



# Studies on the Removal of Nitrogen and COD from Municipal Wastewater by Electrocoagulation

K. Pravallika<sup>1</sup>, A. Rajasekhar Babu<sup>2</sup>, M. Kalyan Kumar<sup>3</sup>

<sup>1,2,3</sup>, Department of Chemical Engineering, JNTUA College of Engineering Ananthapuramu,

<sup>1,2,3</sup> Affiliated to JNTU Anantapur, Ananthapuramu, Andhra Pradesh, 515002, India

(Received: 07 January 2024

Revised: 12 February 2024

Accepted: 06 March 2024)

## KEYWORDS

electrocoagulation, nitrogen, COD, aluminium & iron electrodes, municipal wastewater, eutrophication, response surface methodology (RSM).

## ABSTRACT:

Due to enormous human activities such as industrialization, and the use of excessive fertilizers, the discharge of nutrient-rich wastewater into recipient water bodies is leading to eutrophication. Eutrophication causes a decrease in dissolved oxygen (DO) levels in water bodies, leading to a toxic environment for aquatic life. In this study, an electrocoagulation (EC) cell is used to reduce nitrogen and COD in municipal wastewater employing aluminum and iron electrodes. The effect of the main operational parameters pH, electrolysis time, current density, inter-electrode distance, temperature, concentration, agitation speed, and electrode material are studied. Experimental analysis is carried out using 'Response Surface Methodology' (RSM) by designing experiments using 'Design Expert' software. Mathematical models are developed for COD and ammoniacal nitrogen, achieving high predictive proportions of variance with high  $R^2$  values of 0.9781 and 0.9625 for COD and ammoniacal nitrogen respectively. Process optimization has yielded optimum conditions of pH 7, voltage 8 V, runtime 85 minutes, agitation speed 225 rpm, temperature 57°C, inter-electrode spacing 3 cm, and initial nitrogen concentration of 40 ppm. The application of electrocoagulation for the treatment of Ananthapuramu municipal wastewater with an initial concentration of nitrogen 23.6 ppm under optimal conditions allowed for the removal of 80.17% ammoniacal nitrogen and 84.96% COD. The results demonstrate the effectiveness of electrocoagulation in treating municipal wastewater, making it suitable for discharge into water bodies.

## 1. Introduction

Half of the global population is facing the water crisis, an escalating environmental concern. In India, several districts are currently dealing with water scarcity, attributed to either quality or quantity issues. To address this challenge, there is a significant focus on wastewater treatment to mitigate water contamination problems and promote the reuse of municipal wastewater, thereby easing pressure on traditional water sources [1]. The presence of high levels of ammoniacal nitrogen in various types of wastewater poses a significant threat to both aquatic ecosystems and human health. This nitrogen exists in forms such as unionized ammonia ( $\text{NH}_3$ ) and ammonium ion ( $\text{NH}_4^+$ ), contributing to water pollution and the phenomenon of eutrophication in lakes and rivers. Eutrophication, a widespread environmental concern, results from the excessive input of nutrients like nitrogen and phosphorus into water bodies, often stemming from agricultural practices, wastewater discharge, and improper waste disposal [8]. In response to escalating environmental degradation,

there has been a growing emphasis on finding cost-effective and efficient solutions for wastewater treatment and nutrient recycling. Industrialists, environmentalists, and governments alike are increasingly compelled to explore innovative approaches to mitigate the adverse impacts of wastewater pollution [2].

Electrochemical treatment methods have emerged as promising techniques for removing pollutants like ammonium nitrogen and chemical oxygen demand (COD) from wastewater. The efficacy of these methods is influenced by various factors, including pH, runtime, current density, inter-electrode distance, temperature, agitation speed, electric voltage, and notably, the choice of electrode material, particularly the anode.

Among these factors, the selection of the anode material and the applied electric voltage play pivotal roles in determining both the operational costs and the efficiency of pollutant removal in electrochemical treatment processes. For instance, higher current densities have been observed to enhance pollutant



removal rates and reduce treatment durations significantly [3].

This study focuses on investigating the efficiency of electrocoagulation (EC) using aluminium and iron electrodes for the removal of ammoniacal nitrogen and COD from municipal wastewater. Aluminium and iron are chosen due to their abundance, cost-effectiveness, and proven capability to generate coagulants in situ, aiding in the precipitation and subsequent removal of pollutants. Understanding the performance of EC with these electrodes is crucial for optimizing wastewater treatment processes and addressing the growing challenges of water pollution and scarcity [4].

### Mechanism of COD and Nitrogen Removal in Electrocoagulation

During the electro-dissolution of a sacrificial anode, Aluminum and iron electrodes are used as sacrificial anodes (Fig. 1). Metal cations ( $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ ) react with hydroxide ions ( $\text{OH}^-$ ) to form metal hydroxide flocs. Metal hydroxide flocs act as coagulants and precipitate suspended particles, organic matter, and COD from the water. The formed flocs are easily separable through processes like sedimentation or filtration, resulting in clarified water with reduced COD and nitrogen.

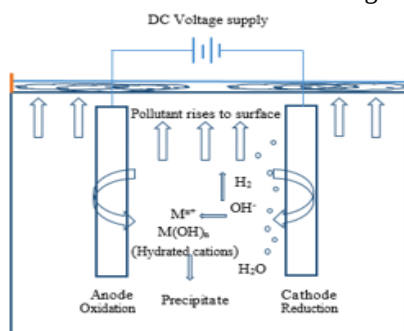
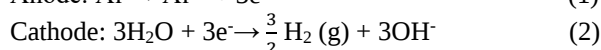
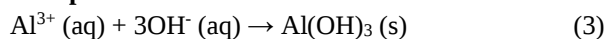


Fig.1. Mechanism of electrocoagulation

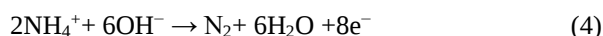
#### Al electrode:



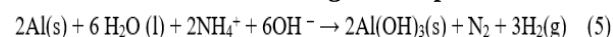
#### Precipitation reaction:



#### Ammonium Ion Oxidation:



#### Overall Reaction with Nitrogen Precipitation:



This represents the precipitation reaction of aluminium ions with hydroxide ions to form solid aluminium hydroxide, along with the oxidation of ammonium ions to produce nitrogen gas and hydrogen gas [5]. Electrocoagulation process, facilitated by the dissolution of aluminium or iron electrodes, creates an environment where the electrochemical reactions transform ammonium ions into nitrogen gas, contributing to the removal of nitrogen from the water.

## 2. Objectives

The objective of the work is to develop an electrocoagulation process for reducing nitrogen and COD in municipal wastewater using response surface methodology. The EC process is carried out while ensuring optimum process parameters to minimize nitrogen and COD levels in Ananthapuramu municipal wastewater.

## 3. Methods and materials

### 3.1 Synthetic wastewater

In 2 litres of distilled water, a mixture of chemical compounds is dissolved. This mixture includes urea at a concentration of 91.74 mg/l, ammonium chloride ( $\text{NH}_4\text{Cl}$ ) at 12.75 mg/l, sodium acetate at 79.37 mg/l, and peptone at 17.41 mg/l. Furthermore, food ingredients such as starch at 122.00 mg/l, milk powder at 116.19 mg/l, yeast at 52.24 mg/l, and soya oil at 29.02 mg/l are added. Additionally, trace metals including manganese sulphate monohydrate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ) at 0.108 mg/l, nickel sulphate hexahydrate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) at 0.336 mg/l, lead chloride ( $\text{PbCl}_2$ ) at 0.100 mg/l, and zinc chloride ( $\text{ZnCl}_2$ ) at 0.208 mg/l are also incorporated. These chemicals are meticulously combined in appropriate proportions within the 2-liter volume of distilled water to mimic wastewater with a defined composition, thereby enabling subsequent analysis of COD and nitrogen levels. The solution is stirred well to disperse the particles in the solution. The pH of the solution is adjusted between 7 and 7.5 using 0.1 M  $\text{H}_2\text{SO}_4$  for decreasing pH and 0.1 M NaOH for increasing pH.

