1 **Electrochemical denitrificacion with chlorides using DSA and**

2 **BDD anodes**

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1 **Abstract**

2 In this work, the electrochemical denitrification of solutions containing chlorides is

3 studied with two different types of anode materials: $O_2$-Dimensionally Stable Anodes

4 (DSA) and Boron Doped Diamond (BDD). First of all, a higher rate of nitrate removal

5 was found when chloride is used as the supporting media, with respect to sulphate.

6 Moreover, it was found that it is necessary a minimum chloride concentration to get an

7 effective treatment and that gaseous-nitrogen is the primary nitrogen species found in

8 the electrolyses. In this process, nitrate is firstly reduced on the cathode surface and next

9 oxidized by the species generated by the anode material. Thus, anode material does not

10 influence on the denitrificacion rate, but it significantly influences on the speciation of

11 chlorine. Furthermore, formation of perchlorates advices against the use of BDD

12 electrochemical denitrification for the production of drinking water. Finally, formation

13 of chlorates in the DSA-electrolyses, due to the ageing of hypochlorite, also limits its

14 use in the production of drinking water, although it does not exclude its use in other

15 applications such as reuse of treated wastewater and treatment of industrial wastes.

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## 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.

1  Another important electrochemical technology is electrolysis. Depending on the anode

2  material, current density, electrolyte concentration and pH, electrolytic reduction of

3  nitrate has been reported to produce ammonium ions, nitrite or different gaseous

4  nitrogen species as the main products [5, 6]. As ammonium is one of the species that are

5  commonly produced, several works have focused on the electrochemical removal of

6  ammonium ions in the presence of chloride, as a consequence of the promotion in the

7  reaction media of the well-known breakpoint chlorination process. This promotion is

8  explained by the anodic formation of hypochlorite and the later combination of this

9  oxidant with ammonia to give different chloramines and gaseous-nitrogen species [7-

10 10]. In those works, the influence of anode material, current density or initial sodium

11 chloride conditions [11-14] has been studied. Thus, the particular working conditions of

12 an electrochemical cell and the influence of these conditions on the removal of

13 ammonium is a topic of the maximum interest.

14

15 In the searching for new applications of the electrochemical technology in the

16 environmental remediation, one additional step is the removal of nitrates using

17 electrolysis or electrochemical denitrification. The presence of chlorine during the

18 electrolytic process of nitrate reduction enhances the breakpoint chlorination reaction,

19 and thus the production of nitrogen gas as the main stable product [15]. At this point,

20 and in spite of the widely studied breakpoint reaction, not many works have dealt about

21 the role of operation conditions and electrode material on the electrochemical

22 denitrification process. Thus, Vanlangendonck et al. [16] determined the optimal

23 operating conditions to reduce the nitrate concentration in wastewaters from power

24 plants, using stainless steel as cathodic material and DSA-$Cl_2$ as anodic material. It was

1   found that a high chloride concentration and a high current density were necessary to

2   convert nitrate into nitrogen gas. Katsounaros and Kyriacou [17] studied the influence

3   of high initial concentrations of nitrates (in chloride medium) during the potentiostatic

4   electrolysis process, using a tin cathode and a platinised Pt foil anode. Li et al. [18]

5   reached the almost complete nitrate conversion to nitrogen gas by using a Cu-Zn

6   cathode and a $Ti/IrO_2$-Pt anode in the presence of sodium chloride as supporting

7   electrolyte. Moreover, Reyter et al. [19] studied the influence of cathode/anode surface

8   area ratio on the efficiency of the conversion of nitrate into nitrogen gas. In addition, it

9   is reported that ammonia oxidation can be enhanced by using BDD or $Ti/PtO_x$-$IrO_2$

10  electrodes if the reaction between active chlorine and ammonia takes place in a reaction

11  zone close to the electrode surface, to reduce the formation of chlorate and perchlorate

12  as by-products [20].

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14  In this context, the main objective of this study is to determine the influence of the

15  anode material on the reduction of nitrate, containing sodium chloride as supporting

16  electrolyte. Previous works of our group characterised the electrolysis in non-chloride

17  media, where the breakpoint chlorination does not occur, and they drew very important

18  conclusions in terms of speciation of nitrogen. In the present work, two different anode

19  materials have been used: $O_2$-dimensionally stable (DSA) and Boron Doped Diamond

20  (BDD) anodes because they correspond to two limit behaviour in oxidation processes.

21  As cathode, and taking into account the results of a previous study [6], stainless steel

22  (AISI 304) was proposed. Likewise, the influence of the concentration of sodium

23  chloride on the process performance (ranging from the typical concentrations of very

1      fresh water to almost brackish water) has been studied, in order to determine the

2      optimum conditions to obtain nitrogen gas as the main final product.

3

4      **2. Experimental**

5      *2.1. Analytical procedure*

6      Nitrogen and chloride inorganic anions ($NO_3^-$, $NO_2^-$, $Cl^-$, $ClO^-$, $ClO_2^-$, $ClO_3^-$, $ClO_4^-$)

7      were measured by ion chromatography using Shimadzu LC-20A equipment (column,

8      Shodex IC I-524A; mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, 1.0 ml min$^-$

9      $^1$). In the case of hypochlorite, its peak interferes with the chloride one; therefore, the

10     determination was carried out by titration with $As_2O_3$ in NaOH 2 M. The same ion

11     chromatography equipment (column, Shodex IC YK-421; mobile phase, 5.0 mM

12     tartaric, 1.0 mM dipicolinic acid and 24.3 mM boric acid; flow rate, 1.0 ml min$^{-1}$) was

13     used to measure the nitrogen inorganic cation ($NH_4^+$). Inorganic chloramines have been

14     measured following the DPD standard method described in literature [21]. The

15     concentration of gaseous species of nitrogen and chlorine were quantified by mass

16     balance. The generation of $NH_3$ was discarded as the gases produced within the tests

17     were conducted through a $H_2SO_4$ trap and no $NH_4^+$ was found in any of the tests.

18

19     *2.2. Electrochemical cell*

20     The electrolysis of nitrogen was carried out in a single-compartment electrochemical

21     flow cell described elsewhere [22]. Boron Doped Diamond (BDD) and dimensionally

22     stable anodes (DSA) were used as anode materials and stainless steel (AISI 304) as

23     cathode material. BDD anodes were supplied by Adamant, Switzerland, (Si substrate; 1

24     mm thickness; 100 mΩ cm resistivity; 500 ppm boron concentration; 1.53 μm CDE-

1  film thickness; 115 CDE-film Raman $sp_3/sp_2$). DSA anodes (supplied by DeNora, Italy)

2  were DSA-$O_2$ type and used a with $IrO_2$ and $RuO_2$ cover. Electrodes had a geometric

3  area of 78 cm$^2$ each one and an electrode gap of 9 mm. The electrolyte was stored in a

4  glass tank (500 ml) and circulated through the electrolytic cell by means of a peristaltic

5  pump. A heat exchanger was used to maintain the temperature at the desired set point.

