



Removal of nitrate from water by electroreduction and electrocoagulation

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Abstract

The aim of this work was to investigate the feasibility of the removal of nitrate from water by applying electrochemical methods such as electroreduction and electrocoagulation. In electroreduction, removal of nitrate to an allowable concentration has been accomplished at the pH range of 5–7 with energy consumption value of 1×10^{-3} kWh g⁻¹. In electrocoagulation, an allowable concentration of nitrate has been achieved at the pH range of 9–11 with energy consumption value of 0.5×10^{-4} kWh g⁻¹. Full removal of nitrate was also possible but with higher energy consumptions for these two methods. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Removal of nitrate; Electroreduction; Electrocoagulation; Water treatment; Surface water

1. Introduction

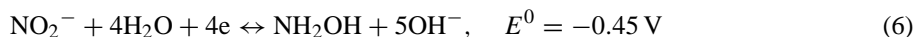
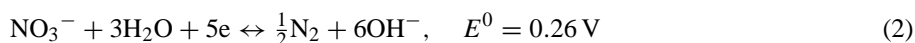
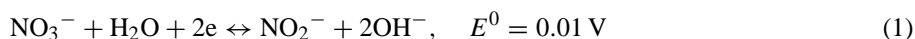
Pollution of ground and surface waters by nitrates is a wide spread and serious problem. Heavy utilization of artificial fertilizers has been known to cause penetration of large quantities of nitrates into ground and surface waters [1]. The nitrate has to be removed since high concentrations of nitrate have a detrimental effect on environment and also limit the usage of water in industry. The maximum allowable concentration of nitrate as NO₃⁻ in drinking water according to the EEC recommendations is 50 mg l⁻¹ (15 mg l⁻¹ for infants).

The current technologies for the treatment of nitrate are ion exchange, biological treatment, reverse osmosis and electrochemical processes. Nitrate ions can be removed from the water on an anion exchange resin. A high excess of regenerant, most notably NaCl, has been required to regenerate the resin periodically. The collected nitrate ends up in the waste solution resulting from the brine regeneration process. Disposal of the waste solution

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may create significant costs and regulatory problems [2]. In biological treatment, a microbiological contamination of water is possible and the control and the effectiveness of the method has some limitations [3]. Reverse osmosis is capable of reducing nitrate concentration. However, resulting brine with high nitrate content can not be discharged into a river or a deep well [4]. The nitrate ion can be destroyed by electrochemical processes through oxidative and reductive reactions into harmless constituents such as water, nitrogen and oxygen [5,6]. Electrodialysis and electrocoagulation is also applicable for the removal of nitrate [7]. Electrochemical methods have advantages such as requirement of no chemicals before and after the treatment, producing no sludge, requirement of small area and low investment cost. One of these methods is the selective electrochemical reduction of nitrate ions to nitrogen and ammonia [8–10].

The main cathodic reactions in the electrochemical reduction of nitrate ions to nitrogen and ammonia have been considered as follows [5]:



The main side reaction at cathode is hydrogen evolution



The main anodic reaction is oxygen evolution



The overall electrochemical reaction is



Electrocoagulation is based on the fact that the stability of colloids, suspensions and emulsions is influenced by electric charges. Therefore, if additional electrical charges are supplied to the charged particles via appropriate electrodes, the surface charge of particles is neutralized and several particles combine into larger and separable agglomerates. The reactions are as follows.

At the cathode



At the anode



In the solution



And with dissolved oxygen in water



Removal of heavy metals and dye stuffs by electrocoagulation has been extensively investigated for last decade [11–14]. In these applications, it has been observed that the nitrate content of effluent decreased significantly [12]. Hence, the electrocoagulation can also be considered as a removal method for nitrate.