### 3.2 Ananthapuramu city waste water sample

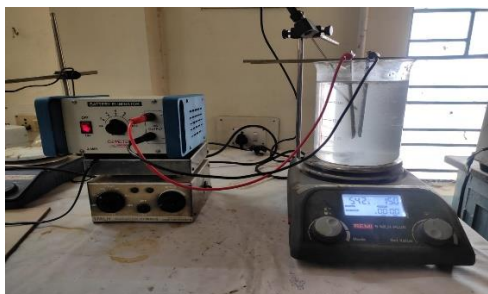
This study prioritizes the utilization of genuine domestic wastewater collected from the sewers of the Ananthapuramu Municipal Corporation. Specifically, the sampling site is located at the coordinates 14.684303°, 77.587821° near the "Nadimivanka," a natural drain coursing through the town's centre (Fig.2).



**Fig.2.** Nadimivanka, Ananthapuramu, Andhra Pradesh (14.684303°, 77.587821°)

### 3.3 Experimental setup and procedure

The experimental setup comprises a 2-liter glass beaker functioning as an electrolytic cell, positioned on a magnetic stirrer. Aluminum and iron plates, measuring 15 cm x 5 cm x 0.2 cm, are utilized as electrodes (Fig.3). Each operation involves two electrodes, submerged in the cell with assistance from a support. These electrodes are linked to an external DC source through alligator clips to facilitate electrolysis. An external DC source, specifically a battery eliminator, is employed, offering various voltage options for the experiment. To ensure adequate agitation of the solution during electrolysis, a magnetic stirring bar is introduced into the cell. The electrocoagulation cell is filled with synthetic wastewater samples, with an effective electrode surface area of 65 cm<sup>2</sup>. The key operational parameters including pH, voltage, temperature, initial concentration of nitrogen, runtime, agitation speed, and inter-electrode distance are meticulously controlled for each experiment.



**Fig.3.** Electrocoagulation setup

### 3.4 Chemical and Analytical methods

#### 3.4.1 pH control

The pH level of the sample significantly impacts the efficiency of COD and nitrogen removal. To adjust the pH, 0.1M sodium hydroxide (NaOH) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) are added to the sample. Systronics 361 digital pH meter is used to measure the pH of the samples.

#### 3.4.2 COD

COD stands for Chemical Oxygen Demand, which is a measure of the amount of oxygen required to oxidize organic and inorganic compounds in water. The method used for COD analysis is reflux method. Visiscan spectrophotometer 167 is employed to measure the absorbance units of the response samples. The absorbance of the solution is measured at 650 nm.

#### 3.4.3 Ammoniacal nitrogen

Ammoniacal nitrogen refers to the concentration of nitrogen present in the form of ammonia (NH<sub>3</sub>) or ammonium ions (NH<sub>4</sub><sup>+</sup>) in water or wastewater. The method used for analysis of Ammoniacal nitrogen is phenate method. Visiscan spectrophotometer 167 is employed to measure the absorbance units of the response samples. The absorbance of the solution is measured at 450 nm.

### 3.5 Experimental design

As there are seven operational parameters, it is difficult and time consuming to conduct the single factor varying experiments. One factor at a time experiments lead to large number of experimental runs, also interactions between the factors and their combined effect on the responses cannot be determined. Design of experiments (DoE) is a statistical tool that provides solution to all the drawbacks that arise in the conventional one-factor-at-a-time approach. The design of experiments is a well planned and structured statistical approach for the smooth conduct of the experiments. 'Design-Expert 8.0.7.1' developed by 'Stat Ease' is used to structure the experiments and evaluate the optimum settings based on the results obtained through RSM. Analysis of variance (ANOVA) plays a crucial role in Design Expert software for analyzing experimental data and determining the significance of factors and interactions. Here the inputs or the factors are pH, conductivity, voltage, run time, temperature, concentration and agitation speed and each factor has seven levels. 'COD removal percentage' and 'Nitrogen removal percentage' are the responses in the experiment. Half fraction 'Central Composite Design (CCD)' is adopted to get the planned experimental design.

## 4. Results and discussion

### 4.1. Statistical analysis

Optimizing process and operational variables enhances the efficiency of the EC process. After conducting characterization studies, experimental data is analysed using Design Expert V13 software. CCD and ANOVA are employed under RSM for process development. After conducting the base experiments, consisting of 88 runs as designed in the Design Expert software, it



was observed that in the 12<sup>th</sup> run, the highest removal percentages of Ammoniacal Nitrogen and COD are achieved. In comparison, the lowest removal percentages of Ammoniacal Nitrogen and COD are observed in the 67<sup>th</sup> and 82<sup>nd</sup> runs. (Table 1). The results of CCD guide the development of empirical second-order polynomial models, where variables A-G represent pH, runtime, agitation speed, voltage, inter-electrode distance, temperature, and initial concentration of nitrogen, respectively (Table 2). Positive coefficients indicate favourable effects on process responses, while negative coefficients imply adverse effects. ANOVA analysis determines the statistical significance of the models, with "P" values consistently below 0.05, affirming their significance at a 95% confidence level after eliminating insignificant variables and interactions (Table 3).

#### 4.2 COD removal

The model F-value of 66.43 implies the model is significant (Table 4). There is only a 0.01% chance that an F-value this large could occur due to noise. A coefficient of determination ( $R^2$ ) of 0.9781 suggests that 97.81% of the variance in efficiency can be explained by the independent variables in RSM, indicating a strong correlation between observed and predicted values. The remaining 2.19% of the variance is unexplained. The adjusted  $R^2$  value of 0.9634 aligns well with  $R^2$ , suggesting a well-fitted statistical model. The Lack of Fit F-value of 1.74 implies the Lack of Fit

is not significant relative to the pure error. There is a 18.94% chance that a Lack of Fit F-value this large could occur due to noise. Low coefficients of variation (CV) at 1.53% demonstrate the model's dependability and reproducibility (Table 3). The model's adequate precision value at 32.5412 exceeds the desired threshold of 4, indicating that the signal-to-noise ratio is sufficient for navigating the desired space [6].

#### 4.3. Nitrogen removal

The model F-value of 64.78 implies the model is significant (Table 5). There is only a 0.01% chance that an F-value this large could occur due to noise. A coefficient of determination ( $R^2$ ) of 0.9776 suggests that 97.76% of the variance in efficiency can be explained by the independent variables in RSM, indicating a strong correlation between observed and predicted values. The remaining 3.24% of the variance is unexplained. The adjusted  $R^2$  value of 0.9625 aligns well with  $R^2$ , suggesting a well-fitted statistical model. The Lack of Fit F-value of 1.39 implies the Lack of Fit is not significant relative to the pure error. There is a 31.14% chance that a Lack of Fit F-value this large could occur due to noise. Low coefficients of variation (CV) at 1.51% demonstrate the model's dependability and reproducibility (Table 3). The model's adequate precision value at 31.4470 exceeds the desired threshold of 4, indicating that the signal-to-noise ratio is sufficient for navigating the desired space [6].

