Optimized Electrocatalytic Degradation of Ciprofloxacin using Co_3O_4 Coated Stainless Steel Electrodes

Submitted By

MUHAMMAD JAWAD

(Registration # 00000320743)

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Science and Technology (NUST)

Islamabad, Pakistan (2021)

Optimized Electrocatalytic Degradation of Ciprofloxacin using Co_3O_4 Coated Stainless Steel Electrodes

Submitted By

MUHAMMAD JAWAD

Reg Number

00000320743

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

In

Environmental Engineering

Institute of Environmental Science and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

Islamabad, Pakistan (2021)

CERTIFICATE

This dissertation submitted by Mr. Muhammad Jawad is accepted in its present form, by the Institute of Environmental Sciences and Engineering (IESE), School of Civil and Environmental Engineering (SCEE), National University of Sciences and Technology (NUST), Islamabad, Pakistan as satisfying the partial requirement for the degree of Master of Science in Environmental Engineering.

Supervisor_____

Dr. Waqas Qamar Zaman

Assistant Professor

IESE, SCEE, NUST

GEC Member _____

Dr. Muhammad Arshad

Professor

IESE, SCEE, NUST

GEC Member _____

Dr. Zeshan

Associate Professor

IESE, SCEE, NUST

THESIS ACCEPTANCE CERTIFICATE

It is certified that the contents and form of the thesis entitled **"Optimized Electrocatalytic Degradation of Ciprofloxacin using Co_3O_4 Coated Stainless Steel Electrodes"** submitted by Mr. Muhammad Jawad, Registration # 00000230743 has been satisfactory, free of errors and plagiarism for the requirements of the degree of Master of Science in Environmental Engineering. It is further certified that necessary amendments, as pointed out by the scholar's GEC members, have also been incorporated in the said thesis.

Signature: _____

Name of the Supervisor: Dr. Waqas Qamar Zaman

Dated: _____

Signature (HOD): _____

Dated: _____

Principal/Dean: _____

Dated: _____

I dedicate this thesis to my beloved parents and siblings, who have always been a source of inspiration and stood beside me at every moment in my life.

ACKNOWLEDGEMENTS

I am thankful to my Creator Allah Subhana-Watala for guiding me throughout this work at every step and for every new thought set in my mind for improvement. Indeed, I could have done nothing without the priceless help and guidance of Allah. Whosoever helped me throughout my thesis, whether my parents or any other individual was His will, so indeed none be worthy of praise but Allah SWT.

I am profusely thankful to my beloved parents, especially my father, who raised me when I could not walk and who struggled his whole life to make me what I am today. He continued to support me throughout every department of my life.

I would also like to express special thanks to my supervisor Dr. Waqas Qamar Zaman for his help throughout my thesis and for teaching me “Design Expert” software for which I had no previous background.

I would also like to pay special thanks to lab Engineer Amir Khan for his tremendous support and cooperation. Each time I got stuck in something, he came up with the solution. Without his help, I would not have completed my thesis. I appreciate their patience and guidance throughout the whole thesis.

I would also like to thank Dr. Zeshan and Dr. Muhammad Arshad for being on my thesis guidance and evaluation committee.

Finally, I would like to express my gratitude to all the individuals who have rendered valuable assistance to my study.

Muhammad Jawad

TABLE OF CONTENTS

Contents

LIST OF ABBREVIATIONS

CIP	Ciprofloxacin
RSM	Response surface methodology
PVDF	Polyvinylidene Fluoride
SDGs	Sustainable development goals
FOs	Fluoroquinolones
NOR	Norfloxacin
ENR	Enrofloxacin
BDD	Boron doped diamond
DCBR	Differential column batch reactor
TOC	Total organic carbon
ECD	Electrical current density
HCl	Hydrochloric acid
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide oxide
Co	Cobalt Oxide
CO_2	Carbon dioxide
pH	Power of Hydrogen
RPM	Revaluations per minute

List of Figures

LIST OF TABLES

ABSTRACT

Currently, increased consumption of antibiotics has escalated their presence in the water environment. Their presence in water can adversely affect human health and aquatic life. Ciprofloxacin (CIP) is one such pollutant that needs consideration due to its increasing concentration in water resources. Further, these emerging contaminants are very persistent against conventional remedial technologies. However, electrochemical degradation of such pollutants is a viable option at current that ensures maximum removal. In this study, the removal of CIP was carried out electrochemically on using stainless steel electrodes coated with cobalt oxide. Also, "Design Expert 11" software was used in this study to optimize the process parameters. The optimization of parameters was done while analyzing them in their effective range. The range of initial concentration of CIP in wastewater (15-35 mg/L), applied voltage (2-8 V) and the diffuse airflow rate was (1.6 -3.5 L/min). By using stainless steel plates, the optimized parameters for the removal of CIP were achieved. The optimum parameters were the initial concentration of ciprofloxacin 25 mg/L, air flow rate 2.5 L/min, and the applied voltage of 6V. Through these optimized parameters, the removal of CIP from wastewater was achieved up to 89% with a hydraulic retention time (HRT) of 27-30 minutes using stainless steel electrodes. Coating of cobalt oxide (Co_3O_4) on stainless steel plates reduced the HRT of process up to 22%. The removal of CIP from wastewater starts at a maximum rate of 21 minutes. Results show that CIP's removal efficiency from wastewater on those optimized parameters was increased to 91.5% due to the coating of Co_3O_4. The different coating of catalyst materials is recommended on stainless steel plates to remove CIP.

Key words: Emerging contaminant, electrochemical degradation, stainless steel plates, cobalt oxide.

Chapter 1

INTRODUCTION

1. Background

Over the past few decades, access to clean drinking water has become a big issue worldwide. The issues related to polluted water are well documented, and these are environmental, economic and health related. Around 1.2 billion people, who are one-fifth of the world population, are suffering from water scarcity, and soon 500 million people are likely to suffer. About 25 % of the world's population is experiencing an economical water shortage. There is also a lack of technologies to treat drinking water and wastewater and their proper use in developing countries (UNDP, 2006).

Water scarcity is the imbalance between availability and demand. The water demand is due to improved living standards with time and urbanization. These imbalances are prominent in Pakistan. Pakistan is among the 36 most water-stressed countries mainly because of prolonged droughts and the lack of efficient treatment technologies [1]. Access to safe drinking water is the right of every person, but about 60% of Pakistanis are deprived of this basic need of life. Also, as Pakistan relies heavily on agriculture, 25% of the GDP, water stress is an issue in terms of food security [2]

In the current era, water pollution is one of the big issues, threatening human health and disturbing the ecological balance. With the increase in water demand due to population growth and decrease in water availability due to climate change, it is necessary to treat the wastewater to reduce the stress on natural water. Wastewater treatment and reuse of water are necessary nowadays to fulfill the required amount of water. Water is one of the main ingredients for the survival of animals and plants. Water pollution is caused by many factors and different waste disposal in the water. Disposal of waste in water or increase in the number of contaminants degrades water quality and remains unfit for drinking purposes.

2. Threat to human and animal health

The pharmaceutical industry has encountered a steady incline in the antibiotic resistance over the past few decades. Various national and global health agencies, including the World Health Organization and US Centre for Disease Control, have verified the increase in resistance of disease-causing microbes, resulting in the decline in the efficacy of antibiotics. In the US, the reported number of deaths from nosocomial diseases increased several folds from 13,300 in 1992 to 98,000 by 2011 due to resistance in bacteria. Some of the pathogens that have contributed to this death toll include *Enterococci, Staphylococcus aureus* and *tuberculosis,* which have developed resistance to vancomycin, methicillin, and multiple drugs, respectively. At least one class of antibiotics is currently resistant to approximately 70% of nosocomial infections. Antimicrobial susceptibility of 13,993 P. *aeruginosa* isolates from 102 healthcare facilities was tested in 2007 [3] for 4 different antibiotics. Of these, 4253 isolates were resistant to CIP, 2967 to imipenem (IPM), 2462 strains were resistant to ceftazidime (CAZ) while Amika (AMK) was ineffective against 2691 isolates.

The presence of resistant bacteria in the water systems poses a significant threat to human health by transferring genes from non-pathogenic to pathogenic bacteria. Streptomycin, tetracycline, and ampicillin are a few medicines to name resistance genes that have been developed, and these antibiotic resistance genes (ARGs) are transferable from bacteria to bacteria. Chlorination is not a guaranteed way for complete sanitization of drinking water. It has been observed that there are certain resistant microbes that survive chlorination and thus enter the drinking water system. Studies show that certain strains of the pathogenic bacteria isolated from the chlorinated drinking water developed resistance to approximately all the antibiotics that were tested.

Although the concentration of pharmaceutical compounds detected in the water system is quite less, their effectiveness at a minute concentration for damaging specific proteins makes their presence even at these low concentrations a risk to human and animal health. Diclofenac is an analgesic that causes a remarkable decrease in the vulture population in Pakistan and India by causing renal failure. The oriental white-backed vulture was the most abundant large bird predator in the late 20th century in India. Its population observed a severe hit due to the drug, diclofenac. Close to 95% of the vulture population was lost due to this drug by 2003 [4]. By 2008, this percentage rose to 99.9%, essentially bringing the species to the brink of extinction in the area.

Due to the nature of the danger and the risk posed by the release of pharmaceutical compounds into the environment, several studies have been conducted on these products' human health and environmental risk assessment. Researchers debate heavily on the level of harm caused by these substances due to their low concentration. Some of the researchers maintain the view that low amount of antibiotics in the environment will not cause considerable damage to human health while others are of the opinion that even the low quantities can affect life, particularly in aquatic ecosystem. There is a dire need to study the harmful effects of pharmaceutical compounds in the long term and develop an effective and accurate risk assessment procedure using the already available models [5].

3. Classification

Classification of antibiotics can be done based on bacterial spectrum, administration route, bactericidal activity, or the origin, whether natural or manufactured. However, the most widely used and significant classification method lies in the chemical structure of the drug. The antibiotics in a specific class developed based on structure usually contain similar characteristics including toxic effects, allergic reactions, and effectiveness patterns.

4. General Use Pattern

Since their discovery in 1900s, antibiotics have been in vigorous use for the protection of public health from microbial infections, disease diagnosis and growth promotion in animals (Fink et al. 2012). This growth promotion is attributed to four major mechanisms [6] namely decrease in microbial utilization of nutrients, enhanced nutrient uptake via thinner intestinal wall of antibiotic fed animals, reduction of infections and a decline in growth inhibiting microbial metabolites. Currently, more than 5000 chemicals are registered for use as medicines for humans and animals [7] with a global annual consumption reported as high as 100,000 to 200,000 tons [8]. Such large consumption has led to significant release of these compounds into the environment. The presence of active compounds of pharmaceutical origin was first reported in 1970 [9] but it gained attention as an emerging pollutant in late mid 1990s with the development of analytical technologies [10].

Due to the inadequacy of conventional water treatment technologies, the concentration of FQs in water aquifers is continuously increasing day by day [11]. Moreover, antibiotics in wastewater also reduce the efficiency of biological treatments due to adverse effects on microbial activities.

Ciprofloxacin (CIP) is one such member of the FQs family that easily escapes the conventional and biological treatment processes [12]. The high concentration of CIP (35.5-64.4 ng/L) in the municipal wastewater was reduced to only 47% in the wastewater treatment plants (WWTP) in Riga (Latvia) after treatment [13]. Researchers have employed many processes for the elimination of CIP such as Electro- Fenton [14], UV and UV/H_2O_2 [15], Peroxydisulfate [16], Electrochemical Peroxidation [17], Photo- Fenton [18], Sono Catalysis [19], Photolytic, and Photocatalytic processes. Among all, the Electrochemical Oxidation process (EO) is contemplated as more efficient with regard to transforming organic compounds into simpler ones or complete mineralization [11].

Process parameters play a very important role in the degradation of CIP. For the degradation of CIP different combinations of parameters were studied by different researchers. In the degradation of CIP through Boron-doped diamond anode the experimental parameters were pH, initial concentration of pollutant and current density [20]. The process parameters used in the electrochemical degradation of CIP through Sb-doped SnO_2 electrodes were effects of electrolyte concentration, coating times and pH [21]. In the degradation of CIP via double sided β-PbO_2 anode in a flow reactor the process parameters were pH, flow rate, temperature and current density [22]. Degradation of CIP through electrochemical peroxidation process, the process parameters were initial concentration, air flow rate and current density [23]. These researchers used different combination of process parameters having different range of parameters. So, for removal of CIP through electrochemical process required a dire need for the optimization of process parameters. In this regard "Design Expert" software was used for Response surface methodology (RSM) to achieve the optimum parameters for the degradation of CIP.

