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Removal of Copper in Aqueous Solution by Apple Wastes

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ABSTRACT

Removal of copper from a solution was investigated to evaluate the cation-exchange capacities of apple residues from agricultural wastes. The effects of solution pH, ionic strength, co-ion, ligands, initial metal concentrations, and particle size of apple residues were studied. The optimal pH range for copper removal by apple residues was shown to be from pH 5.5 to 7.0, and the maximum percentage of copper removal was 91.2%. Increasing ionic strength, up to 0.1 N, has little effect on metal uptake. The presence of co-ions such as lead decreases the removal capacity of copper as expected. The presence of ligands, such as EDTA and ammonia, also reduces metal removal efficiency due to the formation of a metal–ligand complexation in solution. Equilibrium of copper sorption was established very rapidly initially and decreased markedly after 1 hour. Equilibrium isotherms of copper fit the Langmuir equation adequately. Column experiments showed that the dynamic capacity of chemically modified apple residues was four to five times higher than that of raw residues which contained acidic groups such as carboxylic and phenolic functional groups. The adsorbed copper ions were completely recovered with three bed volumes of 0.5 N HCl. Thus, modified apple residues could be applied successfully for metal removal from wastewater.

INTRODUCTION

Public concern over heavy metal pollution has grown constantly since the outbreak of Minamata disease caused by mercury in Japan (1). Man's awareness of the heavy metal hazard now covers a wide spectrum of metals such as lead, cadmium, chromium, copper, and zinc (2). To curtail heavy metal pollution problems, engineerers and scientists have developed processes and measures for the treatment and disposal of metal-containing wastewater: chemical precipitation, ion exchange, membrane separation, adsorption process, and solvent extraction (3–6). However, these methods are relatively expensive, involving either elaborate and costly equipment or high cost operation and energy requirements. Therefore, there is a need for the development of more cost-effective methods.

Recently, recovery and recycling of organic residues (agricultural, urban, fish industry, etc.) has become one of the main fields of investigation in developed countries due to their large waste volume (7, 8). Scott (8) used tobacco and tomato root tissue as biosorbents for the removal of trace amounts of Sr from aqueous streams in nuclear processing facilities. Because apple residues (AR) are solid wastes that must be disposed of, an investigation of its use as a adsorbent seems most appropriate. In the present study, AR were used as a natural cation-exchange material for removing copper ions from aqueous solution. In order to study the feasibility of practical application, batch experiments were performed to see the effect of pH, ionic strength, ligands, co-ions, and particle sizes. Adsorption isotherms were also presented. Chemical treatment of AR was investigated to improve the mechanical strength of the adsorbent and copper removal capacity.

Column experiments were also carried out to investigate the influence of feed concentration, chemical treatment, and elution characteristics.

MATERIALS AND METHODS

AR for these experiments were obtained from an apple-juice processing factory. They consist of the processed skins, seeds, and stems, and contain as much as 12% of the wet weight of original fruit. AR contain 30% of cellulose and 19% of lignin, both with a capacity for binding metal cations due to their carboxylic and phenolic groups. AR were dried overnight at 60°C in a convection oven, ground by a ball mill, and sieved into different fractions. The soluble components (sugars, coloring agents, etc.) were eliminated by washing with 0.5 N HCI and distilled deionized water. In order to improve the structural stability and ion-exchange capacity, AR was chemically modified. The phosphated apple residues (P-AR) were obtained by treatment with phosphorus(V) oxychloride in alkaline medium according to the procedure of Peska et al. (9) for the phosphation of cellulose. Ethylenediamine tetraacetic acid (EDTA) and ammonia were chosen as organic and inorganic ligands. Ionic strength in solution was adjusted with NaCl.

Batch experiments were performed at room temperature, and samples were prepared in duplicate. All the glassware and polyethylene tubes were acid-cleaned and rinsed thoroughly with distilled deionized water before use. Various initial copper concentrations were prepared by dilution of 1000 ppm of a standard solution of Atomic Absorption Spectrophotometer (AAS). The copper solution thus prepared was added to each test tubes containing preweighted AR (0.01 g g AR/10 mL or 20 mL copper solution).

