Adsorption and Desorption of Zinc(II) on Water-Insoluble Starch Phosphates

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ABSTRACT: Water-insoluble starch phosphates (SPs) with different contents of phosphate groups were used as adsorbents of Zn(II). The effects of the adsorption time, dosage of adsorbents, and pH on the removal of Zn(II) by SPs were thoroughly studied. The results showed that the water-insoluble SPs were effective adsorbents for Zn(II) removal. The optimal adsorption effect was achieved at pH = 4.0, and the adsorption equilibrium data agreed well with the Langmuir isotherm model with a maximum adsorption capacity of 2.14 mmol/g. Furthermore, the desorption process and reusability of the adsorbents were studied. HCl (0.5*N*) was found to be an appropriate desorption solution to desorb Zn(II) ions from the adsorbents. After three adsorption/desorption cycles, the Zn(II) adsorption capacities of three SP samples decreased from 0.92, 1.23, and 1.44 to approximately 0.72, 1.02, and 1.29 mmol/g, respectively, and all the desorption percentages were greater than 93%. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1110–1114, 2009

Key words: adsorption; polysaccharides

INTRODUCTION

With the development of modern industry, heavy metals are widely used and are released into the environment either in wastewater or as sludge in landfills. Heavy metals such as lead, mercury, zinc, aluminum, arsenic, nickel, and chromium are not biodegradable, and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals and human beings. Environmental pollution caused by toxic heavy metals in industrial wastewater is one of the most pressing problems, and strict legislation on the discharge of these toxic products makes it necessary to develop various efficient technologies for the removal of heavy metals from wastewater. Among the various water-treatment techniques, adsorption is generally preferred for the removal of heavy-metal ions because of its easy handling, the availability of different adsorbents, and its cost effectiveness. Various adsorptive materials have been studied to remove Zn(II) ions from aqueous solutions. Barsanescu et al.[1] prepared acrylic copolymers with different crosslinking degrees and amine functional groups and found that the maximum Zn(II) retention capacity value (500 mg/g) was obtained with an acrylic copolymer. Activated carbons were prepared from evergreen oak wood and used as adsorbents of Zn(II) with a maximum adsorption capacity of 0.039 mmol/g.[2] Bhattacharya et al.[3] used clarified sludge, rice husk ash, neem bark, and the chemical adsorbent activated alumina as adsorbents for the removal of Zn(II) from aqueous solutions and found that the maximum adsorption capacity was between 13.00 and 16.00 mg/g. Zhang et al.[4] used a graft copolymer of crosslinked starch and acrylonitrile as an adsorbent for the removal of Zn(II) ions from an aqueous solution and found that the adsorption isotherms followed the Freundlich model.

Recently, there has been growing interest in using low-cost, nonconventional alternative adsorption materials based on natural polymers. Polysaccharides, which are abundant, renewable, biodegradable, and easy to modify, have the capacity to adsorb heavy-metal ions by physical and chemical interactions.[5] Wang et al.[6] prepared a new pH-dependent adsorbent based on chitosan and found that the membrane had a maximum sorption capacity for Pb(II) of about 185 mg/g, and the adsorption isotherms could be well fitted by the Langmuir equation. Xing et al.[7] investigated the adsorption behavior of crosslinked cationic starch maleate for chromium(VI) and found that the adsorption process followed a Langmuir isotherm. Nada et al.[8] prepared cotton stalk cation exchangers containing phosphate and sulfonate groups and used them as adsorbents of strontium, arsenic, copper, and nickel ions. Chen and Wang[9] studied the adsorption properties of oxidized carboxymethyl starch and crosslinked carboxymethyl starch for calcium ions

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and concluded that adsorption isotherm models fit the Langmuir model well for oxidized carboxymethyl starch and fit the Freundlich isotherm well for crosslinked carboxymethyl starch. They also studied the adsorption behavior of crosslinked oxidized starch for calcium ions and found that the adsorption process fit the Langmuir model well.[10]

Previous works have mentioned the preparation of water-insoluble starch phosphates (SPs) and valued them as adsorbents of Cu(II)[11] and Pb(II).[12] In this research, water-insoluble SPs with different contents of phosphate groups were used as adsorbents of Zn(II) from aqueous solutions. The effects of the adsorption time, dosage of adsorbents, and pH on the adsorption of Zn(II) by SPs were studied. To better evaluate this modified starch as an adsorbent of Zn(II) for industrial applications, the desorption process and reusability of the adsorbents were also investigated.

