Article

Modelling the impact of inter-electrode spacing on nitrate removal using Response Surface Methodology

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Abstract: Nitrate contamination in water poses a significant concern for environmental engineers, as it has substantial and direct impacts on water quality, the economy, and public health. Consequently, managing nitrate levels in water sources ranks among the top priorities for water authorities. Currently, various treatment methods, including biological treatments and adsorption, are employed to eliminate nitrate from water or wastewater. A substantial body of literature focuses on applying electrocoagulation (EC) for nitrate removal from solutions. This method is favoured for its environmentally friendly attributes and ability to swiftly and cost-effectively remove pollutants. In this study, the EC method was employed to eliminate nitrate from water under varying inter-electrode spacing (I-ES) conditions ranging from 4 to 10 mm and different treatment durations (TD) spanning 5 to 55 minutes. The effects of I-ES and TD on nitrate removal were optimised using Response Surface Methodology (RSM). The study's results demonstrated that the most effective nitrate removal, reaching 91.3%, occurred at an I-ES of 4 mm and a TD of 50 minutes. The agreement between the experimentally observed and predicted removal rates was notably high, with an R^2 value of 0.973.

Keywords: Nitrate; removal; inter-electrode spacing; model; RSM.

1. Introduction

The presence of nitrate contamination in water typically emerges from the natural decomposition of organic matter, an intrinsic process that gradually introduces nitrate pollution into freshwater environments, traditionally at low concentrations. However, a significant shift has occurred in this ecological balance in recent decades. This change can be attributed to the discharge of industrial wastewater, predominantly stemming from human activities – a category known as anthropogenic sources. These wastewater discharges contain notably high levels of nitrogen-based pollutants, presenting a stark departure from the gradual, sustainable release of nitrates in nature [1,2].

The upsurge in nitrate concentrations due to anthropogenic activities has raised considerable environmental and human health concerns. Anthropogenic sources encompass a wide array of industrial processes, including manufacturing, mining, and chemical

production, all generate wastewater laden with nitrogen compounds. Additionally, the agricultural sector contributes substantially to nitrate pollution by extensively using nitrogen-based fertilisers. Runoff from agricultural lands and the leaching of nitrates from soils can introduce substantial quantities of nitrates into nearby water bodies [1,2].

Examples of human-made sources include using nitrogen-based fertilisers in agriculture, using animal waste, and releasing wastewater from both residential and industrial sources. While nitrates are not directly responsible for health issues like "blue baby syndrome," they are significant contributors to many environmental problems [3,4]. For instance, elevated levels of nitrates or phosphates in water can lead to the eutrophication of freshwater ecosystems, resulting in severe water quality degradation. This phenomenon occurs because it rapidly depletes dissolved oxygen by decomposing organic matter in the water. Moreover, the reduced availability of freshwater in rivers and lakes due to climate change exacerbates the concentration of nitrates and other pollutants in these bodies of water [3,5].

Aside from the previously mentioned concerns, nitrates are generally considered safe at reasonable concentrations, with recommended limits set at less than 50 mg/L for adults and 15 mg/L for infants. However, the biological conversion of nitrates into nitrites introduces additional health risks, including conditions such as methemoglobinemia in infants and pregnant women and potential associations with various types of cancer [6-8].

In response to these pressing health concerns, the World Health Organization (WHO) has taken a decisive step by establishing a maximum allowable nitrate concentration in drinking water, with the limit firmly set at 50 mg/L. This regulatory measure aims to safeguard public health by ensuring that nitrate levels in drinking water remain within safe and acceptable ranges. To address the imperative of nitrate removal from water sources, various methodologies have been implemented, driven by the dual goal of mitigating both environmental and health hazards. These diverse methods encompass cutting-edge technologies such as membrane technology, chemical treatment processes, adsorption techniques, and biological digestion mechanisms. However, many traditional nitrate removal techniques grapple with significant limitations despite the available options. For example, membrane technology, while effective, often proves financially burdensome and results in the concentration of nitrates in a separate stream that demands further treatment before disposal. Though efficient, chemical nitrate removal relies on additives that can bear environmental consequences, and the sludge produced in this process can pose a hazard to ecosystems. Meanwhile, while environmentally friendly, biological nitrate removal operates at a slower pace and necessitates an additional disinfection step to eliminate discharged bacteria [9,10]. These challenges have spurred a quest for innovative and sustainable nitrate removal methods that can better address the complex interplay of health and environmental concerns.