Blank tests were also performed without AR to investigate the removal which would occur via copper precipitation and adsorption on the glass wall. The pH in solution of test tubes was adjusted with 0.1 N/1 N NaOH and 0.1 N/1 N HCl to cover the pH range from 2 to 12, and then the test tubes were sealed with caps and placed on a rotary shaker (Roto-Torque model 7637, Coleparmer Instrument Co., USA). Test tubes were removed after shaking for 24 hours and centrifuged for 5 minutes at 3000 rpm. Supernatant was analyzed by flame AAS (Perkin-Elmer, Model 3100) for residual copper contents. Adsorption isotherms were carried out by adding a known amount (0.05–1.2 g) of AR and P-AR to seven different flasks which contained a 100-mL copper solution of 30 ppm at pH 4 and 25°C.

Kinetic studies for copper removal by AR were carried out in a 200-mL copper solution of 10 ppm with 0.2 g AR. A sample was taken periodically from the suspension and centrifuged immediately to remove adsorbents. The column tests for copper removal were carried out in a glass column of 1.5 cm internal diameter and 30 cm length with AR and P-AR. The copper solution was percolated through the packed column at a flow rate of 5 mL/min controlled by a peristaltic pump (EYELA SMP-21 Japan). Effluent samples were collected every 30 minutes for the measurement of pH and copper concentration. After exhaustion of the adsorbent, the adsorbed metal ions were recovered by elution with 0.5 N HCl. After washing with water to eliminate the excess of mineral acid, AR and P-AR were ready for reuse.

RESULTS AND DISCUSSION

Batch Experiments

Sorption Kinetics

The uptake of copper with time at an initial concentration of 10 ppm at pH 3.9, pH 5.9, and pH 6.4 is shown in Fig. 1. The rate of copper sorption

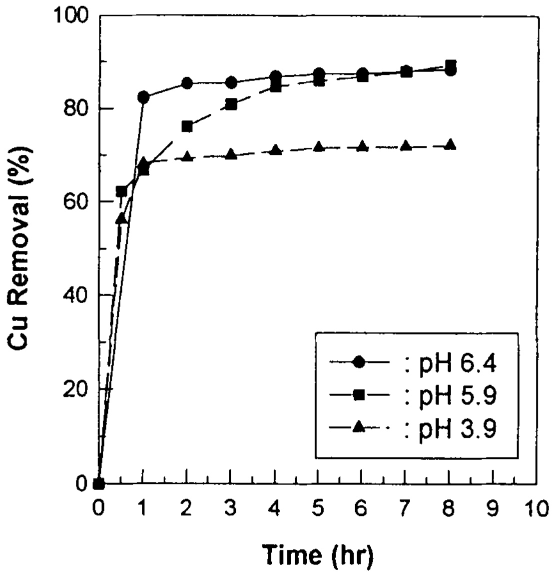

FIG. 1 Kinetics of copper removal at different solution pH (Cu, 10 ppm; AR, 0.2 g/200 mL; I, 0.01 N NaCl).

was very rapid initially and decreased markedly after 1 hour. The functional groups of AR act initially as copper coordination sites. The slower removal rate of copper after an initial rapid uptake can be due to the binding of copper by complexed metal ions. A similar initial rapid uptake of cadmium by chitosan has been reported by Jha et al. (4). Based on the experimental results, an equilibrium contact time of 24 hours was used in all further experiments for copper removal.

Adsorption Isotherms

Figure 2 shows adsorption isotherms for AR and P-AR. The results indicate that copper uptake capacities are 10.8 mg Cu/g AR and 36.2 mg Cu/g P-AR in the present experimental conditions. The isotherms present a very steep rise at low copper concentration which illustrates a high affinity of these residues for copper ions in solution. P-AR were approximately four times higher than that by AR in the removal capacity of copper. Experimental results were fitted to the Langmuir equation in a linear form. Equilibrium isotherms of copper fit the Langmuir equation adequately. The copper binding capacities by AR and P-AR are compared in Table 1 with those of other biomaterials obtained by previous data.

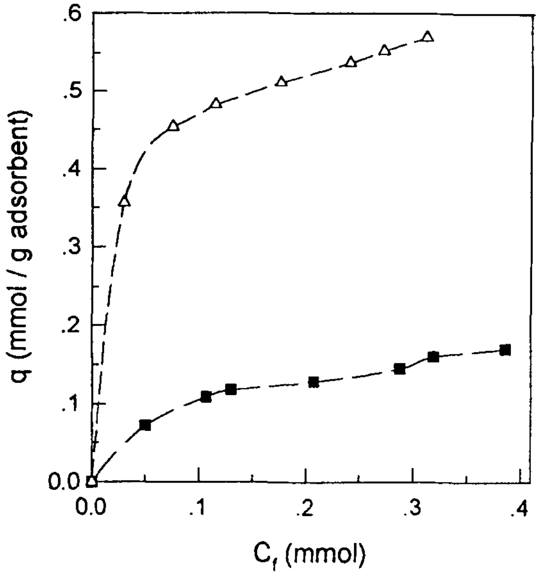

FIG. 2 Copper uptake isotherms for AR and P-AR (Cu, 30 ppm; I, 0.1 N NaCl; pH 4; ■ AR; △ P-AR).

