



Use of nanometer mesoporous MCM-41 for the removal of Pb(II) from aqueous solution

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Abstract

Mobil Composition of Matter (MCM)-41 molecular sieve was successfully synthesized. Power X-ray diffraction, scanning electron microscopy and transmission electron microscopy (TEM) were used to characterize the sample. The sample showed spherical particles, and the morphology was regular. Its average particle diameter was 110 nm. TEM images showed that the sample structure presented a honeycomb pore structure and the average pore diameter was 3.5 nm. Pb²⁺ was adsorbed from water body by the MCM-41. The effects of acidity, contact time, temperature, adsorbent material amount and initial Pb²⁺ concentration on the adsorption rate were studied, and the optimum conditions of adsorption were obtained. The results show that when acidity pH value was 4.5, temperature was 25 °C, contact time was 40 min and the adsorbent material MCM-41/Pb²⁺ = 7.5, the adsorptive effect was the best, the adsorption rate reached 98.78% and the adsorptive capacity was 131.71 mg/g. Kinetic and thermodynamic properties of the adsorptive process were studied. Experimental results show that the adsorption of Pb²⁺ by MCM-41 belongs to the pseudo-second-order adsorption. According to thermodynamic equation, $\Delta G = \Delta H - T\Delta S$, $\Delta H = -24.86$ kJ/mol and $\Delta S = -72.34$ J/(mol K) were obtained by calculation, indicating that the adsorption was exothermic and an entropy reduction process. At the temperature of 298, 308 and 318 K, the free energy change was, respectively, $\Delta G_1 = -3.286$ kJ/mol, $\Delta G_2 = -2.586$ kJ/mol and $\Delta G_3 = -1.86$ kJ/mol, illustrating that at the above temperature the reaction can be carried on spontaneously. Nitric acid, hydrochloric acid and acetic acid were, respectively, used to investigate their effect on desorption. The results show that the desorption effect using nitric acid as a desorption agent was better than those of hydrochloric acid and acetic acid. When desorption was 5 h and the nitric acid concentration was 0.5 mol/l, the desorption rate was the highest that was reached 70.01%.

Keywords Lead · Adsorption · MCM-41 molecular sieve · Kinetics · Thermodynamics

Introduction

Lead is a harmful heavy metal, and pollution caused by lead from various ways to the environment has become a pressing problem. The lead inside body and its compounds content

exceed the standard, which will cause very high toxic effects on the human body many systems. Lead poisoning can cause colic, hepatitis, hypertension, peripheral neuritis, toxic encephalitis, anemia, neurasthenia and other. After many chemicals stop for a little time in the environment, they may be degraded and become harmless final compounds. But lead cannot to be degraded, and once it is discharged into the environment, it remains its availability for a long time. Lead has long been persistent in the environment and is potentially toxic to many living tissues, so lead has been classified as a strong pollutant range (Feng and Zhang 2004; Tian 2000; Wu et al. 1998). The methods of treating heavy metals pollution are chemical precipitation method, oxidation reduction method, solvent extraction separation method, membrane separation technology method, ion exchange method (Feng and Zhang 2004) and biological treatment technique method (Tian 2000; Wu et al. 1998). All these methods have their

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some advantages, but all kinds of methods have their shortcomings, which are given as follows: (1) Chemical precipitation method is easy to produce secondary pollution. (2) In oxidation reduction treatment methods, electrolysis is the main method, but is not suitable for dealing with wastewater with lower concentration of heavy metal ions. High-voltage pulse electrocoagulation method equipment has high cost, the power consumption is high, etc. (3) In solvent extraction separation method, the loss of solvent in the extraction process and the large energy consumption in the regeneration process are some limitations, and its application is greatly limited. (4) For membrane separation technology, as complete sets of equipment are used, the cost is high and the energy consumption is great; this makes its use be limited. (5) In ion exchange treatment method, the manufacture of exchange agent is complex, the cost is high, and the amount of recycling agent consumed is large, which greatly limits its wide application. (6) In biological treatment technology, because the required biology needs domestication, the treatment cycle is relatively long. Adsorption method is one of the most important wastewater treatment methods and has been widely used in various wastewater treatments. The adsorption method processes wastewater and mainly depends on some materials that have a large specific surface area and high surface energy and have a strong adsorption capacity toward pollutants, to separate, remove them from wastewater in order to achieve the goal of purification for wastewater (Feng and Zhang 2004). It is difficult to remove trace lead in water body by the usual method. There have been some materials for the removal of heavy metals, such as activated carbon (Clifford et al. 1986) and agricultural waste (Al-Asheh and Duvnjak 1997; Wafwoyo et al. 1999). However, these materials have many disadvantages, such as low load capacity, weak interaction with metal ions, etc.