Along with optimization electrodes material also play a vital role in the degradation of CIP. For attaining a high oxidation rate and current efficiencies, selecting suitable anode material is very important [24]. The mineralization of organic compounds through the electrochemical process commonly involves the electro-generation of hydroxyl radicles ($OH^{\cdot}$). The oxidative reactivity of these radicles depend upon their interaction with the anode surface [25]. In this regard stainless steel plates coated with cobalt oxide were used for the degradation of CIP. The stainless steel was selected as electrodes because of high ductility, toughness, lower corrosion, and excellent strength [26].

In the current study the electrochemical degradation of CIP was carried out through stainless steel plates electrodes coated with cobalt oxide catalyst. For the optimization of process parameters RSM were used. The range of process parameters for optimization were initial concentration of CIP (15-35) mg/L, diffuse air flow rate (1.6-3.5) L/min, time varied from (1-40) min and range of applied voltage was (2-8) v.

5. Aim of the study

The degradation of wastewater containing antibiotic ciprofloxacin is not achieved in a good amount by using biological or physical treatment processes. Ciprofloxacin degradation is necessary because of its adverse impacts on human health and aquatic animals. Our study aims to degrade CIP electrochemically using stainless steel plates. The stainless-steel plates are highly resistant to corrosion and have high durability.

6. Objectives:

The aims of this study include:

- Optimization of process variables for efficient Ciprofloxacin degradation
- Effect of catalyst Cobalt Oxide on degradation of ciprofloxacin

7. Relevance of national need:

As we know water scarcity increasing day by day. Due to increasing demand of water, we must be focused on recycling and reuse of water. On the other hand, raise in different types of diseases related to use of polluted is rapidly increasing. Therefore, for protection of public health and aquatic life wastewater treatment is necessary.

8. Advantages:

Following are the advantages of this research work:

I. Facile application of the process for pollutant degradation.

II. Robust process ensuring maximum removal efficiency.

III. Overall, environmentally benign process with byproducts of O_2, H_2 and CO_2.

9. Areas of application:

The electrochemical degradation of ciprofloxacin using stainless steel plates is best applicable for water containing CIP. Through this process we can easily and efficiently degrade the contaminants in wastewater. This process can be used to treat CIP effluent from pharmaceutical industries and municipal wastewater. In addition, this process can also be integrated with conventional treatment processes in practice.

Chapter 2

LITERATURE REVIEW

2.1 Pakistan water problems

Approach to a safe and pure water supply is an urgent requirement for the people of Pakistan. In Pakistan, available water is less per person and is deteriorating over time. The country is rated as the highly water-stressed in the world. It is also expected to be rated as “water scarce” in the coming years. This condition may also have adverse implications for energy production concerning the role of water in thermal and hydroelectric power production [27].

In Pakistan, the per capita availability of water is annually 1,017 cubic meters and decreases near 1,000 cubic meters. The Indus basin aquifer is found the second highly overstressed by the NASA researchers and deteriorating with little to no recharge. This aquifer also lies on the world’s resource institute water stress index.

Experts predict that one out of three people in Pakistan is facing critical water shortage, "threatening their very survival"

2.2 Manufacturing Industries/ Human Medicine

Little attention had been paid previously to the pharmaceutical products released from manufacturing plants, but in recent years, concentrations as high as 31 mg/ L, as observed in case of CIP, were found in the effluents released in some of the Asian countries (Larsson et al., 2007; Li et al., 2008a, b). Even the developed countries can have manufacturing facilities as a significant source of antibiotics for sewage treatment plants (Thomas, 2008). The per capita usage of human medicine varies markedly across national boundaries [28]. Medicines used extensively in one country might be used sparsely or be banned completely in another. The use of prescribed and non-prescribed medicines varies greatly in different countries. A large portion of the medicines consumed are excreted out from the body in bioactive form and find their way to the environment.

2.3 Sources of Antibiotics in Environment

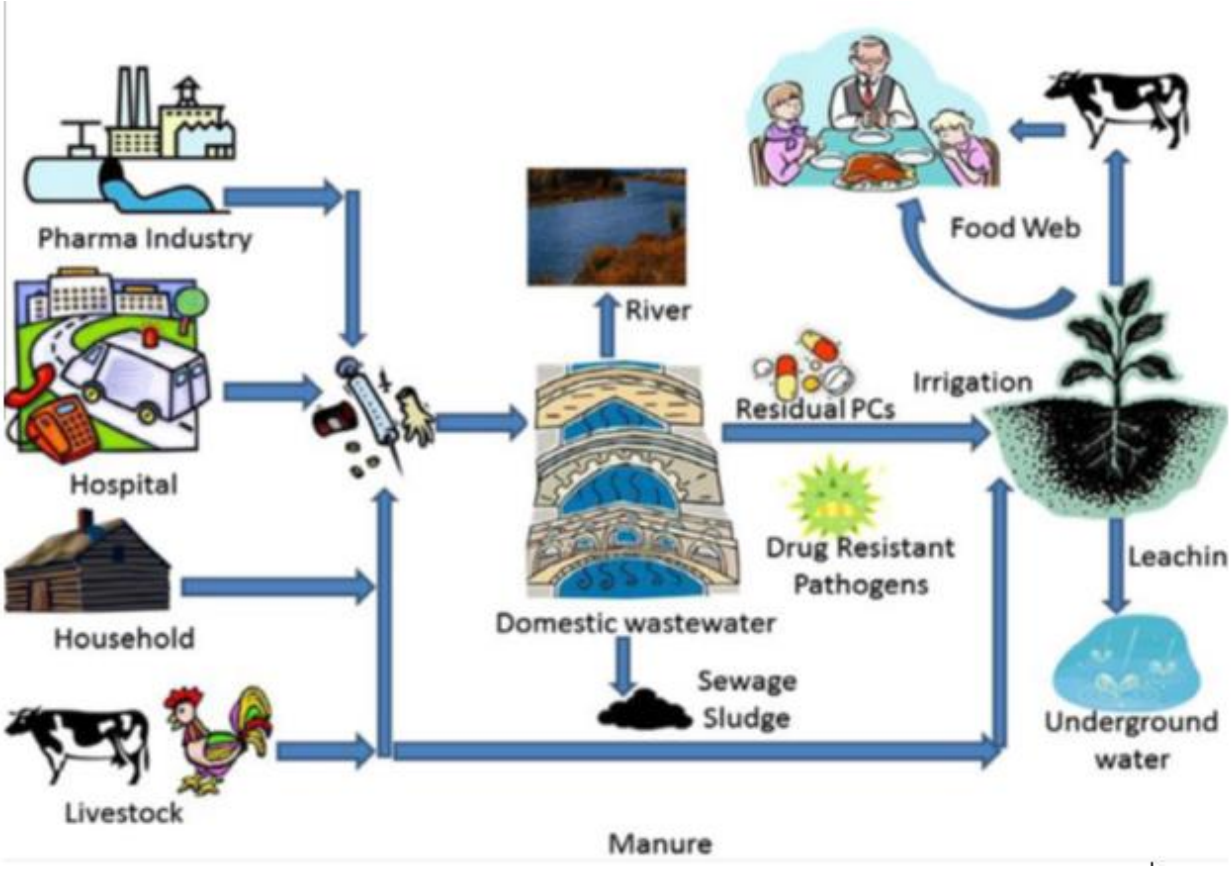

Figure 2.1 Possible routes of antibiotics

Some possible routes of antibiotics to different environmental compartments are shown in figure 2.1 (Rehman et al., 2013).

2.4 Animal husbandry

The use of pharmaceutical products in animal husbandry became popular in the early 1950s as feed additives and for the prevention and control of various diseases to enhance livestock production. The antibiotics consumed by animals are not completely utilized. Drugs, poorly absorbed in the animal gut, along with the feed additives, are excreted (Du et al., 2012), and due to incomplete metabolism, about 25-75% of these are in bioactive form (Zheng et al., 2011). The excretion rate depends on the route of antibiotic consumption, its chemistry, amount of time passed after drug administration and the excreting species. For tetracyclines and sulfonamides, the general excretion rate has been observed to range between 40 and 90% (Sorensen, 2001).

2.5 Fluoroquinolones

Fluoroquinolones (FQs) class of compounds is composed of a growing group of synthetic antimicrobial agents that contains one fluorine molecule at the 6-position of the quinolone nucleus. Despite the similarity in the basic structure of these molecules, their pharmacokinetic characteristics, physicochemical properties, and microbial activities differ significantly among compounds [29]. Due to their excessive use in the treatment of human (since 1980s) and animal diseases (ANSES, 2012; European Medicines Agency, 2012; Pico and Andreu, 2007), FQs have become a serious cause of concern in environmental pollution. They form the third-largest class of antibiotics with a global market share of about 17% and a net share of 7.1 billion US dollars [30]. The FQs consumed are largely excreted and enter the sewage system.

Fluoroquinolones target bacterial cells by inhibiting two of the enzymes associated with the synthesis of bacterial DNA. Fluoroquinolones are specific in their action as they 16 target the enzymes topoisomerases essential to bacterial DNA replication but are absent in human cells. DNA topoisomerases separate the two DNA strands at the time of replication and reseal the parent strands after inserting another DNA strand through the break (Rocha *et al*., 2011). Fluoroquinolones create conformational changes by interacting with the enzyme-bound DNA complex, thereby inhibiting normal enzyme activity. The antibiotic-enzyme-DNA complex formed prevents DNA replication by blocking the replication fork and resulting in obstruction of DNA synthesis leading to quick cell death.

2.5.1 Environmental Presence & Transformation

The presence of FQs in the environment has been reported frequently due to their extensive use and accumulation. In Switzerland, the concentration of CIP detected in domestic sludge, and wastewater treatment plants (WWTP) was 249-405 and 45-567 ng/L, respectively, while that of norfloxacin (NOR) was 45-120 and 34-367 ng/L, respectively [31]; [32]. In US, FQs as high as 0.6-2 μgL^{-1} were detected in wastewaters. From the samples taken from 139 US streams, the CIP and NOR concentrations were 0.02 and 0.12 $\mu g\ L^{-1,}$ respectively. Fink *et al*. (2012) reported the range of 0.7-124.5 $\mu g\ L^{-1}$ for CIP in the wastewater of a Swiss hospital.

On entering the environment, FQs are degraded by various processes. Three of the most common ways these are transformed in the environment are biodegradation, photolysis, and oxidation via mineral oxides. The hydrolysis process is not involved in the breakdown of FQs [33]. Photolysis

primarily comes into effect in the degradation of FQs in surface water ([34, 35]. However, the process is effective only for a few millimetres of depth of sediment surface, making the process slow. The half-life reported for photolysis degraded FQs in surface waters ranges from 6-24d ([36]; Xu *et al*., 2009). Oxidation of FQs by mineral oxides is another important process of FQ transformation in the environment (Zhang and Huang, 2007). Biodegradation of FQs sobbed to the soil sediments has been observed to be ineffectual (Lai and Lin, 2009). The half-life times of more than 217 days have been reported for FQs in studies where sludge and manure were applied as a fertilizer for plants 17 (Rosendahl *et al*., 2012). As a result, despite the various processes for the degradation of FQs, the strong sorption of these antibiotics to soil sediments and their unavailability to microbes by their migration to nano-pores in the soil matrix makes FQ highly persistent, with half-lives 200 times more than the FQs in aqueous sediment matrices (Alexander, 2000).

2.6 Ciprofloxacin

Ciprofloxacin (CIP), belonging to the fluoroquinolone class of antibiotics, was patented by Bayer in 1983. It possesses a broad range of use for human and animal diseases against gram-positive and negative bacteria [37]. Ciprofloxacin with a half-life of 4 h in the human body has been identified by WHO (2007) as a crucial antibacterial human medicine. It is the most frequently prescribed FQ in European countries [38]. It is used to treat bone and joint infections, sexually transmitted diseases, tuberculosis, and typhoid fever to name a few diseases (Rocha *et al*., 2011). It is a proven genotoxic drug that is regularly detected in the natural environment [39]. It has been included in an EU project as a crucial substance in the eradication of pharmaceutical residues from the healthcare sector, with its concentration detected in the range up to 0.083 mg L^{-1} (Hartmann *et al*., 1998).

