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Al ve Fe Plaka Elektrotlar Kullanılarak Kesikli Elektrokoagülasyon Prosesiyle Sulu Çözeltilerden Nitrat Giderimi

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Removal of Nitrate from Aqueous Solutions by Batch Electrocoagulation Process Using Al and Fe Plate Electrodes

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Abstract

Nitrate (NO_3^-) is the most common water pollutant in the world, which has a serious threat to human health due to its high solubility in water. Electrocoagulation (EC) process is an impressive method for removal of pollutants from water. This study is focused on the mechanism of NO_3^- removal from aqueous solutions by electrocoagulation process with using aluminum (Al) and iron (Fe) electrodes. Effects of operational parameters such as electrode material, pH and conductivity on the EC process were evaluated. The process carried out by batch method at room temperature (25 ºC). The experimental results for Al–Al (anode-cathode) electrode reveal that nitrate removal efficiencies are 85.94% and 75.29% at 240 min reaction time, for pH of 3 and 10, respectively. Under the same conditions, for Fe-Fe (anode-cathode) electrode combination, the removal efficiencies are 23.1% and 2.66% at pH of 3 and 10, respectively. NO_3^- removal process was carried out at 5V-1A electrical current. According to the results of the study, it was observed that the Al plate electrode was better than Fe plate electrode in NO_3^- removal. In addition, electrocoagulation at low pH was found to be more effective for nitrate removal in the Al-electrode-operated reactor. In addition, pH values and nitrate removal percentages at Al-electrode-operated reactor increased continuously during 240 minutes at low initial pH. On the iron electrode, steady changes were not observed for pH and nitrate removal rates during process period.

Al ve Fe Plaka Elektrotlar Kullanılarak Kesikli Elektrokoagülasyon Prosesiyle Sulu Çözeltilerden Nitrat Giderimi

Öz

Nitrat (NO_3^-), sudaki yüksek çözünürlüğünden dolayı insan sağlığına ciddi bir tehdit oluşturan dünyadaki en yaygın su kirleticisidir. Elektrokoagülasyon prosesi sulardan kirleticilerin giderilmesinde etkili bir yöntemdir. Bu çalışma, alüminyum (Al) ve demir (Fe) elektrotları kullanılarak elektrokoagülasyon işlemi ile sulu çözeltilerden NO_3^- uzaklaştırılması mekanizmasına odaklanmıştır. Al ve Fe elektrotlar, elektrot malzemesi, pH ve iletkenlik gibi operasyonel parametrelerin değerlendirilmesinde kullanılmıştır. Sistem kesikli olarak oda sıcaklığında (25 ºC) işletilmiştir. Deney sonuçları, 240 dakikalık reaksiyon süresinde, pH 3 ve 10'da Al-Al (anot-katot) elektrot için sırasıyla %85,94 ve %75,29 NO_3^- giderme verimi olduğunu ortaya koymuştur. Aynı koşullar altında, Fe-Fe (anot-katot) elektrot kombinasyonu için ise giderim verimleri pH 3 ve 10'da sırasıyla %23,1 ve %2,66'dır. Nitrat giderim verimi, 5V-1A elektrik akımında değerlendirilmiştir. Yapılan çalışma sonuçlarına göre NO_3^- gideriminde Al plaka elektrotun Fe plaka elektrota göre daha iyi performans gösterdiği görülmüştür. Ayrıca Al elektrot ile işletilen reaktörde düşük pH'da çalışılan elektrokoagülasyonun nitrat giderimi için daha etkili olduğu belirlenmiştir.

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1. INTRODUCTION

During routine agricultural practices, water pollution from nitrate (NO_3^-) is a widespread and growing problem in large agricultural areas in the world. [1]. The increase in nitrate levels can be associated with a variety of human activities, particularly the use of fertilizers in agriculture, septic systems and commercial activities which leads to higher nitrate pollution of water resources [2-5].

Excessive nitrate in water causes methemoglobinemia for children and once accumulated into the human body, it causes digestive system cancers in adults. Maximum admissible level of nitrate in groundwater is accepted as 50 mg L^{-1} according to the World Health Organization [6-8].

