

# Adsorption behavior of gel-type weak acid resin (110-H) for $\text{Pb}^{2+}$

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Received 2 January 2008; accepted 2 June 2008

**Abstract:** The adsorption properties of a novel gel-type weak acid resin (110-H) for  $\text{Pb}^{2+}$  were investigated using chemical methods and IR spectrometry. The optimal adsorption condition of 110-H for  $\text{Pb}^{2+}$  is at  $\text{pH}=6.49$  in  $\text{HAc-NaAc}$  medium and the statically saturated adsorption capacity is  $485 \text{ mg/g}$  at  $298 \text{ K}$ .  $\text{Pb}^{2+}$  adsorbed on 110-H resin can be eluted with  $0.025 \text{ mol/L HCl}$  quantitatively. The adsorption rate constants determined under the temperatures of  $288$ ,  $298$ ,  $308$  and  $318 \text{ K}$  are  $2.46 \times 10^{-5}$ ,  $3.82 \times 10^{-5}$ ,  $4.46 \times 10^{-5}$  and  $5.71 \times 10^{-5} \text{ s}^{-1}$ , respectively. The apparent activation energy,  $E_a$ , is  $18.1 \text{ kJ/mol}$  and the thermodynamic parameters of adsorption,  $\Delta H=20.9 \text{ kJ/mol}$ ,  $\Delta S=161 \text{ J/(mol}\cdot\text{K)}$  and  $\Delta G_{298 \text{ K}}=-48.0 \text{ kJ/mol}$ , respectively. The adsorption behavior of 110-H resin for  $\text{Pb}^{2+}$  accords with the Langmuir isotherm. Infrared spectra show that the oxygen atoms of the functional group of resin coordinate with  $\text{Pb}^{2+}$  to form the coordination bands.

**Key words:** gel-type weak acid resin; adsorption; lead; mechanism

## 1 Introduction

Heavy metal contamination in various water resources is of great concern because of the toxic effect on the human beings, and other animals and plants. Lead is among the most toxic elements and it is of particular interest because of its toxicity and widespread presence in the environment[1]. Methods like precipitation, membrane separation, electrochemical reduction[2–4] are available for treating water contaminated with heavy metals. Most of these methods involve high capital cost with recurring expenses, which are not suitable for small-scale industries. Studies on treatment of effluents bearing heavy metals have revealed that adsorption is a highly effective, cheap and easy method among the physicochemical treatment processes. A variety of adsorbents have been used for removal of heavy metals from metal-contaminated effluents. However, adsorbents such as activated carbon and oxides are generally expensive in spite of their high metal adsorption capacities[5]. Efforts are being directed towards finding other alternative low-cost effective adsorbents. And polymeric materials have been demonstrated to be such kind of adsorbents[6–8].

Because nucleophilic atoms such as oxygen,

nitrogen, sulphur and phosphorus atoms can coordinate directly to metal atoms, the functional polymer that combines those atoms has high affinity towards heavy metal ions and can be used as a sorbent for adsorbing metal ions. The synthesis and adsorption property of polymeric materials have been reported by the author and other researchers in recent years[9–17]. The adsorption ability of functional polymer used to enrich metal ion is strong and the operation of the functional polymer is convenient. The polymer adsorbed metal ion can be recovered by using acid or alkaline solution and the recovered polymeric material can be reused. The adsorption ability of the polymer with various functional groups is different for distinct metals.

In this work, the adsorption of lead ion on gel-type weak acid resin (110-H) that contains a functional group  $[-\text{COOH}]$  is investigated systematically. The adsorption mechanism of 110-H for  $\text{Pb}(\text{II})$  is examined by infrared spectrometry and chemical analysis. Some of basic adsorption parameters are determined.

## 2 Experimental

### 2.1 Materials

The gel-type weak acid resin (110-H) was provided by Nankai University, China. Standard solutions of lead

(II) was prepared from  $\text{Pb}(\text{NO}_3)_2$ , with a purity of AR grade. Buffer solution of pH 3.00–6.49 was prepared by mixing HAc-NaAc. Other reagents were of AR grade.

## 2.2 Instruments

Shimadzu UV-2550 UV-Visible spectrophotometer; DSHZ-300A temperature constant shaking machine; THZ-C-1 temperature constant shaking machine; Mettler Toledo Delta 320 pH meter; SK5200LH ultrasonic cleaning instrument; and IR Nicolet 380 were used.

