Energy, Resources and Environmental Technology

Adsorption of Methyl Orange on Magnetically Separable Mesoporous Titania Nanocomposite ☆

Libo Gao [1,2], Qiang Zhang [1,2], Junyang Li [1,2], Ruiting Feng [1,2], Hongyan Xu [3], Chenyang Xue [1,2,*]

[1] Key Laboratory of Instrumentation Science and Dynamic Measurement of Ministry of Education, North University of China, Taiyuan 030051, China
[2] Science and Technology on Electronic Test & Measurement Laboratory, North University of China, Taiyuan 030051, China
[3] School of Materials Science and Engineering, North University of China, Taiyuan 030051, China

A B S T R A C T

The adsorption of mesoporous Fe_3O_4–SiO_2–TiO_2 (MFST), which can be separated easily from solution by a magnet, for the removal of methyl orange (MO) was investigated. The nitrogen adsorption–desorption measurement shows successful synthesis of MFST with an average pore size of 3.8 nm and a large specific surface area of 55 $m^2 \cdot g^{-1}$. About 95% adsorption percentage of MO is achieved with an initial concentration of 10 $mg \cdot L^{-1}$ in the dark and the MFST exhibits superior adsorption ability under acid conditions. The adsorption data fit well with the pseudo-second order model for adsorption. After 4 cycles, the adsorption rate for MO remains 74% in the dark and the MFST can be recovered in a magnetic field with a recovery of about 80 % (by mass). It demonstrates that the samples have significant value on applications of wastewater treatment.

1. Introduction

Titanium dioxide (TiO_2) exhibits a stable chemical structure, and it is bio-compatible, nontoxic and cost effective [1,2]. It is useful for removal of many organic contaminants from wastewater such as dyes and volatile organic compounds with photocatalytic oxidation [3–5]. Considerable hydroxyl groups (OH) are present on TiO_2 surface and the pollutants in water can be adsorbed on the surface *via* interaction with OH. With large specific surface area, more active sites and highly porous structure, mesoporous TiO_2 should present high photocatalytic activity [6]. It is expected to possess higher removal capability than non-porous TiO_2. Therefore, mesoporous TiO_2 has been an area of intense interest for the past years, particularly for photocatalysis, water purification, and environmental remediation [7–9].

However, much less research has been devoted to the adsorption of TiO_2 compared to photocatalysis for organic compounds [10–12]. TiO_2 nanoparticles have large adsorption capacity due to their large surface area, so they may be effective metal sorbents compared to bulk particles [13–15]. Recently, TiO_2 nanomaterial is developed as adsorbent for high-chroma crystal violet, showing higher removal capacity than the raw material P25 [16]. Also, mesoporous TiO_2 is found to be an effective adsorbent for organic compounds with carboxy groups [17]. Asuha *et al.* synthesized mesoporous TiO_2 by a hydrothermal method and investigated its adsorption for Cr(VI) and methyl orange (MO) [18]. The adsorption capacity for MO was approximately 11 times higher than that of commercial TiO_2 and the specific surface area was about 4 times larger, which may be the reason for high adsorption capacity. However, their mesoporous TiO_2 had a poor reusability for adsorption of MO. In addition, removing nano-sized TiO_2 from large volumes of water is difficult and expensive, which restricts its applications [19]. Magnetic separation provides a convenient method for removing and recycling magnetic particles by applying external magnetic fields [20]. Hence TiO_2 with magnetic particles may solve such a problem in separation from treated water, simply by applying an external magnetic field [21]. The crystallization of sol–gel TiO_2 is usually performed at high temperature and the magnetic materials, such as Fe_3O_4, may transform to α-Fe_2O_3 rapidly if treated concurrently. Fe_3O_4 is much more sensitive and unstable compared with TiO_2, especially under acidic conditions [22], so it is helpful to insert a passivation layer, such as a silica layer, between the magnetic core particle and TiO_2 coating.

In this paper, we report the preparation of Fe_3O_4 nanoparticles as the magnetic core via the carbon reduction method and the fabrication of mesoporous Fe_3O_4–SiO_2–TiO_2 (MFST) with excellent adsorption ability and recyclability through the sol–gel method. The adsorption ability of MFST in the dark for removal of MO is examined after each cycle. The MO is chosen as the representative model compound (Fig. 1) because it is a typical water-soluble anionic dye.
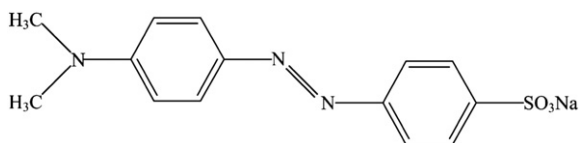
Fig. 1. The structure of methyl orange dye.

2. Experimental

2.1. Materials

Ferric chloride, tetraethoxysilane (TEOS), tetra-butyl ortho-titanate (TBOT), ethanol, hydrochloric acid, nitric acid, and MO (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Sample preparation and characterization

Fe_3O_4 nanoparticles were prepared by a novel method named carbon reduction method as reported in our previous paper [23]. Fe_3O_4 particles and 100 ml of alcohol were put into a beaker in an oven. When the temperature was raised to 50 °C, 15 ml TEOS was added. Then 0.97 ml of hydrochloric acid and a little deionized water were added into the collosol. The residual collosol was removed from the beaker while the particles at the bottom were attracted by magnet after 3 h. Finally, wet particles were put in a quartz Petri dish and kept under 500 °C and 2.6×10^{-5} MPa vacuum conditions for 2 h. Fe_3O_4–SiO_2 particles were obtained after milling. The MFST coated with three TiO_2 layers was prepared as follows. Fe_3O_4–SiO_2 particles were put into the beaker with TBOT and alcohol. The beaker with collosol and particles was in an ultrasonic bath for 10 min and stirred for 20 min. Deionized water was added with slow stirring. The ratio of ester, alcohol to water was 30.3:12.5:1. At last, the particles were heated at 500 °C for 2 h at 2.6×10^{-5} MPa. After milling, the MFST was obtained. The procedure was repeated for three times to obtain the MFST coated with three TiO_2 layers.

