



Research paper

Sequestration of heavy metal cations on montmorillonite by thermal treatment

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ABSTRACT

Clay minerals are low-cost, high-efficient, and environmentally-friendly adsorbents for heavy metal cations. Proper disposal of the spent clay minerals, however, is still a big challenge holding back their wide applications in environmental remediation. In this work, the spent montmorillonites (Mt) after the adsorption of Cu^{2+} or Cd^{2+} were thermally treated, with the aim of in-situ sequestering the adsorbed heavy metal cations. The structural characteristics of the calcined Mt samples were investigated using X-ray diffraction and X-ray photon spectroscopy, and the sequestration efficiency was tested by ammonium acetate and HCl washing. The results of this work demonstrate that Cu^{2+} cations could migrate into both the ditrigonal cavities on the tetrahedral sheet and vacant sites on the octahedral sheet of Mt after thermal treatment due to its small ion radius. In this case, Cu^{2+} cations could be efficiently sequestered on Mt layers, e.g., less than 3.2% desorption by ammonium acetate washing and less than 5% desorption by HCl washing for the 400 °C treated Cu–Mt. As for Cd^{2+} cations, they could hardly migrate into Mt layers, and thus much higher calcination temperature (e.g., 700 °C) was needed to efficiently sequester them on Mt. In this case, Cd^{2+} cations were mainly sequestered by the collapse of Mt layers and/or the deformation of Mt structure, which could block the desorption pathway for Cd^{2+} cations. Interestingly, as the thermal treatment temperature increased to a critical value (i.e., 400 °C for Cu–Mt and 500 °C for Cd–Mt), the structural Al^{3+} could be preferably dissolved by HCl than the adsorbed heavy metal cations; ammonium acetate could hardly dissolve the structural Al^{3+} . This work demonstrated that thermal treatment could be a practical method for safe disposal of the spent Mt after the adsorption of heavy metal cations.

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1. Introduction

Montmorillonite (Mt) belongs to the 2:1 clay mineral group that each layer comprises two sheets of inward pointing SiO_4 tetrahedral which sandwich a third sheet of octahedrally coordinated cations. Isomorphous substitution on Mt layers generates a net negative surface charge on the layers, which should be balanced by exchangeable inorganic cations (e.g., Na^+ , Ca^{2+} , and Mg^{2+}) (Mosser et al., 1997; Li et al., 2011; Brigatti et al., 2013; Skoubris et al., 2013). Mt therefore can effectively adsorb heavy metal cations by cation exchange. Combining with other merits such as low-cost, environmentally-friendly, and rich in reserves, Mt has been considered as promising adsorbents for heavy metal cations in pollution control areas (Abollino et al., 2008; Bhattacharyya and Gupta, 2008; Wu et al., 2009; Zhu et al., 2011a,b). Proper disposal of the spent Mt after adsorption of heavy metal cations, however, is still a challenge holding back the wide application of Mt as adsorbents for heavy metal cations. For example,

direct landfill disposal of the spent Mt may cause serious secondary pollution to soil and groundwater by the desorbed heavy metal cations; while desorption by washing with salts will produce large volume of wastewater that needs further treatment.

Considering the factor that the adsorbed heavy metal cations are mostly located within the nano-sized interlayer space of Mt, one possible method for the disposal of the spent Mt is to in-situ sequester the adsorbed heavy metal cations within the interlayer space. Zhang et al. (2007, 2013) adopted microbial reduction of structural Fe(III) in smectites, finding that thermophilic methanogen enhanced Fe(III) bioreduction (i.e., increase of smectite's layer charge), which then led to the transformation of smectite into illite. In this case, the adsorbed heavy metal cations could be effectively sequestered within the interlayer space of illite. This treatment is limited to Fe-rich montmorillonites, however. In addition, Jaisi et al. (2011) suggested that six months might be needed for the smectite to illite conversion as catalyzed by thermophilic microbes, which indicated that long time was indispensable for sequestration of heavy metal cations by this microbial reduction method.

Previous studies have demonstrated that upon thermal treatment, small cations (e.g., Li^+) within the interlayer space of smectite can irreversibly migrate into the smectite layers (i.e., trapped in the

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ditrigonal cavities or in the vacant octahedral sites), resulting in an overall decrease of the layer charge, which is also known as the Hofmann–Klemen effect (Herling et al., 2012; Hofmann and Klemen, 1950; Komadel et al., 2005; Skoubris et al., 2013). In addition, some cations may even form chemical bonds with Mt upon calcination (Chorom and Rengasamy, 1996; A. Karakassides et al., 1999; Madejová et al., 2006), which can further reduce the desorption of the pre-adsorbed cations from the calcinated Mt. As such, heavy metal cations with relatively small ion radius (e.g., Ni^{2+} , Cu^{2+}) may be in-situ sequestered within smectite layers by thermal treatment. While for many other heavy metal cations with relatively large ion radius (e.g., Cd^{2+} , Pb^{2+}), generally they cannot migrate into the smectite layers by thermal treatment (Madejová et al., 2006). In this instance, one may expect that these cations cannot be as efficiently sequestered by smectite as those small cations. Madejová et al. (1999) showed that after heating at 300 °C for 24 h, the cation exchange capacity (CEC) of the resulting Cu–Mt decreased 63.6%, while that of the heated Cd–Mt only decreased 23.3%. On the other side, previous studies also demonstrated that thermal treatment of smectite under high temperature could lead to complete collapse of the layers, or even deformation of the crystal structure of smectite layers (Emmerich et al., 2001; Noyan et al., 2006; Ōnal and Sarıkaya, 2007; Příšková et al., 2010), which then may close the pathway for the desorption of the adsorbed heavy metal cations. In this instance, large heavy metal cations may still be efficiently sequestered within the interlayer space as long as the thermal treatment reaches a critical high temperature.

