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Contribution to the study of the ammonium electro-oxidation in aqueous solution

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ABSTRACT

Ammonia and ammonium ions are potentially dangerous for the natural ecosystem due to their extreme toxicities to some aquatic species and human health. Several studies were focused for the treatment of these pollutions by application of various methods. Among them, the electro-catalytic oxidation was proposed as a novel advanced treatment technology for the NH_3 and NH_4^+ removal from wastewaters owing to its several advantages such as: degradation of several pollutants types, minimal generation of secondary wastes, easy and rapid performance. In this context, we have studied the direct electrochemical oxidation of NH_3 and NH_4^+ in aqueous solution using an electrochemical system by measurement of cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chrono amperometry (CA). The results suggested that the electro-oxidation of both NH_3 and NH_4^+ was efficient at Pt electrode compared with that performed by the other electrodes materials. However, the presence of chloride ions in the electrolytic medium inhibited the electro-oxidation of NH_3 and NH_4^+. Thus, the pH variation has affected the oxidation peak relating to the change in the NH_4^+ ionization state. Moreover, the initial NH_4^+ concentration and the applied potential value affected the current intensity of the characteristic oxidation peaks. The ammonia nitrogen (NH_3 and NH_4^+) concentration was significantly reduced from 100 to 31.039 mg-NH_4^+/L after an electrolysis time of 60 min and at an applied potential of –0.7 V/saturated calomel electrode (SCE) suggesting that the NH_3 and NH_4^+ were effectively oxidized.

Keywords: Ammonium; Ammonia; Electro-catalytic oxidation; Platinum; Aqueous solution

1. Introduction

Ammonia nitrogen (NH_3 and NH_4^+) was considered as the most toxic forms of the mineral nitrogen due to its extreme effect on the aquatic fauna, environment and human. The origin of this nitrogen pollution is principally caused by the excessive introduction of nitrogen fertilizers and composts issued from the animal farmers. Consequently, the contamination of groundwaters and the surface waters conduct to several inappropriate environmental states, such as: strongly promotion of eutrophication and proliferation of nitrifiers bacteria that could transform the ammonia nitrogen to undesired products such as: nitrites and nitrates [1–8]. Therefore, different techniques were elaborated for ammonia and ammonium treatment, such as: biological nitrification [9,10], chemical precipitation [11,12], membranes processes [13], adsorption [14,15] and catalytic oxidation methods [16]. However, these techniques can present certain disadvantages, including high operational costs and high sludge production [17].

Recently, electrochemical treatment methods have considered as the most efficient and proper technology for wastewaters treatment, owing to their easy operating and large applications for several pollutants degradation.

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The use of this technique in the decomposition of ammonium and ammonia to nitrogen gas is possible, because the Gibbs energy of ammonia nitrogen (NH_4^+ and NH_3) is higher than that of the nitrogen molecule (N_2) [18–20].

According to the literatures, different anodes materials were investigated, including the catalytic oxide alloy electrodes or so-called dimensionally stable anode (DSA) [21], boron-doped diamond (BDD) [21–25], platinum and well-dispersed platinum nanosheets [20], platinum submonolayer on the gold electrode [26], platinum nanocubes deposited on glassy carbon electrodes [27], platinum-Me binary and tertiary alloy [28–30], IrO_2 and thermally decomposed iridium oxide films [19,16,31], coated TiO_2 anode, TiO_2 and Pt/TiO_2 nanotubes for electro- and photo-electro-catalytic oxidation [32–34], RuO_2/Ti [17] and alloys based on Ni [35].

The application of this technique can act directly upon the effluents at the electrodes surface according to the Eq. (1) or indirectly by production of strong oxidants during the *in situ* treatment of chemical compounds present in the electrolytic solution (chloride or hydroxyl radicals) [18–20].

$$\begin{array}{llll} NH_3 \leftrightarrow NH_2OH_{ads} \leftrightarrow NOH_{ads} \leftrightarrow & NO & & \leftrightarrow NO_2 \leftrightarrow NO_2^- \leftrightarrow NO_3^- \\ \updownarrow & \downarrow \ \downarrow & & \\ NH_4^+ & N_2 ; N_2O \rightarrow N_2 & & \end{array} \quad (1)$$

The mechanism of the direct electro-catalytic oxidation of total ammonia nitrogen passes through three successive steps: (i) adsorption of ammonia nitrogen molecules onto the catalysis surfaces; (ii) decomposition of N–H links and (iii) desorption of N_2 molecules [35].

