

1 **Effect of the cathode material on the removal of nitrates by**
2 **electrolysis in non chloride media**

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7 **Abstract**

8
9 In this work, the effect of the cathode material (conductive diamond, stainless steel,
10 silicon carbide, graphite and lead) and current density (150-1400 A m⁻²) on the removal
11 of nitrates from aqueous solutions is studied by electrolysis in non-divided
12 electrochemical cells equipped with Conductive-Diamond Anodes, using sodium
13 sulphate as electrolyte. Results show that cathode material influences very strongly on
14 both the process performance and the product distribution, being gaseous nitrogen (NO,
15 N₂O, NO₂) and ammonium ions the main products obtained. Nitrate removal follows a
16 first order kinetic which indicates that electrolysis process is controlled by mass transfer.
17 Furthermore, stainless steel and graphite present a great selectivity towards the production
18 of ammonium ion whereas silicon carbide leads to the highest formation of gaseous
19 nitrogen, being this speciation promoted at low current densities.

20
21 **Keywords.**

22 Electrolysis, conductive diamond electrodes, nitrates, reduction, water treatment

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1 **1. Introduction**

2 Inorganic nitrogen pollution in water has become a significant problem around the world.
3 It is important to highlight that the total nitrogen deposition on the Earth's surface was 32
4 million metric tons (mostly from natural emission sources) in 1860 while in the early
5 1990s, total nitrogen deposition had risen up to 100 million metric tons [1]. This great
6 difference was entirely due to anthropogenic activities such as an excessive application
7 of fertilizers in agriculture, animal wastes produced in intensive farming, leachates from
8 urban solid waste dumps and/or untreated industry wastewaters [2]. The main nitrogen
9 species that are present in water are nitrates, nitrites and ammonium ions, although the
10 most common pollutant is nitrate.

11 Among other technologies, the removal of these nitrogen compounds can be carried out
12 by biological processes [3,4], ion exchange resins or reverse osmosis [5]. In addition,
13 conventional chemical coagulation using aluminium or iron salts are also employed to
14 remove inorganic nitrogen pollutants [6]. In recent years, electrochemical technologies
15 have become developing technologies for the removal of inorganic nitrogen pollutants.
16 In this way, electrocoagulation can efficiently remove nitrogen using aluminium or iron
17 electrodes [7-10]. In addition, electrochemical reduction of nitrate has been studied. Thus,
18 several cathode materials, such as Fe, Cu or Ti, have been used in electrochemical
19 denitrification [11]. The main final product obtained is usually ammonium ion because
20 the simultaneous electrolysis of ammonium to nitrogen gas (the target product) is reported
21 to be difficult [12-14].

22 The chemical and electrochemical reactivity of inorganic nitrogen pollutants in aqueous
23 solution has been widely described in literature, but it is not completely clear due to the
24 high reactivity and instability of nitrogen intermediates. For instance, Ferapontova and

1 Fedorovich [15] described the rate of reduction of NO_3^- and other anions, taking into
2 account that this reaction is controlled by the simultaneous transfer of both electron and
3 proton from a proton donor. The rate of this reduction depends on the type of
4 electrocatalytic material, the cathode potential and the pH of the solution. For the case of
5 electrocatalytic materials, metals with high overpotential for hydrogen evolution achieve
6 the highest reduction rates.

7 However, ammonia is the main product in the electrochemical reduction of nitrate, above
8 all when its concentration is high [16, 17]. Likewise, the presence of relatively small
9 amounts of copper clearly enhances the nitrate reduction process. Copper exhibits a
10 catalytic effect that limits the adsorption of hydrogen on the cathode surface, enhancing
11 the adsorption of nitrate [17]. After this step, copper has a negative influence over both
12 activity and selectivity towards N_2 production because the electrochemical oxidation of
13 ammonia to nitrogen is a difficult reaction when the potential of electrolysis is constant
14 [18].

15 Katsounaros et al. [19] determined that the reduction of nitrate follows a first order
16 kinetics at -2.5V and that NO could act as an intermediate of the reaction. Thus, NO
17 would be the precursor of ammonia and nitrogen formation, although ammonia is the
18 main product at potentials from -2.0 to -2.2V, being nitrogen gas the final product at more
19 negative potentials. In this way, Kuwabata et al. [20] proposed a reduction pathway of
20 nitrate to ammonia and nitrogen gas using a [Mo-Fe]/GC electrode. This pathway is
21 schematically shown in Figure 1. Nevertheless, nitrogen reactivity is complex and there
22 are different pathways of nitrate reduction reported in literature. Thus, Bockris and Kim
23 [21] found that nitrite plays a key role as an intermediate product in the nitrate reduction
24 process. Likewise, nitrite (instead of nitric oxide) would be further reduced to ammonia

1 or nitrogen, being the yield for ammonia or nitrogen dependent on the electrocatalytic
2 effect of the electrode material.

