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Europium-doped ZnO as a visible light responsive nanocatalyst: Sonochemical synthesis, characterization and response surface modeling of photocatalytic process

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ABSTRACT

Pure and Eu-doped ZnO nanostructures with different amounts of Eu were synthesized using a simple sonochemical method. The as-synthesized samples were characterized by X-ray diffraction, scanning electron microscopy, UV–Vis spectroscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The photocatalytic activity of as-prepared Eu-doped ZnO was investigated based on the decolorization of Acid Red 17 (AR17) under visible light irradiation. The decolorization efficiency was found to be 25.2%, 55.6%, 63.1% and 30.3% for undoped, 1% Eu-ZnO, 3% Eu-ZnO and 5% Eu-ZnO, respectively. Using 3% Eu-doped ZnO nanoparticles, the decolorization efficiency reached 100% by adding 0.1 mM $S_2O_8^{2-}$. Response surface methodology based on five-level central composite design was applied to model and optimize the decolorization of AR17 over 3% Eu-doped ZnO/$S_2O_8^{2-}$. Accordingly, the value of correlation coefficients (R^2 = 0.970 and adjusted-R^2 = 0.935) obtained from analysis of variance confirmed the adequacy of fitted model. The maximum decolorization efficiency of 99% was achieved at an initial dye concentration of 5 mg/L, catalyst dosage of 1.25 g/L, $S_2O_8^{2-}$ concentration of 0.25 mM and reaction time of 150 min. The decolorization efficiency decreased only 7% after 4 repeated runs.

1. Introduction

The presence of organic dye in aqueous environments can cause detrimental effects on aquatic life and subsequently human health. Therefore, in recent years, advanced oxidation processes (AOPs) have been applied widely for the degradation of organic dyes in aqueous phase [1]. One of the most effective AOPs for the degradation of organic dyes is photocatalysis. Among various photocatalysts used in the photocatalysis, ZnO as a semiconductor has gained more attention due to its large area-to-volume ratio, wide band gap (E_g = 3.37 eV), high photosensitivity and large excitation binding energy (60 meV) [2–4]. Moreover, ZnO has a hexagonal wurtzite crystalline structure and its nanostructures are commonly used in the fields of photocatalysis, sensors and desensitized solar cells because of its good optical, electrical and chemical properties [5,6].

When ZnO nanoparticles are irradiated with UV light or solar irradiation containing photonic energy of equal to or greater than their E_g, the excitation of electrons from the valence bands to conduction bands generates electron–hole pairs. The reaction between generated holes and H_2O or OH^- forms hydroxyl radicals (•OH), and the combination of generated electrons with O_2 forms superoxide radicals ($•O_2^-$). These radicals both are strong oxidizing agents to degrade refractory organic compounds like organic dyes and convert them into harmless materials such as H_2O and CO_2 [7].

One of the main drawbacks of pure ZnO is high recombination rate of the generated electron–hole pairs. Accordingly, the improvement of photosensitivity of ZnO nanoparticles under visible light irradiation using doping agents has been considered [1]. Doping with metals or metal oxides is an effective technique to prevent the recombination of photo-induced electron–holes, reduction of band gap energy, and so shifting the absorption band to the visible region in photocatalysis [8–10]. The physical and chemical properties, such as luminescence, electronic and optical properties

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of semiconductors can be modified by doping with an appropriate element. In the last years, among various dopants, the rare earth elements as trivalent lanthanide (Ln^{3+}) ions have been investigated to improve the photocatalytic activity of ZnO [8,11–14].

In the literatures, different techniques have been reported to synthesize ZnO such as solvothermal [15,16] and hydrothermal reactions [17,18], micro-wave radiation [19,20], ultrasonic and microwave combination [21,22] and sol–gel method [23]. In this regard, the development of other facile methods for the synthesis of materials with short reaction time under a moderate condition is of great interest. Sonochemistry is one of the promising methods to synthesize nanomaterials such as ZnO. Under ultrasonic radiation, molecules undergo chemical reaction by acoustic cavitation-formation (nucleation) of bubbles, growth by diffusion of solute atoms into the bubbles and mechanical collapse of critical-sized bubbles in the bulk solution. The temperature and cooling rate during collapsing (<1 ns) are very high (5000–25,000 K, >1011 K/s), leading to the breaking of chemical bonds. When volatile precursors are used, gas phase reactions are predominant and amorphous nanomaterials are prepared. For non-volatile precursors, the nanoamorphous particles and nanocrystals are synthesized. The molecules vibration during sonication process can cause homogenization of concentration and temperature in the solution. In addition, the radiation improves the reaction rate and results in the fabrication of pure products [24–26].

