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Efficiency of electrochemical denitrification using electrolysis cell containing BDD electrode

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ABSTRACT

In the present study, the efficiency of nitrates and nitrites removal was investigated in two types of electrochemical cell containing boron-doped diamond (BDD) anode/cathode or BDD anode and stainless steel (SS) cathode. The nitrates and nitrites removal rate was more than 90% using BDD cathode after 4 h of electrolysis using Na_2SO_4 as electrolyte. A low amount of NH_3 was obtained for high initial concentration, and an important amount was rejected in the form of $N_{gaseous}$. The nitrates removal was more affected when SS was used as cathode but nitrite removal remained higher, about 80%, with initial nitrites solution. An important amount of by-products was formed, and a low amount of $N_{gaseous}$ was rejected. A high amount of $HO^•$ radicals was produced at BDD anode/cathode, which promoted the direct oxidation of ammonia into $N_{gaseous}$. Kinetic of nitrates reduction at BDD anode/cathode fitted well to pseudo-first order for 2 h of electro-reduction. Using BDD anode/cathode, current efficiencies are higher by contrast of energy consumption. The efficiency was confirmed from three initial concentrations of $NaNO_3$ and $NaNO_2$ in sulfates medium.

Keywords: BDD electrode; Stainless steel; Nitrates; Nitrites; $HO^•$; Current efficiency; Energy consumption

1. Introduction

Recently, a huge quantity of nitrogen compounds is being used in several sectors, such as agriculture, and some industrial activity, like nuclear and aquaculture, and it became an important environmental issue due to the pollution of different water sources such as groundwater, rivers, lakes, and seas [1–3]. Depending on their concentration, nitrate ions and related compounds (NO_2^- and NH_3) may promote detrimental effects on human health and disruption of aquatic ecosystems as they cause serious diseases such as methemoglobinemia, liver damage, and cancer [4]. For aquatic animals, this contamination with nitrates causes progressively their death after the storage of oxygen in their body [5].

Different conventional technologies are used for the nitrate removal essentially biological denitrification [6,7]. Continuous monitoring of the addition of a source of carbon, pH control, and temperature is necessary. Extractive methods like reverse osmosis

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and ion exchange resins are also largely used to eliminate nitrates [8,9]. But, these processes produce a large amount of effluents rich with nitrates, which must be treated later and therefore, increase the overall cost of the process and limit its use.

In the last few years, the attention was given to the electrochemical process for the nitrates, nitrites, and ammonia removal, thanks to its advantages, such as the easy implementation, no requirement for chemicals addition, and efficiency either with high quantity of in treated effluent [10–16].

A lot of researchers have been focusing their study on the efficiency of electrochemical treatment, limitation, and the kinetics [11–16].

Electrochemical treatment depends on many factors. Among them, the electrode material is crucial parameter that can strongly affect the efficiency of an anodic oxidation of organic pollutant [17,18]. Therefore, several cathodes have been used such as Fe, Cu, Al, Cu–Zn, and stainless steel (SS) [13–15]. Some of them like SS, Cu, and Fe are known as relatively efficient electrodes for nitrate electro-reduction into nitrogen gaseous [10,13,15,19]. Boron-doped diamond (BDD) is largely studied, and its efficiency as anode has been reported in different works [20,21] due to its electrochemical properties, such as wide working potential window, low and stable voltametric background current, high overpotential for oxygen and hydrogen evolution in aqueous electrolytes and high stability. BDD electrode is used for electrochemical disinfection [22], removal of emerging pollutants [23,24], and removal of other refractory pollutants [25–27]. Using BDD as cathodes [19,20,28] for the elimination of nitrates, nitrites, and ammonia is recently studied and discussed [12,13,28,29]. The major electrochemical reactions involved in the electrochemical nitrate reduction using BDD as cathode and anode material are [12,30]:

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_{3(aq)} + 9OH^- \quad (1)$$

$$NO_3^- + H_2O + 2e^- \rightleftharpoons NO_2^- + 2OH^- \quad (2)$$

$$NO_3^- + 3H_2O + 5e^- \rightarrow \frac{1}{2}N_2 + 6OH^- \quad (3)$$

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_{3(gas)} + 9OH^- \quad (4)$$

The nitrites formed are an intermediary by-products, and it can react to give ammonia, nitrogen gaseous, and also nitrates according to those reactions [12,30]:

$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7OH^- \quad (5)$$

$$2NO_2^- + 4H_2O + 6e^- \rightarrow N_2 + 8OH^- \quad (6)$$

When pH values are between 7 and 11.5, equilibrium between ammonia and ammonium can be established as follows [31]:

$$NH_{4(aq)}^+ + OH^- \rightleftharpoons NH_{3(aq)} + H_2O \quad (7)$$

At this pH, the reduction in nitrate to ammonium is possible:

$$NO_3^- + H_2O + 6H^+ + 3e^- \rightarrow NH_4^+ + 4OH^- \quad (8)$$

However, the objective of this paper is to compare the electrochemical denitrification efficiency of different types of electrodes (BDD and SS) in two electrolytic cells, applying high concentration of nitrates and nitrites for potential application in industrial effluents. The investigation is based on SS and BDD electrodes, the related removal of nitrogen compounds, and elimination pathways. The current efficiencies (η) and energy consumption (EC) have been also evaluated.

