

ELECTROCHEMICAL DENITRIFICATION METHOD FOR NITRATE REMOVAL FROM WATER

Ilie VLAICU¹, Aniela POP¹, Florica MANEA²

¹S.C. Aquatim S.A., Gheorghe Lazar Str., no 11 A, 300081, Timisoara, Romania
²"Politehnica" University of Timisoara, P-ta Victoriei no. 2, 300006, Timisoara, Romania



Problem statement

Because nitrate can cause serious health problems in humans such "blue baby syndrome" in infants, liver damage and cancer, developments in denitrification technology are currently required.

Recently, electrochemical reduction of nitrate increasing attention as alternative denitrification method because allows the high treatment efficiency, no sludge production, small area occupied and relatively low investment costs. In general, applications of the electrochemical process for denitrification are limited due to generation of ammonia and nitrite, and the difficulty is to find the proper condition to perform both cathodic reduction of nitrate and anodic oxidation of the produced ammonia.

The aim of the study

The purpose of this work is to characterize three types of electrode materials to maximize transformation of nitrate from aqueous solution to nitrogen gas by electrochemical denitrification.

Experimental

The Ag-modified zeolite-expanded graphite-epoxy and Cu-modified zeolite-expanded graphite-epoxy (EGZAg and EGZCu) composite electrodes were obtained from two-component epoxy resin mixed with conductive expanded graphite (EG) fillers powder and copper/silver ion-exchanged zeolite (clinoptilolite). Discs with a surface area of 19.63 mm² were embedded in polyethylene and electrical contacts were made using copper wire. Then the epoxy was cured at 50 °C for 60 minutes.

The boron-doped diamond electrode (BDD) with the surface area of 7.07 mm² was provided by Windsor Scientific Ltd, UK.

The electrochemical behaviour of the working electrodes in the presence of nitrate was studied by cyclic voltammetry (CV) in 0.1 M Na₂SO₄ supporting electrolyte.

The controlled potential experiments were carried out by chronoamperometry (CA) and multiple-pulsed amperometry (MPA) techniques using an undivided cell of 50 cm³ volume, for 2 mM nitrate concentrations in 0.1 M Na₂SO₄ supporting electrolyte.

The quantitative assessment of nitrogen as nitrate (N-NO₃) was carried out according to the Romanian standard SR ISO 7890-1/1998 and total nitrogen was analyzed by using a Multi N/C 2100/2100 analyser, provided by Analytik Jena.

Results

The electrochemical behaviour of the electrodes by cyclic voltammetry

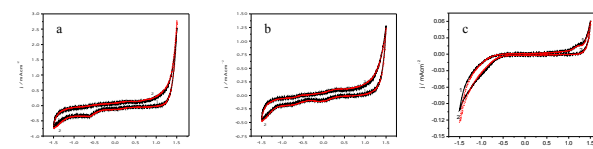


Figure 1. Cyclic voltammograms (CVs) recorded with a potential scan rate of 0.05 Vs⁻¹ between -1.5 V and 1.5 V vs. SCE in a 0.1 M Na₂SO₄ supporting electrolyte (curve 1) and in presence of 2 mM NO₃⁻ (curve 2) at (a) EGZAg; (b) EGZCu and (c) BDD electrodes.

Chronoamperometry and multi-pulsed amperometry data

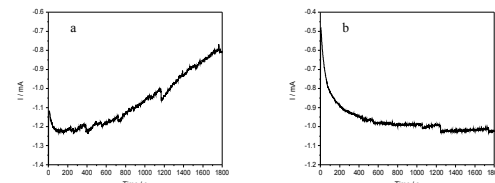


Figure 2. Chronoamperograms (CAs) recorded in 0.1 M Na₂SO₄ supporting electrolyte and in the presence of 2 mM nitrate at E=-2 V vs. SCE at the electrodes: (a) EGZAg; (b) EGZCu.