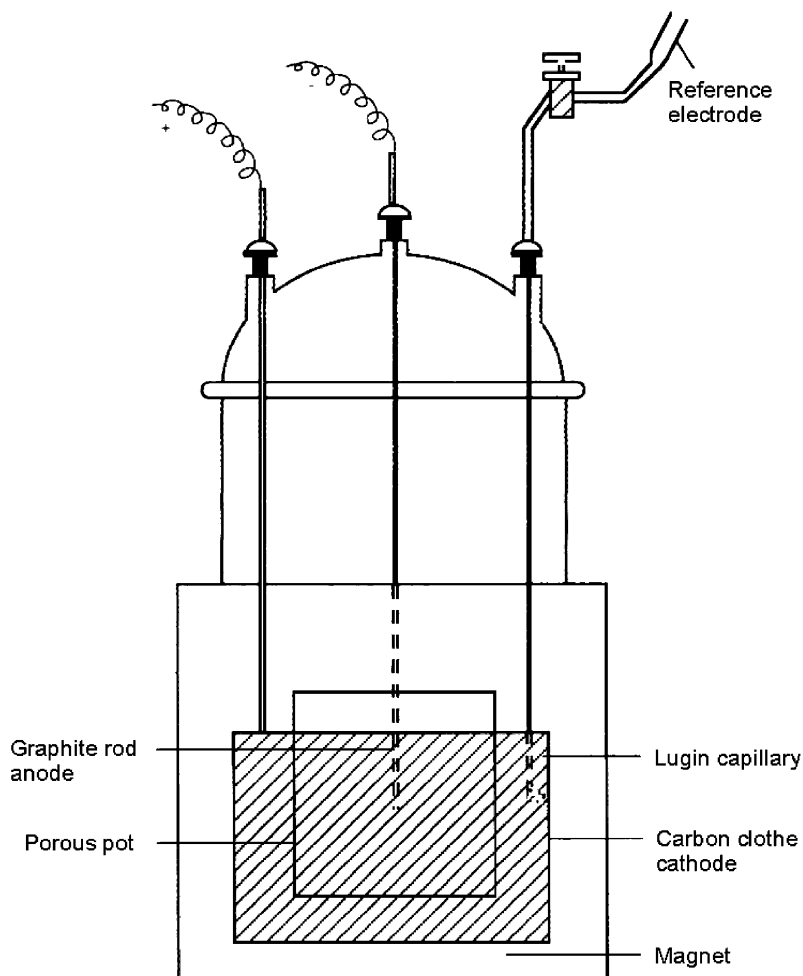


Fig. 1. Electrochemical cell used in electroreduction of NO_3^- .