**Table 1.** Highest and lowest responses of central-composite design for the given factors (Out of total runs 88)

| Std Run No. | Variables |                |                           |                 |                                   |                      |                         | Responses       |                                 |
|-------------|-----------|----------------|---------------------------|-----------------|-----------------------------------|----------------------|-------------------------|-----------------|---------------------------------|
|             | pH (A)    | Time (min) (B) | Agitation speed (rpm) (C) | Voltage (V) (D) | Inter electrode distance (cm) (E) | Temperature (°C) (F) | Concentration (ppm) (G) | COD removal (%) | Ammoniacal nitrogen removal (%) |
| 12          | 7         | 85             | 225                       | 8               | 2                                 | 57                   | 40                      | 89.77**         | 88.92**                         |
| 67          | 8         | 40             | 300                       | 4               | 4                                 | 50                   | 20                      | 64.37           | 63.81*                          |
| 82          | 6         | 40             | 150                       | 4               | 4                                 | 50                   | 20                      | 63.48*          | 64.28                           |

\* Lowest value. \*\* Highest value.

**Table 2.** RSM models obtained for the responses.

| Response             | Equation with significant term                                                                                                                                                                                                                                                                                                                                                                                               |
|----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| COD removal (%)      | 86.22 +0.0098A +1.54B -0.3276C +2.89D -2.81E +1.20F +1.78G -0.1313AB -0.2234AC +0.0191AD +0.2313AE +0.1534AF +0.6544AG -0.3100BC -0.4031BD +0.3591BE -0.1912BF +0.4797BG -1.16CD +0.2825CE +0.3634CF -0.1213CG +0.5669DE -1.48DF +0.0725DG -0.4025EF -0.1784EG +0.0469FG -0.8528A <sup>2</sup> -3.49B <sup>2</sup> -0.7778C <sup>2</sup> -2.51D <sup>2</sup> -0.6778E <sup>2</sup> -0.3678F <sup>2</sup> -1.34G <sup>2</sup> |
| Nitrogen removal (%) | 85.92+0.0344A+1.83B-0.3718C+2.86D+2.56E+1.38F+1.85G-0.0533AB-0.3317AC-0.0814AD+0.1489AE+0.1083AF+0.7592AG+0.1067BC-0.2330BD+0.2961BE-0.1127BF+0.4264BG-1.29CD+0.1802CE+0.3989CF-0.1552CG+0.3367DE-1.37DF+0.0089DG-0.334EF-0.1789EG+0.0186FG-0.0676A <sup>2</sup> -3.24B <sup>2</sup> +0.2774C <sup>2</sup> -2.07D <sup>2</sup> -1.20E <sup>2</sup> -1.03F <sup>2</sup> -2.09G <sup>2</sup>                                   |

**Table 3** ANOVA results for the obtained regression equations.



| Response             | S. D | Mean  | C.V % | R <sup>2</sup> | Adjusted R <sup>2</sup> | Predicted R <sup>2</sup> | Adequate precision | P value model | F value model |
|----------------------|------|-------|-------|----------------|-------------------------|--------------------------|--------------------|---------------|---------------|
| COD removal (%)      | 1.21 | 78.71 | 1.53  | 0.9781         | 0.9634                  | 0.9319                   | 32.5412            | < 0.0001      | 66.43         |
| Nitrogen removal (%) | 1.19 | 78.86 | 1.51  | 0.9776         | 0.9625                  | 0.9299                   | 31.4470            | < 0.0001      | 64.78         |

Table 4. ANOVA table for COD removal percentage.

| Source            | Sum of Squares | df | Mean Square | F-value | p-value  |                 |
|-------------------|----------------|----|-------------|---------|----------|-----------------|
| <b>Model</b>      | 3392.73        | 35 | 96.94       | 66.43   | < 0.0001 | significant     |
| A-pH              | 0.0064         | 1  | 0.0064      | 0.0044  | 0.9474   |                 |
| B-Time            | 155.57         | 1  | 155.57      | 106.62  | < 0.0001 |                 |
| C-Agitation speed | 7.08           | 1  | 7.08        | 4.85    | 0.0320   |                 |
| D-Voltage         | 552.28         | 1  | 552.28      | 378.50  | < 0.0001 |                 |
| E-Distance        | 521.26         | 1  | 521.26      | 357.24  | < 0.0001 |                 |
| F-Temperature     | 94.61          | 1  | 94.61       | 64.84   | < 0.0001 |                 |
| G-Concentration   | 210.26         | 1  | 210.26      | 144.10  | < 0.0001 |                 |
| AB                | 1.10           | 1  | 1.10        | 0.7556  | 0.3887   |                 |
| AC                | 3.20           | 1  | 3.20        | 2.19    | 0.1450   |                 |
| AD                | 0.0233         | 1  | 0.0233      | 0.0159  | 0.9000   |                 |
| AE                | 3.42           | 1  | 3.42        | 2.35    | 0.1317   |                 |
| AF                | 1.51           | 1  | 1.51        | 1.03    | 0.3142   |                 |
| AG                | 27.41          | 1  | 27.41       | 18.78   | < 0.0001 |                 |
| BC                | 6.15           | 1  | 6.15        | 4.22    | 0.0451   |                 |
| BD                | 10.40          | 1  | 10.40       | 7.13    | 0.0101   |                 |
| BE                | 8.25           | 1  | 8.25        | 5.65    | 0.0211   |                 |
| BF                | 2.34           | 1  | 2.34        | 1.60    | 0.2109   |                 |
| BG                | 14.73          | 1  | 14.73       | 10.09   | 0.0025   |                 |
| CD                | 86.54          | 1  | 86.54       | 59.31   | < 0.0001 |                 |
| CE                | 5.11           | 1  | 5.11        | 3.50    | 0.0670   |                 |
| CF                | 8.45           | 1  | 8.45        | 5.79    | 0.0197   |                 |
| CG                | 0.9409         | 1  | 0.9409      | 0.6448  | 0.4256   |                 |
| DE                | 20.57          | 1  | 20.57       | 14.09   | 0.0004   |                 |
| DF                | 140.01         | 1  | 140.01      | 95.95   | < 0.0001 |                 |
| DG                | 0.3364         | 1  | 0.3364      | 0.2305  | 0.6331   |                 |
| EF                | 10.37          | 1  | 10.37       | 7.11    | 0.0102   |                 |
| EG                | 2.04           | 1  | 2.04        | 1.40    | 0.2427   |                 |
| FG                | 0.1406         | 1  | 0.1406      | 0.0964  | 0.7575   |                 |
| A <sup>2</sup>    | 1.69           | 1  | 1.69        | 1.16    | 0.2866   |                 |
| B <sup>2</sup>    | 28.37          | 1  | 28.37       | 19.45   | < 0.0001 |                 |
| C <sup>2</sup>    | 1.41           | 1  | 1.41        | 0.9643  | 0.3306   |                 |
| D <sup>2</sup>    | 14.63          | 1  | 14.63       | 10.02   | 0.0026   |                 |
| E <sup>2</sup>    | 1.07           | 1  | 1.07        | 0.7323  | 0.3961   |                 |
| F <sup>2</sup>    | 0.3146         | 1  | 0.3146      | 0.2156  | 0.6443   |                 |
| G <sup>2</sup>    | 4.16           | 1  | 4.16        | 2.85    | 0.0972   |                 |
| <b>Residual</b>   | 75.87          | 52 | 1.46        |         |          |                 |
| Lack of Fit       | 67.74          | 43 | 1.58        | 1.74    | 0.1894   | not significant |
| Pure Error        | 8.14           | 9  | 0.9044      |         |          |                 |
| <b>Cor Total</b>  | 3468.61        | 87 |             |         |          |                 |

