



# Removal of nitrate using an activated rotating cylinder electrode



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## ABSTRACT

The removal of nitrate from a synthetic effluent,  $30 \text{ mmol dm}^{-3} \text{ KNO}_3$  in  $0.1 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$  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  $-1.2 \text{ V}$ , 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  $\text{mmol dm}^{-3}$   $\text{KNO}_3$  in 0.1  $\text{mol dm}^{-3}$   $\text{K}_2\text{SO}_4$  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  $\text{mmol dm}^{-3}$   $\text{KNO}_3$  in 0.1  $\text{mol dm}^{-3}$   $\text{K}_2\text{SO}_4$  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  $\text{mg NO}_3\text{-N dm}^{-3}$ , 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  $\text{mg NH}_3\text{-N dm}^{-3}$ . 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

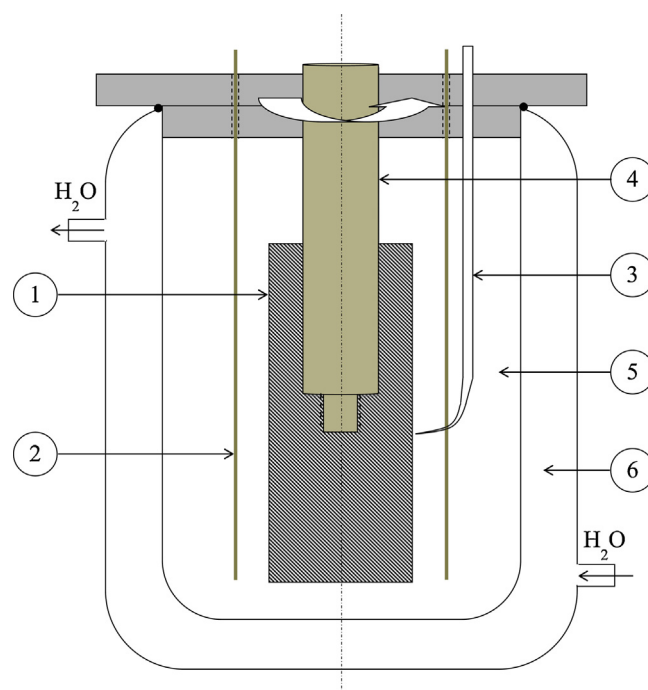
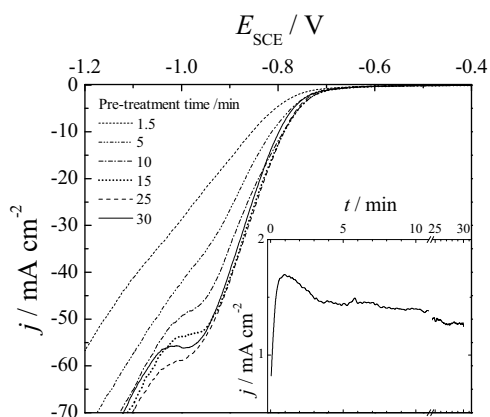


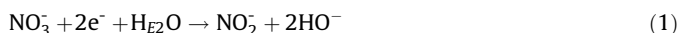
Fig. 1. Schematic representation of the electrochemical reactor. 1, Rotating cylinder electrode; 2, counter electrode; 3, Haber-Luggin capillary; 4, electrode shaft; 5, electrolyte container; 6, heating jacket.



**Fig. 2.** Cathodic current density as a function of the electrode potential for a rotating disc electrode pre-treated at different times. Previous to each experiment the working electrode was maintained at a potential of  $E_{SCE} = 0\text{ V}$  during the time in minutes given in the figure.  $T = 30^\circ\text{C}$ . Rotation speed: 1000 rpm. Potential sweep rate:  $10\text{ mV s}^{-1}$ . Inset: anodic current density as a function of time during a 30 min pre-treatment period.

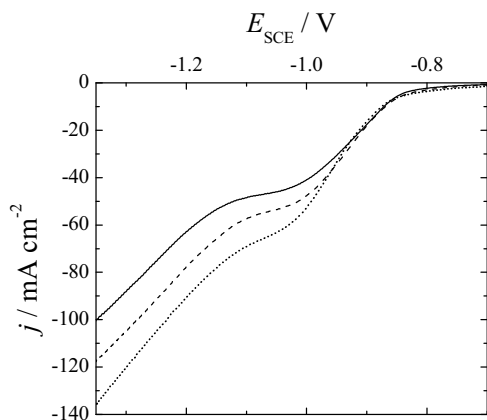
maintained at  $E_{SCE} = 0\text{ V}$  during 30 minutes showed a close concordance between them revealing that the pre-treatment is effective to obtain reproducible results.

