Journal of Non-Crystalline Solids 357 (2011) 136–139

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Synthesis, characterization and dye adsorption of ilmenite nanoparticles

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ARTICLE INFO

Article history:
Received 27 January 2010
Received in revised form 11 August 2010
Available online 10 November 2010

Keywords:
Ilmenite nanoparticles;
Physical properties;
Dye adsorption

ABSTRACT

$FeTiO_3$ nanoparticles (nano-$FeTiO_3$ or nano-ilmenite) can be synthesized by the sol–gel method. In this study, the physical properties and dye adsorption characteristics of nano-$FeTiO_3$ are investigated. A synthesized nano-ilmenite has a particle size of approximately 20 to 60 nm with a polycrystalline structure. The $FeTiO_3$ nanoparticles exhibit weak ferromagnetism and show high adsorption capacity for methylene blue. Experimental data are fitted to pseudo-first-order and pseudo-second-order equations; the pseudo-first-order model is found to be more suitable. It also suggests that the Langmuir isotherm is more adequate than the Freundlich isotherm in simulating the adsorption isotherm of organic dye. The maximum adsorption capacity is 71.9 mg/g, therefore, the magnetic $FeTiO_3$ nanoparticles show a considerably high adsorption capacity for organic dyes in a solution. These findings indicate that the nano-ilmenite is an effective material for dye removal and can be used to alleviate environmental problems.

1. Introduction

Environmental issues such as water and air pollution are becoming increasingly important. Numerous treatment technologies have been developed to eliminate or reduce environmental problems, for example, membrane separation, ion-exchange methods, photocatalysis, and adsorption methods [1–6]. Among these methods, adsorption, in particular, has been intensively studied because of its simplicity, low cost, and high removal efficiency. Therefore, the adsorption process has been extensively used for the elimination of organic substances or heavy metal ions from water and wastewater [7–9]. The common adsorbents used in remediation techniques include oxides, hydroxides, activated carbon, porous materials, and nanominerals [10–13].

The development of nanotechnology at the end of the 20th century has added to the variety of adsorbents. The removal of heavy metals using nanoparticles has shown promising results with nanocrystalline titanium dioxide [14], nanoscale zero-valent iron [15], etc. Recently, it has been discovered in the USA that it is possible to remove As species using nanoparticles, and the adsorption capacity is very high [16–18]. Moreover, nano-maghemite has been found to be very effective in the removal of Cr(VI). The advantages of using nanoparticles as adsorbents are as follows: (a) they can be easily synthesized at a low cost, (b) the amount of nanoparticles required for removal is considerably less, and (c) their adsorption capacity is considerably high because of their large surface area. Since nanomaterials exhibit unique properties, research on nanomaterials has gradually become more popular and significant.

Ilmenite ($FeTiO_3$) is one of the most common minerals in the Earth's crust. It is also a wide bandgap (2.58–2.9 eV) antiferromagnetic semiconductor [19,20], and it has potential applications in spintronics, high temperature integrated circuits, high power electronic devices, chemical catalysts, and photocatalysts [21–24]. Therefore, it has been extensively studied in all its varieties. The structure of $FeTiO_3$ is derived from that of α-Fe_2O_3 by replacing every other layer of Fe atoms in the (001) planes by a layer of Ti atoms. Natural ilmenite contains a large amount of hematite (Fe_2O_3) [25], and thus, preparation of ilmenite is not easy; one of the major obstacles in the preparation of ilmenite is the instability of the Fe^{2+} ion. Therefore, there are few reports on the synthesis of $FeTiO_3$ powders in the literatures. As for the synthesis of ilmenite nanoparticles (nano-ilmenite), there are quite few researches studied on this topic.

Although there have been some studies on the nano-ilmenite, only a few have focused on the photocatalysis of the nano-ilmenite; further, there are no published reports on the adsorption of organic materials using the nano-ilmenite. In this study, ilmenite nanoparticles were synthesized by employing a sol–gel method. We then investigated the physical properties and dye adsorption efficiency of the nano-ilmenite. It is found that the dye adsorption activity of ilmenite nanoparticles gives the compound a great potential for applications in environmental remediation.

