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Research paper

Removal of Heavy Metal Ions from Aqueous Solutions by Bamboo Wastes

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【Summary】

In the present study, the ability of wastes of 5 local bamboo species (*Dendrocalamus latiflorus*, *Phyllostachys makinoi*, *P. pubescens*, *Bambusa stenostachya*, and *B. dolichoclada*) to remove heavy metal ions of Cu (II), Pb (II), Cd (II) and Ni (II) from aqueous solutions, with different reaction times, particle sizes, and pH values were evaluated and compared with 4 known biosorbents of activated carbon, bark, exhausted coffee, and exhausted tea by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results showed that the absorptive capacity of bamboo waste for heavy metal ions increased with prolongation of the reaction times and a decrease in the particle size. The optimum pH value for metal adsorption was in the range of 4~6. *Phyllostachys pubescens* was the most effective in removing heavy metal ions from aqueous solutions among the wastes of the 5 bamboo species. By hot-water-extraction treatment, the available volume and surface area of the raw bamboo materials greatly increased which effectively improved the metal-removal efficiency. The performance of hot-water-extracted bamboo for removing heavy metal ions was even better than those of bark, exhausted coffee, and exhausted tea. Therefore, the use of hot-water-extracted bamboo waste as an adsorbent may be an alternative to other more-costly materials.

Key words: bamboo waste, heavy metal ions, ICP-AES, hot-water-extracted treatment.

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研究報告

以竹廢材移除溶液中重金屬

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摘　要

本研究以感應耦合電漿原子發射光譜儀評估五種台灣常見竹材-麻竹、桂竹、孟宗竹、莿竹與長枝竹等廢材在不同反應時間、粒徑大小及不同pH值等條件下，對溶液中銅(II)、鉛(II)、鎘(II)與鎳(II)等重金屬之移除效果，並與四種已知生物性吸附材料之活性碳、樹皮、咖啡渣與茶渣等進行比較。試驗結果顯示延長試材與溶液反應時間或選用較小粒徑試材皆可提升重金屬吸附效果，而溶液之pH值在4~6範圍時具有最佳吸附效果。五種試材中以孟宗竹對重金屬吸附效果最佳；竹材經熱水萃取處理後，因釋出更多金屬可接觸表面積及空間，而可有效提升其重金屬吸附率，其效果甚至較樹皮、咖啡渣與茶渣等為佳，顯示竹材經熱水萃取處理後，具有做為移除重金屬材料之潛力。

關鍵詞：竹廢材、重金屬離子、感應耦合電漿原子發射光譜儀、熱水萃取處理。

許富蘭、彭于珍、李鴻麟。2009。以竹廢材移除溶液中重金屬。台灣林業科學24(3):159-68。

INTRODUCTION

In recent years, the presence of toxic heavy metals in the environment has emerged as a major concern on a global scale. Heavy metals can be distinguished from other toxic pollutants, since they are not biodegradable and tend to accumulate in living tissues, causing various diseases and disorders (Walker et al. 2001).

Conventional methods of removing heavy metals from industrial effluents, such as chemical precipitation, solvent extraction, electrolysis, membrane separation, ion exchange, and adsorption, are either too expensive or unsuitable for large volumes of wastewater containing low concentrations of heavy metals. Cost-effective alternative technologies or sorbents for treating heavy metal-contaminated wastes are needed (Seco et al. 1999, Chu and Hashim 2000).

Recently, inexpensive biological materials such as algae (Holan et al. 1993), nut wastes, sawdust (Dikshit 1989), exhausted tea, exhausted coffee, and bark (Masri et al. 1974, Randall et al. 1974) were found to efficiently adsorb and accumulate heavy metals. Among these, bark is an effective adsorbent because of its high tannin content. Polyhydroxy polyphenol groups of tannin are thought to be the active species in the adsorption process. Ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups; forming a chelate (Randall et al. 1974, Vázquez et al. 1994). Lignocellulosic materials contain hemicellulose, cellulose, and lignin as major constituents, and each of them plays a different role in metal removal. In general, cellulose makes the least contribution to ion exchange, while hemicellulose, lignin, and extractives are the major players (Yu et al. 2008). These constituents contain polar functional groups, such as alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers that may be involved in chemical bonding. Because of these properties, lignocellulosic materials tend to have a high cation exchange capacity, and are effective adsorbents for removing heavy metals. In addition to chemical properties, the efficacy of biosorbents is closely related to their physical properties (Masri et al. 1974, Randall et al. 1974, Vázquez et al. 1994, Han 1999). In that regard, Han (1999) concluded that the lower the lignin content is, the higher the sorption efficiency; a low lignin content indicates a low density and easy accessibility of ions to active sites.

