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Synthesis of rectorite/Fe_3O_4-CTAB composite for the removal of nitrate and phosphate from water

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ABSTRACT

The rectorite/Fe_3O_4-CTAB composite (REC/Fe_3O_4-CTAB) was fabricated by introducing cetyl trimethyl ammonium bromide (CTAB) and Fe_3O_4 onto the layers of raw rectorite (REC). The layers of rectorite were intercalated or exfoliated, and CTAB enhanced the electrostatic attraction by quaternary ammonium cations towards nitrate and phosphate anions. The order of Fe_3O_4 and CTAB introduction had great effect on the adsorption. When Fe_3O_4 was loaded before CTAB on REC, the obtained composites exhibited better adsorption. The maximum adsorption capacities could reach 182.1 mg/g for NO_3^- and 174.5 mg/g for PO_4^{3-}. Besides, REC/Fe_3O_4-CTAB composite could be easily regenerated with NaOH solution.

Introduction

Agricultural nitrate and phosphate pollution has become the most predominant source of water pollution in China. Excessive use of nitrogenous and phosphorous fertilizers causes eutrophication, which stimulates the overgrowth of algae and aquatic plants, leading to human health disorders, such as blue-baby syndrome, infant methemoglobinemia as well as cancer [1]. The present available methods for the removal of nitrate and phosphate include ion exchange [2–4], reverse osmosis [5], adsorption [6–13], catalytic [14,15] and biological denitrification [16]. Among all the methods studied, adsorption method was attached great importance due to its high efficiency, simple equipment required and good reliability [17]. Many natural materials can be good adsorbents for nitrate and phosphate in water, especially when they are modified, such as bamboo powder charcoal [18], Fe_3O_4/ZrO_2/chitosan composites [19], mixed lanthanum/aluminum modified montmorillonite [20], Fe(III)-montmorillonites [21], positively charged kaolinites [22].

Rectorite (REC) is an interstratified natural clay mineral composed of a regular stacking of dioctahedral mica-like layer and dioctahedral smectite-like layer in a ratio of 1:1. As the smectite-like layers in REC are readily intercalated, REC possesses good adsorption capacity for cationic metals and dyes [23–26] by exchanging interlayer Na^+ with either organic or inorganic cations. Previous work proved that modified REC is a good adsorbent for MB (methylene blue) and Pb^{2+}, with maximum adsorption values of 277 mg/g and 180.8 mg/g, respectively [27].

However, REC exhibited weak adsorption for anionic contaminants such as nitrate, phosphate, sulfate and dichromate. Therefore, it is of great necessity to modify REC in order to meet the demand for the removal of nitrate and phosphate contaminants in water. Recently, many studies focused on tackling such similar problem, and quaternary ammonium salt is a very commonly used and advisable modifier [28]. By ion exchange between organic cations and Na^+ in the interlayer of REC, the adsorption capacity of REC for anionic contaminants can be greatly enhanced. In addition, another disadvantage of REC adsorbent is its difficult withdrawal from water after the adsorption process. By introducing magnetic Fe_3O_4 into REC, REC composites can be easily separated from water with the magnetic field, thus avoiding secondary pollution [29]. In this work, magnetic Fe_3O_4 was introduced into the interlayer of REC for the facile separation from water. At the same time, Fe_3O_4 particles could improve the interlayer spaces of REC, which would be beneficial for intercalating quaternary ammonium salt into the enlarged interlayer of REC. The REC/Fe_3O_4 composite was then treated with CTAB to obtain REC/Fe_3O_4-CTAB composite. The modifications were expected to improve the adsorption capacities for nitrate (NO_3^-) and phosphate (PO_4^{3-}). In this process, magnetic REC actually acted

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as the support of CTAB, while CTAB on magnetic REC was the adsorbent for nitrate and phosphate.

Experimental

Materials

Sodium rectorite was purchased by Hubei Zhongxiang Rectorite Mine (Wuhan, China). All other reagents were of analytical grade and commercially available.

Preparation of REC/Fe_3O_4 composite

REC/Fe_3O_4 composites were fabricated in a modified method of Ref. [29]. 1 g REC, 1.165 g $FeCl_3{\cdot}6H_2O$ and 0.6 g $FeSO_4{\cdot}7H_2O$ were added into 20 mL distilled water. 20 mL NH_3H_2O solution (8 M) was added dropwise to produce magnetic iron oxide under N_2 atmosphere. The pH of the mixture was approximately 11–12. The suspension was held at 70 °C for 4 h and then washed with distilled water several times. The obtained REC/Fe_3O_4 composite was dried at 50 °C for 4 h.

Preparation of REC-CTAB composites

REC-CTAB composites were prepared in a modified method of Ref. [30]. 4 g REC was dispersed in 200 mL 0.014 mol/L CTAB solution using ultrasonication for 10 min. The pH of the mixture was adjusted to 2, 7 and 13 with hydrochloric and sodium hydroxide solution. Then the mixture was shaken on an immersion oscillator registration at 100 rpm for 12 h at 60 °C. After washed for 6–8 times, the sample was dried at 50 °C for 4 h. The obtained REC-CTAB composites were labeled as CTAB-REC-2, CTAB-REC-7 and CTAB-REC-13, respectively.