The present study is to determine the effect of thermal treatment on the in-situ sequestration of the adsorbed heavy metal cations on Mt. Cu^{2+} and Cd^{2+} were selected as representatives of heavy metal cations of different ion radii. The spent Cu–Mt and Cd–Mt were calcined at different temperatures, which were then followed by ammonium acetate and HCl desorption to test the sequestration efficiency. Ammonium acetate can effectively exchange inorganic cations from clay minerals and has been often used to determine their CEC (Madejová et al., 1999). In addition, the calcined Mt may face extremely acidic environment after being disposed in the nature, and acid desorption experiments were therefore conducted as well. The calcined samples were characterized with X-ray diffraction (XRD) and X-ray photon spectroscopy (XPS) to determine the potential sequestration sites of these cations. The results of this work showed that calcination treatment can effectively sequester the adsorbed heavy metal cation on the spent Mt.

2. Materials and methods

2.1. Materials

The original Ca^{2+} form Mt was obtained from Inner-Mongolia, China, with the cation exchange capacity (CEC) of 108 meq/100 g and purity >95% (Zhu et al., 2009, 2011b). CuCl_2 , CdCl_2 , $\text{CH}_3\text{COONH}_4$, and HCl of analytical grade were supplied by Tianjing Chemical Co. (China), and they were used as received.

2.2. Preparation of thermal treated Mt samples

To obtain the adsorption isotherms, the raw Mt was equilibrated with CuCl_2 or CdCl_2 solution of various concentrations (i.e., 0.31–18.88 mmol/L for Cu^{2+} and 0.09–8.90 mmol/L for Cd^{2+}) in centrifuge tubes. The tubes were placed on a thermostat water bath shaker at 25 °C and shaken for 24 h. Preliminary experiments showed that the adsorption equilibrium was reached within 24 h. Then, the Mt dispersion was centrifuged and the concentrations of heavy metal cations were determined using an atomic absorption spectrophotometer. Lower concentration range was used for Cd^{2+} in the adsorption experiments because its adsorption amount could reach relatively constant within this concentration range.

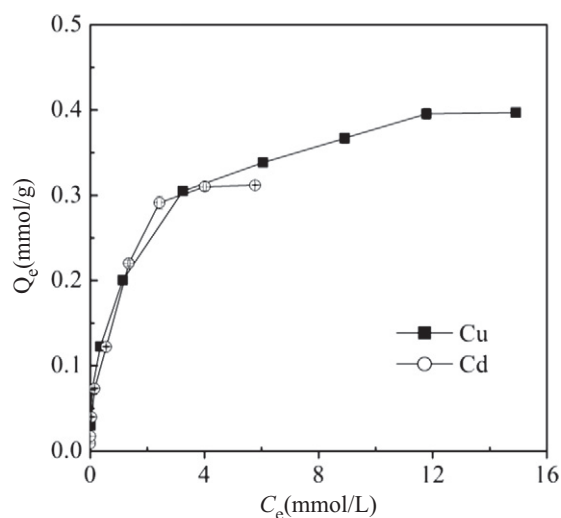


Fig. 1. The adsorption isotherms of Cu^{2+} and Cd^{2+} on Ca-Mt.

According to the above adsorption results (Fig. 1), $\text{CuCl}_2/\text{CdCl}_2$ of a certain concentration (i.e., 15.74 mmol/L for Cu^{2+} and 5.34 mmol/L for Cd^{2+}) were chosen to obtain the spent Cu–Mt/Cd–Mt (with relatively large amount of adsorbed cations). In particular, the specified amount of raw Mt powder was dispersed in a solution of 15.74 mmol/L Cu^{2+} or 5.34 mmol/L Cd^{2+} , and then the dispersion was shaken for 24 h at 25 °C. After being centrifuged, the resultant samples were dried at 50 °C. The finely powdered samples were divided into several portions, and each portion was separately calcined for 16 h at particular temperatures, i.e., from 200 to 600 °C for Cu–Mt and from 300 to 1000 °C for Cd–Mt. Relatively low calcination temperature was chosen for Cu–Mt because Cu^{2+} can migrate into the Mt layers at relatively low temperature, and it might be sequestered much easier (Madejová et al., 1999). According to the calcination temperature, the calcined samples were denoted as xCu–Mt or xCd–Mt (here x represents the calcination temperature, e.g., 400Cu–Mt, 400Cd–Mt).

2.3. Desorption by ammonium or acid washing

Desorption washing was performed in 1.0 M ammonium acetate solution or HCl solution (pH = 2) at desired intervals up to 336 h. The supernatants were collected after centrifugation and then the solution pH and the concentration of Al^{3+} , Cu^{2+} , and Cd^{2+} were analyzed. The concentration of Al^{3+} was detected using a UV–vis spectrophotometer at the wavelength of 640 nm (tested using Chrome azulol S spectrophotography) (Hawke et al., 1996; Pakalns, 1965). The concentrations of Cu^{2+} and Cd^{2+} were determined by atomic absorption spectrophotometer (performed on Shimadzu AA7000).

2.4. Structural characterization of the samples

The XRD patterns of the dry samples were recorded on a Rigaku D/Max 2500 X-ray diffractometer, operating at 40 kV and 40 mA with Cu K α radiation. The 2θ range between 5° and 25° was recorded, at a scanning speed of 2°/min. The basal spacing values of the samples were determined from the 2θ values of the corresponding basal reflections.

The XPS measurements were performed on a K-Alpha from Thermo Fisher Scientific with an Al X-ray source of 100 W. The electron energy analyzer was operated with a pass energy of 30 eV enabling high resolution of the spectra to be obtained.

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