



Preparation of novel polysulfone capsules containing zirconium phosphate and their properties for Pb^{2+} removal from aqueous solution

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ABSTRACT

Zirconium phosphate (ZrP) was immobilized by microencapsulation process of polysulfone (PSF) to form the polysulfone capsules containing ZrP (PSF@ZrP capsules) successfully by using phase inversion precipitation technique, and the PSF@ZrP was employed as capsules adsorbents to remove Pb^{2+} presented in aqueous solution. The result shows that an encapsulation capacity of 50% (mass ratio, PSF: ZrP = 1:1) should be the optimal proportion of ZrP encapsulated with PSF. The characterization of the macroscopical and microcosmic physical properties of the resulting PSF@ZrP capsules was carried out by the DTA-TG, XRD, BET and SEM. Meanwhile, the adsorption properties of the PSF@ZrP capsules for Pb^{2+} were investigated by batch methods. It was found that the adsorption of the PSF@ZrP capsules for Pb^{2+} would be pH dependent due to the ion-exchange mechanism, and the uptake of Pb^{2+} was slightly influenced with the concentration of coexisting cations (Na^+ , K^+) in a low range. Furthermore, the calculated thermodynamics parameters exhibit that the nature of the adsorption process is spontaneous and exothermic. After six times of adsorption–regeneration cycles, no significant loss of adsorption capacity was observed, indicating the good stability of the PSF@ZrP capsules. Consequently, the PSF@ZrP capsules in this work can provide a potential application for treatment process of Pb^{2+} -containing wastewater.

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1. Introduction

Nowadays one of the most common problems afflicting people around the world is the lack of clean water and unacceptable sanitary conditions of water supplies. Problems with water have received much more attention than ever before both from the public and from the chemists, with water scarcity occurring globally and the increasing worldwide contamination of freshwater systems with thousands of industrial and natural chemical compounds. One of the most important classes of the pollutants is toxic heavy metals due to their life threatening, non-degradable and persistence nature. Lead compounds as important industrial chemicals are widely used in many industries and applications [1,2] because of their excellent properties. However, heavy lead compounds usage also causes lots of industrial waste water containing high quantity of lead. It is reported that high concentration of lead can do serious harm to human being and animals, and it's especially dangerous for children since their nervous systems are still developing [3].

The major industrial-scale techniques for the separation and recovery of lead are liquid–liquid extraction and resins [4–7]. While

from a practical point of view there is a major drawback of solvent extraction that an organic solvent is needed which generates important secondary wastes. Although the chelating resin as a traditional adsorption tool has been used for the recovery of lead in water environment for many years, its economic cost is still relatively high when the metals are dissolved in large volume of solution with relatively low concentration. By addressing these problems, a tremendous amount of research has been conducted in the past decades, in the area of natural and synthetic inorganic compounds as excellent ion exchangers [8], due to their large specific interfacial area and microporous structure. Those inorganic compounds generally are zirconium salts [9] and the oxides of Al, Fe, Mn, Ti and Si [10–12], of which zirconium phosphate ($\text{Zr}(\text{HPO}_4)_2$, denoted ZrP) demonstrates a high affinity for Pb^{2+} [13]. However, those inorganic materials are commonly obtained in the form of very fine powder, which limits their practical application in fixed-bed operation because of the great pressure drop. The usual solution is to load the inorganic compounds on the support, usually on the ion exchange resin [14–17]. For example, DeMarco and co-workers [18] have loaded nanoscale hydrated Fe oxide on sulfonic acid cation exchange resin to remove trace concentrations of arsenic from contaminated groundwater. But using ion exchange resin as supporting material results in an expensive operating cost and the loss of ion-exchange function of the resin itself. Consequently, a

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new method of loading inorganic sorbents is needed at lower cost and with less energy, while at the same time minimizing the use of chemicals. In this framework, the utilization of encapsulating the extractant into the porous structure or cavities of the support has been intensively investigated since 1990s [19]. Indeed, their potential use in water treatment is remarkable. Nevertheless, most of the applications focus on the immobilization of organic solvent and Ionic Liquid [20–22]. To our knowledge, the encapsulation of the inorganic compounds mentioned above from water samples has rarely been reported by now.

In this present work, a new kind of capsule has been synthesized by phase inversion precipitation technique, using polysulfone (PSF) as a shell material, ZrP as the core, and N-methyl-2-pyrrolidinone (NMP) as solvent. Moreover, the adsorption properties of the capsules obtained towards Pb^{2+} have been investigated by using batch techniques. The adsorption behavior has been further discussed according to kinetic and isotherm models.

2. Experiment

2.1. Materials

Aqueous solutions of Pb^{2+} at various concentrations were prepared from $Pb(NO_3)_2$. Reagent grade of $ZrOCl_2 \cdot 8H_2O$ and phosphoric acid were used for the preparation of zirconium phosphate (ZrP) according to Ref. [13]. Then the obtained ZrP powder was further milled, and passed through a 220-mesh sieve as standby. Polysulfone (PSF) with intrinsic viscosity of 0.56 was purchased from Dalian Polysulfone plastic Co. Ltd. (China). Sodium lauryl sulfate (SDS) and all other reagents were analytical grade and were used as received.

