PHOTOCATALYTIC ACTIVITY OF CU_2S/ZnO/XC COMPOSITE UNDER UVC RADIATION FOR DEGRADATION OF SALICYLIC ACID

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ABSTRACT

This study aims to investigate the application of the Cu_2S/ZnO/XC composite in the photocatalytic degradation of the emerging pollutant salicylic acid in an aqueous medium, under UVC light irradiation. The synthesis of the material was characterized using X-ray diffractometry (XRD) and FTIR, which confirmed the presence of distinct crystal structures and specific interactions between Cu_2S and ZnO. Degradation tests carried out in a 0.5 L reactor under UVC light showed efficient degradation of salicylic acid. Electron microscopy and energy dispersive spectroscopy (EDS) mapping revealed a uniform distribution of elements, which is essential for efficient charge transfer in the heterojunctions, improving photocatalytic performance, so the integration of Cu_2S with ZnO proved effective in promoting charge separation. These results show the potential of Cu_2S/ZnO composites as advanced photocatalysts, validated by detailed structural analysis and photocatalytic efficiency tests, indicating their suitability for sustainable pollutant remediation technologies. Within environmental biotechnology, the effort to detect and degrade emerging micropollutants through advanced oxidative processes has proven both promising and essential.

Keywords: Heterogeneous photocatalysis. Photocatalytic degradation. Salicylic acid. Carbon xerogel. Heterojunction.

1 INTRODUCTION

Nowadays, with globalization, a variety of toxic components are regularly released into bodies of water. Among these substances, emerging pollutants of pharmaceutical and cosmetic origin stand out. These pollutants are so named because they are not regulated and are found in the environment in extremely low concentrations, but still pose a significant threat to humans and ecosystems[1]. Environmental biotechnology increasingly recognizes the importance of advanced methods for detecting and degrading emerging micropollutants. Advanced oxidative processes have emerged as a promising approach to tackle challenges related to environmental pollution. These methods not only enhance efficiency in removing and degrading persistent substances but also advocate for more effective waste management practices that uphold principles of environmental conservation and public safety[1-2].

Salicylic acid is widely used in dermatological product formulations due to its mild antibiotic, bactericidal, and antiseptic properties[2]. The degradation of this pollutant is of great importance due to its widespread detection in aqueous environments, which is a significant problem due to its ototoxicity and its association with diseases of the nervous system[3].

Heterogeneous photocatalysis is an economical and sustainable alternative for the mineralization of pollutants[4]. ZnO has emerged as a promising semiconductor for mitigating pollution in aquatic environments, but it has limitations, which have prompted research into improving its photocatalytic activity. Heterojunction technology offers a solution to intensify this activity, optimizing the transfer and separation of photogenerated charges[5].

2 MATERIAL & METHODS

Initially, to prepare the unary material, Cu_2S, at room temperature, pre-defined quantities of copper (II) nitrate trihydrate ($Cu(NO_3)_2$ -$3H_2O$, 99% w/w, CAS No. 10031-43-3) were dissolved in 100 ml of deionized water and corresponding stoichiometric concentrations of Ammonium Sulfide P.A. Solution 20% w/w $(NH_4)_2S$ were added, using a magnetic stirrer. The resulting precipitates were then washed repeatedly with deionized water until the filtrate reached neutral pH. The washed material was then dried in an oven (100 °C, 24 h), ground and then sieved through a 325 mesh analytical sieve.

The ternary materials were produced from 8.098 g of zinc chloride ($ZnCl_2$, 97% w/w, CAS No. 7646-85-7) dissolved in 30 mL of deionized water using a magnetic stirrer at room temperature, then 0.392 g of Cu_2S unary material was dispersed over this solution, corresponding to a mass fraction of 7.5%. Separately, 0.250 g of black wattle tannin (PHENOTAN AP, Tanac SA) was dissolved in 20 mL of deionized water and then added to the previously prepared solution of $ZnCl_2$ and Cu_2S. The ternary material was then, precipitated using 50 mL of potassium hydroxide (KOH) solution (85% w/w, CAS No. 1310-58-3) with 7.197 g of material. The precipitates obtained were washed repeatedly with deionized water until the filtrate was free of chloride ions and had a neutral pH. The washed materials were dried in an oven (100 °C, 24 h), ground and then sieved through a 325 mesh sieve. Finally, the materials were compacted in closed crucibles and calcined in a Sppencer muffle furnace at a temperature of 600 °C for 30-minute, using a heating rate of 10 °C min^{-1} and a nitrogen-rich atmosphere (flow rate of 0.5 L min^{-1}).

