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Thermodynamics and kinetics of Zn(II) adsorption on crosslinked starch phosphates

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ABSTRACT

Crosslinked starch phosphates (CSP) with different contents of phosphate groups were used to adsorb Zn(II) from aqueous solution. Effects of adsorption time, initial concentration of Zn(II) ion, and temperature on the adsorption of Zn(II) by CSP were studied, and the equilibrium, thermodynamics and kinetics of the adsorption process were further investigated. It showed that crosslinked starch phosphates can effectively remove Zn(II) from the solution. The adsorption equilibrium data correlate well with the Langmuir isotherm model with a maximum adsorption capacity of 2.00 mmol g^{-1}. The adsorption of Zn(II) on CSP is endothermic in nature. The pseudo-first-order and pseudo-second-order kinetic models were applied to test the experimental data. The pseudo-second-order kinetic model provided a better correlation of the experimental data in comparison with the pseudo-first-order model.

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1. Introduction

Zinc is an important metal, which is widely used in metal plating facilities, battery manufacturing processes, production of paints and pigments, and so on. However, excessive zinc has toxic effects on the environment and human life by joining the food chain after entering the wastewater. Among all the techniques for the removal of metal ions from wastewater, adsorption method is generally preferred due to its high efficiency, easy handling, and availability of different adsorbents.

Recently, adsorbents based on starch have attracted more and more attention with the aim to develop low-cost adsorbents and decrease the dependence on petroleum. Zhang et al. studied the adsorption of Cu(II) from aqueous solutions onto a graft copolymer of crosslinked starch/acrylonitrile, and found that the adsorption process obeyed first-order reversible kinetics and the adsorption isotherms followed the Freundlich model [1]. Xing et al. investigated the adsorption behavior of crosslinked cationic starch maleate for chromium(VI), and found that the adsorption process followed Langmuir isotherm and was exothermic [2]. Chen et al. studied the adsorption properties of oxidized carboxymethyl starch and crosslinked carboxymethyl starch for calcium ion, and concluded that the adsorption process was exothermic and adsorption isotherm models fit well in Langmuir model for oxidized carboxymethyl starch and Freundlich model for crosslinked carboxymethyl starch, respectively [3]. Xu et al. investigated the adsorption behaviors of some dyes on crosslinked amphoteric starch, and concluded that the pseudo-second-order model fits the experimental data better than the pseudo-first-order model [4,5]. Actually, adsorption thermodynamics determines the final extent of an adsorption process and mass transfer kinetics controls the cycle time of an adsorption process. A good understanding of adsorption equilibrium and thermodynamics is required to design and operate an adsorption process.

Therefore, the objective of this study was to evaluate the adsorption potential of CSP for Zn(II) ions from aqueous solution. The equilibrium and kinetic data of adsorption process were studied to better understand the adsorption mechanism of Zn(II) on crosslinked starch phosphates. As a branch of adsorption thermodynamics, the adsorption equilibrium was also investigated.

2. Materials and methods

2.1. Materials

Corn starch (Zhucheng Xingmao Corn Developing Co., Ltd., food-grade) was dried at 105 °C before it was used. $ZnCl_2$ (analytic reagent grade) was used to prepare the adsorbate solution. Urea, phosphoric acid, and all other commercial chemicals were analytic reagent grade and used without further purifica-

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tion. All solutions and standards were prepared using deionized water.

2.2. Synthesis of crosslinked starch phosphates

Crosslinked starch phosphates were prepared according to the method described in previous work [6]. Epichlorohydrin was used as crosslinker to prepare crosslinked starch and then crosslinked starch phosphates were prepared using crosslinked starch, urea and phosphoric acid as materials via dry process. Phosphorus content of adsorbents was determined according to spectrophotometry (GB 12092–1989) [7].

Three samples with different quantity of phosphate groups were prepared to be used as adsorbents. Three samples were named SP1, SP2 and SP3, with the amount of phosphate groups 1.21, 1.87 and 2.46 mmol g^{-1}, respectively. The surface area of adsorbents was determined according to Juszczak' method [8] using Surface Area and Porosity Analyzer (ASAP2020, USA). The nitrogen BET surface areas of SP1, SP2 and SP3 were 0.26, 0.34 and 1.43 $m^2\,g^{-1}$, respectively.

