

# Adsorption Mechanism of Heavy-Metal Ion by Microspherical Tannin Resin

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## SYNOPSIS

The spherical tannin resin (STR) resulting from the reaction between Mimosa (*Acacia Mollissima*) tannin (condensed-type tannin) and formaldehyde was very porous. The specific surface area of the STR made from 37.5% of tannin was 139.2 m<sup>2</sup>/g (1 g of the resin in this is wet resin corresponding to 1 g of dried resin). Properties such as specific surface area and average pore radius could be controlled by adjusting the tannin concentration. The apparent activation energy of Cu<sup>2+</sup> ion adsorption by STR was 3 kcal/mol, and that of Cr<sup>6+</sup> ion was 2 kcal/mol. Since the energy was small, we concluded that the adsorption of metal ions was not influenced significantly by the adsorption temperature. The heat of adsorption for Cu<sup>2+</sup> ions was only 1.6 kcal/mol, which suggests that the adsorption was a physical phenomenon. It was thought that the diffusion of heavy-metal ions into the porous resin was the rate-determining step of the adsorption since the elution profile of the column method was analogous to the profile of active carbon, which adsorbs physically, the heavy metal ions gradually leaking through the column. The surface and cross section of the STR were observed before and after Cu<sup>2+</sup> ion adsorption with the scanning electron microscope. The pores of the spherical resin were clogged with adsorbed copper, suggesting that the Cu<sup>2+</sup> ions were adsorbed during the formation of a multimolecular layer. The adsorption may therefore have been due to physical attractive forces. The rate of adsorption and adsorption isotherms of Cu<sup>2+</sup> ions from copper salts having various anions was found to vary depending on the type of anion. These phenomena were not thought to be due to the properties of the spherical resin but to differences in the hydration state of copper ions.

## INTRODUCTION

In a previous study we described how spherical tannin resin (STR) prepared from Mimosa tannin (MT) and formaldehyde adsorbed heavy-metal ions from solutions of Cr<sup>6+</sup> ions, Cu<sup>2+</sup> ions, Cd<sup>2+</sup> ions, and Fe<sup>2+</sup> ions.<sup>1,2</sup> The adsorption mechanism was unknown.

It has been suggested that when tannin is in the presence of heavy-metal ions, a tannin-ion complex precipitate is produced.<sup>3</sup> We know that tannin and polyphenols reduce metal ions; even if the tannin coexists with the metal ions, the produced precipitate may redissolve depending on the type of tannin.<sup>4</sup>

Since the tannin in this study was immobilized by the reaction with formaldehyde in the spherical resin, it was thought that redissolution of the produced precipitate was unlikely. Consequently, we sought to clarify the mechanism of adsorption of heavy-metal ions by STR.

## EXPERIMENTS

### Materials

Mimosa tannin (condensed-type tannin) was used. The technique of purification and the properties of the tannin were identical to those shown previously.<sup>1</sup> Heavy metals and the reagents for buffer solutions were special grade reagents, toluene and methanol used for the preparation of STR were first grade reagents, and polybutene (54 cp, at 60°C) was tech-

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nical grade. Solutions of 0.1N CH<sub>3</sub>COOH and 0.1M CH<sub>3</sub>COONa were used as the buffer solutions at pH 4, 5, and 6.

### Experimental Methods

Preparation of STR was by a similar method as in the first report.<sup>1</sup> Formaldehyde and MT were reacted under conditions such that the molar ratio of formaldehyde to flavonoid skeleton was 1, reaction temperature at 60°C, and reaction time was 200 min with stirring in polybutene medium. Tannin concentrations on preparing the resin were 37.5, 45.0, 46.0, and 55.8%, and the effects of tannin concentration on adsorption properties were studied. The spherical resins were made to a similar size by stirring speed control, using 300 rpm for 37.5% tannin, 390 rpm for 45 and 46% and 480 rpm for 55.8%.