There are many nitrate removal technologies recommended and tested in a worldwide, such as, membrane processes [9,10], biological processes [11,12] electrodialysis [13,14], adsorption [15,16], ion exchange [17,18], coagulation and electrocoagulation [19,20]. Membrane processes has high pressure requirements and energy consumptions. So, this method is expensive and unattractive [21, 22]. The biological removal method has some disadvantages including pH and temperature problems and necessity of specific working conditions [23-26]. The adsorption process necessitates large volumes of adsorbents for nitrates removal. For this reason, this method is not convenience [27]. The electrocoagulation process is an electrochemical method for the treatment of contaminated water and is an old water treatment technology used to remove a wide variety of contaminants [28]. EC technology develops as a promising alternative because it provides advantages that eliminate the disadvantages of conventional methods [29]. EC process is preferable because of its environment-friendly, efficient, cost-effective and simple installation and operation. It has simple configuration with an EC reactor consisted of an electrolytic cell with one anode and one cathode [30].

In the present study, aluminum (Al) and iron (Fe) electrode materials were selected and their performances were compared for the removal of nitrate from water. The effects of operating parameters such as electrode materials, pH, reaction time and conductivity for EC process on the nitrate removal efficiencies were studied.

2. MATERIAL AND METHODS

Experimental set-up includes electrodes, reactor and power supply [31]. The EC reactor was made of glass with dimension of 100 x 100 x 250 mm. Seven Al and Fe plate electrodes with dimension of 90 x 200 x 3 mm (purity P 99.5%) and 96 x 180 x 1.5 mm were used in the study, respectively. The distance between the electrodes was 10 mm. The electrodes were connected to a digital power supply (Rigol DP832A model, 30V, 3A).

The chemicals (H_2SO_4, NaOH, NaCl) and nitrate standard solution (1000 mg L^{-1}) were provided from Merck. 1500 ml of synthetic nitrate solution (25 mg L^{-1}) was prepared with diluting of standard nitrate solution. Nitrate ions were analyzed with ion chromatography while Al and Fe were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). pH of the solution was adjusted to 3 and 10 prior to the experiment and agitated with a magnetic stirrer at 250 rpm (IKA RH basic 2) in the EC process. To adjust the conductivity 1g NaCl was added at pH 10. EC tests were performed by batch method. Prior to each set-up, the oxide layer on the Al and Fe electrode surfaces was removed by the solution of the HCl (37%) and the hexamethylenetetramine aqueous solution (3%) for 5-minute immersion. The voltage of EC reactor was set to 5V-1A and the experimental set-up was started at room temperature (25 ºC). The duration of the experiment was 240 min and samples were taken 30 min intervals. The samples were filtered using 0.45 µm syringe filters. Initial and final pH and conductivity of samples were measured with Portable Hach-Lange HQ40d multi-measurement device. At the end of the experiment, the electrodes were washed with water to remove pollutants on the surfaces. A schematic diagram of the electrochemical reactor is shown in Fig.1.

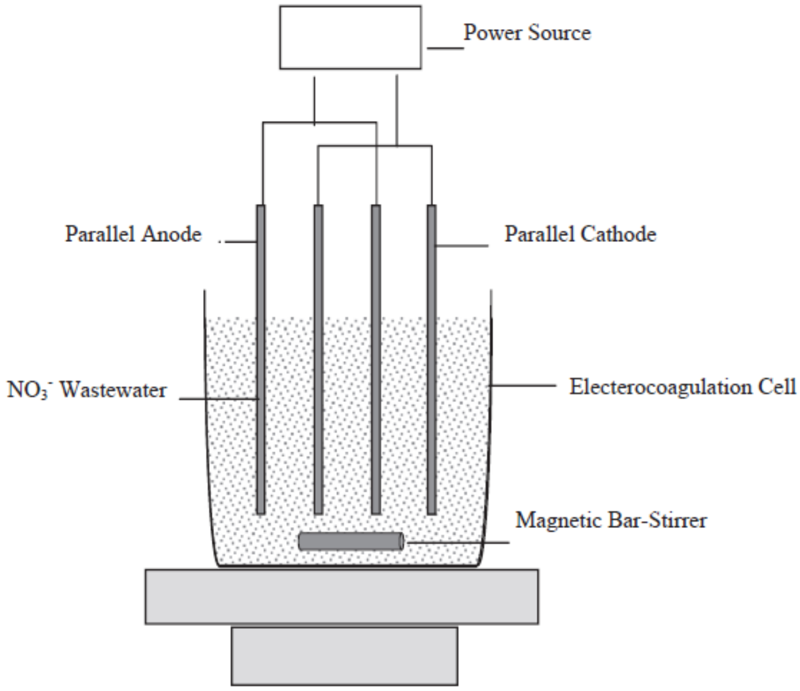


Figure 1. *A schematic diagram of the electrochemical reactor [32]*

The experimental set-up and operational conditions of EC experiments are given at Table 1.

