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Removal of Some Heavy Metals from Wastewater Using Hydrothermally Synthesized Zirconium Phosphate As Ion Exchange Material

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Abstract—Ion exchange materials based on zirconium phosphate were synthesized by mixing zirconyl chloride (0.5 M) with 1 N phosphoric acid with or without addition of poly(vinylpyrrolidone). The physicochemical properties of this materials were determined using scanning electron microscopy (SEM) and infrared (IR) spectroscopy, and distribution behavior was also studied to understand the cation-exchange behavior of the two samples. Sorption studies showed that the cation-exchanger has high selectivity to Pb(II) in comparison to other metal ions. Its selectivity was examined in binary separations. The thermodynamic parameters such as ΔG^*, ΔS^*, and ΔH^* were calculated from the data on the adsorption of Pb(II), Cu(II), and Fe(II) on the studied samples.

Keywords: preparation, characterization, adsorption, thermodynamic parameters

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INTRODUCTION

The presence of heavy metals in the environment pose serious public health and ecological concerns in many countries of the world [1, 2]. Heavy metals are highly toxic and nondegradable. They easily accumulate and persist in water and soils in the environment from where they are easily transferred through food chains to humans [2]. Lead(II) pollution, in particular, poses a threat to biological systems. Lead(II) is considered the most toxic heavy metal pollutant after cadmium and mercury, it is more likely to be encountered in industrial effluents than either of the other two metals, as it is more versatile in its industrial applications [3]. For this reason, increasingly more stringent legislations are being placed upon industries to reduce metal discharge into the environment through industrial effluents [4]. The industries are, as a consequence, required to implement more efficient effluent treatment practices in order to conform to required heavy metal standards. Conventional technologies used in removal of metals' ions from wastewater include: coagulation, precipitation, contact precipitation, electro-coagulation, electrodialysis, reverse osmosis, solar distillation, adsorption, ion-exchange, and other membrane technologies. Most of these technologies are, however, either grossly inefficient or too expensive for small industries, such as those found in developing countries [5]. The use of more affordable alternative technologies has, for that matter, become the focus of environmental research, especially in the most recent years [6]. The media that is desired for easy and safe use for the removal of toxic metal ions from water should be affordable, potent, safe and usable in wide spectrum of wastewater conditions [7]. Clays and similar materials such as the one used in the present work have therefore attracted the scientific attention in the recent and past wastewater treatment protocols because of their ready availability, good adsorbent capacities, surface stability and ease of preparation for used in metal adsorption procedures [8]. On the other hand, lead(II) ions have one of the highest selectivity and affinity for soil surfaces when compared to those of most other metal pollutants [9]. Lead(II) typifies most of the metal pollutants in toxicity, environmental distribution and in potential uptake by natural adsorbents. Pb(II) is, for this reason, often used to evaluate new adsorbents for heavy metal removal from water [10]. In the present work, removal of lead(II) ions from water was used to assess the capacity of AlSiM to sorb pollutant metal species from wastewater. The criteria used was based on analyses of the effect of change in adsorbate concentration, pH, temperature (T), contact time (t), and mass of adsorbent (m) [7]. The kinetics and equilibrium characterization of the process was also performed. The results indicate that AlSiM could be used as a plausible inexpensive media for heavy metal decontamination of wastewater streams.

EXPERIMENTAL

Reagents and Chemicals

Zirconyl chloride [$ZrOCl_2·8H_2O$], phosphoric acid H_3PO_4, cupper(II) chloride, iron(II) chloride, and lead(II) chloride were obtained from CDH (India). While hydrochloric acid (37%) from Egypt. All other reagents and chemicals were of analytical grade purity.

Preparation of the reagent solutions. Solutions of zirconyl chloride (0.5 M) were prepared in demineralized water.