Bamboo, a cheap and rapidly renewable lignocellulosic material, is abundant and produced in great quantities in Taiwan. Because of its high porosity and multiple functional groups, bamboo can be a potential candidate as a biosorbent to remove heavy metals from wastewater. The purpose of this research was to compare the heavy metal-removal efficiency of 5 major local bamboo species and to evaluate their potency as biosorbents of wastewater.

MATERIALS AND METHODS

Bamboo specimens, including *Dendrocalamus latiflorus* (Dl), *Phyllostachys makinoi* (Pm), *Bambusa stenostachya* (Bs), *B. dolichoclada* (Bd), and *P. pubescens* (Pp), were collected, and their abbreviations are listed in Table 1. Activated carbon was purchased from Acros (Geel, Belgium). The bark of *Acacia confusa* was obtained from the Experimental Forest, National Taiwan University, Sitou, Taiwan. Commercial coffee and tea were boiled in hot water for 1 h to imitate exhausted waste. All test materials were ground, sieved, washed with deionized water, and air-dried. Standard metal ion solutions of copper [Cu (II)], lead [Pb (II)], cadmium [Cd (II)], and nickel [Ni (II)] at 1000 ppm were purchased from Merck (Darmstadt, Germany) and were diluted to 10 ppm prior to the adsorption test.

Chemical composition analysis

Components, including cold- and hot-water extractives, ethanol/benzene extractives, lignin, and holocellulose of the wastes of 5 bamboo species, were analyzed according to TAPPI test methods (1994) of T 207 om-93, T 204 om-88, T 222 om-88, and T 249, respectively.

A thermal gravimetric analyzer (TGA, Mettler-Toledo TGA-851, Zurich, Switzerland) was used as an indirect tool to analyze changes in the chemical compositions of the bamboo wastes by hot-water-extraction treatment. Five milligrams of a specimen was used for each test in the TGA at a nitrogen flow rate of 50 mL min^{-1}. The pyrolysis temperature was programmed from room temperature to 600℃ at an increasing temperature of 10℃ min^{-1}. A derivative thermogravimetric analysis (DTG) provided a derivative form (rate

Table 1. Main components of 5 local bamboo species

Specimen		Extractives (%)		Lignin (%)	Holocellulose (%)
Species	Abbreviation	Hot water	Ethanol /benzene		
Dendrocalamus latiflorus	Dl	9.85	1.69	24.17	73.45
Phyllostachys makinoi	Pm	7.11	3.40	26.29	73.68
Bambusa stenostachya	Bs	8.60	3.77	26.21	70.65
Bambusa dolichoclada	Bd	11.66	4.07	25.41	69.73
Phyllostachys pubescens	Pp	5.46	2.63	29.20	69.16

of mass loss) of the thermogravimetric signal and was calculated using a computer.

The surface chemistry of the hot-water-extracted specimens was investigated by electron spectroscopy (ESCA, Perkin Elmer PHI-1600, Waltham, Massachusetts, USA) with an unmonochromated magnesium Kα x-ray source, at 15 kV and 250 W. Specimens were mounted on a holder with double-sided adhesive tape and placed in a vacuum below 2×10^{-8} torr. Each specimen was analyzed at a take-off angle of 45° relative to the electron detector, and the spectra were deconvoluted using a curve-fitting program by PHI-Multi-Pak software Version 8.0 (ULVAC-PHI, Inc. Chigasaki City, Japan).

Preparation of hot-water-extracted bamboo wastes

In addition to the air-dried bamboo, hot-water-extracted bamboo was prepared by boiling bamboo for 1 h in a Soxhlet apparatus and then drying it in a 60℃ oven for 48 h.

Porosity analysis

The effect of hot-water-extraction treatment on the porosity of bamboo was analyzed by a mercury/non-mercury porosimeter (PMI 60K-A-Z, Ithaca, New York, USA). Particles sizes ranging 40~60 mesh were used.

