Journal of the Taiwan Institute of Chemical Engineers 58 (2016) 324–332

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Photocatalytic activity of zinc stannate: Preparation and modeling

M.H. Rasoulifard*, M.S. Seyed Dorraji**, S. Taherkhani[1]

Research Laboratory of Applied Chemistry, Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran

ARTICLE INFO

Article history:
Received 14 February 2015
Revised 1 June 2015
Accepted 7 June 2015
Available online 26 June 2015

Keywords:
Zn_2SnO_4
Photocatalysis
Response surface methodology
Dye

ABSTRACT

Zn_2SnO_4 particles with the cubic shape are prepared via a two-step process, including co-precipitation and high-temperature solid state reaction procedures. The prepared photocatalyst has been characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), UV–vis diffuse reflectance spectroscopy and Fourier transform infrared (FT-IR) spectroscopy. Response surface methodology (RSM) was used to model and optimize four key independent variables, namely catalyst dosage, pollutant initial concentration, pH and distance between UV source and surface of solution (D) for photocatalytic degradation of Basic Red 46 as model pollutant. The proposed quadratic model was in accordance with the experimental results with correlation coefficient of 98.4%. The Pareto analysis indicated that the most important variable for the photocatalytic degradation of BR 46 was the distance between surface of solution and UV source (34.536%), followed by pure quadratic interactions of catalyst dosage (21.049%) and pH (14.309). Optimal experimental conditions found for dye removal were ZTO dosage of 110 mg/l, initial dye concentration of 17 mg/l, $D = 10$ cm and pH of 8.5. The predicted degradation efficiency under the optimal conditions determined by the proposed model was 95.3%. Confirmatory experiment was carried out under the optimal conditions and the degradation efficiency of 94.7% was observed, which closely agreed with the predicted value.

1. Introduction

Zinc stannate, also called zinc–tin oxide (ZTO), is an *n*-type transparent semiconductor material with a band gap energy of 3.6 eV, a typical inverse spinel structure and high electron mobility which make it suitable for wide range of potential applications, including gas sensing material [1,2], anode materials for batteries [3] adsorbent [4] and photocatalyst [5–9] for dye removal.

The preparation of ZTO has been reported by various procedures such as high-temperature solid-state reaction [10], thermal evaporation [11], mechanical and thermal activation [12] vapor chemical deposition [13], co-precipitation [14] and hydrothermal synthesis [15].

Ever since the 1970s, semiconductor photocatalysis has appeared as one of the most promising technologies to address the issue of environmental pollution [16,17]. Photocatalysis is a light-induced catalytic process for reducing organic materials through redox reactions of the process and contains electron–hole pair creation on the surface of a semiconductor by the absorption of photons and its subsequent loss to an adsorbed molecule [6,18].

To date, most of the researches are dominated by TiO_2 because of its chemical stability, low cost and relatively high activity [19]. However, the practical application of the TiO_2 photocatalytic process is restricted by the low quantum efficiency and the slow electron transfer rate [20]. Therefore, it is urgent to seek the photocatalysts with excellent activity. It is clear that a wider separation of the electron and the hole improves photocatalyst performance. Also, it has been confirmed that oxygen vacancies and defects strongly affect light-induced catalytic reactions [7,21].

Zinc stannate is a promising candidate as a photocatalyst because it is chemically stable [6] and has a high electron mobility [22] essential for enhanced photocatalysis. Complex crystal structure of Zn_2SnO_4 has improved its stability in adverse conditions [23] as compared to oxides and binary oxides [24,25].

There are some reports of photocatalytic activity of ZTO [5–9,25], but, to the best of our knowledge, the modeling and optimization of the degradation of any molecule in the UV/ZTO process, using response surface methodology has never been reported. The modeling of process contributes significantly to the improvement and better understanding photocatalytic processes.

Based on the above consideration, Zn_2SnO_4 photocatalyst was prepared in this work by a two-step process, including co-precipitation and high-temperature solid state reaction procedures. The crystal structure and morphology of the prepared photocatalyst were characterized systematically. The photocatalytic activity of prepared ZTO toward degradation of Basic Red 46 (BR46) was modeled

* Corresponding author. Tel.: +98 24 3305 2591; fax: +98 24 3305 2477.
** Corresponding author. Tel.: +98 24 3305 2477; fax: +98 24 3305 2477.
E-mail addresses: m_h_rasoulifard@znu.ac.ir (M.H. Rasoulifard), dorraji@znu.ac.ir, saeed_dorraji@yahoo.com (M.S.S. Dorraji), taherkhani_s@ymail.com (S. Taherkhani).
[1] Tel.: +98 24 3305 2477; fax: +98 24 3305 2477.

http://dx.doi.org/10.1016/j.jtice.2015.06.008
1876-1070/

Table 1
Real and coded levels of variables.

Independent variable	Symbol	Coded levels				
		−2	−1	0	1	2
Catalyst dosage (mg/l)	*A*	80	95	110	125	140
Initial dye concentration (mg/l)	*B*	12	14	16	18	20
pH	*C*	3	5	7	9	11
Distance between surface of solution and UV source (cm)	*D*	10	12.5	15	17.5	20

Light intensity at the surface of solution was 16.3, 15, 11.2, 9.3, 8.7 (W/m^2) at D = 10, 12.5, 15, 17.5 and 20 (cm), respectively.

by response surface methodology. Basic Red 46, a cationic azo dye, was selected as a model due to its extensive use in textile industry. Important factors, such as pH values, ZTO loading, dye concentration, and light intensity were investigated in this research as well as the interactions between these different factors. Also, this study presents effective information about the optimized reaction conditions for the degradation of Basic Red 46.

