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Removal of Nitrate from Simulated Groundwater using Chitosan as Coagulant Aid in Electrocoagulation Process

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Nitrate contamination on groundwater has been an increasing global concern particularly in industrialized and developing nations. This study investigates the efficiency of electrocoagulation for nitrate removal from simulated groundwater, with chitosan applied as a natural coagulant aid. The process used aluminum as electrodes at constant agitation speed of 260 rpm, inter-electrode distance of 10 mm, 2.5 ppm chitosan and initial nitrate concentration of 39 ppm. The effects of pH, applied voltage, and operation time were systematically evaluated. Optimal conditions—pH 2, 30 V, and 90 min—achieved a nitrate removal efficiency of 98.14 %, a substantial improvement over the 73.99 % removal observed under similar conditions without chitosan. The significant increase in removal efficiency at lower pH values can be attributed to the increased protonation of chitosan and the increased formation of positive aluminum hydroxide complexes which improved coagulation. Moreover, higher voltage enhanced current density, promoting faster electrode dissolution and metal hydroxide generation. Statistical analysis via ANOVA confirmed the significant influence of all independent variables (pH: $p = 2.12 \times 10^{-8}$; voltage: $p = 2.51 \times 10^{-6}$; operation time: $p = 5.20 \times 10^{-5}$). These findings demonstrate that the combined use of electrocoagulation and chitosan offers a highly effective and synergistic approach for nitrate remediation in groundwater which is aligned with sustainable development goal 6: clean water and sanitation.

1. Introduction

Excessive nitrate contamination in groundwater poses a critical global challenge, particularly in agricultural regions where it consistently surpasses safe drinking water standards (Zhang et al., 2013). In the Philippines, research shows widespread nitrate pollution in groundwater across farming areas, with concentrations often surpassing the 50 ppm safety threshold (Mendoza et al., 2012). Sources are diverse, ranging from agricultural runoff and animal manures to sewage, with shallow groundwater being particularly vulnerable to agricultural wastewater infiltration (Hosono et al., 2010). As nitrate pollution continues to threaten vital groundwater supplies worldwide, the necessity for efficient and sustainable methods to treat nitrate-laden groundwater has become paramount.

Numerous methods have been explored for nitrate reduction including adsorption, chemical coagulation, nanofiltration, biological denitrification, reverse osmosis, electrochemical reduction, and electrocoagulation (Amarine et al., 2020). Among these, electrocoagulation stands out for its operational simplicity, cost-effectiveness, and high removal efficiency (Mohammed and Aljaberi, 2018). Electrocoagulation (EC) is an advanced water treatment technique that integrates electrochemical reactions, coagulation, and flocculation into a single process. It operates by applying an electrical current across metal electrodes, typically aluminum (Al) or iron (Fe), where oxidation occurs at the anode and reduction at the cathode (Ortenero and Choi, 2022). These reactions generate coagulant species without the need for chemical additives. Specifically, the sacrificial anode undergoes oxidation to release metal cations into the solution, while hydrogen gas and hydroxide ions are produced at the cathode as shown in Eq(1), Eq(2) and Eq(3):

$$\mathrm{Al_{(s)}} \rightarrow \mathrm{Al^{3+}_{(aq)}} + 3\mathrm{e^-} \quad (1)$$

$$2\mathrm{H_2O_{(l)}} + 2\mathrm{e^-} \rightarrow \mathrm{H_{2(g)}} + 2\mathrm{OH^-_{(aq)}} \quad (2)$$

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$$Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3 \quad (3)$$

According to Priya et al. (2020), the pH of the aqueous solution significantly influences the speciation and formation of metal hydroxides during the EC process. In particular, the formation of amorphous and neutral aluminum hydroxide ($Al(OH)_3$), is most favorable within the pH range of 4 to 6 as represented in Eq(3). At lower pH levels (2 to 4), the formation of soluble aluminum species such as $Al(OH)^{2+}$, and $Al(OH)_2^+$ predominate, corresponding to Eq(4) and Eq(5), respectively. Conversely, in alkaline conditions, the formation of negatively charged species like $Al(OH)_4^-$ becomes dominant, as described by Eq(6).