2.2. Instruments

The obtained capsules were observed by means of a scanning electron microscope (SEM), JSM-6701F, JEOL, Japan, operating at 5.0 kV. Thermogravimetric analysis (TGA) was conducted with a TA Instruments STA449 and experiments were carried out on approximately 5 mg of samples in flowing air (flowing rate = $100 \text{ cm}^3/\text{min}$) at a heating rate of $20^\circ\text{C}/\text{min}$. The Brunauer–Emmett–Teller (BET) surface area of capsules was obtained from N_2 adsorption isotherms at 77 K with a Micromeritic chemisorb2750 analyzer. X-ray diffraction (XRD) patterns were obtained using a Philips MPD 18801 diffractometer using $Cu K\alpha$ radiation. Also, a HQD150LB temperature controlled flask – shaker (Beijing Zhongxi Glass Co., China) was used. In this study, the concentration of metal ions was determined with an inductively coupled plasma spectrometer (ICP/IRIS Advantage, Thermo).

2.3. Preparation of PSF@ZrP capsules

PSF@ZrP capsules were prepared by phase inversion precipitation technique [23]. The concrete preparation process was as follows: 3 g of PSF was dissolved in 22.5 mL of N-methyl-2-pyrrolidinone (NMP) to obtain the PSF solution. Then different proportions of ZrP were added into the PSF solution, and the PSF–ZrP mixture was stirred for 60 min under the room temperature to make the ZrP powder disperse equably in the PSF solution. After that, the dispersed phase consisting of ZrP and PSF was injected into the continuous phase (0.5 wt% SDS in the ethanol–water solution) using a 0.8-mm diameter syringe needle to obtain the PSF@ZrP capsules. Finally, after the obtained capsules were cured fully in the continuous phase, they were washed with deionized water several times and dried at 45°C for 24 h as standby. In order to investigate the effect of ZrP content in capsules on the amount of Pb^{2+} adsorption, PSF–ZrP mixture was varied according

to the following weight ratios – 1:0, 1:0.2, 1:0.5, 1:1 and 1:1.5 (PSF to ZrP). And these capsules were abbreviated to be PSF, PSF@0.2ZrP, PSF@0.5ZrP, PSF@1.0ZrP and PSF@1.5ZrP in this paper, respectively. Without special clarification, the PSF@ZrP capsules used in adsorption experiments were the capsules whose mass ratio of PSF to ZrP was controlled at 1:1.

2.4. Adsorption experiments using batch methods

Batch experiments of Pb^{2+} adsorption were carried out by placing 0.05 g of PSF@ZrP capsules in a series of flasks containing 50 mL of Pb^{2+} at the desired initial concentration and pH. Then the contents of the flasks were shaken in a flask – shaker at specific temperature for a given time with a speed of 130 rpm. The residual concentration of Pb^{2+} in the solution was determined by ICP. The amount of Pb^{2+} sorbed per gram of capsules was calculated according to the following Eq. (1):

$$Q = \frac{(C_0 - C)V}{W} \quad (1)$$

where Q is the adsorption capacity (mg g^{-1}); C_0 , the initial concentration of Pb^{2+} (mg L^{-1}); C , the residual concentration of Pb^{2+} in solution (mg L^{-1}); V , the volume of the solution used; W , the weight of capsules (g).

The operating variables studied were pH, contact time, initial concentration, temperature and competing ions. The desired pH was adjusted using HNO_3 ranging from 1.10 to 5.75. From these studies, the working concentration of Pb^{2+} was used in the range of $100\text{--}300 \text{ mg L}^{-1}$ for kinetic studies and $50\text{--}1000 \text{ mg L}^{-1}$ for isotherm studies. In addition, in order to determine the impacts of Na^+ and K^+ on Pb^{2+} adsorption, the initial concentration of Pb^{2+} was kept at 50 mg L^{-1} and the content of NaCl and KCl varied.

2.5. Regeneration of PSF@ZrP capsules

An amount of capsules (about 0.05 g), loaded with a known amount of Pb^{2+} , was placed in a series of flasks containing 20 mL different eluents, then the mixture was shaken at 30°C for 6 h. After that time, the Pb^{2+} concentration in the solution was determined.

3. Results and discussion

3.1. Characterization of PSF@ZrP capsules

The ZrP powder encapsulated in polysulfone capsules was analyzed by XRD. As seen in Fig. 1, the XRD pattern of ZrP implies

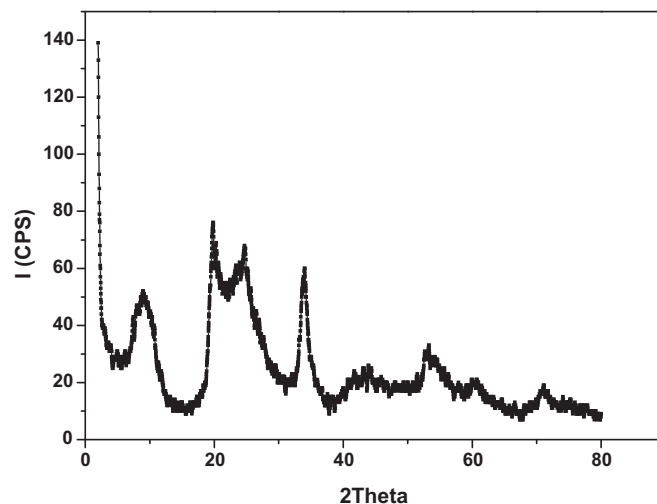


Fig. 1. XRD analysis of the ZrP powder prepared in the current study.

