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Original Research Article

Optimizing Nutrient Removal in Agriculture Wastewater Using Electrocoagulation Technology

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Abstract.
Water pollution contributes to water crises at the global level by reducing the quantity and quality of freshwater resources available to humans and ecosystems. Agricultural wastewater can contain chemicals such as pesticides, herbicides, fertilizers, and organic matter. If discharged without treatment, it can contaminate water sources such as rivers, lakes, and groundwater. This study aims to optimize operating parameters in the form of voltage, electrocoagulation time, and calcium concentration to maximize the removal rate of nitrogen compounds in agricultural wastewater. This study used response surface methodology (RSM) to optimize the operational conditions of electrocoagulation and achieve a high level of allowance without the need for additional coagulants from outside. The results showed that the lowest nitrate concentration was 2.960 mg/L (an 88.37% reduction from the initial concentration) under the conditions of 45 V voltage, 15 minutes of electrocoagulation time, and a calcium concentration of 7 mg/L.. The lowest ammonia concentration was 0.016 mg/L (99.37%) at variations in voltage, electrocoagulation time, and calcium concentration of 30 V, 1.5 minutes, and 4.5 mg/L, respectively. The addition of calcium can react with ions produced from the anode to form coagulants, such as calcium hydroxide, which helps remove nitrogen compounds. The optimal operating conditions for EC to set aside nitrate and ammonia concentrations of 3.709 mg/L and 1.338 mg/L, respectively, are 45 V, 15 minutes, and calcium concentrations are 5.09 mg/L. Agricultural wastewater treatment using EC succeeded in removing iron up to 96.73% of the initial concentration. The magnesium concentration is very low at 0.001 mg/L.

Keywords: Nitrogen; agriculture wastewater; electrocoagulation; RSM

1. Introduction

Water is the most important resource for sustaining life on earth (Verma et al., 2023) Water pollution contributes to water crises at the global level by reducing the quantity and quality of freshwater resources available to humans and ecosystems. Agricultural wastewater can contain chemicals such as pesticides, herbicides, fertilizers, and organic matter from livestock waste (Widjajanto et al., 2016). If discharged without treatment, it can contaminate water sources such as rivers, lakes, and groundwater. Irrigation of agricultural wastewater can have both positive and negative consequences, including the accumulation of potentially toxic elements in the soil and their transfer to flora and fauna. Excess nitrogen can trigger excessive algae growth, causing eutrophication, which can harm aquatic ecosystems and reduce water quality. Eutrophication can damage aquatic ecosystems by causing algae growth (Prasetya, 2023). Nitrogen in wastewater can turn into water-soluble ammonium, nitrite and nitrate compounds (Burghate and Ingole, 2014). High nitrate levels in drinking water can be a public health concern as it can cause health problems such as methemoglobinemia (blue baby syndrome) in children (Knobeloch et al., 2000).

Several methods have been developed to treat and manage nitrogen compounds generated by agricultural wastewater (Usman et al., 2022). In wastewater treatment, physic-chemical and biological techniques are used to remove nitrogen, and hybrid treatments incorporating these strategies have shown promise (Tripathy and Remya, 2020). The use of solid waste as an adsorbent for nitrogen recovery from wastewater and its subsequent use in agricultural land is also being explored (Rajmohan et al., 2018). Management of nitrogen-containing fertilizers and soil management with the adoption of conservation agricultural practices can help overcome nitrogen pollution (Chen et al., 2022). Nitrate in agricultural wastewater undergoes biological nitrification using reactors. In addition, using autotrophic hydrogen-oxidizing bacteria has demonstrated efficient removal of nitrates from wastewater. However, biological processes require a long time to decompose organic substances in wastewater.