TABLE 1
Binding Capacities of Several Biomaterials

Biomaterials	(mg Cu)/ (g biomaterial)	Source
Datura innoxia[a]	7.2	Lujan et al. (10)
Alfalfa sprouts[a]	18.0	Lujan et al. (10)
Sphagnum peat moss[a]	30.4	Lujan et al. (10)
MTW leaves[a]	9.0	Lujan et al. (10)
Visible *S cerevisiae*[b]	1.9	Huang et al. (11)
AR	10.8	This study
P-AR	36.2	This study

[a] Higher plant tissues, samples of 5 mg biomaterial were suspended in a solution of 0.31 mM Cu(II) at pH 5.

[b] Yeast, sample of 2 g/L was suspended in a solution of 0.05 mM Cu(II) at pH 4.

Effect of pH

The pH of a solution has been identified as the most important variable which governs metal adsorption on hydrous solids. This is partly due to the fact that hydrogen ions themselves are strong competing adsorbates, and partly that the solution pH influences the speciation of metal ions and the ionization of surface functional groups.

In Fig. 3 the effect of pH for copper removal in a ligand-free system is illustrated. The optimal pH range for copper removal was from 5.5 to 7.5. The maximum removal was 91.2% for the copper ion concentration of 10 ppm. These results have a connection with the speciation of copper ions. Copper forms soluble complexes with hydroxide. The distribution of copper species is a function of pH. As shown in Fig. 4, the divalent cation, Cu^{2+}, and a monovalent cation, $Cu(OH)^+$, are dominant metal species at the optimal pH range from 5.5 to 7.5. Based on the experimental results and speciation of copper ions, copper removal by AR may occur by complexation between the negative charged functional group and copper cations such as Cu^{2+} and $Cu(OH)^+$. Monovalent cation $Cu(OH)^+$ may be the dominant metal species for copper removal by AR. Blank tests are also shown in Fig. 3 to verify that the removal mechanism is purely bio-

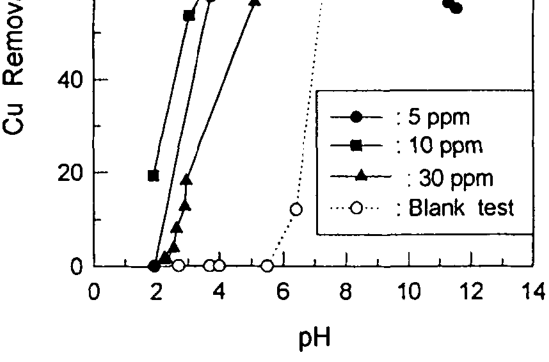

FIG. 3 Effect of pH on the removal of copper. (AR, 0.01 g/10 mL; I, 0.01 N NaCl).

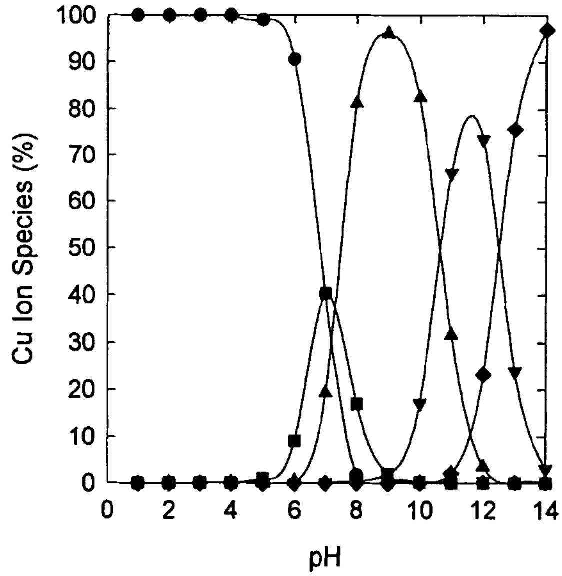

FIG. 4 Speciation of copper ions. [Cu, 10 ppm; I, 0.01 N NaCl; ● Cu^{2+}; ■ $Cu(OH)^+$; ▲ $Cu(OH)_2$; ▼ $Cu(OH)_3^-$; ● $Cu(OH)_4^{2-}$; the numerical values of metal compex formation constants used in the calculation of speciation curves were obtained from chemistry handbooks (13, 14)].

sorption. As indicated in the plot, precipitation occurs at a pH greater than 5.5. However, if precipitation does contribute to the removal mechanism, the removal capacity should not have decreased at a pH greater than 7.5. The decrease in copper removal capacity at pH > 7.5 may be caused by the complexation of copper with hydroxide. Copper anions, $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$, may be dominant ion species.