6

7  *2.3. Experimental procedure*

8  Bench scale electrolyses of 0.60 dm$^3$ of synthetic wastewater were carried out under

9  galvanostatic conditions (30 mA cm$^{-2}$). The concentration of $NaNO_3$ was 1.76 mN and

10  NaCl was used as supporting electrolyte with concentrations ranging from 0.51 to 51.3

11  mM. The cell voltage did not vary during each electrolyses significantly, indicating that

12  appreciable deterioration of electrode or passivation phenomena did not take place. The

13  electrolyte flow rate through the cell was 1.5 dm$^3$ min$^{-1}$. A heat exchanger coupled with

14  a controlled thermostatic bath (Digiterm 100, JP Selecta) was used to maintain the

15  temperature at the desired set point (25 °C).

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17  **3. Results and discussion**

18

19  Figure 1 shows the effect of the electrolyte anion (sulphate or chloride) and of the anode

20  material (DSA or BDD) on the removal of nitrates from aqueous solution in a single

21  compartment electrochemical cell, when a high concentration of electrolyte salt is added

22  to the target solution (simulating a brackish water containing nitrates). These tests were

23  carried out at an initial pH of 2, in order to compare the results obtained with chloride

1   with a previous work carried out with sulphate [6]. This figure also shows the values of

2   the calculated rate of nitrate removal.

3

4   As it can be observed, a huge influence of the anode material on the process

5   performance is observed when sulphate is used as supporting electrolyte, being the

6   BDD much more efficient than the DSA-$O_2$ electrode. Initially, this behavior is difficult

7   to explain, because the removal of nitrates to gaseous-nitrogen species is a reduction

8   process. However, this observation was explained in a previous work [6] in terms of the

9   important role of electro-generated species in the overall reactivity of the system,

10  specifically, in terms of the occurrence of peroxosulphates, which easily decompose to

11  hydrogen peroxide. This hydrogen peroxide reacts with nitrites (generated from the

12  reduction of nitrates) to give gaseous nitrogen species. At this point, it is important to

13  point out that nitrite becomes in a key compound to explain the electrolytic removal of

14  nitrates in sulphate medium. Nevertheless, ammonium ions and nitric oxide were also

15  found as significant species involved in the electrolysis with both anode materials [6].

16

17  In the case of chloride-containing solutions, differences obtained in the electrolyses with

18  both anodes become smaller, being the efficiencies obtained with both anode materials

19  closer between them and higher than those obtained in sulphate medium, even with

20  BDD. This behavior can be also observed in the value of the rates of nitrate removal,

21  which have been added in Figure 1. As it can be observed, the rates of nitrate removal

22  obtained with both electrodes are quite similar when chloride is used as electrolyte, and

23  considerably higher than those obtained in sulphate medium. In addition, the

24  exponential decay of the concentration of nitrates, observed in the electrolyses of nitrate

1  solutions with sulphate as supporting electrolyte, turns into an almost linear trend when

2  chloride is used as supporting electrolyte. This suggests that kinetic order (respect to the

3  nitrates) changes from a first order kinetic (which can be explained by a mass transfer

4  and/or mediated oxidation control of the reaction rate) to a zero-order, which can only

5  be explained assuming a key effect of the chloride concentration on the kinetics of the

6  process.

7

8  To clarify this point, Figure 2 shows the products speciation during the same

9  electrolyses with BDD (Fig. 2.a) and DSA (Fig. 2.b), of nitrate solutions containing

10  NaCl as supporting electrode. As it is explained in section 2.1, the quantification of

11  gaseous species of chlorine and nitrogen were carried out by mass balance, the same

12  method used in our previous study with sulphate ions [6]. Although this method of

13  quantification can originate some experimental errors, its accuracy is high enough to

14  evaluate the influence of the anode material and the nature of the anions present in the

15  target effluent. Moreover, the occurrence of other nitrogen, which has been reported in

16  literature, such as hydroxylamine, Angeli's salt, azide, hydrazine or hyponitrite [17], has

17  been checked in every sample with nil results.

18

19  Very important differences are observed between both electrolyses in terms of the

20  speciation of chlorine. Oxidation of chlorides is very effective in the case of BDD, and

21  it leads to a very significant production of gaseous-chlorine and to a smaller formation

22  of hypochlorite, which clearly behaves as an intermediate and almost disappears for

23  large applied currents, and chlorates, which behaves as a final product, as no perchlorate

24  was detected in the reaction system. Removal of chloride is almost complete at the end

1    of the electrolyses (for applied currents larger than 30 Ah dm$^{-3}$). Conversely, in the

2    electrolyses with DSA-O$_2$, chloride concentration decreases rapidly during the very first

3    moments of the electrolyses, and then, it starts decreasing at a significantly smaller rate.

4    Consequently, at large applied currents (30 Ah dm$^{-3}$) merely 20% of the initial chloride

5    was transformed into other species, being gaseous-chlorine and hypochlorite the most

6    significant species, although it is also important to mark that some chlorate (in very

7    small concentrations) was also detected at large current applied.

8

9    With regard to the speciation of nitrogen, gaseous nitrogen species are the most

10   significant species in both electrolyses, reaching almost 90% conversion in the case of

11   BDD and 75% in the case of DSA-O$_2$. The concentration of ammonium and nitrite ions,

12   which are the most significant species in the electrolyses of sulphate-containing

13   solutions, is negligible. Moreover, combined nitrogen seems to become into very

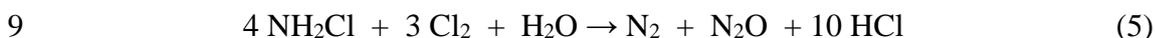14   important species, which plays an important role on the overall process.

15

16   The formation of both significant amounts of ammonium ions by reduction of nitrates

17   and high concentrations of hypochlorite by oxidation of chlorides, is known to take

18   place in this electrochemical system. Hence, the chemical reaction of ammonium ions

19   with hypochlorite through the well-known chemical breakpoint chlorination reaction

20   [23], which involves the formation of chloramines, may explain the negligible

21   concentration of ammonium during both electrolyses. This reaction shows that chloride

22   is recovered after the complete oxidation of nitrogen to gaseous nitrogen (eq. 1). During

23   the process, monochloramine, dichloramine and trichloramine are known to be

24   produced by successive and competitive reactions between these species (Eqs. 2 to 4).

