Electrochemical removal of nitrate ions in waste solutions after regeneration of ion exchange columns

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Abstract

Electrochemical reduction of nitrate ions in synthetic regenerating solutions after ion exchange column regeneration was studied. The influence of current density on the current efficiency was determined in the range 2.8–7.6 mA cm^{-2} in a diaphragmless flow-through electrolyser in a batch recirculation mode. A Cu cathode and a Ti/Pt anode was used, the temperature being maintained at 25 °C. Highest integral current efficiency occurred at 2.8 mA cm^{-2}. The presence of about 6 mg dm^{-3} Cu ions in treated solution was found to prevent a decrease in cathode activity and, consequently, in electrolysis efficiency. The catalytic influence of Cu ions was verified by potentiodynamic polarisation experiments on a copper rotating disc electrode and by chronopotentiometry performed during the course of electrolysis.
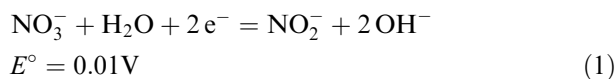
1. Introduction

Nitrates are serious environmental pollutants. Excessive application of agricultural fertilisers has been known to cause penetration of large quantities of nitrates into underground and surface waters [1–3]. High concentrations of nitrates have a detrimental effect on the environment and also constitute a problem in industrial water use. According to the 'Drinking Water Concentration Limits' proposed in the 1987 EEC Recommendations, the maximum allowable concentration of NO_3^- in drinking water is 50 mg dm^{-3} (15 mg dm^{-3} for infants).

At present ion exchange represents the most widespread method for the removal of nitrates [4]. To regenerate ion-exchangers a high excess of a regeneration agent (commonly NaCl) has to be used. Consequently, the salinity of waste water originating from this process is increased substantially. In addition, the used regenerating solution is contaminated by the nitrates released from the ion-exchangers. At present, a means of removing the nitrate in a closed cycle stream is being studied [5].
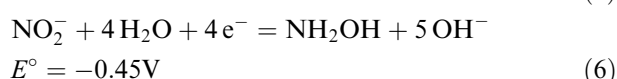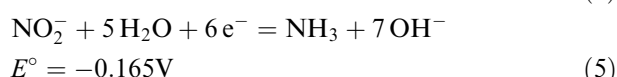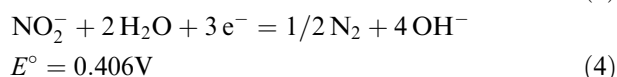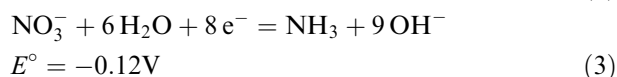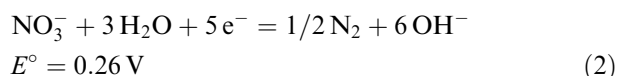
Several methods have been proposed for the reduction of nitrates to nitrogen or ammonium. The application of microorganisms [4, 6] and heterogeneous catalysis [4, 7] are the two groups of methods most often referred to. However, the application of these methods is limited mainly by their sensitivity to the operating conditions and/or by the use of expensive catalysts based on platinum group metals. Such methods are often unacceptable in drinking water treatment; for example, the application of a reducing agent like methanol and/or microbiological contamination of the ion-exchange bed. Furthermore, it may prevent repeated use of the solution for the regeneration of the ion exchange columns.

An alternative method of removing nitrate ions from industrial and waste waters is selective electrochemical reduction to nitrogen or ammonia [8–10]. This represents a relatively simple technology consisting of a minimum number of steps.

