PARAMETRIC STUDY FOR THE TREATMENT OF CETIRIZINE SIMULATED WASTEWATER USING ELECTROCHEMICAL METHODS

M.Tech. Dissertation

Submitted in the partial fulfillment of the requirements for the award of Degree of

MASTER OF TECHNOLOGY

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CHEMICAL ENGINEERING

by

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Certificate

This is to certify that the dissertation work entitled "**Parametric study for the treatment of cetirizine simulated wastewater using electrochemical methods**" submitted by **Shivani Agnihotri (Roll. No. 601611003)** in partial fulfillment for the award of degree of Master of Technology in Chemical Engineering from Thapar Institute of Engineering and Technology, Patiala, Punjab, has been carried out under my supervision. This work has not been submitted partially or wholly to any other university or institute for the award of this or any other degree or diploma.

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Declaration

I hereby declare that the work being presented in the dissertation report entitled "**Parametric study for the treatment of cetirizine simulated wastewater using electrochemical methods"** in the partial fulfillment of the requirements for the award of degree of Master of Technology in Chemical Engineering from Thapar Institute of Engineering and Technology, Patiala, Punjab, is an authentic record of the work carried under the supervision of Dr.Vikas Kumar Sangal, Associate Professor, Department of Chemical Engineering, Thapar Institute of Engineering and Technology, Patiala. The matter presented in this dissertation has not been submitted in any other University/ Institute for the award of any degree / diploma.

Shivani Agnihotri

Dated: 14-07-2018

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Abstract

Pharmaceuticals are consumed worldwide for the treatment and prevention of human and animal diseases. The presence of pharmaceutical compounds in waters poses a potential eco toxicological risk. Due to the low pharmaceuticals removal efficiency of traditional wastewater treatment plants concerns calls are raised for efficient and eco-friendly technologies. Electrochemical advanced oxidation processes, such as electro-floatation, electro-oxidation, electro-coagulation and electro-Fenton attracted a growing interest over the last two decades, to achieve almost complete destruction of the pollutants studied. Cetrizine is an antihistamine widely used for allergic problems, it is a stable drug and very difficult to remove from water. The present study involves parametric study of electro-oxidation and electro-fenton processes for the degradation of cetrizine simulated wastewater. Electro-oxidation and electro-fenton studies were performed on cetrizine containing wastewater with RuO_2 coated Ti electrode (Ti/RuO_2). The selected operational parameters for electro-oxidation process were pH, cetirizine concentration (C_{CE}), current (i) and time (t) whereas, the selected operational parameters for electro-fenton process were cetirizine concentration (C_{CE}), fenton reagent concentration (C_{FE}), current (i) and time (t). % degradation was selected as a response for the optimization of process parameters. Optimization was performed by using RSM with desirability function. The optimum parameters obtained for EO process at C_{CE}=30ppm were pH=7.09, t=100minutes and i=0.93 A. The optimum parameters obtained for EF process at C_{CE}=30ppm were C_{FE}=0.39mMol, pH=3, t=90minutes and i=1.03A. At the optimum conditions the % degradation was found to be 63.86% for electro-oxidation process and for electro-fenton the % degradation was 77.27% for reaction time of 100 minutes and 90 minutes respectively. The energy consumption for the EO process was 21.7 Wh whereas for EF was 20.87 Wh. Therefore, EF is comparatively economical than EO process. The results were verified by the experimental results. A close relationship was observed between the predicted and experimental results.

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Abbreviations

CPCB	Central pollution control board
PPCP	Pharmaceutical and personal care product
EO	Electroxidation
EF	Electrofenton
EC	Electrocoagulation
BBD	Box Benhken Design
RSM	Response surface methodology
ANOVA	Analysis of Variance
DF	Degree of freedom
Prob	Probability
DC	Direct Current
Ti/RuO_2	Ruthenium Oxide coated with Titanium
BOD	Biological oxygen Demand
COD	Chemical Oxygen demand
DSA	Dimensionally stable anode
AOP	Advanced oxidation processes
HPLC	High performance liquid chromatography
i	Current
C_{CE}	Concentration of cetrizine
C_{FE}	Fenton reagent concentration
t	Time
% D	Percentage degradation of cetirizine

CHAPTER 1

INTRODUCTION

1.1 General Background

Water being a vital source of life contributes to around 71% of the planet earth. Water getting perturbed by industrial, domestic and sewage effluents leads to increase in the formation of wastewater. A recent UN report (Ye et al. 2012) mentions that the world's freshwater use is sustainable and baptizes for an essential rethink of strategies to manage competing demands. Minor concentrations of numerous organic substances and endocrine disrupting substances such as pharmaceuticals, prescription drugs, nutraceuticals and cosmetics are accounted as different effluents of wastewater and marine systems. These substances and their bioactive usually metabolites are recurrently being introduced into the marine environment as complicated mixtures.

Suspended solids, bacteria, biodegradable organics, dissolved inorganic, heavy metals etc are predominantly concerned adulterants found in wastewater treatments. Secondary treatment criterion for wastewater is in agreement among the elimination of suspended solids, biodegradable organics and bacteria. Several of the additional rigorous standards introduced in recent times deal with the exclusion of preferential contaminants (Levine et al. 1985). The rising stages of naturally available organic materials precisely associated with societal nutrient management activities have grave affects on management of water resources (Caliman and Gavrilescu 2009).

1.2 PPCP's of major concern in wastewater as a pollutant

It has been found that pharmaceuticals and personal care products universally abbreviated as PPCP's were the major contaminants bothering in wastewater. India being the top 5^{th} largest producer of pharmaceuticals leads to rapid growth of this sector results the depletion of freshwater resources. Water is an essential source of raw material for manufacturing of drugs in pharmaceutical industries. The requirement of water resources includes the production of chemicals, processing of materials, and cooling of products and effluent water. There is a need to have uniform and superior standards for the supply of water. The variety of treatments can be done for feed water utilities, drinking water, process water and water recycling. Though the total available per capita water has

decreased but disposal of pharmaceuticals in the water matrices has increased. The sources of pharmaceutical waste generation in water resources can be broadly classified as waste generated during manufacturing of pharmaceuticals, has passed recommended shelf life, is no longer required by the public or it is discarded due to contaminated packaging.

1.3 Pathways for the entry of pharmaceuticals in water resources

Several pathways constituting of STPs, aquaculture amenities, industrial effluents, hospitals, runoff from fields into surface of waters, and manure applications (Figure 1.1) allow the entry of pharmaceuticals into the environment (Price et al. 2010). Pharmaceuticals enter into the freshwater resources in the form of human consumption resulting into waste, dumping of pharmaceuticals utilized in medical treatment, agricultural usage and industry production (Klavarioti et al. 2009). Pharmaceuticals result into the habitat via human faeces or urine or animals excreta, into the sewage system leading to deterioration of water resources. Other pathway can also be in the form of influent into wastewater treatment plants as partly active metabolites or as in unmetabolized form (Mompelat et al. 2009). Veterinary pharmaceuticals in discrepancy add to the adulteration by directly entering soil by the means of manure, surface and ground waters from fields run offs (Khetan and Collins 2007). It was found that variety of pharmaceutical industries are sources of elevated concentrations of pharmaceuticals into the environment than those originated by the drug's use (Kessler 2010). The chief trail of pharmaceuticals into the environment and marine sources is the discharges from pharmaceutical industries, the WWTP and lastly as municipal effluents.

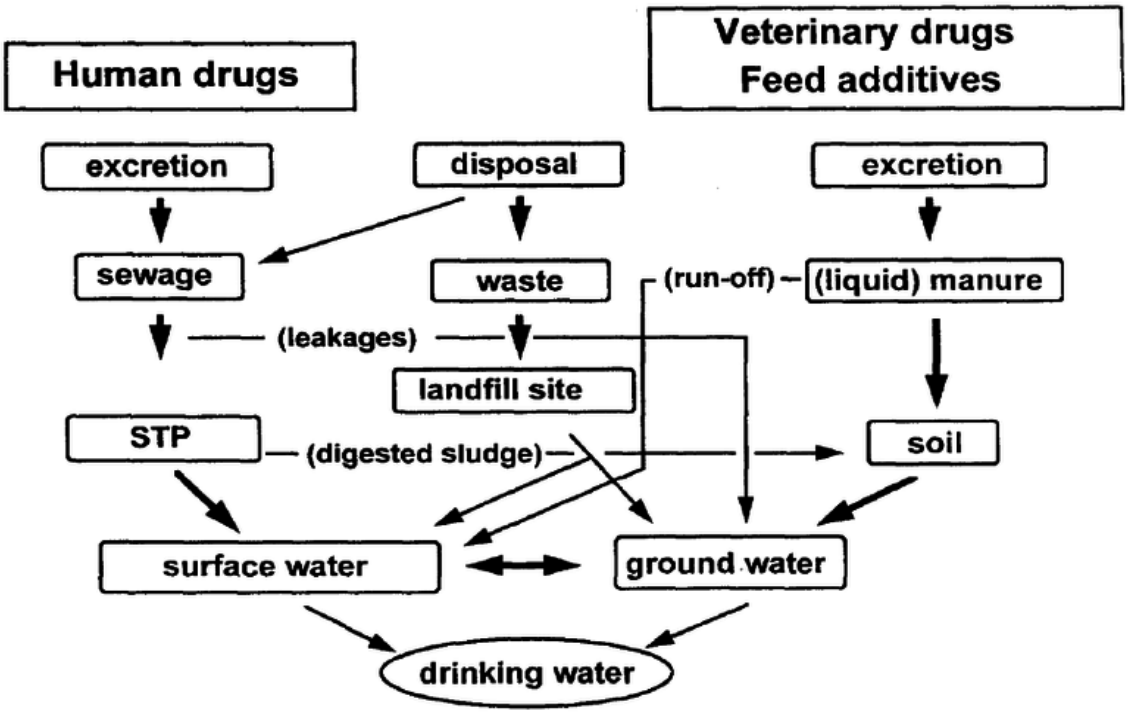

Figure 1.1: Pathways of PPCP entry into water resources (Price et al. 2010)

1.4 Wastewater discharge standards for a pharmaceutical effluent

As environmental regulations become stricter, a suitable procedure is employed to treat waste before discharging it as effluent. Some national standards have been given by the government which are to be followed by every pharmaceutical industry has been mentioned in Table 1.1.

1.5 Pharmaceuticals detected in freshwater resources

It has been accounted that the concentrations around 90-31,000 mg/l for numerous drugs like citalopram, metoprolol, ofloxacin, enoxacin, norfloxacin, lomefloxacin, enrofloxacin, cetirizine, ciprofloxacin and ranitidine as effluents from STP at Patancheru Enviro Tech Ltd. (PETL) located in Hyderabad (Larsson et al. 2007). The pharmaceutical substances with measured concentrations discovered in ground water and in surface water have been mentioned in Table 1.2.

Table 1.1: National Environment Quality standards of a pharmaceutical effluent (www.cpcb.nic.in)

	Parameter	**Concentration levels not to be surpassed (mg/l)**
Compulsory	pH	6.5-8.5
	COD	250
	Oil & Grease	10
	BOD(3days at 27^0C)	100
	Total suspended solids	100
Additional	Mercury	0.01
	Arsenic	0.2
	Lead	0.1
	Cyanide	0.1
	Phosphates (as P)	5.0
	Phenolics(C_6H_5OH)	1.0
	Chromium	0.1
	Sulphides (as S)	2.0

CPCB standards

It is of great importance to determine the existence of the pharmaceuticals in marine environment as they have less volatility, high solubility with major transformation products strewn in the food chain therefore greatest potential to cause a threat on the living individuals (Cunningham et al. 2009). Synergistic or antagonistic effects could occur as the pharmaceuticals present in a blend with other contaminants in the water present on the surfaces (Cleuvers 2003, Jonker et al. 2005). So, their enduring effects are also being taken into contemplation.

Table: 1.2: Drugs concentrations detected and measured in freshwater resources for different countries (Larsson et al.2007)

Pharmaceutical	**Extraction method**	**Country**	**Concentration**	**Extraction Instrument**
Ground water	-	USA		-
Acetaminophen	Solid phase extraction		-	HPLC-MS
Caffeine			1.89 mg/l	
Carbamazepine			0.29 mg/l	
Codeine			0.42 mg/l	
P-xanthine			0.214 mg/l	
Sulfamethoxazole			0.12 mg/l	
Trimethoprim			0.17 mg/l	
Surface water			0.018 mg/l	
Ibuprofen	Solid phase extraction using high performance extraction disks (SBD-XD)	South Korea		HPLC with tandem MS
Carbamazepine			414 ng/l	
Atenolol			595 ng/l	
Clarithromycin			690 ng/l	
Mefenamic acid			443 ng/l	
Erythromycin			326 ng/l	
Fluconazole			137 ng/l	
Levofloxacin			111 ng/l	
Indomethacin			87.4 ng/l	
Propranolol			33.5 ng/l	
Ifenprodil			40.1 ng/l	
Finofibric acid	Oasis HLB solid phase Reverse Phase extraction diode array detector Estuary		35.4 ng/l	HPLC through Douro River 44 with C18 column
Carbamazepine			3.20 mg/l	
Diazepam			0.60 mg/l	
Fluoxetine			1.60 mg/l	
Propranolol			32.00 mg/l	
Sulfamethoxazole			0.80 mg/l	
Trimethoprim			1.40 mg/l	HPLC-MS,

The countries like Canada relied on the fact “dilution being the solution” for releasing micropollutants. But with growing inhabitants along chief waterways, escalating masses

of micro contaminants with high demands of water, diluting is no longer proving to be an economical and practical solution. The presence of micropollutants possesses problems in aspects of water management, security of water from its origin point, vast municipal reusability and effluents of industrial wastewater. The degree by which pharmaceuticals and personal care products are separated using treatment processes is not efficiently empathized. Most of the pollutants discharged are non-biodegradable and hence efficient removal by conventional treatment techniques is leading to adverse accumulation in the marine environment.

The conventional treatment plants are chiefly not designed comprising of tertiary treatment technique that abolishes the pharmaceuticals along with their metabolites (Celiz et al. 2009). Consequently, WWTPs act as foremost pharmaceuticals dispensing emitters into environment. It is of utmost importance to supply the modified techniques to clean the pharmaceuticals in WWTPs ahead of unleashing them into aquatic system. Nonetheless, elevated concentration is formerly compensated to pharmaceuticals even as a category of rising environmental adulterants (Heberer 2002).

1.6 Treatment technologies involved in treating pharmaceutical waste

Conventional wastewater treatment methods do not deal with chemical transformations rather a transfer in between the phases may occur generally, thus resulting into secondary loading of environment and waste disposal problem (Sun et al. 2007). Some of conventional techniques initially used has been given below.

- Coagulation/Flocculation
- Adsorption and biological treatment
- Chlorination
- Membrane separation etc.

The conventional treatment technologies resembling secondary biodegradation are not effective to remove numerous pollutants of rising concern substantially. Whilst AOP's like activated carbon treatment and reverse osmosis technique can generate superior quality water. But the pollutants are only transmitted and concentrated from one phase to another. Supplementary dispensation is required to deliver the substances passive. Comparative simple wastewater treatment techniques could be designed to grant low cost sanitation with environmental protection. The cleansing techniques of various effluent

types have applications owing to assure the exclusion of the contaminant with the aim of reaching the stringent permitted levels for releasing these discharges. The standard limits of contaminants allowable for discharging water are precisely associated with the category of pollutant present in the discharges of wastewater source.

Generally, the exclusion of organics as contaminants in liquid solution requires one or more root treatment technology (Mahamuni and Pandit 2006). The decomposition of organic substances to the required minor levels perhaps attained using numerous processes has been mentioned below.

- Wet air oxidation
- Membrane separation
- Ozonation
- Peroxidation
- Fenton oxidation
- Electrochemical oxidation
- Radiolysis
- Photocatalytic oxidation
- Sonication.

The process could be used individually or in contrast with some other technique to attain minimum levels of toxic contaminants in aquatic systems. But in all the processes there are intrinsic limitations like low degradation rates with lower mineralization and high operating cost.

