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Enhanced removal of Pb^{2+} from water by adsorption onto phosphoric acid-modified PS-EDTA resin: mechanism and kinetic study

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ABSTRACT

The present study aimed to analyze the behavior of phosphoric acid-modified PS-EDTA resin (PS-EDTA/P resin), in the adsorption and removal of Pb^{2+} ions from an aqueous solution in order to identify the parameters that determine this process. The effects of solution pH, initial metal concentration, temperature, contact time, ionic strength, and competing ions on Pb^{2+} sorption were investigated in batch experiments. The results indicated that Pb^{2+} sorption on PS-EDTA/P resin was strongly dependent on pH and weakly dependent on ionic strength. The abundant phosphorus-containing functional groups on the surfaces of PS-EDTA/P resin played an important role in Pb^{2+} sorption. The presence of Hg^{2+}, Zn^{2+}, Cu^{2+}, and Cd^{2+} reduced the Pb^{2+} sorption slightly on PS-EDTA/P resin. The maximum sorption capacities (Q_{max}) of Pb^{2+} sorption on PS-EDTA/P resin at pH 6.0 and $T = 318\,K$ were about 190.95 mg/g, higher than PS-EDTA resin. Studies on adsorption mechanism revealed that surface adsorption and intraparticle diffusion were involved in the adsorption of Pb^{2+} on PS-EDTA/P resin. It was concluded that the adsorption mechanism could be the specific reaction between Pb^{2+} and the functional groups on the surface of PS-EDTA/P resin which forms inner-sphere complexation. The thermodynamic parameters calculated from temperature-dependent sorption isotherms suggested that Pb^{2+} sorption on PS-EDTA/P resin was spontaneous and endothermic in nature. The Pb^{2+} adsorbed on PS-EDTA/P resin could be desorbed effectively by 0.05 M HNO_3, which indicated that PS-EDTA/P resin was a promising candidate for removing Pb^{2+} from wastewater.

Keywords: Phosphoric acid-modified; PS-EDTA resin; Pb^{2+} ions; Adsorption; Mechanisms

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1. Introduction

Heavy metals pollution has been a worldwide concern and results in a serious threat to ecological systems and public health. Heavy metals can be distinguished from other toxic pollutants because they are nonbiodegradable, and can be accumulated in living organisms, causing various diseases and disorders. Lead is one of the toxic heavy metals, which may cause serious damages to the central nervous system, kidney, liver, and brain [1,2]. The Environmental Protection Agency requires the concentration of lead in drinking water not to exceed 0.015 mg/L [3]. While the allowance of lead concentration recommended by the World Health Organization for drinking water is less than 0.01 mg/L [4]. But the lead concentration in industrial wastewater is usually higher than the permissible level. Thus, the removal of lead from industrial effluents is inevitable before that the wastewater is discharged into the environment. Many treatment technologies such as chemical precipitation, ion exchange, membrane filtration, and adsorption have been developed for the removal of lead from aqueous solutions. In particular, adsorption is considered as an effective and economic method for the removal of heavy metal ions from industrial wastewaters. A variety of adsorbents have been studied for lead removal including mango peel waste [5], fly ash [6], acorn waste [7], olive pomace [8], activated carbon [9], grape stalk waste [10], sawdust [11], chitosan-coated sand [12], clay minerals [13,14], various chelating resins [15,16], and microorganisms [17–19]. Among these, resins have been widely used to remove heavy metals from aqueous solution because of higher adsorption capacity, good reusability, and easy separation [20].

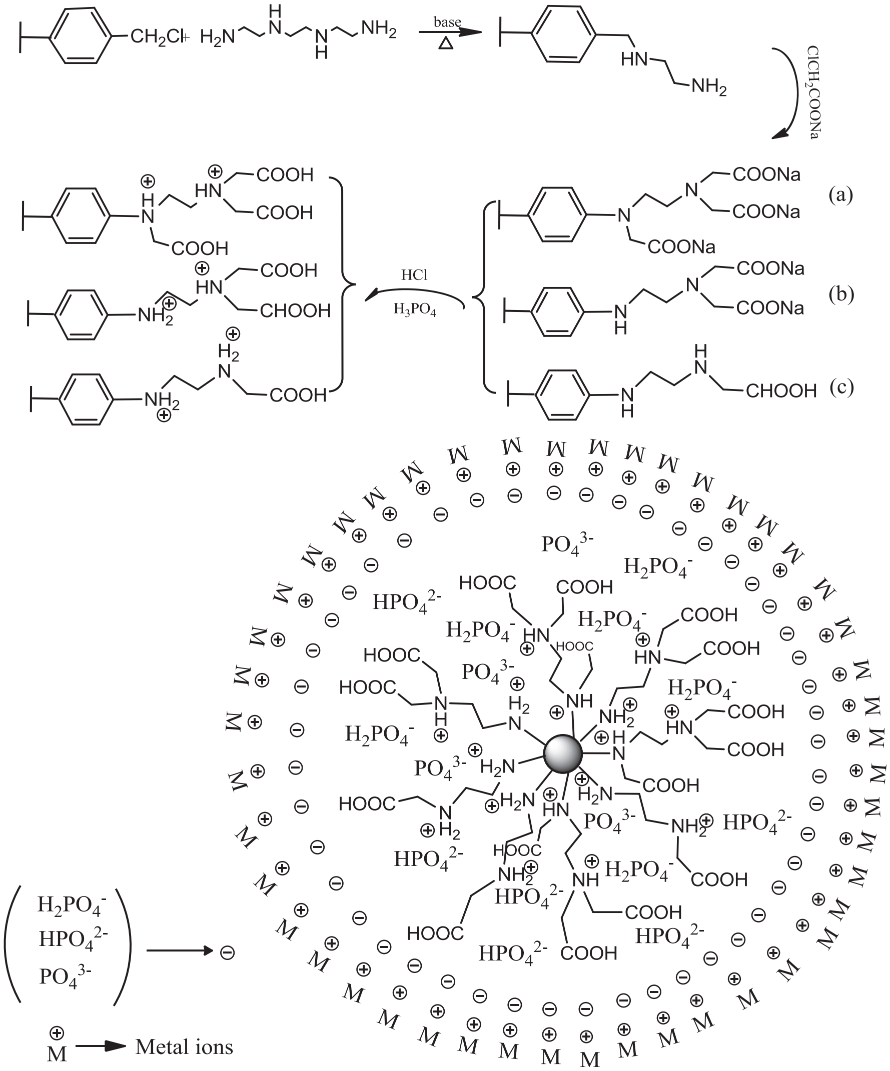

Fig. 1. The proposed structure of PS-EDTA/P resin and combination with metal ions.

