ELECTROCATALYTIC ACTIVITY SURVEY OF SOME CATHODE MATERIALS FOR THE REDUCTION OF NITRITES AND NITRATES IN AQUEOUS SOLUTION

Yassmina ANGAR,[a]* Sofiane DAOUDI,[b] Salima KEBBOUCHE-GANA[c] and Nacer-Eddine DJELALI[a]

[a]Laboratory of treatment and formatting of polymers, Faculty of engineering sciences, University of M'Hamed Bougara, Boumerdes 35000, Algeria
[b]Chemistry department, Faculty of Sciences, University of M'Hamed Bougara, Boumerdes 35000, Algeria
[c]Laboratory of VALCOR, Faculty of sciences, University of M'Hamed Bougara, Boumerdes 35000, Algeria

The electrochemical techniques are the subject of increasing interest on the environmental remediation methods thanks to their efficiency and their selectivity. It was classified among the cleanest methods because it does not produce sludge and undesirable intermediate byproducts. For these reasons, we have chosen this technology for the reduction of nitrites and nitrates ions from aqueous solutions. The objective of our study is the comparison of several cathodes materials performances, in order to promote an optimal electro-reduction of these ions. Indeed, we have used the copper, graphite, stainless steel and zinc as cathodes; among them, we have selected the most efficient on which we have optimized the operational conditions. The results suggested that the copper cathode was the most efficient for the reduction of both tested ions compared to the other tested materials. Therefore, the optimization of operational conditions allows us to fixed them at: scan rate=50 mV/s, initial effluent concentration=100 mg/L, pH=7 and potential range of the cyclic voltammetry scanning of [-1,+1]V/SCE for both ions. Under these optimal parameters, the reduction yield after 45min was important that can achieve 96.5% and 99% for nitrites and nitrates respectively.
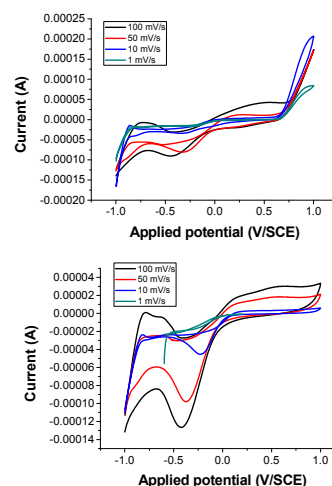
INTRODUCTION

Nitrites and nitrates are considered as essential nutrients for the growth of plants and certain microorganisms. However, the excessive use of these nitrogen forms as fertilizers leads to the imbalance of the nitrogen cycle and thus conduct to several pollution problems by; their accumulation in the soil as organic and mineral matters and consequently the pollution of the water reservoirs because of the high solubility of nitrites and nitrates in cold water.[1,2] Moreover, some studies have shown that 10% of this pollution is attributed to industrial activities including; food industry that used nitrites as antimicrobial agents, heavy industry that generate these pollutions during various processes, pharmaceutical industry that made these oxide nitrogen during the synthesis of certain drugs.[3,4] The water pollution by these matters conduct to the development of eutrophication phenomena that leads to asphyxiation and consequently the disappearance of certain aquatic species by default of oxygen and light.[4] Furthermore, the nitrate could be transformed to

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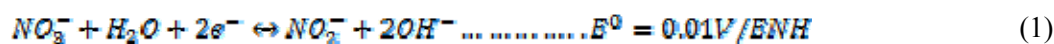* Corresponding author: y.angar@univ-boumerdes.dz

nitrites by bacteria that are naturally present in the digestive system, the formed nitrites can cause methemoglobinemia malady.[5]

Indeed, researches have been devoted to combat the exponential propagation of nitrite and nitrate in water and also in soil. Over the past four decades, science has opened several doors to treat this pollution in biology by dentrifications reactions (heterotrophic,[6–8] autotrophic[9–11] and physicochemistry by application of several techniques such as; ionic exchange,[12–14] membrane treatment,[15] nanofiltration[16] and other). Thus, each method has their advantages and disadvantages depending of their effectiveness and their environmental consequences. So, some treatment methods can only move the pollution from the aquatic environment to another medium. Other methods can lead to the production of undesirable byproducts that require further processing.

Among the nitrate and nitrite treatment methods, the electrochemical techniques are known as the cleanest advanced treatment, it used to remove nitrites and nitrates and several other pollutants from the electrolytic medium by oxidation or reduction without producing sludge or toxic byproducts.[17–19]

The electrochemical reduction of nitrate ions at the cathode surface could gave various products, such as nitrites, ammonia or nitrogen gas depending to the applied potential, the reaction mechanisms of these reductions are presented in the following equations (1)–(3).[18, 20–22]

$$NO_3^- + H_2O + 2e^- \leftrightarrow NO_2^- + 2OH^- \ldots\ldots\ldots\ldots E^0 = 0.01V/ENH \tag{1}$$

$$NO_3^- + 3H_2O + 5e^- \leftrightarrow \frac{1}{2}N_2 + 6OH^- \ldots\ldots\ldots\ldots E^0 = 0.26V/ENH \tag{2}$$

$$NO_3^- + 6H_2O + 8e^- \leftrightarrow NH_3 + 9OH^- \ldots\ldots\ldots\ldots E^0 = -0.12V/ENH \tag{3}$$
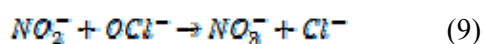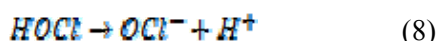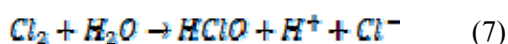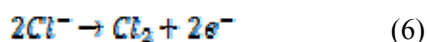
In the other hand, the principal cathodic reactions of the electrochemical reduction of nitrites ions depending of the applied potential are shown in the equations (4) and (5).

