



JIMMA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

JIMMA INSTITUTE OF TECHNOLOGY

FACULTY OF CIVIL AND ENVIRONMENTAL ENGINEERING

ENVIRONMENTAL ENGINEERING PROGRAM

**INVESTIGATION OF PULSED ELECTROCHEMICAL PROCESS FOR THE
TREATMENT OF WET COFFEE PROCESSING WASTEWATER**

A Thesis Submitted to the School of Graduate studies of Jimma University in Partial Fulfillment
of the Requirements for the Degree of Master of Science in Environmental Engineering.

Prepared by: Kassahun Tadesse Asefaw

July, 2022

Jimma, Ethiopia

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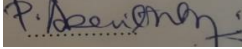
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ABSTRACT

Electrochemical technology for treating wastewater provide number of advantages over traditional treatment processes, including environmental compatibility, energy efficiency, adaptability, safety, selectivity, ease of scale up, mechanization, cost effectiveness, and excellent settling and filterability. In this study, the pulsed electrochemical method is a hopeful treatment strategy because of its high effectiveness, cheap and speedy outcomes. The aim of this research is to investigate the effect of independent variable to remove contaminants from wet coffee processing industry. The independent variables such as pH, time, electric current, and electrolyte dosage on the removal efficiency of Chemical Oxygen Demand (COD), % Color, % Turbidity, phosphate, nitrate, and power consumption were investigated by the pulsed electrochemical process treatment method and the potential of these methods was obtained as COD (98.75 %), color (99.92 %), turbidity (99.00 %), phosphate (99.02 %), and nitrate (98.83 %), with a power consumption of 0.971 kWh/m³ has a high removal efficiency depending on the result. The optimum values for removal was obtained using response surface methodology (RSM) Vis central compost design (CCD): pH 7, electrolyte dosage of 0.75g, electrolysis time of 45min, and current of 0.45Amp). 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 pulsed electrochemical process (PECP) with CaCl₂ as an electrolyte is an effective treatment technique for pollutant removal, and it was discovered that increasing the electrolyte charge from +1 to +2 increases pollutant removal and decreases voltage, which was effective for pollutant removal. Pulsed electrochemical process is an effective treatment particularly to wet coffee wastewater.

Keywords: coffee processing, pulsed electrochemical, Power consumption, Removal of pollutant, Optimization,

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ACRONYM AND ABBREVIATION

APHA	American Public Health Association
AOP	Advanced Oxidation Process
AC	Alternating Current
BOD	Biological Oxygen Demand
CPI	Coffee Processing Industry
COD	Chemical Oxygen Demand
CCD	Central Composite Design
DC	Direct Current
ECAOP	Electrochemical and Advanced Oxidation process
EO	Electro Oxidation
EC	Electro Conductivity
EC	Electrocoagulation
FCCD	Face Central Composite Design
IPECP	Investigation of Pulsed Electrochemical Process
RSM	Response surface methodology
TSS	Total suspended Solid
TDS	Total Dissolved Solid
WHO	World Health Organization
WCPWW	Wet Coffee Processing Wastewater

CHAPTER ONE

1 Introduction

Water resources are the primary sources of potentially usable water, so water is used in a variety of ways, including agriculture, industrial, domestic, and leisure activities. Naturally available water is overused and poisoned by these operations' effluent (Bhagawan *et al.*, 2018). Water is one of nature's most abundant resources and is essential for humans, plants, and animals. Lack of clean water slows economic growth and has negative environmental consequences for people's health and livelihoods. Chemical pollution of surface water, primarily due to industrial and agricultural discharges, is a severe health problem in some developing countries. The main issue is that water, which is required for human consumption, is scarce, especially in developing countries like Ethiopia. Due to a lack of monitoring infrastructure, wastewater created by various processing industries is frequently dumped directly into water bodies in Ethiopia. Water contamination occurs, posing a threat to the entire natural system as well as the human well-being of the entire society. As a result, pollution of water bodies is gradually increasing as a result of industrialization and urbanization (Rajkumar and Palanivelu, 2004).

Water pollution is becoming a major global concern as a result of rapid population expansion, urbanization, ineffective and expensive treatment methods, and poor management. Distilleries, wet coffee processing, oil mills, and the textile, food processing, chemicals, soft drinks, paper, and metal sectors are all major contributors to wastewater generation in Ethiopia (Gebeyehu *et al.*, 2018).

The rapid development of industries such as wet coffee processing industries and other pesticide industries in Ethiopia means directly or indirectly discharging waste and heavy metals from these industries is becoming a bigger hazard for the environment (Mosivand *et al.*, 2018).

Water is one of the most abundantly available resources in nature. Nowadays, the worldwide production and use of chemical compounds has increased significantly, which means they find their way into the environment and many of these compounds are biologically non-degradable. Therefore, the major concern is to treat the wet coffee wastewater before it is discharged into the environment (Rajkumar and Palanivelu, 2004).

Industries produce a large number of pollutants, including bio-refractory organic compounds, which harm the aquatic environment and ecosystem by causing toxicity, color, and odor concerns. An ever-increasing amount of effluent from various industries, while on the hand,

there are severe legislative regulations for its disposal. As a result, treating the effluent before dumping it into the environment is required (Asaithambi *et al.*, 2012).

Coffee is one of the most popular beverages in the world, with a global consumption of 7 million tons per year (Villanueva-Rodríguez *et al.*, 2014). Coffee is an important agricultural crop for coffee-producing countries around the world. Ethiopia produces 6.4 percent of the world's yearly coffee production, which is estimated to be 5.5 million tons. The western, southern, and eastern parts of the country produce 55.35% of total yearly production, respectively. Coffee is grown on about 600,000 hectares of the country's agricultural area (Villanueva-Rodríguez *et al.*, 2014).

The incorrect handling of huge amounts of garbage generated by diverse anthropogenic activities is one of the most serious problems facing emerging countries. The hazardous disposal of these pollutants into the environment is even more difficult. Freshwater reservoirs, in particular, are particularly vulnerable. In Africa, organic pollution of inland water systems is frequently caused by economic and social underdevelopment.

Coffee processing plants are one of the biggest agro-based sectors that pollute the environment. In many coffee-processing countries, effluent from pulping, fermenting, and washing of coffee beans is disposed of, posing a number of issues for the receiving environment, particularly water bodies (Woldesenbet,*et.al.*,2014).

Coffee that has been wet processed is said to be of higher quality than coffee that has been dry processed. There are currently more than 400 coffee processing facilities in Ethiopia, many of which are located near rivers (Woldesenbet,*et.al.*,2014).

Coffee effluent contains a high concentration of organic chemicals that can pollute the environment. The pulp and mucilage of coffee cherries are removed during wet coffee processing. The high quantity of organic compounds in coffee wastewater might contaminate the environment. Because of high percentage of organic matter in this process, a huge volume of acidic waste is produced, which is particularly harmful to the environment. As a result, treatment is required before discharge into water bodies (Tacias-Pascacio *et al.*, 2018).

Pollution is removed by either direct or indirect oxidation processes using pulsed electrochemical procedures. Electrochemical treatments on their own are interesting and promising techniques for removing harmful organic chemicals using a simple, cost-effective, and easy-to-use technology (Bernal-Martínez *et al.*, 2013).

Pulsed electrochemical wastewater treatment method is one of the most widely used electrochemical procedures in wastewater treatment is electrocoagulation. The electrochemical

dissolution of sacrificial metal electrodes (iron or aluminum) into soluble or in soluble spaces, depending on the pH, is the basis of EC. Electro Fenton is one of the electrochemical advanced oxidation processes (EAOPs) that has gotten a lot of attention in the wastewater treatment in world (Afanga *et al.*, 2020). An electrochemical technique that uses sacrificial soluble iron (Fe) and aluminum (Al) as anodes and/or cathodes to release metal ions by anodic oxidation, these ions reacts with the cathode's released aluminum hydroxide, which aids in flock formation. The goal of this research was to look at the effect of alternating current on the electrochemical process in terms of color, COD, turbidity, phosphate, and nitrate removal, as well as electrical energy consumption from wet coffee processing factory effluent. As a result, the pulsed electrochemical process is more efficient at removing color and COD while using less energy than the DCE technique. However, for removing contaminants from industrial effluent, the pulsed electrochemical process is the best option. One of these techniques is electrochemical coagulation, which is the electrochemical reaction of destabilizing agents that cause charge neutralization for pollutant removal and has been employed in wastewater treatment (Vasudevan, 2012). Because of their availability and expansive cost, iron and aluminum are the most commonly utilized electrode materials in the EC process (Zhang *et al.*, 2021).

According to (Sahana *et al.*, 2018) Environmental compatibility, energy economy, adaptability, safety, selectivity, ease of scale-up, automation, cost-effectiveness, and high settling and filterability are all advantages of the electrochemical approach for treating wastewater over traditional treatment methods.

Pulsed electrochemical treatment alone is an interesting and preprocessing method for removing hazardous and organic compounds using a technology that is effective, adaptable, cost-effective, simple, and clean (Bernal-Martínez *et al.*, 2013). As a result, pulsed electrochemical (PEC) was successful in eliminating color and COD removal while using less electricity (Asaithambi *et al.*, 2021).

Because of its safe and environmentally friendly nature, electrochemical technology can be used to clean wastewater. Depending on the nature of the composition, electrochemical oxidation and electrocoagulation are used for various industrial effluents (Asaithambi *et al.*, 2012).

EC is an electrochemical process that destabilizes the charge of the pollutants through applied electric current, causing electrode dissolution and trapping pollutants that can be separated from the electrolytic mixture (Tahreen, Jami and Ali, 2020).

When untreated water is released, many metal ions are poisonous, and it's a major risk for the environment. Because of their high solubility, these ions are easily absorbed by fish and vegetables, and they can accumulate in the human body via the food chain. Heavy metals in waste have long been a source of concern for the environment (Mosivand *et al.*, 2018).

The physiochemical method is not cost-effective, requires chemical overuse, and creates a significant amount of sludge at the same time. High dilution is needed by the biological treatment method, which is a slow and time-consuming procedure. So, it is important to look for a cost-effective way to handle industrial waste. From the point of view of high performance and low resource usage, pulsed electrochemical technology can be used from the point of view of high performance and low resource usage, either as a primary approach to increase the pollutant's biodegradability or an advanced form of treatment to further minimize COD, turbidity, color, nitrate, and phosphate in wastewater to achieve sufficient effluent consistency.

The process of electrochemistry has received a great deal of attention for the treatment of different forms of industrial waste, such as wet coffee processing, paper, distiller organic fertilizer, automotive industry, potentially toxic metals and tanner metal, metal plating wastewater, and real industrial waste by using the pulsed electrochemical process (PECP). Electrochemical treatment, or electro oxidation, has been proposed as a viable option for a variety of industrial effluents. The treatment of pesticide processing industrial waste was carried out in the current study by utilizing an electrochemical method as well as a combination of other advanced technologies (Science, 2018).

Wet coffee processing wastewater is made up of caffeine-rich coffee fruits, sugars, phenolic compounds, fatty acids, lignin, cellulose, pectic chemicals, and other macromolecules that are undesirable for disposal in soil and water bodies (Sahana *et al.*, 2018).

Excess phosphate and nitrate concentrations in coffee wastewater effluents directed to the environment create eutrophication, which is one of the most common problems in the monitoring of environmental water sources today (Chen *et al.*, 2014).

Wet coffee processing wastewater (WCPWW) treated by using pulsed electrochemical processes (PECP) was reused for a variety of purposes. This can reduce the scarcity of pressure on groundwater and surface water bodies. The wastewater treatment process aims to achieve treated effluent and sludge quality that is environmentally safe for disposal (Hassen and Asmare, 2018).

1.1 Background

The electrochemical method with direct current (DC) and pulsed presented well, but pulsed electrochemical method is a promising treatment strategy because of its high effectiveness, low maintenance costs, low labor requirements, and speedy outcomes. Electrochemical treatment is a promising treatment method that has the potential to effectively treat a variety of waste streams, including tannery, chemical industries, bulk drug manufacturing, restaurant, food, and potato chip manufacturing waste (Comninellis and Plattner, 2015).

Electrochemical treatments methods have been successfully used for the treatment of industrial waste. Because of their adaptability, environmental compatibility, and possible cost effectiveness electrochemical techniques are becoming more popular as wastewater treatment solutions. However, coffee wastewater is used by the electrochemical treatment method to remove contaminants from industrial waste. In the case of this research, a pulsed electrochemical technique is used to clean coffee processing wastewater. Pollutants, toxic ions, and nutrients make up a high percentage of the coffee waste removed in electrochemical wastewater treatment methods. The coffee wastewater treatment system relies on the use of electrochemical techniques to remove phosphate, nitrate, color, COD, and turbidity from the wastewater (Comninellis and Plattner, 2015).

Previous research has shown removal of contaminants from wastewater using electrochemical methods. The pulsed current supply was shown to be a viable strategy for organic elimination by electrochemical oxidation since it resulted in a significant reduction in specific energy consumption when compared to the continuous current supply. In addition, when compared to DC, the lower deposition rate of particles under pulsed current has been demonstrated. As a result, direct current is employed for a substantial portion of electric consumption. Cost-effectiveness, environmental compatibility, and potential safety are all advantages of electrochemical procedures. They are becoming more popular as wastewater treatment solutions due to their versatility. Previous studies have shown that electrochemical methods can remove contaminants from wastewater. When compared to the continuous current supply, the pulsed current supply was demonstrated to be a viable technique for organic elimination by electrochemical oxidation since it resulted in a significant reduction in specific energy consumption. Furthermore, the reduced particle deposition rate under pulsed current has been observed when compared to DC, as direct current consumes more electricity than pulsed current (Lu *et al.*, 2015).

For this type of electrode, aluminum was chosen over other electrode materials such as stainless steel, copper, iron, titanium, and others. Aluminum is used for the coffee wastewater treatment method to remove phosphate, nitrate, turbidity, and COD removal efficiency and to be more cost-effective and effective (Manoj Kumar, 2015).

At least two electrodes make up an electrochemical system. Cathode and anode (Muddemann *et al.*, 2019). Selection of the proper electrode materials is critical. Aluminum is the most popular electrode material used in electrocoagulation. They are inexpensive, readily available, and effective. In recent years, the use of aluminum or iron as an electrode in phosphate removal by the EC has received a lot of attention. However, in this study, the phosphate was removed utilizing an electrochemical technique with aluminum as the electrode. In this study, dimension of aluminum electrodes are (13 cm x 6 cm x 0.01 cm) and a gap of 1 cm were employed as alternating electrodes and placed vertically in the reactor. The anode and cathode were changed every 15 minutes to improve the effectiveness of the pulsed electrochemical process procedure (Chen *et al.*, 2014).

1.1.1 Electrochemical Oxidation and Reduction

Electrochemical oxidation processes aim at the mineralization of organic compounds in process waters and wastewaters whereby, in particular, the electrochemical advanced oxidation processes (E-AOP) have moved into the focus of research and application. These are characterized by the generation of very strong oxidizing agents such as hydroxyl radicals, preferably using the reaction at the anode. The in situ electrochemically generated oxidants occur either directly at the anode surface or indirectly by subsequent reactions with inorganic components (Muddemann *et al.*, 2019).

1.2 Statement of the problem

The coffee processing method can be either dry or wet. The wet processing system uses large volumes of water and generates a high volume of polluted effluent, which is traditionally discharged easily into the nearby stream or river. This effluent is generally composed of a high concentration of organic matter and suspended solids and is highly acidic. Another major issue with wet coffee processing is the large amount of water required for processing, approximately 15–20 liters per 1 kilogram of coffee beans. If water is not recycled, the resources themselves are exposed. Consequently, the pollution resulting from the discharge of colored effluent is responsible for its capacity and high chemical and biological oxygen demand, causing eutrophication, blocking light and affecting photosynthesis. Also, the problems caused by

wastewater discharging into the environment are high concentrations of turbidity, nitrate, and phosphate (Ijanu, Kamaruddin *et al*, 2020). The effects of wet coffee processing wastewater are high levels of toxic ions. These ions pose risks to human and plant life when they are discharged from untreated wastewater. The toxic chemicals must be treated before being discharged to the water body. Currently, the development of various sectors leads to economic progress in countries, but our environment is contaminated due to a lack of adequate wastewater treatment from various processing units. For example, coffee is one of Ethiopia's most important exports, but due to a lack of technology for treating wet coffee processing wastewater, water resources are polluted, and various organisms are harmed, particularly due to eutrophication. Additionally, coffee processing wastewater can cause bad odor and sludge in the water body. To address these issues, creating low-cost, easy-to-use, and environmentally friendly technologies, enhanced pulsed electrochemical techniques for waste discharges from wet coffee processing. The gap between pulsed electrochemical processes and other treatment methods or advanced treatment technologies is that the pulsed electrochemical method is easily applicable and can be done at a cheap cost. Previous research has only relied on direct current electrocoagulation (DC-EC). It has disadvantages such as easy passivation of electrodes and high energy consumption, which limit its use in polyvinyl alcohol wastewater. Therefore, alternating pulse current electrocoagulation (APC-EC) has been developed to overcome these problems. In this study, the influencing factors and energy consumption of polyvinyl alcohol treatment by APC-EC and DC-EC were explored, and the best operating conditions for PECP were obtained via the response surface method (RSM). Compared with DC-EC, the application of AC-EC can reduce electrode passivation and production of sludge and operating costs, improve electrode stability, and improve polyvinyl alcohol removal efficiency. Pulsed electrochemical (PEC) treatment technology is an effective wastewater treatment method based on conventional EC, compared with direct current electrocoagulation (DC-EC); it can eliminate and reduce passivation, and can also reduce energy consumption and achieve high processing efficiency. It is simple to implement and inexpensive to implement. Displaying a board prospect for the use of a pulsed electrochemical process to remove wet coffee processing wastewater, Secondly, existing technologies in Ethiopia for coffee processing wastewater treatment are less efficient methods like screening and oxidation ponds, which cannot treat wastewater within the range of WHO standards for wastewater discharges, so to overcome these problems, this research is necessary.

1.3 Research Question

1. What are the characteristics and how to treat wastewater generated from wet CPI?
2. What is the pollutant removal efficiency of the pulsed electrochemical process from CPWW?
3. What is the effect of Independent variables on removal of contaminants and how it can be analyzed by using RSM?
4. What is the optimum value of pollutant removal by using a pulsed electrochemical process for CPWW?

1.4 Objective of the research

1.4.1 General objective

The main objective of this study is to investigate the effect of a pulsed electrochemical process to treat wastewater generated from wet coffee processing

1.4.2 Specific objectives

- To characterize wastewater generated from wet coffee processing industry.
- To determine the removal efficiency of dependent variable and power consumption.
- To analyze effects of pH, time. Current Electrolytes concentration on removal efficiency of Contaminants by using RSM/CCD.
- To optimize and select the best removal efficiency of the pulsed electrochemical process for the treatment of coffee processing wastewater.