In recent years, many studies have shown that chemically modified material could be an effective and promising adsorbent for water purification and wastewater treatment. Especially, chemical modification of adsorbents with phosphate has gained considerable attention. Kalavathy et al. [21] indicated that rubber wood sawdust activated with H_3PO_4 could be effectively employed for the adsorption of Cu^{2+} ions. Adebowale et al. [22] modified kaolinite clay with KH_2PO_4 in order to enhance adsorption of Pb and Cd ions from aqueous solutions. Li et al. [23] treated goethite by phosphate and the results showed that phosphate-modified goethite possessed a higher adsorption capacity for Cu^{2+} and Cd^{2+}. Unuabonah et al. [24] showed that the pretreatment of kaolinite clay with tripolyphosphate increased the cation exchange capacity of kaolinite clay from 13.45 to 128.7 meq/100 g and presented higher selectivity for Pb^{2+} ions than Cd^{2+} ions in the presence of electrolytes. However, to our knowledge, few study investigates the adsorption of Pb(II) with phosphoric acid-modified PS-EDTA resins and the data is of importance for the potential application in wastewater treatment plants.

In this study, PS-EDTA resins were used as the adsorbent for Pb(II) removal. PS-EDTA resin was considered as an environmentally friendly, low-cost and efficient adsorbent as it was synthesized in aqueous-phase by an economical and effective method without using any other toxic organic agent. Our earlier studies revealed that PS-EDTA resins prepared by this novel method showed a good capacity for the adsorption of Ag^+ [25]. To improve adsorption performance, phosphorus atoms were introduced at the surface of PS-EDTA resins by the reaction with phosphoric acid. The objective of the present work was to evaluate equilibrium, kinetic, and thermodynamic parameters of phosphoric acid-modified PS-EDTA resin for the removal of Pb^{2+} from aqueous solutions. The parameters that influence adsorption such as solution pH, initial metal concentration, contact time, temperature, ionic strength, and competing ions were investigated. In addition, the desorption efficiency and reusability of the adsorbent were studied.

2. Materials and methods

2.1. Preparation of phosphoric acid-modified PS-EDTA (PS-EDTA/P) resin

All chemicals used in this study were of analytical grade. Distilled water was used to prepare all the solutions. PS-EDTA resins were prepared as described previously [25]. Phosphoric acid-modified PS-EDTA resins were prepared by the following procedures (as shown in Fig. 1): PS-EDTA resins (10 g) were equilibrated with 250 mL of 3.5 mol/L of H_3PO_4, in a rotary shaker (140 rpm) for 24 h at 303 K. Thereafter, the resin samples were washed with distilled water several times till the pH of the effluent became almost constant. PS-EDTA/P resins obtained were subsequently dried in an oven at 343 K. The phosphorus content of the resulting materials was extracted by a mixture of hydrofluoric acid and nitric acid, and measured by inductively coupled plasma atomic emission spectroscopy (ICP, IRIS Advantage, Thermo Co. Ltd., USA). The elemental analyses were determined with a Perkin–Elmer model 2400 CHN analyzer. The surface morphologies of PS-EDTA/P and PS-EDTA resins were analyzed by scanning electron microscopy (SEM, JSM-6701F, JEOL, Japan).

2.2. Batch adsorption experiments

A stock solution of 1,000 mg/L Pb(Ⅱ) was prepared by dissolving 1.6148 g of lead nitrate ($Pb(NO_3)_2$, 99%) in distilled water. The stock solution was diluted as required to obtain the standard solutions of concentrations ranging from 50 to 400 mg/L.

The adsorption characteristics of PS-EDTA/P and PS-EDTA resin for Pb^{2+} ions from aqueous solution were investigated in detail by a batch method. All adsorption experiments were carried out in a temperature-controlled shaker at 120 rpm. In the pH studies, 0.1 g PS-EDTA/P or PS-EDTA resin and 50 mL Pb(II) solution (100 mg/L) with a range of pH values from 2.0 to 6.0 which was adjusted with 0.1 M HCl or 0.1 M NaOH solution were transferred into a conical flask (250 mL) and shaken at 120 rpm for 24 h at 298 K.

Adsorption isotherm studies were carried out by mixing 0.1 g of adsorbents with a fixed volume of solutions (50 mL) containing different initial concentrations of Pb(II) (50–400 mg/L, pH 6.0) at different constant temperatures (298, 308, and 318 K).

Kinetic experiments were carried out in the time range of 5–480 min at 298 K by contacting 0.3 g of PS-EDTA/P or PS-EDTA resin with 150 mL of Pb^{2+} solution of different initial concentrations (50, 100, 150, and 200 mg/L) at pH 6.0. Moreover, the effect of temperature on the kinetics of the adsorption of Pb^{2+} was studied by adding 0.3 g of PS-EDTA/P or PS-EDTA resin into 150 mL of 150 mg/L Pb^{2+} solution at 298, 308, and 318 K. Samples (1.0 mL) were taken at predetermined time intervals for the analysis of residual metal concentration in the aqueous solution.

The ionic strength of the solution was adjusted to the range of 0.1–5.0 g/L by adding an appropriate amount of $NaNO_3$. 0.1 g of adsorbents and 100 mg/L of Pb^{2+} solution with diverse ionic strength were shaken at 298 K for 24 h. The adsorption behavior of Pb^{2+} from binary mixtures of Pb^{2+}–Cu^{2+}, Pb^{2+}–Hg^{2+}, Pb^{2+}–Zn^{2+}, and Pb^{2+}–Cd^{2+}, respectively, was studied using PS-EDTA/P or PS-EDTA resin at normal pH. The initial concentration of the mixture was 100 mg/L. The mixture was shaken at 298 K for 24 h. The concentrations of metal ions in the solution were measured using ICP.

In the present study, the lead concentration was determined using a UnicoUV/Vis-721spectrophotometer (Shanghai Unico Co. Ltd., Shanghai, China) by monitoring the absorbance at 580 nm. The equilibrium adsorption capacity (Q_e, mg/g) and the removal percentage of Pb^{2+} (R, %) can be calculated according to the following Eqs. (1) and (2), respectively:

$$Q_e = \frac{(C_o - C_e)V}{M} \tag{1}$$

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100\% \tag{2}$$

where Q_e is the amount of Pb^{2+} ions adsorbed by the adsorbent (mg/g), C_o and C_e are the initial and equilibrium concentrations of Pb^{2+} ions in the solution (mg/L), respectively, V is the volume of metal ions solution (L), and M is the weight of adsorbent (g). All the batch experiments were performed in triplicate and the average values were used in data analysis.

