

Optimization of Nitrate Reduction by Electrocoagulation Using Response Surface Methodology

Hooshyar Hossini¹; Abbas Rezaee^{1,*}

¹Department of Environmental Health, Tarbiat Modares University, Tehran, IR Iran

*Corresponding author: Abbas Rezaee, Department of Environmental Health, Tarbiat Modares University, Tehran, IR Iran. Tel: +98-2182883575, Fax: +98-2182883575, E-mail: rezaee@modares.ac.ir

Received: January 23, 2014; Revised: April 24, 2014; Accepted: April 25, 2014

Background: The presence of nitrate and its intermediates are considered undesirable compounds in the environment. Various methods have been proposed to remove nitrate from wastewater and water streams.

Objectives: In this study, we investigated removal of nitrate from an aqueous solution by the process of electrocoagulation, using aluminum/graphite as the anode/cathode electrodes.

Materials and Methods: We applied response surface methodology (RSM) as the statistical method for modeling, and optimizing the applied variables. All experiments were performed according to the standard methods for the examination of water and wastewater. To prepare the optimum condition, we considered the following amount of compounds and conditions: NaCl, 1 g/L; nitrate concentration range, 50-200 mg/L; applied electric current range, 0.05-0.2 A; anode, aluminum; cathode, graphite; and detention time: 120 minutes.

Results: The results showed that by applying electric current of 0.14 A for 120 minutes, the nitrate content would reduce down to 97%. The obtained R² for the nitrate removal model was higher than 0.99. With regard to supporting electrolytes, more nitrate reduction is obtained with NaCl. The oxidation reduction potential (ORP) was changed from 220 to -375 mV and this range is suitable for denitrification and nitrate reduction.

Conclusions: The results of this study show that it is possible to remove nitrate, and its intermediates from waste water. Regarding the desirability of the process, the field scale study is proposed.

Keywords: Electrocoagulation; Nitrate Removal; Waste Water; Water

1. Background

Nitrate and its intermediates are considered undesirable compounds in water and wastewater. The nitrate contamination is an environmental problem in many sources of water (1, 2). The ecological effects and toxicology of the nitrate compounds have been reported in different studies (3, 4). Major sources of nitrate can be used for agricultural fertilizers and wastewater discharges (5, 6). The most adverse effects of nitrate can be mentioned as: eutrophication, methemoglobin, toxicity to aquatics and potential health hazards to infants and pregnant women (2, 5).

Hence, nitrate removal from water and wastewater is considered as an environmental health concern. According to the World Health Organization (WHO) recommendations, the maximum allowable concentration of nitrate in drinking water is 50 mg/L (7). Various methods for nitrate elimination were reported such as ion exchange, biological treatment, reverse osmosis, chemical reduction, and electrochemical processes (7-9). These conventional technologies have some disadvantages such as generating a large amount of intermediates, which require further treatment, continuous monitoring, and slow kinetics rate (8-11).

Electrochemical method is preferred, because of the advantages such as 1) environmentally-friendly technology,

2) high effectiveness process, 3) no addition of chemical requirements, 4) small occupied area, 5) generating small volume of sludge, 6) simplicity of the operation and maintenance, and 7) relatively low investment cost (12, 13). Electrocoagulation is an efficient, credible and low-cost method for treating a large variety of wastewater bodies such as industrial wastewater, municipal wastewater, chemical oxygen demand (COD) removal, dyes, oil-water emulsions, and heavy metal-containing solutions (14, 15). Nitrate removal was reported using different electrodes (16, 17).

2. Objectives

During this study, we investigated the following subjects:

- 1) Evaluation of electrochemical potential for elimination of nitrate and its intermediates using aluminum-graphite electrodes,
- 2) Evaluation of combining affinity of electrocoagulation and air stripping,
- 3) Statistical analysis of experimental data using response surface methodology.

To the best of our knowledge and based on the literature review, optimization of electrocoagulation-reduc-

tion treatment of nitrate from wastewater using the response surface method has not been reported yet.