Synthesis of the Ion-Exchange Material

Synthesis of zirconium phosphate. Zirconium phosphate was prepared through hydrothermal process. In a typical experiment, 0.5 M $ZrOCl_2·8H_2O$, 1 N H_3PO_4 and continuously stirred for 30 min to form a homogeneous solution. Then, the resulting solution was transferred into 400 mL Teflon-lined stainless steel autoclave and kept at 100°C temperature for 24 h to form sample (I). Sample (II) was prepared through the same process, but 0.5 g of polyvinylpyrorolidone (PVP) was added to the initial mixture. After the autoclave was allowed to cool to the room temperature naturally, the product was collected, washed with distilled water and dried at 60°C in drying oven for two days. The product was rewashed with near boiling deionized water (70 ± 1°C) in order to remove the air trapped and adherent fine particles. The excess acid was removed after several washing with DMW, dried at 50°C.

Distribution and selectivity studies. Batch procedure for ion exchange technique the experiments were performed to obtain primary ion exchange data such as distribution coefficients (K_d), and to demonstrate the effect of pH, temperature, and initial concentration of solution (10–1000 ppm). Known weight of ion exchanger was placed in a vial with metals chloride solution containing 50 ppm of Pb(II), Fe(II), and Cu(II) ions with different pH values. The solution volume was 100 mL per 1 g of adsorbent. The mixture was placed in shaker thermostat adjusted at 30 ± 1°C. After overnight standing (sufficient to attain equilibrium), the system obtained equilibrium after about 5 h. The distribution coefficients (K_d) of Pb(II), Fe(II), and Cu(II) ions for two samples were determined by batch equilibration. The liquid phases were separated and metal ion concentrations were measured using inductively coupled plasma spectrometer (ICPS-7500). It can also represent an experimental way of determining the affinity of a sorbent material for a specific ion. The batch distribution coefficient (K_d) was calculated from batch experiments using the following equation.

$$K_\mathrm{d} = \frac{[C_0 - C_e]}{C_e} V/m, \text{ mL/g},$$

where C_0 is the initial concentration of the metal ions in solution; C_e is the concentration in the equilibrated solution after phase separation; V is the volume of the solution, mL; m is the weight of the exchanger, g.

Separation factor. The separation factor may be considered as the relative tendency of two ions to be adsorbed in an exchanger from solutions of equal concentration. It is used as a measure of possibility of chromatographic separation and is also expressed as the ratio of the distribution coefficients of the elements to be separated as:

$$\text{Separation factor } (\alpha_B^A) = K_\mathrm{d}(A)/K_\mathrm{d}(B),$$

where $K_d(A)$ and $K_d(B)$ are the distribution coefficients for the two competing species A and B in the ion-exchange system.

Physical characterizations were carried out on the prepared materials. Some physical and chemical properties of the prepared samples were investigated by using different techniques such as infrared (IR) and scanning electron microscopy (SEM).

Infrared spectra. The IR spectra of the materials were measured in KBr pellets in the wavenumber range of 400–4000 cm^{-1}.

ICPs-7500. An inductively coupled plasma emission spectrometer ICPs-7500 (Shimadzu, Japan) was used for measuring the trace concentrations of metal ions.

RESULTS AND DISCUSSION

This work was studding the preparation and characterization and its selectivity behavior towards the adsorption of Pb(II), Cu(II), and Fe(II) ions onto two sample of zirconium phosphate. The FTIR spectrum of the zirconium phosphate of sample (I) and sample (II) are shown in Figs. 1 and 2. The IR spectra show that the band at about 3500 cm^{-1} assigned to H–O–H stretching vibration of water molecules weakly hydrogen bonded to the M–O [4]. A sharp band at about 1622.9 cm^{-1} corresponds to the deformation vibration of free water molecules. A strong sharp band centered at 1050 cm^{-1} corresponds to P–O stretching vibration for zirconium phosphate of sample (I) and sample (II) [5]. However, the observed bands 546 and 544 cm^{-1} from zirconium phosphate of sample (I) and sample (II) correspond to the defor-

