

Adsorption of Heavy Metals by a Porous Bioadsorbent from Lignocellulosic Biomass Reconstructed in an Ionic Liquid

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S Supporting Information

ABSTRACT: A novel porous bioadsorbent for metal ion binding (Pd²⁺ and Cd²⁺) was successfully prepared from lignocellulosic biomass in ionic liquid by homogeneous succinylation and sequent chemical cross-linking. The morphology of the bioadsorbent and the interaction between bioadsorbent and metal ions was revealed by scanning electron microscopy and Fourier transform infrared spectroscopy. Results showed that the adsorption mechanism of the bioadsorbent was an ion exchange. A lower dose of cross-linker or higher carboxyl content increased the adsorption capacities of Pd²⁺ and Cd²⁺. The adsorption capacities of Pd²⁺ and Cd²⁺ remarkably increased as the pH of metal ion solutions increased. The pores in the bioadsorbent greatly favored the diffusion and adsorption of metal ions, and the adsorption equilibrium time was about 50 min. The adsorption of metal ions could be well explained by the Langmuir model, and the maximum adsorption capacities of Pd²⁺ and Cd²⁺ were 381.7 and 278.6 mg/g.

KEYWORDS: lignocellulosic biomass, bioadsorbent, ionic liquid, heavy metal ion

INTRODUCTION

Various industries, including mining, metal plating, electric device manufacturing, battery, and chemical catalysis are releasing a large amount of heavy metal ions such as cadmium, lead, nickel, and zinc into the environment, which is of great concern because the serious threat of heavy metal ions to plants, animals, and human beings. Because conventional methods for the removal of heavy metal ions from aqueous solutions such as chemical precipitation, chemical oxidation/reduction, reverse osmosis, electrodialysis, and ultrafiltration have disadvantages such as low efficiency, high cost, and generation of toxic waste products, research into developing cheaper and more efficient adsorbents is attracting great attention of scientists. Bioadsorbents based on renewable resources are low cost, biodegradable, and highly efficient and thus recently have spurred great interest in the removal and/or recovery of metal ions from aqueous solutions.^{1–3}

Lignocellulosic biomass, which is mainly composed of lignin, hemicelluloses, and cellulose as the main constituents, is the most popular renewable resource for the preparation of low-cost bioadsorbents.^{1,3,4} Extensive work reveals that lignocellulosic biomass-based bioadsorbents show high adsorption capacity, show efficient regeneration, and are comparable, in many instances, to commercial ion exchange resins.^{2,3} However, cellulose crystalline and the compact structure of the plant cell wall make lignocellulosic biomass very difficult to dissolve in common solvents; therefore, lignocellulosic biomass is commonly used in the form of flake or powder.^{2,5,6}

Extensive work on conventional adsorbents indicates that a compact structure of synthetic resins or polymers restricts the diffusion of metal ions into the interior of matrix and reduces the accessibility of reactive sites for metal ion complexation.^{7–10} Therefore, from a structural point of view, the compact structure of lignocellulosic biomass poses a strong steric

hindrance for metal ion transport and adsorption into the interior of bioadsorbents. If the compact lignocellulosic cell wall can be dissolved and biopolymers (cellulose, hemicelluloses, and lignin) can be reconstructed into porous materials, metal ion adsorption will occur on both the exterior and the interior of the materials, and more highly efficient bioadsorbents can be obtained. Unfortunately, this aim cannot be achieved in common solvents due to the compact plant cell wall.

Room temperature ionic liquids (ILs) are emerging as green solvents, frequently display low vapor pressure, wide liquidus range, and efficient dissolution for cellulose.¹¹ It is also found that ILs could directly dissolve lignocellulosic biomass,^{12–14} and the chemical modification of biomass could be carried out in a more homogeneous way.^{15–17} This provides a novel technological platform for the development of various materials and thus has spurred great interest due to the highly efficient utilization way of lignocellulosic biomass.^{15–18} However, there have been very limited studies on directly preparing biomaterials from lignocellulosic biomass in IL. In this study, an attempt was made to directly prepare a novel porous bioadsorbent from lignocellulosic biomass by dissolving lignocellulosic biomass in IL and then chemically modifying and reconstructing the dissolved biopolymers (cellulose, hemicelluloses, and lignin).

Succinylation of biopolymers can introduce considerable carboxylic functions for binding metal ions; therefore, succinylated biopolymers have been used as bioadsorbents for heavy metal removal.^{19–22} It is, however, that the compact structure of lignocellulosic biomass does not allow succinoy-

