



Electro-generation of hydrogen peroxide using a graphite cathode from exhausted batteries: Study of influential parameters on electro-Fenton process

Ibrahima Diouf, Oumar Dia, Moussa Bagha Diedhiou, Patrick Drogui, Alpha Ousmane Toure, Sidy Mambaye Lo, Michel Rumeau & Codou Gueye Mar/Diop

To cite this article: Ibrahima Diouf, Oumar Dia, Moussa Bagha Diedhiou, Patrick Drogui, Alpha Ousmane Toure, Sidy Mambaye Lo, Michel Rumeau & Codou Gueye Mar/Diop (2018): Electro-generation of hydrogen peroxide using a graphite cathode from exhausted batteries: Study of influential parameters on electro-Fenton process, Environmental Technology, DOI: [10.1080/09593330.2018.1537309](https://doi.org/10.1080/09593330.2018.1537309)

To link to this article: <https://doi.org/10.1080/09593330.2018.1537309>



Accepted author version posted online: 16 Oct 2018.



Submit your article to this journal [↗](#)



View Crossmark data [↗](#)

Publisher: Taylor & Francis & Informa UK Limited, trading as Taylor & Francis Group

Journal: *Environmental Technology*

DOI: 10.1080/09593330.2018.1537309



Electro-generation of hydrogen peroxide using a graphite cathode from exhausted batteries: Study of influential parameters on electro-Fenton process

Ibrahima DIOUF¹, Oumar DIA², Moussa Bagha DIEDHIOU¹, Patrick DROGUI^{2*}, Alpha Ousmane TOURE¹ Sidy Mambaye LO¹, Michel RUMEAU¹, Codou GUEYE MAR/DIOP¹

1 Laboratoire d'Electrochimie et des Procédés Membranaires, Ecole Supérieure Polytechnique, Université Cheikh Anta Diop, B.P : 5085, Dakar-Fann, Senegal.

2 Institut national de la recherche scientifique (INRS-Eau Terre et Environnement), Université du Quebec, 490 rue de la Couronne, Quebec QC G1K 9A9, Canada

*Corresponding author: Patrick DROGUI patrick.drogui@inrs.ca

Ibrahima DIOUF ibaradiouf@yahoo.fr

Oumar DIA Oumar.Dia@ete.inrs.ca

Patrick DROGUI patrick.drogui@inrs.ca

Sidy Mambaye LO sidymambaye.fara@gmail.com

Alpha Ousmane TOURE alpha2re@gmail.com

Michel RUMEAU mj.rumeau@gmail.com

Moussa Bagha DIEDHIOU diebagha@yahoo.fr

Abstract

In this work, the study of hydrogen peroxide (H_2O_2) electro-generation using graphite from exhausted batteries (Gr-Bat) was conducted. Linear sweep voltammetry and electrolysis experiments were carried out in a single compartment electrochemical cell. Study of the possibility to use this electrode revealed that it presents, as vitreous carbon (VC) electrode, a reduction of oxygen with two successive waves (bi-electronic reduction). The first wave corresponds to the reduction of O_2 to H_2O_2 , while the second one corresponds to the reduction of H_2O_2 to H_2O . The cathodic potentials for electro-generation of H_2O_2 appeared at -600 mV and -700 mV *vs* Ag/AgCl for Gr-Bat and VC electrodes, respectively. Subsequently, electrolysis experiments were conducted by imposing the potentials required for H_2O_2 formation. The effect of several operating parameters on H_2O_2 production, such as the nature and concentration of the electrolyte, the pH, the presence of ferrous ions and O_2 injection were studied using Gr-Bat and VC electrodes, respectively. For both electrodes, the acidic medium was more favorable for H_2O_2 electro-generation. The oxygen injection in solution promoted an increase of H_2O_2 concentration, but its effect was more pronounced in the case of VC electrode. Application for crystal violet degradation by electro-Fenton revealed that Gr-Bat had the best purification performance. A removal rate of 73.18% was obtained with Gr-Bat electrode against 62.27% with VC electrode for an electrolysis time of 120 min. This study has demonstrated the possibility of recycling Gr-Bat by using them as cathode materials in the electro-Fenton process.

Keywords: Exhausted batteries, Hydrogen peroxide, Electro-Fenton, Electro-reduction of O_2 , Crystal violet

1. Introduction

Many treatment methods had been developed in order to tackle the issue of aquatic environment degradation by refractory organic pollutants. Among these innovations, Advanced Oxidation Processes (AOPs) play an important role [1, 2]. AOPs are new treatment

technologies that can be used to effectively remove pollutants from surface waters and refractory micro-pollutants found in many influents [3,4].

AOPs are based on *in situ* generation of radical hydroxyls that are very powerful and non-selective oxidants capable to degrade organic compounds present in influents [5]. Hydroxyl radicals (OH^\bullet), the most powerful oxidants used in water and wastewater treatment, have a high potential ($E^\circ_{\text{OH}^\bullet/\text{H}_2\text{O}} = 2.8 \text{ V/ENH}$) and they enable to oxidize organic compounds until their last stage of mineralization to CO_2 , H_2O and other inorganic ions [6, 7]. OH^\bullet can be generated *via* a process called electro-Fenton (EF). It is an electrochemical process that has received a considerable attention in recent years [8, 9, 10]. Its principle is based on the use of Fenton reagent (hydrogen peroxide H_2O_2 and ferrous ions Fe^{2+}) in order to generate hydroxyl radical as shown in the following reaction (Eq. 1):



The main advantage of this process is the *in situ* electro-generation of hydrogen peroxide using only dissolved oxygen as reagent [11]. A cathodic reduction will then occur on the appropriate electrodes such as carbon felt, graphite, reticulated vitreous carbon, activated carbon fiber, carbon nanotube [12, 13, 14, 15] as mention in the following reactions (Eq. 2 and 3).



The ferric ions (Fe^{3+}), cogenerated from the hydroxyl radical formation (Eq. 1), are electrochemically reduced back at the cathode to ferrous ions (Fe^{2+}) (Eq. 4). In this way, the iron is recycled in the redox cycle and the amount of iron hydroxide sludge is considerably reduced [16].



The main advantages of this process are the possibility to continuously generate H_2O_2 and Fe^{2+} in the reactor that reduced risks and costs associated with transportation, acquisition, storage, production and disposal of hazardous waste [17, 18, 19]. Therefore, EF process is an interesting alternative for the treatment of effluents containing high refractory organic compounds [20]. However, it is worth mentioning that this process is hindered by some

drawbacks such as the production of hydrogen peroxide which is controlled by the electro-reduction of dissolved oxygen.

The dissolved O_2 electro-reduction reaction is highly depended to the cathodic material [21]. Thus a judicious choice of the cathode material is required during the implementation of this method. The selected cathode should present two waves of oxygen reduction and have high hydrogen overpotential. In addition to be non-toxic and have a good chemical resistance, the cathodic material should also have less interaction with the generated H_2O_2 in order to facilitate its diffusion in the solution and avoid its eventual self-destruction on the cathode [17]. A good electrical conductivity and an affordable cost are to be taken account for the cathodic material choice [22, 23].

In order to find a way to recycle waste from the batteries industry, we tried, in this study, to investigate the capacity of carbon rods (graphite), from exhausted batteries, to produce H_2O_2 by O_2 reduction. Furthermore, the possible use of this material was tested as an alternative cathode in the EF process. The effect of some influential parameters such as the cell voltage, the solution pH, the electrolyte concentration, and the O_2 bubbling on H_2O_2 production was investigated. Later on, this approach was used to evaluate the degradation of crystal violet pollutant in synthetic solution.

2. Material et methods

2.1. Electrochemical cell and analytical methods

Experiments were conducted in a 250 mL non compartmental cell. The anode was made of Ti/RuO₂-IrO₂ electrode with a surface area of 7.15 cm². The two cathodes used in this study were graphite carbon from exhausted batteries (Gr-Bat) provided by the company SIGELEC-Senegal, and vitreous carbon (VC) having both a surface area of 9.5 cm².

The two chosen electrodes (anode and cathode) were immersed in the aqueous solution with a third Ag/AgCl reference electrode and the reactor was kept under magnetic stirring in order to improve oxygen mass transfer to the surface of the cathode. The electrodes were connected to a potentiometer Radiometer Analytical Voltalab PGZ-100 ALL IN ONE controlled by the Master 4 software. The crystal violet concentration was determined using a UV-visible spectrophotometer Analytik Jena model SPECORD 200 PLUS with a wavelength set at 592 nm. The pH was measured by a pH meter HANNA Instruments HI223 and the conductivity was measured by EC 214 Conductivity meter HANNA Instruments.

In order to estimate the concentration of electro-generated H_2O_2 over the time, the system was stopped and a sample was taken and analyzed using a manganimetry based method [24]. It is a titrimetric determination of H_2O_2 based on the reduction of MnO_4^- ions to Mn^{2+} under acidic medium according to the following reaction (Eq. 5):



The concentration of H_2O_2 was expressed by the following relation (Equation 6):

$$[\text{H}_2\text{O}_2] (\text{g.L}^{-1}) = \frac{5}{2} \times \frac{N_{\text{KMnO}_4} \times V_{\text{KMnO}_4}}{V_{\text{H}_2\text{O}_2}} \times 34 \times 10^{-3} \quad (6)$$

Where N_{KMnO_4} is the molar concentration of the potassium permanganate solution (mol L^{-1}) and V_{KMnO_4} and $V_{\text{H}_2\text{O}_2}$ are the volumes of potassium permanganate solution and the sample respectively.