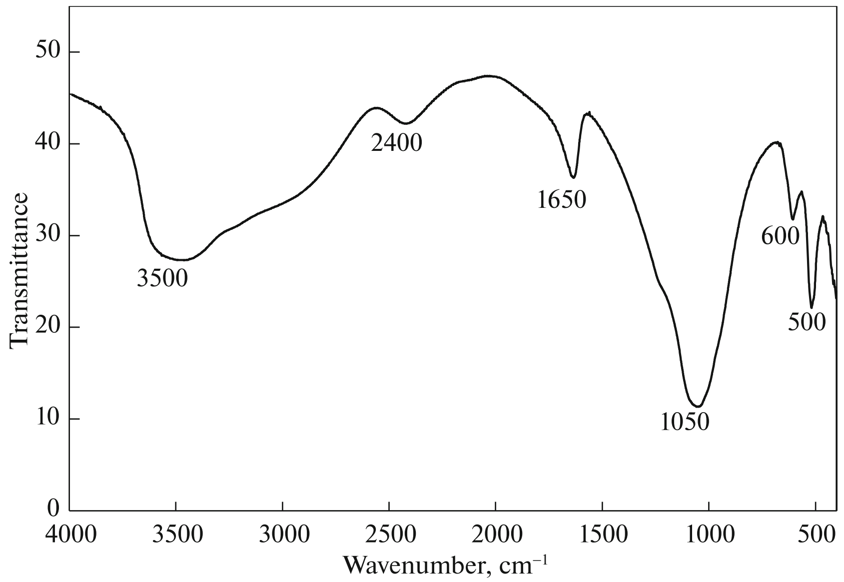

Fig. 1. IR spectrum of sample (I) of zirconium phosphate.

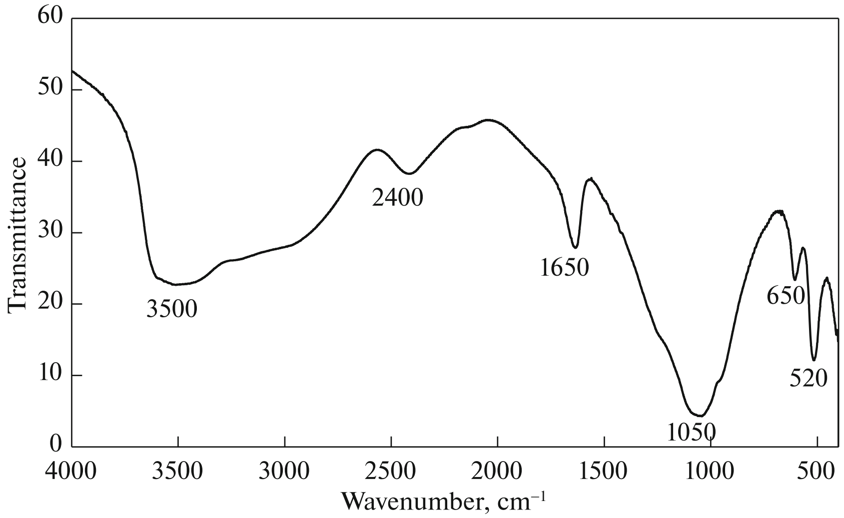

Fig. 2. IR spectrum of sample (II) of zirconium phosphate.

mation vibrations of P—O bonding of the PO_3 terminal groups [11, 12].

SEM micrographs of the synthesized zirconium phosphate of sample (I) and sample (II) are shown Figs. 3 and 4. The resulting products were analyzed as for their morphology, showing a different particle shape in each batch in indicating the binding of the inorganic ion-exchange.

Distribution and Selectivity Studies

The distribution coefficient (K_d, mL/g) of Pb(II), Cu(II), and Fe(II) ions on zirconium phosphate was determined at different pH values. The preliminary studies indicated that the equilibrium time for the exchange of Pb(II), Cu(II), and Fe(II) ions on zirconium phosphate were attained within 5 h in a shaker thermostat adjusted at 25 ± 1°C. In order to investigate the selectivity for Pb(II), Cu(II), and Fe(II) ions, K_d for metal ions was calculated and the results are shown in Table 1.

