JIMMA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

JIMMA INSTITUTES OF TECHNOLOGY

FACULTY OF CIVIL AND ENVIRONMENTAL ENGINEERING

ENVIRONMENTAL ENGINEERING CHAIR

Investigation of coffee processing wastewater treatment by using photo- electro chemical oxidation process

A thesis submitted to the School of Graduate Studies of Jimma University in partial fulfillment of the requirements for the degree of masters of science in environmental engineering.

By:

Firomsa Bidira Abdi

July, 2021

Jimma, Ethiopia

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DECLARATION

This final thesis is my original work and has not been presented for a degree or masters in any of the Ethiopian Universities.

I have recognized all material in this thesis, which are not my own work, through appropriate referencing and acknowledgement.

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Firomsa Bidira Abdi .... 12 /07/2021

Candidate Signature Date

This Final Thesis will be submitted for examination with my approval as a University Supervisor.

Dr. Zerihun Asmelash (PhD) .... 12 /07/2021

Main advisor Signature Date

Mr. Seifu Kebede (MSc.) …………… 12/07/2021.

Co-advisor Signature Date

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ABSTRACT

Water is a limited natural resource that is essential for human life as well as environmental sustainability. It is both a qualitative and quantitative component of every ecosystem. Water quality, whether utilized for home, irrigation, or recreational reasons, is crucial for health in both developing and developed countries around the world. For the treatment of coffee processing wastewater, photo- electrochemical oxidation process is used, which involves the generation and use of powerful oxidizing species, primarily the hydroxyl radical (OH), for contaminant destruction. This technology, when combined with ultraviolet light and with hydrogen peroxide (UV/H_2O_2*), improves the performance of the coffee processing wastewater treatment process. The effect of UV/*H_2O_2 *on an electrochemical process was studied, as well as the effects of various parameters such as PH, time, current,* H_2O_2*, and electrolytes. The trial runs and findings were planned using the response surface methodology (RSM) based on Central Composite Design (CCD). Additionally, the findings were computed and analyzed using Microsoft Excel. The hybrid Photoelectrochemical oxidation (PECO) with Ultraviolet and Hydrogen peroxide (UV/*H_2O_2*) method removed more COD (99.991 %), color (99.898%), nitrate (99.823%), and phosphate (99.982%). These results were obtained at an ideal pH of 7, a current of 0.40 Ampere, 3ml of* H_2O_2 *,1.5g calcium chloride, after 40 minutes of electrolysis and calcium chloride (*$CaCl_2$*) was the best ectrolyte. In eliminating organic compounds from coffee processing wastewater,* $CaCl_2$ *was more effective than (Sodium Chloride) NaCl. Analysis of variance (ANOVA) with 95 percent confidence limits was used to determine the significance of independent variables and their interactions. As a result, the combination of electrochemical oxidation (ECO), ultraviolet light, and hydrogen peroxide (UV/*H_2O_2*) has been shown to be effective treatment techniques for pollutant removal, and it was discovered that combining ultraviolet light with the powerful oxidizing agent hydrogen peroxide could improve pollution attenuation.*

Key words*: Electrochemical Oxidation; Hydrogen Peroxide; Hydroxyl Ions; Ultraviolet Light; Response Surface Methodology.*

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ACRONYMS AND ABBRIVATIONS

ACS	Active Chlorine Species
AOPs	Advanced Oxidation Processes
APHA	American Public Health Association
BBD	Box–Behnken Design
BOD	Biological Oxygen Demand
CCD	Central Composite Design
COD	Chemical Oxygen Demand
CSA	Central Statistical Authority
DC	Direct Current
DO	Dissolved Oxygen
DOE	Design of Experiments
E-AOP	Electrochemical advanced oxidation processes
EC	Electrical Conductivity
ECO	Electrochemical Oxidation
EPA	Environmental Protection Authority
ETB	Ethiopian Birr
FCCD	Face Central Composite Desig
HAOPs	Hybrid Advanced Oxidation Processes
IWWT	Industrial Waste Water Treatment
MMO	Mixed Metal Oxide
OEP	Oxygen Evolution Potential
PECO	Photo Electrochemical Oxidation

RSM	Response Surface Methodology
TDS	Total Dissolved Substance
US	Ultra Sound/ Ultra Sonication
UV	Ultra Violet

CHAPTER ONE

1 INTRODUCTION

Water is a vital resource that can be found in many places, including surface water, ground water, oceans, lakes, springs, and other bodies of water. It was utilized in irrigated agriculture, drinking water, industries, manufacturing, and construction. The main sources of wastewater are industrial wastewater, commercial wastewater, and domestic wastewater, processing wastewater. Coffee production, for example, produces a significant amount of wastewater.

The effluents from various wastewater sources may be had a lot of sludge, a large level of organic or inorganic load, and were acidic due to the fermentation process. Industrial effluents containing significant quantities of hazardous heavy metals are of great concern due to their persistence and non-degradability, but sewage is a more generic word that refers to any polluted water (including wastewater) that may contain organic and inorganic chemicals (Iloms *et al*., 2020). Coffee processing produces two byproducts: coffee pulp and wastewater (also known as honey water or effluent). This wastewater is acidic, killing the microorganisms and plants. Coffee wastewater is discharged directly into local water bodies, producing serious health problems such as overexcitation, skin irritation, stomach pain, nausea, and breathing difficulties, as well as eutrophication of water bodies (Duguma and Chewaka, 2019).

Because of the wide range of compounds and high quantities that industrial wastewater (IWW) effluents contain; treatment their effluents were a difficult task. AOPs are typically tiny in size and can be easily combined with other therapeutic methods. They might be employed to get rid of non-biodegradable contaminants that linger after biological treatment (Cardenas *et al.*, 2020a). The photo electrochemical oxidation method is best recognized as an industrial technique that is widely employed in waste water treatment procedures. Regardless, this electrochemical process has proven to be an effective solution for removing organic contaminants from aquatic environments, whether they are residential or industrial in origin (Marchante *et al.*, 2020) . The maximum organic matter removal was achieved by combining ECO/UV light, and the H_2O_2 oxidant. The coupling of the ECO process with the UV/H_2O_2 process produced some synergetic effects than using in single (Alfonso-Muniozguren *et al.*, 2020a).

1.1 Back ground

Water covers more than three-quarters of the Earth's surface. Although the oceans and seas have 97.2 % of the world's water, potable water makes up only about 2.8% of the total. Water is a vital natural resource for life, not only in terms of human drinking water, but also in terms of agricultural and industrial development (Moradi *et al.*, 2020). In future scenarios, two significant aspects concern drinking water supply. The first is population growth, and the second is linked to the unavoidable consequences of climate change: temperature rises, shorter rains, seasonal shifts, and so on (Spellman and Frank, 2003). Water contamination is still one of our civilization's most serious issues. Acid rain waste, agricultural pesticides, industrial operations, commercial and home waste, and other pollutants all flow into rivers. This is a major issue in both developed and developing countries, due to the number and variety of toxins produced and insufficient technologies in both.

Wastewater treatment is becoming an increasingly important aspect of industrial manufacturing activities. Contamination affects a wide spectrum of components. The environment and human life could be harmed if this wastewater is not properly treated before being discharged into water bodies. Electrochemical oxidation for wastewater treatment has been studied since the nineteenth century. The oxidation efficiency and electrochemical stability of electrode materials, factors affecting process performance, and the examination of the processes and kinetics of pollutant degradation have all been the focus of research during the last three decades (Patel *et al*, 2013a). Electrochemical oxidation has been identified as one of the most successful strategies for contaminant degradation in textile wastewater, landfill leachate, simulated wastewater, olive mill wastewater, paper mill wastewater, and industrial paint wastewater (Bashir *et al.*, 2014). The OH radical can change the chemical structure of stubborn organic molecules, transforming them into simpler compounds with a reduced molecular mass and lesser toxicity to microbes. Hydrogen peroxide (H_2O_2) has been used to remove organic matter from industrial wastewater and to provide water for many years (Botelho *et al*, 2012).

1.2 Statement of the problem

Wet processing of coffee fruit produces large amounts of with high-strength effluent, which necessitates careful treatment before disposal. Due to a lack of monitoring infrastructure, waste generated by coffee processing enterprises is frequently dumped straight into rivers, resulting in massive amounts of liquid waste being wasted in water bodies. As a result, water contamination occurred, posing a threat to the entire natural system as well as human life. These liquids contain a variety of pollutant substances that pollute the environment and are distinguished by a high sludge content, a high organic load, an acidic nature, a high COD, phosphorus, nitrates, turbidity, and a highly colored.

Some existing waste water treatment methods for coffee processing industries include oxidation pond, sedimentation and screening, with finally disposing to water bodies or discharging on open area. But these methods were very old and have no efficiency to remove pollutants exist in coffee processing waste water. When disposed of in natural water, this wastewater contaminates aquatic life and the ecosystem. To discharge wastewater into bodies of water, adequate and latest technology for treatment is required. Otherwise, it may have a negative impact on the environment and human life (Bhagawan *et al.*, 2018b). Eutrophication, aquatic life mortality, human health difficulties, and other important issues have arisen as a result of coffee liquid wastes generated without treatment.

1.2.1 The knowledge gap between photo-electrochemical oxidation with another treatment methods

The addition of H_2O_2 to ECO enhanced the contaminants' removal effectiveness marginally (Muniozguren *et al.*, 2020a). Many advanced oxidation processes were previously carried out using electrochemical oxidation, but now it is possible to improve removal efficiency from coffee processing wastewater and other wastewater by combining ECO (Electrochemical Oxidation with Ultraviolet and hydrogen peroxide (UV/H_2O_2). Photoelectrochemical treatment was simple to implement and could be completed at a low cost and in a short period of time; additionally, photo electrochemical AOPs are generally simple, clean, and more efficient than traditional chemical AOPs (Oturan and Aaron, 2014a). Previously conducted studies relied solely on electrochemical or UV/H_2O_2 wastewater treatment. Organics that have been treated with H_2O_2 have less toxicity and are more biodegradable (Bischel *et al.*, 2013).This study combined both technologies and enhanced the removal efficiency of pollutants from coffee processing industry, based on existing expertise. Because this technique can be employed in a variety of ways as selective separation technology and/or degrading processes, allowing chemical free wastewater treatment, the combined technology ECO/UV/ H_2O_2 will be able to make a significant contribution to this challenge. Furthermore, there has been a significant growth in new advances in electrochemical processes recently (Muddemann *et al.*, 2019a).

Second, many studies have been done on liquid wastes from cafeterias, industries, and hospitals; however, this study focuses on coffee processing wastewater, which contains nutrients and COD as the key dependent variables by considering locally available materials and easily controlled independent variables.

1.3 Objectives of the study

1.3.1 General Objective

The main objective of this study is to investigate coffee processing wastewater treatment by using photo-electrochemical oxidation process.

1.3.2 Specific objectives

- To investigate the efficiency of photo-electrochemical Oxidation process for the removal of turbidity, COD, color and nutrients (phosphates and nitrates) from coffee processing wastewater
- To characterize the effect of experimental parameters such as reaction time, electrolyte, PH, current and UV/H_2O_2 on removal efficiency.
- To optimize the parameters of the processes statistically by adopting response surface methodology (RSM).
- To select and validate the best parameter on removal efficiency of coffee processing wastewater.

1.3.3 Research questions

- What is the efficiency of photo-electrochemical oxidation for removal of pollutants in coffee processing liquid wastes?
- What is the effect of operating parameters on the efficiency of the photo-electrochemical oxidation process?

- How can response surface methodology (RSM) statistically analyze and optimize from input laboratory results?
- What is the optimum value of the operating parameters?

1.4 Significance of the Study

The study's main purpose was to promote a healthy environment for the community by developing new technology which had more efficiency to remove pollutant and preventing water bodies from being affected by improper liquid discharge from coffee processing firms because of the pollution and significant number of debris it includes.

However, when wastewater was treated with proper equipment that was simple to install and maintain, these issues were eliminated. In other words, the research bridges the gap between photo-electrochemical processes and pollutant removal from wastewater, allowing it to make a significant contribution to resolving the problem by supporting a healthy environment and human health.

1.5 Scope of the Study

For the analysis, a sample was acquired from the Jimma Zone, Yabbu town Coffee processing factory. The results of experimental parameters such as reaction duration, electrolyte concentration, solution pH, and electrical current were studied, response surface methodology (RSM) analyses the laboratory result and optimum value was selected.

In order to complete the analysis, which was limited by the material and equipment available, as well as time and budget. In general, the goal is to demonstrate how the ECO process be improved when paired with UV/H_2O_2 as effective treatment strategies for removing color, COD, turbidity, nitrate, and phosphate from wastewater.

1.6 Limitation of the study

The variance of electric power makes the result of the experiment to be vary due to the fluctuating temperature of the sample stored in the refrigerator and reagents prepared for the study. And also, it has interrupted the experimental session and made the session over the planned time. Secondly some materials available in laboratory were not very latest and some measurement difference could be occurred.

CHAPTER TWO

2 LITERATURE REVIEW

2.1 Water sources

Water is the center of sustainable growth, but a resource that is scarce. World population growth and climate change have given rise to an unprecedented decrease in the supply and availability of freshwater resources, posing a major global challenge. The frequency and severity of droughts have risen significantly over the past 35 years due to the effects of global warming (Cardenas *et al.*, 2020b). One of the most pressing issues of the twenty-first century is the provision of safe drinking water to millions of people around the world. The treatment of agro-industrial wastewater is receiving a lot of attention these days because of its increased contamination potential as a result of rapid industrialization and various human activities. Uncontrolled waste water disposal into the atmosphere can harm humans, animals, and plants (Amor *et al.*, 2019a)

2.2 Physicochemical characteristics of Wastewater

2.2.1 Turbidity

Turbidity is a significant visual property of potable water that can also be used to determine the quality of drinking water.A turbidity meter was used to measure turbidity (Hossain,2011). Water turbidity is caused by the presence of suspended particles of various dimensions, ranging from very small colloidal particles to vast flocks, which distribute and absorb electromagnetic radiation in the IR and VIS bands. Surface water particles can be mineral or organic, however organic suspended matter is most commonly seen in effluent treatment plants (Mucha, 2016).

2.2.2 Total solids (TS)

Solids is a phrase that is often used to describe any substance suspended or dissolved in water or waste water that can be physically separated by filtration or evaporation. Filterable and nonfilterable solids can be classified. Filterable solids can be settled or unsettled. Organic and inorganic solids can be classified. After a sample has been evaporated and dried at a specific temperature in an oven, the term "complete solids" is used to describe the residue of the substance left in the vessel (Baxter, 2017).

2.2.3 Total dissolved solids (TDS)

Materials that are totally dissolved in water are referred to as total dissolved solids. These solids are naturally filterable. It is defined as the residue left over after a filterable sample has evaporated. Total suspended solids refer to items that are not dissolved in water and are therefore non-filterable (Anjum *et al*,2016).

2.2.4 Electrical Conductivity (EC)

The salinity of natural and wastewaters is frequently determined using electrical conductivity measurements. EC samples of raw and processed waste water were measured using a salinometer. When a non-filterable sample evaporates on a filter paper, it is referred to as residue (Aniyikaiye *et al.*, 2019). Temperature affects electrical conductivity. The mobility of ions increases as the temperature of liquids rises, resulting in an increase in conductivity (Prieto *et al.*, 2001).

2.2.5 Dissolved oxygen (DO)

Dissolved oxygen is one of the most important measures of the biological health of rivers with considerable changes across a wide range of geographical and temporal scales. It is primarily dependent on water temperature; however, this dependence is influenced by changing hydrometeorological conditions and the rate at which biological processes such as photosynthesis, respiration, and organic matter breakdown occur (Rajwa et al, 2015).

2.2.6 Chemical oxygen demand (COD)

The chemical oxygen demand is a frequently used method for indirectly determining organic molecules in water. The oxygen equivalent of a sample's organic composition that is vulnerable to oxidation by a powerful chemical oxidant is measured by chemical oxygen demand. It's a method of determining how much organic stuff has contaminated water. It measures the amount of oxygen absorbed per liter of fluid in milligrams per liter (mg/L). The amount of oxygen absorbed in water by pollutant. chemical oxidation is calculated using the COD formula. COD describes how much oxygen is required to oxidize organic matter in a sample of water or waste water under specific conditions (Aniyikaiye et al., 2019).

2.2.7 Phosphorus (P)

Phosphorus is a non-metal that belongs to the 15th group of the periodic table, sometimes known as the "nitrogen family," and is one of the most important components for daily existence, influencing every organism on the planet. Phosphorus is a necessary nutrient for all living things on Earth, but it is also a potential environmental problem that can promote eutrophication of water bodies. Wastewater treatment plants all throughout the world fail to remove phosphorus from effluents at a significant expense (Campiglio *et al*., 2018). Large volumes of phosphorus and nitrogen are released into wastewater as a result of mandatory anaerobic treatment of home and agro-industrial waste. Eutrophication (abundant algae development as a result of excess nutrients in water bodies) of rivers, lakes, and other bodies of water is caused by these nutrients (Luz and Bashan, 2004).

2.2.8 Phosphates ($PO_4{}^{3-}$)

Coffee processing wastewater plants discharge high levels of nutrients such as phosphates into the environment, and this is the principal source of eutrophication in seas, lakes, and rivers. Algal and plankton development expands (algal bloom) when nutrient pollution has affected the quality of the water, limiting oxygen for the ecosystem's other aquatic species. To reduce phosphate discharge into the environment, a group of microorganisms that can absorb and metabolize phosphate intracellularly are added to wastewater (Kingdom *et al,* 2012).

2.2.9 Nitrogen (N)

Eutrophication is a main issue of aquatic ecosystem management in rivers, lakes, and estuaries around the world that is caused by surface water nutrient loading of N and P and contributes to higher primary production in rivers and lakes. Ecosystem services such as drinking water availability,fisheries,aquaculture, and tourism can all be negatively impacted by eutrophication (Puijenbroek *et al*,2019).

2.2.10 Nitrate (NO_3^-)

Nitrate is an important component of the nitrogen cycle because it connects the nitrification and denitrification processes. The amount of nitrate seeping from fields into rivers and ground waters is increasing as nitrate fertilizers are increasingly employed in agriculture. Because nitrate is not hazardous to humans, it is a legal food ingredient for curing meat. However, after nitrate has entered the body, bacteria in the stomach can convert it to nitrite, which can then be integrated into carcinogenic N-nitrosamine molecules. Nitrate is a significant analyte for environmental, food, and human but if discharged to water bodies together with wase water, it can leads ecological and human health problems (Kingdom *et al* , 2012).

2.3 Coffee processing waste water characteristics

Coffee is the most popular drink in the world, with millions of people drinking it every day. To remove the cherries out of the coffee, a lot of water is needed throughout the processing (R and Devanna, 2017). The removal of coffee cherry pulp and mucilage is part of wet coffee processing. This method generates a large volume of acidic waste water that is particularly harmful to the environment due to its high level of recalcitrant organic materials. As a result, prior to discharge into aquatic bodies, treatment is required (sanchez *et al*, 2019).

Due to the fact that washed coffee requires significant amounts of water during processing to receive the cherries and hydraulically transport them through the pulping machines, the main and popular coffee producing region in Ethiopia, the Jimma area, has a variety of small-scale coffee pulping industries located along the banks of rivers and/or streams with varying degrees of hydraulic gradients (Tekle *et al.*, 2015).

2.3.1 Major contents (impurities) in coffee processing waste water

Coffee processing companies produce high pollutant load wastewater because they are one of the largest water users and produce a large volume of waste water with high concentrations of organic matter, nutrients, suspended particles, and extremely acidic wastewater,BOD_5, COD, N, P, TDS, and TSS are all important components in coffee wastewater, as are pH, temperature, turbidity, and electrical conductivity (Tekle *et al.*, 2015). The organic loadings and acidity of coffee waste waters are both considerable. Untreated effluents from the processing of washed or semi-washed coffee in high quantities much exceed the natural streams' ability to purify themselves (Calvert *et al*).

Table 2-1 Characteristic of Raw Coffee processing Wastewater (Asha and Kumar, 2015)

	Concentration	
Parameter	Arabica	Robusta
pH	3.92-4.99	4.56-5.04
Turbidity	50-60	80-90
COD, mg/L	8320 -12840	15360 - 26240
BOD_5, mg/L	940-1500	3000 – 4200
Total Solids, mg/L	5000	4758
Total Dissolved Solids, mg/L	4500	4208
Ammonia -Nitrogen, mg/L	50-84	120 to 180
Nitrate -Nitrogen, mg/L	32-52	135 to 163
Phosphorous, mg/L	60-94	688 to 800

2.4 Waste water treatment methods

Depending on the shape and quality of agro-industrial waste, treatment systems may employ traditional technologies such as physical, biological, and chemical methods. Sophisticated technologies, such as membrane separation procedures, reverse osmosis, ultrafiltration, and advanced oxidation processes, can be employed in addition to traditional approaches (Amor et al., 2019a). Rapid urbanization and uncontrolled industrialization have resulted in a high rate of waste generation, hastening the intensification of human activities fueled by the expanding human population. Global water bodies are the primary source of effluent disposal. These effluents change the water receiving body's physical, chemical, and biological characteristics. As technological advancements occur, many compounds are generated by industrial processes that are difficult and expensive to treat using traditional wastewater treatment methods. The amount of heavy metals and synthetic organic compounds produced by industrial operations has increased, and new organic compounds are added on a regular basis (Patel *et al.*, 2013b).

2.4.1 Advanced oxidation process (AOP) wastewater treatment methods

Advanced oxidation processes (AOPs) are effective, promising, and environmentally friendly ways for removing persistent organic pollutants (POPs) from water and wastewater. In general, AOPs are based on the in situ creation of a powerful oxidizing agent, such as hydroxyl radicals

(•OH), at a sufficient concentration to successfully cleanse water (Oturan and Aaron, 2014b). AOPs that require the generation of highly reactive radicals such as hydroxyl radical (HO•) in sufficient quantities to affect water purification for the removal of a wide range of recalcitrant and toxic compounds have been productively explored for the removal of a wide range of recalcitrant and toxic compounds in order to reduce toxicity and increase biodegradability have been productively explored for the removal of a wide range of recalcitrant and toxic compounds in order to reduce toxicity (Amor *et al.*, 2019b)

The mineralization of organic compounds in process fluids and wastewaters is the goal of electrochemical oxidation processes, and electrochemical advanced oxidation processes (E-AOP) have been a focus of research and application. The formation of highly strong oxidizing agents, such as hydroxyl radicals, is a characteristic of these reactions, which are preferably carried out at the anode. In situ electrochemical oxidants are produced either directly at the anode surface or indirectly through subsequent interactions with inorganic components (Muddemann *et al.*, 2019b).

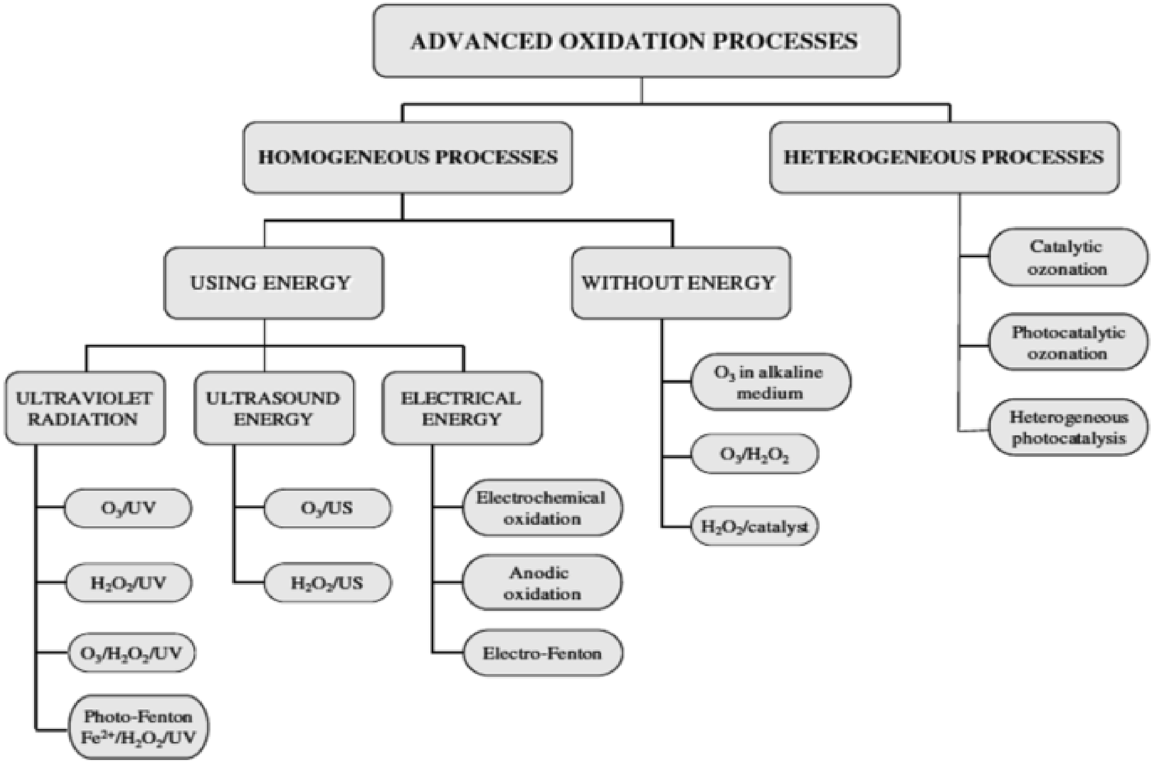


Figure 2-1 Classifications of advanced oxidation process (Amor et al., 2019b)

2.4.2 Photo-electrochemical waste water treatment

Photo-chemical methods have the advantages of being simple, clean, relatively inexpensive, and generally more effective than other chemical AOPs. They are also capable of disinfecting water and destroying contaminants. UV radiation has therefore been coupled with powerful oxidants such as O_3 and H_2O_2, including, in some instances, Fe^{3+} or TiO_2 catalysis, resulting in various types a significant amount of photo-chemical treatment. Three different reactions are capable of degrading and/or destroying pollutants: photo-decomposition based on UV irradiation, excitation and degradation of pollutant molecules, oxidation by direct action of O_3 and H_2O_2, and oxidation by photocatalysis (with Fe^{3+} or TiO_2), inducing the formation of •OH radicals (Oturan and Aaron, 2014b). any AOP's purpose is to create and utilize hydroxyl free radical (OH) as a powerful oxidant to destroy compounds that cannot be destroyed by ordinary oxidizing agents. Hydroxyl radicals are extremely reactive entities that attack the majority of organic molecules with ease and have a low selectivity of attack, which is a good property for an oxidant employed in wastewater treatment (Hassaan *et al*, 2017).

