

Effect of the cathode material on the removal of nitrates by electrolysis in non-chloride media

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ABSTRACT

In this work, the effect of the cathode material (conductive diamond, stainless steel, silicon carbide, graphite or lead) and the current density ($150\text{--}1400\text{ A m}^{-2}$) on the removal of nitrates from aqueous solutions is studied by electrolysis in non-divided electrochemical cells equipped with conductive diamond anodes, using sodium sulphate as the electrolyte. The results show that the cathode material very strongly influences both the process performance and the product distribution. The main products obtained are gaseous nitrogen (NO , N_2O and NO_2) and ammonium ions. Nitrate removal follows first order kinetics, which indicates that the electrolysis process is controlled by mass transfer. Furthermore, the stainless steel and graphite cathodes show a great selectivity towards the production of ammonium ions, whereas the silicon carbide cathode leads to the highest formation of gaseous nitrogen, which production is promoted at low current densities.

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1. Introduction

Inorganic nitrogen pollution in water has become a significant problem around the world. It is noteworthy that the total nitrogen deposition on the Earth's surface was 32 million metric tons (mostly from natural emission sources) in 1860, whereas in the early 1990s, the total nitrogen deposition had risen to 100 million metric tons [1]. This great difference was entirely due to anthropogenic activities such as the excessive application of fertilisers in agriculture, animal wastes produced in intensive farming, leachates from urban solid waste dumps and/or untreated industry wastewaters [2]. The main nitrogen species that are present in water are nitrates, nitrites and ammonium ions, although the most common pollutant is nitrate.

Amongst other available technologies, these nitrogen compounds can be removed by biological processes [3,4], ion exchange resins or reverse osmosis [5]. In addition, conventional chemical coagulation using aluminium or iron salts are also employed to remove inorganic nitrogen pollutants [6]. In recent years, electrochemical technologies have been developed for the removal of inorganic nitrogen pollutants. Electrocoagulation can efficiently remove nitrogen using aluminium or iron electrodes [7–10]. In addition, the electrochemical reduction of nitrate has been studied. Thus, several cathode materials, such as Fe, Cu or Ti, have been used in electrochemical denitrification [11]. The main final product

obtained by this process is usually the ammonium ion because the simultaneous electrolysis of ammonium to nitrogen gas (the target product) has been reported to be difficult [12–14].

The chemical and electrochemical reactivities of inorganic nitrogen pollutants in aqueous media have been widely described in the literature but are not completely clear due to the high reactivity and instability of nitrogen intermediates. For example, Ferapontova and Fedorovich [15] described the rate of reduction of NO_3^- and other anions, taking into consideration that this reaction is controlled by the simultaneous transfer of both an electron and a proton from a proton donor. The rate of this reduction depends on the type of electrocatalytic material used, the cathode potential and the pH of the solution. When considering the electrocatalytic materials, metals with a high overpotential for the evolution of hydrogen achieve the highest reduction rates.

However, ammonia is the main product in the electrochemical reduction of nitrate, particularly when the nitrate concentration is high [16,17]. Likewise, the presence of relatively small amounts of copper clearly enhances the nitrate reduction process. Copper exhibits a catalytic effect that limits the adsorption of hydrogen onto the cathode surface, enhancing the adsorption of nitrate [17]. After the adsorption of nitrate, copper has a negative influence over both the activity and selectivity of nitrate reduction towards N_2 production because the electrochemical oxidation of ammonia to nitrogen is a difficult reaction when the potential of electrolysis is constant [18].

Katsounaros et al. [19] determined that the reduction of nitrate follows first order kinetics at -2.5 V and that NO could act as an intermediate of the reaction. Thus, NO would be the precursor to

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Nomenclature

j_{lim}	limiting current density (A m^{-2})
n	number of electrons exchange in the process
F	Faraday's constant (C mol^{-1})
k_m	mass transport coefficient (m s^{-1})
Q	applied electrical charge (A h dm^{-3})
j	current density (A m^{-2})
$\text{NO}_3^-(t)$	nitrate concentration at time t (mol m^{-3})
t	time (s)

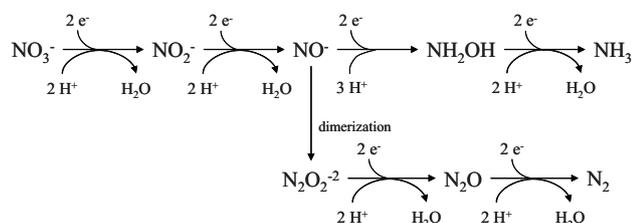


Fig. 1. The reduction pathway of nitrate proposed by Kuwabata et al. [20].

the formation of ammonia and nitrogen, being ammonia the main product at potentials from -2.0 to -2.2V , whereas nitrogen gas is the final product at more negative potentials. Kuwabata et al. [20] proposed a reduction pathway of nitrate to ammonia and nitrogen gas using a [Mo–Fe]/GC electrode. This pathway is schematically represented in Fig. 1. Nevertheless, nitrogen reactivity is complex, and there are different pathways of nitrate reduction reported in the literature. For example, Bockris and Kim [21] found that nitrite plays a key role as an intermediate product in the nitrate reduction process. Likewise, nitrite (instead of nitric oxide) is further reduced to ammonia or nitrogen, as the yield for ammonia or nitrogen is dependent on the electrocatalytic effect of the electrode material.

