Abstract of the Thesis presented to the Postgraduate Program in Chemistry of the Federal University of Rio Grande do Norte and to the International Doctorate School of the University of Castilla-La Mancha as part of the requirements to obtain the double degree, in Chemistry by the UFRN and in Chemical and Environmental Engineering by the UCLM.

TREATMENT OF RESIDUAL GASEOUS EMISSIONS BY ELECTRO-ABSORBENT TECHNOLOGIES

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The electrochemical technologies characterized by their simple instrumentation, environmental compatibility and high efficiencies (hydroxyl radicals are electro-generated acting as a powerful oxidizer), have been highly studied in recent decades to treat wastewater from different sources, seeking to minimize their contamination and toxicity before giving them final disposal or that they can be reused. However, few studies have been devoted to the degradation of pollutants present in gaseous streams using electrochemical methods. The projection of these technologies in the treatment of gases at pre-pilot scales offers a promising alternative to solve the problems caused by the large volumes of waste streams generated both at the domestic and industrial levels. In this sense, this work aimed to evaluate the efficiency of electrochemical oxidation coupled to absorbent devices as a treatment technology for the degradation of pollutants in gaseous streams, from two important sources of contamination worldwide (perchloroethylene and toluene), using electrochemical systems in resized. The results obtained are presented in 13 chapters, of which 7 correspond to papers.

Chapter 1 is dedicated to the introductory part; here, atmospheric pollution is contextualized as a research problem in this work, the importance of adequate management of waste gases is justified, and it is briefly exposed how the electrochemical treatment technology coupled with absorbent systems will be used to approach the degradation of pollutants present in gaseous streams.

Chapter 2 presents the general and specific objectives pursued in this Thesis, justifying the development of each stage of the work.

Chapter 3 exposes a brief discussion on the importance of air for life on the planet and its pollution problems and shows a general review of the technologies currently used for the treatment of gaseous streams, where the absorption technology is commented with greater emphasis. Meanwhile, the fundamentals of electrochemical oxidation as effluent and wastewater treatment, are also commented on. Then the importance of the electrodic material in the generation of oxidizing species and the influence of the presence of metallic mediators in solution are discussed.

Chapter 4 describes the proposed electro-absorption facilities, as well as the methodology, developed, the experimental conditions and, the equipment that will be used to monitor the organic compounds studied (perchloroethylene and toluene) and the products and intermediates obtained in this work. Next, the results of this Thesis are presented in chapters 5 to 11, in the form of papers.

Chapter 5 presents the current panorama in the mode of a mini-review, of the new methodology that combines absorption technology with the electrochemical treatment for the elimination of VOCs and unpleasant smelling gases from polluted air streams, a combination on which the research of this Thesis. In these electro-scrubbers, it is suggested that the system for capturing contaminants present in the gas by the electrolyte/absorbent is as important as the efficiency of this electrolyte in contributing to the electrochemical degradation of the captured compounds. Thus, regarding the absorbent device used, the use of packed columns leads to the number of investigations, however, recently Ventury injectors have begun to be used. On the other hand, most published studies suggest that the presence of metallic pairs in the electrolyte/absorbent formulation leads to a higher degradation efficiency of contaminants. The results of this chapter were published in the *Current Opinion in Electrochemistry* journal.

In Chapter 6 the catalytic effect of the Silicon and Tantalum substrates in boron-doped diamond (BDD) electrodes to the electrochemical oxidation of Co(II) was studied. Cobalt is selected because this metal stands out in electrolyte/absorbent formulations used so far in the

electro-scrubbing studies. As a result, it was found that the Ta/BDD anode presents greater efficiency in the conversion of Co(II) to Co(III), which suggests an important influence on the global contribution of electrochemical reactions. The charge transfer resistance in the metallic Co(II)/Co(III) pair and the diffusion control for each anode are discussed. This difference in the behavior of the electrodes, caused by the substrate on which the diamond coating is deposited, opens a line of research to improve the efficiency of mediated electrolytic treatments, based on the use of redox systems. The article resulting from this research was published in the *Journal of Electroanalytical Chemistry*.

