

CARBON FLOW-THROUGH ELECTRODES FOR ELECTROCHEMICAL REMOVAL OF NITRATE IONS FROM AQUEOUS SOLUTIONS

Yu. Basova, H. Kanoh, K. Ooi

*National Institute of Advanced Industrial Science and Technology
2217-14 Hayashi-cho, Takamatsu, Kagawa 761-0395, Japan*

Introduction

Nitrate contamination is one of the major water quality problems due to their health and environment effects. Electrochemical reduction of nitrates on various electrodes (i.e. metals, metal complexes and carbon materials modified with platinum group metal catalyst), configured in a parallel plate, a packed bed or a gas diffusion electrode mode, is one of the method used to remove nitrates from water [1-4]. Capacitive deionization method by electroadsorption of nitrate ions on the surface of carbon aerogel electrode has also been proposed [5]. In the present work, electrochemical separation techniques using synthetic granulated carbons as fluidized-bed electrode in the reactor with flow through arrangement is applied for potential-dependant elimination of nitrate ions from neutral aqueous solutions. Electrodes used in this study were found to possess chemical and inertness and allow application in a wide range of the electrical potentials; are characterized by a high fluid permeability and accessibility for electrochemically active species; can be easily shaped as required by cell design consideration; possess high electrical conductivity and continuity of electrical contact throughout the electrode bed. Two approaches for removal of nitrates are considered: (a) electrochemical reduction of NO_3^- ions by the external potential and (b) electroadsorption of NO_3^- ions on the carbon surface.

Experimental

Synthetic granulated carbon materials SCN and SCN carbon modified with macrobicyclic trisdimethylglyoximate cobalt(III) complex (CoDmg) were used as electrode materials in this work (Table 1). Surface-modified carbon electrode was prepared by adsorption of complex on the surface of the plain carbon granulars. Details of the procedure has been reported elsewhere [6]. The electrolyte solutions were prepared with ACS grade reagents of sodium nitrate (NaNO_3) and sodium perchlorate (NaClO_4).

All cyclic voltammetry experiments were conducted in a typical three-electrode electrochemical cell with a single carbon sphere as the working electrode and a Pt wire as a counter electrode. A schematic diagram of equipment used and cell for a fluidized-bed electrode employed here

are shown in Fig. 1. The desired flow rate, $1 \text{ cm}^3 \text{ s}^{-1}$, was adjusted to effectively provide electric-transfer conditions and mass-exchange between the electrode particles and liquid-media components during the electrolysis. The height of motionless layer of the carbon particles was estimated to be about 10 mm. A platinum plate was used as a counter electrode. The reference electrode was saturated Ag/AgCl reference electrode system. All voltages are reported with respect to Ag/AgCl.

Results and discussion

Cyclic voltammeteries (CVs) were recorded at 1 to 100 mVs^{-1} in 10^{-4} to $10^{-1} \text{ mol dm}^{-3} \text{ KNO}_3$ in $1.0 \text{ mol dm}^{-3} \text{ NaClO}_4$ solutions.

Typical CVs of nitrate reduction at the plain and modified SCN carbon electrodes are shown in Fig. 2. At the plain SCN electrode a nitrate reduction current occurred at ca. -0.6 to -0.8 V. The reduction current at modified electrode (Fig. 2 b) was initiated at -0.5V and it reached maximum at ca. -0.65 to -0.7 V.

The reduction of nitrate occurs through the formation and accumulation of nitrites as the intermediate products at the surface of the electrode. The desired objective in the electroprocessing of nitrate solution is to totally reduce the nitrates and nitrites to nitrogen or ammonia. The reduction of nitrate ions using electrochemical cell with fluidized-bed electrode was carried out at two selected constant potentials (i.e. -0.6 V and -0.8 V). The percentage of removal of NO_3^- ions, was calculated from the following equation: $\alpha_{\text{NO}_3^-} = (C_{\text{st}} - C_{\text{fin}})100/C_{\text{st}}$, %, in which C_{st} and C_{fin} are the NO_3^- ion concentrations before and after contact of the solution with the carbon fluidized-bed layer.

The adsorption of nitrate ions in the control experiments was rather low. Figure 3 a shows the variation of nitrate ions at the constant potential of -0.6 V as a function of time for the reduction of the solution containing $0.01 \text{ mol dm}^{-3} \text{ KNO}_3$ at various carbon fluidized-bed electrodes. The concentration of nitrate ions diminished in 2 - 4 h and then remained constant. From Fig. 3 b, the reduction is substantially enhanced at more negative potential. Cathodic potential of -0.8V applied here to the carbon layer is sufficient to reduce not only the nitrate to nitrite but also nitrite formed further to ammonia or N_2 gas. As

seen from Fig. 3, the amount reduced is slightly higher for the modified specimen presumably because of some catalytic effect of modified agent on the reduction process or formation of fresh surface sites produced due to hydrogen evolution during electrolysis, which occurs at less negative potentials than that observed for other specimens.