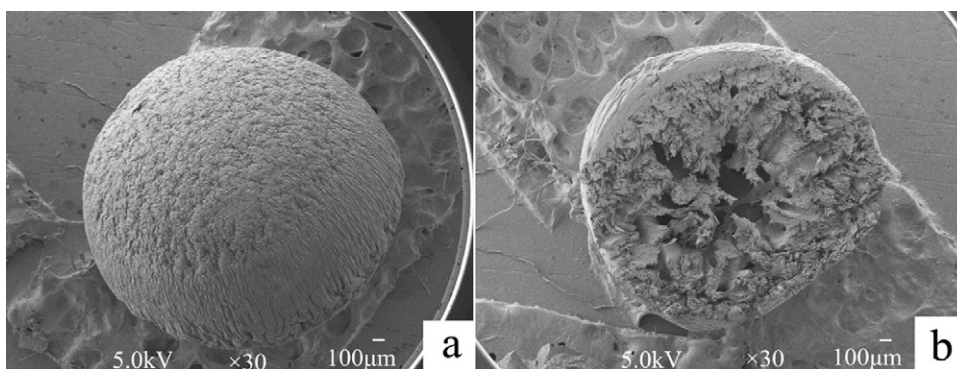


Fig. 2. SEM images of the PSF@ZrP capsules: image of the entire capsule (a) and cross-section (b).

Table 1
BET surface area of capsules.

Capsules	PSF/ZrP ratios (w/w)	BET surface area (m ² /g)
PSF	1:0	16.8
PSF@0.2ZrP	1:0.2	7.39
PSF@0.5ZrP	1:0.5	8.42
PSF@1.0ZrP	1:1	5.27
PSF@1.5ZrP	1:1.5	5.29

that ZrP dispersed within the PSF@ZrP capsules is essentially in the amorphous state though some broad diffraction peaks appear in the pattern, as illustrated by Trobajo et al. [24] and Zhao et al. [25]. Moreover, according to Ref. [13], the Zr/P ratio in ZrP prepared by rigorously following the bibliographic descriptions was confirmed as 1:2. Judging from the BET test results summarized in Table 1, the PSF@ZrP capsules exhibit great surface area which provides large interface between the sorbents and the Pb²⁺ in water, whereas the surface area of capsules encapsulated with ZrP is obviously lower than that of the capsules without ZrP, because of the blockage of some fraction of pores caused by ZrP. However, there are still abundant pores evenly distributed on the surface of the PSF@ZrP capsules, which is further evidenced by SEM images.

Fig. 2a is an image of an entire PSF@ZrP capsule, which clearly shows the capsules are perfectly spherical with a rough surface. Fig. 2b, a cross-sectional view, demonstrates the hollow structure

of the PSF@ZrP capsules. The SEM images (shown in Fig. 3) visually exhibit morphological differences of the PSF capsules and PSF@ZrP capsules both on the outer surface and on the cross-section. It is interesting to observe that the exists of ZrP have great influence on surface morphology of the capsules due to the preparation mechanism of the PSF@ZrP capsules, as revealed in Fig. 3a and e. In addition, compared to the relative smooth surface of the PSF capsules, the wrinkle on the surface of the PSF@ZrP capsules enlarges surface area and also benefits mass transfer performance. As stated above, macroporous structures uniformly distributed on the surface of the PSF@ZrP capsules are still visible in Fig. 3f. By comparison with pure PSF capsules (Fig. 3c), the pore structures on the cross-section of the PSF@ZrP capsules disappear (Fig. 3g), which are accompanied by the presence of many light areas of apparent small ZrP particles inside the capsules (Fig. 3h). Obviously, ZrP was almost uniformly dispersed from outer surface to inner part of the PSF@ZrP capsules, indicating that ZrP was successfully enclosed in the PSF capsules.

In order to observe the heat stability of the PSF@ZrP capsules, thermogravimetric analysis (TGA) of capsules was carried out. In the TGA curve of the PSF@ZrP capsules (Fig. 4), no obvious mass loss can be observed in the temperature range of 100–480 °C, except for one turning point around 491 °C which attributed to the decomposition of PSF, which is indicative of the excellent thermostability of the PSF@ZrP capsules.

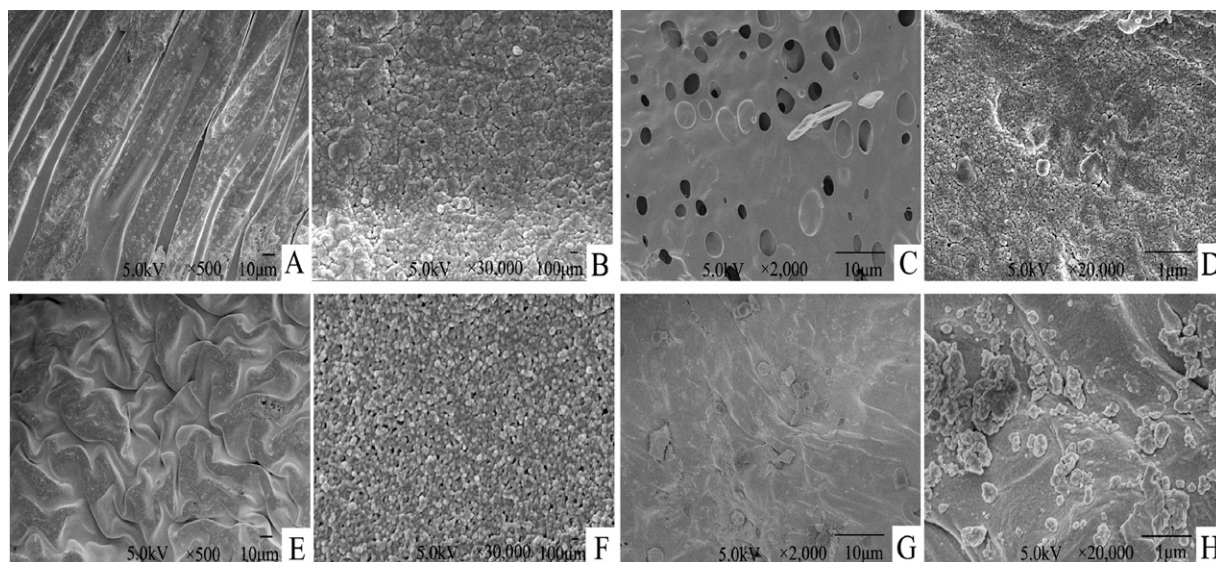


Fig. 3. SEM images of the outer surface morphologies of the PSF capsules (a, b) and PSF@ZrP capsules (e, f); the cross-section of PSF capsules (c, d) and PSF@ZrP capsules (g, h).