2.4.3 Combination of ultraviolet with hydrogen peroxide (H_2O_2/UV)

The activation of hydrogen peroxide is critical in EAOPs because this species is formed on the electrochemical cell's cathode, and if appropriately activated, it can double the efficiency of oxidation processes (raw hydrogen peroxide is not very active). The encouragement of the production of highly active species by UV light irradiation is known as light irradiation activation. This irradiation can be applied either naturally (from the sun) or artificially (from a generator) (using UV lamps) (Sirés *et al.*, 2014).

UV light is frequently employed in conjunction with O_3, H_2O_2, Fenton's (H_2O_2/Fe^{2+}) reagent, and a TiO_2 catalyst to speed up radical production and so cause indirect photolysis. UV energy activates H_2O_2, resulting in the creation of the •OH in the UV/H_2O_2 combination process.

The UV/H2O2 system takes advantage of the combined action of two chemical processes:

a. UV photolytic ability (direct or indirect), and

b. dissolved pollutants reacting with OH radicals formed by the homolytic cleavage of the O-O bond in H_2O_2 (González *et al*, 2020).

UV/H_2O_2 oxidation involves the breakdown of H_2O_2 into two hydroxyl radicals (OH) in a single step. Hydroxyl radicals can oxidize organics (RH) by removing protons, resulting in highly reactive organic radicals (R), which can be further oxidized. The various reactions which exist during UV/H_2O_2 oxidation are as follows (Venkatadri *et al*, 1993) .

$$H_2O_2 + h \rightarrow 2OH^{\circ} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \ldots .1$$

$$H_2O_2 \rightarrow HOO^{-} + H^{+} \ldots\ldots\ldots\ldots\ldots\ldots\ldots .2$$

$$OH^{O} + H_2O_2 \rightarrow HOO^{\circ} + H_2O \ldots\ldots\ldots\ldots .3$$

$$OH^{O} + HOO^{-} \rightarrow HOO^{\circ} + OH^{-} \ldots\ldots\ldots\ldots .4$$

$$2HOO^{\circ} \rightarrow H_2O_2 + O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots .5$$

$$2OH^{O} \rightarrow H_2O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .6$$

$$HOO^{\circ} + OH^{O} \rightarrow H_2O + O_2 \ldots\ldots\ldots\ldots\ldots .7$$

$$RH + OH^{\circ} \rightarrow H_2O + e - R^{\circ} \ldots\ldots\ldots\ldots .8$$

The efficiency of the UV/H_2O_2 process is affected by a number of factors that influence its ability to destroy organic molecules. The kind and quantity of organic pollutants or dissolved inorganics (such as carbonates and metallic cations), as well as the light transmittance of the solutions, pH, temperature, and hydrogen peroxide dose, are all factors to consider. A high concentration of H_2O_2 acts as a radical scavenger, slowing the rate of oxidation, whereas a low dose of H_2O_2 causes insufficient hydroxyl radical production, slowing the rate of oxidation. (Collivignarelli *et al.*, 2017).

2.4.4 Combination of Titanium dioxide with ultraviolet (TiO_2/UV) System

Photocatalytic oxidation, which involves combining air or oxygen, UV radiation, and a semiconductor (most commonly TiO_2) to remove a variety of compounds, is a well-known method for removing a variety of compounds, but it has yet to be fully developed on a large scale due to the need to separate the photocatalyst, as mentioned above. TiO_2 is most effective when used as a powder (particle size in the powder ranges from tens to hundreds of nanometers). It is also necessary for the incident radiation on the photocatalyst's surface to have a low energy so that electrons in the semiconductor's valence band can be promoted to the conduction band and hole–electron pairs can be generated.

Radiation in the near-ultraviolet is necessary in the case of titanium dioxide. This is because of its relatively large bandgap, TiO_2 can only absorb about 5% of the solar spectrum (i.e., near UV radiation with a wavelength of 380 nm). As a result, the scientific community has been paying close attention to the enhancement of TiO_2's catalytic activity in the visible zone of the solar spectrum in recent years. To increase the photocatalytic capabilities of TiO_2 under visual irradiation, many techniques have been used, such as surface modification with organic molecules or nanoparticles, or doping with metal and nonmetal ions (Cuerda,*et al*, 2020).

2.5 Previously investigated related researches

Hespanhol *et al*., (2012) states that, the pollutant from wastewater removals obtained using the UV/H_2O_2 oxidation method were close to 90%. The rate of total organic carbon (TOC) degradation increased when the pretreatment techniques were used, indicating that effluent pretreatment is required to improve UV/H_2O_2 oxidation performance. The following were discovered to be the best settings for ECO; pH 5, current density 49.1mA cm^2, and operating time 60 minutes. The trials revealed that the EO procedure removed 75 percent of COD, TOC, and 71 percent of COD (Sharma and Simsek, 2020a).

Nitrophenol photodegradation by H_2O_2 has pseudo-first order kinetics, with more than 98 percent of 4-NP removed in 12 minutes and up to 94 percent of TOC eliminated in 106 minutes. The use of just the right amount of hydrogen peroxide can speed up 4-NP breakdown, but too much hydrogen peroxide slows it down (Zhang et al., 2003).

The use of a sequential EC and UV treatment of tannery effluent has been shown to reduce COD. These method of treatment reduced COD by 94.1 percent, compared to 85.7 and 55.9% for the solo EC and UV treatments, respectively. A sequential EC and UV treatment of tannery wastewater has been proven effective in the reduction of the COD. These treatments reduced COD by 94.1 percent, whereas the solo EC and UV treatments reduced COD by 85.7 and 55.9%, respectively (Jallouli et al., 2020).

The ECO and chemical oxidation processes are both suitable for treating wastewater from the sugarcane sector. At pH 6.5, electrode gap 20 mm, and current density 156 Am^2, 76 percent chemical oxygen demand and 79 percent color removal were obtained with ECO treatment. The addition of a 0.5M (NaCl) electrolyte concentration improved treatment efficacy by 85% chemical oxygen demand and 89 percent color elimination.

When considering the overall setup, a 0.375 L volumetric flow rate resulted in a 60% COD reduction and a 64% color decrease when the EC was operated in continuous mode. Ferrous sulphate and ferric chloride were utilized to increase pollution reduction. At pH 6.5 and 5mM mass loading, a total COD reduction of 98 percent and a color reduction of 99.7% were achieved using a combination of ferric chloride (Sahu, 2019).

CHAPTER THREE

3 MATERIALS AND METHODS

3.1 Materials and apparatus

The equipment's used for this study were beaker, magnetic stirrer (model RHB2), desiccator, Drying oven, filter paper, COD reactor (Hatch 45600-02), COD kit, DO meter, electrode (Al-Al), DC-power supply (WYJ-o-15V/5A),spectrophotometer (model 6700), vacuum pump, vacuum hood, multimeter, Heaters, conical flasks, pH meter , spectrophotometer, standard flasks, Erlenmeyer flasks, measuring cylinder, plastic bottles, burettes, thermometer, funnel, suction flask, wash bottle, porcelain dish, weighing balance (model Pw -124), filtration apparatus, graduated cylinder, turbidity meter (Wag-WT3020),PH meter (pH 3310),conductivity meter (Cond 3110), and ultultraviolet (UV) lamp(model PUV-1022 Heraeus) was used for the investigation of samples throughout the experiment.

3.1.1 Chemicals and reagents

Chemicals used for coffee processing waste water treatment and analyses were, Mercury sulphate ($HgSO_4$), ferrous ammonium sulphate (Fe (NH_3) SO_4), silver sulphate (Ag_2SO_4), ferroin indicator (Fe(o-phen)$_3SO_4$), potassium dichromate ($K_2Cr_2O_7$), and sulphuric acid (H_2SO_4) are used for COD, hydrogen per oxide (H_2O_2) as oxidizing agent and The supporting reagents (Catalyst),will be used for the treatment are sodium sulfate (Na_2SO_4),KOH, NaOH, NaCl,HCl, sodium hydrogen carbonate ($NaHCO_3$),phenolphthalein,stannous chloride, ammon ium molbidate,Phenol ,buffer solutions and distilled water.

Figure 3-1 Chemicals used for COD determination

3.1.2 Software

Version 7 of design-expert software - response surface methodology (RSM), Edraw Max 7 and Microsoft excel 2013 was used.

3.2 Methodology

3.2.1 Study design

Laboratory based (experimental) study design was conducted in Jimma university, Environmental engineering laboratory room, focusing on the evaluating the performance of the integrated UV-Electro-oxidation Process.

3.2.2 Sample size

To get the best representative for coffee processing wastewater, sample was collected by using composite sampling method by different intervals of time. Also depending on number of experimental runs about 156L of coffee processing waste water was collected for the research. This sample volume was taken depending on the number of experimental runs (N)

$N = N_a + N_o + N_c$ .... 3-1 (Simsek, *et al*, 2020).

whereas N= number of experimental runs

$N_{a=}$number of experimental full Factoria, N_o =number of axial and Nc= number of center point. Depending on these number of experimental runs become 156 which is equal to amount of sample size. Its calculation was done under equation 3-2.

3.2.3 Sample collection, transportation and preparation

I. Sample collection

Composite sampling type was applied in this study due to the type of the wastewater to be taken. The wastewater is taken from Jimma Zone, Yabbu town coffee processing waste water discharge point by plastic Jerrycans for three days according to water quality analysis manuals. Totally about 200L including extra volume necessary for tests is taken during the study period. The jerrycans were soaked with 10% HCl for 24 h and then thoroughly cleaned and rinsed with distilled water.

Figure 3-2 Collected coffee processing wastewater sample

II. Sample transportation and preservation

Sample containing plastic bottles were placed in a box during transportation to the laboratory. Plastic boxes were used to protect samples from sunlight, and allowed at temperature of 4°C to be maintained during transport. The sample is transported to the laboratory according to the preservation of samples for characterization. A laboratory manual is used as a guidance for the sample transportation.

III. Sample preparation

The sample was prepared for analysis on the performance of the UV/H_2O_2 and electrochemical oxidation process separately and in combined systems. The sample was preserved by keeping its maximum holding time until the beginning of laboratory measurement process for each parameter. The maximum holding time is kept and performed based on (WHO/UNEP, 2004) standard protocol and water quality laboratory manuals.

3.2.4 Experimental setup

The systems consist electrochemical oxidation, UV/H_2O_2 and integrated UV/ H_2O_2-oxidation process. The experimental setup of hybrid UV/ H_2O_2-oxidation process is schematically shown in below Figure 3.3. The experimental set up consists of electro-chemical reactor and UV lamp. The wastewater is analyzed for COD, pH, EC, color, turbidity and temperature for wastewater. The working electrode, reference and counter electrode (Al) and the pipette (for bubbling) is inserted through the holes in the rubber stopper.

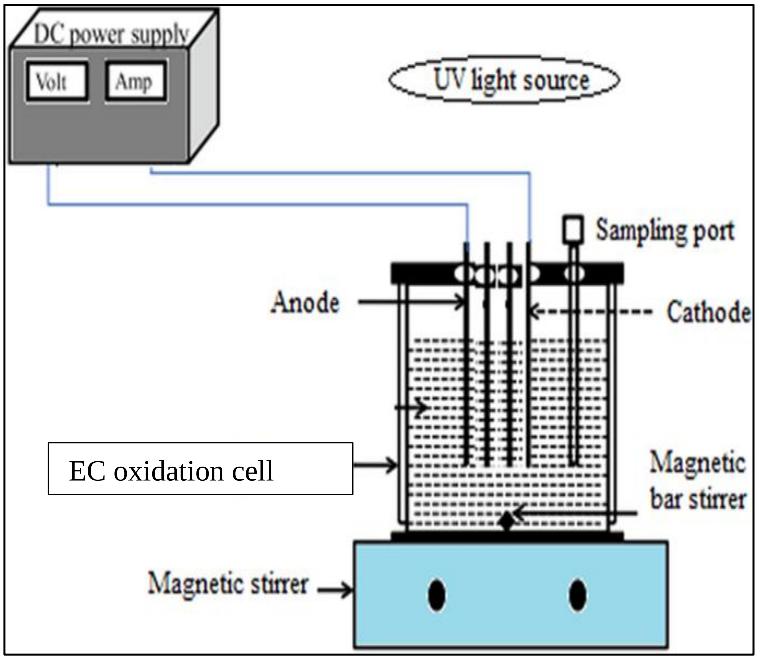


Figure 3-3 photo electrochemical oxidation process set up (Talaat *et al.*, 2011)

3.3 Study variables

a) Dependent variable

COD, turbidity, color, Nitrate and Phosphates were dependent variables or the results after treatment process.

b) Independent variables: Operating parameters such as Electrolyte concentration, time, PH, UV/ H_2O_2 and Current were controlling variables which determine removal ability of the method.

3.4 Method of data analysis and presentation

Upon successful complete of the data collection, the collected data will be analyzed and interpreted by using Microsoft excel office and Response Surface Methodology (RSM) software. Its optimization and analysis were done by using both qualitative and quantitative data analysis methods. All the results were compared with standard limits recommended by WHO (2004). Parameters and measurement methods used were given in the Table 3- 1 below.

Table 3-1 Parameters to be tested and measurement methods

Parameters	
Physical Parameters	Instrument used to measure
pH	pH meter
Turbidity	Nephelometer
Color	spectrophotometer
Electrical conductivity	Conductivity meter
Temperature	Thermometer
Chemical Parameters	
Chemical Oxygen Demand (COD)	LCK 114 kit method
Nitrate	Gravimetric method
Phosphate	Stannious chloride method

3.4.1 Analysis by empirical formula

The performance of the process was evaluated based on the responses of COD, Color, Turbidity, Nitrate and Phosphate removal efficiencies. RSM was a software used for modelling and analysis of the data's obtained from the laboratory by using empirical formulas:

I. Percentage COD removal

The COD test is an indicator of organic component in wastewater.is estimated as equation 3-1:

$$\% \text{ COD removal} = \frac{\text{COD}_i - COD_O}{COD_i} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(Eq. 3-2)}$$

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 (Jallouli *et al.*, 2020).

COD (mg/l) of each run was determined by the following formula

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

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

II. Percentage color removal

$$\% \text{ Color removal} = \frac{Abs_i - Abs_t}{Abs_i} * 100 \ldots\ldots\ldots\ldots \text{(Eq. 3-4)}$$

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

$$\% \text{ Turbidity removal} = \frac{Tur_i - Tur_t}{Tur_i} * 100 \ldots\ldots\ldots\ldots \text{(Eq. 3-5)}$$

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. percentage of nitrate removal

$$\% \text{ Nitrate removal} = \frac{\mathrm{NO3}_i - NO3_t}{NO3_i} * 100 \ldots\ldots\ldots\ldots \text{(3-6)}$$

where NO_3i and NO_3t are concentration of nitrate before treatment and after treatment respectively

V. percentage of phosphate removal

$$\% \text{ Phosphate removal} = \frac{\mathrm{PO3}_i - PO3_t}{PO3_i} * 100 \ldots\ldots\ldots\ldots \text{(3-7)}$$

where PO_3i and PO_3t are concentration of Phosphate before treatment and after treatment respectively

3.4.2 Experimental design and statistical analysis

RSM is a technique for optimizing a response that is influenced by a number of independent variables. As a result, the response is used to describe a performance metric or a quality attribute. The input variables are also known as independent variables, and they are under the scientist's or engineer's control. Response-surface approach is a set of strategies for using experimental methods to find the best operating conditions. Typically, this entails conducting a series of experiments and using the results of one to guide the following steps (Lenth, 2009) In this study, laboratory experiments were carried out using photo electrochemical oxidation process by varying parameters in their interval: pH (5 - 9), electrolytic concentration (0.5 – 2.5) g of NaCl/ $CaCl_2$), current ampere (0.2 – 0.6 A) and reaction time (20 – 50 minute).

As shown in table 3-2-3-3 these inputs give number of experimental runs, range of pH, time, current and electrolyte which was generated by using RSM software.

Table 3-2 Experimental design for electrochemical oxidation using Nacl/$CaCl_2$

Factor	Name	Units	Type	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	pH		Numeric	5.00	9.00	-1 ↔ 5.00	+1 ↔ 9.00	7.13	1.57
B	Time	min	Numeric	20.00	50.00	-1 ↔ 30.00	+1 ↔ 50.00	40.00	10.50
C	Current	amp	Numeric	0.2000	0.6000	-1 ↔ 0.30	+1 ↔ 0.50	0.4033	0.0928
D	Electrolyte	g	Numeric	0.5000	2.50	-1 ↔ 1.00	+1 ↔ 2.00	1.50	0.4549

Table 3-3 Experimental design for electrochemical oxidation combination with UV/H_2O_2

Factor	Name	Units	Type	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	pH		Numeric	5.00	9.00	-1 ↔ 5.00	+1 ↔ 9.00	7.00	1.65
B	Time	min	Numeric	20.00	50.00	-1 ↔ 30.00	+1 ↔ 50.00	40.00	10.11
C	Current	amp	Numeric	0.2000	0.6000	-1 ↔ 0.30	+1 ↔ 0.50	0.4021	0.093
D	Electrolyte	g	Numeric	0.5000	2.50	-1 ↔ 1.00	+1 ↔ 2.00	1.50	0.461
E	H_2O_2	ml	Numeric	1.0000	5.00	-1 ↔ 2.00	+1 ↔ 4.00	3.04	0.966

Therefore, as shown in table 3-2 these inputs give range of pH, time, current and electrolyte which was generated by using RSM software with number of experimental runs. Those parameters were considered to determine the removal efficiency of COD, color, turbidity, Nitrate and phosphate. The order of experiments was arranged randomly.

Totally one hundred fifty-six experiments (sixty for electrochemical oxidation by using NaCl/ $CaCl_2$ and Ninety-six by combination of electrochemical oxidation NaCl/$CaCl_2$ and UV/H_2O_2 were performed in the laboratory using Aluminum-Aluminum electrode combination with electrode distance of 1 cm.

Five dependent variables were evaluated as the response to establish the ideal values of the process' independent variables: COD, color, turbidity, nitrate, and phosphates removal. Input variables were electrolyte, hydrogen peroxide, electric current, electrolysis time, and pH. As stated in the table 3-2 and 3-3, the rotatable experimental plan was carried out with the four independent variables at three coded levels (-1, 0, and +1). Actual values are the original values assigned to various factors, while code values are assigned to different levels of factors (Sharma and Simsek, 2020a).Additional factor H_2O_2 was added in table 3-3.

In this research, the CCD model with four factors was applied to optimize the parameters. The experimental design was based on three-level full factorial design to which central and star points were also added. The total number of experiments (N) can be calculated by:

$N = N_a^n + N_o + N_c = > (2^n+2n+c)$ …………… (Eq. 3-8) (Simsek *et al*,2020)

where, N_a represents the number of two-level experiments in a full factorial design or replicates of factorial points ($2^4=16$), N_0 is the number of replications in the central point (6 replications) for evaluation of net error, and N_c denotes the number of replicates of axial (star) points (2*4=8) by using alpha value = 2, twenty-four (16+8 = 24) factorial points and 6 replicates of central point, total 30 experimental runs were provided by software for single process. That means, for ECO 60 experiments (30 by using NaCl and 30 by using $CaCl_2$)

For combined photo-electron chemical oxidation process by using electrolytes; NaCl and $CaCl_2$ with UV/H_2O_2 = (2^5+(2*5) +6) = 48) because H_2O_2 was added as additional factor and 48 runs(trials) for UV/NaCl and 48 runs for UV/$CaCl_2$ total for combination was 96 experiments. 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 were analyzed using RSM algorithm and were fitted to the predictive quadratic polynomial Equation.

Second-order model equation for prediction of the optimal conditions can be expressed by the following equation

$$Y_i = \beta_0 + \sum_{i=1}^{4} \beta_i \,.\, X_i + \sum_{i \le j}^{4} \sum_{j}^{4} \beta_{ij} . X_i . X_j + \sum_{i=1}^{4} \beta_{ii} \,.\, X_i^2 + e \ldots\ldots\ldots\ldots \text{ (Eq. 3-9)}$$

where Y_i is the response variable, 0 represents the model (regression) constant, i represents the linear terms, i_i represents the squared terms (second-order), i_j represents the interaction terms, X_i and X_j represent independent variables, e represents random error, and k=4 represents the number of parameters (Fallahzadeh *et al.*, 2019a).

Response surface plots are a tool for predicting wastewater removal efficiency. The contours of the plots also aid in identifying the types of interactions that exist between these variables. The maximum expected yield was achieved, as demonstrated by the surface restricted in the smallest curve of the contour diagram. The relevant figures show variation in target responses due to changes in operational parameter levels.

3.4.3 Data quality assurance

According to (APHA), proper quality assurance procedures and precautions were performed to assure the results' credibility. A field work manual was utilized to check every step of the process in order to improve the data quality. In addition, carefully selected assistants were chosen to handle the data. The acquired data was further double-checked for accuracy and reliability. To avoid data errors, a laboratory test procedures manual was used. Laboratory instruments were calibrated; for the quality of the data triplicate experiments were carried out during each set of experiments and average of the triplicate measurements was reported. At each set of experiments, calibration (standardization) is conducted for analysis.

3.5 Ethical considerations

For the study to be sound and ideal, ethical consideration was taken into account. Following approval from the Environmental Engineering Department and JiT to proceed with the work, the research and data collection were carried out. Before the collection of the data, the purpose of the data was clearly described to the interested party. The data was kept confidential and used only for research purpose. Each and every of data collection, processing, and analysis follow scientific methods and procedures. Finally, the result of laboratory analysis was honestly recorded and interpreted based on scientific procedures.

3.6 Dissemination of the results

In the presence of examiners, the research will be presented publicly for postgraduate studies at Jimma Institute of Technology, Faculty of Civil and Environmental Engineering, Environmental Engineering Chair. Following the completion of the research presentation, the paper will be disseminated in nationally and internationally recognized journals of Environmental Engineering. In addition, the findings will be presented to the community, stake holders, governmental and non-governmental organizations through different means.

CHAPTER FOUR

4 RESULTS AND DISCUSSION

4.1 Removal efficiency of photo-electrochemical oxidation process for coffee processing wastewater

Coffee processing waste water is one of industrial waste water which carry pollutants that can affect ecosystem after generated to the environment.as a result waste water taken from coffee processing plant before treated carries the following water quality parameters. Physical parameters include color, odor, temperature, turbidity, and Chemical parameters associated with the organic content of wastewater include the chemical oxygen demand (COD), chemical characteristics of wet processing of coffee associated with Nutrients such as Phosphates and nitrates were analyzed. Depending on analysis Color very black with 2.95abs., Temperature 43^{o}C, very bad smell, Turbidity 144.5 NTU, pH 5.41, COD 7680mg/l nitrate 23.21mg/l and Phosphate 9.2mg/l.

4.1.1 Removal efficiency of electrochemical oxidation using NaCl

Sodium chloride (NaCl) is a chemical used as an electrolyte and used to increase conductivity and decrease amount of voltage supplied to the wastewater by forming Na^{+} and Cl^{-1} during treatment process. The conductivity of wastewater is developed by the addition of different concentrations of NaCl as a supportive electrolyte (Asaithambi *et al.*, 2020).

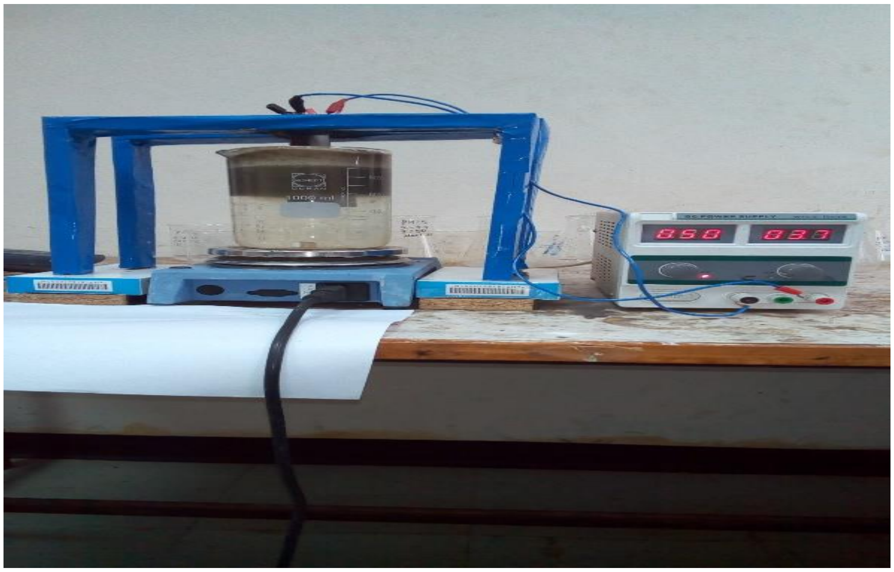


Figure 4-1 Coffee processing waste water sample after treatment

Table 4-1 FCCD for COD, color, turbidity, NO_3 and PO_3 removal by ECO/NaCl

Factors					Responses (Removal efficiency by %)				
Run	A: PH	B: Time (Min)	C: Current (amp)	D: Electrolyte (Nacl)g	COD %	Color %	Turbidity %	Nitrate %	Phosphate %
1	7	60	0.5	1.5	94.991	90.635	95.870	86.607	87.735
2	9	30	0.3	1	91.708	81.950	92.785	72.494	81.950
3	7	40	0.4	2.5	94.951	91.065	95.450	86.878	89.165
4	5	30	0.5	1	89.937	74.811	85.941	67.688	74.811
5	7	40	0.4	1.5	94.241	91.165	94.837	87.975	88.456
6	7	40	0.2	1.5	94.166	87.079	93.768	85.933	87.079
7	5	30	0.3	2	89.566	74.158	84.154	67.835	74.158
8	9	30	0.5	2	92.833	82.821	93.705	74.857	82.821
9	9	50	0.5	2	93.750	83.907	94.4983	74.589	83.907
10	7	40	0.4	1.5	94.525	89.933	95.536	86.899	89.033
11	9	40	0.4	1.5	94.083	83.823	92.858	73.975	83.923
12	7	20	0.4	1.5	94.625	88.079	93.802	84.104	86.079
13	5	50	0.3	2	89.916	74.375	84.517	68.964	74.375
14	9	30	0.3	2	92.500	81.690	92.084	72.470	81.690
15	5	50	0.3	1	89.006	74.158	84.992	67.024	74.158
16	7	40	0.4	0.5	92.083	88.161	92.683	85.417	87.165
17	7	60	0.4	1.5	94.925	89.142	95.643	86.941	89.142
18	5	50	0.5	2	90.511	76.221	86.029	68.988	76.221
19	9	50	0.3	2	93.375	82.930	93.195	73.902	83.930
20	5	50	0.5	1	89.291	75.567	86.608	66.313	75.567
21	5	30	0.3	1	88.545	74.484	85.557	66.958	74.484
22	7	40	0.4	1.5	94.995	90.564	94.121	86.751	90.564
23	5	30	0.5	2	89.770	75.352	85.865	68.919	75.352
24	9	50	0.3	1	92.091	82.121	92.075	72.270	83.821
25	7	40	0.6	1.5	94.915	88.165	95.802	86.978	88.165
26	7	40	0.4	1.5	93.051	89.685	94.871	85.005	89.685

27	9	40	0.4	1.5	93.752	82.987	92.802	74.475	83.987
28	7	20	0.4	1.5	93.125	86.842	93.887	84.991	85.342
29	9	30	0.5	1	92.875	83.016	91.545	72.285	82.016
30	9	50	0.5	1	93.841	83.319	92.837	75.591	83.319

4.1.2 Removal efficiency of electrochemical oxidation using $CaCl_2$

Calcium Chloride ($Cacl_2$) is a chemical used as an electrolyte and used to increase conductivity and decrease amount of voltage supplied to the wastewater by forming Ca^{+2} and Cl^{-1} during treatment process to increase removal efficiency.

