

JIMMA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
JIMMA INSTITUTE OF TECHNOLOGY
FACULTY OF CIVIL AND ENVIRONMENTAL
ENGINEERING
ENVIRONMENTAL ENGINEERING CHAIR

DEVELOPMENT OF SONO-ELECTROCHEMICAL OXIDATION
PROCESS FOR DOMESTIC WASTEWATER TREATMENT:
OPTIMIZATION THROUGH RESPONSE SURFACE METHODOLOGY

By:

Gelana Kora Sime

A Thesis Submitted to the Faculty of Civil and Environmental Engineering of
Jimma Institute of Technology in Partial Fulfillment of the Requirements for
the Degree of Masters of Science in Environmental Engineering.

April 2020
Jimma, Ethiopia

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Advisor: Prof. Dr.-Ing Esayas Alemayehu

Co-advisor: Mrs. Kidist Jemal (MSc.)

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Jimma, Ethiopia

DECLARATION

I, Gelana Kora, declare that this work entitled “**Development of Sono-Electrochemical Oxidation Process for Domestic Wastewater Treatment: Optimization through Response Surface Methodology**” is the outcome of my own effort and study. All sources of materials used for the study have been duly acknowledged and through appropriate referencing.

This Thesis is my original work and has not been submitted for any other Degree in this and any other Universities.

Gelana Kora Sime

.....

.....:

Candidate

Signature

Date

APPROVAL SHEET

We, the undersigned confirm that the Thesis entitled: “**Development of Sono-Electrochemical Oxidation Process for Domestic Wastewater Treatment: Optimization through Response Surface Methodology**” is the work of Gelana Kora and we hereby recommend for the approval by school of Post Graduate Studies of Jimma University in partial fulfillment of the requirements for the Degree of Master of Science in Environmental Engineering.

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As member of Board of Examiners of the MSc. Thesis Open Defense Examination, we certify that we have read, evaluated the Thesis prepared by Gelana Kora and examined the candidate. We recommended that, the Thesis could be accepted as fulfilling the Thesis requirement for the Degree of Master of Science in Environmental Engineering.

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(Internal Examiner)	Signature	Date

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(Chairman)	Signature	Date

ACKNOWLEDGMENTS

Above all, I would like to thank the Almighty GOD for his wordless gift and helping me in all my life.

I am happy to acknowledge and thanks my main Advisor Dr.-Ing Esayas Alemayehu, Professor in Water Resources & Environmental Engineering, Jimma Institute of Technology, Jimma University. Because of his efforts, valuable ideas and encouragements that provided me respected guidance and incalculable support in advising my research.

I wish to thank my Co-Advisor Kidist Jemal (MSc.), since she helped me a lot in developing this paper by giving appreciated comments. My appreciation also goes to Dr. P. Asaithambi for his effort on the Research topic by providing me relevant literature, guidance in laboratory work and for his constructive comments on my document. I am particularly grateful to laboratory technicians Mr. Firomsa Bidira and Mrs. Yohana Taddese for their assistance in laboratory work.

My special acknowledgement is to the Ethiopian Road Authority (ERA) for giving me this golden chance and Jimma University (JU), Jimma Institute of Technology (JiT) is appreciative to be volunteer to accept and teach students from ERA. In addition, I wish to express my gratitude to Environmental Engineering laboratory in JiT & Environmental Health laboratory in main campus for their support with lab facilities.

Finally, I am grateful to all, including my family and friends, who helped me during research work and for their countless motivation in achieving this educational level.

ABSTRACT

In this study, the elimination of organic compounds in wastewater using electrooxidation (EO) and a combination of electrochemical oxidation (EO) and ultrasonic (US) was investigated in terms of percentage removal of COD, color and turbidity with power consumption. The influence of experimental parameters including initial pH, electrolysis time, current ampere and NaCl/ CaCl₂ concentration has studied to find out the optimum conditions leading to maximum percentage removal efficiency. The response surface methodology (RSM) based on Central Composite Design (CCD) was used to plan the experimental runs and optimization of results. According to the study, the optimum values of COD, Color and turbidity with power Consumption for US/EO were 99.70 %, 99.79 % and 99.28 % with 0.003 kWhr/m³ using CaCl₂. These results were obtained at optimal conditions of pH 5.85, electrolysis time 47.15 minutes, current 0.57 Ampere and electrolytic concentration 1.42 g/L using aluminum as electrode. The significance of independent variables and their interactions were tested by means of the analysis of variance (ANOVA) with 95% confidence limits. Quadratic regression equation was suggested as a good model for prediction of chemical oxygen demand (COD), color and turbidity removal efficiency with power consumption. A good agreement between the model prediction and experimental results confirms the soundness of the developed model, which indicates that CCD could be effectively used to optimize the EO and US/EO parameters. Therefore, the combination of EO and US based AOPs has been proved to be efficient treatment techniques for removal of pollutant from domestic wastewater.

Key words: Central Composite Design, Domestic wastewater, Optimization, Pollutant removal, Sono-electrochemical

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ACRONYMS

ANOVA	Analysis of Variance
AOPS	Advanced Oxidation Processes
APHA	American Public Health Association
BBD	Box–Behnken Design
CCD	Central Composite Design
CM	Centimeter
COD	Chemical Oxygen Demand
DC	Direct Current
DF	Degree of Freedom
EO	Electrochemical Oxidation
EPA	Environmental Protection Authority
ERA	Ethiopian Road Authority
FCCD	Face Central Composite Design
FI	Factor of Interaction
G	Gram
HZ	Hertz
JIT	Jimma Institute of Technology
JU	Jimma University
KWH	Kilowatt Hour
L	Liter
ML	Milliliter
NM	Nanometer
PRESS	Predicted Residual Sum of Squares
RPM	Revolution per Minute
RSM	Response Surface Methodology
US	Ultra Sonic/ Ultra Sound
US/EO	Sono-Electrochemical Oxidation
WGS	World Geodetic System

CHAPTER ONE

INTRODUCTION

1.1 Background

The water bodies are being contaminated due to industrial and domestic discharges. To protect water reservoirs and living organism from life threatening diseases, various treatment methods were designed (Wang *et al.*, 2017). Today, a simple turn of the tap provides clean water that is a precious resource. Engineering advances in managing this resource, profoundly in this century, virtually eliminating waterborne diseases in developing nations, and providing clean and abundant water for communities, farms, and industries (Asaithambi *et al.*, 2017).

Nowadays, the main challenge for environmental research and development is to identify new sources of water, especially in those countries where there are lack of water resources. As EPA's (2015) report, with a limited amount of drinking water available for use, water that is available must be used and reused; else, the world will face with poor supply to meet the needs of all users. In order to treat different types of wastewater in efficient manner, many types of technologies have developed by many researchers.

The conventional treatment technologies developed before have faced difficulties such as high operating cost and producing secondary wastes to be disposed. Advanced oxidation processes (AOPs) are one of those developing advanced technologies applied for treatment of different types of wastewaters. Because, the strong oxidants can readily degrade recalcitrant organic pollutants and remove certain inorganic pollutants in wastewater (Chakma *et al.*, 2015).

Electrochemical process is one of the alternative methods of AOPs for wastewater treatment, aiding from advantages such as versatility, environmental compatibility and potential cost efficiency. Still, the polarization and passivation of electrodes due to poor mass transfer are the main troubles of the method (Lee *et al.*, 2016).

According to Lee *et al.* (2016), polarization can be caused by gas accumulation near to the electrode surface and as a result depletion of pollutant in the electrode's boundary layer. Whereas, passivation can be caused by the deposition of reaction products on the surface of electrodes, which results in diminishing of the process efficiency.

Moreover, ultrasound can reduce polarization and passivation by enhancing mass transfer of electro-active species near to the electrode surface and can activate catalytic surface of electrodes. Raschitor *et al.* (2014) argues ultrasound combined with electrochemical degradation process removes electrode contamination because of the continuous mechanical cleaning effect produced by the formation and collapse of acoustic cavitation bubbles near to the electrode surface.

As Steter *et al.* (2014) also witnesses, the combination of electrochemical with other oxidation processes is a promising treatment technology having its advantages such as strong oxidation ability, fast reaction rate, easy to automate and high efficiency. A combination of Sonication and electrochemical oxidation is a hybrid developing technology used for the treatment of very toxic organic pollutant (wastes).

Sono-electrochemical oxidation (US/EO) degradation is a technique employing electric energy as the main driving force. This degradation process is without the need for additional chemicals, which is the weakness of many conventional methods such as nano-filtration, adsorption, fenton and biological treatment processes. When compared to those conventional technologies, the US/EO methods do not generate secondary waste; hence, it involves very strongly oxidizing agents (Thokchom *et al.*, 2015).

Advanced oxidation processes produces powerful hydroxyl (OH^{\bullet}) or sulfate radicals ($\text{SO}_4^{\bullet-}$) as a major oxidizing agent were first proposed in the 1980s for potable water treatment (Chakma *et al.*, 2015). In addition to active radicals, it can provide the complete oxidation of pollutants formed by oxidative species and thermal decomposition. Hydroxyl radical, chemical species containing hydrogen and oxygen, differentiated from hydroxide ion (OH^-) because it has an unpaired electron in its outer shell. The unpaired electron makes it a powerful, unselective electrophile that is able to oxidize a wide range of organic compounds.

According to the Yang *et al.*, (2014), the core benefit of radical's generation during Sono-electrochemical (US/EO) degradation experiments is the ability to mineralize harmful pollutants into simple inorganic compounds such as H_2O or CO_2 , which are natural for the environment. Mineralization of organic pollutants is generally better option than just transferring pollutants from one phase to another, which takes place in traditional water treatment methods such as adsorption, filtration or coagulation.

Response surface methodology (RSM) was adopted to optimize the US/EO parameters chosen for the study statistically and mathematically. RSM procedures employed for the modelling and optimization of different chemical, physical and even biological processes for the treatment of various pollutants (Liu *et al.*, 2019).

The two most common designs extensively used in RSM are the Central Composite Design (CCD) and the Box–Behnken Design (BBD). The CCD is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points (Asaithambi *et al.*, 2016). It can be used for predicting the functional link between a set of experimental design variables and a response variable. It is useful for developing, improving, modeling, analysis and optimizing processes having numerous variables influencing the response (Jamali *et al.*, 2018).

Consequently, the EO and US/EO were chosen to treat domestic wastewater. The impact of operational variables including initial pH, electrolysis time, current ampere and electrolyte concentration (NaCl and CaCl₂) on the % removal of COD, color and turbidity with power consumption was analyzed. Meanwhile, the main goal of this research is to enhance the efficiency of EO processes, in the case of pollutant removal from wastewater, by assisting it with ultrasound irradiation. It helps to eliminate the main drawbacks of an electrochemical oxidation such as electrodes polarization and passivation (Steter *et al.*, 2014).

Although the removal of pollutants from wastewater by using each process separately and jointly has been a largely studied topic, many researchers have recommended as further studies have to be done in this promising combination of both technologies.

1.2 Statement of the Problem

Nowadays, the need for clean water is growing universally due to numerous causes such as population growth, rapid development of industrial activities, urbanization and climate change. Being accessible with suitable water for human consumption becomes a big challenge especially in developing countries like Ethiopia. The reason behind this truth is different types of pollutants are polluting the natural water. In the future, the big source of water might be wastewater due to the rate of pollution of existing water unintentionally.

Increasing demands on water for various uses make the conventional water resources impossible to meet these demands. For this reason, new resources are to be used to close the gap between volume of water available and volume of water needed for consumption. Obviously, many countries, including our country Ethiopia, are introducing new technologies to their country in order to fulfill the need of their peoples. The influence of those newly coming technologies on the environment is unmeasurable. Moreover, the conventional technologies are producing secondary wastes due to the chemical they use, which is risk for the environment.

In recent years, the appearance of pollutants that are recalcitrant to conventional biological and chemical treatments together with the stricter restrictions imposed by new legislation have caused much research work to focus on waste-water treatment by electro-oxidation processes. The electro-oxidation of organic compounds often occurs by applying high potential; oxygen evolution is a competitive pathway to the degradation process. However, these removal methods often generate sub-products, which are not eliminated completely by the processes or can be even more toxic than the original compound.

Wastewater must be treated prior to being released back into the environment in order to remove contaminants. otherwise pose a risk to the environment or public health. Everybody have to run to keep the environment clean and to prevent natural resources depletion. Therefore, the current mission of technological processes should be avoiding the secondary contamination of the environment with harmful side products, improve the effective recycling of materials and use energy saving solutions.

1.3 Objectives of the Study

1.3.1 General Objective

The main objective of this study was to develop integrated electrochemical oxidation process with ultrasonic process for the domestic wastewater treatment by optimizing through response surface methodology (RSM).

1.3.2 Specific Objectives

- i. To estimate the efficiency of electrochemical Oxidation process for the removal of COD, color and turbidity with power consumption from domestic wastewater by analyzing the effect of experimental parameters.
- ii. To evaluate the efficiency of Sono-electrochemical Oxidation process for the removal of COD, color and turbidity with power consumption from domestic wastewater by analyzing the effect of operating factors.
- iii. To optimize the parameters of the processes statistically by adopting Response Surface Methodology (RSM).

1.4 Research Questions

- i. What is the removal efficiencies of COD, color, and turbidity, and how much power is consumed in kWh/m³ by electrochemical oxidation process?
- ii. What is the removal efficiencies of COD, color, and turbidity, and how much power is consumed in kWh/m³ by Sono-electrochemical oxidation process?
- iii. What are the optimum values of the operating parameters by RSM software?

1.5 Significance of the Study

Delivering clean environment for the community by avoiding water bodies from contamination due to improper discharge of liquid was the main importance of the study. Environment was affected severely by direct discharge of the wastewater without treatment due to the poisonousness and high quantity of waste it contains. However, these difficulties were eliminated if wastewater was treated with suitable technology with regarding to installation and maintenance simplicity and cost.

The discharge of a treated water to the environment makes the community beneficial in using this water directly for different purpose. Moreover, the entire environment especially aquatic species lives in water bodies were saved from danger. Maintaining water quality is important because water pollution is not only harmful to health, but also to recreation; commercial fishing; aesthetics; and private, industrial, and municipal water supplies.

In other way, the study fills the gap with electrochemical process in the case of pollutant removals from wastewater to contribute much in solving the problem in this area and used as a reference after publication. Generally, the formation of the clean environment keeps health of people and reduce ground and surface water contamination; if the waste water generated from domestic like JiT café's is treated by proper technology before discharging to the environment.

1.6 Scope of the Study

The study has been carried out in Jimma institute of Technology, Jimma town, Oromia region Southwest of Ethiopia. The effluents from Jimma institute of Technology student cafeteria have been used as a sample of domestic wastewater for the study. Due to the material and equipment available, allocated time and budget only the effect of some experimental parameters such as initial pH, reaction time, current ampere and concentration of electrolyte have been analyzed in order to complete the study.

They were analyzed to know the percentage removal of COD, color and turbidity with power consumption. Operating cost calculations including cost of chemicals used, electrode consumption, and sludge disposal have not been made to this treatment process. The study was carried out only in small-scale laboratory level. Generally, it was to show the enhancement of EO process when combined with US as efficient treatment techniques for the removal of pollutant from wastewater.

1.7 Limitations

The variations of electric power have an effect on the temperature of the samples and reagents stored in the refrigerator. In addition, it have interrupted the experimental session and made the session over the planned time. Finally, when the same electrodes have been used for different runs, the effects of decreasing in size of the electrodes were not considered.

CHAPTER TWO

LITERATURE REVIEW

2.1 Overview

In recent years, demand for pure water increases globally due to various factors such as population growth, rapid development of industrial activities, urbanization, and climate change. A daily activity uses water, which in turn increases the need for efficient wastewater treatment facilities (Asaithambi *et al.*, 2017). To keep the environment clean and prevent natural resources depletion, the technological processes should avoid the secondary contamination of the environment with harmful side products. In wastewater treatment processes, electrochemical and particularly electro-catalytic oxidation of organic compound meets these requirements (Wang *et al.*, 2017).

Combustion via high temperature incineration is one of the oldest historical means of disposing of pollutants and it indicates full mineralization of the compound to its most elementary form, carbon dioxide (CO₂). Ambient combustion or conversion of pollutants leads to mineralization through oxidation reactions at ambient temperature and pressure. When the oxidation treatment involves very strongly oxidizing agents, such as ozone (O₃), photolytic (ultra violet), chemical addition (oxidation), hydrogen peroxide (H₂O₂), or hydroxyl radical (OH[•]), this is known as an advanced oxidation process, or AOP (Ghatak, 2014).

Advanced oxidation involves the use of hydroxyl radicals as strong oxidant to oxidize complex organic matter into simpler products. Strong oxidizing agents such as ozone, hydrogen peroxide, hypochlorite, etc. in the presence of ultraviolet rays, ultrasonics or photo-catalysts produce the hydroxyl radicals. The hydroxyl radicals react with the dissolved contaminants, instigating a chain of oxidation reactions until the contaminants are completely mineralized. The hydroxyl group has a non-selective mode of attack and can work at normal temperature and pressure (Butkovskyi *et al.*, 2014).

The main advantage of AOPs over biological wastewater treatment is the ability of these methods to mineralize highly toxic compound, which are dangerous for microorganisms. Sathishkumar *et al.*, (2016) have argued their benefits and weaknesses as in the table below.

Table 2-1 Advantages and disadvantages of different AOPs methods

Treatment methods	Advantages	Disadvantages
AOPs EO	<ul style="list-style-type: none"> • Complete decomposition and high mineralization is achievable • Ease of implementation and automation • No chemicals required in industrial WW applications 	<ul style="list-style-type: none"> • Electrodes corrosion • Electrodes polarization and contamination • Energy-intensive process
US	<ul style="list-style-type: none"> • Ease of implementation and automation • Fast decomposition reactions • Multicomponent degradation mechanism by OH[•] radicals, pyrolytic reactions, physical effect of bubble collapse. • No chemicals required 	<ul style="list-style-type: none"> • Cooling is required • Energy-intensive process • Formation of toxic by-products is possible • Low mineralization and degradation rates • Strong-reproducibility dependence on reactor types
Fenton	<ul style="list-style-type: none"> • Complete mineralization is achievable • Fast decomposition reactions • No energy input required 	<ul style="list-style-type: none"> • Require chemicals • Ferric hydroxide sludge should be utilized • pH-dependent degradation
Photo-degradation and Photo-catalysis	<ul style="list-style-type: none"> • Complete mineralization is achievable • No chemicals required 	<ul style="list-style-type: none"> • Non-applicable for turbid and colored wastewaters • pH-dependent degradation • Separation of photo-catalyst is required
Ozonation	<ul style="list-style-type: none"> • Fast decomposition reactions • High degradation efficiencies are achievable • No chemicals required • No pH changes in during the treatment • Simultaneous disinfection effect 	<ul style="list-style-type: none"> • Energy-intensive process • Ozone toxicity and fire hazards issues • Formation of toxic by-products
Radiolysis	<ul style="list-style-type: none"> • Fast decomposition reactions • Non-selective process 	<ul style="list-style-type: none"> • Hazards of radioactive personnel exposure • High investment cost of electron accelerator • High resistant materials are required

Electrochemical technologies have been investigated as the effluent treatment processes for over a century. Recently, there has been an increased interest in electrochemical techniques such as electro-oxidation, electro-deposition, electrocoagulation, electro-flotation, electro-photo-oxidation and electrodisinfection as an alternate wastewater treatment method due to the non-biodegradable nature of some industrial wastewaters. The major influencing factors in the electrochemical treatment process are electrode material, input current, pH, conductivity, electrolyte concentration and initial concentration of the pollutants (Steter *et al.*, 2014).

Electrochemical technologies have been widely used for degradation of toxic compounds intended for its versatility, environmental compatibility and potential cost effectiveness (Nair *et al.*, 2014). Several researchers have examined the application of electrochemical oxidation process for degradation of a variety of persistent organic contaminants in wastewater and landfill leachate treatments (Butkovskiy *et al.*, 2014).

2.2 Electrochemical Oxidation Process

Study on electrooxidation for wastewater treatment goes back to the 19th century, when electrochemical decomposition of cyanide was investigated. Extensive investigation of this technology commenced since the late 1970s. During the last two decades, research works have been focused on the efficiency in oxidizing several pollutants on different electrodes, improvement of the electro-catalytic activity and electrochemical stability of electrode materials, investigation of factors affecting the process performance, and exploration of the mechanisms and kinetics of pollutant degradation (Nair *et al.*, 2014).

Electrochemical oxidation (EO) is developing technology of AOPs that use electricity in combination with electrodes where electron transfer occurs through generation of reactive oxygen species or directly at the surface of the anode. It is an effective method for reducing the pollutant load of water containing soluble organic matter. This technology is capable of degrading a wide range of organic contaminants, requires no auxiliary chemicals, does not produce waste, and is more easily adjusted to variations in influent composition than other AOPs (Moreira *et al.*, 2017).

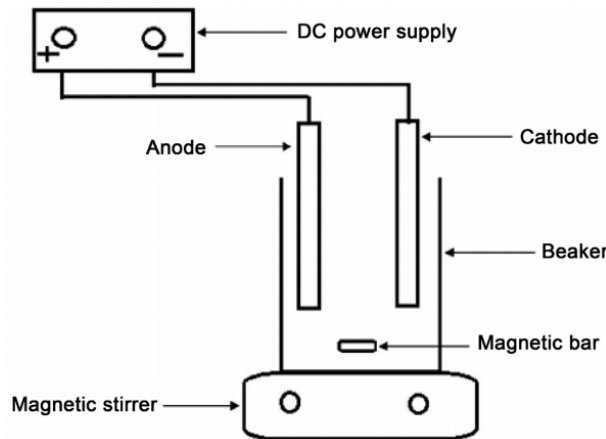
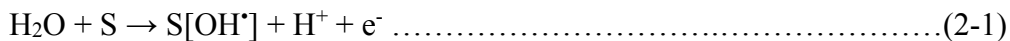


Figure 2-1 Schematic setup for electrochemical oxidation process (Source: Canizares *et al.*, 2006)

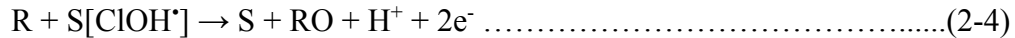
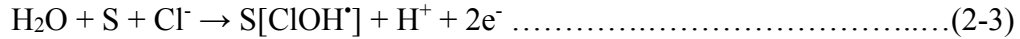
EO has been found to be an environmentally nonthreatening technology which able to mineralize completely non-biodegradable organic matter and to eliminate nitrogen species (Asaithambi, *et al.*, 2017). Moreover, due to the growing development of more efficient electrodes, EO is able to destroy several practically recalcitrant organic pollutants such as polyphenols and fatty acids. In electrochemical treatment processes, organic pollutants could be removed from wastewater by two ways: direct and indirect oxidation (Moreira *et al.*, 2017).

2.2.1 Indirect Electrooxidation Processes

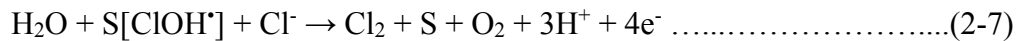
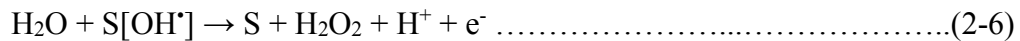
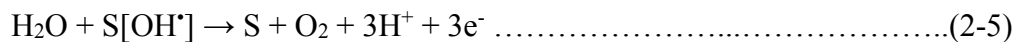
Indirect oxidation has been shown to take place by reactive oxygen species such as hydroxyl radicals (OH[•]) in the bulk solution (Wu *et al.*, 2014). It occurs in the liquid bulk phase by the mediated oxidants, and direct oxidation at the anode surface. Most electrochemical processes are based on indirect oxidation because direct oxidations of organic pollutants are very slow on inert anodes due to limiting reactions and reaction kinetics (Körbahti and Taşyürek, 2015). Hydroxyl radicals are produced by the anodic discharge of water in indirect electrochemical oxidation of organic pollutants at anodes. Hydroxyl radicals are adsorbed on the anode surface [S], and oxidize the organic material. This reaction could also occur in acidic medium at high current densities. Oxidation process continues by the formation of hydroxyl radicals with anodic discharge of water molecules (Wang and Xu, 2012).



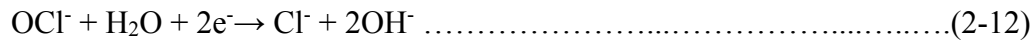
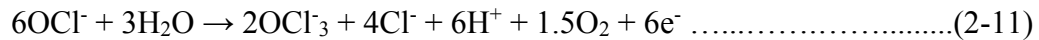
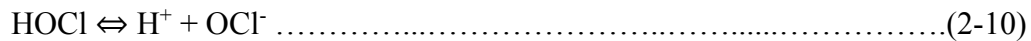
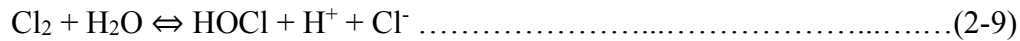
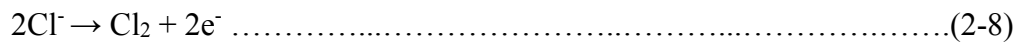
Chloro-hydroxyl radicals are also produced with the presence of chloride ions, adsorb on the active sites of the anode surface [S], and then oxidize the organic material (Thokchom *et al.*, 2015).



Therefore, electrochemical oxidation of wastewater results in removal of pollutants with the formation of Chloro-hydroxyl and hydroxyl radicals. The reactions can also yield O₂, H₂O₂, and Cl₂ (Steter *et al.*, 2014).



Indirect oxidation also occurs with the formation of HOCl/OCl⁻ redox mediators by the presence of NaCl that provides the anodic evolution of Cl₂. The percentage distribution of HOCl/OCl⁻ depends on the initial pH. Chloride-chlorine hypochlorite-chloride cycle occurs in neutral to moderate pH solutions, which maintain the initial concentration of chlorides, stable (Wang and Xu, 2012).



Indirect oxidation is still a viable technology for treating toxic or bio-refractory pollutants. Although there are concerns about the creation of chlorinated intermediates in the case of using Cl⁻ ions or about the complex facilities in the case of using electrically formed H₂O₂ or O₃. This technique can effectively oxidize many inorganic and organic pollutants at high chloride concentration (Nair *et al.*, 2014).

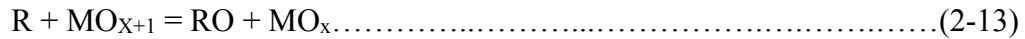
The possible formation of chlorinated organic compounds intermediates or final products hinders the wide application of this technique. Moreover, if the chloride content in the raw wastewater is low, a large amount of salt must be added to increase the process efficiency. In addition, there exists the secondary pollution from the heavy metals added. These disadvantages limit its application (Wu *et al.*, 2014).

2.2.2 Direct Anodic Oxidation

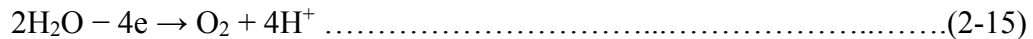
Electrooxidation of pollutants can also occur directly on anodes by generating physically adsorbed “active oxygen” (adsorbed hydroxyl radicals, OH[•]) or chemisorbed “active oxygen” (oxygen in the oxide lattice, MO_{x+1}). This process is usually called anodic oxidation or direct oxidation. In many studies, the anode in an electrolytic cell is used to oxidize the target compound (Moreira *et al.*, 2017).

