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Removal of Cd^{2+} from aqueous solution with carbon modified aluminum-pillared montmorillonite

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ABSTRACT

To clarify the effect and mechanism of pillared montmorillonite on Cd^{2+} adsorption in aqueous solution, carbon modified alumina-pillared montmorillonite has been prepared by incorporating hydroxyl–aluminum cations into the lamellar spaces of montmorillonite via ion-exchanging together with polyvinyl alcohol (PVA), followed by calcining in N_2 atmosphere. The pillared montmorillonites were characterized by XRD, FT-IR, TG–DTA and sorption isotherms. Uptake of Cd^{2+} from aqueous solution was analyzed by means of atomic absorption spectroscopy. The experimental results indicated that the pillared montmorillonites show better properties on both Cd^{2+} adsorption and desorption than the unpillared, which made them the promising recycling Cd^{2+} adsorbents. Moreover, adjusting the pH value of the solution could control the adsorbed amount of Cd^{2+}. The adsorption process fitted the second-order kinetics well, and the two isotherm equations due to Freundlich and Langmuir showed good fits with the experimental data.

1. Introduction

Recently increased concern of the toxic effects of heavy metal pollution of the environment and particularly bodies of water stimulated extensive efforts to develop routes for their separation and removal from aqueous solutions. Usually, activated carbon and ion exchange resins are employed in heavy metal adsorption processes. However, the high costs on both capital and regeneration limit their industrial application, and so that inspired continuous development on ideal sorbing materials [1–4].

Various physicochemical and biological methods were studied for metal removal. Natural clay minerals due to their low cost, high-specific surface area, high chemical and mechanical stability, various surface and structure properties and higher values of cation exchange capacities become the excellent materials for metal adsorption [5–9] and have been extensively studied as sorbents for the removal of various pollutants from wastewater and aqueous solutions [10]. Clays are hydrous aluminosilicates that make up the colloid fraction (<2 μm) of soil, sediment, rocks and water [11].

Intercalating metal hydroxide into the lamellar space of montmorillonite (MMT) followed by calcinations at certain temperature will result in metal oxide pillared montmorillonite, which may have improved porosity, specific surface area and stability. Pillared montmorillonite first tested as cracking catalyst with regard to their acidic properties have recently been studied as sorbents for the heavy metal ions [12–14]. Hydroxyl–aluminum intercalated montmorillonite is one of the most common one, and shows higher adsorption capacity for some heavy metals than that of natural montmorillonite [15–17]. However, very little is known about the heavy metal removal on further modified aluminum–pillared montmorillonite as well as the sorption mechanism. Polyvinyl alcohol (PVA) is a potential complexant for the Keggin-like Al_{13} oligomeric cations, could be a good choice for the modification of aluminum-pillared montmorillonite. Upon calcination in N_2 atmosphere, PVA would change to carbon resulting in a carbon modified aluminum-pillared montmorillonite, which might affect the metal adsorption capacity.

Therefore, this work investigated the removal of Cd^{2+} by the aluminum-pillared montmorillonite from aqueous solutions under kinetic and equilibrium conditions. In order to identify the mechanisms of cadmium sorption on pillared montmorillonites, with or/and without carbon modification the pillaring conditions were varied and different forms of pillared montmorillonites were prepared and tested in sorption experiments.

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2. Experimental

2.1. Clay and reagents

The montmorillonite was purchased from Beijing Montmorillonite Company of Science and Technology. The clay fraction is <2 μm, and its composition is as follows: SiO_2 50.90%, Al_2O_3 18.36%, Fe_2O_3 1.03%, CaO 3.97%, MgO 4.14%, MnO 0.007%, TiO_2 0.02%, K_2O 0.72%, Na_2O 1.18%, P_2O_5 2.15%. The BET specific surface area was measured to be 73.7 m^2/g from N_2 sorption isotherms with a sorptionmeter (AUTOSORB-1). Analytical grade reagents, sodium hydroxide (NaOH), aluminum chloride ($AlCl_3{\cdot}6H_2O$), polyvinyl alcohol (1750 ± 50) and nitric acid (HNO_3) were used. A stock solution of Cd^{2+} prepared by dissolving $Cd(NO_3)_2{\cdot}4H_2O$ in deionized water was taken as the adsorptive solution.