Table 1. *The set-up and operation conditions of EC experiments*

		Operation conditions					
Set-up	Set-up mode	Material	Initial pH	Final pH	Initial Conductivity (µS/cm)	Final Conductivity (µS/cm)	Reaction time (min)
1	Batch	Al-Al	3	7.13	885	154.1	240
2	Batch		10	10.04	218	187.4	240
3	Batch	Fe-Fe	3	3.08	805	577	240
4	Batch		10	9.7	221	202	240

3. RESULTS AND DISCUSSION

The effects of various parameters (electrode materials, pH and conductivity) on the removal of nitrate were investigated. The results are presented and discussed below.

3.1. Effect of electrode materials

The concentrations of Al and Fe were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The Fe concentrations were found below 0.05 mg L^{-1} in all experiments and the results of Al are given in Fig.2. Initial pH was 3 and increased to 7 at the end of 240 min in Fig.2(a). pH was increased from 9 to 10 between 30 and 240 minutes in Fig.2(b). As shown in Fig.3, Al-Al electrode combination has a significant effect on EC process. The nitrate removal percentages of Al-Al and Fe-Fe electrodes were obtained as 85.94 and 23.10% respectively. It was found that an Al-Al electrode has the higher efficiency on the removal of nitrate. In the literature the researchers observed high removal efficiency by Al-Al electrodes in electrochemical process [33,34].

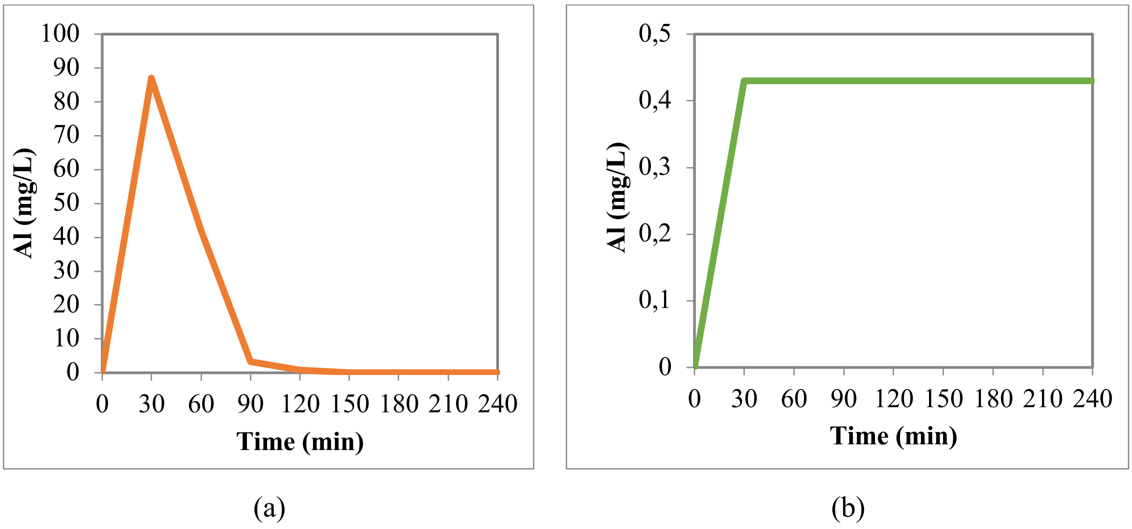


Figure 2. *The concentration of Al in the reactor: (a) initial pH of 3, (b) initial pH of 10*

