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Adsorption behavior of Cr(VI) on organic-modified rectorite

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Abstract

The natural rectorite (REC) was modified with the surfactant of dodecyl benzyl dimethyl ammonium chloride, hexadecyl trimethyl ammonium bromide and octadecyl trimethyl ammonium bromide, respectively. Three kinds of organic-modified rectorite (OREC), termed OREC1, OREC2 and OREC3, respectively, were prepared. Three kinds of OREC were used as adsorbents for Cr(VI) removal in aqueous solution. Through FTIR and X-ray diffraction (XRD) analyses, it was confirmed that they indeed carried out cation exchange reaction between REC and surfactant. Through the research of Cr(VI) adsorption, the removal percentage (%) of Cr(VI) increased with increasing adsorbents dose. The adsorption efficiency of OREC adsorbent was greatly affected by the initial solution pH value. According to thermodynamics study, it can be concluded that the adsorption of Cr(VI) with three adsorbents was carried out spontaneously. The research of adsorption isotherm demonstrated that, adsorption reactions of three prepared OREC adsorbents belonged to Langmuir model. The kinetic data of Cr(VI) with OREC adsorbents were well fitted to the Lagergren rate equation, which indicated that the three adsorption processes belonged to first-order adsorption reaction. Values of coefficients of intra-particle diffusion and mass transfer have been determined for three different OREC adsorbents. Intra-particle diffusion analysis demonstrated that Cr(VI) ions diffused quickly at the beginning of the adsorption process, and then intra-particle diffusion slowed down and stabilized. Mass transfer analysis showed the process of transfer of Cr(VI) removal onto the adsorbents surface was rapid enough.

Keywords: Surfactant; Rectorite; Chromium; Adsorption kinetic; Adsorption isotherm

1. Introduction

Chromium ion, especially Cr(VI), present in the effluents of electroplating, tanning, mining and fertilizer industries and causing problems of skin dermatitis, liver damage, carcinogenicity, etc. [1–5], is a kind of toxic inorganic pollutants. Treatment processes for Cr(VI) contaminating waste water included chemical precipitation, membrane filtration, ion exchange, carbon adsorption [6–9], coprecipitation [8] and adsorption in layered double hydroxides [10,11]. But all these means were all expensive, cost effective alternative technologies or adsorbents for treatment of Cr(VI) contaminated waste water were needed. Clay was chosen to decrease the pollutant of Cr(VI) released into the environment, owing to their high specific surface area, low cost and ubiquitous presence in most soils [12–18]. But these clays mainly were montmorillonite (MMT) and Kaolinite, it was necessary to study adsorption of Cr(VI) with another kind of clay mineral of rectorite (REC).

Structure and characteristics of REC are much similar to that of MMT [19]. REC is a sort of regularly interstratified clay mineral with alternate pairs of dioctahedral mica-like layer (non-expansible) and dioctahedral smectite-like layer (expansible) existing in 1:1 ratio. The cations of Na^+, K^+ and Ca^{2+} lie in the interlayer region between 2:1 mica-like layers and 2:1 smectite-like layers, while the exchangeable hydrated cations reside in the latter. The REC structure can also cleave easily between smectite-like interlayers, forming monolithic REC layers (2 nm thick). However, nearly no attention has been paid to the research of REC on adsorption study until the high quality of REC mineral was discovered in 1983.

Until now, there have been few reports on adsorption study of REC. So in this paper, we studied the adsorption of Cr(VI) from aqueous solution with REC modified by dodecyl benzyl dimethyl ammonium chloride, hexadecyl trimethyl ammonium bromide and octadecyl trimethyl ammonium bromide, respectively, reviewed the effect of adsorbents dose, initial solution pH, adsorption time and temperature on the adsorption, and

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discussed adsorption kinetics and adsorption isotherm of three adsorbents for Cr(VI).

2. Experimental

2.1. Materials

Sodium rectorite (Na-REC) was refined from clay minerals in Wuhan, China. The CEC was found to be 45 meq/100 g, and the *d*-spacing 2.22 nm. Dodecyl benzyl dimethyl ammonium chloride, hexadecyl trimethyl ammonium bromide and octadecyl trimethyl ammonium bromide were supplied by Xi'an Chemistry Glass Station, China. All chemicals used in this work, were of analytical reagent grade and were used without further purification.