2.3. Desorption and reusability studies

In the desorption experiments, Pb^{2+} loaded samples were contacted with 50 mL of 0.05 mol/L HNO_3 solution and shaken at 120 rpm for 2 h, the concentration of Pb^{2+} ions in the desorbed solution was determined to investigate the desorption efficiency. The solid samples were separated and washed thoroughly with distilled water. Then, they were soaked in 0.6 g/L NaCl solution and shaken for 12 h. The regenerated adsorbents were reused in the next cycle of adsorption experiments.

3. Results and discussion

3.1. Characterization of PS-EDTA/P resin

The contents of C, H, and N for PS-EDTA resin were 67.46, 7.219, and 6.83%, respectively, and for PS-EDTA/P resin they were 51.325, 6.137, and 6.22%, respectively. While the phosphorus content in PS-EDTA/P resin was calculated to be 2.435%. It was

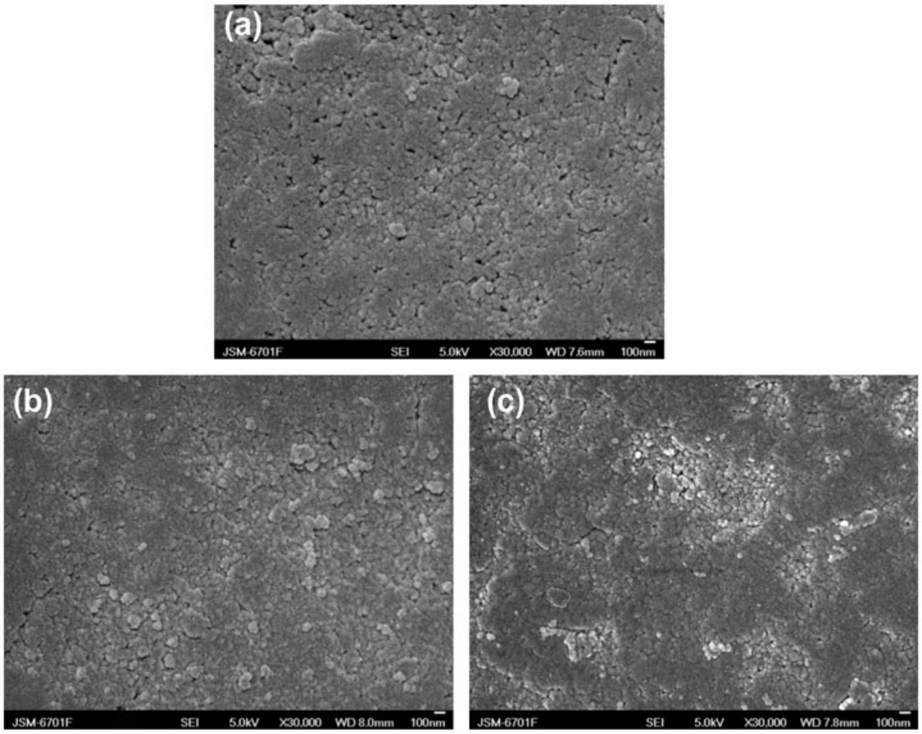

Fig. 2. Surface morphologies of (a) PS-EDTA, (b) PS-EDTA/P resin and (c) PS-EDTA/P resin after Pb^{2+} ions adsorption.

found that there was a slight decrease in the percentage of C, H, and N elements after modification. Fig. 2 (a)–(c) showed the SEM images of PS-EDTA resin, PS-EDTA/P resin, and PS-EDTA/P resin after Pb^{2+} adsorption, respectively. It can be seen from the figure, there are many pores on the surface of PS-EDTA resin (Fig. 2(a)), but some of them disappeared after modification (Fig. 2(b)). This may indicate that parts of the pores were blocked by phosphate anions. These pores could provide convenient diffusion channels for Pb^{2+} ions into the inner of resin. After Pb(Ⅱ) adsorption, SEM image of PS-EDTA/P resin was shown in Fig. 2(c). It was evident that the white particles were unevenly distributed on the surface of resin, which may be due to the formation of water insoluble metal-phosphate complexes between Pb^{2+} ions and phosphate species.

3.2. Pb^{2+} adsorption

3.2.1. Effect of pH

Solution pH is one of the most important factors affecting the removal of heavy metals from aqueous solution. Thus, the influence of pH on adsorption capacity was studied over a range of pH values from 2.0 to 6.0 to avoid lead precipitation. Based on Fig. 3, it was found that the adsorption of Pb^{2+} ions was highly dependent on the solution pH because it affected the solubility of the metal ions and the ionization states of the functional groups. Compared with PS-EDTA resin, the adsorption edges on PS-EDTA/P resin were significantly shifted to lower pH values. Similar phenomenon had been reported by Li et al. [23]. Adsorption capacities of PS-EDTA/P and PS-EDTA resin for Pb^{2+} ions increased with increasing solution pH and the maximum adsorption occurred at pH 6.0. The low adsorption capacities of Pb^{2+} ions observed at lower pH of the solution may be attributed to the partial protonation of the functional groups and the competition of H^+ with Pb^{2+} ions for active sites on the adsorbents. With an increase in pH, the negative charge density on the adsorbent surface increased due to deprotonation of the metal binding sites and thus increased Pb^{2+} adsorption. Pb^{2+} can be effectively removed by PS-EDTA/P resin over a wider range of pH compared to PS-EDTA resin. This may be explained by the fact that phosphoric acid treatment increased the surface negative charge and decreased the electrostatic potential of adsorbent surface [23,26], which caused an increase in Pb^{2+} adsorption. Therefore, subsequent experiments were carried out at pH 6.0.c

3.2.2. Effect of ionic strength

The presence of salts in wastewaters is one of the important factors that may affect the adsorption performance of the adsorbent. The ionic strengths of 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, and 5.0 g/L were used to test their effects on Pb^{2+} adsorption by PS-EDTA/P and PS-EDTA resin at initial Pb^{2+} concentration of 100 mg/L. In Fig. 4 it can be seen that the amount of Pb^{2+} ions adsorbed onto both samples was not affected by the variations of the ionic strength. It therefore indicated that PS-EDTA/P and PS-EDTA resin could efficiently remove Pb^{2+} from solutions with high salt concentration. It is reported that chemical binding reaction between the metal ions and the surface functional groups may be specific that it forms inner-sphere surface complexes and electrostatic binding reaction may be nonspecific with less selectivity forming outer-sphere adsorption. The fact that the metal ions removal from solution by adsorbents is independent on ionic strength may indicate the

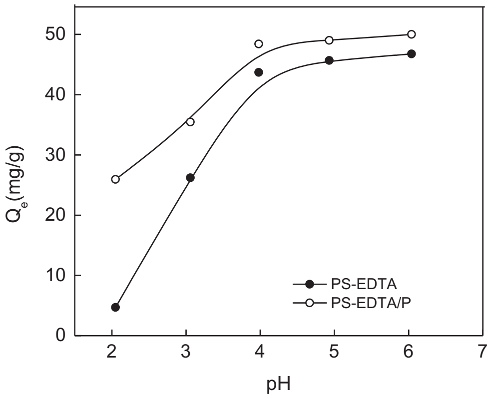

Fig. 3. Effect of pH on the adsorption of Pb^{2+} ions onto PS-EDTA resin and PS-EDTA/P resin.

