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Behavior and mechanism of Cd(II) adsorption on loess-modified clay liner

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ABSTRACT

Cadmium is a toxic heavy metal which is common in landfill leachate and it has caused serious public health problems. It is necessary to find a cost effective method to deal with landfill leachate containing Cd(II). The loess-modified clay is proved to be effective to remove Cd(II) removal from landfill leachate. The adsorption capacity of loess-modified clay towards Cd(II) has been determined to be about 7.08 mg/g. Factors affecting the adsorption of Cd(II) include loess proportion, slurry concentration, initial solution pH, temperature and event duration. The adsorption isotherms and kinetic data are well fit with the Langmuir model and pseudo-second order kinetics model, respectively. The thermodynamic behavior reveals that the adsorption process is spontaneous and endothermic and the system disorder increases with time. The adsorption of Cd(II) on loess-modified clay involves chemical reaction and surface complexation with clay minerals. Chemical precipitation is considered as the dominant mechanism at pH>9. Further studies using X-ray diffraction, Fourier transform infrared spectra have confirmed the adsorption mechanism. The material used in this paper is economic and environmental protection, which is proved to be appropriate for landfill liner material.

Keywords: Adsorption; Loess-modified clay; Cadmium; Kinetics; Isotherm; Thermodynamics; Landfill liners

1. Introduction

Landfill leachate has been found to contain many heavy metals. These heavy metals may pollute the aquifer underlying the landfill and pose a potential threat to human health [1]. Cd(II) is a non–essential and highly toxic heavy metal element, which can usually be found in landfill leachate [2,3]. Cadmium which is more easily absorbed by crops than other heavy metals can enter the human body through the food chain with deleterious effects [4]. Cadmium poisoning can happen under specific concentrations. Cadmium can bring a number of acute and chronic disorders that result in pathological symptoms and severe damage to kidneys, lungs, and the liver [5].

Landfills are commonly lined with clay liners to prevent the transport of contaminants from presenting in the leachate. Conventional liners are designed by focusing on minimizing permeation of leachate through the liner, which can't prevent heavy metals from polluting the groundwater by diffusion through landfill liner. Hence, a new landfill liner that can effectively prevent the transport of heavy metals is need. Many researchers has tried the method by adding materials capable of strongly adsorbing pollutants to the liner [6,7]. Activated carbon is the most widely used sorbent because of its high

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specific surface area and convenient regeneration from spent carbon, however, it's not economic [8–12]. Other adsorbents applied in heavy metal adsorption have been studied recently to ascertain their adsorption capacity for Cd(II), including goethite, montmorillonite, zeolite, bentonite, calcite, sludge–soil, and phosphate rock [13–22]. Several typical soils also have been reported to remove Cd(II) and other heavy metals [23–26].

Loess is widely distributed in northwestern China. This soil is also common in other countries such as Russia, the United States, the Middle East, and South Africa. Removal of Cu(II), Zn(II) and Cd(II) from aqueous solutions has recently been reported and loess soil has shown a high affinity for heavy metals [27–29]. Now that loess is an effective adsorbent, it is meaningful to build landfill liner with clay modified by loess. The loess-modified clay is abundant, economic and environmental protection. No researches about adsorption on loess-modified clay have been done before.

The objective of this study is to investigate the adsorption mechanism of Cd(II) on clay landfill liners containing loess soil. Factors affecting cadmium removal include loess proportion, slurry concentration, pH value, reaction time, and temperature. The interaction mechanism between Cd(II) and loess-modified clay was discussed with the assistance of X–ray diffraction (XRD) and Fourier transform infrared (FT–IR) spectral analysis.

2. Materials and methods

2.1. Preparation of adsorbent and adsorbate

Red clay and loess soil were used as adsorbent in this study. They were sampled from the suburban area of Dalian and Xi'an city of China respectively. The loess soil sample was taken from 1.65 m below ground surface known as Malan loess (Q3). These two kinds of soil were dried by air, sieved through a 0.5 mm sieve, oven–dried at 105°C for 24 h, cooled to room temperature, and then sealed in plastic bags for storage.

The stock solution (1 g/l) of Cd(II) was prepared by dissolving cadmium nitrate (analytical reagent grade) into deionized water (DW). DW was bubbled with N_2 to eliminate dissolved CO_2. Flasks (1 l) were rinsed with 1mol/l HCl solution for 24 h and then cleaned with deionized water.

2.2. Characterization of adsorbent

The chemical constituents, mineral components and surface functional groups of the soil samples were tested by XRF (SRS–3400, Bruker AXS Corp., Germany), XRD (DX–2000, Dandong Fangyuan Corp., China, equipped with a Cu K tube and Ni filter) and FT–IR (Avatar–360, Nicolet, USA), respectively. The solution pH was measured with a glass electrode potentiometer (Starter 2C, Ohaus Instruments (Shanghai) Co., Ltd., China). The Cd(II) loaded soil samples were prepared as follows: the adsorbent (1 g) was mixed with Cd(II) solution (50 ml, 100 mg/l) and then equilibrated at 25°C for 24 h on a shaking box at 160 rpm. The supernatant was poured out for centrifugation and the bottom sludge was oven-dried at 105°C. Both the modified clay and Cd(II) loaded modified clay samples were send to the chemical laboratory of Dalian University of Technology for XRD and FT–IR test.