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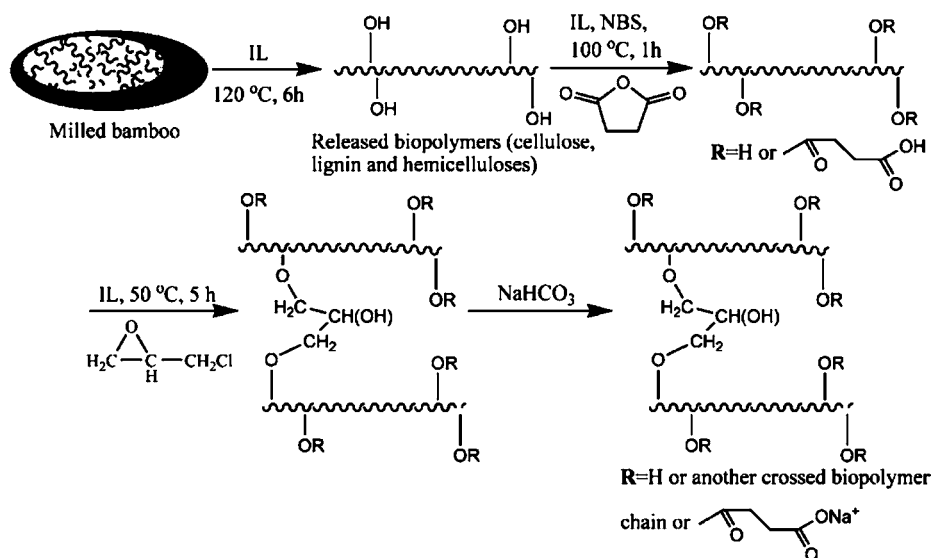


Figure 1. Synthetic route of bioadsorbent from lignocellulosic biomass.

lation to be performed homogeneously in common solvents.^{19–21} In this work, the succinylation of lignocellulosic biomass was carried out in a homogeneous way by directly dissolving biomass in IL. We reported herein for the first time that a porous bioadsorbent was successfully prepared from lignocellulosic biomass in IL and was used for effective removal of metal ions from aqueous solutions. This work provides a novel strategy for manufacturing biomaterials and the full utilization of agriculture wastes.

MATERIALS AND METHODS

Materials. Bamboo (*Dendrocalamus membranaceus* Munro, *DmM*) was kindly provided by a pulp and papermaking factory (Yunnan, China). The compositions (% w/w) of the bamboo were 45.68% cellulose, 25.60% hemicelluloses, 26.33% lignin, 1.53% ash, and 1.40% wax on a dry weight basis. It was dried in sunlight and then cut into small pieces. The cut bamboo was ground and screened to obtain 40–60 mesh size particles and then dried in a cabinet oven with air circulation for 16 h at 55 °C. Afterward, the dried bamboo particles were extracted with toluene/ethanol (2:1, v/v) to remove extracts and further pulverized with a vibratory ball mill for 6 h in a stainless steel jar.

IL 1-ethyl-3-methylimidazolium acetate [C_2mim][OAc] with 99% purity was purchased from Cheng Jie Chemical Co., Ltd. (Shanghai, China). Succinic anhydride and epichlorohydrin were purchased from Shaanxi Chemical Co., Ltd. *N*-Bromosuccinimide (NBS) was purchased from Sigma-Aldrich Co., Ltd. All other solvents are of analytical reagent grade and directly used without further purification.

Dissolution of Lignocellulosic Biomass and Preparation of Bioadsorbent. The dissolution and chemical modification of lignocellulosic biomass are illustrated in Figure 1. A 1.0 g amount of milled bamboo was added to 30 g of IL, and the mixture was stirred at 120 °C up to 6 h to guarantee the complete dissolution of milled bamboo under a nitrogen atmosphere. Upon completion of the dissolution, the required quantities of succinic anhydride (succinic anhydride to dried milled bamboo were 1:1, 2:1, 3:1, 4:1, and 5:1, g/g), catalyst NBS (0.05 g) was added at 100 °C, and the reaction ran for 60 min. When the mixture was cooled to 50 °C, required epichlorohydrin (epichlorohydrin to dried milled bamboo were 1:2, 1:1, 2.5:1, 5:1, and 7.5:1, mL/g) was added to the mixture and stirred for 5 h. The resulting mixture was then poured into 200 mL of methanol under vigorous agitation. The solid products were centrifuged and then thoroughly rinsed with methanol and dried. The products were treated with saturated sodium bicarbonate solution (0.1 M) for 2 h under constant stirring. Soon afterward, the products

were centrifuged, washed with deionized water and acetone, and finally dried in an oven at 80 °C and stored in a desiccator.

Carboxyl Content Determination. The concentration of carboxylic functions per gram of bioadsorbent was determined by retro-titration.²⁰ Briefly, to a 100 mL NaOH solution (0.01 M), 100 mg of product was added before saturated sodium bicarbonate solution treatment, and the mixture was stirred at 50 °C for 1 h. After it was cooled to room temperature, the mixture was filtrated, and three aliquots (20 mL) of each obtained solution were titrated with HCl solution (0.01 M). The concentration of carboxylic functions was calculated using eq 1:

$$C_{COOH} = \frac{C_{NaOH} \times V_{NaOH} - 5 \times C_{HCl} \times V_{HCl}}{W} \quad (1)$$

where C_{NaOH} is the concentration of NaOH solution (mol/L), V_{NaOH} is the volume of NaOH solution (L), C_{HCl} is the concentration of HCl solution (mol/L), V_{HCl} is the volume of HCl (L) spent in the titration of excessive nonreacted NaOH, and W is the mass of bioadsorbent (g).