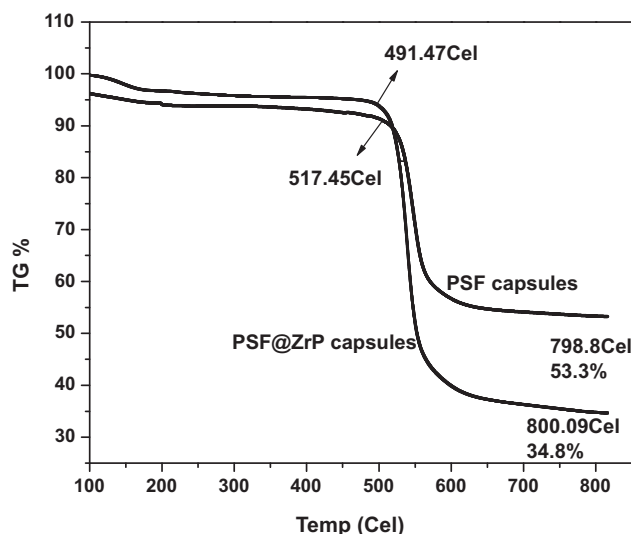


Fig. 4. TGA of the PSF@ZrP capsules.

3.2. Adsorption studies

3.2.1. The contribution of ZrP content in capsules for Pb^{2+} adsorption

In this study, the PSF@ZrP capsules include PSF and ZrP. In order to probe the adsorption capacity contribution of them for Pb^{2+} , PSF capsules enclosing different amounts of ZrP were prepared and used to adsorb Pb^{2+} . As shown in Fig. 5, pure PSF capsules revealed extremely low affinity to Pb^{2+} , and the adsorption amount increased enormously from 12.18 to 62.26 $mg\ g^{-1}$ on increasing the mass ratio of PSF to ZrP in the capsules from 1:0 to 1:1. However, with additional ZrP further added to a ratio of 1–1.5 (PSF to ZrP), the adsorption capacity of the capsules for Pb^{2+} decreased sharply. This finding is strongly associated with the characters of the PSF@ZrP capsules used in this paper.

It has been verified in Fig. 3 and Table 1 that, comparing with the pure PSF capsules, the addition of ZrP caused partial blockage of the micropores and lowered the specific surface area of the PSF@ZrP capsules. Although this situation is of no advantage for adsorption process, the modest increment of ZrP content in the capsules offsets the negative aspects it brings and plays the leading role in the adsorption of Pb^{2+} . While the weight proportion of PSF to ZrP reached 1:1.5, the surface characteristic of PSF@1.5ZrP cap-

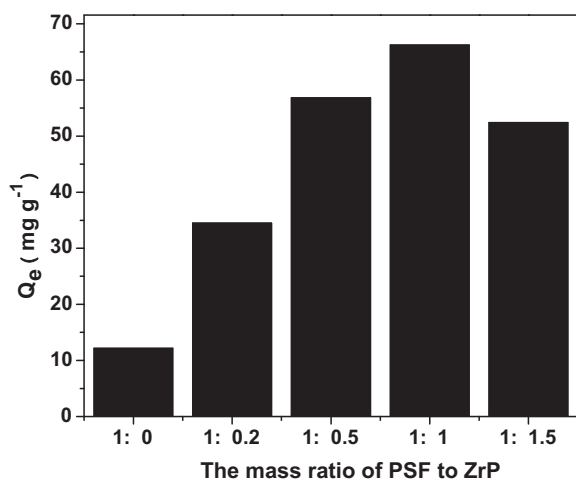


Fig. 5. Effect of the different mass ratios (PSF to ZrP) on the adsorption of Pb^{2+} by 0.05 g capsules with an initial concentration of $100\ mg\ L^{-1}$ at $40\ ^\circ C$ and pH 5.75.

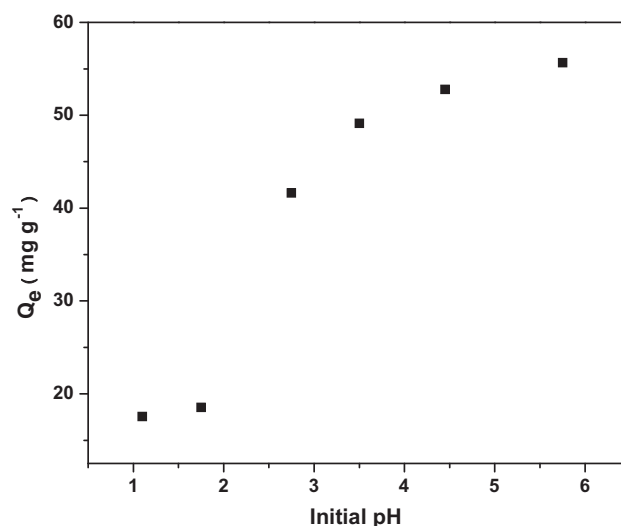
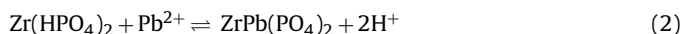


Fig. 6. Effect of initial pH on Pb^{2+} adsorption by 0.05 g PSF@ZrP capsules with an initial concentration of $100\ mg\ L^{-1}$ at $30\ ^\circ C$.

sules seriously repressed the contact of Pb^{2+} with adsorption sites on the capsules and led to a large part of ZrP could not maximize its adsorption performance. Therefore, the capsules obtained at a ratio of 1:1 (PSF to ZrP) are the optimal choice for adsorption in this study and are used for the rest of the adsorption experiments.