According to several researches, the mechanism of the direct electro-oxidation on Pt and Pt–Me binary alloys based electrodes depended of the medium pH [30,35,36]. In alkaline solution, the NH_3 is the dominant species according to the Eq. (2). The mechanism of its electro-oxidation proposed by Gerischer and Mauerer [37] consists of the dehydrogenation of adsorbed NH_3 to N_2 as final product (Eqs. (3)–(5)). Both formed intermediates (NH_x and NH_y, with x = 1 or 2 and y = 1 or 2) can be also chemically recombined to form $N_2H_{(x+y)}$, which is further electrochemically oxidized into N_2, according the Eqs. (7) and (8) [31,38]. Besides N_2, oxide nitrogen species (such as NO and N_2O) may be formed when the electrode surface is oxidized.

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O \quad pk_b = 4,74 \quad (2)$$

$$NH_{3ads} \rightarrow NH_{2ads} + H^+ + e^- \quad (3)$$

$$NH_{2ads} \rightarrow NH_{ads} + H^+ + e^- \quad (4)$$

$$NH_{x,ads} + NH_{y,ads} \rightarrow N_2 + (x+y)H^+ + (x+y)e^- \quad (5)$$

$$NH_{ads} \rightarrow N_{ads} + H^+ + e^- \quad (6)$$

$$NH_{x,ads} + NH_{y,ads} \rightarrow N_2H_{x+y,ads} \quad (7)$$

$$N_2H_{x+y,ads} + (x+y)OH^- \rightarrow N_2 + (x+y)H_2O + (x+y)e^- \quad (8)$$

$$NH_{ads} + OH^- \rightarrow N_{ads} + H_2O + e^- \quad (9)$$

The NH_3 oxidation potential depended on the anode material. According to the literature, the NH_3 oxidation potential values are summarized in Table 1.

$$2NH_4^+ \rightarrow N_2 + 8H^+ + 8e^- \quad (10)$$

$E^0 = -0.6$ to -0.75 V vs. SCE

Several studies have been devoted to the development of efficient electro-catalysts for ammonia nitrogen oxidation in alkaline and neutral solutions [20,26,27,30,32,39,40].

Different factors can affect the direct electro-oxidation of ammonia nitrogen, such as: the chemical nature of working electrode, temperature, electrolytic medium composition, applied potential, cell configuration and the hydrogen evolution. This last can affect the electro-oxidation in immediately consecutive scans by providing hydrogen molecules. The produced protons could be consumed increasing the local pH of the medium. This process could inhibit the ammonia nitrogen oxidation including oxygen evolution and the direct oxidation itself [19].

Furthermore, the chloride ions could affect the electro-oxidation of ammonia nitrogen by formation of active chlorine and hypochlorite (Eqs. (11) and (12)), which could react with NH_3 and NH_4^+ by indirect chemical oxidation producing undesired products (nitrate) in the electrolytic medium, according to Eq. (14) [18,22–25].

$$2Cl^- \leftrightarrow Cl_2 + 2e^- \quad (11)$$

$E^0 = +1.6$ V vs. SCE

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \quad (12)$$

Table 1
Oxidation potential values of NH_3 according to the literature

Anode material	Ammonia oxidation potential	References
$IrO(OH)_2/IrO_2(OH)$	0.3–0.7 V vs. MSE	[19]
Pt	–0.30 to –0.37 V vs. SCE –0.67 V vs. MSE 0.50–0.75 V vs. SHE	[20,26–30,32]
Pt	0.8 V vs. SCE	[36]
Pt	–0.25 V vs. Hg/HgO	[38]

Note: In neutral and acid medium.
MSE - mercury-mercurous sulfate electrode; SCE - saturated calomel electrode; SHE - standard hydrogen electrode.

$$2NH_4^+ + 3HClO \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \quad (13)$$

$$NH_4^+ + 4HClO \rightarrow NO_3^- + H_2O + 6H^+ + 4Cl^- \quad (14)$$

$$2NH_3 + 3HClO \rightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \quad (15)$$

In this work, various electrochemical techniques were carried out in order to investigate the electro-oxidation of ammonia nitrogen (NH_3 and NH_4^+) to atmospheric nitrogen. The CV and LSV measurement methods were used to evaluate the electro-catalytic activities of several anode materials behavior ammonia nitrogen oxidation. Therefore, to study the electro-oxidation method of ammonia nitrogen in aqueous solution, various experimental variables have been considered. At the platinum anode, the direct electro-oxidation of the desired substances was evaluated by variation of the pH, applied potential, scan rate, electrolysis time, initial ammonia nitrogen concentration in the solution and in the presence of chloride ions in the electrolytic solution.

2. Experimental setup

Electrolysis experiments were carried out in a single-compartment with three-electrode cell (200 mL) using Autolab PGSTAT 302 N and a maximum output of 5 A and 30 V. The counter electrode was a Pt wire, and the reference electrode was saturated calomel electrode (SCE; Radiometer Analytical), which has a potential of +0.2415 V vs. standard hydrogen electrode (SHE). The three-electrode configuration had a 5-mm electrode gap between the cathode and the anode, and 2-mm electrode gap between the anode and the reference electrode. The cell was filled by 100 mL of the electrolytic solution containing ammonium ions (NH_4Cl or $(NH_4)_2SO_4$) at well-defined concentration.

