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Chemical Modification and XPS Study for Lead(II) Binding by Wheat Stems Biomass

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Abstract: Increasing concern over heavy metal contamination of the aquatic environment is urging the more effective and environmentally friendly methods of remediating heavy metals from contaminated waters. The use of plant materials as metal adsorbents may be a possible solution. In this study, wheat stems biomass has been utilized as bioadsorbent to bind lead(II) from aqueous solution. Selected binding conditions such as reaction time and solution pH were optimized. The effect of chemical modification on lead(II) binding capacity of the biomass was investigated. Results showed that the lead(II) binding process by wheat stems biomass is fast and the process is strongly affected by the solution pH. After esterification of the biomass, the lead(II) binding capacity decreased dramaticly, while the lead(II) binding capacity increased greatly after base hydrolyzation of wheat stems. FTIR spectra showed that hydroxyl groups and carbonyl groups in wheat stems biomass may play an important role in the binding of lead(II). In addition, XPS analysis also supports this explanation. These studies are useful for determining ligands that may involve in lead(II) ions binding by wheat stems, thus aiding in our understanding of the mechanisms involved in the removal of metal ions from contaminated waters through biosorption.

Keywords: Chemical modification; Lead; Metal binding; Wheat stem

INTRODUCTION

Heavy-metal contamination of the aquatic environment has become an important issue with respect to environmental and human health. Lead contamination of the environment deserves special attention because lead is one of the most toxic heavy metals. At high concentrations, lead has

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been shown to damage the nervous system and cause physical and mental birth defects.

Conventional methods for removing heavy metals from aqueous solutions include chemical precipitation, ion exchange, filtration and membrane technologies. These processes may be ineffective or unduly expensive (1). The use of biological systems to remediate heavy metal contaminated waters has been studied for some time. Many researchers have found that non-living biomaterials can be used to remove heavy metal ions from the environment. Biomass of algae, fungi, bacteria, aquatic ferns and seaweeds, and waste biomass originated from plants and mycelial wastes from fermentation industries are potential biosorbents for removal of heavy metals from aqueous solutions and wastewater (2–5). Among biosorption materials, those based on plant biomass deserve special attention because of their low cost, availability, and renewable nature (6–14).

Wheat is the first main crop in the world and the second main crop in China. Every year large amounts of wheat stems are produced. Usually, the waste wheat stems are burned directly in the field, which constitutes serious atmospheric pollution and wastage of a potentially valuable resource. Like other biomaterials, wheat stems may also be used as biosorbent for the removal of heavy metals from aqueous solutions. However, there are only few reports on adsorption of heavy metals by wheat stems (15).

The objective of this study was to investigate the binding of lead(II) from aqueous solution by wheat stems biomass. Batch laboratory experiments were performed to study the effect of pH on the adsorption capacity of lead(II) by wheat stems. In order to identify the possible binding mechanisms, wheat stems were chemically modified and analyzed by infrared and X-ray photoelectron spectroscopy (XPS). In addition, the interference with lead(II) binding to wheat stems by naturally occurring cations such as calcium and magnesium was examined.

EXPERIMENTAL PROCEDURE

Sample Collection

The wheat stems were collected from a field at Shuangliu Farm, Sichuan Province. The wheat stems and leaves were washed carefully and then dried in an oven at 80°C for 48 h. The biomass was then ground to pass a 100-mesh sieve to achieve uniform particle size. Powdered wheat stems material was washed once with 0.01 M nitric acid (HNO_3) and twice with deionized water. The washing was performed to remove any soluble material that might eventually interact with the adsorption of lead ions in solution. The powdered and washed wheat stems material was then dried in an oven at 80°C; for 48 h prior to further use.