1 $$NH_4^+ + 3HClO \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \tag{1}$$

$$NH_3 + HClO \leftrightarrow NH_2Cl + H_2O \tag{2}$$

$$NH_2Cl + HClO \leftrightarrow NHCl_2 + H_2O \tag{3}$$

$$NHCl_2 + HClO \leftrightarrow NCl_3 + H_2O \tag{4}$$

2

3  In addition, these chloramines can be further oxidized to produce gaseous nitrogen

4  species (Eqs. 5 to 8), explaining the best results obtained in the case of the electrolyses

5  in chloride medium when compared with the same electrolyses in sulphate-containing

6  solutions. At this point, it is important to state that not only dinitrogen (Eqs. 5 and 6),

7  but also nitrogen oxides (Eqs. 7 and 8) can be formed during this reaction.

8

9  $$4\ NH_2Cl + 3\ Cl_2 + H_2O \rightarrow N_2 + N_2O + 10\ HCl \tag{5}$$

10  $$NH_2Cl + NHCl_2 \rightarrow N_2 + 3\ HCl \tag{6}$$

11  $$NH_2Cl + NHCl_2 + HOCl \rightarrow N_2O + 4\ HCl \tag{7}$$

12  $$2\ NH_2Cl + HOCl \rightarrow N_2O + 3\ HCl \tag{8}$$

13

14  From these results, it is clear that chloride ions have a very significant effect on the

15  electrolytic removal of nitrates. In the supplemental material section, some additional

16  information about the chemical chlorination of ammonium solutions can be found, in

17  order to support the importance of this chlorination reaction, and to provide the data

18  required to understand the results shown in this work for the particular range of

19  concentrations used.

20

1    However, experiments shown in Figure 1 and 2 are carried out for very high

2    concentration of chloride (concentrations which practically can only be found in some

3    industrial wastes or in brackish waters). Thus, at this point it is important to know the

4    effect of the chloride concentration on the results, especially if applications for fresh

5    waters or for low conductivity wastewaters are looked for.

6

7    Figure 3 shows the influence of chloride concentration on the electrolyses with BDD

8    and DSA-$O_2$ anodes of nitrate solutions for three different cases including a typical

9    fresh water (300 ppm NaCl, 5.13 mM) and a fresh water with a very low salinity (30

10   ppm NaCl, 0.51 mM). Furthermore, these results are also compared with fresh water

11   with an important salinity (3000 ppm NaCl, Fig.1). These tests were carried out at

12   neutral pH because, according to literature (also checked in supplementary material),

13   the ratio $ClO^-/NH_4^+$ necessary to transform completely ammonium into nitrogen gas is

14   minimized at pH between 7 and 8 [24]. This pH was controlled by the addition of small

15   amounts of $H_2SO_4$.

16

17   As it can be observed, the concentration of sodium chloride plays an important role on

18   the rate of $NO_3^-$ removal and, thus, on the efficiency of this process. There are no

19   significant differences between the results obtained in the electrolyses of typical fresh

20   water and of high-salinity fresh water. On the contrary, marked differences can be found

21   when a very low content of salts is used as supporting electrolyte, suggesting the key

22   role of the concentration of chlorinated species on the removal of nitrates. This

23   behaviour is also checked by the evolution of the total voltage of the electrochemical

24   cell. Thus, total voltage of the cell remains unaltered when passing form 51.3 mM to

1  5.13 (average voltage of 8 V for BDD and 6 V for DSA), meanwhile it dramatically

2  increases for the experiment carried out at 0.51 mM of NaCl (average voltage of 19.7 V

3  for DSA and 12.8 V for BDD). This increase in voltage is directly related to the

4  decrease in conductivity due to the lower concentration of NaCl, and may be related to

5  the appearance of side reactions which diminish the efficiency and the rate of the

6  process. Likewise, as reported previously for brackish water, anode material does not

7  produce important differences in the rate of removal of nitrates.

8

9  Figures 4 and 5 show the speciation of chlorine and nitrogen during the electrolyses of

10  nitrate solutions with 5.13 mM and 0.51 mM of NaCl, when using DSA and BDD as

11  anode materials, respectively.

12

13  In the case of the DSA electrolyses, chloride is not completely oxidized to other

14  chlorinated species during the process. Similarly to the electrolyses of the brackish

15  water, a first rapid decrease in the concentration of chloride is observed in both

16  electrolyses and then, the oxidation process of chloride becomes less efficient and a

17  slower and constant oxidation rate is clearly observed. Although hypochlorite and

18  gaseous chlorine are the most relevant species during the initial stages of the

19  electrolyses, formation of chlorates is clearly observed in both cases. Moreover, this

20  species becomes in the final product because the formation of perchlorates is not

21  observed at any time. The smaller the concentration of chlorides, the higher the ratio of

22  chlorates formed for the same current charge applied (although the total concentration is

23  smaller due to the smaller initial concentration of chlorides). This helps to explain that

24  no chlorate was observed in the electrolyses of the brackish water.

1

2  At this point, it is important to state that chlorate ions are species typically found in

3  drinking water as they are known to be formed from the decomposition of hypochlorite.

4  This is a well-known disproportionation process [25], promoted during ageing of

5  hypochlorite solutions and summarized in equation (9).

6  $$3\ ClO^- \rightarrow ClO_3^- + 2\ Cl^- \qquad (9)$$
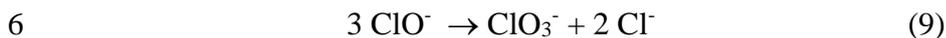
7  This process consists of two consecutive stages (eq 10 and 11), being chlorite an

8  important intermediate. No chlorite was observed in the electrolyses carried out in this

9  work, which can be explained by a promotion in reaction (11) at the conditions used in

10  the electrolyses. Consequently, in conventional disinfection processes with

11  hypochlorite, as the reagent solution ages, the amount of chlorate added to the treated

12  water increases.