2.3. Experimental methods

2.3.1. Batch tests

Batch tests were conducted to investigate the adsorption behavior of Cd(II). Dry soil samples (0.5–16 g) and aqueous solutions (50 ml) of various concentrations of Cd(II) were mixed in each flask (100 ml). Temperature experiments were carried out between 25 and 60°C . The pH value of landfill leachate is generally 4.5–9 from actual investigations, so the initial pH values, pH_0 of the solutions were then adjusted from 3 to 12 by adding 0.001–0.1 M HNO_3 or NaOH solution. A Starter 2C model pH meter was used to adjust a desired pH value. The sample flasks were then put into a temperature controlled shaking box which was rotated at 160 rpm for a predetermined time period. Afterwards, the solutions were transferred into PVC tubes for centrifugation at a speed of 5000 rpm for 5 min to obtain the supernatant. The atomic absorption spectroscopy (AAS) (Shanghai, China) was then used to determine the equilibrium Cd(II) concentration. Blank tests were conducted to evaluate Cd(II) adsorption on the inner surface of the flasks. Two groups of parallel tests were performed to obtain an average value for equipment adsorption. The adsorption of Cd(II) on the adsorbent was calculated from the mass balance:

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{1}$$

where q_t is the amount of Cd(II) adsorbed onto the soil samples at time t; C_0 is the initial Cd(II) concentration; C_t is aqueous phase concentration of Cd(II) at time t; V is the volume of the aqueous phase and M is the weight of the soil samples. The Cd(II) removal efficiency, R_e was calculated by the following equation:

$$R_e(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_e is the equilibrium Cd(II) concentration.

2.3.2. Permeability tests

The hydraulic conductivity as a key parameter for clay landfill liners is required to be less than 1 nm/s. Permeability tests were performed on a loess-modified clay liner. The specimens with various water contents were compacted in the permeameter molds. A changing-head permeability test using flexible-wall permeameters was conducted to measure the hydraulic conductivity following the procedure in SL237-1999.

3. Results and discussion

3.1. Characterization of adsorbent

Both the red clay and loess soil specimens had no history of exposure to Cd(II). The chemical composition of red clay was 45.8% of SiO_2, 26.5% of Al_2O_3, 22.4% of Fe_2O_3, 2.56% of TiO_2, 1.15% of MgO, 0.930% of K_2O, 0.274% of SO_3, 0.183% of CaO, 0.0916% of Cl, 0.0553% of ZrO_2, 0.0439% of NiO and 0.0177% of ZnO. The natural pH of red clay, 4.71, indicating its acidic characteristic, makes it an effective buffer material for alkaline solutions. The chemical composition of loess was 51.0% of SiO_2, 15.4% of CaO, 14.2% of Al_2O_3, 8.77% of Fe_2O_3, 4.21% of K_2O, 3.03% of MgO, 1.34% of Na_2O, 1.07% of TiO_2, 0.254% of SO_3, 0.134% of BaO, 0.119% of MnO, 0.113% of P_2O_5, 0.0927% of Cl, 0.0632% of NiO, 0.0605% of ZrO_2, 0.0576% of SrO, 0.0298% of Rb_2O and 0.0218% of ZnO. The natural pH of loess, 9.19, indicating its alkaline characteristic, makes it an effective buffer material for acidic solutions.

3.2. Effect of loess proportion

Loess soil shows a high affinity for heavy metals as reported in recent papers, so the adsorption effect of mixed soil varies with different proportion of loess. Fig. 1 shows the effect of loess proportion on Cd(II) removal from aqueous solutions that are mixed with soil. The percentage Cd(II) removal of loess increased to 86.3% compared with that of clay 48.9%. The curve is comprised of two linear stages with different slope coefficients. At the first stage, the percentage Cd(II) removal increased rapidly from 48.9% to 65.2% when the proportion of loess increases from 0 to 5%, which shows a remarkable improvement of adsorption. The removal percentage of Cd(II) increased relatively slowly from 65.8% to 86.3% at the second stage when the proportion of loess increases from 7% to 100%. Considering the collapsibility of loess and the structural performance requirement of landfill liners, the proportion of loess should not be very big. The optimum proportion was obtained as 6% at which the maximum metal uptake could be achieved with the structural performance of the mixed soil not destroyed. The proportion of loess in loess-modified clay used later in this paper is 6% if there is no special explanation.

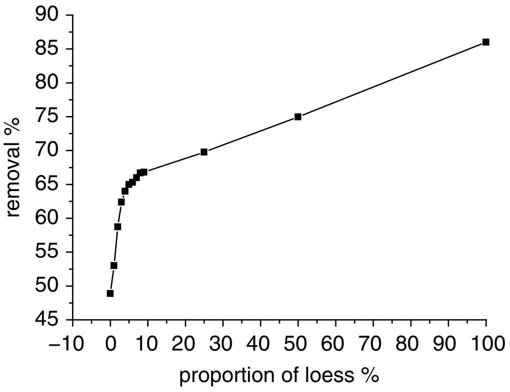

Fig. 1. Effects of loess proportion on Cd(II) removal percentage. Conditions: Cd(II) concentration 100 mg/l, slurry concentration 20 g/l, temperature 298K, time 24 h and natural pH.