The electroadsorption of nitrate ions was studied at two constant potentials +0.4 and +0.6 V. Figure 4 shows the variation of the concentration of NO_3^- ions as a function of applied potential. Overall, tests demonstrated that nitrate ions can be effectively removed by both methods. The best results were achieved by reduction of nitrate ions at -0.9 V and electroadsorption at $+0.6$ V, with relatively poor performance at -0.6 V and $+0.4$ V. It is noteworthy that, the electroadsorption of nitrate ions was found to be reversible by applying low cathodic potentials.

Conclusions

Elimination of nitrate ions from aqueous solution using granulated synthetic carbon as fluidized-bed electrode in the electrochemical cell with flow through arrangement has been demonstrated for the first time. The elimination of nitrate ions was achieved by applying an external potential to the fluidized-bed carbon layer: cathodic (electrochemical reduction) and anodic (electroadsorption).

The effect was more pronounced at negative potential of -0.8 V.

References

1. Prasad S, Weidner W and Farel AE. A boundary-layer model of a parallel plate electrochemical reactor for the destruction of nitrates and nitrites in alkaline waste solutions. *J. Electrochem. Soc.* 1995;142(11):3815-3824.
2. Bockris JO'M and Kim J. Electrochemical treatment of low-level nuclear waste. *J. Appl. Electrochemistry* 1997;27:623-634.
3. Genders JD, Hartsough D and Hobbs DT. Electrochemical reduction of nitrates and nitrites in alkaline nuclear waste solution. *J. Appl. Electrochemistry* 1996;26:1-9.
4. Kalu EE, White RE, and Hobbs DT. Use of hydrogen anode for nitrate waste destruction. *J. Electrochem. Soc.* 1996;143(10):3094-3099.
5. Farmer JC, Fix DV, Mack GV, Pecala RW and Poco JF. Capacitive deionization of NaCl and NaNO_3 solutions with carbon aerogel electrode. *J. Electrochem. Soc.* 1996;143(1):159-169.
6. Basova YuV and Tomizuka I. Electrochemical Behavior of Catalysts Based on Macrobicyclic Trisdimethylglyoximate Cobalt(III) Complex. *Electrochemistry* 2000;68(5):328-332.

Table 1. Carbon materials used in this study

Carbons specimen	BET surface area, $\text{m}^2 \text{g}^{-1}$	Diameter, mm	Specimen code
SCN	5-12	0.5-1.0	SCN1
SCN	200	0.5-1.0	SCN2
SCN	1320	0.3-1.0	SCN3
SCN+CoDmg	1115	0.5-1.0	SCN4

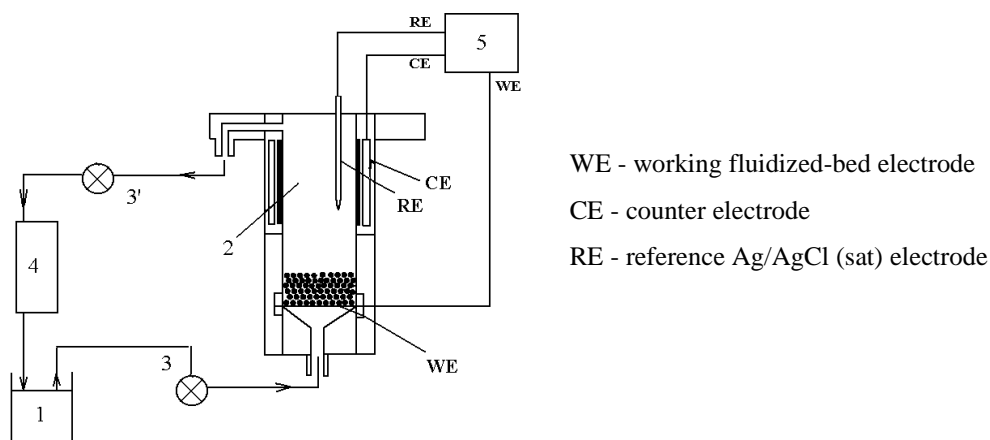


Figure 1. Schematic diagram of the electrochemical fluidized-bed cell flow system: (1) reservoir of working electrolyte, (2) electrochemical cell, (3, 3') pump, (4) pH/ion analyser, and (5) potentiostat and function generator.

