Photocatalytic properties of Bi$_2$O$_3$ powders obtained by an ultrasound-assisted precipitation method

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Abstract

Bi$_2$O$_3$ nanoplates were synthesized by an ultrasound-assisted precipitation method in aqueous solution with different times of exposure to ultrasound radiation. The formation of Bi$_2$O$_3$ oxide with a monoclinic structure was confirmed by X-ray powder diffraction (XRD), which was also used to determine the crystallite size and lattice strain. The characterization of Bi$_2$O$_3$ samples was complemented with scanning electron microscopy (SEM), which revealed the morphology of the particles as irregular, ovoid and rectangular nanoplates as a function of the time of exposure to ultrasound radiation. Infrared spectroscopy (FT-IR) was used to confirm the elimination of the bismuth nitrate used in the synthesis. The specific surface area was determined by the BET method. Diffuse reflectance spectroscopy (DRS) was used to determine the band-gap energy ($E_g$) of the Bi$_2$O$_3$ samples. The photocatalytic activity of Bi$_2$O$_3$ samples was evaluated with respect to the degradation reactions of rhodamine B (rhB), indigo carmine (IC) and tetracycline hydrochloride (TC) in aqueous solution under Xe lamp irradiation. The highest photocatalytic activity was identified for the sample exposed to 2 h ultrasound radiation, i.e., the sample that presented the highest crystallinity, smaller particle size and a more homogeneous morphology. The mineralization degree of organic dyes and antibiotic by Bi$_2$O$_3$ was determined by the total organic carbon analysis (TOC), reaching percentages of 40% for rhB, 13% for IC and 72% for TC after 24 h of Xe lamp irradiation.

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1. Introduction

The environmental pollution caused by human activities has continued to increase, which has necessitated the implementation of sustainable processes. Heterogeneous photocatalysis, which is a clean, green and sustainable technology for the elimination of organic pollutants present in water as dyes, medicine and pesticides, has been introduced [1]. This technology uses a material semiconductor called a photocatalyst for the degradation of organic contaminants active under irradiation with UV and visible light. Recently, the development of material photocatalyst have been oriented toward the use of the solar radiation, including simple oxides, such as Bi$_2$O$_3$ [2], CuO [3], ZnO [4] and WO$_3$ [5], and some mixed oxides such as Bi$_2$MoO$_6$ [6], BiVO$_4$ [7] and Bi$_2$WO$_6$ [8]. Bi$_2$O$_3$ has attracted the most attention because it has the advantages of being economically and environmentally viable for use as a photocatalyst in the remediation of contaminated water [4,9]. Bi$_2$O$_3$ is active under irradiation with visible light due to having an $E_g$ of approximately 2.7–2.8 eV [9,10]. This oxide presents the polymorphism phenomenon with the phase α-Bi$_2$O$_3$ being more stable at ambient temperature [11]. There are a few studies in the literature about the use of Bi$_2$O$_3$ as a photocatalyst in the degradation of organic compounds, such as dyes, and even less for the degradation of antibiotics. Bi$_2$O$_3$ has been regularly used when doped or mixed with other oxides. Therefore, Bi$_2$O$_3$ is a good candidate to further explore the degradation of organic pollutants in aqueous media. The synthesis of Bi$_2$O$_3$ has attracted special attention, and researchers have attempted to prepare it through various methods, including precipitation [12],
refluxing [13], urea [14], citrate [15], sonochemical [16], electrospinning [17] and hydrothermal [18]. The precipitation method is the simplest to obtain Bi₂O₃ with good crystallinity but with the disadvantage of obtained particle size and morphology being highly variable. However, this variability can be controlled and improved with the assistance of other methods, such as ultrasound. This combination of synthesis methods potentiates the preparation of materials because it is possible to exploit the advantages of both methods to achieve synergy that minimizes the disadvantages of the individual methods, thus obtaining materials with unique properties.

Therefore, in this work, Bi₂O₃ nanoplates were successfully prepared by ultrasound-assisted precipitation in aqueous solution with different times of exposure to ultrasound radiation. The samples were characterized, and their photocatalytic properties were evaluated in the degradation of two dyes and an antibiotic: rhodamine B (rhB, CAS 81-88-9), indigo carmine (IC, CAS 860-22-0) and tetracycline hydrochloride (TC, CAS 64-75-5) under Xe lamp irradiation as a simulated sunlight source.

