Journal of Photochemistry and Photobiology A: Chemistry 318 (2016) 71–76

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

BiOI microspheres for photocatalytic degradation of gallic acid

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ARTICLE INFO

Article history:
Received 29 July 2015
Received in revised form 4 November 2015
Accepted 13 December 2015
Available online 15 December 2015

Keywords:
BiOI microspheres
Gallic acid
Multivariate analysis
Photocatalysis
pH

ABSTRACT

The photocatalytic degradation of gallic acid using BiOI microspheres under simulated solar radiation was studied. Response surface methodology (RSM) was applied to optimize the amount of photocatalyst and initial pH. To evaluate the interaction between these two parameters, and to optimize these parameters during the process, a factorial design central composite (CCC) and response surface methodology were developed. The results show that initial pH has a significant effect on the degradation of gallic acid, while the amount of photocatalyst presents a less significant effect. The optimized conditions were: amount of BiOI 560 mg L^{-1} at initial pH around 3.2. In addition, a BiOI synthesized with ionic liquid 1-butyl-3-methylimidazolium iodide ([bmim]I) was used to compare photocatalytic efficiency. Under these conditions, the maximum degradation percentage at 5 min of photocatalytic reaction was of 73% and 82% for BiOI synthesized with inorganic salt KI and ionic liquid [bmim]I respectively. Furthermore, the theoretical and experimental isoelectric points (IEP) of BiOI were obtained to analyze the influence of pH on the degradation of gallic acid, which was used as a winery effluent model pollutant.

1. Introduction

The synthesis of BiOI microspheres has been increasingly attracting attention because of their potential use for water decontamination, as they can be activated with visible light [1,2]. These structures can be obtained by solvothermal synthesis starting from bismuth nitrate and using KI or ionic liquids ([bmim]I) as iodine source, as these materials present high specific surface areas and a band gap energy around 1.8 eV, allowing the use of visible light [3–6]. In addition, present higher photocatalytic efficiencies in visible region than Evonik TiO_2 P25 (former Degussa), the most used photocatalyst during years worldwide [7–9]. BiOI is a ternary compound that generally crystallizes in tetragonal structures, organized in layers with $[Bi_2O_2]$ plates interleaved with two iodine atoms forming well organized microspheres [10].

Finding the optimal values for the operational parameter (initial pH and amount of catalyst) in the photocatalysis of refractory organic substances using BiOI microspheres is a huge challenge. A valuable alternative to this approach is the use of experimental factorial design, a statistical tool that allows for the simultaneous change of more than one variable. This methodology, known as multivariate analysis, has been used in the experimental design of photocatalytic oxidation of various pollutants and industrial effluents [11–14].

Gallic acid (3,4,5-trihydoxybenzoic acid) is a phenolic compound commonly present in agricultural wastewater released from olive oil and wine processing industries [15,16]. This model compound confers a refractory character to agricultural effluents and is responsible for the inhibitory effects on microbial activity in biological treatment systems [17,18].

This article aims to use multivariate design to determine the optimal pH value and the amount of catalyst (BiOI) to get higher photocatalytic efficiency degrading gallic acid. In addition, the theoretical and experimental isoelectric points (IEP) are determined for BiOI microspheres. The obtained information has not yet been reported for these nanostructured materials.

2. Experimental

2.1. Synthesis of BiOI microspheres

The preparation of BiOI microspheres was carried out by solvothermal synthesis. All reagents used were of analytical grade

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http://dx.doi.org/10.1016/j.jphotochem.2015.12.005
1010-6030/

Table 1
Some characteristics the materials of BiOI microspheres synthesized.

Material	Crystalline phase	Eg (eV)	Average particle size (μm)	Surface area (m^2/g)
BiOI/KI	Tetragonal system	1.90	4.45	57
BiOI/[Bmim]I	Tetragonal system	1.80	4.83	63

(AR) and used as received without additional purification. 1 mmol of bismuth nitrate pentahydrate [$Bi(NO_3)_3{\cdot}5H_2O$] (Sigma–Aldrich, 99.0%) was dissolved in ethylene glycol (10 mL, Merck 99.5%) and poured in a solution of 10 mL of ethylene glycol containing 1 mmol of KI (99.0% Merck). The mixture was stirred at room temperature for 30 min and then transferred to a 23 mL Teflon autoclave reactor. The autoclave was heated at 126 °C (at autogenous pressure) for 18 h and finally cooled to room temperature. The final products were separated by vacuum filtration and extensively washed using distilled water and absolute ethanol (Merck, 99.5% v/v). The material obtained was dried at 60 °C for 24 h. The same procedure was used to synthesize BiOI using ionic liquid 1-butyl-3-methylimidazolium iodide ([bmim]I) as an iodide source.