3.3. Effect of pH

The pH value of a solution is very important and it has a significant influence on complexation reactions and electrostatic interactions in physisorption processes at the adsorption surface. The initial pH values of the solutions were adjusted from 3 to 12. Fig. 2 shows that equilibrium pH values lie above the diagonal line at $pH_0 < 5.5$ and below the diagonal at $5.5 \le pH_0 < 12.0$. The value of pH_e increases with pH_0 and there is a sudden rise of pH_e at pH_0 is 11. The value of pH_e remains all the same when pH_0 increases from 3 to 9, which means the loess-modified clay soil can maintain the pH of the solution at a relatively constant value in these conditions. The soil shows a high buffering effect in an alkaline solution and the pH_e values could be lower than the corresponding pH_0 values in these conditions.

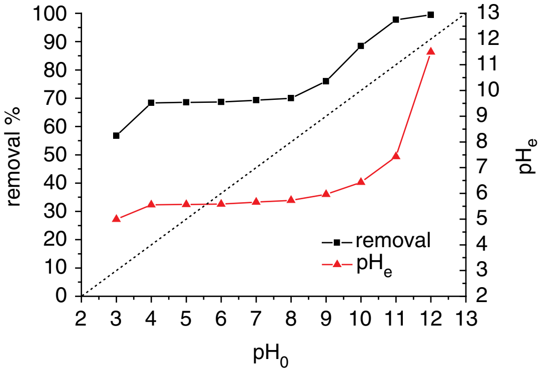

Fig. 2. Variation of Cd(II) removal percentage with varied initial pH values. Conditions: Cd(II) concentration 100 mg/l, slurry concentration 20 g/l, temperature 298K and time 24 h.

Fig. 2 shows the effect of pH_0 on the adsorption of Cd(II) on loess-modified clay. The Cd(II) adsorption increased from 56.2 to 99.7% with the increase of pH from 3.0 to 12.0. The curve plateaus at 70.2% Cd(II) removal when pH_0 is between 4.0 and 8.0. Further increase of pH_0 leads to a continual increase of Cd(II) removal efficiency. When the pH_0 increases from 8.0 to 12.0, the removal percentage of Cd(II) shows a rapid increase from 70.2% to 99.4%. Precipitation may be formed to cause this significant increase in Cd(II) removal efficiency. When the initial pH values are over 12.0, cadmium ions in aqueous solutions can be nearly completely removed, which means effective removal of Cd(II) requires a high alkaline environment.

The increased adsorption of Cd(II) by loess-modified clay relative to adsorbate solution pH may be caused by several reasons. There are a large number of active sites at the surface of the modified clay sample and may become positively charged at very low pH. Thus, competition between H^+ and the metal ions for available adsorption sites is strong. However, this competition decreases as these surface active sites become more negatively charged when pH increases and the adsorption of the positively charged metal ions through electrostatic force of attraction are enhanced.

3.4. Effect of slurry concentration

Fig. 3 shows the effect of slurry concentrations (*S/L*) on Cd(II) removal. The slurry concentrations varied from 10 to 320 g/l and the Cd(II) concentration was kept at 100 mg/l. The percentage removal of Cd(II) increased from 42.03% to 95.11% as the concentration of the adsorbent increased from 10 to 320 g/l. More Cd(II) was removed for larger adsorbent concentration. The Cd(II) removal increases rapidly at first and then moderates as the adsorbent concentration exceeds a critical value of 80 g/l. The results showed that Cd(II) could be almostly removed when the slurry concentration reached 80 g/l. However, the unit adsorption amount of Cd(II) on loess-modified clay decreases as the slurry concentration increases. As shown in Fig. 3, q_e decreases from 4.20 to 0.30 mg/g when the concentration of the adsorbent increases from 10 to 320 g/l. This phenomenon has been reported previously, which is caused by the interaction between colloidal particles in the soil [30].

3.5. The effect of contact time and adsorption kinetics

Fig. 4 shows the variation of unit adsorption amount q_t with contact time. As it can be seen from the figure that the adsorption of Cd(II) on loess-modified clay happened in a fairly short time. The unit adsorption amount reaches a relatively high value within 30 min and then reaches a plateau. It is also possible to say that adsorption equilibrium is attained within the first 30 min. The unit adsorption amount appears to be lower when the slurry concentration is larger during the reaction. At the equilibrium time, the value of q_t is found to be 4.46, 3.26, 1.91 and 1.09 mg/g with different slurry concentration of 10, 20, 40 and 80 g/l.

Adsorption process could be dependent on and controlled with different kinds of mechanisms, like mass transfer, diffusion control, chemical reactions and particle diffusion. The test data were further analyzed to investigate the possible adsorption mechanism and to find the best suitable model. Several adsorption models were applied to evaluate the test data, i.e., the pseudo–second order model, the Eovich model and the intraparticle diffusion model.

The pseudo–second order kinetic equation is given by [31,32]:

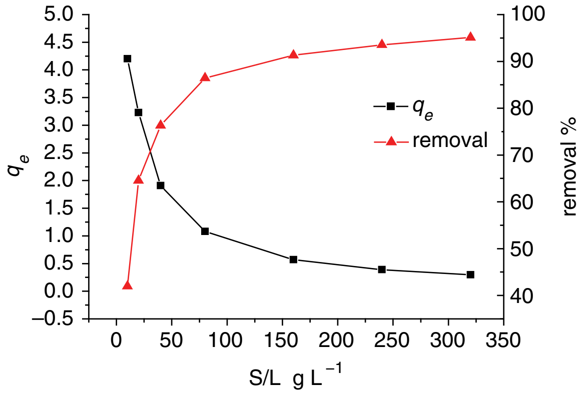

Fig. 3. Effect of slurry concentration on removal percentage of Cd(II). Conditions: Cd(II) concentration 100 mg/l, temperature 298K, time 24 h and natural pH.

