APPLICATIONS OF NOVEL COMPOSITE SUPPORT MATERIALS CAPABLE OF INCORPORATING IN-SITU DUAL EFFECT FOR DEGRADATION OF ISOPROTURON

Thesis

Submitted for the fulfilment of the Degree

of

Master of Science

By

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CERTIFICATE

This is to certify that the dissertation entitled **“Applications of novel composite support materials capable of incorporating in-situ dual effect for degradation of isoproturon”** being submitted by Miss Alisha Shandil to School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala in partial fulfilment of the requirements for the award of degree of **Master of Science in Chemistry,** is an authentic record of bonafide work carried out by her under my guidance and supervision. She has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results embodied in the thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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DECLARATION

I, the undersigned, hereby declare that the research work presented in M.Sc. project entitled **“Applications of novel composite support materials capable of incorporating in-situ dual effect for degradation of isoproturon”** has been carried out by me under the supervision and guidance of **Dr. Anoop Verma (School of Energy and Environment)** and **Dr. Soumen Basu (School of Chemistry and Biochemistry), TIET Patiala.**

Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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ABSTRACT

An unprecedented concept of integrated process by coupling photocatalysis and photo-Fenton especially in fixed mode has been presented in the current study for the removal of contaminants like isoproturon from aqueous solution in reduced treatment time. For fixed-bed studies spherical beads were prepared by combining definite proportions of clay, foundry sand (FS) which was utilized as an iron source and fly ash (FA) for TiO_2 immobilization. The parametric optimization was carried out using Box–Behnken design model (BBD) and response surface methodology. The process of degradation followed the first order kinetics with optimized condition for the integrated degradation of isoproturon with 0.444 ml dosage of H_2O_2, 42 spherical beads and 190ml of solution for duration of 176 min at pH 3.7. Approximately 80.96% reduction in the concentration of compound was observed after inducing the optimized conditions. The experiment was performed both in the presence of artificial UV light and natural sunlight to check the comparative efficiency of both the processes. The integrated treatment was also carried out in solar batch reactor under optimized conditions to expand its application to the industries for treating bio-recalcitrant compounds. The mineralization of isoproturon was validated through generation of nitrite, nitrate and nitrogen along with a definite reduction in COD. The recyclability of catalyst was confirmed by recycling the spherical beads characterized by the SEM/EDAX. The presence of iron along with TiO_2 on the surface of beads was confirmed through SEM-EDS, UV, DRS and FTIR. A tentative pathway for the degradation of isoproturon was also proposed based on the identification of intermediates through GC–MS analysis.

Keywords- In-Situ Dual process, Isoproturon, mineralization, Immobilized beads, Synergy

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ABBREVIATIONS

- AOP’s – Advanced Oxidation Processes
- BBD – Box Behken Design
- cm- centimetres
- cm^2- square centimetres
- eV- Electron volts
- E_g – Band gap energy
- eq- equation
- ft- feet
- gm- grams
- GC-MS- Gas Chromatography Mass Spectroscopy
- Hr^{-1}- per hour
- i.e.- That is
- kg- kilogram
- L- litre
- L^{-1}- per litre
- SEM-EDS- Scanning Electron Microscopy- Electron Dispersive Spectroscopy
- FTIR- Fourier Transform Infrared Spectroscopy
- UV/DRS- Ultraviolet Diffusive Reflectance Spectroscopy
- mg – Milligram
- min-1 - Per minute
- μL – Microlitre
- mL – Millilitre
- nm – Nanometres

- ^{o}C - Degrees Celsius
- $OH^{\bullet}$- Hydroxyl radical
- ppm - Parts per million
- RSM-Response Surface Methodology
- TiO_2- Titanium Oxide

CHAPTER 1

INTRODUCTION

Rapid growth in population and high prominence on attaining food grain sufficiency has pressurized the Indian farmers to switch to the considerable use of pesticides. It has been estimated that almost 100,000 tons of DDTs has been utilized in India alone, predominantly for agricultural purposes, due to their cost effectiveness and excessive toxicity, making them effectual for the control of pests and diseases **(Abhilash and Singh, 2009).** However, certain features such as persistency, instability and atmospheric distribution of the pesticides has brought about contamination of air ,water, and soil **(Singh and Singh, 2008).** India being an agricultural land, its surface fresh water bodies has become extremely prone to pollution, due to increased utilization of pesticides in agriculture.

Pesticides are certain substances or a mixture of substances, of chemical or biological origin, used by humans to mitigate or repel pests which destruct or interfere with the growth of crops, fruits and other vegetation. Pesticides are ought to be lethal to the targeted organisms only but excessive application of these compounds tend to harm the ecosystem and kill the live forms which are prerequisite to be beneficial. Pesticides get washed away with water from the fields which gets drained off into rivers imparting it with high toxic content and hence cause pollution that affects land and aquatic ecosystems in particular as the food for the fishes become susceptible to pesticides **(Ademola and Gideon, 2012).** Pesticides enter the food chain and hence effects our health has become a serious issue which is sure to become more crucial in time to come. These pesticides cause severe affects on humans and are highly lethal to aquatic life and soil flora and fauna **(Geerdink et al., 2002).** Depending on the type and concentration of pesticides their effects can be chronic, mild or acute.

Pesticides are an inescapable part of modern agriculture and the solution for pollution caused by these compounds is either to switch to biodegradable, non-toxic pesticides or limit the use of pesticides and treat the wastewater viably before releasing in to the environment.

Isoproturon 3-(4-isopropylphenyl)-1, 1-dimethylurea is a selective herbicide which belongs to the family of substituted ureas. The herbicide is intended for use in cereals by controlling annual grasses and broad-leaved weeds in them. The chemical is readily absorbed by roots and leaves of the weeds and hence inhibits photosynthesis. Various studies have confirmed presence of isoproturon in fresh water due to production plant discharges, surface runoff and runoff from agricultural sources **(Sharma et al., 2008).**

The increased application of pesticides has lead the water bodies to be extremely susceptible to pollution, hence conventional water treatment methods are most commonly used in industries in order to facilitate pesticide removal. The term is used generally to cover an assortment of treatment techniques, which have been used with success over more extended time scale to benefit a scope of industrial and municipal requirements. Conventional wastewater treatment strategies are typically classified as 1) preliminary treatment 2) primary treatment 3) secondary treatment 4) Tertiary treatment.

Conventional wastewater treatment techniques are not competent enough to totally expel many of these toxic pollutants introduced in urban wastewaters possessing certain drawbacks:

- In case of appliance of coagulants to raw water. Improper dilution of the solution, inadequate doses and inaccurate dosing are the most commonly recognized errors.
- Cleaning is a hassle.
- Sedimentation tanks are usually not well-devised for their applications.
- Short circuiting and inaccurate water abstraction may lead to operational resistibility and overloading of the consequent filters.
- In developing countries like India there is utilization of inoperative chlorination equipments.
- Temperature changes influence the tank greatly **(Zinicovscaia, 2016).**

The illustrated difficulties generally encountered with conventional water treatment results in the generation of water of erratic quality that is generally unsafe for consumption**.** More effective and efficient treatment techniques are required to diminish the environmental and potential effect of effluents. Degradation of these non biodegradable natural compounds is not possible by regular conventional wastewater treatments, hence Advanced oxidation processes (AOPs) are employed to evacuate natural and inorganic toxins as well as for complete mineralization **(Gogate and Pandit, 2004).**

(AOPs) are known as oxidation techniques involving creation of hydroxyl radicals by distinct approach which is utilized for pollutant expulsion **(Chatterjee and Dasgupta, 2005; Herrmann, 2005).** Heterogeneous photocatalysis is a form of AOP which serves as an efficient tool for effective degradation **(Gaya and Abdullah, 2008).** However concerns regarding recombination of charge carriers, increase in the treatment time, and cumbersome catalyst separation restricts the commercial visualization of the perspective model. Photo-Fenton is another AOP technique utilized for effective degradation of contaminants but these studies usually face problem in maintaining high dose of H_2O_2, there is production of high concentration of anions in the treated wastewater and large amounts of ferrous iron sludge **(Nidheesh, 2015).**

In order to overcome these drawbacks we have taken up studies involving immobilization of the catalyst on an effectual support material. Various studies related to TiO_2 immobilization have been studied over a list of different support materials. Present study has introduced a new concept of in-situ dual effect (photocatalysis + photo-Fenton) in fixed form for the degradation of herbicide isoproturon. The drawbacks of individual processes can be used efficiently to execute the dual effect more effectively in less time. In so called dual effect the idea is to extract the photo generated electrons from support to convert ferric to ferrous so that the Fenton reaction starts taking place along with photocatalysis. This has been taken up in the recent study of in-situ degradation of isoproturon.

CHAPTER 2

APPLICATIONS OF ADVANCED OXIDATION PROCESSES

2.1 Introduction

The ordinarily utilized conventional treatment techniques were not sufficiently proficient to deliver water that incorporates toxins within an acceptable limit. AOPs reported in the Figure 2.1 can be employed for the effective removal of contaminants, which involves oxidation of hydroxyl radicals. AOPs are recommended in the case of wastewater containing compounds of low biodegradability and high persistence. A chemical wastewater treatment system using AOPs mineralize the pollutants completely to CO_2 and water. In certain cases, the non-biodegradable contaminants are effectively converted to give biodegradable compounds by application of combination of AOP and biological treatment techniques **(Gogate, 2007).**

AOP is an oxidative approach which involves the formation of an intermediate radical or the hydroxyl radical ($OH^{\bullet}$). It’s typical oxidation potential is greater than the conventional oxidants makes them highly efficient in oxidation of large number of organic pollutants **(Devipriya and Yesodharan, 2005).** Hydroxyl radicals are extremely sensitive species and powerful oxidants. They react with target molecules with rate constants in the order 10^7 -10^{10} L/mol s **(Herrmann and Guillard, 2000; Lhomme et al., 2008)**. These hydroxyl radicals are also characterized as non-selective oxidizing agents and can react with organic compounds by electrophilic addition of $OH^{\cdot}$ Group, by hydrogen atom abstraction, or by electron transfer **(Legrini et al., 1993):**

$$^{\cdot}OH + R \rightarrow ROH \qquad [1]$$

$$^{\cdot}OH + RH \rightarrow {}^{\bullet}R + H_2O \qquad [2]$$

$$^{\cdot}OH + RX \rightarrow RX^{\bullet+} + {}^{-}OH \qquad [3]$$

In general, reactions [1] and [2] are extremely fast and result in new oxidized intermediates with lower molecular weight or are completely mineralization to give carbon dioxide and water. Electron transfer reactions Eq. [3] of hydroxyl radical with organics are uncommon **(Pignatello et al., 2006)**. These radicals are generated from oxidizing agents for example ozone or hydrogen peroxide, which are generally combined with metallic or semiconductor catalysts in presence of UV radiation **(Kim et al., 2009).**

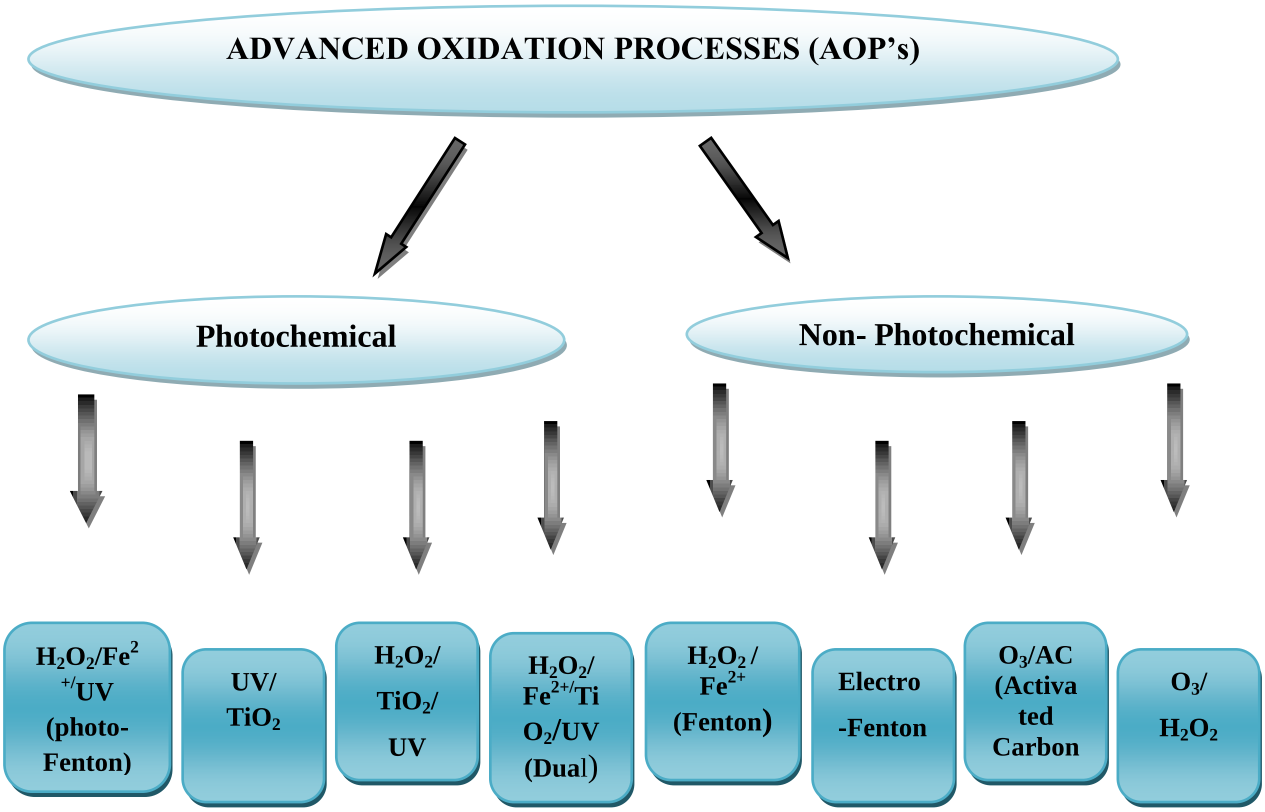


Figure 2.1: Classification of Advanced Oxidation Processes

2.2 UV photolysis and H_2O_2/UV process:

The photolysis is the process of degradation of organic compounds induced due to the presence of natural or artificial light. There are two types of photo-induced processes which can occur in aqueous matrices: direct photolysis and indirect photolysis. Direct photolysis involves, the absorption of UV light occurs by the organic compounds, which would react with components of aqueous solution to undergo self-decomposition. While in the latter case, there is photodegradation by photo-sensitizers e.g. hydroxyl or peroxyl radicals. In H_2O_2/UV process hydroxyl radicals are originated by the photolytic dissociation of hydrogen peroxide in water by UV irradiation **(Legrini et al., 1993).** This process employs the formation of hydroxyl radicals through the degradation of H_2O_2 in the presence of UV light.

2.3 Fenton Process:

The reaction between addition of H_2O_2 and iron was first described by the Fenton in 1895. Fenton and photo-reaction depends not only on the amount of H_2O_2 and iron combined but also depends upon the driving pH value. A homogeneous photo-catalytic degradation of H acid was done using Advanced Oxidation Processes (AOPs) such as UV/H_2O_2, UV, UV/H_2O_2/Fe^{2+} (photo-Fenton process). The experimental results showed degradation of dyes under UV light at pH= 3 after 90 min **(Gogate and Pandit, 2004; Oller et al., 2006).** The most often employed AOPs is the Fenton process wherein Ferrous ions is utilized as a catalyst and H_2O_2 as an oxidant. This process has been extensively utilized for the efficient eradication of dyes, pesticides, pigments, etc.

The overall Fenton reaction can be simplified by the following equation**:**

$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$ [4]

This equation demonstrates that the Fenton reaction is pH driven, mostly near the acidic pH (3) the hydroxyl radical would serve as a principal oxidant **(Neyens and Baeyens, 2003).**

It acquires various advantages such as immense performance rate and simple operation conditions like room temperature. The hydroxyl radicals would readily oxidise the pollutants to generate environmentally safe species like CO_2, water and certain intermediate compounds. Albeit of the wide studies and successful performances on wastewater treatments, it still comprises of certain disadvantages such as extravagant operating costs, small pH range, complications involved during recycle of the catalyst and large quantities of iron sludge formed. Including these disadvantages the Ferrous and Ferric ion concentration ranges from 50–80 ppm for batch processes, that is more than the limit which has been imposed by the European Union directives for direct release of wastewater into the environment **(Brillas et al., 2007).**

2.4 Photo-Fenton Process:

The limitations of the Fenton process can be diminished by the application of ultraviolet irradiation or solar irradiation, which are broadly recognised as Photo-Fenton process **(Soon and Hameed, 2011).**The prominent downside of the Fenton process involves the formation of iron sludge. Photo-Fenton method makes use of UV light together with Fenton reagent (H_2O_2 andFe^{2+}). There is an effective increase in the efficiency of the process predominantly due to renaissance of ferrous ions and additional production of hydroxyl radicals due to photolysis of ferric complex by UV radiation. It reduces the formation of iron sludge with the aid of converting the Fe^{3+} formed back to Fe^{2+} as specified in equation [5].

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + {}^{\bullet}OH \qquad [5]$$

The pH plays an important role in defining the rate of the photo-Fenton reaction, because it firmly determines which iron complexes are to be formed. The formation of extra hydroxyl radicals reduces the requirement of H_2O_2 and iron needed for the removals of pollutants.These studies usually have certain drawbacks like:

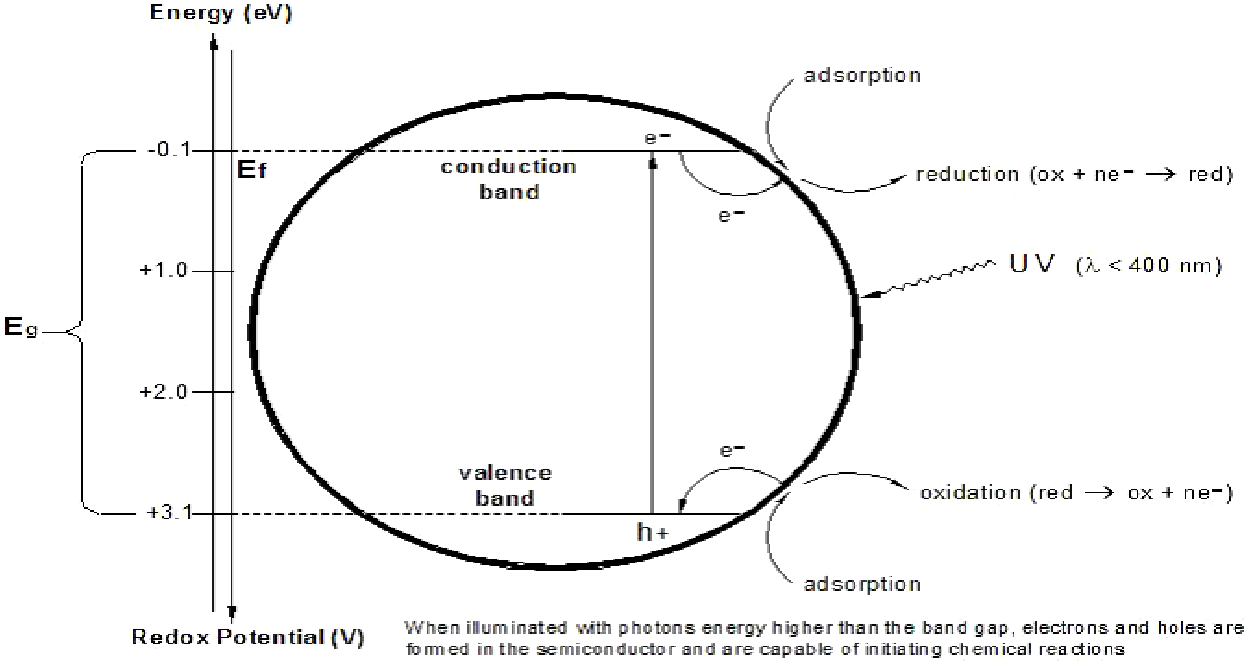
- It faces problem in maintaining high dose of H_2O_2
- the production of a large concentration of anions in the treated wastewater
- large amounts of ferrous iron sludge **(Devipriya and Yesodharan, 2005).**

2.5 Heterogeneous Photocatalysis:

Heterogeneous photocatalysis is an efficient tool for effective degradation of both aquatic as well as atmospheric organic contaminants. It comprises of acceleration by photo induced reaction in presence of semiconductor photocatalyst **(Gaya and Abdullah, 2008).** Semiconductors such as TiO_2, SnO_2, ZnO_2 are employed for the purpose to serve as a photocatalyst, although TiO_2 is predominantly the first preference for the reaction. The photocatalytic characteristic of TiO_2 was first discovered by Fujishima and Honda in 1972. They disclosed the photoinduced degeneration of water on TiO_2 electrodes, principally known as Honda- Fujishima impact. In 1977 Frank and Bard explored the similarity of utilizing TiO_2 to decay cyanide in water.

