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Influence of Al substitution on magnetism and adsorption properties of hematite

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ABSTRACT

A series of Al-substituted hematite was prepared. The structures and properties of as-prepared samples were characterized by various techniques. The magnetic property of the samples was determined and the adsorption of three dyes Acid Blue 74, Methylene Blue and Phenol Red onto the samples was investigated. The results showed that Al incorporation into the crystal structure of hematite occurs via isomorphous ionic substitution of Al for Fe. With increasing Al content, the particle size of samples decreases, the magnetization increases and the remanent magnetization remains unchanged. The coercivity of the samples increases with Al substitution up to n_{Al}/n_{Fe} 0.03, and then decreases as Al content further increases. Compared with Al-free hematite, Al-substituted samples exhibit better adsorption ability to all of the three dyes. The adsorption rates of the three dyes on the surface of Al substituted samples depend on the structure of dye, pH and Al content in hematite.

1. Introduction

Iron oxides, significant minerals of the solid earth and the main constituent of the soil, are thought to play a significant role in controlling the concentration, migration, and conversion of the pollutants in the surface environment [1–3]. However, in natural environments, Fe(III) (hydr)oxides rarely exist as pure iron oxide phases, and often contain several metal impurities, such as Al, Si, and Mn [4–6]. For example, Al-substituted α-Fe_2O_3 occurs in nearly all soils and substitution content lower than 10–15% of Fe sites is typical [4]. The common hematite has known stable isostructural corundum analogs, suggesting that Al(III) and Fe(III) have similar enough chemistry to readily enable substitution. The ionic substitution of Al for Fe in the structure of hematite was found to influence the structural development and anion exchange capacity and subsequently their sorption and photocatalytic characteristics. Chubar et al. [7] synthesized $Fe_2O_3 \cdot Al_2O_3 \times H_2O$ by a hydrothermal method and found that this product shows good uptake of phosphate ions. Li et al. [8] synthesized Fe_2O_3–Al_2O_3 compounds by co-precipitation and investigated their photocatalytic functions. For bisphenol degradation in aerated aqueous suspension under UV light, the samples containing 5–10 wt% of Fe_2O_3 were more active than other samples prepared in parallel, including bare α-Fe_2O_3. El-Sharkawy et al. [9] prepared Fe_2O_3–Al_2O_3 binary compounds containing 10, 20, 30, 50 and 80 wt% Fe_2O_3. The results indicated that their textural, acidic properties and catalytic activities depend on the thermal treatment and the ratio of iron oxide to aluminum oxide. Hong et al. [10] compared Fe–Al binary oxide and corresponding single oxide for As removal and found that Fe–Al mixed oxide showed four times higher As (V) and As(III) adsorption capacity than conventional iron oxide.

In the present paper, a series of Al-substituted hematite was prepared. The as-prepared products were characterized by XRD, SEM, HRTEM, XPS, and BET. The magnetic properties of the products were determined. Three dyes with different structures (Acid Blue 74(AB 74), Methylene Blue (MB) and Phenol Red (PR)) were used as model pollutants to investigate the effect of Al content on the adsorption performance of Al-substituted hematite. The results of the present research must serve to understand the role played by Al-substituted hematite in controlling the concentration and migration of the pollutants in the natural environment.

2. Experimental

2.1. Materials

All chemicals were analytical grade, purchased from the commercial market, and used without further purification before utilization. The ferric salt ($Fe(NO_3)_3 \cdot 9H_2O$) and aluminum salt

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($Al(NO_3)_3 \cdot 9H_2O$) solutions were filtered through a 0.22 μm millipore filter to remove any particulate contaminants before utilization. AB 74, MB and PR were of guaranteed reagent grade and they were used without further purification.

2.2. Synthesis

A series of Al-substituted hematite were prepared by co-precipitation method, followed by calcination at 600 °C. 100 mL of 2.0 mol/L Fe^{3+} solution were mixed with 0, 3, 8, and 14 mL of 2.0 mol/L Al^{3+} solution, respectively. Then 6.0 mol/L NaOH solution were added to the mixed solution dropwise until pH 9. The above process was carried out under vigorous stirring at room temperature. The gels were collected, thoroughly washed with deionized water and dried at about 50 °C. The xerogels were ground and sintered at 600 °C for 3 h.

2.3. Characterization of samples

X-ray diffraction (XRD) measurement was carried out at room temperature using a D8ADVANCE diffractometer with Cu*K*α radiation ($\lambda = 0.15418$ nm). The surface area of all samples were measured with a NOVA 4000e measuring instrument (Quantachrome Instruments) using N_2 adsorption–desorption technique at 77 K. Scanning Electron Microscopy (SEM) images were taken with a S-4800 scanning electron microscope (Japan Hitachi Ltd). The high-resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED) pattern were obtained with a JEM-2010 TEM operated at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data were acquired by using a PHI-5000 Versa Probe.