The following reactions may be considered to proceed on the cathode during electrolysis [11]:
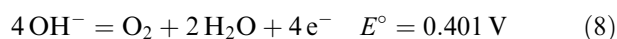
$$NO_3^- + H_2O + 2\,e^- = NO_2^- + 2\,OH^-$$
$$E^\circ = 0.01\,V \tag{1}$$

$$NO_3^- + 3\,H_2O + 5\,e^- = 1/2\,N_2 + 6\,OH^-$$
$$E^\circ = 0.26\,V \tag{2}$$

$$NO_3^- + 6\,H_2O + 8\,e^- = NH_3 + 9\,OH^-$$
$$E^\circ = -0.12V \tag{3}$$

$$NO_2^- + 2\,H_2O + 3\,e^- = 1/2\,N_2 + 4\,OH^-$$
$$E^\circ = 0.406V \tag{4}$$

$$NO_2^- + 5\,H_2O + 6\,e^- = NH_3 + 7\,OH^-$$
$$E^\circ = -0.165V \tag{5}$$

$$NO_2^- + 4\,H_2O + 4\,e^- = NH_2OH + 5\,OH^-$$
$$E^\circ = -0.45V \tag{6}$$

Hydrogen evolution, (Equation 7) represents the main parasitic cathodic reaction:

$$2\,H_2O + 2\,e^- = H_2 + 2\,OH^- \quad E^\circ = -0.83\,V \tag{7}$$

Oxygen evolution (Equation 8) is the main anodic reaction

$$4\,OH^- = O_2 + 2\,H_2O + 4\,e^- \quad E^\circ = 0.401\,V \tag{8}$$

We consider Equations 2 and 8 to be the main reactions and the desired overall electrochemical reaction is given by Equation 9:

$$4\,NaNO_3 + 2\,H_2O = 2\,N_2 + 5\,O_2 + 4\,NaOH \tag{9}$$
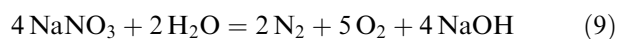
During electrolysis, the electrolyte gradually becomes alkaline (Equation 9). Hence, $NaHCO_3$ present in the used solution (for the composition of the solution see below) is converted to carbonate (Equation 10):

$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O \tag{10}$$
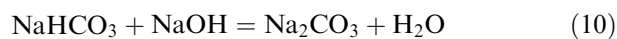
Adding Equations 9 and 10, we obtain the overall cell reaction (Equation 11):

$$4\,NaNO_3 + 4\,NaHCO_3 = 2\,N_2 + 5\,O_2 + 4\,Na_2CO_3$$
$$+ 2\,H_2O \tag{11}$$
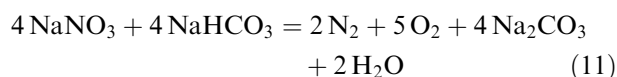
The desired cathodic process is the reduction of nitrate to nitrogen according to Equation 2, but, according to Chebotareva and Nyokong [12], the nitrate reduction mainly follows Equation 3 and the process requires eight electrons. Since it is not possible to estimate with sufficient accuracy that part of the electrical charge passed used for the five (Equation 2) and eight (Equation 3) electron reduction steps, the current yield was calculated according to Equation 2. It thus represents the lowest value.

Three different ways of electrocatalytic reduction of nitrates are known:

(i) Addition of electrocatalyticaly active ions (VO_3^-, MoO_4^{2-}, WO_4^{2-} or organic Co compounds) directly to the treated solution [13, 14].

(ii) Immobilization of the catalyst on the cathode surface, for example, carbon electrode modified with phthalocyanide complexes [12].

(iii) Selection of electrode materials with appropriate catalytic properties [8, 9, 15–17].

The last mentioned method seems to be the most appropriate in the present case. Copper was chosen as the cathode material since it has high electrocatalytic activity for nitrate reduction [17]. At the same time it is also acceptable for drinking water treatment.

Originally the electrochemical reduction of nitrates was studied mainly in acidic solutions [18–21]. At present research in this field is focused on alkaline solutions [8, 9, 12, 14–17, 22]. The main advantage of this approach is that ammonia, being a weak base, will volatilize to the atmosphere from basic solutions. Moreover, HCO_3^- ions are more suitable for drinking water treatment when compared to Cl^- or SO_4^{2-}. Therefore, a solution of $NaHCO_3$, suitable for the regeneration of a strongly basic anion exchanger used for the removal of nitrates from drinking water [23], was chosen for this study.

