Int. J. Electrochem. Sci., 9 **(2014)** 7916 - 7924

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrooxidation of Free Sulfite by an Integrated System of Glassy Carbon Modified Electrodes with Nickel Phthalocyanines and Membrane Absorber in Red Wine

Roxana Arce[1,*], *María J. Aguirre*[2], *Julio Romero*[1]

[1] Universidad de Santiago de Chile, Departamento de Ingeniería Química, Facultad de Ingeniería, Av. B. O'Higgins 3363, 9170022, Estación Central, Santiago, Chile
[2] Universidad de Santiago de Chile, Departamento de Química de los Materiales, Facultad de Química y Biología, Av. B. O'Higgins 3363, 9170022, Estación Central, Santiago, Chile.
[*]E-mail: roxana.arce@usach.cl

Received: 22 September 2014 / *Accepted:* 18 October 2014 / *Published:* 28 October 2014

At basic pH values, the integrated system modified electrode / membrane absorber, it is possible to obtain a sensor of sulfite in actual red wine samples. This quantification method consumes small amounts of sample, it is fast and shows good linearity with r^2 of 0.998 and good accuracy. This integrated approach can separate free sulfite red wine matrix with the absorption system of the membrane and, moreover, can be quantified using the electrochemical sensor using NiTSPc modified electrodes, obtaining a concentration of sulfite free 29.8 ± 0.2 mg·L^{-1}.

Keywords: electrooxidation of sulfite, membrane absorber, modified electrodes, phtalocyanines, wine.

1. INTRODUCTION

The treatment of the species that contain sulfur has called the attention of scientists both on the chemical industries and on biological areas [1, 2]. Sulfur anion oxidation has been carried out on the homogeneous phase through different chemical and photochemical methods [3, 4]. It has also been catalyzed through different soluble macrocyclic complexes, making SO_4^{2-} species their main product [5]. On the other hand, electrochemical techniques appear as a good alternative for the transformation of these species and, particularly, of sulfite in the wine industry [6]. Sulfite is an antiseptic commonly used in wines and food. It can be found free or bound to phenols, aldehydes and other organic compounds [7]. Its concentration at high levels has toxic effects, such as breathing problems in asthmatic patients, hypotension and gastrointestinal problems [8]. For that reason, it is useful to electrochemically determine its concentration.

On the field of quantification, transformation and oxidation of sulfite, electrodes modified with transition metal complexes have gained interest [9-11], demonstrating to be good catalyzers on heterogeneous phase [12].

To determine the sulfite oxidation wave, a glassy carbon electrode modified with Ni phthalocyanines [13, 14] will be used. In our laboratory, sulfite has been determined with nickel phthalocyanines polymeric films, obtaining, from this modification, an increase in the response to the sulfite oxidation wave current, a research that has not been reported by other laboratory teams.

Squarewave voltammetry allows to determine oxidation or reduction waves more precisely than cyclic or differential pulse voltammetry does, reason why it is widely used in analytical determinations [15-17]. Along with squarewave voltammetry, the method of calibration curve will be applied [18].

Previous studies done in the laboratory [10, 19] show that it is possible to find an interval potential where SO_3^{-2} shows a growing response (in current) to basic pHs, the pH at which the adsorbent solution or 0.02 $mol\cdot L^{-1}$ NaOH solution is precisely at.

On the other hand, a system of membrane absorber will be used, aiming to stop the effect of interfering substances on the electrochemical determination. As it is known, there is a high phenol content in wine and these species appear in the same potential zone where sulfite appears when electrochemically measured [11].

In this way, the content of sulfites in wines will be determined in a fast and reliable way by a system of modified electrodes based on NiTSPc polymers which will be coupled to a membrane absorber for the instant separation of interferers, offering an integral control solution for export wine production.

The absorbent solution is placed inside of the membrane absorption system used in this research (see Figure 1).