Approximately 45-62% of this drug is excreted by human urine and 15-25% of it is removed from the body in the form of feces [40]. Hence, CIP finds its way into the environment via sewage systems, water treatment plants, or drug manufacturing facilities. Other pathways of CIP to the environment include applying livestock manure, irrigation of land with contaminated water, and leaching in landfills (Boxall *et al.*, 2003;[41].

2.6.1 Mechanism of Action

CIP shows bactericidal action against a wide range of gram positive and negative bacteria. In gram-positive bacteria, it prevents bacterial multiplication by targeting DNA gyrase (a topoisomerase II) which is involved in the super coiling of circular DNA while in Gram-negative bacteria, it targets topoisomerase IV enzyme, that unwinds the super coiled circular DNA [42] thus disrupting enzymes necessary for the replication, transcription, repair, and recombination of DNA [43].

2.6.2 Clinical Particulars

CIP is used for the treatment of infections of respiratory tract [44], kidney, urinary tract [45], middle ear, genital organs, and abdominal cavity. Some other diseases treated by CIP include infections of eyes, skin and soft tissue, bones and joints and diarrhea. It is also used to treat pneumonias caused by bacterial species including *Escherichia coli*, *Enterobacter* spp., *Pseudomonas aeruginosa* and *staphylococci* (Medicine pamphlet).

2.6.3 Side Effects

Detailed results from clinical trials showed certain side effects including nausea (2.5%), diarrhea (1.6%), abnormal liver function tests (1.3%), vomiting (1.0%) and rash (1%) cases (Medicine pamphlet).

2.6.4 Environmental Presence

The oral consumption of CIP has increased up to 30% over the last few years [46]. Most of the data regarding the presence of FQs in the soil is on enrofloxacin (ENR) and CIP with CIP ranging from 4 to 40.7% in chicken manure and from 0.65 to 2.1 mg kg^{-1} in poultry manure (Leal *et al*., 2012). Wu *et al*. (2014) reported the ubiquitous presence of four quinolones in the soils of 5 organic vegetable farms in Southern China. The selected antibiotics were detected at a frequency of >97% at concentrations ranging from 0-42 µg/kg. The frequency of drug appearance frequency decreased in the order of ENR>CIP>NOR. The concentrations of CIP detected in different environments is listed in Table 2.1

Table 2.1: Concentrations of CIP in environment Concentrations are reported as: mg/L; values with * indicate mg/kg

Matrix	Detected Conc	Regions	Reference
WWTP effluents	31	India	[47]
Agricultural soils	0.75 *	Austria	[48]
River	$6.7x10^{-3}$ - $1.02x10^{-3}$	Portugal	[49]
Sewage treatment plants (STPs)	0.056-0.211	Coimbra	[50]
Ground water	$7x10^{-3}$-$14x10^{-3}$	India	[51]
Surface water	0.36	US	[52]
Chicken dung	0.7 to 45.6 *	China	[53]
Production facility wastewater	4.9	Korea	[54]
Hospital effluents	0.007-0.1245	Swiss	[55]
Poultry manure	0.65-2.1*	Brazil	[56]
River	$1.25x10^{-3}$	Pakistan	[57]

The ecotoxic risk value defined by Veterinary Medicine International Coordination commission for antibiotics is 100 µg/kg. As shown by (Golet et al. 2002), CIP persists in the environment, who observed their presence on land even 13 months after biosolid application. This finding was later corroborated by [58]and [59].

2.6.5 Bacterial Resistance to CIP

The difference in structure and properties of fluoroquinolones from other medicines and their different modes of action implies that the microbes are resistant to the medicines such as tetracyclines, aminoglycosides, macrolides, etc. Cephalosporins might be susceptible to CIP. The development of microbial resistance against CIP and other FQs, on the other hand, usually results from reduced outer membrane permeability and mutations in DNA gyrases.

2.7 Degradation of ciprofloxacin

Antibiotics on reaching the aquatic environment face the natural elements that can bring about their degradation. The fate of fluoroquinolones, including CIP, on the degradation front, can be understood only by contemplating biotic and abiotic factors. Biotic factors involve biodegradation by microorganisms present in the aquatic environment, while photochemical reactions play a vital role in degradation by abiotic factors in the surface layers. The mechanism involved here (Figure 2.2) is the replacement of piperazinyl ring present in the seventh position [60].

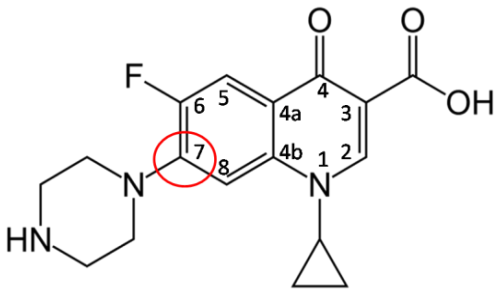

Figure 2.2 Degradation mechanism of CIP

Degradation mechanism of CIP by removal of piperazinyl ring at the seventh position [60].

The maximum number of electrochemical oxidation processes were used to remove contaminants, which are not degradable either by using biological degradation or physical processes. A boron-doped diamond (BDD) anode/Ti cathode were prepared and set in differential column batch reactor (DCBR) was used for the electrochemical oxidation of CIP. The feed in the DCBR system was in uniform flow condition confirmed through computational fluid dynamics (CFD) simulation analysis. The results obtained through this set-up show that the BDD anode/Ti cathode is useful for removing CIP from wastewater, having high removal efficiency. The total removal of CIP was achieved within 20 minutes.

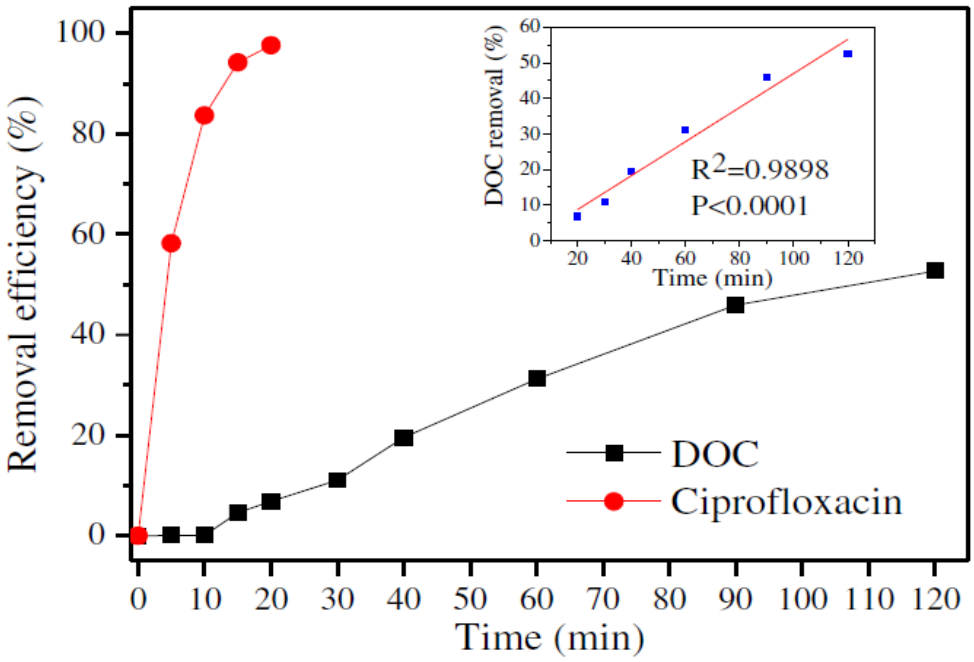

Figure 2.3 Time Vs removal efficiency

The parameters that effect the removal of CIP is initial concentration of contaminant, pH, current density, and the concentration of electrolyte [61].

For the electrocatalytic degradation of CIP electrodes were prepared of Sb-doped SnO_2 by using of the practical sol-gel method. The degradation of CIP was achieved in an aqueous solution. Electrochemical characterization of electrodes having different layers coated, electrode having 16 times coating had the highest O_2 generation potential of 2.2 V and the highest active area for the electrochemical purpose of 3.74 cm^2. The experimental results of scanning electron microscopy and X-ray diffraction showed that the coating time affects the crystal structure and surface morphology of the electrodes and affects the removal efficiency of ciprofloxacin. SSO-electrode having 16 coatings had a denser surface, smaller grain size (28.6) and higher crystallinity. The performance of these electrodes was optimized and achieved the best removal efficiency of almost 100% within 60 minutes. The durability and reusability of electrodes were also assessed. The result shows that the preparation of sol gel coating method is valuable for the electrochemical degradation of antibiotics [21].

The results of BDD anodes having different boron doping as of ppm of 100, 500 and 2500 ppm and sp^3/sp^2 carbon ratios of 215, 325 and 284 respectively were assessed for the electrochemical

degradation of CIP (0.5 L of 50 mg/L in 0.10M Na_2SO_4 at 25°C) in a filter press reactor and using a recirculating flow system. The process's performance was monitored by calculating the remaining concentration of CIP, total organic carbon (TOC) concentration, and oxidation intermediates. The parameters affecting the performance of the process are the pH and current density. All the anodes were affected while varying the pH and the current density. The results concluded that the BDD 100 anode is the more efficient anode for the removal of CIP. By increasing the turbulence in the reactor, enhanced mass transport was achieved at a low flow rate. Ciprofloxacin removal at the fastest rate was achieved within 20 minutes having the other parameters flux of j= 30 mA/cm^2, pH =10 and qv = 2.5 L/min and providing bypass turbulence [62].

By using double-sided Ti-Pt/β-PbO_2 anode in a filter press reactor, the electrochemical degradation of CIP (25 mg/L in 0.10 mol/L Na_2SO_4) was investigated by monitoring oxidation intermediates and follow-up of antimicrobial activity against Escherichia coli. The assessed performance affecting parameters are solution pH, current density, flow rate, and temperature. These parameters were affecting the removal of CIP. For the removal of CIP, the optimized parameters were identified these are pH=10, qv= 6.5 L/min, j=30 mA/cm^2 and the temperature was 25°C. CIP removal was achieved within 2 h [22].

The removal of CIP through electrochemical peroxidation process was investigated. The performance and removal efficiency of the process was monitored. Different conditions were checked for the removal of CIP. The process was carried out in an electrolytic cell with stainless-steel plate electrodes. The required amount of oxygen was supplied from the bottom of electrolytic cell. The parameters which were assessed in the process was H_2O_2 (25-1000 mg/L), the current density of (ECD) (19.71-164.26 A/m^2), Fe^{+2} (0.5 and 2.0 mg/L), pH of the solution (2.5-9.0) and electrolysis treatment time was varied between (5-90 min). These parameters were varied and checked the efficiency of the process. The best suitable parameters for the process were selected upon varying these parameters. During the process, the concentration of CIP, total organic carbon (TOC) and pH of the solution were monitored. During the monitoring stage, other different by products and intermediates by-products was

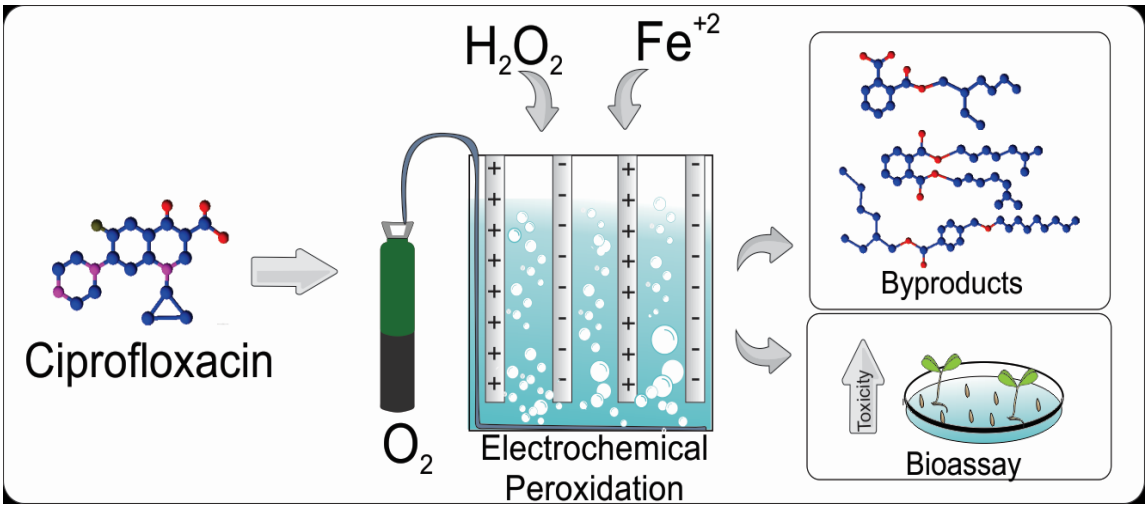

Figure 2.4 Electrochemical Peroxidation of CIP

identified and quantified. The solution's final concentration was checked in terms of median lethal concentration. Lactuca sativa was used as base for the bioassays test for this test. The parameters upon which efficiency of the process is maximum was ECD 32.85 A/m^2, initial concentration of H_2O_2 100 mg/L, initial pH of the stock solution 3 and time for electrolysis was 30 minutes. These optimal parameters were attained for the removal of CIP. The low toxicity level of the CIP was achieved at an initial time means less than 45 minutes. Through this process the toxicity level of the CIP reduced to a considerable level [23].