$$NO_2^- + 2H_2O + 3e^- \leftrightarrow \frac{1}{2}N_2 + 4OH^- \ldots\ldots\ldots\ldots E^0 = 0.406V/ENH \tag{4}$$

$$NO_2^- + 5H_2O + 6e^- \leftrightarrow NH_3 + 7OH^- \ldots\ldots\ldots\ldots E^0 = -0.165V/ENH \tag{5}$$

Moreover, the elimination of nitrite could be effectuated by indirect chemical reaction in the presence of the chloride in the medium according to the following mechanism.[20–22]

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{6}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{7}$$

$$HOCl \rightarrow OCl^- + H^+ \tag{8}$$

$$NO_2^- + OCl^- \rightarrow NO_3^- + Cl^- \tag{9}$$

Nitrites ions are chemically oxidized to nitrates by the intermediate of hypochlorite ion (eq. 9), the produced nitrate transforms to atmospheric nitrogen according the eqs. (1), (2) and (3).

Therefore, researches have focused on studying of the activity and the selectivity of cathode materials for the reduction of nitrates and nitrites. Thus, the most effective materials for this treatment are the noble metals such as; platinum,[23] lead,[24] nickel.[25,26] Moreover, certain transition metals have presented an important activity for these reductions such as; copper[27,28] and their alloys with palladium (Pd-Cu),[27,29,30] some of which are very active in acidic medium.

In the present work, we have elaborated four materials of copper, graphite, stainless steel and zinc as cathodes, in order to evaluate their electrocatalytic effectiveness for the electrochemical reduction of nitrates and nitrites in aqueous solution.

The selection of these materials is related to their availability, electroactivity, non passivity in the nitrites and nitrates reduction ranges and their effectiveness without production of harmful products. The use of our selected materials is beneficial compared to that studied in previous researches, such as; noble metals[23,26] and alloys[27,29] that required a post fabrication, several chemical reagents for their treatments and the high costs of the raw materials.

We have compared the performance of each material to select the best one among them that gave significant reductions of both ions; nitrate and nitrite. Using this cathode, we have studied the effect of the operating conditions on the reaction in order to provide a favorable reaction medium for a significant electro-reduction of the desired ions.

MATERIALS AND METHODS

Reagents and solutions

The reagents used in this work are; Sodium nitrate ($NaNO_3$), sodium nitrite ($NaNO_2$), Sodium hydroxide ($NaOH$), sodium salicylate ($C_7H_5NaO_3$), potassium nitrate (KNO_3), potassium sodium tartrate ($C_4H_4KNaO_6$). All these reagents are solid salts with average purities of 99%. Thus, the solutions of these reagents used for our manipulations were prepared by distilled water.

Elaboration of the cathodes

Copper electrode

The copper electrode used in this work is a plate lamina with dimensions of 6 cm × 2 cm and a thickness of 1mm. So, we have limited the active surface of this lamina at 4.4×2 cm^2, this surface are polished manually by abrasive papers of increasing grit sizes of 120; 220 and 400 in order to eliminate large scratches to obtain uniform surface. After that, the active surface of copper electrode is polished in the polishing machine using different abrasive papers started by 600, 800 and then 1200 during 5 min of each one with a rotator speed of 500 RPM under a continuous water flow. Subsequently, we plunged the polished electrode into an acetone solution for 30 min to remove any organic matter that may be present on the surface. Finally, the electrode was polished once again by sandpaper of 1200 and rinsed with distilled water.

Zinc, graphite and stainless steel electrodes

These three materials have not a uniform surface, for this reason they have been reformed in order to obtain easily usable electrodes with a well-defined active surface area. So, we have attached the materials by a current-conducting wire to connect it to the potentiostat. In the other hand, we have prepared the epoxy resin to isolate the unwanted surfaces of the electrodes. In addition, we covered the electric cable with a plastic pipe to prevent any contact with the electrolytic solution. Then we have put our electrode in a mold previously lubricated with Vaseline to facilitate the electrode demoulding, and we have introduced the resin in the mold all around the electrode to cover the sides. The resin was dried in the open area for 12 hours until the solidification of the resin and the easily demoulded of the electrodes.

The obtained electrodes had irregular contact surfaces, which require several polishing in order to eliminate exceed resin and to uniform the active area. For that, the electrodes were firstly manually polished by abrasive paper of 120 and 220, and then by polishing machine using different abrasive papers started by 600, 800 and then 1200 during 5 min for each one with a rotator speed of 500 RPM under a continuous water flow to obtain very smooth and homogeneous electrode surfaces. The electrodes were immersed in acetone solution for 30 min and polished once again by sandpaper of 1200 and then rinsed with distilled water. The characteristics of these electrodes are presented in the following table (Table 1).

Construction of the electrochemical chain

Electrochemical cell used in this study is a double wall Pyrex glass with a capacity of 100 ml, equipped with a lid that contains three necks. For the anode, we used platinum as anode of the oxidation reactions, and the saturated calomel electrode as reference electrode.

The electrodes are connected to the potentiostat and the resulting graphs are executed on a computer recorder, which is connected to the potentiostat. All electrochemical experiments were performed at open air.

