Research Article

Photodegradation of Methylene Blue by TiO_2 - Fe_3O_4 -Bentonite Magnetic Nanocomposite

Wei Chen,^{1,2} Hongyao Xiao,^{1,2} Hang Xu,^{1,2} Tonggang Ding,^{1,2} and Yanmei Gu²

¹Key Laboratory of Integrated Regulation and Resource Development on Shallow Lake of Ministry of Education, College of Environment, Hohai University, Nanjing 210098, China

²College of Environmental Science, Hohai University, Nanjing 210098, China

Correspondence should be addressed to Hang Xu; 23060096@qq.com

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Fe_3O_4 -bentonite nanoparticles have been prepared by a coprecipitation technique under a nitrogen atmosphere. An aqueous suspension of bentonite was first modified with FeCl_2 and FeCl_3 . TiO_2 was then loaded onto the surface of the Fe_3O_4 -bentonite by a sol-gel method. After sufficient drying, the colloidal solution was placed in a muffle furnace at 773 K to obtain the TiO_2 - Fe_3O_4 -bentonite composite. The material has been characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, and vibrating sample magnetometry (VSM). Morphological observation showed that Fe_3O_4 and TiO_2 nanoparticles had been adsorbed on the surface of bentonite nanoneedles. The material was then applied for the photodegradation of the azo dye methylene blue (MB). It was found that the removal efficiency of MB exceeded 90% under UV illumination, and that only a 20% mass loss was incurred after six cycles. The composite material thus showed good photocatalytic performance and recycling properties.

1. Introduction

Among environmental contaminants, dyestuffs constitute a major component and are of particular concern [1]. Azo dyes are widely applied in the printing and dyeing industries [2–4]. Some azo dyes can be reduced to aromatic amines, which are potent carcinogens [5]. Therefore, they need to be completely removed from wastewater from printing and dyeing. Due to its good catalytic effect, stable chemical performance, ready availability, and nontoxicity, TiO_2 has been regarded as an ideal kind of catalyst since the 1940s [6]. Under illumination, the crystal surface of TiO_2 generates electrons (e^-) and holes (h^+), allowing the production of reactive oxygen species (ROS) such as hydroxyl free radicals or oxygen free radicals [7, 8]. Such species react with the nitrogen double bonds in azo dyes, and the dyes are thereby decomposed into nontoxic small-molecule chemicals [9]. However, pure TiO_2 is of limited use because of its low specific surface area and low adsorption rate [10–13]. Various catalyst supports have been applied for loading with TiO_2 . Xia et al. examined TiO_2

supported on layered double hydroxides that shows over 85% removal rate of azo dyes [14]. Janus et al. loaded TiO_2 on the surface of powder activated carbon and used it to remove azo dyes [15–18]. Xu et al. synthesized a new composite material, hydroxy-iron-aluminum pillared bentonite (H-Fe-Al-Ben), by ion exchange, and studied its 99.5% removal rate of azocarmine B [19].

Due to their adsorption abilities and catalytic activities, natural clays have been widely used as adsorbents and catalyst supports. Bentonite is a clay mineral, the main component of which is montmorillonite [20, 21]. Due to its unique structure, bentonite has good mechanical properties, high thermal stability and acid and alkali resistance, large surface area, and other favorable characteristics. Hence, it has been widely used in adsorbents, catalysts, adhesives, catalyst supports, and so on [22]. Bentonite is abundant in China, notably in Wuxi, Jiangsu, and Zhejiang provinces [23]. Researchers have modified the surface of bentonite to enhance its dispersibility and selectivity. Toor et al. studied acid and thermal activation that leads to approximately 25% increase in

the Congo-red adsorption capacity of natural bentonite [24]. Li et al. synthesized Fe-pillared bentonite and Al-Fe-pillared bentonite and found that these composite materials were effective in removing azo dye X-3B [25]. Liu et al. found that the adsorption capacity of bentonite was greatly increased by 90.55% after interaction with attapulgite [26]. Xu et al. studied that when ZnO/bentonite particles catalyst was used, the removal rate of Acid Yellow II reached to 90% under UV irradiation, which was remarkably effective [27].