2. Experimental details

2.1. Apparatus

A diaphragmless flow-through electrolyser with plate electrodes in a recirculation mode arrangement was used during experiments dealing with the current efficiency with respect to the nitrate ion (reduction). The electrode dimensions were $11.1\,cm \times 22.5\,cm$ (active cathode area of $500\,cm^2$). A schematic diagram of the apparatus is shown in Figure 1. A Straton RTF 3217 (Germany) was used as a stabilized current source.

Polarization curves were measured using a rotating disc electrode (RDE) made of 99.5% purity copper, 4 mm in diameter, embedded in a Teflon disc 12 mm in diameter. A Pt counter electrode was used and a saturated calomel electrode (SCE) served as reference. The potential was controlled by means of a Wenking LB 75 H potentiostat (Elektronik Göttingen, Germany). An IBM Compatible PC equipped with an 8 bit D/A converter (Advantec, UK) was used as the reference signal generator. The current-voltage dependence was recorded using an X–Y recorder.
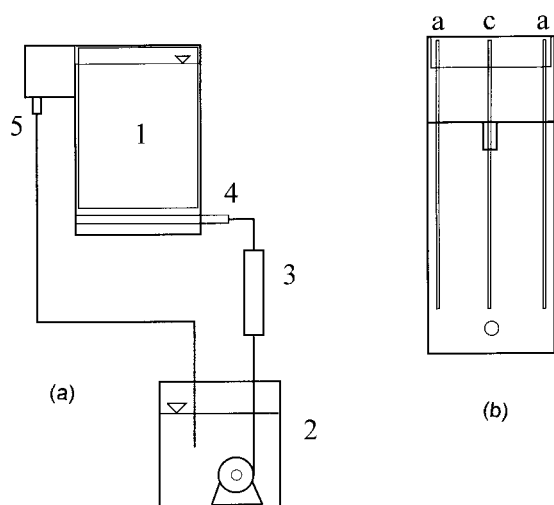
Fig. 1. (a) Scheme of the apparatus: (1) cell, (2) electrolyte reservoir with pump, (3) rotameter, (4) inlet and (5) outlet. (b) Sideview of the cell: (a) anode and (c) cathode.

2.2. *Experimental procedure*

2.2.1. *Electrolysis*
The electrolyte simulated a waste solution after the regeneration of a strongly basic anion exchanger with NaHCO$_3$. Its composition was as follows: 8.0 g dm^{-3} NaHCO$_3$, 0.4 g dm^{-3} NaCl, 0.4 g dm^{-3} Na$_2$SO$_4$ and 0.6 g dm^{-3} NO$_3^-$ (as NaNO$_3$). The composition of the electrolyte containing Cu ions was identical. Additionally about 0.5 g dm^{-3} of CuCO$_3$.Cu(OH)$_2$.3H$_2$O were added to the electrolyte shortly before the electrolysis began. Since the electrolyte is alkaline, copper is not present as Cu^{2+}. We may expect the presence mainly of copper hydroxide Cu(OH)$_2$, which dissolves in weakly alkaline solutions in colloidal form. The experiments were carried out at a constant temperature of 25 °C. A fresh electrolyte was used for each electrolysis. The electrolyte volume was 3 dm^3. The distance between the electrodes was set in the range 5 to 25 mm.

Prior to the first experiment, the copper cathode was treated with dilute H$_2$SO$_4$ (1:1) and rinsed thoroughly with distilled water. Between the subsequent experiments the cathode was not treated. In the electrolysis procedure with addition of Cu ions the cathode pretreatment was identical to the previous case. Afterwards the cathode was treated for 6 h in a solution with Cu ions added by cathodic polarization at a current density of 2.8 mA cm^{-2}. The experimental results were reproducible only after sufficient pretreatment.

Samples were taken at regular time intervals and were analysed for dissolved Cu, NO$_3^-$, NO$_2^-$, NH$_3$ and pH.