Systematically, ciprofloxacin's electrochemical degradation was investigated using SnO_2-Sb/Ti electrodes. The parameters effecting the removal efficiency of the process was studied and monitored. These parameters are initial concentration, current density, and pH of the solution. From the results it was achieved that SnO_2-Sb/Ti electrodes are highly effective for removing CIP. The best optimum parameters for the removal of CIP were CIP initial concentration 50 mg/L, current density of 30 mA/cm^2 and time required for the process is 30 minutes. The removal of CIP achieved was 99.5 %. The reaction followed a first order kinetics model. The effect of current density and initial concentration of CIP were prominent for the removal efficiency. The effect of pH on the removal efficiency were observed and shows prominent effect. Finding the final CIP concentration after treatment was observed and noted using ion chromatography and liquid chromatography and combined with mass spectrometry (LC-MS) [17].

Contaminants from the pharmaceutical industry are the main source of diseases and mortality to aquatic animals and causes several diseases to the human community. For the treatment of such

type of water still now proper treatment technology is developed which is cost-effective and efficient removal of contaminants take place. To remove complete detoxification of CIP a combined treatment technique (electrochemical oxidation and adsorption processes) was developed. For the electrochemical degradation of CIP, a Titanium-based tri-metal oxide mesh type anode was used. The time required for the treatment and pH for the process were evaluated thoroughly. The byproducts generated during the degradation of CIP such as Sulfate, fluoride ions and other toxic byproducts were removed through a simple adsorption process. For the adsorption of these byproducts, activated charcoal was used for 90 min.

At different time intervals through nematode Caenorhabditis elegans species the toxicity of water was assessed by noting the expressions of important stress-responsive genes viz., sod-3, hsp-16.2, ctl-1,2,3, and gst-4. This method combines electrochemical degradation of CIP and adsorption of byproducts, the degradation of CIP was achieved better, and the cost of process is less. [63].

In all the studied literature it has been observed that along implying different electrode materials varying process parameters have been used for degradation of CIP.

Chapter 3

MATERIALS AND METHODS

The aim of this study was to electrochemically degrade the anthropogenic antibiotic, ciprofloxacin in wastewater. The concentration of FOs detected in wastewater is in µg/L to mg/L. However, their continued release into the environment and permanent presence makes them pseudo-persistent contaminants. The current study was based on removal of CIP using stainless steel from wastewater using different concentration of CIP (15-35 mg/L).

3.1 Chemicals preparation

Ciprofloxacin (CIP) Sigma Aldrich (>99.4% purity), selected for the current study, was obtained from Biotechnology lab IESE NUST Islamabad Pakistan. It was used in powder form for the preparation of different stock solutions in ultrapure water. Sodium Hydroxide (NaOH), and Hydrochloric acid (HCl) were used to adjust the pH of the solution. To increase the electrical conductivity of the solution, Sodium Chloride (NaCl) was added into the solution. Hydrogen per Oxide (H_2O_2) was added to promote the reaction.

For the preparation of catalyst soluble starch 2.5g was dissolved in 150 mL deionized water. Cobalt Hexahydrate ($CoCl_2.6H_2O$) 0.1 molar solution was added to boiling starch solution. For the pH adjustment few drops of ammonia were added into the solution [64].

For coating the catalyst on stainless steel plates the chemicals were used Polyvinylidene Fluoride (PVDF) (International laboratory, USA) as a binder in organic solvent N, N-Dimethylacetamide solution (>99%, Merck, USA) [65].

3.2 Electrochemical reactor and experimental setup

A rectangular box of acrylic was prepared with dimensions 12, 7 and 6 cm. Then four 304 stainless steel plates of dimension 7, 3 and 0.2 cm were put upright in the acrylic box. An Air diffuser was provided at the bottom of the box to provide diffuse oxygen to enhance the efficiency of the process. Terminals of variables voltage supply was connected at the top of stainless-steel plates.

For the experimental procedure, different stock solutions of CIP were prepared with different CIP concentrations developed through Stat Ease Design Expert software. To prepare stock solution,

various amounts of CIP were added into distilled water. The stock solution was prepared in 1liter (1000ml) of distilled water. Stock solution of 450ml was used for the experimental procedure. The different parameters used in the experiment were concentration of ciprofloxacin, applied voltage, flowrate of diffuse air and pH of the solution. The combination of these parameters and the number of runs was developed through "Design Expert" software shown in the table 3.1. The range of parameters put in the software were voltage (2-8V), air flowrate (1.6-3.5 L/min), the concentration of CIP (15-35 mg/L) and having a constant value of pH 3. The designed parameters developed through software are shown in table 3.1.

Table.3.1 Combination of Experimental parameters generated through Design

	Factor 1	**Factor 2**	**Factor 3**
Run	A: Conc; of CIP (mg/L)	B: Air flow rate (L/min)	C: Voltage (V)
1	25	2.55	6
2	8	2.55	6
3	25	2.55	2.63
4	35	1.6	4
5	35	1.6	8
6	15	3.5	8
7	41	2.55	6
8	25	3.5	6
9	35	3.5	4
10	15	1.6	4
11	25	1.6	6
12	35	3.5	8
13	25	2.55	9.36
14	15	3.5	4
15	25	2.55	6
16	15	1.6	8
17	25	2.55	6
18	25	2.55	6
19	25	2.55	6
20	25	2.55	6

3.3 Analytical determination

The initial pH of the solution was measured through a digital pH-meter (Eutech Instruments, model PH 700). A diluted solution of CIP was prepared to span from 1-25 mg/L at a pH of 5.7 for the UV-vis analysis, spectrophotometer UV-vis (Dynamica DB-20) was used to determine the concentration of CIP at an absorbance of 275 nm wavelength [23].

By using the different combination of parameters developed through Design Expert software different value of response achieved in laboratory. The designed experiments were performed one by one in laboratory. The time required for each experiment was selected 30 minutes form the literature [23]. After 30 minutes of treatment, a sample of 5ml was taken from the treated wastewater. After collecting the sample, it was kept in the centrifuge for 2 minutes at an rpm of 2800. Through spectrophotometry, the absorbance of the sample was checked at 275 nm wavelength [23]. The same procedure was performed for all the 20 designed experiments. After getting the final concentrations of CIP the best parameters for the removal of ciprofloxacin were selected through RSM.

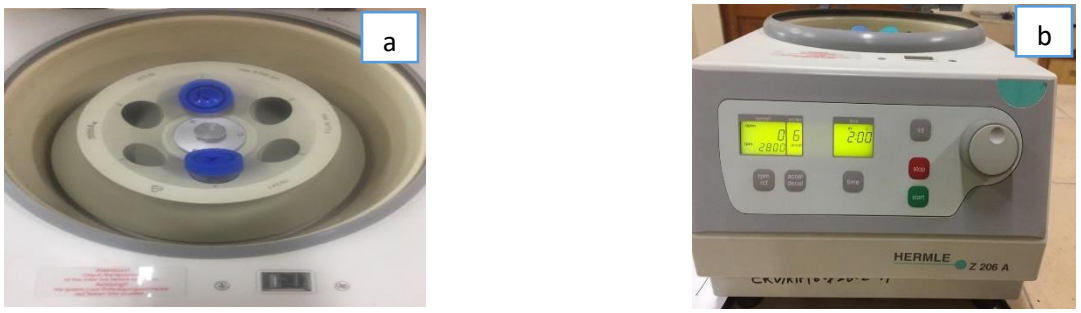

Figure 3.1 a and b Centrifuge

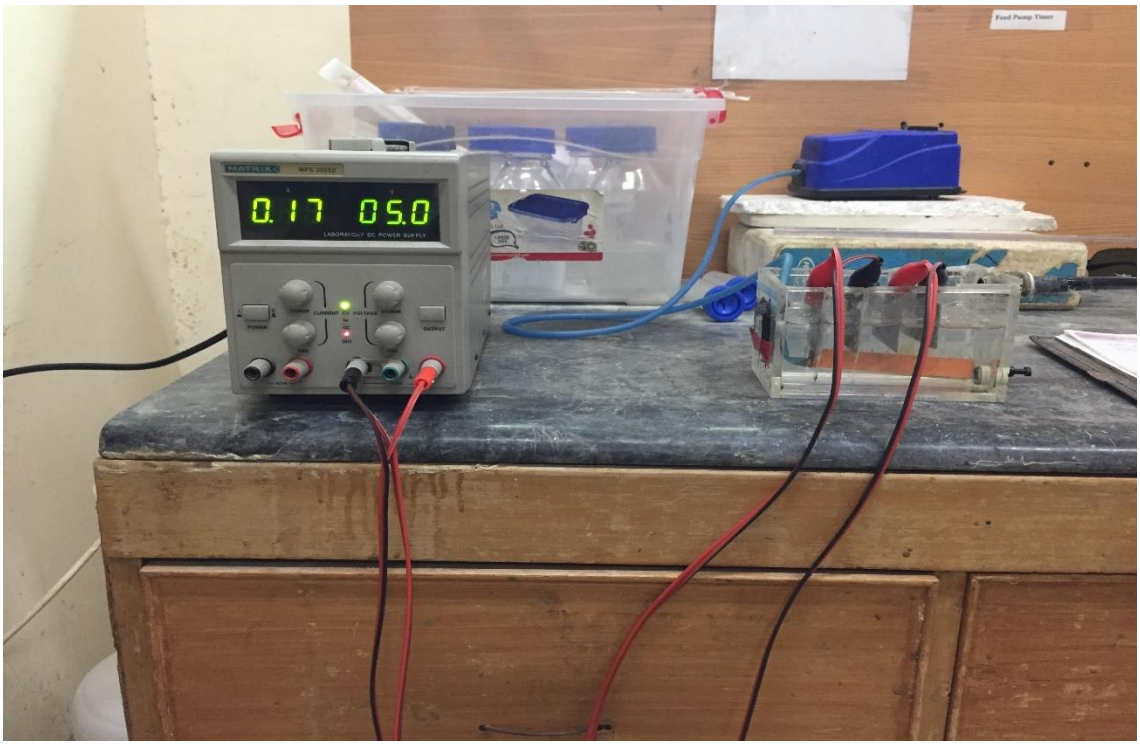

Fig. 3.2 Experimental setup

3.4 Optimization of parameters

Optimizing refers to improving the output of a process, a system, or a product to achieve maximum benefits. Optimization means discovering conditions at which the procedure produces the best possible result [66]. Through Design Expert software using the data collected from laboratory after performing 20 numbers of experiments, the parameters for the removal of CIP were optimized. After optimization those parameters were validated again in the laboratory to check the model's efficiency.

3.5 Preparation of Catalyst

For the preparation of catalyst 2.5g of soluble starch were dissolved in deionized water. After complete mixing of starch in water the solution was kept in water bath for 1 hour at a temperature of 100℃. Then 0.1 molar solution of Cobalt Chloride hexahydrate ($CoCl_2.6H_2O$) of 13 ml was added into the boiled starch solution. After that this mixture was stirred for 10 minutes at a temperature 80℃. For the adjustment of pH few drops of ammonia solution was added and after that the final mixture was stirred at a temperature 80℃ for further 40 minutes. To viscous this

solution it was heated at 150℃. When the solution became viscous, then it was kept in the oven at a temperature 110℃ to get dried solution. After drying the material, it was calcined in the furnace for 4 hours at temperature 500℃. The final materials of Cobalt oxide (Syn-CO) were obtained after the calcination process [64].

