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# Study on the adsorption of $Pb^{2+}$ from aqueous solution by D113-III resin

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#### ABSTRACT

The adsorption and desorption behaviors of Pb<sup>2+</sup> on D113-III resin were investigated with various chemical methods. The influence of operational conditions such as contact time, initial concentration, initial pH of solution, and temperature on the adsorption of Pb<sup>2+</sup> has also been examined. The results show that the maximum uptake capacity of Pb<sup>2+</sup> is 476.2 mg/g on D113-III resin at 298 K at pH=4.5 in HAc–NaAc medium. The adsorption of Pb<sup>2+</sup> fitted the Langmuir isotherm better than the Freundlich isotherm. And kinetics on the adsorption of Pb<sup>2+</sup> has been studied. The apparent activation energy  $E_a$  and adsorption rate constant  $k_{298}$  values are 5.22 kJ/mol and  $5.82 \times 10^{-5} \text{ s}^{-1}$ , respectively. The data of thermodynamic parameters whose  $\Delta S$  value is 0.255 kJ/mol K and  $\Delta H$  value is 45.29 kJ/mol indicate the endothermic nature of the adsorption process. And the negative value of  $\Delta G$  showed that the adsorption of Pb<sup>2+</sup> ions onto D113-III resin was spontaneous. The Thomas model was applied to experimental data obtained from column adsorption experiments. Finally, Pb<sup>2+</sup> can be eluted by using 0.5 mol/L HCl solution and the resin can be regenerated and reused. And the sorption of Pb<sup>2+</sup> on D113-III resin from simulated seawater is studied.

Keywords: D113-III resin; Pb<sup>2+</sup>; Adsorption; Sorption kinetics; Thermodynamic

#### 1. Introduction

Heavy metal ions such as Pb, Cd, Hg, Cr, Ni, Zn, and Cu are non-biodegradable; they can be toxic and carcinogenic even at very low concentrations. In addition, they tend to accumulate in living organisms, causing various diseases and disorders [1], hence, usually pose a serious threat to the environmental and public health [2]. Due to industrial activity and technological development, releases of heavy metal ions to the environment are on the rise [3]. Among those heavy metal ions, Pb<sup>2+</sup> is extremely toxic, the permis-

sible limit for which is no more than 1 mg/L (total lead). When accumulated at high levels, Pb<sup>2+</sup> can generate serious health problems. Pb<sup>2+</sup> poisoning causes damage to liver, kidney, and reduction in hemoglobin formation, mental retardation, infertility, and abnormalities in pregnant women [4,5]. Thus, to remove the hazardous Pb<sup>2+</sup> ion from industrial wastewater is the major course that cannot be ignored.

For years, many methods have been developed to remove heavy metals from the effluents including chemical precipitation, reverse osmosis, electrodialysis, and adsorption on several low-cost adsorbents such as activated carbons [6–9]. However, many problems still remain unsolved, for example, the low

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durability and unsatisfactory selectivity of the electrodialysis membrane [10]. Alternatively, ion exchange adsorption was chose as one of the most effective and common methods for this purpose because of its simplicity, facility, and the characteristic that it can be easily recovered and reused by the regeneration operation [11,12]. Ion exchange resins with specific functional groups, like iminodiacetic acid (IDA). aminophosphonic acid, and amidoxime, have been widely used to recover heavy metals from wastewaters [13]. They are very powerful because the functional groups can form coordination bonds with many heavy metals. It is often the particular kind of heavy metal that is selectively removed from wastewater.

D113-III resin, as a typical ion exchange resin, possesses the advantages of polymeric adsorbent such as the relatively low cost and effectiveness in removing heavy metal ions [14]. D113-III resin is a polymeric material containing a functional group (-COOH). It not only has proton that can exchange with cation, but also oxygen atom that can coordinate directly with metal ions. Its principal characteristics are great chemical and physical stability, high exchange capacity, and good ability of regeneration so it can be very suitable to remove heavy metals from water and industrial wastewater. Study of the adsorption of Pb<sup>2+</sup> on D113-III resin is carried out in the form of batch and column processes. Factors affecting adsorption, such as contact time, initial pH of solution, initial concentration of Pb<sup>2+</sup>, and temperature, have also been examined. The experimental results present a new combined operating mode of resin adsorption with desalination of seawater system.