In practice, such adsorbents are difficult to recycle and are liable to cause secondary pollution and a waste of resources [28]. Iron oxide, with the formula Fe_3O_4 , consists of magnetic black crystals. Its good magnetic properties are often applied to modify materials, allowing for improved recycling performance. Pan et al. studied the recovery performance of Fe_3O_4 -attapulgite used for the degradation of 2,4-dichlorophenol and found the mass loss of adsorbent to be just 7.53% after five cycles [29]. Wu et al. used a solution copolymerization technique to synthesize a bentonite- Fe_3O_4 PSA magnetic nanocomposite, which proved that a small amount of bentonite could improve the swelling ability for the removal of Th(IV) [30].

Using bentonite as a catalyst support, iron oxide for enhanced recovery performance, and TiO_2 for catalytic decomposition, we have prepared a TiO_2 - Fe_3O_4 -bentonite composite photocatalyst material by a simple combined precipitation-coating and sol-gel method. This composite has been investigated by SEM, XRD, and VSM.

2. Materials and Methods

2.1. Materials. Bentonite (average size 200 mesh) was purchased from Oilbetter (China). $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were purchased from Sinopharm Chemical Reagent Co. (China); the latter was stored under a nitrogen atmosphere to avoid the oxidation of Fe(II). Azo dyes were procured from Dye Company (Dystar). The test solution was prepared by dissolving azo dye (30 mg) in distilled water (1 L). Methanol, ethanol, acetylacetone, tetrabutyl titanate, and sodium hydroxide were purchased from Sigma-Aldrich Corporation. All experiments were performed using deionized ultrapure water from an ultrapure water preparation device. All reagents were of analytical grade purity and were used directly without further purification.

2.2. Preparation of the Catalyst

2.2.1. Pretreatment of Bentonite. Bentonite clay powder (particle size 0.074 mm) was finely sieved, a 5% suspension in water was prepared, and this was allowed to age for 24 h. The bentonite powder was then recovered by centrifugation and placed in an oven at 378 K until it completely dehydrated. It was kept dry until its subsequent loading with TiO_2 .

2.2.2. Loading of Bentonite with Fe_3O_4 . Fe_3O_4 -bentonite was prepared by a coprecipitation method.

Step 1. At 343 K under nitrogen atmosphere, bentonite powder (1.0 g) was added to 200 mL of aqueous solution

containing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.0 g) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (2.5 g). Aqueous NaOH solution (10 mL, 8 mol/L) was then added dropwise to adjust the pH to 11 and the mixture was stirred continuously for 1 h.

Step 2. The mixture was aged at 343 K for 4 h. The particles were then washed with distilled water until neutral and dried in an oven at 373 K for 3 h to afford Fe_3O_4 -bentonite crystals.

2.2.3. Loading of Fe_3O_4 -Bentonite with TiO_2

Step 1. Fe_3O_4 -bentonite (2.5 g) was placed in a beaker, and ethanol (80 mL) was added. The mixture was sonicated for 20 min and then left to stand.

Step 2. Ethanol (80 mL) and tetrabutyl titanate (20 mL) were mixed in a beaker and sonicated for 20 min. Further ethanol (80 mL) and aqueous nitric acid (obtained by diluting 10 M HNO_3 (1 mL) with distilled water (16 mL)) were then added to form a colloidal solution. The mixture was vigorously stirred for 30 min and then left to stand for 24 h.

Step 3. The mixture was placed in an oven at 353 K until completely dry and then transferred to a muffle furnace and heated at 773 K for 3 h to afford TiO_2 -loaded magnetic bentonite.

2.3. Analytical Methods. The crystal structure of the product was determined on a Thermo X'TRA type X-ray diffractometer. The crystal size and morphology of the samples were examined using a scanning electron microscope (Hitachi Ltd., S-4800). The magnetic properties of the samples were determined using a vibrating sample magnetometer (VSM) (Lake Shore VSM7410).