Biological methods are amendable only for biodegradable pollutants as in the category of wastewater from households and industrial effluent in a limited ways. Activated sludge process cannot eradicate complex chemical structures that cause solemn human health hazards specifically in marine and terrestrial animals. The aftermath lies in the hormonal systems principally in endocrine systems where the same materials imitates the natural hormones, leading to adverse health hazards in reproductive system, prostate cancer and breast cancers (Ji et al. 2009). These substances exist in plastics, contraceptives, and personal care products like cosmetics, soaps, dyes, and shampoos etc being used every day (Campbell et al. 2006). The list of life forms getting influenced by disruptors of endocrine systems includes fishes that are majorly damaged by gonadal abnormalities.

The tracking of these compounds along with their removal before they occupy the entire environment is important.

It is essential to ratify reactive systems that are to a great extent effective, and assigned in traditional processes of purification. In these cases exclusive category of techniques in oxidation are termed as AOP that typically works at atmospheric temperature and pressure conditions were developed. AOPs are more efficient and ecofriendly in the degradation of any kind of toxic pollutants.

Advanced Oxidation Processes commonly termed as AOP's is defined as a group of oxidative treatments of water used in treating poisonous discharges at industries, hospitals and WWTPs. AOPs chiefly convert venomous organic substances like medicines, pesticides, insecticides etc into biologically degradable compounds. AOPs universally are cost effective to install ,although engrossed with high cost of operation as the participation of chemicals and energy are required (Comninellis et al. 2008). For limiting the costs, processes are frequently used as primary treatment mutually joined with biological treatment (Pulgarin et al. 1999). It is basically a refining step to eradicate micro-pollutants from the discharges of urban treatment plants for wastewater and disinfection the water. The classification of several AOPs has been depicted in Figure 1.2 is an effective way to enhance contaminant removal by reducing costs.

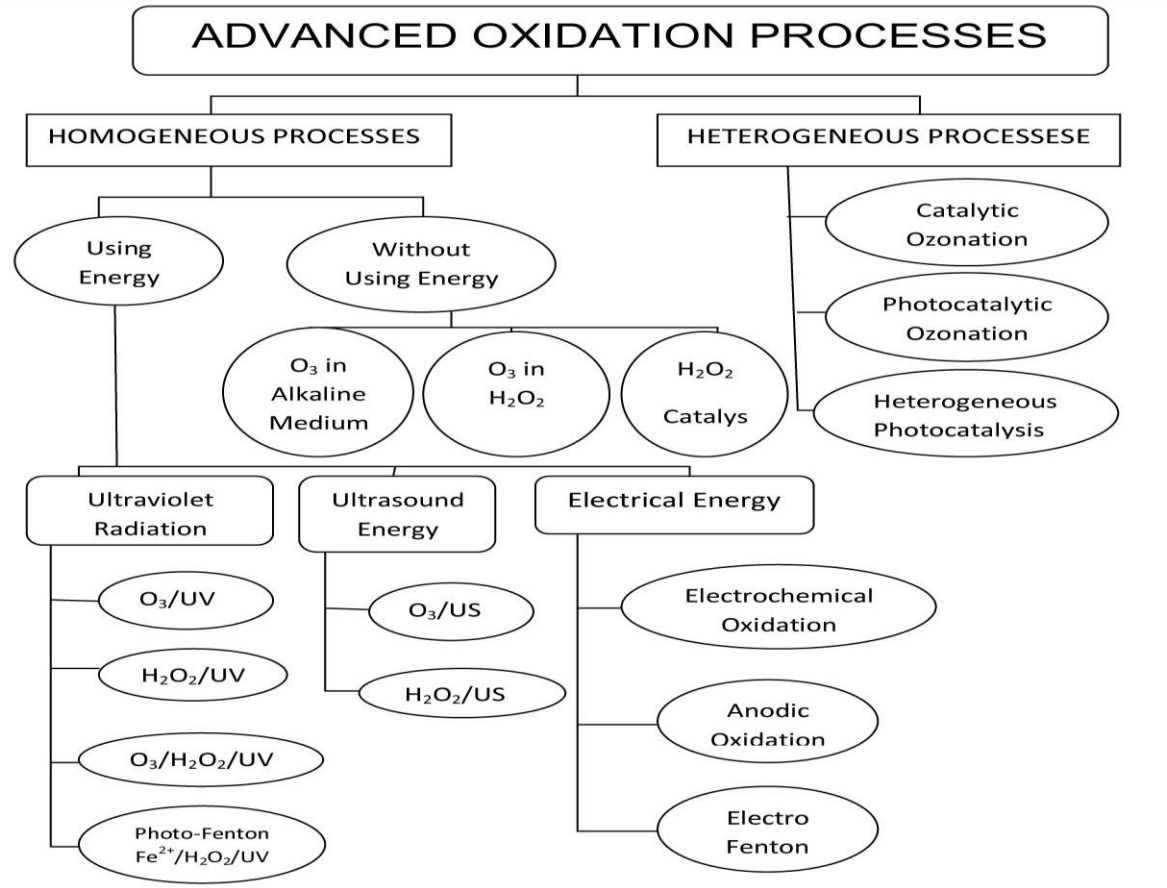

Figure 1.2: Classification of Advanced Oxidation Processes (Bokare and Choi 2014)

Amongst all the AOP's is electrochemical advanced oxidation processes (EAOPs), the most eco-friendly methods, which have recently gathered much attention for water remediation. The EAOPs have advantages like prevention and remediation of pollution, as the electron released in the process is a clean reagent. The process includes high energy efficiency, easy handling as the equipment is simple and safe. The processes operate at room temperature and pressure. The most popular electrochemical advanced oxidation process is the electro-fenton process and electro-oxidation process.

CHAPTER 2

ELECTROCHEMICAL TREATMENT

2.1 Electrochemical Methods

Electrochemical treatment may be the promising water treatment technology. Electrochemical treatment is a budding technology for treatment of water. The major monitored off area in the electrochemical treatment has been mentioned in the list below:-

- Electro-Flotation
- Electro-Coagulation (EC)
- Electro-Oxidation (EO)
- Electro-Fenton (EF)

2.1.1 Electro-Floatation

The effectual electro-flotation is predominantly endorsed in production of consistent and miniature bubbles. It's illustrious that the effectiveness of separation for a flotation technique relies sturdily on size of bubble. Slighter bubbles offer corpulent surface area for the coupling of particle. The bubble sizes produced in the electro-floatation process were diagnosed to be lower than normally distributed. Above 90 % of the bubbles sizes for titanium-based DSA® anode are in the range of 15–45m^2 (Chen et al. 2002). EF is a simpler process where hydrogen (H_2) and oxygen (O_2) are produced from electrolysis of water. These particles move upwards and take alongside the pollutant particles to liquid body's surface.

2.1.2 Electro-Coagulation

Electro-coagulation deals with the production of coagulants within the system on dissolution of Al^{3+} ions from aluminum electrodes or Fe^{3+} ions from iron electrodes by means of electricity. At anode the metal ions are produced, and from the cathode H_2 gas gets evolved. The flocculated particles will float out of water with the help of hydrogen gas and hence, the process is occasionally called electro-flocculation. The electrodes may be assorted in either monopolar or bipolar mode. For electro-coagulation technique the oxidation takes place at anode and therefore, the formation of variety of metal hydrolyzed

both monomeric and polymeric species takes place. The hydroxides of metal eliminate organics in wastewater with the help of sweep coagulation and, therefore aggregate amongst colloidal particles forming bigger flocks that finally get removed by settling.

2.1.3 Electro-Oxidation

Electro-oxidation method involves production of hydroxyl radical (•OH) as the main oxidant, which is the second strongest oxidizing agent known after fluorine. It reacts with most organic contaminants by hydroxylation or dehydrogenation until the total mineralization takes place (Anglada et al. 2009). Research works in the last two decades deeply focused on the improvement of efficiency of oxidation of various pollutants using various electrodes and enhancement of the electro-catalytic activity. Moreover it concentrates on improving the electrochemical adherence of electrode materials, investigating the factors influencing the effectiveness of process, and venturing into the working and kinetics for degradation of contaminant.

2.1.3.1 Types of Electro-Oxidation Process

Treatment of organic contaminants using EO on the surface of the electrode requires the generation of oxidizing agent taking place electrochemically to perform oxidation. Complete decomposition of organic material by the oxidation of organics produces carbon dioxide and water or other oxides (Quiroz et al. 2011). Therefore, no generation of secondary pollutants takes place. The EO of wastewater or wastes can be subdivided in two categories:

- Indirect anodic oxidation (destruction of organics at the electrode surface)
- Direct oxidation (generation of mediators electrochemically to enhance oxidation)

Indirect electro-oxidation involves the generation of chloro species (Cl_2, HOCl and ClO^-) at anode. The presence of hydrogen peroxide (H_2O_2) acts as a source of oxygen supply in the system as in equation (2.1). The anodes in the case of H_2O_2 technique are usually Pb coated on PbO_2, Ti embedded on the Pt coated PbO_2 or Pt individually is preferred.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (2.1)$$

This technology would effectually oxidize most of the inorganic as well as organic contaminants at elevated chloride concentrations. Strong oxidants like HOCl, Cl_2, H_2O_2 and ozone electrochemically gets produced in an indirect oxidation process. The adulterants further get degraded in the bulk solution on generation of oxidant by an oxidation reaction. All the oxidants created inside are consumed spontaneously. Along the oxidants, hypochlorite production is economical, as almost all the effluents have a specific amount of chloride which gets reduced to Cl_2/HOCl. The Cl/HOCl generated by this reaction oxidizes the contaminants and reduces to Cl^- ions.

For direct anodic oxidation, the adulterants get adsorbed on the surface of anode followed by destruction via reaction in which the anodic transfer of electron takes place as in equation (2.2, 2.3, 2.4). Electro-oxidation of pollutants by direct anodic oxidation leads to production of hydroxyl radicals adsorbed physically which is in the form of active oxygen or chemically adsorbed active oxygen inside the latticework of oxide, MO_{x+1}. Following reactions mentioned below are involved in the direct anodic oxidation.

$$MO_x + H_2O \rightarrow MO_x(\bullet OH) + H^+ + e^- \quad (2.2)$$

$$R + MO_x(\bullet OH) \rightarrow CO_2 + H^+ + e^- + MO_x \quad (2.3)$$

$$R + MO_{x+1} \rightarrow RO + MO_x \quad (2.4)$$

2.1.3.2 Electrode Material

The material for the choice of electrode is of major relevance as it influences the selectivity and the effectiveness of the technique. Material of electrode should have properties like elevated physical and chemical stability with high electrical conductivity. It should have resistance towards erosion and corrosion. Selectivity with its catalytic activity should be elevated with less value of cost/life ratio. The material of the electrode used should be economical and have long lasting time. Different types of electrodes used with their properties are listed below.

- Doped-SnO_2 electrodes: SnO_2 conductivity is less, and should be stupefied to achieve high conductivity allowing it to function effectively. (Chaplin 2014).

- PbO_2 electrodes: PbO_2 electrodes oxidation utilizes packed-bed reactors filled with oxidized lead pellets at the earlier stages. But lately exploration was done by PbO_2 and doped-PbO_2 anodes on a various substrates.

- Doped in addition with sub-stoichiometric TiO_2: TiO_2, and doped-TiO_2 having conductive Magneli phase is very potential electrode material required in water treatment (Chaplin 2014).

- Boron-doped diamond electrodes: BDD produced by the chemical vapor deposition (CVD) method is mostly in use these days (Chaplin 2014).

- Ruthenium coated on titanium metal (RuOx–TiOx) electrodes is effectual in the elimination of organic and inorganic adulterants.

- Others electrodes are like Pt foil electrode, Ti/SnO_2–Sb–Pt, graphite electrode etc are also considered in electro-oxidation.

2.1.3.3 Advantages of Electro-Oxidation

Degradation by both direct and indirect electro-oxidation for hazardous wastewater treatment has several advantages in comparison with other treatment methods.

- Electro-oxidation treatment is able to remove extremely toxic wastes

- This process can usually operate at atmospheric pressure in accordance with room temperature.

- A clean technique not requiring any chemical reagent, harmful or expensive.

- It can be easily operated and also optimum safety condition prevails since the oxidizing agents are produced inside the system and utilized during the electro-oxidation process.

- It neither produces any undesirable reaction co-products and sludge.

2.1.3.4 Disadvantages of Electro-Oxidation

- The major hindrance of the process is that operating cost is very high, reason being energy consumption is very high. Furthermore, necessary consideration is required in the process of indirect oxidation as there is a potential for the emergence of chlorinated organic via active chlorine.

- The effluent to be treated should be conducting in nature. Regrettingly, all waste streams would not have adequately conductive; therefore there is necessity for addition of an electrolyte.

- Fouling of electrodes might occur owing to carbon material deposition on the electrode surface.

2.1.4 Electro-Fenton Process

Fenton reaction basically comprises reaction of peroxides (usually H_2O_2) with Fe^{2+} ions to form active oxygen species like $^{\cdot}OH$ that could lead to oxidization of organic and inorganic substances. H.J.H Fenton in 1894 suggested that Fe^{2+}salts could be used to oxidize tartaric acid (Fenton 1894) Recently it's use has been started in removal of hazardous organics from wastewater (Sychev and Isak 1995). Traditional fenton mechanism with rate constants and rate of reaction as in equation (2.5) :- (Fenton 1894)

Ions are reduced with excess hydrogen peroxide into hydroperoxyl ions which are less energetic as in equation (2.6) but follow the same mechanism as fenton and commonly named as fenton like or slow fenton reaction. It is noted that the small amount of ferrous ions acts as catalyst whereas the hydroxyl ions are consumed in the reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \quad k_{1,1} = 40\text{-}80\ Lmol^{-1}sec^{-1} \qquad (2.5)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{2+} + O_2H^{\cdot} + H^+ \quad k_{2,2} = 9.1 \times 10^{-7}\ Lmol^{-1}sec^{-1} \qquad (2.6)$$

The fenton chemistry is as in equation (2.7-2.9):-

$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^- \qquad k_{2,3} = (2.5\text{-}5) \times 10^8\ Lmol^{-1}sec^{-1} \qquad (2.7)$$

$$Fe^{2+} + O2H \rightarrow Fe^{3+} + HO_2 \qquad k_{2,4} = (0.72\text{-}1.5) \times 10^6\ Lmol^{-1}sec^{-1} \qquad (2.8)$$

$$Fe^{3+} + O_2H \rightarrow Fe^{2+} + O_2\ H^+ \qquad k_{2,5} = (0.33\text{-}2.1)\ 10^6\ Lmol^{-1}sec^{-1} \qquad (2.9)$$

Fenton process is indomitably based upon the pH of solution. The fenton reaction has an optimum pH around 3 irrespective of the contaminant being treated (Rivas et al. 2001). A greater interest is to develop effectual electrochemical treatments for the obliteration of bio-refractory organics and toxic chemicals (Pulgarin and Kiwi 1996). In EF process, adulterants get deteriorated by the mechanism of fenton's reagent in group

leading to anodic oxidation at the surface of anode. EF process is categorized into four groups based upon the contact type of Fenton's reagent.

- Usage of sacrificial anode for electrically generating H_2O_2 and ferrous ions being produced by oxygen sparging cathode (Pulgarin and Kiwi 1996).
- External addition of hydrogen peroxide followed by formation of ferrous ions from sacrificial anode (Kurt et al. 2007)
- Ferrous ions are externally added and oxygen sparging cathodes could be used for production of hydrogen peroxide (Brillas and Casado 2002).
- Hydroxyl radical are generated in an electrolysis cell using Fenton reagent, Fe^{2+} ions are being reformed by the diminution of Fe^{3+} ions from the cathode (Zhang et al. 2006).

However, processes like electro-Fenton pose little problems related to H_2O_2 as it has less solubility of oxygen in water. Moreover, the current efficiency gets decreased when pH is less than 3 (Ting et al. 2008). This is due to the generation of $Fe(OH)_3$ leading to slight reduction in production of Fe^{2+} ions. The fundamental disadvantage of fenton reaction being the need of acidic environment could be surmounted by addition of stoichiometric quantity of Fe^{2+} ions. In principle, the most confidential method is the fourth type where at the cathode the ferric ions get reduced to ferrous ions. Although, even at optimum current density the regeneration of Fe^{2+} is slow (Ting et al. 2008). The parameters deciding the electro-fenton process efficiency are nature of electrode, electrolytes added to increase conductance, temperature, pH of the sample, catalyst concentration, DO levels and current density.

