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Spectroscopic study for a chromium-adsorbed montmorillonite

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ABSTRACT

Samples of purified montmorillonite with trace amounts of quartz were subjected to different concentrations of chromium sulphate solutions for one week to allow cation exchange. The chromium-bearing montmorillonites were verified and tested using powder X-ray diffractometry (XRD), X-ray fluorescence spectrometry, electron spin resonance (ESR) spectrometry and Fourier transformation infrared (FTIR) spectroscopy to explore the occupation sites of the chromium. The ESR spectra recorded before and after the chromium exchange show clear differences: a strong and broad resonance with two shoulders at the lower magnetic field side was present to start, and its intensity as well as that of the ferric iron resonance, increased with the concentration of added chromium. The signals introduced by the chromium, for example at $g = 1.975$ and 2.510 etc., suggested that the chromium had several occupational sites. The ESR peak with $g = 2.510$ in the second derivative spectrum suggested that Cr^{3+} was weakly bounded to TOT with the form of $[Cr(H_2O)_3]^{3+}$ in hexagonal cavities. This was verified by comparing the FTIR spectra of the pure and modified montmorillonite. The main resonance centred at $g = 1.975$ indicated that the majority of Cr^{3+} occupied the interlayer region as $[Cr(H_2O)_6]^{3+}$. The substitution of Ca^{2+} by Cr^{3+} also greatly affected the vibration of the hydrogens associate to water, ranged from 3500 to 2600 cm^{-1} in FTIR. Furthermore, the presence of two diffraction lines in the XRD results (specifically those with d-values of 1.5171 and 1.2673 nm) and the calculations of the size of the interlayer space suggested the presence of two types of montmorillonite with different hydration cations in the sample exposed to 0.2 M chromium sulphate. The two diffraction lines were assigned to $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_3O_3]^{3+}$, respectively. This also suggested that the species of hydration cation was constrained by the concentration of the chromium solution.

1. Introduction

Montmorillonite is a phyllosilicate mineral comprising a crystal structure of TOT layer. It requires extra interlayer cations to balance the charge due to the substitution of Al^{3+} for Si^{4+} in tetrahedral sites and substitution of Al^{3+} or Mg^{2+} for cations with lower charge in octahedral sites [1,2]. The interlayer cations are usually hydrated and can be exchanged. Montmorillonite and its various modified forms have been widely used as chemical catalysts, medicine carriers and adsorbents in medicine and environmental engineering. Their usefulness results from their huge BET surface area and extraordinary capacity for adsorption [3–5]. These excellent properties allow montmorillonite to be used to gather heavy metals, such as Cu, Zn, Pb, Cr and Cd, from polluted rivers and lakes [3–12]. Note that the sorption of heavy metals is strongly constrained by pH and ionic strength. For example, the sorption of Cu^{2+} is dominated by ion exchange or outer-sphere complexation at low pH and inner-sphere complexation at high pH, and is strongly dependent on ionic strength at acidic pH [11]. The outer-sphere and inner-sphere complexation means ions bind indirectly or directly to the surface of material, with or without intervening water molecules, respectively [13–15]. A study of the competitive sorption on Na-montmorillonite of a ternary system of Cu, Pb and Cr under conditions of different pH and different concentrations of the heavy metal and also other cations found that the competitive sorption of the three metals was ranked Cr > Cu > Pb. The competitive adsorption was weakened with the rise of pH, but intensified with the increase of concentration of the heavy metals [16]. Furthermore, the amount of adsorbed cations was affected by the solution pH [16]. The adsorption of heavy metals by Ca-montmorillonite has been reported to improve significantly upon the clay's modification with humic acid, and the mechanism of adsorption was well described by a pseudo-second-order equation and interpreted using the Langmuir model [10]. Furthermore, oxide/hydroxide pillared or modified clays have been used to adsorb ions from polluted water [17–19]. The pillaring using ferric aluminium oxide greatly increased its capacity to adsorb the arsenate ion (AsO_4^{3-}) [19], with the adsorption occurring on the external surface of monomeric and polymeric Fe^{3+} species in the interlayer space [17]. The

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adsorption of picloram on iron-oxide-pillared montmorillonite increases with the increasing acidity of the solution [18].

Research has mainly aimed to improve adsorption or modify the structural charge of montmorillonite to allow the adsorption of oppositely charged ions. Study of the adsorption sites has been generally overlooked, which has led to ambiguity over the interpretation of the mechanism. To some extent, the site of heavy cations substitution in montmorillonite has been reported, such as Cu substitution [6,20–24]. The presence of Cu^{2+} in a restricted site inaccessible by water was confirmed by the occurrence of $g = 2.33$ and 2.05 signals. And the $g = 2.05$ signal does not disappear during the dehydration of montmorillonite, which indicates that it is the start of the Cu^{2+} migration into the inner structural sites, at least near the OH position at the bottom of a hexagonal cavity [6,24].

An understanding of the adsorption sites of heavy metals could help to elucidate the adsorption mechanism and to evaluate the ecological side effects of sludge treatment. It would also aid the development of effective processes to produce and settle sludge.

2. Materials and methods

2.1. Materials

The raw light-grey montmorillonite was collected from Anji county in Zhejiang province, China. The main mineral phase was Ca-montmorillonite; some quartz, andesine and calcite were also detected by X-ray diffractometry (XRD). The weight fractions calculated with the use of TOPAS based on the Rietveld refinement technique were 49.3%, 34.2%, 15.4 and 1.1% (wt%) for montmorillonite, quartz, andesine and calcite, respectively. The fraction smaller than 2 μm was obtained from raw clay which was purified by the combination of gravity sedimentary and centrifugation, and then its chemical composition was tested by X-ray fluorescence (XRF). The cation exchange capacity (CEC) of the clay was 87.6 mmol/100 g, determined by leaching with 1 M ammonium acetate at pH 7, washing with 90% ethanol, displacing the NH^{4+} with 1 M NaCl [6,25] and measuring the amount displaced with ICP-AES.

