Occlusion of Transition Metal Ions by New Adsorbents Synthesized from Plant Polyphenols and Animal Fibrous Proteins

MASATOSHI GOTO AND KYOZO SUYAMA*

Department of Applied Bioorganic Chemistry, Division of Life Science, Graduate School of Agricultural Science, Tohoku University, 1-1 Tsutsumidori Amamiyamachi, Aoba-ku, Sendai, 981-8555 Japan, E-mail: suyama@bios.tohoku.ac.jp

Abstract

Removing and collecting heavy and rare metal ions from industrial effluents and waste aqueous solutions are important problems. Our previous studies showed that animal fibrous proteins (AFPs) such as hen eggshell membrane, chicken feather (CF), wool, and silk were stable and insoluble proteins and had an excellent ability to bind not only hard (Mn^{2+} and Fe^{3+}) but also soft (Ag^+, Au^+, Pd^{2+}, Pt^{2+}, and Hg^{2+}) acids from aqueous solutions. In this study, we synthesized some adsorbents for transition (Cr^{6+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) and heavy (Cd^{2+}) metal ions from AFPs (gelatin, CF, and wool) and plant polyphenols (lignin and tannin) by heating a mixture of AFPs and plant polyphenols under acidic conditions. In batch experiments, pH profile, time dependency, and isotherm analysis were performed to determine binding properties of adsorbents for transition and heavy metal ions. Column experiments were also performed to remove copper ion from aqueous solution. The results showed that the new adsorbents were effective for collecting and removing transition and heavy metal ions from aqueous solutions.

Index Entries: Transition metal; animal fibrous protein; plant polyphenol.

Introduction

Metals such as Cr, Mn, Co, Ni, Cu, and Cd are used in various industrial field applications such as chromium plating (Cr), dry cell depolarizers (Mn), magnets (Co), nickel-cadmium batteries (Ni and Cd), and electrical wires (Cu). However, many municipal corporations regulate the discharge of these metal ions into environmental water because of their toxicity as

*Author to whom all correspondence and reprint requests should be addressed.

endocrine disrupters. Therefore, to remove these metal ions from aqueous solutions, various methods exist, including ion exchange, active carbon adsorption, precipitation, and reverse osmosis.

Recently, the removal of heavy metal ions from waste aqueous solutions by biomass such as fungi *(1,2)*, bacteria *(3)*, algae *(4,5)*, and chitosan *(6)* has been drawing the attention of many researchers. This method is called *biosorption*, and adsorbents composed of biomass are called *biosorbents*. The advantages of biosorption are that the use of biosorbents contributes to the good use of natural resources because most of the biomass for removing heavy metal ions is composed of industrial byproducts, the production cost of biosorbents is cheaper than that of chemical adsorbents, and biosorbents are never exhausted.

To collect heavy and precious metal ions from aqueous solutions, we studied biosorption by animal fibrous proteins (AFPs) such as hen eggshell membrane (ESM) and chicken feather (CF) in our laboratory *(7–9)*. ESM and CF are insoluble proteins and are stable in water both mechanically and chemically because ESM and CF have an intricate lattice network of protein fibers. ESM and CF could collect heavy and precious metal ions effectively from aqueous solutions owing to an excellent ability of AFPs to chelate these metal ions.

Plant polyphenol lignin, which comprises 17–33% of wood, is a complex aromatic polymer and has a role in cementing the polysaccharide components in cell walls both chemically and physically, thus increasing the mechanical strength of wood as a composite material and its decay resistance toward microorganisms. A large amount of lignin is included in wastewater from wood-pulp production, and such lignin is mainly used as a heat energy resource. Plant polyphenol tannin is included in tea leaves, but tannin, the bitter component of tea, is barely extracted by hot water, and, therefore, almost all the tannin is scrapped with tea leaf dregs. These plant polyphenols, especially tannin, are known to form insoluble products with protein by tanning reaction *(10,11)* and increase the chemical and physical stability of protein. Moreover, plant polyphenols also have an ability to form coordination bonds to metal ions *(12)*.

In the present study, to remove transition and heavy metal ions from waste aqueous solutions more effectively and cheaply, we synthesized the new adsorbents from AFPs (gelatin, CF, and wool) and plant polyphenols (lignin and tannin) and investigated the binding properties of these adsorbents for various metal ions.

Materials and Methods

Materials and Reagents

Gelatin powder (food grade, particle size <800 μm) and tannic acid powder were purchased from E. Merck. Alkaline lignin (water soluble) was purchased from Nacalai Tesque, Inc., Kyoto, Japan. CF was obtained from the waste of a local chicken industry in Sendai, Japan. Wool was obtained
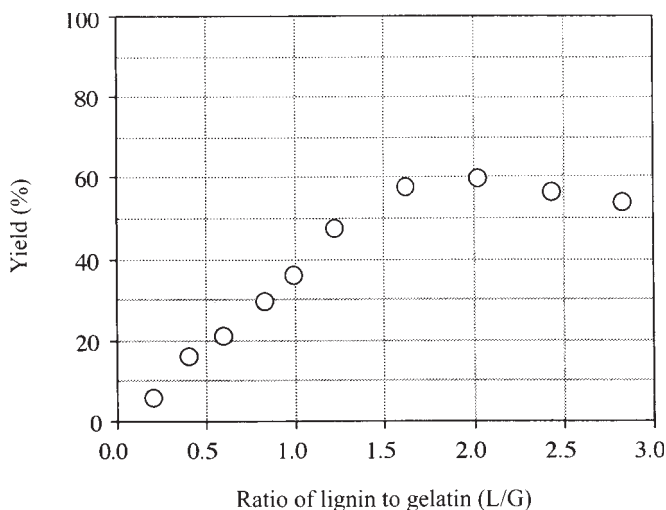
Fig. 1. Effect of the ratio of alkaline lignin to gelatin on the yield of G/L-1 resin. Alkaline lignin and gelatin were each dissolved in distilled and deionized water and mixed in various ratios. The mixture was heated at 95–98°C under 2% HCl condition for 12 h. The products were washed with distilled and deionized water and dried at 110°C.

from the Tohoku University stock farm. K_2CrO_4, $MnCl_2·4H_2O$, $CoCl_2·6H_2O$, $NiCl_2·6H_2O$, $CuCl_2·2H_2O$, $CdCl_2·1/2H_2O$, which were guaranteed reagent grade and used as received, were purchased from Nacalai Tesque and dissolved with distilled and deionized water. Metal ion concentrations of stock solutions were adjusted to 1000 mg of metal/L and diluted to a suitable concentration when adsorption experiments were conducted.

Adsorbents

The production method of the adsorbent, which was composed of gelatin and alkaline lignin, was determined by the data of preliminary experiments in our laboratory (Figs. 1 and 2). All other adsorbents were also synthesized using this production method as references. Figure 1 shows that the yield of gelatin/lignin-1 (G/L-1) resin composed of gelatin and alkaline lignin was the best value (60%) when gelatin and alkaline lignin were at a 1:2 ratio. Figure 2 shows that the yield of G/L-1 resin was the best when the reaction time was 12 h and the HCl concentration was 2%.