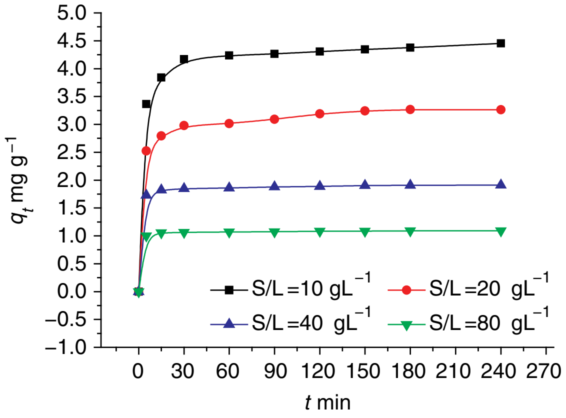

Fig. 4. Effect of contact time on unit adsorption amount of Cd(II). Conditions: Cd(II) concentration 100 mg/l, temperature 298K and natural pH.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

where q_e and q_t are the amount of solute adsorbed on per unit adsorbent at the equilibrium and elapsed time, t respectively (mg/g) and k_2 is the pseudo–second order rate constant (g/mg min). After integrating Eq. (3) with the conditions $q_t = 0$, $t = 0$, we have:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

The Eovich kinetic equation is from [33]:

$$q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{\ln t}{\beta} \tag{5}$$

where α is the initial adsorption rate (mg/gmin) and β is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

The equation for the intraparticle diffusion model is from [34]:

$$q_t = k_i t^{1/2} + C \tag{6}$$

where k_i is the rate constant of intraparticle diffusion (mg/gmin$^{1/2}$) and C is the intercept.

Figs. 5–7 show the simulated curves of the test data with pseudo-second-order kinetic, Eovich model and intraparticle diffusion models, respectively. The predicted model constants are shown in Table 1.

According to the correlation coefficients, the pseudo-second order kinetics is found to be best-fit with the test data. The correlation coefficients are 0.999 attained from pseudo-second order kinetics under various slurry concentrations. This result can be expected because the ordinary type of exchange processes are more rapid and controlled mainly by diffusion, whereas, those in a chelating exchanger are slower and controlled either by particle diffusion mechanism or by a second order chemical reaction [35]. There is a significant increase in the rate constant k_2 from 0.077 to 0.084, 0.433 and 0.893 g/mgmin when increasing the initial slurry concentration from 10 to 20, 40 and 80 g/l. This implies that the equilibrium time is shorter with bigger slurry concentration.

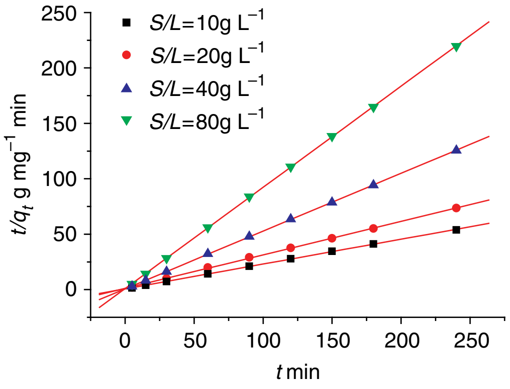

Fig. 5. Simulated curves with pseudo-second-order kinetics.

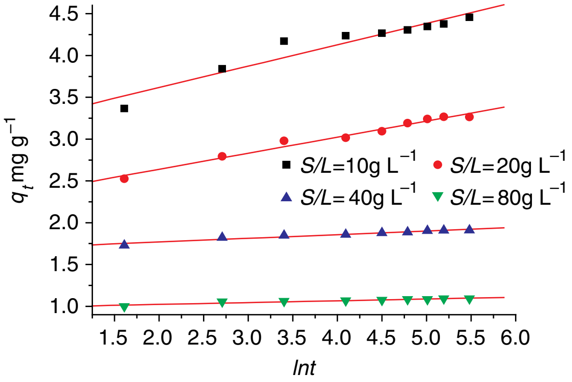

Fig. 6. Simulated curves with Elovich kinetics.

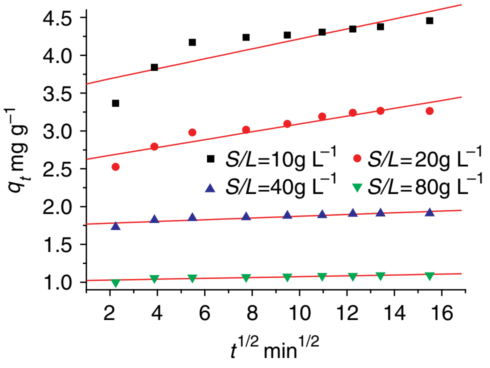

Fig. 7. Simulated curves with intraparticle diffusion kinetics.

The test data fit well with the intraparticle diffusion model and shows a relatively high correlation coefficient more than 0.863. This indicated that gradual internal diffusion inside the micropores dominates the adsorption of Cd(II). This phenomenon has been previously observed for Cu(II), Zn(II) and Cd(II) adsorption on loess [27–29]. The rate constants, contrary to pseudo-second order kinetics, decrease from 0.066 to 0.052, 0.011, and 0.006 mg/g min$^{1/2}$ with increasing slurry concentrations from 10 to 20, 40, and 80 g/l, respectively. This observation shows the increasing of slurry concentration results in a decreased amount of solute capable of diffusing inwards.