In all experiments, the feed tank was kept regulate at room temperature and at neutral pH, unless in the experiments of pH effect.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out in the potential range from −1 V to +0.4 V vs. SCE. The chrono amperometry (CA) measurement was applied for the electrolysis tests at well-defined potential and at various electrolysis times.

The effect of working electrode material on the ammonium electro-catalytic oxidation was studied using the following pure anodes: zinc, aluminum, graphite, stainless steel and platinum, with the surfaces area of 0.635, 1.62, 0.282, 0.785 and 4 cm^2, respectively. All electrodes were mechanically polished before used and washed several times with distilled water. Before and after all electro-analysis experiment, the electrodes were abraded with emery paper, rinsed thoroughly with water, immersed in acetone and finally dried. The pH of the solution was kept constant at neutral; the scan rate was 50 mV/s; and the initial ammonium concentration was 272.72 mg-NH_4/L (using $(NH_4)_2SO_4$) ranging the voltage of the LSV measurement from –2 to +2 V.

The effect of initial ammonium concentration on the process was investigated varying the initial ammonium concentrations from 10 to 1,000 mg-NH_4^+/L at the scan rate of 50 mV/s. The pH was kept constant at 7 using a Pt anode.

For the study of scan rates effects on the electro-oxidation process, the results were obtained after five consecutive scans at the following scan rates: 5, 10, 50, 100 and 500 mV/s in neutral electrolytic solution containing 100 mg-NH_4/L (using $(NH_4)_2SO_4$).

The effect of chloride ions on the process was investigated by CV measurement of two electrolytic solutions, containing $(NH_4)_2SO_4$ 272.72 mg-NH_4^+/L and NH_4Cl 336.44 mg-NH_4^+/L. The pH and the scan rate were kept constant at 7 and 50 mV/s, respectively, using a Pt anode.

The study of pH effect on the ammonium electro-oxidation was carried out at three pH values: acid = 3, neutral = 7 and alkaline = 11, with an initial ammonia nitrogen concentration of 100 mg-NH_4^+/L.

Optimization of the time electrolysis was realized by variation of its value from 0 to 3,600 s with an initial ammonium concentration of 100 mg-NH_4^+/L. The pH was kept constant at 7; the scan rate of the CV measurement of the solution before and after electrolysis was regulated at 50 mV/s using a Pt as anode.

Ammonia nitrogen analyses were carried out by UV-Visible spectrophotometer (Thermo scientific Genesys 10S UV-Vis) at a wavelength of 630 nm according to the water effluents dosage norms [41].

3. Results and discussion

3.1. Anode material effect

The anode nature influences significantly the electro-oxidation process; for this reason, the materials of platinum, zinc, aluminum, graphite and stainless steel were tested against the ammonium electro-oxidation. The LSV curves are shown in Fig. 1(B), respectively, and the CV measurement of the control solution (without ammonia nitrogen) is shown in the Fig. 1(A).

According to Fig. 1, the anodic peak that corresponds to the NH_4^+ oxidation was appeared only for the platinum electrode at approximately –0.7 V vs. SCE (Eq. (10)). For the other anodes, the voltammograms did not present any characteristic peak of NH_4^+ oxidation.

Therefore, the increase of the current intensity at above –1.1 V vs. SCE and −0.8 V vs. SCE for the zinc electrode, and at –1.4 V vs. SCE and 1.3 V vs. SCE for the Al electrode (Fig. 1(B)) are due to the passivation of the materials and not to the ammonium oxidation processes, which was clearly visualized on the electrode's surfaces, especially at low scan rate (data not shown).

Therefore, the increase of current intensity at about 1.3 V vs. SCE for the Al electrode was related to the aluminum oxidation according to Eq. (16). Thus, the oxidation peak observed at +0.5 V vs. SCE was due to the formation and the growth of an aluminum oxide film layer (Eqs. (17) and (18)) [42,43].

