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Original Research Paper

Adsorption of Cadmium (Cd^{2+}) Ions from Aqueous Solutions on the Modified Montmorillonite

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ABSTRACT

Heavy metal pollution has become one of the most serious environmental problems today due to its difficulty in removal, especially in aquatic environments. The technologies for heavy metal ion removal from aqueous solutions are, chemical treatment, physico-chemical treatment and biological treatment. However, the existing methods are relatively expensive. Therefore, there is an urgency that some environmentally sound and practically feasible technologies or sorbents are needed to be developed. In this study, a modified montmorillonite was used for the removal of Cd^{2+} ions from aqueous solutions. The influence of various operating parameters on the adsorption process was investigated. The kinetics and equilibrium adsorption of Cd^{2+} ions from aqueous solutions using the modified montmorillonite were also discussed in detail. The objective of this study is to provide fundamental information on the adsorption of heavy metals from aqueous solution on the modified montmorillonite and to investigate the possible mechanisms.

INTRODUCTION

Heavy metal pollution has become one of the most serious environmental problems today, for its difficulty in degrading into harmless under natural conditions, especially in aquatic environments (Xia et al. 2014). Excessive accumulation of metal ions in living organisms, including the human body, and ecological systems can cause decreased stabilization and vegetation of soils, health disorders, and physical, chemical, and biological damage. Heavy metals are non-biodegradable, making them accumulate to toxic levels in the soil available for plant and animal uptake when they are released into the water and soil fluids. This process allows heavy metals to enter the food chain, which end with human consumption (Pablo et al. 2011). The removal of metal ions from different effluents has permanently attracted a great interest of researchers dealing with water pollution and purification (Dragana et al. 2013).

The main technologies for heavy metal ion removal from aqueous solutions are chemical treatment (such as electrochemical and chemical precipitation), physico-chemical treatment (such as ion-exchange and membrane filtration) and biological treatment (such as biomaterial adsorption). However, the existing methods are relatively expensive. Therefore, there is an urgency that some environmentally sound and practically feasible technologies or sorbents are needed to be developed.

Clay minerals are hydrous aluminium, iron and magnesium silicates with layered structures and are hydrophilic, which impart plasticity to the particles. They occur in different environmental compartments such as rocks, soil, sediment and water, acting as scavengers of organic and inorganic pollutants. So, they have well recognized adsorption capabilities that have extensive industrials, technological, agricultural, and environmental application. The smectite minerals, namely montmorillonite, have been broadly investigated as adsorbents of heavy metals from aqueous solution. They have been proven for efficiency in removal of heavy metals (Martin et al. 2011, Vanessa et al. 2014). Various attempts have been made to improve the quality and characteristics of the clays such as replacing the interlayer inorganic cations with iron nitrate, aliphatic and aromatic ammonium bromide, and using acid activation under high temperature (Wu et al. 2011).

In this study, the modified montmorillonite was used for the removal of Cd^{2+} ions from aqueous solutions. The influence of various operating parameters on the adsorption process was investigated, such as contact time, Cd^{2+} ion concentration and temperature. The kinetics and equilibrium adsorption of Cd^{2+} ions from aqueous solutions using the modified montmorillonite are discussed in detail. The objective of this study is to provide fundamental information on the adsorption of heavy metals from aqueous solution on the modified montmorillonite and to investigate the possible mechanisms.

MATERIALS AND METHODS

Preparation of the modified montmorillonite: The montmorillonite was obtained from City of Jingzhou Liaoning province. The chemical composition of the montmorillonite is given in Table 1.

The 50 g montmorillonite was treated in the 10% H_2SO_4 solution for 24 h at room temperature. It was washed with water until the solution reached around pH 7, and dried at 333 K. The treated montmorillonite was immersed in 200 mL of 5% $FeCl_3$ for 24 h. Then, it was filtered and washed repeatedly. It was dried again at 333 K for 12 h to constant weight and was carbonized at 673 K in a muffle furnace for 60 min. The product of modified montmorillonite was thus obtained and then stored for later adsorption experiments.

