Adsorption of copper and lead in aqueous solution onto bentonite modified by 4′-methylbenzo-15-crown-5

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Abstract

The adsorption of heavy metal ions (Cu^{2+} and Pb^{2+}) onto organobentonite modified by 4′-methylbenzo-15-crown-5 (MB15C5) from bentonite compared with natural bentonite (N-Bentonite) is described in this paper. The kinetic parameters of the models are calculated and discussed, and closely fitted a pseudo-second-order model in all cases. For bentonite modified with MB15C5 (MB15C5-Bentonite) and N-Bentonite, the equilibrium data closely fitted the Langmuir model and showed the following affinity order: $Pb^{2+} > Cu^{2+}$, and the adsorption capacity of MB15C5-Bentonite is higher than that of N-Bentonite for Pb^{2+} and Cu^{2+}. The effect of pH is examined over the range 1.5–6. The adsorption of Cu^{2+} and Pb^{2+} increases with increasing pH and the adsorption of Cu^{2+} and Pb^{2+} reaches a maximum at pH 3.5–6.
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Keywords: 4′-Methylbenzo-15-crown-5; Adsorption; Bentonite; Heavy metal

1. Introduction

Toxic metals at trace levels contamination of soil and potential fouling of groundwater is a complex and common problem, and it is well known that heavy metal pollution is a serious threat to the environment. Pb, Cd, Cu, Hg, Cr, Ni and Zn are the main trace elements that are of greatest concern.

In order to prevent contamination of subsoil, groundwater and surface water by these elements, there has recently been a growing interest in the development of materials capable of adsorbing heavy metals [1–3]. Effective adsorbents with a strong affinity and, subsequently, a high loading capacity for targeted metal ions have been prepared by modifying the surface of various substrates, such as silica gel [4], aerobic granules [5,6], zeolite [7] and clay [8,9], with heavy metal complexing agents (e.g., surfactant [10] and thiols [11,12]).

Because of high specific surface areas, low cost and ubiquitous presence in most soils, clay is usually chosen to prevent heavy metals being released into the environment [13]. One such clay is bentonite, which is a 2:1 type of clay, and its unit layer structure consists of one Al^{3+} octahedral sheet placed between two Si^{4+} tetrahedral sheets. The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the clay [14]. This charge imbalance is offset by exchangeable cations (e.g. H^+, Na^+ and Ca^{2+}) at the clay surface. The most important factors regulating heavy metals in clay include the type of clay, the metal involved, its concentration and pH [15,16]. Many research studies have focused on clay and clay constituents, such as clay minerals, metal (hydr)oxides and organic matter [17–21].

Crown ether is known to complex with numerous metals [22]. Bruening and co-workers [23] and Izatt et al. [24] used silica gel modified by crown ether to remove metal cations from organic solvents and aqueous solution. Crown ether modified bentonite was first reported in 1978 by Ruiz-Hitzky and Casal [25]. They pointed out that crown ethers could be intercalated between the layers of 2:1 bentonite saturated with alkaline or alkaline-earth cations. They also found that crown ether modified bentonite was very stable. Sivaiah et al. has studied adsorption of cesium and strontium to dicyclohexano-18-crown-6 modified bentonite [26]. However, few research studies have focused on the interactions of heavy metal with the surface of bentonite modified by 4′-methylbenzo-15-crown-5 (MB15C5).

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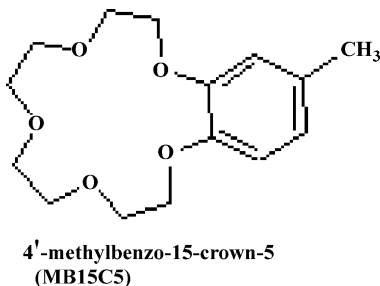
4′-methylbenzo-15-crown-5
(MB15C5)

Fig. 1. Molecular structure of 4′-methylbenzo-15-crown-5 (MB15C5).

In the present study, MB15C5-Bentonite was prepared and the adsorption kinetics and equilibrium of metal ions (Cu^{2+} and Pb^{2+}) on MB15C5-Bentonite and natural bentonite (N-Bentonite) were investigated. The kinetic and equilibrium parameters were calculated, such as the rate constant, the maximum capacities and adsorption affinity. The influence of pH on adsorption was also investigated.

