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A novel magnetically separable composite photocatalyst: Titania-coated magnetic activated carbon

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Abstract

A novel magnetically separable composite photocatalyst, titania-coated γ-Fe_2O_3 magnetic activated carbon, was prepared by depositing of anatase titania onto the surface of magnetic activated carbon (MAC) which was prepared by a simple route: directly adsorbing of magnetic γ-Fe_2O_3 nanoparticles onto activated carbon (AC). The prepared samples were characterized by XRD, SEM, BET and vibrating sample magnetometer (VSM). The photocatalytic activity of the samples was determined by degradation of model contaminant water of phenol aqueous solution, and compared to Degussa P25. The effect of γ-Fe_2O_3/AC mass ratio on the photocatalytic activity was also studied. Results illustrated that photocatalyst with γ-Fe_2O_3/AC mass ratio of 1:7 showed the highest degradation rate, which was nearly twice to that of P25. The photocatalyst can be separated easily by an external magnetic field. It can also be re-dispersed into aqueous solution by stirring after the removing of external magnetic field. The photocatalyst can be recycled with a little decreasing of photocatalytic activity, and the degradation rate of phenol was still higher than 80% after six cycles.

Keywords: Photocatalysis; Magnetically separable; Magnetic activated carbon; Titania; γ-Fe_2O_3

1. Introduction

Titania-mediated photocatalytic oxidation and reduction offers potentially a facile and cheap method for removing inorganic and organic pollutants from wastewaters. It has been an area of intense interest for the past 20 years, particularly for removing organic compounds as they can be completely mineralized under photocatalytic oxidation [1–5].

Typically, a photocatalytic reaction is conducted in a suspension of submicrometer-sized titania, and therefore requires an additional separation step to remove the catalyst from the treated water. Removing such fine particles from large volumes of water involves further expense and manpower. This presents a major drawback to the application of the photocatalytic processes for treating wastewaters [6]. Pozzo et al. [7] stated that the cost of the separation might invalidate altogether the claimed energy savings for a solar-induced decontamination process due to the small particle size of the used photocatalyst.

To solve the problem of separation of photocatalyst, investigators had carried out many researches on immobilizing titania onto various substrates such as glass beads [8], sand, silica gel, activated carbon fibers [9], and quartz optical fibers [7]. Although this approach provides a solution to the solid–liquid separation problem, slurry-type reactors offer significant advantages over immobilized catalyst-type reactors because of the catalyst surface availability and superior mass-transfer properties [10]. Some investigators prepared nanoparticles with magnetic core and photoactive shell using magnetic granules and titania [11–15]. They proved that the composite nanoparticles had magnetic property and could be separated easily by magnetic materials. Kostedt et al. [15] pointed out that the magnetic composite photocatalyst can also be magnetically agitated by an alternating magnetic field in a suspension system. But Beydoun et al. [14] found the photocatalytic activity of the nanoparticles declined because the magnetic particles experienced photodissolution. Matos et al. [16] investigated the photocatalytic activity of a suspended mixture of titania and activated carbon. They found

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that there were a synergistic effect and a common interface, which contributed to the higher photocatalytic activity, between titania and activated carbon. Then, some others investigated the photocatalytic degradation of aqueous organic pollutants by titania-coated activated carbon [17–20]. They also found enhanced photocatalytic activity of the composite photocatalyst. The separation problem still existed because the catalyst was size in micron grade, although it could be separated more easily than the slurry titania system.

Our work is concerned on fabricating composite photocatalyst with enhanced photoactivity and recycles activity. So, we combine the adsorption activity of activated carbon with the magnetic separability of γ-Fe_2O_3 and photocatalytic activity of titania. The separation problem of the photocatalysts would be solved easily and the photocatalytic activity of them would enhance a lot at the same time.

In the present work we prepared magnetic activated carbon firstly by dispersing powder activated carbon in γ-Fe_2O_3 sol, which was prepared by co-precipitation of iron(II) and iron(III) in the presence of ammonium hydroxide. The process was conducted under vacuum. Then the anatase titania, which prepared at low temperature by hydrolyzing titanium-*n*-butoxide ($Ti(OBu)_4$) in abundant acidic aqueous solution, was deposited onto the MAC before it was dried into powders in a rotatory evaporator under vacuum. The photocatalytic activity of as-prepared photocatalyst was compared to P25 titania by degradation of phenol in aqueous solution. The influence of mass of γ-Fe_2O_3 adsorbed on activated carbon on the photoactivity of the photocatalyst was also investigated.

