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# Novel negatively charged hybrids. 3. Removal of Pb<sup>2+</sup> from aqueous solution using zwitterionic hybrid polymers as adsorbent

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# ABSTRACT

Using zwitterionic hybrid polymers as adsorbent, the adsorption kinetics and isotherm, thermodynamic parameters of  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the removal of Pb<sup>2+</sup> from aqueous solution were investigated. It is indicated that the adsorption of Pb<sup>2+</sup> ions on these zwitterionic hybrid polymers followed the Lagergren second-order kinetic model and Freundlich isotherm model, demonstrating that the adsorption process might be Langmuir monolayer adsorption. The negative values of  $\Delta G$  and the positive values of  $\Delta H$  evidence that Pb<sup>2+</sup> adsorption on these zwitterionic hybrid polymers is spontaneous and endothermic process in nature. Moreover, the zwitterionic hybrid polymers produced reveal relatively higher desorption efficiency in 2 mol dm<sup>-3</sup> aqueous HNO<sub>3</sub> solution, indicating that they can be recycled in industrial processes. These findings suggest that these zwitterionic hybrid polymers are the promising adsorbents for Pb<sup>2+</sup> removal and can be potentially applied in the separation and recovery of Pb<sup>2+</sup> ions from the waste chemicals and contaminated water of lead-acid rechargeable battery.

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#### 1. Introduction

With the wide application of lead-acid rechargeable battery in everyday life and the rapid development of electronic industry, water pollution caused by Pb<sup>2+</sup> ions has become a major environmental issue. As one of high toxic heavy metal ions, lead cannot be biodegraded and easily accumulate in human body to induce lead poisoning [1,2]. Removal of lead ions from aqueous solution is thus significantly important and highly needed. To remove or eliminate such type of toxic heavy metals from water resources, various techniques have been developed in the past. Among these, adsorption using inorganic/polymer hybrid materials as adsorbents is regarded as one of the most effective, low-cost and environmental friendly methods to remove this pollutant from wastewater. Consequently, a variety of innovative approaches have been developed for Pb<sup>2+</sup> removal [1–5]. For example, Pan and co-workers [2] prepared a novel hybrid sorbent ZrP-001 by loading zirconium phosphate (ZrP) onto a strongly acidic cation exchanger D-001 and investigated the sorption behaviors for Pb<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> ions. It is indicated that the sorption order followed  $Pb^{2+} \gg Zn^{2+} \approx Cd^{2+}$ . Tao et al. [5] investigated the removal of Pb (II) from aqueous solution using chitosan/TiO<sub>2</sub> hybrid film adsorbent.

As one important type of inorganic/organic charged hybrid materials, zwitterionic hybrid polymer has drew much attention in recent years [6–8]. This type of hybrid polymer not only combines the advantages of organic and inorganic materials, but also exhibits some distinguished properties, such as structural flexibility, thermal and mechanical stability. Its unique feature such as pendent-side structure of ionic groups of opposite sign on the polymer chains allows its application in the separation and recovery of heavy metal ions from contaminated water via electrostatic effect. However, little work is done so far to remove and recover Pb<sup>2+</sup> ions from aqueous solution or wastewater using zwitterionic hybrid polymers as a sorbent.

Recently, many efforts have been made to prepare and characterize zwitterionic hybrid polymer and membranes [7.9–11]. In the previous article [11], a series of zwitterionic hybrid polymers were prepared from the ring-opening polymerization of pyromellitic acid dianhydride (PMDA) and phenylaminomethyl trimethoxysilane (PAMTMS), and a subsequent sol-gel process. Their application for Cu<sup>2+</sup> removal from aqueous solution was examined. It is indicated that their adsorption for Cu<sup>2+</sup> ions followed Lagergren second-order kinetic model and Langmuir isotherm model. To continue the previous job and have an insight into the adsorption properties of zwitterionic hybrid polymers for heavy metal ions, herein, the application of zwitterionic hybrid polymers for Pb<sup>2+</sup> removal is investigated as the model metal for the separation and recovery of heavy metal ions from aqueous solution. Meanwhile, the adsorption kinetics and isotherm, thermodynamic parameters such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  were calculated to evaluate the adsorp-

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tion properties of Pb<sup>2+</sup> ions. Such investigation expects to be used in the disposal of contaminated water from lead-acid rechargeable battery.