In the present paper, the role of the cathode material in the nitrate reduction process was evaluated in a single-compartment electrochemical flow cell. The behaviour of conductive diamond, stainless steel, silicon carbide, graphite and lead was studied, and special attention was given to the rate of nitrate removal, the product speciation and the process efficiency.

2. Experimental

2.1. Analytical procedure

Inorganic nitrogen anions (NO_3^- , NO_2^-) were measured by ion chromatography using a Shimadzu LC-20A instrument (column, Shodex IC I-524A; mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, 1.0 ml min^{-1}). The same ion chromatography equipment was used to measure the inorganic nitrogen cation, NH_4^+ , (column, Shodex IC YK-421; mobile phase, 5.0 mM tartaric acid, 1.0 mM dipicolinic acid and 24 mM boric acid; flow rate, 1.0 ml min^{-1}). The total nitrogen concentration was monitored using an Analytikjena multi N/C 3100 analyser. Gaseous nitrogen compounds were identified by a Teledyne API chemiluminescence $\text{NO}/\text{NO}_2/\text{NO}_x$ analyser and were quantified by a mass balance. In addition, the nitric oxide in the aqueous solution was qualitatively determined by chemiluminescence by bubbling a high quantity of ozone into the sample, using the reaction shown in Eq. (1) [22]. Here, the intensity of the light detected is directly proportional to the nitric oxide concentration.



Table 1
Conductivity of the electrode materials.

Material	Conductivity (S cm^{-1})
CDE	1.0×10^1
Stainless steel	1.4×10^4
Graphite	1.7×10^2
Lead	4.9×10^4

2.2. Electrochemical cell

The electrolysis of nitrogen was carried out in a single-compartment electrochemical flow cell described in Fig. 2 [23]. The anode was composed of a conductive diamond electrode (CDE, Adamant Technologies, Switzerland), whereas the cathodes were composed of the CDE (Adamant Technologies, Switzerland), stainless steel AISI 304 (Mervilab, Spain), silicon carbide (3-ONE-2, USA), porous graphite POCOfoam® (Poco Graphite SARL, France) or lead (Mervilab, Spain). The conductivity of these materials is shown in Table 1. To clean the surface of the electrodes, a solution containing 5000 mg dm^{-3} of sodium sulphate at pH of 2 was passed through the electrochemical cell for 10 min and at a current density of 30 mA cm^{-2} before each experiment. Each electrode had a geometric area of 78 cm^2 and an electrode gap of 9 mm. The electrolyte was stored in a glass tank (500 ml) and was circulated through the electrolytic cell by means of a peristaltic pump. A heat exchanger was used to maintain the temperature at the desired set point.

2.3. Experimental procedure

Bench-scale electrolysis of 0.60 dm^3 synthetic wastewater was carried out under galvanostatic conditions. The concentration of nitrogen was 25 mg dm^{-3} (150 mg dm^{-3} NaNO_3), 3000 mg dm^{-3} Na_2SO_4 was used as a supporting electrolyte and H_2SO_4 was dosed in suitable amounts to set the pH at 2. The current density was varied from 150 to 1400 A m^{-2} ; 150 and 300 A m^{-2} are the typical current densities used in the electrochemical treatment of wastewater. A current density of 1400 A m^{-2} was selected to study the influence of a high current density on the species generated in the reaction media and thus on the nitrogen speciation.

The cell voltage did not significantly vary during each electrolysis experiment, indicating that no appreciable deterioration of the electrode or passivation phenomena took place. The electrolyte flow rate through the cell was $1.5\text{ dm}^3\text{ min}^{-1}$. A heat exchanger coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta) was used to maintain the temperature at the desired set point (25°C).

