Effect of N and Fe_3O_4 on BiOBr for photocatalytic degradation of endocrine disruptors

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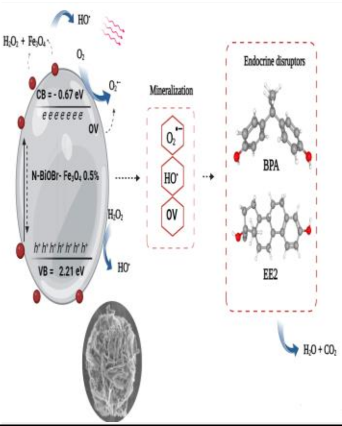

N and Fe_3O_4 incorporation on BiOBr catalyst promoted the effective degradation of a mixture of 17α-ethinylestradiol (EE2) and bisphenol A (BPA) in water by heterogeneous photocatalysis and heterogeneous photo-Fenton process. Materials were synthesized by microwave-assisted solvothermal method, and characterized by different techniques. Results revealed the successful incorporation of N into BiOBr and Fe_3O_4 on its surface, improving the charge transfer and photocatalytic activity. Also, that reduced the recombination of e^-/h^+ pairs, and the Eg value. N-BiOBr catalyst showed the best photocatalytic activity; however, in the presence of H_2O_2, the degradation and mineralization were enhanced with N-BiOBr- Fe_3O_4 due to a synergistic effect with the Fenton reaction. The $O_2^{\bullet-}$ radical was identified as the main oxidant specie favored by the oxygen vacancies, and that was influenced by the synthesis method.

Introduction

The presence of endocrine-disrupting compounds (EDCs) in the aquatic environment has been reported in several studies. They are a group of substances able to act on the endocrine system, causing reproductive and hormonal anomalies. They are introduced into the environment after their consumption through wastewater discharges, some of them have even been detected in effluents from wastewater treatment plants [1]. Among them, bisphenol A (BPA) and 17α-ethinyl estradiol (EE2) are the most detected in water.

To eliminate persistent contaminants, different technologies have been developed and evaluated. In this work, the heterogeneous photocatalysis (FH) and the heterogeneous photo-Fenton process (FFH) were tested, since these processes can take advantage of the activation of semiconductor materials with low-cost radiation sources such as sunlight [2]. Bismuth-based semiconductors have gained relevance as catalysts due to their high photocatalytic activity under visible light. Among them, BiOBr stands out; however, its photocatalytic activity can be improved by incorporating non-metallic or metallic elements [3, 4].

In this work, the effect of nitrogen and Fe_3O_4 in the photocatalytic activity of BiOBr was tested on the degradation of BPA and EE2 mixture, as well as the presence and absence of H_2O_2.

Material and Methods

The N-BiOBr- Fe_3O_4 (0.5% wt.) materials were synthesized by a microwave-assisted solvothermal method using $Bi(NO_3)_3{\bullet}5H_2O$, magnetite (Fe_3O_4), urea and hexadecyltrimethylammonium bromide (CTAB) as precursors. Briefly, solutions of Bi3+ and CTAB with urea were dissolved separately in ethylene glycol. Then, these solutions were mixed drop by drop. Fe_3O_4 was added and sonicated for 30 min. The mixture was transferred to a Teflon container and placed in a microwave oven (MARS 6, CEM Corp. USA) at 160 °C/20 min at 450 W. Materials were recovered and washed with absolute ethanol and deionized water, then dried at 80 °C/24 h. BiOBr-Fe3O4, N-BiOBr and BiOBr were also synthesized as reference materials. The materials were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), N_2 adsorption desorption, atomic absorption spectroscopy (AAS), UV-Vis reflectance spectroscopy, and Electron paramagnetic resonance spectroscopy (EPR).

