Degradation studies of paracetamol using novel Fe-TiO_2 composite

A Dissertation

Submitted in the partial fulfillment of the requirement for

the award of the degree of

Master of Science

In

Biochemistry

Submitted

by:

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Candidate declaration

I, hearby declare that the work presented in the thesis entitled **"Degradation studies of paracetamol using novel Fe-TiO_2 composite"** in partial fulfillment of the award of the degree of Master of Science in Biochemistry, School of chemistry and Biochemistry , Thapar institute of engineering and technology, Patiala. This is an authentic record of my work during the period of six months from Jan, 2019 to July, 2019 under the guidance of **Dr. Anoop Verrma and Dr. Sanghamitra Barman,** Thapar institute of engineering and technology, Patiala. I have not submitted the matter embodied in the thesis for award of any other degree or diploma.

Place: Patiala
Date: 15/07/19

Sonali
(301707018)

Certificate

This is to certify that the thesis entitled submitted **"Degradation studies of paracetamol using novel Fe-TiO_2 composite"** submitted by Sonali in partial fulfillment of the award of the degree of Master of Science in Biochemistry, School of chemistry and Biochemistry, Thapar institute of engineering and technology, Patiala in record of student's own work carried out by her. The report has not submitted for the award of any other degree or certificate in this or any other University or Institute.

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Abstract

A novel composite Fe-TiO_2 was made by mixing fly ash (FA), foundry sand (FS), and, Bentonite clay in required amounts. This composite acts a surface for immobilizing the TiO_2 (using dip-coating method) besides facilitates leaching of iron (FA and FS). leached iron promotes the photo-Fenton (with the presence of H_2O_2 in the system) while surface active TiO_2 layer lead to photocatalysis. Degradation of paracetamol was acquired by dual process combining photocatalysis and photo-Fenton happening at same place and same time. This dual process showed best results of 96.6% degradation at optimized conditions i.e. H_2O_2 dose (525mg/L), number of beads (80), degradation time (215 minutes), volume (200 mL). The enhancement of degradation and decrease in degradation time over first order rate constant (k) was achieved. To be sure, even a couple of overlay augments in 'k' value was seen by using novel Fe-TiO_2 composite for the paracetamol degradation confirming in-situ impact. The stability of catalyst was confirmed by several characterizations like XRD and SEM/EDAX. Moreover mineralization of paracetamol included nitrate, nitrite, total iron estimation, and products formed during degradation were confirmed by GC-MS analysis.

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Chapter 1

Introduction

General

In developing countries like India there is a huge consumption of pharmaceuticals due to poor hygiene and health problems. To cater the ever growing demands of these kinds of pharmaceuticals, the industries are producing the drugs in unregulated ways. The unregulated drugs are being consumed by huge population which has poor health status hence require medications. Such medications are not properly utilized by the body they are being excreted out by means of urine or some other routes that is how they found their way to the drinking water or the surface water. There are wide number of reports on presence of these kind of pharmaceuticals in drinking or surface water **(Abdel-wahab et al.,2017; Fick et al., 2009; Huerta-fontela et al., 2011; Mompelat et al.,2009).**

As the growth of pharmaceutical industries increases, the consumption of pharmaceutically active compounds leads to development of new compounds that have worse effects on the environment. Pharmaceutical industries produce many products by chemical synthesis, research and development, natural product extraction and formulation. Due to research and development a huge amount of laboratory waste is produced on the daily basis which includes chemical and biological waste **(Desale et al., 2013; Huerta-Fontela et al., 2011).**

Moreover the industries which are producing these pharmaceuticals are also responsible for discharging directly or indirectly such pharmaceuticals ultimately finding their routes into drinking or surface water (**Vulliet et al., 2011).**

Numerous kinds of pharmaceuticals are utilized in our nation for a wide assortment of uses to profit people and animals. Significant classes of human pharmaceuticals consist of: antimicrobials, analgesics, beta-blockers, cytostatics, lipid regulators, antibiotics, estrogens etc.**(Wang et al.,2011).** Paracetamol, amoxicillin, ofloxacin etc. are most commonly prescribed medicines by the specialists **(Westergaard et al., 2014; Ranieri et al., 2011)**.

There are widespread reports of presence of antibiotics like ciprofloxacin in the treated sewage **(Subedi et al., 2017; Mutiyar et al., 2014)**. This resulted in contaminating the water bodies and animals like fishes as well; vultures after eating those fishes started getting less in number with each passing day. This finally gets noticed after a huge loss of the several generations of an aquatic life **(Mutiyar et al., 2014)**

According to a report in USA it has been discovered that around 70 billion NSAIDs (Non-Steroidal Anti-inflammatory Drugs) are endorsed by the specialists and about 30 trillion are being sold each year. The amount of Paracetamol in treated wastewater was found between 20 ngL^{-1} to 4.3 µgL^{-} **(Sokol et al., 2016)**. It was evaluated that the centralization of Paracetamol in surface water can stretch up to78.17 µgL^{-1}**(Sokol et al., 2016)**. Presence of these kinds of contaminants in water clearly depicts the inefficacy of conventional methods **(Petra et al., 2015).**

Conventional treatment methods like preliminary, primary, secondary, and tertiary treatments transforms the pharmaceuticals like compounds from one form to another while not completely degrading the compounds. Other shortcomings includes sludge formation and the non-evacuation of the toxicity from the waste water producing some unenviable disinfection by-products which can be deleterious for humans and marine species **(Petra et al.,2015; Lee et al.,2014; Liu et al.,2010; Delacruz et al.,2012).** To overcome these disadvantages several studies on advance treatment technology has been reported **(Poyatos et al., 2010; Torun et al., 2014; Deng et al., 2015).**

In the recent past advanced treatment technologies approved their potential for treatment of wide variety of compounds. Various advance treatment technologies like sonolysis **(De Bel et al.**, **2009)** Fenton **(Segura et al., 2013)**, photo-Fenton and heterogeneous photocatalysis **(Moya et al., 2010; Jallouli et al., 2018)** etc. mentioned in the literature are used for degradation of various compounds in wastewater**.** These methods reduce the reaction time and increments oxidation potential during degradation **(Amr et al., 2012).**

One of the efficacious advanced oxidation process used to detoxify the pestilent and recalcitrant pollutants in wastewater is the photo-Fenton method that combines the Fenton reagent (Fe^{2+}/H_2O_2) and the light energy. The wide range of interest has attracted by the undiversified photo-Fenton method attributable to its comparatively low value and high performance in generation of •OH for decomposing the recalcitrant organic composite **(Banic et al., 2011; Hansson et al., 2012).** Same time photocatalytic oxidation employs a metal oxide semiconductor like Titanium oxide (TiO_2) as photocatalyst which degrades organic compounds into water and CO_2. TiO_2 is widely used photocatalyst as it can efficiently eradicate hepatoxic organic and inorganic pollutants from waste water. TiO_2 is both chemically and biologically inactive, cheap, photostable and extremely photoactive **(Gupta et al., 2011; Choi et al., 2014).**

Although these advanced technologies have shown their capability in treating almost all range of harmful compounds **(Amr et al., 2012; Gupta et al.,2011; Daghrir et al.,2013)** , yet their commercial visualization is still debatable. There are some downsides of advanced oxidation technique like the quick recombination of electron/hole generated, high iron sludge formation, catalyst cost, separation and reusability of the catalyst **(Daghrir et al., 2013; De Souza et al., 2010).**

To eradicate the disadvantages of AOPs, there is wide assortment of papers reported on the catalyst immobilization on the support **(Hir et al., 2017; Namdeo et al., 2009; Scotti et al., 2009; Wang et al., 2009).** Although successful but problems like mass transfer limitations, low degradation efficiency, moderately low selectivity, and increment in treatment time are concerns which limit their time for degradation **(Homaei et al., 2013).**

Hence, to solve these limitations to some extent combination of both the processes i.e. photocatalysis and photo-Fenton is employed in a way which thereby utilizing the limitations in the other process to give better results by reducing the treatment time with enhancement of degradation efficiency. Also with this dual process, the electron-hole recombination in photocatalysis turns infrequent resulting in increasing efficiency of degradation (**Bansal et al., 2018)**. Moreover this process leads to enhanced rate of reaction along with reducing the treatment time.

In the present study, the in-situ dual effect investigations of pharmaceutical compound Paracetamol have been performed using fixed-bed catalysis. In-situ dual method being cost effective gives good yield and can be successful for large scale applications.

Chapter 2

Pharmaceutical industry and Dual process

2.1 Overview

The pharmaceutical assembling industry delivers a wide scope of items to be utilized as human and animal drugs. In these business, different sorts of procedures are associated with the assembling of pharmaceutical items, for example, innovative research work, substance amalgamation, common item extraction and detailing. In research work a large amount of wastes are created by the laboratories. The release of waste from pharmaceuticals into natural environment is a major issue for controllers and the pharmaceutical industries **(Desale et al., 2013)**.

People take few medications without prescription such as analgesics, antibiotics and antimicrobial etc. These medications are partially digestible and therefore excrete in the fecal matter either in intact or metabolite form, which may pollute the water bodies. The effect of a medication varies with age and sex **(Manchikanti et al., 2010)**.

In year 2014 in India a study on wastewater were done **(Subedi et al., 2017; Mutiyar et al., 2014)** which turns out to be a very dangerous conclusion not only for birds like vultures but also for human beings. As there is a huge amount of an antibiotic ciprofloxacin found even in the treated sewage. This resulted in contaminating the water bodies and animals like fishes as well; vultures after eating those fishes started getting less in number with each passing day. This finally gets noticed after a huge loss of the several generations of an aquatic life **(Mutiyar et al., 2014)**

In USA, specialists endorse around 70 million NSAIDs yet 30 trillion altogether are being sold pointing that people are taking quite a bit of it without any prescription **(Sokol et al., 2016)**. Abuse of CNS depressants and stimulants is a typical matter in United States. In 2017, National survey on Drug Use and Health reported that about 2 million Americans have been abused with pain relievers annually.

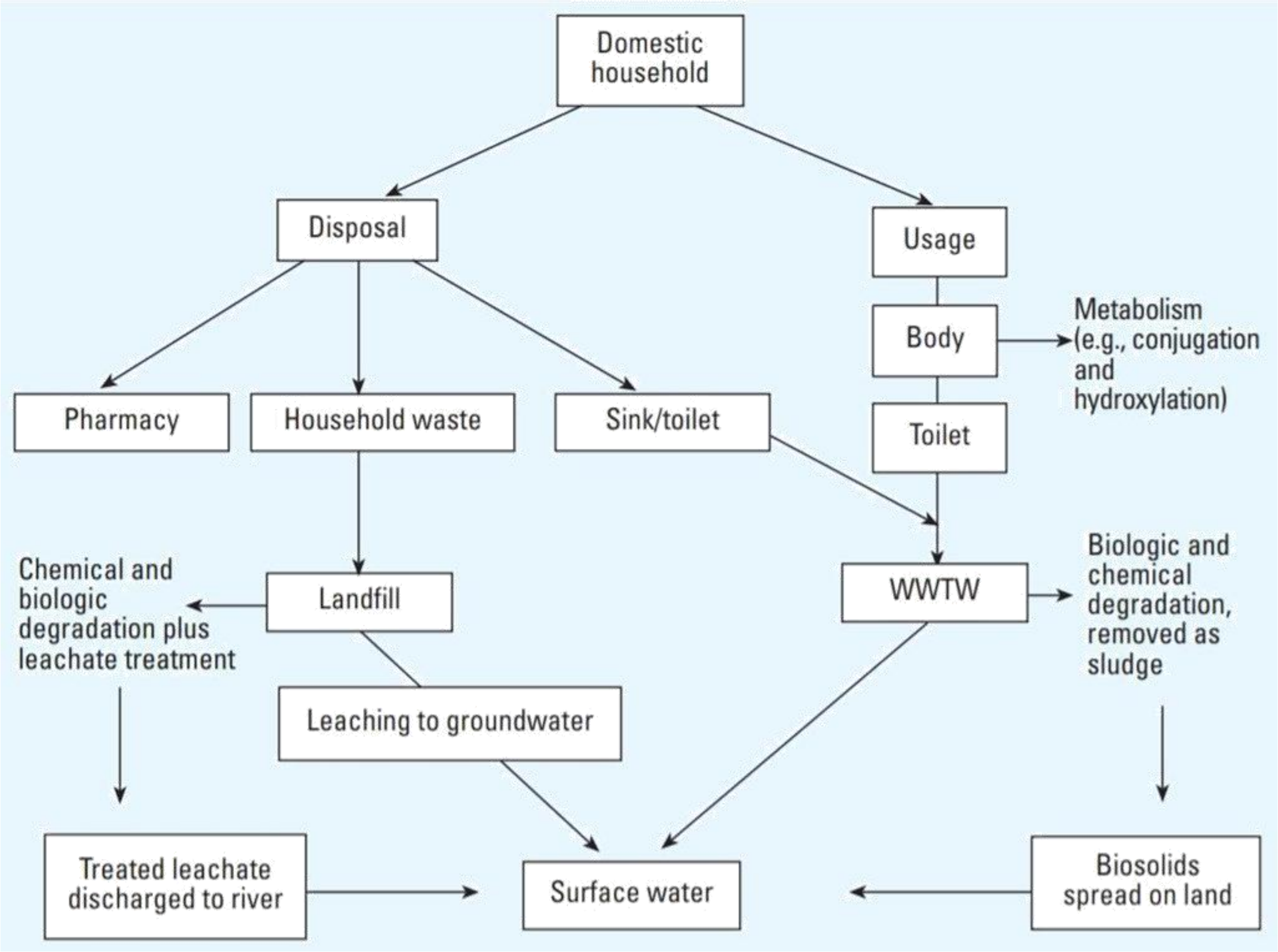


Figure2.1: Pathways of drugs contaminating the environment (WWTW: Waste water treatment works) (Source: Bound et al., 2009).