Study of operating conditions effect on the nitrite and nitrate reduction

This study was carried out on a cell containing 100 mL of the contaminated solution (with nitrites or nitrates) at a concentration of 100 mg/l using cyclic voltammetric technique.

Table 1

Characteristics of tested counter electrodes

	Base area (cm^2)	Weight (g)
Zinc	0.635	65,4
Graphite	0.811	18.48
Stainless steel	0,785	17,33

The scanning range of voltammetry was optimized in order to delimit the range of scanning potential, for this reason we have scanned the potential of the cyclic voltammetry in the interval of -2 V to a high potential of +2 V returned to a started value of -2 V/SCE for the copper cathode.

Therefore, for the scan rate effect study, at the delimitated scanning range, different scan rate were considered (1, 10, 50 and 100 mV/s).

Moreover, we tested four cathode materials to select the best among them for the optimal reduction of the desired ions. Under the optimal scan rate and scanning range the electrodes of copper, zinc, stainless steel and graphite were tested for these reductions reactions.

For the effluent concentration effect study, the previous parameter were maintained at their optimal values with different concentrations of the contaminated solutions (10 mg/L, 50 mg L, 100 mg/L, 200 mg/L, 300 mg/L) respectively. The pH is an important factor in the equilibrium of the reactions. The pH of the contaminated solution were changed at different levels starting with acid solutions (3 and 5), neutral solutions pH= 7 and alkaline solutions (9 and 11).

After selecting the best cathode materials for both solutions and optimal values of initial concentration and pH, multi-cycle voltammetric tests of: 10, 30, 60 and 100 were applied during well-defined times at optimal potential range and scan rate.

The residual nitrates concentrations were determined after each multi cycle by SHIMADZU UV-1800 spectrophotometer, and the residual nitrite concentrations was determined by a LANGE DR-1900 kit spectrophotometer using prepared reagent kits. The reduction percentages were calculated by the following equation (eq. 10)

$$\% = \frac{C_i - C_f}{C_f} \times 100\% \tag{10}$$

where; C_i is the initial concentration and C_f is the final concentration.

RESULTS AND DISCUSSION

Cathodes preparation

The obtained cathodes of zinc, stainless steel and graphite, were covered by 1 cm thick layer of the resin which serves to isolate the electrical wires and to delimit the active surface area (as shown in Fig. 1A, B and C). For the copper electrode that had a rectangular shape of double facet (Fig. 1 D and E), we didn't covered them by the resin, it was impregnated in half in the electrolytic solution and their upper part was connected with an electric cable, which was connected to the electrical chain.

The cathodes were polished and rinsed after each assay to eliminate any products and intermediate products that could issue from the reduction.

Optimization of the potential range

We have effectuated the optimization of the applied potential range before the study of the other operating parameters effect, in order to delimit the applied potentials range and to avoid the parasitic reactions. Therefore, we have proceeded by blank test that we have used distilled water as electrolytic solution using the copper electrode as cathode. After that, we have tested two contaminated solution by 100 mg/L of nitrites and nitrates respectively. For these tests, the potential sweep of the cyclic voltammetry was fixed between -2 to +2 V/SCE with a scan rate of 100 mV/s. The resulting voltammograms are shown in Fig. 2.

According to the Fig. 3C, we noticed that the nitrate reduction peak is located between the potential range of -1V/SCE to + 1V/SCE which is located exactly at -0.3V/SCE. For nitrite ions, the reduction peak is not clearly shown in the voltamogram spectrum because of their overlap with other peak that have higher intensities than nitrite reduction. So, we can see a small deviation of reduction path from 0 until -1V/SCE comparing to blank voltammogram. For this reason, we have delimited the potential range at [-1; +1] V/SCE for the two voltammetric reduction tests.

Study of the operating conditions effect on the electrochemical reduction of nitrites and nitrates

Effect of scan rate

The influence of scan rate has been studied for the four elaborated cathodes. The voltammograms obtained at different scan rate of the two solutions contaminated by 100 mg/l of nitrates and nitrites respectively are superimposed and shown in the Fig. 3.

All the Figures 3A for the different tested cathodes showed the effect of different scanning rates on nitrite reduction. According to the results presented in these figures, we have noticed that the nitrite reduction peak that appeared at -0.4V/SCE, was almost identical at a scan rate of 50 mV/s for all the tested electrodes, except graphite cathode that haven't shown any reduction peak. However, two large oxidation peaks were noted at -0.7V/SCE and +0.1V/SCE with the zinc electrode at a scan rate of 10mV/s. Similarly, at the scan rate of 100mV/s we observed an oxidation peak at -0.7V/SCE for all tested electrodes. These oxidation peaks were attributed to the non-voluntary oxidation of nitrites and thus conducted to the appearance of undesirable by-products in the electrolytic solution.
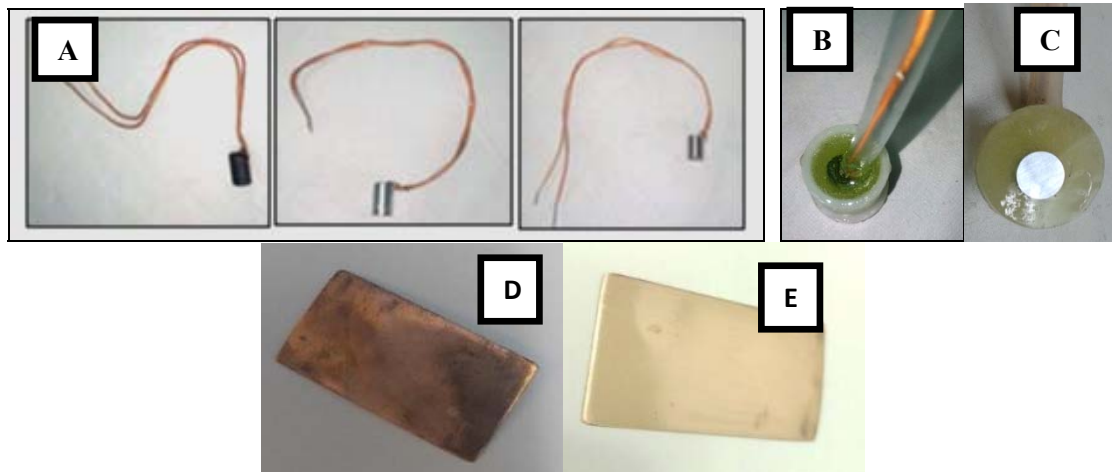