2.3. Adsorption experiments

Adsorption experiments were carried out by batch methods. The desired dose of CSP was added to 50 mL of aqueous $ZnCl_2$ solution in a series of 100 mL glass-stoppered Erlenmeyer flasks. The suspension was stirred on a magnetic stirrer at a uniform speed of 120 rpm in a constant temperature bath. After certain adsorption time, the suspension was filtered by suction and the concentration of Zn(II) ions in the aqueous phase was analyzed by complexometric titration method [9]. pH was adjusted to 4.0 by adding either 0.1 M HCl solution or 0.1 M NaOH solution before adding the adsorbent.

The adsorption capacity was calculated from the following expression:

$$Q = \frac{(C_i - C_t)V}{m},$$

where Q is the adsorption capacity of the adsorbent (mmol g^{-1}), C_i and C_t (mmol L^{-1}) the initial and terminal concentrations of the Zn(II) ions in the adsorption solution, respectively, and V (mL) and m (mg) are the volume of the adsorption solution and the dose of the adsorbent, respectively.

3. Results and discussion

3.1. Adsorption equilibrium studies

Adsorption equilibrium data are mainly about the adsorption capacities of the adsorbents at different Zn(II) concentrations. The effect of initial Zn(II) concentration on the adsorption capacity is shown in Fig. 1. The error bars mark the absolute deviations between different measurements, as also do the error bars in Figs. 4 and 6. It can be found that equilibrium adsorption capacities of CSP for Zn(II) increase with a rise in the initial Zn(II) concentration, which means the adsorption process is highly concentration dependent. When the initial Zn(II) concentration is increased from 1.5 up to 4.0 mmol L^{-1}, the adsorption capacities of SP1, SP2 and SP3 increase from 0.76 to 1.14 mmol g^{-1}, 0.88 to 1.44 mmol g^{-1}, and 1.00 to 1.70 mmol g^{-1}, respectively. The increase in adsorption capacity of CSP with relation to Zn(II) concentration is probably due to a high driving force for mass transfer. Besides, there was little increase in adsorption capacities for initial Zn(II) concentration changes from 3.5 to 4.0 mmol L^{-1}. The adsorption of Zn(II) on CSP is an ion exchange process, as can be showed in the following

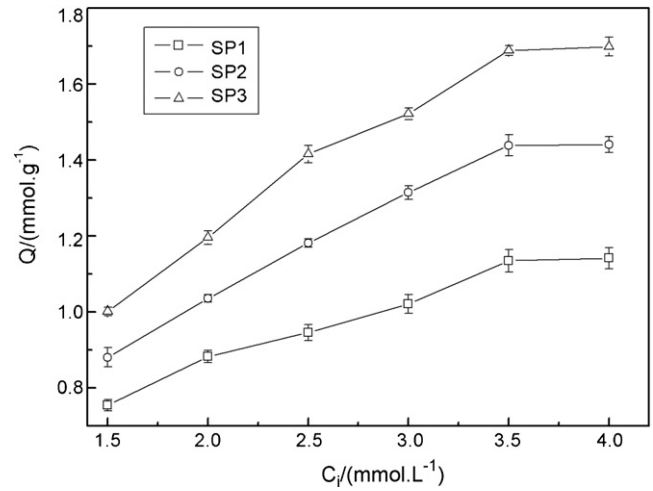

Fig. 1. Effect of the initial Zn(II) concentration on the adsorption capacities (T = 293 K; adsorption time, 40 min; dose of CSP, 60 mg).

expression:

$$\text{St-O-PO}_3\text{R}_2 + \text{Zn}^{2+} \rightleftharpoons \text{St-O-PO}_3\text{Zn} + 2\text{R}^+, \quad \text{R} = \text{H}^+ \text{ or } \text{NH}^{4+}$$

The adsorption performance of metal ions on CSP mainly depends on the active phosphate groups, which was mentioned in the previous papers [6,10]. The adsorption capacities of Zn(II) therefore tend to saturated values with decrease in the content of available phosphate groups when the initial Zn(II) concentration beyond 3.5 mmol L^{-1}.