2. Methods

2.1. Experimental procedure

Synthetic solutions were prepared by dissolving commercial sodium nitrate ($NaNO_3$, Sigma–Aldrich; purity ≥ 99.0%) or commercial sodium nitrite ($NaNO_2$, Sigma–Aldrich; purity ≥ 98.0%) in ultrapure water. Three concentrations of nitrate (65, 250, and 500 mg L^{-1} of N-NO_3^-) and three others of nitrite (25, 75, and 150 mg L^{-1} of N-NO_2^-) were prepared. Sodium sulfate Na_2SO_4 (0.1 M) was used as a supporting electrolyte. The temperature was maintained constant at 25 ℃, and the initial pH is equal to 6.0 ± 0.2.

2.2. Electrochemical setup

All the experiments were performed under galvanostatic mode and with a feed volume of 1 L recirculated through electrolytic cells by peristaltic pump (Fig. 1). A constant current density value ($j = 40$ mA cm^2) was applied by a power supply (Adamant Technologies). Synthetic solutions of nitrate and nitrite were carried in two different cells; the first cell was divided into three equal compartments, BDD was used as cathode and anode materials, the active surface was ($70\,cm^2 \times 3$), and the electrode gap was 1 mm. The second cell was an undivided cell, BDD was used as anode and stainless steel as cathode, the active surface was $12.5\,cm^2$, and the electrode gap was 3 mm. Electrolysis time was fixed at 4 h.

2.3. Analytical procedure

All analyses were done according to standard methods [32]. Nitrate concentrations (NO_3^-) were determined by sodium salicylate method, nitrite concentration was measured by reagent of diazotation method, ammonium and ammonia concentrations were monitored by Nessler method using UV–visible spectroscopy (Thermo Spectronic model) at wavelengths of 415, 543, and 420 nm, respectively [33–35]. Total nitrogen in treated solution was quantified by mass balance. Existing amount of ion hydroxyls is the experimental value in treated solution at different time of electrolysis. It is calculated using pH values determined *in situ* during the experiment. Produced amount of ion hydroxyls is the theoretical value, calculated based on the produced amounts of N-compounds and related generation of OH^- according to corresponding reactions. In this case, the ionic strength effect was considered, and the ionic activity was evaluated using Debye–Hückel formula [36].

$$\log(\gamma_i) = \frac{-Az_i^2\sqrt{I}}{1 + Ba\sqrt{I}} - AI \text{ where } I = \frac{1}{2}\sum C_i z_i^2$$

The possible formation of hydrazine and hydroxylamine was not investigated because the treated solutions were changed into basic after electrolysis, in which hydrazine and hydroxylamine will not be reduced [37].

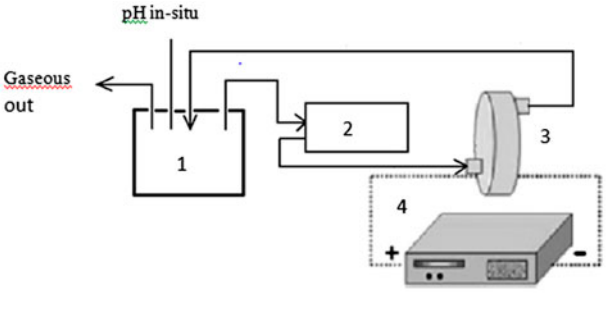

Fig. 1. Experimental setup: (1) back of solution, (2) pump, (3) electrochemical cell, and (4) power supply.

3. Results and discussion

3.1. Nitrate removal and by-products formed

3.1.1. BDD anode/cathode

The mechanism of nitrates reduction at BDD anode/cathode is studied using three initial concentrations of nitrate 65, 250, and 500 $mg\,L^{-1}$ N-NO_3^-, and the obtained results of nitrates elimination, nitrites, and ammonia produced vs. time are presented.

When the initial concentration was 65 $mg\,L^{-1}$ (Fig. 2(a)), nitrates were rapidly reduced to 6.2 $mg\,L^{-1}$ (around 90%) after 1.5 h leading to ammonia as the main by-product according reaction (1).

However, the ammonia formed represented 43.6% (28.3 $mg\,L^{-1}$ N-NH_3) of the total initial N-nitrates. This quantity produced increased with the experimental time. It reached a maximum after 1.5 h then remained stable until the end of electrolysis time. At this concentration, only a trace of nitrites was formed (0.05 $mg\,L^{-1}$ N-NO_2^-) since the beginning and the reaction (2) related to nitrates reduction can be considered as (i) not very important pathway for nitrates degradation, (ii) NO_2^- degradation occurred very fast, or (iii) NO_2^- was oxidized on BDD anode.