For all metal ions studied, the values of distribution coefficient and the separation factor at different pH values are presented in Table 1 on the basis of K_d values, separation factor for some metal ion were calculated and given in Table 1. The most promising prop-

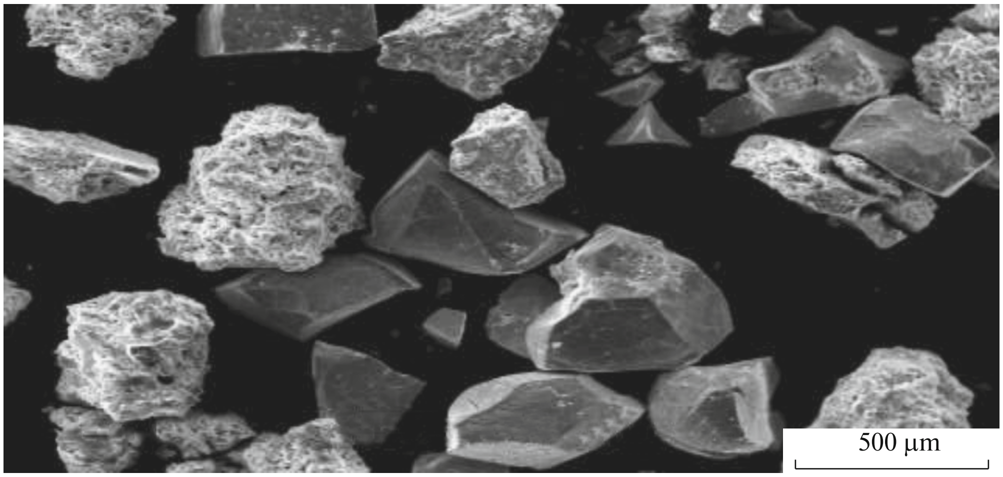

Fig. 3. Scanning electron microphotographs (SEM) of sample (I) of zirconium phosphate.

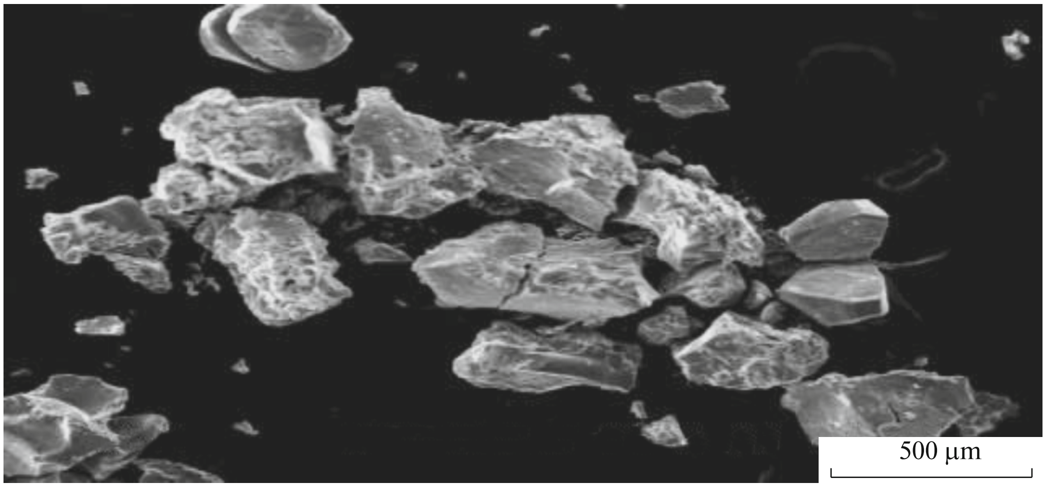

Fig. 4. Scanning electron micrographs of sample (II) of zirconium phosphate.

erty of these materials was found to be the high selectivity towards Pb(II) on sample (I) than sample (II), indicating its importance in environmental studies [13]. The plots of $\log K_d$ against pH for zirconium phosphate of sample (I) and sample (II) are shown in Figs. 5–10 for Pb^{2+}, Cu^{2+}, and Fe^{2+} ions of sample (I) and sample (II), a linear relationship with slope values smaller than the valence of the metals studied are obtained indicating deviation from ideality of the ion exchange reaction for all metals studied.

