Pb^{2+} Binding by Polyaspartyl Polymers and Their Application to Pb^{2+} Removal from Glycyrrhizin

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ABSTRACT: Polyaspartate is an excellent Pb^{2+}-binding agent in comparison with some polyaspartamide derivatives with different side chains, in that it possesses a higher Pb^{2+} uptake and a lower Pb^{2+} equilibrium concentration. Equilibrium sorption data for Pb^{2+} on polyaspartate can be well fitted with the Freundlich and Langmuir models. Experimental results show that a crosslinked polyaspartate hydrogel is superior to poly(acrylic acid)-based resins and polystyrene-based chelating resins. IR spectra and X-ray photoelectron spectra reveal that the polyaspartate hydrogel binds Pb^{2+} by both an ion-exchange mechanism and a chelating mechanism. The polyaspartate hydrogel is also an effective agent for the removal of Pb^{2+} from glycyrrhizin. J Appl Polym Sci 97: 2215–2220, 2005

Key words: gels; hydrogels; hydrophilic polymers; adsorption

INTRODUCTION

A large number of heavy-metal entrapment materials have been developed, including various ion-exchange resins and sorbents and specialized chelating agents. However, with respect to green chemistry, all of these have several disadvantages. Many do not have atomic efficiency; that is, the heavy-metal-binding capacity per gram of the material is not high enough. Additionally, the requirement for the regeneration of these materials is a serious disadvantage as it produces a large amount of waste solution. Moreover, most of these materials do not exhibit biodegradability. Thus, they are widely scattered and released, polluting the natural world, with grave environmental consequences.

Polyaspartates are typical of environmentally friendly chemicals and have attracted a great deal of attention. One of the primary characteristics that make them valuable is that they are biodegradable. They have been used as scale inhibition agents and corrosion inhibition agents in water treatment applications, dispersing agents in paints and coatings, detergents, plant-growth promoters, medical materials, cosmetic ingredients, and so on.[1–4]

With both carboxyl and amide groups, it is possible for polyaspartate to be used as a heavy-metal-binding agent because of its ion-exchange function and complexing function. In particular, its theoretical uptake capacity is about 7.2 mequiv/gram; that of ethylenediaminetetraacetic acid (EDTA) is only 6.0 mequiv/gram (based on the sodium salt). Although poly(acrylic acid) also has a quite high capacity, it shows poor efficiency at a low ion concentration because only an ion-exchange mechanism exists in its structure. Moreover, high-molecular-weight samples are not readily biodegradable.

In this study, several α,β-poly(DL-aspartamide)s with different side chains were synthesized and used to investigate the effects of their structures on their Pb^{2+}-binding performances. An attempt to apply polyaspartate hydrogels to the Chinese herbal medicine glycyrrhizin for heavy-metal removal was also made.

EXPERIMENTAL

Reagents and materials

Polysuccinimide (PSI) was obtained by the acid-catalyzed polycondensation of L-aspartic acid.[5] D418 (chelate ion exchanger), D113 (weakly acidic cation-exchanger carboxylic functionality, macroporous type), and 110 (weakly acidic cation-exchanger carboxylic functionality, gel type) were purchased from the Chemical Plant of NanKai University (Nankai Group, China). Glycyrrhizin pellets were purchased from the hospital pharmacy. All other reagents were obtained from Tianjin Chemical Reagent Co., Inc. (Tianjin, China), and were used as received.

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TABLE I
Instrumental Parameters and Operating Conditions for ICP-OES

Radio frequency (RF) power	1.2 kW
Plasma gas flow rate	15 L/min
Flow rate of argon auxiliary	1.5 L/min
Nebulizer gas flow rate	0.9 L/min
Precision (general)	1–3%
Detection limit	0.01 mg/L
Pb element analytical line (λ)	220.353 nm

Measurements

Fourier transform infrared (FTIR) spectra were recorded with a Nicolet Magna-560 FTIR spectrometer (Madison, WI) in KBr pellets over a wave-number range of 4000–400 cm^{-1} with a 4-cm^{-1} resolution.

