Adsorption behavior and mechanism of Cd(II) on loess soil from China

Yan Wang, Xiaowu Tang*, Yunmin Chen, Liangtong Zhan, Zhenze Li, Qiang Tang

MOE Key Laboratory of Soft Soils and Geoenvironmental Engineering, Department of Civil Engineering, Zhejiang University, Yuhangtang Road 388, Hangzhou 310058, PR China

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ABSTRACT

Cadmium is a toxic heavy metal that has caused serious public health problems. It is necessary to find a cost effective method to deal with wastewater containing Cd(II). Loess soils in China have proven to be a potential adsorbent for Cd(II) removal from wastewater. The adsorption capacity of loess towards Cd(II) has been determined to be about $9.37\,mg\,g^{-1}$. Slurry concentration, initial solution pH, reaction time and temperature have also been found to significantly influence the efficiency of Cd(II) removal. The adsorption isotherms and kinetics of loess soil from China can be best-fit with the Langmuir model and pseudo-second order kinetics model, respectively. The thermodynamic analysis revealed that the adsorption process was spontaneous, endothermic and the system disorder increased with duration. The natural organic matter in loess soil is mainly responsible for Cd(II) removal at pH < 4.2, while clay minerals contribute to a further gradual adsorption process. Chemical precipitation dominates the adsorption stage at pH > 8.97. Further studies using X-ray diffraction, Fourier transform infrared spectra of Cd(II) laden loess soil and Cd(II) species distribution have confirmed the adsorption mechanism.

1. Introduction

Heavy metal contamination has aroused considerable public concern with respect to potential damage to human health and ecosystems. Cd is a non-essential and highly toxic heavy metal element which can be released into the environment by a series of different ways. Metallurgical alloying, ceramics, metal plating, photograph development, pigment works, textile printing industries, lead–zinc mining and alkaline batteries and electroplating are major sources of cadmium contamination [1,2]. Cadmium is more easily absorbed by crops than other heavy metals and can enter the human body through the food chain with deleterious effects [3]. Cadmium poisoning can happen when concentrations reach a specific value. Cadmium can bring a number of acute and chronic disorders that result in pathological symptoms and severe damage to kidneys, lungs, and the liver [4]. There have been cadmium pollution cases occurring in the Beijiang River region of Guangdong province due to excessive discharge from a smelting plant, and along the Xiangjiang river, Hunan province, cadmium pollution due to improper treatment of the effluent has adversely impacted human life. Greater attention needs to be paid to the problem of cadmium contamination.

Many techniques have been developed to remove heavy metals from wastewater. These techniques involve chemical precipitation, ion exchange, filtration, membrane separation, solvent extraction, electroflatation and adsorption [5,6]. Adsorption is one of the methods that is feasible for removing heavy metals from wastewater and water supplies. Adsorption has been found to be both efficient and cost effective in that the process does not involve the production of sludge which will add to the cost of recovery of the metal ions [7,8]. Activated carbon is the most widely used sorbent because of its high specific surface area and convenient regeneration from spent carbon [9–13], however, its high cost necessitates seeking for inexpensive and effective sorbents as potential replacement. In recent years, numerous materials have been studied to ascertain their adsorption capacity for Cd(II), such as goethite [14,15], montmorillonite [16], sludge-soil [17], zeolite [18–20], bentonite [19], calcite [21,22], and phosphate rock [23]. Several typical soils also have been reported to remove Cd(II) and other heavy metals [24–27]. Loess soil is widely distributed throughout northwestern China, Middle Asia, Russia, the Middle East and North America. Loess soil is rather abundant in China, covering an area of approximate $640,000\,km^2$. Removal of Cu(II) and Zn(II) from aqueous solutions has recently been reported and loess soil shows a high affinity for heavy metals [28,29]. However, the adsorption capacity of loess towards Cd(II) remains unknown.

This study is aimed at investigating the adsorption mechanism of Cd(II) on loess soil. Factors affecting efficient removal of cadmium are slurry concentration, pH value, reaction time, and reaction temperature. The interaction mechanism between Cd(II) and loess was studied with the aid of X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectral analysis of both the original loess soil and the Cd(II) loaded loess.

* Corresponding author. Tel.: +86 571 88208791; fax: +86 571 85023966.
E-mail address: tangxiaowu@zju.edu.cn (X. Tang).

2. Materials and methods

2.1. Preparation of adsorbent and adsorbate

The adsorbent utilized in this study, Chinese loess, was sampled from the suburban area of Xi'an, China. The soil sample was taken from 5 m below ground surface in the unsaturated soil zone. It has been reported that the soil is typical Quaternary loess located on the Chinese Loess Plateau [30]. The soil was oven-dried at 105 °C for 24 h to remove bulk water, cooled to room temperature, and then sealed in plastic bags for storage.

Flasks (1 L) were immersed in 1 mol L^{-1} HCl solution for 24 h and then rinsed with deionized water (DW) three times. DW was bubbled with N_2 to eliminate dissolved CO_2. Cd(II) stock solution (1 g L^{-1}) was prepared by dissolving cadmium nitrate (analytical reagent grade) into deionized water.

2.2. Characterization of adsorbent

The organic matter was determined by burning at 650 °C for 8 h in an oven in the presence of O_2 gas. The weight loss was assigned to the organic content. The surface area of the sorbent was determined by N_2 adsorption method using Autosorb 1-MP apparatus (Quantachrome Corporation, USA), and the results were analyzed by Brunauer–Emmett–Teller (BET) adsorption theory.

To determine the cation exchange capacity (CEC), 20 g dried soil sample was saturated with 1.0 M ammonium acetate for 30 min, washed with ethanol several times at first, and then saturated with 1.0 M KCl solution to exchange the adsorbed ammonium ions. The obtained slurry was centrifuged and the NH_4^+ concentration of the supernatant was determined using GDYS 101SA (China) by colorimetric analysis based on the character of selective absorption towards visible light of colored complex (i.e., the reaction product of NH^{4+} with chromogenic agent). The relevant CEC was equal to the amount of exchangeable ammonium per 100 g soil.

The natural pH (pH$_{na}$) of loess soil was determined by mixing 20 g loess soil with 50 mL DW, and the pH$_{pzc}$ of loess was determined by acid–alkaline titration of the sorbent. The solution pH was measured with a glass electrode potentiometer (Shanghai Precision & Scientific Instrument Co., Shanghai, China). The chemical constituents, mineral components and surface functional groups of loess samples were tested by ICP-MS (ICP-MS PQ3, Thermo Electron Corp. USA), XRD (D/MAX-RA, Rigaku Corp., Japan, equipped with a Cu K tube and Ni filter) and FT-IR (Nexus-670, Nicolet, USA), respectively. The Cd(II) loaded loess soil samples were prepared following the procedure: three sets of batch tests were carried out separately by equilibrating solutions (40 mL) including loess soil (0.4 g) and cadmium ions (25, 50 and 100 mg L^{-1}) in a thermostat at 25 °C for 24 h and the supernatant was poured out when the equilibrium solutions were centrifuged. While, the bottom sludge was oven-dried at 100 °C and then was send to the Analytical and Testing Center of Zhejiang University for XRD and FT-IR test.