13  $$2\ ClO^- \rightarrow ClO_2^- + Cl^- \qquad (10)$$

14  $$ClO^- + ClO_2^- \rightarrow ClO_3^- + Cl^- \qquad (11)$$

15

16  At this point, it is important to point out that the concentration of both gaseous chlorine

17  and chlorate obtained here are high, taking into account the conditions selected in the

18  present work, especially with regard to the value of pH (neutral pH), and compared to

19  other works [26, 27]. The high formation of gaseous chlorine can be explained by gas

20  stripping. The formation of gaseous species produced on the surface of the electrodes

21  may favor the desorption of chlorine and, thus, may shift the reaction of chlorine

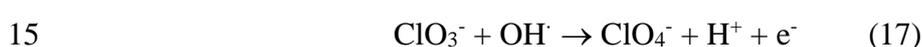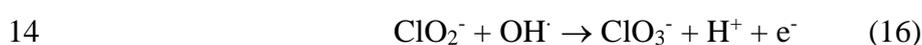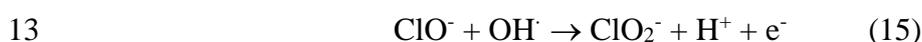22  dissolution (Eq. 12) to the formation of gaseous chlorine.

23

24  $$Cl_2 + H_2O \rightarrow ClO^- + H^+ + Cl^- \qquad (12)$$

1

2    Nevertheless, the observed differences between these results and some of the previously

3    published works may suggest different characteristics for different lots of DSA

4    electrodes, in the same way that it was previously reported for BDD electrodes [28].

5

6    There is no regulation in EU for chlorates. Nevertheless, several studies inform about

7    the importance of limit the concentration of this compound in drinking waters, and

8    report  that very different values can be found depending on the source of water and on

9    the particular conditions of the treatment. At this point, and taking into account

10    preliminary studies, the provisional guidelines of World Health Organization for

11    chlorate in drinking water is 0.7 mg Cl dm$^{-3}$. This means that, although nowadays there

12    is no regulation against the occurrence of this compound, electrochemical

13    denitrificacion with DSA may not be a good treatment for drinking water.

14

15    Respect to the nitrogen speciation, gaseous nitrogen is clearly the final product,

16    although some nitrites were also found during the treatment in the electrolyses of the

17    water with very low concentration of chloride, suggesting that it is necessary a

18    minimum ratio of chloride/nitrate in order to assure the complete conversion of nitrates

19    into gaseous nitrogen. This also indicates that intermediates found do not differ

20    significantly from those obtained during the electrolyses with sulphate, although the

21    chemical reactivity of the system is completely influenced by the presence of the

22    different chlorinated species, which help to transform nitrate into gaseous nitrogen.

23

1    In the case of BDD electrolyses, results are very different and speciation of chlorine

2    shows the complete oxidation of chloride to perchlorates. This is a key difference

3    between DSA and BDD electrodes and it has been previously explained in literature

4    [27] in terms of the occurrence of hydroxyl radicals (Eq. 13), which are reported to be

5    formed in large quantities during electrolyses of aqueous solutions [29]. These radicals

6    can oxidize other compounds in a region close to the anode surface or, in the presence

7    of chlorides, they can oxidize this anion successively to different oxochlorinated

8    compounds (Eq. 14-17). This may explain the occurrence of the perchlorates when

9    using conductive-diamond as anode material, and not with DSA anodes, in which the

10   occurrence of hydroxyl radicals during electrolyses of aqueous solutions is doubtful.

11   $$H_2O \rightarrow OH\cdot + H^+ + e^- \qquad (13)$$

12   $$Cl^- + OH\cdot \rightarrow ClO^- + H^+ + e^- \qquad (14)$$

13   $$ClO^- + OH\cdot \rightarrow ClO_2^- + H^+ + e^- \qquad (15)$$

14   $$ClO_2^- + OH\cdot \rightarrow ClO_3^- + H^+ + e^- \qquad (16)$$

15   $$ClO_3^- + OH\cdot \rightarrow ClO_4^- + H^+ + e^- \qquad (17)$$

16

17   Although the formation of perchlorate is favored at higher values of pH and higher

18   values of current densities that those used in the present work [27], some works have

19   reported the synthesis of this compound from diluted chloride solutions at neutral pH

20   values (even at acid pHs) [27] and at lower values of current density [26].

21

22   The occurrence of perchlorates during the electrolyses of chlorine with diamond

23   electrodes is of a great importance. It means that, initially, this type of electrodes should

24   be avoided for this application [30, 31], at least in conditions in which perchlorates can

1 be formed, because perchlorates are associated to several serious health problems and

2 even to potential risks to environment.

3

4 This particular speciation of chlorine during the electrolyses of nitrates solutions is very

5 important to explain the speciation of nitrogen. Contrarily to DSA-electrolyses,

6 ammonium ions and nitrites appear in a very significant concentration during the

7 electrolyses, being even more important than gaseous nitrogen species. This is just the

8 same behaviour observed in the electrolyses in non-chloride supporting electrolyte and

9 it may be explained in terms of the smaller reactivity of perchlorates, compared to

10 hypochlorite and gaseous chlorine. Thus, although perchlorate is a strong oxidizing

11 agent due to its high redox potential (+1.38 V) [32], its oxidizing power is retarded

12 because of its high activation energy (120 kJ mol$^{-1}$) [33]. Consequently, this compound

13 is not active in the oxidation of ammonia and it is accumulated in the system. In the case

14 of the lowest NaCl concentration and using a DSA anode, the lower conversion of Cl$^-$

15 anions lowers the concentration of hypochlorite and, thus, the rate of ammonium

16 oxidation and nitrate reduction. As a consequence, under these conditions both anodes

17 present a similar behavior. The accumulation of nitrites in the case of BDD electrode

18 can be also explained because of the low concentration of hypochlorite generated.

19 Nitrite can be easily oxidized to nitrate by many chemicals, hypochlorite amongst them,

20 so for higher NaCl concentrations nitrite may be qualitatively converted into nitrate.

21

22 Finally, the specific power consumption has been calculated. This value is related to the

23 potential application of this technology and it has been defined as the power

24 consumption needed to convert one kg of NO$_3^-$ into gaseous nitrogen. This parameter

1    has been calculated until a final concentration of 50 ppm of nitrate, the reference value

2    established by the WHO to avoid health risks in drinking water. It can be observed that

3    this consumption is higher in the case of BDD electrodes (681 kWh kg$^{-1}$ for BDD vs.

4    481 kWh kg$^{-1}$ for DSA and 51.3 mM NaCl) and it depends mainly on the selectivity of

5    the process to convert nitrate into gaseous nitrogen. Moreover, the optimal

6    consumption, found for DSA and a NaCl concentration of 5.13 mM, was 386 kWh kg$^{-1}$

7    (40.6 kWh m$^{-3}$), in the same order than consumption values that can be found in

8    literature for the treatment of waste waters by electrochemical technologies [34,35].

9

10    **4. Conclusions**

11

12    From this work, the following conclusions can be drawn:

13    - Electrolyses of nitrate aqueous solutions containing chlorides anions lead

14      primarily to the formation of gaseous-nitrogen species. Electrochemical

15      formation of hypochlorite and ammonia and the well-known breakpoint

16      chlorination reaction allows explaining this process.

