Harnessing metal tungstates for efficient photocatalytic degradation of propranolol

POSTER
Ph.D. Student: N
Journal: JECE

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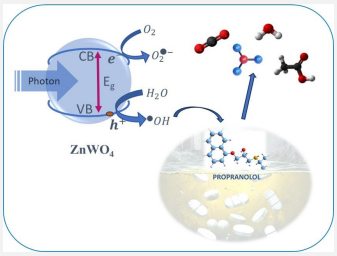

The photocatalytic activity of $ZnWO_4$ synthesized by the coprecipitation method was evaluated on propranolol degradation in aqueous medium under visible radiation. The obtained material was characterized using X-ray diffraction (XRD), N_2 physisorption, and diffuse reflectance UV-Vis spectroscopy (UV-Vis-DRS). Photocatalytic experiments were conducted in 10 mg/L propranolol solution using a catalyst dosage of 1 g/L for 3 h. The degradation process was monitored by high-performance liquid chromatography (HPLC). Results showed that the $ZnWO_4$ photocatalyst achieved a 70 % degradation rate of propranolol within 3 h. In contrast, control experiments indicated that only 8 % degradation occurred via photolysis and 12 % via adsorption under the same conditions. These findings demonstrate that $ZnWO_4$ is significantly more effective in degrading propranolol compared to photolysis and adsorption, underscoring its potential as a photocatalyst for removing emerging contaminants.

Introduction

Emerging contaminants pose a growing concern in water bodies worldwide, with pharmaceuticals representing a significant category. Propranolol, a beta-blocker used to manage cardiovascular conditions, has emerged as a notable contributor to this issue [1], with its widespread presence in water sources, including effluents from wastewater treatment plants, reporting concentrations of 34 ng/L [2,3]. This underscores the urgent need for effective management strategies to safeguard water quality. Understanding the impact of propranolol and other emerging contaminants is crucial for mitigating potential risks to ecosystems and public health.

Heterogeneous photocatalysis offers a versatile and environmentally friendly treatment technology for removing propranolol and other emerging contaminants from water. Tungstates such as $ZnWO_4$ are important classes of visible light-responsive photocatalysts; these materials have attracted much attention due to their good stability, long afterglow to luminescence, and photocatalytic activity [4]. Therefore, this study aims to synthesize $ZnWO_4$ via the coprecipitation method, assess its photocatalytic activity, and evaluate its efficacy in degrading propranolol under visible radiation in an aqueous medium.

Material and Methods

Synthesis of $ZnWO_4$

The materials were synthesized using equimolar amounts of $Na_2WO_4 \cdot 2H_2O$ (solution A) and the precursor salt of the divalent metal: $Zn(NO_3)_2 \cdot 6H_2O$ (solution B) dissolved in 30 mL of distilled water. Subsequently, solution A was added dropwise to solution B at room temperature with constant stirring. The formed solid was washed and centrifuged at 8500 rpm for 10 min. It was then dried in an oven at 100 °C for 15 h and calcined at 600 °C for 2 h using a heating ramp of 5 °C/min.

The obtained material was characterized using X-ray diffraction (XRD), nitrogen physisorption, and diffuse reflectance UV-Vis spectroscopy (UV-Vis/DRS).

Photocatalytic experiments

The photocatalytic tests were conducted in a 250 mL batch reactor with constant stirring under visible radiation, utilizing a lamp emitting wavelengths ranging from 350 to 850 nm at an intensity of 300 W/m^2. The reaction duration was standardized to 3 h. In all experiments, the initial concentration of the propranolol solution was set at 10 mg/L, and the pH was maintained at 5.0. A catalyst dosage of 1 g/L was added. Prior to irradiation, the propranolol solution underwent a 30 min dark period to achieve adsorption/desorption equilibrium. In addition, the corresponding control tests for photolysis (light radiation only) and adsorption (photocatalyst only) were conducted.

Degradation monitoring was performed using HPLC (YL9100 HPLC System), with samples collected every 30 min. Chromatographic separation was performed at room temperature using a reversed-phase C18 column (250 x 4.6 mm, 5 µm, Phenomenex Inc.), with a flow rate of 1.0 mL/min and an injection volume of 20 µL, monitored at 220 nm. The mobile phase consisted of acetonitrile (HPLC grade) and ammonium acetate (10 mM) in a ratio of 40:60 v/v using isocratic elution mode.

