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Optimization of temperature and supporting electrolyte for ammonium removal using bioelectrochemical systems

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Original Article

Abstract

High concentrations of ammonium in drinking water can cause many diseases and environmental problems such as eutrophication. Therefore, high-performance and eco-friendly methods for purification are of great importance and must be considered. Recently, bioelectrochemical systems have been successfully applied for the removal of many pollutants from water and wastewater. In the present work, ammonium was treated using the bioelectrochemical process. The two effective factors of temperature and supporting electrolyte dose were optimized using response surface methodology (RSM). The optimal conditions were electrolyte dosage of 250 mg/l and temperature of 26.5 °C. Under optimized conditions, the maximum ammonia removal percentage was 99.6%. Analysis of variance indicated a reasonable correlation coefficient (R^2) between the predicted and actual values. R^2 (0.8913), adjusted R^2 (0.8137), and coefficient of variation (8.32 %) were calculated based on statistical analysis. The results indicate that the bioelectrochemical process is the most useful and effective method for the removal of ammonium from wastewater.

KEYWORDS: Ammonium Treatment, Waste Water, Bioelctrochemical, Response Surface Methodology

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Introduction

Ammoniacal nitrogen is an essential element for living organisms, but it can contribute to dissolved oxygen depletion, accelerated eutrophication of lakes and rivers, and fish toxicity in water bodies.[1,2] High concentrations of ammonia have been reported in the wastewater of various industries such as coke plant, landfill leachate, textile, and tannery, and municipal and domestic wastewater, urban water run-off, and agriculture drainage.[3,4] The commonly used processes for nitrogen removal are biological process, chemical treatment, ion exchange, and ammonia volatilization by air stripping.[5] Among treatment methods, biological processes are more sustainable approaches due to their lower impact on the surrounding environment and lower cost compared to other physical and chemical processes.[6] The combination of biological processes and electrochemistry in a bioelectrochemical system is a novel approach to the treatment of various contaminants and

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pollutants of water and wastewater. The bioelectrochemical system is composed of an electrochemical reactor and microorganism agents (biocatalyst) that are placed on the electrode surface. In recent years, this process has been widely applied for the removal of many pollutants such as organic carbon, metal, and nutrient compounds.[7-13] The 2 most common bioelectrochemical systems are the microbial fuel cell (MFC) and the microbial electrolysis cell (MEC). In the MFC, energy can be obtained, but in the MEC, electrical energy must be supplied using a power supply.[14] Among nutrient compounds, the treatment of nitrogen compounds (ammonia/ammonium, nitrite, and nitrate) are considered in the present work. Depending on treatment goals, many successful studies have been reported on bioelectrochemical systems' removal of nitrogen compounds from water and wastewater. For example, using a MFC reactor, Xie et al. were successfully able to remove about 97.4% ammonium from synthetic wastewater.[15] In a similar study that was performed by Yan et al., simultaneous nitrification and denitrification without extra energy input was reported.[16] In this case, more than 96.8% ammonia removal was reported.[16]

Various statistical experimental design techniques have been proposed in the optimization of experimental studies. In recent years, response surface methodology (RSM) has been applied successfully in many scientific fields such as chemistry, biology, medicine, and economy.[17] It was originally developed in the 1950s.[18] RSM is based on the experimental design with the final goal of evaluating optimal functioning of industrial facilities using minimum experimental effort.[17] RSM was described by Wilson as an experimental approach to identifying the optimum conditions for a multivariable system using minimum experimental samples.[18] Nitrifying bacteria are sensitive to temperature which is a key influential parameter in ammonium removal rates in bioreactor systems.[19] On the other hand, the amount of salt or supporting electrolyte dose can affect the electrochemical/bioelectrochemical reaction progress. However, in the present study, the 2 factors of temperature and supporting electrolyte dose were optimized using RSM.

Materials and Methods

All chemicals used in this study were analytical reagent grade and were used without further purification. An aqueous stock solution of ammonia (from NH_4Cl salt) was prepared in deionized distilled water. Different concentrations of ammonia were obtained by diluting the stock solution.