It represents one of the simplest technologies in the pollutant mineralization providing that the anode materials are stable and have high over potential of oxygen evolution. The oxidation reaction occurs directly at the anode surface where the target compound undergoes electron transfer or reacts with surface-associated reactive oxygen species (Butkovskiy *et al.*, 2014).

The physically adsorbed “active oxygen” causes the complete combustion of organic compounds (R) and the chemisorbed “active oxygen” (MO_{x+1}) participates in the formation of selective oxidation products (R, organic compounds; z, number of adsorbed OH on anode):



Oxygen evolution reaction is



The reaction at the cathode is



In general, OH[•] is more effective for pollutant oxidation than O in MO_{x+1}. Because oxygen evolution, reaction, can also take place at the anode, high over potentials for O₂ evolution is required in order for reactions to proceed with high current efficiency.

Otherwise, most of the current supplied will be wasted to split water. The anodic oxidation does not need to add a large amount of chemicals to wastewater or to feed O₂ to cathodes, with no tendency of producing secondary pollution and fewer accessories required. These advantages make anodic oxidation more attractive than other electrooxidation processes (Nair *et al.*, 2014). As reported based on experimental evidence, hydroxyl radicals produced in the electrolytic process will non-selectively oxidize organic compounds more quickly than will other strong oxidants such as O₃.

This aggressive reactivity has benefits and risks because although it may helpfully oxidize persistent contaminants. The non-selective oxidation in the presence of salts may form halogenated by-products that may themselves be harmful contaminants. Halogenated by-product yield is one of the key disadvantages of the electrolytic process, but is common among AOPs (Butkovskiy *et al.*, 2014). Corrosion of electrodes due to a use of improper materials or formation of corrosive product on the surface of electrodes is other weakness of EO. However, other researchers have shown that by-products can be minimized by selection of the proper electrode material (Wu *et al.*, 2014).

As all processes, electro-catalytic oxidation processes have disadvantages such as polarization of electrodes due to poor mass transfer and gases accumulation. As a result, the reaction products and reagent/pollutant depletion in electrode's boundary layer or surface affect the efficiency of this technology (Lee *et al.*, 2016). The surface of electrodes is prone to foul with polymeric and oligomeric deposition products formed during electrode reactions. These, however, can be suppressed by powerful agitation generated for example by ultrasound.

In recent years, EO has gained increasing interest due to its outstanding technical characteristics for removing a wide variety of pollutants typically present in wastewaters such as refractory organic matter, nitrogen species and microorganisms. Electrochemical treatment method may be considered as an economically alternate process under such conditions when conventional treatment fails to reduce pollution (Liu *et al.*, 2019).

2.3 Sonolysis

Sound waves are defined as longitudinal pressure waves travelling through a substance. Ultrasound is a term applied to the sound waves above the frequency at which human ears are capable of hearing (20 Hz - 20 kHz). The ultrasonic band can be grouped into two sections power (20 kHz - 1 MHz) and diagnostic ultrasound (>1MHz) (Yang *et al.*, 2014). In the figure provided below the spectrum of sound is shown in a definitive diagram.

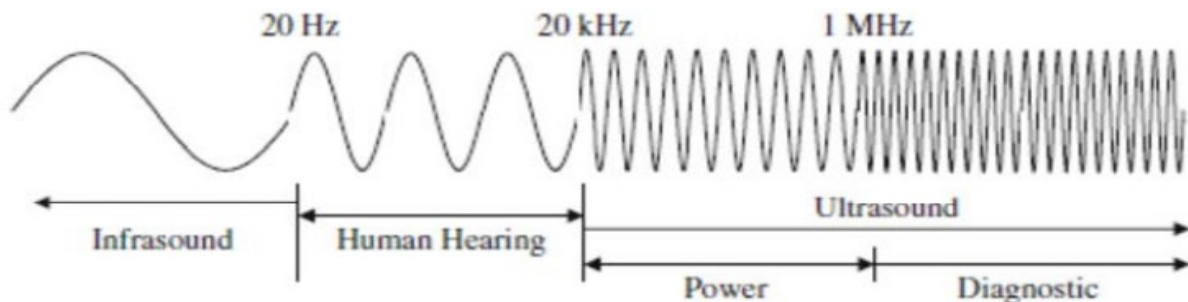


Figure 2-2 The classification of sound spectrum (Source: Sathishkumar *et al.*, 2016)

Sonolysis or Sonochemistry is a formation of radicals using ultrasound to break apart chemical bonds of organic compounds, causing oxidation or cavitation phenomenon. The cavitation is a process that involves the formation, expansion (rapid growth) and implosive collapse of microscopic bubbles in the solvent. That is caused by the periodic change of pressure in aqueous phase with ultrasonic wave application, causing turbulent motion (Barros *et al.*, 2014). Some areas, localized in specific regions such as inside the cavitation bubble and at the interface, encounter high temperatures and pressure. It can enhance chemical reactivity, because of the association between the degradation of the organic compound and free radical generation (Sathishkumar *et al.*, 2016).

The degradation process consists of a complex mechanism that can occur by pyrolysis inside the cavity of the bubble and in the interfacial region due to thermolysis or oxidation mediated via radical species (OH^{\bullet}). In addition, in the bulk solution and near the interface, due to reactions with radical species (OH^{\bullet}). There are chemical and physical effects involved with ultrasound at various frequencies. The chemical effects contain the chemical changes in vapor phase, cavitation bubbles and the surrounding medium (Moreira *et al.*, 2017).

Ultrasonic action can be affected by several factors, including the power and frequency applied, the nature of the electrolyte, the presence of dissolved gas, and the volatility of the compounds formed. Ultrasonic power is the most important parameter since there is a direct relation with the current value of the redox process. Ultrasonic sources of high frequency produce a great quantity of hydroxyl radicals in aqueous media in relation to those with low frequency using the same ultrasonic power (Moreira *et al.*, 2017).

High frequency generally favors the chemical mechanisms involving radicals (cleavage of substrate ligations or by water Sonolysis). On the other hand, low frequencies are more efficient for mechanical effects, as gases elimination and the cleaning of the electrodes surfaces. Yang and his co-authors (2014) have discussed the main parameters that influence the cavitation as table below.

Table 2-2 The main parameters that influence the cavitation

Parameter	Effect of different parameters of cavitation process
Frequency	Higher frequency leads to shorter acoustic cycles, smaller cavitation bubble size, shorter bubble collapse time, higher OH [*] formation. Lower frequencies provide collapse that is more violent.
Dissolved gases	Reduced tensile strength of the liquid initiates the cavitation process at lower pressures. The more gas nuclei in the liquid the lower intensity of generated shock waves. Monatomic gases yield more energy on collapse than multi-atomic gases, which is related to the heat conductivity of gases.
Intensity	There is a minimum level of intensity, which is required to initiate cavitation. Higher intensity generates more bubbles. However, too many bubbles may prevent the distribution of ultrasonic power into entire solution; therefore, an optimal level of intensity should be found.
Temperature	Higher ambient temperature reduces viscosity of the liquid and surface tension, which results in cavitation threshold decrease and higher bubbles formation; however, bubble collapse is less violent. Too many bubbles may reduce the distribution of ultrasonic power into entire solution. A temperature above the boiling point of the media significantly reduces the effect of Sonochemical reactions.
Pressure	Higher ambient pressure reduces the number of bubble collapses at the same intensity. However, collapses are more violent.

Ultrasound technique is among different advanced oxidation processes used for the treatment of wastewater. It does not require addition of chemicals to the treatment process and can be easily automated. In chemistry, it has been applied in several research fields like Sono-electro-synthesis cell disruption, organic synthesis, degassing, polymerization, nanotechnology, chemical reactions, food preservation, ultrasonic imaging, sonar detection, preparation of catalysts, and others (Chakma *et al.*, 2015).

Generally, Ultrasound technology is widely accepted for the degradation of pollutants and for the enhancement of other oxidation processes through cavitation. However, ultra-sonication alone often cannot achieve complete mineralization of organic pollutants and has low degradation rates. Moreover, Ultrasound alone cannot be used to oxidize the pollutants present in effluents containing complex organic and inorganic compounds. Many researchers have demonstrated that, efforts have been made to improve the efficiency of Sonication by combining it with other oxidation processes (Sathishkumar *et al.*, 2016).

2.4 Sono-Electrochemical Process

Conventional treatment methods suffer from some disadvantages such as high operating cost and transfer of pollutants from one phase to another. To overcome the disadvantages of the conventional treatment techniques, various hybrid technologies such as ozone assisted electrocoagulation (Bernal-Martínez *et al.*, 2010), Sono assisted electro-coagulation (Raschitor *et al.*, 2014), electrochemical advanced oxidation processes (AOPs) (Wang and Xu, 2012), and Sonication based AOPs (Chakma *et al.*, 2015) has gained considerable attention in the effort to improve treatment efficiency and effluent quality.

In order to improve mass transfer to the surface of the electrode, combination of Sonication and electrochemical oxidation has been tested and proven enhancement was achieved. Sono-electrochemical process is one of the hybrid technology developed for the treatment of organic pollutant. This field was born through the marriage of electrochemistry and ultrasound and increasingly gained the interest of electrochemists as well as engineers (Ghatak, 2014).

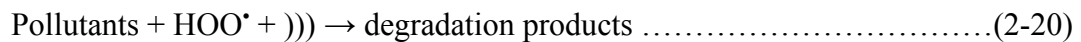
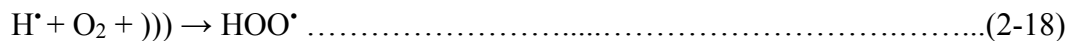
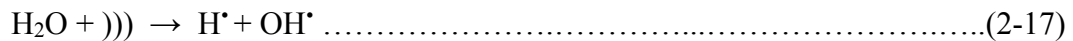
Namgoong and Chun were among those of first to make an effort towards the analysis of the effect of ultrasound implementation to an electrochemical system. When Ultrasound is combined with electrochemical process (US/EO), there is faster removal of pollutants compared to separate application of the treatment process (Raschitor *et al.*, 2014).

The combination tackles the problem of mass transfer to the electrode surface and suffers from fouling of the electrode surface limitation. By simply increasing its rate to the electrode, reducing the diffusion layer thickness and elevating the limiting current density it tackles the problem. In addition, the formation of radicals which could improve the coagulation behaviors of the flocs after the chemical interaction with their surface (Thokchom *et al.*, 2015).

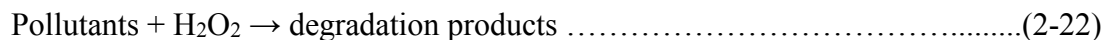
According to Barrera-Díaz *et al.*, (2014), the sonication in the electrochemical process promotes the benefits such as the ultrasonic agitation via cavitation within the bulk interrupts the diffusion layer and stops the diminution of electro-active species. Also, the transfer of ions across the electrode double layer is made available more evenly via ultrasonic agitation, ultrasonic degassing prevent the accumulation of gas bubbles at the electrode, and the electrode surface is continuously activated and cleaned via ultrasonic irradiation.

US/EO process uses electricity as the main reactant and treats very toxic wastes at mild conditions and effluents with low conductivity without auxiliary chemicals or electrolytes (Chakma *et al.*, 2015). EO and US processes are relatively safe for operating personnel, compared with the processes of radiolysis and ozonation. Integration of EO and US has prerequisites of EO enhancement due to the physical effect of US, which can activate electro-catalytic properties of electrodes and reduce their polarization.

The Sonochemical process applied to the oxidation of organic compounds consists of OH[•] radical production by water decomposition, under ultrasonic action, represented by (1), according to the following equations (Wu *et al.*, 2014):



The formation of hydrogen peroxide, a secondary oxidant species, occurs by the recombination of the OH[•] radical species and can help in the degradation process (Raschitor *et al.*, 2014).



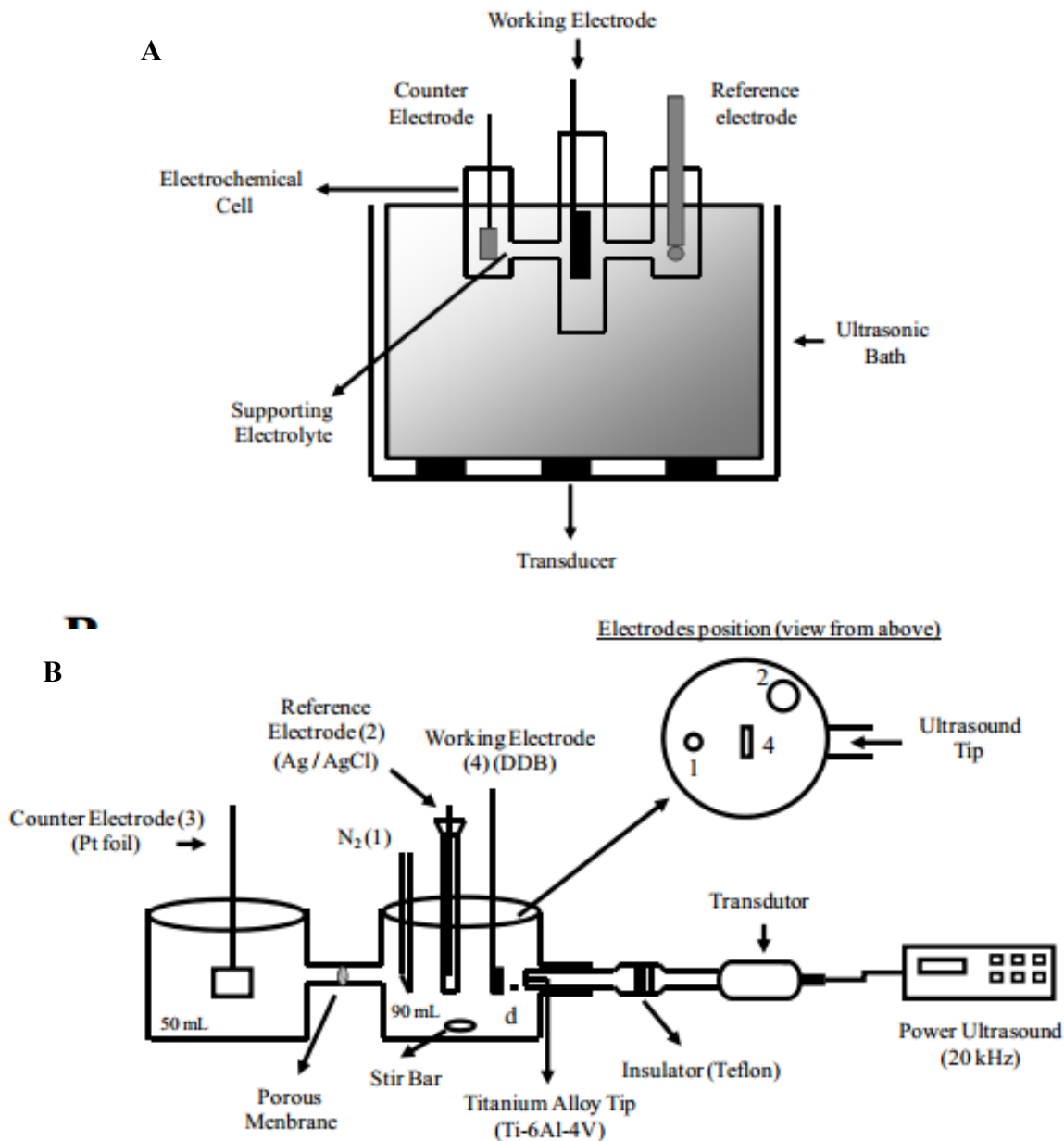


Figure 2-3 (A) Ultrasonic bath containing an EO cell and (B) US/EO cell (Source: Garbellini *et al.*, 2010)

The sources of ultrasound should be considered when the power ultrasound is applied to an electrochemical system. Power ultrasound is introduced into an electrochemical cell by two major sources; they are either ultrasonic baths or ultrasonic immersion horn probes. The ultrasonic bath (Figure A) consists of a number of fixed frequency (20-100 kHz) transducers below the physical exterior of the bath unit and it has the capacity to clean surfaces and to help the dissolution of substances (Chakma *et al.*, 2015).

The bath is filled with distilled water and the conventional electrochemical cell is placed into a fixed position. In this arrangement, the cell is electrically separated and the sound waves penetrate a glass wall before entering the electrochemical reactor. This type of source has been used in polymerization reactions (Barros *et al.*, 2014), metal electro-depositions (Liu *et al.*, 2019) and in studies showing the effect of ultrasound in the sono-electrochemical response of some compounds (Sathishkumar *et al.*, 2016).

On the other hand, studies with the ultrasonic horn transducer as a tip shape (Figure B) are very frequent. This titanium alloy tip (Ti-6Al-4V) is properly insert in the electrochemical cell. The instrument that produces ultrasound converts 50/60 Hz at a high frequency of electric energy, which is transmitted to a piezoelectric transducer, transforming in mechanical vibrations. The probes, creating pressure waves on liquids, intensify these vibrations (Barrera-Díaz *et al.*, 2014).

This action produces millions of microscopic waves (cavities) that expand during the negative pressure and implode violently during the positive pressure. As the bubbles implode, millions of shock waves are produced, generating extreme pressures and temperatures in the implosion sites, with a huge energy liberation. In this way, in front of the horn tip, the formation of a cavitation bubbles cloud can be observed at at sufficiently high intensities (Wu *et al.*, 2014).

As present previously, many studies have focused on oxidative degradation of organic compounds by coupled techniques as Sono-electrochemical. Moreover, the goal of the research is to enhance the efficiency of electro-catalytic degradation processes by assisting it with ultrasound in order to eliminate the main drawbacks of a single electrochemical oxidation such as electrodes polarization and passivation (Raschitor *et al.*, 2014).

2.5 Response Surface Methodology (RSM)

In classic optimization method, one variables changes at a time, while other parameters are kept constant. However, the classic method is not able to determine the complex interaction between the variables and responses (Moradnia *et al.*, 2016). Response surface methodology (RSM) has been derived from statistical and mathematical techniques, which can be used for studying the effect of different factors at various levels and their interactions (Emamjomeh *et al.*, 2017).

Nowadays, RSM, an important branch of experimental design, has been used for modelling and optimizing a variety of water and wastewater treatment processes. It is applied for building models, evaluating the effects of several variables, and obtaining the values of process variables that produce desirable values of the response (Nair *et al.*, 2014).

RSM is a designed regression analysis to predict the value of a dependent variable based on the controlled values of the independent variables. From the parameter estimates, one can determine which variable contributes most to the estimated value, thereby allowing the product researcher to focus on the variables that are most important to the product acceptance. The procedures of RSM are employed for the modelling and optimization of different chemical, physical and even biological processes for the treatment of various pollutants (Liu *et al.*, 2019).

The two most common designs extensively used in RSM are the Central Composite Design (CCD) and the Box–Behnken Design (BBD). CCD is one of the most frequently used technique among RSM due to the need for fewer numbers of experiments (Jamali *et al.*, 2018). Since, is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points (Asaithambi *et al.*, 2016). This method consists of four main stages including experiment design, model fitting, model verification, and determining the optimal conditions (Jamali *et al.*, 2018).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The study has been conducted in Jimma town at Jimma institute of Technology (JiT). Jimma town is found in Oromia regional state, located 352 km southwest of Addis Ababa the capital city of Ethiopia. Jimma town is lying between Latitude 7°39' - 7°83' North and Longitude of 36°49' - 36°61' east and with an elevation of 1700 m - 1850 m above sea level. Whereas, JiT is located at 7°68'23"N Latitude and 36°85'15" E longitude (GeoDatos, 2020).

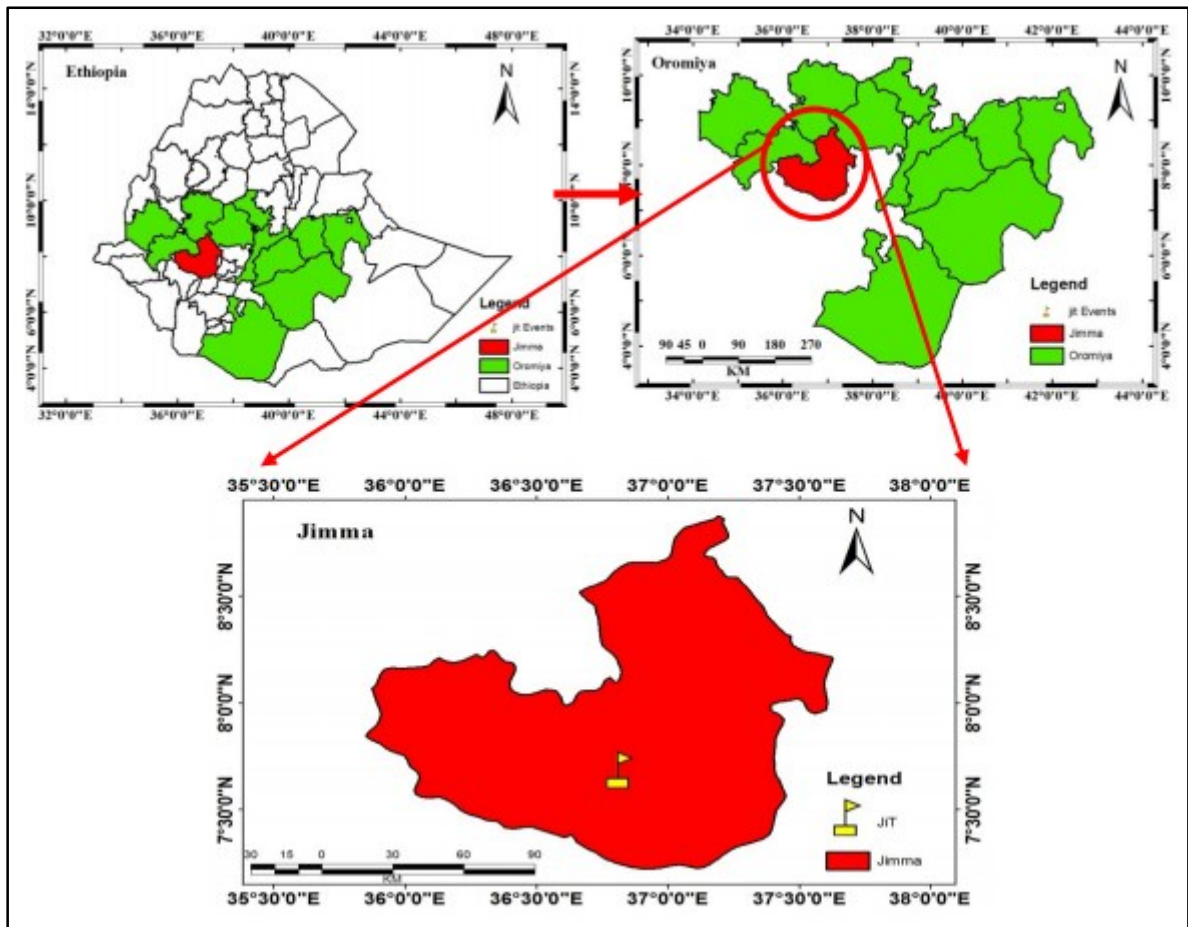


Figure 3-1 Map of study area (Source: WGS 1984)

3.2 Study Period

The study has been conducted from August 2019 to February 2020 in Jimma Institute of Technology (JiT), Environmental Engineering laboratory.

3.3 Study Design

Laboratory based (experimental) study was conducted, focusing on the evaluating the performance of both electro-oxidation and Sonoelectrooxidation process in removing the COD, color and turbidity from wastewater with its power consumption. All important preparation and physico-chemical analyses for water sample have been made during laboratory assessment. While running the experiments, laboratory manuals were used properly to reduce redundancy and errors.

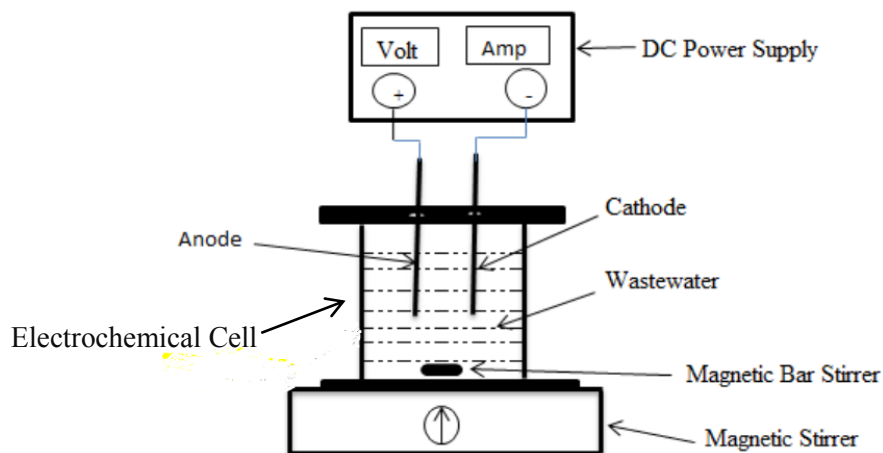


Figure 3-2 The schematic setup of Electrooxidation process (Source: Canizares *et al.*, 2006)

This study was performed in a cylindrical batch reactor separately to check their performance. The net volume of this batch reactor was 1 L. The first system was electrochemical oxidation process that consist electrochemical cell and DC-power supply. The 1000 mL sample was used for each run and the required concentration of electrolyte (NaCl or CaCl₂) was added in it. After the initial pH of the run was adjusted by using diluted H₂SO₄ or NaOH, the initial conductivity and temperature of the system were measured.

The electric power supply was provided by the laboratory direct current ampere (DC) equipped with current–voltage monitoring. Each of the aluminum (Al) electrodes (anode and cathode) connected to a power supply and immersed into the reactor containing the sample. The distance between Al electrodes were kept constant (1 cm) throughout the experiment. The current (Ampere) was adjusted and the initial voltage was taken for each run. Stopwatch was used to control the reaction time and all runs were performed at normal temperature and pressure.



Figure 3-3 Electro-chemical oxidation experimental setup

The reactor was placed on a magnetic stirrer (constant speed of 140 rpm and room temperature) to mix its content during the experiment in order to maximize mass transport for EO process. All chemical experiments were performed according to the standard instructions (APHA, 2005). The experimental setup of EO reactor was shown in Figure 3-3.