1.5 Significance of study

The main purpose of the study is to promote a clean environment for the community, environment protection and land investment office, and other institutions by preventing water bodies from contamination due to improper liquid discharge. The environment has been severely affected by the direct discharge of wastewater due to the poisonous and high amount of waste it contains. However, the discharge of wastewater into a river negatively affects the quality of water or water resources, including human, animal, and plant life. These problems are eliminated when wastewater is handled with appropriate technology in terms of simplicity and cost of installation and maintenance. As a result, you can make a significant contribution to resolving the problem in these and downstream communities. But this technology is to remove the pollutants and to have a clean environment, which keeps the health of people and reduces ground

and surface water contamination. Generally, wastewater generated from wet coffee processing should not be discharged into the environment without treatment with effective technology.

1.6 Scope of the study

A sample was taken from the Bedele wet coffee processing factory for the analysis. A small-scale laboratory setup is used by considering the materials and equipment available and the allocated time and budget. Only the results of particular experimental factors such as reaction time, pH, electrolyte, and current were studied in order to identify the major operating factors for the treatment and removal efficiency. Then removal efficiencies of color, COD, turbidity, phosphate, nitrate, and power consumption were calculated by using standard formulas and data generated from laboratory work. Finally, all data and removal efficiency were analyzed by using response surface methodology (RSM) and optimized to select the best removal efficiency of the pulsed electrochemical process.

1.7 Limitation of the study

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

CHAPTER TWO

2 LITERATURE REVIEW

2.1 Electrochemical treatment

Electrochemical treatment is generally characterized by simple equipment, ease of operation, short retention times, and small equipment for adding chemicals. Also, electrolytic cells can be easily automated and coupled with other processes, including chemical and physical processes, to enhance the efficiency of the treatment. Benefits from using electrochemical techniques include environmental compatibility, versatility, energy efficiency, safety, selectivity, responsiveness to mechanization, and cost effectiveness (Drogui, *et al*, 2007).

Electrochemical systems for treating wastewater provide a number of advantages over traditional treatment processes, including environmental compatibility, energy efficiency, adaptability, safety, selectivity, ease of scale up, automation, cost effectiveness, and excellent settling and filterability (Sahana *et al*, 2018).

According to (Bui, 2017) optimize three of most important operating variables, namely electrolysis time, current density, and initial pH, response surface methodology was used in combination with a central composing design (CCD). Statistical analysis showed that the quadratic models for COD removal were significant at very low probability values ($p < 0.0001$) and a high coefficient of determination ($R^2 = 0.9621$). In addition, the statistical results showed that all three variables, as well as the interaction between initial pH and electrolysis time, were significant in COD decrease. With an electrolysis time of 10 minutes, a current density of 108.3 A/m^2 , and an initial pH 7, the maximum predicted COD removal using the response function was 93.3%. The removal efficiency value agreed well with the experimental value of COD removal (90.4%) under the optimum conditions.

The optimization of this research is carried out by using central composite design methodology to determine the optimum operating conditions to treat coffee industry wastewater using the pulsed electrochemical treatment (PECT) method for simultaneous optimization of response. The optimum value or maximum removal efficiency was chosen for the process parameters of pH 7, electrolyte dosage of 0.75g, electrolysis time of 45 min, and current of 0.45Amp, respectively. The optimum values under this condition are COD (98.75 %), color (99.92 %), turbidity (99.00 %), phosphate (99.02 %), and nitrate (98.83 %), with a power consumption of 0.971 kWh/m^3 . The significance of independent variables and their interactions was determined

with 95 percent confidence limits using response surface methodology (RSM), central composite design (CCD), and analysis of variance (ANOVA).

According to (Kumar, 2015), As previously investigated, an aluminum electrode can be used for the treatment of coffee wastewater using an electrocoagulation technique. Utilizing electrochemical techniques, an aluminum electrode can be utilized to efficiently treat coffee waste. The electrolytic efficiency was mostly determined by the COD elimination efficiency. After 120 min of electrolysis at a voltage of 16 V and a pH 4.56, the aluminum electrode's efficiency in terms of COD removal was 90%. The removal of nitrate, ammonia nitrogen, and phosphorus over time ranged from 87% to nearly 100% for nitrate and 91% to 100% for phosphorus. Nitrate nitrogen was lowered from 34 mg/l to 29 mg/L in the first 12 minutes, and phosphorus was reduced by 63 mg/l, which should be reduced to 54 mg/l. After 60 minutes, nitrate and phosphorus levels were lowered to 3.49 mg/l and 6.7 mg/l, respectively, after 60 min. In particular, the best phosphorus removal percentage was 92%, while the best nitrate nitrogen removal percentage was 89%.

2.2 Water pollution

Water pollution is becoming a major global concern as a result of rapid population expansion, urbanization, ineffective and expansive treatment methods, and poor management. Coffee, distilleries and tanning, oil mills and textiles, food processing chemicals, soft drinks, paper. And the metal sectors are all major contributors to waste creation in Ethiopia (Gebeyehu *et al.*, 2018). Water pollution is caused by the presence of organic, inorganic, biological, radiological, or physical substances in the water that tend to degrade its quality. The presence of undesirable and hazardous materials and pathogens beyond a certain limit also causes water pollution. Water bodies, especially freshwater reservoirs, are the most affected. Organic pollution of inland water systems in Africa is often the result of economic and social underdevelopment (Woldesenbet *et al.*, 2014).

The coffee processing industry is one of the major agro-based industries that are responsible for water pollution. In many coffee processing countries, the wastewater is disposed of after pulping, fermentation, and washing of coffee beans and presents a series of problems for the receiving environment, especially on water bodies (Woldesenbet *et al.*, 2014).

2.3 Physiochemical wastewater characteristics of wet coffee wastewater

2.3.1 Turbidity

Suspended particles, such as clay, silt, finely divided organic and inorganic matter, soluble colored organic compounds, and plankton and other microscopic organisms, generate turbidity in wastewater. Turbidity rises as sewage gets more powerful, and turbidity poses significant difficulty in wastewater treatment. Turbidity is caused by suspended sediment, such as silt, as well as organic compounds, such as algae. Colored dissolved organic matter measurements can also cause turbidity (Mullins *et al.*, 2018).

2.3.2 Total suspended solid (TSS)

The total suspended solid concentration measures the amount of particles suspended in water, which can range from silt and plankton to industrial pollution and sewage. Total suspended solids in river water can reduce light penetration, reducing photosynthesis (Teshome, Gelanew and Abayneh, 2020).

2.3.3 Total dissolved solid (TDS)

Total dissolved solids are found naturally in water as a result of mining and industrial wastewater. TDS is made up of mineral and organic molecules that might be beneficial or harmful, such as poisonous metals and organic pollutants. Total dissolved solids are measured in a water sample by filtering it through a 2.0 μ m particle size filter, evaporating the excess filtrate, and drying what is left to a consistent weight at 180 °C (Weber-Scannell *et al.*, 2007).

2.3.4 Electro conductivity (EC)

Electro conductivity is an indirect measure of ion concentration and refers to the ability of water to conduct an electric current. The more ions are present, the more electricity the water can conduct (Teshome, *et al.*, 2020).

2.3.5 Dissolved oxygen (DO)

The amount of dissolved oxygen in rivers is one of the most important measures of their biological health, with considerable change over a wide range of spatial and temporal scales. It is primarily dependent on the water temperature. However, this reliance shifts with changing hydro climatic conditions and the intensity of biological processes like photosynthesis, respiration, and organic matter decomposition (Rajwa-Kuligiewicz *et al.*, 2015).

2.3.6 Chemical oxygen demand (COD)

The chemical oxygen demand is commonly employed in order to indirectly determine organic molecules in water. The oxygen demand is a measurement of how much oxygen is needed to thoroughly oxidize both biodegradable and non-biodegradable organic and inorganic materials (Teshome, *et al*, 2020).

2.3.7 Phosphate (PO_4^{3-})

High amounts of nutrients, including phosphate, are released into the environment by wet coffee processing wastewater plants and the primary source of eutrophication in oceans, lakes, and rivers. When the quality of the water is harmed due to nutrient pollution, the development of algae and plankton changes dramatically, or algal bloom, depleting oxygen for other aquatic life in the ecosystem (Teshome, *et al* . 2020).

2.3.8 Nitrate (NO_4^{3-})

Nitrate is found in a trace amount in surface water, with the majority of it coming from organic and inorganic waste. Excess nitrate in river water supports high primary productivity of eutrophication or algal blooms (Teshome, *et al.*, 2020).

2.4 Coffee

Coffee is the second most traded product in the world after petroleum, which has made it easier for many countries to cultivate and produce coffee in commercial quantities. Coffee represents an agricultural crop of significant economic importance to the coffee-producing countries of the world. Global annual coffee production is estimated at 5.5 million tons, of which 6.4% is produced in Ethiopia (Woldesenbet, *et al.*, 2014).

2.4.1 Wet coffee processing wastewater characteristics

A large amount of water is used in the manufacturing process, which results in contaminated water. Coffee processing is the prime agro-based industry that utilizes large quantities of water, which is characterized by a high organic load in terms of COD and color. It also contains high total dissolved solids, total suspended solids, and nutrients like nitrogen and phosphorus. Coffee wastewater is also rich in sugars and pectin, caffeine, fat and peptic substances, macromolecules like lignin, tannin, humic acid, alkaloids and polyphenols. The final disposal of the pulp and wastewater containing mucilage and pulp extracts generated by the coffee agro industry is an increasing environmental problem due to the recalcitrant nature of the compounds in the effluents (Asha and Kumar, 2015). Because the wet processing system utilizes a lot of water, it produces a lot of polluted effluent, and this can be easily discharged into a nearby stream or

river. The removal of coffee cherries, pulp, and mucilage is part of wet coffee processing. This waste generates a large volume of acidic materials. As a result, prior to discharge into an aquatic body, treatment is required. Therefore, treatment before discharge to water bodies is required (Ijanu *et al.*, 2020).

Table 2-1 Characteristics of wet coffee wastewater processing

Parameter	Range of Value
pH	3.9- 4.99
Turbidity (NTU)	56 - 85
COD (mg/L)	1,400 – 1990
TS (mg/L)	3,400 – 3550
TDS (mg/L)	3,150 – 3280
Phosphate (mg/L)	53 – 84
Nitrate (mg/L)	87 – 147
Color (abs)	6,800 – 9,200

Source (Villanueva-Rodríguez *et al.*, 2014)

2.5 Effect of wet coffee wastewater processing

Wet coffee wastewater is physically or biologically processed, and the coffee by-products are dumped into the river. The use of the oxygen in the water by the organic residual in the process of the coffee causes the following problem: Due to a lack of oxygen, the proliferation of undesirable microorganisms, non-potable and insufficient water for domestic use; insufficient water for industrial use, including coffee processing in other coffee mills; bad odors; the attraction of flies and other insects; and the deterioration of the landscape (Woldesenbet, *et al.*, 2014).

2.6 Environmental impacts of wet coffee processing industry

According to (Gebrehiwet, 2019) the primary environmental impacts that can be attributed to the production of wet coffee are discharges into water bodies. The discharge of nutrient-rich domestic and industrial waste can have a negative impact on the ecological balance and functioning of the receiving environment as well as the public health of downstream end-users of polluted water sources. Toxicity to fish and other aquatic organisms; depletion of dissolved oxygen in receiving water bodies as ammonia or ammonium ions consume oxygen; eutrophication

n when nitrogen, phosphorus, and bade simile release toxic substances in water bodies; dissolved oxygen in water bodie and potential public health risk are some of the devastating consequences.

2.7 Metal electrodes used for coffee processing wastewater treatment

According to (Kumar, 2015) coffee pulping wastewater uses aluminum as an electrode since it is more economical when compared to other electrodes such as copper, iron, and titanium, etc. Previous researchers have tried electrochemical treatment of different high-strength industrial waste streams with different types of electrodes with varying degrees of pollutant removal. The implementation of electrochemical processes in the treatment of wastewater can result in the destruction of organic contaminants and lead to the efficient removal of color and COD. The visible color removal of coffee pulping wastewater in electrochemical treatment was found to be good. Physicochemical treatment leads to color removal from the wastewater.

2.8 Response surface methodology (RSM)

RSM is typically used to evaluate the efficient factors for optimizing their outcome to the desired responses, and it was combined with the CCD method to improve the series of tests using Excel software. Response surface plots are a tool for predicting wastewater removal efficiency. The contours of the plots also aid in determining the various types of interactions that exist between these variables. The restricted surface in the contour diagram's smallest curve indicates that the maximum expected yield was obtained. RSM generates a three-dimensional surface from input and response variables (Darvishmotevalli *et al.*, 2019) .

CHAPTER THREE

3 MATERIALS AND METHODS

3.1 Study of setting area

Bedele town is located in the Buno Bedele zone of southwest Ethiopia's Oromia region, with latitude 8.450°N 36.350°E and longitude $8^{\circ}27'\text{N}$ $36^{\circ}21'\text{E}$, and meters (6,601 – 7,093 ft) above sea level. According to the central statistical agency's population projections, the Buno Bedele zone Badele city population will be 204, 223 by 2017, with 101,112 men and 103,111 women. The zone has 1.6 million ha of land, of which 10% is high land, 67% is medium land, and 23% is low land. The altitude of the zone ranges from 500 to 2575 meters above sea level. The Buno Bedele zone is divided into ten districts and is known for its coffee, livestock, and cereal grain-livestock mixed farming systems. There are two major rainy seasons in the zone (short and long), and annual precipitation ranges between 1500 and 2200 mm (El-Hosainy, Zahran and Sabry, 2017).

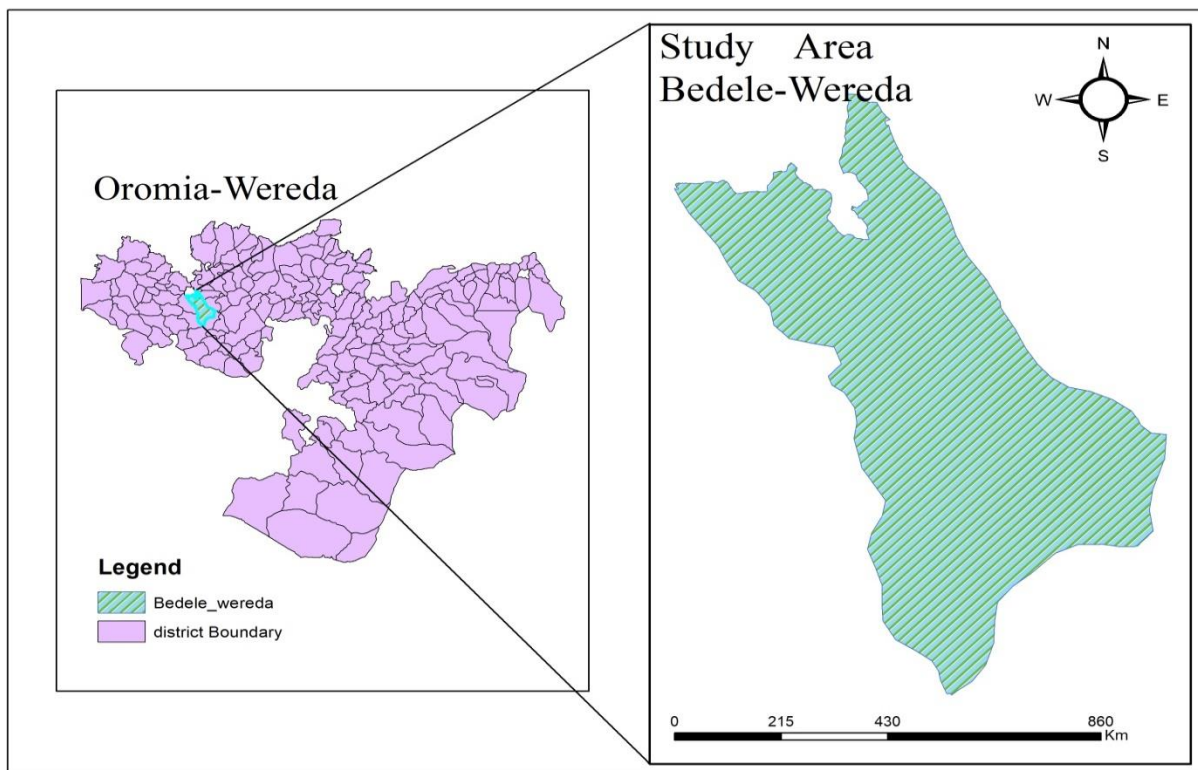


Figure 3-1 Location of study area from GIS

3.2 Material and Methods

The equipment's used for this study were magnetic stirrer, (model RHB2), desiccator, dray oven, filter paper, beaker, desiccator, COD reactor (Hatch 45600-02), COD kit, DO meter, conductivity meter (Cond 3110), electrode (Al), DC-power supply, multi-meter, conical flasks, pH meter, spectrophotometer (model 6700), vacuum pump, multi meter, 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 (Wage-WT3020), pH meter (pH3310), ultraviolet (UV), was used for the investigation of samples throughout the experiment.

3.3 Chemical and reagent

Chemical used for coffee processing wastewater treatment and analyses are mercury sulfate (HgSO_4), ferrous ammonium sulfate ($\text{Fe}(\text{NH}_3)\text{SO}_4$), sulphuric acid (H_2SO_4) silver sulfate (Ag_2SO_4), ferroin indicator ($\text{Fe}(\text{o-phen})_3\text{SO}_4$), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) are used for COD removal , hydrogen per oxide (H_2O_2), oxidizing and supporting reagents (Catalyst), was used for the treatment are sodium sulfate (Na_2SO_4), KOH, NaOH, NaCl, sodium hydrogen carbonate (NaHCO_3), phenolphthalein, stannous chloride, ammonium molbdate, phenol, buffer solution and distilled water.



Figure 3-2 Chemical used for determination of COD

3.4 Software

The software was used with version 7 of design-expert software- response surface methodology (RSM) and Microsoft Excel 2010.

3.5 Methodology

3.5.1 Research Design

Laboratory based experimental study design was conducted in the Jimma University environmental laboratory, focusing on evaluating the performance of the pulsed electrochemical process. All the important preparation and physio-chemical analyses for the wastewater sample were made ready for laboratory testing. The next step was to conduct experiments for all parameters and check the removal efficiency of the process. While running the experiments, lab manuals are used properly to reduce redundancy and errors. The data obtained from both the onsite measuring and laboratory tests was analyzed and optimized by using response surface methodology.

3.6 Sampling design and size

The best representative for wet coffee processing wastewater sampling was collected using a composite sampling method at different intervals of time. The experimental runs were 60 liters of wet coffee wastewater collected for the research. This sample volume was taken depending on the number of experiments run (N). According to (Darvishmotevalli *et al.*, 2019)

$$N = N_a + N_o + N_c \quad (\text{Eq. 3 - 1})$$

Where N represents the number of experimental runs, N_a represents the number of experimental factorials, N_o , represents the number of axial and N_c represents the number of center points. On these, the number of experimental runs became 60, which is equal to the amount of sample size to be calculated for the above equation (3-1). This sample volume was taken to depend on the number of experiments or runs.

$N = [2^n + 2n + C]$ Where, N, number of run, n- number of factor, and C number of center. Based on the above equation number of experiment run becomes 60, which is equal to the sample size. It was calculated using the above equation.

