

Research Article

Photocatalytic Degradation of Humic Acid by Fe-TiO₂ Supported on Spherical Activated Carbon with Enhanced Activity

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Fe-TiO₂ supported on spherical activated carbon (Fe-TiO₂/SAC) with different Fe contents was prepared by heat treatment process after ion exchange method. The prepared Fe-TiO₂/SAC was characterized by SEM, EDS, and BET. Batch experiments for photocatalytic degradation of humic acid by Fe-TiO₂/SAC were carried out in the fluidized bed photoreactor. It was found that 0 wt% Fe-TiO₂/SAC had high photocatalytic activity in the wavelength range of 100~280 nm. However, Fe-TiO₂/SAC with Fe contents of 0.4, 0.6, and 0.8 wt% exhibited higher photocatalytic activity than 0 wt% Fe-TiO₂/SAC in the wavelength range of 315~400 nm compared to that of 100~280 nm. The optimum Fe content was 0.6 wt% for maximum photocatalytic degradation of humic acid. Moreover, Fe-TiO₂/SAC does not require an additional process step for separation of photocatalyst from treated water after photocatalysis.

1. Introduction

Photocatalysis using UV-irradiated semiconductors has been receiving attention in the area of environmental pollutants removal in water purification and solar energy conversion [1, 2]. Among the various semiconductor materials, titanium dioxide (TiO₂) is the most widely used as a photocatalyst to remove aqueous organic contaminants or air pollutants due to its strong oxidizing power, nontoxicity, low cost, chemical inertness, and photostability [2–6]. However, pure TiO₂ powder type has two major problems in the practical application. The first drawback associated with pure TiO₂ is that it acts as photocatalyst with ultraviolet (UV) light due to its large band gap (3.2 eV for anatase and 3.0 eV for rutile) [7–9]. It is well known that UV light accounts for only small fraction (3–5%) of solar energy compared to visible light (about 45%) [2, 10–12]. Therefore, the development of photocatalyst with photocatalytic activity under visible-light irradiation is required. In order to improve utilize solar energy, visible-light active photocatalysts involved in the doping of nonmetal element such as N, C, and S or transition metal ions such

as Ag, Co, Ni, Pt, and Fe into TiO₂ have been developed [13–21]. Among them, Fe-doped TiO₂ has been the most extensively examined because Fe dopants can act as hole and electron traps to inhibit recombination of the photogenerated electron and hole, leading to enhanced photoactivity [5, 9]. The second drawback associated with TiO₂ powder is that it has difficulty in recycling and reusing of TiO₂ powder. To enhance the separation of TiO₂, recent studies have been focused on the immobilization of photocatalyst on certain supporting materials [22–29].

In this study, to overcome the two major limitations associated with poor separation and weak visible-light responsiveness, we have developed Fe-TiO₂/SAC. The degradation of humic acid by Fe-TiO₂/SAC with different Fe contents (0, 0.4, 0.6, and 0.8 wt%) under 100~280 nm and 315~400 nm wavelength irradiation was investigated. Also, the photocatalytic activities of Co-TiO₂/SAC and Ni-TiO₂/SAC were evaluated to compare with that of Fe-TiO₂/SAC. Humic acid, which is a main precursor of carcinogenic material such as trihalomethanes producing during water disinfection processes, was selected as a model target substance.

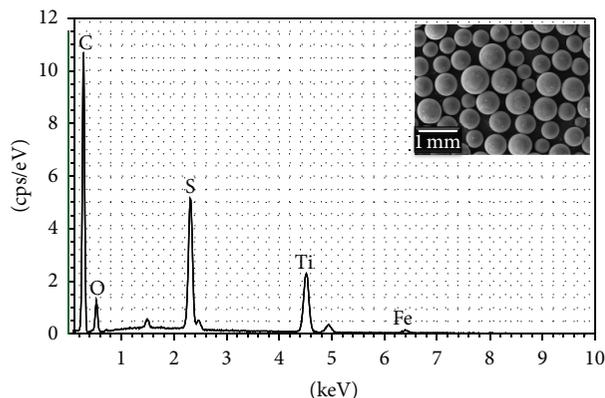


FIGURE 1: SEM image and EDS spectrum of 0.6 wt% Fe-TiO₂/SAC.

