STUDIES ON THE PHOTOELECTROCATALYSIS INDUCED DEGRADATION OF PHARMACEUTICAL DRUG USING FABRICATED TiO_2 ELECTRODE

A Dissertation

Submitted in partial fulfillment of the requirement

for the award degree of

Masters of Technology

in

Environmental Science and Technology

Submitted
By

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Certificate

This is to certify that thesis entitled, **"Studies on the photoelectrocatalysis induced degradation of pharmaceutical drug using fabricated TiO_2 electrode"** submitted by Ms. Jayishnu Singla in partial fulfillment of the requirements for the award of Masters in Technology Degree in Environmental Science & Technology at Thapar University, Patiala is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied in this thesis has not been submitted to any other university/ institute for award of any degree or diploma.

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I, the undersigned, hereby declare that the research work presented in the M.Tech project entitled **"Studies on the photoelectrocatalysis induced degradation of pharmaceutical drug using fabricated TiO_2 electrode"** has been carried out by me under the supervision and guidance of *Dr. Amit Dhir, School of Energy and Environment* and *Dr. V.K.Sangal, Department of Chemical Engineering*, Thapar University, Patiala. Further, I declare that no art of this dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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ACKNOWLEDGEMENT

Firstly, I express my gratefulness to the “**Almighty**” for his blessings and kindness. It’s my pleasure to acknowledge my indebtedness to my teachers and Supervisors, Dr. Amit Dhir, Assistant Professor, School of Energy and Environment and Dr.V.K.Sangal, Assistant Professor, Department of Chemical Engineering, Thapar University, Patiala for their unflinching support & guidance regarding basic principles, constructive ideas and understanding financially and emotionally that made it possible for me to be successful in the initiation and completion of this project. I am thankful for their encouragement to keep going and constantly learn new things and correcting my mistakes along the way.

I would like to extend my gratitude towards Dr. A.S.Reddy, Head, School of Energy and Environment, Thapar University, for his kind cooperation and support and give the opportunity to work industrial application project successfully.

I am also thankful to Ms. Vibhu Bhatia and Ms. Parminder Kaur, Research Scholar for there invaluable inputs, regarding the finer parts of my work and non-teaching staff of department for their cooperation and help throughout my research study.

I would also like to thank the lab technicians of both departments for their technical support and provide a suitable environment to work in.

I am thankful to my friends Amanjit Singh, Khushboo Sharma and Ramandeep Kaur for their help and moral support throughout this period.

At last but not least, I would like to express my gratitude to my parents for their unconditional affection and moral support and blessings bestowed upon me for successful completion of this thesis.

Jayishnu Singla

ABSTRACT

Photoelectrocatalytic degradation of Ornidazole using Ti/TiO_2 photoanode and copper as cathode was investigated in the present study. The degradation rate was observed to follow first-order kinetics. Anodic oxidation technique was used for the fabrication of TiO_2 electrode for the degradation of Ornidazole. The crystal structure, morphology, bandgap energy and flatband potential characterized by X-Ray diffraction, scanning electron microscopy, UV-Vis spectroscopy and electrochemical impendence spectroscopy, respectively. The performance of photoelectrocatalysis was evaluated in terms of %degradation along with operating parameters such as pH, initial concentration and degradation time. Optimization was done by using BBD under response surface methodology. Under optimum conditions the actual %degradation and COD removal during photoelectrocatalytic degradation of Ornidazole by the proposed Ti/TiO_2 electrode were 95.34% and 75% respectively. The predictions agree well with the experimental results. Through comparison among PEC, EC and PC, it was found that photoelectrocatalytic oxidation was convenient and effective way to treat and mineralize the pharmaceutical compound present in wastewater.

Keywords:-

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ABBREVATIONS

- AOPs- Advanced Oxidation Processes
- EAOPs- Electrochemical Advanced Oxidation Process
- ORZ- Ornidazole
- MNSPMAFI- Minimal National Standards Pharmaceutical Manufacturing and Formulation Industry
- TSS- Total Suspended Solids
- BOD – Biological Oxygen Demand
- COD- Chemical Oxygen Demand
- PPs- Pharmaceutical Products
- Fig- Figure
- eq- Equation
- OH^- - Hydroxyl ion
- $OH^\bullet$- Hydroxyl radical
- PEC- Photoelectrocatalysis
- PC- Photocatalysis
- EC- Electrocatalysis
- $h_{vb}{}^+$- holes(valance band)
- $e_{cb}{}^-$ electron (conduction band)
- TiO_2- Titanium Oxide
- UV- Ultraviolet
- RSM-Response Surface Methodology
- BBD- Box-Behnken Design
- HPLC- High Performance Liquid Chromatography

CHAPTER-1
INTRODUCTION

1.1 General

The continued exponential growth in human population has increase the demand of fresh water which becomes one of the most essential environmental issues of 21st century. In past few years many industries which are being set up at a greater extent due to globalization, urbanization and industrialization which have brought more concerns towards human health and environment because more production leads to more waste generation as well as large amount of wastewater. These include pesticides, dyes, chemicals, pharmaceuticals, industrial byproducts etc which are intentionally released in water, air via regulated (wastewater treatment plants or domestic septic systems) and unregulated (directly discharge in river water). So it is necessary to restore the water quality to avoid further water pollution and by reuse we can decrease the dependency on fresh water consumption. Many researchers analyzed that the ever growing problem of pollution in environment is mainly due to increasing amount of pharmaceuticals found in water. Drug and pharmaceutical manufacturing industry plays important key role to the society as a whole. India is one of the top 20 leading producers of pharmaceutical products in world. However production of drugs is also associated with generation of pollutants which pollute the receiving water bodies if not treated properly. Pharmaceutical products have been extensively used for both humans and animals. The use of pharmaceuticals and personal care products is on rise with an estimated increasing from 2 billion to 4 billion annual prescriptions from 1999 to 2009 in U.S alone.

For the past 25years there have been various attempts made to determine the concentration of pharmaceutical compounds in drinking water (Webb et al., 2003). This problem was first brought to light in the 1990's in Europe when pharmaceutical compounds were found not only in drinking water but in abundance in wastewaters, streams, surface water, groundwater resources across Europe. These compounds are getting into water because they are not treated in the water treatment plant. Earlier it was not well known problem neither discussed much but with time the adverse effects on environment is seen due to increasing levels of these drugs in water. Hence this issue has been steadily gaining attention in recent years both within academic community and among general public to get rid of these increasing levels of pharmaceutical compounds in water. Research in this area is only possible because of more reliable and sensitive analytical techniques and due to advances which came in these techniques. The term pharmaceutical covers a wide ranging class of compounds with substantial variability in structures; function, behavior and activity. Each one of these has different impact on people and the environment and with ever growing levels these problems are getting worse. Pharmaceutically active compounds(PhACs) such as antibiotic, pain killers, muscle relaxants, hormonal drugs, anesthetics etc which are meant to cure diseases are not completely metabolized within the body and 90% of the drugs can enter into municipal and natural wastewater via human and animal excretion, residential or commercial discharges (Raloff et al., 1998).The drugs which are of single types in water are not dangerous but when different chemicals are consumed together or when they metabolized in liver and as a consequence gluconoride and sulfate conjugates of the parent drug are excreted produce a magnified effect. Many tests have been done by researchers and various pieces of data were collected on the effect of these pharmaceuticals but because of the large number of variables in the different chemicals and also due to its low level conc.(i.e. in nanogram) in water they cannot accurately estimate the full threat (Xu et al., 2009).

The potential impact of pharmaceutical compounds like nitro-imdazole (ornidazole) in the aquatic environment as well as on public health is matter of great concern. Ornidazole chemically known as 1-chloro-3-(-2-methyl-5-nitroimidazole-1-yl) propan-2-ol is an antiprotozoal drug used in veterinary and human medicine. It is believed that this drug possess genotoxic, carcinogenic and mutagenic properties. Hence determination of trace residues of these drugs in edible and animal tissue has been of growing concern over past few years (Rodriguez et al., 2010). The presence and concentration levels of these compounds are still not known properly due to its complex structure but long term ingestion of these compounds in drinking water is serious issue. Fig 1-2 shows the origin of PPs and the pathways by which these pharmaceutical compounds (waste) enter into environment and in water cycle. Aquatic toxicity, development of resistance in pathogenic bacteria, genotoxicity, endocrine disruption etc are some hazards caused by pharmaceutical compounds.

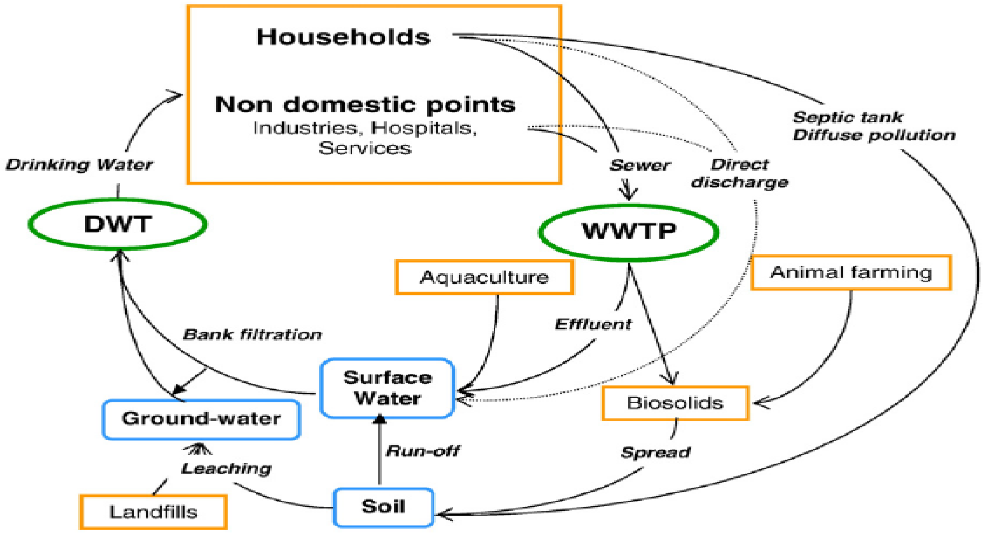
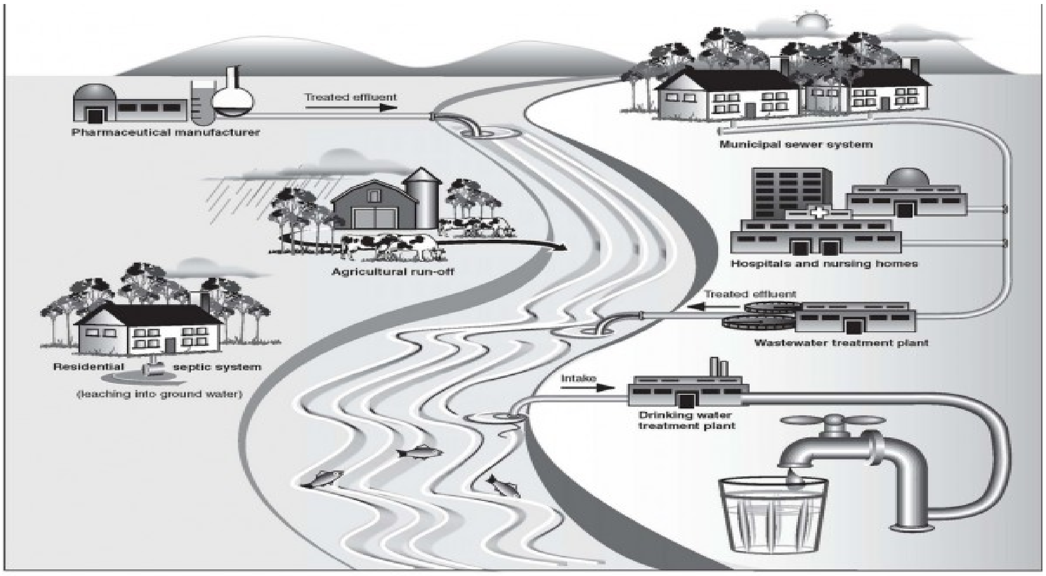


Fig1: Origin and routes of PPs (Source: Petrović et al., 2003).



Source: GAO.

Fig 2: Different pathways by which pharmaceutical enter into water cycle (Source: GAO)

Most of these organic compounds are not biodegradable and are resistant to degradation through biological or conventional treatment methods and need alternative treatments to make them biodegradable.

1.2 Pharmaceutical wastewater generation

The pharmaceutical industries consume large quantity of water and generate wastewater in considerable amount. Table 1 and 2 two different table shows how much wastewater generates from pharmaceutical plants.

1.2.1 Physical process

Table 1: Wastewater generation from pharmaceutical formulation unit.

S.No.	Source of wastewater generation	Average flow of wastewater(cum/hr)	Range of average characteristics except pH	Effluent in mg/l
1	Sterile products	1.0 to 10	BOD TSS	50 to 100 20 to 260
2	Syrup preparation	10 to 25	COD Cl^-	150 to 2500 20 to 150
3	Malt preparation	1 to 5	BOD, SO_4^{2-}	300 to 2000 20 to 200
4	Pastilles preparation	10 to 25	BOD heavy metals TSS pH	2000 to 2500 1 to 20 100 to 300 4.0 to 8.0

Source: **MNSPMAFI**

1.2.2 Fermentation

Wastewater generate from this unit mainly from recovery and purification is about 5cum/kg

Table 2: Wastewater generation from an antibiotic plant.

S.No.	Source of wastewater generation	Nature of wastewater and solid waste	Ranges for average characteristics except pH	effluent in mg/l
1	Fermentation block	Floor & equipment washings, leakages of valves machines, contaminated batches, cooling waters, laboratory & utility wastes	pH TSS BOD	4 to 8 100 to 1000 500 to 6000
2	Filtration/ centrifugation	Mycelium cakes, filter washing , floor washings	BOD	Up to 10,000
3	Recovery & purification block	Faecal wastes, acid and alkali wastes(from regeneration of ion-exchangers), floor washings laboratory wastes	CN^- Heavy metals Oil & grease	0.1 to 1 1 to 5 20 to 50
4	Style and finishing block	Floor and equipments washing and other utility wastes	Phenol (after mycelium cake separation)	1 to 5

Source: MNSPMAFI

1.2.3 Vaccination, microbial suspension antitoxin preparation

The waste generated from these sections contains high BOD, COD and bad odors. High total solids and chlorides are also there as a result of washing operations. Antiseptic and antibacterial agents contribute to toxicity.

1.2.4 Organic synthesis

Table 3: Shows different process effluent.

S.No.	Source	Nature	Effluent in mg/l	Flow(cum/hr)
1	Acidic and alkaline effluents	HCl,H2SO4,organic acids SO_4,Cl^-	2500 to 30,000	20
2	General process liquors	Toxicity	High	-
3	Strong process liquors	COD Organic load	High	-
4	Emulsified effluents	Oils, emulsions, extractable materials	Variate	-
5	Toxic effluents	Phenol, cresol, benzene, germicidal agents	Toxic	-

Source: MNSPMAFI

Effluent characteristics of pharmaceutical wastewater depend upon the processes that are going to be used in the pharmaceutical industries.

1.3 Environment Levels and Standards

Wastewater discharged from Pharmaceutical industries, domestic and commercial industries, hospital and ETPs has become environmental concern. Pharmaceuticals in water are relatively became new concern hence government has been putting regulations into effect to help in keeping water clean. There are few regulations because of little concern about the possible effects of the drugs that were being disposed of on the environment such as Clean Water Act (CWA) established under EPA act to reduce discharges of pollutants from industries to surface waters, other act under which disposal of unused drugs known as ‘Management and Disposal of unused pharmaceuticals, 2008.Also Drug Enforcement Administration(DEA) makes regulations that effect the amount of pharmaceuticals entering the water due to following acts: The controlled Substance Act (CSA), The Resource Conservation and Recovery Act(RCRA) and The Health Insurance Portability and Accountability Act(HIPAA). A few states prohibit these acts and most have strict regulations such as making sure they are uncontaminated. Other states that require the destruction of unused pharmaceuticals do not specify the process to actually get rid of the product. This obviously becomes problem that may cause increasing amounts of drugs in the water. Under the Environment Protection Rules 1986 the Minimal National Standards (MINAS) are developed for effluents from pharmaceutical wastewater are in tab no.4

Table 4: Standard for effluents from pharmaceutical industries (CPCB).

4.1) Compulsory effluent parameters	
Compulsory parameters	Limiting concentration in mg/l, except pH
pH	5.5-9.0
Oil and grease	10
Total suspended solids	100
BOD(5days at 20^0C)	30
Bio assay test	90% survival after 96hrs.
4.2) Operational effluent parameters	
Operational parameters	Limiting concentration in mg/l, except pH
Mercury	0.01
Arsenic	0.2
Chromium	0.1
Lead	0.1
Cyanide	0.1
Phenolica	1.0
Sulphides (as S)	2.0
Phosphate (as P)	5.0

Source: MNSPMAFI

The operational parameters are applicable to pharmaceutical manufacturing units depending upon the process and products. The state board may prescribe limit for COD, BOD and dissolved solids depending upon uses of recipient water body. The limits should be complying with the terminal of the treatment unit before letting out of the boundary limit.

