Continuous Heterogeneous Solar Photo-Fenton Reactor with Electrodeposited Magnetite on Stainless Steel Mesh as Catalyst

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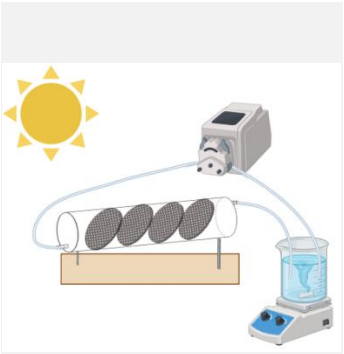
Thais Betoni [1], *Caio César Gonçalves Silva*[1], *Juliana Ferreira de Brito*[1] *Raquel Fernandes Pupo Nogueira*[1] *(1) São Paulo State University (UNESP), Institute of Chemistry, Araraquara 14800-060, São Paulo, Brazil.*



This study proposes the use of magnetite electrodeposited on stainless steel mesh (SS) for application in solar heterogeneous photo-Fenton recirculating reactor applied for degradation of the antibiotic cephalexin (CEX). The material characterization was performed using X-ray diffraction and scanning electron microscopy, verifying the formation of a crystalline phase characteristic of magnetite. The electrodeposition was evaluated applying three different charges, -186, -296, and -462 coulombs, and electrodeposition with -296 C resulted in best performance considering deposited mass and pharmaceutical removal. The prepared meshes were applied in the tubular reactor recirculating a 1 mg L^{-1} CEX solution using 5 mmol L^{-1} H_2O_2 at a flow rate of 200 mL min^{-1}, resulted in the removal of 97% after 120 kJ m^{-2} of sun exposure (90 min) with 6 or 8 SS.

Introduction

The problem of antibiotic contamination in aquatic environments is aggravated by the high global volume of consumption of these pharmaceuticals, estimated at between 100,000 and 200,000 tons per year.[1] The high consumption of antibiotics and improper disposal in domestic, agricultural and industrial sectors results in the presence of these compounds in effluents and surface waters.

Cephalexin (CEX), a first-generation and semi-synthetic cephalosporin, stands out as one of the most consumed antibiotics globally, being the third most prescribed in the world. This popularity also results in its detection in surface waters, as evidenced by studies in the state of São Paulo, where CEX has been found in concentration ranges between 11-29 ng L^{-1} [2].In this context, it is evident that conventional effluent treatment methods often have limited efficacy in the removal of pharmaceutical compounds, highlighting the importance of more innovative approaches, with advanced oxidative processes such as Fenton and photo-Fenton processes being major highlights in the removal of emerging contaminants[3].

The present study aims to evaluate the application of the magnetite (Fe_3O_4) immobilized on stainless steel mesh obtained by the electrodeposition technique in three different charges, and its application in a flow reactor, assessing the flow rate and the amount of catalyst applied in a tubular reactor exposed to sunlight for the degradation of CEX.

Material and Methods

The electrodeposition experiments were conducted in a 500 mL beaker, utilizing a 0.043 mol L^{-1} solution of iron III chloride with the complexing agent triethanolamine (1 mol L^{-1}) in a 2 mol L^{-1} sodium hydroxide solution, maintained at 80 °C with 200 rpm agitation. Three different charges of -186, -296, and -462 coulombs were employed in an electrolytic bath with three electrodes: stainless steel mesh (7 cm in diameter), Ag electrode (AgCl, 3 mol L^{-1}), and DSA (Dimensionally Stable Anodes) electrode and deposited mass was measures in each case. The catalyst was characterized by X-ray diffraction (XRD) using a PAN analytical Aeris diffractometer to identify the crystallographic composition and the morphological characterization was performed using field emission scanning electron microscope (FE-SEM) Auriga, Zeiss. To assess the efficacy of stainless steel mesh with electrodeposited magnetite for solar photo-Fenton degradation, experiments were conducted in a 250 mL beaker with a 1 mg L^{-1} cephalexin solution at pH 5.5, and 5 mmol L^{-1} H_2O_2 using black light lamps under magnetic agitation in a horizontal position. After determining the best electrodeposition condition, the application of 4, 6, and 8 SS in a 1.5 L glass tubular reactor was studied, fixed on a wooden support, with a flow rate of 200 mL min^{-1} and the same condition of the last experiment in terms of pH and H_2O_2. Cephalexin degradation, hydrogen peroxide consumption, and iron leaching were determined using high-performance liquid chromatography (HPLC) with a DAD detector,

and spectrophotometry with ammonium metavanadate and 1,10-phenanthroline methods, respectively.