Hence, the EC technique is employed for eliminating various contaminants, including heavy metals, fluoride, organic substances, and biological pollutants [11-14]. As a result, the EC method is chosen for use in this research to eliminate nitrate from synthetic water. The study incorporates the Box-Behnken Design method (BBD) to optimise the impact of three variables: the pH of synthetic water (pHSW) within the range of 6 to 10, the duration of electrolysis (ET) ranging from 20 to 80 minutes, and the current density (CD) varying from 1 to 3 mA/cm2 on the removal of nitrate.

2. Materials and Methods

The EC setup employed in this research is depicted in Figure 1 and comprises a glass container with a total capacity of 2000 cm^3. This container is outfitted with four aluminium electrodes, each measuring 20 cm by 10 cm. These electrodes are partially submerged in the water within the container. To enhance the treatment process and ensure thorough mixing, the container is placed on a magnetic stirrer, which operates at a consistent speed of 150 rpm.

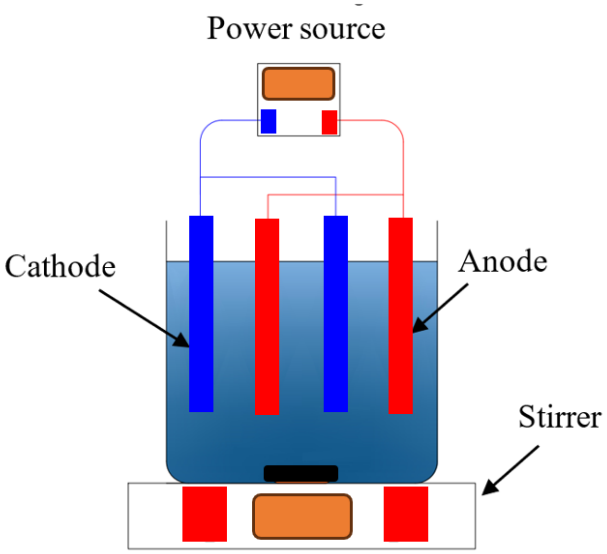

Figure 1. The EC cell.

In the electrocoagulation procedure, the electrodes are connected to a direct current (DC) power source, which delivers the requisite electric current to initiate the electrolysis. Two of the four electrodes serve as anodes, while the remaining two function as cathodes. The selection of aluminium electrodes is deliberate, as aluminium offers the dual advantages of cost-effectiveness and the provision of essential coagulants necessary for efficient nitrate removal [42].

In this study, the nitrate solution was meticulously prepared by precisely blending the required quantity of KNO_3, sourced from Sigma Aldrich in Germany, with deionised water, resulting in a precisely 100 mg/L nitrate concentration. Following this precise preparation, the solution was promptly transferred into the glass container of the electrocoagulation (EC) cell and the treatment process was executed strictly to the predefined experimental design, which incorporated controlled variations in I-ES and TD. The pH of the solution was adjusted to 6, ensuring precise control over this crucial parameter.

The EC experiments were rigorously planned and executed, employing the well-established Central Composite Design methodology. The primary objective was to optimise the influences of I-ES, with a range spanning from 4 to 9 mm and TD spanning from 10 to 50 minutes, all aimed at achieving the efficient removal of nitrate from the water sample. This optimisation process was conducted with the indispensable assistance of Minitab software, enabling a thorough and systematic assessment of the various experimental parameters. The outcomes of this optimisation process, including the minimum, mean, and maximum values for each pivotal factor, are meticulously documented in Table 1.