Determination of nitrate content was based on light absorption at 210 nm [24]; nitrite was allowed to react with sulfanilic acid and α-naphthol in a weakly acidic solution yielding an orange-coloured azo dyestuff with an absorption maximum at 480 nm [24]. Ammonia was determined by the Nessler method [24] and Cu ions were determined by atomic absorption spectroscopy.

2.2.2. *Potentiodynamic measurement*
Prior to the polarization measurements, the surface of the Cu RDE was polished with a metallographic paper (600 Sianor B, Switzerland) and rinsed with dilute H$_3$PO$_4$ (40%). The polarization curves were measured at 1200 rpm, a scan rate of 5 mV s^{-1} and a temperature of 25 °C.

3. Results and discussion

3.1. *Electrolytic reduction in recirculation mode electrolyser*

The first series of experiments was performed using an artificial regenerating solution without the addition of Cu ions. It was found that nitrate reduction proceeds with very low efficiency. The lowest nitrate concentration of 449 mg dm^{-3} was reached after 7 h of electrolysis at 3.8 mA cm^{-2}, which represents an integral current yield of 6.9% with respect to a five electron reduction. This concentration is far above the limit enabling efficient anion exchanger regeneration (∼50 mg dm^{-3} [23]). Moreover, a substantial increase in the nitrite ions concentration in the treated solution was observed during the course of electrolysis, as discussed later.

The existence of such a high limiting value of nitrate concentration in the treated solution was explained by a gradual deactivation of the cathode surface. Only a few compounds causing a deterioration in electrocatalytic activity can be formed on the electrode surface during cathodic polarisation of the Cu electrode in the solution under study. CuH or CuH$_2$ are considered to be the most probable. X-ray diffraction, together with infrared spectrometry, did not directly confirm this assumption. Only a surface layer of amorphous copper was detected. This is in agreement with the results reported by Vaškelis et al. [25] and is probably caused by the instability of CuH, which decomposes in water forming amorphous copper powder and hydrogen [26]. Another reason for the presence of amorphous copper is the destruction of the metal surface layer crystalline structure by the evolved hydrogen.

An alternative explanation was offered by Petrii and Safonova [27] who studied nitrate reduction in acidic

solutions. They considered that active sites on the cathode surface are preferentially occupied by adsorbed hydrogen molecules, which hinder further nitrate reduction. This does not correspond to our observation of the formation of a thick layer consisting of fine particles covering the cathode surface.

Different methods were tested to avoid gradual deactivation of the Cu cathode, for example, introduction of repeated cathode activation by periodic application of an anodic square wave current pulse [28]. The addition of Cu ions in the form of $CuCO_3 \cdot Cu(OH)_2 \cdot 3H_2O$ to the treated solution was found to be the most suitable. The average Cu ion concentration in the treated solution during electrolysis was 6.0 ± 1.2 mg dm^{-3}. This Cu ion concentration does not complicate application of this technique in drinking water treatment because the solution is used in a closed cycle. Also the ion exchange resins employed for the removal of nitrate ions are not seriously affected by Cu ions at this concentration.

The change in nitrate concentration with time of electrolysis using electrolyte with added Cu ions was reproducible during repeated experiments. The average dependence is shown in Figure 2. It follows from this figure that the addition of Cu ions effectively prevents a decrease in the cathode activity and provides a reproducible decrease in nitrate concentration in the treated solution during repeated electrolysis. At the studied conditions the nitrate concentration decreases below the limit for successful ion exchanger regeneration (50 mg dm^{-3}) after 8 h electrolysis.

The effect of Cu ions can be explained by slow continuous Cu deposition on the cathode surface. The deposited copper forms new active sites on the cathode surface thus maintaining electrocatalytic activity independent of electrolysis duration.