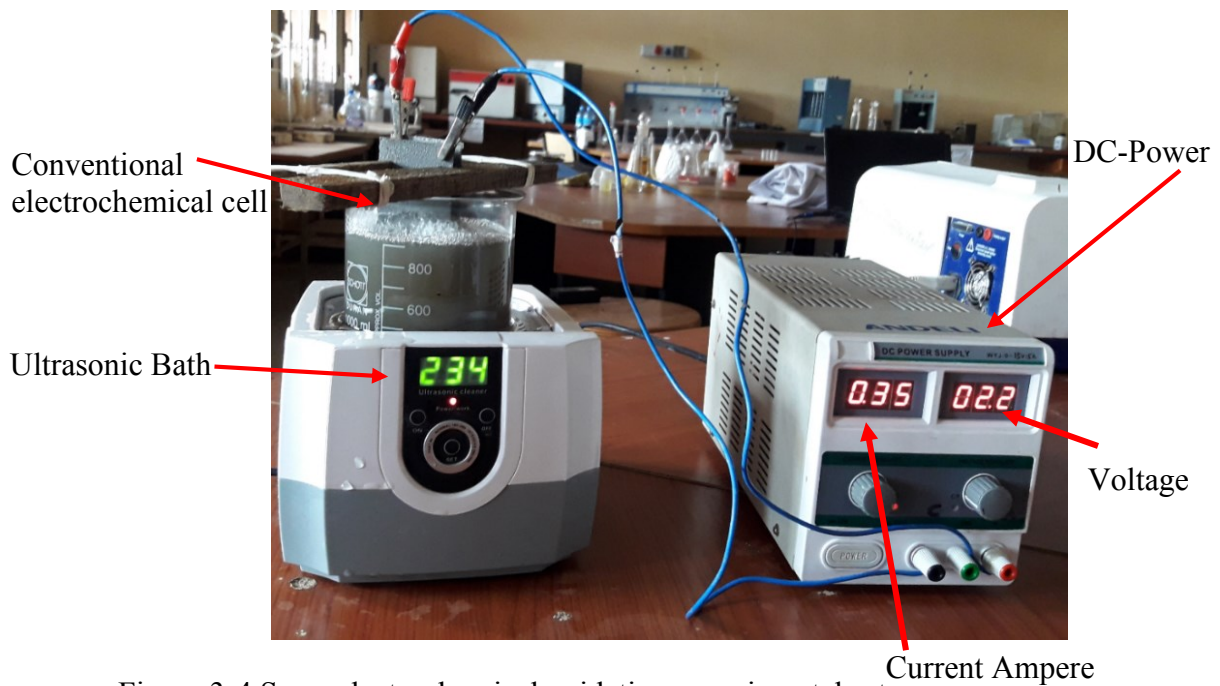


Figure 3-4 Sono-electrochemical oxidation experimental setup

During electrolysis, the samples taken/ ejected at different time intervals by pipette into a glass beaker. Moreover, all the experimental runs were performed at room temperature and distilled water was used to wash the apparatus before and after each usage of any apparatus. In the second system, all the experimental setup were similar to EO, but the magnetic stirrer was replaced by Ultrasonic cleaner for US/EO. The experimental setup of US/ EO process consists of electro-chemical oxidation reactor and ultrasonic water bath was as shown in Figure 3-4.

To simplify the experimental design, variables like distance between electrodes (1 cm), wavelength (420 nm), area of electrode (13 cm x 5cm), stirring rate (140 rpm), temperature (room), ultrasonic power (70 Watt) with frequency (50 Hz) and volume of sample (1 L) taken were kept constant. The data obtained from both the onsite measuring and laboratory test analyzed and optimized by using response surface methodology (RSM) based on Central Composite Design (CCD) using the four independent parameters.

3.4 Materials and Equipment's

3.4.1 Instruments

The equipment's used for the investigation of samples were beakers (80, 100, 400, 500, 800, 1000 mL), desiccator, 250 mL conical (Erlenmeyer) flask, pipettes with elongated tip, pipette bulb, tissue paper, magnetic stirrer (model RHB2), distiller, COD Vials with stand, COD kit, electrode (Al), measuring cylinder, sample cell, plastic bottles and wash bottle. Weighing balance (model Pw 124) was used to weigh the powdered chemicals.

To measure the pH, conductivity, turbidity, color (absorbance and transmittance) and COD of each runs pH meter (pH 3310), Conductivity meter (Cond 3110), Turbidity meter (Wag-WT3020), spectrophotometer (model 6700) and COD digester (Hatch 45600-02) were used respectively. The digital DC power supply (WYJ-o-15V/5A) was used to perform EO and US/EO experiments to adjust the current ampere and voltage. A constant-temperature magnetic mill stirrer (model RHB2) was used to perform agitation of the solution during EO process.

The Al (anode and cathode) were used to perform both EO and US/EO experiments with dimensions of 13 cm (length) x 5 cm (width). Ultrasonic cleaner (CD-4800) with volt - AC 220-240 V with 50 Hz of frequency and power option of 70 Watt were replaced for US/EO process instead of magnetic stirrer (for EO).

Copper wires were connected to DC power source and at one end; the wires are connected to electrodes by electrical clips. After that, the two electrodes were dipped in the sample. Then, the power was supplied and the result was conducted at different affecting parameters.



Figure 3-5 a) Distiller b) pH and conductivity meter c) spectrophotometer d) Reagents e) Al electrodes f) Laboratory refrigerator g) COD reactor used in Laboratory

3.4.2 Chemicals and Reagent Preparation

Analyses have been conducted for samples taken from the effluents of Jimma Institute of Technology (JiT) student's cafeteria. The initial pH of the solutions was adjusted using sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄). Sodium chloride (NaCl) and calcium chloride (CaCl₂) were used as the supporting electrolyte. All the solutions were prepared by using deionized/ distilled water of conductivity of 3 to 5 ms/cm (milli Siemen's/centimeter). Buffer solutions were used for calibration, to check whether the pH meter and conductivity meter were working properly or not.

Chemicals such as Mercury sulphate (HgSO₄), ferrous ammonium sulphate (Fe(NH₃)SO₄), silver sulphate (AgSO₄), ferroin indicator (Phenanthroline mono hydrate and Ferric Sulphate) (Fe(o-phen)₃SO₄), potassium dichromate (K₂Cr₂O₇) and sulfuric acid (H₂SO₄) were used for COD analysis (APHA, 2005).

I. Preparation of Reagents

K₂Cr₂O₇ oxidizes organic matter present in sample completely in the presence of H₂SO₄, AgSO₄ and HgSO₄ to produce CO₂ and H₂O. The sample was refluxed with known amount of K₂Cr₂O₇ in the H₂SO₄ medium and the excess K₂Cr₂O₇ was determined by titration against Fe(NH₃)SO₄, using Fe(o-phen)₃SO₄ as an indicator. The dichromate consumed by the sample was equivalent to the amount of O₂ required to oxidize the organic matter.

a. Standard Potassium Dichromate Reagent –Digestion Solution

4.913 g of K₂Cr₂O₇ and exactly 33.3 g of AgSO₄ weighed and transferred to a beaker one after the other. 167 mL of concentrated sulphuric acid was measured accurately and transferred to the beaker using clean dry measuring cylinder. The contents dissolved and cooled to room temperature. Standard measuring flask (1000 L) was taken and a funnel was placed over it. The contents carefully transferred to the standard flask and made up to 1000 mL using distilled water. This was the standard potassium dichromate solution to be used for digestion.

b. Sulphuric Acid Reagent – Catalyst Solution

5.5 g silver sulphate crystals was weighed accurately to a standard flask (1000 mL) and about 500 mL of concentrated sulphuric acid was added carefully to it. It was allowed to stand for 24 hours, so that the silver sulphate crystals were dissolved completely.

c. Standard Ferrous Ammonium Sulphate Solution

39.2 gram of ferrous ammonium sulphate crystals weighed accurately and dissolved in distilled water. Standard measuring flask (1000 mL) taken and a funnel was placed over it. The contents transferred carefully to the standard flask and made up to 1000 mL mark using distilled water.

II. Procedure for Chemical Oxygen Demand Test

To analyze the Chemical Oxygen Demand (COD) value of each runs, first 2.5 mL wastewater sample taken in COD vials and 2.5 mL of distilled water (blank) in another COD vial with stopper. Then, 1.5 mL of potassium dichromate added to both the tubes and 3.5 mL of sulphuric acid reagent added carefully to both vials. The hot COD vials tightly closed and kept in COD digester at 150 °C for 2 hours.

After cooling to room temperature, the solution transferred to the conical flask and 3 drops of Ferroin indicator added to it. The bluish green colored content was titrated against ferrous ammonium sulphate continually until the color changes to reddish brown. This fashion repeated for all experimental runs. Finally, the COD concentration calculated for each by taking the reading.

3.4.3 Software

The software's used to perform the Research was Version 11 Design Expert software - Response Surface Methodology (RSM) and Microsoft Office 2013.

3.5 Study Variables

3.5.1 Dependent Variable

- ✓ Efficiency

3.5.2 Independent Variables

- ✓ Removal efficiency of electrooxidation process for domestic wastewater treatment for COD, Color and Turbidity with power consumption.
- ✓ Removal efficiency of Sono-electrooxidation process for domestic wastewater treatment for COD, Color and Turbidity with power consumption.
- ✓ Optimization of the operating parameters

3.6 Sample Collection, Transportation and Preparation

3.6.1 Sample Collection

Composite sampling types applied in this study for establishing the reliability of the sample. The wastewater taken from discharge point of JiT student cafeteria in plastic bottles for three days according to the manuals. About one hundred liters of wastewater sample taken by bottles during the study period. The bottles rinsed with distilled water in order to take the sample according to the laboratory guideline.

3.6.2 Sample Transportation

The taken sample transported to the laboratory by plastic container according to the preservation of samples for characterization. The sample was stored at a temperature of 4°C in the laboratory refrigerator (EPA, 2015).

3.6.3 Sample preparation

The sample has been prepared for analysis of the performance of the Ultrasonic and electrochemical oxidation process separately and in combined systems. The sample preserved by keeping its maximum holding time for each parameter and performed (EPA, 2015).

3.7 Method of Data Analysis

3.7.1 Analysis by Empirical Formula

The aim of this study was to optimize the parameters, which affect the performance of EO and US/EO process based on the responses of COD, color and turbidity removal efficiencies with power consumption to improve the treatment of domestic wastewater using RSM. RSM is environmental modelling applied for analysis of the data's from the laboratory by using empirical formulas:

- i. Percentage COD Removal (Banacha, 2018)

The COD test is an indicator of organic component in wastewater. It is estimated as:

$$\% \text{ COD removal} = \frac{\text{COD}_i - \text{COD}_t}{\text{COD}_i} * 100 \dots\dots\dots(3-1)$$

Where, COD_i and COD_t are the chemical oxygen demand in mg/L at initial ($t = 0$) and at any reaction time (t) respectively.

COD (mg/L) of each run was determined by the following formula (Aslam, 2013)

$$COD = \frac{(A-B)}{\text{Volume of a Sample}} * N * 8 * 1000 \dots\dots\dots (3-2)$$

Where, volume of FAS for blank (A), for Sample (B) and Volume of sample = 2.5 mL

$$\text{Normality of FAS (N)} = \frac{\text{Weight of FAS used in FAS solution preparation}}{\text{Equivalent Weight of FAS}} = \frac{39.2g}{392g} = 0.1N$$

ii. Percentage Color Removal (Steter *et al.*, 2014)

$$\% \text{ Color removal} = \frac{Abs_i - Abs_t}{Abs_i} * 100 \dots\dots\dots (3-3)$$

Where, Abs_i and Abs_t are absorbance of samples for corresponding wavelength (λ = 420 nm) at initial (t = 0) and at any reaction time (t) respectively.

iii. Percentage Turbidity Removal (Murat, 2009)

$$\% \text{ Turbidity removal} = \frac{Turb_i - Turb_t}{Turb_i} * 100 \dots\dots\dots (3-4)$$

Where, Tur_i and Tur_t are the turbidity of the sample (NTU) at initial (t = 0) and at any reaction time (t) respectively.

iv. Power Consumption

For the removal of one kg of COD, it is calculated (Santos *et al.*, 2013) as follows:

$$E_{EO} = \left(\frac{[tVI/V_S]/1*10^3}{\Delta COD/1*10^6} \right) \dots\dots\dots (3-5)$$

Where, E_{EO} is energy consumption for electrooxidation (EO) process (kWh/m³), t is the time of electrolysis (hour); V and A are the average cell voltage and the electrolysis current; V_S is the sample volume (l), and ΔCOD is the difference in COD (mg/L).

The electrical energy per order defined as the electrical energy (in kWh) required for reducing the concentration of a pollutant by one order of magnitude in one m³ of wastewater (Asaithambi *et al.*, 2017). E_{US} calculated using:

$$E_{US} = \frac{P_{el} * t * 1000}{V' * 60 * \log\left(\frac{COD_i}{COD_t}\right)} \dots\dots\dots (3-6)$$

Where, E_{US} is energy consumption for sonication (US) process (kWh/m³), P_{el} is the rated power in kW (70 Watt), t is the reaction time (hour), and V' stands for the reactor volume (L).

3.7.2 Experimental Design and Statistical Analysis

RSM used to optimize a response is influenced by several independent variables. Thus, performance measure or quality characteristic is called the response. The input variables are called independent variables, and they are subject to the control of the scientist or engineer (Liu *et al.*, 2019).

Table 3-1 Experimental ranges and levels of independent variables

Factor	Name/ Units	Minimum	Maximum	Coded Low (-1)	Mean (0)	Coded High (+1)
A	pH	3.00	11.00	-1 ↔ 3.00	7.00	+1 ↔ 11.00
B	Time (minute)	20.00	60.00	-1 ↔ 20.00	40.00	+1 ↔ 60.00
C	Current (Amp)	0.1000	0.6000	-1 ↔ 0.10	0.3500	+1 ↔ 0.60
D	CaCl ₂ / NaCl (g/L)	1.0000	3.00	-1 ↔ 1.00	2.00	+1 ↔ 3.00

In this research, CCD model with four factors applied to optimize the parameters. To determine the optimal values of the independent variables of the process, four dependent variables: COD, color, turbidity removal and power consumption analyzed as the response. Whereas, the pH, electrolysis time, current ampere and electrolyte concentration were selected as input variables.

The rotatable experimental plan was performed with the four independent variables at three coded levels (-1, 0, +1) as shown in the Table 3-1. Actual values are original values that given to different factors and code values given for the levels of factors. The experimental design was based on two-level full factorial design to which central and star points were also added. Liu *et al.* (2019) can calculate the total number of experiments (N):

$$N = N_a + N_o + N_c \dots\dots\dots (3-7)$$

Where, N_a represents the number of two-level experiments in a full factorial design or replicates of factorial points ($2^4 = 16$), N_o is the number of replication in the central point (6 replications) for evaluation of net error, and N_c denotes the number of replicate of axial (star) points ($2 * 4 = 8$) by using alpha 0.5. Twenty-four ($16 + 8 = 24$) factorial points and six replicates of central point in the total thirty ($24 + 6 = 30$) experimental runs provided by software for single process.

Six center point of the design to evaluate the pure error and consequently the lack of fit. Lack of fit test was performed to assess the fit of the final model. The experimental results analyzed using RSM algorithm was fitted to the predictive quadratic polynomial Equation. Second-order model equation for prediction of the optimal conditions can be expressed by the following equation (Liu *et al.*, 2019):

$$Y_i = \beta_0 + \sum_{i=1}^4 \beta_i \cdot X_i + \sum_{i \leq j}^4 \sum_j^4 \beta_{ij} \cdot X_i \cdot X_j + \sum_{i=1}^4 \beta_{ii} \cdot X_i^2 + e \dots \dots \dots (3-8)$$

Where Y_i , is the response variable, β_0 is the model (regression) constant, β_i is the linear terms, β_{ii} are the squared terms (second-order), β_{ij} is the interaction terms, X_i and X_j are independent variables, e is random error and $k = 4$ is the number of parameters.

3.8 Data Quality Assurance

According to APHA (2005), proper quality assurance procedures and precautions were taken to ensure the reliability of the results. In order to increase the quality of the data, a fieldwork and laboratory manuals have been used in order to avoid error of data. Moreover, to handle the data's carefully, assistants have been there. At each set of experiments, standardization (calibration) was conducted for analysis. The collected data was analyzed and interpreted using both qualitative and quantitative data analysis methods by using RSM.

3.9 Ethical Considerations

All literatures taken from others were properly cited according to the legislation. Each and every of data collection, processing, and analysis follow scientific methods and procedures. Finally, the results of laboratory analysis have been honestly recorded and interpreted based on scientific procedures.

3.10 Dissemination of the Results

The research will be presented publically for postgraduate studies of Jimma Institute of Technology, Faculty of Civil and Environmental Engineering, Environmental engineering chair in the presence of examiners. Finally, the paper will be disseminated or published using nationally and internationally known journals of Environmental Engineering.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 COD, Color and Turbidity Removal Efficiency and Power Consumption for Electrochemical Oxidation Process

In this study, laboratory experiments were carried out using electrochemical process (EO) and Sono-electrochemical oxidation process (US/EO) by varying parameters in their interval: pH (3 - 11), electrolytic concentration (1 – 3 g of NaCl/ CaCl₂), current ampere (0.1 – 0.6 A) and reaction time (20 – 60 minute). Those parameters were considered to determine the removal efficiency of COD, color (absorbance and transmittance) and turbidity with power consumption. The order of experiments was arranged randomly.

All experiments (for EO and US/EO) were performed in the laboratory using Aluminum-Aluminum electrode combination with electrode distance of 1 cm. All laboratory results were tabulated under appendices (Appendix A1 for EO and Appendix A2 for US/EO) that consist affecting parameters and COD titrated, absorbance of color at 420 nm wavelength and turbidity with power consumption. This study was mainly aimed to determine the optimum values of operating parameters of efficient treatment condition for domestic wastewaters.

As shown in the Table 4-1 and 4-2, the removal efficiency of COD, color and turbidity with power consumption varied within the ranges of 11.44 – 83.51 %, 40.61 – 95.36 % and 34.05 – 98.91 % with 0.0002 – 0.0104 kWh/m³ for EO process using CaCl₂. On the other way, they were varied within the ranges of 8.48 – 71.92 %, 60.23 – 93.81 % and 73.41 – 97.37 % with 0.0002 – 0.0051 kWh/m³ for EO process using NaCl.

The maximum removal efficiencies of COD, color and turbidity with power consumption were 79.89 %, 97.38 % and 97.37 % for EO with 0.0075 kWh/m³ using NaCl, respectively. Those optimum results were obtained at pH=3, electrolysis time of 60 minute, current of 0.6 Ampere and 1g of NaCl. Whereas, using CaCl₂, the maximum removal efficiencies of COD, color and turbidity with power consumption for EO process were 77.51 %, 94.50 % and 98.12 % with 0.0050 kWh/m³ respectively. Those optimum results were obtained at pH=3, electrolysis time of 60 minute, current of 0.6 Ampere and 3 g of CaCl₂ at the degree of desirability of the model was equal to 1.

Table 4-1 FCCD for COD, color and turbidity removal with Power Consumption for EO process using CaCl₂

Run	A:pH	B:Time minute	C:Current Amp	D:CaCl ₂ g/L	COD %	Color %	Turbidity %	Power Consumption kWh/m ³
1	7	40	0.35	2	66.72	86.44	93.71	0.002
2	7	40	0.35	1.5	62.24	90.34	94.11	0.002
3	7	40	0.35	2	66.72	86.44	93.71	0.002
4	7	50	0.35	2	64.27	88.71	83.77	0.0025
5	3	60	0.1	1	49.17	77.69	83.84	0.0007
6	11	60	0.1	1	15.76	49.19	56.99	0.0009
7	11	20	0.6	3	18.84	53.66	52.94	0.0067
8	7	40	0.35	2	66.72	86.44	93.71	0.002
9	11	20	0.6	1	20.84	52.14	62.47	0.0047
10	7	30	0.35	2	65.03	89.32	88.36	0.0013
11	11	60	0.6	3	35.65	73.02	75.99	0.0104
12	11	60	0.6	1	28.54	68.45	85.31	0.0094
13	7	40	0.35	2	66.72	86.44	93.71	0.002
14	3	20	0.1	3	18.72	56.48	67.61	0.0005
15	11	60	0.1	3	15.46	44.43	50.12	0.0009
16	7	40	0.35	2.5	68.36	84.14	96.67	0.0021
17	7	40	0.475	2	72.39	88.11	94.23	0.0031
18	11	20	0.1	1	11.44	45.24	43.09	0.0005
19	3	60	0.1	3	48.87	74.01	85.49	0.0011
20	3	20	0.6	3	65.97	84.34	87.45	0.0018
21	3	20	0.1	1	21.09	60.27	65.01	0.0002
22	7	40	0.35	2	66.72	86.44	93.71	0.002
23	5	40	0.35	2	68.59	82.27	95.59	0.0021
24	3	60	0.6	3	83.51	95.36	98.91	0.005
25	3	60	0.6	1	79.46	91.46	96.31	0.0071
26	7	40	0.35	2	66.72	86.44	93.71	0.002
27	3	20	0.6	1	67.47	81.95	92.97	0.003
28	9	40	0.35	2	47.09	63.87	77.11	0.0031
29	7	40	0.225	2	52.93	70.56	89.13	0.0018
30	11	20	0.1	3	14.53	40.61	34.05	0.0002

Table 4-2 FCCD for COD, color and turbidity removal with Power Consumption for EO process using NaCl

Run	A:pH	B:Time minute	C:Current Amp	D:NaCl g/L	COD %	Color %	Turbidity %	Power Consumption kWh/m ³
1	11	20	0.6	3	13.04	62.83	75.91	0.0029
2	7	40	0.35	2	44.44	74.41	81.55	0.0043
3	3	20	0.6	1	66.17	78.18	86.34	0.003
4	3	60	0.1	1	47.37	80.04	86.69	0.0009
5	11	20	0.1	3	19.8	62.58	77.86	0.0002
6	7	40	0.35	1.5	36.09	77.35	82.56	0.0021
7	3	60	0.6	3	69.45	92.01	95.52	0.0037
8	7	40	0.35	2	44.44	74.41	81.55	0.0043
9	3	20	0.1	1	13.55	62.61	73.41	0.0007
10	7	40	0.35	2.5	43.61	77.36	84.21	0.0007
11	11	20	0.1	1	8.48	69.37	75.89	0.0002
12	7	50	0.35	2	47.37	78.71	82.46	0.0047
13	7	40	0.475	2	43.84	73.01	80.45	0.0048
14	7	40	0.225	2	31.39	66.13	76.69	0.0044
15	11	20	0.6	1	12.03	71.52	75.08	0.0033
16	3	60	0.1	3	47.37	83.09	85.99	0.0016
17	7	40	0.35	2	44.44	74.41	81.55	0.0043
18	3	20	0.6	3	62.4	76.55	89.23	0.0015
19	11	60	0.6	3	17.48	67.87	77.29	0.0051
20	7	40	0.35	2	44.44	74.41	81.55	0.0043
21	5	40	0.35	2	63.39	78.11	81.83	0.0024
22	9	40	0.35	2	30.91	70.23	78.81	0.0024
23	11	60	0.1	1	11.28	65.46	75.33	0.0007
24	7	30	0.35	2	45.49	72.37	79.05	0.0029
25	3	20	0.1	3	32.86	60.23	74.52	0.0008
26	7	40	0.35	2	44.44	74.41	81.55	0.0043
27	7	40	0.35	2	44.44	74.41	81.55	0.0043
28	11	60	0.1	3	22.81	61.94	74.87	0.0022
29	11	60	0.6	1	15.04	71.43	80.32	0.0046
30	3	60	0.6	1	71.92	93.81	97.37	0.0041

4.2 COD, Color and Turbidity Removal Efficiency and Power Consumption for Sono-Electrochemical Oxidation Process

Predominantly, the study was done to evaluate the simultaneous effect of ultrasonic and electrochemical processes on removal efficiency using NaCl and CaCl₂. The results of experiments in the form of removal rate of COD, color and turbidity with power consumption for EO and US/EO were provided in Tables 4-1 to 4-4. Their removal efficiencies were varied within the ranges of 10.75 – 97.61 %, 58.54 – 99.43 % and 73.04 – 99.25 % with 0.0012 – 0.0167 kWh/m³ respectively for US/EO process using CaCl₂. In addition, they were varied within the ranges of 33.83 – 87.06 %, 75.55 – 96.02 % and 81.15 – 98.3 % with 0.0018 – 0.0074 kWh/m³ respectively for US/EO process using NaCl.

The maximum removal efficiencies of COD, color and turbidity with power consumption were 87.06 %, 98.10 % and 98.30 % for US/EO with 0.0015 kWh/m³ using NaCl, respectively. Those optimum results were obtained at pH = 3, electrolysis time of 60 minute, current of 0.6 Ampere and 1g of NaCl. Whereas, using CaCl₂, the maximum removal efficiencies of COD, color and turbidity with power consumption for US/EO were 97.61 %, 99.43 % and 99.25 % with 0.0077 kWh/m³ respectively. Those optimum results were obtained at pH=3, electrolysis time of 60 minute, current of 0.6 Ampere and 3g of CaCl₂.

The experimental results indicate that, the combination of US and EO has a remarkable synergistic effect on the removal efficiencies of COD, color and turbidity. As supporting electrolyte, CaCl₂ was more efficient than NaCl for both EO and US/EO processes. The synergism observed between US and EO, to clarify the hybrid results in a higher removal efficiency than electrochemical oxidation, can be associated with following three reasons.

Primarily, the formation of chloride radical by ultrasonic irradiation in the presence of Cl⁻ when NaCl or CaCl₂ used as supporting electrolyte (Yang *et al.*, 2014). Secondly, ultrasonic waves facilitated the mass-transfer on the electrode surface, resulted in increasing diffusion of the produced hydroxyl radicals (OH[•]), which increased the OH[•] concentration in the solution (Barros *et al.*, 2014). Finally, cleaning of the electrode surface by cavitation bubbles. The mechanical effects of cavitation lead to cleaning of the electrode surface and inhibit any passive layer formation. These effects guarantee the normal electrochemical operation process with a stable current ampere in the period of the treatment time (Ren *et al.*, 2013).

Wastewater sonicated by varying the pH, electrolysis time, current ampere, and electrolyte concentration by constant power of ultrasound (70 Watt).