2. Experimental

2.1. Synthesis of Bi₂O₃

Bi₂O₃ powders were synthesized by ultrasound-assisted precipitation in aqueous solution with different times of exposure to ultrasound radiation. The Bi₂O₃ samples were prepared by the following procedure: 6.25 g (0.0129 mol) of bismuth(III) nitrate pentahydrate (BiN₃O₉·5H₂O, ≥98% purity, Sigma-Aldrich) was dissolved in 100 mL of a nitric acid solution (10% v/v, HNO₃) under continuous stirring at 80 °C in an electric oven. Then, the pH of the solution was adjusted to 11 with a 2 M NaOH solution, causing the formation of a white precipitate. The precipitated was maintained without stirring in an ultrasonic bath (42 kHz, 6%, 100 W) for 1, 2 or 3 h. The precipitate was then washed several times with distilled water to neutralize the pH of the solution and was dried in air at 80 °C for 24 h. Finally, the material was thermally treated at 300 °C for 4 h from room temperature to the specified temperature at a heating rate of 10 °C min⁻¹ to obtain Bi₂O₃. For comparative purposes, commercial Bi₂O₃ was used (99.9% purity, 10 μm, Sigma-Aldrich).

2.2. Characterization of the samples

Structural characterization of the Bi₂O₃ samples was performed by X-ray powder diffraction (XRD) analysis using a BRUKER D8 ADVANCED diffractometer with CuKα radiation (λ = 1.5418 Å) equipped with a high-speed Vantec detector. X-ray diffraction data were collected in the 2θ range of 10°–70° with a scan rate of 0.05° and 0.5 s⁻¹. To estimate the crystallite size and lattice strain behavior, the Bi₂O₃ samples were followed by means of the half-width of the strongest line of the XRD pattern of oxide. Using these data, the crystallite size of the particles of the samples was calculated through the Scherrer equation [19,20], as follows: 

\[ L = \frac{kλ}{β\cos(θ)} \]

where \( L \) is the crystallite size, \( k \) is the Scherrer constant, usually taken as 0.89, \( λ \) is the wavelength of the X-ray radiation (1.5418 Å), \( β \) is the full width at half-maximum (FWHM) of the diffraction peak measured at 2θ and \( θ \) is the diffraction angle. The lattice strain of the samples was calculated by the following equation: 

\[ ε = \frac{β}{4\tan(θ)} \]

where \( ε \) is the lattice strain, and \( β \) and \( θ \) are the same values used to determine the crystallite size. Infrared spectroscopy (NICOLET 380 FT-IR) was used to confirm the elimination of the bismuth nitrate used in the synthesis. The morphology and particle size were investigated by scanning electron microscopy using JEOL Instruments model JSM 6490.

The band-gap energy \( E_g \) was determined by means of the UV–vis diffuse reflectance absorption spectra of the Bi₂O₃ samples, which were taken using a Cary 500 UV–vis NIR spectrophotometer equipped with an integrating sphere. The \( E_g \) value was calculated for direct transition from the UV–vis spectrum by extrapolating a straight line to the slope of the x-axis using the following equation: 

\[ E_g = \frac{1240}{λ_g} \]

where \( λ_g \) is the wavelength (nm) of the exciting light, and \( E_g \) is the band-gap energy [19]. The BET surface area of the Bi₂O₃ samples was determined by adsorption–desorption N₂ isotherms using a BELSORP-mini II surface area and pore size analyzer. The isotherms were evaluated at −196 °C after degassing the samples by thermal treatment at 150 °C for 12 h.

2.3. Photocatalytic tests

The photochemical reactor employed in this work consisted of a glass borosilicate beaker surrounded by a water jacket to maintain the reaction temperature at 25 °C ± 1. A 35 W Xe lamp of 6000 K with a luminous flux of 36,000 lux was used as a simulated sunlight source. The emission spectrum of the Xe lamp was measured by an Ocean Optics Jaz Spectrometer (see Fig. 1). A negligible contribution of UV radiation was observed (< 390 nm).