Adsorption experiments: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 1.0 g of modified montmorillonite and 100 mL of Cd^{2+} ion solutions with various initial concentrations (between 50mg/L and 500mg/L). The initial pH was adjusted to 3.0 with 1 mol/L HCl. The flasks were placed in a shaker at a constant temperature (293, 303 and 313K) and 150 rpm. The samples were filtered and analysed.

Analytical methods: The textural characteristics of the modified montmorillonite including surface area, pore volume, pore size distribution were determined using standard N_2-adsorption techniques. The surface physical morphology of the modified montmorillonite was observed by a scanning electron microscope. The concentration of Cd^{2+} ion was analysed by atomic absorption spectrophotometry (AAS).

The amount of adsorbed Cd^{2+} ion q_t (mg/g) at different time, was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad ...(1)$$

where C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of Cd^{2+} ion respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

Statistical analyses of data: All experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by Excel Software. All error estimates given in the text and error bars in figures are standard deviation of means (mean±SD). All statistical significance was noted at α=0.05 unless otherwise noted.

RESULTS AND DISCUSSION

Characterization of the modified montmorillonite: The surface morphology of the natural montmorillonite and modified montmorillonite is shown in Fig.1 and Fig.2 respectively. It is shown that the modified montmorillonite is a heterogeneous material consisting largely of small spheres, and is irregular and porous. The adsorption capacity of modified montmorillonite is improved.

Additionally, average particle size of the modified montmorillonite is 10.52 nm. The BET surface area is 24.6 m^2/g. The total pore volume is 0.0854 cm^3/g. This result can be attributed to the adsorption of heavy metals in aqueous solution.

Effect of contact time: In order to investigate the effect of contact time on the adsorption of Cd^{2+} ion from aqueous solution by the modified montmorillonite, the adsorption experiments were carried out. Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 1.0 g of modified montmorillonite and 100 mL of 100 mg/L of Cd^{2+} ion solutions. The initial pH was adjusted to 3.0 with 1 mol/L HCl. The flasks were placed in a shaker at a constant temperature (303 K) and 150 rpm. The samples were filtered and analysed at a various contact time ranged from 5 min to 120 min. Effect of contact time is shown in Fig. 3.

As shown in Fig. 3, it can be concluded that the adsorption rate was increased quickly at a various contact time between 3 min and 10 min. However, when the contact time is ranged from 10 min to 60 min, the adsorption rate was increased slowly. After 60 min, the adsorption process reached equilibrium.

Effect of initial concentration of Cd^{2+} ion: To investigate the effect of initial concentration of Cd^{2+} ion on the adsorption of Cd^{2+} ion from aqueous solution by the modified montmorillonite, the experiments were carried out. The initial concentrations of Cd^{2+} ion from aqueous solution were 50, 100, 200, 300, 400 and 500 mg/L. The other operation conditions were 1.0 g of modified montmorillonite, initial pH 3.0, 303 K, contact time of 120 min and 150 rpm. The experimental results are shown in Fig. 4.

From Fig. 4, it can be concluded that the adsorption capacity of Cd^{2+} ion from aqueous solution by the modified montmorillonite was increased along with the increasing of initial concentration of Cd^{2+} ion. When the equilibrium ap-

Table 1: Chemical composition of the montmorillonite.

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	MnO	Na_2O	K_2O
46.21%	18.15%	4.8%	0.39%	2.64%	1.63%	0.06%	0.46%	0.74%

proached, the adsorption process slowed down. It was mainly ascribed to the higher concentration gradient which acted as a driving force for the adsorption process (Foo & Hameed 2012).

Effect of temperature: To investigate the effect of temperature on the adsorption of Cd^{2+} ion from aqueous solution by the modified montmorillonite, the experiments were carried out. The adsorption process of temperature was 298 K, 303 K and 313 K respectively. The other operation conditions were 1.0 g of modified montmorillonite, initial pH 3.0, 100 mg/L of initial concentration of Cd^{2+} ion, contact time of 120 min and 150 rpm. The experimental results are shown in Fig. 5.