Inoculum mass for growth and enrichment of denitrifying bacteria was collected from the Shahrak Gharb Wastewater Treatment Plant, Tehran, Iran. The sludge was added to a 1 l flask containing synthetic wastewater. For enrichment, synthetic wastewater was prepared by dissolving (in terms of g/l) 0.3 KH_2PO_4, 1 $Na_2HPO_4.12H_2O$, 0.1-0.5 NaCl, 0.1 $MgSO_4.7H_2O$, and 0.1-0.4 NH_4Cl. $NaHCO_3$. NH_4Cl was added into the reactor to achieve a carbon/nitrogen ratio of equal to 2:1. In order to supply the required oxygen, an aerator with constant flow rate (0.9 l/minute) was used. During this period, nitrifying bacteria were enriched and used in the bioelectrochemistry reactor.[20]

A 2 l glass vessel (with effective volume of 1.8 l) was utilized for bioelectrochemical nitrification. The schematic of bioelectrochemical cell (BEC) system with its related parts is illustrated in figure 1. The anode and cathode were placed vertically at a fixed distance of 5.5 cm without any separated membrane. A DC power supply (TEK-8051, 30 V, and 5 A double) was set for startup process. Flow rate and hydraulic retention time (HRT) were maintained at approximately 0.9 l/minute and 24 hours, respectively. Batch bioelectrochemical nitrification system (BNS) was operated for 3 weeks and ammonia concentration was determined daily. Growth medium was inoculated to reactor with a mixed liquor suspended solids (MLSS) of about 3000 mg/l. Startup was operated using an electric current of 5 mA/cm^2 and ammonium

concentration of 38.88 mg-N/l (50 mg-NH_4^+/l). The BNS was fed with growth medium containing 0.45 g/l Na_2HPO_4, 0.15 g/l KH_2PO_4, 0.1 g/l $MgSO_4$ $7H_2O$, and 0.015 g/l $CaCl_2$ $7H_2O$. In addition, 1 ml/l trace nutrients solution consisted of 1.5 g/l $FeCl_3 \cdot 6H_2O$, 0.15 g/l H_3BO_3, 0.03 g/l $CuSO_4 \cdot 5H_2O$, 0.18 g/l KI, 0.12 g/l $MnCl_2 \cdot 4H_2O$, 0.06 g/l $Na_2MoO_4 \cdot 2H_2O$, 0.12 g/l $ZnSO_4 \cdot 7H_2O$, 0.15 g/l $CoCl_2 \cdot 6H_2O$, and 10 mM acetate.[21]

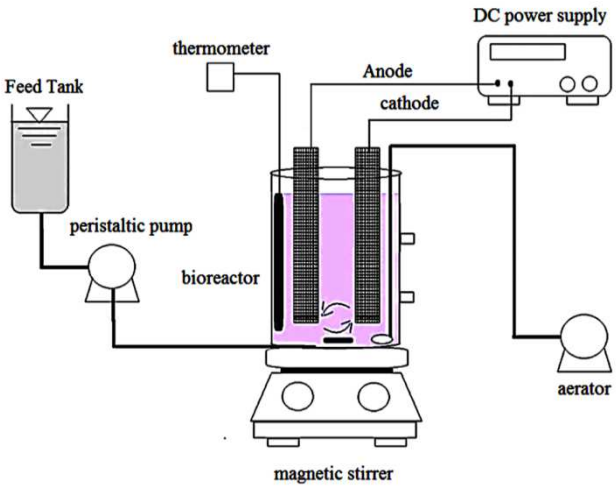

Figure 1. Schematic plan of bioelectrochemical nitrification system (BNS)

Samples were analyzed according to standard methods for water and wastewater. To determine the ammonium content, the phenate method at λ_{max} 640 nm was used. Nitrate concentration was determined using a spectrophotometer at λmax 220 and 275 nm. The nitrite content was analyzed through the colorimetric method using sulfanilamide and naphthylethylenediamine dihydrochloride regents at λ_{max} 543 nm.[11]