The sudden increases in the pH value from 6 to 11.3, depicted in Fig. 2(e) and then its stability due to the high OH^- produced, enhanced the fast reduction in nitrates into ammonia and nitrogen gaseous (around 55%), according to reactions (3) and (4).

When the initial nitrate concentration was 250 mg L^{-1} (Fig. 2(b)), 89% of N-NO_3^- removal was obtained after 1.5 h. In the first 30 min of electrolysis, a significant amount of nitrites was formed and the quantity increased with increasing the initial nitrates concentration, reaction (2) (in direct sense). Fig. 2(b) shows that at the beginning of electrolysis, ammonia was not formed until nitrites concentration reached a maximum after 30 min; at this time, ammonia started to form and the amount of nitrites formed was decreased to obtain traces, which may confirm that nitrites is an intermediary by-products and the amount formed is fastly transformed into ammonia and nitrogen gaseous according to the reactions (5) and (6) [12]. For the initial nitrates concentration of 500 $mg\,L^{-1}$ N-NO_3^-, same results were obtained (Fig. 2(c)), which less NH_3 by-products were formed and more amount of $N_{gaseous}$ was rejected; the amount of N-NO_2^- was reduced at the surface of BDD cathode to give gaseous nitrogen and ammonia according to reactions (5, 6) [12]. Results obtained revealed that nitrates were directly reduced into nitrites which then reduced into ammonia and nitrogen gaseous.

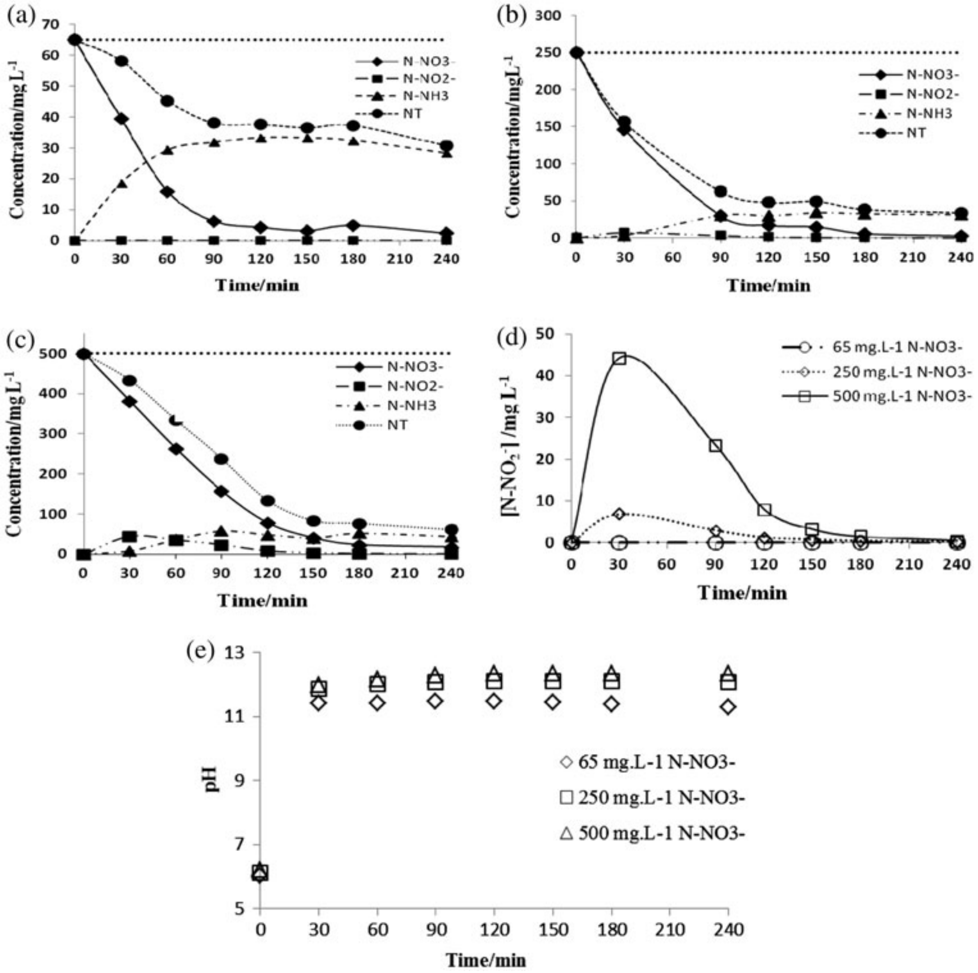

Fig. 2. Concentrations of nitrate removal (♦) N-NO_3^- and by-products formed: (■) N-NO_2^-, (▲) N-NH_3 during the electrolysis of 65 mg L^{-1} (a), 250 mg L^{-1} (b), and 500 mg L^{-1}(c). Change of the concentration of nitrite formed (d) and the evolution of pH with electrolysis time (e) for three feed nitrate solutions. Experimental conditions: BDD anode/cathode; $j = 40$ mA cm^{-2}; supporting electrolyte Na_2SO_4 (0.1 M); $pH_0 = 6.0 \pm 0.2$.