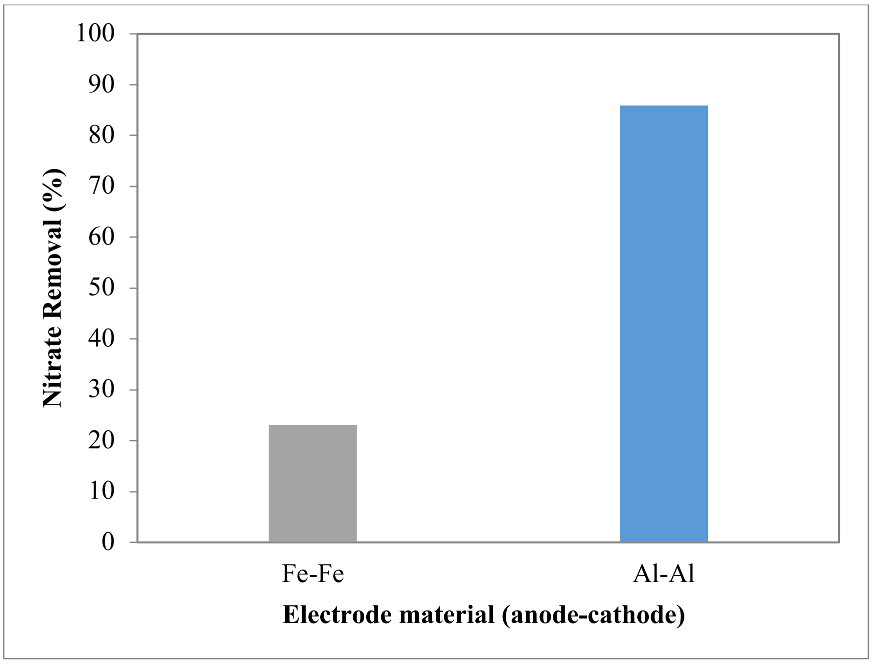
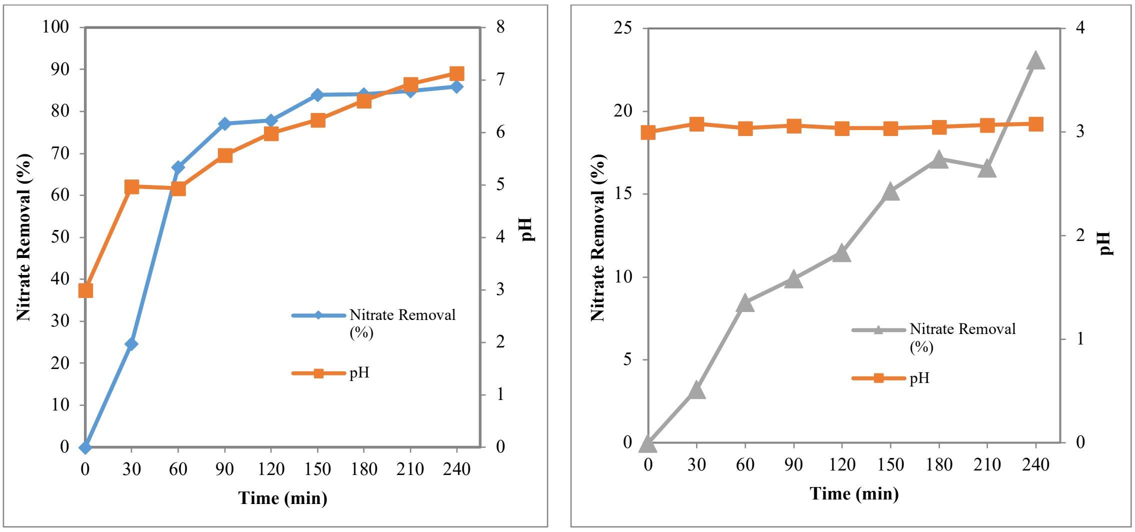


Figure 3. *The effect of electrode materials on the removal of nitrate (at pH: 3 and reaction time:240 min)*