3. Materials and Methods

3.1. Materials

The materials, including KNO_3 , NaCl , KCl , Na_2CO_3 , HCl , H_2SO_4 , HgI_2 , KI , NaOH , NH_4OH , $(\text{NH}_4)_2\text{SO}_4$, and NH_4NO_3 were purchased from Merck company in analytical grade. Stock solutions of nitrate were prepared by adding the specific values of potassium nitrate (KNO_3) in deionized water. The pH was adjusted to the desired value with 1 M HCl and 1 M NaOH . The NaCl , KCl and Na_2CO_3 solutions were prepared as the supporting electrolytes.

3.2. Reactor Set-Up

In this study, electrocoagulation process was combined with the air stripping system (Figure 1). The process consists of the electrochemical reactor (1 L), DC power supply (TEK-8051, 30 V and 5 A), peristaltic pump (Watson Marlow 101 U/R), and graphite and aluminum electrodes. The air stripping periods are considered 5, and 15 minutes between the two cycles. These periods were selected, to eliminate ammonia and other intermediates produced around the cathode during the process.

The process used four electrodes with the arrangement of graphite/Al/graphite/Al. The dimensions of the graphite and aluminum electrodes were $150 \times 60 \times 5$ mm and $150 \times 60 \times 2$ mm, respectively. The distance between anode and cathode electrodes was fixed to 1 cm. Before the starting-up of the process, the anode electrodes were cleaned with 1 M H_2SO_4 and rinsed with deionized water to eliminate impurities from the surface of the electrodes.

3.3. Analysis

All experiments were performed according to standard methods for the examination of water and wastewater. The samples were collected from the reactor and filtered to remove solid material. The nitrate and ammonium contents were measured by UV-spectrophotometer with an absorption maximum at $\lambda = 220$ and $\lambda = 640$ nm, respectively (Rayleigh UV 9200, China) (18). The pH and ORP were measured with a pH meter (Eutech) and an ORP probe.

3.4. Response Surface Methodology

Response Surface Methodology (RSM) includes the mathematical and statistical methods for modeling and determining the model equations. Also, this method is commonly used for improving and optimizing processes (19). We find a suitable function between the responses and a set of independent variables. This approximate function must be a polynomial of independent variables. Central composite design (CCD) was used to fit this model as the most famous design. In CCD, low axial, high axial, factorial and a central point are coded as -2, +2, -1, +1, and 0, respectively.

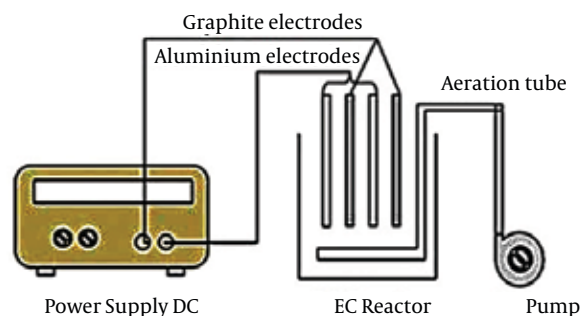


Figure 1. Schematic Diagram of Electrochemical Reactor

3.5. Evaluation of Variables

For modeling and optimization, two important factors were considered: initial concentration of nitrite, and applied electric current. Based on CCD, low axial, high axial, factorial and a central point were chosen as follows:

Initial concentrations of nitrite were ≥ 50 , ≥ 72 , ≥ 125 , ≥ 178 , and ≥ 200 mg/L;

Applied electric currents were ≥ 0.05 , ≥ 0.072 , ≥ 0.125 , ≥ 0.178 , and ≥ 0.2 A;

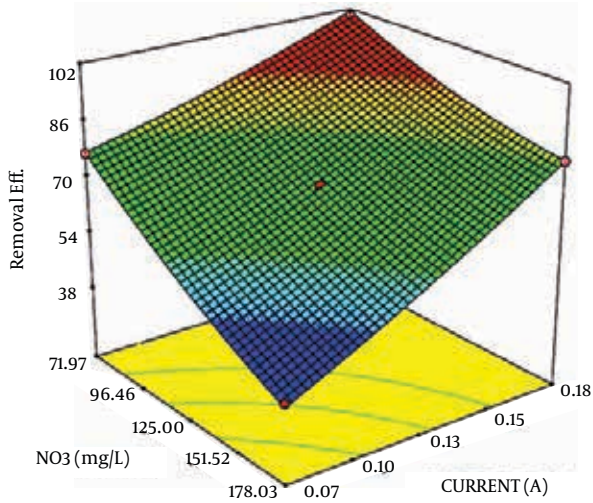
To determine the optimum conditions, supporting electrolyte ($\text{NaCl} = 1$ g/L), anode/cathode: Al/graphite and detention period of 120 minutes were considered.