X-ray photoelectron spectroscopy (XPS) spectra were acquired with a PerkinElmer PHI-1600 electron-spectroscopic-chemical analysis (ESCA) (Wellesley, MA) equipped with a hemispherical electron energy analyzer and a Mg Kα monochromator source (light quantum energy = 1253.6 eV). The pressure in the analysis chamber during data acquisition was approximately 10^{-7} Pa. The analysis area was 0.8 mm^2. The survey spectra were carried out with a pass energy of 187.85 eV. The contaminative C_{1s} peak at 284.6 eV was used to calibrate the energy shift. The accuracy of the binding energy was estimated to be ±0.2 eV. All the data of the spectra were treated with PHI Multipak software (version 6.0, Wellesley, MA).

The total concentration of Pb^{2+} in an aqueous solution was determined with a Vista MPX Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) spectrometer (Varian, Inc., Palo Alto, CA). The instrumental operating conditions are shown in Table I. The free Pb^{2+} concentrations in an aqueous solution were measured by potentiometer determination with a pHS-25 pH Meter (Shanghai Rex Instruments Factory, Shanghai, China) with a 0.01-mV resolution. With the potentials between the lead-ion-selective electrode and saturated calomel electrode (SCE) recorded, they were determined with the aid of a calibration curve of the potential versus the log concentration.[6]

Preparation of an aqueous solution of polyaspartate (1)

To a suspension of 1.0 g (0.01 mol) of PSI [weight-average molecular weight = 9640, as measured by gel permeation chromatography (GPC)][5] in 5 mL of water, 12 mL of 1 mol/L (0.012 mol) NaOH in water was added dropwise with vigorous stirring at room temperature. Maintained for 2 h, the mixture was neutralized with 0.1 mol/L HNO_3 to pH 6–7.

Preparation of aqueous solutions of α,β-poly[(2-hydroxyethyl)-DL-aspartamide] (2) and α,β-poly[(2-aminoethyl)-DL-aspartamide] (3)

Except for the fact that water was substituted for dimethylformamide (DMF), the preparation of the aqueous solutions of **2** and **3** was the same as that reported in the literature.[7] For the reaction with ethylenediamine, more water was needed to prevent crosslinking.

Synthesis of a polyaspartate hydrogel (4)

To a 100-mL flask were charged 25 mL of DMF and 4.85 g (0.05 mol) of PSI with an average molecular weight of 22,000, as measured by GPC.[5] The flask contents were heated to 50°C with agitation to ensure total dissolution. A solution of 1.46 g (0.01 mol) of L-lysine and 0.4 g (0.01 mol) of NaOH in an appropriate amount of water was added to the flask at room temperature with stirring. Then, the reaction mixture was promptly placed in a microwave oven and kept at 120 W for about 3 min. After it cooled to about room temperature, the reaction mixture was poured into about 80 mL of methanol with stirring. The precipitate was filtered, washed several times with methanol, and then dried at 40°C under reduced pressure. About 6.5 g of a solid was obtained.

This material was used for alkaline hydrolysis with the addition of 25 mL of NaOH in water (2 mol/L); it was pH-controlled at 11–12 until a clear, yellow solution formed. After 80 mL of absolute methanol was poured into the solution, precipitation took place. The precipitate was isolated, washed with methanol, and then dried *in vacuo*. About 5.6 g of a yellow solid was collected.

One gram of this material was dissolved in 5 mL of distilled water, and then 0.4 mL of 50% glutaraldehyde was added. The reaction mixture was kept at room temperature overnight until a stable gel formed. The gel was washed several times with distilled water until the pH of the washing medium was 7. Then, it was dried to a constant weight at 40°C *in vacuo*.

Synthesis of a polyaspartamide derivative hydrogel (5)

PSI (2.43 g, 0.025 mol), with an average molecular weight of 22,000 as measured by GPC,[5] was dissolved in 15 mL of DMF at about 50°C. A solution of 1.22 g (0.02 mol) of ethanolamine and 0.3 g (0.005 mol) of ethylenediamine in 5 mL of DMF was added with stirring at room temperature, and the mixture was allowed to stand overnight. Then, 80 mL of absolute methanol was poured into the mixture. The precipitate was isolated, washed with methanol, and then dried *in vacuo*. The procedure was the same as that described in the previous paragraph.