Results and Discussion

In the XRD analysis, recorded in the 2θ range 20-70°, it was verified that the deposited material presents peaks are in agreement with magnetite as previously reported[4] thus indicating that the desired iron oxide was formed (Figure 1). In the SEM images (Figure 2), the stainless-steel mesh before (a and c) and after electrodeposition (b and d) can be observed, showing the iron oxide increase and an homogeneous layer on the SS surface in all conditions.

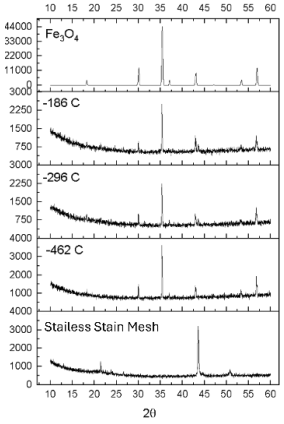


Figure 1: XRD of stain steel meshes before and after electrodeposition using Fe(III)-TEA solution.

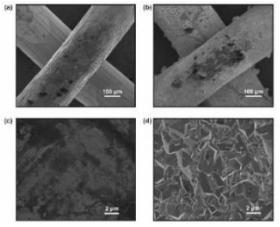


Figure 2: FE-SEM images of magnetite electrodeposited on the stain steel mesh at applied - 1,05 V. (a) and (c) stain steel mesh and (b) and (d) electrodeposited magnetite.

After electroplating at three different charges, the catalysts were tested in a small reactor of 250 mL of 1 mol L^{-1} solution in photo-Fenton experiments. The results demonstrated that the catalysts obtained by electrodeposition under currents of -296 C and - 462 C resulted in CFX concentrations below the detection limit within 60 min reaction, confirming the superior performance of the catalyst deposited under -296 C, so it was chosen to be applied in the tubular reactor under solar irradiation.

The volume of 3 L of CEX solution at pH 5.5, and H_2O_2 5 mmol L^{-1} was circulated in the reactor using 4, 6, or 8 magnetite SS, with samples collected for analysis as a function of energy dose, at a flow rate of 200 mL min^{-1}. It was observed that approximately 95% degradation was achieved, with 4, 6, or 8 SS applied, indicating that the quantity of SS did not significantly alter the degradation kinetics (Figure 3). It is important to mention that no significant degradation was achieved with meshes without electrodeposited magnetite.

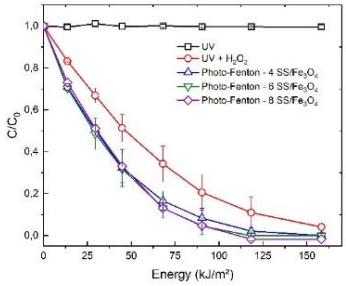


Figure 3: Degradation of cephalexin by solar photo-Fenton process with application of stainless steel mesh with magnetite electrodeposition; Experimental conditions: [CFX]: 1 mg L^{-1}; [H_2O_2]: 5.0 mmol L^{-1}; pH: 5,5; Flow: 200mL min^{-1}.

In the absence of SS (UV and H_2O_2 experiment), cephalexin was removed in 90% at an energy dose of 155 kJ m^{-2}. However, when the catalyst was applied, it is possible to verify that the removal of CEX was improved achieving 97% at a lower dose of energy (120 kJ m^{-2}), denoting the importance of the catalyst applied on the degradation kinetics of cephalexin compared to the UV and H_2O_2 experiment.

Conclusions

Magnetite electrodeposited on stainless steel mesh under the -296 coulombs showed an iron oxide homogenously, which promoted complete degradation of CFX (below detection limit) within 60 min reaction when applied in the photo-Fenton system. Additionally, when the catalyst was applied in a reactor exposed to sunlight using 4, 6, or 8 SS sequentially, it achieved 97% CFX degradation in 120 kJ m^{-2}.

Acknowledgments

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