3.1.1.1. Role of radicals produced in BDD electrode. The performance of BDD as cathode to reduce nitrate into nitrogen gaseous, even at high quantity, was proved in the previous section. This behavior can be also related to the efficiency of BDD used as anode material to produce radicals [20,38]. The amount of ion hydroxyl, which supposed to be produced during nitrates electro-reduction, was calculated using reactions (1–7), occurring at the surface of BDD cathode. The amount existing in treated solution at different electrolysis times was also calculated using pH values which reflects the real amount of OH^- existing in electrolyte and reacted on BDD to produce hydroxyl radicals according to the reaction (9) [20].

$$\mathrm{BDD} + \mathrm{OH}^- \rightarrow \mathrm{BDD}(\mathrm{HO}^\bullet) + \mathrm{e}^- \qquad (9)$$

The amount of radicals could be estimated by the subtraction between the quantity produced and existing of ion hydroxyls. Fig. 3 shows the large difference between the amount of ion hydroxyls (HO^-) produced and existing, which can be explained by the oxidation into $HO^\bullet$, within 4 h of electrolysis. The radicals were rapidly produced and reached a maximum after 30 min, the amount of radicals produced were equal, in respect to the initial concentrations 206.27, 724.23, and 1,673,31 mg L^{-1}. Then, it decreased until the end of electrolysis. The $HO^\bullet$ produced has oxidized NH_3 into N_2 according to reaction (10) [39,40].

$$3\mathrm{HO}^\bullet + \mathrm{NH}_{3(\mathrm{aq})} \rightarrow \frac{1}{2}\mathrm{N}_2 + 3\mathrm{H}_2\mathrm{O} + 3\mathrm{e}^- \qquad (10)$$

The $HO^\bullet$ evolution was similar to NO_2^- evolution (same optimum was obtained in 30 min), which can

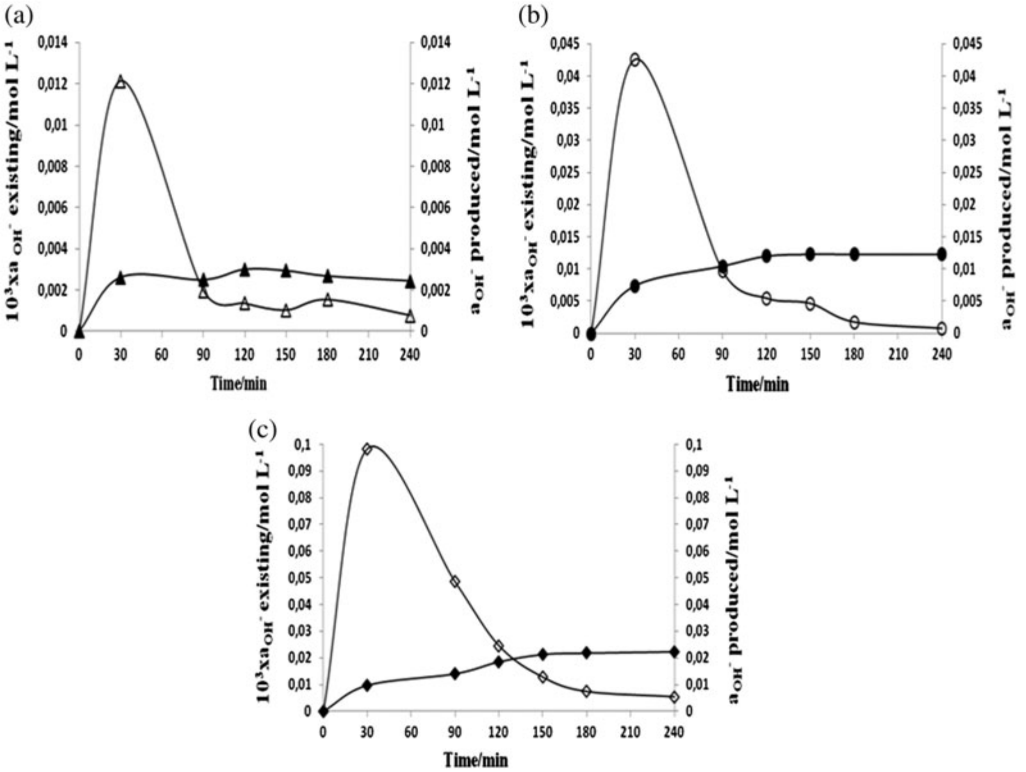

Fig. 3. Comparison between the quantity produced (open symbols) and existing (solid symbols) of ion hydroxyl with electrolysis times during the electro-reduction in: 65 mg L^{-1} (a), 250 mg L^{-1}(b), and 500 mg L^{-1} (c) of N-NO_3^- at BDD anode/cathode.

favorite reactions consuming nitrites (reactions (5) and (6)) via the oxidation of OH^- to $HO^{\bullet}$.