$$Al^{3+} + H_2O \leftrightarrow Al(OH)^{2+} + H^+ \quad (4)$$

$$Al(OH)^{2+} + H_2O \leftrightarrow Al(OH)_2^+ + H^+ \quad (5)$$

$$Al(OH)_3 + H_2O \leftrightarrow Al(OH)_4^- + H^+ \quad (6)$$

Previous research has demonstrated the capability of EC to reduce nitrate levels to below 10 mg/L using iron and aluminum electrodes (Koparal and Ogutveren, 2002), with removal primarily attributed to adsorption onto precipitating metal hydroxides (Lacasa et al., 2011). Innovations such as combining EC with ultrasonic irradiation have further boosted removal efficiency (Al-Marri et al., 2020), and studies have highlighted the superior performance of Al-Al electrode combinations over Fe-Fe in nitrate removal (Yazici Karabulut et al., 2021). Despite its advantages, EC faces two significant limitations: high energy consumption and the necessity for periodic replacement of sacrificial anodes (Shamaei et al., 2018). To mitigate these drawbacks, the integration of EC with chemical coagulation (CC) has garnered considerable interest. Hybrid EC-CC systems have shown promising results in enhancing removal efficiencies for various contaminants, with studies demonstrating improved humic acid removal with chitosan (Seid-Mohammadi et al., 2014) and enhanced total organic carbon removal with $AlCl_3$ (Shamaei et al., 2018). Furthermore, the use of carboxymethyl chitosan has not only boosted heavy metal removal in EC but also inhibited anode corrosion (Sun et al., 2018).

Building upon these developments, the present study investigates the synergistic effect of chitosan as a coagulant aid in the electrocoagulation of simulated nitrate-contaminated groundwater. To the best of the authors' knowledge, this is the first study to evaluate the combined application of electrocoagulation and chitosan (EC-CC) for nitrate removal. The primary objective was to systematically evaluate the impact of chitosan addition on nitrate removal efficiency under controlled parameters: agitation speed, inter-electrode distance, fixed chitosan concentration, and constant initial nitrate concentration. This research specifically explores the influence of three independent variables—pH, voltage, and operation time—to find the best conditions of this hybrid EC-CC process for enhanced nitrate remediation.

2. Research Methodology

The conceptual framework for this study is shown in Figure 1. Simulated groundwater was prepared by dissolving potassium nitrate (KNO_3) in distilled water. 12.71 g of KNO_3 was used to prepare 1 L of 7800 ppm stock solution. This was then used to prepare 20 L of 39 ppm diluted solution for the EC process. This concentration, while below the 50 ppm safety threshold for drinking water, was deliberately chosen to accurately simulate realistic nitrate levels observed in groundwater influenced by moderate agricultural activity, as documented by Hosono et al. (2010) and further supported by Amarine et al. (2020). Other controlled variables include: Al-Al as electrodes, inter-electrode distance of 10 mm, fixed chitosan concentration of 2.5 ppm, and agitation speed of 260 RPM. These parameters were selected based on established methodologies from previous studies of Yazici Karabulut et al. (2021) and Seid-Mohammadi et al. (2014). The independent variables were pH (2,4,6, and 8), voltage (10 V, 20 V, and 30 V), and operation time (30, 60, 90, and 120 min). The dependent variable, final nitrate concentration, was quantified using a HANNA Instruments nitrate high-range checker (HC-HI782), and subsequently employed to calculate the nitrate removal efficiency. All experiments were performed in two trials, each with two replicates. The results of all replicates and trials were subjected to ANOVA at 95 % confidence level with respect to the independent variables. Subsequently, post-hoc Tukey's Honestly Significant Difference (HSD) tests were applied at a 99 % confidence level to ascertain which pairs of treatment groups exhibited statistically significant differences in their mean results.

The EC process was carried out in a 1 L Pyrex glass with Al-Al electrodes with fixed dimensions of 90 mm x 200 mm x 3 mm clamped to an iron stand and a hot plate on the bottom, as illustrated in Figure 2. The electrodes were connected to a DC power supply via alligator clips. All experiments were conducted at ambient room temperature (25 °C) and atmospheric pressure. Following the EC process, the treated solution underwent a 10-min sedimentation period prior to filtration of supernatant liquid. The resultant filtrate was subsequently collected and used for nitrate concentration analysis.