EXPERIMENTAL

Materials

Corn starch (Zhucheng Xingmao Corn Developing Co., Ltd., Shandong Province, China; food-grade) was dried at 105°C before it was used. $ZnCl_2$ (analytical reagent grade) was used to prepare the adsorbate solution. Urea, phosphoric acid, and all other commercial chemicals were analytical reagent grade and were used without further purification. All solutions and standards were prepared with deionized water.

Preparation of the adsorbents

Water-insoluble SPs were prepared with crosslinked starch, phosphoric acid, and urea as materials according to a method described in a previous article.[11] The phosphorus content of the adsorbents was determined according to spectrophotometry (GB 12092-1989).[13] Three samples with contents of phosphate groups of 1.20, 1.90, and 2.46 mmol/g were prepared to be used as adsorbents; they were named SP1, SP2, and SP3, respectively.

Adsorption experiments

Adsorption experiments were performed with a batch method. The desired dose of adsorbents was added to 50 mL of an 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. After the desired contact time, the suspension was filtered, and the concentration of Zn(II) ions in the aqueous phase was analyzed by a complexometric titration method.[14] The pH was adjusted to a certain value by the addition of either a 0.1*N* HCl or 0.1*N* NaOH solution before the addition of the adsorbent.

The adsorption capacity was calculated according to the following expression:

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

where Q is the adsorption capacity of the adsorbent (mmol/g); C_i and C_t (mmol/L) are 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.

Desorption experiments

Batch desorption experiments were carried out through the stirring of 100 mg of Zn(II)-loaded SP3 in 100-mL HCl solutions of different concentrations. The adsorption capacity of Zn(II)-loaded SP3 was 1.44 mmol/g. After the desired desorption time, the suspension was filtered, and Zn(II) ions in the aqueous phase were analyzed with the aforementioned method.

Circular experiments

After adsorption for 40 min according to the aforementioned method by the addition of 100 mg of SP to a 50-mL 5 mmol/L Zn(II) solution, the suspension was filtered, and the adsorbent was washed with deionized water. Then, the Zn(II)-loaded adsorbent was cautiously transferred to a Erlenmeyer flask with a 100-mL 0.5*N* HCl solution. After desorption for 90 min, the desorption suspension was filtered and washed. Then, the adsorbent was reused to adsorb Zn(II). The amounts of Zn(II) ions were determined according to the aforementioned method.

All the adsorption, desorption, and circular experiments were carried out at 293 K, and each process was replicated two times to reduce the error.

RESULTS AND DISCUSSION

Effect of the treatment time

The residual Zn(II) concentration decreased with increasing adsorption time and attained balance in about 40 min, as shown in Figure 1. The error bars mark the absolute deviations between different measurements, as do the error bars in the rest of the figures. The majority of Zn(II) ions were adsorbed in approximately the first 30 min. The adsorption capacity of the SPs for metal ions mainly depended on the active phosphate groups, as reported in previous articles.[11,12] The rate of metal-ion removal was

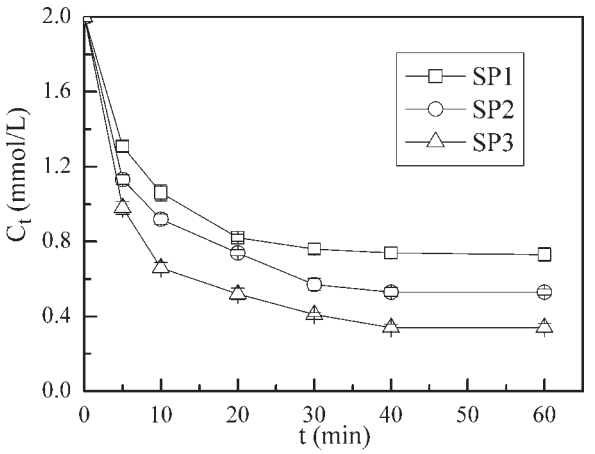

Figure 1 Effect of the adsorption time (t) on the residual Zn(II) concentration ([Zn^{2+}] = 2 mmol/L; pH = 4.0; dose of adsorbents = 60 mg).

higher in the beginning because more active groups of the SPs were available for adsorption. After 30 min, the rate of Zn(II) concentration reduction became almost insignificant because of a gradual exhaustion of the active adsorption groups. For the following experiments, the adsorption time was maintained at 40 min to ensure that equilibrium was really attained.