Assembly of REC-CTAB/Fe_3O_4 composite

1 g as-obtained CTAB-REC-13, 1.165 g $FeCl_3{\cdot}6H_2O$ and 0.6 g $FeSO_4{\cdot}7H_2O$ were added into 20 mL distilled water, and 20 mL NH_3H_2O solution (8 M) was added dropwise to produce magnetic iron oxide under N_2 atmosphere. The pH of the mixture was approximately 11–12. The suspension was held at 70 °C for 4 h and then washed with distilled water several times. The obtained REC-CTAB/Fe_3O_4 composite was dried at 50 °C for 4 h.

Assembly of REC/Fe_3O_4-CTAB composite

1 g as-obtained REC/Fe_3O_4 composite was dispersed in 50 mL 0.014 mol/L CTAB solution using ultrasonication for 10 min. The pH of the mixture was adjusted to 13 with sodium hydroxide solution. Then the mixture was shaken on an immersion oscillator registration at 100 rpm for 12 h at 60 °C. After washed for 6–8 times, the obtained REC/Fe_3O_4-CTAB composite was dried at 50 °C for 4 h.

X-ray diffraction (XRD)

X-ray diffraction patterns for REC, REC-CTAB, REC/Fe_3O_4, REC-CTAB/Fe_3O_4 and REC/Fe_3O_4-CTAB were recorded in reflection mode in the angular range of 1–40° (2θ), at room temperature by a D/MAX-2500 operated at a CuKα wavelength of 1.542 Å.

Fourier transform infrared spectroscopy (FTIR) spectra

FTIR analysis of REC, REC-CTAB, REC/Fe_3O_4, REC-CTAB/Fe_3O_4 and REC/Fe_3O_4-CTAB were performed on a BIO-RAD FTS3000 IR spectra scanner. The sample powders were dispersed in KBr and pressed into transparent sheets for testing.

Thermogravimetric analysis (TGA)

Thermal properties of REC, REC-CTAB, REC/Fe_3O_4, REC-CTAB/Fe_3O_4 and REC/Fe_3O_4-CTAB were measured using a ZTY-ZP type thermal analyzer. Sample weights ranged from 10 to 15 mg. Samples were heated from ambient temperature to 800 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

Vibrating sample magnetometer (VSM)

The magnetic properties of REC/Fe_3O_4, REC-CTAB/Fe_3O_4, and REC/Fe_3O_4-CTAB were tested on a vibrating sample magnetometer (LDJ 9600-1, LDJ Electronics Inc., USA).

Scanning electron microscope (SEM)

Powders of REC, REC-CTAB, REC/Fe_3O_4, REC-CTAB/Fe_3O_4 and REC/Fe_3O_4-CTAB were immobilized in a sample holder, coated with gold, and viewed with an S-4800 scanning electron microscope.

Transmission electron microscope (TEM)

REC, REC-CTAB, REC/Fe_3O_4, REC-CTAB/Fe_3O_4, REC/Fe_3O_4-CTAB powders were dispersed in alcohol. Sample suspensions were dropped into a copper grid, dried in air, and tested with a JEM-2100F transmission electron microscope.

Energy dispersive spectroscopic (EDS) mapping

The composition of REC-CTAB/Fe_3O_4 and REC/Fe_3O_4-CTAB was measured with energy dispersive spectroscopic mapping with a JEM-2100F transmission electron microscope.

Specific surface area

The specific surface area of REC, REC-CTAB/Fe_3O_4 and REC/Fe_3O_4-CTAB were measured with an Autosorb-1 specific surface area analyzer (Quantachrome Instruments, USA) using the BET method on the base of N_2 adsorption data.

The point of zero charge (pH_{ZPC})

The point of zero charge (pH_{ZPC}) of adsorbent REC/Fe_3O_4-CTAB was determined. 10 mg REC/Fe_3O_4-CTAB composite was added to 10 mL of 0.1 mol/L KNO_3 solution at different initial pH from 3 to 10. The initial pH of solutions were adjusted with NaOH or HCl solution, and measured by pH meter (PHSJ-4A, China). Afterwards, the mixtures were shaken on a rotary shaker at 100 rpm for 12 h at 30 °C and the final pH values of solutions were measured at equilibrium [31].

Adsorption of nitrate (NO_3^-)

Adsorption experiments were conducted using glass bottles containing 10 mg adsorbents and 10 mL nitrate solution (NO_3^- 100 mg/L) at pH 5. During the adsorption process, the glass bottles were placed on a slow-moving platform shaker and nitrate solutions were taken at intervals to analyze the effect of contact time on equilibrium adsorption capacity. The NO_3^- concentrations were tested using UV–vis spectrometry at 204 nm to determine the adsorbed amounts of NO_3^- at 30 °C [32].

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