The coefficients of the response functions for different dependent variables were determined through correlating the experimental results using the Design-Expert regression software. The central composite design (CCD) was used to introduce this model as a specific design.[10] The CCD of the main parameters (x_1: supporting electrolyte of 100-500 mg/l and x_2: wastewater temperature of 22-32 ˚C) have been displayed in table 1. According to the design proposed by the Design-Expert software (version 7.0, Stat-Ease, Inc., Minneapolis, MN, USA), 13 experiments were conducted that is presented in table 2. Total number of experiments in CCD method was calculated based on $2k + n_\alpha + n_0$, where k is the number of independent variables, n_α axial points, and n_0 center points.[12,13] In this study, a 4 (2^2) factorial design, 4 (2 × 2) axial points, and 5 central points were selected. In order to ensure the validation of the obtained model, an experiment was performed at optimal factor levels and the result was compared with that predicted by the model.

Results and Discussion

Startup and optimum time

Primary startup of the bioelectrochemical process was performed in certain conditions for about 3 weeks and ammonium removal efficiency was controlled daily. A quasi-steady state was reached at the end of this period, and 78% ammonium removal was achieved (data are not shown). Scanning electron microscope (SEM) images of biofilm-electrode are illustrated in figure 2. The performance of the ammonium removal in the bioelectrochemical nitrification process at HRT of 0-72 hours is shown in figure 3. According to this figure, ammonium removal efficiency was about 80% in HRT of 24 hours. This was considered as optimized condition due to the lack of a significant difference in ammonium removal efficiency at the greater amount of 38.88 mg-N/l.

Table 1. Experimental range and levels of variables

Variable	Low axial (-1.41) −α	Low factorial (-1)	Center point (0)	High factorial (+1)	High axial (+1.41) +α
x_1 (mg/l)	100	160	300	440	500
x_2 (˚C)	22	24	27	30	32

x1: Supporting electrolyte; x2: Temperature

ANOVA

In order to determine responses, 13 experimental conditions of the runs proposed by the CCD were conducted in the laboratory. The response surface models were validated statistically for adequacy using ANOVA. Table 3 presents ANOVA of regression parameters of the predicted response surface quadratic model for bioelectrochemical ammonium removal efficiency. The high F value (11.48) and a low P value (0.0029) that is lower than 0.05 show that the ammonium removal model was significant.

The final second-order polynomial regression in terms of coded and actual factors is shown by equations 1 and 2.

Final equation in terms of coded factors:

$$\text{Ammonia Removal} = 95.6 - (9.24 \times x_1) - (3.5 \times x_2) - (2.35 \times x_1 \times x_2) - (13.69 \times {x_1}^2) - (10.17 \times {x_2}^2) \quad (1)$$

Final equation in terms of actual factors:

Ammonia Removal = -550.805 + (0.4724 × Supporting Electrolyte) + (44.34879 × Temperature) – (4.70E - 03 × Supporting Electrolyte × Temperature) – (6.85E - 04 × Supporting Electrolyte^2) – (0.8135 × Temperature^2) (2)

Table 2. Central composite design (CCD) consisting of 13 experiments for the study of two experimental factors in coded units along with observed values

Run	x_1	x_2	Ammonium removal efficiency (%)	
			Actual	Predicated
1	1.00	1.00	65.7	56.65
2	0	-1.41	83.0	80.21
3	1.00	-1.00	72.1	68.35
4	0	0	98.6	95.60
5	1.41	0	46.5	55.15
6	0	0	96.6	95.60
7	0	0	94.0	95.60
8	-1.41	0	88.0	81.29
9	0	0	95.4	95.60
10	-1.00	-1.00	75.0	82.13
11	0	0	93.4	95.60
12	-1.00	1.00	78.0	79.83
13	0	1.41	65.6	70.31