Effect of the adsorbent dose

The adsorbent dose is an important parameter that determines the adsorption capacity for a given initial concentration of the adsorbate under the operating conditions. The effect of the adsorbent dose on the residual Zn(II) concentration is shown in Figure 2. An increase in the adsorbent dose led to a decrease in the residual Zn(II) concentration. When the adsorbent dose was increased from 20 to 80 mg, the residual Zn(II) concentration decreased from 0.97 to 0.31 mmol/L for SP3. Meanwhile, the removal percentage reached 84.5% when the dose of SP3 was 80 mg. The decrease in the residual Zn(II) concentration with an increase in the adsorbent dose was due to an increase in the active groups on the adsorbent, which made the adsorption of the metal ions to the active groups easier.

Langmuir isotherm models

The Langmuir equation is widely applied to quantify the adsorption capacity, and it was used here to describe the equilibrium data obtained for the adsorption of Zn(II) on SPs. The linear expression is presented as follows:[15]

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

where C_e and Q_e are the equilibrium Zn(II) concentration (mmol/L) and equilibrium adsorption capacity (mmol/g), respectively, and Q_m and b are the Langmuir constants representing the maximal adsorption capacity (mmol/g) and energy of adsorption (L/mmol), respectively. Figure 3 shows the Langmuir isotherms obtained via the plotting of C_e/Q_e versus $1/C_e$. The values of Q_m and b were calculated according to the intercept and slope of these lines, respectively, as shown in Table I. The correlation coefficients (r^2) of all three samples were very close to 1, and this indicated that the equilibrium data fit the Langmuir model well. The maximum adsorption capacities of SP1, SP2, and SP3 were 1.49, 1.97, and 2.14 mmol/g, respectively. The maximum adsorption capacities of the adsorbents were lower than the contents of phosphate groups on the adsorbents, and this means that some phosphate

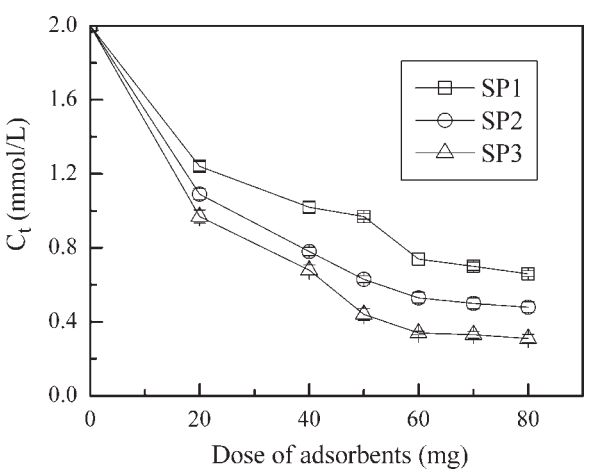

Figure 2 Effect of the dose of adsorbents on the residual Zn(II) concentration ([Zn^{2+}] = 2 mmol/L; pH = 4.0; adsorption time = 40 min).

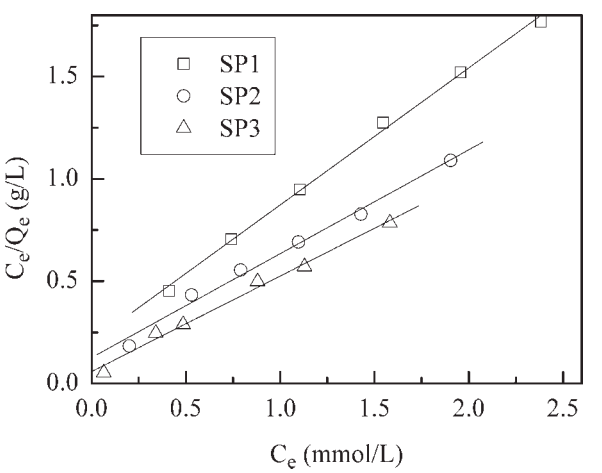

Figure 3 Langmuir adsorption isotherms for the adsorption of Zn(II) on SP at 293 K (dose of adsorbents = 60 mg; pH = 4.0; adsorption time = 40 min).

