stirring time of 90 min. Oxidation of the acetamiprid in water samples by Fenton process was reported by Mistika et al. (2013).

The main future challenges for using this process in the wastewater treatment could be the adoption of strategies for process integration, the targeting of new classes of pollutants and the commercialisation of processes which have been so far used in the laboratory (Pignatello et al., 2006).

2.6.2 UV Treatment

This method of pollutant removal is based on supplying energy to the chemical compounds as radiation. The compounds will absorb the radiation passing to excited state promoting reactions (Legrini et al., 1993). Degradation can happen either by direct photolysis or indirect photolysis.

Effectiveness of UV treatment for the removal of 41 pharmaceuticals from real wastewater was investigated by Kim et al. (2000). Good removal was obtained only for some of the pharmaceuticals such as ketoprofen, diclofenac and antipyrine. Esplugas et al. (2002) used this method for phenol degradation. The best results were obtained at free pH. Benitez et al. (2002) investigated the use of UV for the degradation of carbofuran.

The efficiency and applicability of this process depends on the stability (structure) of the compound to be removed, pH of the system and the nature of light source used.

2.6.3 UV / H_2O_2 Process

When H_2O_2 is used in presence of UV, hydroxyl radicals are formed by the photolysis of H_2O_2.The oxidation of organics can occur by either direct photolysis or reaction with hydroxyl radicals (Ray et al., 2004; Poyatos et al., 2010).

The suggested mechanism of the reactions is as follows

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \quad \text{......}(2.8)$$

$$H_2O_2 + OH^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad \text{......}(2.9)$$

$$H_2O_2 + HO_2^{\bullet} \rightarrow OH^{\bullet} + H_2O + O_2 \quad \text{......}(2.10)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad \text{......}(2.11)$$

The pH, intensity of UV light and the H_2O_2 dosage are the parameters affecting the system performance. The configuration of reactor often decides the path length. It is generally believed that an acidic condition favours UV/ H_2O_2 process as the acidic pH favours the hydroxyl radical formation. But varying reports are available about the pH dependency of the process.

The rate of photolysis of H_2O_2 (equation 2.8) is pH dependent and increase when more alkaline conditions are used (Glaze et al., 1987; Legrini et al., 1993). But at higher pH H_2O_2 auto decomposes forming water and oxygen (Tiruvenkatachari et al., 2007). Chidamabararaj et al. (2005) reported an increase in TOC reduction with increase in pH when tetrahydrofuran (THF) was degraded with UV/ H_2O_2. Saritha et al. (2007) reported highest removal of 4-chloro-2-nitrophenol at neutral pH and also that removal was more or less constant when pH was increased. It can be seen that the optimum pH for the UV/ H_2O_2 process depends on the nature of the compounds present in the water, mainly the pKa values and hydrolysis rate. So laboratory experiments are necessary for fixing the pH for the treatment.

H_2O_2 has an exceptionally low molar absorptivity within the wavelength range of 200-300 nm. Thus wasting of light by the compounds contained in the water to be treated is one of the greatest disadvantages of this method (Andreozzi et al., 1999; Poyatos et al., 2010). A UV/ H_2O_2 system can totally mineralise any organic compound, reducing it to CO_2 and water. However generally, in real life scenarios such a drastic process is not necessary (Vogelpohl, 2007).

H_2O_2 also act as a scavenger for hydroxyl radicals (equation 2.9), hence an excessive H_2O_2 dose will reduce the degradation of pollutants. At the same time, sufficient H_2O_2 is necessary so that it absorb UV to accelerate the generation of hydroxyl radicals. Hence a trade-off between them is necessary to find out the optimum H_2O_2 dosage for effective removal of pollutants.

Removal of more than 93 % naproxen, an anti-inflammatory drug was reported at a pH of 6 after a 3 min treatment using 200 W UV light (Felis et al., 2007). The initial pollutant concentration was 1.06 μg/l and the hydrogen peroxide dose was 1 mg/L.

Kroger and Fels (2007) investigated the photochemical degradation of TNT and aminodinitrotoluene (ADNT) and diaminonitrotoluene (DANT) metabolites using a xenon lamp of 150 W. They observed that the mineralization of ADNT was quicker than that of TNT itself. It was possible to achieve a conversion greater than 90% in 24 h.

Muruganandham et al. (2007) used this method for the degradation of an industrial solvent N-methyl-2-pyrolidone (NMP). They used a H_2O_2

concentration of 500 mg/L, pH of 10 with a UV radiation intensity of 5.5 mW/cm^2 and a temperature of 25^{0}C. The initial concentration of NMP in water was 1 g/L. They found that reaction was slower compared to other AOPs. This method was effectively used also for the degradation of atrazine (Beltran et al., 1993), acetone (Hernandez et al., 2002), cyanide (Sarla et al., 2004), dimethyl sulfoxide (Wu et al., 2007) and terephthalic acid (Tiruvenkatachari et al., 2007).

H_2O_2/UV system is considered to be a viable option for the removal of nonbiodegradable compounds from wastewater because of its simplicity. The only reagent required is H_2O_2 and that is available in liquid form which is readily miscible with water. In cases where the water contains materials that strongly absorb UV, this process may not be effective.

2.6.4 Photo-Fenton Process

Fenton process is one of the simplest processes and hence it is applied widely to remove recalcitrant compounds. But the formation of iron sludge often restricts its application. Separation of this sludge and its disposal will add to the cost of the treatment. Photo-Fenton process was developed with an intention to reduce this sludge formation, which uses UV or solar light for the conversion of Fe^{3+} back to Fe^{2+} resulting in a drastic reduction of the sludge waste (Poyatos et al., 2010; Chitra et al., 2012).

The degradation rate of organic compounds is significantly enhanced when UV-Visible light is added to the reaction. The main reactions involved in the process are

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \quad \text{(2.12)}$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH^{\cdot} + H^{+} \quad \text{(2.13)}$$

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \quad \text{(2.14)}$$

As the rate of the reaction is increased, the size of the reactor is also reduced in addition to the benefit of sludge reduction.

Perez et al. (2002) used photo-Fenton process for the TOC removal of textile effluents. The effect of pH, H_2O_2 and Fe^{2+} dosages, temperature and intensity of light was investigated by the authors. They could obtain more than 70 % TOC reduction at optimised conditions

Degradation of Reactive Red 45 (RR45) by photo-Fenton was reported with initial RR45 dye concentration of 80 mg/L (Peternel et al., 2007). Complete decolourisation was observed after 1 h at a range of Fe^{2+}/ H_2O_2, varying between 1:20 and 1:100. The ratio of Fe^{2+}/ H_2O_2 1:60 was found to be optimal at pH 3, a concentration of Fe^{2+} at 0.5 mM, and an incident UV-light flux at 7.36×10−6Einstein/s.

Malato et al. (2002) studied the degradation of water soluble pesticides diuron, imidacloprid, formetanate and methomyl using photo-Fenton process using solar energy. Total disappearance of parent compound and 90% mineralisation could be achieved for all the pesticides.

González et al. (2007) used this process for the total removal of the antibiotic sulfamethoxazole (SMX) from wastewater at an H_2O_2 dose of over 300 mg/L and 10 mg/L of Fe^{2+}. They could obtain a final concentration of SMX less than 1 mg/L at an H_2O_2 dose of 300 mg/L. Haseneder et al. (2007) used photo-Fenton process for the degradation of Poly Ethylene Glycol (PEG). Almost 93 % degradation of PEG was obtained after 2 hours of treatment at pH 3 and H_2O_2: Fe ratio of 10:1.

Badawy et al. (2006) compared Fenton process, UV/ H_2O_2 and photo-Fenton process for the degradation of organophosphorous pesticides from wastewater. The photo assisted Fenton process produced the highest photochemical elimination rate of pesticides. The optimum operating conditions obtained for the best degradation rate was pH =3, COD: H_2O_2 =1:2.2, H_2O_2: Fe^{2+} ratio = 50:1 using 150 W medium pressure mercury lamp.

Photo-Fenton was used by Abdessalem et al. (2010) for the treatment of a mixture of three pesticides: chlortoluron, carbofuran and bentazon. They could achieve 90 % removal of TOC after 2 hrs of treatment at optimised conditions. Chitra et al. (2012) investigated the kinetics of degradation of 1-4 dioxane by different AOPs. They observed that Fe^{2+}/H_2O_2/sunlight was found to be the fastest. Reactions were carried out at pH 3 using optimised quantity of Fe^{2+} (0.03g) for 0.1 M 1, 4 –dioxane. They observed complete degradation of 1, 4-dioxane at 5.5, 2.25, 1.75 and 8h for samples treated with UV(15W) /H_2O_2, UV (15W) /Fe^{2+}/H_2O_2, sunlight /Fe^{2+}/ H_2O_2 , Fe^{2+}/ H_2O_2 respectively.

Degradation of antibiotic sulfamonomethoxine sodium (SMMS) in aqueous solution by Photo- Fenton oxidation was investigated by JianHui et al. (2012). They could obtain 98.5% SMMS degradation at the optimised conditions.

Photo-Fenton is a suitable technique that can be applied to the removal of recalcitrant compounds from wastewater. The use of the suitable reactor is an important criterion to achieve the target of complete removal of pollutants.

2.6.5 Heterogeneous Photocatalysis

Photocatalytic oxidation of organic compounds is made possible with the use of photocatalysts such as TiO_2. Semiconductors such as SnO_2, ZnO_2 are also used as photocatalyst. But still TiO_2 remain as the first choice for the environmental applications. photocatalytic property of TiO_2 was first reported by Fujishima and Honda in 1972. They reported the photoinduced decomposition of water on TiO_2 electrodes, famously known as Honda-Fujishima effect. In 1977 Frank and Bard examined the possibility of using TiO_2 to decompose cyanide in water. Following this extensive research has been happening in the environmental applications of this effect.

TiO_2 has high reactivity and chemically stability under UV light. The band gap (gap between valence band and conduction band) in titanium dioxide is 3.3 eV. When TiO_2 is photoexcited by photons having energy greater than this band gap, an electron is promoted from valence band to conduction band (Elmolla et al., 2010). This will result in the formation of an electron-hole pair. These electron-hole pairs can recombine or migrate to the surface and react with the adsorbed species on TiO_2 surface. Variety of reactive species will be formed by this process which includes hydroxyl radical, hydrogen peroxide, single oxygen and superoxide anion radical

(Fujishima et al., 2000; Jiang et al., 2013). These principles are illustrated in the diagram below.

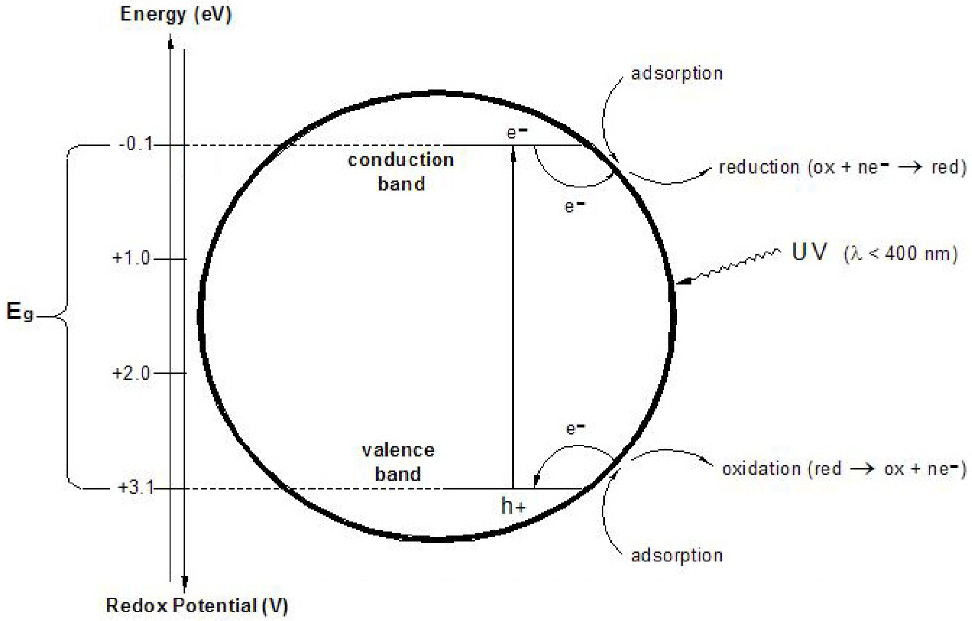


Fig. 2.2 Illustration of principles of photocatalysis showing the energy band diagram of TiO_2 spherical particles (source: Zaleska, 2008)

Among these reactive species, hydroxyl radical is generally responsible for the degradation during TiO_2 photocatalysis under UV radiation. The possible reactions taking place are

$$TiO_2 + h\nu \rightarrow TiO_2(h^+ + e^-) \quad \text{...} (2.15)$$

$$TiO_2h^+ + (OH^-) \rightarrow TiO_2 + OH^\bullet \quad \text{...} (2.16)$$

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^- \quad \text{...} (2.17)$$

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \quad \text{...} (2.18)$$

Park et al. (2001) reported the complete photocatalytic oxidation of ethylene to CO_2 and water. They also investigated the effect of presence of O_2 and H_2O and the addition of Pt on the rate of oxidation. Degradation of oxalic acid and citric acid by UV/ H_2O_2/ TiO_2 process was reported by Lee et al. (2003). They also investigated the use of H_2O_2 mediated photocatalysis for the decontamination and observed a first order reaction during the process.

Degradation of rosolic acid by photocatalysis was studied by Amat et al. (2007). They have used different solar photo catalysts such as Fe(III), Cr(III), Cr(VI), and TiO_2. The best results were obtained using Fe (III). This process was utilized for the treatment of effluent from textile industry (García et al. 2007). They used H_2O_2 along with the UV/TiO_2 system and could obtain a COD reduction levels higher than 90%. Additional advantages of this process were that it totally consumed the added peroxide and that it led to a final non-toxic residue. Treatment of textile effluent by photoctalysis was also reported by Riga et al. (2007).

Abdennaouri et al. (2007) used photocatalytic process for the degradation of pesticides by titanium dioxide prepared by sol-gel process and titanium pillared purified clays. The results of the study indicated that the process is efficient for removal of pesticides.

Photocatalytic degradation of acetamiprid, was studied by Guzsvány et al. (2009). It was found that the reaction in the investigated concentration range (0.5-2.0 mg cm^{-3}) is of a pseudo-first order and beside acetaldehyde, formic and acetic acid, pyridine-containing intermediates (e.g. 6-chloronicotinic acid) formed during the process. Khan et al. (2010) reported the use of TiO_2 photocatalysis for the removal of acetamiprid from waste water. They have compared different grades of TiO_2 and found that the commercially available Degussa P25 is superior to others.

Photocatalytic degradation of amoxicillin, ampicillin and cloxacillin antibiotics was investigated by Elmolla et al. (2010) using TiO_2 catalysts under UVA (365 nm) irradiation. Addition of H_2O_2 at pH 5 and TiO_2 1.0 g/L resulted in complete degradation of amoxicillin, ampicillin and cloxacillin in 30 min.

Bernabeu et al. (2011) reported the use of solar photocatalysis as tertiary treatment for the removal of nine emerging pollutants from wastewater treatment plant effluents. They could obtain significant removal of these pollutants and the faecal bacteria elimination was close to 100%.

2.6.6 TiO_2 Preparation Methods, Modification by Doping and Applications

The photocatalytic activity of TiO_2 depends on its ability to absorb photons producing electron-hole pairs. This electron-hole pairs should be used effectively without causing recombination. The surface area of TiO_2 plays a very important role in this. Use of nanosized TiO_2 is found to be very effective as it has high surface area. Doping of TiO_2 with metal and non-metal ions is also found to be effective in increasing the photocatalytic activity of TiO_2 by reducing the recombination of electron-hole pair. Most of them reduces the band gap of the TiO_2 extending its application to visible region.

Various methods are available for the preparation of ultra-fine TiO_2 based photocatalysts.

The methods include electrochemical (Karuppuchamy et al., 2009), thin films and spin coating (Cheng et al., 1998; Patil et al., 2003), dip coating (Kluson et al., 2006), thermal (Zhu et al., 2006), solvothermal (Li and Gray, 2007), chemical vapour decomposition (Ghorai et al., 2007), sol-gel, modified sol-gel (Chandraboss et al., 2013) etc. Of these sol-gel method has the advantages of preparation of high purity nano sized titania at relatively low temperature, possibility of stochiometry controlling process etc. (Zhang et al., 2004a).

So-gel is one of the most exploited methods. It has been widely used for the preparation of powdered and thin film photocatalysts.

Gombac et al. (2007) prepared TiO_2 co-doped with boron and nitrogen by sol-gel method. The prepared photocatalyst was used for the degradation of methyl orange and found to be effective. Cu-doped TiO_2 was prepared by sol-gel method and was used for the degradation of Rhodamine-B under UV light (Xin et al., 2008). The researchers could obtain about 10 % increase in the removal over undoped TiO_2 and also observed that when Cu concentration increased above 0.06 mol %, it was detrimental.

Colmenares et al. (2006) prepared TiO_2 doped with transition metals viz., Ag, Fe Pd, Pt, Zn, Zr at extremely low temperature by sol-gel method. The photocatalytic activity of the prepared samples were analysed by using it for the selective oxidation of 2-propanol. Pd, Pt and Ag doped TiO_2 gave better results under UV light. Rengaraj and Li (2006) used the Ag doped TiO_2 prepared by ultrasonic assisted sol-gel method for the degradation of bisphenol A. They could obtain 100 % degradation with 2 hr UV irradiation.

Xu et al. (2002) prepared TiO_2 doped with rare earth elements such as La^{3+}, Ce^{3+}, Er^{3+}, Pr^{3+}, Gd^{3+}, Nd^{3+}, Sm^{3+}. The photocatalytic activity was evaluated by using it for the nitrite degradation under UV light. TiO_2 doped with 0.5 % Gd^{3+} gave better performance than commercially available Degussa P25 at 60 min irradiation. TiO_2 doped with lanthanides was prepared by Saif and Abdel-Mottaleb (2007) and used it for the degradation of Remazol Red RB-133dye under UV light. All doped TiO_2 samples showed better performance than undoped TiO_2. Effect of alkaline earth metal doping on the phtocatalytic activity of TiO_2 was studied by Li et al. (2007). Be, Ca, Mg, Sr and Ba doped TiO_2 were prepared by sol-gel method and used for the production of hydrogen. Be- TiO_2 at 1.25 % gave the best results.

Reports on doping of TiO_2 with non metals such as vanadium and boron (Bettinelli et al., 2007), nitrogen (Yu et al., 2007; Gomabac et al., 2007) are also available. The researchers observed that doping method is influencing the phtotocatalytic activity.

Rengaraj and Li (2007) used Bi^{3+} doped TiO_2 for the degradation of methyl parathion and found that at optimum dopant level of 1.5 % complete degradation was obtained within 90 min.

In general it is reported that doping enhances the photocatalytic activity of TiO_2. A detailed investigation is necessary to fix the type of dopant, optimum concentration, applicability etc.

2.6.7 UV Systems

UV light has wavelength less than that of visible light and greater than that of X-ray. Because of its high energy it can destroy the organic contaminants in water. The degradation can happen either by direct photolysis or indirect photolysis. The commonly used UV sources are Low pressure mercury vapour lamps (LP-UV), Medium Pressure Mercury Vapour lamps (MP-UV) and pulsed –UV Xenon arc lamps P-UV). Characteristics of UV sources are given in Table 2.2

Table 2.2 Characteristics of typical Low Pressure (LP), Medium pressure (MP) and Pulsed UV-lamps (P-UV)

Characteristics	Low Pressure	Medium Pressure	Pulsed-UV
Emission	Monichromatic (85-90% at 253.7 nm)	Polychromatic (185-1,367 nm)	Polychromatic (185-1,000 nm)
Peak output wavelength (nm)	253.7	200-400	~ 450
Mercury vapour pressure (torr)	10^{-3} to 10^{-7}	10^{2} to 10^{4}	N/A
Operating temperature	40 to 60 ^{0}C	500 to 800 ^{0}C	~15000 ^{0}C
Arc length (cm)	40 to 75	5 to 195	15
Lifetime	8,000 to 10,000 hrs	2,000 to 5,000 hrs	>100x10^{8} pulses
Light intensity (relative)	Low	High	High

(Source: Sunil Kommineni et al., 2002)

For most of the applications LP-UV and MP-UV lamps are used. MP-UV lamps produce outputs over a wider range of wavelengths

(200-400nm) compared to LP-UV lamps. If H_2O_2 is used in association with UV, use of MP-UV lamps helps in the formation of more hydroxyl radicals as H_2O_2 absorbs more in the lower wavelengths (Glaze et al., 1987). Furthermore, MP-UV systems requires less number of lamps, less space, less maintenance compared to LP-UV lamps even though LP-UV lamps are more electrically efficient.

The removal efficiency of UV lamps is expressed in Electrical energy per order of removal (EE/O). It is defined as the kilowatt-hours (kWh) of electricity required to reduce the concentration of target compound by one order of magnitude (or 90 percent) in 1000 m^3, which can be expressed as (Saritha et al., 2007)

$$EE/O(kWh/m^3) = \frac{P \times t \times 1000}{V \times 60 \times log(C_{init}/C_{fin})} \quad \text{..................}(2.19)$$

where, P is rated power (kW), t is the time (min), V is the volume (Litres), C_{init} and C_{fin} are initial and final concentration of the compound to be treated.

For designing a UV system for AOP treatment, two major variables are to be taken care of. First one is the UV power radiation required per unit volume of water to be treated and the second one is the dosage of oxidizer (H_2O_2, O_3 etc). The first one is defined by the term UV dosage and is a measure of total lamp electrical energy required for fixed volume of water which is expressed as

$$\text{UV dose (kWh/m}^3\text{)} = \frac{1000 \times P \times t}{V \times 60} \quad \text{..}(2.20)$$

where, P is rated power (kW), t is the time (min) and V is the volume (litres)

2.6.8 Kinetic Modeling

Understanding the kinetics of the reactions happening in the processes is necessary to design a suitable system for the removal of pollutants using AOPs. Eventhough a lot of research is happening in this area, commercialisation of the technology is less. One thing that can be done to improve the commercialisation of the process is automatisation of the operation. For that it should be possible to predict the outcome of the processes i.e., it should be possible to predict the treatment time required, reagents required, extent of removal etc. in advance.

Different approaches are used by the researchers for this. The simplest method is use of pseudo-steady state assumption for predicting the performance. The pseudo-first first order model generally gives a prediction with sufficient fit (Glaze et al., 1995). Another method is to describe the process by using all the elementary reactions and the knowledge of the intermediate composition mixtures (Kang et al., 2002b; Kusic et al., 2009). An another alternative is to use empirical modeling using regression where response surface methods and design of experiments can be made use of (Perez-Moya et al., 2008). Even more sophisticated methods based on computational fluid dynamics have been tested for the design of photochemical reactors (Alpert et al., 2010; Mohajerani et al., 2012). Development of kinetic models for Fenton and photo-Fenton process using known kinetic pathways and reaction rate data are also reported (Cabrera Reina et al., 2012; Carra et al., 2014).

In the present study a pseudo-first order model was used for comparing the process performance of various AOPs. An attempt was also made to develop a kinetic model for photo-Fenton process using experimental data and the kinetic data reported in the literature.

2.7 Summary

This chapter has presented the problems associated with the use of various pesticides and the uses and impacts of acetamiprid in detail. A detailed literature survey in the area of selected processes viz., Fenton process, UV treatment, UV/H_2O_2 process, photo-Fenton process and TiO_2 photocatalysis has also been presented. The various researches on the preparation methods and applications of doped TiO_2 and the important UV systems employed in the area of AOPs are also been discussed.

The different approaches used for kinetic modeling of the processes are also discussed in this chapter. The extensive researches in the last decades in the application of AOPs in the area of wastewater treatment proved that it is a viable option for the removal of recalcitrant compounds from wastewater. AOPs has a history of success where biological treatment fails. Next chapter gives the methodology adopted for the present study.

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Chapter 3

Materials and Methods

3.1 Introduction

Advanced oxidation process (AOP) is a class of oxidation techniques where oxidation by hydroxyl radicals is employed and there are a large number of methods for producing hydroxyl radicals. The AOPs selected should be capable of removing the pollutant to below the permissible limit and at low cost.

3.2 Selection of Model Compound for Study

Pollution of surface and ground water sources with pesticides has become the most discussed environmental issue at present.