To verify that the increase in current efficiency of the cathodic nitrate reduction by Cu ion addition is caused not only by the formation of a porous surface layer and by the corresponding increase in surface area, a series of experiments with artificial regenerating solution without Cu addition was performed employing a cathode which had been previously activated by electrolysis in an electrolyte with added Cu ions. The results for three subsequent electrolyses are shown in Figure 2. A decrease in the catalytic activity of the cathode surface is clearly evident. The integral current efficiency decreased from a value of 26.5%, reached during 6 h of electrolysis with Cu ions added, to a value of 8.0% reached at the sixth subsequent electrolysis without adding Cu. This represents an increase in the final nitrate concentration from 97 to 450 mg dm^{-3} after 7 h under otherwise identical conditions. This behaviour is similar to the
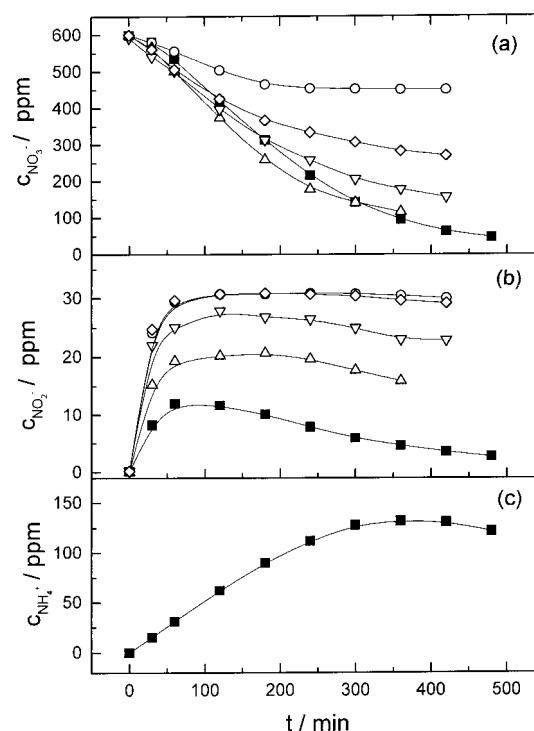

Fig. 2. Concentration against time of electrolysis for nitrate (a), nitrite (b) and ammonia (c). Electrolysis with and without addition of Cu ions into the electrolyte; interelectrode gap 20 mm; current density 3.8 mA cm^{-2}; (■) average values from the 1st, 2nd and 3rd consecutive electrolysis tests with addition of Cu ions; (△), (▽) and (◇) represent 1st, 2nd and 3rd consecutive electrolysis tests without addition of Cu ions, cathode activated by cathodic polarization in an electrolyte containing Cu ions prior to the 1st electrolysis, (○) steady state electrolysis without addition of Cu ions.

steady state experiments without added Cu ions, and thus similar cathode surface properties may be expected.

As mentioned in the theoretical part, one of the possible electrode reactions is the reduction of nitrate to nitrite, that is, Equation 1 [11]. Since nitrite is an even more dangerous pollutant than nitrate, it is desirable to keep its concentration in the treated solution as low as possible. The maximum allowable concentration of nitrite for drinking water is 0.1 mg dm^{-3} [2]. It was found that the addition of Cu ions also has a positive influence on the concentration of nitrite in the treated solution. The nitrite concentration reaches a maximum within the first hour, as seen in Figure 2(b). With Cu ions added, see Figure 2(b), a rapid decrease in nitrite concentration occurs after the first hour. A concentration of about 3.5 mg dm^{-3} was reached after 7 h. This is still above the allowed limit for drinking water [2]. However, we intend to reuse the treated solution in a closed cycle for regeneration of the ion exchange resins, so this does not represent a serious problem. Moreover,

the nitrite concentration still shows a decreasing trend and the final concentration of nitrate may be expected to decrease below the allowable limit for prolonged electrolysis. However, without the addition of Cu ions, see Figure 2(b), the nitrite concentration in the solution decreased only slowly after the first hour. This decrease was even slower during repeated electrolysis. The final nitrite concentration was as high as 20–30 $mg\,dm^{-3}$ at the end of the third subsequent test without added Cu ions. This behaviour is attributable to a selective decrease in cathode activity for the consecutive steps of nitrate reduction.