3.2.2. Effect of initial solution pH on adsorption

According to Clearfield [8] and Kullberg' [26] reports, it has been proved that the adsorption mechanism of zirconium hydrogen phosphate for metal ions was ion-exchange process. Pan and co-workers have investigated polymer loaded ZrP for the removal of Pb^{2+} , and the related ion exchange reaction was expressed as follows [14]:



Therefore, the acidity of the medium is one of the most important key factors, which affects the adsorption equilibrium as well as the surface charge of the adsorbents. Fig. 6 shows the results of the adsorption of Pb^{2+} with the PSF@ZrP capsules at various pH of the solution. It is clear to see that the adsorption amount increased enormously from 17.57 to 55.68 $mg\ g^{-1}$ on increasing the pH value from 1.10 to 5.75, and the maximum adsorption of Pb^{2+} was observed at natural pH 5.75. This phenomenon indicates that the optimal pH condition of Pb^{2+} solution is the original pH of the solution without changing with acid or base, which is time-saving and energy-saving from a practical point of view. Hence the rest of adsorption experiments were done without adjusting the pH. As shown in Fig. 6, it is also noteworthy that strong acidic environments do not favor the adsorption by displaying negligible variation of Pb^{2+} uptake, whereas it suggests the used PSF@ZrP capsules may be regenerated by a strong acid solution. As highlighted above, the pH-dependent trend could be explained by the ion-exchange process between the solution and the PSF@ZrP capsules.

3.2.3. Effect of initial Pb^{2+} concentration on adsorption

Fig. 7 presents the uptake of Pb^{2+} versus contact time, by the PSF@ZrP capsules, at different initial concentrations of 100, 150 and $300\ mg\ L^{-1}$, respectively. It appears that the equilibrium time is independent of initial Pb^{2+} concentration. Moreover, the initial rate of adsorption seems to increase with the increment of initial concentration because of the increased drive force, resulting from the concentration variance of Pb^{2+} between the solution and the capsules. Although the amount of Pb^{2+} adsorbed at equilib-

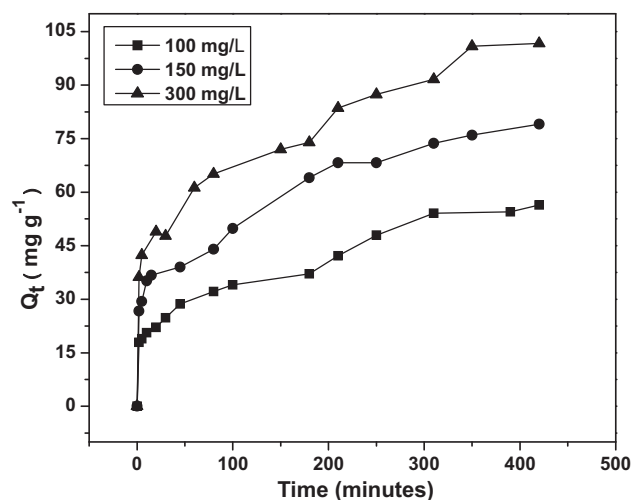


Fig. 7. Effect of contact time on Pb^{2+} adsorption with different initial concentrations at 30°C .

rium increased from 56.39 to 101.66 mg g^{-1} with the increase of Pb^{2+} concentration from 100 to 300 mg L^{-1} , the removal percentage of Pb^{2+} from solution decreased from 56.4% to 33.9% . Based on these observations, we infer that the initial Pb^{2+} concentration has important influence on the adsorption. In addition, from the applicant prospective, it is unsatisfying that the PSF@ZrP capsules need longer equilibrium time than the reported ion exchange resin supported ZrP [14]. Fortunately, further investigation is under going to work this problem.

3.2.4. Adsorption kinetics

In order to estimate the efficiency of the studied PSF@ZrP capsules for removing Pb^{2+} , kinetic data for above three initial concentrations were modeled by pseudo-first-order equation, pseudo-second-order equation and intraparticle diffusion equation [27–29], at initial concentration of $300, 600, 800\text{ mg L}^{-1}$, using Eqs. (3)–(5):

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1 t}{2.303} \quad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (4)$$

$$Q_t = k_i t^{1/2} + C \quad (5)$$

where Q_e and Q_t are the sorption capacity (mg g^{-1}) at equilibrium time and at time t , respectively; k_1 , k_2 and k_i are the pseudo-first-order rate constant (min^{-1}), pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$) and intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$), respectively; C (mg g^{-1}) is a constant of intraparticle diffusion model.