2.2. Preparation of the pillared montmorillonites

The PVA modified aluminum-pillared montmorillonite (Al–PVA–MMT) was prepared as follows: at first, to get the Al_{13} oligomers, 120 mL of 0.2 M NaOH was added dropwise to 50 mL of 0.2 M $AlCl_3$ solution under vigours stirring at 70 °C for 24 h. Then 50 mL of 1% PVA solution was added to the Al_{13} solution. The pillared clay was then synthesized by adding a 2% of clay suspension with the ratio of aluminum to clay of 10 mmol/g. After stirring for 2 h, the suspensions were allowed to age overnight. The products were collected by centrifugation, washed until chloride free, and finally air-dried on a glass plate. The products (coded as Al–PVA–MMT) were then calcined in a programmable oven in N_2 atmosphere at 400 °C for 3 h with the heating rate of 1.5 °C/min to obtained carbon modified aluminum oxide pillared montmorillonites (C–Al–PVA–MMT). Aluminum-pillared montmorillonite (Al–MMT) and its calcined product aluminum oxide pillared montmorillonite (C–Al–MMT) were prepared for comparison.

2.3. Characterization

X-ray diffraction patterns were obtained for oriented powder samples using a diffractometer X'Pert PRO MPD with Cu Kα radiation (λ = 1.54178 Å).

FTIR analyses (400–4000 cm^{-1}) were performed on an EQUINOX55 FTIR spectrophotometer using KBr pellets. Spectral outputs were recorded either in absorbance or transmittance mode as a function of wave number.

Nitrogen adsorption–desorption experiments were carried out at 77 K using a Quantachrome AUTOSORB-1 instrument. The samples were out gassed at 200 °C for 2 h under vacuum prior to adsorption measurement.

An atomic absorption spectrophotometer Perkin Elmer Analyst 200 was used to analyze the amount of metal in the solution. Standardized experimental procedures for cadmium were adopted.

2.4. Cd^{2+} sorption–desorption experiments

The adsorption experiments were carried out by mixing preweighted adsorbents with a Cd^{2+} solution of a giving concentration. And then the mixture was agitated for a constant time. After centrifuging, the Cd^{2+} remaining in the supernatant liquid was determined with the atomic absorption spectrophotometer. The experiment's parameter variation including pH of the solution, agitation time, initial concentration of Cd^{2+} and the amount of the adsorbent have been investigated. For maintaining pH of the solution, either 0.1 M NaOH or 0.1 M HNO_3 was added dropwise before carrying out adsorption and pH was monitored both before and after adsorption.

In order to estimate the reversibility of Cd^{2+} adsorption on the synthesized pillared montmorillonites, desorption experiments using solutions with different pH and sodium contents were performed. Firstly, clay was loaded with cadmium to the equilibration with the 60 mg/L cadmium solution. After centrifugation, the solid residue was dried at 105 °C. Secondly, 0.1 g of the obtained solid phase was added to 50 mL of leaching solution and agitated for 24 h. Six extractants were employed. Two acidic solutions were prepared with acetic acid with pH of 2.93 ± 0.05 and 4.93 ± 0.05 following the technique for preparation of extraction fluids for toxicity characteristic leaching procedure [18]. The other four are NaCl solutions with different concentrations.

2.5. Theoretical basis

The kinetics of the adsorption process was tested with respect to the following well-known models:

(a) Pseudo-first-order kinetics using the Lagergren equation is as follows [19,20]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

where q_e and q_t are the amounts adsorbed per unit mass at equilibrium and at any time t, and k_1 is the pseudo-first-order adsorption rate constant. The value of k_1 can be obtained from the slope of the linear plot of $\ln(q_e - q_t)$ vs. t.

(b) The second-order kinetics is applied when $\ln q_e$ is not equal to the intercept of the first-order plot based on Eq. (1). The second-order kinetics is given by the following equation [21]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{2}$$

where $k_2 q_e^2$ is described as the initial adsorption rate as $t \to 0$. The plot of t/q_t vs. t gives a straight line, which allows computation of q_e and k_2.

