

## ELECTROCHEMICAL DENITRIFICATION OF WATER FOR DRINKING PURPOSE

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### Abstract

Electrocoagulation was used as method of groundwater denitrification for the purpose of obtaining drinking water. The experiments were carried out by using both synthetic solutions and groundwater from the West of Romania. The sacrificial anode was made of aluminium and the cell was equipped either with stainless steel or aluminium cathodes. Also, Linear Scan Voltammetry (LSV) experiments were carried out in order to know the behaviour of aluminium sacrificial anode during the anodic process.

### Introduction

Groundwater is an important supply for drinking water and it is necessary to be aware of various components present in it for practical treatment approaches. The contamination of groundwater with nitrates has become a growing global challenge as a result of excessive fertilization, industrial activity and uncontrolled discharge of wastewaters [1]. The presence of nitrates in groundwater above the limits allowed by regulations in use can lead to health problems. In the human body, nitrates can easily be transformed into nitrites which react with red blood cells and methemoglobin is yielding. If the concentration of methemoglobin is above a certain limit the capacity of blood to transport oxygen to cells and tissues is impacted causing hypoxia and cyanosis [2,3]. Also, nitrites can react with secondary or tertiary amines to produce carcinogenic nitrosamines [4].

The chemical properties of nitrate make it difficult to remove from water using conventional processes such as filtration or activated carbon adsorption. As a result, more complex treatment processes must be considered. Thus, adsorption experiments have been carried out using functionalized chitosan-clinoptilolite nanocomposites [5] or applying electrostatic regeneration of functionalized adsorbent [6]. Denitrification of nitrate-contaminated groundwater using bioelectrochemical systems have been intensively studied [7-12]. Also, electrodialysis [13], hybrid nanofiltration-reverse osmosis filtration [14] and photocatalysis [15] alongside electrochemical processes [16] are suitable and effective alternatives for denitrification of groundwater.

Electrochemical processes because of their advantages, e.g., versatility, energy efficiency, easy operation, automation and environmental compatibility, are promising tools for water treatment. The aim of this study was the denitrification of nitrate-contaminated groundwater by electrocoagulation in order to develop an effective alternative to conventional methods.

### Experimental

LSV experiments were performed by using a Princeton Applied Research VersaSTAT<sup>3</sup>-400, software VersaStudio 2.54.2, potentiostat-galvanostat and a Metrohm three electrode cell. A

silver/silver chloride electrode (Ag/AgCl) was used as reference electrode and a platinum plate of 1 cm<sup>2</sup> as a counter electrode. The working electrode was an aluminium plate with active surface area of 0.49 cm<sup>2</sup>. Prior to the electrochemical measurements, the working electrode was carefully cleaned, degreased and treated by polishing with alumina powder (0.1 mm), and finally washed with distilled water. The interface of the working electrode with the aqueous medium was stabilized by repeated scans in the supporting electrolyte. The LSV experiments were carried out in either 0.1 M Na<sub>2</sub>SO<sub>4</sub> or 0.1 M Na<sub>2</sub>SO<sub>4</sub> + 0.01 M NaCl supporting electrolyte, in a potential range either between -2 → +2 V vs. Ag/AgCl or 0 → +2V vs. Ag/AgCl, potential scan rate either 0.02 or 0.05 V/s and pH of 7.

The electrocoagulation experiments were carried out in a Plexiglas cell. It was equipped with three vertical anodes made of aluminium, each of 4.5x10.2 cm, and four cathodes made of stainless steel or aluminium having the same size as the anodes. The distance between the electrodes was 1 cm.

Volumes of 300 ml working solutions were introduced in the cell, and the applied current densities were 50, 75 and 100 A/m<sup>2</sup> when stainless steel cathodes were used and 10, 25 and 50 A/m<sup>2</sup> for the aluminium ones. Electrolysis duration was 60 minutes and samples were taken at every 15 minutes. All samples were filtered through a low porosity (0.2 µm) filter prior the analysis. The experiments were carried out with synthetic solutions and groundwater from the West of Romania. The synthetic solutions were of 100 mg/L nitrate in 0.1 M Na<sub>2</sub>SO<sub>4</sub> + 0.01 M NaCl as supporting electrolyte. The groundwater was of 175 mg/L (F1) and 152 mg/L nitrate (F2), respectively.