Table 4-2 FCCD for COD, color, turbidity, NO_3 and PO_3 removal by by ECO/$CaCl_2$

	Factor				**Response (Removal efficiency by %)**				
Run	A: PH	B: Time (min)	C: Current (amp)	D: Electrolyte $Cacl_2$g	COD %	Color %	Turbidity %	Nitrate %	Phosphate %
1	7	60	0.5	1.5	96.381	95.806	97.1664	89.966	90.0267
2	9	30	0.3	1	93.204	88.170	94.481	76.853	84.2414
3	7	40	0.4	2.5	95.945	94.385	97.346	90.236	92.456
4	5	30	0.5	1	90.333	80.031	86.637	71.047	77.102
5	7	40	0.4	1.5	95.537	95.856	97.533	90.334	92.747
6	7	40	0.2	1.5	95.662	92.299	96.464	89.292	89.370
7	5	30	0.3	2	88.962	79.378	86.850	71.194	76.449
8	9	30	0.5	2	93.329	90.042	95.402	77.216	86.112
9	9	50	0.5	2	94.245	90.128	96.1945	77.947	88.198
10	7	40	0.4	1.5	95.175	95.154	97.232	90.258	91.324
11	9	40	0.4	1.5	93.579	89.043	94.554	78.734	86.214

12	7	20	0.4	1.5	95.620	93.299	96.499	87.463	88.370
13	5	50	0.3	2	90.912	79.596	87.213	72.223	76.666
14	9	30	0.3	2	93.095	87.910	94.080	77.828	85.981
15	5	50	0.3	1	89.062	79.378	87.688	70.382	76.449
16	7	40	0.4	0.5	94.579	92.385	95.280	87.676	90.456
17	7	60	0.4	1.5	96.220	94.362	96.339	89.900	91.433
18	5	50	0.5	2	90.995	82.441	88.725	72.346	78.512
19	9	50	0.3	2	94.370	89.150	95.492	78.261	86.221
20	5	50	0.5	1	89.125	80.787	89.304	71.972	77.858
21	5	30	0.3	1	88.041	79.704	87.253	69.317	76.775
22	7	40	0.4	1.5	96.325	95.784	96.817	89.909	92.855
23	5	30	0.5	2	90.966	81.573	88.561	71.077	77.643
24	9	50	0.3	1	93.287	89.042	94.771	78.629	85.112
25	7	40	0.6	1.5	95.791	94.385	96.9992	90.136	90.4562
26	7	40	0.4	1.5	96.387	94.905	96.5691	89.334	91.9761
27	9	40	0.4	1.5	93.245	89.207	95.499	77.834	87.278
28	7	20	0.4	1.5	95.620	92.062	95.0837	88.349	87.6331
29	9	30	0.5	1	94.370	89.736	93.7415	78.643	85.3073
30	9	50	0.5	1	93.53	89.539	95.533	78.949	87.610

4.1.3 Removal efficiency of electrochemical oxidation using NaCl and combination with UV/H_2O_2

Under this stage it needs combination of an electrolyte NaCl with ultra violet light and hydrogen peroxide (UV/H_2O_2) to increase the destruction of Hydroxyl ion and increase Pollutant removal efficiency.

Table 4-3 FCCD for COD, color, turbidity, NO_3 and PO_3 removal by ECO/NaCl with UV/H_2O_2

Factor						Response				
Run	A: PH	B: Time min	C: Current amp	D: Electrolyte g	E: H_2O_2 ml	COD %	Color %	Turbidity %	NO_3 %	PO_3 %
1	5	30	0.3	1	2	91.246	94.170	94.687	83.192	91.430
2	9	30	0.5	2	4	95.783	95.692	97.496	96.342	97.215
3	9	30	0.3	1	4	93.708	95.153	97.101	96.319	97.194
4	5	30	0.5	2	4	92.408	95.361	95.274	85.980	93.537
5	9	50	0.3	2	4	95.025	97.424	96.595	96.684	96.507
6	7	40	0.4	1.5	3	96.683	98.000	98.761	98.886	98.209
7	5	30	0.3	2	2	91.471	94.034	95.025	86.062	92.976
8	9	30	0.5	2	2	93.593	94.678	96.640	96.673	97.669
9	7	60	0.5	1.5	3	98.158	98.287	97.582	98.815	97.166
10	7	40	0.4	1.5	3	97.067	97.254	98.541	97.486	98.298
11	7	40	0.6	1.5	3	98.467	97.932	98.619	98.862	98.022
12	5	30	0.5	2	2	92.575	95.271	95.128	85.162	93.088
13	5	30	0.5	1	4	92.708	95.780	95.343	86.146	91.298
14	7	20	0.4	1.5	3	97.179	96.034	99.359	98.174	97.171
15	5	50	0.3	2	4	91.571	94.576	95.265	88.157	93.794
16	7	40	0.4	1.5	5	98.640	97.639	98.713	98.186	97.177
17	9	30	0.3	2	4	95.438	96.000	97.073	96.273	97.091
18	5	50	0.3	1	4	93.179	94.339	94.547	84.861	93.417
19	7	20	0.5	1.5	3	97.204	96.848	98.759	98.080	97.300
20	9	30	0.3	1	2	94.455	94.881	96.542	95.951	97.337
21	5	50	0.5	1	2	92.575	94.805	93.645	84.908	94.314
22	5	50	0.3	1	2	91.579	94.000	93.630	84.128	93.219
23	5	50	0.3	2	2	91.129	94.017	94.671	87.062	94.336
24	9	50	0.3	1	4	94.458	96.017	96.969	97.838	97.055
25	7	40	0.2	1.5	3	95.063	95.468	97.731	97.072	97.164
26	5	30	0.3	2	4	93.071	94.814	94.642	84.048	93.680

27	5	30	0.5	1	2	92.025	93.309	94.409	83.944	92.614
28	9	30	0.3	2	2	95.354	95.414	97.374	95.291	97.048
29	9	50	0.5	2	2	94.413	95.763	97.031	96.672	97.541
30	7	40	0.4	1.5	3	98.558	98.339	98.758	98.497	98.158
31	7	40	0.4	0.5	3	96.954	95.407	97.974	96.508	98.262
32	9	50	0.5	2	4	95.654	97.059	96.977	95.506	97.191
33	9	30	0.5	1	2	95.079	95.450	96.816	96.350	97.746
34	5	50	0.5	2	2	94.250	94.339	94.683	87.098	94.548
35	9	50	0.3	1	2	95.294	95.831	96.678	96.639	97.151
36	5	30	0.3	1	4	90.294	94.780	94.190	85.110	92.417
37	7	40	0.4	1.5	3	98.379	98.170	99.454	98.462	99.022
38	7	40	0.4	1.5	1	95.096	96.046	98.702	97.126	98.143
39	9	30	0.5	1	4	92.779	95.627	97.374	97.873	97.311
40	7	60	0.5	1	3	98.300	98.007	98.041	96.684	98.207
41	9	50	0.5	1	4	95.279	96.898	97.532	96.531	97.268
42	9	50	0.3	2	2	95.813	96.764	96.756	96.660	97.260
43	7	40	0.4	2.5	3	98.196	97.539	99.154	98.880	98.252
44	5	50	0.5	1	4	92.846	94.322	95.231	87.275	92.309
45	7	40	0.4	1.5	3	98.796	96.220	98.345	98.286	98.275
46	9	50	0.5	1	2	93.454	96.203	96.709	97.168	97.746
47	5	50	0.5	2	4	94.213	94.978	95.518	87.169	92.967
48	7	40	0.4	1.5	5	97.771	98.119	98.119	98.669	98.198

4.1.4 Removal efficiency of electrochemical oxidation using cacl$_2$ and combination with UV/H_2O_2

This stage it needs combination of an electrolyte Cacl$_2$ with ultra violet light and hydrogen peroxide (UV/H_2O_2) increase the destruction of Hydroxyl ion and increase Pollutant removal efficiency.

Table 4-4 FCCD for COD, color, turbidity, NO_3 and PO_3 removal by ECO/$CaCl_2$ and UV/H_2O_2

Factor						**Response**				
Run	PH	Time min	Current amp	Electrolyte g	H_2O_2 ml	COD %	Color %	Turbidity %	NO_3%	PO_3 %
1	5	30	0.3	1.0	2.0	91.904	95.729	95.156	84.129	92.390
2	9	30	0.5	2.0	4.0	96.442	97.251	97.965	97.280	98.175
3	9	30	0.3	1.0	4.0	94.367	96.712	97.570	97.257	98.155
4	5	30	0.5	2.0	4.0	93.067	96.920	95.743	86.917	94.498
5	9	50	0.3	2.0	4.0	95.683	98.983	97.064	97.621	97.467
6	7	40	0.4	1.5	3.0	99.342	99.859	99.230	99.823	99.170
7	5	30	0.3	2.0	2.0	92.129	95.593	95.494	87.000	93.936
8	9	30	0.5	2.0	2.0	94.251	96.237	97.109	97.611	98.629
9	7	60	0.5	1.5	3.0	98.817	99.846	98.052	99.753	98.127
10	7	40	0.4	1.5	3.0	99.725	99.814	99.010	98.423	99.259
11	7	40	0.6	1.5	3.0	99.125	99.492	99.089	99.800	99.911
12	5	30	0.5	2.0	2.0	93.233	96.831	95.597	86.100	94.048
13	5	30	0.5	1.0	4.0	93.367	97.339	95.812	87.083	92.259
14	7	20	0.4	1.5	3.0	97.838	97.593	99.828	99.111	98.132
15	5	50	0.3	2.0	4.0	92.229	96.136	95.734	89.095	94.754
16	7	40	0.4	1.5	5.0	99.298	99.198	99.182	99.123	98.138
17	9	30	0.3	2.0	4.0	96.096	97.559	97.542	97.210	98.051
18	5	50	0.3	1.0	4.0	93.838	95.898	95.016	85.798	94.377
19	7	20	0.5	1.5	3.0	97.863	98.407	99.228	99.017	98.260
20	9	30	0.3	1.0	2.0	95.113	96.441	97.011	96.888	98.297
21	5	50	0.5	1.0	2.0	93.233	96.364	94.115	85.846	95.274
22	5	50	0.3	1.0	2.0	92.238	95.559	94.099	85.065	94.180
23	5	50	0.3	2.0	2.0	91.788	95.576	95.141	88.000	95.296
24	9	50	0.3	1.0	4.0	95.117	97.576	97.438	98.775	98.015
25	7	40	0.2	1.5	3.0	95.721	97.027	98.201	98.010	98.125
26	5	30	0.3	2.0	4.0	93.729	96.373	95.111	84.986	94.641
27	5	30	0.5	1.0	2.0	92.683	94.868	94.878	84.882	93.574

28	9	30	0.3	2.0	2.0	96.013	96.973	97.844	96.228	98.008
29	9	50	0.5	2.0	2.0	95.071	97.322	97.500	97.610	98.502
30	7	40	0.4	1.5	3.0	99.217	99.898	99.227	99.435	99.982
31	7	40	0.4	0.5	3.0	97.613	96.966	98.443	97.446	99.222
32	9	50	0.5	2.0	4.0	96.313	98.619	97.446	96.444	98.151
33	9	30	0.5	1.0	2.0	95.738	97.009	97.286	97.287	98.706
34	5	50	0.5	2.0	2.0	94.908	95.898	95.152	88.036	95.508
35	9	50	0.3	1.0	2.0	95.952	97.390	97.147	97.576	98.112
36	5	30	0.3	1.0	4.0	90.952	96.339	94.659	86.048	93.377
37	7	40	0.4	1.5	3.0	99.992	99.829	99.187	99.823	99.149
38	7	40	0.4	1.5	1.0	95.754	97.605	99.172	98.064	99.104
39	9	30	0.5	1.0	4.0	93.438	97.186	97.844	98.811	98.271
40	7	60	0.4	1.5	3.0	99.192	99.566	98.510	97.621	99.167
41	9	50	0.5	1.0	4.0	95.938	98.458	98.002	97.468	98.228
42	9	50	0.3	2.0	2.0	96.471	98.324	97.225	97.598	98.220
43	7	40	0.4	2.5	3.0	99.454	99.098	99.922	99.818	99.212
44	5	50	0.5	1.0	4.0	93.504	95.881	95.700	88.212	93.270
45	7	40	0.4	1.5	3.0	98.875	97.780	98.814	99.223	99.236
46	9	50	0.5	1.0	2.0	94.113	97.763	97.178	98.105	98.706
47	5	50	0.5	2.0	4.0	94.871	96.537	95.988	88.107	93.928
48	7	40	0.4	1.5	5.0	99.181	99.678	98.588	99.135	99.159

4.2 Effect of operating parameters on % removal efficiency

The operating parameters, that highly affect the ECO and UV/H_2O_2 processes, such as solution pH, electrolyte concentration (NaCl/ $CaCl_2$), electric current and reaction time was studied in terms % COD, color, turbidity NO_3, and PO_3 removal at room temperature.

4.2.1 Effect of electrode

Aluminum electrodes are more successful at removing nitrate and phosphorus because they can be quickly ionized and coupled with the phosphate ion to generate aluminum phosphate ($AlPO_4$) for precipitation. It is obvious that COD and ammonia are removed simultaneously during electrolysis by indirect oxidation, with ammonia removal being the main process (Kumar *et al.*, 2012)

4.2.2 Effect of pH

The term pH refers to the severity of a liquid's acid or alkaline condition. Waters with a higher alkalinity have a higher pH. The pH of the solution plays a critical role in the elimination of pollutants in the ECO and UV/H_2O_2 processes).To evaluate the effect of pH on process performance, it is altered in the range of 5 to 9 by integrating NaOH or H_2SO_4 solution (Kumar *et al.*, 2012).

The effect of pH with COD, color, nitrate and phosphate % removal potency is shown below

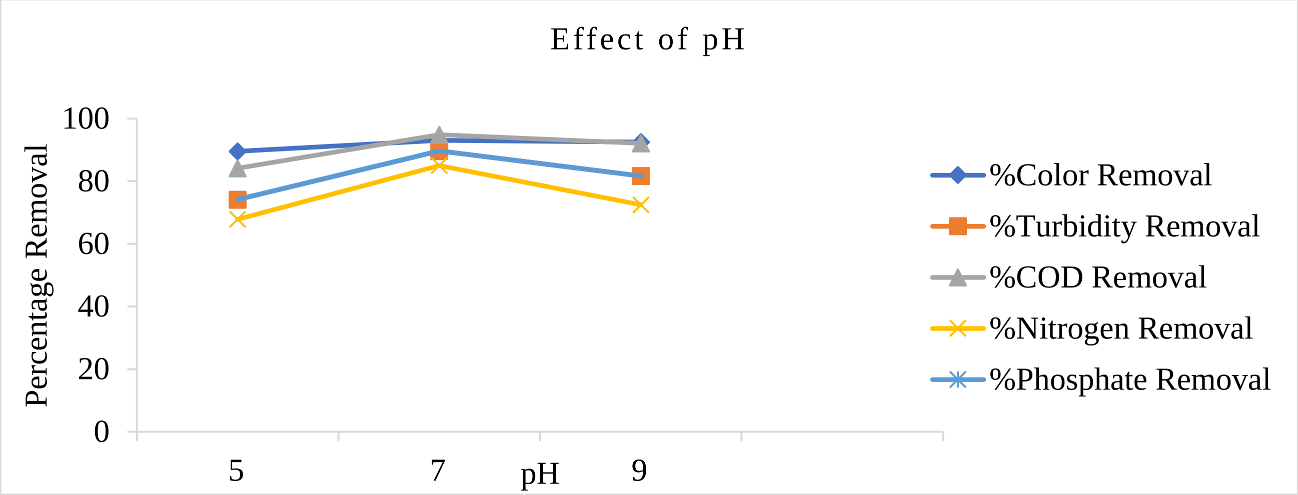


Figure 4-2 Effect of pH on removal efficiency by using NaCl as electrolyte

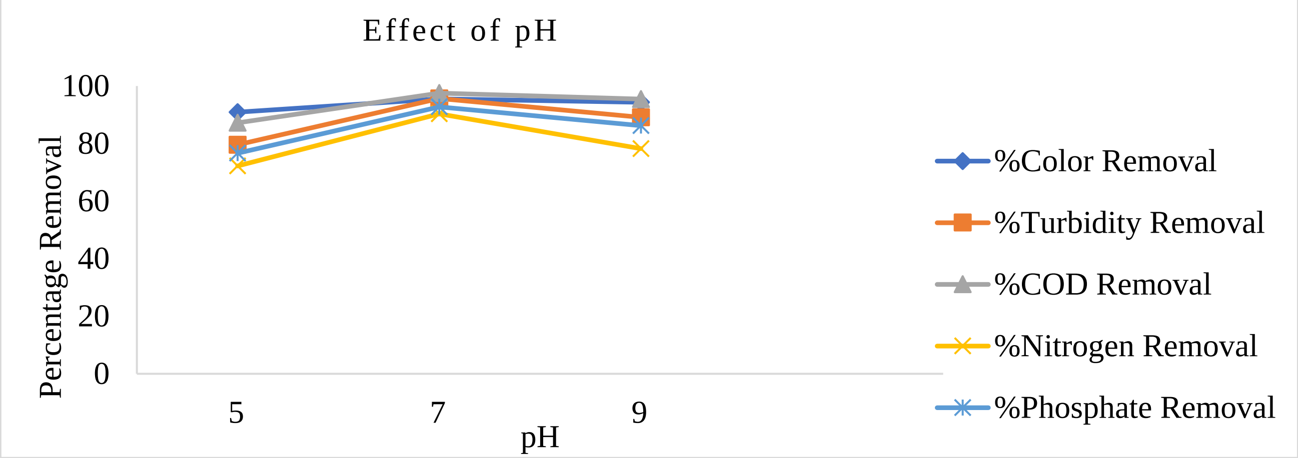


Figure 4-3 Effect of pH on removal efficiency by using $CaCl_2$

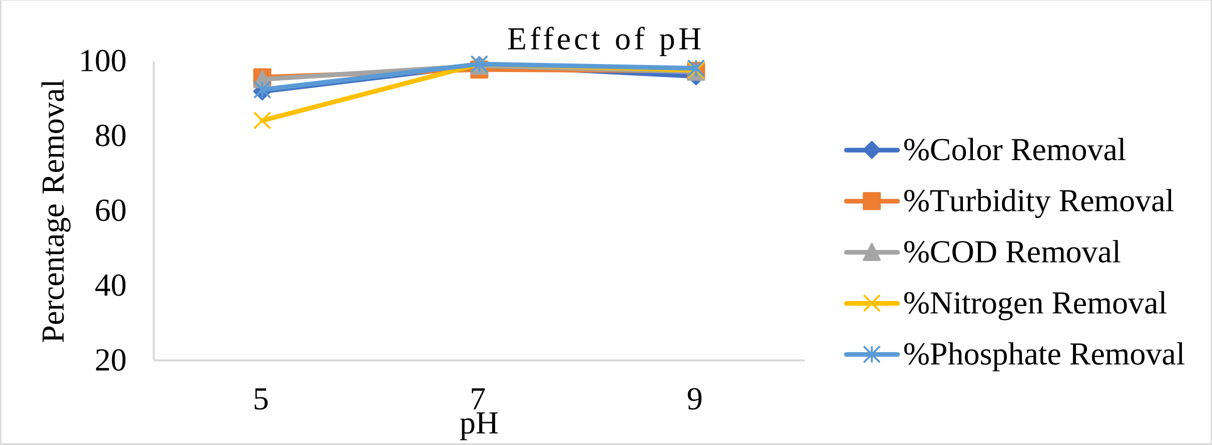


Figure 4-4 Effect of pH on removal efficiency by using UV/H_2O_2 and NaCl

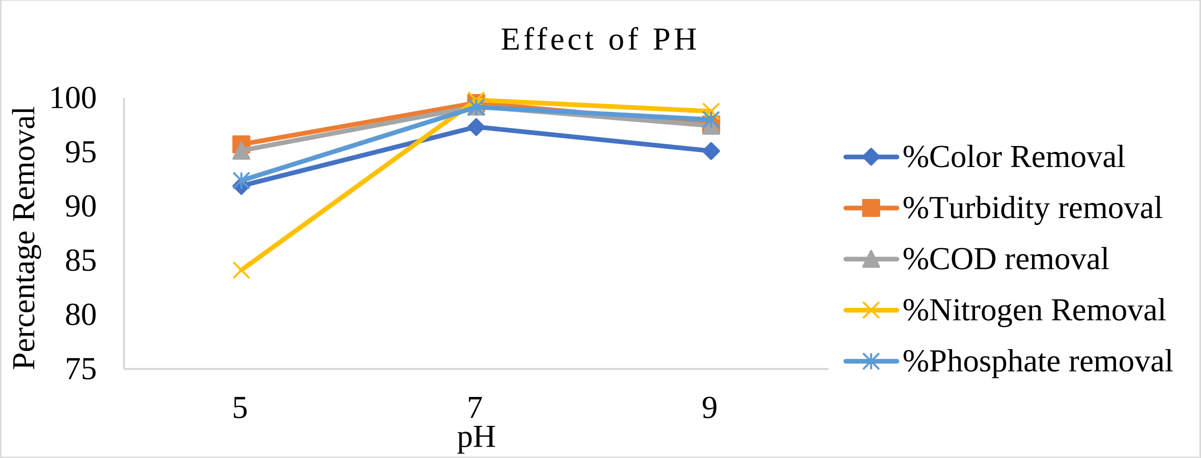


Figure 4-5 Effect of pH on removal efficiency by using UV/H_2O_2 and $CaCl_2$

4.2.3 Effect of electrolysis time

The structure of the sludge may alter over time, impacting the efficacy of pollutant removal as well as the flocs' settleability and floatability. Very long reaction times result in lower removal percentages, according to the study, which could be due to metal hydroxide sequestration at the electrode level (Bhatti *et al.*, 2009). In case of coffee processing waste water treatment long time and very short time have low removal efficiency. Regarding to this research 40 minute is the optimum removal time.

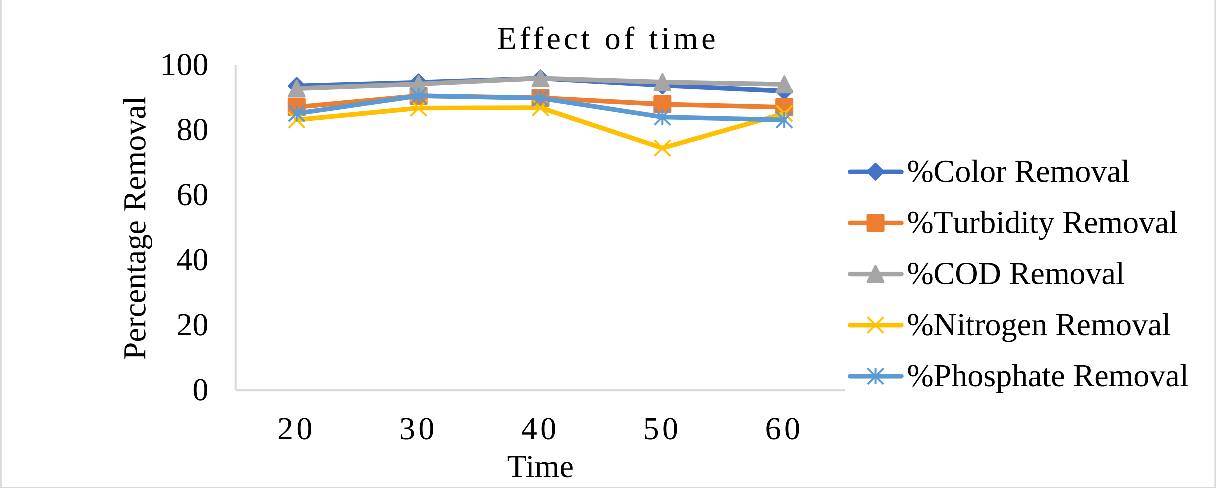


Figure 4-6 Effect of time on removal efficiency by using NaCl

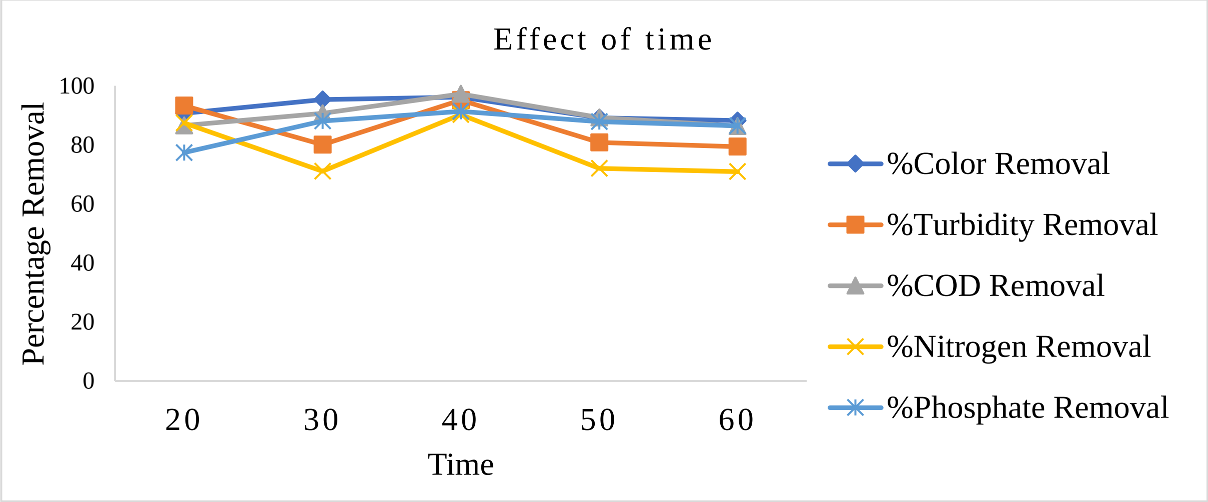


Figure 4-7 Effect of time on removal efficiency by using $CaCl_2$

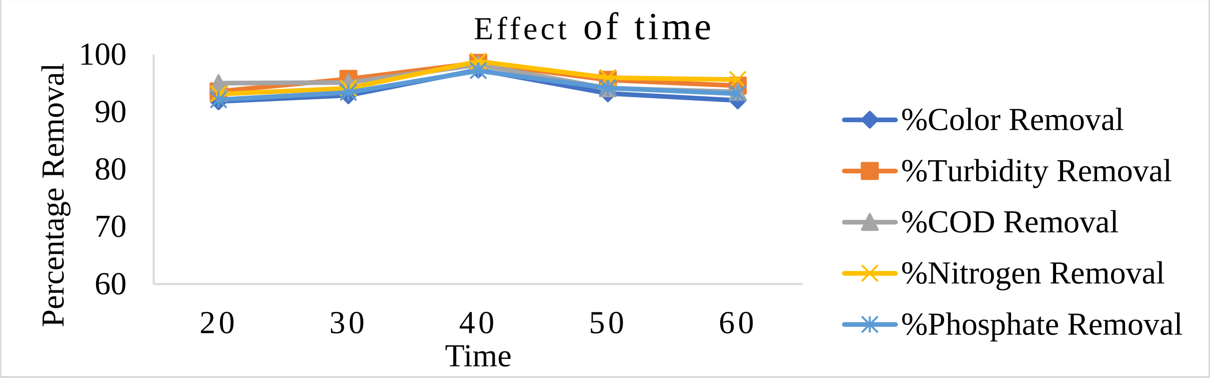


Figure 4-8 Effect of time on removal efficiency by using UV/H_2O_2 and NaCl

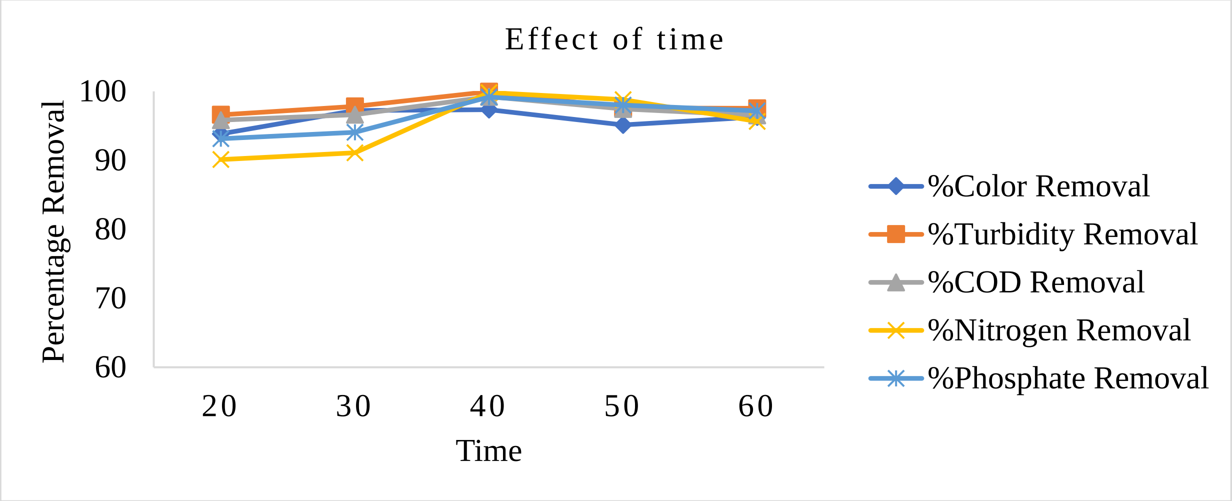


Figure 4-9 Effect of time on removal efficiency by using UV/H_2O_2 and $CaCl_2$

4.2.4 Effect of electric current

In actuality, current was proportional to voltage. As the current grew, so did the amount of aluminum dissolve. As a result, the formation of Al $(OH)_3$ hydroxide is accelerated. The effectiveness of organic oxidation decreases when a higher voltage is applied because oxygen evolution occurs. When the process is carried out at higher voltages, however, poisoning products formed at the anode surface are oxidized. Extremely high current negatively affects(decrease) on the treatment of waste water from the coffee industry. Current is one of the most important factors in electrochemical processes (Vasudevan, 2014)