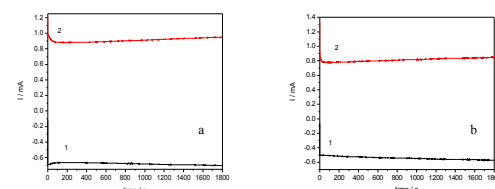


Figure 3. Multiple-pulsed amperograms (MPAs) recorded in 0.1 M Na₂SO₄ supporting electrolyte and in the presence of 2 mM nitrate at two potential levels, E_{appl}=-1.5 V vs. SCE (curve 1) and E_{ox}=1.5 V vs. SCE (curve 2) at the electrodes: (a) EGZAg; (b) EGZCu.

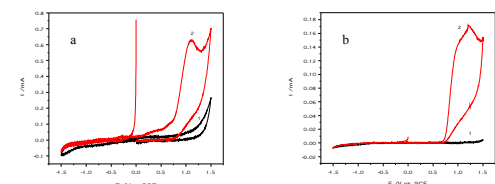


Figure 4. Cyclic voltammograms (CVs) (first scan) recorded with a potential scan rate of 0.05 Vs⁻¹ between -1.5 V and 1.5 V vs. SCE in a 0.1 M Na₂SO₄ supporting electrolyte and in presence of 2 mM NO₃⁻ before (curve 1) and after electrolysis at -2 V/SCE (curve 2) at (a) EGZCu and (b) BDD electrodes.

Table 1. Electrochemical efficiencies of total nitrogen removal (E_{TN}) and nitrate reduction (E_{N-NO3}) for all studied electrodes using CA and MPA techniques

Electrode material	Electrochemical technique	E _{TN} mgC ⁻¹ cm ⁻²	E _{N-NO3} mgC ⁻¹ cm ⁻²	k* %
EGZAg	CA	0.14	0.87	16
	MPA	0.08	0.17	47
EGZCu	CA	0.31	0.69	45
	MPA	0.22	0.4	55
BDD	CA	5.66	17.7	32
	MPA	8.05	16.1	50

* k - effective total nitrogen removal ratio (E_{TN} × 100 / E_{N-NO3}).

Conclusions

The electrochemical nitrate reduction and total nitrogen removal at Ag-doped zeolite-expanded graphite-epoxy, Cu-doped zeolite-expanded graphite-epoxy composite and boron-doped diamond electrodes in 0.1 M Na₂SO₄ supporting electrolyte were investigated by chronoamperometry and multiple-pulsed amperometry.

The electrochemical behaviour of the electrodes in the presence of nitrate was studied by cyclic voltammetry, which allowed selecting the potential value for the controlled potential electrolysis. The experimental results showed that BDD electrodes exhibited the best performance for the electrochemical nitrate reduction and total nitrogen removal under all working potential conditions. Alternating the application of oxidation potential with reduction one achieved by MPA led to improvement the effective total nitrogen removal based on minimization reduction products resulted from nitrate reduction. The high electrochemical performance of BDD electrode for total nitrogen removal from aqueous solution noticed the great potential for its practical application in electrochemical denitrification treatment of groundwater.

Selected references

- Badea, G.E. (2009), *Electrochim. Acta*, **54**(3), 996-1001.
- Li, M., Feng, C., Zhang, Z. and Sugiura, N. (2009) *Electrochim. Acta*, **54**, 4600-4606.
- Manea, F., Pop, A., Radovan, C., Malchev, P., Bebeslea, A., Burtica, G., Picken, S., Schoonman, J. (2008), *Sensors* **8**, 5806-5819.
- Massai, H., Loura, B.B., Ketcha, M.J., Chtaini, A. (2009), *Port. Electrochim. Acta*, **7**(6), 691-698.
- Polatides, C. and Kyriacou, G. (2005), *J. Appl. Electrochem.* **35**(5), 421-427.
- Pop, A., Manea, F., Malchev, P., Proca, C., Burtica, G., Picken, S., Schoonman, J. (2009), *J. Optoelectron. Adv. M.-Symposia* **1**(1), 96-100.
- Souza-Garcia, J., Ticianelli, E.A., Climent, V. and Feliu, J.M. (2009), *Electrochim. Acta* **54**(7), 2094-2101.

Acknowledgements

This study was supported by the Romanian National Research Programs - PN II: STEDIWAT, no. 32-125/2008; NANO-ZEOREZID, no. 72-156/2008.