Fig. 1 – Elaboration of the cathodes of zinc, graphite and stainless steel, the first step (A), the second step (B) and the last step (C) and the Copper cathode before (D) and after (E) polishing.
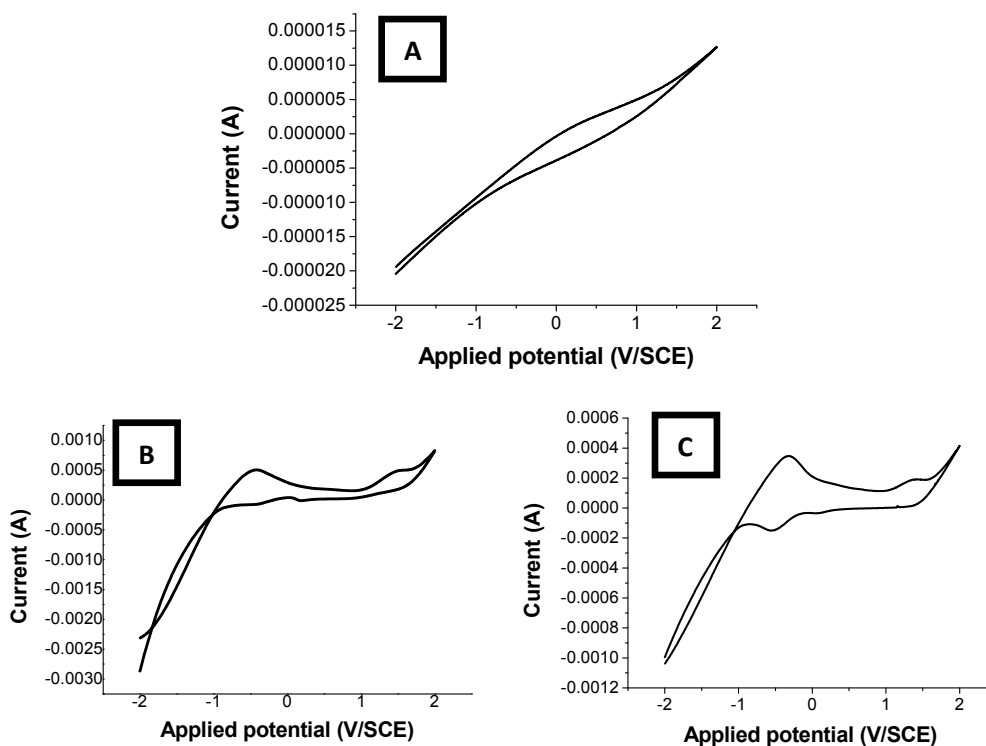