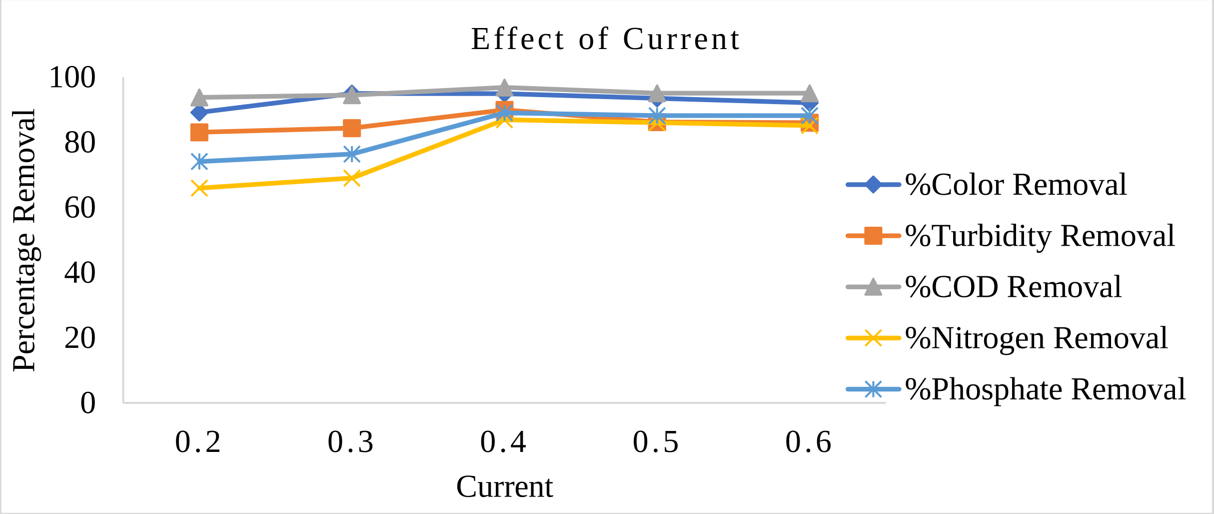


Figure 4-10 Effect of current on removal efficiency by using NaCl

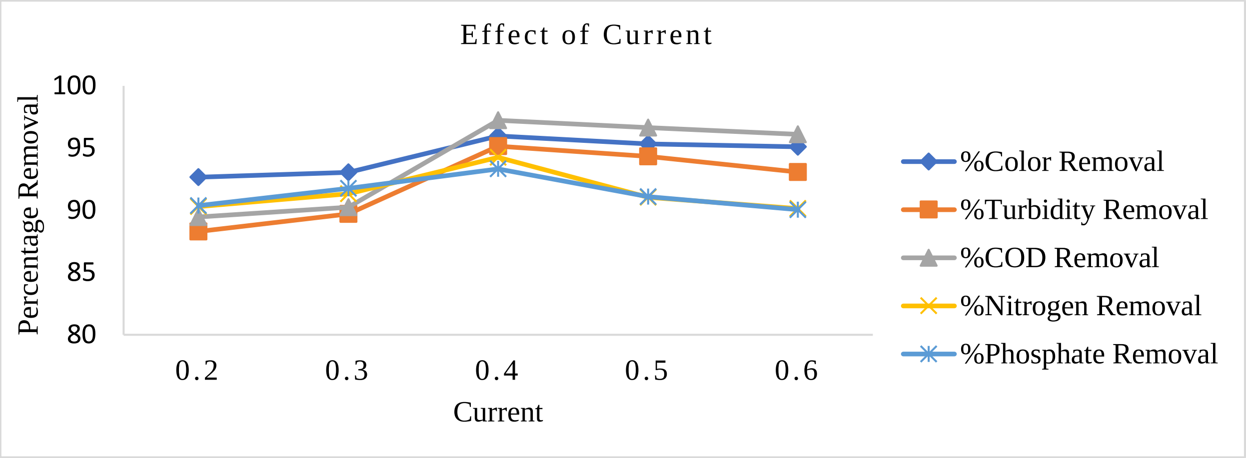


Figure 4-11 Effect of current on removal efficiency by using $CaCl_2$

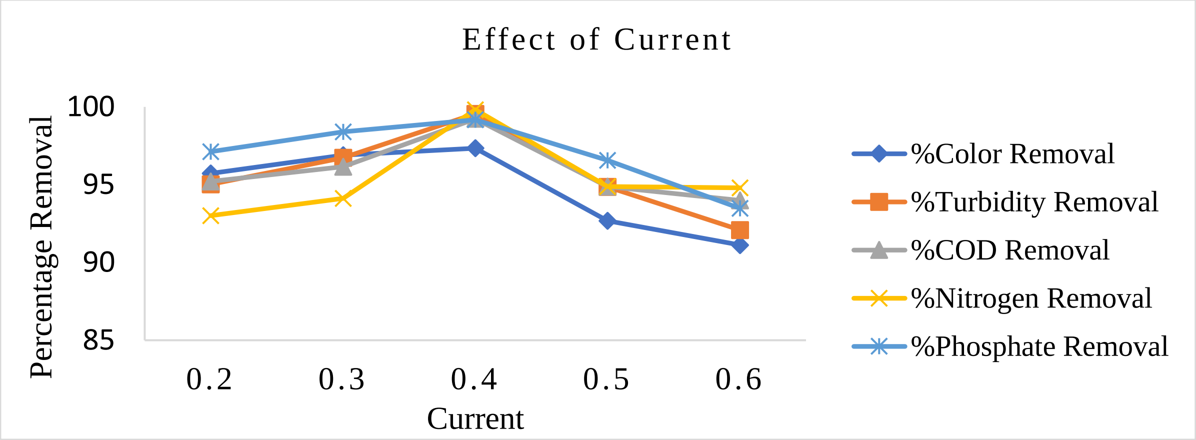


Figure 4-12Effect of current on removal efficiency by using UV/H_2O_2 and NaCl

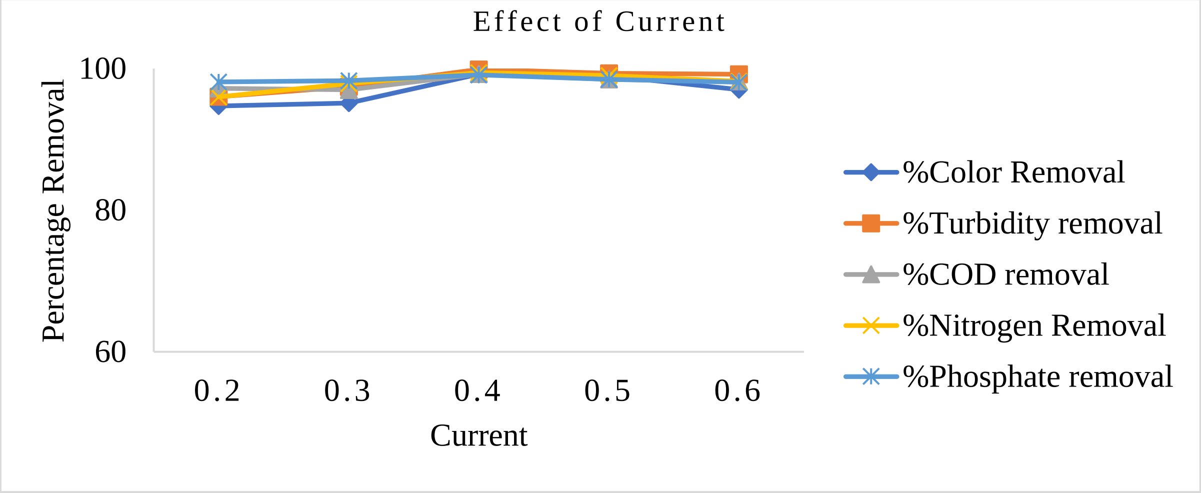


Figure 4-13 Effect of Current on removal efficiency by using UV/H_2O_2 and $CaCl_2$

4.2.5 Effect of electrolyte concentration

To increase the conductivity of the water or wastewater to be treated, table salt was commonly used. Chloride ions were discovered to greatly diminish the negative effects of other anions such as HCO_{3-} and $SO_4^{2-,}$ in addition to their ionic involvement in carrying the electric charge. The presence of carbonate or sulfate ions causes the precipitation of Ca^{2+} or Mg^{2+} ions on the electrodes' surfaces, forming an insulating layer. Energy usage is reduced as electrolyte concentration rises. In the AO and AO-H_2O_2 processes, organic compound elimination and mineralization occur more quickly in the presence of NaCl or $Cacl_2$ than in the absence of Na_2SO_4 (Fallahzadeh *et al.*, 2019b).

The voltage between electrodes would be substantially increased by this insulating layer, resulting in a significant reduction in current efficiency. Because of the increase in conductivity, the addition of NaCl and $CaCl_2$ would also result in a reduction in power usage. Furthermore, chlorine produced electrochemically has been demonstrated to be useful in water disinfection. (A., R. and A., 2011)

As a result, for the tests, a concentration of 0.5–2.5 g/L NaCl and $CaCl_2$ was used. When compared to the other components, the amount of electrolyte factor has a bigger impact on response. This is because NaCl/ $CaCl_2$ raises the conductivity of the EO system, which improves the removal of percent color, COD, Nitrate, Phosphate, and Turbidity. Due to the increase in ions from +1 (NaCl) to +2 ($CaCl_2$), $CaCl_2$ produces a more efficient result than NaCl The addition of a supporting electrolyte (NaCl or $CaCl_2$) was done to boost the solution's conductivity (Sahu, 2019).

By incorporating an appropriate amount of electrolyte, the conductivity of the effluent was adjusted to the correct values. Secondary reactions, such as direct oxidation of organic molecules and Cl ions present in wastewater, may occur if the anode potential is sufficiently high. Within the powerful advanced oxidation technologies, indirect electro-oxidation processes represent a viable alternative for the destruction of high molecular weight substances and, in particular, the elimination of COD, making it a promising technology for the treatment of high conductivity wastewaters (Universiti *et al.*, 2014). Strong oxidants, such as active chlorine species, destroy organic load in these processes (ACS). An electron transfer to the anode (Reaction 1) generates ACS from chloride in water, which interacts with water to produce hypochlorous acid (reaction 2) The equilibrium between hypochlorous acid and hypochlorite ion in water is dependent on the concentration and pH of the solution, according to the speciation of chlorine in water. Reaction 3 is next aside from these active species, the chloride radical is produced by anode direct oxidation (Reaction4).

$$2Cl^- \rightarrow Cl_{2\ (aq)} + (2e^-) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

$$HClO \leftrightarrow ClO^- + H^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

$$Cl^- \rightarrow Cl + e^- \ldots\ldots\ldots\ldots 4$$ (Salmerón, Oller and Malato, 2020)

Thus, the generated chlorine gas can oxidize pollutants. It is clear that, for aluminum, the energy consumption is higher and electrode consumption is lower. It is observed that higher conductivity favors high process efficiency

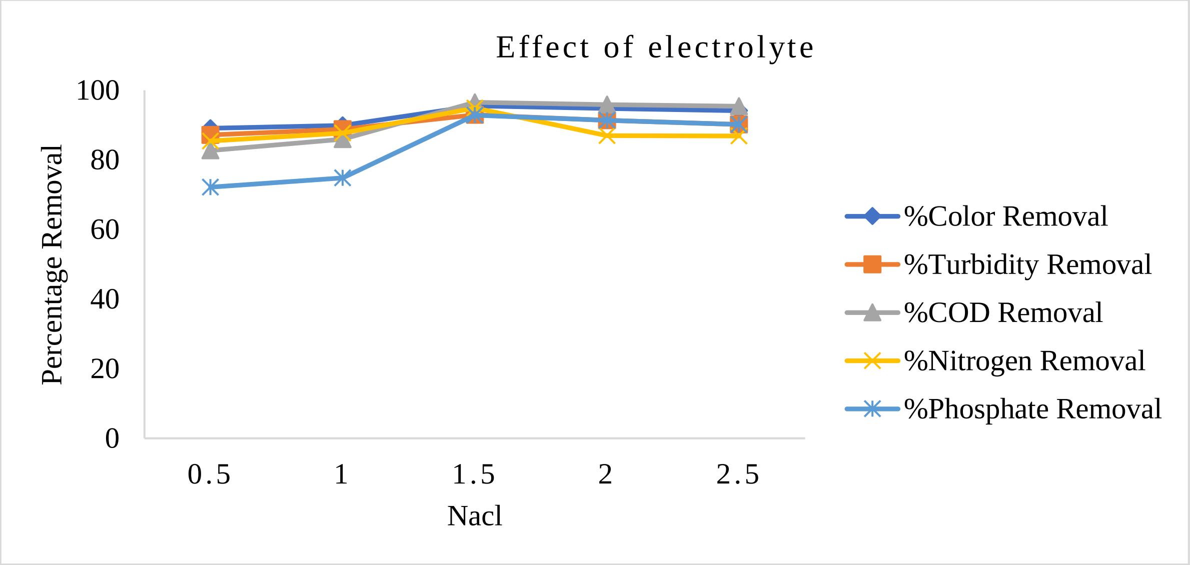


Figure 4-14 Effect of electrolyte concentration on removal efficiency by using NaCl

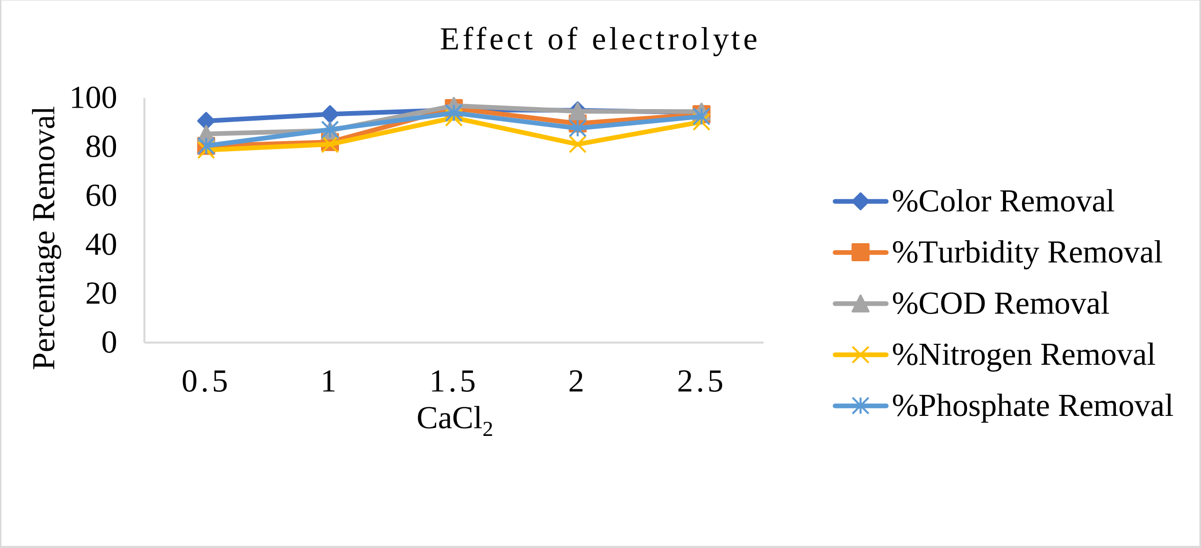


Figure 4-15 Effect of Electrolyte concentration on removal efficiency by Using $CaCl_2$

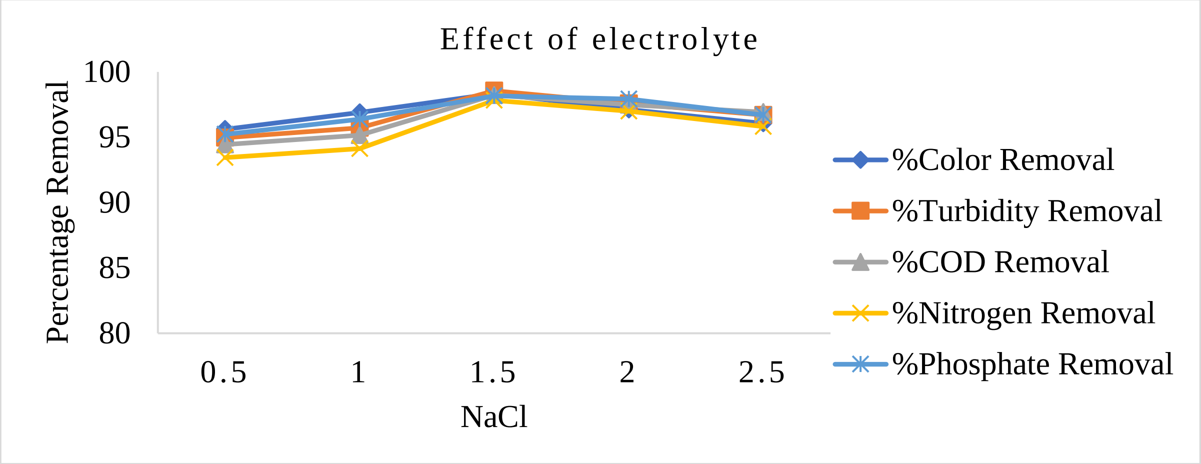


Figure 4-16 Effect of electrolyte on removal efficiency by using UV/H_2O_2 and NaCl

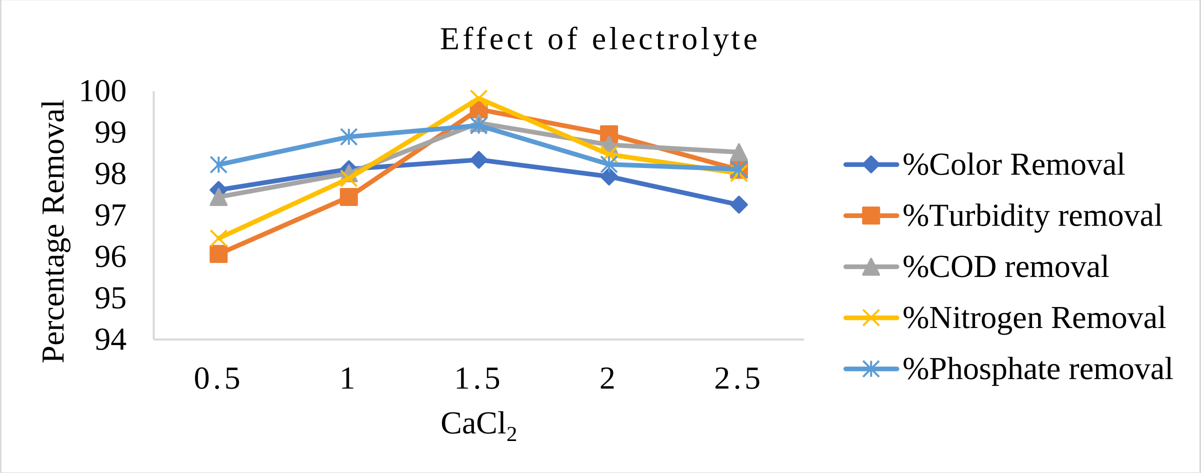


Figure 4-17 Effect of electrolyte on removal efficiency by using UV/H_2O_2 and $CaCl_2$

The percentage removal of color, COD, Nitrate, and Phosphate increased with an increase in dosage of g/l of electrolyte and maximum amount of electrolyte have no more significant with removal efficiency. in the current ampere; this is due to the oxidation of the organic compound did occur directly on the electrode surface.

4.2.6 Effect of ultraviolet light/hydrogen peroxide (UV/H_2O_2)

Because these coupled technologies might create synergistic effects for the removal of organic matter, ECO performance could be increased by pairing it with hydrogen peroxide (H_2O_2) and UV light (Alfonso-Muniozguren *et al.*, 2020b). The elimination of organic contaminants present in water from an advanced primary treatment (APT) was accomplished using both a batch photo-reactor and systems that processed samples with UV light and H_2O_2 variables. (Fernando *et al.*, 2014).

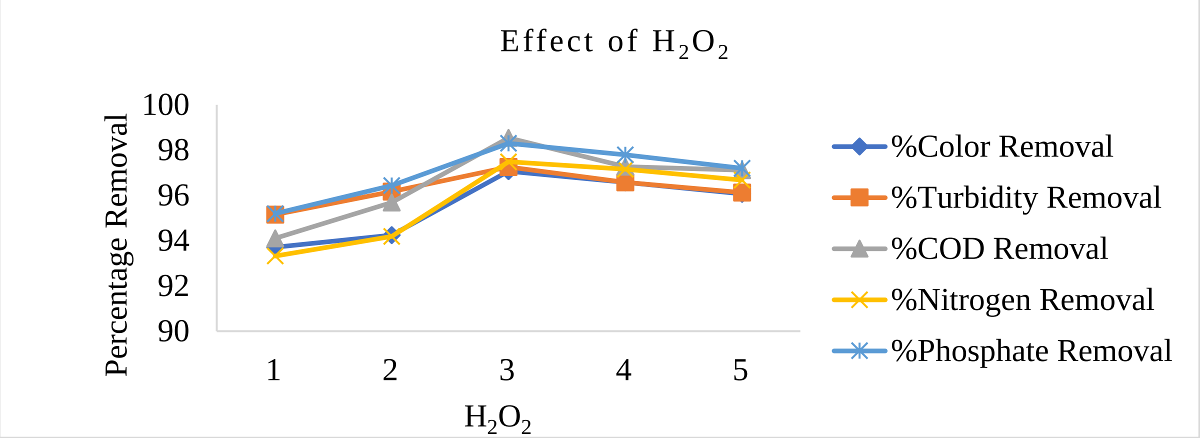


Figure 4-18 Effect of hydrogen peroxide on removal efficiency by using UV/H_2O_2 and NaCl

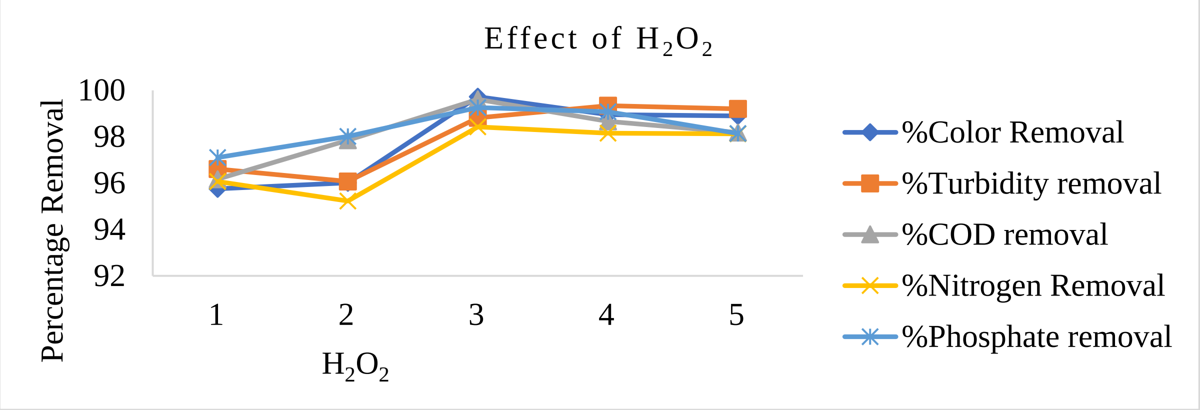


Figure 4-19 Effect of hydrogen peroxide on removal efficiency by using UV/ H_2O_2 and $CaCl_2$

In the photoelectrochemical experiments reactor was used, with a maximum capacity of 1 L of coffee processing waste water, it is equipped with a UV lamp; (model PUV-1022 Heraeus) which is 40cm length, with an emission spectrum in the region from 254 to 380 nm, 50 Watts, 220 Volts and 11.4 amperes of current. The photo-reactor has a demineralized coffee processing waste. Therefore, as dosage of hydrogen peroxide increase removal of organic substance and color also increases but after optimum value of dosage reached no more increase of removal efficiency.