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

8

9 **2. Experimental**

10 *2.1. Analytical procedure*

11 Nitrogen inorganic anions (NO_3^- , NO_2^-) were measured by ion chromatography using a
12 Shimadzu LC-20A equipment (column, Shodex IC I-524A; mobile phase, 2.5 mM
13 phthalic acid at pH 4.0; flow rate, 1.0 ml min^{-1}). The same ion chromatography equipment
14 was used to measure the nitrogen inorganic cation, NH_4^+ , (column, Shodex IC YK-421;
15 mobile phase, 5.0 mM tartaric acid, 1.0 mM dipicolinic acid and 24 mM boric acid; flow
16 rate, 1.0 ml min^{-1}). The total nitrogen concentration was monitored using an Analytikjena
17 multi N/C 3100 analyser. Nitrogen gaseous compounds were identified by Teledyne API
18 chemiluminescence NO/NO₂/NO_x analyzer and were quantified by mass balance. In
19 addition, nitric oxide in aqueous solution was qualitatively determined by
20 chemiluminescence bubbling a high quantity of ozone into the sample, taking into
21 account Eq. 1 [22]. Hence, the intensity of the light detected is directly proportional to
22 nitric oxide concentration.



24

1 2.2. *Electrochemical cell*

2 The electrolysis of nitrogen was carried out in a single-compartment electrochemical flow
3 cell described in Figure 2 [23]. Conductive Diamond Electrode (CDE, Adamant
4 Technologies, Switzerland) was used as anode material whereas CDE (Adamant
5 Technologies, Switzerland), stainless steel AISI 304 (Mervilab, Spain), silicon carbide
6 (3-ONE-2, USA), porous graphite POCOFoam® (Poco Graphite SARL, France) and lead
7 (Mervilab, Spain) were used as cathode materials. The conductivity of these materials is
8 gathered in Table 1. Before each experiment, a solution containing 5000 mg dm^{-3} of
9 sodium sulphate at pH 2 was passed through the electrochemical cell, during 10 min and
10 at a current density of 30 mA cm^{-2} , in order to clean the surface of electrodes. Electrodes
11 had a geometric area of 78 cm^2 each one and an electrode gap of 9 mm. The electrolyte
12 was stored in a glass tank (500 ml) and it was circulated through the electrolytic cell by
13 means of a peristaltic pump. A heat exchanger was used to maintain the temperature at
14 the desired set point.

15

16 2.3. *Experimental procedure*

17 Bench scale electrolysis of 0.60 dm^3 of synthetic wastewater was carried out under
18 galvanostatic conditions. The concentration of nitrogen was 25 mg dm^{-3} (150 mg dm^{-3}
19 NaNO_3), 3000 mg dm^{-3} Na_2SO_4 was used as supporting electrolyte and H_2SO_4 was also
20 dosed in suitable amounts to set a pH of 2. The current density was varied from 150 to
21 1400 A m^{-2} , being 150 and 300 A m^{-2} the typical current densities used in wastewater
22 treatment by means of electrochemical technologies. 1400 A m^{-2} was selected in order to
23 study the influence of a high current density in the species generated in the reaction media
24 and, thus, in the nitrogen speciation.

1 The cell voltage did not significantly vary during each electrolysis, indicating that
2 appreciable deterioration of electrode or passivation phenomena did not take place. The
3 electrolyte flow rate through the cell was $1.5 \text{ dm}^3 \text{ min}^{-1}$. A heat exchanger coupled with
4 a controlled thermostatic bath (Digiterm 100, JP Selecta) was used to maintain the
5 temperature at the desired set point ($25 \text{ }^\circ\text{C}$).

6

7 **3. Results and discussion**

8 Figure 3a compares the evolution of the concentration of nitrates with respect to the
9 applied electrical charge, using different cathode materials. Current density was
10 maintained constant at 150 A m^{-2} and sodium sulphate was added as supporting
11 electrolyte. In this figure, it can be observed that nitrates are removed with all the cathode
12 materials tested, but with not very high current efficiencies. However, this range of
13 current efficiencies can be easily explained taking into account the initial concentration
14 of nitrate, using a single mass transfer model for the overall process [24, 25]. The mass-
15 transfer coefficient was calculated from a standard $\text{Fe}(\text{CN})_6^{3+}/\text{Fe}(\text{CN})_6^{2+}$ limit current test,
16 obtaining a value of $1.2 \cdot 10^{-5} \text{ m s}^{-1}$ [26] for the experimental setup and conditions used.
17 Under these conditions, the limit current density (which can be calculated from the
18 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
19 ($n=2 \text{ mol e}^-/\text{mol NO}_3^-$), and 16.5 A m^{-2} if ammonium is assumed to be the final product
20 ($n=8 \text{ mol e}^-/\text{mol NO}_3^-$). This leads to a maximum efficiency between 2.7-11%, according
21 to a simple model of the electrochemical process based on mass transfer control [27,28].
22 Thus, the maximum reachable current efficiency is limited to this range of values.

23

1 Next, another important point to be highlighted from Figure 2a is the marked differences
2 found in the performance of the five electrodes studied. Graphite is clearly the most
3 efficient, with current efficiencies over 10%, and conductive diamond is the least one.
4 Figure 3b shows that the evolution of nitrates follows a first order kinetics (linear fitting
5 in semi-logarithmic plot). According to literature, this fact may suggest that the process
6 is controlled by mediated reagents (oxidative/reductant agents in the target solution) or
7 by mass transfer [23, 29, 30].