Neonicotinoid insecticides are relatively a new class of insecticides. Because of the stringent environmental legislations and adverse effect of human and aquatic health, organophosphorous pesticides are now being replaced by neonicotinoids. Neonicotinoids are selective and attack nervous systems of target species. Because of this, their use is increasing widely and is increasingly found in the environment. Acetamiprid, the selected compound belongs to this class, has high solubility in water and potential to pollute surface and ground water. Important physical and chemical properties of acetamiprid are already discussed in chapter 2.

3.3 Processes and Operating Parameters Selected for Study

In this work following five methods were selected for the removal of acetamiprid from wastewater based on the literature survey and preliminary degradation studies conducted.

3.3.1 Fenton Process (Fe^{2+}/H_2O_2)

Fenton process is the simplest of all AOPs where H_2O_2 (reactant) and Fe^{2+} (catalyst) are used. This process does not require any sophisticated set up and can be performed at room temperature. The main factors affecting the processes are found to be pH, H_2O_2 dosage and Fe^{2+} dosage. The optimum pH for the Fenton process was reported as 2.8-3 in all literature studied and it was confirmed by conducting preliminary experiments. Hence a pH of 3 is used in this study. The experiments were conducted by varying H_2O_2 and Fe^{2+} dosages at a pH of 3.

3.3.2 UV Treatment

Most of the organic pollutants in water undergo degradation by photolysis under natural sunlight. This can be enhanced by employing a powerful light source. This has the advantage of absence of chemical agents. The experiments were conducted using 125 W medium pressure mercury vapour lamp at different pH to study the effect of pH on degradation rate.

3.3.3 UV/ H_2O_2 Process

The photolysis of organic compounds under UV light is generally slow. The degradation can be enhanced by oxidation with hydroxyl radicals by the addition of hydrogen peroxide. This fact is made use in the UV/ H_2O_2 process. Effects of pH and initial H_2O_2 concentration on the removal of acetamiprid and TOC were studied by conducting experiments at different values of pH and H_2O_2 concentration in the presence of UV source.

3.3.4 Photo-Fenton Process (Fe^{2+}/ H_2O_2/UV)

Fenton process has the disadvantage of sludge formation due to iron hydroxide. Use of UV light along with Fenton (photo- Fenton) reduces the formation of this sludge by converting the Fe^{3+} formed back to Fe^{2+}, which will react again to form more hydroxyl radicals. This reduces the amount of reagents (H_2O_2 and Fe^{2+}) required and sludge formed. In this work experiments were conducted at pH 3 for different $H_2O_2$and Fe^{2+} dosages using a medium pressure mercury lamp of 125 W.

3.3.5 Photocatalysis Using Undoped and Cu, Fe Doped TiO_2

Photocatalysis using semiconductor materials such as TiO_2, ZnO_2, SnO_2 had been used for the removal of recalcitrant compounds from water/wastewater. TiO_2 being inexpensive, stable and inert material finds major application in the water and wastewater treatment. TiO_2 has a band gap of 3.3 eV and hence it shows relatively high activity in the presence of ultraviolet light. Doping of TiO_2 with metals and non- metals are employed widely to enhance the photocatalytic activity of TiO_2. Here doping of TiO_2 with Cu and Fe has been attempted and used for the removal of acetamiprid from wastewater. TiO_2 has a neutral and stable state at a pH 6 (Cao et al., 2008). Hence degradation studies were conducted at pH 6 for different catalyst loading and dopant concentration.

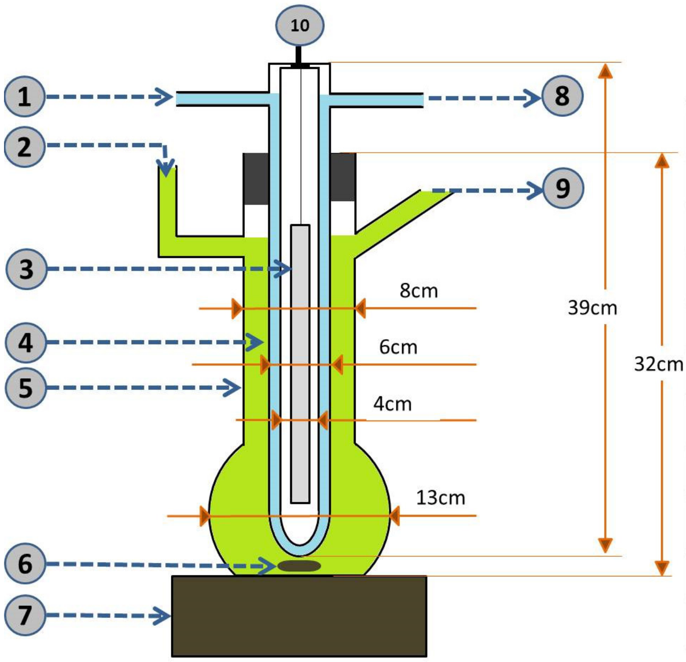
3.4 Materials Used

Acetamiprid (Technical grade, 97%) was received from Rallis India and it was used as such without further purification**.** Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) was used in Fenton and photo-Fenton reactions as a source of Fe^{2+}. Acetonitrile (HPLC grade) received from Fisher Scientific. Ultrapure water was produced in situ using Millipore Direct-Q 3 UV system device. Sulphuric acid, sodium hydroxide used for pH adjustment and hydrogen peroxide solution (30% w/w) used were of analytical grade received from Merck. Acetamiprid of required concentrations were prepared by serial dilution of stock solution using double distilled water.

For preparation of titanium dioxide, titanium isobutoxide ($Ti(OBu)_4$) was purchased from Sigma Aldrich. $CuCl_2$ and $FeCl_3$ were used as the source of Cu an Fe for doping. Analytical grade isopropyl alcohol, Nitric acid, $Cucl_2$ and $FeCl_3$ were from Merck.

3.5 Experimental Set Up

The experiments were conducted in a 1000 ml flat bottom borosilicate glass vessel. The schematic diagram is shown in Fig. 3.1. An immersion well made of high purity quartz was placed inside the glass reactor fitted with a standard joint at the top. A medium pressure mercury vapour lamp of 125 W was kept inside the immersion well as a source of UV radiation. The content of the reactor was kept agitated throughout the reaction using a magnetic stirrer. The temperature of the reaction mixture was maintained at room temperature (28±2^{0}C) by circulating cooling water through the annular space of the immersion well. The entire set up was housed in wooden chamber to protect the operating personnel from UV radiation. The experimental set up is shown in Fig. 3.2.



No:	Label
1	Cooling water inlet
2	Sample inlet
3	UV lamp
4	Quartz immersion well
5	Borosilicate glass vessel
6	Magnetic stirrer bar
7	Magnetic stirrer
8	Cooling water outlet
9	Sample outlet
10	Power supply

Fig. 3.1 Schematic diagram of reactor

Fig. 3.2 Experimental set up used

3.6 Preparation of Photocatalysts

TiO_2 was prepared by the controlled hydrolysis of titanium isobutoxide. The procedure was as follows. 20 ml of titanium isobutoxide was slowly added to 80 ml isopropyl alcohol with continuous stirring. 0.3 ml concentrated. HNO_3 was added to the mixture followed by dropwise addition of 2 ml of water. The resulting mixture was sonicated for 5 minutes and then agitated vigorously for 30 minutes. The sol formed was kept for ageing at room temperature for 24 hours. The gel formed was dried at 80-100^{0}C for 2 hours to evaporate the solvent. The dried precipitate was calcined at required temperature for 2 hours and ground to get fine TiO_2 powder. $CuCl_2$ and $FeCl_3$ solutions of required concentrations were used instead of water for preparing Cu doped and Fe doped TiO_2 respectively. The gel obtained after hydrolysis is shown in Fig. 3.3 and the fine powder obtained after calcination is shown in Fig 3.4

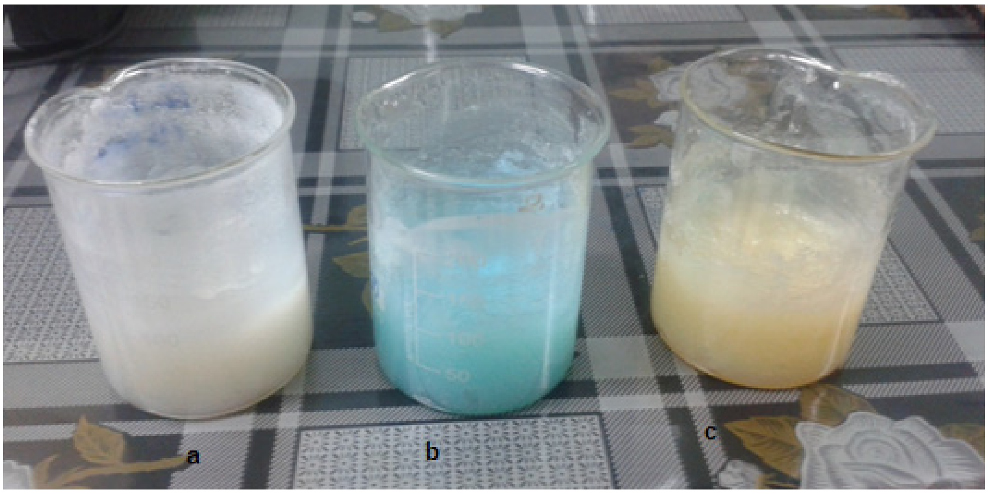


Fig. 3.3 The gel obtained after hydrolysis a)undoped TiO_2 b) Cu doped TiO_2 c) Fe doped TiO_2

Fig. 3.4 TiO_2 obtained after calcination a) undoped TiO_2 b) Cu doped TiO_2 c) Fe doped TiO_2

3.7 Experimental Procedure

Synthetic solution of acetamiprid of 50 mg/L was prepared using distilled water to simulate the heavily loaded industrial wastewater. The reactor was filled with 500 ml of the solution. The desired pH was adjusted using 0.1 N sulphuric acid. Then the required amount of $FeSO_4.7H_2O$ (for Fenton process and photo-Fenton process) was added and mixed well followed by addition of the required amount of hydrogen peroxide. In the case of photocatalysis required amount of catalyst was added after pH adjustment. Then the UV lamp was switched on. A preheating time of 1-2 minutes was given for UV lamp to achieve the stable output. Reaction start for the Fenton reaction was the time when hydrogen peroxide added while for the processes involving UV the time when the lamp achieved stable output was taken as time zero. The mixture was kept stirred throughout the experiment. The reaction time for the processes was selected so as to get at least 95% removal of acetamiprid. All the experiments were conducted in triplicate and the average result is used for representation.

3.8 Analytical Procedure

Samples were collected at required intervals and analysed for acetamiprid concentration and Total Organic Carbon (TOC). The pH of solution after Fenton and photo-Fenton processes was increased immediately to 10 to stop the reaction. Residual hydrogen peroxide in each sample was decomposed by adding one drop of 0.1 N $Na_2S_2O_3$ (Badawy et al., 2006). The samples collected in the photocatalysis experiments were filtered through 0.45 μm filters using a vacuum filtration assembly.

3.8.1 PesticideAanalysis

Pesticide analysis for preliminary studies was carried out using UV-VIS spectrophotometer (Hitachi U 900) with a band pass of 1.5 nm. The absorbance measurement was done at 245 nm. High Performance Liquid Chromatograph (HPLC) was used for determining the pesticide concentration in the detailed study. Hitachi Elite Lachrome HPLC with UV detector was used for the analysis and is shown in Fig 3.5.

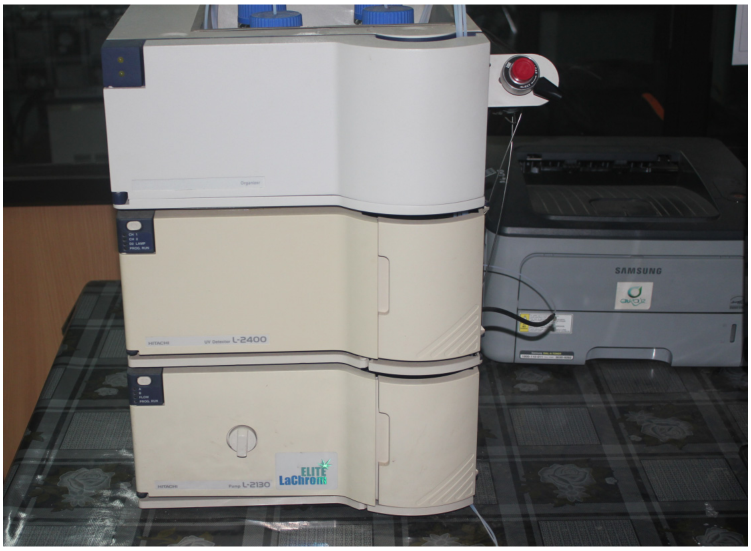


Fig.3.5 HPLC system used for pesticide analysis

The samples collected were filtered through 0.22 µm filter paper and injected manually using Rheodyne injector. A mixture of acetonitrile and water (30:70) was used as the mobile phase. The samples were eluted through the C18 column (Shodex, 5 µm, 4.6 x150 mm) at a flow rate of 1 mL/min. The signals of acetamiprid were detected at 4.4 min at a wavelength of 245 nm. The concentration was calculated from the area of the peak at 4.4 min. Linear relationship between area of the peak and concentration of the pesticide were confirmed by preparing a calibration curve (Annexure 1).

3.8.2 Total Organic Carbon Analysis

Total organic carbon (TOC) measurements were carried out using a Schimadzu TOC-L analyser. It is based on catalytic combustion of the organic material to CO_2 in an oxygen rich environment at 680^0C with a platinum catalyst. The carbon dioxide generated is cooled and dehumidified, and then detected by the NDIR detector. The system used for the measurement is shown in Fig.3.6.

Fig. 3.6 TOC system used for TOC analysis

3.8.3 Characterisation of Undoped and doped TiO_2

X-ray diffraction patterns were recorded for the prepared photocatalysts to identify and determine the crystalline phase using X-ray diffractometer (Bruker, AXS D8 Advance). The patterns were recorded over a 2θ range 20 - $70^{0.}$ The crystalline sizes could be calculated by Scherrer's equation

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \text{..(3.1)}$$

Where D is the crystalline size, λ is the wavelength of the X-ray diffraction (1.5406 A^0), K is the usually taken as 0.9 and β is the line width at half maximum height (Zhang et al., 2004). The micro structure examination was done using scanning electron microscope (SEM) (JEOL JSM- 6390LV).

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the obtained precipitate was carried out to understand the changes happened during heating and to study the thermal stability of catalysts. PerkinElmer system (STA 6000) was used for this purpose and is shown in Fig. 3.7. The samples were heated from 30-800 ^{0}C at rate of 6^0C/ min. The change in weight of the sample and the amount of heat added/rejected was recorded.

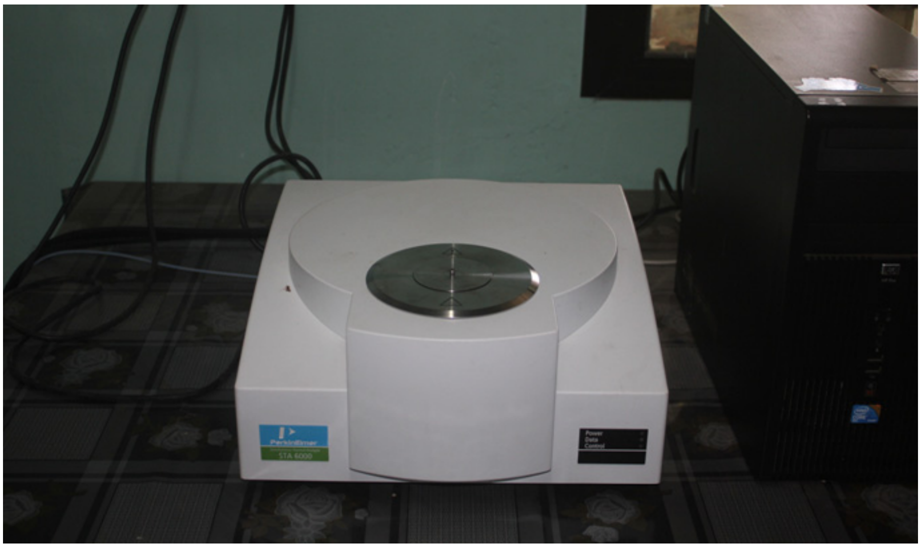


Fig. 3.7 TG-DTA system used for the analysis

3.9 Design of Experiments

The conventional method of conducting experiments is to vary one variable at a time and noting the response. It is time consuming and labour intensive. Moreover, it does not enable the study of combined effects or interaction of two or more variables on the response (Jiang et al., 2013; Montgomery, 2001). An interaction is the failure of one factor to produce the same effect on the response at different levels of another factor. The correct approach is to conduct factorial experiment if response is affected by several variables.

3.9.1 Response Surface Methodology

Response surface methodology (RSM) is a collection of mathematical and statistical tools useful for developing, optimising and improving the processes (Deniz et al., 2007).

RSM is extensively used when some performance measure or quality characteristic of a system (response) is influenced by several input variables (independent variables). The field of RSM consists of the experimental strategy for exploring the space of the process or independent variables, empirical statistical modeling to develop an appropriate approximating relationship between the response and the independent variables and optimisation methods for finding the values of the process variables that produce desirable values of the response. It involves mainly three steps. First step is the design of the experiments statistically using the selected design and conducting the experiments, second is the determination of coefficients in the proposed model and the last step is the validation of the model.

The general relationship between response and the independent variables can be written as

$$y = f(x_1, x_2, \ldots\ldots x_k) + \varepsilon \quad \ldots\ldots(3.2)$$

where x_1, $x_2 \ldots x_k$ are independent variables affecting the system, y is the response and ε the error or noise in the system.

The surface represented by $f(x_1, x_2, \ldots x_k)$ is known as response surface.

Since the true functional relationship between the response and the independent variables is unknown an approximate relationship has to be found out from experimental data. Generally a first order or second order function is used. The first order model is used when the range of variable used is small and the probability of curvature in f is negligible. In the case of two independent variables, the first order function in coded variables can be written as

$$y = A_0 + A_1 x_1 + A_2 x_2 + \varepsilon \quad \text{...}(3.3)$$

The equation 3.3 is known as main effects model, since it considers only main effects of the variable x_1, x_2 and interaction of the variable is not considered.

The equation can be modified by incorporating interaction between variables as

$$y = A_0 + A_1 x_1 + A_2 x_2 + A_{12} x_1 x_2 + \varepsilon \quad \text{..........................} (3.4)$$

The interaction term introduces curvature in the response. When the curvature in the true response is strong, the first order model even with interaction is inadequate to represent in the system. A second order model may be required in such situations.

It can be written as

$$y = A_0 + A_1 x_1 + A_2 x_2 + A_{11} x_1^2 + A_{22} x_2^2 + A_{12} x_1 x_2 + \varepsilon \quad \text{......}(3.5)$$

The second order model is widely used in response surface methodology because of the following reasons (Carley et al., 2004)

1) The second-order model is very flexible. It can take on a wide variety of functional forms, so it will often work well as an approximation to the true response surface.
2) It is easy to estimate the parameters (the A's) in the second-order model. The method of least squares can be used for this purpose.

3) There is considerable practical experience indicating that second-order models work well in solving real response surface problems

In general the second order model for a response can be written as

$$y = A_0 + \sum_{i=1}^{k} A_i x_i + \sum_{i=1}^{k} A_{ii} x_i^2 + \sum_{i=1}^{k} A_{ij} x_i x_j + \varepsilon \quad \text{..................................}(3.6)$$

To find out unknown A's, the data systems has to be collected, generally by experiments. The data received are used to obtain an approximate model for the true response surface. It is usually done by multiple regression analysis

3.9.2 Central Composite Design (CCD)

The central composite design (CCD) is the most popular second order class of RSM. This design is well suited for fitting quadratic surfaces and usually works well for process optimisation. CCD helps to develop a model and optimise the effective parameters with a minimum number of experimental runs. In general, for k factors, CCD requires 2^k factorial runs with $2k$ axial or star runs and n_c center runs (Montgomery, 2001)

A Box-Wilson central composite design, commonly called 'a central composite design', contains an imbedded factorial or fractional factorial design with centre points that is augmented with a group of `star points' that allow estimation of curvature. If the distance from the centre of the design space to a factorial point is ±1 unit for each factor, the distance from the centre of the design space to a star point is $\pm\,\alpha$ with $|\alpha| > 1$. The precise value of α depends on certain properties desired for the design and on the number of factors involved.

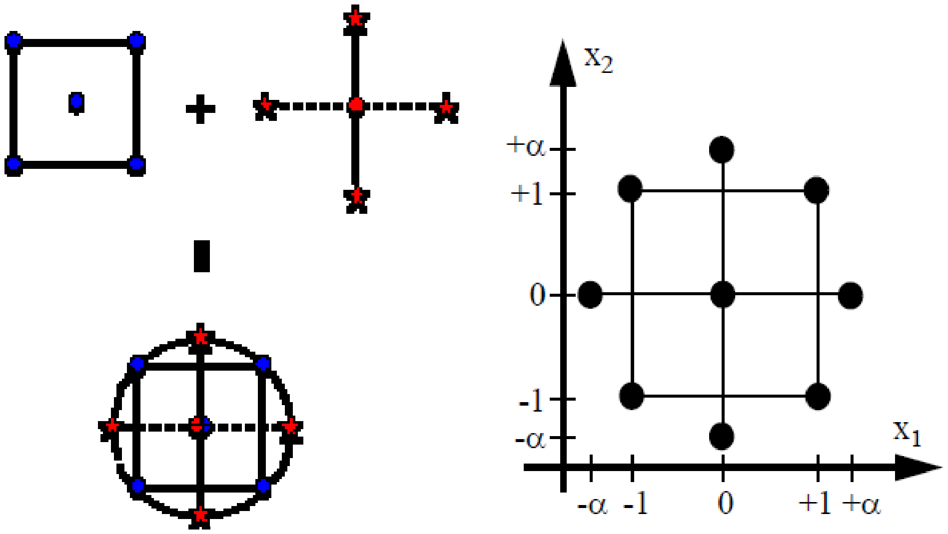


Fig. 3.8 Generation of a central composite design for two factors

An illustration of central composite design is shown in Fig. 3.8. Central composite design always contains twice as many star points as there are factors in the design. The star points represent new extreme values (low and high) for each factor in the design. The value of α is chosen to maintain rotatability and its value depend on the number of experimental runs in the factorial portion of the central composite design:

In the present investigation the effect of parameters on acetamiprid removal and TOC removal was determined using RSM. Central composite design with two factors at five levels was applied using Minitab 14 (PA, USA).

The independent variables are converted into corresponding coded variables x_1 and x_2, between $-\alpha$ and $+\alpha$ in five levels as $-\alpha$, -1, 0. $+1$, and $+\alpha$ using the equation given below (Ahmed Basha et al., 2009).

$$x_i = \frac{2\alpha X_i - \alpha(X_{i,\max} + X_{i,\min})}{(X_{i,\max} - X_{i,\min})} \quad \text{..}(3.7)$$

Where $X_{i,max}$ and $X_{i,min}$ are the maximum and minimum values of the variable X_i.

The value of α used for Fenton, UV/ H_2O_2 and photo-Fenton processes was 1.2 while for photocatalysis it was 1.4. The change in value of α was done to avoid negative values of the variables.

Operating ranges of the variables of the experiments were selected based on the results of the preliminary experiments. Operating parameters and ranges selected for the experiments are given in Table 3.1.

Table 3.1 Operating parameters and ranges selected for the experiments

Independent Variable	**Symbols used**	**Coded levels**				
		-α	**-1**	**0**	**+1**	**+ α**
	a) Fenton process and photo-Fenton process					
H_2O_2 (mg/L)	X_1, X_5^*	2	20	110	200	218
Fe^{2+} (mg/L)	X_2, X_6^*	0.2	2	11	20	21.8
	b) UV-H_2O_2 process					
pH	X_3	2.4	3	6	9	9.6
H_2O_2 (mg/L)	X_4	2	20	110	200	218
	c) Photocatalysis					
Catalyst loading (mg/L)	X_7	300	500	1000	1500	1700
Dopant concentration (mol %)	X_8	0.3	0.5	1.0	1.5	1.7

* X_5 and X_6 are used for photo-Fenton process

Thirteen experiments were conducted including five replicates at centre point. Pure error is calculated based on the results at centre point. Analysis

Of Variance (ANOVA) has also been studied using RSM. A second order polynomial of the following form is fitted to the experimental data

$$y = A_0 + A_1 x_1 + A_2 x_2 + A_{11} x_1^2 + A_{22} x_2^2 + A_{12} x_1 x_2 \quad \text{....(3.8)}$$

where y is the response variable of acetamiprid removal (%) or TOC removal (%) in coded units, A_1, A_2 are regression coefficient for linear effects, A_{11}, A_{22} are quadratic coefficients., A_{12} is interaction coefficient.

