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

Engracia Lacasa, Pablo Cañizares, Javier Llanos and Manuel A. Rodrigo


Abstract

In this work, the effect of the cathode material (conductive diamond, stainless steel, silicon carbide, graphite and lead) and current density (150-1400 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 electrolyte. Results show that cathode material influences very strongly on both the process performance and the product distribution, being gaseous nitrogen (NO, N$_2$O, NO$_2$) and ammonium ions the main products obtained. Nitrate removal follows a first order kinetic which indicates that electrolysis process is controlled by mass transfer. Furthermore, stainless steel and graphite present a great selectivity towards the production of ammonium ion whereas silicon carbide leads to the highest formation of gaseous nitrogen, being this speciation promoted at low current densities.

Keywords.

Electrolysis, conductive diamond electrodes, nitrates, reduction, water treatment
* To whom correspondence should be addressed. Tel. +34 902204100

Fax: +34 926 29 52 56

E-mail: Manuel.Rodrigo@uclm.es
1. Introduction

Inorganic nitrogen pollution in water has become a significant problem around the world. It is important to highlight that the total nitrogen deposition on the Earth's surface was 32 million metric tons (mostly from natural emission sources) in 1860 while in the early 1990s, total nitrogen deposition had risen up to 100 million metric tons [1]. This great difference was entirely due to anthropogenic activities such as an excessive application of fertilizers 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.

Among other technologies, the removal of these nitrogen compounds can be carried out 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 become developing technologies for the removal of inorganic nitrogen pollutants. In this way, electrocoagulation can efficiently remove nitrogen using aluminium or iron electrodes [7-10]. In addition, 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 is usually ammonium ion because the simultaneous electrolysis of ammonium to nitrogen gas (the target product) is reported to be difficult [12-14].

The chemical and electrochemical reactivity of inorganic nitrogen pollutants in aqueous solution has been widely described in literature, but it is not completely clear due to the high reactivity and instability of nitrogen intermediates. For instance, Ferapontova and
Fedorovich [15] described the rate of reduction of NO$_3^-$ and other anions, taking into account that this reaction is controlled by the simultaneous transfer of both electron and proton from a proton donor. The rate of this reduction depends on the type of electrocatalytic material, the cathode potential and the pH of the solution. For the case of electrocatalytic materials, metals with high overpotential for hydrogen evolution achieve the highest reduction rates.

However, ammonia is the main product in the electrochemical reduction of nitrate, above all when its 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 on the cathode surface, enhancing the adsorption of nitrate [17]. After this step, copper has a negative influence over both activity and selectivity 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 a first order kinetics at -2.5V and that NO could act as an intermediate of the reaction. Thus, NO would be the precursor of ammonia and nitrogen formation, although ammonia is the main product at potentials from -2.0 to -2.2V, being nitrogen gas the final product at more negative potentials. In this way, 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 shown in Figure 1. Nevertheless, nitrogen reactivity is complex and there are different pathways of nitrate reduction reported in literature. Thus, 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) would be further reduced to ammonia.
or nitrogen, being the yield for ammonia or nitrogen 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, paying
a special attention to the rate of nitrate removal, the product speciation and the process
efficiency.

2. Experimental

2.1. Analytical procedure

Nitrogen inorganic anions (NO\textsubscript{3}\textsuperscript{-}, NO\textsubscript{2}\textsuperscript{-}) were measured by ion chromatography using a
Shimadzu LC-20A equipment (column, Shodex IC I-524A; mobile phase, 2.5 mM
phthalic acid at pH 4.0; flow rate, 1.0 ml min\textsuperscript{-1}). The same ion chromatography equipment
was used to measure the nitrogen inorganic cation, NH\textsubscript{4}\textsuperscript{+}, (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\textsuperscript{-1}). The total nitrogen concentration was monitored using an Analytikjena
multi N/C 3100 analyser. Nitrogen gaseous compounds were identified by Teledyne API
chemiluminescence NO/NO\textsubscript{2}/NO\textsubscript{X} analyzer and were quantified by mass balance. In
addition, nitric oxide in aqueous solution was qualitatively determined by
chemiluminescence bubbling a high quantity of ozone into the sample, taking into
account Eq. 1 [22]. Hence, the intensity of the light detected is directly proportional to
nitric oxide concentration.