# 2. Experimental

## 2.1. Materials

Phenylaminomethyl trimethoxysilane (PAMTMS, purity:  $\geq$ 95.0%) was purchased from Silicone New Material Co. Ltd of Wuhan University (Wuhan, China) and used without further purification. Pyromellitic acid dianhydride (PMDA, purity:  $\geq$ 99.5%), bromoethane (C<sub>2</sub>H<sub>5</sub>Br, purity:  $\geq$ 98.0%) were purchased from National Pharmaceutical Group Corp. of China (Shanghai, China) and used as received. Other reagents were of analytical grade.

## 2.2. Preparation of zwitterionic hybrid polymers

The composition and cation-exchange capacities (CIECs) of zwitterionic hybrid polymers used in this case were listed in Tables 1 and 2, respectively. The preparation procedure of these zwitterionic hybrid polymers was discussed in detail in a previous paper [11]. The preparation involved three steps (as illustrated in Scheme 1) and was described briefly as follows.

Firstly, proper PMDA was dissolved in 15 ml DMF solution and stirred vigorously for 1 h at room temperature, and then the prescribed amount of PAMTMS solution was added dropwise into the above-prepared DMF mixed solution within 1 h (the ratio of PMDA and PAMTMS was listed in Table 1). Subsequently, the DMF mixed solution was stirred vigorously for additional 30 min to perform the ring-opening polymerization of PMDA and PAMTMS. After that, a homogeneous sol could be observed. During this process, the sol-gel reaction occurs between Si and O to produce the Si–O–Si bonds in the hybrid precursor. Followed, excess bromoethane  $(C_2H_5Br)$  was added to conduct the quaternary amination reaction of tertiary amine groups for 24 h to create the positively charged group in the polymer chains. Finally, the obtained product was washed and dried at 70 °C to acquire the final zwitterionic hybrid polymer.

### 2.3. Adsorption experiments

The adsorption experiments of zwitterionic hybrid polymers for  $Pb^{2+}$  ions were conducted in similar way as our previous studies, in which aqueous solution containing  $Cu^{2+}$  and  $Pb^{2+}$  ions were used as the adsorption medium [12]. The procedure can be described briefly as follows: about 1.0 g of particle sample was immersed in a 0.01 mol dm<sup>-3</sup> aqueous Pb(NO<sub>3</sub>)<sub>2</sub> solution at pH 5 for 24 h; subsequently, it was taken out and washed with deionized water. An

 Table 1

 Composition of the investigated zwitterionic hybrid polymers.

Sample	PMDA (g)	PAMTMS (ml)	$C_2H_5Br(ml)$
А	10.12	5	30
В	10.12	2.5	30
С	15.18	2.5	30
D	20.24	2.5	30

 Table 2

 Cation-exchange capacities (CIECs) of the investigated zwitterionic hybrid polymers.

Sample	А	В	С	D
CIECs (mmol g <sup>-1</sup> )	2.50	4.75	6.51	8.65



**Scheme 1.** The preparation steps of zwitterionic hybrid polymers; step 1 was the ring-opening polymerization of PMDA and PAMTMS; step 2 was the hydrolysis and condensation of hybrid precursor by sol–gel process; step 3 was the quaternary amination reaction to create the positively charged groups in the polymer chains [11].

EDTA solution (0.01 mol dm<sup>-3</sup>) was used to determine the adsorption capacity ( $q_{\rm Pb^{2+}}$ ) of Pb<sup>2+</sup> ions.

The adsorption capacity  $(q_{Pb^{2+}})$  of  $Pb^{2+}$  ions can be calculated by Eq. (1):

$$q_{\rm Pb^{2+}} = (C_0 - C_R)V/W \tag{1}$$

where *V* is the volume of aqueous  $Pb(NO_3)_2$  solution,  $C_0$  and  $C_R$  are the concentration of initial and remaining  $Pb(NO_3)_2$ , respectively; *W* is the weight of polymer.