Figure. 3.3. Digital Balance

Figure. 3.4. Water bath

Figure 3.5. Stirrer & heating plate

Figure. 3.6. Prepared catalyst materials

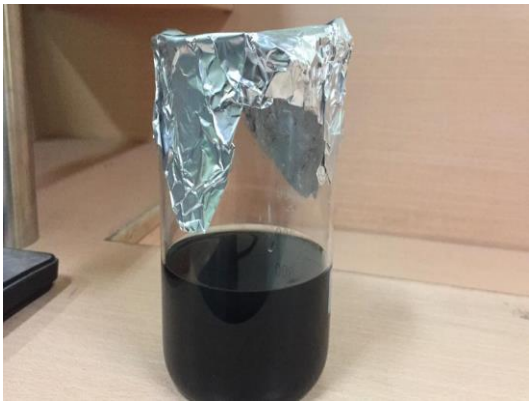

Figure. 3.7 Dissolved material

3.5.1 Coating of catalyst on stainless steel plates

The chemicals used for coating of catalyst Syn-CO on stainless steel plates were PVDF as a binder and N-N Dimethylacetamide organic solvent. The PVDF and the prepared material (catalyst) were thoroughly mixed in the solvent. The thoroughly mixed solution was kept in sonicator bath for 1 hour to dissolve the materials completely. The dissolved materials in an organic solvent were then coated on the stainless-steel plates and kept the plates in the oven for 30 minutes for drying. The amount of the catalyst material of Co_3O_4 coated on each plate was 10 mg. Then the plates were fixed in the reactor to check the removal efficiency and time to remove CIP following the same procedure.

3.5.2 Characterization of catalyst

For the identification of phase and structure of the catalyst before and after the application in the degradation of CIP the X-ray diffraction (XRD) were used having powder diffractometer (D/max 2550 V apparatus) with CuKα ($\lambda = 0.154$ nm radiation). The applied voltage of 40 kV and current 40 mA were used to operate the instrument. The angle 2θ ranging from 10° to 80° having spanning speed of 5° min^{-1} were used for analysis. Diffraction lines were matched with reference patterns of JCPDS (Joint Committee of Powder Diffraction Standards) Cards to identify the key phases. Scanning electron microscope (SEM, JSM-630LV, Tokyo, Japan) were used for the study of morphological characteristics of prepared catalyst before and after use in the degradation of CIP.

Chapter 4

RESULTS AND DISCUSSION

4.1 Response Surface Methodology (RSM)

Through Design Expert software using Response Surface Methodology (RSM), different combinations of experimental parameters were generated. The range for those parameters were voltage (2-8 V), air flowrate (1.6-3.5 L/min), the concentration of CIP (15-35 mg/L) and having a constant value of pH 3. Using the different combinations of these parameters, the result was obtained for all these combinations. The standard calibration curve was used to calculate the final concentration for each combination.

4.2 Model development

For the regression analysis of experimental data and to draw the response surface plot "Design Expert 11" software has been used. By using ANOVA, the statistical parameters were estimated. For the removal of CIP, the range of parameters are shown in table 4.2. The designed experiments and its result have shown table 4.4. The final equation for the remaining concentration of CIP in terms of coded factor is shown in Eq.1

Final concentration (mg/L) =

$$-3.49+0.38A+1.83B-0.16C-0.07A*B-0.04A*C-0.62B*C+0.004289A^2+0.701196B^2+0.1922C^2 \quad (1)$$

The positive sign indicates the synergistic effects whereas the negative sign indicates the antagonistic effects.

To build a good model, there was a lack of fit test for the coefficient of the model, and a test for the significance of the regression model. The ranking of significant factors was based on P-values or F-values. The Model F-value of 28.52 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, C, AB, AC, BC, A^2, B^2, C^2 are significant model terms as shown in table 4.6.

Table 4.1 Limits of experimental parameters

Name	Units	Low	High
Initial Concentration of CIP	mg/L	15	35
Air Flow rate	L/min	1.6	3.5
Voltage	V	2	8

Table 4.2 Calibration data

Calibration curve data	
Concentration (mg/L)	Absorbance
1	0.136
2	0.139
3	0.1416
5	0.1452
10	0.1594
15	0.1736
25	0.1982

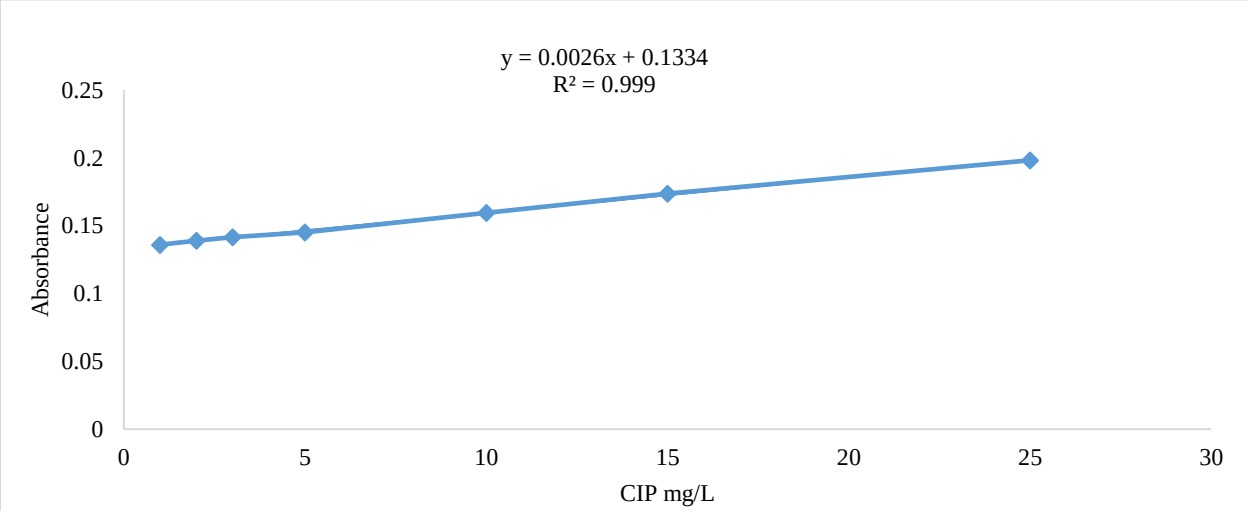

Figure 4.1 Calibration Curve of ciprofloxacin concentration range (1-25 mg/L) in terms of absorbance.

Table 4.3 Response of experimental parameters in laboratory

	Factor 1	**Factor 2**	**Factor 3**	**Response 1**
Run	A: Conc; of CIP (mg/L)	B: Air flow rate (L/min)	C: Voltage (V)	Final Conc; of CIP (mg/L)
1	25	2.55	6	2.53
2	8	2.55	6	1.76
3	25	2.55	2.63	7.53
4	35	1.6	4	7.5
5	35	1.6	8	5.8
6	15	3.5	8	2.92
7	41	2.55	6	6.38
8	25	3.5	6	3.69
9	35	3.5	4	8.69
10	15	1.6	4	1.38
11	25	1.6	6	5.61
12	35	3.5	8	3.65
13	25	2.55	9.36	2.53
14	15	3.5	4	5.61
15	25	2.55	6	3.3
16	15	1.6	8	3.69
17	25	2.55	6	2.92
18	25	2.55	6	3.3
19	25	2.55	6	2.88
20	25	2.55	6	2.5

Table 4.4 Final removal of %CIP

Run	Initial Conc; of CIP (mg/L)	Absorbance	Final Conc; of CIP (mg/L)	% Removal
1	25	0.14	2.53	89.84
2	8	0.138	1.76	78.37
3	25	0.153	7.53	69.84
4	35	0.1529	7.5	78.57
5	35	0.1485	5.80	83.40
6	15	0.141	2.92	80.51
7	41	0.15	6.38	84.45
8	25	0.143	3.69	85.23
9	35	0.156	8.69	75.16
10	15	0.137	1.38	90.76
11	25	0.148	5.61	77.53
12	35	0.1429	3.65	89.56
13	25	0.14	2.53	89.84
14	15	0.148	5.61	62.56
15	25	0.142	3.30	86.76
16	15	0.143	3.69	75.38
17	25	0.141	2.92	88.30
18	25	0.142	3.30	86.76
19	25	0.1409	2.88	88.46
20	25	0.1399	2.5	90

By using the equation of standard curve, the final concentration of ciprofloxacin was calculated as shown in table 4.4.

Table 4.5 Data of generated Model through software

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	82.44	9	9.16	28.52	< 0.0001	Significant
A-conc	25.56	1	25.56	79.61	< 0.0001	
B-air flow	0.2505	1	0.2505	0.7801	0.3979	
C-voltage	20.27	1	20.27	63.13	< 0.0001	
AB	3.83	1	3.83	11.94	0.0062	
AC	6.96	1	6.96	21.67	0.0009	
BC	11.19	1	11.19	34.85	0.0002	
A^2	2.65	1	2.65	8.25	0.0166	
B^2	5.77	1	5.77	17.97	0.0017	
C^2	8.52	1	8.52	26.53	0.0004	
Residual	3.21	10	0.3211			

4.3 Actual vs predicted removal of CIP

The actual and predicted removal of CIP is shown in Fig. 4.2. The values of R^2 and adjusted R^2 were 0.97 and 0.92 respectively. The R^2 means that up to what extent the model can estimated the experimental data, and adjusted R^2 means the amount of variation about the mean explained by the model. The Predicted R^2 of 0.75 is in reasonable agreement with the Adjusted R^2 of 0.92; i.e., the difference is less than 0.2.

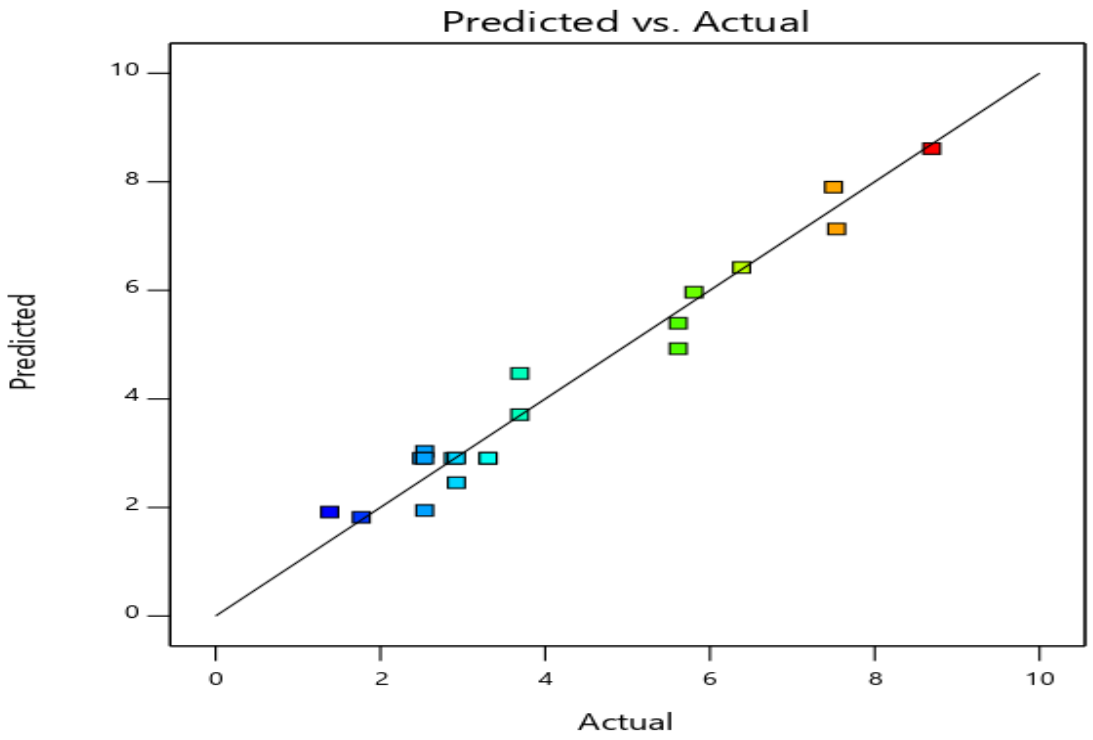

Figure 4.2 Actual vs Predicted removal of ciprofloxacin

Table.4.6 ANOVA data from Design Expert software

Std. Dev.	0.56	**R^2**	0.96
Mean	4.16	**Adjusted R^2**	0.92
C.V. %	13.63	**Predicted R^2**	0.75
		Adequate Precision	16.95

It was concluded that the experimental data fitted well with the value of the model for the removal of CIP. The standard deviation for the model was 0.5 as shown in table 4.7. The statistical parameters obtained from ANOVA are shown in table 4.7.