x_1: Supporting electrolyte; x_2: Temperature

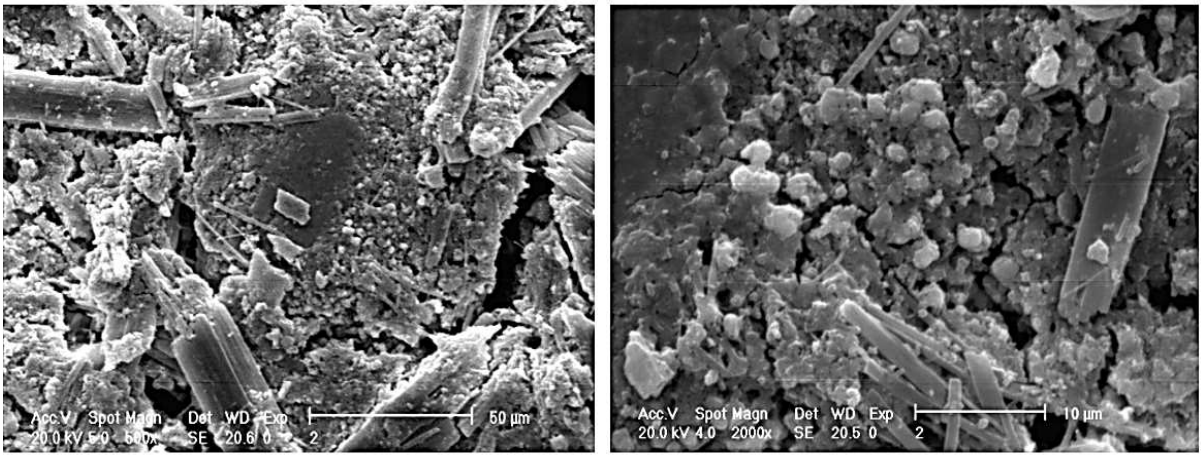

Figure 2. Scanning electron microscope (SEM) images of bio-electrode

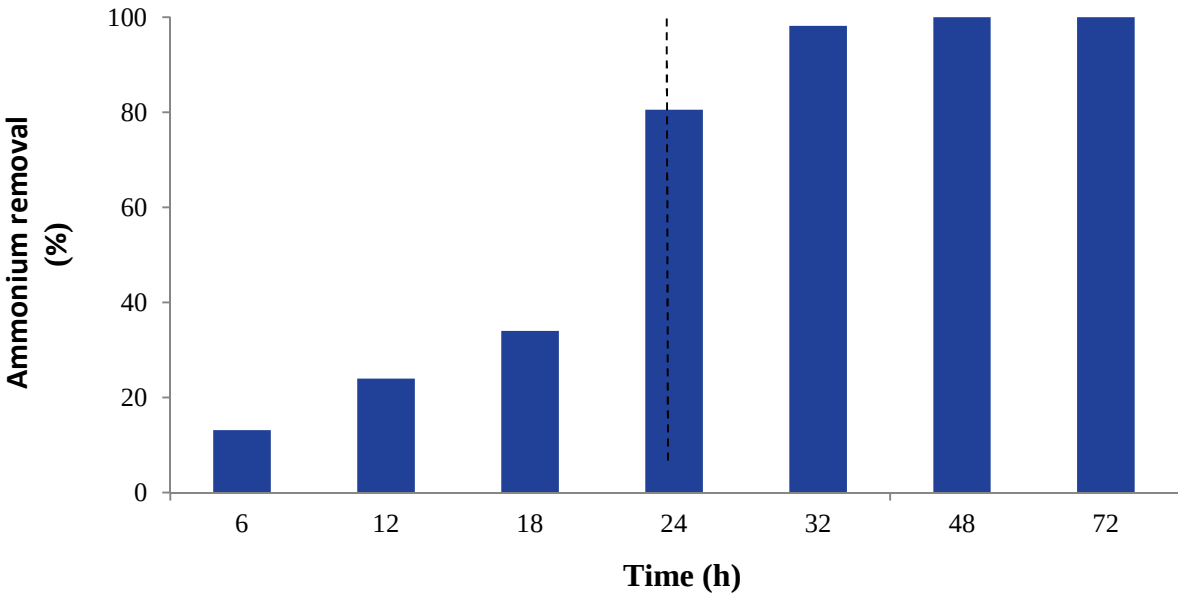

Figure 3. Ammonium variation via reaction time

Table 3. Analysis of variance (ANOVA) for quadratic model

Source	df	F	P Probability > F
Model	5	11.48	0.0029
x_1-Supporting Electrolyte	1	15.05	0.0061
x_2-Tempreature	1	2.16	0.1849
x_1x_2	1	0.49	0.5078
x_1^2	1	28.76	0.0010
x_2^2	1	15.86	0.0053
Residual	7		
Lack of fit	3	22.94	0.0056
Pure error	4		
Cor total	12		
Standard Deviation		6.73	
Mean		80.92	
C.V. %		8.32	
R^2		0.89	
Adjusted R^2		0.81	

Df: Degree of freedom; x_1: Supporting electrolyte; x_2: Temperature; CV: Coefficient of variation

According to R^2 and adjusted R^2, the experimental analysis value indicates a good agreement with the predicted values. The predicted R^2 of 0.8913 is in reasonable agreement with the adjusted R^2 of 0.8137. In addition, the coefficient of variation (CV) is the value of the reproducibility of the model and should be lower than 10%. Accordingly, CV of 8.32% indicates reliability and high precision of the experimental data. Adequate precision is the ratio of signal to noise, and it should be greater than 4 to be desirable. Adequate precision of about 8.78 was obtained in the present study. In figure 4 a, predicted versus actual ammonia removal efficiency are observed. The predicted values were calculated from the final coded model equation (Equation 1). The respective R^2 (0.8137) and its fitted equation indicate the reasonability

of experiments. Usually, the adequacy of the model can be evaluated by diagnostic plots, such as a normal probability plot of the studentized residuals and a plot of predicted versus actual values. The normal probability plots of the studentized residuals for bioelectrochemical ammonium removal are presented in figure 4. This plot indicates that residuals follow a normal distribution and in this case the points will fall along a straight line.[22]

