



Magnetic modification of acid-activated kaolin: Synthesis, characterization, and adsorptive properties



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ABSTRACT

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles were synthesized onto the surface of acid-activated kaolin (AAK), prepared by calcination and acid activation of a coal bearing kaolin, by immobilizing an Fe–urea complex ($[\text{Fe}(\text{NH}_2\text{CONH}_2)_6](\text{NO}_3)_3$) and subsequent calcination. The obtained samples were characterized by X-ray diffraction (XRD), N_2 adsorption–desorption, X-ray photoelectron spectroscopy (XPS), vibrating sample magnetic measurements, and transmission electron microscopy (TEM). The results confirm the formation of ferromagnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles, approximately 18 nm in size, onto the AAK surface. The obtained $\gamma\text{-Fe}_2\text{O}_3/\text{AAK}$ nanocomposite has a high Brunauer–Emmett–Teller (BET) surface area of $99.4\text{ m}^2/\text{g}$ and possesses ferromagnetic characteristics with a maximum magnetization of 26.5 emu/g . The adsorption ability of $\gamma\text{-Fe}_2\text{O}_3/\text{AAK}$ nanocomposite was investigated using methylene blue (MB) as a typical pollutant. Owing to its high surface area, the $\gamma\text{-Fe}_2\text{O}_3/\text{AAK}$ nanocomposite showed higher removal efficiency for MB than for parent kaolin, with a maximum adsorption capacity of 50.2 mg/g . The adsorption kinetics of MB fit well with the pseudo-second-order kinetic model, and the equilibrium data can be well described by the Langmuir adsorption model.

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1. Introduction

Kaolin is one of the most important and useful natural clays. Owing to its good chemical and mechanical stability, layered structure, and high cation exchange capacity, kaolin is widely used to fabricate materials such as rubber, plastic, paper, ceramics, catalysts, cosmetics, and adsorbent materials [1,2]. Kaolin can also be used in the environment as a natural scavenger of pollutants by removing pollutants either through ion exchange or adsorption, which makes it a very promising low cost adsorbent for water treatment [3].

Kaolinite-rich deposits, found in coal seams of coal mines, are abundant in the Inner Mongolia area of northern China. This type of kaolin is called coal bearing kaolin. In general, it has a high concentration of impurities, which limits its use in the above-mentioned applications. For this reason, coal bearing kaolin is discarded as a waste in some areas, and its accumulation is creating new environmental problems. Therefore, the utilization of coal bearing kaolin for wastewater treatment is desirable. However,

coal bearing kaolin is inactive, and therefore, for applications in adsorption, its surface properties, including surface area, and surface exchange sites, must be improved. The reactivity of kaolin is related to several factors including structural order, concentration of impurities, and type of intercalated molecules, which makes it possible to be activated by physical or chemical processes. For example, milling, heat treatment, and acid treatment have proven to be effective methods for the activation of kaolin [4–6]. Of these, acid treatment, which mainly leads to the elimination of mineral impurities and removal of octahedral Al^{3+} in kaolinite, is the most effective method for altering the structure and composition of kaolin. However, the activation of raw kaolin by acid treatment is difficult because it is inert [7]. It has been reported that amorphous metakaolinite (MK), obtained by the calcination of kaolinite, is more reactive to acid attack than parent kaolinite (PK) [8]. Therefore, the calcination of kaolin is usually carried out prior to acid treatment in order to obtain activated kaolin with a high reactivity. The acid treatment of MK yields a porous solid mainly composed of an amorphous silica phase. Acid-activated kaolin (AAK) has a wide range of industrial uses and is very promising as an adsorbent or catalyst; hence, the study of AAK is becoming one of intense interest in material science [9–11].

Removal of industrial pollutants (e.g., heavy metals and organic compounds) from water is becoming more and more important to

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the world's health, and considerable attention has therefore been paid to water treatment in recent years [12,13]. As a low-cost and convenient method, adsorption is very promising for the removal of pollutants from wastewater, and it is widely used in water treatment [14–16]. It is known that the adsorption capacity of an adsorbent mainly depends on the surface area available for adsorption. Materials with many ion exchange sites and high surface area usually possess high removal abilities. Additionally, the separation and recovery of adsorbents from treated water should be easily achieved when using adsorption for water treatment. Based on such considerations, the synthesis of magnetically modified nanocomposites with high surface area would undoubtedly be welcome since the adsorbent materials used can be readily separated from treated water with an external magnetic field.

In this study, we report a novel method for the synthesis of γ -Fe₂O₃/AAK nanocomposite with high surface area using coal bearing kaolin as PK and describe the removal ability of the material for methylene blue (MB). The proposed method is based on the *in situ* formation and thermal decomposition of an Fe–urea complex ([Fe(NH₂CONH₂)₆](NO₃)₃) on the AAK surface, which allows a homogenous generation of γ -Fe₂O₃ nanoparticles on the solid surface and maintains the adsorption ability of AAK together with the ferromagnetic properties of the γ -Fe₂O₃ nanoparticles.