2.1.5 Advantages of Electro- fenton process

- There is no energy input required in activating hydrogen peroxide.
- Ferrous sulphate is relatively inexpensive.
- The reaction time is very small in comparison with other electrochemical processes.
- There is no hindrance due to mass transfer because of homogeneous nature of catalyst.

2.1.6 Disadvantages of Electro-fenton process

- The ferrous ions generated in the electro-fenton process are consumed before they are generated in the process.
- The process is operated in a narrow pH range of 2-3.

CHAPTER 3

LITERATURE SURVEY

3.1 Pharmaceuticals detected in wastewater

It was investigated that the manifestations of pollutants were of increasing concern. The concentration of PPCP is usually higher in spring season than in other seasons but on the other hand groundwater concentrations remain unaffected with the change in seasons. The mean concentrations of most commonly identified pharmaceuticals in wastewater are carbamazepine 5 μg/l, sulfamethoxazole 252 ng/l, ibuprofen 1.5 μg/l, caffeine 9.8 μg/l, and diclofenac 121 ng/l. It was denoted that PPCPs having extremely elevated frequencies of detection with their analogous concentrations in groundwater are constant for all the other countries. Antibiotics, lipid regulators, anti-inflammatory, analgesics, and N, N-diethyl m-toluamide were often found in groundwater (Sui et al. 2015). Sulphonamides comprised the class of antibiotics commonly detected in higher concentrations (García-Galán et al. 2010). The major frequently detected compounds included anti-inflammatories or analgesics in groundwater constituting salicylic acid, ibuprofen, carbamazepine, diclofenac and cetrizine as they have large and frequent consumption. Many other pharmaceuticals with their metabolites like ibuprofen along with ketoprofen were spotted with concentrations in mg/l. 98% salicylic acid was detected in the Guangzhou city of China. The concentration ranges between 43.7 to 2014.7 ng/l (Zhang et al. 2014).

It is indicated that the contamination through pharmaceuticals and personal care products along with its consequent ecological risk pose a grave concern regarding groundwater near landfill sites (Holm et al. 1995). Growing concerns for health and environmental are making PPCP's of meticulous interest as low levels of PPCPs having long-term exposure would lead to adverse effects on marine and global ecosystems or human health. For that matter, in Canadian lake systems the fish population showed feminism due to chronic exposure to low levels between 2-6 ng/L of the fake estrogen ethynylestradiol-EE2, a compound in birth control pills (Kidd et al. 2007).

3.2 Pharmaceuticals treated by Electro-Oxidation

Kaur et al. (2018) investigated the deterioration potential of synthetic ofloxacin wastewater using Ti/RuO_2 electrodes. The operational parameters were studied like preliminary concentration of ofloxacin in wastewater, pH value of ofloxacin sample, electric current supply and concentration of supporting electrolyte on efficiency of removal and percentage of TOC removal. SEC was calculated to be 1120-766.7 Wh for 1 g TOC removed whereas mineralization current efficiency was calculated to be 7.8% to 4.9%. Cost analysis was also performed and it was found that the operating cost for 1g of TOC removal was Rs 35.38 and mineralization cost was calculated 32.67 (g TOC removed)$^{-1}$. The rate constant was found to increase from 0.017 to 0.12 min^{-1} with a current increase from 0.25 to 1 A.

Ji et al. (2017) compared the deterioration studies of diclofenac using two different electrodes i.e. BDD and Ta/PbO_2. The consequences of different operating parameters were investigated like current density, temperature, pH of diclofenac sample, diclofenac's initial concentration in wastewater. The deterioration effectiveness increased on increasing temperature and current density. The efficiency of degradation increases with decrease the initial concentration of Diclofenac in wastewater and pH. Electro-oxidation using Ta/PbO_2 was found to have better anodic oxidation capacity than BDD electrodes. Therefore, he concluded that the electro-oxidation of pharmaceutical waste showed more promising results with Ta/PbO_2. It was also found that the deterioration reaction was dependent on kinetics and obeyed pseudo-first order. The rate limiting step was mass transfer. The technique used to analyze efficiency of degradation was COD measure for initial sample and degraded sample.

Sopaj et al. (2015) performed a comparative analysis on deterioration efficiencies of amoxicillin using different electrode materials. The deterioration efficiency of amoxicillin using BDD anode was much effective than DSA. The increase in deterioration efficiency was significant during the initial stages of electrolysis process even at high current density. It was found mass transfer was the controlling step in the reaction mechanism which helped in calculating the rate constants for all anode types. The effectiveness of the anodes was in the following decreasing order. BDD was most efficient in an oxidation process followed by platinum showing comparatively less oxidation capacity. Carbon fiber and carbon graphite were with little lesser oxidation capacities whereas DSA showed

least oxidation capacity. Large amount of hydroxyl ions were produced on supply of electric current which enhanced the oxidation power of BDD. This deterioration using BDD was 100% in 100 minutes.

Coria et al. (2014) performed an oxidation of diclofenac via hydroxyl radicals on BDD anode. The electrolysis reaction was carried in FM01-LC reactor indicating current density between 10-20 mA cm^{-2}. Diclofenac deterioration along with the current efficiency for the mineralization rate was not dependent on the hydrodynamics. The oxidation of diclofenac engaged a complex mechanism. The 100 % diclofenac mineralization obtained at rate of 29.2 cm s^{-1} along with the current efficiencies of 78%, and energy consumed was 2.54 KWh m^{-3}. The FM01-LC reactor contained an anode of BDD that improved continuum yield leading to better interaction with BDD (•OH) and organics. Hence, process results in increasing organic efficiency of mineralization.

Chen et al. (2013) measured the effects of BDD electrode on the electrochemical degradation of ofloxacin. A study on the effect of oxidation of ofloxacin at different initial ofloxacin concentrations, current densities, electrolyte temperatures, and anodes was done. The deterioration of ofloxacin was found to follow the kinetics of pseudo-first-order yielding 1.2×10^{-3} s^{-1} as rate constant at current density 100 mA/cm^2 in 0.1M Na_2SO_4 electrolyte concentration at 30^oC. With an increasing current density from 20−100 mA/cm^2 and temperature ranging 30−70°C, the deterioration efficiency and the rate constant was observed to increase. The activation energy of deterioration for ofloxacin on BDD was 4.79 kJ/mol. In addition, the efficiency of deterioration for ofloxacin was observed decrease with the increasing initial ofloxacin concentration. The performance of deterioration efficiency of ofloxacin for different anodes was tested and results were obtained as BDD > Pt > DSA. On the usage of BDD electrode no ofloxacin residual were detected at 90 min for the constant current electrolysis. Nevertheless, the efficiency of deterioration of ofloxacin was only about 50.5% on the Pt anode and 13.3% on DSA anodes. Therefore, the BDD electrode has showed marvellous results for the ofloxacin deterioration than anodes of Pt and DSA in aqueous solutions.

Cofan and Radovan (2011) investigated using chronoamperometry (CA) and differential pulse voltammetry (DPV). Acetylsalicylic acid (ASA) was treated using mildly oxidized electrode of boron-doped diamond (BDD) containing a neutral solution of sodium sulphate behaving as a supporting electrolyte In differential pulse voltammetry,

the plots of linear calibration of anodic current were achieved for the concentration ranging between 0.01mMol–0.1mMol. The results of experiments for CA versus concentration were found to have a very significant correlation coefficients and good values for sensitivity. The detection limits lied around 1 μM.

Brillas et al. (2005) studied that the100ml solutions containing paracetamol chemically named as N-(4-hydroxyphenyl) acetamide showed degradation till 1g/l for the pH range 2.0–12.0 via oxidation at anode. In a cell, BDD as an anode and cathode is of graphite, each having an area of 3 cm^2 for applied current values as 100, 300 and 450mA for temperature ranging 25 to 45 ^{0}C mineralization is attained. In this case because of high generation of OH^- ions at the surface of BDD releasing ammonium and nitrate ions, high mineralization was attained. Pt completely degraded paracetamol following the kinetics of pseudo first order independent of the pH of system.

3.3 Pharmaceuticals treated by Electro-Fenton

An AOP category popularly termed as fenton method is basically when a hydroxyl radical (•OH) is generated by decomposition of hydrogen peroxide or by addition of ferrous ion catalytically. The introduction of ferrous ions is because of its high oxidation power, reasonable cost and ease of operation. The advantages above makes the process extensively used. The electrochemical generation of Fe^{2+} ions was consecutively increased by reducing the amount of dissolved oxygen, thereby increasing the capacity of oxidation of fenton process.

Gong et al. (2016) confirmed that the ACF cathode in EF process is an effectual method for both decline and increase in the biodegradability of a wastewater. BOD_5/COD ratio increased with an elevated electrolysis time achieving biodegradability 0.41 for electrolysis time of 600 minutes. The optimum time for complete removal by EF process was 120 minutes following the kinetics as pseudo-first-order. The rate constant of 2.37 × 10^{-2} min^{-1} comparatively greater than that of AO or AO-H_2O_2 processes. The optimum parameters for an EF treatment was current density of 6.67 mA/cm^2, 1.0 mM of catalyst $Fe^{2+,}$ pH of sample 3.0, saturated with 100 ml/min O_2 for 61% TOC removal was in 360 minutes.

Cheng et al. (2013) investigated the degradation behaviour of metronidazole using advanced oxidation process aiming increase in mineralization efficiency using Ce/SnO_2–

Sb/Ti. It was used for anodic oxidation under fenton process and the electro-fenton process. EF process was found to be most effective. The optimum parameters were found to be catalyst concentration 2.0 mMol, molar ratio H_2O_2/Fe^{2+} were 10:1. The total organic carbon was mineralized to 37 % at optimum conditions. The change in biodegradation was studied on the basis of the BOD_5/COD ratio. The ratio of BOD_5/COD of raw MNZ aqueous (0.227) was found to increase from 0.252 in EC and 0.345 by the EF systems.

George et al. (2013) investigated that the oxidation of salicylic acid in an aqueous medium by the EF process in a CSTR under various operating conditions. Continuous experiments performed in saturated air conditions were used to determine the optimal values for the oxidation of SA as 5 mg/L Fe^{2+}, pH 2.5, voltage 2.5V, and electrode spacing of 3 cm. Under these optimized conditions, a maximum SA oxidation was 70 %. It was obvious that CSTR was capable to work without process performing problems. It attained a good SA oxidation depending on the residence time leading to lack in accumulation of other oxidizing agents.

Dirany et al. (2012) studied that the electro-fenton treatment of SCP using carbon felt electrodes or Pt/ BDD. The aim was to show the kinetics, electro degradation by-products and toxicity studies. On the supply of electric current to H_2O_2 in the presence of Fe^{2+} ions, hydroxyl ion production started in the solution. The $OH^{\cdot}$ radicals got deposited at anode leading to the oxidation of SCP. The value of $k_{abs,SCP} = (1.58 \pm 0.02) \times 10^9\ M^{-1}\ s^{-1}$) was calculated for oxidative degradation of SCP. The carboxylic acids formation engaged an incisive toxicity decrease leading to overall detoxification.

Isarain-Chávez et al. (2011) prepared 0.25 mMol solutions of metoprolol tartrate with 0.5 mMol Fe^{2+} including 0.1 mMol Cu^{2+} at pH 3.0 were relatively destroyed under EF and PEF conditions. Two systems were employed to carry out the electrolysis process. The employment of a single cell consisting of BDD as an anode and an air-diffusion cathode for hydrogen peroxide electrical generation. The second assembly comprised of a combined cell constituting a BDD/ADE in a group attached with Platinum over carbon felt (CF) cell. The overall mineralization attained for both systems reached an effective generation of •OH radicals via Fenton's reaction. Complete mineralization was possible using the combined cell in 0.1 mM Cu^{2+} ions. This is to due parallel fast oxidation of Cu(II) carboxylate by •OH following a pseudo-first-order reaction. Ionic chromatography

was used to quantify complexes of final carboxylic acids like formic, oxamic and NH^{4+} ion formed using Fe (III) and Cu (III) in a fenton process.

Several investigations on the treatment of pharmaceuticals using electro-oxidation technique has been shown in Table 3.1

Table 3.1: Literature reviewed for electro-oxidation process for different pharmaceuticals

S.No	Pollutant type	Electrode type	Current Density (mA/cm^2)	pH	Time (min)	Results	Reference
1.	Aspirin	PbO_2 doped with rare earth La-Y	50	-	150	COD 82.12%, TOC removal 50.32%, Degradation efficiencies 43%	(Dai et al. 2016)
2.	Aspirin	Hydrogen Peroxide along with Modified PbO_2 Electrode	50	7	150	aspirin removal 94%, COD 81% TOC 61%	(Dai et al. 2012)
3.	Paracetamol	Vitreous carbon electrodes along TiO2 and Al_2O_3 /CuO/TiO_2	-	3	120	TOC removal 80-99% Current efficiency	(Valdez et al. 2012)
4.	Diclofenac	BDD	-	6.7	240	mineralization degree 72%	(Zhao et al. 2009)
5.	Ibuprofen	$Ti/Pt/PbO_2$ a nd Si/BDD	30	-	360	TOC removal 48-92%	(Ciríaco et al. 2009)
6.	Propham	BDD	30	6	500	pseudo-first-order rate constant 4.8/sec	(Özcan et al. 2008)
7.	Salicylic Acid	Pt and BDD as anode hydrogen peroxide at cathode (H_2O_2)	33	3.0	360	First order decay with 100% mineralization	(Guinea et al. 2008)

The several other pharmaceuticals treated with electro-fenton process has been depicted in Table 3.2

Table 3.2: Literature reviewed for electro-fenton process for different pharmaceuticals

S.No	Pollutant Type	Electrode Type	Fenton reagent (mM)	Current Density (mA/cm^2)	Time (min)	Reference
1.	Enoxacin	cathode carbon-felt anode platinum	0.2	8.6	180	Annabi et al. 2016
2.	Ketoprofen	BDD/carbon felt Pt/carbon felt, AO with BDD anode	0.1	22.22	40	Feng et al. 2014
3.	Amoxicillin	carbon-felt cathode Pt or BDD anode	0.2	13.33	30	Panizza et al. 2014
4.	Sulphanilic acid	BDD	0.4	100	420	El-Ghenymy et al. 2012
5.	Ibuprofen	platinum and boron-doped diamond	0.5	33.3	60	Skoumal et al. 2009

3.4 Technologies employed in treating cetirizine

A general drug cetirizine dihydrochloride of the class antihistamine habitually detected in waste water samples was treated using lacasse enzyme ultrasound treatment and photodegradation.

Sutar and Rathod (2015) concluded that under the effect of ultrasound irradiation with a new technology of laccase enzyme as a catalyst, the degradation of cetirizine dihydrochloride increased rapidly. The parameters were optimized at 0.02 % enzyme

loading (w/v), 50% duty cycle with 200 rpm, at 50 ^{0}C temperature having input of power around 100 W, 25 kHz frequency, the maximum degradation 91 % was achieved. Results from experiments concluded that, under the impact of ultrasound irradiation the enzymatic degradation using lacasse enzyme for Cetirizine dihydrochloride gets enhanced. Also there is a reduction in the time of degradation as compare with conventional techniques

Mead et al. (2014) analyzed the rate of photo degradation of the anti-histamine cetirzine (Zyrtec 1) in various water compositions. Initial observation of first order photo degradation rate coefficient (k_{obs}) 0.024 h^{-1} in deionised water of cetirizine concentration versus irradiation time in simulated sunlight, linear regression of the logarithmic transformation were obtained. The study with various water compositions also measured no statistical difference in K_{obs} in coastal seawater and deionised water with dissolution of the chromophoric organic matter. Gradual yield of cetirizine photodegradation decreased drastically with an increase in wavelength. The standard range of values is from $5.28*10^{-4}$ to $6.40*10^{-3}$ in ultraviolet regime (280-366 nm). The energy of activation for photodegradation of cetirizine was 10.3 kJ/mol and degradation increased with rise in temperature.

