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Photocatalytic activity of AgI sensitized ZnO nanoparticles under visible light irradiation

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ABSTRACT

Nanoparticles of zinc oxide (ZnO) sensitized with silver iodide (AgI) were synthesized by a chemical precipitation method and were found to be a visible light driven photocatalyst. The characterization of prepared photocatalyst was studied using UV–visible diffuse reflectance spectroscopy (UV–vis-DRS), X-ray powder diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS). Average crystallite size determined by XRD was 21.56 nm for ZnO and 23.44 nm for AgI sensitized ZnO (AgI-ZnO). The photocatalytic efficiency of AgI-ZnO was evaluated by the decolorization of rosaniline hydrochloride dye (RA) under visible light irradiation. The influence of various operational parameters such as the effect of pH, catalyst dosage and initial dye concentration on the photodecolorization was investigated in detail. The removal percentage of chemical oxygen demand (COD) and total organic carbon (TOC) was determined to evaluate the mineralization of RA during photodecolorization. Maximum decolorization, COD removal and total organic carbon (TOC) reduction were 88%, 75% and 68% respectively, under the optimum conditions.

1. Introduction

Almost every industry uses dyestuffs to dye their products. Over 7×10^5 tons and approximately 10,000 different types of dyes and pigments are produced worldwide annually. It is estimated that 10% to 15% of the dye is lost in the effluent during the dyeing process. Recent reports reveal that several color-causing substances are microtoxic to aquatic biota [1,2]. Amongst the different industrial wastewaters with different types of color-causing substances, synthetic textile organic dye wastes occupy a prominent position. As international environmental standards are becoming more stringent, technological systems for the removal of such dyes have been developed. The treatment of textile wastewaters in order to reduce visual color and dissolved organic contaminants to meet the increasing environmental demands has continued to attract the interest of research groups [3,4]. Traditional techniques, such as coagulation/flocculation, membrane separation (ultrafiltration, reverse osmosis) and biological methods are totally ineffective to decolorize these dyes due to its stability and complex atomic structure.

In recent years, advanced oxidation processes (AOPs) have been identified as an attractive option for wastewater purification, particularly in cases where the contaminant species are difficult to be removed using biological or physicochemical processes. AOP generates powerful oxidizing agent (hydroxyl radical), which completely destroys the pollutants in wastewater quickly and nonselectively [5–7]. Moreover, this process utilizes cheaply available nontoxic semiconductors (TiO_2, ZnO) for total mineralization of organic compounds to CO_2, water and mineral acids. Though TiO_2 is the most commonly used photocatalyst for a wide range of organic compounds, ZnO is found to be a suitable alternative to TiO_2. ZnO is a potential semiconductor with a wide band gap (3.37 eV) and a large exciton binding energy of 60 meV [8], used in solar cells [9], gas sensors [10], optoelectronic devices [11], light emitting diodes [12] and also used as photocatalyst for the degradation of microorganisms [13,14]. Its higher efficiency than TiO_2 has been found in the photocatalytic oxidation of pulp mill bleaching wastewater [15], 2-phenylphenol [16] and phenol [17]. When irradiation has energy greater than the band-gap energy of ZnO, the electrons in the valence band (VB) will be excited to the conduction band (CB), and thus form electron-hole pairs. These energetically excited species are mobile and capable of initiating surface chemical reactions, usually by the production of highly oxidative hydroxyl and superoxide radicals at the semiconductor interface. They are unstable, and recombination of electron-hole pair occurs very fast, dissipating the input energy as heat. Photocatalytic efficiency depends on the competition between these two processes, that is, the ratio of surface charge carrier transfer rate to the electron-

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hole pair recombination rate. If recombination process occurs too fast, the other surface chemical reactions do not occur. In order to improve the dispersion and to avoid the fast recombination of photogenerated electron-hole pairs and increase the photocatalytic efficiency, it is necessary to modify the surface of ZnO nanoparticles [18–22].

Silver halide (AgX; X = Cl, Br, I) is an important photosensitive material extensively used in photography. Under visible light, AgX absorbs a photon and generates an electron and a positive hole. If the photographic process (i.e. interstitial ions combined with electrons to form silver atoms) is inhibited, the generated electron and hole can be used in the photocatalytic process. Recently, a great deal of attention has been paid to certain variety of AgX based composite photocatalysts. The general way is loading AgX grains as visible light active components on different substrates, like SiO_2 [23], TiO_2 [24–31], Al_2O_3 [32–34], Al-MCM-41 [35], Y-zeolite [36], Fe_3O_4 [37], BiOI [38], H_2WO_4 [39,40] and Bi_2WO_6 [41,42] to form composite catalysts. Such supported AgX catalysts can display high photocatalytic activity and also maintain optical stability to some extent. The probable reason is that electron-hole pairs are efficiently separated by the metal silver on the surface of the catalysts or the heterojunction structure is formed between AgX and substrate.

The dye “rosaniline hydrochloride (RA)” was chosen as a model compound for the present study. RA is used to color fabrics, paper and as biological stain, also used as disinfectant and topical antifungal agent. Though, RA has several advantages in textile and photographic industries, it causes severe health problems. It is considered as a highly toxic dye and its touch can cause skin and eye irritations to human beings. M. Saquib and M. Muneer have reported the photocatalytic degradation of RA in aqueous suspensions of TiO_2 [43].