In Chapter 7 a gas stream polluted with perchloroethylene (PCE), generated from bubbling an aqueous solution, was electrochemical treated in a system coupled to a packed column, with the airflow circulating in a discontinuous mode. The effect of the substrate (Ta and/or Si) of diamond electrodes and the contribution of cobalt as a source of oxidizing species were studied. With mediated electroabsorption, it was obtained that using the Si/BDD anode 79,0% of the PCE is removed while using the Ta/BDD anode 95,9% was reached; this difference in the catalytic effect of the substrates had already been suggested in the results presented in chapter 6. The article resulting from this research was published in *Chemosphere* journal.

In Chapter 8 the removal of PCE (of a gaseous stream generated from bubbling an aqueous solution) by absorption and electroabsorption was studied, comparing two absorbent devices: a packed column and a Venturi injector, in installations with the airflow circulating in continuous mode and using an Si/BDD anode. The tests in the absence of the electrolyte/absorbent indicated reactivity of the PCE in the wet gas phase, and this effect was considered in the electro-absorbers evaluated. In both systems, the electrochemical assistance allowed to degrade the pollutant, achieving better efficiencies in the case of the Venturi injector. Another important result in this study was that the addition of cobalt mediators did not improve the degradation efficiency. The article resulting from this research was published in the *Journal of Electroanalytical Chemistry.*

In Chapter 9 the removal of toluene (of a gaseous stream generated by bubbling a fixed volume of pure reagent) was studied using an Si/BDD anode in an electrochemical cell coupled to a packed column as an absorbent device, with continuous air circulation. The

toluene concentration recovered from the system with and without absorption, with electroabsorption, and with mediated electroabsorption by cobalt was evaluated. The results showed that 87,4% of the toluene present in the gaseous stream is retained in the electrolyte/absorbent, of which 97,0% is degraded by electrochemical oxidation in an acid medium and about 99,6% is eliminated through electrochemical oxidation mediated with cobalt. The current efficiency results obtained in the absence of cobalt suggest that, in addition to the mediating effect of the metal, the redox sulfate/persulfate pair also plays an important role in the degradation of toluene. These studies gave an article that was published in the *Journal of Electroanalytical Chemistry*.

In Chapter 10 the removal of toluene (a gaseous stream generated by bubbling a fixed volume of pure reagent) by electroabsorption in facilities with airflow circulating in continuous mode. For this, the performance of a packed column and a Venturi injector, with an acid medium as electrolyte/absorbent, coupled to an electrochemical cell with Si/BDD anode, was compared. It was obtained that the packed column showed a better performance in the electrochemical degradation, while the Venturi injector showed a greater capacity to retain toluene in the electrolyte/absorbent, reaching levels of supersaturation. It was obtained that both absorbent systems allowed an efficient degradation of toluene, however, the flow rate of the gas stream considerably influenced the efficiency of each system. The results of this chapter were published in the *Journal of Environmental Chemical Engineering*.

Chapter 11 shows the results of the development of a proposed mathematical model, based on the simplified Petersen's matrix, to evaluate the physical and chemical parameters that control the processes involved in the combination of absorption technology with anodic oxidation. For this, the removal with and without electrochemical assistance is analyzed, as well as the effect of the electrolyte/absorbent used, considering part of the experimental results with PCE and toluene, presented in chapters 7 to 10. These studies gave an article that was published in *Separation and Purification Technology* journal.

In chapter 12 there is a summary of the considerations and conclusions reached with the results presented in chapters 5 to 11. Some perspectives for future work are proposed.