TABLE I
Langmuir Parameters for the Adsorption of Zn(II) on SPs at 293 K

Sample	Q_m (mmol/g)	b (L/mmol)	r^2
SP1	1.49	3.29	0.9975
SP2	1.97	4.00	0.9906
SP3	2.14	7.95	0.9906

Dose of adsorbents = 60 mg; pH = 4.0; adsorption time = 40 min.

groups had no effect on the removal of Zn(II) from the aqueous solutions. The reason for this is that some phosphate groups on the adsorbents exist in diphosphates and triphosphates.[16] The adsorption effect of diphosphates and triphosphates is lower than that of monophosphates.

Effect of pH

The pH of a solution is the most important variable affecting metal-ion adsorption. This is partly because hydrogen ions themselves are strongly competing with metal ions. Figure 4 shows the effect of pH on the adsorption of Zn(II) to SPs. The adsorption capacities were highly dependent on pH. When the initial pH values of the Zn(II) solutions were increased from 2.0 to 7.0, the adsorption capacities of Zn(II) on the SPs increased first, then decreased, and attained a maximum value at a pH value around 4. At low pHs, because of the protonation on the phosphate groups, electrostatic repulsion was high during the uptake of metal ions, and this resulted in a lower adsorption efficiency. With increasing pH, electrostatic repulsion decreased because of a reduction of the positive charge density on the adsorption groups, and this resulted in an enhancement of Zn(II) adsorption. At pH values higher than 7, there were inflection points for the adsorption capacities of the three samples. Under a basic condition, OH^- ions competed for Zn(II) with the active groups on the surface of the adsorbents. At pH 8.0, the adsorption capacities of the three samples achieved almost the same value, and this indicated a change in the mechanism for Zn(II)-ion removal. When the pH was beyond 7.0, metal precipitation contributed more to Zn(II) removal than adsorption on SPs.

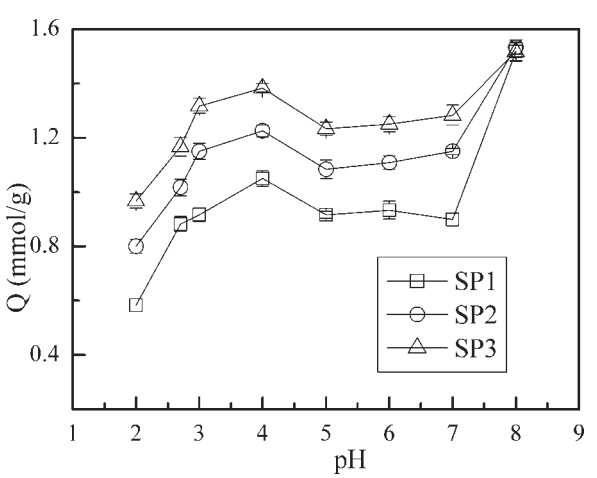

Figure 4 Effect of pH on the adsorption capacity of SP ($[Zn^{2+}]$ = 2 mmol/L; dose of adsorbents = 60 mg; adsorption time = 40 min).

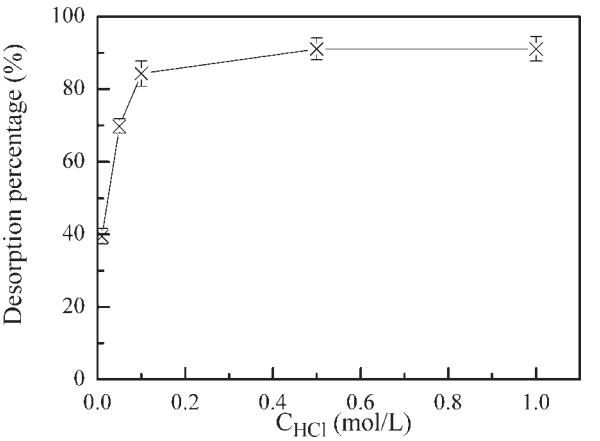

Figure 5 Effect of the HCl concentration (C_{HCl}) on the desorption percentage of Zn(II) (adsorption capacity of SP3 = 1.44 mmol/g; dose of adsorbents = 100 mg; desorption time = 60 min).

