



Magnetic mesoporous clay adsorbent: Preparation, characterization and adsorption capacity for atrazine



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ABSTRACT

Fe₃O₄/sepiolite magnetic composite (MSEP) was prepared by chemical co-precipitation method in air and used as adsorbent to remove atrazine from aqueous solution. The composite was characterized by using X-ray diffraction, X-ray fluorescence, specific surface area, Fourier transform infrared spectroscopy, scanning electron microscope, magnetic hysteresis loop and zeta potential measurements. The results show that the specific surface area, average pore diameter and pore volume increased from 70.92 m²/g, 6.4441 nm and 0.1143 cm³/g for the natural sepiolite (NSEP) to 112.44 m²/g, 8.6703 nm and 0.2437 cm³/g for MSEP because of the loading of Fe₃O₄ particles on the surface of sepiolite particles. The electrokinetic property of sepiolite in an aqueous solution was promoted and the isoelectric point of MSEP was obtained at pH 7.7. The values of saturation magnetization, remanent magnetization and coercivity for MSEP were 31.82 emu/g, 1.12 emu/g and 11.77 Oe, respectively. The adsorption experiments of atrazine onto MSEP show that the adsorption process followed the Langmuir isotherm model and the maximum adsorption capacity can reach 15.9 μg per unit BET surface area of adsorbent.

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1. Introduction

Atrazine, a selective triazine herbicide used to control weeds in various crops, was first manufactured in 1950s, and then introduced into China around 1980. Since then, the amount of atrazine applied in China has increased 20% per year because of its low cost and high effectiveness [1]. Due to its long half-life, apparent mobility, moderate water solubility, great leaching potential and high chemical stability in soils and aquifers, atrazine has been detected in water bodies across the world, including China [2]. Some studies have indicated that atrazine is toxic to animals and humans. It has been classified as a potential human carcinogenic by United States Environmental Protection Agency (USEPA) [3]. In China, atrazine has been included in the standards for surface water quality with a maximum concentration of 3 ppb [4]. Removing atrazine from water bodies has become a critical environmental issue worldwide. However, due to its high chemical and biological stability, most conventional water treatment techniques, except for adsorption, have low removal efficiency for atrazine from water. More and more efforts have been focused on preparing novel adsorbents with natural materials such as clay minerals [5–7].

Sepiolite, a magnesium hydrosilicate with the unit cell formula of Si₁₂O₃₀Mg₈(OH,F)₄(OH₂)₄·8H₂O, is known to occur in many countries including Turkey, Spain, USA, Portugal and China [8–10]. Natural sepiolite (NSEP) has a general structure formed with alternated blocks and tunnels that grow up in the fiber direction and each block consists of two SiO₄ tetrahedral sheets enclosing a central MgO₆⁴⁻ octahedral sheet [11]. Like other clay minerals, NSEP has an electronegative surface because of isomorphous substitutions. In addition, the abundant channels bring sepiolite a large specific surface area, and the large amount of exchangeable cations endows it with favorable ion-exchange capacity. As a result, sepiolite can be used to remove organic and inorganic species from water environment. In particular, it is a promising adsorbent for those chemically and biologically stable contaminants which cannot be effectively disposed from water environment by traditional technologies. Some examples include using sepiolite as an adsorbent to remove surface oil-spill [12], pesticides [13], pharmaceutical [14], organic dyestuff [11,15], heavy metal ions [16], and so on.

During the past few years, magnetic separation technology has attracted a lot of attention and made progress in water treatment because of its easy and fast separation. In this technology, magnetic adsorbents are prepared by loading magnetic nanoparticles on the surface of carrier. Then, the adsorbents are placed into aqueous solutions containing contaminants, collected and separated by an external magnetic field after the adsorption is carried out.

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At present, many kinds of clay minerals have been used as carrier to prepare magnetic composites and to adsorb contaminants from water, such as magnetic attapulgite molecularly imprinted polymers to remove 2,4-dichlorophenol [17], attapulgite/iron oxide magnetic composites to remove U(VI) [18], montmorillonite–Cu(II)/Fe(III) oxides magnetic material to remove humic acid [19] and *Microcystis aeruginosa* [20], magnetic bentonite to remove acid red 138 [21] and metal ions [22], magnetic zeolite to remove metal ions [23]. Also, recently, some researchers have focused on modifying sepiolite with iron to better remove pollutants from water. Wang et al. [24] and Huang et al. [25] prepared magnetic sepiolite composites by chemical co-precipitation technique and investigated the adsorption capacity for Cd²⁺ and Cu²⁺, respectively. Esteban-Cubillo et al. [26] synthesized magnetic iron-coated sepiolite by thermal treatment of the iron-containing sepiolite at 500 °C in a reducing H₂/Ar atmosphere. Iglesias et al. [27] and Li et al. [28] developed nonmagnetic iron-loaded sepiolite composites by ferric ions adsorption onto natural sepiolite to enhance adsorption capacity for Reactive Black 5 dye and antimony, respectively. In addition, other researchers synthesized nonmagnetic Fe-sepiolite composites in which iron exists as a goethite phase, by adding natural sepiolite into an iron nitrate or iron chloride solution under strongly basic conditions [29–33]. Unfortunately, a full-scale characterization for these iron-modified sepiolite composites mentioned above is lack, and studies on their adsorption capacity for herbicides are still scarce.

