



Photocatalytic Degradation of Reactive Dyes Using the Novel Hexagonal Magnetic Titanium Dioxide Composites

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(Received: 11 October 2010;

Accepted: 20 July 2011)

AJC-10169

The novel magnetic photocatalysts, $\text{TiO}_2/\text{Fe}_3\text{O}_4$ and $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ composites were prepared for degradation of reactive dyes. The photoactive TiO_2 was deposited onto the magnetic Fe_3O_4 or $\text{SiO}_2/\text{Fe}_3\text{O}_4$ cores by using a sol-gel coating technique. The morphologies and structures of the photocatalysts were characterized by transmission electron microscopy and X-ray diffraction. The photocatalytic activities of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ under UV light irradiation were investigated by studying the effects of the initial pH values of the solutions and irradiation times on the degradation rates of various of reactive dyes. Compared with TiO_2 , the $\text{TiO}_2/\text{Fe}_3\text{O}_4$ and $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ composites expressed excellent photocatalytic activities for various reactive dyes. The recycling experimental results showed that $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ was a highly effective decolouring agent and could effectively be separated from wastewater under the external magnetic field. After being recycled many times, the novel photocatalyst could hold on the degradation rate of 85 % on reactive brilliant blue.

Key Words: Magnetic TiO_2 , Magnetic separation, Reaction dye, Photocatalysis.

INTRODUCTION

The textile industry consumes large volumes of water in different wet processes. Therefore, large amounts of textile wastewater, which is heavily charged with unconsumed dyes and other chemicals are produced¹.

Reactive dyes are a class of synthetic dyes extensively used in the textile industry due to their characteristic of fixation in the fibers. This kind of dyes exhibit a reactive group, which binds to the textile fibers through covalent bonds. The major environmental problem associated with the use of these reactive dyes is due to their inefficient fixation to the fibers. Therefore, significant losses (12-20 % of the annual dye production) occur during the manufacture and processing with dyes being discharged as effluents into publicly owned water treatment plants^{2,3}.

Thus, there is a need to search for new and economical process that could efficiently remove reactive dyes. A photocatalytic method for the oxidation of dyes in wastewater using TiO_2 under UV or solar irradiation has also been investigated⁴⁻⁶. A major disadvantage of semiconductor oxides is the need of an additional and expensive separation step involving the removal of the photocatalyst from the treated water. In order to overcome this problem, magnetically separable photocatalysts have been developed to enable the easy recovery

of the photocatalyst by an external magnetic field⁷⁻¹². The magnetic photocatalysts can also be easily separated from the terminal solution by magnetic separation, making it available for flow-bed technologies.

In this work, we reported the photodegradation of reactive dyes using titania-supported Fe_3O_4 particles by sol-gel technique. It was found that the new hexagonal magnetic TiO_2 catalysts have the high photocatalytic activities and could be recycled by applying a magnetic field after the degradation process.

EXPERIMENTAL

All the chemicals were analytical grade, purchased from Shanghai Chemical Reagent Co. (Shanghai, China) and used as received without any purification. Doubly distilled water was used throughout this study.

Preparation of photocatalysts: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (2.7838 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.4145 g) were dissolved in distilled water (10 mL) and then dropped by 8M NH_4OH under mechanical stirring at room temperature. The pH 10 of the solution was maintained by the addition of NH_4OH . The precipitates were heated at 80 °C for 0.5 h. The black products were collected, rinsed by distilled water and then dried at 80 °C for 3 h, which were Fe_3O_4 particles.

The as-prepared Fe_3O_4 (50 mg) was ultrasonic dispersed in ethanol (20 mL), and cetyltrimethylammonium bromide (CTAB 40 mg), ethanol (20 mL) and ethylene glycol (40 mL) were added to the above solution subsequently. The solution was mechanically stirred at 65 °C for 1 h and added by dilute sulfuric acid in order to control the pH value of the solution in the range of 3-4 and then slowly dropped by butyl titanate (6 mL). After stirring for 2 h, the mixture was added by distilled water (20 mL) and again stirred for another 4 h. The product was left for over night, then rinsed by distilled water and finally dried at 80 °C for 8 h, which was $\text{TiO}_2/\text{Fe}_3\text{O}_4$ composite. And the synthesis of TiO_2 sample was in the same way as that of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ composite without Fe_3O_4 .