Batch adsorption test

In each adsorption experiment, different dosages (0.05, 0.1, 0.2, and 0.4 g) of a specimen were added to 20 mL of a known concentration and pH value of metal ion solutions. The effect of pH on biosorption was evaluated in the pH range of 2.0~13.0. The pH of the metal solutions was adjusted to the desired value with either an NaOH or HCl solution. After vibrating the samples for 1, 2, 4, 8, and 24 h at room temperature, the mixture was filtered. All biosorption experiments were run in triplicate. The metal ion concentrations in the filtrate and the initial concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Spectro Ciros 120, Kleve, Germany). The removal efficiency and absorption capacity were calculated according to the following equations (Yang et al. 2005):

Removal efficiency (%) = $(Cb - Ca) \div Cb \times 100$ and

Adsorption capacity (Q, mg g^{-1}) = $V (Cb - Ca)/M$;

where Cb and Ca are the concentrations of metal ions before and after adsorption (mg L^{-1}), Q is the absorption capacity (mg metal ions (g absorbent)$^{-1}$), V is the volume of the metal ion solution (L), and M is the weight of the test sample (g).

RESULTS AND DISCUSSION

Chemical composition of the bamboo wastes

The main chemical compositions of the 5 bamboo species are shown in Table 1. Among them, Bd contained higher amount of extractives when extracted with either hot water or ethanol/benzene (1/2, v/v); Pp contained a higher amount of lignin; while Dl and Pm contained higher amounts of holocellulose.

Effects of hot-water-extraction treatment on the bamboo's chemical structure

Variations in the chemical structure of the bamboo specimens before and after hot-water-extraction treatment were evaluated by ESCA and TGA.

The 3 components of the C_{1s} peak can be assigned to 3 different classes of carbon atoms present in the test specimens: the C_1 peak corresponds to a carbon atom bound to a hydrogen atom or to another carbon atom, i.e., C-H or C-C bonds; the C_2 peak corresponds to a carbon atom singly bound to an oxygen atom, i.e., C-O; and the C_3 peak corresponds to carbon doubly bonded to an oxygen atom, i.e., C = O, or to 2 oxygen atoms, i.e., O-C-O (Bouanda et al. 2002). The ESCA spectrum of the control and hot-water-extracted bamboo Dl demonstrated that the relative amounts of both C_2 (C-O) and C_3 (C = O or O-C-O) increased from 37.0 and 5.2 to 39.2 and 8.3%, respectively (Table 2). This indicates that hot-water-extraction treatment played a positive effect in the metal removal efficiency as more metal binding-related functional groups were exposed.

Changes in the chemical compositions by the hot-water-extraction treatment were also evidenced by the TGA test. Figure 1A shows that the maximum temperature peaks in the pyrolysis of hemicellulose, holocellulose, and lignin of bamboo Dl were 291, 337, and 368℃, respectively. The combination of these 3 peaks is shown in Fig. 1B, and its pyrolysis peak was 313℃. However, the pyrolysis peak of hot-water-extracted bamboo Dl shifted to a higher temperature (Fig. 1C), and resulted in the lack of a partial peak. Meanwhile, the onset temperature of hot-water-extracted bamboo Dl increased from the control of 235.1 to 324.3℃ and had a lower weight-loss rate during the initial pyrolysis stage. All results from TGA indicated that low-molecular-weight materials like hemicellulose in the bamboo specimens were removed during hot-water-extraction treatment.

Table 2. Relative intensities of C_{ls} peak components of bamboo Dl before and after hot-water-extraction treatment

Treatment	C_{ls}, %		
	C_1	C_2	C_3
	C-C C-H	C-O	C=O O-C-O
Dl (control)	57.8	37.0	5.2
Hot-water extracted Dl	52.5	39.2	8.3

Effects of reaction time, pH value, and sample particle size on the metal removal ability of bamboo wastes

Simple batch kinetic experiments for determining the removal efficiency of Cu (II), Pb (II), Cd (II), and Ni (II) by bamboo Dl were conducted as illustrated in Fig. 2.

