Co-precipitation synthesis of BiOI/Fe_3O_4 heterojunction: Optimization and application in ciprofloxacin removal from water

ORAL
Ph.D. Student: NO
Journal: NONE

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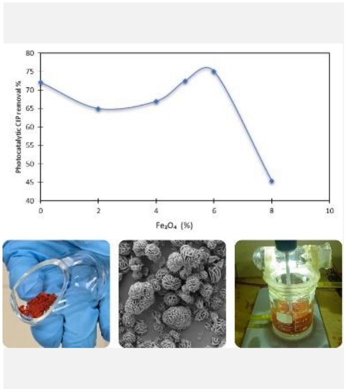

Antibiotics have been detected in various water sources due to increased consumption and the limited efficiency of wastewater treatment plants in removing them. Ciprofloxacin (CIP) is one of the most widely consumed antibiotics in Chile. Heterogeneous photocatalysis (HP) is a promising technology for removing emerging pollutants from water. However, the nanometric size of photocatalytic powders used in HP, such as bismuth oxyiodide (BiOI), poses a challenge for industrial applications. An alternative to overcoming this limitation is coupling BiOI with a magnetic material, which facilitates the separation of the photocatalyst from treated water by applying an external magnetic field. Therefore, in this study, a magnetic photocatalyst (BiOI/ Fe_3O_4) was synthesized via coprecipitation to remove CIP from water, achieving a removal rate of 75.1% with the incorporation of 6% magnetite into the heterojunction.

Introduction

Microbial Resistance to Antibiotics (AMR) poses a serious global challenge to human health and the ecosystems. According to the United Nations (UN), it is estimated that by 2050, AMR could lead to up to 10 million deaths annually worldwide[1].

In Chile, conventional wastewater treatment plants are ineffective in removing antibiotics. Biological systems are currently considered breeding grounds for the proliferation of antibiotic-resistant bacteria [2]. According to the Chilean Institute of Public Health, ciprofloxacin (CIP) is one of the most widely consumed antibiotics in the country. CIP has a highly stable molecular structure and is non-biodegradable, which means it remains in the environment for an extended period of time [3]. Considering the aforementioned, exploring and implementing efficient treatment technologies to remove CIP from the aquatic environment is essential. In this regard, heterogeneous photocatalysis (HP) is a promising technology for removing antibiotics from water.

The semiconductor bismuth oxyiodide (BiOI) is one the most studied materials in HP due to its high photocatalytic efficiency under visible and solar radiation[4]. However, one limitation is its nanometric size, which hinders its recovery from treated wastewater for subsequent reuse. Consequently, for industrial applications, additional operations such as microfiltration are necessary to recover the photocatalyst powders from treated water, thereby increasing treatment costs. To overcome this challenge, in this study, BiOI was coupled to magnetite (Fe_3O_4) using the coprecipitation method to remove CIP from water. This innovative approach enables scalability to industrial levels and facilitates the recovery of photocatalyst powders using an external magnetic force due to the incorporation of magnetite. Thus, it offers a practical and sustainable solution for addressing the removal of antibiotics from water.

Material and Methods

Heterostructures BiOI/Fe_3O_4 were synthesized using the coprecipitation method, varying the proportion of synthetic magnetite (2, 6 and 8%). Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\bullet}5H_2O$) was mixed with 20 mL of absolute ethanol under magnetic stirring; then synthetic magnetite was added and mechanically stirred. A potassium iodide (KI) solution in deionized water was prepared and added dropwise to the $Bi(NO_3)_3{\bullet}5H_2O$ + ethanol + Fe_3O_4 solution. The pH was adjusted to 8.5 with a 20% ammonia solution and mechanically stirred for 180 minutes. The synthesized material was separated with a magnet, washed with ethanol, and dried in a vacuum oven at 60°C for 60 minutes.