2. Experimental

2.1. Sample preparation

Anatase titania sol was prepared by sol–gel method under mild conditions (i.e. 75 °C and ambient pressure), the detailed process described as follows: $Ti(OBu)_4$ was chosen as a Ti precursor, which is less reactive than titanium chloride and titanium isopropoxide. Nitric acid (HNO_3) and isopropanol (PrOH) were analytical reagent grade. Distilled water was additionally cleaned prior to its use with a quartz sub-boil high purity water purification system. $Ti(OBu)_4$ diluted with PrOH was added dropwise into the distilled water under vigorous stirring, whose acidity was adjusted with HNO_3. The molar ratios of PrOH and water to $Ti(OBu)_4$ were 1.42 and 151, respectively. Then, the solution was kept under reflux condition (around 75 °C) for 24 h. Finally, pure TiO_2 sol was obtained, which was used to deposit on the magnetic activated carbon, after PrOH and *n*-butyl alcohol were removed from the solution in a rotatory evaporator under vacuum.

Coconut shell activated carbon, which was purchased from ShangHai Activated Carbon Ltd., was washed for three times by distilled water before using. Then, magnetic activated carbon was prepared in following way: definite amount of AC was added into 200 ml of diluted γ-Fe_2O_3 sol whose concentration was $3\ g\,l^{-1}$. Then the admixture was stirred for 1 h before kept at vacuum for 30 min. After that, we can see the magnetic particles were all adsorbed by AC because all solid sedimented to the bottom of the container. The solid phase of γ-Fe_2O_3/AC was separated by a magnet and dried at 40 °C. MACs with different γ-Fe_2O_3/AC mass ratio were thus prepared.

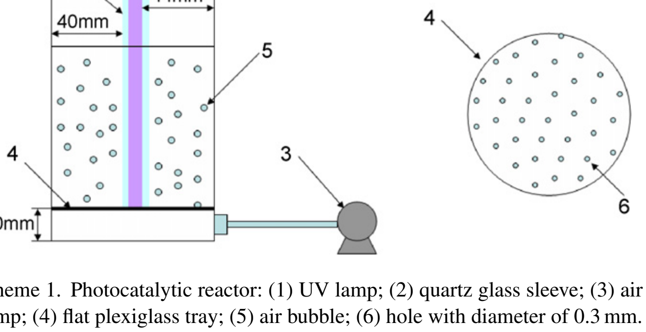
To obtain titania-coated magnetic activated carbon (TMAC), the coating procedure of titania onto MAC was as following: 3 g of MAC was dispersed in 200 ml titania sol in an ultrasonic bath for 1 h. Then, it was dried into powders in a rotatory evaporator under vacuum at 75 °C. At last, the mass ratio of MAC and titania was 1:3 in all samples.

2.2. Reactor

The photoactivity of the prepared samples was assessed using a photocatalytic reaction system newly designed and built in the laboratory (as shown in Scheme 1). The main part of the experimental rig is a cylindrical stainless steel reactor whose diameter is 160 mm. Above 20 mm of the reactor bottom, there is a flat plexiglass tray with symmetrical holes of 0.3 mm. Between the tray and the reactor bottom, there is an entry connects to an air pump. The 20 W ultraviolet lamp (with a wavelength peak at 365 nm) covered by a quartz glass sleeve is placed at the center of the reactor. Before the UV illumination, 0.75 g photocatalyst was added into 500 ml of a 100 ppm solution of phenol under aerating and it was maintained in the dark for 1 h to reach complete adsorption equilibrium because most of adsorption occurred within 30 min. Then the UV illumination start, and samples of the suspension (5 ml) were removed at regular intervals of 1 h for analysis.

2.3. Analysis

The dried samples (γ-Fe_2O_3, γ-Fe_2O_3/AC, γ-Fe_2O_3/AC/TiO_2 powder obtained above) were analyzed for their magnetic properties, composition and microstructure. The magnetic measurements were carried out with a vibrating sample magnetometer (VSM, PARR, Model 4500). The crystalline structure was determined by X-ray diffractometer (XD-3A, Shimadazu Corporation, Japan) using graphite monochromatic copper radiation (Cu Kα) at 40 kV, 30 mA over the 2θ range 20–80°. The morphologies were characterized with a scanning electron microscopy (SEM, Sirion, FEI). BET surface area measure-



Scheme 1. Photocatalytic reactor: (1) UV lamp; (2) quartz glass sleeve; (3) air pump; (4) flat plexiglass tray; (5) air bubble; (6) hole with diameter of 0.3 mm.