TABLE II
Equilibrium Sorption Data for Pb^{2+} on Polyaspartate (18 °C)

Amount of PSI (mg)	Concentration of free Pb^{2+} ion in solution (mg/L)[a]	Pb^{2+} uptake (g/g)[b]
1.25	77.0	0.92
2.50	60.0	0.85
3.75	40.0	0.80
5.00	27.0	0.70
7.50	9.0	0.60
12.5	2.0	0.40
15.0	1.5	0.33
17.5	0.85	0.28
20.0	0.60	0.25
30.0	<0.25	—

[a]Potentiometric assay conditions: initial concentration of Pb^{2+} = 100 mg/L; V total volume of $Pb(NO_3)_2$ solution = 50 mL; concentration of $NaNO_3$ = 0.1 mol/L; pH = 6; temperature = 18°C.
[b] Based on amount of PSI.

Preparation of an aqueous solution of glycyrrhizin

Small pieces of glycyrrhizin (50 g) were soaked in 500 mL of deionized water in a 1000-mL, round-bottom flask equipped with a condenser and allowed to stand at room temperature for 0.5 h. Then, the contents of the flask were heated and maintained at reflux for 1 h. The mixture was cooled and left overnight. The upper liquid layer was carefully decanted and concentrated with a rotary evaporator to a volume.

RESULTS AND DISCUSSION

Effect of the structure of linear polyaspartamide on pb^{2+} binding

Although the performance of a polymer material is closely related to its three-dimensional configuration, its primary structure (or short-range structure) is still an essential factor. Thus, an investigation of the effects of the structure of linear polyaspartamides on Pb^{2+} binding was first made.

The backbone of polyaspartamides is an amide linkage as well as a polypeptide linkage resembling a protein. A study of the effects of some functional groups in side chains, such as —CONH—, —OH, and —NH_2, on Pb^{2+} binding was carried out.

Table II lists equilibrium sorption data for Pb^{2+} on polyaspartate, and Table III is devoted to a direct comparison of the polyaspartyl structures in terms of Pb^{2+} binding.

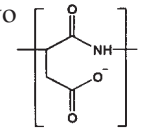
The results in Table II show that polyaspartate possesses both a higher uptake (ca. 0.92 g/g, based on the amount of PSI) and a lower equilibrium concentration (<0.25 mg/L). Moreover, the uptake is still high in the range of lower concentrations of Pb^{2+}. However, the Pb^{2+} uptake decreases rapidly with an increase in the amount of polyaspartate. Thus, it is suited for use in continuous operation or multiple-stage operation.

Under the assumption that the macromolecules of polyaspartate in an aqueous solution consist of an imaginary phase, the data sets listed in Table II were fitted with the Freundlich equation.[8] The following expression was obtained:

$$C_e = K\left(\frac{q}{Q}\right)^m \quad (1)$$

where q is the equilibrium uptake of Pb^{2+}on 1 g of polyaspartate (g/g), C_e is the equilibrium concentration of Pb^{2+} in solution (mg/L), Q is the total number of active sites in 1 g of polyaspartate (g/g), and K and m are the attribute constants of the system.

As long as two



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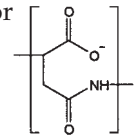

units bind one Pb^{2+} ion, the theoretical uptake capacity of polyaspartate will be about 1.0 g/g (based on the amount of PSI). This is very close to the experimental result (0.92 g/g). If the amount of polyaspartate is small enough, all the active sites can be considered occupied:

$$C_e = K\left(\frac{q}{Q}\right)^m = Kq^m \quad (2)$$

The data sets in Table II provided the experimental basis for the fitting of the model. The m and K values obtained from the fitting of the experimental data with

TABLE III
Comparison of the Polyaspartyl Structure in Terms of Pb^{2+} Binding

Polyaspartamide	Amount of PSI (mg)	Final concentration of free Pb^{2+} ion in solution (mg/L)	Pb^{2+} uptake (g/g)[a]
Polyaspartate	10	4.5	0.48
	20	0.6	0.25
2	10	30	0.35
	20	10	0.22
3	10	50	0.25
	20	30	0.17

[a] Based on the amount of PSI.
[b] The assay conditions were the same as those listed in Table II.