3.7 Sample collection, transportation and preparation

3.7.1 Sample collection

Wet coffee processing wastewater samples were collected in sterilized plastic containers from the Bedele wet coffee processing factory, located in Buno Bedele zone, Bedele city. The composite sample will be applied in this research due to the type of wastewater to be taken. According to the water quality manuals, wastewater was collected from the Bedele wet coffee processing discharge point and stored in a plastic jar can for three days. Generally, about 60 liters of wastewater samples were taken for this research. The plastic jar can was soaked in 10% HCl for 24 hours and thoroughly cleaned and rinsed with distilled water.



Figure 3-3 Collected coffee processing wastewater sample

3.7.2 Sample transportation and preservation

Sample-containing bottles were placed in a box for transportation to the laboratory. Plastic boxes were used to protect the sample from sunlight, prevent the breaking of a plastic jar, and should allow a 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 guidance for sample transportation.

3.7.3 Sample preparation

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

3.8 Experimental setup

The goal of this experiment is to determine the contribution of pulsed electrochemical processes in wastewater treatment, as well as to assess the efficiency of color, COD, turbidity, nitrate, and phosphate removal from Bedele coffee processing wastewater effluent by using an aluminum electrode. The schematic arrangement of the experimental set up is shown in figure 3 2. The experiment was carried out in a 1 L batch mode electrochemical reactor with a pair of rectangular shap

ed aluminum electrodes with a total area of 90 cm^2 . The electrodes were connected vertically with an adjustable gap of 1 cm between them and were powered by a DC power supply in monopolar mode. The electrodes were thoroughly cleaned and washed with HCl and water for about 15 min before and after each run. Magnetic bids were placed in the reactor to preserve uniformity.

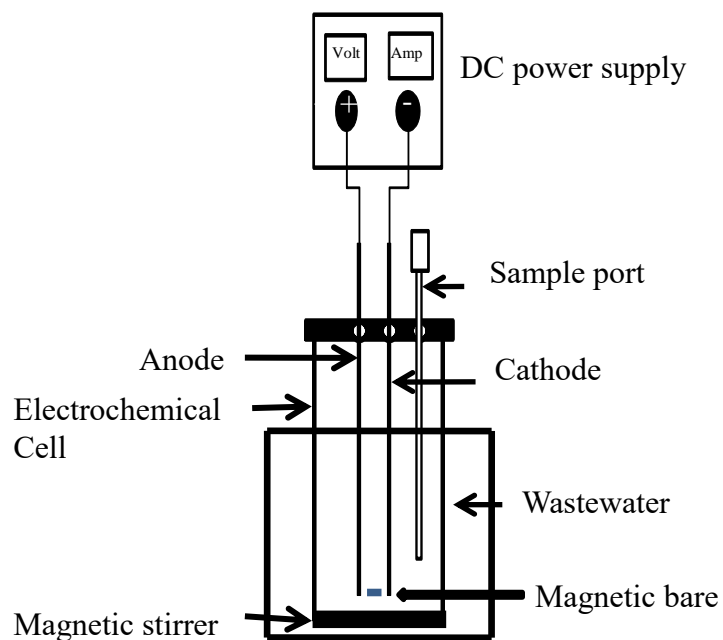


Figure 3-4 Pulse electrochemical processing setup

3.9 Study of variable

3.9.1 Dependent variable

Color, turbidity, COD, phosphate, nitrate, and electricity consumption were dependent variables to investigate removal efficiency or the performance of wastewater treatment technology using a pulsed electrochemical process.

3.9.2 Independent variable

The operating parameters, such as time, pH, current, and electrolyte, are controlling variables which determine the removal ability of the method.

3.10 Method of data analysis and presentation

The study of data processing and analysis was interpreted by using Microsoft Excel Office and Response Surface Methodology (RSM) software. Its optimization and analysis can be done using both qualitative and quantitative data analysis methods. All results are compared with the WHO (2004) standard. The parameters and measurement methods used are given below in table 3-1.

Table 3-1 The parameters to be tested and measurement method

Physical Parameter	Instruments used to measure
pH	pH meter
Color	UV- vis Spector photometer
Current	Milt meter
Turbidity	Turbidity meter
Electrical conductivity	Conductivity meter
Chemical parameter	
Chemical oxygen demand (COD)	Close reflex method
Nitrate	Gravimetric method
Phosphate	Stannous chloride method

3.11 Experimental design and statistical analysis

The performance of the process was evaluated based on the response of COD, color, turbidity, nitrate, and phosphate by removal efficiencies; response surface methodology was used as a soft war model; and analysis of the data obtained from the laboratory by using empirical formulas: -

I. Percentage of COD Removal

The equation (3 - 1) used to determine % of COD removal efficiency (Asaithambi *et al.*, 2021).

$$\% \text{ COD removal,} = \left(\frac{COD_i - COD_o}{COD_i} \right) * (100) \quad (Eq. 3 - 2)$$

Where, COD_i and COD_o are the COD (mg/L) at initial (t=0) and at any reaction time (t) respectively. COD (mg/L) of each run was determined by the following formula

II. Percentage of Color removal

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

Where Abs_i and Abs_t are absorbance of sample for corresponding weave length ($\lambda=420\text{nm}$) at initial (t=0) and at any reaction time (t) respectively.

III. Power consumption (kWhr/m³)

On the practical and economic perspective, the consumption of electrical energy is an important factor in the ACE process and it was calculated using equation.

$$\text{power consumption} = \left(\frac{VI_t}{V_s} \right) \quad (Eq. 3 - 5)$$

Where V cell voltage (volt), I applied current (amp), t – ACE treatment time (hr), and V_s, volume of wastewater used (L)

IV. Percentage of Turbidity removal

$$\text{Turbidity removal,} = \left(\frac{\text{Tur}_i - \text{Tur}_t}{\text{Tur}_i} \right) * (100) \quad (\text{Eq. 3 - 6})$$

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

V. Percentage of nitrate removal

$$\text{Nitrate removal, \%} = \left(\frac{\text{NO}_4^{3-}{}_i - \text{NO}_4^{3-}{}_t}{\text{NO}_4^{3-}{}_i} \right) * (100) \quad (\text{Eq. 3 - 7})$$

Where, NO₄³⁻_i and NO₄³⁻_t are concentration of nitrate before treatment respectively.

VI. Percentage of phosphate

$$\text{Phosphate removal, \%} = \left(\frac{\text{PO}_4^{3-}{}_i - \text{PO}_4^{3-}{}_t}{\text{PO}_4^{3-}{}_i} \right) * (100) \quad (\text{Eq. 3 - 8})$$

Where, PO₄³⁻_i and PO₄³⁻_t are the concentration of phosphate treatment respectively

3.12 The experimental design and statistical analysis

Response surface methodology (RSM) is a procedure for analyzing the relationship between the process variables and the responses. As a result, the response is used to describe a performance metric or quality attribute. The input variables are also known as independent variables, and they are under the scientist's or engineer's control. The Response-surface approach is a set of strategies for using experimental methods to find the best-operating conditions. Typically, this requires conducting a series of experiments and using the results of one to guide the following steps (Bähre, Weber and Rebschläger, 2013). In this study, laboratory experiments were carried out using a pulsed electrochemical process by varying parameters in their interval pH (3–11), electrolyte concentration (0.3–0.6) g of NaCl or CaCl₂, current (0.5–1 Amp), and reaction time (30–60 min). As shown in table 3-2 and 3-3 these inputs give some experimental runs, range of pH, time, current, and electrolyte which was generated by using RSM software.

Table 3-2 Experimental design for pulsed electrochemical process by using CaCl₂

Factor	Name	Units	Type	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	pH		Numeric	3.00	11.00	-1 ↔ 3.00	+1 ↔ 11.00	7.00	1.82
B	Time	Min	Numeric	15.00	75.00	-1 ↔ 30.00	+1 ↔ 60.00	45.00	13.65
C	Current	Amp	Numeric	0.1500	0.7500	-1 ↔ 0.30	+1 ↔ 0.60	0.4500	0.1365
D	Electrolyte	g	Numeric	0.2500	1.25	-1 ↔ 0.50	+1 ↔ 1.00	0.7500	0.2274

Table 3-3 Experimental design for pulsed electrochemical process by using NaCl

Factor	Name	Units	Type	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	pH		Numeric	3.00	11.00	-1 ↔ 3.00	+1 ↔ 11.00	7.00	1.82
B	Time	min	Numeric	15.00	75.00	-1 ↔ 30.00	+1 ↔ 60.00	45.00	13.65
C	Current	Amp	Numeric	0.1500	0.7500	-1 ↔ 0.30	+1 ↔ 0.60	0.4500	0.1365
D	Electrolyte	g	Numeric	0.2500	1.25	-1 ↔ 0.50	+1 ↔ 1.00	0.7500	0.2274

Therefore, as shown in tables 3-2 and 3-3, these inputs have a given range of pH, time, current, and electrolyte, which were generated by using RSM software with some experiments run. Those parameters were considered to determine the removal efficiency of COD, color, turbidity, phosphate, and nitrate. The order of experiments was arranged randomly.

A total of 60 experiments (30 for electrochemical oxidation by using NaCl and 30 for electrochemical oxidation by using CaCl₂) were performed in the laboratory using an aluminum electrode, and the electrode distance was 1cm. According to the previous investigation, NaCl and CaCl₂ were used as electrolytes to increase the salt concentration and increase the removal efficiency dependent variable, which is due to indirect oxidation caused by the production of chloride or hypochlorite in response to the electrolysis process occurring in the reactor, which, together with the produced hydroxyl radical and hydrogen ion, causes degradation of organic compounds. NaCl and CaCl₂ increase the amount of conductivity and power consumption (Darvishmotevalli *et al.*, 2019).

It depends on the above previous investigation; the sports electrolytes used were NaCl and CaCl₂. There are six dependent variables that were evaluated as the response to establish the

ideal values of the process. Those dependent variables are COD, color, turbidity, phosphate, nitrate, and electricity consumption. Input variables were electrolyte, electric current, electrolysis time, and pH. As stated in tables 3-2 and 3-3, the rotatable experiment plan was carried out with the four independent variables at the three coded levels (-1, 0, and +1). Actual values are the original values assigned to various factors, while code values are assigned to a different level of factors (Sharma and Simsek, 2020).

To optimize the parameters in this study, the CCD model with four factors was used. The experimental design was based on a three-level full factorial design with the addition of a central and star point. The total number of experiments can be estimated using the formula.

$$(Darvishmotevalli \textit{ et al.}, 2019) N = N_a + N_o + N_c \Rightarrow (2^n + 2n + c)$$

Where N_a is the number of tow level experiments in a full factorial design or replicates of factorial point ($2^4 = 16$), N_o is the number of replications in the center point (6 replications) for evaluation of net error, and N_c is the number of replications of the axial (star) point ($2*4 = 8$) by using alpha value = 2. Twenty-four ($16+8 = 24$) factorial points and 6 replicates of the center point were provided by software for a single process. That means there are a total of 60 experiments (30 by using NaCl and 30 by using CaCl_2). For the combined pulsed electrochemical process using electrolytes NaCl and CaCl_2 , the combination of two electrolytes is 60 experiments. 6 center points of the design were evaluated to the pure error and, consequently, the lack of fit. A lack of fit taste was performed to assess the fit of the final model.

The RSM algorithm was used to analyze the experimental results, which were then fitted to the predictive quadratic polynomial equation. To correlate the relationship between independent variable and response, a second-order polynomial equation was fitted. The following is the general mathematical form of a second-order polynomial equation.

$$Y_i = \beta_0 + \sum_i^4 \beta_{0i} \cdot X_i + \sum_{i \leq j}^4 \sum_j^4 \beta_{ij} \cdot X_i \cdot X_j + \sum_{i=1}^4 \beta_{jj} \cdot X_i^2 + e \quad \text{Eq. 3.9}$$

Where Y_i is the response, X_i and X_j are response independent variables, β_0 is the model (regression) constant, I is the linear term, ii is the squired term (second-order), i_j is the interaction term, X_i is the linear term, e is random error, and k is the number of independent variables (k=4 in this study). After fitting the data to models, the model was validated and used to create (3D) response surface contour plots to predict the relationship between independent and dependent variables (Sivakumar, *et.,al* 2015).

Response surface plots are a tool for predicting the efficiency of wastewater removal. The contours of the plots also help to identify the different types of interactions that exist between these variables. The surface restricted in the smallest curve of the contour diagram shows that the maximum expected yield was achieved. The relevant figures show how target responses vary as operational parameter levels change.

3.13 Data quality assurance

According to the American Public Health Association (APHA), proper quality assurance procedures and precautions are taken to ensure the reliability of the results. A fieldwork manual is used to check every step of the process in order to improve the quality of the data. In addition, assistants were chosen to carefully handle the data. The collected data was reviewed for accuracy and reliability. A laboratory test procedures manual is used in order to eliminate data errors. Laboratory instruments were calibrated; triplicate experiments were performed during each set of studies to ensure data quality, and the average of the triplicate measurements was reported. For analysis, calibration or standardization is performed after each set of experiments.

3.14 Ethical consideration

The study was conducted after approval was given from the environmental engineering chair for further investigation of this research. The procedure of the lab manual was mandatory at all stages of experiment result, from title approval to final document submission, so ethical consideration was familiar and sociable to the lab assistant. During this time, all activities performed were done in parallel with good ethics. Finally, the result of laboratory analysis was honestly recorded and interpreted based on scientific procedures.

CHAPTER FOUR

4 RESULT AND DISCUSSION

4.1 Characteristics of wet coffee processing wastewater generated from coffee industry

Wet coffee is an example of industrial effluent which contains pollutants that can harm ecosystems. Coffee processing wastewater produces a huge amount of waste. This huge amount wastewater can affected directly and indirectly to human being, animal and plant life so it produces a large amount of contaminated effluent, which is typically released into a nearby stream or river. As a result, if not treated, wastewater from coffee processing industries can cause for the following water quality indicators.

Characteristics of wastewater processing are large amount of water is used in the manufacturing process, which results in contaminated water. Coffee processing is the prime agro-based industry that utilizes large quantities of water, which is characterized by a high organic load in terms of COD and color. It also contains high total dissolved solids, total suspended solids, and nutrients like nitrogen and phosphorus. Coffee wastewater is also rich in sugars and pectin, caffeine, fat and peptic substances, macromolecules like lignin, humic acid, alkaloids and polyphenols.

Table 4-1 Bedele wet coffee wastewater characteristics before and after the treatment

Before treatment (influent)	Units	After treatment (effluent)	Units	% removal		
Color	2.042	abs	Color	0.004 Abs	99.92	
Turbidity	631	NTU	Turbidity	6.63	NTU	99.00
COD	2980	mg/l	COD	53.23	mg/l	98.75
Phosphate	17.45	mg/l	Phosphate	0.17	mg/l	99.02
Nitrate	14.491	mg/l	Nitrate	0.21	mg/l	98.83

According to the above table 4-1, wastewater taken from Bedele wet coffee processing industry was indicated by the following characteristics; this means color is very black with 2.042abs, turbidity of 631NTU, pH 4.5, COD 2980 mg/l, phosphate 17.45 mg/l, and nitrate 14.491mg/l. This shows that the water sample absorbs high amount of light due to high turbidity and color; also it is very acidic, contain large amount of COD and phosphate which is above WHO standards and needs treatment.



Figure 4-1 Sample of wastewater before treatment

As a result of properly conducted laboratory tests, the maximum removal efficiency of color, COD, turbidity, phosphate, and nitrate was 99.92 percent, 98.75 percent, 99.00 percent, 99.02 percent, and 98.83 percent, respectively, using CaCl_2 as an electrolyte. At pH 7, contact time of 45min, electrolyte dosage of 0.75g, current of 0.45Amp, and total power consumption of 0.972 kWh/m^3 , this efficiency is obtained.

4.2 Removal efficiency of pulsed electrochemical for coffee processing wastewater

Wastewater from the Bedele coffee processing industry was treated in a laboratory by taking into account the effects of independent variables and using electrolytes with varying charges, as shown below.

4.2.1 Removal efficiency of pulsed electrochemical process by using NaCl

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



Figure 4-2 Coffee processing wastewater sample after the treatment

Table 4-2 FCCD for color, COD, Turbidity, PO_4^{3-} , and NO_4^{3-} , removals of PECP by using NaCl

Run	Factors				Responses (Removal efficiency by %)					
	A: pH	B: Time (min)	C: Current (Amp)	D: Electrolyte (g)	Color %	COD %	Turbidity %	Phosphate %	Nitrate %	Power kwh/m ³
1	9	60	0.3	0.5	97.13	93.51	96.27	97.49	96.76	0.73
2	5	30	0.3	0.5	82.80	85.29	86.49	86.95	84.26	0.44
3	7	75	0.45	0.75	97.47	96.50	98.33	98.89	98.48	1.60
4	9	30	0.6	0.5	96.62	93.83	95.27	97.60	96.40	1.27
5	7	45	0.45	0.75	98.02	96.84	98.94	98.99	97.66	1.09
6	7	15	0.45	0.75	90.62	90.05	96.81	95.64	95.38	0.38
7	7	45	0.45	0.75	98.92	96.89	98.84	98.40	97.97	0.97

8	7	45	0.45	0.75	98.07	97.906	98.43	98.94	97.98	1.09
9	9	60	0.3	1	97.49	93.55	96.47	97.93	97.55	0.66
10	7	45	0.15	0.75	95.07	95.62	94.81	97.57	95.97	0.18
11	9	60	0.6	1	97.75	96.09	97.76	98.83	96.30	2.29
12	11	45	0.45	0.75	88.54	89.69	85.50	87.08	88.86	0.87
13	9	30	0.3	0.5	95.66	94.87	94.07	95.62	96.90	0.36
14	7	45	0.75	0.75	99.81	97.91	96.98	98.97	97.87	2.67
15	9	60	0.6	0.5	98.05	96.03	96.33	97.99	97.48	2.35
16	5	60	0.6	1	88.66	89.53	88.35	89.81	88.88	2.04
17	9	30	0.3	1	96.72	93.81	96.48	96.20	96.84	0.29
18	5	60	0.6	0.5	88.56	89.56	87.54	87.90	87.85	2.09
19	5	30	0.6	0.5	87.95	88.05	86.45	87.67	86.92	1.50
20	7	45	0.45	1.25	98.96	96.86	97.72	98.19	98.41	0.69
21	7	45	0.45	0.75	96.12	95.97	98.42	98.99	97.95	0.97
22	5	30	0.6	1	88.19	87.62	87.78	87.56	88.79	1.00
23	7	45	0.45	0.75	98.22	96.88	98.33	98.99	97.09	1.11
24	5	60	0.3	1	88.83	88.80	88.65	87.99	87.91	0.61
25	7	45	0.45	0.75	97.12	98.21	98.46	98.99	97.93	1.09
26	5	60	0.3	0.5	87.19	84.94	87.56	87.61	87.46	0.88
27	3	45	0.45	0.75	70.12	73.62	68.27	68.44	68.80	1.04
28	9	30	0.6	1	97.55	94.72	97.24	97.98	96.69	1.14
29	5	30	0.3	1	89.51	88.62	87.94	86.89	87.89	0.45
30	7	45	0.45	0.25	90.40	91.94	97.01	97.67	95.22	1.04

As shown in table 4-1, the removal efficiency dependent variables are (COD, nitrate, color turbidity, and phosphate) were the maximum removal efficiency response variables such as color 98.92%, COD 96.89%, turbidity 98.84%, nitrate 97.97%, and phosphate 98.40% by using independent variables. The optimum values were pH 7, contact time of 45min, current 0.45amp,

and electrolyte dosage of 0.75g, but all values were varied with various independent variables. This means at the lower value of pH3 or acid to neutral, the removal efficiency increased and at the optimum value at pH7 for pH 11, the removal efficiency decreased. As well as maximum time, electrolyte and current have low removal efficiency in NaCl as an electrolyte.