TiO_2 is extremely reactive and chemically stable under the UV light. There is a band gap of 3.3 eV between valence band and conduction band in titanium dioxide. When TiO_2 is irradiated by UV light the photoexcited photons acquiring energy greater than the given band gap results in promotion of an electron from valence band to conduction band **(Elmolla and Chaudhuri, 2010).** This will ultimately result in the production of an electron-hole pair as depicted in Figure 2.2. The electron-hole pairs produced may recombine or migrate towards the surface and hence exhibiting reaction with the adsorbed species. This would lead to the production of various reactive species which incorporates hydrogen peroxide, single oxygen, hydroxyl radical and superoxide anion radical **(Fujishima et al., 2000; Jiang et al., 2013).**

These principles are illustrated in the diagram below:



When illuminated with photons energy higher than the band gap, electrons and holes are formed in the semiconductor and are capable of initiating chemical reactions

Figure 2.2: Interpretations of principles of photocatalysis displaying the energy band diagram of TiO_2 spherical particles (source:**(Zaleska, 2008)**)

The initiation of photocatalytic reaction is when an electron gets excited due to absorbance of a photon of energy hυ which is equal to or more than the band gap of the given photocatalyst. The excited electron moves from the valence band of semiconductor photocatalyst to the empty conduction band leaving a hole behind in the valence band. Thus in brief there is generation of electron and hole pair (e^-, h^+). The following chain reactions initiate the mechanism by production of reactive species (eq 6-9).

Photoexcitation: $TiO_2 + h\nu \rightarrow e^- + h^+$ [6]

Oxygen ionosorption: $(O_2) + e^- \rightarrow O_2^{\cdot -}$ [7]

Ionization of water: $H_2O \rightarrow OH^- + H^+$ [8]

Protonation of superoxides : $O_2^{\cdot -} + H^+ \rightarrow HOO\cdot$ [9]

Oxidation and reduction takes place on the surface of the photoexcited semiconductor photocatalyst. There can be recombination of electrons and holes unless oxygen is available to scavenge the electrons leading to the formation of superoxides ($O_2^{\cdot -}$), hydroperoxyl radical ($HO_2^{\cdot}$) and H_2O_2 **(Gaya and Abdullah, 2008).**

There are certain drawbacks of photocatalytic degradation of majority of organic pollutants using TiO_2 in slurry.

- Separation of the catalyst from the aqueous solution post treatment is the principle limitation that restricts its useful application.
- Recombination of electrons and holes is the other limitation which controls the rate of degradation
- Large amount of time consumption **(Mecha et al., 2016).**

Hence, in order to overcome the hurdles of photocatalysis and Photo-Fenton process, an integrated process was studied in order to merge the pros of both the processes (photocatalysis and photo-Fenton process) and thereby attaining higher degradation of the pollutant. Researchers suggested working on fixed-bed photocatalysis, where catalyst is being coated on foundry sand and subsequently used for degradation. Studies related to fixing of catalyst on supports are extensively cited in literature **(Bansal and Verma, 2018) .** The dual process prompts the generation of hydroxyl radical in large numbers, because of the combined effect of TiO_2 Photocatalysis and Photo-Fenton. It prevents the frequent recombination of the electrons and holes by concentrating the electrons in the production of Fe^{2+} ions which are essential for Photo-Fenton reaction **(Bansal and Verma, 2017).**

Taking into consideration the cons of individual process the dual treatment was taken into consideration, fixed bed giving higher rate of degradation then the respective individual processes.

2.6 Dual Effect of photocatalysis and photo-Fenton

Research in this specific area of interest is always focused towards diminishing the treatment time along with optimizing the cost of the process. In the present study the idea of incorporating the dual effect (photocatalysis and photo-Fenton) was proposed in order to reduce the treatment time of the target pollutant. The dual process has excellent degradation efficiency but the field is not explored well yet. The cost of process and high dose of these chemicals can be substantially reduced if the two different processes (photo-Fenton and photocatalysis) are integrated together in one system which would simultaneously increase the degradation rate and reduce the degradation time **(Bansal et al., 2018).** The approach of binary effect has been recently suggested in a few studies for intensifying the degradation efficiency **(Adish Kumar et al., 2014).** The better degradation efficiency can be attributed to the fact that there is greater production of hydroxyl radicals which are generated simultaneously by both ongoing processes. Moreover, presence of iron would suppresses the recombination of electron and holes in TiO_2 and hence would enhance its photocatalytic activity.

There are limited studies on incorporation of dual processes for the wastewater treatment. Therefore, the proposed study would maximize the photocatalytic efficiency of the system by including the dual effect (photo-Fenton and photocatalysis) which can be well explained by the following equations (eq10-16):

$$\mathrm{Fe^{2+}_{aq} + H_2O_2 \rightarrow Fe^{3+}_{aq} + OH^- + OH^{\cdot}} \qquad [10]$$

$$\mathrm{Fe^{3+}_{aq} + H_2O_2 + H_2O \rightarrow Fe^{2+}_{aq} + H_3O^+ + HO_2^{\cdot -}} \qquad [11]$$

$$\mathrm{Fe^{3+}_{aq} + H_2O \overset{h\nu}{\rightarrow} Fe^{2+}_{aq} + H^+ + OH^{\cdot}} \qquad [12]$$

$$\mathrm{TiO_2 \overset{h\nu}{\rightarrow} e^- + h^+} \qquad [13]$$

$$\mathrm{TiO_2 + H_2O \rightarrow Ti\,OH^- + OH^{\cdot}} \qquad [14]$$

$$\mathrm{Ti\,OH^- + h^+ \rightarrow Ti\,OH^{\cdot}} \qquad [15]$$

$$\mathrm{TiO_2 + O_2 + e^- \rightarrow TiO_2 + O_2^-} \qquad [16]$$

Although these methods are successful in achieving high degradation efficiency yet there are many operational as well design implications which require improvement in the field scale visualization. Complicated mass transfer limitations, durability of the support, more time consumption etc are the points of concern for scale up studies. Over and above most scale up studies have been performed in recirculation mode **(Marugán et al., 2009)** thus offers more treatment time for a given batch. Thus keeping in mind the above concerns as well as field scale applications of this technology, the process was implied achieving high degradation.

CHAPTER 3

LITERATURE REVIEW

3.1 Presence of Pesticides in the environment

Pesticide-related pollution is an insistent environmental issue **(Dijkstra et al., 2002).** Pesticides tend to penetrate in the aquatic environment via agricultural runoff, during heavy rainfall and may also enter the fresh water bodies through accidental spills and wastewater discharges from industries as depicted in Figure 2.1 **(Haylamicheal and Dalvie, 2009; Lhomme et al., 2007).** Pesticides are extensively used and detected throughout the world in the freshwater bodies. Pesticide pollution is a significant contributor to poor water quality especially in India which is primarily an agricultural land. India is the largest manufacturer of pesticides in Asia and ranks 12th all over the world for the application of pesticides. The pesticides intake in India has shown a great hike during a small duration of time from 434MT to 46195.16MT in over last 50years **(P. Abhilash and Singh, 2009).** The pattern of utilization of various pesticides in India profoundly varies from rest of the world.

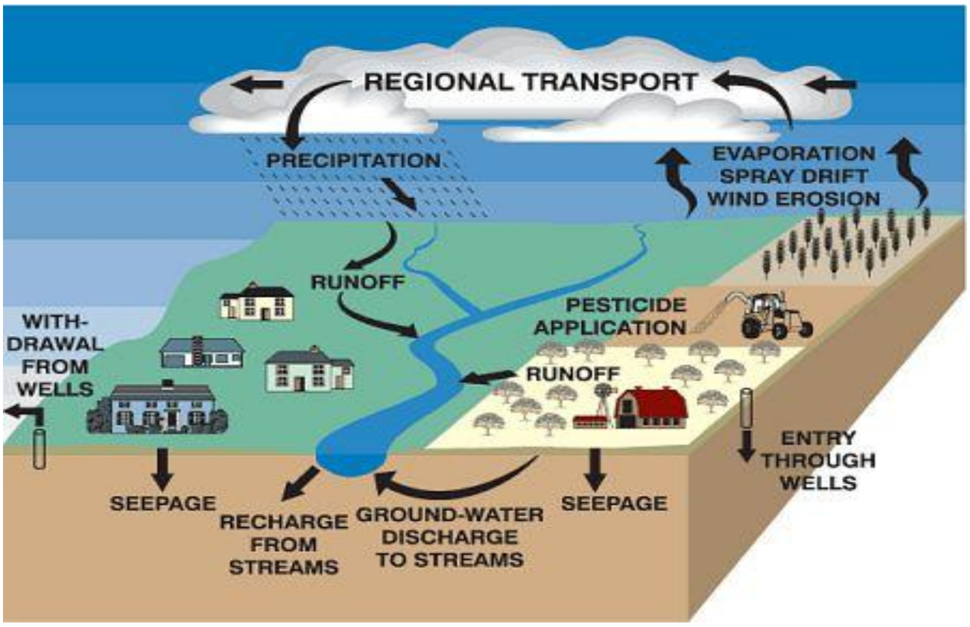


Figure 3.1: Routes of pesticide movement in the water cycle, Source:(**Resek, 1996)**

Research data shows only 0.1% of pesticides application target the pest’s rest 99.9% gets incorporated in the environment. Pesticides show hazardous effects on non-target organisms which includes humans, animals and the environment, showing a large range of toxic effects such as carcinogenicity **(Rathore et al., 2002)** and endocrine disturbing capabilities. A study which was conducted by the Centre for Environment and Science, New Delhi acknowledged an alarming increase in levels of pesticides in the blood samples of villagers in Punjab **(Pathak et al., 2011).** It has been estimated that 3 million people worldwide are poisoned due to the continuous use of pesticides and almost 20,000 people die every year due to pesticide consumption **(Jeyaratnam, 1990).**

Conventional water treatment does not facilitate efficient eradication of pesticides from freshwater bodies, therefore some alternative approaches were investigated. The most competent pesticide removal techniques involves adsorption and Advanced Oxidation Processes **(Sixto Malato et al., 2002; Rosal et al., 2008).**

3.2 Removal of Pesticides from wastewater utilizing AOP's

Oxidation is a chemical process which involves a net elimination of at least one electron from the molecular entity with a consequent increase in the oxidation number of an atom by gaining an oxygen atom or loss of hydrogen atom in any organic compound**.** (AOPs) are categorized as oxidation techniques which involves creation of hydroxyl radicals by distinct approach and are utilized for pollutant expulsion **(Echavia et al., 2009)**. These techniques are highly viable when wastewater incorporates compounds of high durability and low biodegradability. AOPs are estimated to be productive for the efficient mineralization of the pollutants to give CO_2 and water. The mechanism of AOPs chosen for the illustrated study and their applications has been reported in the literature given below.

3.2.1 Heterogeneous Photocatalysis

Photocatalysis is defined as the advancement in a photochemical change utilizing a catalyst like TiO_2 or Fenton's reagent **(Chatterjee and Dasgupta, 2005; Herrmann, 2005).** Despite the fact that heterogeneous photocatalysis has emerged in various forms photodegradation of organic pollutants is the most widely investigated topic. Most of the photocatalysts are semiconductor metal oxides such as SnO_2, ZnO_2 and TiO_2 which usually possess a narrow band gap. Radicals that are generated react with impurities in the wastewater and degrade them unselectively as depicted in Figure 3.2. Till now, Titania is the most frequently utilized semiconductor photocatalyst due to its cost effectiveness, inertness and photostability **(Gaya and Abdullah, 2008).** Photocatalysis exhibited by Titania is also referred as the "Honda-Fujishima effect" was first unraveled by the pioneering research of Fujishima and Honda**.** TiO_2 can either be used in slurry form or supported form.

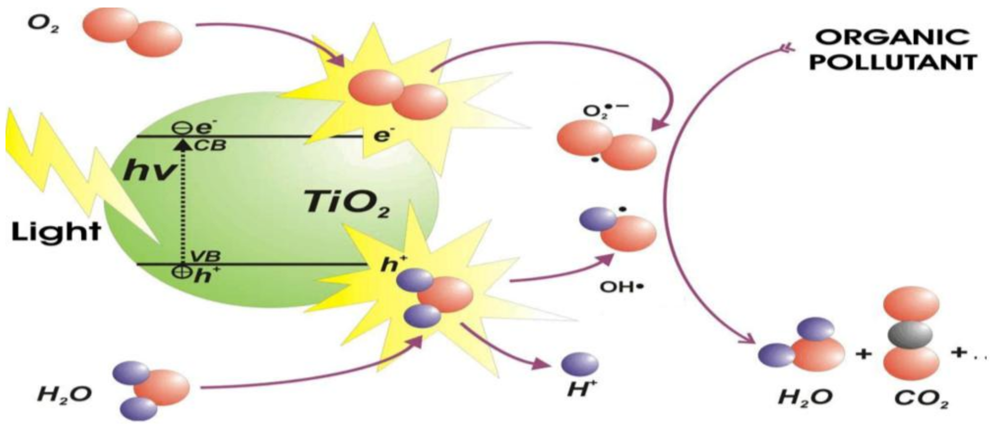


Figure 3.2: Mechanism for photocatalytic degradation of organic contaminants

Source: **(Ibhadon and Fitzpatrick, 2013)**

Fang et al., (2007) investigated the photocatalytic degradation of dye sulforhodamine-B (SRB) was carried out in aqueous solution in the presence of three different categories of light sources namely: UV light, natural solar light, and visible light at pH=2.5 utilizing titanium dioxide. Through the experimental results it was clear that a higher degradation of SRB was possible under artificial UV and natural solar light when compared with that of visible light as confirmed by COD and TOC analysis. The degradation rate constants for UV light, natural sunlight and visible light were found out to be 0.197 min^{-1}, 0.152 min^{-1}, 0.027 min^{-1}, respectively. The mineralization study was confirmed by the formation of amine products as indicated by infrared spectrophotometry.

Photocatalytic degradation of the antibiotic drug Chloramphenicol, was investigated **(Chatzitakis et al., 2008)** in aqueous form using semiconductors such as Titanium as photocatalysts. It was visible that, utilizing TiO_2 as a catalyst lead to a quantitative degradation of the organic compound following Pseudo-first-order kinetics. The dechlorination of the substrate was complete when the organic N was recovered in the form of NO_3^- and NH_4^+ ions. The effect of temperature on the rate of degradation of Chloramphenicol depicted similar activation energies when ZnO_2 and TiO_2 were used as photocatalysts. While the Kirby–Bauer method showed that there was 100% reduction in the drug activity after 90 min of photocatalytic treatment.

The photocatalytic decay of antibiotics such as amoxicillin, ampicillin and cloxacillin were investigated **(Elmolla and Chaudhuri, 2010)** by making use of TiO_2 catalysts under UVA (365 nm) irradiation. When there was addition of H_2O_2 at pH 5 and TiO_2 1.0 g/L it ensured a complete reduction in the concentration of amoxicillin, ampicillin and cloxacillin in 30 min.

The sonolytic, sonophotocatalytic as well as photocatalytic degradation of 4-chloro-2-nitrophenol was investigated **(Verma et al., 2015)** using TiO_2 in slurry mode. Experiments were performed using artificial UV light coupled with ultrasound for the purpose of sonicating the slurry. The optimum conditions for better degradation of the compound were determined as catalyst dose at 1.5 gL^{-1}, pH 7 and oxidant dose at 1.5 gL^{-1} at which 80 % degradation was obtained after 120 min of irradiation. Sonication imparted synergistic effect as degradation was improved to 96 % increase after 90 min of treatment in sonophotocatalysis.

Abdennouri et al., (2016) illustrated the use of photocatalytic process for effective degradation of pesticides utilizing titanium dioxide as a catalyst which is processed by sol-gel process and titanium pillared clarified clays. The outcome of the study determined that the process was efficient for degradation of pesticides.

Verma et al., (2014) carried out research for the photocatalytic degradation of a herbicide, Isoproturon in aqueous solution using TiO_2. The optimum conditions obtained for the better degradation of compound were TiO_2 dose of 0.5 gL^{-1}, pH 5.0, and C0 25 mgL^{-1}. The mineralization studies were also performed which were confirmed by the reduction in COD (96%) and TOC (90 %) along with the generation of ammonium ions whereas various intermediates formed were confirmed by the data of HPLC and LC-MS study.

However concerns regarding recombination of charge carriers, increase in the treatment time, complex reactor configuration, cumbersome catalyst separation restricts the commercial visualization of the perspective model **(Fukahori and Fujiwara, 2015; Sarkar et al., 2015).**

3.2.2 Photo-Fenton process

Fenton process is most widely applied degradation process for the removal of recalcitrant contaminants. But the development of iron sludge frequently restricts its operation. Hence, its cost effectiveness would be overshadowed by the cost required for sludge separation and its disposal. Photo-Fenton process was established with a motive to reduce the sludge accumulation, by the application of UV or solar light for the effective conversion of Fe^{3+} to Fe^{2+} ultimately causing a drastic reduction in the concentration of sludge waste **(Poyatos et al., 2010).**

The rate of decomposition of the organic compounds is significantly intensified in the presence of UV-Visible light in the reaction. The rates of the principal reactions involved in the process of degradation are increased and consequently the size of the reactor is reduced due to the reduction in sludge formation.

Pérez-Moya et al., (2008) utilized the photo-Fenton process considering the effective TOC eradication of textile effluents. The consequence of the change in pH of the solution, H_2O_2 and Fe^{2+} dosage, temperature of the reaction and intensity of light was inspected by the authors. They obtained 70 % TOC decrement at optimised conditions.

Concentration reduction of Reactive Red 45 (RR45) was carried out by photo-Fenton process with a primary RR45 dye concentration of 80 mg/L **(Peternel et al., 2007).** Total decolourisation of the dye was detected after duration of 1hr in a range of varying Fe^{2+} and H_2O_2 concentration. The ratio of Fe^{2+}/ H_2O_2 concentration was optimized at 1:60 at pH 3 and incident UV-light flux at 7.36×10^{-6}Einstein/s.