In the next step, based on optimum factors in RSM, effect of different supporting electrolytes (NaCl , KCl and Na_2CO_3), nitrate intermediates, and oxidation reduction potential were optimized.

4. Results

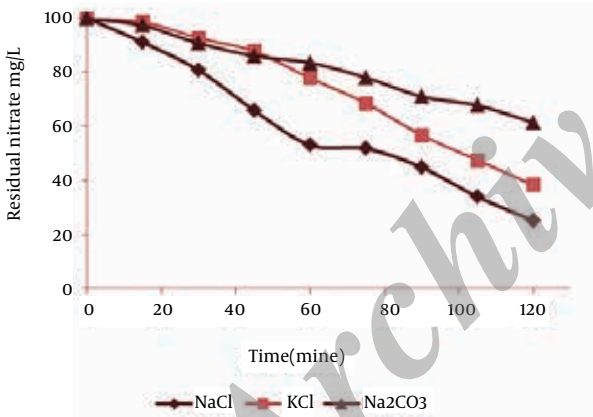
Table 1 shows CCD and responses of each experiment. In this study, the electric current and nitrate concentration were optimized by RSM and designed thirteen runs for developing the model and coded removal equation. Figure 2 displays the contour and 3D response surface plots for the variables. The removal trend indicated the effects of two significant variables on cathodic reduction of nitrate. The statistical values as the R-squared, adjusted R-squared and C.V% that derived from experimental data are shown in Table 2. The R-squared, adjusted R-squared, the mean and C.V% were 0.998132, 0.996798, 72.92% and 1.449454, respectively. As seen in Table 3, the prediction value is observed for models with 95% confidence interval (CI) and prediction interval (PI). Figure 3 displays the effect of different supporting electrolytes such as NaCl , KCl , and Na_2CO_3 on nitrate removal efficiency. Ammonia is the main intermediate of the nitrate in an electrochemical process, and its variations are illustrated in Figure 4. Finally, the variation of the oxidation reduction potential (during the electrocoagulation process at the optimum state) was investigated which its results can be seen in Figure 5.

Figure 2. Three Dimensions Diagram of the Variables for Nitrate Removal Efficiency



Conditions: NaCl = 1 g/L, nitrate concentration range = 50-200 mg/L, applied current range = 0.05-0.2 A, anode = Al and cathode = graphite, detention time = 120 minutes.

Figure 3. Effect of Supporting Electrolyte on Nitrate Removal



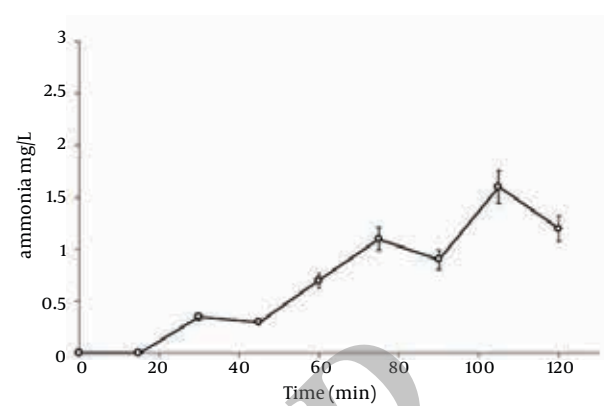
NaCl, KCl, and Na₂CO₃ = 1 g/L, nitrate concentration = 100 mg/L, applied current = 0.10 A, anode = aluminum and cathode = graphite.