The significance of regression coefficients are analysed by '*p*' test.

The quality of fit of the model is represented by correlation coefficient (R), average absolute relative error (AARE), average root mean square error (RMSE) and scatter index (SI) expressed as follows.

$$R = \sum_{i=1}^{N} \frac{(E_i - \overline{E})(P_i - \overline{P})}{\sqrt{\sum_{i=1}^{N} (E_i - \overline{E})^2 \sum_{i=1}^{N} (P_i - \overline{P})^2}} \quad \text{.......(3.9)}$$

$$AARE(\%) = \frac{1}{N} \sum_{i=1}^{N} \frac{(|E_i - P_i|)}{E_i} \times 100 \quad \text{.......(3.10)}$$

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^{N} (P_i - E_i)^2 \right]^{1/2} \quad \text{.......(3.11)}$$

$$SI = \frac{RMSE}{\overline{E}} \quad \text{.......(3.12)}$$

where E is the response obtained from experiment, P is the predicted response obtained from the model, $\overline{E}$ and $\overline{P}$ are the mean values of E and P respectively. N refers to the number of experimental runs. The value of *R* is commonly used to represent the strength of linear relationship between the experimental and predicted variables. But higher value of *R* might not necessarily indicate the better performance of the model because of the tendency of a model to be biased towards higher or lower values. Hence *AARE* and *RMSE* are also computed for measuring the predictability of the model. Since *AAR*E and *RMSE* are calculated through a term by term comparison, they represent unbiased statistics (Srinivasulu and Jain, 2006; Ahmed Basha et al., 2009).

3.10 Kinetic Modeling of Photo-Fenton Process

One of the commonly used methods for kinetic modeling of the process is description of the process using information from individual reactions. In this study, the model was developed based on the simplified reactions that take place in photo-Fenton treatment.

3.10.1 Proposed Reaction Scheme and Mass Balance Equations

The major reactions taking place in photo-Fenton process are given in Table 3.2

Table 3.2 Reaction scheme of the proposed model

Reaction	No.
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^-$	(3.13)
$Fe^{3+} + H_2O \ + h\nu \rightarrow Fe^{2+} + OH^{\cdot} + H^+$	(3.14)
$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^-$	(3.15)
$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HO_2^{\cdot}$	(3.16)
$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+$	(3.17)
$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^-$	(3.18))
$HO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + O_2$	(3.19)
$AMP + OH^{\cdot} \rightarrow AMP^{*\cdot}$	(3.20)

The reaction (3.14) is responsible for the enhancement in the efficiency of removal by photo-Fenton process

Kinetic schemes were written for the oxidation of the acetamiprid (AMP) and the mineralisation of the AMP to CO_2 and water was not considered. The reaction rate expressions and the mass balance equations written are given Table 3.3 and 3.4. Intensity of radiation used in photo-Fenton process is represented by the term '*I*'. The proposed model assumes eight processes and five species: - Fe^{2+}, H_2O_2, Fe^{3+} AMP and radicals formed from peroxide –*R*, (in whatever form) (Cabrera Reina et al., 2012).

Table 3.3 Kinetics expressions for each reaction

Kinetic expression	No.
$r_1 = k_1[Fe^{2+}][H_2O_2]$	(3.21)
$r_2 = k_2[Fe^{3+}]I$	(3.22)
$r_3 = k_3[Fe^{2+}][R]$	(3.23)
$r_4 = k_4[H_2O_2][R]$	(3.24)
$r_5 = k_5[Fe^{3+}][R]$	(3.25)
$r_6 = k_6[Fe^{2+}][R]$	(3.26)
$r_7 = k_7[R][R]$	(3.27)
$r_8 = k_8[AMP][R]$	(3.28)

Table 3.4 Mass balance equations for photo-Fenton process

Mass balance equation	No.
$\frac{d[Fe^{2+}]}{dt} = -r_1 + r_2 - r_3 + r_5 - r_6$	(3.29)
$\frac{d[H_2O_2]}{dt} = -r_1 - r_4$	(3.30)
$\frac{d[Fe^{3+}]}{dt} = r_1 - r_2 + r_3 - r_5 + r_6$	(3.31)
$\frac{d[AMP]}{dt} = -r_8$	(3.32)
$\frac{d[R]}{dt} = r_1 + r_2 - r_3 - r_4 - r_5 - r_6 - r_7 - r_8$	(3.33)

3.10.2 Modeling

The objective of the model was to predict the variation of acetamiprid concentration with time for different H_2O_2 and Fe^{2+} concentration. For this, values of eights reaction constants used in the model (*k_1, k_2, k_3, k_4 k_5, k_6, k_7 and k_8*) were to be obtained. The values of these parameters were to be optimised for the present study as these constants changes within a wide range. The mass balance and rate expressions were solved using MATLAB® and the model parameters were optimised with error rate as objective function. The program will search for suitable values of the parameters within the range available in the literature. These values were used for finding simulated profiles for process variables (Carra et al., 2014). Then the simulated profiles were compared with experimental data obtained for the identification runs (Table 3.5). The error rate objective function is

$$e_n = \alpha_n \sum_{i=1}^{k} \sum_{t=0}^{t=tf} \left[\frac{X_{sim,t} - X_{exp,t}}{X_{exp,t}} \right]^2 \quad \text{...}(3.34)$$

The above function will calculate the sum of the errors for process variables. Where *k* represents the number of identification runs, *t* is the time when the variable was measured, *sim* stands for the simulated value, *exp* stands for experimental value and α is the weighting parameter used to represent the importance and contribution of each parameter to the model.

Table 3.5 Identification and verification runs for photo-Fenton process modeling

Sl No	H_2O_2, mg/L	Fe^{2+}, mg/L	Use
1	5	2	I
2	10	2	V
3	20	2	V
4	50	2	I
5	50	5	I
6	100	2	I
7	100	5	V
8	100	10	I

(I-Identification, V-Verification)

Model validation was done by comparing the simulated and experimental values for verification runs (Table 3.5).

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Chapter 4

Results and Discussion

4.1 Introduction

AOPs are considered to be a viable solution for the removal of pesticides from wastewater. In the present study, five processes are selected for the removal of acetamiprid from wastewater as given in Chapter 3. The effectiveness of the processes depends on number of parameters as discussed in Chapter 2. The important factors affecting the processes were selected here for the study. If the process is influenced by more than one variable it is important to study the effect of their interaction. Hence Response Surface Methodology (RSM), a tool that helps in designing, analysing and optimising the processes were used here. The detailed methodology for conducting the experiments is given in chapter 3. The results obtained from the experiments conducted by the selected processes are presented and discussed in this Chapter.

4.2 Fenton (H_2O_2/Fe^{2+}) Process

4.2.1 Effect of Operating Parameters

pH, Concentartion of H_2O_2 and Fe^{2+} are the main variables affecting the process. It is proven that the optimum pH for the Fenton process is 2.8-3 (Badawy et al., 2006; Chammaro et al., 2001). Hence all the experiments were conducted at pH 3.

Experiments were carried out as per the design obtained by Central Composite Design (CCD) of RSM. The design table and the results of the experiments are given in Table 4.1. It requires 13 experimental runs including four replicates at the centre point.

Table 4.1 The design of experiment and experimental responses for Fenton process (reaction time: 60 minutes)

Run No	H_2O_2 concentration (mg/L), X_1	Fe^{2+} concentration (mg/L) X_2	Acetamiprid removal %	TOC removal, %
1	20	2	17.5	2.5
2	200	2	62.5	11.1
3	20	20	34.5	5.0
4	200	20	99.9	26.0
5	2	11	17.5	2.0
6	218	11	85.0	18.7
7	110	0.2	49.3	9.7
8	110	21.8	78.2	19.0
9	110	11	75.4	20.0
10	110	11	75.6	20.5
11	110	11	75.0	20.3
12	110	11	75.2	20.6
13	110	11	75.5	20.4

It is evident from the results that both factors influenced the removal of pesticide positively. An increase in removal of acetamiprid (%) from 17.5 to 62.5 was observed when H_2O_2 concentration increased from 20 to 200 mg/L at Fe^{2+} concentration of 2 mg/L (run no:1 and 2). Removal of acetamiprid increased with an increase in Fe^{2+} concentration also (run no: 2 and 4). This may be due to the increase in hydroxyl radical formation with increasing H_2O_2 and Fe^{2+}concentration as given in equation 4.1 (Neyens and Baeyens, 2003; Badawy et al., 2006; Chitra et al., 2012).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad \text{...}(4.1)$$

Acetamiprid removal of 99.9 % was obtained when H_2O_2 concentration of 200 mg/L and Fe^{2+} concentration of 20 mg/L (run no: 4) was used. Use of optimum H_2O_2 and Fe^{2+} is important since excess use of H_2O_2 and Fe^{2+} results in scavenging of hydroxyl radicals as given in equation 4.2 and 4.3 (Neyens and Baeyens, 2003). Excess use of H_2O_2 also results in auto decomposition (equation 4.4).

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

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \quad \text{..}(4.3)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad \text{...}(4.4)$$

4.2.2 Combined Effect of Variables

Combined effect of variables from the results of the experiments for Fenton process for 60 minutes duration is shown in Fig. 4.1a and b. It shows that the removal of acetamiprid increases with increase in H_2O_2 and

Fe^{2+} concentrations as explained above. This may be due to the increase in hydroxyl radical formation with increase in H_2O_2 and Fe^{2+} concentration. Highest removal efficiency of acetamiprid was obtained for an initial H_2O_2 and Fe^{2+} concentrations of 200 mg/L and 20 mg/L respectively. TOC removal was only 26 % at these operating conditions. It shows that even though the acetamiprid could be effectively removed, the mineralisation efficiency was low because of the presence of intermediates formed.

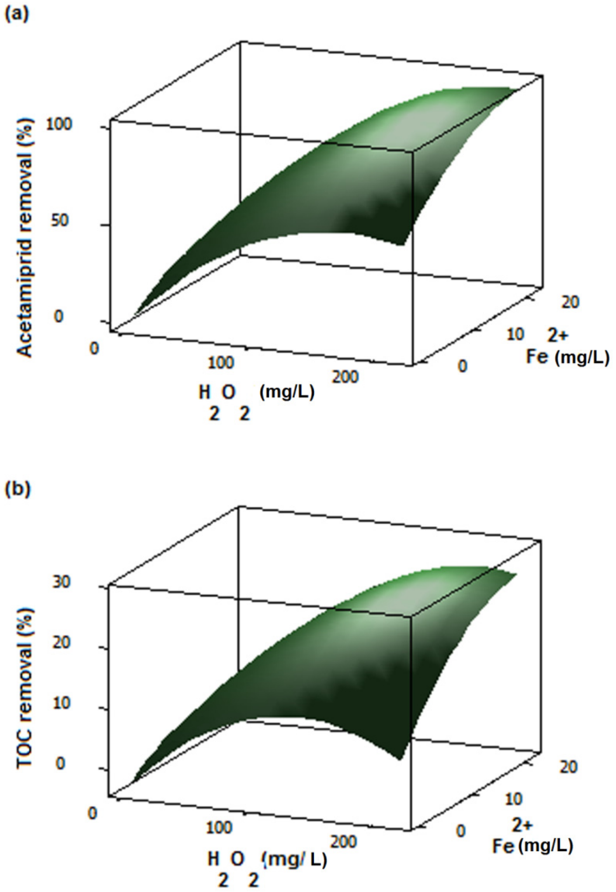

Fig. 4.1 Combined effect of H_2O_2 and Fe^{2+} by Fenton process on a) acetamiprid removal b) TOC removal

4.2.3 Empirical Modeling and Statistical Analysis

Response surface methodology helps in identifying the significant parameters used in the study. In this study, the analysis was done using coded units. Use of coded units helps in eliminating the statistical errors that result from using different measurement scale for different parameters. It also makes the interpretation easier (Malik et al., 2011). The model can be represented in the form

$$y = A_0 + A_1 x_1 + A_2 x_2 + A_{11} x_1^2 + A_{22} x_2^2 + A_{12} x_1 x_2 \quad ..(4.5)$$

where y is the response variable of acetamiprid removal (%) or TOC removal (%) in coded units, A_1, A_2 are regression coefficient for linear effects, A_{11}, A_{22} are quadratic coefficients., A_{12} is interaction coefficient.

The coefficients of fitted second order model in coded terms for Fenton process are given in Table 4.2. By using this model it is possible to predict the acetamiprid removal (%) or TOC removal (%) for any combination of two variables within the experimental domain of study. '*p*' values for all the terms are less than 0.05 (95 % confidence level). So it can be concluded that all the terms are significantly affecting the response of the system.

Table 4.2 Estimated regression coefficients and corresponding *'p'* values for acetamiprid removal and TOC removal by Fenton process (reaction time : 60 minutes)

Response	Factor	Coefficient of the model in coded factors	*'p'* value	significance level
Acetamiprid Removal (%)	A_0	75.191	0.000	>99%
	A_1	27.833	0.000	>99%
	A_2	12.961	0.000	>99%
	A_{11}	-15.637	0.000	>99%
	A_{22}	-6.957	0.000	>99%
	A_{12}	5.123	0.000	>99%
TOC removal (%)	A_0	20.198	0.000	>99%
	A_1	7.355	0.007	>99%
	A_2	4.378	0.003	>99%
	A_{11}	-6.305	0.013	>98%
	A_{22}	-3.007	0.000	>99%
	A_{12}	3.1	0.000	>99%

The equation can be written in uncoded terms as

$$Y_1 = -0.7662 + 0.6640\,X_1 + 2..63387\,X_2 - 0.00193\,X_1{}^2 - 0.08588\,X_2{}^2 + 0.00632\,X_1X_2 \;.....(4.6)$$

$$Y_2 = -3.4224 + 0.2109\,X_1 + 0.8821\,X_2 - .0.00078\,X_1{}^2 - 0.03712\,X_2{}^2 + 0.00382\,X_1X_2 \;..(4.7)$$

Where Y_1 is the acetamiprid removal (%) and Y_2 is the TOC removal (%) after Fenton process in uncoded units, X_1 and X_2 are the initial H_2O_2 concentration and Fe^{2+} concentration in mg/L respectively

The Analysis of the variance (ANOVA) of the models for acetamiprid removal and TOC removal is given in Table 4.3. It shows a higher F value for regression of 640.6 for acetamiprid removal and 1054.4 for TOC removal than the tabulated value of 3.97 in standard statistical table. It shows that the models can navigate the design space well.

Table 4.3 ANOVA results for Fenton process

Source	Degree of freedom	Sum of squares	Mean squares	F value	p value
Acetamiprid removal					
Regression	5	7988.35	1597.67	640.61	0.000
Linear	2	6485.42	3242.71	1300.21	0.000
Square	2	1397.97	698.99	280.27	0.000
Interaction	1	104.96	104.96	42.09	0.000
Residual Error	7	17.46	2.49		
Lack of Fit	3	17.43	5.81	12.08	0.053
Pure error	4	0.03	0.01		
Total	12	8005.81			
TOC removal					
Regression	5	775.957	155.191	1054.4	0.000
Linear	2	504	104.639	710.96	0.001
Square	2	233.510	116.755	793.29	0.000
Interaction	1	38.44	38.44	261.18	0.001
Residual Error	7	1.03	0.147		
Lack of Fit	3	0.882	0.294	7.95	0.069
Pure error	4	0.148	0.037		
Total	12	776.988			

The predictability of the models is quantified by calculating the standard statistical parameters. The values of correlation Coefficient (R), average absolute relative error (AARE), root mean square error (RMSE) and scatter Index (SI) for the two models are given in Table 4.4. The values of the parameters show that both the models are able to predict the responses with adequate accuracy.

Table 4.4 Standard statistical evaluation of the model for Fenton Process

Factor	Acetamiprid removal	TOC removal
R	0.9998	0.9954
AARE	0.7185	5.0400
RMSE	0.4015	0.7645
SI	0.0063	0.0507

4.2.4 Validation of the Model

Apart from the statistical analysis, experimental verification of the model is also important. So experiments were conducted at different combinations of independent variables which were not used to formulate the model, but were within the experimental range. The acetamiprid removal and TOC removal obtained from model predictions were compared with the experimental values and it was in good agreement with each other (Table 4.5). These validations confirmed the suitability of the model for predicting the performance of Fenton process.

Table 4.5 Comparison of predicted and observed values for verification experiments by Fenton process

	Parameters		Acetamiprid removal (%)		TOC removal (%)	
Sl. No.	**H_2O_2 concentration, mg/L**	**Fe^{2+}concentration, mg/L**	**Predicted value**	**Observed value**	**Predicted value**	**Observed value**
1	50	10	48.52	46	12.19	11
2	75	15	65.47	68	17.18	19.0
3	100	5	60.51	62	15.26	14.5
4	100	15	75.99	78	20.48	21.5
5	125	15	84.11	83	22.80	24
6	150	10	82.63	85	21.5	23

4.2.5 Optimisation of Operating Parameters

The optimisation of parameters for the process was done using response optimiser of Minitab®. Response optimiser helps in identifying the combination of independent variables that optimises the responses. The optimisation plots for the process obtained are given in Fig. 4.2. It gives the variation of the predicted responses with the variables. The optimum conditions are obtained by taking the top summit point of the response surface plots. For Fenton process it gives a maximum acetamiprid removal of 97.65% at an optimum initial H_2O_2 and Fe^{2+} concentrations of 190 mg/L and 19 mg/L respectively (Fig. 4.2a) which is very close to the experimentally observed optimum value of 200 mg/L and 20 mg/L. Increasing H_2O_2 and Fe^{2+}

beyond this value decreases the removal slightly because of the scavenging effect of H_2O_2 and Fe^{2+}. Auto-decomposition of H_2O_2 can also contribute to the decrease in removal.

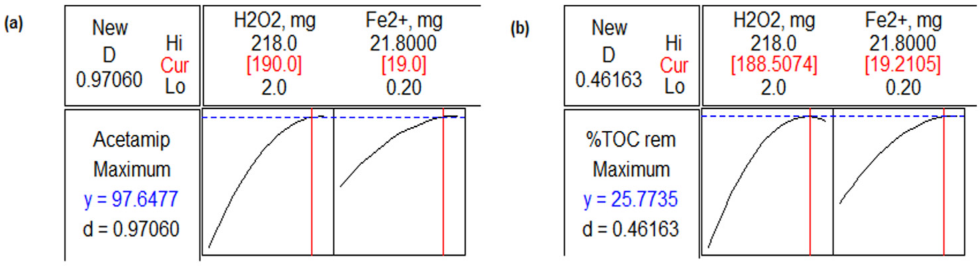

Fig. 4.2 Optimisation plots for Fenton process a) acetamiprid removal b) TOC removal

Experiments were conducted at the predicted optimum conditions. The acetamiprid removal and TOC removal obtained by experiments were 99.98% and 26.54% respectively, whereas the predicted values are 97.65 % and 25.77 %.

4.3 UV Treatment

Photolysis of the compounds under UV light is an important mechanism of degradation of pesticides. pH of the system is an important parameter affecting the degradation. Effect of pH on the degree of removal of by UV photolysis was studied by changing the pH varying the pH between 3 and 9. It was found that pH doesn't have much effect on the degree of removal of acetamiprid. It may be due to very low pKa value of acetamiprid (0.2 @25^{0}C). But a slightly higher removal was noticed in the range of pH 5-6. The effect of pH is shown in the Fig. 4.3.

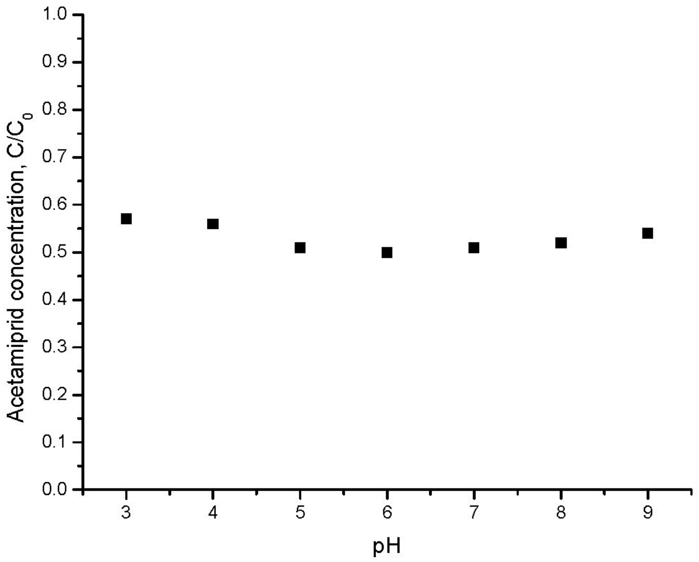

Fig.4.3 The effect of pH on the removal of acetamiprid by UV treatment

Guohong et al. (2009) reported a higher degradation rate for acetamiprid at a pH of 4-5. In this work pH 5-6 was found to give a better removal and hence pH 6 being closer to free (unbuffered) pH was chosen for further studies.

4.4 UV/ H_2O_2 Process

4.4.1 Effect of Operating Parameters

The results of the experiments conducted are given in Table 4.6. It shows the effect of initial pH and H_2O_2 on degree of removal of pesticide and TOC removal. A slight increase in the pesticide removal was noticed when pH increased from 3 to 9 at an initial H_2O_2 concentration of 20 mg/L (run no: 1 and 2). No significant increase in removal was noticed when pH increased from 3 to 9 at an initial H_2O_2 concentration of 200 mg/L (run no: 3 and 4). It is reported that photolysis rate of H_2O_2 increases in more alkaline conditions (Glaze et al., 1987; Legrini et al., 1993; Andreozzi et al., 1999). At higher H_2O_2 concentration, the effect of pH is not significant which shows the predominance of H_2O_2 over pH. Maximum acetamiprid removal of 99.9 % was obtained at a pH value of 6 and H_2O_2 concentration of 110 mg/L (run no: 9). Since acetamiprid is not liable to hydrolyse at pH below 10 it can be concluded that degradation at this condition is due to the oxidation by UV/ H_2O_2 process (Mistika et al; 2013). Use of higher pH is generally not recommended for UV/ H_2O_2 process, since at higher pH, H_2O_2 photo-decomposes into oxygen and water (Tiruvenkatachari et al., 2007). Increasing H_2O_2 concentration beyond optimum results in scavenging of hydroxyl radicals and it is evident in the Fig. 4.4 (Hernandez et al., 2002). TOC removal is also showing similar trend and the maximum TOC removal is obtained at a pH of 6.0 and H_2O_2 concentration of 110 mg/L.

Table 4.6 The design of experiment and experimental responses for UV/ H_2O_2 process (reaction time: 30 minutes)

Run No.	pH	H_2O_2 (mg/L)	Acetamiprid removal (%)	TOC removal (%)
1	3.0	20	80.00	9.5
2	9.0	20	84.00	10.0
3	3.0	200	95.00	28.0
4	9.0	200	96.00	28.7
5	2.4	110	94.90	28.0
6	9.6	110	99.00	28.8
7	6.0	2	77.50	6.0
8	6.0	218	95.00	27.4
9	6.0	110	99.90	30.1
10	6.0	110	99.90	30.2
11	6.0	110	99.80	30.4
12	6.0	110	99.70	30.5
13	6.0	110	99.90	30.5

4.4.2 Combined Effect of Variables

Combined effect of pH and initial H_2O_2 concentration on acetamiprid removal and TOC removal is shown Fig. 4.4. It is evident from the figure that the effect of H_2O_2 is more predominant than that of pH. Removal of pesticide increased initially with increasing H_2O_2 concentration and reached maximum and then decreased. Initial increase is in pesticide removal is because of the formation of more hydroxyl radicals with increase in H_2O_2 concentration. But increase beyond optimum is detrimental due to the scavenging effect of H_2O_2.

