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Removal of Copper Ions from Simulated Wastewater by Electrocoagulation Technique with Different Types of Electrodes

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by

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بسم الله الرحمن الرحيم

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The Head of the Departments Certification

*Given the available recommendations, I forward the project entitled “**Removal of Copper Ions from Simulated Wastewater by Electrocoagulation Technique with Different Types of Electrodes**” for debate by the examination committee.*

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Supervisor Certification

I *certify that this thesis entitled (**Removal of Copper Ions from Simulated Wastewater by Electrocoagulation Technique with Different Types of Electrodes**) had been carried out under his supervision at the University of Babylon/ College of Engineering / Department of Chemical Engineering in partial fulfillment of the requirements for the degree of Master in Engineering/Chemical Engineering.*

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Marwa Abd Aljaleel

/ /2022

Dedication

To

My Husband

A strong and gentle soul who taught me to trust in Allah, believe in hard work and that so much could be done with little

My parents

My Family

My Children's

My friends

For being my guardian during my educational career

With respect and love.

Marwa Abd Aljaleel

/ /**2022**

Abstract

Water pollution can be defined as the contamination of a stream, river, lake, ocean or any other stretch of water, depleting water quality and making it toxic for the environment and humans. The environmental effects of water pollution primarily involve the damage that pollution does to the surrounding ecosystem. Many of the organisms that depend on a supply of relatively healthy water will die. When bodies of water become too heavily polluted, it’s common for crabs, dolphins, seagulls, and fish to wash up ashore. Pollution is also damaging to the economy since it increases the costs of treating the water, leads to losses in tourism, lowers local real estate values, and damages commercial fishing. Likely the most effective way to reduce water pollution is by treating some of the water before it’s reintroduced into the waterways. This is a highly effective solution because wastewater treatment facilities are able to remove nearly all pollutants in wastewater via a chemical, physical, or biological process. Sewage will be taken through several chambers of the facility to slowly reduce its toxicity levels.

There are many variables described as affected factors on electrocoagulation reaction EC. Therefore, this study includes investigation impact of eight variables on the EC process; contact time, current density, the voltage supplied, stirring rate, initial copper concentration, solution pH, reaction temperature, and type of anode was chosen as controlled variables on EC reaction, while copper removal efficiency used as a process response. The feed is simulated wastewater prepared by adding copper nitrate as a copper ions source. Two levels identified the most influential variables on copper removal during EC reaction according to Plackett-Burman design PBD. Results show that the initial copper concentration, solution pH, reaction temperature, and contact time are the most significant variables on EC reaction. On the other hand, the predicted results show that maximum removal efficiency (98%) will obtain at optimum operation conditions; contact time (40 minutes), current density (3 A/cm^2), voltage supply (10 volts), initial copper concentration (400 ppm), reaction temperature (70°C) with no stirring rate and using Fe as an anode. The most affected variables that appeared during the application of PBD in the previous step were studied more deeply via applied Box-Behnken experimental design to explore the initial concentration, temperature, and pH on energy consumption and the efficiency of removing heavy metals (Copper) from simulated.

Box-Behnken Design-based wastewaters, was selected fifteen (15) experiments have been performed, and every experiment takes ٤٠minutes. The findings have been utilized to model the efficiencies of Heavy metals removal and energy consumption for this method with the Minitab support. Numerical Optimization indicates that the optimal energy consumption of ٠.٥٦ kWh/m^3 and highest removal efficiencies for Copper was achieved 97% respectively at operating situations of 200, 350, and 500 ppm Cu concentrations and 50, 40, and 60 ^{o}C from temperature and 3, 7 and 11 from pH gradients. The EC reaction kinetics and thermodynamics parameters were estimated; the reaction obeys second order reaction with rate constants are (k) are 0.6572, 0.6829 and 0.8308 $[(mol/L)\ sec^{-1}]^{-1}$ at 50, 60, and 70 °C respectively, and the apparent activation energy value is 10.719 kJ/mol obtained for the process according to the Arrhenius equation. EC reaction obtained a negative entropy change ΔS (-0.218 kJ/mol K) with the positive enthalpy change ΔH and Gibbs free energy ΔG values.

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List of Abbreviations and Symbols

Abbreviations and Symbols	Details
(PCB)	Printed circuits board
(v)	applied voltage
EC	Electrocoagulation
pH	potential of hydrogen
CCD	Charge-coupled device
PVC	Polyvinyl chloride
COD	Chemical Oxygen Demand
HCl	Hydrochloric acid
BDD	Behavior-driven development
ANOVA	Analysis of variance
T	Temperature (°C)
CC	Chemical Coating
INR	International Normalized Ratio
SEC	Specific Energy Consumption
RSM	Response Surface Methodology

Chapter One

Introduction

Chapter One

Introduction

1.1. Introduction

Water and energy are the two most pressing issues facing the twenty-first century. Water quality has become a critical issue as a result of increased contamination from non-pointed and pointed sources, especially in developing countries (Chaturvedi, 2013).

Wastewater is described as the flow of spent water directed to remediation facilities from households, industries companies, commercial activities, and institutions. This effluent is further classified and characterized in terms of its origins (Abdel-Ghani & Elchaghaby, 2007).

Domestic wastewater relates to flows that are mostly discharged from home sources and are produced by activities including food preparation, washing, cleaning, and personal hygiene. Commercial and industrial operations including food and printing processing produce and discharge industrial/commercial effluent (Abdel-Ghani & Elchaghaby, 2007).

Water contamination may come from a variety of sources, however, there are two main types: indirect and direct pollutant sources. Waste outfalls from waste remediation plants, refineries, factories, and other direct sources are examples. Pollutants, which enter the water supplement through the soil/groundwater system and create the atmosphere throught water of rain are examples of indirect sources (Rao et al., 2012). Heavy metal refers to a set of minerals (and metals-like elements) having a density higher than 5 g/cm3 and an atomic number larger than 20 (Raut et al., 2012). Toxic substances must be removed from industrial effluent as soon as possible. Natural materials used to remove heavy metals have become a source of worry in all nations. Natural materials in vast numbers or agricultural waste might have could be employed as low-cost adsorbents since they are underutilized resources that are widely accessible and ecologically acceptable (Kerri, 2004). The water of acceptable quality is needed for agriculture, industry, home, and commercial uses, and great-quality water was essential for human life. Each of these actions contributes to water contamination. Hundreds of millions of dollars The need for water is growing, but all water resources are gradually becoming unsuitable for use as gallons of trash from all of these sources are being dumped into freshwater bodies each day. incorrect trash disposal The job of establishing appropriate remediation facilities for all pollutant emissions is tough and costly, therefore there is an urgent need for low-cost, low-maintenance, and energy-efficient new solutions. Because the monitoring system is minimal, the adsorption method is both cost-effective and technically simple to separate. The technological feasibility of a variety of low-cost adsorbents for the removal of heavy metals from polluted water is examined in this study (Renge et al., 2012).

Heavy metals were discharged in large quantities into the environment as a result of increasing industrialization, posing a significant worldwide issue. Chromium, mercury, lead, nickel, copper, zinc, and cadmium are frequently found in industrial wastewaters originating from smelting, mining, metal plating, battery manufacturing, petroleum refining, paint manufacturing, tanneries, pesticide manufacturing, pigment manufacturing, photographic manufacturing, and printing, and so on (Ngah & Hanafiah, 2008). Adsorption is a Physico-chemical remediation method for eliminating heavy metals from aqueous solutions that has been shown to be successful. If an adsorbent is plentiful in nature, needs minimal processing, and is a waste product from the waste industry, it may be called inexpensive or low-cost. Plant waste is cheap because it has no or very little economic value (Bailey et al., 1999). Grape stalk waste (Villaescusa et al., 2004), rice husk ashes, Neem bark (Bhattacharya et al., 2006), and peanuts hull pellets (Johnson et al., 2002) were the most often studied untreated plant wastes. Tea trash (Adelaja et al., 2011), sago wastes (Quek et al., 1998), Imperata cylindrical leaves (Hanafiah et al., 2007), papaya woods (Saeed et al., 2005), Moringa Olivera pods (Wasewar, 2010), etc. Industries that conduct procedures such as electroplating, metal/surfaces finishing, and solid-state wafer manufacturing produce wastewater that is polluted with dangerous heavy metals. Some hazardous concentrations of metals, such as Zn, Ni, and Cu, are greater than permitted discharge limits in these wastes. As a result, before having to release these wastewaters into the surrounding areas, it is vital to eliminate these toxic metals via proper remediation (Li et al., 2013).

Heavy metal toxicity: Toxic substances in groundwater and surface sources were designated as significant environmental pollutants owing to their movement in marine toxicity and ecosystems to greater living systems. Although once they were available in relatively, undetectable amounts, their recalcitrance and subsequent perseverance in bodies of water indicate that amounts may get raised to the point where they become hazardous due to natural processes including biomagnification. These metals are present in their elemental form, indicating that they have been not susceptible to further biodegradation or bonded in different salt complexes. Metals could be mineralized in either case. Aside from surrounding areas' considerations, technological elements of metal recovery from industrial waterways should be taken into account (Johnson et al., 2002).

Hazards and Human Health: Chromium, Arsenic, Cadmium, Mercury, Lead, Nickel, Zinc, and Copper are some of the heavy metals that are harmful to people. These metals were present in trace amounts in the soil naturally, posing little concerns. Nevertheless, when concentrated in certain locations, they pose a significant threat. Cancer may be caused by cadmium and arsenic, for example. Mercury may induce genetic damage and mutations, while zinc, nickel, and copper could harm the brain and bones (Goldblatt, 1958; Ngah & Hanafiah, 2008).

Toxic impact on aquatic species: Toxic metals in the surrounding areas harm aquatic organisms. The surface water toxicity is mainly determined by the sediment composition and water chemistry (Volesky, 2003). Microorganisms mineralize the metals that are then carried by plankton and then by aquatic organisms. Eventually, once man eats fish from polluted water, the metals have been biomagnified multiple times.

i.) Sublethal impacts on aquatic species might well be caused by slightly increased metal levels in natural waters: Changes in tissue histology or morphology;
ii.) Alterations in physiology, including development and growth inhibition, decreased swimming performance, and circulation modifications;
iii.) Changing in biochemistry, including blood chemistry and enzyme activity;
iv.) Changing in behavior; and
v.) Changing in imitation (Connell & Miller, 1984).

1.4 Heavy Metals Waste Source

Heavy metals-containing industrial waste streams have been produced by a range of businesses. Heavy metals (including titanium, silver, platinum, vanadium, copper, nickel, chromium, lead, zinc, and cadmium) are produced in large amounts by electro-plating and surface metals remediation procedures in a range of applications (Chuah et al., 2005).

Electroplating, electroless depositions, etching, milling, anodizing-cleaning, and conversion-coating are only a few examples. Printed circuits board (PCB) manufacture is another major source of toxic substances waste. The most often utilized resistant over-plates were nickel, lead, and tin solder plates. Other sources of metal wastes involve the industry of processing wood that also produces arsenic-having waste from wood remediation by chromate copper-arsenates; inorganic pigments industrial production that also produces pigments usually has chromium compounds and cadmium sulfides; refining of petroleum that also products change catalysts polluted with nickel, vanadium, and chromium; and photographic processes that also produce the film with great silver and ferrocyanide amounts. All of these sources generate significant amounts of sludge, residue, and wastewater that may be classified as hazardous waste materials that need substantial waste remediation (Rana et al., 2004).

Copper: In their effluents, the metalworking and electroplating factories release substantial quantities of toxic substances, including ions of nickel (Ni) and copper (Cu) (Hsu, 2009). Metal plating, pipe corrosion, fiber manufacturing, metallurgical, printed circuits, and mining sectors all contribute to copper pollution in the environment (Barrell, 1975). Pulp and paper, petroleum refineries, and woods preservation are the other main sectors that discharge copper in their industrial effluent.

Copper contamination is also caused by sources of agriculture like animal manure, fungicidal sprays, and fertilizers. Copper might well be found in foods such as chocolates, nuts, mushrooms, liver, and shellfish as a pollutant. Copper-based packing containers might pollute products including beverages, water, and food (Kabata-Pendias & Pendias, 1992).

Copper accumulation in the brain lenticular nucleus has been linked to neurotoxicity, often described as "Wilson's disease," as well as renal failure

(Timberlake & Orgill, 2009). Copper poisoning has caused jaundice and an enlarged liver in certain people, however the acceptable amount of Copper in the potable water is (1.3 ppm). One type of metallic fume fever is thought to be caused by it (Goldblatt, 1958). Sprays that contain Copper have been related to the increase in the cancer of lung amongst employees who have been subjected to them (Onundi et al., 2010).

Electro-coagulation reactors come in a variety of shapes and sizes. Every system has its own set of benefits and drawbacks. The first significant difference among electrocoagulation reactors is whether a reactor has been designed as a batch or a batch system, which is critical for optimum efficiency. The bulk of applications, with a constant input of wastewater and working under steady-state conditions, clearly fall into the latter group. The fact that the coagulant needs of these reactor systems have been basically set is a significant benefit in terms of both operation and design. Batch reactors generally treat a set amount of wastewater each treatment cycle that has the apparent drawback of changing conditions inside the reactor over time (Comninellis & Chen, 2010).

1.5 Objectives

The major goal of this investigation is to explore and inspect the characteristics of Coppe removal from wastewater using a batch flow electrocoagulation reactor. Also, this study is supposed to achieve the following objectives:

1. To study the combined effects of applied voltage (v), current density, stirring rate, initial copper concertation, PH, temperature, and type of anode on the efficiency of EC for the copper removing from aqueous solution by batch flow reactor and aluminum as anode and stainless steel as the cathode.

2. To investigate the best-operating conditions of the batch electrocoagulation method of the copper removal.

1.6 Thesis structure

The thesis's structure consists of five chapters, as follows:

1- **Chapter (1)** is the introduction, which shows an overview of the subject wastewater background, Copper, and electrocoagulation. In addition, other heavy metals, objectives of this thesis, and thesis structure.

2- **Chapter (2);** the removal of Coppers, deals with the theory of electrocoagulation, mechanism of electrocoagulation, comparison between batch and batch process, and literature review.

3- **Chapter (3):** Experimental methods used to determine the concentration of copper ions, as well as the materials used in this thesis and apparatus.

4- **Chapter (4):** Results and Discussion, deal with the results of the electrocoagulation batch reactor experiment, and analyses also, Factors affecting Copper removal are studied throughout this chapter. These factors are applied voltage (v), current density, temperature, pH, initial copper concertation, stirring rate, and anode's type.

5- **Chapter five:** Conclusions and Recommendations, provides the conclusions and recommendations suggestions for future work.

Chapter Two

Theoretical part and literature review

Chapter Two

Theoretical part and literature review

2.1 Introduction

Across several developing and developed nations, contamination by Coppers is a severe issue. Evaporation, ion exchange, solvent extraction, reverse osmosis, electrochemical remediation, chemical reductions or oxidation, and Chemical precipitation are some of the traditional techniques for extracting metals from aqueous solutions (Ozsoy & van Leeuwen, 2009).

EC treatment of wastewater was used for much of the twentieth century, with varying degrees of effectiveness and popularity. This method has been more popular in South America and Europe in the past decade for the treatment of industrial wastewater containing metals. It should also be mentioned that in North America, EC has predominantly been utilized to treat effluent from pulp and paper mills, as well as mining and metal processing. EC has also been used to treat water that has food wastes, oil wastes, colors, suspended particles, chemical and mechanical polishing waste, organic matter from landfill leachates, defluorination of water, synthetic detergent effluents, mining wastes, and Copper-containing solutions. EC is often used to identify main operational parameters for wide groups of polluted water or waste streams via empirical investigations (M) (Mollah et al., 2001).

Electrocoagulation is a complicated process that involves many processes working together to remove contaminants from water. In the literature, there are many different viewpoints on critical mechanisms and reactor designs. An absence of a systems process would also have led to a plethora of designs for electro-coagulation reactors that do not take into account the system's complexity. Understanding electrocoagulation and its regulating factors require a methodical, comprehensive approach (anode, temp, initial concentration, contact time, stirring rates, current density, voltage, and pH). In electrocoagulation, a current is passed via electrodes in water. The anode dissolves as a consequence of this (either iron or aluminum). These ions subsequently form hydroxides that bind to pollutants and/or adsorb them, causing them to precipitate out. The pollutants may then be removed from the water by settling, decantation, or filtering of the precipitation (Etiégni et al., 2010).

The charged particles in colloidal suspension were neutralized by mutual impact with metal hydroxides ions and agglomerated, followed by flotation or sedimentation, in chemical coagulation (CC) and EC. The fundamental distinction between chemical coagulation and electrocoagulation is the delivery method for iron or aluminum ions (Avsar et al., 2007).

2.2 The difference between chemical coagulation and electrocoagulation (Liu et al., 2010)

Electrocoagulation	Chemical coagulation
1- Because of the pH neutralizing impact, it worked across significantly wider pH ranges (3-10).	1- Since hydrolysis of the metal salt causes a pH reduction, the final pH must constantly be adjusted. Chemical coagulation is very sensitive to pH changes, and successful coagulation is only possible when the pH is kept constant (7).
2- Electrocoagulated flocks are	2- EC flocs were greater

substantially bigger than chemically coagulated flocks, contain less bound water, seem to be acid-resistant, and more stable, and thus may be readily extracted by filtering.	compared with chemical coagulation flocs.
3- Sedimentation or flotation might be used after the electrocoagulation procedure.	3- Filtering and sedimentation are always performed after the chemical coagulation procedure.
4- The contaminant may be carried to the solution's top by the gas bubbles formed throughout electrolysis, where it could have been focused, gathered, and eliminated more readily.	4- There will be no bubbles created.
5- The gas bubbles generated throughout electrolysis could indeed conduct the contaminant to the solution's top, where it could be more easily mainly focused, collect, and remove.	5- Sludge generation is high.
6- The electrocoagulation technique is used to treat low-turbidity water, low-temp.	6- When the temp and turbidity are low, chemical coagulation has a hard time producing a satisfactory outcome.
7- Electrocoagulation is a basic procedure that needs little equipment and is straightforward to perform.	7- High-level operational issues.

2.3 Theory of electrocoagulation process

A direct current supply is processed by EC between metal electrodes submerged in wastewater. The dissolving of metal electrodes, most often aluminum and iron, into water is caused by an electrical current. At an adequate pH, dissolved metal ions may produce a broad spectrum of coagulated species and metal hydroxides, which destabilize and agglomerate suspended material or precipitated and adsorb dissolved pollutants (Katal & Pahlavanzadeh, 2011).

This method uses a coagulant as a sacrificial anode (typically aluminum or iron) that is formed in situ (Figure 2.1). Anodes have often been made of aluminum or iron that dissolve to generate polymeric hydroxides, oxy-hydroxides, and hydroxides. In EC, settling has been the most typical method, although flotation might well be accomplished using H2 (electroflotation) or with the help of air injection (Essadki, 2012).

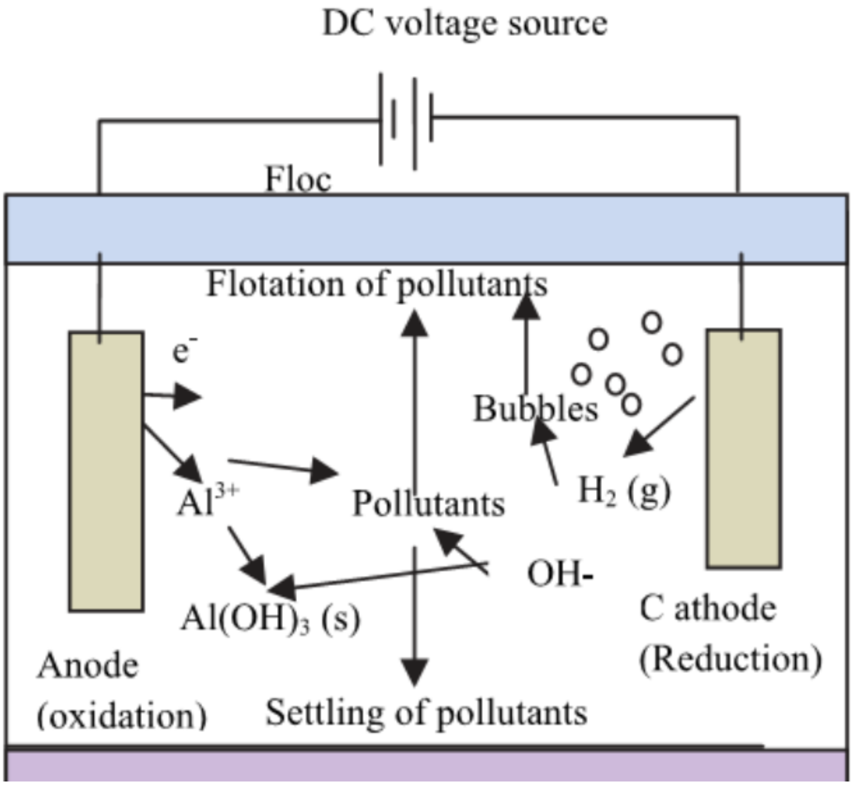

Figure 2.1:Two-electrodes EC cell schematic illustrations (Essadki, 2012).

