Comparative study of P25/BiOCl mixtures as photocatalysts in Acid Orange 7 degradation

Estudio comparativo de mezclas de fotocatalizadores (P25/BiOCl) en la degradación del Naranja ácido 7

MENDEZ-ALVARADO, Lorena[†], RIVERA-FLORES, Miguel A. [´], SANDOVAL, Miguel A. ^{´,´} and FUENTES, Rosalba^ˆ*

^ˆUniversidad de Guanajuato, Natural an Exact Sciences division, Department of Chemical Engineering, Mexico.

^{´´}Universidad de Santiago de Chile, Faculty of Chemistry and Biology, Department of Materials Chemistry, Chile.

ID 1st Author: Lorena, Mendez-Alvarado / ORC ID: 0000-0002-7046-7285, CVU CONACYT ID: 557364

ID 1st Co-author: Miguel A., Rivera-Flores / ORC ID: 0000-0001-5473-5860

ID 2nd Co-author: Miguel A., Sandoval / ORC ID: 0000-0001-9659-5827, CVU CONACYT ID: 386022

ID 3rd Co-author: Rosalba, Fuentes / ORC ID: 0000-0003-0520-3387, CVU CONACYT ID: 202669

DOI: 10.35429/JSTA.2021.19.7.25.28

Received: January 25, 2021; Accepted: June 30, 2021

Abstract

Objectives. Among strategies used to improve the photocatalytic properties of titanium dioxide (TiO₂), coupled semiconductor has been widely studied. Bismuth oxychloride (BiOCl) semiconductor has been highlighted, specially, with hierarchical structures (3D), because it has been shown to have higher performance in the photodegradation of organic dyes in wastewater. Therefore, in this work the degradation efficiency of acid orange 7 (AO7) was studied using TiO₂ (P25 Degussa), synthesized BiOCl with hierarchical structure, and mixtures of them as photocatalysts. **Methodology.** BiOCl was synthesized by the solvothermal method. The BiOCl was characterized by different techniques such as X-ray diffraction (XRD) and scanning electron microscopy (SEM). In addition, the pore distribution and the surface area were determined. Photocatalytic experiments were carried out with a photocatalyst dose of 1 g·L⁻¹, initial dye concentration of 50 mg·L⁻¹, and UV light illumination. **Contribution.** The interaction of P25 Degussa with BiOCl microspheres (75/25, respectively) improved the photocatalytic degradation achieving a 50% degradation efficiency.

Resumen

Objetivos. Con la finalidad de mejorar las propiedades fotocatalíticas del dióxido de titanio (TiO₂), se han propuesto diversas estrategias, una de ellas ha sido el acoplado de TiO₂-semiconductor. Un material semiconductor que ha ganado atención en la fotocatálisis es el oxiclورو de bismuto (BiOCl), especialmente con morfología jerárquica (3D), debido al gran desempeño en la degradación de colorantes orgánicos en aguas residuales. En el presente trabajo se estudió la eficiencia de degradación del colorante naranja ácido 7 (AO7) usando los fotocatalizadores: TiO₂ (P25 Degussa), BiOCl sintetizado de estructura jerárquica, y mezclas de ellos. **Metodología.** El BiOCl fue sintetizado mediante una ruta solvotermal. Este material se caracterizó mediante diferentes técnicas: difracción de rayos X (XRD), microscopia electrónica de barrido (SEM), y se determinó la distribución de poro y área superficial. Las pruebas fotocatalíticas se llevaron a cabo con 1 g·L⁻¹ de fotocatalizador, una concentración inicial de 50 mg·L⁻¹ del AO7 y empleando luz ultravioleta (UV). **Contribución.** La interacción de las microesferas del BiOCl con el P25 Degussa mostró una mayor eficiencia de degradación del naranja ácido 7, en una relación de peso de P25/BiOCl de 75/25.

Titanium dioxide, Bismuth oxychloride, Photocatalysis

Dióxido de titanio, Oxiclورو de bismuto, Fotocatálisis

Citation: MENDEZ-ALVARADO, Lorena, RIVERA-FLORES, Miguel A., SANDOVAL, Miguel A. and FUENTES, Rosalba. Comparative study of P25/BiOCl mixtures as photocatalysts in Acid Orange 7 degradation. Journal of Scientific and Technical Applications. 2021. 7-19:25-28.

* Correspondence to Author (Email: rosalba@ugto.mx)

[†] Researcher contributing as first author.

Introduction

Rapid industrial development has brought with it an increase in the release of chemical pollutants into the environment. These pollutants are often highly harmful to the environment and difficult to degrade by conventional treatments.