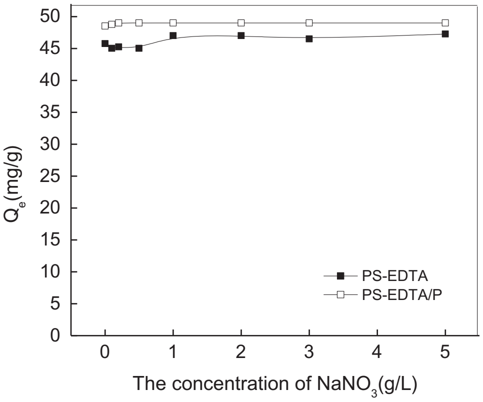

Fig. 4. Effect of ionic strength on the adsorption of Pb^{2+} on PS-EDTA resin and PS-EDTA/P resin.

Table 1
The separation factors for Pb^{2+} ions over other studied metal ions

Metal system	$\alpha_{M1/M2}$-PS-EDTA	$\alpha_{M1/M2}$-PS-EDTA/P
Pb + Hg	0.007	17.951
Pb + Cd	0.061	24.004
Pb + Zn	6.538	19.407
Pb + Cu	0.905	3.292

specific adsorption [27]. Hence, it was concluded that the adsorption of Pb^{2+} ions by both samples may mainly proceed through inner-sphere complexation.

3.2.3. Effect of competing ions on Pb^{2+} removal

Some co-existing ions present in wastewaters may interfere with the adsorption of desired ions, therefore selective separation of Pb^{2+} from binary mixtures of Pb^{2+}–Cu^{2+}, Pb^{2+}–Hg^{2+}, Pb^{2+}–Zn^{2+} and Pb^{2+}–Cd^{2+}, respectively, was studied at normal pH and other conditions similar to those in batch adsorption experiments. The adsorption selectivity of the resulting resin for Pb^{2+} was studied by the means of the separation coefficient, α, given by the equation below:

$$\alpha_{M1/M2} = \frac{\alpha_{M1}/\alpha_{M2}}{C_{eM1}/C_{eM2}} = \frac{\alpha_{M1} \cdot C_{eM2}}{\alpha_{M2} \cdot C_{eM1}} \quad (3)$$

where α_{M1} and α_{M2} (mg/g) are the concentrations of Pb^{2+} and coexisting cations in the solid phase, respectively. C_{eM1} and C_{eM2} (mg/L) are the concentrations of Pb^{2+} and coexisting cations in the solution, respectively. Generally, if $\alpha > 1$, the resin exhibits selectivity for M1 cations, and vice versa.

The values of the separation coefficient ($\alpha_{M1/M2}$) for the adsorption of Pb^{2+} over Hg^{2+}, Zn^{2+}, Cu^{2+}, or Cd^{2+} were calculated and presented in Table 1. From the obtained data it was found that the values of $\alpha_{M1/M2}$ were higher for PS-EDTA/P resin than that for PS-EDTA resin. For example, from Table 1, the value of $\alpha_{M1/M2}$ for Pb^{2+} over Hg^{2+} was 17.951 which implied that PS-EDTA/P resin had selectivity for Pb^{2+} which is about 18 times more than Hg^{2+}. The higher selectivity of PS-EDTA/P resin towards Pb^{2+} over other metals may be due to the introduction of phosphate and formation of more stable complexes which was also reported by Wan Ngah and Fatinathan [28]. These results indicated that Pb^{2+} could be selectively removed by PS-EDTA/P resin from the contaminated water in the presence of Hg^{2+}, Zn^{2+}, Cu^{2+}, or Cd^{2+}.

3.3. Adsorption kinetics and effects of contact time

The rate of metal adsorption is one of the important parameters for successful use of the adsorbent for practical application. The equilibrium adsorption of Pb^{2+} on PS-EDTA/P and PS-EDTA resin as a function of contact time and initial Pb^{2+} concentration was shown in Fig. 5. From the figures it can be seen that, within the expectation, the amount of Pb^{2+} adsorbed, Q_t (mg/g) increased with an increase in contact time. It was also observed that modification of PS-EDTA resin with phosphoric acid not only increased the adsorption of Pb^{2+} but also accelerated the adsorption rate of Pb^{2+} on the adsorbent. The adsorption of Pb^{2+} on PS-EDTA/P resin was very rapid within the first 60 min (78–84% of total metal ions adsorbed) and reached equilibrium after 150 min. While for Pb^{2+} adsorption on unmodified PS-EDTA resin, the time required to reach equilibrium was dependent on the initial Pb^{2+} concentration. The contact time needed for

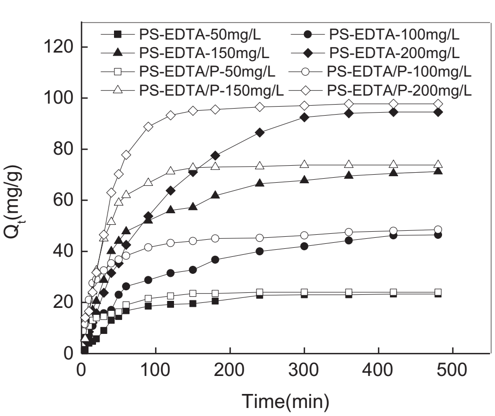

Fig. 5. Effect of contact time on Pb^{2+} adsorption under different initial concentrations (50–200 mg/L).

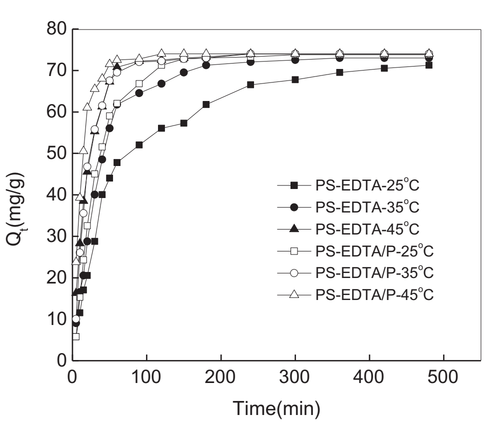

Fig. 6. Effect of temperature on kinetics of Pb^{2+} ions adsorption.

