Ultrasonics Sonochemistry 29 (2016) 27–38

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

Sonocatalytic degradation of Acid Blue 92 using sonochemically prepared samarium doped zinc oxide nanostructures

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ARTICLE INFO

Article history:
Received 2 July 2015
Received in revised form 28 July 2015
Accepted 29 July 2015
Available online 28 August 2015

Keywords:
Sonocatalysis
Degradation
Sm-doped ZnO
Nanocatalyst
Sonocatalyst
Kinetic modeling

ABSTRACT

Pure and Sm-doped ZnO nanoparticles were synthesized applying a simple sonochemical method. The nanocatalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) techniques which confirmed the successful synthesis of the doped sonocatalyst. The sonocatalytic degradation of Acid Blue 92 (AB92), a model azo dye, was more than that with sonolysis alone. The 6% Sm-doped ZnO nanoparticles had a band gap of 2.8 eV and demonstrated the highest activity. The degradation efficiency (DE%) of sonolysis and sonocatalysis with undoped ZnO and 6% Sm-doped ZnO was 45.73%, 63.9%, and 90.10%, after 150 min of treatment, respectively. Sonocatalytic degradation of AB92 is enhanced with increasing the dopant amount and catalyst dosage and with decreasing the initial AB29 concentration. DE% declines with the addition of radical scavengers such as chloride, carbonate, sulfate, and tert-butanol. However, the addition of enhancers including potassium periodates, peroxydisulfate, and hydrogen peroxide improves DE% by producing more free radicals. The results show adequate reusability of the doped sonocatalyst. Degradation intermediates were recognized by gas chromatography–mass spectrometry (GC–MS). Using nonlinear regression analysis, an empirical kinetic model was developed to estimate the pseudo-first-order constants (k_{app}) as a function of the main operational parameters, including the initial dye concentration, sonocatalyst dosage, and ultrasonic power.

1. Introduction

In recent decades, ultrasonic (US) process as an advanced oxidation process (AOP) has been introduced as a possible method for water treatment, and its successful utilization has been reported for the destruction of halogenated hydrocarbons, pesticide components, and dyes. The extensive applications of these dyes lead to the serious pollution of surface and ground water due to the release of colored and toxic effluents, which are resistant to biological treatment [1–3].

Cavitation is induced by ultrasonic irradiation and results in the generation, growth, and collapse of micro-bubbles. These bubbles function as micro-reactors (hot-spot approach) and produce high temperatures in the gaseous contents of a collapsing cavity and the immediate liquid surroundings. Transient supercritical water can also be formed as a consequence of the high localized pressures. These sever conditions can be used to the oxidization of various organic or inorganic contaminants by the dissociation of dissolved oxygen and water molecules to produce reactive oxygen species (ROS), such as $^{\cdot}O_2^-$, $^{\cdot}O$, $^{\cdot}OOH$, and $^{\cdot}OH$ radicals [4,5].

However, degradation rate of organic contaminants by application of sonication is low and hence needs high time and energy; in addition, their complete mineralization rarely occurs [6,7]. To overcome the above-mentioned limitations, the ultrasonic method has been combined with Fe^{2+}, H_2O_2, Fenton reagent, and semiconductor oxides [8,9]. For instance, the presence of appropriate catalysts like semiconductors increases the degradation of organic pollutants considerably, it can be related to the synergistic effect of ultrasound and solid semiconductor named as sonocatalytic process which is an environmentally friendly technique [5,7].

The properties of zinc oxide (ZnO) nanoparticles make it suitable as a sonocatalyst including a wide band gap (3.37 eV), high exciton binding energy (60 meV), and high UV absorption potential [10,11]. However, the main restriction of using undoped ZnO is the

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http://dx.doi.org/10.1016/j.ultsonch.2015.07.026
1350-4177/

fast recombination of the formed electron–hole pairs. Doping the ZnO with rare earth ions is a practical way to enhance its catalytic efficiency [11,12].

Nanoparticles of ZnO have been synthesized via diverse methods, such as chemical precipitation [13], microwave radiation [14], hydrothermal [15] and sol–gel [16] methods. These methods have some drawbacks, including a need for high temperatures and long reaction times. In contrast, the sonochemical technique is very simple, quick, and low-cost [17].

Non-linear regression analysis can be applied to develop an empirical kinetic model for a process when modeling based on exact understanding of the intrinsic elementary reactions is complicated. This method has been used to model several combined AOPs [18,19].

In this study, a convenient sonochemical method has been used to prepare undoped and Sm-doped ZnO nanoparticles. The dopant was incorporated into the ZnO lattice to improve its sonocatalytic activity. Scanning electron microscopy (SEM), and X-ray diffraction (XRD) were utilized to characterize the as-prepared sonocatalysts. X-ray photoelectron spectroscopy (XPS) was used to verify the presence of Sm in the structure of the sonocatalyst. Acid Blue 92 (AB92) was used as a model azo dye to investigate the sonocatalytic activity of the undoped and Sm-doped ZnO nanoparticles compared to the sonication process. To the best of our knowledge, the usage of a sonocatalytic process applying Sm-doped ZnO nanoparticles to degrade AB92 has not been reported previously. The effect of the operational parameters on the DE% was investigated, including the amount of dopant, initial dye concentration, catalyst dosage, ultrasonic irradiation intensity, and also the presence of various radical scavengers and process enhancers. A kinetic model was developed to estimate the reaction rate constant according to nonlinear regression analysis. Eventually, degradation intermediates were identified by gas chromatography–mass spectrometry (GC–MS).

