

Highly Effective Adsorption of Heavy Metal Ions from Aqueous Solutions by Macroporous Xylan-Rich Hemicelluloses-Based Hydrogel

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ABSTRACT: Xylan-rich hemicelluloses-based hydrogel was developed as a novel porous bioadsorbent by graft co-polymerization of acrylic acid (AA) and xylan-rich hemicelluloses for adsorption of heavy metal ions (Pd²⁺, Cd²⁺, and Zn²⁺) from aqueous solutions. The chemical structure, the interaction between the hydrogel and metal ions, and the porous structure of xylan-rich hemicelluloses-g-AA hydrogel were revealed by Fourier transform infrared spectroscopy and scanning electron microscopy. The effects of AA and cross-linker dosage, pH value, contacting time, and initial concentration of metal ion on the adsorption capacity were studied. The adsorption equilibrium time was about 60 min from the adsorption kinetics study. The maximum adsorption capacities of Pd²⁺, Cd²⁺, and Zn²⁺ were 859, 495, and 274 mg/g, respectively. Furthermore, xylan-rich hemicelluloses-g-AA hydrogel also exhibited highly efficient regeneration and metal ion recovery efficiency and can be reused without noticeable loss of adsorption capacity for Pd²⁺, Cd²⁺, and Zn²⁺ after quite a number of repeated adsorption/desorption cycles.

KEYWORDS: Xylan-rich hemicelluloses, hydrogel, metal ion, bioadsorbent, acrylic acid

1. INTRODUCTION

The serious threat of heavy metal ions, such as cadmium, lead, nickel, and zinc, to the environment is of special concern worldwide. Unlike organic wastes, heavy metals ions are recalcitrant and can be accumulated in the environment and living tissues, causing various diseases and disorders of living organisms even at a trace level.^{1,2} Conventional methods for the removal of metal ions from aqueous solutions include chemical precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electrodialysis, and ultrafiltration. However, these techniques have inherent disadvantages, such as less efficiency, high costs, and further generation of toxic sludge or other waste products.³ Therefore, developing cheaper, higher efficient, and more environment-friendly adsorbents or technologies are attracting considerable attention of scientists.

Bioadsorption is emerging as a potential alternative to conventional technologies for the adsorption of metal ions from aqueous solutions. Recently, a great deal of attention has been diverted toward the production of bioadsorbents from renewable resources, such as starch,⁴ cellulose,¹ lignin,⁵ chitin/chitosan,⁶ and agricultural wastes.⁷ These bioadsorbents have many advantages over conventional adsorbents, such as hydrophilic, low costs, biodegradability, high efficiency, minimization of chemical or biological sludge, and good reusability.⁸

Recently, the application of hydrogel with a three-dimensional cross-linked polymer network as adsorbents for highly effective removal of heavy metal ions has been paid special attention because of the facility of the incorporation of different chelating groups into the polymeric networks, porous structure, and high internal specific surface area.⁹ Especially, the hydrogels

obtained from bioresources, such as cellulose and chitosan, have spurred great interest in the adsorption of heavy metal ions from aqueous solutions because they are eco-friendly, cost-effective, and highly efficient in adsorption and reusability.^{10,11}

Xylan-type hemicelluloses are the main noncellulose polysaccharides of the cell walls of hardwoods and herbaceous plants (constituting about 20–35 wt % of the biomass) and, thus, can be available in huge amounts as low-cost products from forestry, agriculture, and pulp and paper industries. In contrast to cellulose, xylan-type hemicelluloses are amorphous, consist of branched chains of various sugars, and thus, can be more easily dissolved in common solvents [e.g., alkaline solution, dimethyl sulfoxide (DMSO), and DMF/LiCl], which allows xylan-type hemicelluloses to be more easily modified in suitable solvents. Therefore, xylan-type hemicelluloses have potential application in producing bioadsorbents for the removal of metal ions from aqueous solutions.

In view of these facts mentioned above, the aim of this work was to develop a novel and high-loading bioadsorbent based on xylan-type hemicelluloses for metal ion removal and recovery from aqueous solutions. Previously, a xylan-type hemicelluloses-g-acrylic acid (AA) ionic hydrogel by graft co-polymerization of AA and xylan-type hemicelluloses was prepared.¹² The interest of the further work was focused on investigating the adsorption properties of this xylan-type hemicelluloses-g-AA hydrogel for metal ions (Pd²⁺, Cd²⁺, and Zn²⁺) from aqueous solutions, and