The degradation tests of BPA and EE2 mixture (5 mg/L each) were carried out in 150 mL. The pH was adjusted to 3, and 0.5 g/L of catalyst was dispersed and stirred for 30 min in the dark. Subsequently, 60 mmol/L of H_2O_2 was added and it was irradiated with a solar simulator at an intensity of 30 W/m^2. Samples were taken and filtered, and the EDCs were quantified by HPLC in reverse phase. The level of mineralization of the mixture was quantified by measuring total organic carbon (TOC-VCSH analyzer Shimadzu Corp). Other tests were performed without the addition of H_2O_2.

Results and Discussion

With the synthesis method, materials with flower-like structures (particle size of 3.8 to 4.8 μm) were obtained with the successful incorporation of N into BiOBr and Fe_3O_4 on the surface. The incorporated amount of Fe_3O_4 was similar to the theoretical incorporation, and caused an increase in crystallite size. The Eg value decreased in the presence of N and Fe_3O_4, promoting its activation under visible light. Also, Fe_3O_4 incorporation reduced the recombination of e^-/h^+ pairs, while N promoted the generation of oxygen vacancies, increased specific surface area (SSA), and enhanced the photocatalytic activity (Table 1).

In the photocatalytic tests, N-BiOBr-Fe_3O_4 (0.5 wt.%) in the absence of H_2O_2, achieved constant rate (K_{ap}) of 0.011 and 0.023 min^{-1} for BPA and EE2, respectively. However, by adding H_2O_2 reached 0.0406 min^{-1} and 0.0487 min^{-1} for BPA and EE2, respectively, and 52.9% of mineralization (Fig 1). This enhancement in K_{ap} is attributed to the synergistic process between heterogeneous photocatalysis and the Fenton process. And these results were better than by using BiOBr, N-BiOBr and BiOBr- Fe_3O_4 (Table 1, Fig 1).

The main identified oxidant species that participates in the degradation of EDCs is the $O_2^{\bullet -}$ radical, which is consistent with the scavengers test and EPR analysis. The second responsible specie was the $HO^{\bullet}$ radical, which was generated mainly during the Fenton reaction. Finally, N-BiOBr- Fe_3O_4 0.5% demonstrated stability to degrade contaminants after four cycles.

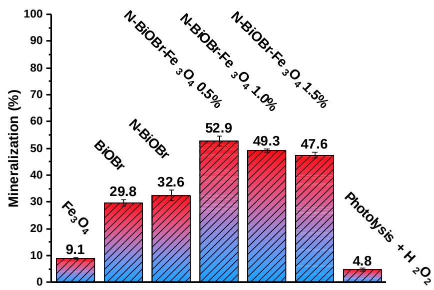

Figure 1. Mineralization of the EDCs mixture by different treatments. Catalyst loading 0.5 g/L, pH 3, 60 mmol/L H_2O_2.

Table 1. Properties of the obtained materials, kinetic degradation and mineralization of BPA and EE2.

Catalyst	SSA (m^2/g)	Eg (eV)	K_{ap} BPA (min^{-1}) 60 min	K_{ap} EE2 (min^{-1}) 60 min	Mineralization (%) 180 min
BiOBr	12.13	3.10	0.0016* 0.0192	0.0023* 0.0261	29.8
N-BiOBr	14.3	3.01	0.0025* 0.0194	0.0037* 0.0269	32.6
BiOBr-Fe_3O_4 0.5%	5.64	2.95	No data	No data	41.9
N-BiOBr-Fe_3O_4 0.5%	6.49	2.87	0.011* 0.0406	0.0023* 0.0487	52.9

Conditions: pH 3 and 60 mmol/L of H2O2, *in absence of H_2O_2.

Conclusions

N-BiOBr-Fe_3O_4 0.5% showed the higher photocatalytic activity for the degradation and mineralization of BPA and EE2 mixture in the presence of H_2O_2 due to the synergistic effect between heterogeneous photocatalysis and Fenton reaction. Results indicated that this semiconductor is a suitable and stable iron source to eliminate EDCs. In addition, the incorporation of nitrogen and the synthesis method favored the generation of oxygen vacancies, and the increase of photocatalytic activity of BiOBr.

Acknowledgments

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