Electrochemical denitrification with chlorides using DSA and BDD anodes

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Abstract

In this work, the electrochemical denitrification of solutions containing chlorides is studied with two different types of anode materials: O₂-Dimensionally Stable Anodes (DSA) and Boron Doped Diamond (BDD). First of all, a higher rate of nitrate removal was found when chloride is used as the supporting media, with respect to sulphate. Moreover, it was found that it is necessary a minimum chloride concentration to get an effective treatment and that gaseous-nitrogen is the primary nitrogen species found in the electrolyses. In this process, nitrate is firstly reduced on the cathode surface and next oxidized by the species generated by the anode material. Thus, anode material does not influence on the denitrification rate, but it significantly influences on the speciation of chlorine. Furthermore, formation of perchlorates advises against the use of BDD electrochemical denitrification for the production of drinking water. Finally, formation of chlorates in the DSA-electrolyses, due to the ageing of hypochlorite, also limits its use in the production of drinking water, although it does not exclude its use in other applications such as reuse of treated wastewater and treatment of industrial wastes.

Keywords.

Nitrates, breakpoint chlorination, electrolyses, dimensionally stable anodes, boron doped diamond anodes.
1. Introduction

The treatment of polluted water effluents, in order to reach the composition that allows its disposal to the environment, is a current and important topic of chemical engineering due to the increase in the worldwide water demand and the decrease in the availability of god-quality water resources. Specifically, the removal of nitrate is usually carried out by the well-known biological denitrificacion process, which uses anoxic biological reactors in order to transform nitrates into gaseous-nitrogen. This is a very effective process, although this technology requires a continuous maintenance of parameters such as pH and carbon source, and it is very sensitive to temperature [1]. Cleaner technologies include ion exchange resins or reverse osmosis [2]. Both can remove nitrate from waters, although they have the important drawback of the rejection-water produced, with a very high nitrogen concentration that has to be treated later with another technology. Likewise, conventional chemical coagulation using aluminium or iron salts are used to remove nitrate [3] but the addition of chemicals increases significantly the salinity of water.

At this point, electrochemical technologies have recently become important processes for the removal of nitrate pollution from water because they show an easy operation mode and a high efficiency on the pollutants removal. In particular, electro-coagulation has shown to be an effective technology in the removal of nitrates. In a recent study of our group [4], it was demonstrated that this electrochemical technology avoids the increase in the conductivity and improves the efficiency as compared with coagulation, allowing the complete removal of nitrates contained in a water effluent.
Another important electrochemical technology is electrolysis. Depending on the anode material, current density, electrolyte concentration and pH, electrolytic reduction of nitrate has been reported to produce ammonium ions, nitrite or different gaseous nitrogen species as the main products [5, 6]. As ammonium is one of the species that are commonly produced, several works have focused on the electrochemical removal of ammonium ions in the presence of chloride, as a consequence of the promotion in the reaction media of the well-known breakpoint chlorination process. This promotion is explained by the anodic formation of hypochlorite and the later combination of this oxidant with ammonia to give different chloramines and gaseous-nitrogen species [7-10]. In those works, the influence of anode material, current density or initial sodium chloride conditions [11-14] has been studied. Thus, the particular working conditions of an electrochemical cell and the influence of these conditions on the removal of ammonium is a topic of the maximum interest.