2. Experimental

Fe-TiO₂/SAC were prepared by ion exchange method and heat treatment process. Titanium trichloride (TiCl₃, 20%, Kanto Chemical) was diluted thirty times with double-distilled water. Strong acid ion exchange resin (Diaion SK1BH, Samyang Co., Ltd.) was added to TiCl₃ solution, and was continuously stirred at 150 rpm for 1 h at room temperature and then the product was rinsed many times. Ti containing ion exchange resin was put into FeCl₃ solution under vigorous stirring 150 rpm for 1 h at ambient temperature. It was rinsed severally with distilled water until a neutral pH was reached. Fe and Ti-containing ion exchange resin was dried at 110°C for 24 h in an oven. The dried product was heated using a tube furnace in order to convert it to a carbonaceous porous material as previously described [27]. Co-TiO₂/SAC and Ni-TiO₂/SAC were prepared by the above-mentioned experimental procedure. All reagents were of analytical grade purity and were used without any further purification. Fe-TiO₂/SAC with various contents of Fe was prepared. According to different Fe contents of 0, 0.4, 0.6, and 0.8 wt%, the Fe-TiO₂/SAC were assigned: 0 wt% Fe-TiO₂/SAC, 0.4 wt% Fe-TiO₂/SAC, 0.6 wt% Fe-TiO₂/SAC, and 0.8 wt% Fe-TiO₂/SAC, respectively.

The surface morphology and size of Fe-TiO₂/SAC were examined by scanning electron microscopy (SEM, JSM-6700F, JEOL), and also chemical composition of Fe-TiO₂/SAC was analyzed by energy-dispersive X-ray spectroscopy (EDS, Bruker Quantax 200). The specific surface area and total pore volume of Fe-TiO₂/SAC were measured by the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2010 apparatus. In order to compare and evaluate the compressive strength of each sample, the single sphere strength of each sample was measured using compressive strength meter, as described in [26].

Batch photocatalysis experiments for degradation of humic acid by Fe-TiO₂/SAC under UV irradiation were performed in the fluidized bed photoreactor (10 cm diameter, 40 cm height, and 2.4 L capacity), and by adding 20 g of Fe-TiO₂/SAC to 1 L of humic acid aqueous solution with initial humic acid concentration of 10 mg/L. Humic acid was purchased from Aldrich Chemical Company, which has

TABLE 1: Specific surface area and total pore volume of Fe-TiO₂/SAC with different Fe contents.

Photocatalyst	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)
0 wt% Fe-TiO ₂ /SAC	584	0.355
0.4 wt% Fe-TiO ₂ /SAC	486	0.221
0.6 wt% Fe-TiO ₂ /SAC	487	0.269
0.8 wt% Fe-TiO ₂ /SAC	483	0.218

carbon, hydrogen, and nitrogen content of 39.44%, 4.74%, and 0.79%, respectively. Low pressure mercury lamp (UV-C, $\lambda = 100\sim 280$ nm) and black light blue lamp (UV-A, $\lambda = 315\sim 400$ nm) used as light sources were placed in the middle of the photoreactor. Air was bubbled to reaction solution through the bottom of the reactor with an air flow of 4 L/min. A schematic diagram of the photocatalytic reactor is shown in [29]. At regular intervals, certain volume of the samples was withdrawn from the photoreactor. In order to examine change of total organic carbon (TOC) concentration in solution according to reaction time, TOC of the solution was analyzed with a total organic carbon analyzer (TOC-5000A, Shimadzu). Chemical oxygen demand (COD) was also measured using COD test kit (C_{mac}).

3. Results and Discussion

Figure 1 shows SEM image and EDS spectrum of Fe-TiO₂/SAC with Fe content of 0.6 wt%. Fe-TiO₂/SAC showed smooth surfaces and good spherical shapes without cracks. A diameter of Fe-TiO₂/SAC observed under SEM was in the range of 0.31~0.57 μ m. The amount of Ti and Fe elements obtained from EDS analysis was in agreement with the doping content. The average compressive strength of Fe-TiO₂/SAC was high as a 9~10 kg/unit. It can enhance durability and the floating of Fe-TiO₂/SAC is beneficial in the fluidized-bed photoreactor system.

