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Photocatalytic degradation of phenol in aqueous solutions by Pr-doped TiO_2 nanoparticles

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Abstract

Photocatalytic degradation of phenol in water was examined using Pr-doped TiO_2 nanoparticles. These photocatalysts were synthesized by an acid-peptized sol–gel method from titanium tetra-isopropoxide with different concentrations of Pr(III) dopant and calcination temperatures. Several tools such as XRD, BET surface area, SEM, and EDX, were used to evaluate particle structure, size distribution, and composition. The optical absorption properties of the prepared particles were also measured. Photocatalytic activity of the particles was studied in a batch reactor containing phenol solution with 400 W UV irradiation. Parameters affecting photocatalytic process such as the catalyst crystallinity, light absorption efficiency, the dosage of catalyst, dopant and phenol concentrations were investigated. The Pr-doped TiO_2 showed high activity for photocatalytic degradation of phenol. The presence of Pr ions in the TiO_2 particles would cause a significant absorption shift towards the visible region. The degradation process was optimized using 1 g/L Pr-doped TiO_2 with a Pr(III) concentration of 0.072 mol% after 2 h irradiation. It was shown that photodegradation followed a pseudo-first-order kinetics and the rate constant changed with phenol concentration.

Keywords: Photocatalytic degradation; Phenol; Pr-doped TiO_2; Sol–gel method; Nanoparticles

1. Introduction

The presence of phenolic compounds in aqueous solutions has caused several environmental problems. A representative of this class of compounds is phenol. Sources of phenol include the discharges of chemical process industries such as coal gasification, polymeric resin production, oil refining, coking plants, paper mill, herbicides and fungicides production [1]. Phenol and their degradation products in the environment are major aquatic pollutants. When phenol-containing water is chlorinated, toxic polychlorinated phenols can be formed; hence, such effluent requires proper treatment before being discharged into the environment. Since they are stable and soluble in water, their removal to reach safety levels in the range 0.1–1.0 mg/L is not easy [2]. Traditional methods such as solvent extraction, activated carbon adsorption, and common chemical oxidation often suffer from serious drawbacks including high cost or formation of hazardous by-products [1,3]. Biological degradation is environmental friendly and cost effective; but it is usually time-consuming [3]. Among the methods available, oxidative degradation using photocatalysts appears cost effective, which has thus been an increasingly important process in pollution prevention [4–7].

Photocatalytic degradation of such organic pollutants with TiO_2 semiconductor has been proved to be the most efficient and popular method because it is a stable and low-cost photosensitized material [8]. The effective photoexcitation of TiO_2 particles requires the application of light with energy higher than its band gap energy; moreover, such photoexcitation results in the formation of electrons (e^-) in the conduction band and positive holes (h^+) in the valence band, and formation of OH radicals [9]. Photogenerated electron-hole pairs also recombine; therefore, inhibiting the recombination of electron–hole pairs and prolonging lifetime of carriers are essential for improving the efficiency of net charge transfer at the semiconductor/electrolyte interface. The hydroxyl ions (OH^-) are the likely traps for holes, leading to the formation of hydroxyl radicals that are strong oxidizing agents, while the traps for electrons are adsorbed oxygen species, leading to the formation of superoxide species (O_2^-) which are unstable [6]. The reactive radical species generated

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(OH^-, $O_2{}^-$) attack phenolic molecules present in suspensions and cause its hydroxylation, oxidation, and finally mineralization occur in forming to carbon dioxide and water [10,11].

Several researchers have studied the photocatalytic degradation of phenol and chlorinated phenols in aerated suspensions of TiO_2 upon illumination with near-UV light [12–14]. In most of the above studies, the Langmuir–Hinshelwood model was often applied to characterize the reaction [15,16], which describes the degradation rate in terms of the disappearance of compounds or the formation of CO_2. It has been indicated that catalyst dosage, initial concentration of organic pollutants, pH, UV light intensity, and concentration of charge trapping species are the main parameters affecting the degradation rate of phenol in TiO_2 suspension [17–19]. Previous work generally uses near-UV as the light source; however, only about 3% of the solar light is absorbed in solar energy applications [20]. Tryba et al. [21] have used an activated carbon as adsorbent, combined with TiO_2 photocatalyst, to improve the efficiency of phenol degradation.