Table 4-3 FCCD for COD, color and turbidity removal with Power Consumption for US/EO process using CaCl₂

Run	A:pH	B:Time minute	C:Current Amp	D:CaCl ₂ g/L	COD %	Color %	Turbidity %	Power Consumption kWh/m ³
1	7	40	0.35	2	77.58	89.17	94.55	0.0017
2	7	40	0.35	2	77.58	89.17	94.55	0.0017
3	3	60	0.6	3	97.61	99.43	99.25	0.0077
4	7	40	0.225	2	91.65	94.77	92.55	0.003
5	3	60	0.1	3	49.35	77.92	92.62	0.0095
6	3	20	0.1	3	19.92	65.01	85.69	0.0051
7	11	60	0.1	3	56.81	72.41	77.02	0.0153
8	7	50	0.35	2	84.39	89.83	96.15	0.0023
9	7	30	0.35	2	72.48	88.78	94.37	0.0012
10	11	20	0.1	1	13.85	58.54	79.38	0.0116
11	11	20	0.6	1	32.49	69.15	88.93	0.0042
12	9	40	0.35	2	48.81	76.35	87.03	0.0092
13	3	60	0.6	1	86.99	94.44	95.55	0.0065
14	7	40	0.35	2	77.58	89.17	94.55	0.0017
15	7	40	0.35	2.5	85.27	90.29	94.11	0.0015
16	7	40	0.35	2	77.58	89.17	94.55	0.0017
17	3	20	0.6	3	68.19	89.72	91.64	0.0039
18	7	40	0.35	2	77.58	89.17	94.55	0.0017
19	7	40	0.35	1.5	76.83	85.93	92.07	0.0013
20	7	40	0.35	2	77.58	89.17	94.55	0.0017
21	11	60	0.6	1	56.99	75.65	91.23	0.0119
22	11	20	0.1	3	10.75	58.73	73.04	0.0132
23	11	60	0.1	1	46.21	68.63	83.91	0.0167
24	3	20	0.6	1	88.62	97.72	96.01	0.0021
25	11	60	0.6	3	60.56	79.16	89.91	0.0146
26	11	20	0.6	3	36.91	70.19	78.83	0.0106
27	5	40	0.35	2	61.74	83.99	94.87	0.0037
28	3	60	0.1	1	73.32	93.46	93.87	0.0094
29	7	40	0.475	2	91.59	94.09	95.15	0.0019
30	3	20	0.1	1	64.41	84.81	91.28	0.0028

Table 4-4 FCCD for COD, color and turbidity removal with Power Consumption for US/EO process using NaCl

Run	A:pH	B:Time minute	C:Current Amp	D:NaCl g/L	COD %	Color %	Turbidity %	Power Consumption kWh/m ³
1	7	40	0.35	2.5	61.71	83.63	91.95	0.0027
2	3	60	0.1	3	58.85	86.68	89.95	0.0033
3	7	40	0.35	2	68.97	80.09	87.81	0.0029
4	7	40	0.35	2	68.97	80.09	87.81	0.0029
5	7	40	0.35	2	68.97	80.09	87.81	0.0029
6	9	40	0.35	2	59.8	76.12	83.07	0.0038
7	3	60	0.6	1	87.06	96.02	98.3	0.0032
8	11	60	0.6	1	54.89	83.09	88.75	0.0069
9	11	60	0.6	3	53.3	79.24	87.15	0.0073
10	7	40	0.35	2	68.97	80.09	87.81	0.0029
11	7	40	0.225	2	59.55	82.29	89.19	0.0035
12	11	20	0.6	3	43.47	75.55	81.55	0.0059
13	7	40	0.35	2	68.97	80.09	87.81	0.0029
14	11	60	0.1	1	36.14	77.89	83.74	0.0074
15	3	20	0.6	1	69.92	88.67	91.7	0.0018
16	7	40	0.35	2	68.97	80.09	87.81	0.0029
17	3	60	0.6	3	82.24	92.99	96.86	0.0037
18	11	20	0.1	3	33.83	77.62	81.15	0.0041
19	11	20	0.6	1	53.42	76.03	83.67	0.0041
20	3	20	0.6	3	64.22	88.69	91.36	0.0028
21	3	20	0.1	1	47.96	80.29	84.37	0.0029
22	5	40	0.35	2	69.89	82.82	85.61	0.0025
23	7	40	0.35	1.5	68.05	81.58	90.82	0.0032
24	11	20	0.1	1	41.65	76.94	85.11	0.0062
25	11	60	0.1	3	34.53	77.19	82.25	0.0048
26	3	20	0.1	3	43.06	80.03	82.75	0.0027
27	7	50	0.35	2	77.47	83.4	88.31	0.0031
28	7	40	0.475	2	73.04	82.71	89.28	0.0034
29	3	60	0.1	1	65.73	87.55	89.73	0.0046
30	7	30	0.35	2	71.56	79.15	83.51	0.0024

4.3 Optimization of Operating Parameters

Determining the optimal operating parameters for the maximum % COD, % color and % turbidity removal with the minimum of power consumption from domestic wastewater using the electrochemical process and sono- electrochemical oxidation process was one objective. During the laboratory experiments, the optimum values for the removal of contaminants were obtained using the regression equation of Response Surface Methodology (Design Expert 11) based on the Central Composite Design.

The optimization of operating parameters such as pH (A), electrolysis time (B), current ampere (C) and electrolytic concentration (D) were selected as within range. In addition, the responses were optimized by maximizing the removal efficiency of COD, color, and turbidity by minimizing the power consumption using aluminum electrode.

The selected maximum values of COD, Color and turbidity with minimum power consumption for US/EO using CaCl_2 were 99.70 %, 99.79 % and 99.28 % with 0.003 kWhr/m^3 respectively. These optimum values were obtained at pH 5.85, electrolysis time 47.15 minutes, current 0.57 Ampere and electrolytic concentration 1.42 g/L at the degree of desirability of the model (equal to 1).

Correspondingly, the selected optimum values of COD, Color and turbidity with power consumption were 91.05 %, 97.55 % and 99.98 % with 0.003 kWhr/m^3 respectively for US/EO using NaCl. These optimum values was obtained at pH 3.99, electrolysis time 60 minutes, current 0.55 Ampere and electrolytic concentration 1.00 g/L.

Additionally, the optimum values of COD, Color and turbidity with power consumption for EO using CaCl_2 were 80.93 %, 98.55 % and 98.91 % with 0.003 kWhr/m^3 respectively. These optimum values were obtained at pH 5.52, electrolysis time 58.75 minutes, current 0.33 Ampere and electrolytic concentration 3 g/L.

Finally, the selected optimum values of COD, Color and turbidity with power consumption for EO using NaCl were 72.69 %, 91.77 % and 97.61 % with 0.003 kWhr/m^3 respectively. These optimum values were obtained at pH 3.05, electrolysis time 50.78 minutes, current 0.47 Ampere and electrolytic concentration 2.97 g/L. According to the study, the optimal values of COD, color and turbidity with power consumption for US/EO using CaCl_2 were more efficient.

4.4 Effect of Operating Parameters on Percentage Removal of Pollutants

The operating parameters, that highly affect the EO and US/EO processes, such as initial pH, reaction time, current ampere and electrolyte concentration (NaCl/ CaCl₂) was studied in terms % COD, color and turbidity removal associated with power consumption. Aluminum (Al) electrode was used because it has a potential for complete oxidation, but also the durability and corrosion resistance of the electrode and the operating current densities.

4.4.1 Effect of pH

pH is the term used to express the intensity of the acid or alkaline condition of liquid. In the EO and US/EO processes, the pH value of the solution plays a fundamental role in the pollutants removal (Kobyra *et al.*, 2012). Therefore, it was adjusted in the range from 3 to 11 by integrating NaOH or H₂SO₄ solution to investigate the effect of pH on process performance.

The acidic conditions were more promising for the reduction of COD, color and turbidity. This was because more of the oxidant was produced under the acidic medium. Whereas, it decreases in the alkaline medium due to significant decrease in the redox potentials of HOCl and ClO⁻ with the increase in pH. This was due to the decreased production of chlorine and hypochlorite and also the formation of chlorate and perchlorate (Asaithambi *et al.*, 2012).

The % color removal of wastewater was significantly affected by the variation in pH levels as compared to COD. The best COD removal was obtained in acidic pH value with Al electrodes. In addition, when initial pH was increased to seven, removal rates decreased dramatically. When Al was used as the electrode material, acidic pH values were more convenient for the removal kinetics due to predominant form of Al(OH)₃(s). The result was in accordance with other studies in literature (Kumar, 2017).

It was observed that % removal of color increases during the process in acidic medium and decreases in the basic medium due to the (H⁺) and (OH⁻) consumption and formation during the processes, respectively (Kobyra *et al.*, 2012). By increasing the pH values, COD, color and turbidity removal percentage was increased. However, this ascending trend was predicted for pH values up to 7, after which the removal percentage continues in a descending trend.

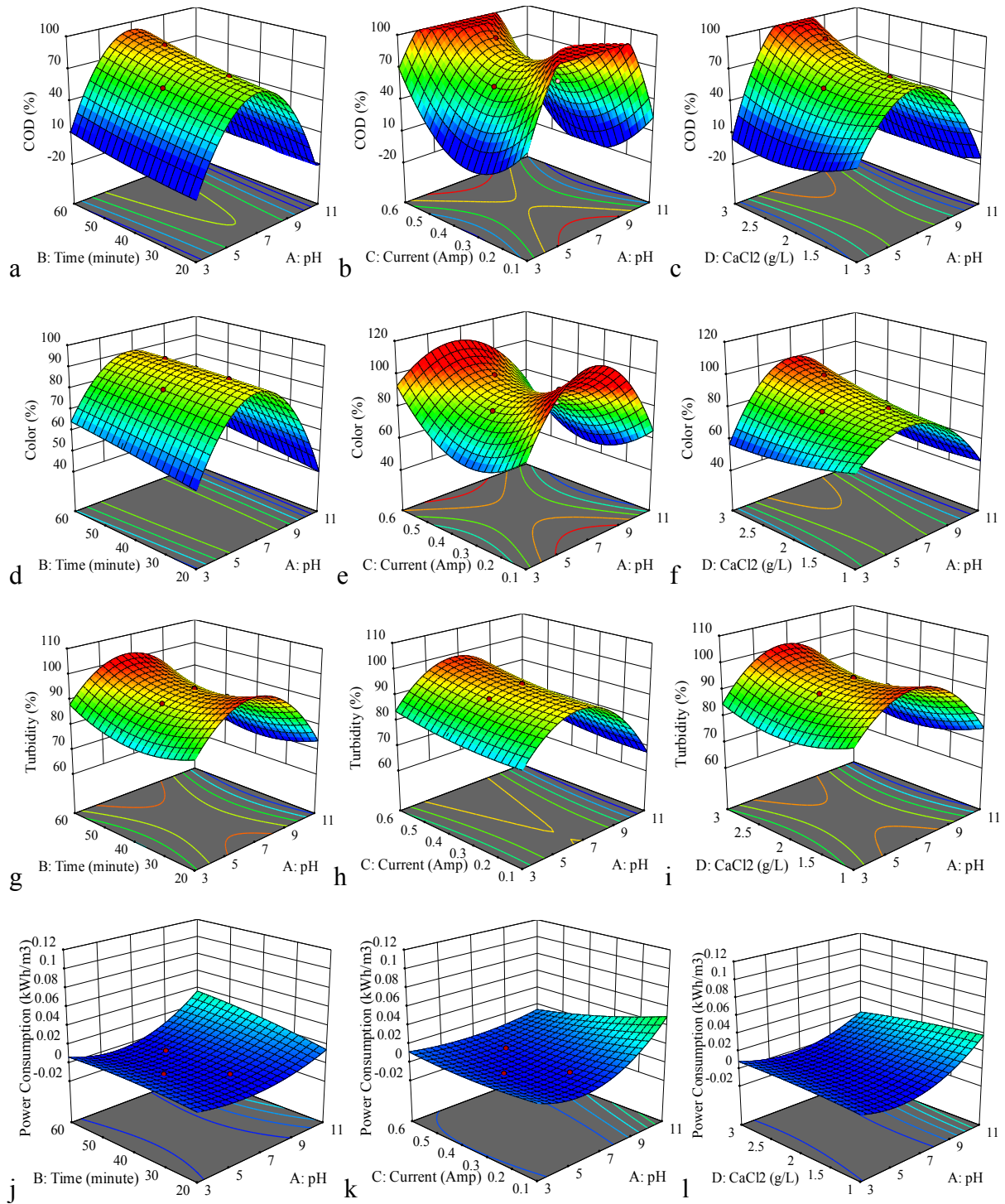
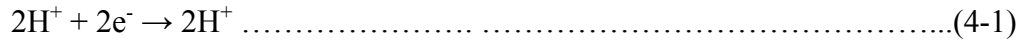


Figure 4-1 Response surface plots for % removal of COD, Color and Turbidity with Power Consumption for US/EO using CaCl₂

During the processes, neutralization of pH of the system describes that the pH of acidic medium (EO system) increases due to the water hydrolysis and H₂ (gas) evolution (Wang and Xu, 2012), thus producing OH⁻:



The effect of pH with other factors on % COD, % color and % turbidity removal potency were shown in Figure 4.1 (a - c), (d - f) and (g - i) respectively. The effect of pH with other factors on % power consumption effectiveness was shown in Figure 4.1 (j - l).

4.4.2 Effect of Electrolysis Time

Time for electrolysis have an effect on pollutant removal and the amount of sludge to be settled after the process. The time for attaining maximum oxidation also could be reduced by introducing turbulence during the process. Turbulence can be accomplished by mechanical agitation, including stirring, aeration, and sonication. For long electrolysis times, the structure of the sludge may change, altering the efficiency of pollution removal and the settle-ability and floatability properties of the flocs. According to the study, a shorter less than 30 minute and longer reaction times more than an hour have a lower removal percentage, which might be due to sequestration of metal hydroxides at electrode level (Chakma *et al*, 2015).

4.4.3 Effect of Current Ampere

In fact, current was directly proportional to voltage (Dalvand *et al*. 2011). When current increases, there was an increase in aluminum dissolution. So, it enhances the formation of hydroxide Al(OH)₃ in the process. By applying higher voltage, evolution of oxygen results in decreasing efficiency of organic oxidation. On the other hand, performing the process at higher voltages causes oxidation of poisoning products formed at the anode surface. According to Figure 4-1, the higher removal rates occurred in high current ampere values, even if energy consumption strongly increases with increasing current ampere.

Solution conductivity influences current efficiency, applied cell voltage, and electrical energy consumption. More energy was required for overcoming high ohmic resistance between anode and cathode when the ionic conductivity of the solution was low. This behavior could be attributed to the increase of ionic conductivity of the reaction medium, and decrease of electrical resistance and applied cell voltage as well (Moreira *et al.*, 2017).

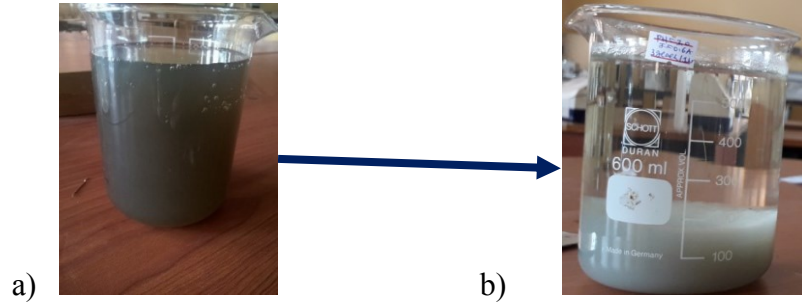


Figure 4-2 Sample a) before treatment and b) after treatment

4.4.4 Effect of Electrolyte Concentration

Table salt was usually employed to increase the conductivity of the water or wastewater to be treated. Besides its ionic contribution in carrying the electric charge, it was found that chloride ions could significantly reduce the adverse effect of other anions such as carbonate (HCO_3^-) or sulfate (SO_4^{2-}) ions. The existence of both ions would lead to the precipitation of Ca^{2+} or Mg^{2+} ions that forms an insulating layer on the surface of the electrodes.

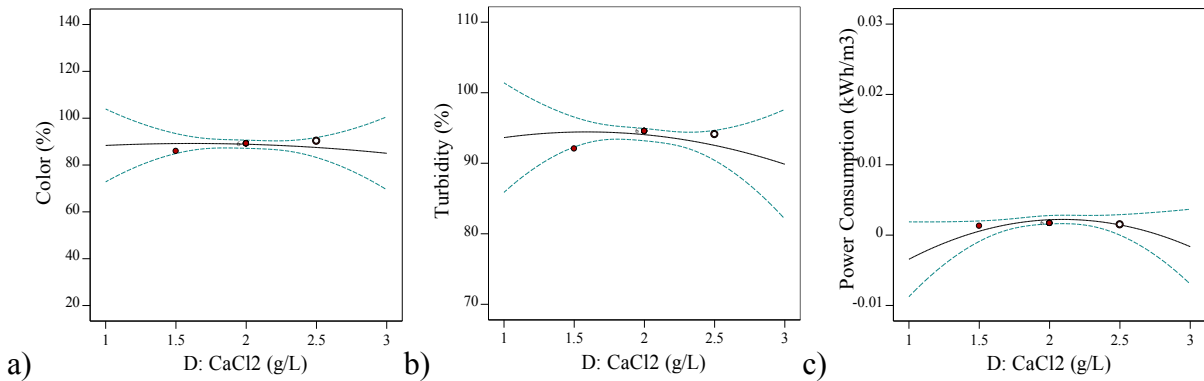


Figure 4-3 Effect of Amount of Electrolyte on of a) % Removal of Color b) Turbidity & c) Power Consumption

The addition of NaCl and CaCl₂ would also lead to the decrease in power consumption, because of the increase in conductivity of the EO system and enhances the percentage COD, color and turbidity removal. It was observed that higher conductivity favors high process efficiency. Moreover, the electrochemically generated chlorine was found to be effective in water disinfections (Körbahti and Taşyürek, 2015). Thus, a concentration of 1 – 3 g/L NaCl and CaCl₂ was chosen for the experiments. The amount of electrolyte factor has a greater effect on response compared to the other factors. Using CaCl₂ was more efficient than NaCl due to the increment of ions from +1 (NaCl) to +2 (CaCl₂) and as it is more environmentally friendly.

4.4.5 Effect of Power Ultrasound

The sources of ultrasound considered when the power of ultrasound is applied to an electrochemical system. Ultrasonic power is the most important parameter since there is a direct relation with the current value of the redox process. Ultrasonic sources of high frequency produce a great quantity of hydroxyl radicals in aqueous media in relation to those with low frequency using the same ultrasonic power (Moreira *et al.*, 2017).

EO makes use of US that result in the cavitation phenomenon that was the formation, growth, and subsequent collapse of micro-bubbles or cavities occurring in an extremely small interval of time about microseconds. The bubble collapse leads to surprisingly high temperature and pressure. These extreme conditions were short-lived; however, in an aqueous system, several reactive species, including hydrogen peroxide (H_2O_2), H^\bullet , and OH^\bullet were produced. These species were capable of oxidizing the organic pollutants (Sathishkumar *et al.*, 2016).

The propagation of ultrasound in a liquid medium has generated cavitation. The ultrasonic cavitation has induced effects such as micro mixing which could have provided better mixing and dispersion of the medium. Ultrasonic cavitation taking place at the electrode surface may reduce the electrode passivation and may enhance the efficiency. In this research, ultrasonic power of 70W with frequency 50 Hz was used for US/EO.

As seen in the figure 4-2 for the treatment of domestic wastewater, US/EO was found to be more efficient method than EO hence it was seen that introduction of the power of ultrasound during sonication could enhance pollution attenuation.

4.5 Validation of the Process by Response Surface Methodology

This wastewater treatment system or process was modelled using RSM. It applied to generate a response surface model that predicts a response based on a combination of factor levels and to find optimum operating conditions that maximizes the performance of a system. Further, it gives the relative magnitude and effect of different factors on the response and their interactions. Estimation models performed optimization of the responses for determining optimized points for operational conditions and achieving the maximum removal percentage.

To achieve the highest removal performance of independent variables; COD, color and turbidity removal percentage were selected at maximum value by minimizing power consumption. The target values of four independent variables including initial pH, reaction time, current ampere and salt concentration were selected in the range state. Optimization of the operating parameters was essential to maximize pollution attenuation consuming relatively less energy.

4.5.1 Fit Summary

The Fit Summary collects the important statistics used to select the correct starting point for the final model. The degrees of freedom for the mean will be one. The degree of freedom (df) for the linear, quadratic, special cubic and cubic models was the number of additional terms added to the model.

As shown in the Table 4-5 to 4-8 for each source, the mean square was the sum of squares divided by the degrees of freedom. This was used to calculate the F-value for the models. The “Model Summary Statistics” table lists other statistics used to compare models. It was recommended to select the highest order polynomial where the additional terms were significant and the model was not aliased.

As a result, quadratic model was the model maximizing the Adjusted R^2 and the Predicted R^2 . Quadratic model was suggested for all responses for US/EO process using CaCl_2 , sequential sum of squares for the quadratic (A-squared, B-squared, etc.) terms. The F-value tests the significance of adding quadratic terms to the 2FI model, sequential sum of squares for the two-factor interaction (AB, BC, etc.) terms.

A small p-value ($\text{Prob}>F$) indicates that adding quadratic terms has improved the model. Experimental data were analyzed by sequential model sum of squares and model summary statistics to obtain the most suitable models among various models such as linear, interactive, quadratic and cubic. The results are tabulated in Tables 4-5 to 4-8 for the % COD, color, turbidity removal and power consumption, respectively. From those tables, it can be seen that quadratic model gives the highest R^2 , adjusted R^2 and predicted R^2 values when compared to the other models after excluding the cubic model.

Table 4-5 Sequential model sum of squares and model summary statistics of % COD removal for US/EO using CaCl₂

Sequential Model Sum of Squares						
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	1.256E+05	1	1.256E+05			
Linear vs Mean	8373.52	4	2093.38	6.87	0.0007	
2FI vs Linear	1712.17	6	285.36	0.9182	0.5035	
Quadratic vs 2FI	5387.18	4	1346.80	39.01	< 0.0001	
Cubic vs Quadratic	477.72	8	59.72	10.40	0.0029	
Residual	40.21	7	5.74			
Total	1.416E+05	30	4720.07			
Model Summary Statistics						
Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	
Linear	17.46	0.5236	0.4474	0.2783	11541.07	
2FI	17.63	0.6307	0.4364	-0.3953	22311.48	
Quadratic	5.88	0.9676	0.9374	0.7412	4138.89	
Cubic	2.40	0.9975	0.9896	0.3639	10171.12	

The Quadratic model was suggested as good model for percentage removal of COD, color and turbidity with power consumption. Whereas, the cubic model cannot be used for further modeling of experimental data because it was found to be aliased. An aliased model was a result of insufficient experiments run independently estimate all the terms of the model. Thus, not all parameters can be estimated and it is unwise for further studying an aliased model.

Table 4-6 Sequential model sum of squares and model summary statistics of % Color removal for US/EO using CaCl₂

Sequential Model Sum of Squares						
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	2.073E+05	1	2.073E+05			
Linear vs Mean	2313.49	4	578.37	10.19	< 0.0001	
2FI vs Linear	317.99	6	53.00	0.9151	0.5054	
Quadratic vs 2FI	969.35	4	242.34	27.75	< 0.0001	
Cubic vs Quadratic	124.05	8	15.51	15.58	0.0008	
Residual	6.97	7	0.9953			
Total	2.111E+05	30	7035.66			
Model Summary Statistics						
Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	
Linear	7.53	0.6199	0.5591	0.4198	2165.37	
2FI	7.61	0.7051	0.5500	-0.1564	4315.39	
Quadratic	2.96	0.9649	0.9321	0.7364	983.75	
Cubic	0.9976	0.9981	0.9923	0.5509	1675.98	

Table 4-7 Sequential model sum of squares and model summary statistics of %
Turbidity removal for US/EO using CaCl₂

Sequential Model Sum of Squares					
Source	Sum of Squares	df	Mean Square	F-value	p-value
Mean vs Total	2.469E+05	1	2.469E+05		
Linear vs Mean	806.93	4	201.73	13.42	< 0.0001
2FI vs Linear	68.20	6	11.37	0.7021	0.6516
Quadratic vs 2FI	274.99	4	68.75	31.61	< 0.0001
Cubic vs Quadratic	27.98	8	3.50	5.27	0.0205
Residual	4.64	7	0.6632		
Total	2.481E+05	30	8270.51		
Model Summary Statistics					
Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS
Linear	3.88	0.6822	0.6314	0.5128	576.25
2FI	4.02	0.7399	0.6030	-0.1035	1305.12
Quadratic	1.47	0.9724	0.9467	0.8093	225.55
Cubic	0.8144	0.9961	0.9837	0.2590	876.36

The highest order polynomial from the sequential model sum of squares, quadratic model, was selected for modeling the treatment of domestic wastewater using Sono-electrochemical process where the additional terms are significant and the model is not aliased.

Table 4-8 Sequential model sum of squares and model summary statistics of power
consumption for US/EO using CaCl₂

Sequential Model Sum of Squares					
Source	Sum of Squares	df	Mean Square	F-value	p-value
Mean vs Total	0.0011	1	0.0011		
Linear vs Mean	0.0003	4	0.0001	4.91	0.0046
2FI vs Linear	0.0000	6	2.895E-06	0.1454	0.9878
Quadratic vs 2FI	0.0004	4	0.0001	88.95	< 0.0001
Cubic vs Quadratic	0.0000	8	1.538E-06	3.59	0.0548
Residual	3.002E-06	7	4.288E-07		
Total	0.0018	30	0.0001		
Model Summary Statistics					
Source	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS
Linear	0.0040	0.4398	0.3502	0.1833	0.0006
2FI	0.0045	0.4644	0.1825	-1.2106	0.0016
Quadratic	0.0010	0.9783	0.9581	0.8491	0.0001
Cubic	0.0007	0.9958	0.9824	0.3510	0.0005

4.5.2 Adequacy of the model

The significance and adequacy of the model was analyzed by the analysis of variance (ANOVA) and the results for % COD, color, turbidity removal and power consumption are given in Tables 4-9 to 4-12, respectively. This test was performed to study the influence of all factors on target response. To prevent systemic error, the experiments were performed randomly.

The interaction effect of input variables, which were statistically designed by using CCD method were studied through different combination of experimental parameters. Results were assessed with various descriptive statistics such as the p-value, F-value, and the degree of freedom (df). The determination coefficient (R^2) of each coefficient was determined by Fisher's F-test and values of probability $>F$.

In Table 4-9 to 4-12 and under appendix B, the results of ANOVA were summarized to test the soundness of the model. The mean squares values were calculated by dividing the sum of the squares of each variation source by their degrees of freedom, and a 95% confidence level ($= 0.05$) was used to determine the statistical significance in all analyses.

The coefficients were analyzed using analysis of variance and $p < 0.05$ was determined as the significance level. As shown in Table 4-9 to 4-12, a small probability value ($p < 0.001$) indicates that the model was highly significant and could be used to predict the response function accurately. Lack of fit test describes the changes in data around the fitted model. If the model has not been fitted well, this test was significant (Jamali *et al.*, 2018).

The significance of each model parameter was mainly determined by means of Fischer's F-value and p-value. The F-value was the test for comparing the curvature variance with residual variance and probability $>F$ (p-value) was the probability of seeing the observed F-value if the null hypothesis was true. Small probability values call for rejection of the null hypothesis and the curvature was not significant. Therefore, the larger the value of F and the smaller the value of p, the more significant the corresponding coefficient is (Liu *et al.*, 2019).

As shown in Table 4-9, it was concluded that the independent variables of the quadratic model, including the pH value (A), electrolysis time (B) and current ampere (C) and the second-order effect of the pH value (A^2), were highly significant parameters because $p < 0.0001$.

Table 4-9 ANOVA for % COD Removal of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	15472.88	14	1105.21	32.01	< 0.0001	Highly significant
A-pH	3499.79	1	3499.79	101.36	< 0.0001	Highly significant
B-Time	2391.75	1	2391.75	69.27	< 0.0001	Highly significant
C-Current	2274.16	1	2274.16	65.86	< 0.0001	Highly significant
D-CaCl ₂	207.83	1	207.83	6.02	0.0269	Significant
AB	228.31	1	228.31	6.61	0.0213	Significant
AC	352.31	1	352.31	10.20	0.0060	Significant
AD	549.43	1	549.43	15.91	0.0012	Significant
BC	104.14	1	104.14	3.02	0.1029	Insignificant
BD	259.37	1	259.37	7.51	0.0152	Significant
CD	218.60	1	218.60	6.33	0.0237	Significant
A ²	1385.99	1	1385.99	40.14	< 0.0001	Highly significant
B ²	0.3169	1	0.3169	0.0092	0.9249	Insignificant
C ²	487.43	1	487.43	14.12	0.0019	Significant
D ²	23.33	1	23.33	0.6756	0.4240	Insignificant
Residual	517.93	15	34.53			
Lack of Fit	517.93	10	51.79			
Pure Error	0.0000	5	0.0000			
Cor Total	15990.81	29				

The Model F-value of 32.01 implies the model was significant. There was 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 were significant. In this case A, B, C, D, AB, AC, AD, BD, CD, A², C² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms, model reduction may improve the model.