TABLE IV
Comparison of Some Absorbents for Pb^{2+} Removal

Absorbent	Amount (g)	Initial concentration of Pb^{2+} in solution (mg/L)	Final concentration of Pb^{2+} in solution (mg/L)	Pb^{2+} uptake (mg/g)
Gel **4**	0.1	200	105	47.5
	0.2	200	50	37.5
	0.2	50	5	11.2
Gel **5**	0.2	200	110	22.5
110	0.2	200	140	15.0
	0.2	50	30	5.0
D113	0.2	200	150	12.5
D418	0.2	200	140	15.0

Total volume of $Pb(NO_3)_2$ solution = 50 mL; exchange time = 1 h; temperature 18°C; pH = 6.

the Freundlich equation were 3.77 and 92.6, respectively.

Therefore,

$$C_e = 92.6q^{3.77} \tag{3}$$

The relative coefficient (R^2) value, 0.986, indicates that the model fits the experimental data relatively well. This result also assists in elucidating the biosorption of Pb^{2+} ion by organisms.

The same data sets shown in Table II were also fitted with the Langmuir equation:[8]

$$\frac{q}{q_m} = \frac{k_1 C_e}{1 + k_1 C_e} \tag{4}$$

or

$$\frac{1}{q} = \frac{1}{q_m k_1} \cdot \frac{1}{C_e} + \frac{1}{q_m} \tag{5}$$

where q_m is the maximum uptake of polyaspartate (based on the amount of PSI; g/g), q and C_e have the same meanings as they do for the Freundlich equation, and k_1 is the constant in the Langmuir model.

The obtained q_m and k_1 values were 0.860 (below the experimental value) and 0.366, respectively. R^2 was 0.975, indicating that the model also fit the experimental data well.

The results given in Tables II and III show that the Pb^{2+} uptake of polyaspartate is higher than that of any other polyaspartamide at the same dosage. This might be due to the fact that the electrostatic charge effect of —COO^- in side chains is stronger than that of —CONH—, —OH, or —NH_2. Additionally, the molecular weight of NaOH is less than that of ethanolamine or ethylenediamine, so it is obvious that the Pb^{2+} uptake per gram of polyaspartate is larger than that of any other polyaspartamide.

An excessive number of carboxyl groups in molecules are no better for the improvement of the Pb^{2+}-uptake capacity. For example, EDTA has four carboxyl groups, but if it reacts with divalent metal cations, only a 1:1 (molar ratio) complex is formed.

Entrapment of Pb^{2+} on the polyaspartate hydrogel

A comparison of **4**, **5**, 110 (polyacrylate cation resin in a gel form), D113 (polyacrylate cation resin in a porous form), and D418 (polystyrene chelating resin in a porous form) for the removal of Pb^{2+} from an aqueous solution is shown in Table IV.

The following conclusions can be drawn:

1. Upon the conversion into the polyaspartate hydrogel, the Pb^{2+} uptake of the resulting product decreases rapidly. It is therefore inferred that the movement of the polyaspartate molecule in gels is so restricted that its Pb^{2+}-binding activity is restrained greatly.
2. The Pb^{2+} uptake of the polyaspartate hydrogel is higher than that of other polyaspartamide derivative hydrogels. This result is consistent with those shown in Table II and III.
3. The polyaspartate hydrogel is superior to the other materials listed in Table IV.