17    - DSA and BDD electrodes get the same efficiency in the removal of nitrates

18      when NaCl is used as electrolyte, although speciation observed during the

19      electrochemical treatment is different and depend importantly on the initial

20      chloride concentration. There are significant differences in the speciation of

21      chlorine species.

22    - BDD electrolyses lead to the formation of perchlorate, being this reaction

23      promoted at low concentration of chlorides. This observation advises against the

1     use of this particular technology for the production of drinking water, due to the

2     hazardous risk associated to this species.

3     -   DSA electrolyses lead to the formation of chlorate but no perchlorate was found

4     when using this material as anode. As a consequence, this process could be

5     potentially used for purposes different from drinking water production, such as

6     water reuse or treatment of industrial wastes. Nevertheless, an accurate study

7     and an economical balance for every single process should be carried out to

8     confirm its applicability.

9

14  **References**

15  [1] S. Ghafari, M. Hasan, M.K. Aroua, Bio-electrochemical removal of nitrate from

16  water and wastewater-a review, Bioresour. Technol. 99 (2007) 3965-3974.

17  [2] S. Samatya, N. Kabay, Ü. Yüksel, M. Arda, M. Yüksel, Removal of nitrate from

18  aqueous solution by nitrate selective ion exchange resins, React. Funct. Polym. 66

19  (2006) 1206-1214.

20  [3] M.I. Aguilar, J. Sáez, M. Lloréns, A. Soler, J.F. Ortuño, Nutrient removal and

21  sludge production in the coagulation–flocculation process, Water Res. 36 (2002) 2910–

22  2919.

1  [4] E. Lacasa, P. Cañizares, C. Sáez, F. J. Fernández, M. A. Rodrigo, Removal of

2  nitrates from groundwater by Electrocoagulation, Chem. Eng. J., In press (2011),

3  DOI:10.1016/j.cej.2011.04.053.

4  [5] R. Tenne, K. Patel, K. Hashimoto, A. Fujishima, Efficient electrochemical reduction

5  of nitrate to ammonia using conductive diamond film electrodes, J. electroanal. Chem.

6  347 (1993) 409-415.

7  [6] E. Lacasa, P. Cañizares, J. Llanos and M.A. Rodrigo, Removal of nitrates by

8  electrolysis in non chloride media. Effect of the anode material, Sep. Purif. Technol. 80

9  (3) (2011) 592-599.

10  [7] T.A. Pressley, D.F. Bishop, S.G. Roan, Ammonia-nitrogen removal by breakpoint

11  chlorination, Environ. Sci. Technol. 6 (1972) 622-628.

12   [8] A. Cabeza, A. Urtiaga, M-J. Rivero, I. Ortiz, Ammonium removal from landfill

13  leachate by anodic oxidation, J. Hazard. Mater. 144 (2007) 715-719.

14  [9] Y. Liu, L. Li, R. Goel, Kinetic study of electrolytic ammonia removal using $Ti/IrO_2$

15  as anode under different experimental conditions, J. Hazard. Mater. 167 (2009) 959-

16  965.

17  [10] A. Kapalka, A. Katsaounis, N.L. Michels, A. Leonidova, S. Souentie, Ch.

18  Comninellis, K.M. Udert, Ammonia oxidation to nitrogen mediated by electrogenerated

19  active chlorine on Ti/PtOx-IrO2, Electrochem. Commun. 12 (2010) 1203-1205.

20  [11] K.W. Kim, Y.J. Kim, I.T. Kim, G.I. Park, E.H. Lee, The electrolytic decomposition

21  mechanism of ammonia to nitrogen at an IrO2 anode, Electrochim. Acta 50 (2005)

22  4356-4364.

[12] Y. Liu, L. Li, R. Goel, Kinetic study of electrolytic ammonia removal using Ti/IrO2 as anode under different experimental conditions, J. Hazard. Mater. 167 (2009) 959-965.

[13] A. Cabeza, A. Urtiaga, M-J. Rivero, I. Ortiz, Ammonium removal from landfill leachate by anodic oxidation, J. Hazard. Mater. 144 (2007) 715-719.

[14] V. Díaz, R. Ibáñez, P. Gómez, A.M. Urtiaga, I. Ortiz, Kinetics of electro-oxidation of ammonia-N, nitrites and COD from a recirculating aquaculture saline water system using BDD anodes, Water Res. 45 (2011) 125-134.

[15] M. Li, C. Feng, Z. Zhang, N. Sugiura, Efficient electrochemical reduction of nitrate to nitrogen using Ti/IrO2-Pt anode and different cathodes, Electrochim. Acta 54 (2009) 4600-4606.

[16] Y. Vanlangendonck, D. Corbisier, A.V. Lierde, Influence of operating conditions on the ammonia electro-oxidation rate in wastewaters from power plants (ELONITATM technique), Water Res. 39 (2005) 3028-3034.

[17] I. Katsounaros, G. Kyriacou, Influence of nitrate concentration on its electrochemical reduction on tin cathode: Identification of reaction intermediates, Electrochim. Acta 53 (2008) 5477-5484.

[18] M. Li, C. Feng, Z. Zhang, X. Lei, R. Chen, Y. Yang, N. Sugiura, Simultaneous reduction of nitrate and oxidation of by-products using electrochemical method, J. Hazard. Mat. 171 (2009) 724-730.

[19] D. Reyter, D. Bélanger, L. Roué, Nitrate removal by a paired electrolysis on copper and Ti/IrO2 coupled electrodes-Influence of the anode/cathode surface area ratio, Water Res. 44 (2010) 1918-1926.

[20] A. Kapalka, L. Joss, A. Anglada, Ch. Comninellis, K.M. Udert, Direct and mediated electrochemical oxidation of ammonia on boron-doped diamond electrode, Electrochem. Commun. 12 (2010) 1714-1717.

[21] APHA-AWWA-WPCF, Standard Methods for the Examination of Water and Wastewater. (L.S. Clesceri, et al., eds.) 17th ed. American Public Health Association, Washington, DC. (1989)

[22] P. Cañizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Sáez, Electrochemical oxidation of phenolic wastes with boron-doped diamond anodes, Water Res. 39 (2005) 2687-2703.

[23] W.J. Eilbeck, Redox control in breakpoint chlorination of ammonia and metal ammine complexes, Water Res. 18 (1984) 21-24.

[24] G.C. White, The Handbook of Chlorination and Alternative Disinfectants, fourth edition, John Wiley & Sons, Inc. (US) (1999).