Gelatin/Lignin-1

Gelatin powder (10 g) and alkaline lignin (20 g) were dissolved with 90 mL of distilled and deionized water in separate flasks at 95–98°C. Both solutions were then mixed. After cooling at room temperature, concentrated HCl (35%, 10 mL) was added to the solution (final HCl concentration was 1.8%). The solution was heated in a 500-mL round bottomed flask at 95–98°C with a temperature-controlled mantle heater (Type AS-5; Sibata Co., Ltd., Sendai, Japan) for 12 h, attached with a reflux condenser. G/L-1
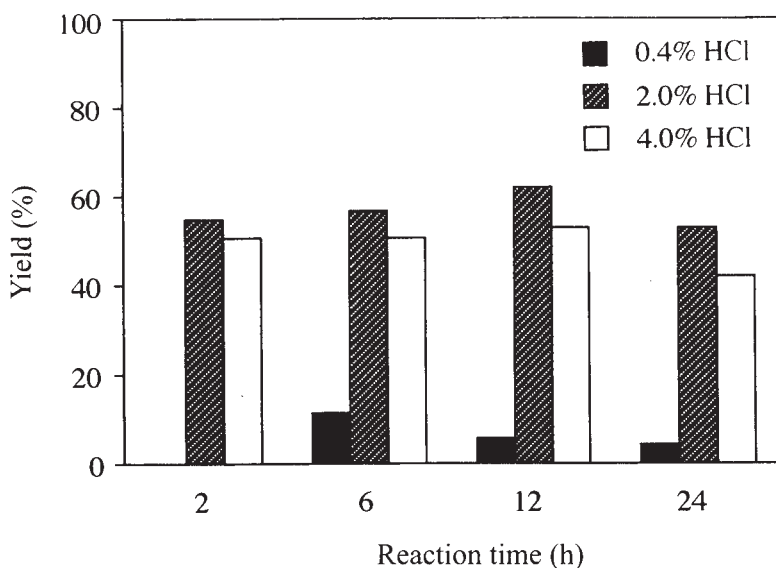
Fig. 2. Effect of catalyst (HCl) concentration and reaction time on the yield of G/L-1 resin. Alkaline lignin (1 g) and gelatin (0.5 g) were each dissolved with 4.5 mL of distilled and deionized water and mixed. These mixtures were heated at 95–98°C under 0.4, 2.0, and 4.0% HCl conditions for 2, 6, 12, and 24 h. The products were washed with distilled and deionized water and dried at 110°C.

resin was washed with distilled and deionized water, and then dried in a temperature-controlled oven (Model TS-6; Toyo Kagaku Sangyo Co., Ltd., Kouhu, Japan) at 110°C. Dried G/L-1 resin was crushed into small particles (particle size was <500 μm).

Gelatin/Lignin-2

Gelatin powder (10 g) and alkaline lignin (20 g) were dissolved with 45 mL of 0.01 *M* NaOH in separate flasks at 95–98°C. Both solutions were then mixed. After cooling at room temperature, 15 mL of a 37% formaldehyde/concentrated HCl mixture (2:1 [v/v]) was added to the solution. The solution was heated at 95–98°C for 3 h in a 500-mL round-bottomed flask attached with a reflux condenser. Gelatin/lignin-2 (G/L-2) resin thus obtained was treated the same as the G/L-1 resin.

Gelatin/Tannin

Tannic acid powder (20 g) was dissolved with 20 mL of distilled and deionized water in a flask at 95–98°C, the solution was cooled at room temperature, and 20 mL of 37% formaldehyde solution was added to the solution. Gelatin powder (15 g) was dissolved with 60 mL of distilled and deionized water at 95–98°C and then added to the tannic acid/formaldehyde solution. Concentrated HCl (35%, 7.5 mL) was added to the mixture, and the mixture was heated at 95–98°C for 12 h in a 500-mL round-bottomed flask attached with a reflux condenser. Gelatin/tannin (G/T) resin thus obtained was treated the same as the G/L-1 resin.

CF/Lignin

CF (100 g) was washed with water (1 L) containing 5 mL of commercial detergent (Lion Co., Ltd., Tokyo, Japan) to remove dirt from the CF, then washed with distilled and deionized water to remove the detergent from the CF, and finally dried *in vacuo* at room temperature. Insoluble CF (5 g) was solubilized with 100 mL of 0.3 *M* NaOH in a flask at 95–98°C. Alkaline lignin (10 g) was also dissolved with 50 mL of 0.1 *M* NaOH in a flask at 95–98°C, and then both solutions were mixed. Twenty milliliters of a 37% formaldehyde/concentrated HCl mixture (1:1 [v/v]) was added to the mixed solution. The solution was heated at 95–98°C for 12 h in a 500-mL round-bottomed flask attached with a reflux condenser. CF/lignin (F/L) resin thus obtained was treated the same as the G/L-1 resin.

CF/Tannin

Insoluble CF (5 g) was solubilized with 100 mL of 0.3 *M* NaOH in a flask at 95–98°C. Tannic acid powder (10 g) was also dissolved with 50 mL of 0.1 *M* NaOH in a flask at 95–98°C, and then both solutions were mixed. The procedure was then carried out according to the same method as the F/L resin production method.

Wool/Lignin

Wool was washed according to the same method as the CF treatment method. Insoluble wool (5 g) was solubilized with 100 mL of 0.3 *M* NaOH in a flask at 95–98°C. Alkaline lignin (10 g) was also dissolved with 50 mL of 0.1 *M* NaOH in a flask at 95–98°C, and then both solutions were mixed. The procedure was then carried out according to the same method as the F/L resin production method.

Adsorption Experiments

A batch method was used to obtain the optimum pH range for metal ion removal, equilibrium data, and the effect of coexistent salts on the metal ion sorption. A series of 100-mL polyethylene bottles washed with dilute nitric acid solution were employed. The procedure involved filling each bottle with 50 mL of metal ion solution of varying concentrations, adding a known amount of adsorbent (20–604 mg) into each bottle, agitating the solution by a magnetic stirrer (SR100 Advantec Co., Ltd., Tokyo, Japan), adjusting to the desired pH with 1 *M* HCl and 1 *M* NH_3 solution, and adjusting the temperature with a temperature-controlled incubator (LTI-600SD; Eyela, Tokyo, Japan) to 25–30°C. pH values were measured with a pH meter (Model F-21; Horiba Co., Ltd., Kyoto, Japan). After completing the adsorption reaction, the adsorbent was filtered off with a polyvinylidene fluoride (PVDF) membrane filter whose pore size was 0.45 μm, and the metal ion concentration of the filtered solution, which was diluted to a suitable concentration with 0.1 *M* HCl, was analyzed by using an atomic absorption spectrophotometer (AES SAS-727; Seiko Co., Ltd., Tokyo, Japan). Initial metal ion concentrations ranged from 9.90 to 914 mg/L for

Cr, 94.0 to 103 mg/L for Mn, 50.0 to 297 mg/L for Co, 26.0 to 199 mg/L for Ni, 28.0 to 107 mg/L for Cu, and 11.0 to 1000 mg/L for Cd. The adsorption ability for Cu ions (Cu^{2+}) of G/L-1 was compared with that of AFPs (CF, wool, and silk) at pH 6.0 for a 9-h reaction at 25°C. The effect of pH on the sorption was studied over a range of pH 0.0–7.0 for a 3-h reaction at 25–30°C. The effect of salts (sodium acetate and NH_4Cl) on the sorption was also studied at pH 6.0 for a 3-h reaction at 25–30°C. The effect of the concentration of NH_4Cl on the sorption was also studied at pH 6.0 for a 3-h reaction at 25–30°C. Adsorption isotherm analysis was performed at the optimum pH (1.8 for Cr^{6+}; 5.0 for Mn^{2+}; 6.0 for Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}) until the reaction reached equilibrium. Kinetic studies showed that the equilibrium of all adsorbed reactions was attained at the most in 24 h.