2. Materials and methods

2.1. Chemicals

All chemicals in this research were used without further purification. $Sm(N_3O_9).6H_2O$ and C_2H_5OH (99%) were obtained from Sigma Aldrich (USA). $ZnCl_2$ was provided by Merck (Germany). AB92 (molecular formula = $C_{26}H_{16}N_3Na_3O_{10}S_3$, color index number = 13,390, λ_{max} = 571 nm, M_w = 695.58 g/mol), which is an anionic monoazo dye and obtained from Shimi Boyakhsaz Company (Iran).

2.2. Synthesis of pure ZnO and Sm-doped ZnO nanoparticles

The simple sonochemical synthesis method of ZnO and Sm-doped ZnO nanoparticles was as following: (1) a stoichiometric amount of $Sm(N_3O_9).6H_2O$ was added to a zinc chloride solution to yield various amounts of dopant (2–8% Sm); (2) to attain pH 10, NaOH solution (1 M) was added dropwise to the prepared solution; (3) the precursor solution was sonicated by an ultrasonic bath (Ultra 8060, England) with a frequency of 36 kHz for 3 h; and (4) the resulting white crystalline product was washed with absolute ethanol and with double distilled water and then dried at 80 °C for 12 h.

2.3. Nanocatalyst characterization

SEM was carried out using a TESCAN, MIRA3 (Czech Republic). Microstructure distance-measurement software was applied to determine the size distribution of the as-prepared nanoparticles. XRD analyses of the undoped and Sm-doped ZnO were performed using a Siemens X-ray diffractometer (D8 Advance, Bruker, Germany) with Cu K_α radiation (l = 1.54065 Å) at an accelerating voltage of 40 kV and an emission current of 30 mA.

X-ray photoelectron spectroscopy (XPS) measurements were conducted utilizing a Thermo Scientific spectrometer (K-ALPHA, UK). The band gap of the nanocatalysts was measured by mixing a sample in distilled water and sonicating the solution for 15 min to yield a homogeneous mixture. The absorbance was then recorded between 200 and 800 nm using a UV–vis spectrophotometer (WPA Lightwave S2000, England). The intermediates generated during the AB92 degradation process were detected by an Agilent 6890 gas chromatograph with a 30-m to 0.25-mm HP-5MS capillary column coupled with an Agilent 5973 mass spectrometer (Canada).

2.4. Sonocatalytic degradation procedure

The degradation of AB92 was studied in the presence of different ZnO nanoparticles applying an ultrasonic bath (Ultra 8060, England) at the natural pH of the dye and process time of 150 min. For this experiment, a distinct amount of nanocatalyst was added to 100 mL of AB92 solution with a certain concentration. To eliminate the photocatalysis effect, experiments were performed in the dark. The dye solution containing catalyst was magnetically stirred in the dark for 30 min to establish an adsorption/desorption equilibrium of the dye. Samples of the ultrasonicated solution were withdrawn at particular time intervals, and the solution absorbance was measured by a UV–vis spectrophotometer at maximum absorbance wavelength of the dye (λ_{max} = 571 nm).

3. Results and discussion

3.1. Characterization of ZnO and Sm-doped ZnO samples

Fig. 1(a) and (b) demonstrate the SEM images of the ZnO and 6% Sm-doped ZnO nanoparticles, respectively. Fig 1(a) shows that the pure ZnO nanoparticles are irregular in shape and size compared to the Sm-doped ZnO nanoparticles, which can be attributed to the growth of irregular crystalline grains during the synthesis and their aggregation. As shown in Fig. 1(b), the incorporation of Sm into the ZnO lattice can reduce the aggregation and crystal size and increase the shape uniformity of the doped nanoparticles. moreover, the de-aggregation of the particles by the sonochemical synthesis of the catalyst provides more active sites [20]. Fig. 1(c) demonstrates that most of the size distribution of the 6% Sm-doped nanoparticles is in the range of 40–60 nm with a frequency of 70%.

Fig. 2 illustrates the XRD patterns of the pure and 6% Sm-doped ZnO nanoparticles. The main dominant peaks were identified for pure ZnO at 2θ values of 31.92, 34.6, 36.48, 47.68, 56.72, 63, 66.08, 68, 68.28, 71.64, and 75.96°, which are related to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) planes of hexagonal wurtzite ZnO, respectively (JCPDS Card 36-1451) [21]. The identical peaks were observed for the doped ZnO without any diffraction peaks from samarium oxides or other impurities. The diffraction values of the (100), (002), and (101) planes revealed a shift to lower angles in the case of the Sm-doped ZnO in comparison with the pure ZnO, indicating the proper doping of Sm^{3+} ions into the ZnO. This shift can be described by the expansion of the ZnO lattice through samarium doping due to the larger ionic radius of Sm^{3+} (0.964 Å) compared to Zn^{2+} (0.74 Å).

Fig. 3 shows the XPS survey spectra of 6% Sm-doped ZnO nanoparticles, where it is obvious that there are Zn, O, C, and Sm peaks on the surface of the sample. The corresponding energies