Fourier Transform Infrared (FT-IR) Analysis. FT-IR spectra were performed by Nicolet 750 spectrophotometer (Thermo Fisher Nicolet, FL) within the frequency range 400–4000 cm^{-1} by the method of transmission. A 1% sample (w/w) was mixed with 99% KBr (w/w), finely ground, and pressed for measurement.

Morphological Characteristics of Bioadsorbent. Bioadsorbent immersed in deionized water for 60 min was withdrawn and then freeze-dried for morphological analysis. The morphology of bioadsorbent was investigated by scanning electron microscopy (SEM, S3700, Hitachi High-Technologies Corp., Tokyo, Japan). The specimen was coated with gold for 30 s in SEM coating equipment.

Preparation of Pb^{2+} and Cd^{2+} Solutions. Pb^{2+} and Cd^{2+} solutions in specific concentrations (25–300 mg/L) were prepared by dissolving solid $Pb(NO_3)_2$ and $CdCl_2 \cdot 2.5H_2O$ in deionized water. Diluted HNO_3 and NaOH solutions (0.01 M) were used for pH adjustment. In all experimental works, deionized water was used.

Adsorption Experiments. Batch experiments were carried out (at room temperature) by agitating a fixed mass of dry bioadsorbent (20 mg) in 50 mL of metal solutions at 100 rpm for 90 min. The initial pH values (2–6) of the solutions were previously adjusted with diluted HNO_3 (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 amount of metal ions adsorbed on the bioadsorbent at adsorption equilibrium, q_e (mg/g), was calculated according to eq 2:

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (2)$$

where C_0 and C_e are the initial and equilibrium metal ion concentrations (mg/L) obtained from atomic absorption spectrophotometer (Z-5000, Tokyo, Japan), respectively. V is the volume of metal ion solution (L), and W is the weight of bioadsorbent (g). Data are representative of at least three experiments performed in duplicate, which varied by less than 5% in all of the cases studied.

Adsorption Kinetics. Twenty milligrams of dry bioadsorbent was added to 50 mL of metal ion solution (100 mg/L), and the mixture was agitated continuously for 10–120 min. The amount of metal ions adsorbed on the bioadsorbent was calculated according to eq 2.

Adsorption Isotherms. The effects of initial concentrations of metal ions on the adsorption capacities of Pb^{2+} and Cd^{2+} were investigated by variation of initial concentrations of metal ions at optimum pH values and equilibrium time obtained from above sections. Twenty milligrams of bioadsorbent was added to 50 mL of metal ion solution (25–300 mg/L). The suspension was centrifuged and filtered, and the amount of metal ions adsorbed on the bioadsorbent was calculated according to eq 2.

RESULTS AND DISCUSSION

Preparation and FT-IR Spectra of Bioadsorbent.

Lignocellulosic biomass is mainly composed of three biopolymers: cellulose, hemicellulose, and lignin. Various covalent bonds between lignin and carbohydrate polymers hold them together in a firmly cross-linked network, preventing them from direct dissolution or fractionation in common solvents. Lignocellulosic biomass without ball-milling treatment can only be partially dissolved in ILs,²³ while ball-milling treatment allows them to be completely dissolved in ILs.¹⁴ It was found that $[C_2mim][OAc]$ was an efficient solvent for lignocellulosic biomass, and both softwood and hardwood could be completely dissolved in $[C_2mim][OAc]$ after mild grinding.^{14,24} In this work, lignocellulosic biomass was directly dissolved in $[C_2mim][OAc]$ at 120 °C in 6 h, and then, the dissolved biopolymers (cellulose, hemicelluloses, and lignin) were homogeneously modified (succinylation) and reconstructed (cross-linking) into a porous material. Epichlorohydrin was used as a cross-linker to connect these biopolymers together to prevent the hydrophilic chains from dissolving into aqueous phase. The reaction is illustrated in Figure 1.

Figure 2 shows the FT-IR spectra of milled bamboo (spectrum A) and bioadsorbents before (spectrum B) and after adsorbing metal ion Cd^{2+} (spectrum C) and Pb^{2+} (spectrum D). In the spectra of milled bamboo (MB), a strong band at 1047 cm^{-1} corresponds to C–O stretching in cellulose, hemicelluloses, and lignin or C–O–C stretching in cellulose and hemicelluloses. The adsorption at 3422 cm^{-1} originates from hydroxyl groups, while the absorption at 2928 cm^{-1} arises from C–H stretching. Bands at 1605, 1510, and 1252 cm^{-1} correspond to aromatic skeletal vibrations and C=O stretch.²⁵ As compared with the spectrum of milled bamboo, strong adsorption at 1735 cm^{-1} in the spectrum of bioadsorbent (spectrum B, SA-MB), which is indicative of carbonyl groups, suggests the introduction of the succinyl groups in the bioadsorbent. The arising bands at 1578 cm^{-1} and between 1420 and 1385 cm^{-1} in the bioadsorbent correspond to asymmetric and symmetric stretching of carboxylate ion. The band at 1160 cm^{-1} is attributed to the C–O stretching in ester and carboxylic groups. These changes confirm the occurrence of the succinylation reaction of lignocellulosic biomass with succinic anhydride. After Pb^{2+} and Cd^{2+} were adsorbed, the band at 1578 cm^{-1} , the asymmetric vibration absorption of carboxylate groups, shifts to lower wavenumbers of 1561 cm^{-1} for Cd^{2+} (spectrum C) and 1560 cm^{-1} for Pb^{2+} (spectrum D),