1.4 Pharmaceutical Wastewater Treatment Processes

The wastewater from pharmaceutical has large amount of complex structure with high concentration of total solids, BOD, COD, odors. Biodegradable compounds can be treated by various treatment but some toxic compounds are there which are redundant and fretful known as bio-recalcitrant compounds as a result the wastewater generate from pharmaceutical industries is matter of great concern for human bodies as well as animals. In past few years many new techniques have been came into existence which are efficient for the degradation of such pollutants e.g. physiochemical, chemical, biological and other technologies. Fig 3 and Fig 4 shows the effective convention wastewater treatment process working in pharmaceutical industries.

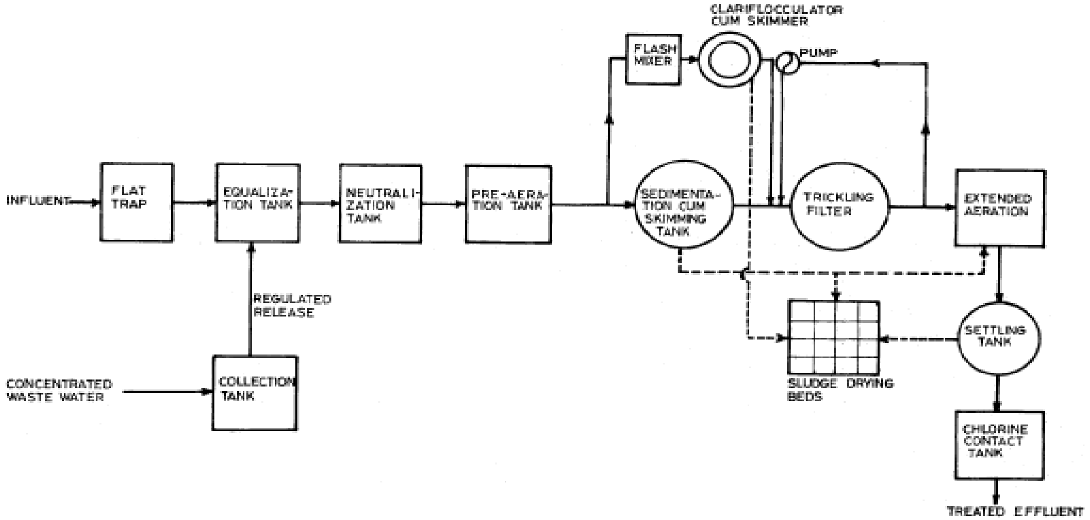


Fig 3: Schematic flow diagram for the treatment of effluent from bulk drugs units (Source: MNSPMAFI)

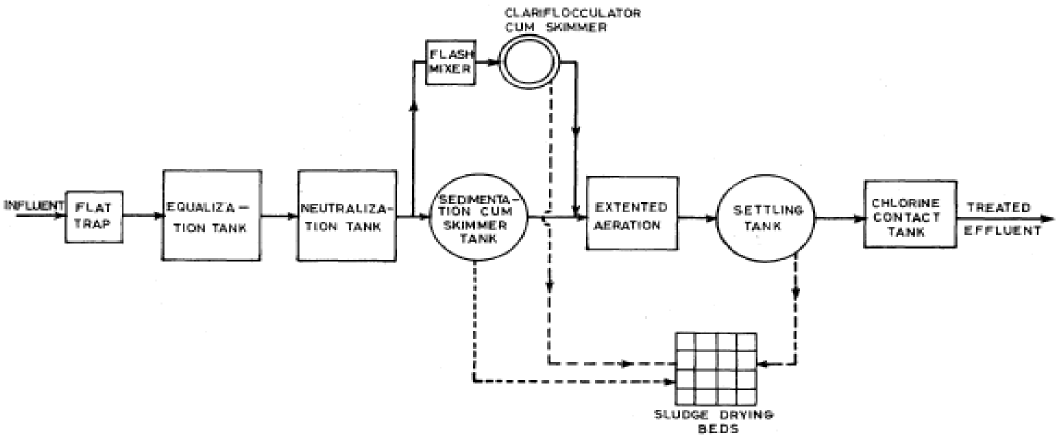


Fig 4: Schematic flow diagram for the treatment of effluent from Formulation units. (Source: MNSPMAFI)

In the last few decades extensively research has taken place in the water treatment. This can be seen in a notable increase in both research and the number of businesses concerned in the field. Because of the extremely diverse features waste that usually contains a mixture of organic and inorganic compounds, no universal strategy of reclamation is feasible and it mainly depends on the nature and concentration of pollutants. With increase in pharmaceuticals and personal care products (PPCPs) found the wastewater streams (Morrissey et al., 2011). The Wastewater treatments for these kinds of “especial” pollutants are discussed below.

1.5 Conventional Technologies

1) Biological treatment methods

They have traditionally been used for the management of pharmaceutical wastewater (Suman Raj and Anjaneyulu, 2005). They may be subdivided into aerobic and anaerobic processes. Aerobic applications include activated sludge, membrane batch reactors and sequence batch reactors (LaPara et al., 2002; Raj and Anjaneyulu., 2005; Noble., 2006; Chang et al., 2008 and Chen et al., 2008). Anaerobic methods include anaerobic sludge reactors, anaerobic film reactors and anaerobic filters (Gangagni et al., 2005; Enright et al., 2005; Chelliapan et al., 2006; Oktem et al., 2007; Sreekanth et al., 2009).

a) Activated Sludge Process

Conventional activated sludge with a long hydraulic retention time (HRT) has historically been the method of choice for the treatment of pharmaceutical industry wastewater (El Gohary and Abou-Elea, 1995; Oz et al., 2004). It has a lower capital cost than more advanced treatment methods and a limited operational requirement; it is generally more environmentally friendly than chlorination. However, high energy consumption, the production of large amounts of sludge (Sreekanth et al., 2009) and operational problems including color, foaming and bulking in secondary clarifiers are associated with activated sludge plants (Oz et al., 2004).

The impact of pharmaceuticals on the AS process appears to be negligible under normal operating conditions (Stamatelatou et al., 2003). Activated Sludge is an efficient method for the removal of some APIs, but not all from municipal facilities (Zwiener and Frimmel., 2003; Castiglioni et al., 2006; Watkinson et al., 2007). In a WWTP in Brisbane Australia, β-Lactam antibiotics showed high biodegradability due to hydraulic cleavage of the β-lactam ring. Lincomycin and sulphonamides were the least affected by AS treatment (Joss et al., 2005).

b) Sequence batch reactors (SBRs) & Membrane bioreactors (MBRs)

A number of pilot scale studies were conducted using Sequence batch reactors (SBRs) and Membrane bioreactors (MBRs) in an attempt to improve the effectiveness of AS treatment (Clara et al., 2005; Radjenovic et al., 2007). SBR is an activated sludge method of treatment in which separate tanks for aeration and sedimentation are not required and there is no sludge return. The main advantages of MBRs over AS is that they require less space for operation (Yang et al., 2006), and can also treat variable wastewater compositions (Chang et al., 2008). One explanation for this is that pharmaceutical compounds are generally smaller than the membrane pores and so only substances sorbed on particles are retained (Radjenovic et al., 2007).

c) Up-flow anaerobic stage reactors (UASRs)

Up-flow anaerobic stage reactors (UASRs) used as a pre-treatment to activated sludge for industrial effluent have been shown to be efficient for the removal of pharmaceuticals even at high concentrations (Chelliapan et al., 2006; Oktem et al., 2007). A UASR fed with real pharmaceutical wastewater containing the antibiotics tylosin and avilamycin showed a high degree of COD and drug removal (Chelliapan et al., 2006). A hybrid Up-flow anaerobic sludge blanket reactor (USABR) which combines a UASR and anaerobic filter technology showed significant removal of COD at a much higher OLR from pharmaceutical wastewater (Oktem et al., 2007).

2) Physio-chemical treatment

Biological wastewater treatment systems can be effective in removing some, but not all pharmaceuticals from wastewater. Therefore, other treatment technologies have been explored with the intention of finding suitable polishing techniques to further reduce pharmaceuticals concentrations.

a)Membrane processes

Several membrane types and applications were evaluated for the removal of APIs at pilot and full scale, including microfiltration, ultra filtration, nanofiltration, reverse osmosis, electrodialysis reversal, membrane bioreactors and combinations of membranes in series (Bellona and Drewes., 2007; Snyder et al., 2007).

Microfiltration and ultra filtration are generally not fully effective in removing organic contaminants as pore sizes vary from 100-1000 times larger than the micro pollutants which can slip through the membranes.The pressure-driven membrane processes Nanofiltration (NF) and Reverse osmosis (RO) have been the focus of attention of many researchers however the studies on the use of RO/NF for pharmaceutical removal is limited.

RO in different configurations showed efficient removal of thirty-six personal care products and endocrine disrupting chemicals including antibiotics, lipid regulators, hormones and oral contraceptives, antiepileptic and analgesics (Snyder et al., 2007; Watkinson et al.,2007).RO membranes removed the majority of compounds investigated to levels below the limit of detection. However, pentoxifylline, iodopromide, dimethyltoluamide (DEET), meprobamate, phosphanetriyltripropanoic acid (TCEP), gemfibrozil, musk ketone and oxybenzone were detected in the permeate of a variety of the configurations (Snyder et al., 2007). A possible reason for this is short circuiting of the membrane or the failure of membrane support media (Bellona et al., 2004). Though membrane process shows potential as an efficient method for removing pharmaceuticals from the wastewater, the disposal of the sludge which could contain the pollutant in a more concentrated form still remains.

b) Activated carbon (AC)

AC is a recognized conventional technology for the removal of both natural and synthetic organic contaminants (Hrubec et al., 1983; Annesini et al., 1987).It is most commonly applied as a powdered feed or in granular form in packed bed filters. Granular activated carbon (GAC) can be used as a replacement for anthracite media in conventional filters, providing both adsorption and filtration. It can be applied following conventional AS treatment as an adsorption bed. However, carbon regeneration and disposal are environmental considerations (Snyder et al., 2007).

Dutta et al., (1997) studied the adsorption and desorption of 6-aminopenicillanic acid (6-APA) in aqueous solution using activated carbon. They found that the adsorption process was highly reversible, the extent of reversibly adsorbed 6-APA was around 93 %. (Snyder et al., 2007) found that both powdered activated carbon (PAC) (5mg/L) and GAC removed greater than 90 % of estrogens (100–200 ng/L initial concentrations). However, dissolved organic compounds, surfactants and humic acids compete with binding sites and can block pores within the AC structure (Zhang and Zhou., 2005; Snyder et al., 2007).

3) Chemical treatments

a) Chlorination and Ozonation

Chlorination has been shown to be effective for the removal of pharmaceuticals including [17α- ethinylestradiol and 17 β-estradiol (Alum et al., 2004) and Sulfonamides (Qiang et al., 2006)]. Chlorine dioxide is also effective for the removal of sulfamethoxazole, roxithromycin, 17α-ethinylestradiol and diclofenac (Khetan and Collins., 2007). Chlorination and ozonation when compared for the removal of bisphenolA, 17β-estradiol, and 17α-ethinylestradiol and byproduct estrogenicity from distilled water showed comparable results with ozonation resulting in 75-99 % removal (Alum et al., 2004). Acetaminophen, diclofenac, sulfamethoxazole and fluoroquinlone all become oxidized during chlorination but have toxic byproducts like N-acetyl-p-benzoquinine imines and1, 4-benzoquinone (Pinkston and Sedlak., 2004).

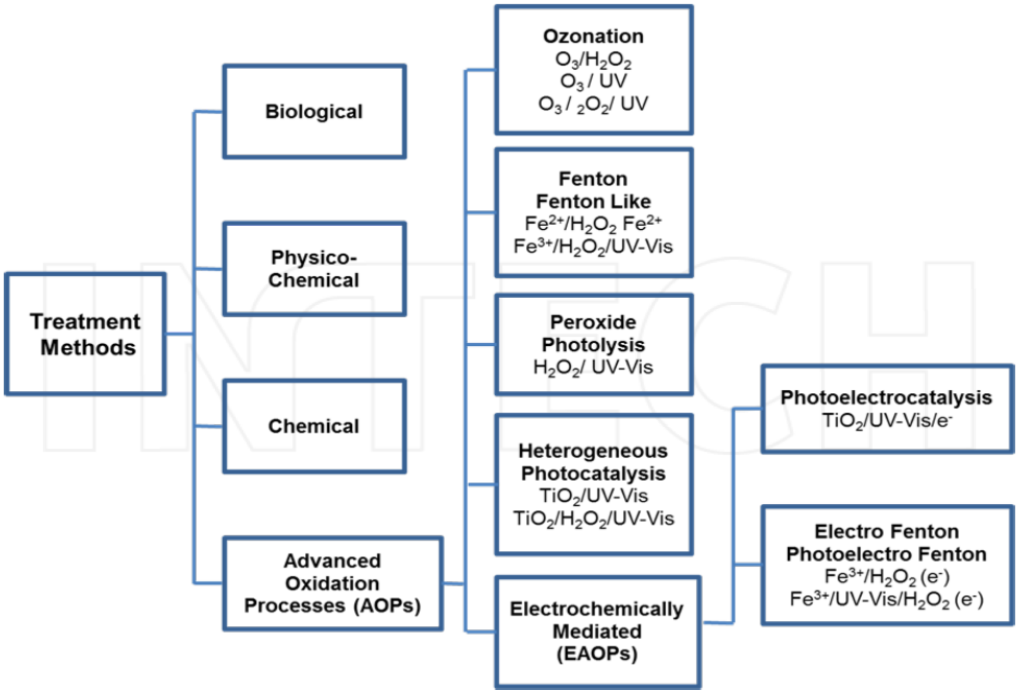


Fig 5: Treatment methods described for the degradation of organic pollutants, including conventional techniques and advanced oxidation processes (Zanoni et al., 2013)

The biological and physiochemical treatment methods discussed previously shown in Fig 5 have shown limited success for the treatment of pharmaceutical wastewater. However, the development of oxidation processes is showing higher removal rates. Oxidation reactions have primarily been used to supplement rather than replace conventional systems and to enhance the treatment of refractory organic pollutants (Balcioglu and Oteker, 2003). This technology has been successfully applied to the treatment of pharmaceuticals (Khetan and Collins, 2007). A chemical agent such as hydrogen peroxide, ozone, transition metals and metal oxides are required for AOPs. In addition, an energy source such as ultraviolet-visible radiation, electric current, gamma-radiation and ultrasound is required. AOPs are based on the production of free radicals, in particular the hydroxyl radical and facilitate the conversion of pollutants to less harmful and more biodegradable compounds (Ikehata et al., 2006).

The ultimate aim of AOPs is the mineralization of pollutants, with conversion to carbon dioxide, water and other minerals. Various studies have confirmed the potential of AOPs for removing pharmaceuticals (Ternes et al., 2002; Huber et al., 2003). AOPs may change a compound’s polarity and the number of functional groups which affect the functionality of the pharmaceutical in the body. Original medicinal modes of action should then disappear e.g. antibiotics which have been hydroxylated should not promote the formation of resistant strains. However, degradation compounds must be identified and monitored as they may be more toxic that the parent compounds (Vogna et al., 2002).

Photo initiated AOPs may be coupled with other biological, physical and chemical methods for mineralization. Pre-treatments such as micro or ultra filtration, reverse osmosis followed by an AOP have proved effective for the treatment of industrial wastewater (Ollis., 2003). AOPs may enhance biodegradability as a pre-treatment method to biological treatment (Oller et al., 2007) or as a tertiary treatment. AOPs also handle fluctuating flow rates and compositions with less difficulty than microbes, as the same level of adaptation to the wastewater is not necessary. Cost of both the chemical agent and the energy source can be a major block to implementation of

AOPs on an industrial scale (Legrini et al., 1993).However, by using solar irradiation the capital cost of AOPs may be substantially reduce. Natural compounds as well as carbonate, bicarbonate and chloride ions may lead to a reduction in treatment efficiency as these compounds may act as antioxidants (Ikehata et al., 2006). AOP is a powerful and environmentally friendly technique for treating pharmaceuticals and there residues with the help of different oxidant species like hydroxyl radicals ($^{\bullet}$OH) and other strong oxidants and leave green chemicals oxygen gas and water as by products after degradation process. Therefore AOP are particularly useful for removing biologically toxic or non-degradable molecules such as aromatics, pesticides, dyes, and volatile organic compounds present in wastewater.