**Table 5.** ANOVA table for Nitrogen removal percentage.

| Source            | Sum of Squares | df | Mean Square | F-value | p-value  |                 |
|-------------------|----------------|----|-------------|---------|----------|-----------------|
| <b>Model</b>      | 3208.59        | 35 | 91.67       | 64.78   | < 0.0001 | significant     |
| A-pH              | 0.0781         | 1  | 0.0781      | 0.0552  | 0.8152   |                 |
| B-Time            | 221.50         | 1  | 221.50      | 156.52  | < 0.0001 |                 |
| C-Agitation speed | 9.12           | 1  | 9.12        | 6.45    | 0.0141   |                 |
| D-Voltage         | 539.40         | 1  | 539.40      | 381.14  | < 0.0001 |                 |
| E-distance        | 432.38         | 1  | 432.38      | 305.52  | < 0.0001 |                 |
| F-Temperature     | 126.58         | 1  | 126.58      | 89.44   | < 0.0001 |                 |
| G-Concentration   | 225.18         | 1  | 225.18      | 159.11  | < 0.0001 |                 |
| AB                | 0.1817         | 1  | 0.1817      | 0.1284  | 0.7216   |                 |
| AC                | 7.04           | 1  | 7.04        | 4.98    | 0.0300   |                 |
| AD                | 0.4241         | 1  | 0.4241      | 0.2997  | 0.5864   |                 |
| AE                | 1.42           | 1  | 1.42        | 1.00    | 0.3213   |                 |
| AF                | 0.7504         | 1  | 0.7504      | 0.5302  | 0.4698   |                 |
| AG                | 36.89          | 1  | 36.89       | 26.07   | < 0.0001 |                 |
| BC                | 0.7289         | 1  | 0.7289      | 0.5150  | 0.4762   |                 |
| BD                | 3.47           | 1  | 3.47        | 2.45    | 0.1233   |                 |
| BE                | 5.61           | 1  | 5.61        | 3.96    | 0.0517   |                 |
| BF                | 0.8123         | 1  | 0.8123      | 0.5739  | 0.4521   |                 |
| BG                | 11.64          | 1  | 11.64       | 8.22    | 0.0060   |                 |
| CD                | 105.81         | 1  | 105.81      | 74.76   | < 0.0001 |                 |
| CE                | 2.08           | 1  | 2.08        | 1.47    | 0.2312   |                 |
| CF                | 10.18          | 1  | 10.18       | 7.20    | 0.0098   |                 |
| CG                | 1.54           | 1  | 1.54        | 1.09    | 0.3016   |                 |
| DE                | 7.26           | 1  | 7.26        | 5.13    | 0.0277   |                 |
| DF                | 119.71         | 1  | 119.71      | 84.59   | < 0.0001 |                 |
| DG                | 0.0051         | 1  | 0.0051      | 0.0036  | 0.9525   |                 |
| EF                | 7.18           | 1  | 7.18        | 5.07    | 0.0286   |                 |
| EG                | 2.05           | 1  | 2.05        | 1.45    | 0.2344   |                 |
| FG                | 0.0221         | 1  | 0.0221      | 0.0156  | 0.9010   |                 |
| A <sup>2</sup>    | 0.0106         | 1  | 0.0106      | 0.0075  | 0.9313   |                 |
| B <sup>2</sup>    | 24.38          | 1  | 24.38       | 17.23   | 0.0001   |                 |
| C <sup>2</sup>    | 0.1790         | 1  | 0.1790      | 0.1265  | 0.7235   |                 |
| D <sup>2</sup>    | 9.99           | 1  | 9.99        | 7.06    | 0.0104   |                 |
| E <sup>2</sup>    | 3.34           | 1  | 3.34        | 2.36    | 0.1308   |                 |
| F <sup>2</sup>    | 2.48           | 1  | 2.48        | 1.75    | 0.1914   |                 |
| G <sup>2</sup>    | 10.14          | 1  | 10.14       | 7.16    | 0.0099   |                 |
| <b>Residual</b>   | 73.59          | 52 | 1.42        |         |          |                 |
| Lack of Fit       | 63.96          | 43 | 1.49        | 1.39    | 0.3114   | not significant |
| Pure Error        | 9.63           | 9  | 1.07        |         |          |                 |
| <b>Cor Total</b>  | 3282.18        | 87 |             |         |          |                 |

Cor total = Corrected Total Sum of Squares.

#### 4.4 Process performance

Using RSM, the impact of seven independent operational variables pH, voltage, runtime, agitation speed, inter-electrode distance, temperature, and initial concentration of ammoniacal nitrogen as well as how they interact with one another on the removal of COD

and nitrogen are evaluated. The RSM approach makes it easy to understand how operational variables interact.

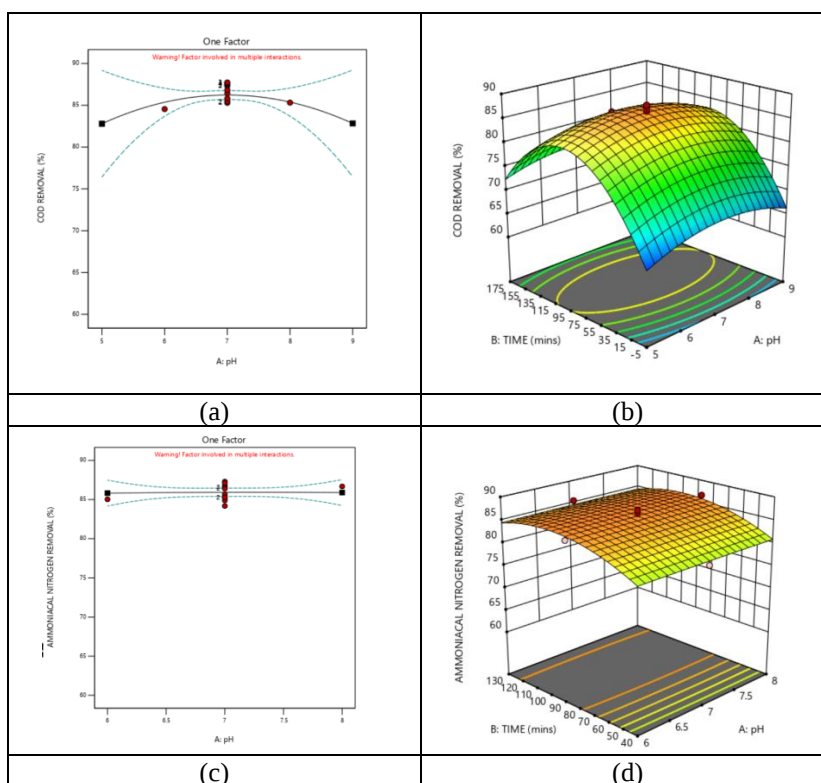
##### 4.4.1 Effect of pH

The efficiency of electrocoagulation in removing COD and nitrogen is significantly influenced by pH [7]. Highest COD removal is identified when the pH is 7, with a corresponding runtime 85 minutes (Fig.4b). In



the EC process, if the wastewater pH is below 7, it tends to increase afterward, while an initial pH above 8 results in a decrease after electrocoagulation. This observation confirms the pH buffering nature of the electrocoagulation process. The removal percentage of COD exhibits an ascending curve when the pH is below 7, reaching its maximum 86.58% at pH 7 (Fig. 4a). Subsequently, the efficiency decreases for pH values

greater than 7, with the lowest recorded at pH 5 is 77.35%. The maximum nitrogen removal is observed when pH ranging 6.5 to 7, runtime is ranging around 80 to 110 min (Fig.4d). The nitrogen removal percentage follows an ascending trend from lower to higher pH values. At pH 5, the lowest nitrogen removal percentage is recorded as 78.72%, while at pH 7, the removal percentage is 87.63%. (Fig.4c).