The point of zero charge of the samples were determined by the solid addition method [11]. 25 mL 0.01 mol/L KNO_3 solution was added to a series of centrifuge tubes. The pH values of the solution were roughly adjusted from 2.0 to 11.0 by adding either 0.1 mol/L HNO_3 or NaOH. The total volume of the solution in each tube was made exactly to 30 mL by adding the KNO_3 solution (0.01 mol/L). The initial pHs of the solutions (pH_0) were accurately recorded. Then, 0.1 g of sample was added to each tube, which was securely capped immediately. The suspensions were then shaken and allowed to equilibrate for 12 h with shaking. The pH values of the supernatant liquid (pH_f) were recorded. The difference between the initial and final pH values ($\Delta pH = pH_0 - pH_f$) was plotted against the pH_0. The point of intersection of the resulting curve with abscissa, at which pH=0, gave the pH_{pzc}.

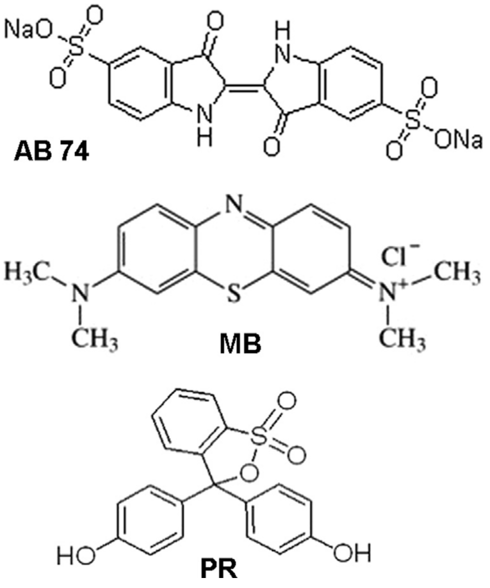

Fig. 1. Chemical structures of AB 74, MB, and PR.

2.4. Adsorption experiments

The adsorption of the dyes AB 74, MB and PR onto as-prepared Al-substituted hematite was investigated by using batch technique in polyethylene tubes sealed with screw-cap. 0.05 g of each sample was respectively added into eight tubes. Then, 1.8, 2.4, 3.0, 3.6, 4.2, 4.8, 5.4 and 6.0 mL of dye stock solution (500 mg/L) were added in turn into the eight tubes. At the same time, the total volume of the system was adjusted to 30 mL and the pH of each system was adjusted to 4.0 by adding dilute HNO_3 or NaOH solutions (1.0 mol/L). The system was shaken at 300 rpm using a thermostatic shaker at 298 K for 12 h. The suspensions were centrifuged and the supernatant liquids were analyzed for the dye concentration by 752 UV–vis spectrophotometer (Shang Hai Xinmao Instruments) at the wavelength of maximum absorption (610 nm for AB 74, 664 nm for MB and 432 nm for PR) of the dye.

The adsorption capacity of samples was calculated by

$$q_e = (c_0 - c_e)V/m \quad (1)$$

where q_e is the equilibrium adsorption capacity of dye on samples (mg/g), c_0 is the initial concentration of dye (mg/L), c_e is the equilibrium concentration in solution (mg/L), m is the mass of sample used (g) and V is the volume of dye solution (L).

The structures of AB 74, MB, and PR are shown in Fig. 1.

3. Results and discussion

3.1. Characterization of Al-substituted hematite

Figs. 2 and 3 present XRD patterns and SEM images of the as-prepared samples. The peaks at 2θ 24.8°, 33.4°, 35.7°, 40.8°, 49.6°, 54.4°, 62.2° and 64.2° in Fig. 2 are indexed to (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (2 1 4) and (3 0 0) planes, respectively, of α-Fe_2O_3 (JCPDS Card no. 00-033-0664). No other phase was observed, indicating that all Al had entered the lattice of hematite. The average particle diameter of Al-substituted hematite evaluated by Scherrer equation decreases from 58.8 to 42.6, 38.4 and then 28.9 nm with increasing molar ratio of Al/Fe from 0 to 0.03, 0.08 and 0.14. As can be seen in Fig. 3a, pure hematite composed of many uniform sphere-like particles with diameters of about 55 nm. As Al^{3+} is incorporated into the crystal lattice of

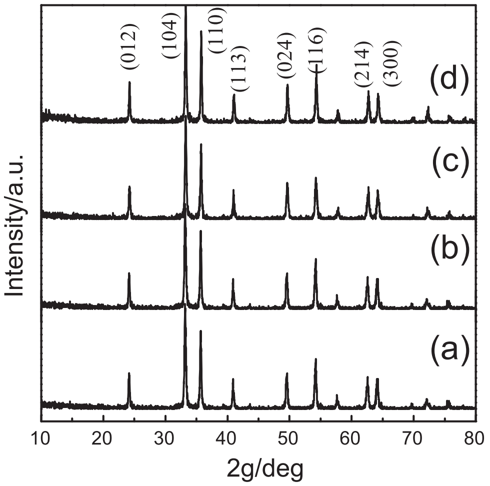

Fig. 2. XRD patterns of as-prepared samples: (a) $n_{Al}/n_{Fe} = 0$; (b) $n_{Al}/n_{Fe} = 0.03$; (c) $n_{Al}/n_{Fe} = 0.08$; and (d) $n_{Al}/n_{Fe} = 0.14$.