Among AOPs, EAOPs were extensively studied at lab scale and several work were published with perspective for up scaling it to pivot plant in near future (Feng et al., 2013). EAOPs are not a direct replacement of AOPs but it has several advantages such as in-situ generation of hydroxyl radical ($^{\bullet}$OH) from water oxidation, no scavenging of $^{\bullet}$OH radical in natural waters, high efficiency, cheaper than traditional AOPs under certain operating conditions, contaminants which are unreactive to $^{\bullet}$OH radical can be treated by EAOPs. Under EAOPs two processes which are widely applied for the treatment of several kind of wastewater are 'Photoelectrocatalysis' in which (hydroxyl radicals are generated directly on electrode via anodic oxidation) and 'Photoelectrofenton' in which (hydroxyl radicals are generated indirectly through Fenton's reagent homogeneously).

1.6 Benefits of using photoelectrocatalysis for pharmaceutical waste

The effect of the mass transfer limitations on the efficiency of anodic oxidation process hence on the economy researchers look for improvements in this process. Rodrigo et al. (2012) has obtained additional improvements in the results when anodic oxidation coupled with the light irradiation while treating Sulfamethoxaole using conductive diamond electrodes because of the enhancement in additional mass transfer. Zhao et al. (2009) studied the degradation of pharmaceutical compound ibuprofen and naproxen by depositing $BiMoO_6$ on BDD electrode under visible light. Results obtained from the experiments showed that degradation rate of these molecules in combined process were larger than the sum of photocatalysis and anodic oxidation. Hence UV and solar irradiation applied in electrochemical process make the decomposition process more rapid and considered as an economical application.

CHAPTER-2
PHOTOELECTROCATALYSIS METHOD

2.1General

Photoelectrocatalysis is one of the most promising alternative electrochemically mediated oxidative advance processes which not only remove organic and inorganic pollutants but also effective in decreasing toxicity and degrade the recalcitrant compounds in short period of time. Photoelectrocatalysis is a combination of electrochemical and photo catalysis technology. Photoelectrocatalytic oxidation is a process in which small positive potential is applied across the photo catalyst due to which water molecules split into hydrogen and oxygen and move upwards and take pollutants along with them to the surface of liquid body. In this process anode material undergoes oxidation and various hydrolyzed species formed. These hydrolyzed metal aggregate with the pollutants and form big colloids or flocs which can be remove by settling. The complete oxidations of organic compounds at end produce CO_2 and water as well other oxide with no secondary pollutant generation (Chen., 2003). In photoelectrocatalysis semiconductor such as (TiO_2) used as photo catalyst for degradation of organic pollutants.

2.2 Mechanism of the photoelectrocatalytic process-

Photoelectrocatalytic process has received considerable attention in environment field because of its ability to retard the recombination of electron-hole pair (e^-_{CB}/h^+_{VB}) and possibility to increase the lifetime of the latter. The key factor which accelerates the photocatalytic process is applied external potential. The basic process of photo catalysis consists of ejecting from valance band to the conduction band of the TiO_2 semiconductor therefore creating "h^+" holes in the valance band. This is because of the UV irradiation which falls on TiO_2 photocatalyst with energy equal or superior to the band gap (3.2ev). These charge carriers (e^- /h^+) then migrate to the surface of catalyst and undergo redox reactions.

$$TiO_2 + h\nu \longrightarrow e^-_{CB} + h^+_{VB} \qquad (1)$$

After that there is formation of extreme reactive radicals (such as OH•) at surface of semiconductor or direct oxidation of the polluting species. Pollutants can be degrade by two ways either directly on the surface of semiconductor or indirectly by reacting with hydroxyl radical. These oxidative species such as OH• (form when holes react with adsorbed water molecule) subsequently attack the pollutant. fig 6 shows the mechanism charge carrier generation.

$$h^{+}_{VB} + H_2O \longrightarrow OH\bullet + H^{+} \qquad (2)$$

$$h^{+}_{VB} + OH^{-} \longrightarrow OH\bullet_{ads} \qquad (3)$$

$$h^{+}_{VB} + R_{ads} \longrightarrow R^{+} \qquad (4)$$

The electrons ejected to the conduction band can either react with electrons acceptors such as adsorbed oxygen (O_2) to form superoxide radicals or react with adsorbed water to form hydroxyl radicals.

$$e^{-}_{CB} + O_2 \longrightarrow O_2\bullet- \qquad (5)$$

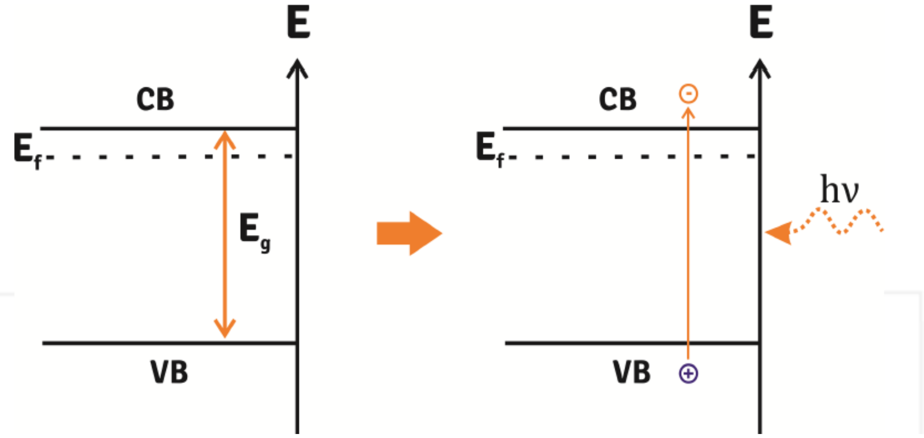


Fig 6: Schematic representation of the energy band diagram in a semiconductor and the mechanism of charge carrier generation by photoexcitation (Zanoni et al., 2013)

The photogenerated electrons (e^-) reduce the recombination rate of the electron-hole pairs and enhance the photocatalytic activity. The time for which this pair exists is few nanoseconds. Hence electron donors or acceptors are require so that they do not recombine otherwise they will release heat or migrate to the surface of semiconductor and react with adsorbed species due to which quantum efficiency decreases as well as limit the application of photocatalysis in wastewater treatment(Zhang et al.,2010).

$$e^-_{CB} + h^+_{VB} \longrightarrow \text{heat} \qquad (6)$$

The recombination of electrons and holes means loss of hole which must be avoided. This is possible by trapping of free charges at intermediate energy levels and this can lead to formation of other oxidant species such as H_2O_2 ,HO_2^- ,HO_2• that can promote oxidizing conditions . As we know the applied potential is a key factor that improves the efficiency of the process is when applied to the Ti/TiO_2 photoanode thereby generation of electrons takes place which are transferred through external circuit instead of oxygen molecule as a result the photogenerated hole or OH• will be left at surface of the TiO_2 electrode. Hence by this way efficiency of oxidation process can be improved at the semiconductor- electrolyte interface (Gogate and Pandit., 2004).

Zanoni et al., 2013 studied how photoelectrocatalysis is efficient in charge separation. When a semiconductor is in contact with an electrolyte there is formation of junction semiconductor /electrolyte interface, which determines the electron hole separation kinetics. The junction in a redox electrolyte causes a change in the electrochemical potential (Fermi level) due to discrepant potentials at the interface (Paramasivm et al.,2012). Thus, the equilibration of this interface needs the flow of charge from one phase to another, and a band-bending is created within the semiconductor phase. The amount of band-bending in this Schottky junction will depend on the difference of the Fermi levels of semiconductor and electrolyte. The region where there is bending is called the space charge layer (SCL), which is characterized by the accumulation of electrons or holes at the surface (Finklea HO, 1988).Fig 7 shows the behavior of these charges in the semiconductor before and after this equilibrium when it is in contact with an electrolyte and fig 8 shows the whole mechanism of photoelectrocatalysis process.

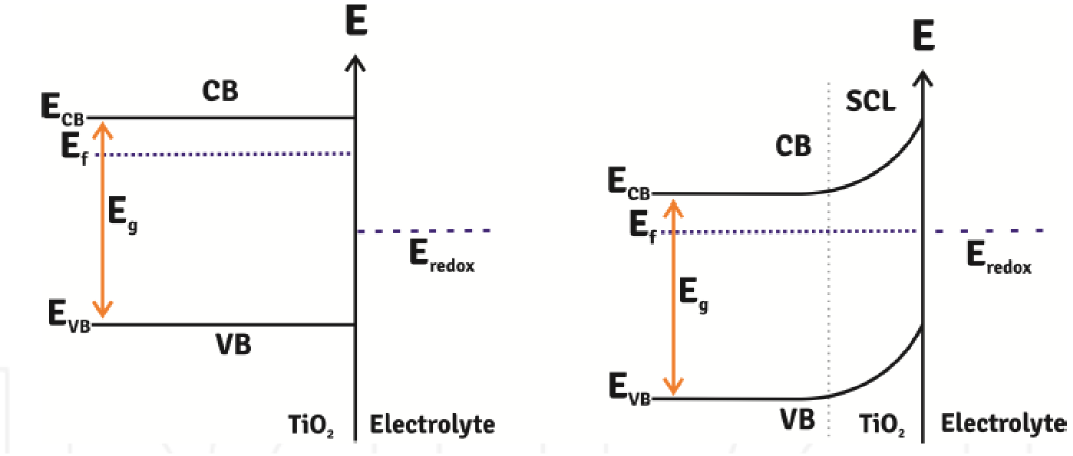


Fig 7: Shows energy band diagram for n-type semiconductor before and after the equilibration of Fermi levels at the interface semiconductor/ electrolyte and appearance of band-bending and SCL (Zanoni et al., 2013).

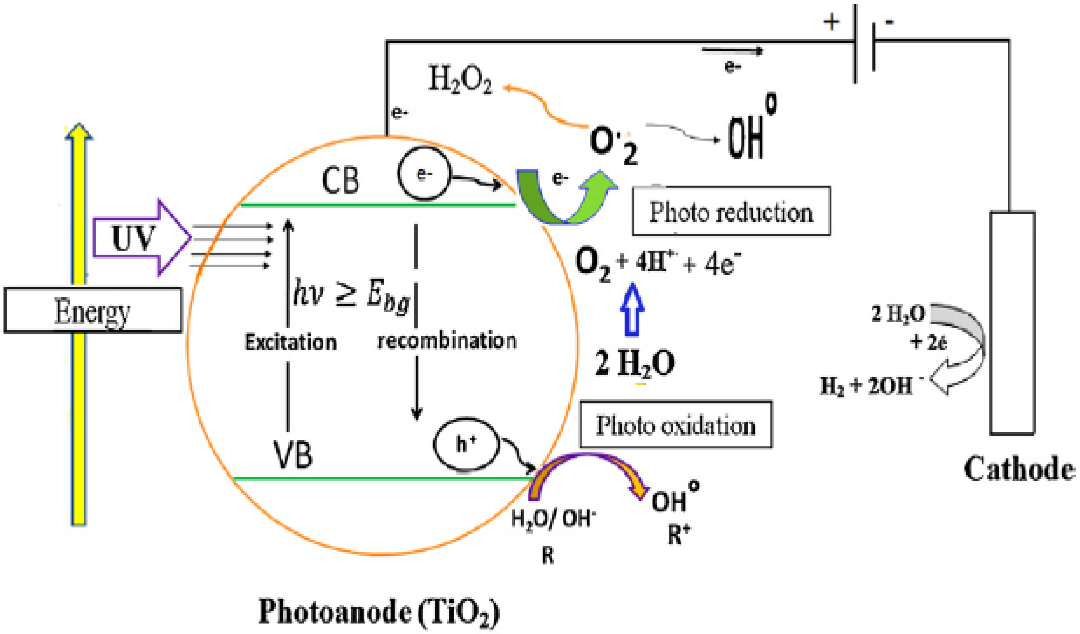


Fig 8: Mechanism of photoelectrocatalysis process using TiO_2 photocatalyst and the reactions that occur at the surface (Drogui et al., 2012).

In the photoelectrocatalysis the rate of conversion depend upon several factors such as applied potential or current intensity, specific feature of semiconductor, diffusion light, intensity of electric field in space charge region and adsorption& desorption of the reactant and products.

2.3 Parameters affecting the photoelectrocatalytic process

i) Effect of external potential applied on TiO_2 or current intensity

In photoelectrocatalysis applying potential prevents charge recombination and increases the lifetime of the active holes. On applying bias potential Fermi level of semiconductor and therefore band bending. For any given semiconductor and electrolyte, there is an exact potential for which the potential drops between the surface and the bulk of the electrode is zero; in other words, there is no space charge layer(Finklea, 1988). Because the band edges are flat, this potential is called flat-band potential, V_{fb} (Figure 9). The application of any potential greater than the flatband potential will increase the band-bending at the n-type semiconductor electrode, such as TiO_2. In this case electrons are depleted and holes enriched at the surface, as we can see in Figure 9. When TiO_2 is irradiated, it is observed that the photogenerated holes have an oxidizing power equivalent to the potential of the valence band edge, and are able to oxidize an RED molecule, whose formal potential is more negative than the valence band. In the case of TiO_2, the H_2O can be oxidized producing ●OH radicals. The electron in the conduction band flows via an external circuit to the counter electrode, where reduction reactions may occur, such as the reduction of H+ ions to H_2. It is important to note that in photoelectrocatalysis the greater the band-bending (and therefore the SCL) the faster the electron/hole separation occurs, and then the recombination of charges is minimized. The influence of current intensity was also put in evidence by (Daghrir et al., 2012) while studying photoelectrocatalytic degradation of some compound using TiO_2 nano-structured photoanode and UV lamp. It was seen that current intensity has significant influence on removal rate of pollutants. If the applied potential increases above optimal value in that case degradation efficiency would be reduce or have no effect on the degradation. The applied potential can be increased up to that level at which it is sure that complete separation of all charge carriers takes place. In electrically biased system (full depletion conditions), the majority of the electrons are drawn inside semiconductor and are extracted at the back contact. Under these conditions, the current under UV radiation cease to increase and the kinetics of there action is only limited by the photon flux. According to (Maeda et al., 1999) the oxidation and reduction reactions could be occurred simultaneously on the illuminated TiO_2 photo-catalyst in an electrically unbiased system, where the consumption of photoexcite electrons is slow in the conduction band (reduction site).

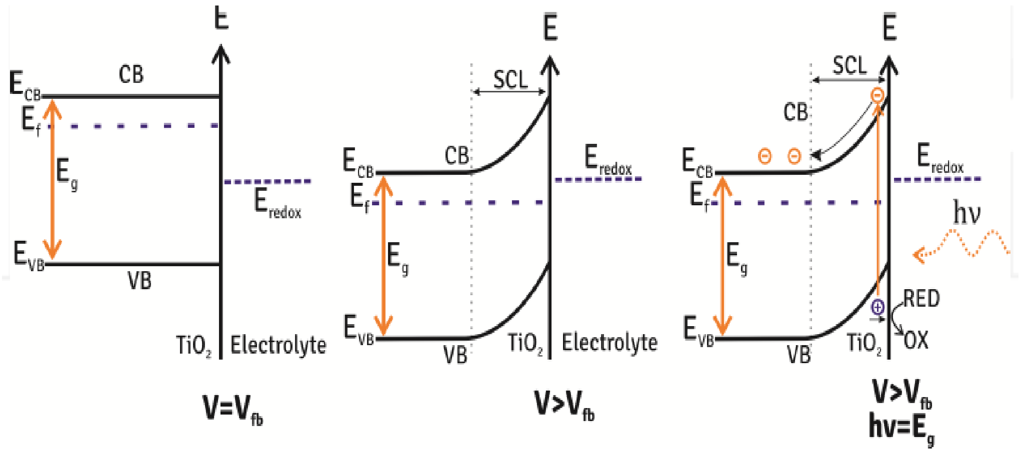


Fig 9: Energy band diagram for n-type semiconductor when the applied potential (V) is equal to flat-band potential (V_{fb}) and when the applied potential (V) is greater than V_{fb}. The last schematic shows the mechanism of charge separation when the electrode is submitted for a potential higher than the Vfb and irradiated with $\lambda \geq Eg$ (Zanoni et al., 2013).

ii) Effect of light intensity

The photocatalytic degradation strongly depends on light intensity applied on photocatalyst surface. With the increase in the intensity of the incident light the probability of excitation of the catalyst and the re-excitation of recombined electrons can be increased (Wang et al., 2010).Moreover, with the increase of UV light intensity, the decomposition of organic compounds or the inactivation rate of bacteria (especially under UVC irradiation) increases due to the increasing concentration of reactive oxygen species and hydroxyl radicals formed on the TiO_2 surface. The degradation rate is directly proportional to light intensity has been proved by (Li et al., 2002). According to some authors it is difficult to maintain uniform light intensity within the reactor. So it is necessary to determine the appropriate light intensity with minimum energy consumption and maximum degradation. For that they have find one solution that is using natural UV irradiation from solar spectrum to minimize the treatment cost. And if light is insufficient then it can be combine with artificial UV lamp (Chong et al., 2008).

iii) Effect of pH

pH is one of the most important parameters that influence the removal rate of pollutants. Also it affects the capacity of adsorption and dissociation of the target compounds, the charge distribution to photocatalyst surface, and the oxidation potential of the valence band. Many researchers found that at pH 6 the surface charge of TiO_2 is neutral and the electrostatic interaction between the pollutant and TiO_2 is absent. At pH below 6 and above 6 surfaces become positive and negative and show repulsion (Sene et al., 2003).However the effect of pH in photoelectrocatalysis process cannot be generalized. Laboratory experiments are carried out to determine optimum pH at which particular compound degrades maximum using previous research (Pandit and Gogate., 2004). In photoelectrocatalysis the three mechanisms i) direct attack of hydroxyl radicals (ii) direct photo-oxidation by the positive hole in the valence band and (iii) direct photo-reduction by the electron in the conduction band depends on the pH value and the nature of the substrate.

iv) Effect of dissolved oxygen

The dissolved oxygen play important role of electron acceptors and participates in formation of oxidative species. In photoelectrocatalysis the dissolved oxygen is source of aeration (Anderson et al.,2003).The electrons ejected in conduction band react with electron acceptor and form superoxide radical as well as other radicals.