Among these chemical pollutants are the organic dyes. There are a large variety and high production of organic dyes, around 280,000 tons per year worldwide, of which from 2 to 20% are directly discharged into wastewater causing an environmental damage.

Several techniques have been used to treat wastewaters. Photocatalysis (PC) is one of them and it has been considered as a good and effective alternative for water remediation. PC is based on the photoactivation of semiconductor materials (photocatalyst) by irradiation of suitable energy to generate electrons and holes, and highly oxidant species like hydroxyl radical ($\bullet\text{OH}$), responsible of degradation of organic dyes (1).

Titanium dioxide (TiO_2) is the most studied photocatalyst due to its biocompatibility, low cost, and high chemical stability. However, TiO_2 has showed some drawbacks. For example, it can only be photoactivated under UV-light irradiation considering its large band gap ($\sim 3.2\text{eV}$) and high charge recombination rate. Thus, several strategies have been employed to improve the photocatalytic activity of TiO_2 (2,3).

In recent years, bismuth-based photocatalysts, particularly the bismuth oxychloride (BiOCl) with hierarchical structures (3D), have demonstrated to be more effective in the photodegradation of organic dyes in wastewater compared to the commercial TiO_2 (4–6).

For this reason, in this work the photocatalytic activity of mixtures of TiO_2 -P25/ BiOCl hierarchical structure (3D) was studied to degrade acid orange 7 (AO7) dye under UV light.

Methodology

Synthesis

Solvothermal method was used to synthesize BiOCl ⁷. This procedure consisted in 5 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ which was dissolved in 30 mL of methanol.

Then, 5 mmol of KCl and 5 mmol of citric acid were added to the solution maintaining a constant stirring for 3 h. The mixture was transferred to Teflon-lined stainless autoclave. The solvothermal reaction was maintained at 150°C for 12 h. After, it cooled down to room temperature. Finally, the product was washed with distillate water and ethanol and dried at 60°C for 12 h.

Characterization

Scanning electron microscopy (SEM), X-ray diffraction (XRD), and N_2 adsorption-desorption were used as characterization techniques for synthesized BiOCl . The surface area (BET, Brunauer-Emmett-Teller method) and porosity of BiOCl were determined by from nitrogen adsorption-desorption isotherms data, which were obtained at 77K (Micromeritics TriStar II Plus equipment). The diffraction patterns were obtained by Rigaku MiniFlex® powder diffractometer with $\text{Cu K}\alpha$ radiation, $\lambda = 1.54 \text{ \AA}$ at 40 kV tube voltages and 100 mA tube current. The XRD data were collected in a 2θ range from 10 to 70° with a speed of 5° per minute. The morphology of BiOCl was analysed by the field emission Scanning Electron Microscopy (FE-SEM; ZEISS, Sigma HD VP), equipped with an angle selective backscatter (AsB) detector. The following experimental conditions were used: voltage 10 kV, aperture size: 30 μm and magnification 10 kX.

Experimental

P25/ BiOCl mixtures were prepared with different weight relation of each semiconductor: 0/100, 25/75, 50/50, 75/25 and 100/0.

For each photocatalytic experiment, 0.1 g of pure and mixture of photocatalyst (pure or in mixture) was dispersed into 100 mL of AO7 ($50 \text{ mg}\cdot\text{L}^{-1}$) dye. The solution (photocatalyst and dye) was stirred in darkness for 30 min to establish adsorption-desorption equilibrium between photocatalyst and dye.

Oxygen supply to the solution was carried out using an air pump and UV lamps (4 W) were used for system illumination. The change of dye concentration over time was followed by UV-vis spectroscopy (wavelength of 483 nm).

Results

Characterization of BiOCl

N₂ adsorption-desorption isotherm was obtained for synthesized BiOCl. The presence of micro- and meso-pores was observed. Moreover, a value of 41.4 m²·g⁻¹ specific surface area was determined.

Figure 1 X-ray diffraction pattern of the BiOCl synthesized

Figure 1 shows X-ray pattern of BiOCl, which all peaks coincide with the tetragonal phase of BiOCl (JCPDS 00-006-0249 with crystallographic parameters of $a=b=3.8910$ Å and $c=7.369$ Å). It is important to highlight that the solvothermal synthesis method promoted the growth of the (110) plane. The Scherrer equation through X'pert Highscore Plus (2.2a) software was used for calculated the crystal's size of 19.1 nm.