It was found that the adsorption rate of Cd^{2+} ions decreased with increasing solution temperature from 298K to 313K. It indicated that higher temperature was not suitable for adsorption process. High temperature might lead to the breaking of the existing intermolecular bonding between Cd^{2+} and the modified montmorillonite, which is an important contribution to the adsorption process.

Adsorption kinetics: Kinetic studies are necessary to optimize different operating conditions for the absorption. To investigate the possible mechanisms that control the adsorption process and potential rate controlling steps, the pseudo first order and pseudo second order were used to interpret the experimental data.

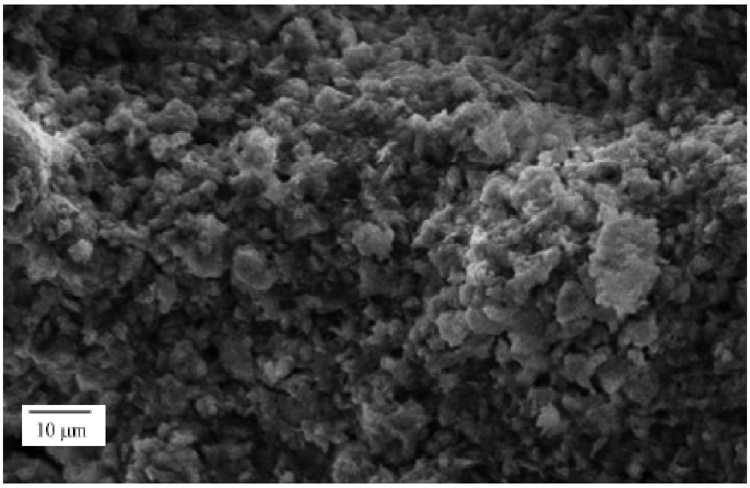

Fig.1: SEM micrographs of the nature montmorillonite.

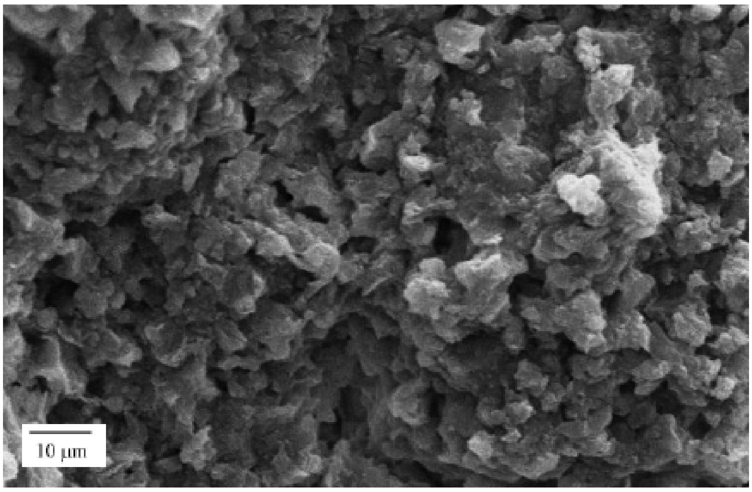

Fig.2: SEM micrographs of the modified montmorillonite.

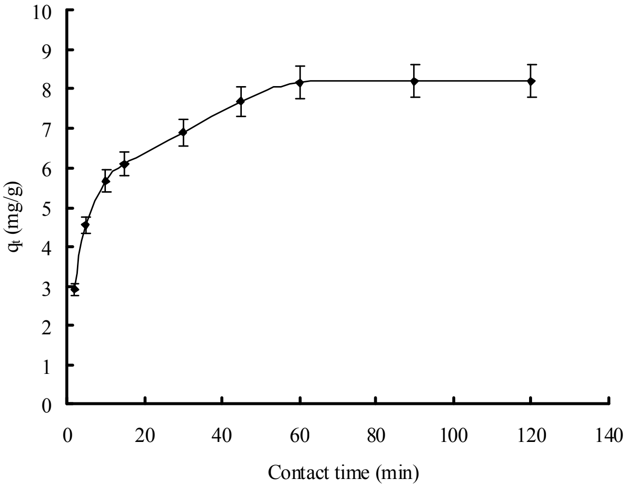

Fig. 3: Effect of contact time on the adsorption of Cd^{2+} ion from aqueous solution by the modified montmorillonite.