Moreover hydrogen peroxide is electro generated by cathodic reduction of dissolved oxygen on electrode.

$$2H_2O \rightarrow O_2 + 4H+ + 4e- \quad (1)$$

$$e- + O_2\ (ads) \rightarrow O_2\bullet- \quad (2)$$

$$O_2\bullet- + H+ \rightarrow HO_2 \quad (3)$$

$$2HO_2\bullet \rightarrow H_2O_2 + O_2 \quad (4)$$

$$O2\bullet- + HO2\bullet \rightarrow O_2 + HO_2- \quad (5)$$

$$HO_2- + H+ \rightarrow H_2O_2 \quad (6)$$

$$O_2 + 2e_{CB} + 2H+ \rightarrow H_2O_2 \quad (7)$$

$$2H_2O + 2H^{+}_{VB} \rightarrow H_2O_2 + 2H+aq \quad (8)$$

The presence of reactive oxygen species in high quantity can limit the recombination of photo-generated electron–hole and improve the efficiency oxidation at the semiconductor interface (Zhang et al., 2006).

v) Effect of electrolyte

In an electrolytic process, the conductivity of the solution affects the efficiency of current intensity, voltage, and the consumption of electrical energy. The conductivity must be high in order to ensure good ion transfer in the effluent is there (Wang et al., 2009).If the conductivity is too low, the resistance is too high and consequently, an increase of the applied voltage is observed. NaCl and Na_2SO_4 are the two electrolytes commonly used. During the photoelectrocatalysis the addition of an electrolyte improves treatment efficiency because it modifies the conductivity of the solution and facilitates the passage of the electrical current in solution, which in turn prevents the fast recombination of photo-generated electrons and holes (Philippidis et al., 2010).

2.4 Typical reactor design

The main advantage of using photoelectrocatalytic processes the simplicity of the reactor in terms of construction and management that is the bi-polar cell. Besides plane electrodes, the cylindrical electrodes can also be employed. In order to design an electrochemical oxidation system, the electrode material, the configuration of the cell and the operating conditions have to be taken into account. Cell configuration one of the most important issues in cell design is to maintain high mass transfer rates as the main reactions that take place in electrochemical oxidation processes take place on electrode surfaces(Anglada et al., 2009). Two types of electrodes, mainly of two-dimensional and three dimensional constructions exist. The latter guarantee a high value of electrode surface to cell volume ratio. Besides the electrode geometry and configuration, the configuration of the cell, divided and undivided cells has to be considered in the reactor design. In divided cells, the anode and cathode are separated by a porous diaphragm or an ion conducting membrane. For divided cells the choice of the separating diaphragm or membrane is as important as the appropriate choice of electrode materials for proper functioning of the electrolytic process (Curtis et al., 2003).Overall, the use of divided cells should be avoided whenever possible, because separators are costly and tightening of a divided cell is difficult and encounters a host of mechanical and corrosion problems. With the exception of the photo-reactor in the experimental units the UV lamp or UV tubes are also used. The position UV light also influences the efficiency of photoelectrocatalysis. Indeed, UV radiations absorbed by H_2O molecules allow the generation of powerful oxidizing species such as H_2O_2 and OH• The direct contact of UV light with polluted water induced high oxidation of pollutant. Using internal UV configuration for laboratory scale applications enhances the distribution of irradiation across the photo-catalyst and consequently increases the generation rate of reactive oxygen species. The large distance between the light source and the working electrode in a practical photo-reactor reduces the radiation flux and consequently reduces the efficiency of the process. The turbulent effect required promoting mass transfer and to minimize fouling can be achieved in the reactor using mesh electrodes and gas sparging with small bubbles (Daghrir et al., 2012).

2.5 Electrodes:

2.5.1 Electrode material

In the photoelectrocatalysis process the choice of electrode have great importance since it affects the efficiency of the process. The electrode material should possess following properties these are:

1) High electrical conductivity
2) High physical and chemical stability
3) Resistance to corrosion, erosion and formation of passivation layers
4) High catalytic activity and selectivity.
5) Low cost/life ratio. The use of electrode materials that are inexpensive and durable must be favored.

2.5.2 Different methods for preparing TiO_2 electrodes

Several methods are used for preparation of electrodes they are-

a) Aerosol Pyrolysis

Kavan and Gratezel., (1993) used this method to form TiO_2 layer on F-doped SnO_2 electrode taking two different electrolyte solutions one is di-iso-propoxy titanium-bis(acetylacetone) and titanium tetra(isopropoxide) in ethanol and isopropanol with different concentration and other one is acidic aqueous solution of titanyl nitrate Containing(1.35to 13.5% TiO_2). Layers were formed by spin or dip coating the electrodes and after that pyrolysis were done at 500^0C for 1hr.

b) RF Sputtering

Li et al., (2006) made TiO_2 layer on ITO conductive glass using radio frequency magnetron sputtering in which Ti plate sputtered in a gaseous mixture of argon and oxygen at 2.0pa. After this TiO_2 suspension loaded on an ITO glass by dip casting method and then dried for 15mins on hot plate of temp 100^0C and then sintered in a muffle furnace at 500^0C for 2hr.

c) Anodic or thermal oxidation method

Sulka et al., (2002) fabricate TiO_2 film on titanium metal using anodization technique. Ti substrate was taken as anode and platinum as cathode with 3cm distant apart. Anodization takes place with applied potential of 40V for 3hr in ethylene glycol solution as electrolyte at 20^0C.

2.6 Advantages of photoelectrocatalysis

Photoelectrocatalytic degradation of wastewater has several advantages compared with other treatment methods.

i) PEC process is able to treat toxic wastes

ii) This process can operate at room temperature and atmospheric pressure.

iii) It is a clean technique; it does not need any chemical reagent which may be harmful or expensive.

iv) It can be easily operated and also optimum safety condition prevails since the oxidizing agents are generated in-situ and utilized during the electro-oxidation process.

v) It neither produces any undesirable reaction co-products and sludge

vi) Reaction time for this process is short.

vii) More efficient than other methods

2.7 Disadvantages of photoelectrocatalysis

i) The effluent has to be conducting. Unfortunately, not all waste streams will have sufficient conductance and the addition of an electrolyte may be necessary.

ii) Electrode fouling may occur due to deposition of material on the electrode surface.

CHAPTER-3
LITERATURE REVIEW

Several investigations have been worked on fabrication of photoanode as well as the treatment of pharmaceutical waste and other wastes by photoelectrocatalysis method are reported below. This literature review is divided into three sections:-

a)Fabrication of Ti/TiO_2 using anodic oxidation:

Zhou et al., (2009) conducted experiments for the preparation of short, robust and highly ordered TiO_2 nanotube arrays using sonoelectrochemical anodization of titanium in a n electrolyte solution of HF-H_2O(referred as short TNAs, STNAs). Titanium sheets used in experiments were of size 20mmX50mm degreased in 1:1 acetone and ethanol solution in a sonicator followed by rinsing in DI water and then dried in a stream of air. Electrochemical anodization was carried out at different voltage 0-20V and current (0-5Amp) using DC power supply at room temperature. STNs obtained was amorphous in nature were crystallized by annealing in air atmosphere for 3hr at 450^0C. The prepared SNTs were characterized using XRD and it was concluded that the electron transport process within the STNAs electrode material is much favorable compared to LTNAs prepared with conventional magnetic agitation method.

Sulka et al., (2010) studied the fabrication of nanoporous TiO_2 by electrochemical anodization. Anodization process was carried out in three steps at constant cell potential ranging from 30 to 70V at a temperature of 20^0C in an ethylene glycol electrolyte containing 0.38wt% of NH_4F and 1.79%H_2O. Nanoporous TiO_2 array was obtained after short duration of 10mins of third step. The influence of anodizing potential on the structural parameters of porous anode were studied which includes pore diameter, wall thickness, porosity and pore density. The best arrangement of nanopore was observed at 40V. It was also concluded that if anodization would carried out for longer periods then instead of nanoporous TiO_2 nanotubes/ nanowires were formed on Ti surface.

Table 5: Shows reported investigation on fabrication of TiO_2 electrode by anodizing method and its application on PEC degradation.

Anode & Cathode	Polishing	Anodization electrolyte	Voltage & current density	Anodization time	Calcination time &temp	Conclusion	Reference
TiO_2/Ti & Cu	Sand paper, HF:HNO_3:H_2O 1:3:6 for 2mins	NH4FO(27M) , 4% aqueous distillate	25V	For different hours 2,4,6,8,10 hr	500^{0}C	Nanotube anatase crystalline structure formed on TiO2 plate anodized for 4hrs as well as high degradation was seen on this plate.	Nurdin et al., 2014
TiO_2/Graphite & gold sheet	Immerse in 10M NaOH for 30mins,Ultrasonically cleaned in distilled water	Titanium tetrachloride +Distilled H_2O(1:10) continuous stirring for 10hrs		1hr	343K for 20mins and then calcined 673K for 3hrs	Stable layer was formed and electrodes were used for 6months without any drop in reaction rate and 4-NP removed efficiently by PEC than individual utilization of EC and PC	Augugliaro et al., 2009
TiO_2/Si , TiO_2/SiC & Pt	Ultrasonically cleaned with acetone and then rinse with distilled water	Aqueous electrolyte [HF acid sol with different conc. ranging from 0.1-2.0wt%], Neutral electrolyte[1	0-9V	30mins	500-600^{0}C for 3hrs	Discrete nanotubes were formed due to attack of F$^-$ ions to the interpore regions during long anodization process in case of TiO_2/Si while in case of TiO_2/SiC a layered structure was formed due to intrinsic properties of	Li et al.,2008

		M(NH$_4$)$_2$SO$_4$ & 0.5wt% NH$_4$F]				the Ti film deposited on SiC.	
TiO$_2$/Ti & Pt	HF & distilled H$_2$O	0.5M H$_2$SO$_4$	150V, 100mA/cm^2 (1st stage), 40m A/cm^2 (2nd stage)	Till voltage reach 150V	Ist plate calcined at 105^{0}C for 30mins in oven and other plate calcined by laser beam for 30mins	Anatase crystalline TiO2 structure was formed on laser calcined plate. 97.3% MB degradation& 87% COD removal was seen after 150mins.	Jin et al., 2007
TiO$_2$/Ti & Pt	Alcohol, Distilled water and acetone solution & then submerged in 0.2M HF solution for 2mins	Process A - [H$_2$SO$_4$(0.1M) ,H$_3$PO$_4$(0.3M) , H$_2$O$_2$(0.6M), HF(0.03M)] & Process B- [H$_3$PO$_4$(0.5M) , HF(0.1M)]	Process A- (20-40V) & Process B- (10-50V)	Process A- (6hrs long anodization) & Process B- (30mins short time anodization)	Process B- 723K for 2hrs	Crystalline micro-structured TiO$_2$/Ti thick-film electrodes were formed in case of long-time anodization at low voltage without subsequent calcination. While in case of process B crystallized nano-structured TiO2/Ti thin-film electrodes were formed	Li et al.,2006

b) Photoelectrocatalytic degradation of industrial waste

An et al., (2003) investigated the photoelectrocatalytic process efficiency to removes color and COD from the reactive brilliant orange K-R in a new continuous flow PEC reactor. The reactor was developed to check the feasibility of an electrochemically assisted photocatalytic process in degradation of reactive brilliant orange K-R dye in 0.5 mmol l^{-1} NaCl solution. It was found that the dye could be degraded more efficiently by this photoelectrochemical process than the degradation obtained by photocatalytic oxidation or by electrochemical oxidation alone, as well as both decoloration and TOC removal were high in case of photoelectrocatalysis. Various parameters, such as applied cell voltage, initial concentration of chloride ion and the dye, pH value and airflow were the major factors affecting the oxidation rate of the dye. The aim of this work is to prove that the photocatalytic degradation of RBOKR in a salt solution can be substantially improved by the three-dimensional electrode technology. The degradation results shows that there is enhancement effect rather a scavenging effect on the photoelectrocatalytic degradation of RBOKR existed in the photoelectrocatalytic reactor in the presence of a high concentration of chloride ion.

Jorge et al., (2005) degraded p-nitrophenol using titanium dioxide thin film. The effects of different parameters such as supporting electrolyte, pH, applied potential and PNP concentration were examined. The best condition at which maximum degradation of PNP was found in perchlorate medium at pH 2 with applied potential 1.0V on Ti/TiO_2 photoanode. Based on initial concentration 1 X 10^{-4} of PNP solution the mineralization of organic compound achieved was 60% after 3hrs experiment. It can be concluded that photoelectrocatalysis appears to be promising for the degradation toxic compounds which are relatively resistant to biological degradation.

Godinez et al., (2009) studied the photoelectrocatalysis for the destruction of pollutants present in wastewater using modified optical fiber electrode incorporated in photochemical reactor. The aim of this study is to develop a new TiO_2 based photoanode using optical fiber support. TiO_2 layer was positioned on top of a surface modified optical fiber substrate, allowed the construction of a photoelectrochemical reactor that works on the basis of an internally illuminated approach. In this way, a semi-conductive optical fiber modified surface was prepared using 30 mm thickness SnO_2: Sb films on which the photoactive TiO_2 layer was electrophoretically deposited. UV light transmission experiments were conducted to evaluate the transmittance along the optical fiber covered with SnO_2: Sb and TiO_2 showing that 43% of UV light reached the optical fiber tip.

With different illumination configurations (external or internal), it was possible to get an increase in the amount of photo-generated H_2O_2 close to 50% as compared to different types of TiO_2 films. At last the electro-Fenton photoelectrocatalytic Oxidation process studied in this work. Results reveal that total color removal of Azo orange II dye (15 mg L_1) and a 57% removal of total organic carbon (TOC) within 60 min of degradation time.

Zhao et al., (2009) investigated the degradation of aqueous methyl orange by combining TiO_2 and CdS electrode in a photoelectrocatalytic reactor under UV and Visible light irradiation. TiO_2 film and CdS film were made by two different methods magnetron sputtering method and Chemical bath deposition method respectively. The film structure and surface morphologies were characterize by different techniques XRD, FESEM, Raman. The overall experimental study indicate that the efficiency of PEC is higher than that of PC which is due to that the applied electric field is helpful to separate the photo-induced electrons and holes. Furthermore, the two-beam induced PEC (PC) is better than the sum of PEC (PC) induced by UV or visible light, indicating that the synergistic function of two-beam light could improve photocatalytic activity to an greater extent.

Table6: Reported investigations of with the effect of Time and pH on the % compound degradation and TOC removal using photoelectrocatalysis of Textile and microbial waste.