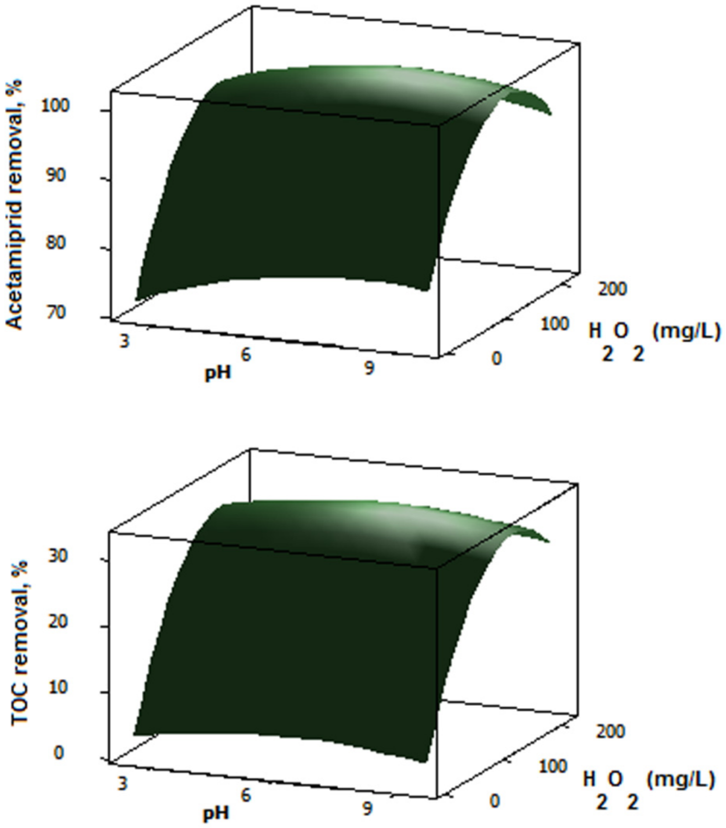

Fig. 4.4 Combined effect of pH and H_2O_2 concentration in UV/ H_2O_2 process on a) acetamiprid removal b) TOC removal

4.4.3 Empirical Modeling and Statistical Analysis

As explained in section 4.2.3 models were developed by regression for predicting acetamiprid removal and TOC removal and the results are given in Table 4.7 .Analysis was done using coded units.

Table 4.7 Estimated regression coefficients and corresponding ‘*p*’ values for acetamiprid removal and TOC removal by UV/ H_2O_2 process

Response	Factor	Coefficient of the model in coded factors	‘*p*’ value	significance level
Acetamiprid Removal (%)	A_0	99.7543	0.000	>99%
	A_3	1.5988	0.000	>99%
	A_4	7.064	0.000	>99%
	A_{33}	-1.994	0.000	>99%
	A_{44}	-9.2858	0.000	>99%
	A_{34}	-0.7500	0.058	>94%
TOC removal (%)	A_0	30.388	0.000	>99%
	A_3	0.3140	0.032	>96%
	A_4	9.1395	0.000	>99%
	A_{33}	-1.5294	0.000	>99%
	A_{44}	-9.6554	0.000	>99%
	A_{34}	0.050	0.756	>24%

In both models the coefficient term for the effect of H_2O_2 (A_4) is larger than that of pH (A_3), showing the predominance of H_2O_2 concentration in the process.

The equation can be written in uncoded terms as

$$Y_3 = 64.5895 + 3.3641X_3 + 0.3497X_4 - 0.2099X_3^2 - 0.0012X_4^2 - 0.0030.X_3X_4 \quad \ldots\ldots.(4.8)$$

$$Y_4 = -1.8276 + 2.1234X_3 + 0.3627X_4 - 0.16993X_3^2 - 0.00119X_4^2 - 0.000185.X_3X_4 \ldots(4.9)$$

Where Y_3 and Y_4 are the acetamiprid removal and TOC removal after UV/ H_2O_2 process, X_3 and X_4 are the pH and H_2O_2 concentration in mg/L respectively.

The analysis of the variance of the models for acetamiprid removal and TOC removal is given in Table 4.8. A higher F values for regression of 357.81 for acetamiprid removal and 2123.12 for TOC removal are obtained than the tabulated value of 3.97 in standard statistical table. It shows that the models can navigate the design space well.

Table 4.8 ANOVA results for UV/ H_2O_2 process

Source	Degree of freedom	Sum of squares	Mean squares	F value	p value
Acetamiprid removal					
Regression	5	782.894	156.579	357.81	0.000
Linear	2	360.895	180.448	412.35	0.000
Square	2	419.748	209.874	479.59	0.000
Interaction	1	2.250	2.250	5.14	0.058
Residual Error	7	3.063	0.438		
Lack of Fit	3	3.031	1.010	12.63	0.051
Pure error	4	0.032	0.008		
Total	12	785.957			
TOC removal					
Regression	5	1016.52	203.303	2123.12	0.000
Linear	2	575.37	287.686	3004.34	0.001
Square	2	441.14	220.568	2303.42	0.000
Interaction	1	0.01	0.01	0.10	0.756
Residual Error	7	0.67	0.096		
Lack of Fit	3	0.54	0.179	5.44	0.068
Pure error	4	0.13	0.033		
Total	12	1017.19			

The quality of the model is quantified in terms of R, AARE, RMSE and SI. The calculated values are given in Table 4.9

Table 4.9 Standard statistical evaluation of the model for UV/ H_2O_2 process

Factor	Acetamiprid removal	TOC removal
R	0.9997	0.9996
AARE	0.1684	1.4343
RMSE	0.1883	0.2272
SI	0.0020	0.0093

From the values of the parameters in Table 4.9, it is evident that the models are adequate to predict the system response with required accuracy.

4.4.4 Validation of the Model

Eventhough it is proved statistically that the models are of good quality, experimental validation was also done to confirm the predictability. The predicted and observed values of acetamiprid removal and TOC removal are given Table 4.10.

Table 4.10 Comparison of predicted and observed values for verification experiments by UV/ H_2O_2 process

Sl. No:	Parameters		Acetamiprid removal		TOC removal	
	pH	H_2O_2 concentration, mg/L	Predicted value	Observed value	Predicted value	Observed value
1	3	30	81.93	79	12.80	12
2	4	50	88.57	86	19.07	18
3	5	70	93.71	95	24.03	25
4	6	100	98.39	97	29.05	31
5	7	110	99.49	100	30.06	31

4.4.5 Optimisation of Operating Parameters

Response optimiser of Minitab was used for the optimisation of parameters for UV/ H_2O_2 process. Optimisation plots give the variation of predicted responses with the variables. The optimisation plot for the process obtained is given in Fig. 4.5.

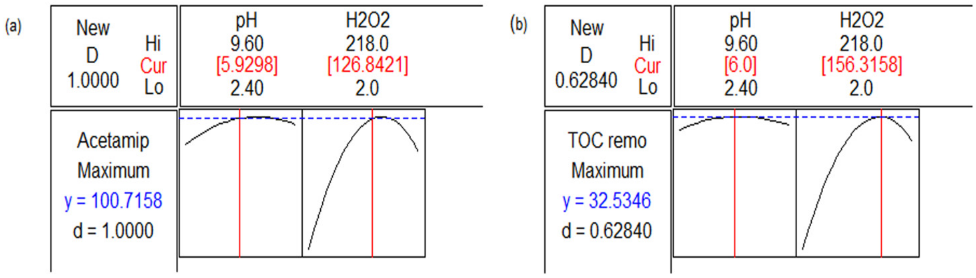

Fig. 4.5 Optimisation plots for UV/ H_2O_2 process a) acetamiprid removal b) TOC removal

The effect of pH and H_2O_2 on the predicted acetamiprid removal and TOC removal is given in the optimisation plots. Removal is maximum in the pH range 5-7 and pH of 6 being closer to the pH of unbuffered solution is taken as optimum. It predicts pesticide removal of 100 % at a pH 5.93 and H_2O_2 concentration of 126.8 mg/L, whereas the maximum TOC removal of 32.53 is predicted at a pH of 6 and 156.32 mg/L. Low TOC removal shows that the intermediates formed by the oxidation of parent compound (acetamiprid) were not degraded fully and it requires further treatment for complete removal. The predicted optimum conditions were verified by conducting experiments and found to be in good agreement with the observed value.

4.5 Photo-Fenton (UV/ H_2O_2/ Fe^{2+}) process

4.5.1 Effect of Operating Parameters

The experimental values obtained for the photo-Fenton experiments are given in Table 4.11.

It clearly shows an increase in acetamiprid removal and TOC removal compared to Fenton and UV/ H_2O_2 process at lower H_2O_2 and Fe^{2+} concentrations. At higher concentrations the removal was reduced due to scavenging effect of H_2O_2 and Fe^{2+} on hydroxyl radicals. For 99% pesticide removal Fenton process required 200 mg/L H_2O_2 and 20 mg/L Fe^{2+} while photo-Fenton process required 20 mg/L H_2O_2 and 2 mg/L Fe^{2+} only. There was almost 10 times reduction in the reagent requirement by using photo-Fenton process within 30 minutes of reaction time.

Table 4.11 The design of experiment and experimental responses for photo-Fenton process (reaction time: 30 minutes)

Run No	H_2O_2concentration (mg/L), X_5	Fe^{2+}concentration (mg/L) X_6	Acetamiprid removal %	TOC removal, %
1	20	2	99.0	14.8
2	200	2	84.0	39.6
3	20	20	85.0	12
4	200	20	84.0	32
5	2	11	89.0	10
6	218	11	82.0	36
7	110	0.2	91.0	42
8	110	21.8	87.0	36
9	110	11	93.0	47.5
10	110	11	93.2	47.8
11	110	11	93.4	47.3
12	110	11	93.5	47.9
13	110	11	93.0	47.5

Maximum TOC removal obtained was only 47.9 % after 30 minutes of reaction (run no: 12). It shows that total mineralisation of the compound is difficult to achieve at the experimental conditions and/or it requires more stringent oxidising conditions. It is reported that mineralisation requires 5-10 times reagents compared to that for acetamiprid removal (Mistika et al., 2013).

4.5.2 Combined Effect of Variables

The combined effect of H_2O_2 and Fe^{2+} concentration on acetamiprid removal and TOC removal by photo-Fenton after 30 minutes are shown in Fig. 4.6a and b. It clearly indicates the reduction in requirement of H_2O_2 and Fe^{2+} concentration for acetamiprid removal compared to Fenton process.

As shown in equation 4.1, in Fenton process one molecule of H_2O_2 and one molecule of Fe^{2+} react to give one molecule of hydroxyl radical.

In photo-Fenton, the UV radiation contributes in converting Fe^{3+} complex formed back to Fe^{2+} and hydroxyl radicals by the equation 4.10 (Malato et al., 2002; Gonzalez et al., 2007; Jiang Hui et al., 2012). Fe^{2+} formed can further react with H_2O_2 to form more hydroxyl radicals.

$$H_2O + Fe^{3+} + h\nu \rightarrow OH^{\cdot} + H^{+} + Fe^{2+} \quad \text{..} (4.10)$$

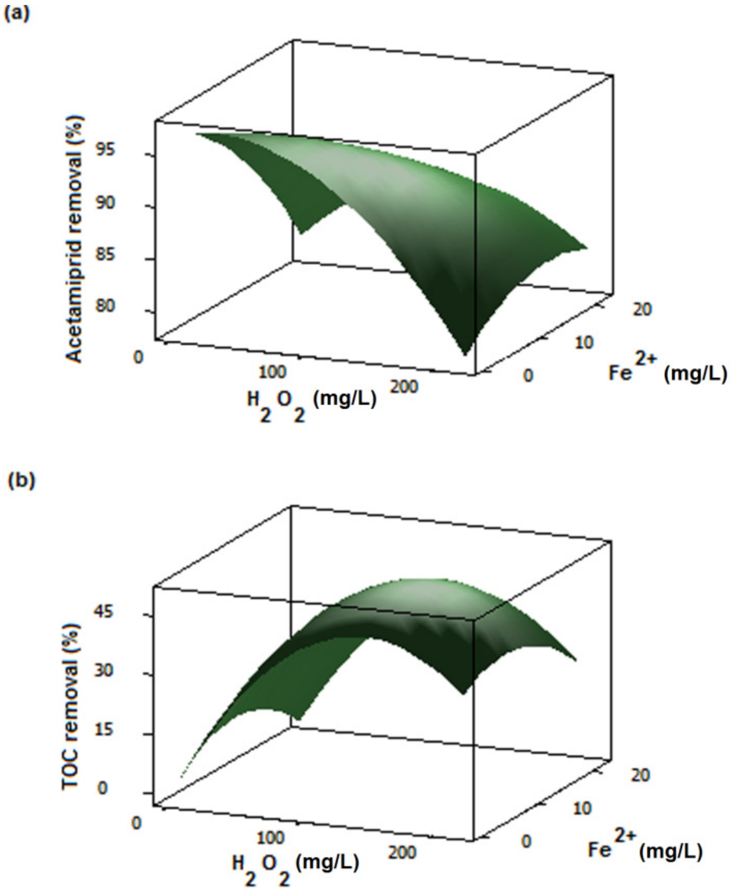

Fig. 4.6 Combined effect of H_2O_2 and Fe^{2+} concentration in photo-Fenton process on a) acetamiprid removal b) TOC removal

This increase in hydroxyl radical formation explains the reduced requirement of H_2O_2 and Fe^{2+} for the removal by photo-Fenton process. In addition to oxidation by hydroxyl radicals, photolysis by UV radiation also contributes in removal of acetamiprid and TOC (Chitra et al., 2012).

4.5.3 Empirical Modeling and Statistical Analysis

The coefficients of fitted second order model in coded terms for photo-Fenton oxidation process are given in Table 4.12. From the values of '*p*', given in Table 4.12 it can be concluded that all the terms are significantly affecting the response of the system.

Table 4.12 Estimated regression coefficients and corresponding '*p*' values for acetamiprid removal and TOC removal by photo-Fenton process

Response	Factor	Coefficient of the model in coded factors	'*p*' value	significance level
Acetamiprid Removal (%)	A_0	92.907	0.*000*	>99%
	A_5	-3.547	0.001	>99%
	A_6	-2.733	0.004	>99%
	A_{55}	-4.172	0.001	>99%
	A_{66}	-1.742	0.067	>93%
	A_{56}	3.5000	0.004	>99%
TOC removal (%)	A_0	47.539	0.000	>99%
	A_5	10.581	0.000	>99%
	A_6	-2.849	0.000	>99%
	A_{55}	-17.199	0.000	>99%
	A_{66}	-6.436	0.000	>99%
	A_{56}	-1.7	0.000	>99%

The equation can be written in uncoded terms as

$$Y_5 = 96.9753 + 0.02638X_5 - 0.30589X_6 - 0.0005151X_5^2 - 0.0215014X_6^2 + 0.00432X_5X_6 \quad ..(4.11)$$

$$Y_6 = 0.24227 + 0.607801X_5 + 1.66224X_6 - .0.0021233X_5^2 - 0.07945X_6^2 - 0.002098X_5X_6 \quad ...(4.12)$$

Where Y_5 is the acetamiprid removal (%) and Y_6 is the TOC removal (%) after photo-Fenton process in uncoded units, X_5 and X_6 are the initial H_2O_2 concentration and Fe^{2+} concentration in mg/L respectively.

The ANOVA of the models for predicting acetamiprid removal and TOC removal is shown in Table 4.13. For both models F value for regression is higher than that of value (3.97) in the standard statistical table. It shows that the models can navigate the design space well.

Table 4.13 ANOVA results for photo-Fenton process

Source	Degree of freedom	Sum of squares	Mean squares	F value	P value
Acetamiprid removal					
Regression	5	284.228	56.8456	19.72	0.001
Linear	2	137.907	68.9535	23.92	0.001
Square	2	97.321	48.6606	16.88	0.002
Interaction	1	49	49	17	0.004
Residual Error	7	20.175	2.8821		
Lack of Fit	3	19.967	6.6557	12.79	0.055
Pure error	4	0.208	0.052		
Total	12	304.403			
TOC removal					
Regression	5	2436.78	487.357	2360.93	0.000
Linear	2	826.16	413.081	2001.12	0.000
Square	2	1599.06	799.53	3873.21	0.000
Interaction	1	11.56	11.56	56.00	0.000
Residual Error	7	1.44	0.206		
Lack of Fit	3	1.20	0.402	6.69	0.059
Pure error	4	0.24	0.060		
Total	12	2438.23			

The statistical parameters are calculated to quantify the quality of the model and the values are given in Table 4.14

Table 4.14 Standard statistical evaluation of the models by photo-Fenton process

Factor	Acetamiprid removal	TOC removal
R	0.9663	0.9997
AARE	0.9889	0.8818
RMSE	0.3057	0.3335
SI	0.0034	0.0095

From the values of R, AARE, RMSE and SI it can be confirmed that quality of model is adequate to predict the responses within the experimental domain of study.

4.5.4 Validation of the Models

Validation of the models was done by conducting experiments at different combinations of independent variables which were not used to formulate the model, but were within the experimental range. It was found that predicted and observed values were in good agreement with each other. Comparison between predicted and observed values are given Table 4.15

Table 4.15 Comparison of predicted and observed values for verification experiments by photo-Fenton process

Sl. No:	Parameters		Acetamiprid removal		TOC removal	
	H_2O_2 concentration, mg/L	Fe^{2+}concentration, mg/L	Predicted value	Observed value	Predicted value	Observed value
1	10	2	96.57	95.0	9.07	8.6
2	50	2	96.74	98.0	28.12	29.5
3	75	10	94.08	97.0	40.99	42.5
4	100	5	94.55	93.0	45.06	47.0
5	125	15	90.90	93.0	46.16	48.0
6	150	10	90.61	94.0	49.17	51.0

4.5.5 Optimisation of the Operating Parameters

Optimisation of the operating parameters was done using response optimiser of Minitab®. It gives the variation of predicted responses with operating parameters. Optimisation plots for the photo-Fenton process obtained using response optimiser is given in Fig. 4.7

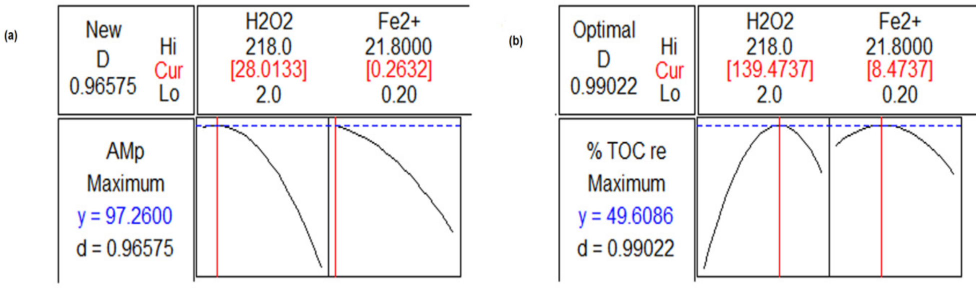

Fig. 4.7 Optimisation plots for photo-Fenton process a) acetamiprid b) TOC removal

The optimum initial H_2O_2 and Fe^{2+} concentrations for acetamiprid removal by photo-Fenton process were predicted to be 28.01mg/L and 0.26 mg/L respectively. The optimum values obtained by conventional experimental technique were 20 mg/L of H_2O_2 and 2 mg/L of Fe^{2+}. The predicted optimum conditions for TOC removal for photo-Fenton process were 139.4 mg/L H_2O_2 and 8.4 mg/L Fe^{2+}. It predicted a maximum removal of 49.6% at optimised conditions. The experimental values obtained after 30 minutes were 99.99% acetamiprid removal and 51.5% TOC removal while the predicted values were 97.26 % and 49.61 % respectively. There was a reduction in the optimum value of H_2O_2 and Fe^{2+} when photo-Fenton was used. This can be explained by additional hydroxyl radical formation when UV was used.

4.6 Heterogeneous Photo-catalysis Using Undoped and Doped TiO_2

4.6.1 Effect of Calcination Temperature

It was reported by researchers that calcining temperature of 400 ^{0} C gives TiO_2 of better performance (Wilke and Breuer, 1999; Su et al., 2004; Qiu, 2006), while some reported a temperature of 500 ^{0}C (Liu et al., 2005; Colmenares at al., 2006) as the optimum temperature. To select the suitable calcining temperature TiO_2 samples were prepared at calcining temperatures of 400 ^{0} C and 500 ^{0}C and XRD patterns were recorded between 2θ values of 20 to 70 degrees. XRD patterns obtained are shown in Fig. 4.8.

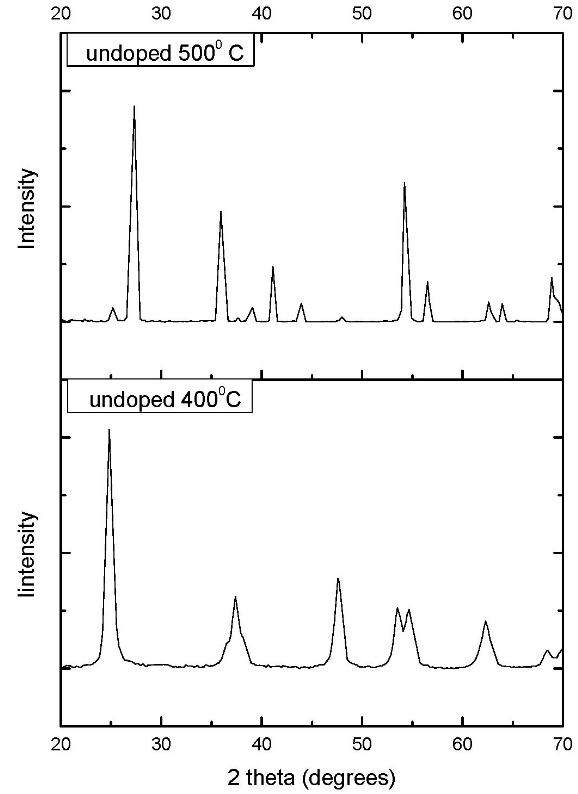

Fig. 4.8 XRD patterns of TiO_2 calcined at 400 ^{0}C and 500 ^{0}C

The patterns were compared with standard pattern of TiO_2 and it was found that the anatase phase (2θ values of 25^0, 37^0, 48^0 and 63^0) was predominant in the TiO_2 calcined at 400 ^{0}C whereas rutile phase (2θ values of 28^0, 36^0, 39^0, 54^0, 57^0) predominated in the TiO_2 calcined at 500 ^{0} C. This is in line with the observation by Zhang et al. (2004a). Anatase phase is generally considered to be more photoreactive (Lakshminarayana et al., 2011). Moreover, diffraction peaks became sharper at 500 ^{0}C due to coarsening of crystallites. Hence calcination temperature of 400 ^{0}C was selected for further studies.

4.6.2 Characterisation of Undoped and Doped TiO_2

The X-ray diffraction patterns obtained for pure (undoped), Cu and Fe doped TiO_2 calcined at 400 ^{0}C are shown in Fig. 4.9. Major peaks were obtained at 2θ values of 25^0, 37^0, 48^0 and 63^0 corresponding to anatase phase of TiO_2 for all samples. It shows that doping of Fe and Cu did not affect the crystalline structure of TiO_2. The XRD patterns obtained for doped TiO_2 samples coincided almost with the pure TiO_2 and it showed no diffraction patterns corresponding to Cu and Fe. So it can be concluded that dopants were not incorporated directly onto the structure but were placed onto TiO_2 surface (Katarzyna et al., 2013) and it also indicates that the dopant particles at the TiO_2 surface were very small and highly dispersed (Zhou and He, 2012) or the concentration of dopant was too low for the XRD to reveal (Wu et al., 2011). Zhang et al. (2004b) reported that < 65.97 wt % Cu in TiO_2 has no significant copper oxide peaks in XRD powder diffraction patterns

The presence of rutile phase in the prepared samples was very less and anatase phase is generally considered to be more photoactive. The average grain size was calculated from the broadening of the peak at 2θ value of 25 degrees using Scherrer's formula and it was found that doped TiO_2 has smaller size compared to the pure one. Pure TiO_2 size is in the order of 36 nm while Cu doped has 25 nm and Fe doped has 23 nm.

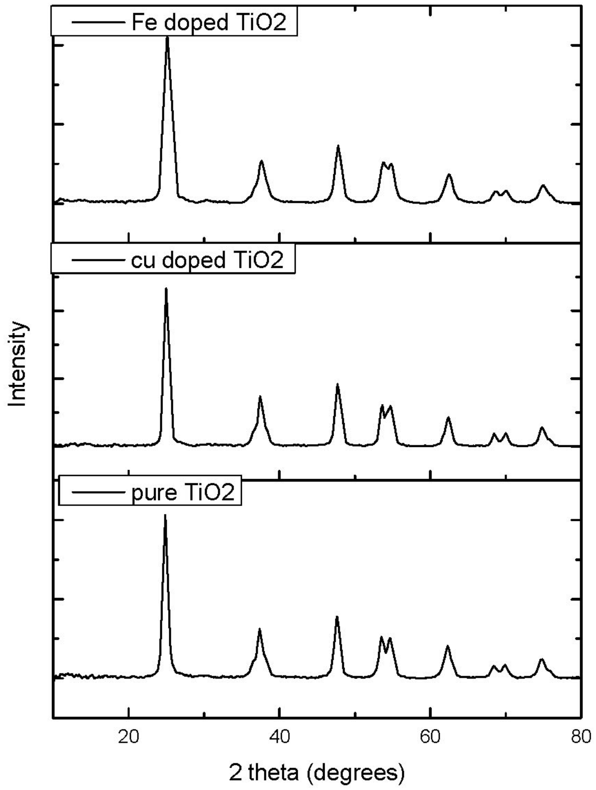

Fig. 4.9 XRD patterns for pure, Cu doped and Fe doped TiO_2

The microstructure and particle size of TiO_2 powders were observed by scanning electron microscope (SEM).The pictures obtained by SEM are shown in Fig. 4.10. It was observed that doping has restrained the growth of particle.