Malato et al., (2002) investigated the percentage degradation of water dispersible pesticides diuron, imidacloprid, formetanate and methomyl utilizing photo-Fenton process in the presence of solar energy. There was dissipation of the parent compound and 90% mineralization was attained for all the given pesticides.

González et al., (2007) illustrated the photo-Fenton process for the effective removal of the antibiotic sulfamethoxazole (SMX) from the wastewater when the H_2O_2 dose was kept to be $300mgL^{-1}$ and Fe^{2+} dose was $10mgL^{-1}$. The consequence of the given reaction was that the antibiotic concentration was reduced to 1mg/L at an H_2O_2 dose of $300mgL^{-1}$.

Badawy et al., (2006) undertook a comparison of Fenton process, UV/ H_2O_2 (photolysis) and photo-Fenton process in order to decompose organo phosphorous pesticides from wastewater. This resulted to a maximum percent of degradation exhibited by the photo assisted Fenton process. The optimized operation conditions were inspected to be pH 3, COD: H_2O_2 =1:2.2, H_2O_2: Fe^{2+} ratio = 50:1 utilizing 150 W of otimum pressure mercury lamp.

Photo assisted Fenton process was carried out **(Abdessalem et al., 2010)** for degradation of mixture of three pesticides namely chlortoluron, carbofuran and bentazon and hence, achieving 90 % of TOC removal after a duration of 2 hrs at optimised conditions**.**

These studies usually face problem in maintaining high dose of H_2O_2, there is production of high concentration of anions in the treated wastewater and large amounts of ferrous iron sludge **(Nidheesh, 2015).**

3.2.3 Fixed bed Catalysis

Numerous studies in the recent past have reported the applications of homogenous **(Alalm et al., 2015)** and heterogeneous photocatalysis **(Haroune et al., 2014)** for the treatment of pesticides. In all types, reactions leading to the formation of $OH^{\cdot}$ radicals which are main oxidizing agents, quantities of which are supposed to be maximum. Various authors have reported the photocatalytic treatment of pharmaceuticals for various rector using TiO_2 as a catalyst **(Prieto-Rodriguez et al., 2012).** However concerns regarding recombination of charge carriers, increase in the treatment time, complex reactor configuration, cumbersome catalyst separation restricts the commercial visualization of the perspective model **(Sarkar et al., 2015).**

Problems concerning the catalyst segregation from slurry can be solved by immobilizing the catalyst on an effectual support material. Various studies related to TiO_2 immobilization have been studied over a list of different support materials. Therefore, it is covetable to have a photocatalyst that can be easily substituted, cost effective and easy to produce. Different materials for supports of catalysts have been studied in literature for the degradation of wide variety of pollutants using glass beads, woven glass fabric **(Wang et al., 2007)** activated carbon, pumice stone, steel mesh **(Hosseini et al., 2008)**, clay materials **(Bouna et al., 2013)** and many more.

Veréb et al., (2014) investigated the photocatalytic degradation of phenol (100 ppm) using TiO_2 supported Al_2O_3-based ceramic paper. A titanium alkoxide was used as a fixing agent for immobilization. The photocatalytic efficiency of the coated ceramic paper was constant up to five 2hr cycles. Pilot-scale flow reactor employing impregnated ceramic sheet was also developed in which 60-95% degradation of model pollutants (phenol, oxalic acid, monuron) was achieved after 4hr of treatment.

Mukherjee et al., (2013) evaluated five distinct cross-linked polymer/TiO_2 composites for the photocatalytic degradation of aspirin under artificial UV and natural solar light. The freeze dried films had porous structure and exhibited highest degradation capability but they were not strong enough to maintain their stability after seven hours.

However, the prolonged use of immobilized catalyst and the durability of support material to be used for longer period are the major concerns to be looked carefully for field-scale applications. On the other hand the photocatalytic degradation sometimes does not completely degrade the pollutants having large structures **(Ziemiańska et al., 2010).** Therefore, subsequent removal of the organic compounds from the treated wastewater before discharge to water bodies is necessary. Sometimes there are several other limitations associated with the photocatalysis including increase in the treatment time for degradation of priority pollutant, mass transfer limitations, inertness of the support and durability. These drawbacks are not really attempting the fixed bed photocatalysis applications to work on commercial scale. Homogenous photocatalysis (mostly photo-Fenton) offers certain advantages in terms of homogenous nature, faster reaction rate wide working spectrum. The photo-Fenton systems which consist of irradiation by UV/Visible light strongly accelerate the degradation of large number of pollutants. This behavior is attributed to the irradiation which causes photochemical reduction of Fe (III) back to Fe (II), for which the reaction is summarized as (eq 17):

$$Fe^{3+} + H_2O + h\upsilon \rightarrow Fe^{2+} + H^{+} + {}^{\bullet}OH \qquad [17]$$

The photo-Fenton process involves certain operational and environmental advantages. The photo-Fenton process produces no new pollutants and requires only small quantities of iron salt **(Pignatello et al., 2006).** At the end of the reaction, if necessary, the residual Fe(III) can be precipitated as iron hydroxide by increasing the pH **(Babuponnusami and Muthukumar, 2014)**. These studies usually face problem in maintaining high dose of H_2O_2, the formation of a high concentration of anions in the treated wastewater and large amounts of ferrous iron sludge **(Nidheesh, 2015).** A recent novel concept has suggested the concept of dual effect i.e photocatalysis and photo-Fenton. The drawbacks of one process can be used efficiently to run the second process simultaneously. In so called dual effect the idea is to extract the photo generated electrons to convert ferric to ferrous so that the Fenton reaction starts taking place as shown in the Figure 3.3.

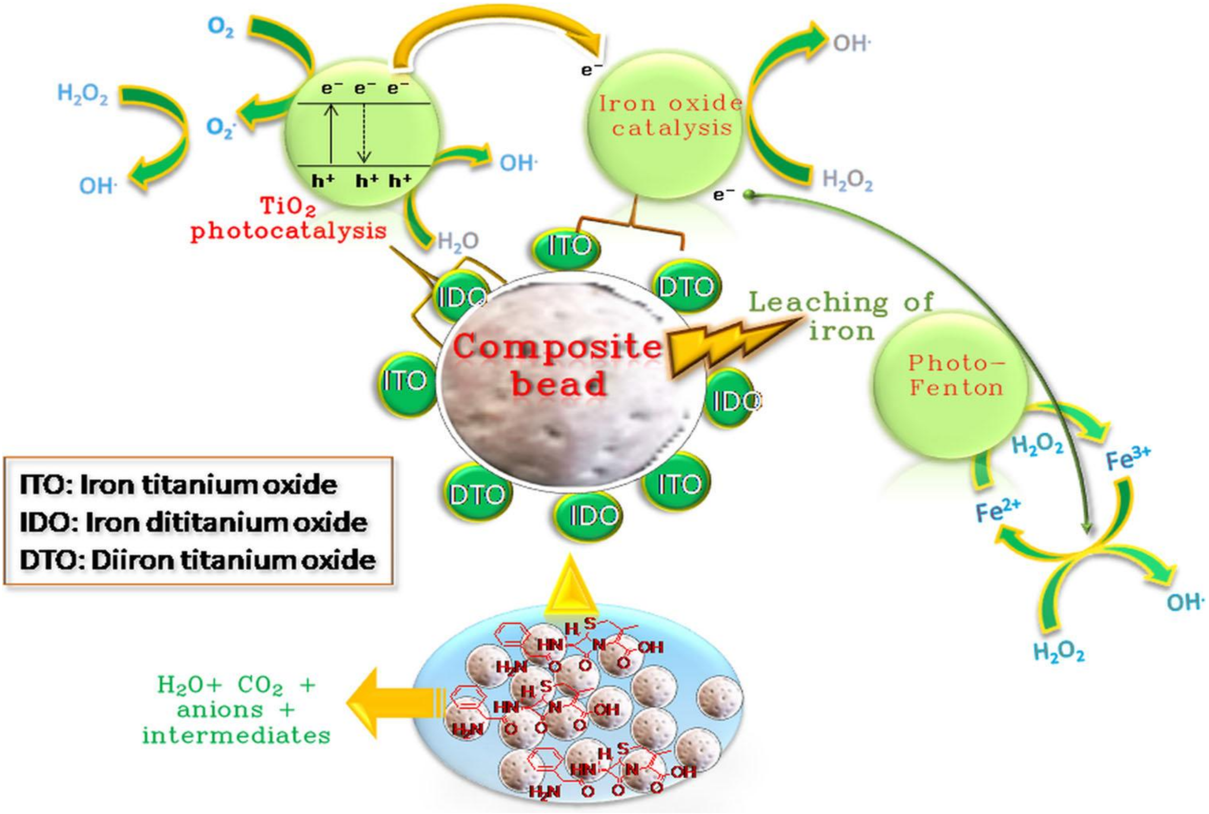


Figure 3.3: Proposed mechanism of Dual degradation (Source: **(Bansal et al., 2018)**)

Mazille et al., (2010) carried out the photocatalytic reduction of phenol, nalidixic acid, mixture of pesticides, and various other emerging water contaminants by use of immobilized TiO_2 and iron oxide on functionalized polyvinyl fluoride films (PVF–TiO_2–Fe oxide) in a compound parabolic collector (CPC) solar photoreactor. During the process of degradation iron was efficiently leached, but the degradation of different compounds followed different trends on variable of parameters. The discrepancy in degradation rates was justified due to the presence of different intermediates and chelating groups.

Kumar et al., (2014) investigated that solar/TiO_2/$Fe^{2+/}H_2O_2$ process displayed increased efficiency due to the synergetic effect of homogeneous and heterogeneous photo-catalytic reaction. The combination increased the photo process efficiency, by decreasing the reaction time of the separate operations and decreased the cost of treatment. The optimal conditions enabling over 99% reduction of chemical oxygen demand (COD).

Mineralization of congo red and malachite green was carried out by **(Hadjltaief et al., 2015),** by analyzing a novel structure of TiO_2–Fe-plate catalyst by immobilization of iron and TiO_2 on a natural clay plate. Effective mineralization was possible on a wide range of operational parameters. Irradiation by UV and presence of oxidants like H_2O_2 enhanced the reaction. The efficiency of the reaction could be proved by synergistic effect between photocatalytic and photo-Fenton activities.

Bansal et al., (2018) investigated an integrated process of coupling two individual catalytic degradation processes i.e. photocatalysis and photo- Fenton by immobilization of the catalyst for degradation of cephalexin (CEX) from aqueous solution. The use of waste materials like FS was undertaken as a substitute for iron with TiO_2. Optimization of various parameters was carried out using Box–Behnken design model (BBD) and response surface methodology. Various supports were compared to show best recyclability efficiency in the minimum treatment time.

3.2.4 Fixed bed reactors

Two different types of heterogeneous photoreactors are available, first one in which the TiO_2 is present in the form of a suspension or slurry and the second one in which it is immobilized on durable support. Both types of reactors have distinct advantages. Although the degradation efficiency in the case of immobilized system is less than the slurry system, but it can be utilized continuously for different reactions without any separation issue. Therefore, there is a need of designing an efficient photocatalytic reactor which would optimize the area covered by photocatalytic particles and the light dissemination. The properties of the reactor must involve (i) excellent vertical mixing, (ii) immense surface area per unit volume, and (iii) no shadowing effect. Many investigations have been carried out for the advancement of different types of photocatalytic reactors which work in the presence of solar or artificial illumination **(Rao et al., 2012)**. The photocatalytic reactors investigated has been successfully used for detoxification and disinfection of contaminated water. Most of the reactors make use of the UV region for the disinfection of the waste water **(Alrousan et al., 2012).** Among all types of photocatalytic reactors the solar reactor is considered to be most efficient due to its property of light harvesting. Fixed bed catalysis makes use of immobilized catalysts which acquires certain advantages like no separation and filtration are required and allow continuous operations. But there are certain drawbacks in reference with this system which includes difficulty in radiating of the entire and mass transfer limitations due to the catalyst thickness. In order to overcome all the drawbacks, the combination of AOPs can be utilized in order to drastically enhance the $^{\bullet}OH$ production which can be proved by the synergistic reaction routes which involves $^{\bullet}OH$ formation. The dual effect caused by merging of AOP’s has been very less investigated upon therefore the present study attempts to study certain advances in the field of wastewater treatment utilizing AOPs. The finest efforts are made to reduce the treatment time by integrating the in-situ dual effect (photocatalysis and photo-Fenton).

3.2.5 Scaling up of photocatalytic reactors

On a larger spectra commercial utilization and successful applications of advanced oxidation processes can be employed for large scale treatment of wastewater globally. Further, the discommodity caused by mass transfer rates can be counterbalanced by developing certain useful design procedures for large-scale applications **(Motegh et al., 2014).** But the main hurdle is that the scaling up solar photocatalytic reactors is comparatively more complicated than scaling up conventional reactors. Hence in order to achieve maximum degradation temperature, duration of exposure of the catalyst to solar irradiation and area of the catalyst exposed are essential for effective application **(Miyawaki et al., 2016)**.

RESEARCH GAPS

On the basis of literature review following research gaps has been identified:

I. Studies related to the applications of dual effect for the degradation of pesticides or any other compounds have not been reported yet.
II. Moreover degradation studies using inert composite beads made of FA+FS+clay has not been reported yet (Fixed bed in-situ dual effect)
III. Process durability in terms of catalyst stability on the support always put a constraint on field-scale applications of AOP

CHAPTER 4

OBJECTIVES

On the basis of Literature review we have extended our study on in-situ dual degradation of isoproturon on fixed bed reactor. The following objectives have been set for further work:

- Selection of inert support material for immobilization of catalyst along with presence of iron source and its subsequent applications for the degradation of isoproturon
- Process optimization for the effective degradation of isoproturon using RSM.
- Scale-up studies for the degradation of isoproturon using fixed bed solar baffled reactor.
- Catalyst stability and durability in terms of number of recycles of immobilized catalyst.

CHAPTER 5

MATERIALS AND METHODS

In this chapter the materials and methods adopted for carrying out the dual degradation of the wastewater has been portrayed. The instruments used their applications and the material study has been depicted in detail. The procedures and the methodologies required to carry out the degradation has been discussed.

5.1 Materials

5.1.1 Isoproturon: Isoproturon is a selective herbicide which belongs to the family of substituted ureas. It is used for the pre- and post-emergence control of annual grasses and weeds specifically for wheat and barley. Isoproturon is used for plant protection like all the other active substances under a variety of different commercial products. Its frequent use can be explained by the fact that it is cheap and easy to use herbicide. It is detected in fresh water bodies at low concentrations due to applications in agricultural activities and is highly stable possessing low biodegradability. Hence, its removal through conventional techniques is difficult.

Maximum absorbance of the compound was obtained at 239 nm after scanning it over a range of 190 to 700 nm.

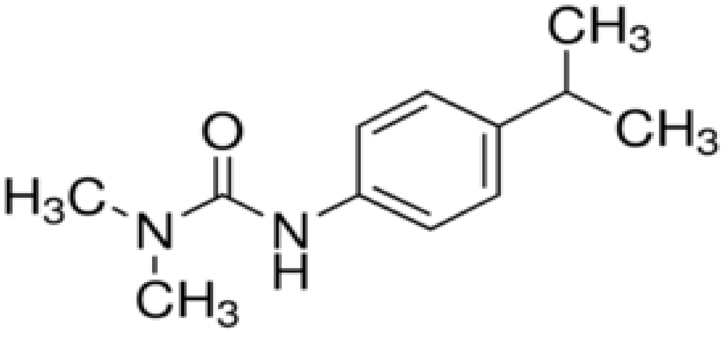


Figure 5.1: Chemical structure of isoproturon

5.1.2 Reagents and Chemicals

Isoproturon grade (90%) was brought from Pioneer Pesticides Pvt. Ltd, Delhi (India) and was usilized as such without any further purification. TiO_2 P-25 was utilised as a catalyst obtained from Evonik (India). Foundry sand (FS) and Fly ash (FA) were collected as such from a local industry IN Patiala (India) and Hydrogen Peroxide (H_2O_2) (40% w/v) was utilized as an oxidant was bought from Ranbaxy (India). Fuller's earth was brought from a local vendor, Patiala (India). Sodium acetate 97% purity and acetic acid 99.5% purity, acquired from TCI Chemicals (India) was used for preparing acetate buffer in order to maintain the pH of the solution. The double distilled water was used for preparation of all solutions.

5.2 Instruments used

5.2.1 Spectrophotometer: In order to determine the concentration of pesticide in water its absorbance was measured using a UV- visible Spectrophotometer by Hitachi V-500 UV/VIS double-beam spectrophotometer at 239nm.

5.2.2 Magnetic Stirrer: A magnetic stirrer is a device which is required for stirring of a solution with the assistance of a magnetic bead using the magnetic forces in order to solve the problem of mixing of a solution.

5.2.3 pH meter: The pH meter (purchased from Eutech instrumentation) was used in order to maintain the pH of the solution with the help of Acetate buffer. The instrument was calibrated with the help of a buffer solution after every use.

5.2.4 Air sparger: In order to maintain the consistency of the reaction there was regular supply of air through the solution with the help of air spargers.

5.2.5 Filters: After the dual treatment of wastewater containing pesticide, the suspended TiO_2 particles and iron particles must be separated from the treated sample before measuring its absorbance. Hence, it is made to pass through filters of 0.45µm pore size.

5.2.6 Sonicator: Ultrasonic bath Tank (Fisher Brand, model no.FB11201) with frequency of 33 KHz was used for formation of a homogenous solution of catalyst (TiO_2) suspension in the process of catalyst coating on beads.

5.2.7 COD Digester: COD Digester (HACH DRB200) was used for the digestion of samples in the process of COD determination.

5.2.8 SEM-EDS Analyser: is used for the identification of TiO_2 composite beads (freshly coated and recycled). The model utilized for SEM-EDS was JSM-6510LV, JEOL, Japan while that of EDS was INCAX-act, Oxford Instruments, UK.

5.2.9 FTIR Spectrometer: Fourier Transform Infrared spectroscopy was performed in order to determine the morphological features of composite beads when compared to fresh TiO_2. The model utilized for FTIR was Spectrum Two FTIR Spectrometer L160000F.

5.2.10 UV-DRS Analyser: UV-Visible Diffuse Reflectance Spectroscopy is used for evaluation of band gap energy for freshly TiO_2 coated and recycled composite beads. The model utilized for UV– DRS is, UV-2600, Shimadzu (Asia Pacific) in the UV–visible region ranging from 200 to 800 nm.

5.3 Immobilized Beads

Beads showing both photocatalysis and photo-Fenton were prepared by mixing sand, foundary sand and fly ash in the ratio 2:1:1 respectively with water. Around 300 beads were made of identical sizes. When the beads were semi-dry small holes were made on the surface to undergo effective TiO_2 coating when the dried beads were immersed completely into TiO_2 sonicated solution. Some beads were kept uncoated in order to determine the efficiency of alone photo-Fenton reaction. The figure shows the images of uncoated 5.2 and coated beads 5.3.

Figure 5.2: Image of Uncoated beads

Figure 5.3: Image of Coated beads

5.4 Photo reactors: We have worked upon two types of reactors:

5.4.1 Shallow pond batch reactor: A lab scale set up for shallow pond reactor was made as shown in Figure 5.4. The binary degradation studies were carried out using a borosil glass vessel of 8 cm diameter, 2.6 cm height and 500 ml capacity and UV rays were irradiated on the glass vessel. For the dual reaction to be carried out optimized number of catalyst coated beads were kept in the reactor with the given volume of solution (25mgL^{-1}) pH was maintained up to 3.6 and quantified amount of H_2O_2 was added. The reactor was covered with the help of a plastic film to avoid any evaporation and proper penetration of UV light.

