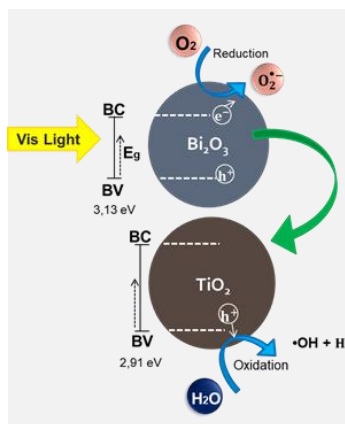


Photocatalytic oxidation of cyanide ion using a Bi₂O₃/TiO₂ co-catalyst supported on activated carbon.

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A co-catalyst Bi₂O₃/TiO₂ supported on activated carbon (AC) was prepared by combining two semiconductors Bi₂O₃ and TiO₂ varying the Bi₂O₃/TiO₂ molar ratio. Two sources of irradiation were applied: UV with a mercury lamp ($\lambda=254$ nm) and sunlight ($\lambda\approx 534$ nm) to the oxidation of cyanide ions (CN⁻). The co-catalyst Bi₂O₃/TiO₂ supported on activated carbon (AC) were characterized using X-ray diffraction and UV-Visible diffuse reflectance spectroscopy. Five co-catalysts were prepared via direct impregnation. The prepared samples present values of the band gap between Bi₂O₃ and TiO₂ pure samples. It was observed that the co-catalysts could absorb in the visible region of the solar spectrum. The composite was optimized to 10:90 (Bi₂O₃:TiO₂) ratio with a commercial activated carbon as support. A high photocatalytic efficiency of 90 % was reached by using sunlight irradiation during 10 hours for the CN⁻ oxidation, while 80 % of CN⁻ was removed with UV as irradiation source. The use of the Bi₂O₃/TiO₂ mixtures contributes to a better CN⁻ photocatalytic degradation in the visible spectrum region.

Introduction

In Ecuador, sodium cyanide solutions are used in concentrations of 110-550 mg L⁻¹ in gold leaching processes [1]. The cyanide ion (CN⁻) is highly toxic to humans and aquatic organisms, as it is a potent inhibitor of respiration [2]. It is estimated that 7,000 L of water contaminated with cyanide is generated for every 10 g of leached gold, generating significant negative environmental impacts in the country, which produces discharges with cyanide concentrations of 300 – 600 mg L⁻¹ [3], while the legislation establishes that the tolerable limit of cyanide concentration is 0.1 mg L⁻¹ for the discharge of effluents into a fresh water system [4]. Photocatalytic degradation of organic pollutants on semiconductor surfaces has attracted much attention as a non-pollutant technique. Photocatalysts usually work under UV-light ($\lambda < 420$ nm) with limitations and poor efficiency [5]. The development of photocatalysts with better activity under visible-light irradiation as sunlight is required. In this work the photocatalytic oxidation of cyanide ion was realized by using a co-catalyst Bi₂O₃/TiO₂ supported on activated carbon (AC).

Material and Methods

Co-catalysts preparation

Bi₂O₃ was synthesized by using oxalic acid and bismuth nitrate in a molar ratio 1:3. The mixture was heated at 280-500 °C for three hours to obtain Bi₂O₃ in a tubular furnace Nabertherm P300. Based in the methodology proposed by Chakraborty, et al., a Bi₂O₃/TiO₂ composite photocatalyst was prepared utilizing maleic acid as an organic binder. Three molar ratios were proposed for the Bi₂O₃/TiO₂: 5:95 (Co5), 10:90 (Co10) and 20:80 (Co20). Finally, the co-catalysts supported on activated carbon were prepared by wet impregnation of Bi₂O₃/TiO₂ composite on activated carbon (AC, CALGON GRC-20 ®). Co-catalysts were calcinated in a furnace at 400 °C for 1 hr, washed and dried at 100 °C for 2 hours [6]. Additionally, for comparison, two co-catalysts Bi₂O₃ and TiO₂ supported on CA separately were prepared.

Physical and chemical characterization of Bi₂O₃/TiO₂

co-catalyst supported on activated carbon

Crystalline phases of the prepared samples were analyzed by X-ray Diffraction (XRD) technique (D8 ADVANCE Bruker) operated with the monochromatized Cu-K α radiation ($\lambda=1.541874$ Å). The scanning 2 θ angle range was 3.0° to 80.0° using a step size of 0.02° and counting time of 2s/step. The measured XRD diffractograms were analysed with EVA and TOPAS software programs for identification. Diffuse reflectance spectra (DRS) were obtained using a UV-Visible spectrometer (Ocean Optics).

