Development of an empirical kinetic model for sonocatalytic process using neodymium doped zinc oxide nanoparticles

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ABSTRACT

The degradation of Acid Blue 92 (AB92) solution was investigated using a sonocatalytic process with pure and neodymium (Nd)-doped ZnO nanoparticles. The nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). The 1% Nd-doped ZnO nanoparticles demonstrated the highest sonocatalytic activity for the treatment of AB92 (10 mg/L) with a degradation efficiency (DE%) of 86.20% compared to pure ZnO (62.92%) and sonication (45.73%) after 150 min. The results reveal that the sonocatalytic degradation followed pseudo-first order kinetics. An empirical kinetic model was developed using nonlinear regression analysis to estimate the pseudo-first-order rate constant (k_{app}) as a function of the operational parameters, including the initial dye concentration (5–25 mg/L), doped-catalyst dosage (0.25–1 g/L), ultrasonic power (150–400 W), and dopant content (1–6% mol). The results from the kinetic model were consistent with the experimental results ($R^2 = 0.990$). Moreover, DE% increases with addition of potassium periodate, peroxydisulfate, and hydrogen peroxide as radical enhancers by generating more free radicals. However, the addition of chloride, carbonate, sulfate, and t-butanol as radical scavengers declines DE%. Suitable reusability of the doped sonocatalyst was proven for several consecutive runs. Some of the produced intermediates were also detected by GC–MS analysis. The phytotoxicity test using *Lemna minor* (*L. minor*) plant confirmed the considerable toxicity removal of the AB92 solution after treatment process.

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1. Introduction

The application of ultrasonic processes in advanced oxidation processes (AOPs) has been proposed recently for the treatment of various hazardous organic compounds, including halogenated hydrocarbons, pesticides components, and dyes in aqueous mediums [1–3]. Considerable amounts of dyes (up to 20%) can be lost in effluents during dyeing processes in the textile industry, which results in serious pollution of surface and ground waters that are resistant to biological treatment [4]. Sonication with a simple mechanism is an inexpensive solution to overcome this problem that can be used in ambient conditions.

The origin of the sonochemical effects is cavitation, which involves the generation, growth, and implosion of micro-bubbles within the liquid medium acting as localized micro-reactors (a hot-spot approach). This collapse generates high temperature and pressure in the collapsing cavities and in the liquid immediately surrounding them (the interface area) [5,6]. Consequently, thermal cleavage of water occurs as the liquid and dissolved oxygen molecules produce reactive oxygen species (ROS), including $\cdot O_2^-$, $\cdot O$, $\cdot OOH$, and in particular $\cdot OH$ radicals. The hydroxyl radical ($\cdot OH$) as a strong oxidizing agent, reacts with pollutants effectively and unselectively to degrade them without generating secondary waste. [7,8].

However, the degradation rate of organic pollutants by ultrasonic processes is low, and complete mineralization rarely occurs [9,10]. To overcome these drawbacks, the ultrasonic method can be combined with Fe^{2+}, H_2O_2, Fenton reagent, and semiconductor oxides to increase the production of $\cdot OH$ radicals [11,12]. For example, using appropriate catalysts (heterogeneous catalysis) like semiconductors (heterogeneous catalysis) can accelerate the sonochemical reactions by a synergistic effect of ultrasound and the solid semiconductor in the sonocatalytic process in an environmentally friendly coupled technique [8,9].

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Among the diverse catalysts, zinc oxide (ZnO) nanoparticles have attracted particular attention for properties such as a wide band gap (3.37 eV), high UV absorption potential, and high exciton binding energy (60 meV) [13]. Doping with rare-earth metals (REMs) is a practical way to increase the catalytic activity of ZnO by preventing fast recombination of the electron–hole pairs in the doped semiconductor [10,14]. The advantages of sonochemical methods for nanostructured material synthesis are the simple experimental conditions, quick procedure, and low cost compared to conventional methods [15].

Using intrinsic elementary reactions as a basis for a kinetic model is one of the best methods for model development because it involves exact understanding of the process reactions and the influences of the operational parameters [16–18]. However, this kind of modeling is sometimes difficult due to the diversity of reactions, particularly for coupled processes [19,20]. Empirical kinetic modeling of a process via non-linear regression analysis provides a nonlinear model that can be used for complicated combined AOPs, including photoelectro-Fenton and US/UV/H_2O_2 processes [19,21]. The validity of empirical modeling has been evaluated by comparing experimental and theoretically calculated data [22].