2.2. Reduction of dissolved oxygen on graphite and carbon vitreous electrodes

The objectives of this part were as following: 1) to verify whether the carbon-graphite electrode from exhausted batteries (Gr-Bat) had two waves O_2 reduction kinetic allowing a production of H_2O_2 ; 2) to determine the electrochemical potential region for O_2 reduction to H_2O_2 ; 3) to evaluate the impact of the use of NaCl as electrolyte on the production of hydrogen peroxide. To do this, firstly, a comparison had been made between Gr-Bat cathodic polarization curves and curves obtained with carbon vitreous described in the literature as a cathode showing two waves oxygen reduction kinetic [19]. Secondly, we compared the cathodic polarization curves of O_2 reduction using Gr-Bat cathode obtained with NaCl as supporting electrolyte and those recorded with Na_2SO_4 generally used in the electro-Fenton process as supporting electrolyte [13].

2.3. Chemicals

All the reagents used in this work were analytical grade. Sulfuric acid (H_2SO_4), sodium chloride (NaCl), and crystal violet ($\text{C}_{25}\text{H}_{30}\text{ClN}_3$) were purchased from Sigma Aldrich. Potassium permanganate (KMnO_4) and sodium sulfate (Na_2SO_4) were purchased from Scharlau Company while iron sulfate (FeSO_4) from Merck and sodium hydroxide (NaOH) from Fisher Scientific. A 14 m^3 nitrogen bottle (N_2) supplied by AIR-LIQUIDE- Senegal company and a 7 m^3 oxygen cylinder (O_2) supplied by EUROSAF OXYGEN were used in the experiments. Distilled water was also employed throughout the aqueous solutions preparation.

3. Results and discussion

3.1. Study of the electrochemical region of H₂O₂ production and effect of influential parameters

3.1.1. Comparative study of O₂ reduction kinetics

The kinetic study of oxygen reduction on both electrodes (VC and Gr-Bat) was conducted using a linear sweep voltammetry under the different following conditions: **a)** 3 g L⁻¹ of Na₂SO₄; **b)** 3 g L⁻¹ of Na₂SO₄ + O₂ bubbling; **c)** 3 g L⁻¹ of Na₂SO₄ + N₂ bubbling. The potential varied from 0 to -2500 mV *V/s* Ag/AgCl reference electrode with a scan rate of 10 mV s⁻¹.

The results obtained from linear voltammetry study on VC and Gr-Bat electrodes are recorded in Figures 1A and 1B, respectively.

Figure 1 (A and B)

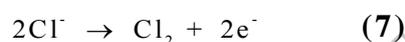
The results revealed that, like VC electrode, the Gr-Bat electrode shown two waves oxygen reduction kinetic. Thereby, it can be used for H₂O₂ electro-generation. The first wave, corresponding to the reduction of O₂ to H₂O₂, was obtained between -684 and -920 mV for VC electrode and between -522 and -850 mV for Gr-Bat electrode. This shows that the Gr-Bat electrode have the lowest O₂ reduction potential. In both cases the oxygen bubbling did not change significantly the shape of the curves; a two steps reduction was always observed. However, it has the effect of increasing the value of the diffusion limit currents. For example, in the case of Gr-Bat electrode, at a potential of -1000 mV, the O₂ sparging increased the current limit from -2.04×10^{-3} to -3.32×10^{-3} mA and lowered the hydrogen overvoltage value. N₂ bubbling removed the dissolved oxygen in the solution. In both cases, the disappearance of the first wave with the nitrogen sparging confirmed that the first step was due to the reduction of oxygen to hydrogen peroxide.

Results from Figures 1A and 1B revealed also that the Gr-Bat electrode has the highest hydrogen overvoltage with -1836 mV against -1770 mV for vitreous carbon and the latter had limited diffusion currents sometimes ten times higher than those for Gr-Bat electrode. Indeed, at a potential of -2000 mV, the diffusion limited currents without O₂ sparging were $-7.41 \cdot 10^{-2}$

and $-6.36 \cdot 10^{-3}$ mA for the VC and Gr-Bat electrodes respectively. This can be attributed to the intrinsic characteristics of these two materials such as their texture and difference in electrical conductivity.

3.1.2. Influence of type and concentration of electrolyte

The effect of type and concentration of the electrolyte on O_2 reduction had been studied using different NaCl and Na_2SO_4 concentrations. The use of NaCl in electrochemical treatment processes such as electro-oxidation and electro-Fenton leads to very interesting results [25]. It allows an *in situ* generation of other oxidizing agents such as hypochlorite ion ClO^- and hypochlorous acid HClO *via* the following reactions (Eqs. 7, 8 and 9):



Hence, these electro-generated oxidants can contribute to the degradation of the dissolved organic pollutants. Therefore, the use of such electrolytes improves the efficacy of the treatment [26]. Results obtained using NaCl are shown in Figure 2A. The cathodic scanning was carried out from 0 to -2500 mV with a scan rate of 10 mV s^{-1} .

Figure 2 (A and B)

These results show that similarly to Na_2SO_4 , NaCl can be used as an electrolyte in the production of hydrogen peroxide. The polarization curves show that the two waves of O_2 reduction were always present, reflecting the formation of hydrogen peroxide. By comparing the curves of Figure 2A with those obtained in Figure 1B using Na_2SO_4 as electrolyte, it can be seen that the use of NaCl had an effect on the oxygen reduction potential. Indeed, a diminution of this potential was observed with the use of NaCl. Depending on the electrolyte type, the value of the current limits varied due to the difference in conductivity of the two supporting electrolytes, Na_2SO_4 (3.52 mS) and NaCl (4.77 mS).

Moreover, study of the effect of electrolyte concentration was carried out using Na_2SO_4 at the same scan rate as above with continuous O_2 sparging. Results, plotted in Figure 2B, revealed that the increase of electrolyte concentration did not change the curves shape. The reduction of O_2 at two levels was always observed but the diffusion limited currents increased with the electrolyte concentration. This was expected because the electrolyte role consists to reduce the electrical resistance by facilitating the passage of the current in the solution. Hence, the limited currents increased when the solution was more and more concentrated in electrolyte. However, it should also be noted that the potentials reduction became lower and lower as the solution became more and more concentrated in electrolyte.

3.1.3. Influence of pH

The effect of pH on oxygen reduction was studied using Na_2SO_4 as electrolyte; the concentration was fixed at 3 g L^{-1} . This study was conducted in order to determine in which regional of pH the hydrogen peroxide generation was optimal. It was carried out on solutions having pH of 3, 5.4 (initial pH), 7, and 10 with continuous O_2 sparging. Sulfuric acid (H_2SO_4) was used to acidify the medium to pH 3 while sodium hydroxide (NaOH) was used to raise the pH to 7 and 10. The obtained results are shown in Figure 3A.

Figure 3A

These results revealed that the diffusion limited currents were higher in acidic medium (initial solution and pH 3) showing the quantity of dissolved oxygen participating in the reaction was more important and leading to higher H_2O_2 production. The increase of diffusion limited currents in acidic solutions can be attributed either to oxygen which is much more soluble in acid medium [20] or to the high concentration of H^+ protons in acid medium.

Indeed, as shown by the Equation 2, the hydrogen peroxide is generated from H^+ protons and dissolved O_2 in the solution, and these two species are more available in solution when the pH medium is acidic. However, the increase of the amount of hydrogen peroxide can also be attributed to the intrinsic properties of the material [20] such as its adsorption ability of

dissolved oxygen and desorption of hydrogen peroxide generated from its surface to the solution or to the synergism effects of these phenomena.

These findings are interesting for an eventual use of this electrode in the electro-Fenton process. Indeed, several recent studies have shown that this process is more efficient when the pH is around 3 [1, 10, 13]. In addition, results revealed that hydrogen overvoltage is much lower in acidic solutions. Qiang et al [17] explained this by the high concentration of H^+ protons that facilitates the hydrogen evolution reaction and thus reduce the efficiency of hydrogen peroxide formation.

3.1.4. Effect of ferrous ions concentration

In order to have an idea about the behavior of these electrodes during their use in the electro-Fenton process, the effect of ferrous ions concentration on O_2 reduction reaction had been investigated. In the electro-Fenton process, these ions are used to generate hydroxyl radicals OH^\bullet from hydrogen peroxide according to Equation 1 called the Fenton reaction. However, the concentration of ferrous ions should be optimized. Several studies have shown that it greatly influences the electro-Fenton process [16, 22]. The study of the effect of iron sulfate concentration was conducted using 3 g L^{-1} of Na_2SO_4 with O_2 sparging and a scan rate of 10 mV/s at room temperature.

Figure 3B

The results presented in Figure 3B show that the presence of iron sulfate in the solution affected the reduction of oxygen. In all experiments, the presence of iron sulfate caused an increase of the limit of the diffusion current in comparison to the initial solution, but the shape of the reduction curves did not change. This can be explained by the increase of conductivity with the presence of Fe^{2+} and SO_4^{2-} ions [27]. In addition, the presence of ferrous and sulfate ions reduced both the hydrogen overvoltage and the potential corresponding to oxygen peroxide reduction in comparison to the control solution. This was also observed in the case of increase in electrolyte concentration, it can be explained by the decrease of the cell resistance when the solution is more and more conductive.