Figure 2.1 depicts that by two chief ways pharmacological compounds can enter in the water bodies: waste water treatment works (WWTW) and disposing medicines into sink/latrine **(Bound et al., 2005).**

Traditionally the pharmaceuticals in water from hospitals and industries are removed by waste water treatment plant before releasing into the environment. But some compounds are not removed by using this treatment. In order to circumvent this issue, advance oxidation techniques can be used for degradation of harmful substances in the wastewater **(Behera et al., 2011).**

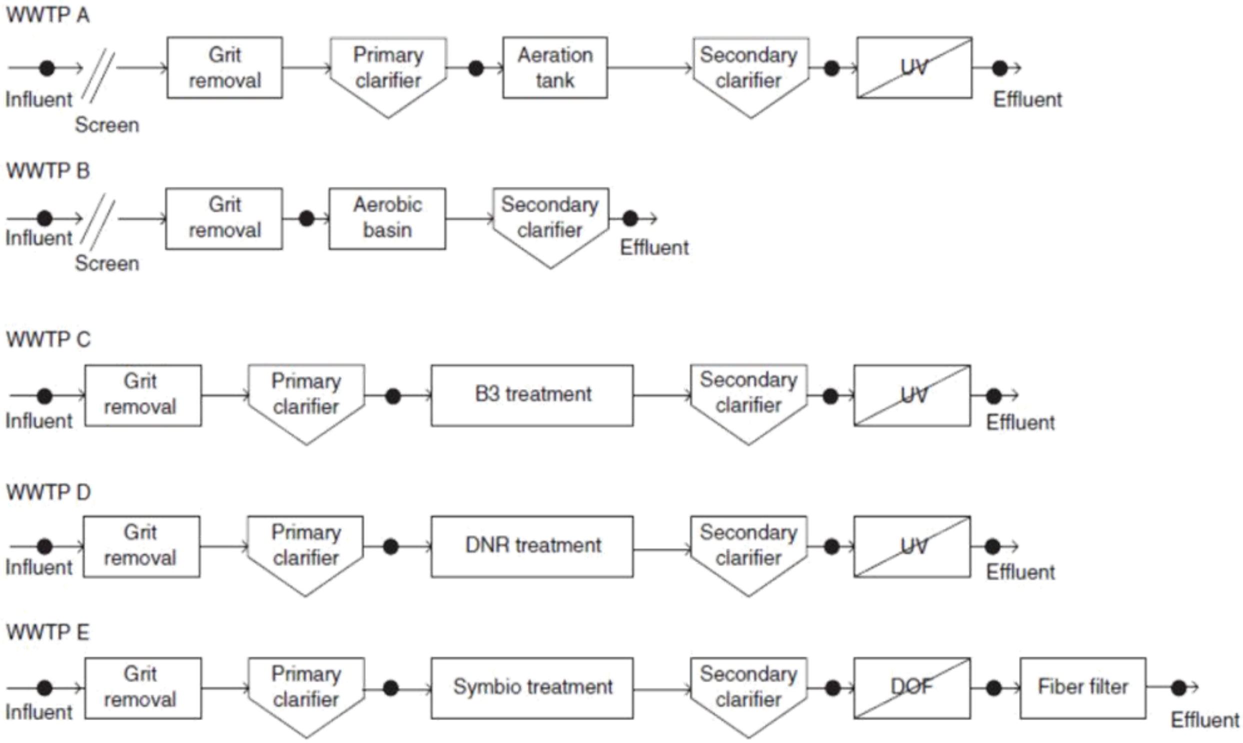


Figure2.1.1: Schematic diagram of five WWTPs processes (Source: Behera et al., 2011)

Figure 2.1.1. shows that WWTPs A and B uses conventional activated sludge process for the treatment, WWTP C uses Bio Best Bacillus (B3) process, WWTP D uses a modified process which removes nitrogen and phosphorus at the same time and WWTP E uses Symbio treatment process **(Behera et al., 2011).** But because of less efficacy and sensitivity of WWTPs, various pharmaceuticals are found in the WWTP discharge.

2.2. Application of advance oxidation techniques:

Wastewater consists of various fine suspended solids, metals, pollutants, inorganic and natural particles. The filtration and settling of small sized particles is difficult due to the close surface charge. The expulsion of these particles becomes major venture for industries. Coagulations or flocculation is widely used for expulsion of these particles from wastewater, but exhibits several flaws, therefore Advances oxidation processes are used **(Lee et al, 2014).** .

2.2.1 Photo-Fenton:

Photo-Fenton is extremely efficient process for wastewater treatment due to its low cost and high efficiency. In the incidence of ferrous ions, decomposition of H_2O_2 takes place. This process involves the transfer of electron between H_2O_2 and ferrous ion. Furthermore under UV light the effectiveness of process increases due to regeneration of ferrous ions and more hydroxyl radical production takes place

$$Fe^{2+} + H_2O_2 \longrightarrow Fe(OH)^{2+} + \bullet OH \qquad (2.1)$$

$$Fe(OH)^{2+} + \text{ɧʋ} \longrightarrow Fe^{2+} + \bullet OH \qquad (2.2)$$

Even the Fenton and photo-Fenton responses have been connected for wide kinds of natural contaminants, their utilization for the decadence of pharmaceutical mixes has been applied to a small degree than different AOPs like photocatalysis or then again O_3. Moreover Fenton is accounted to be lesser effective than photo-Fenton. This process has pulled in wide intrigue due to its generally minimal effort and elite in producing •OH for the deterioration of unmanageable natural mixes **(Banic et al., 2011; Poyatos et al., 2009; Arriaga et al., 2009).**

2.2.2 Heterogeneous photocatalysis:

In last few decades the process called heterogeneous photocatalysis has extended quickly and has experienced numerous developments particularly in relevance to energy and environment **(Ibhadon et al., 2013)**.In this process the acceleration of a photoreaction occurs in the existence of a photocatalyst **(Augugliaro et al., 2012).** Degradation is done with the help of a semiconductor TiO_2 which acts as a catalyst and carry out series of redox reactions. TiO_2 has large band gap and is commonly found as anatase (band gap 3.4 eV) and rutile (band gap 3.0 eV) **(Ibhadon et al., 2013).** In this study upon light irradiation on catalytic site the target compounds get oxidized forming radicals/holes (h^+) **(Augugliaro et al., 2012).** In this process the catalyst is available as solid while reaction occurs at the interface between solid-fluid/solid-gas. The essential responses in such catalysis are reduction reactions or electrochemical oxidation including hole and movement of electron from photo-energized semiconductor **(Byrne et al., 2015).**

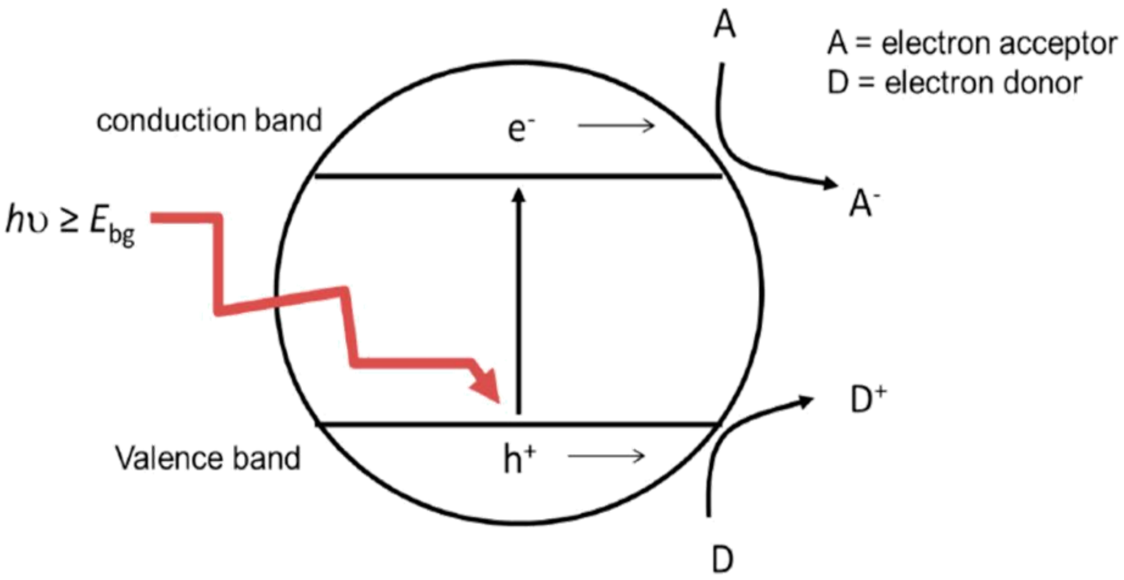


Figure 2.2.2: Basic heterogeneous photocatalysis mechanism. (Byrne at al., 2015)

Figure 2.2.2 shows that the semiconductor is energized by the ingestion of electromagnetic radiation with vitality equivalent to or more prominent than the band gap vitality. These outcomes in the advancement of an electron from the valence band to the conduction band, leaving a positive opening in the valence band. The electron/gap sets may recombine with the vitality being re-transmitted as warmth or light, or the charge transporters can relocate to the molecule surface **(Byrne et al., 2015).**

The particular wavelengths that can be utilized with TiO2 photocatalysis have been referenced in the table 2.1:

Table 2.1: UV classifications and comparing energies in eV

Spectral Sub Category	**Wavelength range (nm)**	**E in (ev)**
UV-A	400-350	3.09-3.93
UV-B	315-280	3.93-4.42
UV-C	280-100	4.42-12.39

2.2.3 Dual effect of Photocatalysis and Photo-Fenton:

To solve the limitations of photo-Fenton and photocatalysis to some extent combination of both the processes is employed in a way which thereby utilizing the limitations in the other process to give better results by reducing the treatment time with enhancement of degradation efficiency. Also with this dual process, the electron-hole recombination in photocatalysis turns infrequent resulting in increasing efficiency of degradation (**Bansal et al., 2018)**. Moreover this process leads to enhanced rate of reaction along with reducing the treatment time **(Sirtori et al., 2009)**. Research in this particular area has been constantly drawn towards diminishing the treatment time with cost viability of the procedure. In this examination, clever thought of actuating dual effect (photocatalysis and photo-Fenton) proposed in setting of decline in treatment time for the goal contaminant. The dual procedure has colossal degradation adequacy anyway very little connected well yet. The expense of procedure and high measure of these engineered mixes can be impressively diminished if the two methods (photo- Fenton and photocatalysis) are applied simultaneously in one system which would along these lines assemble the degradation rate as well. The possibility of dual effect has been proposed recently by couple of examinations for improving the effect of degradation **(Bansal and Verma, 2017)**.

Different examinations are based on the scaling technique using TiO2 especially in suspension stage joins annular photo reactor **(Autin et al., 2013),** fixed-bed photo reactor **(Borges et al., 2015)**, photocatalytic Taylor vortex reactor **(Jia et al., 2011)**, fluidized bed reactor **(Kang et al., 2011)**, secured fiber optic connection reactor, falling film reactor **(Luna et al., 2014)**,

Meager film settled bed inclining plate reactor **(Khan et al., 2012)**, furrowed plate reactor **(Passalía et al., 2011).** Though powerful to the extent achieving total degradation still there are various operational and furthermore plan recommendations those renders their field scale discernment. Confused mass trade constrainments, strength of the support, extra time use, etc are the components of worry for scale examinations. A long ways past most scale up study have been worked in circulation mode **(Marugán et al., 2009; McCullagh et al., 2011)** along these lines offers more prominent treatment time for a given plot. Therefore keeping in thought the above mentioned elements and furthermore field scale employments of this development, attempts would be made to think about the in-situ dual strategy. In this technique, the bunch will be managed in reliable mode so it could be urged to the natural reactor as well.The proposed thought would prompt lessening in treatment time of degradation of paracetamol.