## 2.3 Experimental method

### 2.3.1 Adsorption equilibrium experiment

A desired amount of treated resin was weighed and added into a conical flask, in which a desired volume of buffer solution with pH 5.4 was added. After 24 h, a required amount of standard solution of  $\text{Pb}(\text{II})$  was added. The flask was shaken in a DSHZ-300A temperature constant shaking machine at the constant equilibrium. The upper layer of clear solution was taken for analysis until adsorption equilibrium. The adsorption capacity ( $Q$ ) and distribution coefficient ( $D$ ) were calculated by the following equations:

$$Q = \frac{(\rho_0 - \rho_e) \cdot V}{m} \quad (1)$$

$$D = \frac{Q}{\rho_e} \quad (2)$$

where  $\rho_0$  and  $\rho_e$  are the initial and equilibrium contents of  $\text{Pb}^{2+}$  in solution (mg/mL),  $V$  is the total volume of solution (mL), and  $m$  is the mass of the resin (g).

### 2.3.2 Analytical method

A solution containing less than 100  $\mu\text{g}$  of  $\text{Pb}^{2+}$  was accurately added into a 25 mL colorimetric tube, and then 2 mL of 0.1% xylenol orange solution and 10 mL pH 5.4 methanamine- $\text{HNO}_3$  buffer solution were added. After the addition of redistilled water to 25 mL, the absorbency was determined in a 1 cm cell on a Shimadzu UV-2550 UV-VISIBLE spectrophotometer at the wavelength of 560 nm and compared with the blank sample[18].

### 2.3.3 Elution test

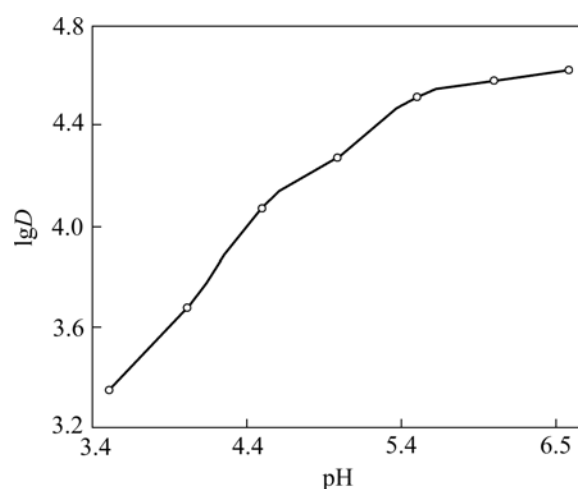
A desired amount of resin was added into a mixed solution composed of pH 6.49 buffer solution and desired amount of standard solution of  $\text{Pb}^{2+}$ . After the equilibrium, the concentration of  $\text{Pb}^{2+}$  in the aqueous phase was determined, and then the adsorption capacity of the resin for  $\text{Pb}^{2+}$  was obtained. The resin separated from aqueous phase was washed three times with pH 6.49 buffer solution. The resin adsorbed  $\text{Pb}^{2+}$  was shaken with eluant. After reaching equilibrium, the concentration of  $\text{Pb}^{2+}$  in aqueous phase was determined and then the

percentage of elution was obtained.

## 3 Results and discussion

### 3.1 Influence of pH on distribution coefficient ( $D$ )

The adsorption behavior of lead onto the 110-H resin in HAc-NaAc medium was studied in the pH range of 3.40–6.49 and the results are shown in Fig.1. The results indicate that the distribution coefficient  $D$  increases with the increase of the pH value. The maximum adsorption is attained at pH 6.49, and then the adsorption capacity almost keeps constant when pH is over 6.49. In order to prevent  $\text{Pb}^{2+}$  from hydrolyzing, all the following experiments were carried out at pH 6.49 ( $[\text{Pb}^{2+}][\text{OH}^-]^2 < K_{\text{sp}}[\text{Pb}(\text{OH})_2]$ ).



**Fig.1** Influence of pH on adsorption capacity of  $\text{Pb}^{2+}$  (resin 20.0 mg,  $T=298\text{ K}$ ,  $\rho_0=0.4\text{ mg/mL}$ ,  $r=100\text{ r/min}$ )

### 3.2 Isotherm adsorption curve

Five samples of 20.0 mg resin were added into a mixed solution composed of pH 6.49 buffer solution individually. After 24 h,  $[\text{Pb}^{2+}]_0=0.33, 0.40, 0.47, 0.53$  and  $0.60\text{ mg/mL}$  of standard solutions were added. When the adsorption equilibrium arrived, the concentration of  $\text{Pb}^{2+}$  was determined.