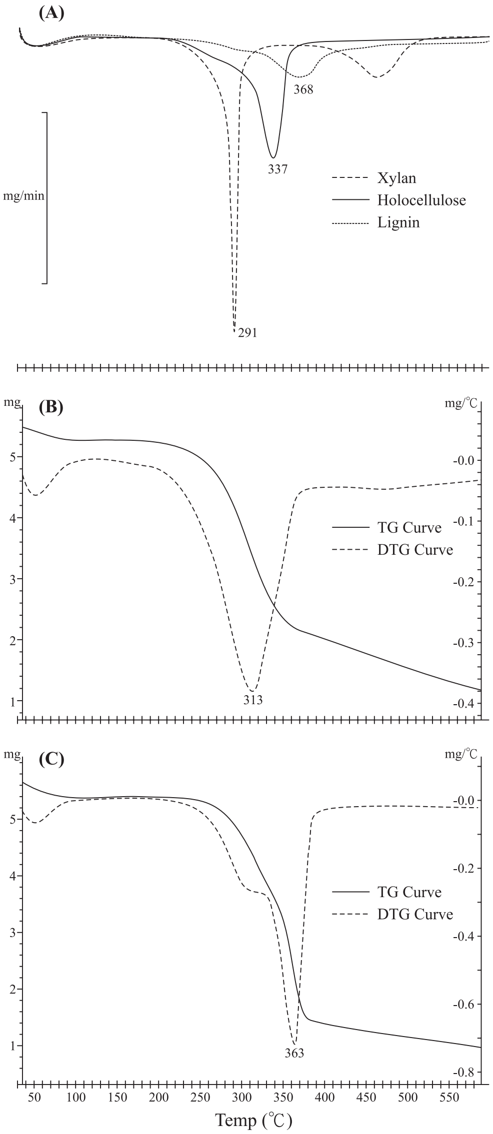

Fig. 1. TGA and DTG curves for nitrogen of (A) xylan, lignin, and holocellulose of *Dendrocalamus latiflorus*; (B) *D. latiflorus*; (C) hot-water-extracted *D. latiflorus*.

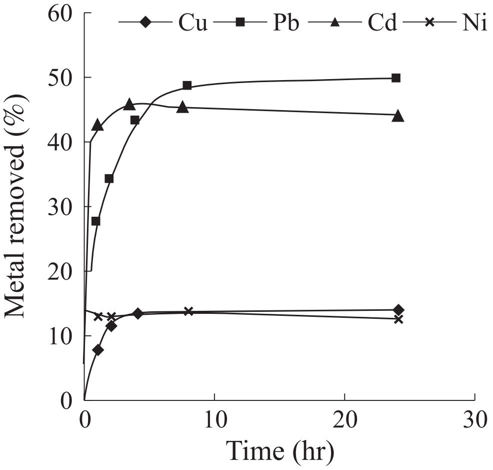

Fig. 2. Cu (II), Pb (II), Cd (II), and Ni (II) adsorption kinetics on *Dendrocalamus latiflorus* (0.4 g of specimen was added to 20 mL of metal ion solutions at pH 4).

Among the 4 tested metal ions, Dl adsorbed more Cd (II) and Pb (II) than Ni (II) and Cu (II). The removal efficiency of bamboo Dl increased with a longer reaction time. It was found that metal ions were rapidly absorbed by bamboo Dl during the first 4 h, and after exposure for 4~8 h, the adsorption of metal ions reached an equilibrium. Furthermore, extending the exposure time beyond the equilibrium point did not further increase the metal removal efficiency by bamboo Dl. Similar results were also found in Yang's (2005) study.

Figure 3 showed the effect of pH values on metal ion adsorption by bamboo Dl. The optimum pH value for metal adsorption of bamboo Dl was in the range of 4~6. There was a tendency for the removal efficiency of metal ions to significantly decrease at a lower pH. The absence of adsorption at low pH values can be explained by the fact that at lower pH, the H^+ ion concentration is high, which can compete with metal cations for exchange sites in the system. On the contrary, rapid precipitation of ions occurred when pH values exceeded 8.0, so the results could not be used.

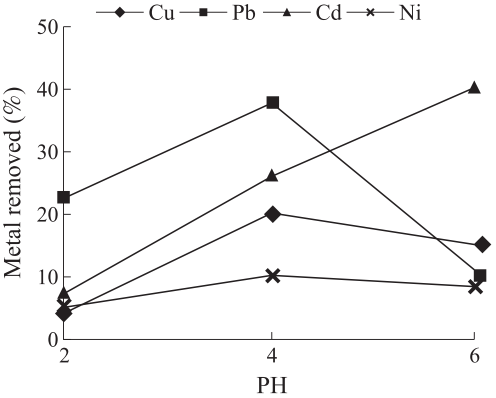

Fig. 3. Effects of pH on the adsorption of Cu (II), Pb (II), Cd (II), and Ni (II) by *Dendrocalamus latiflorus* (0.4 g of specimen was added to 20 mL of metal ion solutions).