To the best of our knowledge, the photodecolorization of RA using AgI-ZnO has not been studied. Hence, in the present work we intent to study the photodecolorization of RA in water under visible light irradiation using AgI-ZnO. Influence of operating parameters on the photodecolorization, such as the pH, catalyst dosage and initial concentration of RA was all evaluated in detail. In addition the decolorization was also assessed in terms of chemical oxygen demand (COD) and total organic carbon (TOC).

2. Materials and methods

2.1. Materials

All the chemicals employed were of analytical grade and applied without further purification. Double distilled water was used throughout for all experiments.

2.2. Synthesis of photocatalyst, AgI-ZnO

ZnO nanoparticles were synthesized according to the procedure described by Chen et al. [44]. In a typical synthesis, 4.16 g of $ZnSO_4 \cdot 7H_2O$ (0.1 M) and 3.36 g of $NaHCO_3$ (0.2 M) were separately dissolved in 200 mL of water. Then $NaHCO_3$ solution was added drop wise into zinc sulfate solution with constant stirring. And then, the precipitates derived from the reaction between $ZnSO_4 \cdot 7H_2O$ and $NaHCO_3$ solutions were collected by filtration and rinsed three times with water and ethanol. Subsequently, the washed precipitates were dried at 80 °C to form the precursors of ZnO. Finally, the precursors were calcined at a temperature of 350 °C for 3 h in a muffle furnace to obtain the nano-sized ZnO particles.

AgI-ZnO was prepared by the deposition–precipitation method. ZnO with 10% Ag content was prepared by the following procedure: 1 g quantity of ZnO was added to 100 mL of distilled water, and the suspension was sonicated for 30 min. Then, 0.205 g of KI was added to the suspension, and the mixture was stirred magnetically for 30 min, then, 0.21 g of $AgNO_3$ in 2.3 mL of ammonium hydroxide (25 wt.% NH_3) was quickly added to the mixture with vigorous stirring. The molar ratio of Ag^+/I^- was 1:1. The resulting pale yellow color suspension was stirred at room temperature for 12 h. The product was filtered, washed with water, dried at 75 °C, and subsequently sintered in a muffle furnace at 100 °C for 2 h.

2.3. Characterization

The UV–vis-DRS spectral measurements were performed with a JASCO V-550 double beam spectrophotometer with PMT detector. X-ray diffractions were collected at 25 °C using XPERT PRO X-RAY diffractometer with Cu k_α radiation. Scanning electron microscopy (SEM) observations were performed by means of a JSM 6701F-6701 instrument in both secondary and backscattered electron modes. The elemental analysis was studied by an energy dispersive X-ray spectroscopy (EDS) attached to the SEM. pH was monitored using EUTECH instrument pH meter. Photocatalytic experiments were performed in a HEBER immersion type photoreactor (HIPR-Compact — p-8/125/250/400). Absorption spectra were recorded using a JASCO V-530 UV–vis spectrophotometer. Total organic carbon (TOC) was determined using a TOC analyzer (TOC-VCSH-Shimadzu) programmed by TOC-Control-V software.

2.4. Procedure for evaluation of photocatalytic activity

100 mL of aqueous solution of RA was put into the cylindrical glass vessel equipped with a circulating water jacket to maintain constant temperature, in which air was bubbling continuously from the bottom of the reactor. Then, AgI-ZnO was added into the vessel. Before irradiation, the aqueous suspensions containing RA and catalyst were continuously stirred for 30 min in dark to reach an adsorption–desorption equilibrium. After that, the mixture was subjected to visible irradiation and the source of visible light was 150 W tungsten lamp. During irradiation, 5 mL of aliquot samples were withdrawn from the reaction mixture at a regular time interval of 30 min. The sampled suspensions were then centrifuged at 4000 rpm for 20 min to remove the catalyst and the residual dye concentration was analyzed by UV–vis spectrophotometer.

The decolorization efficiency (%) has been calculated as:

$$\text{Decolorization efficiency} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of RA and C is the concentration of RA after photoirradiation. The COD of the photodecolorized solution was determined by the usual procedure (digesting sample using $K_2Cr_2O_7$/H_2SO_4 and subsequent titration) [45].

3. Results and discussion

3.1. UV–vis-DRS

Fig. 1(a) shows the UV–vis DRS of ZnO and AgI-ZnO. The absorption onset is observed at about 364 nm for ZnO whereas the absorption onset is red shifted for AgI-ZnO (426 nm). The absorption coefficients of the ZnO and AgI-ZnO are analyzed by Tauc's approach [46], and the direct band gap is calculated using the following equation:

$$\alpha = \frac{C\left(h\nu - E_g^{bulk}\right)^2}{h\nu} \quad (2)$$

where α is the absorption coefficient, C is a constant, $h\upsilon$ is the photon energy and E_g^{bulk} is the band gap. Fig. 1(b) and Fig. 1(c) show the Tauc plots of ZnO and AgI-ZnO. Extrapolation of the linear region of Tauc plot gives a band gap of 3.05 eV for ZnO and 2.73 eV for AgI-ZnO.