Chapter 13 presents the scientific contributions and parallel works carried out during the development of this Thesis. Of these productions, it should be noted that in a set of studies electrochemical technology was used for the treatment of organic compounds in solution, both in effluents of real origin (wastewater from the washing machine) and in synthetic effluents (water/ petroleum, caffeine, and mixture of antibiotics in synthetic and real urine). Below is a brief description of the work carried out:

- A real washing machine effluent was treated by electro-oxidation, with a pre-pilot scale flow reactor using anodes (Ti/Pt) and (BDD). The effect of the anode material and the applied current density were studied, as well as the active species produced electrochemically, both from the effluent itself (as received) and from the addition of Na_2SO_4. The contribution of the electrogenerated species in the degradation of the organic load present was evaluated.

- A synthetic water/petroleum effluent was electrochemically treated, evaluating the effect of adding sodium dodecyl sulfate (SDS) as a surfactant and as a source of sulfate species, proposing a promising approach for the treatment of wastewater with low solubility organic pollutants.

- The electro-oxidation of an aqueous caffeine solution was studied, evaluating the synergistic effect of SDS and Na_2SO_4, used as support electrolyte, proposing reaction mechanisms to explain the contribution of the sulfate, persulfate, and hydroxyl radical species, in the oxidation of this model organic molecule, using active and non-active anodes.

- Electrochemical degradation of the mixture of the antibiotics rifampicin and isoniazid, prepared in samples of synthetic urine and real human urine, using boron-doped diamond anodes (BDD) and Ti/Pt, was evaluated as a promising approach for the treatment of hospital effluents, which represent a considerable fraction of the total municipal effluents. The results of this work are in the writing phase.

- Finally, the electrochemical production of persulfate was studied, using active and non-active anodes, in treatments at room temperature and 60°C, from a Na_2SO_4 0.05 M solution. The results indicated that the persulfate production routes are highly dependent on the electrode material and experimental conditions. This work is in the writing phase.

Objetives

General: Developing and evaluating residual gaseous emission treatment systems using electrochemically assisted absorption devices.

Specific:

1-Carry out a bibliographic review on the problem of atmospheric pollution and the existing technologies for the control and treatment of VOCs and unpleasant smelling gases. Chapter 3.

2-Structure the experimental methodology and analytical procedures to monitor both the organic compounds to be studied (perchloroethylene and toluene) and the products and intermediaries expected with the electrochemical treatment. Chapter 4.

3-Analyze the latest advances on the electrochemical oxidation methodology coupled to absorption devices, better known as *electro-scrubbing*, used to treat polluted gaseous streams. Chapter 5.

4-Study the catalytic effect of Tantalum (Ta) and Silicon (Si) substrates, in boron-doped diamond electrodes (BDD), on the electrochemical oxidation of Co(II) to Co(III), a metallic pair that then will be used as a mediator in the formulation of the electrolyte/absorbent. Chapter 6.

5-Compare the contribution of Co(III), electrogenerated in BDD anodes with Ta and/or Si substrates, for treating a synthetic current contaminated with PCE, in an electroabsorption system operating in discontinuous mode. Chapter 7.

6-Contrast the differences in PCE removal obtained by absorption and electroabsorption with two different absorbents devices: a packed column and a Venturi injector, in facilities operating in continuous mode and using an Si/BDD anode. Chapter 8.

7- Evaluate the catalytic effect of the cobalt mediator and the sulfate/persulfate pair in the removal of toluene present in a synthetic gas stream, circulating in continuous mode, using a Si/BDD anode coupled to a packed column as an absorbent system. Chapter 9.

8-Investigate the influence of gas flow variation on toluene removal by electroabsorption in an acid medium, using a Si/BDD anode with two absorbents devices: a packed column and a Venturi injector, operating in continuous mode. Chapter 10.

9-Propose the development of a mathematical model, using the simplified Petersen's, matrix to evaluate the physical and chemical parameters that control the processes involved in the new electro-scrubbing technology. Chapter 11.