In this research, polypropylene (PP) membranes are used in order to put them in contact with the red wine and the receiving solution [20]. The principle of wine sulfite quantification is the following: the feeding, which is red wine, is acidified by a H_2SO_4 solution in order to ensure the formation of volatile sulfites since the presence of volatile SO_2 increases as the pH decreases. The analyzed case for sulfite quantification is based on the extraction of free and bound sulfite in wine through pH modification to extract the non-volatile forms (HSO_3^- y SO_3^{2-}), changing them to the volatile form, SO_2. In this way, the volatile form is transferred through the membrane contactor and is recovered as free sulfite in the receiving solution [10, 21]. Besides, the effect of process parameters such as temperature, circulation speed, the concentration of receiving solution and the configuration of the solution circulations on the sulfite quantification efficiency, have been investigated in order to estimate the optimal conditions.

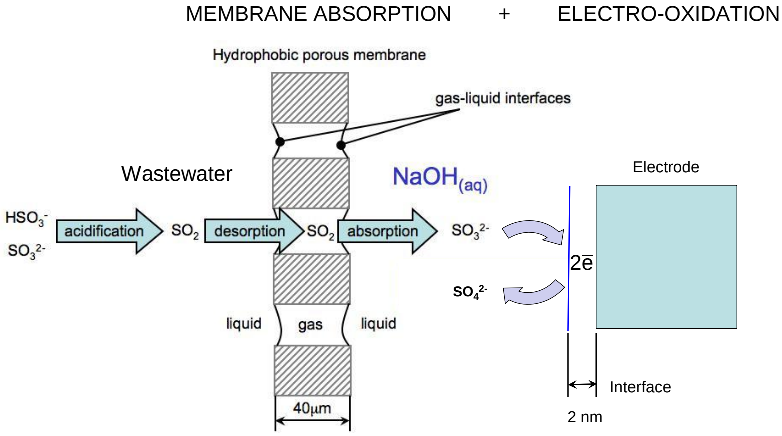

Figure 1. Principle of integrated system electrode / membrane absorber used in this study.

On the other hand, the receiving solution with its total free sulfite content was measured, later with the electrode modified with nickel phthalocyanine electroformed using a potentiostat/biopotentiostat.

2. EXPERIMENTAL

Initially, all the material was washed and the electrodes were cleaned. In the case of the working electrode, it was polished with an alumina suspension and felt. The counter electrode was put under fire and, in that way, impurities (organic compounds) were eliminated. The reference electrode was maintained submerged in a KCl 3 M solution on a compartment coupled by a Lugging capillary to the working electrode.

Then, voltammetry was performed to a 0.02 $mol\cdot L^{-1}$ NaOH solution (receiving solution) (see Figure 1) on all the pH range adding NaOH or HCl drops, respectively, and in that way the optimal pH was obtained that presented the sulfite oxidation with best response at current related to pH.

Later, a calibration curve was prepared with a set of 6 sodium sulfite solutions at different concentrations: $1\cdot10^{-4}$ - $3\cdot10^{-4}$ - $5\cdot10^{-4}$ - $7\cdot10^{-4}$ - $8\cdot10^{-4}$ - $9\cdot10^{-4}$ - $1\cdot10^{-3}$ $mol\cdot L^{-1}$. The respective voltagramms were obtained and with this calibration curve the sulfite concentration was determined on the soda previously measured at pH 10. In all respective analyses, N_2 was bubbled.

The glassy carbon electrode was polished to a mirror finish on a felt pad using alumina slurries (3 mm). The modified electrode was obtained by electrodeposition of 1mM NiTSPc in NaOH (0.1 $mol\cdot L^{-1}$) on the glassy carbon electrode surface, 20 repetitive cyclic voltammetry to 10 $mV\cdot s^{-1}$.

The modified electrodes were carefully rinsed with water to remove excess and electrolyte. The modified electrode was stabilized in carbonate buffer to pH 10 by cycling the potential within the potential window at which sulfite oxidation is performed, i. e., -1.0 to 1.0 V vs. Ag/AgCl.