2.3. Experimental methods

2.3.1. Effect of slurry concentration

Batch tests were conducted to investigate the adsorption behavior of Cd(II). Four different slurry concentrations (i.e., 2, 10, 20, and 40 g L^{-1}) were studied in order to determine appropriate adsorbent dosages. The initial Cd(II) concentration was set at 100 mg L^{-1} and the solution pH was not adjusted. The sample flasks were then put into a temperature controlled shaking box which was rotated at 160 rpm. The reaction temperature was maintained constant at 25 ± 0.2 °C and the reaction duration was 24 h. Afterwards, the slurry was centrifuged at a speed of 3000 rpm for 5 min to obtain the supernatant. The atomic absorption spectroscopy (AAS) was

then used to determine the equilibrium Cd(II) concentration. The Cd(II) removal efficiency, R was calculated by dividing the difference between the initial concentration, C_0 and the equilibrium Cd(II) concentration, C_e by the initial concentration (i.e., units of mg L^{-1}: $R(\%) = [(C_0 - C_e)/C_0] \times 100$). Blank tests were conducted to evaluate the adsorption of Cd(II) on the inner surface of the flasks and two groups of parallel tests were performed to obtain an average value for equipment adsorption.

2.3.2. Effect of pH

The same amount of sorbent (i.e., 0.500 ± 0.002 g) and Cd(II) solution (100 mg L^{-1}, 50 mL) were put into several pretreated conical flasks. The initial pH values, pH$_0$ of the solutions were adjusted from 2.3 to 12 by adding 0.1 M HCl or NaOH solution. The sample flasks were then placed into a controlled temperature shaking box and rotated at 160 rpm for 24 h. The temperature was controlled at 25 °C throughout the duration. The pH of solutions was measured at the end of the test using a glass electrode potentiometer. The solutions were transferred into PVC tubes for centrifugation at 3000 rpm for 5 min. The supernatants were sampled to determine the Cd(II) concentration by atomic absorption spectroscopy.

2.3.3. Adsorption kinetics

The adsorbent dosage was selected to be 10 g L^{-1} and the initial solute concentrations were 50 and 100 mg L^{-1}. The solution pH was not adjusted and the reaction temperature was maintained at 25 °C. The equilibration times were set increasing from 30 to 1680 min. Specific samples were taken out of the controlled temperature environment at intervals. The samples were then centrifuged at 3000 rpm for 5 min. The concentration of cadmium in supernatant liquids was detected using an atomic absorption spectrophotometer (AAS) at various times.

In order to investigate the rate law describing Cd(II) adsorption by loess soil, the kinetic data were analyzed using three kinetic equations, i.e., the pseudo-first order kinetics, the pseudo-second order kinetics and the intraparticle diffusion model.

The pseudo-first order kinetic equation is from [31]:

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

The above equation can be linearized as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

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^{-1}) and k_1 is the pseudo-first order rate constant for the adsorption process (min^{-1}).

The pseudo-second order kinetic equation is from [31]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{3}$$

where k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}).
The equation for the intraparticle diffusion model is from [32]:

$$q_t = k_{int}t^{1/2} + C \tag{4}$$

where k_{int} is the relevant rate constant (mg g^{-1} min$^{-1/2}$) and C is the intercept.

2.3.4. Adsorption isotherms at different temperatures

Batch tests were carried out to study the Cd(II) adsorption. Five sets of adsorption tests were conducted at five temperatures (i.e., 5, 15, 25, 35 and 45 °C). The slurry concentration was fixed as 10 g L^{-1} and the initial solute concentration ranged from 25 to 150 mg L^{-1}. All samples were equilibrated for 24 h in the controlled temperature shaking box and the equilibrium Cd(II) concentrations were measured by AAS to calculate the Cd(II) adsorption amount on the

sorbent. Control tests and parallel tests were conducted and the results were averaged.

The adsorption isotherms were simulated by the mathematical equations of Langmuir, Freundlich and Dubinin-Radushkevich (D-R). The Langmuir isotherm model assumes that homogeneous monolayer surface adsorption occurs and can be written as [31]

$$\frac{C_e}{q_e} = \frac{1}{bQ} + \frac{C_e}{Q} \tag{5}$$

where q_e is the mass ratio of the adsorbed solute on the adsorbent ($mg\,g^{-1}$), C_e the equilibrium solute concentration ($mg\,L^{-1}$), Q the maximum adsorption capacity of the adsorbent ($mg\,g^{-1}$), and b the Langmuir constant ($L\,mg^{-1}$).

The Freundlich isotherm model assumes a heterogeneous and patch-wise surface that is independent from one another. The equation can be written as [31]

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_F is the Freundlich constant ($mg\,g^{-1}$) indicating the adsorption capacity and strength of the adsorptive bond and n is the heterogeneity factor.

The D-R (Dubinin-Radushkevich) isotherm model assumes a uniform pore-filling adsorption and can predict the free adsorption energy change. The D-R model can be written as [31]

$$\ln q_e = \ln q_m - k\varepsilon^2 \tag{7}$$

where q_m is the maximum adsorption capacity ($mol\,g^{-1}$), k a model constant related to the free adsorption energy and ε the Polanyi potential, which is written as

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{8}$$

where the unit of C_e should be translated into $mol\,L^{-1}$.

The mean free energy of adsorption E is

$$E = -\frac{1}{\sqrt{2k}} \tag{9}$$

The adsorption is basically ascribed to surface adsorption by means of ion exchange when $|E|$ is between 8.0 and $16.0\,kJ\,mol^{-1}$, while, the mechanism is physical adsorption for $|E|$ ranging from 1.0 to $8.0\,kJ\,mol^{-1}$.

3. Results and discussion

3.1. Characterization of sorbent

The basic elemental constituents of the sorbent are listed in Table 1. The content of silicate and aluminum oxide was 63.68% and 12.77% of the total weight respectively, corresponding to clay minerals such as illite and kaolinite which was confirmed by the XRD spectrum of loess soil [33]. Calcium was the third most abundant element (9.56% in oxide form). The organic matter in loess was determined as $5.5\,mg\,g^{-1}$. The zero point of surface charge was observed at pH 2.82, indicating the negative surface charge of Chinese loess. The surface area and CEC were determined as $24.1\,m^2\,g^{-1}$ and $11.2\,cmol\,(+)\,kg^{-1}$ respectively.