In the searching for new applications of the electrochemical technology in the environmental remediation, one additional step is the removal of nitrates using electrolysis or electrochemical denitrification. The presence of chlorine during the electrolytic process of nitrate reduction enhances the breakpoint chlorination reaction, and thus the production of nitrogen gas as the main stable product [15]. At this point, and in spite of the widely studied breakpoint reaction, not many works have dealt about the role of operation conditions and electrode material on the electrochemical denitrification process. Thus, Vanlangendonck et al. [16] determined the optimal operating conditions to reduce the nitrate concentration in wastewaters from power plants, using stainless steel as cathodic material and DSA-Cl₂ as anodic material. It was
found that a high chloride concentration and a high current density were necessary to convert nitrate into nitrogen gas. Katsounaros and Kyriacou [17] studied the influence of high initial concentrations of nitrates (in chloride medium) during the potentiostatic electrolysis process, using a tin cathode and a platinised Pt foil anode. Li et al. [18] reached the almost complete nitrate conversion to nitrogen gas by using a Cu-Zn cathode and a Ti/IrO$_2$-Pt anode in the presence of sodium chloride as supporting electrolyte. Moreover, Reyter et al. [19] studied the influence of cathode/anode surface area ratio on the efficiency of the conversion of nitrate into nitrogen gas. In addition, it is reported that ammonia oxidation can be enhanced by using BDD or Ti/PtO$_x$-IrO$_2$ electrodes if the reaction between active chlorine and ammonia takes place in a reaction zone close to the electrode surface, to reduce the formation of chlorate and perchlorate as by-products [20].

In this context, the main objective of this study is to determine the influence of the anode material on the reduction of nitrate, containing sodium chloride as supporting electrolyte. Previous works of our group characterised the electrolysis in non-chloride media, where the breakpoint chlorination does not occur, and they drew very important conclusions in terms of speciation of nitrogen. In the present work, two different anode materials have been used: O$_2$-dimensionally stable (DSA) and Boron Doped Diamond (BDD) anodes because they correspond to two limit behaviour in oxidation processes. As cathode, and taking into account the results of a previous study [6], stainless steel (AISI 304) was proposed. Likewise, the influence of the concentration of sodium chloride on the process performance (ranging from the typical concentrations of very
fresh water to almost brackish water) has been studied, in order to determine the
optimum conditions to obtain nitrogen gas as the main final product.

2. Experimental

2.1. Analytical procedure

Nitrogen and chloride inorganic anions (NO$_3^-$, NO$_2^-$, Cl$^-$, ClO$_2^-$, ClO$_3^-$, ClO$_4^-$) were measured by ion chromatography using 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$^{-1}$). In the case of hypochlorite, its peak interferes with the chloride one; therefore, the determination was carried out by titration with As$_2$O$_3$ in NaOH 2 M. The same ion chromatography equipment (column, Shodex IC YK-421; mobile phase, 5.0 mM tartaric, 1.0 mM dipicolinic acid and 24.3 mM boric acid; flow rate, 1.0 ml min$^{-1}$) was used to measure the nitrogen inorganic cation (NH$_4^+$). Inorganic chloramines have been measured following the DPD standard method described in literature [21]. The concentration of gaseous species of nitrogen and chlorine were quantified by mass balance. The generation of NH$_3$ was discarded as the gases produced within the tests were conducted through a H$_2$SO$_4$ trap and no NH$_4^+$ was found in any of the tests.

2.2. Electrochemical cell

The electrolysis of nitrogen was carried out in a single-compartment electrochemical flow cell described elsewhere [22]. Boron Doped Diamond (BDD) and dimensionally stable anodes (DSA) were used as anode materials and stainless steel (AISI 304) as cathode material. BDD anodes were supplied by Adamant, Switzerland, (Si substrate; 1 mm thickness; 100 mΩ cm resistivity; 500 ppm boron concentration; 1.53 μm CDE-
film thickness; 115 CDE-film Raman sp3/sp2). DSA anodes (supplied by DeNora, Italy) were DSA-O2 type and used a with IrO2 and RuO2 cover. Electrodes had a geometric area of 78 cm2 each one and an electrode gap of 9 mm. The electrolyte was stored in a glass tank (500 ml) and 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 electrolyses of 0.60 dm3 of synthetic wastewater were carried out under galvanostatic conditions (30 mA cm-2). The concentration of NaNO3 was 1.76 mN and NaCl was used as supporting electrolyte with concentrations ranging from 0.51 to 51.3 mM. The cell voltage did not vary during each electrolyses significantly, indicating that appreciable deterioration of electrode or passivation phenomena did not take place. The electrolyte flow rate through the cell was 1.5 dm3 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

Figure 1 shows the effect of the electrolyte anion (sulphate or chloride) and of the anode material (DSA or BDD) on the removal of nitrates from aqueous solution in a single compartment electrochemical cell, when a high concentration of electrolyte salt is added to the target solution (simulating a brackish water containing nitrates). These tests were carried out at an initial pH of 2, in order to compare the results obtained with chloride
with a previous work carried out with sulphate [6]. This figure also shows the values of the calculated rate of nitrate removal.