Moreover, D (electrolyte concentration), AC (the interactions between the pH value and current ampere), AD, BD (the interactions between electrolysis time and electrolyte concentration), CD and C² (second-order effect of the current ampere value) were significant because $p < 0.05$.

Table 4-10 ANOVA for % Color Removal of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3600.82	14	257.20	29.45	< 0.0001	Highly significant
A-pH	1434.91	1	1434.91	164.29	< 0.0001	Highly significant
B-Time	278.23	1	278.23	31.85	< 0.0001	Highly significant
C-Current	554.02	1	554.02	63.43	< 0.0001	Highly significant
D-CaCl ₂	46.33	1	46.33	5.30	0.0360	Significant
AB	7.91	1	7.91	0.9057	0.3564	Insignificant
AC	36.81	1	36.81	4.22	0.0579	Insignificant
AD	137.30	1	137.30	15.72	0.0012	Significant
BC	34.31	1	34.31	3.93	0.0661	Insignificant
BD	33.96	1	33.96	3.89	0.0674	Insignificant
CD	67.69	1	67.69	7.75	0.0139	Significant
A ²	191.80	1	191.80	21.96	0.0003	Significant
B ²	1.12	1	1.12	0.1279	0.7256	Insignificant
C ²	88.73	1	88.73	10.16	0.0061	Significant
D ²	0.7975	1	0.7975	0.0913	0.7667	Insignificant
Residual	131.01	15	8.73			
Lack of Fit	131.01	10	13.10			
Pure Error	0.0000	5	0.0000			
Cor Total	3731.83	29				

The Model F-value of 29.45 implies the model was significant. There was 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 were significant.

In this case A, B, C, D, AD, CD, A², C² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table 4-11 ANOVA for % Turbidity Removal of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1150.12	14	82.15	37.77	< 0.0001	Highly significant
A-pH	464.86	1	464.86	213.72	< 0.0001	Highly significant
B-Time	94.32	1	94.32	43.36	< 0.0001	Highly significant
C-Current	188.98	1	188.98	86.88	< 0.0001	Highly significant
D-CaCl ₂	58.77	1	58.77	27.02	0.0001	Highly significant
AB	1.70	1	1.70	0.7829	0.3902	Insignificant
AC	17.14	1	17.14	7.88	0.0133	Significant
AD	18.36	1	18.36	8.44	0.0109	Significant
BC	0.3906	1	0.3906	0.1796	0.6777	Insignificant
BD	26.63	1	26.63	12.24	0.0032	Significant
CD	3.98	1	3.98	1.83	0.1962	Insignificant
A ²	19.65	1	19.65	9.03	0.0089	Significant
B ²	6.76	1	6.76	3.11	0.0982	Significant
C ²	0.0898	1	0.0898	0.0413	0.8417	Insignificant
D ²	0.8844	1	0.8844	0.4066	0.5333	Insignificant
Residual	32.63	15	2.18			
Lack of Fit	32.63	10	3.26			
Pure Error	0.0000	5	0.0000			
Cor Total	1182.75	29				

The Model F-value of 37.77 implies the model was significant. There was 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 were significant.

In this case A, B, C, D, AC, AD, BD, A² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table 4-12 ANOVA for Power Consumption of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0008	14	0.0001	67.16	< 0.0001	Highly significant
A-pH	0.0002	1	0.0002	244.05	< 0.0001	Highly significant
B-Time	0.0001	1	0.0001	132.65	< 0.0001	Highly significant
C-Current	0.0000	1	0.0000	51.79	< 0.0001	Highly significant
D-CaCl ₂	0.0000	1	0.0000	15.97	0.0012	Significant
AB	8.556E-07	1	8.556E-07	1.03	0.3264	Insignificant
AC	0.0000	1	0.0000	12.51	0.0030	Significant
AD	9.506E-07	1	9.506E-07	1.14	0.3018	Insignificant
BC	3.306E-07	1	3.306E-07	0.3978	0.5377	Insignificant
BD	5.641E-06	1	5.641E-06	6.79	0.0199	Significant
CD	5.641E-06	1	5.641E-06	6.79	0.0199	Significant
A ²	0.0000	1	0.0000	48.34	< 0.0001	Highly significant
B ²	1.771E-06	1	1.771E-06	2.13	0.1649	Insignificant
C ²	3.560E-08	1	3.560E-08	0.0428	0.8388	Insignificant
D ²	3.618E-06	1	3.618E-06	4.35	0.0544	Insignificant
Residual	0.0000	15	8.311E-07			
Lack of Fit	0.0000	10	1.247E-06			
Pure Error	0.0000	5	0.0000			
Cor Total	0.0008	29				

The Model F-value of 67.16 implies the model was significant. There was 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 were significant.

In this case A, B, C, D, AC, BD, CD, A² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

4.5.3 Fit Statistics

Statistical significance of the model equation and model terms was evaluated by ANOVA. As Jamali *et al.*, (2018) report, the quality of the model fitting was controlled by determination coefficients (R^2 and Adj. R^2), while the statistical significance was controlled by Fischer test (F-test). Validation of the final model was established using predicted R-squares (R^2), which estimates the prediction power of the model with new observations based on the leave-one-out technique. The experimental and the predicted responses correlation was quantitatively evaluated by coefficient (R^2).

The coefficient of determination (R^2) which represents the ratio of the total changes in the predicted response by the model shows the sum of squares regression (SSR) to the total sum of squares (SST) ratio. Largeness of R^2 and its closeness to 1 was desirable and a desired correspondence with adjusted R^2 (Adj. R^2) was necessary. The quality of fitness of second-order polynomial model was expressed by R^2 .

Goodness-of-fit for the model was also evaluated by coefficients of determination R^2 (correlation coefficient) and adjusted coefficients of determination R^2_{adj} . According to Moradnia and his co-authors (2016), for a good fitness of model R^2 should be at least 0.8 and high R^2 values suggest a great accordance between the experimental data and data estimated by the model.

In this study, all of the values of R^2 were above 0.9. For instance, as indicated in the table 4-9, a large value of the correlation coefficient (R^2) for COD is 0.9676. This indicates a high reliability of the model in predicting of removal percentages, by which 96.76% of the response variability can be explained by the model. Therefore, high R^2 values and their accordance with Adj. R^2 in this study suggest the high significance of the suggested model.

The Adequate precision that has been shown in Table 4-13 to Table 4-16 was “signal-to-noise ratio” index. In other word, Adequate precision compares the range of values predicted at design points with the mean prediction error. Model Summary (Fit Statistics) for % removals of US/EO using CaCl_2 was shown in Table 4-13 to Table 4-16, but for other process US/EO using NaCl , EO using CaCl_2 and EO using NaCl were show under appendices C.

Table 4-13 Model Summary for % COD removals of US/EO using CaCl₂

Std. Dev.	5.88	R ²	0.9676
Mean	64.71	Adjusted R ²	0.9374
C.V. %	9.08	Predicted R ²	0.7412
		Adeq Precision	21.3503

The Predicted R² of 0.7412 was in reasonable agreement with the Adjusted R² of 0.9374; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 21.350 indicates an adequate signal. This model can be used to navigate the design space.

Table 4-14 Model Summary for % Color removals of US/EO using CaCl₂

Std. Dev.	2.96	R ²	0.9649
Mean	83.13	Adjusted R ²	0.9321
C.V. %	3.55	Predicted R ²	0.7364
		Adeq Precision	20.0044

The Predicted R² of 0.7364 was in reasonable agreement with the Adjusted R² of 0.9321; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 20.004 indicates an adequate signal. This model can be used to navigate the design space.

Table 4-15 Model Summary for % Turbidity removals of US/EO using CaCl₂

Std. Dev.	1.47	R ²	0.9724
Mean	90.73	Adjusted R ²	0.9467
C.V. %	1.63	Predicted R ²	0.8093
		Adeq Precision	26.7398

The Predicted R² of 0.8093 was in reasonable agreement with the Adjusted R² of 0.9467; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 26.740 indicates an adequate signal. This model can be used to navigate the design space.

Table 4-16 Model Summary for Power Consumption of US/EO using CaCl₂

Std. Dev.	0.0009	R ²	0.9843
Mean	0.0061	Adjusted R ²	0.9696
C.V. %	14.91	Predicted R ²	0.8990
		Adeq Precision	28.2210

The Predicted R² of 0.8990 was in reasonable agreement with the Adjusted R² of 0.9696; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 28.221 indicates an adequate signal. This model can be used to navigate the design space.

Ratios above 4 suggest precision of the signal for models to find design space (Liu *et al.*, 2019), which in this study for COD, color, turbidity and power consumption were 21.350, 20.004, 26.74 and 28.221, respectively that implies the existence of sufficient signal and the high power of the model in prediction of the results.

The ANOVA analysis showed that all the four quadratic models were significant ($p < 0.05$) and can be used to predict the % of COD, color, turbidity removal, and also power consumption. The quality of predicted points was verified by the R² value, where the R² values were 0.96, 0.96, 0.97 and 0.98 for % of COD, color, turbidity removal, and power consumption, respectively.

4.5.4 Effects of Model Parameters and Their Interactions

The response surface (3D surfaces and 2D contour) plots were graphical representations of the regression equation for the optimization of reaction conditions and were the most useful approach in revealing the conditions of the reaction system. Moreover, the contours of the plots help to check the effect of each variable on responses and to identify the type of interactions between these variables. The maximum predicted yield was obtained and it was indicated by the surface confined in the smallest curve of the contour diagram (Nair *et al.*, 2014).

In such plots of the quadratic model, the response functions of two factors were presented by varying within the experimental ranges while all other factors were kept constant at their levels. The optimal values of the operation parameters were estimated by the three-dimensional response surface analysis of the independent variables and the dependent variable.

A series of three-dimensional (3D) response surface graphs were generated and were presented in Figure 4-1 (a - l) which shows the relationship between removal efficiency and electrolysis parameters. In the Figure 4-4 for US/EO using CaCl_2 , the surface and contour plots obtained from the linear models built from the experimental results was shown using pH vs time.

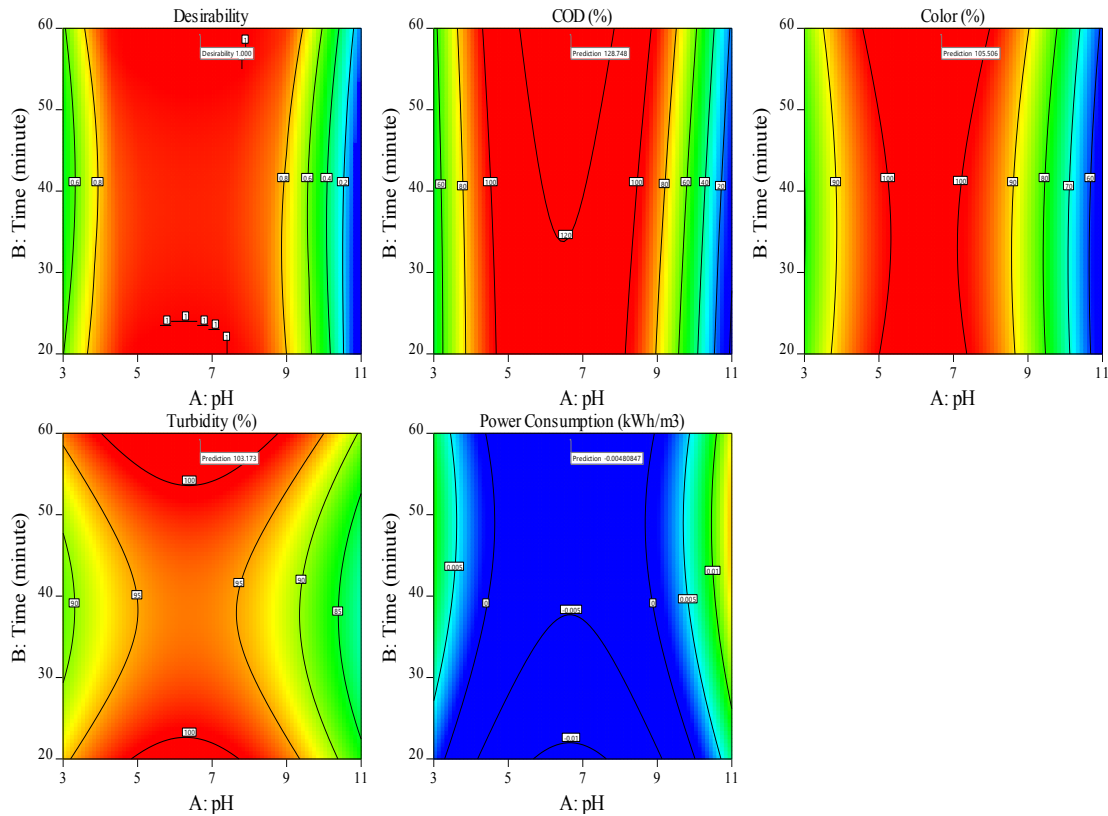


Figure 4-4 The surface and contour plots obtained from the linear models built from the experimental results

The results of the interactions between four independent variables and the dependent variable (COD) were shown in Figure 4-4. As it can be seen in this figure, depending on the initial pH, electrolysis time, current ampere and salt concentration may have a positive or negative effect on the COD, color and turbidity removal and power consumption.

As it can be seen in the plots, there was an increase in the COD removal rate with an increase of pH from acidic medium to neutral medium and with a decrease of pH from basic medium to neutral. The maximum COD, color, turbidity removal rate and power consumption was confirmed at pH range of 3 to 5, time interval range 50 to 60 minute as shown in the Figure 4-5 B.

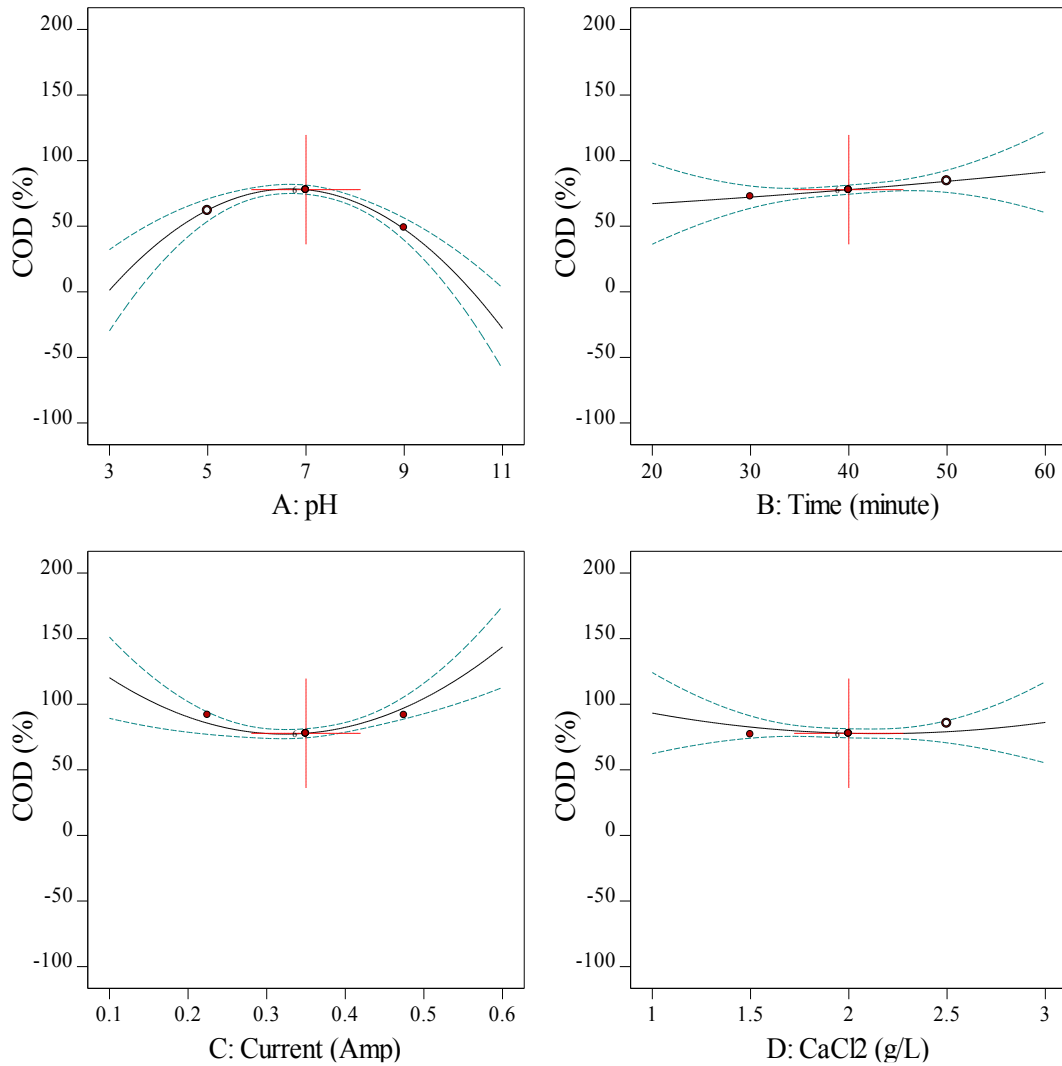


Figure 4-5 Effects of pH, time, current and electrolyte concentration on COD for US/EO using CaCl₂.

Figure 4-5 indicates the interactive effects between the variables influencing COD removal which demonstrate the effect of changes in pH, time of electrolysis, current ampere and salt concentration on the reduction of COD.

As can be seen in the Figure 4-5, with the increase in the salt concentration, COD increases, which was due to indirect oxidation caused by production of chloride or hypochlorite in response to electrolysis process of NaCl occurring in the reactor, which together with produced hydroxyl radical, causes degradation of organic compounds (Un *et al.*, 2008).

4.5.5 Regression Equations

The optimum values of the final model were calculated using numerical methods. In this regard, the experimental range predictors were divided into a grid and then the final model was calculated for all possible combinations of predictors in the grid.

According to the results, many of the model terms were significant for responses which include: pH (A), reaction time (B), current ampere (C), salt concentration (D), square terms of pH (A^2), reaction time (B^2), current ampere (C^2), salt concentration (D^2), and interaction terms of AB, AC, AD, BC, BD and CD. Therefore, the experiment were investigated in terms of these parameters to determine optimum operating conditions for maximum removal efficiency of COD, color and turbidity with minimum power consumption.

In Sono-electrooxidation process, to achieve high removal efficiency, all affecting factors were optimized based on the second order polynomial model. An empirical relationship between the response and independent variables for US/EO using CaCl_2 was approximated by quadratic polynomial as follows:

$$\begin{aligned} \text{COD} = & 77.86 - 14.56 A + 12.04 B + 11.74 C - 3.55 D + 3.78 AB - 4.69 AC + \\ & 5.86 AD - 2.55 BC + 4.03 BD + 3.70 CD - 91.26 A^2 + 54.12 C^2 + 11.84 D^2 \\ & \dots\dots\dots (4-1) \end{aligned}$$

$$\begin{aligned} \text{Color} = & 88.89 - 9.33 A + 4.11 B + 5.79 C - 1.68 D + 0.7031 AB - 1.52 AC + \\ & 2.93 AD - 1.46 BC + 1.46 BD + 2.06 CD - 33.95 A^2 + 2.59 B^2 + \\ & 23.09 C^2 - 2.19 D^2 \dots\dots\dots (4-2) \end{aligned}$$

$$\begin{aligned} \text{Turbidity} = & 94.06 - 5.31 A + 2.39 B + 3.38 C - 1.89 D + 0.3263 AB + 1.04 AC - \\ & 1.07 AD + 0.1563 BC + 1.29 BD + 0.4988 CD - 10.87 A^2 + 6.37 B^2 + \\ & 0.7347 C^2 - 2.31 D^2 \dots\dots\dots (4-3) \end{aligned}$$

$$\begin{aligned} \text{Power Consumption} = & 0.0022 + 0.0035 A + 0.0026 B - 0.0016 C + 0.0009 D + \\ & 0.0002 AB - 0.0008 AC + 0.0002 AD - 0.0001 BC - 0.0006 BD + \\ & 0.0006 CD + 0.0155 A^2 - 0.0033 B^2 - 0.0005 C^2 - 0.0047 D^2 \dots\dots\dots (4-4) \end{aligned}$$

After elimination of the terms which were not statistically significant ($p > 0.05$), the modified quadratic model, for COD (Y_1), color (Y_2) and turbidity (Y_3) removal efficiency involving power consumption (Y_4) were obtained as shown in equation 4-5 to 4-8. The terms in the models were in a coded format. The model suitability was tested using the ANOVA test.

$$Y_1 = +77.86 - 14.56 A + 12.04 B + 11.74 C - 3.55 D + 3.78 AB - 4.69 AC + 5.86 AD + 4.03 BD + 3.70 CD - 91.26 A^2 + 54.12 C^2 \dots\dots\dots (4-5)$$

$$Y_2 = +88.89 - 9.33 A + 4.11 B + 5.79 C - 1.68 D + 2.93 AD + 2.06 CD - 33.95 A^2 + 23.09 C^2 \dots\dots\dots (4-6)$$

$$Y_3 = +94.06 - 5.31 A + 2.39 B + 3.38 C - 1.89 D + 1.04 AC - 1.07 AD + 1.29 BD - 10.87 A^2 \dots\dots\dots (4-7)$$

$$Y_4 = +0.0022 + 0.0035 A + 0.0026 B - 0.0016 C + 0.0009 D - 0.0008 AC - 0.0006 BD + 0.0006 CD + 0.0155 A^2 \dots\dots\dots(4-8)$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors were coded as +1 and the low levels were coded as -1. The coded equation was useful for identifying the relative impact of the factors by comparing the factor coefficients.

Model validity was confirmed by using the lack of fit test, as indicated in Table 4-9 to 4-12. On the regression model, was highly significant ($P < 0.001$), and ANOVA for the lack of fit was insignificant ($P > 0.05$). All the results indicate that this model well fit the experimental data. These findings indicate that US/EO was the most effective method for treatment of wastewater due to the higher percentage COD, color and turbidity removal value and least power consumption within the shortest time. Means with different letters within the same row indicate significant differences ($P \leq 0.05$).

4.5.6 Evaluation of Experimental Results with Design of Experiments

The result from Table 4-17 shows that, there was a good agreement between the predictive and experimental results at the optimum levels, giving a high validity of the model. Backward elimination method was used to achieve a parsimonious model (validating the simplest explanation that describes the process) with significant predictors.

The coefficient of determination obtained for the predicted model indicated a quadratic relationship between responses and parameters with a good regression coefficient. The comparison between experimental and predicted value proposed by the CCD was shown in Table 4-17 and Fig. 4-5 for US/EO process using $CaCl_2$. For US/EO process using NaCl, EO process using $CaCl_2$ and NaCl, the predicted versus experimental results was shown under appendices D.

Table 4-17 Experimental runs and predicted values proposed by the CCD for US/EO process using CaCl₂

Run Order	COD removal (%)		Color removal (%)		Turbidity removal (%)		Power Consumption (kWhr/m ³)	
	Actual Value	Predicted Value	Actual Value	Predicted Value	Actual Value	Predicted Value	Actual Value	Predicted Value
1	77.58	77.86	89.17	88.89	94.55	94.06	0.0017	0.0022
2	77.58	77.86	89.17	88.89	94.55	94.06	0.0017	0.0022
3	97.61	88.96	99.43	95.91	99.25	98.85	0.0077	0.0081
4	91.65	85.52	94.77	91.76	92.55	92.55	0.0030	0.0027
5	49.35	53.81	77.92	80.11	92.62	92.84	0.0095	0.0084
6	19.92	24.13	65.01	67.46	85.69	86.44	0.0051	0.0050
7	56.81	53.34	72.41	71.75	77.02	78.66	0.0153	0.0164
8	84.39	84.23	89.83	91.59	96.15	96.85	0.0023	0.0025
9	72.48	72.19	88.78	87.48	94.37	94.46	0.0012	0.0002
10	13.85	19.38	58.54	60.81	79.38	80.46	0.0116	0.0109
11	32.49	31.18	69.15	68.18	88.93	87.99	0.0042	0.0057
12	48.81	47.77	76.35	75.74	87.03	88.69	0.0092	0.0077
13	86.99	92.34	94.44	98.10	95.55	96.90	0.0065	0.0068
14	77.58	77.86	89.17	88.89	94.55	94.06	0.0017	0.0022
15	85.27	79.05	90.29	87.50	94.11	92.54	0.0015	0.0015
16	77.58	77.86	89.17	88.89	94.55	94.06	0.0017	0.0022
17	68.19	69.49	89.72	89.12	91.64	91.83	0.0039	0.0044
18	77.58	77.86	89.17	88.89	94.55	94.06	0.0017	0.0022
19	76.83	82.60	85.93	89.18	92.07	94.43	0.0013	0.0006
20	77.58	77.86	89.17	88.89	94.55	94.06	0.0017	0.0022
21	56.99	49.66	75.65	71.96	91.23	91.15	0.0119	0.0117
22	10.75	8.55	58.73	56.29	73.04	70.96	0.0132	0.0132
23	46.21	48.06	68.63	70.45	83.91	83.00	0.0167	0.0165
24	88.62	88.97	97.72	97.13	96.01	95.04	0.0021	0.0007
25	60.56	69.73	79.16	81.49	89.91	88.81	0.0146	0.0140
26	36.91	35.14	70.19	71.89	78.83	80.49	0.0106	0.0103
27	61.74	62.33	83.99	85.06	94.87	94.00	0.0037	0.0044
28	73.32	71.97	93.46	90.52	93.87	92.89	0.0094	0.0094
29	91.59	97.26	94.09	97.56	95.15	95.93	0.0019	0.0014
30	64.41	58.39	84.81	83.69	91.28	91.65	0.0028	0.0037

From Fig. 4-6, it can be seen that the model-predicted values matched the experimental data in which all the points are closed to the diagonal line. Moreover, good correlations between predicted values and real values regarding COD removal and other responses confirm the adequacy of the models in predicting the removal of pollutants.