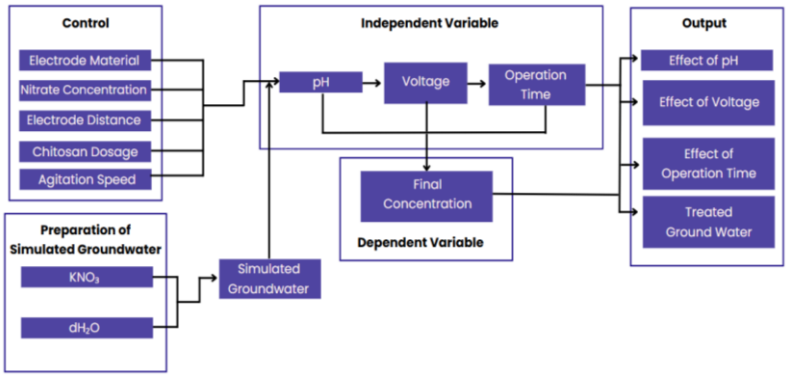

Figure 1: Conceptual framework of the present study

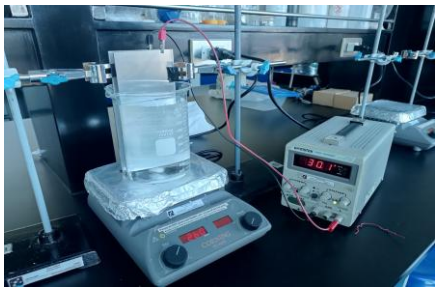

Figure 2: Electrocoagulation setup

3. Results and Discussion

Figure 3a illustrates the changes in appearance observed in the simulated groundwater after the EC process. This increase in turbidity was consistently observed across all experimental trials conducted in this study which confirms the effective coagulation and flocculation of contaminants. The subsequent decrease in turbidity after the sedimentation step further validates the successful agglomeration and settling of these newly formed flocs, as shown in Figure 3b.

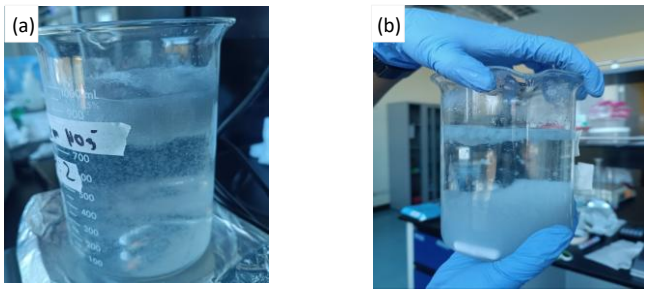

Figure 3: Simulated groundwater (a) after EC process; (b) after sedimentation

3.1 Effect of pH

The effect of pH was initially investigated using constant voltage of 30 V and operation time of 60 min. Figure 4 presents the removal efficiency of nitrate under varying pH. The box plots represent the interquartile range (IQR) of experimental values (Q1 to Q3), while the red line indicates the mean removal efficiency for each treatment. Error bars represent the range from the median to the minimum and maximum observed values. It can be observed that the highest removal efficiency (90.90 %) was obtained at pH 2. This finding contrasts with the results of Karabulut et al. (2021) which reported optimal removal at pH 6 after 210 min. Interestingly, the removal efficiency at pH 6 after 60 min closely matches the results of the present study, suggesting that the electrocoagulation behavior under neutral conditions is consistent with what has been reported in the literature. The enhanced removal efficiency at pH 2 can be attributed to the protonation of the amino groups of chitosan, transforming it into a soluble cationic polymer which attracts the nitrate anions (Khnifira et al., 2022). Additionally,

the increased production of Al3+, Al(OH)2+, and Al(OH)2+ species at this pH significantly improved the destabilization and aggregation of the contaminant (Priya et al., 2020). In contrast, higher pH levels lead to the predominant formation of $Al(OH)_4^-$, which is less effective for coagulation, thereby reducing nitrate removal efficiency. While nitrate can form into HNO3 at low pH, it readily dissociates into its ionic form (NO3-) as a strong electrolyte (Wang et al., 2018). Therefore, low pH does not inhibit nitrate availability for adsorption. Statistical analysis using ANOVA confirmed that the effect of pH on nitrate removal efficiency was highly significant (p = 2.12 x10-8). Moreover, Table 1 shows that the results for all pH were statistically different from each other except for pH 4 and 6. This could be attributed to the formation of similar metal coagulant species (i.e. Al(OH)3) which is dominant on both pH levels. Thus, pH 2 was used for subsequent experiments.