Molecular sieve is a kind of new, highly adsorptive selective adsorbent, which can, according to molecular size and configuration, carry on selective adsorption and has a strong adsorption action to unsaturated molecules, polar molecules and polarizable molecules. The open framework structure of mesoporous molecular sieve material and large internal and outside specific surface area makes it have unique adsorption function. At the same time, the good physical and chemical stable performance of molecular sieve makes it have excellent regeneration function (Liu et al. 2012). Mesoporous molecular sieve MCM-41 is a new type of the synthesized molecular sieve with one-dimensional pore structure of the hexagonal regular arrangement and pore size uniformity. Also, by adjusting the synthesis conditions, the pore size is adjusted. The very good adsorption selectivity and stability can be guaranteed. The pore channels of MCM-41 are rich and have very good adsorption ability. These advantages make it have wide applied prospect (Kresge et al. 1992; Beck et al. 1992). Nanoscale MCM-41 (Cai et al. 2001)

has larger specific surface area; it is expected that nano-MCM-41 should have better adsorption performance. In this study, cetyltrimethylammonium bromide is used as the template agent with liquid phase method to synthesize nano-MCM-41. With the MCM-41, Pb^{2+} was adsorbed and the influence of experimental conditions on the adsorption effect was studied. The kinetic and thermodynamic properties of the adsorption have been investigated, and desorption conditions have been studied. This work is of great significance and potential applied value for the removal of water body lead(II) pollution and the study of sewage treatment. Compared with the commonly used activated carbon method, the present method has the advantages of MCM-41 low cost and strong regeneration of the adsorbent and has higher applied value.

Experimental

Reagents

1. Materials for the synthesis of nano-mesoporous MCM-41

Cetyltrimethylammonium bromide (CTMAB), tetraethyl orthosilicate (TEOS) and sodium hydroxide were used.

2. Reagents for the determination of lead

Pb^{2+} standard solution (1 mg/ml): 0.1599 g of $Pb(NO_3)_2$ [Chinese Pharmaceutical (Group) Shanghai Chemical Reagent Company] was weighed and placed in a beaker and dissolved in deionized water. Then, 1 ml of concentrated HNO_3 was added; the solution was transferred into a 100-ml volumetric flask, diluted with 100 ml of deionized water and shaken well. Xylenol orange (XO) solution (0.1%, w/v): 0.050 g of XO (Xiya Reagent, China) was weighed and dissolved in a small amount of deionized water. After dissolution, 1 ml of concentrated hydrochloric acid was added and filtered. The solution was diluted with 50 ml of deionized water for use. XO solution is prepared when it is in use and it should not be stored for a long time. Buffer solution (pH 6.0): 0.054 g of sodium acetate (NaOAc) was weighed and dissolved in water. 0.56 ml glacial acetic acid (HOAc) was added, and 100 ml of deionized water was added and shaken well. 0.25% (w/v) of *o*-phenanthroline solution: 0.25 g of *o*-phenanthroline was dissolved in 7.5 ml of acetone and diluted with 100 ml of deionized water.

Nitric acid and sodium hydroxide were used for adjusting the acidity of adsorption.

The reagents used in the experiments were of analytical purity. Unless stated, the reagents were purchased from

Beijing Chemical Plant, China. The water used was deionized water.

Characterization technique

The determination of lead content was spectrophotometrically made with a 722S spectrophotometer (Shanghai Lengguang Technology Co. Ltd., China). D5005 X-ray diffractometer (XRD, SIEMENS, Germany) was used for powder X-ray diffraction experiments. Through the spectrum of sample to X-ray diffraction, the crystalline phase structure, periodic arrangement, etc., information about sample was determined with Cu-K α target, $\lambda = 1.5418 \text{ \AA}$, operating voltage (tube voltage) 30 kV and operation current (tube current 20 mA). The scanning range was 0° to 10° , and the step length was 0.02° . Netherlands Philips XL30-type field emission scanning electron microscope (SEM) was used to determine and obtain the SEM images in order to observe the particle size and morphology of the samples. The operating voltage was 20 kV. The sample was prepared by ethanol, and the sample was dropped on the slide glass to conduct the conductive layer. Transmission electron microscopy (TEM) photograph was obtained on FEI Tecnai, G2 F20-type field emission transmission electron microscope in order to observe the structural morphology of the sample with a working voltage of 200 kV.

Experimental procedure

Synthesis of MCM-41

In this study, MCM-41 was synthesized by the hydrothermal method, and the specific method is as follows:

Nanometer MCM-41 sample was prepared according to the literature procedure (Cai et al. 2001) with CTMAB as template under basic conditions. A 1.0 g of CTMAB was dissolved in 480 ml of deionized water at 80°C under vigorous stirring until the solution became homogeneous. To this solution, 3.5 ml of NaOH (2 mol/l) was added with stirring. After the solution became homogeneous, 5 ml of TEOS was slowly dropped, giving rise to a white slurry. Then, the reaction mixture was kept at 80°C for 2 h with stirring, and then the solid products were recovered by filtering and dried overnight at room temperature. The surfactant was removed by calcination at 550°C for 4 h in air, yielding the final white parent powder, nanometer MCM-41.