2. Experimental

2.1. Synthesis

All chemical reagents used in this experiment were of analytical grade and used without further purification. According to a typical co-precipitation synthesis [14], zinc nitrate ($Zn(NO_3)_2 \bullet 3H_2O$) and tin tetrachloride ($SnCl_4 \bullet 5H_2O$) were dissolved with the mole rate of 2:1 in a minimum amount of distilled water as zinc and tin sources, respectively. The mixture was added dropwise into ammonia aqueous solution ($V_{ammonia}$:V_{water} = 2:3) under magnetic stirring. The pH of final solution was adjusted to about 8 by adding ammonia solution to make the reagents react completely. The wet synthesized precursor was filtered and washed with distilled water to remove undesirable anions and dried at about 150 °C in air for 2 h. Finally, the precursor was calcined in air at a certain temperature (1000 °C for 1 h) to produce ZTO photocatalyst. The reactions for formation of Zn_2SnO_4 can be summarized as follows:

$$2Zn^{2+} + Sn^{4+} + 8OH^- \rightarrow 2Zn(OH)_2 + Sn(OH)_4 \quad (1)$$

$$2Zn(OH)_2 + Sn(OH)_4 \rightarrow Zn_2SnO_4 + 4H_2O \quad (2)$$

2.2. Characterization

The crystallographic information of the prepared ZTO was obtained with X-ray diffraction (XRD) of Cu K_α radiation λ = 0.154,598 nm (Siemens D-5000 diffractometer). Scanning electron microscopy (Seron Technology, AIS 2100) was used for examining the morphology and size of the synthesized sample. Further characterization of the morphology of prepared ZTO was carried out using TEM (ZEISS EM 10, Germany).

Varian Cary 5 Series E UV–Vis Spectrophotometer was used to investigate the optical absorption of prepared photocatalyst. UV–visible absorption spectra of powder samples were recorded using pure $BaSO_4$ pellet as the reference.

UV–vis diffuse reflectance spectrum was recorded on the Cary 300 UV–vis spectrophotometer.

2.3. Photocatalytic measurements

The photocatalytic activity of ZTO was evaluated by photocatalytic degradation of a representative of azo dyes, Basic Red 46 ($C_{18}H_{21}BrN_6$; M_w = 401.3; λ_{max} = 530 nm; type: cationic). The tests were performed in a 200 ml batch slurry reactor. Irradiation was carried out with a 30 W (UV-C) mercury lamp (Philips, Holland), which was put above the photoreactor.

In order to monitor the rate of degradation, optical absorption spectra were determined after various light-exposure durations using a UV–vis spectrophotometer by recording the reduction in the absorption intensity of BR 46 at maximum wavelength.

Degradation efficiency (R) was calculated as $R = (A_o - A)/A_o$, where A_o shows initial absorbance and A shows final absorbance at λ_{max} = 530 nm.

2.4. Modeling and optimization of photocatalytic process

The response surface methodology (RSM) was employed to model and optimize the photocatalytic degradation of BR 46. The RSM was used for evaluation of combined effects of pH, ZTO dosage, initial dye concentration and distance between UV lamp and surface of solution on the degradation efficiency of photocatalyst. Initially preliminary experiments were conducted following single factor study method to decide the most influential experimental parameters affecting the photocatalytic process and to find out their ranges.

The ranges and levels of independent variables are shown in Table 1.

A response surface model was developed to correlate the degradation efficiency dependency on the four different parameters according to the statistical regression as shown in (Eq. (3))

$$R(\%) = b_o + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i}^{k} \sum_{j}^{k} b_{ij} X_i X_j \quad (3)$$

where $R(\%)$ is the predicted degradation efficiency, b_o is the constant, b_i is the linear effect of the factor X_i (i = 1, 2, 3 and 4), b_{ii} is the quadratic effect of the factor X_i, b_{ij} is the linear interaction effect between the input factors X_i and X_j (i = 1, 2, 3 and 4; j = 1, 2, 3 and 4).

3. Results and discussion

3.1. Structural characterization of Zn_2SnO_4 particles

The phase composition of the ZTO obtained following above experimental procedure was determined by X-ray powder diffraction. Fig. 1(a) gives the XRD pattern of prepared ZTO. The dominant diffraction peaks could be indexed by cubic spinel crystal structure (JCPDS no. 24-1470). The diffraction peaks of the XRD pattern are strong and narrow, indicating high crystallinity of the prepared Zn_2SnO_4 particles. The small residual peaks marked with black triangle symbols can be assigned to SnO_2 (JCPDS 41-1445). The presence of SnO_2 may be attributed to the two facts (*i*) evaporation of a part of ZnO, and (*ii*) thermal decomposition of the as-prepared precursor [14].

FTIR spectroscopy (Fig. 1(b)) provides some structural and surface information about the prepared ZTO. A broad band centers at about 3400 cm^{-1} is observed, which can be attributed to the stretching vibration of the O–H groups on the surface of ZTO. The absorption peaks located at 565 and 615 cm^{-1} are corresponding to Zn–O and Sn–O vibrations. Also, the other characteristic absorption band has appeared around 1120 cm^{-1} due to both symmetric and antisymmetric stretching vibrations of Zn–O–Sn [2]. Thus, the formations of ZTO can be further confirmed here by the FTIR result.