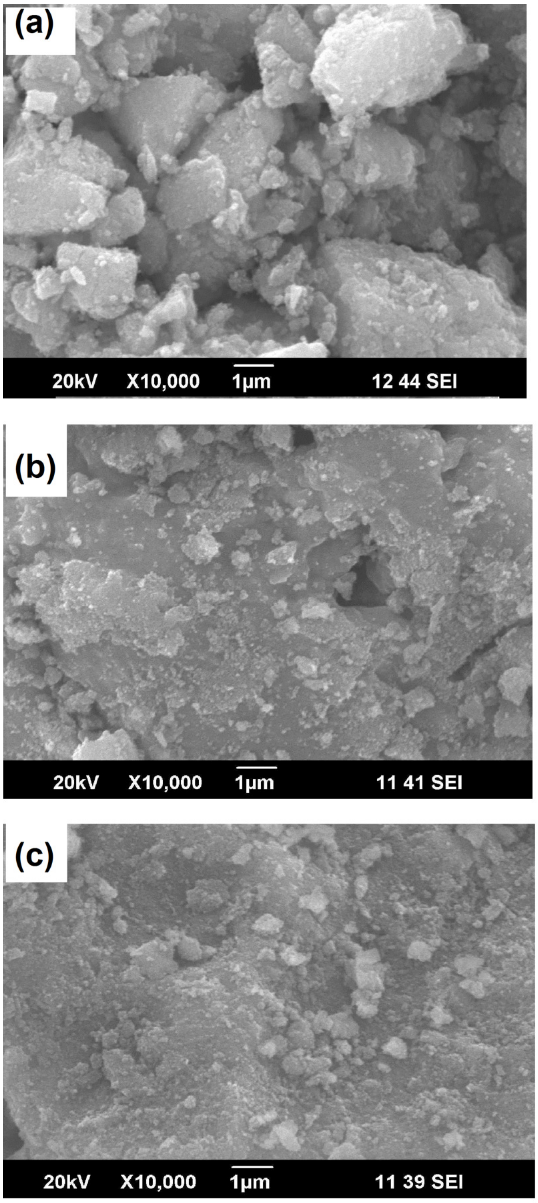

Fig. 4.10 SEM photographs of a) Pure TiO_2 b) Cu doped TiO_2 c) Fe doped TiO_2

To understand the changes happening during heating and to study the thermal stability of the catalysts DTA and thermogravimetic analysis were carried out. The plots obtained are given in Fig. 4.11, 4.12 and 4.13. It was found that the major weight loss occured below 200 ^{0}C. This may be due to the loss of water molecules and solvent from the matrix. A small endothermic peak was obtained near to 100 ^{0}C corresponding to the loss of solvents. It was also observed that reaction was complete around 400 ^{0}C. All samples (pure and doped TiO_2) showed the same pattern.

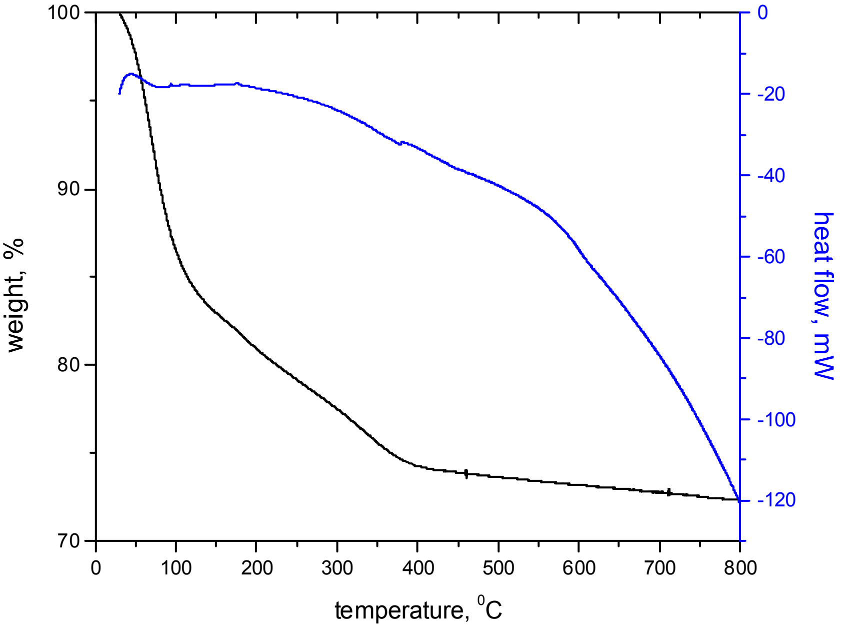

Fig. 4.11 DTA-TGA thermograms obtained for pue TiO_2

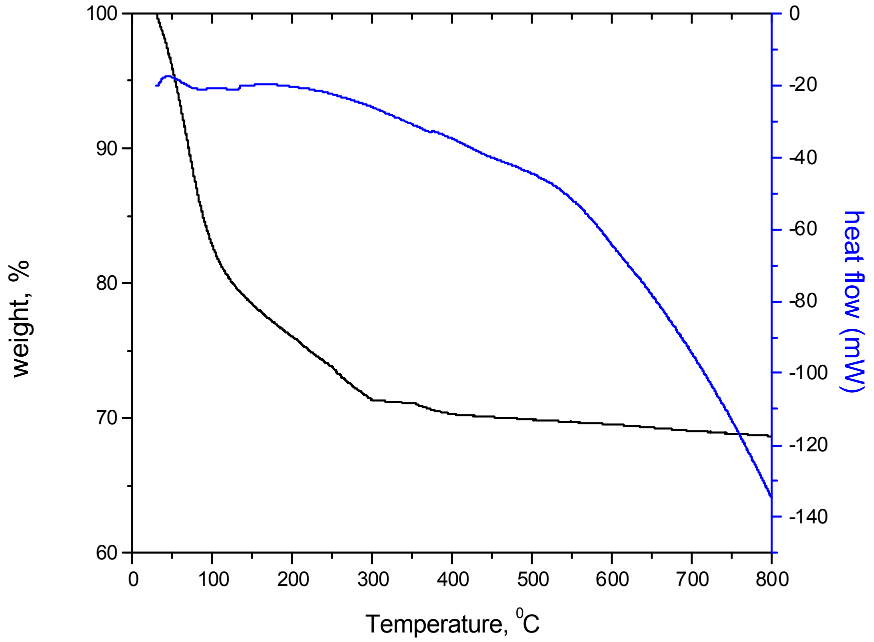

Fig. 4.12 DTA-TGA thermograms obtained for Cu doped TiO_2

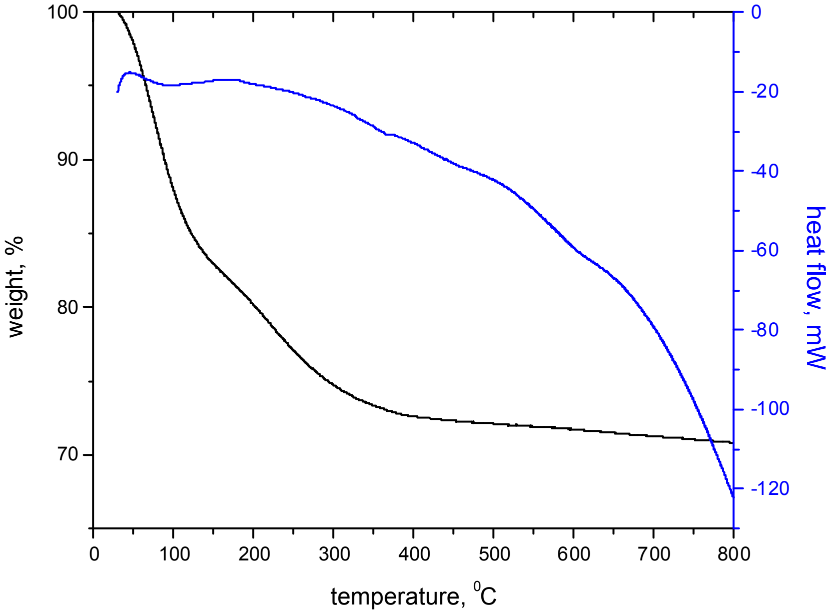

Fig. 4.13 DTA-TGA thermograms obtained for Fe doped TiO_2

4.6.3 Effect of Catalyst Loading

Effect of catalyst loading was studied by varying the amount of pure TiO_2 used from 0.5 g/L to 2 g/L for the removal of acetamiprid from wastewater samples. All the experiments were conducted at pH 6 owing to its stability (Cao et al., 2008). The variation of concentration of acetamiprid with time for different catalyst loading is shown in Fig. 4.14.

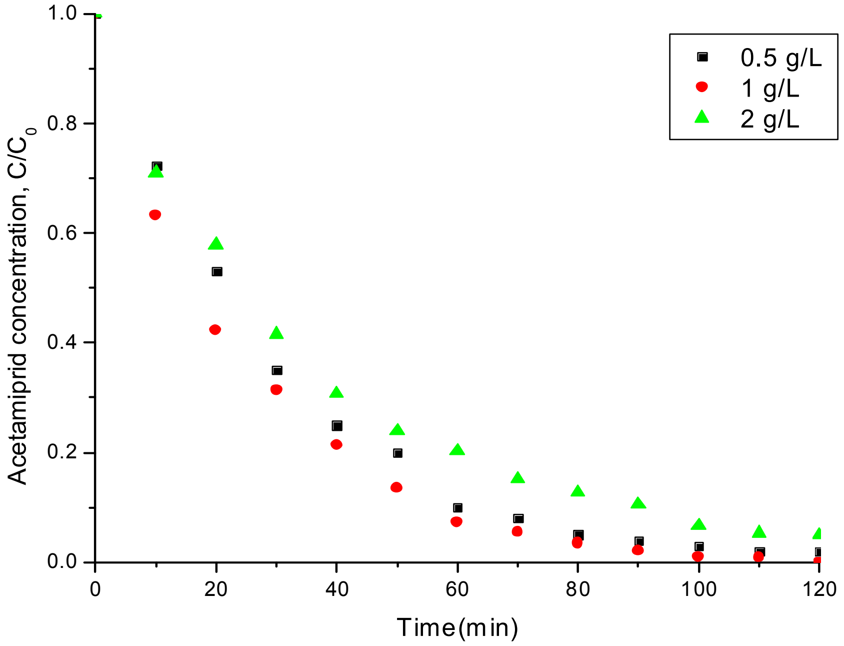

Fig. 4.14 The effect of catalyst loading on the removal of acetamiprid

It was found that concentration of pesticide decreases slowly with time. Increase in removal with increase in catalyst loading was noticed up to a certain catalyst loading. This may be because of the increase in the number of active sites on the catalyst surface with increase in catalyst concentration

(Akpan et al., 2010). Maximum removal of acetamiprid was noticed for TiO_2 concentration of 1 g/L and the rate of removal was also better. Increase in TiO_2 concentration above 1 g/L decreased the rate of removal slightly. This may be due to the decrease in transparency of solution and light scattering by the particles at higher concentrations. The decrease in interfacial area due to aggregation of the particle is another reason for decrease in removal at higher catalyst loading (Saritha et al., 2007).

4.6.4 Effect of Doping

As the doping is an efficient method for improving the photo catalytic activity of TiO_2, before optimising the parameters, the effect of doping was studied. Experiments were conducted with pure (undoped), Cu doped and Fe doped TiO_2 at a catalyst loading of 1g/L. The variation of concentration of acetamiprid with photocatalysis using doped and undoped TiO_2 is shown in Fig. 4.15. It was found that Cu doping enhanced the rate of removal of the pollutant slightly while there was a decrease in the rate of removal with Fe doping. This may be due to high electron density of Fe about the nucleus. The atomic radius of Fe is same as that of Ti. This electron density can act as a repulsive force against Ti interaction (Akpan et al., 2010).

It is also reported that recombination of photogenerated electron/hole pairs takes place quickly in the Fe-doped TiO_2, while the charge separation of the photogenerated electron/hole pairs takes place effectively in the Cu-doped TiO_2 (Maeda and Yamada, 2007).

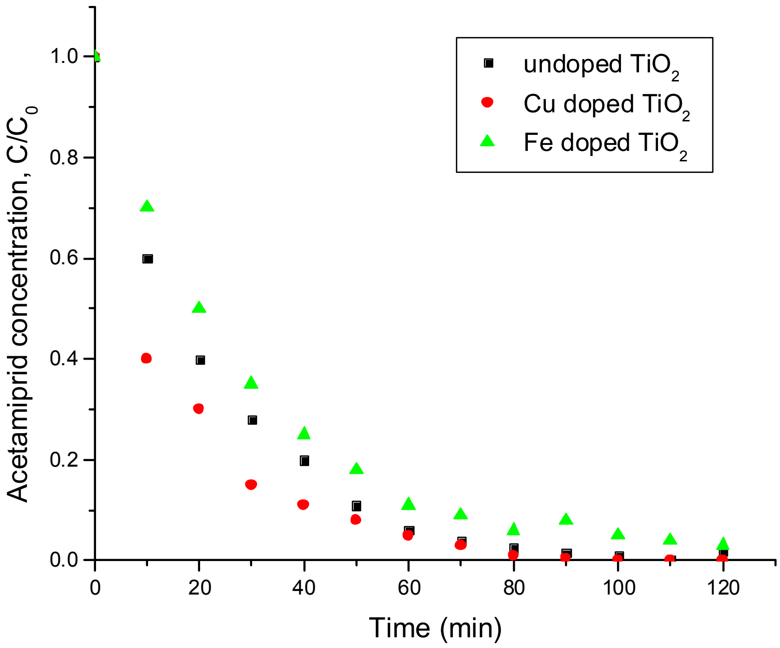

Fig. 4.15 Effect of doping of TiO_2 on acetamiprid removal

4.6.5 Effect of Dopant Concentration

As it was observed that the doping of TiO_2 influenced the photocatalytic activity of TiO_2, the effect of concentration of doping agents on the photocatalytic activity was studied. Catalysts were prepared at different concentration of Cu and Fe viz., 0.5, 1.0, 1.5 wt%.

The prepared catalysts were used to study the effect of dopant concentration on the removal of pesticide. Experiments were conducted at a catalyst loading of 1g/L.

The effect of concentration of Cu on the removal efficiency is shown in Fig. 4.16.

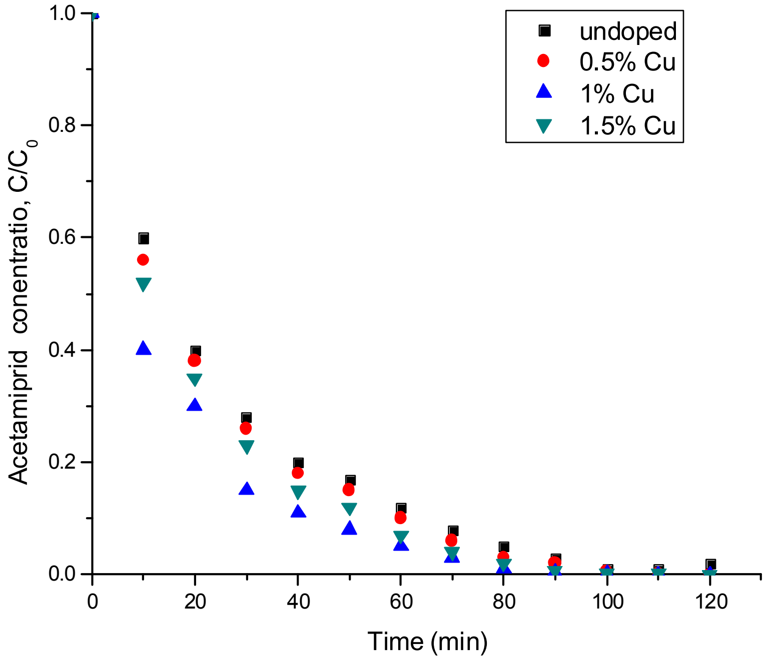

Fig. 4.16 Effect of Cu (dopant) concentration on the removal of acetamiprid

It can be seen from the plot that the rate of removal increased slightly when the Cu concentration increased from 0.5 to 1 %. Further increase in Cu decreased the removal rate by a small degree. Excessive usage of dopant can cover the catalyst surface resulting in low interfacial area (Liu et al., 2005). This explains the decrease in removal at higher Cu concentration.

The increase in concentration of Fe in the doped TiO_2 decreased the removal of pesticide as shown in Fig. 4.17. This may be due to recombination of electron-hole pairs as explained before.

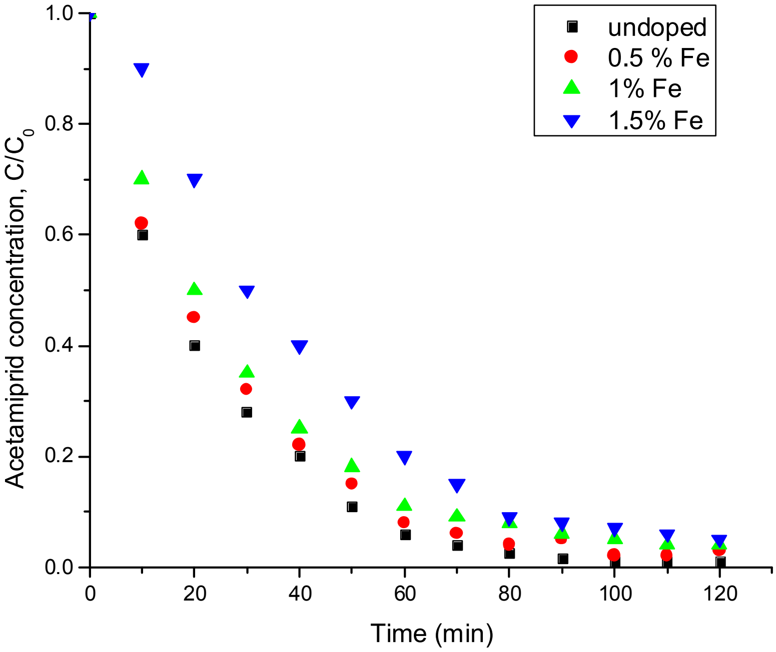

Fig. 4.17 Effect of Fe (dopant) concentration on the removal of acetamiprid

4.6.6 Empirical Modeling Using RSM and Statistical Analysis

As it was observed that Cu doping of TiO_2 enhanced the photocatalytic activity of TiO_2 modeling and optimisation of the process using RSM was tried with varying catalyst loading and dopant concentration. Experiments were conducted as demanded by CCD with replicates at central point as given in Table 4.16. As no improvement in photocatalytic activity was noticed with Fe doping, optimisation with Fe doping was not tried.

Table 4.16. The design of experiment and experimental responses for photo-catalysis using Cu doped TiO_2 (reaction time: 60 minutes)

Run No	Catalyst loading (mg/L/), X_7	Dopant (Cu) concentration (weight %), X_8	Acetamiprid removal %	TOC removal, %
1	500	0.5	85.0	12
2	1500	0.5	93.0	20
3	500	1.5	92.0	15
4	1500	1.5	93.0	22
5	300	1.0	87.0	10
6	1700	1.0	91.0	18
7	1000	0.3	88.0	20
8	1000	1.7	95.0	22
9	1000	1.0	96.0	25
10	1000	1.0	97.0	26
11	1000	1.0	96.5	25
12	1000	1.0	96.0	24
13	1000	1.0	97.0	26

The variation of acetamiprid removal and TOC removal with catalyst loading and dopant (Cu) concentration is given in Table 4.16. It is evident from the responses that the catalyst loading and dopant concentration affected the acetamiprid removal and TOC removal. The removal increased initially with increase in catalyst loading. This may be because of the increase in the number of active sites with increase in catalyst concentration as explained in section 4.6.3. Increase in catalyst concentration beyond a certain value decreases the removal because of the reduction in transparency of solution and light scattering by the particles at higher catalyst concentration.

Reduction in removal with excessive usage of dopant may be because of the covering of the catalyst surface resulting in low interfacial area. This emphasizes the importance of using optimum conditions for the process. Maximum removal was obtained for a catalyst loading of 1000 mg/L and 1 wt% Cu concentration.

The combined effect of catalyst loading and dopant (Cu) concentration on acetamiprid removal and TOC removal is shown in Fig. 4.18.

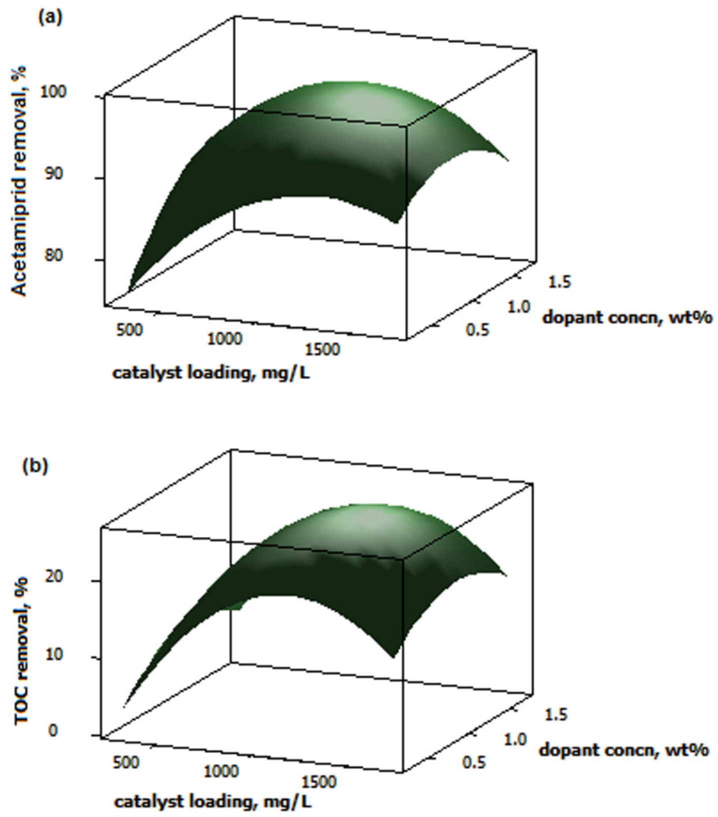

Fig. 4.18 Combined effect of catalyst loading and dopant (Cu) concentration on a) acetamiprid removal b) TOC removal

The study using RSM revealed a mathematical relation between the responses (acetamiprid removal and TOC removal) and the independent variables (catalyst loading and dopant concentration). A second order model was fitted and the coefficients of the model and the significance level of the parameters are given in Table 4.17.

Table 4.17. Estimated regression coefficients and corresponding 'p' values for photocatalysis using Cu doped TiO_2 (reaction time- 60 minutes)

Response	Factor	Coefficient of the model in coded factors	'*p*' value	significance level
Acetamiprid Removal (%)	A_0	96.495	0.000	>99%
	A_7	1.843	0.000	>99%
	A_8	2.121	0.000	>99%
	A_{77}	-3.664	0.000	>99%
	A_{88}	-2.388	0.000	>99%
	A_{78}	-1.750	0.003	>99%
TOC removal (%)	A_0	25.2007	0.000	>99%
	A_7	3.3081	0.000	>99%
	A_8	0.9848	0.013	>98%
	A_{77}	-5.7383	0.000	>99%
	A_{88}	-2.1669	0.000	>99%
	A_{78}	-0.2500	0.571	>43%

From the values of '*p*', it can be concluded that all the terms are significantly affecting the response of the system.

The equation can be written in uncoded terms as

$$Y_7 = 57.3562 + 0.03999X_7 + 30.3499X_8 - 0.00001465X_7^2 - 9.55372X_7^2 - 0.007X_7X_8 \text{....}(4.13)$$

$$Y_8 = -16.0062 + 0.05352X_7 + 20..3050X_8 - 0.0000229X_7^2 - 8.6676X_7^2 - 0.001X_7X_8 \text{..}(4.14)$$

Where Y_7 is the acetamiprid removal (%) and Y_8 is the TOC removal (%) after photocatalysis using Cu doped TiO_2 after 60 minutes in uncoded units. X_7 and X_8 are the catalyst loading in mg/L and dopant (Cu) concentration in weight % respectively.

The Analysis of the variance of the models is given in Table 4.18. It shows a higher F value for regression 63.53 for acetamiprid removal and 93.68 for TOC removal than the tabulated value of 3.97 in standard statistical table. It shows that the models can navigate the design space well.