[25] M. Bolyard, P. Snyder Falr., Occurrence of Chlorate in Hypochlorite Solutions Used for Drinking Water Disinfection, Environ. Sci. Technol. 26(8) (1992) 1663-1665.

[26] A. M. Polcaro, A. Vacca, M. Mascia, F. Ferrara, Product and by-product formation in electrolysis of dilute chloride solutions, J. Appl. Electrochem. 38 (2008) 979-984.

[27] A. Sánchez-Carretero, C.Sáez, P. Cañizares, M.A. Rodrigo. Electrochemical Production of Perchlorates using Conductive Diamond Electrolyses. Chem. Eng. J. 166(2) (2011) 710-714.

[28] P. Canizares, C. Sáez, F. Martínez, M. A. Rodrigo, The role of the characteristics of p-si BDD anodes on the efficiency of wastewater electro-oxidation processes, Electrochem. Solid State Lett. 11, (7) (2008) E15-E19

1   [29] P. Cañizares, C. Sáez, A. Sánchez-Carretero, M.A. Rodrigo, Synthesis of novel

2   oxidants by electrochemical technology, J. Appl. Electrochem. 39 (2009) 2143-2149.

3   [30] M.E.H. Bergmann, J. Rollin, T. Iourtchouk, The occurrence of perchlorate during

4   drinking water electrolysis using BDD anodes, Electrochim. Acta 54 (2009) 2102-2107.

5   [31] M.E.H. Bergmann, J. Rollin, Product and by-product formation in laboratory

6   studies on disinfection electrolysis of water using boron-doped diamond anodes, Catal.

7   Today 124 (2007) 198-203.

8   [32] J.H. Espenson, The problem and perversity of perchlorate. In: E.T. Urbansky,

9   Editor, Perchlorate in the Environment, Kluwer Academic/Plenum, New York (2000),

10  pp. 1–7.

11  [33] B. Gu, W. Dong, G.M. Brown and D.R. Cole, Environ. Sci. Technol. 37 (2003),

12  pp. 2291–2295.

13  [34] P. Cañizares, R. Paz, C. Sáez, M. A. Rodrigo, Costs of the electrochemical

14  oxidation of wastewaters: A comparison with ozonation and fenton oxidation processes.

15  J. Environ. Manage., 90(1) (2009) 410-420.

16  [35] M. A. Rodrigo, P. Cañizares, A. Sánchez-Carretero, C. Sáez, Use of conductive-

17  diamond electrochemical oxidation for wastewater treatment, Catalysis Today 151, (1-

18  2) (2010) 173-177.

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2 **Figures caption**

3 Figure 1. Influence of supporting electrolyte and the anode material on the variation of
4 nitrate concentration during the electrolysis of 1.76 mM $NaNO_3$ with 51.3mM NaCl
5 (solid points) or 51.3mM $Na_2SO_4$ (open points). Experimental conditions: j=30mA $cm^{-2}$;
6 acid $pH_0$. Anode: (■,□)BDD, (▲,Δ)DSA.

7

8 Figure 2. Percentage of products formed during the electrolysis of 1.76 mM $NaNO_3$.
9 Experimental conditions: anode: (a)BDD, (b)DSA; cathode: SS; j=30mA $cm^{-2}$; acid
10 $pH_0$; 51.3mM NaCl; ■ $NH_4^+$ - N; ▲ $NCl_3$ - $N_{combined}$; ● N gaseous; □ $Cl^-$ - Cl; Δ $ClO^-$ -
11 Cl; ◊ $ClO_3^-$ - Cl; ○ $ClO_4^-$ - Cl; x Cl – gaseous.

12

13 Figure 3. Influence of supporting media concentration and anode material on the
14 variation of nitrate molar concentration with respect to electric charge applied during
15 the electrolysis of 1.76 mM $NaNO_3$. Experimental conditions: cathode: SS; supporting
16 media: NaCl; j=30mA $cm^{-2}$; neutral pH; Molar concentration of NaCl: ● 51.3 mM; ■
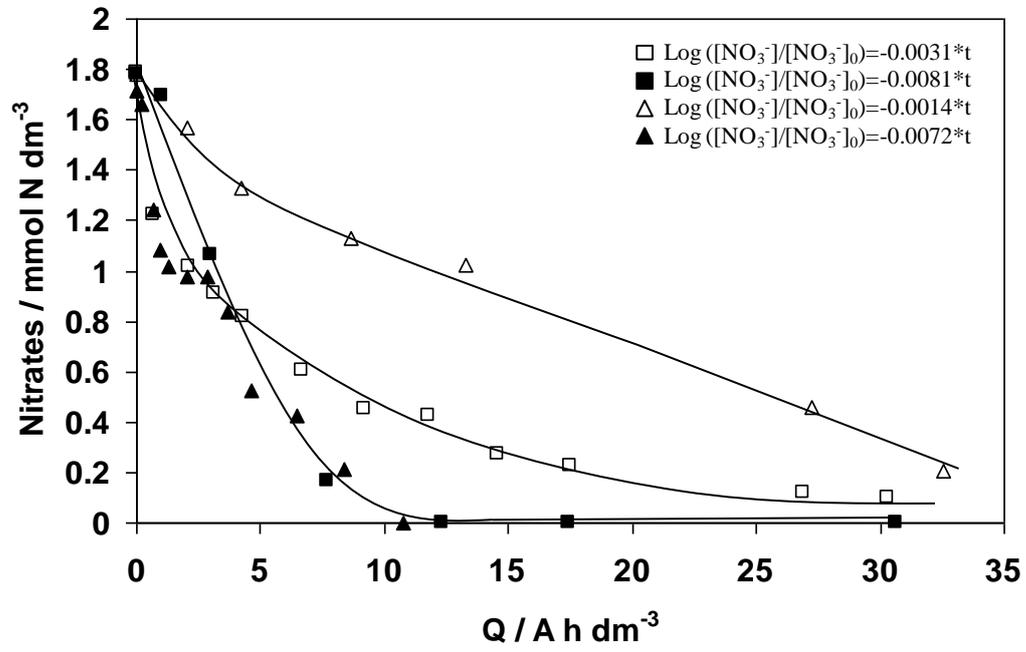17 5.13 mM; ▲ 0.51 mM; BDD: solid symbols; DSA: open symbols.

18

19 Figure 4. Percentage of products formed during the electrolysis of 1.76 mM $NaNO_3$.
20 Experimental conditions: anode: DSA; cathode: SS; j=30mA $cm^{-2}$; acid $pH_0$; (a)5.13
21 mM NaCl, (b)0.51 mM NaCl; ■ $NH_4^+$ - N; ▲ $NO_2^-$; ● N gaseous; □ $Cl^-$ - Cl; Δ $ClO^-$ -
22 Cl; ◊ $ClO_3^-$ - Cl; ○ $ClO_4^-$ - Cl; x Cl – gaseous.