3.2. Effect of slurry concentration

Fig. 1 shows the effect of slurry concentrations on Cd(II) removal from aqueous solutions that were mixed with loess. The percentage Cd(II) removal increased linearly from 59.03% to 98.03% when the dosage of loess increased from 2 to $40\,g\,L^{-1}$. More Cd(II) was eliminated from larger dosages of loess. The results showed that Cd(II) could be thoroughly removed when the slurry concentration reached $40\,g\,L^{-1}$. However, the unit adsorption amount of

Table 1
Constituents and basic parameters of loess in China.

Constituent	Mass percentage (%)
SiO_2	63.68
Al_2O_3	12.77
CaO	9.56
MgO	3.14
K_2O	3.01
Fe_2O_3	2.74
Na_2O	2.35
FeO	0.89
TiO_2	0.78
MnO	0.09

Parameter	Value
Organic ($mg\,g^{-1}$)	5.5
Specific density	2.75
Specific surface area ($m^2\,g^{-1}$)	24.1
CEC ($cmol\,(+)\,kg^{-1}$)	11.2
pH_{na}	8.16
pH_{pzc}	2.82

Cd(II) on loess decreased as the slurry concentration increased. This phenomenon has been previously reported and ascribed to the interaction between colloidal particles in the soil [34].

3.3. Effect of pH

Fig. 2 shows the effect of pH_0 on the adsorption of Cd(II) on loess. The initial pH of the solution has a significant influence on the amount of Cd(II) equilibrium adsorption. The cadmium ions in the aqueous solution were gradually removed by increasing the initial pH of the solution. The removal of Cd(II) is less than 50% at a pH < 4.2 and changes little when pH is <4.2. Further increase of pH_0 leads to a continual increase of Cd(II) removal efficiency. The removal percentage of Cd(II) shows a rapid increase from 71.2% to 97.4% when the pH_0 increases from 9.0 to 10.0. The significant increase in Cd(II) removal efficiency indicates the possibility of precipitation. The curve then plateaus at 98.9% Cd(II) removal with continuously increasing pH_0. Thus, cadmium ions in aqueous solutions can be nearly completely removed when the initial pH values are over 10.0. In other words, effective removal of Cd(II) requires a high alkaline environment.

Fig. 2 shows that equilibrium pH values lie above the diagonal line at $pH_0 < 7.5$, below the diagonal at $7.5 \leq pH_0 < 10.0$ and approximately on the diagonal when $pH_0 \geq 10.0$. The high buffering effect of loess is related to the abundance of calcite and the pH_e values could be higher than the corresponding pH_0 values in an acidic solution.
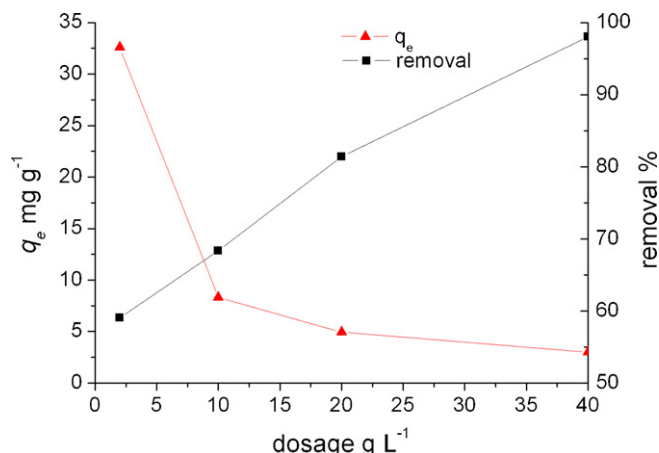

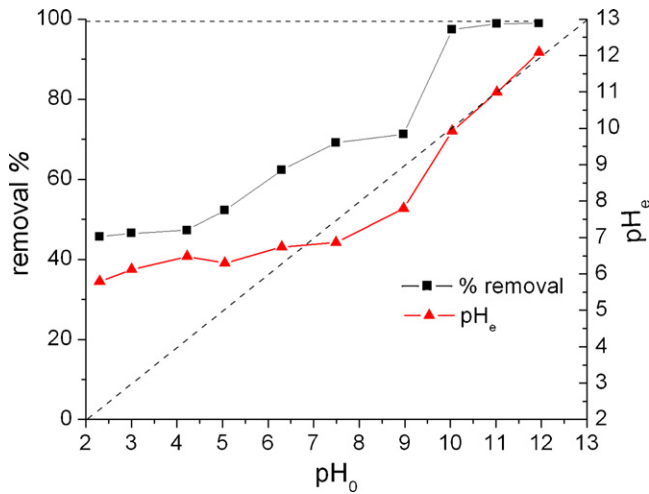**Fig. 1.** Effects of slurry concentrations on Cd(II) removal percentage.

Fig. 2. Variation of Cd(II) removal percentage with varied initial pHs.

While under very strong alkaline conditions, the equilibrium pH_e had no change when compared with the initial pH value.

3.4. Isothermal adsorption kinetics

Fig. 3 shows the variation of q_t of Cd(II) on loess with reaction time. The adsorption amount of Cd(II) on loess reaches a relatively high value within a fairly short time period (i.e., less than 1 h) and then slowly increases until it reaches a plateau after 1440 min. The unit adsorption amount appears to be higher when the initial solute concentration is larger during reaction. The test data were further analyzed using three kinetic models (i.e., pseudo-first order kinetics, pseudo-second order kinetics and intraparticle diffusion model). The predicted parameters are shown in Table 2. The pseudo-second order kinetics best-fit the test data with the highest correlation coefficients. There was a slight decrease in the rate constant k_2 from 3.81×10^{-3} to 3.66×10^{-3} g mg^{-1} min^{-1} when increasing the initial Cd(II) concentration from 50 to 100 mg L^{-1}. This implies that the solution with smaller solute concentration is likely to reach equilibrium in a shorter time period.

The test data fit with the intraparticle diffusion model showed a correlation coefficients higher than 0.942. This indicated that the adsorption of Cd(II) is dominated by gradual internal diffusion inside the micro pores. This phenomenon has been previously observed for Cu(II) and Zn(II) adsorption on loess [28,29].
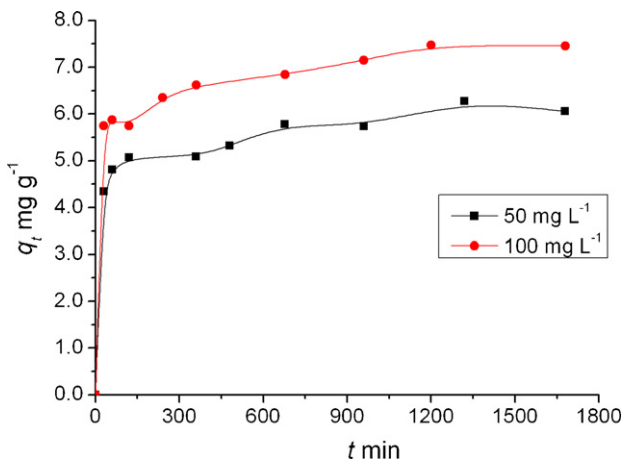

Fig. 3. Test data of adsorption kinetics.