Two isotherm equations were used to find out the relation between the equilibrium concentrations of the adsorbate in the liquid phase and in the solid phase. These isotherms [22,23] are as follows:

$$\text{Freundlich isotherm}: q_e = k_f C_e^n \tag{3}$$

where C_e and q_e are the equilibrium concentrations of Cd^{2+} in the liquid and the solid phases, respectively; the coefficients k_f and n represent the capacity and the intensity of adsorption.

$$\text{Langmuir isotherm}: \frac{C_e}{q_e} = \frac{1}{b q_m} \left(\frac{1}{q_m}\right) C_e \tag{4}$$

where b and q_m are Langmuir coefficients representing the equilibrium constant for the adsorbate–adsorbent equilibrium and the monolayer capacity. The linear Freundlich and Langmuir plots are obtained by plotting $\log q_e$ vs. $\log C_e$ and C_e/q_e vs. C_e, respectively, from which the adsorption coefficients could be evaluated.

3. Results and discussion

3.1. Characteristics of clay adsorbents

3.1.1. Structure and composition of pillared montmorillonites

The XRD patterns (Fig. 1) of aluminum-pillared montmorillonites indicated that the d_{001} value increases from 13.9 Å to 18.9 Å after pilling with aluminum, which suggests the successful intercalation of Al_{13} units. For pillaring together with PVA, the

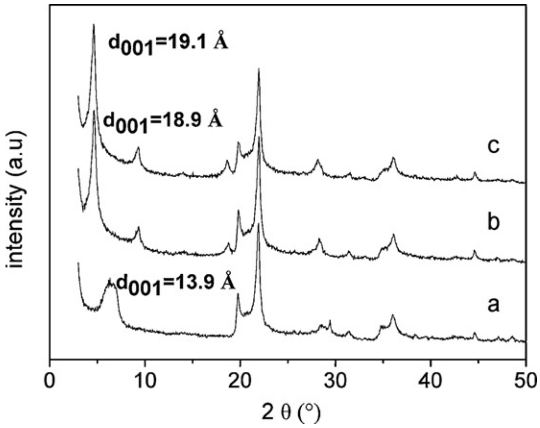

Fig. 1. XRD patterns of (a) raw montmorillonite, (b) aluminum-pillared montmorillonite and (c) aluminum-pillared montmorillonite pillaring with PVA.

basal spacing further increases to 19.1 Å, the slight increase may be due to the complexation of PVA to the Al_{13} oligomeric cations. The peaks obtained are sharper than the raw material showing a better ordered structure. The FT-IR measurements gave additional support of the intercalation (Fig. 2). Both of the pillared montmorillonites showed Si–O–Al modes around 519 cm^{-1} and 467 cm^{-1}, and Al–O stretching band at 789 cm^{-1}. With PVA intercalated, the band for $-CH_2$ stretching appeared at 2955 cm^{-1}.

3.1.2. N_2 adsorption–desorption isotherm

The adsorption isotherms for the samples are well fitted by the BET equation, and the BET specific surface area (Table 1) of aluminum-pillared montmorillonite calculated from the N_2 adsorption isotherm is 221.1 m^2, the high surface area confirms the presence of aluminum polycations in the interlayer space. When pillaring together with PVA a smaller specific surface area of 192.1 m^2 was obtained. After calcination, both the as-synthesized samples have decreased in the surface area (113.9 m^2 for Al–MMT and 70.4 m^2 for Al–PVA–MMT), but since the PVA was converted to porous active carbon, the corresponding specific surface area decrease of the sample is less. The pore diameter and total pore volume were calculated by BJH method (Table 1). The total pore volume for both the as-synthesized samples decreased after calcinations (from 0.32 to 0.29 mL/g for Al–MMT, and from 0.45 to 0.31 mL/g for Al–PVA–MMT), which is in accordance with the surface area changes, and is mainly caused by the decreases of the basal spacing upon calcination. At the mean time, the pore diameter just changed slightly (from 3.82 to 3.75 nm for Al–MMT, and from 3.73 to 3.79 nm for Al–PVA–MMT), suggesting that the aluminum oxide pillars are dominant for the pore size in the final products.