Effects of main parameters

Figure 5 illustrates the three-dimensional and related contour plot of response surface. Accordingly, the interaction between temperature and supporting electrolyte on ammonium removal efficiency is observed. It is clear that the increase in temperature and supporting electrolyte dosage promotes an increase in ammonium removal efficiency. The maximum observed removal of ammonium (optimum point for nitrification) was around center point (300 mg/l of NaCl and 27 ˚C). According to plot, the ammonium removal percentage decreased to a minimum with the increase in supporting electrolyte dosage to 500 mg/l. It is clear that the higher NaCl dose has adverse effects on biological population. Bacterial activity is improved by increasing of ambient temperature. The oxidation rates of specific ammonium and its byproducts were also highly dependent on solution or ambient temperature. The variations of ammonia-oxidizing bacteria (β-Proteobacterial AOB) and nitrite-oxidizing bacteria (NOB) (Nitrobacter spp.) are sensitive and affected by temperature changes.[19] Zhang et al. suggested that the activity of AOB increased more than that of NOB by the increasing of temperature from 7.2 to 28.3 ˚C, but was inhibited more below 5.0 ˚C.[19] Moreover, Xiao et al. reported that increase in temperature could benefit the anode microbes when heat is transferred into the anode compartment through electrolyte.[23] In temperatures higher than 26.5 ˚C, nitrification rate declined. This can be due to the decreasing of ohmic resistance. As a result, electric current increased and this can have adverse effects on nitrifying bacteria. On the other hand, this phenomenon is intensified by the increasing of supporting electrolyte dosage. Dincer and Kargi reported that in a continuous flow nitrification/denitrification system, rates of nitrification/denitrification dropped significantly with salt dosage of more than 1000 mg/l.[24]