All reagents were of analytical grade and the synthetic solutions were prepared with distilled water. The pH was adjusted to 7. No adjustment of the pH of groundwater was made, and it was 7.9 (F1) and 7 (F2), respectively.

The nitrate concentration was determined by using a Thermo Scientific Orion nitrate ion selective electrode.

## Results and discussion

When aluminium is used as sacrificial anode it is important to know its behaviour during the anodic process as well as in the sequence of processes that occur in the electrocoagulation cell. Sulfate is widespread in groundwater. The aluminium behaviour in the anodic process and in presence of 0.1 M Na<sub>2</sub>SO<sub>4</sub> is shown in Figure 1. The variation of current intensity as the potential was ranged from -2 to +2 V/Ag/AgCl showed that the aluminium dissolution was practically blocked in presence of Na<sub>2</sub>SO<sub>4</sub>.

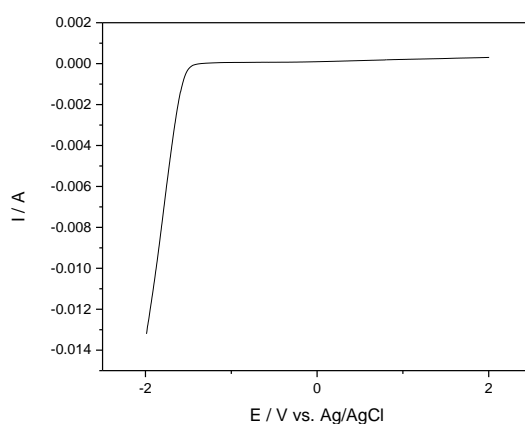


Fig. 1. Linear scan voltammogram of aluminium electrode in 0.1 M Na<sub>2</sub>SO<sub>4</sub> potential scan rate: 0.02 V/s; potential range: -2 → +2 V/Ag/AgCl; pH 7

The experiments carried out did not lead to the expected results when the potential scan rate was increased in order to notice some activation and passivation of the electrode. At low polarization speed, namely 0.02 V/s, in 0.1 M Na<sub>2</sub>SO<sub>4</sub>, the electrode remained practically passive in a large potential range. The increase of the current (Figure 2), with the increase of the polarization speed to 0.05 V/s, can be interpreted by a compromise between the formation of an insulating superficial layer and the limitation of the processes by mass transport.

At a polarization rate of 0.05 V/s, the addition of 0.01 M NaCl did not change the shape of the polarization curves (Figure 3), but the current increased, that signifies the aluminium active dissolution by adding NaCl in the solutions subjected to electrocoagulation.

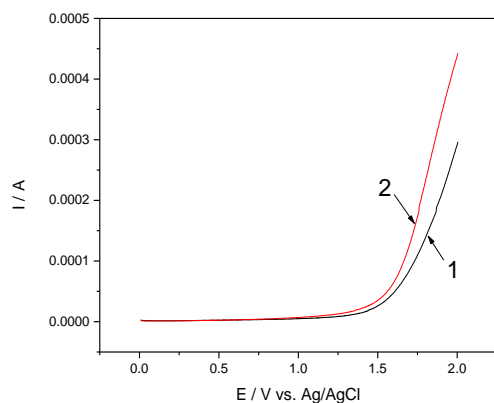


Fig. 2. Linear scan voltammograms of aluminium electrode in 0.1 M Na<sub>2</sub>SO<sub>4</sub> potential scan rate: 0.02 V/s (1) and 0.05 V/s (2); potential range: 0 → +2 V/Ag/AgCl; pH 7

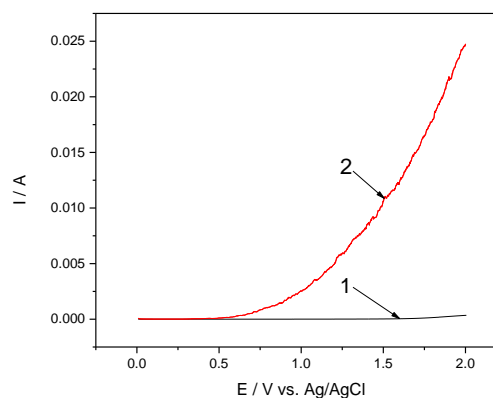


Fig. 3. Linear scan voltammograms of aluminium electrode in 0.1 M Na<sub>2</sub>SO<sub>4</sub> (1) and 0.1 M Na<sub>2</sub>SO<sub>4</sub> + 0.01 M NaCl (2) potential scan rate: 0.05 V/s; potential range: 0 → +2 V/Ag/AgCl; pH 7

When nitrate was added in 0.1 M Na<sub>2</sub>SO<sub>4</sub> + 0.01 M NaCl supporting electrolyte in concentration of 30, 60 and 90 ppm N, respectively, it was found that the current decreased compared to the experiments in which the pollutant was not present (Figure 4). This behavior could be explained by a possible adsorption of the pollutant on the electrode surface.