Pb^{2+} removal from glycyrrhizin by the polyaspartate hydrogel

Because the polyaspartate hydrogel possesses excellent behavior for Pb^{2+} removal, especially at low Pb^{2+} concentrations, an attempt to remove Pb^{2+} from herbal medicines has been made. It has been reported[9] that there exists binding between glycyrrhizin acid and Pb^{2+}. In our work, the potential between an ion-selective lead electrode and an SCE in a 100 mg/L $Pb(NO_3)_2$ aqueous solution was measured to be 13.69 mV before water-extracted liquor of glycyrrhizin was added, whereas the potential was 13.31 mV after 10 mL of the liquor (solid content = 35 g/L) was added; this corresponded to a 5 mg/L free Pb^{2+} concentration. This result confirms that binding between glycyrrhizin acid and Pb^{2+} does exist. Thus, glycyrrhizin

TABLE V
Results of Pb^{2+} Removal from Glycyrrhizin with the Polyaspartate Hydrogel

Amount (g)	Initial concentration of Pb^{2+} in solution (mg/L)	Final concentration of Pb^{2+} in solution (mg/L)	Pb^{2+} removal (%)
0.18	20	3.47	82.6
0.3	4	0.75	81.2

Total volume of $Pb(NO_3)_2$ solution = 50 mL; exchange time = 1 h; temperature = 18 °C; pH = 6.

was chosen to investigate the Pb^{2+}-removal performance of the polyaspartate hydrogel. The results are shown in Table V.

As shown in Table V, the polyaspartate hydrogel can effectively remove Pb^{2+} from glycyrrhizin. If a multiple-stage operation is adopted, the percentage of Pb^{2+} removal will be even higher.

In general, herbal liquor contains small quantities of amino acids and peptides, in addition to the main components. Polyaspartate possesses a protein-resembling structure and much denser carboxyl groups in its side chains than natural proteins, and this results in more active sites for binding metal ions and stronger effects and thus lower equilibrium concentrations of heavy-metal ions. It can recapture heavy-metal ions from natural proteins, and so heavy-metal ions in herbal medicines can be removed.

Characterization of the polyaspartate hydrogel and investigation of its Pb^{2+}-binding effect

The IR spectrum of the polyaspartate hydrogel shows strong absorption at 1605.8 and 1396.5 cm^{-1} (—COO^-) and strong and wide absorption at 3426.8 cm^{-1} (—NH—), whereas the IR spectrum of the Pb^{2+}-binding polyaspartate hydrogel shows strong absorption at 1558.1 and 1396.5 cm^{-1} (—COO^-) and strong and wide absorption at 3388 cm^{-1} (—NH—), shifting to a lower wave-number region. It can be inferred that the N atom in the amide group participates in binding Pb^{2+}.

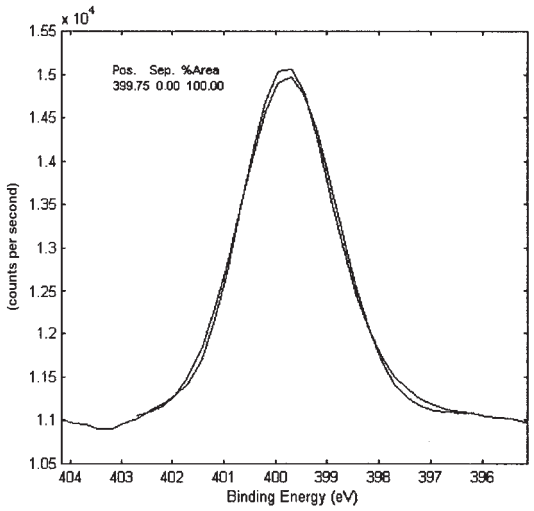

Figure 1 XPS spectrum of N(1s) before sorption.