Electrochemical technology has been a promising technology over the past three decades for purifying wastewater and recovering nutrients, metals, energy, and heat (Chaplin, 2019; Liu et al., 2021). Electrocoagulation (EC) is considered a wastewater treatment method due to its ability to remove organic and inorganic contaminants. The use of EC is based on its flexibility, easy setup, environmentally friendly nature, and does not require large land (Shokri and Fard, 2022). The presence of calcium ions in the EC process effectively reduces contaminant concentrations (Anwer and Abdulmajeed, 2020). However, EC with helix electrode configuration and the addition of calcium for nitrogen removal is limited by several limitations, including the impact of voltage and time. This study aims to optimize operating parameters in the form of voltage, electrocoagulation time, and calcium concentration to maximize the removal rate of nitrogen compounds in agricultural wastewater. This study used response surface methodology (RSM) to optimize the operational conditions of electrocoagulation and achieve a high level of allowance without needing additional external coagulants.

2. Methods

2.1. EC reactor design

The scheme of the EC reactor in this study is shown in Figure 1. The blindest EC reactor of acrylic is cylindrical in shape with a diameter of 12 mm and a thickness of 3 mm. The EC reactor is equipped with a cover made of polyurethane. The top and bottom lids are hooked using 4 iron rods. Reactor volume 1500 mL. The cathode uses a spiral-shaped stainless still, and the anode is made of cylindrical magnesium (Mg). The reactor is equipped with outlet gas produced Tuesday by the electrocoagulation process. Copper wires connect Both electrodes to the power supply (KXN-6010D). Power supply with voltage input: AC 220 V 50Hz; Output voltage: DC 0~60 V; Output current: DC 0~10A; and Power: 240 Watts. The distance between the anode cathodes is 10 mm.

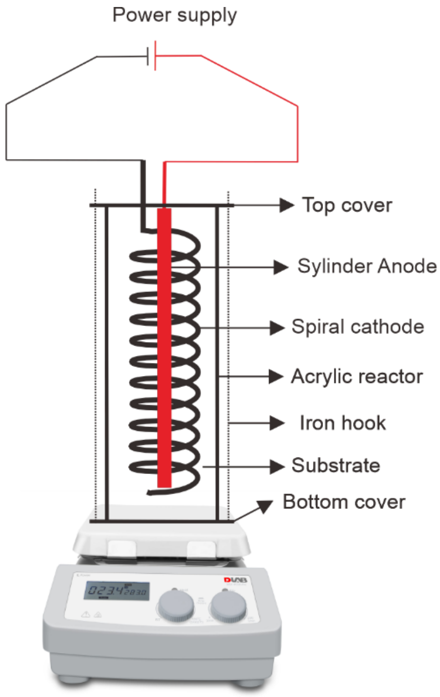


Figure 1 The scheme of the EC tool is cylindrical in shape with a total volume of 1500 mL

2.2. Experimental setup

Design-Expert statistical software (version, State-Ease Inc., USA) is used to perform statistical analysis and modeling using central composite design (CCD). This method allows optimization of multiple quadratic models simultaneously using the measurement of a group of results at once rather than individual optimization (Bhatt et al., 2020). The relationship between the independent variable and the response variable (Y) is estimated using a second-order polynomial model. This model allows the determination of the effect of variables such as calcium concentration, electrical power and operating time on the efficiency of removal of target pollutants. Coded level and independent variables of the model are shown in Table 1.

Table 1 Coded level and independent variables

Factor	Variable	level		
		-α	0	α
A	Voltage, V	15	30	45
B	Time, min	5	10	15
C	Calcium concentration, mg/L	2	4.5	7

Agricultural wastewater plus calcium (p.a) (Merck, Germany) with the concentration according to the Central Composite experiments in Table 1 which is 0.295 mg / L; 2 mg/L; 4.5 mg/L; and 7 mg/L. Wastewater from agricultural activities is drained into the EC reactor using pumps up to a total volume mark of 1500 mL. The power supply is connected to an AC power source, then regulates the mains voltage. The other voltage variations are 15V, 30V, 45V, and 55.23 V. The electrocoagulation time is set to vary by 1.59 minutes, 5 minutes, 10 minutes, 15 minutes, and 18.41 minutes. We use this voltage based on previous research conducted by (Phiri et al., 2021) and (Krishnamoorthy et al., 2021). They use voltages between 3-40 volts.

