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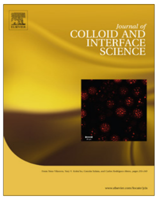

Preparation and characterization of bifunctional Ti–Fe kaolinite composite for Cr(VI) removal

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ABSTRACT

A novel bifunctional Ti–Fe kaolinite composite with excellent adsorption and photocatalytic properties was synthesized by a simple precipitation method. X-ray diffraction analysis and high-resolution transmission electron microscope analysis confirmed the existence of rutile phase TiO_2 and amorphous iron in the composite. The specific surface area of the Ti–Fe kaolinite composite is 5.5 times higher than that of the original kaolinite. The composite was used as an adsorbent as well as photocatalyst for Cr(VI) removal. The results indicate that the low pH is favorable to the Cr(VI) removal by the composite and the removal rate of Cr(VI) reached 87% at pH 3.0. Visible light irradiation obviously increased the removal of Cr(VI) by the composite and greatly shortened reaction equilibrium time, which may be attributed to the photocatalytic reduction of Cr(VI) to Cr(III) by TiO_2 associated with simultaneous redox cycle of Fe(III)/Fe(II). Various common co-existing ions did not show obvious effects on the removal of Cr(VI) by the composite. The composite exhibited very high stability for the Cr(VI) removal. The adsorption models and thermodynamics of Cr(VI) onto the composite were studied.

1. Introduction

Chromium is widely distributed in the earth's crust, and is extensively used in many industries including paints, dyes, metal plating, automobile spare parts, stainless steel, leather tanned and petroleum refining. Hexavalent chromium Cr(VI) has been reported to be toxic as well as carcinogenic [1,2]. Chronic exposure to high level of chromium may cause serious health problems, including respiratory tract, stomach, small intestine, male reproductive system and developmental disorders in children [3]. Maximum permissible intake level of chromium in drinking water set by World Health Organization (WHO) is 0.05 mg/L [4]. Due to its high toxicity and a potential carcinogenic activity, removal of Cr(VI) from aqueous media has attracted strong environmental concerns. Many technologies such as chemical precipitation, phytoextraction, electrodialysis, reverse osmosis, ion exchange, membrane filtration and adsorption are widely used for removal of chromium(VI) from water and wastewater [5]. Among these, adsorption seems to be more promising because of its cost effectiveness, high efficiency, ease of recovery and reusability [6]. Several conventional as well as nonconventional materials including red mud [7], coconut coirpith [8], sewage sludge [9], fly ash [10], biomass [11], zeolites and modified zeolites [12], tree fern [13], bone char [14], clay and modified clay [15], have been used as adsorbent for chromium removal.

Clays and their modified forms have been employed extensively for removal of chromium because of the low-cost and higher efficiency [16]. Natural and Na-purified smectite and kaolinite were employed for Cr(III) removal, adsorption capacity was 117.5 and 61.4 mg/g, respectively for natural and modified clays [17]. Langmuir adsorption capacities for Cr(III) on montmorillonite modified by poly(hydroxoaluminium) and cetyltrimethylammonium bromide were 26.67 and 25.51 mg/g, respectively [18]. Wu et al. [19] reported Ca-montmorillonite modified with humic acid for the adsorption of Cr(III). Turkish montmorillonite showed higher adsorption capacity for Cr(VI) removal at pH 1.0 [20]. Many modified forms of kaolinite including acid-activated, polyoxozirconium, and tetrabutylammonium kaolinite, were also investigated as a potential adsorbents for Cr(VI) in aqueous medium [21]. Modified organo-bentonite was also found to be an efficient adsorbent for the removal of Cr(VI) [22]. However, to the best of our knowledge, there is no report regarding the preparation and application of the Ti–Fe kaolinite composite for Cr(VI) removal to date.

In this work, we report the preparation of the novel bifunctional Ti–Fe kaolinite composite by a facile precipitation method. For the first time, this composite was used as adsorbent and photocatalyst for the removal of Cr(VI). The effects of the Fe/Ti ratio in the

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composite, adsorption conditions and visible light irradiation on the Cr(VI) removal by the composite were studied. A possible photocatalytic mechanism for the reduction of Cr(VI) to Cr(III) supported by XPS results was proposed.

2. Materials and methods

All reagents were analytical grade and used as received without any further purification. Deionized water was used throughout the experiments. The original kaolinite sample used in this study was obtained from Jiangsu Province (China) and was sieved through a 325-mesh prior to its use in the experiments.

2.1. Preparation of the Ti–Fe kaolinite composite

The Ti–Fe kaolinite composite was synthesized in two steps. In the first step, 0.5 M $NaHCO_3$ was added into the mixed solution of $TiCl_4$ and $FeCl_3$ in different Ti^{4+}/Fe^{3+} molar ratios (0.05:0.1, 0.1:0.1, 0.2:0.1, 0.3:0.1, 0.1:0.2, 0.1:0.3 and 0.1:0.4) with constant stirring. Then, the as-obtained mixed solution was aged for 3 h at 55 °C and added drop wise to the suspension of kaolinite (2 wt%) under vigorous stirring followed by aging for 24 h. The precipitate was collected by filtration and washed with deionized water for several times, until no chlorides were detected by $AgNO_3$ test. The as-obtained product was dried in oven at 105 °C for 12 h, and was ground to a fine powder, which was hereinafter named as the Ti–Fe kaolinite composite.