Drawing of working curve of lead

In a 25-ml volumetric flask, in order 0.02, 0.04, 0.06, 0.08 and 0.10 mg of Pb(II) working solution, 3.75 ml of 0.25% (w/v) *o*-phenanthroline solution, 5 ml of HOAc–NaOAc

buffer solution of pH = 6.0 and 1.0 ml of 0.1% (w/v) XO solution were added, respectively, diluted with deionized water to the scale and shaken well for measurement. The absorbance value was measured with 1-cm cells at 535 nm by using the corresponding reagent blank as reference. The working curve for the determination of lead was drawn by absorbance against Pb(II) solution concentration. A linear regression equation was calculated according to the data experimentally obtained (Du et al. 2009).

Study of adsorption of Pb²⁺ by MCM-41 molecular sieve

Twenty milliliters of 2 mg/l Pb²⁺ working solution was taken and placed into a 100-ml beaker. The pH value was adjusted to 4.5 using 6 mol/l HNO₃ or 6 mol/l NaOH solutions. The final solution volume was adjusted with water to be 40 ml. 0.30 g of MCM-41 molecular sieve was accurately weighed, added to the above-stated sample, stirred at room temperature ($25 \pm 1^\circ\text{C}$) for 40 min and filtered. The Pb²⁺ content in the filtrate was determined by the above-stated spectrophotometric method, and the adsorption rate and adsorption capacity were calculated.

When the effects of experimental conditions were studied, the experimental parameters variables values used were: the initial pH (1.0–10.0), the contact time (0–60 min), the amount of adsorbent MCM-41 (0–1.000 g), the initial concentration of Pb²⁺ (0–10 mg/ml) and the temperature (15 – 55°C).

Lead desorption in (MCM-41)–Pb

Desorption of the lead from (MCM-41)–Pb was studied with three kinds of desorption agents HNO₃, HCl and HOAc. The experimental material of desorption (MCM-41)–Pb was prepared by the method in “[Study of adsorption of Pb²⁺ by MCM-41 molecular sieve](#)”, denoted as sample A. The sample A was placed in a 100-ml beaker containing 30 ml of 0.1 mol/l HNO₃ (or HCl, HOAc), soaked for 0, 1, 3, 5, 7, 8 and 10 h and filtered. The content of lead in the filtrate was determined by spectrophotometry, the desorption rate was calculated, and the desorption time–desorption ratio curve was plotted.

Experimental method of influence of HNO₃ concentration on the desorption of lead in (MCM-41)–Pb

The preparation method of desorption (MCM-41)–Pb experimental material was the same as the experiment procedure of “[Study of adsorption of Pb²⁺ by MCM-41 molecular sieve](#)”. It was denoted as sample A. The sample was placed in a 100-ml beaker containing 30 ml of 0.1, 0.3, 0.5, 0.7 and 1.0 mol/l HNO₃, soaked for 5 h and then filtered. The content of lead in the filtrate was determined by the spectrophotometric

method, the desorption rate was calculated, and the desorption time–desorption ratio curve was plotted.

Results and discussion

Powder X-ray diffraction (XRD)

The analysis results of sample XRD are shown in Fig. S1 (see Supporting Materials), indicating that for the molecular sieve obtained four peaks emerged, which can be assigned to the peaks obtained by (100), (110), (200) and (210) crystal plane diffraction. The diffraction peak locations are basically the same as those reported by the literature (Cai et al. 2001), proving that the synthesized material was MCM-41.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) study

SEM can well reflect the morphology and size of sample particles. From Fig. S2 (see Supporting Materials), the scanning electron micrograph of sample, it can be seen that the morphology of the sample is mainly a spherical grain structure with regular morphology, and the average particle diameter is 110 nm. Figure S3 (see Supporting Materials) is the TEM diagram of nanometer MCM-41. The sample hole presents a honeycombed structure, and the average pore diameter is 3.5 nm.

Working curve for the determination of lead

The test results show that Beer's law is obeyed over the concentration range of 0–4.0 $\mu\text{g/ml}$ for Pb^{2+} . The linear regression equation of method is $A = 0.0288C + 0.0035$ (C : $\mu\text{g/ml}$), A is the absorbance, C is the lead concentration ($\mu\text{g/ml}$), and the correlation coefficient $R = 0.9998$. The apparent molar absorptivity of the method for the determination of lead is $2.01 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, expressing the ability of lead complex to absorb light at a wavelength of 535 nm.

$$C = (A - 0.0035)/0.0288 \quad (1)$$

By formula (1), the Pb^{2+} concentration in the solution to be determined can be calculated.