As presented in Figure 1 [20, 21], the device for sulfite measurement couples either a membrane absorption system, in which the previously acidified wine circulation occurs, or a model solution by the enclosure of a hollow fiber contactor module, by whose membrane internal fiber side a SO_2 absorbent solution circulates. In this case, a NaOH diluted aqueous solution was used. In this way, the acidified wine releases the sulfite in its SO_2 form, which is transfered through the membrane and is absorbed as SO_3^{2-} in the absorbent solution.

The membrane used in this research is compound of a minimodule Celgard Liquicel® G542 of 7400 polypropylene fibers (PP) and 0.58 m^2 of effective contact area. Besides, two Preston Manostat® peristaltic pumps were used for making circulate both the analyzed solution (wine solution) and the receiving phase (NaOH(ac)), which are in contact to the minimodule.

3. RESULTS AND DISCUSSIONS

3.1. Electropolymerization of polyNiTSPc on glassy carbon. Preparation and Characterization by Repetitive Cyclic Voltammetry (RCV).

The completely flat aromatic skeleton of soluble sulphonated phthalocyanines allows them to form columnar aggregates in which π-stacking interactions between the macrocycles predominate [22].

Nickel tetraazamacrocyclic complexes are exceptionally efficient and selective electrocatalysts, probably because nickel easily changes from a square planar to an octahedral conformation [23]. Repetitive cyclic voltammetry (RCV) in alkaline solution of a soluble macrocycle on an inert electrode, such as glassy carbon (GC), yields at higher potentials, at which Ni(II) is oxidized to Ni(III) (in Figure 2, I_a) and the first steps of oxygen evolution occur, oligomers that become firmly attached to the GC [24]. The cathode process is observed to invest potential, such as I_c. The oxidation and reduction processes appear approximately at 0.0 V vs. Ag/AgCl. At the same time, a current decrease at higher potentials is observed, suggesting that the thin film may decrease the excited energy levels of the hydroxyl anion (in Figure 2, II).

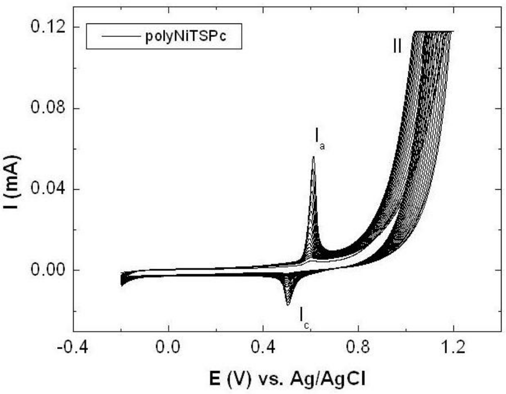

Figure 2. Voltammetric profile of electropolymerization of polyNiTSPc on a glassy carbon electrode in 0.1 mol·L^{-1} NaOH solution. v = 10 mV·s^{-1}. 20 RCVs.

Ni(III) needs a highly hydrophobic environment [25] and, in this case, this will be provided by the aromatic environment around Ni(III), which collaborates in the formation of a stacked structure, film growth probably occurring via Ni-O-Ni oxo bridges [24]. Thus, the water-soluble Ni(II)TSPc polymerize in strongly alkaline aqueous media, yielding a film when the positive limit is high enough for the formation of adsorbed OH, facilitating the formation of the O-Ni-O bridges [26].

The first 20 CVs of electroformation of the different polymeric films are shown in Figure 2. In all cases there is a non-Nernstian process whose currents increase with increasing number of cycles, indicating the growth of a film.