**Fig. 3** displays polarization curves at different rotation speeds. When the electrode potential is near  $-1.0\text{ V}$ , against SCE, a limiting current is observed which increases with the rotation speed. Similar results were reported by Milhano and Pletcher [3] for a copper disc in an acidic media. These limiting current densities are close to those predicted by the Levich equation,  $57\text{ mA cm}^{-2}$  at 1000 rpm, assuming the physicochemical parameters reported in **Table 1**. In the calculation, 2 was assumed as the number of exchanged electrons per nitrate molecule with a diffusion coefficient from Paidar et al. [9]. Then, in this potential region the formation of nitrite could be assumed as follows



Taking into account **Fig. 3**, a further reduction of nitrate to oxidation states of nitrogen lower than to nitrite cannot be identified in the polarization curves with this electrolyte because they are masked by hydrogen evolution.

**Fig. 4** shows the current density as a function of time for a given electrode potential, where it can be observed that the cathode is



**Fig. 3.** Cathodic current density as a function of the electrode potential for a rotating disc electrode at different rotation speeds. Full line: 500 rpm. Dashed line: 1000 rpm. Dotted line: 1500 rpm. The working electrode was pre-treated at a potential of  $E_{SCE} = 0\text{ V}$  during 30 min before each experiment.  $T = 30^\circ\text{C}$ . Potential sweep rate:  $10\text{ mV s}^{-1}$ .

deactivated being the effect more marked at more negative potentials. To overcome the deactivation of the electrode surface, additional experiments were performed with the rotating disc electrode maintaining the cathode potential during 5 minutes at  $E_{SCE} = -1.2\text{ V}$ , and then it was suddenly changed to a lower value during a given time. This procedure was cyclically repeated three times. **Fig. 5**, Part (a) displays the current density as a function of time when the reactivation was made at  $E_{SCE} = -0.8\text{ V}$  during 2.5 minutes. It can be noted that current density in the second cycle continues the curve of the first one and the same tendency is repeated in the next cycle. Then, the initial activity is not recovered. **Fig. 5**, Part (b) shows the same information as above, but the reactivation was performed at  $E_{SCE} = 0\text{ V}$  during 5 minutes, where a small anodic current flows. However, under this working condition the initial activity of the electrode is completely restored. Likewise, the first cycle of Part (a) is also re-plotted in Part (b) as a dotted line showing a close concordance between them. Further experiments carried out either at different potentials for the reactivation, or changing the frequency of the cycle have not improved the results of **Fig. 5** Part (b). From **Figs. 4 and 5** it can be concluded that for nitrate reduction at a copper electrode, it is convenient to activate the electrode at  $E_{SCE} = 0\text{ V}$  previous to the experiment and during it, it is also necessary its reactivation at the same potential.

The high current density and the narrow range of potentials where nitrate reduction takes place under limiting current conditions, without a noticeable hydrogen evolution as a secondary reaction, both suggest that it should not be necessary the use of a three-dimensional cathode to carry out this reaction. The same conclusion can be drawn for the operation at potentials more negative than  $-1.0\text{ V}$ , where nitrate reduction is overlapped to hydrogen evolution. Thus, a reactor with a rotating cylinder electrode becomes an attractive device to remove nitrate.

### 3.2. Studies with a rotating cylinder electrode

Considering the results obtained with the rotating disc electrode, previous to each experiment the copper cylinder was pre-treated in a  $0.1\text{ mol dm}^{-3}\text{ K}_2\text{SO}_4$  solution controlling the potential at  $0\text{ V}$ , against SCE, at 1000 rpm and  $30^\circ\text{C}$ . The pH at the end of the pre-treatment was approximately 10. The copper cylinder was covered with a pale brown adherent layer, also detected by previous authors [17], which was dissolved when the cylinder was immersed in a solution of ammonia rendering a deep blue solution. From this experimental evidence and taking into account the Pourbaix diagram for copper [18], it can be inferred that the layer produced during the pre-treatment is formed by cupric oxide. Similar catalytic layers were previously reported [19]. During this pre-treatment, the solution shows a slight change in colour attributed to the presence of copper ions, revealing that a portion of the anodic current is used for the dissolution of the copper.