#### 2. Experimental

#### 2.1. Materials and instruments

D113-III resin was supplied by Jiangsu Suqing Water Treatment Engineering Group Co., Ltd, and the properties are shown in Table 1. Acetic acid–sodium acetate buffer solutions with pH 3.0–5.0 were prepared from the acetic acid (HAc) and sodium acetate (NaAc) solutions. All other chemicals were of analytical grade and purified water was used throughout. The Pb<sup>2+</sup> was determined with Shimadzu UV-2550 UV–vis spectrophotometer. Mettler Tolledo Delta 320 pH Meter was used for measuring the pH of solutions. The sample was shaken in the DSHZ-300A temperature constant shaking machine and the THZ-C-1 temperature constant shaking machine. The water used in the present work was purified using Molresearch analysis-type ultra-pure water machine.

 Table 1

 General description and properties of resin

Items	Properties
Resin	D113-III resin
Functional group	-COOH
Volume capacity (m mol/ml)	4.3
Mass capacity (m mol/g)	≥11.0
Moisture (%)	45–52
Bulk density (g/ml)	0.74-0.80
Specific density (g/ml)	1.14-1.20
Particle size (≥95%)	0.315–1.25 mm
Whole bead after osmotic attrition (%)	≥95

#### 2.2. Adsorption experiments

Experiments were conducted in a certain range of pH, temperature, and contact time. The operation for the removal of  $Pb^{2+}$  is usually carried out in batch vessels and glass columns [15].

Batch experiments were performed under kinetic and equilibrium conditions. A desired amount of treated D113-III resin was weighed and added into a conical flask, in which a desired volume of buffer solution with pH 4.5 was added. After 24 h, a required amount of standard solution of Pb<sup>2+</sup> was put in. The flask was shaken in a shaker at constant temperature. The upper layer of clear solution was taken for analysis until adsorption equilibrium was reached. The procedure of kinetic tests was identical to that of the equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of Pb<sup>2+</sup> were similarly measured. Continuous flow adsorption experiments were conducted in a vertical glass column filled with D113-III resin (the diameter height ratio was 1/6). At the bottom of the column, a stainless sieve was attached followed by a layer of cotton wool. The particles were dropped in from the top of the column. The Pb<sup>2+</sup> ion solution was fed from the top at a fixed flow rate. The Pb<sup>2+</sup> solutions at the outlet of the column were collected periodically and analyzed for the Pb<sup>2+</sup> concentration using a UVvisible spectrophotometer at 570 nm. The flow through the column was continued till the inlet and outlet concentrations were equal. All the experiments were carried out at room temperature.

#### 2.3. Analytical method

A solution containing lower than  $75 \mu g$  of  $Pb^{2+}$  was accurately added into a 25 mL colorimetric tube, and then 2.0 mL xylenol orange visualization reagent and 10 mL hexamethylenetetramine the buffer solution were added. After the addition of deionized water to the mark of colorimetric tube, the absorbency was determined in a 1 cm colorimetric vessel at a wavelength of 570 nm and compared with the blank test. The adsorption capacity (Q) of Pb<sup>2+</sup> ions on D113-III resin was calculated with the following formula:

$$Q = \frac{C_{\rm o} - C_{\rm e}}{W} V. \tag{1}$$

The distribution coefficient (*D*) of  $Pb^{2+}$  ions between the aqueous phase and the solid phase can be directly obtained using:

$$D = \frac{C_{\rm o} - C_{\rm e}}{C_{\rm e}} \times \frac{V}{W},\tag{2}$$

where  $C_o$  (mg/mL) and  $C_e$  (mg/mL) are the initial and equilibrium Pb<sup>2+</sup> concentrations, respectively, *V*/ *W* is the ratio of the volume of metal solution (mL) to the amount of D113-III resin (g) in a batch.

#### 3. Results and discussion

#### 3.1. Influence of pH on the distribution coefficient for $Pb^{2+}$

The effect of initial pH on the adsorption process is presented in Fig. 1. The pH of the solution is an important factor in the adsorption process, which affects surface charge of the adsorbent and the degree of ionization and speciation of adsorbate [16]. As seen in Fig. 1, for Pb<sup>2+</sup>, the highest statically saturated sorption capacity was achieved at a pH of about 4.5 with HAc–NaAc. Above this pH a decrease in the sorption of metal ion was observed, and it can be deduced that



Fig. 1. Influence of pH on the distribution coefficient of  $Pb^{2+}$  (resin 15.0 mg,  $C_o = 10 \text{ mg}/30.0 \text{ mL}$ , T = 298 K, 100 rpm).