4.4 Graphical presentation of optimized paramters

The optimized paramters through RSM is presented in the below graphs. The optimized value of the paramters is voltage 6V, air flow rate 2.5 L/min and the intial concentration of CIP is 25 mg/L.

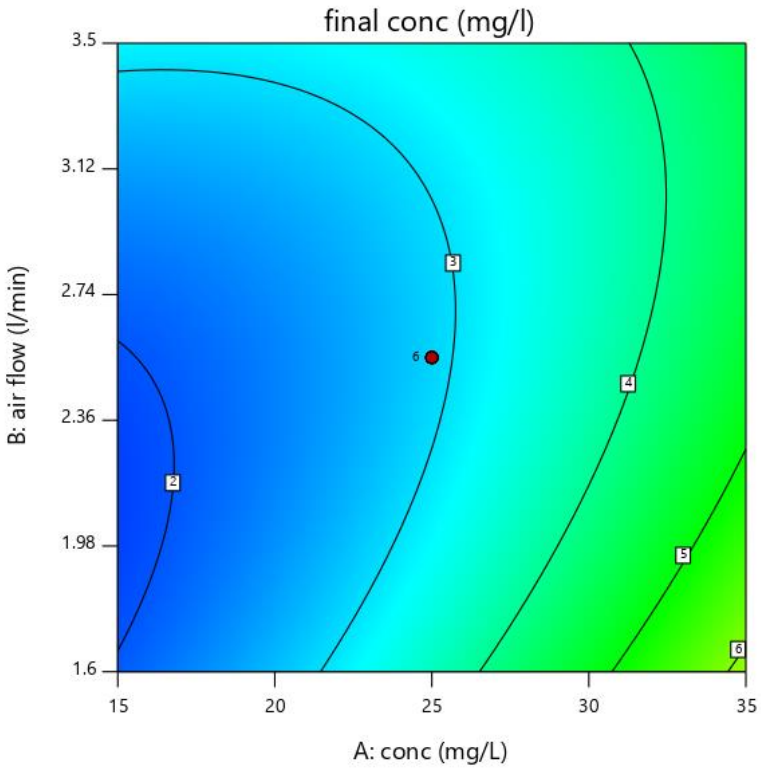

Figure 4.3 Contour of Optimized parameters

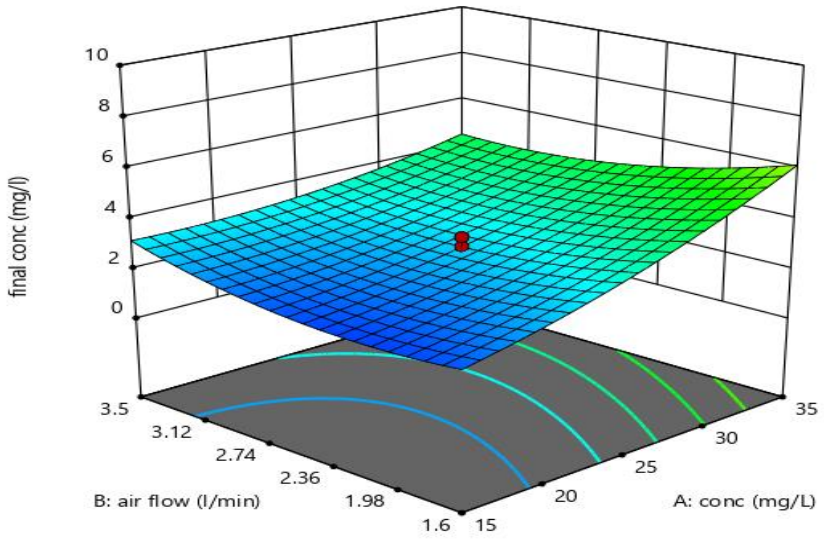

Figure 4.4 3D surface of Optimized parameters

4.5 Relation of time and degradation rate

The electrochemical degradation of CIP through stainless steel plates was slowly at the start of the process and gradually the removal of CIP increased with time. After some time, the degradation rate of CIP remain constant and shows degradation with a slower rate. This relation is presented in below figure 4.5.

Table 4.7 Time vs Removal efficiency of CIP

Time(minutes)	Absorbance	Initial Conc; of CIP (mg/L)	Final Conc; of CIP (mg/L)	% Removal
3	0.180	25	18.30	26.76
6	0.179	25	17.73	29.07
9	0.178	25	17.26	30.92
12	0.175	25	16.11	35.53
15	0.170	25	14.26	42.92
18	0.165	25	12.26	50.92
21	0.155	25	8.65	65.38
24	0.149	25	6	76
27	0.140	25	2.73	89.07
30	0.140	25	2.57	89.69
33	0.139	25	2.5	90

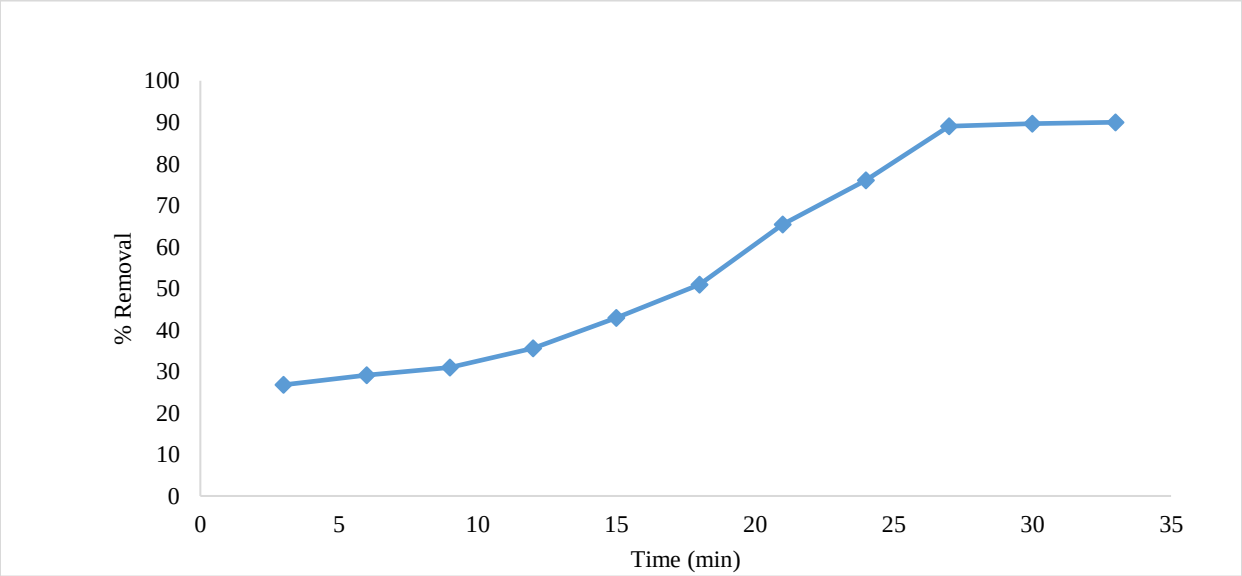

Figure 4.5 Time vs removal efficiency of CIP

4.6 Wavelenght vs absorbance

Table 4.8 Absorbance against different wavelength

Absorbance Au	Wavelength nm
0.136	200
0.139	225
0.1416	250
0.1982	275
0.1794	300
0.1736	325
0.1703	350
0.1654	375
0.1509	400

The relation between wavelength and absorbance was calculated by using the value of absorbance generated through spectrophotometer with respect to different wavelength. The maximum absorbance due to the structure of CIP was achieved at wavelength of 275 nm. This wavelength was furhter used for calculating the final concentration of ciprofloxacin.

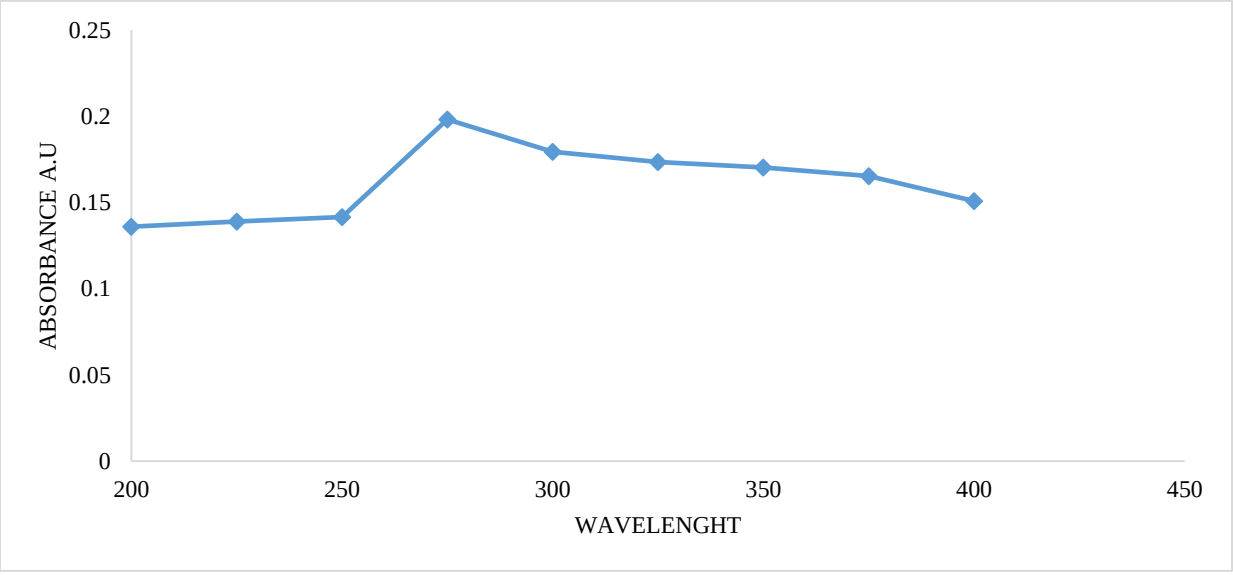

Figure 4.6 Graph of absorbance vs wavelength

4.7 Effect of catalyst coating on the degradation of ciproflxacin

The effect of coated catalyst Syn-CO having a quantity of 10mg on each plate for the removal of CIP from wastewater was reduction in HRT upto 22% and enhanced removal of CIP to 91.5%.

4.7.1 Characterization of catalyst structure

The catalyst prepared in this study were examined for phase identification using X-ray diffraction (XRD) as shown is Fig.7. In the XRD patterns, the prominent peaks at 2Θ values of 18.95°, 53.25°and 64.35° at point A, B and C respectively were observed. These peaks were attributed to the standard peaks of Co_3O_4. The graph also shows XRD pattern of catalyst after application consisting of the same number of peaks at similar diffraction angle however the peaks of Co_3O_4 after the treatment were relatively broaden. that shows increase in the amorphousasity of synthesized catalyst [67]. Through SEM images its clear that after application structure of the catalyst became amorphous.