The Langmuir isotherms are represented by the following equation:

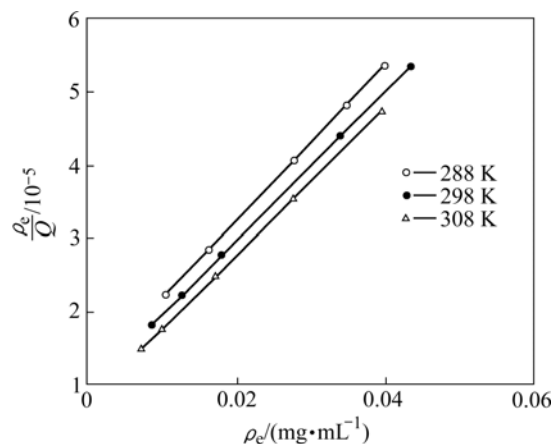
$$\rho_e/Q = \rho_e/Q^0 + 1/(Q^0 b) \quad (3)$$

where  $\rho_e$  is equilibrium content of metal ion,  $Q$  is the adsorbing capacity in equilibrium state,  $Q^0$  is the saturated sorbing capacity and  $b$  is the Langmuir constant.

The plots of  $\rho_e/Q$  vs  $\rho_e$  give a straight line. The results shown in Fig.2 and Table 1 indicate that the Langmuir-type adsorption isotherm is suitable for equilibrium studies.

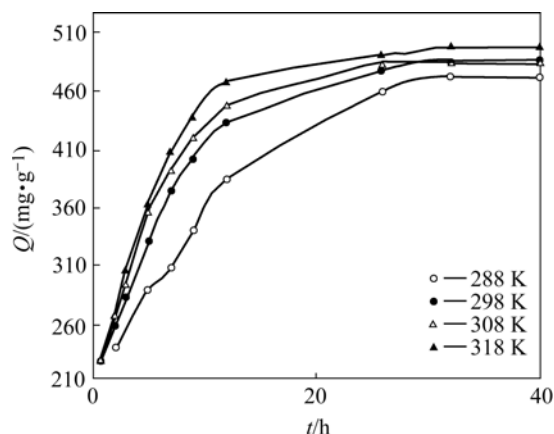
**Table 1** Linearity relation of  $\rho_e/Q$  (y) and  $\rho_e$  (x)

T/K	Linear relation of $\rho_e/Q$ and $\rho_e$	$R^2$
288	$y = 0.00113x + 0.000010$	0.9910
298	$y = 0.00101x + 0.000009$	0.9958
308	$y = 0.00101x + 0.000008$	0.9978

(resin 20.0 mg,  $r=100$  r/min, pH=6.49)**Fig.2** Langmuir isotherm curve (resin 20.0 mg,  $r=100$  r/min, pH=6.49)

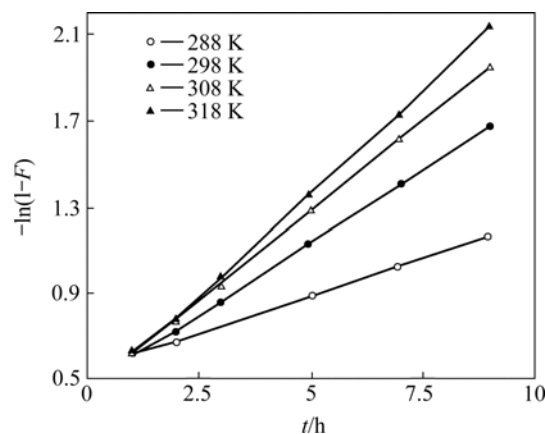
### 3.3 Determination of adsorption rate constant at different temperatures and apparent activation energy

The tests were carried out with 40.0 mg resin under conditions of  $T=288, 298, 308, 318$  K,  $[\text{Pb}^{2+}]=0.4$  mg/mL by the method mentioned above. 0.2 mL of the upper-layer clear solution was taken out at intervals for the determination of remaining concentrations. The results are shown in Fig.3.