5. Discussion

5.1. Statistical Analysis

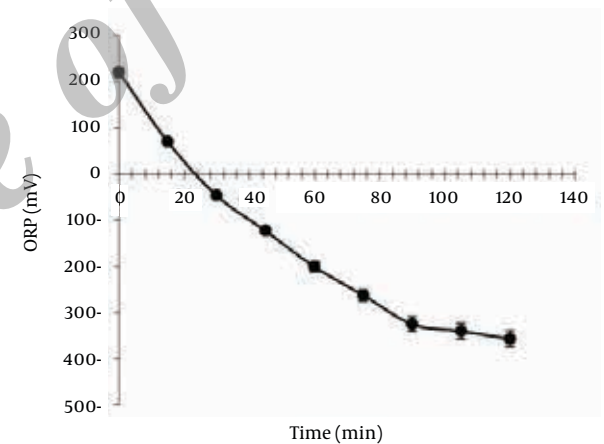
The percentage of reduced nitrate, P Value and the variance analysis of the obtained data showed a significant value (Table 1). The P Value, lack of fit and F value of the model were achieved < 0.0001, 0.0729, and < 748.1962, respectively. Regarding the statistical values for nitrate reduced model, it displayed a high significant conformity (Table 2). Difference between R² (0.998) and adjusted R² (0.996) should be lower than 0.2. In addition, the coefficient of the variation percentage (CV% ~ 1.5) is the

Figure 4. Development of Ammonium During the Electroreduction of Nitrate at Optimum State



Condition: NaCl = 1 g/L, nitrate concentration range = 176 mg/L, applied current range = 0.14 A, anode = Al and cathode = graphite, detention time = 120 minutes.

Figure 5. ORP Variations During the Electrocoagulation Process at Optimum State



Condition: NaCl = 1 g/L, nitrate concentration range = 176 mg/L, applied current = 0.14 A, anode = Al and cathode = graphite, detention time = 120 minutes.

value of the reproducibility of the model and should be lower than 10% (20). Accordingly, the CV% indicates the reliability and high precision of the experimental data. Adequate precision (about ~ 88.26) is the ratio of signal, and the figure should be greater than 4 in order to be desirable. The model removal was calculated from the coded factors equation (Equations 1).

Final equation in terms of coded Factors:

Equation 1.

$$\text{Removal Percentage: Eq} = + 70.4 - 14.90x_1 + 16.79x_2 + 4.75x_1x_2 + 2.68x_1^2 + 1.43x_2^2$$

According to the Figure 2, the higher removal efficiency occurred in lower initial concentration and high applied

current. Also, lower removal rates can be seen in higher concentrations. Nitrate reduction rate shows a direct relation to the applied current and has reverse relationship by initial concentration. So, the 99% removal rate is observed in high current and low concentration. Bazrafshan et al. reported that the most effective removal capacities of nitrate

(96%) could be achieved at 40 Volt, pH10, and reaction time 60 minutes for initial concentration of 5 mg/L nitrate (20). The results of Lacasa et al. indicated that electrocoagulation is an effective technology for nitrate removal because nitrate anions preferentially are adsorbed onto the surfaces of growing metal-hydroxide precipitates (21).

Table 1. The Central Composite Design and its Responses in Experimental and Coded Equation Condition

Run	x_1	x_2	Experimental Removal	Model Removal
1	0	0	71.2	70.4
2	0	1	98	88.62
3	0	1	100	88.62
4	0	0	69.6	70.4
5	0	-1	49	55.04
6	2	1	81	79.04
7	0	-1	54	55.04
8	0	0	70	70.4
9	0	0	70.8	70.4
10	-1	-1	70.4	77.37
11	-1	-1	77	77.37
12	1	0	58	58.18
13	0	-2	39	42.54