The theory about positive influence of the added Cu ions on the nitrate reduction process is also supported by the dependence of the cathode potential on the electrolysis duration shown in Figure 3. During approximately the first 10 min of electrolysis with added Cu ions, the cathode potential exhibited a continuous decrease with one apparent delay. This probably corresponds to the reduction of copper oxides and/or hydroxides to metallic form, thus forming electrocatalyticaly active sites. After reaching a maximum, the potential decreased continuously during electrolysis due to continuous build-up of an active surface layer during cathodic polarisation. The slow initial potential decrease is in agreement with the initial (nitrate reduction) inductive period observed during the first 30 min of electrolysis.

The dependence of the nitrate concentration on the time of electrolysis in the current density range 2.8–7.6 $mA\,cm^{-2}$ was studied for a 20 mm interelectrode gap. The observed dependence of nitrate and nitrite concentration on the total charge for several studied current densities is shown in Figure 4. A current density of 2.8 $mA\,cm^{-2}$ gave the highest current efficiency with respect to nitrate reduction. It follows from Figure 4

that the current yield decreases with increasing current density. At 7.6 $mA\,cm^{-2}$, the current yield exhibited a much stronger decrease when compared to the lower current density range. A current density of 3.8 $mA\,cm^{-2}$ was used in further study of the nitrate reduction efficiency. This was because it still exhibited a relatively high current efficiency, together with a fairly rapid reduction in the nitrate concentration with time. At all current densities the time dependence of the cathode potential showed a shape identical with that in Figure 3 for the case of added Cu ions. The following average cathode potentials were found for the respective current densities of 2.8, 3.8, 5.7 and 7.6 $mA\,cm^{-2}$ − 1.076, −1.175: −1.208 and −1.247 V vs SCE.

As already mentioned, the pH of the treated solution became gradually more alkaline during electrolysis, that is its value changed from 8.3 to 9.1, within the first 200 min of electrolysis and then remained at this value.

One of the possible products of nitrate reduction is ammonia. The ammonia concentration against time of electrolysis in the treated solution exhibited an apparent increase during the first 6h of electrolysis. A maximum concentration of 132 $mg\,dm^{-3}$ was reached, followed by a continuous decrease. In 4h after the end of electrolysis, the ammonia concentration in the treated solution cir-

Fig. 4. Concentration against electric charge for nitrate (a) and nitrite (b). Electrolysis test with addition of Cu ions in the electrolyte; interelectrode gap 20 mm; current densities: (□) 2.8, (○) 3.8, (△) 5.7 and (▽) 7.6 $mA\,cm^{-2}$.
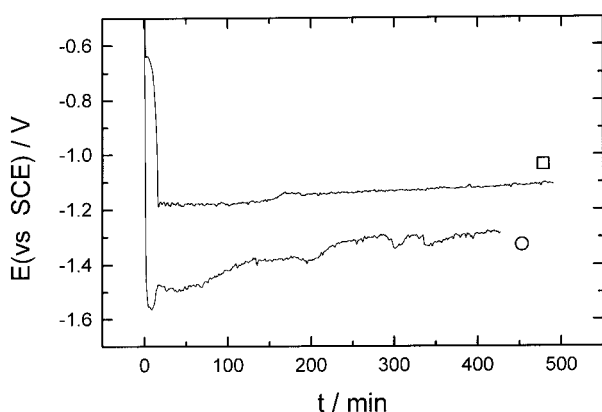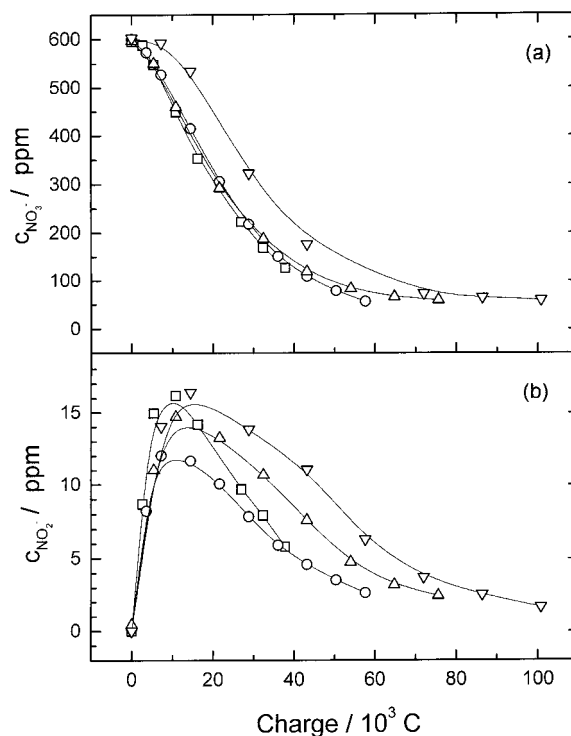