There was an increase of the limit of the diffusion current when the iron concentration varied from 0 to 7.2×10^{-3} M. However, when the iron concentration increases (from 7.2×10^{-3} to 10.8×10^{-3} M) a decrease of the limit of the diffusion current was recorded.

3.2. Study of the effect of the operating parameters on the quantity of electro-generated H_2O_2

3.2.1. Effect of applied voltage

The comparative study of the voltage influence on H_2O_2 electro-generation was carried out in 250 mL solution containing 3 g L^{-1} of Na_2SO_4 during 90 min of electrolysis time. The results presented in Figure 4A show that the production of H_2O_2 was strongly correlated with the voltage applied across the electrodes. In both electrodes, the amount of generated H_2O_2 increased with the cathodic potential until an optimal voltage specific to each electrode. These optimum voltages were -600 mV for Gr-Bat electrode and -700 mV for VC electrode. When the applied voltage was higher than the optimum voltage, the amount of generated H_2O_2 decreased immediately resulting in a lower current efficiency in both cases. This observation is attributed to the appearance of undesirable secondary reactions such as O_2 reduction to H_2O and H_2 evolution reaction occurring on the cathode surface [28, 20].

Figure 4A

These results revealed also that in the investigated potential region, Gr-Bat electrode was more able to generate hydrogen peroxide than VC electrode. The maximum concentrations of H_2O_2 achieved were $5.1 \times 10^{-3} \text{ g L}^{-1}$ for Gr-Bat against $4.25 \times 10^{-3} \text{ g L}^{-1}$ for VC. The best current efficiency over the entire electrochemical region was obtained with the Gr-Bat electrode. However, it can be noted that the potential region allowing the produce more than 50% of the maximum value was much wider for vitreous carbon electrode than the graphite electrode.

3.2.2. Effect of electrolyte concentration

The electrolyte promotes the passage of the current in the solution by reducing the ohmic resistance and facilitating the electrochemical reactions. Its effect on the electro-generation of hydrogen peroxide was investigated by fixing the cathodic potential at -600 mV for the Gr-Bat electrode and -700 mV for the VC electrode. Different Na₂SO₄ concentrations were then experimented (1 to 6 g L⁻¹) during 90 min of electrolysis time.

The results obtained in Figure 4B show that the electro-generation of H₂O₂ was not significantly affected by the concentration of the supporting electrolyte. Indeed, for both electrodes, a slight variation in the amount of hydrogen peroxide was noted when the electrolyte concentration was increased to its maximum value (6×10⁻³ g L⁻¹). These results are consistent with those reported by Azri and Zerouali [29]. These authors shown that, the increase of electrolyte concentration had only an effect on the conductivity of the solution and on migration phenomena of species. Given that the increase of the conductivity *via* Na₂SO₄ addition had no significant effect on H₂O₂ production, the concentration of 3 g L⁻¹ had been retained for the following experiments.

Figure 4B

3.2.3. Effect of the pH

The pH is a very important parameter for an electrochemical oxidation processes. Several authors had studied the effect of pH on electrochemical oxidation of organic matter in aqueous media [8, 20]. In order to identify in which pH range the production of hydrogen peroxide was maximum, the effect of this latter was investigated using four different pH values: 3, initial solution (5.4), 7 and, 10. Sulfuric acid and sodium hydroxide were respectively used to acidify or alkalinize the solution.

Figure 4C

The results plotted in Figure 4C revealed that the pH had a significant influence on hydrogen peroxide generation. However, the variation of H_2O_2 concentration according to the pH depends on the type of electrode. The variation was more stressed for the Gr-Bat electrode than VC electrode. For both electrodes, the acidic medium seemed to be more favorable for H_2O_2 generation and an optimum pH of 5.4 for the Gr-Bat and 3 for VC had been observed. Similar observations had been reported by Petrucci et al [30], Xu et al [20], and of Liu et al [31]. Hsiao and Nobe [32] have studied the degradation of phenol and chlorobenzene using the EF process; they concluded that the current efficiency and the generation of H_2O_2 are promoted by the decrease of pH. Xu et al [20] attributed the increase in hydrogen peroxide concentration in acidic medium to the concentration of dissolved oxygen which is higher in acidic medium. These studies have also associated the increase of H_2O_2 production in acidic medium with the high availability of H^+ protons necessary for the production of hydrogen peroxide according to Eq. 2. Nevertheless, it should be pointed out that if the quantity of H^+ is so important, the hydrogen evolution reaction will be facilitated on the cathode and it will hinder O_2 reduction into H_2O_2 . Other authors have reported that the improvement of H_2O_2 electro-generation in acidic medium might be linked to the intrinsic characteristics of the electrode materials, such as their O_2 adsorption ability that is improved in acidic medium [33].

3.2.4. Effect of oxygen sparging

The study of the impact of O_2 sparging on H_2O_2 generation was carried out on the two electrodes for three experimental conditions: 3 g L^{-1} of Na_2SO_4 , 3 g L^{-1} of $\text{Na}_2\text{SO}_4 + \text{O}_2$ sparging, and 3 g L^{-1} of $\text{Na}_2\text{SO}_4 + \text{O}_2$ sparging with pH adjustment at 3. Experiments were performed by maintaining the voltage at -600 and -700 mV for Gr-Bat and VC electrodes respectively. The results obtained are shown in Figures 5A and 5B.

Figure 5 (A and B)

These results indicated that O_2 sparging had influence on the production of hydrogen peroxide. Its influence depends on the type of electrode; in fact it is much more pronounced in the case of vitreous carbon electrode where the concentration of peroxide increased from 4.25×10^{-3} to $6.38 \times 10^{-3} \text{ g L}^{-1}$ for an electrolysis time of 90 min. Under the same operating conditions, only a small evolution of H_2O_2 production was observed in the case of the

graphite electrode. This increase of the amount of H_2O_2 was attributed to the increase in dissolved oxygen concentration in solution during the sparging. Indeed, Petrucci et al [30] have shown that the pure oxygen sparging considerably increased the concentration of dissolved oxygen in the solution [34] resulting to the increase in the amount of hydrogen peroxide.

These results show that the VC material presents a better dissolved oxygen adsorption capacity than that Gr-cell. In fact, O_2 reduction reaction being a process that takes place on the electrode surface, the more the cathode has the ability to adsorb oxygen the more hydrogen peroxide production will be important. This difference can also be attributed to the electrical conductivity of the two electrodes. Since the oxygen reduction reaction is dependent to the current intensity, the vitreous carbon electrode being more conductive than Gr-Bat as shown in section 3.1.1., will allow the current to pass more easily. That will accelerate the electrochemical reactions kinetics on its surface and thus increase the quantity of hydrogen peroxide with the oxygen bubbling.

Moreover, these results revealed that the oxygen sparging with pH adjustment to 3 improved the amount of hydrogen peroxide produced in both cases. This improvement could be explained by the synergistic effect of the three phenomena which are the increase of the solubility of oxygen [33], the high presence of H^+ protons in acid medium, and the improvement of the materials adsorption capacity at this pH [33].

3.3. Application for the degradation of crystal violet by electro-Fenton

In order to compare the efficiency of the two electrodes, the electrolysis of 7.5×10^{-5} M crystal violet solution was carried out at pH 3, 5.10^{-2} M of Na_2SO_4 , 10^{-4} M of Fe^{2+} , and a current of intensity of 300 mA. The residual crystal violet concentration was monitored by UV-visible spectroscopy. Electrolysis experiments were performed using a Ti/IrO₂-RuO₂ anode under these three conditions: a) Gr-Bat cathode without Fe^{2+} , b) Gr-Bat cathode + Fe^{2+} , and c) VC cathode + Fe^{2+} . Figure 6 shows the evolution of crystal violet concentration as a function of the electrolysis time.

Figure 6

The results revealed that the presence of Fe^{2+} ions in the solution allows a faster degradation of the crystal violet. This shows that these ferrous ions have allowed the generation of additional oxidizing species in solution proving that these electrodes can be used in the implementation of the electro-Fenton process. In fact, considering an electrolysis time of 120 min with the Gr-Bat electrodes, the addition of the ferrous ions increased the crystal violet degradation rate from 45.75 to 73.18%. In addition, these results also reveal that, under the actual electrolysis conditions, the Gr-Bat electrode remains more effective than VC electrode regarding the removal of crystal violet. For the same electrolysis time (120 min), the crystal violet removal rate was 62.27% using the VC electrode. Based on the previous preliminary study, these results were somehow expected. In fact, the Gr-Bat electrode produced more H_2O_2 than VC electrode. The production of H_2O_2 is required for hydroxyl radical formation in the presence of ferrous ions during electro-degradation of pollutants (electro-Fenton process).

4. Conclusion

The purpose of this study was to find a way to recycle exhausted batteries by using their graphite contain as a cathode material in the electro-Fenton process. Voltammetry studies of dissolved oxygen reduction reaction on this cathode showed that this material has a kinetic of oxygen reduction with two waves revealing the passage through H_2O_2 formation. Some operating parameters such as nature and concentration of the electrolyte, pH and ferrous ion concentration had a significant influence on the diffusion-limited currents and the overvoltage potentials.

