Preparation of Fe₃O₄/TiO₂ magnetic mesoporous composites for photocatalytic degradation of organic pollutants

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ABSTRACT

Fe₃O₄/TiO₂ magnetic mesoporous composites were synthesized through a sol-gel method with tetra-n-butyl titanate as precursor and surfactant P123 as template. The as-prepared Fe₃O₄/TiO₂ composites were characterized by X-ray diffraction, diffuse reflectance spectroscopy, nitrogen adsorption-desorption isotherm and pore size distribution. The as-synthesized products were applied as photocatalysis for the degradation of Acid Black ATT and tannery wastewater under UV lamp irradiation. Fe₃O₄/TiO₂-8 composites containing Fe₃O₄ of 8 wt% were selected as model catalysts. The optimal catalyst dosage was 3 g/L in this photocatalytic system. The magnetic Fe₃O₄/TiO₂ composites possessed good photocatalytic stability and durability. This approach may provide a platform to prepare a magnetic composite to optimize the catalytic ability.

Key words | Fe₃O₄/TiO₂, magnetic mesoporous composites, organic pollutants, photocatalytic degradation

INTRODUCTION

Tannery wastewater, containing heavy metals, toxic chemicals and organic dye compounds, is considered as one of the most hazardous pollutants (Song et al. 2000; Dixit et al. 2015). It would severely pollute the environment if not properly treated. Although many conventional physical and chemical treatment processes, including coagulation and biological oxidation, have been employed to abate the pollution, incomplete degradation and sludge generation are still inevitable problems (Martinez-Huitle & Ferro 2006; Elabbas et al. 2016; Thankappan et al. 2015). The technical challenge of wastewater treatment is growing with the increase in contaminants with industrial development. So far, developing a new technology to efficiently eliminate organic pollutants from the wastewater is a huge challenge.

Photocatalytic oxidation, as a representative advanced oxidation process, has the ability to degrade the most recalcitrant organic dye molecules into carbon dioxide and H₂O (Gogate & Pandit 2004; Sauer et al. 2006; Oturan & Aaron 2014). Mesoporous TiO₂ has been well studied in photocatalytic degradation of pollutants (Guo et al. 2010; Xiang et al. 2015). However, it still possesses a severe failing, for those TiO₂ samples are difficult to completely recycle and reuse with durability due to their small particle size. In recent years, magnetic separation technology has provided a convenient approach for removing and recycling magnetic particles/composites by applying an appropriate magnetic field (Jing et al. 2013; Li et al. 2016). This method may effectively prevent the agglomeration of the catalysts during recovery and can increase the durability of the catalysts. Among them, Fe₃O₄ nanoparticles, with a rapid and efficient magnetic response, can enable the separation of catalysts from the reaction mixture efficiently and without trouble (Xuan et al. 2009). Thus, a Fe₃O₄/TiO₂ magnetic mesoporous composite is required to be recoverable and an efficient photocatalyst towards pollutant degradation.

Herein, we report the synthesis of a Fe₃O₄/TiO₂ magnetic mesoporous composite with different Fe₃O₄ wt%. Acid Black ATT was selected as a contamination model because it is extensively used in the leather industry and consists of Acid Black 10B and acid orange. In addition, the photocatalytic performance of the Fe₃O₄/TiO₂ samples is also evaluated towards the degradation of diluted tannery wastewater.
EXPERIMENTAL

Materials

All chemicals were of analytical grade and used as received without further purification. Acid Black ATT and tannery wastewater were obtained from Tianjin Fusheng Leather Co., Ltd (Tianjin, China). Distilled water was used throughout the experiment. Tannery wastewater was collected from the equalisation tank of a treatment plant designed to treat 2,500 m$^3$/d of tannery wastewater generated from about 128 tanneries. First, the raw tannery wastewater was pre-treated with conventional coagulants for the amendment of suspended solids and precipitation of chromium. Then, the pre-treated wastewater was used as feed to the sequencing batch reactor. The average chemical composition of raw and pre-treated tannery wastewater is shown in Table S1 (available with the online version of this paper). The parameters were measured according to Standard Methods (1995) (APHA, AWWA & WEF 1995; Ganesh et al. 2006).