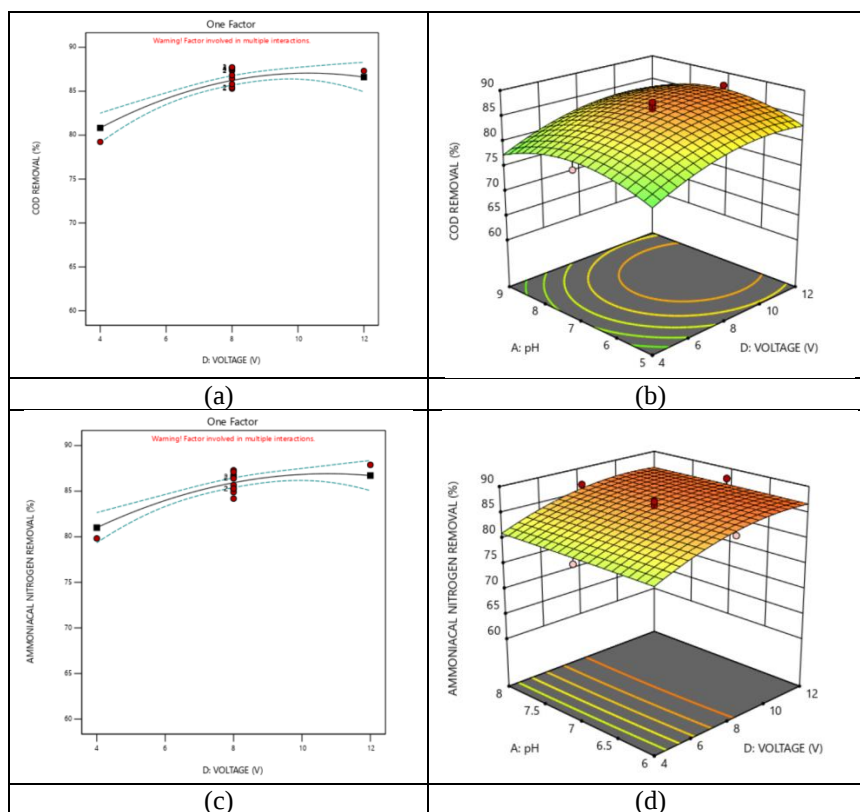
**Fig.4.** Response surface (RS) plots for the effect of pH on COD removal % (a, b), Ammoniacal nitrogen removal % (c, d)

#### 4.4.2. Effect of voltage

A key parameter affecting EC efficiency is current density, which is the current, applied per effective electrode surface area [8]. Highest COD removal percentage is identified when the voltage range is 10 to 12 V, with pH of 7 (Fig. 5b). At a cell voltage of 4.0 V, COD removal 67.35 %. These values increase to 90.58 % at a cell voltage of 12 V (Fig.5a.). The optimal cell voltage for COD removal is determined to be 8 V. The peak efficiency for nitrogen removal is evident when the values for pH and voltage fall within the range of 6.5 to 7.5 and 8.0 to 12 V respectively (Fig.5d). As cell voltage is increased from 4 to 12 V, nitrogen removal increased from 68.62 % to 91.33 % (Fig.5c). The optimal cell voltage for nitrogen removal is found to be 8 V, with a removal percentage of 87.72%.

#### 4.4.3 Effect of Runtime

The efficiency of pollutant removal relies significantly on the duration of EC operation [9]. Extended operation durations result in a higher rate of pollutant removal by generating more metal coagulants and flocs at a constant current density. Maximum COD removal percentage can be found when the agitation speed range is 240 to 270 rpm and the EC time is between 75 and 95 minutes (Fig.6b). A runtime increases, the COD removal increases (Fig. 6a). After 30 minutes, the COD removal is 79.51%. During the 130 minutes maximum runtime, the COD removal is found to be 91.89%. The optimal nitrogen removal identified when the run time ranges from 78 to 110 minutes, and the agitation speed is between 210 and 240 rpm (Fig.6d).



**Fig. 5.** Response surface (RS) plots for the effect of voltage on COD removal % (a, b), Ammoniacal nitrogen removal % (c, d)

The nitrogen removal after 30 minutes is 79.51%. The removal of nitrogen increased to 92.41% in the course of 110 minutes runtime (Fig. 6c).

#### 4.4.4 Effect of Agitation speed

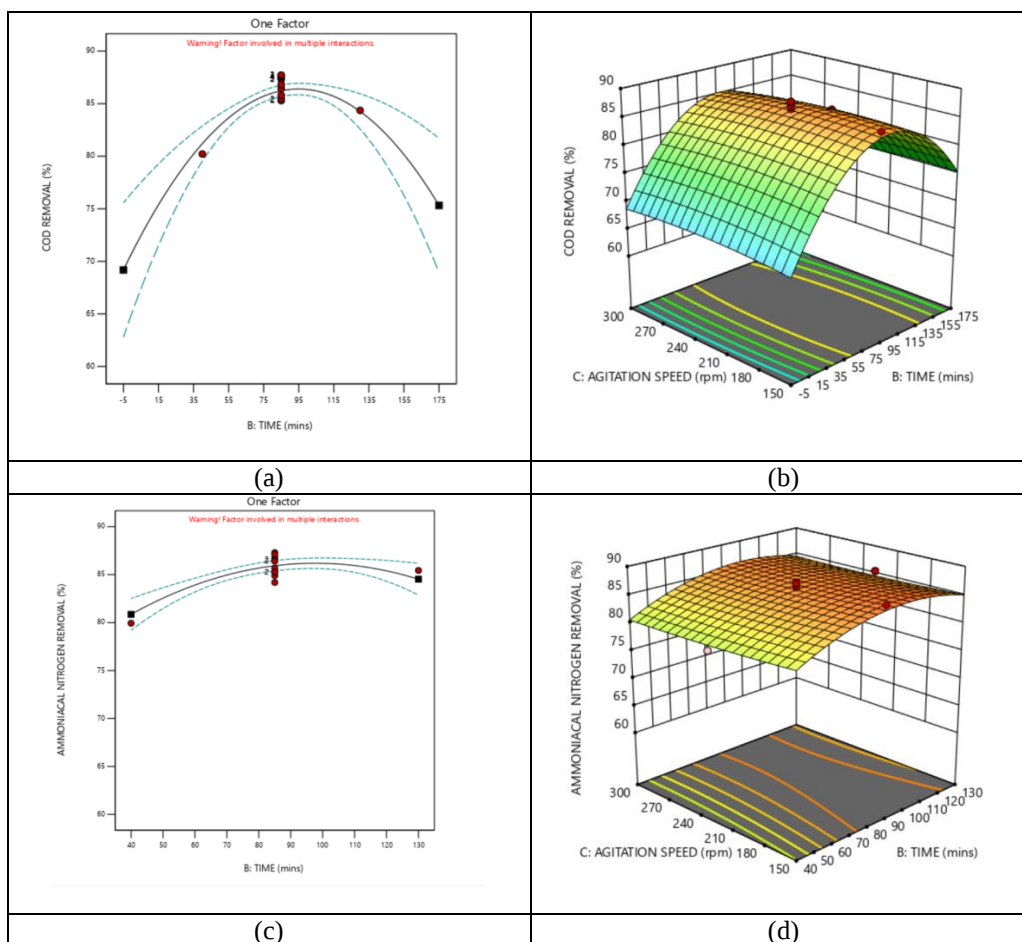
Stirring speed is essential in EC to achieve uniformity in the reactor mixture and accelerate the rate of pollutant removal through agitation [10]. The RS plots a & b reveal the effect of agitation speed on the removal of COD (Fig. 7). COD removal is 67.18% at 150 rpm stirring (Fig. 7a). The maximum COD removal is 90.26% at 250 rpm and at 350 rpm, it is 73.69%. Beyond 250 rpm the rate of COD removal gradually declined. The optimal range for maximizing nitrogen removal for agitation speed 150 to 250 rpm, pH 6.5 to 7 (Fig. 7d). The RS plots c & d evaluate how agitation speed affects the removal of nitrogen. At 250 rpm nitrogen removal peaks at 89.47%. As speed of agitation is increased further, the removal of nitrogen decreased continuously to reach 75.23% at 350 rpm.