Specific surface area was determined by the solvent adsorption method.<sup>5</sup> Small amounts of wet STR, prepared from the 37.5, 46.0, and 55.8% MT solution, were equilibrated in methanol. The resins were further equilibrated in *n*-hexane, the amount of *n*-hexane contained in the resin being measured by filtration with G2 glass filter before weighing.

From 0.5 to 2 g of the spherical resin and 50 mL of 0.026 mol/L iodine *n*-hexane solution were mixed while stirring with a 360° somersault stirrer for 72 h at 23°C, during which time iodine was adsorbed by the resin. The supernatant was collected, the residual iodine in a set volume of the solution being titrated with 0.1N sodium thiosulfate while stirring vigorously. The difference between the initial and residual iodine concentrations was calculated, thus allowing the amount of iodine adsorbed by the resin to be determined. The specific surface area (*S*) of the STR was calculated from the amount of adsorbed iodine by substituting the value of 21.1 Å<sup>2</sup> for the occupied area of the adsorbed iodine in *n*-hexane solvent.<sup>6</sup>

The measurement of total pore volume (*V<sub>g</sub>*) and average pore radius ( $\bar{r}$ )<sup>7</sup> was as follows. About 2 g of the resin was weighed out and equilibrated in *n*-hexane as previously described. The suspended resin in *n*-hexane was heated in a water bath and filtered out with G3 glass filter from boiling *n*-hexane. The resulting resin was then weighed. The density of *n*-hexane was determined to be 0.645 g/cm<sup>3</sup>. Any increase in weight of the spherical resin judged to be the amount of *n*-hexane remaining in the pore of the resin, allowing the *V<sub>g</sub>* to be calculated. The total pore volume in water was measured too. The average pore radius ( $\bar{r}$ ) was calculated from the relationship between *S* and *V<sub>g</sub>* on the assumption that the pores

were of the straight pipe type, using the formula  $\bar{r} = 2V_g/S$ .

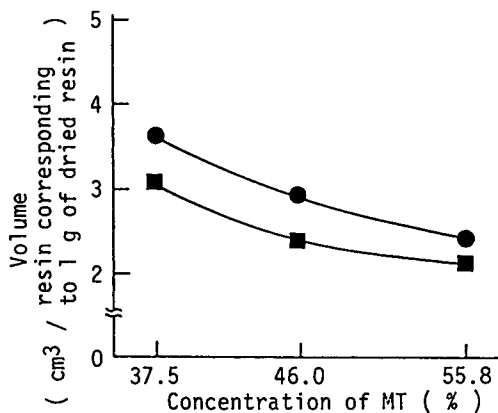
The amount of adsorbed heavy-metal ion was determined as follows. The prescribed amount of wet STR was weighed, and the prescribed amount of the required heavy-metal ion buffer solution was added, and the vessel was stoppered. The heavy-metal ions were adsorbed by the spherical resin during somersault stirring at 23°C or with the shaker in a thermostat at the prescribed temperature. The supernatants were then collected and the concentration of inadsorbed heavy-metal ions determined with the atomic absorption spectrophotometer (AAS) (Nihon Jourrel Ash Co. Ltd. AA-500 type). The amount of adsorbed heavy-metal ion was calculated as the difference in concentration before and after treatment.

The apparent activation energies for adsorption were determined as follows. The wet STR corresponding to oven-dried weight 0.25 g was weighed and Cr<sup>6+</sup> ion solution (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, pH 4, 495 ppm) or Cu<sup>2+</sup> ion solution (CuCl<sub>2</sub>, pH 4, 495 ppm) at the required concentration was added. The adsorption treatments were performed with shaking at 19.5, 34.5, and 50.0°C. An aliquot of the solution was removed at the prescribed time. The amounts of adsorbed Cr<sup>6+</sup> ion or Cu<sup>2+</sup> ion were determined by AAS. The time taken until resin corresponding to 1 g of oven-dried resin adsorbed 2 mmol of Cr<sup>6+</sup> ion and the time until the same amount of resin adsorbed 0.1 mmol of Cu<sup>2+</sup> ions were measured at the three temperatures described previously. The logarithms of the reciprocal of each time were plotted against the absolute temperature (Arrhenius plot). The apparent activation energies of each heavy-metal adsorption were calculated from the slopes of the curves.