2.2. Characterization of the composite

The structure and crystallinity of the Ti–Fe kaolinite composite were analyzed by powder X-ray diffraction (XRD) on a D/MAX-RB X-ray powder diffractometer (Rigaku, Japan) with Cu Kα radiation. The morphology of the Ti–Fe kaolinite composite was analyzed by scanning electron microscope (SEM) (JSM5610LV). High-resolution transmission electron microscopy (HRTEM) image was recorded with a HRTEM at an accelerating voltage of 200 kV. The nitrogen adsorption/desorption isotherms were measured on an AUTOSORB-1 nitrogen adsorption apparatus (Quantachrome, USA). X-ray photoelectron spectroscopy (XPS) analysis was carried out using an ESCALAB II XPS system with a monochromatic Mg Ka source and a charge neutralizer. All binding energies were referred to the C 1s peak at 284.5 eV of the surface adventitious carbon. Peak deconvolution was performed using Gaussian–Lorentzian components after a Linear background subtraction. The FTIR spectra were collected by Nexus, Thermo Nicolet. Thermogravimetry (TG) analysis of the samples was carried out on a Netzsch STA 449C Jupiter Aeolos (German) coupled to mass spectrometer with a heating rate of 5 °C/min under N_2.

2.3. Adsorption studies

A definite amount 2 g/L (0.2 g) of the Ti–Fe kaolinite composite was added into a flask with 100 mL of 50 mg/L Cr(VI) aqueous solution for adsorption experiments. The same amount was maintained throughout the whole study unless otherwise specified. The flasks were shaken on a shaker at 25 °C with speed of 190 rpm. After filtration, the concentration of Cr(VI) was determined using atomic absorption spectrophotometer (AAS, Analytik Jena ZEEnit 700). In order to make a comparison, we took random samples from adsorption experiment and analyzed Cr(VI) in the samples by 1,5-diphenyl carbazide method at a wavelength of 540 nm using visible spectrophotometer and AAS method separately. The as-obtained results were comparable within 5% [23]. The pH of the Cr(VI) solution was adjusted by adding 0.1 M NaOH or 0.1 M HCl solution. The effect of common coexisting ions including sodium, potassium, iron, nitrate, chloride, sulfate and bicarbonate on the adsorption of Cr(VI) by the composite was also studied.

2.4. Adsorption isotherms

Adsorption isotherms are expressed in terms of the relationship between the concentration of adsorbate in the solution and the amount adsorbed by the unit mass of the adsorbent at a constant temperature. The isotherms models such as Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich equations were applied to investigate the adsorption mechanism of Cr(VI) over the composite.

$$\text{Langmuir equation} \quad \frac{C_e}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right)C_e \tag{1}$$

$$\text{Freundlich isotherm} \quad \log q_e = \log K_f + \frac{1}{n}\log C_e \tag{2}$$

$$\text{Tempkin equation} \quad q_e = B_T \ln A_T + B_T \ln C_e \tag{3}$$

$$\text{Dubinin—Radushkevich} \quad q_e = Q_d \times \exp\left(B_D\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2\right) \tag{4}$$

2.5. Photocatalytic experiment

The photocatalytic activity of the as prepared Ti–Fe kaolinite composite was evaluated by the Cr(VI) removal from aqueous solution under the visible light irradiation (300 W Dy lamp with a 420 nm cutoff filter). In a typical experiment, 200 mg of the composite was dispersed in 100 mL of 50 mg/L Cr(VI). During irradiation, 2 mL of sample was taken at different time intervals and centrifuged immediately to remove the composite particles. The residual concentration of Cr(VI) in the supernatant was measured by AAS.

2.6. Desorption and regeneration of the adsorbent

For the desorption study, 200 mg of the composite was contacted with 100 mL of 50 mg/L Cr(VI) solution. After the adsorption experiment, the adsorbent was collected by filtration using 0.45 μm millipore filter. Then it was transferred into 50 mL aqueous solution with deionized water, 0.1 M NaCl, 0.1 M HNO_3 and 0.1 M HCl, respectively [24]. The mixtures were shaken at room temperature overnight, and the filtrates were analyzed to determine the concentration of Cr(VI) after desorption, the same experiment was repeated for six times.

3. Results and discussion

3.1. Characterization of the Ti–Fe kaolinite composite

The Fe–Ti kaolinite composites with different Ti^{4+}/Fe^{3+} molar ratios (0.05:0.1, 0.1:0.1, 0.2:0.1, 0.3:0.1, 0.1:0.2, 0.1:0.3 and 0.1:0.4) were prepared and their sorption capacity for Cr(VI) was evaluated. As observed from Fig. 1, the increase of the Ti^{4+}/Fe^{3+} molar ratio in the composite has no effect on the adsorption capacity of the composite. However, the adsorption capacity increased from 21.05 to 24.8 mg/g with increasing the Fe^{3+} molar ratio in the composite from 0.1 to 0.4. Meanwhile, the iron leaching of the composite showed an increase with increasing the Fe^{3+} molar ratio. The composite with 1:1 molar ratio of Ti^{4+}/Fe^{3+} was selected for further study because of its good adsorption capacity as well as