Table 2. ANOVA and Statistical analysis for Response Surface Model

Source	Sum of Squares	Mean Square	F Value	P Value Prob > F
Model	4179.503	835.9005	748.1962	< 0.0001
x_1 -NO ₃	1776.837	1776.837	1590.408	< 0.0001
x_2 -Current	2254.443	2254.443	2017.902	< 0.0001
x_1x_2	90.25	90.25	80.78079	< 0.0001
x_1^2	49.77826	49.77826	44.55543	0.0003
x_2^2	14.12609	14.12609	12.64395	0.0093
Residual	7.820547	1.117221	-	-
Lack of Fit	6.220547	2.073516	5.183789	0.0729
Pure Error	1.6	0.4	-	-
Cor Total	4187.323	-	-	-
Result, Mean \pm SD	72.92308 \pm 1.056987	-	-	-
C.V., %	1.449454	-	-	-
Press	46.735	-	-	-
R ²	0.998132	-	-	-
Adjusted R ²	0.996798	-	-	-
Pred R ²	0.988839	-	-	-
Adequate precision	88.26366	-	-	-

Table 3. Prediction and Experimental Values with 95% Confidence Interval (CI) and Prediction Interval (PI)

Prediction	95% CI Low	95% CI High	95% PI Low	95% PI High
82.8064	81.52	84.09	80	85.62

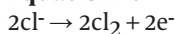
5.2. Optimum Condition

The optimum condition for nitrate removal using electroreduction-flotation process was achieved using 176 mg/L nitrate and 0.14 A electric current. The nitrate removal efficiency was gained 82.8% in the optimum conditions with regard to 95% confidence interval and prediction interval (Table 3). The experimental results obtained from optimum conditions revealed the precision of the resulting data and models.

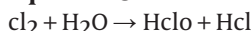
5.3. Effect of Supporting Electrolyte

The use of supporting electrolyte can decrease interior resistance of electrolyte, lower energy consumption, and increase applied frequency in an electrochemical experiment. Although the nitrate ions can serve as a supporting electrolyte in the transfer of electrons during the electrochemical process, but addition of certain salts such as NaCl, KCl and Na₂CO₃ can reduce the internal resistance of the electrolyte (22). According to Figure 3, nitrate reduction due to NaCl, is better than KCl and Na₂CO₃. Higher elimination of nitrate in the presence of NaCl may be due to higher ionization of this compound. The nitrate reduction of NaCl and KCl can occur because of chlorine reaction on the anode electrode as follows (Equations 2 and 3):

Equation 2.



Equation 3.



5.4. Removal of Ammonia as an Intermediate

The main intermediates of nitrate in an electrochemical process are nitrite, NH₂OH, and ammonia (Equations 4-9).

Equation 4.



Equation 5.



Equation 6.



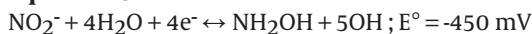
Equation 7.



Equation 8.



Equation 9.



The nitrogen gas is the final environmental friendly product (23, 24). Generally, ammonia is produced during the electrochemical removal process of nitrate. It can be removed by air stripping. Figure 4 shows the various ammonia compounds during the process. The variation of the produced ammonia is due to the intermittent aeration that occurred after air is turned off. The dissolution

of anode (aluminum) and produced monomeric, polymeric and amorphous species, such as Al(OH)₃, Al(OH)₂⁺, Al(OH)₂²⁺, Al₂(OH)₂⁴⁺, Al(OH)₄⁻, Al⁶(OH)₁₅³⁺, Al₇(OH)₁₇⁴⁺, Al₈(OH)₂₀⁴⁺, Al₁₃O₄(OH)₂₄⁷⁺, and Al₁₃(OH)₃₄⁵⁺ is the main reason for the pH increase of the process (25, 26). Because of the dissolution of anode, Al³⁺ ions are released. The amount of aluminum released into the solution from the anode can be calculated by Faraday's law (Equation 10).

Equation 10.

$$W_A = I.t.m / n.F$$

Where W_A is the amount of dissolved anode (g); I is the current intensity (A); t is the run time (s); m is the specific molecular weight (g/mol); F is Faraday's constant (96485 A-s/mol); and n is the number of electrons involved. The overall weight loss of anode ratio during the electrochemical process to theoretical state obtained about 1.3: 1. Near the surface of cathode, the water is hydrolyzed to H₂ and OH⁻ (Equations 11 and 12). The aluminumhydroxide (Equation 13) is the final product of the reaction (27).

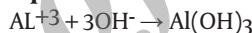
Equation 11.