#### 4.4.5 Effect of inter-electrode distance

The distance between electrodes is crucial in electrocoagulation (EC), influencing the electrostatic field between the anode and cathode [12]. Maximum COD removal percentage can be found when the distance is between 3 and 3.5 cm and the pH is 7 (Fig. 8b). The optimal range for maximizing nitrogen removal is identified at pH ranging 6.5 to 7; inter electrode distance 2 to 3 cm (Fig. 8d). The removal percentages of COD and nitrogen at a distance of 2 cm are 89.35% and 89.21%, respectively. The removal of nitrogen dropped to 87.53% and the COD decreased to 87.92% at a distance of 3 cm. At a distance of 5 cm, the removal efficiencies of COD and nitrogen are 80.5% and 81.28%, respectively (Fig. 8a and 8c).

#### 4.4.6 Effect of temperature

Temperature is always considered an important parameter in any chemical or electrochemical separation process [8, 11]. Highest COD removal percentage is identified when the temperature is between 58 to 60 °C, with pH of 7 (Fig. 9b). At temperature of 50 °C, COD removal 86.23%.

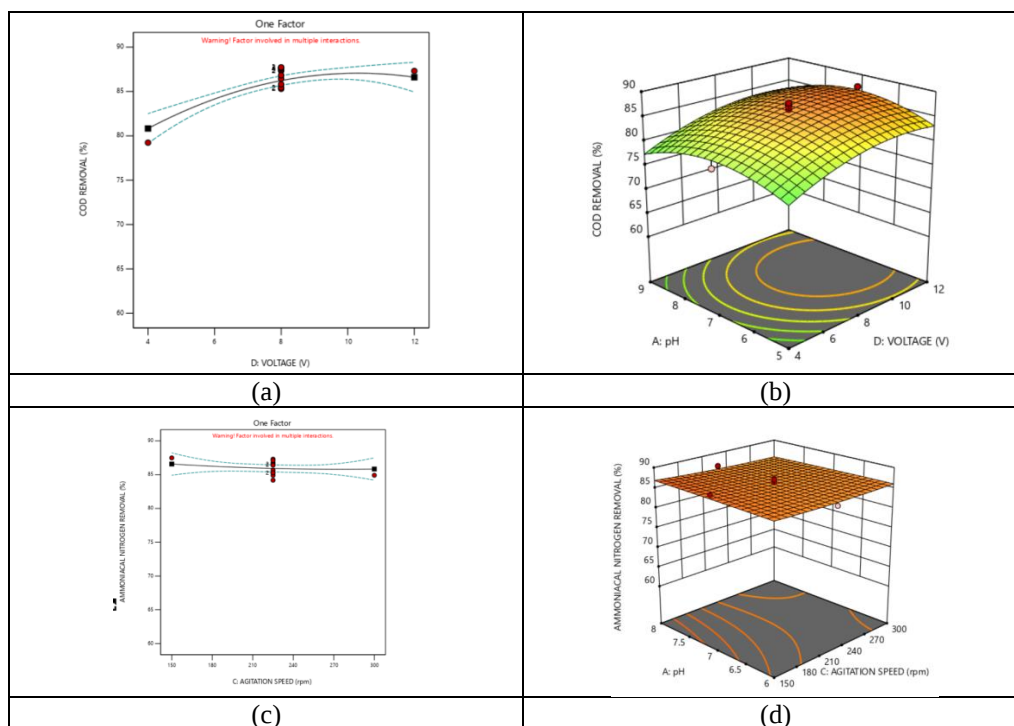


**Fig. 6.** Response surface (RS) plots for the effect of runtime on COD removal % (a, b), Ammoniacal nitrogen removal % (c, d)

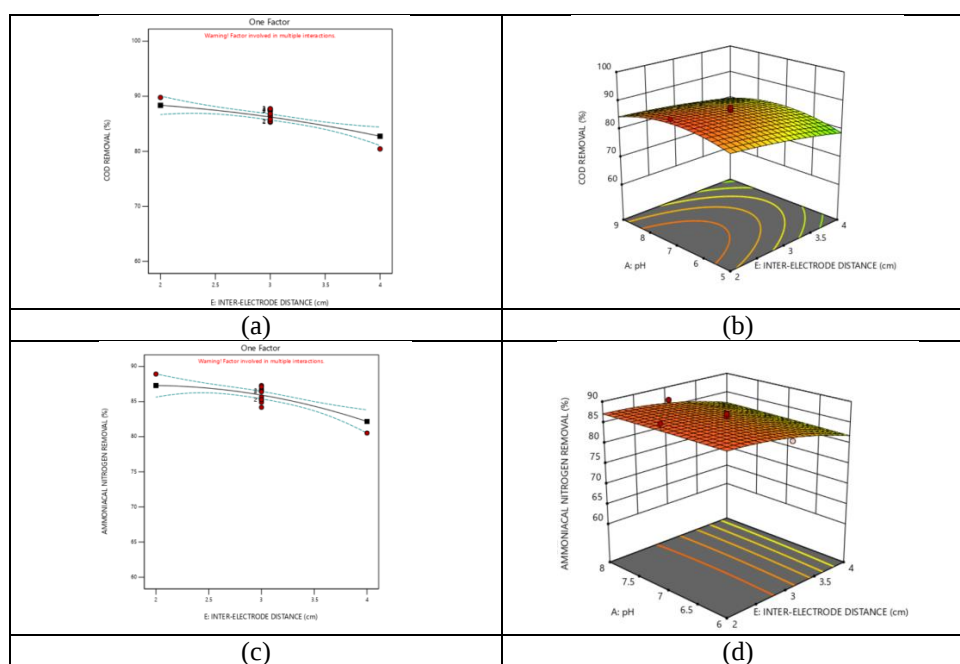
These values increase to 90.23 % at temperature of 54°C (Fig. 9a.). The optimal temperature for COD removal is determined to be 54°C. The peak efficiency for nitrogen removal is evident in the RS plot when the values. for pH and temperature fall within the range of 6.5 to 7.5 and 54 to 58 °C, respectively (Fig. 9d). As temperature is increased from 50 to 54 °C, nitrogen removal increased from 86.91% to 90.41% (Fig. 9c). The optimal temperature for nitrogen removal is found to be 54°C, with a removal percentage of 90.41%.