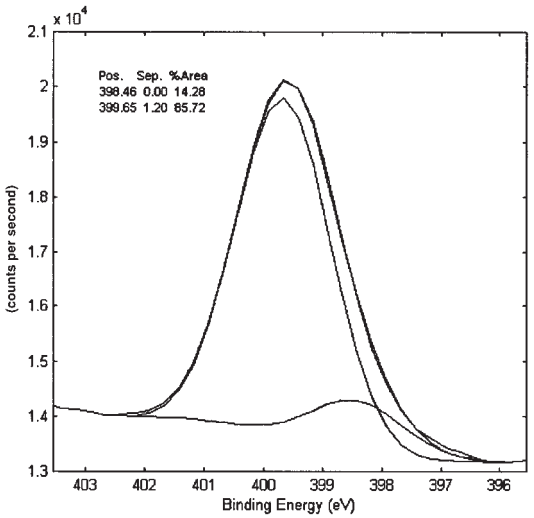

Figure 2 XPS spectrum of N(1s) after sorption.

Meanwhile, the XPS measurements of the surface of gels before and after sorption were also carried out. Before sorption, the N(1s) peak appeared at 399.75 eV (Fig. 1), whereas after sorption, the N(1s) peak was separated into two sets of peaks (Gaussian curve) centered at 399.65 and 398.46 eV, respectively (Fig. 2). The peak at 398.46 eV may come from the N atoms in the coordination state.

Surface atomic ratios from XPS are given in Table VI. An atomic ratio of 2.8% Pb^{2+} uptake on the surface is close to that in the bulk calculated from the results of the chemical analysis. This suggests that Pb^{2+} was adsorbed uniformly in the gel.

On the basis of the results given in Table II and those from IR, it can be concluded that the polyaspartate hydrogel binds Pb^{2+} by both an ion-exchange mechanism and a chelating mechanism. That is one reason that it has a lower equilibrium concentration of

TABLE VI
Surface Atomic Ratios of the Pb^{2+}-Binding Gel from XPS

Element	atom %
C	68.7
O	21.6
N	6.9
Pb	2.8

Pb^{2+} uptake of the sample was about 40 mg/g of dry gel (atomic ratio = 2.2%) based on polyaspartate.

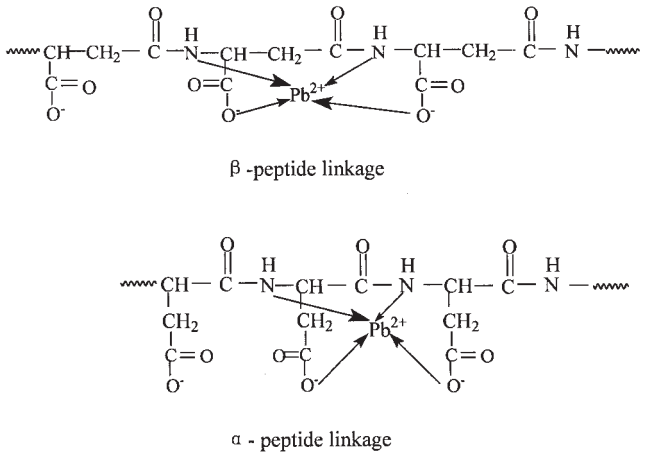

Figure 3 Deduced structure of the complex from Pb^{2+} and the polyaspartate hydrogel.

heavy-metal ions. We speculate that the complex is formed between Pb^{2+} and the polyaspartate hydrogel and that the coordination number of Pb^{2+} is 4. The deduced structure of the complex is shown in Figure 3.

Additionally, intermolecular linking may occur. A solution becomes turbid when the dosage of linear polyaspartate is low enough (or the concentration of Pb^{2+} in the solution is high enough). Pb^{2+} can be regarded as a crosslinking agent, resulting in the formation of water-insoluble crosslinked polyaspartate.

CONCLUSIONS

The results of this study show that the Pb^{2+} uptake of linear polyaspartate is higher than that of any other polyaspartamide at the same dosage. A crosslinked polyaspartate hydrogel has also been demonstrated to be superior to poly(acrylic acid)-based resins and polystyrene-based chelating resins. An analysis based on FTIR and XPS has indicated that the polyaspartate hydrogel binds Pb^{2+} by both an ion-exchange mechanism and a chelating mechanism. It has also been verified that the polyaspartate hydrogel is an effective agent for Pb^{2+} removal from glycyrrhizin.

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