Electrolyte	Pollutant	Intensity	C_0 (mg/ dm^{-3})	pH	J (mA/cm^2)	Electrodes	Treatment time	Result	Flow rate	Reference
-	Rose Bengal	20W UV lamp(365) 1.4-2.2mW/ cm^2	20mg/l	-	-	TiO_2(anode), Pt(cathode)	6hr	- RB(65%) after 0.5hr & 85% after 6hr	-	Liu et al.,2000
Na_2SO_4 0.5g/l	Textile effulent, Brillant Blue X-BR(RBB)	11W Xe-Hg lamp(254nm) power(15mW/cm^{-2}	20-150mg/l	10	0.6-1.0V	TiO_2(anode), Cu(cathode)	2hr	85%, 96% 44-83% RRB(aqu filmPEC reactor), 12-75% RRB(conventional PEC reactor)	7.7L/hr	Xu et al.,2008
Na_2SO_4 0.05M	Azo dye Orange 11	8W Hg medium pressure lamp(365)	15mg/l	3	0-1.5mA	Ti/TiO_2(anode),carbon cloth(cathode)	60min	57%(TOC) 100%	80l/hr,640ml	Martinez et al.,2009
Na_2SO_4 0.1M/L	Dispersal orange dye, dispersal ruby dye,	125W medium pressure mercury lamp	DOD(77ppm), DRD(72ppm), DRR(92ppm	2-10	1.0V	Ti/TiO_2(anode), Pt(cathode)	6hr	DOD (90% color removal, 63% TOC), DRD (94% ,45%),DRR(100	-	Anderson et al.,2009

	borax,emulsogen, dispersal red dye		),borax(1500 ppm),emulsogen(800ppm)					%,61%)		
NaCl 0.05mol/l	Microcystin aeruginosa	125W Philips medium pressure Hg lamp(365)	50µg/l	4	30mA/cm^{-2}	Ti/TiO_2(anode), Pt(cathode)	150min	TOC (90%) color decrease (93%) 100 %(MA), COD (96%)		Fraga et al.,2009
Na_2SO_4 0.1m/l	Escherichia coli XL-Blue	9W/78 UV lamp(365)	10^3-10^7 CFU	5.6-	1.0V	Ti/TiO_2(anode), Pt-TiO_2/Ti(anode), R-TiO_2/Ti(anode), Pt(cathode)	3hr 25^{0}C	- EO(5% after 3hr), PO(80% after 1hr), PEO(100% after 1hr)	40ml/min	Philippiis et al.,2010

c) Photoelectrocatalytic degradation of pharmaceutical waste

The degradation of Rhodamine B by photoelectrochemical process in a visible light on Bi_2WO_6 nanoplate film electrode was studied by (Li & Zhang., 2007). The Bi_2WO_6 nanoplate film electrode was prepared by hydrothermal method combined with spin coating technique. The PEC reactor based Bi_2WO_6 nanoplate film electrode could degrade 87.2% of Rhodamine B with initial concentration of 5mg/l in 120mins. Also significant synergetic effect in degrading RhB via electro-oxidation and photocatalysis under visible light irradiation were also investigated. The degradation results obtained from these two processes were 36.8% and 35.9% respectively. The conclusion that made from this study was that utilizing solar light for the removal of aqueous organic pollutants is an effective and efficient approach.

Zhou et al., (2009) studied the photoelectrocatalytic (PEC) behaviors of typical PPCPs, tetracycline (TC) using highly effective TiO_2 nanopore arrays (TNPs) electrode and compare with electrochemical (EC) and photocatalytic (PC) process. A significant photoelectrochemical synergetic effect in Tetracycline degradation was observed on the TNPs electrode and the rate constant for the PEC process of TNPs electrode was ∼6.7 times as high as its Photocatalytic process. The TC removal rate achieved was 80% within 3 h PEC reaction which is∼25% higher than that obtained for a conventional coated TiO_2 nanofilm electrode fabricated by sol–gel method. TNPs electrode also shows enhanced photocurrent response compared with that for the coated TiO_2 nanofilm electrode. From this investigation it was concluded that TiO_2 nonporous will have many potential applications in various areas as an outstanding photo electrochemical material.

Yao et al., (2012) investigated the degradation pathway of Ornidazole using doped Bi5Nb3O15 photocatalyst. Nanoparticle of Bi5Nb3O15 doped with Y3+ was prepared for the first time by the sol–gel method combined with impregnation. The degradation of Ornidazole reacting with Y3+-Bi5Nb3O15 was investigated to explore the feasibility of using Y3+-Bi5Nb3O15 to treat antibiotics in wastewater. The products were characterized by X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, high-resolution transmission electron microscopy, UV–Vis diffuse reflectance spectrum and X-ray photoelectron spectroscopy. The results obtained reveal the feasibility of application of doped photocatalyst in the decomposition of Ornidazole. Fig 10 shows the degradation pathway of compound Ornidazole.

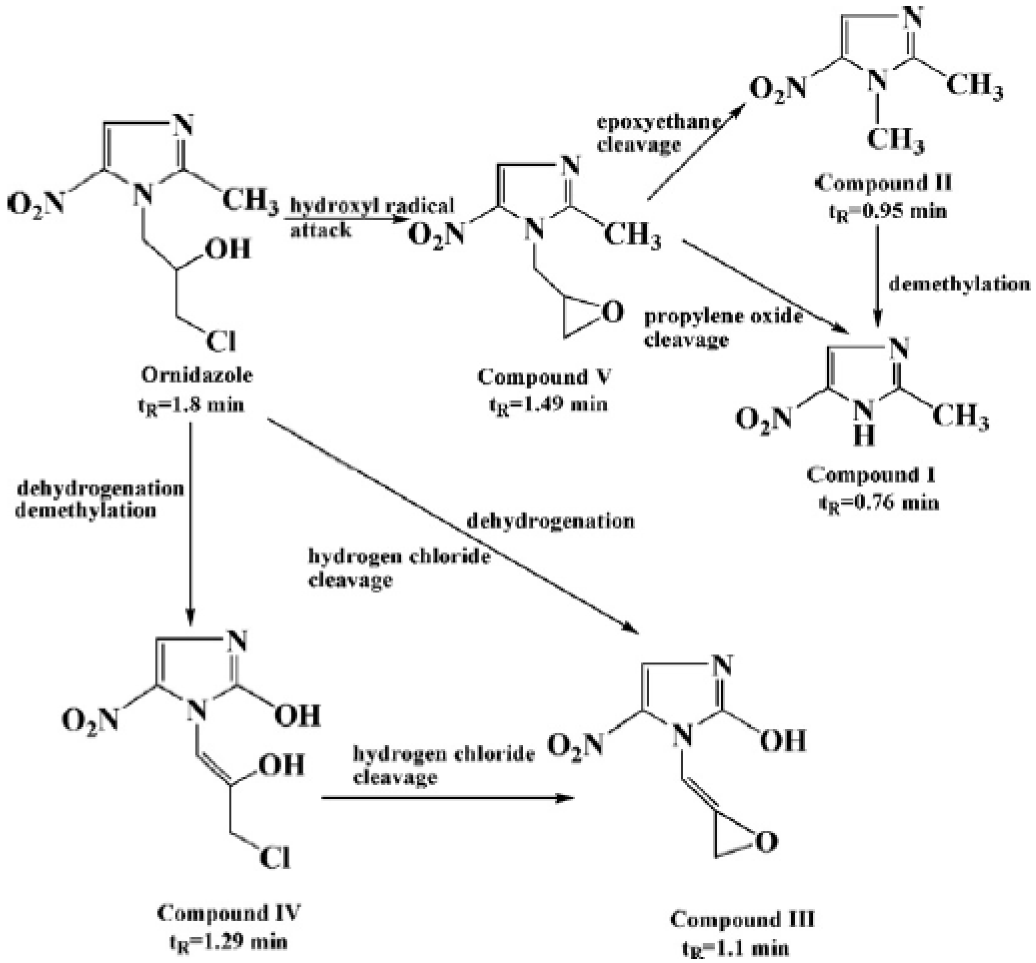


Fig 10: Proposed degradation pathway of Ornidazole (Zhao et al., 2012).

Several investigations have been worked on the treatment of pharmaceutical, textile-waste by photoelectrocatalysis method shown in Table 6 and 7, respectively.

Table 7: Reported investigations of with the effect of Time and pH on the % compound degradation and TOC removal using photoelectrocatalysis of pharmaceutical waste.

Pollutant	Intensity	C_0 (mg/ dm^{-3})	pH	J (mA/cm^2)	Electrodes	Time	Results	Reference
4-chlorophenol, oxalic acid	45W Hg medium pressure lamp(365)	-	7	-	TiO_2(anode), Ag/AgCl	5hr	- Oxalic acid100%(TOC), less CO_2 detected(4-chlrophenol)	Waldner et al.,2003
Humic Acid	450W Xe-Hg UV light lamp(254nm&400nm)	25mg/dm^{-3}	7	0-2V	TiO_2(anode), Pt(cathode)	2hr	TOC removal (85%), Color removal (96%) Acid removal (98%)	Sene et al.,2003
Aspirin	-	-	-	-	Pt(cathode), Carbon fiber (anode)	-	The progressive oxidation increased biological availability	Rosenwinkle et al., 2004
Paracetamol	-	1gm/l	2-12	-	BDD/Pt (anode), graphite bar (cathode)		100% removal	Cabot et al., 2005
Bisphenol A	8W Hg medium pressure lamp(365)	1.12mg/l	6.17	0-1.5mA	Ti/TiO_2(anode), RVC or Pt(cathode)	180min	- Bisphenol removal (13-99%)	Li and Xie.,2006
Rhodamine	30W	-	2-10	0.05-0.5V	Ti/TiO_2(anode),	30min	-	Zheng et

B	mercury UVA lamp				Pt(cathode)		Rhodamine B (100%)	al.,2006
Pentachlorophenol(PCP)	8W Hg high pressure lamp(365)	20ppm	3.25-8.00	0-0.6V	Ti/TiO_2(anode), Pt(cathode)	2hr	EO (0%), DP (44%) PO (62%), PEO (82-86%)	Chen et al.,2007
2,4-dichlorophenol	8W Hg high pressure lamp(365)		-		Ti/TiO_2(first anode), Fe (2nd anode)graphite(cathode)	60min	- 78% mineralization4-DP (93%)	Zhao et al.,2007
Benzotriazole(BTA)	30W UV lamp(253.7nm	$2x10^{-4}$ M	2-10	0-0.8V	Ti/TiO_2(anode), Pt(cathode)	180min	- EO (0%) DP (65%) PO (70%), PEO (89-90%)	Yang et al.,2010
Ketoprofen	-	-	3-11	0-320 mA/cm^2	BDD/Pt (anode), Pt (cathode)	-	ketoprofen degraded to CO_2 and H_2O,poor mineralization at both BDD and Pt anodes in the presence of NaCl as SEC, while complete mineralization was achieved using Na_2SO_4 as SEC	Latha et al., 2010
Diclofenac	15W low pressure Hg lamp emitting at 253.7 nm	-	6.5	20-30mA/cm^2	BDD, Ti/Pt/PbO_2(anode), stainless steel(cathode)	6hr	COD (60%), TOC (95%), diclofenac (95.3%)	Anjo et al., 2009 & Zhang et al., 2011

CHAPTER-4
OBJECTIVES

This present study focuses on the degradation of the pharmaceutical compound using novel technique photoelectrocatalysis. Photoelectrocatalytic degradation of pharmaceutical compound was studied under UV- light. The present work is carried out under the following objectives:

1) Fabrication of Ti/TiO_2 electrode using anodic oxidation (anodization).
2) To study the effect of process parameters such as pH, compound concentration and time (t) on % degradation by photoelectrocatalysis.
3) Optimization of process parameters for photoelectrocatalysis degradation using RSM.

CHAPTER-5
EXPERIMENTAL SETUP AND PROCEDURE

5.1General

The photoelectrocatalytic process for the pharmaceutical wastewater treatment can be oxidized directly on the surface of the photocatalyst or degraded by reacting with hydroxyl radicals. This chapter describes the use of semiconductor TiO2 as photoanode and copper as cathode for the treatment of pharmaceutical compound in photoelectrocatalytic reactor. Different analytic techniques necessary for the compound assessment and its pathway are also used. Experiments were conducted in a batch system to study the consequence of pH, time and initial concentration on % degradation of compound, COD removal etc.

5.2 Pharmaceutical compound

Ornidazole chemically known as 1-chloro-3(2-methyl-5-nitroimidazole-1yl) propan-2-ol is well known antiparasitic drug is commonly used for the treatment of giardiasis, trichomoniasis, amoebiasis and anaerobic infections as well as used in abdominal and gynaecological surgery. Because of its many uses several analytical procedures are reported in the literature. Ornidazole has been detected in wastewater, surface water, ground water and drinking water as well as in soils and river bed sediment (Eurin et al., 2011). Its continuous accumulation in water leads to negative effects on ecosystem hence it has to be eliminated completely from environment. So far Ornidazole removal by oxidant and its photolytic stability in solution has been reported. But there was no much information available on degradation of Ornidazole by oxidant from its kinetic and mechanistic point of view (Yao et al., 2012).

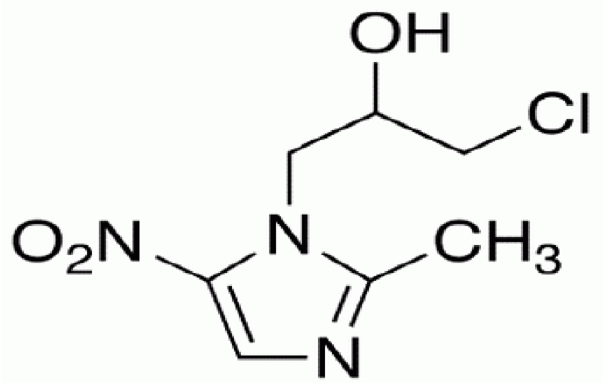


Fig 11: Chemical structure of Ornidazole.

The compound was scanned over a range of 190nm -500nm with the help of UV- Vis spectrophotometer and maximum absorbance was seen at 319nm.

5.3 Reagents and Chemicals

The compound which is used in the present study was purchased from SNG labs, Chandigarh. The various reagents used in all experiments were prepared in double distilled water. pH of the solution was adjusted using 0.2M NaOH and 0.2M H_2SO_4.

5.4 Instruments and Equipment Used

5.4.1 pH meter

A digital desktop, used to measure the pH of the solution. Instrument was calibrated with freshly prepared buffer solution of pH 4, 7, 9 from time to time throughout the research work.

5.4.2 Radiometer

Eppley (model no. 33013, USA) radiometer used to measure the intensity of UV light and solar light hourly during research study.

5.4.3 UV-Vis Spectrophotometer

UV-Vis spectrophotometer (LABINDIA, Model no. T60**)** was used for analyzing the compound degradation studies using 1cm quartz cell at 319nm wavelength.

5.4.4 Muffle Furnace

Rate controlled muffle furnace (temperature range 50- 1000^0C) used for fixing the coated catalyst on electrode. Temperature 500^0C was used for this study.

5.4.5 Reactor

Reactor used for experimental work was rectangular having dimensions of 12cm*12cm*15cm with 0.5cm thickness and was made up of polycarbonate sheet having 1.5cm and 2.5cm inlet and outlet respectively absorbs maximum UV light. The working volume of the reactor is 1500 ml.

5.4.6 UV light chamber

The chamber was made up of wood and had outer and inner lining of plywood. The whole chamber was painted black from inside which act as sink and absorb excessive heat. The reactor used was rectangular having dimensions of (138cm*52cm). Reactor contains 12 UV tubes (36 watts each, 255-370nm) as irradiation source attached with side walls. Temperature inside the chamber was maintained by an exhaust fan attached to the roof.

5.4.7 DC supply

The direct current power supply (DIGITECH, Roorkee, India, Model: 4818A10) was used to supply the current during experiments as well as control the experimental voltage in the electrochemical process.

5.4.8 Magnetic stirrer

Magnetic stir was used to agitate the wastewater sample.

5.4.9 HPLC

The samples were also analysed using HPLC [Shimazdu, communication module (CBM-20A), diode array detector (SPD-M20A), pump (LC-20AD)] for the confirmation of Ornidazole degradation. HPLC was performed on binary HPLC system with C-18 column (250 mm x 4.60 mm), particle size 5 µm using 1% formic acid and acetonitirile as mobile phase with UV detector at 319 nm for Ornidazole. Flow rate was maintained at 1.0 mL min^{-1} with 10% acetonitrile. Each analysis lasted 20 min and the injection volume was 20µL.

5.4.10 XRD (X-Ray Diffraction)

The samples were checked for crystalline structure using XRD XPERT-PRO (SAI Labs, TU). The samples chosen were normal Ti plate, and anodized Ti plate both before calcination and after calcination.

5.5 Materials and Methods

5.5.1 Sample preparation

Ornidazole solution was prepared by dissolving 23mg of Ornidazole (powder form) in 1*l* of distilled water.

5.5.2 Fabrication of TiO_2 Electrode

In this research work Ti/TiO_2 and Cu electrodes having dimension 10cm*7.5cm*0.1cm were used as anode and cathode respectively. Ti/TiO_2 electrode was prepared by anodic oxidation (anodization). Reagents used for the preparation of electrode were glycerol (20ml), ammonium fluoride (40ml), hydrofluoric acid (20ml), water (100ml). After that volume was made up to 2000ml. electrodes were put in above electrolyte solution and connected to DC supply by giving potential bias of 20V for 45mins. The final stage was furnishing the electrode for 3hrs at a temperature of 500^0C to evaporate residual electrolyte solution as well to obtain anatase TiO_2 crystal structure.

