Piezo-photocatalysis: a winning solution for organic pollutants mineralization under solar light irradiation

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Introduction

Nowadays, freshwater contamination is a global concern. Pharmaceutical and personal care products (PPCPs), steroids, and hormones are pollutants found in water.[1] Among the former, nonsteroidal anti-inflammatory drugs (NSAIDs) are characterized by a broad scope of properties widely used in medicine. Ibuprofen (IBU) belongs to this category: it is the most marketed over-the-counter drug in the world, whose market size value is projected to reach USD 110.7 million by 2030.[1] Generally, traditional wastewater treatment plants are not very effective in removing contaminants of emerging concern, such as PPCPs and their recalcitrant metabolites, due to their chemical stability. So, efforts in developing new methods for their abatement is a current challenge. Among the different approaches, heterogeneous photocatalysis has emerged, since it can mineralize organic contaminants to CO_2 and H_2O.[2] However, the fast photo-induced electron-holes recombination limits its use, since it leads to the diffusion of the produced charges at the photocatalyst surface, strongly reducing the photocatalytic activity. The urgency to identify novel photocatalysts able to reach complete and fast mineralization of IBU by sustainable approaches is thus evident. In this context, combining different techniques enhances the process efficiency, contributing to the reduction of hazardous byproduct formation. Piezophoto-catalysis is an innovative strategy, requiring a proper photo-piezoelectric catalyst, for degrading pollutants in wastewaters. Ultrasound vibrations promote the formation of an internal electric field in the material, enhancing the photoinduced charge separation. The free charges accumulated on the material surface thus promote redox reactions involved in the degradation of organic pollutants. [3]

Herein, we present for the first time the fast and efficient mineralization properties of the bismuth oxybromide nanosheets as piezophotocatalyst (BiOBr, Figure 1a) in the IBU degradation in ultrapure (UW) or simulated drinking water to evaluate its potentialities in real environments.

Materials and Methods

BiOBr was prepared by co-precipitation.[3] Its physico-chemical properties were elucidated by targeted characterization techniques. Different IBU abatement tests were approached by BiOBr: *i)* piezocatalytic by sonication (pulsed 5 s on/5 s off, US output power 23 W), *ii)* photocatalytic under solar light, and *iii)* piezo-photocatalytic by sonication and light.[3]

Results and Discussion

Figure 1b resumes the mineralization capacity values obtained in the presence of different BiOBr dosages. High efficiency of BiOBr nanosheets in the mineralization process was detected. At low concentration (0.125 g/L) BiOBr showed good mineralization efficiency (*ca.* 45%), reaching 100% by BiOBr content increase up to 0.50 g/L. Data collected in the presence of 0.25 g/L catalyst dose also clearly highlighted an important synergistic effect in the mineralization process, demonstrating the fast mineralization process that reaches more than 60% final mineralization value after 30 min. Electrochemical impedance spectroscopy, transient photocurrent measurements, and Mott-Schottky analyses helped to furtherly understand the electrochemical features of BiOBr and proposing a detailed mechanism for IBU degradation (Figure 1c). Considering the IBU oxidation potential (E_{Ox}) equal to *ca*. 1.6V *vs* SCE, the photogenerated holes in BiOBr have sufficient driving force (≥800 mV) to oxidize the organic pollutant and produce at same time a certain amount of ·OH radical species (E(HO−/•OH) = +2.25 V *vs* SCE) that can play a role in the IBU degradation. Then, radical trapping investigations demonstrated that h^+ photogenerated charge carriers were mainly involved in the IBU piezo-photocatalytic degradation. The identification of the produced transformation products produced during the process demonstrated that decarboxylation, oxidation, and hydroxylation are the main processes involved in drug degradation.

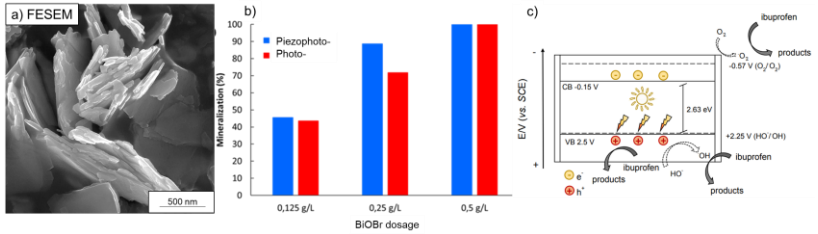

Figure 1. a) FESEM images (left); b) Percentage of IBU mineralization (50 mg·L^{-1} in UW) at the process end (30 min dark *plus* 180 min solar irradiation, 35 W·m^{-2}); c) Proposed mechanism of IBU photodegradation over BiOBr.

The extraordinarily promising results obtained demonstrated that the ultrasounds use enhances the IBU degradation by BiOBr, acting on: boosting charge separation, reducing particle aggregation, improving the availability of active sites, promoting mass transfer between the catalyst's surface and the solution reaction, and active radical formation.

Significance

The coupling of piezo- and photo-catalysis, not requiring the use of costly materials prepared by expensive procedures, is exploited for wastewater treatment. Here, developing materials with tuned physico-chemical properties is the key point.

References

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