Table 2
Predicted kinetic constants for Cd(II) adsorption on loess.

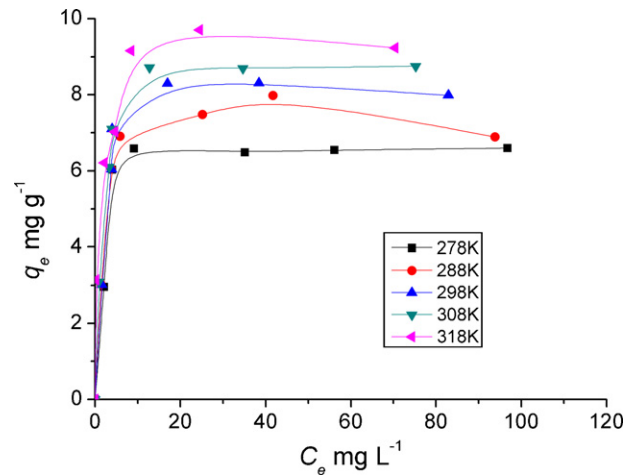|	C_0 (mg L^{-1})	
	50	100
Pseudo-first order kinetics		
q_e (mg g^{-1})	5.57	6.75
k_1 ($\times 10^{-3}$ min^{-1})	44.59	55.70
R	0.970	0.966
Pseudo-second order kinetics		
q_e (mg g^{-1})	6.21	7.56
k_2 ($\times 10^{-3}$ g mg^{-1} min^{-1})	3.81	3.66
R	0.998	0.999
Intraparticle diffusion model		
k_i (mg g^{-1} min$^{-1/2}$)	0.048	0.054
C	4.31	5.43
R	0.942	0.977

Fig. 4. Isotherms of Cd(II) adsorption on loess.

3.5. Adsorption isotherms and effect of temperature

Fig. 4 shows adsorption isotherms of Cd(II) on loess at different temperatures. The unit adsorption of Cd(II) on loess shows a gradual ascending trend and eventually achieved a maximum adsorption amount with an increase equilibrium solute concentration. Three general isothermal adsorption models including the Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) models were used to evaluate the test data and to interpret the possible adsorption mechanism. The predicted isothermal constants for Cd(II) adsorption on loess are listed in Table 3. The Langmuir model was found to show the best-fit to the test data based on calculated correla-

Table 3
Predicted isothermal constants for Cd(II) adsorption on loess.

	278 K	288 K	298 K	308 K	318 K
Langmuir model					
Q (mg g^{-1})	6.68	7.03	8.17	8.90	9.37
b (L mg^{-1})	0.913	−3.032	1.073	0.922	1.668
R	0.999	0.997	0.999	0.999	0.999
Freundlich model					
K_F (mg g^{-1})	3.80	4.02	4.05	4.26	4.87
n	6.900	5.937	5.067	4.747	4.951
R	0.695	0.759	0.772	0.865	0.927
D-R model					
q_m (mg g^{-1})	11.17	13.93	17.22	19.27	19.32
k (mol^2 kJ^{-2})	0.0016	0.0017	0.0018	0.0018	0.0015
E (kJ mol^{-1})	−17.85	−16.30	−16.57	−16.90	−18.57
R	0.724	0.796	0.803	0.898	0.955
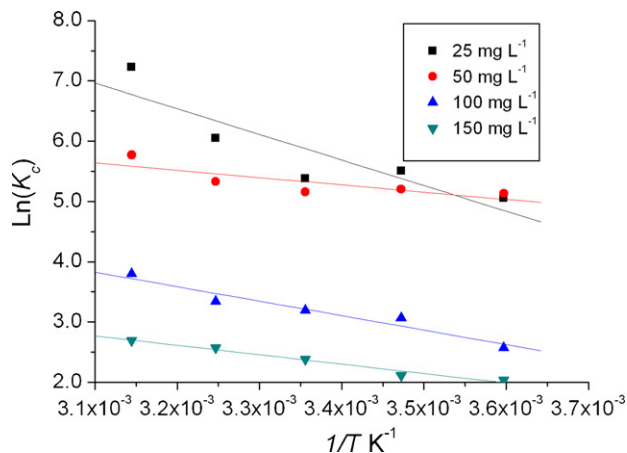
Fig. 5. Linear fit of thermodynamics for Cd(II) adsorption on loess.

Table 4
Thermodynamics parameters for Cd(II) adsorption on loess.

C_0 (mg L^{-1})	T (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	R
25	278	−11.69			
	288	−13.18			
	298	−13.33	35.34	167.45	0.892
	308	−15.50			
	318	−19.11			
50	278	−11.87			
	288	−12.46			
	298	−12.78	10.04	78.00	0.818
	308	−13.65			
	318	−15.26			
100	278	−5.95			
	288	−7.34			
	298	−7.90	19.97	93.70	0.970
	308	−8.55			
	318	−10.04			
150	278	−4.71			
	288	−5.05			
	298	−5.90	12.96	63.18	0.986
	308	−6.58			
	318	−7.11			

tion coefficients. The correlation coefficients for linear curves with both the Freundlich isotherm and the D-R models became larger and came closer to 1.00 when temperatures increased from 278 to 318 K. This implies that the Freundlich and D-R models are more appropriate under relatively high temperature conditions.

Based on the analysis with the Langmuir isotherm model, the maximum Cd(II) adsorption capacities of loess were estimated to be 6.68, 7.03, 8.17, 8.90 and 9.37 mg g^{-1} at temperatures ranging from 278, 288, 298, 308 and 318 K, respectively. The increasing temperature contributes to improved adsorption capacity. The adsorption capacities estimated by the D-R isotherm were 11.17, 13. 93, 17.22, 19.27 and 19.32 mg g^{-1} at temperatures ranging from 278, 288, 298, 308 and 318 K, respectively. These values are considerably higher than those obtained with the Langmuir model. This phenomenon may be due to the inherent assumption in the D-R model that all micro/macropores are filled with solute. However, this ideal state is difficult to realize in practice. The absolute values of estimated free adsorption energy were basically a little more than 16 kJ mol^{-1}, implying a chemisorption type that the chemical bond between loess and Cd(II) plays an important role.

