

APPLICATION OF ELECTROCHEMICAL OXIDATION OF SULFIDE FOR THE TREATMENT OF INDUSTRIAL WASTE WATERS

Eveline Martins Mattiusi, evelinemattiusi@yahoo.com.br

Nice Mika Sakamoto Kaminari, nice.kaminari@gmail.com

Maria José Jerônimo de Santana Ponte, mponte@ufpr.br

Haroldo de Araújo Ponte, hponte@ufpr.br

Federal University of Parana, Laboratory of Environmental Technology (LTA), PO Box 19011, ZIP CODE 81531-990, Curitiba, PR, Brazil

Abstract. *The growing demand for energy inputs has led oil companies to process heavy oils with higher sulfur content. The effluent from condensing gas processing oil are composed of dissolved hydrogen sulfide (H_2S), a highly toxic and corrosive gas. Thus, the objective is study the application of electrochemical oxidation process for the neutralization of H_2S from industrial waste waters. However, in the tests we used a synthetic solution and the first step of the study was the voltammetry curves obtained from the registries of current versus potencial. Through this study, the current required to be applied in solution to occur the electrochemical oxidation of H_2S to sulfuric acid and/or elemental sulfur is determined. The voltammetric study, the main purpose of work, is fundamental to the development of future works using industrial reactors.*

Keywords: *sulfide, electrochemical oxidation, voltammetry study*

1. INTRODUCTION

The growth in energy consumption due to industrial development and population growth, is leading oil companies to take actions to ensure increased production with environmental conservation. Fossil fuels, including solids, liquids and gases are the majority of this demand.

Among the gases from the processing of fossil fuels is hydrogen sulfide (H_2S). The hydrogen sulfide is a colorless, unpleasant smell, flammable, toxic and highly corrosive gas. Because its toxicity, the hydrogen sulfide is able to act on nervous and respiratory systems and can kill a human in few minutes (Mainier e Viola, 2005).

The hydrogen sulfide is found in the environment as sulfide dissolved in wastewater and as hydrogen sulfide in gas effluents (Dutta et al., 2008). The dissolution of sulfide depends on the conditions of system, as by example, the pH, which is a determining factor for the separations of aqueous solutions.

The hydrogen sulfide is one of the forms that the sulfur may occur in petroleum. Among other sulfur compounds are the polysulfides and elemental sulfur, rarely. The sulfur, independent of the form that is presented, is the third most abundant element in petroleum, and its medium concentration is 0,65% in weight, with a range presenting values between 0,02% and 4,00% (Thomas, 2004; Cardoso, 2005).

The sulfur compounds are present in all types of oil, and in general, the higher the density of the oil the higher the oil content of sulfur. The sulfur compounds are responsible for the corrosion of equipment in the refineries, by the contamination of catalysts used in the transformation processes and determine the color and smell of the final products. They are toxic and produce SO_2 and SO_3 through combustion, gases high pollutants of the atmosphere, which can form H_2SO_3 and H_2SO_4 (sulfuric acid) in aqueous solution (Thomas, 2004).

The oil refineries, as well as other industries such as paper and cellulose, tanneries, slaughterhouses, fertilizer industries and sewage treatment of wastewater, are anthropogenic sources of hydrogen sulfide. Already the H_2S found in the nature (natural sources) is the result of volcanic activity, decomposition of organic matter and the action of sulfate reducing bacteria (SRB) to sulfide in anaerobic medium. As an example of natural sources of hydrogen sulfide are the reservoirs of oil and natural gas and natural hot water.

With this significant number of industrial processes involving hydrogen sulfide and its damage to health, environment and integrity of equipment, its removal becomes an indispensable procedure, aiming the adapting to environmental laws, worker and industrial components protection.