Table 1
Specific surface area, pore diameter, total pore volume of the pillared montmorillonites before and after calcinations in N_2

Sample	Specific surface area (m^2/g)		Total pore volume (mL/g)		Pore diameter (nm)
	Measured	Decrease	Calculated	Decrease	
Al–MMT	221.1	113.9	0.32	0.03	3.82
C–Al–MMT	107.2		0.29		3.75
Al–PVA–MMT	192.1	70.4	0.45	0.14	3.73
C–Al–PVA–MMT	121.7		0.31		3.79

3.2. Adsorption of cadmium

3.2.1. Effect of pH

Adsorption of cadmium was examined with the pH variation up to 8.0 with clay amount of 2 g/L and Cd^{2+} concentration of 60 mg/L. As shown in Fig. 3, the amount adsorbed increased in the pH range with no indication of precipitation of cadmium hydroxide. This was in conformity with the results of a blank experiment without the presence of the clay. When the pH is lower than 6, the Cd^{2+} adsorption amount is low and increases slowly with the pH increase. This could be attributed to the high concentration of H^+ ions, which exceeds that of Cd^{2+} by several times, so that the metal ions can hardly compete with H^+ for the binding sites on the clay adsorbents. While as the pH is higher than 6, along with its increase, the Cd^{2+} uptake increased sharply, which might be because of the relatively low H^+ concentration that has made the clay surface negatively charged and could bond strongly with Cd^{2+} [24,25]. With larger spaces provided by the calcined pillared montmorillonites than the raw material, under higher pH (6–8), much more enhanced Cd^{2+} adsorption could be achieved. Additionally, carbon modified aluminum-pillared montmorillonite showed higher Cd^{2+} uptake capacity than that without modification, indicating that carbon helped the better utilizing of the pore spaces for Cd^{2+} adsorption.

3.2.2. Effect of agitation time and kinetics of adsorption

For an adsorbent amount of 2 g/L and initial Cd^{2+} concentration of 60 mg/L, adsorption was taken up with different agitation times

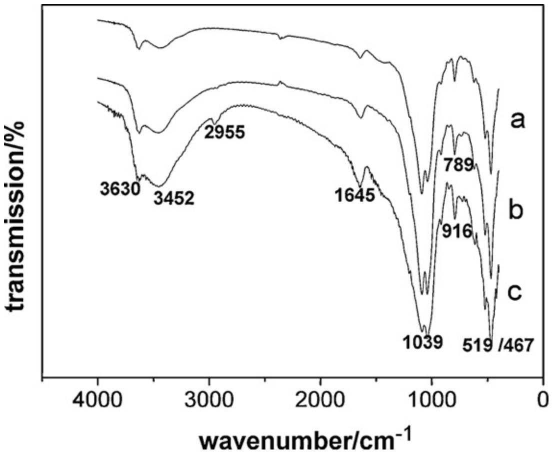

Fig. 2. FT-IR spectra of (a) raw montmorillonite, (b) aluminum-pillared montmorillonite and (c) aluminum-pillared montmorillonite pillaring with PVA.

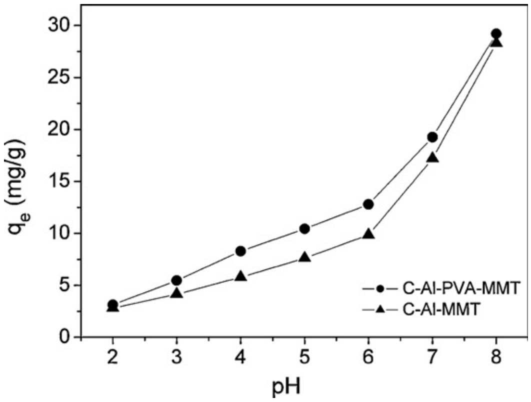

Fig. 3. Effect of pH on the amount of Cd^{2+} adsorbed on per unit mass of pillared montmorillonite (q_e).

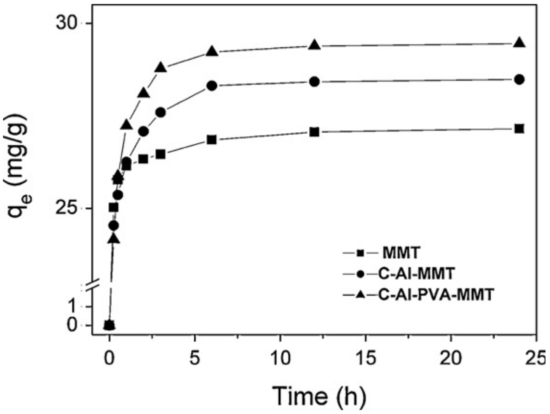

Fig. 4. Variation of amount of Cd^{2+} adsorbed per unit mass (q_e) with time at pH 8.0.

and at the solution pH of 8.0. The uptake of Cd^{2+} was very fast in the first 30 min, and it continued to slowly increase up to 6 h, when equilibrium was reached (Fig. 4). The initial uptake of Cd^{2+} is very high, since a large number of adsorption sites are available for adsorption. As the sites are gradually filled up, adsorption becomes slow and the kinetics becomes more dependent on the rate at which the adsorptive is transported from the bulk phase to the actual adsorption sites [26].