8

9 Figure 4 (data also gathered in Table 2) shows the effect of current density on the removal
10 of nitrates using a silicon carbide cathode. Part a) depicts the progress of the electrolysis
11 with respect to nitrate concentration and Part b) summarizes the efficiency of NO_3^-
12 removal at different stages of the electrolysis. This efficiency has been calculated as the
13 mass of nitrate (mg NO_3^-) removed per unit of applied electrical charge (expressed in A
14 h). Moreover, the maximum efficiency of NO_3^- removal reachable if the reduction product
15 is ammonium (oxidation state -3), nitrite (oxidation stage +3) or gaseous nitrogen
16 (oxidation state 0) is also shown, for comparison purposes. Note that this maximum
17 efficiency of NO_3^- removal would correspond to an electrical efficiency of 100% (100%
18 of the electrons applied used to the target reduction reaction).

19

20 This figure is very important to discern between a mass transfer and a mediated
21 electrolysis control of the process. Mediated electro-reagents should be produced more
22 intensively at higher current densities, and hence, their effect should increase with current
23 density. On the contrary, direct electrochemical process becomes less efficient at higher
24 current density, in the region in which mass transfer rate is below the electron supply rate.

1 As it can be observed, the process is less efficient at higher current densities. This
2 observation discards mediated reduction as the primary reduction mechanism when using
3 SiC as cathode, and it clearly supports that the process is mass transfer controlled.

4
5 Figures 5 and 6 show the effect of current density and reaction progress on the efficiency
6 of the reduction of nitrates with the other four cathode materials studied in this work (data
7 included in tables 3 and 4). Figure 5 is focused on lead (Figure 5a) and conductive
8 diamond (Figure 5b) cathodes. Both electrodes show a very similar behaviour to that
9 observed with silicon carbide. In both cases, mass transfer clearly controls the process
10 rate, and efficiencies are comparable to those of silicon carbide, although they decrease
11 in the series SiC>Pb>CDE. On the contrary, results corresponding to electrolysis with
12 stainless steel (Figure 6a) and graphite carbon (Figure 6b) electrodes show a very different
13 behaviour, which suggests a significant role of mediated processes in the nitrate removal.
14 In both cases, efficiencies do not decrease but increase in the range from 150 to 300 A m⁻².
15 This could mean that mediated reduction processes are occurring and they compensate
16 the loss of efficiency caused by mass transport limitations. This behaviour is more
17 significantly observed in the case of stainless steel. It is worth mentioning that current
18 efficiency is almost constant with current density at the highest value of the electric
19 charge applied. This observation supports, even more strongly, the important role of the
20 mediated oxidation processes (the electron transference to the pollutant takes place
21 chemically from an oxidative or reductant inorganic agent).

22
23 Product distribution is the other important point in the study of the electro-catalytic
24 properties of the different cathodes. Figure 7 shows the time-course of the different

1 products during the electrolysis of nitrate at different current densities using silicon
2 carbide cathode. In every case, ammonium ion is the primary product obtained, although
3 different nitrogen gaseous species are initially formed at a high rate. These species are
4 quantified by mass balance, but some qualitative gas analyses allow identifying NO, N₂O,
5 NO₂ as the primary nitrogen components of these evolved gases. The particular
6 composition of each sample of gases changes with time, due to the well-known
7 decomposition of NO into N₂O and NO₂, and the further reactions to yield N₂O₅. This
8 places NO as the main gaseous product formed during the electrochemical process. In
9 addition, an ozonation test [22] was carried out to the liquid samples taken during the
10 electrochemical process. In these samples, chemiluminiscence tests confirm that NO
11 concentration increases with time. This is consistent with the high solubility of nitric
12 oxide in aqueous medium, and confirms NO as a key component in the gaseous nitrogen
13 flow. Nitrite concentration is negligible (merely traces in some of the determinations),
14 what suggests its high reactivity when it behaves as intermediate.

15

16 Figure 8 reports, for the lowest current density (150 A m⁻²), the changes in the products
17 speciation with the electric charge passed (progress of the electrolysis), in terms of the
18 ammonium selectivity. This variable is the most deeply influenced by the electrode
19 material, especially in the cases of stainless steel and SiC, which show limit behaviours.
20 On the one hand, ammonium ion is almost the unique final product from the very early
21 stage when stainless steel is selected as cathode material. On the contrary, in the case of
22 using the SiC electrode, gaseous nitrogen species are the main products in the first
23 moment and afterwards, selectivity of the process changes and ammonium ions become
24 in the primary products. This behaviour is also observed at higher current densities, as it

1 is shown in Figure 9 (parts a and b). However, a key difference is that for larger current
2 densities, smaller differences are observed in the role of gaseous nitrogen compounds at
3 large current passed.

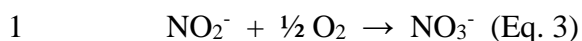
4
5 Taking into account these results, a single mechanistic model can be proposed for the
6 main processes occurring on the cathode surface. Nitrates are reduced to ammonium ions
7 and to nitrites regardless of the cathode used, although the selectivity depends on the
8 particular cathode studied. Then, under high concentrations of nitrates, nitrites are
9 transformed into nitric oxide according to the reaction showed in equation 2 [31].