Table 4.18 ANOVA results for photo-catalysis using Cu doped TiO_2

Source	Degree of freedom	Sum of squares	Mean squares	F value	p value
Acetamiprid removal					
Regression	5	191.548	38.3096	63.53	0.000
Linear	2	62.551	31.2753	51.86	0.000
Square	2	116.748	58.3738	96.80	0.000
Interaction	1	12.25	12.25	20.31	0.003
Residual Error	7	4.221	0.603		
Lack of Fit	3	3.221	1.0737	4.29	0.097
Pure error	4	1.000	0.25		
Total	12	195.769			
TOC removal					
Regression	5	332.114	66.423	93.68	0.000
Linear	2	94.354	47.177	66.54	0.000
Square	2	237.510	118.755	167.48	0.000
Interaction	1	0.25	0.25	0.35	0.571
Residual Error	7	4.963	0.709		
Lack of Fit	3	2.163	0.721	1.03	0.469
Pure error	4	2.800	0.700		
Total	12	337.077			

Standard statistical analysis of the models was done for checking the predictability of the model. The values obtained for R, RMSE, AARE (%), SI are given in Table 4.19.

Table 4.19 Standard statistical evaluation of the model for photocatalysis

Factor	Acetamiprid removal	TOC removal
R	0.9892	0.9926
AARE	0.532	2.91
RMSE	0.5697	0.6179
SI	0.0061	0.0303

From the values of statistical parameters in Table 4.19, it is evident that models for predicting acetamiprid removal and TOC removal after photocatalysis using doped TiO_2 are adequate to predict the responses with required accuracy.

4.6.7 Validation of the Model

Statistical analysis shows good quality models for predicting the responses. To confirm the results experimental validation was done by conducting the experiments at operating conditions which were not used to formulate the model. The predicted and observed values of acetamiprid removal and TOC removal are given Table 4.20.

Table 4.20 Comparison of predicted and observed values for verification experiments by photocatalysis using Cu doped TiO_2

Sl. No:	Parameters		Acetamiprid removal (%)		TOC removal (%)	
	Catalyst loading, mg/L	Dopant (Cu) concentartion, wt %	Predicted value	Observed value	Predicted value	Observed value
1	400	0.2	76.13	78	5.37	5.0
2	700	0.5	88.50	90	17.8	18.5
3	1000	1.2	96.96	95	25.29	26.0
4	1000	1.5	96.22	94	24.06	25.0
5	1200	1.5	95.67	93	24.39	24.0

4.6.8 Optimisation of Operating Parameters

The optimisation plots for the process are prepared using response optimiser tool of RSM and is shown in Fig.4.19. It gives the variation of the predicted responses with the variables. The optimum conditions were obtained by taking the top summit point of the response surface plots. It predicts a maximum acetamiprid removal of 96.96 % at an optimum catalyst loading of 1000 mg/L and a dopant concentration of 1.22 weight %. The prediction was verified experimentally and acetamiprid removal of 97.5 % was observed at the optimum conditions after 60 minutes. The predicted maximum TOC removal was 25.6 % at catalyst loading of 1081mg/L and dopant concentration of 1.01 wt %.

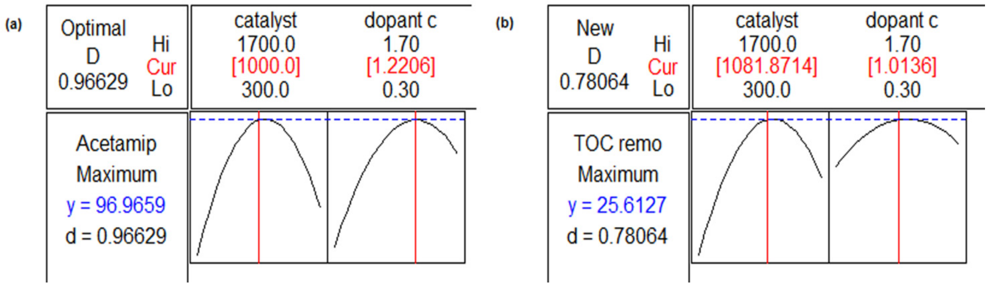

Fig. 4.19 Optimisation plots for photocatalysis using Cu doped TiO_2

4.7 Kinetic Analysis of Acetamiprid Oxidation

The understanding of kinetics of the reactions happening in the process is very much essential in the process analysis and the design of suitable reactor for the process. Hence kinetic studies were carried for all the processes selected for study for the oxidation of acetamiprid. Reaction constants were calculated for the processes by measuring the concentration of acetamiprid at different times during the reaction. The comparison of the processes were done on the basis of kinetic data obtained at optimum conditions

4.7.1 Fenton Process

The change in the concentration of acetamiprid with time for varying amount of H_2O_2 and Fe^{2+} is shown in Fig. 4.20 and 4.21 An increase in removal from 36 % to 99.9 % was observed when the H_2O_2 concentration increased from 20 to 250 mg/L for a Fe^{2+}concentration of 20 mg/L (Fig. 4.20). A slight decrease in removal of acetamiprid was observed when H_2O_2 concentration increased from 200 to 250 mg/L. It may be due to scavenging effect of H_2O_2 at higher concentrations.

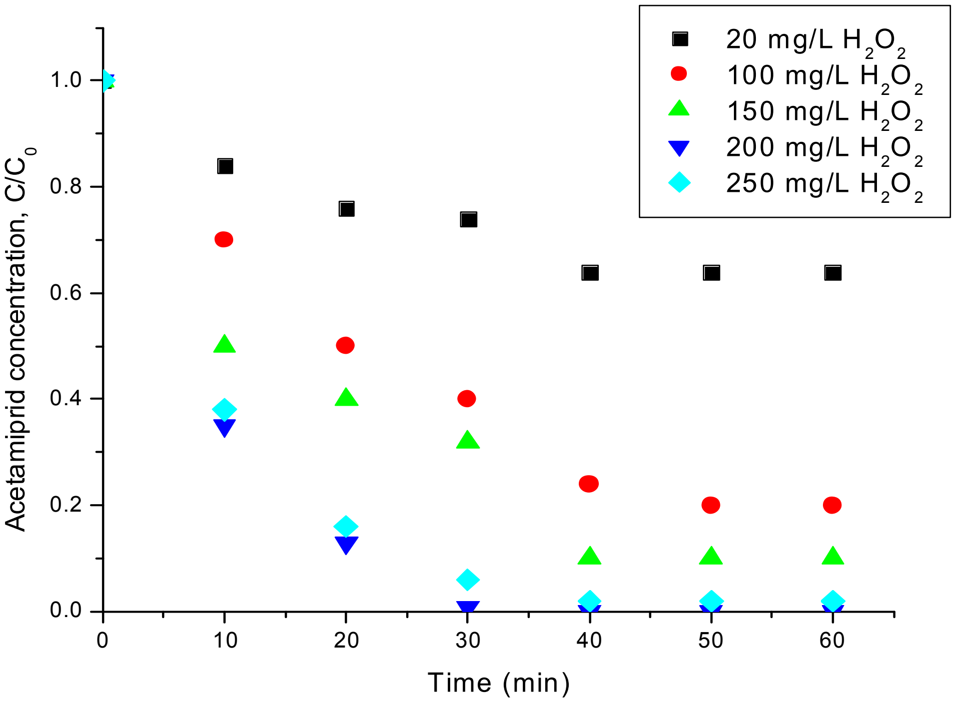

Fig.4.20 Effect of initial H_2O_2 concentration on acetamiprid removal at Fe^{2+} concentration of 20 mg/L for Fenton process

The effect of Fe^{2+} concentration on acetamiprid removal is shown in Fig. 4.21. An increase in removal of insecticide from 62 % to 99.99 % was observed when the Fe^{2+} concentration increased from to 2 to 25 mg/L. Complete removal of acetamiprid was achieved when the concentration of Fe^{2+} was 20 mg/L. The use of minimum amount is recommended to reduce the sludge formation and scavenging effect of reagents (Neyens and Baeyens, 2003).

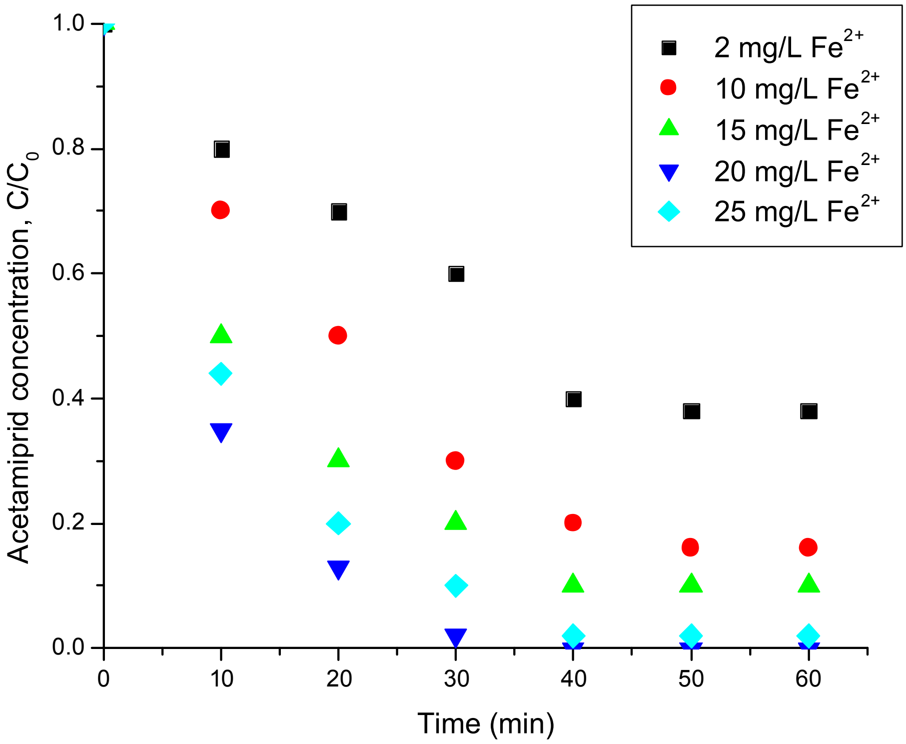

Fig. 4.21 Effect of initial Fe^{2+} concentration on acetamiprid removal at H_2O_2 concentration of 200 mg/L for Fenton process

The time dependent chromatograms of the samples after Fenton process at initial concentrations of 200 mg/L H_2O_2 and 20 mg/L Fe^{2+} is shown in Fig.4.22. The peak intensity corresponding to acetamiprid (retention time- 4.4 min) reduces as the time passes and it disappears completely after 40 minutes

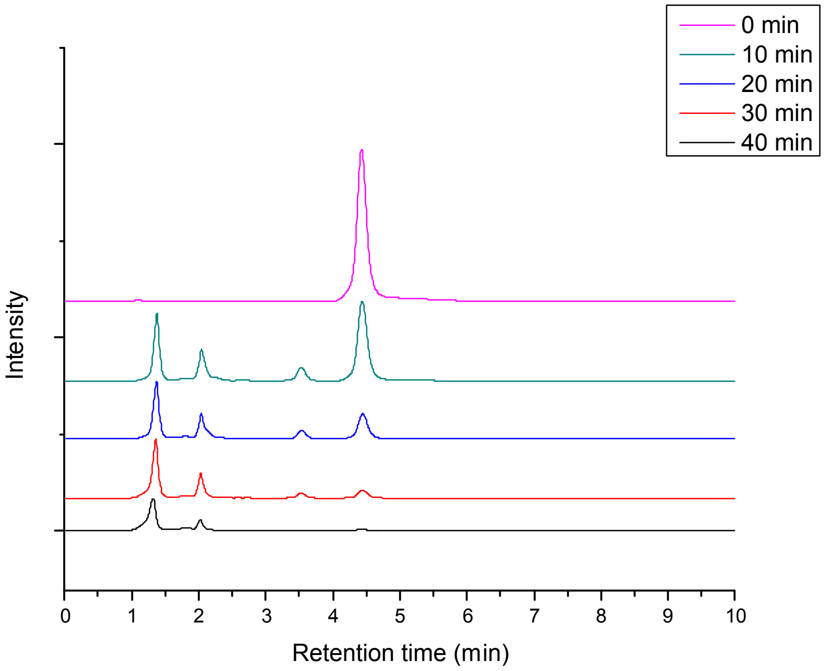

Fig.4.22 Time dependent chromatograms of the samples after Fenton process

The effect of initial concentration of acetamiprid was studied by varying the concentration of acetamiprid at initial H_2O_2 concentration of 200 mg/L and Fe^{2+} concentration of 20 mg/L and is shown in Fig.4.23. At low concentrations of 5 mg/L the pesticide disappeared very fast, whereas at higher concentration of 75 mg/L complete removal could not be achieved even after 60 minutes.

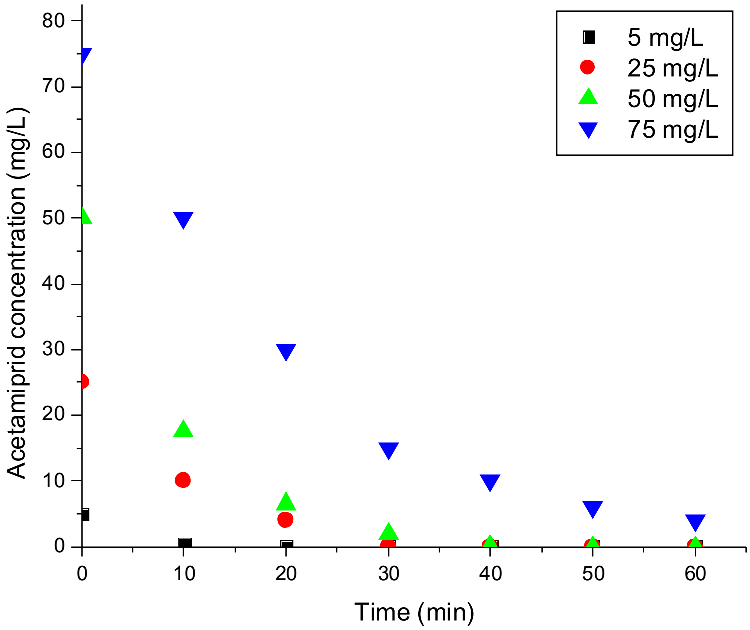

Fig. 4.23 Effect of initial concentartion of acetamiprid on the degradation acetamiprid by Fenton process

4.7.2 UV Treatment

The variation of concentration of acetamiprid with time under UV treatment at pH 6 was recorded using HPLC. The variation with time is depicted in Fig. 4.24 and it shows slow removal of acetamiprid. The chromatograms recorded for one hour treatment are shown in Fig. 4.25. Acetamiprid concentration decreases initially at a faster rate and then the rate of removal decreases.

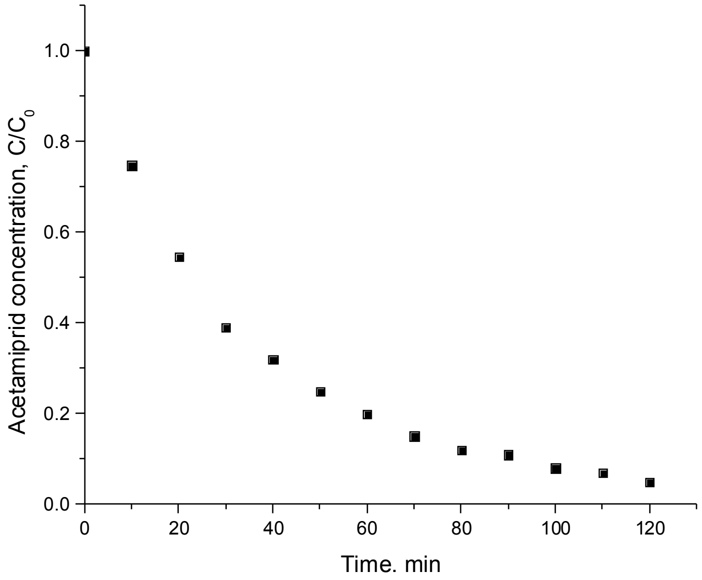

Fig. 4.24 Variation of concentration of acetamiprid with time for UV treatment at pH 6

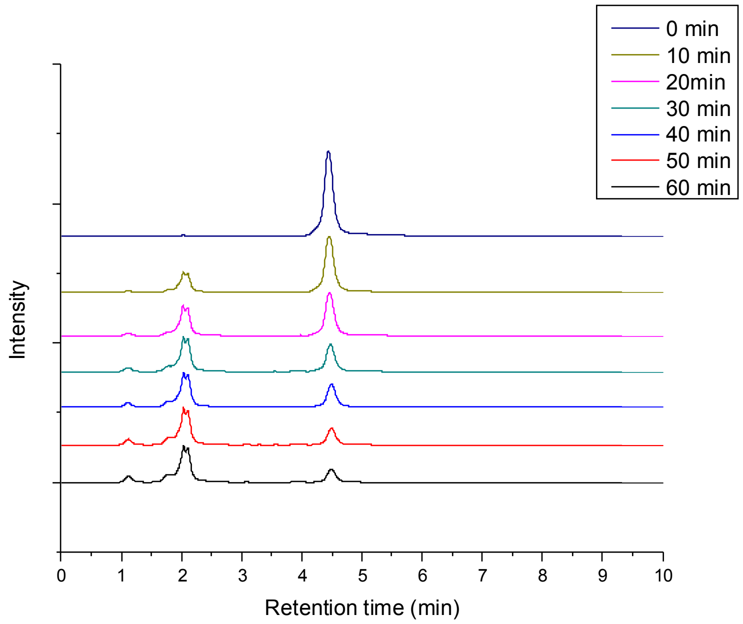

Fig. 4.25 Time dependent chromatograms after UV treatment at pH 6

The effect of variation of initial acetamiprid concentration on the removal of acetamiprid by UV treatment is shown in Fig. 4.26. At pH 6, when the pesticide concentration is 5 mg/L, the acetamiprid disappeared after 100 min treatment whereas at higher concentration of 75 mg/L only 75% removal could be achieved after 120 minutes of treatment.

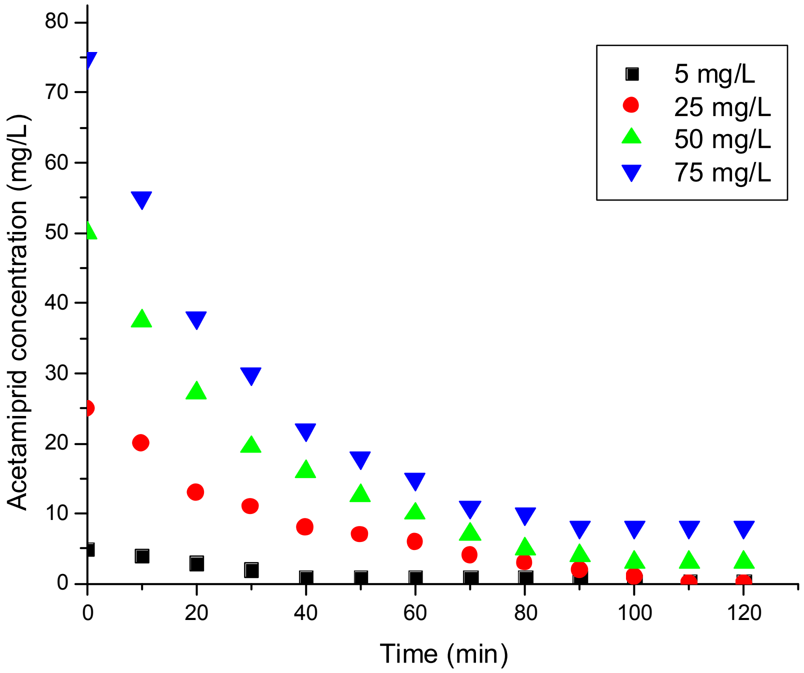

Fig. 4.26 Effect of initial acetamiprid concentartion on the degradation of acetamiprid by UV treatment

4.7.3 UV/ H_2O_2 Process

The effect of pH on the rate of removal of acetamiprid with H_2O_2/UV treatment is shown in Fig. 4.27. It shows a slight improvement in the removal when pH was increased from 3 to 9. The increase may be because of the higher photolysis rate of hydroxyl radicals at alkaline pH. But a slightly better removal rate was noticed at pH 6 as explained in section 4.4.1.

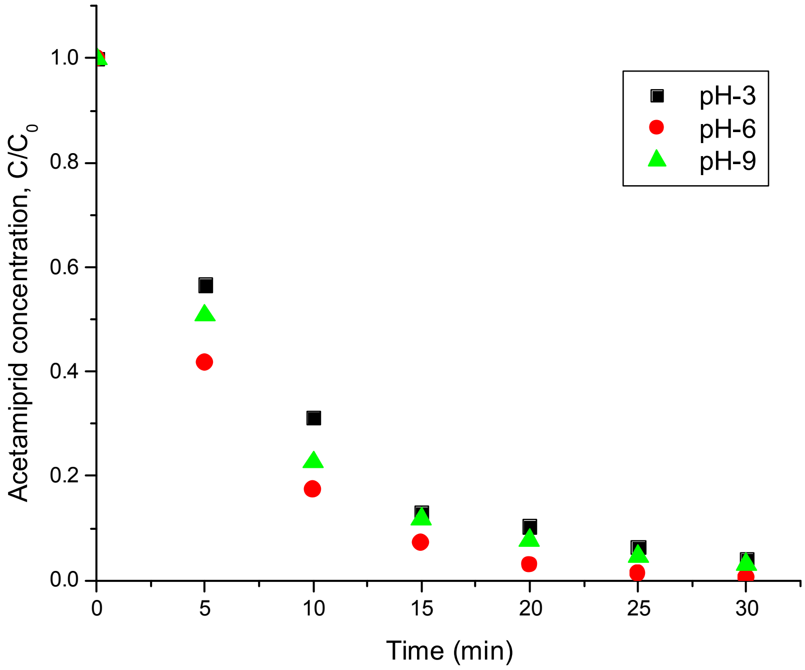

Fig.4.27 Effect of pH on acetamiprid removal at initial H_2O_2 concentration of 110 mg/L for UV/ H_2O_2 process

The effect of varying H_2O_2 concentration on the removal of acetamiprid with UV/ H_2O_2 process is shown in Fig. 4.28. An increase in removal from 85 to 99 was noticed when H_2O_2 concentartion increased from 20 to 100 mg/L. No significant increase in the removal was noticed when H_2O_2 increased from 100 to 200 mg/L. The use of H_2O_2 more than the optimum decreases the removal due to scavenging effect and also results in increase in the treatment cost (Hernandez et al., 2002).

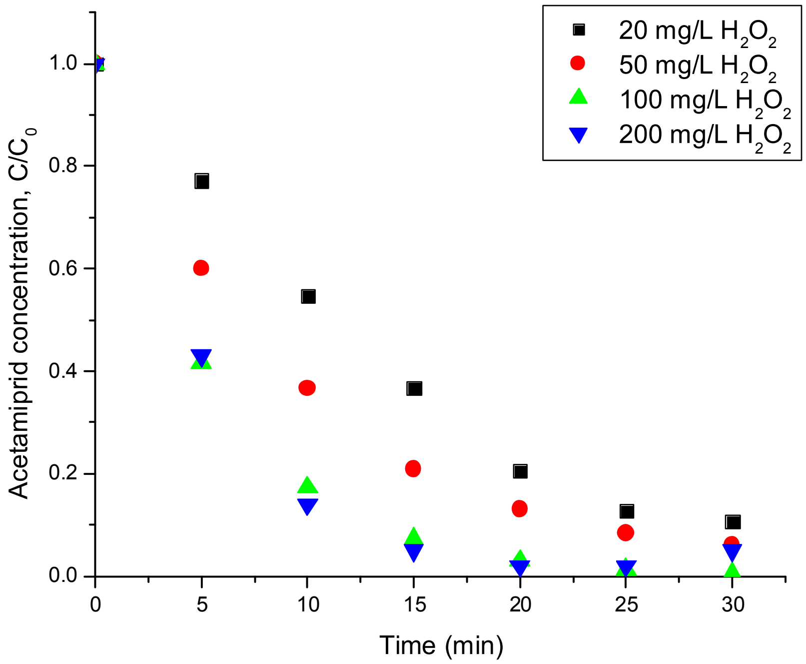

Fig.4.28 Effect of initial H_2O_2 concentration on acetamiprid removal at pH 6 for UV/ H_2O_2 process

The chromatograms for the samples collected at different times during UV/ H_2O_2 treatment were recorded and is plotted as shown in Fig. 4.29. The peak corresponding to acetamiprid is absent in the chromatogram of the sample collected after 30 min of the reaction.