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 + \text{light} \quad \text{(Eq. 1)} \]
2.2. Electrochemical cell

The electrolysis of nitrogen was carried out in a single-compartment electrochemical flow cell described in Figure 2 [23]. Conductive Diamond Electrode (CDE, Adamant Technologies, Switzerland) was used as anode material whereas CDE (Adamant Technologies, Switzerland), stainless steel AISI 304 (Mervilab, Spain), silicon carbide (3-ONE-2, USA), porous graphite POCOFoam® (Poco Graphite SARL, France) and lead (Mervilab, Spain) were used as cathode materials. The conductivity of these materials is gathered in Table 1. Before each experiment, a solution containing 5000 mg dm\(^{-3}\) of sodium sulphate at pH 2 was passed through the electrochemical cell, during 10 min and at a current density of 30 mA cm\(^{-2}\), in order to clean the surface of electrodes. Electrodes had a geometric area of 78 cm\(^2\) each one and an electrode gap of 9 mm. The electrolyte was stored in a glass tank (500 ml) and it 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\(^3\) of 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\(_2\)SO\(_4\) was used as supporting electrolyte and H\(_2\)SO\(_4\) was also dosed in suitable amounts to set a pH of 2. The current density was varied from 150 to 1400 A m\(^{-2}\), being 150 and 300 A m\(^{-2}\) the typical current densities used in wastewater treatment by means of electrochemical technologies. 1400 A m\(^{-2}\) was selected in order to study the influence of a high current density in the species generated in the reaction media and, thus, in the nitrogen speciation.
The cell voltage did not significantly vary during each electrolysis, indicating that appreciable deterioration of electrode or passivation phenomena did not take place. The electrolyte flow rate through the cell was 1.5 dm$^3$ 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 ºC).

3. Results and discussion

Figure 3a compares the evolution of the concentration of nitrates with respect to the applied electrical charge, using different cathode materials. Current density was maintained constant at 150 A m$^{-2}$ and sodium sulphate was added as supporting electrolyte. In this figure, it can be observed that nitrates are removed with all the cathode materials tested, but with not very high current efficiencies. However, this range of current efficiencies can be easily explained taking into account the initial concentration of nitrate, using a single mass transfer model for the overall process [24, 25]. The mass-transfer coefficient was calculated from a standard Fe(CN)$_6^{3-}$/Fe(CN)$_6^{2+}$ limit current test, obtaining a value of 1.2 $10^{-5}$ m s$^{-1}$ [26] for the experimental setup and conditions used. Under these conditions, the limit current density (which can be calculated from the expression $j_{\text{lim}}(t) = n F k_m \text{NO}_3^-(t)$) is 4.1 A m$^{-2}$ if nitrite is assumed as the final product (n=2 mol e$^-$/mol NO$_3^-$), and 16.5 A m$^{-2}$ if ammonium is assumed to be the final product (n=8 mol e$^-$/mol NO$_3^-$). This leads to a maximum efficiency between 2.7-11%, according to a simple model of the electrochemical process based on mass transfer control [27,28]. Thus, the maximum reachable current efficiency is limited to this range of values.
Next, another important point to be highlighted from Figure 2a is the marked differences found in the performance of the five electrodes studied. Graphite is clearly the most efficient, with current efficiencies over 10%, and conductive diamond is the least one. Figure 3b shows that the evolution of nitrates follows a first order kinetics (linear fitting in semi-logarithmic plot). According to literature, this fact may suggest that the process is controlled by mediated reagents (oxidative/reductant agents in the target solution) or by mass transfer [23, 29, 30].

Figure 4 (data also gathered in Table 2) shows the effect of current density on the removal of nitrates using a silicon carbide cathode. Part a) depicts the progress of the electrolysis with respect to nitrate concentration and Part b) summarizes the efficiency of NO₃⁻ removal at different stages of the electrolysis. This efficiency has been calculated as the mass of nitrate (mg NO₃⁻) removed per unit of applied electrical charge (expressed in Ah). Moreover, the maximum efficiency of NO₃⁻ removal reachable if the reduction product is ammonium (oxidation state -3), nitrite (oxidation stage +3) or gaseous nitrogen (oxidation state 0) is also shown, for comparison purposes. Note that this maximum efficiency of NO₃⁻ removal would correspond to an electrical efficiency of 100% (100% of the electrons applied used to the target reduction reaction).