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

21

22 At larger current charge passed, when the concentration of nitrates is smaller, this reaction
23 is not promoted, and a simple transformation of nitrites into nitrates (with the consequent
24 decrease in the efficiency) is obtained (equation 3).



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

6

7 To sum up, reduction of nitrates to ammonium ions is promoted when using stainless steel
8 as cathode material, while the production of nitrites is favoured with silicon carbide
9 cathode. Other cathodes show an intermediate behaviour between those observed for
10 stainless steel and silicon carbide. Taking into account their selectivity to ammonium in
11 the first stage, they can be classified in the following series: stainless steel>conductive
12 diamond>graphite>lead>silicon carbide.

13

14 The increase observed in the efficiency of the reduction of nitrates from 150 to 300 A m⁻²
15 is not explained by a mediated oxidation process, but by the preferential transformation
16 of nitrites into nitric oxide. Production of reducing compounds is not promoted at the
17 lowest current density (merely ammonium formation), which justifies the high selectivity
18 obtained. Nitrites formed are reverted into nitrates under these conditions. At 300 A m⁻²
19 both mechanisms are fully active, explaining the higher efficiency in the removal of
20 nitrates and also the lower selectivity towards the production of ammonium. In the case
21 of graphite, the explanation can also be related with the formation of hydrogen or
22 hydrogen peroxide, which in this case is enhanced at low current densities, explaining the
23 high selectivity towards NO at low current densities and the selectivity to ammonium at
24 larger values of this variable.

1

2 **4. Conclusions**

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

5 - Ammonium cation is the main reaction product in the electroreduction of nitrates
6 when conductive diamond, stainless steel, graphite, silicon carbide and lead are used as
7 cathode materials. Nitrogen oxides are secondary products, being silicon carbide the
8 material that leads to the highest yield in the production of these species. This yield is
9 promoted at lower current densities.

10 - Graphite is the most efficient cathode in terms of nitrate removal, with current
11 efficiencies close to 10%, whereas conductive diamond presents the lowest efficiency,
12 with values lower than 5%. In every case, nitrate removal follows a first order kinetics,
13 which can be explained by mass transport control or by mediated processes.

14 - During electrolysis with stainless steel and graphite, a complete reduction of
15 nitrates to ammonium was observed, without significant production of gaseous nitrogen
16 compounds.

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

19

20 **Acknowledgements**

21 This work was supported by the MCT (Ministerio de Ciencia y Tecnología, Spain) and
22 by the EU (European Union) through projects CTM2010-18833/TECNO and CSD2006-
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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 ($A m^{-2}$)
$NO_3^-(t)$	Nitrate concentration at time t ($mol m^{-3}$)
t	Time (s)

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19 List of Figures

20 Figure captions

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

2 **Figure 2.** Layout of the electrolysis bench-scale plant (1: Absorber, 2: Feed tank, 3:
3 Peristaltic pump, 4: Electrochemical cell, 5: Sampling, 6: Thermostatic bath, 7: Heat
4 exchanger, 8: Power supply). Detail of the electrochemical cell.

5 **Figure 3.** Variation of NO_3^- -N concentration with applied electrical charge (a) and time
6 (b) during electrolysis of nitrate solutions. Operation conditions: $25 \text{ mg dm}^{-3} \text{ NO}_3^-$ -N +
7 $3000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; pH_0 2; 150 A m^{-2} ; anode: conductive diamond; cathode materials:
8 ◆conductive diamond, *stainless steel, ●silicon carbide, ■graphite, ▲lead.

9 **Figure 4.** (a) Variation of NO_3^- -N concentration with applied electrical charge (▲ 150 A
10 m^{-2} , ○ 300 A m^{-2} , ■ 1400 A m^{-2}). (b) Influence of the current density on the efficiency of
11 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}).
12 Operation conditions: $25 \text{ mg dm}^{-3} \text{ NO}_3^-$ -N + $3000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; pH_0 2; anode:
13 conductive diamond; cathode: silicon carbide.

14 **Figure 5.** Influence of the current density on the efficiency of the removal of nitrates
15 (◆ 2.5 A h dm^{-3} , * 5 A h dm^{-3} , ● 10 A h dm^{-3} , ▲ 20 A h dm^{-3}). Operation conditions: 25
16 $\text{mg dm}^{-3} \text{ NO}_3^-$ -N + $3000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; pH_0 2; anode: conductive diamond; cathodes:
17 (a) lead, (b) conductive diamond.

18 **Figure 6.** Influence of the current density on the efficiency of the removal of nitrates
19 (◆ 2.5 A h dm^{-3} , * 5 A h dm^{-3} , ● 10 A h dm^{-3} , ▲ 20 A h dm^{-3}). Operation conditions: 25
20 $\text{mg dm}^{-3} \text{ NO}_3^-$ -N + $3000 \text{ mg dm}^{-3} \text{ Na}_2\text{SO}_4$; pH_0 2; anode: conductive diamond; cathodes:
21 (a) stainless steel, (b) graphite.

