

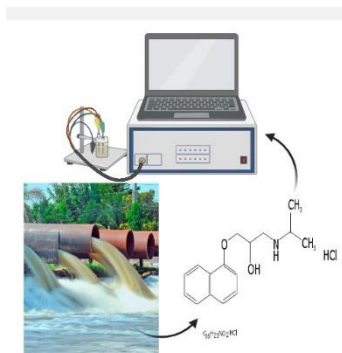
Electrodeposition of polypyrrole and samarium on stainless steel electrodes for photoelectrocatalytic degradation of propranolol hydrochloride in aqueous solution

POSTER

Ph.D. Student: N

Journal: XXX

E. L. D. Provenzi¹, V. G. Cunha², C. M. Gris², K. Petkowicz², V. Fante², J. M. M. de Mello², L. L. Silva², M. Zanetti², M. P. Belançon³, M. A. Fiori³, G. L. Colpani². (1) Unochapecó, Servidão Anjo da Guarda, 295 D, Chapecó, Brazil, eduarda.p@unochapeco.edu.br. (2) Unochapecó, Servidão Anjo da Guarda, 295 D, Chapecó, Brazil. (3) Universidade Tecnológica Federal do Paraná – Campus Pato Branco, Via do Conhecimento, km 1, Pato Branco, Brazil.



Advanced oxidative processes have gained prominence in the study of contaminant degradation in surface and wastewater. Among the various methods explored, photoelectrocatalysis stands out, which combines electro-oxidation and photocatalysis processes to minimize the recombination of the electron/vacancy pair through the potential difference generated at the photoanode. In this study, the degradation of the pharmaceutical compound propranolol hydrochloride in aqueous medium was evaluated using stainless steel electrodes electro-deposited with polypyrrole and samarium, achieving approximately 25% degradation, highlighting the potential application of this system in water and wastewater treatments.

Introduction

Advanced treatments improve the quality of effluents, surpassing the limited efficacy of conventional methods in completely removing contaminants^[1]. Therefore, Advanced Oxidative Processes (AOPs) have been studied due to their high potential to oxidize other molecules, reducing them in a non-selective manner^[2]. Among AOPs, photoelectrocatalysis stands out by combining the photocatalytic process with electro-oxidation. In this process, a photoactive material is employed as the photoanode and then irradiated with light of suitable wavelength along with the passage of electrical energy through the electrode^[3]. To enhance its performance and prolong its lifespan, electrodes are often subjected to modifications, such as coatings with various materials^[4]. Among the compounds that can be electrodeposited, samarium oxides and hydroxides and polypyrrole have attracted interest for potential application in electro-oxidation and photoelectrocatalysis due to their electrical conductivity and ability to absorb electromagnetic radiation at wavelengths in the range of ultraviolet and visible light^[5,6].

Material and Methods

The stainless steel AISI 316 plates, with dimensions of 5.00 x 1.50 x 0.15 cm, were previously cleaned by physical and chemical

treatments. The electrodeposition studies of polypyrrole and samarium were conducted using a potentiostat (Metrohm Autolab - PGSTAT 204) and an electrolytic cell, employing solutions of 0.1 M pyrrole and 0.05 M samarium hexahydrate nitrate ($\text{Sm}(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$). The electrodeposition of pyrrole was investigated by voltammetry and subsequently by chronoamperometry at a potential of 0.9 V for 60 seconds. After the electrodeposition of polypyrrole, samarium was electrodeposited on the surface through 03 sequential pulses at -1.5 V for 10 seconds^[7]. For the degradation assays of propranolol hydrochloride, an aqueous solution containing 10 mg/L of the drug and 0.1 M sodium sulfate (Na_2SO_4) as an electrolyte was prepared. First, a voltammetry assay was performed using this solution to determine the oxidation potential of propranolol. The assays were conducted at room temperature for 60 minutes, assisted by ultraviolet radiation, using a stainless-steel electrode only, a stainless-steel electrode with polypyrrole only, and another containing polypyrrole and samarium. Samples collected from the aqueous medium were analyzed by UV-Vis spectrophotometer.

Results and Discussion

Figure 1 presents the cyclic voltammograms resulting from the deposition of polypyrrole at a

concentration of 0.1 M over 04 cycles.