Figure 2 SEM image of hierarchical microspherical-like structure BiOCl

SEM image of the synthesized BiOCl is displayed in Figure 2. It can be observed that BiOCl has hierarchical structures (3D) that were made up of irregular nanosheets, interconnected with each other. SEM image shows that there are particles in the sample with different morphologies, from microspherical to irregular shapes, both constructed from the assembly of nanosheets. This result suggests that the BiOCl microspherical structures may provide reaction sites where the photodegradation of AO7 is carried out.

Evaluation of photocatalytic degradation of AO7 dye

Preliminary to photodegradation experiments, the photolysis of AO7 dye under UV light illumination was examined. Only 2.5% of initial dye concentration decreased. Photodegradation of AO7 dye was evaluated using TiO₂-P25 and synthesized BiOCl photocatalysts. The photodegradation efficiency is shown in Figure 3. The micro-spherical structure of BiOCl offered a higher photodegradation efficiency than P25.

Figure 3 Photodegradation efficiency of AO7 dye (50 mg·L⁻¹) using P25 and BiOCl as photocatalysts

Figure 4 Photocatalytic activity of P25/BiOCl mixtures in degradation of AO7 dye (50 mg·L⁻¹)

Figure 4 shows the photodegradation efficiency of AO7 (50 mg·L⁻¹) under UV light using the P25/BiOCl mixtures. The maximum degradation achieved for AO7 dye was using 75/25 weight relation of photocatalysts P25/BiOCl, respectively. It is important to note that load of BiOCl synthesized played an important role, diminishing synthesized BiOCl concentration an increase in the photodegradation efficiency of AO7 dye under UV light illumination was observed.

Acknowledgment

The authors are grateful to the University of Guanajuato (UG) for its financial support of this work (252/2020). Lorena N. Mendez-Alvarado acknowledges to Mexican Council for Science and Technology (CONACyT) for her PhD scholarship (grant 448004).

Conclusions

In summary, the obtention of BiOCl was successful by solvothermal method, obtained a hierarchical structure like-microspheres with a particle size of 1 - 4 µm and surface area of 41.4 m²·g⁻¹.

The photocatalytic degradation of AO7 dye was improved using coupled semiconductors (P25/BiOCl). A maximum degradation efficiency (50.8%) was obtained at a weight relation of 75/25. This result suggests, that at low weight loading of microspheres BiOCl promoted the separation of photogenerated charge (electron-holes) and reaction sites, for photodegradation to take place.

This enhancement in the photodegradation of AO7 dye with the photocatalysts mixtures (P25/BiOCl) under UV light, allows to propose the photoactivity evaluation of this mixtures under visible light illumination. Additionally, photocatalysts mixtures can be tested in the degradation of other organic pollutants, such as: drugs and pesticides.

References

1. Cheng M, Zeng G, Huang D, et al. Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: A review. *Chem Eng J.* 2016;284:582-598. doi:10.1016/j.cej.2015.09.001

2. Khalid NR, Majid A, Tahir MB, Niaz NA, Khalid S. Carbonaceous-TiO₂ nanomaterials for photocatalytic degradation of pollutants: A review. *Ceram Int.* 2017;43(17):14552-14571. doi:10.1016/j.ceramint.2017.08.143
3. Nguyen CH, Fu C-C, Juang R-S. Degradation of methylene blue and methyl orange by palladium-doped TiO₂ photocatalysis for water reuse: Efficiency and degradation pathways. *J Clean Prod.* 2018;202:413-427. doi:10.1016/j.jclepro.2018.08.110
4. Li K, Liang Y, Yang J, et al. Controllable synthesis of {001} facet dependent foursquare BiOCl nanosheets: A high efficiency photocatalyst for degradation of methyl orange. *J Alloys Compd.* 2017;695:238-249. doi:10.1016/j.jallcom.2016.10.204
5. Song J, Fan Q, Zhu W, Wang R, Dong Z. Preparation of BiOCl with high specific surface area and excellent visible light photocatalytic activity. *Mater Lett.* 2016;165:14-18. doi:10.1016/j.matlet.2015.11.093
6. Mendez-Alvarado LN, Medina-Ramirez A, Manriquez J, Navarro-Mendoza R, Fuentes-Ramirez R, Peralta-Hernandez JM. Synthesis of microspherical structures of bismuth oxychloride (BiOCl) towards the degradation of reactive orange 84 dye with sunlight. *Mater Sci Semicond Process.* 2020;114(March):105086. doi:10.1016/j.mssp.2020.105086
7. Sun D, Wang T, Xu Y, Li R, Sato T. Hierarchical bismuth oxychlorides constructed by porous nanosheets: Preparation, growth mechanism, and application in photocatalysis. *Mater Sci Semicond Process.* 2015;31:666-677. doi:10.1016/j.mssp.2014.12.046