Effect of Ionic Strength

Figure 5 shows the influence of ionic strength on the removal of copper by AR. The result indicate that up to 0.1 N NaCl, there was no significant decrease in copper removal. But increasing ionic strength over 0.1 N NaCl results in about a 40% decrease of copper removal capacity. Adsorption is sensitive to the change in concentration of the supporting electrolyte if the electrostatic attraction is a significant mechanism for metal removal. Based on the result of this experiment, electrostatic attraction in a low concentration of sodium chloride plays a negligible role in the removal of copper, but at a high ionic strength the increased amount of electrolyte

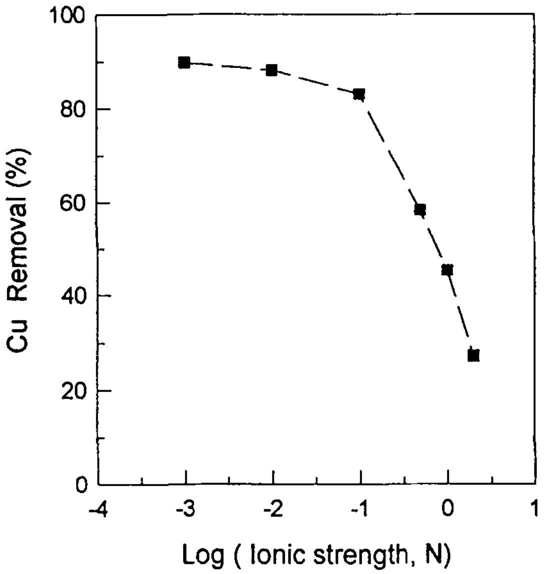

FIG. 5 Effect of ionic strength on the removal of copper (Cu, 10 ppm; AR, 0.01 g/10 mL; pH 6.2).

can swamp the surface of the AR, decreasing copper ions access to the AR surface for adsorption. Thus, copper removal may be decreased significantly. These results can also be explained by considering the competitive effect of Na^+ ions for copper binding. The ion exchanger tends to prefer the counterion of higher valance (12). Therefore, Cu^{2+} ion is more selective than Na^+ ions for a cation exchanger. Based on experimental results, AR may prefer Cu^{2+} ions to Na^+ ions. Therefore, the competitive effect of Na^+ ions for copper removal by AR may be low, especially at low ionic strength.

Effect of Ligands

The effects of organic and inorganic ligands were investigated for copper removal by AR. Figure 6 shows the effects of organic (EDTA) and inorganic (ammonia) ligands for copper removal by AR. From Fig. 7 which indicates copper ion speciation in the presence of EDTA, we can see EDTA is a strong cheating agent and forms complexes with copper ions over the 2 to 12 pH range. Copper removal by AR in this pH range was significantly decreased due to the formation of the copper–EDTA com-

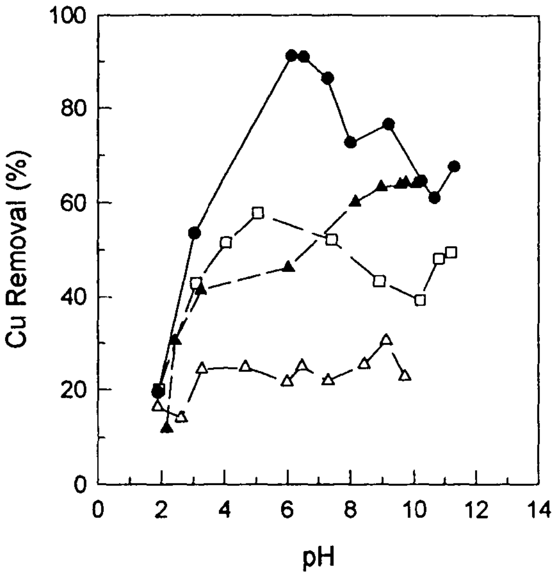

FIG. 6 Effect of ligands on the removal of copper [Cu, 10 ppm; AR, 0.01 g/10 mL; I, 0.1 N NaCl; ● ligand-free; □ Cu:EDTA (1:1 molar ratio); △ Cu:EDTA (1:10 molar ratio); ▲ Cu:NH_3 (1:3 molar ratio)].

