Studies on Two-Dimensional Coordination Polymer Cadmium Phosphate and Its High Efficient Adsorption of Pb(II) Ions from Aqueous Solutions

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ABSTRACT: The two-dimensional coordination polymer cadmium phosphate with the morphology of rectangle layers was prepared by solid-state template reaction at room temperature, and was characterized by XRD, FTIR, and TEM techniques. The as-synthesized sample is a layered cadmium phosphate material, in which the structure is poly ($CdPO_4^-$) anion framework with ammonium ions and water species residing in the space between the layers, and cadmium ions are coordinated by the phosphate oxygen atoms. This article also presents the adsorption of Pb(II) ions from aqueous solution on the as-synthesized coordination polymer cadmium phosphate, and the results showed that this inorganic polymer adsorbent had good adsorption capacity. It could reach to the saturation adsorption capacity within an hour, and its excellent adsorption capacity for Pb(II) was 5.50 mmol/g when the initial solution concentration was 1.68×10^3 μg/mL at $T = 278$K. Moreover, the adsorption kinetics and adsorption isotherms were studied, it revealed that the adsorption kinetics can be modeled by pseudo second-order rate equation wonderfully. The apparent activation energy (E_a), ΔG, ΔH, and ΔS were 3.16 kJ mol^{-1}, −13.97 kJ mol^{-1}, −11.84 kJ mol^{-1}, and 7.66 J mol^{-1} K^{-1}, respectively. And it was found that Langmuir equation could well interpret the adsorption of the as-synthesized coordination polymer cadmium phosphate for Pb(II) ions. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 4054–4059, 2008

Key words: coordination polymer; inorganic polymer; morphology; template; adsorption

INTRODUCTION

Two- and three-dimensional coordination polymers have received increased attention during the last decades because of their potential applications in the fields of catalysis, separation, and adsorption.[1–3] After the discovery of crystalline aluminum phosphate in 1982,[4] as a synthetic alternative of the natural zeolites, a large number of other zeolite-like inorganic polymer material metal phosphates, including transition metal phosphates, have been prepared and characterized. The most typical examples include the extensive families of open-framework cobalt-aluminum-, vanadium-, cobalt-, zinc-, and gallium-phosphates,[5–12] which are generally prepared under hydrothermal condition, and have their structural diversity.

Interestingly, so far, only a few reports are involved in coordination polymer cadmium phosphates, they include the one-dimensional Cd(phen)$(H_2PO_4)_2 \cdot H_2O$ and Cd(2,2′-bipy)$(H_2PO_4)_2$ with different chain-like architecture,[13,14] the layered $K_4[Cd_3(HPO_4)(H_2PO_4)_2]$ and $CdBa_2(HPO_4)_2(H_2PO_4)_2$,[15,16] and the three-dimensional $CdVO_2(H_2O)PO_4$[17] and $[C_3H_{12}N_2]_4CdMo_{12}O_{24}(HPO_4)_6(PO_4)_2(OH)_6][Cd(H_2O)_2] \cdot 3H_2O$.[18]

Despite the richness of the crystal chemistry of the open-framework metal phosphates, their properties, especially the adsorption properties for heavy metal ions, are still a rarely studied area.[3,19] Recently, the removal and recovery of heavy metal ions from industrial wastewater have been significant concerns in all industrial factories because of economic and environmental factors. Toxic metals such as lead, chromium, and arsenic are dangerous environmental pollutants because of their toxicity and strong tendency to concentrate in environment, and in food chains. Wastewaters from a chemical industry polluted by heavy metal Pb(II) ions represent a hazard for all living organisms especially for human, and

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adsorption is the one of the important procedure for the removal of the traces heavy metal ions. In the previous work of our group, focusing on the investigation of metal ions adsorbents, we have prepared two novel chelating resins, polystyrene G1.0 diethanolamine-typed dendrimer (PS-DEA) and G2.0 diethanolamine-typed dendrimer (PS-$(DEA)_2$), and found they had good adsorption capacities for Cu^{2+}, Ag^{+}, and Hg^{2+}.[20] However, the adsorption properties of these chelating resins for Pb(II) ions were not good, and their saturation adsorption capacities were only about 0.5 mmol g^{-1}. Then, we tried to look after high efficient inorganic coordination polymer absorbents for Pb(II) ions.