2.4. Photocatalytic Reactions. Experiments on the degradation of methylene blue were performed to investigate the photocatalytic effect of the TiO_2 - Fe_3O_4 -bentonite. A 350 W xenon lamp equipped with a 288 K constant temperature circulator was used. TiO_2 - Fe_3O_4 -bentonite (30 mg) and 30 mg/L methylene blue solution (100 mL) were mixed for 30 min in a dark environment. After the solution had reached equilibrium, it was placed in a batch stirrer for several minutes under UV light irradiation. Aliquots (2 mL) of the supernatant were withdrawn at intervals to measure the methylene blue concentration by UV spectrophotometry at a wavelength of 664 nm. No catalyst was added in a blank test.

3. Results and Discussion

3.1. SEM Analysis of TiO_2 - Fe_3O_4 -Bentonite. Figure 1 shows the XRD patterns of different samples. From the figure, it is evident that the modification of bentonite did not change its structure. Comparing Figures 1(a) and 1(b), it can be seen that the bentonite surface had been successfully loaded with Fe_3O_4 and TiO_2 by the concerted precipitation-coating and sol-gel method.

FIGURE 1: XRD patterns of (a) bentonite, (b) $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$. ◇ Bentonite; △ Fe_3O_4 ; ☆ TiO_2 (rutile).

FIGURE 2: SEM images of (a) bentonite, (b) $\text{Fe}_3\text{O}_4\text{-bentonite}$, (c) $\text{TiO}_2\text{-bentonite}$, and (d) $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$.

Figure 2 shows SEM images of the samples. Figure 2(a) shows a bentonite particle of diameter about 2–3 μm . When 5% aqueous suspensions of bentonite were aged for 24 h, the surface area of the crystals was significantly increased, providing a good surface for the loading of TiO_2 and Fe_3O_4 [31]. From Figures 2(a) and 2(b), it can be seen that the $\text{Fe}_3\text{O}_4\text{-bentonite}$ surface was more rough and that the crystal size was smaller after loading with Fe_3O_4 . Many Fe_3O_4 particles were adsorbed on the bentonite surface. Figure 2(c) shows a surface image of $\text{TiO}_2\text{-bentonite}$, from which it is evident that the bentonite particles had a good surface condition

for the loading of TiO_2 . Figure 2(d) shows that the crystal surface morphology was not significantly changed when a large number of TiO_2 particles of diameter 10–20 nm were adhered on the surface of the $\text{Fe}_3\text{O}_4\text{-bentonite}$.

3.2. Magnetic Properties of $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-Bentonite}$. Figure 3 shows the magnetic hysteresis loop of $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$. The magnetic properties of the composite were measured by vibrating sample magnetometry (VSM) at room temperature, at magnetic field strengths in the range $-20\text{ kOe} \leq H \leq 20\text{ kOe}$. The magnetic saturation (M_s), residual

FIGURE 3: Magnetic hysteresis loop of $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$ at 298 K.

magnetization (M_r), coercivity (H_c), and M_r/M_s ratio (S_r) of the composite were 33.29 emu/g, 0.87 emu/g, 7.973 G, and 0.026, respectively. Low residual magnetism and coercivity showed the sample to have ferromagnetic behavior at room temperature. Weak hysteresis attributed to a single magnetic domain of nanocrystalline nature was observed, which indicates that $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$ is a strongly paramagnetic material. The magnetism of Fe_3O_4 was weakened after loading with TiO_2 , but was still 33.29 emu/g, so that it could be attracted by a commercial magnet. Thus, the $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$ composite can be recovered by a simple magnetic separation technique, greatly reducing secondary pollution and the material cost of wastewater treatment.

3.3. Adsorption Kinetics of $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-Bentonite}$. The Langmuir-Hinshelwood kinetic model is commonly used to describe the photocatalytic degradation of organic compounds. The relationship between the reaction rate r and the concentration C is expressed as follows:

$$r = -\frac{dC}{dt} = \frac{k_r K_{ad} C}{1 + K_{ad} C}, \quad (1)$$

where k_r is the intrinsic rate constant and K_{ad} is the adsorption equilibrium constant. When the adsorption is weak or the adsorbate concentration is low, $K_{ad} C$ is negligible and the adsorption kinetic equation can be simplified to a first-order model:

$$r = k_r K_{ad} C = K_{app} C, \quad (2)$$

where K_{app} is the apparent adsorption constant.