plex. The degree of decrease in copper removal capacity increased with an increase of the copper–EDTA molar ratio. As in the case of EDTA, the presence of ammonia in solution reduced copper removal capacity due to the formation of the copper–ammonia complex. These results can also be explained by copper ion speciation in the presence of ammonia as shown in Fig. 8. In the pH range of 2 to 7, the removal capacity of copper by AR was dramatically decreased due to copper–ligand complex formation. However, in the pH region beyond pH 7, the degree of copper–ligand complex formation was decreased since the monovalent cation $Cu(OH)^+$ becomes the dominant species. Thus, the capacity for copper removal by AR increased gradually.

Effect of Co-ion

The effect of co-ions (Ni and Pb) on copper removal by AR is indicated in Fig. 9. In the control case, the removal of copper ion was approximately 69% at an initial concentration of 10 ppm at pH 5.2. When nickel ion was present as a competing metal at a molar ratio of 1:1, a small reduction of

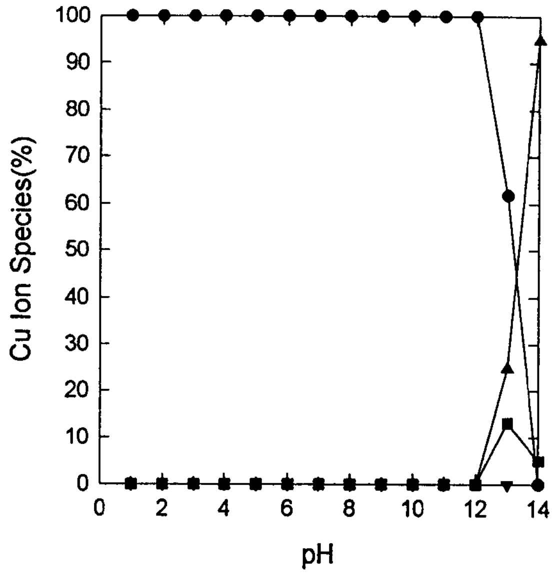

FIG. 7 Speciation of copper in the presence of EDTA [Cu, 10 ppm; I, 0.1 N NaCl; EDTA, 1.57E(−4) mole; ● Cu(EDTA); ■ $Cu(OH)_3^-$; ▲ $Cu(OH)_4^{2-}$; the numerical values of metal–ligand compex formation constants used in the calculation of speciation curves were obtained from chemistry handbooks (13, 14)].

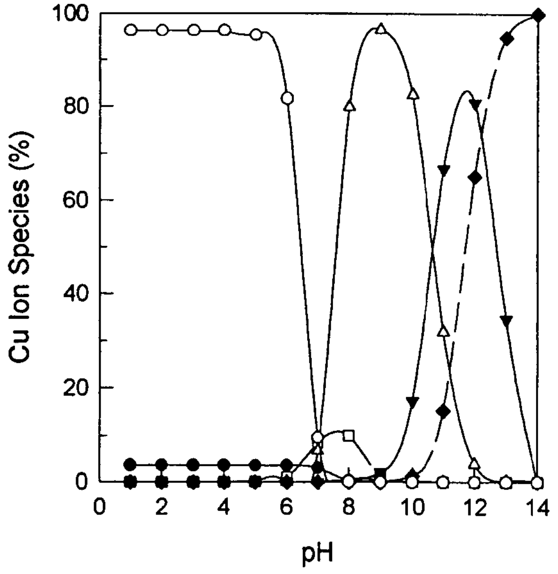

FIG. 8 Speciation of copper in the presence of ammonia [Cu, 10 ppm; I, 0.1 N NaCl; NH_3, 4.71E(−4) mole; ● Cu^{2+}; ○ $Cu(NH_3)$; □ $Cu(OH)^+$; △ $Cu(OH)_2$; ▼ $Cu(OH)_3^-$; ● $Cu(OH)_4^{2-}$; the numerical values of metal–ligand compex formation constants used in the calculation of speciation curves were obtained from chemistry handbooks (13, 14)].