For adsorption kinetic studies, the prepared sample was immersed in 0.01 mol dm<sup>-3</sup> aqueous Pb(NO<sub>3</sub>)<sub>2</sub> solution for different adsorption times at pH 5. Meanwhile, the adsorption isotherm was conducted by changing the solution concentration ranging from 0.05 to 0.5 mol dm<sup>-3</sup> at room temperature for 24 h at pH 5. The adsorption data were analyzed using Lagergren first-order and second-order kinetic model, Langmuir and Freundlich isotherm models. Based on the adsorption data, the thermodynamic parameters such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  at different temperatures for Pb<sup>2+</sup> removal were examined. In addition, desorption efficiency of Pb<sup>2+</sup> ions was also measured using HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl acidic solutions (2.0 mol dm<sup>-3</sup>), respectively.

### 3. Results and discussion

#### 3.1. Adsorption kinetics

To determine the dependency of adsorption capacity for Pb<sup>2+</sup> ions and CIECs of these samples, the adsorption capacity of zwitte-



**Fig. 1.** Adsorption capacity of zwitterionic hybrid polymers A–D for Pb<sup>2+</sup> ions; 1.0 g samples were immersed in  $40 \text{ dm}^3$  aqueous Pb(NO<sub>3</sub>)<sub>2</sub> solution (0.01 mol dm<sup>-3</sup>) at  $25 \degree C$  for 24 h.



**Fig. 2.** Adsorption kinetic curves of  $Pb^{2+}$  on samples A–D at pH 5; the concentration of aqueous  $Pb(NO_3)_2$  solution was 0.01 mol dm<sup>-3</sup>.

rionic hybrid polymers A–D for Pb<sup>2+</sup> ions was tested and presented in Fig. 1. It is interesting to find that the adsorption capacity of samples A–D increases with an increase in CIEC values, suggesting that the adsorption of these samples for Pb<sup>2+</sup> ions is related to the content of ionic groups and high CIECs will conduce to Pb<sup>2+</sup> adsorption. The reason can be ascribed to the increasing amount of carboxylic groups grafted on the polymer chains, resulting in an increase in the electrostatic attraction between the metal ions and ionic groups.

Fig. 2 illustrates the adsorption kinetic curves, i.e. the relationship between adsorption capacity and adsorption time. As shown in Fig. 2, at the same adsorption time, different samples indicate different changing trends. Among them, sample D shows the largest adsorption capacity, and the adsorption capacity of  $Pb^{2+}$  follows such order as: sample D > sample C > sample B > sample A. Whereas, for different samples, the time for adsorption equilibrium is different although the adsorption kinetic curves all rise as the adsorption time elapses. For example, for sample D, the time for adsorption equilibrium is about 6 h. But the equilibriums of samples A–C will take longer more than 15 h.



Fig. 3. Lagergren second-order kinetic model for Pb<sup>2+</sup> adsorption on samples A–D.

It is well accepted that Lagergren adsorption kinetic model is a useful tool to describe the adsorption property of a species [13,14], and the adsorption mechanism can be predicted by the intraparticle diffusion model [15,16] or the diffusion-controlled adsorption mechanism [17]. The Lagergren first-order and second-order equation can be linearly expressed as Eqs. (2b) and (3b), respectively.

$$q_t = q_e(1 - e^{-k_1 t})$$
(2a)

or,

$$\log(q_{\rm e} - q_t) = \log q_{\rm e} - \frac{k_1}{2.303}t \tag{2b}$$

$$q_t = \frac{q_e^2 k_2 t}{(1 + q_e k_2 t)}$$
(3a)

or,

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

where  $k_1$  and  $k_2$  are the first-order and second-order rate constant, respectively;  $q_t$  and  $q_e$  are the adsorption capacity of Pb<sup>2+</sup> ion at time *t* and at equilibrium state, respectively.