FTIR Spectroscopy and XPS Analysis

Infrared spectrum of the wheat stems biomass were acquired on a Nicolet 5700 FTIR Spectrophotometer (Thermo Electron Corporation) under ambient conditions. Each sample was examined using reflection mode in the wavenumber range of $400 \sim 4000\,\mathrm{cm}^{-1}$. The XPS of lead on biomass surface was performed using a Kratos XSAM 800 and Mg K_{α} X-rays (charge-correcting the spectra on the basis of the adventitious hydrocarbon C 1s signal at 284.8 eV).

Chemical Modification

The wheat stems were methanol esterified following a simple method described in the literatures (16–18). In brief, 9 g of the biomass was suspended in 633 ml of 99.9% pure methanol and 5.4 ml of concentrated hydrochloric acid (HCl) was added to maintain the final acidic concentration of 0.1 M HCl. While continuously stirring the solution, the samples were heated to 60°C for 48 h. The biomass samples were then washed three times with deionized water to quench the reaction. Then the biomass was dried in an oven at 80°C and stored in a desiccator until further use.

Base hydrolysis of the biomass was performed on 9 g of the biomass reacted with 100 ml of 0.1 M sodium hydroxide for 1 h at room temperature. The hydrolyzation reaction was quenched by washing the biomass with deionized water three times. The biomass was then dried in an oven at 80°C and stored in a desiccator for further batch metal binding experiments.

Lead Binding Experiments

Batch sorption experiments were carried out in 100-ml beakers, each of which contained 25 ml of lead solution prepared with $Pb(NO_3)_2$. A 100-mg sample of wheat stems biomass was added to each beaker. The effect of solution pH (2.0–6.0) on lead binding by wheat stem was investigated at an initial lead concentration of $20\,\mathrm{mg\,l}^{-1}$. Also, controls consisting of just lead(II) nitrate were made at each pH. All of the metal-biomass solutions and controls were equilibrated for 30 min. After equilibration, all of the solutions were filtered and the filtrates were collected and analyzed for metal content.

Other batch experiments were implemented as described above to determine the effect of chemical modification on the wheat stems binding capacity for lead(II). In these experiments, 100-mg samples of unmodified and modified wheat stems, respectively were reacted with 25 ml of lead(II) solution containing different lead(II) concentrations at pH 5.0. The concentrations of the lead(II) solution were as follows: 5, 10, 20, 40, 80, 120, and 200 mg l^{-1}. Metal solution controls were also carried out throughout these experiments for the data quality control. All of the solutions were equilibrated for 30 min. The equilibrated solutions were filtered and the filtrates were analyzed for lead concentration.

Lead Binding Interference Studies

Lead(II) (20 mg l^{-1}) solutions used in the interference studies were made with the following concentration of both calcium(II) and magnesium(III) ions: 0, 20, 50, 100, and 200 mg l^{-1}. A 100-mg sample of unmodified wheat stems was added to each solution and the pH of each solution was adjusted to 5.0 using 0.01 M HNO_3. Controls consisting of various cations were made and reacted in the same way. After equilibration, the solutions were filtered and the filtrates were collected for lead analysis.

Metal Analysis

A SOLAAR M6 MK2 atomic absorption spectrometer (Thermo Electron Corporation) was utilized to determine the lead concentration in filtrates from binding experiments. The wavelength used for lead analysis was 217.0 nm. The concentration of each sample was read three times and the mean values, as well as the relative standard deviation, were computed. The difference between the initial and the remaining metal ion concentration was assumed to be bound to the biomass. The lead(II) equilibrium binding capacity q_e (mg lead/g of biomass) was calculated as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{w \times 1000} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentration of Pb^{2+} respectively ($mg \cdot l^{-1}$), and V is the volume of solution in ml and w the mass of wheat stems biomass in g.