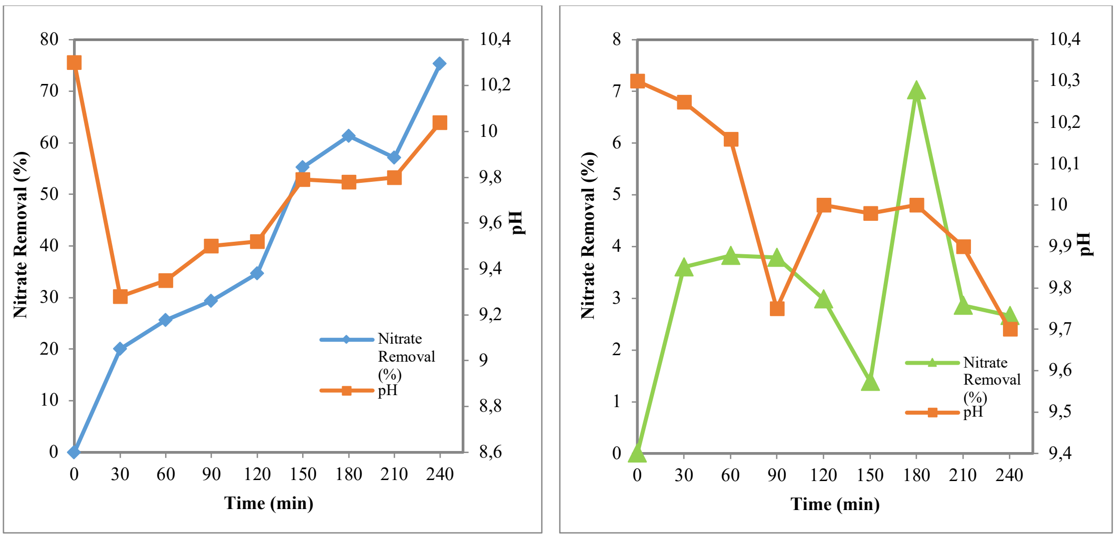
3.2. Effect of pH

pH has a significant effect in electrocoagulation process [35,36]. Especially in this study pH affected the removal of nitrate. Controlling the pH of the water was very difficult during the EC process. The initial pH changed from 3 to 7 for Al-Al electrode at the end of the process. Fe-Fe electrode combinations are not effective on the nitrate removal (Fig.4-5). In the study with initial pH of 3 for Al electrode, pH increased to 7 while the nitrate removal reached approximately 86% for 240 min. However, for Fe electrode, pH has not changed at the end of 240 min and nitrate removal was only about 23%. For Al electrode with initial pH of 10, the pH value increased from 9.3 to 10 while the nitrate removal reached to 75%. The pH and nitrate removal for Fe electrode were found variable for 30 min intervals. In addition, pH values and nitrate removal percentages at Al-electrode-operated reactor increased continuously during 240 minutes at low initial pH. On the iron electrode, steady changes were not observed in pH values and nitrate removal percentages during process period.



(a) (b)

Figure 4. *Nitrate removal for initial pH: 3 with (a) Al-Al electrode, (b) Fe-Fe electrode*



(a) (b)

Figure 5. *Nitrate removal for initial pH: 10 with (a) Al-Al electrode, (b) Fe-Fe electrode*

3.3. Effect of Conductivity

Conductivity was measured in order to examine the treated water quality in electrocoagulation. During each experimental run, it was observed that the conductivity of the solution decreased with time for both Al and Fe-electrode-operated reactors for 3 and 10 initial pH. For Al-Al electrodes, the initial conductivity was 885 µS/cm and 218 µS/cm (additive 1g NaCl) for pH of 3 and 10, respectively. On the other hand, the initial conductivity was 805 µS/cm and 221 µS/cm (additive 1g NaCl) under the same conditions (pH: 3 and 10) for Fe electrodes (Fig.6). As shown in Fig.6 the conductivity decreases as the nitrate removal increases, this is because the ions which cause the increase in conductivity, come together to form the insoluble compounds and reduce the amount of nitrate and conductivity in electrocoagulator.