To investigate the adsorption kinetic property in this case, Lagergren adsorption kinetic model is calculated according to the dependency of adsorption capacity on adsorption time. It is interesting to find that the Lagergren first-order model for Pb<sup>2+</sup> adsorption on samples A–D exhibited poor regression coefficient ( $R^2$ ) (the data were not presented in the text); suggesting that Pb<sup>2+</sup> adsorption on these samples does not follow Lagergren first-order kinetic equation. In contrast, the regression coefficient ( $R^2$ ) of Lagergren second-order model fitted well for these samples (as presented in Fig. 3). Meanwhile, the experimental and calculated Lagergren second-order kinetic parameters for Pb<sup>2+</sup> adsorption demonstrate approximate values (cf. Table 3). Based on these data, it can be concluded that Pb<sup>2+</sup> adsorption on these zwitterionic hybrid polymers followed Lagergren second-order kinetic model.

Furthermore, the effect of intraparticle diffusion on adsorption rate can be calculated based on the relation of adsorption capacity

#### Table 3

Lagergren second-order kinetic model parameters for Pb<sup>2+</sup> adsorption.

Sample	$k_2$ (hg mmol <sup>-1</sup> )	$h^{\mathrm{a}}$ (hg mmol <sup>-1</sup> )	$q_{\rm e}$ (experimental) (mmol g <sup>-1</sup> )	$q_{\rm e}$ (calculated) (mmol g <sup>-1</sup> )	<i>R</i> <sup>2</sup>
А	0.58065	17.0096955	5.33675	5.4124	0.99908
В	0.817977	17.911517	4.66925	4.679457	0.99618
С	0.374195	7.047216	4.22875	4.3397	0.99801
D	0.1244595	1.68472	3.36025	3.67917	0.96554

<sup>a</sup> Initial adsorption rate  $(h) = k^2 q_e^2$ .



Fig. 4. Intraparticle diffusion curves for Pb<sup>2+</sup> adsorption on samples A–D.

and time, which usually is expressed as Eq. (4) [15]:

$$q_t = x_i + k_{\rm p} t^{0.5} \tag{4}$$

where  $q_t$  is the adsorbed amount (mmol g<sup>-1</sup>) at time t,  $k_p$  is the intraparticle diffusion rate constant and  $x_i$  is the intercept of straight line, which is related to the boundary layer thickness [15,16].

Fig. 4 illustrated the intraparticle diffusion curves for  $Pb^{2+}$  adsorption. As shown in Fig. 4, different trends are observed for samples A–D. For samples A and B, the straight lines (R=0.977 and 0.955, respectively) indicate that  $Pb^{2+}$  adsorption on them is controlled by intraparticle diffusion within the pores of the hybrid polymers [15]. Nevertheless, for samples C and D, two step adsorption curves are clearly observed (from the beginning to adsorption equilibrium and at the period of equilibrium state), suggesting that  $Pb^{2+}$  adsorption on samples C and D is not governed by intraparticle diffusion; diffusion-controlled adsorption mechanisms might be the major process as reported in a article [17]. The reason might be related to the formation of hybrid matrix and the elevating content of ionic groups in the polymer backbone.

#### 3.2. Adsorption isotherms

To further explain the above trends, Langmuir and Freundlich isotherm models are used to analyze the tested adsorption data. The Langmuir isotherm equation is based on monolayer adsorption on the active sites of the adsorbent; which can be expressed as Eq. (5) [13,15]:

$$\frac{c_{\rm e}}{q_{\rm e}} = \frac{c_{\rm e}}{Q_m} + \frac{1}{Q_m b} \tag{5}$$

where  $q_e$  and  $c_e$  are the equilibrium concentrations of metal ion in the adsorbed and liquid phases, respectively.  $Q_m$  and b are the Langmuir constants, which can be calculated from the intercept and slope of the linear plot based on  $c_e/q_e$  vs.  $c_e$ .