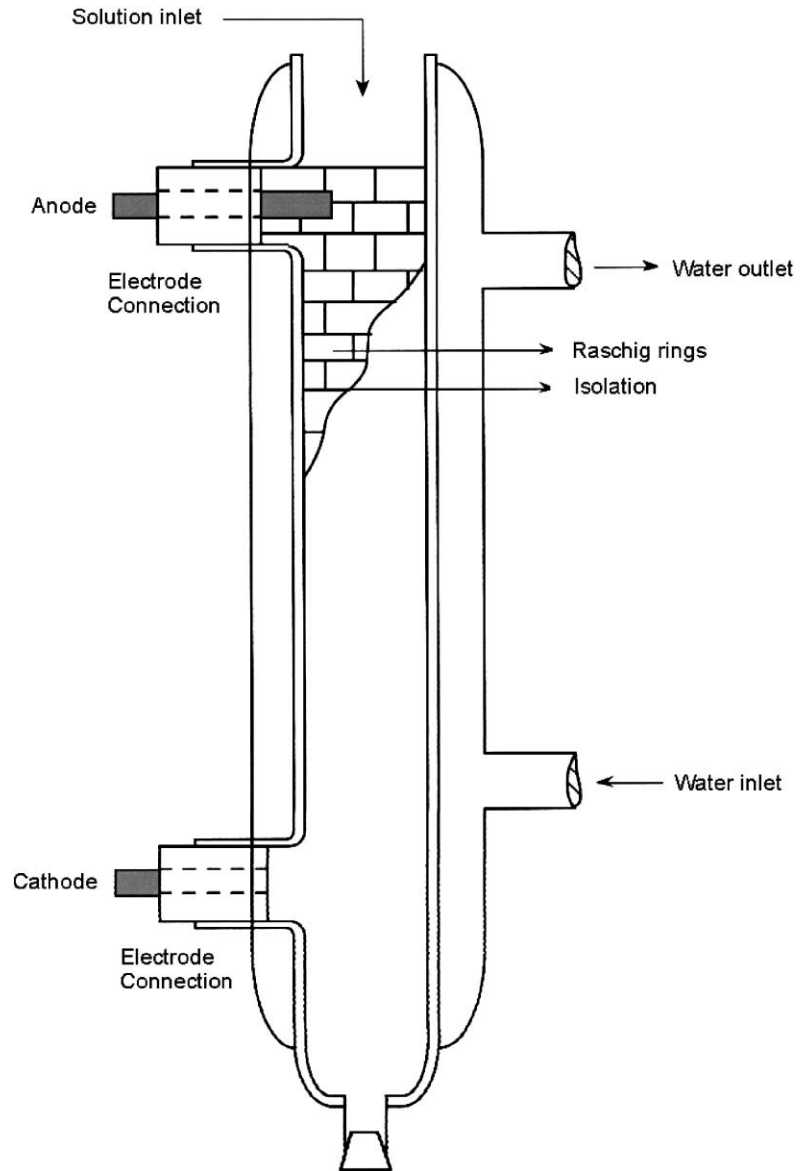


Fig. 2. Bipolar trickling tower electrochemical cell used in electrocoagulation.

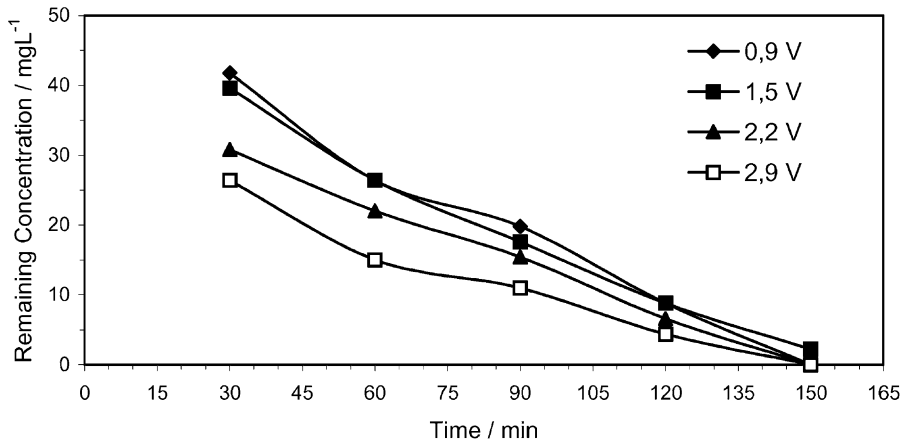


Fig. 3. The variation of removal rate with applied potential (initial concentration, 100 mg l^{-1} ; pH 7).

In the present work, the performance of electroreduction and electrocoagulation systems for the removal of nitrate from water has been investigated.

2. Experimental

2.1. Electrochemical reduction

A model solution containing nitrate as NaNO_3 in two different concentrations has been treated in a batch reactor of 160 cm^3 consisting of graphite rod anode and carbon cloth

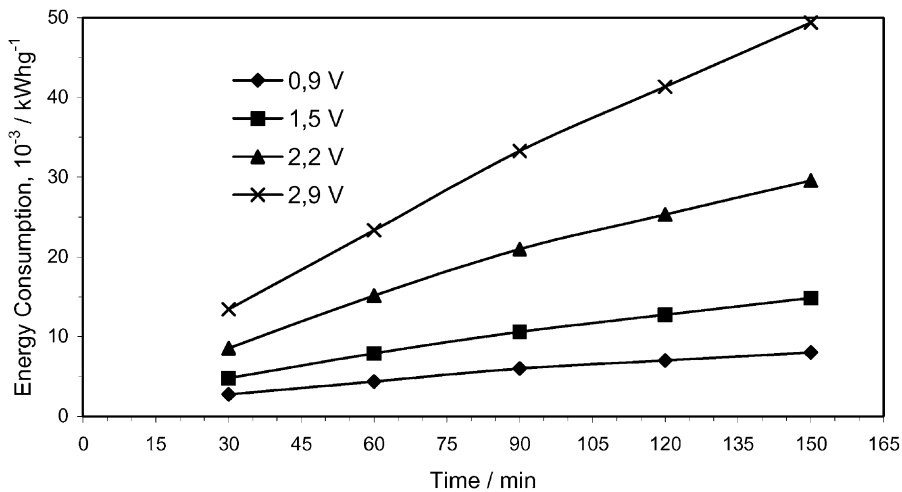


Fig. 4. The effect of applied potential on the energy consumption (initial concentration, 100 mg l^{-1} ; pH 7).

