Sonochemical synthesis of Pr-doped ZnO nanoparticles for sonocatalytic degradation of Acid Red 17

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ABSTRACT

Undoped and Pr-doped ZnO nanoparticles were prepared using a simple sonochemical method, and their sonocatalytic activity was investigated toward degradation of Acid Red 17 (AR17) under ultrasonic (US) irradiation. Synthesized nanoparticles were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) techniques. The extent of sonocatalytic degradation was higher compared with sonolysis alone. The decolorization efficiency of sonolysis alone, sonocatalysis with undoped ZnO and 5% Pr-doped ZnO was 24%, 46% and 100% within reaction time of 70 min, respectively. Sonocatalytic degradation of AR17 increased with increasing the amount of dopant and catalyst dosage and decreasing initial dye concentration. Natural pH was favored the sonocatalytic degradation of AR17. With the addition of chloride, carbonate and sulfate as radical scavengers, the decolorization efficiency was decreased from 100% to 65%, 71% and 89% at the reaction time of 70 min, respectively, indicating that the controlling mechanism of sonochemical degradation of AR17 is the free radicals (not pyrolysis). The addition of peroxydisulfate and hydrogen peroxide as enhancer improved the degradation efficiency from 79% to 85% and 93% at the reaction time of 50 min, respectively. The result showed good reusability of the synthesized sonocatalyst.

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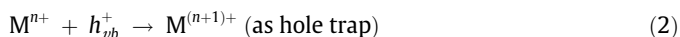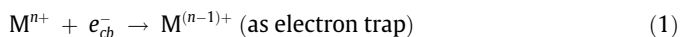
1. Introduction

Organic dyes are one of the many new chemicals which have been widely used in leather, textile, pulp and paper, cosmetic and pharmaceutical industries [1]. Due to their large-scale production and extensive applications, organic dyes have become an integral part of industrial wastewaters which are generally toxic and resistant to degradation by biological treatment methods. Therefore, conventional treatment methods are ineffective for degradation and mineralization of organic dyes [2,3]. Recently, great attention has been paid to the application of ultrasound as an advanced oxidation process (AOP) for water and wastewater treatment due to its high efficiency and easy to operation. Ultrasonically induced cavitation effects can be very effective in the degradation of organic compounds in aqueous phase [3]. Sonochemical degradation involves ultrasound waves to produce rapid growth and collapse of a bubble producing extremely high temperature and pressure conditions inside the bubble [4]. The temperature near the bubbles is high and the resulting thermal dissociation of water results in the formation of hydroxyl radicals which oxidize the substances near them [5]. Ultrasound has been used for the wastewater treatment of various pollutants e.g. organic dyes, organic sulfur compounds, aromatic compounds and so on [6]. However, degradation of organic compounds using ultrasound consumes large amounts of energy and complete mineralization of organic pollutants rarely happens by applying sonolysis alone [3,7]. To overcome these limitations, ultrasonic treatment of wastewater can be used in the presence of suitable catalyst (sonocatalyst). According to literature, semiconductors are used as efficient sonocatalysts [8–10]. Researches indicate that there is similarity in the mechanisms of sonocatalytic and photocatalytic reactions. Sonocatalytic reactions involve the formation of electron–hole pairs on the surface of catalyst, which their formation is critical during sonocatalytic

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degradation [9,11,12]. Among different catalysts, ZnO has been widely used in the catalytic processes for removing organic dyes because of its wide band gap (3.37 eV) and low cost [8,13–16]. The main disadvantage of pure ZnO nanoparticles is the fast recombination rate of the generated electron–hole pairs [17]. Hence, to improve the sonocatalysis efficiency, the electron–hole pair recombination must be hindered. For this purpose, modification of ZnO nanoparticles through metal ion doping is considered as one of possible ways to decrease the probability of recombination of the generated electron–hole pairs as shown in Eqs. (1) and (2) [5,8,18]:

$$M^{n+} + e_{cb}^{-} \rightarrow M^{(n-1)+} \text{ (as electron trap)} \tag{1}$$

$$M^{n+} + h_{vb}^{+} \rightarrow M^{(n+1)+} \text{ (as hole trap)} \tag{2}$$

If the $M^{n+}/M^{(n-1)+}$ pair is less negative than the ZnO conduction band edge and the energy level for $M^{n+}/M^{(n+1)+}$ is less positive than ZnO valence edge, the trapping of electrons and holes would happen on the surface affecting the lifetime of charge carriers.