The cyclic voltammetry at 0.1 V·s^{-1} of the stabilized (or activated) films are also shown in Fig. 3, where there is the evidence for the modification of GC by the higher faradaic charge that the voltamperometric response shows. Two not well defined processes, a and b, can be observed, which correspond to Ni(II) oxidation and, later, to Ni(III) reduction. In this case, at high potentials the formation of hydroxyl groups can be observed (Figure 3, I)

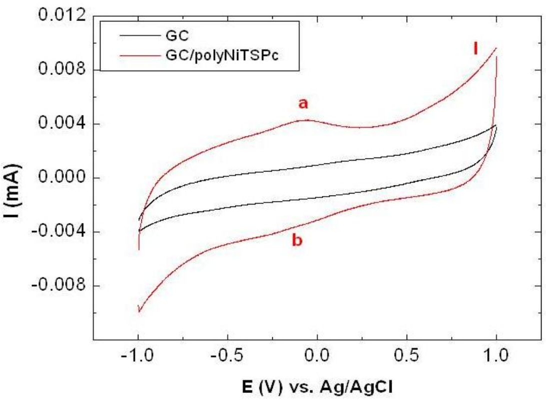

Figure 3. Comparative voltammetric profiles obtained to GC and GC/polyNiTSPc on a glassy carbon electrode in 0.1 mol·L^{-1} NaCl ethanol/water 12% v/v (pH 10) solution. v = 100 mV·s^{-1}. Cycle 1.

The voltamperometric characterization of the polyNiTSPc layers formed indicates the presence of a reversible process which has been associated to the change of the oxidation state Ni(II) ⇔ Ni(III). This process presents a diffusional component and an absorption component that indicate that the process is not only superficial but also there is entrance and exit of OH$^-$ species through the layer, as informed in other studies [27].

3.2. Electrooxidation of sulfite on GC/polyNiTSPc at pH 10.

In Figure 4, the comparison of the modified electrode voltamperometric responses can be observed in absence and presence of sulfite 1 mM. The electrocatalytic activity of the GC electrodes modified with polyNiTSPc for the sulfite oxidation can be seen as an oxidation wave at approximately 0.8 V vs. Ag/AgCl (in Figure 4, green line, c). Besides, processes a and b (green line) that correspond to the redox process Ni(II)/Ni(III) can be observed moved towards more positive potentials, becoming more notorious and reversible indicating greater stability when the polymer film is in the presence of sulfite. This may be because the reaction mechanism is present some molecule that stabilizes the polymeric film and electrocatalysis can happen.

For the sulfite to oxidize, it is concluded that the films on the CG are porous, allowing the sulfite to go through it and to react on the GC surface [24].

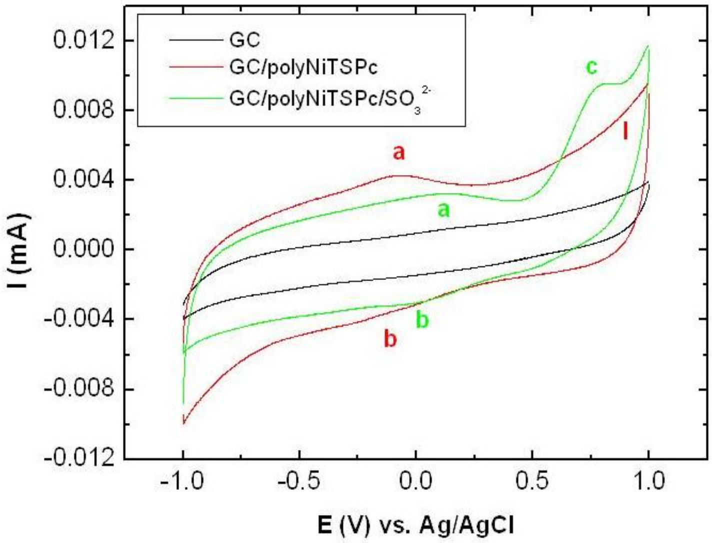

Figure 4. Profiles of comparative voltammetry of glassy carbon electrode modified with polyNiTSPc for the electrooxidation of sulfite in 0.1 mol·L^{-1} NaCl ethanol/water 12% v/v (pH 10) solution. v: 100 mV·s^{-1}. Cycle 1.