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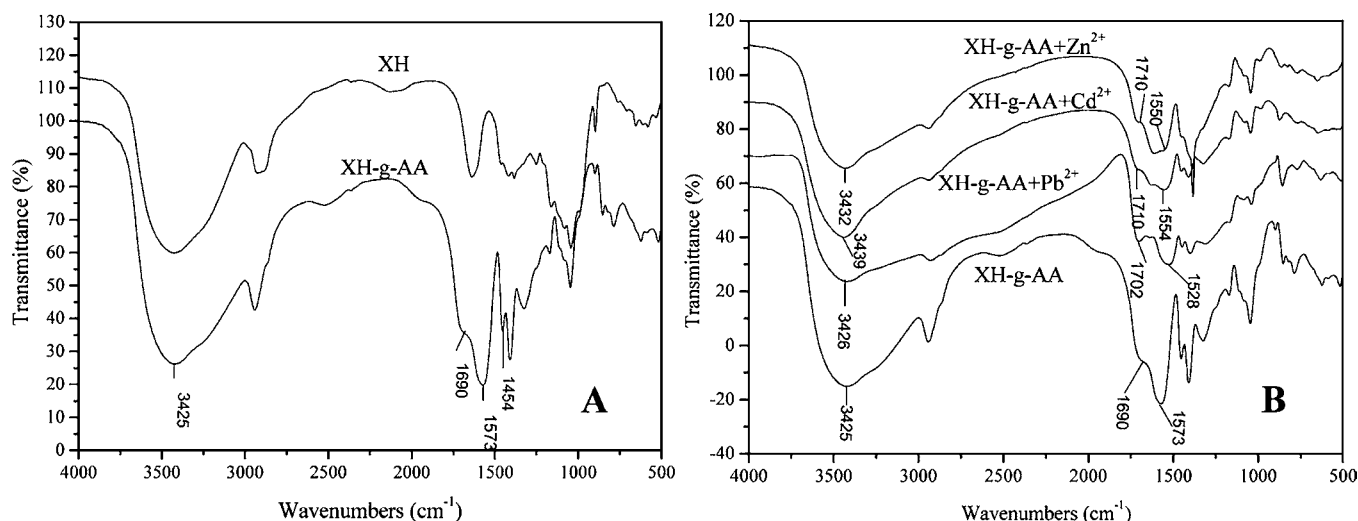


Figure 1. FTIR spectra of xylan-type hemicelluloses and xylan-type hemicelluloses-g-AA hydrogels before (xylan-type hemicelluloses-g-AA) and after adsorption of Pb²⁺ (xylan-type hemicelluloses-g-AA + Pb²⁺), Cd²⁺ (xylan-type hemicelluloses-g-AA + Cd²⁺), and Zn²⁺ (xylan-type hemicelluloses-g-AA + Zn²⁺).

this work provided a highly efficient bioadsorbent for heavy metal ion removal and recovery.

2. MATERIALS AND METHODS

2.1. Materials. Xylan-type hemicelluloses were isolated according to the treatment discussed in a previous work.¹² The sugar composition (relative weight percent, w/w) in xylan-type hemicelluloses was as follows: 89.4% xylose, 5.8% arabinose, 1.9% glucose, 0.7% galactose, 1.8% glucuronic acid, and 0.6% galactose acid.

N,N,N',N'-Tetramethylethylenediamine (TEMEDA) was purchased from Aldrich Chemical Co. (Guangzhou, China). *N,N*-Methylenebisacrylamide (MBA) and ammonium persulfate (APS) were purchased from Shanghai Chemical Reagent Corp. (Shanghai, China). All of these chemicals were used without any further purification. AA (Xi'an Chemical Reagent Factory, Xi'an, China) was purified by distillation under reduced pressure to remove the inhibitor hydroquinone before use. All other reagents used were of analytical grade, and all solutions were prepared with deionized water. Solid Pb(NO₃)₂, CdCl₂·2.5H₂O, and Zn(NO₃)₂·6H₂O were purchased as reagent grade from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Preparation of Xylan-Rich Hemicelluloses-g-AA Hydrogel. The isolated xylan-type hemicelluloses (1.00 g) were dissolved in 30.0 mL of deionized water in a three-necked flask with a magnetic stirrer at 85 °C for 60 min before the solution was cooled to room temperature. The xylan-type hemicellulosic solution obtained was continuously purged with gaseous N₂ for 10 min, and then 0.05 g of APS and 0.05 mL of TEMEDA as an initiator system were added and stirred for 10 min. AA (2.0–16.0 g) and MBA (0.05–0.25 g) were subsequently added and stirred for 2 h under a nitrogen gas atmosphere. Then, the reaction was processed for 24 h without stirring. The hydrogel was washed thoroughly in deionized water for 7 days. The products were then treated by 0.1 M NaOH solution to completely convert COOH groups to COO⁻ groups in the hydrogel. The hydrogel was again carefully washed thoroughly with deionized water and then cut into small fragments with a diameter of about 2 × 2 × 2 mm before being dried to a constant mass at 50 °C in an oven.

2.3. Fourier Transform Infrared (FTIR) Analysis. FTIR spectra of hydrogel before and after adsorption of metal ions were recorded by a Nicolet 750 spectrophotometer (Thermo Fisher Nicolet, Orlando, FL) within the frequency range of 400–4000 cm⁻¹ by the method of transmission. The 1% finely ground hydrogel samples were mixed with KBr to press a plate for measurement.

2.4. Preparation of Pb²⁺, Cd²⁺, and Zn²⁺ Solutions. Pb²⁺, Cd²⁺, and Zn²⁺ solutions (50–800 mg/L) were prepared by dissolving solid Pb(NO₃)₂, CdCl₂·2.5H₂O, and Zn(NO₃)₂·6H₂O in deionized water,

respectively. Diluted HNO₃ and NaOH solutions (0.01 M) were used for pH adjustment. In all experimental works, deionized water was used.