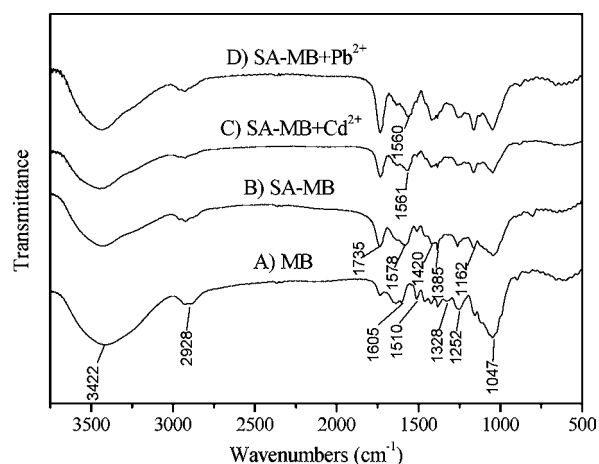


Figure 2. FT-IR spectra of raw material milled bamboo (A) and bioadsorbents (dissolution time of 6 h, epichlorohydrin to milled bamboo ratio of 1:1, and succinic anhydride to milled bamboo ratio of 4:1) before (B) and after adsorbing Cd^{2+} (C) and Pb^{2+} (D). The adsorption conditions were pH 5.0, 120 min, 100 mg/L, and room temperature.

suggesting that the interaction occurs between the COO^- and the metal ions.^{26,27}

SEM Analysis. Figure 3 shows the morphologies of milled bamboo and bioadsorbent. Milled bamboo exhibited a compact structure due to the firm network in cell wall (Figure 3A), which is responsible for its insolubility in common solvents. This compact structure restricts the diffusion of metal ions from the exterior into the interior of the matrix, and thus, metal ion adsorption mainly occurs on the exterior of lignocellulosic biomass. Contrastly, the bioadsorbent had a porous structure (Figure 3B), which is due to the dissolution, homogeneous modification, and reconstruction of biopolymers in IL. Considerable COO^- groups originated from succinyl groups in the bioadsorbent produce strong electrostatic repulsion in the cross-linking network in water, and thus, the polymeric network expands, forming a porous structure. The porous structure of the bioadsorbent will favor the diffusion of metal ions from the exterior to the interior of the material and provides a higher specific surface area and more ligands for metal ion loading.

Effects of Epichlorohydrin and Succinic Anhydride to Milled Bamboo Ratios on Metal Ion Uptake. In this study, succinic anhydride was introduced to the bioadsorbent as active sites for metal ion binding, while epichlorohydrin was incorporated as a cross-linker to form a swelling network. Therefore, succinic anhydride and epichlorohydrin are two important factors that influence the physical and chemical structure as well as the adsorption properties of the bioadsorbent.

The effect of epichlorohydrin to milled bamboo ratio on metal ion uptake is shown in Figure 4A. The adsorption capacities of Pb^{2+} and Cd^{2+} were 273.5 and 196.6 mg/g at epichlorohydrin to a milled bamboo ratio of 1:2 and then decreased to 121.3 and 93.8 mg/g as the ratio increased to 7.5:1. This suggests that the cross-link polymeric network of bioadsorbent significantly influences its metal ion uptake. A higher cross-linker concentration will produce higher cross-linking density and less expanded pores,^{28,29} and consequently, a stronger steric hindrance restricts the diffusion and adsorption of metal ions into the interior of matrix.¹ Therefore, the porous

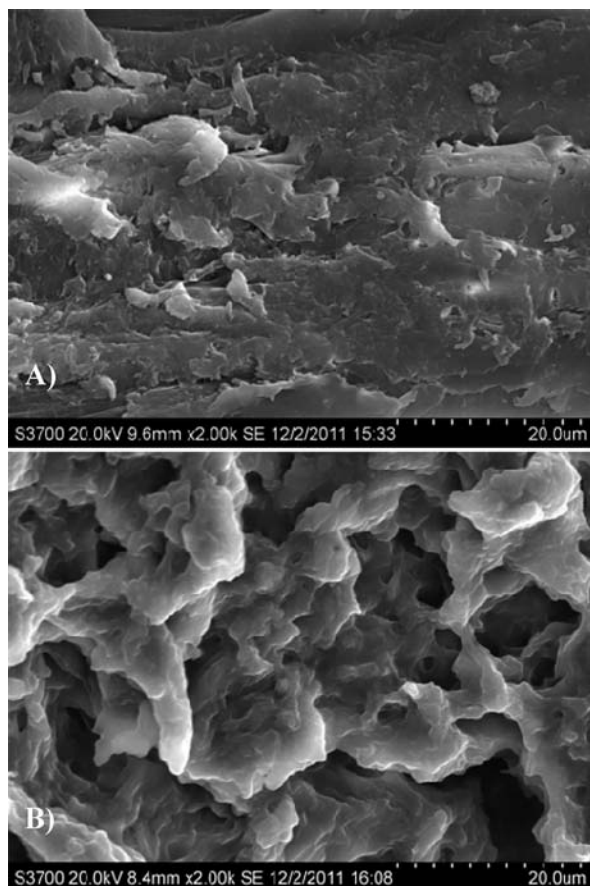


Figure 3. SEM images of raw material milled bamboo (A) and bioadsorbent (B, dissolution time of 6 h, epichlorohydrin to milled bamboo ratio of 1:1 and succinic anhydride to milled bamboo ratio of 4:1). The adsorption conditions were pH 5.0, 120 min, 100 mg/L, and room temperature.