Table 1 At the end of the experiment, the solids are allowed to settle and then filtered. The sample was allowed to settle for 30 minutes then the sample is taken using a pipette from a depth of 2 cm from the surface of the substrate and filtered using filter paper. After filtration, the filtrate is analyzed for nitrate and ammonia levels. Nitrate test using ultraviolet (UV) spectrophotometric (Norman and Stucki, 1981) the indophenol method (APHA, 2017). The colour formed was measured using a UV-Vis spectrophotometer (Genesys 150, Thermofisher Scientific, USA).

3. Result and Discussion

3.1. Optimization of nitrate and ammonium removal in agricultural wastewater using RSM

RSM is employed to enhance the elimination of nitrate and ammonium from agricultural wastewater through electrocoagulation. Within the Central Composite Design (CCD) experiments, the factors of voltage, time, and calcium concentration are evaluated at three levels (a midpoint and two extremities) using a symmetrical design involving three variables, as outlined in the table, with the details of these CCD experiments presented in Table

Table 1

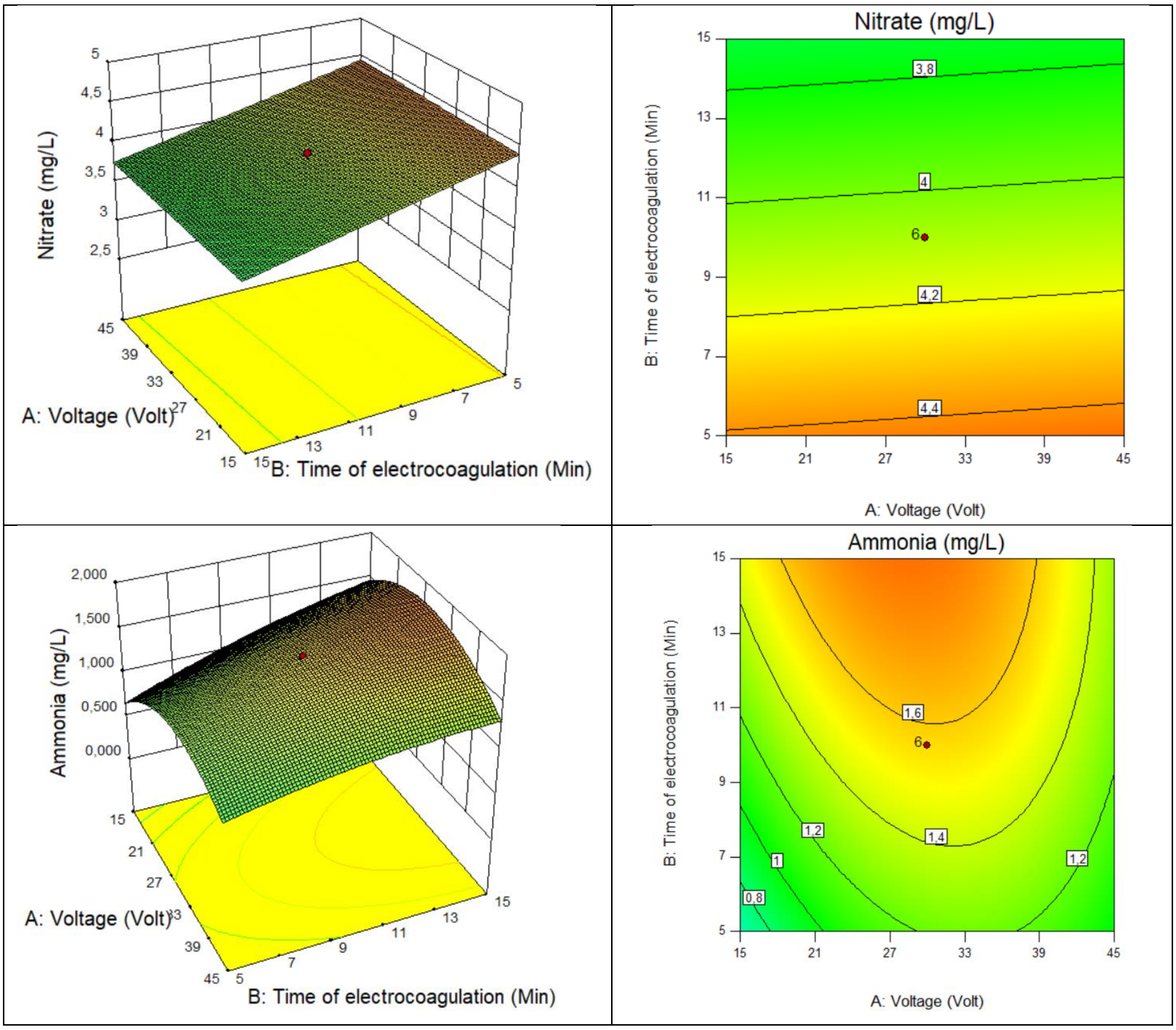
Table 1 Central Composite experiments