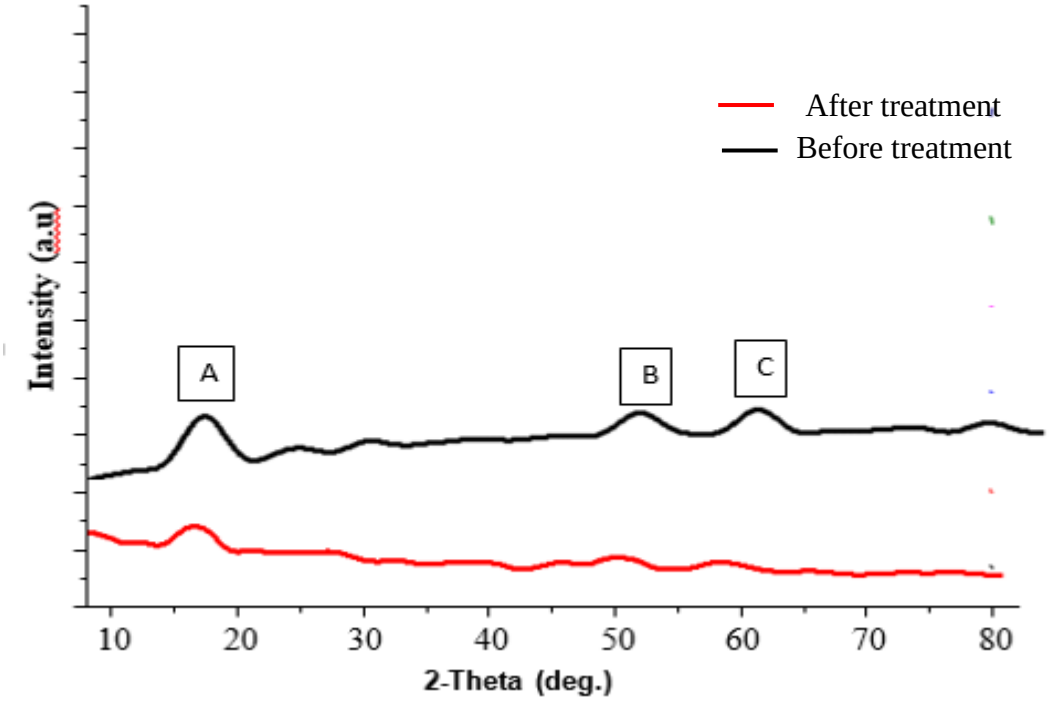

Figure 4.7 XRD pattern of catalyst (Cobalt Oxide)

Figure. (a & b) Shows the SEM images of prepared catalyst before application to degrade CIP. The spherical and polyhedral morphology shows a large surface area and maximum pores which

is beneficial for catalytic activity. The morphology of catalysts after using in the degradation of CIP are shown in Fig. (c & d) which shows the pores occupied by the degraded materials.

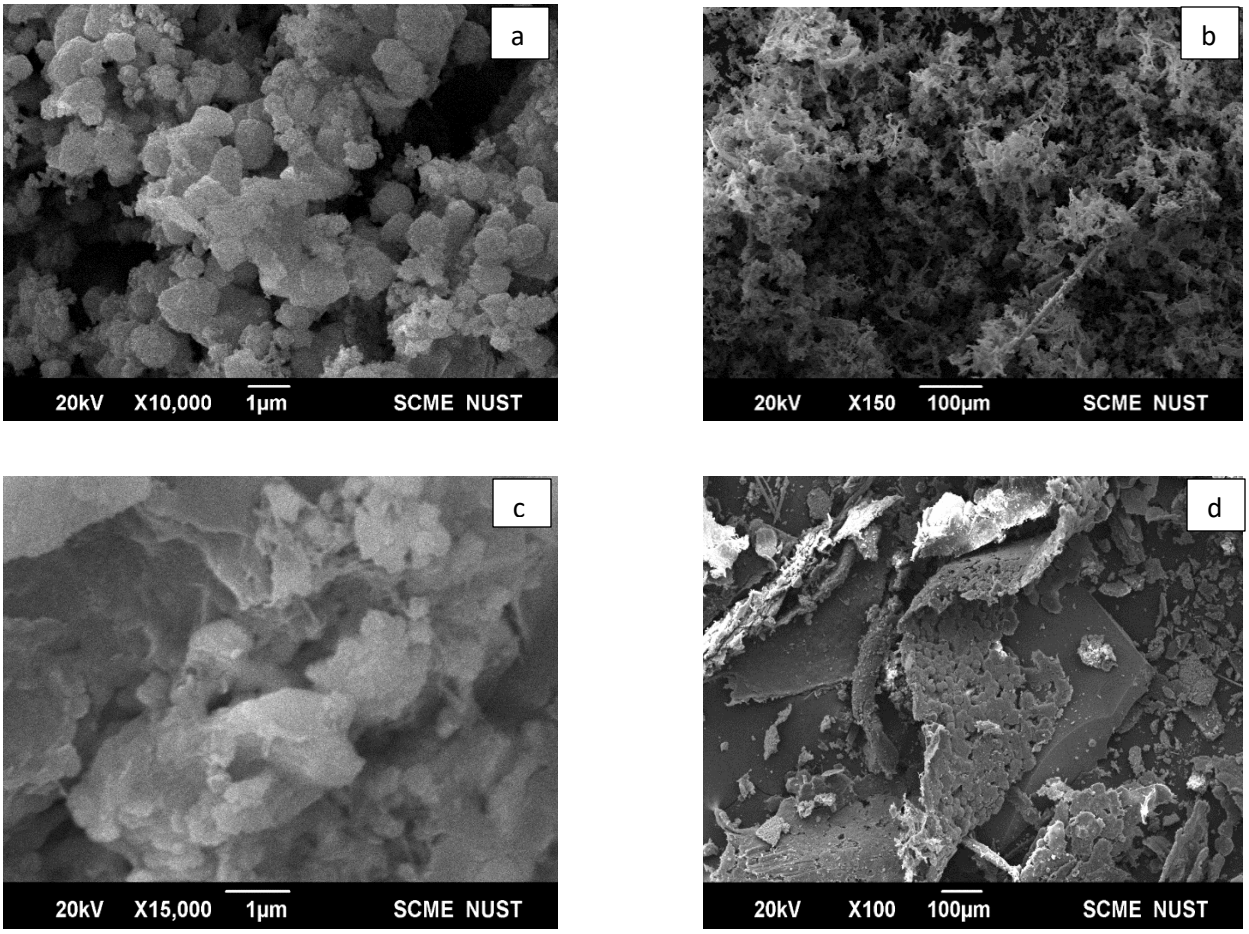

Figure 4.8 SEM images of catalyst before (*a* and *b*) and after treatment (*c* and *d*)

4.7.2 Relation of time vs removal efficiency

The removal of CIP through stainless steel plates coated with catalyst Cobalt oxide became enhanced upon coating. The time taken for removal of CIP from wastewater is also reduced. The maximum degradation of ciprofloxacin was started at 21 minutes of the process.

Table 4.9 Effect of catalyst coating on HRT

Time (minutes)	Absorbance	Initial Conc; of CIP (mg/L)	Final Conc; of CIP (mg/L)	% Removal
3	0.18	25	18.30	26.76
6	0.17	25	17.73	29.07
9	0.17	25	17.26	30.92
12	0.17	25	16.11	35.53
15	0.16	25	11.96	52.15
18	0.15	25	6.88	72.46
21	0.14	25	2.96	88.15
24	0.14	25	2.53	89.84
27	0.13	25	2.42	90.30
30	0.13	25	2.11	91.53

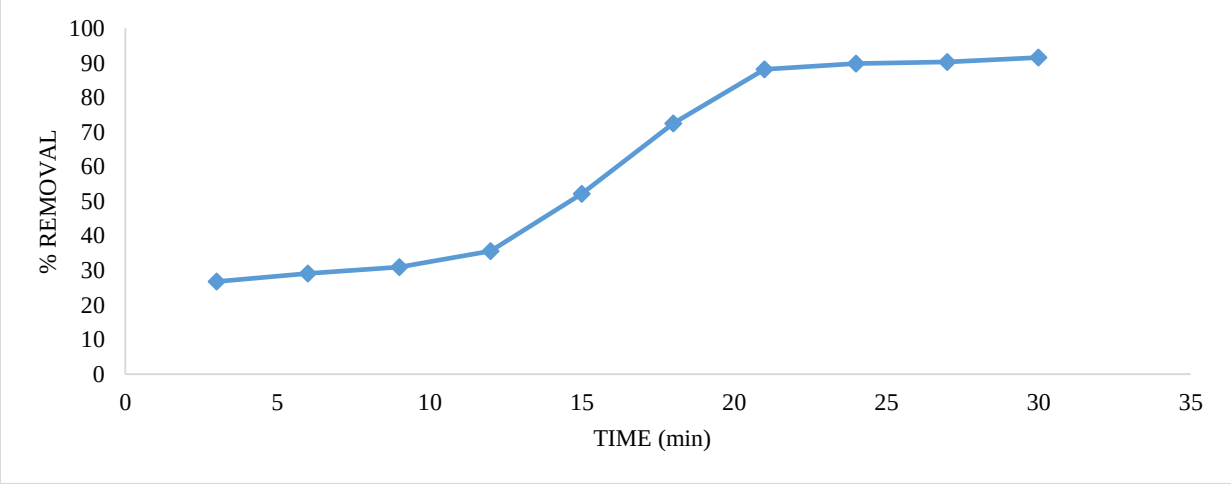

Figure 4.9 Time vs removal of CIP after coating

CIP's removal efficiency with Cobalt Oxide Coated Stainless Steel (CCSS) and that of non coated Stainless Steel (SS) plates with repsect to time are shown in figure 4.10.

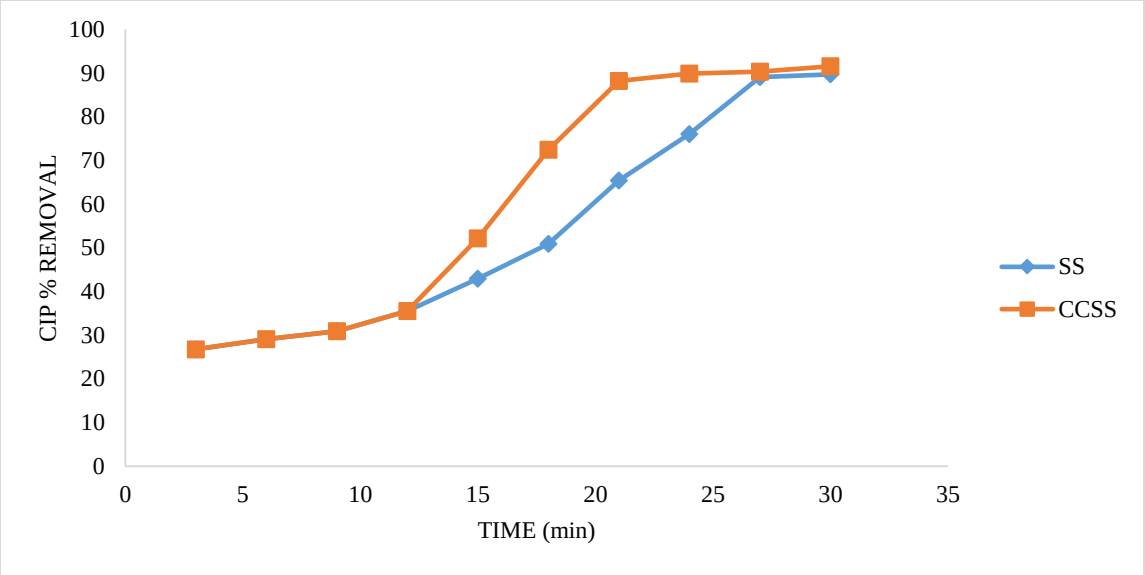

Figure 4.10 Removal efficiencies of coated and without coating stainless steel plates

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The result of this study highlights the removal of CIP from wastewater through electrochemical degradation by stainless steel plates electrodes coated with cobalt oxide catalyst. The electrochemical degradation process for this type of contaminant is economical and quick. The optimized parameters for CIP removal were concluded using software "Design Expert" surface response methodology. The optimized parameters for the removal of CIP with high efficiency of degradation was applied voltage of 25V, diffuse air flow rate 2.5 L/min and the initial concentration of ciprofloxacin was 25 mg/L. By using these optimized parameters, two experiments were performed for the removal of CIP with stainless steel plate's electrodes and coated plate's electrodes with catalyst cobalt oxide, the results were achieved 89% and 91.5% removal of CIP respectively. The HRT of the process was reduced up to 22% due to coating of catalyst cobalt oxide.

Different materials of the catalyst are recommended for coating on stainless steel plates.

5.2 Recommendations

With the increasing consumption and release of FQs, the environmental pollution caused by these drugs and their ensuing detrimental effects will gain even more attention in the coming years. Some of the recommendations for future research are:

- There is a lack of information on the presence of these drugs in various environmental compartments. So, studies should also be conducted to gather this information that helps to determine their fate.
- Other cheaper transition metal oxides should be explored to further economize the process and for improving efficiency.

- The kinetic study of the degradation mechanism can be helpful in unveiling the formation of different metabolites during the process.
- Chronic eco-toxicological effects of pharmaceuticals should be studied.