23

24 Figure 5. Percentage of products formed during the electrolysis of 1.76 mM $NaNO_3$.
25 Experimental conditions: anode: BDD; cathode: SS; j=30mA $cm^{-2}$; acid $pH_0$; (a)5.13
26 mM NaCl, (b)0.51 mM NaCl; ■ $NH_4^+$ - N; ▲ $NO_2^-$; ● N gaseous; □ $Cl^-$ - Cl; Δ $ClO^-$ -
27 Cl; ◊ $ClO_3^-$ - Cl; ○ $ClO_4^-$ - Cl; x Cl – gaseous.

28

29

1    **Figures**

2



Legend (from plot):
- □ Log $([NO_3^-]/[NO_3^-]_0) = -0.0031*t$
- ■ Log $([NO_3^-]/[NO_3^-]_0) = -0.0081*t$
- △ Log $([NO_3^-]/[NO_3^-]_0) = -0.0014*t$
- ▲ Log $([NO_3^-]/[NO_3^-]_0) = -0.0072*t$
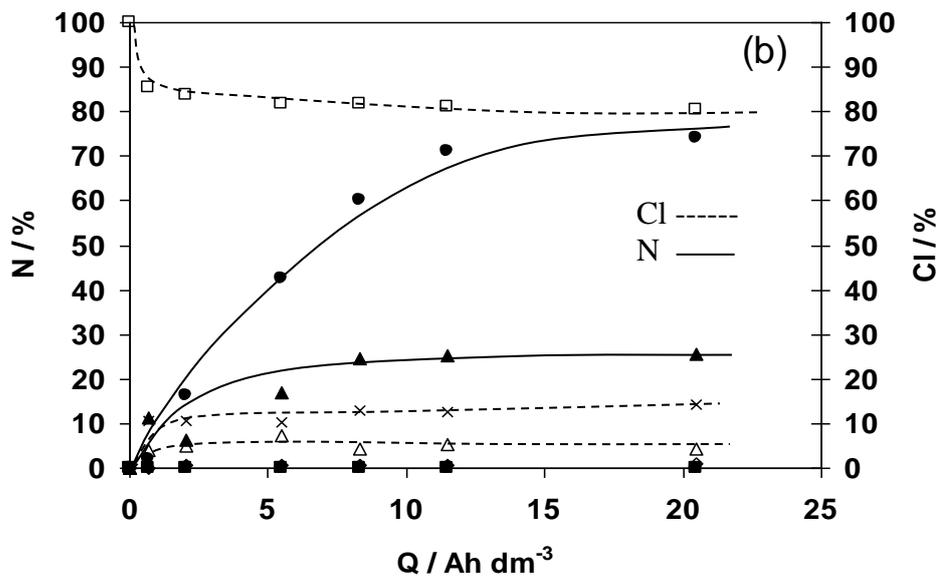
Y-axis: Nitrates / mmol N dm$^{-3}$
X-axis: Q / A h dm$^{-3}$