No	A: Voltage	B: Time	C: [Calcium]	Ammonia	Nitrate
	Volt	minute	Mg/L	mg/L	mg/L
1	30	18.409	4.5	1.998	3.73
2	15	5	7	1.392	4.14
3	30	10	4.5	1.588	4.15
4	45	15	7	1.764	2.96
5	30	10	4.5	1.588	4.15
6	45	15	2	1.409	3.9
7	15	15	2	1.846	3.91
8	30	10	8.70448	1.798	3.91
9	30	10	4.5	1.588	4.15
10	15	15	7	1.366	3.39
11	55.2269	10	4.5	0.045	4.42
12	15	5	2	1.068	4.55
13	30	10	4.5	1.588	4.15
14	30	1.59104	4.5	0.016	4.49
15	30	10	4.5	1.588	4.15
16	45	5	2	1.575	4.64
17	30	10	4.5	1.588	4.15
18	4.77311	10	4.5	0.211	4.14
19	30	10	0.295518	1.643	4.25
20	45	5	7	1.805	4.34

Table 3 The approximate function of nitrate and ammonia removal based on experimental results is evaluated

Parameters (mg/L)	Equation for optimum allowance efficiency	Suggested equations
Nitrate	$Nitrate = +5.099+1.566E\text{-}003 * X_1 - 0.0701 * X_2 - 0.081 * X_3$	Linear
Ammonia	$Ammonia = -0.907 + 0.111 * X_1 + 0.196 * X_2 - 0.241 * X_3 - 1.599E\text{-}003 * X_1 * X_2 + 2.470E\text{-}003 * X_1 * X_3 - 6.792E\text{-}003 * X_2 * X_3 - 1.717E\text{-}003 * X_1\text{^}2 - 3.029E\text{-}003 * X_2\text{^}2 + 0.0282 * X_3\text{^}2$	Quadratic
X_1=Voltage; X_2= Time of electrocoagulation; X_3= Calcium concentration		