Adsorption Modeling

The values of thermodynamic parameters are relevant for the practical application of adsorption process. Isotherm data related to adsorption of Pb(II), Cu(II), and Fe(II) ions onto the sample (I) and sample (II) at various temperatures were analyzed to obtain the values of thermodynamic parameters from Van't Hoff plot of the adsorption of Pb(II), Cu(II), and Fe(II) ions as shown in Figs. 11 and 12.

The values of thermodynamic function ΔS^* and ΔH were evaluated using Van't Hoff's equation [10], which is given by:

$$\ln K_d = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT},$$

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

where ΔG^* change in Gibbs free energy (J mol^{-1}), R universal gas constant (8.314 J K^{-1} mol^{-1}), T temperature (K), ΔH^* change in enthalpy (J mol^{-1}), ΔS^* change in entropy (J mol^{-1} K^{-1}).

The results are given in Table 2. The change of free energy for physisorption is generally between –20 and

Table 1. K_d values and separation factors (α) of Pb(II), Cu(II), and Fe(II) ions as a function of pH on sample (I) and sample (II) of zirconium phosphate at different reaction temperature

T	K_d, mL g^{-1}					
	sample (I)			sample (II)		
	(Pb^{2+})*	(Cu^{2+})**	(Fe^{2+})***	(Pb^{2+})*	(Cu^{2+})**	(Fe^{2+})***
30°C	3459.4	439.5 (7.87)*	399.02 (8.67)* (1.10)**	149279.4	778.03 (191.87)*	281.84 (529.66)* (2.76)**
45°C	19364.2	557.18 (34.75)*	490.9 (39.44)* (1.13)**	157398.3	1210.59 (130.02)*	346.74 (453.94)* (3.49)**
65°C	95719	899.5 (106.41)*	679.2 (140.92)* (1.32)**	172583.78	1555.96 (110.92)*	431.52 (399.94)* (3.61)**

0 kJ mol^{-1}, the physisorption together with chemisorption is at the range of –20 to –80 kJ mol^{-1} and chemisorption is at a range of –80 to –400 kJ mol^{-1} [13, 14]. As can be seen from Table 2, the overall standard free energy changes ΔG^* during the adsorption process were negative for the experimental range of temperatures, corresponding to a spontaneous and a boundary of physisorption process of Pb(II), Cu(II),

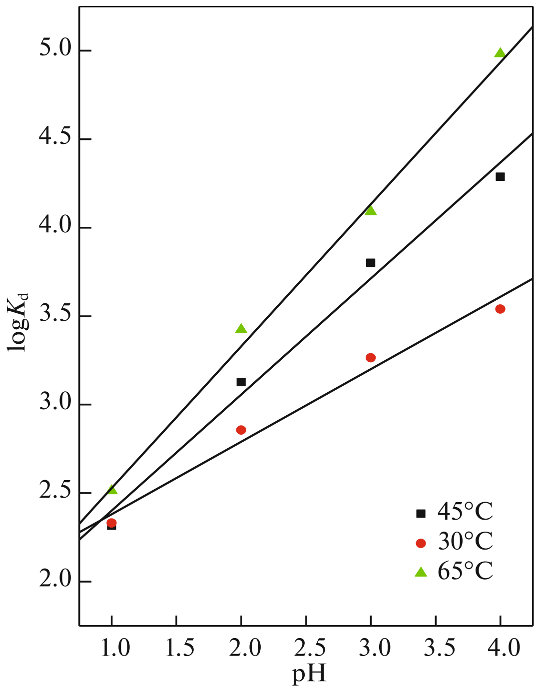

Fig. 5. $\log K_d$ as a function of pH of Pb^{+2} ion on sample (I) of zirconium phosphate at different reaction temperature.