Kinetic Measurements

As in the case of adsorption experiments, kinetics studies were conducted using the batch method because of its simplicity and reliability. A number of 250-mL polyethylene bottles containing a known volume (150 mL) of metal ion solutions of 91–108 mg/L were brought to the desired temperature, 25–30°C, with a temperature-controlled incubator. A known amount of adsorbent (0.3 g) was added into each bottle, and the solution was agitated with a magnetic stirrer until the experiment was completed. At predetermined time intervals, 2 mL of the solution was separated from the adsorbent using a PVDF membrane filter, and the concentration of the filtered solution was analyzed.

Column Experiments

Column operations are essential for industrial-scale designing of technical systems. Moreover, the adsorption isotherms do not necessarily give accurate scale-up data in fixed-bed systems. Therefore, the practical applicability of the adsorbents synthesized in the present study was also ascertained in the column operations. A polypropylene column (2.0 cm diameter, 12 cm length) filled with a known amount of G/L-2 resin (1.86 and 0.37 g, particle size 250–500 µm) was used for metal ion removal. Investigations were carried out by feeding the columns with solutions of Cu^{2+} (10 and 100 mg/L) containing 10 m*M* 2-(*N*-morpholino)ethanesulfonic acid buffer (pH 6.0) at the desired flow velocity (0.30–0.32 cm/min) with a peristaltic pump (Eyela) at the top of the columns (25°C). The Cu^{2+} concentration of effluents, which were diluted to a suitable concentration with distilled and deionized water, was analyzed by an inductively coupled plasma mass spectrometer (ELAN 6000 ICP-MS; Perkin Elmer, Norwalk, CT).

For any adsorption process, one of the most important factors is the recovery of adsorbate material and the ability of the adsorbent to regenerate. Therefore, the recovery efficiency of Cu^{2+} and the ability of the G/L-2 resin to regenerate were also investigated by column operations, which was a repetition of metal adsorption and desorption. The adsorption process was done according to the method previously described. The desorp-
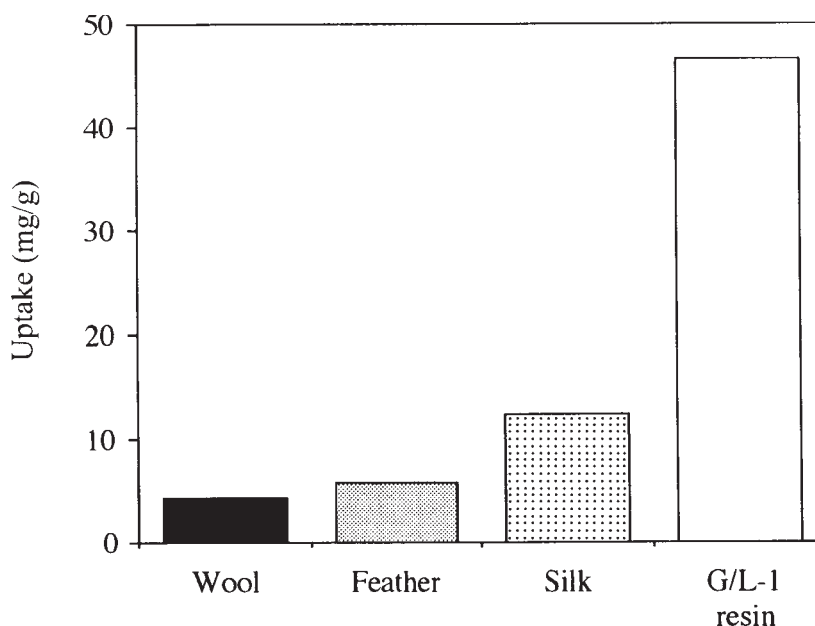
Fig. 3. The Cu uptake of G/L-1 resin was compared with that of AFPs (wool, feather, and silk). Various adsorbents (300 mg) were each suspended in the solution (150 mL) containing Cu^{2+} for 9 h at 25–30°C. Initial concentration of metal ions was 100 mg/L.

tion process was performed by feeding the column, which already adsorbed copper ions, with dilute nitric acid solution (0.2 M) at a desired flow velocity (0.30–0.32 cm/min) with a peristaltic pump at the top of the column (25°C). The concentration of copper ion in the effluents from the column was also analyzed by an inductively coupled plasma mass spectrometer.

Analysis of Metal Ions

The concentrations of the metal ions in solutions before and after the reactions were measured with an atomic adsorption spectrophotometer or an inductively coupled plasma mass spectrometer.

The adsorption capacity of adsorbents for metal ions was calculated according to the following equation:

$$Q = (C_i - C_f)V/m$$

in which Q is the adsorption capacity for metal ions (mg metal/g adsorbent); C_i and C_f are initial and final concentrations of metal ions (mg metal/L); V is the reaction volume (L); and m is the sorbent weight (g).

Results and Discussion

Adsorption Experiments

The adsorption ability of copper ions of G/L resin was compared with that of AFPs (CF, wool, and silk) at pH 6.0 for a 9-h reaction at 25–30°C;
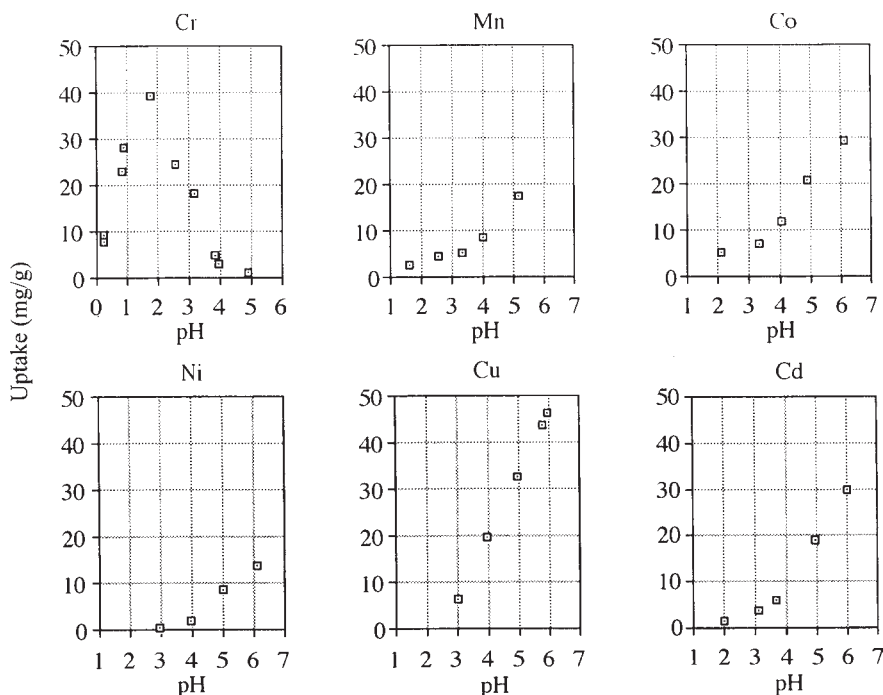
Fig. 4. Effect of pH on the uptake of metal ions. G/L-1 resin (100 mg) was suspended in each metal solution (50 mL) for 3 h (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}) or 12 h (Cr^{6+}) at 25–30°C, agitating the solution with a magnetic stirrer. The pH was adjusted with 1 M HCl and 1 M NH$_3$ solution. The initial concentration of the metal ions was 100 mg/L (Cr^{6+}), 91 mg/L (Mn^{2+}), 99 mg/L (Co^{2+}), 97 mg/L (Ni^{2+}), 100 mg/L (Cu^{2+}), and 96 mg/L (Cd^{2+}).

