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Research Paper

Evaluation of Structural-Optical Properties and Catalytic Performance of BiOI-CuO Heterojunction Photocomposite Embedded in Zeolitic Matrix

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Abstract: In the present study, the impact of immobilizing a BiOI-CuO heterojunction on clinoptilolite zeolite as a support for photocatalytic degradation of the organic pollutant methyl orange (MO) was investigated. To this aim, BiOI-CuO heterojunction photocatalysts with varying weight ratios of BiOI:CuO (2, 3, and 4) were synthesized and embedded in clinoptilolite matrix. Characterization techniques confirmed the successful synthesis of the photocatalysts. FESEM analysis revealed that immobilization of the heterojunction structure on the zeolite support reduced the number of agglomerations. This immobilization not only preserved the morphology of the semiconductors but also led to the formation of a more homogeneous and uniform structure. The results demonstrated enhanced photocatalytic performance for MO degradation due to the formation of a heterojunction between BiOI and CuO semiconductors and their immobilization on clinoptilolite. The combination of 20 wt.% BiOI and 10 wt.% CuO immobilized on clinoptilolite exhibited the highest removal efficiency for MO. This superior performance was attributed to the favorable dispersion and distribution of the active-phase semiconductors on the zeolite support, lower charge carrier recombination and an appropriate bandgap, as confirmed by characterization analyses. Under 2 h of UV light irradiation with a MO concentration of 20 ppm and a photocatalyst dosage of 0.5 g/L, a maximum MO removal efficiency of 85% was achieved under UV light irradiation.

Keywords: Clinoptilolite, Semiconductor CuO, Semiconductor BiOI, Photodegradation, Methyl orange pollutant.

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INTRODUCTION

Wastewater may originate from various sources, such as industrial, agricultural, or residential activities. Organic pollutants are one of the most abundant compounds in the body of wastewater [1]. One type of organic pollutants that should be noted is colored pollutants, which are introduced into the environment each year over 280,000 tons [2]. Methyl orange is a commonly utilized anionic dye in various industrial applications. This dye contains azo groups and can have the potential to cause adverse effects on the health of humans, animals, and plants. Hence, the removal of this substance from aquatic ecosystems holds significant importance [3]. Among the different methods that exist to remove this color, the photocatalytic process has garnered interest from researchers owing to the lack of secondary pollutant production, feasibility for implementation under environmental conditions, and cost-effectiveness. BiOI is a p-type semiconductor that has a band gap of 1.6-1.9 eV and is widely used due to its chemical stability, non-toxicity, unique layered structure, and activity in visible light [4]. Despite the appropriate activity, challenges such as the rapid recombination of charge carriers and the complex separation of nanoparticles from the reaction solution hinder the effective use of this semiconductor. To mitigate recombination rates, enhance the adsorption capacity, and facilitate the separation from the solution, effective strategies include establishing a heterojunction structure between two semiconductors and immobilizing onto the support. CuO has been used for the degradation of pollutants because of its narrow band gap, easy synthesis, widespread availability, and cost-effectiveness, making it a popular choice among various semiconductors. CuO nanoparticles can adsorb oxygen molecules, resulting in the creation of oxygen vacancies, which can improve the photocatalytic performance [5]. Conversely, immobilizing semiconductors on zeolite support is expected to result in decreased aggregation, improved dispersion of photosites, and enhanced recoverability of the catalyst from the reaction solution. The clinoptilolite mineral support stands out as a superior choice compared to other supports, owing to its diverse pores and channels, cost-effectiveness, high mechanical and chemical resistance, proper absorption capacity, and the widespread availability of its mines [6]. In the present study, for the first time, the immobilization effect of CuO-BiOI heterostructures over clinoptilolite as an economical and accessible support, along with the composition impact of the integrated heterostructure, were assessed in the photodegradation of methyl orange pollutant.

METHODS

Initially, the precursors' solutions were prepared by dissolving the desired amount of bismuth nitrate, potassium iodide, and copper acetate in ethanol and distilled water. Next, the required amount of mineral support was dispersed in the bismuth nitrate solution (mixture 1). Potassium nitrate solution was added dropwise to mixture 1 under mixing (mixture 2). Subsequently, copper acetate solution was added to mixture 2, and the resulting mixture underwent mixing (mixture 3). To create precipitation, ammonia solution is added to mixture 3 until pH = 9 is achieved. In the next step, the obtained precipitation was aged under reflux conditions at 80-85 °C for 4 h. Ultimately, the filtrated precipitates were dried and calcined at 350 °C for 3 hours.