Equation 12.



Equation 13.



Increasing the pH by the production of hydroxylated species can facilitate the release of ammonia to the atmosphere. Szpyrkowicz et al. (24) reported that the electroreduction of nitrate can be influenced by pH and cathodic potential. The cathodic potential depends more on anode/cathode material, than the electrolyte conditions and electric potential.

5.5. Effect of Oxidation Reduction Potential

The Oxidation Reduction Potential (ORP) is a main factor in the electrochemistry process. It is very important in the formation of intermediates of nitrogen such as NO₃, NO₂, and NH₃. The nitrate reduction needs a reduction condition with a negative ORP. In the experiments, the ORPs were changed from +220 to -375 mV (Figure 5). With regard to the ORP, the produced nitrogen species mainly consists of the ammonia and nitrogen gases. Based on the relationship between the ORP and the concentrations of reduced and oxidized species involved in denitrification processes can be ensured that the denitrification is performed. The ORP has been widely used as a control parameter for online monitoring and control of nitrification and denitrification since 1980s (28). The operating ORP for nitrification and denitrification have been reported between -100 and +100 mV (28). Also, Ra et al. believed that the complete depletion of nitrate is occurred around -300 to -400 mV (29).

The results of this study shows that it is possible to remove the nitrate and its intermediates from wastewater, using an electrocoagulation process. According to the

obtained results, it can be found that the aluminum/graphite electrodes show nitrate removal with high performance. In this process, many operational factors such as pH, supporting electrolyte, applied current, and initial nitrate concentration were found. RSM was used as an effective method and optimized the applied current and initial concentration of nitrate values at 176 mg/L and 0.14 A, respectively. Furthermore, the RSM has been applied to develop the polynomial regression equations and evaluation the relation between the nitrate reduction and the experimental factors. Finally, with regard to the results, 90% removal efficiency was obtained based on the optimized state, and this amount can be used reliably for field scales. Moreover, this process is able to reduce the nitrate according to WHO guidelines or USEPA MCL. Due to the desirable efficiency of electrocoagulation process the field scale assessment is recommended.

Acknowledgements

The authors acknowledge the financial support of Tarbiat Modares University.

Authors' Contributions

Mr. Abbas Rezaee was the main research designer and corresponding author. Mr. Hooshyar Hossini and Mr. Abbas Rezaee were both equally participated in this research.