The heats of adsorption were determined by combining wet STR (prepared from 37.5% tannin) corresponding to oven-dried weights of 0.2, 0.4, 0.6, 0.8, and 1.0 g with 50 mL Cu<sup>2+</sup> ion [(CH<sub>3</sub>COO)<sub>2</sub>Cu, pH 4, 3050 ppm]. The adsorption treatments were performed with shaking for 24 h at 20 and 30°C. The adsorption isotherms were plotted on the basis of the amount of adsorbed ion. The heats of the adsorption were then calculated from the Clapeyron–Clausius equation throughout the entire range of adsorption at 20 and 30°C. The Clapeyron–Clausius equation<sup>8</sup> is as follows:

Heat of adsorption (*q<sub>iso</sub>*)

$$= \frac{-R}{2.303[(\log p_1 - \ln p_2)/(1/T_1 - 1/T_2)]}$$



**Figure 1** Swelling properties of the spherical resin: (■) in *n*-hexane; (●) in ion-exchanged water.

where  $p_1$ ,  $p_2$  are the concentrations of unadsorbed heavy-metal ions at prescribed adsorption levels, at temperatures  $T_1$  and  $T_2$ , respectively, and  $R$  is the gas constant.

Heavy-metal adsorption with column was determined as follows: 7.8 mL (corresponding to oven-dried weight 2.6803 g) of STR was packed in a  $18 \times 160$  mm column. The packed column was conditioned with acetic acid buffer solution, and  $\text{Cr}^{6+}$  ion solution ( $\text{K}_2\text{Cr}_2\text{O}_7$ , pH 4, 126 ppm) or  $\text{Cu}^{2+}$  ion solution [ $(\text{CH}_3\text{COO})_2\text{Cu}$ , pH 4, 200 ppm] was passed through the column at space velocity (SV) 10. Eluting fractions of 25 mL were collected. The amounts of unadsorbed heavy-metal ion in the prescribed fractions were determined by AAS. The amount of eluted heavy-metal ion (ppm) was plotted against the amount of injected solution, expressed as litres per litre of resin.

It was expected that the rate of adsorption and the amount of adsorbed metal ion would be influenced by the type of the anion in association with the heavy-metal ion. In determining the adsorption

rate, resin prepared at 37.5% tannin concentration and corresponding to 0.25 g of oven-dried resin, was weighed out and  $\text{Cu}^{2+}$  ions in the form of  $\text{CuCl}_2$  (pH 4, 432 ppm, 50 mL in acetic acid buffer solution) or as  $\text{Cu}(\text{NO}_3)_2$  (pH 4, 608 ppm, 50 mL in acetic acid buffer solution),  $(\text{CH}_3\text{COO})_2\text{Cu}$  (444 ppm, 50 mL in acetic acid buffer solution) were added to the resin. The adsorption treatments were performed for 0.5, 1, 4, 8, and 12 h at 23°C with the 360° somersault stirring apparatus. After the adsorption treatment, the amount of unadsorbed heavy-metal ion in the supernatant was determined by AAS. The rate of adsorption was calculated as the amount of adsorbed metal ion per unit weight resin per unit time.

In the determination of the adsorption isotherms, resin corresponding to 0.2, 0.4, 0.6, 0.8, and 1.0 g of oven-dried resin was weighed out, and 50 mL of  $\text{CuCl}_2$  buffer solution (pH 5, 3380 ppm), 50 mL of  $\text{Cu}(\text{NO}_3)_2$  buffer solution (pH 5, 3280 ppm), or 50 mL of  $(\text{CH}_3\text{COO})_2\text{Cu}$  buffer solution (pH 5, 3220 ppm) was added. The adsorption treatments were performed for 24 h at 23°C with 360° somersault stirring, and the unadsorbed heavy-metal ion concentration determined by AAS.