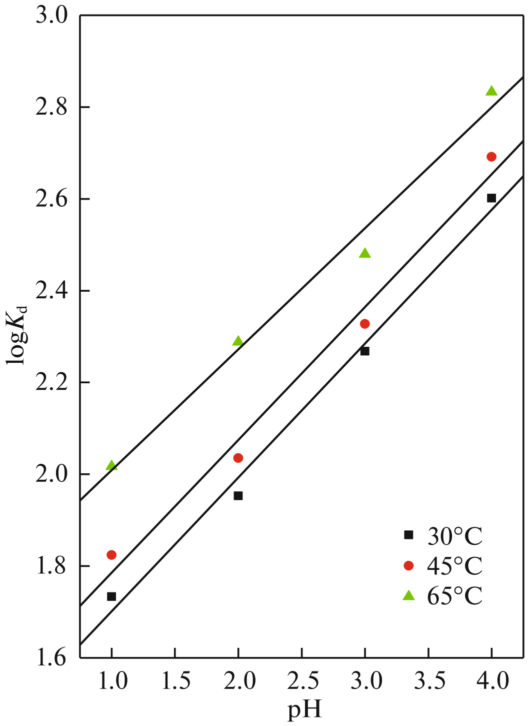

Fig. 6. $\log K_d$ as a function of pH of Fe^{+2} ion on sample (I) of zirconium phosphate at different reaction temperature.

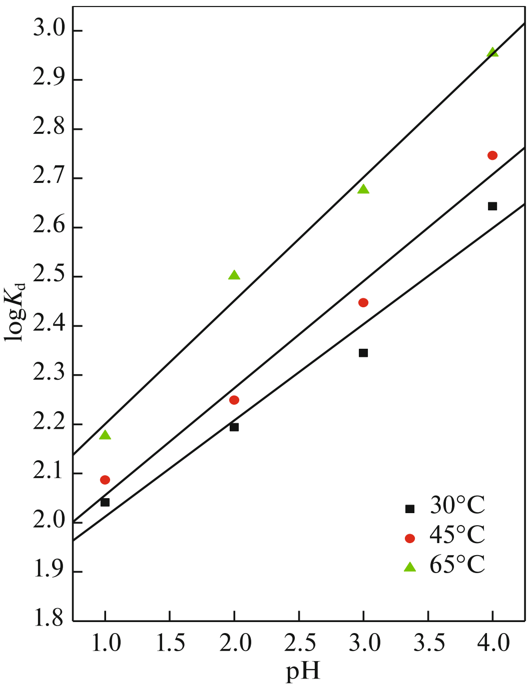

Fig. 7. logK_d as a function of pH of Cu^{+2} ion on sample (I) of zirconium phosphate at different reaction temperature.

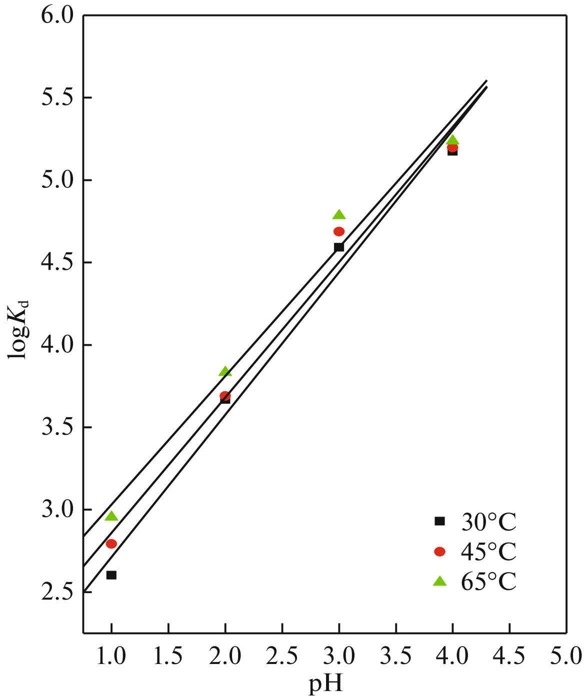

Fig. 8. logK_d as a function of pH of Pb^{+2} ion on sample (II) of zirconium phosphate at different reaction temperature.