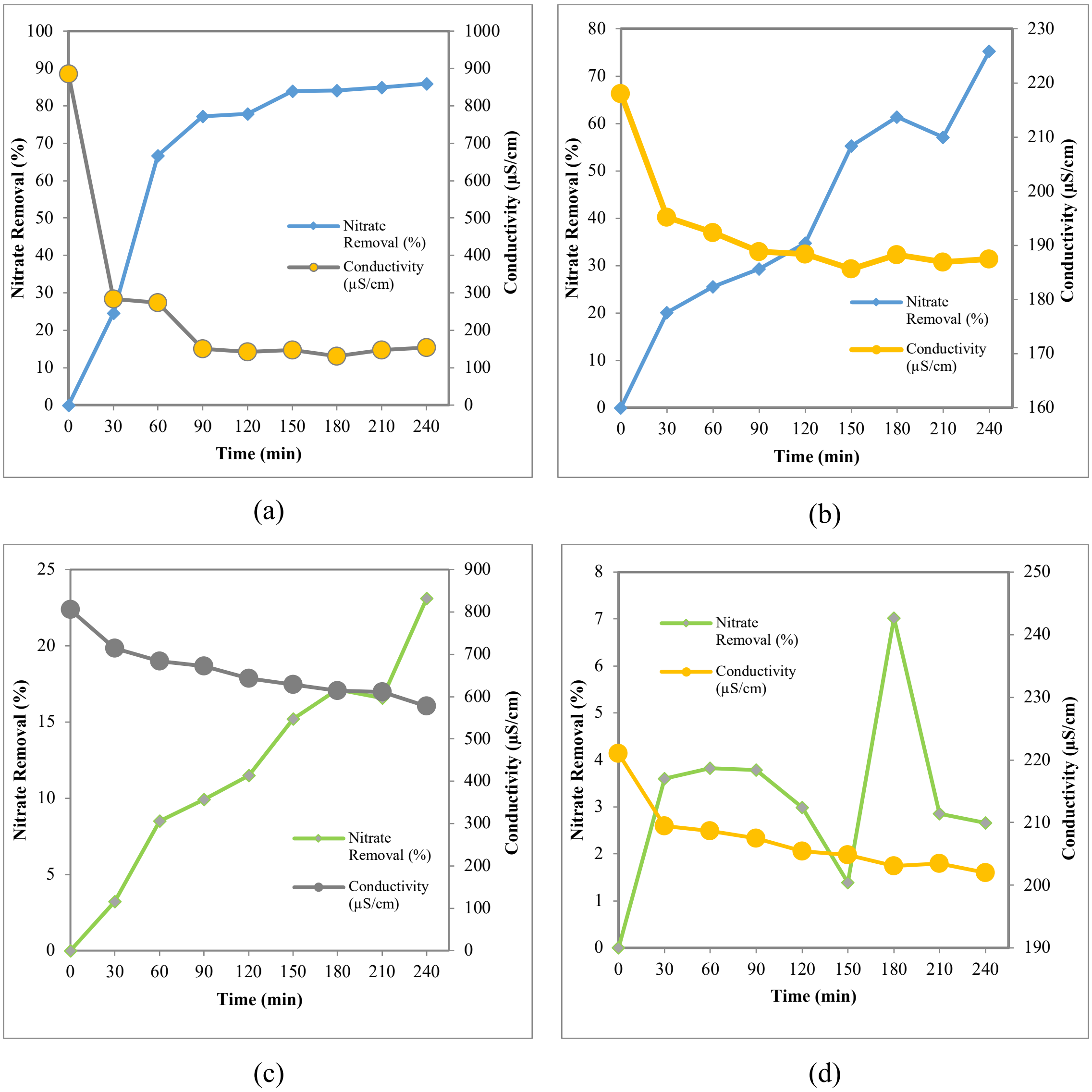


Figure 6. *The effect of conductivity on the nitrate removal: (a) pH: 3-Al electrode, (b) pH: 10-Al electrode, (c) pH: 3-Fe electrode, (d) pH: 10-Fe electrode*

Also, the previous studies carried out in nitrate removal by electrocoagulation method are given in the Table 2.

Table 2. *Previous studies on the removal of nitrate by electrocoagulation*

Method	Objectives	Electrode Type	Results	Reference
Electrocoagulation	Nitrate removal from ground water	Al and Fe	EC method has been as an effective technology in nitrate removal from water.	[21]
	Nitrate removal from water	Al and Fe	Nitrate removal was observed at 92% in the Al-Fe electrodes and 80% in the Fe-Fe electrodes.	[27]
	Nitrate removal from water	Al	Nitrate removal was around 96% at optimum time and pH conditions.	[32]
	Nitrate removal from water	Al	The EC technology for nitrate removal can be an effective process	[37]
	Treatment of nitrate contaminated water	Fe	Under optimum conditions the method can be successful.	[38]
	Treatment of nitrate contaminated water	Al-Fe	Al electrodes were slightly more efficient than Fe electrodes.	[39]

5. CONCLUSION

Electrocoagulation method has been carried out with Al and Fe electrodes in this study. Al-electrode-operated reactor was more effective than Fe-electrode-operated one in nitrate removal. Nitrate removal percentage for low initial pH (pH: 3) was found higher than initial pH of 10 at the end of 240 minute. On the other hand, the Fe electrode was not effective on nitrate removal at low or high pH. Conductivity decreased as the nitrate removal increased in EC process. The experimental results showed that the quality of the EC treated water was closely related to the electrode material, time of electrolysis, conductivity and the pH value. Different modification methods will be applied on our electrode materials and variable operational conditions will be investigated in subsequent studies.

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