 $Pb^{2+}$  might have formed several hydrolysis products, which lead to the polymerizations [17]. Thus, optimum initial pH value of  $Pb^{2+}$  solution was chosen to be 4.5 and adsorption of  $Pb^{2+}$  ions on D113-III was studied at pH 4.5 for subsequent experiments.

#### 3.2. Adsorption isotherms

The adsorption data were analyzed to see whether the isotherm obeyed the Langmuir [18] and Freundlich [19] isotherm models. The linear forms of the Langmuir and Freundlich isotherms are represented by the following equations:

Langmuir isotherm:

$$\frac{C_{\rm e}}{Q_{\rm e}} = \frac{1}{Q_{\rm max}K_{\rm L}} + \frac{C_{\rm e}}{Q_{\rm max}} \tag{3}$$

Separation factor for Langmuir isotherm ( $R_L$ ):

$$R_{\rm L} = \frac{1}{1 + K_{\rm L} C_{\rm o}} \tag{4}$$

Freundlich isotherm:

$$\lg Q_{\rm e} = \lg K_{\rm F} + \frac{1}{n} \lg C_{\rm e},\tag{5}$$

where  $Q_e$  is the equilibrium Pb<sup>2+</sup> ions concentration on the adsorbent (mg/g),  $C_e$  is the equilibrium Pb<sup>2+</sup> ions concentration in solution (mg/mL),  $Q_{max}$  is the monolayer capacity of the adsorbent (mg/g), and  $K_L$ is the Langmuir constant that is related to the free energy of adsorption (mL/mg);  $K_F$  is Freundlich constant (mg/g) and *n* (dimensionless) is the heterogeneity factor.

The plots of  $C_e/Q_e$  vs.  $C_e$  (Langmuir) for the adsorption of Pb<sup>2+</sup> ions onto D113-III resin give a straight line of slope  $1/Q_{max}$  and intercept  $1/Q_{max}K_L$ (Fig. 2, Table 2); by plotting  $lgC_e$  vs.  $lgQ_e$  (Freundlich) to generate  $K_{\rm F}$  and *n* from the intercept and the slope (Fig. 3, Table 3), respectively. It is evident from these data that the adsorption capacity increased with an increase in the temperature. The adsorption of Pb<sup>2+</sup> ions onto D113-III resin fitted better to the Langmuir isotherm model than to the Freundlich isotherm model, as indicated by the  $R^2$  values. The Freundlich constant n is a measure of the deviation from linearity of the adsorption. The numerical values of n at equilibrium lay between 3.15 and 5.14, indicating that  $Pb^{2+}$ ions were favorably adsorbed by D113-III resin at all the studied temperatures [20].

Also the value of separation factor indicates the type of the isotherm and the nature of the adsorption



Fig. 2. Langmuir isotherm curve.

Table 2 Linearity relation of  $C_e/Q_e$  and  $C_e$ 

		•	
T (K)	Linearity relation of $C_e/Q_e$ and $C_e$	$R^2$	$Q_{\rm max}  ({ m mg}/{ m g})$
288	y = 0.0024x + 3E - 06	0.9941	416.7
298	y = 0.0021x + 1E - 06	0.9976	476.2
308	y = 0.0015x + 1E - 06	0.9981	666.7



Fig. 3. Freundlich isotherm curve.

Table 3		
Linearity	relation of $\lg Q_e$ and $\lg C_e$	

T (K)	Linearity relation of $\lg Q_e$ and $\lg C_e$	$R^2$	п
288	y = 0.3174x + 3.2724	0.9935	3.15
298	y = 0.1944x + 5.1066	0.9653	5.14
308	y = 0.3078x + 3.5315	0.9561	3.25

process. Considering the  $R_{\rm L}$  value, adsorption can be unfavorable  $(R_{\rm L}>0)$ , linear  $(R_{\rm L}=1)$ , favorable  $(0 < R_{\rm L} < 1)$ , or irreversible  $(R_{\rm L}=0)$  [21]. In our case, the  $R_{\rm L}$  value was found to be 0.00143 and shows favorable adsorption for Pb<sup>2+</sup> ions.