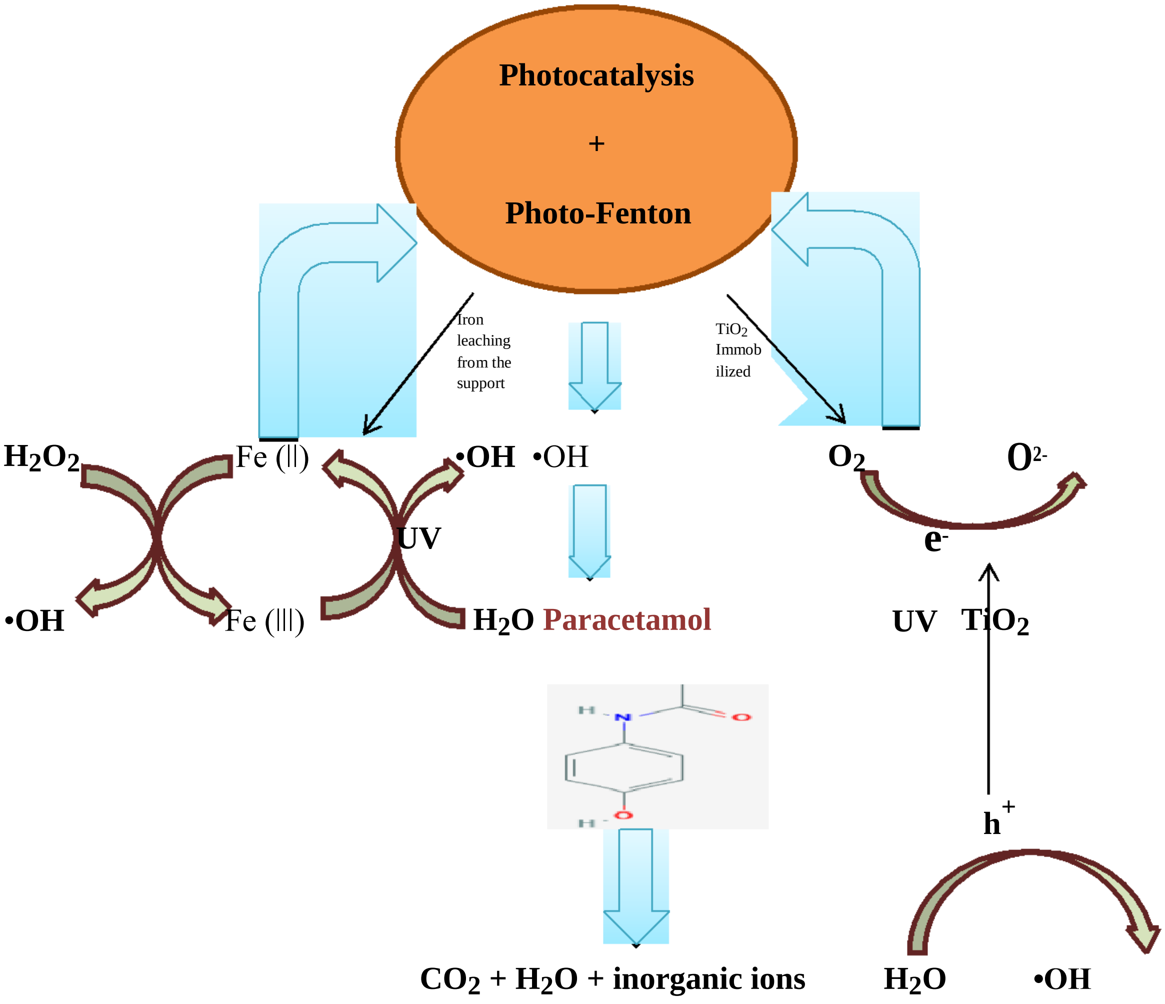


Figure2.2.3: Scheme 1: Dual effect of photocatalysis and photo-Fenton on paracetamol.

Chapter 3

Literature review

3.1 Brief overview

In farming, development, transport, synthetic industry, and in various different routines of the individuals water is sole source of utilization. United Nations indicated that the principal need of poor nations, particularly in Africa, ought to be not budgetary help or mechanical learning yet clean water supply to the citizens. To clean wastewater, there are several average procedures used such as physical, biological and chemical. Each one of these methods can be utilized independently or joined with different procedures to improve the treatment effectiveness **(Gao et al., 2012; Lee et al., 2014; Munoz et al., 2012)**. The decision of the right framework must be done thinking about a few elements, both specialized and affordable. Be that as it may be the ordinary treatment strategies present but a few burdens, which incorporate the accompanying are: (I) mind-boggling expense, (ii) an obvious minimal effort alternative is offered by the natural oxidation, however the natural toxin/s has/need to be biodegradable and of low danger, and (iii) movement of the liquid organics to other stage, leave the taint undestroyed. To beat the bothers of ordinary treatment strategies, different advance oxidation methods have risen in the most recent decades, specifically for the treatment of wastewater from industries. Among these procedures, the advance oxidation procedures have all the earmarks of being a promising field of study, which have been accounted to be viable for the degradation of dissolvable natural contaminants in soil and water. AOPs change artificially pollutants to non-toxic substances, yet present extremely alluring points of interest, for example, the total mineralization of certain pollutants, their oxidation at extremely low concentrations, production of the substances or products which does not harm the environment, and the low utilization of vitality, in correlation with different strategies **(Herney-ramirez et al., 2010).** Among various strategies AOPs have been accurately characterized as water treatment procedures accomplished at room temperature and usual pressure which depends on the in situ production of an amazing oxidizer, for example, hydroxyl radicals (•OH), at an adequate concentration to viably clean water by methods for different photochemical, sonochemical, or electrochemical responses. The most tested and most utilized AOP is the Fenton technique, wherein a blend of a dissolvable Fe

(II) salt and H2O2, called as the Fenton's reagent, is connected to breakdown or destroy various pollutants. Except previous methods there are some more techniques which have been reported like TiO_2 based photocatalysis , ozonolysis and so forth **(Oturan et al.,2014; Dai et al.,2014; Byrne et al.,2015; Shan et al.,2010)**.

3.2 Advance oxidation processes (AOPs):

AOPs includes various processes like ozonation, sonolysis, photolysis, photo-Fenton, and, heterogeneous photocatalysis which degrades various pharmaceuticals by the production of •OH to oxidize the desired compound. •OH is highly unstable and oversensitive so their reactions are exceedingly non-specific and prompt **(Asghar et al., 2015).**

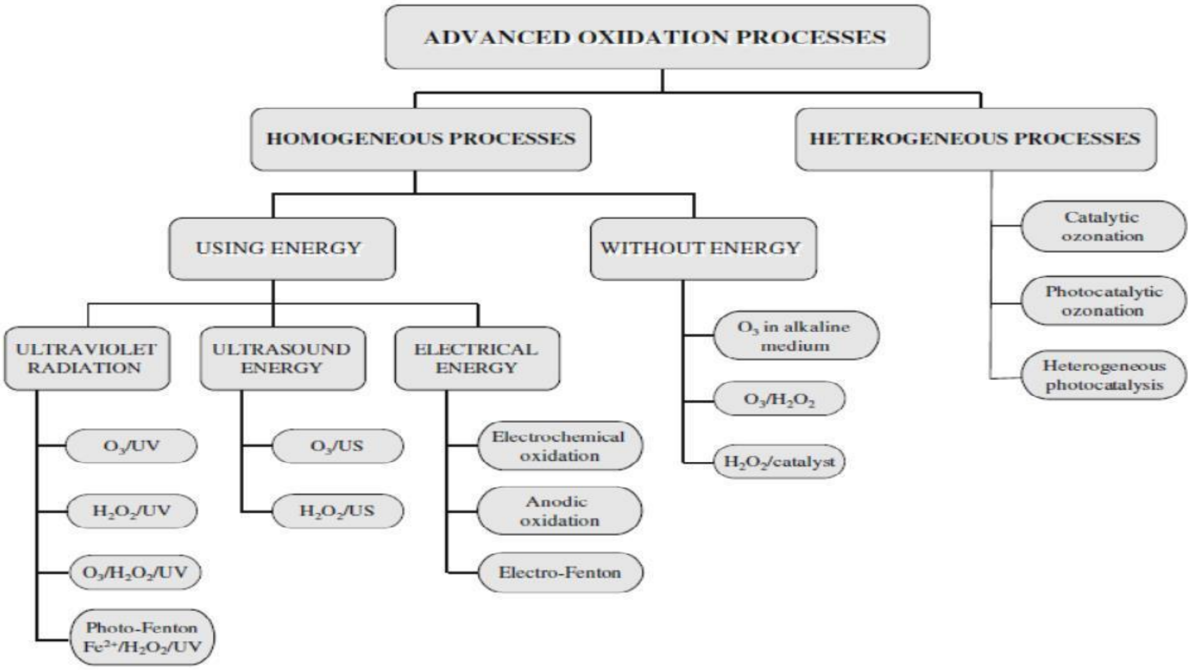


Figure3.2: Advance oxidation forms (AOPs) order. Utilized abbreviations: H2O2 hydrogen peroxide; US ultrasound vitality; particle; O3 ozonation; UV bright radiation; Fe2+ ferrous (Source: Poyatos et al., 2010).

3.2.1 Photo-Fenton:

Photo-Fenton is extremely efficient process for wastewater treatment due to its low cost and high efficiency. In the incidence of ferrous ions, decomposition of H_2O_2 takes place. This process involves the transfer of electron between H_2O_2 and ferrous ion. Furthermore under UV light the effectiveness of process increases due to regeneration of ferrous ions and more hydroxyl radical production takes place **(Elmolla et al., 2009; Bautiz et al., 2007).**

Mechanism **(Hermosilla et al., 2009)**:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + \bullet OH \ k = 76\ M^{-1}\ s^{-1} \quad (3.1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + \bullet OOH + H^{+} \quad (3.2)$$

$$H_2O_2 + \bullet OH \rightarrow \bullet OOH + H_2O \quad (3.3)$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^{-} \quad (3.4)$$

$$Fe^{3+} + \bullet OOH \rightarrow Fe^{2+} + O_2H^{+} \quad (3.5)$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + H_2O_2 \quad (3.6)$$

$$\bullet OOH + \bullet OOH \rightarrow H_2O_2 + O_2 \quad (3.7)$$

$$\bullet OOH + H_2O_2 \rightarrow H_2O + O_2 \quad (3.8)$$

Photo-Fenton is proved as an effective method for degradation of various pollutants like pharmaceuticals compounds **(Klamerth et al., 2010),** dyes **(Peternal et al., 2007),** pesticides **(Navvaro et al., 2011)** etc.

Although successful but photo-Fenton still have some flaws like need of high photoactive species, narrow pH range **(Clarizia et al., 2017),** and, costly process **(Romero et al., 2016).**

3.2.2 Heterogeneous photocatalysis

In last decades this field has been studied widely. In heterogeneous photocatalysis reaction takes place between two phases i.e. solid-liquid but catalyst used is present in the form of solid **(Augugliaro et al., 2012).** Degradation is done with the help of a semiconductor TiO_2 which acts as a catalyst and carry out series of redox reactions. TiO_2 has large band gap and is commonly found as anatase (band gap 3.4 eV) and rutile (band gap 3.0 eV) **(Ibhadon et al., 2013).** In this study upon light irradiation on catalytic site the target compounds get oxidized forming radicals/holes (h^+) **(Augugliaro et al., 2012).** A very less energy is required by TiO_2 for degrading organic pollutants by producing oxidizing species **(Choi et al., 2014).**

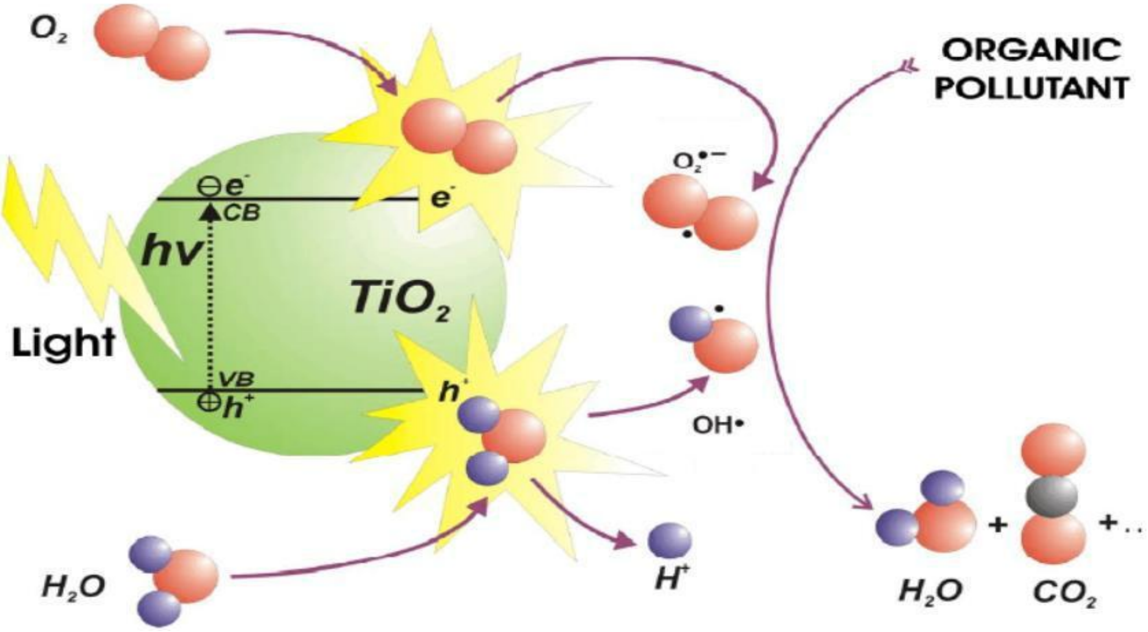


Figure 3.2.2: Mechanism of TiO_2 activation and generation of holes and electrons

Heterogeneous photocatalysis is widely reported for degradation of various pollutants like pharmaceuticals **(Choi et al., 2014; Martinez et al, 2013),** dyes **(Khataee et al, 2010),** pesticides and insecticides **(Ahmed et al., 2011; Sud et al., 2012).**

This method is quite successful but still has several drawbacks like photochemical instability, large band gap etc. **(Qu et al., 2013).**

3.2.3 Dual process for degradation

Combination of two processes for degradation of organic pollutants is called dual process. There are several papers reported on dual processes for degradation of various organic pollutants like:

Degradation of 4-nitrophenol was reported by combination of two processes i.e. electrochemical oxidation and electro-Fenton **(Chu et al., 2011),** degradation of chlorinated solvents using photocatalysis and photo-Fenton **(Rodriguez et al., 2004),** degradation of antibiotics using photo-Fenton and electro-Fenton process **(Liu et al., 2018),** degradation of oxallin by photocatalysis and electrochemical processes **(Serna-Galvis et al., 2016).**

In present study photocatalysis and photo-Fenton are used in fix bed to degrade paracetamol and results were quite impressive. Hence, to solve these limitations to some extent combination of both the processes i.e. photocatalysis and photo-Fenton is employed in a way which thereby utilizing the limitations in the other process to give better results by reducing the treatment time with enhancement of degradation efficiency. Also with this dual process, the electron-hole recombination in photocatalysis turns infrequent resulting in increasing efficiency of degradation (**Bansal et al., 2018)**. Moreover this process leads to enhanced rate of reaction along with reducing the treatment time.