RESULTS AND DISCUSSION

FTIR Analysis

Figure 1 shows the FTIR spectrum of the wheat stems biomass. Peaks at 3344, 2905, 1735, 1457, 1374, 1250, 1163, and 1054 cm^{-1} are observed in the wheat stem spectrum. The broad and strong band at 3344 cm^{-1} is

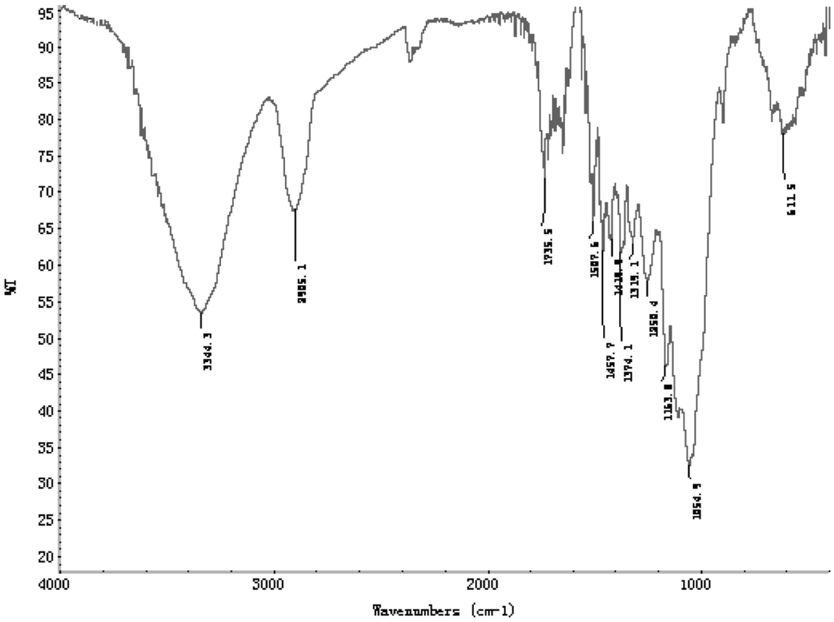

Figure 1. FTIR spectrum of wheat stems biomass.

attributed to the O-H stretching vibration. Peaks at 2905, 1457, and 1374 cm^{-1} are the C-H stretching and bending vibration respectively. The peak at 1735 cm^{-1} is assigned to C=O stretching vibration, especially the carbonyl in ester groups. The peaks at 1250 and 1163 cm^{-1} confirm this conclusion, arising from the C-O-C stretching vibration (19). The peaks at 1054 cm^{-1} is assigned to C-O stretching vibration in carbohydrate. So, it can be concluded that hydroxyl groups and carbonyl groups are present in the wheat stems biomass.

Effect of Solution pH on Lead(II) Binding

The sorption kinetics experiments (data not shown) revealed that the lead(II) binding process by wheat stems biomass is fast in the first 10 min. The sorption of lead(II) reaches equilibrium until 30 min. In the subsequent batch sorption experiments, the sorption time was set at 30 min.

An important parameter affecting metal ions sorption is pH. It not only influences the properties of the sorbent surface, but also affects the metal speciation in solution. In order to determine the effect of pH on lead(II) binding by wheat stems, batch sorption equilibrium experi-

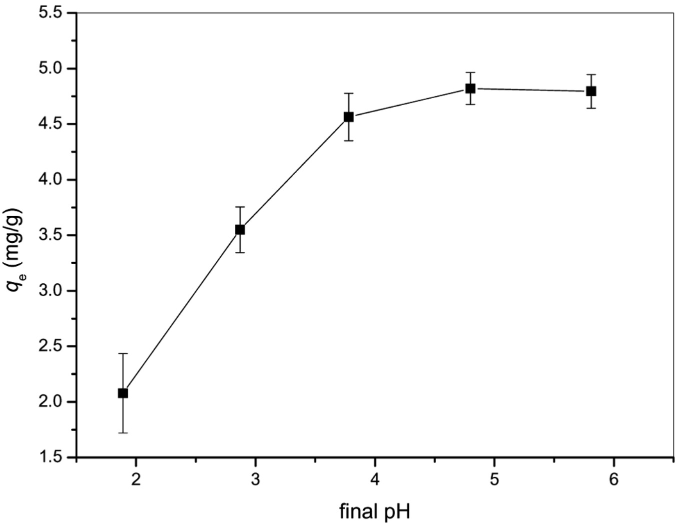

Figure 2. The effect of solution pH on the lead(II) binding by wheat stems biomass.