Different from Langmuir isotherm model, Freundlich isotherm model is considered as the adsorption occurred on a heterogeneous surface with uniform energy; which can be expressed as Eqs. (6a) and (6b) [13,14]:

$$q_{\rm e} = k_{\rm F} c_{\rm e}^{1/n} \tag{6a}$$

$$\log q_{\rm e} = \log k_{\rm F} + \frac{1}{n} \log c_{\rm e} \tag{6b}$$

where  $q_e$  and  $c_e$  are the equilibrium concentrations of metal ion in the adsorbed and liquid phases, respectively.  $k_F$  and n are the



**Fig. 5.** Plot of  $Pb^{2+}$  adsorption capacity vs.  $Pb^{2+}$  concentration at pH 5; the sample was immersed in different concentration aqueous Pb (NO<sub>3</sub>)<sub>2</sub> solution for 20 h, respectively.

Freundlich constants, which can be calculated from the slope and intercept of the linear plot according to  $\log q_e vs. \log c_e$ .

The adsorption isotherm of these samples (i.e. the dependence of  $Pb^{2+}$  adsorption capacity on  $Pb^{2+}$  concentration) was illustrated in Fig. 5. For the same sample, its adsorption capacity for  $Pb^{2+}$ ions has the same changing trend: increasing as  $Pb^{2+}$  concentration increases as expected. However, for different samples, their adsorption capacities for  $Pb^{2+}$  ions increase from samples A to D, following the same changing trend as CIECs (cf. Table 2).

Fig. 6(a) and (b) illustrated the Langmuir and Freundlich adsorption isotherm of samples A–D for Pb<sup>2+</sup> adsorption. The Langmuir and Freundlich isotherm parameters are listed in Table 4. As shown



Fig. 6. Adsorption isotherm of samples A–D for  $Pb^{2+}$  ions, (a) Langmuir, (b) Freundlich model.

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Table	4

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Sample	nple Langmuir		Freundlich			
	$Q_{\rm m} ({\rm mmol}{\rm g}^{-1})$	<i>b</i> (dm <sup>3</sup> /mol)	R <sup>2</sup>	k <sub>F</sub>	n	R <sup>2</sup>
А	4.8652	13.9918	0.982299	10.33832	2.4630	0.7943
В	4.8337	27.6948	0.98575	9.22593	3.7543	0.9157
С	6.1778	30.4840	0.992454	5.84629	2.8315	0.9018
D	7.1633	54.7451	0.99774	6.62827	3.4871	0.9585

in Fig. 6, it can be seen that the experimental data fitted well with Langmuir isotherm model [the regression coefficient ( $R^2$ ) values are in the range of 0.98–0.99]. In contrast, these experimental data fitted worse with Freundlich isotherm model [the regression coefficient ( $R^2$ ) values are within 0.79–0.95]. Based on these results, it can be deduced that the adsorption process is Langmuir mono-layer adsorption rather than heterogeneous surface one. The reason might be related to such major factors: the electrostatic attraction between the ionic groups and the metal ions, the content of ionic groups, etc. [13], as well as the influence of  $-N^+$ – groups on the adsorption of metal ions as discussed in a previous paper [11].

For Langmuir isotherm model, separation factor or equilibrium parameter ( $R_L$ ) can be used to predict the favorability of adsorption, which is defined by Eq. (7) [13,18]:

$$R_{\rm L} = \frac{1}{(1+bC_0)}$$
(7)

where  $C_0$  is the initial Cu<sup>2+</sup> concentration and *b* is the Langmuir adsorption equilibrium constant.

When the  $R_L$  value is within  $0 < R_L < 1$ , it is favorable adsorption. Otherwise, it is unfavorable adsorption [18]. Table 5 lists the calculated  $R_L$  values based on the Langmuir isotherm parameters. Obviously, these  $R_L$  values are all in the range of  $0 < R_L < 1$ , demonstrating that Pb<sup>2+</sup> adsorption on these samples is favorable. Consequently, these zwitterionic hybrid polymers are promising adsorbents for Pb<sup>2+</sup> removal from aqueous solution.

#### 3.3. Thermodynamic parameters

To determine thermodynamic parameters, adsorption experiments at different temperatures for Pb<sup>2+</sup> removal were conducted and presented in Fig. 7.

