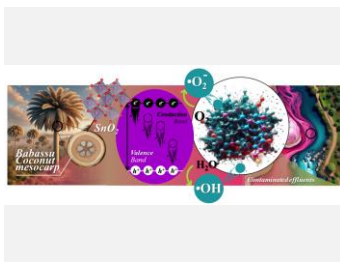


Degradation of emerging contaminants using photocatalysts produced by an environmentally friendly route

POSTER
Ph.D. Student: S
Journal: JECE

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Co-doped SnO₂ materials were synthesized by a green route using babassu mesocarp (*Orbignya Speciosa*) and used in the photodegradation of the mixture of drugs, ofloxacin (OFX) and diclofenac sodium (DCF) prepared in domestic wastewater. X-ray diffraction analysis (XRD) showed materials with a tetragonal rutile-type structure with crystallite sizes of 3.40 nm and 3.95 nm. The band-gap values allowed for the degradation of the drugs under UV-C light irradiation (254 nm). The degradation of emerging contaminants achieved > 94%, with the formation of degraded transformation products (TP) for DCF.

Introduction

Emerging contaminants, such as chemicals generated by the pharmaceutical industry, are the main culprits in contaminating water resources. One way of degrading these contaminants is to use advanced oxidative processes (AOPs), which are innovative technologies in wastewater treatment [1]. Heterogeneous photocatalysis is an advanced oxidation process that uses semiconductors to excite electrons from the valence band to the conduction band, generating an electron/hole pair (e⁻/h⁺) and highly oxidative species such as hydroxyl radicals. Tin dioxide (SnO₂) is an n-type semiconductor with a wide band gap (3.6–4.0 eV) that has become a popular photocatalyst due to its high chemical stability, high conductivity, and low cost [2]. The addition of dopants to the SnO₂ matrix such as cobalt (Co) can result in a narrowing of the gap and consequent improvement in its optical and photocatalytic properties. Among the methodologies by which SnO₂ has already been obtained is the green synthesis route, which makes use of the replacement of alkoxides used in conventional synthesis routes with organic precursors obtained naturally, which act as a chelating and polymerizing agent in the reaction. Gelatine, coconut water, and starch are examples of precursors used in the green synthesis route [3,4]. One organic material that has the potential to be a good chelating and polymerizing agent is babassu mesocarp – BCM (*Orbignya speciosa*), which has a high starch composition (50–70%). In this way, the present work proposed the degradation of emerging contaminants by heterogeneous photocatalysis using Co-doped SnO₂ obtained by a green route.

Material and Methods

To obtain cobalt-modified SnO₂ (Sn_{1-x}Co_xO₂, with x = 0.05 and 0.1 mol), initially, 5.65 g of BCM (Mesovital-MA) were solubilized in distilled water. Then, 5.65 g of SnCl₂·2H₂O followed by 0.31 g of CoCl₂·6H₂O for x = 0.05 mol and 0.63 g for x = 0.1 mol were added to the reaction medium. The mixture was kept stirring at 70 °C for 30 min until it gelatinized. Next up, the mixture was transferred to a microwave-coupled hydrothermal reactor and heated at 120 °C for 5 min. The material was washed

successively with ethanol, dried at 70 °C for 5h, deagglomerated, and calcined at 500 °C for 4 hours at a heating rate of 10 °C/min. The powder was characterized by XRD, and Diffuse Reflectance Spectroscopy (DRS). The photocatalytic activity of powders was performed from a mixture of OFX (1.5 mg L⁻¹), and DCF (1 mg L⁻¹) prepared in domestic wastewater. Then, 50 mg of catalyst was dispersed in 100 mL of the mixture and kept in the dark for 30 min to reach adsorption-desorption equilibrium. Then, the samples were irradiated for up to 60 minutes under UV-C (254 nm) light, and aliquots of 1 mL were taken at different times for chemical analysis. Degradation was monitored by HPLC-RF, and the figures of merit were: LOD = 0.263 µg L⁻¹, LOQ = 0.878 µg L⁻¹, R² = 0.999 for OFX and LOD = 4.79 µg L⁻¹, LOQ = 16.0 µg L⁻¹, R² = 0.999 for DCF.

Results and Discussion

The X-ray patterns of samples (Fig. 1a) confirmed the presence of the SnO₂, being the peaks indexed as rutile-type tetragonal structure (JCPDS 77-050).

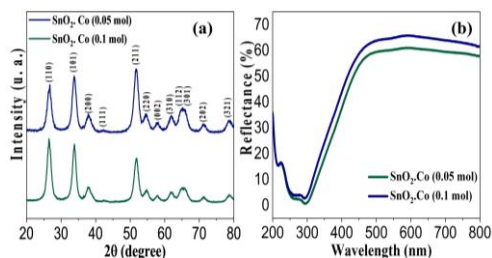


Fig. 1 - a) X-ray diffractogram, b) UV-Vis DRS reflectance spectra.