$$Al^{3+} + 3e^- \leftrightarrow Al \quad (16)$$

E^0 = –1.662 V vs. SCE

$$Al_2O_3 + 3H^+ + 3e^- \leftrightarrow 2Al + 3H_2O \quad (17)$$

E^0 = –1.494 V vs. SCE

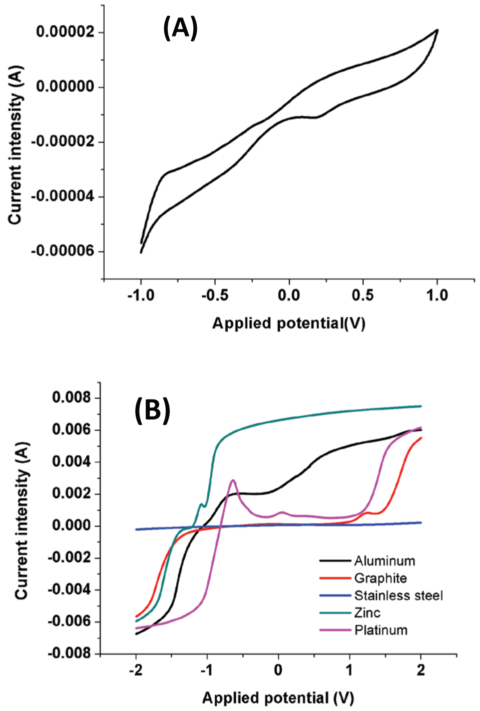

Fig. 1. CV measurement of the control solution (without ammonia nitrogen) (A) and LSV measurement of the solution containing 272.72 mg-NH_4^+/L (B), using various anode materials: scan rate = 50 mV/s and pH = 7 at 25°C.

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^- \tag{18}$$

E^0 = +0.5 V vs. SCE

Moreover, the results of CV and LSV measurements of the Zn electrode indicate that the oxidation of Zn at –1.1 V vs. SCE has degraded its electro-catalytic activity for NH_4^+ oxidation. Even though the NH_4^+ oxidative current is even lower than that of zinc oxidation. As shown in Figs. 1(A) and (B), the Zn electrode was oxidized at –1.1 V vs. SCE forming $Zn(OH)_2$ and ZnO films on the surface layer at –0.8 V vs. SCE according to Eqs. (19)–(21) [44,45]:

$$Zn \rightarrow Zn^{2+} + 2e^- \tag{19}$$

E^0 = –1.1 V vs. SCE

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \tag{20}$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \tag{21}$$

However, the Zn^{2+} and Al^{3+} ions generated by the anodes (Eqs. (16) and (19)) conduct to consumption of the electrodes and the contamination of electrolytic solution by these ions. Also, the oxide layer formed on the electrodes surface could inhibit the NH_4^+ oxidation performance. Consequently, the application of zinc as well as the aluminum, as electro-catalysts for ammonia nitrogen oxidation, is practically infeasible.

So, the platinum electrode was the most active anode for this treatment according our results and several previous researches [38,40,46,47]. Platinum is a noble metal; it has a high affinity and high activity for oxidations processes involving ammonia nitrogen. It is also highly corrosion resistant and very stable [26,27,47,48]. For this reason, the study of the effect of operating conditions on the electrochemical oxidation of ammonia nitrogen was conducted using a Pt as working electrode.

3.2. Chloride effect

The response of the Pt electrode in both solutions containing ammonium chloride and ammonium sulfate, respectively, are shown in Fig. 2.

The rough curve at below –1 V/SCE was usually attributed to the evolution of hydrogen evolved on electrode during the cathodic polarization. In absence of chloride ions, the anodic peak of NH_4^+ oxidation was observed at –0.7 V vs. SCE according to Eq. (10). However, this peak was disappeared in the CV and LSV voltammograms of the electrolytic solution containing chloride ions, as shown in Fig. 2. This observation was attributed to the adsorption and oxidation of Cl^- to Cl_2 on the anode surface, according to Eq. (11) that could affect the NH_4^+ electro-oxidation process. Therefore, the formed active chlorine at the anode (Eq. (11)) could contribute to the NH_4^+ chemical oxidation, because the free chlorine and hypochlorite are sufficiently strong chemical oxidants according

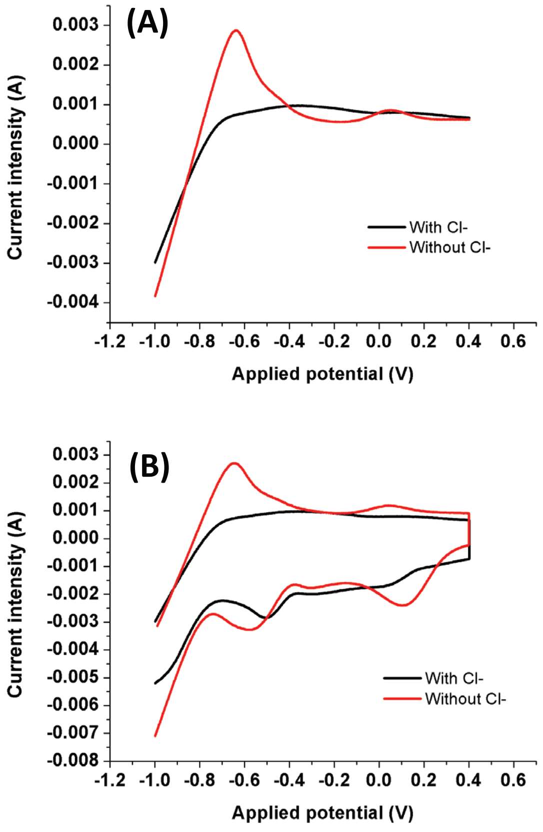

Fig. 2. LSV (A) and CV (B) measurements on Pt electrode, with and without chloride ions: pH = 7 and scan rate = 50 mV/s.

to Eqs. (12)–(14). The chloride ion competes ammonium ions for adsorption sites at the electrode surface and inhibits the decomposition reaction of ammonium to atmospheric nitrogen. Consequently, it could limit or even stop the electrochemical oxidation processes [18,21,25].