2. Materials and methods

2.1. Materials

N-Bentonite was obtained from the Inner Mongolia Autonomous Region, China. It had a high montmorillonite content (>95%) and its cation-exchange capacity (CEC) was 108 meq/100 g. MB15C5 was synthesized in laboratory. The chemical structure of MB15C5 ether is given in Fig. 1.

2.2. Preparation of MB15C5-Bentonite

N-Bentonite fractions less than 100 mesh were treated with 1 mol/L sodium chloride solution to obtain homoionic samples (Na-Bentonite). After complete exchange, the samples were washed with distilled water until free from chloride as shown by the AgNO3 test.

Then 50 g Na-Bentonite was mixed with methanol containing the amount of MB15C5 equivalent to the CEC of bentonite in a beaker. After stirring mechanically for 24 h at 25 °C, the mixture was filtered, and then washed several times with methanol. After drying at room temperature, it was activated for 1 h at 105 °C to dehydrate, MB15C5 still remaining stable [27], and ground with a pestle to less than 100 mesh. This produced MB15C5-Bentonite.

2.3. Characterization of N-Bentonite and MB15C5-Bentonite

An X-ray diffractometer (XRTA, Switzerland) with Cu Kα radiation and a Ni filter was operated at 40 kV, 40 mA and a scanning rate of 0.02° min^{-1}. IR spectroscopy was performed on Nexus 870 FT-IR. Bentonites were obtained using the conventional KBr pellet method. The total organic carbon content of N-Bentonite or MB15C5-Bentonite was analyzed by the wet oxidation method [28].

2.4. Adsorption of Cu^{2+} and Pb^{2+} as a function of pH

A batch of 0.2000 g N-Bentonite or MB15C5-Bentonite was mixed in a 50 mL centrifuge tube with 25 mL Cu^{2+} (initial concentration: 3.227 mmol/L) or Pb^{2+} (initial concentration: 4.344 mmol/L). The pH of the initial solution was adjusted to 1.5–6 with HNO3 or NaOH using a pH meter (Shanghai Second Analytical Equipment Co.). After being shaken at 25 °C for 12 h, the tubes were centrifuged for 10 min, and Cu^{2+} or Pb^{2+} was analyzed by AAS (Hitachi, Z-8100). All experiments were carried out in duplicate.

2.5. Batch kinetic experiments

The kinetic experiments were conducted in batch mode on N-Bentonite and MB15C5-Bentonite. The experimental details were as follows: 0.2000 g N-Bentonite or MB15C5-Bentonite was added to a tube (50 mL) containing 25 mL Cu^{2+} or Pb^{2+} solution. The corresponding Cu^{2+} and Pb^{2+} concentrations were 2.824 and 4.344 mmol/L at pH 5.0, respectively. The suspension was shaken for a period between 2 and 60 min with a rotary shaker at a speed of 150 rpm. After being centrifuged, Cu^{2+} or Pb^{2+} was analyzed by AAS. All experiments were carried out in duplicate. The kinetics of metal uptake can be described by pseudo-first-order and pseudo-second-order model [29,30].

The pseudo-first-order model is given as:

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$

The pseudo-second-order model is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

$$h = K_2 q_e^2$$

where K_1 is the rate constant of pseudo-first-order adsorption (min^{-1}), K_2 (g/mmol min) the rate constant of pseudo-second-order adsorption, h the initial adsorption rate (mmol/g min) and q_e and q_t are the amount of adsorbed Cu^{2+} and Pb^{2+} on adsorbent (mmol/g) at equilibrium and at time t, respectively.

2.6. Adsorption experiments

Adsorption isotherm studies were conducted by adding 0.2000 g N-Bentonite or MB15C5-Bentonite to a solution containing 25 mL of various concentrations of Cu^{2+} (ranging from 0.2 to 6 mmol/L, pH 5.0) or Pb^{2+} (ranging from 0.4 to 10 mmol/L, pH 5.0). The tubes were shaken for 12 h at 25 °C on the rotary shaker at 150 rpm. After being centrifuged, Cu^{2+} or Pb^{2+} was analyzed by AAS. All experiments were carried out in duplicate. The adsorption isotherm can be described by a Langmuir-type isotherm which can be described by the following equation:

$$q = \frac{K Q_{max} C_e}{1 + K C_e}$$

where q is the amount of metal adsorbed (mmol/g of adsorbent), C_e the equilibrium concentration (mmol/L), Q_{max} the maximum