A technique for removal H_2S from wastewaters is the electrochemical oxidation. The biggest advantage of electrochemistry is because its main reagent, the electron, being a clean reagent (Jüttner et al., 2000). The sulfide is an electroactive compound that can be removed by electrochemical oxidation, being the elementary sulfur the main end product in the oxidation of aqueous solutions of sulfide (Dutta et al., 2009). Therefore, the purpose of this work is analyze the results of the voltammetry study and determine the best current range for oxidation of the H_2S .

2. THEORETICAL CONSIDERATIONS

The H_2S gas is denser than air, flammable, accumulates in confined spaces and forms explosive mixture with air at normal temperature and pressure. Due to its solubility and high volatility, the dangerousness of the H_2S has the same order of cyanide gas. The corrosion by H_2S is the most important factor that contributes to the rapid deterioration of tubes and industrial installations.

The H_2S is a very weak dibasic acid, of difficult dissociation. The most metal sulfides can be regarded as salts of H_2S , and how it is a dibasic acid, there are two series of salts: the hydrogen sulfides like $NaHS$, and normal sulfides, like Na_2S . The sulfides of alkali metals are all soluble in water and undergo hydrolysis sharp and therefore strongly basic (Lee, 1997).



In several studies was used sodium sulfide (Na_2S) to obtain synthetic solutions. Authors such as Ateya and Al-Kharafi (2002), Mainier and Rocha (2003), Silva (2007) and Dutta et al. (2009) used Na_2S to obtaining their solutions. The reason for using this methodology in the laboratory is due the operational security, avoiding the use of gas H_2S , due its high toxicity.

The hydrogen sulfide, that is partially soluble in water, dissociates to form chemical species HS^- (acid disulfide or sulfide ion) and S^{2-} (sulfide), so the HS^- is the specie effectively corrosive of the system. The reactions (3) and (4) represent the dissociation of hydrogen sulfide with their respective dissociation constants (Mahan, 1997 and Zhang et al., 2008):



The dissociation is related to temperature and pH. Regarding the pH, the following relationships are established represented by Eq. (5) e (6):



An increase concentration of H^+ ions favors the formation of hydrogen sulfide, as shown in Fig. 1.

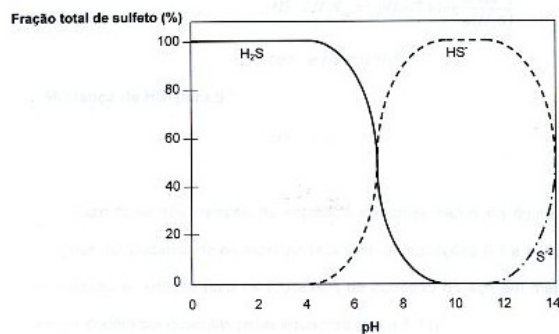
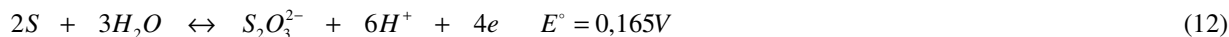
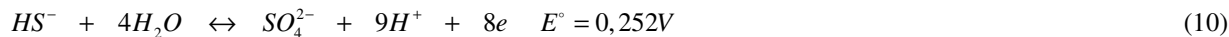


Figure 1. Percent concentration of H_2S , HS^- and S^{2-} in function of the pH in aqueous solution (Boucher apud Silva, 2007).

As it said previously, the hydrogen sulfide is a weak dibasic acid and for an environment with pH between 11 and 12 the predominant species are the ions HS^- . These ions are agents reducers that can be oxidized by O_2 , and also other oxidants such as hydrogen peroxide (H_2O_2), to polysulfides and sulfur. Already in the anodic oxidation, the HS^- ions can result in elemental sulfur, polysulfide or sulfur oxyanions, depending of the potential, temperature and pH of the

electrolyte. The following are the oxidation reactions of disulfide ions and their potential, measured with standard hydrogen electrode (Ateya and Al-Kharafi, 2002; Szpyrkowicz, 2005):