REFERENCES

1. Reig, P., T. Shiao, and F. Gassert, *Aqueduct water risk framework*. 2013, Citeseer.
2. Hayat, S., et al., *Photosynthetic rate, growth, and yield of mustard plants sprayed with 28-homobrassinolide.* 2000. 38(3): p. 469-471.
3. Monico, L., et al., *Degradation process of lead chromate in paintings by Vincent van Gogh studied by means of synchrotron X-ray spectromicroscopy and related methods. 1. Artificially aged model samples.* 2011. 83(4): p. 1214-1223.
4. Oaks, J.L., et al., *Diclofenac residues as the cause of vulture population decline in Pakistan.* 2004. 427(6975): p. 630-633.
5. Bowman, S.M., et al., *Toxicity and reductions in intracellular calcium levels following uptake of a tetracycline antibiotic in Arabidopsis.* 2011. 45(20): p. 8958-8964.
6. Gaskins, H., C. Collier, and D.J.A.b. Anderson, *Antibiotics as growth promotants: mode of action.* 2002. 13(1): p. 29-42.
7. Scholz, S., et al., *A European perspective on alternatives to animal testing for environmental hazard identification and risk assessment.* 2013. 67(3): p. 506-530.
8. Jelic, A., et al., *Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment.* 2011. 45(3): p. 1165-1176.
9. Ghosh, G.C., et al., *Occurrence and elimination of antibiotics at four sewage treatment plants in Japan and their effects on bacterial ammonia oxidation.* 2009. 59(4): p. 779-786.
10. Homem, V. and L.J.J.o.e.m. Santos, *Degradation and removal methods of antibiotics from aqueous matrices–a review.* 2011. 92(10): p. 2304-2347.
11. Wachter, N., et al., *Optimization of the electrochemical degradation process of the antibiotic ciprofloxacin using a double-sided β-PbO2 anode in a flow reactor: kinetics, identification of oxidation intermediates and toxicity evaluation.* 2019. 26(5): p. 4438-4449.
12. Moussavi, G., A. Alahabadi, and K. Yaghmaeian, *Investigating the potential of carbon activated with NH4Cl for catalyzing the degradation and mineralization of antibiotics in zonation process.* 2015. 97: p. 91-99.

13. Reinholds, I., et al., *Determination of pharmaceutical residues and assessment of their removal efficiency at the Daugavgriva municipal wastewater treatment plant in Riga, Latvia.* 2017. 75(2): p. 387-396.
14. Yahya, M.S., et al., *Oxidative degradation study on antimicrobial agent ciprofloxacin by electro-Fenton process: kinetics and oxidation products.* 2014. 117: p. 447-454.
15. Guo, H.-G., et al., *Photochemical degradation of ciprofloxacin in UV and UV/H 2 O 2 process: kinetics, parameters, and products.* 2013. 20(5): p. 3202-3213.
16. Lin, C.-C., M.-S.J.J.o.P. Wu, and P.A. Chemistry, *Degradation of ciprofloxacin by UV/S2O82− process in a large photoreactor.* 2014. 285: p. 1-6.
17. Wang, Y., et al., *The electrochemical degradation of ciprofloxacin using a SnO2-Sb/Ti anode: influencing factors, reaction pathways and energy demand.* 2016. 296: p. 79-89.
18. de Lima Perini, J.A., et al., *Photo-Fenton degradation kinetics of low ciprofloxacin concentration using different iron sources and pH.* 2013. 259: p. 53-58.
19. Hassani, A., et al., *Sonocatalytic degradation of ciprofloxacin using synthesized TiO2 nanoparticles on montmorillonite.* 2017. 35: p. 251-262.
20. Li, G., et al., *Electrochemical degradation of ciprofloxacin on BDD anode using a differential column batch reactor: mechanisms, kinetics and pathways.* 2019. 26(17): p. 17740-17750.
21. Mu, Y., et al., *Electrochemical degradation of ciprofloxacin with a Sb-doped SnO 2 electrode: Performance, influencing factors and degradation pathways.* 2019. 9(51): p. 29796-29804.
22. Sánchez-Montes, I., et al., *Evolution of the antibacterial activity and oxidation intermediates during the electrochemical degradation of norfloxacin in a flow cell with a PTFE-doped β-PbO2 anode: Critical comparison to a BDD anode.* 2018. 284: p. 260-270.
23. Bueno, F., et al., *Degradation of ciprofloxacin by the Electrochemical Peroxidation process using stainless steel electrodes.* 2018. 6(2): p. 2855-2864.
24. Moreira, F.C., et al., *Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters.* 2017. 202: p. 217-261.
25. Kapałka, A., G. Fóti, and C.J.J.o.A.E. Comninellis, *Kinetic modelling of the electrochemical mineralization of organic pollutants for wastewater treatment.* 2008. 38(1): p. 7-16.

26. Hamasaki, H., et al., *Modelling of cyclic plasticity and martensitic transformation for type 304 austenitic stainless steel.* 2018. 146: p. 536-543.
27. Clark, C., et al., *Water use in the development and operation of geothermal power plants*. 2010, Argonne National Lab.(ANL), Argonne, IL (United States).
28. Mölstad, S., et al., *Antibiotic prescription rates vary markedly between 13 European countries.* 2002. 34(5): p. 366-371.
29. Martinez, M., P. McDermott, and R.J.T.V.J. Walker, *Pharmacology of the fluoroquinolones: a perspective for the use in domestic animals.* 2006. 172(1): p. 10-28.
30. Hamad, B.J.N.r.D.d., *The antibiotics market.* 2010. 9(9): p. 675.
31. Golet, E.M., et al., *Environmental exposure and risk assessment of fluoroquinolone antibacterial agents in wastewater and river water of the Glatt Valley Watershed, Switzerland.* 2002. 36(17): p. 3645-3651.
32. Frade, V.M.F., et al., *Environmental contamination by fluoroquinolones.* 2014. 50: p. 41-54.
33. Kümmerer, K.J.C., *Antibiotics in the aquatic environment–a review–part I.* 2009. 75(4): p. 417-434.
34. Babić, S., M. Periša, and I.J.C. Škorić, *Photolytic degradation of norfloxacin, enrofloxacin and ciprofloxacin in various aqueous media.* 2013. 91(11): p. 1635-1642.
35. Sturini, M., et al., *Photolytic and photocatalytic degradation of fluoroquinolones in untreated river water under natural sunlight.* 2012. 119: p. 32-39.
36. LIU, L.-w., X.-l. WU, and C.J.J.o.C.S.U. Wu, *Photocatalytic degradation of quinolone antibiotics in water using TiO2.* 2012. 43(8): p. 3300-3307.
37. Davis, R., A. Markham, and J.A.J.D. Balfour, *Ciprofloxacin.* 1996. 51(6): p. 1019-1074.
38. Ferech, M., et al., *European Surveillance of Antimicrobial Consumption (ESAC): outpatient antibiotic use in Europe.* 2006. 58(2): p. 401-407.
39. Kümmerer, K., A. Al-Ahmad, and V.J.C. Mersch-Sundermann, *Biodegradability of some antibiotics, elimination of the genotoxicity and affection of wastewater bacteria in a simple test.* 2000. 40(7): p. 701-710.
40. Golet, E.M., et al., *Environmental exposure assessment of fluoroquinolone antibacterial agents from sewage to soil.* 2003. 37(15): p. 3243-3249.

41. Topp, E., et al., *Runoff of pharmaceuticals and personal care products following application of biosolids to an agricultural field.* 2008. 396(1): p. 52-59.
42. Singh, R., et al., *Role of persisters and small-colony variants in antibiotic resistance of planktonic and biofilm-associated Staphylococcus aureus: an in vitro study.* 2009. 58(8): p. 1067-1073.
43. Lewis, G., et al., *Environmental metabolites of fluoroquinolones: synthesis, fractionation and toxicological assessment of some biologically active metabolites of ciprofloxacin.* 2012. 19(7): p. 2697-2707.
44. Jones, R.N., et al., *North American (United States and Canada) comparative susceptibility of two fluoroquinolones: ofloxacin and ciprofloxacin: a 53-medical-center sample of spectra of activity.* 1994. 18(1): p. 49-56.
45. Hickerson, A.D. and C.C.J.E.o.o.i.d. Carson, *The treatment of urinary tract infections and use of ciprofloxacin extended release.* 2006. 15(5): p. 519-532.
46. Batt, A.L., S. Kim, and D.S.J.C. Aga, *Comparison of the occurrence of antibiotics in four full-scale wastewater treatment plants with varying designs and operations.* 2007. 68(3): p. 428-435.
47. Larsson, D.J., C. de Pedro, and N.J.J.o.h.m. Paxeus, *Effluent from drug manufactures contains extremely high levels of pharmaceuticals.* 2007. 148(3): p. 751-755.
48. Martínez-Carballo, E., et al., *Environmental monitoring study of selected veterinary antibiotics in animal manure and soils in Austria.* 2007. 148(2): p. 570-579.
49. Krützfeldt, J., et al., *Specificity, duplex degradation and subcellular localization of antagomirs.* 2007. 35(9): p. 2885-2892.
50. Seifrtová, M., et al., *Determination of fluoroquinolone antibiotics in hospital and municipal wastewaters in Coimbra by liquid chromatography with a monolithic column and fluorescence detection.* 2008. 391(3): p. 799-805.
51. Fick, J., et al., *Contamination of surface, ground, and drinking water from pharmaceutical production.* 2009. 28(12): p. 2522-2527.
52. Roig, B., *Pharmaceuticals in the Environment*. 2010: IWA publishing.
53. Wang, L., et al., *Occurrence and risk assessment of acidic pharmaceuticals in the Yellow River, Hai River and Liao River of north China.* 2010. 408(16): p. 3139-3147.

54. Sim, W.-J., et al., *Occurrence and distribution of pharmaceuticals in wastewater from households, livestock farms, hospitals and pharmaceutical manufactures.* 2011. 82(2): p. 179-186.
55. Fink, L., I. Dror, and B.J.C. Berkowitz, *Enrofloxacin oxidative degradation facilitated by metal oxide nanoparticles.* 2012. 86(2): p. 144-149.
56. Leal, R.M.P., et al., *Occurrence and sorption of fluoroquinolones in poultry litters and soils from São Paulo State, Brazil.* 2012. 432: p. 344-349.
57. Ahmad, M., et al., *Role of untreated waste water in spread of antibiotics and antibiotic resistant bacteria in river.* 2013. 65(1): p. 10.
58. Zhang, Z., et al., *Ethanol, corn, and soybean price relations in a volatile vehicle-fuels market.* 2009. 2(2): p. 320-339.
59. Walters, E., K. McClellan, and R.U.J.W.r. Halden, *Occurrence and loss over three years of 72 pharmaceuticals and personal care products from biosolids–soil mixtures in outdoor mesocosms.* 2010. 44(20): p. 6011-6020.
60. Nowara, A., et al., *Binding of fluoroquinolone carboxylic acid derivatives to clay minerals.* 1997. 45(4): p. 1459-1463.
61. Li, G., et al., *Electrochemical degradation of ciprofloxacin on BDD anode using a differential column batch reactor: mechanisms, kinetics and pathways.* 2019. 26(17): p. 17740-17750.
62. Wachter, N., et al., *Electrochemical degradation of the antibiotic ciprofloxacin in a flow reactor using distinct BDD anodes: reaction kinetics, identification and toxicity of the degradation products.* 2019. 234: p. 461-470.
63. Ganesan, S., et al., *Absolute removal of ciprofloxacin and its degraded byproducts in aqueous solution using an efficient electrochemical oxidation process coupled with adsorption treatment technique.* 2019. 245: p. 409-417.
64. Abbas, Z., et al., *Catalytic nonthermal plasma using efficient cobalt oxide catalyst for complete mineralization of toluene.* 2021. 47(6): p. 2407-2420.
65. Ahmad, F., et al., *Desalination of brackish water using capacitive deionization (CDI) technology.* 2016. 57(17): p. 7659-7666.
66. Araujo, P.W. and R.G. Brereton, *Experimental design II. Optimization.* TrAC Trends in Analytical Chemistry, 1996. 15(2): p. 63-70.

67. Kaganer, V., et al., *X-ray diffraction peaks due to misfit dislocations in heteroepitaxial structures.* 1997. 55(3): p. 1793.