Figures show that the highest value of  $Q_{\text{max}}$  obtained at 298 K is 476.2 mg/g. Thus, a comparison of the maximum adsorption capacity of D113-III resin with those of some other adsorbents reported in the literatures is given in Table 4, [22–29], indicating that D113-III resin possesses a good capacity to remove Pb<sup>2+</sup> in aqueous solution. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups, and surface area.

## 3.3. Determination of adsorption rate constant and apparent activation energy

The influence of contact time on the adsorption of  $Pb^{2+}$  ions onto D113-III resins (Fig. 4) was investigated at various temperatures, i.e. 288, 298, and 308 K. It is easily seen that the amount of adsorption increased with increasing contact time. Further, the maximum adsorption was observed after 14 h, beyond which there was almost no further increase in the adsorption. Therefore, this interaction time could be very well taken as equivalent to the equilibrium time.

Adsorption kinetics curves were obtained for Pb<sup>2+</sup> on D113-III resins. The kinetics of adsorption can be described by the liquid film diffusion model [30], using the Brykina method [31]:

Table 4 Comparison of the maximum adsorption capacities of  $\mathrm{Pb}^{2+}$ 

Various adsorbents	Maximum adsorption capacity of Pb <sup>2+</sup> /(mg/g)
Moringa oleifera bark	34.6
Aspergillus versicolor	45.0
8-Hydroxy quinoline-immobilized bentonite	142.9
Pine cone activated carbon	27.5
Polypropylene–clinoptilolite composites	1.2
Modified typha angustifolia biomass	263.9
Chitosan-coated sand	12.3
Modified quebracho tannin resin	86.2
Modified Moringa oleifera tree leaves	209.54
D113-III resin	476.2



Fig. 4. Effect of contact time on adsorption (resin 30.0 mg,  $C_0 = 20.0 \text{ mg}/60.0 \text{ mL}$ ).

$$-\ln(1-F) = kt,\tag{6}$$

where *F* is the fractional attainment of equilibrium  $(F = Q_t/Q_e)$ , where  $Q_e$  and  $Q_t$  are the amounts of Pb<sup>2+</sup> ions adsorbed on the adsorbent at equilibrium and at various times, respectively; *k* is the adsorption rate constant. The experimental results accorded with the equation and a straight line were obtained by plotting  $-\ln(1-F)$  vs. *t* (Fig. 5). Therefore, the adsorption rate constant can be found from the slope of the straight line, which is  $k_{298 \text{ K}} = 5.82 \times 10^{-5} \text{ 1/s}$ . The correlation coefficient ( $R^2 = 0.9901$ ) was obtained via linear fitting. The other results are listed in Table 5.

According to the Boyd equation, it can be deduced from the linear relationship of  $-\ln(1-F)$  vs. *t* that the liquid film spreading was the predominating step of the adsorption process [32]. According to the Arrhenius equation [33]:



Fig. 5. Determination of adsorption rate constant (resin 30.0 mg,  $C_0 = 20.0 \text{ mg}/60.0 \text{ mL}$ ).

Table 5				
Adsorption	rate constants	under	various	temperatures

T (K)	Linearity relation of $-\ln(1-F)$ and $t$	$k \times 10^{-5} (1/s)$	$R^2$
288	y = 0.1919x - 0.0641	5.33	0.9922
298	y = 0.2096x - 0.0344	5.82	0.9901
308	y = 0.2211x + 0.0425	6.14	0.9900

$$\lg k = -E_{\rm a}/2.303RT + \lg A \tag{7}$$

where  $E_a$  is the Arrhenius activation energy for the adsorption process indicating the minimum energy that reactants must have for the reaction to proceed, *A* is the Arrhenius factor, *R* is the gas constant (8.314J/(mol K)), *k* is the adsorption rate constant, and *T* is the temperature. As can be observed in Fig. 6,  $E_a$  and A values can be estimated from the slope and intercept value of this plot lg *K* vs. 1/*T*, respectively. The correlation coefficient of the straight line  $R^2 = 0.9939$  was achieved. The apparent activation energy  $E_a$  was 5.22 kJ/mol, which could be considered as a low-energy barrier in this study. It can be deduced that the adsorption speed accelerated when the temperature rose within the scope of experimental temperature.