Fig. 2 – Voltammograms of the blank solution (A), nitrites (B) and nitrates (C), using copper electrode with scan rate of 100 mV/s.
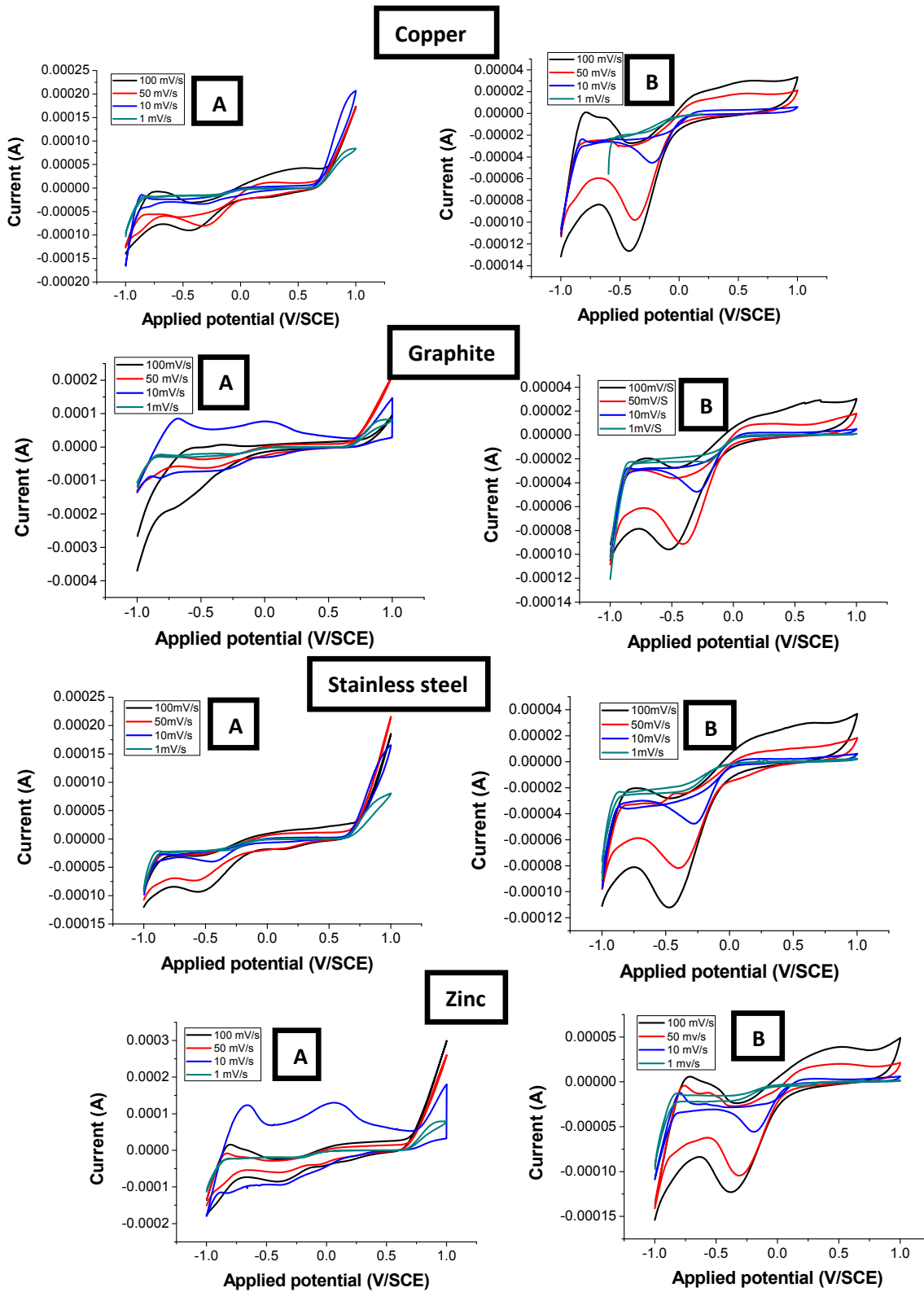
Fig. 3 – Voltammograms presented the scan rate effect on the electrochemical reduction of nitrites (A) and nitrates (B) with an initial concentration of 100 mg/L using different cathode materials (copper, graphite, stainless steel and zinc).

Nevertheless, the reduction of nitrite could contribute to the formation of several other nitrogen forms, such as NO, H_2N-OH, H_2N-NH_2 depending of the electrode materials, pH, reduction potential, etc. like obtained in the studies of Chen *et al.* (2008) and Estudillo-Wong *et al.* (2013)[31,32] that have used Fe nanoparticles and Pt nanoparticles respectively supported on the glass carbon electrode. The authors have obtained a release of NO gas at different potential (-0.6V and -0.78V/SCE[31] and -1.18 V/SCE[32]) in alkaline solution according to the following equation (eq. 11).

$$NO_2^- + H_2O + e^- \rightarrow NO + 2OH^- \ldots \quad (11)$$
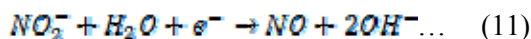
According to Nishimura *et al.* (1991),[33] different volatile compounds could be produced during the NO_2^- depending to the saved potential of reduction, the authors studied the reduction of nitrite in acidic solution they found that N_2 was formed at a potential range of E=0.1–0.6 V/NHE. So, the reduction of NO_2^- to N_2O took place at E = 0.8–0.2 V/NHE and the NO gas was produced at NO at E=0.6–0.1 V/NHE.[33]

Moreover, according to the Figures B of the nitrates reduction, we have noted a reduction peak at -0.3V/SCE for the four cathodes tested, which corresponds to the reduction of nitrates at different scan rates.[34] Hence, the scan rate has an influence on the current intensity. So, at higher scan rate, the reduction peak is so intense. However, at a scanning speed of 100 mV/s, we noticed a moderate oxidation peaks at -1.0V/SCE and -0.7V/SCE. At a scan rate of 50 mV/s the nitrate reduction peak is lower than the other higher speed, but at this scan rate we didn't noticed any undesirable peak. For this raison, we choose the 50mV/s as the optimal scan rate.

According to the literatures, the electroreduction of nitrites ions on an electrode modified with polypyrrole nanowires was improved at high scan rate. So, with increasing of scan rate the reduction peak moved to negative values, the favorable scan rate studied by the authors was similarly with that found in our work, V=50mV/s, this suggests that the reduction process is controlled by diffusion process.[35]

In the other hand, the comparison between the selectivity of the zinc, copper, graphite and stainless steel electrodes revealed that copper cathode is the most efficient for the nitrites reduction. Concerning the nitrates reduction, the four electrodes tested showed a significant efficiency with different peak intensity. Thus, for the other optimization test, we selected the copper electrode for the nitrite and nitrate reductions.

Effect of initial concentration

The initial nitrites and nitrates concentrations effect on the peak intensity was realized on the electrochemical cell containing the contaminated solutions with nitrites and nitrates ions respectively at different concentrations (from 10 mg-NO_x^-/L to 300 mg-NO_x^-/L), using copper as cathode at a scan rate of 50mV/s. The obtained voltammograms were superimposed and represented in Figure 4.