2



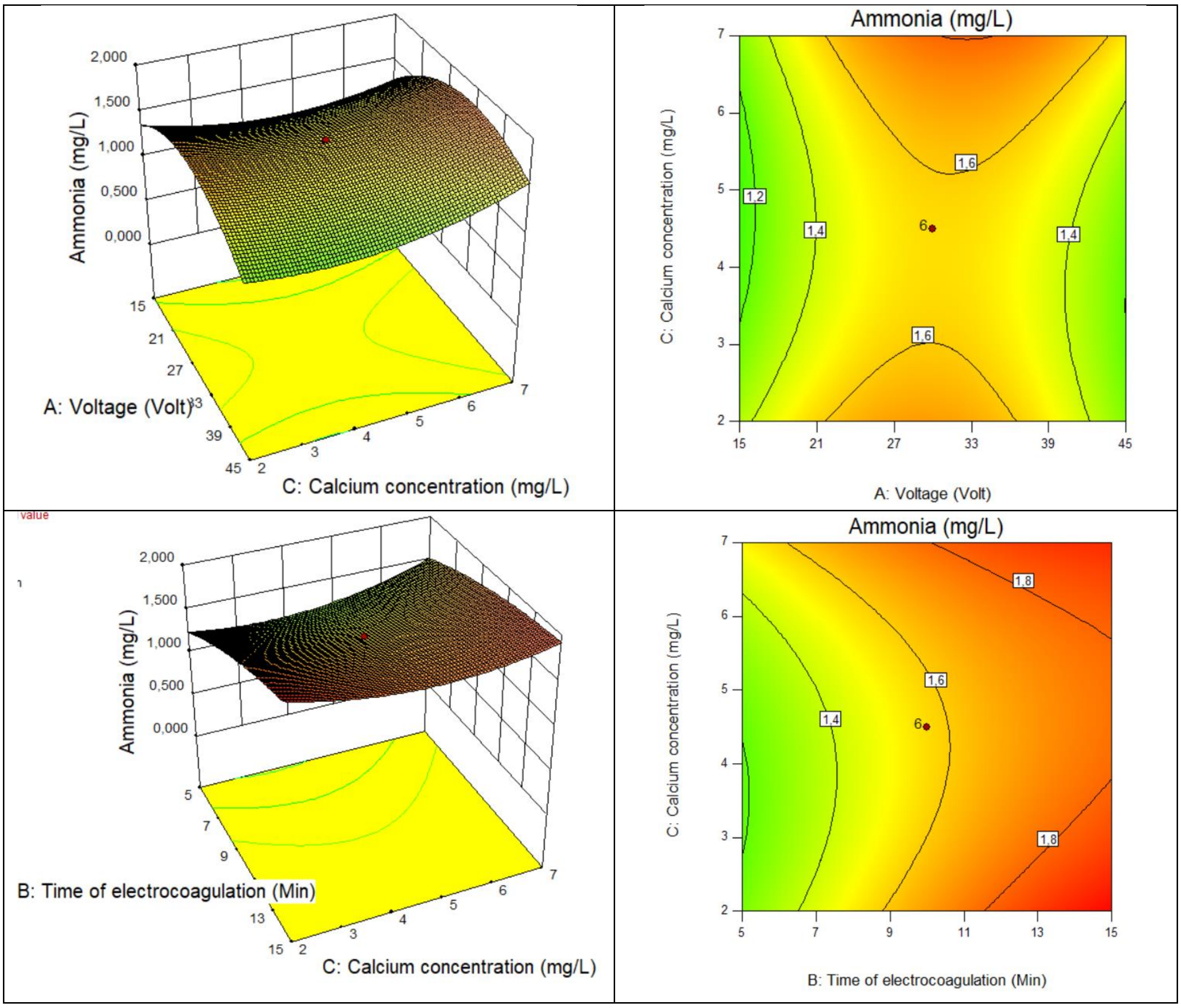
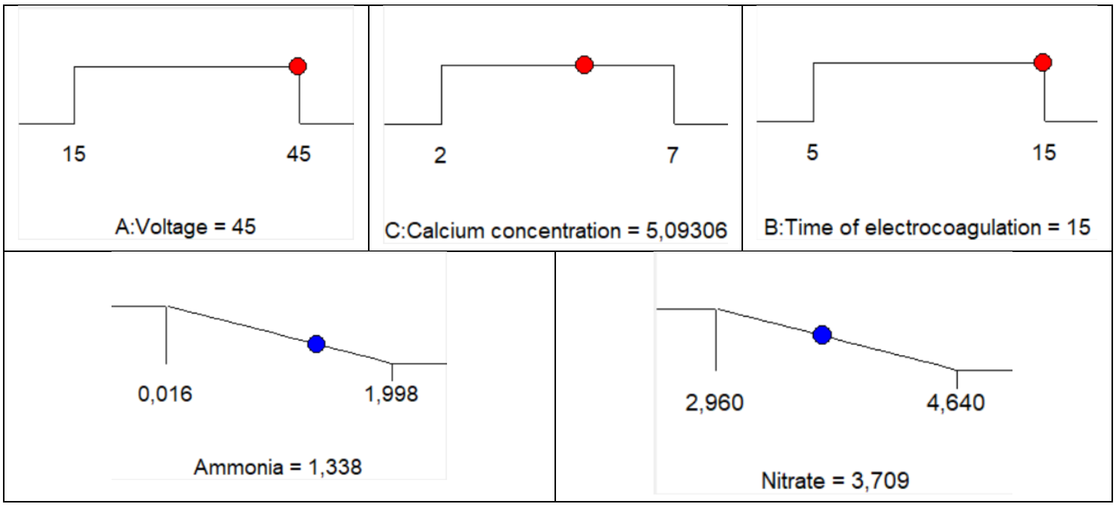