cathode separated by a porous cylinder. The effects of initial nitrate concentrations and pH on the removal efficiency have been investigated and energy consumptions have been calculated.

2.2. Electrocoagulation

Electrocoagulation experiments have been carried out using a bipolar packed bed reactor filled with iron Raschig rings to be consisted of 28 layers. Model nitrate solutions of 100 and 300 mg l⁻¹ have been treated. The effects of applied potential and initial nitrate concentration on the removal efficiency have been investigated, and the energy consumptions have been determined.

Electrochemical cells used in electroreduction and in electrocoagulation have been shown in Figs. 1 and 2, respectively.

3. Results and discussion

3.1. Electrochemical reduction

For an electrochemical reaction, the driving force is the applied potential on the electrodes. It can be seen from Fig. 3 that the removal rate of nitrate has increased as applied potential increased as expected. Much higher potentials cannot be proposed to prevent the nitrogen generated to be reduced to the ammonia according to Eq. (3). Thus, as high potential as 2.9 V can be applied for the removal of nitrate without converting NH₃. Also, energy consumption has increased with an increase in potential as it can be seen from Fig. 4.

The pH is considered to be effective on conversion of nitrate to N₂ gas. The smaller the pH, the conversion of nitrate becomes greater according to Eq. (1). This effect can be seen in Fig. 5. Higher removal rates have been observed at lower pH values with still relatively low energy consumptions as shown in Fig. 6.

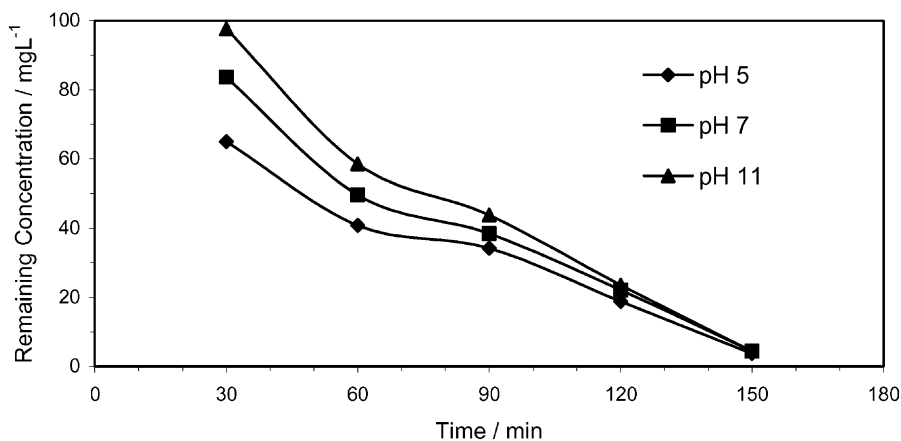


Fig. 5. The variation of removal rate with pH (initial concentration, 300 mg l⁻¹; potential, 2.9 V).