Research gaps

Based on literature studies following gaps have been identified:

1. There are very few reported studies on the use of in-situ dual process for the degradation of pharmaceutical compounds.
2. Catalyst stability and film intactness along with leaching of iron in case of dual effect need to be studied.
3. Durability of the beads need to be covered for its longer use.

Chapter 4

Objectives

Keeping in view the following research gaps the following objectives have been framed:

1. Efficacy of Fe-TiO_2 composite incorporating in-situ dual effect for the degradation of paracetamol.
2. Catalyst intactness and iron leaching studies for subsequent recycles while maintaining dual effect.
3. Durability and stability of support material for number of cycles.

Chapter 5

Materials and Methods

In this chapter, resources and approaches used in degradation of pharmaceutical compound paracetamol by the help of dual process has been explained. The explicitness and properties of pharmaceutical compound received has been clarified in the materials section. In the techniques section the instruments used to implement the photocatalytic degradation of the compound have been examined in detail.

5.1 Materials

5.1.1 Pharmaceutical compound

Paracetamol is a NSAID which is most commonly prescribed drug all over the world. Chemical name of the drug is p-acetamidophenol, N-acetyl-p-aminophenol, 4-hydroxyacetanilide **(Abdel-wahab et al., 2017).** The chemical structure is given in **figure 5.1.**

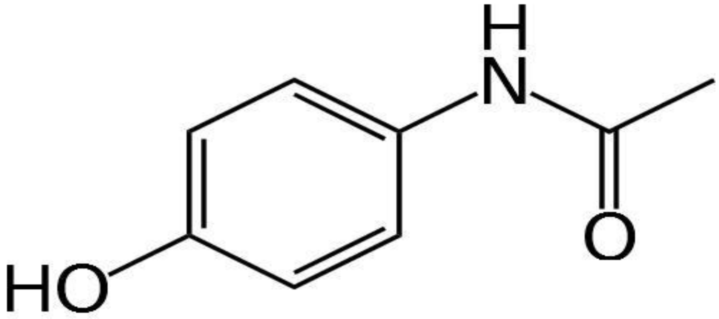


Figure 5.1.1 Structure of paracetamol

The empirical formula of paracetamol is $C_8H_9NO_2$ with a molecular mass of 151.163 g/mol. It is commonly used analgesic which helps in reducing the pain sensation in our body like tooth ache, head ache, muscle aches etc. but the exact mechanism is still unknown. Overuse of paracetamol can cause jaundice, nausea, loss of appetite, liver damage etc. It is overtly used because of its low cost and easy availability. Also, there are no papers reported on degradation of paracetamol by dual process using photocatalysis and photo-Fenton.

5.1.2 Reagents and catalysts used

Degussa P25 TiO_2 used as a catalyst was procured from Evonik Industries (India). Hydrogen peroxide (H_2O_2), 30% w/v purchased from Ranbaxy, India was used as an oxidant. Bentonite was bought from a local dealer while Fly ash was obtained free of cost from a local industry and fly ash was accepted as a gift from an industry based in Gurugram. For maintaining pH NAOH and H_2SO_4 were obtained from Merk. For acetate buffer formation acetic acid (>99.5%) and sodium acetate (>98.5%) were bought from TCI chemicals (India) Pvt. Ltd. For preparation of all the samples Milli-Q water was being used.

5.2 Instruments used

5.2.1 pH meter

The pH of paracetamol solution was set initially by addition of acetate buffer as required and thereafter measured by pH meter of Thermo Scientific Orion Star Series.

5.2.2 UV-Visible Spectrophotometer

Absorbance of solution after degradation of paracetamol was measured by Spectrophotometer (LABINDA, model no. T60U). Calibration curve of different concentrations of paracetamol was made and a particular absorbance value was obtained for 25 ppm at 242 nm.

5.2.3 Branson bath sonicator

While preparing the coating of the suspended catalyst homogenization is must so as to make uniform coating and for that homogenization is done by Ultrasonic bath tank (Model No. EN 60 US) having frequency of 33 KHz.

5.2.4 Muffle furnace

Muffle furnace having temperature range 200-1200 ^{o}C was used. In this study, beads formation and coating of the beads for fixing catalyst was done at 800 ^{o}C and 350 ^{o}C respectively.

5.2.5 UV Chamber and batch reactor

A rectangular wooden chamber of lab scale provided with UV lights was used for degradation of paracetamol by dual effect. Batch reactor has diameter 17.4 cm, height of 5.2 cm and capacity of 1200 mL. A laboratory jack of dimensions 1.37m x 0.9 x 1.0 m was used to adjust the height of the reactors to an equal level. 365 nm wavelength UV tubes of intensity 36 W were used for the degradation reactions. Spargers provided the aeration during the reaction inside the UV chamber and temperature was maintained by an exhaust fan provided inside the chamber.

5.2.6 SEM-EDAX

Presence of TiO_2 amount on both freshly coated and recycled beads is done by the technique SEM-EDAX. SEM generates the images while EDAX show the presence of different compounds on the peaks of graphs. The model of SEM used was JSM-6510LV, JEOL and EDS was INCAX-act, Oxford instruments, UK.

5.2.7 XRD

X-RAY Diffraction (XRD) was done to ensure that catalyst is still active or not after 30 cycles of reaction. XRD gave several peaks representing different phases of TiO_2 i.e. anatase and rutile.

5.2.8 UV-DRS

Band gap energy of freshly coated and recycled beads was evaluated by UV-Vis diffuse reluctance spectra in range of 200-800 nm. Model used for the process was UV-2600 shimadzu (Asia pacific).

5.3 TiO_2 immobilization

Beads are formed by mixing Bentonite, foundry sand (FS), and, fly ash (FA) in ratio of 2:1:1 respectively. The beads were made by mixing all the ingredients and giving them desired shape and size after those beads were muffled at 800 ^{o}C for desired period of time. Afterwards muffled beads were dipped in water for 24 h once cool down. For immobilization, TiO_2 weighed, stirred, and, sonicated as per the requirement. The slurry is coated on the beads by shaking them time to time till it dries. Once dried then they are heated at 350 ^{o}C so that the coating remain intact. The beads used were of same size and shape and binding material was Bentonite. To ensure the presence of iron characterization of FA and FS is done as cited in various studies **(Rajput et al., 2016; Verma et al., 2014)**. TiO_2 film on the surface of beads was ensured by SEM-EDAX analysis. Genuine images of TiO_2 coated and uncoated beads are displayed in Figure 5.3 (a) and (b) respectively.

Figure 5.3: (a) Uncoated beads and (b) TiO_2 coated beads

5.4 Protocol for paracetamol degradation by dual process under UV light and reaction setup

1. From stock solution of 1000 ppm, working solution of 25 ppm was made every day.

2. Covered the surface of batch reactors with desired amount of beads.

3. Required amount of drug solution was added in the reactor containing beads.

4. pH of solution was maintained to 3.5 by using acetate buffer.

5. Required amount of H_2O_2 was added to the solution carefully.

6. Reactors were then placed inside the UV chamber at same height so that all the reactors will get equal intensity of light.

7. Provided the aeration to the reactors using spargers.

8. Turn on the UV lights and collect the samples after certain time intervals using syringe.

9. Filter the samples in test tubes using syringe filters of 4.5µm size.

10. The whole process runs for 240 minutes and the % degradation of paracetamol was estimated by measuring absorbance at 242 nm.

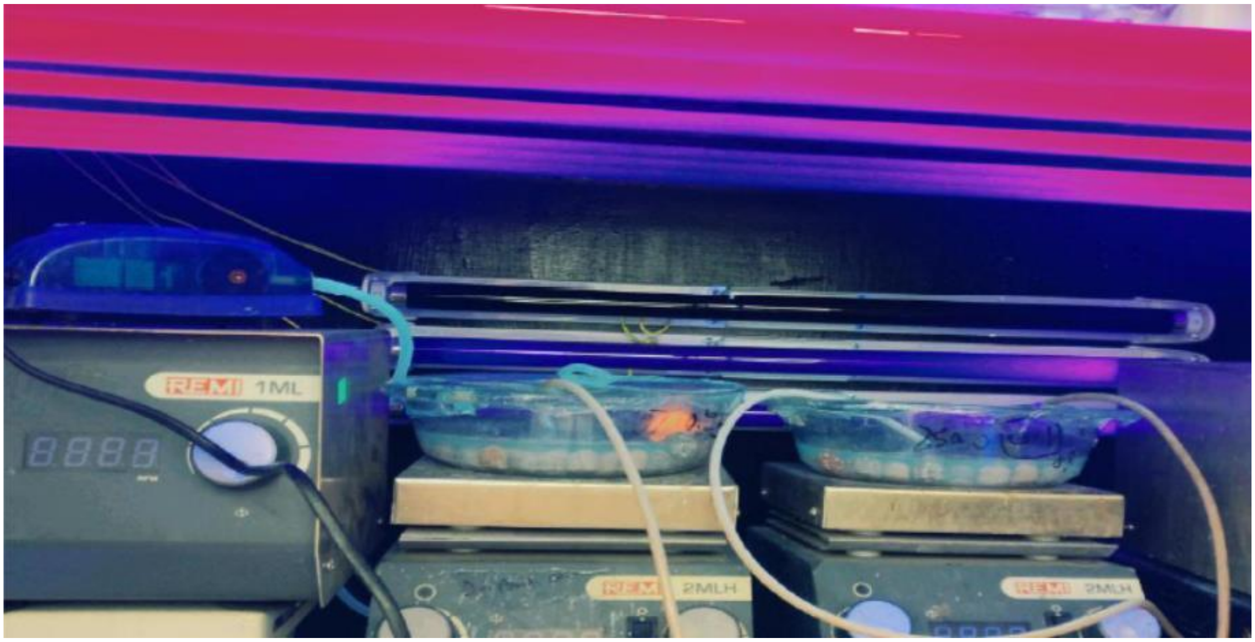


Figure 5.4: Actual image of reaction setup

Chapter 6

Results and discussions

This chapter talks about the degradation of paracetamol by means of fixed-bed dual effect of photocatalysis and photo-Fenton. Specific parameters like no. of beads, degradation time, volume and H_2O_2 dose are taken into consideration and varied to a particular optimized set of conditions.

6.1 Standard calibration curve of paracetamol

A standard graph of known concentrations ($5mgL^{-1}$-$50mgL^{-1}$) of paracetamol was plotted at 242nm using UV-vis spectrophotometer. From figure 6.1 i.e. calibration graph, the concentration of unknown sample can be estimated.

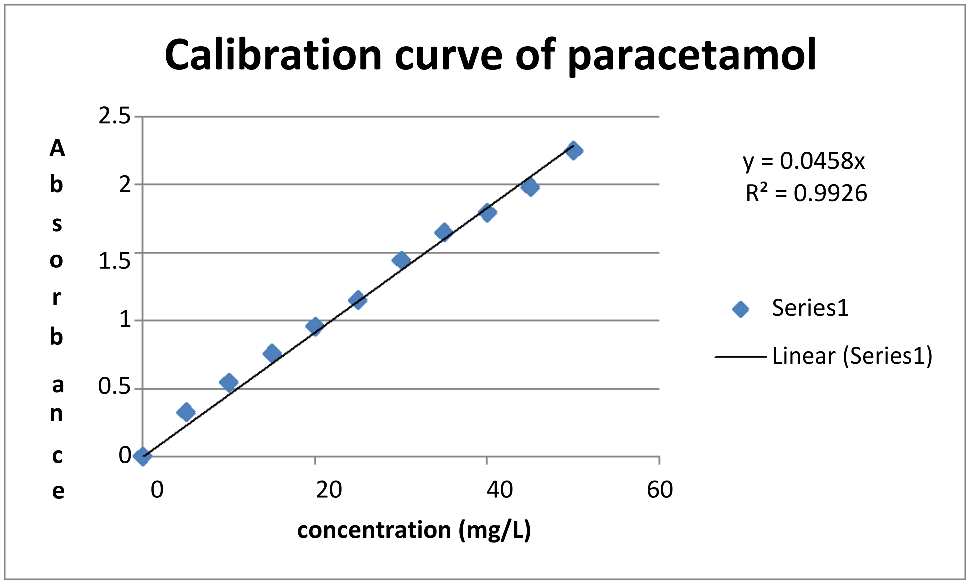


Figure 6.1: Standard graph for paracetamol

6.2 Degradation studies using dual effect

6.2.1 Preliminary studies

For studying the effect of various parameters on the degradation of paracetamol, numerous reactions were performed. On exposure of paracetamol solution to UV light for four hours, no degradation was observed. Similarly, adsorption studies resulted in no degradation.