The resins prepared from 37.5, 46.0, or 55.8% MT solutions, before and after the adsorption of  $\text{Cu}^{2+}$  ions, were vacuum dried and observed with the scanning electron microscope.

## RESULTS AND DISCUSSION

### Results for $S$ , $V_g$ , and $\bar{r}$ of STR, and the Ability to Adsorb Heavy Metal Ion

When the STR was dipped in iodine *n*-hexane solution, the saturated amount of adsorbed iodine was determined from the adsorption isotherms as shown in Figure 1. The saturated adsorption for each resin

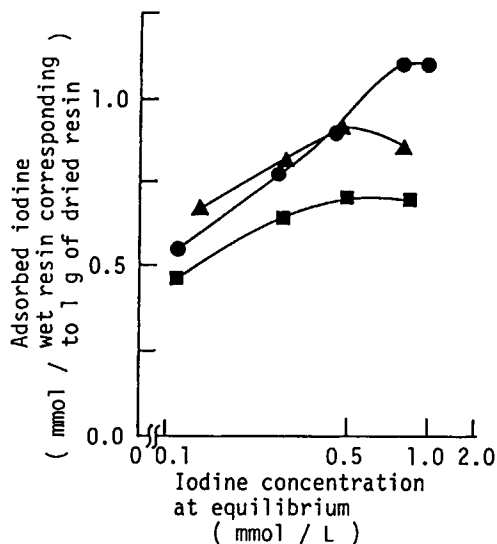
**Table I** Properties of the Spherical Tannin Resin<sup>a</sup>

Concentration of MT (%) <sup>b</sup>	Specific Surface Area ( $\text{m}^2/\text{g}^c$ )	Total Pore Volume ( $\text{cm}^3/\text{g}^c$ )	Average Pore Radius ( $\text{Å}$ )	Total Pore Volume in Water ( $\text{cm}^3/\text{g}^c$ )
37.5	139.2	1.77	254.3	1.90
46.0	117.4	1.15	196.0	1.37
55.8	88.8	0.61	137.4	0.93
Active carbon	500–1500	0.8–2.7	5–10,000	

<sup>a</sup> Specific surface area:  $I_2$  is adsorption method from  $I_2$ -*n*-hexane solution. (Cross-sectional area of  $I_2$ :  $21.1 \text{ Å}^2$ ). Total pore volume: liquid substitution method. (Heating the resin in *n*-hexane, and then drying only the surface of the resin by filtration.) Average pore radius: evaluated by the equation below.  $\bar{r} = 2V_g/S$  where  $V_g$  = total pore volume and  $S$  = specific surface area.

<sup>b</sup> The concentration of MT when the spherical resin were prepared.

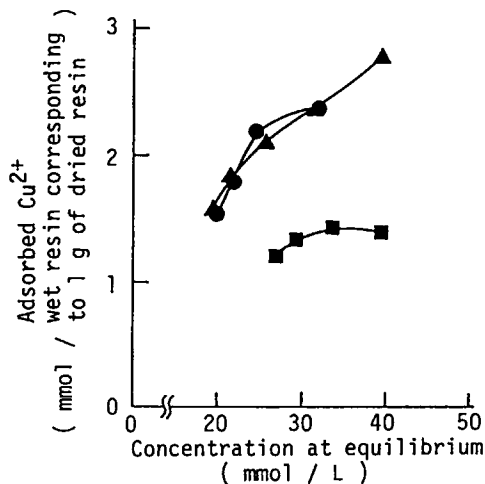
<sup>c</sup> Wet resin corresponding to 1 g of dried resin.