structure of bioadsorbent is an important factor that determines the adsorption capacity of the metal ion. A similar observation was also reported on other adsorbents.^{2,9} Thus, a tunable porous structure can be obtained by dissolving the biomass and reconstructing the dissolved biopolymers in IL, which is in contrast with the compact structure of lignocellulosic biomass.

Figure 4B shows that bioadsorbent without chemical modification showed low adsorption capacities for Pb^{2+} (10.7 mg/g) and Cd^{2+} (6.4 mg/g). With the succinic anhydride to milled bamboo ratio increasing from 1:1 to 4:1, the adsorption capacities of Pb^{2+} and Cd^{2+} increased from 133.8 and 71.5 mg/g to 275.7 and 190.8 mg/g, respectively. The further increase in the succinic anhydride to milled bamboo ratio (5:1) resulted in the decrease of adsorption capacities (167.2 mg/g for Cd^{2+} and 236.4 mg/g for Pb^{2+}). Figure 5 illustrates that the carboxyl content increased from 1.52 mmol/g at succinic anhydride to a milled bamboo ratio of 1:1 to 4.01 mmol/g at succinic anhydride to a milled bamboo ratio of 4:1 and then decreased to 3.21 mmol/g at succinic anhydride to a milled bamboo ratio of 5:1. Yoshimura et al.³⁰ found that the formation of diester between ester carboxylic groups and cellulosic hydroxyl groups was possible due to the fact that excess succinic anhydride in the reaction system might behave as a dehydrating agent under nonaqueous conditions, forming a cross-linking structure. This reaction is responsible for the decrease of carboxyl groups and the adsorption capacities of Pb^{2+} and Cd^{2+} at a higher succinic

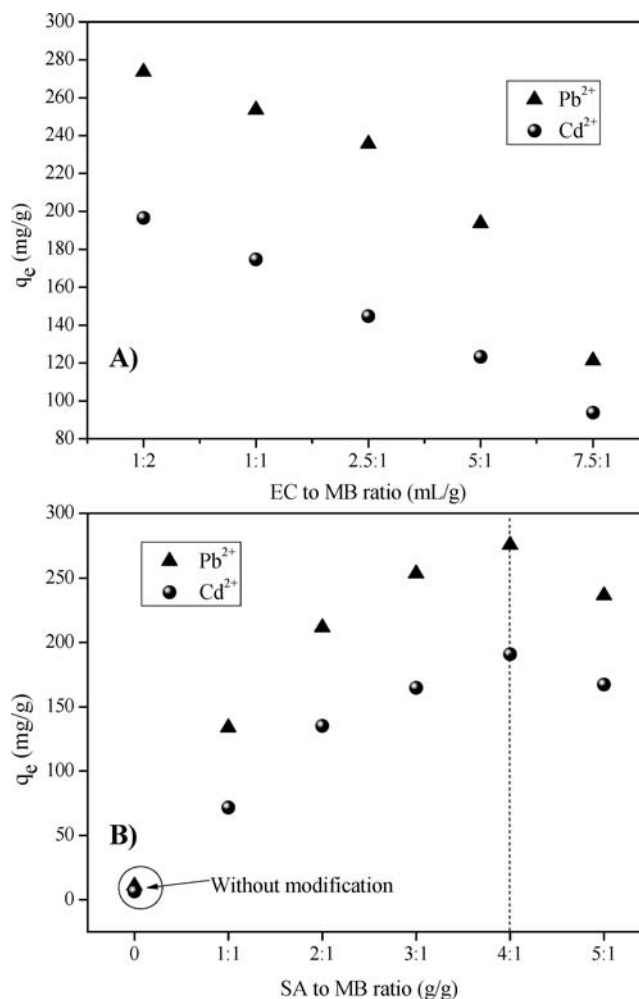


Figure 4. Effects of epichlorohydrin to milled bamboo (EC to MB, A) and succinic anhydride to milled bamboo (SA to MB, B) ratios on metal ion adsorption on the bioadsorbent.