#### 4.4.7 Effect of concentration

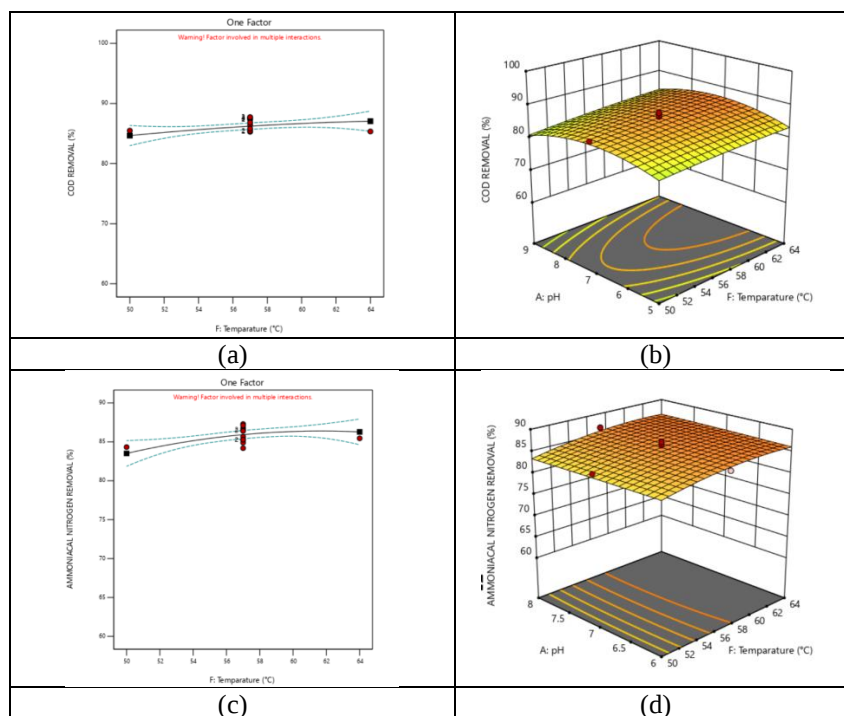
The concentration of contaminants in wastewater plays a vital role in electrocoagulation [12]. Highest COD removal percentage is identified when the concentration of nitrogen is 40 to 50 ppm, with pH of 7 (Fig. 10b). At concentration of nitrogen at 12 ppm, COD removal 74.31%. These values increase to 90.31% at concentration of nitrogen of 60 ppm (Fig.10a.). The peak efficiency for nitrogen removal is evident for pH and concentration of nitrogen fall within the range of 6 to 7.5 and 40 to 60 ppm respectively (Fig. 10d). As concentration of nitrogen is increases from 12 to 60 ppm, nitrogen removal increases from 75.53 to 91.86 % (Fig. 10c). For an initial concentration of nitrogen 60 ppm nitrogen removal is found to be 91.86%.



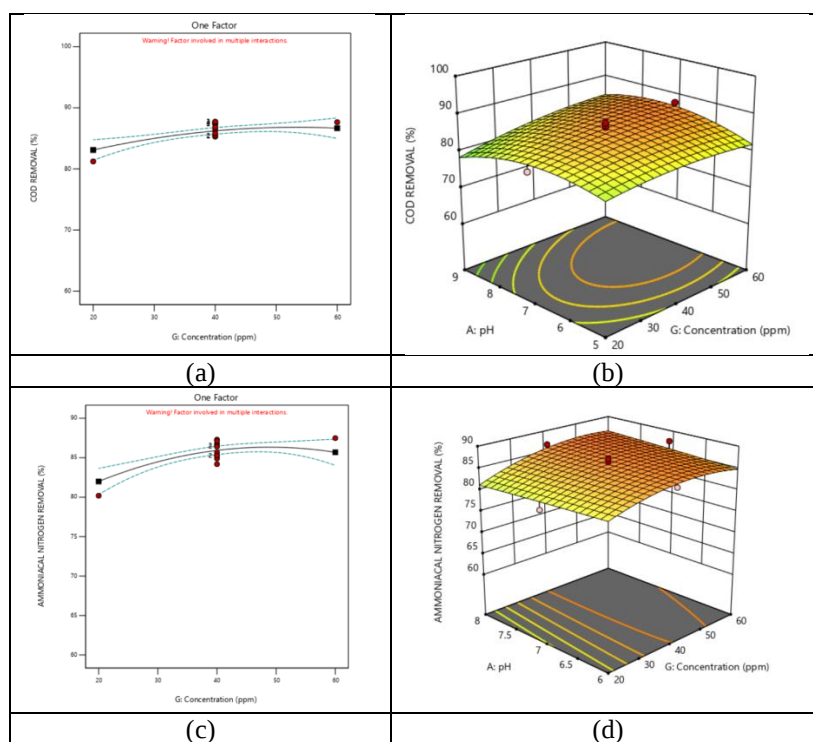
**Fig. 7.** Response surface (RS) plots for the effect of agitation speed on COD removal % (a, b), Ammoniacal nitrogen removal % (c, d)



**Fig. 8.** Response surface (RS) plots for the effect of inter-electrode distance on COD removal % (a, b), Ammoniacal nitrogen removal % (c, d)



**Fig. 9.** Response surface (RS) plots for the effect of temperature on COD removal % (a, b), Ammoniacal nitrogen removal % (c, d)



**Fig. 10.** Response surface (RS) plots for the effect of initial concentration of ammoniacal nitrogen on COD removal % (a, b), Ammoniacal nitrogen removal % (c, d)



#### 4.5 Process optimization

Post-analysis allows for the determination of the process optimization. The optimal factors are found

after post-analysis (Table 6), and these factors when tested in three trial runs produced units better than predicted by the models (Table 7).

**Table 6.** Optimization factors are given by RSM.

| S. No | pH | Time (min) | Agitation speed (rpm) | Voltage (v) | Inter-electrode distance (cm) | Temperature (°C) | Initial Concentration of ammoniacal nitrogen (ppm) |
|-------|----|------------|-----------------------|-------------|-------------------------------|------------------|----------------------------------------------------|
| 1     | 7  | 85         | 225                   | 8           | 3                             | 57               | 40                                                 |

#### 4.6 Validation and verification of predictive model

It is necessary to confirm and test the model equation's dependability. The ideal values for the independent variables are determined once the model has been refined. After entering the target replies, anticipated ideal response values are produced. The response values must be adjusted for optimal efficiency [12]. By using the operational parameters produced by the model to

execute the experimental runs, the COD and nitrogen removal efficiencies predicted by the model are confirmed and validated. The actual or experimental response values and the expected response values for the specified operational parameters are determined to be reasonably in accord. These results confirmed the adequacy of the derived regression model in reflecting the expected optimization (Table 7).