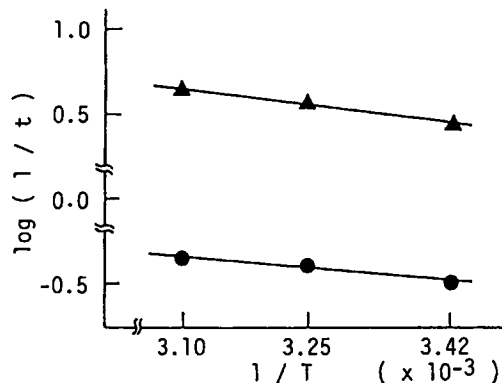
**Figure 2** Adsorption isotherms of iodine from iodine-*n*-hexane solution: (●) 37.5% resin; (▲) 46.0% resin; (■) 55.8% resin. Initial concentration of iodine: 0.026 mmol/L. Adsorption condition: 23°C, 72 h, 360° stirring.

(per gram oven-dried resin) was 1.10 mmol for 37.5% resin, 0.92 mmol for 46.0% resin, and 0.70 mmol for 55.8% resin. The  $S$  values of each resin were calculated from these saturated amounts of adsorbed iodine.

Although the liquid displacement<sup>7</sup> for  $V_g$  determination was only approximate, the data scatter was small (3–9%), which was acceptable. The  $\bar{r}$  values were calculated from  $S$  and  $V_g$ .



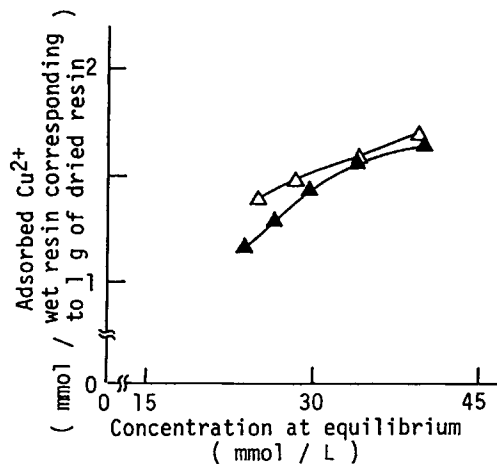
**Figure 3** Adsorption isotherms of the resins prepared from various concentrations of MT. Legends are the same as in Fig. 2. Initial concentration of  $\text{Cu}^{2+}$ : 3220 ppm,  $(\text{CH}_3\text{COO})_2\text{Cu}$ , pH 5. Adsorption condition: 23°C, 24 h, 360° stirring.



**Figure 4** Arrhenius plots of  $\text{Cr}^{6+}$  or  $\text{Cu}^{2+}$  adsorption: (●)  $\text{Cr}^{6+}$ ; (▲)  $\text{Cu}^{2+}$ . 37.5% resin, corresponding to 0.25 g dry weight.  $\text{Cr}^{6+}$ : 495 ppm, pH 4;  $\text{Cu}^{2+}$ : 545 ppm, pH 4. Activation energies:  $\text{Cr}^{6+}$ : 2 kcal/mol;  $\text{Cu}^{2+}$ : 3 kcal/mol.

The  $S$ ,  $V_g$ , and  $\bar{r}$  values are shown in Table I. All three decreased in size with increasing concentration of MT used in the resin preparation. It was shown that the structure of the resin was fine. Comparison with the data of active carbon shows that STR is a reasonably porous spherical resin. The values of  $S$  etc. were presumed to be larger in water than in *n*-hexane because of the larger value of  $V_g$  in water, and comparing the resin's swelling property in water with *n*-hexane (Fig. 2).

The adsorption isotherms of three kinds of resin are shown in Figure 3. The amount of adsorption of  $\text{Cu}^{2+}$  ion by the resin made from 55.8% of tannin was smallest, compared to those of resin made from 37.5 and 46.9%, which were similar. When the resin was made from tannin at concentrations more dilute



**Figure 5** Adsorption isotherms of  $\text{Cu}^{2+}$  heat of adsorption: (Δ) 20°C; (▲) 30°C.  $\text{Cu}^{2+}$ : 3050 ppm, pH 4. Adsorption time: 24 h.