Influence of the adsorption conditions on adsorption impact

Impact of pH value

Acidity of the solution is one of the most important parameters to control the removal of heavy metals from wastewater. It affects the surface charge of the adsorbent and the degree of ionization of the lead ion. According to the standard work

curve of Pb^{2+} obtained, the adsorption rate of lead at different pH (1.0–10.0) was calculated, and the effect results of pH on adsorption impact obtained are shown in Fig. S4 (see Supporting Materials). It can be seen that when the initial pH of solution is in the range of 1.0–4.5, the adsorption rate of MCM-41 to Pb^{2+} increases with the increase in pH value. This is because the adsorption of Pb^{2+} by MCM-41 is always accompanied by the release of H^+ . After pH increases, neutralization to H^+ can reduce the competitive role of H^+ , which is beneficial to the adsorption of Pb^{2+} by adsorbent. At the time of pH 4.5, the adsorption rate of Pb^{2+} by MCM-41 is the highest. After that, with the further increase in pH, the adsorption of Pb^{2+} on the MCM-41 is suppressed due to the hydrolysis of Pb^{2+} , so the adsorption rate of Pb^{2+} decreases and so pH 4.5 is chosen as the optimum adsorption acidity.

Effect of contact time

The effect of contact time on the removal of Pb^{2+} under the condition of $\text{MCM-41/Pb}^{2+} = 7.5$ is shown in Fig. S5 (see Supporting Materials). It can be observed that the initial adsorption rate is very high. As time goes on, the adsorption rate of Pb^{2+} shows an upward trend. With the further increase in contact time, when 40 min is reached, the adsorption rate almost reached a constant value, the adsorption reached an equilibrium and the adsorption rate no longer increased with the increase in time. The adsorption material reached the maximum saturation capacity, and Pb^{2+} reached the maximum adsorption rate. The optimum adsorption time is 40 min. At the beginning time, all the hydroxyl groups on the MCM-41 can be contacted with Pb^{2+} for ion exchange. As time goes on, these hydroxyl groups are gradually consumed. When the adsorption rate is equal to the desorption rate, the adsorption reaches equilibrium and the adsorption reaches the maximum value.

Effect of Pb^{2+} initial concentration and MCM-41 dosage

The effect of the initial concentration of Pb^{2+} on the adsorption results is shown in Fig. S6 (see Supporting Materials). The adsorption rate increases with increasing initial concentration of Pb^{2+} (0–1.0 mg/ml). The initial Pb^{2+} concentration provides the driving force to overcome the Pb^{2+} mass transfer resistance between aqueous and solid phase; increasing the initial concentration of Pb^{2+} can increase the interaction between adsorbent and Pb^{2+} . The adsorption rate reached the maximum 1.0 mg/ml, i.e., the optimum initial concentration of Pb^{2+} was 1.0 mg/ml. Figure S7 (see Supporting Materials) shows the influence of MCM-41 dosage on the Pb^{2+} adsorption rate. It can be seen that when the adsorbent dosage is between 0 and 0.05 g, the adsorption rate of Pb^{2+} increases with the increase in adsorbent amount. This is because with the increase in

adsorbent dosage greater adsorption surface area and more adsorption sites were resulted. When MCM-41 is 0.3 g, the adsorption rate of Pb^{2+} reaches the maximum, so the optimum amount of molecular sieve was set at 0.3 g.

Influence of temperature

Figure S8 (see Supporting Materials) shows the influence of temperature on the adsorption of Pb^{2+} by the adsorption system. The adsorption rate increases with the increase in temperature over the range of 15–25 °C. The maximum is reached when the temperature reaches 25 °C. After that, the adsorption rate decreases with the increase in temperature, indicating that the adsorption process is exothermic. But the change trend is not obvious, and the temperature has little influence on the MCM-41 adsorption performance. The reason may be that the influence of temperature on adsorption has two sides. First of all, when the temperature rises, the thermal motion of Pb^{2+} increases rapidly and the vibration in the solution accelerates, which makes it easier to diffuse into the adsorption material channels. The adsorption rate increases with the increase in temperature, and thus a positive effect is produced. However, the exchange adsorption of Pb^{2+} and the hydroxyl radical in MCM-41 are carried on, which is exothermic. Therefore, the increase in temperature is not conducive to ion exchange adsorption, which results in the decrease in adsorption rate with the increase in temperature and causes a negative effect. Because of the relative cancellation of the two kinds of effects, variation of the adsorption rate with the temperature is not big. Considering that at the high-temperature a large amount of energy is consumed, the adsorption is carried out at room temperature of 25 ± 1 °C.

The optimized adsorption condition of Pb^{2+} on MCM-41 molecular sieve was as follows: 0.3 g of the molecular sieve is used at 25 °C to adsorb Pb^{2+} with 1 mg/ml solution at pH 4.5 for 40 min. The adsorption rate at this time is 98.71%, and the adsorption capacity is 131.71 mg/g.

Kinetic study results of adsorption process

Adsorption kinetics curves of pseudo-first-order model

The kinetic study of an adsorption process is mainly to describe the rate of an adsorbate adsorbed by adsorbent, and the adsorption rate controls the retention time of the adsorbate on the solid–liquid interface. It is necessary to do research on the treatment of wastewater by the adsorption method.