Table 1
Interlayer spacing increases and organic carbon content of N-Bentonite and MB15C5-Bentonite

Bentonite type	d_L (Å)	Δd_L (Å)	Organic carbon contents (%)
N-Bentonite	12.5	3.6	0.23
MB15C5-Bentonite	15.4	5.8	9.85

capacity of the adsorbent (mmol/g) and K is the affinity constant (L/mmol). The Langmuir equation can be rearranged to a linear form for the convenience of plotting and determining the Langmuir constants as below:

$$\frac{C_e}{q} = \frac{C_e}{Q_{max}} + \frac{1}{KQ_{max}}$$

3. Results and discussion

3.1. N-Bentonite or MB15C5-Bentonite characteristics

The organic carbon contents of Na-Bentonite and MB15C5-Bentonite are shown in Table 1. As calculated from the organic carbon content, the amount of MB15C5 in MB15C5-Bentonite is 0.55 mmol/g MB15C5/Bentonite. The IR spectra of bentonite, MB15C5 and MB15C5-Bentonite are as shown in Fig. 2. Comparing MB15C5-Bentonite with bentonite, the spectrum of MB15C5-Bentonite shows extra peaks at 3100–2800 cm^{-1} due to C−H saturated and unsaturated stretching vibration, and 1592.7, 1514.9 and 1459.5 cm^{-1} due to benzene ring char-
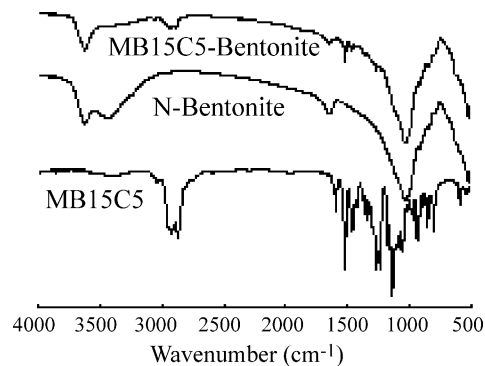

Fig. 2. IR spectra of bentonite, MB15C5 and MB15C5-Bentonite.

acteristic peaks. This demonstrates clearly the attachment of MB15C5 onto bentonite.

The basal spacing of Na-Bentonite and MB15C5-Bentonite are shown in Fig. 3. The basal spacing of Na-Bentonite is 3.6 Å. The observed changes in the basal spacing show an increase in the interlayer spacing changes from 3.6 to 5.8 Å (Fig. 3 and Table 2.). Ruiz-Hitzky and co-workers have studied the structural characteristics of crown ether in the interlayer of bentonite [31]. Their work suggests that crown ether, which forms 1:1 or 2:1 ligand/cation intrastalline complexes, lies flat or tilting between the interlayer of bentonite as can be deduced from the increase in the basal space of silicate.

It is known that the formation of 1:1 or 2:1 ligand/cation complexes is determined by the ratio of the ionic radius to the
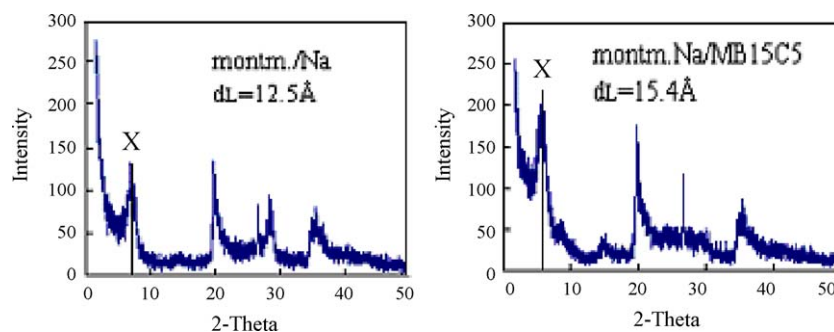

Fig. 3. XRD pattern of MB15C5 intercalated into bentonite.

