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

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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) electroadsoption of NO$_3^-$ ions on the carbon surface.

Experimental

Synthetic granulated carbon materials SCN and SCN carbon modified with macrobicyclic tris-dimethylglyoximate 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 cm$^3$ 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 voltammetries (CVs) were recorded at 1 to 100 mVs$^{-1}$ in $10^{-4}$ to $10^{-1}$ mol dm$^{-3}$ KNO$_3$ in 1.0 mol dm$^{-3}$ 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 ions at the electric processing 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:

$$\alpha_{NO_3^-} = \frac{(C_{st} - C_{fin})}{C_{st}} \times 100 \%,$$

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 mol dm$^{-3}$ 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.
seen form 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 electrod砷sorption 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 electrod砷sorption at +0.6 V, with relatively poor performance at –0.6 V and +0.4 V. It is noteworthy that, the electrod砷sorption 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 (electrod砷sorption).

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

**References**


**Table 1. Carbon materials used in this study**

<table>
<thead>
<tr>
<th>Carbons specimen</th>
<th>BET surface area, m$^2$ g$^{-1}$</th>
<th>Diameter, mm</th>
<th>Specimen code</th>
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<td>SCN+CoDmg</td>
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<td>0.5-1.0</td>
<td>SCN4</td>
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**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 analyther , 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 mol dm$^{-3}$ NaClO$_3$ and 0.01 mol dm$^{-3}$ 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 0.01mol dm$^{-3}$ KNO$_3$. Applied potential: (a) -0.6V, (b) -0.8V.

Figure 4. Averaged diagram of the elimination of NO$_3^-$ ions from 0.01 mol dm$^{-3}$ KNO$_3$ solution depending on the applied potential after circulation for tree hour though the fluidized-bed layer of the polarized carbon electrode.