Pseudo-first-order model:

The adsorption kinetic model can be described by Lagergren first-order rate equation (Lagergren 1898):

$$dq/dt = k_1(q_e - q) \quad (2)$$

Where q_e is the equilibrium adsorption quantity, mg/g; q is the adsorption amount at a certain time, mg/g; and k_1 is the adsorption kinetic rate constant (min^{-1}). For formula (1), integration is made from $t=0$ to $t>0$ ($q=0$ to $q>0$), written in the linear form as follows:

$$\lg(q_e - q) = \lg q_e - k_1 t / 2.303. \quad (3)$$

Pseudo-second-order model of adsorption kinetics

The pseudo-second-order model of adsorption kinetics can be described by using Ho and McKay equation (Celekli et al. 2011; Ho and McKay 1998; Ho and McKay 1999). It is established based on the rate-controlling step and is a second-order kinetic equation on the basis of chemical adsorption through chemical reaction or through sharing of electrons or through getting or losing the electrons. The expression formula of second-order kinetic equation is:

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (4)$$

Formula (4) is integrated from $t=0$ to $t>0$ ($q=0$ to $q>0$); its linear form is written as follows:

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)t \quad (5)$$

Where t is the time (min); q_t is the adsorption amount at a certain time (mg/g); k_2 is the adsorption kinetic rate constant ($\text{g mg}^{-1} \text{min}^{-1}$); and q_e is the equilibrium adsorption quantity (mg/g).

The experiments were carried out to make adsorption studies at the same stirring speed, the temperature 25 °C and the solution pH 4.5 by using 1 and 4 mg/ml Pb^{2+} solutions. Figures 1a, b and 2a, b show, respectively, pseudo-first-order and pseudo-second-order kinetic simulation curves made by different concentrations of Pb^{2+} . The kinetic parameters obtained by correlation calculations are shown in Table 1. After calculation, the correlation coefficient of the 1 mg/ml Pb^{2+} pseudo-first-order kinetic equation is $R=0.8924$ ($R^2=0.7964$), and the coefficient of pseudo-second-order kinetic equation is $R=0.9995$ ($R^2=0.9991$). The correlation coefficients of 4 mg/ml Pb^{2+} pseudo-first-order kinetic equations are $R=0.9248$ ($R^2=0.8553$), and the correlation coefficients of the pseudo-second-order kinetic equations are $R=0.9999$ ($R^2=0.9998$). It can be seen that when the kinetic data were fitted by the pseudo-first-order kinetic equation, the R_1^2 is smaller, the calculated adsorption equilibrium capacity of different concentrations deviated larger from the values of the experimental measurements, and the differences are larger. When the pseudo-second-order

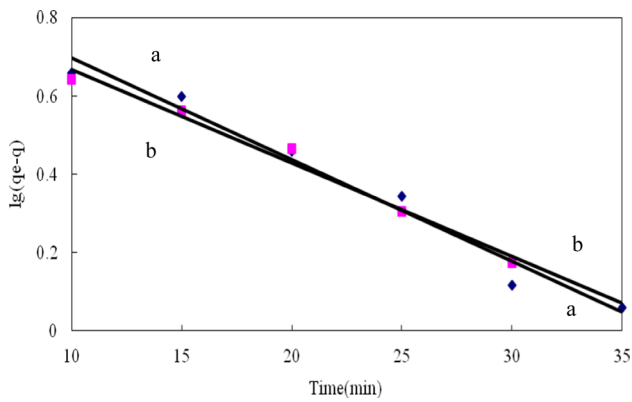


Fig. 1 Pseudo-first-order kinetic simulation; 7.5 g/l of MCM-41, $T=25\text{ }^{\circ}\text{C}$, $\text{pH}=4.5$; **a** Pb^{2+} : 1 mg/ml; **b** Pb^{2+} : 4 mg/ml

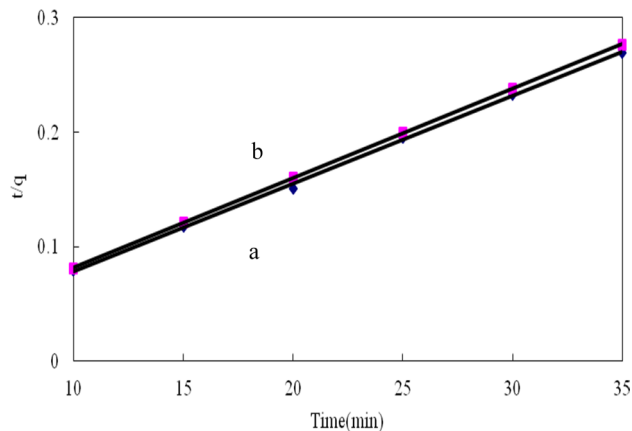


Fig. 2 Pseudo-second-order kinetic simulation; 7.5 g/l of MCM-41, $T=25\text{ }^{\circ}\text{C}$, $\text{pH}=4.5$; **a** Pb^{2+} : 1 mg/ml; **b** Pb^{2+} : 4 mg/ml

kinetic equations were used to fit, all the correlation coefficients R_2^2 are greater than 0.999 and the calculation values of equilibrium adsorption capacities for different concentrations are basically consistent with the actual measured value, so the dynamics of the adsorption system more conform to pseudo-second-order kinetic equation. Therefore, it can be concluded that the process of adsorption toward Pb^{2+} by MCM-41 conforms to the pseudo-second-order kinetic equation, and the pseudo-second-order model can

be utilized and better predict the adsorption behavior of Pb^{2+} on mesoporous MCM-41.