The samples showed good crystallinity and the calculated crystallite size was 3.40 nm for SnO₂.Co (0.05 mol) and 3.95 nm for SnO₂.Co (0.1 mol). In addition, scanning electron microscopy measurements found nanoparticles with a diameter of up to 18.88 ± 6.76 nm. Thus, each particle is made up of more than one crystallite, which can

improve the absorption of light and the photoactivity of the materials. DRS analyses showed that the electronic transition occurs from 300 nm for both materials. Applying the TAUC equation, the band gap energies (E_{gap}) of the $\text{SnO}_2\cdot\text{Co}$ (0.05 mol) and $\text{SnO}_2\cdot\text{Co}$ (0.1 mol) were 4.0 and 3.69 eV respectively. As these values correspond to the ultraviolet region, the photocatalytic assays were carried out under UV-C light (254 nm). The removal of OFX and DCF by the organic matter naturally present in the domestic wastewater was 11% and 7%, respectively, during the adsorption equilibrium time in the dark (Fig. 2a-b). The samples added to the catalysts showed a maximum adsorption of 35% for OFX and DCF in the presence of the $\text{SnO}_2\cdot\text{Co}$ (0.1 mol). When the UV-C light source was activated, the photolytic degradation of OFX was incipient. However, in the presence of the photocatalysts, degradation was 94% for the samples in 45 min (Fig. 2a). Fig. 2b shows the degradation profile of DCF after the adsorption step, which was similar to that observed for OFX under the same conditions. DCF removal was > 95% for photolysis and photocatalysis in up to 20 min, confirming the greater susceptibility of this compound to be degraded in the photolytic process alone (Fig. 2b).

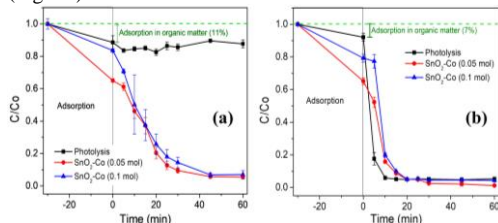


Fig. 2 - Degradation profile of (a) OFX, (b) DCF by photolytic and photocatalytic process under UV-C light. Degradation conditions: $[\text{OFX}]_0 = 1.5 \text{ mg L}^{-1}$, $[\text{DCF}]_0 = 1.0 \text{ mg L}^{-1}$, $V_{\text{sample}} = 100 \text{ mL}$, Catalyst = 50 mg, light = UV-C (254 nm).

The pseudo-first-order kinetic constants ($k = \text{min}^{-1}$) calculated confirm the higher values for DCF degradation (Fig. 3a). In photolysis, degradation over a short period did not allow for an adequate linear fit to the model. However, the k values and fits (R^2) were obtained for $\text{SnO}_2\cdot\text{Co}$ (0.05 mol) and $\text{SnO}_2\cdot\text{Co}$ (0.1 mol) showed the efficiency and suitability of the kinetic model. This behavior was also observed in the degradation of OFX, which reached k values up to 50% lower than those calculated for DCF. Different studies in the literature show that the degradation of DCF is achieved more easily compared to OFX. The latter, in turn, is considered a pollutant with low biodegradability and high environmental persistence. The peaks adjacent to the original compounds (OFX and DCF) were also monitored

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during the chromatographic analyses. No TP was found during the OFX analyses; however, three main TP were found from the degradation of DCF in the photolytic and photocatalytic processes (Fig. 3b-d). TP1 (Fig. 3b) is not formed in the photolytic process but in the presence of $\text{SnO}_2\cdot\text{Co}$ (0.05 mol) and $\text{SnO}_2\cdot\text{Co}$ (0.1 mol), its formation reaches a maximum area in just 15 min, after which it is also degraded. TP2 (Fig. 3c) and TP3 (Fig. 3d) were monitored in photolysis and photocatalysis, showing a similar profile in all processes, but with a slight tendency towards a higher area plateau for the photocatalytic processes. This monitoring of TP is important during degradation assays, as they can be more toxic, less toxic, or inert compared to the original products, as mentioned in the literature for other classes of contaminants [5].

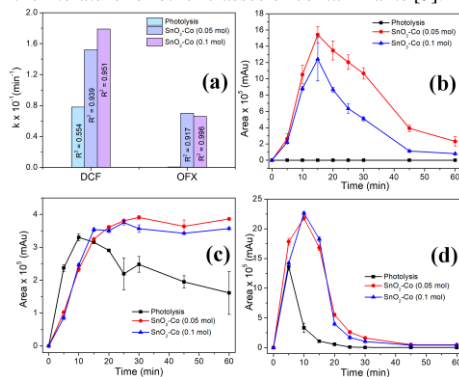


Fig. 3 – (a) Pseudo-first order kinetic constant and TP formed from the degradation of DCF are identified as (b) TP1, (c) TP2, and (d) TP3.

Conclusions

Co-doped SnO_2 oxides were obtained by green synthesis using BCM. The materials obtained confirmed the tetragonal rutile structure through XRD analysis and the UV-Vis DRS spectra indicated application for photocatalysis under UV light. Degradation tests showed > 94% degradation of the emerging contaminants DCF and OFX in a domestic wastewater matrix. The degradation of DCF showed the specific TP for the photocatalytic process is formed and subsequently degraded. Therefore, the SnO_2 semiconductors obtained were effective in degrading emerging contaminants in wastewater.

Acknowledgments

Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP: Processo 2022/06219-3; 2023/17483-6, 2021/06128-5), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).