2.5. Adsorption Experiments. Batch experiments were carried out (at room temperature) by agitating 10 mg of dry hydrogel particles in 50 mL of metal solution (200 mg/L) at 100 rpm for 120 min. The initial pH values (3.5–6.5) of the solutions were previously adjusted with diluted HNO₃ (0.01 M) or NaOH (0.01 M) using a pH meter. At the end of the experiment, the mixture was centrifuged and filtered. The metal ion concentration in the filtrate was determined by titration with standard ethylenediaminetetraacetic acid (EDTA) solution (2 mmol/L) using Erichrome Black T as the indicator.^{13,14} The pH of the titrated solution was kept constantly at 10 with NH₃–NH₄Cl buffer solution (pH 10). The amount of metal ion adsorbed on the hydrogel at adsorption equilibrium, *q_e* (mg/g), was calculated according to eq 1

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where *C₀* and *C_e* are the initial and equilibrium metal ion concentrations (mg/L), *V* is the volume of the metal ion solution used in the adsorption experiment (L), and *W* is the weight of the hydrogel particles (g), respectively. Data are representative of at least three experiments, and standard deviations are less than 5.0%.

2.6. Adsorption Kinetics. The adsorption kinetics experiment was conducted with the following conditions: 10 mg of dry hydrogel particles were added to 50 mL of metal ion solution (200 mg/L), and the mixture was agitated continuously at optimum pH values obtained from section 2.5 for 10–120 min. The amount of metal ion adsorbed on the hydrogel was calculated according to eq 1.

2.7. Adsorption Isotherms. The effect of the initial metal ion concentration on adsorption capacity was investigated by variation of the initial concentration of the metal ion at an optimum pH value and equilibrium time obtained from sections 2.5 and 2.6. A total of 10 mg of sample was added to 50 mL of metal ion solution (50–800 mg/L). The suspension was centrifuged and filtered, and the amount of metal ions adsorbed on the hydrogel was calculated according to eq 1.

2.8. Desorption and Reusability Behaviors of Xylan-Type Hemicelluloses-g-AA Hydrogel. A total of 10 mg of dry hydrogel particles were added to 50 mL of metal ion solution (200 mg/L), and the mixture was agitated continuously at an optimum pH value and equilibrium time to reach its adsorption equilibrium. The hydrogel particles were then withdrawn from the solution and washed with deionized water 3 times. Thereafter, the hydrogel particles were immersed into HNO₃ solution (0.5 M) for 2 h under stirring to remove the adsorbed metal ions from the hydrogel and then treated

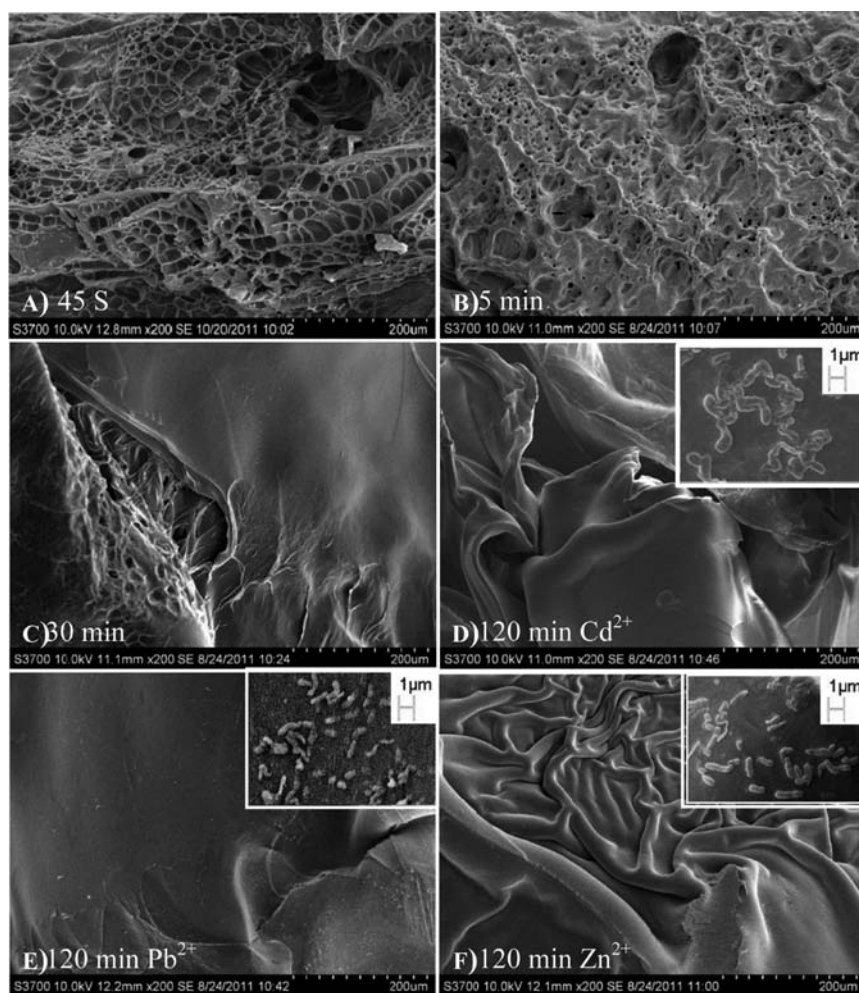


Figure 2. Morphologies of xylan-type hemicelluloses-g-AA hydrogel during the adsorption process in metal ion solutions.

with 0.01 M NaOH for 8 h to completely convert COOH groups to COO⁻ groups. Finally, the hydrogel particles were thoroughly washed with deionized water and again used in the adsorption experiment. The adsorption–desorption process was repeated 8 times, and the amount of adsorbed and desorbed metal ions was calculated according to eq 1.