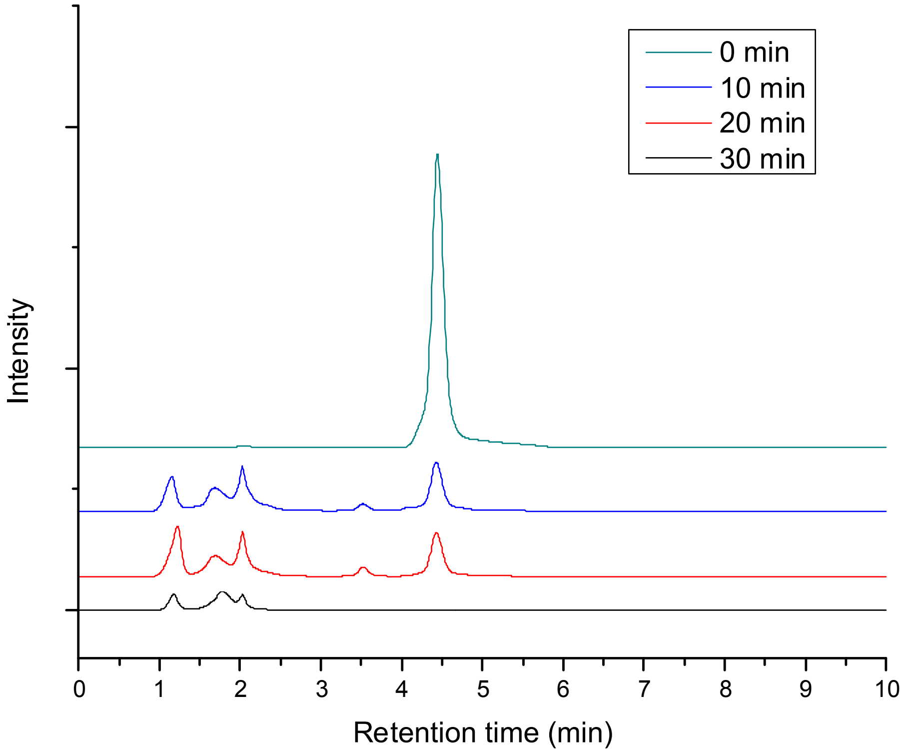

Fig.4.29 Time dependent chromatograms of the samples after UV/ H_2O_2 process

The degree of degradation obtained will obviously depend on the initial concentration of acetamiprid and the effect was studied by conducting the experiments for different initial acetamiprid concentration for a fixed pH and H_2O_2 concentration. As shown in Fig. 4.30, at higher concentration the removal decreased because of the insufficient radical formation.

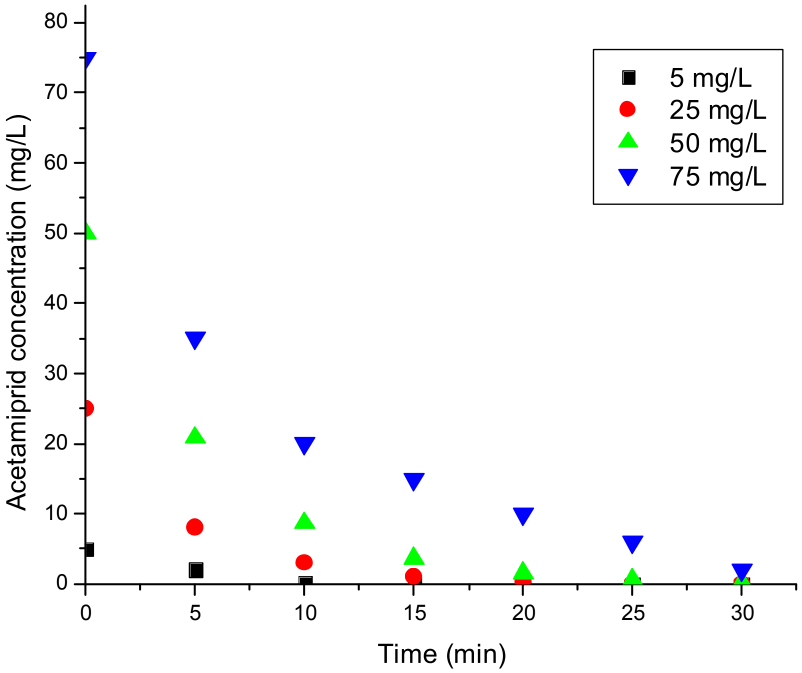

Fig. 4.30 Effect of initial acetamiprid concentartion on the degradation of acetamiprid by UV/ H_2O_2 process

4.7.4 Photo-Fenton Process

The effect of H_2O_2 on acetamiprid removal by photo-Fenton process is depicted in Fig. 4.31. An increase in rate of removal of acetamiprid was observed when H_2O_2 concentration increased from 2 to 20 mg/L. Further increase in H_2O_2 concentration didn't show significant improvement in the rate of removal. At higher concentration of H_2O_2 it shows slight reduction in rate of removal because of the scavenging effect of H_2O_2 as explained before.

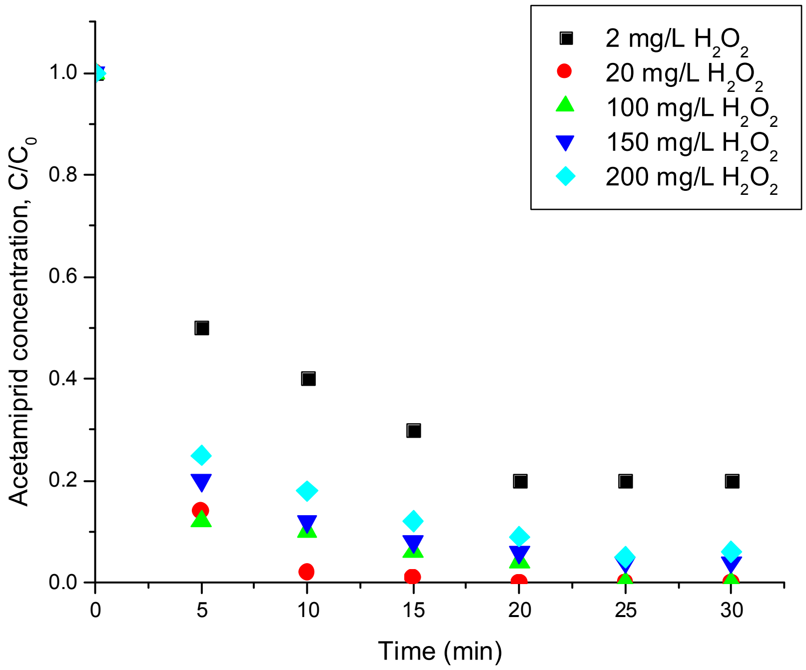

Fig. 4.31 Effect of initial H_2O_2 concentration on acetamiprid removal at Fe^{2+} concentration of 2 mg/L for photo-Fenton process

The effect of initial Fe^{2+} concentration on acetamiprid removal by photo-Fenton process is shown in Fig. 4.32. It shows an increase in removal when Fe^{2+} concentration was increased from 0.2 to 2 mg/L. Increase in H_2O_2 and Fe^{2+} concentrations above the optimum reduces the removal because of the scavenging effect as explained earlier.

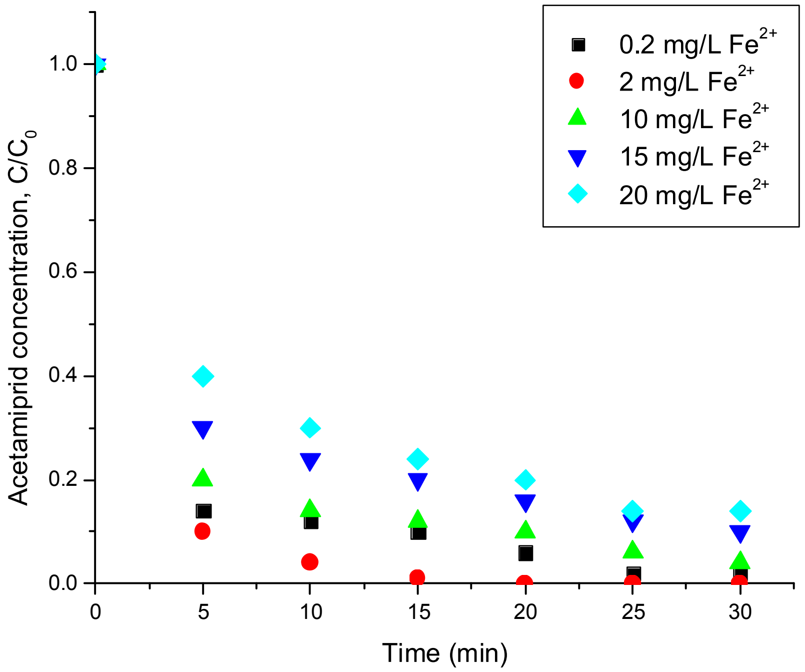

Fig. 4.32 Effect of initial Fe^{2+} concentration on acetamiprid removal at H_2O_2 concentration of 20 mg/L for photo-Fenton process

The chromatograms of the samples collected after photo-Fenton process at H_2O_2 concentrtaion of 20 mg/L and Fe^{2+} concentration of 2 mg/L is shown in Fig. 4.33. The peak corresponding to acetamiprid disappeared very fast in photo-Fenton which shows the high rate of removal in photo-Fenton process

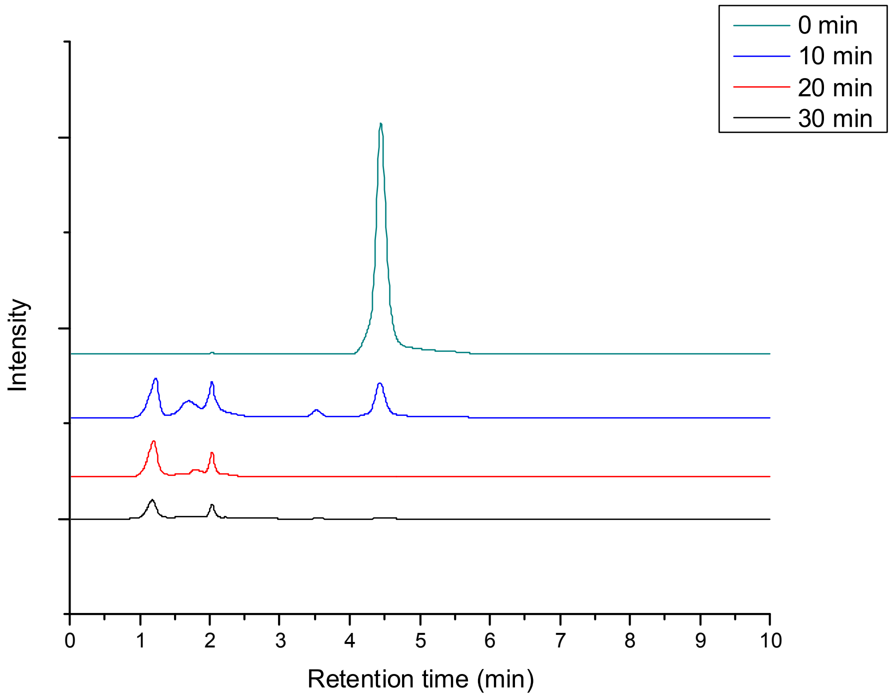

Fig.4.33 Time dependent chromatograms of the samples after photo-Fenton process

The effect of initial concentration of acetamiprid on the removal by photo-Fenton process was analysed by conducting experiments by varying the initial acetamiprid concenetration at fixed H_2O_2 and Fe^2+ concentration. The effect is shown in Fig.4.34. As expected the time required for removal increased with increasing initial acetamiprid concentration and for 75 mg/L the removal obtained was 96% after 30 minutes.

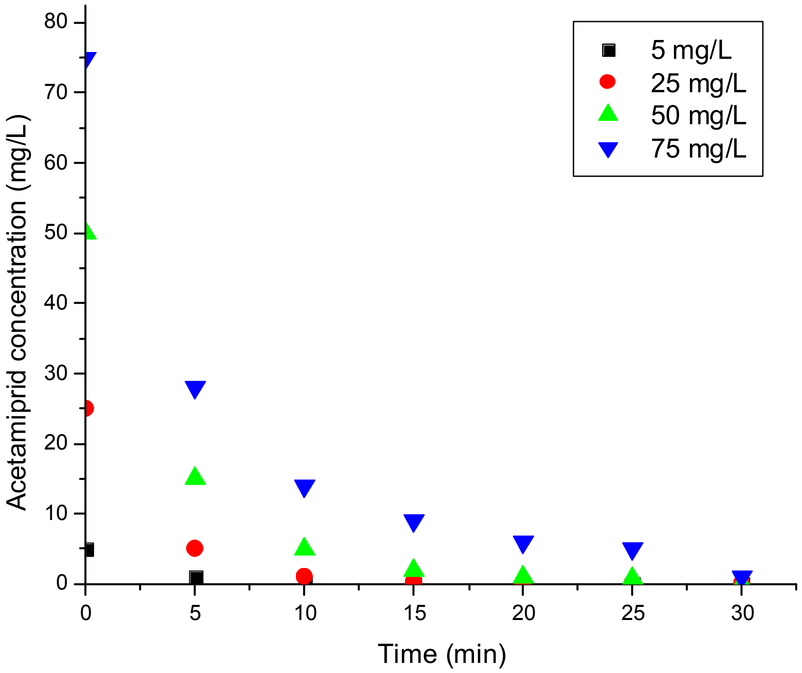

Fig. 4.34 **Effect of initial acetamiprid concentartion on the degradation of acetamiprid by photo-Fenton process**

4.7.5 Heterogeneous Photocatalysis Using Undoped and Doped TiO_2

The effect of operating parameters such as catalyst loading, doping and dopant concentration on the rate of removal of acetamiprid using TiO_2 is already discussed in the sections 4.6.3, 4.6.4 and 4.6.5.

The chromatograms for the samples collected at different times during the treatment using undoped, Cu doped and Fe doped TiO_2 is given Fig.4.35, 4.36 and 4.37 respectively

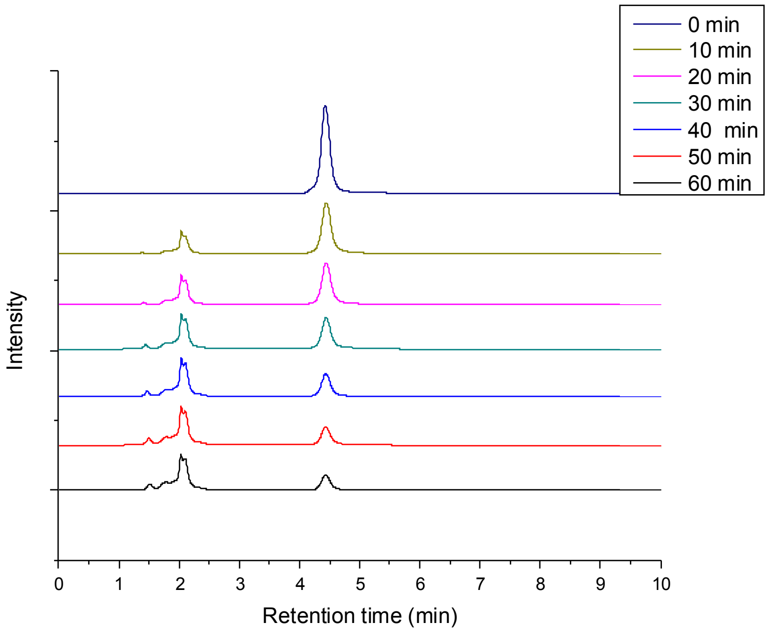

Fig.4.35 Time dependent chromatograms of the samples after photocatalysis using undoped TiO_2

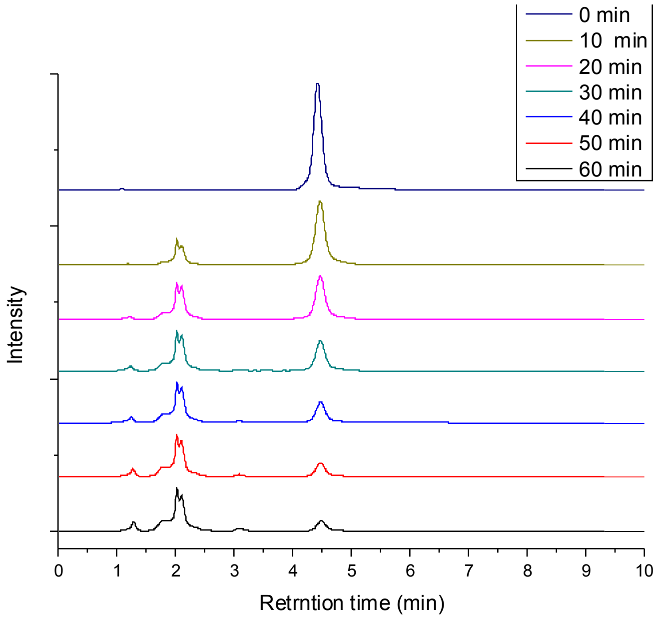

Fig.4.36 Time dependent chromatograms of the samples after photocatalysis using Cu (1 wt%) doped TiO_2

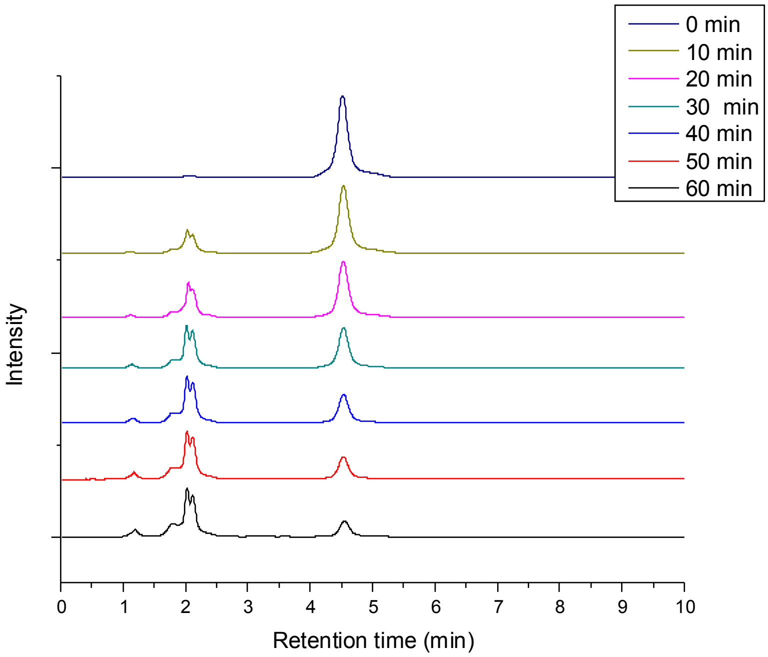

Fig. 4.37 **Time dependent chromatograms of the samples after photocatalysis using Fe (1 wt%) doped TiO_2**

It is evident from the chromatograms that the rate of removal was enhanced by the doping of TiO_2 with Cu whereas rate was decreased slightly by doping with Fe. The reasons are already explained in section 4.6.4.

The effect of initial concentration of acetamiprid on the removal using Cu doped TiO_2 is depicted in Fig. 4.38. The extent of removal decreases as the concentration of acetamiprid increases at fixed catalyst loading and dopant concentration.

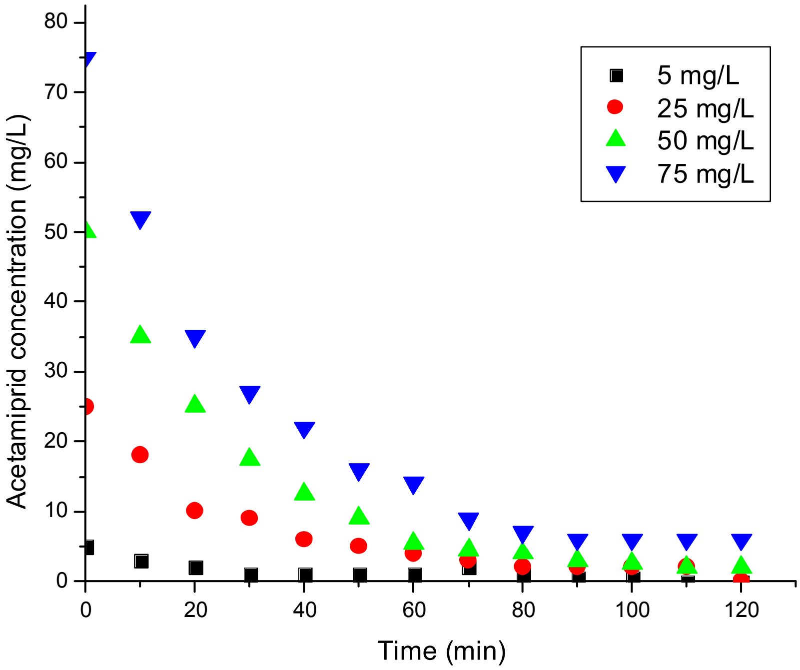

Fig. 4.38 Effect of initial acetamiprid concentartion on the degradation of acetamiprid by photocatalysis using Cu doped TiO$_2$

4.7.6 Comparison of the Processes on the Basis of Rate of Reaction

Hydroxyl radicals play an important role in oxidising the pollutant using AOPs. The rate of reaction depends on the concentration of the acetamiprid and the hydroxyl radical concentration. This can be represented as

$$\frac{dC}{dt} = -k[C][OH^{\cdot}] \quad \text{...} \quad (4.15)$$

where C is the concentration of acetamiprid and '*k*' is second order rate constant. In the presence of excess hydroxyl radicals, the rate equation can be written as

$$\frac{dC}{dt} = -k^{'}[C] \quad \text{...} \quad (4.16)$$

where $k^{'}$ is pseudo-first order rate constant

Thus,

$$ln\frac{C}{C_0} = -k^{'}t \quad \text{..} \quad (4.17)$$

where C_0 is the initial concentration and C is the concentration at time t.

The data obtained from the experiments conducted at optimum conditions of the respective process were fitted to the equation 17 and is plotted as shown in the Fig. 4.39. Half life period is calculated using the equation 17, when $C = C_0/2$ .Values of pseudo-first order rate constant, *k'*, R^2 and half life period for the treatment processes are given in Table 4.21

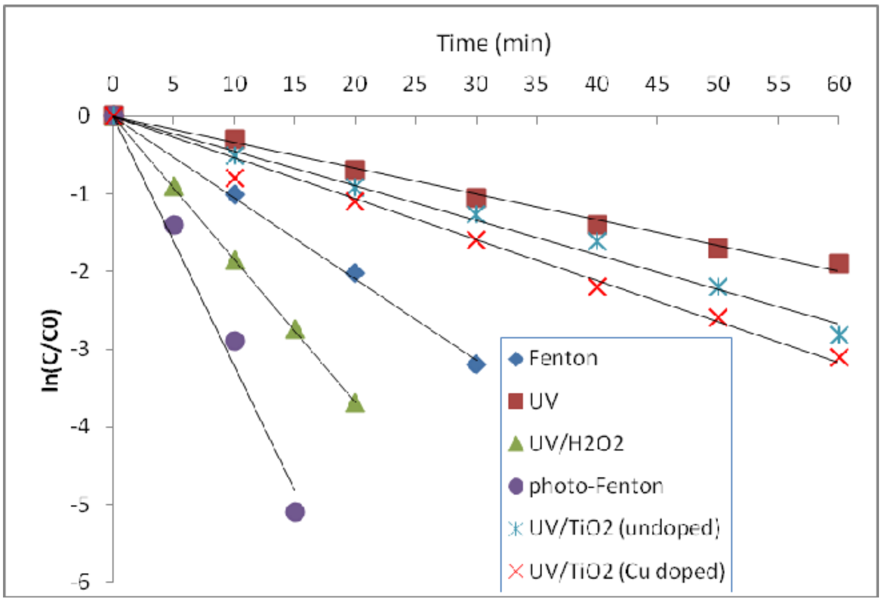

Fig. 4.39 Pseudo first order plot for the treatment processes

Table 4.21 Pseudo first order rate constants and half life period for different treatment techniques

Treatment technique	k' (min $^{-1}$)	R^2	Half life (min)
Fenton	0.1041	0.998	6.7
UV	0.0334	0.997	20.8
UV/ H_2O_2	0.1801	0.987	3.8
Photo-Fenton	0.3174	0.989	2.2
UV/ TiO_2 (undoped)	0.0445	0.989	15.6
UV/ TiO_2(Cu doped)	0.0532	0.987	13.0

It is clear from the kinetic plot (Fig. 4.39) and the data in Table 4.21 that the photo-Fenton process gives the highest reaction rate and hence low half life period. In photo-Fenton process the rate of reaction is increased because of the formation of additional hydroxyl radicals compared to Fenton process, as per the equation 4.10. UV process gives the lowest reaction rate. Addition of TiO_2 to UV process improves the removal rate because of the photocatalytic activity of TiO_2. Use of Cu doped TiO_2 improves the reaction rate slightly which was already discussed in section 4.6.4. Addition of H_2O_2 to UV process improves reaction rate from 0.0334 min^{-1} to 0.1801 min^{-1} due to the formation of hydroxyl radicals by the photolysis of H_2O_2. The rate of removal is in the order photo-Fenton>UV/H_2O_2>Fenton>TiO_2 photocatalysis>UV.