Photocatalytic cyanide ion degradation

First, adsorption tests were carried out in a batch reactor under dark conditions at room temperature. 250 ml of a sodium cyanide solution (500 mg/L) was mixed with 10 gr of the co-catalysts prepared. 10 mL samples were taken during the process to analyze the concentration of free cyanide by potentiometric titration using a standardised silver nitrate solution. Photocatalytic activity was performed with two irradiation sources: UV and sunlight separately, using an initial concentration of sodium cyanide of 500 mg/L and a composite concentration of 40 g/L at pH 10.5 and room temperature. The system was maintained in dark conditions during 24 hours to ensure adsorption-desorption equilibrium. Then, UV lamps were turned on to initiate the photodegradation tests, and for the tests for sunlight irradiation, they were performed outdoors. Samples of 10 mL were taken during the process, and concentration of free cyanide was determined by potentiometric titration using a standardised silver nitrate solution.

Results and Discussion

Figure 1 shows the XRD patterns of TiO₂, Bi₂O₃ and the different Bi₂O₃/TiO₂ co-catalysts prepared. For the TiO₂ it is shown that the diffraction planes clearly indicate the presence of pure anatase (JCPDS #021-1272). Bismuth is present in three compounds as shown in Figure 1. It could be observed that the XRD patterns of the co-catalysts showed the diffraction peaks of phases of α -Bi₂O₃, β -

Bi₂O₃ and TiO₂. The intensity of the major peaks of α -Bi₂O₃ and β -Bi₂O₃ increases with increasing amount of Bi₂O₃ of the co-catalysts prepared. The presence of anatase TiO₂ remains in all the co-catalysts.

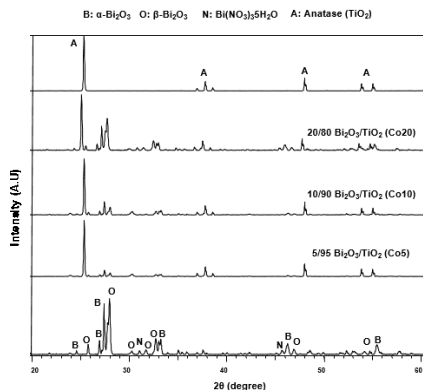


Figure 1. X-ray diffraction pattern of TiO₂, Bi compound and Bi₂O₃/TiO₂ co-catalysts synthesized at 300 °C for 3 hours with various Bi₂O₃/TiO₂ molar ratio.

The UV-Vis diffuse reflectance spectra of the as-prepared co-catalysts powders are shown in Figure 2. The band gap of Bi₂O₃ and TiO₂ were reported to be 2.8 and 3.4 eV, respectively. The optical absorptions of Bi₂O₃/TiO₂ co-catalysts powders start about 400 nm, corresponding to the absorption edge of Bi₂O₃. These results show that with the increasing of the quantity of Bi₂O₃ in the co-catalysts, the absorption in visible-light of the co-catalysts powder also increased. These results revealed that the co-catalysts could absorb the photon in the visible region of the solar spectrum.

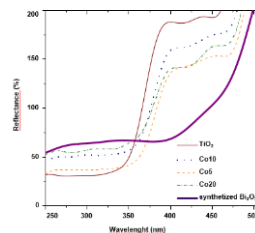


Figure 2. UV-Visible diffuse reflectance spectra of Bi₂O₃/TiO₂ co-catalysts, synthesized Bi compound and TiO₂.

The photocatalytic oxidation of cyanide using the co-catalysts Bi₂O₃/TiO₂/CA system under UV and sunlight are represented in Figure 3.

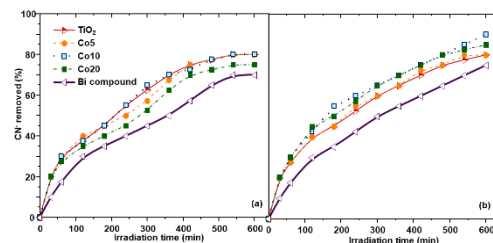


Figure 3. Photocatalytic oxidation of CN⁻ under (a) UV irradiation and (b) sunlight irradiation.

It could be observed that 80 % of CN⁻ was removed in 10 hr with the irradiation of UV light with three of all the co-catalysts, those with the minor percentage of Bi₂O₃ and the blank experiment with only TiO₂ supported in CA. The photocatalytic oxidation of CN⁻ presents better results if the sunlight irradiation was used. 90 % of CN⁻ was removed while using the co-catalysts Co10 and Co20 (the two with more quantity of Bi₂O₃).

Conclusions

Various Bi₂O₃/TiO₂ co-catalysts supported on activated carbon were prepared for the photocatalytic oxidation of cyanide. It was observed that the co-catalysts could absorb in the visible region of the solar spectrum. The Bi₂O₃/TiO₂ CA with 10:90 ratio (Co10) demonstrated higher photocatalytic activity for the oxidation on cyanide under UV and visible light irradiation. After 10 hours of UV irradiation, 80 % of the cyanide was removed. While, by using solar irradiation 90 % of cyanide was removed. The use of the Bi₂O₃/TiO₂ mixture contributes to a better CN⁻ photocatalytic degradation in the visible spectrum region, compared to TiO₂ alone.

Acknowledgments

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