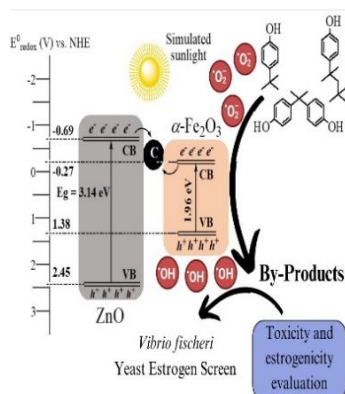


Endocrine disrupting compounds mixture degradation using MOF235(Fe)-derived α -Fe₂O₃/ZnO: Ecotoxicological assessment

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The MOF235(Fe)-derived α -Fe₂O₃ (MIO), ZnO (ZnO), and α -Fe₂O₃/ZnO (MIO@ZO) composite were synthesized by microwave-assisted method followed by calcination at 450 °C. The MIO incorporated during the ZnO synthesis increased specific surface area and improved light absorption in the visible region. The photocatalysts were evaluated in the degradation of bisphenol A (BPA), 4-*tert*-butylphenol (4tBP), and 4-*tert*-octylphenol (4tOP) mixture (5 mg L⁻¹, each) under solar-simulated light. The best performance was observed with MIO@ZO showing 37.76% mineralization in 330 min. The oxalic acid, 2-hydroxyacetic acid, ethane-1,2-diol, and acetic acid were detected at the end of the treatment. The *Vibrio fischeri* and Yeast Estrogen Screen assays showed that the effluent was moderately toxic and non-estrogenic.

Introduction

Natural resources, such as water, are vital for humanity [1] and their development. The water quality has been affected by some emerging contaminants, such as endocrine-disrupting compounds (EDCs) [2]. For their elimination, environmentally friendly photocatalysis can be used since it is a clean technology based on semiconductors. The ZnO has been widely used but presented disadvantages, including the photo-corrosion phenomenon, low surface area, and high electron-hole (e^-/h^+) recombination. The coupling of metal-organic frameworks-derived α -Fe₂O₃ into ZnO has been evaluated to address these inherent limitations, [3]. This study aimed to synthesize the MOF235(Fe)-derived α -Fe₂O₃/ZnO (MIO@ZO) composite for the elimination of BPA, 4tOP, and 4tBP mixture under simulated sunlight, evaluating the acute toxicity and estrogenicity of the effluent.

Material and Methods

The MIO@ZO composite was prepared by microwave-assisted procedure (Mars 6, CEM corporation) at 100 °C for 60 min using zinc acetate dihydrate, hexadecyltrimethylammonium bromide, urea, and MOF235(Fe) (20% wt). The solid was washed with ethanol and water and calcinated at 450 °C for 4 h. ZnO was prepared using the same methodology without MOF235(Fe) addition.

The materials were thoroughly characterized by X-ray powder diffraction (Burker AXS), N₂ physisorption (Micromeritics ASAP 2020), Scanning electron

microscopy (SEM-EDAX JSM-6490LV JEOL), and UV-Vis diffuse reflectance spectroscopy (UV/DRS, Ocean Optic Inc. USB 2000).

The photocatalytic experiments were carried out in an in-batch reactor using the EDCs mixture (5 mg L⁻¹ each) at pH 7 with 0.5 g L⁻¹ of catalyst. The solution was maintained in the dark for 1 h before irradiation under simulated sunlight (SUNTEST, XLS + ATLAS, 300–800 nm) for 330 min. The photocatalytic activity of the prepared materials and photolysis test (control) were evaluated by total organic carbon (TOC) analysis (Shimadzu TOC analyzer) for mineralization assessment. The degradation by-products were identified by GC-MS (Agilent Technologies). The acute toxicity was evaluated using the *Vibrio fischeri* bioluminescence assay according to NBR15411-3 [4]. Meanwhile, the estrogenicity of the effluent was measured using YES assay in a LES Versamax plate reader according to Gomes et al. methodology [5].