4.2.7 The interaction effects

Two or three independent variables that have a significant impact on the study, as well as experimental parameters that were statistically developed using the CCD technique and investigated using various combinations of experimental parameters, are referred to as the interaction effect of input variables. Fisher's F-test and values of probability p determined the determination coefficient (R^2) of each coefficient; Small probability values ($p< 0.001$) suggest that the model was very significant and may be used to predict the response function, as illustrated in Tables 4-6 to 4-21.

The model was very significant and could be used to reliably predict the response function with a minimal probability value ($p < 0.001$). Multiple regressions were used to assess the research data. The coefficients were examined using analysis of variance, and the significance threshold was set at $p < 0.05$. Fischer’s F-value and p-value were used to determine the relevance of each model parameter. If the null hypothesis is true, the F-value is the test for comparing curvature variance with residual variance, and probability (p-value) is the probability of observing the observed F-value. The null hypothesis is rejected when the probability values are small, and the curvature is not significant. Therefore, the larger the value of F and the smaller the value of p, the more significant the corresponding coefficient

4.2.8 Synergistic effect

Four separate pretests were performed to examine the simultaneous influence of UV/H_2O_2 and electrochemical processes on removal efficiency. electrochemical oxidation, Photo-electrochemical oxidation using NaCl, and Photo-electrochemical oxidation using $CaCl_2$. Solution pH, reaction time, electrolyte concentration, and electric current value were used as operating parameters in all studies. Table 4-5 shows the highest COD, color, turbidity, nitrate, and phosphate removal efficiency.

In electrochemical oxidation, the anode undergoes oxidation while the cathode undergoes reduction. This focuses on an overview of electrochemical reactors for water and wastewater treatment.

An electrochemical system consists of at least two electrodes – an anode and a cathode – as well as an electrolyte-filled intermediate region. The system can be supplemented with reference electrodes for electrochemical characterizations (Muddemann *et al.*, 2019b). electrooxidation was found to have limitation in % removal, as the maximum pollution attenuation values, in terms of COD, color, turbidity, Nitrate and Phosphate. % removal was enhanced by applying UV/H_2O_2 on the electrochemical oxidation process.

Rajagopalan Venkatadri,(1993) States Some of the basic concepts about PECO to clarify the results in a higher removal efficiency than electrochemical oxidation as the followings.

- The hydroxyl radicals are possibly created inside the photochemical systems as: UV light /H_2O_2 (Fernando *et al.*, 2014)
- pH, temperature, contact time, and chemical reactivity are all factors that affect the efficiency of H_2O_2 treatment. In general, inorganics react faster with H_2O_2 than organics, with trace organics reacting the slowest due to mass transfer constraints. For large quantities of certain refractory materials, oxidation with H_2O_2 alone is ineffective. H_2O_2 is also used in the surface treatment sector to clean surfaces.
- H_2O_2 can be activated by UV light to create hydroxyl radicals, which are powerful oxidants. The activation of H_2O_2 by salts is used in oxidation processes. Advanced oxidation processes are those that are dependent on the formation of hydroxyl radical intermediates.

Aluminum electrode have a potential for complete oxidation, but also the durability and corrosion resistance of the electrode and the operating current densities.

In electrochemical cells for energy-saving operations, the reaction medium's ionic conductivity is a critical parameter. Current efficiency, applied cell voltage, and electrical energy consumption are all influenced by solution conductivity. When the ionic conductivity of the solution is low, more energy is required to overcome high ohmic resistance between the anode and cathode. The most frequent way for increasing solution conductivity is to add a small amount of supportive electrolyte, which minimizes energy consumption during electrochemical treatment. Energy usage is reduced as electrolyte concentration rises. This behavior could be explained by a rise in the reaction medium's ionic conductivity, as well as a decrease in electrical resistance and applied cell voltage. Energy consumption also increases dramatically with rising applied cell voltage, which has a direct effect on electric current (Fallahzadeh *et al.*, 2019b). Significant interactions between the experimental factors were confirmed by the surface plots, interaction plot and ANOVA.

4.3 Optimization by response surface methodology

The study of electrochemical parameters were statistically optimized using response surface methodology (RSM). RSM is a type of regression analysis that uses the controlled values of the independent variables to predict the value of a dependent variable. RSM was used to optimize an experimental parameter for a different process, which included an advanced oxidation process. It is a highly efficient procedure because it not only finds the optimum operating conditions to maximize a system's performance, but it also generates a response surface model that predicts a response based on a combination of factor levels. It also shows the relative magnitude and impact of various factors on the response and their interactions. As a result, they've been used to mimic a wide range of water and wastewater treatment systems and processes (Asaithambi and Matheswaran, 2016)

All laboratory findings were tabulated in Appendices- 1, which included influencing parameters and color absorbance at 450 nm wavelength, COD titration, phosphate and nitrate readings by spectrophotometer at 690 nm wave length, and turbidity readings by turbidimeter. The results of experiments in the form of removal rate of COD, color, turbidity, nitrate and phosphate for ECO and UV/H_2O_2 were as follows.

Optimization of the responses for determining optimized points for operational conditions and achieving the maximum removal percentage was performed by estimation models. To achieve the highest removal performance at operational conditions of independent variables, COD, color, turbidity, nitrate and phosphate removal percentage were selected at maximum value. As shown on figures 4-2 to 4-19 the target values of five independent variables including reaction time, solution pH, electric current, salt concentration and hydrogen peroxide were selected in in-range state. The values of optimal conditions for independent variables were obtained as follows: pH = 7, reaction time of 40 min, electric current of 0.4 ampere and salt concentration of 1.5 g/L and 3ml of H_2O_2. Under these conditions, the degree of desirability of the model was equal to 1, while the removal percentage of COD, color turbidity,

Table 4-5 Optimum value of pollutant removed by photo-electrochemical oxidation

Treatment designs	Major Pollutants	Coffee Wastewater Before Treated	Coffee Wastewater After Treated	Removal efficiency (%)	permissible WHO standard for effluents
ECO/Nacl	COD (mg/l)	7680	384.384	94.995	250 mg/l
	Color (abs)	2.95	0.261	91.165	50 TCU
	Turbidity (NTU)	144.5	5.966	95.871	300 NTU
	Nitrate (mg/l)	23.21	2.791	87.975	5 mg/l
	Phosphate (mg/l)	9.21	0.869	90.564	5 mg/l
ECO/$Cacl_2$	COD (mg/l)	7680	277.478	96.387	250 mg/l
	Color (abs)	2.95	0.122	95.856	50 TCU
	Turbidity (NTU)	144.5	3.565	97.533	300 NTU
	Nitrate (mg/l)	23.21	2.243	90.334	5 mg/l
	Phosphate (mg/l)	9.21	0.658	92.855	5 mg/l
ECO/ Nacl and UV/H_2O_2	COD (mg/l)	7680	92.467	98.796	250 mg/l
	Color (abs)	2.95	0.049	98.339	50 TCU
	Turbidity (NTU)	144.5	2.789	99.454	300 NTU
	Nitrate (mg/l)	23.21	0.259	98.886	5 mg/l
	Phosphate (mg/l)	9.21	0.090	99.022	5 mg/l
ECO/$Cacl_2$ and UV/H_2O_2	COD (mg/l)	7680	8.294	99.992	250 mg/l
	Color (abs)	2.95	0.003	99.898	50 TCU
	Turbidity (NTU)	144.5	1.11	99.922	300 NTU
	Nitrate (mg/l)	23.21	0.041	99.823	5 mg/l
	Phosphate (mg/l)	9.21	0.008	99.982	5 mg/l

The efficiency of photo-electrochemical oxidation is dependent on many factors, such as pH, electrolyte concentration, electrolysis time, current density, and H_2O_2. Optimization of these operating parameters is essential to maximize pollution attenuation. stirring during electro-oxidation and photoelectrochemical oxidation could provide enhanced oxidation by forming uniform solution.

4.3.1 Analysis of variance test

For graphical analyses of the data, analysis of variance (ANOVA) was employed to determine the interaction between the process factors and the response. The value of the correlation coefficient (R^2) was used to describe the quality of the fit polynomial model, and the F test was used to determine its statistical significance. The P value (probability) was used to evaluate model terms with a 95% confidence level. The analysis of variance (ANOVA) was used to examine the data; it is where descriptive statistics and statistical tests are presented. This test is used to investigate the impact of all factors on the intended response. ANOVA is a statistical method for testing hypotheses about the parameters of a model by dividing the total variance in a set of data into smaller groups and component portions linked with specific sources of variation (Bui, 2017). The experiments were carried out at random to avoid systemic error. The performance of independent variables is determined by the coefficients of the second-order model, which interpret the amount of removal of the researched parameters (responses) (factors). In surface response analysis, it seeks for low p-values to identify key terms in the model. The ANOVA findings for responses with probability values $p < 0.0500$ show that the second-order model is significant. 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.

I.ANOVA for the % removal of ECO quadratic model using NaCl

Table 4-6 ANOVA for the % Removal of COD by quadratic model using NaCl

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	118.76	14	8.48	21.97	< 0.0001	significant
A-PH	51.81	1	51.81	134.17	< 0.0001	
B-Time	1.82	1	1.82	4.71	0.0464	
C-Current	2.52	1	2.52	6.53	0.0219	
D-Electrolyte	4.74	1	4.74	12.26	0.0032	
AB	0.3125	1	0.3125	0.8093	0.3825	
AC	0.0826	1	0.0826	0.2139	0.6503	
AD	0.0678	1	0.0678	0.1756	0.6811	
BC	0.0034	1	0.0034	0.0088	0.9265	
BD	0.1843	1	0.1843	0.4772	0.5003	
CD	0.5955	1	0.5955	1.54	0.2334	
A^2	53.61	1	53.61	138.81	< 0.0001	
B^2	0.0200	1	0.0200	0.0519	0.8229	
C^2	0.0063	1	0.0063	0.0162	0.9004	
D^2	1.55	1	1.55	4.02	0.0632	
Residual	5.79	15	0.3862			
Lack of Fit	3.03	10	0.3032	0.5492	0.8036	not significant
Pure Error	2.76	5	0.5521			
Cor Total	124.55	29				

The model F-value of 21.97 indicates that the model is statistically significant. An F-value of this magnitude has a 0.01 percent chance of occurring due to noise. Model terms with P-values less than 0.0500 are significant. A, B, C, D, and A^2 are important model terms in this situation. The model terms are not important if the value is bigger than 0.1000. The F-value of 0.55 for the Lack of Fit indicates that it is not significant in comparison to the pure mistake. A significant Lack of Fit F-value has an 80.36 percent chance of occurring owing to noise.

Table 4-7 ANOVA for % removal of turbidity by quadratic model using NaCl

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	449.86	14	32.13	103.21	< 0.0001	significant
A-PH	232.98	1	232.98	748.32	< 0.0001	
B-Time	2.54	1	2.54	8.15	0.0121	
C-Current	5.75	1	5.75	18.46	0.0006	
D-Electrolyte	2.19	1	2.19	7.02	0.0182	
AB	0.2153	1	0.2153	0.6917	0.4186	
AC	0.4817	1	0.4817	1.55	0.2326	
AD	2.87	1	2.87	9.21	0.0084	
BC	0.4381	1	0.4381	1.41	0.2540	
BD	0.1910	1	0.1910	0.6134	0.4457	
CD	1.34	1	1.34	4.29	0.0559	
A^2	203.75	1	203.75	654.45	< 0.0001	
B^2	0.0626	1	0.0626	0.2011	0.6603	
C^2	0.0012	1	0.0012	0.0037	0.9521	
D^2	0.7190	1	0.7190	2.31	0.1494	
Residual	4.67	15	0.3113			
Lack of Fit	3.66	10	0.3662	1.82	0.2646	not significant
Pure Error	1.01	5	0.2016			
Cor Total	454.53	29				

The F-value for the model is 103.21, indicating that it is significant. Due to noise, an F-value of this magnitude has a 0.01 percent probability of occurring. Model terms are important when the -value is less than 0.0500. Significant model terms in this scenario are A, B, C, D, AD, and A^2. The model terms are not significant if their values exceed 0.1000. The F-value of 1.82 for the Lack of Fit indicates that it is not significant in comparison to the pure error.

A significant Lack of Fit F-value owing to noise has a 26.46 percent chance of occurring. a minor deficiency of fit is good.as want the model to fit is good.

Table 4-8 ANOVA for % removal of nitrate by quadratic model using NaCl

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1820.26	14	130.02	158.41	< 0.0001	significant
A-PH	143.19	1	143.19	174.46	< 0.0001	
B-Time	4.77	1	4.77	5.81	0.0292	
C-Current	3.77	1	3.77	4.59	0.0490	
D-Electrolyte	6.85	1	6.85	8.35	0.0112	
AB	1.19	1	1.19	1.45	0.2479	
AC	1.60	1	1.60	1.95	0.1830	
AD	0.7857	1	0.7857	0.9572	0.3434	
BC	0.0325	1	0.0325	0.0395	0.8451	
BD	0.0217	1	0.0217	0.0264	0.8730	
CD	0.0690	1	0.0690	0.0841	0.7758	
A^2	1643.99	1	1643.99	2002.93	< 0.0001	
B^2	2.97	1	2.97	3.62	0.0766	
C^2	0.1302	1	0.1302	0.1586	0.6961	
D^2	0.5550	1	0.5550	0.6761	0.4238	
Residual	12.31	15	0.8208			
Lack of Fit	7.26	10	0.7260	0.7186	0.6937	not significant
Pure Error	5.05	5	1.01			
Cor Total	1832.57	29				

The F-value for the model is 158.41, indicating that it is significant. An F-value of this magnitude has a 0.01 percent chance of being caused by noise. Model terms are significant if their P-values are less than 0.0500. Significant model terms in this example are A, B, C, D, and A^2. The model terms are not significant if their values exceed 0.1000. The F-value of 0.72 for the Lack of Fit indicates that it is not significant when compared to the pure error. A large Lack of Fit F-value owing to noise has a 69.37 percent chance of occurring.

Table 4-9 ANOVA for % removal of phosphate by quadratic model using NaCl

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	874.37	14	62.46	171.21	< 0.0001	significant
A-PH	275.96	1	275.96	756.49	< 0.0001	
B-Time	11.37	1	11.37	31.17	< 0.0001	
C-Current	2.22	1	2.22	6.09	0.0262	
D-Electrolyte	1.67	1	1.67	4.58	0.0493	
AB	1.55	1	1.55	4.26	0.0569	
AC	1.05	1	1.05	2.89	0.1100	
AD	0.0015	1	0.0015	0.0041	0.9495	
BC	0.0449	1	0.0449	0.1230	0.7306	
BD	0.0407	1	0.0407	0.1114	0.7431	
CD	0.5076	1	0.5076	1.39	0.2565	
A^2	580.95	1	580.95	1592.54	< 0.0001	
B^2	11.61	1	11.61	31.83	< 0.0001	
C^2	4.92	1	4.92	13.49	0.0023	
D^2	2.13	1	2.13	5.85	0.0288	
Residual	5.47	15	0.3648			
Lack of Fit	2.74	10	0.2743	0.5024	0.8342	not significant
Pure Error	2.73	5	0.5459			
Cor Total	879.85	29				

The F-value of 171.21 for the model indicates that it is significant. Noise-values smaller than 0.0500 suggest that model terms are important, therefore an F-value this large has a 0.01 percent chance of occurring. A, B, C, D, A^2, B^2, C^2, D^2 are important model terms in this situation. The model terms are not important if the value is bigger than 0.1000. The F-value of 0.50 for the Lack of Fit indicates that the Lack of Fit is not significant in comparison to the pure mistake.

II.ANOVA for the % removal of ECO quadratic model using $CaCl_2$

Table 4-10 ANOVA for % removal of COD by quadratic model using $CaCl_2$

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	174.37	14	12.45	118.74	< 0.0001	significant
A-PH	65.16	1	65.16	621.18	< 0.0001	
B-Time	1.26	1	1.26	12.03	0.0034	
C-Current	1.76	1	1.76	16.81	0.0009	
D-Electrolyte	3.12	1	3.12	29.71	< 0.0001	
AB	0.0077	1	0.0077	0.0733	0.7902	
AC	0.5320	1	0.5320	5.07	0.0397	
AD	1.34	1	1.34	12.79	0.0028	
BC	1.81	1	1.81	17.21	0.0009	
BD	1.63	1	1.63	15.54	0.0013	
CD	0.1552	1	0.1552	1.48	0.2427	
A^2	101.28	1	101.28	965.50	< 0.0001	
B^2	1.20	1	1.20	11.41	0.0041	
C^2	0.3099	1	0.3099	2.95	0.1062	
D^2	0.0039	1	0.0039	0.0370	0.8501	
Residual	1.57	15	0.1049			
Lack of Fit	1.40	10	0.1396	3.93	0.0721	not significant
Pure Error	0.1776	5	0.0355			
Cor Total	175.94	29				

The model F-value of 118.74 indicates that the model is statistically significant. Noise-values smaller than 0.0500 suggest that model terms are important, therefore an F-value this large has a 0.01 percent chance of occurring. A, B, C, D, AC, AD, BC, BD, A^2, B^2 are important model terms in this situation. With a Lack of Fit F-value of 3.93, there's a 7.21 percent possibility that a significant Lack of Fit F-value is due to noise.

Table 4-11 ANOVA for % removal of color by quadratic model using $CaCl_2$

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	950.33	14	67.88	136.34	< 0.0001	significant
A-PH	322.80	1	322.80	648.37	< 0.0001	
B-Time	4.55	1	4.55	9.13	0.0086	
C-Current	12.09	1	12.09	24.28	0.0002	
D-Electrolyte	2.55	1	2.55	5.13	0.0387	
AB	0.0146	1	0.0146	0.0294	0.8662	
AC	0.1608	1	0.1608	0.3230	0.5782	
AD	0.3435	1	0.3435	0.6899	0.4192	
BC	0.0670	1	0.0670	0.1345	0.7189	
BD	0.1067	1	0.1067	0.2144	0.6500	
CD	1.18	1	1.18	2.38	0.1441	
A^2	599.21	1	599.21	1203.58	< 0.0001	
B^2	3.02	1	3.02	6.06	0.0264	
C^2	2.98	1	2.98	5.99	0.0272	
D^2	3.15	1	3.15	6.34	0.0237	
Residual	7.47	15	0.4979			
Lack of Fit	6.16	10	0.6161	2.36	0.1781	not significant
Pure Error	1.31	5	0.2614			
Cor Total	957.79	29				

The F-value of 136.34 for the model indicates that it is significant. An F-value of this magnitude has a 0.01 percent chance of occurring due to noise. Model terms with P-values less than 0.0500 are significant. A, B, C, D, A^2, B^2, C^2, D^2 are important model terms in this situation. The F-value of 2.36 for the Lack of Fit indicates that it is not significant in comparison to the pure error. Due to noise, a significant Lack of Fit F-value has a 17.81 percent chance of occurring.

Table 4-12 ANOVA for % removal of nitrate by quadratic model using $CaCl_2$

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1719.42	14	122.82	525.08	< 0.0001	significant
A-PH	199.74	1	199.74	853.94	< 0.0001	
B-Time	7.22	1	7.22	30.87	< 0.0001	
C-Current	1.63	1	1.63	6.98	0.0185	
D-Electrolyte	2.30	1	2.30	9.81	0.0068	
AB	0.0680	1	0.0680	0.2907	0.5977	
AC	0.2866	1	0.2866	1.23	0.2858	
AD	2.21	1	2.21	9.44	0.0077	
BC	0.0866	1	0.0866	0.3701	0.5520	
BD	0.0233	1	0.0233	0.0997	0.7566	
CD	2.52	1	2.52	10.77	0.0050	
A^2	1500.20	1	1500.20	6413.85	< 0.0001	
B^2	2.18	1	2.18	9.34	0.0080	
C^2	0.0240	1	0.0240	0.1027	0.7530	
D^2	1.22	1	1.22	5.20	0.0376	
Residual	3.51	15	0.2339			
Lack of Fit	2.09	10	0.2087	0.7343	0.6838	not significant
Pure Error	1.42	5	0.2842			
Cor Total	1722.93	29				

The 525.08 model F-value indicates that the model is significant. Noise-values smaller than 0.0500 suggest that model terms are important, therefore an F-value this large has a 0.01 percent chance of occurring. A, B, C, D, AD, CD, A^2, B^2, D^2 are important model terms in this situation. The F-value for Lack of Fit is 0.73, indicating that the lack of fit is not significant in comparison to the pure error. There's a 68.38 percent likelihood that a significant Lack of Fit F-value is caused by noise. Non-significant lack of fit is good.

Table 4-13 ANOVA for % removal of phosphates by quadratic model using $CaCl_2$

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	931.59	14	66.54	140.11	< 0.0001	significant
A-PH	333.30	1	333.30	701.80	< 0.0001	
B-Time	8.87	1	8.87	18.68	0.0006	
C-Current	5.98	1	5.98	12.58	0.0029	
D-Electrolyte	3.63	1	3.63	7.64	0.0145	
AB	0.9919	1	0.9919	2.09	0.1690	
AC	0.0502	1	0.0502	0.1056	0.7497	
AD	0.6224	1	0.6224	1.31	0.2703	
BC	0.8609	1	0.8609	1.81	0.1982	
BD	0.0023	1	0.0023	0.0049	0.9450	
CD	0.0014	1	0.0014	0.0030	0.9573	
A^2	575.31	1	575.31	1211.40	< 0.0001	
B^2	17.60	1	17.60	37.06	< 0.0001	
C^2	7.14	1	7.14	15.03	0.0015	
D^2	0.3576	1	0.3576	0.7529	0.3992	
Residual	7.12	15	0.4749			
Lack of Fit	4.74	10	0.4743	0.9961	0.5368	not significant
Pure Error	2.38	5	0.4761			
Cor Total	938.72	29				

The model F-value of 140.11 indicates that the model is statistically significant. Due to noise, an F-value this large has a 0.01 percent probability of occurring. Model terms with P-values less than 0.0500 are considered significant. A, B, C, D, A^2, B^2, C^2 are crucial model terms in this situation. The F-value of 1.00 for the Lack of Fit indicates that the Lack of Fit is not significant in comparison to the pure mistake. A significant Lack of Fit F-value has a 53.68 percent likelihood of being caused by noise. Non-significant lack of fit is good.

III.ANOVA for the % removal for combination of NaCl/UV/H_2O_2 and quadratic model

Table 4-14 ANOVA for % Removal of COD by quadratic model using UV/$H_2O_2$and NaCl

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	245.38	20	12.27	14.07	< 0.0001	significant
A-PH	46.17	1	46.17	52.97	< 0.0001	
B-Time	3.34	1	3.34	3.83	0.0108	
C-Current	4.58	1	4.58	5.26	0.0299	
D-Electrolyte	5.24	1	5.24	6.02	0.0209	
E-H_2O_2	3.61	1	3.61	4.14	0.0519	
AB	0.1716	1	0.1716	0.1969	0.6608	
AC	5.75	1	5.75	6.60	0.0160	
AD	0.1696	1	0.1696	0.1945	0.6627	
AE	0.2396	1	0.2396	0.2748	0.6044	
BC	0.2209	1	0.2209	0.2535	0.6187	
BD	0.4991	1	0.4991	0.5726	0.4558	
BE	0.3459	1	0.3459	0.3968	0.5340	
CD	0.0689	1	0.0689	0.0791	0.7807	
CE	0.3411	1	0.3411	0.3913	0.5369	
DE	0.7876	1	0.7876	0.9035	0.3503	
A^2	114.22	1	114.22	131.03	< 0.0001	
B^2	0.0052	1	0.0052	0.0060	0.9388	
C^2	1.47	1	1.47	1.69	0.2046	
D^2	0.0138	1	0.0138	0.0158	0.9008	
E^2	1.19	1	1.19	1.36	0.2537	
Residual	23.54	27	0.8717			
Lack of Fit	20.28	21	0.9658	1.78	0.2442	not significant
Pure Error	3.25	6	0.5424			
Cor Total	268.92	47				

The model F-value of 14.07 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, C, D, AC, A^2 are significant model terms. The Lack of Fit F-value of 1.78 implies the Lack of Fit is not significant relative to the pure error.

Table 4-15 ANOVA for % removal of turbidity by quadratic model using UV/$H_2O_2$and NaCl

Source	SS	df	Mean Square	F-value	p-value	
Model	121.81	20	6.09	44.66	< 0.0001	significant
A-PH	39.99	1	39.99	293.22	< 0.0001	
B-Time	1.20	1	1.20	8.80	0.0062	
C-Current	0.8642	1	0.8642	6.34	0.0181	
D-Electrolyte	1.48	1	1.48	10.88	0.0027	
E-H_2O_2	0.8264	1	0.8264	6.06	0.0205	
AB	0.0036	1	0.0036	0.0261	0.8729	
AC	0.0370	1	0.0370	0.2710	0.6069	
AD	0.5793	1	0.5793	4.25	0.0491	
AE	0.0762	1	0.0762	0.5585	0.4613	
BC	0.0047	1	0.0047	0.0346	0.8538	
BD	0.0042	1	0.0042	0.0306	0.8623	
BE	0.2739	1	0.2739	2.01	0.1679	
CD	0.0588	1	0.0588	0.4312	0.5169	
CE	0.6802	1	0.6802	4.99	0.0340	
DE	0.4139	1	0.4139	3.03	0.0929	
A^2	51.97	1	51.97	381.05	< 0.0001	
B^2	0.0841	1	0.0841	0.6170	0.4390	
C^2	0.2961	1	0.2961	2.17	0.1522	
D^2	0.0114	1	0.0114	0.0838	0.7744	
E^2	0.0781	1	0.0781	0.5727	0.4557	
Residual	3.68	27	0.1364			
Lack of Fit	3.27	21	0.1557	2.27	0.1570	not significant
Pure Error	0.4121	6	0.0687			
Cor Total	125.49	47				

The 44.66 model F-value indicates that the model is significant. An F-value of this magnitude has a 0.01 percent chance of occurring due to noise. Model terms with P-values less than 0.0500 are significant. A, B, C, D, E, AD, CE, and A^2 are important model terms in this situation. The F-value of 2.27 for the Lack of Fit indicates that it is not significant.