Throughout EC, three steps take place in order (Essadki, 2012):

i. Coagulants are formed when a sacrificial anode is oxidized.

ii. Contaminant destabilization, particle suspension, and emulsion breaking.

iii. The destabilized components clump together to produce flocs.

The contaminants could be in the system of (Essadki, 2012):

1- Particles of a large size By settling, it is simple to extract them from the water.

2- Colloid.

3- Minerals salts dissolved in water and organic compounds.

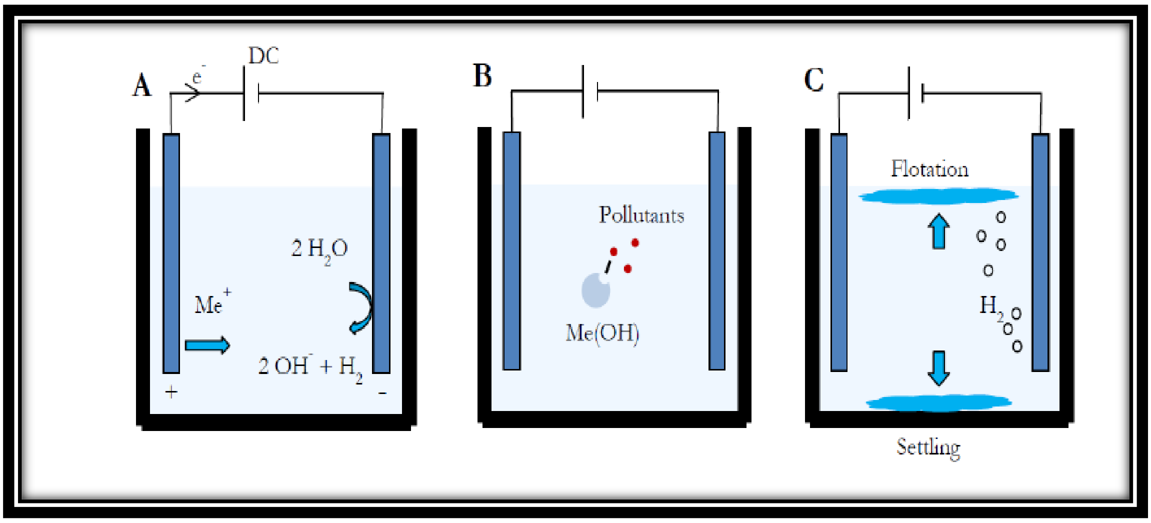

Fig.2.2 Principles of Electrocoagulation (Dubrawski, 2013)

The consumable (sacrificial) metal anodes M was seen in Fig. 2.2 A, in which they are employed to constantly create polymeric hydroxides in the region of the anode. Coagulation takes place once those metal cations interact with the negative particles transported towards the anode using electrophoretic motion, as seen in Fig. 2.2 B. Contaminants in the wastewater stream are treated in Figure 2.2 C either via chemical processes and precipitation or through chemical and physical attachment to colloidal materials created by electrode erosion. Filtering, sedimentation, and Electro-flotation are used to remove them.

It is difficult to employ decantation as a method for removing the greatest number of particles. This is particularly true in the case of colloids. Colloids were mineral or organic particles that range in size from a few nanometers to a few millimeters and are willing to take responsibility for turbidity and color (Essadki, 2012).

2.4 Mechanism of EC

The processes of EC is the remediation of water and wastewater are quite complicated. Apart from EC, electroflotation, electrochemical oxidation, and adsorption were thought to be three additional probable processes at work (Kobya et al., 2011). Throughout this electrocoagulation process, seven primary steps happen:

1. The movement to an electrode with the opposing charging (electrophoresis).
2. Charging neutralization causes aggregation.
3. With the contaminant, the cation or hydroxyl ion (OH) produces precipitation.
4. The metallic cation binds to the contaminant by reacting with OH to generate a hydroxide with strong adsorption characteristics (bridge coagulation).
5. The hydroxides sweep thru the water, forming bigger lattice-like formations (sweeping coagulation).
6. Adhesion to bubbles and removing using electro-flotation or sediment

Iron electrodes were used to study the mechanics of EC (Ni'am et al., 2006). EC is depending on the notion that electrical charges affect the stabilization of emulsions, suspensions, and colloids. As a result, once extra electrical charges are applied to charged particles through suitable electrodes, the surface charge of the particles becomes neutralized, and numerous particles clump together to form larger, separate agglomerates (Koparal & Öğütveren, 2002).

Coagulant has been formed in situ via electrolytic oxidation of the anode material in EC with an electrical current passing between two electrodes. Fe(OH)n with n = 2 or 3 is generated at the anode with an iron anode. The cathode and anode of the iron electrodes have been described by simplification oxidation/reduction processes:

Anodes:

$$Fe_{(s)} \rightarrow Fe^{+2}{}_{(aq)} + 2e^{-} \qquad (2.1)$$

$$Fe^{+2}{}_{(aq)} + 2OH^{-}{}_{(aq)} \rightarrow Fe(OH)_{2(s)} \qquad (2.2)$$

Cathodes:

$$2H_2O_{(l)} + 2e^{-} \rightarrow H_{2\,(g)} + 2OH^{-}{}_{(aq)} \qquad (2.3)$$

Overall:

$$Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_2 \qquad (2.4)$$

Utilizing aluminum electrodes to study the processes of EC (Koparal & Öğütveren, 2002).

The major reactions happening at the aluminum electrodes throughout electrolysis in the EC process have been well recognized:

$Al \rightarrow Al^{+3} + 3e^{-}$ (anode) E^0A = -1.66 V (2.5)

Once the anode potential is reasonably high, oxygen evolution is also conceivable.

$4(OH)^{-} \rightarrow O_2 + 2H_2O + 4e^{-}$ E^0= -0.40 V (2.6)

Concurrently, a cathodic process happens, generally resulting in hydrogen evolution. The pH of the reaction at the cathode seems important. Hydrogen is created by Formula (2.7) at alkaline or neutral pH.

$2H_2O + 2e^- \rightarrow 2OH^- + H_2$ $E^o = -0.83$ V (2.7)

Formula (2.8) best captures hydrogen evolution at the cathode under acidic environments.

$2H^+ + 2e^- \rightarrow H_2$ $E^o = 0$ V (2.8)

Faraday's law states that the metal's dissolved amount is proportional to the electricity amount flowing thru the electrolytic solution (Sakarinen, 2016). In its most basic form, this formula provides:

$Al + 3H_2O \rightarrow Al\,(OH)_3 + 1.5H_2$ (2.9)

$Al + 4H_2O + e^- \rightarrow Al(\,OH)_4 + 2H_2$ (2.10)

$$\mathrm{w(metal)} = \mathrm{I} * \mathrm{t(s)} * \frac{\mathrm{M}}{z * F} \qquad (2.11)$$

w (metal) = the dissolved metal mass (g).

I = the applied current (A).

t (s) = the time remediation (s).

M = the electrode material in molar mass (M (Al) = 26.982 g/mol).

z = the ions valence of the electrodes material (z (Al) = 3).

F = The constant of Faraday, which equal to (96485 C/mol).

2.5 Factors affecting electrocoagulation processes

Much research has demonstrated that electrocoagulation is a complicated process that may be influenced by a variety of factors including temperature, anode, contact duration, initial amount, stirring rates, pH, voltage, and current density.

2.5.1 Impact of Current Density

Current density is an essential factor in EC since it controls the coagulant dose rate, bubble generation rate, floc size, and development, all of which have an impact on the EC's efficiency. The anode dissolving rate rises as the current density increases. As a consequence, the amount of metal hydroxide flocs increases, increasing the effectiveness of pollution removal. Because adequate quantities of metal hydroxide flocs seem to be obtainable for contaminant sedimentation, an increase in current density above the optimal current density does not lead to an increase in pollution removal effectiveness (Doong et al., 1998; Fabbri et al., 2009).

2.5.2 Impact of stirring rate

The main purpose of the rotating electrodes mixing rate is to effectively transfer the coagulant materials dissolved from the electrode to the EC reactor. The instability of flocks produced in the reactor might well be causing the loss in efficiency at greater rates of stirring. The stirring rate has no impact on the final pH. Slight increases in electrode dissolution have been found (Al Qedra, 2015). Generally, when the stirring rate is increased, coagulant matter forms bind together, and disperses in the reactor, making the contents homogeneous. Agitation aids in improving current efficiency, allowing for a greater working current density (Pletcher & Walsh, 2012).

2.5.3 Impact of temperature

The electrocoagulation process is also influenced by the temp of the water. The pace of reaction is increased as the temp is raised during electrocoagulation (Shen et al., 2006). The electrocoagulation process is also influenced by the temp of the water. The breakdown of an aluminum anode was studied at water temperatures ranging from 40 to 60 degrees Celsius. The destructive reaction of the oxide membrane will be accelerated as the temp rises, increasing the current efficiency. Once the temp above 60 degrees centigrade, nevertheless, the current efficiency started to decline. The amount of colloid formed on the anode will decrease in this situation, and pores created on the anode will shut. The aforementioned variables will be to blame for the existing inefficiency (Comninellis & Chen, 2010).

2.5.4 Initial PH.

Researchers have conducted several investigations on electrocoagulation to see how it affects the overall mechanism of the process (Chen et al., 2000). The pH of the wastewater is always taken into account while choosing the coagulation method (Canizares et al., 2005). Maximum removing efficiency is achieved at an appropriate pH level for a given contaminant, and precipitation starts at this pH. When the pH is changed from its optimal magnitude, its removing efficiency diminishes. Optimum effectiveness was reached at neutral pH levels of 6 to 8, whereas removing efficiency is about same at strongly acidic (pH less than 5) and extremely basic (pH more than 9) pH levels. However the pH does not stay constant during the process, it does change over time.

2.5.5 Initial concentration

Investigations have been performed using the CCD design to investigate the influence of initial Cu (II) various concentrations from 100 to 400 mg/L. At lower initial amounts, removing efficiency has been increased; nevertheless, when the initial amount was raised, removing efficiency rose dramatically. Even though the efficiency only increased up to a certain point of the initial amount, beyond that it began to drop. This might be explained by the fact that the number of flocs generated was inadequate for Cu (II) adsorption at extremely high starting concentrations.

2.5.6 Impact of electrodes materials

The current remediation facility's core is the electrode assembly. Stainless steel, aluminum, and In the initial minutes, the effluent treated with an iron electrode looked greenish, and also became yellow and muddy. Fe2+ and Fe3+ ions created during the EC process might well be responsible for the green and yellow colors. Fe^{2+} is the most frequent ion produced during the electrolysis of an iron electrode in situ. It seems to have a high soluble in acidic or neutral situations and could be easily oxidized into Fe^{3+} by dissolved oxygen in water (Babu et al., 2007), in which the effluent treated with aluminum electrode appeared white for the first time and remained white throughout the process, no sludge has been observed, and only white foam founded as the electrode has been eroded and liberated trivalent aluminum (Al^{3+}). (Al^{3+}) created an ionic couple with the wastewater contaminant. The development of a powerful coagulant occurred. There was good coagulation and flocculation.

2.5.8 Contact time:

The effectiveness of pollutant removal is already a function of the electrolysis time. As the electrolysis duration is increased, the effectiveness of pollution removal improves. However, beyond the optimal electrolysis time, the contaminant removing efficiency remains constant and does not improve when the electrolysis duration is increased. The disintegration of the anode produces metal hydroxides. With a constant current density, the number of produced metal hydroxides grows as the electrolysis time increases. The formation of flocs increases as the electrolysis duration is increased, resulting in an improvement in contaminant removing efficiency. The pollutant removing effectiveness does not improve when the electrolysis time exceeds the optimal electrolysis duration because adequate quantities of flocs were accessible for contaminant removal (Khandegar & Saroha, 2013).

2.6 Previous Studies

Research has been conducted to determine the ideal design of electrocoagulation reactors to retain a greater removing efficiency of contaminants and hazardous metals from aquatic environments while keeping ecological and economic principles in mind.

(Rajemahadik et al., 2013) investigated the removing efficiency of toxic metals from electroplating wastewater utilizing an Al and Fe electrode as a material at pH variations of 9, 7.0, 5.0, and 3.0 for half an hour of retention time. Throughout most of the testing, the impacts of retention duration, pH, and electrode material were investigated, as well as energy usage and electrodes. In comparison to Al-Al and Al-Fe removing efficiency and usage cost, the maximum removing efficiency on optimization has been demonstrated throughout pH 9 at 0.1A current utilizing electrode combination of Fe-Fe and Fe-Al 100.0 percent of chromium and nickel removing within 20 minutes for INR 90.0/m^3 for INR 90.0/m^3.

(Escobar et al., 2006) utilized flat commercial laminate steel plates for both electrodes in a monopolar configuration and utilized batch and continuous operational parameters to treat simulated contribute to water pollution 4, 4, and 12ppm of cadmium, lead, and copper, respectively. The pH ranges (4-9) have been investigated, as were the current density=(11-108)A/m^2 and flow rates=(6.3-17)cm^3/min. This research discovered the ideal circumstances for better-removing efficiency: current density=(31-54) A/m^2, flow rate=6.3 cm3/min, and pH=7.

(Petsriprasit et al., 2010) investigated the removing of Coppers from billet manufacturing effluent using the electrocoagulation technique in batch and continuous tests at a lab-scale and ambient temp (30) C. The influence of several factors on metal removing efficiency, such as current density, beginning wastewater pH, and electrolysis duration, has been investigated in a batch experiment. With a current density=98 A/m^2, an initial wastewater pH=5, and a 30 minute electrolysis period, optimal metal ion depletion has been achieved. More than 99 percent of Zn, Cr, and Cu have been removed under these circumstances, and the outlet effluent had less than (0.05, 0.07, 0.01, and 0.02) mg/l of Zn, Pb, Cr, and Cu, respectively. The findings showed that the continuous process achieved steady condition after 2 hr and that the optimal condition for continuous treatment was identified at an initial wastewater pH of 3 and a flow rate of 55 ml/min. Cu and Pb have been completely removed, whereas Cr and Zn had been removed at a rate of better than 99 percent.

Batch electrocoagulation (EC) utilizing monopolar iron electrodes for simultaneous removing of manganese (Mn), zinc (Zn), nickel (Ni), and copper (Cu) from a sample of wastewater were researched by (Al Aji et al., 2012). To find the ideal experimental situations, the impacts of beginning pH (3, 5.68, 8.95), initial metal amount (50-250 mg/L), and current density (2–25) mA/cm^2 on removing efficiency have been investigated in a batch stirred cell. Under the optimal experimental circumstances, the findings demonstrate that EC was extremely efficient in removing toxic metals from the sample of wastewater, which had an initial amount of 250 mg/L for each metal. High pH levels seem to be more favorable for metal removing with EC remediation, depending on preliminary pH measurements.

(Murthy & Parmar, 2011) investigated the removing of strontium utilizing aluminum electrodes and stainless steel inelectrocoagulation. Electrocoagulation has been used to remove strontium up to (100mg/L) from synthetic wastewater. The removing efficiency of aluminum electrodes and stainless steel have been evaluated in terms of electrocoagulation duration, current density, the quantity of electrolyte injected, solution pH, the distance between electrodes, temp, and starting strontium content. For both electrode materials, initial operational cost estimates were discovered. Utilizing adsorption kinetics models for pseudo-second-order and pseudo-first-order, the strontium removing data has been utilized to discover adsorption kinetics. The best operational factors are 50 minutes of process duration, 8mA/cm2 current density, and solution pH 5, with removing efficiency of roughly 77 percent and 93 percent attained utilizing aluminum electrodes and stainless steel, respectively. The results fit the pseudo-second-order kinetic model higher than the pseudo-first-order model.

(Heidmann & Calmano, 2010) explored the efficiency of an electrocoagulation technique for the removal of Cr, Cu, and Ni from galvanic wastewater. Many factors were studied to see how they affected the removing outcomes and electrocoagulation effectiveness. They found that electrocoagulation might be a suitable alternative to traditional techniques for treating heavily polluted wastewater with concentrations up to a few hundred mg/l in this investigation. The findings were eliminated due to the use of Al and Fe electrodes, as well as an initial pH magnitude of more than 5.

(Bayar et al., 2013) explored the viability of electrocoagulation for cadmium removal from water. The impacts of conductivity (j), stirring speed, reaction duration (t), initial amount (C0), and initial solution's pH on cadmium removing from chemically synthesized wastewater having cadmium in the batches EC method have been examined in this work. The initial pH of the solution seems to be a key element impacting cadmium removal, according to the findings of the experiments. In the trials, the pH of the starting solution ranged between 3 and 6. Even though specific energy usage rose as cadmium amount decreased due to poor conductivity, cadmium removing efficiency had also been better at 25 mg/l than 1,000 mg/l. The efficiency of cadmium removal is reduced by stirring speeds below and above 150 rpm. The electrocoagulation approach was shown to be quite successful in removing cadmium from aqueous solutions.

(Wided et al., 2014) evaluated the impact of employing aluminum electrodes to extract lead and copper from a contaminated solution utilizing batches of electrocoagulation reactors with bipolar electrodes. The starting pH (3-7) magnitude, plane electrodes' applied current densities (0.147-1.470) m A/cm^2, reaction duration (0-60) mins, and solutions conductivity (415-1107 mS/cm) have all been investigated. The maximum removing efficiency for each of these contaminants at 70ppm initial amount is 54.1 percent and 91.4 percent for copper and lead ions, respectively, after 30 minutes when pH is 5, the current density is 1.029 mA/cm2, and solution conductivity is 1.107 mS/cm, according to this research.

The influence of reactors design specifications on cadmium removal from industrial wastewater has been explored by (Brahmi et al., 2018). The optimum cadmium removing has been accomplished with a surface area/volume proportion (S/V) of 13.6 m^2/m^3, stirring speed=300 rev/min, monopolar connection mode, inter-electrode spacing= 5 mm, and an initial temp of 50 degrees centigrade, based on an analysis of the design specifications one by one. The electrodes arrangement, inter-electrode spacing, and S/V proportion are the characteristics that influence the operational cost, according to the research. The cost of remediation, energy usage, and pH change have all been investigated. In under 5 minutes, 100 percent cadmium elimination had been achieved.

(Rehman et al., 2015) used iron and aluminum metal to explore the influence of plane electrodes metal on response variables. In a continuous electrocoagulation reactor, bipolar electrodes have been used to investigate additional parameters including current density (0.007-0.04) A/cm^2, hydraulic retention time (20-120) seconds, inter-electrode distance (0.4-24) cm, and pH (3-9). Under current density=0.026 A/cm^2 and pH=6.32, more than 95 percent of the original amount (63 ppm Pb ion, 110 ppm Ni ion, and 105 ppm Cu ion) seems to have been exposed, with a very low power usage (1.6 kW h/m^3).

Chapter Three

Materials and Methodologies

Chapter Three

Materials and Methodologies

3.1 Introduction

In the current chapter, an electrocoagulation reactor (cell) contains two electrodes; mild steel or aluminum was utilized as anodes while stainless steels were utilized as cathodes for removing copper from simulated wastewater by the EC reaction. The study consists of a selection of eight variables which are reported as affected operation variables on EC reaction and screeing which are more significant effects on it. The optimum operating conditions were identified. The kinetics and thermodynamics for EC reaction were investigated. and the Application of the Box-Behnken method to the most influential factors on the copper removal process.

3.2 Chemical Materials

The chemical compositions, the materials' purity utilized in the current investigation have been presented in table **3.1**

Table 3.1: Chemical utilized

NO.	Chemical	Formula
1	**Copper nitrate**	**$Cu(NO_3)_2$**: purity equal to 99.99%wt
2	**Sodium hydroxides**	$\boldsymbol{NaOH}$: pureness=97.5 % wt
3	**Hydrochloric acids**	$\boldsymbol{HCl}$: pureness=38%wt

3.3 Apparatus

The electrocoagulation reactor is electrochemically cells that consist of a 1.0 L glass vessel fixed with a cover of (PVC) that contains holes to install the electrodes, in which the anode iron or aluminum while the cathode is a stainless steel ring

Figure 3.1: Hard anodes of iron and aluminum

In the present work, the diameter of anodes 1cm with 20 cm long, the effective area of the Aluminum and iron electrode was 62.4cm². The area of the submerged part of the anode was 31.2cm²

Figure 3.2: cathode stainless steel ring

The reactor is supplied with the thermometer, pH meter, in which the electrocoagulation reactor (cell) is immersed in the water bath. The cell was equipped by the power supply (Type (TXN-1502D with a ranging of voltage 0-30 V and current ranging from 0-2 A, as to accuracy 0.01%), two multimeters (model number DT 832 and basic accuracy is 0.75% with range 0-10 amperes) for current and voltage measurement, pH sensor (Type: PH - 80 which has a range of pH 0-14), 0.1 resolution and accuracy (± 0.01), thermometer and multi-speed stirring motor. Four digits balance was utilized also.