Therefore, the main aims of this work are: (i) to prepare magnetic clay adsorbent composed of nano-magnetite and clay (sepiolite) by chemical co-precipitation technique, (ii) to investigate the characteristics of MSEP with various instrumental analyses, (iii) to evaluate the adsorption capacity of atrazine onto MSEP with the Langmuir adsorption isotherm model.

2. Materials and methods

2.1. Materials

The natural sepiolite used in this study was obtained from Dongfeng Sepiolite Co., Ltd. (Xinyang, China) with a particle size ≤ 0.075 mm (200-mesh). Ferric chloride (FeCl₃·6H₂O), ferrous sulfate (FeSO₄·7H₂O), sodium hydroxide (NaOH) and ammonium hydroxide (NH₄OH) were purchased from Kelong Chemical Co., Ltd. (Chengdu, China). Atrazine was supplied by Oddfoni Biological Technology Co., Ltd. (Nanjing, China). Deionized ultrapure water used in all experiments was purified with Millipore offered by Purkinje General Co. (Beijing, China). All the reagents were of analytical grade and used as received without further purification.

2.2. Preparation of MSEP

2.4 g FeSO₄·7H₂O and 3.1 g FeCl₃·6H₂O were respectively dissolved in 50 mL deionized water in beaker. 4 g NSEP were dispersed into the Fe³⁺ solution and sat in ultrasonic bath at 40 °C for 15 min to get a well-mixed feed solution. Then the mixture solution was transferred into a 500 mL three-necked flask which was placed in a thermostat water bath. The Fe²⁺ solution was added into the flask and the mixture was stirred (200 rpm) at 60 °C to keep it as sufficient suspension. After 30 min, the stirring speed was increased (400 rpm) followed by drop wise addition of NH₄OH solution (25%, 10 mL). After 60 min, the suspension was aged for 120 min at the same temperature. Finally, the precipitates were collected by magnetic separation and washed immediately with deionized water for several times until the supernatant pH was neutral. After being filtered, dried at 110 °C for 3 h, ground

and screened with 200 mesh standard sieve, the final MSEP products were obtained.

2.3. Material characterization

X-ray diffraction (XRD) patterns were collected on an X'Pert pro X-ray diffractometer (PANalytical, Holland) with Cu K α radiation ($\lambda = 0.15406$ nm) and the 2θ range of 5–80°.

X-ray fluorescence (XRF) was characterized using a wavelength dispersive ARL-9800XP X-ray fluorescence spectrometer (ARL, Switzerland). Prior to measurement, the samples were allowed to dry at 105 °C for 4 h to remove adsorbed water in materials.

Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area by nitrogen adsorption/desorption isotherm on a Micrometrics ASAP 2020 analyzer (Micromeritics, USA) at 77 K. The pore volume and pore diameter distribution were derived from the adsorption branches of isotherms using the Barrett–Joyner–Halenda (BJH) model.

The Fourier transform infrared spectra (FTIR) (4000–400 cm⁻¹) were acquired on a NEXUS870 Fourier Transform Infrared Spectrometer (Nicolet, USA) to observe the surface functional groups using KBr pressing method. KBr pellets were prepared with the 1:200 mass ratio of material and KBr.

The structural morphology and surface characteristics of sepiolite samples were observed using a Hitachi S-4800 scanning electron microscope (SEM) with an accelerating voltage of 5 kV.

Magnetic hysteresis loop measurements of the samples were carried out at room temperature using a 7404 vibrating sample magnetometer (Lakeshore, USA). The magnetic property parameters such as the saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) were obtained from the hysteresis loop.

Zeta potential (ZP) of materials was measured using a ZEN3690 Zeta potential analyzer (Malvern, UK) according to literature [8]. Samples for ZP analysis were prepared by mixing 0.25 g solid sample in 50 mL electrolyte (NaCl, 0.01 M) in an Erlenmeyer flask and pH was adjusted with 0.01 M HCl or NaOH. Then the samples were stirred for 1 h at room temperature. Subsequently, the samples were allowed to stand for 15 min to let larger particles settle and the colloidal suspension was collected for the ZP analysis.

2.4. Isothermal adsorption experiments for atrazine

Atrazine adsorption experiments were carried out to evaluate the adsorption capacity of MSEP. 0.1 g of MSEP was added into 50 mL of atrazine solution with initial concentrations varying from 2 to 28 mg/L. The pH of mixture was 6.5 without any adjustment during experiment. Each mixture was maintained at a setting temperature (25 °C, 45 °C or 65 °C) and stirred at 180 rpm for 120 min. Then the precipitation was separated by an external magnetic field. The supernatant was filled with 0.45 μ m filter and the concentration of remaining atrazine was measured by HPLC [34].

In order to prevent aerobic biodegradation and photochemical decomposition of atrazine during the adsorption process, a certain amount of HgCl₂ (200 mg/L, pH 6.5) were added into samples, and all batch tests were performed in dark. Additionally, blank experiments (without adsorbent) were carried out simultaneously as control. The results showed that no adsorption occurred on the glass wall of the vessels, and the atrazine loss resulting from volatilization was insignificant. All the adsorption experiments were performed in triplicate. The amount of atrazine adsorbed per unit sepiolite surface area (q_e) was calculated as follows:

$$q_e(\text{mg/m}^2) = (C_0 - C_e)V/S_{\text{BET}} \quad (1)$$

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