Table 2
Kinetic parameters for Pb^{2+} ions adsorption onto PS-EDTA resin and PS-EDTA/P resin

Pb con. mg/L	Q_{exp} mg/g	Pseudo-first-order			Pseudo-second-order				Intraparticle diffusion		
		Q_e (mg/g)	K_1	R^2	Q_e (mg/g)	K_2	h	R^2	K_p	C	R^2
PS-EDTA											
50	23.27	15.00	0.73×10^{-2}	0.875	26.52	0.703×10^{-3}	0.495	0.993	0.733	10.751	0.924
100	46.47	43.12	0.91×10^{-2}	0.951	51.81	0.297×10^{-3}	0.798	0.993	1.749	12.286	0.946
150	71.27	50.20	0.72×10^{-2}	0.968	79.36	0.247×10^{-3}	1.559	0.998	2.050	20.280	0.921
200	94.52	99.48	1.15×10^{-2}	0.992	123.45	0.067×10^{-3}	1.027	0.992	4.215	33.368	0.990
PS-EDTA/P											
50	24.03	5.23	0.62×10^{-2}	0.290	25.06	2.479×10^{-3}	1.557	0.999	0.542	16.528	0.917
100	48.53	19.64	0.78×10^{-2}	0.921	49.75	1.206×10^{-3}	2.985	0.999	0.864	33.500	0.979
150	73.78	24.14	0.96×10^{-2}	0.681	79.36	0.491×10^{-3}	3.092	0.995	0.100	58.278	0.921
200	97.78	42.90	1.06×10^{-2}	0.812	99.97	0.328×10^{-3}	3.283	0.994	1.712	73.415	0.889

Pb^{2+} solution with initial concentration of 50 mg/L to reach equilibrium was less than 240 min. However, for Pb^{2+} solution with the initial concentration of 200 mg/L, the time of 420 min was required to reach equilibrium. PS-EDTA/P resin showed a higher adsorption rate for Pb^{2+} compared to the unmodified PS-EDTA resin. This may be due to the existence of more active sites introduced by the modifying reagents. Besides, some pores on the surface of PS-EDTA/P resin were blocked by phosphate anions during modification, as a result, Pb^{2+} would be difficult to diffuse into the interior of adsorbent, which resulted in a shorter equilibrium time and faster adsorption rate. A similar observation was reported by Wang and Xing [26]. Fig. 6 showed the effect of temperature on the adsorption rate of Pb^{2+} ions on PS-EDTA/P and PS-EDTA resin. Increasing temperature from 298 to 318 K increased the adsorption rate of Pb^{2+} onto both samples and decreased the time for the adsorption of Pb^{2+} to reach equilibrium. This may be due to that increasing temperature may increase the driving force of Pb^{2+} onto adsorbents.

In order to investigate the kinetic mechanism that controls the adsorption of Pb^{2+} on phosphoric acid-modified and unmodified PS-EDTA resin, the pseudo-first order, the pseudo-second order, and intraparticle diffusion kinetic models are used to analyze the equilibrium data.

The linear form of the pseudo-first order kinetic model is expressed as:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \tag{4}$$

where Q_e and Q_t (mg/g) are the amounts of Pb^{2+} adsorbed at equilibrium and at time t (min), respectively, and K_1 (1/min) is the adsorption rate constant.

The pseudo-second order equation is expressed as:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{5}$$

where K_2 (g/(mg min)) is the rate constant of second-order. The second-order rate constant is used to calculate the initial adsorption rate, h (mg/(g min)), which is given by:

$$h = K_2 Q_e^2 \tag{6}$$

The intraparticle diffusion model assumes a two-step adsorption process metal ions binding to the adsorbent surface followed by the metal ions' diffusion through its pores [29]:

$$Q_t = K_i t^{0.5} + C \tag{7}$$

where K_i is the intraparticle diffusion constant (mg/(g min$^{0.5}$)), and C represents the boundary layer diffusion effect. The larger the intercept is, the greater the boundary layer effect would be. If the linear plot of intraparticle diffusion passes through the origin, then the intraparticle diffusion is the only rate-limiting step. Otherwise, some other mechanism along with intraparticle diffusion is also involved [30].

The pseudo-first-order constants (Q_e, K_1, and R^2) for Pb^{2+} adsorption on PS-EDTA/P and PS-EDTA resin were presented in Table 2. The theoretical Q_e values calculated from the first-order kinetic model did not agree with the experimental values, and the correlation coefficients were also found to be low (Table 2). These results showed that the adsorption of Pb^{2+} onto PS-EDTA/P and PS-EDTA resin did not follow the pseudo-first-order kinetic model.

The slope and intercept of the linear plot t/Q_t vs. t (Fig. 7) yielded the values of Q_e and K_2. The regression coefficients (R^2) and several parameters obtained from the pseudo-second-order kinetic model were shown in Table 2. Based on Table 2, the theoretical Q_e values were very close to the experimental Q_{exp} values and the obtained R^2 values were higher than 0.99, which indicated that the pseudo-second-order kinetic model described the removal of Pb^{2+} by both the samples. These results indicated that the second-order mechanism was predominant and the chemisorption might be the rate-limiting step that controlled the adsorption process [31]. As shown in Table 2, the values of the initial sorption rate, h, for PS-EDTA/P resin were higher than those for PS-EDTA resin, which indicated that the rate of Pb^{2+} removal by PS-EDTA/P resin was much faster than that by PS-EDTA resin. However, the values of the rate constant, K_2, were found to decrease with the increase of initial Pb^{2+} concentration. Higher K_2 values were obtained for PS-EDTA/P resin than that for PS-EDTA resin. The larger values of h and K_2 indicated that modification of PS-EDTA resin improved the adsorption rate and thus reduced the equilibrium time for the adsorption system. In addition, the adsorption kinetics for both PS-EDTA/P and PS-EDTA resin at different temperatures were found to follow the pseudo-second order model ($R^2 > 0.997$). As temperature increased from 298 to 318 K, the initial adsorption rate, h, increased from 3.092 to $14.970\,\mathrm{mg\,g^{-1}\,min^{-1}}$ and 1.559 to $6.988\,\mathrm{mg\,g^{-1}\,min^{-1}}$ for PS-EDTA/P and PS-EDTA resin, respectively. Moreover, the pseudo-second order rate constant, K_2, for PS-EDTA/P resin were also higher than those for PS-EDTA resin and the value increased with increasing temperature. This may be explained by the fact that increasing temperature may increase the diffusion rate of Pb^{2+} to the binding sites.