5.5.3 Standard curve preparation

To make standard curve various concentration varying from 2 to 25 ppm were made from 30ppm stock solution. Complete wavelength scan was done and maximum absorbance was seen at 319nm. Further readings were taken at 319nm throughout the research study under UV –Vis spectrophotometer.

5.6 Lab scale experimental setup

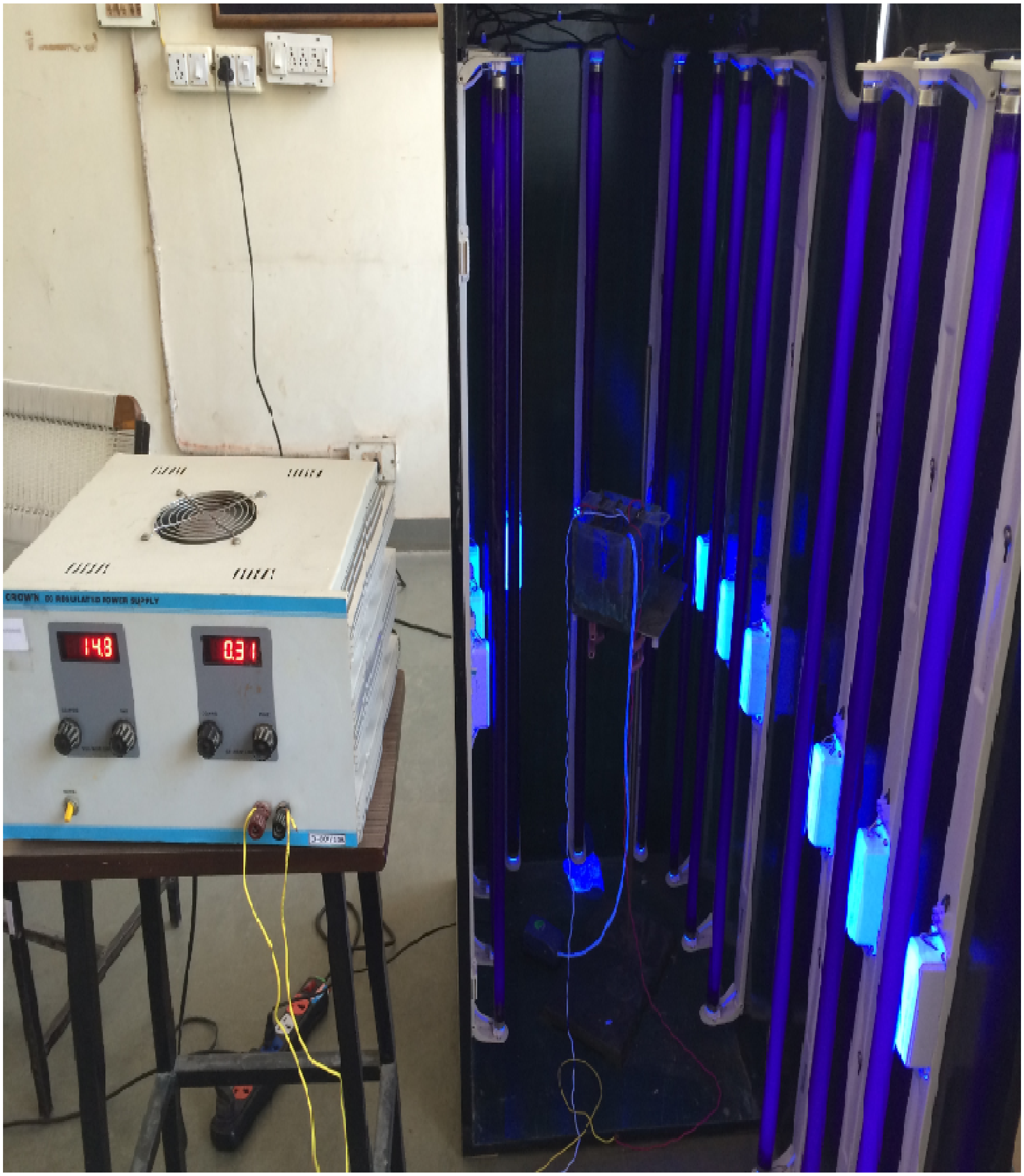


Fig 12: Photoelectrocatalytic experimental setup.

5.7 Experimental Procedure

Photoelectrocatalytic oxidation reaction was accomplished in a 1500ml photoreactor made up of polycarbonate sheet. pH of the solution was set to desired level using 0.2N NaOH or 0.2N H_2SO_4. Conductivity of the solution was maintained to 2.5 mS by adding 2 gm of NaCl. The electrode were placed 2cm apart. DC supply was provided for photoelectrocatalysis. Once electrode was used it was rinse with distilled water to remove carbon deposits during particular reaction and used upto 3 times for further experiments. UV light with moderate intensity was provided throughout the experiment as well as continous airflow was there with the help of Air Spurger. To determine the concentration of compound spectro-photometric technique was used. Absorbance was checked at 319 nm.

5.7.1 Determination of degradation efficiency

The degradation of the compound was evaluated by monitoring the absorbance as a function of irradiation-time using spectrophotometer. The degradation efficiency was studied in terms of absorption at 319nm was calculated as follows:

$\%\text{Degradation} = 100\text{X} \{[C_0 - C]/[C_0]\}$

Where C_0 = initial concentration of solution & C= concentration of solution after photoelectron irradiation.

5.8 Response surface methodology (RSM) Optimization

RSM is a collection of statistical and mathematical method that can be used for studying the effect of several factors at different level and their influence on each other. Hence RSM is a well known efficient experimentation technique which is applied in wide range of fields for the purpose of producing high quality of products or for analyzing engineering problems in a more stable and economical way. The main objective of this technique is to optimize the response surface that is influenced by several process parameters. It also quantifies the relationship between the controllable input parameters and the obtained response surfaces. The design procedure of RSM is divided in four steps.1) designing of a series of experiment for adequate and reliable measurement of the response of interest, 2) developing a mathematical model of the second order response surface with the best fittings, 3) finding the optimal set of experimental parameters that produce maximum or minimal value of response, 4) representing the direct and interactive effects of process parameters through two and three dimensional plot, 5) at last conducting a confirmation experiment to verify the optimal parameters. The choice of the design of experiments can have great influence on the accuracy of the approximation and cost of constructing RSM. Generally these models are polynomial with unknown structure; hence the corresponding experiments are designed only for particular problem. The purpose of this methodology is to identify the design variables that have large effect on further investigation as well as to optimize the response variable y because y is the answer of the system and Xi the variables of action called factors.

$$Y=f(X_1, X_2, X_3 \ldots\ldots\ldots.X_k) \quad \text{(Aslan and Cebeci., 2007)}$$

Some researchers have successfully applied RSM to different oxidation processes to optimize the experimental design. Its application includes TiO_2-coated/UV oxidation (Lanteri et al., 2004; Morvan et al., 2008), TiO_2 slurry/UV oxidation (Muruganandham and Swaminathan., 2006; Daneshvar et al., 2007), O_3 oxidation (Zhao et al., 2006) and electrochemical oxidation (Recotti et al., 2007). However, the application of RSM in Ti/TiO_2 photoelectrocatalysis for pharmaceutical degradation is not yet reported. RSM is a multivariate technique that mathematically fits the experimental domain studied in the theoretical design through response function. The two most common designs used in RSM are the Central Composite design (CCD) and the Box-Behnken design (BBD). BBD is considered as an efficient option in RSM and an ideal alternative to CCD (Box and Hunter., 1957).

5.8.1 Box-Behnken Design

This experimental design developed in 1980 by Box and Behnken. It is a useful method for developing 2^{nd} order response surface models, based on construction of balanced incomplete block designs which requires at least three levels for each factor. In BBD the level of one of the factor is fixed at center level while combinations of all levels of other factors are applied (Myers and Montgomery., 2002). The level of factor C was fixed and then, the combinations of all levels of factor A and B were applied and subsequently this same procedure is applied for factor B and A respectively. Table 8 shows three-factor Box-Behnken design.

Table 8: Coded factor levels for a Box-Behnken design of a three-variable system

Experiment	A	B	C
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0

Source: (Tekindal et al., 2012)

Box-Behnken design is rotatable or nearly rotatable second order design. Rotatability is important for the second order model to provide good predictions throughout the region of interest. So, it is required that the model have a reasonably consistent and stable variance of the predicted response at a point A graphical representation of three factor in two forms is shown in Fig13 a-b (Ferreira et al., 2007).

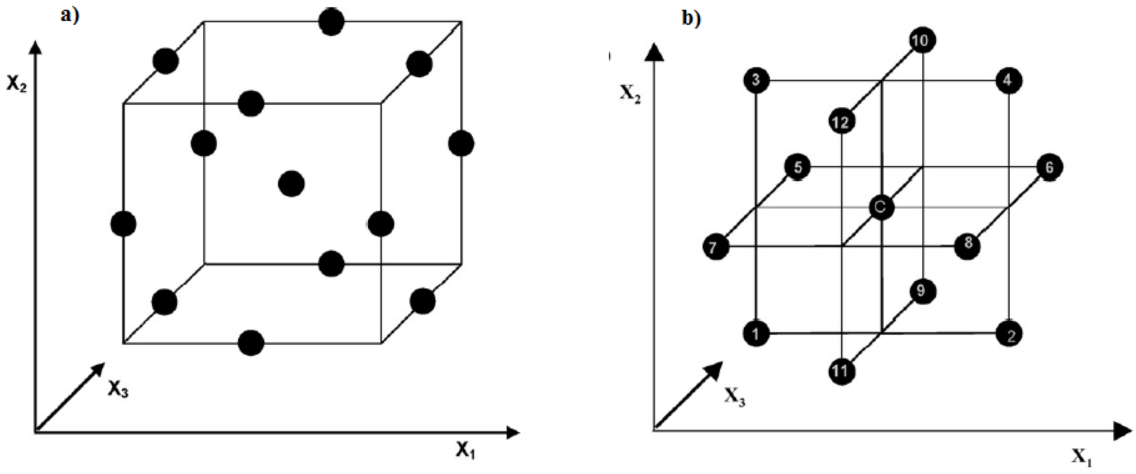


Fig 13: a) A cube for BBD consists of the central point and middle point of the edges; b) Three interlocking 2^2 factorial designs and a central point.

The number of experiments (N) required for the development of BBD is defined as N=2k (k−1) +C_0, (where k is number of factors and Co is the number of central points). For comparison from BBD the equation used for number of experiments in case of a central composite design is N=2k +2k +C_0. There are certain authors, after performing several experiments confirmed that BBD is better and more efficient than other response surface designs such as CCD, Three level full factorial, Doehlert matrix etc.

Advantages of BDD:

1) Avoid extreme conditions of experiments.
2) Lower experimental cost if two or three factors are considered

5.8.2 Desirability

The desirability function approach is one of the most widely used methods in industry for the optimization of multiple response processes. It is an approach to translate the functions to common scale, combine them using the geometric mean and optimize the overall metric. There are three responses therefore multi response process optimization by the desirability function approach was used for the optimization of the photoelectrocatalysis process parameters.

One-sided desirability di is given by:

$$d_i = \begin{cases} 0 & \text{if Yi <=Yi\_min} \\ \left[\dfrac{y_i - y_{i-\min}}{y_{i-\max} - y_{i-\min}} \right]^r & \text{if Yi\_min < Yi < Yi\_max} \\ 1 & \text{if Yi >=Yi\_max} \end{cases}$$

Where Yi is response value, Yi-min and Yi-max are minimum and maximum acceptable values of response i, and r is a weight and a positive constant used to determine scale of desirability. The desirability (di) lies between 0 and 1, representing the closeness of a response to its ideal value. In multi response process optimization, the desirability function transforms each response in to a corresponding desirability value between 0 and 1 (Sangal et al., 2013). All the desirability functions are combined to form a composite desirability function, which converts multi responses into a single response. The individual desirability functions are combined in order to obtain the overall desirability, D as follows: $D= (d_1 \text{ x } d_2 \text{ x } d_3 \text{ x}\ldots\ldots)^{1/k}$.

Where 0<=D<=1 and k is the number of responses. If all of the quality characteristics reach their ideal values di is 1for all i. Consequently, the total desirability is also 1. If any one of the responses does not approach its ideal value, the di is less than 1 for that response and the total desirability is therefore also less than 1(Kaur et al., 2014).

CHAPTER-6
RESULT AND DISSCUSION

6.1 General

In this chapter the experimental results and their interpretation regarding pharmaceutical compound degradation, anode preparation and COD removal using photoelectrocatalysis based Ti/TiO_2 coated plate as an anode and copper plate as cathode has been discussed in detail. Treatment process has shown significant COD removal and compound degradation.

6.2 Standard Curve

The complete wavelength scan of compound Ornidazole was done on UV-Vis spectrophotometer and maximum absorbance was observed at 319nm. Standard curve was made to evaluate the concentration of compound Ornidazole after photoelectrocatalytic degradation by plotting the graph between absorbance and compound concentration using UV-Vis spectrophotometer at predetermined known concentrations of Ornidazole.

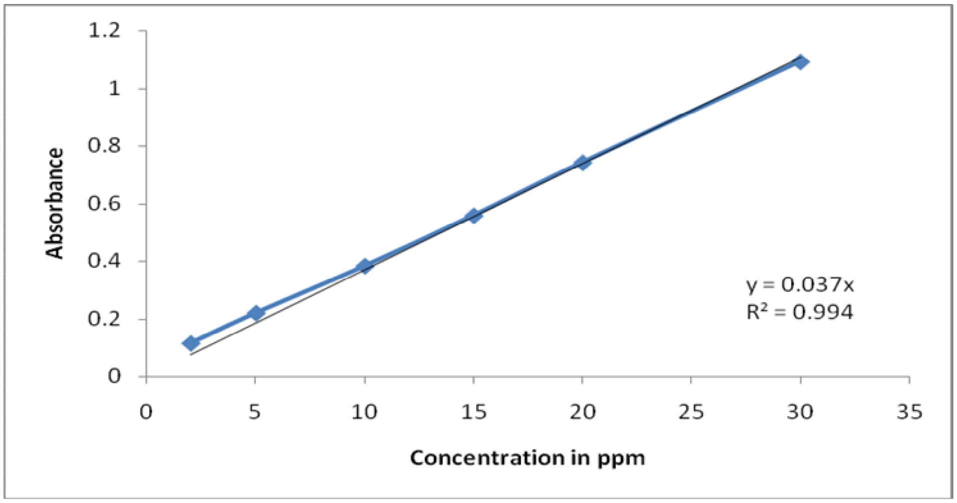


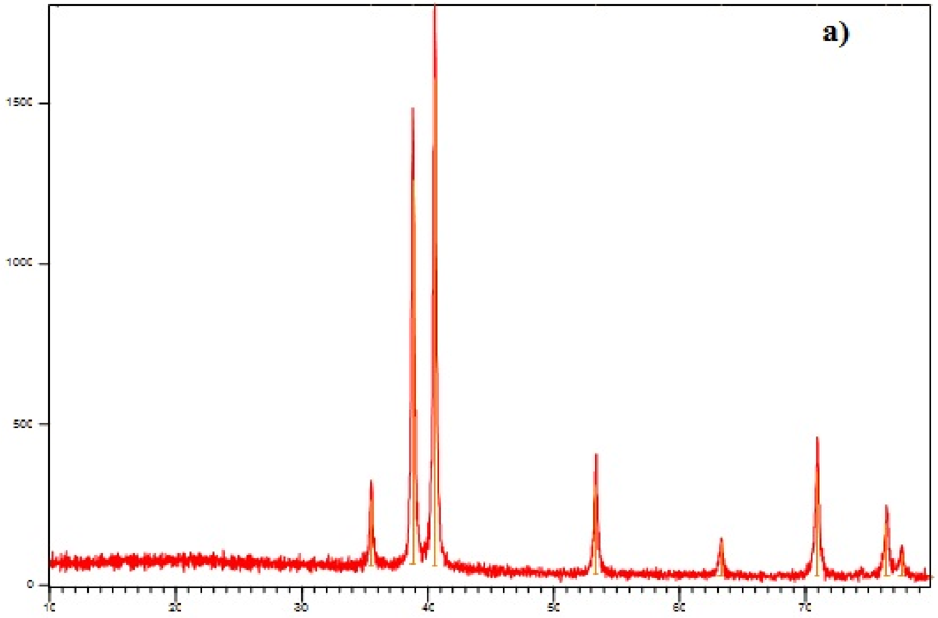
Fig 14: Calibration curve of Ornidazole at wavelength 319nm

6.3 Characterization of TiO_2 Electrodes

The TiO_2 electrodes were characterized by XRD which showed crystalline form of TiO2 long with its percentage. The result as shown in Figure 15 indicates that anodized TiO2 film had good crystallinity even without carination. The prepared TiO2 films have both anatase and rutile phases with anatase being dominant in before calcinations and rutile in after calcinations samples as mentioned in Table no.9.