Adsorption equilibrium isotherm

The adsorption isotherm is a mathematical formula expressing the relationship between the amount of adsorption and the concentration of the solution under the condition of constant temperature fixing. At present, different kinds of mathematical formulas have been put forward, each of which has its applicable range. There are two kinds of commonly used ones: Langmuir adsorption formula and Freundlich adsorption formula. Langmuir and Freundlich equation is commonly used to describe the adsorption isothermal model of adsorption behavior and parameters. In this study, two models were used to test the adsorption properties and adsorption process of adsorbent. The Langmuir adsorption isotherm model assumed that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption. The Langmuir equation is expressed by the following relation (Langmuir 1918).

$$q_e = K_L Q_m C_e / (1 + b C_e) \tag{6}$$

Where q_e (mg/g) is the equilibrium load capacity of adsorbent, Q_m (mg/g) is the maximum adsorption capacity of monolayer coverage, C_e (mg/l) is the equilibrium concentration of adsorbent and K_L (l/g) is the adsorption equilibrium constant.

The linearized form of Langmuir isotherm can be written according to the following equation.

$$C_e/q_e = 1/(K_L Q_m) + C_e/Q_m \tag{7}$$

The slope and intercept of the plot between C_e/q_e versus C_e will give Q_m and K_L , respectively.

The Freundlich adsorption isotherm model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption. The Freundlich adsorption isotherm model is represented as follows (Freundlich 1906):

$$q_e = K_F C_e^{1/n} \tag{8}$$

Table 1 Kinetic parameters for the adsorption of Pb^{2+} onto MCM-41

Concentration (mg/l)	Adsorption capacity determined by experiment $q_{e,exp}$ (mg/g)	Kinetic equation of pseudo-first-order adsorption rate			Kinetic equation of pseudo-second-order adsorption rate		
		k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R_1^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	$q_{e,cal}$ (mg/g)	R_2^2
1	129.967	0.151	13.579	0.7964	2.113×10^3	129.976	0.9991
4	202.078	0.473	66.231	0.8553	2.355×10^3	202.080	0.9998

The linearized form of Freundlich can be expressed as:

$$\lg q_e = \lg K_F + (1/n) \lg C_e \tag{9}$$

where q_e is the amount of adsorbate metal ion adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of adsorbate in solution (mg/l), K_F is the capacity of the adsorbent and n is the intensity of adsorption constant for Freundlich. The plot of $\ln q_e$ versus $\lg C_e$ is employed to determine the K_F and n from intercept and slope, respectively. Generally, the value of the linear regression correlation coefficient R^2 gives an indication as to which model can be chosen to give the best fit.

In this study, the adsorption isotherms of Langmuir and Freundlich obtained by the adsorption of Pb^{2+} by MCM-41 are shown in Figs. 3 and 4. The corresponding parameters of its adsorption isotherm equation are shown in Tables 2 and 3. By the linear fitting results of Langmuir and Freundlich isothermal adsorption equations, the fitting effect of Langmuir adsorption isotherm equation is not good, and the maximum saturated adsorption capacity of theory is largely different from the experimental value. The fitting effect of Freundlich adsorption isotherm equation is better, and all the fitted linear correlation coefficients R are greater than 0.99, showing that the Freundlich adsorption isotherm established according to the multi-molecular layer adsorption model can better express this adsorption process. The process of MCM-41 adsorption toward lead(II) conforms to the Freundlich adsorption model and is multi-molecular layer adsorption. The n value of the Freundlich index of this adsorption system is greater than 1. At the time of $n < 1$, the adsorption is non-preferential adsorption. At the time of $n = 1$, the adsorption is linear adsorption. At the time of $n > 1$, the adsorption is preferential adsorption, meaning that molecular affinity between adsorbate molecules and solid adsorbent drops with the increase in temperature and the isotherm slope drops with the increase in the solute concentration in solution