The Bi₂O₃ photocatalytic activity was evaluated by the degradation reactions of two dyes, rhodamine B (rhB, CAS 81-88-9) and indigo carmine (IC, CAS 860-22-0), and one antibiotic, tetracycline hydrochloride (TC, 64-75-5), in aqueous solution. By taking into account the molar extinction

![Fig. 1. Emission spectrum of: (a) Xe lamp, (b) Xe lamp inside the reactor and (c) solar spectrum.](image-url)
coefficient of the dyes and the antibiotic, the initial concentrations were 5 mg L\(^{-1}\) for rhB, 30 mg L\(^{-1}\) for IC and 20 mg L\(^{-1}\) for TC. The photocatalytic tests were performed as follows: 200 mL of organic compound solution containing 200 mg of Bi\(_2\)O\(_3\) powder was added to a glass beaker and then placed in an ultrasonic bath for 1 min to eliminate aggregates. The solution was then transferred to the photocatalytic reactor. The solution was kept in the dark for 1 h to ensure that the adsorption–desorption equilibrium of the organic compound on the catalyst surface was reached. After this time, the light source was turned on. During the reaction, aliquots were taken from the reactor at different time intervals. The powders were separated by centrifugation, and the filtered solution was analyzed in a UV–vis spectrophotometer following the procedure established in a previous work [21]. Repeatability tests were performed to evaluate the stability of Bi\(_2\)O\(_3\) oxide.

The mineralization degree of the organic compounds was examined by the analysis of the total organic carbon (TOC) content of the solutions at different irradiation times using a SHIMADZU TOC-VSCH analyzer. For these experiments, 200 mL of the organic compound solution (20 mg L\(^{-1}\) for rhB, 30 mg L\(^{-1}\) for IC and 20 mg L\(^{-1}\) for TC) containing 200 mg of photocatalyst was used.

3. Results and discussion

3.1. Structural characterization

The obtained powders of Bi\(_2\)O\(_3\) with exposure for 1, 2 or 3 h to ultrasound radiation were thermally treated at 500 °C. For comparative purposes, commercial Bi\(_2\)O\(_3\) was used (BCOM). The materials presented a light yellow tinge. The formation of the Bi\(_2\)O\(_3\) crystalline structure was followed by the X-ray diffraction pattern. Fig. 2 shows the X-ray diffraction patterns of the Bi\(_2\)O\(_3\) samples exposed for 1, 2 or 3 h to ultrasound radiation and heated at 500 °C (hereafter identified as B1U, B2U and B3U, respectively). For all samples, the materials crystallized as the α-Bi\(_2\)O\(_3\) polymorph with a monoclinic structure, according the JCPDS card no. 01-071-0465. All samples presented main diffraction peaks located at 2\(θ\) = 24.5°, 25.7°, 26.9°, 27.3°, 28°, 33°, 33.2° and 46.3°, which are typical of the α-Bi\(_2\)O\(_3\) polymorph. However, samples B1U and B3U had an additional reflection at 2\(θ\) = 30.7° that corresponded to bismuth nitrate traces, which in these samples was not fully decomposed. It is assumed that longer ultrasound reaction time provokes the partial decomposition of the Bi\(_2\)O\(_3\), therefore the free bismuth react with the ions nitrate, forming bismuth nitrate. Table 1 shows the crystallite size and lattice strain of the synthesized samples. The results revealed that the B2U sample had a higher crystallite size value, which indicates growth of the crystals and increasing crystallinity. This result was corroborated by the XRD pattern, where the B2U sample presented more narrow peaks of higher intensity and the formation of the pure phase. When lattice strain decreases, the crystallinity of the samples increases [22], and sample B2U presented the lowest value of lattice strain.

Fig. 3 shows the FT-IR spectra of the Bi\(_2\)O\(_3\) samples exposed for 1, 2 or 3 h to ultrasound radiation and heated at 500 °C, as well as the commercial Bi\(_2\)O\(_3\). The IR analysis was performed with the aim of identifying the impurities observed by XRD in the B1U and B3U samples, i.e., the presence of nitrate traces. In this sense, Fig. 3 shows that only the B1U and B3U samples presented additional bands compared to commercial oxide. These bands were located at 1340 and 1390 cm\(^{-1}\) and corresponded to N–O, which can be attributed to the NO\(_3^-\) ion.
3.2. SEM morphology analysis