Moreover, investigation of the effects of these operating parameters on the amount of hydrogen peroxide revealed that Gr-Bat cathode had the best current efficiency than VC electrode. Hydrogen peroxide concentrations of 5.1×10^{-3} and 4.25×10^{-3} g L^{-1} were respectively generated by Gr-Bat and VC electrodes. This study also revealed that for potentials set at -600 and -700 mV *Vs* Ag/AgCl for Gr-Bat and VC respectively, the amount of H_2O_2 generated in both cases was not significantly influenced by the electrolyte concentration. For Na_2SO_4 concentration set at 3 g L^{-1} using same previous potentials, it had been observed that acidic medium (pH = 3) was more favorable for H_2O_2 generation in both electrode materials. However, O_2 sparging had more influence on H_2O_2 production when vitreous carbon electrode was used.

Later on, the degradation of crystal violet solution by electro-Fenton process had been performed using these two electrodes. Results showed that the Gr-Bat cathode presents the best removal performance than VC cathode. For a treatment time of 120 min, the removal rates of the crystal violet were 73.18 and 62.27% for Gr-Bat and VC respectively. This study has demonstrated the possibility of recycling the graphite contained in exhausted batteries and valorizes it as a cathodic material in the electro-Fenton process. Very promising results have been obtained with the use of this low cost material. This innovative approach could help to tackle both issues related to exhausted batteries recycling and water treatment. Thereafter it would be interesting to study the state of the surface of the two electrodes before and after analysis and to follow the evolution of the TOC during electrolysis to see if the compound is mineralizing.

However, in view of studying the lifetime of cathode materials (vitreous carbon versus graphite) different characterization techniques should be carried out to evaluate the physicochemical (X-XPS spectroscopy) and morphological (SEM microscopy) properties of the surface of the electrodes (vitreous carbon versus graphite) before and after treatment of dye solution.

Conflict of interest

There are no conflicts of interest to declare.

Acknowledgments

This work was supported by the laboratory of electrochemistry and membrane processes of the polytechnic graduate school of Dakar University, Cheikh Anta Diop.

References

- [1] Brillas E, Mur E, Sauleda R, Sanchez L, Peral J, Domenech X, Casado J. Aniline mineralization by AOP's: anodic oxidation, photocatalysis, electro-Fenton and photo-Fenton processes. *Appl. Catal. B: Environ*, 1998; 16: 31-42.
- [2] Oturan MA, Peirotenn J, Pascal C, Aurel A J. Complete destruction of p-nitrophenol in aqueous medium by electro-Fenton method. *Environ. Sci. Technol*, 2000; 34: 3474-3479.
- [3] Bounab L, Iglesias, Pazos M, Sanroman MÁ, Gonzalez-Romero E. Effective monitoring of the electro-Fenton degradation of phenolic derivatives by differential pulse voltammetry on multi-walled-carbon nanotubes modified screen-printed carbon electrodes. *Appl. Catal. B: Environ*, 2016; 180: 544–550.
- [4] Meijide J, Rodríguez S, Sanromán M A, Pazos M. Comprehensive solution for acetamiprid degradation: Combined electro-Fenton and adsorption process. *J Electroanal Chem*, 2018; 808: 446-454.
- [5] Ioannou LA, Michael C, Vakondios N, Drosou K, Xekoukoulotakis NP, Diamadopoulou E, Fatta-Kassinos D. Winery wastewater purification by reverse osmosis and oxidation of the concentrate by solar photo-Fenton. *Sep. Purif. technol*, 2013; 118: 659-669.
- [6] Bocos E, Pazos M, Sanroman MÁ. electro-Fenton decolourization of dyes in batch mode by the use of catalytic activity of iron loaded hydrogels. *J. Chem. Technol Biotechnol*. 2014; 89 : 1235–1242.
- [7] Oturan MA, Oturan N, Edelahia MC, Podvorica FI, Kacemi KE. Oxidative degradation of herbicide diuron in aqueous medium by Fenton's reaction based advanced oxidation processes. *Chem. Eng. J*. 2011; 171: 127–135.
- [8] Sopaj F, Oturan N, J Pinson, Podvorica FI, Oturan MA. Effect of the anode materials on the efficiency of the electro-Fenton process for the mineralization of the antibiotic sulfamethazine. *Appl. Catal. B: Environ*. 2016; 199: 331–341.
- [9] Yi W, Yuhui L, Tianfu L, Shuqin S, Xuchun G, Hong L, Panagiotis T. Dimethyl phthalate degradation at novel and efficient electro-Fenton cathode. *Appl. Catal. B: Environ*. 2014; 156–157: 1–7.
- [10] Trellu C, Péchaud Y, Oturan N, Mousset E, Huguenot D, van Hullebusch ED, Esposito G, Oturan MA. Comparative study on the removal of humic acids from drinking

water by anodic oxidation and electro-Fenton processes: Mineralization efficiency and modelling. *Appl. Catal. B: Environ.* 2016; 194: 32–41.

[11] Matsue T, Fujihira M, Osa T. Oxidation of alkylbenzenes by electrogenerated hydroxyl radical. *J. Electrochem Soc.* 1981; 128: 2565–2569.

[12] Brillas E, Sirés I, Oturan M. Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry. *Chem Rev.* 2009; 109: 6570–6631.

[13] Mousset E, Wang Z, Hammaker J, Lefebvre O. Physico-chemical properties of pristine graphene and its performance as electrode material for electro-Fenton treatment of wastewater. *Electrochim Acta.* 2016; 214: 217–230.

[14] Soltani RDC, Rezaee A, Khataee AR, Godini H. Electrochemical generation of hydrogen peroxide using carbon black-, carbon nanotube-, and carbon black/carbon nanotube-coated gas-diffusion cathodes: effect of operational parameters and decolorization study. *Res. Chem. Intermed.* 2013; 39: 4277–4286.

[15] Lan H, He W, Wang A, Liu R, Liu H, Qu J, Huang CP. An activated carbon fiber cathode for the degradation of glyphosate in aqueous solutions by the electro-Fenton mode: Optimal operational conditions and the deposition of iron on cathode on electrode reusability. *Water Res.* 2016; 105: 575–582.

[16] Sudoh M, Kodera T, Sakai K, Zhang J Q, Koide K. Oxidative degradation of aqueous phenol effluent with electrogenerated Fenton's Reagent. *J Chem Eng Japan.* 1986; 19: 513–518.

[17] Qiang Z, Chang J-H, Huang C-P. Electrochemical generation of hydrogen peroxide from dissolved oxygen in acidic solutions. *Water Res.* 2002; 36: 85–94.

[18] Zhao H, Chen Y, Peng Q, Wang Q, Zhao G. Catalytic activity of MOF(2Fe/Co)/carbon aerogel for improving H₂O₂ and •OH generation in solar photo-electro-Fenton process. *Appl. Catal. B: Environ.* 2017; 203: 127–137.

[19] Martínez-Huitle CA, Brillas E. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review. *Appl. Catal. B: Environ.* 2009; 87: 105–145.

[20] Xu A, Han W, Li J, Sun X, Shen J, Wang L. Electrogeneration of hydrogen peroxide using Ti/IrO₂-Ta₂O₅ anode in dual tubular membranes Electro-Fenton reactor for the degradation of tricyclazole without aeration. *Chem. Eng. J.* 2016; 295: 152–159.

[21] García-Rodríguez O, Bañuelos J A, Zavala A R, Godínez L A. and Rodríguez-Valadez F J. Electrocatalytic Activity of Three Carbon Materials for the In-situ Production

of Hydrogen Peroxide and Its Application to the Electro-Fenton Heterogeneous Process. *Int. J. Chem. React. Eng.* 2016, 14 (4).

[22] Zhou L, Hu. Z, Zhang C, Bi Z, Jin T, Zhou M. Electrogenation of hydrogen peroxide for electro-Fenton system by oxygen reduction using hemically modified graphite felt cathode. *Sep. Purif. Technol.* 2013; 111: 131–136.

[23] Zhou L, Zhou M, Zhang C, Jiang Y, Bi Z, Yang J. Electro-Fenton degradation of p-nitrophenol using the anodized graphite felts. *Chem. Eng. J. Chemical Engineering Journal.* 2013; 233: 185–192.

[24] Azri MY., Contribution à l'étude de l'incinération des polluants organiques par le procédé d'électrooxydation directe et indirecte sur électrodes modifiées, Thèse UNIVERSITE DES SCIENCES ET DE LA TECHNOLOGIE d'ORAN Mohamed Boudiaf, 2015.

[25] Torres-Palma RA, Sarria V, Torres W, Peringer P, Pulgarin C. Electrochemical treatment of industrial wastewater containing 5-amino-6-methyl-2- benzimidazolone: toward an electrochemical-biological coupling. *Water Res.* 2003; 37: 3118–3124.

[26] Zaviska F, Drogui P, Blais J-F, Mercier G. In situ active chlorine generation for the treatment of dye-containing effluents. *J Appl Electrochem.* 2009; 39: 2397–2408.

[27] Azri M, Zerouali D. Traitement d'effluents pétrochimiques par procédés Electro-Fenton Etude électrochimique sur la réaction de réduction d'oxygène pour la génération du peroxyde d'hydrogène. *Rev. Energ. Renew.* 2013; 16: 11–22.

[28] Kuang F, Zhang D, Li Y, Wan Y, Hou B. Electrochemical impedance spectroscopy analysis for oxygen reduction reaction in 3.5% NaCl solution. *J. Solid. State. Electrochem.* 2009; 13: 385–390.

[29] AZRI MY, ZEROUALI D. Electrochemical incineration of refractory organic pollution by electrochemically generated fenton's reagent. *J. Chil. Chem. Soc.* 2012; 57: 1388-1393.