In this work, we explored the convenient solid-state template synthesis of zeolite-like coordination polymer adsorbent cadmium phosphate with rectangle layers morphology at room temperature. This reaction method has the technical features of not only convenient operation without pollution but also safe and economical production. Moreover, the adsorption properties of the inorganic polymer cadmium phosphate for Pb(II) ions from aqueous solution were investigated in detail. These research results may suggest a new class of facile methods for the preparation of coordination polymer cadmium phosphates with excellent adsorption properties for the heavy metal ions.

EXPERIMENTAL DETAILS

Materials and preparation

All reagents were analytical-grade chemical products and used without further purification. Double deionized water was used for all dilutions. Aqueous solutions containing lead metal ions at various concentrations (10^{-2}–$10^{-3}M$) were prepared from metal salts.

The coordination polymer cadmium phosphate was synthesized by the solid-state reaction at room temperature. Cadmium chloride and 1,4-diazabicyclo (2,2,2) octane were mixed and ground for 30 min at ambient temperature. Fed with ammonium phosphate, the mixture was continually ground for another 20 min, and these reactants (Cadmium chloride,1,4-diazabicyclo (2,2,2) octane and ammonium phosphate) were in a molar ratio of 1.5 : 1.5 : 1.0. There then followed centrifuging washes with distilled water and ethanol, and the product was dried in air. The yield was 96.6%.

Instruments

IR spectrum (KBr pellets) was recorded on a Magna-IR 550 (series II) Fourier transform spectrometer, Nicolet, USA. Powder X-ray diffraction (XRD) data were obtained using a Rigaku MAX-2500VPC diffractometer with Cu-Kα_1 radiation (λ = 1.54056 Å). The morphology of the compounds was examined on JEOL JEM-1230 transmission electron microscope, JEOL, Japan. A GBC-932 atomic adsorption spectrophotometer made in Australia was used, and all measurements were carried out in an air/acetylene flame.

Adsorption procedure

Adsorption experiments were carried out using batch method in a thermostat-cum-shaking assembly. About 0.02 g of the sample cadmium phosphate was shaken with 20 mL of solution containing Pb(II) ions with different concentrations for different hours. Thereafter, the sample was obtained by centrifugalization, 4 mL solution was taken out and put in 25 mL colorimetry-used tube, and the distilled water was put in until the whole volume was 25 mL, and the concentrations of Pb(II) solution were determined on a GBC-932 atomic adsorption spectrophotometer. Adsorption amount (Q) and the coefficient of distribution (D) were calculated according to the eqs. (1) and (2), respectively.

$$Q(\text{mmol/g}) = (C_0 - C)V/W \quad (1)$$

$$D = (C_0 - C)V/(WC) \quad (2)$$

Where C_0 and C are the concentration of Pb(II) ions before and after sorption (mmol/L), respectively; V is the volume of the solution used for sorption (L); and W is the weight of the sample coordination polymer cadmium phosphate (g).

RESULTS AND DISCUSSION

Characterization of synthesized coordination polymer cadmium phosphate

The as-synthesized sample is a layered cadmium phosphate material, in which the structure is poly ($CdPO_4^-$) anion framework with ammonium ions and water species residing in the space between the layers, and cadmium ions are coordinated by the phosphate oxygen atoms. The XRD diffraction peaks of the sample coordination polymer cadmium phosphate corresponded well in position with the standard pattern (JCPDS No. 33-0048), indicating the phase purity of the as-synthesized sample. The strong peaks (2θ) included 10.060, 31.040, 25.540, 38.630, 20.361, and 23.460, whose d values were 8.786 Å, 2.879 Å, 3.485 Å, 2.329 Å, 4.358 Å, and 3.789 Å, respectively. These peaks corresponded to (010), (121), (111), (131), (011), (101) crystal planes. Using the program TREOR90,[21] we calculated the lattice

