



# Removal of nitrate using an activated rotating cylinder electrode



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## ABSTRACT

The removal of nitrate from a synthetic effluent, 30 mmol dm<sup>-3</sup> KNO<sub>3</sub> in 0.1 mol dm<sup>-3</sup> K<sub>2</sub>SO<sub>4</sub> as supporting electrolyte, is analysed by means of its reduction to ammonia using an undivided electrochemical reactor with a copper rotating cylinder cathode. The cathode was activated by a film of cupric oxide, anodically produced at a potential of 0V against saturated calomel electrode, SCE. In some experiments, to avoid the deactivation of the cathode, a periodic potential reversal, PPR, technique was applied making the rotating electrode work 5 min as a cathode and 5 min in reactivation. The application of both strategies, cathode activation and the use of a PPR procedure, improved the reactor performance. Under these working conditions, with this specific synthetic effluent, ammonia was the main product of the reduction of nitrate obtaining a molar yield of 86% and a current efficiency of 90% with a nitrate conversion of 92% in an experiment of 1 h at -1.2V, vs. SCE, as cathodic potential.

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## 1. Introduction

Nitrate contamination represents a very common issue in ground and surface waters. Several strategies were proposed for the removal of nitrate [1]. Rajeshwar and Ibañez [2] outlined the electrochemical reduction of oxynitrogen ions and Milhano and Pletcher [3] presented a comprehensive review on the electrochemistry and electrochemical technology of nitrate. Recently, Reyter [4] reported the state-of-the-art on the electrochemical removal of nitrate. From the above reviews, it is inferred that despite the large number of fundamental contributions devoted to this subject, the cathodic reduction of nitrate has not been well understood. Thus, the type of product depends on the concentration of nitrate as well as on cathode material, electrode potential and charge passed. Likewise, the presence of both cations and anions at a trace or impurity level can change the product spectrum. These circumstances together with the fact that many other reaction parameters are not comprehended have made the course of nitrate reduction difficult to understand. However, considering monometallic electrodes, copper is recognized as the most efficient electrocatalyst for nitrate electroreduction producing ammonium as a final product [5–7]. A drawback of the use of copper as a cathode is the decrease in its electroactivity with time due to the fact that the adsorption of nitrate-reduction products blocks the electrode surface. Nevertheless, the electrode can be

reactivated desorbing the poisoning species by applying a less negative potential at the cathode than that required for nitrate reduction [7].

Aspects of electrochemical engineering to reduce nitrate were also taken into account. Thus, a reactor with parallel plate electrodes was analysed with an electrolyte simulating the waste solution from the regeneration of strongly basic ion-exchange columns for drinking water treatment [8]. The electrolysis efficiency was improved by adding copper ions to the solution to prevent the decrease in cathode activity with electrolysis duration. Additionally, Paidar et al. [9] compared four types of cell construction using a simulated spent solution. The optimal choice of the reactor must provide intensive mass-transfer, and at the same time a continuous renewal of the cathode surface mainly by mechanical friction. They identified a reactor with a fluidised bed of inert particles in the inter-electrode space as optimal from the point of view of cell efficiency coupled with simplicity of construction and operation. Likewise, the transformation of nitrate to nitrogen is efficiently performed in a paired electrolysis. At the cathode, nitrate is reduced to ammonia which is oxidized to nitrogen by the hypochlorite produced *in-situ* at the anode [10]. Abdallah et al. [11] reported the use of a graphite felt coated with copper as cathode, in a flow through cell, for the reduction of nitrate to ammonium with 72% current efficiency and 96% selectivity. However, Reyter [4] considers that in the future, efforts should be made toward the design of electrochemical reactors for nitrate removal.

The rotating cylinder electrode shows widespread acceptance in a number of interdisciplinary fields and its versatility has been

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fully demonstrated [12,13]. This reactor presents good mass-transfer characteristics achieving turbulent flow conditions at low rotation rates, the current and potential distributions are substantially uniform and it is also possible to operate the system with a superimposed axial flow, which does not usually modify mass-transfer behaviour. The aim of this study was to analyse the performance of a batch electrochemical reactor with a rotating cylinder electrode for the removal of nitrate with an activated cathode and using a periodic potential reversal technique, PPR, which permits the maintenance of electrode activation.

## 2. Experimental

### 2.1. Rotating disc electrode experiments

Polarization curves were obtained using a copper rotating disc electrode with a 3 mm diameter embedded in a 10 mm diameter Teflon cylinder. A platinum wire with a 1 mm diameter and 100 mm long was used as a counter electrode. A saturated calomel electrode, SCE, served as reference and the potentials are referred to this electrode.

The surface of the working electrode was polished to a bright mirror finish with slurry of 0.3  $\mu\text{m}$  alumina powder and copiously washed with distilled water. Experiments were performed using a synthetic solution of 30 mmol  $\text{dm}^{-3}$   $\text{KNO}_3$  in 0.1 mol  $\text{dm}^{-3}$   $\text{K}_2\text{SO}_4$  as supporting electrolyte. The temperature and the rotation speed were 30 °C and 1000 rpm, unless otherwise stated, respectively. The experiments were carried out potentiostatically and nitrogen was bubbled in the reactor for 1 h prior to each experiment in order to remove the dissolved oxygen.

