Bismuth Oxychloride Heterostructures doped with Copper for the Photocatalytic Degradation of Methyl Orange: on the Process Optimization and Kinetic Modeling.

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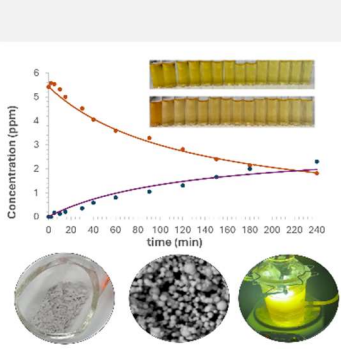

This study explored the photocatalytic degradation of methyl orange (MO) using a BiOCl/CuO heterostructures catalyst. The research focused on optimizing conditions, including pH and photocatalyst concentration, with synthesized heterostructures demonstrating enhanced photocatalytic activity. Characterization techniques such as SEM, EDS, and FTIR confirmed material composition and morphology. A central composite design established optimal experimental conditions (pH 4 and 0.8 g/L photocatalyst dosage). The optimal CuO concentration (0.6%) relative to the BiOCl catalyst achieved a 40% degradation of MO in 60 minutes under solar-simulated light. Kinetic experiments show that the reaction follows a pseudo-second-order model, revealing insights into the practical applicability of BiOCl/CuO for water decontamination.

Introduction

Water pollution has become a pressing global concern over the past few decades, with industrial dyes emerging as significant contributors to organic compound contamination, mainly released by textile, paper, plastic, and leather industries. Among these dyes, methyl orange (MO), a mono-azo anionic dye, stands out among the most used, but its challenge lies in conventional wastewater treatment methods [1]. Photocatalysis emerges as a promising alternative to address pollution [2]. Bismuth-based photocatalysts (BiOX) have gained attention due to their stability, low toxicity, and high photocatalytic activity [3]. Although BiOCl has an energy gap limiting its absorption to UV light, incorporating metal ions or forming heterostructures with semiconductors of lower energy gap, such as copper oxide (CuO), has shown significant improvements [4]. In this context, the degradation of MO by photocatalysis of the BiOCl/CuO material is evaluated, assessing operational conditions of pH and photocatalyst dosage, obtaining kinetic data, and analyzing the physicochemical surface characteristics of the heterostructure material.

Material and Methods

Copper oxide (CuO) nanoparticles were synthesized using high-purity copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) from Merck S.A. in deionized water. For the BiOCl compound, bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) and potassium chloride KCl were used as the Cl- ion precursor. The synthesis was carried out using ethylene glycol supplied by Merck S.A., Germany. The solvothermal method was employed for the BYOB heterostructure at 167.5°C for 18 hours.

Results and Discussion

CuO-doped heterostructures were synthesized with varying concentrations, finding 0.6% CuO optimal for 40% degradation under visible light for 60 minutes. SEM and EDS analysis confirmed BiOCl microspheres and CuO lamellar plates in the structure at this concentration [5,6], contrasting with higher doping levels that showed amorphous morphology and lower degradation rate. The analysis of the zero-point charge of the 0.6% BiOCl/CuO photocatalyst shows a gradual increase in surface charge negativity with increasing alkaline pH. The surface charge approaches zero at acidic pH levels, facilitating contaminant adsorption [7].

Acidic conditions also enhance the reactivity of the photocatalyst's active sites and the formation of reactive species like hydroxyl radicals, which degrade contaminants [8]. Conversely, alkaline pH reduces contaminant adsorption, decreasing photocatalytic efficiency [9]. Experimental findings validate that higher adsorption and degradation occur under acidic pH conditions. The material underwent degradation experiments using a central composite design (CCD) with MODDE PRO 13 software, resulting in 11 experiments varying pH and photocatalyst dosage. Optimal degradation of MO in the study range occurred at pH 4 with a photocatalyst dosage of 0.8 g/L starting from 10 ppm contaminant concentrations (figure 1). The adjusted model showed a strong correlation (R^2) and predictive capability (Q^2), indicating its suitability for anticipating contaminant degradation. Pseudo-first-order and pseudo-second-order kinetics were explored, with the latter providing a more accurate description of degradation behavior, suggesting surface interactions and adsorption of species on the catalyst surface as critical factors. Intermediates may also contribute to this kinetics [10].

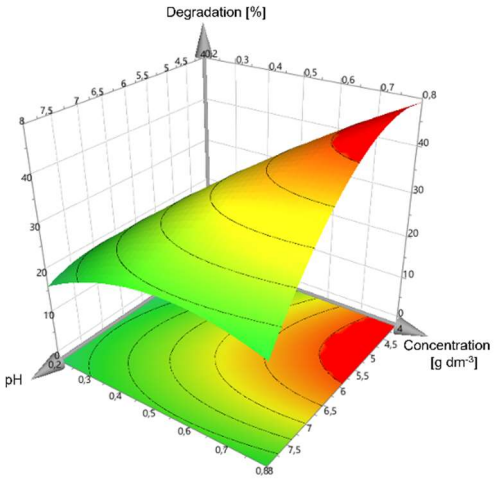

Figure 1. Response Surface for MO degradation as a function of the catalyst load and solution pH.

Conclusions

The synthesis of the BiOCl/CuO compound reveals that concentrations higher than 5% are less effective due to the formation of CuO clusters. In contrast, an optimal concentration of 0.6% may positively affect the coupling between CuO plates and BiOCl microspheres, thereby increasing efficiency in photocatalytic degradation. Pseudo-second order kinetics characterize the degradation process of MO with a 0.6% CuO load, highlighting the positive influence of pH and higher catalyst concentration, with optimal conditions observed at 0.8 g/L and pH 4, indicating the formation of degradation compounds. Several opportunities exist in developing photocatalyst materials with non-toxic, scalable, cost-effective, and industrially adaptable characteristics.

Acknowledgments

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