4.2.2 Removal efficiency of pulsed electrochemical process by using CaCl₂

Calcium Chloride (CaCl₂) is a chemical used as an electrolyte and used to increase conductivity and decrease the amount of voltage supplied to the wastewater by forming Ca⁺² and Cl⁻¹ during the treatment process to increase removal efficiency.

Table 4-3 FCCD for COD, color, turbidity, NO₄³⁻, and PO₄³⁻ removals of PECP by using CaCl₂

Factors					Response (Removal efficiency by %)					
Run	A: pH	B: Time (min)	C: Current (Amp)	D: Electrolyte (g)	Color %	COD %	Turbidity %	Phosphate %	Nitrate %	Power kwh/m ³
1	9	60	0.3	0.5	97.23	94.05	96.32	97.51	97.11	0.73
2	5	30	0.3	0.5	82.90	85.84	86.54	86.97	84.61	0.45
3	7	75	0.45	0.75	93.57	97.04	98.39	98.91	98.83	1.60
4	9	30	0.6	0.5	96.72	94.37	95.33	97.63	96.75	1.27
5	7	45	0.45	0.75	98.12	97.38	99.00	99.02	98.00	1.09
6	7	15	0.45	0.75	90.72	90.59	96.87	95.66	95.74	0.38
7	7	45	0.45	0.75	99.02	97.43	98.90	98.42	98.32	0.97
8	7	45	0.45	0.75	98.17	98.44	98.49	98.96	98.33	1.09
9	9	60	0.3	1	97.59	94.09	96.53	97.95	97.90	0.66
10	7	45	0.15	0.75	95.17	96.17	94.87	97.60	96.32	0.18
11	9	60	0.6	1	99.85	96.63	97.81	98.86	96.65	2.29
12	11	45	0.45	0.75	88.64	90.23	85.56	87.10	89.20	0.87
13	9	30	0.3	0.5	94.16	95.41	94.12	95.64	97.25	0.36
14	7	45	0.75	0.75	95.92	98.45	97.04	99.00	98.22	2.67

15	9	60	0.6	0.5	98.15	96.57	96.39	98.02	97.83	2.35
16	5	60	0.6	1	88.76	90.07	88.41	89.84	89.23	2.04
17	9	30	0.3	1	96.82	94.35	96.53	96.23	97.19	0.29
18	5	60	0.6	0.5	87.66	90.10	87.60	87.93	88.20	2.09
19	5	30	0.6	0.5	86.05	88.60	86.50	87.69	87.26	1.50
20	7	45	0.45	1.25	99.06	97.40	97.78	98.22	98.75	0.69
21	7	45	0.45	0.75	96.22	96.51	98.48	99.01	98.30	0.97
22	5	30	0.6	1	88.29	88.16	87.84	87.58	89.14	1.00
23	7	45	0.45	0.75	98.32	97.42	98.38	99.01	97.43	1.11
24	5	60	0.3	1	88.94	89.34	88.71	88.01	88.26	0.61
25	7	45	0.45	0.75	97.22	98.75	98.52	99.02	98.28	1.09
26	5	60	0.3	0.5	87.29	85.48	87.61	87.63	87.80	0.88
27	3	45	0.45	0.75	70.22	74.16	68.634	68.47	69.15	1.04
28	9	30	0.6	1	94.65	95.26	97.30	98.00	97.04	1.14
29	5	30	0.3	1	89.61	89.16	88.00	86.92	88.24	0.45
30	7	45	0.45	0.25	96.50	93.49	96.07	97.30	96.47	1.04

As shown in table 4-2, the removal efficiency dependent variables are (COD, nitrate, color turbidity, and phosphate) were the maximum removal efficiency response variables such as color 99.02%, COD 97.43%, turbidity 98.90%, nitrate 98.33%, and phosphate 98.44% by using independent variables. The optimum values were pH 7, contact time 45min, current 0.45amp, and electrolyte dosage 0.75g, but all values were varied with in various independent variables. This means at the lower value of pH3 decreased, but acid to neutral, the removal efficiency increased and the optimum value in pH7 for pH 11, the removal efficiency decreased. As well as maximum time, electrolyte and current have low removal efficiency in CaCl₂ as an electrolyte.

4.3 Effect of operating parameters on % of removal efficiency

Depending on Laboratory results; the operating parameters have the greatest influence on PECP, such as solution pH, electrolyte concentration (NaCl/CaCl₂), electric current, and reaction time, were investigated in terms of percent COD, color, turbidity, NO₄³⁻, and PO₄³⁻ removal at room

temperature.

4.3.1 Effect of electrode

Aluminum is the most suitable metal for use as an electrode. Because of its low cost, ease of availability, less oxidation at the anode and cathode, and being less toxic than iron. Aluminum electrodes are more effective at removing phosphates, nitrate, COD, color, and turbidity from wastewater because they can be quickly ionized and coupled with the phosphate ion to generate aluminum phosphate for precipitation (Lacasa *et al.*, 2011).

4.3.2 Effect of pH

pH is one of the most important factors influencing electrochemical process performance. The pH of the water used in the coffee industry is an important operating factor that influences the performance of the electrochemical process. In general, pH refers to a liquid's degree of acidity or alkalinity. Waters with a higher alkalinity have a higher pH. The pH of the solution is critical for pollutant removal in pulsed electrochemical processes. The pH range is varied from 3 to 9 to examine its effect on treatment efficiency (Mouedhen *et al.*, 2008). Depending on the above citation, in this study the pH range was varied from 3 to 11.

The study found that at pH 7, the maximum removal efficiency of COD (98.75%), phosphate (99.02%), nitrate (98.83%), color (99.92%), and turbidity (99.00%) with an aluminum electrode was achieved. Figures 4.2 and 4.3 show this. In the Bedele coffee processing industry, waste water with an acidic pH (pH 3) has lower removal efficiency. However, as the pH moves from acidic to neutral, removal efficiency increases; maximum removal was obtained at pH 7, and removal efficiency begins to decrease when the solution pH becomes basic.

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

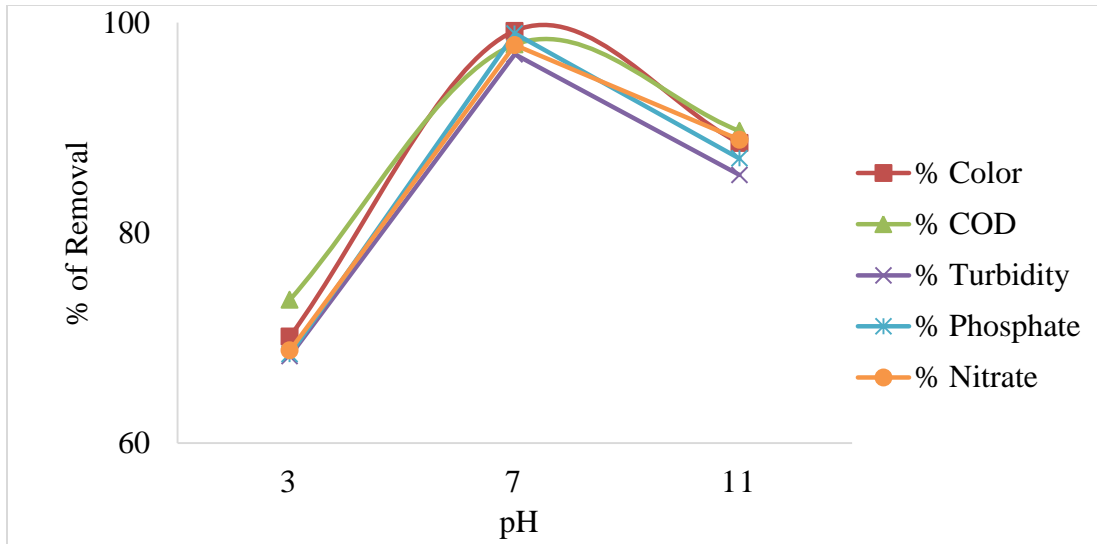


Figure 4-3 Removal efficiency of dependent variable in pH concentration by using NaCl as electrolyte

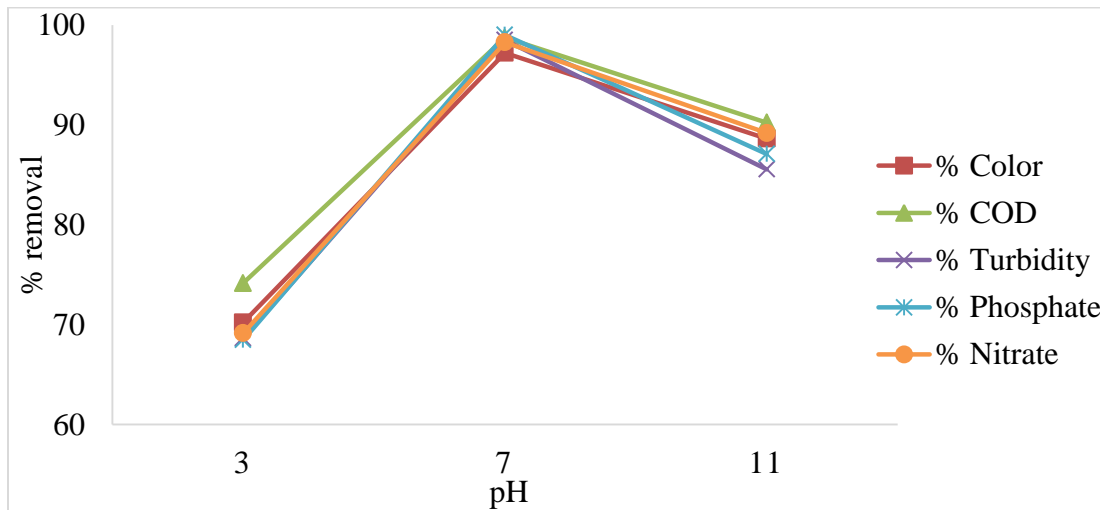


Figure 4-4 Removal efficiency of dependent variable of pH concentration by using CaCl₂

4.3.3 Effect of electrolysis time

Electrolysis time is an important parameter for controlling the reaction rate in an electrochemical treatment process. The experiments were carried out by varying the electrolysis time from 20 to 60 minutes, and the results showed that increasing the electrolysis time up to 45 minutes increases the percentage of absorbance removals (Sivakumar and Maran, 2015). Depend on the above effect of electrolysis time this research was designed 30 to 60min, the reaction time for CPWW has been investigated using Al electrodes at various time intervals (15–75). As shown in

figures 4-3 and 4-4 below, the maximum removal percentage of COD (98.75%), phosphate (99.02%), nitrate (98.83%), color (99.92 %), and turbidity (99.00%) for coffee processing wastewater treatment for a long time and very short time have low removal efficiency. According to this study, 45 minutes is the optimum removal time.

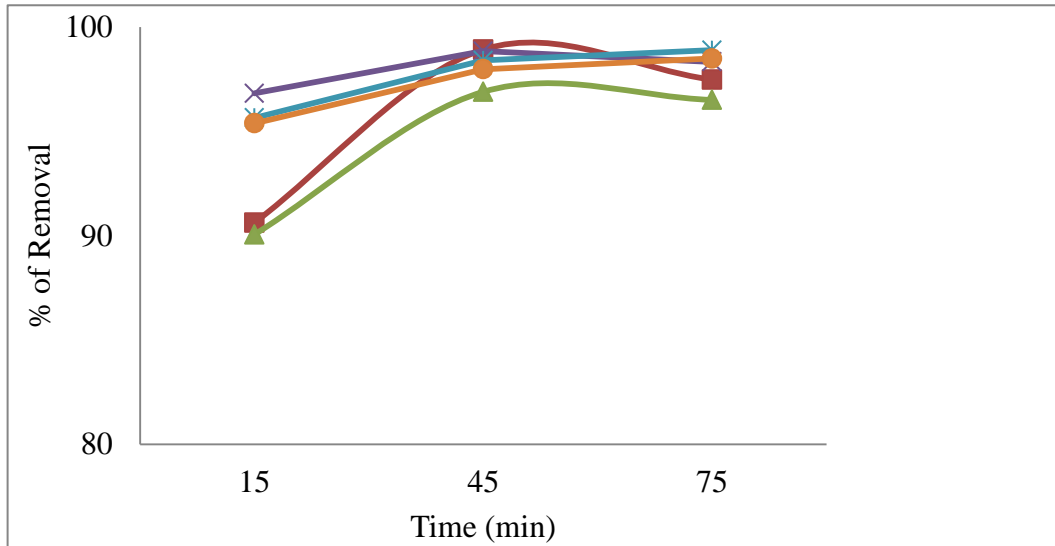


Figure 4-5 Effect of time on removal efficiency by using NaCl

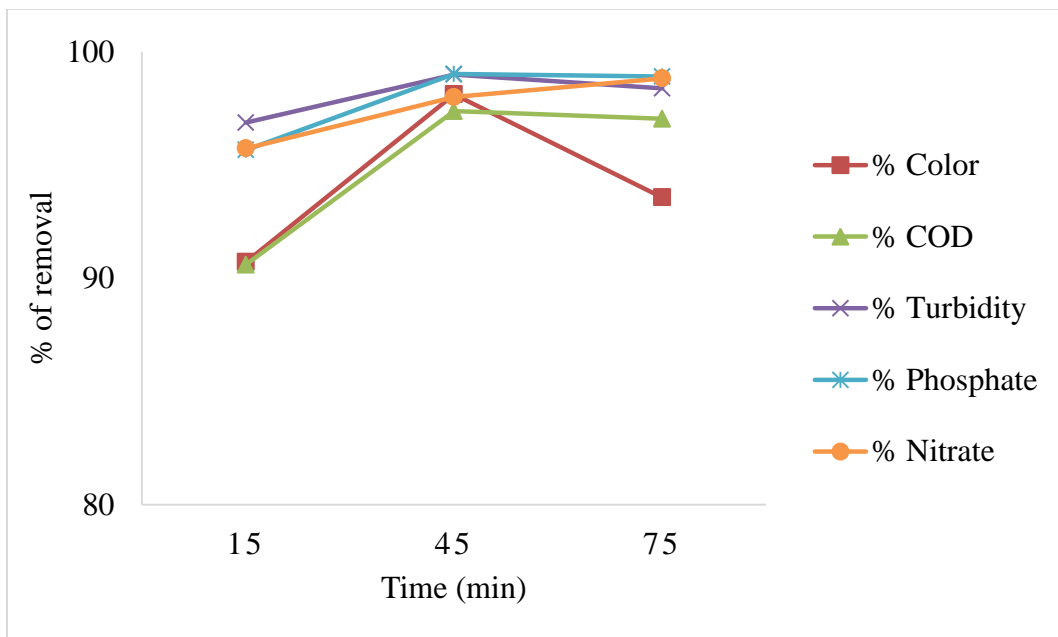


Figure 4-6 Removal efficiency pH of concentration by using CaCl₂

4.3.4 Effect of electric current

Current was, in fact, proportional to voltage. The amount of aluminum dissolved increased as the

current increased. When a higher voltage is applied, the effectiveness of organic oxidation decreases due to oxygen evolution. However, when the process is performed at higher voltages, the poisoning products formed at the anode surface are oxidized. To investigate the effect of current density on the maximum COD and color removal efficiency from coffee processing wastewater (Sivakumar *et al.* 2015). Current density is a critical parameter that influences the electrochemical treatment method used to treat CP industry wastewater, the current range varied from 0.4 to 1 amp. In order to investigate the effect of current density on the maximum COD and color removal efficiency from coffee processing industrial wastewater (Mara *et al.*, 2015). According to the above previously study were designed 0.3 to 0.6amp, as shown, in results depend on figures 4-6 and 4-7, where extremely high current ($I = 0.75$) has a negative or decreased impact on the treatment of wastewater for the CP industry. Current density is a critical parameter that influences the electrochemical treatment method used to treat coffee processing wastewater.

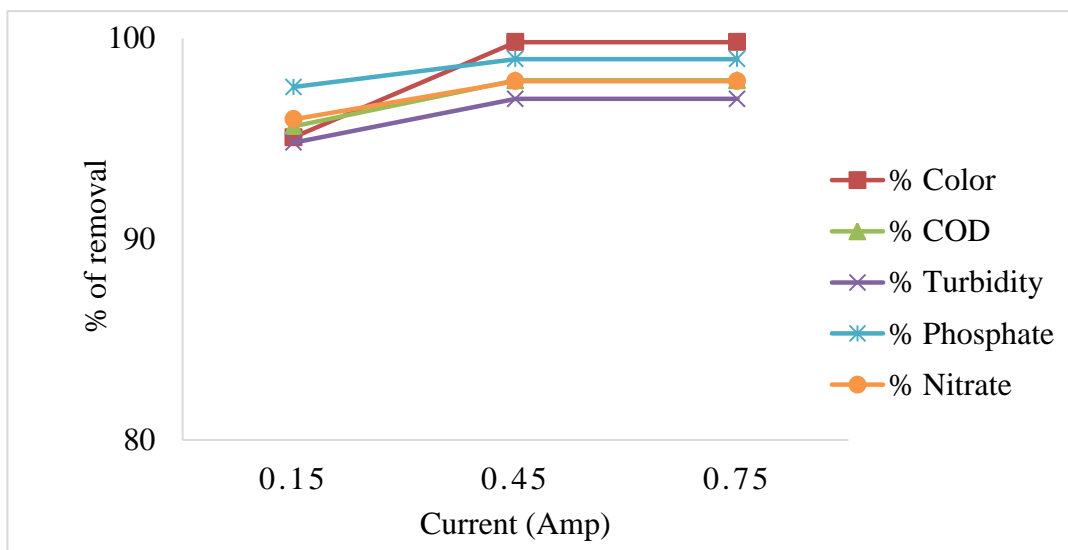


Figure 4-7 Removal efficiency of dependent variable of current concentration by using NaCl

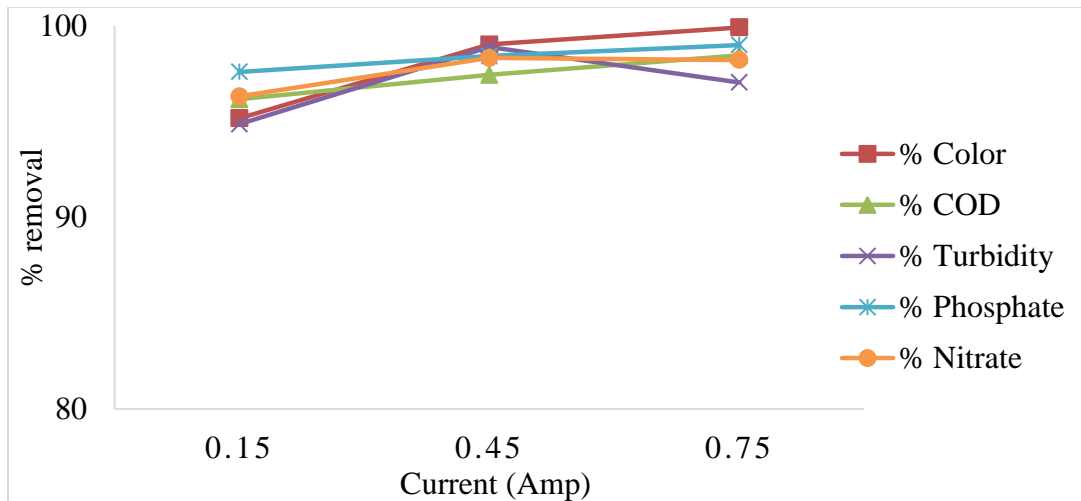


Figure 4-8 Removal efficiency of dependent variable of current concentration by using CaCl_2

4.3.5 Effect of electrolyte concentration

The change in electrical conductivity, which results in a change in the interelectrode resistance and the change in wettability, which affects the mean bubble height, affects the critical voltage and critical current. This insulating layer would significantly increase the voltage between the electrodes, resulting in a significant reduction in current efficiency. The addition of electrolyte would result in a reduction in power usage due to the increase in conductivity. Furthermore, electrochemically produced chlorine has been shown to be useful in water disinfection.