ments were carried out at various pH 2.0–6.0. The lead(II) binding against pH is shown in Fig. 2. It shows that lead(II) binding increased with increasing pH. In addition, the pH of the aqueous solution had decreased after the binding of lead ions, suggesting that lead ions are bound by a cation exchange mechanism and protons are released from the biomass. Figure 2 shows that the optimum pH for lead(II) binding is around 5.0. Although the binding of lead(II) was similar at pH 6.0, pH 5.0 was used in the remaining studies to avoid lead precipitation.

Modification and Adsorption Isotherm

The respective lead(II) binding capacities (q_e, mg/g) of the biomass and the modified biomass as a function of residual lead concentration (c_e, $\mathrm{mg \cdot l^{-1}}$) at pH 5.0 are shown in Fig. 3. The Langmuir isotherm equation was used to fit the experimental data derived from the biomass and the modified biomass (20):

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{2}$$

where K_L is the Langmuir isotherm constant and q_m is the maximum binding capacity of lead(II) in mg per g of the biomass, which represents a practical limiting binding capacity when the surface is fully covered

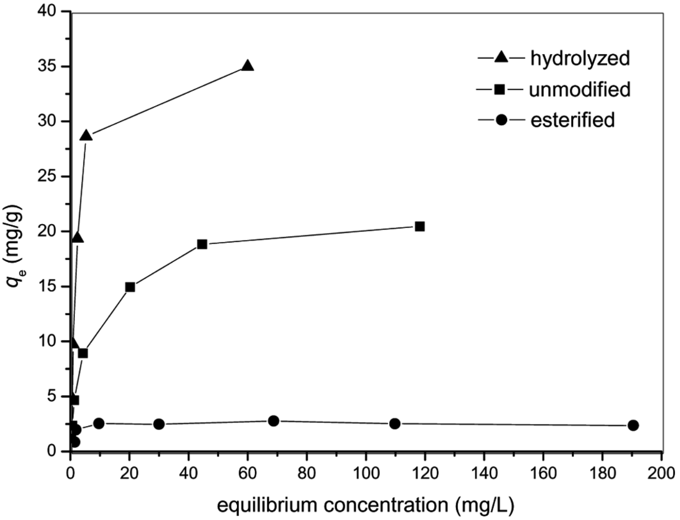

Figure 3. Sorption isotherms of lead(II) ions on unmodified and modified biomass.

with lead(II) ions. Langmuir equation can be described by the linearized form:

$$\frac{1}{q_e} = \frac{1}{K_L q_m}\frac{1}{C_e} + \frac{1}{q_m} \tag{3}$$

By plotting $1/q_e$ versus $1/C_e$, the maximum binding capacity q_m can be determined when a straight line is obtained. The linearized form of Langmuir isotherms are displayed in Fig. 4. The values of q_m, calculated from the experimental data through linear regression analysis, are listed in Table 1. A dramatic decrease in the binding capacity of the esterified biomass was found. The lead binding capacity of the unmodified biomass was 26.95 mg/g, while the esterified biomass had a binding capacity of 2.94 mg/g. However, after hydrolyzation, a significant increase in lead(II) binding was observed from 26.95 to 99.01 mg/g.