3.6. The effect of temperature and adsorption isotherms

Fig. 8 shows adsorption isotherms of Cd(II) on loess-modified clay at different temperatures. The unit

Table 1
Predicted kinetic constants of Cd(II) adsorption on loess-modified clay

	S/L(g/l)			
	10	20	40	80
Pseudo–second order model				
q_e(mg/g)	4.464	3.306	1.917	1.095
k_2(g/mgmin)	0.077	0.084	0.433	0.893
R	0.999	0.999	0.999	0.999
Eovich model				
α(mg/gmin)	4.88E4	2.45E4	2.73E15	1.85E18
β(g/mg)	3.915	5.213	22.98	46.82
R	0.957	0.989	0.973	0.946
Intraparticle diffusion model				
k_i(mg/gmin$^{1/2}$)	0.066	0.052	0.011	0.006
C	3.558	2.574	1.757	1.020
R	0.866	0.937	0.901	0.863

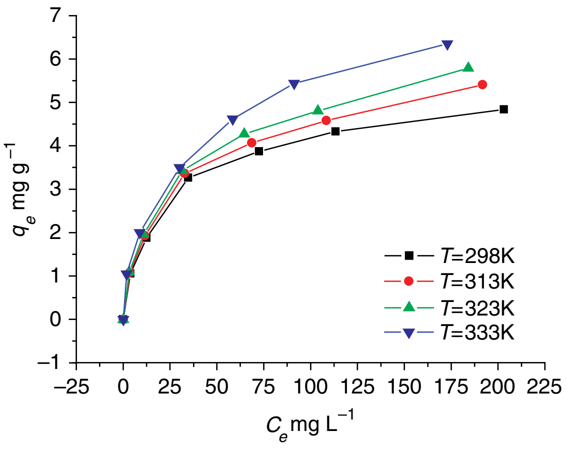

Fig. 8. Isotherms of Cd(II) adsorption on loess-modified clay. Conditions: slurry concentration 20 g/l, time 24 h and natural pH.

adsorption of Cd(II) shows a gradual increasement and then achieved a maximum adsorption amount. The unit adsorption amount increases with temperature, which indicates the endothermic nature of the adsorption. Three general isothermal adsorption models (Langmuir, Freundlich, and Dubinin-Radushkevich (D-R)) are used to evaluate the batch test data and to interpret the possible adsorption mechanism.

Langmuir isotherm models the monolayer coverage of the adsorption surface. This model is based on the assumption that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and all the adsorption sites are energetically identical. The Langmuir adsorption model further assumes that and adsorption occurs on adsorbent of homogeneous structure and intermolecular forces decrease rapidly with the distance from the adsorption surface. Based on those assumptions the linearized form of the Langmuir equation is given as [36]:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQC_e} \tag{7}$$

where q_e is the amount of solute adsorbed on per unit adsorbent at the equilibrium time (mg/g), C_e the equilibrium solute concentration (mg/l), Q the maximum surface density of adsorbent (mg/g), and b the Langmuir constant (l/mg). The plots of $1/q_e$ versus $1/C_e$ give a straight line and the values of b and Q can be calculated from the slope and intercept of the plots, respectively. The Langmuir isothermal constants for Cd(II) adsorption on loess-modified clay are listed in Table 2.

Freundlich equation models the multilayer adsorption and adsorption on heterogeneous surfaces. The equation can be written as [36]:

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

where K_F is the Freundlich constant (mg/g) indicating the adsorption capacity and strength of the adsorptive bond and n is the heterogeneity factor. By taking logarithms of the equation a linear form of the Freundlich equation can be obtained as:

Table 2
Predicted isotherms constants of Cd(II) adsorption on loess-modified clay

	298K	313K	323K	333K
Langmuir model				
Q(mg/g)	5.173	5.735	6.193	7.077
b(l/mg)	0.048	0.044	0.041	0.037
R	0.997	0.994	0.993	0.991
Freundlich model				
K_F(mg/g)	0.903	0.889	0.897	0.975
n	0.327	0.350	0.363	0.371
R	0.979	0.988	0.992	0.995
D–R model				
q_m(mg/g)	13.62	15.11	16.38	16.98
k(mol^2/kJ^2)	0.0039	0.0036	0.0034	0.0030
E(kJ/mol)	11.35	11.83	12.13	12.87
R	0.992	0.996	0.998	0.998

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{9}$$

The plot of the log q_e versus log C_e gives a straight line and the values of K_F and n can be calculated from the intercept and slope, respectively. The Freundlich isothermal constants for Cd(II) adsorption on loess-modified clay are listed in Table 2.

Langmuir and Freundlich isotherms give no idea about adsorption mechanism. The D–R isotherm model can predict the free adsorption energy change based on the assumption of a uniform pore–filling adsorption. The D–R model is given as [36]:

$$\ln q_e = \ln q_m - k\varepsilon^2 \tag{10}$$

where q_m is the maximum adsorption capacity (mol/g), k a model constant related to the free adsorption energy and ε the Polanyi potential, which can be expressed as:

$$\varepsilon = R_i T \ln(1 + \frac{1}{C_e}) \tag{11}$$

where R_i is the ideal gas constant, T is the temperature (K).