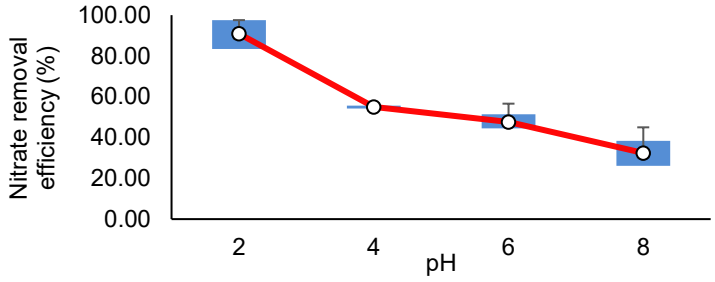

Figure 4: Effect of pH on nitrate removal using EC with chitosan

Table 1: Post-hoc Tukey's HSD Test for pH

Treatment pair	Tukey HSD p-value	Tukey HSD inference (p < 0.01)
2 vs 4	0.0010	Significant
2 vs 6	0.0010	Significant
2 vs 8	0.0010	Significant
4 vs 6	0.2625	Insignificant
4 vs 8	0.0010	Significant
6 vs 8	0.0075	Significant

3.2 Effect of voltage

The influence of applied voltage was further examined at pH 2 with a fixed operation time of 60 min. Figure 5 shows that nitrate removal efficiency increased proportionally with voltage which is consistent with previous findings of Medina Collana et al. (2024) in the removal of nitrates from brackish groundwater through the use of electrodialysis. This trend can be attributed to the rise in current density at higher voltages, which accelerates the dissolution of the aluminum electrodes and promotes the generation of coagulant species such as metal hydroxide complexes which was also highlighted in the study of Ortenero and Choi (2021). The large error bar at 10 V indicates substantial variability among replicates which could be attributed to insufficient and inconsistent generation of coagulant species at low current density. At 20 V, efficiency improved to 56.73 % with reduced variability, while 30 V yielded the highest and most consistent efficiency (90.90 %), reflecting optimal coagulant formation and stable electrochemical conditions. Statistical analysis using ANOVA confirmed that the effect of voltage on nitrate removal efficiency was significant ($p = 2.51 \times 10^{-6}$). Moreover, Table 2 shows that the results for all voltages were statistically different from each other, indicating the importance of voltage as a critical parameter in optimizing both removal efficiency and process stability.

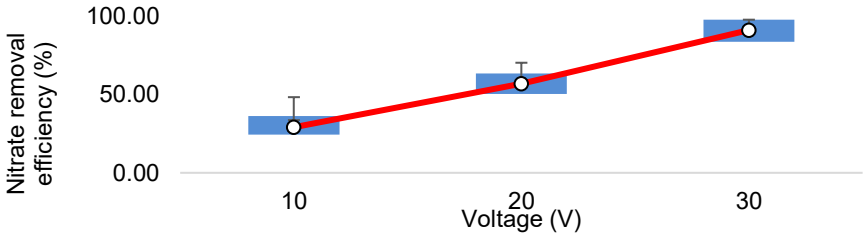

Figure 5: Effect of voltage on nitrate removal using EC with chitosan

Table 2: Post-hoc Tukey's HSD Test for voltage

Treatment pair (V)	Tukey HSD p-value	Tukey HSD inference (p < 0.01)
10 vs 20	0.0010	Significant
10 vs 30	0.0010	Significant
20 vs 30	0.0010	Significant