Table 4-16ANOVA for % Removal of Nitrate by quadratic model using UV/$H_2O_2$and NaCl

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1497.04	20	74.85	117.82	< 0.0001	significant
A-PH	951.21	1	951.21	1497.24	< 0.0001	
B-Time	3.63	1	3.63	5.72	0.0240	
C-Current	2.72	1	2.72	4.29	0.0481	
D-Electrolyte	3.22	1	3.22	5.07	0.0327	
E-H_2O_2	3.73	1	3.73	5.88	0.0223	
AB	2.20	1	2.20	3.46	0.0737	
AC	0.4053	1	0.4053	0.6379	0.4314	
AD	7.74	1	7.74	12.19	0.0017	
AE	0.8534	1	0.8534	1.34	0.2566	
BC	1.40	1	1.40	2.20	0.1493	
BD	0.6951	1	0.6951	1.09	0.3048	
BE	0.0991	1	0.0991	0.1559	0.6960	
CD	1.05	1	1.05	1.65	0.2100	
CE	0.0091	1	0.0091	0.0144	0.9054	
DE	3.25	1	3.25	5.11	0.0320	
A^2	354.68	1	354.68	558.27	< 0.0001	
B^2	0.6146	1	0.6146	0.9674	0.3341	
C^2	0.1418	1	0.1418	0.2231	0.6405	
D^2	0.5437	1	0.5437	0.8558	0.3631	
E^2	0.4877	1	0.4877	0.7676	0.3887	
Residual	17.15	27	0.6353			
Lack of Fit	13.70	21	0.6522	1.13	0.4759	not significant
Pure Error	3.46	6	0.5762			
Cor Total	1514.19	47				

The model F-value of 117.82 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, E, AD, DE, A^2 are significant model termsThe Lack of Fit F-value of 1.13 implies the Lack of Fit is not significant relative to the pure error. There is a 47.59% chance that a Lack of Fit F-value this large could occur due to noise.

Table 4-17 ANOVA for % removal of phosphate by quadratic model using UV/H_2O_2/ NaCl

Source	SS	df	Mean Square	F-value	p-value	
Model	233.11	20	11.66	59.75	< 0.0001	significant
A-PH	137.71	1	137.71	705.93	< 0.0001	
B-Time	1.69	1	1.69	8.67	0.0066	
C-Current	0.9969	1	0.9969	5.11	0.0321	
D-Electrolyte	1.09	1	1.09	5.59	0.0255	
E-H_2O_2	1.14	1	1.14	5.86	0.0225	
AB	2.40	1	2.40	12.28	0.0016	
AC	0.4133	1	0.4133	2.12	0.1570	
AD	2.64	1	2.64	13.54	0.0010	
AE	0.0060	1	0.0060	0.0306	0.8623	
BC	0.0045	1	0.0045	0.0233	0.8799	
BD	0.3388	1	0.3388	1.74	0.1986	
BE	0.9261	1	0.9261	4.75	0.0382	
CD	0.0032	1	0.0032	0.0163	0.8992	
CE	1.35	1	1.35	6.91	0.0140	
DE	0.0202	1	0.0202	0.1035	0.7501	
A^2	58.79	1	58.79	301.34	< 0.0001	
B^2	1.45	1	1.45	7.46	0.0110	
C^2	0.0193	1	0.0193	0.0991	0.7553	
D^2	0.0019	1	0.0019	0.0096	0.9229	
E^2	0.1363	1	0.1363	0.6985	0.4106	
Residual	5.27	27	0.1951			
Lack of Fit	4.19	21	0.1996	1.11	0.4861	not significant
Pure Error	1.08	6	0.1794			
Cor Total	238.38	47				

The model F-value of 59.75 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, E, AB, AD, BE, CE, A^2, B^2 are significant model terms. The Lack of Fit F-value of 1.11 implies the Lack of Fit is not significant.

V. ANOVA of % Removal for combination of $CaCl_2/UV/H_2O_2$ and quadratic model

Table 4-18 ANOVA for % Removal of COD by quadratic model using UV/H_2O_2 and $CaCl_2$

Source	SS	df	Mean Square	F-value	p-value	
Model	261.47	20	13.07	13.40	< 0.0001	significant
A-PH	46.17	1	46.17	47.34	< 0.0001	
B-Time	4.47	1	4.47	4.58	0.0415	
C-Current	4.48	1	4.48	4.59	0.0413	
D-Electrolyte	5.24	1	5.24	5.38	0.0282	
E-H_2O_2	4.85	1	4.85	4.97	0.0343	
AB	0.1716	1	0.1716	0.1759	0.6782	
AC	5.75	1	5.75	5.90	0.0221	
AD	0.1696	1	0.1696	0.1738	0.6800	
AE	0.2396	1	0.2396	0.2456	0.6242	
BC	0.2768	1	0.2768	0.2837	0.5986	
BD	0.4991	1	0.4991	0.5117	0.4806	
BE	0.3459	1	0.3459	0.3546	0.5565	
CD	0.0689	1	0.0689	0.0707	0.7924	
CE	0.3411	1	0.3411	0.3497	0.5592	
DE	0.7876	1	0.7876	0.8075	0.3768	
A^2	125.09	1	125.09	128.24	< 0.0001	
B^2	0.1012	1	0.1012	0.1037	0.7499	
C^2	1.55	1	1.55	1.59	0.2179	
D^2	0.0117	1	0.0117	0.0120	0.9135	
E^2	0.2206	1	0.2206	0.2261	0.6382	
Residual	26.34	27	0.9754			
Lack of Fit	22.59	21	1.08	1.72	0.2581	not significant
Pure Error	3.75	6	0.6243			
Cor Total	287.80	47				

The F-value of 13.40 for the model indicates that it is significant. An F-value of this magnitude has a 0.01 percent chance of occurring due to noise. Model terms with P-values less than 0.0500 are significant. A, B, C, D, E, AC, and A^2 are important model terms in this situation. The F-value of 1.72 for the Lack of Fit indicates that it is not significant in comparison to the pure error. A significant Lack of Fit F-value has a 25.81 percent chance of occurring owing to noise.

Table 4-19 ANOVA for % Removal of Turbidity by quadratic model using UV/$H_2O_2$and $CaCl_2$

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	121.81	20	6.09	44.66	< 0.0001	significant
A-PH	39.99	1	39.99	293.22	< 0.0001	
B-Time	1.20	1	1.20	8.80	0.0062	
C-Current	0.8642	1	0.8642	6.34	0.0181	
D-Electrolyte	1.48	1	1.48	10.88	0.0027	
E-H_2O_2	0.8264	1	0.8264	6.06	0.0205	
AB	0.0036	1	0.0036	0.0260	0.8730	
AC	0.0370	1	0.0370	0.2710	0.6069	
AD	0.5793	1	0.5793	4.25	0.0491	
AE	0.0762	1	0.0762	0.5584	0.4614	
BC	0.0047	1	0.0047	0.0346	0.8537	
BD	0.0042	1	0.0042	0.0306	0.8624	
BE	0.2739	1	0.2739	2.01	0.1679	
CD	0.0588	1	0.0588	0.4312	0.5170	
CE	0.6802	1	0.6802	4.99	0.0340	
DE	0.4140	1	0.4140	3.04	0.0929	
A^2	51.97	1	51.97	381.05	< 0.0001	
B^2	0.0842	1	0.0842	0.6170	0.4390	
C^2	0.2961	1	0.2961	2.17	0.1522	
D^2	0.0114	1	0.0114	0.0838	0.7744	
E^2	0.0781	1	0.0781	0.5727	0.4558	
Residual	3.68	27	0.1364			
Lack of Fit	3.27	21	0.1557	2.27	0.1569	not significant
Pure Error	0.4121	6	0.0687			
Cor Total	125.49	47				

The F-value of 44.66 for the model indicates that it is significant. An F-value of this magnitude has a 0.01 percent chance of being caused by noise. Model terms are significant if their P-values are less than 0.0500. Significant model terms in this scenario are A, B, C, D, E, AD, CE, and A^2. The F-value of 2.27 for Lack of Fit indicates that it is not significant in comparison to the pure error. A large Lack of Fit F-value owing to noise has a 15.69 percent chance of occurring.

Table 4-20 ANOVA for % removal of nitrate by quadratic model using UV/$H_2O_2$and $CaCl_2$

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1492.43	20	74.62	118.32	< 0.0001	significant
A-PH	951.21	1	951.21	1508.28	< 0.0001	
B-Time	3.63	1	3.63	5.76	0.0235	
C-Current	2.72	1	2.72	4.32	0.0473	
D-Electrolyte	3.22	1	3.22	5.11	0.0321	
E-H_2O_2	3.37	1	3.37	5.35	0.0286	
AB	2.20	1	2.20	3.49	0.0727	
AC	0.4053	1	0.4053	0.6426	0.4298	
AD	7.74	1	7.74	12.28	0.0016	
AE	0.8534	1	0.8534	1.35	0.2549	
BC	1.40	1	1.40	2.22	0.1478	
BD	0.6951	1	0.6951	1.10	0.3031	
BE	0.0991	1	0.0991	0.1571	0.6950	
CD	1.05	1	1.05	1.66	0.2083	
CE	0.0091	1	0.0091	0.0145	0.9051	
DE	3.25	1	3.25	5.15	0.0314	
A^2	350.81	1	350.81	556.25	< 0.0001	
B^2	0.6146	1	0.6146	0.9745	0.3323	
C^2	0.1418	1	0.1418	0.2248	0.6392	
D^2	0.5437	1	0.5437	0.8621	0.3614	
E^2	0.8068	1	0.8068	1.28	0.2680	
Residual	17.03	27	0.6307			
Lack of Fit	13.69	21	0.6518	1.17	0.4565	not significant
Pure Error	3.34	6	0.5568			
Cor Total	1509.46	47				

The model F-value of 118.32 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, E, AD, DE, A^2 are significant model terms. The Lack of Fit F-value of 1.17 implies the Lack of Fit is not significant relative to the pure error. There is a 45.65% chance that a Lack of Fit F-value this large could occur due to noise.

Table 4-21 ANOVA for % removal of phosphate by quadratic model using UV/$H_2O_2$and $CaCl_2$

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	233.11	20	11.66	59.75	< 0.0001	significant
A-PH	137.71	1	137.71	705.93	< 0.0001	
B-Time	1.69	1	1.69	8.67	0.0066	
C-Current	0.9970	1	0.9970	5.11	0.0321	
D-Electrolyte	1.09	1	1.09	5.59	0.0255	
E-H_2O_2	1.14	1	1.14	5.86	0.0225	
AB	2.40	1	2.40	12.28	0.0016	
AC	0.4133	1	0.4133	2.12	0.1570	
AD	2.64	1	2.64	13.54	0.0010	
AE	0.0060	1	0.0060	0.0306	0.8624	
BC	0.0045	1	0.0045	0.0233	0.8799	
BD	0.3388	1	0.3388	1.74	0.1986	
BE	0.9261	1	0.9261	4.75	0.0382	
CD	0.0032	1	0.0032	0.0164	0.8992	
CE	1.35	1	1.35	6.91	0.0140	
DE	0.0202	1	0.0202	0.1036	0.7500	
A^2	58.79	1	58.79	301.34	< 0.0001	
B^2	1.45	1	1.45	7.46	0.0110	
C^2	0.0193	1	0.0193	0.0991	0.7553	
D^2	0.0019	1	0.0019	0.0096	0.9229	
E^2	0.1363	1	0.1363	0.6985	0.4106	
Residual	5.27	27	0.1951			
Lack of Fit	4.19	21	0.1996	1.11	0.4861	not significant
Pure Error	1.08	6	0.1794			
Cor Total	238.38	47				

The model F-value of 59.75 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise-values less than 0.0500 indicate model terms are significant. In this case A, B, C, D, E, AB, AD, BE, CE, A^2, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy). The Lack of Fit F-value of 1.11 implies the Lack of Fit is not significant relative to the pure error. There is a 48.61% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

4.3.2 Fit statistics

ANOVA was used to determine the statistical significance of the model equation and model terms. According to Jamali (2018), determination coefficients (R^2 and Adj. R^2) were used to control the model fitting quality, while the Fischer test was used to control the statistical significance (F-test). The resulting model was validated using predicted R-squares (R^2), which uses the leave-one-out technique to evaluate the model's prediction power given new observations. The correlation between experimental and expected responses is quantified using coefficients (R^2). The coefficient of determination (R^2) is the ratio of total changes in the expected response by the model variables. shows the sum of squares regression (SSR) to the total sum of squares (SST) ratio. Largeness of R^2 and its closeness to 1 is desirable and a desired correspondence with adjusted R^2 (Adj.R^2) is necessary. The quality of fitness of second-order polynomial model is 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^2adj. The large value of the correlation coefficient $R^2 = 0.9535$ indicated a high reliability of the model in predicting of removal percentages, by which 95.35% of the response variability can be explained by the model. All of the R^2 values in this investigation were greater than 0.9. According to Mirhosseini *et al*,(2009), R^2 should be at least 0.8 for a satisfactory model fitness. According to Bashir *et al.,* (2010), high R^2 values indicate a high level of agreement between experimental data and model-estimated data. As a result, in this investigation, strong R^2 values and their agreement with Adj.R^2 indicate that the model is highly significant. The “signal-to-noise ratio” index is provided in Table 4-22 to 4-25 as Adequate precision (AP). To put it another way, AP compares the projected range of values at design points to the mean prediction error. Model summary for Color, turbidity, nitrate and phosphate were available under: appendix -2

Table 4-22 Model summary for% COD removals using NaCl

Std. Dev.	0.6214	R^2	0.9535
Mean	92.59	Adjusted R^2	0.9101
C.V. %	0.6712	Predicted R^2	0.8330
		Adeq Precision	14.6749

The Predicted R^2 of 0.8330 is in reasonable agreement with the Adjusted R^2 of 0.9101; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. ratio of 14.675 indicates an adequate signal. This model can be used to navigate the design space.

Table 4-23 Model summary for% COD removals using $CaCl_2$

Std. Dev.	0.3239	R^2	0.9911
Mean	93.39	Adjusted R^2	0.9827
C.V. %	0.3468	Predicted R^2	0.9465
		Adeq Precision	35.1243

The Predicted R^2 of 0.9465 is in reasonable agreement with the Adjusted R^2 of 0.9827; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. ratio of 35.124 indicates an adequate signal.

Table 4-24 Model summary for % COD removals using combination NaCl and UV/H_2O_2

Std. Dev.	0.9337	R^2	0.9125
Mean	94.86	Adjusted R^2	0.8476
C.V. %	0.9842	Predicted R^2	0.6955
		Adeq Precision	12.4325

The Predicted R^2 of 0.6955 is in reasonable agreement with the Adjusted R^2 of 0.8476; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater

than 4 is desirable. ratio of 12.432 indicates an adequate signal. This model can be used to navigate the design space.

Table 4-25 Model summary for % COD removals using combination $CaCl_2$ and UV/H_2O_2

Std. Dev.	0.9876	R^2	0.9085
Mean	95.57	Adjusted R^2	0.8407
C.V. %	1.03	Predicted R^2	0.6837
		Adeq Precision	11.8832

The Predicted R^2 of 0.6837 is in reasonable agreement with the Adjusted R^2 of 0.8407; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. ratio of 11.883 indicates an adequate signal.

In general, the high squared correlation coefficient (R^2) for all models in both ECO and ECO with UV/H_2O_2 suggested that the models could explain the complete variation. The modified R^2 vouched for the models' high significance, and the low coefficient of variation (2%) in all of them demonstrated good precision and dependability of the experiments. High R^2 and R^2 adj values suggested that operating parameters such as current, time, pH, electrolyte, and H_2O_2 dose have a considerable impact on COD, color, turbidity, nitrate, and phosphorus removal (Sharma and Simsek, 2020b).

4.3.3 Effects of model parameters and their interactions

The most useful way in disclosing the conditions of the reaction system is to employ 3D surfaces and 2D contour plots, which are graphical representations of the regression equation for the optimization of reaction conditions. They're also used to see how each variable affects answers. The response functions of two elements are depicted in such quadratic model plots by varying within the experimental ranges while all other factors are kept constant at their values. From the results, it was observed that in all the combined process variables showed the significant effect on the color, COD, turbidity, Nitrate and Phosphate removal with their power consumption in treatment process. 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 are presented in Figure below which shows the relationship between removal efficiency and factors

4.3.3.1 Effects of interractions for ECO/$Cacl_2$ Combination with UV/H_2O_2

Effect of interaction is were more than two independent variables affect positively or negatively the efficiency of pollution removal in coffee processing waste water. Some interaction effects are shown in 3D diagram from Fig 4-20 to 4-24

a. Interaction of PH and Current

As indicated on Fig 4-20 by 3D graph the removal COD efficiency was low at pH 5 and by increasing, high at neutral pH which is indicated by red color and when the amount of current is about 0.4Amp. So, the interaction effect of pH and Current was significant.

Sharma and Simsek, (2020b) shows that the initial pH and current density had a substantial interaction in the removal of COD in ECO as the current density was increased and the pH increased from 4 acidic to neutral 7.It was also shown that increasing pH without increasing current density had little effect on COD elimination.

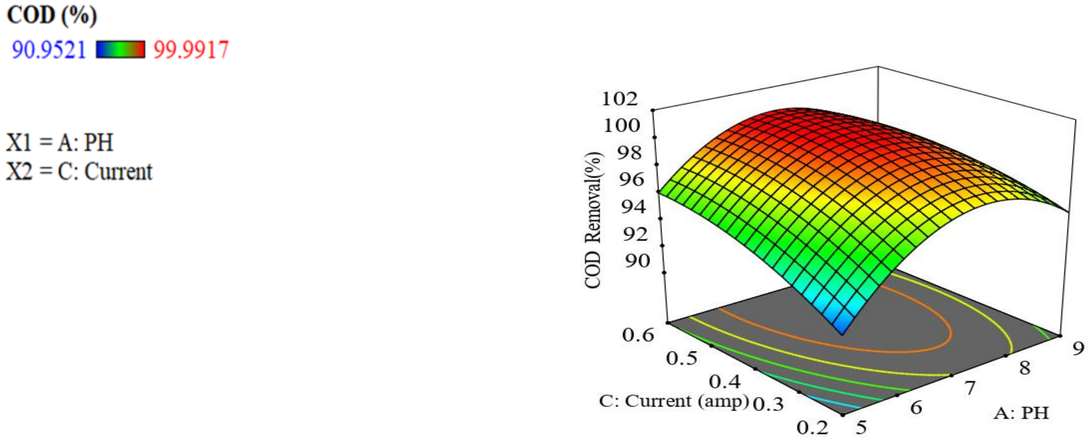


Figure 4-20 Interaction effect of PH with Current plots for % removal of COD, by combination of ECO with UV/H_2O_2 using $CaCl_2$

b. Interaction of Current and time.

This 3D figure shows the color removal efficiency was high at 0.4amp which is indicated by red color and when the time is 40min. increasing time up to the center of graph and increasing time in the same way it comes to the red color where shows the high removal efficient; terminal points indicated by green color shows lower removal efficiency, so, the interaction effect of current and time was significant.

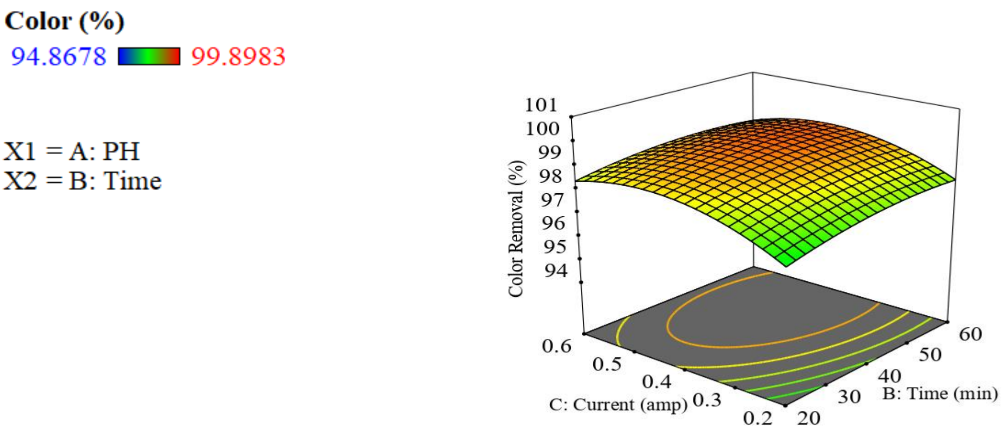


Figure 4-21 Interaction effect time with PH plot for % removal of Color by combination of ECO with UV/H_2O_2 usingCaCl$_2$

c. Interaction of H_2O_2 and Current

This 3D figure shows the Turbidity removal efficiency was maximum when volume of H_2O_2 reaches 3ml and current around 0.4 amp but at corner of the graph were indicated by yellow color i.e., at dosage of hydrogen peroxide 5ml and current 0.6 there is a minimum removal.so maximum dosage and maximum current leads to decrease in removal efficiency. Us understood from the result interaction of H_2O_2 and current have significant on turbidity removal.

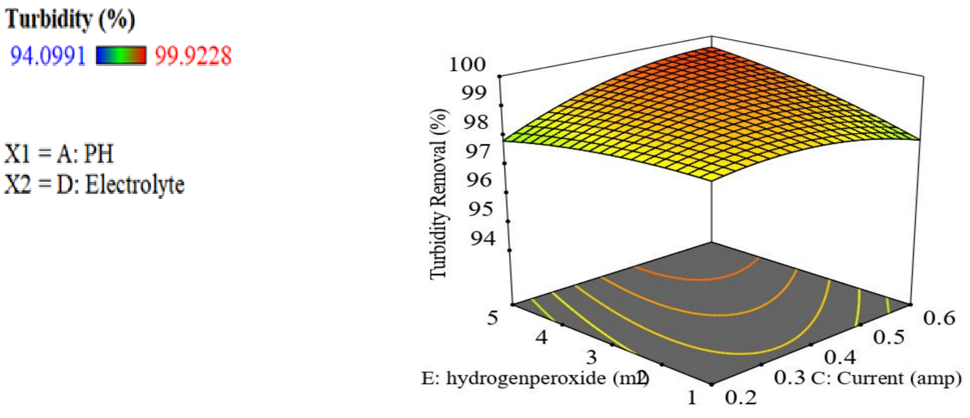


Figure 4 22 Interaction effect electrolyte with PH plot for % removal of turbidity by combination of ECO with UV/ usingCaCl$_2$

d. Interaction of PH and electrolyte

This graph shows NO_3 removal efficiency was increasing when moved from lower pH to higher PH; then maximum removal at neutral were indicated by more red color, however it decreases around maximum pH. Also, it shows little increasing in removal efficiency from small dosage of electrolyte to the maximum and then decrease at maximum dosage. interaction effect of pH and electrolyte have a little significant in nitrate removal process.

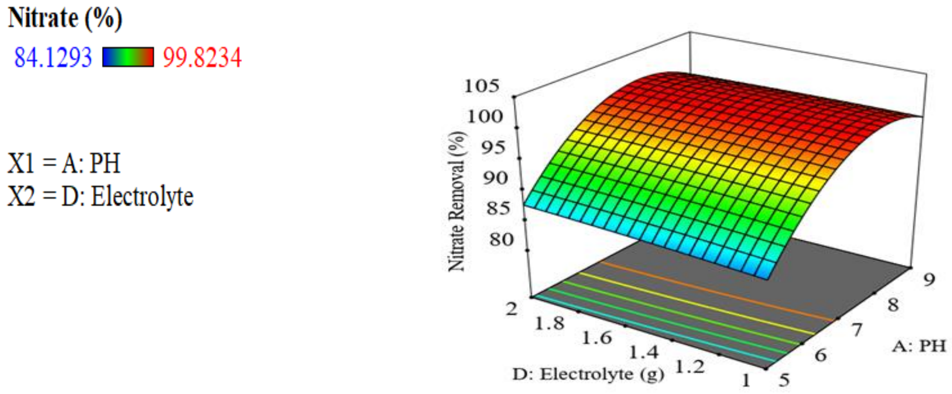


Figure 4-22 Interaction effect electrolyte with pH plot for % removal of Nitrate by combination of ECO with UV/H_2O_2 using$CaCl_2$

e. Interaction of PH and hydrogen peroxide

Figure 4-24 shows PO_3 removal efficiency was high at neutral pH which is indicated by red color and when dosage of H_2O_2 is 3ml. the interaction effect of pH and H_2O_2 have a little significant in PO_3 removal process. The appropriate H_2O_2 dose in the ECO is critical because H_2O_2 is the principal reagent that creates OH radicals, and when combined with pH, their interaction leads to an increase in removal potential.(Simsek *et al*, 2020).

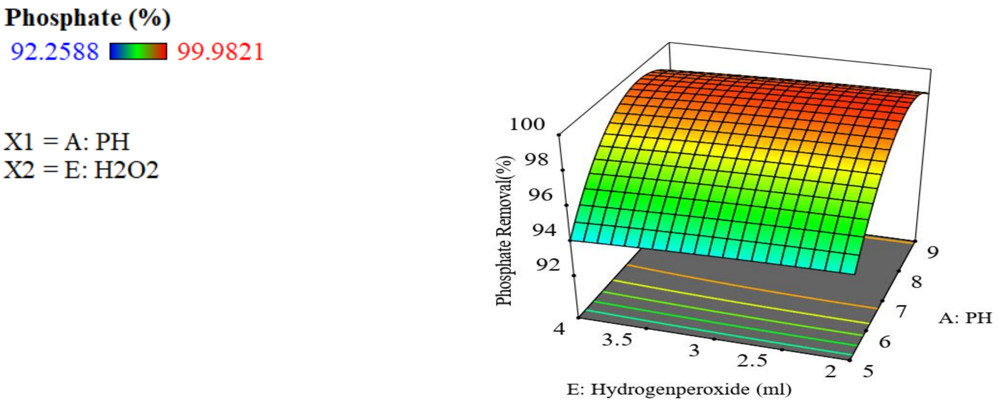


Figure 4-23 Interaction effect H_2O_2 with pH plot for % removal of Phosphate by combination of ECO with UV/H_2O_2 using$CaCl_2$

The results of the interactions between four independent variables and the dependent variable (COD), color, turbidity, nitrate and phosphate with time and PH are shown in Figures (4-20-4-23). As it can be seen in Figures, depending on, current ampere, electrolysis time, solution pH and salt concentration may have a positive or negative effect on the COD, color, turbidity, nitrate and phosphates removal and power consumption.

4.3.4 Regression equations

Regression analysis reveals the link between a response (dependent) variable and one or more (predictor) independent variables, to the extent that information is present in the data. The response variable is modeled as a function of the predictor factors in regression analysis. The data used determines the duality of the fit as well as the precision of the result (Sharma and Simsek, 2020b).

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.