Figure 3 gives the results. The G/L-1 resin adsorbed copper ions more than AFPs did.

The effect of pH on the uptake of metal ions—Cr^{6+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}—by G/L-1 resin was investigated; Figure 4 gives the results. It is apparent that in the case of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}, lower pH values resulted in lower uptake of metal ions from the metal solution, whereas higher pH values resulted in higher uptake of metal ions. However, only in the case of Cr^{6+} did lower pH values result in higher uptake of Cr, and the optimum pH value for the removal of Cr^{6+} was 1.77.

These behaviors can be explained by considering the change in the electric state of the G/L-1 resin surface with a change in the pH values. It is presumed that the G/L-1 resin has various types of chemical groups, such as carboxyl (anion) and amino (cation) groups, derived from AFPs and plant polyphenols. Therefore, the G/L-1 resin can be considered to be one of the dipolar ions. In the solution at a higher pH than the isoelectric point (pI) of the G/L-1 resin, protons of cationic (amino) groups on the G/L-1 resin dissociate, and the electric state of the G/L-1 resin becomes electronegative. Therefore, positively charged aco ions of Mn^{2+}, Co^{2+}, Ni^{2+},
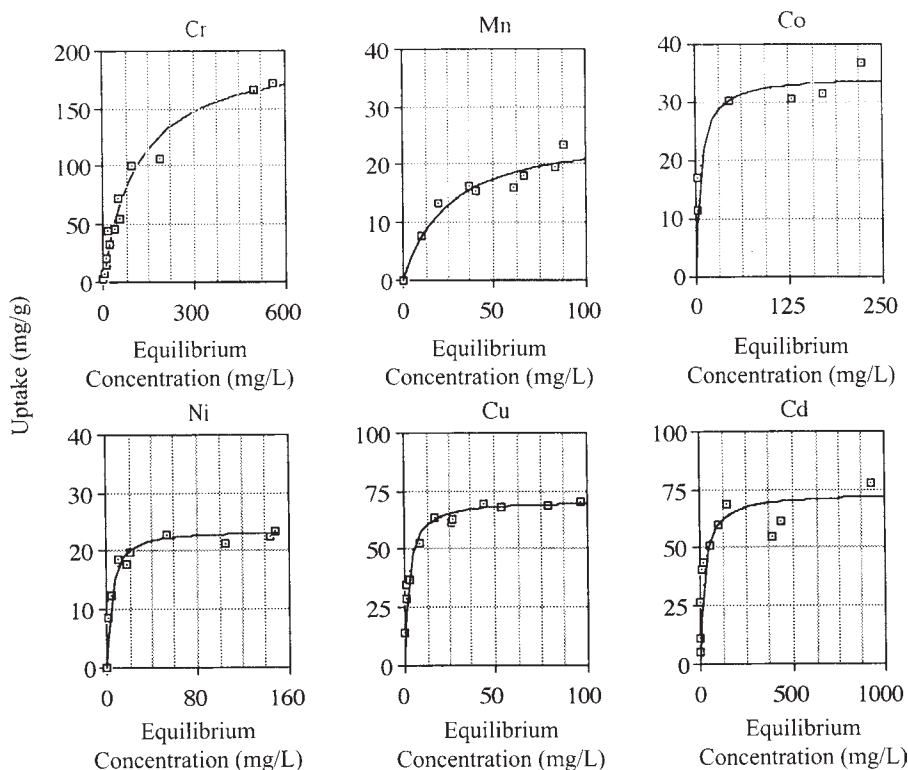
Fig. 5. Isotherm analysis of metal ions for G/L-1 resin. G/L-1 resin was suspended in each solution containing metal ions at optimal pH (1.8 for Cr^{6+}; 5.0 for Mn^{2+}; and 6.0 for Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}) until the adsorbed reactions reached equilibrium (24 h for Cr^{6+}, 6 h for Mn^{2+}, 12 h for Co^{2+}, 24 h for Ni^{2+}, 3 h for Cu^{2+}, and 9 h for Cd^{2+}) at 25–30°C.

Cu^{2+}, and Cd^{2+} are adsorbed more significantly with an increase in pH values. Conversely, in the solution at a lower pH than the p*I* of the G/L-1 resin, anionic (carboxyl) groups receive protons, and the electric state of the G/L-1 resin becomes electropositive. Therefore, negatively charged CrO_4^{2-} or $Cr_2O_7^{2-}$ are adsorbed more significantly at lower pH values. Moreover, in Cr^{6+} solution, the ratio of $Cr_2O_7^{2-}$ increased with the following reaction, when the pH value of the solution became low:

$$2\ CrO_4^{2-} + 2\ H^+ \rightleftarrows Cr_2O_7^{2-} + H_2O$$
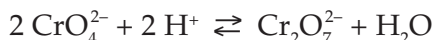
The redox potential of $Cr_2O_7^{2-}$ ($E° = 1.33$ V) is higher than that of CrO_4^{2-} ($E° = -0.13$ V). Therefore, it is presumed that the redox potential of the solution becomes high, when the pH value of the solution becomes low. As a result, chemical groups (such as aldehyde) on the surface of the G/L-1 resin are oxidized, and the stereochemical structure of the G/L-1 resin may be changed to capture chromium more effectively.

Figure 5 presents the results of isotherm analysis. Generally, adsorption isotherms can be presented by various models such as Langmuir,

Table 1
Freundlich, Langmuir, and Correlation Constants
for Adsorption Isotherms for Metal Ions Using G/L-1 Resin[a]

Metal ions	K	n	R^2	Q_{max} (mg metal/g G/L)	K_{eq} (L/mg metal)	R^2
Cr	3.37	0.668	0.906	202.0	0.00888	0.976
Mn	3.30	0.416	0.892	26.2	0.0399	0.925
Co	12.7	0.192	0.920	31.6	0.0208	0.988
Ni	9.62	0.193	0.863	23.8	0.274	0.998
Cu	27.3	0.243	0.892	71.1	0.457	0.999
Cd	20.7	0.211	0.873	73.6	0.0438	0.971

[a]K and n are the Freundlich constants in the equation $Q_{eq} = K \cdot C_{eq}^{n}$. Q_{max} and K_{eq} are the Langmuir constants in the equation $Q_{eq} = K_{eq} \cdot Q_{max} \cdot C_{eq}/(1 + K_{eq} \cdot C_{eq})$. Q_{eq}, uptake (mg metal/g); C_{eq}, metal concentration (mg metal/L).