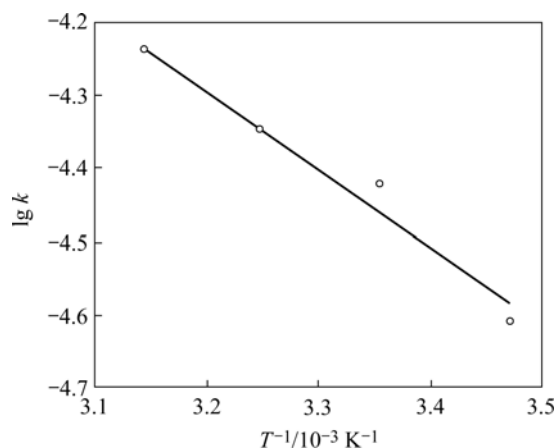
**Fig.3** Adsorption rate curve of  $\text{Pb}^{2+}$  ( $[\text{Pb}^{2+}]=0.4$  mg/mL, resin 40.0 mg, pH=6.49)

According to Brykina method, the adsorption rate constant  $k$  can be calculated from  $-\ln(1-F)=kt$ , where  $F=Q_t/Q_\infty$ ,  $Q_t$  and  $Q_\infty$  are the adsorption capacity at certain time and at equilibrium, respectively. The experimental results accord with the equation and a straight line is obtained by plotting  $-\ln(1-F)$  vs  $t$  (shown in Fig.4), and

the adsorption rate constant of 110-H resin for  $\text{Pb}^{2+}$  can be found from the slope of the straight line, which are  $2.46 \times 10^{-5}$ ,  $3.82 \times 10^{-5}$ ,  $4.46 \times 10^{-5}$  and  $5.71 \times 10^{-5} \text{ s}^{-1}$  at 288, 298, 308 and 318 K, respectively. According to Boyd equation, it can be deduced from the linear relationship of  $-\ln(1-F)$  vs  $t$  that the liquid film spreading is the controlling step in the adsorption process.

**Fig.4** Determination of adsorption rate constant ( $[\text{Pb}^{2+}]_0=0.4$  mg/mL, resin 40.0 mg, pH=6.49)

According to the formula of Arrhenius  $\lg k = -E_a/(2.30RT) + \lg A$ , the apparent activation energy of  $E_a=18.1$  kJ/mol can be calculated (Fig.5). It can be seen from the rate constant that the adsorption speed accelerates as the temperature increases in the experimental temperature range.

**Fig.5** Relationship between  $\lg k$  and  $1/T$  ( $[\text{Pb}^{2+}]_0=0.4$  mg/mL, resin 40.0 mg, pH=6.49)

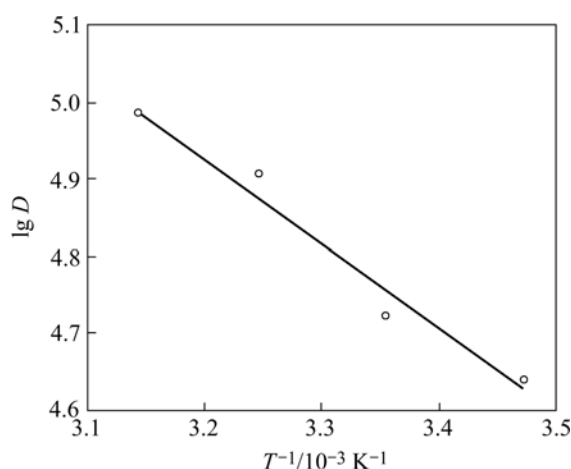
### 3.4 Influence of adsorption temperature on distribution ratio and determination of thermodynamic parameters

The distribution coefficient of the resin for  $\text{Pb}^{2+}$  in the temperature range of 288–318 K was measured, and the result is shown in Fig.6. A straight line was obtained by plotting  $\lg D$  against  $1/T$  with a correlation coefficient

of 0.966 6. The result obviously indicates that it is favorable for the adsorption with the temperature increasing. It implies that the adsorption process is endothermic. So the adsorption reaction is a chemical adsorption. By the following equation,

$$\lg D = -\frac{\Delta H}{2.30RT} + \frac{\Delta S}{2.30R} \quad (4)$$

$\Delta H=20.9$  kJ/mol, and then  $\Delta S=161$  J/(mol·K) can be obtained from the slope and the intercept of the line. In the light of  $\Delta G=\Delta H-T\Delta S$ ,  $\Delta G_{288K}=-46.4$  kJ/mol,  $\Delta G_{298K}=-48.0$  kJ/mol,  $\Delta G_{308K}=-49.6$  kJ/mol and  $\Delta G_{318K}=-51.2$  kJ/mol were obtained. The values reveal that the adsorption reaction is a spontaneous process under the experimental condition.