Therefore, the experiment was investigated in terms of selection of pH (A), reaction time (B), applied current (C), and chemical concentration (D) (supporting electrolytes) and (E) hydrogen peroxide. in order to determine optimum operating conditions for maximum removal efficiency of color, COD, Nitrate, phosphate and turbidity with minimum power consumption. In photo-electrochemical oxidation 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 UV/H_2O_2 using $CaCl_2$ was attained and could be approximated by quadratic polynomial as follows:

$$\begin{aligned}\mathbf{COD} = {} & 98.44 + 1.2\mathrm{A} + 0.3073\mathrm{B} + 0.3322\mathrm{C} + 0.3621\mathrm{D} + 0.3370\mathrm{E} - 0.0732\mathrm{AB} \\ & - 0.1249\mathrm{BD} + 0.1040\mathrm{BE} + 0.0464\mathrm{CD} + 1032\mathrm{CE} + 1569\mathrm{DE} - 3.99\mathrm{A}^2 \\ & + 0.0526\mathrm{B}^2 - 0.2572\mathrm{C}^2 + 0.0226\mathrm{D}^2 + 0.0865\mathrm{E}^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathrm{Eq} - 1\end{aligned}$$

$$\begin{aligned}\boldsymbol{Color} = {} & 99.15 + 0.6863A + 0.2879B + 0.2089C + 0.2221D + 0.3464E \\ & + 0.3502AB0.1109AC + 0.0265AD - 0.0037AE - 0.0228BC + 0.0122BD \\ & - 0.0659BE - 0.0977CD + 0.0596CE + 0.0424DE - 1.63A^2 \\ & - 0.0766B^2 \quad - 0.2196C^2 - 0.2796D^2 \\ & - 0.1387E^2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots Eq - 2\end{aligned}$$

$$\begin{aligned}\boldsymbol{Turbidity} = {} & 99.09 + 1.12A - 0.1593B + 0.1459C + 0.1926D + 0.1392E + 0.0105AB \\ & - 0.0340AC - 0.1346AD - 0.0488AE + 0.0117BC + 0.0114BD \\ & + 0.0925BE - 0.0429CD + 0.1458CE - 0.1137DE - 2.57A^2 - 0.0479B^2 \\ & - 0.1123C^2 + 0.0223D^2 - 0.0515E^2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. Eq - 3\end{aligned}$$

$$\begin{aligned}\boldsymbol{Nitrate} = {} & 99.25 + 5.45A + 0.2771B + 0.2590C + 0.2838D + 0.2811E - 0.2622AB \\ & - 0.1125AC \; - 0.4919AD - 0.1633AE - 0.2013BC + 0.1474BD \\ & - 0.0556BE - 0.1810CD + 0.0169CE - 0.3186DE - 6.69A^2 - 0.1296B^2 \\ & - 0.0777C^2 - 0.1541D^2 \;\; - 0.1654E^2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. Eq \;\; - 4\end{aligned}$$

$$\begin{aligned}\boldsymbol{Phosphate} = {} & 99.18 + 2.07A + 0.1891B + 0.1567C + 0.1651D - 0.1637E - 0.2736AB \\ & + 0.1137AC - 0.2873AD + 0.0137AE - 0.0115BC - 0.1029BD \\ & - 0.1701BE - 0.0100CD - 0.2052CE + 0.0251DE - 0.2052A^2 \\ & - 0.1993B^2 - 0.0287C^2 + 0.009D^2 - 0.068E^2 \dots\dots\dots\dots\dots\dots\dots\dots\dots Eq - 5\end{aligned}$$

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 are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

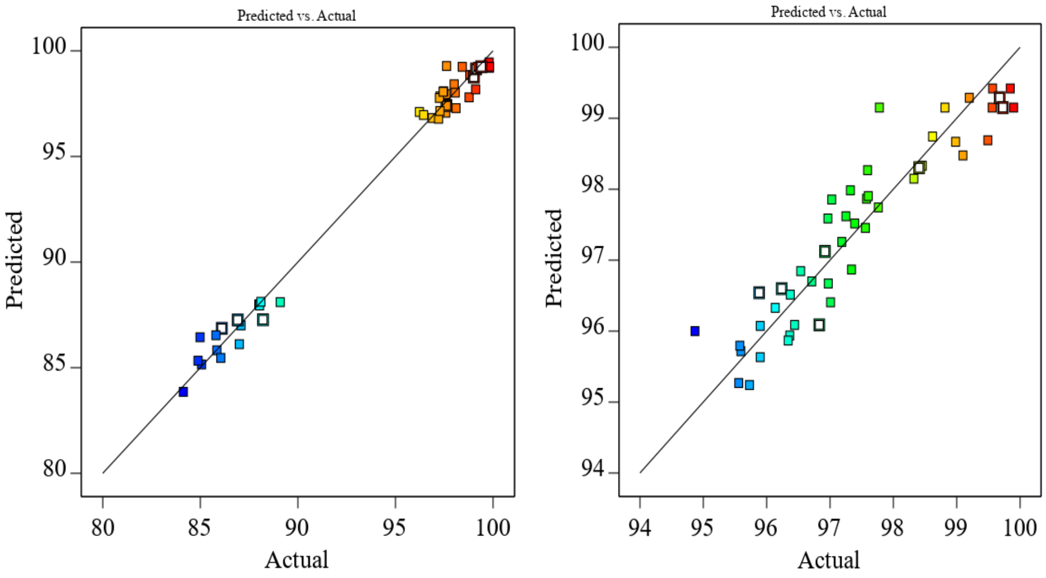
According to the results, many of the model terms were significant for responses which include: pH (A), reaction time (B), Current (C), Electrolyte (D), Hydrogen peroxide (E) and pH (A^2), reaction time (B^2), Current (C^2), Electrolyte (D^2), Hydrogen peroxide (E^2) and interaction terms of AB, AC, AE, BE, BD BC, AD, CD, CE and DE.

The terms in the models are organized in a coding system. The ANOVA test was used to determine the model's appropriateness. The lack of fit test was used to confirm model validity, as seen in the tables above. On the regression model, was extremely significant ($P < 0.001$), but the ANOVA for lack of fit was insignificant ($P > 0.05$). All of the results show that this model is a good fit for the experimental data. These findings indicate that Combination of ECO and UV/H_2O_2 was the most effective method for treatment of wastewater due to the higher percentage COD, color, nitrate, phosphate and turbidity removal value and better extraction yield within the shortest time. Means with different letters within the same row indicate significant differences ($P \leq 0.05$).

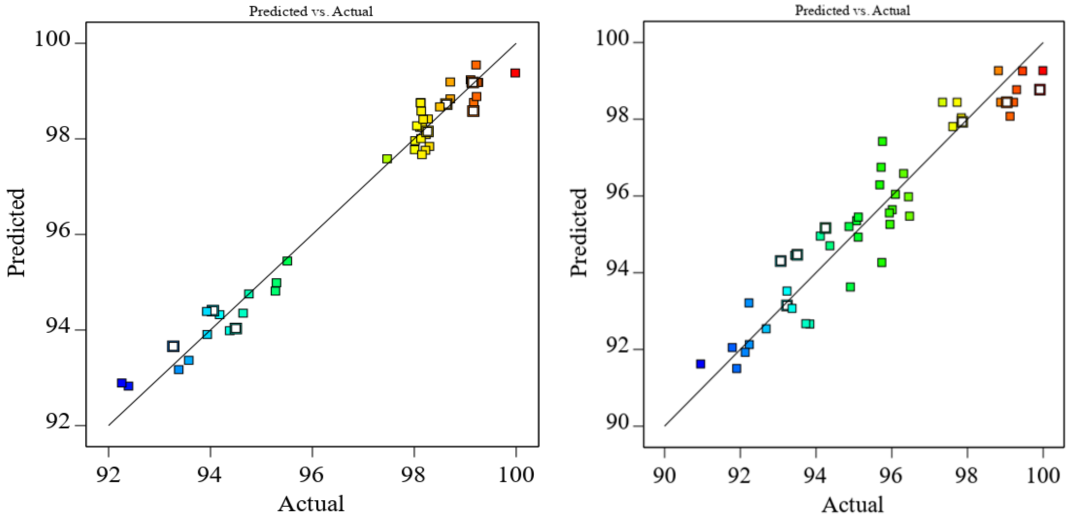
4.4 The desired optimum condition for responses

Figure 4-24 indicates that at the optimum levels, the prediction and experimental findings are in line with straight line and in good agreement, indicating that the model is very valid. This initial model's expected R^2 was 99.09 percent as analyzed by RSM. To build a parsimonious model with meaningful predictors, the backward elimination method was applied. The anticipated model's coefficient of determination revealed a quadratic link between responses and parameters with a good regression coefficient.

The optimum ECO and UV/H_2O_2 conditions were obtained using Design Expert 11.1.2.0 software, and determined as a practical optimum: electrolysis time of 40 min, UV Lamp of 50 W, salt concentration of 1.5g/l, and pH of 7, 3ml H_2O_2 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 which their difference was less than 0.2 and values were not significantly different ($P > 0.05$). Thus, it could be concluded that the established model in this study was appropriate and valid. The following diagram a,b,c and d shows actual and predicted value of NO_3,color,PO_3 and COD.



a. Nitrate b. color



a. Phosphate d. COD

Figure 4-24 Comparison of the predictive and the experimental result for Combination of ECO and UV/H_2O_2 using $CaCl_2$ optimum values on removal efficiency

The models' competence in predicting the removal of these two pollutants is demonstrated by the good correlations between anticipated and actual COD removal values shown in Figure 4-24 Based on regression models and aligned diagrams of the interactive relationships between them and the response variable, the interactive reaction between four independent variables and dependent variables (responses) can be depicted.

Furthermore, the model's adequacy can be evaluated using diagnostic diagrams including normal probability distribution diagram of residuals, the diagram of predicted values versus real values. Fig. 4-25 and 4-26 and 4-27 shows the distribution of normal probability percentage versus studentized residuals for COD, turbidity and Phosphate removal levels. As seen in these diagrams, the points lie on a relatively straight line, suggesting the constancy of the variance and normal distribution. In the normal probability distribution diagram of residuals, the points are aligned along an almost straight line. Some of the scattered points are even expected in normal distribution of the data. As it could be seen from the figures there is no outlier which cross the red line.

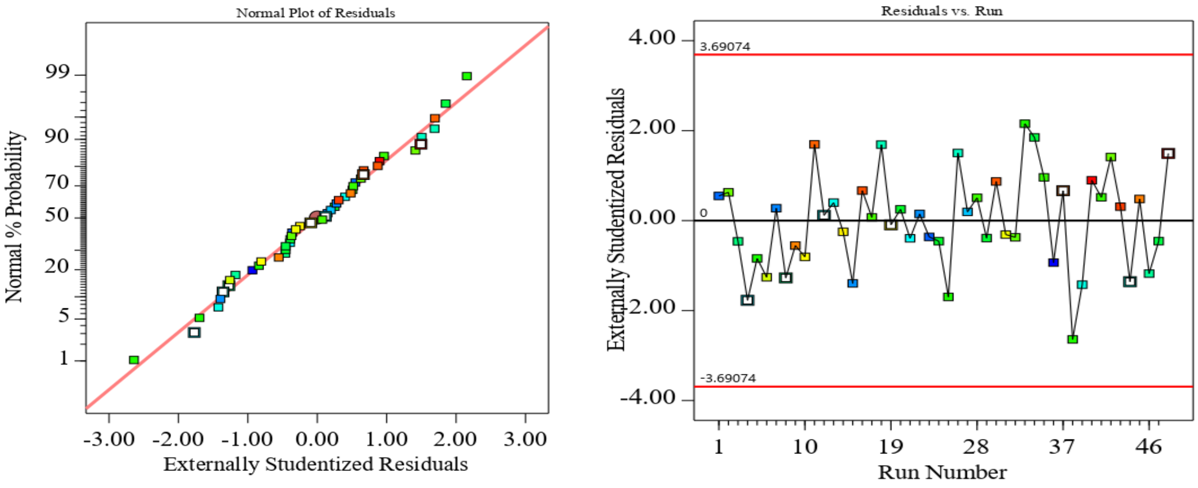


Figure 4-25 Distribution of normal probability percentage and residuals for COD

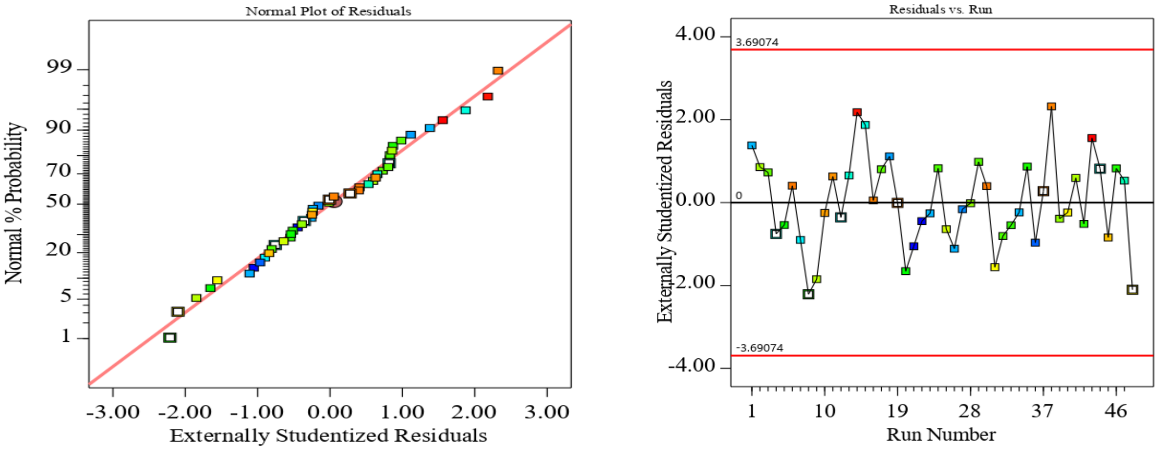


Figure 4-26 Distribution of normal probability percentage and residuals for Turbidity

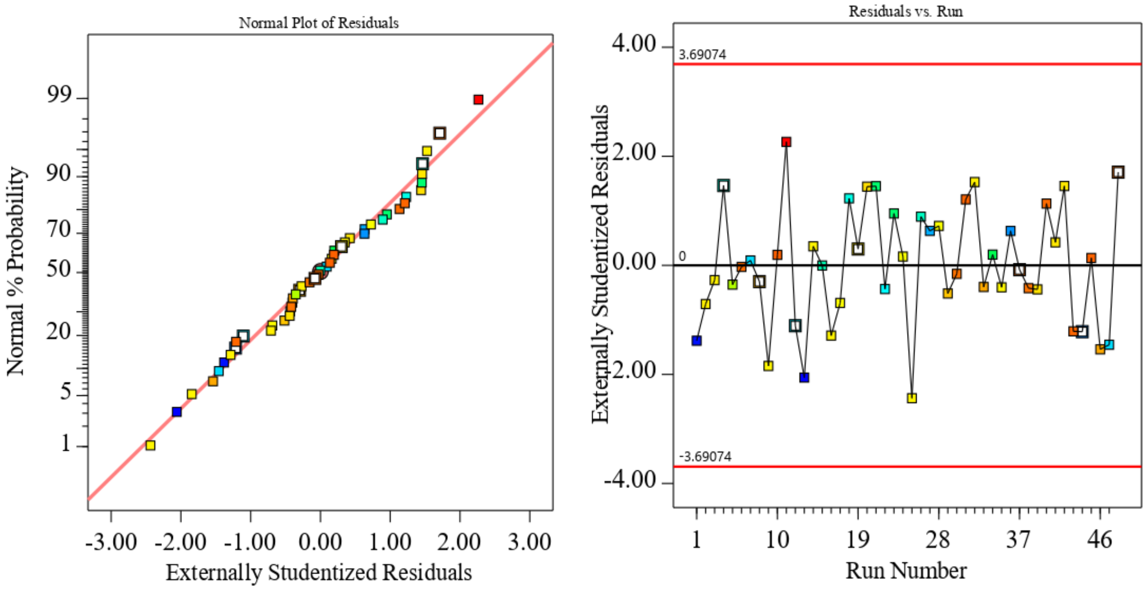


Figure 4-27 Distribution of normal probability percentage and residuals for Phosphate

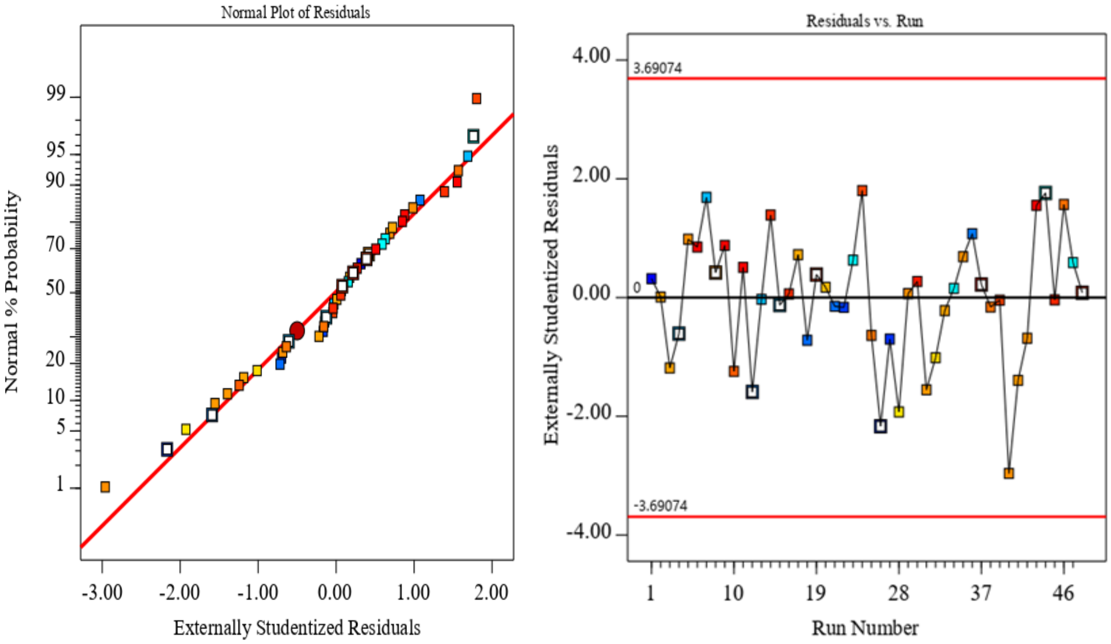


Figure 4-28 Distribution of normal probability percentage and residuals for Nitrate

As shown on above figures 4-25-4-28 results of removal efficiency were nearer to straight line on Distribution of normal probability percentage and residuals graphs for pollutant removals. On the second graph run number versus externally studentized residuals were in uniform variation. As a result, the experimental results were valid.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Photo-electrochemical oxidation process potential for coffee processing wastewater effluent treatment was the best technology which is achieved by considering independent variables such as pH, time, current, electrolytes and hydrogen peroxide.

In this method of coffee processing wastewater treatment independent variables have maximum effect on increasing removal efficiency of pollutants. These variables were control removal efficiency of the method depending on duration of time and amount of dosage. The 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. 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, turbidity, Nitrate and phosphate removal efficiency.

Whereas combining the Maximum removal efficiency of electrochemical oxidation with UV/H_2O_2 using $CaCl_2$ for removal of COD, Color, Turbidity, nitrate and phosphate, gives the maximum efficiency 99.992%, 99.898 99.898%, 99.22%, 99.982 respectively. Those optimum results were obtained at pH=7, electrolysis time of 40 minute, current of 0.4 Ampere, 1.5g $CaCl_2$ and 3ml of H_2O_2.

This indicates that, the combination of ECO With UV/H_2O_2 have a remarkable synergistic effect on the removal. As supporting electrolyte, $CaCl_2$ was more efficient than NaCl for both ECO and UV/H_2O_2 processes. For the treatment of Coffee processing waste water, ECO Combination with UV/H_2O_2 was found to be more efficient method than ECO alone.

5.2 Recommendations

Photoelectrochemical process for coffee processing wastewater is the preferable and economical method of treatment technology some points which need consideration regarding to proper usage of this technology were listed as follow

- coffee processing wastewater, after treated by Photo-electro chemical wastewater, it could be directly discharged to water bodies because it fulfills WHO standard of industrial wastewater effluents.
- During process of treatment electrodes should be Separated for anode and cathode terminals.
- Amount of CO_2 released, sludge sediments, foam created and remain after treatment should be properly managed.
- Operating parameters such like PH, Electrolytes and hydrogen peroxides should be adjusted carefully with accurate measurement to get best result from experiment unless the results were varied with a little mistake.
- To display all outputs from response surface methodology analysis (RSM) was very difficult but selecting the core results from analysis was best for understanding the result.
- To get the exact result and identify the effects of independent variables, power to DC, refrigerator and other laboratory machines those operated by electric power should continuously supplied.

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Appendixes

Appendix A: Experimental data for photo electrochemical oxidation process

Constant parameters

Anode – Cathode electrode = Al – Al
System: Batch system
Reaction time = 20min-1hr.
Mode of electrode connection = Parallel
Length of electrode = 13cm
Width of electrode = 6cm
Distance between electrode = 1cm

Appendix B: Experimental runs and outputs of ECO by using NaCl electrolyte

<u>Experiment 1</u> Date 9/03/2021 • pH=7 • I=0.4A • NaCl=1.5g • T=20 °C • V=2.25V • Cond=4.25µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.276	5.968	1.13	2.843	2.3

<u>Experiment 2</u> Date 9/03/2021 • pH=9 • I=0.3A • NaCl=1g • T=20 °C • V=2.25V • Cond=4.25µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.532	10.425	1.662	5.839	1.51
	50	0.527	11.451	1.490	5.832	1.60

Experiment 3 Date 9/03/2021 - pH=7 - I=0.4A - NaCl=2.5g - T=22.4 ºC - V=1.85V - Cond=4.25µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.261	5.574	0.998	2.768	2.29

Experiment 4 Date 9/03/2021 - pH=5 - I=0.5A - NaCl=1g - T=22.2 ºC - V=4.45V - Cond=3ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.743	20.315	2.32	6.86	1.09
	50	0.721	19.351	2.25	7.152	1.12

Experiment 5 Date 9/03/2021 - pH=7 - I=0.4A - NaCl=1.5g - T=24.7ºC - V=1.8V - Cond=4.4µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.282	7.46	1.063	2.553	1.09

	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD FAS (ml)
Experiment 6 Date 10/03/2021 • pH=7 • I=0.2A • NaCl=1.5g • T=24.4°C • V=1.8V • Cond=3.42ms/cm	0	2.95	144.5	9.21	21.23	0.5
	40	0.381	9.00	1.19	2.986	2.1

	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD FAS (ml)
Experiment 7 Date 10/03/2021 • pH=5 • I=0.3A • NaCl=2g • T=25.1 °C • V=1.85V • Cond=3.32ms/cm	0	2.95	144.5	9.21	21.23	0.5
	30	0.762	22.897	2.380	6.828	1
	50	0.756	22.372	2.360	6.589	1.08

	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD FAS (ml)
Experiment 8 Date 10/03/2021 • pH=9 • I=0.5A • NaCl=2g • T=22.9 °C • V=2.55V • Cond=4.28ms/cm	0	2.95	144.5	9.21	21.23	0.5
	30	0.507	9.095	1.582	5.338	1.78
	50	0.475	7.95	1.485	5.395	2.00

Experiment 10 Date 10/03/2021 pH=7 I=0.4A NaCl=1.5g T=24.7°C V=1.8V Cond=4.4µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.297	6.46	1.013	2.781	1.29

Experiment 11 Date 10/03/2021 pH=7 I=0.4A NaCl=1.5g T=24.7°C V=1.8V Cond=4.4µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.477	7.46	1.483	2.981	1.19

Experiment 12 Date 11/03/2021 pH=7 I=0.4A NaCl=1.5g T=20.9 °C V=2.4V Cond=3.26ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	20	0.352	8.955	1.282	3.375	2.21
	60	0.32	6.295	1.00	2.772	2.28

Experiment 14 Date 12/03/2021 - pH=9 - I=0.3A - NaCl=2g - T=23.1 ºC - V=2.70V - Cond=2.52ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.547	11.438	1.48	5.845	1.70
	50	0.504	9.832	1.48	5.54	1.91

Experiment 15 Date 12/03/2021 - pH=5 - I=0.3A - Nacl=1g - T=21.1 ºC - V=1.55V - Cond=1379µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.735	20.87	2.35	7.001	0.75
	50	0.762	21.686	2.38	7.015	0.86

Experiment 16 Date 12/03/2021 - pH =7 - I=0.4A - NaCl=0.5g - T=23.4ºC - V=2.6V - Cond=1926µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.349	10.572	1.182	3.096	1.6

Experiment 18 Date 12/03/2021 • pH =5 • I=0.5A • NaCl=2g • T=24.1 ºC • V=2.6V • Cond=1374ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.701	20.425	2.27	6.598	1.04
	50	0.727	20.188	2.19	6.584	1.22

Experiment 22 Date 12/03/2021 • pH =7 • I=0.4A • NaCl=1.5g • T=24.7ºC • V=1.8V • Cond=4.4µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.278	8.495	0.869	2.813	2.21

Experiment 25 Date 12/03/2021 • pH =7 • I=0.6A • NaCl=1.5g • T=23.7ºC • V=2.75V • Cond=2.26µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.349	6.056	1.09	2.764	1.75

Experiment 26 Date 14/03/2021 • pH =7 • I=0.4A • NaCl=1.5g • T=24.7°C • V=1.8V • Cond=4.4µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.304	7.41	0.953	3.181	2.112

Experiment 27 Date 14/03/2021 • pH =7 • I=0.4A • NaCl=1.5g • T=24.7°C • V=1.8V • Cond=4.4µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.502	10.46	1.473	2.881	2.00

Experiment 28 Date 14/03/2021 • pH =9 • I=0.4A • NaCl=1.5g • T=25°C • V=1.65V • Cond=5.53µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.388	8.833	1.35	3.168	1.85

Experiment 29 Date 14/03/2021 • pH =9 • I=0.5A • $CaCl_2$=1g • T=24.3 °C • V=2.8V • Cond=4.27 ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.501	12.217	1.656	5.884	1.79
	50	0.491	10.35	1.535	5.182	2.02

Appendix C: Experimental Runs and outputs of ECO by using $CaCl_2$ electrolyte

Experiment 1 Date 15/04/2021 • pH =7 • I=0.4A • $CaCl_2$=1g • T=20 °C • V=3.2V • Cond=2.28ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.122	4.095	0.919	2.13	2.63
Experiment 2 Date 15/03/2021 • pH =9 • I=0.3A • $CaCl_2$=1g • T=20 °C • V=1.95V • Cond=3.55ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.349	7.974	1.451	4.914	1.869
	50	0.323	7.555	1.371	4.537	1.889

Experiment 3 Date 15/03/2021 • pH =7 • I=0.4A • $CaCl_2$=2.5g • T=22.4 °C • V=2.35V • Cond=3.57ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.166	3.834	0.695	2.073	2.527

Experiment 4 Date 15/03/2021 • pH =5 • I=0.5A • $CaCl_2$=1g • T=25.2 °C • V=4.25V • Cond=1388μs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.589	19.309	2.109	6.147	2.18
	50	0.567	15.455	2.039	5.95	0.89