Figure 2 3D 2response surface plots of the interaction effects of voltage vs. time of electrocoagulation on nitrate and ammonia removal.



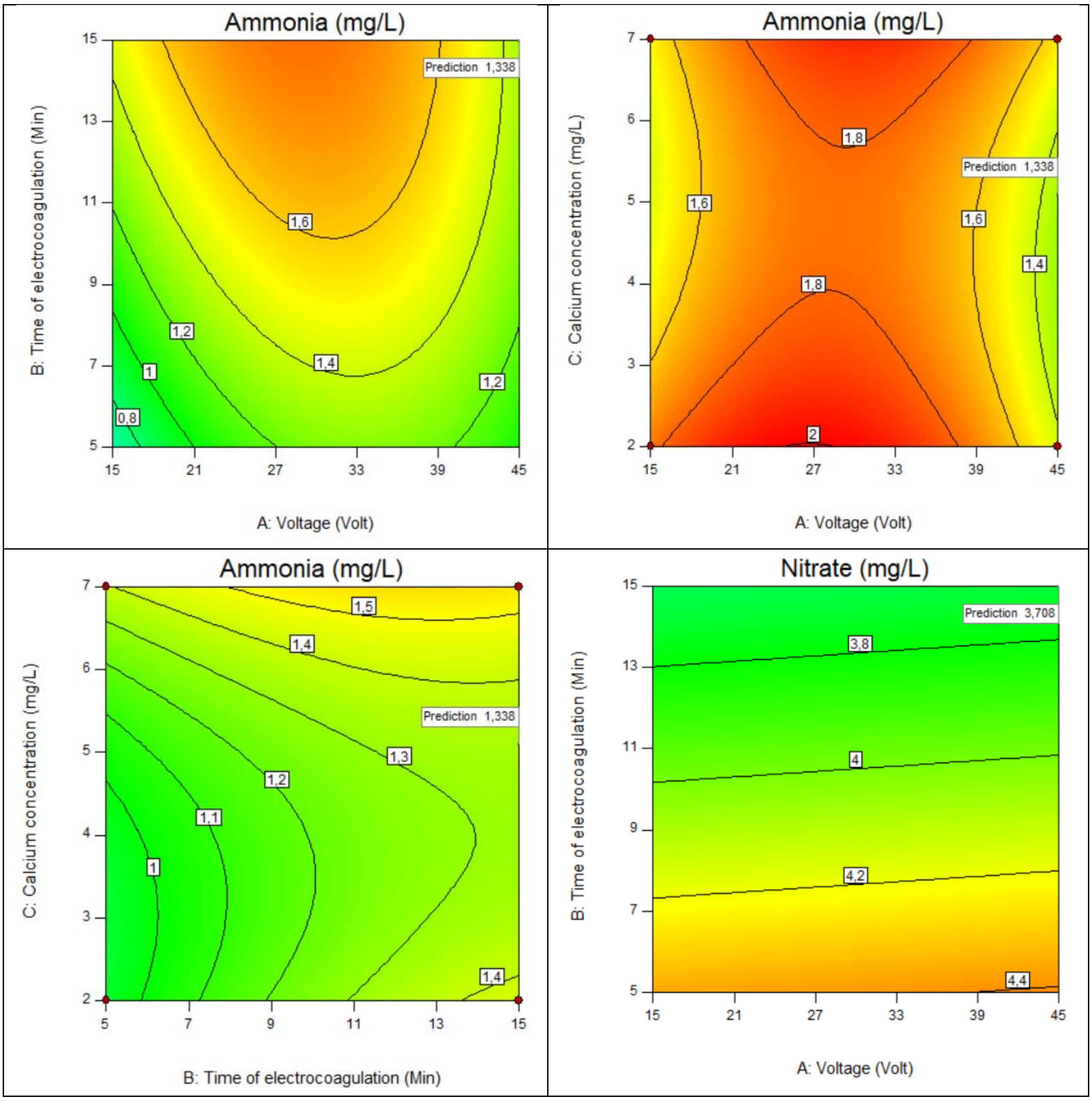


Figure 33 Results of the operational variables' optimization based on CCD-RSM

Table 2 shows that the study was conducted as many as 20 runs on various variations in voltage, electrocoagulation time, and calcium concentration. This run was done to measure its effect on ammonia and nitrate concentrations. With various variations, the results showed that the voltage, duration, and concentration of calcium effectively reduced the concentration of ammonia and nitrates through the process of electrocoagulation. Post-analysis determines the optimal composition between voltage, time, and calcium concentration. Figure 3 shows the results of optimizing nitrate and ammonia removal using the RSM method. The optimal operating conditions for EC to set aside nitrate and ammonia concentrations of 3.709 mg/L and 1.338 mg/L, respectively, are 45 V and 15 minutes, and calcium concentrations are 5.09 mg/L.

3.2. Optimization of nitrate removal in agricultural wastewater

One of the objectives of this study is the optimization of nitrate removal in agricultural wastewater using electrocoagulation. Electrocoagulation is one of the effective methods to reduce nitrate concentrations from wastewater. The efficiency of nitrate removal depends on the voltage used and the surface area of the electrode (Amarine et al., 2020). The results showed that the lowest nitrate concentration was 2,960 mg/L (88.37% removal from initial concentration) at variations in voltage, electrocoagulation time, and calcium concentration of 45 V, 15 minutes, and 7 mg/L, respectively. Agricultural wastewater still contains the highest nitrate (4,640 mg/L) when the operating conditions of voltage, electrocoagulation time, and calcium concentration are 45 V, 5 minutes, and 2 mg/L, respectively.