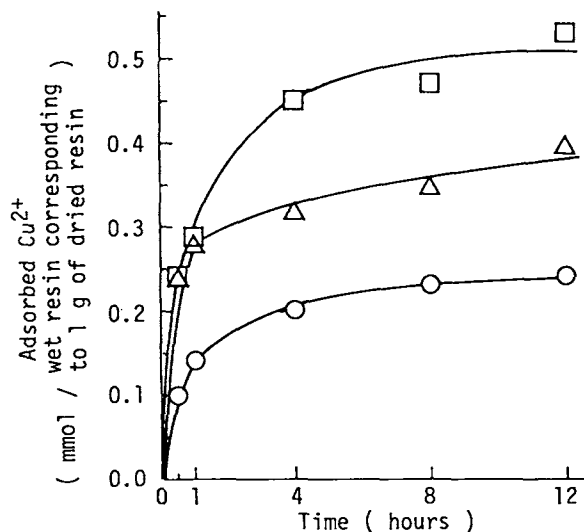
than 45%, it was thought that the diffusion of the metal ion into the pore proceeded at a constant rate, regardless of the values for *S* etc.

**Apparent Activation Energies for the Adsorption**

The Arrhenius plot, where the logarithms of the reciprocal of time were plotted against the reciprocal of the absolute temperature, is shown in Figure 4. The apparent activation energies calculated from these slopes being 2 kcal/mol for Cr<sup>6+</sup> ions, and 3 kcal/mol for Cu<sup>2+</sup>. Since these activation energies were small, the adsorption of heavy-metal ions by STR was little influenced by temperature. If adsorption by the resin was accompanied by chemical reaction, it would require large activation energies. From these facts it was assumed that the adsorption by the resin was accompanied by physical adsorption.

**Heats of Adsorption**

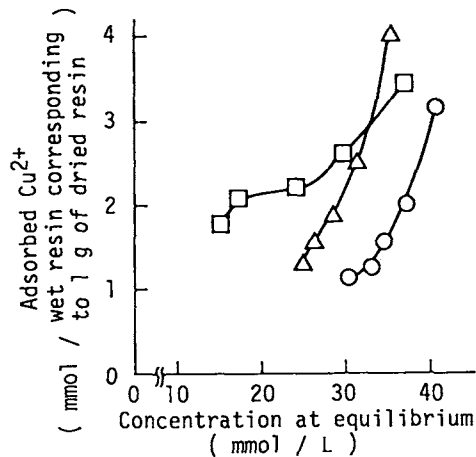
The phenomenon of adsorption is always attended by the evolution of heat, which is called the heat of adsorption.<sup>9</sup> This varies depending upon whether the adsorption occurs by physical or chemical at-



**Figure 6** Comparison of Cu<sup>2+</sup> ion adsorption rate from different copper salts:

Cu salt	ppm × mL
(○) CuCl <sub>2</sub>	432 × 50
(Δ) Cu(NO <sub>3</sub> ) <sub>2</sub>	608 × 50
(□) (CH <sub>3</sub> COO) <sub>2</sub> Cu	444 × 50

Adsorption condition: 37.5% resin: 0.25 g, pH 4, 23°C, 0.5–12 h (5 steps).