Experiment 5 Date 15/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25.1°C • V=2.4V • Cond=2.34ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.128	3.564	0.668	2.052	2.429

Experiment 6 Date 15/03/2021 • pH =7 • I=0.2A • $CaCl_2$=1.5g • T=25.5°C • V=1.9V • Cond=3.42ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.227	5.109	0.979	2.273	2.459

Experiment 7 Date 15/03/2021 • pH =5 • I=0.3A • $CaCl_2$=2g • T=26.1 °C • V=3V • Cond=1736µms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.608	19.001	2.169	6.115	0.851
	50	0.602	18.476	2.149	5.897	0.875

Experiment 8 Date 16/03/2021 • pH =9 • I=0.5A • $CaCl_2$=2g • T=21.1 °C • V=3V • Cond=2.52ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.294	6.644	1.279	4.837	1.899
	50	0.291	5.499	1.087	4.682	2.119

Experiment 10 Date 16/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24.3°C • V=1.8V • Cond=4.4µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.143	3.99	0.799	2.068	2.342

Experiment 11 Date 16/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24.7°C • V=1.8V • Cond=4.4µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.323	7.869	1.27	4.515	1.959

Experiment 12 Date 16/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=19 °C • V=1.8V • Cond=2.26ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	20	0.198	5.059	1.071	2.662	2.449
	60	0.166	5.289	0.789	2.144	2.593

Experiment 14 Date 16/03/2021 • pH =9 • I=0.3A • $CaCl_2$=2g • T=21.1 °C • V=1.55V • Cond=4.42ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.753	20.87	2.35	7.00	0.75
	50	0.320	6.514	1.269	4.615	2.149

Experiment 15 Date 16/03/2021 • pH =5 • I=0.3A • $CaCl_2$=2g • T=21.1 °C • V=3.2V • Cond=1379μs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.599	17.79	1.139	6.514	0.63
	50	0.608	18.419	2.169	6.288	0.875

Experiment 16 Date 16/03/2021 • pH =7 • I=0.4A • $CaCl_2$=0.5g • T=23.4°C • V=2.2V • Cond=1780μs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.225	6.82	0.879	2.616	2.199

Experiment 18 Date 16/03/2021 • pH =5 • I=0.5A • $CaCl_2$=2g • T=22.1 ºC • V=3.4V • Cond=4.21µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.544	16.292	2.059	6.14	1.332
	50	0.518	16.529	1.979	5.871	1.339

Experiment 22 Date 18/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24.7ºC • V=1.8V • Cond=4.4µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.124	4.599	0.658	2.142	2.593

Experiment 25 Date 18/03/2021 • pH =7 • I=0.6A • $CaCl_2$=1.5g • T=23.7ºC • V=3.5V • Cond=3.26µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.166	4.336	0.879	2.094	2.49

Experiment 26 Date 18/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24.7°C • V=1.8V • Cond=4.4μs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.15	4.958	0.739	2.264	2.407

Experiment 27 Date 18/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24.7°C • V=1.8V • Cond=4.4μs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.318	6.504	1.172	4.706	1.879

Experiment 28 Date 18/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25°C • V=2.4V • Cond=3.99ms/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.234	7.104	1.139	2.473	2.449

Experiment 29 Date 19/03/2021 - pH =9 - I=0.5A - $CaCl_2$=1g - T=24.3 ºC - V=3V - Cond=1950µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.303	9.044	1.353	4.534	2.149
	50	0.309	6.454	1.141	4.469	1.949

Appendix D: Experimental outputs of ECO by using combination of ECO and UV/H_2O_2 and NaCl as an electrolyte

Experiment 1 Date 19/03/2021 - PH=5 - I=0.3A - $Cacl_2$=1g - T=25.6 ºC - V=4.5V - Cond=1740µs/cm - H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.172	7.677	0.782	3.568	1.399
	50	0.177	9.205	0.618	3.370	1.479

Experiment 2 Date 19/03/2021 - pH =9 - I=0.5A - $CaCl_2$=2g - T=24.2 ºC - V=4.6V - Cond=1875µs/cm - H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.127	3.20	0.254	0.781	2.488
	50	0.087	4.37	0.256	0.776	2.457

Experiment 3 Date19/03/2021 • pH =9 • I=0.3A • $CaCl_2$=1g • T=24.6 °C • V=3.9V • Cond=2.42ms/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.143	4.20	0.256	0.781	1.99
	50	0.117	4.40	0.269	0.459	2.17

Experiment 4 Date 19/03/2021 • pH =5 • I=0.3A • $CaCl_2$=2g • T=25°C • V=5.98V • Cond=3.20ms/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.137	6.829	0.589	2.976	1.678
	50	0.148	6.476	0.641	2.724	2.111

Experiment 5 Date 19/03/2021 • pH =9 • I=0.3A • $CaCl_2$=2g • T=24.4 °C • V=2.7V • Cond=2.59ms/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.118	4.404	0.265	0.791	2.404
	50	0.076	4.92	0.319	0.704	2.306

Experiment 7 Date 19/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25.6°C • V=4.1V • Cond=2.32ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.059	1.79	0.163	0.263	2.704

Experiment 8 Date 19/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24.8°C • V=4.8V • Cond=2.72ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.081	2.11	0.155	0.534	2.315

Experiment 9 Date 19/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24.8°C • V=4.9V • Cond=2.82ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.049	1.79	0.168	0.319	3.154

Experiment 10 Date 19/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25ºC • V=4.5V • Cond=2.78ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.054	1.853	0.165	0.327	3.11

Experiment 11 Date 20/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25.3ºC • V=4.5V • Cond=2.98ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.111	2.39	0.164	0.364	2.965

Experiment 12 Date 20/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24.3ºC • V=4.5V • Cond=2.68ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.009	2.71	0.159	0.283	2.834

Experiment 13 Date 20/03/2021 • pH =5 • I=0.3A • $CaCl_2$=2g • T=26°C • V=2.8V • Cond=2ms/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.176	7.189	0.641	2.959	1.453
	50	0.177	7.70	0.662	2.748	1.371

Experiment 14 Date 20/03/2021 • pH =9 • I=0.5A • $CaCl_2$=2g • T=24.7°C • V=5.24V • Cond=3.3ms/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.157	4.88	0.213	0.706	1.962
	50	0.125	4.29	0.224	0.707	1.759

Experiment 15 Date 20/03/2021 • pH =7 • I=0.4A • $NaCl_2$=1.5g • T=25°C • V=5.8V • Cond=2.6ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	20	0.077	4.34	0.278	0.259	2.78
	60	0.051	3.50	0.258	0.252	3.05

Experiment 16 Date 21/03/2021 • pH =7 • I=0.6A • NaCl=1.5g • T=25.7ºC • V=4.4V • Cond=1793µs/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.061	2.00	0.089	0.242	3.132

Experiment 17 Date 21/03/2021 • pH =5 • I=0.5A • NaCl=2g • T=25.3ºC • V=5.9V • Cond=3.79ms/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.14	7.04	0.63	3.152	1.718
	50	0.176	7.70	0.517	2.747	1.371

Experiment 18 Date 21/03/2021 • pH =5 • I=0.3A • $NaCl_2$=2g • T=25.8ºC • V=6.1V • Cond=3.14ms/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.153	7.04	0.576	3.387	1.83
	50	0.124	6.84	0.566	2.541	1.60

Experiment 19 Date 21/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24°C • V=4.7V • Cond=4.31ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	20	0.019	5.046	0.277	4.18	6.123

Experiment 20 Date 21/03/2021 • pH =5 • I=0.5A • $NaCl_2$=1g • T=25°C • V=3.2V • Cond=2.91ms/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.124	6.70	0.74	2.94	1.75
	50	0.167	6.89	0.701	2.702	1.78

Experiment 21 Date 21/03/2021 • pH =7 • I=0.4A • NaCl=1.5g • T=24.9°C • V=4.8V • Cond=4.85ms/cm • H_2O_2=5ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.07	1.86	0.257	0.385	3.174

Experiment 22 Date 22/03/2021 • pH =5 • I=0.3A • $NaCl_2$=1g • T=26.6 ºC • V=4.7V • Cond=1940µs/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.154	8.40	0.69	0.714	1.17
	50	0.167	7.88	0.60	3.214	1.86

Experiment 23 Date 22/03/2021 • pH =9 • I=0.3A • $CaCl_2$=1g • T=25.4 ºC • V=3.75V • Cond=2.1ms/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.151	5.00	0.243	0.86	2.20
	50	0.123	4.90	0.26	0.51	2.37

Experiment 28 Date 22/03/2021 • pH =7 • I=0.2A • NaCl=1.5g • T=24.3ºC • V=2.1V • Cond=1280µs/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.128	3.6	0.471	0.542	2.647

Experiment 29 Date 22/03/2021 • pH =5 • I=0.3A • $CaCl_2$=1g • T=25°C • V=2.8V • Cond=2.2ms/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.135	3.80	0.269	0.707	2.38
	50	0.095	4.70	0.249	0.687	2.50

Experiment 31 Date 22/03/2021 • pH =7 • I=0.4A • NaCl=1.5g • T=25.4°C • V=4.8V • Cond=3.18ms/cm • H_2O_2=1ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.081	2.197	0.182	0.241	2.132

Experiment 35 Date 22/03/2021 • pH =7 • I=0.4A • $CaCl_2$=2.5g • T=25.4°C • V=4.35V • Cond=2.98ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.073	2.79	0.159	0.238	3.21

Experiment 42 Date 22/03/2021 • pH =9 • I=0.5A • $NaCl_2$=1g • T=25.3 ºC • V=4.1V • Cond=2ms/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.129	3.794	0.245	0.452	1.767
	50	0.092	3.566	0.245	0.737	2,367

Experiment 45 Date 22/03/2021 • pH =7 • I=0.2A • $CaCl_2$=0.5g • T=24.3ºC • V=2.9V • Cond=1580µs/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.188	3.6	0.571	0.742	2.173

Experiment 48 Date 22/03/2021 • pH =9 • I=0.5A • $CaCl_2$=2g • T=22.7ºC • V=5.2V • Cond=3.3ms/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.157	4.855	0.213	0.706	1.962
	50	0.125	4.25	0.251	0.706	2.159

Appendix E: Experimental outputs of ECO by using combination of ECO and UV/H_2O_2 $CaCl_2$ as an electrolyte

Experiment 1 Date 23/03/2021 • pH =5 • I=0.3A • $CaCl_2$=1g • T=24.6 ºC • V=4.7V • Cond=1640µs/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.126	6.999	0.694	3.37	1.557
	50	0.131	8.527	0.531	3.17	1.776

Experiment 2 Date 23/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25.7ºC • V=1.7V • Cond=1640µs/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.013	1.12	0.076	0.04	2.862
Experiment 3 Date 23/03/2021 • pH =7 • I=0.6A • $CaCl_2$=1.5g • T=25.7ºC • V=4.4V • Cond=1493µs/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.015	1.317	0.002	0.04	3.29

Experiment 4 Date 23/03/2021 • pH =7 • I=0.2A • $CaCl_2$=1.5g • T=25.3°C • V=1.9V • Cond=1580µs/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.088	2.6	0.171	0.42	2.473

Experiment 5 Date 23/03/2021 • pH =5 • I=0.5A • $CaCl_2$=2g • T=25.6 °C • V=3.7V • Cond=1507µs/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.091	6.151	0.502	2.78	1.836
	50	0.102	5.798	0.554	2.52	2.269

Experiment 7 Date 24/03/2021 • pH =9 • I=0.3A • $CaCl_2$=1g • T=25.6 °C • V=3.7V • Cond=2.42ms/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.097	3.511	0.168	0.58	2.148
	50	0.071	3.72	0.181	0.26	2.328

Experiment 8 Date 24/03/2021 • pH =9 • I=0.5A • $CaCl_2$=1g • T=25.6 ºC • V=4V • Cond=2ms/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.081	2.941	0.166	0.58	2.646
	50	0.041	3.691	0.169	0.76	2.651

Experiment 9 Date 24/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25.3ºC • V=3.9V • Cond=2.32ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.09	2.249	0.071	0.54	2.927

Experiment 10 Date 24/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25.3ºC • V=3.9V • Cond=2.32ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.035	1.431	0.171	0.05	3.216

Experiment 11 Date 24/03/2021 • pH =9 • I=0.3A • $CaCl_2$=2g • T=26.4 °C • V=3.15V • Cond=2ms/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.105	4.319	0.155	0.66	2.327
	50	0.108	7.718	0.604	0.51	1.329

Experiment 12 Date 25/03/2021 • pH =9 • I=0.5A • $CaCl_2$=2g • T=24.4 °C • V=4.5V • Cond=1975μs/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.0121	3.116	0.158	0.25	1.925
	50	0.046	2.888	0.162	0.54	2.525

Experiment 13 Date 25/03/2021 • pH =5 • I=0.5A • $CaCl_2$=1g • T=24.4 °C • V=4.5V • Cond=1484μs/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.152	7.401	0.586	3.21	1.744
	50	0.107	8.505	0.431	3.02	1.876

Experiment 14 Date 25/03/2021 • pH =9 • I=0.3A • $CaCl_2$=2g • T=24.4 °C • V=2.5V • Cond=2.69ms/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.097	3.511	0.168	0.58	2.148
	50	0.071	3.702	0.181	0.26	2.328

Experiment 16 Date 25/03/2021 • pH =7 • I=0.4A • $CaCl_2$=2.5g • T=25.4°C • V=4.35V • Cond=2.88ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.027	0.112	0.072	0.04	3.369

Experiment 17 Date 26/03/2021 • pH =5 • I=0.3A • $CaCl_2$=2g • T=25°C • V=2.5V • Cond=2ms/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.131	6.511	0.553	2.76	1.611
	50	0.130	7.022	0.429	2.550	1.529

Experiment 18 Date 26/03/2021 • pH =5 • I=0.3A • $CaCl_2$=1g • T=25ºC • V=4.2V • Cond=1404µs/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.121	6.411	0.541	2.72	1.722
	50	0.122	7.00	0.411	2.44	1.623

Experiment 19 Date 26/03/2021 • pH =9 • I=0.3A • $CaCl_2$=1g • T=25ºC • V=3.65V • Cond=6.03ms/cm • H_2O_2=1ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.066	4.078	0.118	0.05	2.09
	50	0.0544	4.02	0.117	0.045	2.07

Experiment 20 Date 27/03/2021 • pH =5 • I=0.5A • $CaCl_2$=1g • T=25ºC • V=3.2V • Cond=2.91ms/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.078	6.025	0.706	2.74	1.908
	50	0.121	6.213	0.614	2.50	1.941

Experiment 21 Date 27/03/2021 • pH =5 • I=0.5A • $CaCl_2$=2g • T=25^{o}C • V=5.9V • Cond=3.69ms/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.094	6.362	0.543	2.95	1.876
	50	0.093	7.00	0.41	2.54	2.278

Experiment 22 Date 27/03/2021 • pH =5 • I=0.3A • $CaCl_2$=2g • T=25^{o}C • V=5.9V • Cond=3.24ms/cm • H_2O_2=4ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.107	7.074	0.489	3.19	1.995
	50	0.114	6.164	0.478	2.32	1.635

Experiment 23 Date 27/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25^{o}C • V=5.8V • Cond=2.6ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	20	0.071	0.249	0.17	0.19	2.981
	60	0.031	2.153	0.076	0.50	3.25

Experiment 28 Date 29/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25.4°C • V=4.8V • Cond=3.18ms/cm • H_2O_2=1ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.071	1.197	0.082	0.41	2.481

Experiment 29 Date 29/03/2021 • pH =9 • I=0.5A • $CaCl_2$=2g • T=22.7°C • V=5.2V • Cond=3.3ms/cm • H_2O_2=2ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.111	4.177	0.125	0.510	2.12
	50	0.079	3.116	0.181	0.26	2.317

Experiment 30 Date 29/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25°C • V=4.2V • Cond=2.81ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.009	2.04	0.077	0.18	3.123

Experiment 31 Date 29/03/2021 • pH =9 • I=0.5A • $CaCl_2$=1g • T=23.2ºC • V=7.2V • Cond=2.51ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	30	0.088	3.922	0.118	0.580	2.477
	50	0.074	3.811	0.172	0.510	2.522

Experiment 35 Date 29/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=25ºC • V=4.7V • Cond=4.81ms/cm • H_2O_2=5ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.024	1.182	0.170	0.190	3.332

Experiment 42 Date 29/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24ºC • V=5.7V • Cond=4.31ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.008	2.05	0.078	0.180	3.123

Experiment 45 Date 29/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24°C • V=5.7V • Cond=4.31ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.065	1.714	0.07	0.16	3.23

Experiment 48 Date 29/03/2021 • pH =7 • I=0.4A • $CaCl_2$=1.5g • T=24°C • V=4.7V • Cond=4.31ms/cm • H_2O_2=3ml	Time (Min)	Absorbance	Turbidity (NTU)	PO_3 (Mg/L)	NO_3 (Mg/L)	COD
						FAS (ml)
	0	2.95	144.5	9.21	21.23	0.5
	40	0.009	2.046	0.077	0.18	3.123

Appendix F: Fit statistics for some dependent variables

Table F-1 Model Summary for% Color removals using NaCl

Std. Dev.	0.6552	R^2	0.9936
Mean	83.25	Adjusted R^2	0.9877
C.V. %	0.7870	Predicted R^2	0.9680
		Adeq Precision	35.2624

The Predicted R^2 of 0.9680 is in reasonable agreement with the Adjusted R^2 of 0.9877; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. ratio of 35.262 indicates an adequate signal. This model can be used to navigate the design space.

Table F-2 Model summary for% turbidity removals using NaCl

Std. Dev.	0.5580	R^2	0.9897
Mean	91.61	Adjusted R^2	0.9801
C.V. %	0.6091	Predicted R^2	0.9452
		Adeq Precision	29.7299

The Predicted R^2 of 0.9452 is in reasonable agreement with the Adjusted R^2 of 0.9801; i.e. the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. ratio of 29.730 indicates an adequate signal. This model can be used to navigate the design space.

Table F-3 Model summary for% nitrate removals using NaCl

Std. Dev.	0.9060	R^2	0.9933
Mean	77.14	Adjusted R^2	0.9870
C.V. %	1.17	Predicted R^2	0.9726
		Adeq Precision	31.6266

The Predicted R^2 of 0.9726 is in reasonable agreement with the Adjusted R^2 of 0.9870; i.e., the difference is less than 0.2**.** Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 31.627 indicates an adequate signal. This model can be used to navigate the design space.

Table F-4 Model Summary for% Phosphate removals using NaCl

Std. Dev.	0.6040	R^2	0.9938
Mean	82.94	Adjusted R^2	0.9880
C.V. %	0.7282	Predicted R^2	0.9780
		Adeq Precision	36.0989

The Predicted R^2 of 0.9780 is in reasonable agreement with the Adjusted R^2 of 0.9880; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater

than 4 is desirable. Ratio of 36.099 indicates an adequate signal. This model can be used to navigate the design space.

Table F-5 Model Summary for % Color removals using $CaCl_2$

Std. Dev.	0.7056	R^2	0.9922
Mean	88.85	Adjusted R^2	0.9849
C.V. %	0.7942	Predicted R^2	0.9689
		Adeq Precision	32.0326

The Predicted R^2 of 0.9689 is in reasonable agreement with the Adjusted R^2 of 0.9849; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 32.033 indicates an adequate signal. This model can be used to navigate the design space.

Table F-6 Model Summary for% Turbidity removals using $CaCl_2$

Std. Dev.	0.6247	R^2	0.9860
Mean	93.71	Adjusted R^2	0.9728
C.V. %	0.6666	Predicted R^2	0.9367
		Adeq Precision	23.1709

The Predicted R^2 of 0.9367 is in reasonable agreement with the Adjusted R^2 of 0.9728; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 23.171 indicates an adequate signal. This model can be used to navigate the design space.

Table F-7 Model Summary for% Nitrate removals using $CaCl_2$

Std. Dev.	0.4836	R^2	0.9980
Mean	80.78	Adjusted R^2	0.9961
C.V. %	0.5987	Predicted R^2	0.9902
		Adeq Precision	62.0145

The Predicted R^2 of 0.9902 is in reasonable agreement with the Adjusted R^2 of 0.9961; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater

than 4 is desirable. Ratio of 62.014 indicates an adequate signal. This model can be used to navigate the design space.

Table F-8 Model summary for % phosphate removals using $CaCl_2$

Std. Dev.	0.6891	R^2	0.9924
Mean	85.63	Adjusted R^2	0.9853
C.V. %	0.8048	Predicted R^2	0.9730
		Adeq Precision	32.6473

The Predicted R^2 of 0.9730 is in reasonable agreement with the Adjusted R^2 of 0.9853; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 32.647 indicates an adequate signal. This model can be used to navigate the design space

Table F-9 Model Summary for% Color removals using combination NaCl and UV/H_2O_2

Std. Dev.	0.6445	R^2	0.8719
Mean	95.90	Adjusted R^2	0.7770
C.V. %	0.6720	Predicted R^2	0.5697
		Adeq Precision	9.8063

The Predicted R^2 of 0.5697 is not as close to the Adjusted R^2 of 0.7770 as one might normally expect; i.e., the difference is more than 0.2. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response transformation, outliers, etc. A ratio greater than 4 is desirable. Ratio of 9.806 indicates an adequate signal. This model can be used to navigate the design space.

Table F-10 Model summary for% turbidity removals using combination NaCl and UV/H_2O_2

Std. Dev.	0.3693	R^2	0.9707
Mean	96.74	Adjusted R^2	0.9489
C.V. %	0.3817	Predicted R^2	0.8998
		Adeq Precision	21.8900

The Predicted R^2 of 0.8998 is in reasonable agreement with the Adjusted R^2 of 0.9489; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 21.890 indicates an adequate signal. This model can be used to navigate the design space.

Table F-11Model summary for% nitrate removals using combination NaCl and UV/H_2O_2

Std. Dev.	0.7971	R^2	0.9887
Mean	93.41	Adjusted R^2	0.9803
C.V. %	0.8533	Predicted R^2	0.9627
		Adeq Precision	29.6118

The Predicted R^2 of 0.9627 is in reasonable agreement with the Adjusted R^2 of 0.9803; i.e. the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 29.612 indicates an adequate signal. This model can be used to navigate the design space.

Table F-12Model Summary for% PO_3 removals using Combination NaCl and UV/H_2O_2

Std. Dev.	0.4417	R^2	0.9779
Mean	96.11	Adjusted R^2	0.9615
C.V. %	0.4595	Predicted R^2	0.9174
		Adeq Precision	23.0046

The Predicted R^2 of 0.9174 is in reasonable agreement with the Adjusted R^2 of 0.9615; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 23.005 indicates an adequate signal. This model can be used to navigate the design space.

Table F-13 Model Summary for% turbidity removals using Combination $CaCl_2$ and UV/H_2O_2

Std. Dev.	0.3693	R^2	0.9707
Mean	97.21	Adjusted R^2	0.9489
C.V. %	0.3799	Predicted R^2	0.8998
		Adeq Precision	21.8899

The Predicted R^2 of 0.8998 is in reasonable agreement with the Adjusted R^2 of 0.9489; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater

than 4 is desirable. Your ratio of 21.890 indicates an adequate signal. This model can be used to navigate the design space.

Table F-14 Model Summary for % nitrate removals using combination $CaCl_2$ and UV/H_2O_2

Std. Dev.	0.7941	R^2	0.9887
Mean	94.34	Adjusted R^2	0.9804
C.V. %	0.8418	Predicted R^2	0.9628
		Adeq Precision	29.6927

The Predicted R^2 of 0.9628 is in reasonable agreement with the Adjusted R^2 of 0.9804; i.e. the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 29.693 indicates an adequate signal. This model can be used to navigate the design space.

Table F-15 Model Summary for% PO_3 removals using Combination $CaCl_2$ and UV/H_2O_2

Std. Dev.	0.4417	R^2	0.9779
Mean	97.07	Adjusted R^2	0.9615
C.V. %	0.4550	Predicted R^2	0.9174
		Adeq Precision	23.0046

The Predicted R^2 of 0.9174 is in reasonable agreement with the Adjusted R^2 of 0.9615; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 23.005 indicates an adequate signal. This model can be used to navigate the design space.

Appendix G: Some Figures Illustrate Lab activities.

Figure G-1 Aluminum electrode used

Figure G-2 Adjustment and treatment process of coffee processing waste water

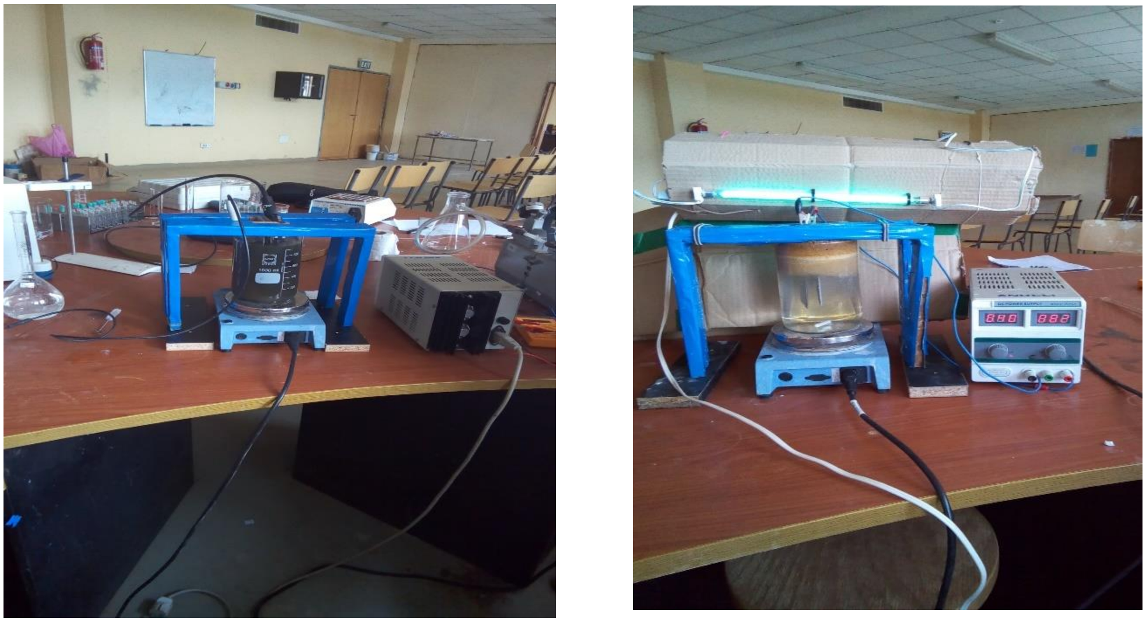

Figure G-3 Adjusting variables and treatment by using combination of UV/H_2O_2

Figure G-4 Before and after treatment of coffee wastewater

Figure G-5 COD determination by titration method

Figure G-6 Phosphate Reading by Spectrophotometric method

Figure G-7 Nitrate Reading by Spectrophotometric