Nitrate reduction can occur through various reactions, including reduction to nitrite or ammonium, as well as adsorption on coagulant floc (Amarine et al., 2020) Coagulant floc produced from the active surface of the electrode plays a role in adsorbing the nitrite, thus causing an increase in the efficiency of nitrate removal. Adsorption of nitrates in coagulant floc is not the main mechanism in nitrate removal because nitrate is an ion dissolved in water and is not easily adsorbed by Priya et al., (2022). However, the coagulation-flocculation process can help eliminate nitrogen in the form of particulates associated with other organic matter. The addition of calcium can cause it to react with ions produced from the anode (Mg) to form coagulants, such as calcium hydroxide ($Ca(OH)_2$(Gupta et al., 2023).

Coagulation involves the interaction between coagulants and pollutants, forming floc that can be easily separated from liquids. The mechanism involves the destabilization of colloids, the Formation of Microflocs, and Floc Growth (Alekseev and Shambina, 2021; Bharath et al., 2018). In the case of effluent treatment, electrocoagulation generates microbubbles that adhere to the suspended solid, allowing it to float to the surface, thereby improving water quality. Previous studies have been conducted to investigate the use of EC as a method to lower nitrate concentrations in wastewater. The results showed a considerable efficiency of nitrate removal. Nitrate removal efficiency in wastewater by 91.6% with utilization of a continuous flow EC reactor operating under optimized conditions (Shaker et al., 2023). Nitrate removal efficiency of 94.41% under certain conditions, including pH 7, electrical voltage 30 V, and submerged surface area 33.75 cm^2 (Amarine et al., 2020; Berkani et al., 2019).