Table 1. Values of the studied parameters.

Run	I-ES (mm)	TD (min)
1	4.00	50.00
2	4.00	10.00
3	6.50	30.00
4	6.50	30.00
5	6.50	30.00
6	6.50	30.00
7	2.96	30.00
8	9.00	10.00
9	6.50	58.28
10	9.00	50.00
11	6.50	1.72
12	10.04	30.00
13	6.50	30.00

The experimental procedures applied a constant current density of 5 mA/cm^2 and an initial pH of 6. The evaluation of nitrate removal entailed the periodic collection of samples from the electrocoagulation (EC) cell, typically at 5-minute intervals. To ensure the accuracy of spectrophotometric measurements, these collected samples underwent an initial filtration step using a 0.45µm filter, effectively separating any floc or particulate matter in the samples.

Subsequently, the resulting clarified water samples were tested using a Hach Spectrophotometer (DR3900), a renowned instrument known for its precision and reliability in this specific analytical context. The efficiency of nitrate removal was precisely quantified using a dedicated equation, Eq. 1.

$$Re\% = \frac{Initial\ nitrate\ concentration - Measured\ nitrate\ concentration}{Initial\ nitrate\ concentration} \times 100 \qquad (1)$$

3. Results

The required experiments to determine nitrate removal by the EC cell were run by applying a constant current density via the DC power source and the initial pH of the solution. At the same time, the rest of the parameters (I-ES and TD) were changed according to Table 1, which was produced using Minitab software.

The removals of nitrate were measured and recorded in Table 2.

Table 2. Values of the studied parameters.

Run	**I-ES (mm)**	**TD (min)**	**Re%**
1	4.00	50.00	91.35
2	4.00	10.00	53.35
3	6.50	30.00	60.6
4	6.50	30.00	59.95
5	6.50	30.00	60.95
6	6.50	30.00	61.35
7	2.96	30.00	84.35
8	9.00	10.00	12.85

9	6.50	58.28	82.1
10	9.00	50.00	60.85
11	6.50	1.72	6.35
12	10.04	30.00	49.05
13	6.50	30.00	60.55

The results presented compelling evidence of a direct relationship between nitrated removal and treatment time (TD) and an inverse correlation with inter-electrode spacing (I-ES). Specifically, as TD increases and I-ES decreases, nitrated removal efficiency shows a noticeable and significant improvement. Notably, the most notable nitrate removal efficiency recorded was 91.35%, a remarkable achievement when the TD was extended to 50 minutes while reducing the I-ES to a mere 4 mm.

The enhancement in nitrated removal observed with increased TD can be attributed to the heightened release of aluminium ions during electrocoagulation. These liberated aluminium ions are pivotal in augmenting nitrated removal [15]. Conversely, the reduction in I-ES contributes to an accelerated corrosion rate of the aluminium electrodes. Consequently, this results in a higher concentration of aluminium ions within the solution, effectively amplifying the removal of pollutants [16]. The intricate interplay between these variables underscores the complexity of optimising nitrated removal through electrocoagulation, offering valuable insights for further research endeavours and practical applications in water treatment.

The analysis of the results in Table 2 yields a model that is shown below:

$$Ref\% = 74.6 - 13.36 \times I\_ES + 2.149\, TD + 0.447\, I\_ES^2 - 0.02111\, TD^2 + 0.0500\, I\_ES \times TD \quad (2)$$

The model presented above was employed to forecast nitrate removal under the conditions specified in Table 2, and the outcomes are documented in Table 3. A notable observation is the striking similarity between the results in Tables 2 and 3.

To affirm the validity of this resemblance between the actual and predicted nitrate removal outcomes, a graphical representation was generated in the form of Fig. 2. Furthermore, a rigorous statistical analysis was conducted, resulting in the calculation of the coefficient of determination (R^2) This analysis revealed an R^2 value of 0.9508, compelling evidence of a robust relationship between the actual and predicted nitrate removal values. This high R^2 value reinforces the accuracy and reliability of the predictive model in capturing the essential trends and dynamics of nitrate removal under the specified experimental conditions.