Electrochemical techniques are applied in the removal of toxic material of gases, liquids and solids in the final stages of the production process. The electrochemistry offers promising approaches for the prevention of pollution in industrial processes. The biggest advantage of electrochemistry is due to the fact that its main reagent, the electron, being a clean reagent. Below are described some of the advantages of electrochemical processes (Jüttner et al., 2000; Zaman and Chakma, 1995):

Versatility: oxidation or indirect reduction (with production of oxidizing agent in the electrochemical cell) or directly (without production of oxidizing agent), phase separation, concentration or dilution, biocidal functionality, applicability to a variety of pollutants in gases, liquids and solids, and treatment of small to large volumes of mililiters to millions of liters;

Energy efficiency: electrochemical processes generally require lower temperatures unlike other physical and chemical processes to remove pollutants, such as incineration. Electrodes and cells can be designed to minimize losses caused by inhomogeneous distributions of current, potential drop and parallel reactions;

Facility of automation: the variables of an electrochemical system, the electrode potential and cell current, are easily capable of automation;

An electrochemical reaction is a heterogeneous chemical process (involving a solid/solution interface) which gives the charge transfer to or from a metal electrode or semiconductor. Thus, the electrochemical purification of gases such as hydrogen sulfide, permits electrochemical conversion in an aqueous environment, since the corresponding potential standards of the corresponding reactions are all inside a range of stability corresponding to aqueous electrolytes.

In anodic oxidation processes many authors use graphite electrodes, graphite modified by copper film deposition (Zhang et al., 1995) and vanadium pentoxide (Kudaish and Al-Hinai, 2006). The use of graphite matrix is justified by its high porosity, which leads to a larger superficial area. There are also the use of *Pt* (Szynkarczuk et al., 1995), *Ti/Pt-Ir* (Szpyrkowicz et al., 2001), *Al* and steel electrodes (Feng et al., 2007). In some cases the anode is graphite and the counter electrode (cathode made of another material, such as platinum or stainless steel). The main product obtained in the oxidation of sulfide, is in its majority, as affirmed in the literature, elementary sulfur.

In the last years have noticed a bigger worry of the authors regarding the passivation of electrodes. The passivation is attributed to an increase in polarization resistance at the interface of the electrode caused by the deposition of elemental sulfur. Dutta et al. (2009), proposes a technique for regeneration of electrodes loaded during removal of sulfide from wastewater.

Most studies are developed in electrochemical cells with small volumes of solution (approximately 100 mL). When they utilized reactors, the volumes do not exceed 3 L. Therefore, Zaman and Chakma (1995) advocate increasing scale and an investigation of the effects of hydrodynamic conditions in the transport rates for additional project information.

3. MATERIALS AND METHODS

In this item presents the methodology used in voltammetric study of the electrochemical oxidation of hydrogen sulfide, defining the experimental conditions and the materials and methods required. The methodology for developing the study proposes the use of dissolved hydrogen sulfide, which simulates the conditions of industrial processes.

At this point is important to make clear that the effluent to be used in laboratory will not be coming from the plant. For the experiments will be used a synthetic solution obtained from sodium sulfide, to ensure operational safety in the laboratory. The sulfide is dissolved in the synthetic solution as reactions (2), (3) e (4).

Materials: with according to the properties of hydrogen sulfide, pH conditions to be neutral or basic dissolution, low solubility and high toxicity, for the voltammograms is suggested an electrochemical cell with three electrodes consisting of glass body with capacity of 100 mL and a lid with five holes (Fig. 2).

The working electrode, which may or may not be in rotation, it is the glassy carbon with a surface area of $0,126 \text{ cm}^2$. The auxiliary electrode is a spiral of platinum and the reference electrode is the $(\text{Ag} / \text{AgCl}) / \text{saturated KCl}$ with a potencial of $+0,199\text{V}$ compared to the normal hydrogen electrode at 25°C .

The working electrolyte used was an aqueous solution of sodium sulfide – prepared from sodium sulfide ninth-hydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and deionized water. As supporting electrolyte was used sodium chloride (NaCl) $0,1\text{M}$. The initial pH of the electrolyte was greater than 12, which according Fig. 1 ensures the dissolution of the H_2S .