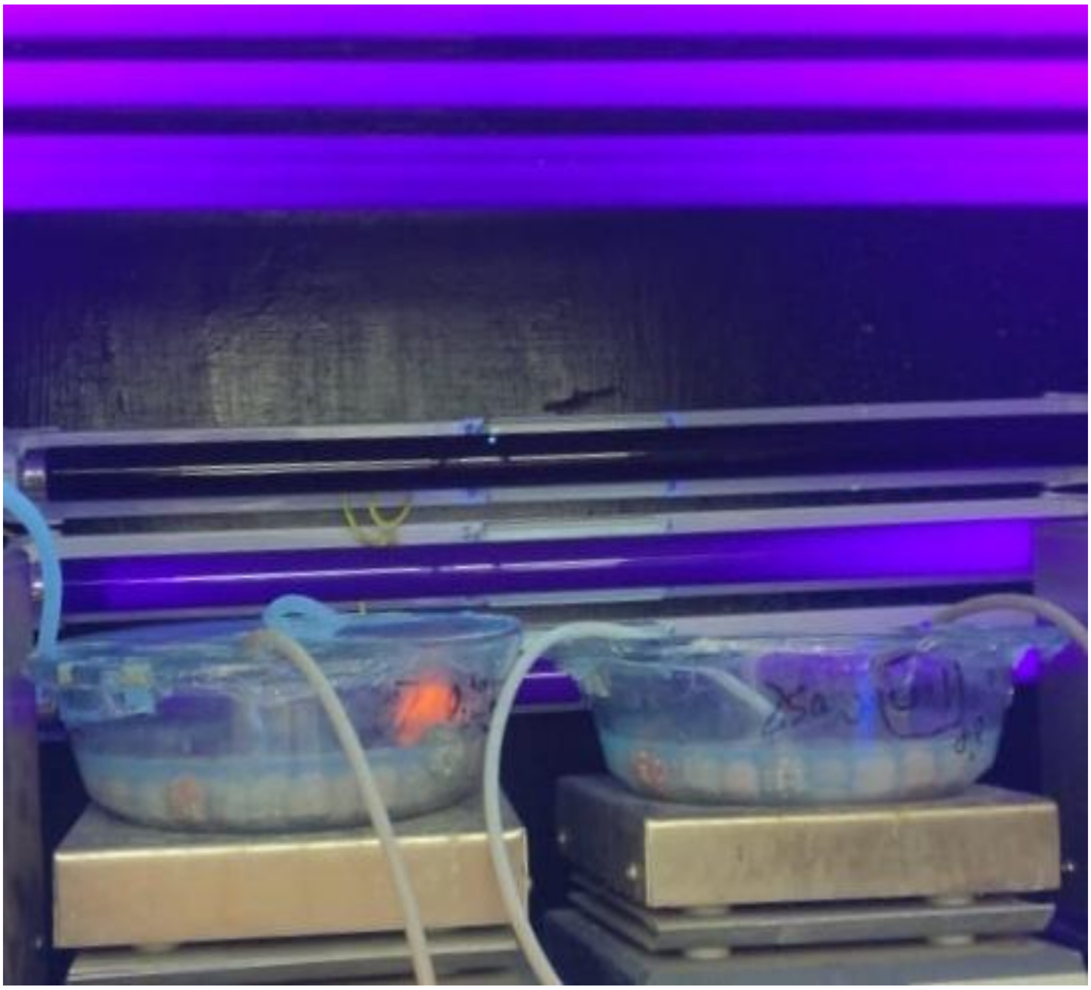


Figure 5.4: Shallow pond batch reactor placed in UV chamber

5.4.2 Solar baffled reactor: The degradation process was also carried out using a pilot scale set-up comprising of a concrete baffled reactor having dimensions of 20cm x 30 cm causing continuous recirculation as shown the (Figure 5.5). The catalyst coated beads were placed in every chamber of the baffled reactor in a manner that they are efficiently immersed in the solution which is pumped in to the reactor to be treated. The flow rate of the solution was maintained in order to attain the desired retention time. It was used to treat 5L of solution to imply its large scale uses. The reactor was shielded with a transparent film for effective penetration of sunlight and for preventing the evaporation losses.

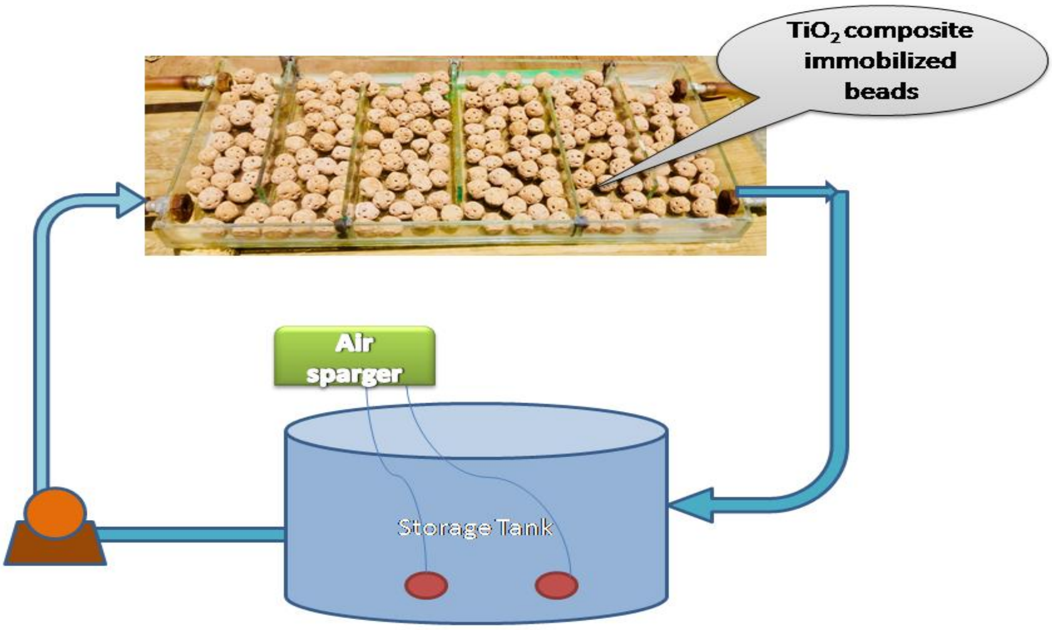


Figure 5.5: Fixed bed solar baffled reactor

5.5 Experimental procedure

5.5.1 Procedure for Dual degradation of Isoproturon utilizing a shallow pond reactor in the presence UV light

The accustomed procedure for the dual experiments was as follows:

1. The stock solution of isoproturon was made by dissolving 25 mg L^{-1} (25 ppm) in distilled water. The solution was kept for overnight stirring for dissolving isoproturon completely in distilled water.

2. Took a quantified number of beads in the shallow pond reactor in order to evenly cover the surface.

3. To it added a given volume of the solution to undergo a dual treatment.

4. Then checked the pH of the solution using the pH meter, original pH of the solution was 5.4 which was further maintained to 3.5 using the buffer.

5. The reactor was then placed on the stand in the UV Chamber and the UV lights were switched on and the door of the UV chamber was closed.

6. After every 30 minutes, took 5ml sample from the reactor with the help of micropipette. The reaction is continued for 180 minutes.

7. In order to prevent any disruption during scanning due to the presence of suspended TiO_2 and iron particles the solution was filtered using a micro filter.

8. Concentration of the collected samples was determined by measuring their absorbance using a computer based UV-Vis spectrophotometer using the following steps:

a) The system is switched on and warmed up.

b) Quartz cuvette was thoroughly cleaned.

c) The cuvette was filled with distilled water and auto zero is done.

d) After this the cuvette is rinsed and filled with the sample whose absorbance is to be measured at λ_{max}.

e) In order to get an explicit relationship between concentration and absorbance of the compound, a calibration curve was made by plotting absorbance against concentration of the calibrated samples. With the help of calibration curves concentration of unknown samples can be calculated directly through absorbance.

9. As we know that the concentration would gradually decrease with time hence parameters like H_2O_2 dose, no. of beads, volume and time were varied in order to determine the optimized conditions for the reaction.

5.5.2 Modeling and optimization

Dual treatment of wastewater containing pesticides is quite complicated as it involves participation of two different processes (Photocatalysis and Photo-Fenton) simultaneously. Hence, there are a large number of factors which would regulates the rate of degradation of a particular compound like the mass transfer mechanisms, amount of $OH^{\cdot}$ radicals formed and various other limiting factors which would be complex to understand. Modeling of the binary degradation process involves a multivariate system, it is evident that this system could not be explained by simple linear multivariate correlation **(Aleboyeh et al., 2005)**. It is necessary to investigate the interactions of parameters at a given time. Hence, optimization was carried out using Response Surface Methodology (RSM) varying various operational parameters to attain a suitable optimised condition.

5.5.3 Optimization by Box-Behnken Design (BBD)

In order to optimize operational parameters Box-Behnken designs (BBD) under response Surface Methodology (RSM) was used **(Pareek et al., 2002)**. The response B_i is the functions of inputs A_1, A_2, A_i...A_f which are attained by using the following relationship:

$B_i = \Phi(A_1, A_2, A_3 ... A_i ... A_f)$ [18]

The relation between the input factors and responses can be interpreted as a quadratic response model. The non-linear regression data was used to analyze the relevant model to fit the responses according to simulated results and input factors. In general, the model was used to find the best fitted in second-order polynomial equation.

$$B = \sum_{i=1}^{k} sA_i + \sum_{i}^{k} s A_i^2 + \sum_{i=1}^{k} s A_i A_i \quad [19]$$

Where, B is response; s is constant coefficients and A_i the uncoded independent variables. Coding followed the three level factor, and coded as -1 (low) and +1 (high). To design the experiments, the Statistical Design-Expert software version 6.06 (STAT-EASE Inc., Minneapolis, US) was used.

CHAPTER -6

RESULTS AND DISCUSSION

Isoproturon 3-(4-isopropylphenyl)-1, 1-dimethylurea is a selective herbicide which belongs to the class of substituted ureas. It is used for limiting the pre- and post-emergence of annual grasses and weeds specifically for wheat and barley. In this chapter we have studied the effect of operating parameters on the percentage degradation of a herbicide (isoproturon) by Dual effect. Pilot-scale studies were also conducted using a baffled solar reactor to see its viability for commercial applications.

6.1 Standard calibration curve of Isoproturon

The total wavelength scan of compound isoproturon was done using UV-Vis spectrophotometer and its maximum absorbance (λ_{max}) was observed at 239nm. A standard calibration curve (Figure 6.1) was made by varying the concentration of the solution ranging from 0mgL^{-1} to 30mgL^{-1} and plotting it against absorbance measured at 239nm. Through the graph we could determine the unknown concentration of any given solution. The regression coefficient (R^2) and the slope (y) of the curve were found to be 0.998 and 0.075 respectively.

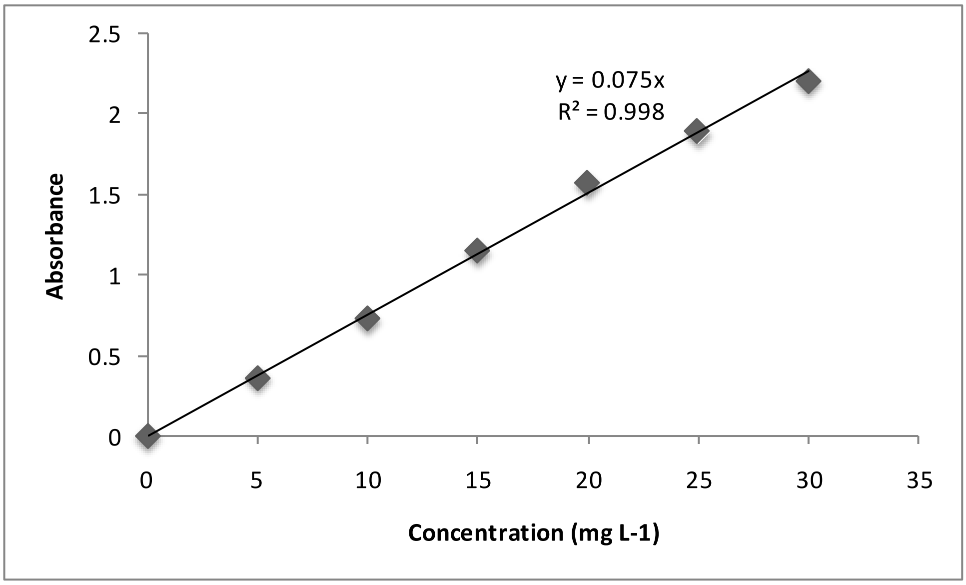


Figure 6.1: Standard calibration curve of isoproturon

6.2 Preliminary experiments

Preliminary studies were performed in order to consider the impact of individual parameters on the degradation of Isoproturon Figure 6.2. All the studies were carried out on fixed bed and a list of preliminary experiments was carried out as follows:

(1)Adsorption (2) Photolysis (3)UV+H_2O_2 (4)Photocatalysis (5) Photo-Fenton (6)Dual Effect

Adsorption studies showed (2.055%) a negligible amount of reduction after 180min and (11.86%) was observed when solution was exposed to UV light (photolysis) in a batch reactor. It was observed from the results that very less degradation was shown in presence of UV+H_2O_2 (18.66) due to restricted production of $OH^{\cdot}$ radicals. While Photo-Fenton studies (Fe+UV+H_2O_2) showed 29.9% reduction in concentration of the compound. Moreover, when photocatalysis (UV + TiO_2 +H_2O_2) was carried out it depicted a reasonable percent of degradation 57.7% which may be due to comparatively larger production of $OH^{\cdot}$ radicals. Hence, the combined effect of both photocatalysis and Photo-Fenton (Fe+UV+TiO_2+H_2O_2) was brought to action in order to attain maximum degradation of (80.96%) due to the substantial increase in the generation of hydroxyl radicals.

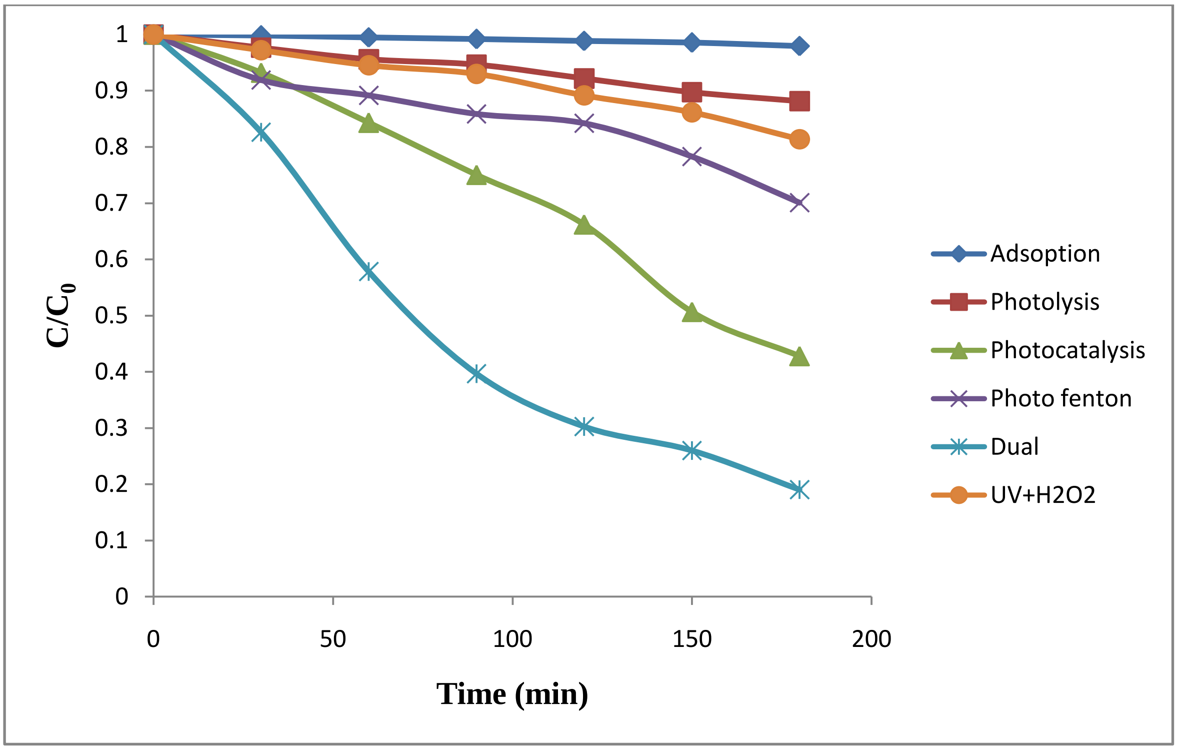


Figure 6.2: Outcome of different preliminary reactions to assess the advantage and effectiveness of each condition

6.3 Optimization by using RSM

6.3.1 Box- Behnken Design (BBD)

Box-Behnken design under Response Surface Methodology (RSM) was used in order to gain optimal values of operational parameters for dual degradation of wastewater containing isoproturon. The four optimum conditions used were H_2O_2 dose, number of beads, volume of solution (wastewater) and degradation time were utilized as input variables and percentage of degradation was taken as response. Table 6.1 shows the various optimum conditions and their maximum and minimum limits.

Table 6.1: Variation of variables and coded levels

Factor	Name	Low Actual	High Actual	Low Coded	High Coded
A	Variation of H_2O_2 (ml)	0.25	0.75	-1.000	1.000
B	Number of beads	30.00	90.00	-1.000	1.000
C	Volume of solution (ml)	150.00	400.00	-1.000	1.000
D	Time	30.00	180.00	-1.000	1.000

A complete factorial design has been used to take a look at dual degradation of isoproturon and depicted in Table 6.2. Overall 29 experiments was suggested by BBD in order to optimize the process parameters such as were H_2O_2 dose from 0.25 to 0.75ml, number of beads from 30 to 90 beads (30 beads covering almost 50% of the reactor surface, 60 beads covering almost 100% and 90 beads covering 150% of the surface area), volume of solution ranging from 150 to 400ml (wastewater) and degradation time 30 to 180 minutes for isoproturon.

Table 6.2: Full factorial BBD matrix

S.No.	**Variation of H_2O_2 (ml)**	**Number of beads**	**Volume of solution (ml)**	**Time (min)**	**% degradation**
1	0.50	90	400	105	44.64
2	0.50	30	275	30	20.34
3	0.50	60	400	180	63.57
4	0.25	60	150	105	60.09
5	0.75	90	275	105	21.56
6	0.50	90	275	180	68.21
7	0.75	60	400	105	28.41
8	0.75	60	275	30	10.24
9	0.50	30	275	180	68.05
10	0.75	60	275	180	79.12
11	0.50	60	275	105	44.87
12	0.75	30	275	105	23.93
13	0.50	90	150	105	15.49
14	0.25	90	275	105	40.53
15	0.25	60	400	105	41.53
16	0.50	60	275	105	52.11
17	0.25	30	275	105	44.86
18	0.50	30	150	105	60.25
19	0.50	60	150	30	24.19
20	0.50	60	275	105	56.44
21	0.50	60	275	105	50.34
22	0.50	60	400	30	5.06
23	0.50	30	400	105	27.53
24	0.25	60	275	30	24.14
25	0.75	60	150	105	26.35
26	0.50	90	275	30	18.97
27	0.25	60	275	180	70.11
28	0.50	60	275	105	48.99
29	0.50	60	150	180	78.33

6.3.2 Statistical analysis

The degradation of isoproturon wastewater was studied utilizing dual effect. A sequence of F-test and other required measures were used in order to select the best Model. The p value for the decomposition of isoproturon was found to be less than 0.01 hence the quadratic model was suggested by sequential model sum of squares. Model summary statistics and sequential model sum of squares and were tested to decide the adequacy of model. A result of adequacy model was shown in Table 6.3 for % degradation of isoproturon. Sequential model sum of squares showed that quadratic model was best fit model for experimental data for % degradation of isoproturon. Cubic model was found to be aliased for the degradation of isoproturon.