Synthesis of Fe$_3$O$_4$

Fe$_3$O$_4$ is prepared through a precipitation method, which uses aqueous ammonia (NH$_3$·H$_2$O) as precipitant; 1.6 g of ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O) and 4.05 g ferric trichloride hexahydrate (FeCl$_3$·6H$_2$O) were dissolved in 100 mL distilled water under vigorous stirring. The solution was kept at 30°C for 30 min and protected by nitrogen. Then, 6 mL of NH$_3$·H$_2$O was added in the solution drop by drop. The mechanical stirring and temperature continued until the color of the solution turned from orange red to completely black. Finally, the suspension was cooled to room temperature. The as-prepared magnetic particles were washed with ethanol and water several times, and then dried in a vacuum at 60°C for 6 h.

Synthesis of Fe$_3$O$_4$/TiO$_2$ magnetic mesoporous composites

Fe$_3$O$_4$/TiO$_2$ magnetic mesoporous composites of different Fe$_3$O$_4$ wt% were prepared by a sol-gel method. The typical process was as follows: a certain amount of Fe$_3$O$_4$ substrate was dispersed in a solution containing 1.0 g of P123, 10 g of tetrabutyl titanate (TBOT), and 20 mL of ethyl alcohol (C$_2$H$_5$OH) to form a suspension. Then, a mixture containing 10 mL of C$_2$H$_5$OH and 1.5 mL of H$_2$O was added. The reaction was maintained in a water bath at 40°C and magnetically stirred until a gel formed. The as-prepared gel was dried in a vacuum at 60°C for 6 h, and calcined at 500°C for 4 h. Six different Fe$_3$O$_4$ wt%, e.g. 1, 2, 4, 8 and 10%, were synthesized. We named them Fe$_3$O$_4$/TiO$_2$-1, Fe$_3$O$_4$/TiO$_2$-2, Fe$_3$O$_4$/TiO$_2$-4, Fe$_3$O$_4$/TiO$_2$-8, and Fe$_3$O$_4$/TiO$_2$-10, respectively.

Characterization

The X-ray diffraction (XRD) pattern was investigated using the Rigaku 97D/max-2500 with Cu Kα radiation ($\lambda = 0.15406$ nm) in the 2θ range from 20 to 80. The operation voltage was kept at 50 KV and the current at 20 mA. N$_2$ adsorption-desorption isotherms were recorded on a Quantachrome autosorb apparatus. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The pore size distribution was determined by the Barrett–Joyner–Halenda (BJH) approach. The UV-vis absorption spectra were recorded on a UV-vis diffuse reflectance spectrophotometer (U-3010 UV-VIS-NIR). BaSO$_4$ was referenced.

Photocatalytic activity

Photocatalytic activity of the prepared samples was evaluated for the decolorization of Acid Black ATT solution and leather wastewater with a 200 W UV lamp at ambient temperature. In the test, a certain amount of photocatalyst was added into the Acid Black ATT solution (200 mL, 10 mg/L) or leather wastewater (the chroma is 150 times and the initial chemical oxygen demand (COD) is 170 mg/L). The UV lamp was surrounded by a quartz thimble in the centre of the reactor, and water was circulated around the thimble in order to avoid the heat of the lamp. Before illumination, the suspension was magnetically stirred in the dark for 1 h to establish an adsorption-desorption equilibrium. Then, at given time intervals, 5 mL of suspension was taken and immediately centrifuged to analyze the supernate by UV-vis spectrophotometer (VIS-2102).

For the photodegradation of Acid Black ATT, the time interval was 1 h. The filtrates were analyzed by recording the variations of the absorption band maximum (618 nm) in the UV-visible spectra. The degradation rate $D(\%)$ was evaluated by the following equation: $D(\%) = (C_0 - C_t)/C_0 \times 100\%$ (where $C_0$ is the initial concentration of the Acid Black ATT solution, and $C_t$ is the concentration of the Acid Black ATT solution at a given time $t$).

The COD and chroma value of tannery wastewater were determined by the potassium dichromate method and dilution method, respectively.
Wastewater chroma was tested in accordance with the dilution multiple method. First, the tannery wastewater was diluted with distilled water into diluted wastewater with different multiple concentrations. Then, they were transferred into 50 mL colorimetric tubes and diluted to the volume. The colorimetric tubes were placed on a white surface and compared with distilled water until the diluted wastewater corresponded to the distilled water. At this time, the dilution multiple was the chroma value of the wastewater samples.