2.9. Morphological Characteristics of Xylan-Type Hemicelluloses-g-AA Hydrogel. Xylan-type hemicelluloses-g-AA hydrogels immersed in metal ion solution were withdrawn at different time intervals and then freeze-dried for morphological analysis. The morphologies of xylan-type hemicelluloses-g-AA hydrogel were characterized by Hitachi S3700 scanning electron microscopy (SEM, Hitachi, Ltd., Tokyo, Japan). Specimens were coated with gold for 30 s in SEM-coating equipment.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis. FTIR spectra obtained from xylan-type hemicelluloses and hydrogel (xylan-type hemicelluloses-g-AA) before and after adsorbing metal ions are shown in Figure 1. In the spectrum of raw material (xylan-type hemicelluloses, Figure 1A), the absorbances at 3426, 2925, 1468, 1418, 1384, 1252, 1162, 1081, 1043, 986, and 895 cm⁻¹ are the typical bands of xylan-type hemicelluloses.¹⁵ In comparison to the spectrum of xylan-type hemicelluloses, new peaks at 1769, 1573, and 1454 cm⁻¹ in the spectrum of xylan-type hemicelluloses-g-AA hydrogel (xylan-type hemicelluloses-g-AA, Figure 1A) are related to the stretching vibration of C=O and asymmetrical stretching vibration and symmetrical stretching vibration of

COO⁻, respectively, indicating the presence of COO⁻ groups in the bioadsorbent.¹⁶ These results indicate that AA monomers were actually grafted onto xylan-type hemicelluloses.

After lead ion adsorption on xylan-type hemicelluloses-g-AA hydrogel (xylan-type hemicelluloses-g-AA + Pb²⁺, Figure 1B), the absorption bands of COO⁻ groups at around 1690 and 1573 cm⁻¹ shift to 1702 and 1528 cm⁻¹, respectively. This can be attributed to the formation of the coordinated COO⁻ and Pb²⁺ complexes (or COO⁻···Pb²⁺).⁸ In the spectrum of bioadsorbents adsorbing Cd²⁺ (xylan-type hemicelluloses-g-AA + Cd²⁺, Figure 1B) and Zn²⁺ (xylan-type hemicelluloses-g-AA + Zn²⁺, Figure 1B), the bands at around 1690 and 1573 cm⁻¹ also shift (from 1690 to 1710 cm⁻¹ and from 1573 to 1554 cm⁻¹ for Cd²⁺ adsorption and from 1690 to 1710 cm⁻¹ and from 1573 to 1550 cm⁻¹ for Zn²⁺ adsorption, respectively), also indicating the formation of the coordinated COO⁻ and metal ion (M²⁺) complexes.^{8,17} Evidently, the negatively charged COO⁻ groups in xylan-type hemicelluloses-g-AA hydrogel are the major ligands for metal ion adsorption. It should be noted that the shift of the adsorption of –OH at around 3425 cm⁻¹ may also be indicative of the involvement of some –OH groups in binding to Cd²⁺ or Zn²⁺.¹⁷

3.2. Morphology of Xylan-Type Hemicelluloses-g-AA Hydrogel. During the adsorption process, xylan-type hemicelluloses-g-AA hydrogel first swelled in metal ion solutions and then gradually shrank as the adsorption proceeded. Figure 2