The resultant parameters and correlation coefficients (R) were given in Table 2. It is noticed that the calculated Q_e values of the pseudo-first-order model at the three initial concentrations are too low compared with experimental Q_{exp} values, and the correlation

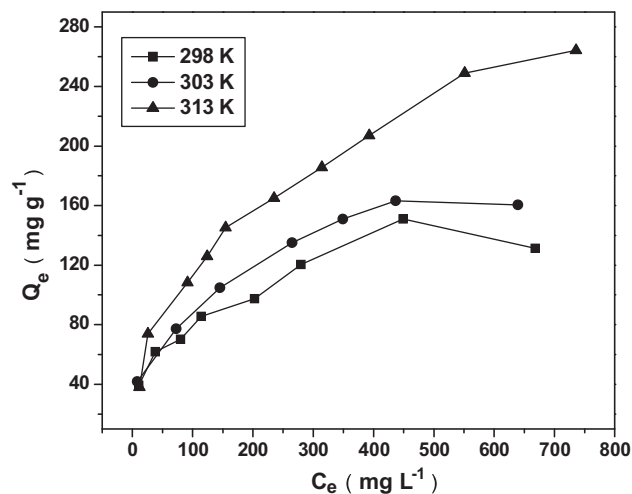


Fig. 8. Adsorption isotherms for the adsorption of Pb^{2+} on the PSF@ZrP capsules at different temperatures.

coefficients (R) are also not high. This indicates that Pb^{2+} uptake onto the PSF@ZrP capsules cannot be approximated favorably by the pseudo-first-order model. While the calculated Q_e value fully agrees with the experimental data (Q_{exp}) in the case of pseudo-second-order kinetics, and the adsorption data are well represented by intraparticle diffusion with a much higher correlation coefficient (0.99) than the pseudo-second-order kinetics. This result suggests adsorption behavior may be controlled by intraparticle diffusion together with the pseudo-second-order kinetics model, which means the chemical adsorption and intraparticle diffusion resistance of Pb^{2+} inside the capsules are both involved to affect the rate of adsorption. Generally, the rapid adsorption of Pb^{2+} to the external surface is followed by slow intraparticle diffusion along the micropore walls.

3.2.5. Adsorption isotherm

To fully understand the adsorption systems, the experiment data in Fig. 8 was treated with the most frequently used two adsorption isotherm models, which are Langmuir [30] and Freundlich and Heller [31] equations, respectively. The Langmuir isotherm was developed on the assumption that all adsorption sites are identically homogeneous and the monolayer adsorption occurred on a surface with a finite number of identical sorption sites. On the contrary, the Freundlich equation is based on the assumption that the adsorption systems are heterogeneous. The linear form of Langmuir and Freundlich equations are given as follows:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{\text{max}}} + \frac{C_e}{Q_{\text{max}}} \quad (6)$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

where Q_e and Q_{max} are the equilibrium adsorption capacity (mg g^{-1}) and maximum adsorption capacity (mg g^{-1}), respectively; C_e is the concentration of metal ions at equilibrium time (mg L^{-1});

Table 2
Parameters of kinetics model for the adsorption of Pb^{2+} on the PSF@ZrP capsules with different initial concentrations.

Initial Conc. (mg L^{-1})	Q_{exp} (mg g^{-1})	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion	
		$k_1 \times 10^3$ (min^{-1})	Q_e (mg g^{-1})	R^a	$k_2 \times 10^4$ ($\text{g mg}^{-1} \text{min}$)	Q_e (mg g^{-1})	R^a	k_i ($\text{mg g}^{-1} \text{min}^{-1/2}$)	R^a
100	56.39	2.46	40.04	0.8418	4.28	57.74	0.9814	2.07	0.9914
150	79.06	2.78	56.33	0.9928	3.91	80.71	0.9896	2.82	0.9909
300	101.66	3.36	76.94	0.9515	2.83	103.41	0.9873	3.43	0.9933

^a The correlation coefficient.

Table 3Parameters of isotherm model for the adsorption of Pb²⁺ on the PSF@ZrP capsules with different temperatures.

Temperature (K)	Langmuir parameters			Freundlich parameters		
	Q_{\max} (mg g ⁻¹)	$K_L \times 10^2$ (L mg ⁻¹)	R^a	K_F (mg g ⁻¹)	1/n	R^a
298	149.70	1.516	0.9868	18.392	0.322	0.9823
303	179.86	1.389	0.9920	20.243	0.333	0.9919
313	302.11	0.6372	0.9821	14.525	0.447	0.9909

^a The correlation coefficient.

K_L is Langmuir constant (L mg⁻¹); K_F (mg g⁻¹) and n are Freundlich constants.

Table 3 compiles the correlation coefficients (R) and parameters of the two models. As we can see, the R values of the two models is close to each other and as high as 0.98. This phenomenon can be explained by the characters of the PSF@ZrP capsules. It is evident from Fig. 5, that PSF as shell material also exhibits tiny amount of Pb²⁺ adsorption. Therefore, the monolayer adsorption is dominant through the entire adsorption process, which is supplemented by a lower importance of physical adsorption resulting from the micropore structure of PSF.

The essential feature of the Langmuir adsorption can be expressed by means of R_L [32]. R_L is a dimensionless constant for predicting whether an adsorption system is favorable or unfavorable which is defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

where C_0 is the initial Pb²⁺ concentration (mg L⁻¹) and K_L is Langmuir constant (L mg⁻¹). The value of R_L reveals the nature of the adsorption process to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). In our study, the calculated R_L values for the adsorption on the PSF@ZrP capsules at different initial concentrations were range from 0.062 to 0.569, 0.067 to 0.590 and 0.136 to 0.758, at the temperature of 298, 303, and 313 K, respectively. As see here, the R_L values obtained were all between 0 and 1, indicating the adsorption is favorable.