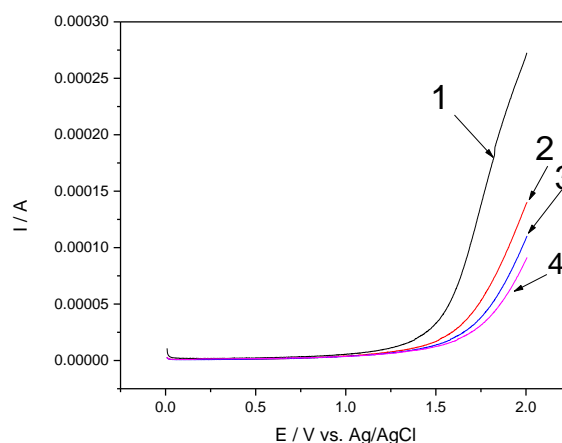


Fig. 4. Linear scan voltammograms of aluminium electrode in 0.1 M Na<sub>2</sub>SO<sub>4</sub> + 0.01 M NaCl (1) and in presence of nitrate: 30 ppm N (2), 60 ppm N (3), 90 ppm N (4); potential scan rate 0.05 V/s; potential range: 0 → +2 V/Ag/AgCl; pH 7

Figures 5-8 show the working conditions and the nitrate removal efficiency obtained in this study. When the electrocoagulation carried out in 0.1 M Na<sub>2</sub>SO<sub>4</sub> + 0.01 M NaCl supporting electrolyte, both stainless steel and aluminium cathodes, for any current density, the nitrate removal efficiency increased with the increase of electrolysis time. The concentration of nitrate was of 33.3 mg/L after 60 minutes of electrolysis by using stainless steel cathodes (Figure 5). This value was under the threshold limit of 50 mg/L nitrate stipulated in Romanian Law 458/2002 concerning the drinking water quality. Concentrations under the threshold limit stipulated in Romanian Law 458/2002 were achieved at lower current densities and shorter electrolysis time when the cell was equipped with aluminium cathodes (Figure 6). Thus, at 10 A/m<sup>2</sup> and 45 minutes of electrolysis, the nitrate concentration was 40 mg/L.

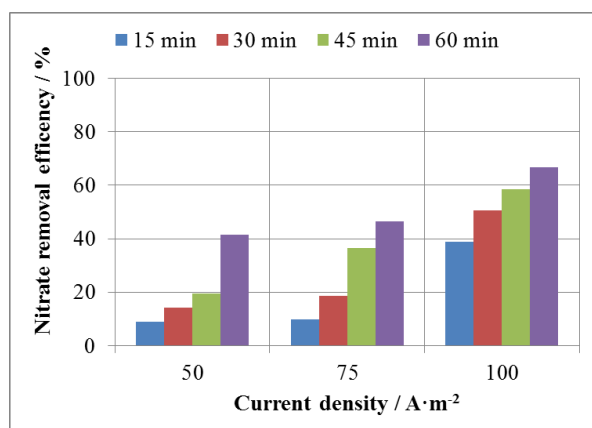


Fig. 5. Nitrate removal efficiency by electrocoagulation with stainless steel cathodes 0.1 M Na<sub>2</sub>SO<sub>4</sub>+0.01 M NaCl supporting electrolyte; nitrate concentration: 100 mg/L; pH: 7