This reaction was improved at both neutral and alkaline pH in the range of 7–12. However, the hypochlorite could contribute to the formation of undesired by-products, such as: nitrogen oxides and oxyanions. Also, it could be further oxidized to chlorate and perchlorate, which are two toxic water contaminants too [40].

Moreover, the chemical reaction between NH_4^+ and free chlorine promotes the formation of chloramines, according to Eqs. (22)–(24), which are considered as very toxic substances [17,22,23,49].

$$NH_4^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+ \tag{22}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \tag{23}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \tag{24}$$

Nevertheless, two cathodic peaks were observed at –0.53 V/SCE and 0.12 V/SCE that can be correspond to the reduction of nitrate to NH_3 (Eq. (25)) and to nitrite (Eq. (26)) [25,26,50].

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \tag{25}$$

$E^0 = -0.248$ V vs. SCE and equilibrium $E = 0.170$ V vs. SCE

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^- \tag{26}$$

$E^0 = -0.6$ V vs. SCE

3.3. Scan rate effect

The results of the scan rate effect were studied by the CV and LSV methods and shown in Fig. 3. The increase of scan rate range increased the peak intensity of the NH_4^+ oxidation at –0.7 V vs. SCE using a Pt anode.

The results indicate the same characteristics, not exactly the same potential value. Differences were also noted in the total current peaks intensities and their sizes, which have increased with increasing of the scan rate value. The oxidation mechanism previously presented in Eq. (10) referred to the appearance of the anodic peak at about –0.6 to –0.75 V vs. SCE, as found in several previous researches [40,36].

The differences in the current intensities during the voltage at various scan rates were related to the size of the diffusion layer that depended of the scan rate. In a slow voltage scan, the diffusion layer was low comparing with that performed at rapid scan rate. This result was related to occurring of intermediate adsorption reactions of the formed species according to Eqs. (2)–(6) that could block some active sites of the electrode surface. The occurred intermediate reactions were related to the presence of NH_3 with the predominant ions of NH_4^+ in the medium at neutral pH according to the equilibrium presented in Eq. (2). On the other hand, the relation between I_p (faraday current density) and v (scan rate) is $I_p = C.v$, where C is the concentration of the species, confirmed this hypothesis. Therefore, the reaction of NH_3 oxidation behavior Pt electrode was occurred by rapid electron transfer kinetic, which was often referred to the reversible processes [28,36]. As the result, the optimal scan rate for this oxidation process was in the range of 50–100 mV/s.

3.4. Initial NH_4^+ concentration effect

The increase of the initial NH_4^+ concentration affected considerably the current intensity and consequently the oxidation efficiency. When the initial NH_4^+ concentration increased from 10 to 1,000 mg-NH_4^+/L, the current intensity increased to 0.0012 A (Fig. 4).

The oxidation peak intensity increased with increasing of the initial ammonium concentration, until obtaining a maximum value at 500 mg-NH_4^+/l. After this value, the peak intensity kept constant with further increasing of the initial ammonium concentration. This observation can be attributed to the excessive formation of adsorbed N_{ads} that can block of the electrode surface [29].

Hence, the NH_4^+ concentration depended of the electrolysis time; according to Mahvi et al. [17], during 10 min of

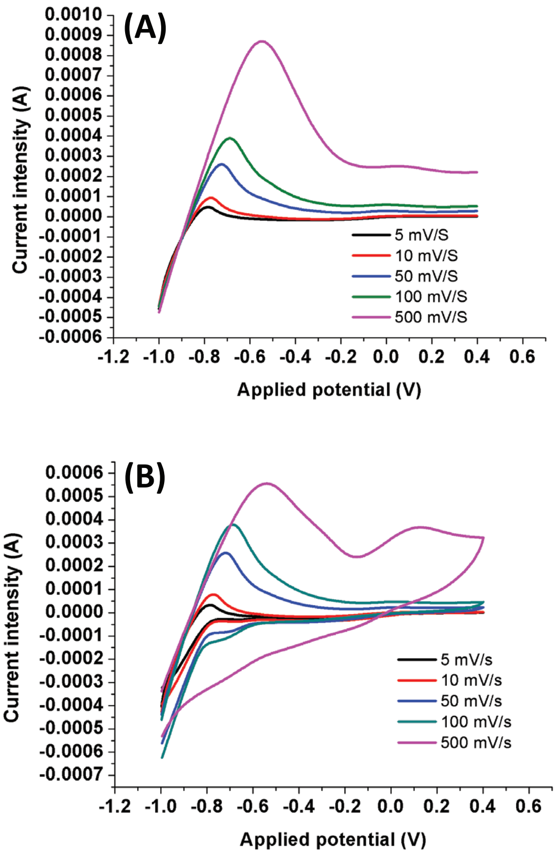

Fig. 3. LSV (A) and CV (B) measurements of the solution of 100 mg-NH_4^+/L at various scan rates, using Pt anode with pH 7 and 25°C.