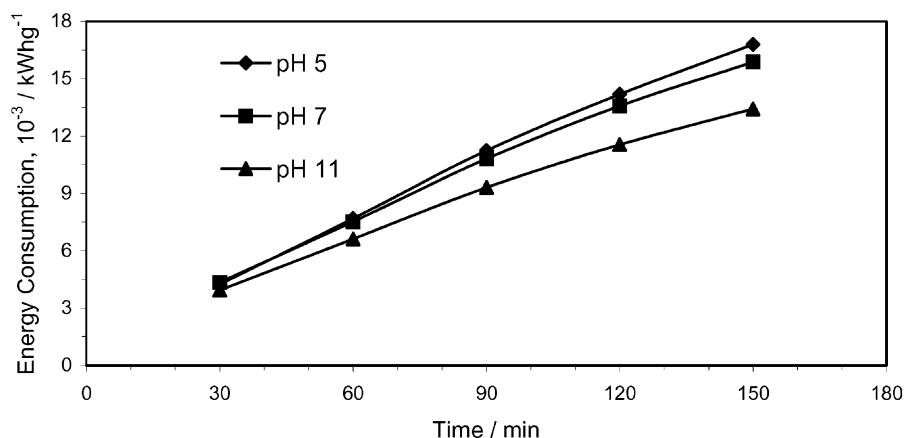


Fig. 6. The effect of pH on the energy consumption (initial concentration, 300 mg l^{-1} ; potential, 2.9 V).

The concentration of nitrate present in water is an important factor effecting the removal of nitrate. Therefore, removal rates of two different initial concentrations have been shown in Fig. 7. As initial concentration decreases, the removal rate has increased as expected in all batch systems. However, energy consumption has been much higher with lower concentrations. In the first 30 min, the concentration of about 30 mg l^{-1} has been achieved with the solution of 100 mg l^{-1} with energy consumption value of $0.5 \times 10^{-4} \text{ kWh g}^{-1}$. Similarly, the concentration of 90 mg l^{-1} has been achieved with energy consumption of $13 \times 10^{-4} \text{ kWh g}^{-1}$ with the solution of 300 mg l^{-1} . The concentration of about 50 mg l^{-1} has been achieved in about 60 min with the solution of 300 mg l^{-1} . At this point energy

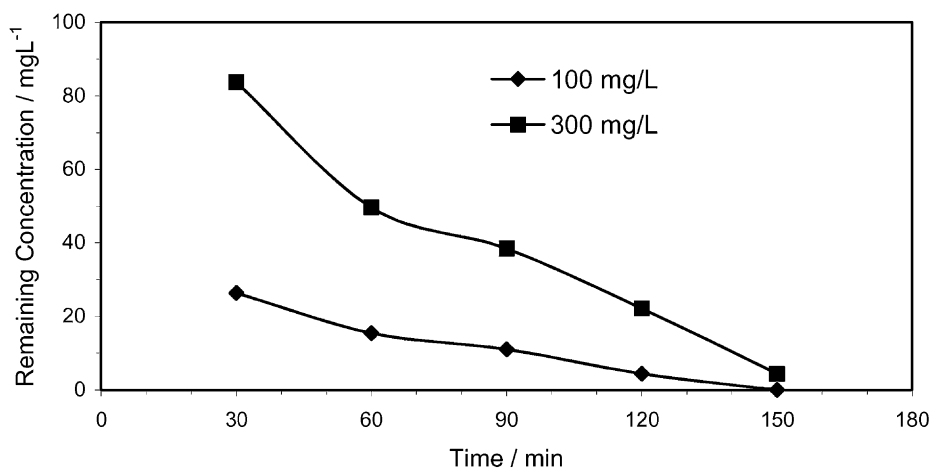


Fig. 7. The variation of removal rate with initial concentration (potential, 2.9 V ; pH 7).

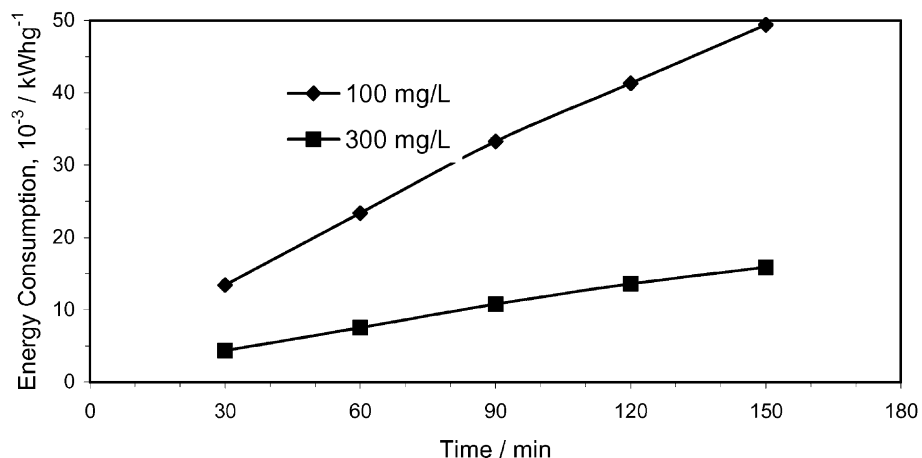


Fig. 8. The effect of initial concentration on the energy consumption (potential, 2.9 V; pH 7).