Table 1 presents the data of specific surface area and total pore volume of the Fe-TiO₂/SAC. It can be seen that specific surface area and total pore volume of Fe-TiO₂ with different Fe contents (0.4, 0.6, and 0.8 wt%) showed similar value, which were slightly lower than that of 0 wt% Fe-TiO₂/SAC. Figure 2 shows the nitrogen adsorption-desorption isotherm and the pore size distribution of 0.6 wt% Fe-TiO₂/SAC. The isotherm exhibits type I according to IUPAC classification, indicating dominant microporous character.

To evaluate the influence of light source, the photocatalytic degradation of humic acid by Fe-TiO₂/SAC photocatalysts under light irradiation with wavelength range of 100~280 nm and 315~400 nm was investigated. These results are presented in Figure 3 and Figure 4. After 6 h irradiation at wavelength of 100~280 nm, 53% of COD was removed by TiO₂/SAC, whereas COD removal by Fe-TiO₂/SAC with Fe content of 0, 0.4, 0.6, and 0.8 wt% was 25~38% (Figure 3). As shown in Figure 4, the photocatalytic degradation of humic acid by TiO₂/SAC under 315~400 nm wavelength irradiation is very low (3.39%). However, the photocatalytic degradation of humic acid by Fe-TiO₂/SAC with Fe content of 0, 0.4,

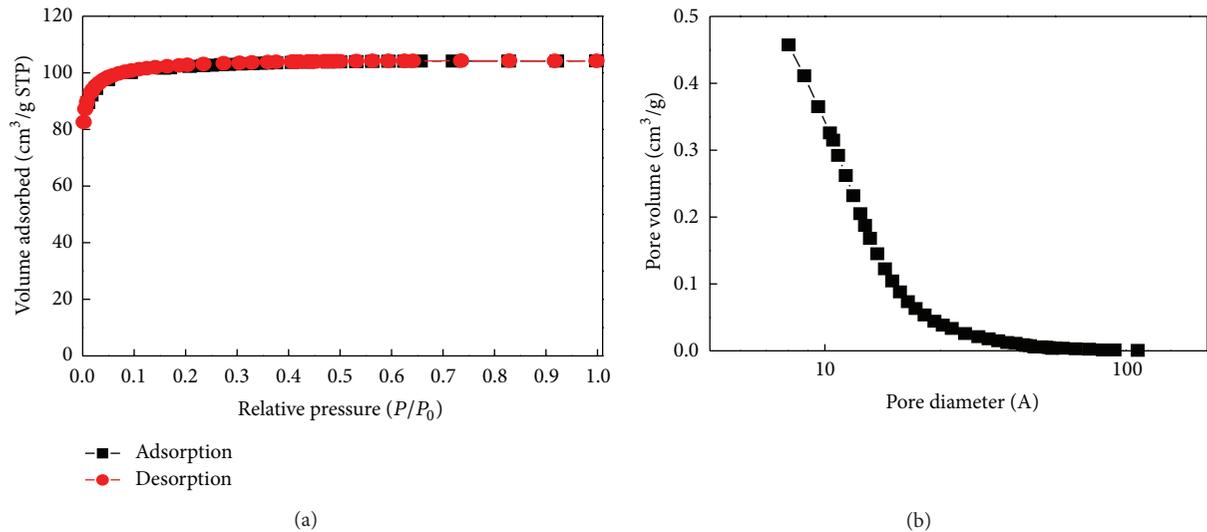


FIGURE 2: (a) Nitrogen adsorption-desorption isotherm and (b) pore size distribution of 0.6 wt% Fe-TiO₂/SAC.