As a result, for the tests, 0.25–1.25 g/l NaCl and CaCl_2 concentrations were used. The amount of electrolyte factor has a greater impact on response when compared to the other components. This is because $\text{NaCl}/\text{CaCl}_2$ increases the ECP system's conductivity, which improves the removal of color, COD, nitrate, phosphate, and turbidity. CaCl_2 produces a more efficient result than NaCl due to the increase in ions from +1 (NaCl) to +2 (CaCl_2). To improve the solution's conductivity disinfection, a supporting electrolyte (NaCl or CaCl_2) was added (Kateb, Fathipour and Kolahtouz, 2020). As shown in figs. 4-8 and 4-9, high concentrations and very small concentrations of electrolyte dosage have low efficiency of removal for coffee processing wastewater treatment (CPWWT).

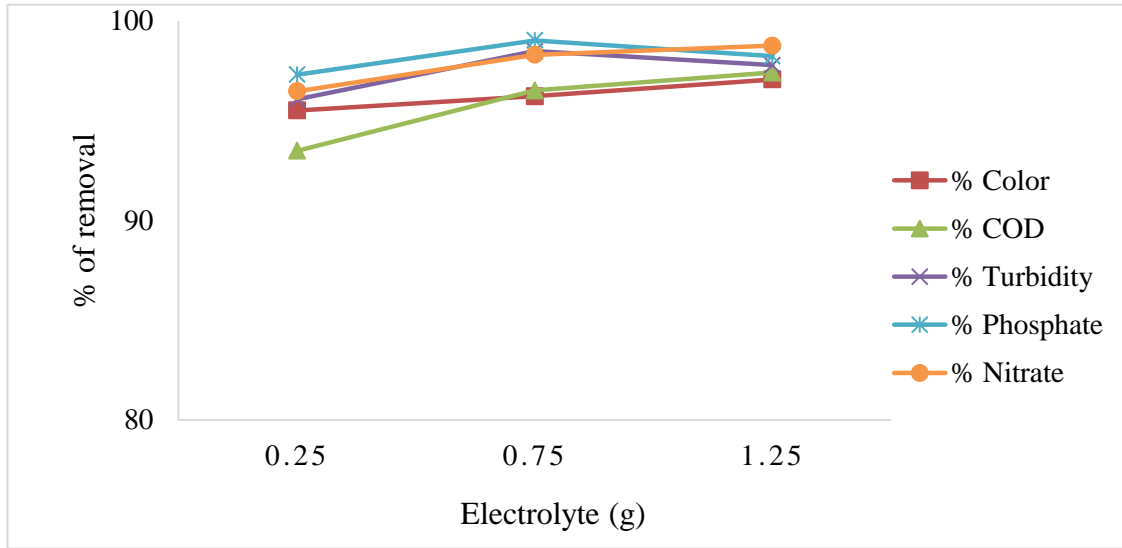


Figure 4-9 Removal efficiency variable of electrolyte concentration by using NaCl

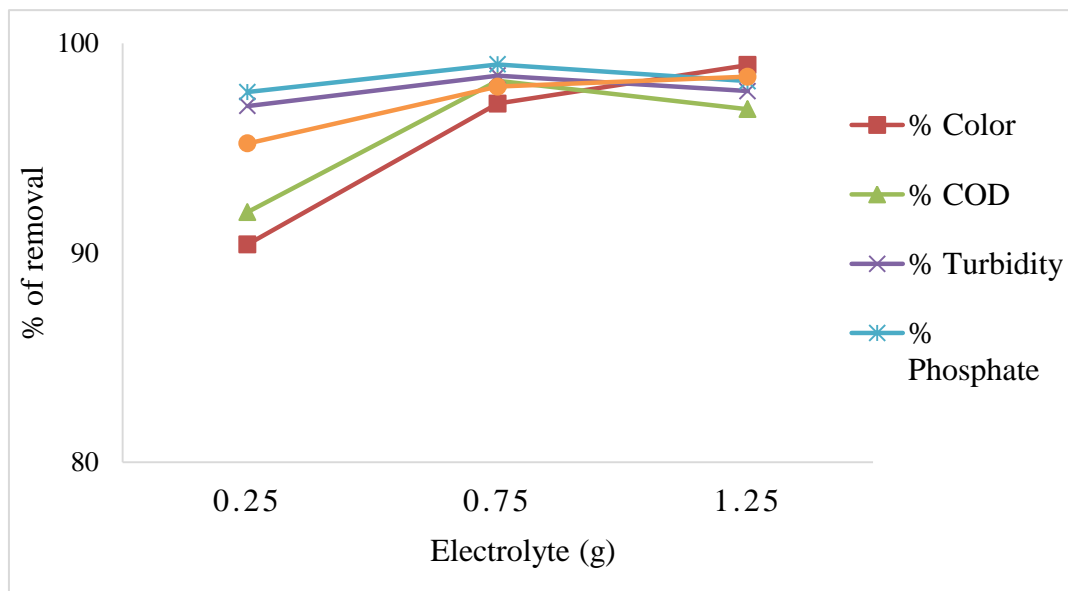


Figure 4-10 Removal efficiency variable of electrolyte concentration by using CaCl₂

4.3.6 The interaction effects

The interaction effect of input variables refers 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. The determination coefficient (R^2) of each coefficient was determined using Fisher's F-test and probability p-values; small probability values ($p < 0.001$) indicate that the model was very significant and could be used to predict the response function, as shown in

Tables 4-4. The model was highly significant and could be used to predict the response function with a low probability ($p < 0.001$). The research data was evaluated using multiple regressions. Analysis of variance was used to examine the coefficients, and the significance level was set at ($p < 0.05$). The relevance of each model parameter was determined using Fischer's F-value and P-value. If the null hypothesis is true, the F-value is the test for comparing curvature variance to residual variance, and the probability (p-value) is the likelihood of observing the observed F-value. When the probability values are small and the curvature is not significant, the null hypothesis is rejected. Show on the result, the greater the value of F and the lower the value of p, the more significant.

4.4 Optimization of response surface methodology

Using response surface methodology, electrochemical parameters were statistically optimized (RSM). RSM is a type of regression analysis that predicts the value of a dependent variable based on the controlled values of the independent variables. RSM was used to optimize an experimental parameter for another process, which included electrochemical oxidation. It is a highly efficient procedure because it not only determines the best operating conditions to maximize system performance, but it also generates a response surface model that predicts a response based on a combination of factor levels. It also depicts the magnitude and impact of various factors on the response, as well as their interactions. As a result, they have been used to simulate a variety of water and wastewater treatment systems and processes (Asaithambi and Matheswaran, 2016).

All laboratory findings, including influencing parameters and color absorbance at 450 nm wavelength, COD titration, phosphate and nitrate readings by spectrophotometer at 690 nm wavelength, and turbidity readings by turbid meter, were tabulated in Appendix 1. The following are the results of the experiments in terms of COD, color, turbidity, nitrate, and phosphate removal rates for PECP.

Estimation models were used to optimize the responses in order to determine optimal points for operational conditions and achieve the highest removal percentage. COD, color, turbidity, nitrate, and phosphate removal percentages were set to their maximum values to achieve the best removal performance under operational conditions. In the in-range state, the target values of four independent variables, including reaction time, solution pH, electric current, and electrolyte, is shown in figure 4-2. The following were the optimal conditions for independent variables: pH7, reaction time 45 min, electric current 0.45amp, and salt concentration 0.75 g/l under these

conditions, the model's degree of desirability was equal to one, while the removal percentage of COD and color turbidity.

Table 4-4 Optimum value of pollutant removed by pulsed electrochemical process

Treatment design	pollutants	Unites	Before treated	After treated	(%) Removal efficiency	WHO standard effluent	Unite
PECP/NaCl	Color	abs	2.042	0.004	99.820	50	TCU
	COD	mg/l	2980	53.235	98.214	250	mg/l
	Turbidity	NTU	631	6.635	98.948	300	NTU
	Nitrate	mg/l	14.491	0.219	98.489	5	mg/l
	Phosphate	mg/l	17.45	0.175	98.998	5	mg/l
PECP/CaCl ₂	Color	abs	2.042	0.002	99.920	50	TCU
	COD	mg/l	2980	3.309	98.756	250	mg/l
	Turbidity	NTU	631	6.277	99.005	300	NTU
	Nitrate	mg/l	14.491	0.169	98.835	5	mg/l
	Phosphate	mg/l	17.45	0.170	99.024	5	mg/l

As shown in table 4-3 before and after treatment, the result and which electrolyte has higher removal efficiency dependent variables such as COD, nitrate, color, turbidity, and phosphate. NaCl and CaCl₂ are used as an electrolyte, so CaCl₂ is the base removal efficiency due to charge +1NaCl and +CaCl₂ were the maximum removal efficiency response variables as CaCl₂ (color 99.92%, COD 98%). The removal efficiency fits the WHO standard for effluent.

4.4.1 Analysis of variance test

Analysis of variance (ANOVA) was used to determine the interaction between the process factors and the response in graphical data analyses. The R² value was used to describe the quality of the fit polynomial model, and the F test was used to determine its statistical significance. With a 95% confidence level, the P value (probability) was used to evaluate model terms. The data was examined using the analysis of variance (ANOVA), which includes descriptive statistics and statistical tests. This test is used to determine the effect of all variables on the intended response. ANOVA is a statistical method for testing hypotheses about model parameters by dividing total

variance in a set of data into smaller groups and component portions that are linked to specific sources of variation (Bui, 2017). ANOVA was used to determine significant values between input factors and responses. To determine whether the recommended design is consistent with the test data, statistical factors such as R^2 , Adj. R^2 , F-test value (F-value), and probability value must be examined (p-value). The higher the F-value and the lower the P-value, the greater the significance of the corresponding term in the recommended correlation for response, so a P value less than 0.05 is considered significant. The mean square values were calculated by dividing the sum of each variation source's squares. To avoid systemic error, the experiments were conducted at random. The coefficients of the second-order model, which interpret the amount of removal of the investigated parameters (responses), determine the performance of independent variables (factors). To identify key terms in the model, surface response analysis looks for low p-values. The ANOVA results for responses with $p < 0.05$ probability values show that the second-order model is significant. The mean square values were calculated by dividing the sum of the squares of each variation source by their degrees of freedom, and the statistical significance was determined in all analyses using a 95% confidence level (0.05).

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

Table 4-5 ANOVA for the % removal of COD by quadratic model using NaCl

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	786.41	14	56.17	41.04	< 0.0001	Significant
A-pH	309.24	1	309.24	225.92	< 0.0001	
B-Time	9.74	1	9.74	7.11	0.0176	
C-Current	11.53	1	11.53	8.42	0.0110	
D-Electrolyte	11.30	1	11.30	8.25	0.0116	
AB	0.1066	1	0.1066	0.0779	0.7840	
AC	0.2981	1	0.2981	0.2178	0.6474	
AD	2.88	1	2.88	2.10	0.1677	
BC	4.82	1	4.82	3.52	0.0802	
BD	0.0910	1	0.0910	0.0665	0.8000	
CD	2.02	1	2.02	1.48	0.2433	

A ²	415.99	1	415.99	303.90	< 0.0001	
B ²	37.13	1	37.13	27.12	0.0001	
C ²	0.3658	1	0.3658	0.2672	0.6127	
D ²	13.71	1	13.71	10.02	0.0064	
Residual	20.53	15	1.37			
Lack of Fit	17.21	10	1.72	2.59	0.1522	Not significant
Pure Error	3.32	5	0.6637			
Cor Total	806.94	29				

The Model F-value of 41.04 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, A², B², D² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 2.59 implies the Lack of Fit is not significant relative to the pure error. There is a 15.22% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good.

II. ANOVA for % removal of turbidity by quadratic model using NaCl

Table 4-6 ANOVA for % removal of turbidity by quadratic model using NaCl

Source	Sum of Squares	df	Mean Square	F-value	p value	
Model	1280.64	14	91.47	451.28	< 0.0001	Significant
A-pH	447.03	1	447.03	2205.37	< 0.0001	
B-Time	4.38	1	4.38	21.59	0.0003	
C-Current	2.13	1	2.13	10.52	0.0055	
D-Electrolyte	6.12	1	6.12	30.19	< 0.0001	
AB	0.0063	1	0.0063	0.0312	0.8621	
AC	0.9168	1	0.9168	4.52	0.0504	
AD	0.1075	1	0.1075	0.5301	0.4778	
BC	0.0329	1	0.0329	0.1621	0.6929	
BD	0.8266	1	0.8266	4.08	0.0617	

CD	0.0091	1	0.0091	0.0451	0.8347	
A ²	806.77	1	806.77	3980.09	< 0.0001	
B ²	1.75	1	1.75	8.62	0.0102	
C ²	12.36	1	12.36	60.97	< 0.0001	
D ²	2.54	1	2.54	12.52	0.0030	
Residual	3.04	15	0.2027			
Lack of Fit	2.72	10	0.2716	4.18	0.0640	not significant
Pure Error	0.3249	5	0.0650			
Cor Total	1283.68	29				

The Model F-value of 451.28 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, A², B², C², D² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 4.18 implies there is a 6.40% chance that a Lack of Fit F-value this large could occur due to noise.

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

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1210.87	14	86.49	221.87	< 0.0001	Significant
A-pH	551.88	1	551.88	1415.69	< 0.0001	
B-Time	5.71	1	5.71	14.65	0.0016	
C-Current	2.37	1	2.37	6.07	0.0263	
D-Electrolyte	7.26	1	7.26	18.62	0.0006	
AB	0.5517	1	0.5517	1.42	0.2527	
AC	2.33	1	2.33	5.98	0.0272	
AD	3.20	1	3.20	8.21	0.0118	
BC	0.2666	1	0.2666	0.6839	0.4212	
BD	1.34	1	1.34	3.44	0.0834	
CD	0.4870	1	0.4870	1.25	0.2813	

A ²	623.02	1	623.02	1598.18	< 0.0001	
B ²	1.58	1	1.58	4.05	0.0625	
C ²	1.61	1	1.61	4.14	0.0599	
D ²	2.00	1	2.00	5.12	0.0389	
Residual	5.85	15	0.3898			
Lack of Fit	5.22	10	0.5223	4.18	0.0638	not significant
Pure Error	0.6241	5	0.1248			
Cor Total	1216.71	29				

The Model F-value of 221.87 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, AC, AD, A², D² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

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

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1353.57	14	96.68	562.48	< 0.0001	Significant
A-pH	546.60	1	546.60	3179.96	< 0.0001	
B-Time	10.11	1	10.11	58.81	< 0.0001	
C-Current	5.47	1	5.47	31.84	< 0.0001	
D-Electrolyte	1.22	1	1.22	7.09	0.0177	
AB	0.0221	1	0.0221	0.1285	0.7250	
AC	0.1739	1	0.1739	1.01	0.3305	
AD	0.0009	1	0.0009	0.0052	0.9432	
BC	0.1620	1	0.1620	0.9426	0.3470	
BD	0.4804	1	0.4804	2.79	0.1153	
CD	0.1753	1	0.1753	1.02	0.3286	
A ²	773.66	1	773.66	4500.95	< 0.0001	
B ²	5.20	1	5.20	30.24	< 0.0001	
C ²	0.9177	1	0.9177	5.34	0.0355	
D ²	1.96	1	1.96	11.39	0.0042	

Residual	2.58	15	0.1719			
Lack of Fit	2.30	10	0.2296	4.06	0.0677	not significant
Pure Error	0.2827	5	0.0565			
Cor Total	1356.15	29				

The Model F-value of 562.48 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, A², B², C², D² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 4.06 implies there is a 6.77% chance that a Lack of Fit F-value this large could occur due to noise.

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

Source	Sum of Squares	df	Mean Square	F value	p-value	
Model	1156.22	14	82.59	31.54	< 0.0001	Significant
A-pH	523.84	1	523.84	200.06	< 0.0001	
B-Time	20.86	1	20.86	7.96	0.0129	
C-Current	12.72	1	12.72	4.86	0.0435	
D-Electrolyte	32.33	1	32.33	12.35	0.0031	
AB	0.0517	1	0.0517	0.0198	0.8901	
AC	0.2653	1	0.2653	0.1013	0.7546	
AD	2.77	1	2.77	1.06	0.3197	
BC	0.6632	1	0.6632	0.2533	0.6221	
BD	3.18	1	3.18	1.22	0.2875	
CD	4.85	1	4.85	1.85	0.1935	
A ²	538.44	1	538.44	205.63	< 0.0001	
B ²	15.49	1	15.49	5.92	0.0280	
C ²	0.2634	1	0.2634	0.1006	0.7555	
D ²	9.62	1	9.62	3.67	0.0745	
Residual	39.28	15	2.62			
Lack of Fit	34.46	10	3.45	3.58	0.0861	not significant

Pure Error	4.82	5	0.9637
Cor Total	1195.50	29	

The Model F-value of 31.54 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, A², B² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 3.58 implies there is a 8.61% chance that a Lack of Fit F-value this large could occur due to noise.