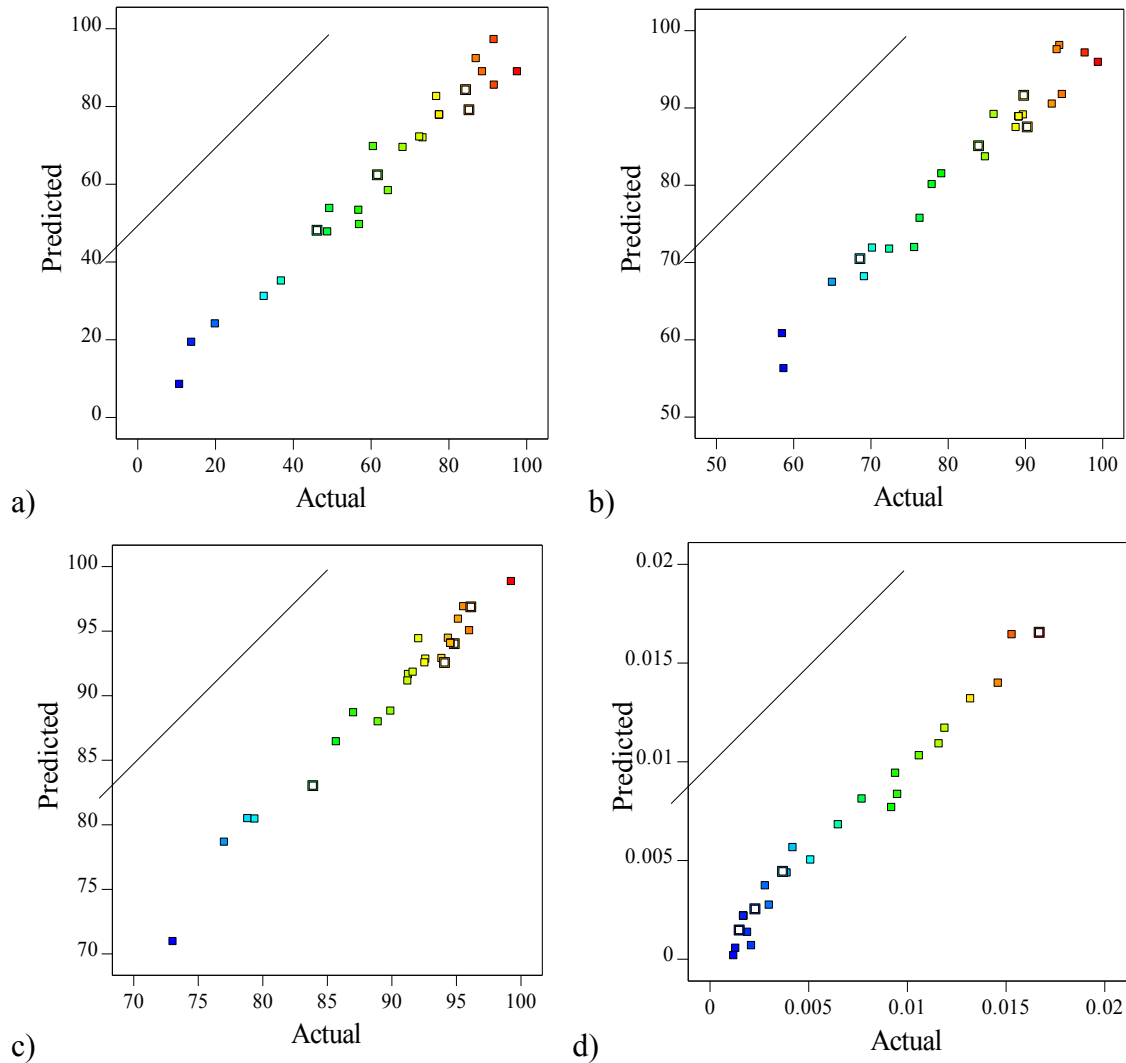


Figure 4-6 Comparison of the predictive and the experimental result for US/EO using CaCl_2 optimum values of a) COD b) Color c) Turbidity % removal and d) Power Consumption.

Verification experiments were performed under optimal conditions, to further validate the reliability of the theoretical model prediction. The results showed that experimental results for removal efficiencies were very close to the predicted values, values were not significantly different ($P > 0.05$). Thus, it concluded that the established model in this study was appropriate and valid.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The main objective of this study was to develop integrated electrochemical oxidation process with ultrasonic process for domestic wastewater treatment by studying on operating parameters. The performance was evaluated by determining the optimal operating parameters for the maximum % COD, color and turbidity removal with the minimum of power consumption from domestic wastewater using the electrooxidation (EO) and sono-electrochemical oxidation (US/EO) process.

In both experiments, independent variables such as initial pH (A), reaction time (B), current ampere (C) and electrolyte concentration (D) were examined as within the range to maximize COD, color and turbidity removal of the effluent with minimal power consumption as the response function. These processes were employed for the treatment of domestic wastewater using both NaCl and CaCl₂ separately as supporting electrolyte. The percentages of those responses for EO and US/EO were compared and the optimum operating conditions to achieve maximum removal were determined.

The maximum removal efficiencies of COD, color and turbidity with power consumption were 79.89%, 97.38% and 97.37% for EO with 0.0075 kWh/m³ and 87.06%, 98.1% and 98.30% for US/EO with 0.0015 kWh/m³ using NaCl, respectively. Those optimum results were obtained at pH=3, electrolysis time of 60 minute, current of 0.6 Ampere and 1g of NaCl.

Whereas, using CaCl₂, the maximum removal efficiencies of COD, color and turbidity with power consumption for EO process were 77.51%, 94.50% and 98.12% with 0.0050 kWh/m³ and for US/EO were 97.61%, 99.43% and 99.25% with 0.0077 kWh/m³ respectively. Those optimum results were obtained at pH=3, time of 60 minute, current of 0.6 Ampere and 3 g of CaCl₂.

This indicates that, the combination of sonolysis and electrochemical oxidation has a remarkable synergistic effect on the removal of pollutants from domestic wastewater when compared with the results of other related studies. As supporting electrolyte, CaCl₂ was more efficient than NaCl for both EO and US/EO processes using aluminum electrode.

Results show that the values of the initial pH, reaction time, current ampere and ultrasonic power were the main parameters affecting the removal, while comparatively electrolyte concentration had a slight effect on the reaction. Moreover, it indicates that US/EO technology increased the % removal of COD, color and turbidity by lowering the power consumption.

Taken together, the US/EO process can be applied as a novel technology to treat domestic wastewater. It was found to be more efficient method than EO, because it was seen that introduction of the power of ultrasound during sonication could enhance pollutant reduction. This hybrid technology will work efficiently in the wastewater treatment process due to the significant improvement over the conventional system.

Response Surface Methodology (RSM) based on Central Composite Design (CCD) was a good tool used to evaluate and optimize the effect of operating parameters on the responses. According to the study, the optimum values of COD, Color and turbidity with power Consumption for US/EO were 99.70 %, 99.79 % and 99.28 % with 0.003 kWh/m³ using CaCl₂. These results were obtained at optimal conditions of pH 5.85, electrolysis time 47.15 minutes, current 0.57 Ampere and electrolytic concentration 1.42 g/L using aluminum as electrode at the degree of desirability of the model equal to 1.

The significance of independent variables and their interactions were tested by means of the analysis of variance (ANOVA) with 95% confidence limits. Quadratic regression equation was suggested as a good model for prediction of chemical oxygen demand (COD), color and turbidity removal efficiency with power consumption.

The coefficients of determination (R^2) for US/EO using CaCl₂ were found to be 0.96 for both COD and color, 0.97 for turbidity and 0.98 for power consumption. Largeness of R^2 and its closeness to 1 was desirable. The model prediction for maximum removal was compared to the experimental result at optimal operating conditions. A good agreement between the model prediction and experimental results confirms the soundness of the developed model, which indicates that the central composite design (CCD) could be effectively used to optimize the electrochemical process and sono-electrochemical process parameters.

Therefore, as an experimental finding showed that, the combination of EO and US based on advanced oxidation processes (AOPs) has been proved to be efficient and alternative treatment techniques for domestic wastewater effluent.

5.2 Recommendations

Even if Sono-electrochemical process was a promising technology, the CO₂ released from the process have to be in concern in order to protect the environment from pollution. Likewise, relatively higher energy consumption of the electro-sonication process may be a disadvantage for the commercial application. It was done by applying a source of energy power from either electric power or solar power depending on their availability. Not only energy consumption, operating cost calculations have to be made to this treatment process including cost of chemicals and electrodes, investment costs, power supplies, electrochemical cell vessels, sludge disposal and sludge separation systems.

Since, the source of energy is electric power; the variation of electric source has an impact on the initial temperature of the sample. If the electric power was switched off suddenly, while doing an experiment, it elongate the period of the laboratory and the effect of current ampere may wrongly recorded. It was recommended to have constant power supply in order to minimize the problem. To cover this source like generator or solar power must be provided to minimize the effect of electric power.

On another way, electrodes are the best material needed in electrochemical process. Hence, there was electrode dissolution in the process, using the same electrode for different tests may have direct influence on the results of the responses. While using the electrode in the process, washing the electrode between each experiments and replacing the electrode regularly for proper treatment was recommended if possible. Hereafter, for the sludge produced during the process applied for wastewater treatment, proper disposal area must be provided.

Finally, this treated water was not recommended for drinking, if it was not further treated as per the criteria for drinking water by WHO. But, it may be recommended for toilet flushing and other household purposes not in direct touch with food. The combination of electrochemical process and ultrasonic need to be studied further by considering additional parameters that affect domestic wastewater for the future.

REFERENCES

- APHA, W. F. (2005). *Standard methods for the examination of water and wastewater*. Washington, DC, USA: American Public Health Association (APHA).
- Asaithambi, P. and Matheswaran, M. (2016). Electrochemical treatment of simulated sugar industrial effluent: Optimization and modeling using a response surface methodology. *Arabian Journal of Chemistry*, 9, 981-987.
- Asaithambi, P., Aziz, A., Sajjadi, B. and Daud, W. (2017). Sono assisted electrocoagulation process for the removal of pollutant from pulp and paper industry effluent. *Environ Sci Pollut Res*, 24, 5168–5178.
- Asaithambi, P., Beyene, D. and Alemayehu, E. (2017). Treatment of landfill leachate waste using sono (US) and photo (UV) based advanced oxidation processes: Studies on various operating parameters. *Desalination and Water Treatment*, 94, 147–155.
- Asaithambi, P., Garlanka, L., Anantharaman, N. and Matheswaran, M. (2012). Influence of Experimental Parameters in the Treatment of Distillery Effluent by Electrochemical Oxidation. *Separation Science and Technology*, 47(3), 470-481.
- Aslam D., Muhammad N. and Muzafar M. (2013). Characterization and Treatment of Wastewater from Sapphire Textile Industry, Pakistan. *Journal of Scientific & Innovative Research*, 2(2), 351-371.
- Banacha, M., Mollazehib, A. and Ahmadib, S. (2018). Survey on the removal of ciprofloxacin from aqueous solutions by nano-sonocatalytic process. *Desalin. Water Treat.*, 136, 207–211.
- Barrera-Díaz, C., Roa-Morales, G., Hernández, P., Fernandez-Marchante C. and Rodrigo, M. (2014). Enhanced electrocoagulation: New approaches to improve the electrochemical process. *J. Electrochem. Sci. Eng.*, X, 000-000.
- Barros, W., Steter, J., Lanza, M. and Motheo, A. (2014). Degradation of amaranth dye in alkaline medium by ultrasonic cavitation coupled with electrochemical oxidation using a boron-doped diamond anode. *Electrochim Acta*, 143, 180–7.

- Bernal-Martínez, L., Barrera-Díaz, C., Solís-Morelos, C. and Natividad, R. (2010). Synergy of electrochemical and ozonation processes in industrial wastewater treatment. *Chemical Engineering Journal*, 165, 71–77.
- Butkovskiy, A., Jermaise, A., Leal, L. and Van der Zande, T. (2014). Electrochemical Conversion of Micropollutants in Gray Water. *Environmental Science and Technology*, 48, 1893-1901.
- Canizares P., Garcia-Gomez J., Fernandez de Marcos I., Rodrigo MA and Lobato J. (2006). Measurement of mass-transfer coefficients by an electrochemical technique. *J Chem Educ*, 83: 1204–1207.
- Chakma, S., Vijayan and Moholkar, S. (2015). Investigation in mechanistic issues of sonocatalysis and sonophotocatalysis using pure and doped photocatalysts. *Ultrasonics Sonochemistry*, 22, 287–299.
- Dalvand, A., Gholami, M., Joneidi, A. and Mahmoodi, N. (2011). Dye Removal, Energy Consumption and Operating Cost of Electrocoagulation of Textile Wastewater as a Clean Process. *CLEAN - Soil, Air, and Water*, 39 (7), 665–72.
- Emamjomeh, M., Jamali, H. and Moradnia, M. (2017). Optimization of nitrate removal efficiency and energy consumption using a batch monopolar electrocoagulation: prediction by RSM method. *J. Environ. Eng.*, 143.
- Garbellini, G., Salazar-Banda, G. and Avaca, L. (2010). Effects of Ultrasound on the Degradation of Pentachlorophenol by Boron-Doped Diamond Electrodes. *Portugaliae Electrochimica Acta*, Vol. 28, No. 6, pp. 405-415.
- GeoDatos. (2020, January 05). *Latitude and longitude of Jimma institute of Technology [Blog post]*. Retrieved from <https://www.geodatos.net/en/coordinates/ethiopia/oromiya/jimma.html>.
- Ghatak, H. (2014). Advanced oxidation processes for the treatment of biorecalcitrant organics in wastewater. *Environmental Science and Technology*, 44, 1167-1219.
- Jamali, H., Dindarloo, K., Fard, M. and Moradnia, M. (2018). Response surface methodology to optimize wastewater treatment in carpet industries by potassium ferrate. *Int. J. Water Wastewater*, 29.
- Kobyas, M., Demirbas, E. and Sahin, O. (2012). Effect of Operational Parameters on the Removal of Phenol from Aqueous Solutions by Electrocoagulation using Fe and Al Electrodes. *Desalination and Water Treatment*, 46, 366-374.
- Körbahti, B. and Taşyürek, S. (2015). Electrochemical oxidation of ampicillin antibiotic at borondoped diamond electrodes and process optimization using response surface methodology. *Environmental Science and Pollution Research*, 22(5), 3265–78.

- Kumar, V. (2017). A Review on the Feasibility of Electrolytic Treatment of Wastewater: Prospective and Constraints. *Constraints*, 2, 52-62.
- Lee, B., Park, H., Choi, I., Cho, M., Kim, H., Yoo, S., ... and Jang, J. (2016). Polarization characteristics of a low catalyst loading PEM water electrolyzer operating at elevated temperature. *Journal of Power Sources*, 309, 127-134.
- Liu B., Aisa H. and Yili A. (2019). Optimization of ultrasound-assisted extraction of sheep abomasum protein concentrates by response surface methodology and evaluation of their properties. *Food Science and Technology*(1678-457X (Online)).
- Moradnia, M., Dindarlo, K. and Jamali, H. (2016). Optimizing potassium ferrate for textile wastewater treatment by RSM. *Environ. Health Eng. Manag. J.*, 3, 137–142.
- Moreira, F., Boaventura, R., Brillas, E. and Vilar, V. (2017). Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters. *Applied Catalysis B: Environmental*, 202, 217-261.
- Murat, S. (2009). Removal of suspended solids and turbidity from marble processing wastewaters by electrocoagulation. Comparison of electrode materials and electrode. Connection systems. *Journal of Hazardous Materials*, 345–352.
- Nair, A., Makwana, A. and Ahammed, M. (2014). The use of response surface methodology for modelling and analysis of water and wastewater treatment processes. *Water Science & Technology*, 69(3), 464-478.
- Namgoong, E. and Chun, J. (1984). Effect of ultrasonic vibration on hard chromium plating in a modified self-regulating high speed bath. *Thin Solid Films*, 120(2), 153-159.
- Raschitor, A., Fernandez, C., Cretescu, I., Rodrigo, M. and Cañizares, P. (2014). Sono-electrocoagulation of wastewater polluted with Rhodamine 6G. *Separation and Purification Technology*, 135, 110–116.
- Ren, Y-Z., Wu, Z-L., Franke, M., Braeutigam, P., Ondruschka, B. and Comeskey, D. (2013). Sono-electrochemical degradation of phenol in aqueous solutions. *Ultrason Sonochem*, 20(2), 715–21.

- Santos, I., Dezotti, M. and Dutra, J. (2013). Electrochemical treatment of effluents from petroleum industry using a Ti/RuO₂ anode. *Chemical Engineering Journal*, 226, 293–299.
- Sathishkumar, P., Mangalaraja, R. and Anandan, S. (2016). Review on the recent improvements in sonochemical and combined sonochemical oxidation processes – A powerful tool for destruction of environmental contaminants. *Renewable and Sustainable Energy Reviews*, 55, 426–454.
- Steter, J., Barros, W. Lanza, M. and Motheo, A. (2014). Electrochemical and sonoelectrochemical processes applied to amaranth dye degradation. *Chemosphere*, 117, 200–207.
- Thokchom, B., Pandit, A., Qiu, P., Park, B., Choi, J. and Khim, J. (2015). A review on sonoelectrochemical technology as an upcoming alternative for pollutant degradation. *Ultrason. Sonochem.*, 27, 210-234.
- Wang, J. and Xu, L. (2012). Advanced Oxidation Processes for Wastewater Treatment: Formation of Hydroxyl Radical and Application. *Environmental Science and Technology*, 42, 251–325.
- Wang, Z., Zhang, Y., Liu, B., Wu, K., Thevuthasan, S., Baer, D., ... and Wang, F. (2017). In situ Mass Spectrometric Monitoring of the Dynamic Electrochemical Process at the Electrode-Electrolyte Interface: a SIMS Approach. *Anal. Chem.*, 89, 960–965.
- WHO. (2017). *Guidelines for drinking water quality* (4th ed.). Geneva: World Health Organization.
- Wu, W., Huang, Z. and Lim, T. (2014). Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water. *Applied Catalysis A: General*, 480, 58-78.
- Yang B., Zuo J., Tang X., Liu F., Yu X. and Tang X. (2014). Effective ultrasound electrochemical degradation of methylene blue wastewater using a nanocoated electrode. *Ultrason Sonochem*, 21(4), 1310–7.

APPENDIXES

Appendix A: Experimental Data

Appendix A-1: Experimental Data for Electrochemical Oxidation Process

Constant operating parameters

- System: Batch system
- Reaction time = 1 hr.
- Wavelength = 420 nm
- Mode of electrode connection = Parallel
- Distance between electrode = 1cm
- Anode – Cathode electrode = Al – Al
- Length of electrode = 13 cm
- Width of electrode = 5 cm

Date: Sept. 03/2019 Exp. Blank (Distilled Water)	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)
pH = 7.65 Conductivity = 3.59mS/cm Temperature = 12.7 °C	0	0	100.0	0.10	0.00

Date: Sept. 16/2019 Exp. 1	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
pH = 3.0 Conductivity = 7.34 mS/cm Temperature = 21.5 °C Current = 0.1 A [NaCl] = 1 g/L Voltage = 2.2 volts	0	1.53	3.0	425.6	230.0	0.00
	20	0.305	49.5	252.0	26.21	0.0007
	60	0.163	68.7	112.0	13.72	0.0009

Date: Sept. 16/2019 Exp. 2	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
pH = 3.0 Conductivity = 10.54 mS/cm Temperature = 21.8 °C Current = 0.1 A [NaCl] = 3 g/L Voltage = 1.2 volts	0	1.53	3.0	425.6	230.0	0.00
	20	0.490	32.3	236.0	40.28	0.0008
	60	0.164	68.6	192.0	15.49	0.0016

Date: Sept. 17/2019 Exp. 3	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
pH = 3.0 Conductivity = 7.03 mS/cm Temperature = 18.6 °C Current = 0.6 A [NaCl] = 1 g/L Voltage = 4.3 volts	0	1.53	3.0	425.6	230.0	0.00
	20	0.057	87.8	128.0	9.20	0.0030
	60	0.044	90.4	80.0	6.43	0.0041

Date: Sept. 17/2019 <u>Exp. 4</u> pH = 3.0 Conductivity = 11.03 mS/cm Temperature = 19.5 °C Current = 0.6 A [NaCl] = 3 g/L Voltage = 2.6 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.088	81.7	144.0	15.82	0.0015
	60	0.059	87.2	80.0	9.63	0.0037

Date: Sept. 17/2019 <u>Exp. 5</u> pH = 3.0 Conductivity = 6.32 mS/cm Temperature = 19.9 °C Current = 0.1 A [CaCl ₂] = 1 g/L Voltage = 1.4 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.751	17.7	352.0	54.88	0.0002
	60	0.163	68.8	144.0	13.99	0.0007

Date: Sept. 17/2019 <u>Exp. 6</u> pH = 3.0 Conductivity = 7.96 mS/cm Temperature = 20.4 °C Current = 0.1 A [CaCl ₂] = 3 g/L Voltage = 1.2 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.753	17.7	368.0	32.56	0.0005
	60	0.318	48.1	224.0	13.75	0.0011

Date: Sept. 19/2019 <u>Exp. 7</u> pH = 3.0 Conductivity = 6.41 mS/cm Temperature = 17.8 °C Current = 0.6 A [CaCl ₂] = 1 g/L Voltage = 4.2 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.043	90.5	132.0	23.15	0.0030
	60	0.018	96.0	80.0	9.69	0.0071

Date: Sept. 19/2019 <u>Exp. 8</u> pH = 3.0 Conductivity = 9.74 mS/cm Temperature = 17.8 °C Current = 0.6 A [CaCl ₂] = 3 g/L Voltage = 2.8 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.085	82.2	144.0	16.29	0.0018
	60	0.059	87.3	80.0	11.31	0.0050

Date: Sept. 19/2019 <u>Exp. 9</u> pH = 11.0 Conductivity = 10.04 mS/cm Temperature = 21.7 °C Current = 0.1 A [NaCl] = 1 g/L Voltage = 1.2 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.470	33.9	228.0	36.94	0.0002
	60	0.712	19.4	184.0	39.3	0.0007

Date: Sept. 20/2019 <u>Exp. 10</u> pH = 11.0 Conductivity = 12.47 mS/cm Temperature = 22.3 °C Current = 0.1 A [NaCl] = 3 g/L Voltage = 1.2 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.441	36.2	345.6	35.03	0.0002
	60	0.596	25.4	272.0	38.5	0.0022

Date: Sept. 20/2019 <u>Exp. 11</u> pH = 11.0 Conductivity = 9.41 mS/cm Temperature = 23.2 °C Current = 0.6 A [NaCl] = 1 g/L Voltage = 4.1 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.431	31.1	288.0	19.9	0.0033
	60	0.381	41.6	192.0	17.9	0.0046

Date: Sept. 20/2019 <u>Exp. 12</u> pH = 11.0 Conductivity = 12.55 mS/cm Temperature = 23.5 °C Current = 0.6 A [NaCl] = 3 g/L Voltage = 2.2 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.577	26.5	256.0	23.4	0.0029
	60	0.516	30.5	176.0	22.0	0.0051

Date: Sept. 20/2019 <u>Exp. 13</u> pH = 11.0 Conductivity = 6.82 mS/cm Temperature = 23.0 °C Current = 0.1 A [CaCl ₂] = 1 g/L Voltage = 1.5 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.766	17.1	281.6	46.6	0.0005
	60	0.406	39.3	207.6	39.6	0.0009

Date: Sept. 23/2019 Exp. 14 pH = 11.0 Conductivity = 8.07 mS/cm Temperature = 22.6 °C Current = 0.1 A [CaCl ₂] = 3 g/L Voltage = 1.4 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.488	32.5	243.2	64.1	0.0002
	60	0.297	50.4	192.0	39.01	0.0009

Date: Sept. 23/2019 Exp. 15 pH = 11.0 Conductivity = 6.81 mS/cm Temperature = 23.2 °C Current = 0.6 A [CaCl ₂] = 1 g/L Voltage = 4.7 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.399	39.9	261.6	39.5	0.0047
	60	0.271	53.6	165.6	21.0	0.0094

Date: Sept. 24/2019 Exp. 16 pH = 11.0 Conductivity = 7.50 mS/cm Temperature = 23.7 °C Current = 0.6 A [CaCl ₂] = 3 g/L Voltage = 4.9 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.525	29.9	293.6	48.5	0.0067
	60	0.242	57.2	197.6	22.8	0.0104

Date: Sept. 24/2019 Exp. 17 pH = 9.0 Conductivity = 5.70 mS/cm Temperature = 22.2 °C Current = 0.35 A [CaCl ₂] = 2 g/L Voltage = 2.7 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.411	38.8	256.0	44.9	0.0031

Date: Sept. 24/2019 Exp. 18 pH = 5.0 Conductivity = 7.82 mS/cm Temperature = 20.6 °C Current = 0.35 A [CaCl ₂] = 2 g/L Voltage = 2.6 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.038	91.7	112.0	5.24	0.0021

Date: Sept. 25/2019 <u>Exp. 19</u> pH = 7.0 Conductivity = 7.05 mS/cm Temperature = 21.9 °C Current = 0.35 A [CaCl ₂] = 2 g/L Voltage = 2.6 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	30	0.206	62.2	112.0	16.54	0.0013
	40	0.189	64.7	97.0	11.1	0.0020
	50	0.174	67.0	57.0	10.17	0.0025

Date: Sept. 25/2019 <u>Exp. 20</u> pH = 7.0 Conductivity = 6.63 mS/cm Temperature = 22.8 °C Current = 0.35 A [CaCl ₂] = 1.5 g/L Voltage = 3.6 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.241	57.5	153.6	20.0	0.0020

Date: Sept. 25/2019 <u>Exp. 21</u> pH = 7.0 Conductivity = 7.11 mS/cm Temperature = 22.7 °C Current = 0.225 A [CaCl ₂] = 2 g/L Voltage = 1.7 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.043	90.6	160.0	16.16	0.0018

Date: Sept. 25/2019 <u>Exp. 22</u> pH = 7.0 Conductivity = 7.62 mS/cm Temperature = 22.7 °C Current = 0.35 A [CaCl ₂] = 2.5 g/L Voltage = 2.7 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.082	82.8	128.0	10.06	0.0021

Date: Sept. 25/2019 <u>Exp. 23</u> pH = 7.0 Conductivity = 7.04 mS/cm Temperature = 19.6 °C Current = 0.475 A [CaCl ₂] = 2 g/L Voltage = 3.2 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.144	71.7	175.2	14.8	0.0031

Date: Sept. 26/2019 <u>Exp. 24</u> pH = 5.0 Conductivity = 8.81 mS/cm Temperature = 20.4 °C Current = 0.35 A [NaCl] = 2 g/L Voltage = 2.5 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.092	80.9	160.0	12.3	0.0024

Date: Sept. 26/2019 <u>Exp. 25</u> pH = 7.0 Conductivity = 8.57 mS/cm Temperature = 20.2 °C Current = 0.35 A [NaCl] = 2 g/L Voltage = 2.6 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	30	0.345	45.2	272.0	25.0	0.0029
	40	0.290	51.3	240.0	21.2	0.0043
	50	0.254	55.7	224.0	18.6	0.0047

Date: Sept. 26/2019 <u>Exp. 26</u> pH = 9.0 Conductivity = 7.62 mS/cm Temperature = 20.9 °C Current = 0.35 A [NaCl] = 2 g/L Voltage = 3.0 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.508	31.1	280.0	37.6	0.0024

Date: Sept. 26/2019 <u>Exp. 27</u> pH = 7.0 Conductivity = 7.78 mS/cm Temperature = 21.5 °C Current = 0.475 A [NaCl] = 2 g/L Voltage = 3.7 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.156	69.8	192.0	15.55	0.0048

Date: Sept. 27/2019 <u>Exp. 28</u>	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
pH = 7.0 Conductivity = 8.50 mS/cm Temperature = 21.6 °C Current = 0.225 A [NaCl] = 2 g/L Voltage = 1.9 volts	0	1.53	3.0	425.6	230.0	0.00
	40	0.271	53.5	220.0	19.9	0.0044

Date: Sept. 27/2019 <u>Exp. 29</u>	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
pH = 7.0 Conductivity = 7.62 mS/cm Temperature = 21.7 °C Current = 0.35 A [NaCl] = 1.5 g/L Voltage = 2.5 volts	0	1.53	3.0	425.6	230.0	0.00
	40	0.188	64.8	272.0	15.37	0.0021