Results and Discussion

The XRD results indicated that MIO presented the hematite rhombohedral phase (JCPDS 33-0664) while ZnO and MIO@ZO exhibited the wurtzite hexagonal phase (JCPDS 01-075-0576). The crystallite size values calculated by the Scherrer equation (Table 1) show that the MIO incorporation during the ZnO synthesis decreased the crystallite size, which can be related to the enhanced surface area. The MIO@ZO composite showed a specific surface area of 37.31 m² g⁻¹ while ZnO of 12.43 m² g⁻¹. The obtained pore size values (20-27

nm) indicated that the materials are mesoporous according to the IUPAC classification.

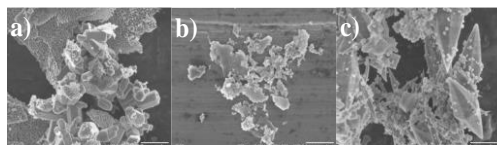


Figure 1. SEM images of a) ZnO, b) MIO, and c) MIO@ZO.

In the SEM images, the MIO presented the pyramidal structure of the MOF235(Fe) and some nanolayers of hematite (Figure 1a) [6], while the ZnO showed nanospheres aggregates (Figure 1b). Otherwise, MIO@ZO consists of nanolayers coated with nanospheres (Figure 1c). The Eg values of the materials were calculated using the Kubelka–Munk function from diffuse reflectance data (Table 1). The MIO@ZO composite shifted to a low Eg value (2.93 eV) compared to ZnO (3.14 eV) related to the coupling of the MIO in ZnO, showing visible light activation.

The mineralization of the EDCs mixture using the prepared catalyst is shown in Figure 2, a). The degradation by photolysis allowed only 5.98% of TOC abatement. The MIO@ZO produced a superior response in mineralization (37.76%) compared with ZnO and MIO semiconductors (32.08% and 28.29%, respectively).

The oxidation and ring opening of aromatic structures by the MIO@ZO mediated photocatalysis resulted in

the formation of low molecular weight compounds as oxalic acid (93.03 m/z), 2-hydroxyacetic acid (76.02 m/z), ethane-1,2-diol (62.07 m/z), and acetic acid (60.02 m/z). Eventually, these products could be mineralized into CO₂ and H₂O [7].

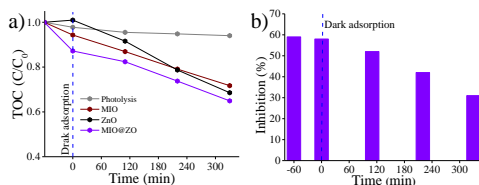


Figure 2. a) Mineralization of the EDCs mixture by photolysis and ZnO, MIO, and MIO@ZO mediated photocatalysis. b) Bioluminescence inhibition (%) using MIO@ZO catalyst.

The *Vibrio fischeri* assay showed 54% of bioluminescence inhibition (related to high toxicity) at the beginning of the reaction, which decreased to 31% at 330 min (Figure 2b). Thus, the effluent was considered moderately toxic to *Vibrio fischeri* [8]. The Yeast Screen Assay confirmed the estrogenicity reduction during the photocatalytic treatment using MIO@ZO. The initial estrogenicity of the solution was 884.24 ng L⁻¹ equivalent estradiol (EQ-E2). After 1 h of adsorption-desorption equilibrium, the solution presented 666.87 ng L⁻¹ EQ-E2; while the estrogenicity was below the limit of quantification after 330 min of reaction.

Table 1. Crystallite size, surface area, pore size, and Eg (eV) values of the synthesized materials.

Materials	Size (XRD, nm)	Surface area	Pore size (nm)	Band gap (eV)
MIO	30.39 (1 0 4)	58.41	20.76	1.96
ZnO	17.60 (1 0 1)	12.43	27.42	3.14
MIO@ZO	14.48 (1 0 1)	37.31	24.38	2.93

Conclusions

The incorporation of MIO into ZnO via the microwave-assisted method showed a slight increase in the surface area, pore size, light absorption in the visible region, and decreased crystallite size. The MIO@ZO photocatalyst presented better efficiency for the mineralization (37.76%) of BPA, 4tOP, and 4tBP mixture solution under simulated sunlight. The intermediates detected in the effluent showed moderate acute toxicity and non-estrogenicity.

Acknowledgments

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