22 **Figure 7.** Effect of the current density on the speciation of nitrogen during electrolysis of
23 nitrate solutions (■ NO_2^- -N, ▲ NH_4^+ -N, ◆ $\text{N}_{\text{gaseous}}$ -N). Operation conditions: 25 mg dm^{-3}

1 NO_3^- -N + 3000 mg dm^{-3} Na_2SO_4 ; pH_0 ; anode: conductive diamond; cathode: silicon
 2 carbide; points: empty-150 A m^{-2} , gray-300 A m^{-2} , full-1400 A m^{-2} .

3 **Figure 8.** Products distribution with applied electrical charge during the electrolysis of
 4 nitrate solutions. Operation conditions: 25 mg dm^{-3} NO_3^- -N + 3000 mg dm^{-3} Na_2SO_4 ; pH_0
 5 2; 150 A m^{-2} ; anode: conductive diamond; cathode materials: ◆conductive diamond,
 6 *stainless steel, ●silicon carbide, ■graphite, ▲lead.

7 **Figure 9.** Products distribution with applied electrical charge during the electrolysis of
 8 nitrate solutions. Operation conditions: 25 mg dm^{-3} NO_3^- -N + 3000 mg dm^{-3} Na_2SO_4 ; pH_0
 9 2; current densities: (a)300 A m^{-2} , (b)1400 A m^{-2} ; anode: conductive diamond; cathode
 10 materials: ◆conductive diamond, *stainless steel, ●silicon carbide, ■graphite, ▲lead.

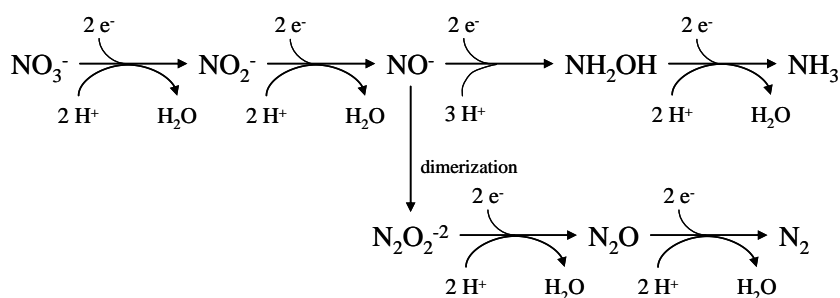
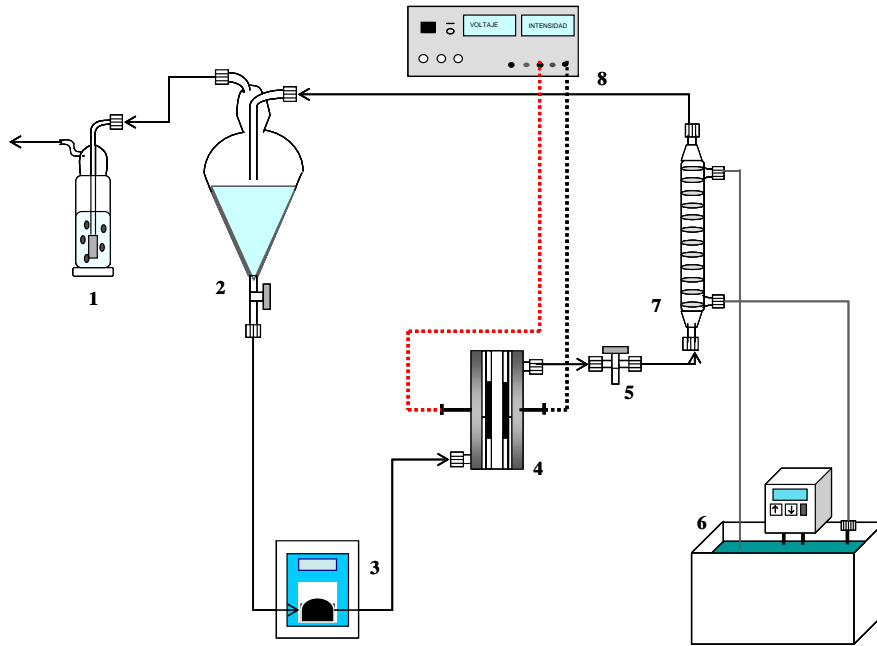
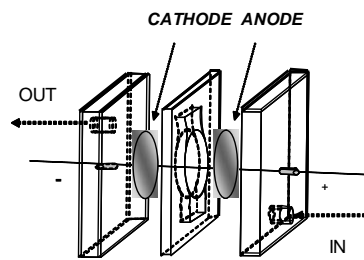


Figure 1.