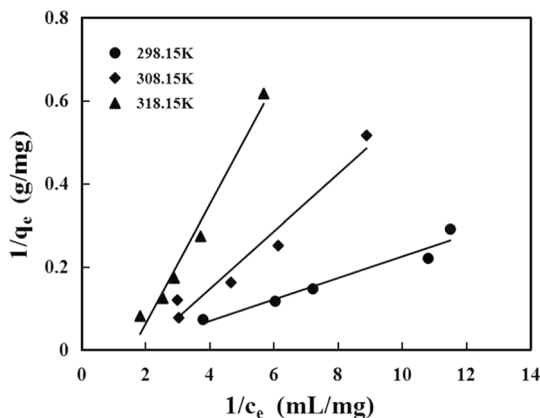


Fig. 3 Langmuir adsorption isotherm

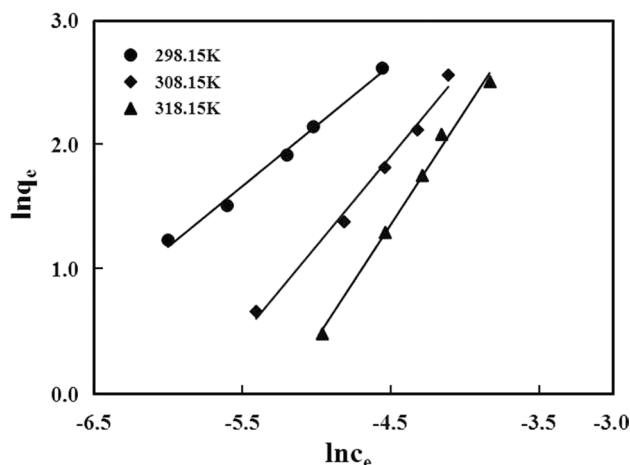


Fig. 4 Freundlich adsorption isotherm

phase. Therefore, the adsorption of lead(II) by MCM-41 can be well represented by the Freundlich isotherm adsorption equation established by basing on the multi-molecular layer adsorption model, and the adsorption process is preferential adsorption.

Thermodynamic properties of adsorption

The thermodynamics of an adsorption process may be obtained from a study of the influence of temperature on the process. The mechanism of adsorption can be deduced from thermodynamic parameters: Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°). The linear equation is listed as follows:

$$K_L = Q_e/C_e \tag{10}$$

$$\Delta G^0 = -RT \ln K_L \tag{11}$$

Where K_L is the adsorption equilibrium constant (K_L is the parameter in the Langmuir equation), Q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/l), T is the thermodynamic absolute temperature and R is a physical constant regarded as a universal gas constant (8.314 J/mol K). ΔG° is the Gibbs free energy change.

The standard enthalpy change and standard entropy change of adsorption process are calculated according to the Van't Hoff Eq. (12)

$$\ln K_L = -\Delta G^0/(RT) = \Delta S^0/R - \Delta H^0/(RT) \tag{12}$$

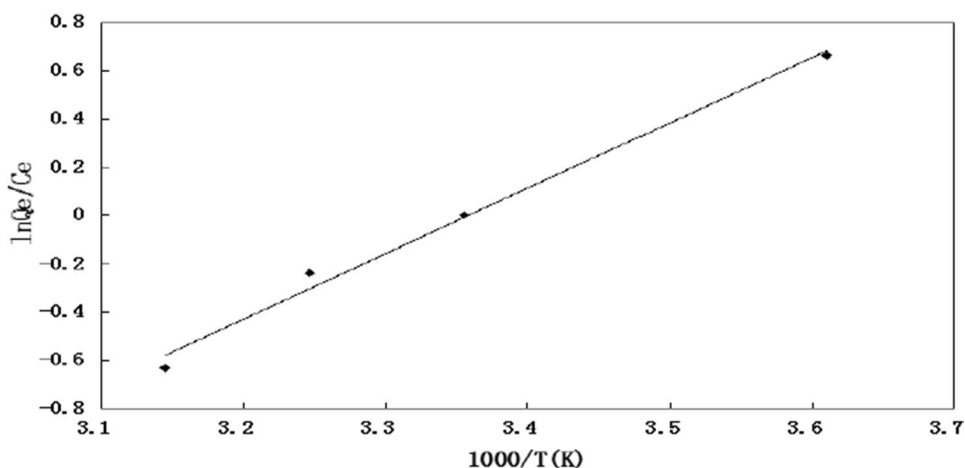
Where ΔH^0 is the enthalpy change, ΔS^0 is the entropy change and ΔG^0 is the Gibbs free energy change.

Table 2 Langmuir adsorption isotherm equation data

T (K)	Equation expression formula	q_m (mg/g)	K_L (l/mg)	R^2	R
298.15	$1/q_e = 0.0297/c_e - 0.0366$	-27.333	-1.233	0.9111	0.9545
308.15	$1/q_e = 0.0802/c_e - 0.1390$	-7.196	-1.733	0.9337	0.9663
318.15	$1/q_e = 0.1506/c_e - 0.2341$	-4.271	-1.555	0.9216	0.9600

Table 3 Freundlich adsorption isotherm equation data

T (K)	Equation expression formula	n	K_F (l/mg)	R^2	R
298.15	$\ln q_e = 0.8996 \ln c_e + 3.8289$	1.1116	46.013	0.9977	0.9988
308.15	$\ln q_e = 1.4047 \ln c_e + 3.5263$	0.7119	33.997	0.9981	0.9990
318.15	$\ln q_e = 1.4977 \ln c_e + 3.3133$	0.6677	27.477	0.9967	0.9983

Fig. 5 Van't Hoff curve; $m(\text{MCM-41}) = 0.3$ g, $t = 40$ min, $\text{pH} = 4.5$, $C_{\text{Pb}^{2+}} = 1$ mg/ml