Previous studies have suggested that the base hydrolyzation process of the biomass may transform the ester groups, which are not active in the metal binding process, into the carboxyl groups, and then increase the metal binding capacity (18). The base hydrolyzation process can be described by the reaction: $R\text{-}COO\text{-}CH_3 + NaOH \rightarrow R\text{-}COO^- + Na^+ + CH_3OH$, where R represents the others component in the biomass. The FTIR spectrum of wheat stems biomass (Fig. 1) shows that ester groups are present in the biomass. Thus the increase of the lead(II) binding capacity after hydrolyza-

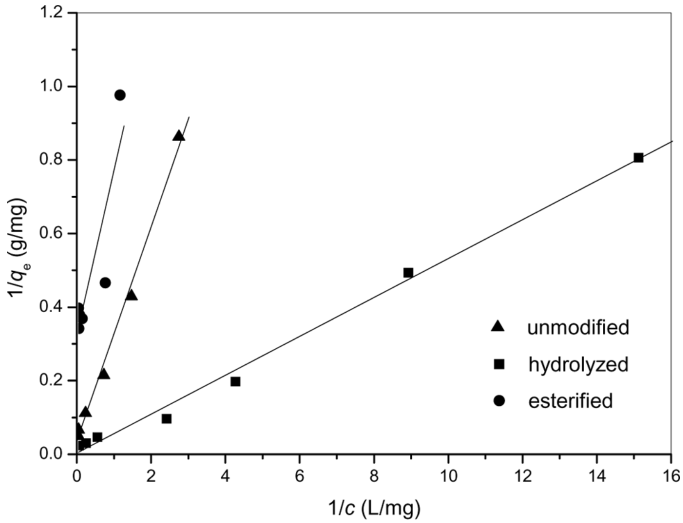

Figure 4. Linearized Langmuir isotherm model for lead(II) binding by unmodified and modified biomass.

tion is possibly attributed to the formation of R-COO$^-$ groups on the biomass which play an important role in the binding of lead(II) ions by the wheat stems biomass.

XPS Analysis

X-ray photoelectron spectroscopy is a relatively new technique for the determination of binding energy of electrons in molecules which depends upon the distribution of valence charges and thus provides information about the oxidation state of an ion (21). The XPS spectrum of wheat stems biomass binding about 22 mg lead per gram of biomass (wheat stems biomass interacted with 400 mg $\cdot$ l^{-1} lead(II) solutions at pH 5.0

Table 1. Comparison of binding capacity for lead of native and chemically modified wheat stems biomass

q_m (mg metal/g of wheat stems biomass)		
Before modification	After esterification	After hydrolysis
26.95 ± 2.44	2.94 ± 1.13	99.01 ± 3.22

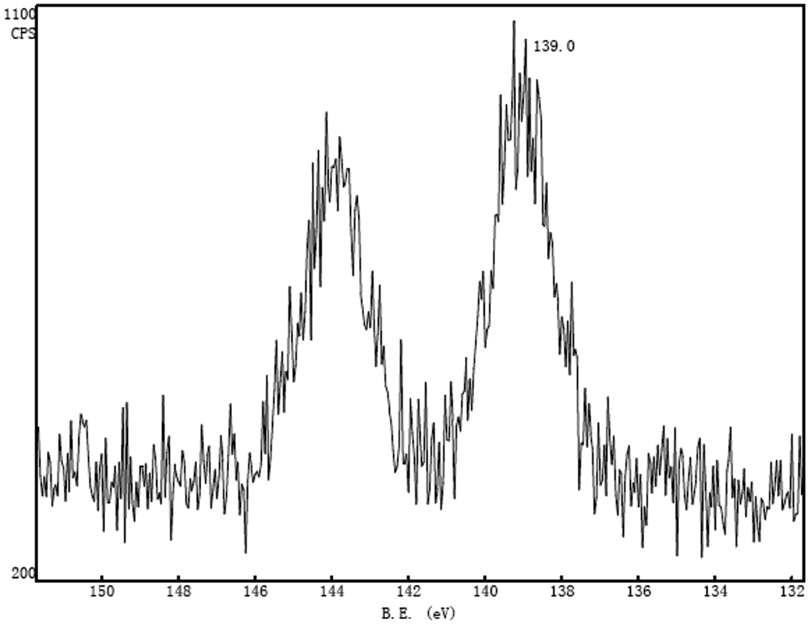

Figure 5. XPS spectrum of wheat stems biomass after binding with lead.