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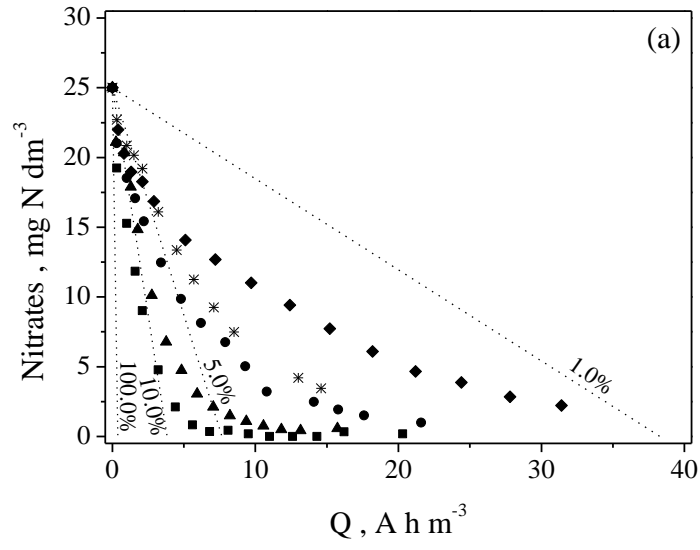
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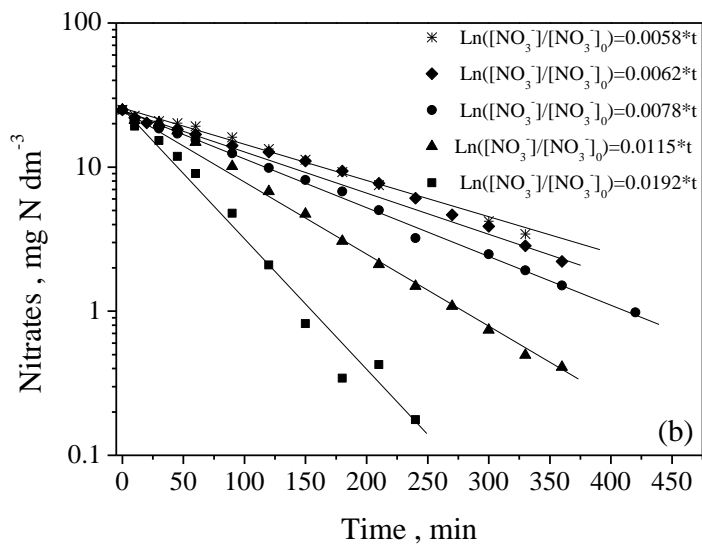
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Figure 2



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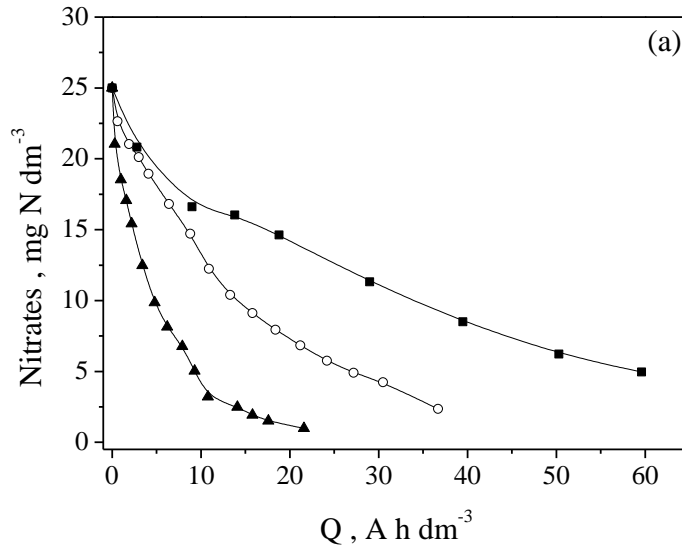
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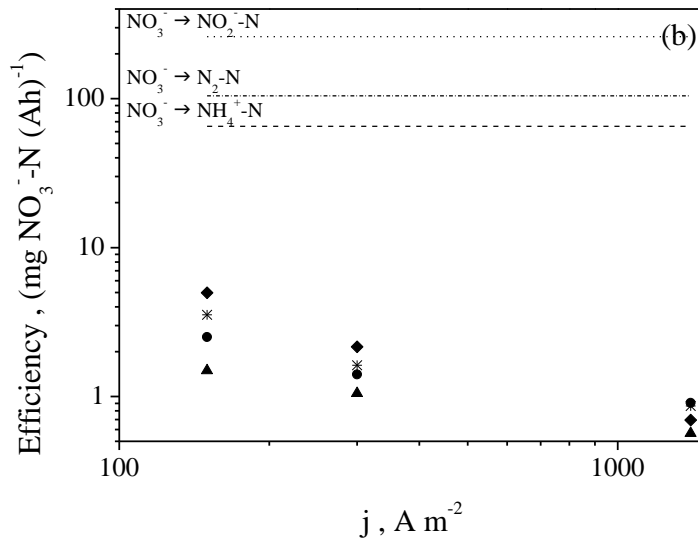
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Figure 3.