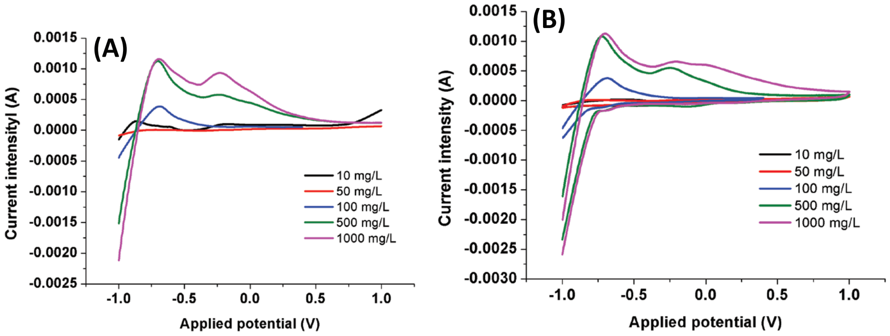

Fig. 4. LSV (A) and CV (B) measurements using Pt anode at various initial ammonium concentrations, with scan rate of 50 mV/s, pH 7 and 25°C.

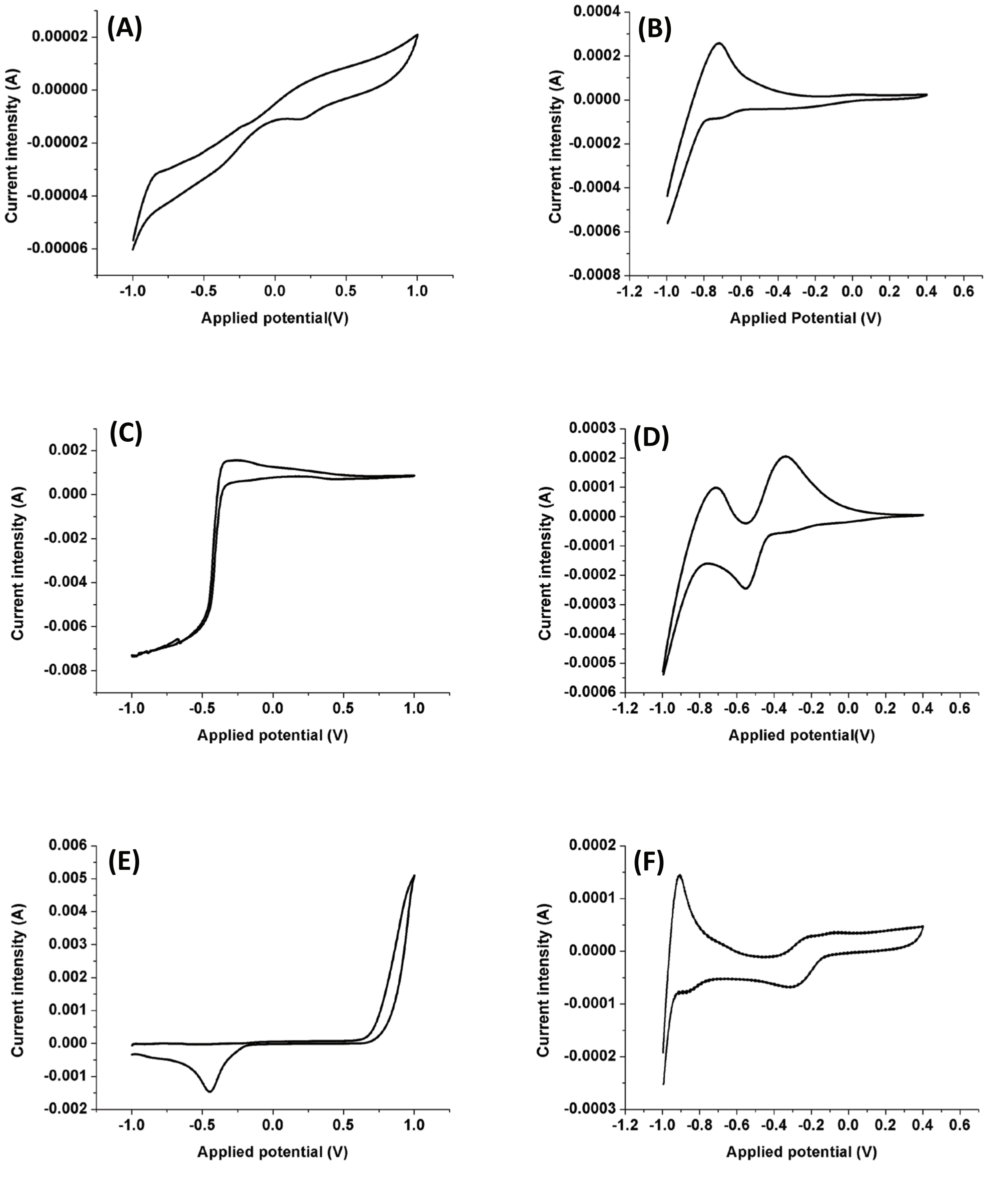

Fig. 5. CV measurements of: control neutral solution (without ammonia nitrogen) (A); solution containing 100 mg-NH_4^+/L of $(NH_4)_2SO_4$ (B); control acid solution (H_2SO_4 0.1 M) (C); solution containing 100 mg-NH_4^+/L of $(NH_4)_2SO_4$ + H_2SO_4 0.1 M (D); control alkaline solution (NaOH 0.1 M) (E) and solution containing 100 mg-NH_4^+/L of $(NH_4)_2SO_4$ + NaOH 0.1 M (F): scan rate = 50 mV/s using Pt anode.

electrolysis, the oxidation efficiency was 30% with an initial NH_4^+ concentration of 15 mg/L. This value was decreased to 10% when the initial NH_4^+ concentration was 100 mg/L. Thus, during 60 min, the electro-oxidation efficiency could attain up to 95% for all tested concentrations.