3.6. Thermodynamics

The thermodynamic behavior of Cd(II) adsorption on loess was evaluated using the following equations:

$$\Delta G^0 = -RT \ln K_c \quad (10)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (11)$$

where K_c is the distribution coefficient of the solute between the adsorbent and the solution in equilibrium (q_e/C_e), R the ideal gas constant, T the temperature (K), ΔH^0 the change of enthalpy, ΔS^0 the change of entropy and ΔG^0 is the change of Gibbs' free energy. Eqs. (10) and (11) can be written in a linearized form between K_c and $1/T$ as

$$\ln(K_c) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (12)$$

The change of enthalpy (ΔH^0) and entropy (ΔS^0) were determined from the slope and intercept of the linearized curves as shown in Fig. 5 fitted with Eq. (12). The initial solute concentration had a great effect on the thermodynamic parameters as can be seen from Table 4. The calculated change of Gibbs' free energy decreased along with an increasing reaction temperature at a fixed initial solute concentration. Moreover, the change of Gibbs' free energy was negative at initial solute concentrations ranging from 25 to 150 mg L^{-1}, indicating that the adsorption process was spontaneous

in the range of temperature from 278 K to 318 K. With increasing initial Cd(II) concentration, the change of Gibbs' free energy for Cd(II) adsorption on loess decreased under constant temperature conditions. The change of enthalpy was 35.34, 10.04, 19.97, and 12.96 kJ mol^{-1} and the change of entropy was 167.45, 78.00, 93.70 and 63.18 J mol^{-1} K^{-1} when the initial Cd(II) concentration increased from 25 to 50, 100 and 150 mg L^{-1} respectively, implying an endothermic character to the adsorption process and increasing disorder in the system.

3.7. Discussion of the mechanisms involved

Fig. 6(a) shows the XRD spectra of original loess and Cd(II) loaded loess with different initial solute concentration, i.e., 25, 50 and 100 mg L^{-1} and (b) shows the partial enlarged detail. The main minerals in loess are quartz, calcite, albite, goethite and kaolinite as determined from the characteristic bands on the XRD spectra. New patterns were observed at $2\theta = 27.40°$, 27.47°, 27.70°, 28.12° and 30.46° compared with original loess sample, however, the patterns at $2\theta = 24.84°$ and 34.36° disappeared when the loess was loaded with Cd(II). The patterns at $2\theta = 27.40°$ can be attributed to CdSiO$_3$, and at $2\theta = 28.12°$ the patterns can be attributed to either CdSiO$_3$ or CdAl$_2$(SiO$_4$)$_2$ according to the MDI Jade software. Cadmium ions could react with aluminum silicate minerals in loess soil to form CdSiO$_3$. The formation of CdAl$_2$(SiO$_4$)$_2$ can be attributable to surface complexes between Cd(II) and the kaolinite mineral. The reaction equations can be written as

$$\equiv SOH + Cd^{2+} \rightarrow \equiv SOCd^+ + H^+ \quad (13)$$

where S denotes the clay mineral constituents in the soil.

Yee [35] studied the adsorption characteristics of quartz with respect to Cd(II) and thought that weak protonation and deprotonation reactions of the silanol group occurred on the surface of quartz. Then cadmium ions can be absorbed in the form of surface complex adsorption:

$$SiOH + Cd^{2+} \rightarrow SiOCd^+ + H^+ \quad (14)$$
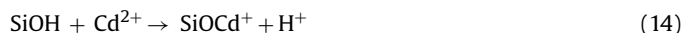
The reaction was weak and the stability constant for this equation was 10$^{-6.09}$. According to the pH-edge curves by Yee [35], Cd(II) whose initial concentration was 0.089 mg L^{-1} was absorbed on the surface of quartz when pH > 7.0, and the removal percentage was only 10% at a pH = 8.0. This phenomenon is not sufficient to explain
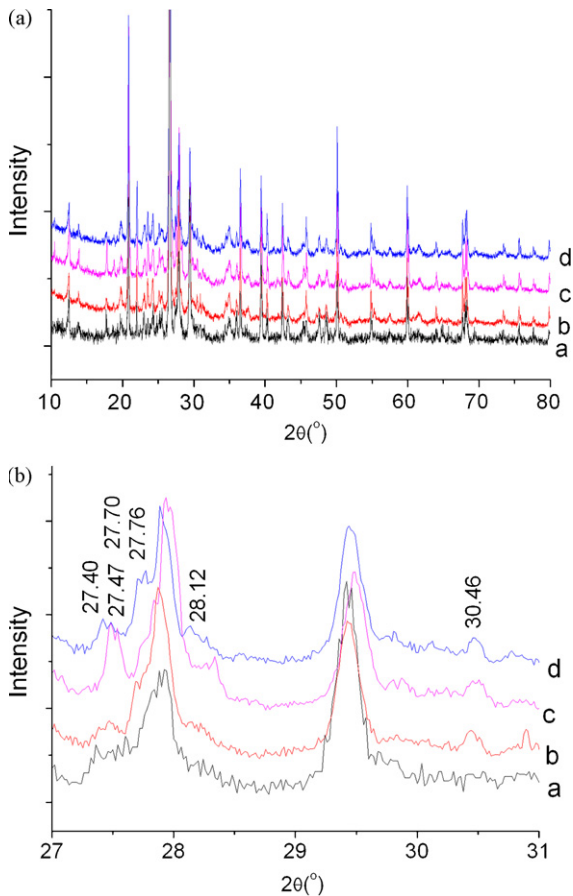
Fig. 6. X-ray diffraction (XRD) spectra of loess and Cd(II) loaded loess. (a) Loess, (b) $C_0 = 25\,mg\,L^{-1}$, (c) $C_0 = 50\,mg\,L^{-1}$, and (d) $C_0 = 100\,mg\,L^{-1}$.

the test results in this paper. Thus, it could be rationalized that aluminum silicate minerals reacted with Cd(II) to form $CdSiO_3$.

Fig. 7 shows the FT-IR spectra of loess and Cd(II) loaded loess with different initial solute concentration, i.e., 25, 50 and $100\,mg\,L^{-1}$. The IR spectrophotometer covered the range from 4000 to $400\,cm^{-1}$. The change of surface functional groups after being loaded with Cd(II) could be seen from the FT-IR spectra.