Different kinetics models such as the Lagergen's first-order equation and second-order equation were tested to find out which model is in agreement with the experimental results of the kinetics study [27,28]. On comparison, the second-order equation gives a better explanation of the interactions. The calculations indicated that the carbon modification did not enhance the rate constant for adsorption, but increased the amount of adsorbed metal ions. Furthermore, theoretically predicted equilibrium sorption is close to that determined experimentally.

3.2.3. Effect of initial Cd^{2+}concentration

The adsorption experiments were carried out with Cd^{2+} concentrations of 10, 20, 30, 40, 50 and 60 mg/L with a constant clay amount of 2 g/L, for 6 h at pH of 8.0. The amount of Cd^{2+} adsorbed per unit mass of clay increases gradually with increase in Cd^{2+} concentration (Fig. 5). At low initial metal ion concentration, the ratio of the metal ions to the available adsorption sites is low and consequently the adsorption is independent on the adsorbents. However, as the number of Cd^{2+} increases, unit mass of the adsorbent exposing to more metal ions, and the adsorbents with more available binding sites would take up more Cd^{2+}.

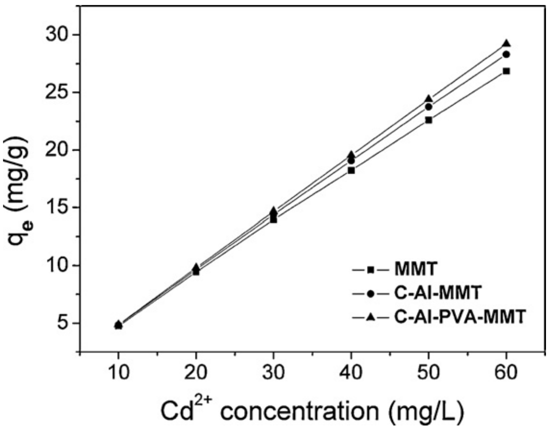

Fig. 5. Amount of Cd^{2+} adsorbed per unit mass (q_e) on different montmorillonite adsorbents in the solutions with different initial metal ion concentrations.

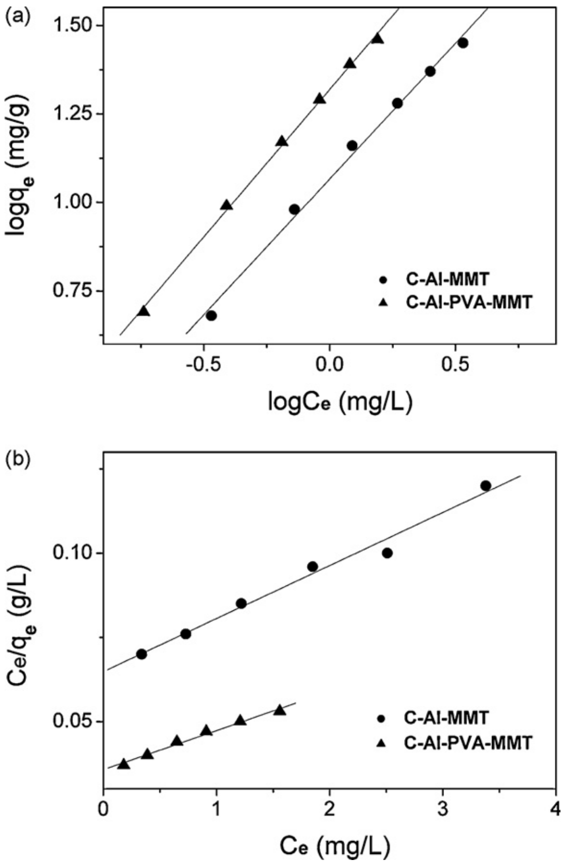

Fig. 6. (a) Freundlich isotherm and (b) Langmuir isotherm for adsorption of Cd^{2+} on pillared montmorillonite adsorbents.