**Fig. 6** shows the current as a function of time for a rotating cylinder electrode at different values of the pre-treatment time. The experiments were made potentiostatically at  $-1.2\text{ V}$  against SCE. After the experiment the electrode remains stable without noticeable changes in its surface morphology. Likewise, the results for a not pre-treated copper cylinder are also reported, as ( $\square$ ), where it is observed that the pre-treatment is able to increase the current four times. As a conclusion, the pre-treatment activates the electrode by forming a layer of cupric oxide. Regarding **Fig. 2**, the best results were obtained for pre-treatment times in the range from 15 min to 30 min, whereas higher values did not improve the electrode performance, which is corroborated in **Fig. 6**.

For a rotating cylinder electrode, the electrolyte is considered to be well-mixed at all times. Assuming a first order reaction for the removal of nitrate, the temporal behaviour of the current for the

**Table 1**  
Physicochemical properties of the electrolyte.

Composition	[KNO <sub>3</sub> ] ≈ 30 mmol dm <sup>-3</sup> in 0.1 mol dm <sup>-3</sup> K <sub>2</sub> SO <sub>4</sub>
Kinematic viscosity, $\nu$ / m <sup>2</sup> s <sup>-1</sup>	8.80 × 10 <sup>-7</sup>
Diffusion coefficient, $D$ / m <sup>2</sup> s <sup>-1</sup>	1.9 × 10 <sup>-9</sup>
Schmidt number, Sc	463

reduction of nitrate in a batch reactor is given by [20]

$$I_{\text{NO}_3}(t) = I_{\text{NO}_3}(0)\exp(-ka_e t) \quad (2)$$

where  $a_e$  is the specific surface area and  $k$  is the kinetic constant according to

$$k = \frac{k_f}{1 + \text{Da}} \quad (3)$$

being  $k_f$  the rate constant and Da the Damköhler number defined as  $k_f/k_m$  [21], where  $k_m$  is the mass-transfer coefficient. The total current is

$$I(t) = I_{\text{NO}_3}(t) + I_{\text{H}_2} \quad (4)$$

being the second term on the right hand side the current for hydrogen evolution, which is assumed to be independent of time providing a very useful simplification for mathematical modelling. Introducing Eq. (2) into Eq. (4), evaluating the resulting equation at  $t=0$  and rearranging yields

$$I(0) - I(t) = I_{\text{NO}_3}(0)[1 - \exp(-ka_e t)] \quad (5)$$

For small values of the argument, the exponential function can be approximated by the two first terms of a MacLaurin's series, resulting

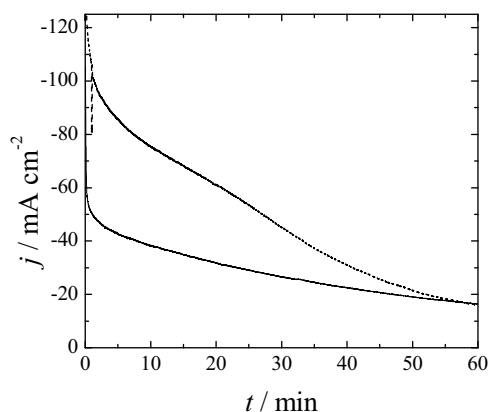
$$I(0) - I(t) \cong I_{\text{NO}_3}(0)ka_e t \quad (6)$$

In the inset of Fig. 6 the data of the experiment with an activation time of 30 min are re-plotted according to Eq. (6). The full line corresponds to the behaviour under limiting mass-transfer conditions, which provides the maximum variation of current with time. The mass-transfer coefficient was calculated with the correlation proposed by Eisenberg et al. [22] according to

$$\text{Sh} = 0.0791 \text{Re}^{0.7} \text{Sc}^{0.356} \text{ for } 112 < \text{Re} < 1.62 \times 10^5 \quad (7)$$

The Sherwood number, Sh, the Reynolds number, Re, and the Schmidt number, Sc, are defined as

$$\text{Sh} = \frac{k_m d}{D} \quad (8)$$



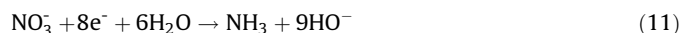
**Fig. 4.** Current density as a function of time for a rotating disc electrode. Full line:  $E_{\text{SCE}} = -1.0$  V. Dashed line:  $E_{\text{SCE}} = -1.2$  V. The working electrode was maintained at a potential of  $E_{\text{SCE}} = 0$  V during 30 min previous to each experiment.  $T = 30$  °C. Rotation speed: 1000 rpm.