As shown in Fig. 7, it can be seen that the adsorption capacity of  $Pb^{2+}$  ions increases with an increase in solution temperature [the linear regression coefficient ( $R^2$ ) values are in the range of 0.91–0.96], suggesting that adsorption process of  $Pb^{2+}$  ions is endothermic in nature [13], which can be confirmed by some thermodynamic parameters as presented later.

To explain the above phenomenon, special attention can be paid to the electrostatic attraction effect between the  $Pb^{2+}$  ions and the ionic groups situated at the molecular backbone, which can be interpreted as follows.

Commonly, the –COOH groups are partially protonated and the partition degree increases with the elevated temperature [19], thus the amount of –COOH groups transformed into –COO<sup>–</sup> groups will

Table 5	
The calculated R	values based on the Langmuir isotherm parameter.

$C_0 ({ m mol}{ m dm}^{-3})$	<i>R</i> <sub>L</sub> value			
	A	В	С	D
0.05	0.5883	0.4193	0.3692	0.2676
0.1	0.4168	0.2653	0.2470	0.1545
0.15	0.3227	0.1940	0.1795	0.1086
0.3	0.1924	0.1074	0.09857	0.05739
0.5	0.1251	0.06735	0.06157	0.03525

be promoted as the temperature enhances, leading to an increase in the electrostatic attraction between the metal ions such as Pb<sup>2+</sup> ions and ion-exchange groups. As a result, the adsorption capacity of Pb<sup>2+</sup> ions increases slightly at high temperature. In this case, the partition or deprotonation-adsorption mechanism will be the dominating control step and can be used to explain the adsorption behaviors (cf. Eqs. (8a), (8b) and (10)). On the other hand, the Pb<sup>2+</sup> ions may directly coordinate with –COOH groups and conduct the ion-exchange with metal ions to produce the metal-complexes, which also gives rise to an improvement in the adsorption capacity when the temperature elevates. Thus they will follow the ionexchange mechanism (cf. Eqs. (9) and (10)) [19]. The proposed adsorption mechanism between the divalent metal ions (Me<sup>2+</sup>) and –COOH groups can be briefly described as follows.

$$R-COOH \rightleftharpoons R-COO^- + H^+$$
 (8a)

or,

$$R-COO^{-} + Me^{2+} \rightleftharpoons R-COOMe^{+}$$
(8b)

or/and,

$$R-COOH + Me^{2+} \rightleftharpoons R-COOMe^{+} + H^{+}$$
(9)

$$R-COOMe^{+} + R-COOH \rightleftharpoons R-COO \cdots Me \cdots OOC - R + H^{+}$$
(10)

Furthermore, the thermodynamic parameters, such as free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ), can be calculated from Eqs. (11) and (12) [13]:

$$\Delta G = -RT \ln K_{\rm c} \tag{11}$$

$$\ln K_{\rm c} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{12}$$

in which,  $K_c$  is the equilibrium partition coefficient and can be calculated from Eq. (13) [13]:

$$K_{\rm c} = \frac{C_{\rm s}}{C_{\rm e}} \tag{13}$$



**Fig. 7.** Plot of  $Pb^{2+}$  adsorption capacity vs. solution temperature, the concentration of aqueous  $Pb(NO_3)_2$  solution was 0.1 mol dm<sup>-3</sup>.

Table 6		
Thermodynamic data for Pb2+	adsorption on samples A-D	).

Sample	Temperature (K)	$\Delta G$ (kJ/mol)	$\Delta S$ (J/mol K)	$\Delta H$ (kJ/mol)	$R^2$
A	298 308 318	7.52366 8.29803 9.59946	103.1019	23.2811	0.9610
В	298 308 318	-10.74428 -11.74831 -12.35572	80.9496	13.3159	0.9352
С	298 308 318	-12.62867 -13.24326 -13.73062	55.2209	3.8071	0.9197
D	298 308 318	-13.03302 -14.4408 -15.26699	112.2481	20.3249	0.9399

where *R* is the gas constant (8.314 J/mol K), C<sub>s</sub> and C<sub>e</sub> are the equilibrium concentrations of Pb<sup>2+</sup> ions in the adsorbent and solution, respectively, and *T* is the solution temperature (K).  $\Delta H$  and  $\Delta S$  can thus be calculated from the slope and intercept of the linear plot according to  $\ln K_c vs. 1/T$  (cf. Fig. 8). The calculated results are presented in Table 6.