Table 6.3: Sequential Model Sum of Squares

Source	**Sum of Squares**	**DF**	**Mean Square**	**F value**	**Prob>F**	
Mean	51177.00	1	51177.00			
Linear	9820.31	4	2455.08	21.75	<0.0001	
2FI	1200.81	6	200.13	2.39	0.0710	
Quadratic	848.82	4	212.21	4.51	0.0151	Suggested
Cubic	513.70	8	64.21	2.65	0.1258	Aliased
Residual	145.41	6	24.23			
Total	63706.05	29	2196.76			

Table 6.4: Model Summary Statistics for % degradation of isoproturon

Source	**SD**	**R^2 value**	**Adjusted R^2**	**Predicted R^2**	
Linear	10.62	0.7838	0.7478	0.6784	
2FI	9.15	0.8796	0.8128	0.6788	

Quadratic	6.86	0.9474	0.8948	0.7211	Suggested
Cubic	4.92	0.9884	0.9458	0.9458	Aliased

Where SD is Standard Deviation

The Prob > F value was 0.0151, which indicated that the quadratic model is significant. The coefficient of determination is 0.94 for quadratic model. This concludes a good correlation between observed and predicted values. The predicted values were quite close to the actual values.

The difference between predicted values and observed values dividing by standard error of the residual has close relationship with percent Normal probability. This advocates a good correlation between the observed and predicted values as shown in Fig 6.3.

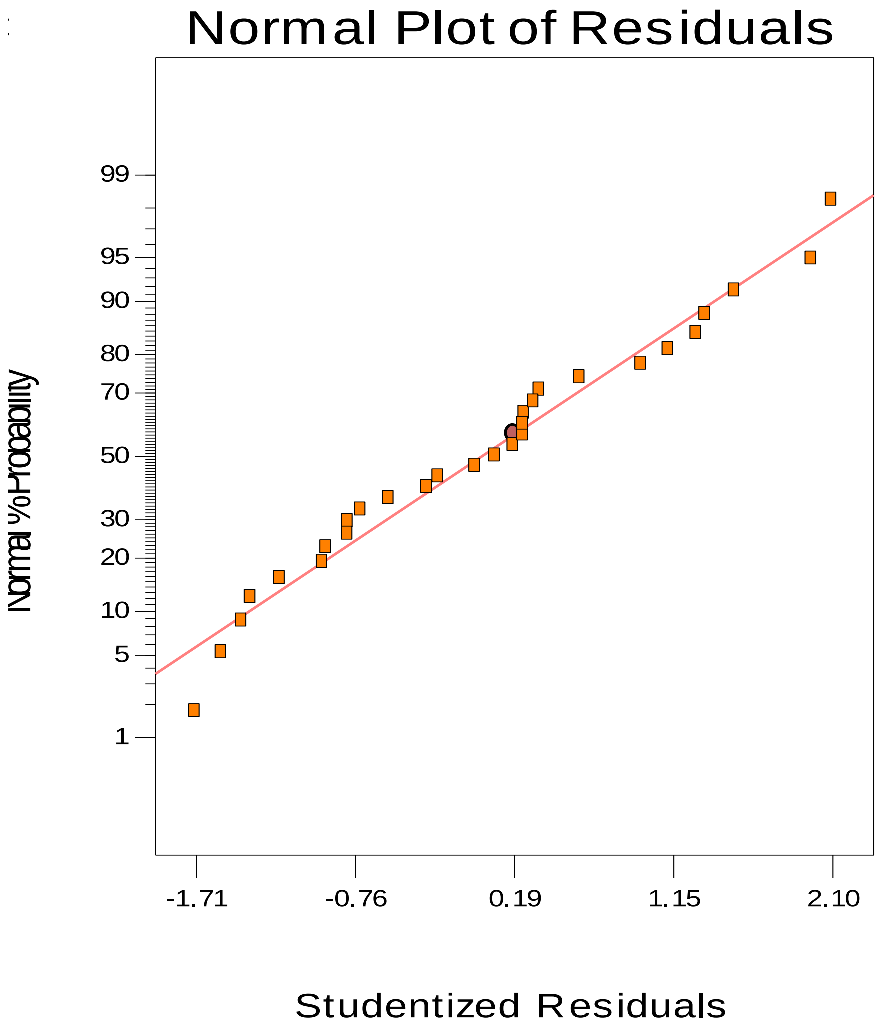


Figure 6.3: Residual plot for dual degradation of isoproturon

The ANOVA (analysis of variance) indicated that the F-value for percent degradation of isoproturon is 18.01 as shown in Table 6.5. The Model F-value of 18.01 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant and "prob>F" values larger than 0.100 indicated that model term are insignificant.

From ANOVA it was clear that Variation of H_2O_2, Volume of the solution, (Variation of $H_2O_2)^2$, (Number of beads)^2, (Volume of solution)^2, (Number of beads× Volume of solution) and time are highly significant for %degradation of isoproturon.

Table 6.5: ANOVA suggested by BBD for the % degradation of isoproturon

		Sum of Square	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Source							
	Model	11869.94	14	847.85	18.01	< 0.0001	Significant
	Variation of H_2O_2	699.98	1	699.98	14.87	0.0017	
	Number of beads	105.38	1	105.38	2.24	0.1568	
	Volume of solution	242.64	1	242.64	5.15	0.0395	
	Time	8772.32	1	8772.32	186.33	< 0.0001	Highly significant
		286.45	1	286.45	6.08	0.0272	
	(Number of beads)^2	492.00	1	492.00	10.45	0.0060	
	(Volume of solution)^2	239.32	1	239.32	5.08	0.0407	
	(Time)^2	4.02	1	4.02	0.085	0.7745	
	Variation of H_2O_2× Number of beads	0.96	1	0.96	0.020	0.8885	
	Variation of H_2O_2× Volume of solution	106.30	1	106.30	2.26	0.1552	
	Variation of H_2O_2× Time	131.22	1	131.22	2.79	0.1172	
	Number of beads × Volume of solution	956.97	1	956.97	20.33	0.0005	

	Number of beads × Time	0.59	1	0.59	0.012	0.9128	
	Volume of solution× Time	4.77	1	4.77	0.10	0.7548	
Residual		659.11	14	47.08			
Lack of Fit		587.24	10	58.72	3.27	0.1325	not significant
Pure Error		71.87	4	17.97			
Cor Total		12529.05	28				

The quadratic model equation obtained in terms of significant process parameters and interaction parameters are given below:

Degradation = 67.68912 – (5.58133 × H_2O_2 Variation) – (0.16436×Volume)+ (0.1361×Time) - (106.3266× H_2O_2 Variation^2) – (9.67685×10^{-3}× No of beads^2)- (3.88747×10^{-4} ×Volume^2)+ (4.12467×10^{-3}× No of beads× Volume) [20]

6.3.3 Effect of variation of H_2O_2, number of beads, volume of solution and time on %degradation of isoproturon

To study the effect of parameters like variation of H_2O_2, number of beads, volume of solution and time on % degradation of isoproturon for dual treatment of a herbicide, the three dimension response surface graph were considered.

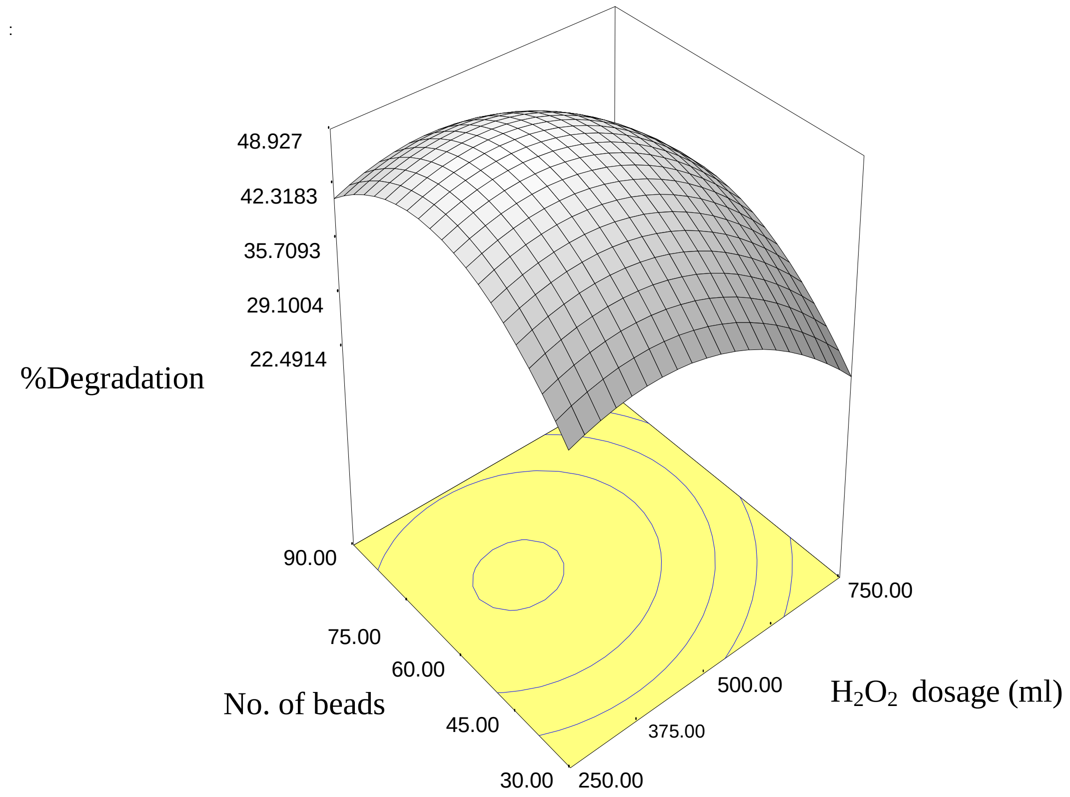


Figure 6.4(a): 3-D response surface graph for % degradation of isoproturon by variation of H_2O_2 dosage and no. of beads

From the 3-D response graph plotted against no. of beads and H_2O_2 dosage for the percentage degradation of isoproturon as depicted in the given Figure 6.4(a) shows that with increase in number of beads initially from 30 to 60 the % degradation of isoproturon would undergo an increment, but with further increase in number of beads there is decrease in % degradation. This is basically due to increase in concentration of iron in the solution which would hinder the reaction due to the formation of dead zones or blockage of active sites. On the other hand with increase in H_2O_2 concentration from 0.25ml to 0.50ml there is slight increase in % degradation which would decrease after further increase in concentration to 0.75ml that may be attributed to the scavenging effect of H_2O_2. This involves the formation of excess of $HO^{\cdot}_2$ radicals when $OH^{\cdot}$ radicals combine with H_2O_2 as signified in the given equation 21:

$$^{\bullet}OH + H_2O_2 \rightarrow HO^{\bullet}_2 + H_2O \qquad [21]$$

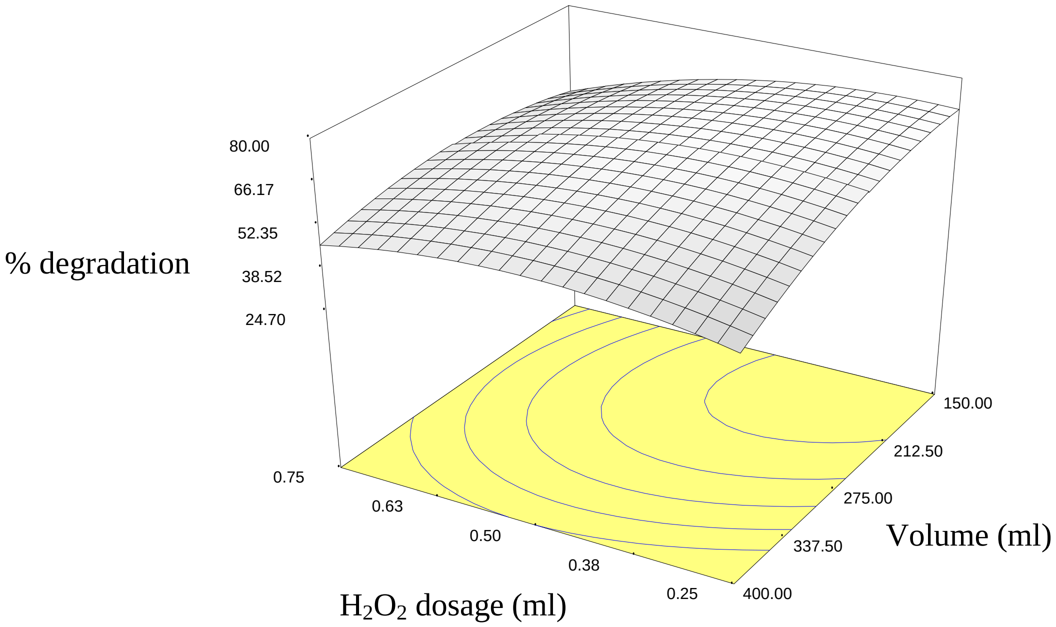


Figure 6.4(b): 3-D response surface graph for % degradation of isoproturon by variation of H_2O_2 dosage and volume of wastewater

From the 3-D response graph plotted against H_2O_2 dosage and volume of solution for the percentage degradation of isoproturon as depicted in the given Figure 6.4(b), indicates that with increase in volume of the solution from 150ml to 275ml there is negligible effect on the % degradation while with further increase in volume % degradation decreases intensely due to improper penetration of UV radiations as the volume of the solution is more ultimately causing lesser degradation. On the other hand change in concentration of H_2O_2 from 0.25ml to 0.50ml causes a slight increase in % degradation which would decrease after further increase in concentration to 0.75ml due to the scavenging effect already explained in equation [21].

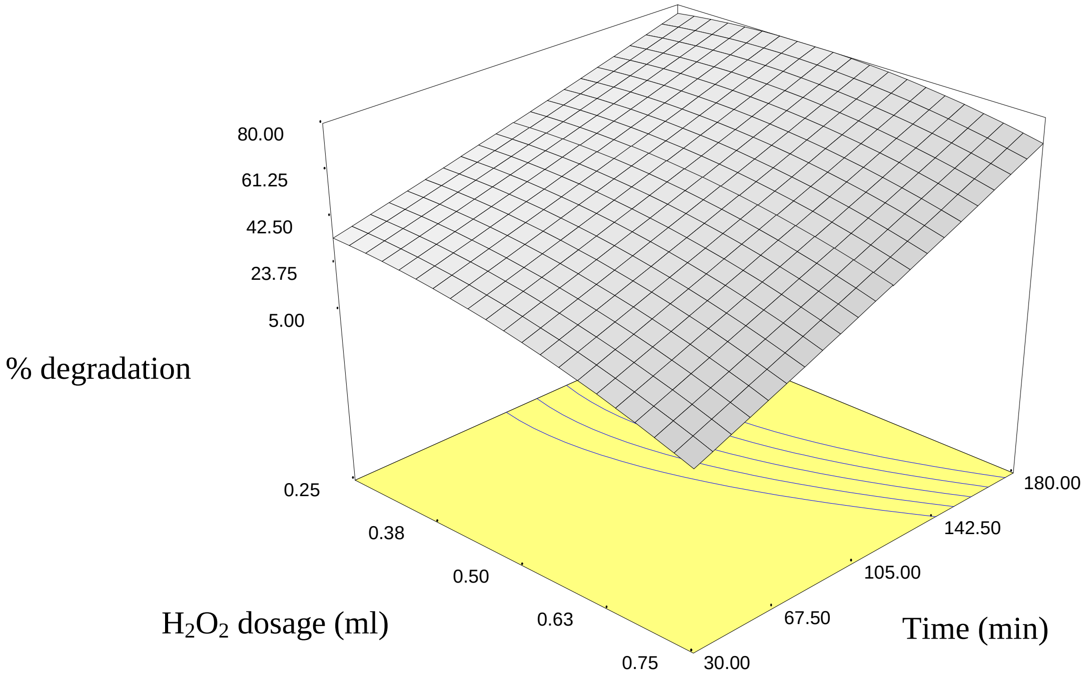


Figure 6.4(c): 3-D response surface graph for % degradation of isoproturon by variation of H_2O_2 dosage and time

From the 3-D response graph plotted against H_2O_2 dosage and time for the percentage degradation of isoproturon shows that there is a sharp increase in % degradation with increment in time as depicted in Figure6.4(c), this can be well explained on the basis of more exposure time experienced by the solution in the UV light and hence more $OH^{\cdot}$ radicals formation leading to more degradation. The variation in H_2O_2 dose would exhibit scavenging effect with increase in volume of H_2O_2 after certain limit.

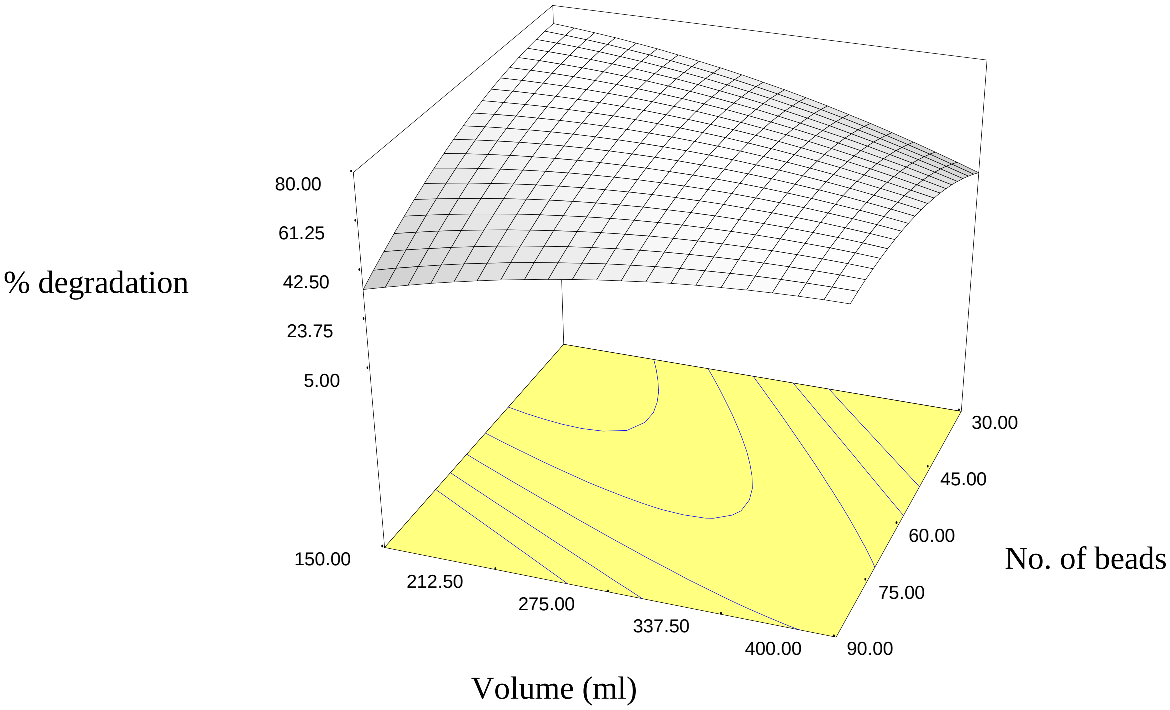


Figure 6.4(d): 3-D response surface graph for % degradation of isoproturon by variation of volume and no. of beads

From the 3-D response graph plotted against volume of solution and number of beads for the percentage degradation of isoproturon as illustrated in the given Figure 6.4(d) it can be depicted that maximum degradation of isoproturon is when the number of beads are in the range 45-60 and volume of the solution is limited between 200-275ml which would further represent the optimised condition due to the favoured conditions required for degradation.