In recent years, many groups have examined the effect of metal doping on photocatalytic properties of TiO_2. The incorporation of transition metals into TiO_2 crystal lattice alters the photoreactivity by shifting the band gap of the catalysts into the visible region [22–25]. For instance, Blazkova et al. [26] doped Pt in TiO_2 immobilized on glass fibers by sol–gel technique to improve phenol photodegradation under UV irradiation. The reflectance spectra of TiO_2-containing Fe have shown increased absorption dependence on annealing temperature and Fe concentration [27]. In addition to the methods of catalyst preparation, the photoactivity of the doped TiO_2 catalysts depends substantially on the nature of the dopant and its concentration [28,29]. Iwasaki et al. [30] reported that TiO_2 doped with a small amount of Co^{2+} has high photocatalytic activity under UV–vis light irradiation at a Co^{2+} doping concentration of 0.03 mol%. In the same subject, Barakat et al. [6] also reported a Co^{3+} doping concentration of 0.036 mol% in TiO_2 particles.

There are many reports on transition metal and noble metal dopants in TiO_2 particles previously. To our knowledge, the doping of rare earth metals, particularly Pr(III), in TiO_2 and their catalytic properties have seldom been presented so far [31]. In this work, we synthesized the Pr-doped TiO_2 nanoparticles *via* a sol–gel technique with various Pr^{3+} concentrations and annealing temperatures. The photocatalytic activity of the prepared Pr-doped TiO_2 was evaluated via the degradation of phenol in aqueous solutions under 400 W UV irradiation. Parameters affecting photodegradation process such as catalyst crystallinity, optical absorption, concentration of the catalyst and dopant, and phenol concentration were examined.

2. Materials and methods

2.1. Materials and solutions

TiO_2 nanoparticles were prepared using 0.12 mol titanium tetra-isopropoxide (Ti[*iso*-OC_3H_7]$_4$, Acros 98%) in a mixture of 2 mol% ethanol (Merck 99.8%) and water. The suspension was stirred for 6 h at room temperature, followed by several centrifuge and washing steps with deionized water (Milli-Q, Millipore). The colloidal solution was then diluted with deionized water and the pH was adjusted to 1.8 by adding 0.1 M HNO_3 (Merck 65%). Pr-doped TiO_2 particles containing 0.018–0.22 mol% Pr^{3+} dopant were synthesized *via* the acid-peptized sol–gel formation method at 85 °C and were calcined at different temperatures [32]. The dopant stoichiometry was controlled by dissolving the precursor $Pr(NO_3)_3{\cdot}5H_2O$ (Acros 99.9%) in deionized water prior to the drop-wise addition of TiO_2 colloidal solution. The resulting suspension was stirred for 18 h at 85 °C, and was allowed to rest and cool to room temperature for settling the precipitate. The precipitate was separated and collected by centrifuge and washing steps with deionized water to remove contaminants. The powder samples were dried from room temperature to 100 °C in an oven and then annealed for 6 h in a tube furnace operating between 100 and 800 °C in ambient atmosphere. During this process, the samples were transformed from anatase to rutile phase. The calcined particles were finally pulverized with mortar and pestle, followed by passing through a 270 mesh.

The reagent-grade phenol was purchased from Merck Co. (99.5% purity). All other chemicals used in this work were also of reagent-grade quality. The light source used was a water-cooled 400 W high-pressure mercury lamp (HL400EH-5, SEN, Japan). The spectral irradiance of the UV lamp ranges from 253.7 to 577 nm, with three dominant peaks locating at 365, 546, and 577 nm, and the illumination distance is 80 mm. The light intensity of the UV lamp used for photodegradation experiments was recorded with a UV–vis spectrophotometer (Shimadzu, UV-2501PC).

2.2. Characterization

The Brunauer–Emett–Teller (BET) surface area of the Pr-doped TiO_2 catalysts was measured from N_2 sorption isotherm at 77 K using a Micrometrics ASAP2010 sorption analyzer. The Barrett–Joyner–Halenda (BJH) approach was applied to obtain pore size distribution from the desorption data. The samples were degassed at 150 °C for 5 h to remove any physically sorbed gases or vapors prior to the measurements. The crystalline phases present in the sample were identified by X-ray diffraction (XRD) analysis. A Siemens D8 XRD system generating monochromatic Cu Kα radiation with continuous scanning mode at a rate of $2\,\text{min}^{-1}$ and the operating conditions of 40 kV and 40 mV was used to obtain XRD patterns. Scanning electron microscopy (SEM, Hitachi S-4800) was applied to observe the morphology of the catalysts. The dopant concentration was verified by energy dispersive X-ray analysis (EDX, Horiba 7593H). Finally, a diffusive reflective UV–vis spectrophotometer (Shimadzu UV-2501PC) was employed to measure the absorbance and estimate the band gap of the catalysts. The samples were diluted with methanol, and the resulting solution was sonicated before the measurements.

2.3. Photodegradation experiments

Degradation experiments were conducted in a batch photocatalytic reactor. This small-scale system consisted of a cylindrical