$$\text{Re} = \frac{\omega d^2}{2\nu} \quad (9)$$

and

$$\text{Sc} = \frac{\nu}{D} \quad (10)$$

here  $\omega$  is the rotation speed and  $d$  is the cylinder diameter. The Reynolds number was 85918 giving  $k_m = 1 \times 10^{-4}$  m s<sup>-1</sup>. The dashed line corresponds to the linear fitting of the experimental results at the beginning of the experiment. From the slope of the dashed line, the kinetic constant is  $5 \times 10^{-5}$  m s<sup>-1</sup> giving a Damköhler number of 0.5. This value shows that the reduction of nitrate, as a global reaction, is under a combined mass and charge transfer kinetic control. The inset also reveals that immediately after the start of the experiment the slope decreases with time, making the reactor performance decline. Thus, the pre-treatment activates the electrode improving the efficiency of the reactor during the early stages of the experiment, but at longer times the electrode is deactivated probably due to the adsorption of the products of the nitrate reduction blocking the electrode surface. However, in the four cases reported in Fig. 6 a similar final solution was obtained, which can be explained considering that the pre-treatment time is only important up to achieving the electrode surface area completely covered with cupric oxide. The nitrate conversion was 83% and the concentration of the different species is given in the first column in Table 2, where it is observed that under these working conditions ammonia results in the main product in the reduction of nitrate according to



Likewise, approximately 42% of nitrate was converted to gaseous nitrogen compounds, which were not analysed in these experiments. The final pH was 12.9 and 9 V was the mean value of the cell voltage with a current efficiency for ammonia production of 58%.

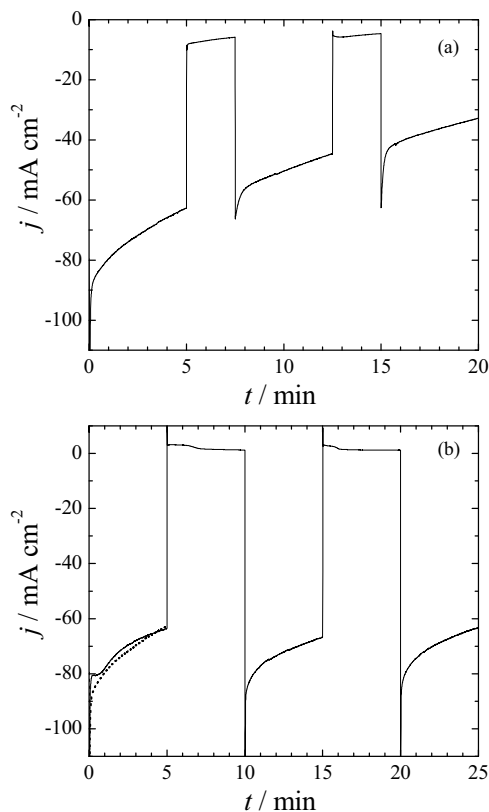
The relevant parameters required to analyse the performance of the electrochemical reactor, called 'figures of merit', are reported in Fig. 7. Thus, the nitrate conversion,  $X$ , current efficiency for ammonia generation,  $CE$ , and molar yield, defined as

$$Y_P = \frac{\text{moles of P formed}}{\text{moles of nitrate reacted}} \quad (12)$$

for the production of nitrite, ammonia and hydroxylamine are given in Fig. 7 as a function of the cathodic potential. The best results are obtained at a potential of  $-1.2$  V, where the nitrate conversion, yield and current efficiency for ammonia production are maximal. Likewise, in all cases the production of hydroxylamine is negligible.

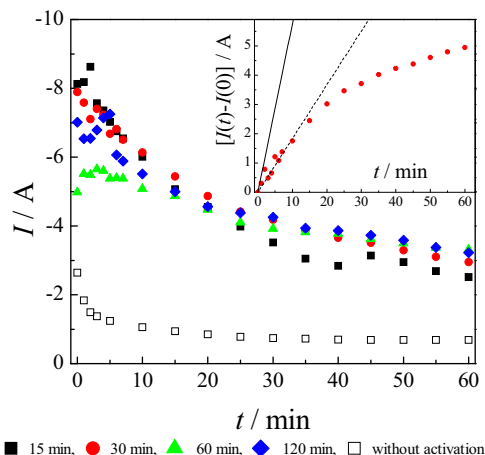
Fig. 8 reports on the current as a function of time using a periodic potential reversal, PPR, procedure. Thus, the electrode potential was controlled at  $-1.2$  V during 5 minutes and the reactivation was made during the same time at 0 V, passing an anodic current. The full line represents the cathodic current, partially used for the reduction of nitrate, and in the upper part the current during the reactivation is shown as a dashed line. The results for an experiment without application of PPR, given in Fig. 6, are also reported as a comparison. At the beginning, both experiments, with and without PPR, show a similar behaviour, but at times higher than 10 min the reactivation of the electrode permits to obtain a higher current, improving the performance of the reactor.