Langmuir and Freundlich models are widely used to describe the equilibrium of an adsorption process between the liquid and solid phases. The Langmuir model is valid for a monolayer adsorption with a homogenous distribution of adsorption sites and sorption energies, without interactions between the adsorbed molecules or ions. The Freundlich model is used for heterogeneous surface energies in which the energy term in the Langmuir equation varies as a function of the surface coverage strictly as a result of variation in the adsorption heat. In order to better design an adsorption system to remove Zn(II) from wastewater, Langmuir and Freundlich models have been tested in the present study.

3.1.1. The Langmuir isotherm

Langmuir equation is widely applied to quantify adsorption capacity and is given as follows [11,12]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m},$$

where C_e and Q_e are equilibrium Zn(II) concentration (mmol L^{-1}) and equilibrium adsorption capacity (mmol g^{-1}), respectively; Q_m and b the Langmuir constants representing maximum adsorption capacity (mmol g^{-1}) and the affinity adsorption constant (L $mmol^{-1}$), respectively. The straight lines were given by plotting C_e/Q_e versus C_e, as shown in Fig. 2, which give the values of b and Q_m in Table 1 according to the intercept and slope of these lines, respectively. The maximum adsorption capacities of SP1, SP2 and SP3 are 1.37, 1.78 and 2.00 mmol g^{-1}, respectively. The good applicability of the Langmuir isotherms to the Zn(II) adsorption shows that both monolayer adsorption and homogeneous distribution of active groups on the surface of the adsorbent are possible.

3.1.2. The Freundlich isotherm

Freundlich isotherm is often used for heterogeneous surface energy systems. A linear form of the Freundlich equation is given

Table 1
Langmuir and Freundlich parameters for the adsorption of Zn(II) on CSP

Sample	Langmuir			Freundlich		
	Q_m (mmol g^{-1})	b (L mmol^{-1})	r^2	n	K_F (mmol g^{-1})	r^2
SP1	1.37	1.87	0.9922	3.35	1.45	0.9745
SP2	1.78	2.01	0.9939	3.08	1.15	0.9807
SP3	2.00	2.99	0.9953	3.51	1.13	0.9794

T = 293 K; adsorption time, 40 min; dose of CSP, 60 mg.

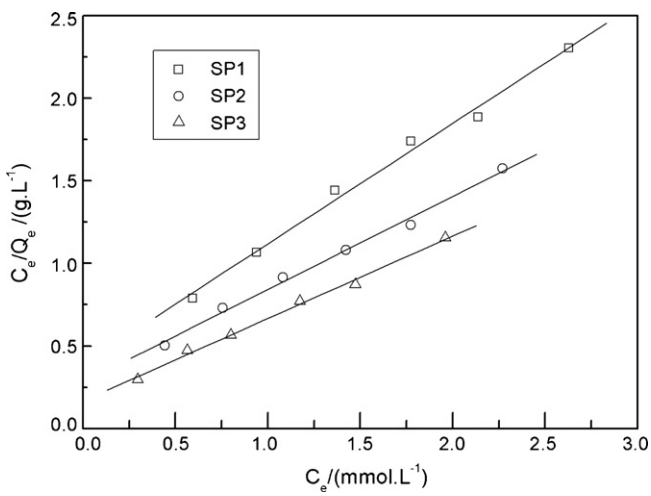

Fig. 2. Langmuir adsorption isotherms for the adsorption of Zn(II) on CSP (T = 293 K; adsorption time, 40 min; dose of CSP, 60 mg).

as [13]:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e,$$

where K_F is the Freundlich dissociation constant (mmol g^{-1}) and n the Freundlich exponent. K_F and n can be determined from the linear plot of $\log Q_e$ versus $\log C_e$. The Freundlich isotherms for adsorption of Zn(II) on CSP are shown in Fig. 3 and the values of the Freundlich constants together with the correlation coefficient (r^2) are presented in Table 1. The values of correlation coefficient are lower than the Langmuir value, which shows that the Langmuir equation represents a better fit of experimental data than the Freundlich equation. The adsorption of Zn(II) on other adsorbents