The characterization of the materials was performed using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). XRD identified the crystalline phases using a PANalytical Empyrean device with CuKα radiation, covering the range of 20 to 70°. The chemical structure was analyzed with a Perkin Elmer Frontier spectrometer, operating in the range of 4000 to 500 cm^{-1}, with a resolution of 4 cm^{-1}. For morphological and compositional analysis, scanning microscopy and energy-dispersive spectroscopy (EDS) were used EDS, using an Oxford Swift ED3000 spectrometer, provided qualitative and quantitative identification of the constituent elements, offering a comprehensive characterization of the studied materials.

Photocatalytic evaluation tests were conducted to assess the photocatalytic activity of the materials in a 0.5 L reactor, with constant magnetic stirring and temperature controlled at 25°C. Each test involved adding 0.1 g of the evaluated photocatalyst and 0.5 L of a solution containing 10 mg L^{-1} of salicylic acid (SA). Firstly, the reactor was kept in the dark to achieve adsorption-desorption equilibrium between the pollutant and the catalyst. After equilibrium was reached, the samples were exposed to irradiation from an Osram HNS L 36W 2g11 bulb to simulate UVC radiation. The concentration of SA was measured with a UV-Vis spectrophotometer at 296 nm after filtering the samples, which were collected every 5 minutes until the 40-minute mark.

3 RESULTS & DISCUSSION

The materials obtained from the synthesis were characterized using x-ray diffractometry, and FTIR, and the structure and morphology were also evaluated using SEM and EDS.

X-ray diffraction (XRD) provided information on the crystal structure of the unary, binary, and ternary materials shown in the diffractograms below in Figure 1A. The peaks and bands of interest in the synthesized materials were identified with reference to the ICDD codes from the literature, according to the High Score Plus database, and FTIR in Figure 1B.

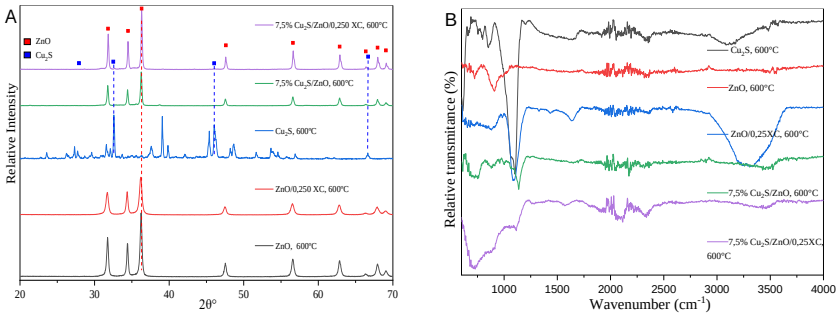

Figure 1 (a) XRD diffractograms (b) FTIR spectra of the synthesized materials.

In (A), it is possible to see the characteristic peaks of the materials, as well as the hexagonal crystal structure (wurtzite) of ZnO, in the following 2Theta positions as 31.84° to 69.26°, corresponding to the HKL planes as (100), (002) and (101). Cu_2S shows characteristic peaks from 32.66° to 66.71° corresponding to the HKL planes as (103), (104), (113). These results confirm the diffraction data known from the literature (ICDD), which confirms the composition and structure of the materials obtained[6].

In Figure 1B, the FTIR spectra of the synthesized materials show characteristic absorption bands attributed to the components of the composites. The ternary material shows a peak at 1380 cm^{-1}, attributed to the Cu-S stretching vibration in the Cu_2S/ZnO nanocomposites, as well as peaks at 1466 cm^{-1} and 719 cm^{-1}, related to the methylene bending and Cu-S stretching vibrations, respectively. Peaks at 680, 669, and 836 cm^{-1}, attributed to the Zn-O stretching vibration, appear in both the binary and ternary materials, indicating the continuous presence of ZnO. The incorporation of Cu_2S is confirmed by the peaks at 1380 cm^{-1} observed only in the ternaries. These observations indicate a strong interaction between the Cu_2S nanoparticles and the ZnO matrix, as well as the presence of XC, evidenced by characteristic C=O, C-N, and C-H peaks in the spectrum[7].