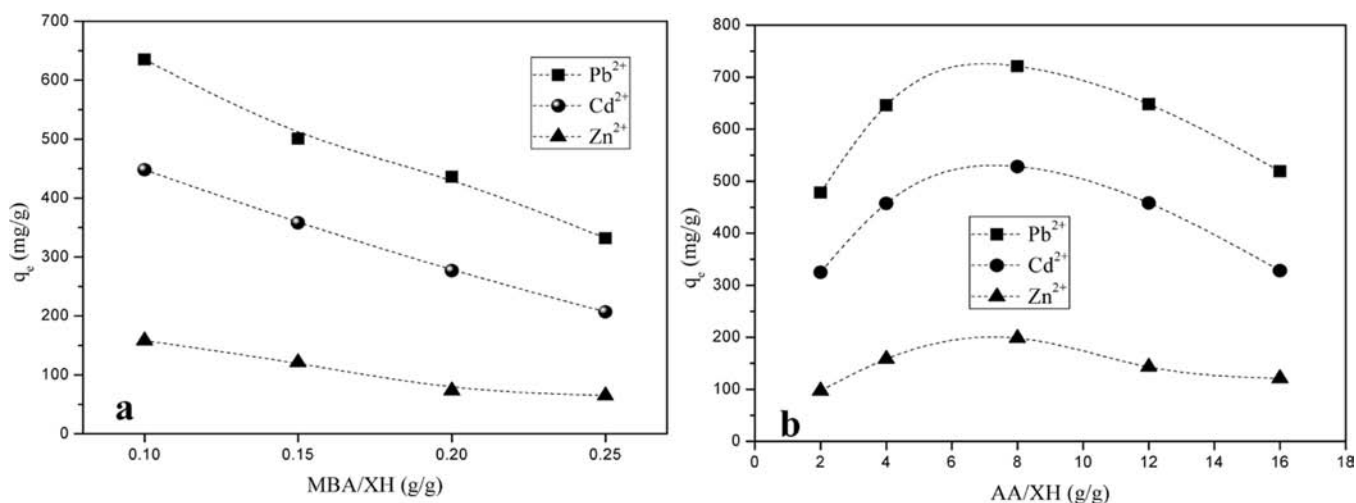


Figure 3. Effects of (a) MBA/xylan-type hemicelluloses and (b) AA/xylan-type hemicelluloses ratios on the metal ion adsorption of xylan-type hemicelluloses-g-AA hydrogel.

shows the morphological change of the hydrogels as the adsorption proceeded at different time intervals in Cd²⁺, Pb²⁺, and Zn²⁺ solutions, respectively. Xylan-type hemicelluloses-g-AA hydrogel exhibited a macroporous structure with a pore diameter of about 10–20 μm in the initial adsorption stage (45 s, Figure 2A). As the adsorption proceeded, the expanded macropores gradually shrank (5 min, Figure 2B) and even collapsed (30 min, Figure 2C). Finally, the pores completely collapsed, and no pores could be observed on the surface of xylan-type hemicelluloses-g-AA hydrogel (120 min, panels D–F of Figure 2). The morphologies of metals Pb, Cd, and Zn adsorbed on xylan-type hemicelluloses-g-AA hydrogel are also shown in the insets of panels D–F of Figure 2.

The presence of COO[−] groups in xylan-type hemicelluloses-g-AA hydrogel produces strong electrostatic repulsion in water, and thus, the expansion of polymer chains occurs, forming a macroporous structure. The interaction between electro-negative COO[−] groups and electro-positive metal ions (Pb²⁺, Cd²⁺, and Zn²⁺) results in the electrostatic screening of anionic groups (COO[−]) in the polymeric network, which leads to the decrease in electrostatic repulsion and the shrinkage of the network or pores.¹⁸ The expansion of the polymeric network and porous structure in the initial adsorption stage will favor the diffusion and adsorption of metal ions from the exterior to the interior of the hydrogel.^{19,20}

3.3. Effect of the MBA/Xylan-Type Hemicelluloses Ratio and the AA/Xylan-Type Hemicelluloses Ratio on the Metal Ion Adsorption. The effect of the MBA/xylan-type hemicelluloses ratio on the metal ion adsorption capacity of xylan-type hemicelluloses-g-AA hydrogel is shown in Figure 3a. The adsorption capacities of Pb²⁺, Cd²⁺, and Zn²⁺ were 635, 448, and 158 mg/g, respectively, at a MBA/xylan-type hemicelluloses ratio of 0.1, exhibiting high adsorption properties. The increase of the MBA/xylan-type hemicelluloses ratio up to 0.25 resulted in the adsorption capacities of Pb²⁺, Cd²⁺, and Zn²⁺ decreasing to 332, 207, and 65 mg/g, respectively. This suggests that the cross-linked polymeric network significantly influences metal ion adsorption. A higher cross-linker concentration produces a hydrogel with a higher cross-linking density and a less expanded network in water,¹⁶ which restricts the diffusion of metal ions from the exterior into the interior of the matrix and, thus, decreases the metal ion

adsorption capacity.²¹ Therefore, xylan-type hemicelluloses-g-AA hydrogel with a more expanded network exhibits a higher metal ion adsorption capacity. However, too low of a MBA/xylan-type hemicelluloses ratio will cause a very weak polymeric network and high water dissolubility, resulting in the difficult handling of the bioadsorbent.

Figure 3b shows that the adsorption capacity of each ion did not increase with the increase of the AA/xylan-type hemicelluloses ratio. The adsorption capacities of Pb²⁺, Cd²⁺, and Zn²⁺ first increased from 478, 325, and 97 mg/g to 721, 528, and 198 mg/g when the AA/xylan-type hemicelluloses ratio increased from 2 to 8 (g/g) and then decreased to 519, 328, and 121 mg/g at the AA/xylan-type hemicelluloses ratio of 16 (g/g), respectively. A similar phenomenon was also found in dendrimer-like polymer.^{21,22} The increase of adsorption capacities with the increase of the AA/xylan-type hemicelluloses ratio is attributed to more carboxyl groups being incorporated into the hydrogel as the AA/xylan-type hemicelluloses ratio increases, whereas the lower adsorption capacities at the AA/xylan-type hemicelluloses ratio of more than 8 is likely due to a higher AA/xylan-type hemicelluloses ratio producing shorter grafting chains and a denser network, which reduces the accessibility of ligands to the active sites of the materials^{16,23,24} and, therefore, lowers the metal ion adsorption capacity. These results indicate that the porous structure is a crucial factor in determining the adsorption capacity of the bioadsorbent.