The COD of tannery wastewater was determined by the potassium dichromate method, according to the standardized method ISO 6060 (ISO 1989).

The wastewater sample (20 mL) was refluxed in the presence of mercury (II) sulphate with a known amount of potassium dichromate (10 mL, 0.2500 mol/L) and silver catalyst in strong sulphuric acid (30 mL) for 2 h. A part of the dichromate was reduced by the oxidizable material present. The residual dichromate was titrated with ammonium iron (II) sulphate (AIS). The COD was calculated from the amount of dichromate reduced. The empirical COD was calculated as follows:

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\text{COD (mg/L)} = \frac{(V_0 - V_1) \times C \times 8 \times 1,000}{V}
\]

where \( C \) is the concentration of AIS standard solution (mol/L), \( V_0 \) is the dosage of AIS standard solution for the titration of the blank (L), \( V_1 \) is the amount of AIS standard solution for the titration of the sample (L), and \( V \) is the volume of the sample (L).

RESULTS AND DISCUSSION

XRD was used to determine the crystal structure of the samples. Figure 1 shows the XRD patterns of Fe3O4, TiO2 and Fe3O4/TiO2 heterostructures. As can be seen in Figure 1(a), a series of diffraction peaks at around \( 2\theta \) of 25.26, 38.00, 47.98, 53.78, 57.08 and 62.78 are observed, which can be indexed to the (220), (311), (400), (422), (511) and (440) planes of magnetite Fe3O4 (JCPDS card no. 01-072-2303) (Ansar et al. 2015; Chen et al. 2015). The as-prepared Fe3O4/TiO2 products with different Fe3O4 wt\% are 1% Fe3O4 for Fe3O4/TiO2-1, 2% Fe3O4 for Fe3O4/TiO2-2, 4% Fe3O4 for Fe3O4/TiO2-4, 8% Fe3O4 for Fe3O4/TiO2-8 and 10% Fe3O4 for Fe3O4/TiO2-10, respectively (Figure S1, available with the online version of this paper). With the contents of Fe3O4 increased from 1 to 10%, the diffraction peak intensity of Fe3O4 becomes enhanced, and the peak corresponding to (311) plane (2\( \theta \) = 35.50°) gradually broadens. In addition, the peak ascribed to the (101) plane (2\( \theta \) = 25.26°) of TiO2 gradually weakens, thus indicating that Fe3O4 is coated by TiO2. A permanent magnet is used to test the magnetism of the Fe3O4/TiO2 samples. It indicates that the samples with higher Fe3O4 content achieve better magnetism.

Figure 2 shows the N2 adsorption/desorption isotherm and the BJH pore size distribution plot of the Fe3O4/TiO2-8 composite. The shape of the isotherm is observed to be a type IV isotherm according to the IUPAC classification (Galán et al. 2013; Gómez et al. 2014; Zhao et al. 2015), indicative of the presence of mesopores. The calculated pore size is about 3.83 nm according to the BJH pore size distribution, judging from the isotherm. The surface area of the Fe3O4/TiO2-8 magnetic mesoporous composites determined by the BET method is 54.36 m²/g. The above results clearly indicate that the obtained Fe3O4/TiO2-8 composites are magnetic mesoporous.
The UV-vis diffuse reflection spectra (DRS) of TiO$_2$ and Fe$_3$O$_4$/TiO$_2$ with different Fe$_3$O$_4$ wt% are displayed in Figure 3. In comparison, Fe$_3$O$_4$/TiO$_2$ exhibits a broad absorption in the whole UV-vis region, while the absorption threshold of TiO$_2$ is located at about 400 nm. It demonstrates that the introduction of a certain amount of Fe$_3$O$_4$ obviously increased and broadened the visible light absorption of TiO$_2$.