Fig. 3. Cathodic potential (vs SCE) against time of electrolysis; interelectrode gap 20 mm; current density 3.8 $mA\,cm^{-2}$; (□) 3rd electrolysis test with addition of Cu ions; (○) steady state electrolysis test without addition of Cu ions.

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culating in the electrolyser decreased to $25 \, mg \, dm^{-3}$. The initial increase in ammonia concentration can be explained by the relatively high production rate, Reactions 3 and 5. The decrease in concentration taking place after 7 h of electrolysis is attributable to the decrease in concentration of nitrate in the treated solution and the consequent gradual decrease in the ammonia production rate.

The dependence of the nitrate, nitrite and ammonium concentrations on electrolysis time was studied for interelectrode gaps varying in the range 5–25 mm. The observed differences between the individual interelectrode gaps were within experimental error. Terminal voltages of 5.38, 5.05, 4.4 and 4.1 V were found for interelectrode gaps of 25, 20, 10 and 5 mm, respectively, which demonstrates the possibility of reducing the energy consumption by lowering the interelectrode gap. In our case a reduction by 24% was attained between the smallest and largest interelectrode gaps.

3.2. Potentiodynamic polarization study of nitrate reduction

The conclusions concerning the increase in cathode catalytic activity due to the addition of Cu ions were verified by potentiodynamic polarization experiments using a copper RDE. The polarization curves for the solution under study with and without nitrate are shown in Figure 5. The curve for the solution without nitrate exhibits one cathodic current wave of half-wave potential $E_{1/2 \, vs \, SCE} = -0.58 \, V$. This corresponds to the reduction of the surface copper oxide layer [22] and coincides with the cathode potential delay during the first 10 min of electrolysis in the case of added Cu ions. The solution containing nitrate ions exhibits an additional second, well developed, cathodic current peak at potential $E_{vs \, SCE} = -1.30 \, V$ corresponding to nitrate reduction. This cathodic peak consists of two individual waves, in agreement with [12, 22]. Figure 5 shows that the catalytic activity of the cathode and, consequently, the height of the nitrate reduction current plateau (or peak) decreases strongly with the duration of cathodic polarisation. Electrode inactivation was already apparent after 10 min. With increasing cathode deactivation two individual peaks corresponding to nitrate reduction became more distinguishable. The peak at the less cathodic potential gradually became predominant. This is probably connected with enhanced nitrite formation during electrolysis without Cu addition.

The addition of Cu ions to the electrolyte causes a reproducible increase in the nitrate reduction current peak not only compared to the inactivated electrode, but also to the freshly activated cathode, see (Figs 5 and 6).
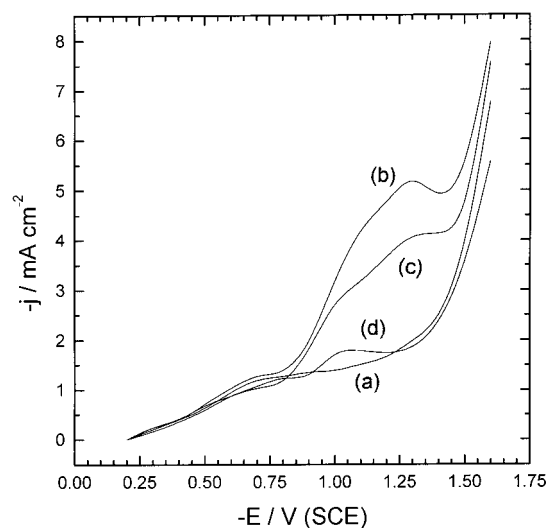