3.4 procedure:

The Experimental objectives of the study work are:

3.5. The Simulated Wastewater Samples

Copper nitrate Cu $(NO_3)_2.3H_2O$ has been dissolved in distilled water to make 1000 ppm copper stocking solutions. 5 grams of copper nitrates have been dissolved to make 1000 ppm copper stocking solutions. the necessary concentration (200 mg copper/l) was calculated using the dilution formula from the stocking solutions:

$$V_1 \times C_1 = V_2 \times C_2 \tag{3.1}$$

3.6. Batch Mode of Electrocoagulation Operations

The basic layout of the apparatus and experimental equipment utilized in this study is depicted in Fig. 3.3, which is a snapshot of the experiment conducted utilized in this study.

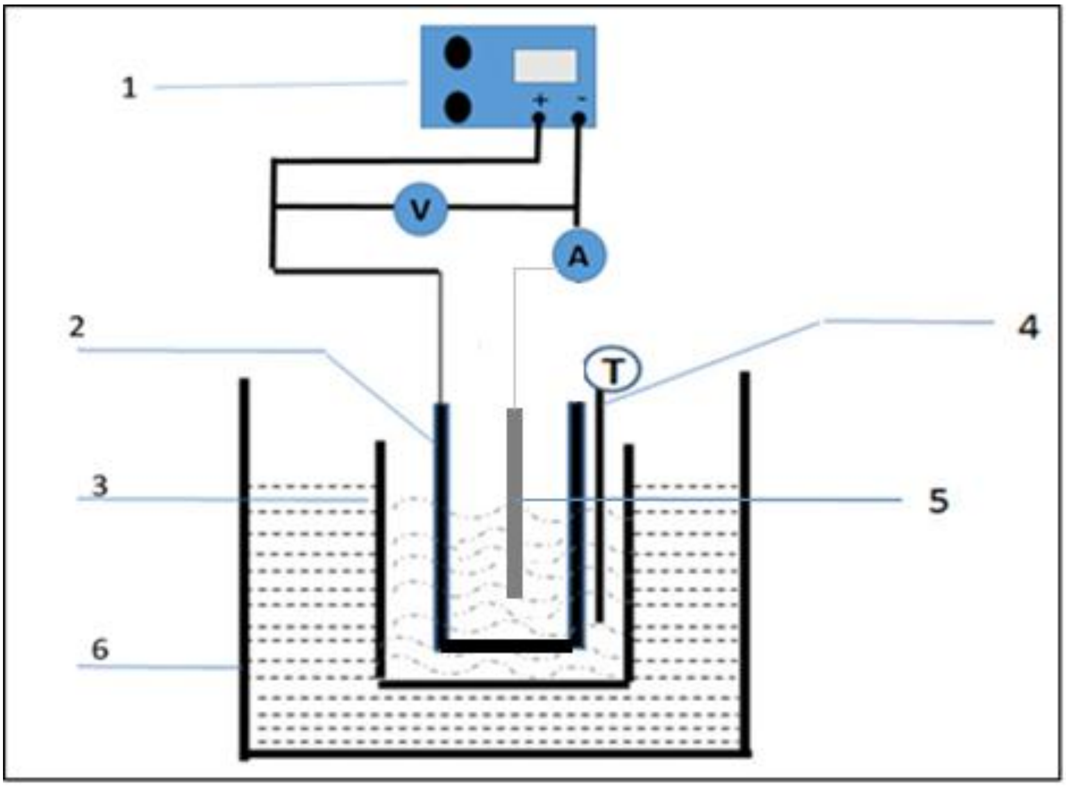

Fig 3.3: EC reaction apparatus plan, 1) power supplier, 2) anodes, 3) electrochemical cell, 4) thermometer sensors, 5) cathodes, 6) water basin, V–voltmeter, A-ammeter.

3.6.1. The General Procedure of Each Experiment

The electrodes were rinsed in before each run; electrodes were washed with sodium hypochlorite solution to remove surface grease. At the end of each run, the electrodes were rubbed with sandpaper and then rinsed with 0.1N HCl solution followed by water to remove any solid residues on the surfaces and dried. Feed stocking solutions have been produced by dissolved copper nitrates $Cu\ (NO_3)_2.3H_2O$ in distilled water. The electrolyte's pH has been fixed, when essential, with 0.9-M in 500 ml water or HCl solutions. All operation conditions were adjusted according to the PBD matrix shown in Table3.3. The electrodes were immersed in an EC reactor (cell) which contains simulated wastewater, and power supply power according to the required voltage and current, as well as the stirring motor switched on at the same time samples were taken at end of each run to determine copper concentration.

The variables chosen in this work are reaction time, current time, voltage supply, stirring rate, initial copper concentration, solution pH and reaction temperature, and type of electrode, which symbolic A, B, C, D, E, F, G, and H respectively as listed in Table 3.2

3.6.2. Analytical Procedure

Copper concentration has been investigated utilizing UV-visible spectrophotometers (Spect roquant Pharo 283; MERCK, Darmstadt, Germany). The equation utilized to calculate the wastewater removal efficiency and COD in the treatment experiments was

$$\text{RE}\ \% = \frac{\text{Initial conc.} - \text{Final conc.}}{\text{Initial conc.}}\ \text{x}\ 100 \qquad (3.2)$$

Where RE % is copper removing efficiency.

3.6.2.1. Screen the variable Plackett –burman design

The investigation of the impact of studied variables is done in three steps; the first step is variables selection with their levels, the second step is to design the experiment matrix and the third step is result analysis. The analysis step consists of the application of Plackett-Burman design PBD, in which PBD is the statistical technique utilized to study studied variables on EC process as well as reduce the number of the repeated experiment, it is a two-level factorial design i.e. -1(low) and, +1(high) that detects significance variables on EC process by screening studied factors (Kennedy & Krouse, 1999). The studied variables chosen were with their level listed in the table and the Plackett-Burman matrix design shown in Table 3.2. The main impact was estimated by calculating the difference between average measurements for each factor at high and low levels, while the design screening variables based on a first-order regression model

$$\mathrm{RE\%} = \beta_0 + \sum \beta_i X_i \qquad (3.3)$$

Where RE% is the response, β_0 and β_i are intercept and variables parameter respectively. The variables screening was done by aim of Minitab software version 17.

Table 3.2: the high and low levels for all selected variables

	Variables (parameter)	Units	Low levels (-1)	Great levels (1)
1	Reaction time (A)	Minutes	10	40
2	Current density(B)	A/cm^2	1	3
3	Voltage supply (C)	Volt	2	10
4	Stirring rate(D)	rpm	0	1000
5	Initial copper concentration (E)	ppm	100	400
6	Solution pH (F)	-	3	10
7	Reaction temperature (G)	°C	50	70
8	Type of anode (H)	-	Al	Fe

Table 3.3–Plackett-Burman design PBD matrix

Run	Contact time A	current density B	voltage supply C	stirring rate D	Initial Copper conc. E	pH F	Temperature G	Anode H
1	-1	-1	-1	1	1	1	-1	Al
2	1	1	-1	1	1	-1	1	Fe
3	-1	1	-1	-1	-1	1	1	Al
4	-1	1	1	-1	1	-1	-1	Fe
5	1	1	1	-1	1	1	-1	Al
6	-1	-1	1	1	1	-1	1	Al
7	1	-1	1	1	-1	1	-1	Fe
8	-1	-1	-1	-1	-1	-1	-1	Fe
9	1	-1	1	-1	-1	-1	1	Al
10	1	-1	-1	-1	1	1	1	Fe
11	1	1	-1	1	-1	-1	-1	Al
12	-1	1	1	1	-1	1	1	Fe

The standard calibration curve was plotted for known concentrations of copper by measuring the absorbent by UV Spectrometry as shown in fig.(3.3) The absorbance value for unknown sample was interpolated to obtain concentration from the calibration curve.

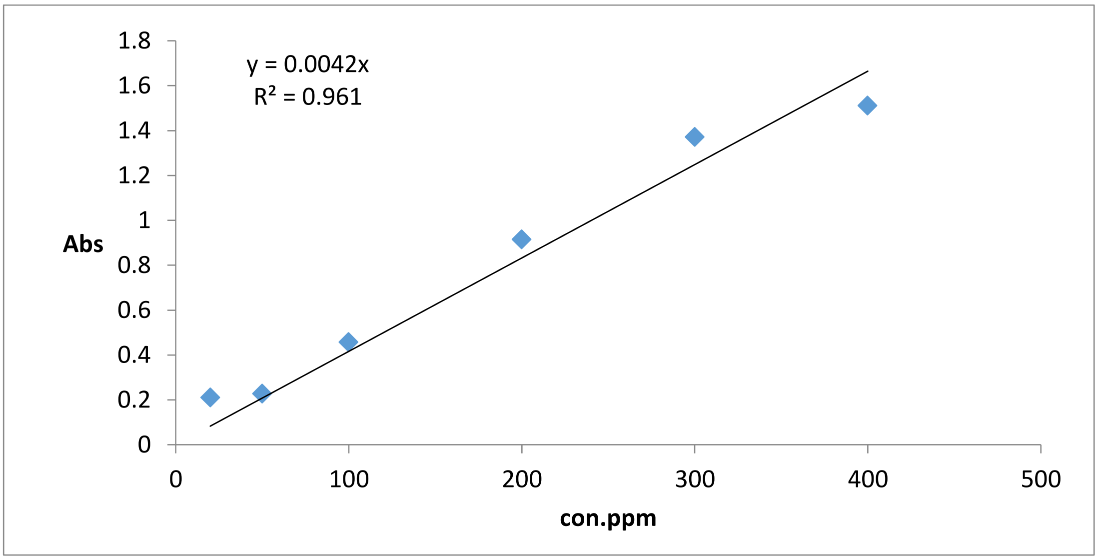

Fig.3.5 Standard Calibration Curve of copper at Different Concentration (20, 50, 100,200, 300, 400and 500 mg/l) (Absorbance Versus Concentration).

3.6.2.2. Application Of Box Behnken Design

The first three variables that most affect removal efficiency, pH, initial concentration, and temp', have been chosen, and researchers performed a new study using the Box-Behnken Design (BBD) 2nd order model design, among many other RSM methods, for modeling work, improvement, and interpretation of findings since its benefits over others that include: taking cognizance of deformation (nonlinear presence) of response that is beyond the skill of the first three factors (Ouhadi et al., 2010). Version 18 for Minitab was the mathematical program utilized to accomplish these above goals. Fifteen tests have been designed with three parameters (independent parameters) utilizing the BBD method: pH value, initial concentration, and temperature

The set of tests needed to cover the range of factors has been estimated using the Box Behnken matrix (Equation) (3.4) (Essa et al., 2013).

$$N = 2k\,(k-1) + r \qquad (3.4)$$

Whereas:

N: the tests numbers,

K: the parameters numbers, and

R: the replicated central points' numbers.

The method suggested that the levels of the variables were modified at just three levels (+1, 0, -1) and the intervals between these levels were similar. The overall experiments number calculated by Formula (3.4) for three Box Behnken model variables is 12 in addition to three central point replication amounts, therefore, the total would be fifteen experiments to determine the impact of independent parameters on the removing process. Corresponding to the experimental designing approach of Box Wilson, 27 tests were required to cover three independent machine parameters.

Table 3.4 Independent (controllable) variables and their levels.

Parameters (unit)	**Character**		**Level**		
	Coded	Actual	-1	0	1
Concentration(ppm)	x_1	X_1	200	350	500
Temperature(G)	x_2	X_2	40	50	60
pH	x_3	X_3	3	7	11

Table 3.4 demonstrates X_1 , X_2 , and X_3 the actual parameters (factor) selected for designing the 3-levels high= (+1), intermediate= (0), and low (-1) magnitudes. The coded parameters (x_1 , x_2 , and x_3) have been connected to parameters by Formula:

$$Xi = \frac{Xi - Xo}{\Delta Xi}\ ; \qquad i = 1,2,3 \tag{3.5}$$

Whereas:

The independent variable real magnitude at the central level= $X0$ and the interval magnitude= ΔX

Table 3.5 Box-Behnken design matrixes.

Run	Design parameters		
	x_1	x_2	x_3
1.0	-1.0	-1.0	0.0
2.0	1.0	-1.0	0.0
3.0	-1.0	1.0	0.0
4.0	1.0	1.0	0.0
5.0	-1.0	0.0	-1.0
6.0	1.0	0.0	-1.0
7.0	-1.0	0.0	1.0
8.0	1.0	0.0	1.0
9.0	0.0	-1.0	-1.0
10.0	0.0	1.0	-1.0
11.0	0.0	-1.0	1.0
12.0	0.0	1.0	1.0
13.0	0.0	0.0	0.0
14.0	0.0	0.0	0.0
15.0	0.0	0.0	0.0

Table 3.5 indicates the Box Behnken matrixes are the experimental discovery organized at random orders to maximize the Copper removal mechanism in terms of estimating the initial concentration, pH, and temperature on the performance of removal of Coppers (Ferreira et al., 2007).

The findings obtained for the impact of initial concentration, pH, and temperature on removing performance could be equipped by Minitab as a second-order polynomial which could be utilized to estimate the optimum for three parameters where Formula reflects the second-order polynomial (3) (Mourabet et al., 2017).

$$y = \beta 0 + \sum \beta i\, xi + \sum \beta ii\, x^2 i + \sum \beta ij\, xi\, x\, j + \varepsilon \qquad (3.6)$$

Whereas:

The response of estimating is y,

The coefficient of intercept is β_0,

The linear influence (slope) of input parameter xi is βi,

The linear interaction is influenced by linear between two input parameters xi is βij, and

βii is squared influence.

Analysis of variation To find variations in the rate of success of the variables tested, ANOVA has been utilized as a mathematical tool for decision-making, at which a total of square and F-statistics have been utilized to explain the relative significance of analyzed data processing and error and unregulated parameter estimation. The machine randomized the tests to be carried out, as seen in Table 3.6, according to the BDD test design.

Table 3.6 Box-Behnken design matrixes.

run	**studied variables**			**Result**	
	Initial concentration	pH	temperature		
1	200	3	50		
2	500	3	50		
3	200	11	50		
4	500	11	50		
5	200	7	40		
6	500	7	40		
7	200	7	60		
8	500	7	60		

9	350	3	40		
10	350	11	40		
11	350	3	60		
12	350	11	60		
13	350	7	50		
14	350	7	50		
15	350	7	50		

3.6.2.3. The procedures of Optimization

The computational optimization has been accomplished by the method steps below:

Step 1: Selecting targets for all of the optimization variables and responses concerned.

Step 2: Entering both high and low variables and response magnitudes limits.

Step 3: Depending on the models produced, the software then explores within the designing space and selects the combination of parameters that best match the specified objectives.

Chapter Four

Result and Discussion

Chapter Four

Result and Discussion

4.1. Introduction

Several groups of experimental have been carried out with different situations to investigate the influence of these variables on the removing efficacies in the electrocoagulation technique. The study is done by obeying the following steps:

1- The first step in the present chapter will clearly illustrate the results impact of studies some affected operation variables on copper removal from simulated wastewater, in which the impact of studied factors was examined to identify the most significant variables from chosen studied variables on the response by applied Plackett-Burman experimental design PBD.

2- The most affected variables that appeared during the application of PBD in the previous step were studied more deeply via applied Box-Behnken experimental design, in which the application of Box-Behnken included result analysis, results fitting, and optimization.

3- The specific energy consumption (SEC) was studied also as an attempt to analyze the energy consumed during the process.

4- The reaction kinetics and thermodynamics parameters were estimated in this study.

4.2. Plackett-Burman design (PBD)

Table 4.1, shows the actual results gain from the experiments designed according to PBD experimental design. The PBD is a basic tool in filtering the effects of process factors on response. The regression model was gained by using PBD, which predicted how variables affect the response, and by the aim of Minitab software the solution of the equation was expressed by coefficient R^2 equal to 0.91, so the model equation can be result by fitting actual results as a first-order equation:

$$RE\% = 67.20 + 3.40\ A + 3.35\ B + 3.39\ C - 0.81\ D + 19.22\ E + 12.10\ F + 4.86\ G - 3.18\ H \quad (4.1)$$

Table 4.1 – Actual result for the 12 runs designed according to Plackett-Burman matrix design

run	Contact time	current density	voltage supply	stirring rate	initial Copper conc.	pH	Temperature	Anode	RE %
1	10	1	2	1000	400	10	50	Al	19
2	40	3	2	1000	400	3	70	Fe	14
3	10	3	2	0	100	10	70	Al	0
4	10	3	10	0	400	3	50	Fe	51
5	40	3	10	0	400	10	50	Al	63
6	10	1	10	1000	400	3	70	Al	57
7	40	1	10	1000	100	10	50	Fe	2
8	10	1	2	0	100	3	50	Fe	97
9	40	1	10	0	100	3	70	Al	89
10	40	1	2	0	400	10	70	Fe	75
11	40	3	2	1000	100	3	50	Al	73
12	10	3	10	1000	100	10	70	Fe	88

The Pareto chart (Figure 4-1) was obtained by the aim of Minitab software, and it can tell us every parameter contribution to the changeability in the copper removing or in another meaning which studied variables are more significant effect on process response. The absolute values of the effects were plotted designated utilizing the line of reference on the diagram. In the findings, stirring rate, anode without substantial impact on copper removing, while initial copper concentration, solution pH, and reaction temperature were the most efficient variables. The copper removing efficiency was optimized by the aim of Minitab software in the application of response optimization, Figure 4-2, shows the predicted operation conditions which lead to the optimum value of copper removing efficiency, the theoretical maximum removal efficiency is 98% (which calculated according to coded variables) which analog for applying operation conditions; contact time (40 minutes), current density (3 A/cm^2), voltage supply (10 volts), initial copper concentration (200 ppm), reaction temperature (70°C) with no stirring rate and using Fe as an anode.

Figure 4-2; also show the impact of studied variables individually, the removal efficiency increasing with the contact time, current density, voltage supply, reaction temperature, and pH, while it was decreased with increasing stirring rate. It can be noted that removal efficiency is higher when using Fe as anode than Al anode.

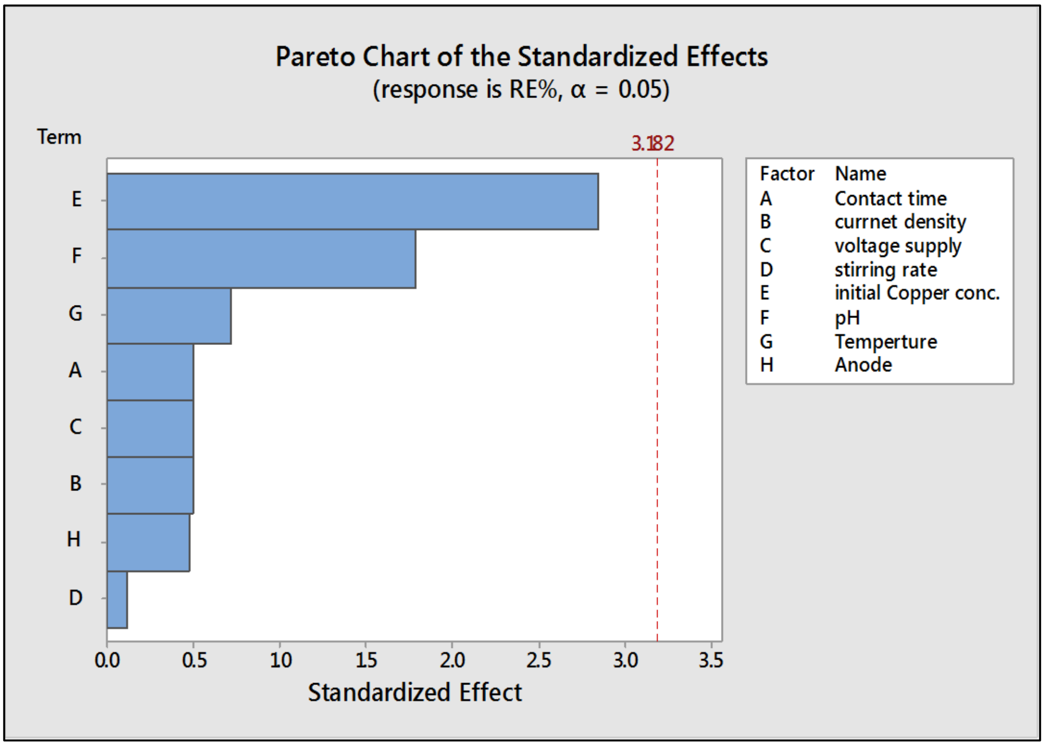

Figure 4-1 – The standardized main effect Pareto chart for PBD.