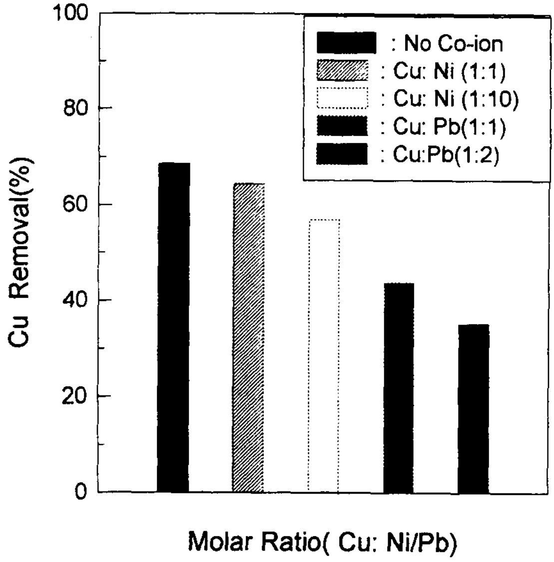

FIG. 9 Effect of co-ions (Ni,Pb) on the removal of copper (AR, 0.01 g/20 mL; Cu, 10 ppm; I, 0.1 N NaCl; pH 5.2).

copper removal was observed. As the molar ratio increased to 1 : 10, even more reduction of copper removal yield was noticed.

In case of lead, as indicated in Fig. 9, a 25% reduction in copper removal yield was observed when the lead ion was present at a molar ratio of 1 : 1. These results can also be explained by the selectivity sequence of the most common cations in a cation exchanger. In general, Pb^{2+} ion is more selective than Ni^{2+} ions in cation exchangers (12). Based on these experimental results, Pb^{2+} ion may be a stronger competitive ion than Ni^{2+} ion for copper removal by AR. AR may prefer Pb^{2+} ion to Ni^{2+} ions.

Effect of Particle Size

The effect of the particle size of AR for copper removal was studied by employing three different particle sizes: 273.5, 460, and 651 μm. Each particle size has a minimum and maximum: 273.5 (250–297), 460 (420–500), and 651 (595–707) μm. As shown in Fig. 10, a decrease in particle size has a favorable effect on copper removal by AR. These results can be explained by an increase in the surface area of AR with a decrease of AR particle size. Therefore, more functional groups on AR can be used to bind metal ions.

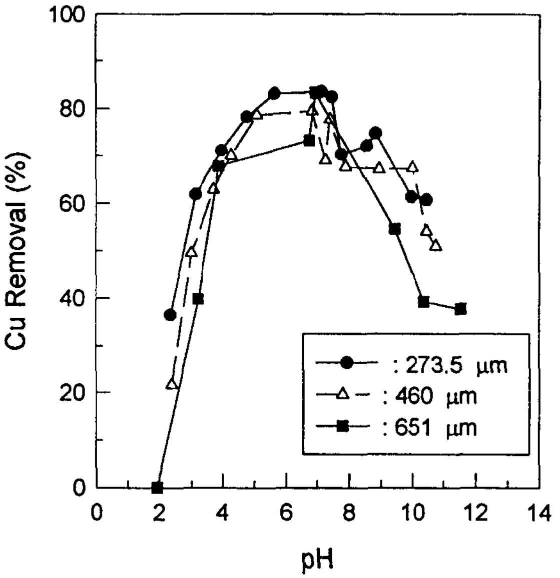

FIG. 10 Effect of AR particle sizes on the removal of copper (Cu, 10 ppm; AR, 0.01 g/10 mL; I, 0.01 N NaCl).

Effect of Chemical Treatment

Because AR consists of the processed skins, seeds, and stems, and contains as much as 12% of the wet weight of the original fruit, these residues have a structural instability on prolonged use. In order to strengthen the structure and increase the low cation-exchange capacity of AR, they were treated with phosphorus(V) oxychloride by Peska method (9).

In this work the effect of chemical treatment for copper removal was investigated using AR and P-AR. Based on the results in Fig. 11, the copper removal capacity by P-AR was higher than that by AR, especially at low pH regions, due to the presence of phosphate groups in P-AR. This can be explained by the speciation of copper. In acidic pH regions the dominant metal ions species is divalent cation, Me^{2+}. Therefore, the phosphate groups in P-AR may effectively bind the free metal ions. The optimal pH zone for copper removal by P-AR was broader and the maximum uptake capacity was higher (98.5%) than by AR.