To evaluate the photocataltic performance, a batch system including a 600 ml Pyrex reactor, magnetic stirrer for proper mixing, cooling system to keep the solution temperature at 20 °C, a 125 W medium pressure Hg lamp as a UV light source, and the aluminium foil–covered frame was used. During each experiment, the photocatalyst was uniformly distributed in the reaction solution at a concentration of 20 ppm with a dosage of 0.5 g/L. The solution undergoes a two-hour testing period in the absence of light to determine the equilibrium between absorption-desorption. Then, the light source is turned on, and the photocatalytic process begins. During designated intervals, sampling is done from the reaction solution, and the concentration of colored pollutants in the samples is determined using a spectrophotometer at 480 nm.

FINDINGS AND ARGUMENT

Photocatalyst Characterization

To investigate the physical and chemical properties of photocatalysts, analyses such as XRD, FESEM, FTIR, DRS, and PL were used. An overview of the XRD results confirmed the presence of BiOI, CuO, and clinoptilolite. Analysis of FESEM findings indicated a reduction in the embedded particle size and an enhancement in the uniformity of the structure as a result of embedding the photophases in the zeolitic matrix. DRS analysis also verified the activity of all photocatalysts in the visible light region and also a blue shift in the absorbance edge of the embedded heterojunction photocatalysts. On the basis of PL analysis (Figure 1), it can be found that the lifetime of electron-hole pairs decreases with an increase in the BiOI:CuO weight ratio.

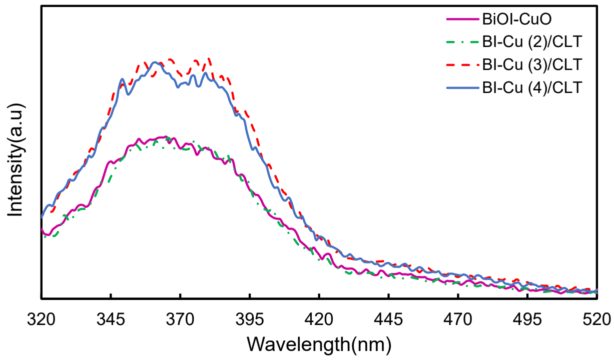

Figure 1. PL analysis of the synthesized samples

Photocatalytic performance

The methyl orange removal efficiency of bare clinoptilolite, BiOI, BiOI-CuO, BI-Cu (2)/CLT, BI-Cu (3)/CLT, BI-Cu (4)/CLT photocatalysts was investigated, and the results are shown in Figure 2. The findings demonstrate the effectiveness of the presence of clinoptilolite and a heterostructure formation between BiOI and CuO. The enhanced efficiency may be due to the improved availability of pollutant molecules to the photosites, facilitated by the more uniform dispersion of active phases across the zeolite matrix and enhanced adsorption capacity. Among the nanostructured composites with different loadings of heterogeneous, the BI-Cu (2)/CLT photocomposite shows the best result by removing 85% of the pollutant under 2 h of irradiation. The improved efficiency in this sample can be attributed to the lower recombination rate, reduction aggregations, and proper distribution of active sites on the zeolite surface. The kinetics of the photocatalytic treatment of wastewater contaminated with methyl orange were studied by zero-order, first-order and second-order models. The results of the correlation coefficients (R^2) showed that the first-order model has a better fit with the data compared to other models.

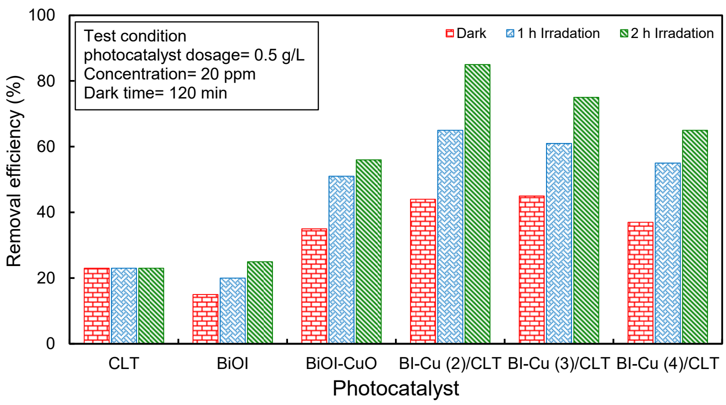

Figure 2. Adsorption and UV-photodegradation of methyl orange over the synthesized samples

CONCLUSIONS

According to the obtained results, it can be stated that the hetero-structure formation between BiOI and CuO and the employ of clinoptilolite as a support, as well as the utilization of the appropriate combination of photophases, improve the performance of BiOI in the photodegradation process of methyl orange pollutant. The photodegradation efficiency for the optimized photocatalyst is approximately 3.4 times that of pure BiOI. The highest amount of colored pollutant removal has been achieved with the BiOI/CuO weight ratio equal to 2. This could be due to the better distribution of the photophase semiconductors on the mineral support, more uniform morphology, and lower rate of charge carrier recombination in this photocomposite. Examining different kinetic models on the optimal photocatalyst efficiency confirms that the data follow the first-order model.

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