Date: Sept. 27/2019 <u>Exp. 30</u>	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
pH = 7.0 Conductivity = 9.22 mS/cm Temperature = 22.7 °C Current = 0.35 A [NaCl] = 2.5 g/L Voltage = 2.9 volts	0	1.53	3.0	425.6	230.0	0.00
	40	0.174	67.0	166.4	13.93	0.0007

Appendix A-2: Experimental Results/ Data for Sono-electrochemical Oxidation Process

Date: Oct. 01/2019 <u>Exp. 1</u> pH = 7.0 Conductivity = 7.42 mS/cm Temperature = 26.0 °C Current = 0.35 A [CaCl ₂] = 2 g/L Voltage = 3.2 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	30	0.211	61.6	153.6	17.1	0.0012
	40	0.183	65.6	137.6	12.14	0.0017
	50	0.161	69.0	64.6	9.28	0.0023

Date: Oct. 01/2019 <u>Exp. 2</u> pH = 7.0 Conductivity = 6.69 mS/cm Temperature = 32.1 °C Current = 0.35 A [CaCl ₂] = 1.5 g/L Voltage = 2.7 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.209	61.8	112.0	12.61	0.0013

Date: Oct. 02/2019 <u>Exp. 3</u> pH = 7.0 Conductivity = 7.10 mS/cm Temperature = 26.7 °C Current = 0.225 A [CaCl ₂] = 2 g/L Voltage = 2.4 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.382	41.5	201.6	26.30	0.0030

Date: Oct. 01/2019 <u>Exp. 4</u> pH = 7.0 Conductivity = 7.42 mS/cm Temperature = 29.2 °C Current = 0.35 A [CaCl ₂] = 2.5 g/L Voltage = 2.8 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.197	63.5	121.6	11.80	0.0015

Date: Oct. 02/2019 <u>Exp. 5</u> pH = 7.0 Conductivity = 6.88 mS/cm Temperature = 26.0 °C Current = 0.475 A [CaCl ₂] = 2 g/L Voltage = 3.8 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.087	81.9	91.6	6.29	0.0019

Date: Oct. 02/2019 <u>Exp. 6</u> pH = 11.0 Conductivity = 6.94 mS/cm Temperature = 30.4 °C Current = 0.6 A [CaCl ₂] = 1 g/L Voltage = 2.9 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.846	14.3	361.6	89.90	0.0042
	60	0.398	40.0	265.6	35.8	0.0119

Date: Oct. 02/2019 <u>Exp. 7</u> pH = 11.0 Conductivity = 8.33 mS/cm Temperature = 33.7 °C Current = 0.6 A [CaCl ₂] = 3 g/L Voltage = 2.9 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	1.064	8.6	393.6	136.0	0.0106
	60	0.405	39.4	297.6	59.7	0.0146

Date: Oct. 03/2019 <u>Exp. 8</u> pH = 11.0 Conductivity = 7.20 mS/cm Temperature = 25.5 °C Current = 0.1 A [CaCl ₂] = 1 g/L Voltage = 1.4 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	1.306	4.9	416.0	154.0	0.0116
	60	0.923	11.9	377.6	109.0	0.0187

Date: Oct. 03/2019 <u>Exp. 9</u> pH = 11.0 Conductivity = 7.61 mS/cm Temperature = 25.2 °C Current = 0.1 A [CaCl ₂] = 3 g/L Voltage = 1.3 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	1.043	9.1	401.0	136.4	0.0132
	60	0.886	13.0	346.6	127.7	0.0173

Date: Oct. 03/2019 <u>Exp. 10</u> pH = 9.0 Conductivity = 6.07 mS/cm Temperature = 24.9 °C Current = 0.35 A [CaCl ₂] = 2 g/L Voltage = 3.3 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.608	24.6	256.0	70.9	0.0092

Date: Oct. 03/2019 <u>Exp. 11</u> pH = 5.0 Conductivity = 7.45 mS/cm Temperature = 28.2 °C Current = 0.35 A [CaCl ₂] = 2 g/L Voltage = 3.2 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.137	72.9	112.0	14.03	0.0037

Date: Oct. 03/2019 <u>Exp. 12</u> pH = 3.0 Conductivity = 6.55 mS/cm Temperature = 21.7 °C Current = 0.1 A [CaCl ₂] = 1 g/L Voltage = 1.6 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.678	21.0	271.2	82.8	0.0028
	60	0.263	54.6	192.0	30.8	0.0094

Date: Oct. 03/2019 <u>Exp. 13</u> pH = 3.0 Conductivity = 8.94 mS/cm Temperature = 26.0 °C Current = 0.1 A [CaCl ₂] = 3 g/L Voltage = 1.9 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.814	15.4	312.4	86.1	0.0051
	60	0.271	53.5	208.0	32.9	0.0095

Date: Oct. 03/2019 <u>Exp. 14</u> pH = 3.0 Conductivity = 6.59 mS/cm Temperature = 26.6 °C Current = 0.6 A [CaCl ₂] = 1 g/L Voltage = 4.3 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.087	81.9	48.0	12.74	0.0021
	60	0.058	87.4	37.0	7.14	0.0065

Date: Oct. 03/2019 <u>Exp. 15</u> pH = 3.0 Conductivity = 8.47 mS/cm Temperature = 26.8 °C Current = 0.6 A [CaCl ₂] = 3 g/L Voltage = 4.0 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.246	56.8	128.0	32.6	0.0039
	60	0.049	89.4	32.0	5.89	0.0077

Date: Oct. 03/2019 <u>Exp. 16</u> pH = 3.0 Conductivity = 7.45 mS/cm Temperature = 27.0 °C Current = 0.1 A [NaCl] = 1 g/L Voltage = 1.1 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.711	19.4	282.4	82.1	0.0029
	60	0.206	62.2	194.0	26.0	0.0046

Date: Oct. 04/2019 <u>Exp. 17</u> pH = 3.0 Conductivity = 7.70 mS/cm Temperature = 18.1 °C Current = 0.6 A [NaCl] = 1 g/L Voltage = 4.0 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.109	77.8	144.0	10.43	0.0018
	60	0.060	87.1	128.0	5.93	0.0032

Date: Oct. 04/2019 <u>Exp. 18</u> pH = 3.0 Conductivity = 11.08 mS/cm Temperature = 22.2 °C Current = 0.6 A [NaCl] = 3 g/L Voltage = 3.6 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.088	81.5	160.0	9.9	0.0028
	60	0.069	85.4	130.0	6.35	0.0037

Date: Oct. 04/2019 <u>Exp. 19</u> pH = 3.0 Conductivity = 7.73 mS/cm Temperature = 22.0 °C Current = 0.1 A [NaCl] = 3 g/L Voltage = 1.5 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.907	12.4	290.0	94.9	0.0027
	60	0.251	56.1	224.0	23.80	0.0033

Date: Oct. 04/2019 <u>Exp. 20</u> pH = 5.0 Conductivity = 8.80 mS/cm Temperature = 21.5 °C Current = 0.35 A [NaCl] = 2 g/L Voltage = 2.6 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.228	59.2	128.0	16.9	0.0025

Date: Oct. 04/2019 <u>Exp. 21</u> pH = 9.0 Conductivity = 8.41 mS/cm Temperature = 18.2 °C Current = 0.35 A [NaCl] = 2 g/L Voltage = 3.0 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.581	26.2	304.0	50.7	0.0038

Date: Oct. 04/2019 <u>Exp. 22</u> pH = 7.0 Conductivity = 8.76 mS/cm Temperature = 19.3 °C Current = 0.35 A [NaCl] = 2 g/L Voltage = 2.2 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	30	0.419	38.1	208.0	40.5	0.0024
	40	0.392	40.5	216.0	31.6	0.0029
	50	0.296	50.5	224.0	26.9	0.0031

Date: Oct. 04/2019 <u>Exp. 23</u> pH = 7.0 Conductivity = 8.48 mS/cm Temperature = 21.0 °C Current = 0.475 A [NaCl] = 2 g/L Voltage = 2.9 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.240	57.6	192.0	17.12	0.0034

Date: Oct. 04/2019 <u>Exp. 24</u> pH = 7.0 Conductivity = 8.79 mS/cm Temperature = 19.8 °C Current = 0.225 A [NaCl] = 2 g/L Voltage = 2.1 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.678	21.0	292.0	76.1	0.0035

Date: Oct. 04/2019 <u>Exp. 25</u> pH = 7.0 Conductivity = 7.68 mS/cm Temperature = 19.3 °C Current = 0.35 A [NaCl] = 1.5 g/L Voltage = 2.1 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.349	44.8	272.0	27.2	0.0032

Date: Oct. 04/2019 <u>Exp. 26</u> pH = 7.0 Conductivity = 9.42 mS/cm Temperature = 19.0 °C Current = 0.35 A [NaCl] = 2.5 g/L Voltage = 2.3 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	40	0.323	47.6	240.0	25.0	0.0027

Date: Oct. 04/2019 <u>Exp. 27</u> pH = 11.0 Conductivity = 12.42 mS/cm Temperature = 14.8 °C Current = 0.1 A [NaCl] = 3 g/L Voltage = 1.7 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.425	37.6	345.6	117.0	0.0041
	60	0.407	39.2	325.1	106.0	0.0048

Date: Oct. 04/2019 <u>Exp. 28</u> pH = 11.0 Conductivity = 8.64 mS/cm Temperature = 17.8 °C Current = 0.1 A [NaCl] = 1 g/L Voltage = 1.8 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.603	24.9	377.6	125.0	0.0062
	60	0.488	32.5	371.2	132.0	0.0074

Date: Oct. 04/2019 <u>Exp. 29</u> pH = 11.0 Conductivity = 8.67 mS/cm Temperature = 18.9 °C Current = 0.6 A [NaCl] = 1 g/L Voltage = 3.0 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.526	29.6	374.4	129.0	0.0041
	60	0.414	38.5	361.6	112.0	0.0069

Date: Oct. 04/2019 <u>Exp. 30</u> pH = 11.0 Conductivity = 11.87 mS/cm Temperature = 20.7 °C Current = 0.6 A [NaCl] = 3 g/L Voltage = 3.0 volts	Time (min.)	Absorbance (% Abs.)	Transmittance %	COD (mg/L)	Turbidity (NTU)	Power C. (kWh/m ³)
	0	1.53	3.0	425.6	230.0	0.00
	20	0.495	32.0	366.2	127.0	0.0059
	60	0.359	43.7	316.5	99.0	0.0073

Appendix B: Analysis of Variance Test

Table B-1: ANOVA for the % COD Removal of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	5624.92	14	401.78	126.32	< 0.0001	Highly significant
A-pH	1810.84	1	1810.84	569.32	< 0.0001	Highly significant
B-Time	370.29	1	370.29	116.42	< 0.0001	Highly significant
C-Current	1428.29	1	1428.29	449.05	< 0.0001	Highly significant
D-NaCl	130.71	1	130.71	41.09	< 0.0001	Highly significant
AB	242.04	1	242.04	76.09	< 0.0001	Highly significant
AC	52.24	1	52.24	16.42	0.0010	Significant
AD	0.1106	1	0.1106	0.0348	0.8546	Insignificant
BC	19.60	1	19.60	6.16	0.0254	Significant
BD	11.34	1	11.34	3.57	0.0785	Insignificant
CD	0.0452	1	0.0452	0.0142	0.9067	Insignificant
A ²	36.16	1	36.16	11.37	0.0042	Significant
B ²	95.38	1	95.38	29.99	< 0.0001	Highly significant
C ²	13.30	1	13.30	4.18	0.0588	Insignificant
D ²	35.47	1	35.47	11.15	0.0045	Significant
Residual	47.71	15	3.18			
Lack of Fit	47.71	10	4.77			
Pure Error	0.0000	5	0.0000			
Cor Total	5672.63	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 126.32 implies the model was significant. There was 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 were significant. In this case A, B, C, D, AB, AC, BC, A², B², D² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table B-2: ANOVA for the % Color Removal of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	682.08	14	48.72	29.05	< 0.0001	Highly significant
A-pH	394.89	1	394.89	235.44	< 0.0001	Highly significant
B-Time	91.97	1	91.97	54.83	< 0.0001	Highly significant
C-Current	79.86	1	79.86	47.61	< 0.0001	Highly significant
D-NaCl	3.38	1	3.38	2.01	0.1763	Insignificant
AB	12.76	1	12.76	7.61	0.0146	Significant
AC	47.44	1	47.44	28.28	< 0.0001	Highly significant
AD	0.0028	1	0.0028	0.0016	0.9682	Insignificant
BC	3.97	1	3.97	2.37	0.1448	Insignificant
BD	4.42	1	4.42	2.64	0.1253	Insignificant
CD	2.39	1	2.39	1.43	0.2507	Insignificant
A ²	9.28	1	9.28	5.53	0.0328	Significant
B ²	0.0101	1	0.0101	0.0060	0.9391	Insignificant
C ²	3.60	1	3.60	2.15	0.1633	Insignificant
D ²	4.28	1	4.28	2.55	0.1309	Insignificant
Residual	25.16	15	1.68			
Lack of Fit	25.16	10	2.52			
Pure Error	0.0000	5	0.0000			
Cor Total	707.24	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 29.05 implies the model was significant. There was 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 were significant. In this case A, B, C, AB, AC, A² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table B-3: ANOVA for the % Turbidity Removal of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	478.24	14	34.16	27.78	< 0.0001	Highly significant
A-pH	169.73	1	169.73	138.04	< 0.0001	Highly significant
B-Time	85.09	1	85.09	69.20	< 0.0001	Highly significant
C-Current	98.60	1	98.60	80.19	< 0.0001	Highly significant
D-NaCl	8.42	1	8.42	6.85	0.0195	Significant
AB	12.69	1	12.69	10.32	0.0058	Significant
AC	31.78	1	31.78	25.85	0.0001	Highly significant
AD	2.24	1	2.24	1.82	0.1969	Insignificant
BC	6.88	1	6.88	5.59	0.0319	Significant
BD	0.8696	1	0.8696	0.7072	0.4136	Insignificant
CD	0.1139	1	0.1139	0.0926	0.7650	Insignificant
A ²	30.80	1	30.80	25.05	0.0002	Significant
B ²	8.93	1	8.93	7.26	0.0167	Significant
C ²	5.94	1	5.94	4.83	0.0440	Significant
D ²	35.36	1	35.36	28.76	< 0.0001	
Residual	18.44	15	1.23			
Lack of Fit	18.44	10	1.84			
Pure Error	0.0000	5	0.0000			
Cor Total	496.68	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 27.78 implies the model was significant. There was 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 were significant. In this case A, B, C, D, AB, AC, BC, A², B², C², D² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table B-4: ANOVA for the Power Consumption of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0001	14	4.554E-06	45.03	< 0.0001	Highly significant
A-pH	0.0000	1	0.0000	299.35	< 0.0001	Highly significant
B-Time	7.400E-06	1	7.400E-06	73.17	< 0.0001	Highly significant
C-Current	7.424E-09	1	7.424E-09	0.0734	0.7901	Insignificant
D-NaCl	4.583E-07	1	4.583E-07	4.53	0.0502	Insignificant
AB	1.406E-07	1	1.406E-07	1.39	0.2567	Insignificant
AC	8.556E-07	1	8.556E-07	8.46	0.0108	Significant
AD	3.906E-07	1	3.906E-07	3.86	0.0682	Insignificant
BC	3.306E-07	1	3.306E-07	3.27	0.0907	Insignificant
BD	7.656E-07	1	7.656E-07	7.57	0.0148	Significant
CD	6.126E-06	1	6.126E-06	60.57	< 0.0001	Highly significant
A ²	7.800E-08	1	7.800E-08	0.7713	0.3937	Insignificant
B ²	1.394E-07	1	1.394E-07	1.38	0.2586	Insignificant
C ²	5.911E-07	1	5.911E-07	5.84	0.0288	Significant
D ²	2.215E-09	1	2.215E-09	0.0219	0.8843	Insignificant
Residual	1.517E-06	15	1.011E-07			
Lack of Fit	1.517E-06	10	1.517E-07			
Pure Error	0.0000	5	0.0000			
Cor Total	0.0001	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 45.03 implies the model was significant. There was 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 were significant. In this case A, B, AC, BD, CD, C² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table B-5: ANOVA for the % COD Removal of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	15160.22	14	1082.87	61.89	< 0.0001	Highly significant
A-pH	4886.52	1	4886.52	279.27	< 0.0001	Highly significant
B-Time	831.62	1	831.62	47.53	< 0.0001	Highly significant
C-Current	2800.73	1	2800.73	160.06	< 0.0001	Highly significant
D-CaCl ₂	7.12	1	7.12	0.4070	0.5331	Insignificant
AB	210.25	1	210.25	12.02	0.0035	Significant
AC	782.32	1	782.32	44.71	< 0.0001	Highly significant
AD	4.02	1	4.02	0.2297	0.6386	Insignificant
BC	5.57	1	5.57	0.3183	0.5810	Insignificant
BD	11.12	1	11.12	0.6356	0.4377	Insignificant
CD	3.55	1	3.55	0.2031	0.6587	Insignificant
A ²	113.81	1	113.81	6.50	0.0222	Significant
B ²	0.1974	1	0.1974	0.0113	0.9168	Insignificant
C ²	7.86	1	7.86	0.4490	0.5130	Insignificant
D ²	2.26	1	2.26	0.1294	0.7240	Insignificant
Residual	262.46	15	17.50			
Lack of Fit	262.46	10	26.25			
Pure Error	0.0000	5	0.0000			
Cor Total	15422.68	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 61.89 implies the model was significant. There was 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 were significant. In this case A, B, C, AB, AC, A² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table B-6: ANOVA for the % Color Removal of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	7690.86	14	549.35	34.99	< 0.0001	Highly significant
A-pH	2522.68	1	2522.68	160.69	< 0.0001	Highly significant
B-Time	589.39	1	589.39	37.54	< 0.0001	Highly significant
C-Current	1575.56	1	1575.56	100.36	< 0.0001	Highly significant
D-CaCl ₂	3.48	1	3.48	0.2218	0.6444	Insignificant
AB	9.06	1	9.06	0.5771	0.4592	Insignificant
AC	17.77	1	17.77	1.13	0.3042	Insignificant
AD	0.2809	1	0.2809	0.0179	0.8954	Insignificant
BC	11.36	1	11.36	0.7234	0.4084	Insignificant
BD	1.29	1	1.29	0.0821	0.7784	Insignificant
CD	53.44	1	53.44	3.40	0.0849	Insignificant
A ²	282.41	1	282.41	17.99	0.0007	Significant
B ²	84.89	1	84.89	5.41	0.0345	Significant
C ²	43.32	1	43.32	2.76	0.1174	Insignificant
D ²	39.91	1	39.91	2.54	0.1317	Insignificant
Residual	235.48	15	15.70			
Lack of Fit	235.48	10	23.55			
Pure Error	0.0000	5	0.0000			
Cor Total	7926.34	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 34.99 implies the model was significant. There was 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 were significant. In this case A, B, C, A², B² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table B-7: ANOVA for the % Turbidity Removal of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	9226.64	14	659.05	41.76	< 0.0001	Highly significant
A-pH	3091.95	1	3091.95	195.94	< 0.0001	Highly significant
B-Time	948.11	1	948.11	60.08	< 0.0001	Highly significant
C-Current	1724.83	1	1724.83	109.30	< 0.0001	Highly significant
D-CaCl ₂	62.64	1	62.64	3.97	0.0648	Significant
AB	37.06	1	37.06	2.35	0.1462	Insignificant
AC	22.02	1	22.02	1.40	0.2559	Insignificant
AD	81.41	1	81.41	5.16	0.0383	Significant
BC	2.24	1	2.24	0.1421	0.7115	Insignificant
BD	5.70	1	5.70	0.3612	0.5568	Insignificant
CD	6.39	1	6.39	0.4048	0.5342	Insignificant
A ²	62.52	1	62.52	3.96	0.0651	Significant
B ²	70.09	1	70.09	4.44	0.0523	Insignificant
C ²	0.6249	1	0.6249	0.0396	0.8449	Insignificant
D ²	46.85	1	46.85	2.97	0.1054	Insignificant
Residual	236.71	15	15.78			
Lack of Fit	236.71	10	23.67			
Pure Error	0.0000	5	0.0000			
Cor Total	9463.35	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 41.76 implies the model was significant. There was 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 were significant. In this case A, B, C, AD were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table B-8: ANOVA for Power Consumption of US/EO quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0002	14	0.0000	41.79	< 0.0001	Highly significant
A-pH	0.0000	1	0.0000	41.47	< 0.0001	Highly significant
B-Time	0.0000	1	0.0000	64.80	< 0.0001	Highly significant
C-Current	0.0001	1	0.0001	362.42	< 0.0001	Highly significant
D-CaCl ₂	1.364E-09	1	1.364E-09	0.0043	0.9488	Insignificant
AB	7.562E-08	1	7.562E-08	0.2363	0.6339	Insignificant
AC	0.0000	1	0.0000	39.93	< 0.0001	Highly significant
AD	1.756E-06	1	1.756E-06	5.48	0.0334	Significant
BC	0.0000	1	0.0000	35.59	< 0.0001	Highly significant
BD	1.406E-07	1	1.406E-07	0.4393	0.5175	Insignificant
CD	3.063E-08	1	3.063E-08	0.0957	0.7613	Insignificant
A ²	4.845E-07	1	4.845E-07	1.51	0.2375	Insignificant
B ²	1.991E-07	1	1.991E-07	0.6220	0.4426	Insignificant
C ²	2.036E-07	1	2.036E-07	0.6362	0.4375	Insignificant
D ²	4.058E-08	1	4.058E-08	0.1268	0.7268	Insignificant
Residual	4.801E-06	15	3.201E-07			
Lack of Fit	4.801E-06	10	4.801E-07			
Pure Error	0.0000	5	0.0000			
Cor Total	0.0002	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 41.79 implies the model was significant. There was 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 were significant. In this case A, B, C, AC, AD, BC were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table B-9: ANOVA for the % COD Removal of US/EO quadratic model using NaCl

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	9626.61	14	687.61	34.92	< 0.0001	Highly significant
A-pH	5725.84	1	5725.84	290.75	< 0.0001	Highly significant
B-Time	343.92	1	343.92	17.46	0.0008	Significant
C-Current	1027.95	1	1027.95	52.20	< 0.0001	Highly significant
D-NaCl	112.74	1	112.74	5.72	0.0303	Significant
AB	143.22	1	143.22	7.27	0.0166	Significant
AC	1115.06	1	1115.06	56.62	< 0.0001	Highly significant
AD	10.94	1	10.94	0.5555	0.4676	Insignificant
BC	71.78	1	71.78	3.65	0.0756	Insignificant
BD	16.75	1	16.75	0.8505	0.3710	Insignificant
CD	126.28	1	126.28	6.41	0.0230	Significant
A ²	36.84	1	36.84	1.87	0.1915	Insignificant
B ²	23.96	1	23.96	1.22	0.2874	Insignificant
C ²	90.04	1	90.04	4.57	0.0494	Significant
D ²	34.13	1	34.13	1.73	0.2078	Insignificant
Residual	295.40	15	19.69			
Lack of Fit	295.40	10	29.54			
Pure Error	0.0000	5	0.0000			
Cor Total	9922.01	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 34.92 implies the model was significant. There was 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 were significant. In this case A, B, C, D, AB, AC, CD, C² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table B-10 ANOVA for the % Color Removal of US/EO quadratic model using NaCl

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1817.29	14	129.81	55.16	< 0.0001	Highly significant
A-pH	575.66	1	575.66	244.64	< 0.0001	Highly significant
B-Time	340.45	1	340.45	144.68	< 0.0001	Highly significant
C-Current	316.98	1	316.98	134.71	< 0.0001	Highly significant
D-NaCl	38.84	1	38.84	16.51	0.0010	Significant
AB	314.89	1	314.89	133.82	< 0.0001	Highly significant
AC	101.40	1	101.40	43.09	< 0.0001	Highly significant
AD	24.50	1	24.50	10.41	0.0056	Significant
BC	0.0056	1	0.0056	0.0024	0.9617	Insignificant
BD	11.66	1	11.66	4.96	0.0417	Significant
CD	2.28	1	2.28	0.9690	0.3405	Insignificant
A ²	0.0296	1	0.0296	0.0126	0.9122	Insignificant
B ²	4.26	1	4.26	1.81	0.1986	Insignificant
C ²	58.95	1	58.95	25.05	0.0002	Significant
D ²	25.25	1	25.25	10.73	0.0051	Significant
Residual	35.30	15	2.35			
Lack of Fit	35.30	10	3.53			
Pure Error	0.0000	5	0.0000			
Cor Total	1852.59	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 55.16 implies the model was significant. There was 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 were significant. In this case A, B, C, D, AB, AC, AD, BD, C², D² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table B-11 ANOVA for the % Turbidity Removal of US/EO quadratic model using NaCl

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	928.90	14	66.35	36.67	< 0.0001	Highly significant
A-pH	369.01	1	369.01	203.95	< 0.0001	Highly significant
B-Time	133.00	1	133.00	73.51	< 0.0001	Highly significant
C-Current	179.22	1	179.22	99.05	< 0.0001	Highly significant
D-NaCl	0.1523	1	0.1523	0.0842	0.7757	Insignificant
AB	95.06	1	95.06	52.54	< 0.0001	Highly significant
AC	116.64	1	116.64	64.47	< 0.0001	Highly significant
AD	0.2862	1	0.2862	0.1582	0.6964	Insignificant
BC	0.4692	1	0.4692	0.2593	0.6180	Insignificant
BD	10.30	1	10.30	5.69	0.0306	Significant
CD	0.5929	1	0.5929	0.3277	0.5755	Insignificant
A ²	0.4755	1	0.4755	0.2628	0.6157	Insignificant
B ²	0.0004	1	0.0004	0.0002	0.9882	Insignificant
C ²	12.57	1	12.57	6.95	0.0187	Significant
D ²	18.59	1	18.59	10.28	0.0059	Significant
Residual	27.14	15	1.81			
Lack of Fit	27.14	10	2.71			
Pure Error	0.0000	5	0.0000			
Cor Total	956.04	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 36.67 implies the model was significant. There was 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 were significant. In this case A, B, C, AB, AC, BD, C², D² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table B-12 ANOVA for the Power Consumption of US/EO quadratic model using NaCl

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0001	14	4.756E-06	10.21	< 0.0001	Highly significant
A-pH	5.097E-07	1	5.097E-07	1.09	0.3122	Insignificant
B-Time	7.602E-06	1	7.602E-06	16.32	0.0011	Significant
C-Current	0.0000	1	0.0000	57.91	< 0.0001	Highly significant
D-NaCl	2.424E-09	1	2.424E-09	0.0052	0.9435	Insignificant
AB	1.806E-07	1	1.806E-07	0.3876	0.5429	Insignificant
AC	1.156E-06	1	1.156E-06	2.48	0.1361	Insignificant
AD	4.556E-07	1	4.556E-07	0.9778	0.3384	Insignificant
BC	6.806E-07	1	6.806E-07	1.46	0.2455	Insignificant
BD	1.051E-06	1	1.051E-06	2.25	0.1540	Insignificant
CD	1.051E-06	1	1.051E-06	2.25	0.1540	Insignificant
A ²	1.461E-06	1	1.461E-06	3.14	0.0969	Significant
B ²	1.157E-06	1	1.157E-06	2.48	0.1359	Insignificant
C ²	5.669E-06	1	5.669E-06	12.17	0.0033	Significant
D ²	8.069E-06	1	8.069E-06	17.32	0.0008	Significant
Residual	6.989E-06	15	4.660E-07			
Lack of Fit	6.989E-06	10	6.989E-07			
Pure Error	0.0000	5	0.0000			
Cor Total	0.0001	29				

Factor coding was coded and Sum of squares was Type III – Partial. The Model F-value of 10.21 implies the model was significant. There was 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 were significant. In this case B, C, C², D² were significant model terms. Values greater than 0.1000 indicate the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Appendix C: Fit Statics

Table C-1 Model Summary for % COD removals of US/EO using NaCl

Std. Dev.	1.78	R ²	0.9916
Mean	60.84	Adjusted R ²	0.9837
C.V. %	2.93	Predicted R ²	0.9365
		Adeq Precision	43.3462

The Predicted R² of 0.9365 was in reasonable agreement with the Adjusted R² of 0.9837; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 43.346 indicates an adequate signal. This model can be used to navigate the design space.