Table 2
Change in Standard Gibbs Free Energy ($\Delta G°$)
for Adsorbed Reaction
Between Metal Ions and G/L-1 Resin

Metal ions	$-\Delta G°$ (kJ/mol)	pH
Cr	15.20	1.8
Mn	19.06	5.0
Co	22.60	6.0
Ni	24.00	6.0
Cu	25.46	6.0
Cd	21.06	6.0

Freundlich, and BET isotherms. Langmuir and Freundlich isotherms are shown in Eqs. 1 and 2:

$$Q_{eq} = Q_{max}K_{eq}C_{eq}/(1 + K_{eq}C_{eq}) \tag{1}$$

$$Q_{eq} = KC_{eq}^{n} \tag{2}$$

in which Q_{eq} (mg/g) is the equilibrium uptake; C_{eq} (mg/L) is the equilibrium concentration of metal ions; Q_{max} (mg/g) and K_{eq} (L/mg) are the Langmuir constants; and K and n are the Freundlich constants. In this study, adsorption isotherms for all metal ions could fit the Langmuir isotherm model well. The maximum uptake of Cr^{6+} was the highest in this study: 171 mg of metal/g of G/L-1 resin. Table 1 gives the Langmuir, Freundlich, and correlation constants for each metal ion in this study.

The changes in standard Gibbs free energy ($\Delta G°$) were calculated using Langmuir isotherms and are shown in Table 2. The changes in standard Gibbs free energy ($\Delta G°$) were obtained using Eq. 3:
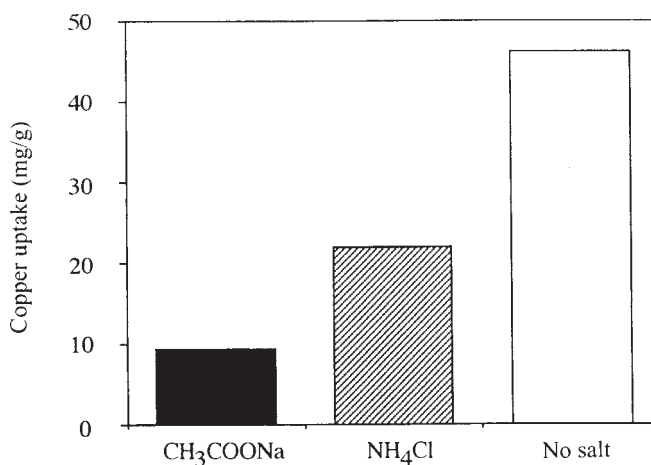
$$\Delta G° = -RT \ln K_{eq} \tag{3}$$

Fig. 6. Effect of salt on the uptake of Cu at pH 6.0. G/L-1 resin (2 mg/mL) was suspended in each solution containing 100 mg/L of Cu^{2+} with 1.0 M sodium acetate (■), 1.0 M NH_4Cl (▨), or without salt (□) for 3 h at 25–30°C.

It is presumed that as the values of $\Delta G°$ decrease, the adsorption reaction between metal ions and the G/L-1 resin progresses more easily. Therefore, the affinity of the G/L-1 resin for metal ions in this study became stronger and stronger in the order $Co^{2+} < Ni^{2+} < Cu^{2+} > Cd^{2+}$, according to the values of $\Delta G°$ in Table 2. The trend resembled the Irving-Williams series:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$
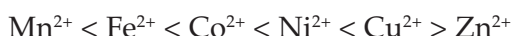
The Irving-Williams series describes an ascending order of the stabilities of divalent metal ion complexes formed regardless of the nature of the complexing agent *(13)*. Precise comparison of the affinity for the G/L-1 resin between two metal species (Cr^{6+} and Mn^{2+}) and four metal species (Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}) is difficult because of the different experimental conditions of pH values.

The effect of sodium acetate and NH_4Cl on the uptake of Cu^{2+} by the G/L-1 resin was investigated; Figure 6 presents the results. The existence of these salts reduced the uptake of Cu^{2+}. Not only the G/L-1 resin but the acetate ion and ammonia can also bind to Cu^{2+}. Therefore, it could be considered that the G/L-1 resin competed with the acetate ion or ammonia for Cu^{2+} adsorption. As a result, the uptake of Cu^{2+} by the G/L-1 resin would be reduced. Cu^{2+} adsorption was suppressed by sodium acetate more than by NH_4Cl, because the acetate ion can form stabler complexes with Cu^{2+} than does ammonia. The chelate formation constants, $log\beta_1$, for Cu^{2+} are 4.04 (ammonia) and 4.76 (acetate ion).

The effect of NH_4Cl concentration on the uptake of Cu^{2+} by the G/L-1 resin was also investigated; Figure 7 presents the results. The uptake of Cu^{2+} decreased from 43.7 to 36.4, 21.9, and 5.6 mg/g in the presence of NH_4Cl at concentrations of 0.10, 1.00, and 4.67 M, respectively. The adsorption of Cu^{2+} was suppressed by a high concentration of NH_4Cl more than by a low

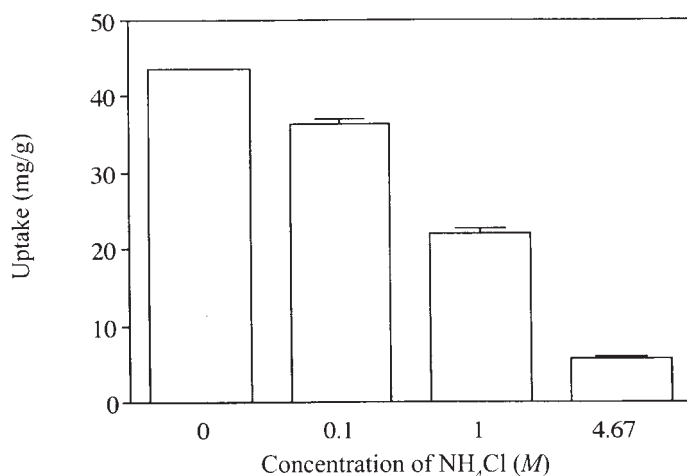Fig. 7. Effect of NH$_4$Cl concentration on the uptake of Cu by G/L-1 resin. G/L-1 resin (2 mg/mL) was suspended in each solution (pH 6.0) containing 100 mg/L of Cu^{2+} with 0.10, 1.00, and 4.67 M NH$_4$Cl or without salts for 3 h at 25–30°C.
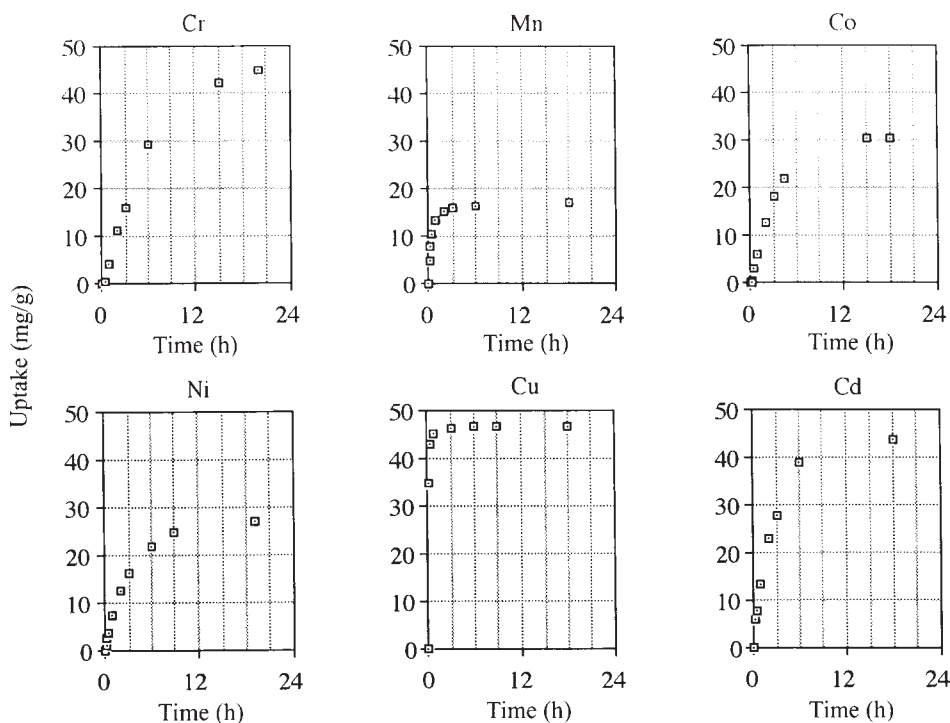