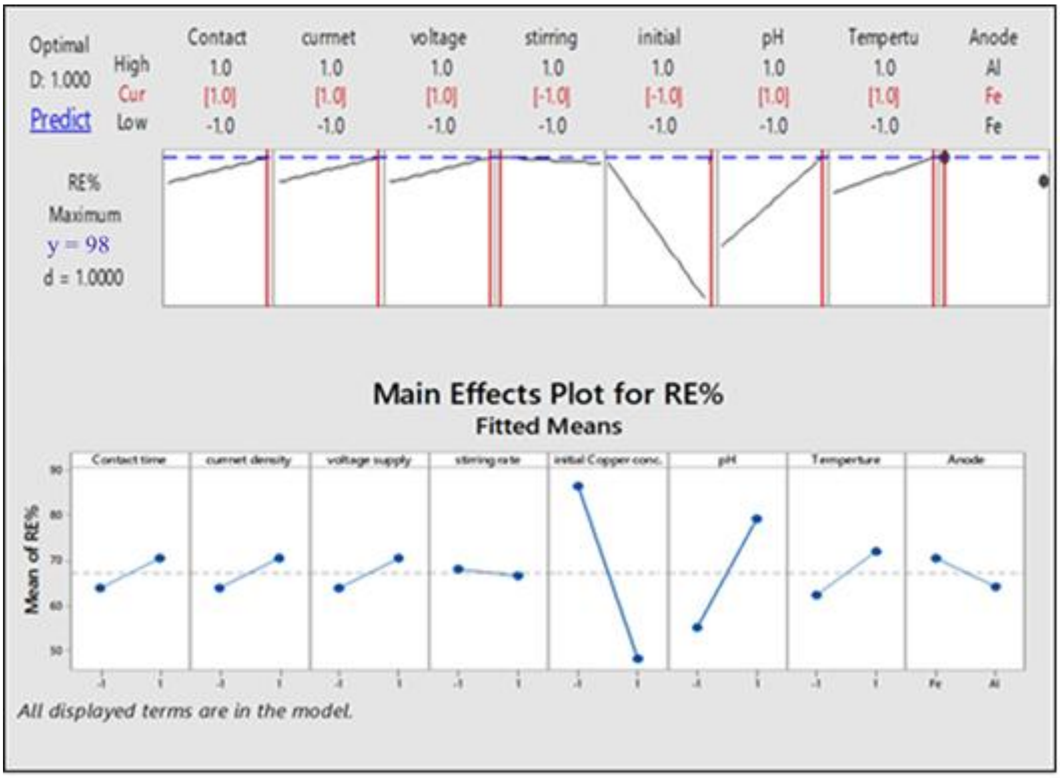

Figure 4-2 Optimum conditions for electrocoagulation reaction for removal of copper from simulated waste water.

Researchers have conducted many experiments on electrocoagulation to investigate the effect of solutions pH on the general mechanism of the processing (Chen et al., 2000). The wastewater pH is always taken into account while choosing the coagulation method (Cañizares et al., 2009). Optimal removing efficiency is achieved at an appropriate pH level for a given contaminant, and precipitation starts at this pH. When the pH is changed from its optimal magnitude, its removing efficiency diminishes. As shown in the three-dimensional graphs (Figures 4-3, and 4-4), the greatest efficiency is attained at neutral pH spanning from 6 to 8, whereas removing efficiency is almost the same at very acidic, that seems to be, pH less than 5, and extremely basic, such that, pH more than 9. However the pH does not stay constant during the process, it does change over time.

Experiments have been carried out as per PBD at different beginning amounts ranging from 100 to 400 mg/L to investigate the influence of the initial Cu (II) amount. Figure 4 shows that lower beginning amounts resulted in poorer removing efficiency; nevertheless, when the initial amount was decreased, the removing efficiency decreased . However, this increase was just temporary, since the efficiency decreased after a certain point of initial focus. This might be owing to inadequate quantities of flocs being generated for Cu (II) adsorption at extremely high starting amounts.

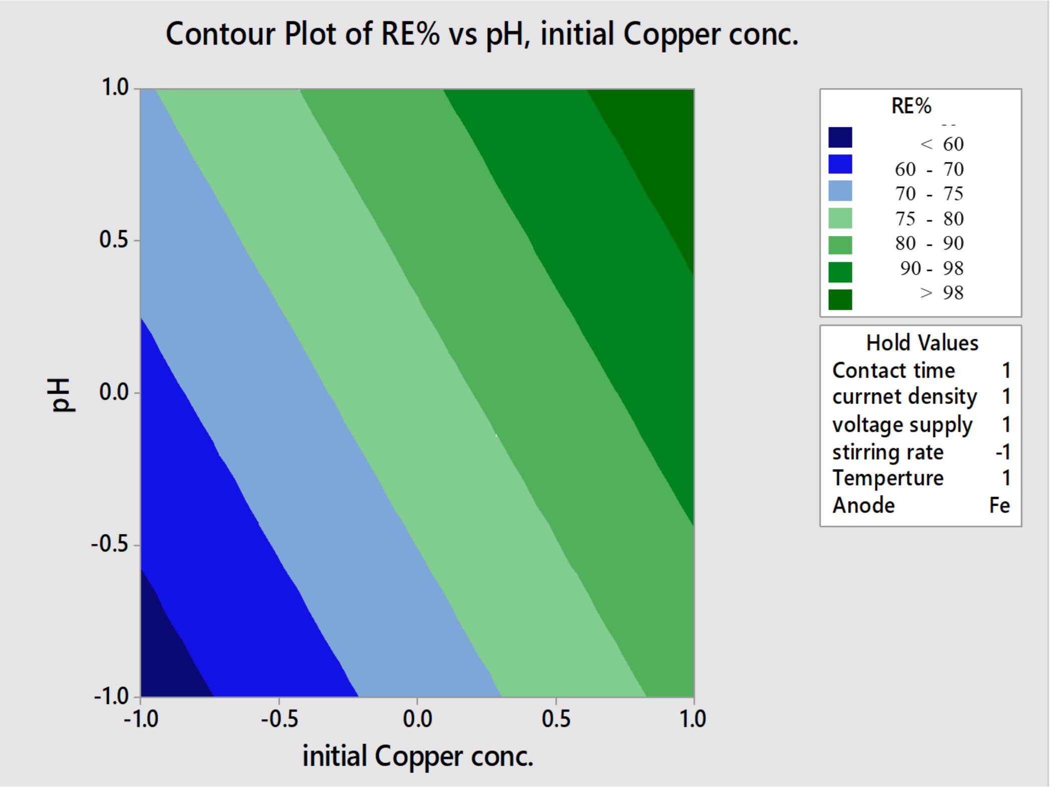

Figure 4-3. Contour chart for the impact of initial copper concentration and solution pH by using Fe as the anode.

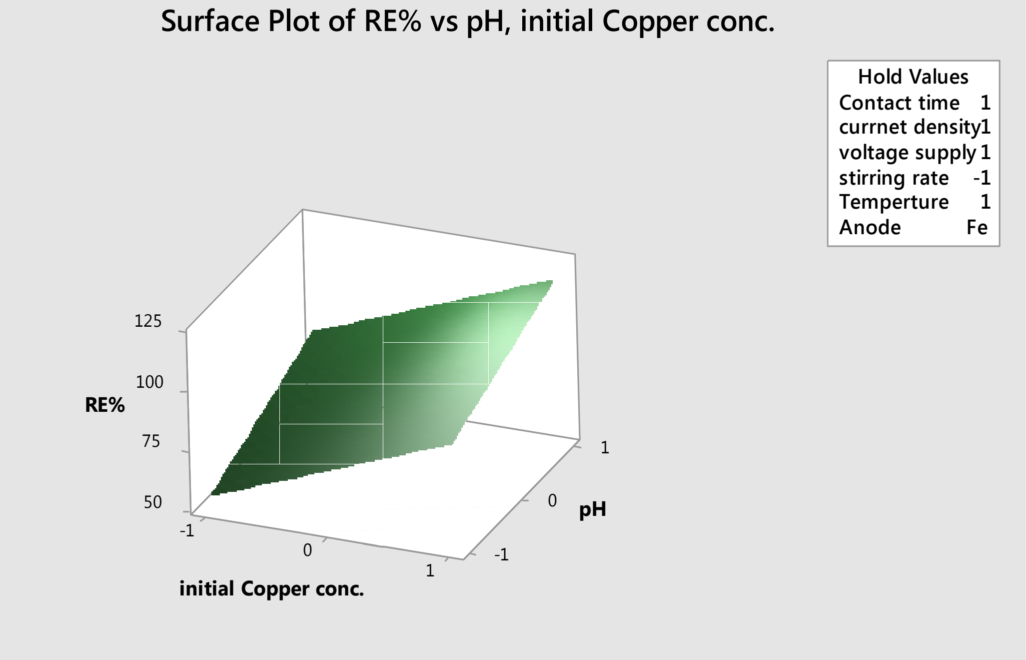

Figure 4-4. Response surface plot for the impact of initial copper concentration and solution pH by using Fe as the anode.

The models become created based on experimental evidence and demonstrated to be true at a 95 percent confidence interval by both statistical tests and hypotheses, providing some degree of confidence depending on the facts acquired from these plots. These graphs allow us to analyze further and appreciate the impact on the reactions in this analysis of the independent Variables of concern (initial concentration, pH, temperature).

The response surface contour and surface response diagrams demonstrating the impact of pH applied initial concentration, and temperature on the removing efficacies of Coppers depending on 12 experimental are seen in figures (4-5) to (4-6). Except for great amounts, which tend to drop for a period leading to a shortage of adequate sites on the surface of the adsorbent materials to obtain a relatively great removing proportion, the great efficiency response of removing along the time of electrolysis for all magnitudes of the initial amounts of copper. The same behavior for changing the magnitude of removing efficiency with pH throughout every experiment, in which it is clear that this response varies depending on the magnitude of the, which is associated to the release of hydroxyl ions from the cathodes and aluminum ions from the anodes as a natural result of the continuous flow of electric current thru the electrodes, as mentioned by (Bayar et al., 2013). The magnitude of the removing efficiency response will be affected by the production of adsorbent material on the other hand, and the changes in the pH magnitude on the other side.

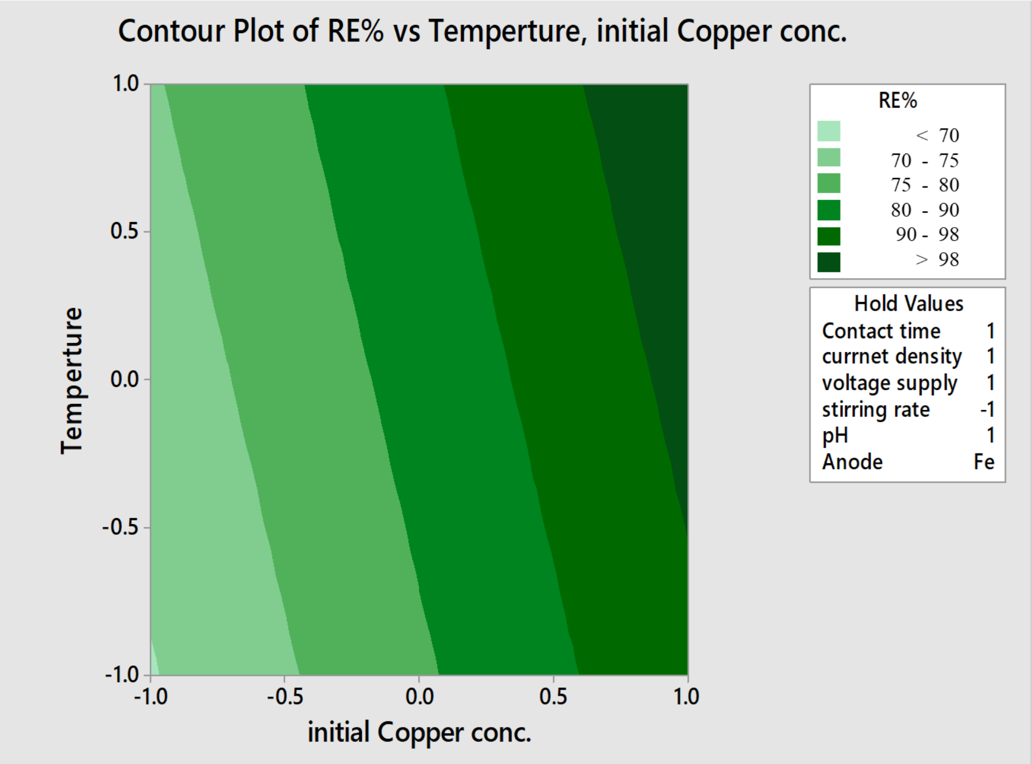

Figure 4-5- Response surface plot for the impact of initial copper concentration and reaction temperature by using Fe as the anode.

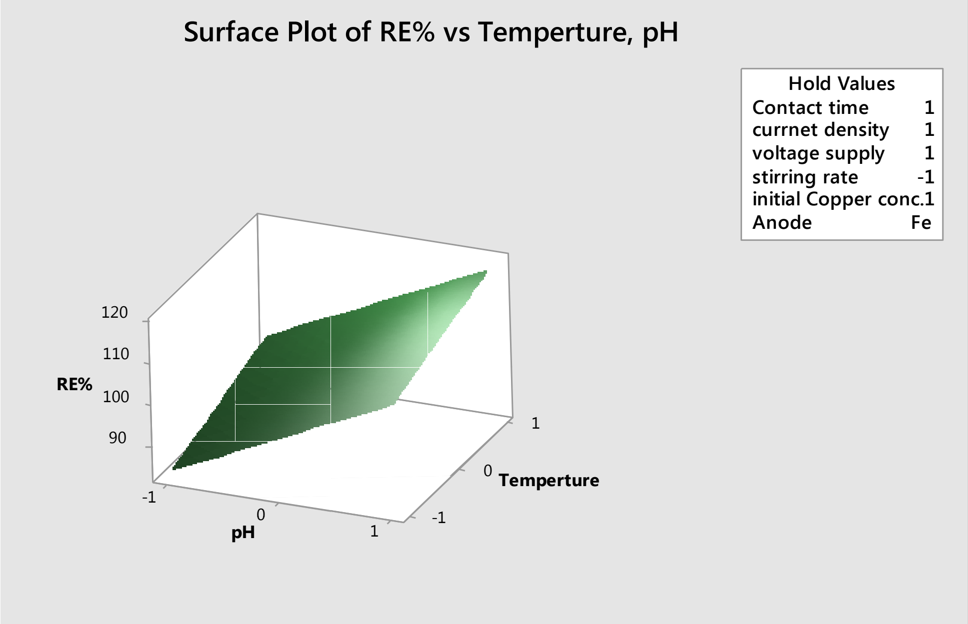

Figure 4-6. Response surface plot for the impact of initial copper concentration and reaction temperature by using Fe as an anode.

4.3. Box-Behnken Design (BBD)

For studying the effects of studied variables more deeply it took the first three variables, and these variables were conducted by the Box-Behnken so that we know their study extensively.

Table 4.2: Experiment Details and Consequences for Behnken Box System (BBD)

Run	Temperature	pH	Initial Conc.	Actual Removal efficiency of Cu%
	T	pH	C	
1	50	3	200	**97**
2	50	3	500	**83**
3	50	11	200	**40**
4	50	11	500	**25**
5	40	7	200	**60**
6	40	7	500	**53**
7	60	7	200	**82**
8	60	7	500	**63**
9	40	3	350	**88**
10	40	11	350	**26**
11	60	3	350	**90**
12	60	11	350	**33**
13	50	7	350	**74**
14	50	7	350	**74**
15	50	7	350	**74**

4.3.1. Statistical Analysis and Models' Fitting

Depending on the experiment design, the results presented in Table 2 are the experiment outcomes. The variance analysis for all the responses modeled that included Cu removing efficiency has been illustrated in Table 3. As identified in the variance analysis table at the 5 % significance level, the response models developed have been evaluated with all the necessary probability and statistical tests. A possibility magnitude (p-magnitude) < 0.05 indicates that a model is statistically effective in predicting response. The model's p-value 0 has arrived at Cu removal. This ensures that all models in their predictions were very significant. The model has been looped many times for each model developed to eliminate the insignificant terms until a final refined model has been developed in which all the terms were significant depending on p-value <0.05.

$$RE\% = -92.1 + 0.3208\,c + 3.78\,PH + 4.67\,T - 0.000633\,c*c - 0.7344\,PH*PH - 0.0525\,T*T - 0.00250\,c*PH + 0.003000\,c*T - 0.0000\,PH*T \quad (4.2)$$

Table (4.3) analyzing of difference table (ANOVA) for Cu removing

Sources	DF	Adj-SS	Adj-MS	F-magnitude	P-magnitude
Models	9	8464.83	940.54	209.01	0.000
Linear	3	7160.50	2386.83	530.41	0.000
C	1	18.00	18.00	4.00	0.102
PH	1	6962.00	6962.00	1547.11	0.000
T	1	180.50	180.50	40.11	0.001
Square	3	1214.33	404.78	89.95	0.000
C^2	1	749.77	749.77	166.62	0.000
pH^2	1	509.77	509.77	113.28	0.000
T^2	1	101.77	101.77	22.62	0.005
2-Way Interaction	3	90.00	30.00	6.67	0.034

Sources	DF	Adj-SS	Adj-MS	F-magnitude	P-magnitude
C × pH	1	9.00	9.00	2.00	0.216
C × T	1	81.00	81.00	18.00	0.008
T × pH	1	0.00	0.00	0.00	1.000
Error	5	22.50	4.50		
Lack-of-Fit	3	22.50	7.50	*	*
Pureness Error	2	0.00	0.00		
Sum	14	8487.33			

The coefficient of the correlation model is obtainable in Table 4 with an R^2 magnitude of 99.73% arrived at for Cu removing. Although R^2 is considered skewed (Lucas, 2010; Zhang et al., 2014), a stronger coefficient of correlation is also used, which is less skewed and more reliable to determine the adequacy of the model named adjusted R^2.

For example, the response surface models for Cu removing has great adjusted R^2 magnitude and Cu removing is in good alignment with the respective predicted R^2, as demonstrated in Table 4.

Table 4.4: Surface reaction model with the coefficient of correlation magnitude for reaction

S	R^2	R^2 (adj)	R^2 (pred)
2.12132	99.73%	99.26%	95.76%

4.3.2. The Validations and Diagnostics of RSM Models’

As a feature used in this study, the proposed models have been analyzed statistically and also have demonstrated to be sufficient for their respective forecasts of the reactions. Such a section reviews the mathematical expectation simulations over which the simulation variance analyzing (ANOVA) relies as well as validates the accuracy of the model in terms of experimental (actual and predicted magnitudes. Figure (4.7) offer the graph for the generalization of simulation and verification for removing Cu. The model's accuracy of the model has been validated utilizing 95 percent limits of confidence.

It's important to note that model validation and diagnostics have become the final parameter used here for model prediction testing of credibility, adequacy, and accuracy of the model. And the developed model followed the requirement that validates the model to predict the dependent variable analyzed below.

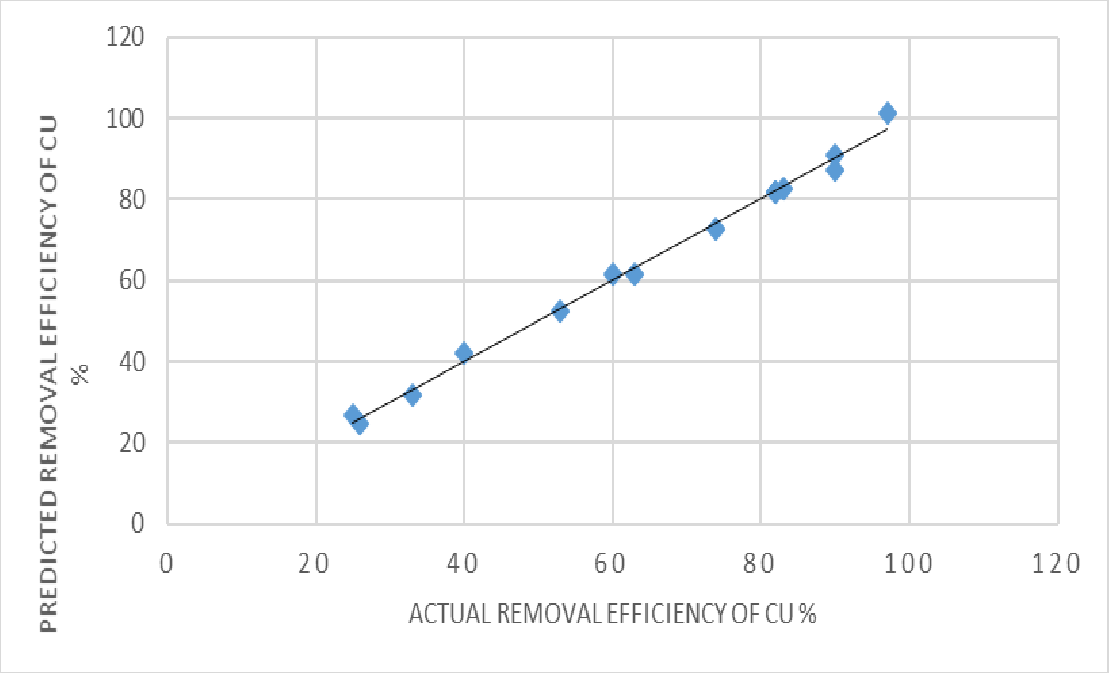

Figure 4.7: Model Validation: Actual vs Predicted removal efficiency

4.3.3. Impact of Factors on Surface Response

Surface response and scatter plots have been created depending on the response surface model produced in this segment (4.2). The model become created based on experimental evidence and demonstrated to be true at a 95 percent confidence interval by both statistical tests and hypotheses, providing some degree of confidence depending on the facts acquired from these plots. These graphs allow us to further analyze and appreciate the impact on the reaction in this analysis of the independent variables of concern (initial concentration, pH, and temperature) on the response of this study from Copper removing efficiency.