3. Results and discussion

Fig. 3a compares the evolution of the concentration of the nitrates with respect to the applied electrical charge, using different cathode materials. The current density was maintained at 150 A m^{-2} , and sodium sulphate was added as a supporting electrolyte. In the figure, it is observed that all the cathode materials tested removed the nitrates, but not with very high current efficiencies. However, this range of current efficiencies can be easily explained when taking into account the initial concentration of the nitrates, using a single mass transfer model for the overall process [24,25]. The mass-transfer coefficient was calculated from a standard $\text{Fe}(\text{CN})_6^{3+}/\text{Fe}(\text{CN})_6^{2+}$ limit current test, obtaining a value of $1.2 \times 10^{-5}\text{ m s}^{-1}$ [26] for the experimental setup and conditions used. Under these conditions, the limiting current density, calculated from the expression $j_{\text{lim}}(t) = nFk_m\text{NO}_3^-(t)$, is 4.1 A m^{-2} if nitrite is assumed to be the final product ($n = 2\text{ mol e}^-/\text{mol NO}_3^-$) and is 16.5 A m^{-2} if ammonium is assumed to be the final product

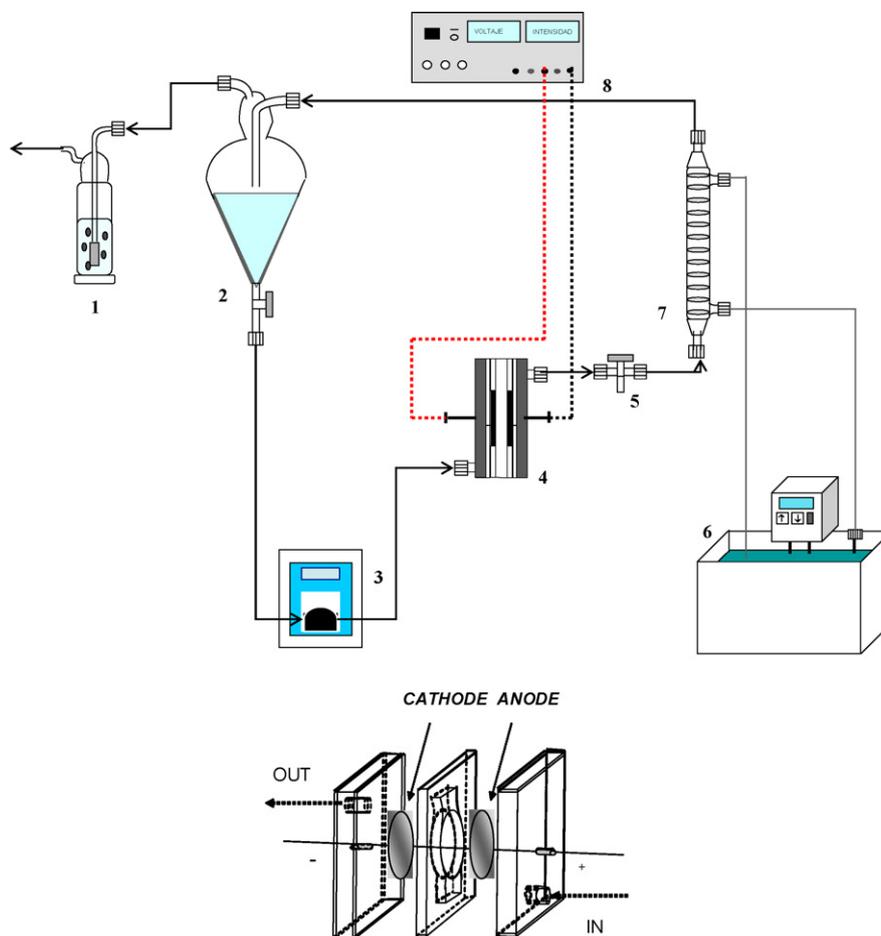


Fig. 2. The layout of the electrolysis bench-scale plant (1: absorber, 2: feed tank, 3: peristaltic pump, 4: electrochemical cell, 5: sampling, 6: thermostatic bath, 7: heat exchanger, 8: power supply). Detail of the electrochemical cell.

($n=8 \text{ mol e}^-/\text{mol NO}_3^-$), thus a maximum efficiency of 2.7–11%, according to a simple model of the electrochemical process based on a mass transfer-controlled process [27,28]. Hence, the maximum achievable current efficiency is limited to this range of values.

Another important point to be highlighted from Fig. 3a is the marked differences found in the performance of the five electrode materials studied. The graphite is clearly the most efficient, with current efficiencies over 10%, and the conductive diamond is the least efficient. Fig. 3b shows that the evolution of nitrates follows first order kinetics (as demonstrated by linear fitting in semi-logarithmic plot), which according to the literature, may suggest that the process is controlled by mediated reagents (oxidative/reductant agents in the target solution) or by mass transfer [23,29,30].

Fig. 4 (data also shown in Supplementary material) shows the effect of the current density on the removal of nitrates using a silicon carbide cathode. Fig. 4a) depicts the progress of the electrolysis with respect to the nitrate concentration and Fig. 4b) summarises the efficiency of the NO_3^- removal at different stages of the electrolysis. This efficiency is calculated as the mass of nitrate (mg NO_3^-) removed per unit of applied electrical charge (expressed in Ah). Moreover, for comparison, the maximum efficiency of the achievable NO_3^- removal is also shown with the reduction product being ammonium (oxidation state -3), nitrite (oxidation stage $+3$) or gaseous nitrogen (oxidation state 0). Note that this maximum efficiency of NO_3^- removal would correspond to an electrical efficiency of 100% (100% of the electrons applied are used for the target reduction reaction).