[30] Petrucci E, Da Pozzo A, Di Palma L. On the ability to electrogenerate hydrogen peroxide and to regenerate ferrous ions of three selected carbon-based cathodes for electro-Fenton processes. *Chem. Eng. J.* 2016; 283: 750–758.

[31] Liu H, Wang C, Xuan X, Jiang C, Cui H. A novel electro-Fenton process for water treatment: reaction-controlled pH adjustment and performance assessment. *Environ Sci Technol.* 2007; 41: 2937–2942.

[32] Hsiao YL, Nobe K. Oxidative reactions of phenol and chlorobenzene with in situ electrogenerated Fentons reagent. *Chem Eng Commun.* 1993; 126: 97–110.

[33] Yu F, Zhou M, Yu X. Cost-effective electro-Fenton using modified graphite felt that dramatically enhanced on H₂O₂ electro-generation without external aeration. *Electrochim Acta.* 2015; 163: 182–189.

[34] Petrucci E, Di Palma L, Lavecchia R, Zuorro A. Treatment of diazo dye Reactive Green 19 by anodic oxidation on a boron-doped diamond electrode. *J. Ind Eng Chem.* 2015; 26: 116-121.

ACCEPTED MANUSCRIPT

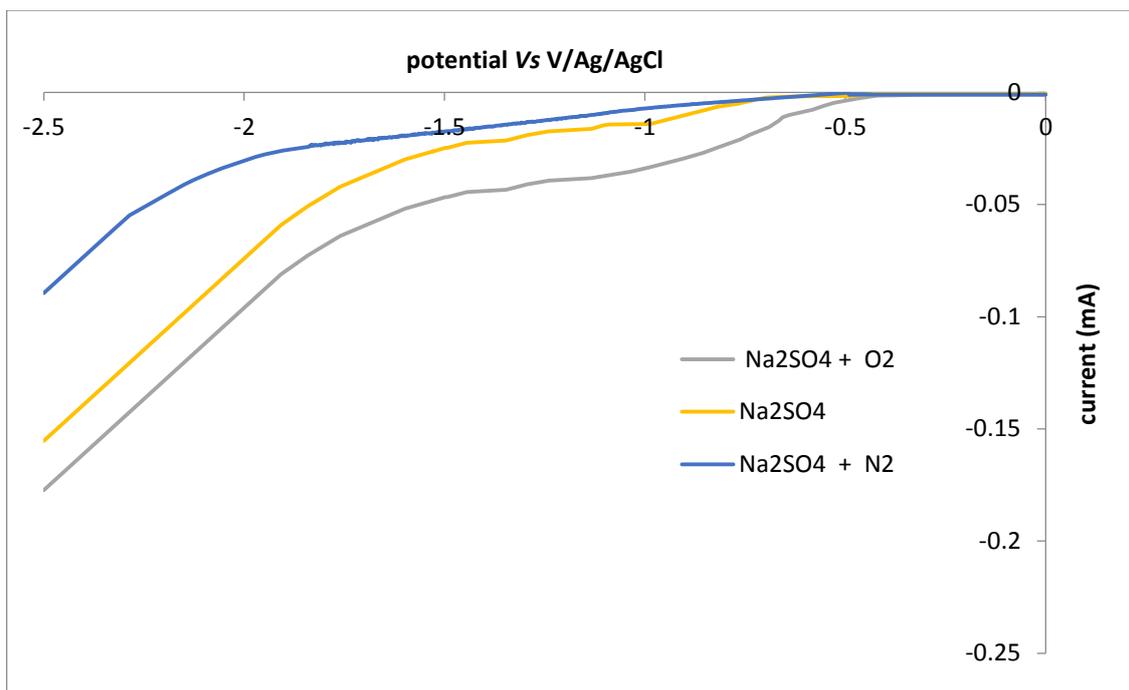


Fig 1 A)

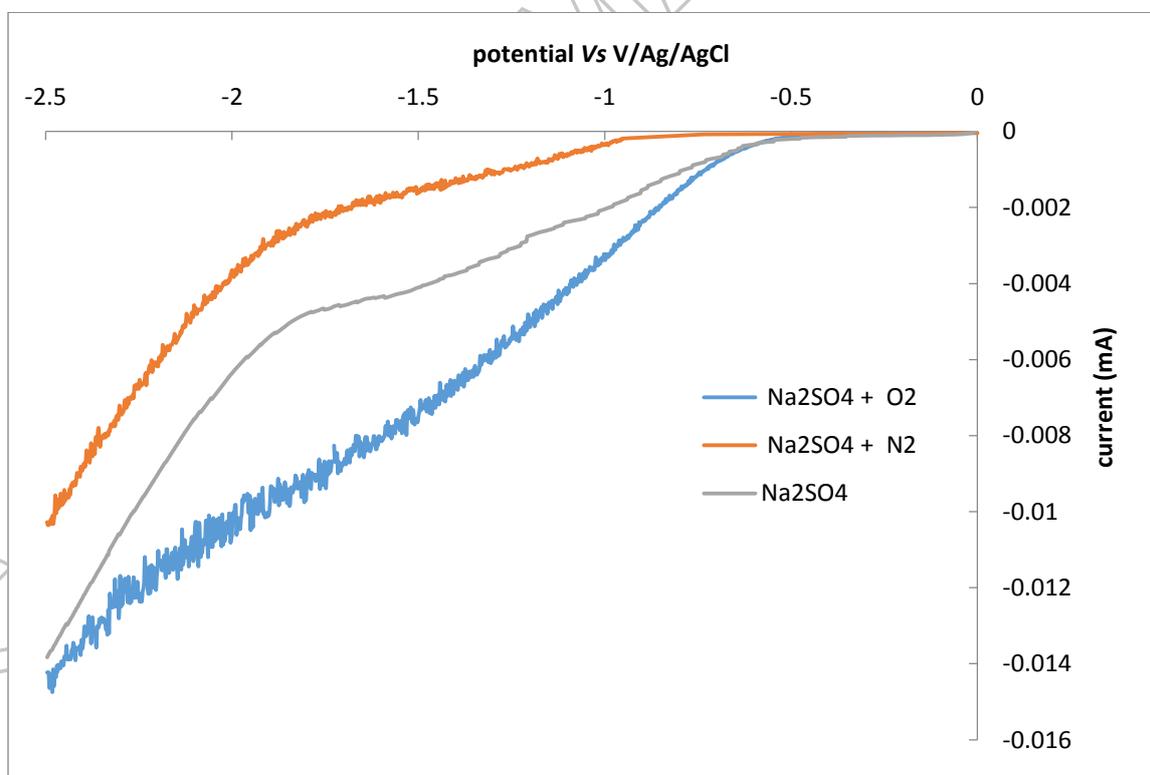


Fig 1 B)

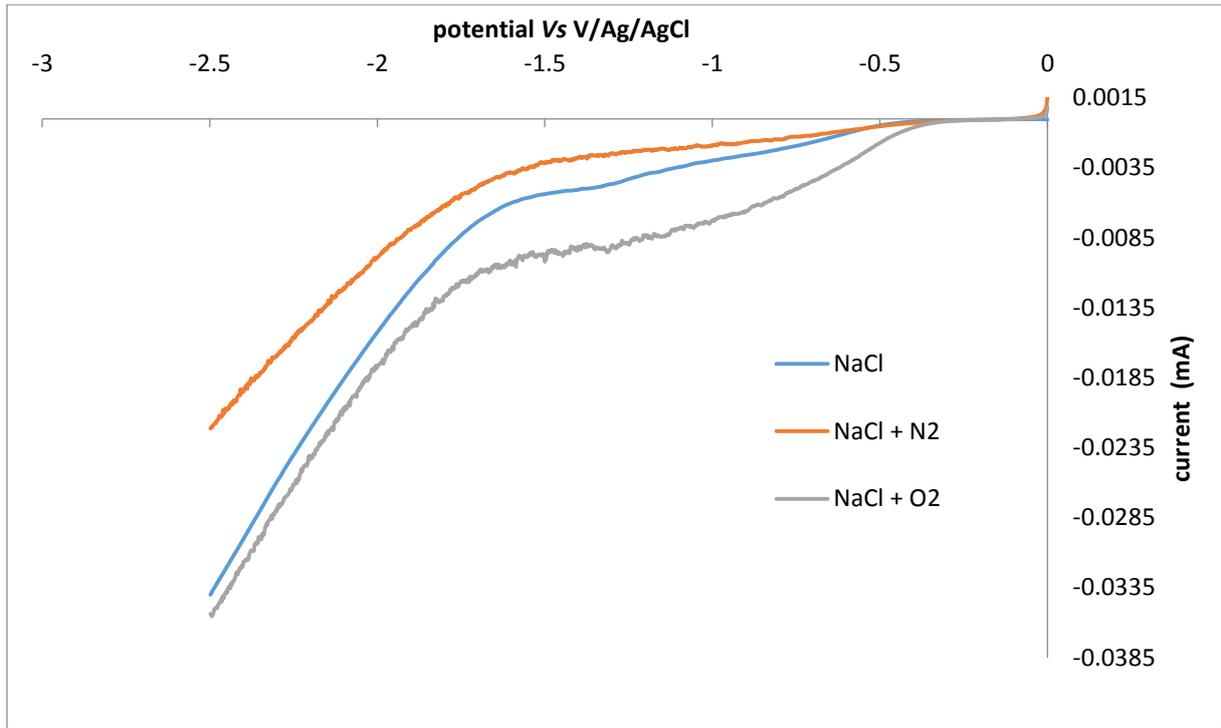


Fig 2A)