During the process (obtaining solution and tests) was made deaeration through bubbling nitrogen gas (N_2), in order to avoid solution contact with oxygen in the air, which could result in parallel reactions.

For acquisition of electrochemical measurements was employed a potentiostat MQPG-01 of the Microquímica. Recalling, that all tests were performed at room temperature.

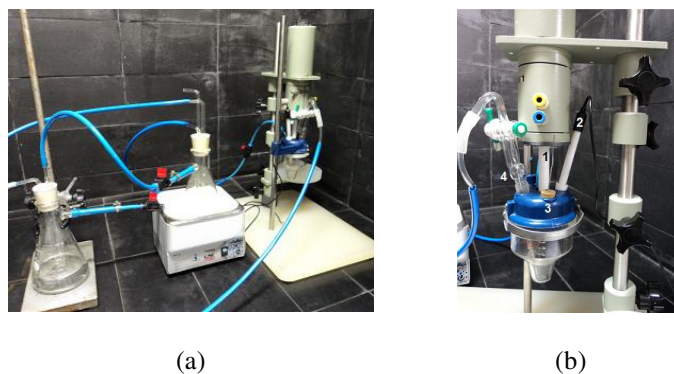


Figure 2. (a) System for obtaining solution and (b) Electrochemical cell: (1) Working electrode; (2) Reference electrode; (3) Auxiliary electrode and (4) Nitrogen bubbler.

Methods: the basic principle of the voltammetry study is the current as a function of applied potential. It is a sensitive technique for investigation of chemical kinetics, because the current contains quantitative information of the mechanisms and the experimental procedure is relatively simple. The potential scan is performed between the potential -1V and 1V , indicated for graphite electrodes in $0,1 \text{ M NaCl}$ solutions (Brett, 1996).

4. RESULTS

In carrying out voltammetry, is limited to the anodic scan, since it comprises the region of interest. In the voltammograms of Fig. 1, current peaks are observed near the potential of $0,50\text{V}$, indicating the oxidation of sulfide present in the synthetic solution. Surface and concentration analysis, such as scanning electron microscopy and ion chromatography should be performed at the working electrode and solution to support this hypothesis and to evaluate which compounds are present before and after the tests. At first, the potential range where there is the reaction of interest is between 0V and 1V , which corresponds to Reactions (8), (9), (10) and (12).

In the voltammetry study, was first investigated what the best potential sweep rate, or, one that shows the highest peaks, but at the same time with the smaller noise. In Figure 1 (a) the best conditions occurs in $15\text{mV} / \text{s}$. In Figure 1 (b) the highest peak currents occurred when the electrode of work was in rest or in rotation of 100rpm , which demonstrates that changes in the hydrodynamics of the system favor the mass transfer (sulfide ions leave the bulk solution to be oxidized on the surface of the electrode). A thorough discussion concerning the mechanisms of convection and diffusion in mass transport, can explain better if the condition of 100rpm is most appropriate for continuing studies.

In the next steps of the study of electrochemical oxidation of hydrogen sulfide, the electrochemical cell should be placed on stream, together with a solution reservoir with a volume 20 times larger than the cell volume. The cell-reservoir system should be modeled as a batch reactor and subjected to different currents and flow rates of electrolyte solution (synthetic solution). The decrease of sulfide concentration, and consequent increase in concentration of H_2SO_4 and/or S , during the tests will be analyzed to evaluate the performance of the system and generate a correlation between dimensionless groups. These groups, which represents the mechanism of mass transport in electrochemical oxidation of H_2S for H_2SO_4 and/or S .