The as-prepared Fe_3O_4 (30 mg), distilled water (3 mL) and ethanol (20 mL) were mixed together and the pH value of the solution was adjusted at 11-12 by dropping the dilute NH_4OH . The mixture was stirred for 0.5 h at the room temperature, then dropped by tetraethoxysilane (0.3 mL) and finally stand for 5 h. The product was rinsed by ethanol for several times and dried at 60 °C for 15 h, which was $\text{SiO}_2/\text{Fe}_3\text{O}_4$ composite. The preparation of $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ was similar with that of $\text{TiO}_2/\text{Fe}_3\text{O}_4$, expect that $\text{SiO}_2/\text{Fe}_3\text{O}_4$ took the place of Fe_3O_4 during the fabrication process.

Characterization of photocatalysts: The as-prepared samples were characterized by transmission electron microscopy (TEM, TECNAL F20 S-TWIN) and X-ray diffraction spectrum (XRD, Shimadzu X-6000 X-ray diffractometer, CuK_α radiation).

Photocatalytic activity: Photocatalytic activities of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ and $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ composites were monitored by decomposing reactive dyes at room temperature. 5 mg of the product was dispersed in 5 mL of aqueous solution of dye (50 mg L^{-1}) in a quartz tubular container. After being stirred without irradiation for 0.5 h, the adsorption/desorption of dye molecules on the samples reached equilibrium. The mixture was further stirred in front of a halogen lamp and cooled by quickly running water to avoid additional heating effects. The concentration of dye was tested by UV-VIS absorption spectra on a UV1800PC UV-VIS spectrophotometer. Under the same experimental conditions, the photocatalytic activity of TiO_2 prepared by the similar method was also measured to estimate the photocatalytic activities of the composites. The chemical formula and the maximum absorption wavelength of reactive dyes, that is reactive yellow, reactive red, reactive black, reactive brilliant blue and reactive orange, were shown in Table-1.

RESULTS AND DISCUSSION

Characterization of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ and $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ composites: TEM images of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ and $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ composites were shown in Fig. 1a-b, respectively. In TEM images the dark colour corresponded to Fe_3O_4 and the light colour to TiO_2 or $\text{SiO}_2/\text{TiO}_2$ layer. As can be seen that the Fe_3O_4 particles were wrapped in the TiO_2 or $\text{SiO}_2/\text{TiO}_2$ layer. Fig. 1c shows the XRD patterns of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ and $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ composites. The diffraction peak at 24.4° can be indexed to hexagonal-phased TiO_2 in good agreement with the data of JCPDS file No. 33-1381. The peaks at 35.6°, 37.2°, 43.3°, 57.1°