RESEARCH GAPS

On the basis of literature survey a following gaps were found:-

1. There lies paucity of literature for the degradation studies of cetirizine with EO and EF treatment methods using dimensionally stable Ti/RuO_2 electrodes.
2. A comparative study, of EO and EF treatment process is lacking in the literature for the degradation of cetirizine.

OBJECTIVES

In the current study, degradation of cetirizine was studied using Ruthenium oxide coated with Titanium (Ti/RuO_2) electrodes. The following were the objectives of study:

- To study the effect of EO process parameters like initial molar concentration (C_{CE}), pH of the sample, current applied (i) and time (t) on the % degradation of cetirizine (D) in simulated cetirizine wastewater using BBD.
- To study the effect of EF process parameters like initial molar concentration (C_{CE}), catalyst concentration (C_{FE}), current applied (i) and time (t) on the % degradation of cetirizine (D) in simulated cetirizine wastewater using BBD.

CHAPTER-4

MATERIAL AND METHODS

The chapter discusses the materials (properties and specifications) and methods used in performing the degradation of synthetically prepared pharmaceutical wastewater of cetirizine. Apart from that the instruments used, their specifications with applications are also provided in detail. This chapter reports the use of electro-oxidation and electro-fenton process for the removal of cetirizine from synthetic wastewater.

4.1 Materials

4.1.1 Pharmaceutical Drug

Cetirizine dihydrochloride is an orally active selective H1-receptor antagonist was purchased directly from market and solution was prepared in double distilled water. The chemical nomenclature was [2-[4-[(4-chlorophenyl)phenylmethyl]-1-piperazinyl] ethoxy] acetic acid, dihydrochloride with a structural formula as depicted in Figure 4.1. Cetirizine dihydrochloride, a racemic compound ($C_{21}H_{25}ClN_2O_3$•2HCl) with a half life of 30 hours. The properties of pharmaceutical drug are enlisted in Table 4.1.

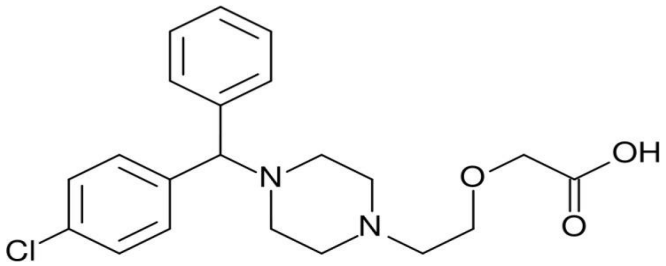

Figure 4.1: Structure of cetirizine

Table 4.1: Physical properties of cetirizine Dihydrochloride (Drugs.com, 2017)

	Units	Typical Value
Appearance		White in colour
Odour		Odourless
Crystallinity		Crystalline powder
Molecular weight	g/mole	388.892
Melting point	^{o}C	112.5
Water solubility	mg/l	101
Solubility		Very soluble in water, chloroform, alcohol

4.1.2 Catalyst

Fenton's reagent is usage of ferrous ions as a catalyst in a compound, to oxidize the pollutants of wastewaters. Fenton's reagent could be used in destroying organic compounds like tetrachloroethylene also commonly called perchloroethylene, PCE. The procedure for performing fenton reaction requires:

- Adjusting of the pH 3-5 for sample wastewater
- Addition of solution of $FeSO_4$ as an iron catalyst
- Slow addition of H_2O_2.

4.1.3 Reagents, Chemicals and Electrodes

Titanium coated Ruthenium oxide electrodes were purchased (Titanium Tantalum Products Limited, Chennai, India) used as anode whereas stainless steel electrodes were used as cathode. The stainless steel electrodes were inert and did not actively participate in the cell reaction. The dimensions of electrodes were same 100*85*1 mm. The electrodes were separated from each other by an optimum distance of 1cm using ceramic beads (Chen, 2004). Ti/RuO_2 as a cathode and stainless steel plate as an anode were used as electrodes in the processes.

Sulphuric acid (H_2SO_4), sodium hydroxide (NaOH) and Fenton Reagent ($FeSO_4$) were purchased from SD Fine Chemicals Limited India utilized in adjusting the pH of the simulated cetirizine wastewater. Distilled water was used to prepare simulated cetirizine solutions for the reaction. Sodium chloride (NaCl) was utilized as an electrolyte to

maintain the conductance of electrolytic cell. Whatman filter paper (180 µm) was used to filter the sample from any other impurities.

4.2 Experimental Setup

4.2.1 Experimental lab scale setup for electro oxidation process

The electro oxidation reactor was fabricated with acrylic plexiglass sheet of thickness 5mm having the effective volume of 1.5 l. The electrodes were Ti/RuO_2 as anode and stainless steel as cathode having the dimensions of 100*85*1 mm. Copper wires were used to connect the electrodes with DC supply. The direct current supply (DIGITECH, Roorkee, India, Model: 4818A10) was used for steady current supply at the time of experiments. Magnetic stirrer was utilized in agitating the wastewater sample. The schematic diagram for reaction setup was shown in Figure 4.2.

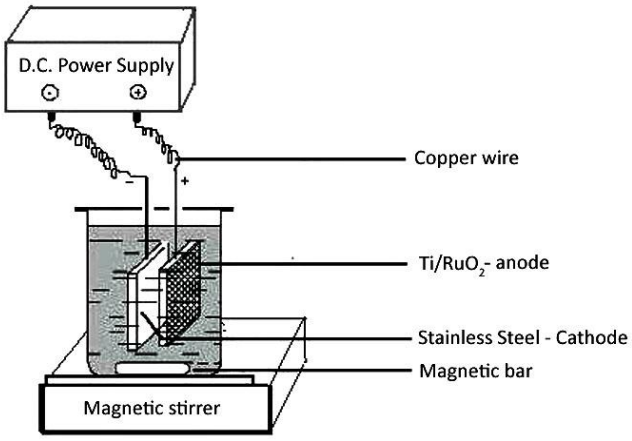

Figure 4.2: Experimental Setup for Electro-oxidation Process

4.2.2 Experimental lab scale setup for Electro-Fenton process

The electro-fenton reactor was fabricated with acrylic Plexiglas sheet of thickness 5mm having the working volume of 1.5 l. Ti/RuO_2 as an anode while, stainless steel electrodes as cathode having the dimensions of 100x85x1 mm were used. Copper wires were used to maintain the flow of current from DC supply to electrodes. The direct current power supply (DIGITECH, Roorkee, India, Model: 4818A10) was used to maintain the current during experiments. Magnetic stirrer was required for agitation of the wastewater sample. A pump along with the air sparger was used for continuous supply of air to enhance the

fenton reaction. The schematic representation of experimental setup was shown in Figure 4.3.

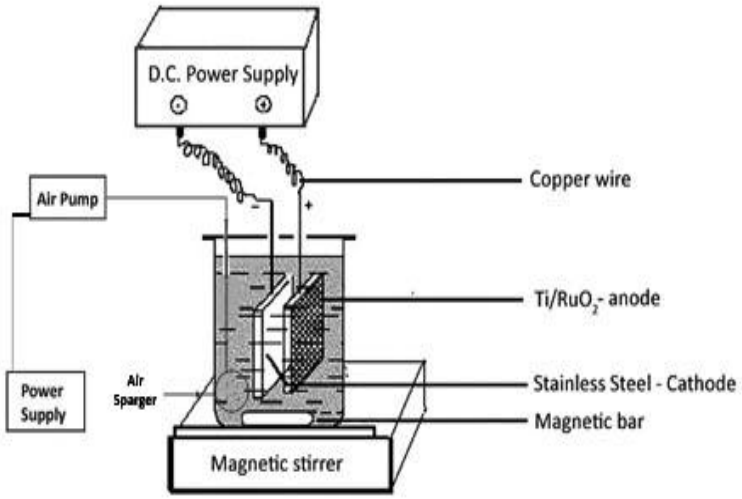

Figure 4.3: Experimental setup for electro-fenton treatment

4.3 Experimental Design and Methodology

4.3.1 Response Surface Methodology

Data collected from the preliminary experiments was used for optimization by Response Surface Methodology (RSM). The Box-Behnken design, a self governing quadratic design which does not have any embedded fractional factorial design was used to design experiments in decided parameter ranges. In Box-Behnken design the treated amalgamation are present at the midpoints, the process space edges and also at the center. Therefore, the three stages of each factor to be optimized are required (Ferreira et al. 2007).

4.3.2 Optimization by Box-Behnken Design (BBD)

For the optimization of parameters in treatment process, a Box-Behnken design (BBD) under response Surface Methodology (RSM) was used. The output (response) Y_i is the dependent on inputs X_1, X_2, X_i .X_f, which are obtained from the below mentioned equation (4.1).

$$Y_i = \Phi (X_1, X_2, X_3 ... Xi ... Xf) \quad (4.1)$$

The relationship amongst the input factors with their responses is expressed in quadratic response model. The non-linear regression analysis was used to identify relevant model to fit the responses. In general, the model used in the study is best fitted in second-order polynomial equation (4.2)

$$Y = S_0 + \sum_{i=1}^{k} S_i X_i + \sum_{i=1}^{k} S_{ii} X_i^2 + \sum \sum_{i<j} X_i Y_i + K_t \quad (4.2)$$

Where, Y is response; S_0, S_i, S_{ii} ,S_{ij} are constant coefficients and X_i the uncoded independent variables . Coding followed the three level factor, coded as -1 (low) and +1 (high). To design the experiments for wastewater treatment, the Statistical Design-Expert software version 6.06 (STAT-EASE Inc., Minneapolis, US) was used.

4.3.3 Desirability

Desirability function is used to optimize multiple responses. It is an approach originally proposed by Harrington used to transform the functions to common scale, and hence combining using geometric mean and optimize the overall matrix. The response of electro-oxidation and electro-fenton was studied and optimized by desirability function. The one sided desirability is calculated by using the equation (4.3).

$$d_i = \begin{cases} 0 & if \quad y_i \leq y_{i-min} \\ \left[\frac{y_i - y_{i-min}}{y_{i-max} - y_{i-min}}\right]^r & if \quad y_{i-min} < y_i < y_{i-max} \\ 1 & if \quad y_i \geq y_{i-max} \end{cases} \quad (4.3)$$

Where y_i is a response value, $yi_{\text{-min}}$ and $y_{\text{i-max}}$ are the minimum and maximum adequate values of response i, and r is a weight and a positive constant used in determining desirability scale. The desirability function lies between 0 & 1. It represents the nearness of the response to its actual value.

4.3.4 Sample preparation

The stock solution of 50 ppm was prepared by dissolving 100 mg of finely crushed cetirizine using mortar and pestle arrangement and dissolved in two liters of distilled water. Constant stirring for half an hour was carried out initially to maintain uniformity of cetirizine in simulated wastewater. A complete wavelength scan was performed using UV

visible spectrophotometer to obtain maximum absorbance at 234 nm. The samples of different concentrations (10-50 ppm) were prepared to obtain the calibration curve.

4.3.5 Procedure for performing Electro-Oxidation treatment

Preliminary reactions were carried out to obtain the parameter variation for an electro-oxidation process. The parameter ranges selected after these reactions were pH of the sample (3-11), initial concentration of cetirizine in simulated wastewater (C_{CE}) (10-30 ppm), current (0.25-1.75) and 120 minutes of reaction time. BBD was used to design the set of experiments considering the range in which parameters are to be varied to study the interaction between operational parameters and responses. The experiments as suggested by BBD under RSM using Design Expert software version 6.06 were performed with procedure below for optimizing the parameters like initial concentration of cetirizine (C_{CE}), pH, current (i) and time of degradation(t).

1. The reaction was performed by withdrawing required amount of solution from freshly prepared stock solution of known concentration. Dilution of stock solution to required concentration was done before performing the reaction.
2. The pH of the sample solution was measured using Thermo Scientific Orion star series pH. The required pH was adjusted by adding 0.5 N Sodium hydroxide (NaOH) and 0.5 N Sulphuric acid (H_2SO_4) solutions respectively by using a micropipette. 1 g/l of sodium chloride as an electrolyte was added to the pharmaceutical sample solution to enhance the conductance of the sample upto 10^{-3} mS.
3. Ti/RuO_2 as a cathode and stainless steel as an anode were used as electrodes in a bipolar arrangement. The electrodes were separated from each other by an optimum electrode spacing of 1 cm using ceramic beads. This assembly was further connected to the terminals of DC supply to allow the flow of current. Electrodes of stainless steel were cleaned using sandpaper and rinsed with water successively after each reaction so as to remove carbon deposits. DC supply was switched on to maintain the constant supply of current into the solution. Time was noted from the point at which supply was switched on.
4. DC supply was switched off. A 3 ml of sample was withdrawn after every 10 minutes with the help of pipette into a glass test tube. The sample was filtered

using whatman filter paper. The time was noted when the supply was switched on again. This electro-oxidation reaction was carried out for 120 minutes.

5. A computer based UV-Visible spectrophotometer was used for the determination of the concentration of cetirizine in the sample.

    - The system is switched on and warmed.
    - Thoroughly cleaned cuvette was taken.
    - Absorbance is checked at λ_{max} with distilled water. Auto zero is done.
    - Then the cuvettes are filled with sample and absorbance is measured at λ_{max} successively.
    - To get the relationship between concentration and absorbance a calibration curve is made by taking absorbance values for standard solutions of known concentrations. The absorbance is plotted against the known concentrations to obtain the calibration curve.

4.3.6 Procedure for performing Electro-Fenton Process

Preliminary reactions were carried out to obtain the parameter variation for an electro-fenton process. The parameter ranges selected after these reactions were initial concentration of cetirizine in simulated wastewater (C_{CE}) (10-30 ppm), fenton reagent concentration (C_{FE}), (0.2-1 mMol), current (0.25-1.75) and reaction time (10-120). The pH of simulated cetirizine wastewater was maintained at 3. BBD under RSM was used to design experiments to study the interaction between the parameters and response. The standard procedure followed to perform the reactions provided by BBD in a full factorial Table for the study of response degradation reaction of cetirizine is given as below:-

1. Each time the reaction was performed; required amount of solution was drawn from freshly prepared stock solution of known concentration. Dilution of stock solution to required concentration was done before performing the reaction.
2. The pH of the sample solution was measured using Thermo Scientific Orion star series pH. The required pH was adjusted by 0.5 N of Sodium hydroxide (NaOH) and 0.5 N Sulphuric acid (H_2SO_4) solutions respectively by using a

micropipette. 1 g of sodium chloride an electrolyte was added to increase the conductance of the solution upto 10^{-3} mS.

3. A known concentration of fenton reagent (C_{FE}) 0.2 mMol, 0.6 mMol and 1.0 mMol as specified in the conditions was added to the reaction mixture. Air sparger was kept into the reactor for continuous supply of air to enhance the ($^{\cdot}OH$) hydroxyl ion formation.
4. Ti/RuO_2 as a cathode and stainless steel as an anode were used as electrodes in a bipolar arrangement. The electrodes were separated from each other by an optimum electrode spacing of around 1 cm using ceramic beads. This assembly was further connected to the terminals of DC supply to allow the flow of current. Electrodes of stainless steel were cleaned using sandpaper and rinsed with water successively after each reaction so as to remove carbon deposits. DC supply was switched on to maintain the constant supply of current into the solution. Time was noted from the point at which supply was switched on.
5. DC supply was switched off and a sample of 3 ml of sample was withdrawn after every 10 minutes with the help of pipette into the glass test tube. The sample was filtered using Whatman filter paper and the funnel was thoroughly washed after each sample. DC supply was then switched on and the time was noted on from that moment. The reaction time was 120 minutes.
6. A computer based UV-Visible spectrophotometer was used for the determination of the concentration of cetirizine in the simulated reaction solution.

    - The system is switched on and warmed.
    - Thoroughly cleaned cuvette was taken.
    - Absorbance is checked at λ_{max} with distilled water. Auto zero is done.
    - Then the cuvettes are filled with sample and absorbance is measured at λ_{max} successively.
    - To get the relationship between concentration and absorbance a calibration curve is made by taking absorbance values for standard solutions of known concentrations. The absorbance is plotted against the known concentrations to obtain the calibration curve.