3.3. Optimization of the removal of ammonia in agricultural wastewater

Ammonia in surface water is a chemical compound that has gained global attention (Purwono et al., 2023; Wang et al., 2020). In this study, agricultural wastewater had an initial ammonia concentration of 2.515 mg/L. The lowest ammonia concentration was 0.016 mg/L (99.37%) at variations in voltage, electrocoagulation time, and calcium concentration of 30 V, 1.5 min, and 4.5 mg/L, respectively. Agricultural wastewater contains the highest ammonia content of 1.998 mg/L when it is treated using EC under operational conditions of voltage, electrocoagulation time, and calcium concentrations of 30 V, 18.4 minutes, and 4.5 mg/L, respectively.

Decreased ammonia concentration due to in situ coagulant production through electrochemical processes. Electrode magnesium as an anode will oxidize and dissolve into wastewater, producing magnesium ions Mg^{2+}. These ions act as coagulants that can neutralize the charge of suspended particles or colloids in water, including ammonia (NH_3) and ammonium ions (NH_4^+), helping to agglomerate them into larger floc (Mamelkina, 2020). The concentrations of ammonium (NH_4^+) and ammonia (NH_3) during the EC process are affected by pH and temperature. An increase in pH leads to the formation of NH_3 (Purwono et al., 2023)

$$NH_4^+ + OH^- \leftrightarrow NH_3.H_2O \leftrightarrow NH_3 + H_2O \quad (3)$$

pH value data support this. The EC process produces the lowest pH of 8.3 at variations in voltage, electrocoagulation time, and calcium concentrations of 30 V, 18.4 minutes, and 4.5 mg/L, respectively. The highest pH was 10.3 at variations in voltage, electrocoagulation time, and calcium concentration of 15 V, 15 minutes, and 2 mg / L, respectively. The presence of calcium ions in the EC process effectively reduces contaminant concentrations (Anwer and Abdulmajeed, 2020).

3.4. Iron and magnesium

Agricultural wastewater contains an initial iron concentration of 0.165 mg/L. The EC process succeeded in reducing iron concentration to 0.005 mg/L (96.73% of initial concentration) at variations in voltage, electrocoagulation time, and calcium concentration of 45 V, 15 minutes, and 2 mg/L, respectively. Based on the CCD design, operational conditions of 15 V, 15 minutes, and 2 mg/L of calcium resulted in iron concentrations of 0.148 mg/L (9.81% of initial concentrations). The EC process uses Mg electrodes so researchers need to analyze the concentration of Mg contained in agricultural wastewater after EC is done. Agricultural wastewater yielded as low as 0.001 mg/L at variations in voltage, electrocoagulation time, and calcium concentrations of 4.8 V, 10 minutes, and 4.5 mg/L, respectively. The highest magnesium concentration was 0.007 mg/L at variations in voltage, electrocoagulation time, and calcium concentration of 45 V, 15 min, and 2 mg/L, respectively.

4. Conclusions

This study aims to optimize operating parameters in the form of voltage, electrocoagulation time, and calcium concentration to maximize the removal rate of nitrogen compounds in agricultural wastewater. The optimal operating conditions for EC to set aside nitrate and ammonia concentrations of 3.709 mg/L and 1.338 mg/L, respectively, are 45 V, 15 minutes, and calcium concentrations are 5.09 mg/L. Agricultural wastewater treatment using EC succeeded in removing iron up to 96.73 % of the initial concentration. The magnesium concentration is very low at 0.001 mg/L. The attention of electrocoagulation to remove other pollutants commonly found in agricultural wastewater, such as pesticides, herbicides, and organic matter, could be a valuable area of research in the future.

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