The morphology and particle size of the Bi$_2$O$_3$ samples were analyzed by SEM. Fig. 4 shows the SEM micrographs of the samples obtained by ultrasound irradiation for 1, 2 or 3 h and calcined at 500 ºC, in addition to the commercial oxide. When the oxide was exposed for 1 h to ultrasound radiation, agglomerated particles were observed with the morphology of irregular nanoplates, with a thickness of approximately 50 nm and a length of 0.5 μm (see Fig. 4a). On the other hand, the samples synthesized with 2 h of ultrasound radiation presented a change in morphology to ovoid nanoplates, with a more homogeneous and smooth surface and a thickness of approximately 50 nm and length of 200 nm, as shown in Fig. 4b. The samples obtained with 3 h in the ultrasonic bath presented a similar morphology to those exposed for 1 h but with a more defined shape and a larger particle size, i.e., mainly rectangular nanoplates with a thickness of approximately 80 nm and a length above 1 μm (see Fig. 4c). The commercial sample had particles with a rod shape with a thickness of approximately 3 μm and a length of 5–10 μm, as shown in Fig. 4d, which is different from the samples synthesized by ultrasound.

Therefore, we can conclude that with the increase of exposure to the ultrasound radiation, the Bi$_2$O$_3$ samples presented a similar morphology of nanoplates with a change of shape in the following order: irregular to ovoid to rectangular (see Fig. 5). The sample exposed for 2 h in the ultrasonic bath had the smallest particle size and a more homogeneous morphology.

3.3. Band-gap energy and BET surface area analysis

The optical properties of the Bi$_2$O$_3$ samples (B1U, B2U and B3U) and commercial oxide were analyzed using UV–vis diffuse reflectance spectroscopy. Table 1 shows the band-gap energy ($E_g$) values of the samples. The $E_g$ values were within the range reported in the literature (i.e., 2.3–2.7 eV [9,10]) and were similar to the $E_g$ value of commercial oxide.

The specific surface areas of the Bi$_2$O$_3$ samples measured by the BET method are also included in Table 1. All of the synthesized samples had a higher surface area value than commercial Bi$_2$O$_3$. The specific surface area value obtained for all samples was low, at 2 m$^2$ g$^{-1}$. All samples presented a type II isotherm (i.e., typical behavior of a material that is not porous, according to the classification previously establish for adsorption–desorption isotherm [23]).

Therefore, these experiments revealed that the textural properties, such as the specific surface area of the Bi$_2$O$_3$ samples, were not influenced by the varying of time exposure in an ultrasonic bath during the synthesis. A similar effect was observed in the optical properties. In contrast, significant differences were observed in the morphology properties with varying exposure time to ultrasound radiation.

3.4. Evaluation of photocatalytic activity

The photocatalytic activity of Bi$_2$O$_3$ samples was evaluated for the degradation reactions of rhB, IC and TC in water under a 6000 K Xe lamp as the radiation source. Fig. 6 shows the temporal
degradation of rhodamine B (5 mg L$^{-1}$) with different synthesized Bi$_2$O$_3$ samples used as photocatalysts. After 180 min of Xe lamp irradiation, all of the samples bleached the rhB solution to a large degree. The best photocatalytic activity was shown by the B2U sample, i.e., the sample that presented the highest crystallinity, smallest particle size and more homogeneous morphology. Therefore, the activity could be attributed to the high crystallinity of the B2U sample because high crystallinity results in a reduced number of defects and prevents the recombination of electron–hole pairs. In the same way, other factors that favor the photocatalytic activity of the B2U sample include its smaller particle size and more homogeneous morphology because minimizing the size of the photocatalyst particles can maximize the number of active sites, causing an increase in photocatalytic performance.

Fig. 7 shows the photocatalytic activity of the Bi$_2$O$_3$ samples for the degradation of IC (30 mg L$^{-1}$) by Xe lamp irradiation. All synthesized samples presented better activity than the commercial oxide. After 180 min of exposure to Xe lamp radiation, the B1U, B2U and B3U samples bleached the IC solution nearly 100%. The sample that presented the best photocatalytic activity was B2U, which is similar to the findings in the evolution of the concentration of rhB. Therefore these results we can conclude that in the degradation of indigo carmine and rhodamine B, the IC has a discoloration less time because it suffers the attack by radicals formed in the photocatalytic process breaking its chromophore group, which is responsible of its coloration [24]. Nevertheless, mineralization becomes slow in concordance with the proposed mechanism by Vautier et al. [25], where it is observed that amino groups and nitro groups bonded to a benzene group, which may be competing in the oxidation processes to transform an amino group, forming a nitro group. While in the case of the rhB a fully de-ethylated rhB molecule occurs causing that the color of the solution disappears, indicating that the chromophore structure of the dye was destroyed [26,27], which occurs slowly.