Table 2
Parameters for adsorption of Cu^{2+} and Pb^{2+} onto N-Bentonite and MB15C5-Bentonite derived from the pseudo-first- and second-order kinetic models and their compatibility to the associates

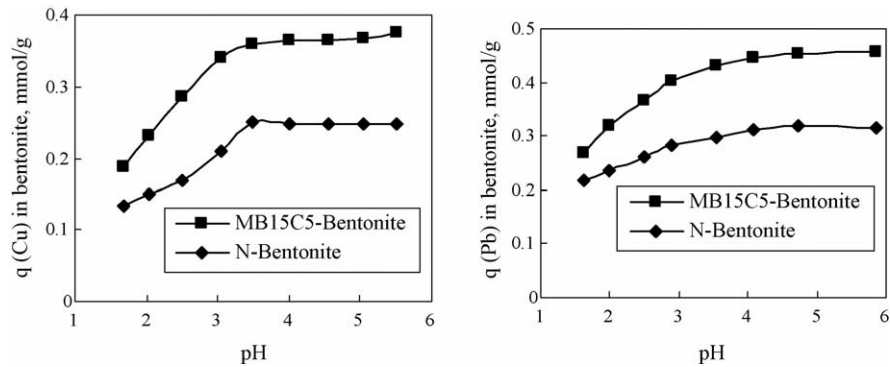|	Cu^{2+}		Pb^{2+}	
	N-Bentonite	MB15C5-Bentonite	N-Bentonite	MB15C5-Bentonite
Pseudo-first-order kinetics				
K_1 (min^{-1})	0.258	0.096	0.090	0.077
r^2	0.568	0.807	0.686	0.771
Pseudo-second-order kinetics				
H (mmol/g min)	0.127	1.121	1.908	2.309
K_2 (g/mmol min)	1.644	9.609	19.502	10.216
q_e (mmol/g)	0.278	0.342	0.313	0.475
r^2	0.9985	1.0000	0.9999	0.9999

Fig. 4. Effect of pH on Cu^{2+} and Pb^{2+} adsorption onto N-Bentonite and MB15C5-Bentonite.

cavity size of the macrocyclic cavity [32]. For the cavity size of the MB15C5 ring (1.7–2.2 Å), sodium ion (diameter, 1.96 Å) can fit tightly into the crown cavity, forming a 1:1 complex. From molecular models, 4 Å was the estimated thickness of the MB15C5 ether. Following intercalation of MB15C5 in bentonite, the value of the interlayer spacing changes to 5.8 Å. This result suggests that MB15C5 can intercalate into the interlayer of bentonite, and tilt in the interlayer with respect to the silicate layers.

3.2. Effect of initial pH

The adsorption of Cu^{2+} and Pb^{2+} onto MB15C5-Bentonite and N-Bentonite as a function of pH is shown in Fig. 4. Cu^{2+} and Pb^{2+} were adsorbed on bentonite over the pH range 1.5–6. It can be seen that the adsorption of Cu^{2+} and Pb^{2+} onto bentonite is markedly pH-dependent. The uptake of Cu^{2+} and Pb^{2+} on MB15C5-Bentonite is better at all pH values compared with N-Bentonite. For N-Bentonite and MB15C5-Bentonite, the adsorption of Cu^{2+} and Pb^{2+} increases with increasing pH, and almost reaches a plateau value around 3.5 for Cu^{2+} and Pb^{2+}. As the surface of bentonite is more protonated at a low pH, it is less able to retain heavy metal ions [33]. The reason for this is that the surface complexation reactions are influenced by the electrostatic attraction between negatively charged groups at the bentonite surface and the ions [34]. When adsorption occurs below pH 5.00, the two ions are below the pH of precipitation [35]. In such a system H^+ competes with metal ions, resulting in active sites becoming protonated to the virtual exclusion of metal binding on the bentonite surface [36]. This means that at higher H^+ concentrations, the bentonite surface becomes more positively charged thus reducing the attraction between surface and metal cations. As the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake [37]. In return, due to some removal of metals by precipitation above precipitation pH 5.00, metals were removed by both adsorption and precipitation.

3.3. Kinetic modeling

Sorption of Cu^{2+} and Pb^{2+} on bentonite may involve a chemical sorption which may control the rate. In order to investigate
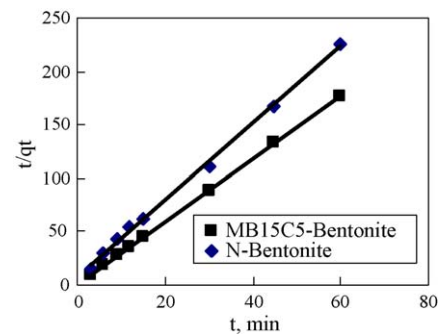

Fig. 5. Pseudo-second-order adsorption kinetics of Cu ion at pH 5.

the mechanism of sorption and potential rate-controlling steps, two kinetic models were tested including a pseudo-first- and second-order equations. The adsorption kinetic constants and linear regression values are given in Table 2.