This figure is very important to discern between a mass transfer and a mediated electrolysis control of the process. Mediated electro-reagents should be produced more intensively at higher current densities, and hence, their effect should increase with current density. On the contrary, direct electrochemical process becomes less efficient at higher current density, in the region in which mass transfer rate is below the electron supply rate.
As it can be observed, the process is less efficient at higher current densities. This observation discards mediated reduction as the primary reduction mechanism when using SiC as cathode, and it clearly supports that the process is mass transfer controlled.

Figures 5 and 6 show the effect of 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 tables 3 and 4). Figure 5 is focused on lead (Figure 5a) and conductive diamond (Figure 5b) cathodes. Both electrodes show a very similar behaviour to that observed with silicon carbide. In both cases, mass transfer clearly controls the process rate, and efficiencies are comparable to those of silicon carbide, although they decrease in the series SiC>Pb>CDE. On the contrary, results corresponding to electrolysis with stainless steel (Figure 6a) and graphite carbon (Figure 6b) electrodes show a very different behaviour, which suggests a significant role of mediated processes in the nitrate removal. In both cases, efficiencies do not decrease but increase in the range from 150 to 300 A m⁻². This could mean that mediated reduction processes are occurring and they compensate the loss of efficiency caused by mass transport limitations. This behaviour is more significantly observed in the case of stainless steel. It is worth mentioning that current efficiency is almost constant with 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 (the electron transference to the pollutant takes place chemically from an oxidative or reductant inorganic agent).

Product distribution is the other important point in the study of the electro-catalytic properties of the different cathodes. Figure 7 shows the time-course of the different
products during the electrolysis of nitrate at different current densities using silicon carbide cathode. In every case, 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 identifying NO, N₂O, NO₂ 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 N₂O and NO₂, and the further reactions to yield N₂O₅. This places NO as the main gaseous product formed during the electrochemical process. In addition, an ozonation test [22] was carried out to the liquid samples taken during the electrochemical process. In these samples, chemiluminescence tests confirm that NO concentration increases with time. This is consistent with the high solubility of nitric oxide in aqueous medium, and confirms NO as a key component in the gaseous nitrogen flow. Nitrite concentration is negligible (merely traces in some of the determinations), what suggests its high reactivity when it behaves as intermediate.

Figure 8 reports, for the lowest current density (150 Å m⁻²), the changes in the products speciation with the electric charge passed (progress of the electrolysis), in terms of the ammonium selectivity. This variable is the most deeply influenced by the electrode material, especially in the cases of stainless steel and SiC, which show limit behaviours. On the one hand, ammonium ion is almost the unique final product from the very early stage when stainless steel is selected as cathode material. On the contrary, in the case of using the SiC electrode, gaseous nitrogen species are the main products in the first moment and afterwards, selectivity of the process changes and ammonium ions become in the primary products. This behaviour is also observed at higher current densities, as it
is shown in Figure 9 (parts a and b). However, a key difference is that for larger current densities, smaller differences are observed in the role of gaseous nitrogen compounds at large current passed.

Taking into account these results, a single mechanistic model can be proposed for the main processes occurring on the cathode surface. Nitrates are reduced to ammonium ions and to nitrites regardless of the cathode used, although the selectivity depends on the particular cathode studied. Then, under high concentrations of nitrates, nitrites are transformed into nitric oxide according to the reaction showed in equation 2 [31].

\[ 3 \text{NO}_2^- + \text{NO}_3^- + 6 \text{e}^- + 10 \text{H}^+ \rightarrow 5 \text{H}_2\text{O} + 4 \text{NO}(g) \] (Eq. 2)

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 reducing compound (e.g., hydrogen) to take place and these compounds are more likely 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 current passed when using larger current densities. When working at these conditions, nitrites formed at the beginning (the stage that marks the difference) can easily react with reducing compounds and, then, be 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 it has been previously described in literature [33].

At larger current charge passed, when the concentration of nitrates is smaller, this reaction is not promoted, and a simple transformation of nitrites into nitrates (with the consequent decrease in the efficiency) is obtained (equation 3).
\[
\text{NO}_2^- + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_3^-(\text{Eq. 3})
\]

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

To sum up, reduction of nitrates to ammonium ions is promoted when using stainless steel as cathode material, while the production of nitrites is favoured with silicon carbide cathode. Other cathodes show an intermediate behaviour between those observed for stainless steel and silicon carbide. Taking into account their selectivity to ammonium in the first stage, they can be classified in the following series: 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. Production of reducing compounds is not promoted at the lowest current density (merely ammonium formation), which justifies the high selectivity obtained. Nitrites formed are reverted into nitrates under these conditions. At 300 A m\(^{-2}\) both mechanisms are fully active, explaining the higher efficiency in the removal of nitrates and also the lower selectivity towards the production of ammonium. In the case of graphite, the explanation can also be related with 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 to ammonium at larger values of this variable.
4. Conclusions

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

- 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 cathode materials. Nitrogen oxides are secondary products, being silicon carbide 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, nitrate removal follows a 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.