The absorption bands at 3620 and $1032\,cm^{-1}$ are characteristic of hydroxyl group and Si–O group respectively which can be
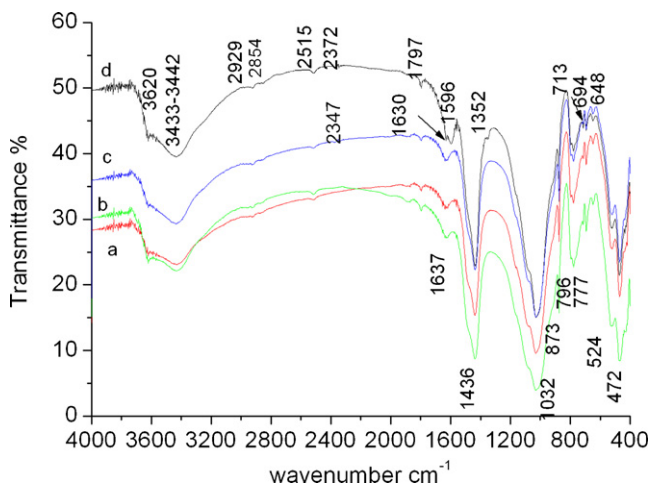

Fig. 7. FT-IR spectra of loess and Cd(II) loaded loess. (a): $C_0 = 25\,mg\,L^{-1}$, (b) $C_0 = 50\,mg\,L^{-1}$, (c) $C_0 = 100\,mg\,L^{-1}$, and (d) loess.
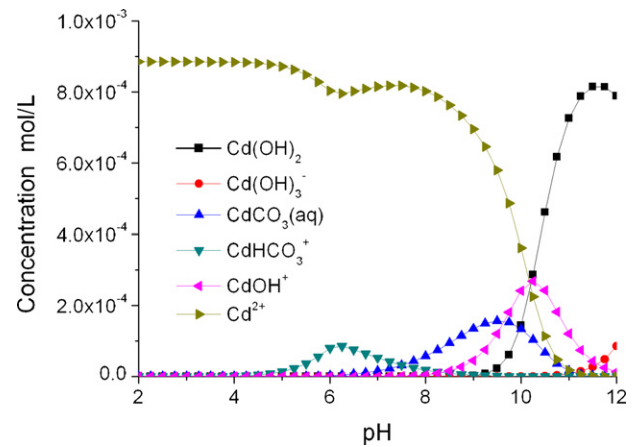

Fig. 8. Species distribution of Cd(II) in the presence of calcite (conditions include: 1.0 atm; 25 °C; $100\,mg\,L^{-1}$ $Cd(NO_3)_2$; $0.02\,mol\,L^{-1}$ calcite).

assigned to clay minerals in loess [36,37]. These bands had no obvious differences indicating that these sites have no contribution to adsorption of Cd(II) on loess.

The broad bands at 3433–3442 and bands at $1630–1637\,cm^{-1}$ are assigned to the stretching vibration and bending stretching of sorbed water. There was no change in the intensities of such bands. Although measures were taken to keep samples dried during the experiment, perhaps some potassium bromide still hydrolyzed in air to bring some water in these species.

The weak absorption bands at 2929 and $2854\,cm^{-1}$ are related to CH stretching vibration [38]. These bands existed in loess and all Cd(II) loaded loess species, indicating that this functional group has no positive effect on adsorption of Cd(II) on loess.

The absorption bands at 2515, 1797, 1436, 873 and $713\,cm^{-1}$ were related to calcite, and the absorption bands at 796, 777, 694, 524 and $472\,cm^{-1}$ were related to quartz. Both calcite and quartz were inherent material in loess and have little effect on Cd(II) adsorption.

The weak absorption bands at 2372 and $2346\,cm^{-1}$ existing in loess disappeared at $C_0 = 25$ and $50\,mg\,L^{-1}$ and then appeared again at $C_0 = 100\,mg\,L^{-1}$. These bands correspond to atmospheric carbon dioxide. Some CO_2 might be dissolved into water and then absorbed into the micropores of loess causing interference.

The absorption bands at 1596 and $1352\,cm^{-1}$ appeared in loess but disappeared in Cd(II) loaded loess. These bands can be regarded as bending vibrations of the carboxyl group [39] which are originally contained in loess in the form of organic matter. The interaction between Cd(II) and the carboxyl group could be

$$-COOH + Cd^{2+} \rightarrow -COOCd^+ + H^+ \qquad (15)$$
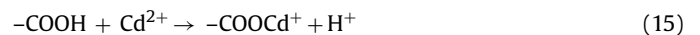
In addition, as can be seen in Fig. 2, the initial solution pH value has a strong relationship to the uptake of Cd(II) on loess. At pH values close to zero charge ($pH_{pzc} = 2.82$), loess exhibited a low affinity for Cd(II). This phenomenon was previously reported [40]. It has been reported that the carboxyl functional groups of organic matter in loess soil played a significant role in the uptake of Cd(II) and the sorption at lower pH depended mainly on the protonation or deprotonation of these carboxyl groups [41], which is also in agreement with Eq. (15).

The patterns of $CdCO_3$ were not found in XRD spectra indicating that Cd(II) adsorption has little to do with calcite. This is different from Cu(II) and Pb(II) adsorption on loess. The Visual MINTEQ was used to analyze the species distribution of Cd(II) in the presence of calcite and Cd(II), and the results are shown in Fig. 8. Cd(II) combined with HCO_3^- to form $CdHCO_3^-$ when the $5.0 < pH < 9.0$, and Cd(II) started to combine with CO_3^{2-} to generate precipitation at

Table 5
Adsorption capacities of Cd(II) on different adsorbents.

Adsorbents	Cd(II) adsorption capacity (mg g^{-1})	References
Eskisehir Esentepe soil	5.72	[43]
Kaolin	1.46	[44]
Hyper-Rhodic Ferralsol	2.05	[26]
Na-bentonite	28.34	[19]
Chinese loess	9.33	Present study

pH = 6.5–7.0. 17.6% of Cd(II) was precipitated in the form of $CdCO_3$ at a pH = 9.5. Cd(II) also combined with OH^- to form $CdOH^+$ when the pH > 8.5. The amount of $CdOH^+$ reached a peak at a pH = 10.25, and then gradually decreased until it disappeared at a pH = 12.0. Cd(II) was precipitated in the form of cadmium hydroxide when the pH > 9.5 and Cd(II) precipitation was as high as 91.46%.

The pH of a loess–Cd(II) solution mixture was less than 7.0 without any pH adjustment. According to the species distribution calculations, it is hard to form cadmium carbonate under such conditions as confirmed by the XRD spectra analysis.
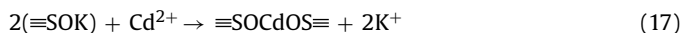
Apart from the effect of calcite, the mineral components responsible for Cd(II) adsorption is clear: quartz, kaolinite, goethite, etc. The adsorption of Cd(II) on goethite could be written as [35]
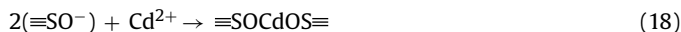
$$FeOOH + Cd^{2+} \rightarrow FeOOCd^+ + H^+ \quad (16)$$
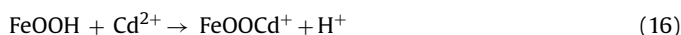
The stability constant of the above equation is $10^{0.47}$, which could be effective to adsorb Cd(II) from solution to the solid phase.