The values of q_m and k are calculated from the intercept and slope of the ln$q$ versus ε^2 plots. The mean free energy of adsorption (E) was calculated from the k values with the equation:

$$E = -\frac{1}{\sqrt{2k}} \tag{12}$$

The adsorption is basically ascribed to physical adsorption for $|E|$ ranging from 1.0 to 8.0 kJ/mol, while, the mechanism is surface adsorption by means of ion exchange when $|E|$ is between 8.0 and 16.0kJ/mol [37]. The D–R isothermal constants for Cd(II) adsorption on loess-modified clay are listed in Table 2.

It is shown in Table 2 that the Langmuir equation gives a better fit to the experimental data than the Freundlich equation in all cases for the adsorption of Cd(II) on loess-modified clay. The maximum Cd(II) adsorption capacities of loess-modified clay estimated by the Langmuir isotherm model were 5.17, 5.74, 6.19 and 7.08 mg/g at temperatures ranging from 298, 313, 323 and 333K, respectively. The adsorption capacity is improved by increasing temperature. Based on the analysis with the D-R isotherm, the adsorption capacities were estimated to be 13.62, 15.11, 16.38 and 16.98 mg/g at temperatures ranging from 298, 313, 323 and 333K, respectively. These values are fairly higher than those obtained with the Langmuir model. This phenomenon may be due to the inherent assumption of the D-R model that all micropores and macropores are filled with solute. However, this ideal state is not easy to realize in practice. The absolute values of E were 11.35, 11.83, 12.13 and 12.87 kJ/mol, which were between the values of ion exchange. Therefore it is possible to say that Cd(II) adsorption mechanism on loess-modified clay can be explained with an ion-exchange process. As temperatures increased from 298 to 333K, the correlation coefficients for linear curves with both the Freundlich isotherm and the D-R models became larger and came closer to 1.00. This phenomenon means that the Freundlich and D-R models suit better with relatively high temperature conditions.

3.7. Adsorption thermodynamics

The thermodynamic equations of Cd(II) adsorption on modified clay are written as [38]:

$$\Delta G^0 = -R_i T \ln K_D \tag{13}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{14}$$

$$\ln(K_D) = \frac{\Delta S^0}{R_i} - \frac{\Delta H^0}{R_i T} \tag{15}$$

where K_D is the distribution coefficient of the solute between the adsorbent and the solution in equilibrium (q_e/C_e), ΔG^0 is Gibbs' free energy change, ΔS^0 is entropy change and ΔH^0 is enthalpy change.

The values of ΔH^0 and ΔS^0 can be calculated from the slopes and intercepts of the linearized curves fitted with Eq. (15) as shown in Fig. 9. The initial Cd(II) concentration had a great effect on the thermodynamic parameters as shown in Table 3. The change of enthalpy was 16.26, 9.39, 9.01, and 9.97 kJ/mol and the change of entropy was 100.41, 72.85, 63.03 and 59.72 J/molK when the initial Cd(II) concentration increased from 25 to 50, 150 and 300 mg ^{1} respectively. The change of entropy decreased along with an increasing initial Cd(II) concentration. The positive value of ΔH^0 confirmed endothermic character to the adsorption process. The positive ΔS^0 suggested the increased randomness at the solid–solution interface during the adsorption of cadmium on the sample [39]. As initial Cd(II) concentration increased from 25 to 300 mg/l, the correlation coefficients for linear curves with Eq. (15) became larger and came closer to 1.00, which shows that Eq. (15) suit better with relatively high Cd(II) concentration conditions.

The change of Gibbs' free energy was negative as the initial Cd(II) concentrations varied from 25 to 300 mg/l, which indicates the spontaneity of the adsorption process. In addition, the change of Gibbs' free energy for Cd(II) adsorption on loess-modified clay samples

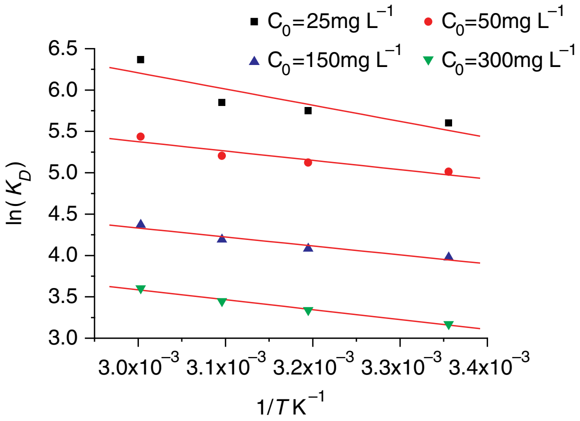

Fig. 9. Linear fit of thermodynamics for Cd(II) adsorption on loess-modified clay. Conditions: slurry concentration 20 g/l, time 24 h and natural pH.

Table 3
Thermodynamics parameters for the adsorption Cd(II) on loess-modified clay

C_0 (mg/l)	T(K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/molK)	R
25	298	–13.66	16.26	100.41	0.888
	313	–15.16			
	323	–16.17			
	333	–17.17			
50	298	–12.32	9.39	72.85	0.943
	313	–13.42			
	323	–14.15			
	333	–14.87			
150	298	–9.78	9.01	63.03	0.969
	313	–10.72			
	323	–11.35			
	333	–11.98			
300	298	–7.82	9.97	59.72	0.993
	313	–8.72			
	323	–9.32			
	333	–9.92			

decreased with increasing initial Cd(II) concentration under constant temperature conditions. The higher negative values reflect a more energetically favorable adsorption process. The reaction is favored and getting easier at higher temperatures. The value of ΔG^0 decreased along with an increasing reaction temperature at a fixed initial Cd(II) concentration, which indicates more driving force of the adsorption reaction and therefore more adsorption capacity of loess-modified clay samples at higher temperatures.