consumption has been 23×10^{-4} kWh g $^{-1}$. It can be concluded that this is still relatively low value for energy consumption for this type of processes (Fig. 8).

3.2. Electrocoagulation

The effect of applied potential on the removal efficiency can be seen in Fig. 9. Energy consumption values for corresponding potentials have been shown in Fig. 10. Increasing applied potential has resulted in an increase in removal efficiency and energy consumption. For the solution of 300 mg l $^{-1}$, the remaining concentration of 50 mg l $^{-1}$ has been achieved in about 10 min with the energy consumption of about 0.7×10^{-4} kWh g $^{-1}$ at

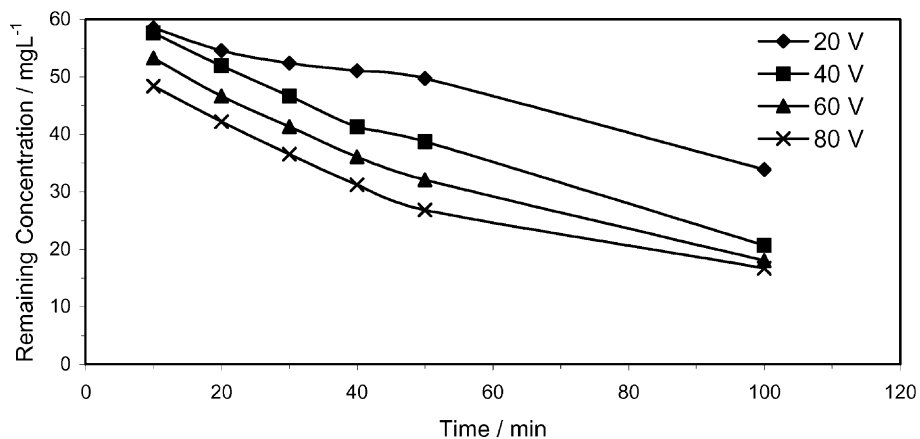


Fig. 9. The variation of removal rate with applied potential (initial concentration, 100 mg l $^{-1}$; pH 7).

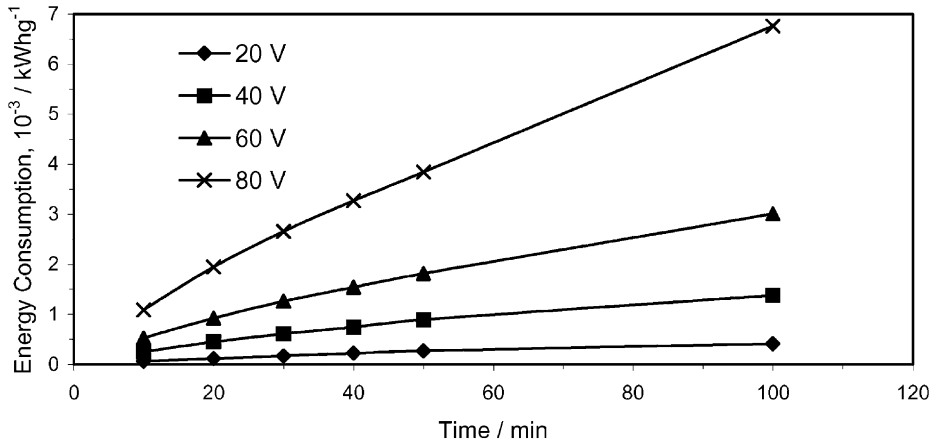


Fig. 10. The effect of applied potential on the energy consumption (initial concentration, 100 mg l^{-1} ; pH 7).