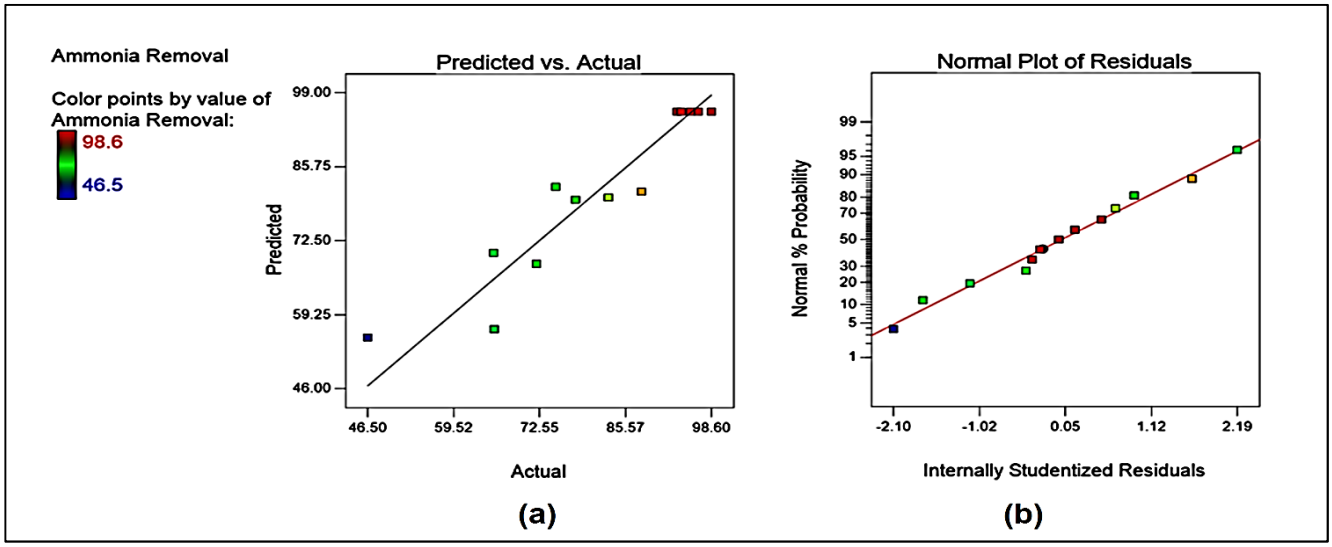

Figure 4. Predicted versus actual values plot (a) and normal probability plot (b) of the studentized residual for bioelectrochemical ammonium removal