While photo-Fenton process resulted in 27.59% degradation in 4h (Figure 6.2.1) where, only the iron and hydroxyl radical production by H_2O_2 resulted in reduction of compound concentration. Furthermore 56.41% paracetamol was degraded by photocatalysis in 4 h. By combining both the processes of photocatalysis and photo-Fenton 72.40% of paracetamol degradation was observed in just 90 minutes. So from this study we can assume that the dual process is pretty effective in degradation of paracetamol. When time of reaction was further increased it resulted in 99% degradation in 240 minutes.

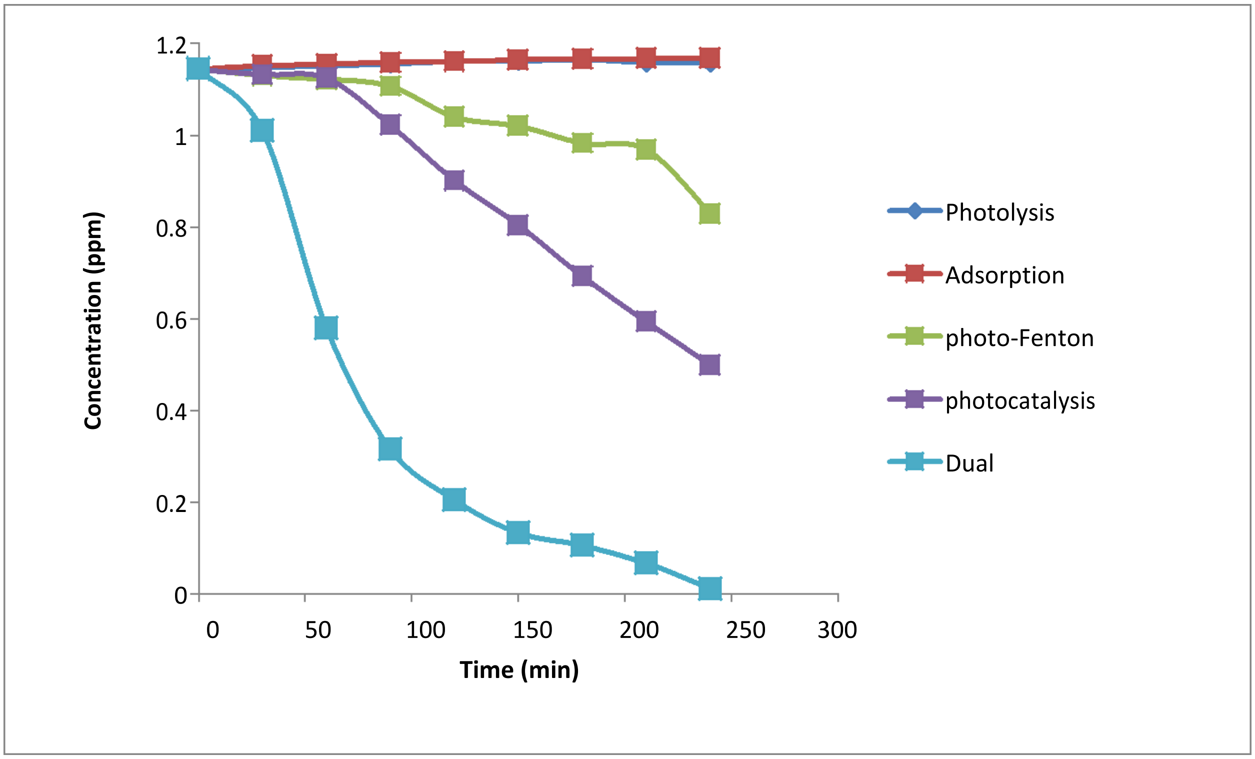


Figure 6.2.1: Photocatalytic degradation of paracetamol in presence or absence of UV, TiO_2 and H_2O_2. Experimental conditions: C_o= 25mgL^{-1}, V = 200ml

6.2.2 Optimization by RSM

6.2.2.1 Box-Behnken design (BBD)

For optimization of catalytic degradation of concerned compound paracetamol in wastewater Box-Behnken Design under Response Surface Methodology (RSM) was used. Four parameters were taken into consideration like H_2O_2 dose, catalyst dose, degradation time, and area/volume ratio as shown in table 6.1.

Table 6.1 Shows levels and types of operational parameters.

Factor	Name	Low Actual	Medium	High Actual
A	Time (min)	30.00	150	240.00
B	H_2O_2 (mg L^{-1})	300.00	750	1200.00
C	No. of Beads	40.00	80	120.00
D	Volume (mL)	150.00	200	250.00

Paracetamol photocatalytic degradation study was done with the help of factorial method/design shown in Table 6.2. RSM suggested 29 set of reactions varying different parameters like H_2O_2 dose, catalyst dose, degradation time, and area/volume ratio for optimization.

Table 6.2: BBD matrix showing % degradation

Std.	Run	Factor 1 A:Time	Factor 2 B: H_2O_2	Factor 3 C: beads	Factor 4 D:Volume	Response 1 degradation
18	1	240.00	750.00	40.00	200.00	92.28
1	2	30.00	300.00	80.00	200.00	35.52
10	3	240.00	750.00	80.00	150.00	93.71
9	4	30.00	750.00	80.00	150.00	13.79
22	5	135.00	1200.00	80.00	150.00	67.77
29	6	135.00	750.00	80.00	200.00	89.00
26	7	135.00	750.00	80.00	200.00	82.79
8	8	135.00	750.00	120.00	250.00	76.06
4	9	240.0	1200.00	80.00	200.00	91.35
15	10	135.00	300.00	120.00	200.00	80.00
23	11	135.00	300.00	80.00	250.00	84.21
19	12	30.00	750.00	120.00	200.00	16.85
28	13	135.00	750.00	80.00	200.00	82.88
13	14	135.00	300.00	40.00	200.00	80.08
5	15	135.00	750.00	40.00	150.00	74.97
14	16	135.00	1200.00	40.00	200.00	54.06
27	17	135.00	750.00	80.00	200.00	82.88
11	18	30.00	750.00	80.00	250.00	7.77
12	19	240.00	750.00	80.00	250.00	92.57
2	20	240.00	300.00	80.00	200.00	96.05
3	21	30.00	1200.00	80.00	200.00	1.39
24	22	135.00	1200.00	80.00	250.00	54.75
21	23	135.00	300.00	80.00	150.00	87.32
16	24	135.00	1200.00	120.00	200.00	71.87
17	25	30.00	750.00	40.00	200.00	2.27
7	26	135.00	750.00	40.00	250.00	70.69
25	27	135.00	750.00	80.00	200.00	82.88

20	28	240.00	750.00	120.00	200.00	92.22
6	29	135.00	750.00	120.00	150.00	86.11

6.2.2.2 Statistical analysis

The plot shows normal probability of paracetamol degradation (Figure 6.2.2.2 (a)). This pattern of figure displays a good residual of paracetamol which is normally distributed and resembles a straight line.

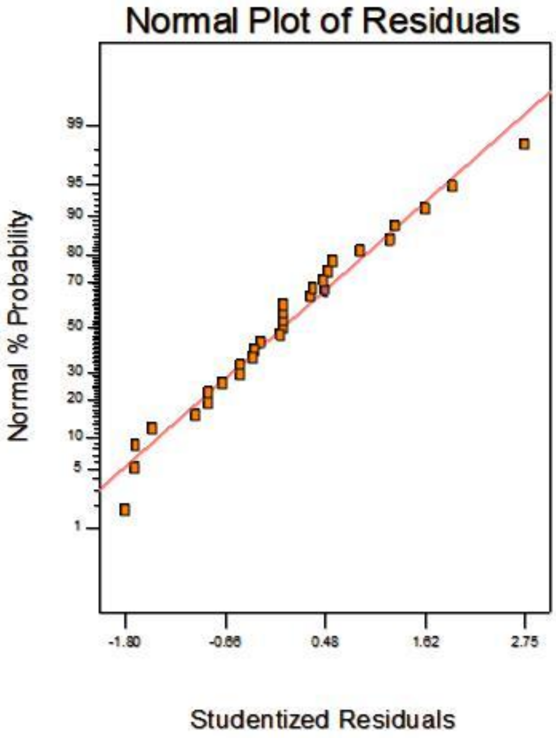


Figure 6.2.2.2 (a): Residual plot showing % degradation of paracetamol.

Paracetamol degradation correlation was displayed in figure 6.2.2.2 (b) showing a good agreement between real and predicted data.

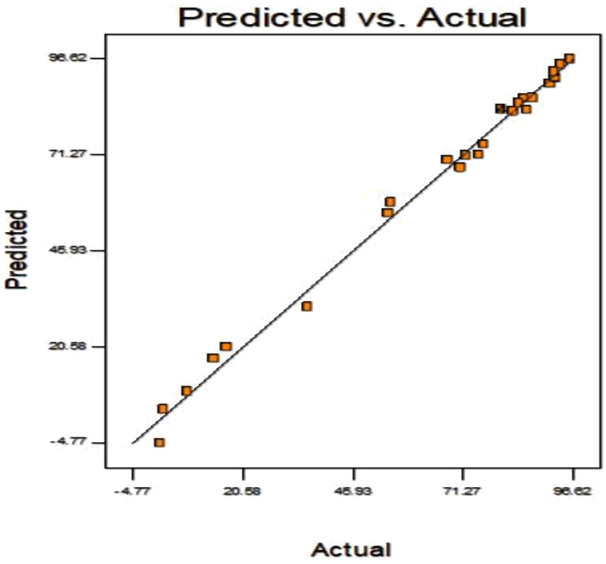


Figure 6.2.2.2 (b) Comparison between predicted and actual values of paracetamol degradation.

6.2.2.2.1 ANOVA (analysis of variance)

ANOVA (analysis of variance) (table 6.3) displays the model F-value test for % degradation of paracetamol. The F value of 152.67 in model shows that it was significant. Various significant model terms represent A (Time), B (H_2O_2), C (Catalyst dose), and, D (Area/volume ratio). Values of "Prob > F" greater than 0.1000 indicate model terms are not significant. $R^2 = 0.9935$ i.e determination coefficient indicated a good correlation between actual and predicted results.

Table 6.3: ANOVA suggested from the response.

Source	Sum of Squares	DF	Mean Square	F value	Prob >F	
Model	25616.29	14	1829.23	117.28	<0.0001	Significant
A	19263.25	1	19263.25	1234.75	<0.0001	
B	1240.13	1	1240.13	79.49	<0.0001	
C	196.51	1	196.51	12.60	0.0032	
D	117.94	1	117.94	7.56	0.0157	
A2	4398.68	1	4398.68	281.95	<0.0001	
B2	161.57	1	161.57	10.36	0.0062	
C2	220.44	1	220.44	14.13	0.0021	
D2	121.17	1	121.17	7.77	0.0145	
AB	216.53	1	216.53	13.88	0.0023	
AC	55.06	1	55.06	3.58	0.0813	
AD	5.95	1	5.95	0.38	0.5467	
BC	80.01	1	80.01	5.13	0.0399	
BD	24.55	1	24.55	1.57	0.2302	
CD	8.32	1	8.32	0.53	0.4772	
Residual	218.41	14	15.60			
Lack of Fit	188.22	10	18.82	2.49	0.1962	Not Significant
Pure Error	30.19	4	7.55			
Cor Total	25834.70	28				

Table 6.4: Different R squares

R-Squared	0.9915
Adj R-Squared	0.9831
Pred R-Squared	0.9562
Adeq Precision	35.366

6.2.2.3 H_2O_2 dose, catalyst dose, volume and, degradation time of paracetamol

The trend of graph shows increment in percent degradation of paracetamol. The rate of degradation from 30-135 minutes displayed progressive increase but after 135 minutes the degradation rate comparatively decreased. With decrease in H_2O_2 dose the rate of degradation shows an increasing pattern because with increasing dose of H_2O_2 scavenging effect takes place which leads to formation of more and more •OH radicals which ultimately interferes with intermediates formation at the time of degradation and create hindrance during absorbance measurement (Fig. 6.2.2.3 (a)).