**Fig.6** Influence of temperature on distribution ratio ( $[\text{Pb}^{2+}]_0=0.4$  mg/mL, resin 40.0 mg, pH=6.49)

### 3.5 Effect of $\text{Na}^+$ on adsorption capacity of 110-H resin

Six samples of 20.0 mg resin were put into conical flasks individually, then 20.0 mL of 0.4 mol/L HAc-NaAc buffer solution with pH 6.49 was added. After 24 h, 5.0 mL standard solution of  $\text{Pb}^{2+}$  was added individually. The flasks were shaken with different NaCl concentrations, as shown in Table 2. The clear upper-layer solution was taken for analysis until adsorption equilibrium. The adsorption capacity is calculated and shown in Table 2 also. The results indicate that the capacity of the resin for  $\text{Pb}^{2+}$  changes little with the increase of  $\text{Na}^+$  concentration under the experimental condition.

### 3.6 Elution

The test was carried out by the above-mentioned method. 30.0 mL eluant was added. The results are listed in Table 3. It can be seen that the elution is different with the change in the concentration of HCl. Considering the environmental pollution, 0.025 mol/L HCl is favourable.

### 3.7 Dynamic adsorption and desorption

#### 3.7.1 Dynamic adsorption curve

The dynamic adsorption test was conducted using a

**Table 2** Effect of  $\text{Na}^+$  on adsorption capacity of 110-H resin

Concentration of NaCl/(mol·L <sup>-1</sup> )	Adsorption capacity/(mg·g <sup>-1</sup> )
0	485
$2.40 \times 10^{-3}$	484
$7.20 \times 10^{-3}$	484
$1.20 \times 10^{-2}$	486
$1.00 \times 10^{-1}$	483
$3.00 \times 10^{-1}$	485

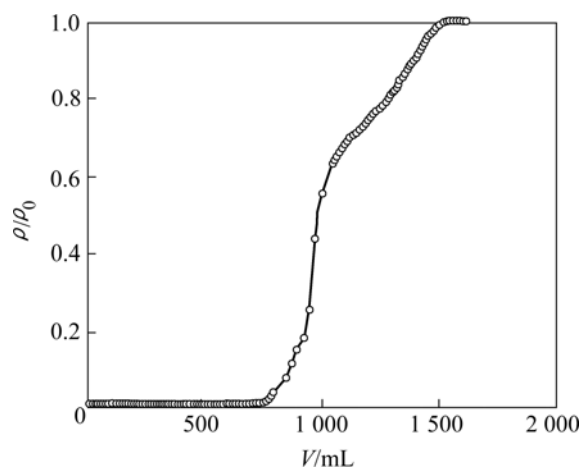
(Resin 20.0 mg, pH=6.49,  $T=298$  K,  $[\text{Pb}^{2+}]_0=0.4$  mg/mL)

**Table 3** Elution test results of Pb (II)

Concentration of HCl/(mol·L <sup>-1</sup> )	0.5	0.25	0.1	0.05	0.025
Elution/%	93.6	94.5	96.8	100	100

(Resin 20.0 mg, pH=6.49,  $T=298$  K)

glass column packed with 300 mg newly prepared 110-H resin at room temperature. After the column was conditioned, a solution containing 0.200 mg/mL  $\text{Pb}^{2+}$  was continuously fed into the column at a constant flow rate of 0.25 mL/min. The effluents from the column were analyzed quantitatively using the above-mentioned method. Breakthrough data were acquired by plotting the volume of solution passing through the column vs the concentration of  $\text{Pb}^{2+}$  in the effluent. When the  $\text{Pb}^{2+}$  concentration from the bottom of the column ( $\rho$ ) is equal to that at the top of the resin bed ( $\rho_0$ ), the experiment was terminated, and a plot of  $\rho/\rho_0$  vs the volume of effluent gives a typical breakthrough curve, as shown in Fig.7.