2.2. Characterization

The two materials obtained were characterized by scanning electron microscopy (SEM, JEOL, JSM-6380) operated at 20 kV to determine the morphology. The particle size of the materials was determined using a laser diffraction particle size analyzer (Microtrac Model S3500) equipped with tri-laser technology operated at 240 V and 50 Hz. The specific surface area of the material was determined by adsorption–desorption isotherms with nitrogen at 77 K using Brunauer–Emmett–Teller (BET) analysis in a Micromeritis TriStar II porosity analyzer. X-ray diffraction (XRD) in a powder diffractometer Bruker D4 equipped with Cu-Kα radiation (λ = 1.5406 Å) and a 2θ scan range of 5–80° was used to determine the crystallinity and phases of the synthesized materials. Diffuse reflectance spectroscopy (DRS) was obtained using PerkinElmer Precisely Lambda 35 UV/Vis spectrophotometer equipped with an integrating sphere.

2.3. Isoelectric point

The isoelectric point (IEP) of BiOI was determined on a Zeta-Meter Inc., Model ZM-3.0+ using 20 mg of solid suspended in 200 mL of KCl, 1×10^{-3} mol L^{-1}. The pH was adjusted with HCl, 0.1 mol L^{-1} or KOH, 0.1 mol L^{-1}.

2.4. Experimental design

The optimization of the photocatalytic conditions for gallic acid degradation using BiOI microspheres was done by simultaneously changing the amount of photocatalyst and initial pH. The design was carried out through the response surface methodology (RSM). The experimental design was a composed central circumscribed design (CCC) which is based on a factorial experimental design with 3 central points and 4 star points. According to this methodology, the variables were coded using unitary values, where −1 and +1 were defined as the lowest and highest values of the variables, respectively. The central point was coded as 0 and determined in triplicate to statistically validate the determinations assuming homoscedasticity of variance [19–21]. The variables were the amount of BiOI (ranging from 200–600 mg L^{-1}) and the initial pH (from 4 at 8). The number of experiments was determined by the expression: $2^n + 2n + 3$, where $n = 2$ (n = number of variables) and considering two levels (−1, +1), giving a total of 11 runs [22]. The degradation percentage of gallic acid (after 5 min of illumination) under simulated solar radiation was chosen as the response factor. The design of experiments is depicted in Table 1. From the CCC design a polynomial was obtained by multiple linear regression (MLR). The software MODDE 7 was used to evaluate the weight of the variables, get the polynomial and the 3D representation of the surface response. The statistical validation was performed by ANOVA test with a 95% confidence level.

2.5. Photocatalytic tests

The photocatalytic degradation of gallic acid was evaluated under light irradiation using a xenon lamp (VIPHID 6000 k, 12 W) with spectral range 380–900 nm. The photocatalysis was carried out in a 300 mL borosilicate reactor containing 250 mL of acid gallic aqueous solution (20 mg L^{-1}). The amount of catalyst was used according to the factorial design in the range between 200–600 mg. The reactor temperature was maintained with circulating tap water and continuous magnetic stirring. Before the light was turned on, the solution was kept in the dark in order to reach the adsorption–desorption equilibrium. The gallic acid concentration in the course of the reaction was monitored by HPLC (Hitachi Elite Lachrom) using a C18 reverse phase column

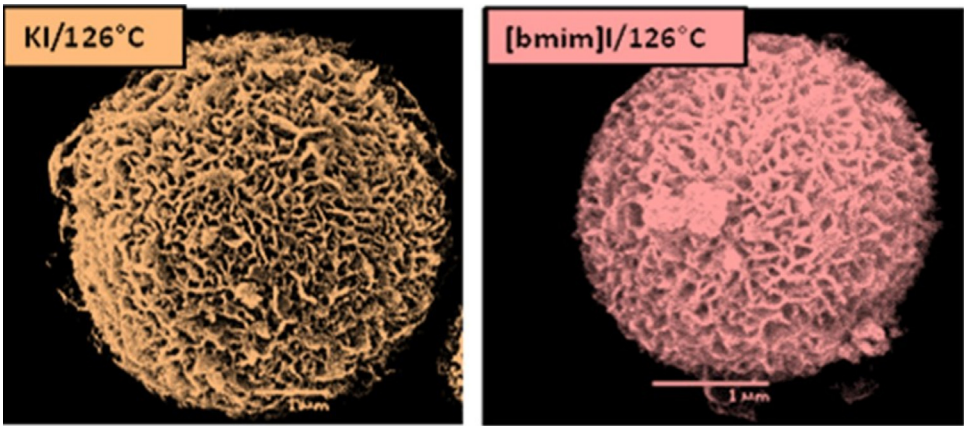

Fig. 1. SEM images of BiOI.