CHAPTER 5

RESULTS AND DISCUSSION

This chapter focuses on the effect of operating parameters on the % degradation of pharmaceutical compound cetirizine by the electro-oxidation (EO) process and electro-fenton (EF) process. The electrodes used were Ti/RuO_2 as an anode and stainless steel as a cathode for both the processes. The experimental results and their interpretation regarding the degradation of pharmaceutical compound cetirizine degradation using EO and EF have been discussed in detail.

5.1Calibration curve

The complete wavelength scan of compound cetirizine was done on UV-Vis spectrophotometer and maximum absorbance was observed at 234 nm. Standard curve was obtained by plotting the graph between absorbance and concentration of cetirizine as shown in figure 5.1.

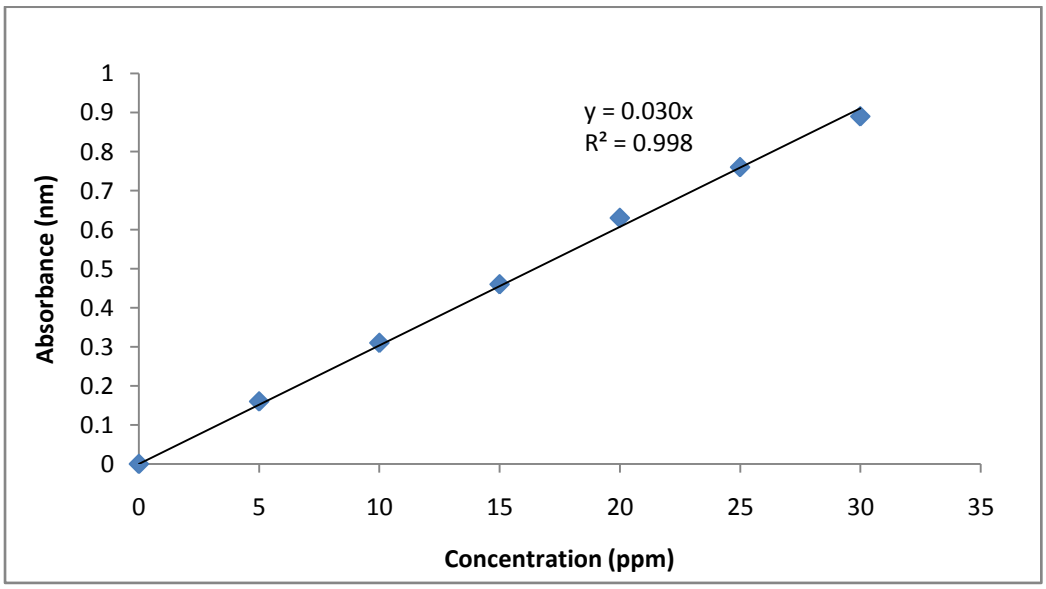

Figure 5.1: Calibration curve for different concentrations of cetirizine

5.2 Degradation of Cetirizine wastewater by EO process

The range of selected operational parameters was determined by performing preliminary experiments. The selected parameters were pH of sample, concentration of cetrizine in simulated sample (C_{CE}), current (i) and time of degradation (t).

5.2.1 Response Surface Methodology (RSM) for EO process

5.2.1.1 Box- Behnken Design (BBD) for EO process

Box-Behnken design under Response Surface Methodology (RSM) was used to design the experiments for the degradation of cetrizine by EO. Three analytical steps were performed adequacy of various models, ANOVA and RSM plotting. The four operational parameters C_{CE} (10-30 ppm), i (0.25-1.75A), pH (3-11), t (10-120 min) were considered as input variables and % degradation of cetirizine (% D) was taken as response. Table 5.1 shows the various operational parameters and their coded levels.

Table 5.1: Range of variables and coded levels for EO process

VARIABLES	**-1**	**0**	**1**
C_{CE}(ppm)	10	20	30
pH	3	7	11
i (A)	0.25	1	1.75
t(min)	10	65	120

A full factorial design has been used to study the EO degradation of cetirizine have been shown in Table 5.2. The parameters to be optimized in the process are i, pH, C_{CE} and t of % degradation of cetirizine. The results obtained after performing the reactions as mentioned in BBD matrix (Table 5.2) was statistically analyzed. Analysis was performed in three analytical steps to find optimum conditions. Sequential model sum of squares and model summary statistics (Adequacy of various models) were used to predict the significance of parameters and their ranges by using F values. F values and "prob F" values were compared and the significance was tested. Analysis of variance (ANOVA) analyzes the adequacy of quadratic model by comparing probability is of 95 % confidence interval. The value of "prob F" > 0.05% proves that the parameters have significant effect on the percentage degradation of cetrizine. The major role is of response surface plotting which provides three dimensional graphs depicting the interaction between the various parameters considered and the responses obtained.

5.2.1.2 Statistical Analysis for EO process

The % degradation of cetirizine by EO was optimized according to the matrix of experiments designed as shown in Table 5.2. The sequential F-test with all other test for measures of adequacy was worked upon for choosing the best model. P value for the % degradation of cetirizine was found to be less than 0.0001, so, the quadratic model suggested by sequential model sum of squares was significant. A result of adequacy model was shown in Table 5.3 for % degradation of cetirizine (D). Sequential model sum of squares showed that quadratic model was best fit model for experimental data for degradation percentage of cetirizine. Cubic model was determined as aliased for degradation of cetirizine. Both model summary statistics along with sequential model sum of squares and were checked adequately to decide the accuracy of model.

The "Prob" > F 0.0001, indicates that quadratic model was found to be significant. The R squared value is observed value was 0.95, adjusted value was 0.9033 and predicted value was 0.8125 for quadratic model. This concludes a good association between observed values and predicted values of the EO reaction. The difference between predicted values and observed values dividing by standard error of the residual has close relation with % Normal probability (Figure 5.2). This indicates a good correlation between the observed and predicted values as shown in Figure 5.3. The predicted values were closer to the actual values depicting that optimization of process parameters for the percentage degradation of cetirizine was performed successfully.

Table5.2: Full factorial BBD matrix used and simulated data response for EO process

Std No	Concentration (C_{CE})	pH	Time (t)	Current (i)	% Degradation (D)
1.	30.00	7.00	65.00	0.25	17.1875
2.	20.00	3.00	120.00	1.00	35.346
3.	10.00	11.00	65.00	1.00	38.028
4.	10.00	11.00	65.00	1.00	38.028
5.	10.00	3.00	65.00	1.00	41.1058
6.	20.00	11.00	65.00	1.75	40.2516
7.	20.00	7.00	65.00	1.00	54.7216
8.	20.00	3.00	10.00	1.00	34.8971
9.	20.00	7.00	10.00	0.25	1.0057
10.	20.00	7.00	65.00	1.00	52.3172
11.	20.00	7.00	65.00	1.00	53.7314
12.	20.00	7.00	65.00	1.00	53.2435
13.	30.00	7.00	65.00	1.75	45.093
14.	20.00	7.00	10.00	1.75	34.0076
15.	30.00	11.00	65.00	1.00	44.4357
16.	30.00	7.00	120.00	1.00	64.3312
17.	10.00	7.00	65.00	1.75	46.3087
18.	10.00	7.00	65.00	0.25	1.73697
19.	20.00	7.00	120.00	0.25	42.0977
20.	10.00	7.00	120.00	1.00	64.0306
21.	30.00	3.00	65.00	1.00	58.1276
22.	20.00	7.00	65.00	1.00	52.9153
23.	30.00	7.00	10.00	1.00	34.607
24.	20.00	11.00	65.00	0.25	11.1457
25.	20.00	11.00	120.00	1.00	47.0508
26.	20.00	7.00	120.00	1.75	40.9222
27.	20.00	3.00	65.00	0.25	9.25645
28.	20.00	11.00	10.00	1.00	14.6774
29.	20.00	3.00	65.00	1.75	43.1429
30.	10.00	7.00	10.00	1.00	41.5816

Table 5.3: Sequential model sum of squares for % degradation of cetirizine for EO process

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Mean	44973.68	1	44973.68			
Linear	3748.03	4	937.01	5.06	0.0042	
2FI	1028.25	6	171.38	0.90	0.5142	
Quadratic	3020.07	4	755.02	26.68	< 0.0001	Suggested
Cubic	266.45	8	33.31	1.54	0.3080	Aliased
Residual	129.71	6	21.62			

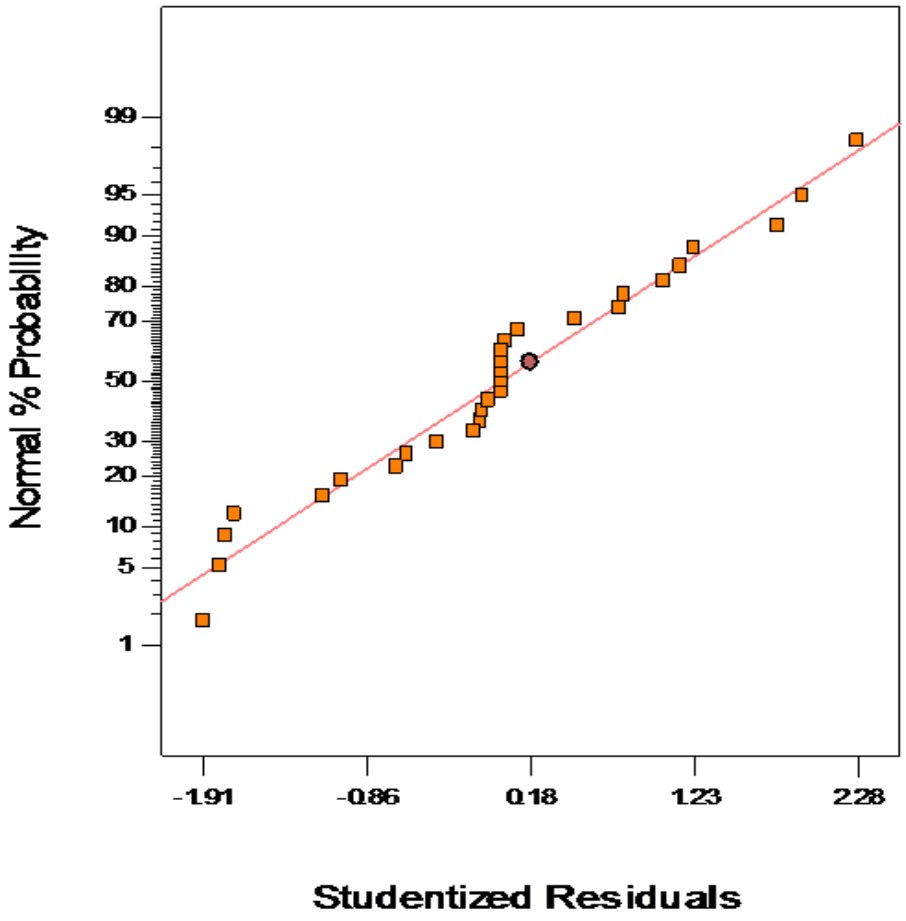

Figure 5.2: Residual plots (normal % probability vs Studentized residuals) for % degradation of cetirizine by EO

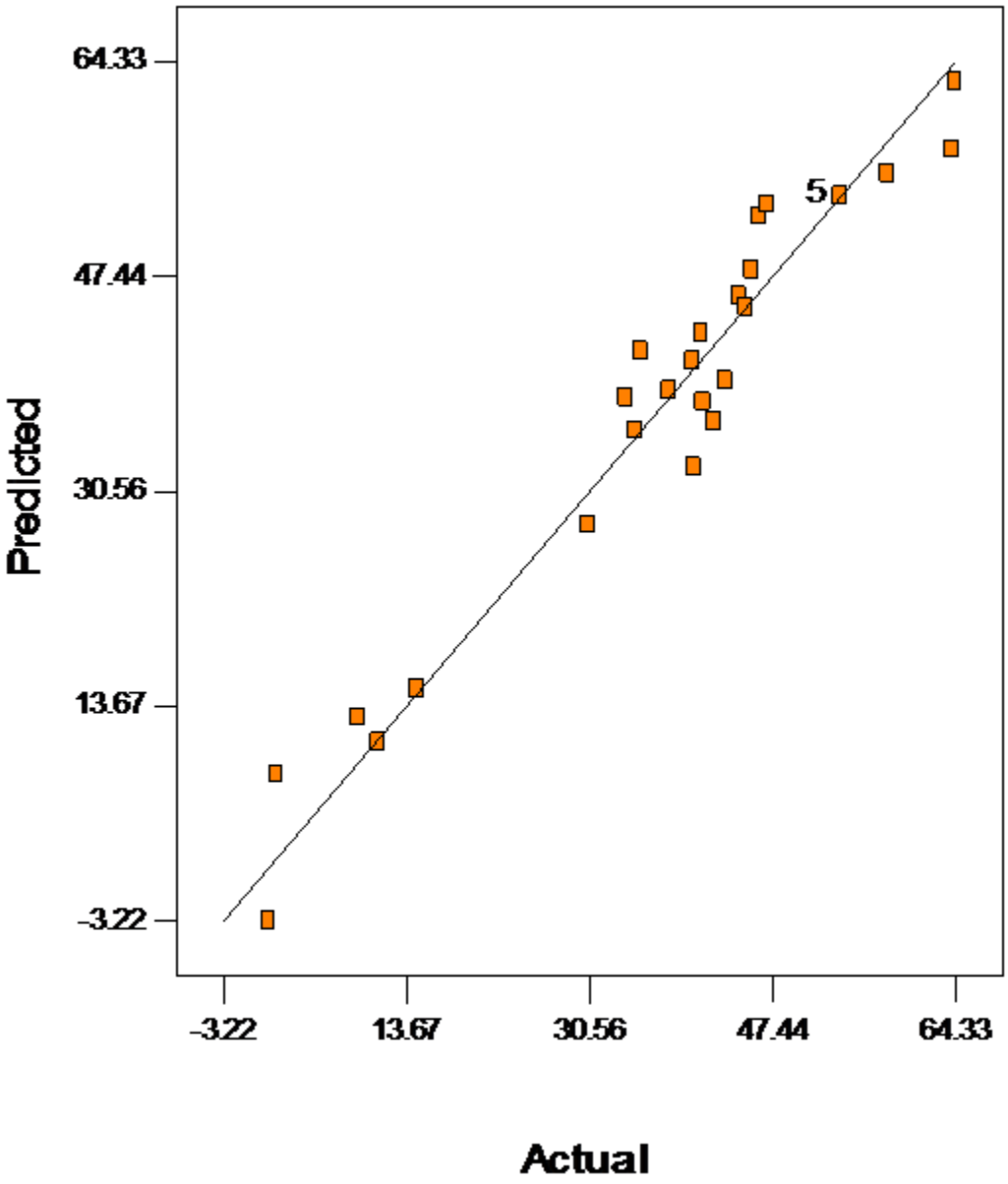

Figure 5.3: Residual plots (predicted vs actual) for % drug degradation of cetirizine by EO

5.2.1.3 Analysis of Variance for EO process

The ANOVA (analysis of variance) shows the model F-value for % D of cetirizine (Table 5.4). This showed that model considered is significant for % degradation of cetirizine. For model terms to be significant, "Prob > F" values should be less than 0.001. "Prob > F" values larger than 0.001 indicates that model term are insignificant. It is clear from ANOVA that the time and current are highly significant terms for % D of cetirizine**.** The Model F-value is noted to be 19.68 entails high significance of the model. There is only a 0.01 % chance that a "Model F-Value" could occur due to noise. Values of "Prob >

F" less than 0.0500 indicate model terms are significant. In this case C_{CE}, i, t, pH^2, i^2, t^2, C_{CE}*t, pH*i, i*t are significant model terms. The "Prob > F" values greater than 0.1000 indicated as the insignificant model terms.