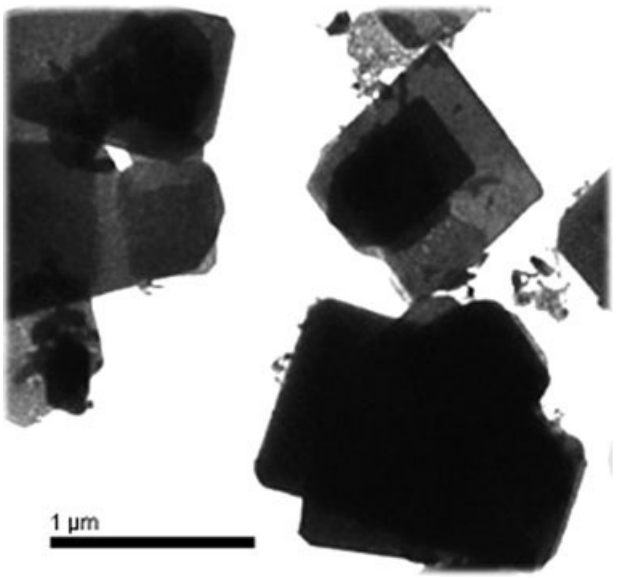

Figure 1 TEM images of the sample coordination polymer cadmium phosphate.

parameters of the above-mentioned sample, they were a = 5.8054 Å, b = 8.8522 Å, c = 5.0051 Å, and $\alpha = \beta = \gamma = 90.0^\circ$, which were in good agreement with the reported data (a = 5.8173 Å, b = 8.8797 Å, c = 5.0134 Å, $\alpha = \beta = \gamma = 90.0^\circ$, JCPDS No. 33-0048). IR spectrum of the compound showed the presence of vibrational bands characteristic of phosphate group, the intense bands at 936.2, 1034.8, and 1074.8 cm^{-1} were caused by the stretching vibrations of P—O bonds.

The TEM images of the powdery sample, as prepared, are showed in Figure 1. It revealed that the sample was consisted of rectangle layers. The length/width of them was within the range of 0.8–1.5 μm. Because the product was bound to be delivered from the solid state reactions at ambient temperature occurring in the mixture of the three given reactants, it is evident that only the template 1,4-diazabicyclo(2,2,2)octane applied in the experiment could be the chemical factor promoting the formation of the rectangle layers for the sample coordination polymer cadmium phosphate. The cause of the rectangle layers was speculated to be the structural direction of the template, which is shown to be a linear ligand. The rectangle layers being produced might originate from the possible formation of infinite rectangle network-like intermediate and the cadmium ions stand at the nodes because of the template's inducement in the course of the solid state reactions. When ammonium phosphate was being added into the reaction system, the phosphate ions replaced the cadmium-bonded nitrogen of the template gradually because there is stronger chemical bonding for cadmium with phosphate ions. Although the displaced templates were washed out, the rectangle layers of coordination polymer cadmium phosphate were produced in the end. As viewed from the chemical kinetics angle, the above-mentioned reactive procedures in the solid state and at room temperature rather than in an aqueous state or at high temperature, which could be advantageous to the product being prevented from further growth and being kept the nanoscale in thickness.