2. Experimental

2.1. Materials

Coal bearing kaolin was obtained from coal seam deposits of Inner Mongolian coal mines in northern China. Its chemical composition (wt.%) is given in Table 1. Fe(NO₃)₃·9H₂O (99%, Tianjin Fengchuan Chemical Reagents Company), urea (99%, Tianjin Shengao Chemical Reagents Company), absolute ethanol (99%, Beijing Chemical Reagents Company), hydrochloric acid (analytical grade, Tianjin Fengchuan Chemical Reagents Company), and methylene blue (MB, 99%, Tianjin Shengao Chemical Reagents Company) were used as received.

2.2. Acid activation of kaolin

First, 6 g of PK was mixed with 180 mL of deionized water in a 250 mL laboratory ball mill, followed by grinding for 24 h. The resultant powder was separated from the solution by filtration and washed several times using deionized water, and dried in an oven at 60 °C, resulting in the formation of a gray powder. Then, the dried powder was calcined at 800 °C in air for 8 h to obtain MK.

In a three-neck flask equipped with a condenser, 5 g of MK was mixed with 90 mL of 6 M HCl solution. It was then slowly heated to 90 °C and kept at that temperature under reflux condition for 4 h. After cooling to room temperature, the acid treated powder was separated from the solution by centrifugation, washed with deionized water until no Cl⁻ ions could be detected, and then dried at 50 °C, resulting in the formation of AAK powder.

2.3. Magnetic modification of AAK

For the synthesis of AAK/ γ -Fe₂O₃ nanocomposite, we calculated the amount of AAK and iron nitrate, which would give products

with 30 wt.% Fe₂O₃ after calcination. Typically, 1.98 g of AAK powder was dispersed in 20 mL of absolute ethanol, and then 4.3 g of Fe(NO₃)₃·9H₂O was added to the mixture under stirring, which continued for 1 h. At the end of that time, 4.2 g of urea was added to the resulting mixture, followed by ultrasonication for 30 min. The molar ratio of Fe³⁺ to urea was set at 1:6 to form [Fe(NH₂CONH₂)₆](NO₃)₃ over the AAK surface. The solid was separated from solvent by filtration, rinsed with ethanol several times to remove the unreacted reactants and dried at room temperature. Finally, the sample was calcined at 200 °C for 1.5 h in air. The final product was attracted to a permanent magnet, indicating the formation of a magnetic solid.

2.4. Characterization

Elemental analysis was carried out by inductively coupled plasma spectroscopy (ICPS) using a Thermo IRIS Interpid II spectrometer. N₂ adsorption–desorption isotherms were measured using a Micrometrics ASAP2020 analyzer. Transmission electron micrographs (TEM) were recorded using a FEI Tecnai G2 F20 S-Twin transmission electron microscope. X-ray diffraction patterns (XRD) were obtained with a Rigaku D/Max-Ultima IV diffractometer using CuK α radiation. Fourier transformed infrared (FTIR) spectra were recorded using a Nicolet Nexus 6700 spectrometer in a dry-nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) spectra were measured using a VG ESCALAB-MKII 250 instrument with a monochromatic Al K α radiation source. Thermogravimetric analysis (TGA) was carried out in air, at a heating rate of 5 °C/min from room temperature to 800 °C, using a Shimadzu DTG-60H apparatus. Magnetic measurements were performed on a Lake Shore 7407 vibrating-sample magnetometer (VSM) at room temperature. The Brunauer–Emmett–Teller (BET) surface area was calculated from the adsorption branches, and the pore size distribution from the desorption branches using the Barrett–Joyner–Halenda (BJH) method.

2.5. MB adsorption

For the adsorption tests, 100 mg of adsorbent was added to 20 mL of MB (50 mg/L) solutions. The mixtures were agitated in a shaking water bath at a constant speed of 300 rpm at room temperature for a certain time. The solution pH was 6.8, and it was not adjusted. After adsorption, solution and adsorbent powders were magnetically separated by using a magnet to measure the concentration of MB in the solution. MB concentrations were determined using a Shimadzu UV–Vis 2550 spectrophotometer by measuring the solution absorbance at 668 nm.

3. Results and discussion

3.1. Synthesis and characterization of AAK/ γ -Fe₂O₃ nanocomposites

The procedure adopted for the synthesis of AAK/ γ -Fe₂O₃ nanocomposites from kaolin is illustrated in Fig. 1, which is based on the ability of [Fe(NH₂CONH₂)₆](NO₃)₃ to be transformed into γ -Fe₂O₃ nanoparticles at a high temperature and mainly comprises the following five steps: (1) preparation of MK by the calcination of PK at 800 °C, (2) preparation of AAK via the acid treatment of MK, (3) wet impregnation of the AAK with iron nitrate, (4) formation of [Fe(NH₂CONH₂)₆](NO₃)₃ complex on the surface of AAK via the reaction of impregnated sample with urea, and (5) calcination of the sample at 200 °C in air to form γ -Fe₂O₃ nanoparticles on the AAK surface. Fig. 2a shows the N₂ adsorption–desorption isotherms of PK, AAK, and AAK/ γ -Fe₂O₃. The isotherm of PK corresponds to type II of the IUPAC classification [17], indicating that the original

Table 1
Chemical compositions (wt.%) of PK and AAK.

Sample	SiO ₂	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	K ₂ O	CaO	MgO	H ₂ O
PK	43.94	38.0	0.50	0.46	0.20	0.16	0.079	15.10
AAK	80.68	0.66	0.06	0.22	0.02	0.055	0.055	18.25

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