Table C-2 Model Summary for % Color removals of US/EO using NaCl

Std. Dev.	1.30	R ²	0.9644
Mean	81.89	Adjusted R ²	0.9312
C.V. %	1.58	Predicted R ²	0.7830
		Adeq Precision	22.6092

The Predicted R² of 0.7830 was in reasonable agreement with the Adjusted R² of 0.9312; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 22.609 indicates an adequate signal. This model can be used to navigate the design space.

Table C-3 Model Summary for % Turbidity removals of US/EO using NaCl

Std. Dev.	1.11	R ²	0.9629
Mean	87.57	Adjusted R ²	0.9282
C.V. %	1.27	Predicted R ²	0.7390
		Adeq Precision	22.0307

The Predicted R² of 0.7390 was in reasonable agreement with the Adjusted R² of 0.9282; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 22.031 indicates an adequate signal. This model can be used to navigate the design space.

Table C-4 Model Summary for Power Consumption of US/EO using NaCl

Std. Dev.	0.0003	R ²	0.9768
Mean	0.0038	Adjusted R ²	0.9551
C.V. %	8.39	Predicted R ²	0.7816
		Adeq Precision	27.0309

The Predicted R² of 0.7816 was in reasonable agreement with the Adjusted R² of 0.9551; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 27.031 indicates an adequate signal. This model can be used to navigate the design space.

Table C-5 Model Summary for % COD removals of EO using CaCl₂

Std. Dev.	4.18	R ²	0.9830
Mean	49.88	Adjusted R ²	0.9671
C.V. %	8.39	Predicted R ²	0.8744
		Adeq Precision	25.7896

The Predicted R² of 0.8744 was in reasonable agreement with the Adjusted R² of 0.9671; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 25.790 indicates an adequate signal. This model can be used to navigate the design space.

Table C-6 Model Summary for % Color removals of EO using CaCl₂

Std. Dev.	3.96	R ²	0.9703
Mean	74.14	Adjusted R ²	0.9426
C.V. %	5.34	Predicted R ²	0.8105
		Adeq Precision	21.6707

The Predicted R² of 0.8105 was in reasonable agreement with the Adjusted R² of 0.9426; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 21.671 indicates an adequate signal. This model can be used to navigate the design space.

Table C-7 Model Summary for % Turbidity removals of EO using CaCl₂

Std. Dev.	3.97	R ²	0.9750
Mean	80.66	Adjusted R ²	0.9516
C.V. %	4.92	Predicted R ²	0.8464
		Adeq Precision	24.0049

The Predicted R² of 0.8464 was in reasonable agreement with the Adjusted R² of 0.9516; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 24.005 indicates an adequate signal. This model can be used to navigate the design space.

Table C-8 Model Summary for Power Consumption of EO using CaCl₂

Std. Dev.	0.0006	R ²	0.9750
Mean	0.0028	Adjusted R ²	0.9517
C.V. %	20.42	Predicted R ²	0.7908
		Adeq Precision	25.3746

The Predicted R² of 0.7908 was in reasonable agreement with the Adjusted R² of 0.9517; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 25.375 indicates an adequate signal. This model can be used to navigate the design space.

Table C-9 Model Summary for % COD removals of EO using NaCl

Std. Dev.	4.44	R ²	0.9702
Mean	37.99	Adjusted R ²	0.9424
C.V. %	11.68	Predicted R ²	0.7903
		Adeq Precision	22.7833

The Predicted R² of 0.7903 was in reasonable agreement with the Adjusted R² of 0.9424; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 22.783 indicates an adequate signal. This model can be used to navigate the design space.

Table C-10 Model Summary for % Color removals of EO using NaCl

Std. Dev.	1.53	R ²	0.9809
Mean	73.31	Adjusted R ²	0.9632
C.V. %	2.09	Predicted R ²	0.8414
		Adeq Precision	30.5080

The Predicted R² of 0.8414 was in reasonable agreement with the Adjusted R² of 0.9632; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 30.508 indicates an adequate signal. This model can be used to navigate the design space.

Table C-11 Model Summary for % Turbidity removals of EO using NaCl

Std. Dev.	1.35	R ²	0.9716
Mean	81.23	Adjusted R ²	0.9451
C.V. %	1.66	Predicted R ²	0.7602
		Adeq Precision	25.7950

The Predicted R² of 0.7602 was in reasonable agreement with the Adjusted R² of 0.9451; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 25.795 indicates an adequate signal. This model can be used to navigate the design space.

Table C-12 Model Summary for Power Consumption of EO using NaCl

Std. Dev.	0.0007	R ²	0.9050
Mean	0.0029	Adjusted R ²	0.8163
C.V. %	23.90	Predicted R ²	0.7191
		Adeq Precision	11.7244

The Predicted R² of 0.7191 was in reasonable agreement with the Adjusted R² of 0.8163; i.e. the difference was less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 was desirable. The ratio of 11.724 indicates an adequate signal. This model can be used to navigate the design space.

Appendix D: Evaluation of experimental results with design of experiments

Table D1: Experimental & predicted values for US/EO using NaCl proposed by the CCD

Run Order	COD % Removal		Color % Removal		Turbidity % Removal		Power Consumption (kWh/m ³)	
	Actual Value	Predicted Value	Actual Value	Predicted Value	Actual Value	Predicted Value	Actual Value	Predicted Value
1	61.71	63.67	83.63	81.82	91.95	91.06	0.0027	0.0028
2	58.85	59.27	86.68	85.94	89.95	89.07	0.0033	0.0030
3	68.97	68.73	80.09	80.78	87.81	87.77	0.0029	0.0029
4	68.97	68.73	80.09	80.78	87.81	87.77	0.0029	0.0029
5	68.97	68.73	80.09	80.78	87.81	87.77	0.0029	0.0029
6	59.80	59.80	76.12	76.47	83.07	82.77	0.0038	0.0038
7	87.06	87.82	96.02	96.71	98.30	98.30	0.0032	0.0032
8	54.89	55.30	83.09	81.73	88.75	88.03	0.0069	0.0069
9	53.30	51.42	79.24	78.97	87.15	86.49	0.0073	0.0070
10	68.97	68.73	80.09	80.78	87.81	87.77	0.0029	0.0029
11	59.55	61.84	82.29	80.85	89.19	88.04	0.0035	0.0034
12	43.47	45.83	75.55	76.09	81.55	81.95	0.0059	0.0057
13	68.97	68.73	80.09	80.78	87.81	87.77	0.0029	0.0029
14	36.14	37.99	77.89	79.00	83.74	84.82	0.0074	0.0074
15	69.92	70.03	88.67	88.16	91.70	91.13	0.0018	0.0013
16	68.97	68.73	80.09	80.78	87.81	87.77	0.0029	0.0029
17	82.24	83.60	92.99	94.01	96.86	98.25	0.0037	0.0040
18	33.83	33.15	77.62	76.90	81.15	81.03	0.0041	0.0043
19	53.42	53.08	76.03	76.74	83.67	84.43	0.0041	0.0046
20	64.22	62.45	88.69	87.56	91.36	90.15	0.0028	0.0030
21	47.96	49.92	80.29	80.54	84.37	84.90	0.0029	0.0034
22	69.89	70.28	82.82	81.36	85.61	85.97	0.0025	0.0024
23	68.05	66.48	81.58	82.28	90.82	91.77	0.0032	0.0030
24	41.65	40.19	76.94	76.01	85.11	83.84	0.0062	0.0057
25	34.53	34.32	77.19	77.79	82.25	82.94	0.0048	0.0051
26	43.06	42.54	80.03	81.48	82.75	83.59	0.0027	0.0025
27	77.47	77.08	83.40	81.90	88.31	87.08	0.0031	0.0030
28	73.04	71.14	82.71	83.05	89.28	90.49	0.0034	0.0034
29	65.73	63.27	87.55	87.10	89.73	89.45	0.0046	0.0047
30	71.56	72.34	79.15	79.54	83.51	84.81	0.0024	0.0024

Table D-2: Experimental and predicted values for EO using CaCl₂ proposed by the CCD

Run Order	COD % Removal		Color % Removal		Turbidity % Removal		Power Consumption (kWh/m ³)	
	Actual Value	Predicted Value	Actual Value	Predicted Value	Actual Value	Predicted Value	Actual Value	Predicted Value
1	66.72	65.42	86.44	84.73	93.71	92.31	0.0020	0.0021
2	62.24	66.01	90.34	88.83	94.11	97.48	0.0020	0.0020
3	66.72	65.42	86.44	84.73	93.71	92.31	0.0020	0.0021
4	64.27	69.24	88.71	93.37	83.77	90.97	0.0025	0.0024
5	49.17	45.16	77.69	74.77	83.84	80.66	0.0007	0.0012
6	15.76	16.47	49.19	50.91	56.99	58.49	0.0009	0.0007
7	18.84	23.91	53.66	56.71	52.94	54.67	0.0067	0.0061
8	66.72	65.42	86.44	84.73	93.71	92.31	0.0020	0.0021
9	20.84	22.32	52.14	54.81	62.47	65.54	0.0047	0.0053
10	65.03	62.14	89.32	87.39	88.36	83.39	0.0013	0.0013
11	35.65	31.35	73.02	69.42	75.99	73.32	0.0104	0.0100
12	28.54	26.42	68.45	66.38	85.31	81.80	0.0094	0.0096
13	66.72	65.42	86.44	84.73	93.71	92.31	0.0020	0.0021
14	18.72	21.90	56.48	58.69	67.61	69.67	0.0005	0.0003
15	15.46	19.52	44.43	46.64	50.12	52.54	0.0009	0.0013
16	68.36	66.67	84.14	88.38	96.67	95.53	0.0021	0.0020
17	72.39	70.22	88.11	85.59	94.23	97.91	0.0031	0.0037
18	11.44	10.01	45.24	42.71	43.09	40.73	0.0005	-0.0002
19	48.87	46.20	74.01	71.03	85.49	83.73	0.0011	0.0005
20	65.97	64.06	84.34	82.31	87.45	87.26	0.0018	0.0020
21	21.09	24.20	60.27	63.57	65.01	68.99	0.0002	0.0006
22	66.72	65.42	86.44	84.73	93.71	92.31	0.0020	0.0021
23	68.59	67.49	82.27	80.62	95.59	94.31	0.0021	0.0021
24	83.51	86.00	95.36	98.02	98.91	99.82	0.0050	0.0056
25	79.46	83.08	91.46	94.45	96.31	99.28	0.0071	0.0065
26	66.72	65.42	86.44	84.73	93.71	92.31	0.0020	0.0021
27	67.47	64.48	81.95	79.88	92.97	89.10	0.0030	0.0026
28	47.09	50.28	63.87	68.25	77.11	80.62	0.0031	0.0030
29	52.93	57.19	70.56	75.81	89.13	87.69	0.0018	0.0010
30	14.53	9.72	40.61	37.31	34.05	32.39	0.0002	0.0008

Table D-3: Experimental and predicted values for EO process using NaCl proposed by CCD

Run Order	COD % Removal		Color % Removal		Turbidity % Removal		Power Consumption (kWh/m ³)	
	Actual Value	Predicted Value	Actual Value	Predicted Value	Actual Value	Predicted Value	Actual Value	Predicted Value
1	13.04	16.29	62.83	64.30	75.91	77.21	0.0029	0.0026
2	44.44	43.88	74.41	74.34	81.55	81.10	0.0043	0.0037
3	66.17	62.61	78.18	77.81	86.34	85.78	0.0030	0.0030
4	47.37	41.67	80.04	79.50	86.69	85.56	0.0009	0.0011
5	19.80	18.58	62.58	61.36	77.86	76.74	0.0002	0.0004
6	36.09	38.99	77.35	78.18	82.56	83.70	0.0021	0.0019
7	69.45	71.44	92.01	94.45	95.52	96.75	0.0037	0.0036
8	44.44	43.88	74.41	74.34	81.55	81.10	0.0043	0.0037
9	13.55	20.27	62.61	63.29	73.41	73.74	0.0007	0.0008
10	43.61	41.61	77.36	76.65	84.21	83.79	0.0007	0.0019
11	8.48	4.04	69.37	67.86	75.89	74.83	0.0002	0.0001
12	47.37	49.16	78.71	77.87	82.46	82.53	0.0047	0.0047
13	43.84	42.01	73.01	71.82	80.45	80.58	0.0048	0.0058
14	31.39	34.12	66.13	67.44	76.69	77.28	0.0044	0.0045
15	12.03	12.98	71.52	72.31	75.08	76.06	0.0033	0.0033
16	47.37	48.81	83.09	81.37	85.99	84.80	0.0016	0.0017
17	44.44	43.88	74.41	74.34	81.55	81.10	0.0043	0.0037
18	62.40	62.61	76.55	74.75	89.23	87.46	0.0015	0.0016
19	17.48	13.16	67.87	66.26	77.29	76.75	0.0051	0.0051
20	44.44	43.88	74.41	74.34	81.55	81.10	0.0043	0.0037
21	63.39	56.91	78.11	77.18	81.83	83.04	0.0024	0.0028
22	30.91	38.28	70.23	71.28	78.81	78.31	0.0024	0.0030
23	11.28	13.47	65.46	66.32	75.33	76.89	0.0007	0.0007
24	45.49	44.60	72.37	73.33	79.05	79.69	0.0029	0.0040
25	32.86	31.51	60.23	61.74	74.52	76.19	0.0008	0.0005
26	44.44	43.88	74.41	74.34	81.55	81.10	0.0043	0.0037
27	44.44	43.88	74.41	74.34	81.55	81.10	0.0043	0.0037
28	22.81	23.92	61.94	63.24	74.87	75.60	0.0022	0.0021
29	15.04	13.94	71.43	70.85	80.32	78.81	0.0046	0.0048
30	71.92	75.53	93.81	94.09	97.37	98.28	0.0041	0.0040

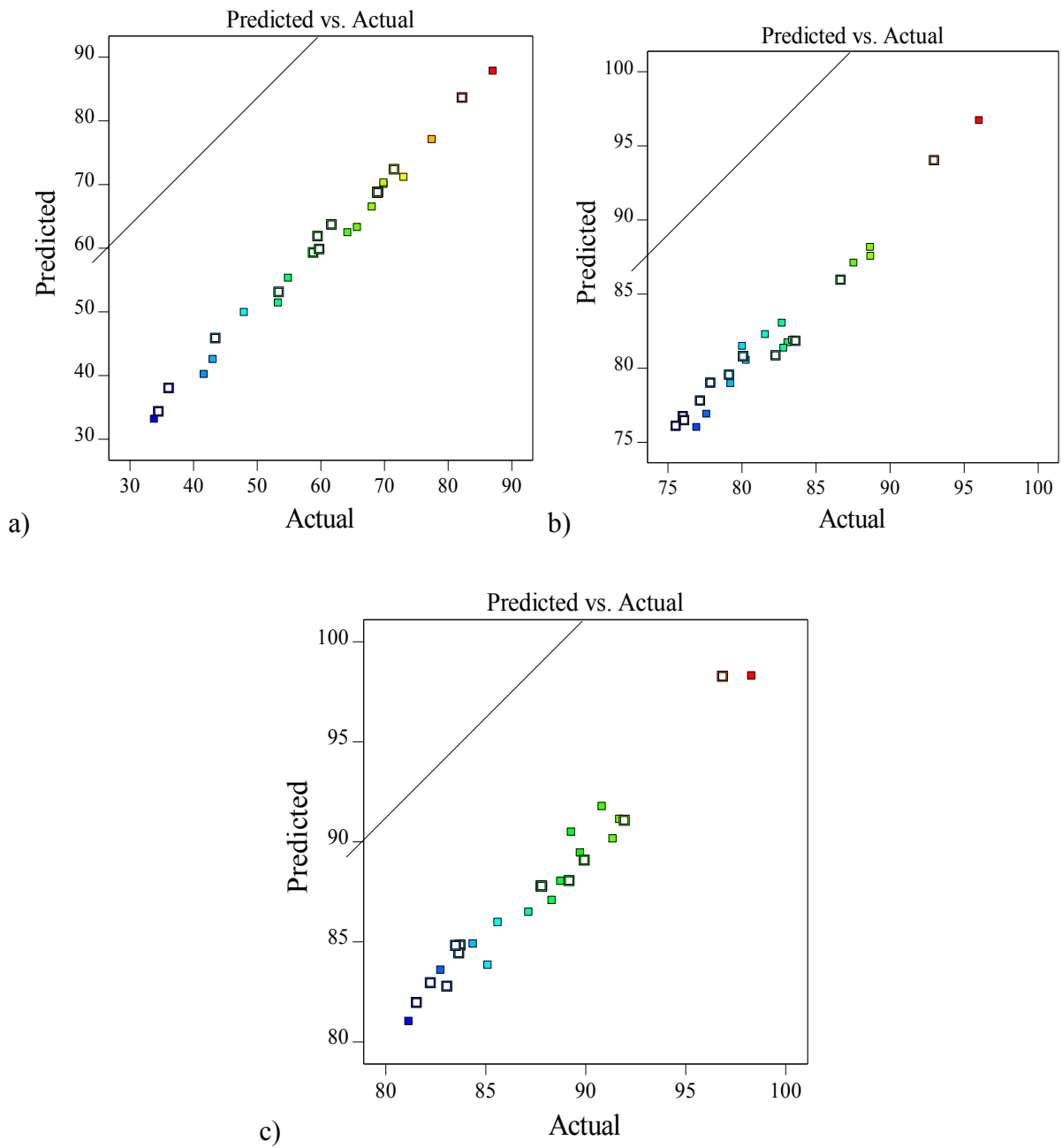


Figure D-1 Comparison of the predictive and the experimental result for US/EO using NaCl optimum values of a) COD b) Color and c) Turbidity % removal.

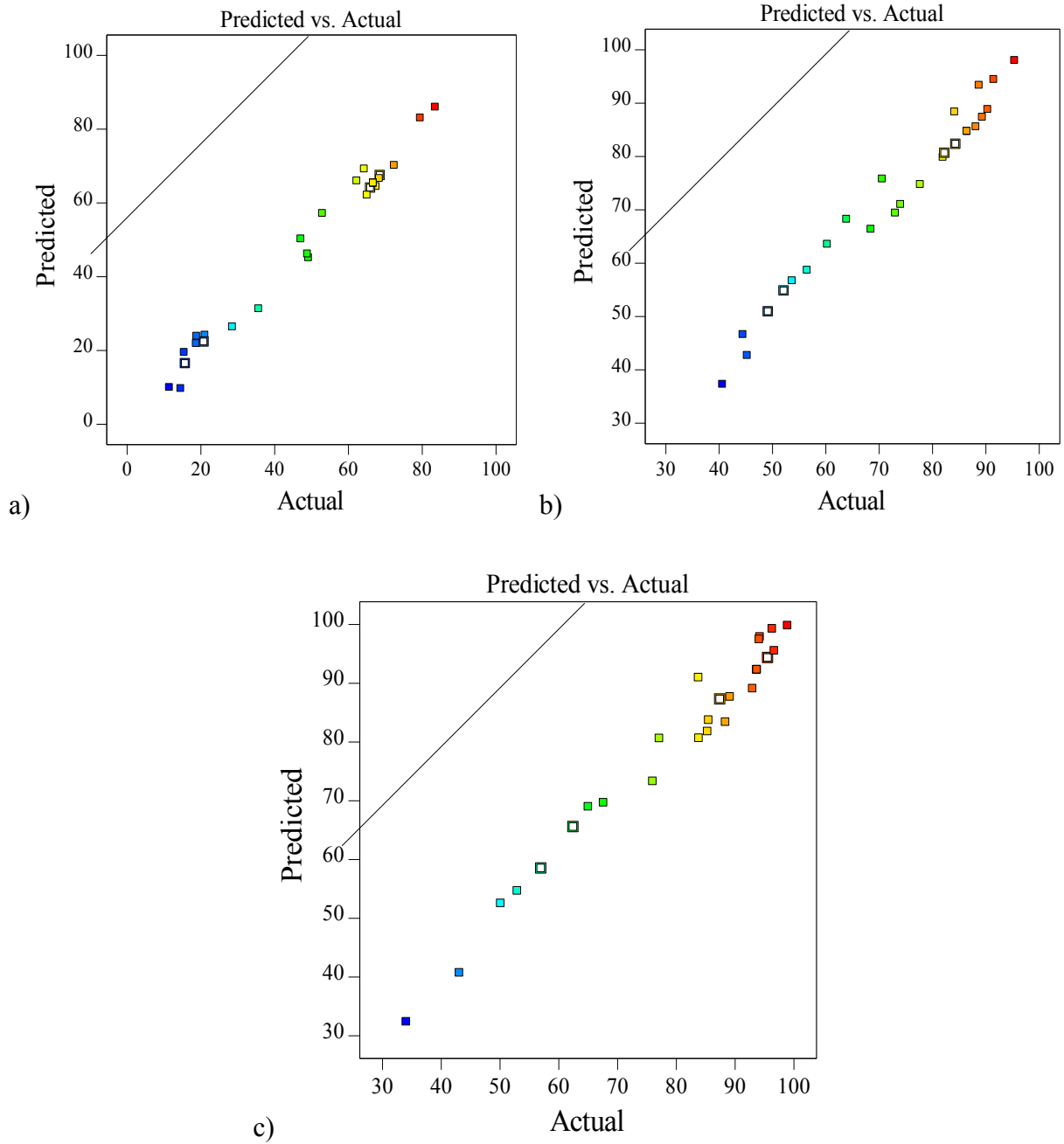


Figure D-2 Comparison of the predictive and the experimental result for EO using CaCl₂ optimum values of a) COD b) Color and c) Turbidity % removal.

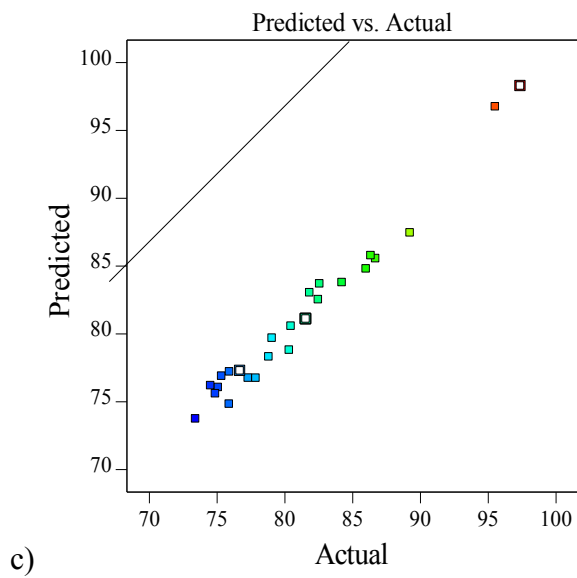
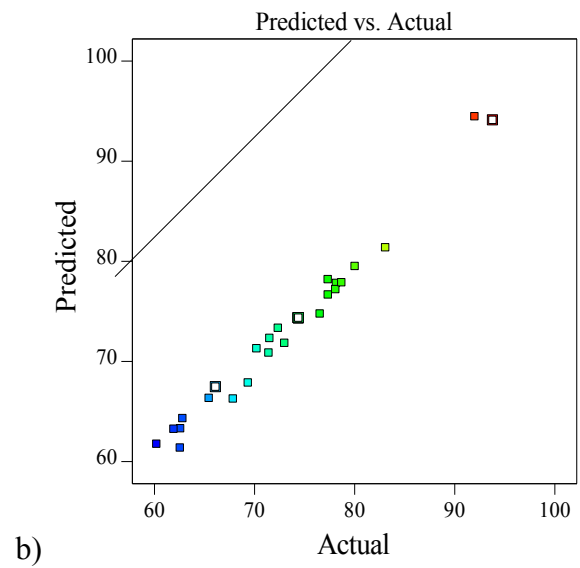
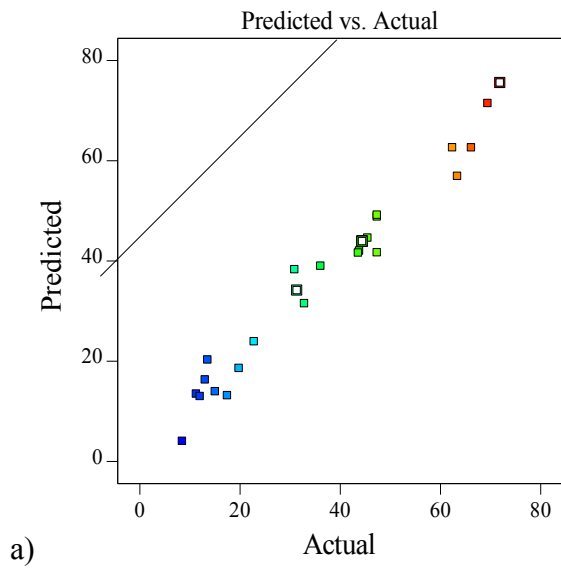


Figure D-3 Comparison of the predictive and the experimental result for US using NaCl optimum values of a) COD b) Color and c) Turbidity % removal

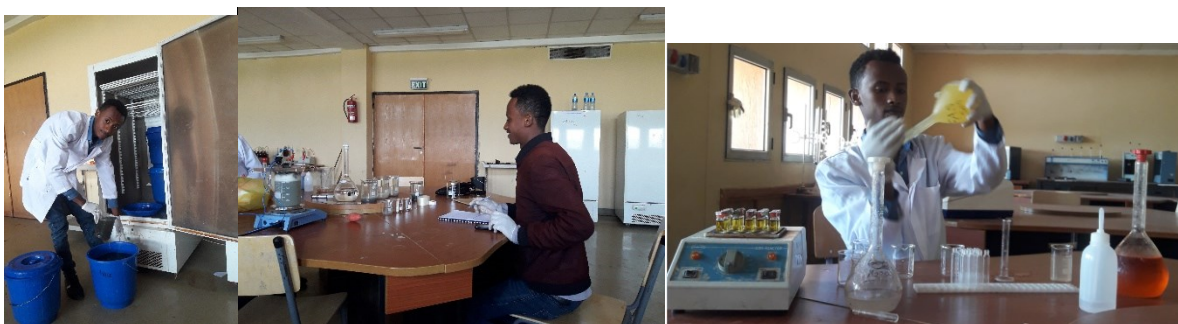


Figure D-4 Laboratory Session of the Researcher