Concluding remarks

The discussion about conventional technologies for the control and treatment of VOCs and gases with an unpleasant odor and the analysis of **the advances of the new methodology** of electrochemical oxidation coupled to absorption systems, currently known as **"electro-scrubbing"**, **allowed** to structure the experimental development of this Thesis to **study the removal of perchloroethylene and toluene from gas streams**. The most important considerations are listed below:

It was obtained that the Tantalum and Silicon **substrates on which the diamond coating is deposited**, **exert** different **catalytic effects in the electrochemical oxidation** of Co(II) and in the degradation of organic compounds in solution, as reported in the case of perchloroethylene. However, more in-depth studies are needed since very little information about it is found in the literature.

The contribution of the Co(III) species was significant in the treatment of PCE with pre-electrolysis and in the oxidation of toluene at the highest current density, in both cases using Si/BDD anodes, which **highlights the relevance of the mechanisms of mediated electro-oxidation and further suggests that** the promotion of oxidants is not always positive from the point of view of their accumulation in the electrolyte. **Ta/BDD anode**

appears to promote sufficient amounts of hydroxyl radicals, making the presence of the metal unnecessary.

Although the contribution of Co(III) species in continuous and discontinuous systems **for toluene removal** was not compared, the results obtained in electroabsorption and mediated electroabsorption for the installation operated with the gaseous circuit in continuous mode, suggested that although the presence of Co(II) leads to higher removals, **the contribution of the sulfate/persulfate pair is considered significant.**

In general, **under the experimental conditions studied, the Venturi injector proved to be a better absorbent device**, where higher amounts of contaminants (perchlorethylene and toluene) were identified in the electrolyte, suggesting a higher mass transfer efficiency, **compared to the packed column.**

The proposed mathematical model fits most of the cases studied satisfactorily, with regression coefficients between 0.85 and 0.99 for PCE and toluene, respectively. The limited number of parameter changes highlights its robustness and allows us to validate its use.

By being a recent methodology, **electro-scrubbing technology still needs to be improved**, requiring studies that deepen each parameter involved. The electrochemical degradation of compounds in solution has already been a well-researched topic; however, **the transfer of pollutants from the gas phase to the liquid phase is one of the main challenges** for the success of this methodology.

Finally, it is known that BDD anode is not a viable anode to be used on larger dimensions due to its high costs. Therefore, **the search for other electrode materials** that can efficiently replace it **would allow electro-scrubbing technology to be applied on a large scale.**

Faced with the results discussed throughout this Thesis, it is considered that **electro-scrubbing technology** as an alternative for the treatment of polluted gaseous streams, **is a promising proposal for environmental remediation**, which was verified by treating two important pollutants, common in the industrial sector. The objectives of this thesis were successfully achieved; allowing us to conclude that electro-scrubbing technology is a line of research **that deserves the opportunity to continue it due to the high potential**

demonstrated so far and the need to develop new gas treatment processes for real applications.

Future research and development needs

The main efforts to optimize this technology should focus on:

1- Formulation of electrolytes/absorbents suitable to favor the formation of species that promote reactive absorption or, alternatively, that increase the solubility of pollutants in the liquid phase (Escalona-Durán et al., 2021). Furthermore, the possibility of subsequently separating the mediator used from the oxidation products should be evaluated.

2- Evaluation of other options of absorption devices that allow a high gas-liquid mass transfer efficiency on a pilot scale. The good results obtained with the Venturi injector raise expectations regarding the use of systems based on the formation of microbubbles.

3- Development of more profitable electrodes with greater active surface areas. The use of three-dimensional electrodes and continuous flow electrodes represent a key point in this technology (Escalona-Durán et al., 2021).

4- Consider the influence of pressure and temperature on the solubility of gases. Evaluate the inclusion of these experimental parameters in new methodologies, studying the challenge that these extreme conditions pose for electrochemical applications (Escalona-Durán et al., 2021). A systematic study of these operating parameters could expand the application possibilities of electroabsorption technology.