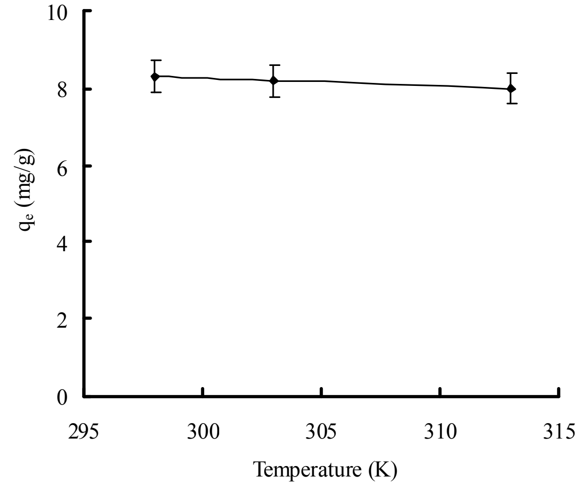

Fig. 5: Effect of temperature on the adsorption of Cd^{2+} ion from aqueous solution by the modified montmorillonite.

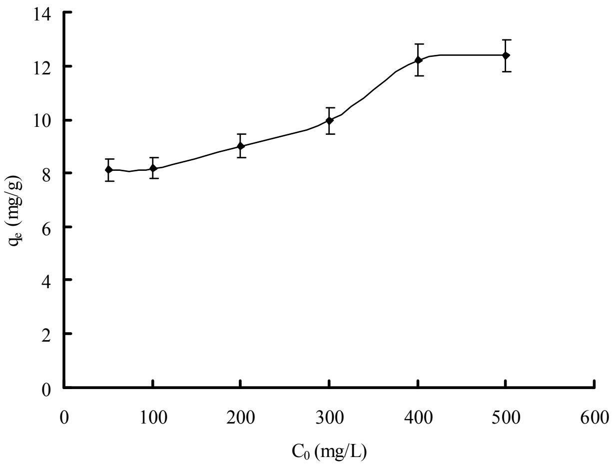

Fig. 4: Effect of initial concentration of Cd^{2+} ion on the adsorption of Cd^{2+} ion from aqueous solution by the modified montmorillonite.

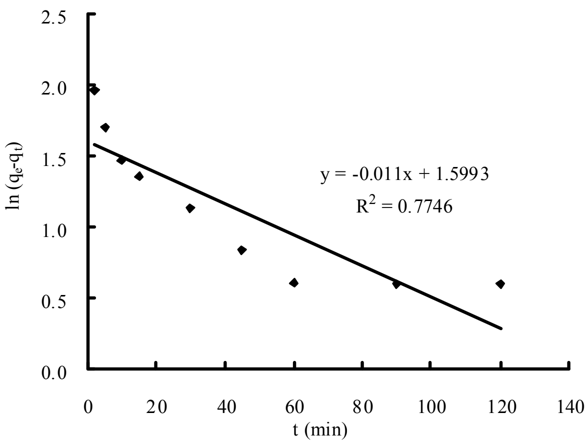

Fig. 6: Pseudo first order kinetic model plots for adsorption of Cd^{2+} ion from aqueous solution by the modified montmorillonite.

The pseudo first order kinetic model has been widely used to predict sorption kinetics. The equation of the model was represented as follows:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad ...(2)$$

Where q_e (mg/g) and q_t (mg/g) are the amounts of the heavy metal Cd^{2+} ion adsorbed on the modified montmorillonite at equilibrium and at any time, t (min), respectively. K_1 (min^{-1}) is the pseudo first order adsorption rate constant. The plots of $\ln(q_e - q_t)$ versus t give the K_1 and q_e values.

The pseudo second order equation expressed by:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad ...(3)$$

Where K_2 ($g \cdot mg^{-1} \cdot min^{-1}$) is adsorption rate constant of pseudo second order model. The constant K_2 and q_e can be obtained from a linear regression plot of $\frac{t}{q_t}$ versus t.