4.8 Cost Estimation

It was found that photo-Fenton gives the better removal within less time with lesser amount of reagents. Use of UV along with Fenton also reduces the sludge formation. But addition of UV increases the cost of the treatment. So a cost analysis is necessary before selecting the process for the treatment. The cost of full scale wastewater treatment plant depends on the nature and concentration of pollutant, the geometry of the reactor utilised, the lamp characteristics (if UV lamp is employed) and the flow rate of the wastewater (Esplugas et al., 2002). An attempt was made to calculate the approximate operating cost for the process based on the cost of materials used (Table 4.22). Calculation of cost for the processes utilising UV was based on electrical energy per order (EE/O) (Saritha et al., 2007) using the equation

$$EE/O(kWh/m^3) = \frac{P \times t \times 1000}{Vx60x\log(C_{init}/C_{fin})} \quad \text{......................}(4.18)$$

where P is rated power (kW), t is the time (min), V is the volume (liters), C_{init} and C_{fin} are initial and final concentration of the compound to be treated. The cost was calculated for the removal of 90% of the pollutant

Table 4.22 Cost of the reagents

Reagent	Basis	Cost (Rs)
H_2O_2	kg	320
$FeSO_4.7H_2O$	kg	300
Electricity	kWh	20

The result of the calculation is given in Table 4.23 (Refer Annexure 2 for sample calculation). It is evident from the cost data that the treatment with Fenton is costlier. It is because of the cost of the chemicals involved (H_2O_2 and Fe^{2+}). UV treatment is also costly because of the high treatment time involved. Use of H_2O_2 along with UV reduces the cost since it produces more hydroxyl radicals reducing the reaction time requirement.

Photo-Fenton process gives the lowest cost because of the improvement in reaction rate overweighs the cost involved in adding UV. The cost can be further reduced if the sunlight is used instead of artificial UV light. The cost for UV/TiO_2 process is not calculated here but it can be seen that since the improvement in rate is not significant by adding pure (undoped) and doped TiO_2, there will not be much reduction in the cost compared to treatment with UV. So it can be concluded that photo-Fenton gives the highest removal rate with lowest operating cost.

Addition of UV to a process requires special set up for the treatment which increases the initial cost. Fenton is the simplest process which does not require any special set up. So a total cost analysis becomes important before selecting the treatment process and that depends on the design of the reactor and the volume of the effluent to be treated.

Table 4.23 Operating cost of the treatment methods

Treatment method	***Cost (Rs/m^3)***
Fenton	95,245
UV	50,000
UV/H_2O_2	33,041
Photo-Fenton	10,056

4.9 Modeling of Acetamiprid Removal by Photo-Fenton Process

The objective of this modeling was to simulate the variation of acetamiprid concentration with time for different H_2O_2 and Fe^{2+} concentration As discussed in section 3.10.2, the values of kinetic constants (k_1, k_2, k_3, k_4, k_5, k_6, k_7 and k_8) were found out. The values obtained are given in Table 4.24

Table 4.24 Model parameters ($M^{-1}\ s^{-1}$)

k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8
76	50	$3.2\text{x}10^6$	$2.5\text{x}10^6$	$0.5\text{x}10^6$	$1.2\text{x}10^6$	$6.6\text{x}10^7$	$3.5\text{x}10^4$

As shown in Table 4.24 the lowest values were obtained for k_1 and k_2 corresponding to photo-Fenton cycle and it shows that the reactions 3.13 and 3.14 are the controlling steps for the process. A value in the range of 53-76 $M^{-1}s^{-1}$ is reported in the literature for k_1 (Kang et al., 2002b; Neyens and Baeyens, 2003; Kusic et al., 2006) and a value of 76 was used in this model. For Fe^{3+} reacting with hydrogen peroxide a value of 0.001-0.02$M^{-1}s^{1}$ is reported (Kusic et al., 2006). Here a value of 50 was obtained because of the enhancement in the reaction rate due to UV radiation. The highest value was obtained for k_7 corresponding to the reaction between hydroxyl and perhydroxyl radicals. The reaction between radicals is very fast and the value obtained is line with the values reported in literature (Cabrera Reina et al., 2006; Kusic et al., 2006). The values of k_3, k_4 k_5, k_6, are also within the range of the values reported in the literature (Neyens and Baeyens, 2003; Kusic et al., 2006).

The validation of the model was done by comparing the simulated concentration profile with that obtained by experiment for the validation runs. Comparison of the experimental values with simulated profiles is shown in Fig. 4.40.

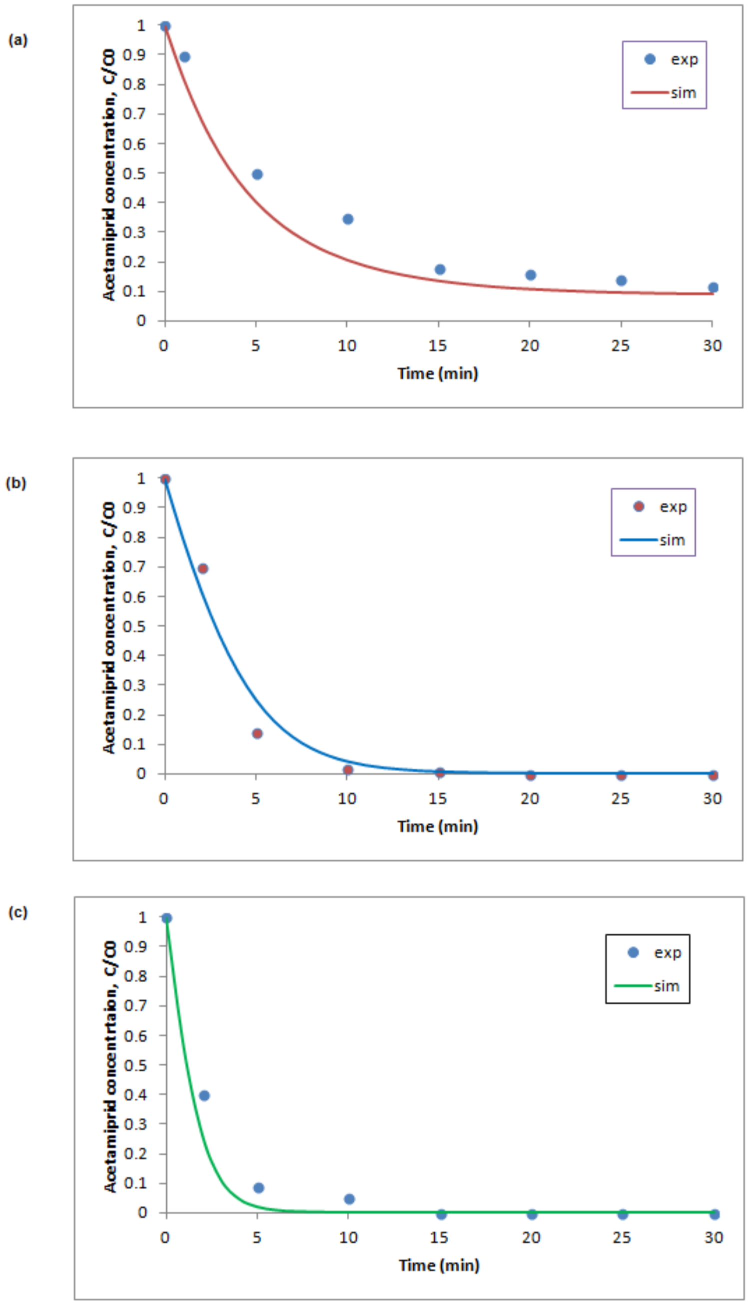

Fig. 4.40. **Experimental and simulated profiles of acetamiprid concentration at a) H_2O_2-10 mg/L, Fe^{2+}- 2mg/L b) H_2O_2-20 mg/L, Fe^{2+}- 2mg/L c) H_2O_2-100 mg/l, Fe^{2+}-5 mg/L**

It is to be noted that the predicted profiles using kinetic modeling gives a concentration profile very close to the experimental values.

The above model parameters mentioned in Table 4.24 were used to simulate the profile of acetamiprid for different initial concentration of acetamiprid to study the effect initial pesticide concentration.

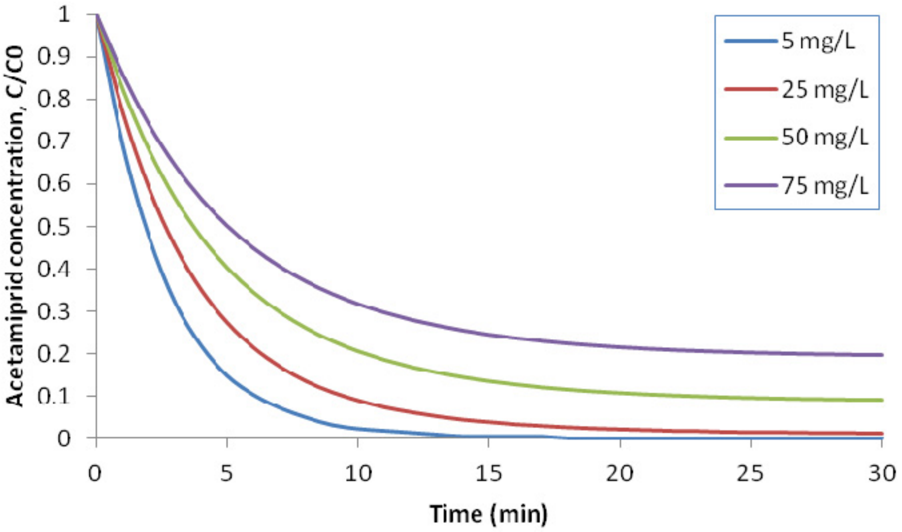

Fig. 4.41 Simulated concentration profiles of acetamiprid for various initial concentration of acetamiprid at fixed H_2O_2 and Fe^{2+} concentration

As expected, the extent of removal of decreases with increase in initial pesticide concentration at fixed H_2O_2 and Fe^{2+} concentration as shown in Fig. 4.41.

The effect of radiation intensity was also studied by simulating the profile at different intensity values. The variation is shown in Fig. 4.42. Simulated profiles shows a significant increase in removal when intensity was increased from 5 to 15 W/m^2. But the concentration profiles obtained for 25 W/m^2 and 40 W/m^2 are very close showing no significant improvement with increase in intensity of radiation. This is in line with the observation by Cabrera Reina et al. (2006) and Carra et al. (2014).

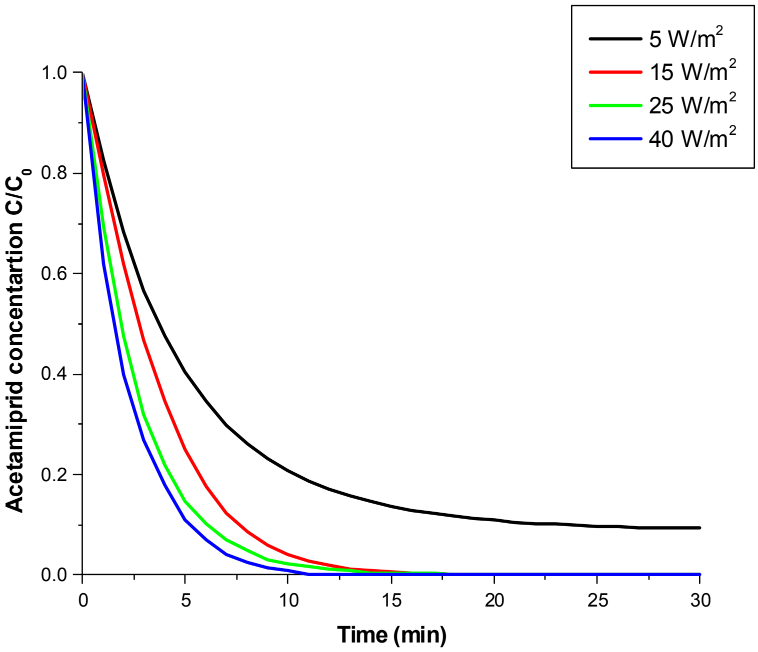

Fig. 4.42 Simulated concentration profiles for acetamiprid with varying intensity

4.10 Summary

The use of AOPs viz., Fenton, UV, UV/H_2O_2, photo-Fenton and heterogeneous photocatalysis for the removal of acetamiprid from wastewater has been investigated. The optimisation of the process parameters was done using response surface methodology (RSM). Second order model equations have been suggested for predicting the removal by the processes. The analysis of the models was done by ANOVA. The quality of the models were analysed statistically as well as experimentally. The kinetic studies were conducted for all the processes and the processes were compared on the basis of reaction rates obtained at optimised conditions. Cost estimation of the process is also presented to aid the comparison. It is observed that photo-Fenton gives highest removal rate. The order of rate of removal is photo-Fenton>UV-H_2O_2>Fenton>UV-Cu doped TiO_2> UV-undoped TiO_2>UV. A kinetic model for photo-Fenton was developed using the reaction rate expressions and mass balance equations for the important elementary reactions taking place in the process. Simulated acetamiprid concentration profiles were compared with the experimental values and were found to be in good agreement.

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Chapter 5

Summary and Conclusions

Contents

5.1 Summary

Conventional wastewater treatment systems based on biological treatment are not efficient to treat the wastewater containing recalcitrant compounds like pesticides. Advanced oxidation processes (AOPs) based on the oxidation of pollutant by hydroxyl radicals can effectively remove these pollutants. In AOPs hydroxyl radicals are produced in situ through different mechanisms. AOPs are showing success where biological treatment fails.

Acetamiprid is a neonicotinoid insecticide widely used to kill sucking type insects on crops such as leafy vegetables, citrus fruits, pome fruits, grapes, cotton, cole crops, and ornamental plants. It is recommended as a substitute for organophosphorous pesticides because of its efficacy and nervous system attacking mechanism. Because of its widespread use it is increasingly found in the environment. It has high water solubility and low photolytic degradation rate. It is stable to hydrolysis at environmental temperature. It belongs to the toxicity category II based on the studies on rats. Even after its increased use, its removal methods are less frequently studied.

Five treatment methods (Fenton process, UV treatment, UV/H_2O_2 process, photo-Fenton process and photocatalysis using TiO_2) were selected for study to remove acetamiprid from wastewater, based on the preliminary experiments conducted and the literature survey. The influence of major operating parameters on the pesticide removal and TOC removal by the selected processes were investigated. Undoped TiO_2 and TiO_2 doped with Cu and Fe were prepared by sol-gel method. Characterisation of the prepared catalysts was done using XRD, SEM and DTA-TGA. All the experiments were designed using central composite design (CCD) of response surface methodology (RSM). Model equations were developed for the processes and were validated statistically as well as experimentally. Optimum operating conditions were found out for all the processes studied. Kinetic studies were carried out and the processes were compared based on reaction rate and approximate operating cost. Photo-Fenton was found to be the fastest method with lowest operating cost. A kinetic model was developed for photo-Fenton process using the elementary reaction constants available in the literature and the kinetic data collected through experiments.Using this model it is possible to predict the variation of acetamiprid concentration with time for different H_2O_2 and Fe^{2+} concentrations

5.2 Conclusions

The conclusions derived from the study are

- The selected AOPs viz. Fenton process, UV treatment, UV/ H_2O_2 process, photo-Fenton and TiO_2 photocatlysis are viable options for the removal of acetamiprid from wastewater.
- The rate of removal with Fenton process increases with increase in initial H_2O_2 and Fe^{2+} concentration.
- Effect of pH on the removal rate of acteamiprid by UV treatment is not much significant.
- Use of UV along with H_2O_2 increases the removal rate of acetamiprid.
- Removal of acetamiprid decreases when H_2O_2 concentration increases beyond a certain value due scavenging of hydroxyl radicals.
- Addition of Fe^{2+} to UV/H_2O_2 process increases the reaction rate.
- There was almost 10 times reduction in the amount of reagents required when photo-Fenton was used instead of Fenton process
- Doping of TiO_2 with Cu enhances the removal rate of acetamiprid by photocatalysis while with Fe doping removal decreases.
- Conducting the treatment at optimum operating conditions is important since excess use of reagents will result in reduction in removal rate and increase in operating cost.

- All the processes follow pseudo-first order kinetics.
- The pseudo-first order reaction constants obtained for the processes at optimised conditions are Fenton- 0.1041 min^{-1}, UV – 0.0334 min^{-1}, UV/ H_2O_2- 0.1801 min^{-1}, photo-Fenton- 0.3174 min^{-1}, UV/undoped TiO_2- 0.0445 min^{-1} and UV/Cu doped TiO_2- 0.0532 min^{-1}
- Photo-Fenton process gives highest removal rate with lowest operating cost.
- The systems using UV require special experimental set up to enhouse the UV lamps and capture the light output, whereas as for Fenton process no sophisticated set up is necessary. Hence total cost analysis should be done before selecting the treatment system.

5.3 Limitations of the study

- Effect of temperature on the removal of pesticide was not studied. All experiments were conducted at room temperature (28 ± 2^0C)
- Surface area determination and the composition analysis of prepared photocatalysts using EPS/EDX etc. were not carried out as the enhancement in the removal rate of acetamiprid with doped TiO_2 was not much significant.
- The improvement in the photocatalytic activity of doped TiO_2 under visible light was not investigated.
- Cost comparison of the processes was done based on operating cost. Initial capital cost was not calculated which depends on the design of the reactor employed.

5.4 Scope for future Research

- Possibility of coupling of two or more AOPs could be investigated to reduce the treatment time and to improve the mineralisation efficiency.
- Studies on the removal using TiO_2 doped with other metals/non-metals could be carried out.
- Pilot plant studies using real wastewater could be done using the optimal range of values for the operating parameters. Scaling up of the laboratory set up to pilot plant could be carried out.

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Annexure

Annexure I

Calibration Details for determining acetamiprid concentration using HPLC

Equipment used: Hitachi Elite Lachrome

Column used: C18 ((Shodex, 5 µm, 4.6 x150 mm)

Mobile phase: Acetoinitrile/ water (70/30)

Flow rate: 1 mL/min

Sample volume: 20µl

Retention time for acetamiprid : 4.4 min

Calibration curve is plotted between concentration of acetamiprid (mg/L) and area of the peak at 4.4 min.

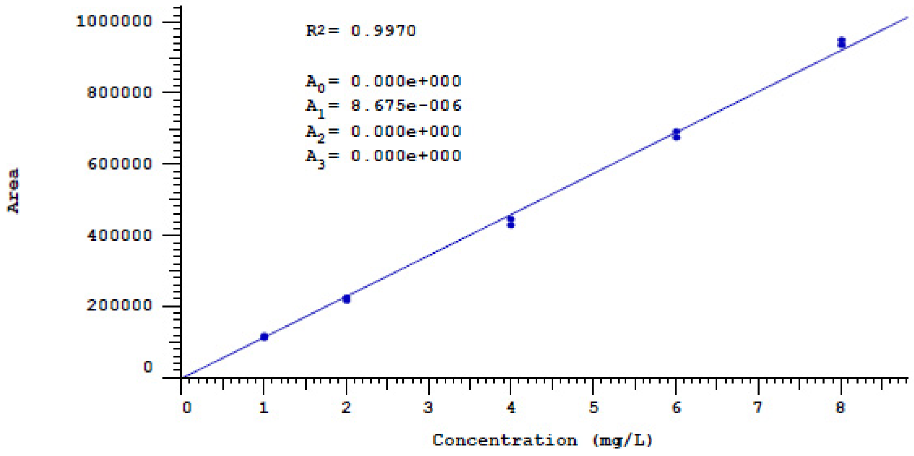

Fig. A1 Calibration curve for acetamiprid using HPLC

Annexure II

Important equations used in the calculation

Initial acetamiprid concentration = C_{init}

Final acetamiprid concentration = C_{fin}

Initial TOC = TOC_{init}

Final TOC = TOC_{fin}

Acetamiprid removal (%) = $\frac{C_{init} - C_{fin}}{C_{init}} * 100$

Acetamiprid removal (%) = $\frac{TOC_{init} - TOC_{fin}}{TOC_{init}} * 100$

Calculation of operating cost (refer table 4.22 and 4.23)

Operating cost calculation for photo-Fenton process

Cost of Electricity =Rs 20/kWh

Cost of H_2O_2= Rs 320/kg

Cost of FeSO4.7H2O= Rs 300/kg

a) Cost of electrical energy

$$EE/O(kWh/m^3) = \frac{P \times t \times 1000}{Vx60x\log(C_{init}/C_{fin})}$$

Lamp power P= 125 W= 0.125kW

Time taken for 90 % removal of acetamiprid = 15 min

Volume of wastewater treated = 0.5 litres

C_{init} / C_{fin} = 10 (90% removal)

$$EE / O(kWh / m^3) = \frac{0.125 \times 15 \times 1000}{0.5x60x \log 10}$$

Cost of electrical energy = (cost of Electricity/KWh) xEE/O

= Rs 625/m^3

b) Cost of H_2O_2

Amount of H_2O_2 used = 20 mg/L

Cost of H_2O_2 = $\frac{20*1000*320}{1000}$

= Rs.6400/m^3

c) Cost of $FeSO_4 . 7H_2O$

Amount of Fe^{2+} used = 2 mg/L

Amount of $FeSO_4$ $7H_2O$ needed = $\frac{277.84*2*1000}{55*1000}$ kg/m^3

Cost $FeSO_4 . 7H_2O$ = $\frac{277.84*2*1000*300}{55*1000}$

= Rs 3031/m3

Total operating cost for the treatment (a+b+c) = Rs 10056/m^3

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List of Publications

Journals

[1] P.A.Fasnabi, G.Madhu, P.A.Soloman (2014), Removal of acetamiprid from wastewater by Fenton and photo-Fenton processes- Optimisation by Response surface methodology and kinetic study, CLEAN- Soil, Air, Water (accepted).

[2] P.A.Fasnabi, G.Madhu, P.A.Soloman (2014), Advanced oxidation processes for the removal of acetamiprid from wastewater- Optimization and kinetic study, Environmental Engineering and Management Journal (accepted).

[3] P.A.Fasnabi, G.Madhu, K.N.Ajeesh, Optimization of Acetamiprid Removal from wastewater using Pure and Cu,Fe doped TiO_2 Photocatalyst under UV radiation by Response Surface Methodology, Journal of Environmental Chemical Engineering (communicated).

Conferences

[1] P. A. Fasnabi**,** G. Madhu**,** Removal of non biodegradable compounds from waste water using fenton oxidation process, International Conference on Materials for Future, 23-25 February 2011, Government Engineering College, Thrissur.

[2] P. A. Fasnabi**,** G. Madhu**,** Fenton Process for the Degradation of neonicotinoid Insecticide , Chemference 2011, 23-24 September , Indian Institute of Science, Bangalore.

[3] P A Fasnabi, Ginna Vincent, G,Madhu: Fenton Process for pesticide removal-Optimization by Statistical methods, NATCON 2012, 9-10th February 2012, Govt. Engineering College, Thrissur,.

[4] Ginna Vincent, P A Fasnabi, Treatment of Acephate by Fenton oxidation, NATCON 2012, 9-10th February 2012 Govt. Engineering College, Thrissur,

[5] P.A.Fasnabi, N.Manoj, G.Madhu, Pesticide Removal by ozonation, National conference on Advances in Manufacturing Systems and Processes (NAIMSAP), 05-07 September 2012, Government Engineering College, Thrissur.

[6] P.A.Fasnabi, G.Madhu, Use of ultraviolet for pesticide Removal, International Conference on Materials for Future 2013 (ICMF 2013), 6-8 November 2013, Government Engineering College, Thrissur.

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Curriculum Vitae

Fasnabi P.A obtained her Bachelor's degree in Chemical Engineering from Government Engineering College, Thrissur in 1997 and M.Tech degree in Energy Engineering from National Institute of Technology, Tiruchirapalli in 2002. She joined as lecturer in Chemical Engineering in Government Engineering College, Kozhikode in 2004. Presently she is working as Assistant professor in Chemical Engineering in Government Engineering College, Thrissur. Her areas of interest include water and wastewater treatment, Energy audit & management and Process integration.

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