The effect of pH on Cd(II) adsorption on loess can be divided into three stages. The Cd(II) removal efficiency remained as 45.6–47.2% when the $pH_0 < 4.2$ and gradually increased to 71.2% as pH_0 increased to 8.97. At the third stage, the Cd(II) removal efficiency increased rapidly until Cd(II) was nearly completely adsorbed with increasing pH_0.

The stable adsorption efficiency at pH < 4.2 implies that some constituents in loess have a strong affinity for Cd(II) and are not affected by the solution pH. These constituents could have high stability and strong surface activity such as natural organic matter in loess. The further gradual adsorption process bears a relationship to the clay minerals (e.g., kaolinite). Angove et al. [42] found that the adsorption of Cd(II) by kaolinite occurred at a pH > 4.0. This observation was confirmed by the adsorption results in the present study. In addition, under such acidic condition at pH near pH_{pzc}, Cd(II) can be immobilized on the loess soil surface to form outer sphere complexes by exchanging background electrolyte cations with cadmium ions or bonding to permanent-charge sites, and the adsorption process can be expressed as

$$2(\equiv SOK) + Cd^{2+} \rightarrow \equiv SOCdOS \equiv + 2K^+ \quad (17)$$

and

$$2(\equiv SO^-) + Cd^{2+} \rightarrow \equiv SOCdOS \equiv \quad (18)$$

With an increase of solution pH, the raise of the negative variable charges on loess surface can lead to the increase of Cd(II) adsorption. Cd(II) started to form precipitate at higher initial pH values (i.e., pH > 8.97), suggesting that this adsorption stage was mainly caused by chemical precipitation.

The Cd(II) adsorption capacities of several reported specific soil adsorbents are listed in Table 5. The Cd(II) adsorption capacities of kaolin, Hyper-Rhodic Ferralsol, Eskisehir Esentepe soil and Na-bentonite were 1.46, 2.05, 5.72 and 28.34 mg g^{-1}, respectively. Chinese loess got a higher capacity than kaolin, Hyper-Rhodic Ferralsol and Eskisehir Esentepe soil by contrast, however, Na-bentonite had the highest Cd(II) adsorption capacity. The Na-bentonite was a clay mineral in which Na replaced Ca in montmorillonite clay. The clays carried a net negative charge due to the broken bonds around the edges of the silica–alumina units that

would give rise to unsatisfied charges, thus, the adsorption capacity of Na-bentonite was largely improved. Taking into account of the economic cost, the wide distribution of Chinese loess makes it an alternative adsorbent for Cd(II) removal from wastewater.

4. Conclusions

(1) Chinese loess is effective for Cd(II) removal from aqueous solutions with the adsorption capacity as 9.37 mg g^{-1} determined by Langmuir model. The adsorption was surface heterogeneous analyzed by Freudlich equation, and was a chemisorption mode suggested by D-R model.
(2) Kinetic studies showed that the Cd(II) adsorption followed pseudo-second order kinetics, and the process was mainly gradual internal diffusion.
(3) The factors including slurry concentration, initial solution pH, initial solute concentration and temperature were found to have great effects on the adsorption capacity of loess.
(4) The thermodynamic study showed that the adsorption process was spontaneous and endothermic and the system disorder increased in the duration.
(5) The natural organic matter is mainly responsible for Cd(II) removal at pH < 4.2, clay minerals contributing to the further gradual adsorption process and chemical precipitation dominating the adsorption stage at pH > 8.97 by the analysis of XRD, FT-IR spectra and Visual MINTEQ.

References

[1] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, Bioresour. Technol. 76 (2001) 63–65.
[2] M. Mohapatra, S. Anand, Studies on sorption of Cd(II) on Tata chromite mine overburden, J. Hazard. Mater. 148 (2007) 553–559.
[3] E.I. Unuabonah, K.O. Adebowale, B.I. Olu-Owolabi, L.Z. Yang, L.X. Kong, Adsorption of Pb(II) and Cd(II) from aqueous solutions onto sodium tetraborate-modified Kaolinite clay: equilibrium and thermodynamic studies, Hydrometallurgy 93 (2008) 1–9.
[4] K. Bedoui, I. Bekri-Abbes, E. Srasra, Removal of cadmium(II) from aqueous solution using pure smectite and Lewatite S 100, the effect of time and metal concentration, Desalination 223 (2008) 269–273.
[5] C. Namasivayam, K. Ranganathan, Removal of Pb(II), Cd(II) and Ni(II) and mixture of metal ions by adsorption onto waste Fe(III)/Cr(III) hydroxide and fixed bed studies, Environ. Technol. 16 (1995) 851–860.
[6] L. Nouri, I. Ghodbane, O. Hamdaoui, M. Chiha, Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran, J. Hazard. Mater. 149 (2007) 115–125.
[7] Y.S. Ho, G. McKay, Batch lead(II) removal from aqueous solution by peat: equilibrium and kinetics, Trans. Chem. Eng. B 77 (1999) 165–173.
[8] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents, Adv. Environ. Res. 6 (2002) 533–540.
[9] C. Cooper, R. Burch, Mesoporous materials for water treatment processes, Water Res. 33 (1999) 3689–3694.
[10] A. Seco, P. Marzal, C. Gabaldon, A. Aucejo, Effect of pH, cation concentration and sorbent concentration on cadmium and copper removal by a granular activated carbon, J. Chem. Technol. Biotechnol. 74 (1999) 911–918.
[11] A.M. Youssef, T. El-Nabarawy, S.E. Samra, Sorption properties of chemically-activated carbons. 1. Sorption of cadmium(II) ions, Colloid Surf. A: Physicochem. Eng. Aspects 235 (2004) 153–163.
[12] H.J. Fan, P.R. Anderson, Copper and cadmium removal by Mn oxide-coated granular activated carbon, Sep. Purif. Technol. 45 (2005) 61–67.
[13] V.C. Srivastava, I.D. Mall, I.M. Mishra, Adsorption of toxic metal ions onto activated carbon: study of sorption behaviour through characterization and kinetics, Chem. Eng. Proc. 47 (2008) 1269–1280.