**Fig.7** Dynamic adsorption curve ( $\rho_0=0.200$  mg/mL, flow-rate 0.25 mL/min)

#### 3.7.2 Dynamic desorption curve

The dynamic desorption curves of 110-H resin for  $\text{Pb}^{2+}$  were obtained based on the volume of desorption solution and the  $\text{Pb}^{2+}$  concentration in the desorption solution. HCl of 0.025 mol/L was employed to strip  $\text{Pb}^{2+}$  from 110-H resin. The elution of  $\text{Pb}^{2+}$  from the column was at a flow rate of 0.25 mL/min. The results are shown in Fig.8.

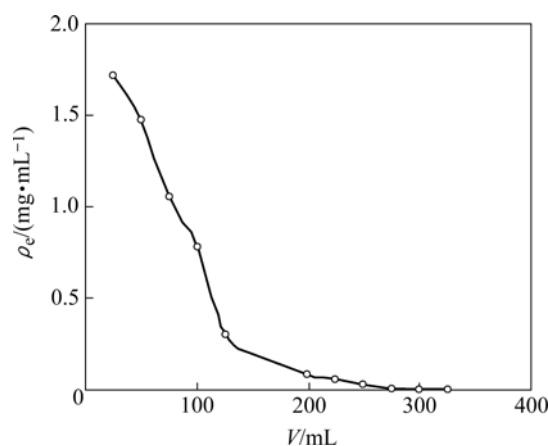


Fig.8 Dynamic desorption curve (flow rate 5.4 BV/h)

### 3.8 Analysis of infrared spectra

It is deduced that the adsorption of  $\text{Pb}^{2+}$  by 110-H ( $\Delta H > 0$ ) belongs to a chemical process. Therefore, the functional groups of 110-H,  $\text{C}=\text{O}$ ,  $\text{C}-\text{OH}$  and  $\text{Pb}^{2+}$  are supposed to form chemical bonds. It is found from Fig.9 that the characteristic adsorption peak of the bond  $\text{C}=\text{O}$  ( $1712\text{ cm}^{-1}$ ) disappears, and a new peak at  $1562\text{ cm}^{-1}$  occurs. The characteristic peak of the bond  $\text{C}-\text{OH}$  shifts from  $1392\text{ cm}^{-1}$  to  $1396\text{ cm}^{-1}$ . These results show that there are coordination bonds between oxygen atoms and  $\text{Pb}^{2+}$ , and H of  $\text{C}-\text{OH}$  is exchanged as a complex compound forms.

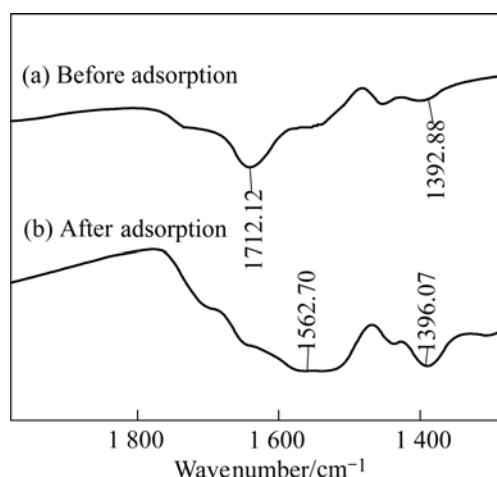


Fig.9 IR spectra of 110-H resin: (a) Before adsorption; (b) After adsorption

## 4 Conclusions

1)  $\text{Pb}^{2+}$  can be adsorbed on 110-H resin in the HAC-NaAc system with the pH value of 6.49, and the statically saturated adsorption capacity is 485 mg/g at 298 K. The  $\text{Pb}^{2+}$  adsorbed on 110-H resin can be eluted by 0.025 mol/L HCl quantitatively.

2) The adsorption behavior of 110-H resin for  $\text{Pb}^{2+}$  obeys the Langmuir isotherm. The apparent adsorption

rate constant  $k_{298\text{K}} = 3.82 \times 10^{-5}$ . The apparent activation energy  $E_a = 18.1\text{ kJ/mol}$ . The thermodynamic parameters of the adsorption are  $\Delta H = 20.9\text{ kJ/mol}$ ,  $\Delta S = 161\text{ J/(mol}\cdot\text{K)}$  and  $\Delta G_{298\text{K}} = -48.0\text{ kJ/mol}$ , respectively.

3) Infrared spectra show that the oxygen atoms of the functional group of resin coordinate to  $\text{Pb}^{2+}$  to form the coordination bands.

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(Edited by YNAN Sai-qian)