3.8. Discussion about the mechanism of Cd(II) adsorption on modified clay

Fig. 10 shows the XRD spectra of modified clay and Cd(II) loaded modified clay with initial solute concentration of 100 mg/l. It is determined from the characteristic bands on the XRD spectra that the main minerals in modified clay are quartz, calcite, albite, goethite and kaolinite. After loaded with Cd(II) new patterns were observed at 2θ = 27.40° and 28.12° compared with original modified clay sample. According to the MDI Jade software, the patterns can be attributed to $CdSiO_3$ at 2θ = 27.40°, and the patterns can be attributed to either $CdSiO_3$ or $CdAl_2(SiO_4)_2$ at 2θ = 28.12°. Aluminum silicate minerals in soil could react with cadmium ions to form $CdSiO_3$. The formation of $CdAl_2(SiO_4)_2$ can be attributable to surface complexes between the kaolinite mineral and Cd(II). The reaction equations can be written as:

$$\equiv \mathrm{SOH} + \mathrm{Cd}^{2+} \rightarrow \equiv \mathrm{SOCd}^{+} + \mathrm{H}^{+} \qquad (16)$$

where S denotes the clay mineral constituents.

Other bands relevant to $Cd(OH)_2$ or $CdCO_3$ were not observed in Fig. 10, which means there were no or limited amount of $Cd(OH)_2$ or $CdCO_3$ precipitation when the samples subjected to XRD patterns were collected.

Fig. 11 shows the IR spectra of modified clay and Cd(II) loaded modified clay with the range from 4000 to 400 cm^{-1}. Patterns at 3620 and 1032 cm^{-1} are observed in both curves. They are characteristic of hydroxyl group and Si–O group respectively, which can be assigned to clay minerals. These patterns have no obvious differences indicating that these sites have no contribution to adsorption of Cd(II) on loess-modified clay.

Patterns at 3436 and 1637 cm^{-1} decline in Cd(II) loaded modified clay, indicating the amount of adsorbed

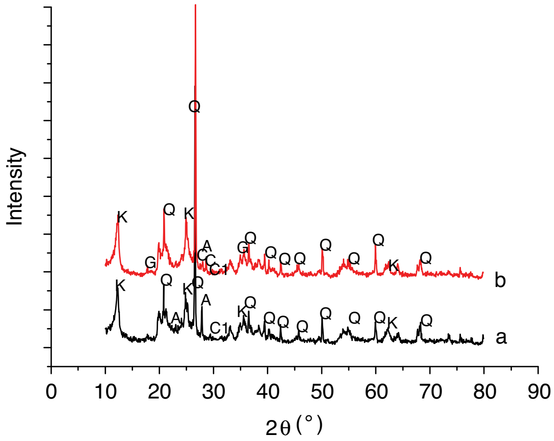

Fig. 10. XRD spectra of modified clay (a) and Cd(II) loaded modified clay (b) (A=albite; C=$CdSiO_3$ or $CdAl_2(SiO_4)_2$; C1=calcite; G=goethite; K=Kaolinite; and Q=quartz).

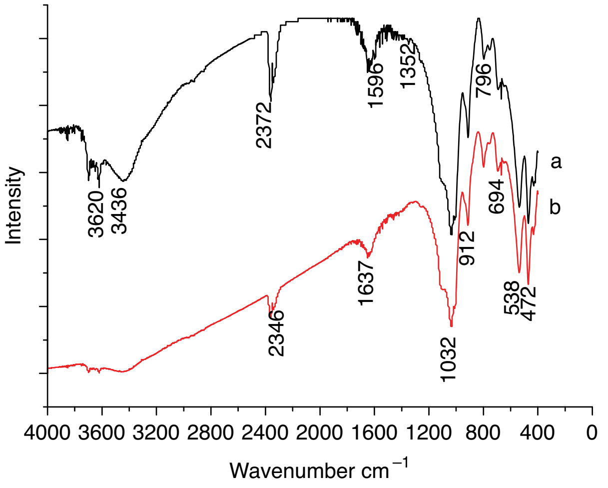

Fig. 11. (a) FT-IR spectra of modified clay and (b) Cd(II) loaded modified clay.

water molecules decreased and the H bonds weakened within contact particles. Measures were taken to keep samples dried during the test. However, some potassium bromide may still be hydrolyzed in air to bring some water in these species.

The absorption bands at 2372 and 2346 cm^{-1} existing both in modified clay and Cd(II) loaded modified clay are related to atmospheric carbon dioxide. Interference might be caused by some CO_2 which was dissolved into water and absorbed into the micropores of soil.

Patterns at 1596 and 1352 cm^{-1} appeared in loess-modified clay can be assigned to the bending vibrations of the carboxyl group, which are originally contained in loess-modified clay in the form of organic matter [40]. These bands disappear after loaded with Cd(II). The interaction between Cd(II) and the carboxyl group could be:

$$-\text{COOH} + \text{Cd}^{2+} \rightarrow -\text{COOCd}^{+} + \text{H}^{+} \tag{17}$$

As to the bands at 912, 796, 694, 538 and 472 cm, it is related to quartz. Quartz was inherent material in loess-modified clay and proved to have little effect on Cd(II) adsorption.