[14] C.R. Collins, K.V. Ragnarsdottir, D.M. Sherman, Effect of inorganic and organic ligands on the mechanism of cadmium sorption to goethite, Geochim. Cosmochim. Acta 63 (1999) 2989–3002.
[15] G. Mustafa, B. Singh, R.S. Kookana, Cadmium adsorption and desorption behaviour on goethite at low equilibrium concentrations: effects of pH and index cations, Chemosphere 57 (2004) 1325–1333.
[16] F. Barbier, G. Duc, M. Petit-Ramel, Adsorption of lead and cadmium ions from aqueous solution to the montmorillonite/water interface, Colloid Surf. A: Physicochem. Eng. Aspects 166 (2000) 153–159.
[17] A. Battaglia, N. Calace, E. Nardi, B.M. Petronio, M. Pietroletti, Paper mill sludge–soil mixture: kinetic and thermodynamic tests of cadmium and lead sorption capability, Microchem. J. 75 (2003) 97–102.
[18] A.M. EI-Kamash, A.A. Zaki, M.A. EI Geleel, Modeling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A, J. Hazard. Mater. B 127 (2005) 211–220.
[19] G.P.C. Rao, S. Satyaveni, A. Ramesh, K.S.N. Murthy, N.V. Choudary, Sorption of cadmium and zinc from aqueous solutions eolite 4A, zeolite 13X and bentonite, J. Environ. Manage. 81 (2006) 265–272.
[20] S. Kocaoba, Y. Orhan, T. Akyuz, Kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite, Desalination 214 (2007) 1–10.
[21] M. Shirvani, H. Shariatmadari, M. Kalbasi, F. Nourbakhsh, B. Najafi, Sorption of cadmium on palygorskite, sepiolite and calcite: equilibria and organic ligand affected kinetics, Colloid Surf. A: Physicochem. Eng. Aspects 287 (2006) 182–190.
[22] M. Shirvani, H. Shariatmadari, M. Kalbasi, F. Nourbakhsh, B. Najafi, Sorption–desorption of cadmium in aqueous palygorskite, sepiolite, and calcite suspensions: isotherm hysteresis, Chemosphere 65 (2006) 2178–2184.
[23] Z. Elouear, J. Bouzid, N. Boujelben, M. Feki, F. Jamoussi, A. Montiel, Heavy metal removal from aqueous solutions by activated phosphate rock, J. Hazard. Mater. 156 (2008) 412–420.
[24] H.B. Bradl, Adsorption of heavy metal ions on soils and soils constituents, J. Colloid Interface Sci. 277 (2004) 1–18.
[25] D.M. Zhou, Y.J. Wang, L. Cang, X.Z. Hao, X.S. Luo, Adsorption and cosorption of cadmium and glyphosate on two soils with different characteristics, Chemosphere 57 (2004) 1237–1244.
[26] J. Liang, R.K. Xu, X. Jiang, Y. Wang, A.Z. Zhao, W.F. Tan, Effect of arsenate on adsorption of Cd(II) by two variable charge soils, Chemosphere 67 (2007) 1949–1955.
[27] C. Appel, L.Q. Ma, R.D. Rhue, W. Reve, Sequential sorption of lead and cadmium in three tropical soils, Environ. Pollut. 155 (2008) 132–140.
[28] X.W. Tang, Z.Z. Li, Y.M. Chen, Behaviour and mechanism of Zn(II) adsorption on Chinese loess at dilute slurry concentrations, J. Chem. Technol. Biotechnol. 83 (2008) 673–682.
[29] X.W. Tang, Z.Z. Li, Y.M. Chen, Y. Wang, Removal of Cu(II) from aqueous solution by adsorption on Chinese quarternary loess: kinetics and equilibrium studies, J. Environ. Sci. Health A 43 (7) (2008) 779–791.
[30] J.M. Sun, Z.L. Ding, Deposits and soils of the past 130,000 years at the desert-loess transition in northern China, Quaternary Res. 50 (1998) 148–156.
[31] D.D. Do, Adsorption Analysis: Equilibrium and Kinetics, Imperial College Press, London, 1998.
[32] Y.S. Ho, G. McKay, A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents, Trans. Inst. Chem. Eng. B 76 (1998) 332–340.
[33] Z.Z. Li, X.W. Tang, Y.M. Chen, Y. Wang, Sorption behavior and mechanism of Pb(II) on Chinese loess, J. Environ. Eng.-ASCE 135 (2009) 58–67.
[34] X.W. Tang, Z.Z. Li, Y.M. Chen, Adsorption behavior of Zn(II) on calcinated Chinese loess, J. Hazard. Mater. 161 (2009) 824–834.
[35] N. Yee, Experimental studies of adsorption in bacteria–water–rock systems: implications for heavy metal transport in the subsurface, Ph.D. Dissertation, University of Notre Dame, Indiana, 2001.
[36] I.S. Ismael, M.K. Abd EI-Rahman, M.S. Hassan, Influence of vibration grinding and calcination on the physico-chemical properties of Egyptian kaolinite, Miner. Petrol. 67 (1999) 45–57.
[37] M.F. La Russa, G. Barone, P. Mazzoleni, A. Pezzino, V. Crupi, D. Majolino, Characterisation and differentiation of pigments employed on the facade of "Noto's Valley monuments (Sicily), Appl. Phys. A 92 (2008) 185–190.
[38] H. Smaoui, H. Guermazi, S. Agnel, Y. Mlik, A. Toureille, Structural changes in epoxy resin polymer after heating and their influence on space charges, Polym. Int. 52 (2003) 1287–1293.
[39] M. Biswas, J.D. Masuda, S. Mitra, Hydrothermal synthesis, crystal structure and magnetic properties of a new one-dimensional polymer, Struct. Chem. 18 (2007) 9–13.
[40] R. Naidu, N.S. Bolan, R.S. Kookana, K.G. Tiller, Ionic strength and pH effects on surface charge and Cd sorption characteristics of soils, J. Soil Sci. 45 (1994) 419–429.
[41] J.T. Matheickal, Q.M. Yu, G.M. Woodburn, Biosorption of cadmium(II) from aqueous solutions by pre-treated biomass of marine alga DurvillAea potatorum, Water Res. 33 (1999) 335–342.
[42] M.J. Angove, B.B. Johnson, J.D. Wells, Adsorption of cadmium(II) on kaolinite, Colloid Surf. A: Physicochem. Eng. Aspects 126 (1997) 137–147.
[43] Y. Aşçl, M. Nurbaş, Y.S. Açlkel, A comparative study for the sorption of Cd(II) by soils with different clay contents and mineralogy and the recovery of Cd(II) using rhamnolipid biosurfactant, J. Hazard. Mater. 154 (2008) 663–673.
[44] Y. Aşçl, M. Nurbaş, Y.S. Açlkel, Sorption of Cd(II) onto kaolin as a soil component and desorption of Cd(II) from kaolin using rhamnolipid biosurfactant, J. Hazard. Mater. B 139 (2007) 50–56.