:

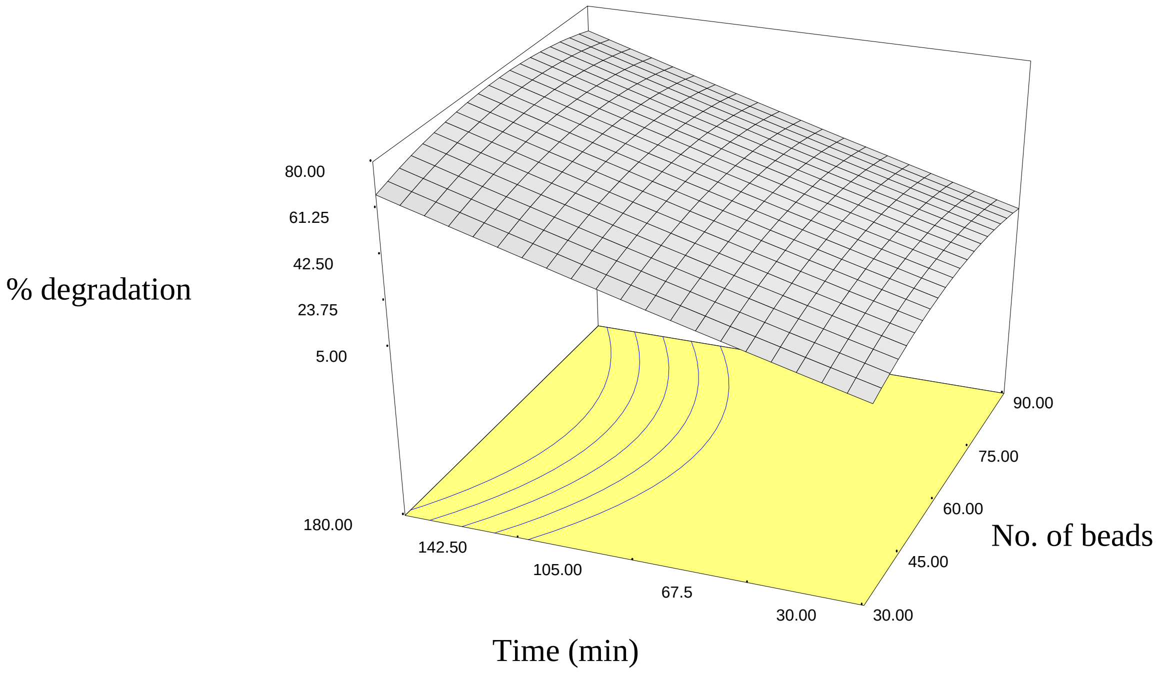


Figure 6.4(e): 3-D response surface graph for % degradation of isoproturon by variation of time and no. of beads

From the 3-D response graph plotted against time and no. of beads for the percentage degradation of isoproturon illustrates that the maximum degradation is visible when the number of beads ranges from 45-60 and exposure time is kept in the interval ranging from 160-180min as shown in Figure 6.4(e), due to extravagant exposure to UV radiations and rare formation of dead zones as the number of beads is less. There is almost 80% degradation when the number of beads is 60 hence ideally covering 100% area of the reactor.

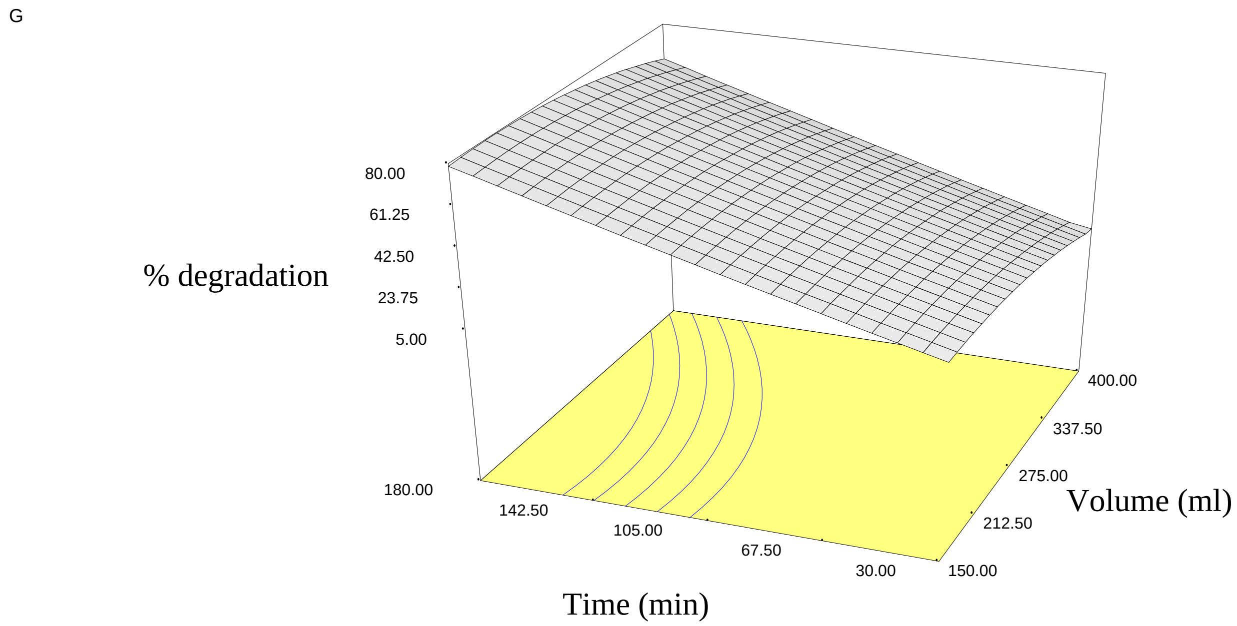


Figure 6.4(f): 3-D response surface graph for % degradation of isoproturon by variation of time and volume of wastewater

From the 3-D response graph plotted against time and volume of solution for the percentage degradation of isoproturon signifies that degradation is maximum when the time of exposure is maximum while % degradation increases with decrease in the volume of solution allowing more penetration of the UV light as interpreted in the given Figure 6.4(f).

6.3.4 Optimization analysis

Dual degradation of Isoproturon was carried out and was optimized by BBD in order to maximise the % degradation. For this consideration some operational parameters were varied as shown in the Table 6.6.

Table 6.6: Variation of operational parameters

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
H_2O_2 Variation	is in range	0.25	0.75	1	1	3

Number of beads	is in range	30	90	1	1	3
Volume	is in range	150	400	1	1	3
Time	is in range	30	180	1	1	3

Through this study, % degradation of Isoproturon was maximised by utilising the optimisation parameters using BBD. The values of optimum parameters are defined in the given table 6.7. At this optimum condition, the % degradation of Isoproturon with concentration of 25ppm was found out to be 80.96%.

Table 6.7: Optimum conditions in order to maximise % degradation

Variables	**Optimum values**
H_2O_2 Dose	0.444ml
No. Of beads	42
Volume of solution	190ml
Time	176min

6.3.5 Confirmation results

Optimum conditions for the dual treatment of wastewater were verified experimentally. Experiment was made to run for 176 min at pH 3.7 with 42 beads, 190ml of wastewater and o.444ml of H_2O_2 dose. The % COD removal is 63.7%. Hence, the predictions agreed well with the experimental optimisation parameters and confirmed effective degradation of contaminant.

6.4 Kinetic study and Synergistic calculations

The kinetics of the dual process (photocatalytic and photo-Fenton), was performed by using pseudo-First order kinetics as depicted below:

$$Rate = -\frac{d(I)}{dt} = k(I) \qquad [22]$$

$$\frac{d(I)}{(I)} = -kdt \qquad [23]$$

$$\int_{(I_0)}^{(I)} \frac{d(I)}{(I)} = \int -kdt \qquad [24]$$

$$\ln(I) - \ln(I_0) = -kt \qquad [25]$$

$$\ln\frac{(I)}{(I_0)} = kt \qquad [26]$$

Where, I_0 is the initial concentration of Isoproturon at t=0, I is the concentration (mg/L) of Isoproturon at any time, t is the time (min) for degradation of isoproturon and k is the pseudo first order rate constant (min^{-1}). The value of slope (k) can be determined by natural log of $(I)/(I_0)$ and time required for degradation. As expected, the value of the pseudo first order rate constant came higher i.e. 0.009 min^{-1} for FE+ FS beads with TiO_2 coating whereas the rate constant for photocatalysis and photo-Fenton were 0.004 and 0.001 respectively.

Synergy of the integrated system over the individual process was studied using the equations 27-29

Synergy of dual over photocatalysis process:

$$\%\,Synergy = 100 \times \{(k_{dual} - k_{photocatalysis})\}/k_{dual} \qquad [27]$$

$$\%\,Synergy = 100 \times \{(0.009 - 0.004)\}/0.009$$

$$\%\,Synergy = 55\%$$

Synergy of dual over photo-Fenton process:

$$\%\,Synergy = 100 \times \{(k_{dual} - k_{photoFenton})\}/k_{dual} \qquad [28]$$

$$\%\,Synergy = 100 \times \{(0.009 - 0.001)\}/0.009$$

$$\%\,Synergy = 88\%$$

Synergy of dual over both photocatalysis and photo-Fenton process i.e overall synergy:

$$\%\,Synergy = 100 \times \{(k_{dual} - (k_{photocatalysis} + k_{photoFenton}))\}/k_{dual} \qquad [29]$$

$$\% \, Synergy = 100 \times \{(0.009 - (0.004 + 0.001))\}/0.009$$

$$\% \, Synergy = 44\%$$

Therefore, the synergetic effects of dual process over both the processes lead to the drastic increase in the rate of reaction. Hence, confirms the feasibility of our process.

6.5 Solar v/s UV irradiation

The 80.96% degradation of isoproturon in wastewater was increased to 87% when the dual process was carried out in natural solar light as depicted in Figure 6.5 this is because now the degradation can be carried out in both visible and UV region due to composite work of the solar light, as photo-Fenton reaction is more active in the visible region due to effective iron leaching in the visible spectra. All the experiments were conducted under solar light in the month of May-June, 2018 from 9 am to 4 pm at Thapar Institute of Engineering and Technology, Patiala, India. Subsequently, the technology utilized is economically attainable and can also give a suitable solution to the industries for treating recalcitrant compounds.

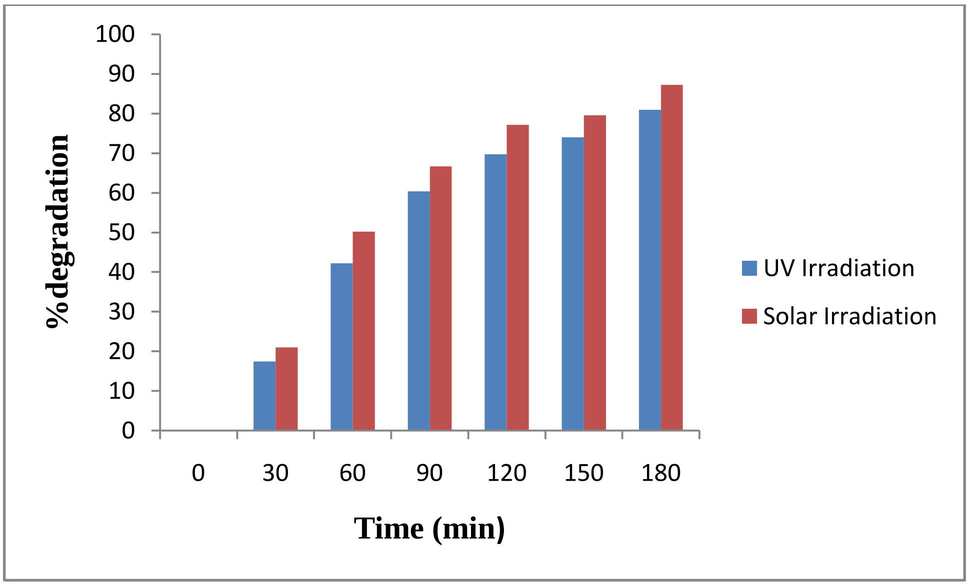


Figure 6.5: Effect of solar v/s UV radiations on %degradation of isoproturon

6.6 Scaling up using a fixed bed reactor

For the large scale use of the dual process reactors are introduced which decomposes wastewater effectively in comparable duration of time. In order to conduct the experiment a baffled glass reactor with dimensions (25cm×30cm×5cm) was designed to handle the total volume of 5 L and the TiO_2 immobilized beads were used to conduct the in-situ dual effect experiments. The untreated wastewater containing an optimised dose of H_2O_2 and maintained acidic conditions with the help of a buffer in order to carry out the Photo-Fenton reaction was pumped from the collection tank with the help of a pump and the flow rate was maintained to be 2.5Lhr^{-1}. The reaction was carried out for duration of 360 minutes and readings were taken in a proper time interval to measure the %degradation which was incremented to 72% for 5L of wastewater as shown in Figure 6.6. All experiments were conducted under solar light in the month of May-June, 2018 from 9 am to 4 pm at Thapar Institute of Engineering and Technology, Patiala, India. Intensity was measured using pyranometer (Apogee: MP-100) and was averaged to 820 Wm^{-2} during that period.

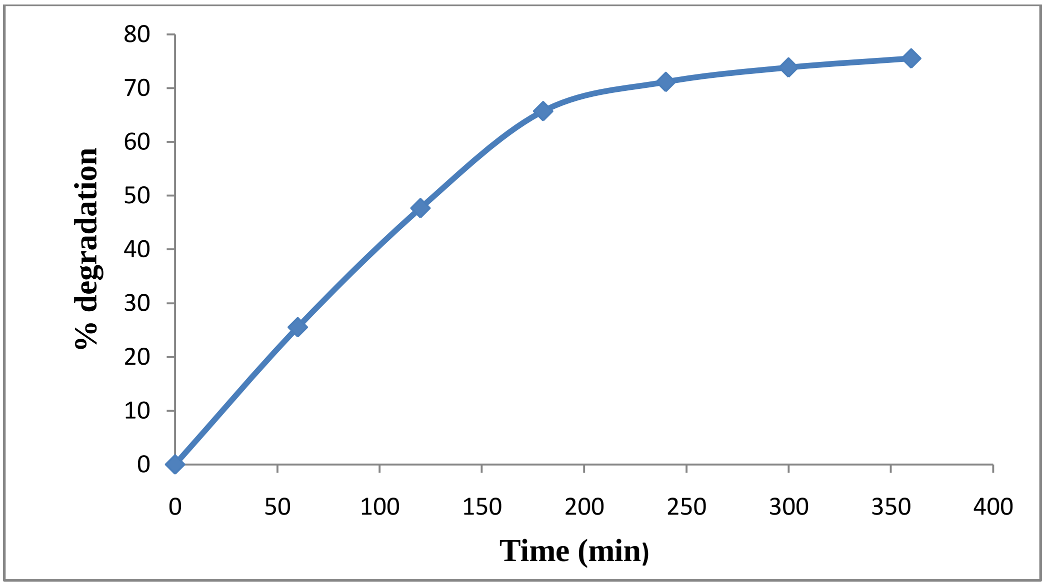


Figure 6.6: % degradation of isoproturon on fixed bed reactor

6.7 Energy Consumption

A comparison could be drawn by measuring the energy consumption (E_{EO}) for the dual effect on the % degradation of isoproturon and energy consumption in the case of individual processes photocatalysis and photo-Fenton. E_{EO} can be described as the electrical energy required for the reduction in the contaminant concentration in cubic meter of the wastewater. The E_{EO} (kW h m^{-3} order^{-1}) can be calculated by utilising the given formula:

$$E_{E0} = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C_i}{C_f}\right)} \qquad [30]$$

Where, P is the power consumed by the UV lamps (kW), t is the irradiation time (min), V is the volume (L) of the water in the reactor and C_i and C_f are the initial and final compound concentration (mgL^{-1}).

Using the equation (30) the estimated value of E_{EO} for the three processes can be depicted as:

Table 6.8: Estimated value of E_{EO} for degradation processes

Degradation processes	Energy consumption (E_{EO}) ($MWh\ m^{-3}$)
Photo-Fenton	25.30
Photocatalysis	10.39
Dual effect	5.28

It can be observed (Table 6.8) that electric energy consumption was comparatively very less in case of dual effect due to the intact coating of TiO_2 and simultaneous leaching of iron from the beads causing the effective degradation.