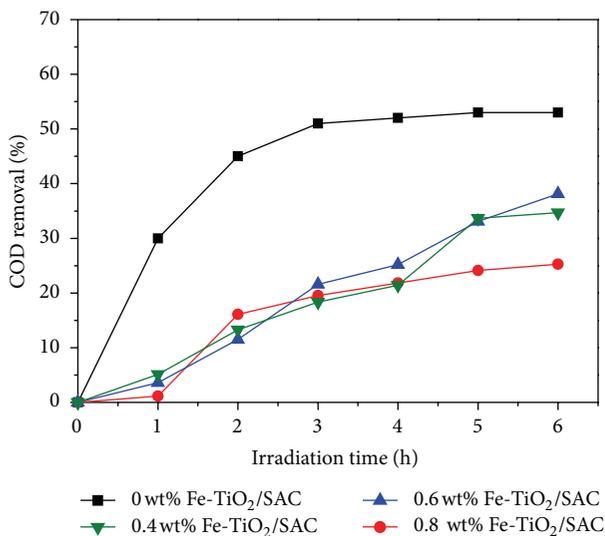


FIGURE 3: COD removal on the photocatalytic degradation of humic acid by Fe-TiO₂/SAC under light irradiation with wavelength range of 100~280 nm.

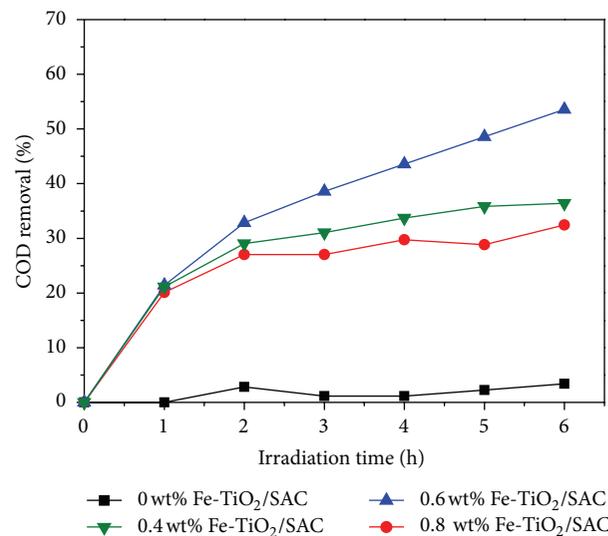


FIGURE 4: COD removal on the photocatalytic degradation of humic acid by Fe-TiO₂/SAC under light irradiation with wavelength range of 315~400 nm.

0.6, and 0.8 wt% was 32–54%, which is superior to that of 0 wt% Fe-TiO₂/SAC, exhibited high photocatalytic activity in the wavelength range of 100~280 nm, whereas 0.4 wt% Fe-TiO₂/SAC, 0.6 wt% Fe-TiO₂/SAC, and 0.8 wt% Fe-TiO₂/SAC exhibited high photocatalytic activity in the wavelength range of 315~400 nm. It is evident that Fe-TiO₂/SAC with Fe content of 0.4~0.8 wt% showed better photocatalytic activity in the range of 315~400 nm compared to that of the wavelength range of 100~280 nm.

In order to assess the effect of doping amounts of Fe on the degradation of humic acid, the photocatalytic activity of Fe-TiO₂/SAC with different Fe contents was evaluated under 315~400 nm wavelength irradiation. Figure 5 shows the result on the TOC removal for irradiation of 6 h. With increase of

the amount of Fe from 0 wt% to 0.8 wt%, the photocatalytic activity was initially increased to reach the amount of 0.6 wt% and then decreased with the further increase of the amount. It can be said that the optimum Fe content is 0.6 wt% for maximum photocatalytic degradation of humic acid in this study conditions. It was reported that when the doping concentration reaches beyond optimum amount, Fe³⁺ mainly acts as recombination center for photogenerated electrons and holes, thus reducing photocatalytic activity [10, 18].