4.3.4 Removal efficiency of Coppers

The surface response and contour diagrams demonstrating the impact of pH, temperature, and initial Copper amount on the removing efficiency of Copper dependent on the fifteen experimental findings are seen in figures (4.8) to (4.13). The statistics suggest that an increase in temperature improves the removing performance, which could be attributed to an increase in the movement of Copper ions as a consequence of an increase in the temperature. With the rise in pH in purification solution, the removing efficiency of all Coppers was demonstrated to decrease, because the ions transportation of metals happened from the cathode's towards the anode as well as the ions amount of metals moved to increase with the decrease of the pH of the solution, since the propensity for ions of the metal to be adsorbed into the solution particles as well as rises as pH increase. Exchanges of ion and precipitation are other potential causes that might contribute to a reduction in removing efficiency.

The temperature and initial copper concentration were caused by decreasing of copper removal efficiency until they are reached the optimum points (temperature 50 °C and initial copper concentration 200 ppm)

(Nwabanne et al., 2018) The solution pH plays an essential function in the efficiency of copper ion removal throughout the electrocoagulation process, as the increase in solution pH leads to reduce in the removing efficiency, whatever in case of studying the interaction effect of temperature with solution pH; the removal efficiency increasing with temperature for the constant value of solution Ph (Prasetyaningrum et al., 2021).

The interaction effect of solution pH and initial copper concentration illustrated via surface response and contour chart, in which the copper removal efficiency decreased as pH solution increased as the initial copper concentration increased until it was reached to about 200 ppm (optimum point) and started decreasing and this is agreed with Prasetyaningrum report (Prasetyaningrum et al., 2021).

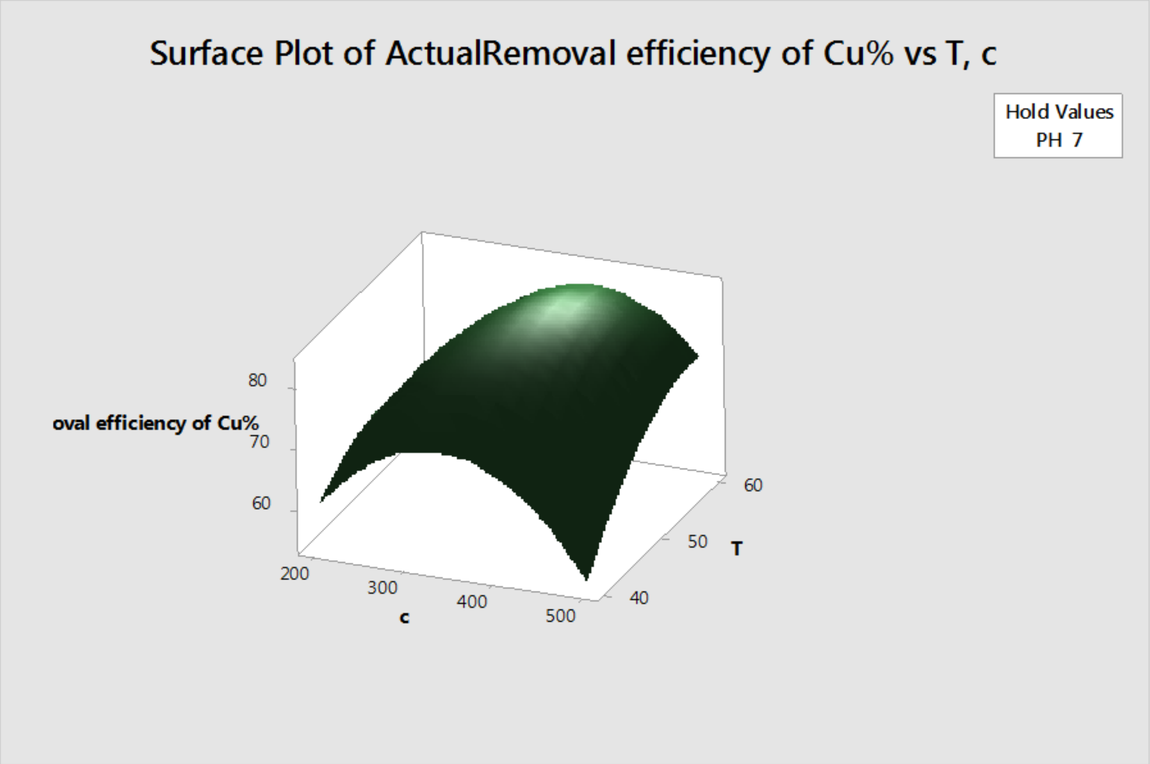

Figure (4.8) surface response diagram showing the interactive effect of initial concentration and temperature on copper removal efficiency with keeping solution pH at 7.

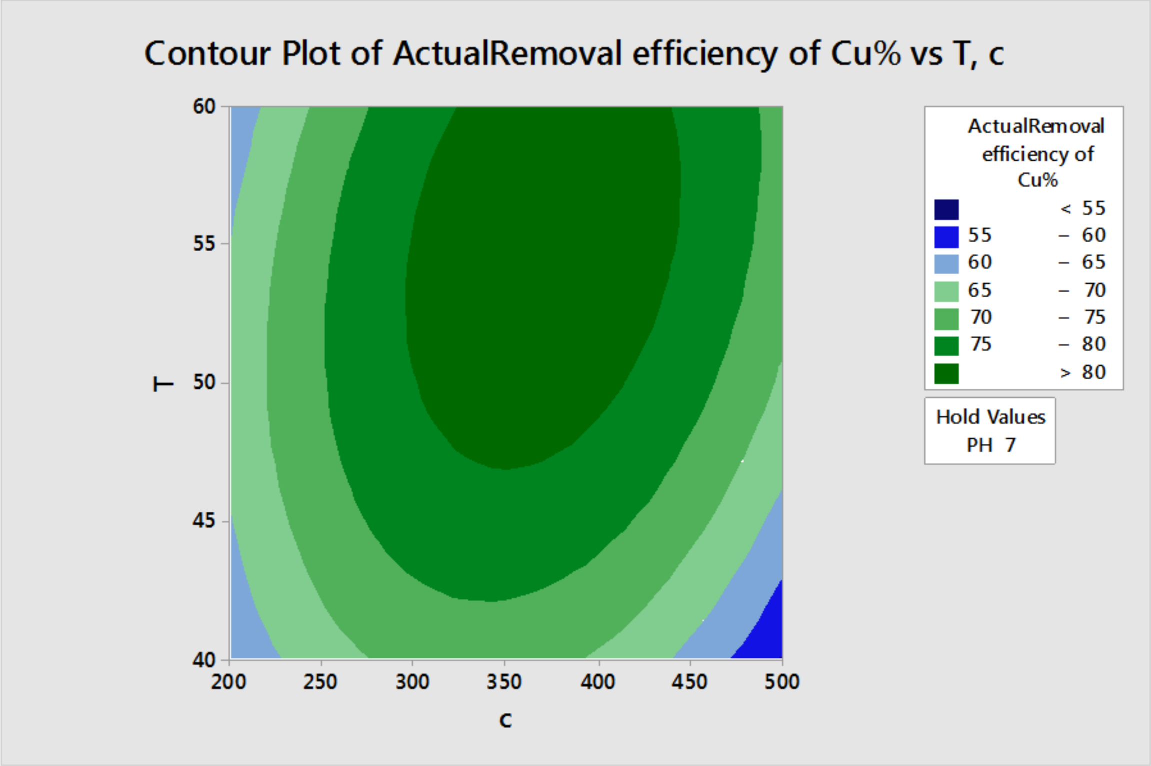

Figure (4.9) contour chart showing the interactive effect of initial concentration and temperature on copper removal efficiency with keeping solution pH at 7

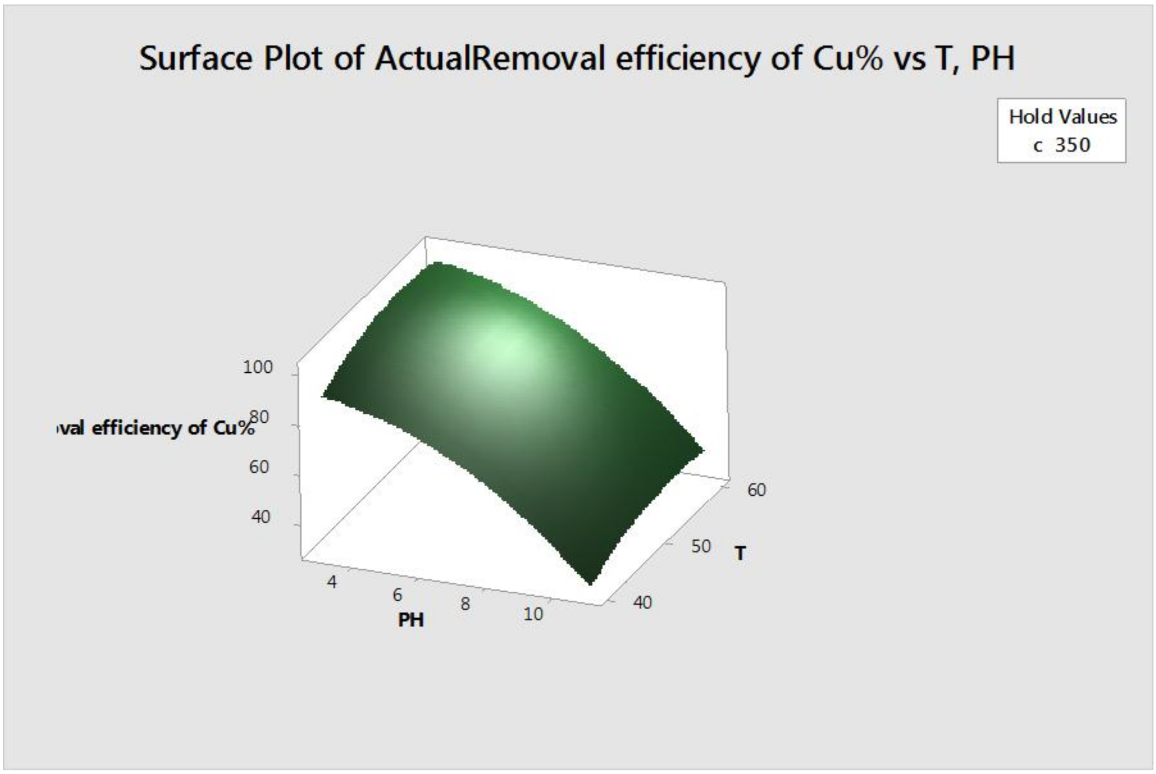

Figure (4.10) surface response diagram showing the interactive effect of solution pH and temperature on copper removal efficiency with keeping initial concentration at 350 ppm.

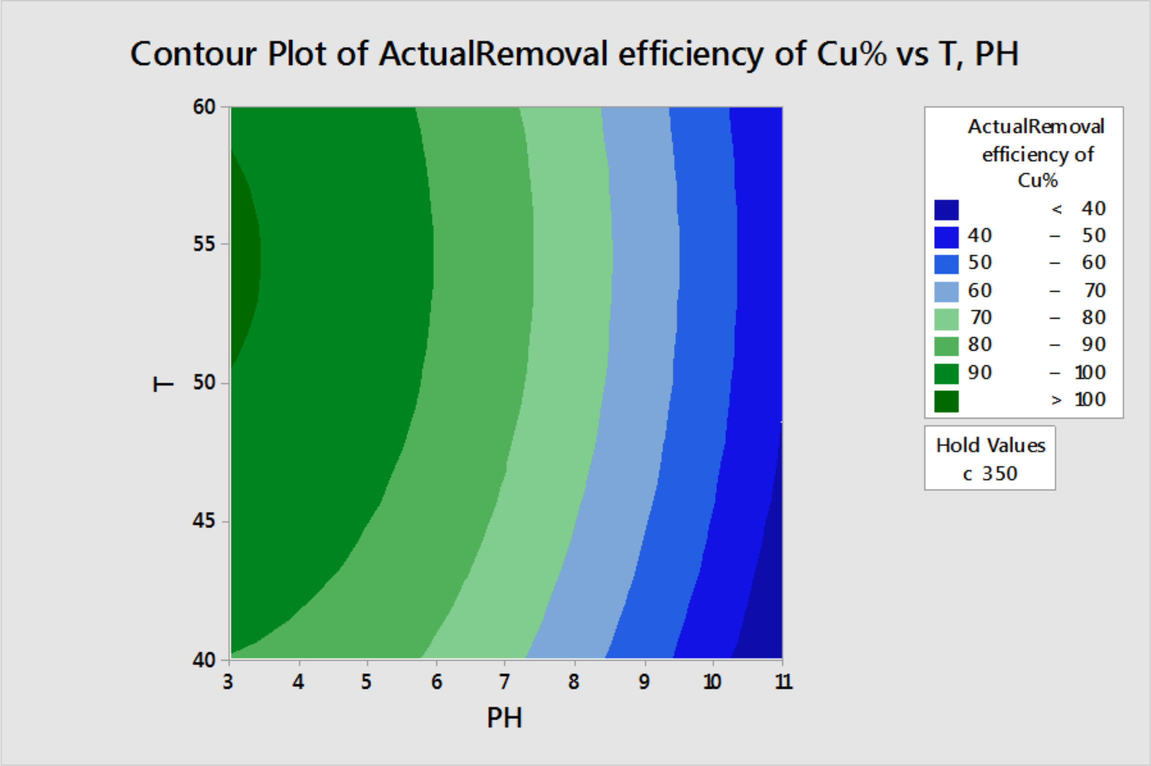

Figure (4.11) contour chart showing the interactive effect of solution pH and temperature on copper removal efficiency with keeping initial concentration at 350 ppm.

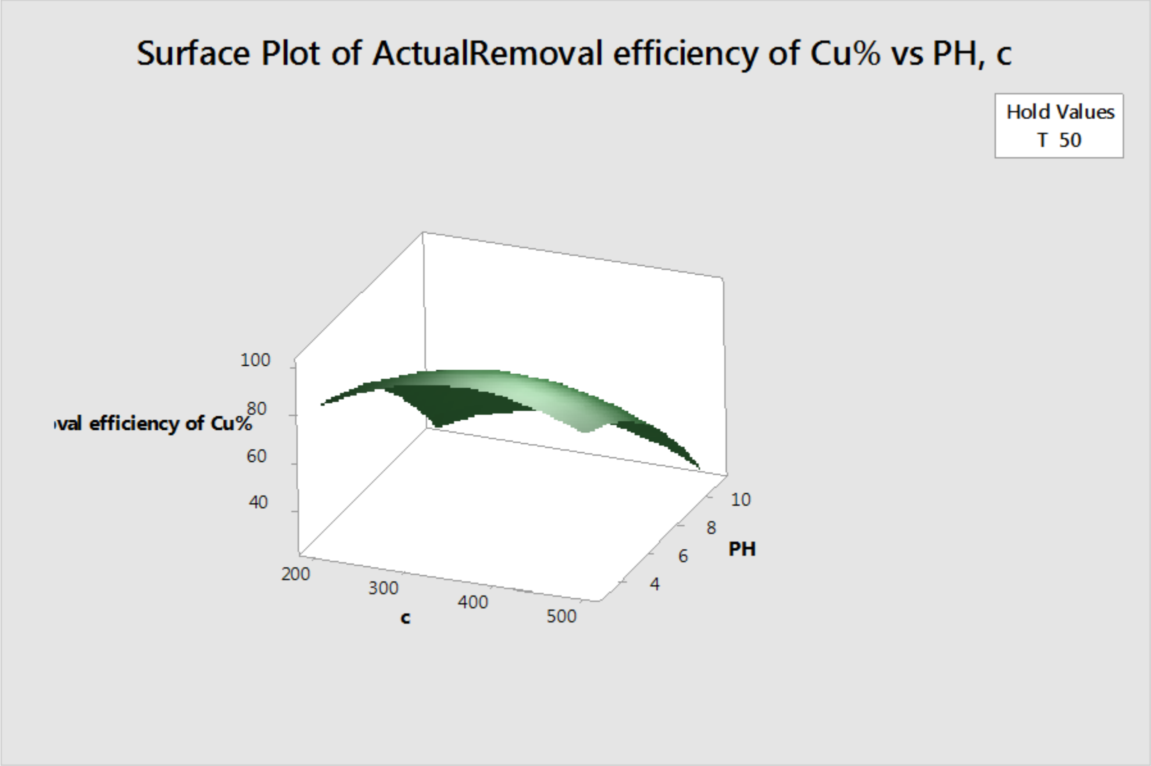

Figure (4.12) surface response diagram showing the interactive effect of solution pH and initial concentration on copper removal efficiency with keeping temperature 50 °C.

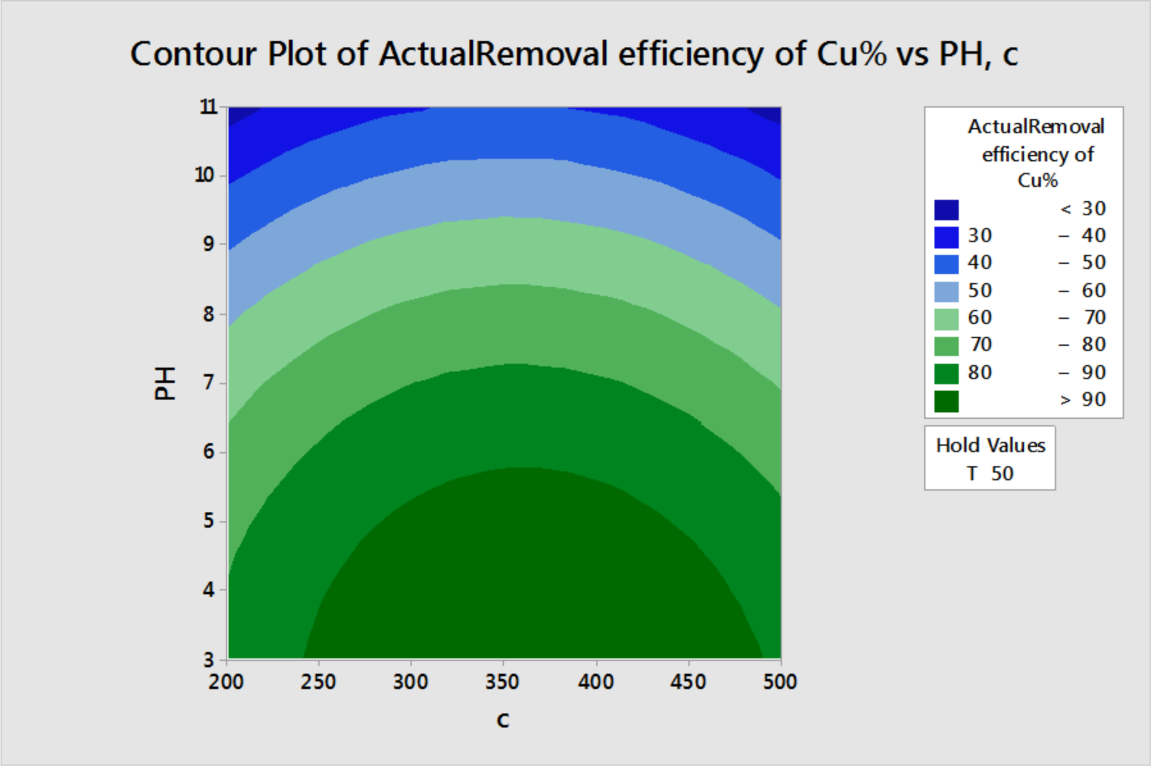

Figure (4.13) contour chart showing interactive effect of solution pH and initial concentration on copper removal efficiency with keeping temperature 50 °C.

4.4 SEC study

The SEC values were calculated according to the equation

$$\mathrm{SEC} = \frac{\mathrm{Pt}}{\mathrm{V}(\mathrm{C_0} - \mathrm{C_f})} \qquad (4-3)$$

Energy usage and operational factors are linked by an empirical numerical relationship:

$$\begin{aligned}\text{specific Energy Consumption} \; = \; & -56.63 + 0.18267\, c - 0.0047\, pH \qquad (4\text{-}4)\\ & + 1.1386\, T - 0.000209\, c*c\\ & - 0.20906\, pH*pH - 0.013325\, T*T\\ & - 0.000250\, c*pH - 0.000542\, c*T\\ & + 0.06931\, pH*T\end{aligned}$$

Table (4.5) analyzing of variance table (ANOVA) for Energy usage Difference Analyzing

Sources	DF	Adj-SS	Adj-MS	F-magnitude	P- magnitude
Models	9	194.230	21.5811	1908.99	0.000
Linear	3	43.821	14.6069	1292.08	0.000
C	1	10.013	10.0128	885.70	0.000
pH	1	25.526	25.5255	2257.90	0.000
T	1	8.282	8.2825	732.64	0.000
Square	3	116.931	38.9771	3447.78	0.000

c*c	1	81.737	81.7367	7230.14	0.000
pH*pH	1	41.313	41.3133	3654.43	0.000
T*T	1	6.556	6.5559	579.91	0.000
2-Way Interaction	3	33.478	11.1592	987.10	0.000
c*pH	1	0.090	0.0900	7.96	0.037
c*T	1	2.641	2.6406	233.58	0.000
pH*T	1	30.747	30.7470	2719.77	0.000
Error	5	0.057	0.0113		
Lack-of-Fit	3	0.057	0.0188	*	*
Pureness Error	2	0.000	0.0000		
Sum	14	194.286			

The coefficients of correlation model are as obtainable in Table 6 with R^2 0.9997 Energy consumption model

Table 4.6: Surface reaction model with the coefficient of correlation for reaction

S	R^2	R^2 (adj)	R^2 (pred)
0.106325	99.97%	99.92%	99.53%

Depending on formula 4-3, Table 7 describes the acquired findings of energy usage response (YENCR) for each of the intended experiments. The coefficient of regression (R2) is 0.9997, and the number of repetitions has reached its limit. Figure 4-14 depicts the relationship between predicted and realized energy usage response magnitudes.