### 2.2. Rotating cylinder electrode experiments

The experiments were performed in an undivided batch reactor, 95 mm internal diameter and 140 mm high, being the reactor thermostated by a heating jacket. Fig. 1 schematically depicts the complete experimental arrangement. The working electrode was a copper rotating cylinder, 38 mm diameter and 90 mm long, with its upper end attached to the motor shaft. Three platinum wires, 1.0 mm diameter and 100 mm long, were used as anode and were symmetrically placed around the working electrode. The inter-electrode gap was 11 mm. This simpler and more economical arrangement of the counter electrode was used because it yielded similar results to those obtained in preliminary experiments with a concentric helical platinum wire as anode.

The experiments were carried out potentiostatically at 30 °C and 1000 rpm. The cathodic potential was controlled against a SCE connected to a Haber-Luggin capillary positioned in the middle region of the cathode. During the experiment, the cell voltage and the current were recorded as a function of time.

The solution was 30 mmol  $\text{dm}^{-3}$   $\text{KNO}_3$  in 0.1 mol  $\text{dm}^{-3}$   $\text{K}_2\text{SO}_4$  as supporting electrolyte with an initial pH of 5.6. The electrolyte volume was 0.90  $\text{dm}^3$ .

### 2.3. Analytical procedures

At the end of the experiment, the concentrations of nitrate, nitrite, ammonium and hydroxylamine were spectrophotometrically determined. Nitrate, nitrite and ammonia concentrations were measured following standard methods [14]. For the determination of nitrate the absorbance of the sample was measured at 220 nm where the nitrate absorbs strongly, and also at 275 nm where its absorption is negligible. The absorption of nitrate was calculated by subtracting twice the absorbance reading at 275 nm, as a correction for organic matter, from that at the shorter wavelength. The calibration curve follows Beer's law up to

11 mg  $\text{NO}_3^- \text{N dm}^{-3}$ , nitrate is referred as nitrogen per  $\text{dm}^3$ . In order to measure nitrite concentration, the solution was diluted and a colour developing reagent containing sulfonamide and N-(1-naphthyl) ethylenediamine dihydrochloride was added. The absorbance of the characteristic peak at 543 nm was used for calculation being the applicable range of the method from 10 to 1000  $\mu\text{g NO}_2^- \text{N dm}^{-3}$ . Ammonia was determined using the phenate method and the absorbance was measured at 640 nm. This method is linear to 0.6 mg  $\text{NH}_3 \text{N dm}^{-3}$ . The determination of hydroxylamine [15] is based on its oxidation to nitrite using sodium arsenate under alkaline condition and the nitrite formed was measured as above.

## 3. Results and discussion

### 3.1. Preliminary studies with a rotating disc electrode

Preliminary experiments carried out with a copper electrode and the synthetic solution corroborated that the reduction of nitrate takes place before hydrogen evolution. However, the current for nitrate reduction decreases at more negative potentials, this is attributed to poisoning by adsorbed hydrogen blocking the electrode surface for further reduction of N-containing molecules [16]. Likewise, it was observed a decrease in the current of polarization curves obtained consecutively, which is explained by the adsorption of nitrate-reduction products that blocks the electrode surface [7].

Fig. 2 reports on polarization curves where, previous to each experiment, the electrode was electrochemically pre-treated. Thus, the electrode potential was controlled at  $E_{\text{SCE}} = 0\text{V}$  during different times as it is given in Fig. 2. After this pre-treatment for times higher than 15 min, all the polarization curves are close. The inset in Fig. 2 illustrates a typical curve of current density as a function of time during the pre-treatment of the electrode, showing an anodic current. Polarization curves obtained consecutively and between experiments the electrode potential was

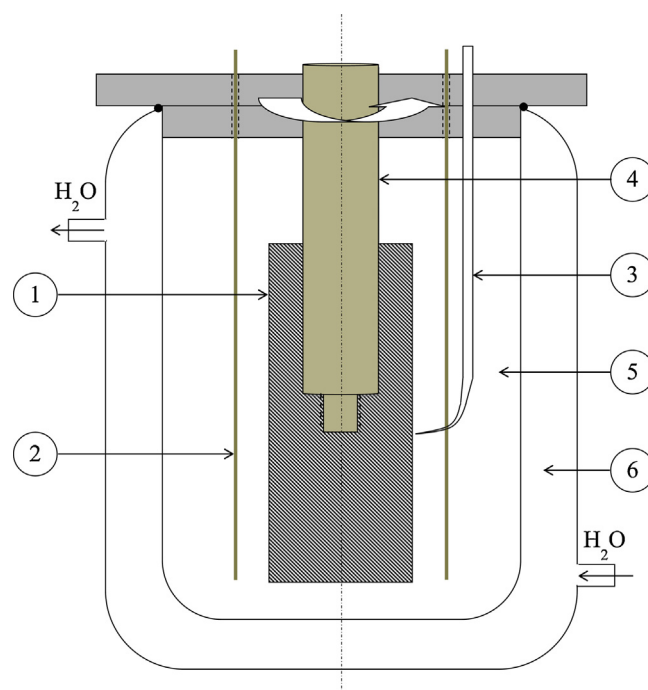


Fig. 1. Schematic representation of the electrochemical reactor. 1, Rotating cylinder electrode; 2, counter electrode; 3, Haber-Luggin capillary; 4, electrode shaft; 5, electrolyte container; 6, heating jacket.

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