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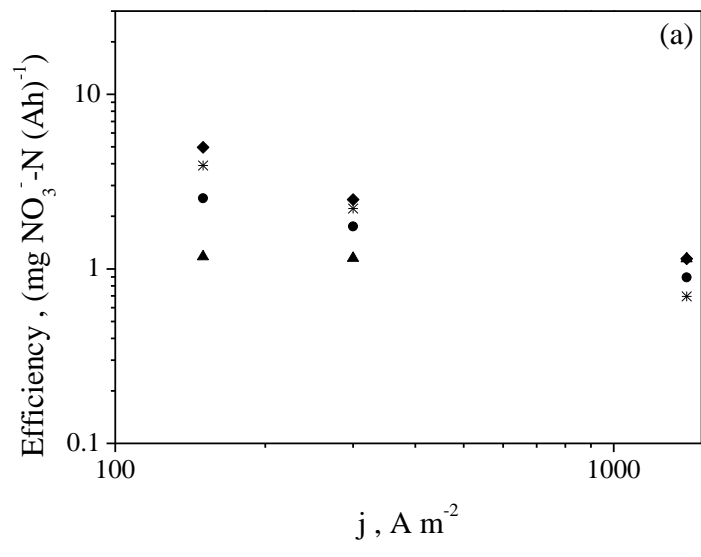
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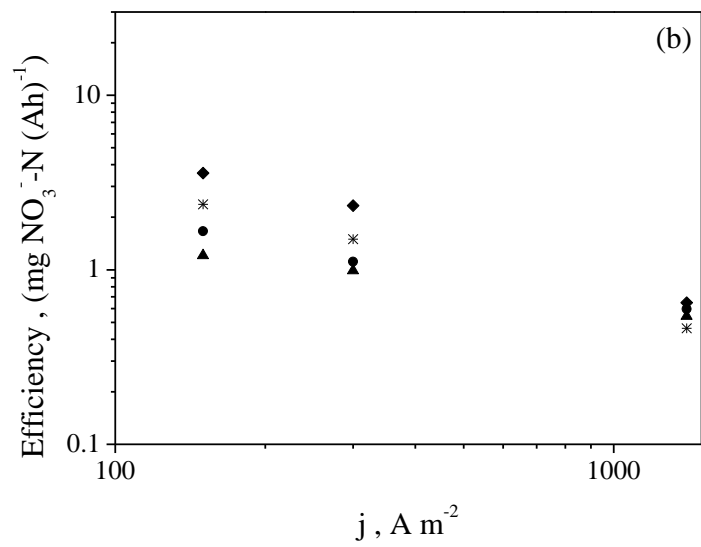
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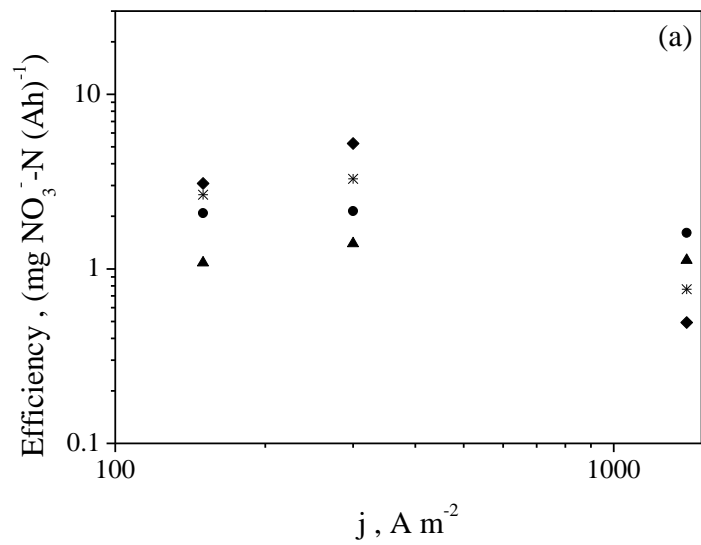
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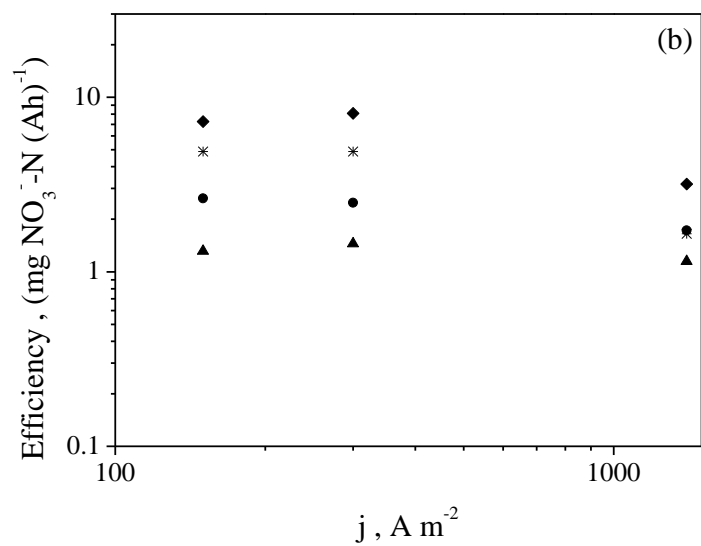
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Figure 5.



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Figure 6.