3.4. Effect of the pH of the Metal Ion Solution on Metal Ion Adsorption. As illustrated in Figure 4, the adsorption capacity of Pb²⁺ remarkably increased from 318 mg/g at pH 3.5 to 806 mg/g at pH 5.5. The adsorption capacities of Cd²⁺ and Zn²⁺ also increased continuously with the increasing pH, and adsorption capacities of 458 mg/g (Cd²⁺) and 255 mg/g (Zn²⁺) could be achieved at pH 6.5. At low pH (less than 4.5), COO[−] groups are converted into COOH, which reduces their ability of binding to positively charged ions. When pH increases, the COOH groups become deprotonated with the result of negatively charged ligands (COO[−]), which easily attracts the positively charged metal ions.^{8,25} Thus, metal ion binding to xylan-type hemicelluloses-g-AA hydrogel is an ion-exchange mechanism, which involves an electrostatic interaction between metallic cations and negatively charged ligands.²⁶ In addition, a more expanded polymeric

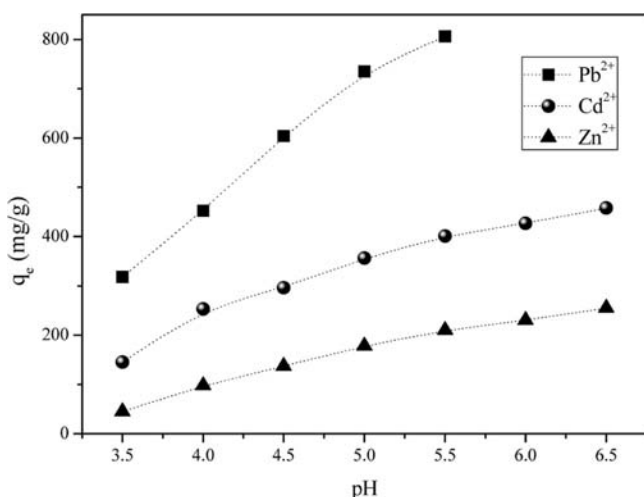


Figure 4. Effect of pH on the metal ion adsorption of xylan-type hemicelluloses-g-AA hydrogel (MBA/xylan-type hemicelluloses ratio of 0.1 and AA/xylan-type hemicelluloses ratio of 8).

network because of the repulsion between negatively charged COO^- groups at higher pH will also favor the diffusion and adsorption of metal ions in the interior of the hydrogel.

3.5. Effect of the Contact Time and Sorption Kinetics.

To establish the equilibration time for maximum adsorption capacity and to know the adsorption kinetics of xylan-type hemicelluloses-g-AA hydrogel, the metal ion adsorption capacities were measured as a function of time, and the results are shown in Figure 5. The increases of the adsorption

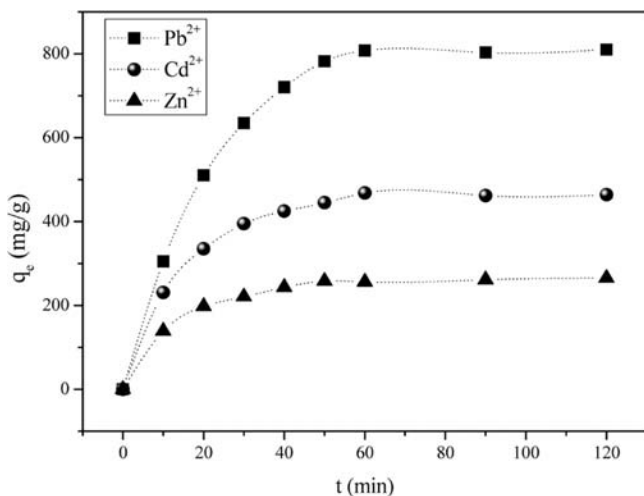


Figure 5. Adsorption kinetics of metal ions onto xylan-type hemicelluloses-g-AA hydrogel (MBA/xylan-type hemicelluloses ratio of 0.1 and AA/xylan-type hemicelluloses ratio of 8) at pH 5.5 (Pb^{2+}) and pH 6.5 (Cd^{2+} and Zn^{2+}).

capacities of Pb^{2+} , Cd^{2+} , and Zn^{2+} as contacting time progressed are remarkable at short time scale and then slowed, and adsorption equilibrium could be achieved within 60 min. The short time period for adsorption equilibrium suggests an excellent affinity of the polymeric network for metal ions in aqueous solutions. According to this result discussed above and the SEM morphologies in Figure 2, the following three stages could be proposed to model the adsorption process. The first stage involved the rapid expansion of the polymeric network and the formation of the macroporous structure because of the highly hydrophilic network and strong electrostatic repulsion. Simultaneously, metal ions began to transport to the external surface of the hydrogel. This stage actually offered considerable macropores for the diffusion of metal ions in the next adsorption stage. The second stage was the diffusion of metal ions into the internal pores of hydrogel through the macropores and then proceeded where they finally adsorbed (the third stage). In the second stage, electrostatic screening resulted in the pores and polymeric network shrinkage. In the last stage, the strong steric hindrance resulted from the internal network shrinkage and made ligands hard to be accessible to metal ions. Therefore, a macroporous structure will favor the diffusion of metal ions and enhance the adsorption capacity of the adsorbent.