2. Experimental

2.1. Preparation and characterization of the nano-ilmenite

In this study, $FeTiO_3$ nanoparticles were synthesized by using the sol–gel method; $Fe(NO_3)_3$ was reacted with $TiCl_4$, and citric acid in

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doi:10.1016/j.jnoncrysol.2010.09.070

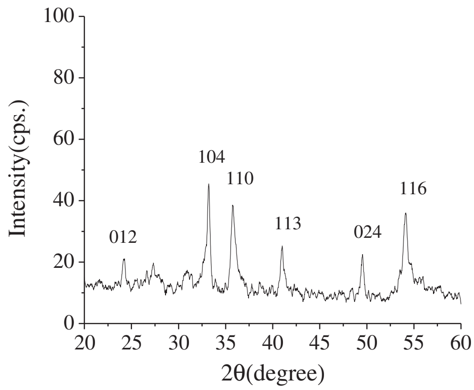

Fig. 1. XRD pattern of the nano-$FeTiO_3$.

deionized water heated to 100 °C for 2 h (the molar ratio of Fe $(NO_3)_3$, $TiCl_4$, and citric acid was 1:1:2). Subsequently, it was calcined at 500 °C for 3 hr and then cooled to room temperature. The crystal structure of the nano-ilmenite was characterized by X-ray powder diffraction (XRD). The morphology and grain size of $FeTiO_3$ nanoparticles were observed by using a transmission electron microscope (TEM). The bandgap of this specimen was examined via a UV–Vis diffuse reflectance spectrometer. The magnetism was measured by a superconducting quantum interference device (SQUID) magnetometer at room temperature (R.T.) within the magnetic field of 1 T. For determining the specific surface area, the nitrogen gas adsorption method was used via the autosorbing nitrogen-adsorption devices.

2.2. Adsorption batch experiment

For the adsorption experiment, methylene blue solution (M.B., $C1_6H_{18}C_lN_3S{\bullet}3H_2O$) was used as the organic dye at various initial concentrations (0.5, 1, 2, 4, 6, and 8 ppm), to which 0.03 g of the nano-ilmenite (adsorbent) was added. The rate of M.B. adsorption onto the nano-ilmenite was studied using batch experiments with varying times. The degradation in the M.B. concentration was measured using a UV–Vis spectrometer.

2.3. Adsorption kinetics and isotherm

Various kinetic models have been suggested for the adsorption process, and two well-known models, pseudo-first-order [26] and pseudo-second-order [27] models, were selected in this study. The pseudo-first-order equation is commonly represented by the following form:

$$\frac{dq}{dt} = k_1(q_e - q_t)$$

where k_1 is the rate constant of the pseudo-first-order model; q_t, the amount of solute adsorbed on the adsorbent at time t; q_e, the amount of solute adsorbed on the adsorbent at the equilibrium state. The variable q_t can be expressed as follows:

$$q_t = \frac{(C_0 - C_t)}{m_s}$$

where C_t is the dye concentration at time t, C_0 is the dye initial concentration, and m_s is the mass of the adsorbent. The concentration of the solute varies with time according to the equation:

$$(C_t - C_0) = \left(1 - \frac{m_s q_e}{C_0}\right) + \left(\frac{m_s q_e}{C_0}\right) e^{-k1t}.$$

The pseudo-second-order equation can be represented in the following:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \text{ or } (C_t - C_0) = \left(1 - \frac{m_s q_e}{C_0}\right)\left(\frac{q_e k_2 t}{1 + q_e k_2 t}\right)$$

where k_2 is the rate constant of the pseudo-second-order model.

The adsorption isotherm is essential for the research of an adsorption process. Numerous isotherm equations have been reported, and two major isotherms, the Langmuir and Freundlich isotherms [28], are tested to fit the experimental data. The Langmuir adsorption isotherm can be expressed as follows:

$$q_e = \frac{(Qk_L C_e)}{1 + k_L C_e}$$

where Q is the adsorption capacity, and k_L is the Langmuir constant.

The Freundlich isotherm, which is in the form:

$$q_e = k_F C_e^{1/n}$$

where k_F is the extent of the adsorption, and n is the degree of non-linearity.

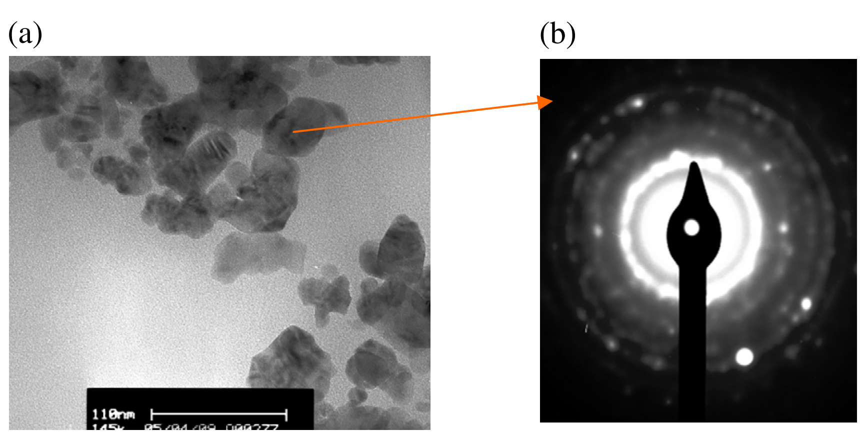

Fig. 2. (a) TEM image and (b) SAED pattern of the nano-ilmenite.