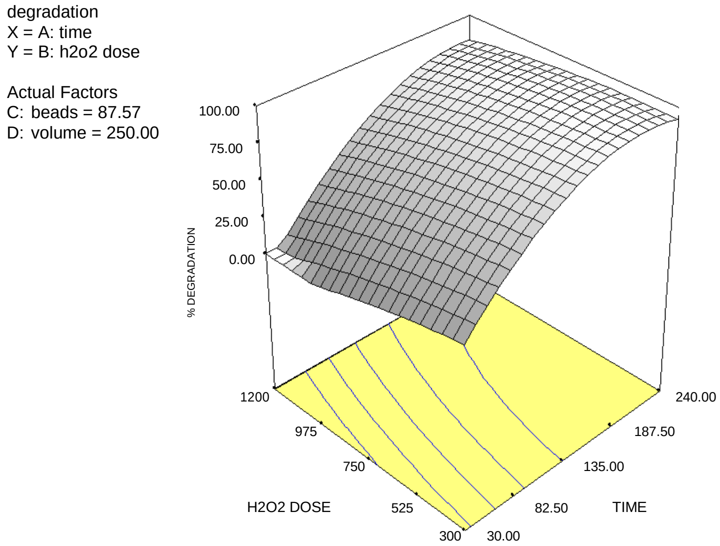


Figure 6.2.2.3 (a): % degradation versus time and H_2O_2 dose

With increasing number of beads reaction rate follows increasing pattern till 80 beads because of increasing catalyst TiO_2 and iron. After increasing number of beads from 80 a little downfall in degradation rate was observed. Reason being the high amount of catalyst which may reduce the amount of light entering inside and, light scattering can be the another reason hence the rate of degradation slows down a bit (Fig 6.2.2.3(b)).

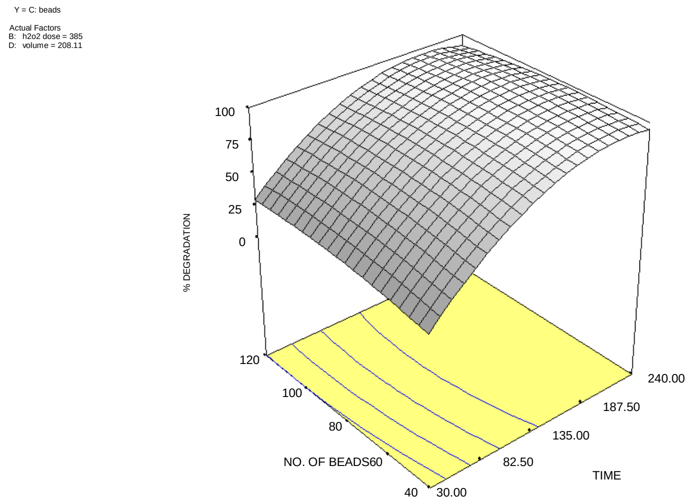


Figure 6.2.2.3 (b): % degradation versus no. of beads and time

Initially a slight raise in degradation rate was seen with increasing volume i.e. from 150-200 ml but as it moved further the degradation rate started falling. Because of increasing volume the light faced a little difficulty in penetrating inside the reactor. Once the volume decreases it shortens the path length of photons ultimately rate of degradation increases (Fig. 6.2.2.3 (c)).

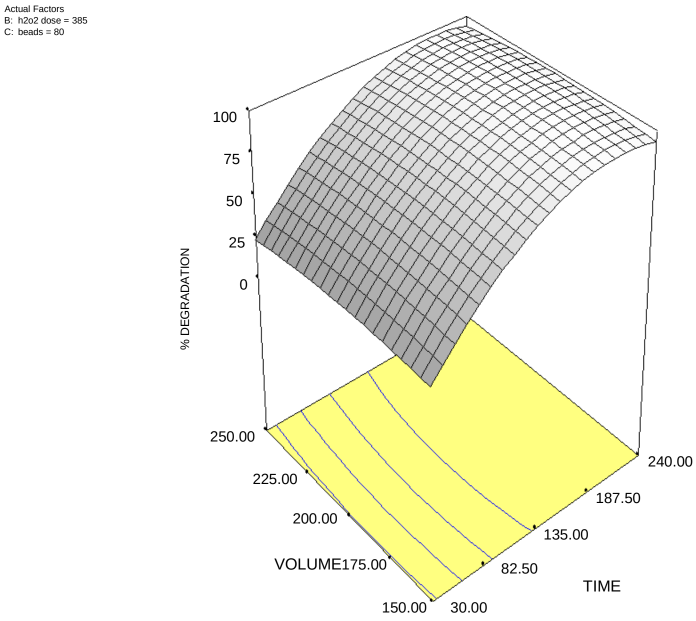


Figure 6.2.2.3 (c): % degradation versus time and volume

Interaction between volume and number of beads shows maximum rate of degradation at 80 no. of beads but before and after 80 the rate of degradation is quite less. Almost similar pattern is followed by other factor i.e. volume before and after the 200 ml there is downfall in the degradation rate. Less catalyst amount cannot degrade efficiently and more creates the hindrance and less volume gives more exposure to the light while more volume creates huddle in light entry (Fig 6.2.2.3 (d)).

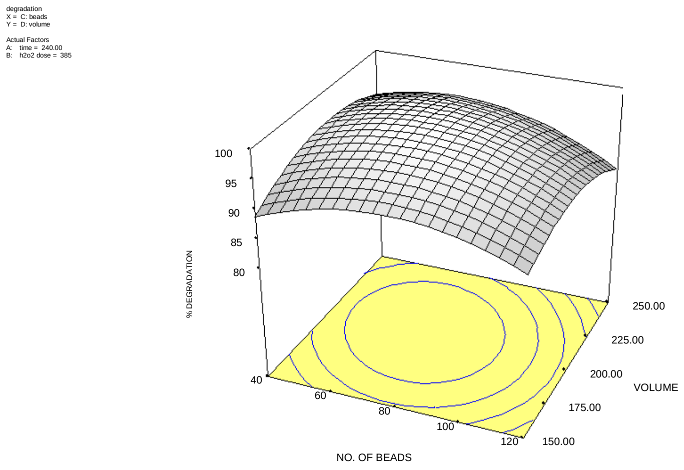


Figure 6.2.2.3 (d): Interaction between volume and no. of beads

Oxidant (H_2O_2) is proven for enhancing the degradation rate by forming •OH radical after accepting the excited electrons from the conduction band **(Bansal et al., 2016).** Varied amount of H_2O_2 from 300-1200 mg/L but good degradation results were witnessed at 525 mg/L. Observed decrement in degradation rate after increasing amount of H_2O_2 was due to scavenging of •OH. Best results with respect to volume came at 200 mL because increase in volume hinders light penetration resulting in downfall of degrdation rate. Interaction between H_2O_2 and volume says that excess of both factors result in little less degradation rate (Fig. 6.2.2.3 (e)).

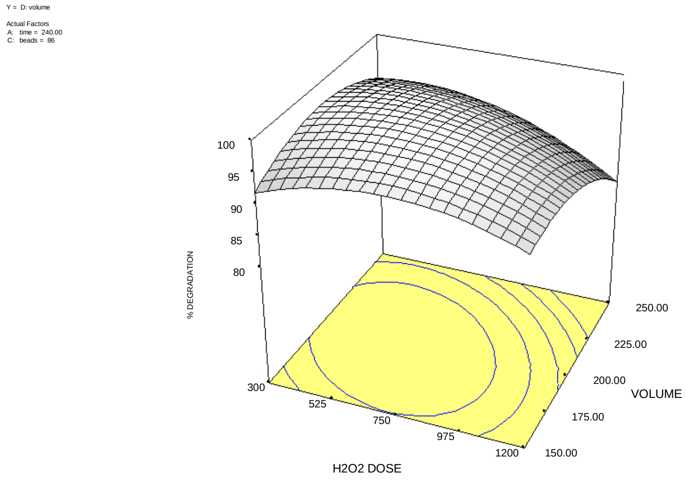


Figure 6.2.2.3 (e): Interaction between H_2O_2 dose AND volume

The interaction between H_2O_2 dose and no. of beads says that with increasing no.of beads the paracetamol degradation rate enhances till 80 beads after that it started decreasing slightly. While increasing dose of H_2O_2 from 525 mg/L shows decrement in paracetamol degradation rate because of scavenging effect. But further increase in no. of beads led to downfall in degradation rate of paracetamol because of scattering of light and reduction in amount of light due to excess of catalyst (Fig. 6.2.2.3 (f)).

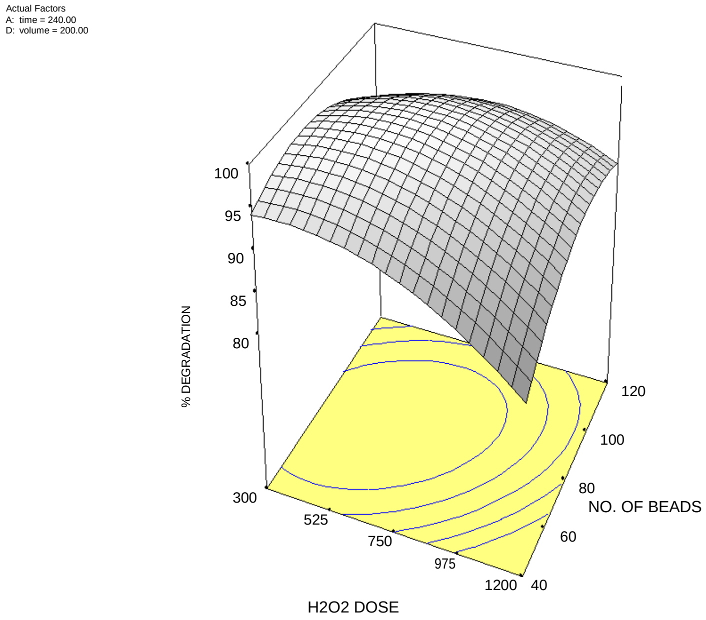


Figure 6.2.2.3 (f): Interaction between H_2O_2 and no. of beads

6.2.2.5 Optimization analysis

The parameters for degradation were optimized by RSM increasing % degradation of paracetamol. To attain this several parameters were applied shown in Table 6.5. These optimized conditions gave 98.16% degradation. The optimized values are given in Table 6.5

Table 6.5: Optimized values of different parameters

Parameters	Optimum values
H_2O_2 dose (mg/L)	525
No. of beads	80
Time (min.)	215
Volume (mL)	200

6.2.2.4:

The kinetic study of paracetamol degradation at optimized condition from BBD by RSM. In this study the first and second order model were tested. According to this model the reaction rate is directly proportional to surface fraction of photocatalyst. Degradation of paracetamol at optimized conditions (No.of beads = 80, degradation time = 215 minutes, H_2O_2 dose = 0.525 mL, and, volume = 200 mL) followed first order kinetics.

$$-dc/dt = KC \qquad 6.1$$

On integrating and arranging following equation of first order is given below:

$$\ln [A] = - kt + \ln [A]_o \qquad 6.2$$

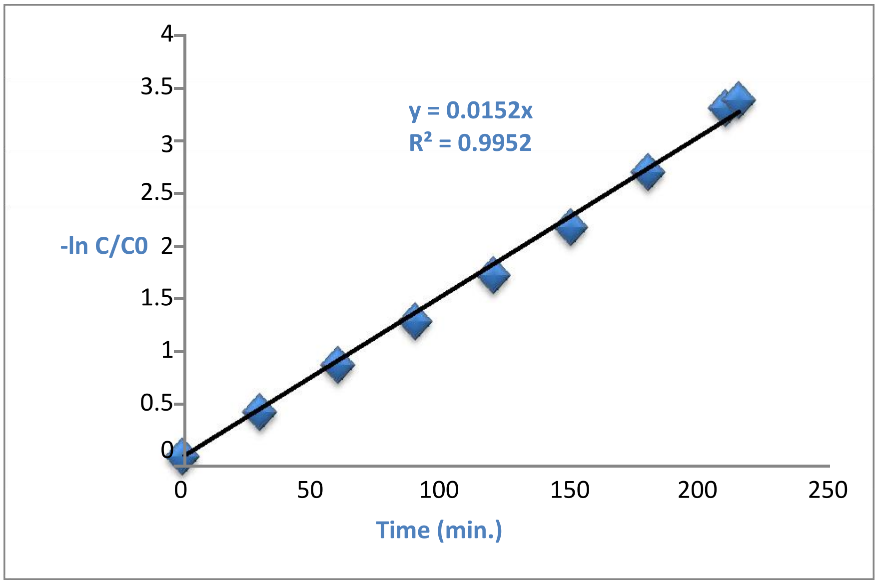


Figure 6.2.2.4: Kinetic study of paracetamol degradation

6.2.2.5 Durability study of beads

Most significant factor in photocatalytic degradation is durability. Beads work as a support system for catalyst and iron source to which catalyst remain intact and iron leaching in solution occurs even after several cycles of reaction making them fit for resuing again and again.

After each reaction the beads were kept into oven to retain their catalytic property. The reactivation of catalyst is not feasible according to literature. In the present study using immobilized TiO_2 and iron in cemented beads, even after 20 cycles there is a very minor reduction in paracetamol degradation as shown in Figure 6.2.2.5. The gradual reduction in degradation after 30 cycles may be due to a lesser amount of iron leaching in solution and catalyst loss. But the catalyst was still intact as a film and iron leaching was also occuring in both freshly coated and recycled beads and is shown by SEM-EDAX.