for 30 min) is depicted in Fig. 5. The relevant Pb 4f photoelectron peak occurs at the binding energies of 139.0 eV, which is the characteristic of lead carbonate and lead oxalate compounds (22), indicating that lead is bound by the wheat stems biomass through the hydroxyl and carbonyl groups. In addition, the only symmetrical peak at 139.0 eV indicates that lead bound on the surface of the wheat stems biomass was present only in one oxidation state of divalent lead. Furthermore, the precipitation of lead(II) ions to form $Pb(OH)_2$ or PbO (Pb 4f at 137.3 eV) can be excluded in the lead(II) binding process by the wheat stems biomass (23).

Interference of Calcium and Magnesium

Hard cations such as calcium and magnesium are readily found in natural waters. Therefore, it is necessary to determine the effects of these hard cations on the lead(II) binding ability of the wheat stems. The results of calcium and magnesium interference on lead(II) uptake are displayed in Fig. 6. The lead(II) binding capacity of the biomass decreased only a little in the presence of $200\,\text{mg}\cdot\text{l}^{-1}$ calcium and $200\,\text{mg}\cdot\text{l}^{-1}$ magnesium (which is 20 times the concentration of lead in solution). These results

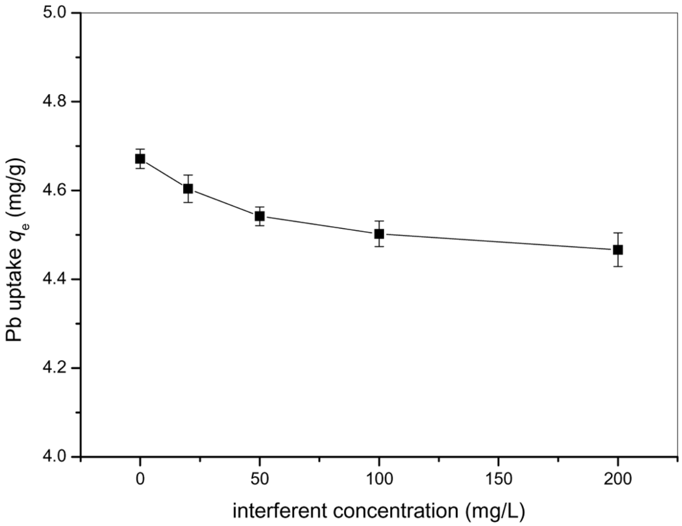

Figure 6. The interference effect of various combined calcium and magnesium concentrations on lead(II) binding by the wheat stems biomass.

indicate that the biomass has a greater affinity toward lead(II) over calcium and magnesium ions.

CONCLUSION

Wheat stems materials have the potential to be used as a biosorbent for lead(II) removal from aqueous solutions and they are low cost and environmentally friendly. The following conclusions are drawn.

1. The pH of solution seriously influences the lead(II) binding by the wheat stems biomass and the optimum pH for lead(II) binding is around 5.0.
2. Esterification of the biomass results in a dramatic decrease in lead(II) binding, while hydrolysis of the biomass lead to an considerable increase in lead(II) binding. FTIR spectrum of the biosorbent material shows that hydroxyl groups and carbonyl groups are present on the biomass surface. These functional groups may play an important role in the binding of lead(II). XPS experiment further indicates that lead is bound by wheat stems biomass through hydroxyl and carbonyl groups.

3. Wheat stems biomass shows high selectivity for lead(II) binding even with calcium and magnesium ions concentrations at 20 times that of lead. Calcium and magnesium ions interfere only very little with lead(II) binding by the wheat stem biomass.

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