Synthesis and Characterization of the Supported Nanocatalyst for Photodegradation of Atrazine: Experimental design and Ecotoxicity

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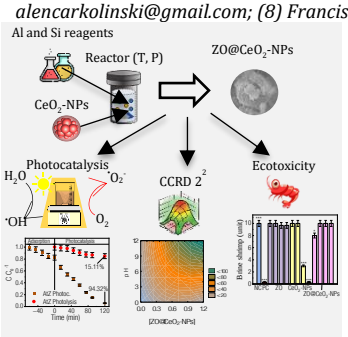
D.M. Druzian[1], *C. dos Santos*[2], *Y.P.M. Ruiz*[3], *A. Galembeck*[4], *G. Pavoski*[5], *D.C.R. Espinosa*[6], *A.K. Machado*[7], *W.L. da Silva*[8]

(1) Franciscan University (UFN), Santa Maria - RS, Brazil, daniel.druzian@ufn.edu.br; (2) Franciscan University (UFN), Santa Maria - RS, Brazil, cristiane.engbio@gmail.com; (3) Federal University of Pernambuco (UFPE), Recife – PE, Brazil, ypmoreno@gmail.com; (4) Federal University of Pernambuco (UFPE), Recife – PE, Brazil, andre.galembeck@ufpe.br; (5) University of the São Paulo (USP), São Paulo, Brazil, giovanipavoski@gmail.com; (6) University of the São Paulo (USP), São Paulo, Brazil, espinosa@usp.br; (7) Franciscan University (UFN), Santa Maria - RS, Brazil, alencarkolinski@gmail.com; (8) Franciscan University (UFN), Santa Maria - RS, Brazil, w.silva@ufn.edu.br



The present work aims to synthesize and characterize a supported nanocatalyst (ZO@CeO_2-NPs) for the photodegradation of Atrazine dye under visible irradiation. ZO@CeO_2-NPs denoted analcime and cerionite crystalline phases, a surface charge of -26.3 mV, and a band gap energy of 2.22 eV. The ideal condition by CCRD 2^2 was of [ZO@CeO_2-NPs] = 0.92 g L^{-1}, pH = 6.5 and T = 298.15 ± 2 K with degradation of 76.75 % (k = 0.0189 min^{-1}) after 120 min, and photocatalytic stability after 5 cycles. The ecotoxicity of ZO@CeO_2-NPs did not demonstrate toxicity and bioaccumulation in *Artemia salina* (10 - 1000 mg mL^{-1}). Therefore, it was possible to synthesize a supported nanocatalyst with great potential for the wastewater treatment with persistent organic molecules under visible radiation.

Introduction

Contamination of the environment and soil by wastewater occurs mainly due to the presence of persistent organic pollutants (e.g., dyes, pharmaceuticals and pesticides), causing serious environmental liabilities [1]. Advanced Oxidative Processes (AOPs) have been applied as an alternative for the correct and adequate treatment of these pollutants through the generation of hydroxyl radicals ($^{\bullet}OH$) onto the catalytic surface, responsible for oxidation-reduction reactions. Cerium dioxide nanoparticles (CeO_2-NPs) present considerable photocatalytic activity (around 90%) in the removal of synthetic dyes [2]. Moreover, supported catalysts have been studied as an alternative to promote increased catalytic activity, due to the increase in available active sites, with zeolite (ZO) catalytic supports with a photoactive phase of metallic nanoparticles [3]. In this context, a supported nanocatalyst (ZO@CeO_2-NPs) of zeolite (ZO) as catalytic support and CeO_2-NPs as photoactive phase was synthesized by impregnation method and characterized for the atrazine (AtZ) photodegradation under visible radiation.

Material and Methods

1) Synthesis and characterization: ZO was synthesized by hydrothermal method [3], and CeO_2-NPs by the biosynthesis process [2]. ZO@CeO_2-NPs were prepared by the impregnation method [4], where 0.01 g of the CeO_2-NPs was mixed with 0.2 g of the ZO under magnetic stirring (200 rpm / 120 min), dried (343.15 ± 2 K / 720 min) and calcined (873.15 K / 180 min). The samples were analyzed by X-ray diffraction (XRD), Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy, N_2 porosimetry, Zeta Potential (ZP), Diffuse Reflectance Spectroscopy (DRS), and Field Emission Gun – Scanning Electron Microscope (FEG-SEM) and dispersive X-ray analysis (EDX).

2) Photocatalytic Activity and Ecotoxicity: Central Composite Rotational Design (CCRD) 2^2 was used to determine the ideal condition for heterogeneous photocatalysis . The kinetic study was determined using the pseudo first-order Langmuir-Hinshelwood (L-H) model. The effect of temperature was evaluated ranging from 288.15-318.15 K by the Arrhenius and Eyring models [5]. Moreover, it was analyzed the electron scavengers and catalyst reuse. *A. salina* was used for ecotoxicity tests ranging from 10 - 1000 mg L^{-1}.