The heterostructures with the most efficient stoichiometric ratio (6% Fe_3O_4), BiOI, and synthetic magnetite (Fe_3O_4) were analyzed using different techniques: SEM, XRD, BET, BJH, and DRS. The photocatalytic efficiency of the materials was determined using a Batch reactor, in which 250 mL of a 10 ppm CIP solution and 800 ppm of the material were added. The solution was kept in the dark for 60 minutes to reach adsorption-desorption equilibrium, after which the system was irradiated with simulated solar radiation for 300 minutes. Samples of 10 mL were taken using a syringe with a 0.22 µm nylon filter at intervals of 0, 5, 10, 15, 20, 30, 60, 90, 120, 180, 240, and 300 min.

The photocatalytic efficiency of materials was evaluated by monitoring the removal of ciprofloxacin in water over a period of 300 min using an Agilent Infinity 1260 HPLC with a diode array detector (DAD), a C-18 column, and a mobile phase consisting of Formic Buffer:ACN (Buffer pH 3.0), 87:13, with a flow rate of 1 mL/min and injection of 20µL.

Results and Discussion

Table 1 shows the CIP removal percentanges using different percentages of magnetite in the heterostructure (2, 6, and 8 %). It was determined that the highest photocatalytic efficiency is achieved with the material containing 6% Fe_3O_4.

Table 1. Results CIP removal by HPLC

Materials	% Removal CIP
BiOI	74.9%
Fe_3O_4	36.2%
Photolysis	15.4%
BiOI/Fe_3O_4 (2% Fe_3O_4)	65.3%
BiOI/Fe_3O_4 (6% Fe_3O_4)	75.1%
BiOI/Fe_3O_4 (8% Fe_3O_4)	45.4%

The characterization of the materials provides insight into the properties and their influence on the obtained photocatalytic efficiency. SEM analysis revealed that the BiOI/Fe_3O_4 heterostructures (Fe_3O_4 6%) exhibit a morphology of three-dimensional microspheres similar to that of individual bismuth oxy iodide, but with a higher presence of BiOI nanoplates, which provides a less porous, more compact, and closed structure

XRD analysis revealed the characteristic diffraction peaks of BiOI, confirming its tetragonal phase as a semiconductor. In addition diffraction peaks of Fe_3O_4 were identified. These peaks in both individual materials indicate high crystallinity and purity in the synthesized materials. However, in the XRD patterns of the BiOI/Fe_3O_4 heterostructures only BiOI was observed, suggesting the coexistence of BiOI and Fe_3O_4 phases. Analysis of the surface properties of the materials showed that the BiOI/Fe_3O_4 heterostructure (6%) presents a higher specific surface area (15 m²/g) compared to individual BiOI (7 m²/g). BET analysis, combined with SEM and XRD, confirmed that the three-dimensional BiOI/Fe_3O_4 heterostructure is formed by the aggregation of BiOI particles in the form of nanoplates on magnetite. The average pore diameter of the BiOI/Fe_3O_4 heterostructure is 17.0 nm, which classifies it as a mesoporous material. The abundance of mesopores in the BiOI/Fe_3O_4 heterostructure provides more exposed active sites, potentially offering an ideal platform for surface reactions and thus favoring improved photocatalytic efficiency. Finally, DRS demonstrated that the coupling of magnetite to BiOI does not affect the optical properties, as all synthesized materials have a narrow bandgap value (BiOI=1.98; Fe_3O_4=1.63; BiOI/Fe_3O_4=1.94), suggesting strong optical absorbance in the visible radiation region.

Conclusions

This study demonstrates that the BiOI/Fe_3O_4 heterostructure (6%), obtained through the co-precipitation method, exhibits the highest photocatalytic efficiency for removing CIP from water. This heterostructure showcases a three-dimensional morphology comprising the aggregation of BiOI nanoplates on a magnetic core. The material's high purity and crystallinity, coupled with a narrow bandgap indicating optical solid absorbance in the visible region, were observed. These findings highlight the potential of BiOI/Fe_3O_4 (6%) heterostructures as efficient magnetic photocatalysts for removing emerging organic contaminants from water. Furthermore, these heterostructures possess the added advantage of scalability at industrial levels.

Acknowledgments

The authors would like to thank the "DIDULS regular 2023. PR 2321510", Grupo Multidisciplinar en Energía y Gestión Ambiental (GIMEGA) and Instituto Multidisciplinar en Investigación y Postgrado (IMIP).

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