Fig. 8 showed the plot of Q_t vs. $t^{0.5}$ for the adsorption of Pb^{2+} on PS-EDTA/P and PS-EDTA resin. It can be seen that the plots were not linear over the whole time range, indicating that intraparticle diffusion was not the only rate limiting mechanism and several processes may affected Pb^{2+} removal. The adsorption process of Pb^{2+} onto both samples followed three steps: the initial curved stage was attributed to rapid external diffusion and surface adsorption, the second region was the gradual adsorption stage where intraparticle diffusion was the rate limiting step, and the third region was the final equilibrium stage where intraparticle diffusion started to slow down due to extremely low metal concentration in the solution. The intraparticle diffusion parameter, K_i ($\mathrm{mg/(g\,min^{-0.5})}$), was calculated from the slope of the second linear portion as shown in Table 2. The intercept of the second portion represented the boundary layer effect. The larger the intercept is, the greater the contribution of the surface adsorption would be [32]. From Table 2, it was observed that the values of K_i were higher for PS-EDTA resin than that for PS-EDTA/P resin, indicating that the effect of intraparticle diffusion reduced for PS-EDTA/P resin. This was probably due to the blockage of the pores of the resin by phosphate anions. As a result, Pb^{2+} may not be able to diffuse further into the pores and this would reduce the rate of intraparticle diffusion. Moreover, the values of the intercept, C, were higher for PS-EDTA/P resin than for PS-EDTA resin, indicating that the contribution of surface adsorption for PS-EDTA/P resin was more than PS-EDTA resin. Based on the results it was suggested that both surface adsorption and intraparticle

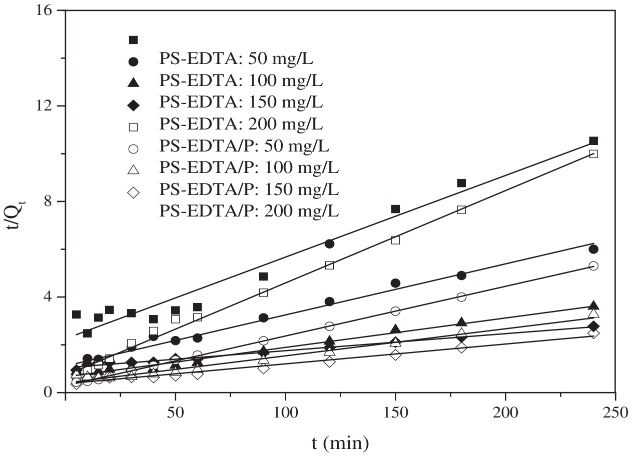

Fig. 7. Pseudo-second-order plot for adsorption of Pb^{2+} ions on PS-EDTA resin and PS-EDTA/P resin.

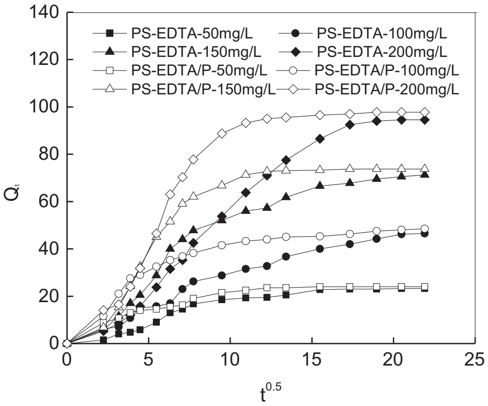

Fig. 8. Intraparticle diffusion plot for the adsorption of Pb^{2+} onto PS-EDTA resin and PS-EDTA/P resin.

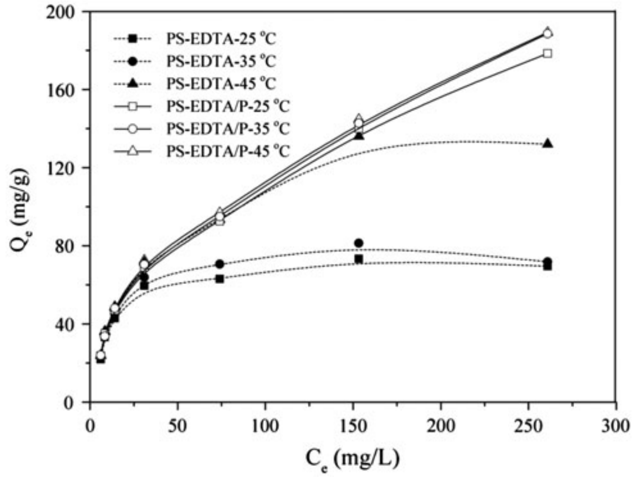

Fig. 9. Plot of Q_e (mg/g) vs. Pb^{2+} ions equilibrium (final) concentrations in the aqueous phase.

diffusion affected Pb^{2+} adsorption by the two samples, while surface adsorption played a greater role in the adsorption of Pb^{2+} on PS-EDTA/P resin.

3.4. Adsorption isotherms and effects of initial metal concentration and temperature

The effects of initial metal concentration on the adsorption of PS-EDTA/P and PS-EDTA resin for Pb^{2+} were shown in Fig. 9. It was found that adsorption capacities of Pb^{2+} on PS-EDTA/P increased from 23.75 to 178.49 mg/g as the initial Pb^{2+} concentration increased from 50 to 400 mg/L at 298 K. However, the adsorption of Pb^{2+} on PS-EDTA resin initially increased with increasing initial metal concentration and then tended to reach a plateau. The adsorption capacity of PS-EDTA/P resin increased by 143% for Pb^{2+} compared with the unmodified PS-EDTA resin, which may be attributed to the higher affinity of phosphate groups to Pb^{2+} ions. It was also observed that increasing initial metal concentration resulted in a decrease in the percent removal of Pb^{2+} by both samples. As the initial metal concentration increased from 50 to 400 mg/L, the equilibrium removal of Pb^{2+} decreased from 95.1 to 89.5% for PS-EDTA/P resin and 87.7–34.7% for PS-EDTA resin. It therefore indicated that PS-EDTA/P resin was more effective than PS-EDTA resin for the removal of Pb^{2+}. In addition, it also can be seen from Fig. 9, the Q_e values of PS-EDTA/P resin and PS-EDTA resin were found to increase with increasing temperature from 298 to 318 K, indicating the endothermic nature of the adsorption process.

Analysis of sorption equilibrium data is important for optimizing the design of adsorption systems. Adsorption isotherm expresses the relationship between metal ions adsorbed onto the adsorbent and metal ions in the solution and provides important design parameters for adsorption systems. Several isotherm models have been widely used to model the equilibrium of adsorption systems. In the present work, Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms were used to describe the equilibrium of Pb^{2+} adsorption onto both samples.

The Langmuir isotherm model assumes a monolayer adsorption with a homogeneous distribution of the sorption sites and sorption energies, and that once the adsorption site is occupied no further adsorption can take place at that site [33,34]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \tag{8}$$

where Q_e (mg/g) and C_e (mg/L) are the equilibrium Pb^{2+} concentrations in the solid and liquid phase, respectively. $Q_{\max}$ (mg/g) and K_L (L/mg) are the Langmuir constants related to saturated monolayer adsorption capacity and the binding energy of the sorption system, respectively. The values of $Q_{\max}$ and K_L were calculated from the slope and the intercept of the linear plot of C_e/Q_e vs. C_e (Fig. 10), respectively.