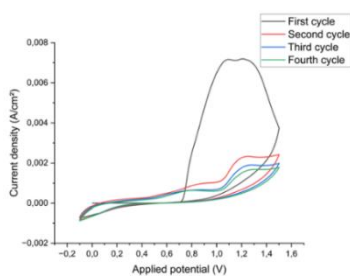


Figure 1. Cyclic voltammogram of the polymerization of polypyrrole at a concentration of 0.1 molar.

Based on these results, a potential of 0.9 V was defined for the chronoamperometry assay with fixed potential, aiming to obtain the ideal time for the formation of a homogeneous electro-deposited film on the surface of stainless steel. Based on the chronoamperometry results, a deposition time of 30 seconds under a potential of 0.9 V was defined. After this step, samarium was electrodeposited. Figure 2 presents the spectra obtained during the degradation process for each of the electrodes, as well as the standard spectrum.

Conclusions

The results demonstrated that the formed films assist in the degradation of contaminants in comparison to the stainless-steel electrode alone, as well as the effect of UV radiation improving the degradation response, achieving approximately 25% removal. This fact may be associated with a lower rate of electron recombination and vacancies due to the synergy between photocatalysis and electro-oxidation.

Acknowledgments

We would like to express our sincere gratitude to the University of the Chapecó Region - Unochapecó for the technical and scientific support. We also thank the funding agencies Capes and Unochapecó for the financial support provided for this study, as well as FAPESC for contributing financial assistance.

References

- [1] ROSA, J. M.; TAMBOURGI, E.; VANALLE, R.; GAMARRA, F.; SANTANA, J.; ARAUJO, M. Application of continuous H₂O₂/UV advanced oxidative process as an option to reduce the consumption of inputs, costs and environmental impacts of textile effluents. *Journal of Cleaner Production*, v. 246, p. 119012, fev. 2020.
- [2] LOZANO-ORNA, E. P.; REYES-VERA, C. H. Avaliação multivariada de um fotocatalisador dopado com nanopartículas de prata para a degradação de compostos orgânicos em uma amostra de efluente. *Ibero-American Journal of Engineering & Technology Studies*, v. 3, n. 1, p. 20–44, 31 mar. 2023.
- [3] YUSUF, T. L. et al. The application of photoelectrocatalysis in the degradation of rhodamine B in aqueous solutions: a review. *RSC Advances*, v. 12, n. 40, p. 26176–26191, 2022.
- [4] MENG, Q.; ZHANG, Y. J.; HE, P. Y.; CHEN, H.; LI, C. J. A novel carbon-fiber geopolymer composite-coated electrodes for photoelectrocatalysis: Fabrication and application. *International Journal of Applied Ceramic Technology*, 28 abr. 2023.
- [5] SANIVARAPU, S. R.; LAWRENCE, J. B.; SREEDHAR, G. Role of Surface Oxygen Vacancies and Lanthanide Contraction Phenomenon of Ln(OH)₃ (Ln = La, Pr, and Nd) in Sulfide-Mediated Photoelectrochemical Water Splitting. *ACS Omega*, v. 3, n. 6, p. 6267–6278, 30 jun. 2018.
- [6] SHANMUGAM, M. et al. Conducting polymeric nanocomposites: A review in solar fuel applications. *Fuel*, v. 325, p. 124899, out. 2022.
- [7] JOO, M. H. et al. Electrochemical behaviors and electrodeposited materials of lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) on terpyridine-functionalized Ti sheets. *Materials Today Communications*, v. 27, p. 102305, jun. 2021.

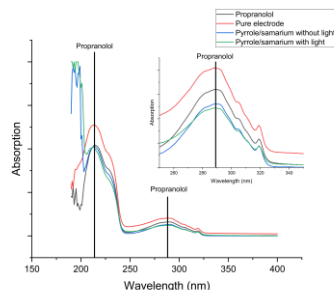


Figure 2. UV-vis spectra of propranolol hydrochloride in a 0.1 Molar Na₂SO₄ medium before and after photoelectrocatalysis.

The spectra exhibit peaks at 214 and 289 nm, indicating the absorption of the naphthalene group of propranolol. Considerable degradation was observed using the stainless steel-polypyrrole-samarium system, especially with light, reaching 23.75%. The degradation rate was 18.43% in the absence of light. There was no degradation with the pure stainless-steel electrode and light. Although further studies are necessary, the new peaks in the spectra suggest drug degradation and the formation of by-products.