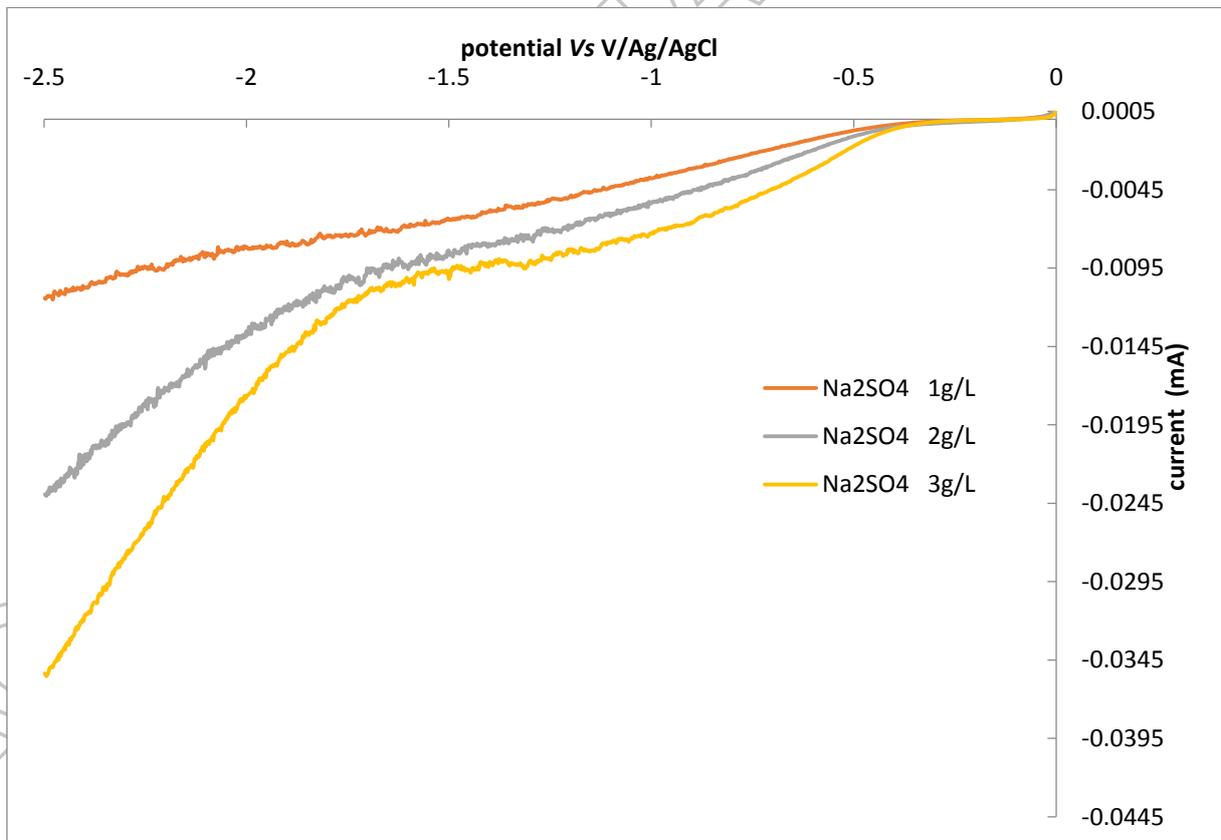


Fig 2B)

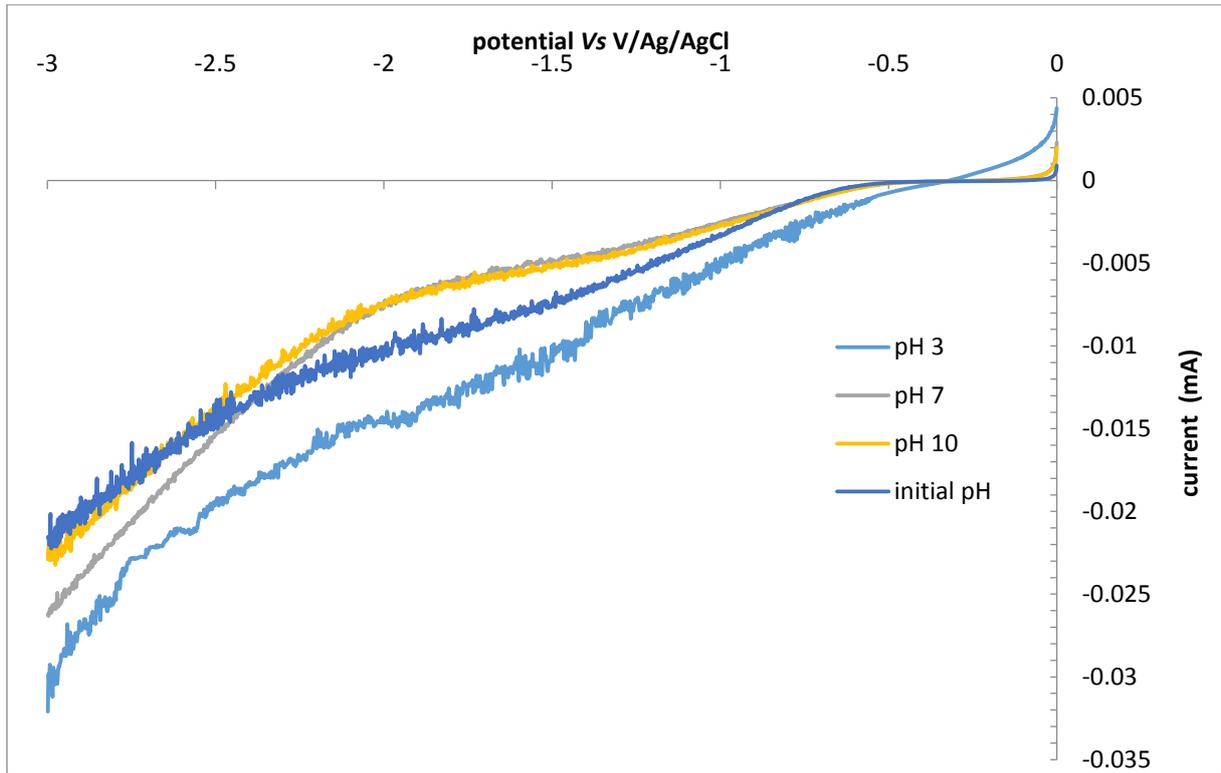


Fig 3A)

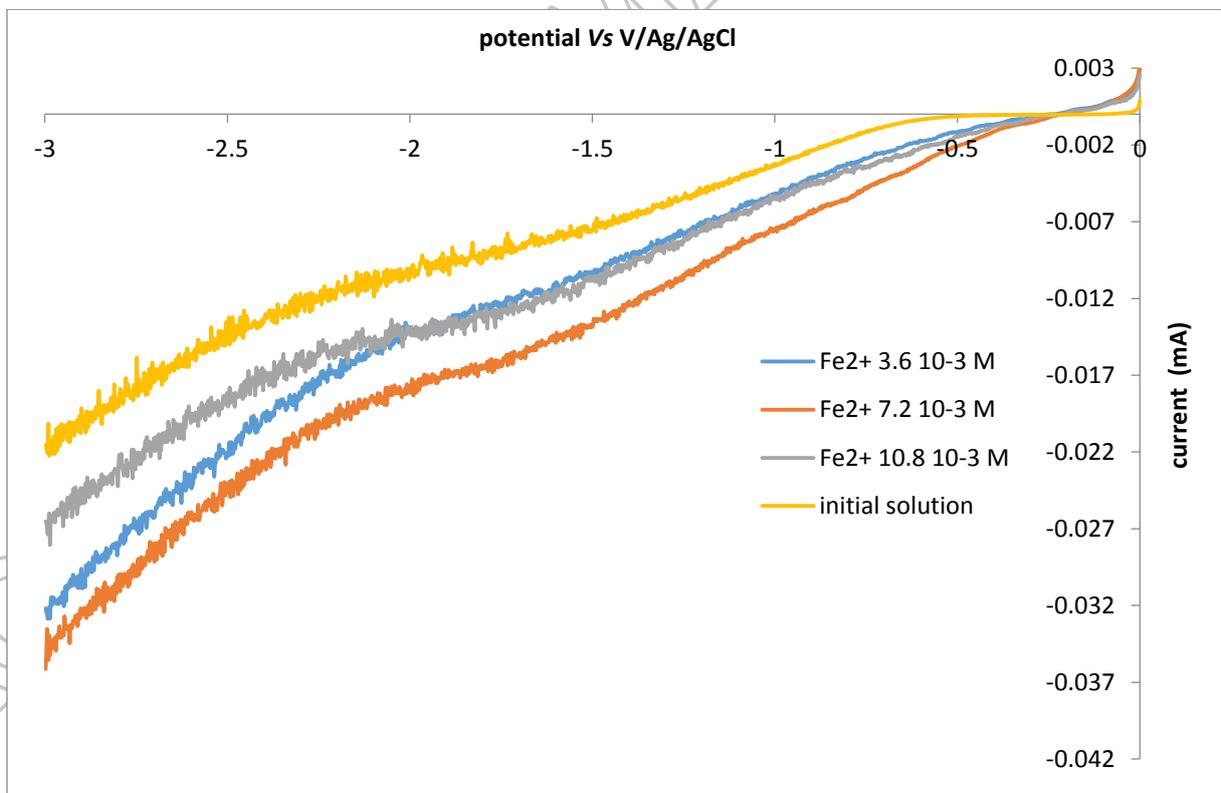


Fig 3B)