Figure 4 shows the effect of sample particle size on metal ion adsorption. The adsorption capacity of bamboo Pp was affected by particle size, and its effectiveness was in the order 80~100 > 60~80 > 40~60 mesh. Apparently, the adsorption capacity of heavy metals by bamboo waste increased as the particle size decreased.

Comparison of the metal-removal ability of bamboo Dl and 4 positive controls at different dosages

The batch adsorption tests of bamboo Dl and 4 positive controls were conducted by shaking 0.05, 0.1, 0.2, and 0.4 g of adsorbents with 20 mL of a 10 ppm metal solution at pH 4, and the results are shown in Fig. 5. Among the test materials, activated carbon was the most effective, followed by exhausted coffee, exhausted tea, and bark, and the last was bamboo Dl. Activated carbon reached almost 100% removal efficiency at all tested dosages. *Acacia* bark, exhausted coffee, and exhausted tea also showed good metal-removal efficiencies with the same tendency: the removal efficiency increased with an increasing dosage.

However, the removal efficiency of bamboo Dl was < 50% at all tested dosages.

Effects of hot-water-extraction treatment on the metal-removal ability of bamboo wastes

Despite exhausted coffee, exhausted tea, and bark showing good metal-removal efficiencies, they leached some organic matter into the water during the adsorption test, resulting in discoloration of the water which could limit their application as a biosorbent. In order to reduce the leaching effect, all of the biomaterials were extracted with boiling water for 1 h in a Soxhlet apparatus before the metal adsorption test. It was interesting to find that the metal-removal efficiency improved after the hot-water-extraction treatment, especially for *Acacia* bark and bamboo Dl. As shown in Fig. 6A, bamboo Dl exhibited a dosage-dependent relationship with the copper-removal efficiency. Hot-water-extraction treatment improved the metal-removal efficiency of bamboo Dl at a dosage of 0.4 g, increasing from 8.65 to > 80%. Moreover, similar results were obtained for *Acacia* bark, and its copper ion-removal efficiency improved from 60.11 to 80.45%, at a dosage of 0.4 g after hot-water-extraction treatment. The results indicated that hot-water-extraction treatment can improve the copper-removal abilities of bamboo Dl and *Acacia* bark. The

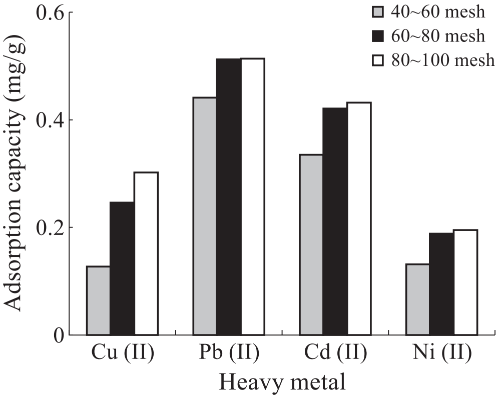

Fig. 4. Effects of particle size on metal adsorption by *Phyllostachys pubescens* (0.4 g of specimen was added to 20 mL of metal ion solutions at pH 6).

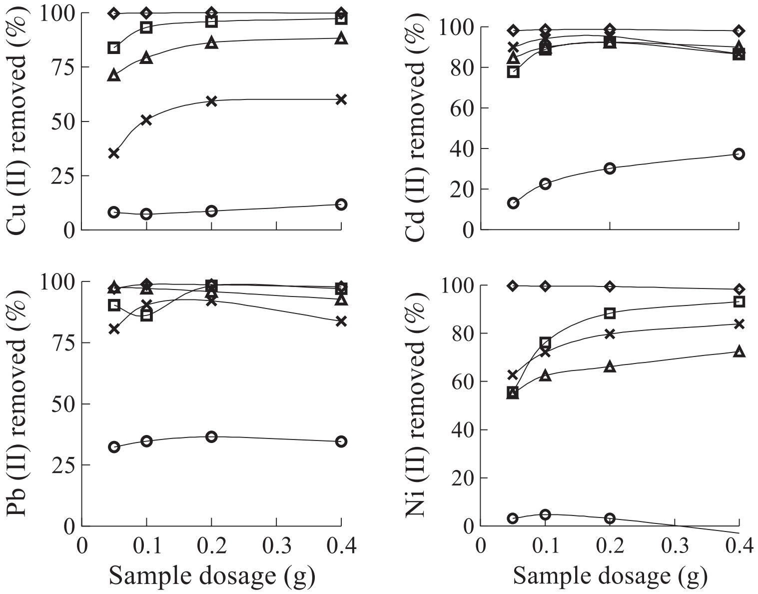

Fig. 5. Effects of specimen dosage on the metal adsorption test. ◇ Activated carbon; □ exhausted coffee; △ exhausted tea; × *Acacia* bark; ○ bamboo (Dl).