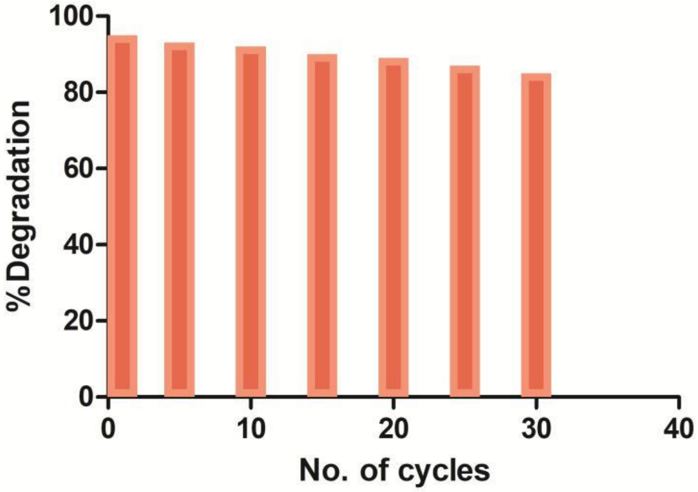
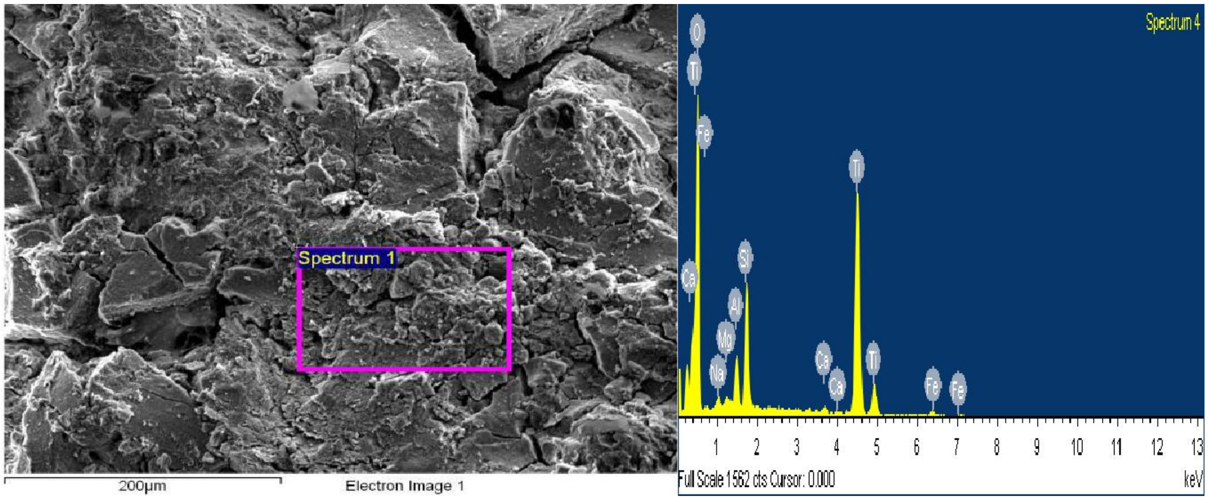


Figure 6.2.2.5: Bar graph showing durability of beads during degradation of paracetamol by dual effect (Co = 25 ppm, volume = 200 mL.

6.3 Characterisatin analysis

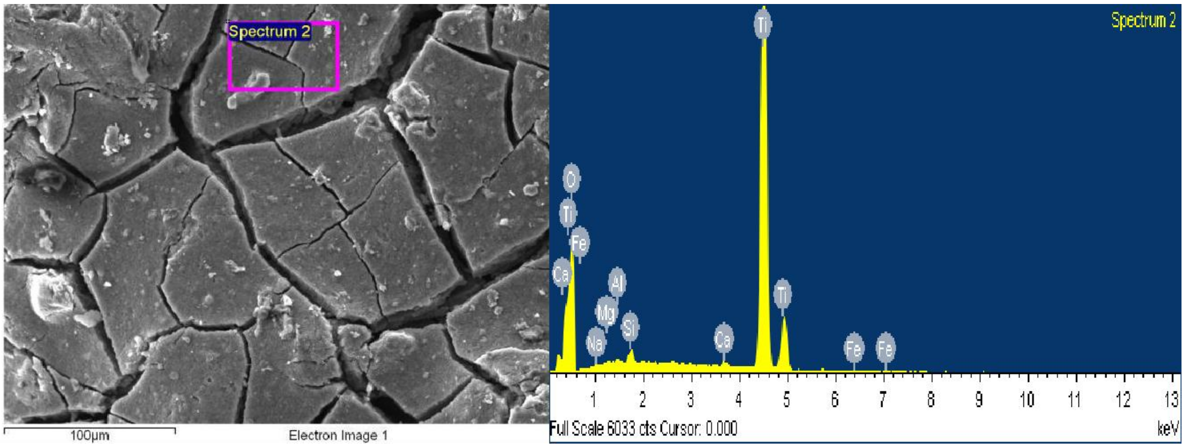
6.3.1 SEM-EDAX

Morphology of freshly coated and used beads were studied by a technique called SEM-EDAX (Scanning Electron Microscopy-Energy Dispersive X-RAY Analysis). SEM employ a beam of electrons to the samples for generating high resolution images and EDAX provides the elemental information (Fig. 6.7).The image of used beads clearly illustrates that TiO_2 is still intact even after 30 reaction cycles. Images of SEM-EDAX have displayed in Fig. 6.7 (a) used beads which have gone through 30 recycles due to which coating of TiO_2 become faded but to a minor degree Fig 6.7 (b) Freshly coated unused spherical beads having Fly Ash + Foundary Sand (FA + FS). EDAX confirmed the presence of Fe, Ti and, O by respective peaks in graph.



Elements	O K	Na K	Mg K	Al K	Si k	Ca K	Ti K	Fe k	Total
Weight	59.5	0.55	0.21	1.95	5.50	0.48	30.96	1.15	100

Figure 6.3.1 (a): SEM-EDAX of used TiO_2 coated beads



Elements	O K	Na K	Mg K	Al K	Si k	Ca K	Ti K	Fe k	Total
Weight	**41.06**	**0.09**	**0.07**	**0.18**	**0.54**	**0.35**	**57.53**	**0.19**	**100**

Figure 6.3.1 (b): SEM-EDAX of unused TiO_2 coated beads

6.3.2 UV-DRS

Band gap energy was evaluated by UV-Vis diffuse reluctant spectra. A comparison of both recycled and fresh Fe-TiO_2 and TiO_2 Degussa P25 was done in the range 200-800 nm with the help of spectrophotometer. Due to presence of iron the light absorbed in the visible region as well. Band gap of both the prepared catalyst and TiO_2 was estimated by an equation:

$$Eg = h\nu = hc/\lambda \tag{6.3}$$

Eg = band gap energy in eV; h = Planck's constant; c = speed of light; λ = wavelength

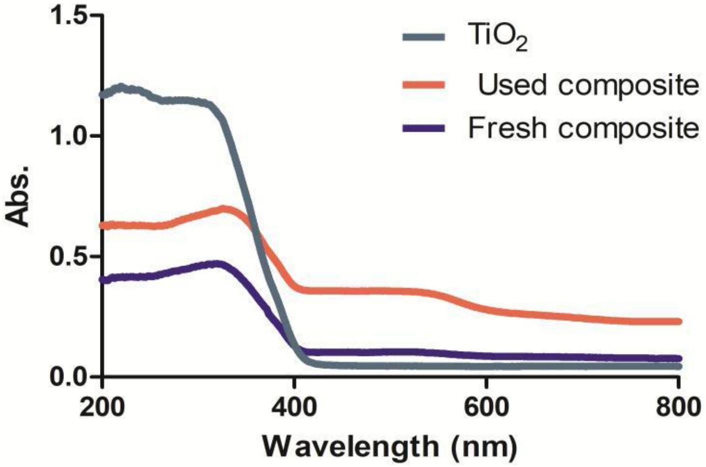


Figure 6.3.2: Graph of UV-DRS for recycled, fresh catalyst and,TiO_2 Degussa P25

6.4 X-Ray Diffraction (XRD)

To check if there is any change in activity of photocatalyst after 30 cycles XRD of recycled and fresh TiO_2 was performed and shown in Figure 6.4 (a). Fresh and recycled samples were extracted from surface of beads. Several peaks have developed representing particular phases of TiO_2 i.e. A represents anatase and R represents rutile. The peaks of A and R shows the retention of catalyst even after various reaction cycles.

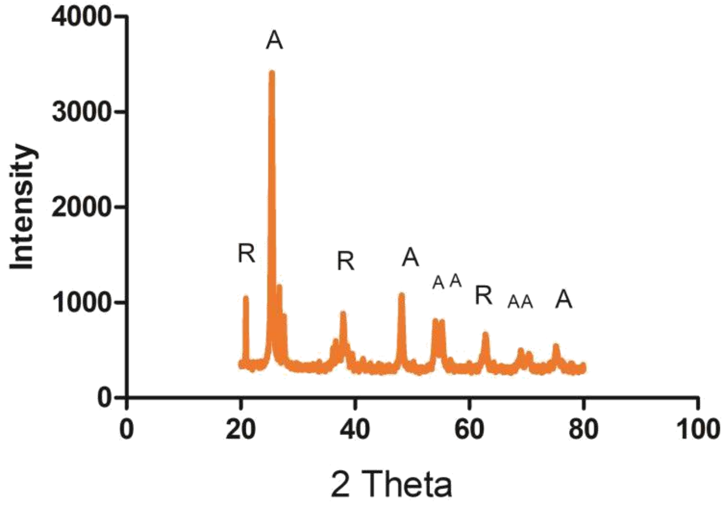


Figure 6.4 (a): XRD pattern of fresh TiO_2

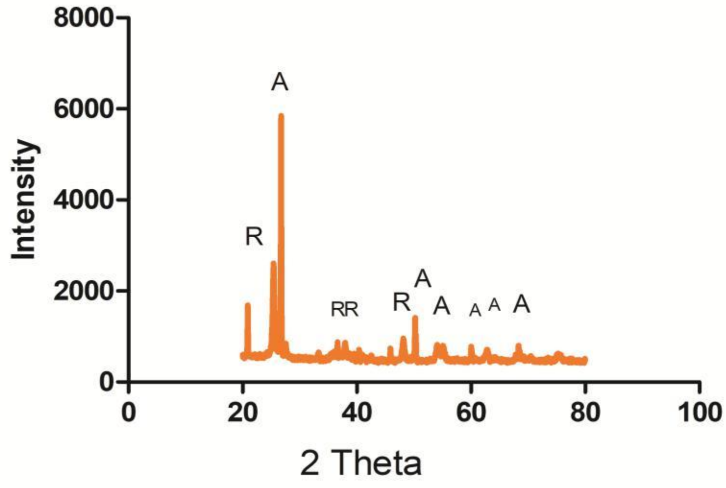


Figure 6.4 (b): XRD pattern of recycled TiO_2

6.5 Mineralization studies

The mineralization studies were done by nitrate, nitrite, and, iron estimation. Moreover the intermediates formed during paracetamol dedgradation were confirmed by GC-MS analysis.

6.5.1 Nitrate and Nitrite estimation

Paracetamol has nitrogen in its structure so during mineralization of paracetamol nitire and nitrate formation occur. The nitrite first increases gradually till 60 minutes then showed a slight fall in value at 150 minutes and again increased slightly from 150 to 240 minutes (Figure 6.5.1(a)). The nitrate is showing gradual increase in the concentration till 150 minutes but after that its concentration started falling with degradation of paracetamol (Figure 6.5.1 (b)) and this concludes the complete mineralization of paracetamol was achieved.

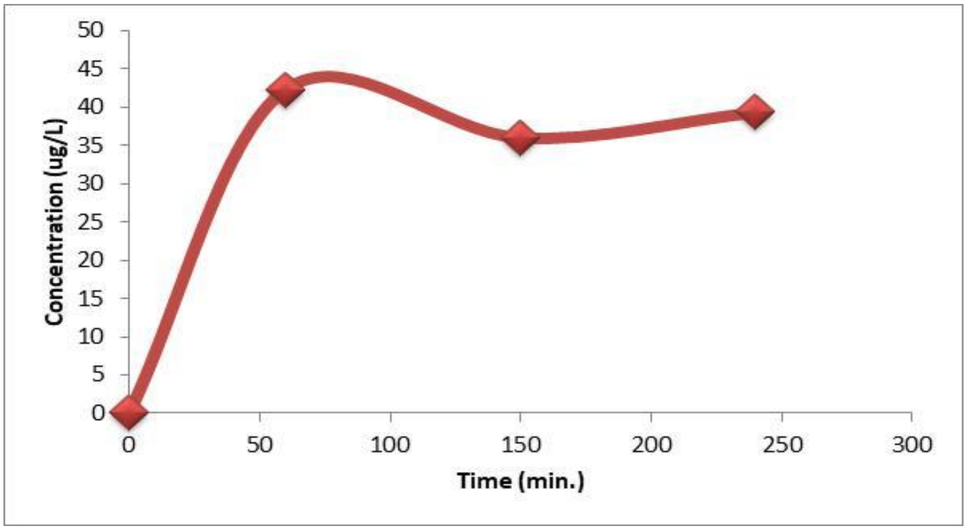


Figure 6.5.1 (a) Nitrite concentration during degradation of paracetamol

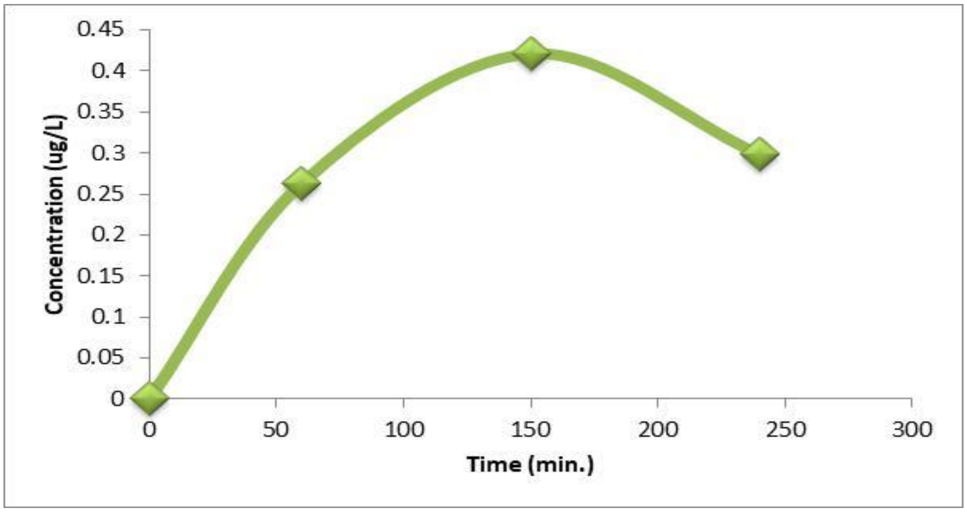


Figure 6.5.1 (b) Nitrate concentration during degradation of paracetamol

6.5.2 Iron estimation

Iron leaching from beads was confirmed during degradation of paracetamol by iron estimation. This study includes measure of Total iron, ferrous and ferric ion concentration. After a reaction of 240 minutes Total iron concentration observed was 27.7 mgL^{-1} . Concentration of ferrous ions were less than total iron but ferric ions were even less than ferros ions concentration. From this figure it can be said that paracetamol mineralization gives more ferrous ions (Figure 6.5.2).