Table 4.7 Box-Behnken design matrixes.

run	**studied variables**			
	Initial concentration	pH	temperature	Energy consumption (kWh/m3)
1	200	3	50	0.56
2	500	3	50	1.32
3	200	11	50	0.82
4	500	11	50	1.79
5	200	7	40	1
6	500	7	40	6.1
7	200	7	60	1.56
8	500	7	60	4.1
9	350	3	40	1.25
10	350	11	40	2.7
11	350	3	60	1.54
12	350	11	60	13.1
13	350	7	50	9.2
14	350	7	50	9.2
15	350	7	50	9.2

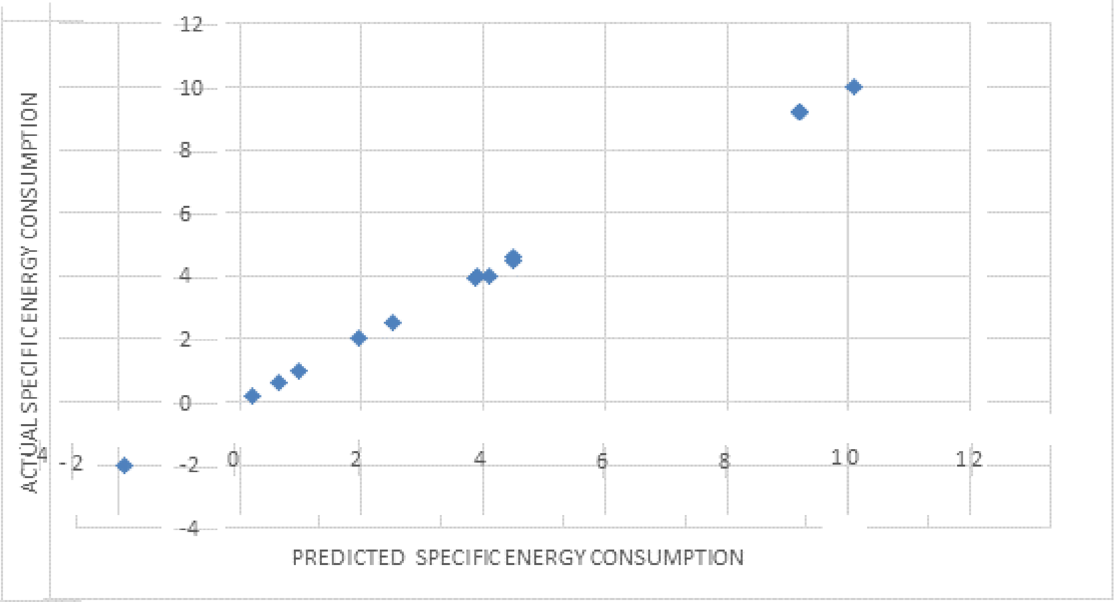

Figure 4-14 . Actual and predicted plot SEC

4.4.1. SEC with temperature, initial concentration, and pH

Figures (4.15), (4.16), (4.17), (4.18), (4.19), and (4.20) demonstrate the variance of the three variables with energy consumption. the energy consumption increases with the increase in the initial concentration of Coppers in simulated wastewater due to an increase in the current generated throughout the experiment due to an increase in water electrical conductivity and this was agreed with (Bazrafshan et al., 2015). As for the temperature, the used-up energy increases with the increase in the temperature. where the greater the temperature, the greater the energy used up, and this was agreed with (Körbahti & Turan, 2016). In terms of pH, the energy used up is large at small pH magnitudes and in the use of low amounts of Coppers, as well as the use of low temperature, while the energy used up increases with an increase in the pH at the use of great amounts of Coppers, as well as at great temperature and this was agreed with (Dermentzis et al., 2011).

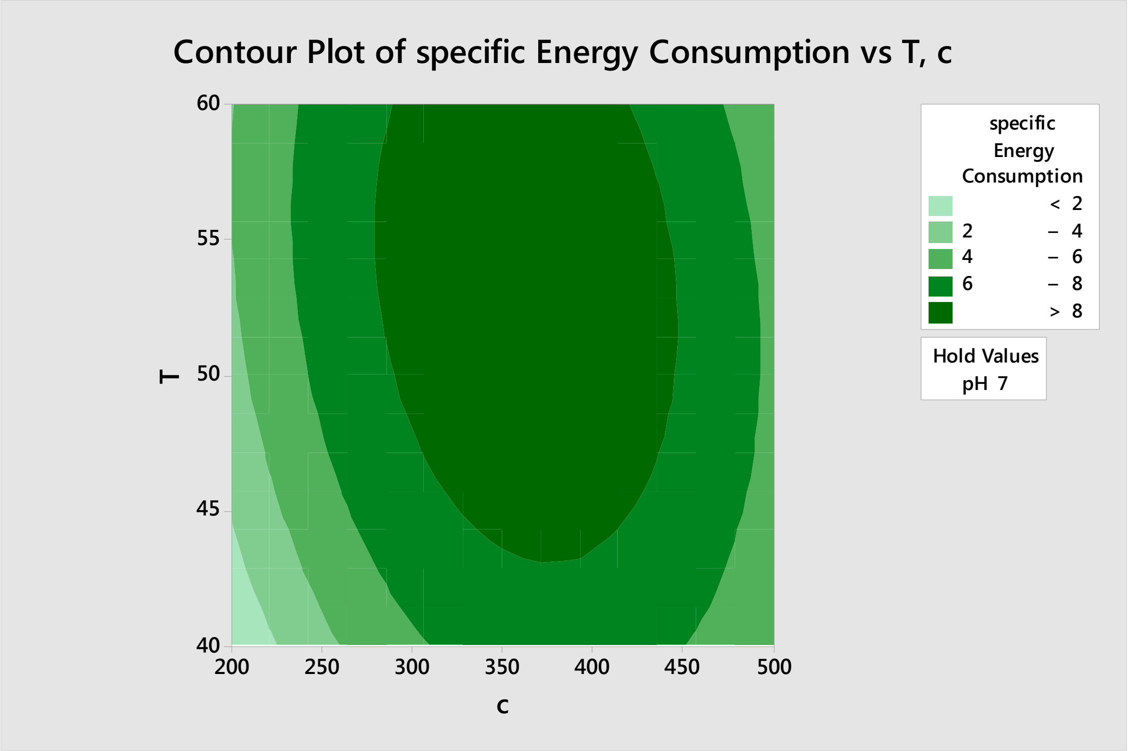

Figure (4.15) contour chart showing interactive effect of initial concentration and temperature on energy consumption with keeping solution pH at 7

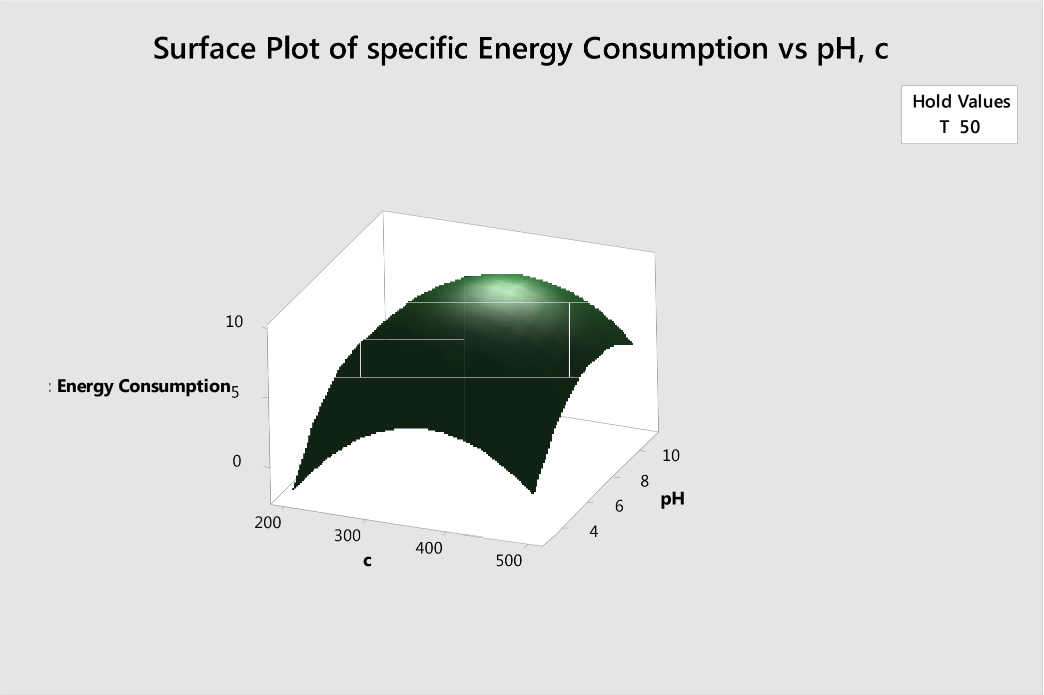

Figure (4.16) surface response diagram showing interactive effect of solution pH and initial concentration on energy consumption with keeping temperature 50 °C.

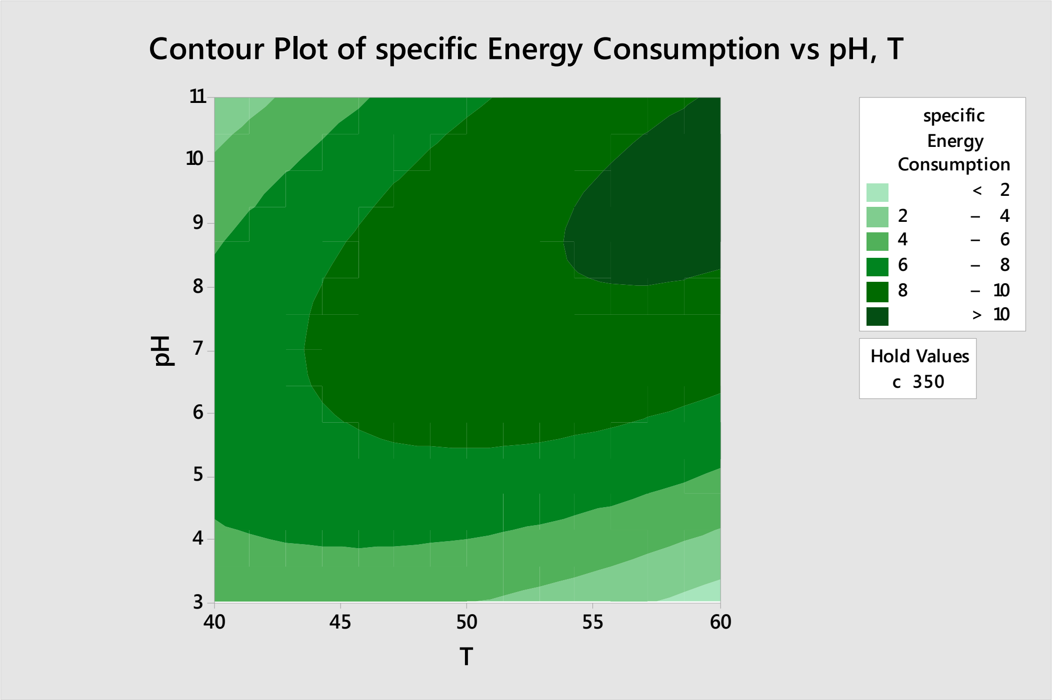

Figure (4.17) contour chart showing the interactive effect of solution pH and temperature on energy consumption with keeping initial concentration at 350 ppm.

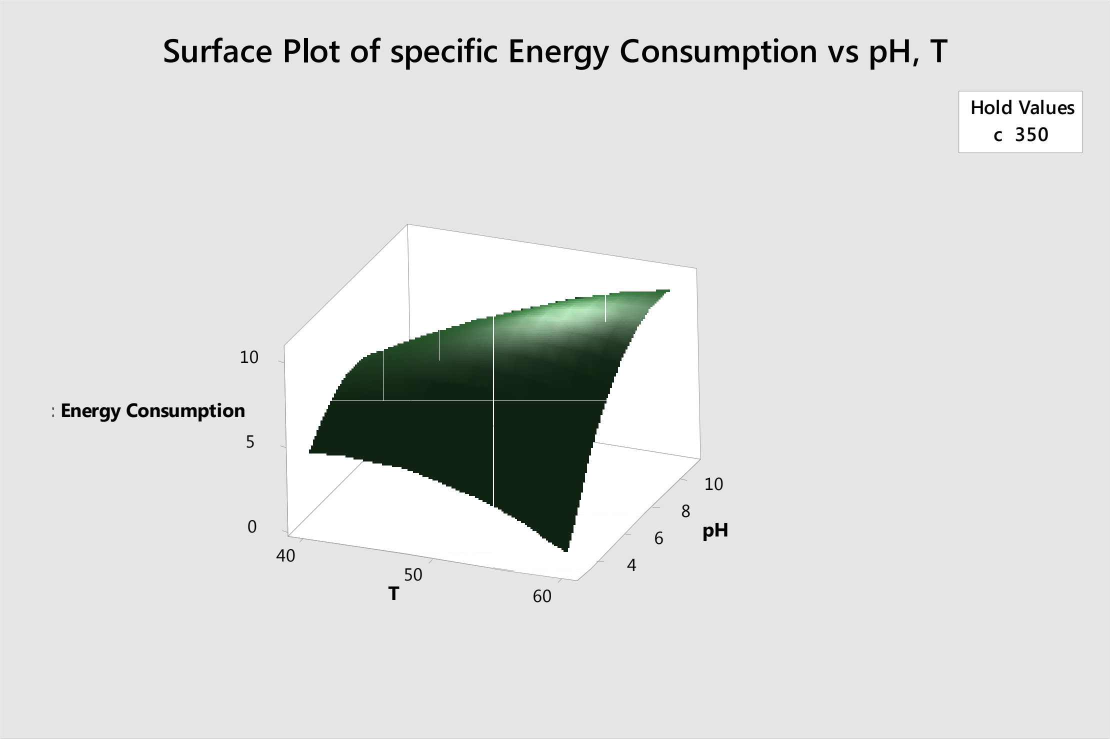

Figure (4.18) surface response diagram showing interactive effect of solution pH and temperature on copper removal efficiency with keeping initial concentration at 350 ppm.

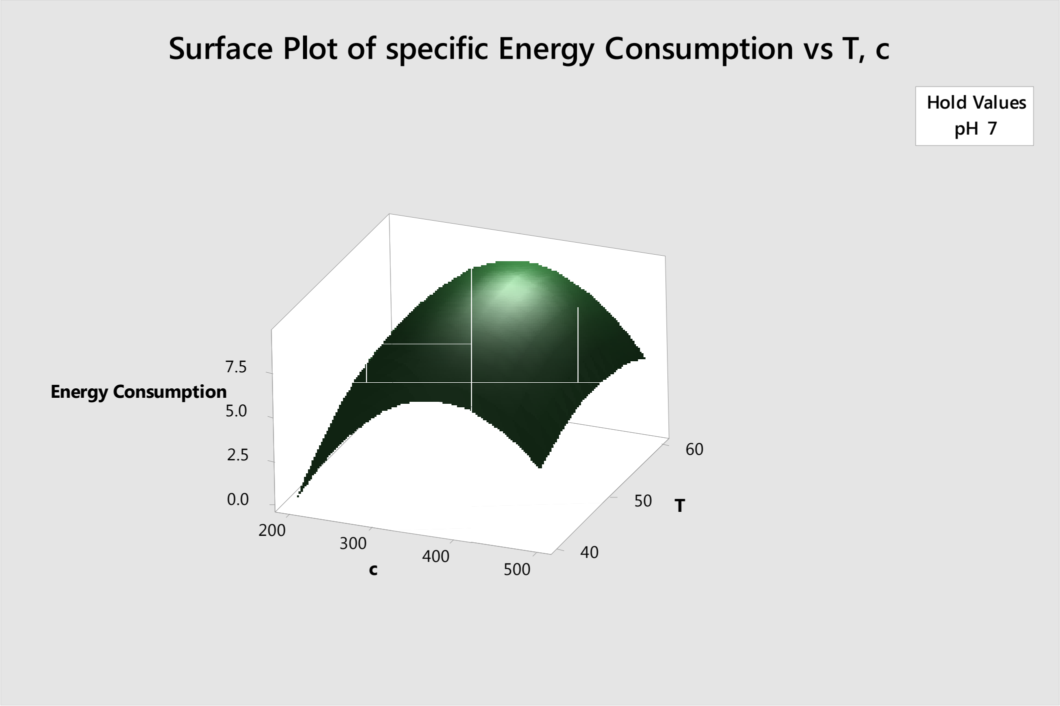

Figure (4.19) surface response diagram showing interactive effect of initial concentration and temperature on energy consumption with keeping solution pH at 7.

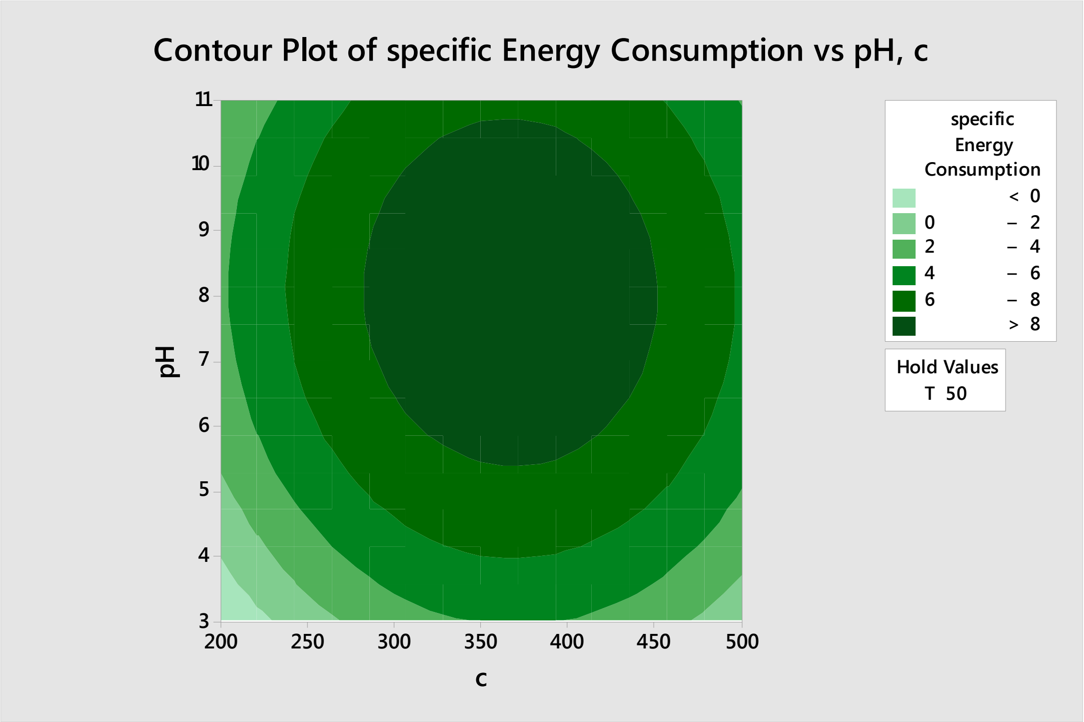

Figure (4.20) contour chart showing interactive effect of solution pH and initial concentration on energy consumption with keeping temperature 50 °C.

4.5. Electrocoagulations Reactors thermodynamics and Kinetic

The rate of reaction parameters of the electrocoagulation processing is evaluated using a kinetic model for the electrocoagulation reactors. The following is the typical kinetic rate formula for describing the rate of elimination of a Copper content from modeled wastewater (Levenspiel, 1998):

$$\frac{d[C_{At}]}{dt} = -kC_{At}^{n} \qquad (4.5)$$

Where C_A is the pollutant amount, k is reactions rating constant, t is contacting time and n is the order of the reaction. The kinetic equation for case of zero, first and second orders reaction was listed in table 8

Table 4.8- Solution of equation for n = 0, 1 and, 2.