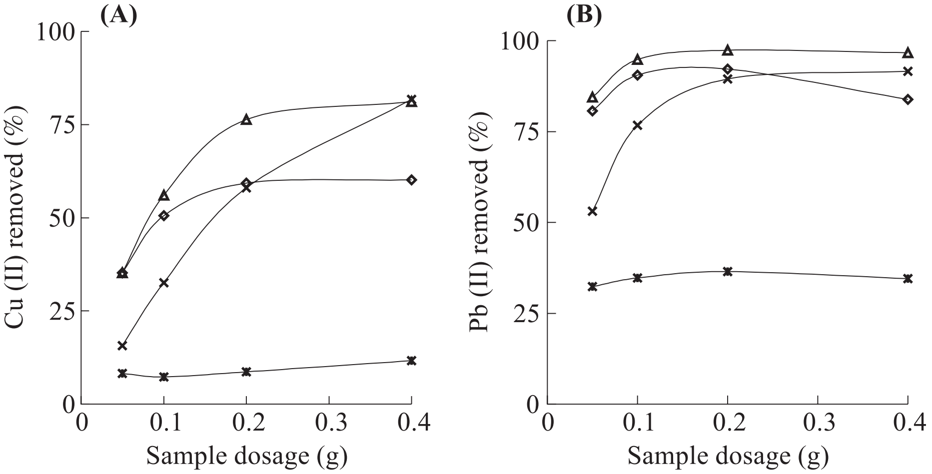

Fig. 6. Effects of hot-water-extraction treatment on (A) copper (II) and (B) lead (II) removal efficiencies of bamboo Dl and *Acacia* bark. ◇ *Acacia* bark; △ hot-water-extracted *Acacia* bark; ✱ Dl; × hot-water-extracted bamboo Dl.

same tendency was also observed in the lead-removal test as shown in Fig. 6B.

The metal removal efficiencies of the other 4 species of bamboo waste after hot-water-extraction treatment were also evaluated. Figure 7 shows the results of copper-removal efficiency between the raw bamboo and hot-water-extracted bamboo wastes. Among the 5 species of bamboo, Pp, which contained the highest amount of lignin, showed the best adsorption capacity, while Dl and Pm, which contained higher amounts of holocellulose, displayed the least ability to remove Cu (II).

As shown in Fig. 7A, the copper-removal efficiencies of bamboo Dl, Bd, and Pm wastes at a dosage of 0.05 g slightly improved with hot-water-extraction treatment, compared to the untreated controls, namely by increasing the respective removal efficiencies from 11.4, 20.5, and 9.4 to 18.4, 22.9, and 18.8%. When the specimen dosage was increased to 0.4 g, the copper-removal efficiency for bamboo Dl, Pp, Bd, Bs, and Pm wastes greatly improved from 13.4, 35.7, 25.1, 33.0, and 6.7 to 81.1, 79.4, 75.3, 89.7, and 50.6%, respectively. The results revealed that increasing the specimen

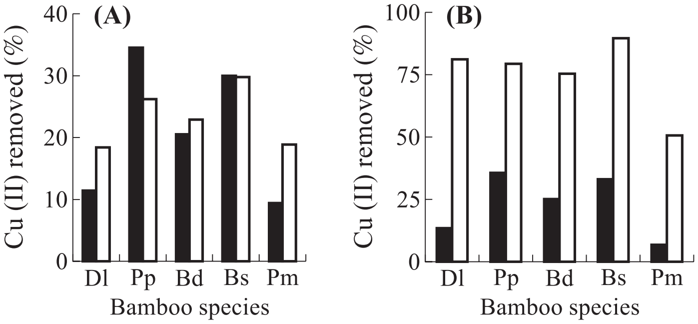

Fig. 7. Effects of hot-water-extraction treatment on the copper (II) removal efficiency of 5 local species of bamboo wastes. (A) At a dosage of 0.05 g and (B) at a dosage of 0.4 g. ■ Control; □ hot-water treated.

dosage of bamboo waste synergistically promoted the hot-water-extraction treatment's effect and thus also improved the copper-removal efficiency in the aqueous solution.