The Freundlich isotherm is an empirical equation based on adsorption on a heterogeneous surface. It is assumed that the stronger binding sites are occupied first and the binding strength decreases with the increasing degree of site occupation [30].The linear form of Freundlich equation is given as:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{9}$$

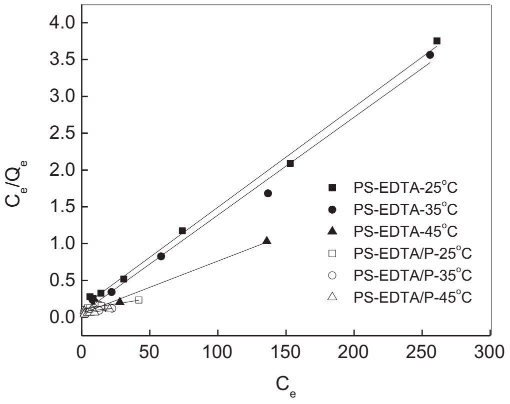

Fig. 10. Langmuir isotherm for Pb^{2+} ions adsorption onto PS-EDTA resin and PS-EDTA/P resin.

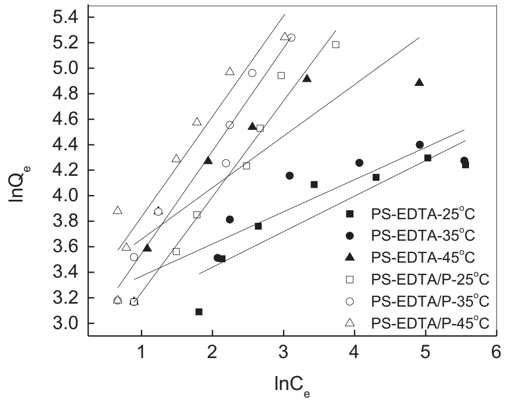

Fig. 11. Freundlich isotherm for Pb^{2+} ions adsorption onto PS-EDTA resin and PS-EDTA/P resin.

where K_f and n are the Freundlich constants, indicating the relative adsorption capacity of the adsorbent related to the bonding energy and the adsorption intensity, respectively. The values of K_f and *1*/*n* were calculated from the intercept and the slope of the linear plot between $\ln Q_e$ and $\ln C_e$ (Fig. 11), respectively. The $1/n$ values are between 0.1 and 1.0, indicating that the adsorption of heavy metals is favorable at studied conditions [35].

The D–R isotherm is more general than the Langmuir isotherm since it does not assume a homogeneous surface or constant sorption potential [36]. It can be applied to distinguish between physical and chemical adsorption. The linear form of D–R isotherm equation is expressed as follows:

$$\ln Q_e = \ln Q_m - \beta\varepsilon^2 \tag{10}$$

where β is a constant related to the mean free energy of adsorption ($mol^2 J^{-2}$), Q_m is the theoretical saturation capacity (mol/g), ε is the Polanyi potential, which is equal to $RT \ln(1 + 1/C_e)$, R is the gas constant ($J mol^{-1} K^{-1}$) and T is the absolute temperature (K).

The mean adsorption energy, E (kJ/mol), was involved in the transfer of free energy of one mole of metal ions from infinity in solution to the surface of the solid. The mean adsorption energy (E) can be determined by the following equation:

$$E = \frac{1}{(2\beta)^{1/2}} \tag{11}$$

where E value gives the information about sorption mechanism [37]. If the value of E is between 8 and 16 kJ/mol, the adsorption process takes place chemically and if the value of E is less than 8 kJ/mol, then the adsorption process takes place physically [38].

The Langmuir and Freundlich isotherm constants along with the correlation coefficients (R^2) have been calculated from the corresponding isotherm plots for the adsorption of Pb^{2+} onto PS-EDTA/P and PS-EDTA resin and the results were presented in Table 3. As can be seen in Table 3, higher correlation coefficients ($R^2 > 0.99$) were obtained from the Langmuir model, indicating that the Langmuir isotherm model correlated quite well with the equilibrium data for Pb^{2+} adsorption on PS-EDTA resin. The values of the theoretical Q_{max} were in good agreement with those obtained experimentally (Table 3). The adsorption of Pb^{2+} onto PS-EDTA resin may be considered as monolayer adsorption. While for the adsorption of Pb^{2+} onto PS-EDTA/P resin, the Freundlich model gave the highest R^2 values (larger than 0.96) at all the temperatures studied, indicating that the adsorption of Pb^{2+} onto PS-EDTA/P resin was best described by this isotherm. It may be attributed to the heterogeneity of various active sites on the surface of the PS-EDTA/P

Table 3
Langmuir, Freundlich and D–R isotherm parameters for Pb^{2+} ions adsorption on PS-EDTA resin and PS-EDTA/P resin

T ℃	Q_{exp} mg/g	Langmuir			Freundlich				D–R	
		Q_{max} (mg/g)	K_L	R^2	K_f	n	R^2	K_p	C	R^2
PS-EDTA										
25	73.37	73.53	0.1001	0.9973	17.8374	3.5855	0.8326	0.818×10^{-3}	13.649	0.8615
35	81.37	75.18	0.2239	0.9942	22.5785	3.9635	0.8380	0.820×10^{-3}	15.555	0.8804
45	136.02	140.84	0.1411	0.9953	25.9118	2.4734	0.7848	2.917×10^{-3}	12.194	0.8305
PS-EDTA/P										
25	178.49	344.82	0.0265	0.8388	12.0564	1.3310	0.9751	14.091×10^{-3}	9.016	0.9766
35	188.58	476.19	0.0281	0.6439	15.4761	1.2408	0.9775	23.897×10^{-3}	8.982	0.9776
45	190.95	454.54	0.0383	0.6948	18.1850	1.1106	0.9641	45.767×10^{-3}	9.023	0.9723

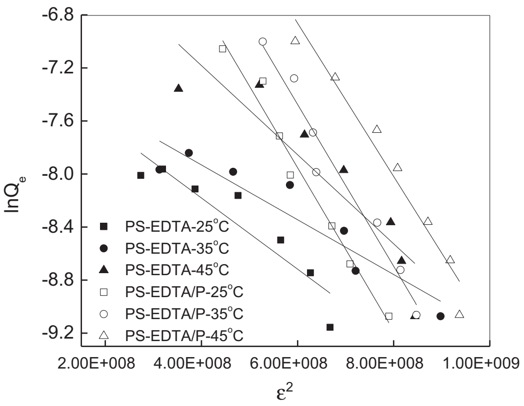

Fig. 12. D–R isotherm for Pb^{2+} ions adsorption onto PS-EDTA resin and PS-EDTA/P resin.

resin. It was notable that PS-EDTA/P resin was a composite material which was prepared with PS-EDTA resin and phosphoric acid. Therefore, it was reasonable that PS-EDTA/P resins have more heterogeneous binding sites. It was also found that the adsorption of PS-EDTA/P resin for Pb^{2+} was significantly higher than that of the unmodified PS-EDTA resin at all the studied temperatures, indicating that chemical modification of PS-EDTA resin with phosphoric acid improved the adsorption capacity for Pb^{2+} due to the higher concentration of active sites of the PS-EDTA/P resin. As can be seen in Table 3, although the D–R isotherm (Fig. 12) gave the higher correlation coefficients, the theoretical Q_m values and the experimental Q_{exp} values were not in agreement with each other indicating a poor D–R isotherm model fit.