Run	I-ES (mm)	TD (min)	Predicted Ref%
1	4.00	50.00	92.99
2	4.00	10.00	49.69
3	6.50	30.00	61.87
4	6.50	30.00	61.87
5	6.50	30.00	61.87
6	6.50	30.00	61.87
7	2.96	30.00	88.84
8	9.00	10.00	14.45
9	6.50	58.28	79.13
10	9.00	50.00	67.74
11	6.50	1.72	10.83
12	10.04	30.00	46.07
13	6.50	30.00	61.87

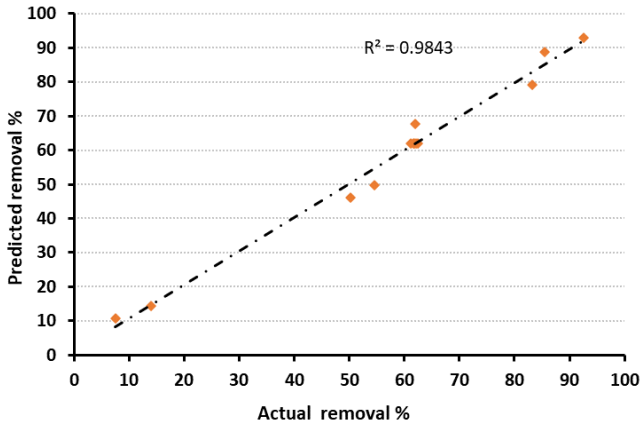

Figure 2. Predicted Vs experimental nitrate removal.

The combined effects of the TD and I-ES on nitrated removal by the EC unit are shown in Fig. 3.

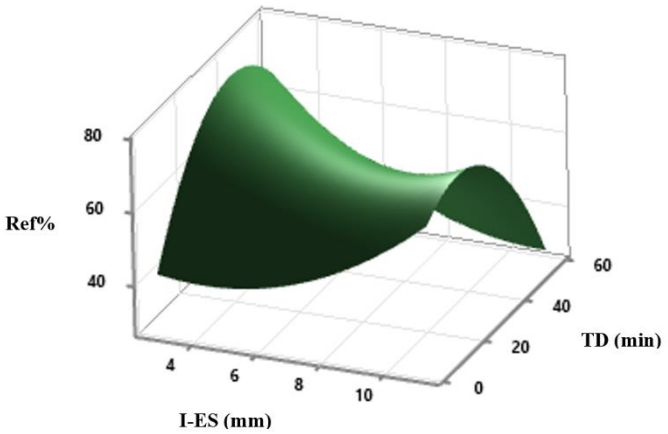

Figure 3. Effects of I-ES and TD nitrate removal.

4. Conclusions

The results obtained in the current study unequivocally establish the effectiveness of the electrocoagulation (EC) method in nitrated removal from water. Significantly, an extended treatment time (TD) exerts a positive influence on improving nitrate removal. Conversely, an increase in inter-electrode spacing (I-ES) adversely affects nitrate removal efficiency.

In light of these findings, it becomes evident that for the optimisation of nitrated removal, it is prudent to prolong the treatment time (TD) to its maximum duration while concurrently maintaining the inter-electrode spacing (I-ES) at minimal values. This strategic approach is poised to yield the most favourable outcomes by efficiently eliminating nitrates from water.

Moreover, using the Response Surface Methodology (RSM), particularly the Central Composite Design (CCD), has demonstrated its suitability and effectiveness for modelling

nitrate removal from water. This method has proven its capacity to offer valuable insights and exhibited a high degree of predictive accuracy in the context of nitrated removal. These findings underscore the potential of RSM, particularly CCD, for future research endeavours and practical applications within water treatment.

Conflicts of Interest: The authors declare no conflict of interest.

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