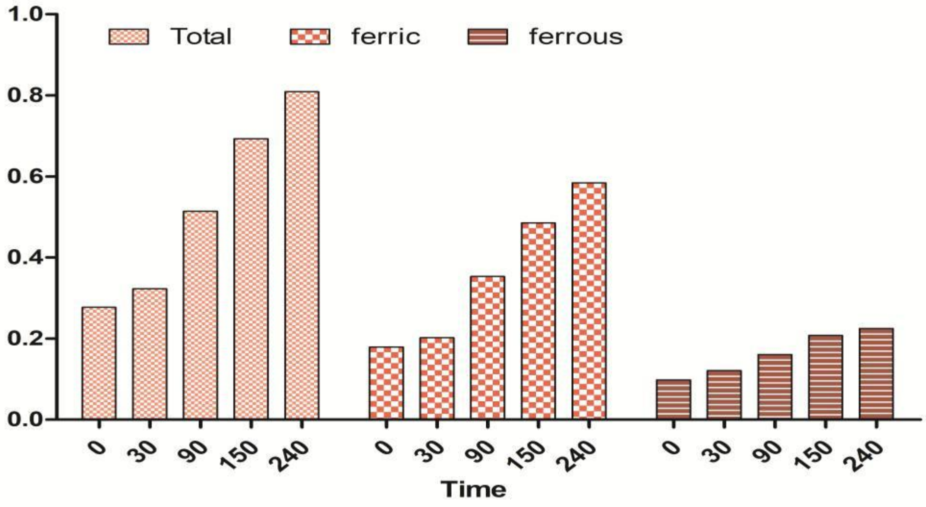


Figure 6.5.2: Bar graph showing different concentrations of iron

6.5.3 GC-MS analysis

GC-MS identified the compounds formed during degradation of paracetamol shown in Figure 6.5.3 (a) and Figure 6.5.3 (b) with chromatograms. The pathway of paracetamol degradation displayed in the Figure 6.5.3 (b) the first compound formed by dehydrogenation was N-phenylacetamide which further formed a compound called aniline by decarboxylation. Further denitrification of aniline formed toluene then hyroxyl attack caused bond breaking and leads to formation of (Z)-buta-1,3-dien-1-ol. At last aldehyde removal lead to formation of final product i.e. but-1-ene (alpha-butylene). The other intermediates formed includes carbon dioxide, water, nitrite, and, nitrate.

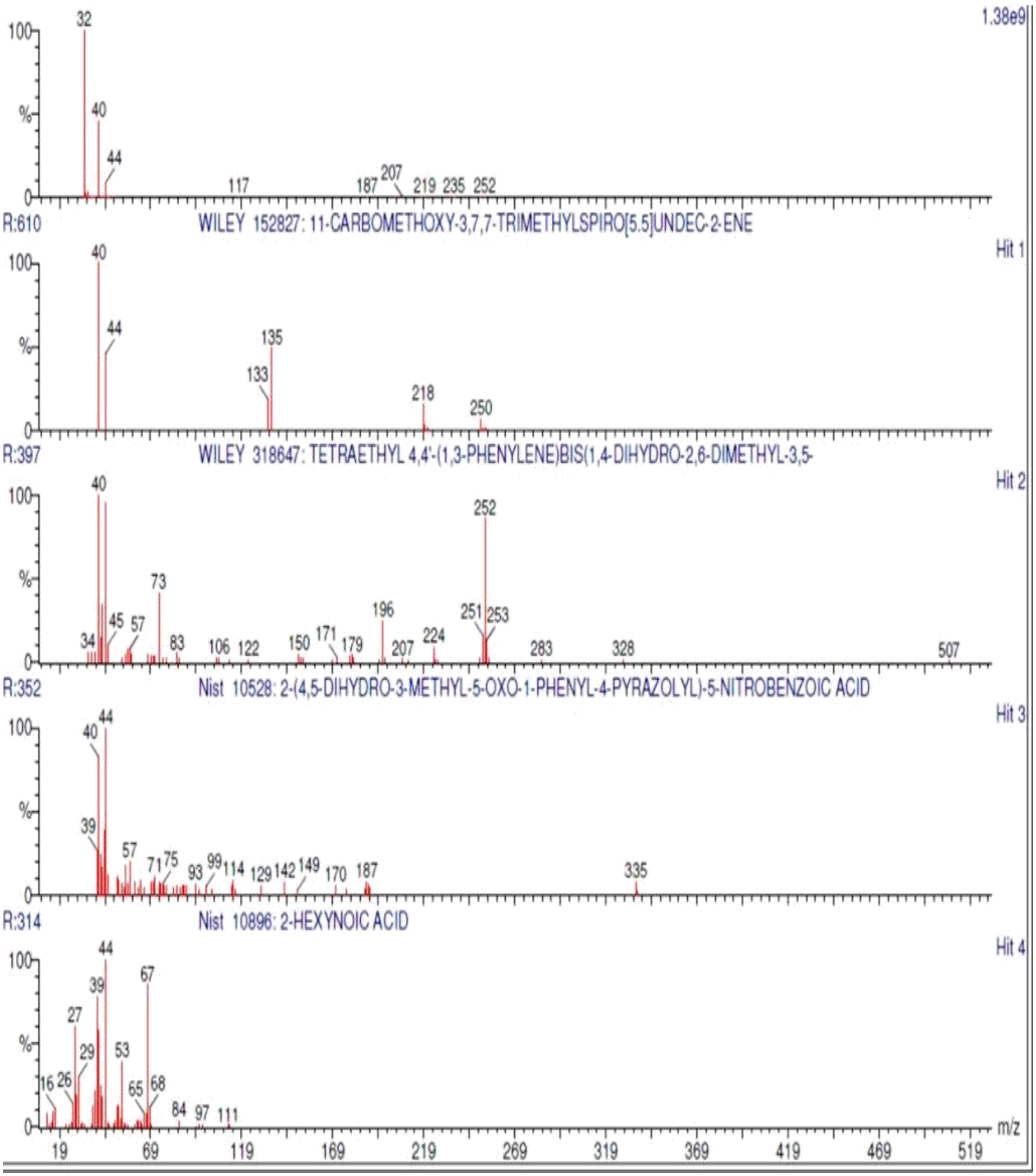


Figure 6.5.3 (a): Intermediates formed in GC-MS is shown by peaks

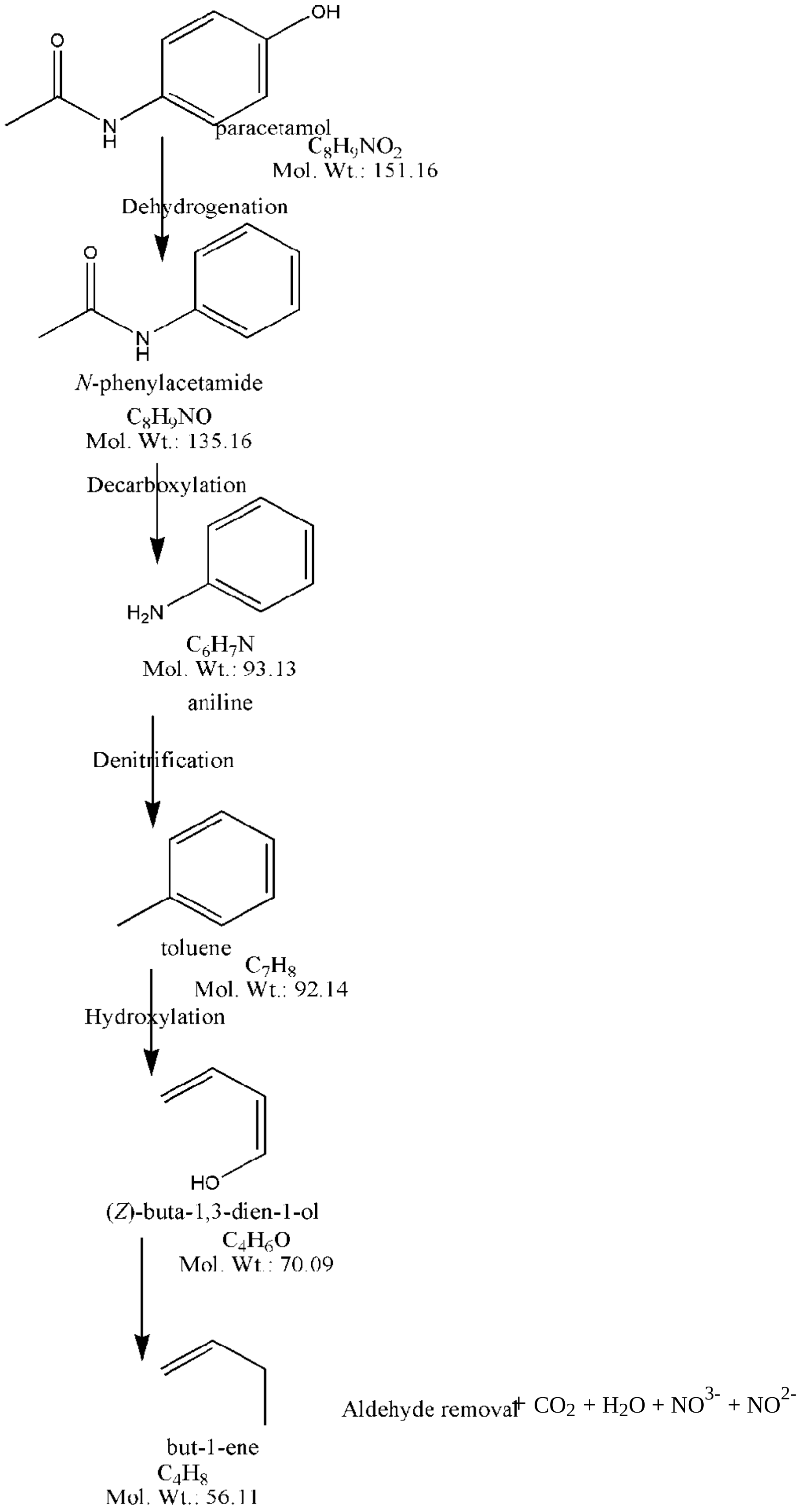


Figure 6.5.3 (b): Mechanism of paracetamol degradation proposed by GC-MS

Chapter-7

Conclusion

Present study demonstrates the use of novel Fe-TiO_2 composite for the degradation of paracetamol. This composite incorporates the in-situ dual effect (photocatalysis and photo-Fenton) through surface active TiO_2 film and iron leaching from the composite. Waste materials like FA, FS in the composite facilitates the iron leaching. The degradation of paracetamol was carried out at optimum H_2O_2 dose (525mg/L), no. of beads (80), degradation time (215 minutes), volume (200 mL). Dual effect prompts the synergistic effect of individual processes by increasing the rate of reaction. Durability studies proved the efficiency of degradation process even after 30 cycles with almost similar degradation efficiency. Characterization of both freshly TiO_2 coated beads and recycled beads was done by SEM/EDAX, UV-DRS, and, XRD. The images and graphs generated showed the intact TiO_2 and confirmed the presence of various compounds including iron. The mineralization of paracetamol was studied by analysis like GC-MS, nitrate, nitrite, and total iron estimation. GC-MS gave us several peaks of intermediates formed during degradation of paracetamol by which a pathway can be made. Nitrate and nitrites are also formed because paracetamol contain nitrogen in its structure. Iron leaching was confirmed by total iron estimation. This process degraded 96.6% drug in 215 minutes. Hence it was concluded that dual method is very effective for wastewater treatment and mineralization studies proved that water is safe from toxic compounds. This dual process could lead to effective waste water treatment options at field-scale through proper reactor designing.

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