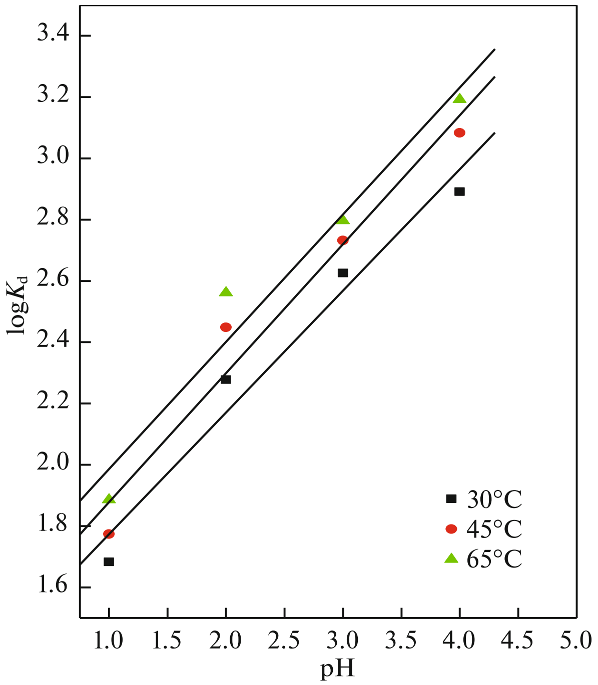

Fig. 9. logK_d as a function of pH of Cu^{2+} ion on sample (II) of zirconium phosphate at different reaction temperature.

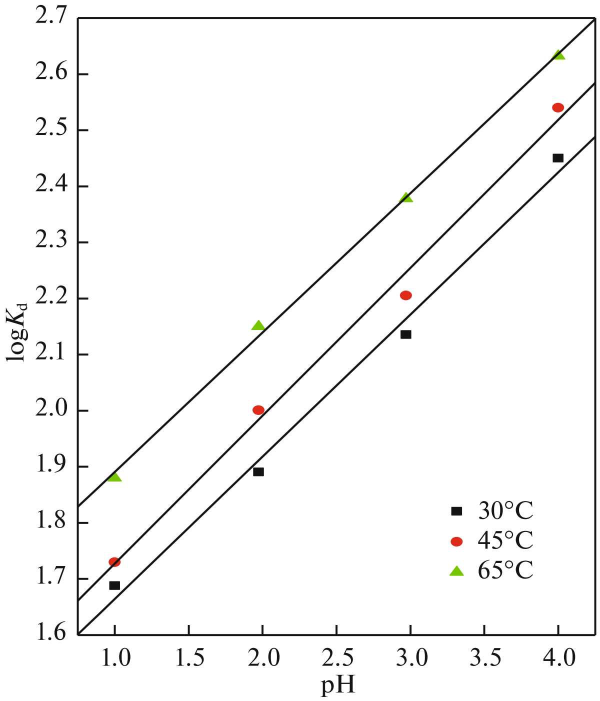

Fig. 10. logK_d as a function of pH of Fe^{2+} ion on sample (II) of zirconium phosphate at different reaction temperature.

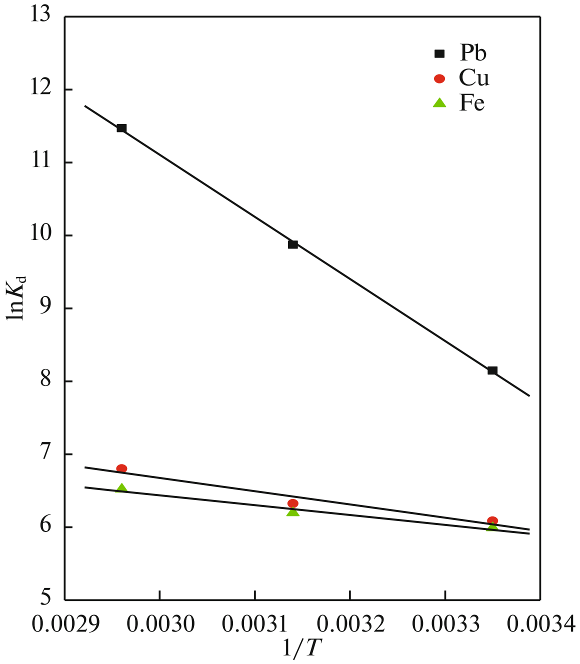

Fig. 11. Van't Hoff plot of the adsorption of Pb^{2+}, Cu^{2+}, and Fe^{2+} on sample (I) of zirconium phosphate.