Effects of hot-water-extraction treatment on the porosity of bamboo wastes

The effect of hot-water-extraction treatment on the physical properties, including pore diameter, pore volume, and pore surface area, of bamboo Dl were evaluated. The pore diameter of bamboo Dl was analyzed from 0 to 100 μm. As shown in Fig. 8A, the volume of small pores (0.005 μm) greatly increased from 6.2 to 27.3 mL g^{-1} after hot-water-extraction treatment. No significant difference between the control and hot-water-extracted sample was observed when the pore diameter was > 0.06 μm (data not shown). A similar result also appeared in the surface area of small pores (0.005 μm), and the volume increased from the control bamboo Dl at 424.2 m^2 g^{-1} to the hot-water-extracted bamboo Dl at 909.1 m^2 g^{-1} (Fig. 8B). When the pore diameter was > 0.25 μm, no difference was observed between the control bamboo Dl and hot-water-extracted bamboo Dl (data not shown). It is clear that increments in the volume and surface area of small pores contributed to an increase in the porosity of hot-water-extracted bamboo Dl. Moreover, the greater volume and surface area present in bamboo specimens after hot-water-extraction treatment may have contributed to the increased metal-binding efficiency.

From the results of TGA, the heavy-metal-removal efficiency partially decreased by hot-water-extraction treatment because of the possible loss of the binding of low-molecular-weight materials, whereas the results of ESCA and porosimeter indicated that the heavy-metal-removal efficiency of bamboo wastes greatly increased by hot-water-extraction treatment because of the release of more functional groups, available volume, and surface area. To sum up, low-molecular-weight materials were easily extracted by water from bamboo wastes, resulting in changes to the chemical compositions, the exposure of more metal binding-related functional groups, and the availability of greater surface area and volume of small pores. Such changes improved the metal-removal efficiency in the long run.

CONCLUSIONS

This study investigated the metal-ion adsorption abilities of wastes of 5 local bamboo species. Results showed that the adsorption

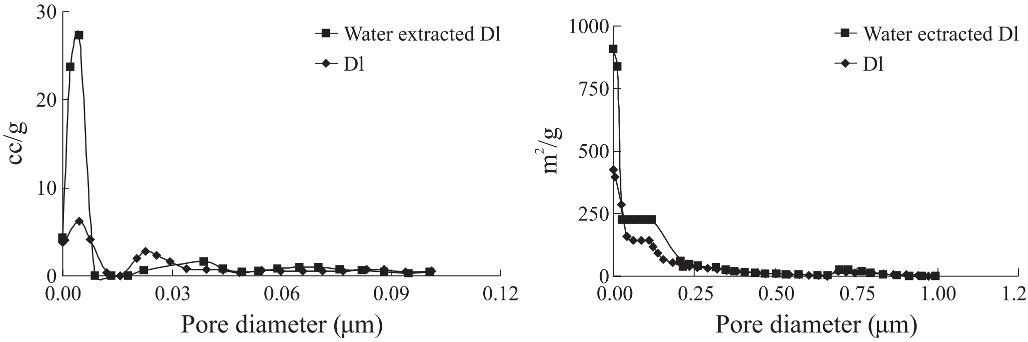

Fig. 8. Changes in the porosity of bamboo Dl after hot-water-extraction treatment. (A) Pore volume; (B) pore surface area.

capacity increased with prolongation of reaction times and decreased as the particle size increased. Optimum pH values for metal adsorption were in the range of 4~6. Among the tested bamboo samples, *Phyllostachys pubescens* was the most effective in removing heavy metal ions from aqueous solutions. The metal-removal efficiency of raw bamboo can be greatly and easily improved by hot-water-extraction treatment. The performance of heavy-metal removal of hot-water-extracted bamboo waste was even better than that of bark, exhausted coffee, and exhausted tea. This may be due, in part, to hot-water-extraction treatment effectively increasing the available volume and surface area of the treated bamboo. Therefore, hot-water-extracted bamboo wastes may be a potential alternative biosorbent to remove heavy metals from industrial effluents.

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