Final Equation in Terms of Actual Factors:

The final equation in terms of actual factors for % D of cetirizine was determined as in equation (5.1).

$$\% D = -98.08+2.17*C_{CE}+0.56*t+125.79*i-0.69207*pH^2-2.12*10^{-3}*t^2 *33.53* i^2 -6.69*10^{-3} * C_{CE} * t -0.39* pH *i -0.21 * t *i \quad (5.1)$$

Table 5.4: ANOVA for response surface quadratic model for % degradation of pharmaceutical drug cetirizine for E process

Source	Sum of Squares	DF	Mean Square	F value	Prob < F	
Model	7796.35	14	556.88	19.68	< 0.0001	Significant
C_{CE}	481.21	1	481.21	17.01	0.0010	
pH	57.58	1	57.58	2.03	0.1756	
i	1474.13	1	1474.13	52.09	< 0.0001	Significant
t	1735.11	1	1735.11	61.32	< 0.0001	Significant
C_{CE}^2	18.53	1	18.53	0.66	0.4319	
pH^2	795.34	1	795.34	28.11	0.0001	Significant
i^2	268.76	1	268.76	9.50	0.0081	
t^2	2307.69	1	2307.69	81.55	< 0.0001	Significant
C_{CE}*pH	28.17	1	28.17	1.00	0.3354	
C_{CE}*i	54.20	1	54.20	1.92	0.1880	
C_{CE}*t	393.35	1	393.35	13.90	0.0022	
pH*i	254.79	1	254.79	9.00	0.0095	
pH*t	5.71	1	5.71	0.20	0.6601	
i*t	292.02	1	292.02	10.32	0.0063	
Residuals	790.35	14	56.45			
Lack of Fit	790.35	10	79.03			insignificant
Pure Error	0.000	4	0.000			
Cor Total	10101.85	28				

5.2.1.4 Parametric study for EO process

The interaction of the operational parameters for the electro-oxidation process i.e pH, initial Concentration of cetirizine (C_{CE}), current (i) and time (t) on % degradation (D) was studied using 3D graphs. From the ANOVA analysis it was found that initial C_{CE}, i and t were found to be significant.

Figure 5.4 depicts that there is a close relation between i and % degradation with the increasing C_{CE}. It is observed that the % degradation was found to be maximum at the current value 0.93 approximately at highest C_{CE}. Also it is observed that as i value increases 0.25, there was a sharp increase in % degradation along with increase in concentration ⇉ 0.93. As i value reaches 0.93 A, there was a decrease in the % degradation even if the C_{CE} is increased. As the current density was increased, the rate of production of $HOCl^-$ ion increased. This increase in hypochlorite ions advances towards equilibrium with degradation of cetirizine.

Figure 5.5 shows the interaction of percentage degradation of cetirizine in accordance with pH and time. It clearly shows that the maximum degradation is observed at natural pH 7 with an increasing time. It is seen the % degradation is visibly increasing with increase in pH upto 7 with the increase in the time of the reaction till 100 minutes approximately. But after that when the pH > 7 the degradation decreases with increase in time. So, the maximum degradation is seen at pH 7 after a period of 100 minutes after which the degradation starts to decrease. In highly acidic pH, cetirizine gets degraded into less molecular weight compounds through the indirect oxidation by the action of oxidants having high oxidation potential like HOCl and direct oxidation by the chemisorbed hydroxyl ions (Kaur et al, 2018). In highly alkaline pH, leading effect of ClO^- mediated oxidation again lowered the % D of cetirizine. From the above explained results, it is resultant that the cetrizine degradation is favoured by highly acidic and alkaline pH; while at neutral pH highest degradation occurred.

Figure 5.6 depicts the interaction between % degradation, time and current simultaneously. It is clearly visible that maximum percentage degradation is observed at current approximately 0.93A and after 103 minutes reaction time. It is observed that the percentage degradation of cetirizine increases with the increase in current from 0.25 to 0.93A, with increasing reaction time. But on further increase in current from 0.93 to higher values till 1.75 A the % degradation decreases. The percentage degradation shows

linear relationship with time as it increases with increase time significantly upto approximately 103 minutes and then on further increase in time the % degradation decreases with increasing current During EO treatment, the contaminants adsorb to the anode surface and mature like a film with the time. Therefore, due to the resistance of this film the execution of the EO process is affected, and hence % D of cetirizine values was limited (Kaur et al. 2018).

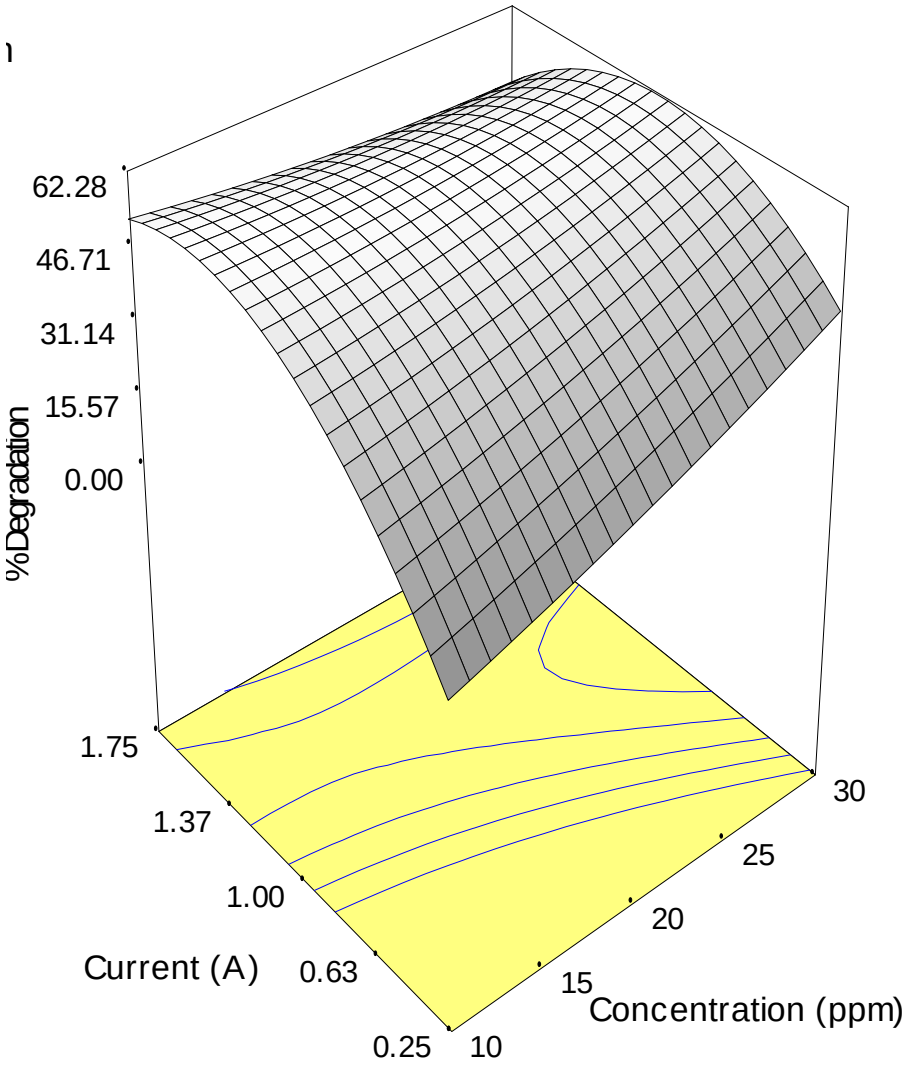

Figure 5.4: 3-D response graph for EO process for % D of cetirizine with respect to C_{CE} (ppm) and i (A)

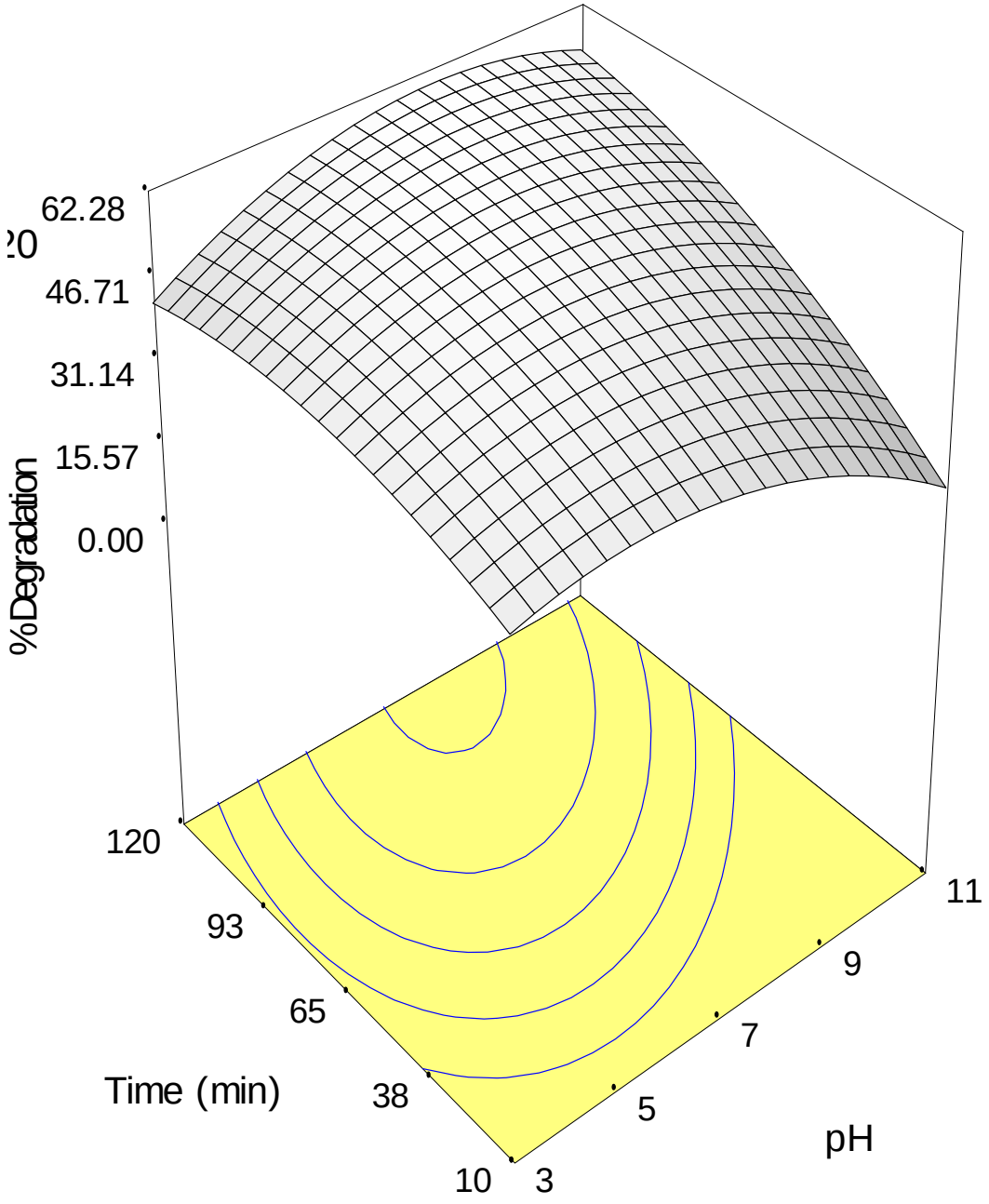

Figure 5.5: 3-D response graph for EO process for % D of cetirizine with respect to t (min) and pH

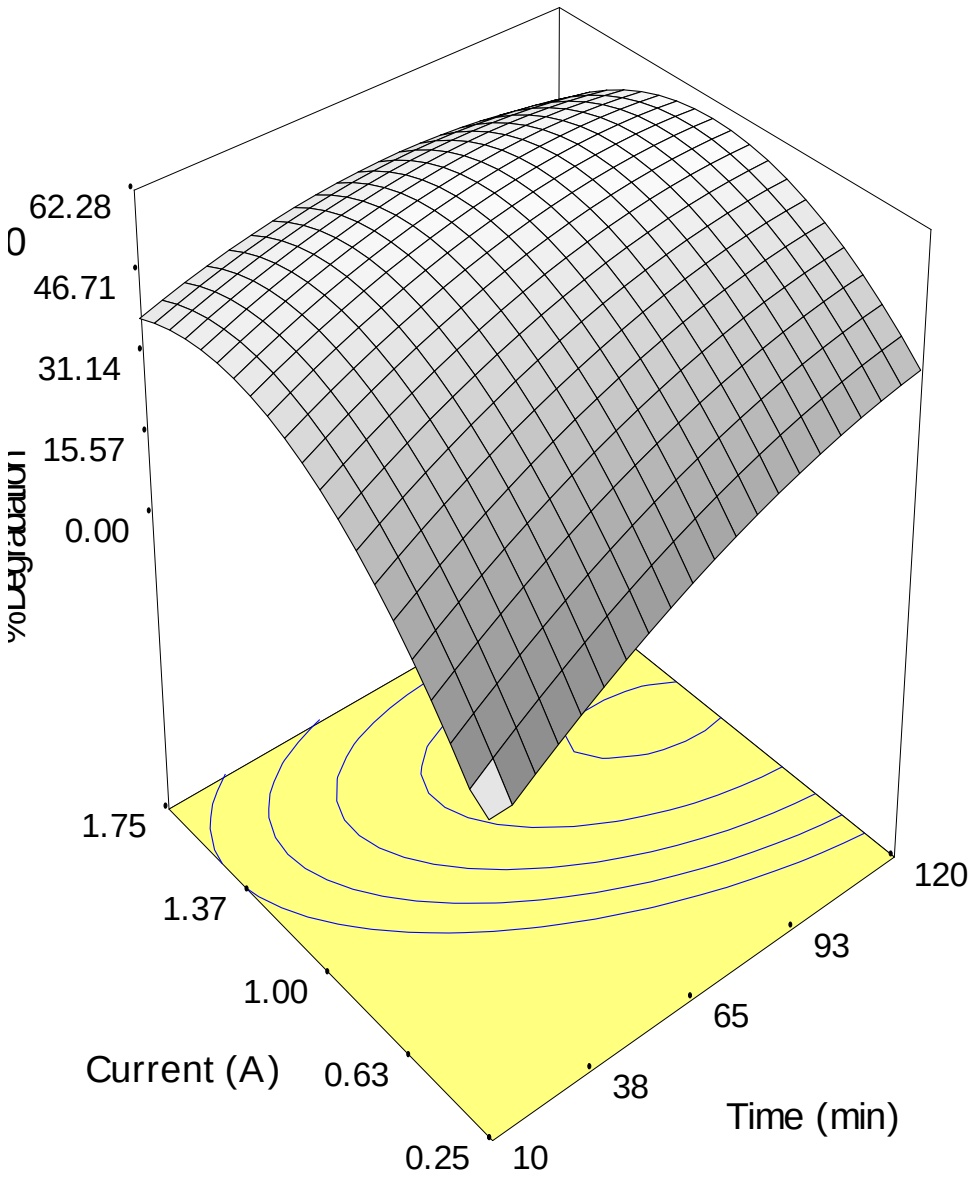

Figure 5.6: 3-D response graph for EO process for % D of cetirizine with respect to t (min) and i (A)

5.2.1.5 Optimization Analysis for EO process

EO of cetirizine wastewater was optimized using RSM in terms of maximising the response % D of cetirizine by using desirability approach. The constraints applied for the degradation of cetirizine has been shown in Table 5.5.

Table 5.5: Constraints applied for optimizing EO of cetirizine in wastewater

Variables	Goal	Lower limit	Upper Limit	Lower Weight	Upper weight	Importance
C_{CE}	is in range	10	30	1	1	3
t	is in range	10	120	1	1	3
pH	is in range	3	11	1	1	1
i	is in range	0.25	1.75	1	1	3
% D	maximize	1.00575	100	1	1	3

5.2.2 Confirmation Results for EO process

The optimum parameters suggested by BBD after complete analysis for a C_{CE} = 30 ppm were pH = 7.09, i = 0.93 for a t = 100 minutes resulted with an optimum % degradation of ceitizine as 64 %. The optimum conditions selected for EO of cetirizine wastewater degradation was experimentally verified. An experiment was run at t = 100 minutes at i = 0.93 and pH = 7 to confirm the practical feasibility of simulated response by BBD. The comparison between the predicted results and experimental results concluded the feasibility of BBD to find optimum conditions as in Table 5.6

Table 5.6: Optimum conditions for EO treatment of cetirizine wastewater

Variables	Predicted Values	Experimental Values
C_{CE}	30 ppm	30 ppm
pH	7.09	7.09
i	0.93 A	0.9 A
t	100 minutes	100 minutes
%D	64.01 %	63.86 %

5.3 Degradation of Cetirizine using EF process

The ranges of the selected parameters were concluded by preliminary experiments. The ranges of the selected parameters were C_{CE} (10-30 ppm), i (0.25-1.75 A), concentration of fenton reagent (C_{FE}) (0.2-1 mMol) and time of degradation (t). The selected operating

parameters were used to model the degradation reactions of cetirizine by electro-fenton processes using BBD.