3.5. pH effect

Three pH medium were tested, and the results of both CV and LSV measurements at 50 mV/s are shown in Fig. 5.

The potential of the oxidation peak was different for the three tested medium: acid, neutral and alkaline, which were, respectively, –0.7; –0.75 and –0.9 V vs. SCE. These peaks were not appeared in the voltammograms of the control solutions confirming that these peaks were attributed to the oxidation of NH_3 and NH_4^+ according to Eqs. (2)–(10). Therefore, in acid medium, another peak was appeared at approximately –0.3 V vs. SCE, which was appeared also in the acid control voltammograms.

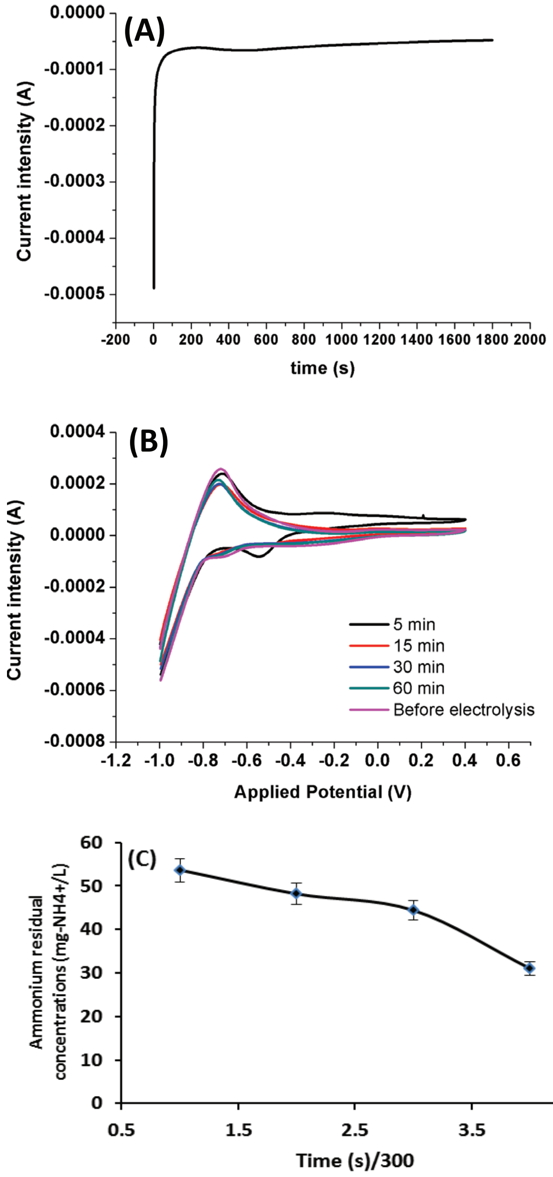

Fig. 6. CA measurement during 60 min at –0.7 V vs. SCE with 100 mg-NH_4^+/L (A); CV measurements after various electrolysis times at scan rate of 50 mV/s (B) and variation of NH_4^+ concentrations as a function of time (C) using Pt electrode at pH 7 and 25°C.