3.3. Evaluation of the integrated electrode/membrane absorber system.

Several tests for absorption by membranes were performed: effect of the solution volume, effect of the absorbent concentration and effect of the circulation flow [21, 28]. With this tests, the membrane adsorption system demonstrated 99,5% of extraction of the sulfite content of 200 mL of solution on approximately 200 seconds of operation.

With the absorber system working, tests were performed to obtain the response of the GC electrode modified with polyNiTSPc with electrocatalytic activity for the oxidation of sulfite in experimental conditions used in this study, that is to say, an electrode modified towards sulfite. Then, these voltamperometric responses were obtained from the sulfite oxidation on the 0.02 mol·L^{-1} NaOH solution at pH 10 from the receiving solution. Responses of the GC electrode modified with polyNiTSPc active for sulfite were obtained, since at this pH the species fraction is 0.998 in aqueous solution, almost a 100% of this species is present. The oxidation peak was deconvolutionated to obtain peak potential and current peak, whose values are 5.031·10^{-6} A / 0.972 V vs. Ag/AgCl.

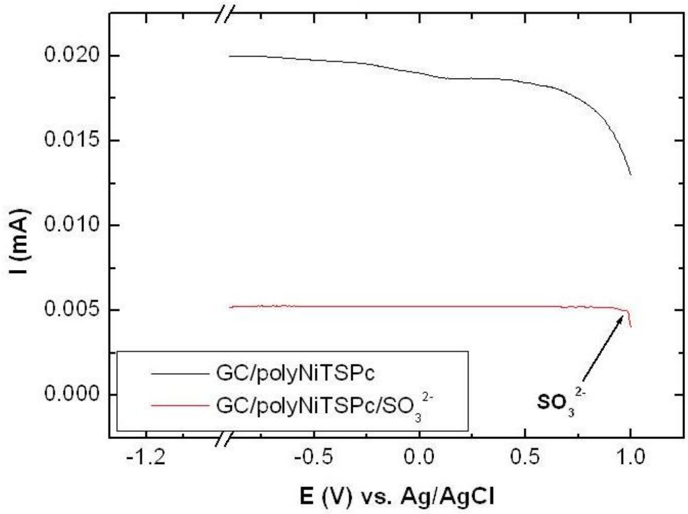

Figure 5. Profiles of the voltammetry of a glassy carbon electrode modified with polyNiTSPc for the electrooxidation of sulfite to pH 10 (receiving solution).

Later, the voltamperometric profiles at pH 10 in 0.1 mol·L^{-1} NaCl ethanol/water 12% v/v solution were obtained at different sulfite concentrations (see Figure 6) and, from these, Ip (peak oxidation current) versus sulfite concentration was mapped. The next chart shows the rising of the sulfite oxidation current with the increase in the analyte concentration, existing a direct proportion between the peak current and the sulfite concentration, in the concentration ranges here used.

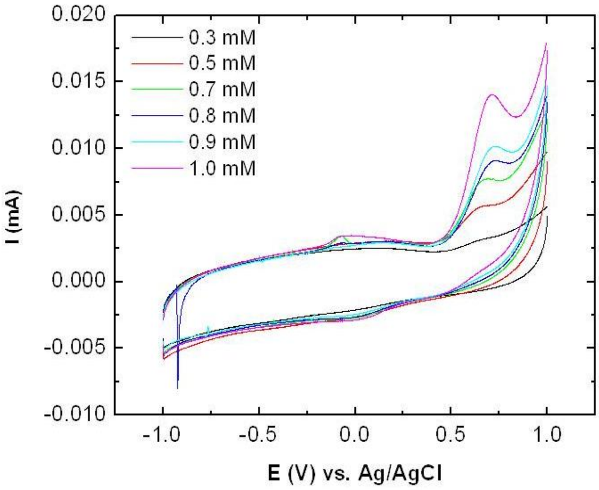

Figure 6. Profiles of the voltammetry of a glassy carbon electrode modified with polyNiTSPc for the electrooxidation of sulfite to pH 10 at different sulfite concentrations.