3.2.4. Adsorption isotherm

The empirical Freundlich and the Langmuir isotherms (Fig. 6) could be used to describe the adsorption of Cd^{2+} on the pillared montmorillonites (C–Al–MMT and C–Al–PVA–MMT). The Langmuir isotherm, applicable strictly to chemisorptive monolayer formation, has also been found to be equally applicable for the adsorption. The Langmuir equilibrium coefficient, *b*, which is characterized the adsorption capability, is larger for C–Al–MMT and C–Al–PVA–MMT (231.4 and 323.5 g/L) than that of the unpillared (215.6 g/L). This may explain the larger adsorption capacity of the pillared adsorbents.

3.3. Desorption

Cadmium desorption from clay adsorbents depends on the composition of the extraction solution (Fig. 7). In all the different extractant, more Cd^{2+} desorption from the pillared montmorillonite than the unpillared could be obtained. The percentage of desorption in acetic acid with pH 2.90 was the highest for all the three adsorbents, this may be attribute to the high concentration of H^+ in the solution, which is more likely to occupy the adsorption sites and finally make the Cd^{2+} desorbed from the adsorbents. In NaCl solutions, with the increase of the Na^+ concentration, the exchangeable Na^+ increased, as a result, more Cd^{2+} can be desorbed. When the concentration of NaCl reached 1.0 M, the highest desorption attained 61.8% of the initial sorbed Cd^{2+} by C–Al–MM, which is much higher than the unpillared montmorillonite. The higher desorption of pillared montmorillonite provides

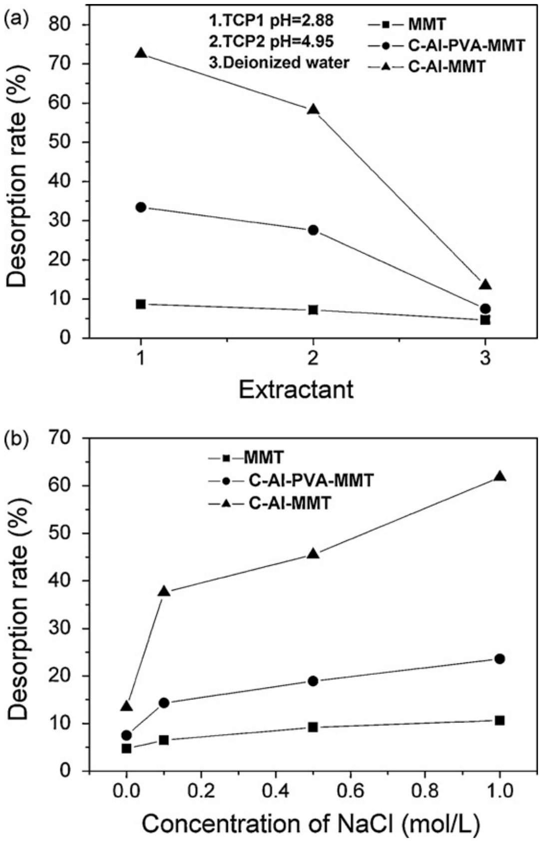

Fig. 7. Desorption rates of Cd^{2+} by using (a) acetic acid aqueous solutions and (b) NaCl solutions.

available condition for repeated use of montmorillonite. However, carbon modified pillared montmorillonite showed a lower desorption, which might be addressed by the obstacle of the carbon. Further controlling the amount and state of carbon might lead to better results.

4. Conclusions

Carbon modified aluminum-pillared montmorillonite was prepared. With the carbon modification, the pillared montmorillonite showed improved specific surface area and pore volume. When used for Cd^{2+} adsorption, the pillared montmorillonites showed a pH dependent Cd^{2+} uptaking. On the other hand, the amount of adsorbed Cd^{2+} increased with the concentration of Cd^{2+}. The Cd^{2+} adsorption followed a mechanism based on second-order kinetics. The Cd^{2+} sorption isotherm can be well described by both Freundlich and Langmuir equation, the adsorption coefficients agree well with the conditions supporting favorable adsorption. The carbon modified pillared montmorillonite showed the higher Cd^{2+} adsorption but lower Cd^{2+} desorption capability than the unmodified. To obtain better Cd^{2+} desorption capability, the carbon amount and state in the pores should be carefully controlled, researches on which is now in progress.

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