According to Fig. 4, the peak reduction intensity is proportional to the increase of the initial concentration. So, at high concentrations (200 and 300 mg-NO_3^-/L) the reduction peak is greater compared to the other tested concentrations.

The comparison between the different initial concentrations of nitrite and nitrate suggested that at very low concentrations the reduction peaks were disappeared. Indeed, the peak reduction intensity is proportional to the increase in the initial concentration, so, at high concentrations (200 and 300 mg/L) the reduction peak is greater compared to the other tested concentrations. However, at very high concentrations of nitrites and nitrates, started from 200 mg/L, an undesirable oxidation peak was appeared at -0.8V/SCE in both obtained voltammograms. Therefore, the optimal concentration was chosen at 100 mg/L for both ions.

Effect of pH

pH optimizing allowed us to fix the favorable pH of the nitrite and nitrate reductions on copper with an optimized initial concentration at 100 mg/L and a scanning rate of 50mV/s. We have tested different pH values, the obtained voltammograms are presented in Fig. 5.

According to the Figs. 5A and 5C, we noticed that the very acid pH (pH = 3) strongly affects the reaction of the reduction of and leads to an unwanted oxidation reactions signified by the appearance of an oxidation peak at -0.3V/SCE with a sharp drop in the current intensity because of the reduction of the hydrogen accompanied by a violent release of the gas H_2. This current drop covered the other reduction reactions for the other tested pHs. For this reason, we have eliminated this pH value in the Figs. 5B and 5D for nitrite and nitrate respectively, in order to compare the voltammograms of the other pHs.
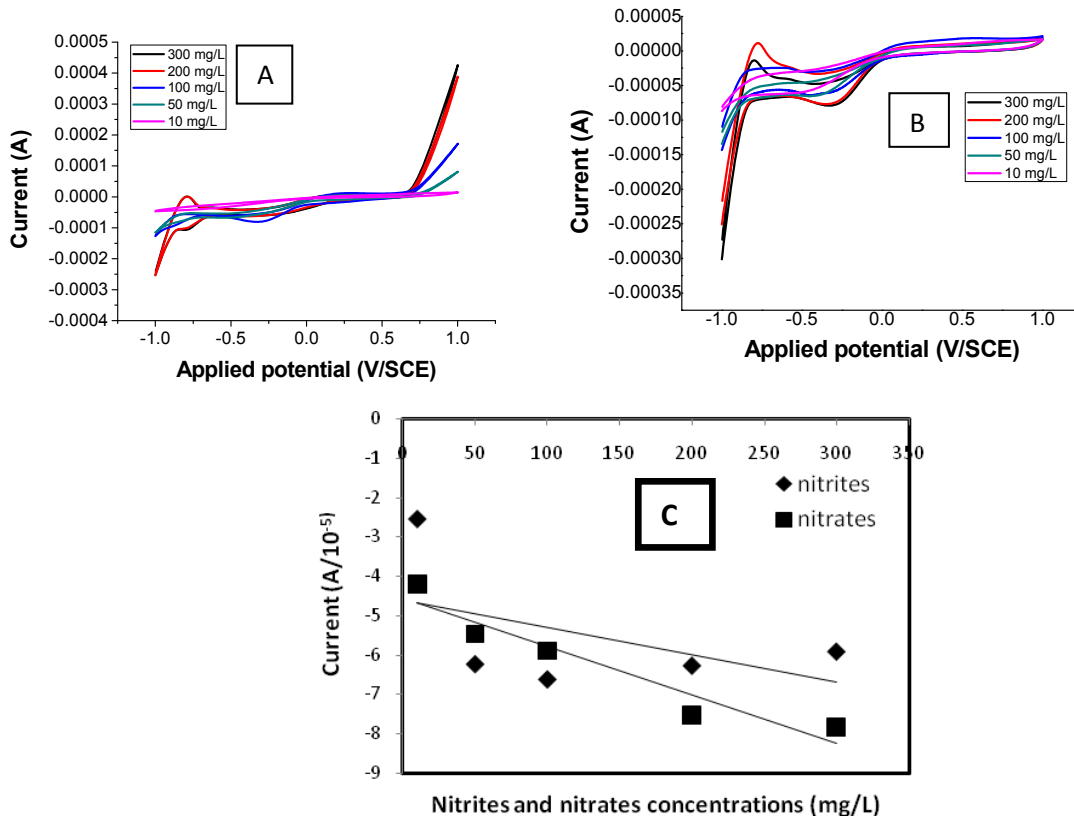
Fig. 4 – Voltammograms presented the initial concentration of nitrites (A) and nitrates (B) effects on the reduction peaks intensities, with a scan rate of 50 mV/s. (C) relationship between current electroreduction and initial concentrations of nitrites and nitrates.
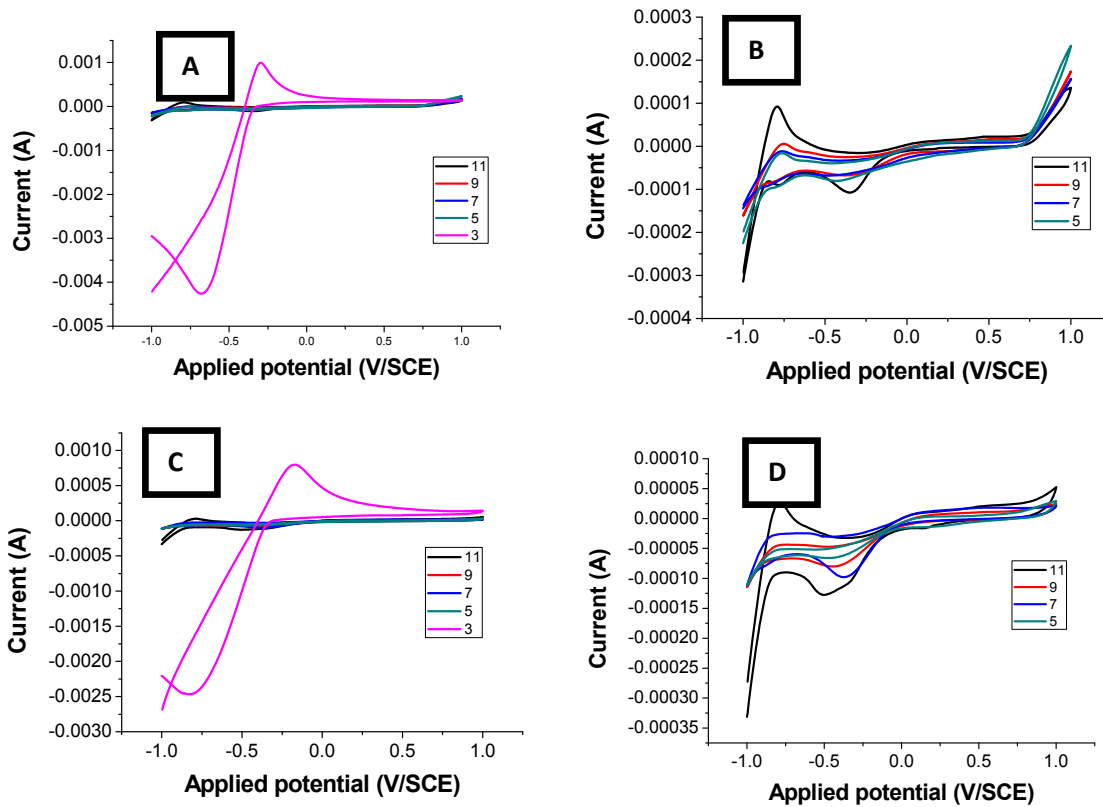

