Heterojunction of BiOCl-CuO by co-precipitation method for the remotion of environmental pollutants.

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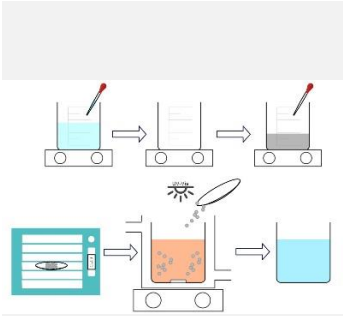


Emerging pollutants, such as organic dyes that generate environmental impact, have been removed from wastewater using new technologies such as advanced oxidation processes (AOP), for example heterogeneous photocatalysis (HP), by using individual semiconductors. However, heterostructures are used in these HP processes to reduce the recombination process and, in this way, increase photocatalytic efficiency. In this research, a BiOCl-CuO heterostructure, which was obtained by the co-precipitation method, is used. Five variations to the method used were carried out, achieving a better degradation of methyl orange (MO) dye from the addition of polyvinylpyrrolidone (PVP). The percentage of photocatalytic degradation of (MO) under up to 150 minutes of simulated solar radiation using the obtained heterostructure (M5) was 98.5%.

Introduction

Among the solutions to solve environmental problems are the AOPs that remove emerging pollutants in water since they are substances of global concern due to the environmental damage they cause **[1]**. The current study uses heterogeneous photocatalysis (HP) since it is efficient in its degradation of organic dyes. However, an associated problem is the recombination presented by the individual semiconductors used in HP. Therefore, in this study, we propose the synthesis of a heterojunction to minimize the recombination process and increase the photocatalytic efficiency in dye degradation. The BiOCl-CuO heterojunction was synthesized by the co-precipitation method using different solvents such as ethanol, acetic acid, and water, as well as by adjusting the pH and adding PVP. The method proposed to obtain this heterostructure has not been previously reported in literature. However, this material was previously synthesized using the solvothermal method. This method uses ethylenglycol as a solvent, which is a toxic compound, and it incurs higher energy costs and economic expenses. Therefore, the co-precipitation method was used in this study, which is more environmentally friendly. Moreover, the heterojunction obtained by the solvothermal route presents a percentage of 81.3% MO degradation, while the heterostructure obtained using co-precipitation shows a 98.5% dye removal.

Materials and Method

In the first method (M1), BiOCl-CuO was synthesized using deionized water (DIW) and ethanol. Subsequently, another synthesis was performed using M1, but ethanol was exchanged for 10% acetic acid (M2). The heterostructure was obtained using a third method based on M2 with the addition of PVP (M3). A fourth procedure (M4) used M1 with the addition of PVP. Finally, the amount of PVP was reduced to 0.1g (M5). It is important to mention that in M2, pH adjustments were made to 1.3 and 2.0 (M2.1 and M2.2, respectively). All procedures are reported in Table 1.

The photocatalytic efficiency was determined with HP assays. The heterostructures obtained using M1-M5 were arranged in a Batch reactor containing 250mL of a 10 ppm solution of MO in DIW, and 0.1g of the heterostructure obtained by the corresponding method was added to the system. The reactor was kept for one hour in the dark to reach the adsorption-desorption equilibrium. Subsequently, a lamp simulating solar radiation was turned on, and samples were taken at specific times of 0,5,10,15,30,40,60,90,120 and 150 min.

The reaction kinetics with each heterostructure obtained were followed using an Agilent Infinity 1260 HPLC equipment with a diode array detector (DAD) and a C-18 column. The mobile phase has Methanol and ammonium acetate (Buffer pH 6.6) in a 60:40 ratio, respectively. The flow rate was 1mL/min, and the injection was 10µL.

Results and Discussion

The results obtained using the HPLC analytical technique allowed the synthesizing of the BiOCl-CuO heterostructures using different procedures (M1-M5).

Figure 1 shows the C/C_0 results using the BiOCl-CuO heterostructure obtained with the procedures reported in Table 1. The material that presented the highest photocatalytic efficiency for MO removal was the one obtained in M5.

In the case of M2.1 and M2.2, the pH adjustment made to 1.3 is the point at which this heterostructure was without making pH changes. When compared with M2.2, a clear difference is observed in the percentages of both removal and degradation, showing that a higher photocatalytic efficiency is achieved without adjusting the pH.

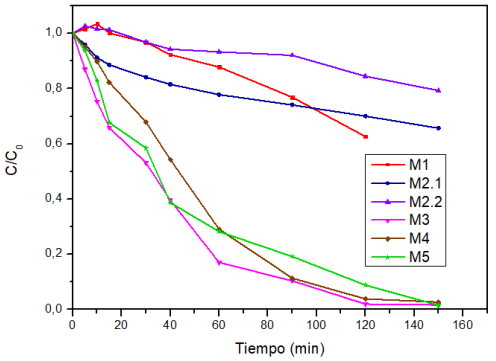
The material with the highest photocatalytic efficiency for MO removal was obtained with M5. The highest degradation percentages are obtained by adding PVP. This is due to the effect that this compound has on the arrangement of the BiOCl nanoparticles, which generates a 3D structure in the form of a flower [2]. This also causes the interaction with the pollutants to be much more effective than without the presence of this polymer.

These results suggest performing a standardization procedure of the amount of PVP and CuO to obtain a BiOCl-CuO heterostructure under optimized conditions with higher photocatalytic efficiency and, on the other hand, reduce the amount of PVP.

Table 1. Results of degradation and removal percentages by different procedures

Type of procedure	pH adjustment	%Degradation	%Removal
M1	8.5	37.3%	35.8%
M2.1	1.3	34.3%	39.6%
M2.2	2	20.7%	29.5%
M3	None	97.6%	97.7%
M4	None	97.3%	97.2%
M5	None	98.4%	98.6%

Figure 1. C/C_0 BiOCl-CuO by different procedures



Conclusions

The BiOCl-CuO heterostructure by M5 shows the highest photocatalytic efficiency; this method (M5), compared to the solvothermal route, shows better MO degradation (81,3%).

The M5 co-precipitation method performed is highly efficient, has low energy consumption, and is environmentally friendly. In addition, it has high potential for industrial scalability.

Acknowledgments

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