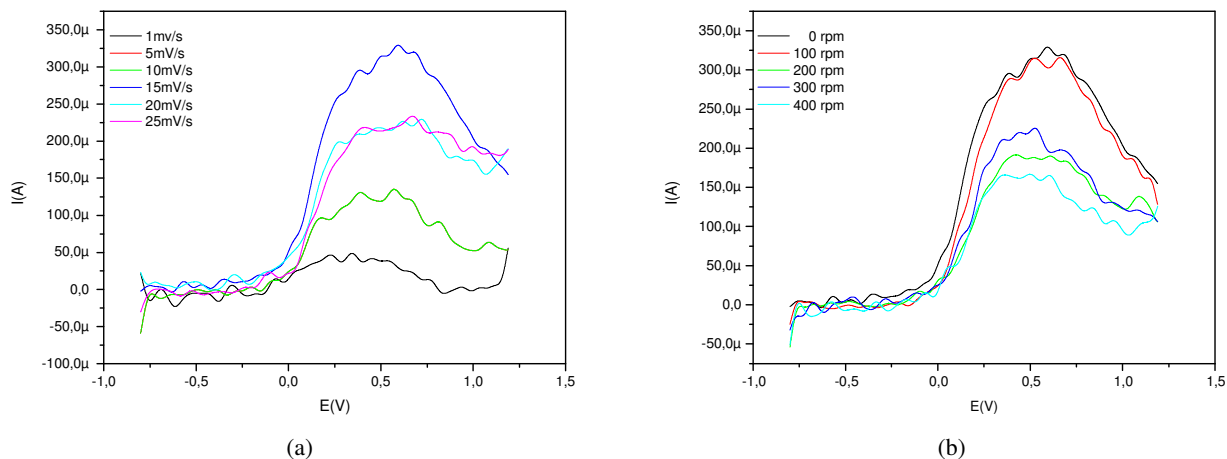


Figure 3. Voltammograms of synthetic solution $[Na_2S.9H_2O] = 0,044M$ and $[NaCl] = 0,100M$: (a) Current versus Potential at different scan rates and (b) Current versus Potential at $15mV/s$ in different rotations of the electrode.

5. CONCLUSIONS

With the processing of oils more and more heavy and with the bigger content of sulfur, the worry in remove H_2S of the industrial plants becomes bigger. A technique to be explored, with the objective of accomplishing this removal, is the electrochemical oxidation to produce products such H_2SO_4 and S . However, to start the study of this technique, the initial step is the voltammetry study, which the current required to occur the reaction of interest is determined.

The present study revealed current peaks near of $0,5V$, comprising a range of $0V$ and $1V$. Then, the next step is to place the cell in stream and submit it to different currents corresponding to the potential range of $0V$ and $1V$.

The voltammetric study is a fundamental phase in the development of studies using electrochemical reactors. From study of cell and small-scale electrochemical reactors is possible obtain correlations between dimensionless groups, that help in the project of industrial reactors, enabling the increase of scale with physical resemblances and economic and time advantages.

6. ACKNOWLEDGEMENTS

The authors acknowledge the financial support of FINEP and ANP – through the Program of Human Resources – PRH 24 of UFPR.