#### 3.4. Thermodynamic parameters

In any adsorption procedure, both energy and entropy considerations should be taken into account in order to determine which process will take place spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process. The amounts of Pb<sup>2+</sup> ions adsorbed at equilibrium at different temperatures, which are 288, 298,



Fig. 6. Relationship between  $\lg k$  and 1/T (resin = 30.0 mg,  $C_0 = 20.0 \text{ mg}/60.0 \text{ mL}$ ,).

and 308 K, have been examined to obtain thermodynamic parameters for the adsorption system.

Thermodynamic parameters, such as changes in the Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) associated to the adsorption process, were determined by using the following equations:

$$\lg D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{8}$$

$$\Delta G = \Delta H - T \Delta S,\tag{9}$$

where R (8.314J/molK) is the gas constant and T is the absolute temperature.

 $\Delta H$  and  $\Delta S$  values can be estimated from slope and intercept value of this plot lg *D* vs. 1/*T* (Fig. 7), and the  $\Delta G$  values at different temperatures were calculated using Eq. (6), respectively. Table 6 shows the values of thermodynamic parameters of Pb<sup>2+</sup> ions adsorption on D113-III resin. The negative value of  $\Delta G$  confirms the spontaneity of the adsorption process with increasing temperature and the positive value of  $\Delta H$  suggests that the adsorption is endothermic in nature. So the adsorption reaction is a chemical adsorption [34].

#### 3.5. Elution tests

Fifteen milligrams of D113-III resin was added into a mixed solution composed of pH 4.5 buffer solution and desired amount of  $Pb^{2+}$  solution. After equilibrium reached, the concentration of  $Pb^{2+}$  in the aqueous phase was determined, and the adsorption capacity of the D113-III resin for  $Pb^{2+}$  was obtained. Then, the D113-III resin separated from aqueous phase was washed three times with pH 6.00 buffer solution. The D113-III resin adsorbed  $Pb^{2+}$  was shaken



Fig. 7. Relationship between  $\lg D$  and 1/T (Resin 15.0 mg,  $C_0 = 10 \text{ mg}/30.0 \text{ mL}$ ).

Table 6 Thermodynamic parameters

		$\Delta G (kJ/mol)$				
$\Delta H$	$\Delta S$					
(kJ/mol)	(KJ/MOLK)	T = 288  K	T = 298  K	$T = 308  {\rm K}$		
45.29	0.255	-28.15	-30.7	-33.25		

with 30.0 mL HCl eluant. After equilibrium reached, the concentration of  $Pb^{2+}$  in aqueous phase was determined and then the percentage of elution for  $Pb^{2+}$  was obtained. The results listed in Table 7 show that the percentages of elution can reach 100%. So  $Pb^{2+}$  adsorbed on D113-III resin can be recovered. Considering the environmental pollution and economic cost, the experimental results show that the 0.5 mol/L HCl is the best.

Reusability is an important factor for an effective absorption material. And the desorption of the adsorbed  $Pb^{2+}$  from the D113-III resin was studied by static experiment. When the 0.5 mol/L HCl solution with a pH value of 4.5 was used as an eluant, the hydrogen bond interaction between  $Pb^{2+}$  and D113-III resin was disrupted and subsequently,  $Pb^{2+}$  was released into the eluant. In order to show the reusability of the D113-III resin, the adsorption–desorption cycle was repeated several times using the same material. The results (Table 8) clearly show that the D113-III resin could be used repeatedly without significantly losing its adsorption capacity.