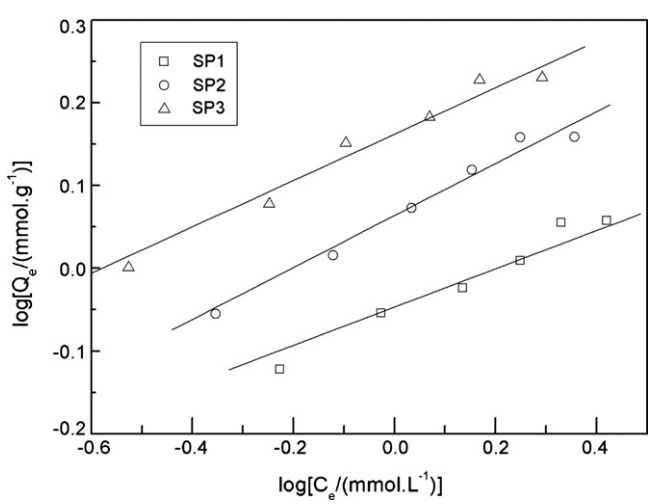

Fig. 3. Freundlich adsorption isotherms for the adsorption of Zn(II) on CSP (T = 293 K; adsorption time, 40 min; dose of CSP, 60 mg).

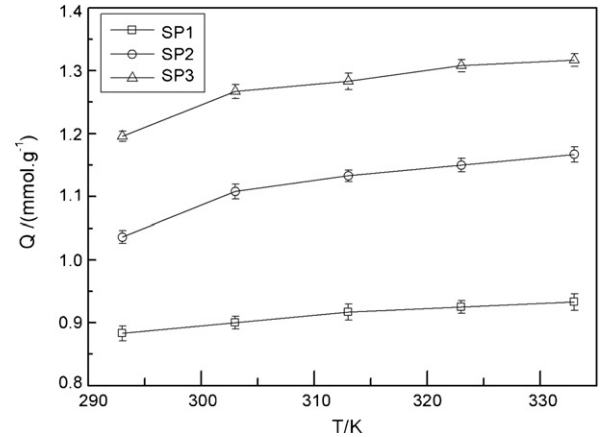

Fig. 4. Effect of the temperature on the adsorption capacity for Zn(II) on CSP ([Zn^{2+}] = 2 mmol L^{-1}; adsorption time, 40 min; dose of CSP, 60 mg).

based on lignin [14] and mineral [15] via ion-exchange mechanism was observed to obey Langmuir equation better than Freundlich equation.

3.2. Adsorption thermodynamic studies

The thermodynamics for the adsorption of Zn(II) on crosslinked starch phosphates was investigated in the range of 293–333 K, and the influence of temperature on the adsorption under the optimized conditions is shown in Fig. 4. It can be found that there is a little increase for the equilibrium adsorption capacity with the temperature increase from 293 to 333 K.

Thermodynamic parameters such as change in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined using the following equations [16]:

$$K_D = \frac{Q_e}{C_e},$$

$$\log K_D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R},$$

$$\Delta G = \Delta H - T\,\Delta S$$

where K_D (L g^{-1}) is the distribution coefficient, Q_e (mmol g^{-1}) and C_e (mmol L^{-1}) are the adsorption capacity and Zn(II) concentra-

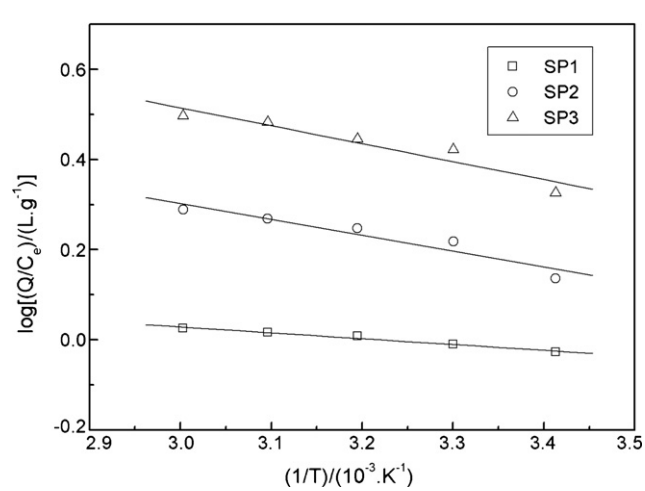

Fig. 5. The plots of $\log K_D$ versus $1/T$ for the adsorption of Zn(II) on CSP ([Zn^{2+}] = 2 mmol L^{-1}; adsorption time, 40 min; dose of CSP, 60 mg).