References

- Koizumi M, Tanaka M, Nishiki Y, Sekimoto M, Furuta T, Inoue H, et al. Reduction of nitrate ion using hydrogen permeating Pd foil electrodes. *Res Chem Inter*. 2006;**32**(5):585-94.
- Rezaee A, Godini H, Jorfi S. Nitrate removal from aqueous solution using mgcl (2) impregnated activated carbon. *Environ Eng Manag J*. 2010;**9**(3):449-52.
- Camargo JA, Alonso A. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. *Environ Int*. 2006;**32**(6):831-49.
- Sparis D, Mystrioti C, Xenidis A, Papassiopi N. Reduction of nitrate by copper-coated ZVI nanoparticles. *Desalination Water Treat*. 2013;**51**(13-15):2926-33.
- Schoeman JJ, Steyn A. Nitrate removal with reverse osmosis in a rural area in South Africa. *Desalination*. 2003;**155**(1):15-26.
- Rezaee A, Godini H, Dehestani S, Yazdanbakhsh AR, Mosavi GR, Kazemnejad A. Biological denitrification by *Pseudomonas stutzeri* immobilized on microbial cellulose. *World J Microbiol Biotechnol*. 2008;**24**(11):2397-2.
- Dash BP, Chaudhari S. Electrochemical denitrification of simulated ground water. *Water Res*. 2005;**39**(17):4065-72.
- Luk GK, Au-Yeung WC. Experimental investigation on the chemical reduction of nitrate from groundwater. *Adv Environ Res*. 2002;**6**(4):441-53.
- Li M, Feng C, Zhang Z, Yang S, Sugiura N. Treatment of nitrate contaminated water using an electrochemical method. *Bioresour Technol*. 2010;**101**(16):6553-7.
- Bi J, Peng C, Xu H, Ahmed AS. Removal of nitrate from groundwater using the technology of electro dialysis and electrodeionization. *Desalination Water Treat*. 2011;**34**(1-3):394-401.
- Li M, Feng C, Zhang Z, Chen R, Xue Q, Gao C, et al. Optimization of process parameters for electrochemical nitrate removal using Box-Behnken design. *Electrochimica Acta*. 2010;**56**(1):265-70.
- Aoudj S, Khelifa A, Drouiche N, Hecini M, Hamitouche H. Electrocoagulation process applied to wastewater containing dyes from textile industry. *Chem Eng Process*. 2010;**49**(11):1176-82.
- Yahiaoui O, Lounici H, Abdi N, Drouiche N, Ghaffour N, Pauss A, et al. Treatment of olive mill wastewater by the combination of ultrafiltration and bipolar electrochemical reactor processes. *Chem Eng Process*. 2011;**50**(1):37-41.
- Rezaee A, Hossini H, Masoumbeigi H, Cheshmeh Soltani R. Simultaneous Removal of Hexavalent Chromium and Nitrate from Wastewater using Electrocoagulation Method. *Int J Environ Sci Develop*. 2011;**2**(4):294-8.
- Adhoum N, Monser L. Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation. *Chem Eng Process*. 2004;**43**(10):1281-7.
- Benhadji A, Taleb Ahmed M, Maachi R. Electrocoagulation and effect of cathode materials on the removal of pollutants from tannery wastewater of Rouiba. *Desalination*. 2011;**277**(1-3):128-34.
- Emamjomeh MM, Sivakumar M. Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. *J Environ Manage*. 2009;**90**(5):1663-79.
- American Public Health Association. AWWA, WPCF. Washington DC, USA: American Public Health Association; 2005.
- Koby M, Demirbas E, Bayramoglu M, Sensoy MT. Optimization of Electrocoagulation Process for the Treatment of Metal Cutting Wastewaters with Response Surface Methodology. *Water Air Soil Pollut*. 2010;**215**(1-4):399-410.
- Bazrafshan E, Soori M, Mostafapour F, Jafarian H, Paseban A. Application of electrochemical process for nitrate removal from aqueous environments. *JNKU*. 2011;**3**(4):25-33.
- Lacasa E, Cañizares P, Sáez C, Fernández FJ, Rodrigo MA. Removal of nitrates from groundwater by electrocoagulation. *Chem Engin J*. 2011;**171**(3):1012-7.
- Soltani R, Rezaee A, Godini H, Khataee AR, Hasanbeiki A. Photo-electrochemical treatment of ammonium using seawater as a natural supporting electrolyte. *Chem Ecol*. 2013;**29**(1):72-85.
- Paidar M. Electrochemical removal of nitrate ions in waste solutions after regeneration of ion exchange columns. *J Appl electrochem*. 1999;**29**(5):611-7.
- Szpyrkowicz L, Daniele S, Radaelli M, Specchia S. Removal of NO₃ - from water by electrochemical reduction in different reactor configurations. *Appl Catal B-Environmt*. 2006;**66**(1-2):40-50.
- Koby M, Can O, Bayramoglu M. Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. *J Hazard Mater*. 2003;**100**(1-3):163-78.
- Katal R, Pahlavanzadeh H. Influence of different combinations of aluminum and iron electrode on electrocoagulation efficiency: Application to the treatment of paper mill wastewater. *Desalination*. 2011;**265**(1-3):199-205.
- Mouedhen G, Feki M, Wery Mde P, Ayedi HF. Behavior of aluminum electrodes in electrocoagulation process. *J Hazard Mater*. 2008;**150**(1):124-35.
- Lackner S, Lindenblatt C, Horn H. 'Swinging ORP' as operation strategy for stable reject water treatment by nitrification-anammox in sequencing batch reactors. *Chem Engin J*. 2012;**180**:190-6.
- Ra CS, Lo KV, Mavinic DS. Real-Time Control of Two-Stage Sequencing Batch Reactor System for the Treatment of Animal Wastewater. *Environ Technol*. 1998;**19**(4):343-56.