Adsorption kinetics

Figure 2 showed the adsorption kinetics of the sample coordination polymer cadmium phosphate for Pb(II) ions. Obviously, the as-synthesized cadmium phosphate with the morphology of rectangle layers had quick adsorption rate, and it could reach to the saturation capacity within an hour, and the saturation capacity decreased while the temperature increased over the range of 278–298 K. After doing many experiments under the conditions of different initial concentrations, it was found that the excellent adsorption capacity for Pb(II) ions on the sample could reach to 5.50 mmol/g when the initial solution concentration was 1.68×10^3 μg/mL at T = 278 K, which was larger than that using our synthesized organic polymer adsorbents PS-DEA and PS-$(DEA)_2$.[20]

The adsorption kinetics of coordination polymer cadmium phosphate for Pb(II) ions at different temperature was studied in detail. The results revealed that the adsorption rates increase with the increasing temperature (see the values of k_2 in Table I). As we mentioned earlier, the saturation capacity decreased with the increasing temperature. Then, the explanation for these facts is that the diffuse rate of Pb(II) is enhanced by increasing temperature, so the Pb(II) can approach and contact the synthesized inorganic

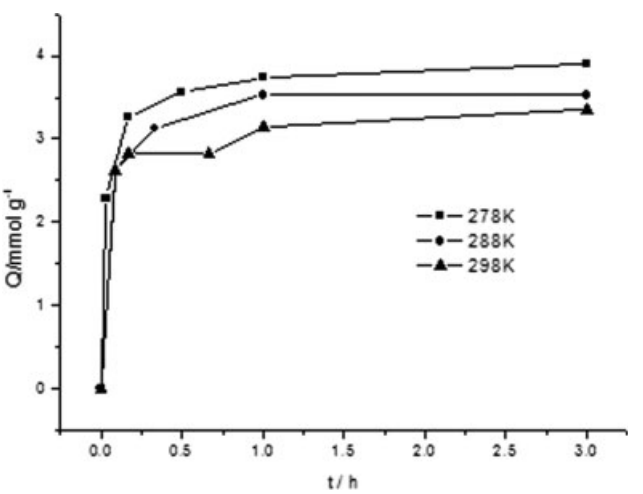

Figure 2 The adsorption kinetics of the synthesized coordination polymer cadmium phosphate for Pb(II) ions.

TABLE I
Parameters of Pseudo Second-Order Kinetic Models and *D* Values of Coordination Polymer Cadmium Phosphate for Pb(II) Ions

		Pseudo second-order model of cadmium phosphate for Pb^{2+}		
Temperature (K)	D	k_2	Q_0	R^2
278	1384.17	4.89	3.94	0.9995
288	1170.08	4.34	3.60	0.9989
298	997.44	5.38	3.16	0.9990

adsorbent much faster at higher temperature. Therefore, the metal ions were adsorbed inside the open framework structures and outer layer of the adsorbent at high temperature prevent the Pb(II) from diffusing into the inside, so the value of adsorption capacities at highest temperature is not the largest.

Adsorption kinetics can be modeled by several models. After our investigations, we finally found that pseudo second-order model was very suitable for the value of R^2 were regarded as the measure of the goodness-of-fit of experimental data on the kinetic models, whose relative eq. (3) was given as follows,

$$t/Q = 1/(k_2Q_0^2) + (1/Q_0)t \tag{3}$$

where k_2 (g/mmol) is the rate constant of pseudo second-order adsorption, Q_0 and Q are the adsorption amount at equilibrium and at time t, respectively.

Figure 3 displayed the straight-lines of pseudo second-order kinetic model, and the parameters calculated according to the model are listed in Table I. It can be seen that the general change trend of k_2 is that increases with the rise of the temperature. On the other hand, its adsorption amount at equilibrium Q_0 decreases while the temperature rises, which implying that the adsorption procedure is an exothermic one. According to Arrhenius equation, $\ln k_2 = -E_a/(RT) + \ln A$, plotting $\ln k_2$ against $1/T$, a straight line could be gotten. The apparent activation energy of adsorption E_a calculated from the linear slope is 3.16 kJ mol^{-1}, which is very small because that of the typical chemical reaction is 65–250 kJ mol^{-1}, then, the adsorption of the as-synthesized coordination polymer cadmium phosphate for Pb(II) ions is a facile procedure.