Results and Discussion

Figure 1 shows the diffraction pattern of the synthesized material. The monoclinic crystalline phase of $ZnWO_4$, known as sanmartinite (PDF 01-075-8595), was obtained with a crystallite size of 50 nm. The point of zero charge (pzc) was found to be 7.43, which suggests that the surface of $ZnWO_4$ is

neutral at this pH. This is significant as the pzc can influence the adsorption of propranolol and other contaminants, potentially affecting the photocatalytic process.

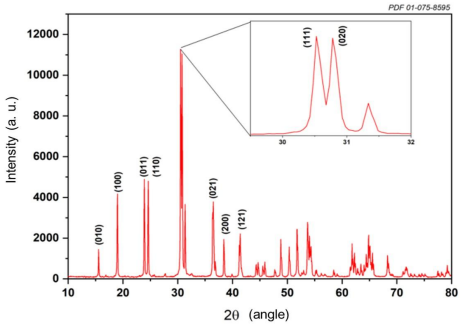

Figure 1. XRD patterns for $ZnWO_4$.

From the N_2 adsorption isotherm, the specific surface area was estimated using the BET method, resulting in a value of 2.02 m^2/g; although this value falls on the lower end for materials typically utilized as photocatalysts, it is noteworthy in understanding the material's surface properties and its potential impact on photocatalytic performance.

Regarding the calculated band gap energy from the Kubelka-Munk function, a value of 3.1 eV was obtained. This indicates that the material possesses a band gap suitable for activation with visible light, corresponding to a wavelength of 400 nm. This characteristic is highly desirable for photocatalysts, as it enables efficient utilization of solar irradiation, thus enhancing the potential for practical applications in environmental remediation. The ability to absorb visible light means that $ZnWO_4$ can utilize a broader spectrum of sunlight, making it more efficient for photocatalytic processes.

Moving on to the evaluation of photocatalytic activity, $ZnWO_4$ demonstrated significant efficacy in degrading propranolol under visible radiation. The material exhibited a degradation efficiency of 70 %, surpassing the degradation achieved through control tests of photolysis and adsorption, which yielded degradation rates of 8 and 12 %, respectively (Fig. 2). The degradation followed a pseudo-first-order kinetics with a rate constant of 0.00532 min^{-1} and a half-life of 130.3 min. This indicates that the reaction rate is proportional to the concentration of propranolol, and the relatively high rate constant suggests a strong photocatalytic performance.

Furthermore, the stability of the material was confirmed by measuring the leaching of Zn, which was found to be 3 mg/L. This value is below the limit established by Mexican regulations, indicating that $ZnWO_4$ is stable under experimental conditions and does not release harmful amounts of Zn into the solution.

Overall, the integration of surface area analysis, band gap energy determination, and photocatalytic activity assessment provides valuable insights into the suitability of $ZnWO_4$ as a photocatalyst. Further research may explore optimization strategies to enhance its photocatalytic efficiency and broaden its applicability in water treatment processes.

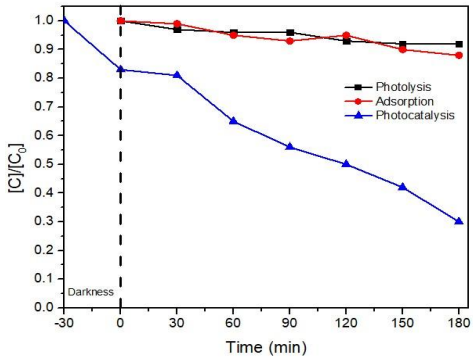

Figure 2. Photolysis, adsorption, and photocatalytic degradation of propranolol (10 mg/L) using $ZnWO_4$ (1 g/L).

Conclusions

In conclusion, the comprehensive characterization and evaluation of ZnWO4 as a photocatalyst have underscored its significant potential for the removal of emerging contaminants from water bodies. The material's well-defined monoclinic crystalline phase, crystallite size, and suitable band gap energy enable efficient activation with visible light, leading to substantial photocatalytic degradation of propranolol. The material's stability, indicated by low zinc leaching, further supports its potential for repeated use without environmental harm. Future research focused on optimizing synthesis methods and enhancing photocatalytic efficiency will be crucial in maximizing the efficacy of $ZnWO_4$ and accelerating its application in real-world water treatment technologies.

Acknowledgments

The authors gratefully acknowledge the financial support by grants: CONAHCYT-Mexico (Master scholarship, 1315023), ProACTI2023-UANL, 27-BQ-2023.

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