Table 2
Thermodynamic parameters for the adsorption of Zn(II) on CSP

Sample	T (K)	Q_e (mmol g^{-1})	K_D (L g^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
SP1	293	0.88	0.94	0.14	2.47	7.96
	303	0.90	0.98	0.058		
	313	0.92	1.02	−0.021		
	323	0.93	1.04	−0.10		
	333	0.93	1.06	−0.18		
SP2	293	1.04	1.37	−0.89	6.72	25.96
	303	1.11	1.65	−1.15		
	313	1.13	1.77	−1.41		
	323	1.15	1.85	−1.67		
	333	1.17	1.95	−1.92		
SP3	293	1.20	2.12	−1.96	7.61	32.67
	303	1.27	2.64	−2.29		
	313	1.28	2.79	−2.62		
	323	1.31	3.04	−2.94		
	333	1.32	3.14	−3.27		

[Zn^{2+}] = 2 mmol L^{-1}; adsorption time, 40 min; dose of CSP, 60 mg.

tion at equilibrium, respectively, T is temperature in Kelvin and R is the gas constant. ΔH and ΔS were obtained from the slope and intercept of the plots of $\log K_D$ versus $1/T$ (Fig. 5). Table 2 shows the calculated values of the thermodynamic parameters. The values of ΔG become more negative with increasing temperature, which indicates that the adsorption process is more favorable at high temperature. The similar results were found in the studies of Wang and Qin [17] and Rakhshaee et al. [18]. The positive values of ΔS indicate that there is an increase in the randomness in the solid/solution interface during the adsorption process. The ΔH values are in the range of 2.47–7.61 kJ/mol with a mean value of 5.60 kJ/mol, which mean the endothermic nature of the adsorption process. In addition, the small values of ΔH are not compatible with the formation of strong chemical bonds between phosphate groups and Zn(II) ions, and the adsorption process is likely to be on account of the weak ionic bond interactions between Zn(II) and phosphate groups.

3.3. Adsorption kinetics studies

To better understand the adsorption mechanism between crosslinked starch phosphates and Zn(II) ions in aqueous solution, adsorption capacities of Zn(II) were measured as a function of time. As shown in Fig. 6, Zn(II) ions are rapidly removed by CSP and the adsorption processes reach equilibrium in about 40 min. Although the quantity of active phosphate groups is different the equilibrium time is almost the same. According to the chemisorption steps [19], transporting within the adsorbent particle is considered as the rate-limiting step. Most of the active groups are on the particle surface [6], and this makes the rate-limiting step rapid.

Predicting the kinetic models for a given adsorption process is probably the most important factor in adsorption system design. A number of kinetic models have been described in an attempt to find a suitable mechanism explanation for solid/liquid adsorption systems, in which Lagergren's first-order [20] and Ho's pseudo-second-order kinetic models [21] are the two most widely applied. Then, the two kinetic models are used to correlate experimental data for the adsorption process of Zn(II) on CSP.

3.3.1. Pseudo-first-order kinetic model

Lagergren's pseudo-first-order equation is the earliest known one describing the adsorption rate based on the adsorption capacity. During the last several decades, the kinetics equilibrium has been widely applied to the adsorption of pollutants from aqueous solutions [22]. The linear form of Lagergren's pseudo-first-order equation is generally expressed as [23,24]:

$$\log(Q_e - Q) = \log Q_e - \frac{K_1}{2.303}t,$$

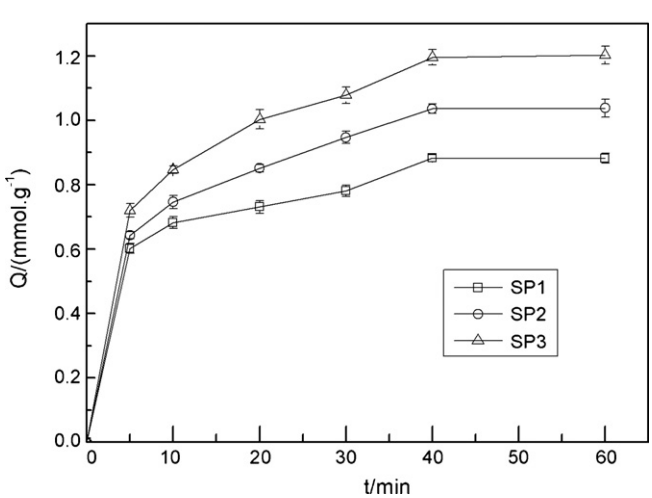

Fig. 6. Effect of the adsorption time on the adsorption capacities of Zn(II) ([Zn^{2+}] = 2 mmol L^{-1}; T = 293 K; dose of absorbents, 60 mg).