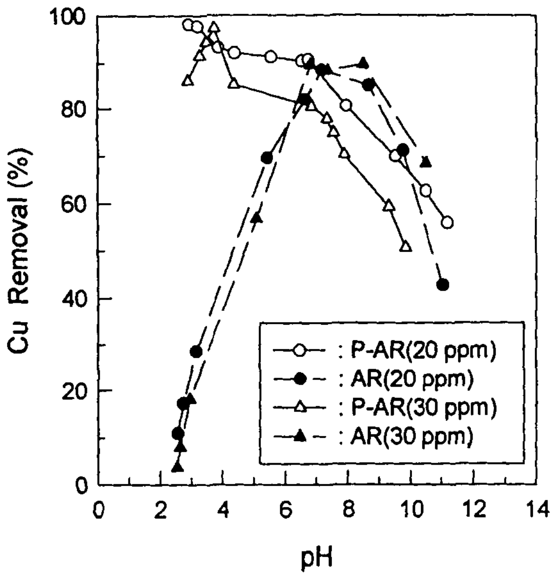

FIG. 11 Effect of chemical treatment of AR on the removal of copper (AR and P-AR, 0.01 g/10 mL; I, 0.1 N NaCl).

Column Experiments

The column tests for copper removal were carried out in a glass column of 1.5 cm internal diameter and 30 cm length with AR and P-AR. When the column was filled with 3 g of AR by the slurry packing method, the bed height immediately swelled to 13 cm from the original height of approximately 5 cm. However, with the same weight of P-AR, the height became 7.2 cm, which indicates a far smaller swelling ratio. The swelling ratio of P-AR decreased several times in comparison with AR. This result could be explained by the fact that phosphorus(V) oxychloride might have acted as a crosslinking agent.

Effect of Feed Concentration

The effect of feed concentration on copper removal by AR is shown in Fig. 12. The flow rate of feed metal solutions was 5 mL/min. The pH of the feed solutions was maintained at 4.12. Breakthrough occurred at 86 bed volumes (1975 mL) when the copper concentration was 10 ppm; it appeared at 13.1 bed volumes (300.8 mL) with 49.5 ppm of copper solu-

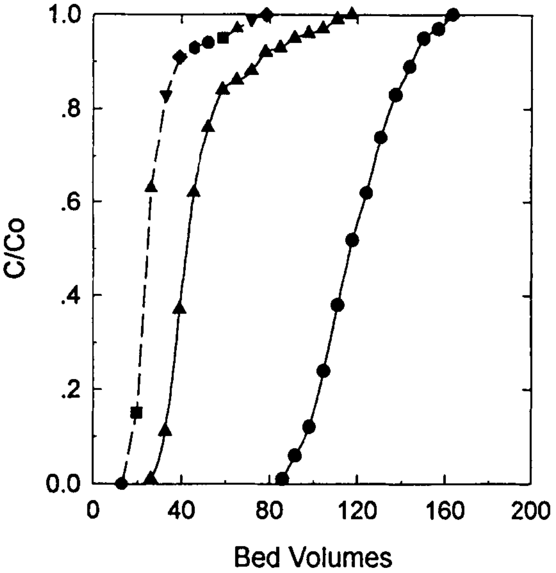

FIG. 12 Effect of feed concentration on the removal of copper by AR (AR, 3 g; I, 0.01 N NaCl; pH 4.12; ● 10 ppm; ▲ 28.3 ppm; ■ 49.5 ppm).

tion. The bed was completely saturated at 163 (3742 mL) and 78.4 bed volumes (1800 mL) with 10 and 49.5 ppm, respectively. The dynamic capacity was 6.58 mg Cu/g AR when the feed concentration was 10 ppm. However, the capacity decreased to 5.63 mg Cu/g AR and 4.96 mg Cu/g AR when the feed concentration was increased to 28.3 and 49.5 ppm, respectively. Dynamic or breakthrough capacity is defined as the amount of copper ions taken up prior to the breakthrough point (12). As expected, the copper removal capacity was relatively low, and a decrease in copper concentration in solution led to an increase in dynamic capacity.

Effect of Chemical Treatment

Figure 13 shows the breakthrough curves obtained by percolating solutions of copper down through two glass columns, each filled with 3 g of AR and P-AR. The cation-exchange capacities of the original AR were very low. The dynamic capacity by AR was 6.58 and 5.63 mg Cu/g when the feed concentrations were 10 and 28.3 ppm, respectively. However, the capacity by P-AR increased to 29.9 and 24.8 mg Cu/g with feed concen-