3.5. Thermodynamic parameters of Pb^{2+} ions adsorption

Thermodynamics parameters can be determined using the equilibrium constant K_d (Q_e/C_e) which depends on temperature. The change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) associated to the adsorption process was calculated using following equations [39]:

$$\Delta G^\circ = -RT \ln K_d \tag{12}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{13}$$

where R is the universal gas constant (8.314 J/(mol K)), and T is the absolute temperature (K). The values of ΔH° and ΔS° can be calculated from the slope and intercept of the plot of ln K_d vs. $1/T$, respectively. The ΔH° values between 20.9 and 418.4 kJ/mol are usually considered, as the comparable values for the chemical adsorption process [40].

The activation energy (Ea) can be calculated from a linear plot of the Arrhenius equation:

$$\ln K_2 = \ln K_o - \frac{Ea}{RT} \tag{14}$$

where K_2 is the rate constant of the pseudo-second order (g/(mg min)), K_o is the independent temperature factor (g/mg min)). The value of Ea can be determined from the slope of the plot of lnK_2 vs. $1/T$.

The thermodynamics of the adsorption of Pb^{2+} onto PS-EDTA/P and PS-EDTA resin were studied at 298, 308 and 318 K at 100 mg/L of initial metal concentration, pH 6.0, and 12 h of contact time and the results were given in Table 4. The negative values of ΔG° at various temperatures indicated the feasibility of the process and spontaneous nature of the adsorption. Moreover, the negative value of ΔG° decreased with an increase in temperature, indicating that the spontaneous nature of Pb^{2+} adsorption was inversely proportional to the temperature. The positive values of ΔH° further confirmed the endothermic nature of adsorption process whereas the positive values of ΔS° suggested that the degrees of freedom increased at the solid–liquid interface during the adsorption and it might be due to the substitution of water hydration molecules of metal ion by different binding sites. The observed larger positive value of ΔS° for PS-EDTA/P resin than that for PS-EDTA resin may be due to the stronger interaction between Pb^{2+} ions and phosphate groups. In addition, the heat of adsorption value between 20.9 and 418.4 kJ/mol indicates the chemisorption process. Hence Pb^{2+} ions adsorption on PS-EDTA/P and PS-EDTA resin was chemical in nature. It was also seen from the table that $\Delta H^\circ < T\Delta S^\circ$ at all

Table 4
Thermodynamic parameters for the adsorption of Pb^{2+} ions onto PS-EDTA resin and PS-EDTA/P resin

Adsorbent	ΔG° (kJ/mol)			ΔH° (kJ/mol)	ΔS° (J/mol K)	Ea (kJ/mol)	$T\Delta S^\circ$		
	298 K	308 K	318 K				298 K	308 K	318 K
PS-EDTA	−2.75	−4.01	−5.23	34.22	124.10	61.48	36.98	38.22	39.46
PS-EDTA/P	−5.12	−6.75	−8.52	45.52	169.87	66.26	50.62	52.32	54.02

temperatures. This indicated that the adsorption process of Pb^{2+} was dominated by entropic change rather than enthalpic change. In this study, the values of Ea were calculated to be 61.48 kJ/mol for PS-EDTA resin and 66.26 kJ/mol for PS-EDTA/P resin. Generally, low activation energies (5–40 kJ/mol) are characteristic of physisorption, while higher ones (40–800 kJ/mol) suggest chemisorption [40]. This indicated that chemical adsorption dominated the process of Pb^{2+} adsorption onto both samples.

3.6. Desorption study

In order to make the adsorption process more economical and feasible, desorption efficiency and regeneration potential of PS-EDTA/P and PS-EDTA resin was investigated. 0.05 M HNO_3 was used as the desorbing agent for the recovery of Pb^{2+} from metal-loaded adsorbents. Desorption of Pb^{2+} from the metal-loaded PS-EDTA/P and PS-EDTA resin for the first cycle resulted in 92.42 and 75.61% of metal recovery, respectively. It was found that only 44–60% of Pb^{2+} was recovered if the desorbed resins were treated with distilled water, while, the treatment with solution of NaCl could restore the adsorption capacity of desorbed resins. About eight adsorption–desorption cycles were carried out in the batch system to evaluate the reusability of PS-EDTA/P and PS-EDTA resin. The results showed that more than 67% of Pb^{2+} was adsorbed by PS-EDTA/P resin after eight adsorption–desorption cycles. It was notable that a small amount of P from PS-EDTA/P resin was lost. While the adsorption capacity of PS-EDTA resin decreased as the cycle number of adsorption–desorption goes higher. At the end of the eighth cycle, only 14% of Pb^{2+} adsorption was obtained. These results indicated that phosphoric acid-modified PS-EDTA resin was a good reusable adsorbent for the removal of Pb^{2+} from wastewaters.

4. Conclusions

The adsorption characteristics of Pb^{2+} on phosphoric acid-modified and unmodified PS-EDTA resin from aqueous solution were evaluated. When compared with unmodified resin, phosphoric acid-modified resin had higher adsorption capacity and faster adsorption rate. The adsorption of Pb^{2+} by phosphoric acid-modified and unmodified PS-EDTA resin was best described by the Freudlich and Langmuir isotherm, respectively. Kinetic data of Pb^{2+} adsorption onto both samples correlated well with the pseudo-second order kinetic model. Adsorption mechanism studies revealed that surface adsorption and intraparticle diffusion were involved in the adsorption of Pb^{2+} onto both samples. Thermodynamic studies showed that the adsorption process was endothermic and spontaneous in nature. All the above results indicated that phosphoric acid-modified PS-EDTA resin was an effective and reusable adsorbent for removal of Pb^{2+} from aqueous solution due to its high adsorption capacity and selectivity, fast kinetics, feasible regeneration. In addition, further investigation is still needed to study the effects of various parameters such as bed height, inlet metal ion concentration on the packed column adsorption, which is expected to lead to its large-scale application.

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