As it can be observed, a huge influence of the anode material on the process performance is observed when sulphate is used as supporting electrolyte, being the BDD much more efficient than the DSA-O₂ electrode. Initially, this behavior is difficult to explain, because the removal of nitrates to gaseous-nitrogen species is a reduction process. However, this observation was explained in a previous work [6] in terms of the important role of electro-generated species in the overall reactivity of the system, specifically, in terms of the occurrence of peroxosulphates, which easily decompose to hydrogen peroxide. This hydrogen peroxide reacts with nitrites (generated from the reduction of nitrates) to give gaseous nitrogen species. At this point, it is important to point out that nitrite becomes in a key compound to explain the electrolytic removal of nitrates in sulphate medium. Nevertheless, ammonium ions and nitric oxide were also found as significant species involved in the electrolysis with both anode materials [6].

In the case of chloride-containing solutions, differences obtained in the electrolyses with both anodes become smaller, being the efficiencies obtained with both anode materials closer between them and higher than those obtained in sulphate medium, even with BDD. This behavior can be also observed in the value of the rates of nitrate removal, which have been added in Figure 1. As it can be observed, the rates of nitrate removal obtained with both electrodes are quite similar when chloride is used as electrolyte, and considerably higher than those obtained in sulphate medium. In addition, the exponential decay of the concentration of nitrates, observed in the electrolyses of nitrate
solutions with sulphate as supporting electrolyte, turns into an almost linear trend when chloride is used as supporting electrolyte. This suggests that kinetic order (respect to the nitrates) changes from a first order kinetic (which can be explained by a mass transfer and/or mediated oxidation control of the reaction rate) to a zero-order, which can only be explained assuming a key effect of the chloride concentration on the kinetics of the process.

To clarify this point, Figure 2 shows the products speciation during the same electrolyses with BDD (Fig. 2.a) and DSA (Fig. 2.b), of nitrate solutions containing NaCl as supporting electrode. As it is explained in section 2.1, the quantification of gaseous species of chlorine and nitrogen were carried out by mass balance, the same method used in our previous study with sulphate ions [6]. Although this method of quantification can originate some experimental errors, its accuracy is high enough to evaluate the influence of the anode material and the nature of the anions present in the target effluent. Moreover, the occurrence of other nitrogen, which has been reported in literature, such as hydroxylamine, Angeli’s salt, azide, hydrazine or hyponitrite [17], has been checked in every sample with nil results.

Very important differences are observed between both electrolyses in terms of the speciation of chlorine. Oxidation of chlorides is very effective in the case of BDD, and it leads to a very significant production of gaseous-chlorine and to a smaller formation of hypochlorite, which clearly behaves as an intermediate and almost disappears for large applied currents, and chlorates, which behaves as a final product, as no perchlorate was detected in the reaction system. Removal of chloride is almost complete at the end
of the electrolyses (for applied currents larger than 30 Ah dm$^{-3}$). Conversely, in the electrolyses with DSA-O$_2$, chloride concentration decreases rapidly during the very first moments of the electrolyses, and then, it starts decreasing at a significantly smaller rate. Consequently, at large applied currents (30 Ah dm$^{-3}$) merely 20% of the initial chloride was transformed into other species, being gaseous-chlorine and hypochlorite the most significant species, although it is also important to mark that some chlorate (in very small concentrations) was also detected at large current applied.

With regard to the speciation of nitrogen, gaseous nitrogen species are the most significant species in both electrolyses, reaching almost 90% conversion in the case of BDD and 75% in the case of DSA-O$_2$. The concentration of ammonium and nitrite ions, which are the most significant species in the electrolyses of sulphate-containing solutions, is negligible. Moreover, combined nitrogen seems to become into very important species, which plays an important role on the overall process.