Fig. 9 shows the figures of merit at different cathodic potentials when the PPR technique is applied. For comparison, the values of these figures of merit without the application of PPR at  $-1.2$  V are also reported on the left hand side and the concentration of the



**Fig. 5.** Current density as a function of time for a rotating disc electrode. Part (a): reactivation at  $E_{SCE} = -0.8$  V during 2.5 min. Part (b): reactivation at  $E_{SCE} = 0$  V during 5 min. The working electrode was maintained at a potential of  $E_{SCE} = 0$  V during 30 min previous to each experiment.  $T = 30^\circ\text{C}$ . Rotation speed: 1000 rpm.

different species is given in Table 2. It can be observed that at a cathodic potential of  $-1.2$  V the application of PPR increases not only the conversion of nitrate, but also current efficiency and the yield to produce ammonia, diminishing the molar yield of nitrite and hydroxylamine. Likewise, taking into account the results with application of PPR, the best behaviour was achieved at a potential of  $-1.2$  V, giving a nitrate conversion of 92% with 86% and 90% for

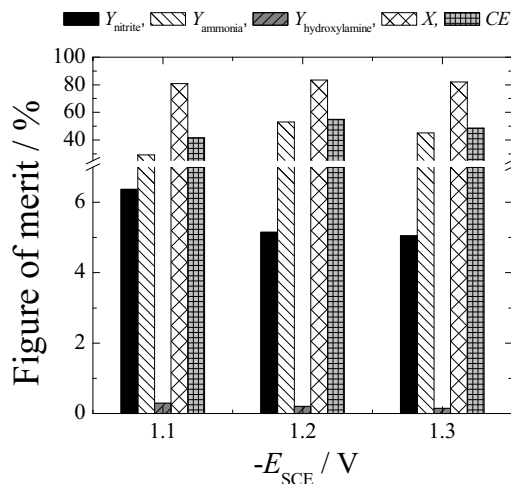


**Fig. 6.** Current as a function of time for a rotating cylinder electrode. Pre-treatment at a potential of  $E_{SCE} = 0$  V in  $0.1 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$  during the time indicated at each curve previous to each experiment.  $E_{SCE} = -1.2$  V.  $T = 30^\circ\text{C}$ . ( $\square$ ): not activated copper cylinder. Rotation speed: 1000 rpm. Inset: difference between the initial current and the value at time  $t$ ; full line: temporal behaviour under limiting current conditions; dashed line: linear fitting of the experimental results at the beginning of the experiment.

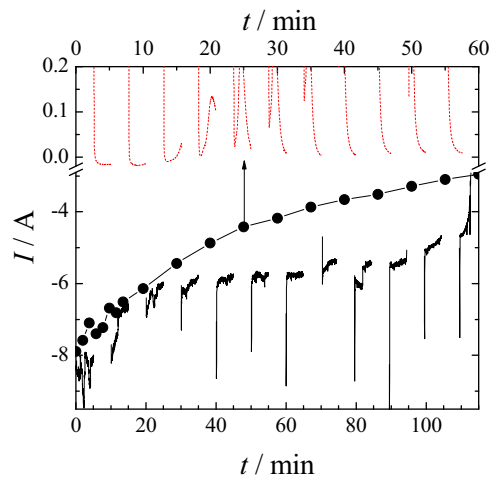
**Table 2**

Final composition of the electrolyte,  $\text{mmol dm}^{-3}$ , after 1 h electrolysis using the rotating cylinder electrode.  $E_{SCE} = -1.2$  V.  $T = 30^\circ\text{C}$ . Rotation speed: 1000 rpm.