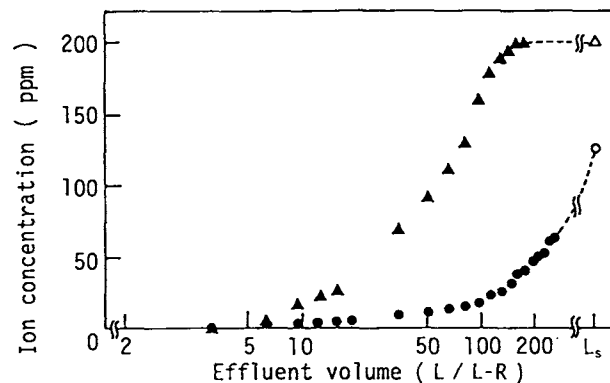
**Figure 7** Comparison of Cu<sup>2+</sup> ion adsorption from different copper salts:

Cu salt	ppm × mL
(○) CuCl <sub>2</sub>	3380 × 50
(Δ) Cu(NO <sub>3</sub> ) <sub>2</sub>	3280 × 50
(□) (CH <sub>3</sub> COO) <sub>2</sub> Cu	3220 × 50

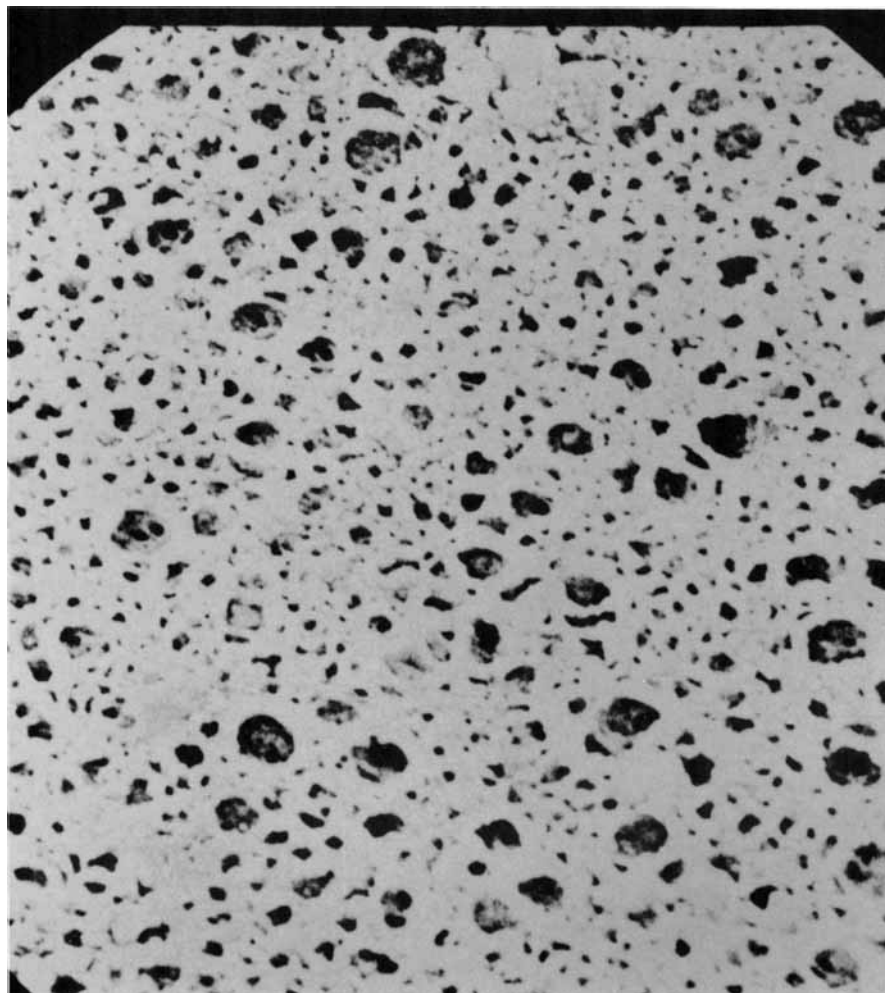
Adsorption condition: pH 5, 23°C, 24 h, 45% resin: 0.2–1.0 g (5 steps).

tractive forces between the adsorbent and the adsorbates. It is said that the heat of adsorption required for physical adsorption is a few kcal/mol, but that in chemical adsorption this may increase several tens to several hundreds kcal/mol.<sup>10</sup>