Fig. 4 is very important to distinguish between a mass transfer-controlled and a mediated electrolysis-controlled process. Mediated electro-reagents should be produced more intensively at higher current densities, and hence, their effect should increase with current density. Conversely, the direct electrochemical process becomes less efficient at a higher current density in the region where the mass transfer rate is below the electron supply rate. As can be observed in this figure, the process is less efficient at higher current densities. This observation rejects the mediated reduction mechanism as the primary reduction mechanism when using the SiC as the cathode, and it clearly supports the mass transfer-controlled mechanism for this process.

Figs. 5 and 6 show the effect of the current density and reaction progress on the efficiency of the reduction of nitrates with the other four cathode materials studied in this work (data included in Supplementary material). Fig. 5 shows the data for the lead (Fig. 5a) and conductive diamond (Fig. 5b) cathodes. Both electrodes show very similar behaviours to that observed with silicon carbide. In both cases, the mass transfer clearly controls the process rate, and the efficiencies are comparable to those of silicon carbide, although they decrease in the order $\text{SiC} > \text{Pb} > \text{CDE}$. However, results corresponding to electrolysis with the stainless steel (Fig. 6a) and graphite carbon (Fig. 6b) electrodes show very different behaviours, which suggests a significant role of the mediated processes in the nitrate removal for these cathode materials. In both cases, the efficiencies do not decrease but rather increase in the range from 150 to 300 A m^{-2} . This could mean that the mediated reduction processes are occurring and that they compensate for

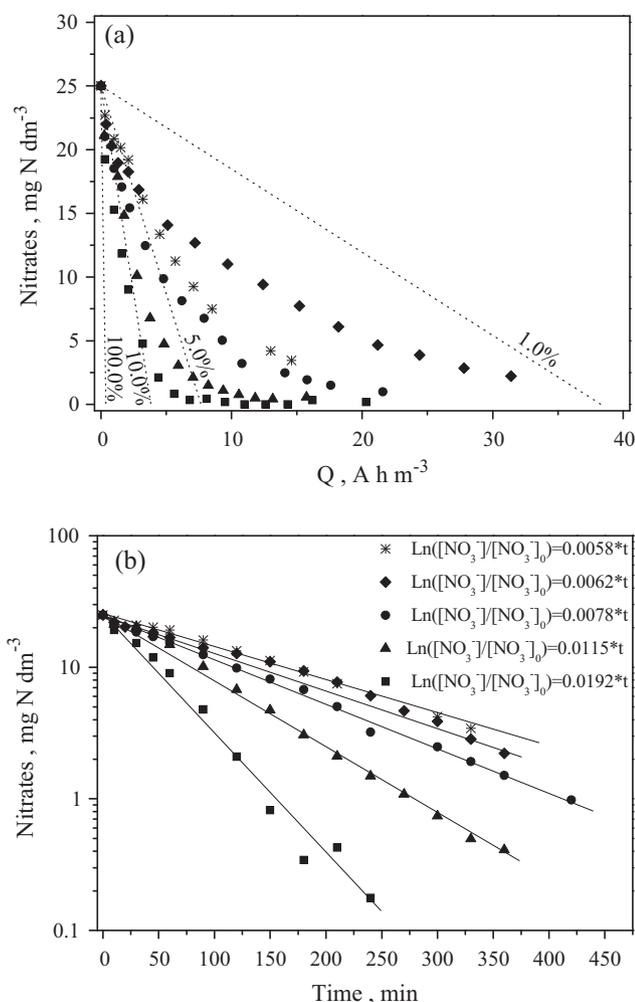


Fig. 3. The variation of the NO_3^- -N concentration with respect to the applied electrical charge (a) and the time (b) during the electrolysis of the nitrate solutions. Operating conditions: $25 \text{ mg dm}^{-3} \text{ NO}_3^-$ -N + $3000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; pH_0 2; 150 A m^{-2} ; anode: conductive diamond; cathode materials: \blacklozenge conductive diamond, $*$ stainless steel, \bullet silicon carbide, \blacksquare graphite, \blacktriangle lead.

the loss of efficiency caused by the mass transport limitations. This behaviour is more significantly observed in the case of stainless steel. It is noteworthy that the current efficiency is almost constant with the current density at the highest value of the electric charge applied. This observation supports, even more strongly, the important role of the mediated oxidation processes (in which the electron transfer to the pollutant takes place chemically from an oxidative or reductant inorganic agent).