**Table 7.** Predicted and actual experimental values of COD and Nitrogen removal percentage.

| Std. Run No. | pH | Run Time (min s) | Agitation Speed (rpm) | Voltage (V) | Inter electrode distance (cm) | Temperature (°C) | Concentration (ppm) | COD removal % (P) | COD removal % (O) | Nitrogen removal % (P) | Nitrogen removal % (O) |
|--------------|----|------------------|-----------------------|-------------|-------------------------------|------------------|---------------------|-------------------|-------------------|------------------------|------------------------|
| 1            | 7  | 85               | 225                   | 8           | 3                             | 57               | 40                  | 86.22             | 88.34             | 85.92                  | 86.61                  |
| 2            | 7  | 85               | 225                   | 8           | 3                             | 57               | 40                  | 86.22             | 86.27             | 85.92                  | 85.03                  |
| 3            | 7  | 85               | 225                   | 8           | 3                             | 57               | 40                  | 86.22             | 87.45             | 85.92                  | 86.89                  |

#### 4.7 Energy consumption

Energy consumption is highly dependent on voltage and runtime. The energy consumption value for the

optimized experimental condition is 2.89 KWh/m<sup>3</sup>. The operational cost will be economical, if the energy consumption is low (Table 8).

**Table 8.** Electrical energy consumption in KWh/m<sup>3</sup> at the optimized experimental conditions.

| Std. Run No. | Voltage (V) | Current (A) | Runtime (min) | Treated volume (m <sup>3</sup> ) | Energy consumption (KWh/m <sup>3</sup> ) |
|--------------|-------------|-------------|---------------|----------------------------------|------------------------------------------|
| 1            | 8           | 0.85        | 85            | 0.002                            | 2.89                                     |

#### 4.8 Treatment of municipal wastewater from Nadimivanka an open channel of Ananthapuramu city in Andhra Pradesh

The urban wastewater is sampled from a natural drain called 'Nadimivanka' passing through the centre of Ananthapuramu city in Andhra Pradesh (14.684303°, 77.587821°).

The electrocoagulation process is conducted at the optimized process conditions. The ammoniacal nitrogen decreased from initial concentration of 24.2 mg/l to 4.8 mg/l with 80.17% removal. The COD decreased from initial concentration of 561.03 mg/l to 84.38mg/l with 84.96% removal (Table 9).

**Table 9.** Ananthapuramu Municipal Wastewater Characteristics.

| Std. Run No. | pH | Run Time (mins) | Agitation Speed (rpm) | Voltage (V) | Inter electrode distance (cm) | Temperature (°C) | Concentration (ppm) | COD removal % | Nitrogen removal % |
|--------------|----|-----------------|-----------------------|-------------|-------------------------------|------------------|---------------------|---------------|--------------------|
| 1            | 7  | 85              | 225                   | 8           | 3                             | 57               | 40                  | 85.32         | 81.23              |
| 2            | 7  | 85              | 225                   | 8           | 3                             | 57               | 40                  | 85.12         | 80.61              |
| 3            | 7  | 85              | 225                   | 8           | 3                             | 57               | 40                  | 84.96         | 80.17              |

## 5. Conclusion

A comprehensive study on urban wastewater treatment employing an electrocoagulation (EC) cell through the systematic application of central composite design and response surface methodology (RSM), identified and optimized key factors influencing the treatment process. The critical parameters affecting wastewater treatment were determined to be initial pH, voltage, runtime, temperature, concentration, and inter-electrode distance. Rigorous experimentation led to the establishment of optimized conditions, specifically: pH 7, voltage 8 V, runtime 85 minutes, agitation speed 225 rpm, temperature 57°C, initial concentration of ammoniacal nitrogen 40 ppm, and inter-electrode distance 3 cm.

Application of these optimized parameters to Ananthapuramu municipal wastewater yielded remarkable results, with removal efficiencies reaching 80.17% for Ammoniacal Nitrogen and 84.96% for Chemical Oxygen Demand (COD). These outcomes not only underscore the efficacy of the batch electrocoagulation method but also demonstrate its ability to meet the stringent norms set by the Central Pollution Control Board (CPCB), Government of India for the release of treated wastewater into natural water bodies. In essence, this work contributed valuable insight into field of urban wastewater treatment, adopting a systematic approach for optimizing electrocoagulation process. The success achieved in meeting regulatory standards further emphasizes the potential applicability of this method in addressing the pressing environmental challenges associated with wastewater discharge.

## Acknowledgment

The authors would like to acknowledge JNT University Anantapur, Ananthapuramu, Andhra Pradesh, India for the financial support provided for this research work under the Research Seed Grant (RSG) scheme.

## References

- Shweta Kumari and R. Naresh Kumar. Electrocoagulation for COD, turbidity, ammonia, and phosphate removal from municipal wastewater. *J. Indian Chem. Soc.*, Vol. 97, April 2020, pp. 527-532
- Raj N.Desai, Dr. D S. Vyas. Removal of Ammonical Nitrogen by Electrocoagulation Method. *IJARIE-ISSN(O)-2395-4396*, Vol-2 Issue-3 2016.
- Umesh Ghimire, Min Jang. Electrochemical Removal of Ammonium Nitrogen and COD of Domestic Wastewater using Platinum Coated Titanium as an Anode Electrode. *Energies* 2019, 12, 883; doi:10.3390/en12050883.
- Edwar Aguilar-Ascon. Removal of Nitrogen and Phosphorus from Domestic Wastewater by Electrocoagulation: Application of Multilevel Factorial Design. Volume 21, Issue 7, October 2020, <https://doi.org/10.12911/22998993/125439>.
- Bharath M, Krishna B M and Manoj Kumar B. A Review of Electrocoagulation Process for Wastewater Treatment. *International Journal of ChemTech Research CODEN (USA): IJCRGG*, ISSN: 0974-4290, ISSN(Online):2455-9555 Vol.11 No.03, pp 289-302, 2018.
- Adjeroud, Nawel, et al. "Improvement of electrocoagulation-electroflotation treatment of effluent by addition of *Opuntia ficus indica* pad juice." *Separation and Purification Technology* 144 (2015): 168-176.
- Amina Tahreen, Mohammed Saedi Jami, Fathilah Ali. Role of electrocoagulation in wastewater treatment: A developmental review. *Journal of Water Process in Engineering* <https://doi.org/10.1016/j.jwpe.2020.101440>
- A. Ronaldo Anuf, K. Ramaraj, Vishnu Sankar Siva Sankara pillai, Ragupathy Dhanusuraman b, J. Prakash Maran, G. Rajeshkumar, Abbas Rahdar, Ana M. Díez-Pascual. Optimization of



- electrocoagulation process for treatment of rice mill effluent using response surface methodology. *Journal of Water Process in Engineering* <https://doi.org/10.1016/j.jwpe.2022.103074>
9. Guohua Chen. Electrochemical technologies in wastewater treatment. 1383-5866/\$ – see front matter © 2003 Elsevier B.V. All rights reserved. doi:10.1016/j.seppur.2003.10.006.
  10. P.I. Omwene, M. Koby. Treatment of domestic wastewater phosphate by electrocoagulation using Fe and Al electrodes: A comparative study. *Process Safety and Environmental Protection* 116 (2018) 34-51. <https://doi.org/10.1016/j.psep.2018.01.005>
  11. Yani Zhao, Liling Zhang, Meng Zhang, Jingya Wu, Shuping Li, Douzhi Ran, Liwei Sun and Guangcan Zhu. Effect of Chemical Oxygen Demand Concentration on Nutrient Removal in Simultaneous Nitrification, Denitrification, and Phosphorus Removal Systems in High-Altitude Areas. *Water* 2021, 13, 2656. <https://doi.org/10.3390/w13192656>
  12. A. Attour. Influence of operating parameters on phosphate removal from water by electrocoagulation using aluminum electrodes. *Separation and Purification Technology*. <http://dx.doi.org/10.1016/j.seppur.2013.12.030>.