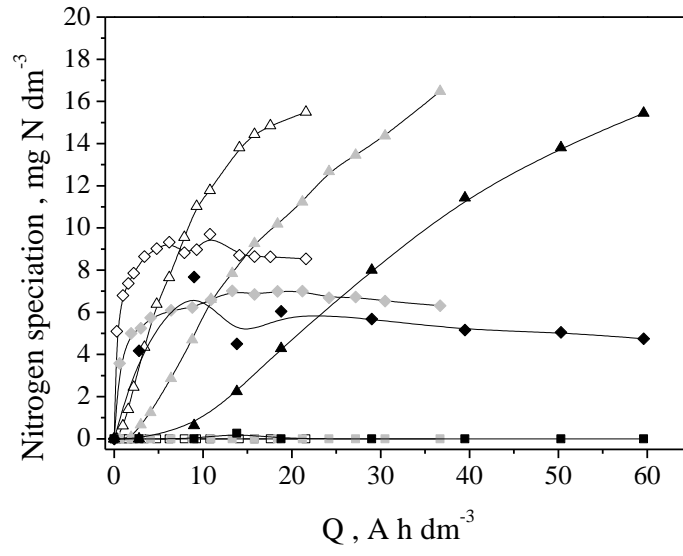


Figure 7.

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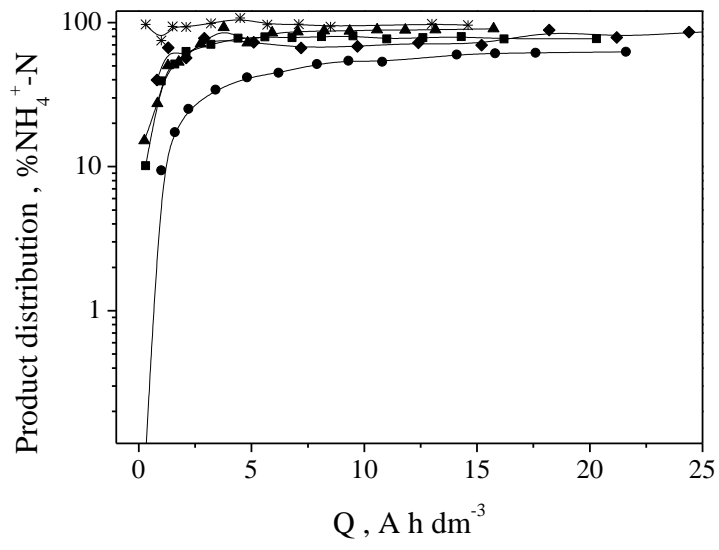
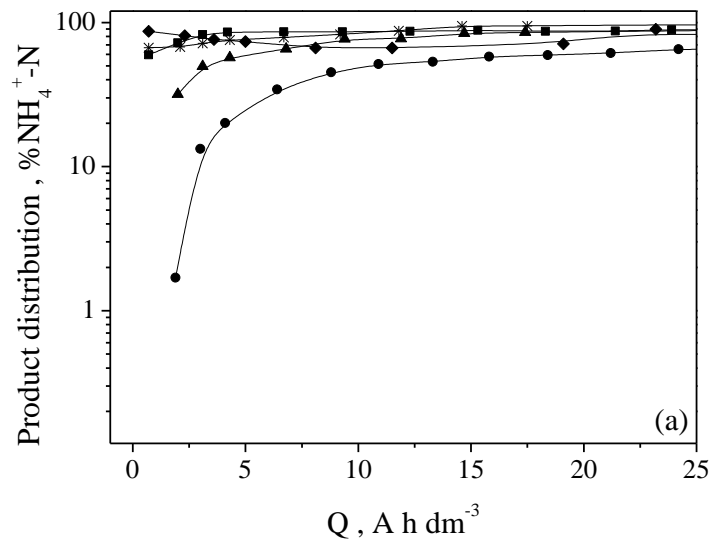
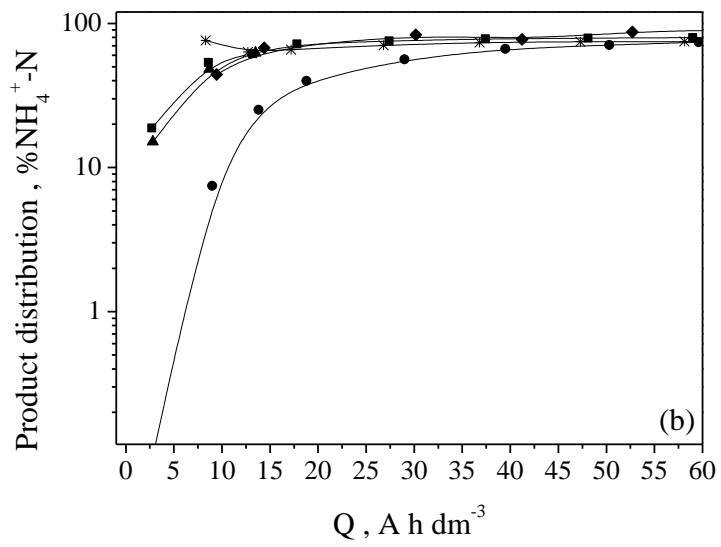


Figure 8.

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Figure 9.

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Table 1. Conductivity of the electrode materials.

Material	Conductivity (S cm⁻¹)
CDE	$1.0 \cdot 10^1$
Stainless steel	$1.4 \cdot 10^4$
Graphite	$1.7 \cdot 10^2$
Lead	$4.9 \cdot 10^4$