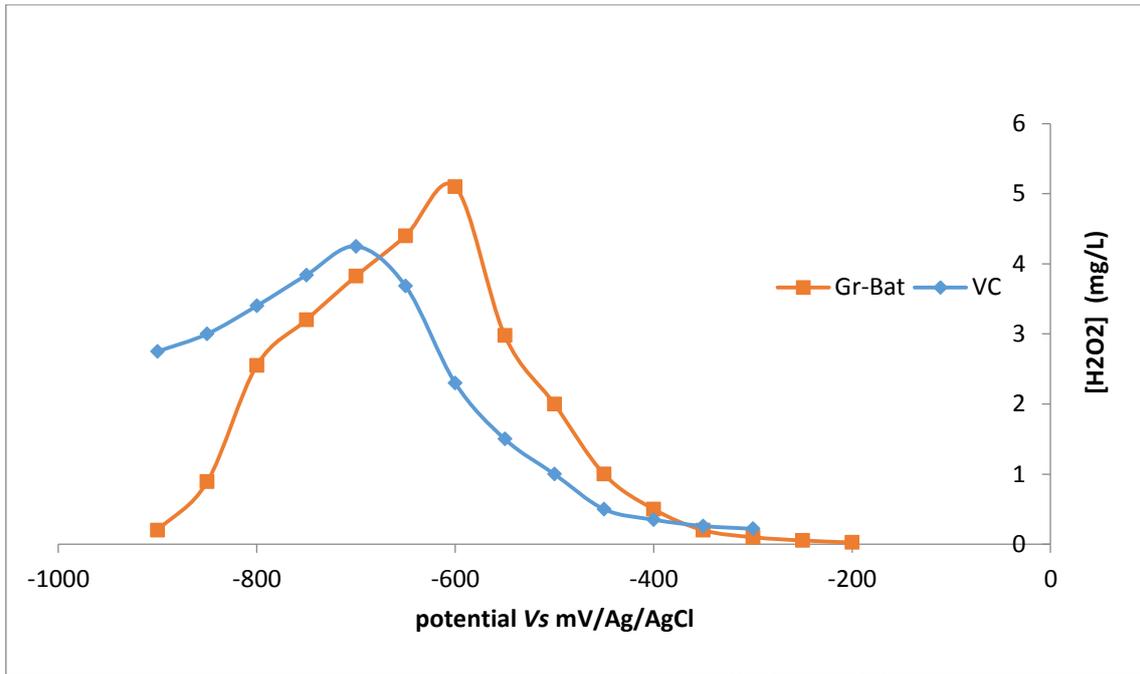


Fig 4A)

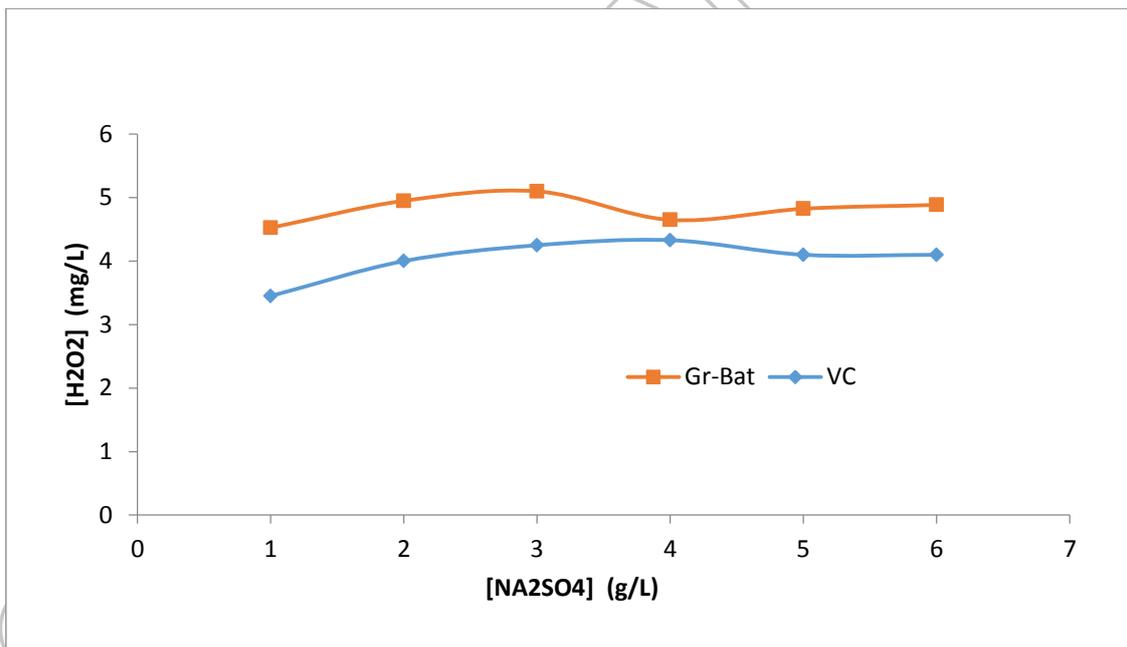


Fig 4B)

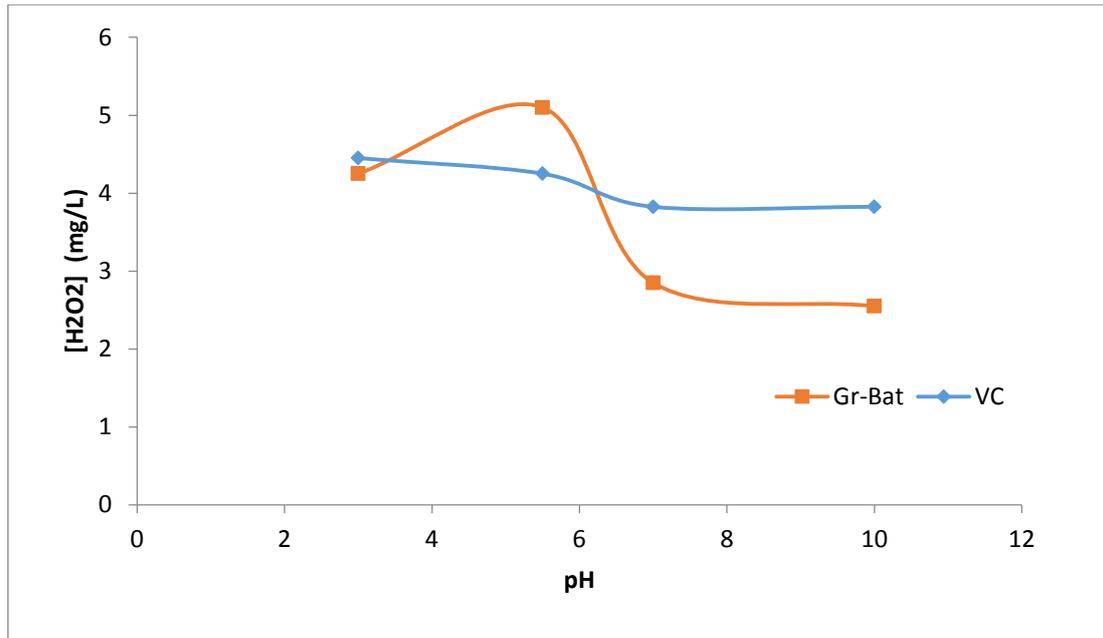


Fig 4C)

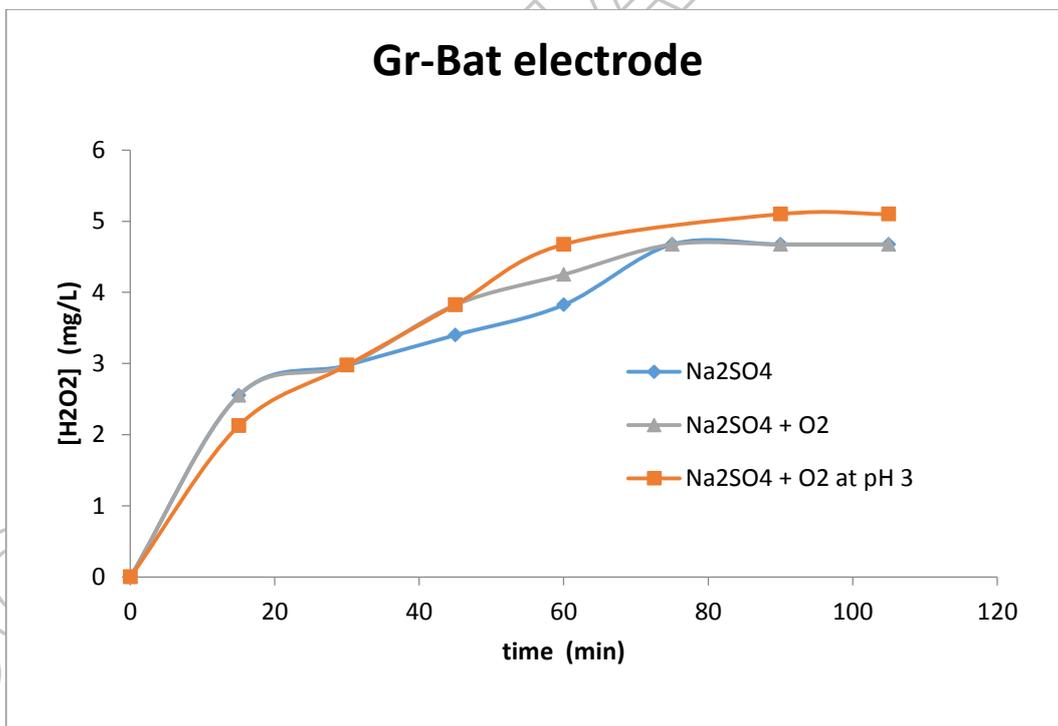


Fig 5A)