From the Table 2, we can see that the degree of fit r^2 for the pseudo-second-order kinetic model ($r^2 > 0.99$) is higher than those of the pseudo-first-order model ($r^2 < 0.90$). Accordingly, the pseudo-second-order kinetic model is applicable, and the plot of t/q_t versus t shows a linear relationship (Figs. 5 and 6). Also, the q_e calculated values fit the experimental data. This suggests that the pseudo-second-order adsorption mechanism is predominant and that the overall rate of the Cu^{2+} and Pb^{2+} adsorption process appeared to be controlled by the chemical process [36]. The calculated q_e values of the first-order model do
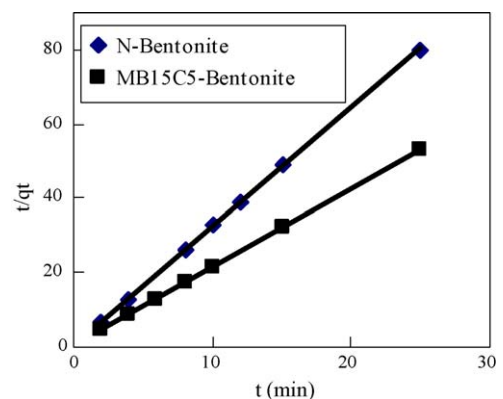

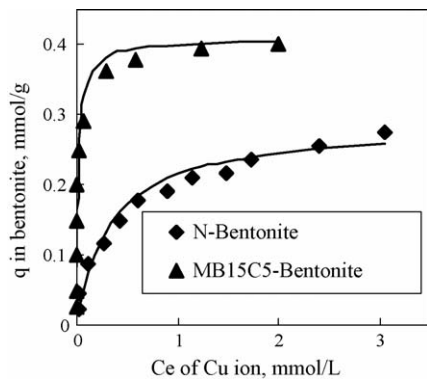Fig. 6. Pseudo-second-order adsorption kinetics of Pb ion at pH 5,.

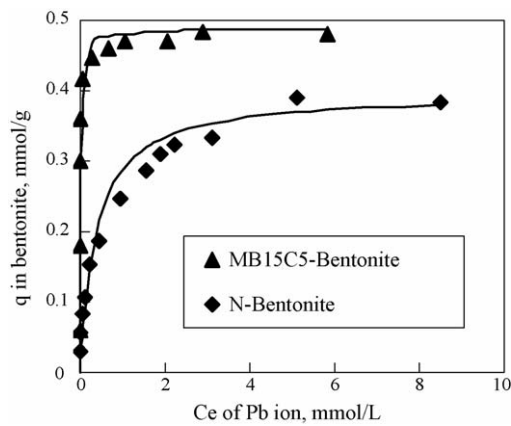Fig. 7. Adsorption Langmuir fit isotherm of Cu ions on bentonite.

Fig. 8. Adsorption Langmuir fit isotherm of Pb ions on bentonite.

not give reasonable values, which are obviously different from the experimental q_e values. So, adsorption of Cu^{2+} and Pb^{2+} onto N-Bentonite and MB15C5-Bentonite is not a pseudo-first-order process.

### 3.4. Metals adsorption studies

The adsorption of Cu^{2+} and Pb^{2+} from solution to N-Bentonite and MB15C5-Bentonite was studied at 25 °C at pH 5.0. Adsorption isotherms for Cu^{2+} and Pb^{2+} were established to compare the adsorption of MB15C5-Bentonite with that of N-Bentonite (Figs. 7 and 8).

The equilibrium adsorption data are fitted to the linear form of the Langmuir equation, and the adsorption parameters of the adsorbents (adsorption capacity Q_{max}, the affinity constant K and a measure of the degree of fit r^2) are shown in Table 3. In all cases, the degree of fit r^2 for the linear regression fits were

found to be >0.99, which is a measure of the goodness-of-fit of the experimental data to the Langmuir isotherm models. For both Cu and Pb, higher K values were observed for MB15C5-Bentonite than N-Bentonite.