I. ANOVA for the % removal of ECO quadratic model using CaCl₂

Table 4-10 ANOVA for % removal of COD by quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	792.43	14	56.60	35.54	< 0.0001	Significant
A-pH	309.24	1	309.24	194.18	< 0.0001	
B-Time	13.63	1	13.63	8.56	0.0104	
C-Current	11.52	1	11.52	7.24	0.0168	
D-Electrolyte	8.72	1	8.72	5.47	0.0335	
AB	0.1066	1	0.1066	0.0669	0.7993	
AC	0.2981	1	0.2981	0.1872	0.6714	
AD	2.88	1	2.88	1.81	0.1989	
BC	4.82	1	4.82	3.03	0.1024	
BD	0.0910	1	0.0910	0.0571	0.8143	
CD	2.02	1	2.02	1.27	0.2778	
A ²	426.74	1	426.74	267.97	< 0.0001	
B ²	29.58	1	29.58	18.57	0.0006	
C ²	0.7501	1	0.7501	0.4710	0.5030	
D ²	10.96	1	10.96	6.88	0.0192	
Residual	23.89	15	1.59			
Lack of Fit	20.57	10	2.06	3.10	0.1118	not significant

Pure Error	3.32	5	0.6637
Cor Total	816.32	29	

The Model F-value of 35.54 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, A², B², D² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 3.10 implies the Lack of Fit is not significant relative to the pure error. There is a 11.18% chance that a Lack of Fit F-value this large could occur due to noise.

Table 4-11 ANOVA for % removal of color by quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	P value	
Model	1155.52	14	82.54	154.85	< 0.0001	Significant
A-pH	509.00	1	509.00	954.95	< 0.0001	
B-Time	10.63	1	10.63	19.94	0.0005	
C-Current	1.07	1	1.07	2.01	0.1765	
D-Electrolyte	12.69	1	12.69	23.81	0.0002	
AB	0.4523	1	0.4523	0.8486	0.3715	
AC	1.24	1	1.24	2.33	0.1475	
AD	14.18	1	14.18	26.60	0.0001	
BC	0.0460	1	0.0460	0.0862	0.7731	
BD	2.84	1	2.84	5.32	0.0357	
CD	12.98	1	12.98	24.36	0.0002	
A ²	557.86	1	557.86	1046.61	< 0.0001	
B ²	48.57	1	48.57	91.13	< 0.0001	
C ²	6.35	1	6.35	11.91	0.0036	
D ²	0.1693	1	0.1693	0.3176	0.5814	
Residual	8.00	15	0.5330			
Lack of Fit	3.18	10	0.3177	0.3296	0.9363	Not significant

Pure Error	4.82	5	0.9637
Cor Total	1163.51	29	

The Model F-value of 154.85 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, D, AD, BD, CD, A², B², C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 0.33 implies the Lack of Fit is not significant relative to the pure error. There is a 93.63% chance that a Lack of Fit F-value this large could occur due to noise.

Table 4-12 ANOVA for % removal of turbidity by quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1260.12	14	90.01	634.38	< 0.0001	significant
A-pH	441.87	1	441.87	3114.27	< 0.0001	
B-Time	4.38	1	4.38	30.84	< 0.0001	
C-Current	2.13	1	2.13	15.03	0.0015	
D-Electrolyte	8.31	1	8.31	58.54	< 0.0001	
AB	0.0063	1	0.0063	0.0446	0.8356	
AC	0.9168	1	0.9168	6.46	0.0226	
AD	0.1075	1	0.1075	0.7573	0.3979	
BC	0.0329	1	0.0329	0.2315	0.6373	
BD	0.8266	1	0.8266	5.83	0.0290	
CD	0.0091	1	0.0091	0.0644	0.8031	
A ²	791.35	1	791.35	5577.41	< 0.0001	
B ²	1.55	1	1.55	10.94	0.0048	
C ²	11.83	1	11.83	83.35	< 0.0001	
D ²	4.71	1	4.71	33.23	< 0.0001	
Residual	2.13	15	0.1419			
Lack of Fit	1.80	10	0.1803	2.78	0.1357	not significant
Pure Error	0.3249	5	0.0650			
Cor Total	1262.25	29				

The Model F-value of 634.38 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, AC, BD, A², B², C², D² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 2.78 implies the Lack of Fit is not significant relative to the pure error. There is a 13.57% chance that a Lack of Fit F-value this large could occur due to noise.

Table 4-13 ANOVA for % removal of phosphate by quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1350.91	14	96.49	604.06	< 0.0001	Significant
A-pH	546.60	1	546.60	3421.77	< 0.0001	
B-Time	10.11	1	10.11	63.28	< 0.0001	
C-Current	5.47	1	5.47	34.26	< 0.0001	
D-Electrolyte	1.61	1	1.61	10.05	0.0063	
AB	0.0221	1	0.0221	0.1383	0.7152	
AC	0.1739	1	0.1739	1.09	0.3133	
AD	0.0009	1	0.0009	0.0056	0.9411	
BC	0.1620	1	0.1620	1.01	0.3298	
BD	0.4804	1	0.4804	3.01	0.1034	
CD	0.1753	1	0.1753	1.10	0.3114	
A ²	771.23	1	771.23	4828.02	< 0.0001	
B ²	5.00	1	5.00	31.31	< 0.0001	
C ²	0.8360	1	0.8360	5.23	0.0371	
D ²	2.62	1	2.62	16.38	0.0011	
Residual	2.40	15	0.1597			
Lack of Fit	2.11	10	0.2113	3.74	0.0793	not significant
Pure Error	0.2827	5	0.0565			
Cor Total	1353.30	29				

The Model F-value of 604.06 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, A², B², C², D² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Table 4-14 ANOVA for % removal of nitrate by quadratic model using CaCl₂

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1215.38	14	86.81	235.79	< 0.0001	Significant
A-pH	551.88	1	551.88	1498.94	< 0.0001	
B-Time	5.69	1	5.69	15.46	0.0013	
C-Current	2.37	1	2.37	6.43	0.0228	
D-Electrolyte	5.41	1	5.41	14.70	0.0016	
AB	0.5517	1	0.5517	1.50	0.2398	
AC	2.33	1	2.33	6.34	0.0237	
AD	3.20	1	3.20	8.69	0.0100	
BC	0.2666	1	0.2666	0.7241	0.4082	
BD	1.34	1	1.34	3.64	0.0757	
CD	0.4870	1	0.4870	1.32	0.2681	
A ²	627.99	1	627.99	1705.66	< 0.0001	
B ²	1.82	1	1.82	4.95	0.0419	
C ²	1.88	1	1.88	5.10	0.0393	
D ²	0.8513	1	0.8513	2.31	0.1492	
Residual	5.52	15	0.3682			
Lack of Fit	4.90	10	0.4899	3.92	0.0722	not significant
Pure Error	0.6241	5	0.1248			
Cor Total	1220.91	29				

The Model F-value of 235.79 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, AC, AD, A², B², C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 3.92 implies there is a 7.22% chance that a Lack of Fit F-value this large could occur due to noise.

4.4.2 Fit statistics

The statistical significance of the model equation and model terms was determined using ANOVA. According to (Darvishmotevalli *et al.*, 2019). Model fitting quality was controlled using determination coefficients (R^2 and Adj. R^2), while statistical significance was controlled using the Fischer test (F-test). The model was validated using predicted R-squares (R^2), which employs the leave-one-out technique to assess the model's prediction power in the face of new observations. Coefficients are used to quantify the relationship between experimental and expected responses (R^2). The coefficient of determination (R^2) is defined as the ratio of total changes in the expected response caused by the model variables. Show the ratio of sum of squares regression to total sum of squares. R^2 should be large and close to 1, and there should be a desired correspondence with adjusted R^2 (Adj. R^2). R^2 expresses the fitness quality of a second-order polynomial model. According to (Mirhosseini *et al.*, 2009). The model's goodness-of-fit was also assessed using coefficients of determination R^2 (correlation coefficient) and adjusted coefficients of determination R^2_{adj} . The high value of the correlation coefficient $R^2 = 0.9707$ indicated that the model was highly reliable in predicting removal percentages, with the model explaining 97.07 percent of the response variability. In this study, all of the R^2 values were greater than 0.9. According (Sivakumar, *et.al.*, 2015) to For a satisfactory model fitness, R^2 should be at least 0.8. R^2 values greater than one indicate a high level of agreement between experimental and model-estimated data. As a result, in this study, high R^2 values and their agreement with Adj, The value of R^2 indicates that the model is highly significant. Tables 4-14 to 4-15 show the "signal-to-noise ratio" index as Adequate precision (AP). In other words, AP compares the predicted range of values at design points to the mean prediction error. Appendix 2 contained a model summary for color, turbidity, nitrate, and phosphate.

Table 4-15 Model summary for % COD removals using $CaCl_2$

Std. Dev.	1.26	R^2	0.9707
Mean	93.04	Adjusted R^2	0.9434
C.V. %	1.36	Predicted R^2	0.8490
		Adeq Precision	26.5383

The Predicted R^2 of 0.8490 is in reasonable agreement with the Adjusted R^2 of 0.9434; 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 26.538 indicates an adequate signal. This model can be used to navigate the design space.

Table 4-16 Model summary for % COD removals using NaCl

Std. Dev.	1.17	R ²	0.9746
Mean	92.41	Adjusted R ²	0.9508
C.V. %	1.27	Predicted R ²	0.8712
		Adeq Precision	28.6244

The Predicted R² of 0.8712 is in reasonable agreement with the Adjusted R² of 0.9508; 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 28.624 indicates an adequate signal. This model can be used to navigate the design space.


4.4.3 Effect of model parameter and their interactions

The most useful method for revealing reaction system conditions is to use 3D surfaces and 2D contour plots, which are graphical representations of the regression equation for optimizing reaction conditions. They're also used to see how each variable influences the results. In such quadratic model plots, the response functions of two elements are depicted by varying within the experimental ranges while all other factors are held constant at their values. According to the findings, all of the combined process variables had a significant effect on color, COD, turbidity, nitrate, and phosphate removal with their power consumption in the treatment process. The three-dimensional response surface analysis of the independent variables and the dependent variable was used to estimate the optimal values of the operation parameters. A series of three-dimensional (3D) response surface graphs were created and are shown in the figure below to demonstrate the relationship between removal efficiency and factors.

A. Interaction of pH and current

The removal COD efficiency was low at pH 3 and increased too much at neutral pH, as indicated by the red color and when the current was around 0.45Amp, according to the 3D graph in figure 4-4. As a result, there was a significant interaction between pH and current. The initial pH and current interacted significantly in the removal of COD in the PEC process. Figure 4-4 shown that increasing the current density from 0.3 to 0.6 Amp and increasing the pH from acidic 3 to neutral 7 has a positive effect on COD removal. The mutual interaction effect of current density, on the

other hand, was critical in the removal of COD and color in the PEC process (Sharma and Simsek, 2020).

COD (%)
 74.1624  98.7557
 X1 = A: pH
 X2 = C: Current

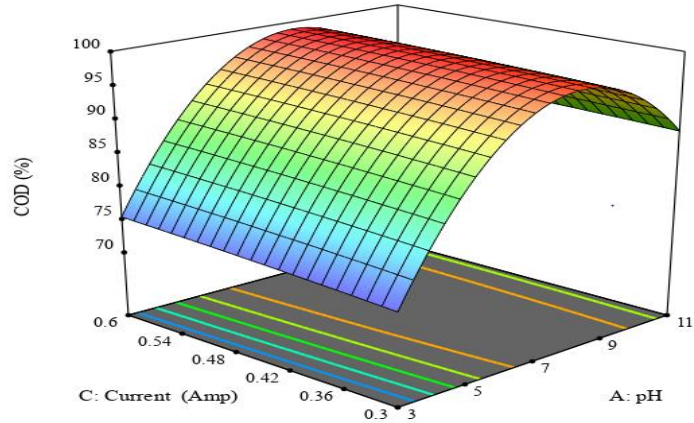


Figure 4-11 Interaction effect of pH with current plots for % removal of COD, by using CaCl_2

B. Interaction of current and time

The color removal efficiency was high at 0.45Amp, which is indicated by the red color, and when the time is 45 min., increasing time up to the center of the graph and increasing time in the same way, it comes to the red color, which shows the high removal efficiency; terminal points indicated by the green color show lower removal efficiency, indicating that the interaction effect of current and time was significant. Through contour plots and 3D response surface plots, the mutual effects of current density and time as an estimate of response removal efficiency are shown in figure 4-11 for PEC processes. Current density and time interacted in the PEC process to achieve significant COD removal (Sharma and Simsek, 2020).

Color (%)

70.2216  99.0673

X1 = B: Time

X2 = C: Current

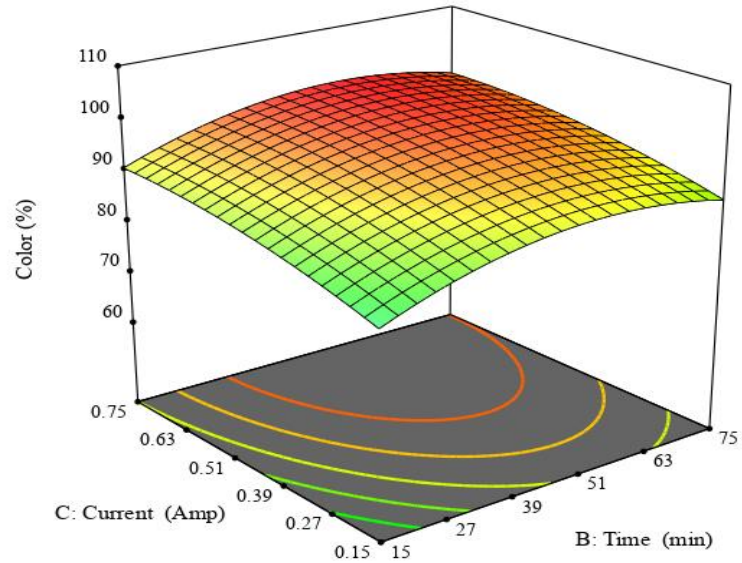


Figure 4-12 Interaction effect time with pH plot for % removal of color by using CaCl_2

C. Interaction of pH and electrolyte

This graph shows that color removal efficiency increased as pH increased from lower to higher; maximum removal at neutral was indicated by more red, but it decreased after and before neutral pH. It also shows a small increase in removal efficiency from a low electrolyte dosage to the maximum, followed by a decrease at the maximum dosage. The interaction effect of pH and electrolyte is only marginally significant in the color removal process.

COD (%)

74.1624  98.71

X1 = A: pH

X2 = D: Electrolyte

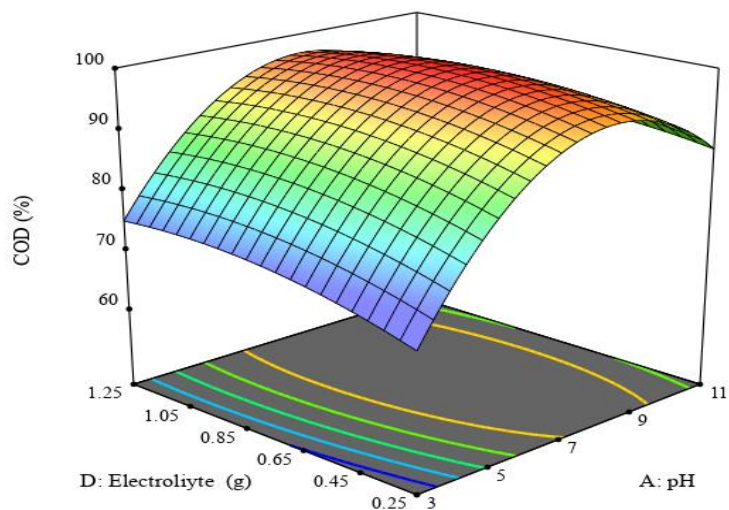


Figure 4-13 Interaction effect electrolytes with pH plot for % removal of color PECP by using CaCl_2

4.4.4 Regression equation

Regression analysis is one of the most commonly used statistical techniques in social and behavioral sciences as well as physical sciences, and it entails identifying and evaluating the relationship between a dependent variable and one or more independent variables, also known as predictor or explanatory variables. It is especially useful for assessing and adjusting for confounding variables. The relationship model is hypothesized, and parameter estimates are used to develop an estimated regression equation. Various tests are then used to determine whether or not the model is satisfactory (Mirhosseini *et al.*, 2009). According to If the model is satisfactory; the estimated regression equation can be used to predict the value of the dependent variable given the independent variable values. Regression analysis is used to explain variability in dependent variables by means of one or more independent or control variables and to analyze relationships among variables to answer the question of how much the dependent variable changes with changes in each of the independent variables, and to forecast or predict the value of the dependent variable based on the values of the independent variables.

Numerical methods were used to calculate the final model's optimum values. In this regard, the experimental range predictors were divided into a grid, and the final model was computed for all possible predictor combinations in the grid.

The experimental results were analyzed using multiple regressions, and the empirical relationship between the response and independent variables was expressed using a second-order polynomial equation. Two empirical models were created to better understand the interactive relationship between responses and process variables (Thirugnanasambandham, *et.,al* 2015). As a result, the experiment was evaluated in terms of pH (A), reaction time (B), applied current (C), and supporting electrolytes (D). All influencing factors were optimized in order to determine optimal operating conditions for maximum color, COD, nitrate, phosphate, and turbidity removal efficiency with minimum power consumption in the pulsed electrochemical process. CaCl₂ was used to achieve an empirical relationship between the response and the independent variables, which could be approximated by a quadratic polynomial as follows:

$$\begin{aligned} \text{COD} = & +97.66 + 3.59A + 0.7536B + 0.6929C + 0.6027D - 0.0816AB - 0.1365AC \\ & - 0.4241AD + 0.5489BC + 0.0754BD - 0.3553CD - 3.94A^2 - 1.04B^2 \\ & - 0.1654C^2 - 0.6321D^2 \end{aligned} \quad \text{Eq - 1}$$

$$\begin{aligned}
\text{Color} = & +97.85 + 4.61A + 0.6655B + 0.2114C + 0.7272D + 0.1681AB - 0.2788AC \\
& - 0.9414AD - 0.0536BC - 0.4211BD - 0.9008CD - 4.513A^2 \\
& - 0.133B^2 - 0.4812C^2 + 0.0786D^2 \qquad \qquad \qquad \text{Eq - 2}
\end{aligned}$$

$$\begin{aligned}
\text{Turbidity} = & +98.63 + 4.29A + 0.4270B + 0.2981C + 0.5883D + 0.0199AB + 0.2394AC \\
& + 0.0820AD - 0.0453BC - 0.2273BD + 0.0239CD - 5.37A^2 - 0.2379B^2 \\
& - 0.6566C^2 - 0.4146D^2 \qquad \qquad \qquad \text{Eq - 3}
\end{aligned}$$

$$\begin{aligned}
\text{Phosphate} = & +98.91 + 4.77A + 0.6490B + 0.4775C + 0.2585D + 0.0372AB + 0.1042AC \\
& + 0.0075AD - 0.1006BC + 0.1733BD + 0.1047CD - 5.30A^2 - 0.4270B^2 \\
& - 0.1746C^2 - 0.3089D^2 \qquad \qquad \qquad \text{Eq - 4}
\end{aligned}$$

$$\begin{aligned}
\text{Nitrate} = & +98.11 + 4.80A + 0.4871B + 0.3141C + 0.4749D - 0.1857AB - 0.3818AC \\
& - 0.4472AD - 0.1291BC - 0.2895BD - 0.1745CD - 4.78A^2 - 0.2576B^2 \\
& - 0.2615C^2 - 0.1762D^2 \qquad \qquad \qquad \text{Eq - 5}
\end{aligned}$$

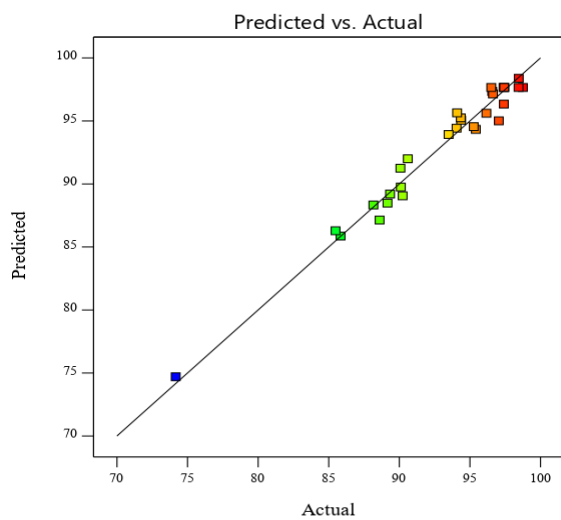
The equation in terms of coded factors can be used to predict the response to different levels of each factor. The high levels of the factors are coded as +1 by default, while the low levels are coded as -1. By comparing the factor coefficients, the coded equation can be used to determine the relative importance of the factors.