2.2. Adsorption and desorption experiments

The adsorption experiments were carried out in volumetric flasks in an electro-thermostatic water bath under continuous shaking for one week at 50 °C. Deionized water and analytical-grade 0.6 M $Cr_2(SO_4)_3$ solution were used to prepare 0.05, 0.10 ($pH = 2.12$) and 0.20 M ($pH = 1.48$) Cr^{3+} solutions. The solid:liquid ratio was 1:25. After the experiments, each Cr-montmorillonite (Cr-M) sample was rinsed with deionized water to leave a stable clay colloid slurry, which was then centrifuged at 5000 rpm and left to dry at 80 °C in an oven. The chromium-bearing montmorillonites were denoted as Cr-M1, Cr-M2 and Cr-M3 corresponding to the samples respectively prepared from the 0.05 M, 0.10 M and 0.20 M Cr^{3+} solutions, with 158.9, 283.6 and 543.3 mmol of Cr^{3+} adsorbed on 100 g of each clay, respectively, as calculated by the Cr^{3+} concentration differences before and after the adsorption. An adsorption experiment was carried out with the CTAB exchanged montmorillonite, the obtained sample was denoted as CTAB-Cr-M.

The desorbing experiments were carried out in a solution with pH 3, respectively. The relict clays were tested by both ESR and FTIR.

2.3. Analytical techniques

XRD analysis was carried out using a Rigaku D/max IIIa diffractometer equipped with a Cu-target tube and curved-graphite monochromator, operated at 40 kV and 25 mA. The wavelength of CuKα is 0.154178 nm. Samples were scanned in 2θ steps of 0.02° from 3° to 36° at a rate of 1 s/step for naturally oriented specimens, and from 3° to 70° in 0.01° 2θ steps at a rate of 0.5 s/step for randomly distributed specimens. The slit systems were 1° (DS/SS) and 0.3 mm for the receiving slit. The randomly oriented specimens were prepared via a side-packing technique proposed by the U.S. National Institute of Standards and Technology (NIST). The

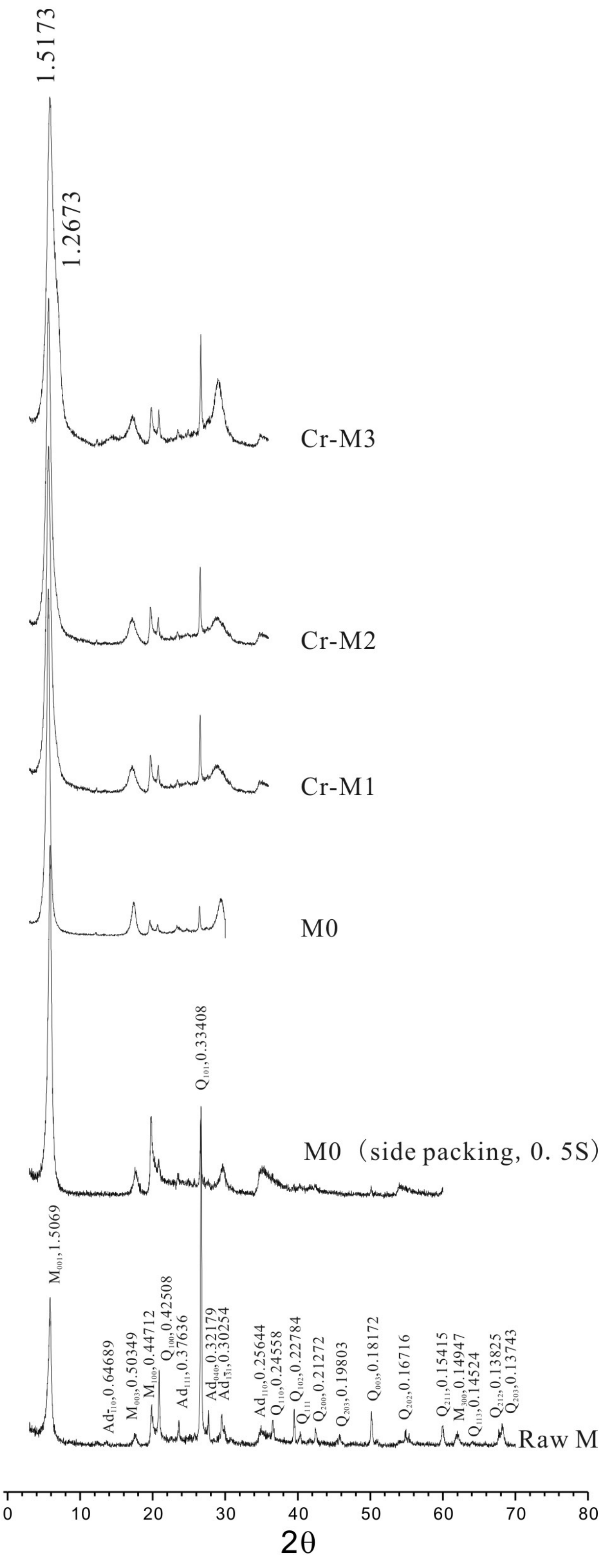

Fig. 1. XRD patterns of (from bottom to top): raw montmorillonite clay, random and orientated slide of purified montmorillonite (M0) and orientated slides of Cr-M1, Cr-M2 and Cr-M3.