Fig. 5 – Voltamogrammes presented the pH effect on the reduction peaks of nitrites (A and B) and nitrates (C and D) with a scan rate of 50 mV/s and initial ammonium concentration of 100mg/L.
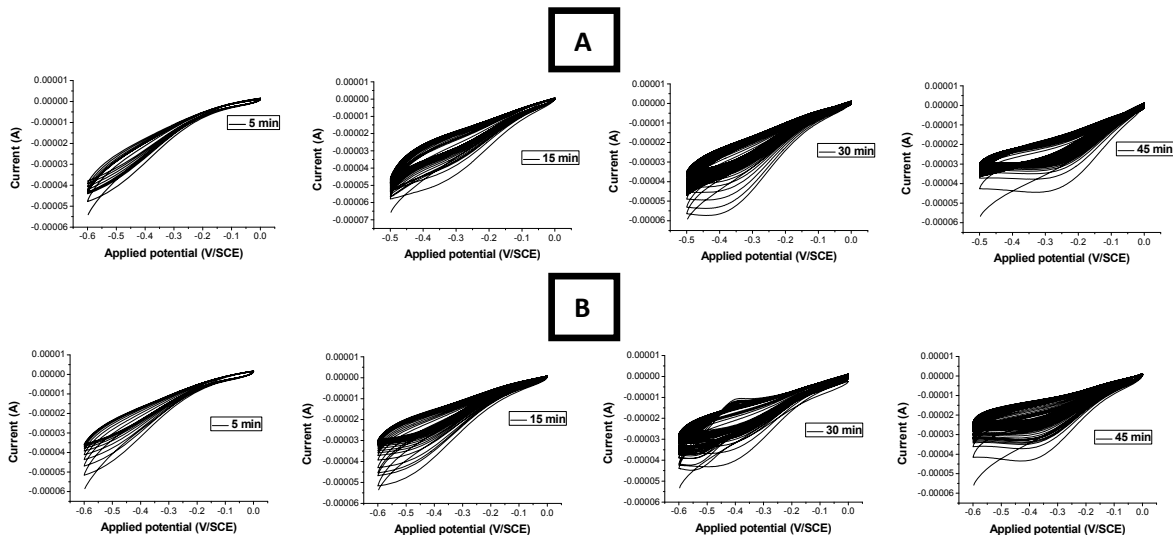
Fig. 6 – Voltamogrammes presented the contact time effect on the reduction peaks of nitrites (A) and nitrates (B) with a scan rate of 50 mV/s, pH=7 and initial ammonium concentration of 100mg/L.

Indeed, we have noticed that our reduction peaks are optimal at a pH =11 accompanied by the appearance of unwanted oxidation peaks at -0.8V/SCE. At pH =7 reduction peaks are less important compared to pH =11 but at neutrality we did not notice any oxidation peak for both tested ions. For these reasons the optimal peak of reduction has been set at pH=7.