The formation of both significant amounts of ammonium ions by reduction of nitrates and high concentrations of hypochlorite by oxidation of chlorides, is known to take place in this electrochemical system. Hence, the chemical reaction of ammonium ions with hypochlorite through the well-known chemical breakpoint chlorination reaction [23], which involves the formation of chloramines, may explain the negligible concentration of ammonium during both electrolyses. This reaction shows that chloride is recovered after the complete oxidation of nitrogen to gaseous nitrogen (eq. 1). During the process, monochloramine, dichloramine and trichloramine are known to be produced by successive and competitive reactions between these species (Eqs. 2 to 4).
NH₄⁺ + 3HClO → N₂ + 3H₂O + 5H⁺ + 3Cl⁻ \hspace{1cm} (1)

NH₃ + HClO ↔ NH₂Cl + H₂O \hspace{1cm} (2)

NH₂Cl + HClO ↔ NHCl₂ + H₂O \hspace{1cm} (3)

NHCl₂ + HClO ↔ NCl₃ + H₂O \hspace{1cm} (4)

In addition, these chloramines can be further oxidized to produce gaseous nitrogen species (Eqs. 5 to 8), explaining the best results obtained in the case of the electrolyses in chloride medium when compared with the same electrolyses in sulphate-containing solutions. At this point, it is important to state that not only dinitrogen (Eqs. 5 and 6), but also nitrogen oxides (Eqs. 7 and 8) can be formed during this reaction.

4 NH₂Cl + 3 Cl₂ + H₂O → N₂ + N₂O + 10 HCl \hspace{1cm} (5)

NH₂Cl + NHCl₂ → N₂ + 3 HCl \hspace{1cm} (6)

NH₂Cl + NHCl₂ + HOCl → N₂O + 4 HCl \hspace{1cm} (7)

2 NH₂Cl + HOCl → N₂O + 3 HCl \hspace{1cm} (8)

From these results, it is clear that chloride ions have a very significant effect on the electrolytic removal of nitrates. In the supplemental material section, some additional information about the chemical chlorination of ammonium solutions can be found, in order to support the importance of this chlorination reaction, and to provide the data required to understand the results shown in this work for the particular range of concentrations used.
However, experiments shown in Figure 1 and 2 are carried out for very high concentration of chloride (concentrations which practically can only be found in some industrial wastes or in brackish waters). Thus, at this point it is important to know the effect of the chloride concentration on the results, especially if applications for fresh waters or for low conductivity wastewaters are looked for.

Figure 3 shows the influence of chloride concentration on the electrolyses with BDD and DSA-O₂ anodes of nitrate solutions for three different cases including a typical fresh water (300 ppm NaCl, 5.13 mM) and a fresh water with a very low salinity (30 ppm NaCl, 0.51 mM). Furthermore, these results are also compared with fresh water with an important salinity (3000 ppm NaCl, Fig.1). These tests were carried out at neutral pH because, according to literature (also checked in supplementary material), the ratio ClO⁻/NH₄⁺ necessary to transform completely ammonium into nitrogen gas is minimized at pH between 7 and 8 [24]. This pH was controlled by the addition of small amounts of H₂SO₄.

As it can be observed, the concentration of sodium chloride plays an important role on the rate of NO₃⁻ removal and, thus, on the efficiency of this process. There are no significant differences between the results obtained in the electrolyses of typical fresh water and of high-salinity fresh water. On the contrary, marked differences can be found when a very low content of salts is used as supporting electrolyte, suggesting the key role of the concentration of chlorinated species on the removal of nitrates. This behaviour is also checked by the evolution of the total voltage of the electrochemical cell. Thus, total voltage of the cell remains unaltered when passing form 51.3 mM to
5.13 (average voltage of 8 V for BDD and 6 V for DSA), meanwhile it dramatically increases for the experiment carried out at 0.51 mM of NaCl (average voltage of 19.7 V for DSA and 12.8 V for BDD). This increase in voltage is directly related to the decrease in conductivity due to the lower concentration of NaCl, and may be related to the appearance of side reactions which diminish the efficiency and the rate of the process. Likewise, as reported previously for brackish water, anode material does not produce important differences in the rate of removal of nitrates.