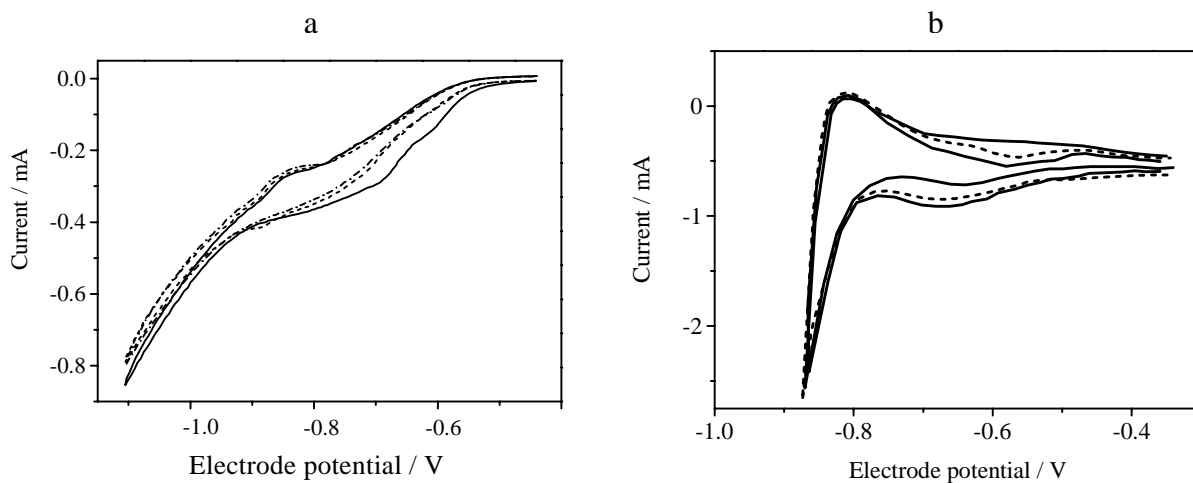


Figure 2. Cyclic voltammograms of (a) plain SCN1 carbon and (b) surface modified SCN4 carbon at 5 mV/c in $1.0 \text{ mol dm}^{-3} \text{ NaClO}_4$ and $0.01 \text{ mol dm}^{-3} \text{ KNO}_3$. (—) First scan, (----) third scan, (.....) fifth scan

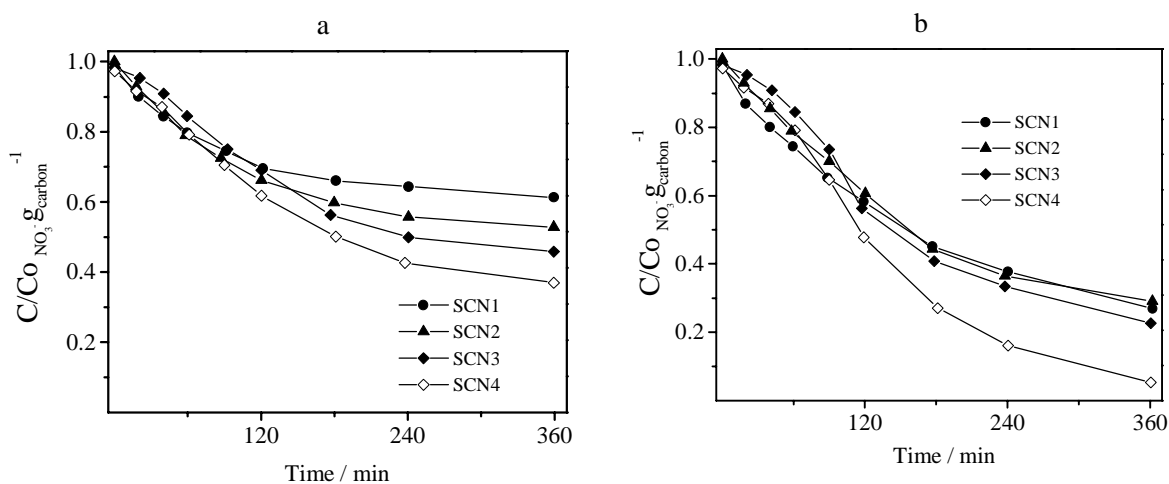


Figure 3. Specific normalized NO_3^- ion concentrations against the time of contact of the fluidized-bed layer of the SCN carbons with $0.01 \text{ mol dm}^{-3} \text{ KNO}_3$. Applied potential: (a) -0.6 V , (b) -0.8 V .

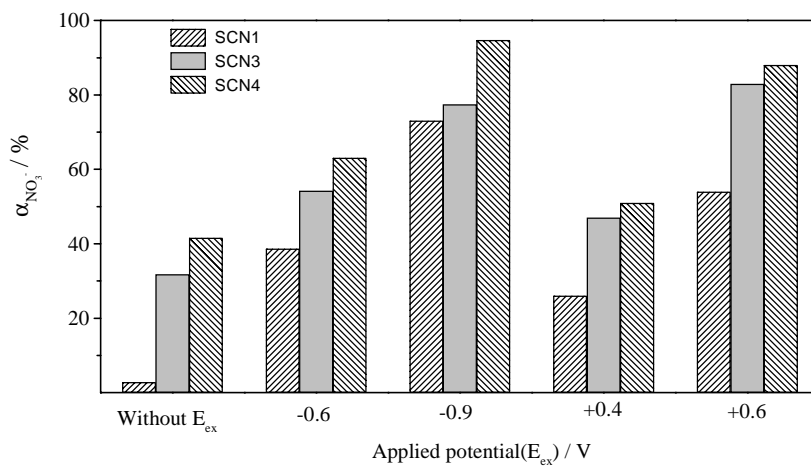


Figure 4. Averaged diagram of the elimination of NO_3^- ions from $0.01 \text{ mol dm}^{-3} \text{ KNO}_3$ solution depending on the applied potential after circulation for three hours through the fluidized-bed layer of the polarized carbon electrode