Fig. 5. Polarization curves of copper RDE. Temperature 25 °C, 1200 rpm, potential scan rate $5 \, mV \, s^{-1}$. Composition of electrolytes: (a) 440 mg dm^{-3} Na$_2$SO$_4$, 400 mg dm^{-3} NaCl; 8 g dm^{-3} NaHCO$_3$.Cu RDE with freshly activated surface; (b) is identical to (a) with addition of 821.6 mg dm^{-3} NaNO$_3$ (600 mg dm^{-3} NO$_3^-$). Cu RDE with a freshly activated surface; (c) is identical to (b). Cu RDE after 10 min of polarization at -1.6 V vs SCE in electrolyte (a); (d) as for (b). Cu RDE after 20 min of polarization at -1.6 V vs SCE in electrolyte (a).
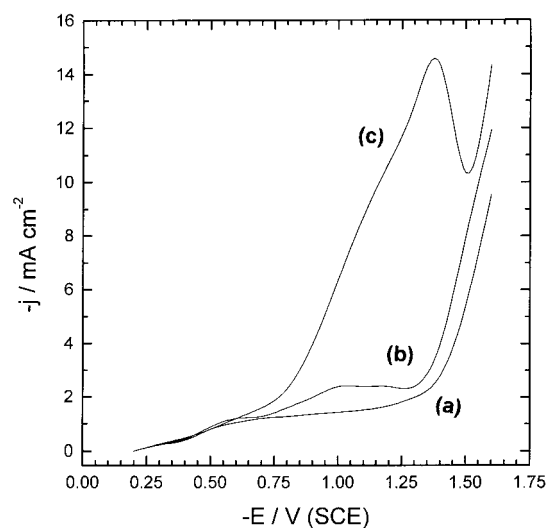

Fig. 6. Polarization curves of Cu RDE. Temperature 25 °C, 1200 rpm, potential scan rate $5 \, mV \, s^{-1}$. Composition of electrolytes: (a) 440 mg dm^{-3} Na$_2$SO$_4$, 400 mg dm^{-3} NaCl, 8 g m^{-3} NaHCO$_3$. Copper RDE with a fresh surface; (b) is identical to (a) with addition of 821.6 mg dm^{-3} NaNO$_3$ (600 mg dm^{-3} NO$_3^-$). Copper RDE after 30 min polarization at -1.6 V vs SCE in electrolyte (a). (c) as for (b). Copper RDE after 40 min polarization at -1.6 V vs SCE, electrolyte composition is identical to (b) with addition of 0.5 g dm^{-3} of CUCO$_3$.Cu(OH)$_2$.

This may be explained by the rapid deactivation of the copper cathode surface already apparent after the first cathodic potential scan when using the electrolyte without Cu addition.

4. Conclusions

It was found that by using a copper cathode it is possible to remove nitrate ions from a solution simulating the waste solution from the regeneration of strongly basic ion-exchange columns for drinking water treatment.

The current yield decreased with increasing cathodic current density in the range 2.8–$7.6\,\mathrm{mA\,cm^{-2}}$. A current density of $3.8\,\mathrm{mA\,cm^{-2}}$ was chosen as optimal with respect to current yield and electrolysis duration. Using this current density, an integral current yield of 22%, during reduction of nitrate concentration from $600\,\mathrm{mg\,dm^{-3}}$ to about $50\,\mathrm{mg\,dm^{-3}}$ was reached.

The presence of Cu ions in the concentration range $6.0 \pm 1.2\,\mathrm{mg\,dm^{-3}}$ was found to prevent decrease in cathode activity with electrolysis duration which otherwise lowers the current efficiency of the process. In the presence of Cu ions, the average current yield remained constant during repeated reduction of nitrate in the batch reactor. It also had a positive influence on the reduction of nitrite concentration in the treated solution.

Acknowledgement

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