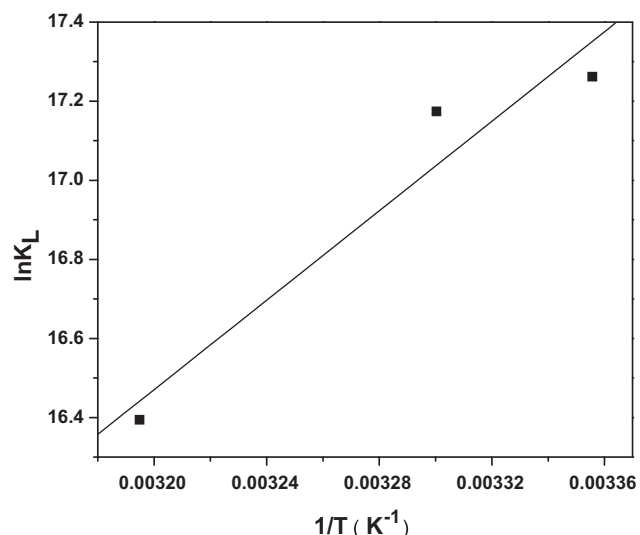
It is evident from the listed Pb²⁺ adsorption capacity values (Table 4), the PSF@ZrP capsules show satisfactory affinity to bind Pb²⁺ by comparing with some other similar sorbents reported. Obviously, the PSF@ZrP capsules have absolute advantage on Pb²⁺ adsorption amount by comparing with alumina and modified alumina [33,34]. Furthermore, the maximum uptake amount of the PSF@ZrP capsules is over hundred times larger than that of ZrP modified silica [35], which means ZrP enclosed in PSF capsules is superior to be loaded on the surface of silica. Although the porous resin supported ZrP [21] gets larger adsorption amount than the PSF@ZrP capsules, it is at the cost of almost losing the ion-exchange function of the resin itself.

3.2.6. Thermodynamics analysis

The thermodynamic parameters are indispensable to evaluate the feasibility and exothermic nature of the adsorption process. Thus, isotherm data related to adsorption of Pb²⁺ onto the PSF@ZrP capsules at various temperatures ranging from 298 K to 313 K, were

Table 4The Pb²⁺ adsorption capacity of sorbents derived from the literature and experimental data.

Sorbent	Q_{\max} (mg g ⁻¹)	Temperature (°C)	Initial pH	Reference
Activated alumina	83.33 ^a	30	5.0	[33]
Alumina immobilized with 1-nitroso-2-naphthol	39.33	Room temperature	7.0	[34]
Zirconium(IV) phosphate modified silica	2.07	25	4.5	[35]
ZrP loaded on chloromethylated polystyrene	556 ^a	15	5.5	[21]
Porous resin loaded with a-ZrP	200	25	Above 2.5	[17]
PSF@ZrP capsules	302.11 ^a	40	5.75	Present work

^a The Langmuir maximum capacity.**Fig. 9.** Van't Hoff plot for the adsorption of Pb²⁺ on the PSF@ZrP capsules.

analyzed to obtain the values of thermodynamic parameters. The values of thermodynamic function ΔS^0 and ΔH^0 were calculated using Van't Hoff's equation as follows:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

where K_L is Langmuir's constant (L mol⁻¹), R is the gas constant, 8.314 (J mol⁻¹ K⁻¹), T is the temperature (K), ΔS^0 denotes the standard entropy change (J mol⁻¹ K⁻¹), and ΔH^0 is the standard enthalpy (J mol⁻¹).

Fig. 9 shows the Van't Hoff plot, illustrating a good correlation of the plotted data ($R = 0.97$). From the Gibbs–Helmholtz equation,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

by using values of ΔH^0 and ΔS^0 from Eq. (9), the Gibbs free energy change (ΔG^0) can be obtained. Table 5 presents the results of these thermodynamic parameters in the studied temperature range. Negative values of ΔG^0 confirm the favorable and spontaneous nature of the adsorption process. Although with the increase in temperature from 298 to 313 K the magnitude of ΔG^0 decreased from 42.99 kJ mol⁻¹ to 42.78 kJ mol⁻¹, the adsorption process was spontaneous at all studied temperatures, which was in agreement with what was seen during the experiments. The entropy change

Table 5
Thermodynamics parameters for Pb²⁺ adsorption onto the PSF@ZrP capsules.

T (K)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	ΔG^0 (kJ mol ⁻¹)
298	-47.03	-13.55	-42.99
303			-42.92
313			-42.78

value (ΔS^0) measured in this study shows that metal adsorbed on the capsules leads to a less chaotic system than ZrP-loaded chloromethylated polystyrene [21]. It is also noted that the negative value of enthalpy change (ΔH^0) indicates the exothermic nature of the adsorption process.

3.2.7. Effect of competing cations

It is fact that many environmentally friendly cations such as Na⁺, K⁺ and Ca²⁺ may reach high levels in waters and industrial wastewater, and these cations have been confirmed to mainly take a negative role in the adsorption process because of their competing with the target ions during the ion-exchange process [21,36,37]. In this study, we tested the effects of Na⁺ and K⁺ on the Pb²⁺ uptake onto the PSF@ZrP capsules. As shown in Fig. 10a, the amount of Pb²⁺ sorbed onto the PSF@ZrP capsules is slightly influenced with