The product distribution is the other important point in the study of the electro-catalytic properties of the different cathodes. Fig. 7 shows the time-course of the different products during the electrolysis of nitrate at different current densities using the silicon carbide cathode. In every case, the ammonium ion is the primary product obtained, although different nitrogen gaseous species are initially formed at a high rate. These species are quantified by mass balance, but some qualitative gas analyses allow for the identification of NO, N_2O and NO_2 as the primary nitrogen components of these evolved gases. The particular composition of each sample of gases changes with time, due to the well-known decomposition of NO into N_2O and NO_2 and their further reactions to yield N_2O_5 . This indicates that NO is the main gaseous product formed during the electrochemical process. In addition, an ozonation test [22] was performed on the liquid samples taken during the electrochemical process. In these samples, the chemiluminescence tests confirm that

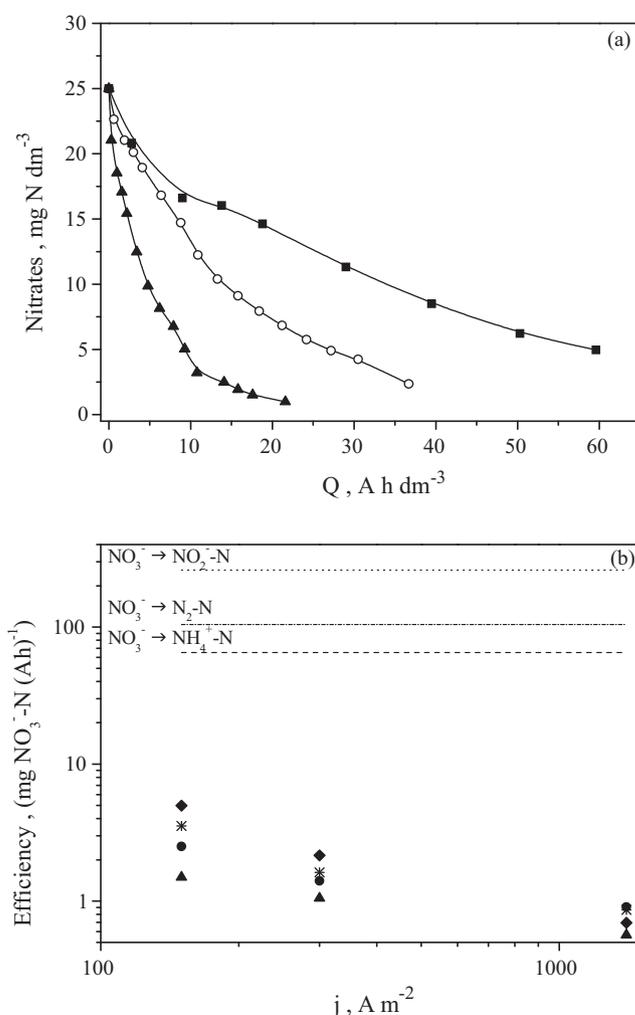


Fig. 4. (a) The variation of the NO_3^- -N concentration with the applied electrical charge (\blacktriangle 150 A m^{-2} , \circ 300 A m^{-2} , \blacksquare 1400 A m^{-2}). (b) The influence of the current density on the efficiency of the removal of the nitrates (\blacklozenge 2.5 A h dm^{-3} , $*$ 5 A h dm^{-3} , \bullet 10 A h dm^{-3} , \blacktriangle 20 A h dm^{-3}). Operating conditions: $25 \text{ mg dm}^{-3} \text{ NO}_3^-$ -N + $3000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; pH_0 2; anode: conductive diamond; cathode: silicon carbide.

the NO concentration increases with time. This is consistent with the high solubility of nitric oxide in an aqueous medium and confirms that NO is a key component in the gaseous nitrogen flow. The nitrite concentration is negligible (there are merely traces in some of the samples), suggesting its high reactivity when it behaves as intermediate.

Fig. 8 reports, for the lowest current density (150 A m^{-2}), the changes in the speciation of the products with the applied electric charge (progress of the electrolysis), in terms of the ammonium selectivity. This variable is most influenced by the electrode material, especially in the cases of stainless steel and SiC, which show limiting behaviours. The ammonium ion is almost a unique final product from the very early stages when stainless steel is selected as the cathode material. In contrast, when using the SiC electrode, the gaseous nitrogen species are initially the main products; afterwards, the selectivity of the process changes and the ammonium ions become the primary products. This behaviour is also observed at higher current densities, as shown in Fig. 9a and b. However, a key difference is that at larger current densities, smaller differences are observed in the role of gaseous nitrogen compounds at large applied currents.