Reaction order	Kinetic rate reaction	Reaction rate constant unit
0	$C_{A0} - C_{At} = k_0 t$ (4.6)	(mol/L) sec.$^{-1}$
1	$-\ln\frac{C_{At}}{C_{A0}} = k_1 t$ (4.7)	Sec.$^{-1}$
2	$\frac{1}{C_{At}} - \frac{1}{C_{A0}} = k_2 t$ (4.8)	[(mol/L) sec.$^{-1}$]$^{-1}$

To estimate the kinetics parameters, measuring the change of pollutant concentration with time while all other variables kept constant at optimum values, followed by plotting concentration difference (C_{A0}-C_A), ln (C_{A0}/C_A), and 1/ C_A versus time for zero, first and second order of reaction respectively, The plot that gives the best straight line will represent the order of the reaction. Figures 4-21, 4-22, and 4-23 show the reaction order testing (Alwan et al., 2020).

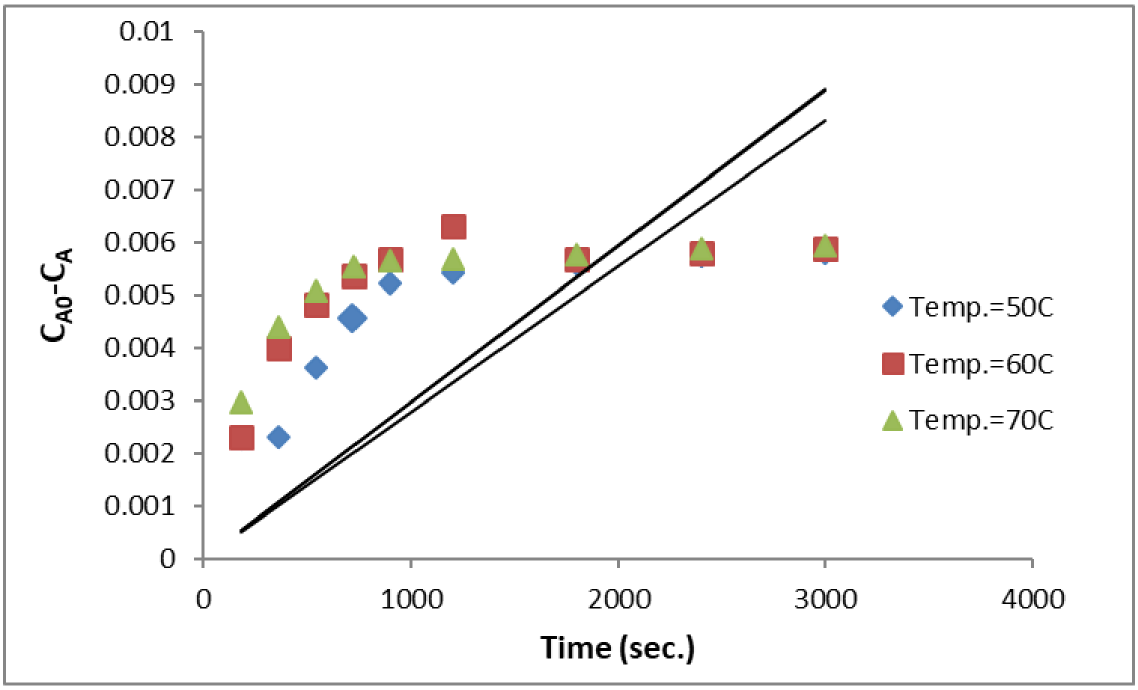

Figure 4.21- Concentration difference versus time for zero-order reaction representing applying of zero-order kinetics equation (C_{A0}-C_A=k_0t).

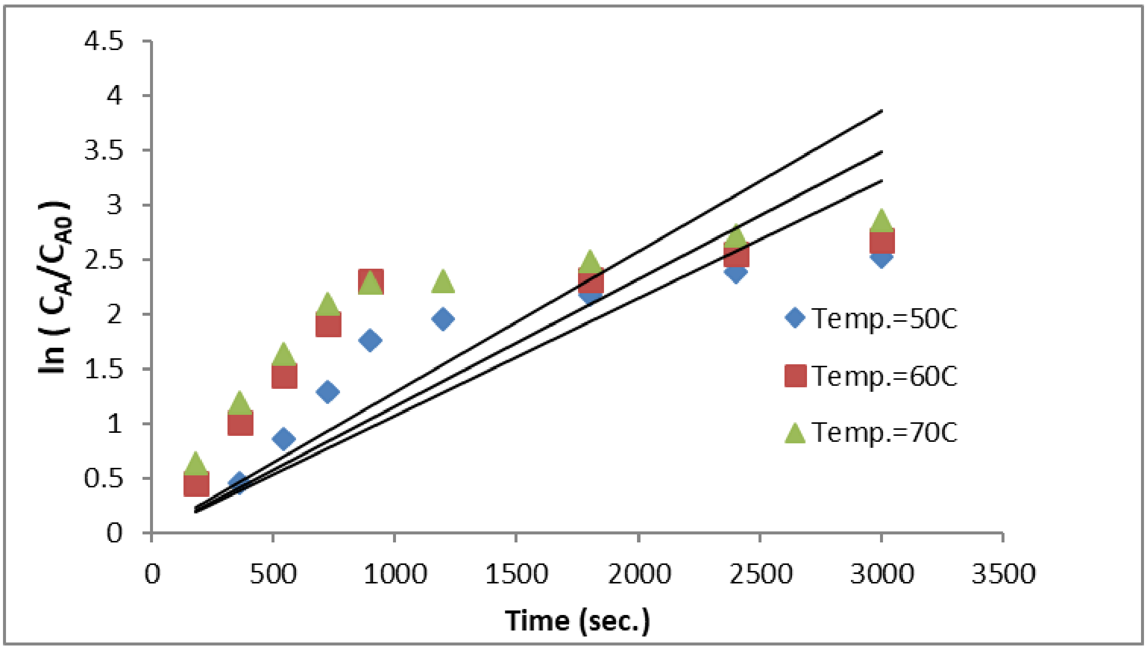

Figure 4.22 - Concentration difference versus time for zero-order reaction representing applying of first-order kinetics equation ($-\ln\frac{C_{At}}{C_{A0}} = k_1 t$).

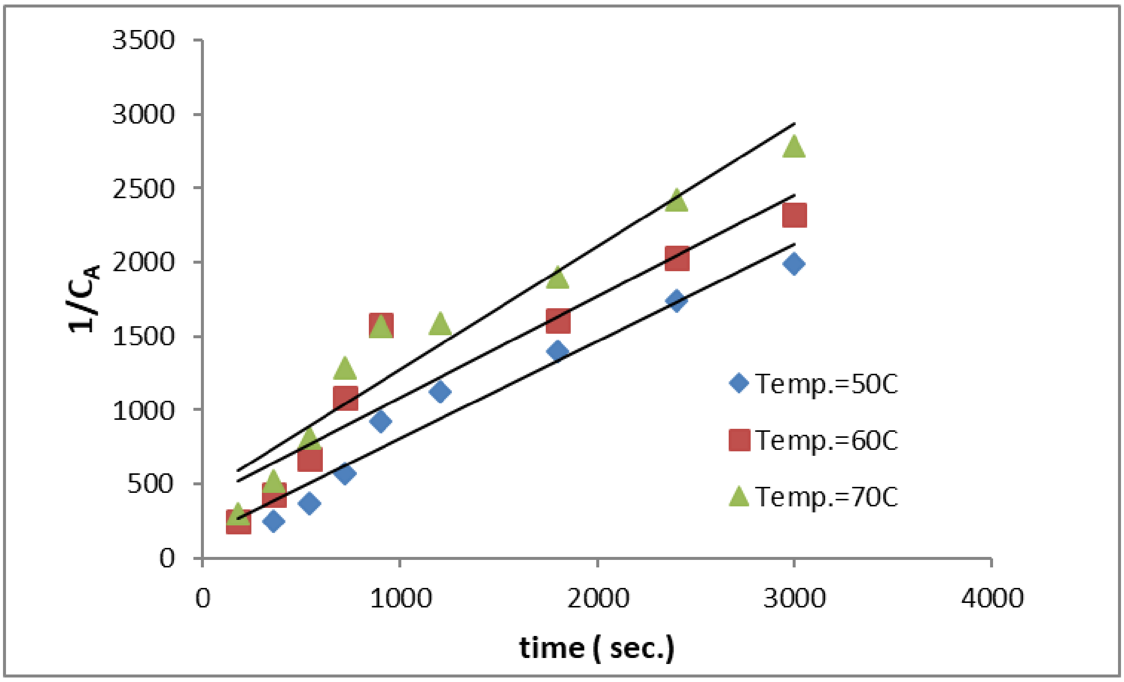

Figure 4.23 - Concentration difference versus time for zero order reaction representing applying of second order kinetics equation ($\frac{1}{C_{At}} - \frac{1}{C_{A0}} = k_2 t$).

As seen from above figures , it was noted that the concentration-time data for electrocoagulation reaction obey second order reaction; the R^2 for fitted data with zero order are -1.174 , -3.869 and -7.528 at 50 , 60,and 70 °C respectively, while its values are 0.605 , 0.033 and 0369 at 50 , 60,and 70 °C respectively , and R^2 vales are 0.963 , 0.875 and 0.931 at 50 , 60,and 70 °C respectively , the slope for straight line represented reaction rate constant (k) are 0.6572 , 0.6829 and 0.8308 [(mol/L) $sec^{-1}]^{-1}$ at 50 , 60 , and 70 °C respectively.

Table 4.9 Constant rates magnitudes with temp with correlation parameter R^2

Temp (ºC)	Temp (ºK)	Constant Rates ([(mol/L) $sec^{-1}]^{-1}$)	R^2
50	323	0.6572	0.963
60	333	0.6829	0.875
70	343	0.8308	0.931

The activation energies (Ea) for electrocoagulation reaction estimated according to Arrhenius equation

$$k = A\exp(-E_a/RT) \qquad (4.9)$$

The linear formula for the Arrhenius equation is as below:

$$\ln(k) = \ln(A) - (E_a/RT) \qquad (4.10)$$

Based on obtained reaction rate (k) values from Figure and by plotting (ln k) versus (1/ T) as shown in Fig4.10, the straight-line slope (Ea/R); so from figure 4-24 apparent activation energy Ea can be estimated; thus apparent activation energy value is 10.719 kJ/mol.

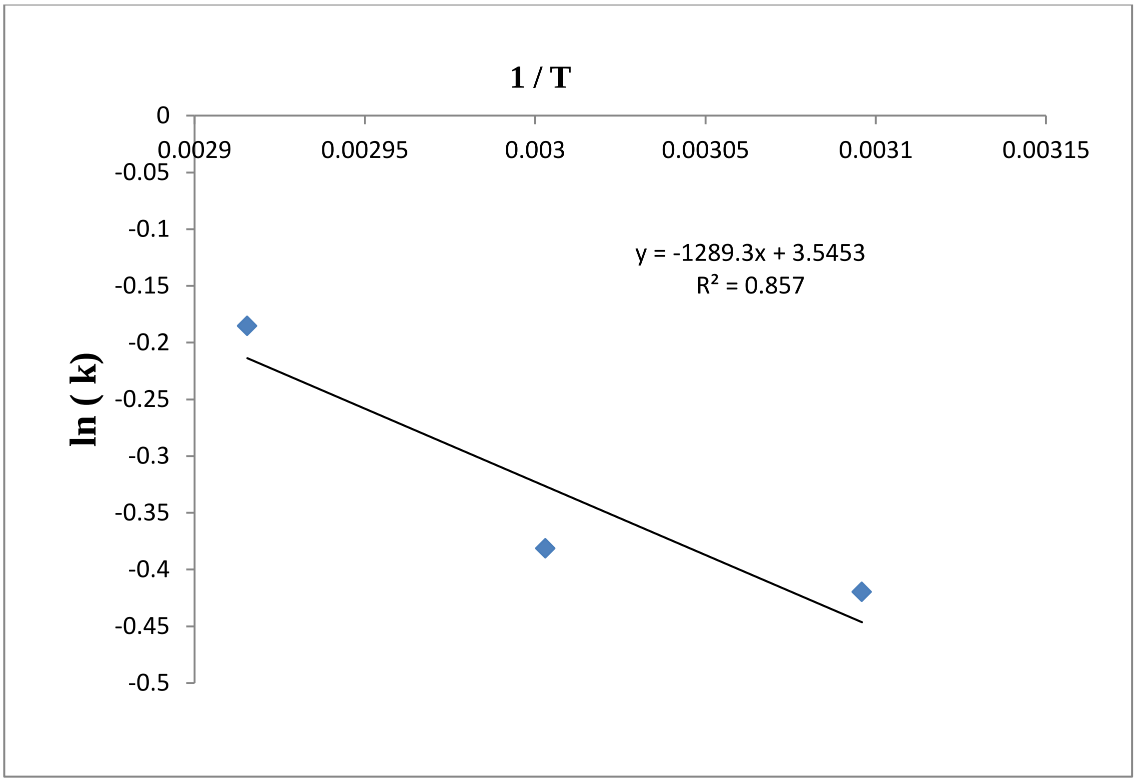

Figure 4.24. Impact of temp on reaction constant rates according to Arrhenius equation

Thermodynamics parameters electrocoagulation reactions could be expected as followed; the enthalpy changes (ΔH) has been determined from the energy of activation (Rezaei & Nezamzadeh-Ejhieha, 2020):

$$\Delta H = E_a + RT \qquad 4.11$$

After that determination of changes in entropy (ΔS) by:

$$\ln\left[\frac{k}{T}\right] = \ln\left(\frac{K_B}{h}\right) + \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right) \qquad 4.12$$

In which constant of Plank is h =(66.26 $\times 10^{-35}$ J sec.) and constant of Boltzmann is (K_B)=(138.07$\times 10^{-25}$ J/K) respectively. Therefore, scheme of ln(k/T) vs (ΔH/RT) could be recognized and straighten line has been gained. The intercept of obtained straight line magnitude help for change of entropy estimation. Eventually, the reactions of free energy Gibbs (ΔG) magnitude has been expected by

$$\Delta G = \Delta H - T\Delta S \qquad 4.13$$

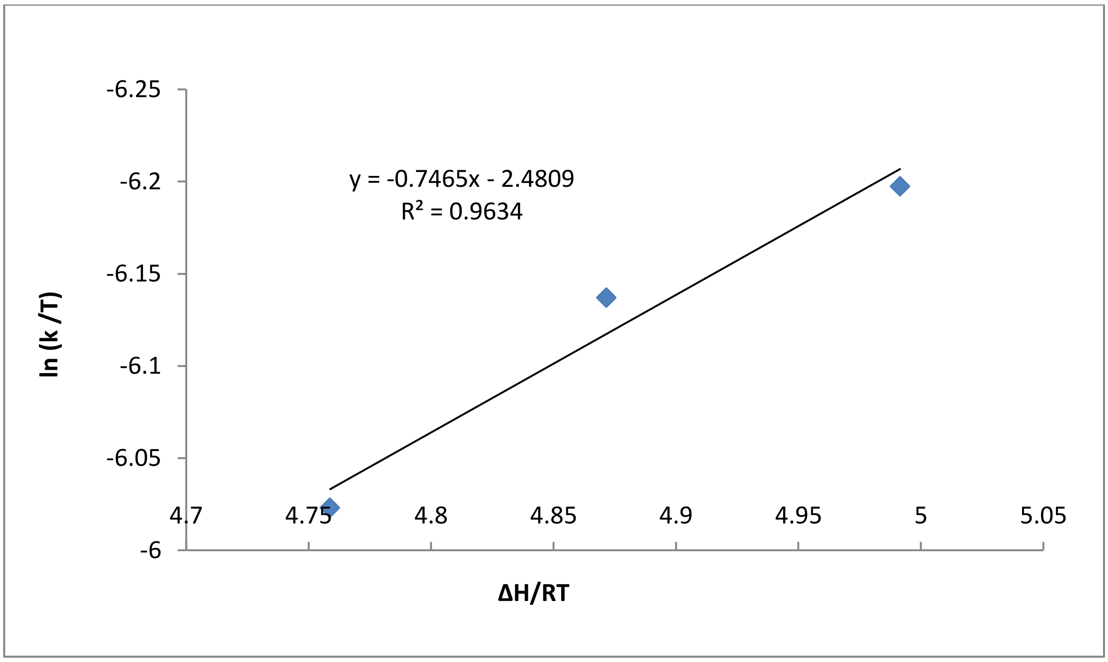

Figure 4.25. Classic curve utilized for an estimate of entropy activation for reactions EC

Table 4.10-kintecs and thermodynamics parameters for electrocoagulation reaction

T (K)	k	Ea ($kJ.mol^{-1}$)	ΔH ($kJ.mol^{-1}$)	ΔS ($kJ.mol^{-1}$)	ΔG ($kJ.mol^{-1}$)
323	0.6572	10.719	13.404	-0.218	13.475
333	0.6829		13.488		13.560
343	0.8308		13.571		13.645

All thermodynamics parameters data are summarized in the table, the copper removal by electrocoagulation reaction achieved by relative high positive activation energy and Gibbs free energy values, and these refer a high level of energy for transition state complex was produced. These positive values for energies confirmed that for transition state complex reaction which cannot produce at normal condition, on the other hand, the negative value for entropy energy (-0.218 kJ/mol. K) is near zero (which is relatively positive) and maybe meaning the activated complex was not much ordered of reactant (Gupta et al., 2016).

Chapter Five

Conclusions and Recommendations

Chapter Five

Conclusions and Recommendations

5.1 Introduction

The current chapter contains the thesis' main findings, as well as suggestions and research directions for future works.

5.2 Conclusions

1. copper as a pollutant was removed from wastewater by EC reaction, eight crucial variables were investigated on EC reaction and they were screened by PBD design.
2. The eight variables are reaction time, current time, voltage supply, stirring rate, initial copper concentration, solution pH reaction temperature, and type of electrode.
3. The screening results show that initial copper concentration, pH, and reaction temperature most significant variables.
4. The optimization by aim of Minitab software shows that theoretical optimum removal efficiency is 98% based on coded values for operation conditions; contact time (40 minutes), current density (3 A/cm2), voltage supply (10 volts), initial copper concentration (400 ppm), reaction temperature (70°C) with no stirring rate and using Fe as an anode.
5. For studying the effects of studied variables more deeply it took the variables that had more effect on removal efficiency and these variables were conducted by the Box-Behnken, so that we know their study extensively.
6. The surface response and contour diagrams demonstrating the impact of pH, temperature, and initial concentration of Copper on the removing efficiency of Copper are dependent on the fifteen experimental findings.

7. An increase in temperature improves the removing performance, which could be attributed to an increase in the movement of Copper ions as a consequence of an increase in the temperature.
8. the rise in pH in purification solution, the removing efficiency of all Coppers was demonstrated to decrease because the ions transportation of metals happened from the cathode's towards the anode as well as the ions amount of metals moved to increase with the decrease of the pH of the solution since the propensity for ions of the metal to be adsorbed into the solution particles as well as rises as pH increase.
9. Exchanges of ion and precipitation are other potential causes that might contribute to a reduction in removing efficiency.
10. The temperature and initial copper concentration were caused by increasing copper removal efficiency until they are reached the optimum (temperature 50 °C and initial copper concentration 350 ppm)
11. The effect of the three variables (initial concentration, temperature, and pH) on energy consumption. the energy consumption increases with the increase in the initial concentration of Coppers in simulated wastewater due to an increase in the current generated throughout the experiment due to increase in water electrical conductivity, As for the temperature, the used-up energy increases with the increase in the temperature, and in terms of pH, the energy used up is large at small pH magnitudes.
12. The kinetics and thermodynamics studies show that EC reaction obeys second-order reaction with 0.6572, 0.6829 and 0.8308 [(mol/L) sec-1]-1 at 50, 60, and 70 °C respectively, and the activation energy is 10.719 kJ / mol, while the entropy change was -0.218 kJ/mol with positive enthalpy change and Gibbs free energy change

5.3. Recommendations

Based on the conclusions arrived at the study recommended the following:

following:

1- Studying the electrocoagulation cell present on a continuous mode process.

2- Studying the effect of reaction time, current time, voltage supply, the distance between anode and cathode, stirring rate, initial copper concentration, solution pH, reaction temperature, and type of electrode on removal effectiveness of pollution from simulated wastewater

3- Studying the effect of the use of programs and designs.

Reference

Abdel-Ghani, N. T., & Elchaghaby, G. A. (2007). Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption. *International Journal of Environmental Science & Technology*, *4*(4), 451–456.

Adelaja, O. A., Amoo dkk, I. A., & Aderibigbe, A. D. (2011). Biosorption of Lead (II) ions from aqueous solution using Moringa oleifera pods. *Archives of Applied Science Research*, *3*(6), 50–60.

Ajjam, R. Z. J. and S. K. (2016). *Removal of Lead Ions from a Synthetic Waste Water by a Batch Electrocoagulation Process September* (Issue September).

Al Aji, B., Yavuz, Y., & Koparal, A. S. (2012). Electrocoagulation of heavy metals containing model wastewater using monopolar iron electrodes. *Separation and Purification Technology*, *86*, 248–254.

Al Qedra, B. (2015). *Boron removal from seawater by Hybrid Solar Photovoltaic Electrocoagulation (SPEC) Process*.