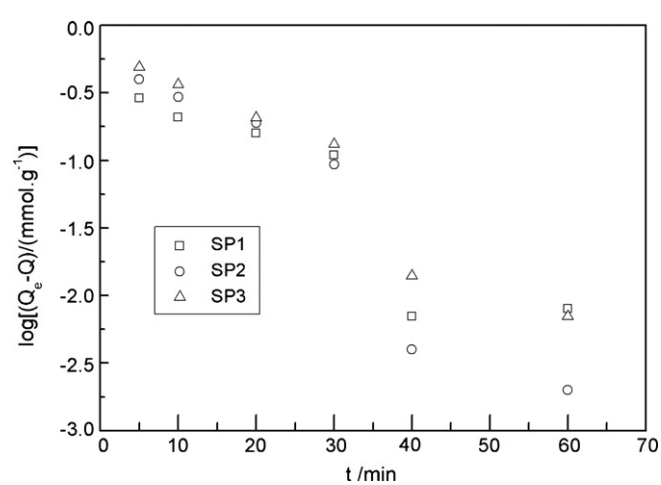

Fig. 7. Pseudo-first-order plots for adsorption of Zn(II) on adsorbents ([Zn^{2+}] = 2 mmol L^{-1}; T = 293 K; dose of absorbents, 60 mg).

Table 3
Pseudo first and second order kinetic parameters for the adsorption of Zn(II) on CSP

Sample	$Q_{e\text{-exp}}$ (mmol g^{-1})	Pseudo first order			Pseudo second order		
		$Q_{e\text{-cal}}$ (mmol g^{-1})	K_1 (min^{-1})	r^2	Q_e (mmol g^{-1})	K_2 (g mmol^{-1} min^{-1})	r^2
SP1	0.89	0.48	0.074	0.8254	0.94	0.26	0.9949
SP2	1.04	0.94	0.11	0.8987	1.13	0.18	0.9969
SP3	1.21	0.88	0.083	0.9282	1.31	0.15	0.9973

[Zn^{2+}] = 2 mmol L^{-1}; T = 293 K; dose of absorbents, 60 mg.

where Q (mmol g^{-1}) is the adsorption capacity at any time t (min); K_1 the pseudo-first-order rate constant of the equation (min^{-1}) and Q_e is the equilibrium adsorption capacity (mmol g^{-1}). The adsorption rate constant K_1 can be determined experimentally by plotting of $\log(Q_e - Q)$ versus t. Fig. 7 shows the Lagergren plots of $\log(Q_e - Q)$ versus t for the adsorption of Zn(II) by CSP. The bad linearity of these dots indicates that a pseudo-first-order mechanism is not fully followed in this process. The rate constants (K_1), equilibrium adsorption capacities ($Q_{e\text{-cal}}$), and the correlation coefficient (r^2) for each system were calculated according to the linear least square method and are given in Table 3 along with equilibrium adsorption capacities ($Q_{e\text{-exp}}$) from the experiments.

3.3.2. Pseudo-second-order kinetic model

Ho's pseudo-second-order model has been successfully applied to the adsorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions. The pseudo-second-order model does not have the problem of assigning an effective adsorption capacity, and furthermore is fit for the chemisorption of divalent metal ions onto adsorbents with polar functional groups [21,23,25,26]. The adsorption of Zn(II) on CSP mainly depends on the chemical bonding between the phosphate groups and Zn(II), so Ho's model is compatible to describe this adsorption process. Ho's pseudo-second-order equation is expressed as [25,27]:

