

Synthesis, characterization and catalytic activity of nano size semiconductor metal oxide in a visible light batch slurry photoreactor

G. Thennarasu, A. Sivasamy*, S. Kavithaa

Chemical Engineering Area, CSIR-Central Leather Research Institute, (Council of Scientific & Industrial Research), Adyar, Chennai-600 020, India

ARTICLE INFO

Article history:

Received 24 August 2012

Received in revised form 19 November 2012

Accepted 1 December 2012

Available online 17 December 2012

Keywords:

Visible light

Zinc oxide

Photo catalyst

Degradation

Azo dye

ABSTRACT

Nano size zinc oxide was prepared employing zinc acetate as the precursor solution and aqueous sodium hydroxide as the medium. The formation of pure ZnO was confirmed through FT-IR and powder X-ray diffraction. Surface morphology was characterized by SEM and TEM analysis. The visible photocatalytic behaviour of the synthesized ZnO was tested through the degradation of AB10B. The disappearance of dye molecules followed pseudo-first-order kinetics. The effect of various parameters namely, pH of the medium, catalyst loading, initial dye concentration and kinetics of photo degradation of AB10B was investigated. The rate of degradation was found to be strongly influenced by all above mentioned parameters. The reduction in the chemical oxygen demand (COD) of the degraded aqueous samples revealed a possibility of complete destruction of the organic molecules along with colour removal. Adsorption of AB10B onto ZnO particles was also carried out and experimental data were analysed by model equations such as Langmuir and Freundlich isotherms and it was found that the Langmuir isotherm model best fitted the adsorption data. Kinetic analyses were indicative of the complex nature of the heterogeneous photo catalytic process. The formation of intermediates during the degradation of the dye was monitored by ESI-Mass and HPLC analysis.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The inadequacy in the degradation of organic pollutants from industrial effluents by conventional biological, physical and chemical treatment methods has resulted in the development of advanced oxidation processes [1–4]. Through heterogeneous photocatalysis, processes used for the complete mineralization of the environmental contaminants and/or for the efficient conversion of a wide range of chemicals into less harmful products were reported elsewhere [5–9]. In comparison with other AOPs semiconductor-mediated/assisted photocatalysis ranks the foremost due to its ability to photosensitize the complete mineralization of a wide range of organic substrates at ambient temperatures and pressures, without the production of harmful by-products [3,10–15].

Studies on semiconductor metal oxides for photocatalytic applications were focused on the UV-driven TiO₂ photocatalyst [16–21]. Since UV light takes up only ca. 4% of the solar energy in comparison with visible-light that takes up ca. 43%, visible-light-driven photocatalysts gained more importance [22–24]. Moreover, widespread use of TiO₂ was not economical for large-scale water treatment resulting in the search of a suitable alternative for TiO₂ [25–28] and the priority of other metal oxides over TiO₂ [29–33] such as the photocatalytic activity of ZnO was higher than nano-TiO₂. The greatest advantage of ZnO is that

it absorbs larger fraction of solar spectrum and more light quanta than TiO₂ [34].

ZnO is a wide band gap semiconductor with an energy gap of 3.37 eV at room temperature and it is relatively cheap, nontoxic and with holes of strong oxidizing power. It has proven to be active in the photocatalytic oxidation of different organic compounds and in the degradation and complete mineralization of environmental pollutants [4,29,33,35–40].

1.1. Mechanism for photo degradation of dye molecules

Studies on mechanism of ZnO-photocatalyzed reactions has been extensively reported [41]. Though detailed mechanism differs from one pollutant to another, it has been widely recognized that hydroxyl radical •OH acts as the active reagent for mineralization of organic compounds. The mechanism behind the radical formation by scavenging of electron-hole pair by moisture upon irradiation (Eqs. (1)–(4)) is described below.

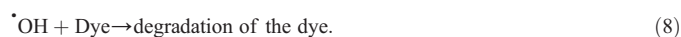


* Corresponding author. Tel.: +91 44 24916706; fax: +91 44 24911589, +91 44 24912150.

E-mail address: arumugamsivasamy@yahoo.co.in (A. Sivasamy).



Furthermore, the electrons present in the conduction band of the catalyst reduce molecular oxygen to superoxide anion (Eq. (5)) which could result in the formation of organic peroxides (Eq. (6)) or hydrogen peroxide (Eq. (7)). Moreover, these electrons are also responsible for the production of hydroxyl radicals (Eq. (8)).



The focus of the present work is to synthesize ZnO and use it in the photocatalytic degradation of AB10B using visible light as the source. The study of AB10B degradation and understanding its reaction kinetics helped to consider actual effluent treatment for the photocatalytic study, in view of its complexity in containing diverse types of dyes and other chemicals. The photo degradation was evaluated by monitoring the changes in the AB10B concentration using UV–Vis spectroscopy and HPLC techniques. The total degradation was assessed in terms of chemical oxygen demand (COD). The present work emphasizes the importance of ZnO as an effective visible photocatalyst for the degradation of AB10B using renewable energy (visible light) as the source.