Figures 4 and 5 show the speciation of chlorine and nitrogen during the electrolyses of nitrate solutions with 5.13 mM and 0.51 mM of NaCl, when using DSA and BDD as anode materials, respectively.

In the case of the DSA electrolyses, chloride is not completely oxidized to other chlorinated species during the process. Similarly to the electrolyses of the brackish water, a first rapid decrease in the concentration of chloride is observed in both electrolyses and then, the oxidation process of chloride becomes less efficient and a slower and constant oxidation rate is clearly observed. Although hypochlorite and gaseous chlorine are the most relevant species during the initial stages of the electrolyses, formation of chlorates is clearly observed in both cases. Moreover, this species becomes in the final product because the formation of perchlorates is not observed at any time. The smaller the concentration of chlorides, the higher the ratio of chlorates formed for the same current charge applied (although the total concentration is smaller due to the smaller initial concentration of chlorides). This helps to explain that no chlorate was observed in the electrolyses of the brackish water.
At this point, it is important to state that chlorate ions are species typically found in drinking water as they are known to be formed from the decomposition of hypochlorite. This is a well-known disproportionation process [25], promoted during ageing of hypochlorite solutions and summarized in equation (9).

\[ 3 \text{ClO}^- \rightarrow \text{ClO}_3^- + 2 \text{Cl}^- \]  

(9)

This process consists of two consecutive stages (eq 10 and 11), being chlorite an important intermediate. No chlorite was observed in the electrolyses carried out in this work, which can be explained by a promotion in reaction (11) at the conditions used in the electrolyses. Consequently, in conventional disinfection processes with hypochlorite, as the reagent solution ages, the amount of chlorate added to the treated water increases.

\[ 2 \text{ClO}^- \rightarrow \text{ClO}_2^- + \text{Cl}^- \]  

(10)

\[ \text{ClO}^- + \text{ClO}_2^- \rightarrow \text{ClO}_3^- + \text{Cl}^- \]  

(11)

At this point, it is important to point out that the concentration of both gaseous chlorine and chlorate obtained here are high, taking into account the conditions selected in the present work, especially with regard to the value of pH (neutral pH), and compared to other works [26, 27]. The high formation of gaseous chlorine can be explained by gas stripping. The formation of gaseous species produced on the surface of the electrodes may favor the desorption of chlorine and, thus, may shift the reaction of chlorine dissolution (Eq. 12) to the formation of gaseous chlorine.

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{ClO}^- + \text{H}^+ + \text{Cl}^- \]  

(12)
Nevertheless, the observed differences between these results and some of the previously published works may suggest different characteristics for different lots of DSA electrodes, in the same way that it was previously reported for BDD electrodes [28].

There is no regulation in EU for chlorates. Nevertheless, several studies inform about the importance of limit the concentration of this compound in drinking waters, and report that very different values can be found depending on the source of water and on the particular conditions of the treatment. At this point, and taking into account preliminary studies, the provisional guidelines of World Health Organization for chlorate in drinking water is 0.7 mg Cl dm$^{-3}$. This means that, although nowadays there is no regulation against the occurrence of this compound, electrochemical denitrification with DSA may not be a good treatment for drinking water.

Respect to the nitrogen speciation, gaseous nitrogen is clearly the final product, although some nitrites were also found during the treatment in the electrolyses of the water with very low concentration of chloride, suggesting that it is necessary a minimum ratio of chloride/nitrate in order to assure the complete conversion of nitrates into gaseous nitrogen. This also indicates that intermediates found do not differ significantly from those obtained during the electrolyses with sulphate, although the chemical reactivity of the system is completely influenced by the presence of the different chlorinated species, which help to transform nitrate into gaseous nitrogen.
In the case of BDD electrolyses, results are very different and speciation of chlorine shows the complete oxidation of chloride to perchlorates. This is a key difference between DSA and BDD electrodes and it has been previously explained in literature [27] in terms of the occurrence of hydroxyl radicals (Eq. 13), which are reported to be formed in large quantities during electrolyses of aqueous solutions [29]. These radicals can oxidize other compounds in a region close to the anode surface or, in the presence of chlorides, they can oxidize this anion successively to different oxochlorinated compounds (Eq. 14-17). This may explain the occurrence of the perchlorates when using conductive-diamond as anode material, and not with DSA anodes, in which the occurrence of hydroxyl radicals during electrolyses of aqueous solutions is doubtful.