Taking into account these results, a single mechanistic model can be proposed for the main processes occurring on the cathode

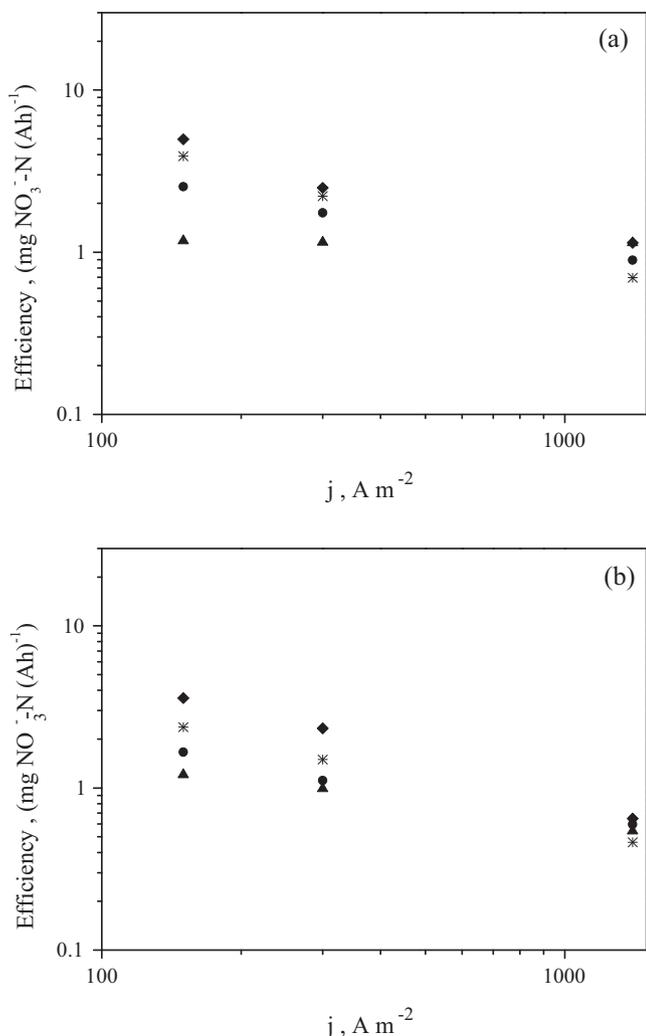
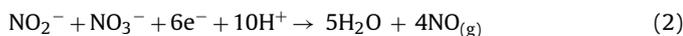


Fig. 5. The influence of the current density on the efficiency of the removal of nitrates (◆ 2.5 A h dm⁻³, * 5 A h dm⁻³, ● 10 A h dm⁻³, ▲ 20 A h dm⁻³). Operating conditions: 25 mg dm⁻³ NO₃⁻-N + 3000 mg dm⁻³ Na₂SO₄; pH₀ 2; anode: conductive diamond; cathodes: (a) lead, (b) conductive diamond.

surface. The nitrates are reduced to ammonium ions and to nitrites regardless of the cathode material used, although the selectivity depends on the particular cathode material chosen. Then, under high concentrations of nitrates, nitrites are transformed into nitric oxide according to the reaction showed in Eq. (2) [31].



Thus, nitric oxide is the key component in the gas flow and, due to its high solubility, it is also present in the liquid reaction medium. Moreover, this reaction needs a reducing compound (e.g., hydrogen), and these compounds are more likely to be produced at higher current densities. This helps to explain the smaller differences observed for the different electrode materials, in terms of the contribution of gaseous nitrogen, at large applied current when using larger current densities. When working under these conditions, the nitrites formed at the beginning of the process (the stage that marks the difference) can easily react with the reducing compounds and are then transformed into nitrogen gas [32]. At this point, it is worth noting that the reaction rate of Eq. (2) is expected to be higher (under the complexity of the reaction system) than has been previously described in the literature [33].

At larger applied current charges, when the concentration of nitrates is smaller, this reaction is not promoted, and a simple