3.1.2. BDD anode and SS cathode

The electro-reduction in the three initial concentrations of nitrates (3.95, 14.88, and 30 mg L^{-1} with respect to the same nitrates concentrations treated by active surface with the first type of cell) was also studied at BDD as anode and SS as cathode.

When initial nitrates concentration was 14.88 mg L^{-1} N-NO_3^-, nitrates were slightly decreased during electrolysis, around 24% after 4 h of treatment (Fig. 4(a)). A small amount of nitrogen gaseous was rejected (26.4%), and ammonium, ammonia, and nitrites were the main by-products produced in a small quantity. Nitrogen gaseous and by-products steel to formed until the beginning of the electrolysis according to reactions (1–3, 5). However, nitrogen gaseous reach a maximum after 1 h then remained stable until to the end, but nitrites, ammonia, and ammonium increased slightly with time until the end of experiment.

The pH values, at this concentration, increased from 6.2 to 7.6, as can be seen in Fig. 4(b), indicating that ammonia and ammonium coexist in the solution at the same time, reaction (9) [31]. Furthermore, the reduction in nitrates into ammonia and ammonium occurred according to reactions (1) and (8).

In Table 1, same results were obtained in the cases of 3.95 and 30 mg L^{-1} of N-NO_3^- (figures not shown), and in three cases, nitrate removal does not exceed 40%.

Nitrates removal using BDD as anode/cathode material fitted the first kinetic order. Values of the apparent rate constant, k ($10^{-4}s^{-1}$), displayed in Table 1 for the three initial nitrates concentration showed that nitrates were eliminated rapidly and the kinetic decreased with the increase in initial concentration. After 2 h of electrolysis, nitrates removal was decreased from 94 to 85% with the increase in initial nitrates concentration from 65 to 500 mg N-NO_3^-. This decrease was also proved by the decrease in estimated kinetics rate presented in Table 1. This can be explained in terms of mass diffusion control and as well as to the saturation of the electrode surface

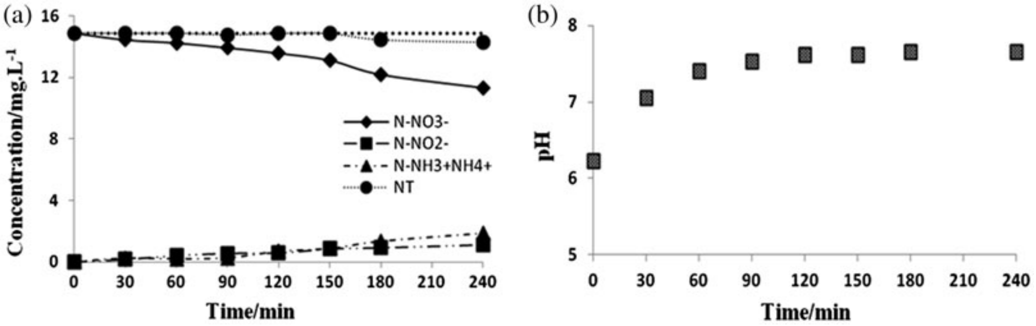

Fig. 4. Concentrations of nitrate removal (♦) N-NO_3^-, by-products formed: N-NO_3^-(■) N-NO_2^-, (▲) N-$NH_3 + NH_4^+$, and (●) total nitrogen (a), during the electrolysis of 14.88 mgL^{-1} of N-NO_3^-. pH evolution with electrolysis time (b). Experimental conditions: BDD anode, SS cathode; $j = 40\ mA\ cm^{-2}$; supporting electrolyte Na_2SO_4 (0.1 M); $pH_0 = 6.0 \pm 0.2$.

Table 1

Current efficiency (η) obtained for reduction in nitrate in BDD anode/cathode and BDD anode/SS cathode

Initial nitrate concentration		*65*	*250*	*500*
BDD anode/cathode	N-NO_3^-removal (%)	96.3	99.1	96.5
	N-NO_2^- formed (%)	0.1	0.1	0.1
	N-NH_3 formed (%)	43.6	12.5	8.8
	N-$N_{gaseous}$ formed (%)	52.6	86.5	87.6
	$HO^\bullet$estimated (mg L^{-1})*	206.27	724.23	1673.31
	η	19.70	128.77	256.77
	k ($10^{-4}s^{-1}$)**	4.15	3.92	2.41
	(R^2)	(0.98)	(0.99)	(0.96)
Initial nitrate concentration		*3.95*	*14.88*	*30*
BDD anode/SS cathode	N-NO_3^- removal (%)	24.3	24.1	34.4
	N-NO_2^- formed (%)	4.5	7.6	15.4
	N-($NH_3 + NH_4^+$) formed (%)	10.6	12.4	17.8
	N-$N_{gaseous}$ formed (%)	6.1	11.7	1.2
	η	0.58	7.07	6.05

*Quantity estimated at 30 min.