The MEV analysis in Figure 2 shows the 7.5% Cu_2S/ZnO/0.250 XC ternary composite treated at 600°C for 0.5h, displaying a combination of spherical nodular particles and some larger polyhedral particles. The presence of these larger particles is attributed to the incorporation of Cu_2S and carbon xerogel. The composites with Cu_2S and carbon xerogel show greater morphological diversity, with larger and more irregular particles, potentially increasing photocatalytic efficiency due to defects at the edges of the particles, which can act as intermediate states for electrons, reducing the recombination of photogenerated charges.

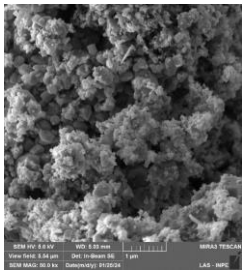

Figure 2 Ternary MEV

EDS mapping of 7.5% Cu_2S/ZnO/0.250 XC ternary composite in Figure 3 shows the uniform distribution of Cu, S, Zn, O, and C, confirming the effective incorporation of Cu_2S and XC into the ZnO matrix. The combination of these materials may offer greater

photocatalytic efficiency due to the synergy between the components, which improves the separation and transport of photogenerated charges.

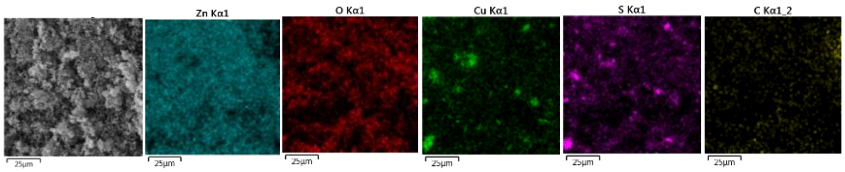

Figure 3 EDS mapping

The correlation between the characterization analyses and the salicylic acid degradation efficiency of each material is evident in Figure 4. The positive impact of doping ZnO with Cu_2S and utilizing XC as a solid-state electronic mediator on catalytic performance is evident in the individual degradation tests.

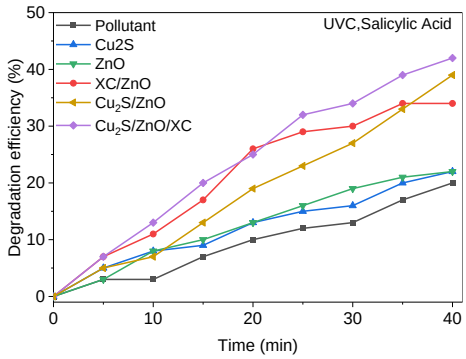

Figure 4 Compared results of photocatalytic tests for the degradation of SA

Structural stability, indicated in the diffractograms, suggests enhanced catalytic properties, leading to improved solar degradation outcomes. The combination of Cu_2S, ZnO, and XC results in more efficient materials for pollutant degradation. The consistency between diffractograms and degradation test results underscores that careful material selection can significantly optimize photocatalyst efficiency under solar irradiation. This integrated approach between structural analysis and catalytic performance establishes a robust foundation for future applications in heterogeneous photocatalysis[8].

4 CONCLUSION

In the field of emerging pollutants, the presence of which in water is causing growing concern due to the lack of effective treatment, the results of this study offer significant insights. In summary, the main aim of this project was to investigate ZnO, Cu_2S, and XC photocatalytic materials, with an emphasis on the potential for salicylic acid degradation. The materials, demonstrated by their structural properties and degradation test performance, lay a solid foundation for future applications in heterogeneous photocatalysis, aiding in pollutant mitigation. The consistency between structural analyses and degradation test results validates the choice of materials and synthesis methodology, establishing a basis for developing sustainable and innovative catalytic technologies. X-ray diffraction patterns and FTIR spectra confirm the distinct crystalline structures of ZnO and Cu_2S, while consistent degradation test results demonstrate high efficiency in degradation salicylic acid. Electron microscopy and EDS mapping reveal a uniform distribution of elements, reinforcing the effectiveness of the heterojunctions in the composites, which is crucial for photocatalytic efficiency. Therefore, the combination of Cu_2S with ZnO shows promise in forming new active sites and enhancing electronic conduction, indicating that doping and composite formation strategies are effective in creating advanced photocatalysts.

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