Calibrate curves were obtained and gave a mean linear regression of:

Ip(A) = (average ± SD)[SO_3^{2-}] + (average intercept ± SD), with a regression coefficient of 0.9984 (Figure 7).

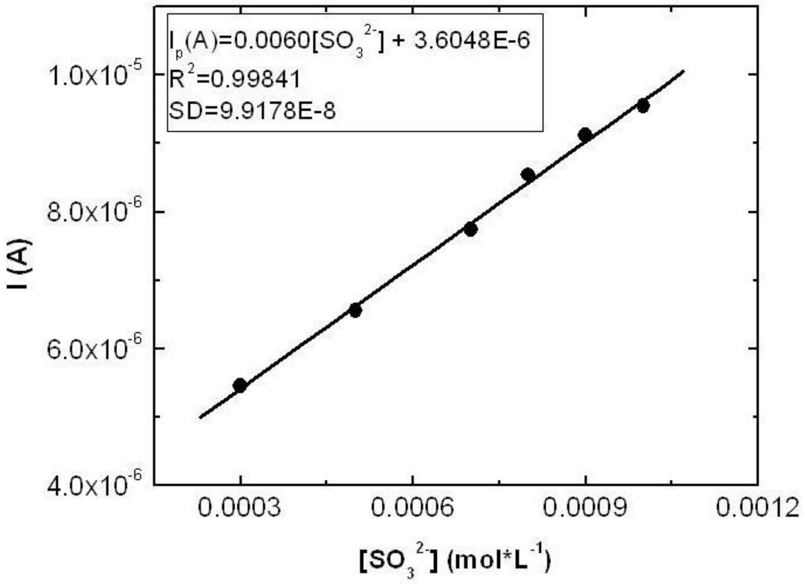

Figure 7. Calibration curve: Ip versus sulfite concentration, at pH 10.

All curves were done in a range of concentrations between $1\cdot10^{-4}$ mol·L^{-1} and $1\cdot10^{-3}$ mol·L^{-1} from various voltammograms obtained. Figure 6 shows a calibration curve obtained, where it can be seen that its correlation coefficient (R^2) is very close to 1, giving evidence of the linearity of the method.

To obtain the concentration in the sample of real red wine passed through the membrane and recovered sulfites, oxidation current in the receiving solution is interpolated. This average value is 29.8 ± 0.2 mg·L^{-1} for free sulfite, value is very close to that delivered by the vineyard where the red wine belongs to.

4. CONCLUSION

When evaluating the integrated electrode/membrane absorber system**,** its application on sulfite sensors on the experimental conditions here used can be obtained. This method of quantification consumes small sample quantities, is fast and shows good linearity and accuracy. Eventually, it can be used in other types of wine since it can separate free sulfite from the with the membrane absorber system and, on the other hand, it is possible to quantify it through the use of the electroanalytic sensor using the NiTSPc modified electrodes.

ACKNOWLEDGEMENTS
Financial support from 3130594 Fondecyt-Postdoctoral and 1120071 Fondecyt-Regular projects. Also, this study has been supported by Project ICM-P10-003-F, CILIS, granted by Fondo de Innovación para la Competitividad, del Ministerio de Economía, Fomento y Turismo, Chile.