To examine the controlling mechanism of the adsorption process, the two most commonly used kinetic models, i.e., the pseudo-first-order and pseudo-second-order models, were used to test the experimental data. The linear pseudo-first-order (eq 2) and pseudo-second-order (eq 3) are illustrated as follows:

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad (2)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (3)$$

where q_t (mg/g) is the adsorption capacity at time t (min), q_e (mg/g) is the adsorption capacity at adsorption equilibrium, and k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the kinetics rate constants for the pseudo-first-order and pseudo-second-order models, respectively. Table 1 lists the computed results obtained from the first- and second-order kinetic models. Clearly, the correlation coefficients (R^2 in Table 1) for the pseudo-second-order kinetic model are higher than those of the pseudo-first-order kinetic model, and the calculated data ($q_{e,\text{cal}}$ in Table 1) from the pseudo-second-order kinetic model generally deviate less from the experimental data ($q_{e,\text{exp}}$ in Table 1), which suggests that this adsorption system is a pseudo-second-order kinetic adsorption process and the adsorption is a chemical process.

3.6. Effect of the Initial Concentration and Sorption Isotherms. The adsorption isotherms are shown in Figure 6. At low initial concentrations (less than 200 mg/L), adsorption capacities of metal ions increased almost proportionally with the increment in the initial concentrations of metal ions,

Table 1. Experimental q_e Values and Kinetic Parameters for the Adsorption Based on the Pseudo-first- and Pseudo-second-Order Kinetic Models

metal ions	$q_{e,\text{exp}}$ (mg/g)	pseudo-first-order model			pseudo-second-order mode		
		$q_{e,\text{cal}}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e,\text{cal}}$ (mg/g)	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
Pb^{2+}	810	844	0.0655	0.807	938	7.23×10^{-5}	0.988
Cd^{2+}	464	287	0.0401	0.948	508	2.18×10^{-4}	0.996
Zn^{2+}	265	147	0.0450	0.901	294	3.58×10^{-4}	0.997

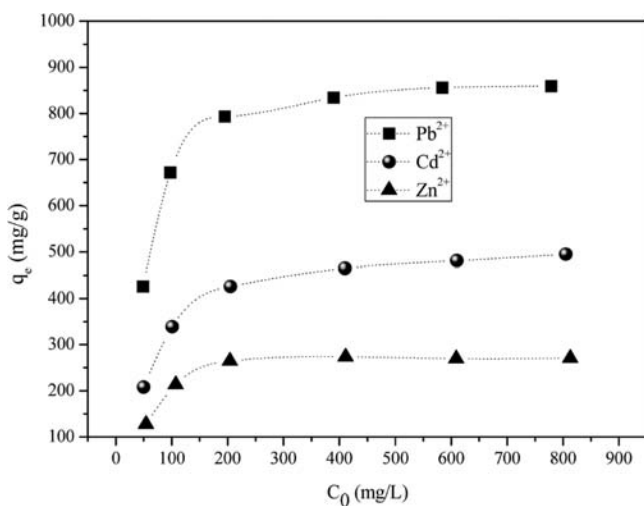


Figure 6. Adsorption isotherms of metal ions onto xylan-type hemicelluloses-g-AA hydrogel (MBA/xylan-type hemicelluloses ratio of 0.1 and AA/xylan-type hemicelluloses ratio of 8) at pH 5.5 (Pb^{2+}) and pH 6.5 (Cd^{2+} and Zn^{2+}).

suggesting that the adsorption process is highly concentration-dependent.²⁷ At higher initial concentrations (more than 200 mg/L), the increase in uptake slowed. In this case, the number of available ligands in the bioadsorbent actually became the limiting factor that controlled the amount of uptake.⁸ The popularly used Langmuir isotherm (eq 4) was used in the adsorption processes

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}} \quad (4)$$

where q_e (mg/g) is the adsorption equilibrium at a specific metal ion concentration, C_e (mg/L) is the concentration of the metal ion in aqueous solution, Q_{\max} is the maximum adsorption capacity, and b (L/mg) is the Langmuir constant related to the binding sites affinity. Table 2 shows the calculated results. The

Table 2. Adsorption Isotherm Parameters Based on the Langmuir Model and Experimental Maximum Adsorption Capacity $Q_{\max, \text{exp}}$ Values

metal ions	$Q_{\max, \text{exp}}$ (mg/g)	Langmuir		
		$Q_{\max, \text{cal}}$ (mg/g)	b	R^2
Pb^{2+}	859	909	0.0255	0.998
Cd^{2+}	495	534	0.0156	0.999
Zn^{2+}	274	288	0.0255	0.996

high correlation coefficients ($R^2 > 0.99$) of the linearized Langmuir equation indicate that this model can explain well metal ion adsorption by xylan-type hemicelluloses-g-AA hydrogel. The $Q_{\max, \text{cal}}$ values calculated from the Langmuir model are very close to the experimental data $Q_{\max, \text{exp}}$. It can be concluded that the Langmuir model can describe the adsorption of Pb^{2+} , Cd^{2+} , and Zn^{2+} onto the bioadsorbent.