Fig. 8. Kinetics of metal ion uptake by G/L-1 resin. G/L-1 resin (300 mg) was suspended in each solution (150 mL) at 25–30°C, and pH was adjusted with 1 M HCl and 1 M NH$_3$ solution. The pH values were 1.8 for Cr^{6+}; 5.0 for Mn^{2+}; and 6.0 for Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}. Initial concentrations of metal ions were 108 mg/L (Cr^{6+}), 94 mg/L (Mn^{2+}), 106 mg/L (Co^{2+}), 103 mg/L (Ni^{2+}), 99 mg/L (Cu^{2+}), and 99 mg/L (Cd^{2+}).

Table 3
Rate Constants of Adsorption
for Metal Ions Using G/L-1 Resin[a]

Metal ions	K (L/[mg metal · h]) ($\times 0.001$)
Cr	0.73
Mn	4.26
Co	3.10
Ni	1.65
Cu	16.10
Cd	3.36

[a]G/L-1 resin was suspended in the solution containing metal ion (pH was 1.8 for Cr^{6+}; 5.0 for Mn^{2+}; 6.0 for Co^{2+}, Ni^{2+}, Cu^{2+}, and Cd^{2+}) at 25°C. Initial concentration of metal ion was 108 mg/L for Cr^{6+}, 94 mg/L for Mn^{2+}, 106 mg/L for Co^{2+}, 103 mg/L for Ni^{2+}, 99 mg/L for Cu^{2+}, and 99 mg/L for Cd^{2+}. Resin density was 2 mg/mL. The rate constants were calculated according to the second-order reaction.

concentration of NH_4Cl. In a high concentration NH_4Cl solution, the chelating reaction between ammonia and Cu^{2+} occurs more easily. Therefore, in a high concentration of NH_4Cl solution, Cu^{2+}, which binds to ammonia, would increase, and Cu^{2+}, which binds to the G/L-resin, would decrease.

Kinetic Experiments

Studies on the rate of uptake of metal ions on the G/L-1 resin indicated that in the case of Mn^{2+} and Cu^{2+}, the process was quite rapid, and typically 78.4–96.9% of the ultimate adsorption occurred within the first hour of contact. Conversely, in the case of Cr^{6+}, the process was quite slow, and only 8.8% of the ultimate adsorption occurred within the first hour of contact. Figure 8 presents adsorption kinetics data of the G/L-1 resin for each metal ion. The initial reaction rate constant of Cu^{2+} adsorption was the highest in this study: 16.1×10^{-3} (L/[mg metal·h]). The initial reaction rate constant of Cr^{6+} adsorption was the smallest in this study (7.3×10^{-4}), but the ultimate uptake of Cr^{6+} almost corresponded with that of Cu^{2+}. Moreover, the adsorption reaction for Cu^{2+} reached equilibrium for only 1 h, whereas the adsorption reaction for Cr^{6+} continued for a long time. It was presumed that the adsorption reaction for Cr^{6+} continued for a long time because the oxidization of the G/L-1 resin by $Cr_2O_7^{2-}$ also continued for a long time. Therefore, the ultimate uptake of Cr^{6+} could almost correspond with that of Cu^{2+}. Table 3 gives the initial reaction rate constants of adsorption for each metal ion.

Column Experiments

Adsorption and desorption for Cu^{2+} by the G/L-2 resin column were performed; Figure 9 presents the results. A Cu^{2+} solution of 10 mg/L was
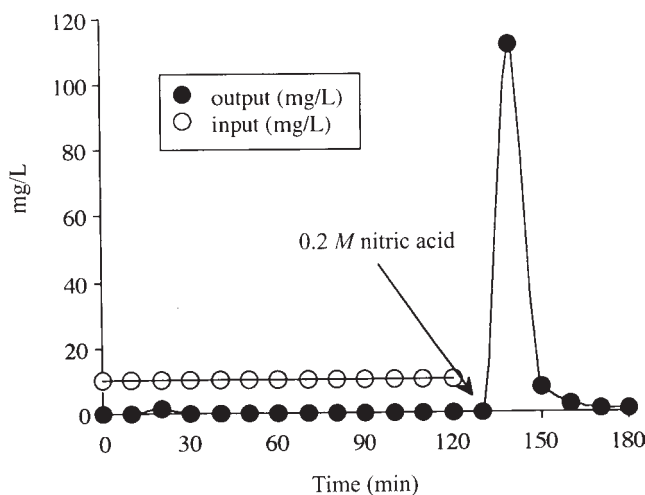
Fig. 9. Column operation for the removal of Cu^{2+} from Cu^{2+} solution (10 mg/L, pH 6.0) and collection of the Cu^{2+} that adsorbed on the G/L-2 resin. The condition for the removal of Cu^{2+} was described in Fig. 6. To collect the Cu^{2+} that adsorbed on the G/L-2 resin, 0.2 *M* nitric acid was supplied to the column at the time indicated by an arrow in Fig. 9 (flow velocity was 0.32 cm/min). Element, copper (II) ion; concentration, 10.00 mg/L; pH, 6.0; flow rate, 1.0 mL/min; flow velocity, 0.32 cm/min; column diameter, 2.0 cm; resin volume, 5.0 mL; resin weight, 1.86 g; temperature, 25°C.
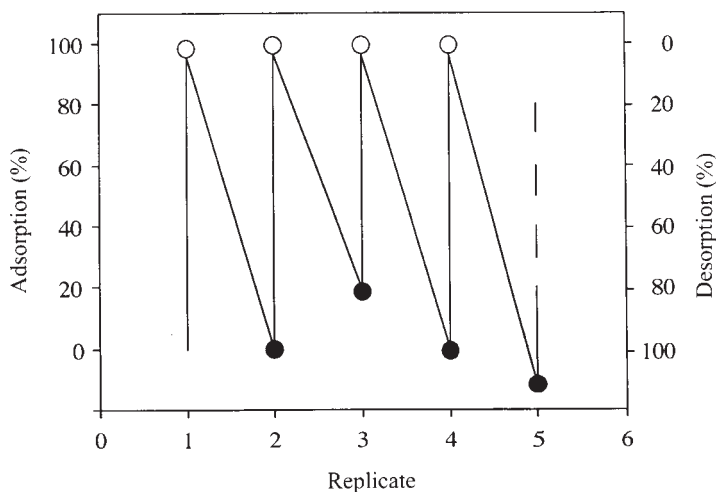