Figure 6 shows the photocatalytic degradation of humic acid over various transition metal-doped TiO₂/SAC under 315~400 nm wavelength irradiation. Co-TiO₂/SAC and Ni-TiO₂/SAC, which contain 6 wt% of Ti and 0.6 wt% of Co, and Ni were prepared to compare with photocatalytic activity

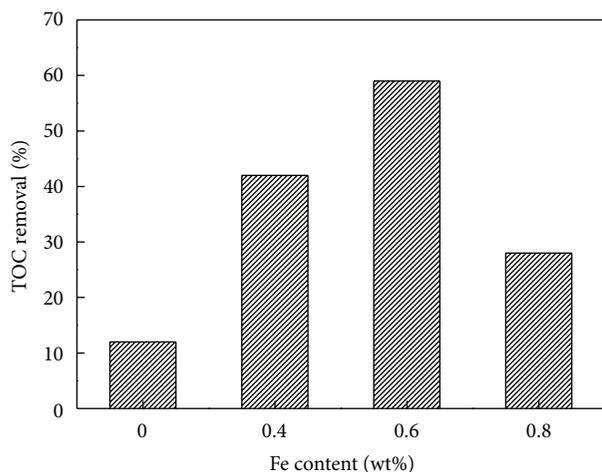


FIGURE 5: TOC removal on the photocatalytic degradation of humic acid by Fe-TiO₂/SAC with different Fe content under light irradiation with wavelength range of 315~400 nm for 6 h.

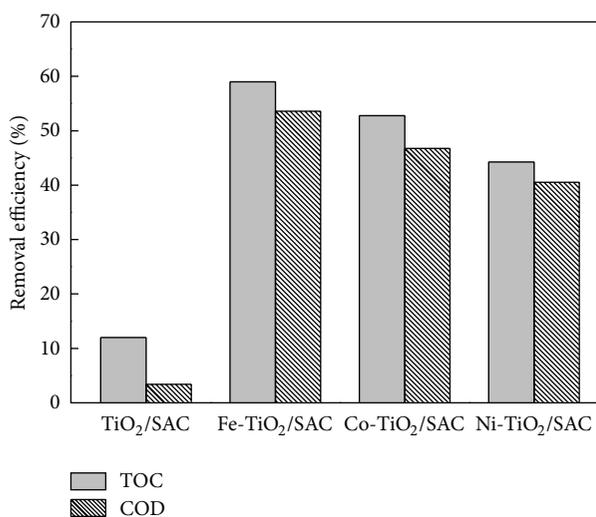


FIGURE 6: TOC and COD removal on the photocatalytic degradation of humic acid by TiO₂/SAC and various transition metal doped-TiO₂/SAC under light irradiation with wavelength range of (a) 100~280 nm and (b) 315~400 nm for 6 h.

of Fe-TiO₂/SAC. It is clear that all of the various transition metal-doped TiO₂/SAC exhibited significantly high photocatalytic activity compared with pure TiO₂/SAC under 315~400 nm wavelength irradiation. Particularly, among the various transition metal-doped TiO₂/SAC, Fe-TiO₂/SAC had relatively the highest photocatalytic activity. This result indicates that doping of transition metal ion with an optimal concentration not only narrows the band gap of TiO₂ to extend the absorption into the long wavelength region but also is beneficial to the photogenerated electron-hole separation [16].

4. Conclusions

The photocatalytic activity of Fe-TiO₂/SAC with different Fe contents (0, 0.4, 0.6, and 0.8 wt%) were examined in the fluidized bed photoreactor for the degradation of humic acid under 100~280 nm and 315~400 nm wavelength irradiation. Fe-TiO₂/SAC had high photocatalytic activity in the wavelength range of 315~400 nm compared to that of the wavelength range of 100~280 nm. The photocatalytic activity increased and then decreased with increasing of Fe content. The optimized amount of Fe content for the highest photocatalytic activity was 0.6 wt%. Moreover, transition metal-doped-TiO₂/SAC exhibited high TOC and COD removal on the photocatalysis of humic acid under 315~400 nm wavelength irradiation. Among the various transition metal-doped-TiO₂/SAC, Fe-TiO₂/SAC had relatively high photocatalytic activity in the long wavelength region. Furthermore, Fe-TiO₂/SAC used in this study is free from a separation process after photocatalytic reaction, and also for possible application as visible light active photocatalyst in water treatment.

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