**Estimated kinetics rate of nitrates removal.

[41,42]. At low initial concentration, the electrochemical reaction was faster than the diffusion. Nitrates were expected to be reduced completely at the interface. When the initial concentration increased, more nitrates were transferred to the surface of electrode and the amount reduced was increased [42]. By contrast, when SS was used as cathode material, the kinetic of nitrate elimination was different.

3.2. Nitrite removal study and by-products formed

3.2.1. BDD anode/cathode

In case of sodium nitrite feed solutions, the efficiency of electrode was studied with three initial concentrations (25, 75, and 150 mg L^{-1} of N-NO_2^-).

The amount of nitrites was rapidly decreased, as shown in Fig. 5(a), that is in accordance with other works [12,43]. After 30 min of electrolysis time, initial nitrite concentration was rapidly decreased, around 90% was removed, it was fast oxidized into nitrates according to reaction (2) (in indirect sense), and we obtained a maximum nitrates concentration, 45.7 mg L^{-1} (around 60%). Moreover, nitrates formed were rapidly reduced on the surface of BDD cathode to nitrites at 1 h. Nitrites formed were increased slightly then reduced (a little concentration was detected) after 1.5 h, and simultaneously, the amount of ammonia reached a maximum and its concentration remained stable until the end of the experiment. Same behavior concerning nitrites trend was found by Pérez et al. and Hu et al. [12,43]. A mechanism of nitrates electro-reduction was proposed following the scheme in Fig. 6.

Same results were obtained with 25 and 150 mg L^{-1} of N-NO_2^- (Table 2), nitrates formed were totally

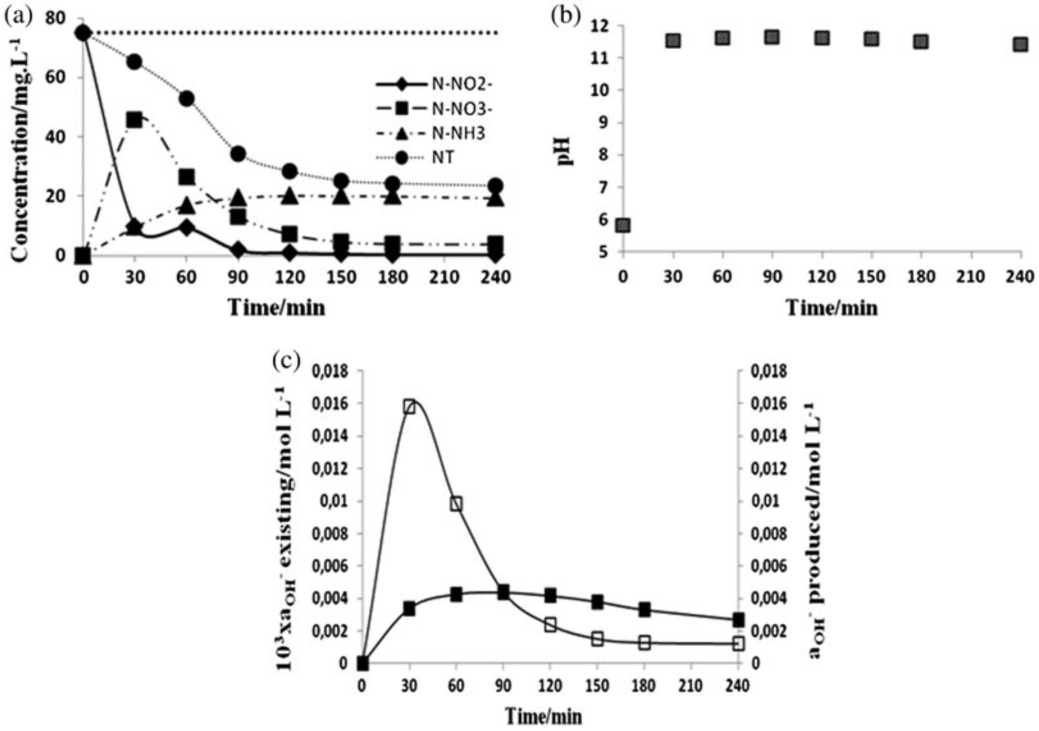

Fig. 5. Concentrations of nitrite removal (♦) N-NO_2^-, by-products formed: (■) N-NO_3^-, (▲) N-NH_3, and (●) total nitrogen, during the electrolysis of 75 mg L^{-1} of N-NO_2^- (a), pH evolution with electrolysis time (b), and comparison between the quantity produced (open symbols) and existing (solid symbols) of ion hydroxyl with electrolysis times during the electro-reduction of 75 mgL^{-1} of N-NO_2^- (c). Experimental conditions: BDD anode/cathode; $j = 40$ mA cm^{-2}; supporting electrolyte Na_2SO_4 (0.1 M); $pH_0 = 6.0 \pm 0.2$.