For MB15C5-Bentonite, the amount of metal (Cu^{2+} or Pb^{2+}) adsorbed increased vertically with a significant increase and level with subsequent increase in its equilibrium concentration belong to H-type isotherms suggesting a very strong metal–bentonite surface interaction, which are actually the extreme case of the L-type ones [38]. According to Veeresha et al. [39], the isotherms which show steep initial slopes that level out with a subsequent increase in the equilibrium concentration of the metal giving rise to a plateau or a linear section with positive slope are classified as L-type isotherms and reflect a relatively high affinity between the metal and soil surface. In the N-Bentonite adsorption test, the rate of Cu^{2+} and Pb^{2+} removal is relatively rapid at the start because of the initially greater availability of the bentonite surface area. As the surface adsorption sites become exhausted, uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the bentonite particles. Also, for both Cu^{2+} and Pb^{2+}, much higher K values were observed for MB15C5-Bentonite than for N-Bentonite. Furthermore, for Cu^{2+} and Pb^{2+} the value of Cu^{2+} and Pb^{2+} adsorbed on MB15C5-Bentonite is about 1.25 and 1.30 times that of Na ions desorbed from MB15C5-Bentonite.

The adsorption mechanisms of MB15C5-Bentonite are complex and the main adsorption mechanisms are involved, i.e., ion exchange, complex formation and precipitation. Accordingly, the adsorption process can be described as follows:

$$A^{n+} + n\text{Na-B} \Leftrightarrow n\text{Na}^+ + \text{A-B}$$
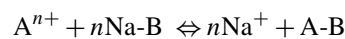
where A^{n+} (Cu^{2+} and Pb^{2+}) and Na^+ are the exchanging cations and B refers to bentonite. In the interlayer of bentonite, some Na ions are fixed in the crown ring of MB15C5, so the equilibrium moves to the right. Also, some MB15C5 ethers that do not complex with Na ions in the interlayer of bentonite can capture A^{n+}, and this enhances the adsorption affinity of MB15C5-Bentonite. And as bentonite has acid-base buffering properties, the final pH of solution after Cu^{2+} (or Pb^{2+}) adsorption onto bentonite is from pH 6 to pH 7 when the initial pH is 5.0. So precipitation is another adsorption mechanism. Due to the above reasons, MB15C5 is the effective modifier to capture Cu^{2+} and Pb^{2+}.

For MB15C5-Bentonite, the adsorption affinity for Pb^{2+}, $K_{Pb^{2+}}$ is greater than for Cu^{2+} and $K_{Cu^{2+}}$, respectively. It is the same order based on the maximum amounts adsorbed expressed in mmol/L. The preferential adsorption order of $Pb^{2+} > Cu^{2+}$ may be attributed to the different adsorption affinities of metals

Table 3
Langmuir parameters for adsorption of Cu^{2+} and Pb^{2+} onto N-Bentonite and MB15C5-Bentonite

Solute	Adsorbent	K (L/mmol)	Q_{max} (mmol/g)	Degree of fit (r^2)
Cu^{2+}	N-Bentonite	2.999	0.287	0.9862
	MB15C5-Bentonite	48.133	0.403	0.9997
Pb^{2+}	N-Bentonite	2.737	0.396	0.9927
	MB15C5-Bentonite	75.693	0.488	0.9987

for the bentonite surface according to their different properties, and metal hydrolysis is generally related to the adsorption affinity [40,41]. However, the hydrated heavy metal ions have diameters (Pb^{2+} 8.02 Å and Cu^{2+} 8.38 Å [42]) that are greater than the interlayer spacing. It is believed that partial dehydration of the hydrated heavy metal ions needs to occur in order for adsorption to the surface of bentonite to take place. So, Pb species with the lower hydration energy may help the hydrated Pb ions to enter the bentonite more easily than Cu ion [43].

4. Conclusions

MB15C5-Bentonite has been prepared by MB15C5 from N-Bentonite. The structure and adsorption performance of N-Bentonite and MB15C5-Bentonite were evaluated. Using Cu^{2+} and Pb^{2+} as heavy metal indicators for adsorption, our experiments prove that the adsorption capacities of MB15C5-Bentonite are dramatically enhanced. The pH is an important factor affecting the adsorption of heavy metals by bentonite, and it can change the affinity of the adsorption sites for heavy metals. The pseudo-second kinetic model is suitable for describing the adsorption system. The Langmuir isotherm provides a good fit for the studied temperature and concentration ranges.

Acknowledgements

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