The models' terms are organized using a coding system. The ANOVA test was used to determine the model's suitability. As shown in the tables above, the lack of fit test was used to confirm model validity. The ANOVA for lack of fit was insignificant ($P < 0.05$) on the regression model. All of the results show that this model fits the experimental data well. Due to the higher percentage of COD, color, nitrate, phosphate, and turbidity removal values and better extraction yield in the shortest time, these findings indicate that PECP was the most effective method for wastewater treatment.

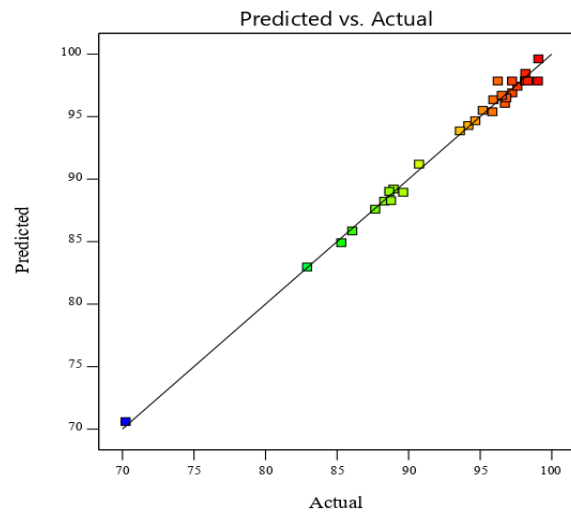
4.5 The desired optimum condition for response

Figure 4.11 shows that at the optimum levels, the prediction and experimental findings are in good agreement and in line with the straight line, indicating that the model is very valid. According to RSM, the expected R^2 for this initial model was 98.91 percent. The backward elimination method was used to construct a parsimonious model with meaningful predictors. The coefficient of determination of the anticipated model revealed a quadratic relationship between responses and parameters with a good regression coefficient.

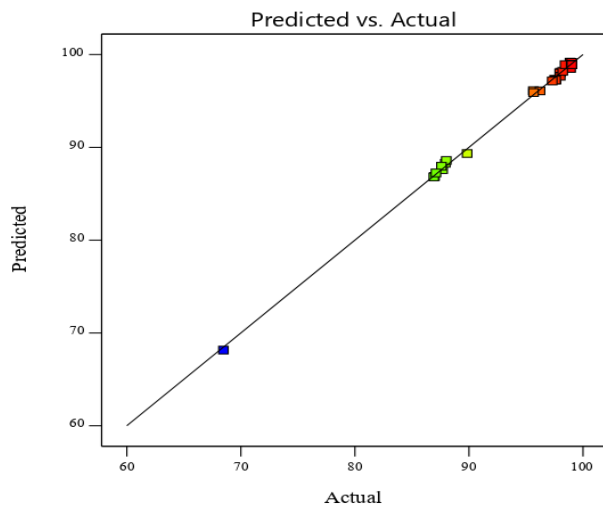
The optimum PECP conditions were determined as a practical optimum using Design Expert 11.1.2.0 software: an electrolysis time of 45 min, salt concentration of 0.75 g/l, and pH of 7. To further validate the predictability of the theoretical model, verification experiments were carried out under optimal conditions. The results showed that experimental removal efficiencies were very close to predicted values, with a difference of less than 0.2 and no significant differences ($P>0.05$). As a result, it was possible to conclude that the established model in this study was appropriate and valid. The diagrams a, b, c, and d show the actual and predicted values of NO_4^{3-} color, PO_4^{3-} , and COD, which are not dispersed from each other and in line with the straight line.



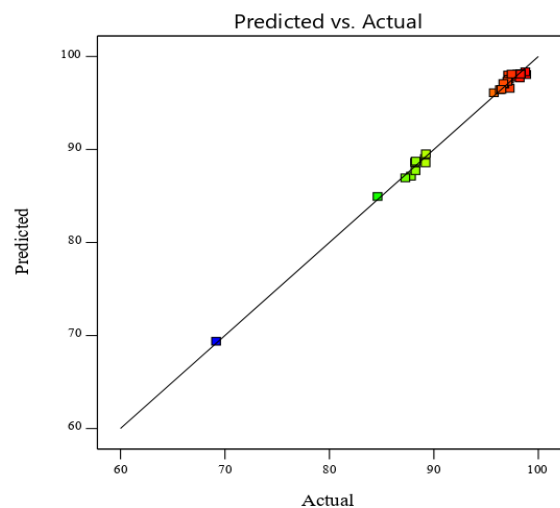
A. COD removal



B. color removal



B. Phosphate removal



D. Nitrate removal

Figure 4-14 the comparison of predictive and the experimental result for the PECP by using CaCl_2 the optimum value on removal efficiency

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. Figure 4-13 and 4-14 and 4-15 show the distribution of normal probability percentage versus studentized residuals for COD, turbidity and Phosphate removal levels. The points in these diagrams are arranged in a relatively straight line, indicating that the variance and normal distribution are constant. The points in the normal probability distribution diagram of residuals are almost straight line aligned. Some of the scattered points are even expected in the data's normal distribution. The figures show that there are no outliers that cross the red line.

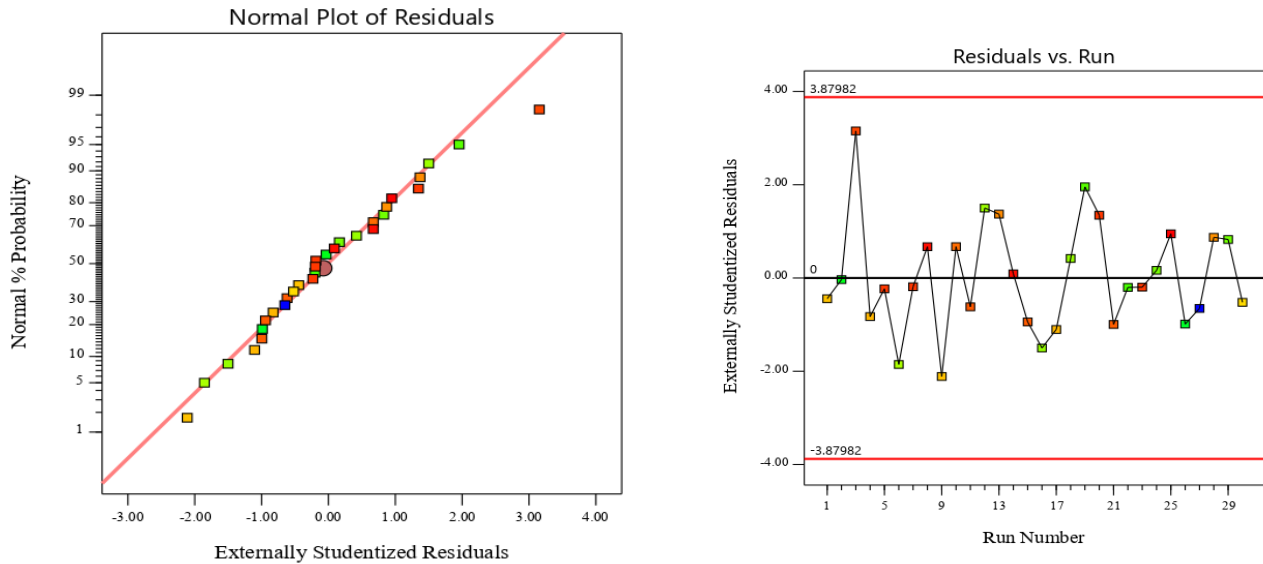


Figure 4-15 Distribution of normal probability percentage and residuals for COD

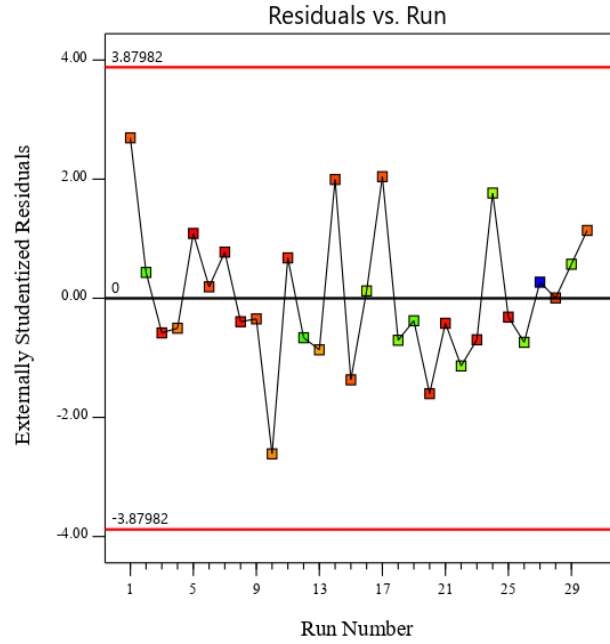
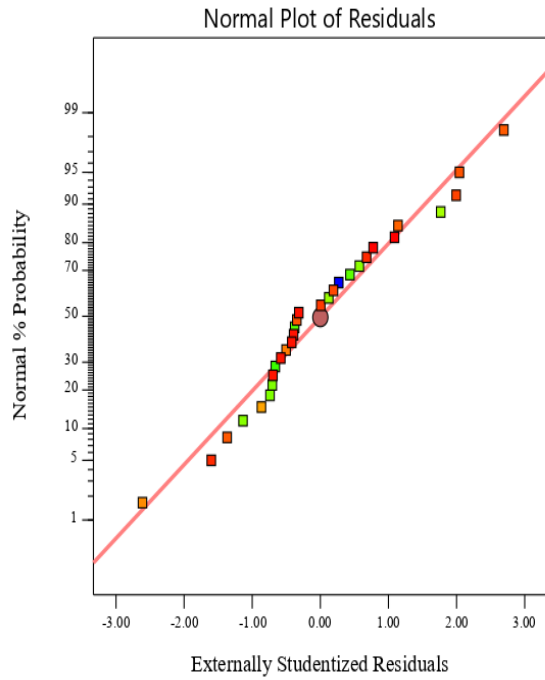


Figure 4-16 Distribution of probability percentage and residuals for Turbidity

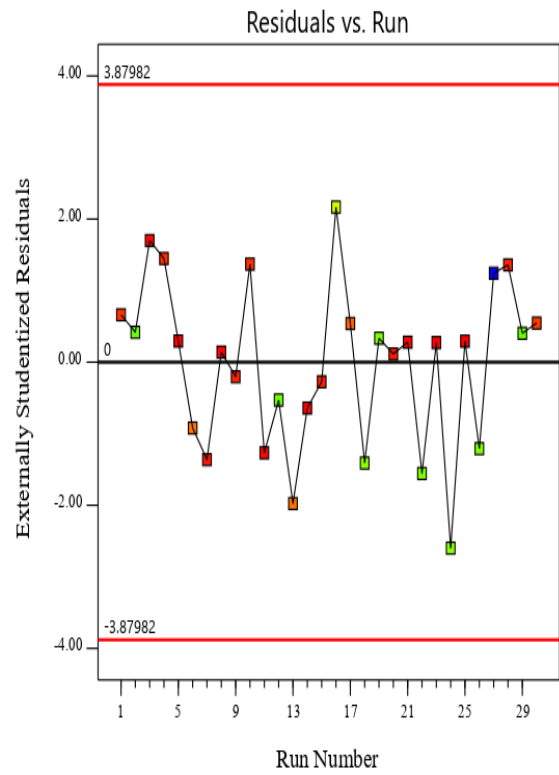
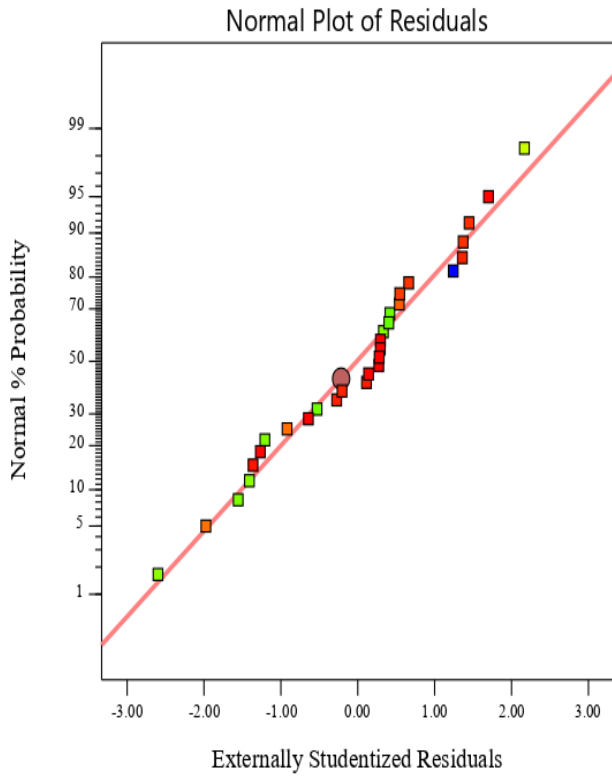


Figure 4-17 Distribution of normal probability percentage and residuals for phosphate

The results of removal efficiency were closer to the straight line on the distribution of probability percentage and residuals graphs for pollutant removal, as shown in figures 4-15 and 4-16 above. The number of externally studentized residuals on the second graph run varied uniformly. Were the experiment results valid.

CHAPTER FIVE

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Pulsed electrochemical process for coffee processing wastewater treatment is the latest technology and consumes low power during the treatment process.

According to laboratory results and analysis, all contaminants such as color, turbidity, COD, phosphate, and nitrate are removed with a high percentage and meet WHO standards for wastewater effluents. This means after treatment, wastewater has no color, odor, turbidity, and contains a very low amount of COD and nutrients.

During the process of treatment by using PECP, operating parameters such as pH, electrolyte dosage, contact time, and current play a major role in removal efficiency. Changing the media of wastewater from basic to acidic or acidic to basic greatly affects the removal efficiency. Aside from the duration of electrolysis, the dosage of electrolyte is also important in the removal of contaminants. In PECP, using CaCl_2 as an electrolyte is more efficient than using NaCl due to the increment of charge from +1 to +2, which leads to increasing conductivity and causes high removal of contaminants.

The Response Surface Methodology (RSM) based on Central Composite Design (CCD) was a useful tool for assessing and optimizing the effect of operating parameters on responses. The analysis of variance (ANOVA) with 95% confidence limits was used to test the significance of independent variables and their interactions.

The quadratic regression equation was recommended as a good model for predicting color, COD, turbidity, phosphate, and nitrate removal efficiency. The model's goodness of fit was validated with high values of squared correlation coefficient for each of color, COD, turbidity, phosphate, and nitrate (R^2). This study suggests that the PECP process could be a successful alternative treatment process for CP wastewater treatment when compared to traditional treatment methods. The comparison of experimental and predicted values by the model for each response demonstrates that results were produced with very little error.

Finally, maximum values were selected by all independent variables in the range and dependent variables were maximized. Then, by conducting a final laboratory experiment, optimum values were obtained. As a result, it is concluded that this technology can be used on a large scale to treat real coffee processing wastewater.

5.2 Recommendation

Pulsed electrochemical process is a useful technology for the removal of contaminants that exist in coffee processing wastewater. Pulsed electrochemical oxidation is the best and latest technology that can replace old technology and operate at a low cost with a high removal efficiency of contaminants. However, to use the technology and conduct the test, the following reality should be considered.

- ❖ Instead of using electric power, renewable energies such as solar energy can be used to minimize cost and power consumption.
- ❖ Since the optimum value was obtained at neutral pH, effluent after treatment can be discharged directly to water bodies or can be used for irrigation purpose.
- ❖ As a weakness of the method, it needs an expert to design and operate properly to run the method properly. The odor released during experimental tests, sludge sediments, foam created and remains after treatment should be properly managed. This means contaminants which generated in the forms of sludge and foams should be disposed in safe place or further treatment can be designed for them.
- ❖ To get the precise result and find the effects of independent variables, power to DC, refrigerators, and other laboratory machines operated by electricity should be continuously supplied.
- ❖ During investigation, accurate measurement of electrolyte and adjustment of pH, time, current, and voltage are very useful to identify and optimize the maximum removal out of overall experimental runs.