The evolution of the concentration of TC (20 mg L$^{-1}$) in presence of the Bi$_2$O$_3$ samples used as photocatalysts under Xe lamp irradiation is shown in the Fig. 8. The synthesized samples presented better activity than BCOM, with the exception of the sample B3U, with a percentage of degradation of approximately 50% after of 180 min of exposure to the Xe lamp. For B1U and B2U, the percentages of degradation were similar at approximately
65%. However, B2U had the best photocatalytic activity. On the other hand, it seems that the degradation reaction of TC stop at 60 min, however degradation continues but it is more slowly as shown in Figs. 8 and 9c. This is due to intermediary products that form the TC structure during its degradation, which become more complex [28]. Therefore, these experiments revealed that the degradation of rhB, IC and TC is possible when Bi$_2$O$_3$ synthesized by ultrasound-assisted precipitation is used as a photocatalyst, and B2U presented the best photocatalytic activity.

Fig. 8 shows the UV–vis absorption spectra of rhB, IC and TC solutions when being photodegraded by B2U. The UV–vis absorption spectra of the three pollutants decreased over the time in the ultraviolet and visible regions. This decrease may be indirectly caused by a direct attack on the aromatic rings of its molecules [29], which leads to the breaking of the bonds and provokes the complete decomposition into small organic/inorganic molecules and/or ion products [30]. However, aromatic ring of the organic molecules remains even after 4 h of reaction; this is due to the intermediary products that are generated during the degradation of the organic contaminants [25,27,28], which are difficult to decompose after this time.

To determine if the mineralization of organic compounds by Bi$_2$O$_3$ exposed under Xe lamp irradiation is feasible, total organic carbon (TOC) content during the photocatalytic test for the degradation reactions of rhB, IC and TC (see Fig. 10) was performed. For these experiments, the sample with the highest photocatalytic activity (B2U) was used as the photocatalyst. After 24 h under Xe lamp irradiation, the mineralization degree was approximately 40% for rhB, 13% for IC and 72% for TC. Therefore, Bi$_2$O$_3$ synthesized by ultrasound-assisted precipitation
method can be used as a photocatalyst to provoke a considerable mineralization degree of organic pollutants. These results were associated with the UV–vis absorption spectra previously explained, where it was observed that Bi$_2$O$_3$ is feasible for the partial degradation of rhB, IC and almost the complete degradation of TC. These results confirm that it is feasible to break the bonds of organic compounds (rhB, IC and TC) during the photocatalytic tests.

4. Conclusions

Bi$_2$O$_3$ powders with monoclinic structure were successfully synthesized by ultrasound-assisted precipitation method with varied times of exposure to ultrasound radiation. The largest crystallite size and lowest lattice strain were obtained in the B2U sample, i.e., the sample with the highest crystallinity. The Bi$_2$O$_3$ samples exposed to ultrasound radiation (1, 2 or 3 h) presented a similar morphology of nanoplates in the following order: irregular to ovoid to rectangular, respectively. The specific surface area of the Bi$_2$O$_3$ samples was not influenced by the varying exposure time in the ultrasonic bath during synthesis. In contrast, significant differences were observed in the morphology properties with varying exposure time. The highest photocatalytic activity was found for the B2U sample, i.e., the sample with the highest crystallinity, smallest particle size and more homogeneous morphology. Therefore, the photocatalytic activity of Bi$_2$O$_3$ was attributed to the crystallinity, particle size and the morphology of rectangular nanoplates. After 24 h under Xe lamp irradiation, the mineralization degree of organic dyes and the antibiotic was: 40% for rhB, 13% for IC and 72% for TC. These results indicate the potential of Bi$_2$O$_3$ synthesized by ultrasound-assisted precipitation method as a good candidate for use as an effective photocatalyst in the removal of organic dyes and antibiotics.

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