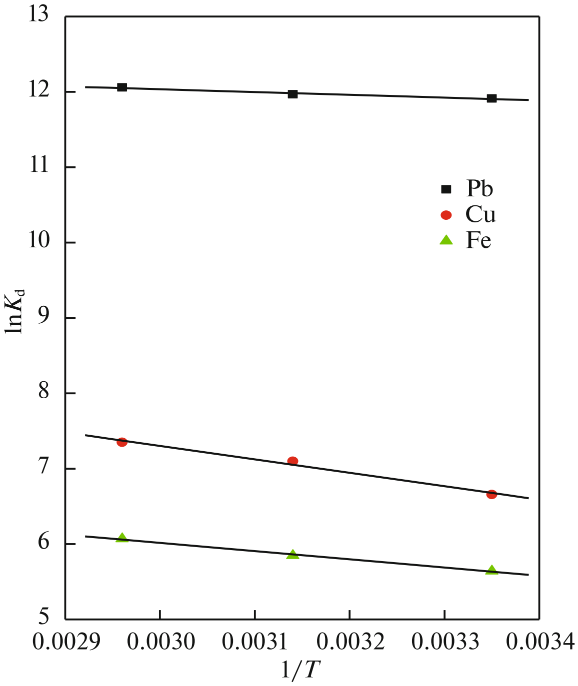

Fig. 12. Van't Hoff plot of the adsorption of Pb^{2+}, Cu^{2+}, and Fe^{2+} on sample (II) of zirconium phosphate.

and Fe(II) ions adsorption onto stannic silico-vanadate [15]. The decrease in the value of ΔG with the increase of temperature shows that the reaction was more spontaneous at high temperature which indicated that the sorption processes are favored when temperature increases [16]. The positive entropy change ΔS^* value corresponds to an increase randomness at the solid/solution interface during the adsorption Pb(II), Cu(II), and Fe(II) ions onto sample (I) and sample (II).

Table 2. Thermodynamic parameters for adsorption of Pb(II), Cu(II), and Fe(II) ions on sample (I) and sample (II) at different reaction temperature

Metal ions	*T*, K	ΔG^*, kJ/mol	ΔH^*, kJ/mol	ΔS^*, J/(mol K)
Sample (I)				
Pb^{2+}	303	−20.53	70.73	301.18
	318	−26.09		314.35
	338	−32.23		304.61
Cu^{2+}	303	−15.33	15.10	100.43
	318	−16.72		100.06
	338	−19.11		100.21
Fe^{2+}	303	−15.09	11.23	86.86
	318	−16.38		86.82
	338	−18.32		87.42
Sample (II)				
Pb^{2+}	303	−30.01	3.06	109.14
	318	−31.64		109.12
	338	−33.88		109.29
Cu^{2+}	303	−16.77	14.83	104.29
	318	−18.77		105.66
	338	−20.65		104.97
Fe^{2+}	303	−14.21	9.06	76.80
	318	−15.46		77.11
	338	−17.05		77.25

CONCLUSIONS

Sorption studies showed that the prepared zirconium phosphate cation-exchanger has high selectivity to Pb(II) on sample (I) than sample (II) in comparison to other metal ions Table 1. The separations factor of Pb(II) higher than Cu(II) and Fe(II) ions on two samples so that the Pb(II) can be separated at this pH. The property of these samples was found to be the high selectivity towards Pb(II), indicating its importance in environmental studies. The Thermodynamic parameters such as ΔG^*, ΔS^*, and ΔH^* have been calculated from the adsorption of Pb(II), Cu(II), and Fe(II) ions onto sample (I) and sample (II).

The positive values of ΔH^* indicated that the studied sorption processes are endothermic in nature. However, the negative values of ΔG^* cleared that the spontaneous behavior of the sorption processes. The positive values of ΔS^* suggest the increase randomness at the solid—solution interface during the sorption process.

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