6.8 Durability studies

The durability studies of supported catalyst are very important in case of fixed-bed catalysis. As the activity of a catalyst decreases with every cycle, but it can be re-activated at high temperature of 480°C but it is not economically feasible. We have made efforts in order to study the durability of TiO_2 coated FS+FA beads used for the degradation of isoproturon in wastewater. The beads were adequately recycled for at least forty to fifty times without any effective decrease in efficiency with respect to % degradation of isoproturon as it depicted adequate amount of iron leaching even after repeated use which was confirmed by Figure 6.7 After every cycle the beads were reactivated by placing them in a heating oven at 100°C for duration of 1hr. A small amount of reduction in the photocatalytic activity is due to loss of TiO_2 coating with every cycle. But it depicted adequate amount of iron leaching even after repeated use which was confirmed by

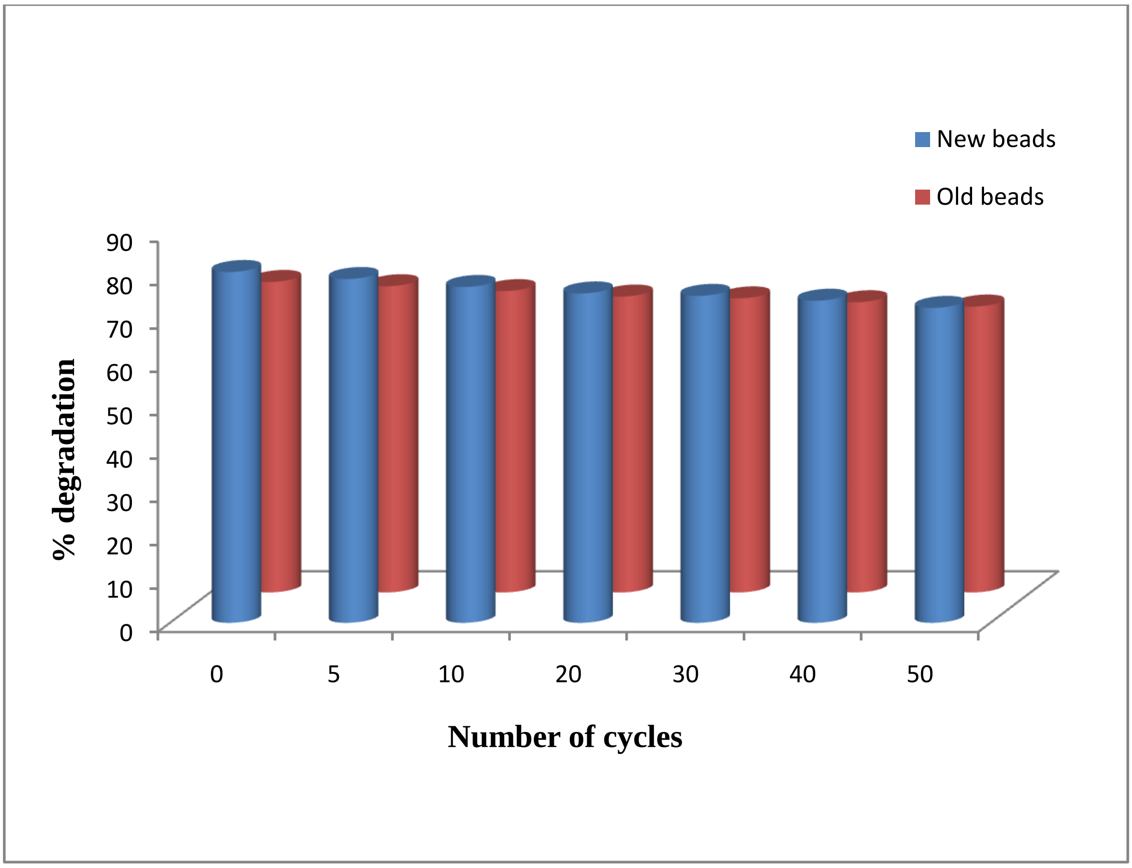
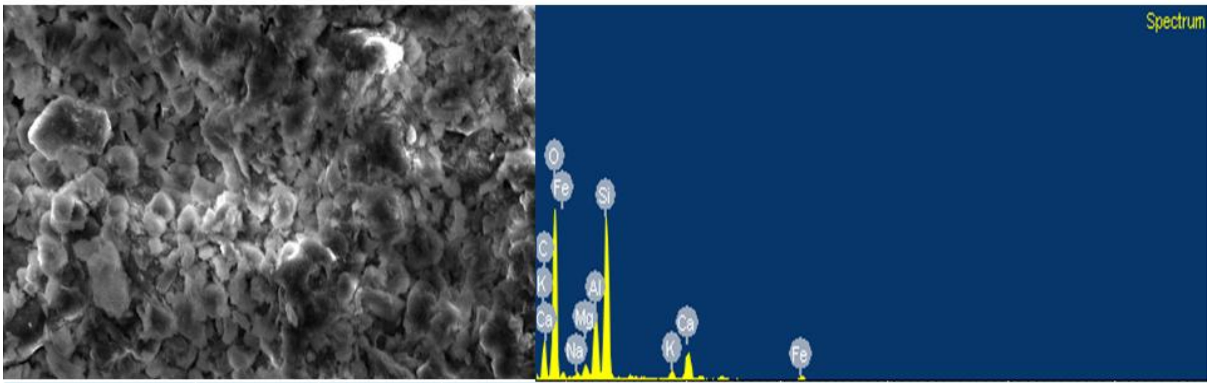


Figure 6.7: Durability studies of fresh and recycled beads for % degradation of isoproturon using dual effect

6.9 Characterisation of Beads

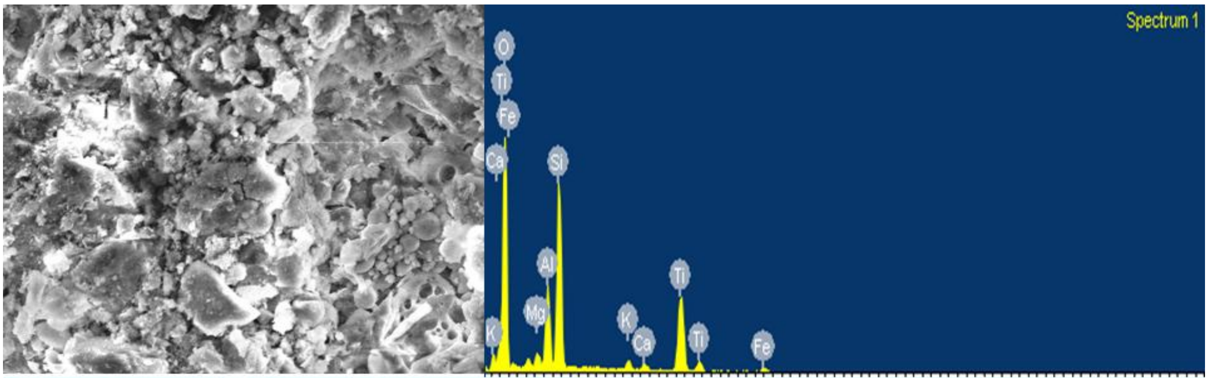
6.9.1 SEM-EDS

The SEM-EDS (Scanning Electron Microscopy -Energy Dispersive Spectroscopy) images as depicted in the Figures 6.8(a), 6.8(b), 6.8(c) of the freshly coated FA+FS spherical beads, as well as the recycled beads (40 cycles) show the uniform coating of TiO_2 over their surface, with a little diminishment of TiO_2 coating after repeated cycles. The confirmation regarding the presence of Fe, Ti, and O was attained by presence of distinct peaks in EDS. Presence of some other compounds were also detected on the surface of the catalyst due to several other contaminants present in wastewater.



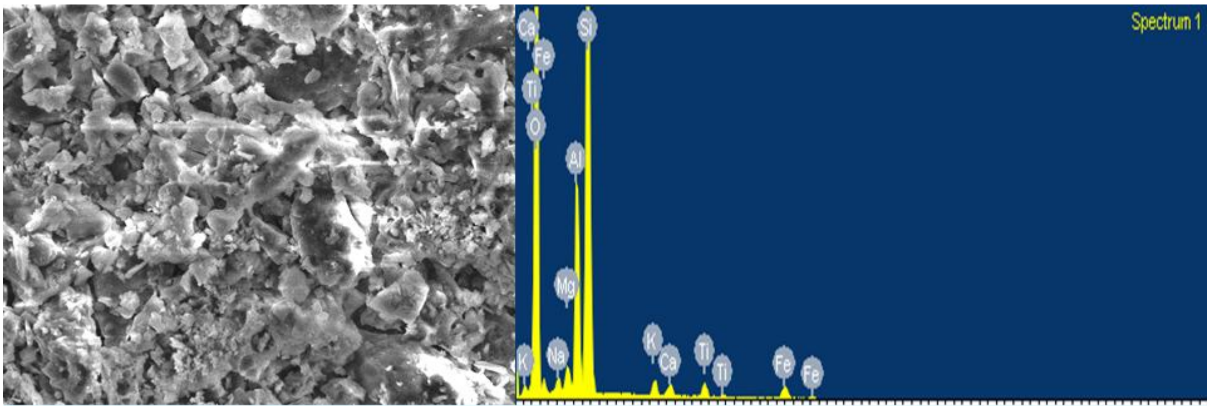
Elements	C K	Na K	Mg k	Al K	Si K	K K	Ca K	Fe K	O
Weight	11.26	0.56	1.16	5.62	15.05	1.47	5.56	2.89	56.44

Figure 6.8 (a): SEM-EDS of uncoated FA+FS spherical beads



Elements	Ti K	Mg k	Al K	Si K	K K	Ca K	Fe K	O
Weight	23.35	1.44	6.98	17.89	1.66	1.08	2.88	44.73

Figure 6.8(b): SEM-EDS of freshly TiO_2 coated FA+FS spherical beads



Elements	Ti K	Mg k	Al K	Si K	K K	Ca K	Fe K	O
Weight	14.1	23	8.74	19.50	1.58	1.29	4.78	48.02

Figure 6.8(c): SEM-EDS after 40 recycles of TiO_2 coated FA+FS spherical beads

6.9.2 UV/DRS Analysis

Evaluation of band gap energy was carried out utilising UV-visible Diffuse reflectance spectroscopy. A comparison was made between band gap energy of the P-25 TiO_2, freshly coated and recycled catalyst coated Fe composite. The scan was carried out ranging from 200-800 nm. There was a slight shift in the spectra of the composite catalyst over alone TiO_2 hence defining the capability of the composite catalyst to absorb light in visible spectrum.

$$E = hc/\lambda \qquad [31]$$

Where,

E = band gap energy (eV), c = speed of light, h = Planck's constant, and k = absorption wavelength.

Utilising the given equation the value of band gap energy was 3.2eV for P-25 TiO_2 , 3.15eV for fresh catalyst (beads) and 3.18 eV for recycled catalyst (beads), confirming the activity of the catalyst even after repeated use.

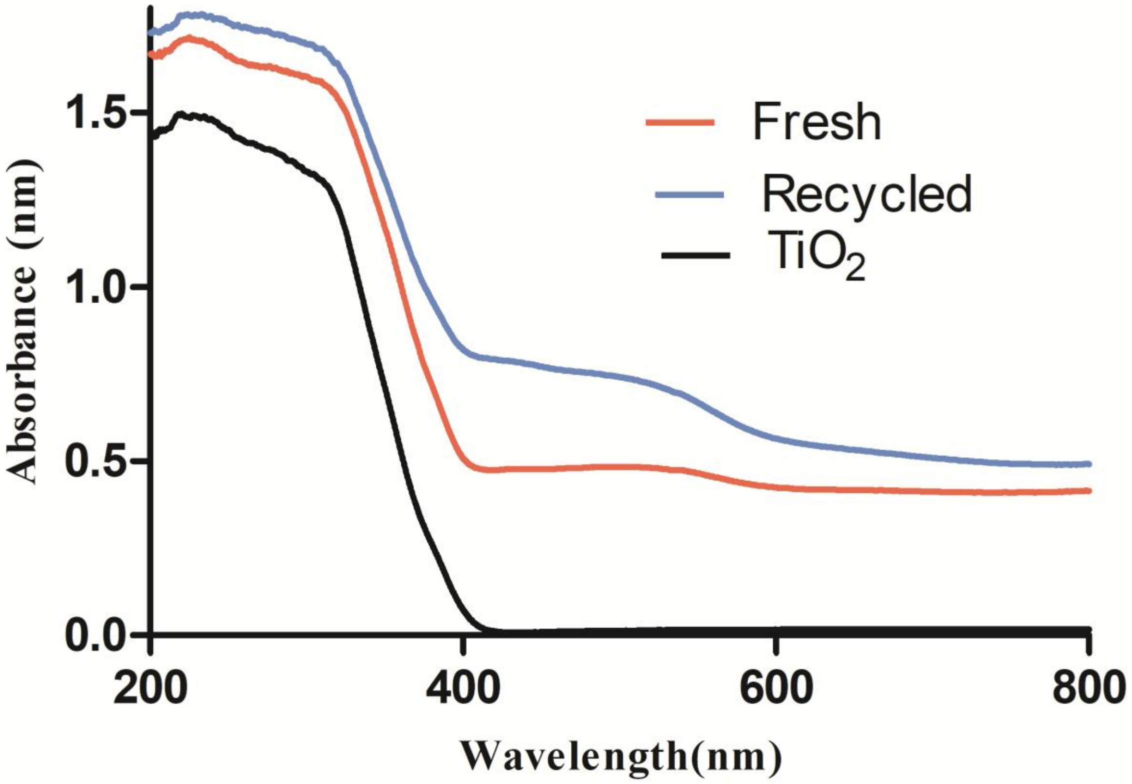


Figure 6.9: UV Visible DRS of fresh TiO_2, composite fresh and recycled beads

6.9.3 FTIR Analysis

FTIR (Fourier Transform Infrared spectroscopy) was performed in order to determine the morphological features of composite beads when compared to fresh TiO_2. The spectra of the TiO_2, fresh beads and recycled beads have been shown in the Figure 6.10.

The scan depicted appearance of peaks in the range 800-1200 cm^{-1} for both the fresh and recycled spectrums, determining the presence of Ti-O-Ti bonds in the both samples which proves the retention of TiO_2 lattice in case of immobilised beads.

The peak existing in the range 450 to 550cm^{-1} confirms the presence of Fe-O bonding which exists in the spectra of fresh and recycled composite beads and are absent in spectra of fresh TiO_2 sample.

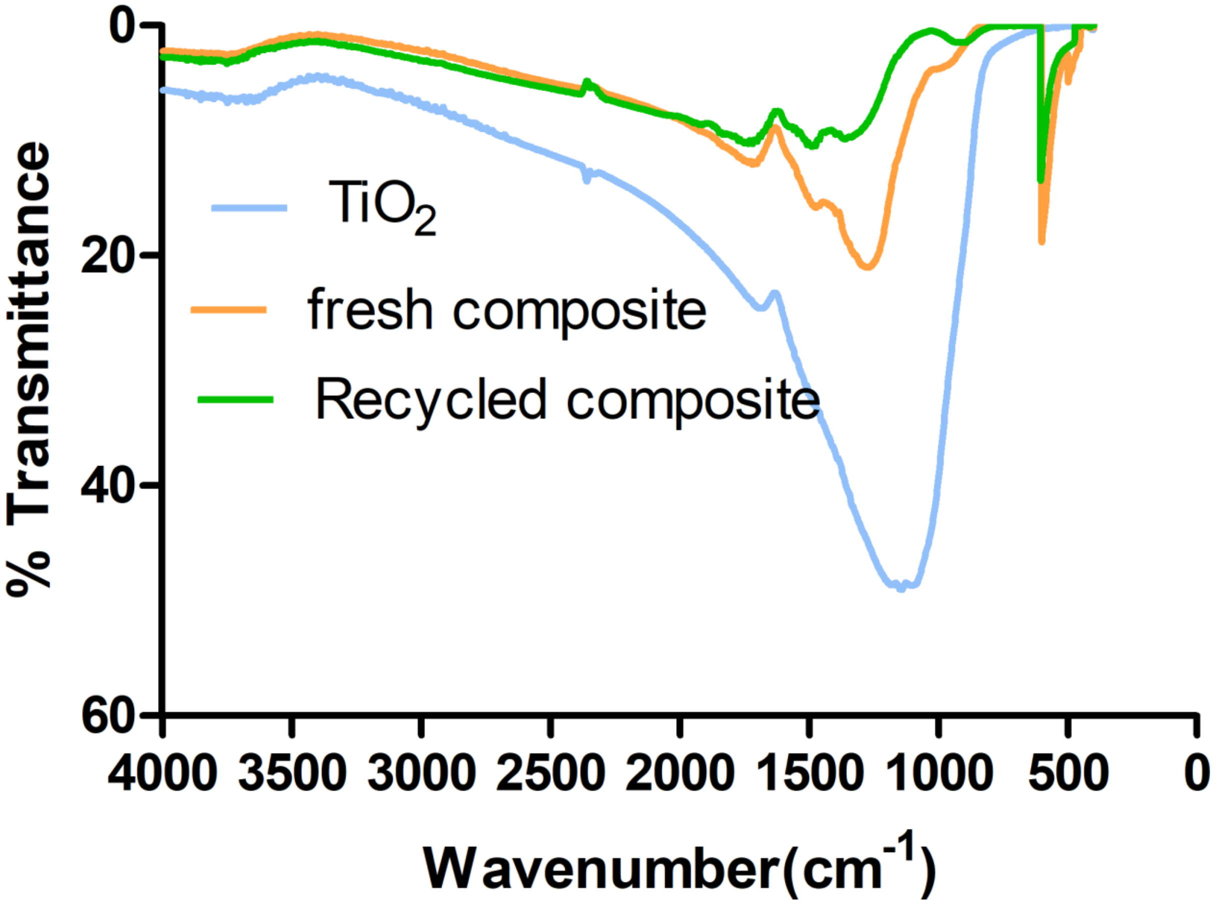


Figure 6.10: FTIR of TiO_2, fresh composite and recycled composite

6.9.4 Iron Estimation

Iron leaching test was carried out to determine the percentage concentration of Fe^{+2} (Ferrous) and Fe^{+3}(Ferric) during the duration of experiment as shown in Figure 6.11. The concentration of ferrous ions was more as compared to the Ferric ions, due to the presence of H_2O_2 which would ultimately convert Ferric ions to Ferrous ions.

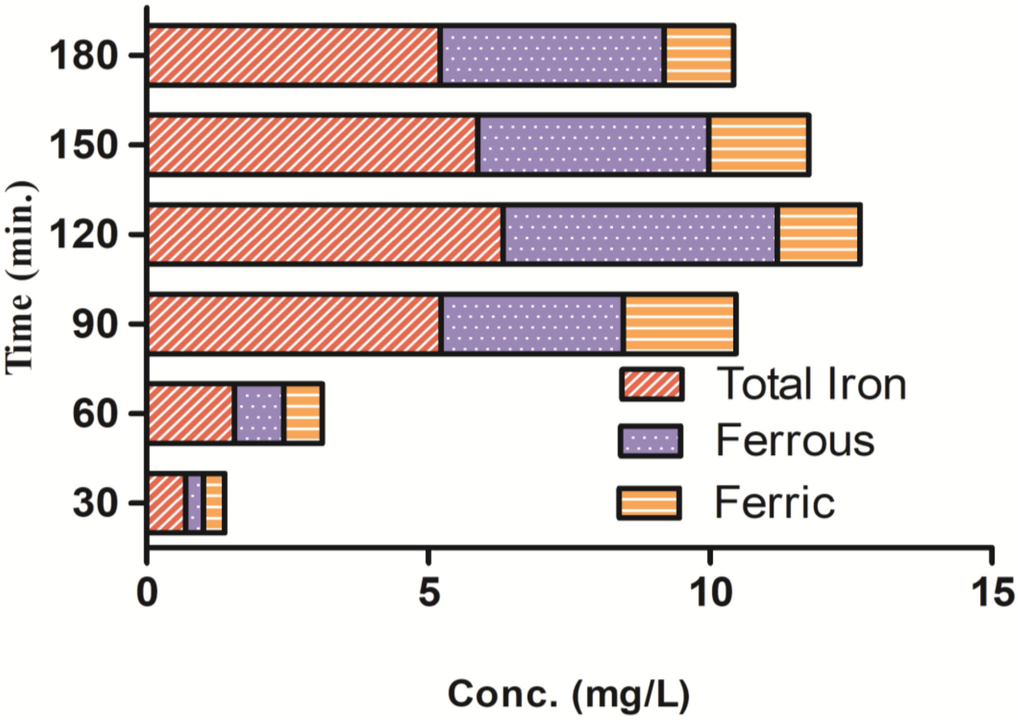


Figure 6.11: Ferrous and Ferric concentration during isoproturon degradation

6.10 Mineralisation Studies

The mineralization study was carried out to determine the complete degradation of contaminant isoproturon. The investigation depicted the presence of nitrate and nitrite ions with a gradual decrease in concentration of nitrate ions during the experiment (Figure 6.12), as there is a possibility of them being converted into nitrite ions which shows a consecutive increase in the concentration (Figure 6.13). There was reduction in 65% of COD during the treatment process hence confirming increase in degradation as shown in the Figure 6.14.