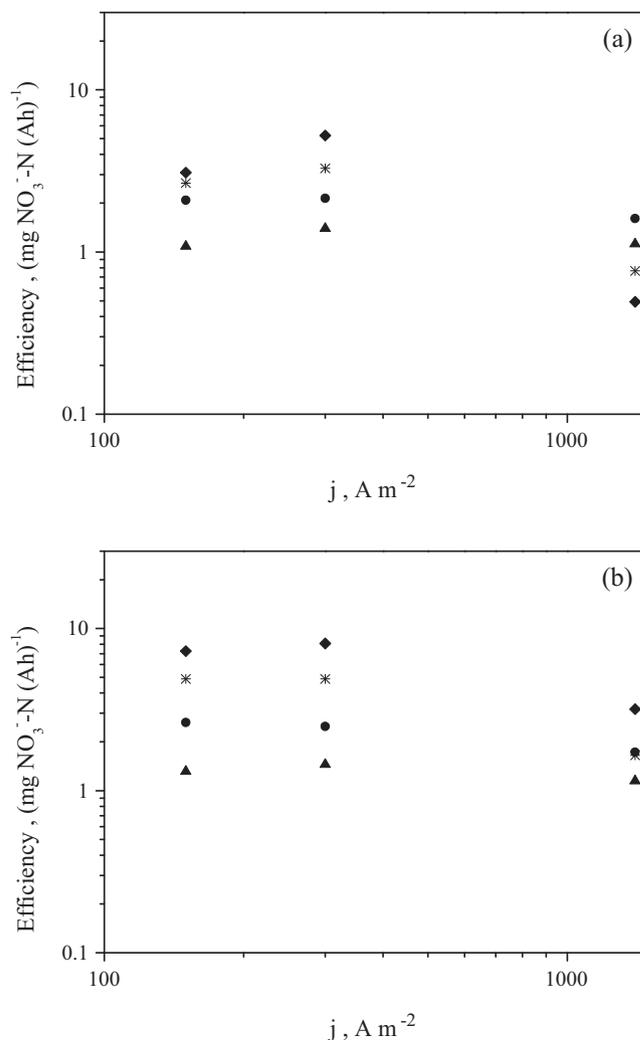


Fig. 6. The influence of the current density on the efficiency of the removal of the nitrates (◆ 2.5 A h dm⁻³, * 5 A h dm⁻³, ● 10 A h dm⁻³, ▲ 20 A h dm⁻³). Operating conditions: 25 mg dm⁻³ NO₃⁻-N + 3000 mg dm⁻³ Na₂SO₄; pH₀ 2; anode: conductive diamond; cathodes: (a) stainless steel, (b) graphite.

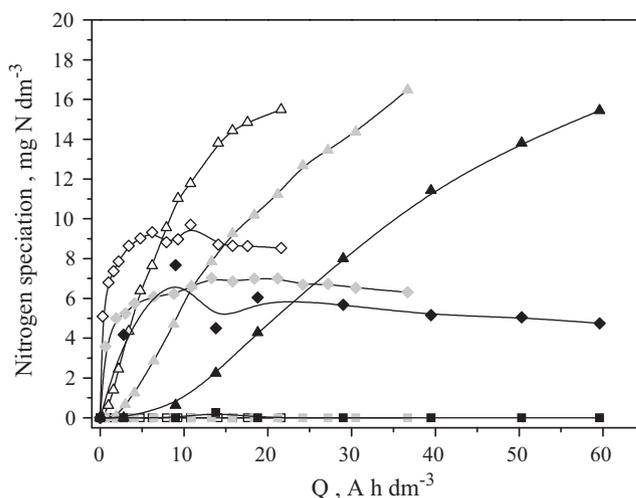


Fig. 7. The effect of the current density on the speciation of nitrogen during the electrolysis of nitrate solutions (NO₂⁻-N, ▲ NH₄⁺-N, ◆ N_{gaseous}-N). Operating conditions: 25 mg dm⁻³ NO₃⁻-N + 3000 mg dm⁻³ Na₂SO₄; pH₀; anode: conductive diamond; cathode: silicon carbide; points: unfilled – 150 A m⁻², grey – 300 A m⁻², filled – 1400 A m⁻².

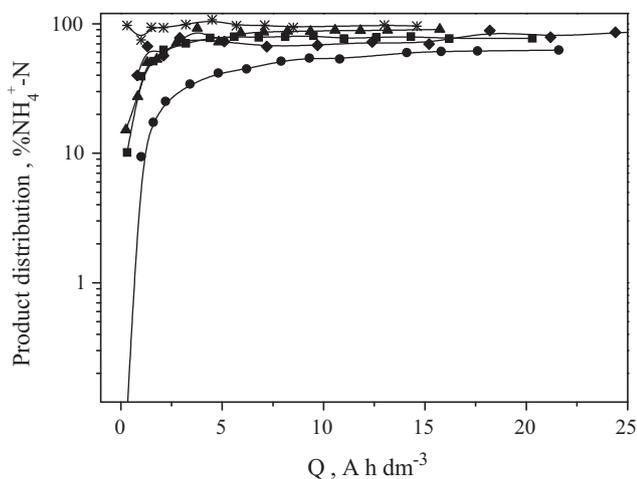


Fig. 8. The distribution of the products with respect to the applied electrical charge during the electrolysis of the nitrate solutions. Operating conditions: 25 mg dm⁻³ NO₃⁻-N + 3000 mg dm⁻³ Na₂SO₄; pH₀ 2; 150 A m⁻²; anode: conductive diamond; cathode materials: ◆ conductive diamond, * stainless steel, ● silicon carbide, graphite, ▲ lead.