5- Optimize the hydrodynamic conditions of the electrochemical cell according to the absorbent device used. Turbulence promotion improves the efficiency of mass transport controlled processes. In this context, 3D printers can help technology, since they offer the possibility of carrying out complex mechanical concepts, tested in simulations (Escalona-Durán et al., 2021).

6- The replacement of the electrochemical cell used in this Thesis by a divided cell with a selective ion membrane, as well as the substitution of the pre-electrolysis

step by a progressive and controlled dosage of oxidant precursors, would be interesting alternatives to evaluate the efficiency of mediated oxidation processes.

7- Control of production and toxicity of unwanted intermediaries, typical of the degradation of VOCs (Escalona-Durán et al., 2021).
8- Projection of the treatments developed at a pre-pilot laboratory scale for resized systems, seeking to raise the Technology Readiness Level (TRL) and thus advance in the value chain necessary for commercialization.
9- Propose new mathematical models for a better understanding of the mechanical, physical and chemical concepts involved in the treatment, offers the possibility of progression of the technology in the stages of research, development and implementation.

Although so far no clear advantage has been found compared to other gas stream treatment methodologies, in the studies of this Thesis, electroabsorption technology was able to remove pollutants efficiently. So far, a limited number of articles on the subject have been published, which becomes an opportunity for future work (Escalona-Durán et al., 2021).

Escalona-Durán, F., Sáez, C., Lobato, J., Martínez-Huitle, C. A., & Rodrigo, M. A. (2021). Electroscrubbers for removing volatile organic compounds and odorous substances from polluted gaseous streams. Current Opinion in Electrochemistry, 28, 100718. https://doi.org/10.1016/j.coelec.2021.100718

Supplementary material

Scientific contributions of this Thesis

Papers

- Durán, F. E., Sáez, C., Lobato, J., Martínez-Huitle, C. A., & Rodrigo, M. A. (2021). Electroscrubbers for removing volatile organic compounds and odorous substances from polluted gaseous streams. Current Opinion in Electrochemistry, 100718. https://doi.org/10.1016/j.coelec.2021.100718

- Escalona-Durán, F., Muñoz-Morales, M., Souza, F. L., Sáez, C., Cañizares, P., Martínez-Huitle, C. A., & Rodrigo, M. A. (2021a). Promoting the formation of Co (III) electrocatalyst with diamond anodes. Journal of Electroanalytical Chemistry, 882, 115007. https://doi.org/10.1016/j.jelechem.2021.115007

- Escalona-Durán, F., Muñoz-Morales, M., Souza, F. L., Sáez, C., Cañizares, P., Martínez-Huitle, C. A., & Rodrigo, M. A. (2021b). Cobalt mediated electro-scrubbers for the degradation of gaseous perchloroethylene. Chemosphere, 279, 130525. https://doi.org/10.1016/j.chemosphere.2021.130525

- Escalona-Duran, F., Muñoz-Morales, M., Saez, C., Cañizares, P., Martinez-Huitle, C. A., & Rodrigo, M. A. (2021). Continuous electro-scrubbers for the removal of perchloroethylene: Keys for selection. *Journal of Electroanalytical Chemistry*, *892*, 115267. https://doi.org/10.1016/j.jelechem.2021.115267

- Escalona-Durán, F., Muñoz-Morales, M., de Freitas Araújo, K. C., Sáez, C., Cañizares, P., Martínez-Huitle, C. A., & Rodrigo, M. A. (2021). Treatment of toluene gaseous streams using packed column electro-scrubbers and cobalt mediators. Journal of Electroanalytical Chemistry, 895, 115500. https://doi.org/10.1016/j.jelechem.2021.115500

- Escalona-Durán, F., Muñoz-Morales, M., de Freitas Araújo, K. C., Sáez, C., Cañizares, P., Martínez-Huitle, C. A., & Rodrigo, M. A. (2021). Comparison of the performance of packed column and jet electro-scrubbers for the removal of toluene. Journal of Environmental Chemical Engineering, 9(5), 106114. https://doi.org/10.1016/j.jece.2021.106114