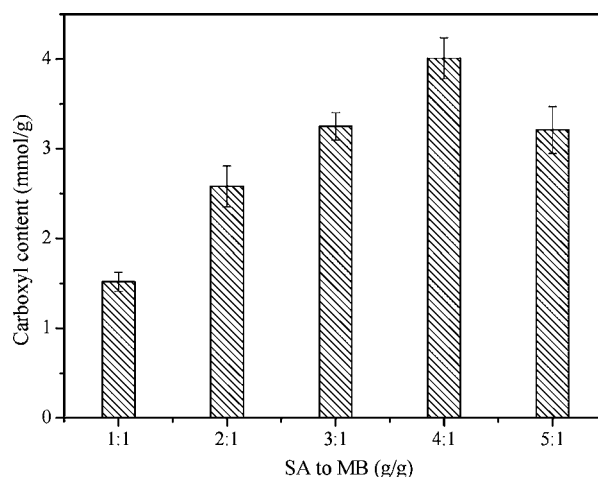


Figure 5. Effect of succinic anhydride to milled bamboo ratio on carboxyl content in bioadsorbent (epichlorohydrin to milled bamboo ratio of 1:1).

anhydride to milled bamboo ratio. These results indicate that both the amount of ligands and the porous structure are required to produce a higher adsorption capacity.

Effect of Dissolution Time on Metal Ion Uptake. To better understand the influences of homogeneous modification and reconstruction on the metal ion uptake, the adsorption capacities of metal ions as a function of dissolution time of milled bamboo in IL were investigated, and the results are shown in Figure 6. It was found that the adsorption capacities

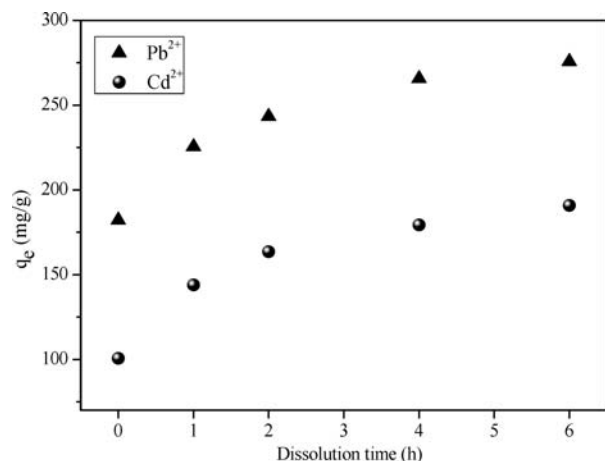


Figure 6. Effect of dissolution time on metal ion adsorption on the bioadsorbent (epichlorohydrin to milled bamboo ratio of 1:1 and succinic anhydride to milled bamboo ratio of 4:1).

of Pb²⁺ and Cd²⁺ on the milled bamboo without previous dissolution in IL were 162.2 mg/g for Pb²⁺ and 90.6 mg/g for Cd²⁺. In this case, small particles and high surface area resulting from ball-milling treatment contribute to the relatively high metal ion loading. As the dissolution time increased from 1 to 6 h, the adsorption capacities of Pb²⁺ and Cd²⁺ increased from 225.4 and 143.9 mg/g to 275.7 and 190.8 mg/g, respectively. For the bioadsorbent without being previously dissolved in IL, the compact structure of biomass was less destroyed and did not allow homogeneous modification and cross-linking. As dissolution preceded, more biopolymers were dissolved in IL and chemical modification and cross-linking could be carried out more homogeneously, which greatly facilitated loading more ligands and forming a more porous structure. These results confirm that homogeneous chemical modification and reconstructing biopolymers into porous material are beneficial for metal ion uptake.

Effect of pH on Metal Ion Uptake. To avoid the generation of hydrolyzed species of lead such as Pb(OH)⁺ or Pb(OH)₂ at higher pH, the pH of Pb²⁺ solution was limited to values less or equal to 5.³¹ As illustrated in Figure 7, the adsorption capacity of Pb²⁺ remarkably increased from 51.3 mg/g at pH 2.0 to 288.7 mg/g at pH 5.0. The adsorption capacity of Cd²⁺ also increased continuously with the increasing pH, and the equilibrium adsorption capacity at pH 6.0 was 195.8 mg/g. At low pH (less than 4.5), carboxyl groups retain their protons (COOH), which weakens the interaction between negatively charged COO⁻ groups and positively charged metal ions. As the pH of metal ion solution increases, carboxyl groups become deprotonated (COO⁻) and easily attract the positively charged metal ions.^{27,32} Therefore, metal ion binding to the bioadsorbent mainly involves electrostatic interaction between metallic cations and negatively charged COO⁻ groups, and the adsorption process is an ion exchange mechanism.³³

Adsorption Kinetics. The adsorption capacities of metal ions were measured as a function of contact time, and the

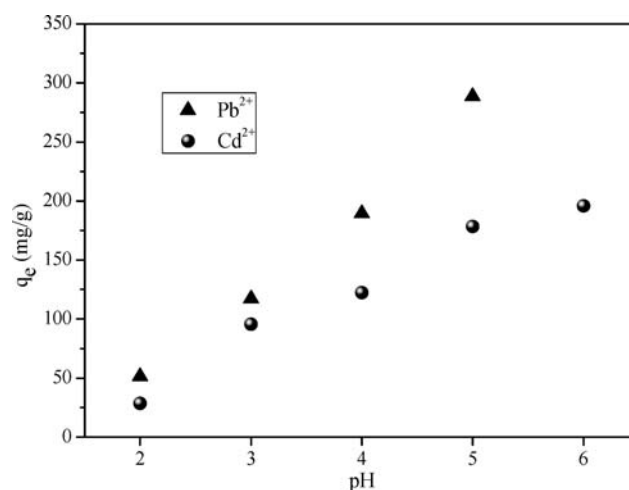


Figure 7. Effects of the pH of metal ion solutions on metal ion adsorption on the bioadsorbent (epichlorohydrin to milled bamboo ratio of 1:1 and succinic anhydride to milled bamboo ratio of 4:1).

results are shown in Figure 8. The adsorption capacities of Pb²⁺ and Cd²⁺ increased rapidly in the first 30 min and then augmented slowly. The adsorption equilibrium could be achieved within 50 min.