3.3 Effect of operation time

Finally, the influence of operation time on nitrate removal was assessed at pH 2 and 30 V. As illustrated in Figure 6a, the removal efficiency increased steadily with longer treatment durations, similar with the trend observed with voltage. This behavior aligns well with previous studies of Yazici Karabulut et al. (2021) and Kumari and Kumar (2021). The improved performance at extended operation times can be attributed to prolonged electrolysis, which promotes continuous generation of metal hydroxide coagulants from the electrodes. Additionally, longer exposure enhances interactions among nitrate ions, chitosan, and the in situ-formed coagulants – improving overall removal efficiency. While the Tukey HSD post-hoc analysis shown in Table 3 indicated no statistically significant difference in mean removal between 60 min and subsequent time points (90 and 120 min), the plot distinctly shows a marked improvement in process consistency beyond 60 min. Specifically, at 90 min, the mean removal efficiency approached 98.14 %. Crucially, this time point exhibited an exceptionally tight IQR and minimal error bar range, demonstrating a highly consistent and reproducible process. Further extending the operation to 120 min resulted in a marginal increase in mean efficiency, reaching approximately 99.62 %, but without a statistically significant improvement over 90 min. This suggests that 90 min emerges as the optimal operational time for this electrocoagulation system, offering almost complete nitrate removal with superior process consistency and reliability. ANOVA results confirmed that the effect of operation time on nitrate removal was statistically significant ($p = 5.20 \times 10^{-5}$). Notably, Figure 6b highlights that the absence of chitosan dramatically decreased the nitrate removal efficiency, having only 73.99 % as the maximum. This validates the effective performance of chitosan as coagulant aid in the electrocoagulation process.

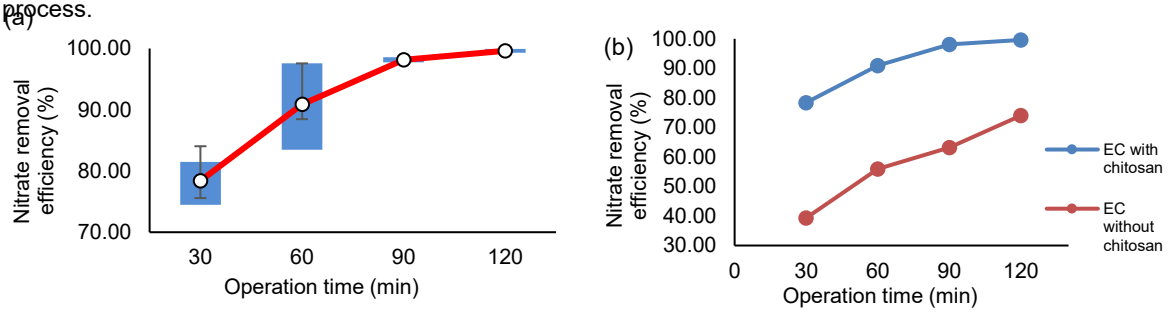

Figure 6: (a) Effect of operation time on nitrate removal using EC with chitosan; (b) Comparison of EC with chitosan and without chitosan

Table 3: Post-hoc Tukey's HSD Test for operation time

Treatment pair (min)	Tukey HSD p-value	Tukey HSD inference (p < 0.01)
30 vs 60	0.0067	Significant
30 vs 90	0.0010	Significant
30 vs 120	0.0010	Significant
60 vs 90	0.1319	Insignificant
60 vs 120	0.0586	Insignificant
90 vs 120	0.9000	Insignificant

4. Conclusions

This study demonstrates the potential of electrocoagulation, enhanced with chitosan as a coagulant aid, as an effective alternative for nitrate removal from contaminated groundwater. The influence of key operating parameters—pH, voltage, and operation time—was evaluated to find the best treatment performance. Results revealed an inverse relationship between pH and removal efficiency, with the highest efficiency (90.90 %) achieved at pH 2. This outcome is attributed to the enhanced protonation of chitosan and the increased formation of positively charged aluminum hydroxide species that promote coagulation. In contrast, both voltage and operation time exhibited a directly proportional relationship with nitrate removal efficiency. 30 V yielded the highest removal efficiency (90.90 %) by increasing electrode dissolution and coagulant generation. Similarly,

extending the operation time to 120 min allowed for prolonged electrolysis, resulting to maximum efficiency of 99.62 %. However, this result shows no statistical difference from the result of 90 min, suggesting that the latter should be considered as the optimal operation time for this study. Overall, the findings highlight the synergistic role of chitosan in improving electrocoagulation performance and support its application as a sustainable and efficient treatment option for nitrate-contaminated water sources. Future works could examine the effect of higher nitrate concentration and the use of actual groundwater sample.

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