- Mediated oxidation process largely affects the product speciation and helps to explain the effect of the current density.

Acknowledgements

This work was supported by the MCT (Ministerio de Ciencia y Tecnología, Spain) and by the EU (European Union) through projects CTM2010-18833/TECNO and CSD2006-044.
1 References


distribution and disinfection during electrochemical removal of dilute ammonia from an

anion electroreduction Part I. Effect of the adsorption of inorganic cations in small
concentrations on the kinetics of anion electroreduction with different elementary steps

[16] C. Polatides, G. Kyriacou, Electrochemical reduction of nitrate ion on various

[17] L. Szpyrkowicz, S. Daniele, M. Radaelli, S. Specchia, Removal of NO$_3^-$ from water
by electrochemical reduction in different reactor configurations, Applied catalysis B:

DEMS and cyclic voltammetry study of NH$_3$ oxidation on platinized platinum,

reduction of nitrate to nitrogen on tin cathode at very high cathode potentials,


List of symbols

- $j_{lim}$: 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)

List of Figures

Figure captions
Figure 1. Reduction pathway of nitrate proposed by Kuwabata et al. [20].

Figure 2. 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.

Figure 3. Variation of NO$_3^-$-N concentration with applied electrical charge (a) and time (b) during electrolysis of nitrate solutions. Operation conditions: 25 mg dm$^{-3}$ NO$_3^-$-N + 3000 mg dm$^{-3}$ Na$_2$SO$_4$; pH$_o$ 2; 150 A m$^{-2}$; anode: conductive diamond; cathode materials: ◆ conductive diamond, ★ stainless steel, ● silicon carbide, ■ graphite, ▲ lead.

Figure 4. (a) Variation of NO$_3^-$-N concentration with applied electrical charge (▲ 150 A m$^2$, ○ 300 A m$^2$, ■ 1400 A m$^2$). (b) 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$^{-3}$). Operation conditions: 25 mg dm$^{-3}$ NO$_3^-$-N + 3000 mg dm$^{-3}$ Na$_2$SO$_4$; pH$_o$ 2; anode: conductive diamond; cathode: silicon carbide.

Figure 5. 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$^{-3}$). Operation conditions: 25 mg dm$^{-3}$ NO$_3^-$-N + 3000 mg dm$^{-3}$ Na$_2$SO$_4$; pH$_o$ 2; anode: conductive diamond; cathodes: (a) lead, (b) conductive diamond.

Figure 6. 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$^{-3}$). Operation conditions: 25 mg dm$^{-3}$ NO$_3^-$-N + 3000 mg dm$^{-3}$ Na$_2$SO$_4$; pH$_o$ 2; anode: conductive diamond; cathodes: (a) stainless steel, (b) graphite.

Figure 7. Effect of the current density on the speciation of nitrogen during electrolysis of nitrate solutions (■ NO$_2^-$-N, ▲ NH$_4^+$-N, ◆ N$_{gaseous}$-N). Operation conditions: 25 mg dm$^{-3}$
NO₃⁻-N + 3000 mg dm⁻³ Na₂SO₄; pH₀; anode: conductive diamond; cathode: silicon carbide; points: empty-150 A m⁻², gray-300 A m⁻², full-1400 A m⁻².

**Figure 8.** Products distribution with applied electrical charge during the electrolysis of nitrate solutions. Operation 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.

**Figure 9.** Products distribution with applied electrical charge during the electrolysis of nitrate solutions. Operation 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.

![Chemical reactions](image-url)
Figure 2
Figure 3.
Figure 4.
Figure 5.
Figure 6.
Figure 7.
Figure 8.
Figure 9.
Table 1. Conductivity of the electrode materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (S cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDE</td>
<td>1.0 (\cdot 10^1)</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>1.4 (\cdot 10^4)</td>
</tr>
<tr>
<td>Graphite</td>
<td>1.7 (\cdot 10^2)</td>
</tr>
<tr>
<td>Lead</td>
<td>4.9 (\cdot 10^4)</td>
</tr>
</tbody>
</table>