The values of the coefficient of distribution D were also listed in Table I, and the thermodynamic parameters (ΔG, ΔH, and ΔS) could be obtained by using the eqs. (4) and (5) later,

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

$$\text{Log } D = \Delta S/R - \Delta H/(2.303RT) \tag{5}$$

where D is the distribution ratio, T the solution temperature (K), and R is the gas constant. ΔH and ΔS could be calculated from the slope and intercept of van't Hoff plots of log$D$ versus $1/T$. The results showed that ΔG was -13.97 kJ mol^{-1}, which meant the adsorption procedure was spontaneous; the value of ΔH was -11.84 kJ mol^{-1}, then the adsorption was exothermic in nature, which was consistent with the above-mentioned discussion. ΔS was 7.66 J mol^{-1} K^{-1}, the positive value implied entropy increased at the solid-solution interface in the procedure.

Isothermal adsorption

The adsorption isotherms were studied and the data were analyzed with Langmuir (6) and Freundlich (7) equations, respectively.

$$C/Q = 1/(bQ_0) + C/Q_0 \tag{6}$$

$$\ln Q = \ln K_F + (\ln C)/n \tag{7}$$

where Q is the adsorption capacity (mmol/g), C the equilibrium concentration of Pb(II) ions (mmol/mL), Q_0 the saturated adsorption capacity (mmol/g), b an empirical parameter, n the Freundlich constant, and K_F the binding energy constant reflecting the affinity of the absorbent to metal ions. It is well known that the Langmuir equation is applicable to homogeneous adsorption, where the adsorption of each adsorbate molecule onto the surface had equal adsorption activation energy. On the other hand, the Freundlich equation is used to describe heterogeneous systems and reversible adsorption, and it is not restricted to the formation of monolayer.

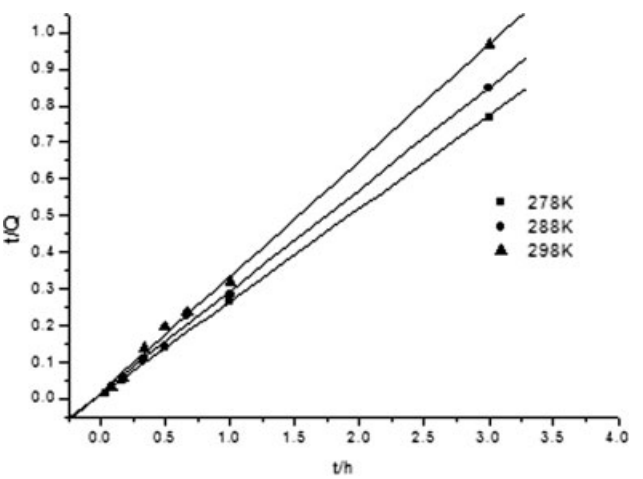

Figure 3 The pseudo second-order kinetic models of the sample coordination polymer cadmium phosphate for Pb(II) ions.

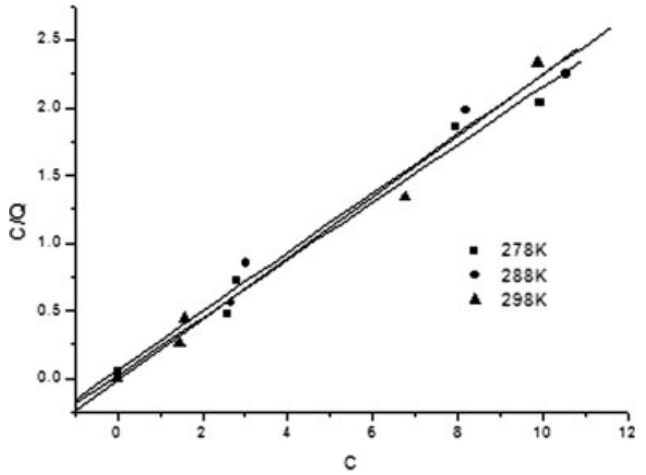

Figure 4 The Langmuir isotherms of the sample coordination polymer cadmium phosphate for Pb(II) ions.