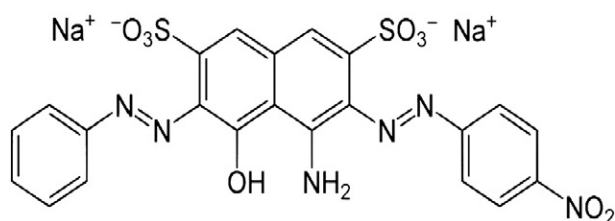
2. Experimental

2.1. Materials

Amido Black 10B dye (AB 10B; C.I. No: 20470; formula weight = 616.5). Zinc acetate ($\text{Zn}(\text{OAc})_2$) was procured from S. D. Fine Chemicals Ltd., Mumbai, India. The chemical structure of AB10B is shown in Scheme 1. Sodium hydroxide (NaOH) was obtained from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. Hydrochloric acid (HCl) was procured from Ranbaxy Fine Chemicals Ltd., New Delhi, India. All the chemicals were of analytical reagent grade quality and were used as received. Solutions were prepared by dissolving appropriate amount of the dye in double distilled water before each experiment.

2.2. Preparation of photo catalyst

ZnO was prepared according to the literature reported elsewhere [42]. The required amount of zinc acetate was taken in a beaker and stirred by a PTFE-coated magnetic paddle at room temperature. NaOH solution was added drop wise to the zinc acetate solution in order to maintain the pH of the mixture at 8. The suspension pH



Scheme 1. Chemical structure of AB10B.

values were adjusted at desired level using dilute NaOH or HCl solutions. The pH values were measured via Digisun pH metre (Model 2001). The white precipitate was filtered and washed several times with double distilled water until the rinses reached to neutral pH and later dried at 110 °C for 12 h. The prepared white powder was ground and calcined at 400 °C for 2 h.

2.3. Analytical methods

The characteristics of the final product of synthesis depend mainly on the experimental parameters [43] like starting materials, experimental temperature, pH of the medium, experimental duration etc. The final product was characterized by X-ray powder diffraction (XRD) analysis employing X' per PRO. Perkin Elmer 6X FT-IR spectrophotometer was used for recording FT-IR spectra. Transmission electron microscope (TEM) images were recorded using a Philips model (Tecna 10) transmission electron microscope and the morphology of catalyst was examined using a JEOL JSM-6360 scanning electron microscope. Diffuse reflectance spectra were recorded using shimadzu UV-2450. The formation of intermediates during the degradation of the dye was monitored by HPLC using a C_{18} column and 25 mM ammonium acetate: methanol (1:1 (v/v)) as mobile phase. The elution profiles were monitored at 254 nm using ESI-Mass spectrometer-LCQ Advantage MAX, Thermo Finnigan.

2.4. Visible light photoreactor studies

The visible light photocatalytic experiments were conducted in a visible light photoreactor equipped with 500 W tungsten lamp as irradiation source supplied by Heber Scientific Company, Chennai, India. The schematic diagram of the visible slurry photoreactor is shown in (SF1). The degradation of AB10B dye with different initial dye concentrations such as 10 ppm, 25 ppm, 50 ppm, 75 ppm and required amount of the catalyst (ZnO) was taken up in glass reactors of which one was exposed to visible light and another was kept in the dark. At specific time intervals aliquot samples were taken from the test solution, filtered and their absorbance was recorded at λ_{max} 619 nm using UV–vis spectrophotometer (Shimadzu UV 2101 PC).

The progress of photo catalytic degradation was also monitored by Chemical Oxygen Demand (COD) analysis measured employing the dichromate closed reflux method [44]. The percentage of degradation (X) was calculated by $X = C_0 - C_e / C_0 \times 100$ where, C_0 is the initial concentration of dye and C_e is the concentration of dye at time interval t .

3. Results and discussion

3.1. Characterization of photo catalyst

The XRD pattern of ZnO catalyst calcined at 400 °C for 2 h in a muffle furnace is shown in (SF2). The sharp and symmetric diffraction peaks observed indicated high crystallinity of the synthesized ZnO and larger particle sizes. Scherrer equation $d = 0.94 \lambda / \beta \cos \theta$ was used to calculate the average crystallite size (30–50 nm) of the calcined sample. λ denotes the wavelength of the radiation equal to 0.154 nm, β is the full width at half maximum (FWHM) and θ is the half diffraction angle. The presence of pure phase of hexagonal zinc oxide (zincite structure) was confirmed from the recorded diffraction peaks.

The SEM picture of the ZnO powders calcined at 400 °C for 2 h in a muffle furnace shown in (SF3) indicated absence of any significant surface porosity. The prepared ZnO was characterized by TEM. As shown in Fig. 1, the size of the ZnO particles uniformly varies from 10 to 20 nm. The FT-IR spectra of ZnO powder (calcined at 400 °C) are shown in (SF4). It was observed that the presence of absorption bands at 532 cm^{-1} confirms the presence of metal–oxide bond in

Download English Version:

<https://daneshyari.com/en/article/5412118>

Download Persian Version:

<https://daneshyari.com/article/5412118>

[Daneshyari.com](https://daneshyari.com)