5.3.1 Box- Behnken Design (BBD) for EF process

To determine the optimum operational parameters by varying C_{CE}, C_{FE}, i and t to maximize the % D, BBD under RSM was used. The range of variables and coded levels were listed below in Table 5.7. The pH of the electrolyte was maintained 3 constantly throughout all the experiments.

A full factorial design used to study the electro-fenton degradation of cetirizine and is shown in Table 5.8. These experiments with the help of design expert software under RSM would help to find the optimum parameter at which the maximum degradation would be obtained.

Table 5.7: Range of variables and levels coded for EF process

VARIABLES	**-1**	**0**	**1**
C_{CE} (ppm)	10	20	30
C_{FE} (mmol)	0.2	0.6	1
i (A)	0.25	1	1.75
t (min)	10	65	120

5.3.2 Statistical Analysis for EF process

The % degradation of cetirizine by EF was optimized according to the matrix of experiments designed in Table 5.7. The sequential F-test with all other test for measures of adequacy was worked upon for choosing the best model. P value for the % degradation of cetirizine was found to be less than 0.0001, so, quadratic model suggested by sequential model sum of squares was significant. A result of an adequacy model was shown in Table 5.9 for % degradation of cetirizine. Sequential model sum of squares depicted that quadratic model was best fit model for experimental data for degradation percentage of cetirizine. Cubic model was considered to be aliased for degradation of cetirizine. Both Model summary statistics along with sequential model sum of squares and was checked adequately to predict the accuracy of model.

Table 5.8: Full factorial design BBD matrix used and simulated data response for EF process

Std No	Concentration (C_{CE})	Fenton Reagent Concentration (C_{FE})	Time (t)	Current (i)	%Degradation (D)
1	20.00	1.00	60.00	1.75	65.177
2	20.00	0.60	60.00	1.00	70.434
3	20.00	1.00	60.00	0.25	54.125
4	20.00	0.20	10.00	1.00	16.137
5	20.00	0.60	10.00	1.75	41.212
6	30.00	0.60	60.00	0.25	24.797
7	20.00	1.00	10.00	1.00	58.76
8	30.00	0.60	10.00	1.00	23.222
9	20.00	0.60	60.00	1.00	71.212
10	20.00	0.60	60.00	1.00	71.005
11	20.00	0.20	60.00	1.75	61.181
12	30.00	0.60	60.00	1.75	69.068
13	30.00	1.00	60.00	1.00	75.175
14	20.00	0.60	60.00	1.00	70.658
15	30.00	0.60	110.00	1.00	76.147
16	20.00	0.60	110.00	0.25	52
17	10.00	0.60	60.00	1.75	63.452
18	20.00	0.60	60.00	1.00	72.215
19	30.00	0.20	60.00	1.00	64.995
20	10.00	0.60	10.00	1.00	38.805
21	10.00	0.60	110.00	1.00	69.154
22	10.00	0.60	60.00	0.25	31.271
23	20.00	1.00	110.00	1.00	71.131
24	10.00	0.20	60.00	1.00	58.891
25	20.00	0.60	10.00	0.25	26.666
26	10.00	1.00	60.00	1.00	57.901
27	20.00	0.20	110.00	1.00	67.989
28	20.00	0.60	110.00	1.75	73.139
29	20.00	0.20	60.00	0.25	20.893

The Prob > F value was 0.0001, which indicates that quadratic model is relevant. The coefficient of determination is 0.9835, adjusted value was 0.9664 and predicted value was 0.9048 for quadratic model. This concludes a good interaction between observed and predicted values. The difference between predicted values and observed values dividing by standard error of the residual has close relation with % Normal probability (Figure 5.7). This indicates a good interaction between the observed and predicted values as shown in Figure 5.8. The predicted values were closer to the actual values. This shows that optimization of process parameters for % degradation of cetirizine was performed successfully.

Table 5.9: Sequential model sum of squares for % degradation of cetirizine for EF process

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	
Mean	90272.46	1	90272.46			
Linear	6445.19	4	1611.30	10.58	< 0.0001	
2FI	809.39	6	134.90	0.85	0.5468	
Quadratic	2056.92	4	514.23	9.11	0.0008	Suggested
Cubic	624.30	8	78.04	2.82	0.1117	Aliased
Residual	166.05	6	27.67			
Total	1.004E+005	29	3461.18			

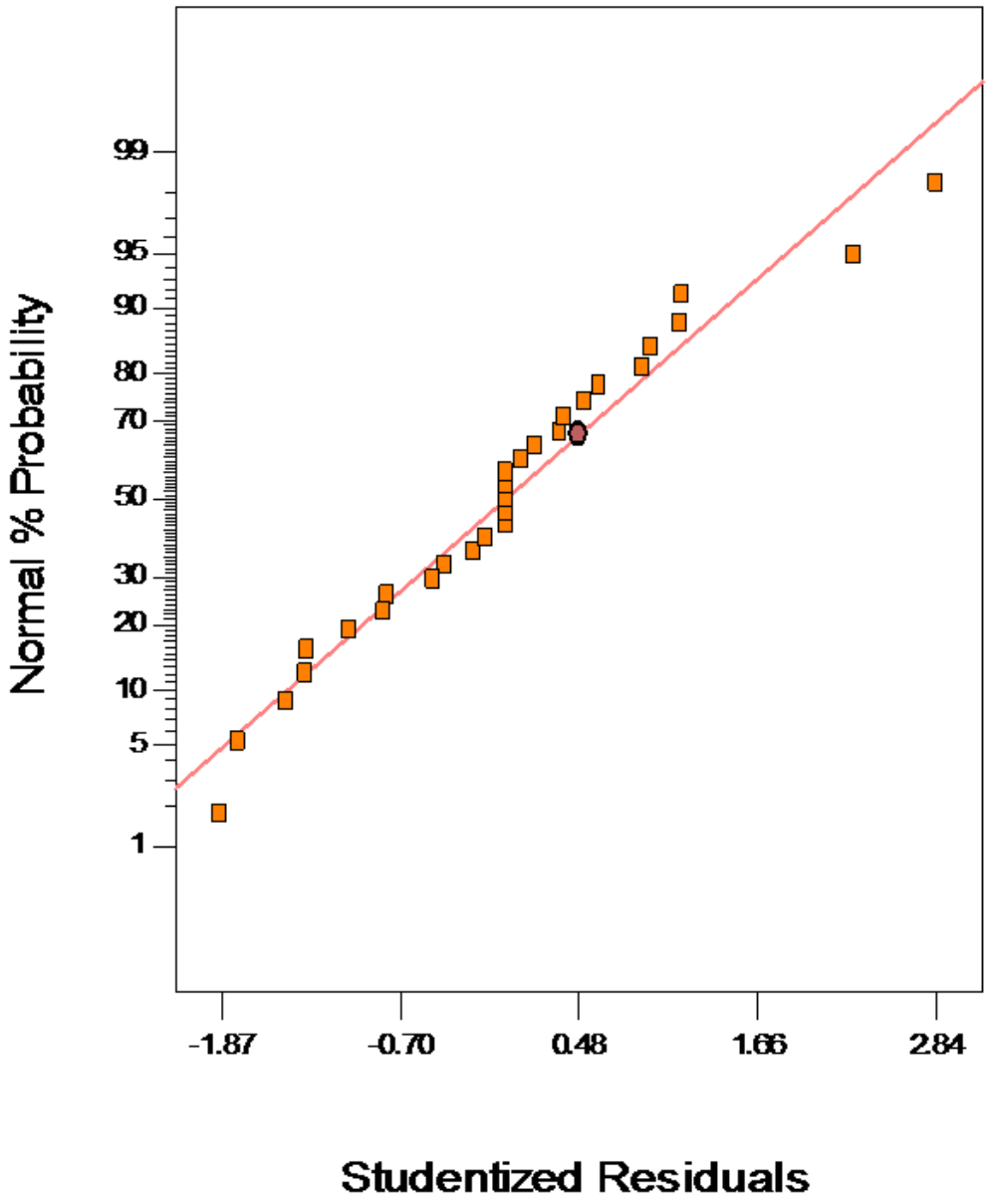

Figure 5.7: Residual plots for EF treatment (normal % probability vs studentized residuals) of pharmaceutical drug for % D of cetirizine

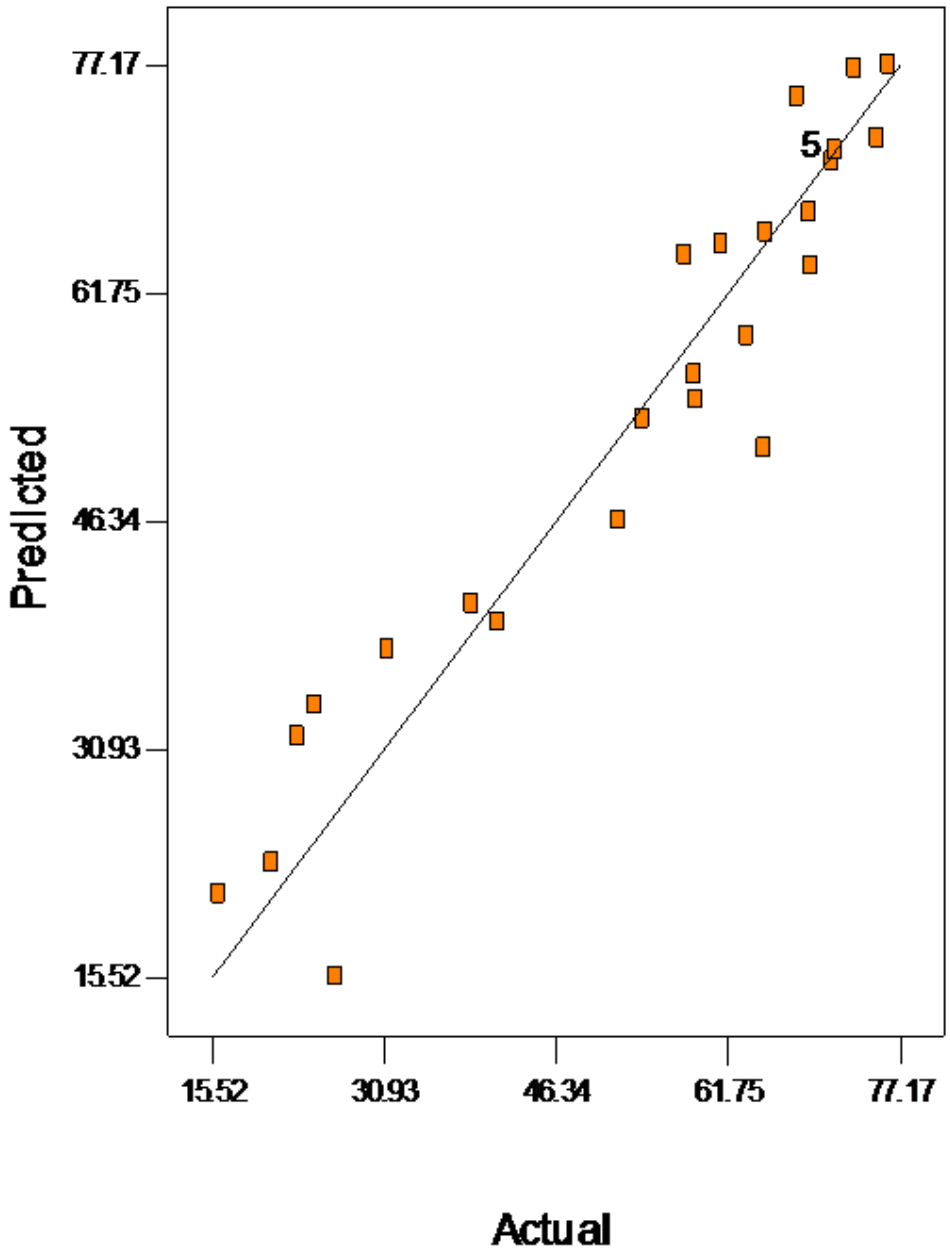

Figure 5.8: Residual plots (Actual vs. Predicted) for EF treatment for % D of cetirizine

5.3.3 Analysis of Variance for EF process

The ANOVA (analysis of variance) shows the model F-value for % D of cetirizine is as shown in Table 5.10. This depicts that model considered is significant for % degradation of cetirizine. For model terms to be significant, prob > F values should be less than prob > F values larger than indicates that model term are insignificant. From ANOVA it is clear that the time and current are highly significant terms for % degradation of cetirizine**.**

The Model F-value of 19.96 signifies that the model is significant. There is only a 0.01% probability that a Model F-value this large could occur due to noise. The values of Prob > F are less than 0.0500 so they were depicted as significant model terms. In this case C_{FE}, i, t, i^2, t^2, C_{FE}^2, C_{FE}* i are significant model terms. If the values were obtained more than 0.1000 were suggested, then the model was considered to be insignificant. Model reduction may be considered if there are numerous insignificant model terms, hence improvement of model.

Final Equation in Terms of Actual Factors:

The concluding equation in quadratic form for EF process in % D in the form of actual factors as suggested by design expert is equation (5.2)

$$\% D = - 60.51+90.56 * C_{FE} +0.91* t +76.66 * i -4.57*10^{-3}*t^2-27.29* i^2 -24.36*C_{FE}*i \quad (5.2)$$

Table 5.10: ANOVA for response surface quadratic model for % D of cetirizine using EF

Source	Sum of Square	DF	Mean Square	F value	Prob > F	
Model	9311.50	14	665.11	11.78	< 0.0001	Significant
C_{CE}	16.17	1	16.17	0.29	0.6009	
C_{FE}	708.14	1	708.14	12.54	0.0033	
I	3493.82	1	3493.82	61.89	< 0.0001	Significant
T	2227.06	1	2227.06	39.45	< 0.0001	Significant
C_{CE}^2	283.79	1	283.79	5.03	0.0417	
C_{FE}^2	113.32	1	113.32	2.01	0.1784	
i^2	847.27	1	847.27	15.01	0.0017	
t^2	1528.67	1	1528.67	27.08	0.0001	
C_{CE}* C_{FE}	31.19	1	31.19	0.55	0.4696	
C_{CE}*i	127.42	1	127.42	2.26	0.1552	
C_{CE}*t	36.54	1	36.54	0.65	0.4345	
C_{FE} *t	389.69	1	389.69	6.90	0.0199	
C_{FE}*t	213.69	1	213.69	3.79	0.0721	
i*t	10.87	1	10.87	0.19	0.6675	
Residual	790.35	14	56.45			insignificant
Lack of Fit	790.35	10	79.03			
Pure Error	0.000	4	0.000			
Cor Total	10101.85	28				

5.3.4 Parametric Study for EF process

To study the response on % D of cetirizine of parameters like C_{CE}, C_{FE}, t and i along with their interactions with each other in an EF process was studied by 3D graphs. Time and current were found to be highly significant parameters for the present study.

Figure 5.9 depict as we increase C_{FE} from 0.2 mMol the % degradation increases with the increasing current but becomes constant at 0.83 mMol with an increase i ≕1.03A. The % D then further decreases with the further increase in the C_{FE} even if the i value increases. This can be explained by the generation of higher amount of •OH in the medium from reaction 2.5, due to the increased H_2O_2 concentration. On further strengthening in the i value the % D value decreases explained by H_2O_2 chemical decomposition to O_2 either on the surface of anode or in the solution following equation 5.1 (Brillas et al 2003).