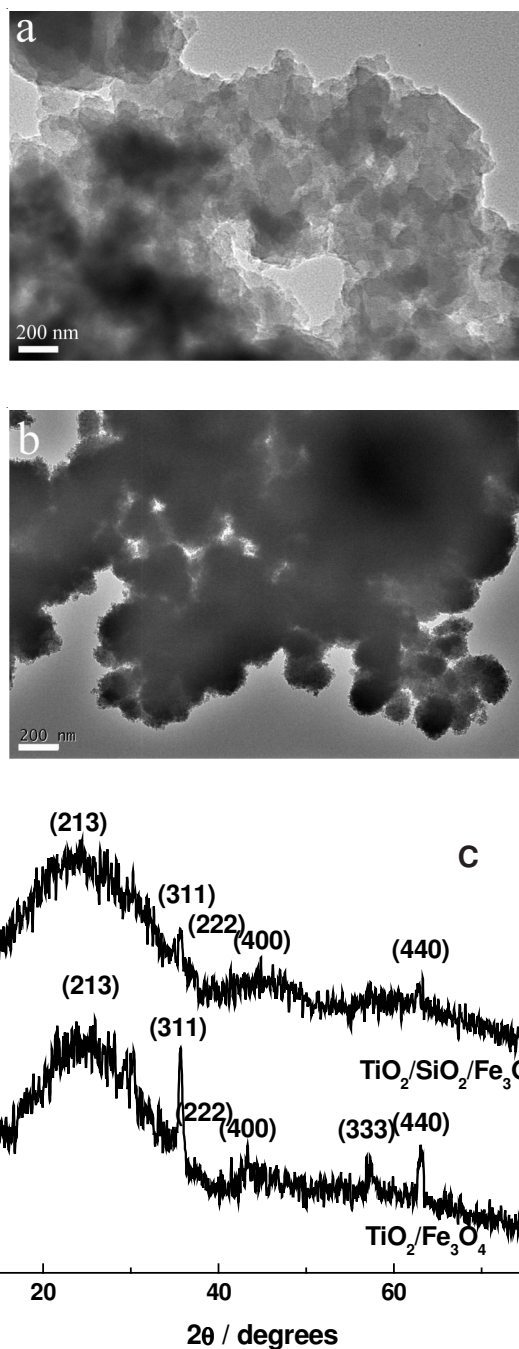
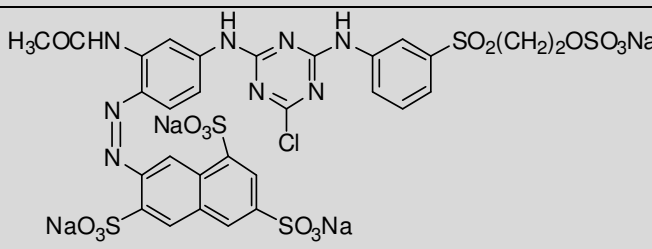
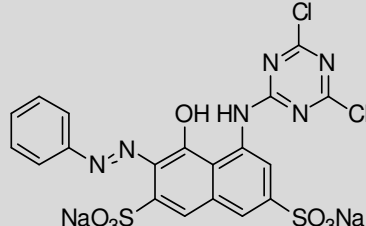
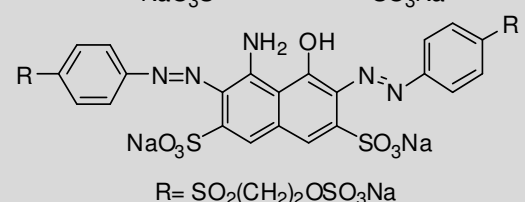
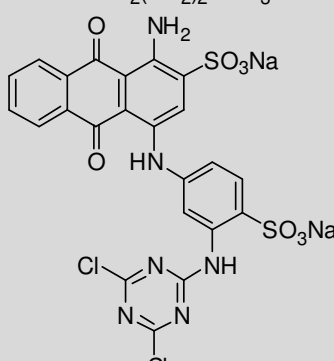
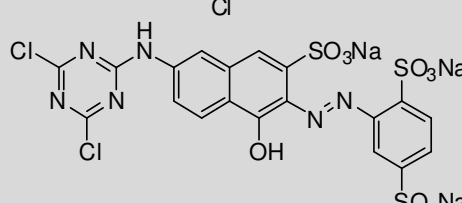


Fig. 1. TEM images (a and b) and XRD (c) patterns of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ (a) and $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ (b) composites

and 63.0° can be indexed to face-centered cubic (fcc) directions of Fe_3O_4 (311), (222), (400), (333) and (440) well corresponding to JCPDS file No. 82-1533, respectively. And the peak strength of Fe_3O_4 in $\text{TiO}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ was obviously weaker than that of Fe_3O_4 in $\text{TiO}_2/\text{Fe}_3\text{O}_4$, which was due to the presence of SiO_2 layer.