MFST particles were characterized by TEM and XRD. The components were measured by advanced X-ray diffraction (XRD) system (Bruker D8) using Cu K_α radiation of wavelength 0.15406 nm. Shapes and sizes of particles were examined using JEOL JEM-1200EX TEM measurements (operated at 120 kV). Magnetic properties were characterized on a Lake Shore 7307 vibrating sample magnetometer. Nitrogen adsorption–desorption isotherms were taken by a Micromeritics ASAP 2020 instrument. Brunauer–Emmett–Teller (BET) surface area was calculated from adsorption branches and pore size distribution was from desorption branches using the Barrett–Joyner–Halenda (BJH) method. The ultraviolet visible adsorption spectra were measured with a UV–Vis–NIR spectrophotometer 5000 (Varian).

2.3. Measurement of adsorption ability

The adsorption ability of MFST was evaluated by measuring the adsorption percentage of MO in an aqueous solution at room temperature. 0.2 g MFST was added with stirring into 50 ml of MO aqueous solution with concentration of 10 mg·L^{-1} and maintained in the dark. 6 mol·L^{-1} of HCl and 6 mol·L^{-1} of NaOH were used to adjust the pH value of the solution. 2 ml suspension solution was removed at regular intervals and filtered through a high-speed desktop centrifuge (TGL-16KZhuhai Black Horse Medical Equipment Co., Ltd) for adsorption analysis. The UV–Vis adsorption spectra were measured with a UV–Vis–NIR spectrophotometer 5000 (Varian) at $\lambda = 462.5$ nm. The experiment was performed until nearly complete adsorption. All the tests were repeated three times; the presented results are the average of three measurements. The adsorption capacity of MFST is calculated by

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

where q_t is the adsorbed amount of MO (mg·g^{-1}), C_0 and C_t represent the initial concentration (mg·L^{-1}) and that at time t, respectively, V is the volume of MO solution (L), and W is the mass (g) of MFST adsorbent.

2.4. Regeneration

The MFST was recovered in a permanent magnetic field and washed with sodium hydroxide and deionized water completely for further experimental runs. Specifically, 0.2 g MFST containing MO was collected in a permanent magnetic field. Then it was added under stirring into 100 ml of NaOH aqueous solution with concentration of 1 mol·L^{-1} and maintained in the dark with stirring for 1 h. The MFST was removed from NaOH solution in a permanent magnetic field and washed with 0.05 mol·L^{-1} acid solution and deionized water. Finally, the recovered MFST was dried at 50 °C in a vacuum oven for further experiments.

3. Results and Discussion

3.1. Characteristics of synthesized MFST

Fig. 2(a) shows the XRD pattern of MFST. The relatively strong and sharp diffraction characteristic peaks of Fe_3O_4 and anatase structural
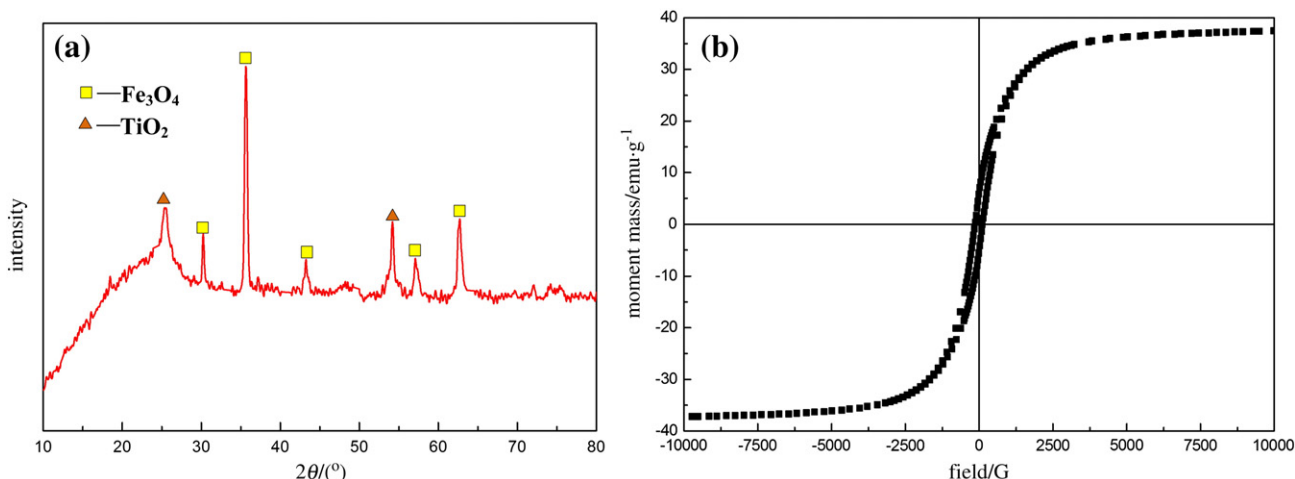

Fig. 2. XRD pattern (a) and magnetization curves (b) of MFST.