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{OH}^- + \text{H}^+ + e^- \quad (13) \\
\text{Cl}^- + \text{OH}^- & \rightarrow \text{ClO}^- + \text{H}^+ + e^- \quad (14) \\
\text{ClO}^- + \text{OH}^- & \rightarrow \text{ClO}_2^- + \text{H}^+ + e^- \quad (15) \\
\text{ClO}_2^- + \text{OH}^- & \rightarrow \text{ClO}_3^- + \text{H}^+ + e^- \quad (16) \\
\text{ClO}_3^- + \text{OH}^- & \rightarrow \text{ClO}_4^- + \text{H}^+ + e^- \quad (17)
\end{align*}
\]

Although the formation of perchlorate is favored at higher values of pH and higher values of current densities that those used in the present work [27], some works have reported the synthesis of this compound from diluted chloride solutions at neutral pH values (even at acid pHS) [27] and at lower values of current density [26].

The occurrence of perchlorates during the electrolyses of chlorine with diamond electrodes is of a great importance. It means that, initially, this type of electrodes should be avoided for this application [30, 31], at least in conditions in which perchlorates can
be formed, because perchlorates are associated to several serious health problems and even to potential risks to environment.

This particular speciation of chlorine during the electrolyses of nitrates solutions is very important to explain the speciation of nitrogen. Contrarily to DSA-electrolyses, ammonium ions and nitrites appear in a very significant concentration during the electrolyses, being even more important than gaseous nitrogen species. This is just the same behaviour observed in the electrolyses in non-chloride supporting electrolyte and it may be explained in terms of the smaller reactivity of perchlorates, compared to hypochlorite and gaseous chlorine. Thus, although perchlorate is a strong oxidizing agent due to its high redox potential (+1.38 V) [32], its oxidizing power is retarded because of its high activation energy (120 kJ mol$^{-1}$) [33]. Consequently, this compound is not active in the oxidation of ammonia and it is accumulated in the system. In the case of the lowest NaCl concentration and using a DSA anode, the lower conversion of Cl$^-\$ anions lowers the concentration of hypochlorite and, thus, the rate of ammonium oxidation and nitrate reduction. As a consequence, under these conditions both anodes present a similar behavior. The accumulation of nitrites in the case of BDD electrode can be also explained because of the low concentration of hypochlorite generated. Nitrite can be easily oxidized to nitrate by many chemicals, hypochlorite amongst them, so for higher NaCl concentrations nitrite may be qualitatively converted into nitrate.

Finally, the specific power consumption has been calculated. This value is related to the potential application of this technology and it has been defined as the power consumption needed to convert one kg of NO$_3^-$ into gaseous nitrogen. This parameter
has been calculated until a final concentration of 50 ppm of nitrate, the reference value established by the WHO to avoid health risks in drinking water. It can be observed that this consumption is higher in the case of BDD electrodes (681 kWh kg\(^{-1}\) for BDD vs. 481 kWh kg\(^{-1}\) for DSA and 51.3 mM NaCl) and it depends mainly on the selectivity of the process to convert nitrate into gaseous nitrogen. Moreover, the optimal consumption, found for DSA and a NaCl concentration of 5.13 mM, was 386 kWh kg\(^{-1}\) (40.6 kWh m\(^{-3}\)), in the same order than consumption values that can be found in literature for the treatment of waste waters by electrochemical technologies [34,35].

4. Conclusions

From this work, the following conclusions can be drawn:

- Electrolyses of nitrate aqueous solutions containing chlorides anions lead primarily to the formation of gaseous-nitrogen species. Electrochemical formation of hypochlorite and ammonia and the well-known breakpoint chlorination reaction allows explaining this process.