80 V. When 60 V has been applied, the time for achieving 50 mg l^{-1} was 15 min and the energy consumption was $0.7 \times 10^{-4} \text{ kWh g}^{-1}$. At 40 V, the time was 25 min, and the energy consumption was $0.5 \times 10^{-4} \text{ kWh g}^{-1}$, at 20 V the time was 50 min and the energy consumption was $0.25 \times 10^{-4} \text{ kWh g}^{-1}$. Thus, optimum removal rate and energy consumption value should be selected according to the preferences.

The effect of pH has been shown in Fig. 11. It can be seen from the figure that the optimum pH was between 9 and 11 as expected according to the nature of the reaction between ferrous and hydroxide ions, and the energy consumption has not changed significantly

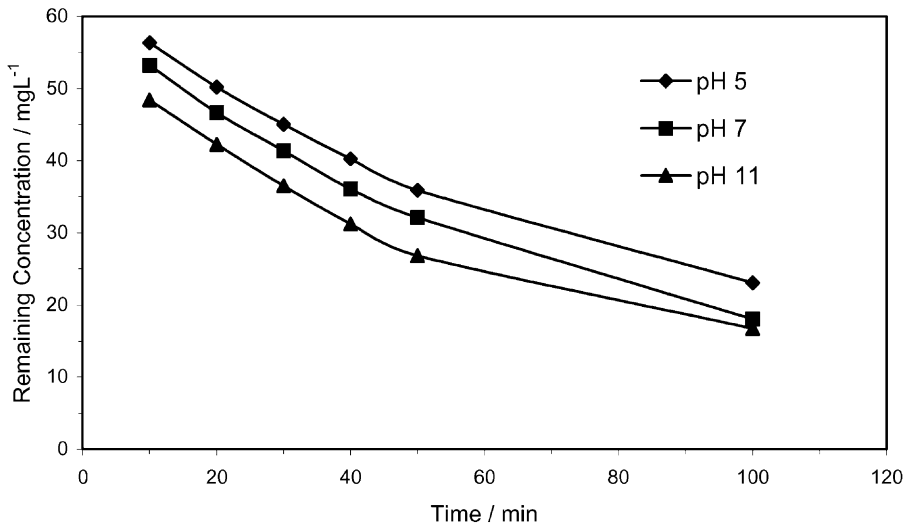


Fig. 11. The variation of removal rate with pH (initial concentration, 100 mg l^{-1} ; applied potential, 60 V).

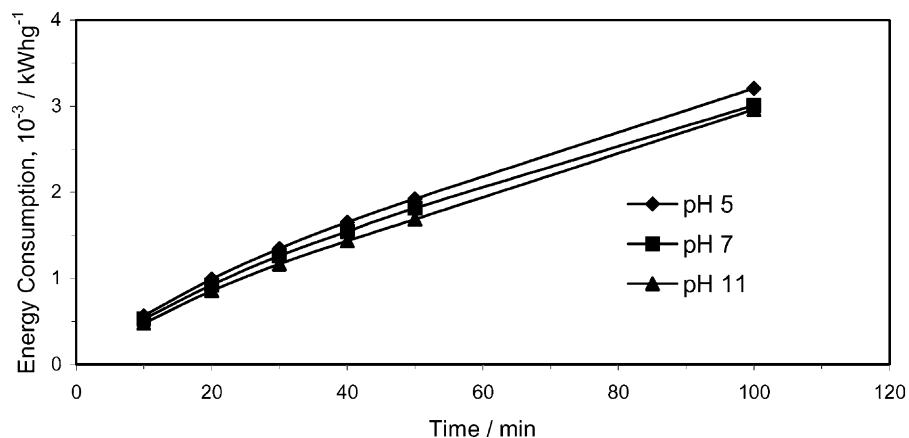


Fig. 12. The effect of pH on the energy consumption (initial concentration, 100 mg l^{-1} ; applied potential, 60 V).

with pH change for especially at the first 10 min of electrocoagulation at which point the concentration of about 50 mg l^{-1} has been achieved (Fig. 12).