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4    **Figure 1**

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4    Figure 2

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Figure 3 legend:
- ○ $\log([NO_3^-]/[NO_3^-]_0) = -0.0072 \cdot t$
- ● $\log([NO_3^-]/[NO_3^-]_0) = -0.0081 \cdot t$
- □ $\log([NO_3^-]/[NO_3^-]_0) = -0.0075 \cdot t$
- ■ $\log([NO_3^-]/[NO_3^-]_0) = -0.0021 \cdot t$
- △ $\log([NO_3^-]/[NO_3^-]_0) = -0.0005 \cdot t$
- ▲ $\log([NO_3^-]/[NO_3^-]_0) = -0.0005 \cdot t$
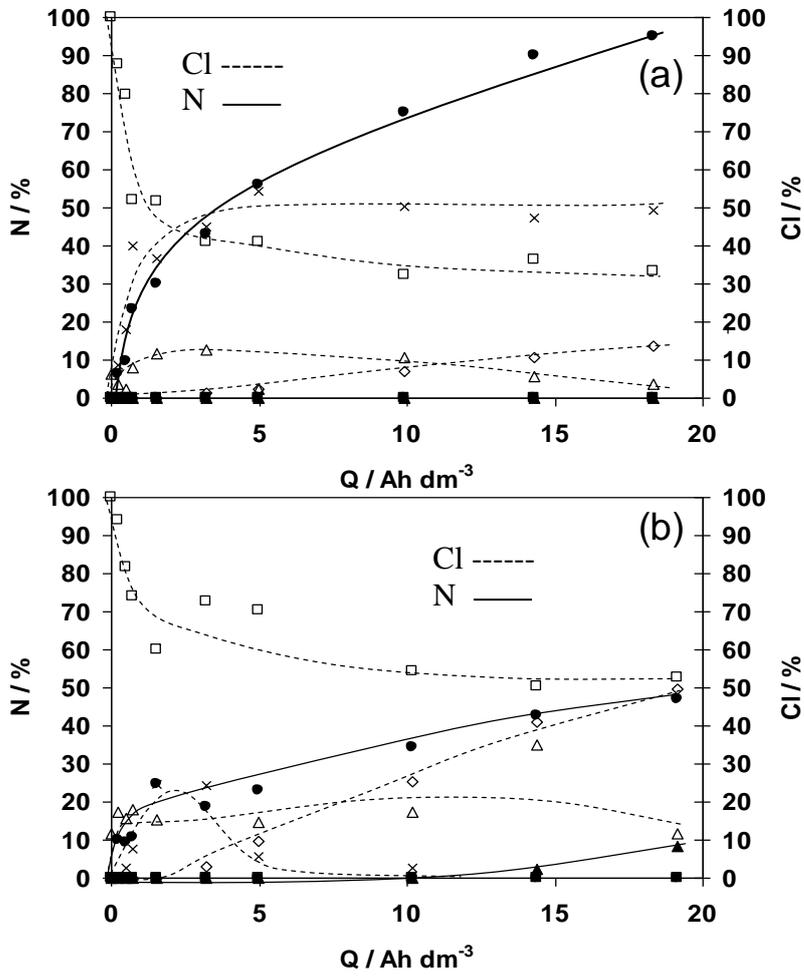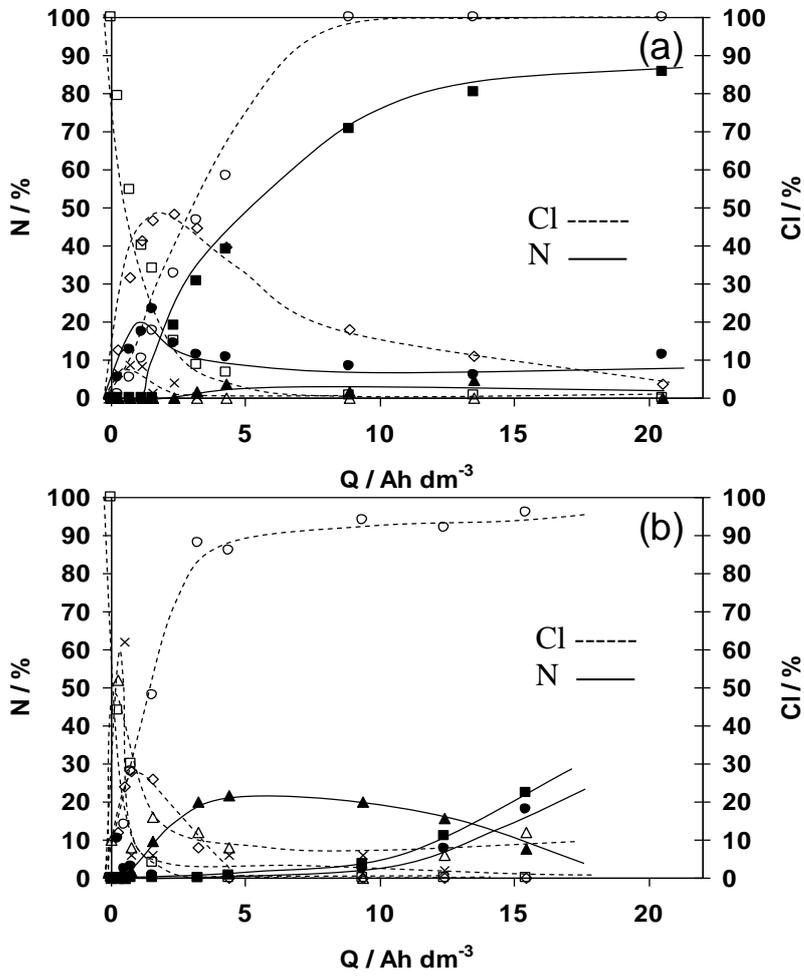
Axes: $NO_3^-\text{-N / mM}$ versus $Q / \text{Ah dm}^{-3}$
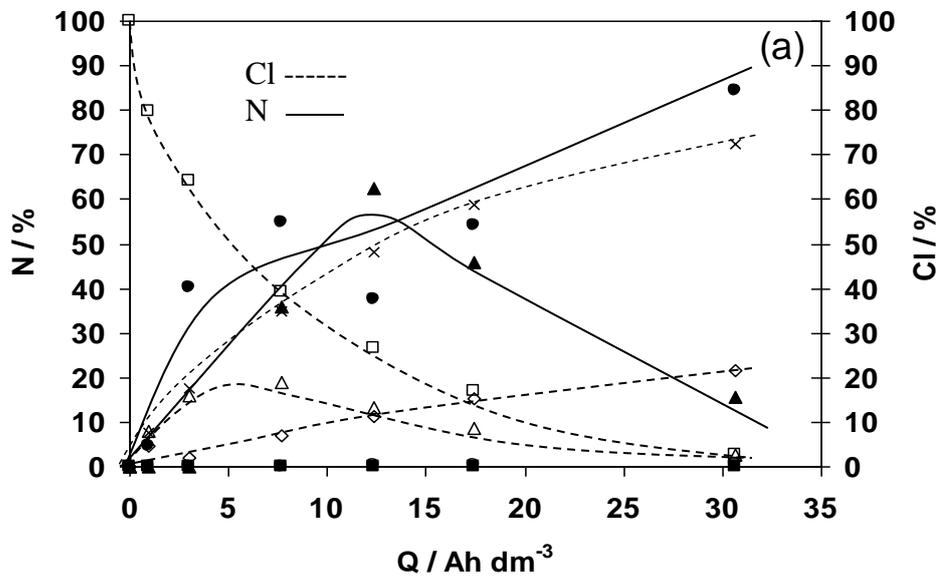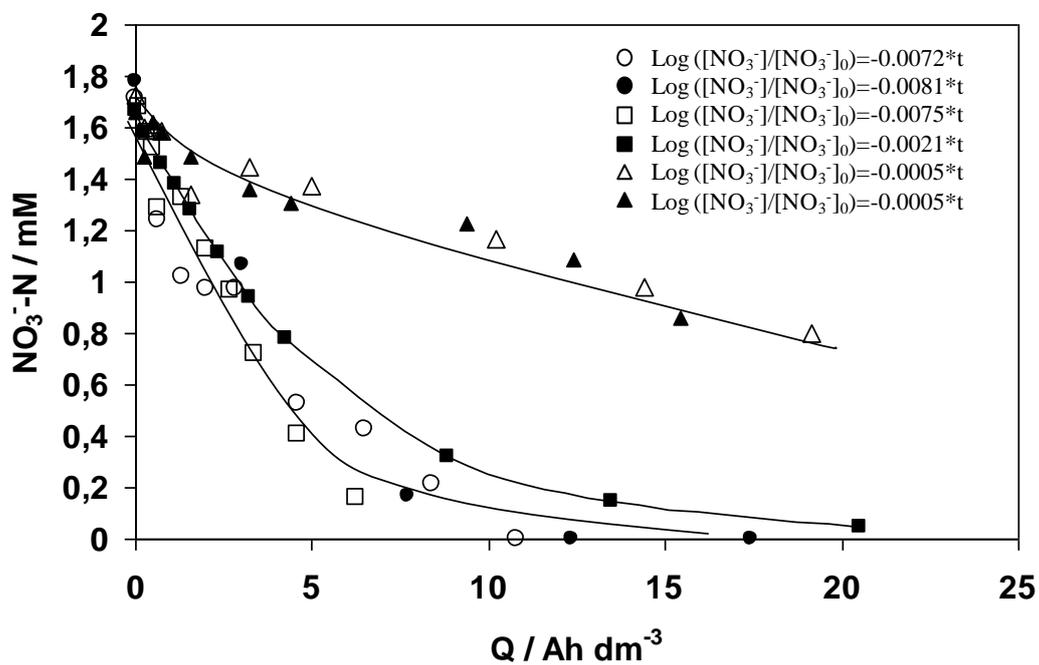
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3    Figure 3

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3    Figure 4

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3    Figure 5

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