As shown in Table 6, the  $\Delta G$  values are all negative and the  $\Delta H$  values are all positive, which evidence that the adsorption of Pb<sup>2+</sup> ions on the zwitterionic hybrid polymers A–D is spontaneous and endothermic process in nature. Moreover, it can be noted that for the same sample, these  $\Delta G$  values become more negative with the elevated temperature. Whereas, at the same temperature, the  $\Delta G$  values also become more negative from sample A to D, implying that Pb<sup>2+</sup> adsorption ability increases with the elevating content of ionic groups, which is consistent with the upward trend in CIECs (cf. Table 2). In addition, it can be found in Table 6 that the  $\Delta S$  values are all positive, suggesting that the randomness increased during the adsorption of Pb<sup>2+</sup> on samples A–D. These findings demonstrate that temperature and the content of ionic groups in the polymer chains have an active effect on Pb<sup>2+</sup> adsorption.

The above trend can be ascribed to the electrostatic attraction between the Pb<sup>2+</sup> ions and ionic groups in the zwitterionic hybrid polymers, and the increase of pore size in the sample surface as the temperature increases [13].

#### 3.4. Desorption experiment

Currently, for the removal of heavy metal ions, the significance consists in the desorption and reuse of metal ion in industrial



**Fig. 8.** Van't Hoff plot of Pb<sup>2+</sup> adsorption on samples A–D, the concentration of aqueous Pb(NO<sub>3</sub>)<sub>2</sub> solution was 0.1 mol dm<sup>-3</sup> at 25, 35 and 45 °C for 24 h, respectively.

## Table 7

Desorption efficiency of sample D for Pb<sup>2+</sup> ions in various desorbents.

Desorbent	Desorption time (min)	Efficiency (%)
HNO <sub>3</sub>	60	64.4
$H_2SO_4$	60	11.1
HCI	60	35.5

processes rather than the simple adsorption and disposal [14]. To regenerate and recycle the adsorbent spent, desorption experiment was conducted using sample D as typical example. The experimental results are shown in Table 7. Obviously, for  $Pb^{2+}$  desorption, the desorption efficiency of sample D using 2.0 mol dm<sup>-3</sup> aqueous HNO<sub>3</sub> solution for 60 min could reach up to 64.4%, indicating an effective regeneration cycle.

Based on the above findings, it can be concluded that these zwitterionic hybrid polymers are promising adsorbent for Pb<sup>2+</sup> removal and have potential applications in the separation and recovery of divalent metal ions from wastewater of lead-acid rechargeable battery.

# 4. Conclusions

The adsorption behaviors of Pb<sup>2+</sup> ions on zwitterionic hybrid polymers were investigated. It is confirmed that the adsorption of Pb<sup>2+</sup> followed Lagergren second-order kinetic model and Langmuir isotherm model, demonstrating that the adsorption mechanism followed Langmuir monolayer adsorption. The electrostatic attraction between the ionic groups and Pb<sup>2+</sup> ions, and the content of ionic groups might be responsible for such trend, which can be confirmed by CIECs. The negative values of  $\Delta G$  and the positive values of  $\Delta H$  evidenced that Pb<sup>2+</sup> adsorption on these zwitterionic hybrid polymers is spontaneous and endothermic process in nature. Meanwhile, from sample A to D, the  $\Delta G$  values become more negative, indicating that Pb<sup>2+</sup> adsorption ability increases with the increasing content of ionic groups, which is consistent with the upward trend in CIECs. The desorption efficiency of sample D for Pb<sup>2+</sup> in 2 mol dm<sup>-3</sup> aqueous HNO<sub>3</sub> solution for 60 min reached up to 64.4%; implying that they are promising sorbents and can be applied to remove and recover  $Pb^{2+}$  ions from aqueous solution. These findings are very useful for the separation and recovery of Pb<sup>2+</sup> ions from the contaminated water of lead-acid rechargeable battery and other environmental field, which will be our further issue.

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