Cd(II) adsorption has little to do with calcite as no patterns of $CdCO_3$ were not found in XRD spectra. The loess-modified clay–Cd(II) solution mixture was acidic without any pH adjustment. As confirmed by the XRD spectra analysis, it is not easy to form cadmium carbonate under such conditions. The other mineral components responsible for Cd(II) adsorption are: kaolinite, goethite, etc. The adsorption of Cd(II) on goethite could be written as [41]:

$$\text{FeOOH} + \text{Cd}^{2+} \rightarrow \text{FeOOCd}^{+} + \text{H}^{+} \tag{18}$$

In addition, Cd(II) can be immobilized on the loess-modified clay soil surface to form outer sphere complexes under acidic conditions by bonding to permanent-charge sites or exchanging background electrolyte cations with cadmium ions, and the adsorption process can be expressed as:

$$2\,(\text{SOK}) + \text{Cd}^{2+} \rightarrow \text{SOCdOS} + 2\text{K}^{+} \tag{19}$$

and

$$2(\text{SO}^{-}) + \text{Cd}^{2+} \rightarrow \text{SOCdOS} \tag{20}$$

As the pH of the solution rises, the negative variable charges on loess-modified clay surface increases, which can lead to the increase of Cd(II) adsorption. Cd(II) precipitate at higher initial pH values (i.e., pH>9), suggesting that chemical precipitation played the most important role on Cd(II) adsorption at this stage.

3.9. Permeability tests

As shown in Fig. 12, the hydraulic conductivity (K) varied with water content. The hydraulic conductivity of the soil specimen decreased and then increased as water content increased gradually. A relatively high hydraulic conductivity was got when the soil specimen was compacted drier than the optimum water content. Increasing water content generally results in reorientation of clay particles and elimination of inter-aggregate pores [42,43]. The minimum hydraulic conductivity is 1.88E-8 cm/s. The appropriate range of water content is between 26% and 34% as required for a hydraulic conductivity less than 1 nm/s of loess-modified clay.

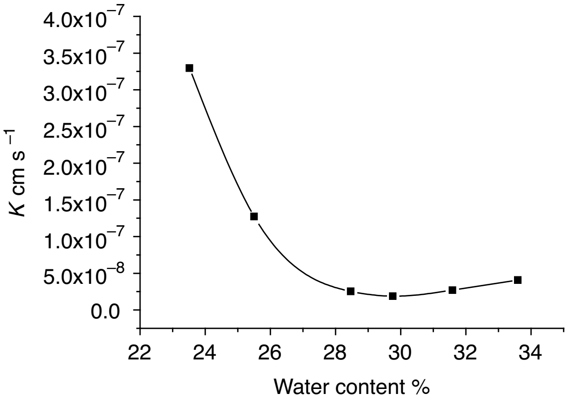

Fig. 12. Influence of water content on hydraulic conductivity of loess-modified clay.

4. Conclusions

1. The factors including loess proportion, slurry concentration, initial solution pH, initial solute concentration, temperature and equilibrating duration were found to have great effects on the adsorption capacity of modified clay. The optimum proportion of loess was found to be 6% for Cd(II) adsorption.
2. The loess-modified clay is effective to remove Cd(II) from aqueous solutions with the adsorption capacity as 7.08 mg/l determined by Langmuir model.
3. Kinetic studies showed that the Cd(II) adsorption followed pseudo-second order kinetics, and the process was mainly gradual internal diffusion. The adsorption was surface homogeneous analyzed by Langmuir equation, and was a chemisorption mode suggested by D-R model. The thermodynamic study showed that the adsorption process was spontaneous and endothermic and the system disorder increased with time.
4. The adsorption capacity of loess-modified clay is promoted significantly compared with clay and the hydraulic conductivity of loess-modified clay can meet the requirement of landfill liners according to permeability tests. The loess-modified clay is abundant, economic and environmental protection. The material used in this paper is proved to be appropriate for landfill liner material.

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Symbols

q_t — the amount of Cd(II) adsorbed onto the soil samples at time t (mg/g)

C_0 — the initial initial Cd(II) concentration (mg/l)

C_t — aqueous phase concentration of Cd(II) at time t (mg/l)

V — the volume of the aqueous phase (l)

M — the weight of the soil samples (g)

t — time (min)

R_e — the removal efficiency (%)

C_e — the equilibrium Cd(II) concentration (mg/l)

q_e — the amount of solute adsorbed on per unit adsorbent at the equilibrium time (mg/g)

q_{t} — the amount of solute adsorbed on per unit adsorbent at the elapsed time (mg/g)

k_2 — the pseudo–second order rate constant (g/mgmin)

α — the initial adsorption rate (mg/gmin)

β — related to the extent of surface coverage and activation energy for chemisorption (g/mg)

k_i — the rate constant of intraparticle diffusion (mg/gmin$^{1/2}$)

C — the intercept of Eq. (6)

Q — the maximum surface density of adsorbent (mg/g)

b — the Langmuir constant (l/mg)

K_F — the Freundlich constant (mg/g)

n — the Freundlich isothermal constant

k — a model constant related to the free adsorption energy

ε — the Polanyi potential

E — the mean free energy of adsorption (kJ/mol)

K_D — the distribution coefficient of the solute between the adsorbent and the solution in equilibrium (l/g)

R_{i} — the ideal gas constant (8.314J/molK)

T — the temperature (K)

ΔG^0 — Gibbs' free energy change (kJ/mol)

ΔS^0 — entropy change (J/molK)

ΔH^0 — enthalpy change (kJ/mol)

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