The catalytic performance of the Fe$_3$O$_4$/TiO$_2$ was investigated by the degradation of Acid Black ATT and leather wastewater under the irradiation of a UV lamp (Table S2, available with the online version of this paper). In a typical run, a certain amount of photocatalyst was added into Acid Black ATT solution (200 mL, 10 mg/L) or leather wastewater (the chroma was 150 times and the initial COD was 170 mg/L). The UV lamp was surrounded by a quartz sleeve in the centre of the reactor and water was circulated around the sleeve in order to avoid the heat of the lamp. Before illumination, the suspension was magnetically stirred in the dark for 1 h to establish an adsorption-desorption equilibrium. Then, at given time intervals, 10 mL of suspension was taken and immediately centrifuged to analyze the supernate by UV-vis spectrophotometer (VIS-2102).

Figure 4 displays the photodegradation performance of Acid Black ATT over the Fe$_3$O$_4$/TiO$_2$ composites with different Fe$_3$O$_4$ wt%. The self-photolysis rate of Acid Black ATT without catalyst can be neglected. The decrease of Acid Black ATT with Fe$_3$O$_4$ nanoparticles was similar to that of the blank test. No apparent photocatalytic activity was detected. It was found that the photodegradation efficiency gradually enhanced as the Fe$_3$O$_4$ wt% decreased. This is mainly ascribed to the heterojunction between Fe$_3$O$_4$ and TiO$_2$, in which electron-hole recombination was increased. The main reason was that Fe$_3$O$_4$ has a lower conduction band and a higher valence band compared with those of TiO$_2$. According to previous reports (Jing et al. 2013), the saturation magnetization of Fe$_3$O$_4$/TiO$_2$ composites enhanced with the increase of the Fe$_3$O$_4$ wt% to TiO$_2$. Therefore, it is vital to select a Fe$_3$O$_4$/TiO$_2$ composite with optimal photocatalytic activity and magnetic property. In the research, we selected Fe$_3$O$_4$/TiO$_2$-8 as a model.

Figure 5 depicts the effect of the catalyst dosage of Fe$_3$O$_4$/TiO$_2$-8 on the photocatalytic activity towards the degradation of Acid Black ATT. It shows that the degradation performance increased as the catalyst dosage changed from 0.5 to

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**Figure 2** | Nitrogen adsorption-desorption isotherm and pore size distribution of Fe$_3$O$_4$/TiO$_2$-8 consisting of 8% Fe$_3$O$_4$.

**Figure 3** | UV-vis DRS of TiO$_2$ and Fe$_3$O$_4$/TiO$_2$ magnetic mesoporous composites.

**Figure 4** | C/C$_0$ versus reaction time for the degradation of Acid Black ATT with Fe$_3$O$_4$/TiO$_2$ samples. (1) TiO$_2$; (2) Fe$_3$O$_4$/TiO$_2$-1; (3) Fe$_3$O$_4$/TiO$_2$-2; (4) Fe$_3$O$_4$/TiO$_2$-4; (5) Fe$_3$O$_4$/TiO$_2$-8; (6) Fe$_3$O$_4$/TiO$_2$-10; (7) Fe$_3$O$_4$; (8) without catalysts.
3 g/L. Also, the colour removal rate increased from 48.7 to 93.3% after illumination for 5 h. When the catalyst dosage sequentially increased to 4 g/L, the results remain unchanged. It is mainly ascribed that excessive catalysts tend to be agglomerated, and thus results in less surface exposure to the light and the light transmittance steps down (Goncalves et al. 1999). Therefore, the optimum catalyst dosage for photocatalytic degradation was 3 g/L.

The durability of Fe₃O₄/TiO₂-8 was evaluated by repetitive use of the catalyst for three runs towards the decomposition of leather wastewater. The Fe₃O₄/TiO₂ composites could be easily collected from the solution by a permanent magnetic bar. The recycle results are shown in Figure 6. The initial colour and COD activity was 87 and 42%. After being used three times, the catalysts still afforded a colour and COD degradation rate of 57 and 21%. The results demonstrate that the Fe₃O₄/TiO₂ composites possess good photocatalytic stability and durability.

CONCLUSIONS

Magnetic mesoporous Fe₃O₄/TiO₂ composites with different Fe₃O₄ wt% were prepared through a sol-gel method. This material showed excellent photocatalytic efficiency. The decolorizing efficiency for the Acid Black ATT solution reached 93%. The colour and COD removal rate for tannery wastewater were 87 and 42% respectively. It was easy to recycle and keep good photocatalytic stability and durability. The present synthetic strategy may allow access to fabricating other composite catalysts with good photocatalytic performance.

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