References

1. C. Lion, L. Da Conceicao, H. Sayag, C.R. Acad. *Sci. Ser. II. C.* 2 (1999) 57.
2. M.H. Ali, M. McDermott, *Tetrahedron Lett*. 43 (2002) 6271.
3. S.-M. Chen, S.-W. Chiu, *Electrochem Acta* 45 (2000) 4399.
4. N. Rea, B. Loock, D. Lexa, *Inorg. Chim. Acta* 312 (2001) 53.
5. S-M. Chen, *J. Molec. Cat. A: Chem*. 112 (1996) 277.
6. C. Montes, J. H. Vélez, G. Ramírez, M. Isaacs, R. Arce, and M. J. Aguirre., *The Scientific World Journal*, 2012 (2012) doi: 10.1100/2012/168148. Available online.
7. I. Hornsey, "The Chmestry and Biology of Wine Making", *The Royal Society of Chemistry*, Thomas Graham House, Cambridge U.K. 2007.
8. Schwartz, H. J., *J Allergy Clin. Immunol.* 71 (1983) 487.
9. J. Henríquez, G. Ramírez, B. Matsuhiro, L. Mendoza, M. Isaacs, C. Arévalo, M.J. Aguirre, *J. Quantum Chemistry*. Sent.
10. R. Arce, P. Márquez, F. Herrera, M. J. Aguirre, J. Romero, *J. Chil. Chem. Soc.* 58(4) (2013), 1982-1985.
11. B. Molinero-Abad, M. A. Alonso-Lomillo, O. Domínguez-Renedo, M. J. Arcos-Martínez. *Analyt Chim Acta*, 812 (2014) 41-44.
12. E. Trollund, P. Ardiles, M.J. Aguirre, S.R. Biaggio, R.C. Rocha-Filho, *Polyhedron* 19 (2000) 2303.
13. J. F. Silva, S. Griveau, C. Richard, J. H. Zagal, F. Bedioui, E*lectrochemistry Communications*, 9 (2007) 1629-1634.
14. N. Navarrete, C. Canales, R. del Río, G. Ramírez, *J. Chil. Chem. Soc.*, 58 (2013)1971.
15. A. J. Bard & L. R. Faulkner, *Electrochemical methods*, Wiley, 2ª edición, 2001.
16. L. Zhu, L. Xu, B. Huang, N. Jia, L. Tan, S. Yao, *Electrochim Acta* 115 (2014) 471-477.
17. G. Bia, L. Borgnino, P. I. Ortiz, V. Pfaffen, *Sens Actuat B: Chem*, 203 (2014) 396-405.
18. S. Douglas, J. Holler, T. Nieman, *"Principios de Análisis Instrumental",* 5º edición, Ed. Mc Graw Hill, 2001.
19. M. Lucero, G. Ramírez, A. Riquelme, I. Azocar, M. Isaacs, F. Armijo, J. E. Förster, E. Trollund, M. J. Aguirre, D. Lexa, *J Mol Catal A: Chem* 221 (2004) 71-76.
20. A Hasanoğlu, J Romero, B Pérez, A. Plaza, *Chem Engin J* 160 (2010) 530-537.
21. A. Hasanoğlu, J. Romero, A. Plaza, W. Silva, *Desalination and Water Treatment* 51 (2013) 5649-5663.
22. K. De Wael, P. Westbroek, P. Bultinck, D. Depla, P. Vandenabeele, A. Adriaens and E. Temmerman, *Electrochem. Comm.* 7 (2005) 87.
23. A.B.P. Lever, M.R. Hempstead, C.C. Leznoff, W. Liu, M. Melnik, W.A. Nevin and P. Seymour, *Pure Appl. Chem.* 58 (1986) 1467.
24. N. Pereira_Rodrigues, V. Albin, M. Koudelka-Hep, V. Auger, A. Pailleret and F. Bedioui, *Electrochemistry Communications* 4 (2002) 922.
25. S-I Mho, B. Ortiz, S-M. Park, D. Ingersoll and N. Doddapaneni, *J. Electrochem. So.*, 142 (1995) 1436.
26. D. Chang, T, Malinski, A. Ulman and K.M. Kadish, *Inorg. Chem.,* 23 (1984) 817.
27. S. Trevin, F. Bedioui, M.G. Gomez-Villegas and C. Bied-Charreton, *J. Mater. Chem.* 7 (1997) 923.
28. Roxana Arce, Julio Romero, María J. Aguirre. *J. Appl. Electrochem.* (2014). doi: 10.1007/s10800-014-0750-7. Available online.