Table 3 shows the maximum adsorption capacities of typical bioadsorbents. Because of the cellulose crystalline and compact structure of the plant cell wall, lignocellulosic biomass is usually used in the form of flake or powder instead of porous materials,^{1,2} resulting in metal ion adsorption mainly taking place on the surface of the bioadsorbent. Cross-linked biopolymers, such as co-polymers and hydrogels, usually

Table 3. Maximum Adsorption Capacities (mg/g) of Metal Ions by Various Adsorbents

adsorbents	Pb^{2+}	Cd^{2+}	Zn^{2+}	reference
modified plant wastes	≤ 313	≤ 313	≤ 83.3	2
sawdust-g-AA		168.0		30
modified cellulose	≤ 105	≤ 169	≤ 27	1
modified sugar cane bagasse	500.0	256.4		13
cross-linked chitosan	559.4			31
cross-linked starch	416.9			32
carrageenan/AA hydrogel	202	239	216	11
chitosan hydrogel	901			29
xylan-type hemicelluloses/AA hydrogel	859	495	274	this work

show higher adsorption capacity because they possess a large amount of ligands and macro- or mesoporous structure.²⁸ The chitosan-based bioadsorbent, which is one of the most important adsorbents, shows the highest adsorption capacity (901 mg/g) for Pb^{2+} ,²⁹ followed by xylan-type hemicelluloses-g-AA hydrogel. Therefore, it is necessary to design a porous bioadsorbent for highly effective adsorption of metal ions from aqueous solutions. Xylan-type hemicelluloses are amorphous and, thus, can be more easily dissolved in common solvents, which greatly facilitates the chemical modification of xylan-type hemicelluloses and reconstructs them into porous materials.

3.7. Desorption and Reusability. Table 4 illustrates the adsorption and desorption behaviors of xylan-type hemicelluloses-g-AA hydrogel for eight cycles. The adsorption capacities of Pb^{2+} , Cd^{2+} , and Zn^{2+} were 774, 441, and 230 mg/g, respectively, after eight cycles, indicating that reuse has little influence on the metal ion uptake of xylan-type hemicelluloses-g-AA hydrogel. The recovery efficiency were high up to 98.9% (Pb^{2+}), 99.1% (Cd^{2+}), and 99.0% (Zn^{2+}) in the first cycle, and then they slightly decreased to 96.7, 96.4, and 97.6% after eight cycles, respectively. In 0.5 M HNO_3 solution, the protons compete with metal ions for carboxyl groups, which is responsible for the easy desorption of metal ions. This again confirms that the main adsorption mechanism is ion exchange. Therefore, xylan-type hemicelluloses-g-AA hydrogel has stable physical and chemical properties and can be reused almost without significantly decreasing the adsorption properties after quite a number of cycles.

This work presents the possibility of preparing a highly efficient bioadsorbent from xylan-type hemicelluloses for heavy metal ion removal and recovery. Further research work should be extended to better understand the influences of physical and chemical structures of bioadsorbents on their adsorption and desorption behaviors and to develop a more efficient xylan-type hemicelluloses-based bioadsorbent for metal ion removal and recovery in more complicated conditions, such as low pH, high ion strength, and competing adsorption.

In summary, a novel hemicelluloses-based hydrogel as a bioadsorbent was developed for adsorption of heavy metal ions from aqueous solutions. Both cross-linker/xylan-type hemicelluloses and AA/xylan-type hemicelluloses ratios significantly affected the adsorption capacity of the metal ion. As the pH of metal ion solutions increased, the adsorption capacities of Pd^{2+} , Cd^{2+} , and Zn^{2+} increased. An adsorption equilibrium time of about 60 min was obtained, and metal ion adsorption on xylan-type hemicelluloses-g-AA hydrogel followed the Langmuir isotherm model. The maximum adsorption capacities of Pd^{2+} , Cd^{2+} , and Zn^{2+} were 859, 495, and 274 mg/g, respectively.

Table 4. Metal Ion Adsorption and Desorption Behaviors of Xylan-Type Hemicelluloses-g-AA Hydrogel (MBA/Xylan-Type Hemicelluloses Ratio of 0.1 and AA/Xylan-Type Hemicelluloses Ratio of 8)

metal ions	cycle 1		cycle 2		cycle 4		cycle 6		cycle 8	
	A ^a (mg/g)	R ^b (%)	A (mg/g)	R (%)	A (mg/g)	R (%)	A (mg/g)	R (%)	A (mg/g)	R (%)
Pb ²⁺	876	98.9	850	99.0	831	98.6	810	97.7	774	96.7
Cd ²⁺	510	99.1	496	98.7	484	98.1	467	97.2	441	96.4
Zn ²⁺	261	99.0	260	98.8	254	98.5	241	98.2	230	97.6

^aAdsorption capacity of the metal ion. ^bRecovery rate (desorption) of the metal ion.

Xylan-type hemicelluloses-g-AA hydrogel could be reused almost without significant loss of adsorption capacity and recovery efficiency.

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Notes

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