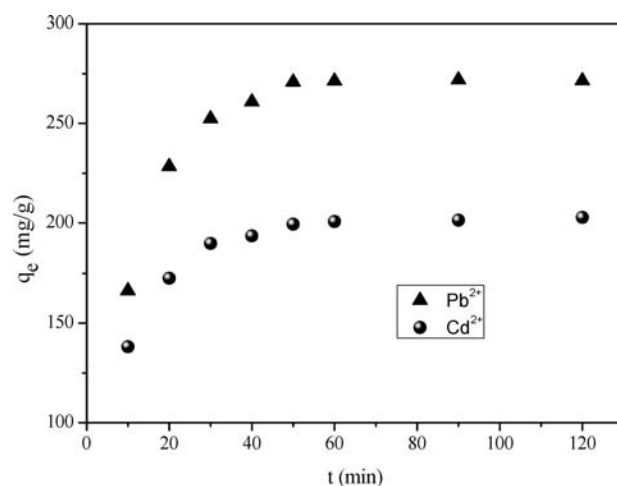


Figure 8. Adsorption of Pb²⁺ and Cd²⁺ on the bioadsorbent (epichlorohydrin to milled bamboo ratio of 1:1 and succinic anhydride to milled bamboo ratio of 4:1) as a function of contact time at pH 5.0 (Pb²⁺) and pH 6.0 (Cd²⁺).

Two most commonly used kinetic models, that is, the pseudofirst-order and pseudosecond-order models, were used to test the experimental data to examine the controlling mechanism of the adsorption process. The linear pseudofirst-order eq 3 and second-order eq 4 are illustrated as following:

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad (3)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (4)$$

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 [g/(mg·min)] are the kinetics rate constants for the pseudofirst-order model and the pseudo-

Table 1. Equilibrium Adsorption q_e and Correlation Coefficient R Values Obtained from Experimental and Adsorption Kinetics and Adsorption Isotherm^a

metal ions	adsorption kinetics (mg/g)					adsorption isotherm (mg/g)			
	$q_{e,exp}$	$q_{e,1st}$	R_{1st}^2	$q_{e,2nd}$	R_{2nd}^2	$q_{e,exp}$	$Q_{max,L}$	R_L^2	R_F^2
Pb ²⁺	271.3	169.1	0.909	287.4	0.998	309.9	381.7	0.973	0.825
Cd ²⁺	202.7	101.8	0.894	210.5	0.999	228.7	278.6	0.979	0.894

^a R_L^2 and R_F^2 are correlation coefficients of Langmuir and Freundlich models.

second-order model, respectively. The results are shown in Figure S1 (see the Supporting Information) and Table 1.

The correlation coefficients for the pseudosecond-order kinetic model (R_{1st}^2) were higher than those of the pseudofirst-order kinetic model (R_{2nd}^2), and the calculated data from pseudosecond-order kinetic model ($q_{e,2nd}$) generally deviated less from the experimental data ($q_{e,exp}$ in Table 1). These results suggest that the adsorption kinetics of Pb²⁺ and Cd²⁺ on the bioadsorbent are well-represented by the pseudosecond-order kinetic model, and the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied ligands. Therefore, the adsorption of Pb²⁺ and Cd²⁺ on the bioadsorbent is dominated by a chemical adsorption process (the interaction occurs between the COO⁻ and the metal ions), which also was confirmed by the FT-IR results. Similar conclusions were also found by other authors.³⁴

Adsorption Isotherms. The adsorption data of Pb²⁺ and Cd²⁺ as a function of metal ion concentration are presented in Figure 9. At low concentrations, the adsorption capacities of

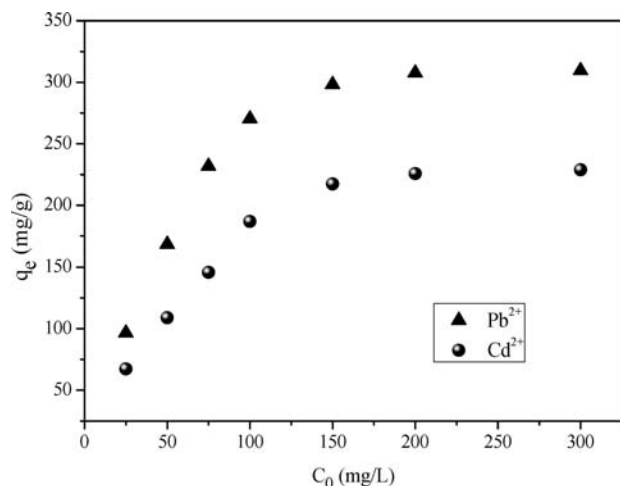


Figure 9. Adsorption of Pb²⁺ and Cd²⁺ on the bioadsorbent (epichlorohydrin to milled bamboo ratio of 1:1 and succinic anhydride to milled bamboo ratio of 4:1) as a function of metal ion concentration at pH 5.0 (Pb²⁺) and pH 6.0 (Cd²⁺).