Photocatalytic activity: The photocatalytic activities of the synthesized magnetic titanium dioxide were evaluated by the degradation of reactive dyes in aqueous solution under UV light irradiation. Before the irradiation, the adsorption/desorption of reactive dyes on photocatalyst was investigated. Fig. 2 shows the concentration decrease of various reactive dyes in aqueous solution (50 mg L^{-1}) in the presence of $\text{TiO}_2/\text{Fe}_3\text{O}_4$ samples without irradiation. As shown in Fig. 2, the

TABLE-1 CHARACTERISTICS OF REACTION DYES		
Reaction dyes	Chemical formula	λ_{\max} (nm)
Reactive yellow		427
Reactive red		519
Reactive black		572
Reactive brilliant blue		598
Reactive orange		527

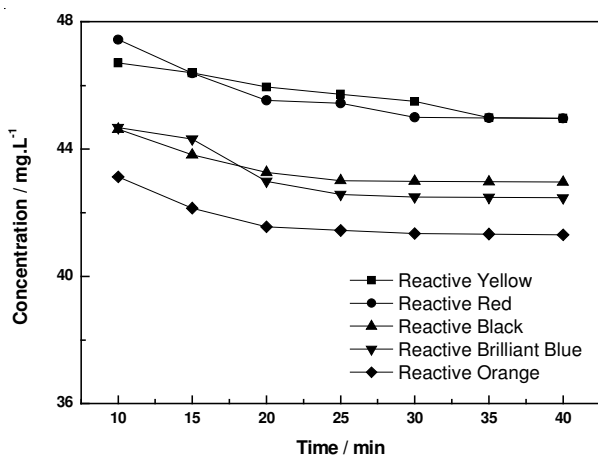


Fig. 2. Degradation rates of various of reactive dyes at different intervals in the presence of TiO₂/Fe₃O₄ composite without irradiation

concentrations of the reactive yellow and reactive red in aqueous solution decrease with the increasing time and about 45 mg L⁻¹ at 0.5 h, after that they were no change occurred. At the same experimental condition the concentrations of the reactive black and reactive brilliant blue reached stable at 25 min and were about 43 mg L⁻¹. And similar to reactive black and reactive brilliant blue, reactive orange with the concentration of 41 mg L⁻¹ at 25 min kept stable. The concentration decreases of reactive dyes without irradiation can be accounted for the adsorption of dye molecules on the photocatalyst. After the adsorption/desorption equilibrium, the concentrations of reactive dyes in aqueous solution hardly changed with the increasing time.

The wastewaters resulted from textile industries usually have a wide range of pH values. Hence, the effect of initial pH values on the photocatalytic degradation of reactive dyes

(50 mg L⁻¹) with UV light irradiation time of 10 min in the presence of TiO₂/Fe₃O₄ composite was studied (Fig. 3). The pH values of the initial solutions were adjusted by dropping hydrochloric acid solution. It can be found that the degradation rates of reactive dyes in strong acid solution were slightly higher than those in neutral solution, which exceeded 90 % in addition to that of reactive yellow. Among them, the degradation rates of reactive brilliant blue and reactive orange were more than 90 % during the whole range of initial pH values. That is to say, the magnetic catalyst could effectively be used in aqueous solution with widely pH values.

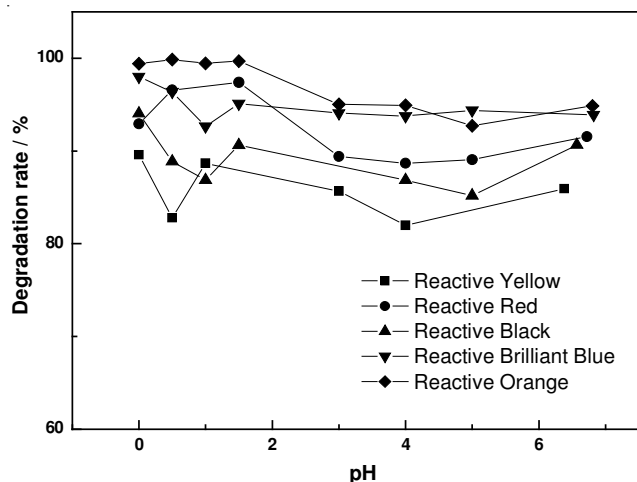


Fig. 3. Effects of initial pH values on degradation rates of reactive dyes in the presence of TiO₂/Fe₃O₄ composite with the irradiation time of 10 min