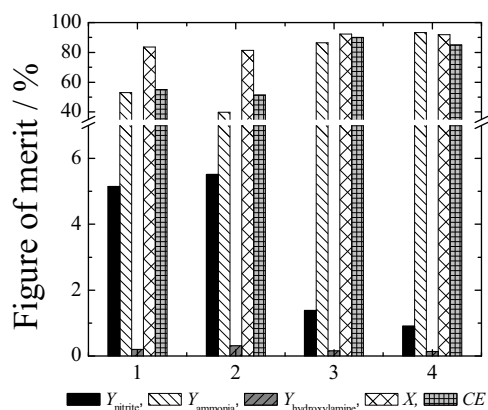
Initial composition	without PPR [KNO <sub>3</sub> ] = 29.8 $\text{mmol dm}^{-3}$ in $0.1 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$	with PPR [KNO <sub>3</sub> ] = 34 $\text{mmol dm}^{-3}$ in $0.1 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$
Nitrate	4.9	2.6
Nitrite	1.3	0.4
Ammonia	13.2	27.2
Hydroxylamine	0.05	0.05



**Fig. 7.** Figures of merit for the nitrate reduction at an activated rotating copper cylinder for different cathodic potentials.  $Y_P$ : molar yield for the production of P;  $X$ : nitrate conversion;  $CE$ : current efficiency for the ammonia production. Pre-treatment at a potential of  $E_{SCE} = 0$  V in  $0.1 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$  during 30 min previous to each experiment. Electrolysis time: 1 h.  $T = 30^\circ\text{C}$ . Rotation speed: 1000 rpm.



**Fig. 8.** Current as a function of time for a rotating cylinder electrode applying a periodic potential reversal, PPR, procedure. Pre-treatment at a potential of  $E_{SCE} = 0$  V in  $0.1 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$  during 30 min previous to the experiment.  $E_{SCE} = -1.2$  V.  $T = 30^\circ\text{C}$ . Rotation speed: 1000 rpm. Full line: cathodic current for the reduction of nitrate. Dashed line: current during the reactivation of the electrode. ( $\bullet$ ): experiment under the same working conditions without PPR reported in Fig. 6.



**Fig. 9.** Figures of merit for the nitrate reduction at an activated rotating copper cylinder for different control strategies.  $Y_p$ : molar yield for the production of P. X: nitrate conversion. CE: current efficiency for the ammonia production. Pre-treatment at a potential of  $E_{\text{SCE}}=0\text{V}$  in  $0.1\text{ mol dm}^{-3}\text{K}_2\text{SO}_4$  during 30 min previous to each experiment. Electrolysis time: 1 h.  $T=30^\circ\text{C}$ . Rotation speed: 1000 rpm. PPR: periodic potential reversal. 1: without PPR at  $E_{\text{SCE}}=-1.2\text{V}$ , 2: with PPR at  $E_{\text{SCE}}=-1.1\text{V}$ , 3: with PPR at  $E_{\text{SCE}}=-1.2\text{V}$ , 4: with PPR at  $E_{\text{SCE}}=-1.3\text{V}$ .

the yield and current efficiency for ammonia formation, respectively. Under these working conditions the final pH was 13, the mean value of the cell voltage was  $10.9\text{V}$  and  $22.1\text{ kWh kg}^{-1}$  for the specific energy consumption, referred to the potassium nitrate reacted, giving a normalized space velocity [23] of  $1.12\text{ h}^{-1}$ . Fig. 9 also shows that similar values for the yield of ammonia and nitrate conversion were obtained at the most cathodic potentials. However, at  $-1.3\text{V}$  the high value of the specific energy consumption,  $26.5\text{ kWh kg}^{-1}$ , becomes inadequate this cathodic potential.

#### 4. Conclusions

Copper electrodes showed a good performance for the reduction of nitrate to ammonia from a specific synthetic effluent,  $30\text{ mmol dm}^{-3}\text{KNO}_3$  in  $0.1\text{ mol dm}^{-3}\text{K}_2\text{SO}_4$  as supporting electrolyte, when they are activated at a potential of  $0\text{V}$  against SCE in a  $0.1\text{ mol dm}^{-3}\text{K}_2\text{SO}_4$  aqueous solution, forming a film of cupric oxide.

The high conversion of nitrate to ammonia with a small production of nitrogen secondary species reveals that an undivided electrochemical reactor with an activated rotating cylinder cathode of copper is promising as a first step for the transformation of this synthetic effluent containing nitrate in fertilizers.

The application of a periodic potential reversal technique, 5 min as cathode and 5 min in reactivation as anode, permits the maintenance of the activation of the cathode and the achievement of a high conversion of nitrate to ammonia.

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