- DSA and BDD electrodes get the same efficiency in the removal of nitrates when NaCl is used as electrolyte, although speciation observed during the electrochemical treatment is different and depend importantly on the initial chloride concentration. There are significant differences in the speciation of chlorine species.

- BDD electrolyses lead to the formation of perchlorate, being this reaction promoted at low concentration of chlorides. This observation advises against the
use of this particular technology for the production of drinking water, due to the hazardous risk associated to this species.

- DSA electrolyses lead to the formation of chlorate but no perchlorate was found when using this material as anode. As a consequence, this process could be potentially used for purposes different from drinking water production, such as water reuse or treatment of industrial wastes. Nevertheless, an accurate study and an economical balance for every single process should be carried out to confirm its applicability.

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References


Figures caption

Figure 1. Influence of supporting electrolyte and the anode material on the variation of nitrate concentration during the electrolysis of 1.76 mM NaNO$_3$ with 51.3mM NaCl (solid points) or 51.3mM Na$_2$SO$_4$ (open points). Experimental conditions: $j=30$mA cm$^{-2}$; acid pH$_0$. Anode: (■,□)BDD, (▲,Δ)DSA.

Figure 2. Percentage of products formed during the electrolysis of 1.76 mM NaNO$_3$. Experimental conditions: anode: (a)BDD, (b)DSA; cathode: SS; $j=30$mA cm$^{-2}$; acid pH$_0$; 51.3mM NaCl; ■ NH$_4^+$ - N; ▲ NC$_3^-$ - N$_{combined}$; ● N gaseous; □ Cl$^-$ - Cl; Δ ClO$^-$ - Cl; ◊ ClO$_3^-$ - Cl; ○ ClO$_4^-$ - Cl; x Cl – gaseous.

Figure 3. Influence of supporting media concentration and anode material on the variation of nitrate molar concentration with respect to electric charge applied during the electrolysis of 1.76 mM NaNO$_3$. Experimental conditions: cathode: SS; supporting media: NaCl; j=30mA cm$^{-2}$; neutral pH; Molar concentration of NaCl: ● 51.3 mM; ■ 5.13 mM; ▲ 0.51 mM; BDD: solid symbols; DSA: open symbols.

Figure 4. Percentage of products formed during the electrolysis of 1.76 mM NaNO$_3$. Experimental conditions: anode: DSA; cathode: SS; $j=30$mA cm$^{-2}$; acid pH$_0$; (a)5.13 mM NaCl, (b)0.51 mM NaCl; ■ NH$_4^+$ - N; ▲ NO$_2^-$; ● N gaseous; □ Cl$^-$ - Cl; Δ ClO$^-$ - Cl; ◊ ClO$_3^-$ - Cl; ○ ClO$_4^-$ - Cl; x Cl – gaseous.

Figure 5. Percentage of products formed during the electrolysis of 1.76 mM NaNO$_3$. Experimental conditions: anode: BDD; cathode: SS; $j=30$mA cm$^{-2}$; acid pH$_0$; (a)5.13 mM NaCl, (b)0.51 mM NaCl; ■ NH$_4^+$ - N; ▲ NO$_2^-$; ● N gaseous; □ Cl$^-$ - Cl; Δ ClO$^-$ - Cl; ◊ ClO$_3^-$ - Cl; ○ ClO$_4^-$ - Cl; x Cl – gaseous.
Figures

![Graph showing the reduction of nitrate concentrations over time](image)

\[
\log\left(\frac{\text{NO}_3^-}{\text{NO}_3^-_0}\right) = -0.0031 \times t
\]

\[
\log\left(\frac{\text{NO}_3^-}{\text{NO}_3^-_0}\right) = -0.0081 \times t
\]

\[
\log\left(\frac{\text{NO}_3^-}{\text{NO}_3^-_0}\right) = -0.0014 \times t
\]

\[
\log\left(\frac{\text{NO}_3^-}{\text{NO}_3^-_0}\right) = -0.0072 \times t
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Figure 2
Figure 3
Figure 4
Figure 5