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APPENDIXES

APPENDIX A: EXPERIMENTAL DATA FOR INVESTIGATION OF PULSED ELECTROCHEMICAL PROCESS

CONSTANT PARAMETER

Anode –Cathode electrode = Al-Al

System : Batch system

Reaction time 30min - 1hr

Mode of electrode connection = parallel

Length of electrode 13cm

Width of electrode = 6cm

Distance between electrode 1cm

Appendix B: Experimental run and output of ECO by using NaCl electrolyte

<u>Experiment .1</u>	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
Date 1/04/2022 pH=9 I=0.3Amp NaCl=0.5g T=14.3°C V=0.5 Cond=2.88µs/cm	0	2.042	631	17.45	14.491	6.45
	60	0.058	23.520	0.438	0.468	0.400

<u>Experiment.2</u>	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD (FAS)ml
Date 2/04/2022 <ul style="list-style-type: none"> • pH=5 • I=0.3Amp • NaCl=0.5g • T=13°C • V=0.96 • Cond=2.21µs/cm 	0	2.042	631	17.45	14.491	6.45
	30	0.351	85.230	2.276	2.280	0.300

<u>Experiment.3</u>						
Date 3/04/2022 • pH=7 • I=0.45Amp • NaCl=0.75g • T=17°C • V=2.81 • Cond=2.81µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD (FAS)ml
	0	2.042	631	17.45	14.491	6.45
	75	0.052	10.510	0.194	0.219	3.550

<u>Experiment.4</u>						
Date 4/04/2022 • pH=9 • I=0.6Amp • NaCl=0.5g • T=13.3°C • V=4.25 • Cond=2.68µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.069	29.810	0.418	0.521	0.700

<u>Experiment .5</u>						
Date 5/04/2022 • pH=7 • I=0.45Amp • NaCl=0.75g • T=13.4°C • V=3.25 • Cond=2.88µs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.040	6.635	0.175	0.339	3.500

<u>Experiment.6</u>						
Date 6/04/2022 <ul style="list-style-type: none"> pH=7 I=0.45Amp NaCl=0.75g T=13.4°C V=3.25 Cond=3.04µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	15	0.191	20.070	0.760	0.669	3.700

<u>Experiment. 7</u>						
Date 7/04/2022 <ul style="list-style-type: none"> pH=7 I=0.45Amp NaCl=0.75g T=13.5°C V=2.88 Cond=2.88µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.022	7.276	0.278	0.293	3.550

<u>Experiment.8</u>						
Date 8/04/2022 <ul style="list-style-type: none"> pH=7 I=0.45Amp NaCl=0.75g T=13.5°C V=3.25 Cond=2.88µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.039	9.860	0.185	0.292	3.560

<u>Experiment.9</u>						
Date 9/04/2022 <ul style="list-style-type: none"> • pH=9 • I=0.3Amp • NaCl=1g • T=14.8°C • V=2.2 • Cond=2.13µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.051	22.250	0.361	0.354	2.300

<u>Experiment. 10</u>						
Date 10/04/2022 <ul style="list-style-type: none"> • pH=7 • I=0.15Amp • NaCl=0.75g • T=14°C • V=1.6 • Cond=2.86µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.101	32.720	0.423	0.583	3.300

<u>Experiment. 11</u>						
Date 11/04/2022 <ul style="list-style-type: none"> • pH=9 • I=0.6Amp • NaCl=1g • T=14.3°C • V=3.83 • Cond=3.06µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.046	14.130	0.203	0.535	2.800

<u>Experiment. 12</u>						
Date 13/04/2022 <ul style="list-style-type: none"> pH=9 I=0.3Amp NaCl=0.5g T=14.3°C V=2.46 Cond=2.88µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₃ (mg/l)	NO ₃ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.088	37.410	0.764	0.448	2.600

<u>Experiment. 13</u>						
Date 12/04/2022 <ul style="list-style-type: none"> pH=11 I=0.45Amp NaCl=0.75g T=15°C V=2.62 Cond=3.62µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.234	91.440	2.254	1.614	1.500

<u>Experiment. 14</u>						
Date 14/04/2022 <ul style="list-style-type: none"> pH=7 I=0.75Amp NaCl=0.75g T=14.5°C V=4.75 Cond=2.88µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.004	19.000	0.179	0.308	3.850

<u>Experiment. 16</u>						
Date 16/04/2022 <ul style="list-style-type: none"> • pH=5 • I=0.6Amp • NaCl=1g • T=14.6°C • V=3.4 • Cond=3.24µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.231	73.450	1.777	1.610	0.420

<u>Experiment. 17</u>						
Date 17/04/2022 <ul style="list-style-type: none"> • pH=9 • I=0.3Amp • NaCl=1g • T=14.8°C • V=2.65 • Cond=2.13µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.067	22.200	0.661	0.457	0.680

<u>Experiment. 18</u>						
Date 18/04/2022 <ul style="list-style-type: none"> • pH=5 • I=0.65Amp • NaCl=0.5g • T=17°C • V=5.15 • Cond=19.39µs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.234	78.570	2.111	1.760	0.450

<u>Experiment. 19</u>						
Date 19/04/2022 <ul style="list-style-type: none"> • pH=5 • I=0.6Amp • NaCl=0.5g • T=17°C • V=5 • Cond=19.39μs/cm 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.246	85.500	2.151	1.895	0.350

<u>Experiment. 20</u>						
Date 20/04/2022 <ul style="list-style-type: none"> • pH=7 • NaCl=1.25g • Cond=4.33μs/cm • T=13.6°C • I=2.07Amp • V=4.75 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.021	14.360	0.314	0.230	3.800

<u>Experiment. 21</u>						
Date 21/04/2022 <ul style="list-style-type: none"> • pH=7 • NaCl=0.75g • Cond=2.88μs/cm • T=13.5°C • I=0.45Amp • V=2.88 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.079	9.920	0.176	0.296	3.620

<u>Experiment. 22</u>						
Date 22/04/2022 • pH=5 • NaCl=1g • Cond=3.24 μ s/cm • T=14.6°C • I=0.6Amp • V=3.35	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.241	77.070	2.170	1.623	0.500

<u>Experiment. 23</u>						
Date 23/04/2022 • pH=7 • NaCl=0.75g • Cond=2.88 μ s/cm • T=17°C • I=0.45Amp • V=3.3	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.036	10.520	0.176	0.421	3.540

<u>Experiment. 24</u>						
Date 24/04/2022 • pH=5 • NaCl=1g • Cond=2.62 μ s/cm • T=20.6°C • I=0.3Amp • V=2	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.228	71.580	2.096	1.751	1.600

<u>Experiment. 25</u>						
Date 25/04/2022 <ul style="list-style-type: none"> pH=7 NaCl=0.75g Cond=2.88μs/cm T=13.5°C I=0.45Amp V=3.25 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.059	9.690	0.175	0.299	0.660

<u>Experiment. 26</u>						
Date 26/04/2022 <ul style="list-style-type: none"> pH=5 NaCl=0.5g Cond=2.21μs/cm T=13.1°C I=0.3Amp V=2.96 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.261	78.489	2.161	1.817	0.800

<u>Experiment. 27</u>						
Date 27/04/2022 <ul style="list-style-type: none"> pH=3 NaCl=0.75g Cond=2.27μs/cm T=13°C I=0.45Amp V=3.7 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.610	200.170	5.506	4.520	0.500

<u>Experiment. 28</u>						
Date 28/04/2020 • pH=9 • NaCl=1g • Cond=2.27 μ s/cm • T=13°C • I=0.6Amp • V=3.8	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.050	17.380	0.352	0.479	0.600

<u>Experiment. 29</u>						
Date 29/04/2022 • pH=5 • NaCl=1g • Cond=2.62 μ s/cm • T=22.5°C • I=0.3Amp • V=2	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.214	76.060	2.287	1.754	0.500

<u>Experiment. 30</u>						
Date 30/04/2022 • pH=7 • NaCl=0.25g • Cond=2.24 μ s/cm • T=14.4°C • I=0.45Amp • V=3.1	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.196	18.830	0.405	0.692	3.600

Appendix C: Experimental run and output of ECO by using CaCl₂electrolyte

<u>Experiment. 1</u>	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
Date 1/05/2022 • pH=9 • CaCl ₂ =0.5g • Cond=2.75µs/cm • T=15.3°C • I=0.3Amp • V=2.5	0	2.042	631	17.45	14.491	6.45
	60	0.056	23.162	0.433	0.418	0.409

<u>Experiment. 2</u>	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
Date 2/05/2022 • pH=5 • CaCl ₂ =0.5g • Cond=19.40µs/cm • T=18°C • I=0.3Amp • V=3.1	0	2.042	631	17.45	14.491	6.45
	30	0.349	84.872	2.272	2.230	0.209

<u>Experiment. 3</u>						
Date 3/05/2022 <ul style="list-style-type: none"> pH=7 CaCl₂=0.75g Cond=2.62μs/cm T=18°C I=0.3Amp V=3.1 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	75	0.049	10.152	0.189	0.169	3.559

<u>Experiment. 4</u>						
Date 4/05/2022 <ul style="list-style-type: none"> pH=9 CaCl₂=0.5g Cond=2.51μs/cm T=19°C I=0.6Amp V=4.15 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.067	29.452	0.413	0.471	0.709

<u>Experiment. 5</u>						
Date 5/05/2022 <ul style="list-style-type: none"> pH=7 CaCl₂=0.75g Cond=2.54μs/cm T=15.4°C I=0.45Amp V=3.4 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.038	6.277	0.170	0.289	3.509

<u>Experiment. 6</u>						
Date 6/05/2022 <ul style="list-style-type: none"> • pH=7 • CaCl₂=0.75g • Cond=2.54μs/cm • T=18.3°C • I=0.45Amp • V=3.3 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	15	0.189	19.712	0.756	0.617	3.709

<u>Experiment. 7</u>						
Date 7/05/2022 <ul style="list-style-type: none"> • pH=7 • CaCl₂=0.75g • Cond=2.54μs/cm • T=13.3°C • I=0.45Amp • V=3.3 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.020	6.918	0.274	0.243	3.559

<u>Experiment. 8</u>						
Date 8/05/2022 <ul style="list-style-type: none"> • pH=7 • CaCl₂=0.75g • Cond=2.54μs/cm • T=13°C • I=0.45Amp • V=3.3 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.037	9.502	0.180	0.242	3.569

<u>Experiment. 9</u>						
Date 9/05/2022 • pH=9 • CaCl ₂ =1g • Cond=2.67μs/cm • T=13.3°C • I=0.3Amp • V=2.5	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.049	21.892	0.356	0.304	2.309

<u>Experiment. 10</u>						
Date 10/05/2022 • pH=7 • CaCl ₂ =0.75g • Cond=2.09μs/cm • T=12.3°C • I=0.15Amp • V=2	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.098	32.362	0.418	0.533	3.309

<u>Experiment. 11</u>						
Date 11/05/2022 • pH=9 • CaCl ₂ =1g • Cond=2.3μs/cm	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45

<ul style="list-style-type: none"> • T=18.1°C • I=0.6Amp • V=4.1 	60	0.044	13.772	0.198	0.485	2.809
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<u>Experiment. 12</u>						
Date 12/05/2022 <ul style="list-style-type: none"> • pH=11 • CaCl₂=0.75g • Cond=2.08μs/cm • T=20.4°C • I=0.45Amp • V=4.1 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.232	91.082	2.250	1.564	1.509

<u>Experiment. 13</u>						
Date 13/05/2022 <ul style="list-style-type: none"> • pH=9 • CaCl₂=0.5g • Cond=2.75μs/cm • T=15°C • I=0.3Amp • V=2.5 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.086	37.052	0.759	0.398	2.609

<u>Experiment. 14</u>						
Date 14/05/2022 <ul style="list-style-type: none"> • pH=7 • CaCl₂=0.75g • Cond=2.5µs/cm • T=25°C • I=0.75Amp • V=4.4 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.002	18.642	0.174	0.258	3.859

<u>Experiment. 15</u>						
Date 15/05/2022 <ul style="list-style-type: none"> • pH=9 • CaCl₂=0.5g • Cond=2.51µs/cm • T=19.2°C • I=0.6Amp • V=4.15 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.038	22.765	0.345	0.314	2.759

<u>Experiment. 16</u>						
Date 16/05/2022 <ul style="list-style-type: none"> • pH=5 • CaCl₂=1g • Cond=2.4µs/cm • T=16.4°C • I=0.6Amp • V=4.05 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.229	73.093	1.773	1.560	0.429

<u>Experiment. 17</u>						
Date 17/05/2022 • pH=9 • CaCl ₂ =1g • Cond=2.67μs/cm • T=13.4°C • I=0.3Amp • V=2.5	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.065	21.842	0.657	0.407	0.689

<u>Experiment. 18</u>						
Date 18/05/2022 • pH=5 • CaCl ₂ =0.5g • Cond=17.29μs/cm • T=13.5°C • I=0.6Amp • V=6.3	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.231	78.212	2.106	1.710	0.459

<u>Experiment. 19</u>						
Date 19/05/2022 • pH=5 • CaCl ₂ =0.5g • Cond=17.29μs/cm • T=13.5°C • I=0.6Amp • V=7.1	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.244	85.142	2.147	1.845	0.359

<u>Experiment. 20</u>						
Date 20/05/2022 • pH=7 • CaCl ₂ =1.25g • Cond=2.81μs/cm • T=13.3°C • I=0.45Amp • V=3.2	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.019	14.003	0.310	0.180	3.809

<u>Experiment. 21</u>						
Date 21/05/2022 • pH=7 • CaCl ₂ =0.75g • Cond=2.54μs/cm • T=15.4°C • I=0.45Amp • V=3.3	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.077	9.562	0.171	0.246	3.629

<u>Experiment. 22</u>						
Date 22/05/2022 • pH=5 • CaCl ₂ =1g • Cond=2.4μs/cm • T=16.4°C • I=0.6Amp • V=4.1	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.239	76.712	2.166	1.573	0.509

<u>Experiment. 23</u>						
Date 23/05/2022 • pH=7 • CaCl ₂ =0.75g • Cond=2.54μs/cm • T=15.4°C • I=0.45Amp • V=3.3	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.034	10.162	0.172	0.371	3.549

<u>Experiment. 24</u>						
Date 24/05/2022 • pH=5 • CaCl ₂ =1g • Cond=17.67μs/cm • T=21°C • I=0.3Amp • V=3.05	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.226	71.222	2.091	1.701	1.609

<u>Experiment. 25</u>						
Date 25/05/2022 • pH=7 • CaCl ₂ =0,75g • Cond=2.54μs/cm • T=13.3°C • I=0.45Amp • V=3.25	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.057	9.332	0.170	0.249	3.669

<u>Experiment. 26</u>						
Date 26/05/2022 <ul style="list-style-type: none"> • pH=5 • CaCl₂=0.5g • Cond=19.4μs/cm • T=18°C • I=0.3Amp • V=3.1 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	60	0.259	78.132	2.157	1.767	0.809

<u>Experiment. 27</u>						
Date 27/05/2022 <ul style="list-style-type: none"> • pH=3 • CaCl₂=0.75g • Cond=17.6μs/cm • T=13°C • I=0.45Amp • V=3.8 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.608	197.919	5.502	4.470	0.509

<u>Experiment. 28</u>						
Date 28/05/2022 <ul style="list-style-type: none"> • pH=9 • CaCl₂=1g • Cond=2.3μs/cm • T=18.1°C • I=0.6Amp • V=2.3 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.048	17.022	0.348	0.429	0.609

<u>Experiment. 29</u>						
Date 29/05/2022 <ul style="list-style-type: none"> • pH=5 • CaCl₂=1g • Cond=2.3μs/cm • T=21°C • I=0.3Amp • V=3.1 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	30	0.212	75.702	2.282	1.704	0.509

<u>Experiment. 30</u>						
Date 30/05/2022 <ul style="list-style-type: none"> • pH=7 • CaCl₂=0.25g • Cond=2.07μs/cm • T=16.5°C • I=0.45Amp • V=4.8 	Time (Min)	Absorbance	Turbidity (NTU)	PO ₄ ³⁻ (mg/l)	NO ₄ ³⁻ (mg/l)	COD FAS(ml)
	0	2.042	631	17.45	14.491	6.45
	45	0.194	24.783	0.470	0.511	3.609

Appendix D: Fit statistics for some dependent variables

Table D-1 Model summary for % Color removal using NaCl

Std. Dev.	1.62	R ²	0.9671
Mean	93.21	Adjusted R ²	0.9365
C.V. %	1.74	Predicted R ²	0.8282
		Adeq Precision	25.2702

The Predicted R² of 0.8282 is in reasonable agreement with the Adjusted R² of 0.9365; 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 25.270 indicates an adequate signal. This model can be used to navigate the design space.

Table D-2 Model summary for % turbidity removal using NaCl

Std. Dev.	0.4502	R ²	0.9976
Mean	93.26	Adjusted R ²	0.9954
C.V. %	0.4828	Predicted R ²	0.9875
		Adeq Precision	95.2559

The Predicted R² of 0.9875 is in reasonable agreement with the Adjusted R² of 0.9954; 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 95.256 indicates an adequate signal. This model can be used to navigate the design space.

Table D-3 Model summary for % nitrate removals by using NaCl

Std. Dev.	0.6244	R ²	0.9952
Mean	93.35	Adjusted R ²	0.9907
C.V. %	0.6688	Predicted R ²	0.9745
		Adeq Precision	64.9510

The Predicted R² of 0.9745 is in reasonable agreement with the Adjusted R² of 0.9907; 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 64.951 indicates an adequate signal. This model can be used to navigate the design space.

Table D-4 Model summary for % phosphate removals by using NaCl

Std. Dev.	0.4146	R ²	0.9981
Mean	93.93	Adjusted R ²	0.9963
C.V. %	0.4414	Predicted R ²	0.9899
		Adeq Precision	105.8883

The Predicted R² of 0.9899 is in reasonable agreement with the Adjusted R² of 0.9963; 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 105.888 indicates an adequate signal. This model can be used to navigate the design space.

Table D-5 Model summary for % COD removals by using NaCl

Std. Dev.	1.17	R ²	0.9746
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Mean	92.41	Adjusted R ²	0.9508
C.V. %	1.27	Predicted R ²	0.8712
		Adeq Precision	28.6244

The Predicted R² of 0.8712 is in reasonable agreement with the Adjusted R² of 0.9508; 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 28.624 indicates an adequate signal. This model can be used to navigate the design space.

Table D-6 Model summary for % Color removals by using CaCl₂

Std. Dev.	0.7301	R ²	0.9931
Mean	92.86	Adjusted R ²	0.9867
C.V. %	0.7862	Predicted R ²	0.9783
		Adeq Precision	56.2111

The Predicted R² of 0.9783 is in reasonable agreement with the Adjusted R² of 0.9867; 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 56.211 indicates an adequate signal. This model can be used to navigate the design space.

Table D-7 Model summary for % COD removals by using CaCl₂

Std. Dev.	1.26	R ²	0.9707
Mean	93.04	Adjusted R ²	0.9434
C.V. %	1.36	Predicted R ²	0.8490
		Adeq Precision	26.5383

The Predicted R² of 0.8490 is in reasonable agreement with the Adjusted R² of 0.9434; 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 26.538 indicates an adequate signal. This model can be used to navigate the design space.

Table D-8 Model summary for % turbidity removals by using CaCl₂

Std. Dev.	0.3767	R ²	0.9983
Mean	93.29	Adjusted R ²	0.9967
C.V. %	0.4038	Predicted R ²	0.9914

Adeq Precision	112.8853
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The Predicted R^2 of 0.9914 is in reasonable agreement with the Adjusted R^2 of 0.9967; 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 112.885 indicates an adequate signal. This model can be used to navigate the design space.

Table D-9 Model summary for % phosphate removals by using CaCl_2

Std. Dev.	0.3997	R^2	0.9982
Mean	93.94	Adjusted R^2	0.9966
C.V. %	0.4254	Predicted R^2	0.9907
		Adeq Precision	109.7815

The Predicted R^2 of 0.9907 is in reasonable agreement with the Adjusted R^2 of 0.9966; 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 109.781 indicates an adequate signal. This model can be used to navigate the design space.

Table D-10 Model summary for % nitrate removals by using CaCl_2

Std. Dev.	0.6068	R^2	0.9955
Mean	93.73	Adjusted R^2	0.9913
C.V. %	0.6474	Predicted R^2	0.9762
		Adeq Precision	67.5328

The Predicted R^2 of 0.9762 is in reasonable agreement with the Adjusted R^2 of 0.9913; 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 67.533 indicates an adequate signal. This model can be used to navigate the design space.

Appendix E: Some figure illustrate lab activities



Figure E- Aluminum electrode used



Figure E-2 adjustment and treatment process of coffee processing wastewater



Figure E-3 Adjusting variable and treatment by using pulsed electrochemical process



Figure E-4 before and after treatment of coffee processing of wastewater



Figure E-5 COD determination by titration method



Figure E-6 phosphate reading by spectrophotometric method



Figure E-7 Nitrate reading by spectrophotometric method