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (5.1)$$

Figure 5.10 depicts the marginal interaction of C_{FE} and C_{CE} with the % D of cetirizine. It was observed that as C_{FE} increased from 0.2 mMol the %D of cetirizine increases with the increase in the C_{CE} upto ≕ 27 ppm. But on further increasing the value from 0.83mMol the % D decreases even though the C_{CE} increases. The decrease in %D of cetirizine on increasing C_{FE} beyond 0.83mMol could be explained by the rapid utilization of •OH with the extreme amount of reformation of Fe^{2+} according to reaction 2.7 (Brillas et al. 2003).

Figure 5.11 depicts that on increasing the value of i the degradation percentage will increase upto 1.08 A with increasing C_{CE} = 30 ppm. But with the further increase in current the % degradation of cetirizine started decreasing. The maximum degradation was observed at i = 1.03 A and the C_{CE} 30 ppm.

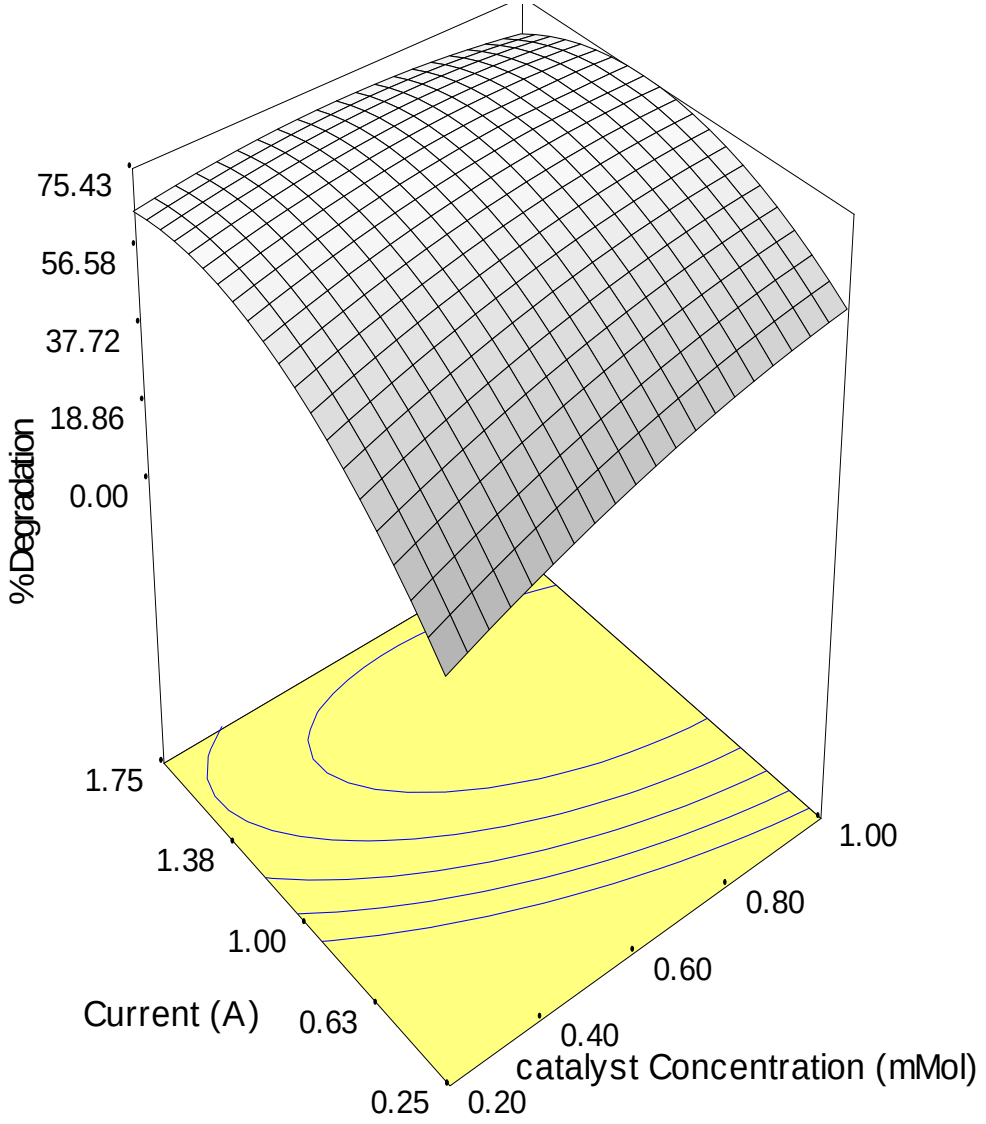

Figure 5.9: 3-D response graphs for EF process for % D of cetirizine with respect to C_{FE} (mMol) and i (A)

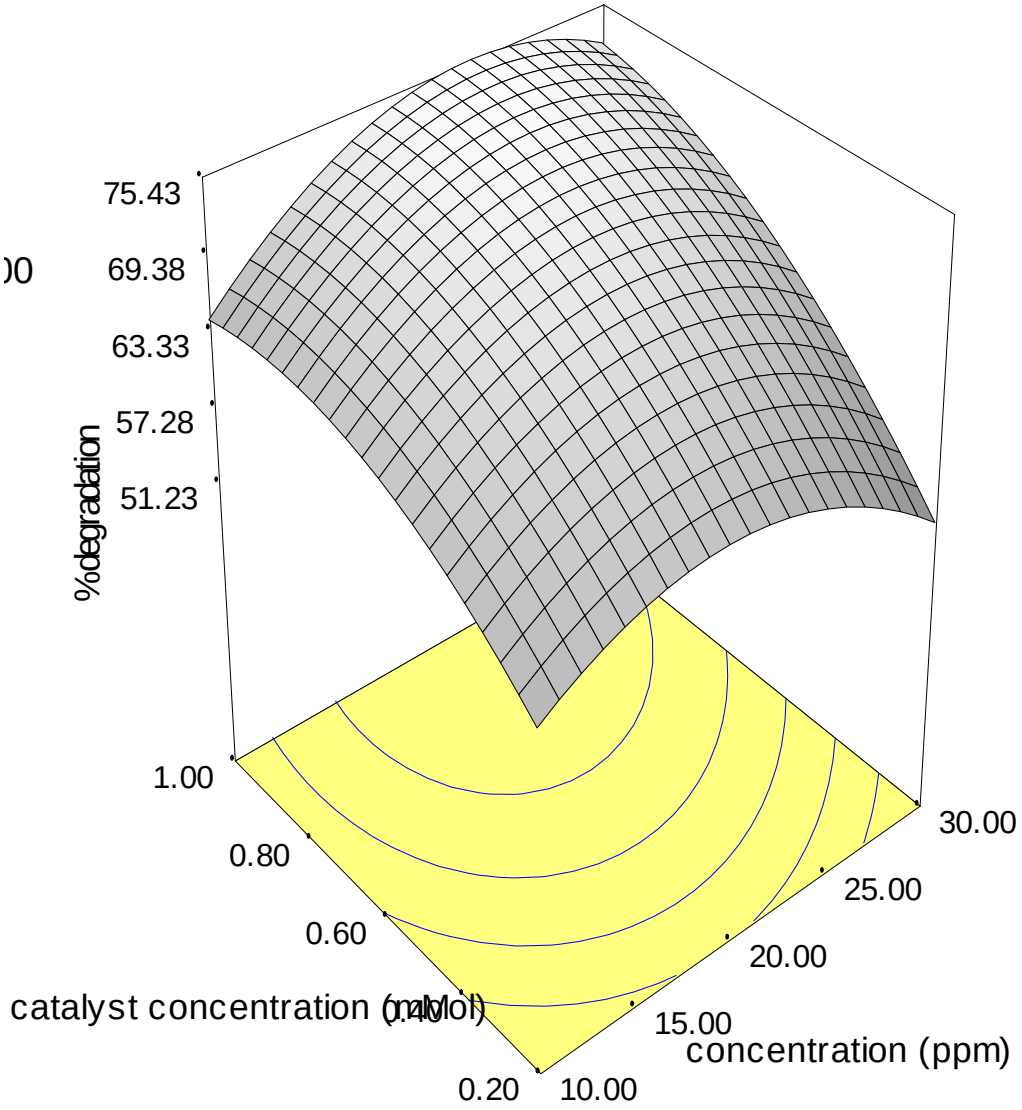

Figure 5.10: 3 D response graphs for EF process for % D of cetirizine with respect to C_{CE} (ppm) and C_{FE} (mMol)

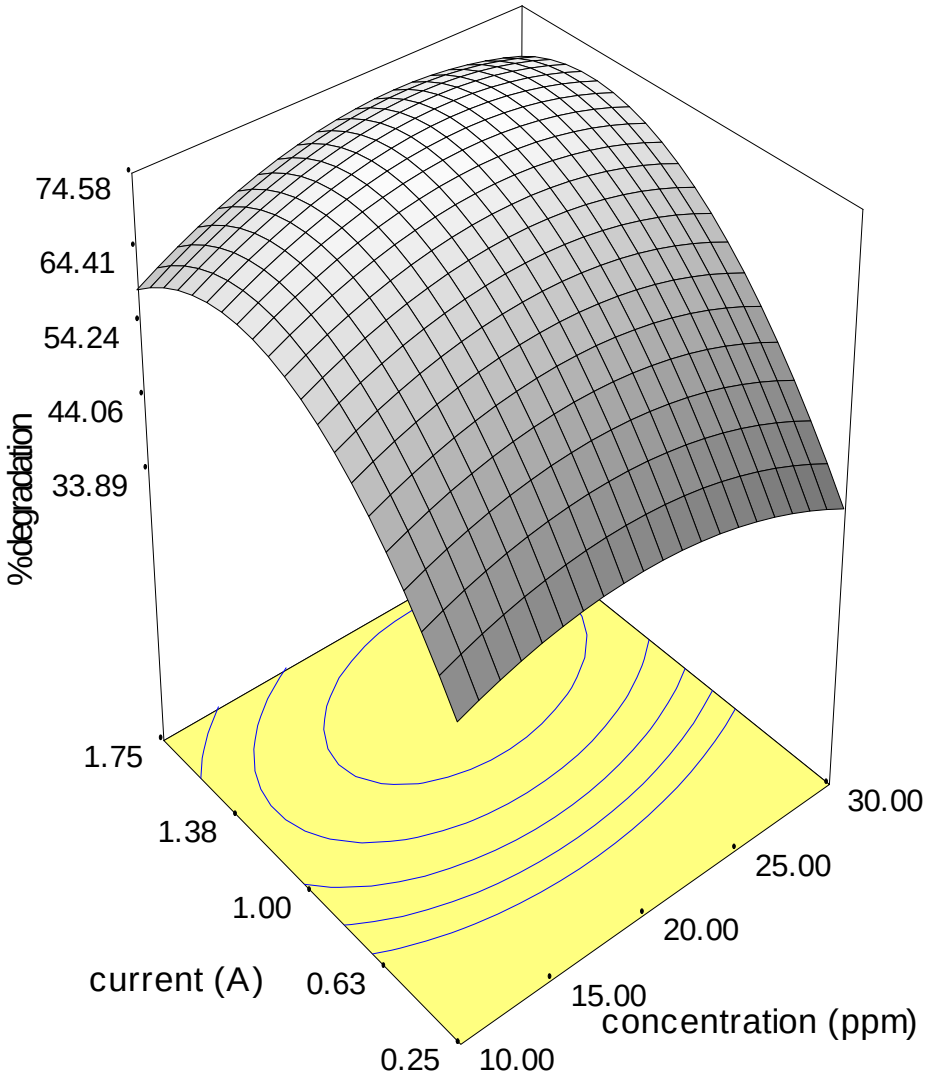

Figure 5.11: 3 D response graphs for EF process for % D of cetirizine with respect to C_{CE} (ppm) and i (A)

5.3.5 Optimization Analysis for EF process

The results obtained using RSM were studied for EF degradation of cetirizine. The three dimensional graphs were studied and optimized results were obtained. BBD was used to optimize the input variables so as to maximize the degradation. For this consideration, set of constraints for operational parameters was applied as 0in Table 5.12.

Table 5.11: Constraints applied for optimization of EF process

Variables	Goal	Lower limit	Upper Limit	Lower weight	Upper weight	Importance
C_{CE}	is in range	10	30	1	1	3
C_{FE}	is in range	0.2	1	1	1	3
t	is in range	10	110	1	1	3
i	is in range	0.25	1.75	1	1	3
% D	maximize	16.137	100	1	1	5

5.3.6 Confirmation Results for EF process

In this study of % D for cetirizine was optimized in terms of maximizing using BBD. The optimum values for the variables were suggested to be C_{CE} = 30 ppm, C_{FE} = 0.89 mMol, pH 3, t = 90 minutes and i = 1.03 A. At this optimum concentration, the % D of cetirizine was 80 %. The optimum conditions for the EF treatment of cetirizine wastewater were verified experimentally. Experiment was run for 90 minutes at i 1.03 A, pH 3, C_{FE} 0.89 mMol to confirm the simulated data. The optimum process response was studied experimentally and then reconfirmed with estimated results. Estimated percentage degradation of cetirizine at the above mentioned parameters was 80 % and experimental values for the same were 77.269 %. Optimization by BBD under response surface methodology distinctly underscores interactions of variables with their effects on % D of cetirizine by EF process. The predicted results synchronize well with the experimental results as shown in Table 5.12

Table 5.12: Optimum conditions of EF treatment of cetirizine wastewater

Variables	Predicted values	Experimental values
C_{CE}	30 ppm	30 ppm
C_{FE}	0.89 mMol	0.89 mMol
i	1.03 A	1.03 A
t	90 min	90 min
%D	80%	77.27%

5.4 Comparison between the degradation of simulated cetirizine wastewater using both EO and EF processes

The % degradation of simulated cetirizine wastewater was degraded using electrochemical treatments at optimum conditions are depicted in Table 5.13. The optimum parameters were obtained using Design Expert software. The experiment was performed at C_{CE} of 30 ppm by both EO and EF process. In EO process the optimized parameters were pH = 3, i = 0.93 A for a reaction time of 100 minutes. Whereas, in EF process the optimized parameters were C_{FE} = 0.89 mMol, pH = 3, i = 1.03 A for a reaction time of 90 minutes. The maximum degradation of 63.86 % and 77.27 % was obtained for EO and EF process simultaneously.

Table 5.13: Comparative optimized results for electro-oxidation and electro-fenton process

Parameters	**EO**	**EF**
C_{CE} (ppm)	30	30
C_{FE}(mMol)	-	0.89
pH	7.09	3
t (min)	100	90
i(A)	0.93	1.03
%D	63.86	77.27
Energy Consumption (Wh)	21.7	20.85

CONCLUSIONS

Degradation of cetirizine was studied using EO and EF process. Based on the study the following conclusions were made:-

- The optimization of the process parameters of EO and EF (using dimensionally stable Ti/RuO_2 anodes) was performed successfully using BBD under RSM.
- The model's coefficient of determination R^2 for both EO and EF processes was found to be 0.9033 and 0.9218 respectively.
- Current and time are highly significant operational parameters for the EO treatment of cetirizine simulated wastewater. Whereas, in case of EF current, time and fenton reagent concentration are significant model terms.
- The optimum parameters selected for EO process in treating 30 ppm of simulated cetirizine wastewater were pH = 7.09, time = 100minutes and a current supply of 0.93 A.
- The EO process effectively degrades cetirizine at neutral pH, HOCl and $OH^{\cdot}$ radicals were responsible for the degradation of cetirizine. These two radicals are prominent at the neutral pH.
- It is concluded that, during the EO treatment hydroxyl radical oxidation is prominent as compare to the chloro-oxidation. So, the generation of chloro-compounds during the EO treatment of cetirizine is nearly negligible.
- The optimum parameters selected for EF process in treating 30 ppm of simulated cetirizine wastewater at pH 3 were fenton concentration 0.89 mMol, time = 90 minutes and current supply of 1.03 A.
- The optimum pH of the EF process is 3 and the prominent oxidants were hydroxyl radical, Cl^- . The hydroxyl radicals have strongest oxidation potential as compare to other generated oxidant species so, % D increases ~ 16 % as compare to EO treatment process.

- At the optimum EO operational parameters, the % D was found to be 63.86 but in case of EF at the optimum operational parameters the maximum % D was 77.26 %.

- The energy consumption of EO process at optimum parameters was 21.7 Wh whereas in EF process at optimum parameters was 20.87 Wh.

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