According to the literatures, the pH affect also the formed species in the electrolytic medium and conduct to the appearance of unwanted by product such as NO that could form in alkaline solution form the reduction of nitrite ions[31,32] and in acidic solution using copper-containing nitrite reductase model complex incorporated into collagen film as electrode.[36] For the nitrates ions, in alkaline solution the reduction could produce ammonia as final product according to the following equations (12 and 13).[37]

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (12)$$

$$NO_2^- + 5H_2O + 6e^- \rightarrow NH_3 + 7H_2O \quad (13)$$
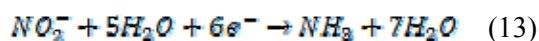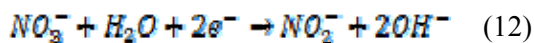
In acidic solution, the nitrates reduction could produce different nitrogen gas according to the reduction potential, such as N_2O and N_2 at the potentials $E < 0.4$ V/NHE.[33]

Effect of contact time

After optimization of the scan rate, the initial concentration and the pH of the electrolytic medium, we proceeded to the reduction of nitrite and nitrate by application of several cycles voltammetry during well-defined time intervals on

a copper electrode. In addition, we defined the potential range at -0.6V/SCE to 0.0V/SCE for the reduction of both ions. The results of the obtained voltammograms are presented in Fig. 6.

According to the voltammograms shown in Figure 6, we have noticed a decrease in peak reduction intensity as a function of time and of the cycle's number. Indeed, in the voltammograms of the nitrite reduction, the peak intensity decreased from -0.0445 mA to a current value of -0.0347mA during 5 min of scanning (Fig. 6 B1). On the other hand, the peak intensity could reach a value of -0.0301 mA and -0.0228 mA after the 30th and 60th potential scan cycles respectively. These values could reach a minimum value of- 0.0218 mA after the 100th scan cycle. These results suggest that the concentration of nitrites decreased during sweeps and as a function of applied cycle numbers.

In addition, in the voltammograms of Fig. 7B of the nitrate reduction, the reduction peak intensity decreased from -0.0486 mA to -0.0335 mA after 5 min of scan. This value remained to decrease to -0.0277 mA and to -0.0207 mA after 15 min and 30min which correspond to 30th and 60th cycles respectively. Thus, these values could reach a minimum value of -0.0187 mA after the 100th scan, which indicates that the concentration of nitrates decreased in the reaction medium during sweeps and as a function of the applied cycle's number.

Moreover, dosages of the residual concentrations of nitrites and nitrates respectively after each applied cycle have been effectuated, in order to confirm the results found by cyclic voltammetry.
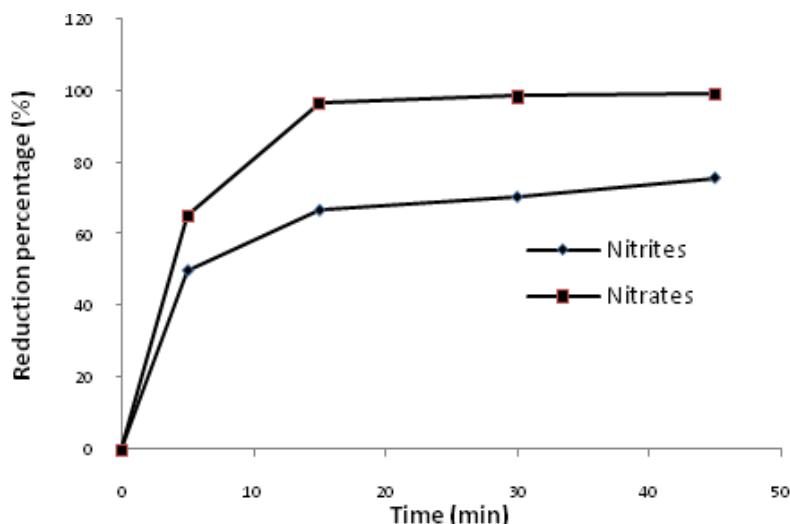
Fig. 7 – Reduction percentage of nitrites and nitrates as a function of time.

Study of nitrites and nitrates electrochemical reduction on the copper cathode

In order to confirm our interpretations, dosages of residual nitrite and nitrate after each voltammetric test were carried out. The results are exploited in the form of the trend curves and presented in Figure 7.

According to the Fig. 7 we noted that the increase in cyclic potential sweep number improved the rates of nitrite and nitrate reductions. At a scan of 10 cycles, about 50% and 65.33% of nitrite and nitrate respectively were reduced. Beyond the 30th cycle, the yield exceeded 70.4% until the elimination of 75.7% of nitrites and from 96.8% to about 99% for the nitrates at the 100th cycle sweep. These results suggest that under successive cyclical scans of potential, the yield of the reduction of our ions is important.

CONCLUSIONS

In this work, we treated nitrite and nitrate in aqueous solution by the electrochemical technique, comparing the performance of different electrode materials. On the most efficient electrode, which is copper, we optimized the various operating parameters of cyclic voltammetry, such as the scanning rate, the applied potential range, the pH, the initial effluent concentration and the time. Indeed, the application of different scanning speeds allowed us to deduce the type of reaction and thus to select the optimal speed of the reduction of both ions for the different tested cathode materials. From the results obtained, we conclude that our reductions reactions are rapid and spontaneous. However, high scanning rates lead to undesirable intermediate reactions. Moreover, the optimization of the initial concentration of the contaminated solutions and pH allowed us to maintain them at 100 mg/L and 7 respectively. The effect of reduction contact time or the applied cycle number suggests that the increase in the cycle number improves nitrate and nitrite reduction rates which can reach 99% and 96.5% respectively in the 100th cycle. Our treatment process has proven a remarkably effective in reduction of nitrite and nitrate, which can be applied in the water treatment rich in both contaminants.

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