Fig. 10. Repetition of adsorption (○) and desorption (●) for Cu^{2+} by G/L-2 resin column. Cu^{2+} solution (120 mL, 10 mg/L, pH 6.0), nitric acid solution (60 mL, 0.2 *M*), and MES buffer (180 mL, 10 m*M*, pH 6.0) were supplied to the column in turn.

supplied to the G/L-2 resin column to remove Cu^{2+} from the solution, and then 0.2 *M* nitric acid solution was supplied to desorb Cu^{2+}, which was adsorbed in the G/L-2 resin column. The Cu^{2+} concentration of effluents from the G/L-2 resin column was about 30 µg/L, whenever the Cu^{2+} solution was supplied, and the adsorption efficiency was 98.3%. The space
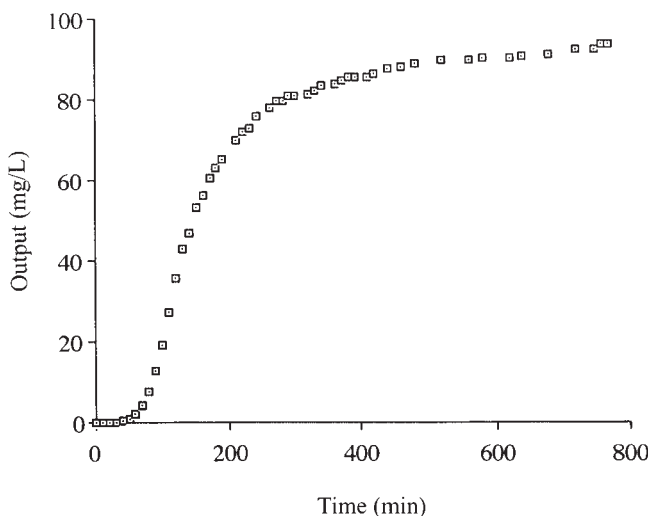
Fig. 11. Breakthrough curve of the effluents of Cu. Cu^{2+} solution (100 mg/L, pH 6.0) was supplied to the G/L-2 resin column. The experimental conditions were as follows: element, copper (II) ion; concentration, 100 mg/L; pH, 6.0; flow rate, 0.95 mL/min; time, 770 min; column diameter, 2.0 cm; resin volume, 1.0 mL; resin weight, 0.37 g; temperature, 25°C; buffer, 10 m*M* MES; resin size, 250–500 μm.

time in this study was 5 min, i.e., almost all the Cu^{2+} in the solution could be adsorbed for at least 5 min. The supply of 0.2 *M* nitric acid solution in the G/L-2 resin column could desorb about 100% of the Cu^{2+} kept in the G/L-2 resin. The Cu^{2+} concentration of effluents with nitric acid solution was 112 mg/L; that is, the Cu^{2+} concentration became 11.2 times as dense as that of the Cu^{2+} solution of 10 mg/L.

A regeneration experiment of the G/L-2 resin column for Cu^{2+} removal was performed; Figure 10 presents the results. Repetition of the adsorption and desorption for Cu^{2+} was performed in four cycles. The adsorption capacity for Cu^{2+} could be maintained, and the average of the adsorption ratio for Cu^{2+} was 99.2%. Therefore, it was suggested that the G/L-2 resin column had an excellent reuse ability. However, the use of oxidizing acids (HNO_3) may cause damage to the G/L-2 resin.

A Cu^{2+} solution of 100 mg/L was supplied to the G/L-2 resin column, and the concentration of the effluents was analyzed; Figure 11 presents the results. The breakthrough curve of Cu^{2+} effluents was a general S curve type. Finally, 58.6 mg of Cu^{2+} was adsorbed per gram of G/L-2 resin for 13 h.

Adsorption Studies Using the Other Adsorbents

The effect of pH on the uptake of metal ions, Cu^{2+} and Cd^{2+}, by G/T, F/L, CF/tannin (F/T), and wool/lignin (W/L) resins was investigated; Figure 12 presents the results. G/T and F/T adsorbed Cu^{2+} more effectively than Cd^{2+}. Conversely, F/L adsorbed Cd^{2+} more effectively than Cu^{2+}. The results showed that in the case of F/L and F/T resins, with an increase in
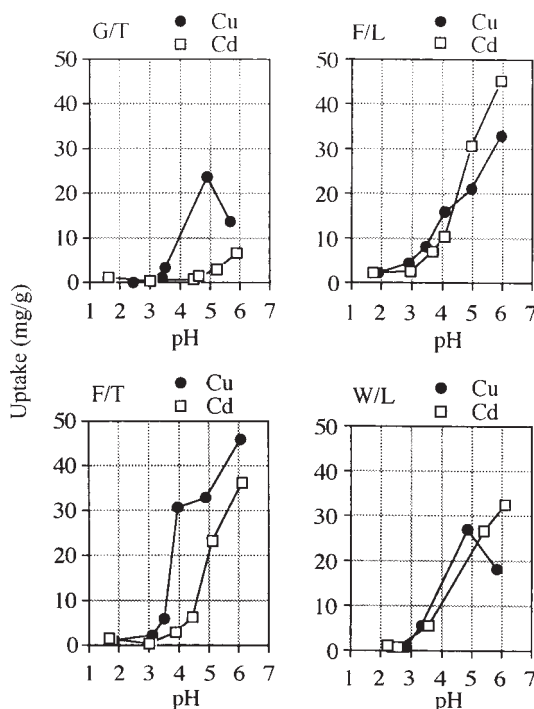
Fig. 12. Effect of pH on the uptake of Cu and Cd ions. G/T, F/L, F/T, and W/L resin were suspended in each solution containing 99 mg/L of Cu^{2+} or 100 mg/L of Cd^{2+} for 3 h at 25–30°C. Resin density was 2 mg/mL.
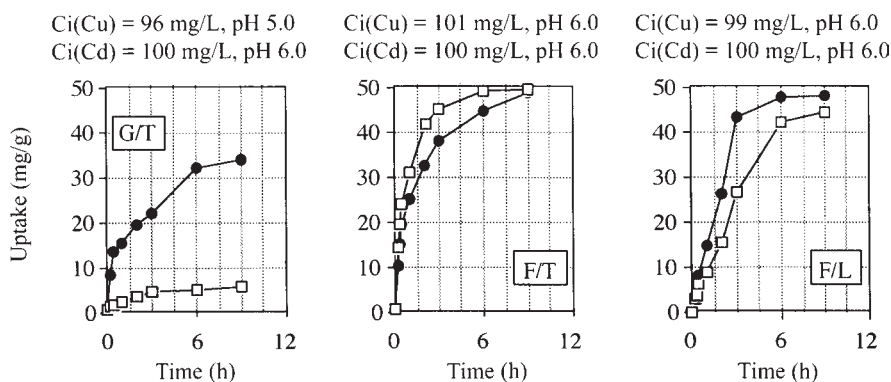

