Journal of Industrial and Engineering Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Photocatalytic removal of cefazolin using Ag_3PO_4/BiOBr under visible light and optimization of parameters by response surface methodology

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ARTICLE INFO

Article history:
Received 8 August 2016
Received in revised form 17 September 2016
Accepted 21 September 2016
Available online xxx

Keywords:
Photodegradation
Ag_3PO_4/BiOBr
Cefazolin
Response surface method
Box–Behnken design

ABSTRACT

The degradation of cefazolin (CFZ) by Ag_3PO_4/BiOBr composites under visible-light irradiation was explored. The main and interaction of parameters (catalyst dosage, pH, CFZ initial concentration and degradation time) on removal of CFZ were studied by Box–Behnken design combined with response surface methodology. The pH was the most influential factor and both h^+ and $^{\bullet}OH$ played a role in the photocatalytic process. The high correlation coefficients ($R^2 = 0.9986$ and adjusted $R^2 = 0.9973$) demonstrated close fit between the predicted and experimental values. The exceptional efficiency of Ag_3PO_4/BiOBr composite in removing CFZ represents a promising technique for treatment of CFZ-containing wastewater.

Introduction

Recently, the frequently detected antibiotics and their resistant microbes in aquatic environments raise an alarming environmental risk, which poses a new challenge to wastewater and drinking water treatment systems [1]. Cephalosporins are important β-lactam antibiotics that have been extensively used both in humans and in animals [2]. The persistence and increasing amount of cephalosporins in surface water and wastewater systems have been reported in many countries [3–7] . This has prompted a growing public concern about their potential risks to aqueous organisms and humans due to their acute and chronic effects on ecosystems [8–10] as well as increased antibiotic resistance of microorganisms in the environment [11,12]. The US Food and Drug Administration (FDA) has prohibited certain uses of cephalosporins in farm animals including cattle, pigs, chickens and turkeys since 5 April, 2012 [13]. Notably, higher toxic byproducts of cephalosporins may form during their photodegradation in aqueous environment [14]. As a result, the presence of trace amounts of cephalosporins also may be a risk because of higher toxicity of their photobyproducts during natural attenuation processes. It therefore impels us continuously to investigate the degradation techniques to eliminate cephalosporins from wastewater.

Cefazolin (CFZ), a representative of the first generation cephalosporins, has relatively high residue level in environmental media, and exhibits some adverse effects to aquatic organisms [6,15–17]. Wastewater treatment plants (WWTP) are main sources of CFZ entry into the environment, because of inadequate removal efficiencies in the plants [18]. For example, residual level of CFZ in influent WWTPs in Taiwan was 0.083–8.79 μg/L, while its maximum effluent concentration was higher than 2.0 μg/L [16]. Besides, the intermediates formed after chlorination disinfection process of CFZ have higher toxicity than the parent CFZ [15]. Thus, WWTPs confront an array of immediate challenges associated with the treatment of CFZ-containing wastewaters before discharge.

However, only a few works have been devoted to remove CFZ. For instance, Fakhri et al. [19] employed CdS-MWCNT nanocomposites as an adsorbent to eliminate CFZ, and maximum surface coverage of 59.10% for CFZ was obtained. Nonetheless, this technique only transferred the pollutant from one phase to another without destroying it. Li et al. [20] utilized permanganate (Mn (VII)), a common oxidant in water pre-oxidation treatment, to

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http://dx.doi.org/10.1016/j.jiec.2016.09.032
1226-086X/

oxidize CFZ. But, they exclusively focused on the transformation characteristics rather than reduction of CFZ during oxidation by Mn(VII). Moreover, the (di-)sulfoxide and sulfone containing products formed in Mn(VII) oxidation may have potential genotoxicity to animals and human beings. In contrast, Gurkan et al. [21] reported a more competitive process to reduce CFZ by employing a heterogeneous photocatalytic system [ultraviolet (UV) or sunlight/N-doped TiO_2], in which 80% of CFZ was transformed to CO_2, water and inorganic compounds in 30 min with N-doped TiO_2 under direct sunlight irradiation. Thereafter, some studies have examined ceftiofur sodium removal with TiO_2 photocatalysis [22,23]. Clearly, heterogeneous photocatalysis has turned out to be more effective strategy for WWTPs addressing the cephalosporins-containing wastewater, through impurity doping or metal deposition heterojunction broadening the visible-light absorption of photocatalysts. While doping or metal deposition has greatly improved the availability of visible light, the sensitivity of photocatalysts to doping or metal deposition level and homogeneity make it a less suitable method. However, heterojunction of two semiconductors, such as Ag_3PO_4/BiOX [24–27], Ag_3PO_4/TiO_2 [28], has found evidence that can effectively tune the electronic properties of composites and are less sensitive to component homogeneity.