#### 3.6. Dynamic adsorption and desorption

#### 3.6.1. Dynamic adsorption curve

The performance of packed beds is described through the concept of the breakthrough curve. The breakthrough curve shows the loading behavior of Pb<sup>2+</sup> to be removed from solution in a fixed bed and is usually expressed in terms of adsorbed Pb<sup>2+</sup> concentration ( $C_{ad}$  = inlet Pb<sup>2+</sup> concentration ( $C_o$ ) – outlet Pb<sup>2+</sup> concentration ( $C_e$ )) or normalized concentration

Table 7 The elution tests of Pb<sup>2+</sup>

Composition of HCl (mol/L)	Elution percentage (%)
0.1	99.3
0.5	100
1.0	100
2.0	100
3.0	100

Table 8	
Adsorption–desorption cycle of Pb <sup>2+</sup>	

Repeat time	1	2	3
Adsorption capacity (mg/g)	406.3	394.5	396.2
Desorption percentage (%)	100	100	100

defined as the ratio of effluent  $Pb^{2+}$  concentration to inlet  $Pb^{2+}$  concentration ( $C_e/C_o$ ) as a function of time or volume of effluent for a given bed height [35]. The area under the breakthrough curve obtained by integrating the adsorbed concentration ( $C_{ad}$ ; mg/mL) vs. the throughput volume (V; mL) plot can be used to find the total adsorbed  $Pb^{2+}$  quantity (maximum column capacity). Total adsorbed  $Pb^{2+}$  quantity (Q; mg/ g) in the column for a given feed concentration and flow rate is calculated from Eq. (10) as follows:

$$Q = \int_0^v \frac{(C_o - C_e)}{m} dV \tag{10}$$

where *m* (g) is the mass of the adsorbent. The capacity value *Q* was obtained by graphical integration as 457 mg/g (Fig. 8). Traditionally, the Thomas model is used to fulfill the purpose. The model has the following form [36]:

$$\frac{C_{\rm e}}{C_{\rm o}} = \frac{1}{1 + \exp[K_T(Qm - C_{\rm o}V)/\theta]},\tag{11}$$

where  $K_{\rm T}$  (mL/(min·mg)) is the Thomas rate constant and  $\theta$  (mL/min) is the volumetric flow rate. The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_{\rm o}}{C_{\rm e}} - 1\right) = \frac{K_{\rm T}Qm}{\theta} - \frac{K_{\rm T}C_{\rm o}}{\theta}V \tag{12}$$



Fig. 8. Breakthrough curve for adsorption of  $Pb^{2+}$  (Resin 150 mg,  $C_0 = 0.197$  mg/mL, flow rate 0.208 mL/min).



Fig. 9. Plot of  $\ln [(C_o/C_e) - 1]$  vs. *t* (resin 150 mg,  $C_o = 0.197$  mg/mL, flow rate 0.208 mL/min).

The kinetic coefficient  $K_{\rm T}$  and the adsorption capacity of the bed Q can be determined from a plot of  $\ln [(C_{\rm o}/C_e) - 1]$  vs. t at a certain flow rate as shown in Fig. 9. The Thomas equation coefficients for Pb<sup>2+</sup> adsorption were  $K_{\rm T} = 2.94 \times 10^{-2}$  mL/(min·mg) and Q = 383.8 mg/g.

#### 3.6.2. Dynamic desorption curve

Efficient elution of adsorbed solute from D113-III resin in column was essential to ensure the reuse of D113-III resin for repeated adsorption/desorption cycles. With respect to the stripping of  $Pb^{2+}$  from D113-III resin, the 0.5 mol/L HCl eluant was employed. Desorption curve was plotted using the effluent concentration ( $C_e$ ) vs. elution volume from the column at a certain flow rate. It can be seen from Fig. 10 that the adsorption flow rate was less so that the volume of elution was less which helped in easy handling and high in concentration for economical recovery of Pb<sup>2+</sup>. It was observed that the total vol-



Fig. 10. Dynamic desorption curve (flow rate 0.21 mL/min).

ume of eluant was 60 mL and the desorption process took 60 h, after which further desorption was negligible. Therefore, the 0.5 mol/L HCl eluant could help in easy handling and removal of Pb<sup>2+</sup>.

#### 3.7. Analysis of infrared spectra of sorption of resin for $Pb^{2+}$

The spectra analysis of D113-III resin, before and after  $Pb^{2+}$  is adsorbed, is conducted (Fig. 11). It is found that the characteristic sorption peaks of the bonds C–OH shift from 3,438 cm<sup>-1</sup> to 3,436 cm<sup>-1</sup> and the peak of bonds C=O (1,705 cm<sup>-1</sup>) disappeared on the whole. The IR studies performed on D113-III resin previously loaded with  $Pb^{2+}$  indicated that the complexing main sites are the carboxyl functional groups, and the adsorption mechanism might be partly a result of the ion exchange or complexation between the  $Pb^{2+}$  ions and carboxyl groups of D113-III resin.