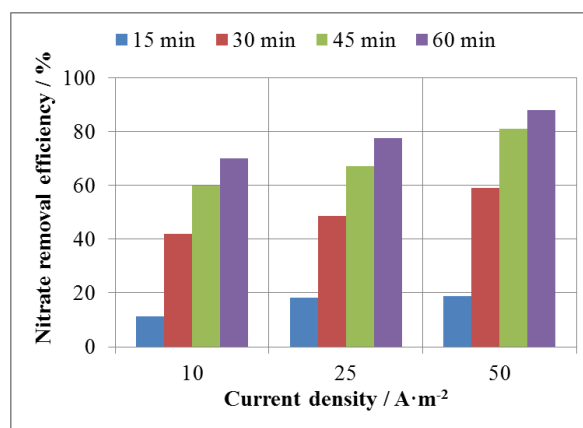


Fig. 6. Nitrate removal efficiency by electrocoagulation with aluminium cathodes 0.1 M Na<sub>2</sub>SO<sub>4</sub>+0.01 M NaCl supporting electrolyte; nitrate concentration: 100 mg/L; pH: 7

The results obtained by using synthetic solutions provided useful information regarding the best working conditions for electrochemical denitrification of nitrate-contaminated groundwater from West part of Romania. Nitrate concentration under the threshold limit stipulated in Romanian Law 458/2002 were recorded for both groundwater samples (F1 and F2) at 50 A/m<sup>2</sup> and electrolysis time of 60 and 45 minutes, respectively (Figures 7 and 8).

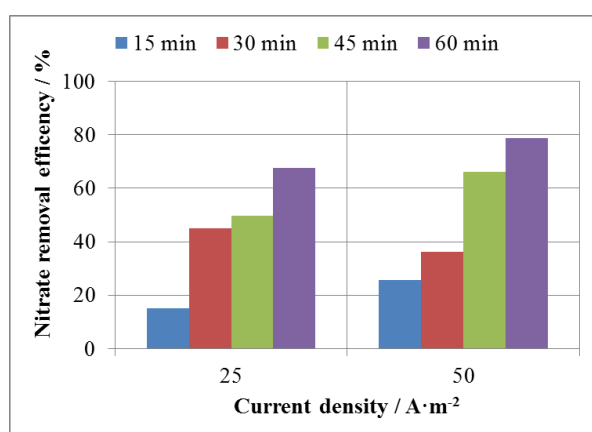


Fig. 7. Nitrate removal efficiency by electrocoagulation from groundwater (F1) nitrate concentration: 175 mg/l; pH: 7.9; cathodes: aluminium

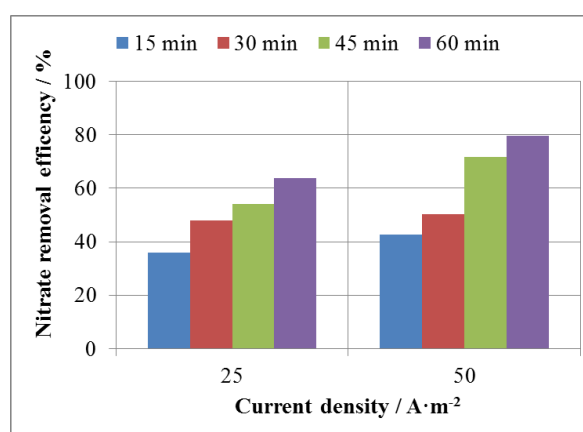


Fig. 8. Nitrate removal efficiency by electrocoagulation from groundwater (F2) nitrate concentration: 152 mg/L; pH: 7; cathodes: aluminium

The specific energy consumption was calculated according to equation (1) by using as working conditions: applied current density of 50 A/m<sup>2</sup> (1.15 A), electrolysis time of 60 minutes, cell voltage of 4 V, groundwater sample of 300 ml and it was of 15.3 kWh/m<sup>3</sup>. The pH of groundwater was in the range 7-8. In these conditions, the concentration of nitrate in the treated groundwater was under the threshold limit of 50 mg/L.

$$Q = U \cdot I \cdot t \cdot 10^{-3} / V \cdot 3600 \quad (1)$$

where:

Q = specific energy consumption, kWh/m<sup>3</sup>; U = cell voltage, V; I = current intensity, A; t = electrolysis time, s; V = electrolyzed solution volume, m<sup>3</sup>

### Conclusion

Electrocoagulation with aluminium sacrificial anode was applied to denitrification of groundwater for drinking water purpose. The best results were achieved when aluminium cathodes were used. The best nitrate removal efficiency from groundwater from two sites in West of Romania was of about 80% and the concentration of nitrate was under the limit allowed by the regulations in use. The LSV experiments showed the aluminium sacrificial anode behaviour in the presence of sulfate and chloride that are often accompanying anions of nitrate in groundwater.

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