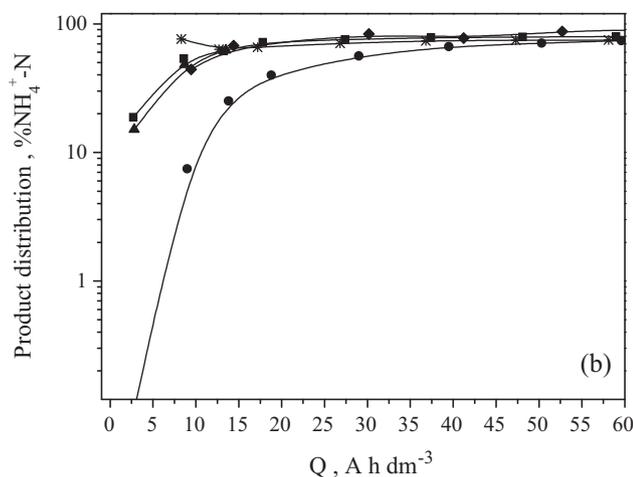
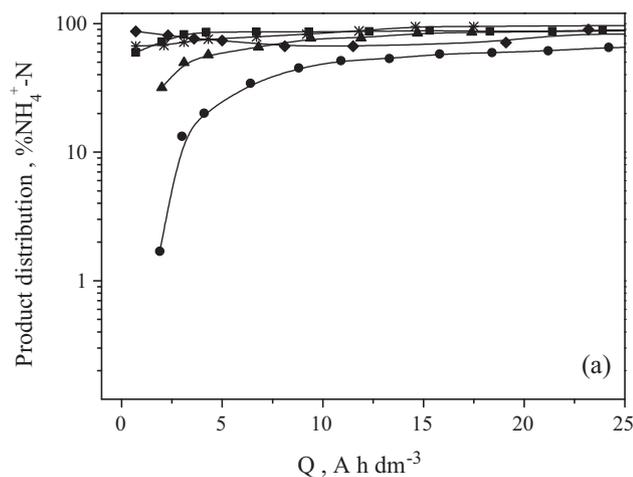


Fig. 9. The distribution of the products with respect to the applied electrical charge during the electrolysis of nitrate solutions. Operating conditions: 25 mg dm⁻³ NO₃⁻-N + 3000 mg dm⁻³ Na₂SO₄; pH₀ 2; current densities: (a) 300 A m⁻², (b) 1400 A m⁻²; anode: conductive diamond; cathode materials: ◆ conductive diamond, * stainless steel, ● silicon carbide, ■ graphite, ▲ lead.

transformation of nitrites into nitrates (with the consequent decrease in the efficiency) occurs (Eq. (3)).



This explains that, in every case, the selectivity towards the ammonium ions increases progressively during the electrolysis up to a constant value; it also explains the smaller differences observed at larger current densities and higher values of the applied electric charge.

To summarise, the reduction of nitrates to ammonium ions is promoted when using stainless steel as the cathode material, whilst the production of nitrites is favoured with the use of a silicon carbide cathode. Other cathodes show an intermediate behaviour between those observed for stainless steel and silicon carbide. When considering their selectivity to ammonium in the first stage, the cathode materials can be placed in the following order: stainless steel > conductive diamond > graphite > lead > silicon carbide.

The increase observed in the efficiency of the reduction of nitrates from 150 to 300 A m⁻² is not explained by a mediated oxidation process, but by the preferential transformation of nitrites into nitric oxide. The production of reducing compounds is not promoted at the lowest current density (merely ammonium formation occurs), which justifies the high selectivity obtained. The formed nitrites revert into nitrates under these conditions. At 300 A m⁻², both mechanisms are fully active, explaining the higher efficiency in the removal of nitrates as well as the lower selectivity towards the production of ammonium. In the case of graphite, the explanation can also be related to the formation of hydrogen or hydrogen peroxide, which in this case is enhanced at low current densities, explaining the high selectivity towards NO at low current densities and the selectivity for ammonium at larger current densities.

4. Conclusions

From the results gathered in the present work, the following conclusions can be highlighted:

- The ammonium cation is the main reaction product in the electroreduction of nitrates when conductive diamond, stainless steel, graphite, silicon carbide and lead are used as the cathode materials. Nitrogen oxides are secondary products, and silicon carbide is the material that leads to the highest yield in the production of these species. This yield is promoted at lower current densities.
- Graphite is the most efficient cathode in terms of nitrate removal, with current efficiencies close to 10%, whereas conductive diamond presents the lowest efficiency, with values lower than 5%. In every case, the nitrate removal follows first order kinetics, which can be explained by mass transport control or by mediated processes.
- During electrolysis with stainless steel and graphite, a complete reduction of nitrates to ammonium was observed, without significant production of gaseous nitrogen compounds.
- The mediated oxidation process largely affects the product speciation and helps to explain the effect of the current density.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jhazmat.2012.02.034.

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