$$\frac{t}{Q} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e},$$

where K_2 is the pseudo-second-order rate constant of adsorption (g mmol^{-1} min^{-1}), Q_e equilibrium adsorption capacity (mmol g^{-1}), and Q is the adsorption capacity at any time, t (mmol g^{-1}). Linear plots of t/Q versus t curves (Fig. 8) were used to determine the rate constants and equilibrium adsorption capacity. Table 3 shows the pseudo-second-order rate constants, equilibrium adsorption capacity and correlation coefficients for removal of Zn(II) from aqueous solutions. The values of correlation coefficient indicate a better fit of pseudo-second-order model with the experimental data compared with the pseudo-first-order model. Moreover, the equilibrium adsorption capacity calculated from the pseudo-second-order kinetic model fitting is nearer equilibrium adsorption capacity from the experiments ($Q_{e\text{-exp}}$) than the pseudo-first-order kinetic model fitting. It means that chemisorption is the determining step of the adsorption process rather than mass transfer in solution [28]. The similar results were obtained to adsorb Zn(II) ions from aqueous solution using adsorbents with active groups [29,30].

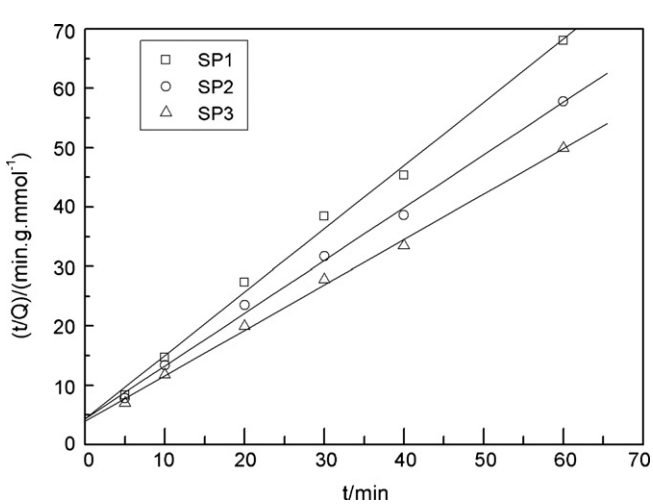

Fig. 8. Pseudo-second-order plots for adsorption of Zn(II) on CSP ([Zn^{2+}] = 2 mmol L^{-1}; T = 293 K; dose of absorbents, 60 mg).

Table 4
Previously reported adsorption capacities and time to reach equilibrium for various adsorbents for Zn(II) adsorptions

Adsorbents	Q_m (mmol g^{-1})	Time (min)	Refs.
Spray-dried chitosan microspheres	0.17	600	[30]
Crosslinked chitosan	0.16	240	[31]
Calcium hydroxyapatite	1.57	20	[32]
Barium hydroxyapatite	0.56	60	[32]
Moringa oleifera	0.80	50	[33]
Clarified sludge	0.24	60	[34]
Rice husk ash	0.22	180	[34]
Activated alumina	0.21	240	[34]
Neem bark	0.20	240	[34]
CSP3	2.00	40	Present study

3.4. Comparison with other adsorbents

In order to justify the validity of crosslinked starch phosphates as an adsorbent of Zn(II), its adsorption potential must be compared with other various adsorbents reported in literature. Table 4 shows the values of maximum adsorption capacity and the time to reach equilibrium for the adsorption of Zn(II) ions on different adsorbents cited in the literature compared with that of the present study. The maximum adsorption capacity is from the Langmuir isotherm, and the time to reach equilibrium is estimated from the effect of adsorption time on the adsorption capacities. It shows that CSP3 has good adsorption capacity and a relatively short adsorption time when compared with other adsorbents.

4. Conclusions

The results of this study show that crosslinked starch phosphates can be successfully used for the adsorption of Zn(II) from aqueous solutions. The adsorption process can be well described by Langmuir isotherm with a maximum adsorption capacity of 2.00 mmol g^{-1}. The values of ΔG become more negative with increasing temperature, which indicates that the adsorption process is more favorable at high temperature. The small values of ΔH mean weak electrovalent bond interactions between phosphate groups and Zn(II) ions in the adsorption process. Pseudo-first-order and pseudo-second-order kinetic models were tested to investigate the adsorption mechanism. The pseudo-second-order kinetic model fits very well with the dynamical adsorption behavior of Zn(II). Crosslinked starch phosphates may be used as cost-

effective and biodegradable adsorbents for the removal of Zn(II) from wastewater.

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