## 3.8. Effect of Na<sup>+</sup> on the adsorption of D113-III resin for $Pb^{2+}$

In order to determine the adsorption capacity of the method, the proposed procedure has been applied. Na<sup>+</sup> is a common ion in natural water systems, an investigation of the effect of this ion is very important. Here the sorption equilibrium of Pb<sup>2+</sup> ions is investigated in a series of NaCl solutions, in which the concentration of Pb<sup>2+</sup> ions is  $0.2 \mu g/ml$ , which is the highest concentration in heavily polluted seawater. The results in Table 9 show that the adsorption capacity of the resin for Pb<sup>2+</sup> significantly decreases with increasing NaCl concentration at pH 4.5. As the solution containing NaCl with the concentration of 3.5% can be regarded as simulated seawater, the results



Fig. 11. Infrared spectra of D113-III resin. (a) Before adsorption. (b) After adsorption.

Table 9 Adsorption capacitic concentrations of Na <sup>+</sup>	es of	Pb <sup>2+</sup>	under	different
Composition of NaCl solutions (g/L)	1.50%	2.50%	3.50%	4.50%
Adsorption capacity (mg/g)	298.02	265.29	249.78	241.17

also indicate that D113-III resin can be of great interest in the case of natural waters. The Pb<sup>2+</sup> concentrations were found to be not higher than the maximum allowable levels restricted by international regulations (GB3838-88, water).

#### 4. Conclusion

Pb<sup>2+</sup> adsorption by D113-III resin is highly dependent on pH. In addition, initial Pb<sup>2+</sup> concentration influences the adsorption process. The maximum adsorption capacity of the resin for Pb<sup>2+</sup> for the Langmuir model is evaluated to be 476.2 mg/g at 289 K. And it is found that 0.5 mol/L HCl solution provides effectiveness of desorption of Pb2+ from D113-III resin. Isotherm studies show that the adsorption process of D113-III resin for Pb2+ follows the Langmuir model. And the kinetics of adsorption can be described by the liquid film diffusion model. The apparent activation energy  $E_a$  was 5.22 kJ/mol, indicating that the adsorption had a low potential barrier. Thermodynamic parameters including standard enthalpy ( $\Delta H$ ), standard entropy ( $\Delta S$ ), and standard free energy ( $\Delta G$ ) indicate that the adsorption of Pb<sup>2+</sup> on D113-III resin is a spontaneous reaction and is endothermic in nature. Column experiments show that it is possible to remove Pb<sup>2+</sup> ions from aqueous medium dynamically. The D113-III resin could be used repeatedly without significantly losing its adsorption capacity. And the resin can be used in heavily polluted seawater system.

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**Symbols** 

Q	_	adsorption capacity, mg/g
D		distribution coefficient
$C_{0}$		initial Pb <sup>2+</sup> ions concentration, mg/mL
C <sub>e</sub>	_	equilibrium $Pb^{2+}$ ions concentration, mg/
c		mL
V		volume of metal solution, mL
W		amount of D113-III resin in the batch, g
$Q_{e}$		adsorption capacity at equilibrium time,
		mg/g
Q <sub>max</sub>		monolayer capacity of the adsorbent, mg/g
$K_{\rm L}$		langmuir constant, mL/mg
$K_{\rm F}$		freundlich constant, mg/g
Ν		freundlich constant, the deviation from
		linearity of the adsorption
$R^2$		correlation coefficient
$\Delta H$		change in the enthalpy
$\Delta S$		change in the entropy
$\Delta G$		changes in the Gibbs free energy
R		gas constant, 8.314 J/mol K
Т	—	absolute temperature
F		fractional attainment of equilibrium, $(F = Q_t/$
		Q <sub>e</sub> )
$Q_t$		adsorption capacity at various times, mg/g
k		adsorption rate constant
Ea		Arrhenius activation energy for the
		adsorption process
Α		Arrhenius factor
V		throughput volume
$K_{\rm T}$	_	Thomas rate constant, mL/(min·mg)
$\theta$	_	volumetric flow rate, mL/min
т		amount of D113-III resin in the column, g

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