Fig. 4 showed the effects of irradiation times on degradation rates of various reactive dyes in neutral aqueous solution in the presence of the TiO₂/Fe₃O₄ sample, respectively. As shown in Fig. 4, at first the degradation rates of various dyes quickly went up with the increasing irradiation times and at about 7 min tended to balance. The degradation rates of reactive yellow, reactive red, reactive black, reactive brilliant blue and reactive orange at the irradiation time of 10 min were 89.3, 99.1, 96.4, 96.2 and 96.6 %, respectively. It was indicated that the TiO₂/Fe₃O₄ photocatalyst was universal to various reactive dyes.

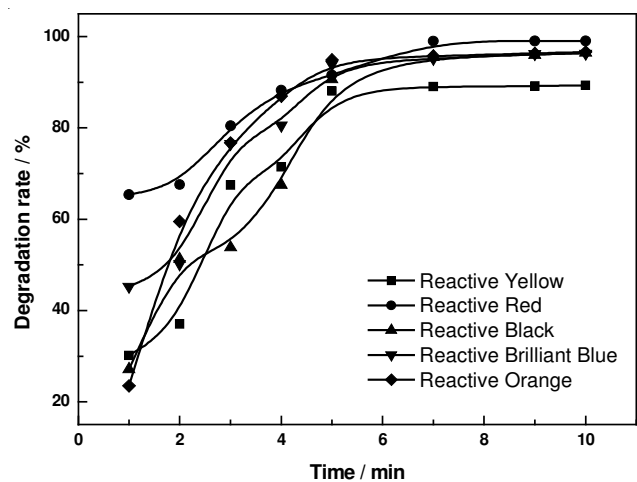


Fig. 4. Degradation rates of various of reactive dyes at different intervals in the presence of TiO₂/Fe₃O₄ composite with irradiation

In order to estimate the photocatalytic activity of the composites, the degradation rates of various reactive dyes in the presence of TiO₂, TiO₂/Fe₃O₄ or TiO₂/SiO₂/Fe₃O₄ samples at the different irradiation times were listed in Table-2. As shown in Table-2, the degradation rates of various dyes in the presence of TiO₂/Fe₃O₄ or TiO₂/SiO₂/Fe₃O₄ composites were obviously more than those in the presence of TiO₂, indicating the good photocatalytic performance of the composites. The photocatalytic capacities of TiO₂/Fe₃O₄ samples were slightly more than those of TiO₂/SiO₂/Fe₃O₄ ones apart from that of reactive yellow. As shown in Table-2, the degradation rates of various of reactive dyes exceeded 90 % in the presence of TiO₂/SiO₂/Fe₃O₄ sample and expressed good photocatalytic properties.

TABLE-2
DEGRADATION RATES OF VARIOUS OF REACTIVE DYES IN THE PRESENCE OF TiO₂, TiO₂/Fe₃O₄ or TiO₂/SiO₂/Fe₃O₄ SAMPLES, RESPECTIVELY