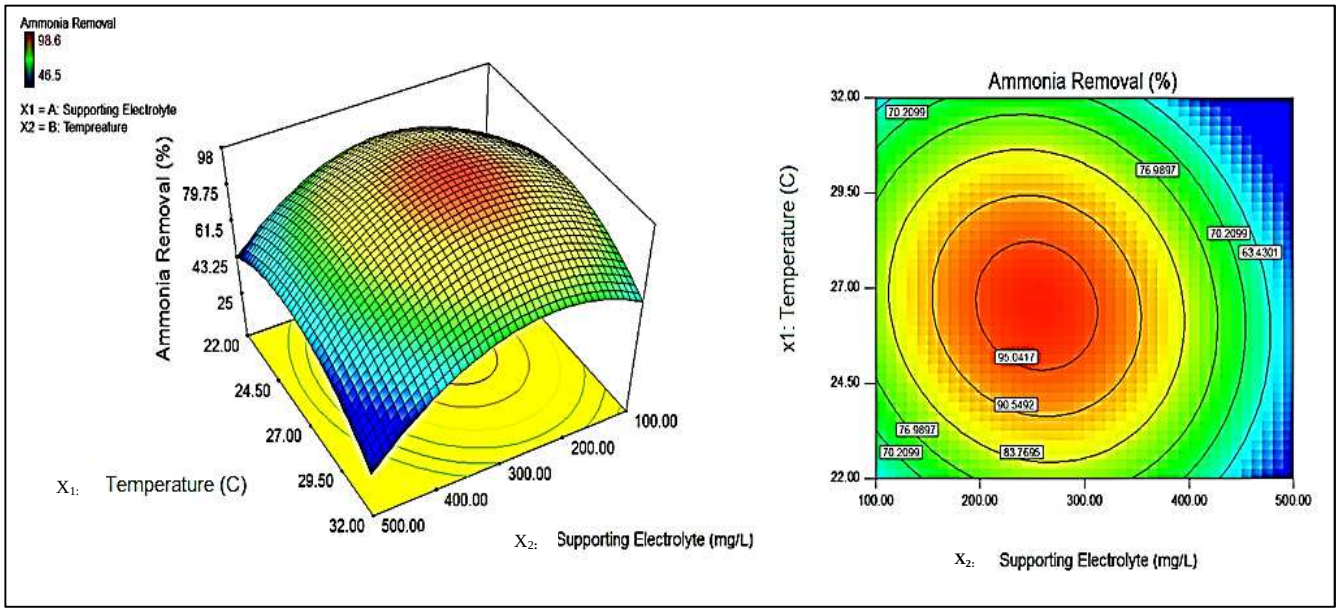

Figure 5. Three-dimensional and related contour graphics of response surface for bioelectrochemical ammonium removal

Optimization and confirmatory experiment

To achieve optimal nitrification, the desired goal for desired parameters was considered to be the "within the range" status, while for ammonium efficiency percentage it was "maximum". Therefore, the optimal values of working conditions and predicated removal efficiencies of ammonium were established. Figure 6 and table 4 indicate the optimal processing conditions and verification actual test. Regarding figure 6 that shows the overlay plot, optimal acquired condition for nitrification was about 250 mg/l of NaCl and 26.5 ˚C. Figure 7 shows the removal efficiency of ammonium in time. According to this figure, the experimental analysis value (99.6% at 24 hours) represents a good compatibility with the predication values (97.34%) and is in close agreement at a 95% confidence and prediction interval. The generation rate of nitrate and nitrite were determined. Nitrite is an unstable form of nitrogen which can be converted into other nitrogen compounds. This fact can be seen in figure 7 in which nitrite is converted to nitrate. Final concentrations of nitrite and nitrate were determined around 9.8 and 103 mg/l, respectively.

Conclusion

The present study showed that a desirable rate of ammonium removal from aqueous solution could be achieved using bioelectrochemical nitrification method. Effects of the two operational parameters of temperature and supporting electrolyte dosage were evaluated to obtain the maximum efficiency using RSM. Accordingly, the optimal amounts of desired parameters were 250 mg/l of NaCl and 26.5 ˚C. Under these conditions, a 99.6% experimental value was obtained.

Conflict of Interests

Authors have no conflict of interests.

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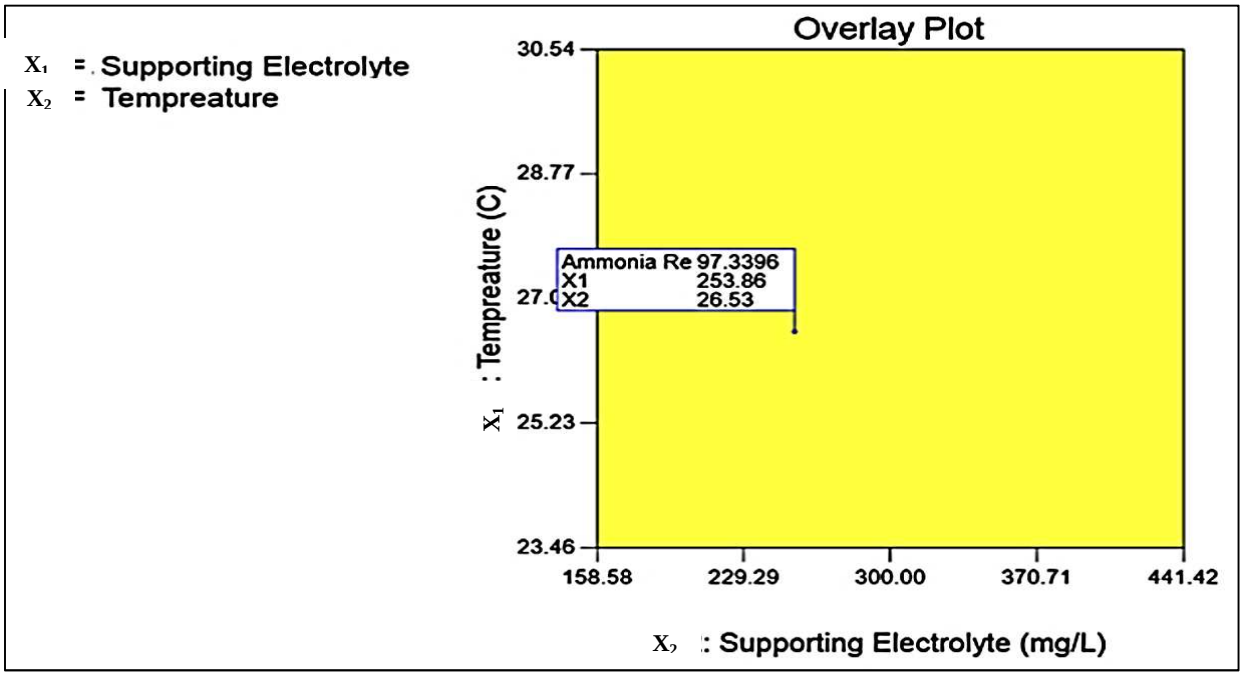