In this study, a simple sonochemical method was used to synthesize pure and Nd-doped ZnO nanoparticles. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the prepared sonocatalysts. X-ray photoelectron spectroscopy (XPS) was used to confirm the presence of Nd in the catalyst structure. AB92 was treated as a model organic azo dye to determine the sonocatalytic activity of pure and Nd-doped ZnO nanoparticles, and the results were compared to those of sonolysis alone. To the best of our knowledge, sonocatalysis using Nd-doped ZnO nanoparticles for the degradation of AB92 has not been studied previously. Non-linear regression analysis was used to develop an empirical kinetic model considering the effect of the main operational parameters on k_{app}, including initial dye concentration, doped-catalyst dosage, ultrasonic power, and dopant content. The effects of various process enhancers and radical scavengers on the dye degradation efficiency (DE%) were studied. Finally, some of the intermediates generated during the sonocatalytic process were detected by GC–MS technique.

2. Materials and methods

2.1. Chemicals

All chemicals were analytical grade and used without further purification. $ZnCl_2$ was provided by Merck, Germany. Ethanol (C_2H_5OH, 99%) and neodymium chloride ($NdCl_3.6H_2O$) were purchased from Sigma Aldrich, USA. Acid Blue 92 (molecular formula = $C_{26}H_{16}N_3Na_3O_{10}S_3$, λ_{max} = 571 nm, M_w = 695.58 g/mol, color index number = 13,390), as an anionic monoazo dye, was obtained from Shimi Boyakhsaz Company (Iran).

2.2. Undoped ZnO and Nd-doped ZnO nanoparticles synthesis procedure

Undoped ZnO and Nd-doped ZnO nanoparticles were sonochemically synthesized as follows: (1) a molar pre-specified amount of $NdCl_3 \cdot 6H_2O$ was added to an aqueous solution of zinc chloride, (2) NaOH solution (1 M) was added dropwise to the prepared solution to set the pH to 10, (3) the obtained solution was sonicated for 3 h by an ultrasonic bath (Ultra 8060, England) with a frequency of 36 kHz, and (4) the resulting white crystalline product was washed with double distilled water and ethanol and dried at 80 °C for 12 h.

2.3. Characterization of nanocatalysts

XRD of the undoped and Nd-doped ZnO was conducted using a Siemens X-ray diffractometer (D8 Advance, Bruker, Germany) with Cu K$_\alpha$ radiation (l = 1.54065 Å), an accelerating voltage of 40 kV, and an emission current of 30 mA. The surface morphology of the synthesized catalysts was investigated by SEM (TESCAN, MIRA3, Czech Republic), and a thermo scientific spectrometer (K-ALPHA, UK) was used for XPS measurements. The band gap of the nanocatalysts was measured by preparing a sample solution in distilled water and sonicating it for 20 min to obtain a homogeneous mixture. Microstructure distance-measurement software (Microstructure Measurement version 1.0) was applied to determine the size distribution of the as-prepared nanoparticles. The solution absorbance was recorded between 200 and 800 nm using an UV–Vis spectrophotometer (WPA lightwave S2000, England). Some of the intermediates during the sonocatalytic degradation of AB92 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 of the dye

Sonocatalytic degradation experiments of AB92 were done for 150 min each using an ultrasonic bath (Ultra 8060, England) with a frequency of 36 kHz at the natural pH of the dye in the presence of various ZnO nanoparticles. A certain amount of nanocatalyst was added to 100 mL of AB92 solution with a specified concentration, and the prepared solution was sonicated in the dark to eliminate the photocatalysis effect. A typical sample of the ultrasonically treated solution was withdrawn at distinct process times, and the AB92 solution absorbance was measured using the UV–Vis spectrophotometer at its maximum absorbance wavelength (λ_{max} = 571 nm).

3. Results and discussion

3.1. Characterization of undoped ZnO and Nd-doped ZnO

Fig. 1 illustrates the X-ray diffraction patterns of pure and 1% Nd-doped ZnO nanoparticles. The main peaks were identified for undoped ZnO at 2 θ 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) [23]. Identical peaks for the doped ZnO were seen without any diffraction peaks from neodymium oxides or other impurities. The diffraction values of the (100), (002), and (101) planes revealed a shift to lower angles in the case of Nd-doped ZnO compared to pure ZnO, indicating appropriate doping of Nd ions into the ZnO lattice. This shift can be explained by the expansion of the ZnO lattice through doping by neodymium due to the larger ionic radius of Nd^{3+} (0.983 Å) in comparison with Zn^{2+} (0.74 Å).

Fig. 2a and b demonstrate SEM images of the undoped ZnO and 1% Nd-doped ZnO nanoparticles, respectively. Fig. 2a shows that the undoped ZnO nanoparticles are irregular in shape and size in comparison with the Nd-doped ZnO nanoparticles, which is related to the growth of irregular crystalline grains during the synthesis and their aggregation. Fig. 2b shows that the incorporation of Nd into the crystal structure of ZnO can decrease the aggregation phenomenon and hence reduce the size of nanoparticles and improve the shape uniformity of them. The presence of the Nd dopant decreases the crystal size of Nd-doped ZnO sample, which was mainly attributed to the generation of Nd–O–Zn on the surface of