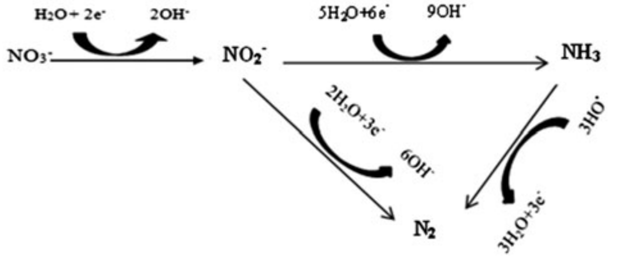

Fig. 6. Mechanism of electro-reduction in nitrate at BDD anode/cathode.

reduced, the percentage of ammonia produced decreases with the initial nitrate concentration opposite to $N_{gaseous}$ which the percentage increased with the increase in initial nitrate concentration that proved the selectivity into $N_{gaseous}$.

Estimated quantity of radicals (Fig. 5(c) and Table 2), in the case of feed solutions with nitrite, increased rapidly and reached a maximum after 30 min, as was obtained in case of nitrate solutions. The ammonia was adsorbed at the surface of electrode, which facilitated the direct oxidation to nitrogen gas by radicals [40].

3.2.2. BDD anode and SS cathode

Using cell with SS cathode and BDD anode, electrochemical nitrite removal was studied with three initial nitrite concentrations, 1.49, 4.46, and 8.92 mg L^{-1} of N-NO_2^-.

Nitrites were fast oxidized into nitrate (around 55% after 30 min) and reduced into ammonia and ammonium. In the first hour of electro-reduction, nitrites removal was around 91.5%, nitrates formed reached a maximum (2.5 mg L^{-1}) and then remained stable (Fig. 7(a)). Conversely to the results obtained at BDD anode/cathode, a high percentage of nitrates was formed, around 64.3%, and was slightly reduced to ammonia and nitrogen gaseous. Nitrites were also reduced into ammonia and ammonium, around 0.61 mg L^{-1} (13.4%). A low amount of nitrogen gaseous was rejected, 0.16 mg L^{-1} (14.6%) after 4 h of electrolysis. Results obtained (Figs. 5 and 7) clear the difference between results obtained at BDD cathode and SS

Table 2
Current efficiency (η) obtained for reduction/oxidation in nitrite in BDD anode/cathode and BDD anode/SS cathode

Initial nitrite concentration		*25*	*75*	*150*
BDD anode/cathode	N-NO$_2^-$ removal (%)	99.7	99.6	99.8
	N-NO$_3^-$ formed (%)	8.9	6.6	6.6
	N-NH$_3$ formed (%)	32.0	24.1	19.3
	N-N$_{gaseous}$ formed (%)	58.8	70.9	73.8
	HO$^\bullet$ estimated (mg L^{-1})*	99.21	268.75	773.10
	η	6.97	31.65	76.61
Initial nitrite concentration		*1.49*	*3.95*	*8.92*
BDD anode/SS cathode	N-NO$_2^-$ removal (%)	82.3	92.4	93.1
	N-NO$_3^-$ formed (%)	42.9	64.3	46.3
	N-(NH$_3$ + NH$_4^+$) formed (%)	19.1	13.4	27.9
	N-N$_{gaseous}$ formed (%)	20.3	14.6	18.8
	η	0.85	2.04	5.18

*Quantity estimated at 30 min.

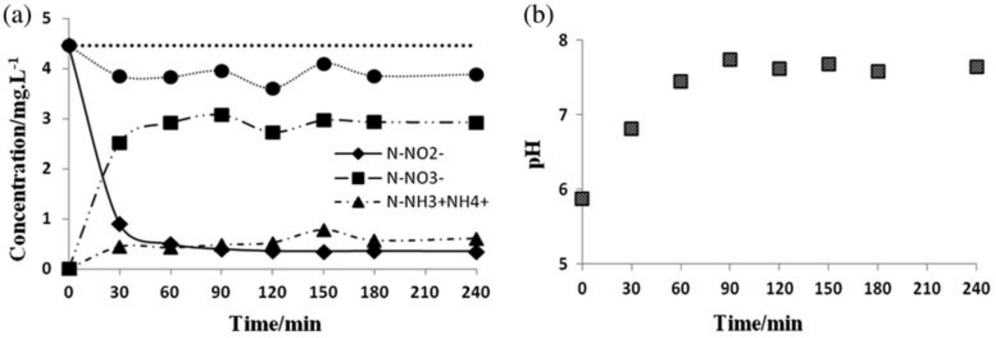

Fig. 7. Concentrations of nitrite removal (♦) N-NO$_2^-$, by-products formed:, (■) N-NO$_3^-$, (▲) N-NH$_3$, and (●) total nitrogen (a) during the electrolysis of 4.46 mg L^{-1}.pH evolution with electro-reduction time (b). Experimental conditions: BDD anode, SS cathode; $j = 40$ mA cm^{-2}; supporting electrolyte Na$_2$SO$_4$ (0.1 M); pH$_0$ = 6.0 ± 0.2.

cathode concerning the reduction in nitrates formed according to reaction (2) that nitrates formed at BDD cathode was reduced into ammonia and nitrogen gaseous, and the percentages were higher than 20 and 60%, respectively, (reactions (1–3) are favored). By contrast, at SS cathode, the reduction of nitrates into ammonia and nitrogen gaseous was not favored.