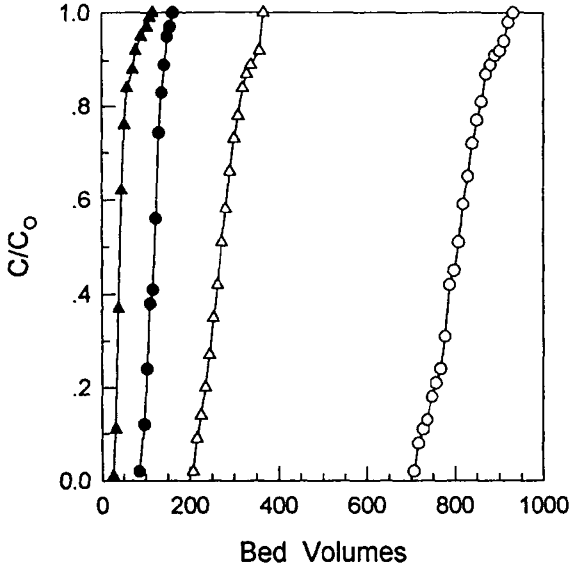

FIG. 13 Effect of chemical treatment of AR on the removal of copper [AR, P-AR, 3 g; I, 0.01 N NaCl; pH 4.12; feed rate, 0.5 mL/min; ● AR (10 ppm); ○ P-AR (10 ppm); ▲ AR (28.3 ppm); △ P-AR (28.3 ppm)].

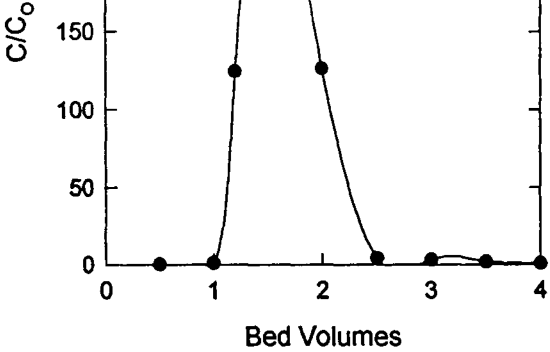

FIG. 14 Elution curve through a packed bed of AR. (C_0, Cu 10 ppm).

trations of 10 and 28.3 ppm, respectively. Based on experimental results, the dynamic capacity by P-AR was four to five times higher than that by AR in the removal of copper.

The significant increase of copper removal capacity by P-AR is attributed to the presence of phosphate groups on P-AR due to chemical treatment.

Elution Test

Figure 14 shows the result of an elution test through a packed column of AR. As shown in the figure, only four bed volumes of 0.5 N HCl were necessary for the almost complete recovery of metal ions. Similar results were obtained for the elution of a saturated P-AR packed column. The breakthrough capacity of regenerated AR and P-AR packed beds decreased less than approximately 6% from the previous column. Thus, P-AR could be successfully applied to the heavy metal removal process.

SUMMARY AND CONCLUSION

Characteristics for copper removal by AR and P-AR were investigated in conical tubes and glass columns in a ligand-free system and in the presence of ligands (EDTA and ammonia), competing metals (Ni and Pb), and various ionic strengths and pH values. Structural instability and low cation-exchange capacity were improved by chemical treatment with phosphorus(V) oxychloride according to the procedure of Peska et al. (9). Removal of copper by AR and P-AR was shown to be pH dependent. The copper removal yield by P-AR was higher than that of AR, especially at low pH regions, due to the presence of the phosphate group on P-AR by chemical modification. An increase in ionic strength reduced copper removal capacity at ionic strengths over 0.1 N NaCl since the swamp phenomenon decreased copper ion access to the AR surface. The effect of organic and inorganic ligands on copper removal was dependent on the ligand type and concentration. The presence of ligands significantly decreased the copper removal yield due to copper–ligand complex formation. The copper removal yield increased with a decrease in the particle size of AR. Equilibrium isotherms of copper fit the Langmuir equation adequately. Copper uptake capacities were 10.8 mg Cu/g AR and 36.2 mg Cu/g P-AR at the experimental limit.

In column tests the copper removal capacity by AR increased from 4.96 to 6.58 mg Cu/g with a decrease of feed concentration from 49.5 to 10 ppm. When the feed concentration was 10 ppm, the copper removal capacity by P-AR (29.9 mg Cu/g) was four to five times higher than that by AR (6.58

mg Cu/g) due to the presence of phosphate groups formed by chemical treatment with phosphorus(V) oxychloride. The adsorbed copper ions were almost completely recovered with three to four bed volumes of 0.5 N HCl. The dynamic capacity of regenerated AR and P-AR packed bed decreased less than approximately 6% from the previous column.

P-AR were shown to be effective and cheap adsorbents for copper removal from aqueous solution, especially at low concentrations. Thus, P-AR can be used to remove heavy metal ions from aqueous effluents.

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