In this study, the thermodynamic properties of nano-MCM-41 adsorption lead(II) process were calculated. Figure 5 shows the Van't Hoff equation curve of this adsorption; the curve equation is $y = 2.6024x - 10.0744$ with a correlation coefficient of $R = 0.9977$. The calculated results of related thermodynamic parameters are listed in Table 4. $\Delta H^0 = -24.86$ kJ/mol < 0 indicates that the process of MCM-41 adsorption Pb^{2+} is an exothermic reaction. $\Delta S^0 = -72.34$ J mol $^{-1}$ K $^{-1}$ < 0 shows that the adsorption is a process of entropy reduction. After MCM-41 adsorbed Pb^{2+} , the degree of order for material arrangement increased. It has been known (Table 4) that ΔG^0 is less than zero, showing that the MCM-41 adsorption Pb^{2+} process has a spontaneous property. With the increase in temperature, the absolute value of ΔG^0 decreased, showing that the higher the temperature, the smaller the spontaneous trend of adsorption process.

Desorption results

The desorption results of (MCM-41)-Pb by nitric acid are shown in Fig. S9. The desorption efficiency of Pb^{2+} increases gradually with the increase in time. This is mainly due to the

Table 4 Thermodynamic parameters at different temperatures

T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 [J/(mol K)]
298	-3.28	-24.86	-72.34
308	-2.58		
318	-1.86		

fact that the Pb^{2+} electron density is too concentrated, there is an empty orbital in the outer layer, and the complexes formed by Pb^{2+} and the hydroxyl groups in MCM-41 are not stable enough. With the increase in time, Pb^{2+} in the solution is gradually liberated, the Pb^{2+} concentration in solution increases gradually and the desorption rate increases. When desorption time reached 5 h, the desorption rate reached the maximum value of 63.38%. But as time increased, Pb^{2+} desorption rate decreased. This is probably because as time elapsed, the Pb^{2+} desorbed in the solution was adsorbed in MCM-41 in the form of physical adsorption, resulting in a decrease in the Pb^{2+} concentration in the solution, thereby reducing the adsorption rate of Pb^{2+} .

The effect results of nitric acid concentration on desorption of Pb^{2+} (Fig. S10) show that the desorption rate of Pb^{2+}

increases gradually with the increase in nitric acid concentration. When the concentration of nitric acid is 0.5 mol/l, the desorption rate is the maximum, which is 70.01%. After that, when the concentration of nitric acid was continued to increase, the adsorption efficiency of Pb^{2+} was decreased. This is mainly because the H^+ and Pb^{2+} in the solution have competitive adsorption action. When the acidity of solution is smaller, the concentration of H^+ solution is smaller. The hydroxyl in the modified MCM-41 molecular sieve mainly combines with Pb^{2+} . The Pb^{2+} content in solution was decreased, and the desorption rate was low. With the increase in acidity, the Pb^{2+} content in solution increased and the desorption rate also changed to be high. When the acidity continues to grow, the H^+ concentration in solution is excessively large, which has an impact on the internal structure arrangement of molecular sieve and thus makes desorption rate be decreased.

To sum up, the optimum desorption acidity is 0.5 mol/l HNO_3 . If the acidity is too high or too low, this is not beneficial to the desorption. The reason is that the acidity is low, H^+ number is small, the capacity of replacement for Pb^{2+} is low, and therefore, the desorption rate is low. If acid concentration is too high, which causes the change of mechanical strength and the physicochemical properties of adsorbent. This is not conducive to the desorption neither. In addition, the desorption effect of HCl on Pb^{2+} showed that when the maximum desorption rate time 5 h was reached, the desorption rate was 54.97%. When acetic acid was used as desorbent and the time reached 3 h, the desorption rate reached 52.95%. The effects of both these two desorbents are lower than that of nitric acid.

Conclusions

In this study, mesoporous MCM-41 molecular sieve was successfully prepared. The morphology of the sample was mainly spherical crystal particle structure, with regular morphology and average particle diameter of 110 nm. The optimum conditions for the adsorption of Pb^{2+} by MCM-41 molecular sieve are MCM-41/ Pb^{2+} (m/m) = 7.5, starting pH = 4.5, at room temperature of 25 ± 1 °C and stirring 40 min. In the kinetic study, it was found that the adsorption of Pb^{2+} by nanomaterial MCM-41 conforms to the quasi-second-order equation. The adsorption agrees with the Freundlich adsorption isotherm and belongs to a heterogeneous adsorption. The thermodynamic results showed $\Delta H^0 = -24.86$ kJ/mol and $\Delta S^0 = -72.34$ J/(mol K). At the temperatures of 298, 308 and 318 K, $\Delta G^0 < 0$, indicating that the adsorption belongs to endothermic entropy reduction spontaneous reaction process. After MCM-41 adsorbed Pb^{2+} , the ordered degree of material arrangement increased. The desorption effect of using nitric acid as desorption agent

is better than those of hydrochloric acid and acetic acid. When desorption is 5 h and the concentration of nitric acid is 0.5 mol/l, the desorption rate is the highest, reaching 70.01%.

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Compliance with ethical standards

Conflict of interest No potential conflict of interest was reported by all the authors.

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