Reaction dyes	Catalysts	Irradiation times (min)	Degradation rates (%)
Reactive yellow	TiO ₂	5	72.7
	TiO ₂ /Fe ₃ O ₄	5	88.0
	TiO ₂ /SiO ₂ /Fe ₃ O ₄	5	92.1
Reactive red	TiO ₂	7	65.7
	TiO ₂ /Fe ₃ O ₄	7	99.0
	TiO ₂ /SiO ₂ /Fe ₃ O ₄	7	96.8
Reactive black	TiO ₂	10	69.1
	TiO ₂ /Fe ₃ O ₄	10	96.4
	TiO ₂ /SiO ₂ /Fe ₃ O ₄	10	94.1
Reactive brilliant blue	TiO ₂	10	79.7
	TiO ₂ /Fe ₃ O ₄	10	96.2
	TiO ₂ /SiO ₂ /Fe ₃ O ₄	10	94.8
Reactive orange	TiO ₂	10	77.5
	TiO ₂ /Fe ₃ O ₄	10	96.6
	TiO ₂ /SiO ₂ /Fe ₃ O ₄	10	95.2

Taking a sample of reactive brilliant blue (50 mg L⁻¹), the recycling capacities of the TiO₂/Fe₃O₄ and TiO₂/SiO₂/Fe₃O₄ composites at the irradiation time of 10 min were shown in Fig. 5. The experimental results showed that the degradation rates of reactive brilliant blue in the presence of TiO₂/Fe₃O₄ sample kept stable at first three-time cycles and achieved 96 % and then they quickly decreased to 48 % at the 7th cycle. It resulted from an unfavourable electronic heterojunction between the core-shell TiO₂/Fe₃O₄, which led to the electron-hole recombination^{13,14}. However, the degradation rates of reactive brilliant blue in the presence of TiO₂/SiO₂/Fe₃O₄ sample gradually decreased to 92 % at first three-time cycles, after seventh cycles they held on 85 % and hardly changed. It was indicated that the presence of SiO₂ layer prevent electron-hole from recombining. Comparing to the TiO₂/Fe₃O₄ sample, the TiO₂/SiO₂/Fe₃O₄ composite was more stable and had excellent recycling stability.

Conclusion

The novel hexagonal TiO₂/Fe₃O₄ and TiO₂/SiO₂/Fe₃O₄ composites were synthesized by sol-gel technique. The presence of Fe₃O₄ was in favour of separation and recovery of catalysts from wastewaters under the magnetic field and the silica was coated on magnetic core in order to facilitate catalyst

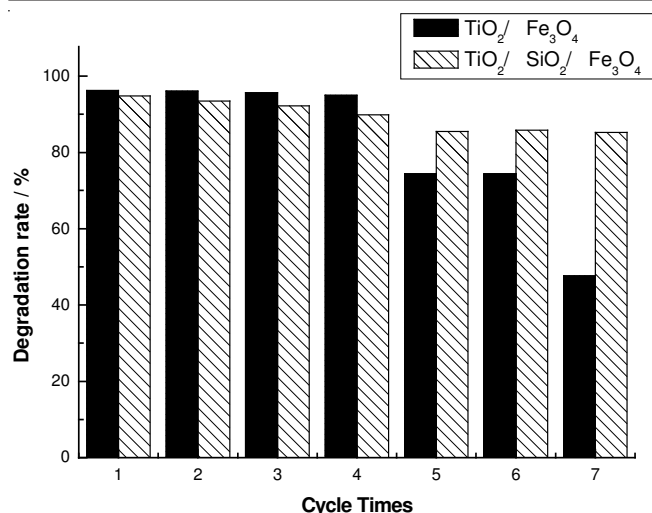


Fig. 5. Effects of the different cycle times on degradation rates of reactive brilliant blue in the presence of TiO₂/Fe₃O₄ or TiO₂/SiO₂/Fe₃O₄ composites at the irradiation time of 10 min

to recover and reuse. The experimental results showed that the TiO₂/Fe₃O₄ composite had high photocatalytic activity and were universal to various reactive dyes in the solutions with different pH values. And the reused results of the composites indicated that the TiO₂/SiO₂/Fe₃O₄ sample was more stable and had excellent recycling stability.

ACKNOWLEDGEMENTS

This research was financially supported by Foundation of Zhejiang Educational Committee of China (Grant No. Y200805544) and the National Science Foundation for Young Scientists of China (Grant No. 20901051).

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