2.2. The synthesis of organic clay

Na-REC was screened with a sieve of 300-mesh in order to remove impurities. Certain amount of screened clay was suspended in deionized water in glass vessel using a glass-rod. Surfactant was dissolved in certain amount of water, and then added into the suspended clay–water solution, stirring vigorously for several minutes at room temperature. The mixture was transferred into three-necked flask, heated to 85 °C, and stirred for additional 8 h. Then the treated products were washed and filtered repeatedly in order to ensure a complete removal of chloride or bromide ions, and the filtrate was titrated with $AgNO_3$ until no AgCl or AgBr precipitate was found. The product was then dried under vacuum at 90 °C for several hours, and the product, termed OREC1, OREC2 and OREC3, were obtained. In the modification experiment, weight of 30 g REC needs water of 1700 mL, while the molar of surfactant was about 75% of cation exchangeable capability (CEC).

2.3. Characterization

FTIR studies were performed using a WQF-310 machine over the wave number range 4000–400 cm^{-1}. The IR spectra of REC or OREC was obtained using KBr wafer which was prepared by mixing a given weight of the REC or OREC with KBr crystals. The resulting mixture was then ground into powder and heated for 1 h at 373 K. Finally, the mixture was pressed into a KBr wafer under vacuum conditions and used as such for IR studies. X-ray diffraction (XRD) measurements of REC and OREC were conducted with a Rigaku D/max-3C using nickel-filtered Cu K_α ($\lambda = 0.154$ nm) radiation (40 kV, 40 mA) and a scan range of 1–10°.

2.4. Adsorption procedure

Various weights of the OREC adsorbents ranging from 0.2 to 1.0 g/L were used to study the effect of adsorbent dose on the adsorption of Cr(VI) with the concentration of 100 mg/L. The stock solution of Cr(VI) (500 mg/L) was prepared in distilled water using analytical grade reagent of $K_2Cr_2O_7$.

Fifty-milliliter solutions of 100 mg/L of Cr(VI) were adjusted to various pH ranging from 3 to 12. These were added to 1 g/L of OREC sample in 120 mL polyethylene plastic containers. They were agitated for enough time at room temperature (26 ± 1 °C) and centrifuged at 1500 rpm for 10 min. The amount of Cr(VI) adsorbed by the adsorbents was calculated by difference about initial and final solution concentrations.

The effect of temperature on adsorption equilibrium was studied by varying temperature from 20 to 80 °C.

Kinetic studies were carried out for 50 mL working solution at constant pH 6 with initial concentration (100 mg/L) and the adsorbent dose of 1 g/L. After shaking, the samples were centrifuged for 10 min at 1500 rpm.

Working solutions of 50–130 mg/L were subsequently prepared from the stock solution. The various working solutions were adjusted pH 6 with 0.1 M HCl. A 50 mL of the various working solutions were introduced into 1.0 g/L of the OREC sample in 120 mL polyethylene plastic containers. They were agitated for 60 min at room temperature (26 ± 1 °C). The suspensions were then centrifuged for 10 min at 1500 rpm. The supernatants collected were analyzed for Cr(VI). The amount of the Cr(VI) adsorbed by the adsorbents was calculated by difference about initial and final solution concentrations.

3. Results and discussion

3.1. FTIR and XRD analysis of OREC

In the present work, three different surfactants were used for ion exchanging of Na^+ to modify the REC. The structure of REC and OREC can be characterized by FTIR spectra, and are shown in Fig. 1. For OREC, there appeared two peaks at 2927 and 2853 cm^{-1}, which represent the stretching vibration of $–CH_3$ and $–CH_2$, respectively. The characteristic peaks confirmed that the organic cations of quaternary ammonium salt of surfactant were exchanged with the interlayer Na^+ of REC.

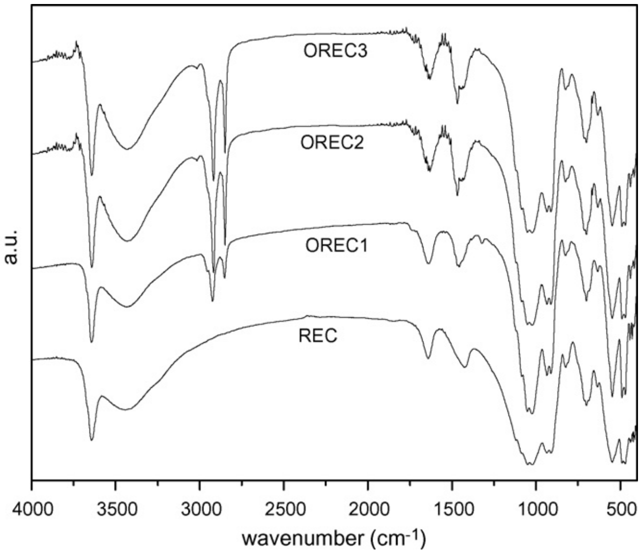

Fig. 1. FTIR spectra of REC, OREC1, OREC2 and OREC3.