The electrochemical oxidation of the NH_3 in alkaline solution on Pt working electrode was studied in several researches; it showed an important electro-activity compared with the other ionization state of ammonia nitrogen [38,47]. However, some intermediate reactions that conduct to the formation of N_{ads} could affect the NH_3 oxidation on Pt anode and inhibit the N_2 formation, because the adsorption energy of N_{ads} on Pt is too high for allow the recombination of two N atoms. Consequently, N_{ads} is considered as poisoning species because it can block the active electrochemical sites on the Pt anode surface [19,27,35,38].

Therefore, neutral pH is the most preferable medium for this electro-treatment because the electro-oxidation do not produce poisoning species [14,17,29].

3.6. Time electrolysis effect

The time electrolysis effect was studied by the CA measurement, at an initial NH_4^+ concentration of 100 mg-NH_4^+/L, an applied potential of –0.7 V vs. SCE and pH = 7 at various time electrolysis periods. The CV measurement of the solution before and after electrolysis was conducted in order to show the influence of the electrolysis on the oxidation peak intensity. The CA and CV voltamogramms are shown in Fig. 6. Thus, determination of residual NH_4^+ concentration is also provided in Fig. 6(C).

After 5 min of electrolysis, the NH_4^+ electro-oxidation was realized until above 50% with a residual NH_4^+ concentration of 53.67 mg-NH_4^+/L. This percentage was improved by increasing of the electrolysis time until a removal efficiency of above 70% with a residual NH_4^+ concentration of 31.03 mg-NH_4^+/L during 60 min of electrolysis. This result is in accordance with that found in the literatures.

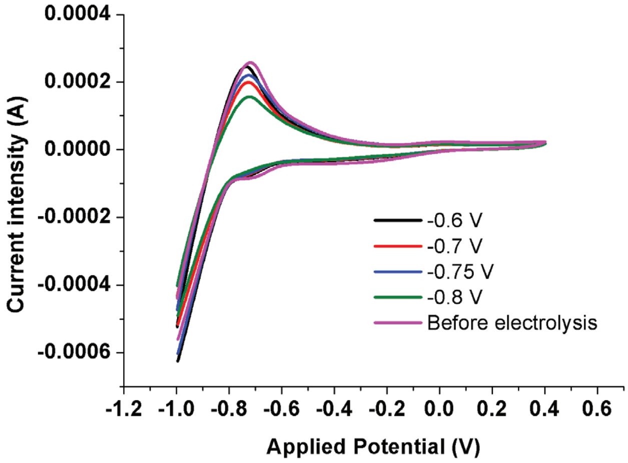

Fig. 7. CV measurement of the solution after 30 min of electrolysis at different applied potentials: pH = 7, initial NH_4^+ concentration = 100 mg-NH_4^+/L and scan rate = 50 mV/s.

Therefore, prolonged electrolysis time improved the NH_4^+ electro-oxidation yield [17].

3.7. Applied potential effect

The applied potential effect on the NH_4^+ electro-oxidation during 30 min of electrolysis was studied by application of the CA method at various applied potential values, ranging from –0.6 to –0.8 V vs. SCE. After electrolysis, the resulted solutions were analyzed by CV, as shown in Fig. 7.

According to Fig. 7, the increase in the applied potential value from –0.6 to –0.8 V vs. SCE increased the NH_4^+ electro-oxidation efficiency, which was clearly appeared by the decrease of the current peak intensity. The applied potential has the same effect on the process as the current intensity. According to several researches, the current was positively correlated with the NH_3 and NH_4^+ removal until attain a certain limit value of current when the oxidation electro-activity loses its efficiency [14,17].

4. Conclusion

In the present work, the feasibility and the different experimental factors affecting the ammonia nitrogen removal from aqueous solution were studied by electrochemical oxidation method using Pt electrode, at neutral pH and without Cl^- in the electrolytic solution. The results of anode nature effect allow selecting the Pt as the most electro-active material, the voltamogramms of ammonia nitrogen oxidation using this anode material showed the characteristic oxidation peak of NH_4^+ at around –0.7 V vs. SCE. The chloride ions could affect the NH_4^+ electro-oxidation reaction and acting upon the indirect NH_3 and NH_4^+ oxidation that conduct to the formation of undesired by-products. Moreover, the NH_4^+ ionization state was changed according to the pH of the solution, so each state had its oxidation potential. The initial NH_4^+ concentration and the applied potential value affected the current intensity of the characteristic oxidation peaks. The effect of time electrolysis revealed that the increase in the electrolysis duration increased the NH_4^+ removal efficiency, which could attain above 70% during about 60 min. Furthermore, the applied potential has a considerable effect on the current intensity of the NH_4^+ oxidation peak; the results suggested that the increase of the applied potential increased the NH_4^+ electro-oxidation, which was clearly proved by the CV measurements. However, at very high applied potentials, the system has not revealed any electro-activity for NH_4^+ oxidation, and poisoning species could be formed on the anode surface conducting to its passivation.

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