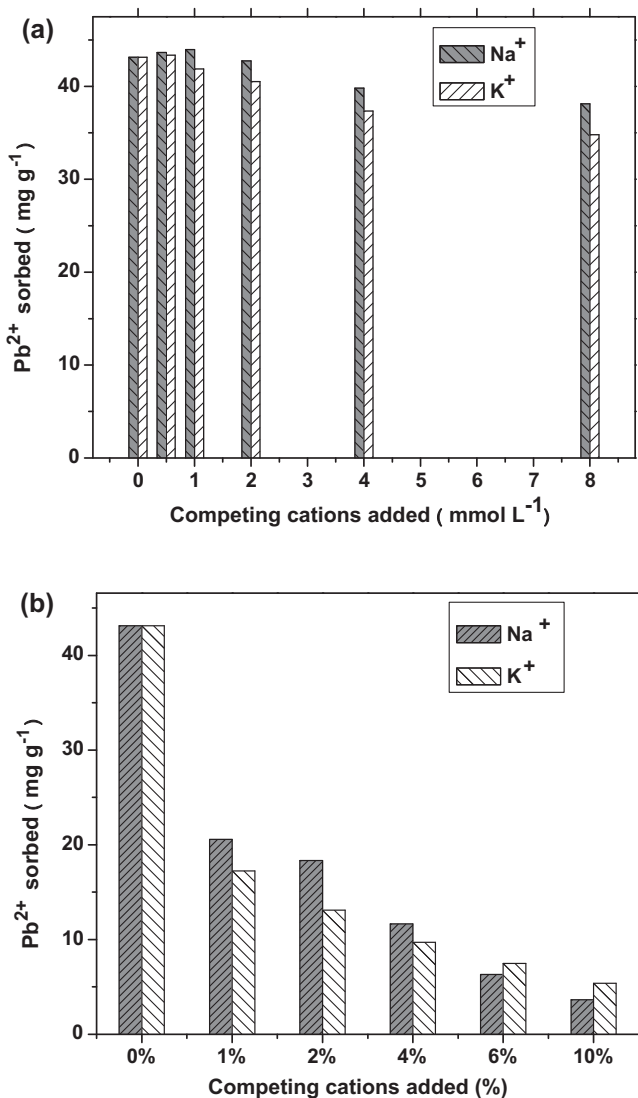


Fig. 10. Effect of competing cations (Na⁺ and K⁺) on Pb²⁺ adsorption capacity by 0.05 g PSF@ZrP capsules at 30 °C with the initial concentration of 50 mg L⁻¹ for Pb²⁺.

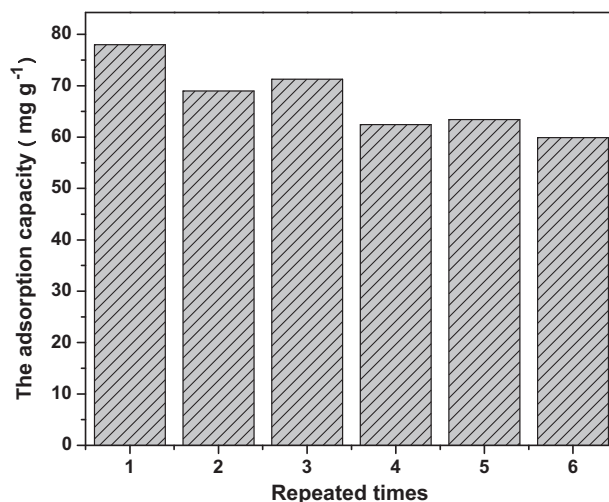


Fig. 11. Effect of regeneration on the adsorption capacity of Pb²⁺ onto the PSF@ZrP capsules using batch experiments with an initial concentration of 100 mg L⁻¹ at 30 °C.

the concentration of coexisting cations in a low range, which is in agreement with the previous report [36]. Contrarily, the uptake of Pb²⁺ decreased obviously as the concentration of additional Na⁺ and K⁺ further added was hundreds of times more than Pb²⁺ (Fig. 10b). Of particular note is that competing capacities of the added cations essentially yield the sequence as K⁺ > Na⁺. Such a sequence can be explained by the ionic hydration radii of the alkaline ions [37]. Due to the smaller hydrated ion radii of K⁺, it can easier diffuse into the capsules for ion exchange.

From what has been discussed above, we may safely draw the conclusion that the PSF@ZrP capsules are qualified to remove Pb²⁺ from normal salinity water, and lead-containing wastewater with high salinity needs to be pre-desalinated before the use of the PSF@ZrP capsules, for extending the regeneration cycle of sorbents.

3.3. Regeneration of the capsules

The regeneration test of the spent PSF@ZrP capsules was conducted by 3 M HNO₃ at 30 °C using batch experiments. In adsorption–regeneration cycles, the adsorption capacity of Pb²⁺ onto the PSF@ZrP capsules every time is calculated and the results are plotted in Fig. 11. It is observed that adsorption–regeneration cycles were performed six times with no significant loss of adsorption capacity. This result suggests the PSF@ZrP capsules can be effectively desorbed for repeated use and they may be potential candidates for Pb²⁺ removal from water.

4. Conclusions

In the present study a novel kind of capsules with ZrP, an efficient ion exchanger immobilized in the porous structure, was successfully prepared with a phase inversion method for enhanced removal of Pb²⁺ from water. The results show more favorable adsorption of Pb²⁺ onto the PSF@ZrP capsules can be obtained at weak acid environment and high temperature. The magnitude of the influence of Na⁺ and K⁺ on adsorption is dependent on their concentration. Furthermore, adsorption kinetics indicate the chemical adsorption and intraparticle diffusion resistance of Pb²⁺ inside the capsules are both involved to affect the rate of adsorption. It is found that the spent sorbent can be readily regenerated for reuse by dilute HNO₃ solution and after six times of regeneration the sorbent may still be reused without significant loss of their initial properties. All the results reveal that the studied capsules could be

massively used for removing Pb^{2+} from waste water owing to their simple and low-cost synthesis method and satisfactory adsorption properties for Pb^{2+} .

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