Indeed, the Ag_3PO_4/BiOBr heterostructures have seen important enhancements in visible-light absorption and photocatalytic performance compared to pure BiOBr and Ag_3PO_4 for degrading typical organic pollutants such as Rhodamine B and phenol [24,27]. These hetero-photocatalysts facilitate the surface separation of photoexcited electron and hole pairs derived from matching band potentials between BiOBr and Ag_3PO_4 rather than bulk phase separation. Most importantly, the Ag_3PO_4/BiOBr heterojunctions exhibited almost no loss of activity even after 6 recycling runs [24]. Considering the high stability and enhanced visible-light-driven photocatalytic activity, it is possible and meaningful to apply this composite for CFZ removal in WWTPs. From critical review of published data, research on CFZ heterogeneous photocatalytic degradation has not been mentioned utilizing the suspended Ag_3PO_4/BiOBr heterojunction.

It is known that, the outcome of the photocatalysis depends upon numerous operational parameters such as catalyst loading, pollutant concentration, medium pH, light intensity, temperature and irradiation time, etc [29,30]. The conventional one-parameter-at-a-time (OPAT) approach is mostly used to the optimization of operation parameters on photocatalytic antibiotics. Though the OPAT approach is widely acceptable, it does not take into account the effects of the parameters combination, consequently, the obtained outcomes could be insignificant and have less predictive power if the condition for one operating parameter changes [29]. Also OPAT approach is costly in light of time and reagents, and not that efficient because of a large number of experiments [31]. Recently, response surface methodology (RSM) is a very useful and capable tool for the optimization of photocatalysis process [29,31,32], which combines mathematics and statistics to analyze the relative significance of influencing factors in a system. Compared to other designs in RSM, Box–Behnken design (BBD) shows the most-frequently used in pioneering studies [33]. Such statistical analysis is more efficient and helpful, since it accounts for interaction effects between the studied variables and determine more accurately the combination of levels that produces the optimum of the process [31]. But to our knowledge, RSM has not been applied previously to optimize operating parameters of photocatalysis process using Ag_3PO_4/BiOBr heterojunction as a photocatalyst.

In present study, a simple coprecipitation method was used for the preparation of Ag_3PO_4/BiOBr heterojunction photocatalyst. The CFZ removal under the influence of operating parameters such as Ag_3PO_4/BiOBr dose, initial CFZ concentration, pH and irradiation time was studied. The oxidative species during photodegradation of CFZ was also determined by scavenger experiments. For optimization, the photocatalytic degradation process was statistically designed adopting RSM analysis method based on BBD in order to reach the best combination of operating parameters that could achieve maximum CFZ removal.

Materials and methods

Reagents and chemicals

Cefazolin (CFZ) was procured from Ehrenstorfer GmbH. Tetrabutylammonium bromide (TBAB) was obtained from Aladdin Reagent Company, China. All other chemicals were analytical grade and purchased from Beijing Chemical Factory, China, which were used as received without any further purification. Deionized water was used throughout the study.

Preparation and characterization of Ag_3PO_4/BiOBr composite

BiOBr powders were prepared by a simple solvothermal method using ethanol as the solvent [34]. Briefly, 0.9 g $Bi(NO_3)_3{\cdot}5H_2O$ was dispersed uniformly in 80 mL absolute ethanol under sonication, and 1.2030 g TBAB was added and dispersed completely by keeping sonication. The mixture was transferred to a 100-mL Teflon-lined stainless autoclave, which was heated to 145 °C and maintained at 145 °C for 4.5 h, and then cooled to room temperature. The resulting precipitates were collected and washed with ethanol and hot deionized water thoroughly, and dried at 60 °C for 10 h.

The preparation method of Ag_3PO_4/BiOBr was as follows: A certain amount of BiOBr was dispersed into 20 mL of water by sonication and the corresponding quantities of $AgNO_3$ and Na_3PO_4 were added into the suspension to make the Ag/Bi weight ratio of 0.7, and then stirred for 6 h at room temperature. The products were collected by centrifugation and washed with deionized water followed by absolute ethanol then vacuum dried at 60 °C for 10 h. For comparison pure Ag_3PO_4 photocatalyst was prepared using the same method without adding the BiOBr powders.

The crystalline structure and phase purity of the above prepared samples were analyzed by X-ray diffraction (XRD) using Germany D8 advance diffractometer with Cu Kα radiation (λ = 1.5406 Å). The microstructure of the samples was observed by Dutch Philips XL30 field emission scanning electron microscope (SEM). Elemental analysis was probed using energy-dispersive spectroscopy (EDS) attachment on FEI Quanta 200 ESEM. The UV–vis diffuse reflectance spectra (UV-DRS) reflecting the optical property of the samples were obtained by a Hitatchi U-3010 spectrophotometer.

Photocatalytic degradation experiment

All photocatalytic experiments were performed in an XPA photo-reactor (Xujiang Electromechanical Plant, Nanjing, China) with a 400 W metal halogen lamp. The experiments were carried out with Ag_3PO_4/BiOBr (10 mg/L) suspended in CFZ solution (30 mL, with concentration of 10 mg/L) under continuous stirring in the presence of visible light (>420 nm). The metal halogen lamp was irradiated perpendicularly to the surface of solution, and the distance between the lamp and vessel containing reaction mixture was fixed at 10 cm. Prior to irradiation, the suspension was equilibrated under darkness for 30 min to reach adsorption equilibrium. Aliquots of 0.5 mL were collected after every 5 min of illumination and then filtered through 0.22 μm filter. The filtrate was determined by HPLC-UV (Agilent 1220, USA) at 272 nm with a

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