The variation of removal rate for two different initial concentrations has been shown in Fig. 13. It can be seen from the Fig. 14 that energy consumption for achieving the remaining concentration of 50 mg l^{-1} was lower for the solution of higher concentrations because of the greater amount removed than that of the solution of lower concentration. However, the duration of electrolysis was much shorter for the lower concentration being one sixth of that of the higher concentration.

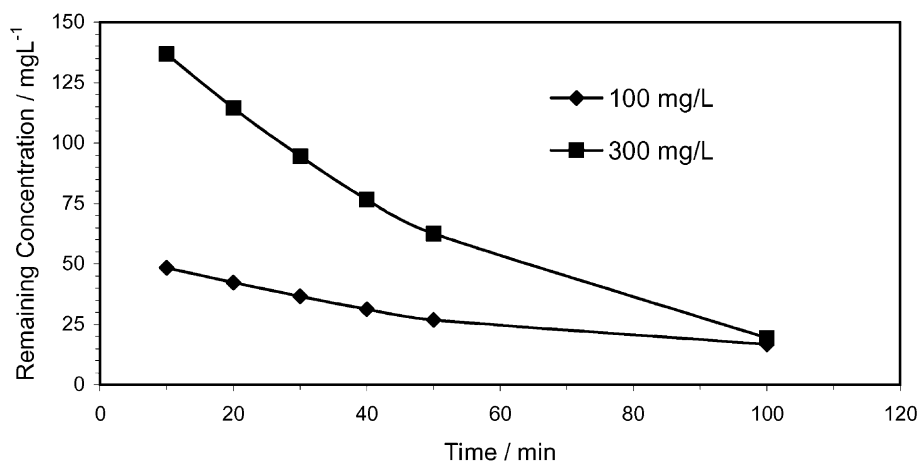


Fig. 13. The variation of removal rate with initial concentration (applied potential, 80 V; pH 7).

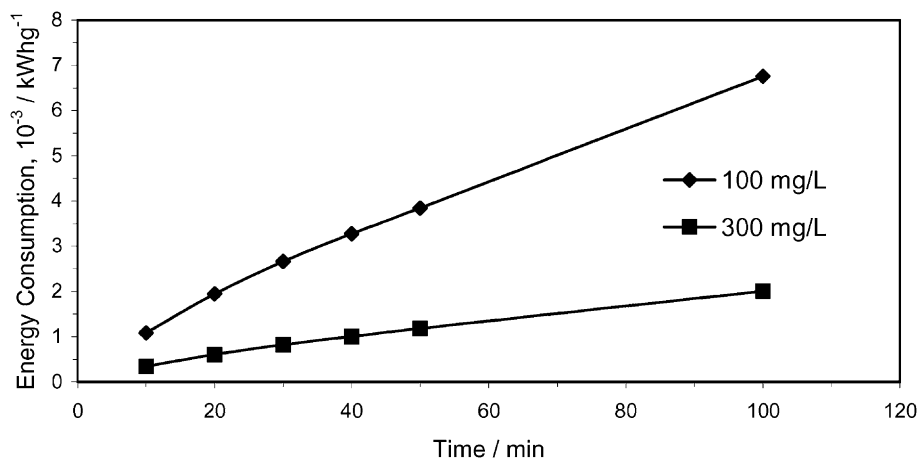


Fig. 14. The effect of initial concentration on the energy consumption (applied potential, 80 V; pH 7).

4. Conclusions

It can be concluded that the nitrate can be removed completely from water by using electrochemical methods such as electroreduction and electrocoagulation. In electroreduction, the main reaction is the conversion of nitrate to N_2 gas which is evolved to the atmosphere. In electrocoagulation, nitrate removal has been accomplished accompanying with the precipitation of $Fe(OH)_3$ produced in water by soluble anode. Reduction of nitrate to N_2 gas can also be possible in this process. Energy consumption for the removal of nitrate has been relatively low for these two methods being typical value for about 0.5×10^{-4} kWh g^{-1} .

It can also be concluded that the electrocoagulation seems to be more cost efficient method comparing electroreduction. However, the former has zero discharge although electrocoagulation has a sludge problem even if unimportant compared with the classical methods.

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