Pb²⁺ and Cd²⁺ increased linearly with increasing concentrations, suggesting that the amount of metal ions adsorbed was dependent on the number of metal ions. A higher initial metal ion concentration enhances the adsorption capacities of metal ions. At higher concentrations (higher than 150 mg/L), the adsorption capacities no longer increased proportionally with the initial concentrations, indicating that the number of ligands accessible to metal ions in the bioadsorbent actually controlled the amount of metal ion uptake.

The Langmuir (eq 5) and Freundlich isotherm models (eq 6) have widely been used in adsorption isotherm studies and were also used in this work to fit the experimental isotherm

data for Pb²⁺ and Cd²⁺ adsorption on the bioadsorbent. The results are presented in Figure S2 in the Supporting Information and Table 1.

$$\frac{c_e}{q_e} = \frac{1}{Q_{max} \times b} + \frac{c_e}{Q_{max}} \quad (5)$$

$$\ln q_e = \ln k + \frac{1}{n} \ln c_e \quad (6)$$

where q_e (mg/g) is the adsorption capacity of metal ion at equilibrium, c_e (mg/L) is the concentration of metal ion, Q_{max} and b are the Langmuir equation parameters, and k and n are the Freundlich equation parameters.

The higher correlation coefficients (R_L^2) of the linearized Langmuir equation than those of the Freundlich equation (R_F^2) indicate that the Langmuir model can better fit the experimental results. The maximum values (Q_{max}) of Pb²⁺ and Cd²⁺ calculated from Langmuir model were 381.7 and 278.6 mg/g, deviating somewhat from the experimental data ($q_{e,exp}$ in Table 1). These results therefore suggest that the phenomenon of metal ion adsorption on the bioadsorbent was somewhat complex due to the complexity of the contribution of components (i.e., cellulose, hemicelluloses, and lignin) in the matrix to the chemical and physical structure of the bioadsorbent.

Generally, plant wastes with and without chemical modification show low adsorption capacities for metal ions in aqueous solutions (4.51–100 mg/g for Cd²⁺ and 4.48–200 mg/g for Pb²⁺).² Therefore, the bioadsorbent that we prepared shows a great advantage over traditional bioadsorbents for the removal of metal ions (228.7 mg/g for Cd²⁺ and 309.9 mg/g for Pb²⁺). It is interesting, however, that sugar cane bagasse-based bioadsorbents exhibit much higher adsorption capacities (189–313 mg/g for Cd²⁺ and 164–313 mg/g for Pb²⁺), which may be attributed to its physical and chemical structure and composition.² For these probable reasons, high adsorption capacities (256.4 mg/g for Cd²⁺ and 500.0 mg/g Pb²⁺ according to Langmuir model) were reported for sugar cane bagasse modified with succinic anhydride.¹⁹ These results in combination with our findings indicate that the adsorption properties of bioadsorbent can be further improved by tailoring the chemical and physical structure.

The findings presented here suggest that, besides the amount of ligands, porous structure is also an important factor that determines the adsorption properties of metal ions. A porous structure can greatly facilitate the diffusion of metal ions and the accessibility of ligands to metal ions. The dissolution of lignocellulosic biomass in IL opens up the possibility to prepare materials with precise porous structure from the compact plant cell wall by homogeneous modification and reconstruction. The further work especially will be focused on adjusting the porous structure of the bioadsorbent for higher metal ion-loading capacity.

In summary, lignocellulosic biomass was directly dissolved in IL and then homogeneously modified (succinylation) and reconstructed (cross-linking) into a porous bioadsorbent. COO⁻ groups were the main functional groups participated in metal ion binding, and the adsorption process was an ion exchange mechanism. The bioadsorbent exhibited porous structure, which greatly favored the diffusion and uptake of metal ions. Both network structure and carboxyl content significantly influenced the adsorption capacity of the bioadsorbent. The adsorption equilibrium could be achieved in 50 min, and the maximum adsorption capacities of Pd²⁺ and Cd²⁺ were 309.9 and 228.7 mg/g.

■ ASSOCIATED CONTENT

● Supporting Information

Adsorption kinetics of Pb²⁺ and Cd²⁺ on the bioadsorbent (epichlorohydrin to milled bamboo ratio of 1:1 and succinic anhydride to milled bamboo ratio of 4:1) as a function of contact time (Figure S1). Adsorption isotherms of Pb²⁺ and Cd²⁺ on the bioadsorbent (epichlorohydrin to milled bamboo ratio of 1:1 and succinic anhydride to milled bamboo ratio of 4:1) as a function of metal ion concentration (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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