Figure 6. Overlay plot for ammonium removal

Table 4. Optimum condition verification and additional experiments

Response	Prediction	95% CI		95% PI		Conformity experiment
		Low	High	Low	High	
Ammonia removal	97.34%	90.34	100	79.94	100	99.6%

CI: Confidence interval; PI: Predicted interval

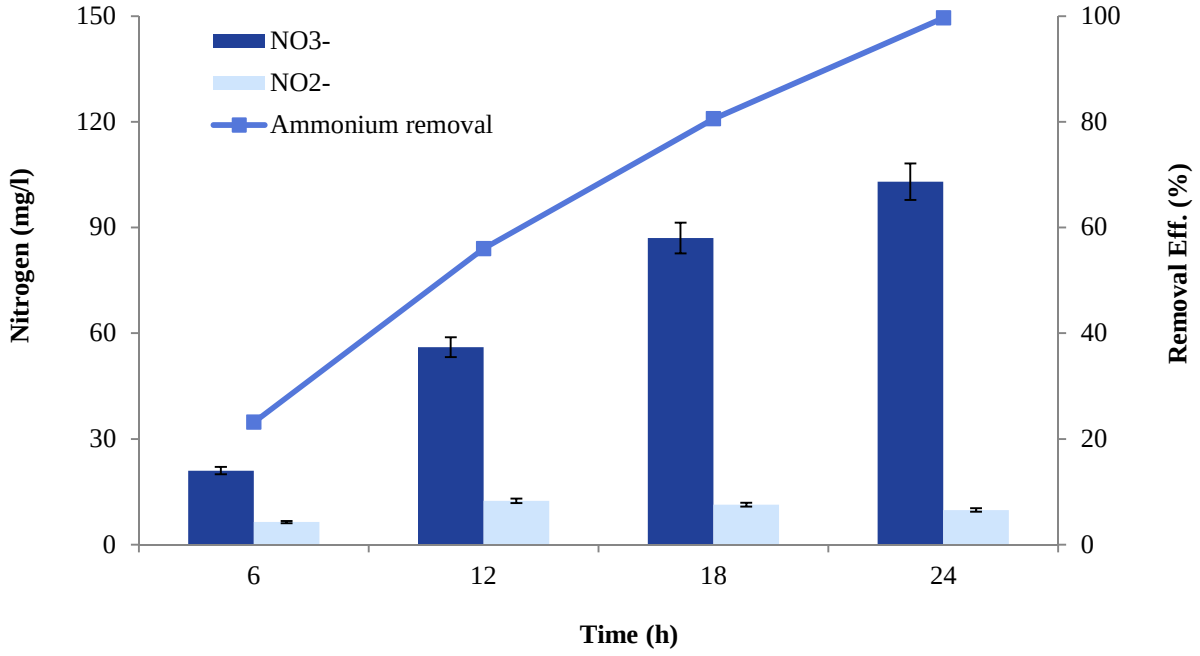

Figure 7. Variation of nitrogenous compounds during ammonia removal

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