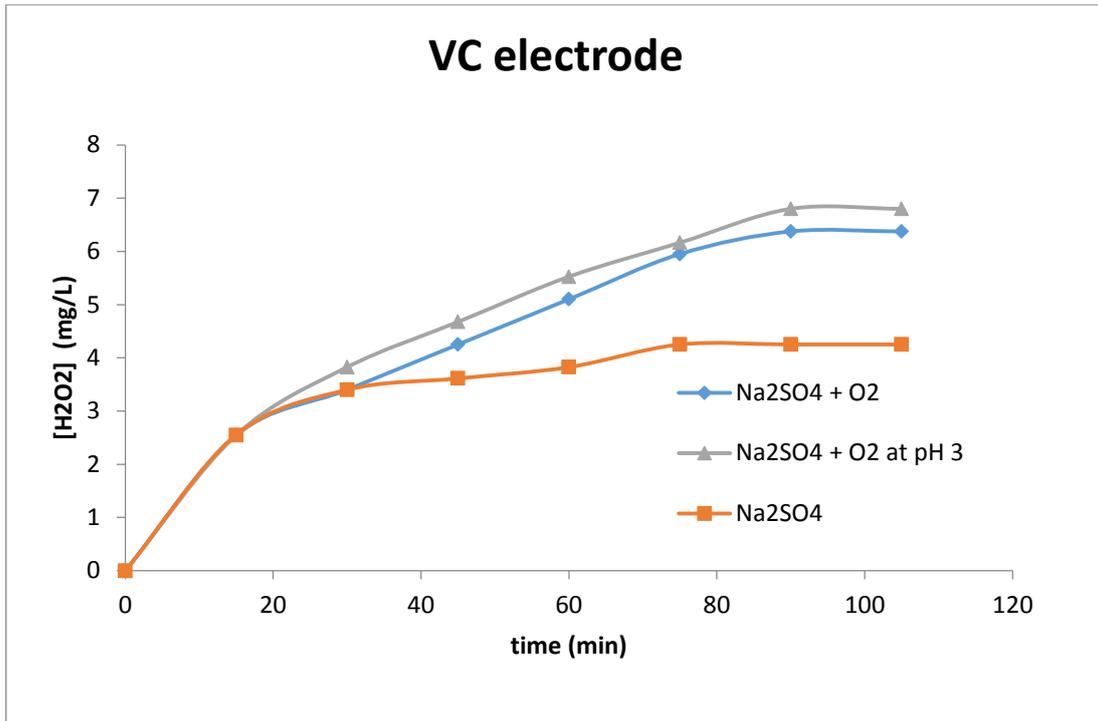


Fig 5B)

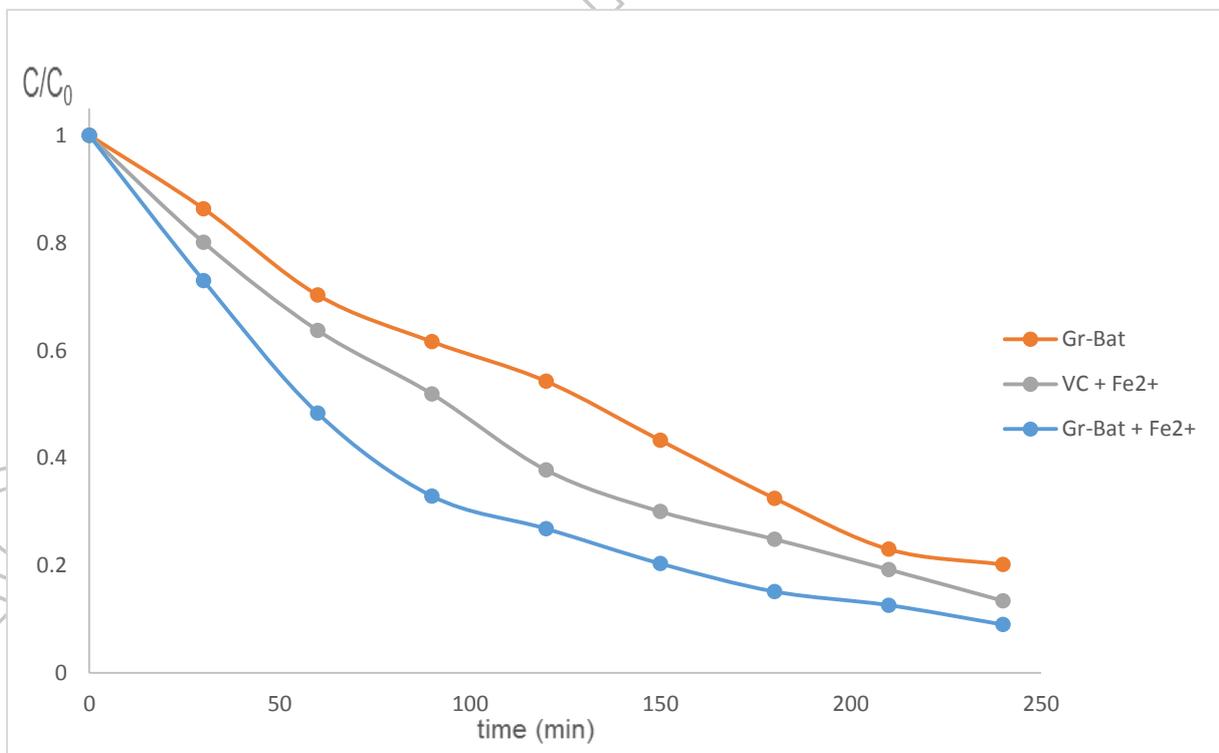


Figure 6

Figure captions

Figure 1. Cathodic polarization curves of oxygen reduction for three experimental conditions a) $[\text{Na}_2\text{SO}_4] = 3 \text{ g L}^{-1}$; b) $[\text{Na}_2\text{SO}_4] = 3 \text{ g L}^{-1} + \text{O}_2$; c) $[\text{Na}_2\text{SO}_4] = 3 \text{ g L}^{-1} + \text{N}_2$; $v = 10 \text{ mV s}^{-1}$ **A)** on Gr-Bat electrode **B)** on VC electrode

Figure 2: Cathodic polarization curves of oxygen reduction on Gr-Bat electrode. **A)** For three experimental conditions a) $[\text{NaCl}] = 3 \text{ g L}^{-1}$; b) $[\text{NaCl}] = 3 \text{ g L}^{-1} + \text{O}_2$; c) $[\text{NaCl}] = 3 \text{ g L}^{-1} + \text{N}_2$; $v = 10 \text{ mV s}^{-1}$ **B)** Electrolyte concentration effect on oxygen reduction. Conditions: O_2 sparging, $[\text{Na}_2\text{SO}_4] = 1, 2 \text{ and } 3 \text{ g L}^{-1}$; $v = 10 \text{ mV s}^{-1}$

Figure 3: Effect of parameters on oxygen reduction using Gr-Bat electrode **A)** Effect of pH. Conditions: $[\text{Na}_2\text{SO}_4] = 3 \text{ g L}^{-1}$; O_2 sparging for different pH (3, 5.4, 7, and 10); $v = 10 \text{ mV s}^{-1}$ **B)** Effect of Fe^{2+} concentration. Conditions: $[\text{Na}_2\text{SO}_4] = 3 \text{ g L}^{-1}$; $[\text{Fe}^{2+}] = (0; 3.6 \times 10^{-3}; 7.2 \times 10^{-3} \text{ and } 10.8 \times 10^{-3} \text{ M})$; $v = 10 \text{ mV s}^{-1}$

Figure 4: Effect of parameters on the amount of electro-generated H_2O_2 ; electrolysis time = 90 min. **A)** Effect of cathodic potential. Conditions: 3 g L^{-1} of Na_2SO_4 . **B)** Effect of the electrolyte concentration (Na_2SO_4). Conditions: Gr-Bat potential = -600 mV; VC potential = -700 mV. **C)** Effect of different pH values (3, initial solution (5.4), 7 and, 10). Conditions: $[\text{Na}_2\text{SO}_4] = 3 \text{ g L}^{-1}$; Gr-Bat potential = -600 mV; VC potential = -700 mV.

Figure 5: Effect of O_2 bubbling on the production of H_2O_2 . Conditions: $[\text{Na}_2\text{SO}_4] = 3 \text{ g L}^{-1}$ with and without pH adjustment to 3. **A)** on Gr-Bat electrode; Voltage = -600 mV *Vs* Ag/AgCl **B)** on VC electrode; Voltage = -700 mV *Vs* Ag/AgCl.

Figure 6: Evolution of crystal violet concentration as a function of electrolysis time. Conditions: pH = 3; $[\text{Na}_2\text{SO}_4] = 5.10^{-2} \text{ M}$; $[\text{Fe}^{2+}] = 10^{-4} \text{ M}$; $I = 300 \text{ mA}$.