Fig. 13. Kinetics of metal ion uptake. G/T, F/L, and F/T resin were suspended in each solution containing Cu^{2+} or Cd^{2+} at 25–30°C. The pH value and initial concentration of the metal solution are given. Resin density was 2 mg/mL.

pH values, the uptake of Cu^{2+} and Cd^{2+} was significantly increased. However, in the case of the G/T and W/L resins, there was an optimum pH for the removal of Cu^{2+} at 4.89 (G/T) and 4.81 (W/L). The enhancement of metal ion uptake at a high pH can be explained by the same reason as in the case of the G/L-1 resin, as previously described.
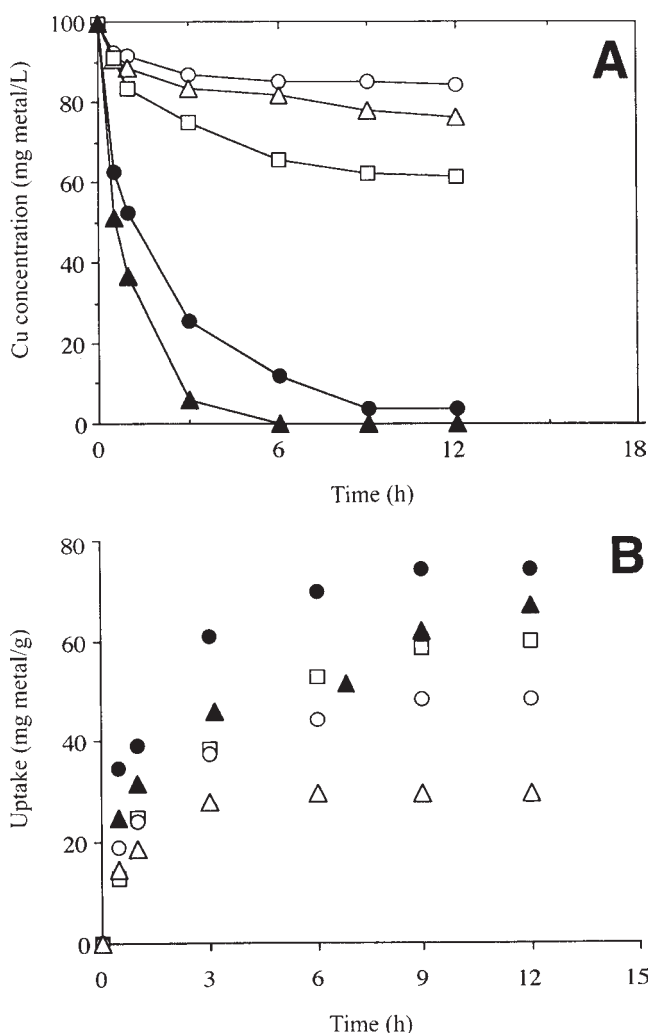
Fig. 14. **(A)** Effect of the amount of adsorbent on the rate of metal ion removal using F/L resin. F/L resin was suspended in each solution (pH 6.0) containing 100 mg/L of Cu^{2+} at 25–30°C. Resin density was 0.21 (○), 0.35 (△), 0.64 (□), 2.0 (●), and 3.3 (▲) mg/mL. **(B)** Effect of the amount of adsorbent on the kinetics of Cu uptake using F/L resin. F/L resin was suspended in each solution (pH 6.0) containing 100 mg/L of Cu^{2+} at 25–30°C. Resin density was 0.21 (●), 0.35 (▲), 0.64 (□), 2.0 (○), and 3.3 (△) mg/mL.

Adsorption kinetics for Cu^{2+} and Cd^{2+} by G/T, F/L, and F/T resins were investigated; Figure 13 presents the results. The results showed that the G/T resin barely adsorbed Cd^{2+}, but that the other adsorbents could effectively adsorb both Cu^{2+} and Cd^{2+}. It is presumed that the G/T resin has few soft ligands. Therefore, it is difficult for a soft acid (such as Cd^{2+}) to be adsorbed in the G/T resin. However, Cu^{2+}, which has a nature between hard and soft acid, could be effectively adsorbed by the G/T resin.

Figure 14 depicts the effect of the amount of adsorbent on the removal rate of copper ion and the uptake rate of copper ion using the F/L resin.

It seemed that the removal rate of Cu^{2+} increased with an increase in the amount of adsorbent. However, the uptake rate of Cu^{2+} per gram of the F/L resin decreased with an increase in the amount of adsorbent.

Conclusion

This study indicates that the adsorbents synthesized from AFPs and plant polyphenols are effective for the removal and collection of transition and heavy metal ions from industrial effluents and waste aqueous solutions. Further chemical studies of these adsorbents by methods such as functional group analysis are needed.

References

1. Rao, C. R. N., Iyengar, L., and Vevkobachar, C. (1993), *J. Environ. Eng.* **2,** 369–377.
2. Delgado, A., Anselmo, A. M., and Novaris, J. M. (1998), *Water Environ. Rec.* **70,** 370–375.
3. Noberg, A. and Rydin, S. (1984), *Biotechnol. Bioeng.* **26,** 265–268.
4. Leusch, A., Holan, Z. R., and Volesky, B. (1995), *J. Chem. Technol. Biotechnol.* **62,** 279–288.
5. Laube, V., Ramamoporthy, S., and Kusher, D. J. (1979), *Bull. Environ. Contam. Toxicol.* **21,** 763–770.
6. Guibal, E., Milot, C., and Roussy, J. (1999), *Water Environ. Rec.* **71,** 10–17.
7. Suyama, K., Fukazawa, Y., and Umetsu, Y. (1994), *Appl. Biochem. Biotechnol.* **45/46,** 871–879.
8. Suyama, K., Fukazawa, Y., and Suzumura, H. (1996), *Appl. Biochem. Biotechnol.* **57/58,** 67–74.
9. Ishikawa, S. and Suyama, K. (1998), *Appl. Biochem. Biotechnol.* **70–72,** 719–728.
10. Kawamoto, H., Nakatsubo, F., and Murakami, K. (1996), *Phytochemistry* **41(5),** 1427–1431.
11. Makkar, H. P., Dawra, R. K., and Singh, B. (1987), *Anal. Biochem.* **166(2),** 435–439.
12. Krisper, P., Tisler, V., Skubic, V., Rupnik, I., and Kobal, S. (1992), *Basic Life Sci.* **59,** 1013–1019.
13. Templeton, D. M. (1990), *J. Biol. Chem.* **265(35),** 21,764–21,770.