Desorption of Zn(II)

The desorption of Zn(II) from SPs was studied with HCl solutions as desorption agents. The desorption efficiency was investigated with respect to the HCl concentration and desorption time, as shown in Figures 5 and 6, respectively. Sample SP3 was chosen to optimize the desorption condition, and the adsorption capacity of Zn(II)-loaded SP3 was 1.44

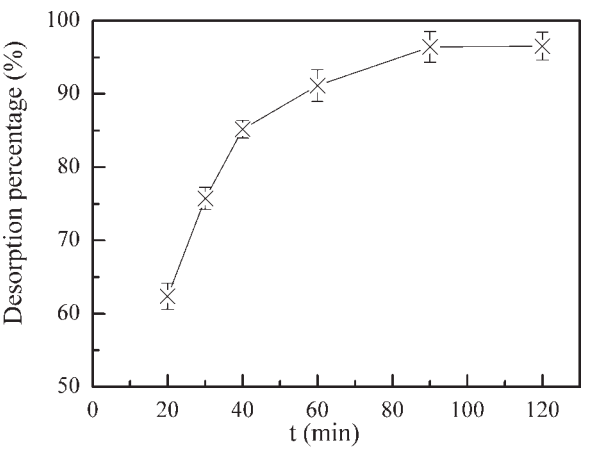

Figure 6 Effect of the desorption time (t) on the desorption percentage of Zn(II) (adsorption capacity of SP3 = 1.44 mmol/g; dose of adsorbents = 100 mg; HCl concentration = 0.5 mol/L).

TABLE II
Three Cycles of Adsorption and Desorption of Zn(II) on SP

Sample	Adsorption and desorption	Cycle		
		First	Second	Third
SP1	Q (mmol/g)	0.92	0.81	0.72
	Desorption percentage	94.6	94.4	93.1
SP2	Q (mmol/g)	1.23	1.13	1.02
	Desorption percentage	96.3	95.6	94.1
SP3	Q (mmol/g)	1.44	1.39	1.29
	Desorption percentage	96.5	98.5	96.1

Desorption agent = 0.5 mol/L HCl; treatment time = 90 min.

mmol/g. The desorption percentages increased with the HCl concentration increasing. Under strongly acidic conditions, Zn(II) ions were desorbed effectively because of the replacement of Zn(II) ions adsorbed onto the active groups with H_3O^+ ions in the solution. On the other hand, a high-concentration HCl solution could enhance the hydrolyzation of phosphate groups on the adsorbents and reduce the reusability of the adsorbents. Balancing the two aspects, we found that 0.5*N* HCl was optimal for the desorption of Zn(II) from SPs. As shown in Figure 5, the desorption of Zn(II) from SP3 was rapid, and equilibrium was achieved within 90 min with a desorption percentage of 96.4%. A longer desorption time was disadvantageous for the adsorbents for the aforementioned reason.

Reusability of the adsorbents

An important characteristic of adsorbents for industrial applications is reusability. The aforementioned desorption experiments proved that adsorbed Zn(II) ions can be easily desorbed in about 90 min with 0.5*N* HCl as a desorption solution. Three adsorption/desorption cycles were performed to examine the reusability of the adsorbent and Zn(II) recovery efficiency, and the results are shown in Table II. The desorption percentages of SP1, SP2, and SP3 were all greater than 93%, and the Zn(II)-ion adsorption capacities of SP1, SP2, and SP3 decreased from 0.92, 1.23, and 1.44 to about 0.72, 1.02, and 1.29 mmol/g, respectively, after three cycles. The main functional groups on the adsorbents were ether and phosphate groups, which were unstable under acidic conditions. Therefore, the decrease in the adsorption capacities of the adsorbents was mainly due to the hydrolyzation of the active groups. However, the high desorption percentages during the three cycles made the adsorbents very suitable for the recovery of Zn(II) from aqueous solutions.

CONCLUSIONS

In this study, water-insoluble SPs were used as adsorbents of Zn(II) ions. The removal rate of Zn(II) was very high, and the adsorption balance was obtained in about 40 min. The adsorption equilibrium data correlated well with the Langmuir isotherm model, and the maximum adsorption capacity was 2.14 mmol/g. The adsorption capacities of Zn(II) on the SPs were highly dependent on the pH. When the initial pH values of Zn(II) solutions were increased from 2.0 to 7.0, the adsorption capacities increased first, then decreased, and attained a maximum value at a pH value around 4. Zn(II) ions adsorbed onto the adsorbent could be easily desorbed with 0.5*N* HCl as a desorption solution. The results of adsorption/desorption cycle experiments showed that the adsorbents had good reusability for the recovery of Zn(II) from aqueous solutions. The desorption percentages of the adsorbents were all greater than 93% in three circles. Water-insoluble SPs have potential as effective adsorbents for the removal and recovery of Zn(II) from wastewater.

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