In our recent related studies, we have studied the sonocatalytic degradation of textile dyes by Gd-doped and Pr-doped ZnO nanoparticles synthesized through sonochemical process [27,28]. The relatively high energy consumption in the sonocatalytic process may restrict its application in large scales. So, it is very important to investigate and introduce the conditions in which these catalysts can degrade the pollutants under a mild condition and low energy consumption. Therefore, in this study, we focused on the photocatalytic activity of europium (Eu)-doped ZnO under visible light only. In this regard, Eu-doped ZnO nanoparticles were first synthesized through sonochemical method. The structural and optical characteristics of as-prepared samples were systematically examined. Then, to investigate the photocatalytic activity of undoped and Eu-doped ZnO nanoparticles under visible light irradiation, Acid Red 17 (AR17) as an azo dye was used. A one-factor-at-a-time statistical approach requires a large number of experiments; which is time-consuming. Additionally, evaluation of the interactive effects of operational parameters is not possible [29]. Thus, to better evaluate the efficiency of the decolorization process, response surface methodology (RSM) based on central composite design (CCD) was used to assess the effect of studied parameters (initial dye concentration, catalyst dosage, peroxydisulfate concentration and retention time) on the photocatalytic degradation of AR17. CCD was used due to its advantages over the conventional "one-factor-at-a-time" method, including reduced the number of experimental runs and subsequently low experimental costs, capability to evaluate the interactive effects of the operational parameters and possibility to optimize the operational parameters for maximum removal efficiency. In this respect, five-level CCD was applied to model and optimize the process in a batch flow mode reactor.

2. Materials and methods

2.1. Materials

All used chemicals were of analytical grade and used without further purification. $C_6H_9EuO_6{\cdot}xH_2O$ and C_2H_5OH (99%) were purchased from Aldrich, USA. NaOH and $ZnCl_2$ (99.5%) was purchased from Merck, Germany and AR17 (a mono-azo dye with molecular weight of 502.435 g/mol and λ_{max} of 510 nm) was purchased from Shimi Boyakhsaz Co. (Iran). The characteristics of the AR17 are displayed in Table S1 (Supplementary data).

2.2. Sonochemical synthesis of undoped and Eu-doped ZnO

Undoped and Eu-doped ZnO nanostructures with variable Eu mole fractions (0, 1, 3 and 5% mol) were synthesized through sonochemical method as follows: $ZnCl_2$ was dissolved in double distilled water and different amounts of $C_6H_9EuO_6{\cdot}xH_2O$ were added to the above solution. NaOH solution (1 M) was added to the resulted mixture until the pH reached 10. Then, the mixture was sonicated in a bath type sonicator (sonica, 2200 EP S3, Italy) with a frequency of 40 kHz for 3 h. Finally, the resulted white solid products were washed with distilled water and absolute ethanol and dried at 80 °C for 12 h.

2.3. Characterization methods

To identify the crystalline structure and phase purity of the synthesized photocatalyst samples, XRD characterization was carried out at room temperature using a Siemens X-ray diffractometer (D5000, Germany), Cu Kα radiation (l = 1.54065 Å), an accelerating voltage of 40 kV and an emission current of 30 mA. Scanning electron microscopy (SEM) was applied to evaluate morphology and surface structure of undoped and Eu-doped ZnO nanoparticles using a Hitachi microscope (Model: S-4200, Japan). Chemical composition of the samples was analyzed using X-ray photoelectron spectroscopy (XPS) by thermo scientific spectrometer (K-ALPHA, UK). Fourier transform infrared spectroscopy (FT-IR) was carried by a Bruker spectrometer (Tensor 27, Germany), in the wavenumber range of 400–4000 cm^{-1} on KBr pellets with a 2 cm^{-1} resolution. Furthermore, a UV–Vis spectrophotometer)lightwave S2000, England) was applied to record UV–Vis spectra of the samples.

2.4. Photocatalytic activity and experimental procedure

The photocatalytic performance of undoped and Eu-doped ZnO nanoparticles was investigated by the decolorization of aqueous solution of AR17 under visible light irradiation. In a typical approach, 0.1 g of the photocatalyst was mixed with 100 mL of solution containing 5 mg/L AR17. Then, the mixture of photocatalyst and AR17 was stirred in a quartz photoreactor in the dark for 20 min to reach an adsorption/desorption equilibrium. The results of our preliminary studies showed that the adsorption of AR17 onto as-prepared photocatalyst reached equilibrium within 20 min. The light source was a 100 W visible lamp (Pars Co, Iran). The intensity of the lamp with a distance of 4.5 cm from the surface of solution was 25 W/m^2. The radiation intensity was measured with a UV–Vis radiometer purchased from Cassy Lab Company (Germany).

The residual concentration of AR17 in the solution was measured by using a UV–Vis spectrophotometer at a maximum wavelength of 510 nm. The color removal efficiency (CR %) was calculated using Eq. (1):

$$CR(\%) = \left[1 - \left(\frac{C}{C_0}\right)\right] \times 100 \quad (1)$$

where C_0 and C are the initial and final concentration of the AR17 in the solution, respectively. All of the experiments were performed thrice and the mean values were written down to check precision of the obtained results.