Table 2 depicts that the same results were obtained when the initial nitrites concentrations were 1.49 and 8.92 mg L^{-1} of N-NO$_2^-$ (figures not shown), and the big difference between the efficiency of the electro-reduction at the surface of two materials of cathode used was also proved.

3.3. Current efficiency (η) and EC

The main object of this study was to eliminate a maximum of nitrates and nitrites and to transform them into nitrogen gaseous. At the same time to obtain the minimum amount of by-products formed essentially ammonia and nitrites. Currents efficiencies (η), presented in Tables 1 and 2, were calculated according to Eq. (11) [5,44,45], for studying the efficiency of applied current to reduce nitrates and oxidize nitrites into nitrogen gaseous. For the determination of η, reactions (2) and (6) were considered.

$$\eta = \frac{Q(C_{f,NO_3^-} - C_{NO_3^-})}{I/nF} \tag{11}$$

where C_{f,NO_3^-} and $C_{NO_3^-}$ are influent and effluent concentrations of nitrate (mol cm^3), Q is the volumetric flow rate (cm^3 s^{-1}), I is the current (mA), n is the stoichiometric coefficient ($n = 5$), and F is Faraday's constant (C mol^{-1}).

Considering nitrates reduction at BDD anode/cathode, an important amount of nitrates was reduced into N$_{gaseous}$, and the currents efficiencies (η) were important and increase with initial nitrate concentra-

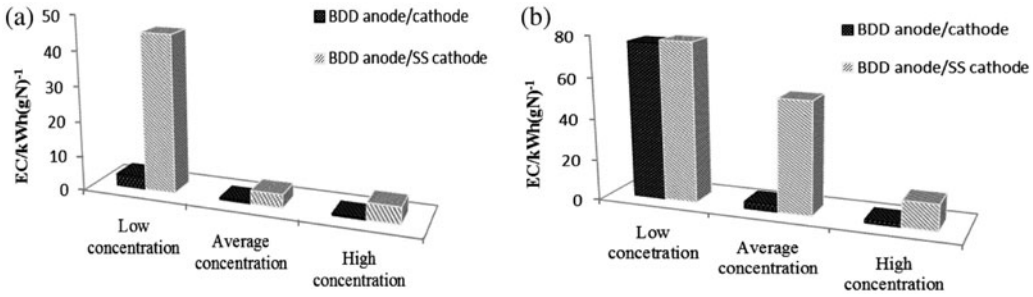

Fig. 8. Histograms of EC ($EC/kWh(gN)^{-1}$) in case of nitrate (a) and nitrite (b) reduction at BDD anode/cathode and at BDD anode/SS cathode.

tion. η was higher than 100%. This behavior could be attributed to the presence of bipolar BDD electrode (self-polarized) with $C_{N\text{-}NO_3^-} \geq 250\ \text{mg L}^{-1}$. In the case of nitrites reduction/oxidation at BDD anode/cathode, the current efficiency was low, by contrast of the amount of nitrogen gaseous formed, which demonstrates that reduction in nitrites to nitrogen gaseous is not favored but, it formed according to the reduction in nitrates formed (reaction (2)).

Moreover, when SS was the cathode and BDD was the anoden η was low in the case of electro-reduction in nitrates and nitrites, which may be due of the low reduction in NO_3^- and NO_2^- into N_2.

EC by two cells during elimination of nitrates and nitrites was calculated according Eq. (12) [28,46]:

$$EC(kWh(gN)^{-1}) = \frac{IEt}{\Delta C_N V_s} \tag{12}$$

where I is the applied current (A), V is the average cell voltage (V), t is the electrolysis time (h), V_s is the solution volume (dm^3), and ΔC_N is the decay in nitrogen ($g\,dm^{-3}$).

Fig. 8 shows that EC using SS cathode is more important than using BDD cathode. Increasing the initial concentration of nitrates reduced the EC in two cells used. This provides clear evidence of an attenuation of both the ionic species mobility and electric conductivity due to pronounced reaction mixture viscosity [45].

4. Conclusion

From the previously displayed results, it could be concluded that:

- BDD as material of cathode was efficient in terms of electro-reduction in nitrates and reduction/oxidation in nitrites into nitrogen gaseous, and the percentage of by-products formed essentially ammonia was low; it decreased with the increasing of initial concentrations. Nitrites formed disappeared after nearly 2 h of electro-reduction on BDD electrode.
- The production of radicals $HO^\bullet$ was more important using BDD anode/cathode than using BDD anode/SS cathode.
- The high quantity of radicals produced in the case of BDD anode/cathode was accompanied with the highest oxidation state of ammonia into $N_{gaseous}$, which increased the selectivity of nitrates reduction into $N_{gaseous}$.
- Finally, obtained results proved the efficiency of BDD cathode to remove all the amount of nitrates, even at high quantity by contrast of SS cathode; the nitrate reduction was not favored.

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