Table 9: Shows the crystalline nature of Ti plate before and after calcinations.

Sample	**Ref. Code**	**Compound Name**	**Displacement [°2Th.]**	**Scale Factor**	**Chemical Formula**	**Semi Quant [%]**
Initial metal	01-071-4632	Titanium	0.622	1.034	Ti	100
Before Calcination	01-076-0324	Rutile, syn	-0.379	0.341	TiO_2	39
	01-075-2553	Anatase	0.125	0.826	TiO_2	61
After Calcination	01-075-2546	Anatase	0.137	0.432	$Ti\ O_2$	20
	01-076-0323	Rutile, syn	-0.377	1.175	$Ti\ O_2$	80



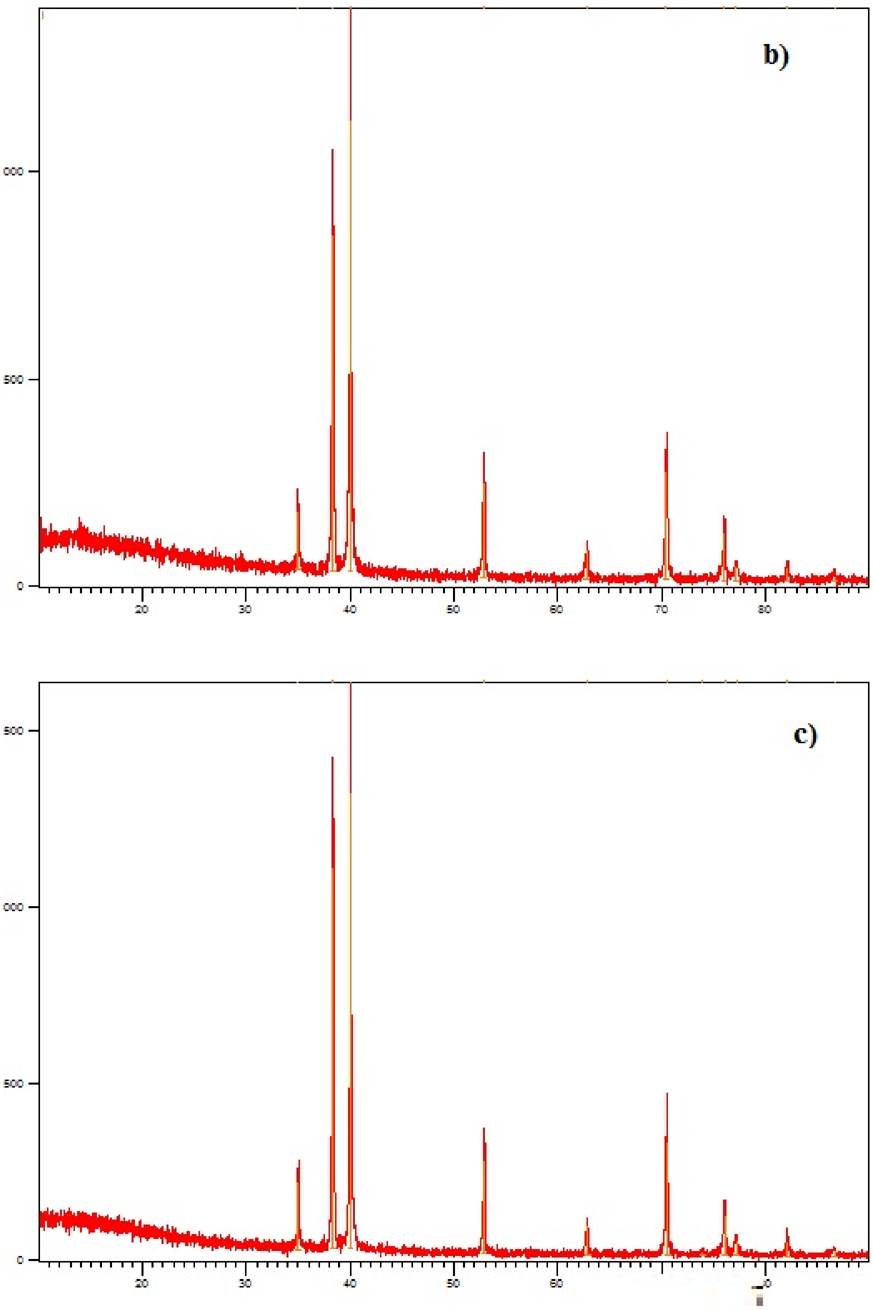


Fig.15 XRD pattern of TiO_2 films a) Intial Ti plate b)before calcination TiO_2 film formed on Ti plate c) after calcination TiO_2 film formed on Ti plate

6.4 Photoelectrocatalytic degradation of Ornidazole

The number of experiments were carried out in order to find the optimum conditions for the photoelectrocatalytic degradation of Ornidazole using Ti/TiO_2 as anode and cu as cathode under UV light with varying pH, initial concentration of compound , time of degradation etc by using RSM technique.

6.5 RSM OPTIMIZATION

6.5.1. Box- Behnken design (BBD)

Box-Behnken design which is based on RSM was used for this experimental design. For assessing the optimum conditions for the response three analytical steps were performed i) adequacy of various model test(sequential model sum of squares and model summary statistics), ii) analysis of variance (ANOVA) and the last step was the response 3-D surface plotting. The three operational parameters were variable pH 4-10, degradation time 20- 180mins and compound concentration 10-30ppm were considered as input parameters and % of degradation was taken as response. Table no. 10 shows the various operational parameters and there levels.

The total 17 number of experiments designed by RSM to study the effect of three parameters pH, concentration and time on response % compound degradation. Full factorial design used to study the photoelectrocatalytic degradation of pharmaceutical compound shown in table no. 11.

Table 10: Range of variables and levels of the design model

Factors	**Variables**	**Range of actual and coded variables**		
		Coded(-1)	**Mean(0)**	**Actual(+1)**
A	pH	4	7	10
B	C(ppm)	10	20	30
C	T(mins)	20	100	180

Table 11: Full Factorial design used for photoelectrocatalytic degradation of Ornidazole.

Std	Run	Factor 1 A:pH	Factor 2 B:Conc.	Factor 3 C:T	Response % degradation
4	1	10	30	100	78.43
17	2	7	20	100	79.62
14	3	7	20	100	79.62
1	4	4	10	100	81.81
6	5	10	20	20	28.88
8	6	10	20	180	93.75
2	7	10	10	100	80.45
7	8	4	20	180	90.07
11	9	7	10	180	90.33
5	10	4	20	20	34.74
12	11	7	30	180	90.75
9	12	7	10	20	16.97
15	13	7	20	100	79.62
13	14	7	20	100	79.62
16	15	7	20	100	79.62
10	16	7	30	20	10.27
3	17	4	30	100	71.77

6.5.2 Statistical Analysis

The response % degradation by photoelectrocatalysis of pharmaceutical compound using Ti/TO$_2$ as anode and copper as cathode were calculated according to the arrangement of operational parameters in a design matrix of experiments and results are shown in table no.11. Quadratic model was fitted to the experimental data to obtain regression equations. Sequential model sum of squares and model summary statistics were tested to decide the adequacy of model. A result of adequacy model was shown in table no.12 for response % compound degradation. Sequential model sum of squares showed that quadratic model was best fit model for experimental data for response %degradation. Higher order models were found aliased for response (%degradation).

Table 12: Sequential model sum of squares for % compound degradation.

Source	Sum of Squares	DF	Mean Square	F value	Prob>F	
Mean	80981.17	1	80981.17			
Linear	9916.86	3	3305.62	18.63	<0.0001	
2FI	30.37	3	10.12	0.044	0.9868	
Quadratic	2157.60	3	719.20	42.27	<0.0001	Suggested
Cubic	119.10	3	39.70			Aliased
Residual	0.000	4	0.000			
Total	93205.09	17	5482.65			

The model gives coefficient of determination that is predicted R^2 value, adjusted R^2 value and R^2 value shown in table no.13. This concludes a good correlation between observed and predicted values. The predicted values were closer to actual ones. fig 16-17 shows close relation between %normal probability and Studentized residual. Which implicit that the difference between predicted value and observed value dividing by standard error of the residual have close relation with % Normal probability.

Table 13: Model summary statistics

Source	**Standard Deviation**	**R^2 value**	**Adjusted R^2**	**Predicted R^2**	
Linear	13.32	0.8113	0.7677	0.6493	
2FI	15.09	0.8138	0.7020	0.2274	
Quadratic	4.12	0.9903	0.9777	0.8441	Suggested
Cubic	0.000	1.0000	1.0000		Aliased

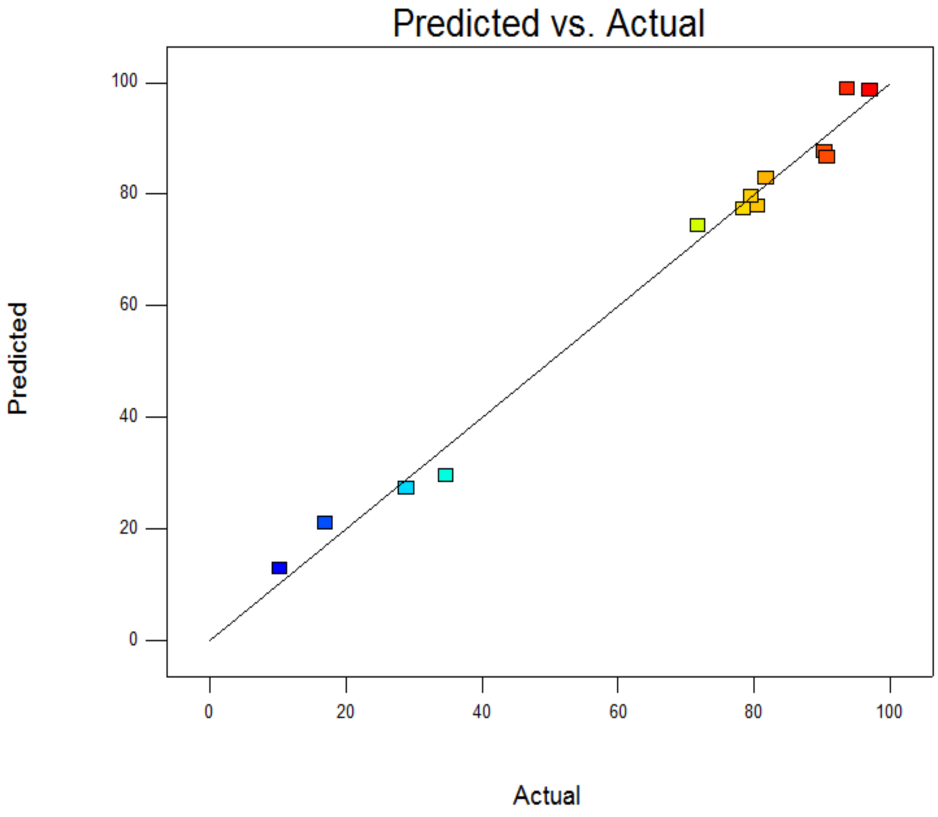


Fig 16: Residual plots (actual vs. predicted) for photoelectrocatalysis of Ornidazole for % compound degradation

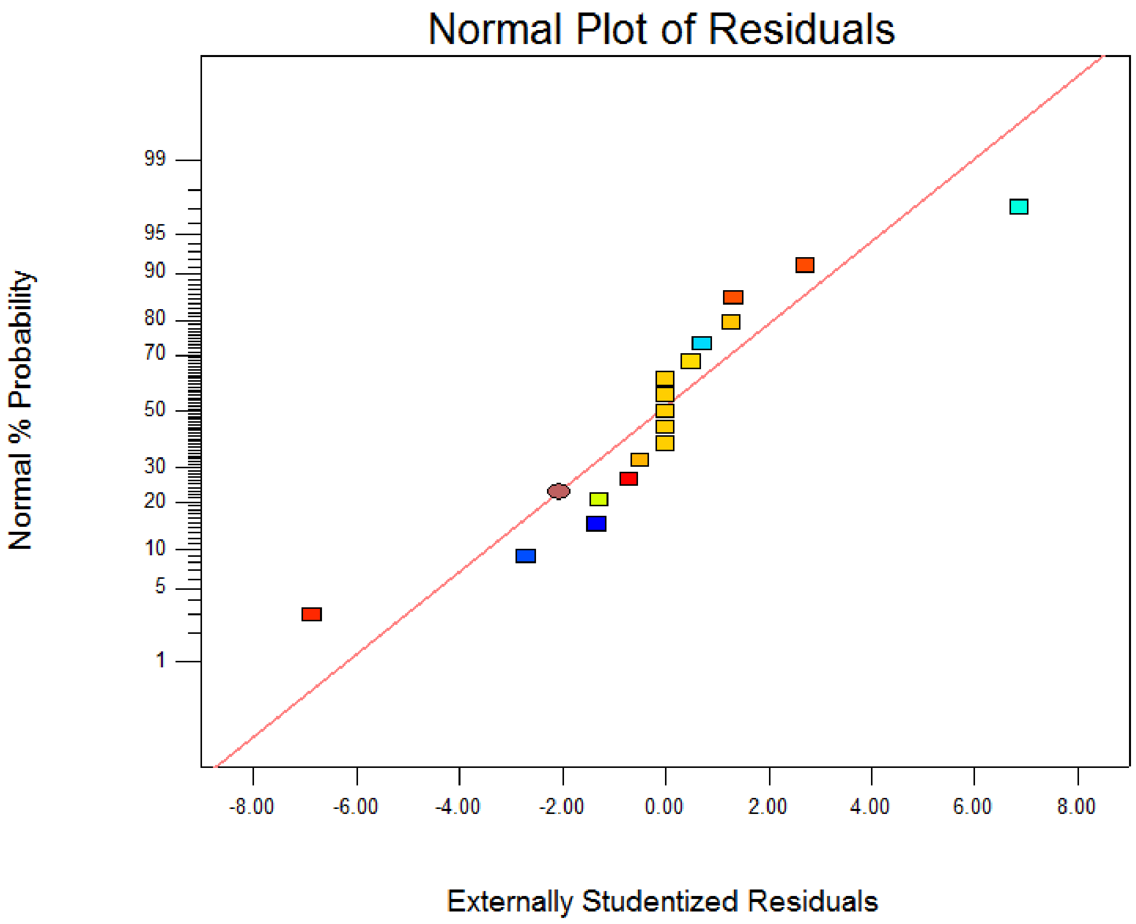


Fig 17: **Residual plots for photoelectrocatalysis of Ornidazole of % compound degradation.**

The analysis of variance (ANOVA) shows the model F-values for %degradation shown in table no. 14. After studying the table it was confirmed that this model is significant for response (% degradation). For model to be significant “prob>F” values should be less than 0.05. If “prob>F” values come larger than 0.100 indicate that model terms are insignificant. The response surface model shows that time and time^2 were highly significant for response (%degradation) while pH^2 and conc^2 were significant for response (% degradation).

Table 14: ANOVA for response surface quadratic model for % degradation of pharmaceutical compound

Source	Sum of Squares	DF	Mean square	F-value	P-Value Prob>F	
Model	12104..83	9	1344.98	79.05	<0.0001	Significant
pH	1.88	1	1.88	0.11	0.7492	
Concentration	42.04	1	42.04	2.47	0.1599	
Time(T)	9872.94	1	9872.94	580.29	<0.0001	Significant
pH*concentration	16.08	1	16.08	0.95	0.3634	
pH*time	1.61	1	1.61	0.095	0.7671	
Concentration*time	12.67	1	12.67	0.74	0.4167	
pH^2	105.79	1	105.79	6.22	0.0414	
Concentration^2	178.85	1	178.85	10.51	0.0142	
Time^2	1860.82	1	1860.82	109.37	<0.0001	Significant
Residual	119.10	7	17.01			
Lack of Fit	119.10	3	39.70			
Pure error	0.000	4	0.000			
Core total	12223.93	16				

The final quadratic equation in terms of coded factors for %age of compound degradation is given below.

Final Equation in Terms of Coded Factors:

%degradation=+79.620.48*pH2.29*concentration+35.13*time+2.01*pH*concentration+ 0.64*pH*time+1.78*concentration*time+5.01*pH^2-6.52*concentration^2-21.02*time^2 .