Aljaberi, F. Y. (2018). Novel method for electrocoagulation removal of lead from simulated wastewater by using concentric tubes electrodes reactor. *Desalination and Water Treatment*, *101*(July), 86–91. https://doi.org/10.5004/dwt.2018.21812

Alwan, H. H., Ali, A. A., & Makki, H. F. (2020). Optimization of Oxidative Desulfurization Reaction with Fe2O3 Catalyst Supported on Graphene Using Box-Behnken Experimental Method. *Bulletin of Chemical Reaction Engineering & Catalysis*, *15*(1), 175–185.

Avsar, Y., Kurt, U., & Gonullu, T. (2007). Comparison of classical chemical and electrochemical processes for treating rose processing wastewater. *Journal of Hazardous Materials*, *148*(1–2), 340–345.

Babu, R. R., Bhadrinarayana, N. S., Begum, K., & Anantharaman, N. (2007). Treatment of tannery wastewater by electrocoagulation. *Journal of the University of Chemical Technology and Metallurgy*, *42*(2), 201–206.

Bailey, S. E., Olin, T. J., Bricka, R. M., & Adrian, D. D. (1999). A review of potentially low-cost sorbents for heavy metals. *Water Research*, *33*(11), 2469–2479.

Barrell, D. C. (1975). Atomic Spectrophotometer Analysis of Heavy Metals Pollutants in Water. *Ann Arbor Science Publishers Inc., Ann Arbor, MI*, *25*.

Bayar, S., Yilmaz, A. E., Boncukcuoğlu, R., Fil, B. A., & Kocakerìm, M. M. (2013). Effects of operational parameters on cadmium removal from aqueous solutions by electrochemical coagulation. *Desalination and Water Treatment*, *51*(13–15), 2635–2643.

Bazrafshan, E., Mohammadi, L., Ansari-Moghaddam, A., & Mahvi, A. H. (2015). Heavy metals removal from aqueous environments by electrocoagulation process–a systematic review. *Journal of Environmental Health Science and Engineering*, *13*(1), 1–16.

Bhattacharya, A. K., Mandal, S. N., & Das, S. K. (2006). Adsorption of Zn (II) from aqueous solution by using different adsorbents. *Chemical Engineering Journal*, *123*(1–2), 43–51.

Brahmi, K., Bouguerra, W., Harbi, S., Elaloui, E., Loungou, M., & Hamrouni, B. (2018). Treatment of heavy metal polluted industrial wastewater by a new water treatment process: ballasted electroflocculation. *Journal of Hazardous Materials, 344*, 968–980.

Canizares, P., Carmona, M., Lobato, J., Martinez, F., & Rodrigo, M. A. (2005). Electrodissolution of aluminum electrodes in electrocoagulation processes. *Industrial & Engineering Chemistry Research*, *44*(12), 4178–4185.

Reference

Cañizares, P., Jiménez, C., Martínez, F., Rodrigo, M. A., & Sáez, C. (2009). The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters. *Journal of Hazardous Materials*, *163*(1), 158–164.

Chaturvedi, S. I. (2013). Electrocoagulation: a novel waste water treatment method. *International Journal of Modern Engineering Research*, *3*(1), 93–100.

Chen, X., Chen, G., & Yue, P. L. (2000). Separation of pollutants from restaurant wastewater by electrocoagulation. *Separation and Purification Technology*, *19*(1–2), 65–76.

Chuah, T. G., Jumasiah, A., Azni, I., Katayon, S., & Choong, S. Y. T. (2005). Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview. *Desalination*, *175*(3), 305–316.

Comninellis, C., & Chen, G. (2010). *Electrochemistry for the Environment* (Vol. 2015). Springer.

Connell, D. W., & Miller, G. J. (1984). *Chemistry and ecotoxicology of pollution* (Vol. 65). John Wiley & Sons.

Dermentzis, K., Christoforidis, A., & Valsamidou, E. (2011). Removal of nickel, copper, zinc and chromium from synthetic and industrial wastewater by electrocoagulation. *International Journal of Environmental Sciences*, *1*(5), 697–710.

Doong, R., Wu, Y.-W., & Lei, W. (1998). Surfactant enhanced remediation of cadmium contaminated soils. *Water Science and Technology*, *37*(8), 65–71.

Dubrawski, K. L. (2013). *Reactor design parameters, in-situ speciation identification, and potential balance modeling for natural organic matter removal by electrocoagulation*. University of British Columbia.

Escobar, C., Soto-Salazar, C., & Toral, M. I. (2006). Optimization of the electrocoagulation process for the removal of copper, lead and cadmium in natural waters and simulated wastewater. *Journal of Environmental Management*, *81*(4), 384–391.

Essa, M. H., Al-Zahrani, M. A., & Nesaratnam, S. (2013). Optimisation of activated carbon production from date pits. *International Journal of Environmental Engineering*, *5*(3), 325–338.

Essadki, A. H. (2012). Electrochemical Probe for Frictional Force and Bubble Measurements in Gas-Liquid-Solid Contactors and Innovative Electrochemical Reactors for Electrocoagulation/Electroflotation. *Electrochemical Cells–New Advances in Fundamental Researches and Applications. Janeza Trdine*, *9*(51000), 45–70.

Etiégni, L., Senelwa, K., Balozi, B. K., Oricho, D. O., Ofosu-Asiedu, K., & Orori, B. O. (2010). TREATMENT OF WASTEWATER BY ELECTROCOAGULATION METHOD AND THE EFFECT OF LOW COST SUPPORTING ELECTROLYTES. *FLUID WASTE DISPOSAL*, 0.

Fabbri, D., Crime, A., Davezza, M., Medana, C., Baiocchi, C., Prevot, A. B., & Pramauro, E. (2009). Surfactant-assisted removal of swep residues from soil and photocatalytic treatment of the washing wastes. *Applied Catalysis B: Environmental*, *92*(3–4), 318–325.

Ferreira, S. L. C., Bruns, R. E., Ferreira, H. S., Matos, G. D., David, J. M., Brandão, G. C., da Silva, E. G. P., Portugal, L. A., Dos Reis, P. S., & Souza, A. S. (2007). Box-Behnken design: an alternative for the optimization of analytical methods. *Analytica Chimica Acta*, *597*(2), 179–186.

Goldblatt, M. W. (1958). Occupational carcinogenesis. *Caribbean Medical Journal*, *20*(1/4), 81–91.

Gupta, A., Joia, J., Sood, A., Sood, R., Sidhu, C., & Kaur, G. (2016).

Microbes as potential tool for remediation of heavy metals: a review. *J Microb Biochem Technol*, *8*(4), 364–372.

Hanafiah, M. A. K., Ngah, W. S. W., Zakaria, H., & Ibrahim, S. C. (2007). Batch study of liquid-phase adsorption of lead ions using Lalang (Imperata cylindrica) leaf powder. *J. Biol. Sci*, *7*(2), 222–230.

Heidmann, I., & Calmano, W. (2010). Removal of Ni, Cu and Cr from a galvanic wastewater in an electrocoagulation system with Fe-and Al-electrodes. *Separation and Purification Technology*, *71*(3), 308–314.

Hsu, T.-C. (2009). Experimental assessment of adsorption of Cu2+ and Ni2+ from aqueous solution by oyster shell powder. *Journal of Hazardous Materials*, *171*(1–3), 995–1000.

Johnson, P. D., Watson, M. A., Brown, J., & Jefcoat, I. A. (2002). Peanut hull pellets as a single use sorbent for the capture of Cu (II) from wastewater. *Waste Management*, *22*(5), 471–480.

Kabata-Pendias, A., & Pendias, H. (1992). Trace elements in soils and plants–CRC Press. *Boca Raton, FL*, 356.

Katal, R., & Pahlavanzadeh, H. (2011). Influence of different combinations of aluminum and iron electrode on electrocoagulation efficiency: Application to the treatment of paper mill wastewater. *Desalination*, *265*(1–3), 199–205.

Kennedy, M., & Krouse, D. (1999). Strategies for improving fermentation medium performance: a review. *Journal of Industrial Microbiology and Biotechnology*, *23*(6), 456–475.

Kerri, K. D. (2004). *Operation of wastewater treatment plants: a field study training program* (Vol. 1). California State University.

Khandegar, V., & Saroha, A. K. (2013). Electrocoagulation for the treatment of textile industry effluent–a review. *Journal of Environmental Management*, *128*, 949–963.

Kobya, M., Ulu, F., Gebologlu, U., Demirbas, E., & Oncel, M. S. (2011). Treatment of potable water containing low concentration of arsenic with electrocoagulation: Different connection modes and Fe–Al electrodes. *Separation and Purification Technology*, *77*(3), 283–293.

Koparal, A. S., & Öğütveren, Ü. B. (2002). Removal of nitrate from water by electroreduction and electrocoagulation. *Journal of Hazardous Materials*, *89*(1), 83–94.

Körbahti, B. K., & Turan, K. M. (2016). Electrochemical decolorization of reactive violet 5 textile dye using Pt/Ir electrodes. *Journal of the Turkish Chemical Society Section A: Chemistry*, *3*(3), 229–246.

Levenspiel, O. (1998). *Chemical reaction engineering*. John wiley & sons.

Li, L., Wei, D., Wei, G., & Du, Y. (2013). Transformation of cefazolin during chlorination process: products, mechanism and genotoxicity assessment. *Journal of Hazardous Materials*, *262*, 48–54.

Liu, H., Zhao, X., & Qu, J. (2010). Electrocoagulation in water treatment. In *Electrochemistry for the Environment* (pp. 245–262). Springer.

Lucas, J. M. (2010). *Response surface methodology: process and product optimization using designed experiments*. Taylor & Francis.

Mollah, M. Y. A., Schennach, R., Parga, J. R., & Cocke, D. L. (2001). Electrocoagulation (EC)—science and applications. *Journal of Hazardous Materials*, *84*(1), 29–41.

Mourabet, M., El Rhilassi, A., El Boujaady, H., Bennani-Ziatni, M., & Taitai, A. (2017). Use of response surface methodology for optimization of fluoride adsorption in an aqueous solution by Brushite. *Arabian Journal of Chemistry*, *10*, S3292–S3302.

Murthy, Z. V. P., & Parmar, S. (2011). Removal of strontium by electrocoagulation using stainless steel and aluminum electrodes. *Desalination*, *282*, 63–67.

Ngah, W. S. W., & Hanafiah, M. A. K. M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresource Technology*, *99*(10), 3935–3948.

Ni'am, M. F., Othman, F., Sohaili, J., & Fauzia, Z. (2006). Combined magnetic field and electrocoagulation process for suspended solid removal from wastewater. *Proc. of the 1st International Conference on Natural Resources Engineering & Technology (INRET), July*, 24–25.

Nwabanne, J. T., Igwegbe, C. A., & Okpo, S. O. (2018). Removal of copper, nickel, and chromium from simulated wastewater using electrocoagulation technique. *International Conference Proceedings: Faculty of Engineering, Unizik*, 448–4580.

Onundi, Y. B., Mamun, A. A., Al Khatib, M. F., & Ahmed, Y. M. (2010). Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbon. *International Journal of Environmental Science & Technology*, *7*(4), 751–758.

Ouhadi, V. R., Yong, R. N., Shariatmadari, N., Saeidijam, S., Goodarzi, A. R., & Safari-Zanjani, M. (2010). Impact of carbonate on the efficiency of heavy metal removal from kaolinite soil by the electrokinetic soil remediation method. *Journal of Hazardous Materials*, *173*(1–3), 87–94.

Ozsoy, H. D., & van Leeuwen, J. (2009). Pb (II) ions removal by dried rhizopus oligosporus biomass produced from food processing wastewater. *Fluid Waste Disposal*.

Petsriprasit, C., Namboonmee, J., & Hunsom, M. (2010). Application of the electrocoagulation technique for treating heavy metals containing wastewater from the pickling process of a billet plant. *Korean Journal of Chemical Engineering*, *27*(3), 854–861.

Pletcher, D., & Walsh, F. C. (2012). *Industrial electrochemistry*. Springer Science & Business Media.

Prasetyaningrum, A., Ariyanti, D., Widayat, W., & Jos, B. (2021). Copper and Lead Ions Removal by Electrocoagulation: Process Performance and Implications for Energy Consumption. *International Journal of Renewable Energy Development*, *10*(3).

Quek, S. Y., Wase, D. A. J., & Forster, C. F. (1998). The use of sago waste for the sorption of lead and copper. *Water Sa*, *24*(3), 251–256.

Rajemahadik, C. F., Kulkarni, S. V, & Kulkarni, G. S. (2013). Efficient removal of heavy metals from electroplating wastewater using electrocoagulation. *International Journal of Scientific and Research Publications*, *3*(10), 1–5.

Rana, P., Mohan, N., & Rajagopal, C. (2004). Electrochemical removal of chromium from wastewater by using carbon aerogel electrodes. *Water Research*, *38*(12), 2811–2820.

Rao, D. G., Senthilkumar, R., Byrne, J. A., & Feroz, S. (2012). *Wastewater treatment: advanced processes and technologies*. CRC Press.

Raut, N., Charif, G., Amal Al-Saadi, S. A.-A., & Abrar, A.-A. (2012). A critical review of removal of Zinc from wastewater. *Proceedings of the World Congress on Engineering*, *1*, 4–6.

Rehman, A., Jingdong, L., Shahzad, B., Chandio, A. A., Hussain, I., Nabi, G., & Iqbal, M. S. (2015). Economic perspectives of major field crops of Pakistan: An empirical study. *Pacific Science Review B: Humanities and Social Sciences*, *1*(3), 145–158.

Renge, V. C., Khedkar, S. V, & Pande, S. V. (2012). Removal of heavy metals from wastewater using low cost adsorbents: a review. *Sci. Revs. Chem. Commun*, *2*(4), 580–584.

Rezaei, M., & Nezamzadeh-Ejhieha, A. (2020). The ZnO-NiO nano-composite: a brief characterization, kinetic and thermodynamic study and study the Arrhenius model on the sulfasalazine photodegradation.

International Journal of Hydrogen Energy, *45*(46), 24749–24764.

Saeed, A., Akhter, M. W., & Iqbal, M. (2005). Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. *Separation and Purification Technology*, *45*(1), 25–31.

Sakarinen, E. (2016). *Humic acid removal by chemical coagulation, electrocoagulation and ultrafiltration*.

Shen, Z. M., Wu, D., Yang, J., Yuan, T., Wang, W. H., & Jia, J. P. (2006). Methods to improve electrochemical treatment effect of dye wastewater. *Journal of Hazardous Materials*, *131*(1–3), 90–97.

Timberlake, K. C., & Orgill, M. (2009). *Chemistry: An introduction to general, organic, and biological chemistry*. Pearson/Prentice Hall.

Villaescusa, I., Fiol, N., Martínez, M., Miralles, N., Poch, J., & Serarols, J. (2004). Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. *Water Research*, *38*(4), 992–1002.

Volesky, B. (2003). Sorption and biosorption, BV Sorbex. *Inc., St. Lambert, Quebec*, *326*.

Wasewar, K. L. (2010). Adsorption of metals onto tea factory waste: a review. *Int J Recent Res Appl Stud*, *3*, 303–322.

Wided, B., Khawla, M., Eya, B. K., & Béchir, H. (2014). Evaluation of boron removal by coagulation-Flocculation and Electrocoagulation. *International Journal of Engineering Research*, *3*(2).

Zhang, T., Zou, H., Ji, M., Li, X., Li, L., & Tang, T. (2014). Enhanced electrokinetic remediation of lead-contaminated soil by complexing agents and approaching anodes. *Environmental Science and Pollution Research*, *21*(4), 3126–3133.

الخـــلاصـــــة

يمكن تعريف تلوث المياه على أنه تلوث مجرى أو نهر أو بحيرة أو محيط أو أي امتداد آخر للمياه ، مما يؤدي إلى استنزاف جودة المياه وجعلها سامة للبيئة والبشر. تشمل الآثار البيئية لتلوث المياه في المقام الأول الضرر الذي يلحقه التلوث بالنظام البيئي المحيط. تموت العديد من الكائنات الحية التي تعتمد على إمدادات المياه الصحية نسبيًا. عندما تصبح المسطحات المائية شديدة التلوث ، فمن الشائع أن تغسل السرطانات والدلافين وطيور النورس والأسماك على الشاطئ. كما يضر التلوث بالاقتصاد لأنه يزيد من تكاليف معالجة المياه ويؤدي إلى خسائر في السياحة ويقلل من قيمة العقارات المحلية ويضر بالصيد التجاري. من المحتمل أن تكون الطريقة الأكثر فعالية للحد من تلوث المياه هي معالجة بعض المياه قبل إعادة إدخالها في المجاري المائية. هذا حل فعال للغاية لأن مرافق معالجة مياه الصرف الصحي قادرة على إزالة جميع الملوثات تقريبًا في مياه الصرف الصحي عبر عملية كيميائية أو فيزيائية أو بيولوجية. سيتم نقل مياه الصرف الصحي من خلال عدة غرف بالمنشأة لتقليل مستويات السمية ببطء.

هناك العديد من المتغيرات الموصوفة بالعوامل المتأثرة في تفاعل التخثر الكهربي .EC لذلك ، تتضمن هذه الدراسة التحقيق في تأثير ثمانية متغيرات على عملية EC ؛ تم اختيار وقت التلامس ، وكثافة التيار ، والجهد الموفر ، ومعدل التحريك ، وتركيز النحاس الأولي ، ودرجة حموضة المحلول ، ودرجة حرارة التفاعل ، ونوع الأنود كمتغيرات خاضعة للتحكم في تفاعل EC ، بينما تم استخدام كفاءة إزالة النحاس كاستجابة للعملية. يتم محاكاة التغذية بمياه الصرف الصحي المحضرة عن طريق إضافة نترات النحاس كمصدر أيونات النحاس. حدد مستويان المتغيرات الأكثر تأثيرًا على إزالة النحاس أثناء تفاعل EC وفقًا لتصميم Plackett-Burman PBD. تظهر النتائج أن تركيز النحاس الأولي ، ودرجة الحموضة في المحلول ، ودرجة حرارة التفاعل ، ووقت التلامس هي أهم المتغيرات في تفاعل .EC من ناحية أخرى ، تظهر النتائج المتوقعة أن الحد الأقصى من كفاءة الإزالة (٩٨٪) ستتحقق في ظروف التشغيل المثلى ؛ وقت التلامس (٤٠ دقيقة) ، كثافة التيار (٣ أمبير / سم ٢) ، إمداد الجهد (١٠ فولت) ، تركيز النحاس الأولي (٤٠٠ جزء في المليون) ، درجة حرارة التفاعل (٧٠ درجة مئوية) بدون معدل تقليب واستخدام الحديد كقطب موجب. تمت دراسة المتغيرات الأكثر تأثرًا التي ظهرت أثناء تطبيق PBD في الخطوة السابقة بشكل أعمق من خلال التصميم التجريبي Box-Behnken التطبيقي لاستكشاف التركيز الأولي ودرجة الحرارة ودرجة الحموضة على استهلاك الطاقة وفعالية إزالة المعادن الثقيلة (النحاس) من المياه الملوثة.

مياه الصرف. تم إجراء خمسة عشر (١٥) تجربة قائمة على تصميم Box-Behnken ، وتستغرق كل تجربة ٤٠ دقيقة. تم استخدام النتائج لنمذجة كفاءة إزالة المعادن الثقيلة واستهلاك الطاقة لهذه الطريقة بدعم Minitab. يشير التحسين العددي إلى أن استهلاك الطاقة الأمثل البالغ ٠.٥٦ كيلو واط ساعة / متر مكعب وأعلى كفاءة لإزالة النحاس قد تم تحقيقه بنسبة ٩٧٪ على التوالي في حالات التشغيل ٢٠٠ و ٣٥٠ و ٥٠٠ من تركيزات النحاس و ٥٠ و ٤٠ و ٦٠ من درجة الحرارة و ٣ ، ٧ و ١١ من تدرجات الأس الهيدروجيني. تم تقدير حركية تفاعل EC ومعلمات الديناميكا الحرارية ؛ يخضع التفاعل للترتيب الثاني مع ثوابت معدل التفاعل (k) هي ٠.٦٥٧٢ و ٠.٦٨٢٩ و ٠.٨٣٠٨ [(مول / لتر) ثانية -١] -١ عند ٥٠ و ٦٠ و ٧٠ درجة مئوية على التوالي ، قيمة طاقة التنشيط الظاهرة هي ١٠.٧١٩ كيلو جول / مول تم الحصول عليها لهذه العملية بواسطة معادلة أرهينيوس. حصل تفاعل EC على تغيير إنتروبيا سالب ΔS (-0.218 kJ / mol K) مع تغير المحتوى الحراري الإيجابي ΔH وقيم Gibbs الخالية من الطاقة ΔG.

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قسم الهندسة الكيمياوية

إزالة ايون النحاس من مياه الصرف الصحي المحاكاة بتقنية التخثير الكهربي بأنواع مختلفة من الاقطاب الكهربائية

رسالة

مقدمة إلى كلية الهندسة / جامعة بابل وهي جزء من متطلبات نيل شهادة الماجستير في
الهندسة /الهندسة الكيمياوية

من قبل

مروة عبد الجليل عبد الرحيم حسين

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1443 **2022**