7. REFERENCES

- Ateya, B. G., Al-Kharafi, F. M., 2002. "Anodic Oxidation of Sulfide Ions from Chlorine Brines". *Electrochemical Communications*, vol. 4, pp. 231-238, 2002.
- Brett, A. M. O., Brett, C. M. A., 1996. "Electroquímica: Princípios, Métodos e Aplicações". Coimbra: Livraria Almedina, Portugal.
- Cardoso, L. C., 2005. "Petróleo do Poço ao Posto". Editora Qualitymark, Rio de Janeiro, Brazil.
- Dutta, P. K., Rabaey, K., Yuan, Z., Keller, J., 2008. "Spontaneous Electrochemical Removal of Aqueous Sulfide". *Water Research*, vol. 42, pp. 4965-4975.
- Dutta, P. K., Rozendal, R. A., Yuan, Z., Rabaey, K., Keller, 2009. "Electrochemical Regeneration of Sulfur Loaded Electrodes". *Electrochemical Communications*, doi: 10.1016/j.elecom.2009.05.024.
- Feng, J., Sun, Y., Zheng, A., Zhang, J., Li, S., Tian, Y., 2007. "Treatment of Tannery Wastewater by Electrocoagulation". *J. Environmental Science*, vol. 19, pp. 1409-1415.
- Jüttner, K., Galla, U., Schmieder, H., 2000. "Electrochemical Approaches to Environmental Problems in the Process Industry". *Electrochimica Acta*, vol. 45, pp. 2575 – 2594.
- Khudaish, E. A., Al-Hinai, A. T., 2006. "The Catalytic Activity of Vanadium Pentoxide Film Modified Electrode on the Electrochemical Oxidation of Hydrogen Sulfide in Alkaline Solutions". *J. Electroanalytical Chemistry*, vol. 587, pp.108-114.
- Lee, J. D., 1997. "Química Inorgânica não tão Concisa". Tradução da 4ª edição Inglesa, Editora Edgard Blücher LTDA. São Paulo, Brazil.
- Mahan, B. M., Myers, R. J., 1997. "Química um Curso Universitário". Tradução da 4ª Edição Americana. Editora Edgard Blücher LTDA; São Paulo, Brazil

- Mainier, F. B.; Rocha, A. A., 2003. “ H_2S : Novas Rotas de Remoção Química e Recuperação de Enxofre”. 2º Congresso Brasileiro de P&D em Petróleo & Gás. Rio de Janeiro, Brazil.
- Mainier, F. B., Viola, E. D. M., 2005. “O sulfeto de Hidrogênio e o Meio Ambiente”. II Simpósio de Excelência em Gestão e Tecnologia – SEGeT.
- Silva, P. R., 2007. “Estudo Laboratorial da Estabilidade de Filmes de Sulfeto de Ferro Visando o Monitoramento da Corrosão em Unidades de Craqueamento Catalítico Fluido”. DSc. thesis, Universidade Federal do Paraná, Curitiba, Brazil.
- Szpyrkowicz, L., Kaul, S. N., Neti, R. N., Satyanarayan, S., 2005. “Influence of Anode Material on Electrochemical Oxidation for the Treatment of Tannery Wastewater”. *Water Research*, vol. 39, pp. 1601-1613.
- Szpyrkowicz, L., Kelsall, G. H., Kaul, S. N., De Faveri, M., 2001. “Performance of Electrochemical Reactor for Treatment of Tannery Wastewaters”. *Chemical Engineering Science*, vol. 56, pp. 1579-1586.
- Szynkarczuk, J., Komorowski, P. G., Donini, J. C., 1995. “Redox Reactions of Hydrosulphide Ions on the Platinum Electrode – II. An Impedance Spectroscopy Study and Identification of the Polysulphide Intermediates”. *Electrochimica Acta*, vol. 40, n°. 4, pp. 487 – 494.
- Thomas, J. E., 2004. “Fundamentos da Engenharia de Petróleo”. 2ª edição, Editora Interciência, Engenho Novo, Brazil.
- Zaman, J., Chakma, A., 1995. “Production of Hydrogen and Sulfur from Hydrogen Sulfide”. *Fuel Process. Technol.*, vol. 41, pp. 159-198.
- Zhang, J., LEVER, A. B. P., PIETRO, W. J., 1995. “Surface Copper Immobilization by Chelation of Alizarin Complexone and Electrodeposition on Graphite Electrodes, and Related Hydrogen Sulfide Electrochemistry, Matrix Isolation of Atomic Copper and Molecular Copper Sulfides on a Graphite Electrode”. *J. Electrochem. Chem.*, vol. 385, pp. 191-200.
- Zhang, L., De Schryver, P., De Gussemé, B., De Muynck, W., Boon, N., Verstraete, W., 2008. “Chemical and Biological Technologies for Hydrogen Sulfide Emission Control Sewer Systems: A Review”. *Water Research*, vol. 42, pp. 1-12.

8. RESPONSIBILITY NOTICE

The authors are the only responsables for the printed material included in this paper.