According to the experimental data, kinetics of adsorption Cd^{2+} ion from aqueous solution by the modified montmorillonite are shown in Fig. 6, Fig. 7 and Table 2.

From Fig. 6, Fig. 7 and Table 2, it can be confirmed that the adsorption of Cd^{2+} ion from aqueous solution by the modified montmorillonite better fits to pseudo second order kinetic model. It implies that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent.

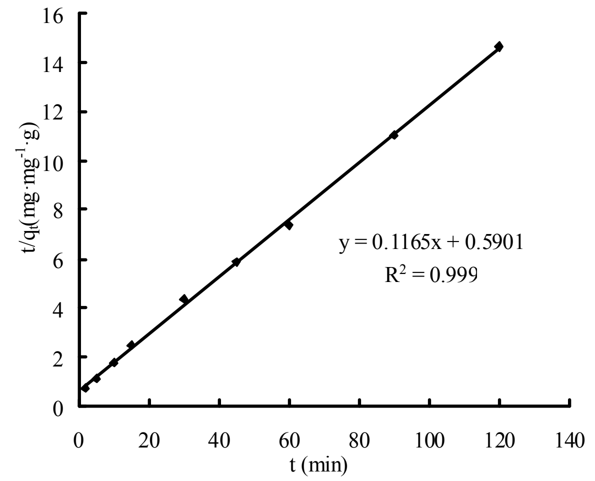

Fig. 7: Pseudo second order kinetic model plots for adsorption of Cd^{2+} ion from aqueous solution by the modified montmorillonite.

Adsorption isotherm: The adsorption isotherm was described with Langmuir isotherm and Freundlich isotherm. The Langmuir isotherm equation is represented by the following Eq. (4):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad ...(4)$$

Where C_e is the equilibrium concentration of Cd^{2+} ion (mg/L), q_e is the amount of Cd^{2+} ion adsorbed (mg/g), q_m is the maximum adsorption capacity of Cd^{2+} ion (mg/g), and K_L is the Langmuir adsorption equilibrium constant (L/mg) related to the affinity of the binding sites (Langmuir 1918).

The Freundlich isotherm equation is described by the following Eq. (5):

$$q_e = K_F C_e^{\frac{1}{n}} \quad ...(5)$$

Where K_F and n are the Freundlich adsorption isotherm constants, which are indicators of adsorption capacity and adsorption intensity respectively (Freundlich 1906).

According to the experimental data, the adsorption parameters were obtained from the Langmuir adsorption isotherm and Freundlich adsorption isotherm. They are listed in Table 3.

It was shown that the Langmuir adsorption isotherm model was more suitable for the Cd^{2+} ion from aqueous solution than the Freundlich adsorption isotherm model. It was also suggested that the adsorption process was homogeneous adsorption. The Cd^{2+} ion from aqueous solution adsorption on the modified montmorillonite was monolayer adsorption (Tan et al. 2009).

Table 2: The kinetic parameters for the adsorption of Cd^{2+} ion from aqueous solution by the modified montmorillonite.

Pseudo first order		Pseudo second order	
K_1(min^{-1})	R^2	K_2(g. min^{-1}.min^{-1})	R^2
0.011	0.7746	0.023	0.999

Table 3: The adsorption parameters for Cd^{2+} ion from aqueous solution adsorption on the modified montmorillonite by Langmuir adsorption isotherm and Freundlich isotherm.

Langmuir parameters			Freundlich parameters		
q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F	R^2
12.36	22.65	0.9713	8.97	5.68	0.8512

CONCLUSIONS

In this study, the modified montmorillonite was used for the removal of Cd^{2+} ions from aqueous solutions. The modified montmorillonite is a heterogeneous material consisting largely of small spheres, and is irregular and porous. The adsorption capacity of modified montmorillonite is improved. The influence of various operating parameters on the adsorption process was important for the adsorption rate, such as contact time, Cd^{2+} ions concentration and temperature. The adsorption of Cd^{2+} ion from aqueous solution by the modified montmorillonite better fits to pseudo second order kinetic model. The Langmuir adsorption isotherm model was more suitable for the Cd^{2+} ion from aqueous solution than the Freundlich adsorption isotherm model.

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