- Escalona-Durán, F., Muñoz-Morales, M., Fernández-Marchante, C. ., Lobato, J., Martínez-Huitle, C. A., & Rodrigo, M. A. (2021). Modelling electro-scrubbers for removal of VOCs. Separation and Purification Technology, 277, 119419. https://doi.org/10.1016/j.seppur.2021.119419

Oral Presentations

Florymar Escalona-Durán, Cristina Saez, Manuel Rodrigo, Carlos A. Martinez-Huitle. *Desarrollo de un proceso combinado de electro-lavado para el tratamiento de compuestos orgânicos clorados* (IX Jornadas Doctorales de la Universidad de Castilla-La Mancha, Ciudad Real, España), 2019.

Florymar Escalona-Durán, Manuel Rodrigo, Carlos A. Martinez-Huitle. *Development of a combined electro-scrubbing process for the treatment of volatile organic compounds* (XIV Young Science Symposium, virtual edition), 2020.

F. Escalona-Durán, C. Saez, M. A. Rodrigo, C. A. Martínez-Huitle. *Development of a scrubbing processes using absorbents-electrolytes to the elimination of volatile organic contaminants* (12th European Symposium on Electrochemical Engineering, Leeuwarden virtual edition) 2021.

Poster Presentations

Florymar Escalona-Durán, Cristina Saez, Manuel Rodrigo, Carlos A. Martinez-Huitle. *Development of a Combined Electro-Scrubbing Processes (*Advanced Electrochemical Oxidation for Water Reuse, virtual edition), 2020.

Florymar Escalona-Durán, Martín Muñoz-Morales, Cristina Sáez, Carlos Alberto Martínez-Huitle, Manuel Andrés Rodrigo. *Desarrollo de sistemas absorbentes asistidos electroquímicamente para el tratamiento de corrientes gaseosas contaminadas.* (V Workshop de la Red E3TECH/I Workshop Iberoamericano a Distancia 'Aplicaciones Medioambientales y Energéticas de la Tecnología Electroquímica' (V E3TECH), edición virtual), 2020.

Parallel works

Escalona-Durán, Florymar, de Araújo, D. M., do Nascimento Brito, C., Santos, E. V., Ganiyu, S. O., & Martínez-Huitle, C. A. (2018). Electrochemical technology for the

treatment of real washing machine effluent at pre-pilot plant scale by using active and non-active anodes. Journal of Electroanalytical Chemistry, 818(December 2017), 216–222. https://doi.org/10.1016/j.jelechem.2018.04.029

Escalona-Durán, Florymar, Ribeiro da Silva, D., Martínez-Huitle, C. A., & Villegas-Guzman, P. (2020). The synergic persulfate-sodium dodecyl sulfate effect during the electro-oxidation of caffeine using active and non-active anodes. Chemosphere, 253. https://doi.org/10.1016/j.chemosphere.2020.126599

Escalona-Durán, Florymar, Villegas-Guzman, P., dos Santos, E. V., da Silva, D. R., & Martínez-Huitle, C. A. (2019). Intensification of petroleum elimination in the presence of a surfactant using anodic electrochemical treatment with BDD anode. Journal of Electroanalytical Chemistry, 832(October 2018), 453–458. https://doi.org/10.1016/j.jelechem.2018.11.045

Escalona-Durán, F., Villegas-Guzman, P., dos Santos, E. V., da Silva, D. R., & Martínez-Huitle, C. A. Electrochemistry as a revolutionary field for contamination issues: analytical and treatment application against anti-TB drugs in urine (*em fase de escrita)*.

Escalona-Durán, F., Villegas-Guzman, P., dos Santos, E. V., da Silva, D. R., & Martínez-Huitle, C. A. Persulfate production using active and non-active anodes (*em fase de escrita)*.

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