In the initial condition ($t = 0$, $C = C_0$),

$$\ln \frac{C_0}{C} = K_{app} t, \quad (3)$$

where C_0 and C are the initial dye concentration and the concentration at time t , respectively. The values of K_{app} can

FIGURE 4: Pseudo-first-order kinetics for the degradation of methylene blue.

TABLE 1: Pseudo-first-order kinetic parameters for the photodegradation of MB dye.

Sample	MB		R^2
	K_{app} [min^{-1}]	$t_{1/2}$ [min]	
$\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$	0.03236	21.4	0.9848

thus be calculated from regression analysis of the reaction time t and $\ln C_0/C$.

Figure 4 shows the linear relationship between $\ln C_0/C$ and t for the degradation of methylene blue at 298 K, as befits the first-order adsorption model (linear correlation constant > 0.98). The apparent adsorption constant and $t_{1/2}$ value are shown in Table 1. The degradation of methylene blue was 90% complete after 90 min of reaction. Specifically, the rate of degradation of methylene blue adsorbed on the $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$ composite material was 0.0324 min^{-1} ($t_{1/2} = 21.4 \text{ min}$); that is, it was 50% degraded in just 21.4 min. This synthetic clay composite material thus showed considerable photocatalytic degradation efficiency.

3.4. The Photocatalytic Properties of $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-Bentonite}$. We investigated the catalytic effects of bentonite, $\text{Fe}_3\text{O}_4\text{-bentonite}$, $\text{TiO}_2\text{-bentonite}$, and $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$ on the degradation of methylene blue under xenon lamp light, and the results are shown in Figure 5. It can be seen that the reaction almost reached completion after 90 min with $\text{TiO}_2\text{-bentonite}$ and $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$; the removal of methylene blue was 90% complete after 90 min. Comparison of these four adsorbents for the removal of methylene blue indicates that $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$ is better than bentonite. The TiO_2 crystals loaded on the surface of bentonite are mainly responsible for the decomposition of methylene blue. Studies have indicated that azo dyes are first adsorbed and then a surface-catalyzed reaction ensues, which is favorable for their removal. From Figure 5, it is also evident that $\text{TiO}_2\text{-Fe}_3\text{O}_4\text{-bentonite}$ and $\text{TiO}_2\text{-bentonite}$ removal rate shows superior removal efficiency compared to $\text{Fe}_3\text{O}_4\text{-bentonite}$

FIGURE 5: Photocatalytic degradation of methylene blue by bentonite, Fe₃O₄-bentonite, TiO₂-bentonite, and TiO₂-Fe₃O₄-bentonite under Xe light.

FIGURE 6: TiO₂-Fe₃O₄-bentonite regeneration experiment.

and bentonite, and that the little difference between TiO₂-Fe₃O₄-bentonite and TiO₂-bentonite is led by little contribution of Fe₃O₄ to photocatalytic removal efficiency.

The regeneration performance of TiO₂-Fe₃O₄-bentonite was tested by carrying out six cycles of adsorption and desorption. The eluent consisted of methanol and acetic acid (9.5:0.5). After separating the catalyst from the aqueous solution by means of a magnet at the end of each experiment, the catalyst was washed for 30 min with 10 mL of eluent under ultrasonication. The experimental results are shown in Figure 6. It can be seen that the mass loss of the composite material over the six cycles was only 20%. The composite material retained its stable structure during the process, indicating good regeneration properties.

4. Conclusions

A TiO₂-loaded magnetic clay composite material has been synthesized by a simple ion coprecipitation and sol-gel method. The catalyst has proved to be effective for the removal of methylene blue under irradiation with a xenon lamp. The absorption of methylene blue on the composite material showed pseudo-first-order kinetics, with an adsorption rate r of 0.0324 min⁻¹. In methylene blue degradation experiments, the removal efficiency of a 30 mg/L methylene blue solution reached 90% after 90 min at 298 K and pH 7.0. In addition, the composite material incurred only 20% mass loss after six cycles of repeated use, which shows good recycling properties. Therefore, the described TiO₂-loaded magnetic clay material showed not only good adsorption

decomposition performance for azo dyes under visible light, but also excellent recycling properties. It thus has great potential application in the azo dye treatment industry and is worthy of further study.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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