Figures 4 and 5 displayed the Langmuir and Freundlich isotherms for the studied system, and the relative parameters were listed in Table II. It can be seen that the regression coefficient R^2 obtained from Langmuir model is much higher than that from Freundlich model, suggesting the Langmuir model is better than Freundlich model, and could well interpret the studied adsorption procedure. The values of Q_0 also decreased with the increasing temperature, which further verified the above discussion.

CONCLUSIONS

A convenient solid-state template method for synthesis of coordination polymer cadmium phosphate with rectangle layers morphology at room temperature has been developed, and the nature of the sample was characterized by XRD, FTIR, and TEM techniques. The synthesized cadmium phosphate showed the average length/width of the layers within the range of 0.8–1.5 μm. There must be some interesting mechanism deserving further attention. Such a simple method may have potential applications, in physics and chemistry, and it is helpful in searching for different feasible ways of achieving morphology control.

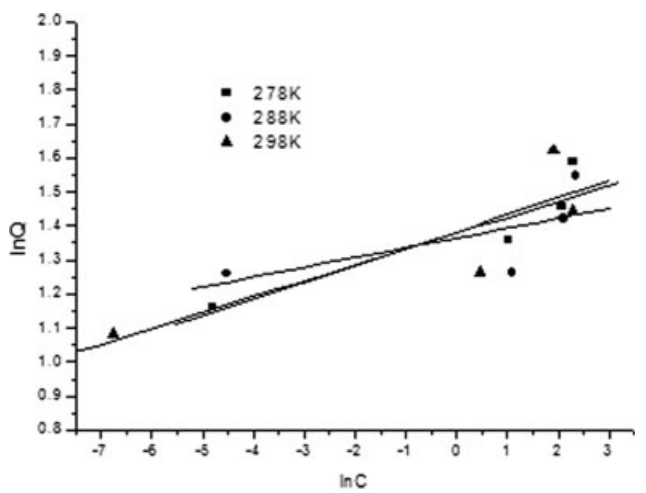

Figure 5 The Freundlich isotherms of the sample coordination polymer cadmium phosphate for Pb(II) ions.

TABLE II
Langmuir and Freundlich Parameters of the Sample Coordination Polymer Cadmium Phosphate for Pb(II) Ions

Temperature (K)	Langmuir parameters			Freundlich parameters		
	Q_0	b	R^2	K_F	$1/n$	R^2
278	4.69	8.67	0.9941	3.99	0.05	0.9195
288	4.58	3.57	0.9916	3.92	0.03	0.6695
298	4.42	4.32	0.9923	3.97	0.05	0.8506

The results of the adsorption of Pb(II) ions from aqueous solution on the as-synthesized coordination polymer cadmium phosphate showed that this high efficient inorganic adsorbent had good adsorption capacity. It can reach to the saturation adsorption capacity within an hour, and its excellent adsorption capacity for Pb(II) could reach to 5.50 mmol/g when the initial solution concentration was 1.68×10^3 μg/mL at $T = 278$K. The adsorption kinetics and adsorption isotherms were studied, the results showed that the adsorption kinetics can be modeled by pseudo second-order rate equation wonderfully, The apparent activation energy (E_a), ΔG, ΔH, and ΔS were 3.16 kJ mol^{-1}, −13.97 kJ mol^{-1}, −11.84 kJ mol^{-1}, and 7.66 J mol^{-1} K^{-1}, respectively. Moreover, it is found that Langmuir equation could well interpret the adsorption of the sample coordination polymer cadmium phosphate for Pb(II) ions. The obvious characters of this zeolite-like inorganic polymer material cadmium phosphate are its facile preparation with low costs and low pollutions, and its rapid, high efficient adsorption for Pb(II). On the basis of these results, it was concluded that this material had a significant potential for removing Pb(II) from wastewater using adsorption method.

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