Results and Discussion

Figs. 1(a) – 1(d) show the cubic cerionite and hexagonal analcime crystalline phases with an average crystallite size of around 29 nm; isotherms type IV with S_{BET}= 11 ± 0.3 m^2 g^{-1}, D_p = 22.2 nm, ZP= -26.3 ± 1.42 mV, E_g = 2.22 eV. The morphology was denoted for small clusters and spherical morphology with average particle size of 103.5 ± 27.9 nm and elemental composition of Si/Al = 1.57 and Ce 1.59 wt.%, confirming the obtaining of the supported nanocatalyst. Fig. 1(e) and 1(f) demonstrated the ideal condition for the AtZ ([ZO@CeO_2-NPs] = 0.92 g L^{-1}, pH = 6.5 and T = 298.15 ± 2 K) with degradation of 76.75% and pseudo first-order kinetic of 0.0189 min^{-1}. The effect of temperature of 288.15 to 318.15 K for the AtZ photodegradation was significantly demonstrated in Fig. 1(g) and 1(h), where the increment of temperature increased the pseudo first order kinetic degradation of AtZ from 26.98 % at 308.15 K to 61.37 % at 318.15 K. In this regard, the nanocatalyst synthesized denoted an E_a of 32.65 J mol^{-1}, ΔH of -6.97 J mol^{-1} and Gibbs free energy (ΔG ≈ -5648.14 J mol^{-1}), indicating that the process is spontaneous. The effects

of reusing the nanocatalyst in Fig. 1(i) demonstrated the photocatalytic activity and reusability after 5 cycles with degradation of 76.75 to 61.02% (k = 0.0189 – 0.0121 min^{-1}). Additionally, the electron scavengers (Fig. 1j) showed that the isopropanol (IPA) scavenger's lowest degradation value of 26.05 % of the AtZ indicating that the main mechanism of degradation is the formation of ˙OH. Concerning to Fig. 1(k), toxicity tests in *A. Salina* after 24 hours demonstrated a toxicity effect on CeO_2-NPs of 100 and 1000 mg L^{-1} and ZO@CeO_2-NPs of 10 mg L^{-1} assigned the particle size particularly the increase in the concentration of metallic nanoparticles of CeO_2-NPs.

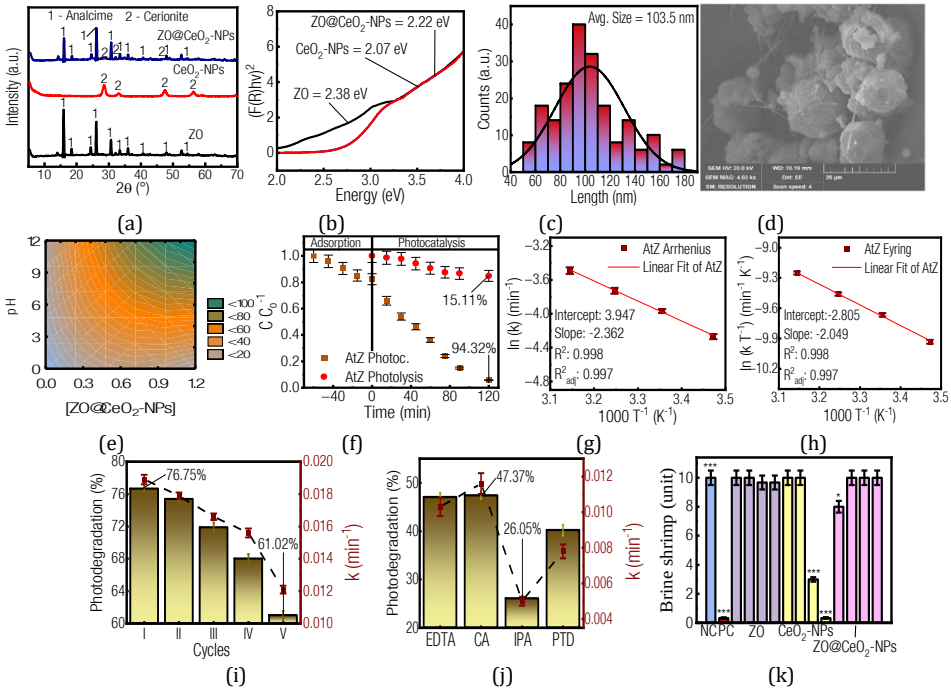


Figure 1. (a) X-ray diffractogram; (b) DRS spectra; (c) Average particle size; (d) FEG-SEM micrographs; (e) 2D response surface; (f) Photocatalytic activity; (g) Arrhenius plot; (h) Eyring plot; (i) Effect of reuse of nanocatalyst; (h) Charged species-trapping experiments and (k) Acute toxicity.

Conclusions

A supported nanocatalyst was synthesized by the impregnation method for the photodegradation of AtZ, demonstrating good photocatalytic activity for AtZ and the absence of acute toxicity in *Artemia salina*. It is worth mentioning that heterogeneous photocatalysis systems are difficult to transpose from bench to industrial scale due to intrinsic thermodynamic limitations, such as the relatively short life of reactive oxygen species [6]. Therefore, possible recombination of catalytic metals and non-metals have been adopted as alternatives to prevent the recombination of electron pairs. Furthermore, the possibility of combining POAs increases applicability across industries.

Acknowledgments

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