In the present study, a simple sonochemical method has been introduced to the synthesis of undoped and Pr-doped ZnO nanoparticles. Pr was incorporated into ZnO lattice to improve its sonocatalytic activity. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to characterize as-prepared sonocatalysts. In addition, X-ray photoelectron spectroscopy (XPS) was utilized to verify the presence of Pr in the sonocatalyst structure. Acid Red 17 (AR17) was used as model organic dye to evaluate sonocatalytic activity of undoped and Pr-doped ZnO nanoparticles under ultrasonic irradiation. To the best of our knowledge and on the basis of the literature review, the application of sonochemical method for the preparation of Pr-doped ZnO nanoparticles and its potential for the sonocatalytic degradation of AR17 has not been investigated. In the following, the effect of various parameters such as amount of dopant, catalyst dosage, initial dye concentration, initial pH, intensity of ultrasonic irradiation and presence of various radical scavengers and process enhancers on the decolorization efficiency was investigated.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were of analytical grade and used without further purifications. $C_2H_5OH\cdot4H_2O$ (%99) solution and $Pr(NO_3)_3\cdot6H_2O$ (99.99%) were purchased from Sigma Aldrich, USA. NaOH and $ZnCl_2$ (%99.5) was purchased from Merck, Germany. AR17 was prepared from Shimi Boyakhsaz Co., Iran. The characteristics of the dye are reported in Table 1.

2.2. Synthesis of ZnO and Pr-doped ZnO nanoparticles

ZnO and Pr-doped ZnO nanoparticles were synthesized using a simple sonochemical method. For preparation of Pr-doped ZnO nanoparticles with different amount of dopant (0–5%), stoichiometric amount of $Pr(NO_3)_3\cdot6H_2O$ was added to $ZnCl_2$ solution. Then, 1 M NaOH solution was added dropwise to above solution until the pH reached to 10. The precursor solution was then irradiated by a bath type sonicator (sonica, 2200 EP S3, Italy) with a frequency of 50–60 Hz for 3 h. Finally, the obtained white precipitate was washed thrice with absolute ethanol and distilled water, and dried at 80 °C for 12 h to achieve the crystalline structure.
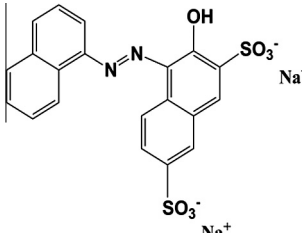
2.3. Characterization of the synthesized samples

The crystalline phase composition of as-prepared samples was identified through X-ray diffraction (XRD) by using a Siemens X-ray diffractometer (D8 Advance, Bruker, Germany), Cu Kα radiation (l = 1.54065 Å), an accelerating voltage of 40 kV, and an emission current of 30 mA. The surface morphology of ZnO and Pr-doped ZnO samples were examined via scanning electron microscopy (SEM) by means of a Hitachi microscope (Model: S-4200, Japan). For TEM observations, the as-prepared sample was dispersed in the ethanol using ultrasonic vibration (Sonorex Bandelin Digi Tec, UK) for 15 min, and then a drop of dispersed sample was placed on a copper grid coated with a layer of amorphous carbon. TEM images were recorded by a Cs-corrected high-resolution TEM (Model: JEM-2200FS, JEOL, Japan) operated at 200 kV. Chemical compositions and chemical states of the samples were analyzed using X-ray photoelectron spectroscopy (XPS) by Thermo Scientific spectrometer (Model: K-ALPHA, UK). A Tensor Fourier transform infrared (FT–IR) spectroscope (Model: Tensor 27, Bruker, Germany) was employed to examine the chemical bonds on the samples, in the wavenumber range of 400–4000 cm^{-1} on pellets obtained by mixing the samples in KBr. For determination of band gap of undoped and Pr-doped ZnO nanoparticles, the sample was well dispersed in distilled water by sonication for 15 min to form a homogeneous suspension, and then optical absorption spectra of samples were recorded using UV–Vis spectrophotometer (WPA lightwave S2000, England) in wavelength range between 200 and 700 nm at room temperature.

2.4. Sonocatalytic degradation of AR17

Decolorization of AR17 was investigated in the presence of undoped ZnO and Pr-doped ZnO nanoparticles using ultrasonic bath (Sonica, 2200 EP S3, Italy). In a typical manner, 100 mL of AR17 solution with initial concentration of 10 mg/L containing 100 mg sonocatalysts was sonicated with a frequency of 50–60 Hz and 400 W output power at natural pH. The reactions were performed in dark environment to eliminate the effects of

Table 1
Characteristics of Acid Red 17.

Dye	Chemical structure	Molecular formula	Color index number	λ_{max} (nm)	M_w (g/mol)
C.I. Acid Red 17		$C_{20}H_{12}N_2Na_2O_7S_2$	16180	510	502.435