6.5.3 Effect of pH, time and concentration on %degradation

To study the effect of parameters i.e. pH, concentration of compound and time on % degradation (response) for photoelectrocatalysis of pharmaceutical compound, 3-D response surface graph were considered

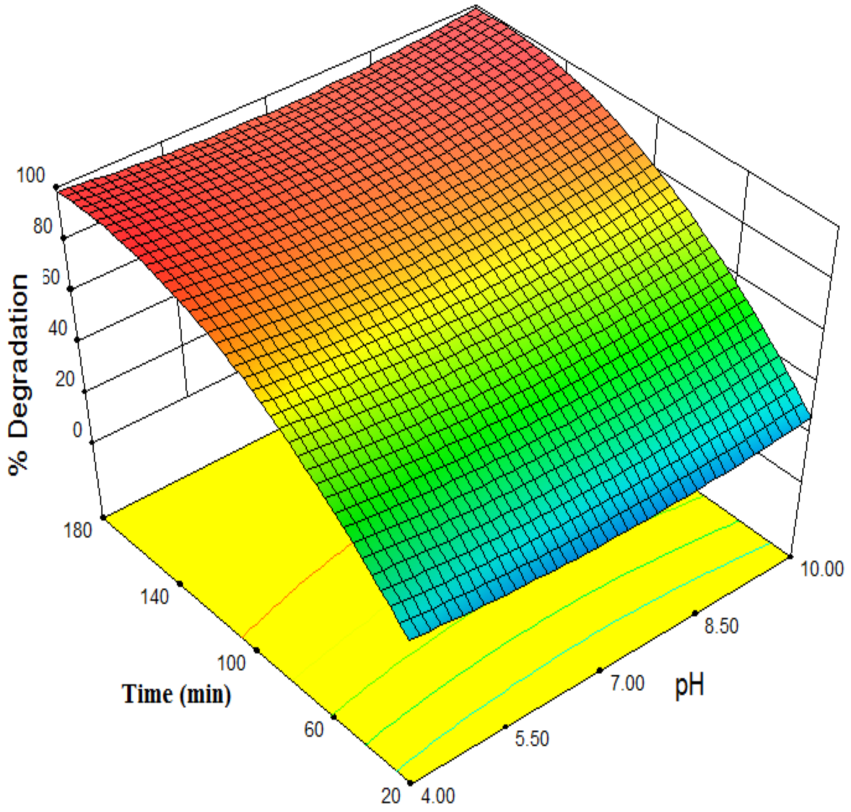


Fig 18: Three dimensional response surface graphs for photoelectrocatalysis of pharmaceutical compound for % degradation.

Fig 18 shows the 3-D response surface graph for time and pH versus %degradation. The graph shows with increase in time %degradation increases till the optimum value of time after which the degradation becomes constant. The little higher degradation was observed in case of highly acidic and basic solutions. Even as the reaction proceeds the pH of the solution decreases. With effect of the final degraded solution to be neutral the optimized condition was chosen as the alkaline.

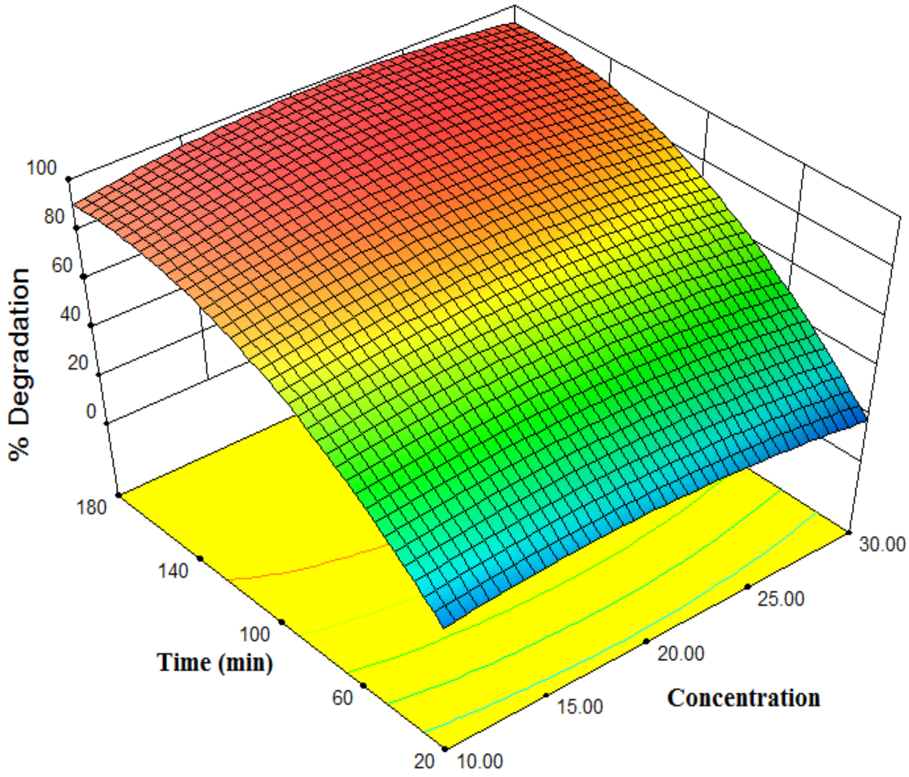


Fig 19: Three dimensional response surface graphs for photoelectrocatalysis of pharmaceutical compound for % degradation.

Fig 19 shows the 3-D response surface graph for time and concentration versus % degradation. With increase in concentration little decrease in degradation was observed as we deviate from the optimal value (~ 23 ppm) due to mass transfer limitations. While in case of time with increase in time %degradation increases till the optimum value of time after which the degradation becomes constant. The maximum degradation was observed till 170min.

Fig 20 shows the 3-D response surface graph for pH and concentration versus % degradation. It was seen that in acidic and basic medium there was little effect on the % degradation. The maximum %degradation was observed at pH 9.5. While in case of concentration little decrease in degradation was observed as we deviate from the optimal value (~ 23 ppm) due to mass transfer limitations.

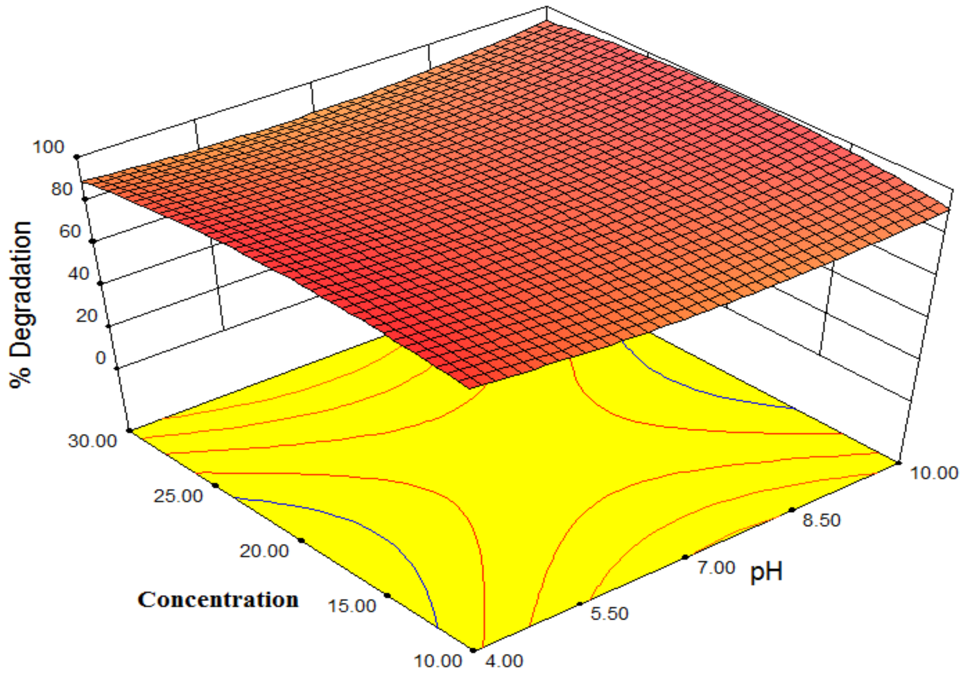


Fig20: Three dimensional response surface graphs for photoelectrocatalysis of pharmaceutical compound degradation for % degradation.

6.5.4 Optimization Analysis

Photoelectrocatalysis of pharmaceutical was optimized by RSM in terms of maximization of response %degradation. For this purpose some constraints for operational parameters were applied shown in table no. 15.

Table 15: Constraint applied for PEC of Ornidazole

Variables	Goal	Lower limit	Upper limit
pH	Is in range	4	10
Time(mins)	Is in range	20	180
Concentration(ppm)	Is in range	10	30
%degradation	Maximize	10.27	97.31

The overall desirability (D) was 0.9985. The optimum values of operational parameters suggested by RSM as shown in table no. 16. The optimized values of process parameters were time (t) = 170mins, pH =9.5 and concentration= 23ppm. The response at these conditions was 97.31% compound degradation.

Table 16: Optimum conditions for PEC of Ornidazole

Variables	Optimum values
pH	9.5
Time(t)	170mins
Concentration	23ppm

6.5.5 Confirmation Results

Optimum condition for photoelectrocatalysis of Ornidazole was verified experimentally. Experiment was run for 170mins at pH 9.5 and initial concentration was 23ppm. Optimum response for optimum parameters was %degradation 97.31%. An experiment result for optimum process parameters for response (% degradation) was 95.34%.

The comparison between the optimum and experimental results is shown in table no. 17.

Table 17: Comparisons between the results for PEC

Response	Predicted	Experimental
% compound degradation	97.31%	95.34%

Optimization by BBD under RSM clearly indicates the interaction between variables and their effects for the degradation of Ornidazole by photoelectrocatalysis process. The predictions correlate well with experimental result.

6.6 Mineralization

Mineralization of compound during photoelectrocatalysis treatment is important. In this context, COD reduction was study for the mineralization of Ornidazole. 75% reduction of COD was achieved after three hours. Moreover, HPLC chromatograms, Figure no. 21 indicated the disappearance of peak for the parent compound at 319 nm.

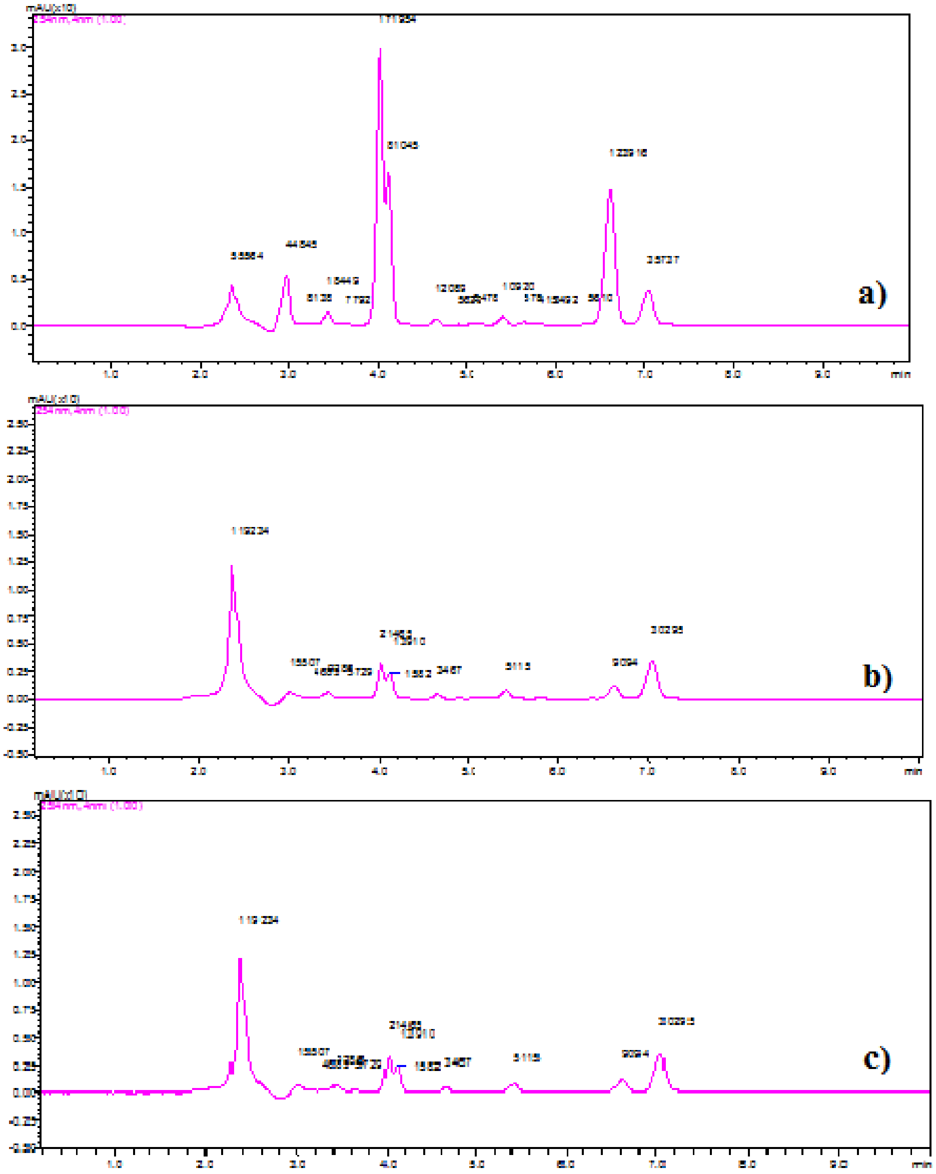


Fig 21: Shows HPLC chromatogram for Ornidazole. a) initial (0mins), b) 90mins c) 180mins

6.7 Comparison among three processes PEC, EC & PC

Fig 22 shows that photoelectrocatalytic, photocatalytic and electrocatalytic effect of TiO_2 on %degradation of pharmaceutical compound Ornidazole. It can be seen that the efficiency of PEC is higher than that of EC and PC at optimal conditions which is due to the applied electric field is helpful to separate the photo-induced electrons and holes.

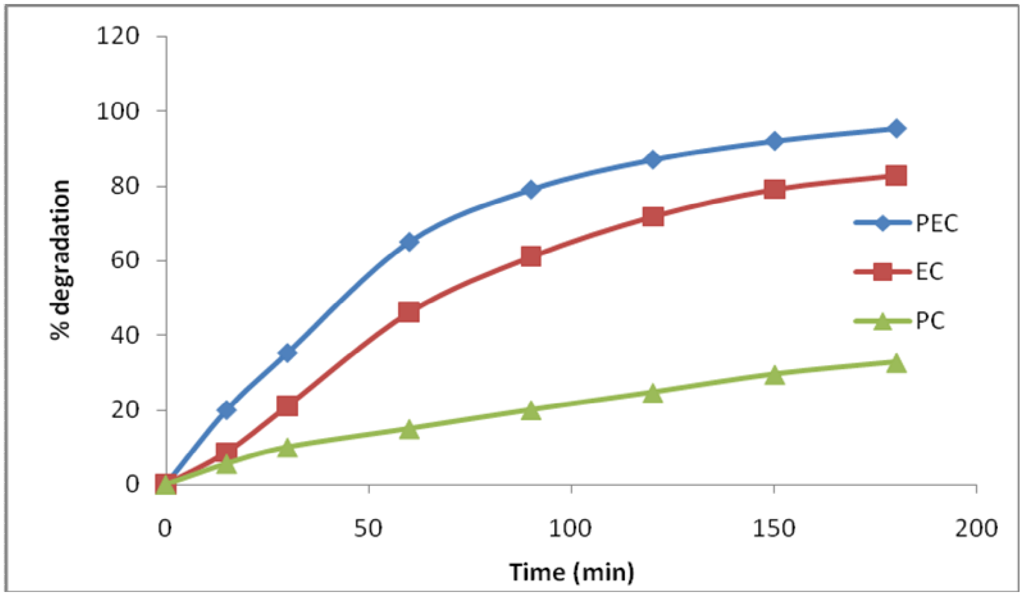


Fig 22: Synergic effect of PEC, EC and PC

CHAPTER-7
CONCLUSION

In the present study the heterogeneous photoelectrocatalytic degradation for the pharmaceutical compound Ornidazole with Ti/TiO_2 coated plate as anode and Cu as cathode was assessed. The following major conclusions were drawn.

The target was to compare the degradation efficiency of PEC, EC and PC for compound Ornidazole under two different light sources. Ti/TiO_2 was fabricated first by anodic oxidation at 20V in alkaline electrolyte solution combined with annealing process examined by SEM and XRD and it illuminated that proposed electrodes were consist of both anatase and rutile Ti/TiO_2 nanocrystalline structure and exhibited better photocatalytic properties. .The residual concentration of compound in solution was measured by UV-Vis spectrophotometer at 319nm at different time intervals. The degradation was performed at different range of pH, concentration and time using BBD under response methodology. The optimized conditions at which maximum degradation was observed were 23ppm concentration, 9.5pH after 170mins. Using these optimal conditions series of experiments were carried out to study the degradation behavior of three processes. The comparing experiments results exhibit that the photoelectrocatalytic degradation for Ornidazole was better than other two processes. Hence photoelectrocatalysis has proven efficient and promising method for the treatment of pharmaceutical compounds present in wastewater as well as economical.

CHAPTER-8
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