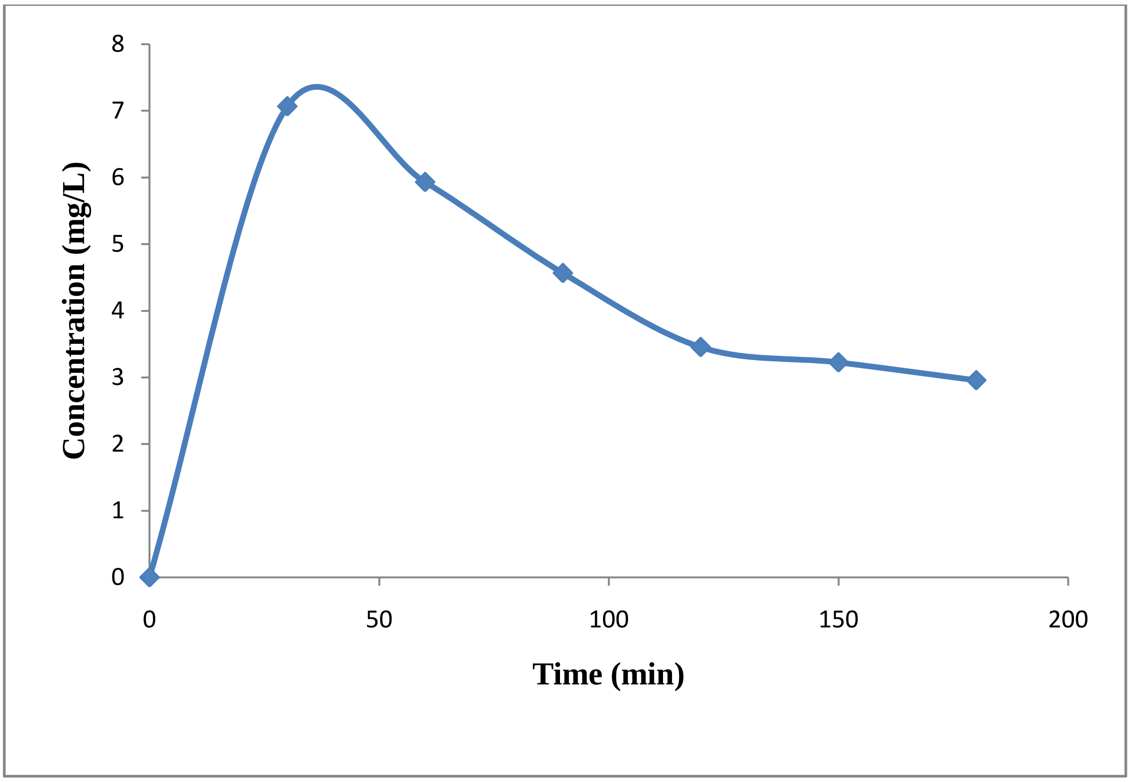


Figure 6.12: Concentration of nitrate ions during degradation of isoproturon

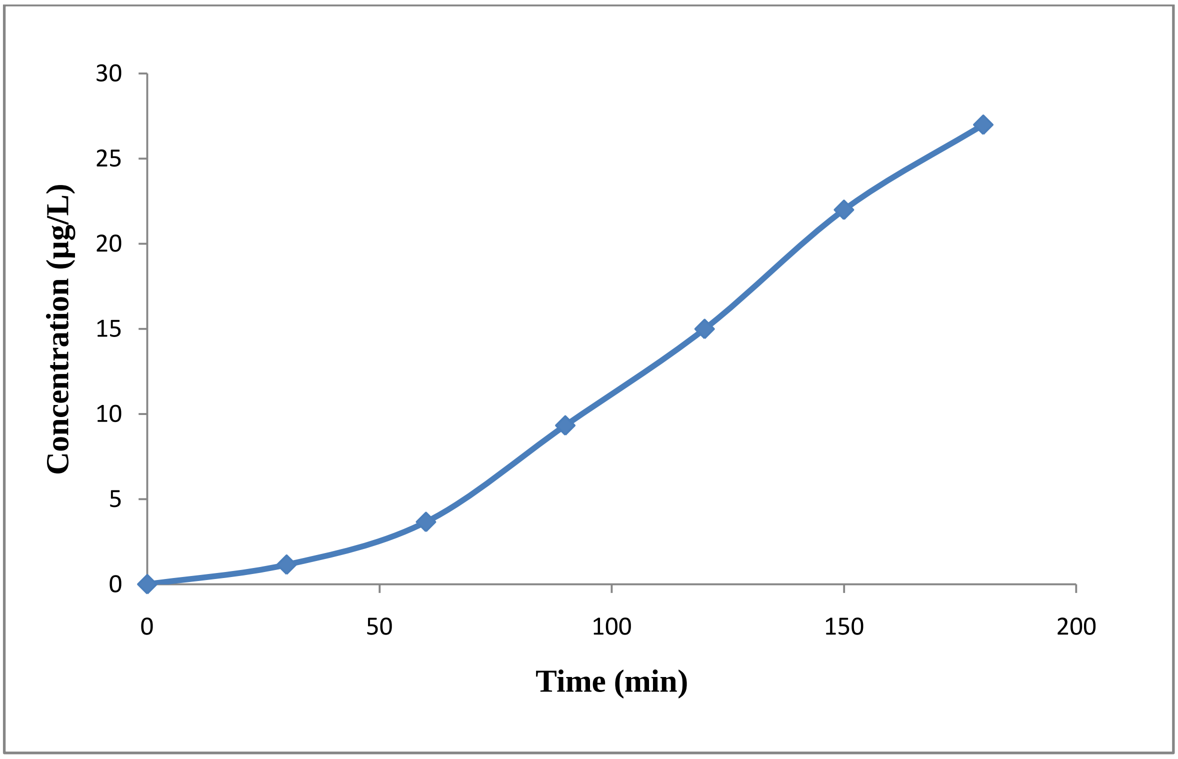


Figure 6.13: Concentration of nitrite ions during degradation of isoproturon

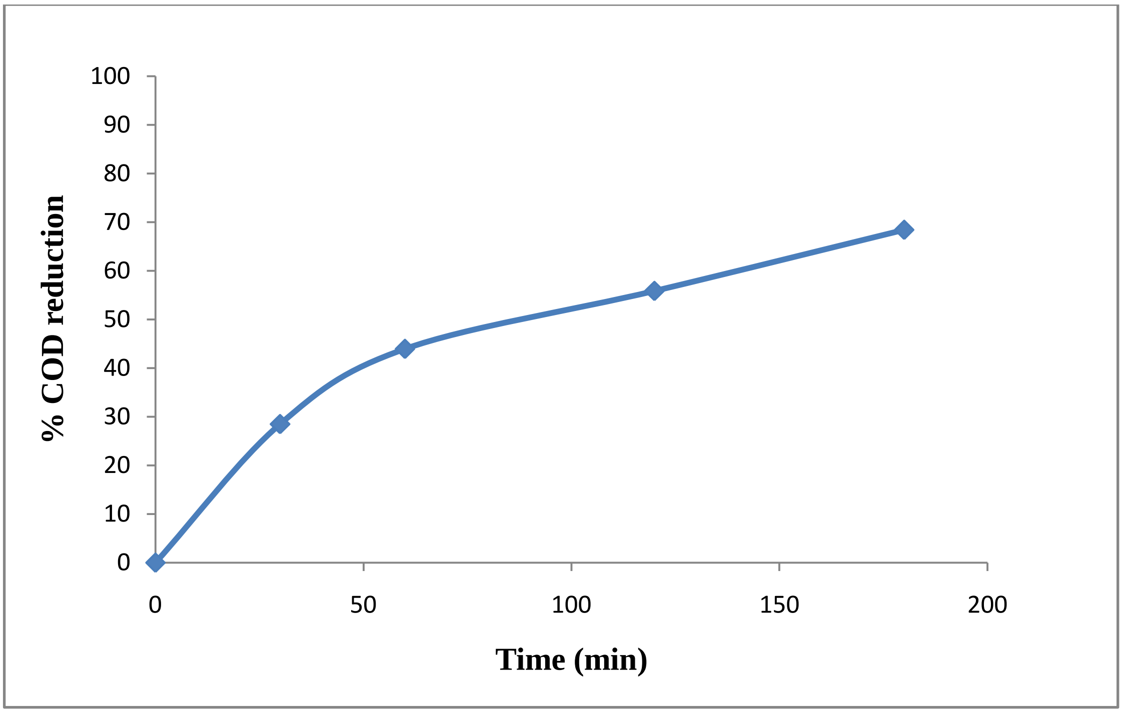


Figure 6.14: Increase in % COD reduction during the degradation of isoproturon

Ammonical estimation was done to confirm the complete mineralization of isoproturon during the course of reaction. The figure 6.15 determines that there is an acute increase in the ammonical concentration during the degradation process. Ranging from negligible concentration of ammonia at 0 minutes to almost 2.7μg/L after 180minutes.

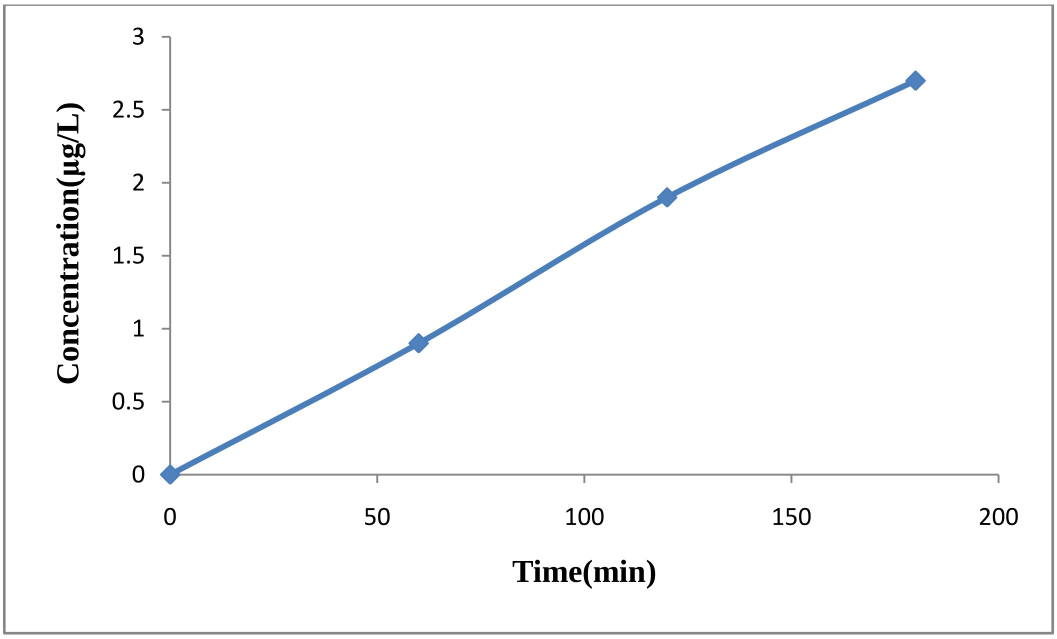


Figure 6.15: Concentration of Ammonia during integrated degradation of isoproturon

The complete mineralization of the compound could be proved by GC-MS (Gas chromatography-Mass spectroscopy) analysis for identification of compounds formed during degradation as shown in figure 6.16 along with chromatograms. The proposed degradation mechanism (figure 6.17) can follow two distinct routes of hydroxylation, which further undergoes fragmentation by hydrodenitrogenation and gives 2-amino-5-isopropylbenzene-1,4-diol. The intermediate formed undergoes final fragmentation to give acetaldehyde, 2-methyl butane, nitrate, nitrite, nitrogen, carbon dioxide and water.

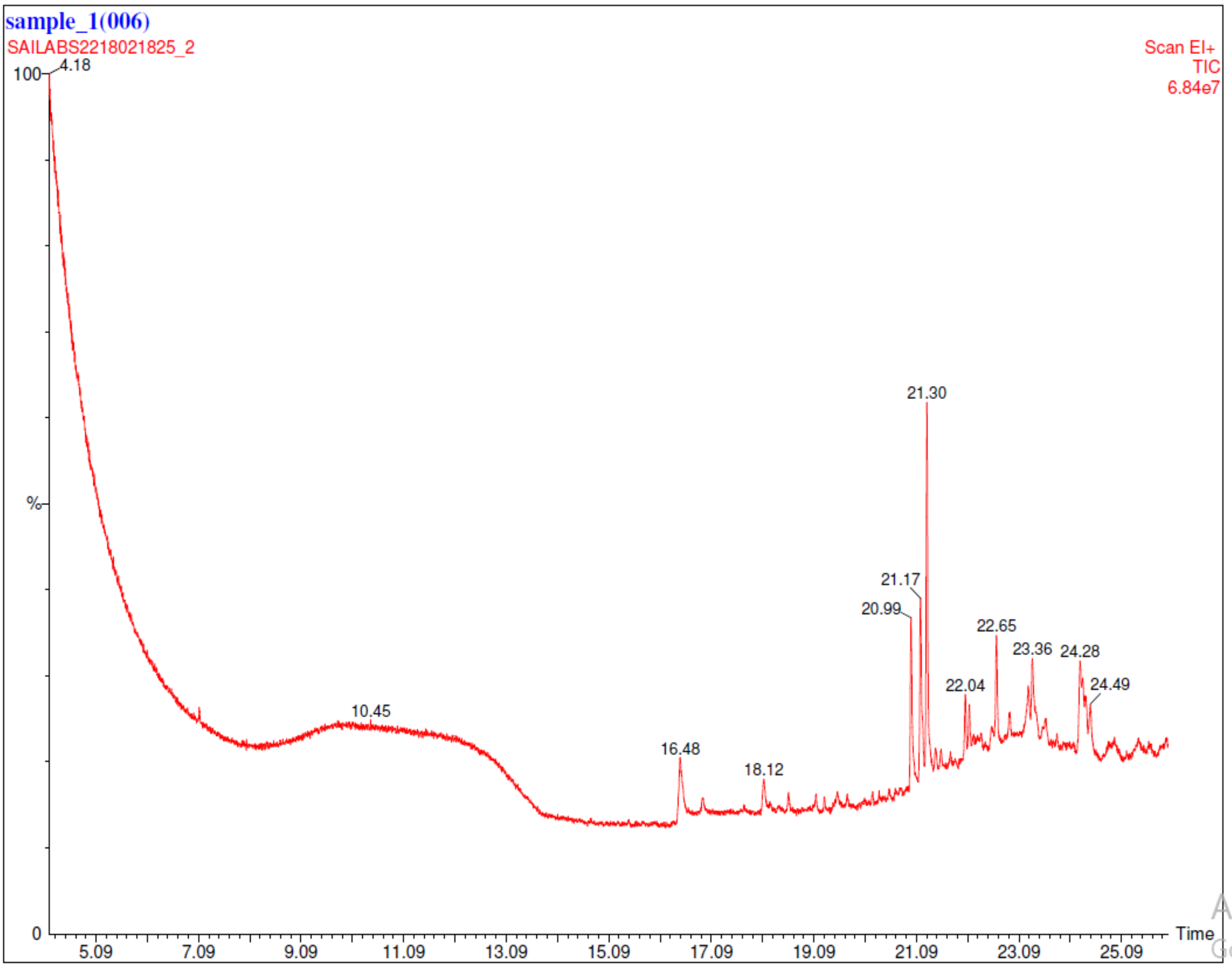


Figure 6.16: Intermediates formed during GC-MS analysis of isoproturon

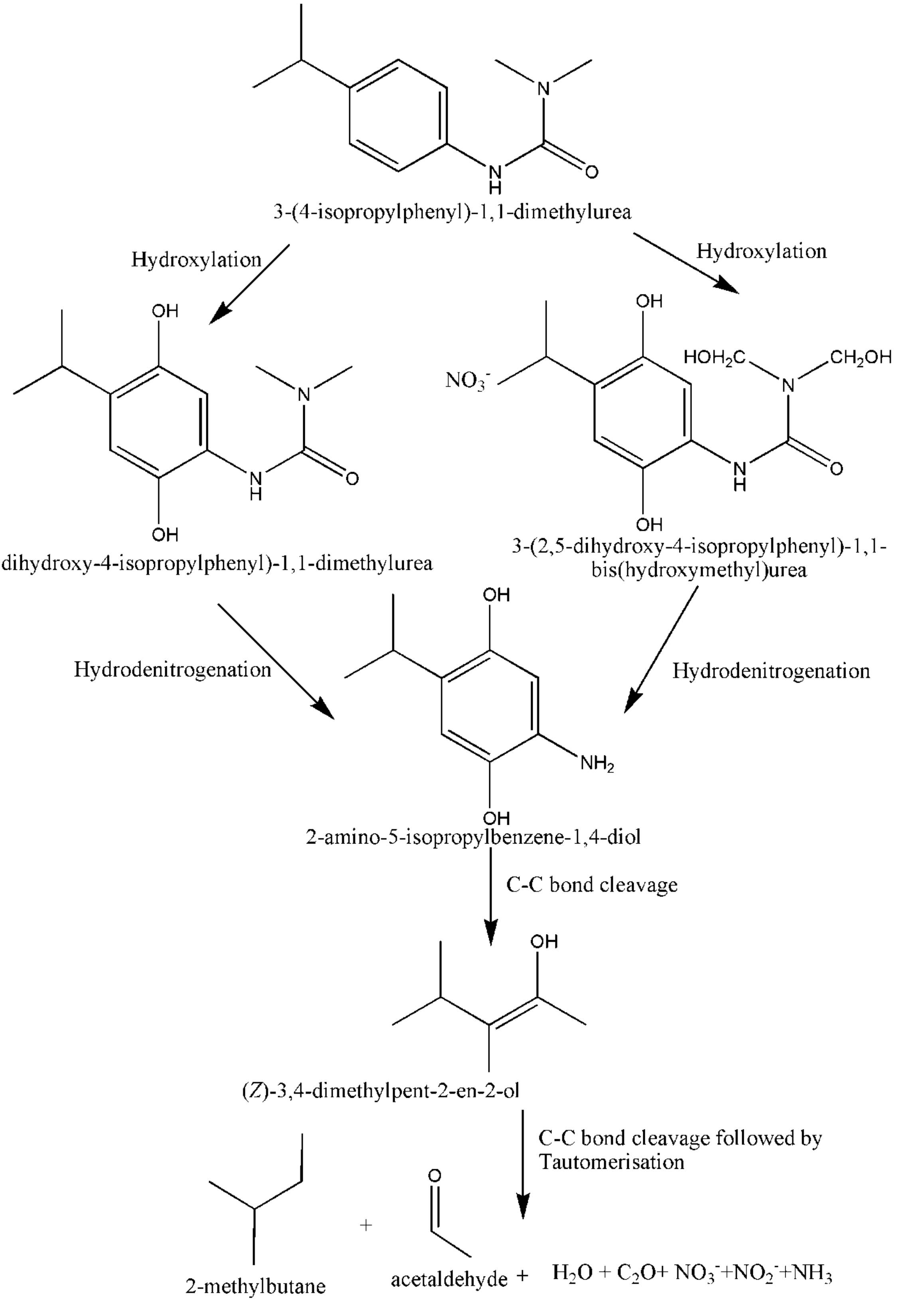


Figure 6.17: Proposed mechanism for degradation of isoproturon

CHAPTER-7

CONCLUSION

An advanced concept of integrating in-situ dual effect of photo-Fenton and photocatalysis utilizing waste materials like FS and FA has been successfully incorporated for degradation of compound isoproturon by successful reduction in the degradation time as compared to individual processes. The optimized conditions were specified using RSM based on BBD which included: H_2O_2 dose (0.444ml), number of composite beads (42) i.e covering 75% of the reactor's area, volume of wastewater (190ml) and treatment time (176min) showing degradation up to 80.96%. The integrated binary process followed pseudo first order kinetics and overall 44% synergy was obtained over the respective individual processes. Through the characterization of composite beads using SEM/EDS, UV/ DRS and FTIR the presence of iron along with TiO_2 on the surface of beads were confirmed, hence proving the stability and utility of integrated process. Mineralization of isoproturon by production of nitrate, nitrite and ammonia along with reduction in COD confirmed the degradation of the compound. Presence of Ferrous and Ferric in the solution determined the photo-Fenton reaction. The degradation mechanism was suggested by identifying intermediates through GC–MS analysis. Hence, the integrated binary process using composite beads would provide a better alternative for various industries releasing contaminants into the fresh water.

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