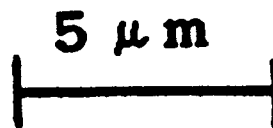
The adsorption isotherm at 20 and 30°C are shown in Figure 5. The calculated heat of adsorption for Cu<sup>2+</sup> was consequently 1.6 kcal/mol in the range



**Figure 8** Elution profile of Cr<sup>6+</sup> or Cu<sup>2+</sup> from a spherical tannin resin column: (●) Cr<sup>6+</sup>; (▲) Cu<sup>2+</sup>. 45.0% resin, wet resin corresponding to 2.68 g of dry resin (7.8 cm<sup>3</sup>). Column: 18 × 160 mm. SV: 10. Temperature: 23°C. L<sub>s</sub>: Loading solution: Cr<sup>6+</sup>: pH 4, 128 ppm; Cu<sup>2+</sup>: pH 5, 200 ppm.



Surface  
(A) Before adsorption



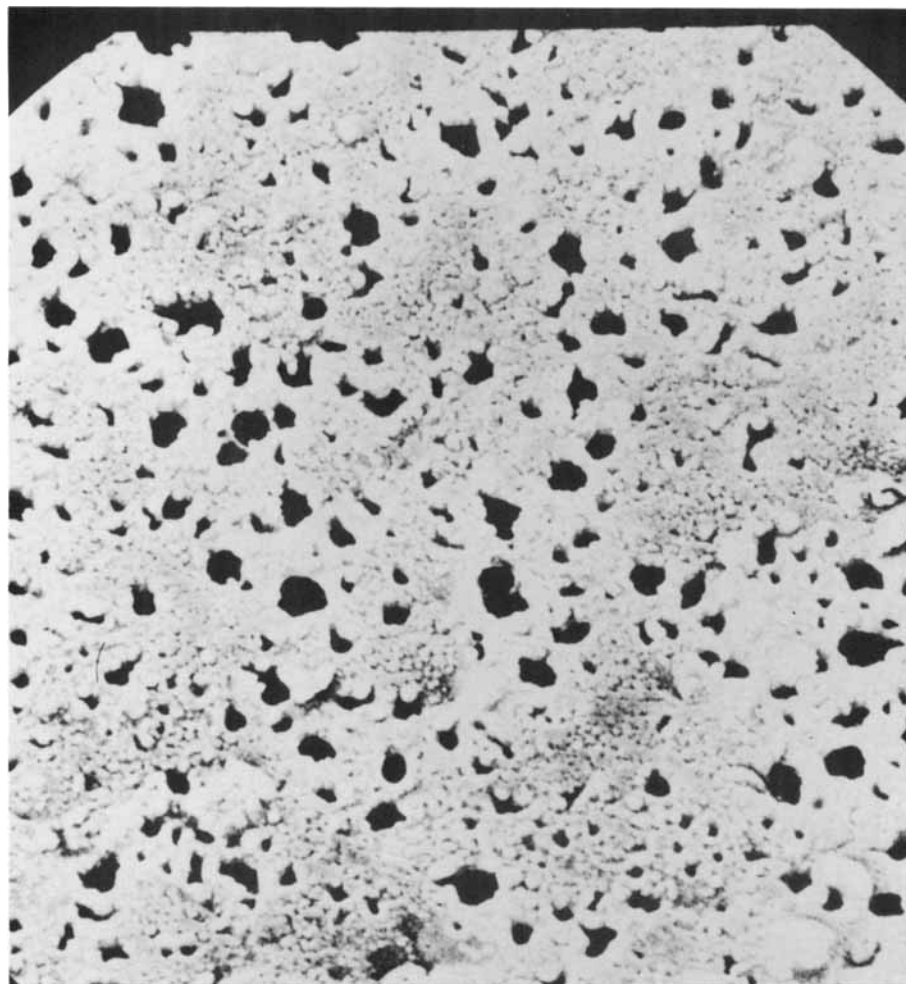
**Plate 1** Spherical tannin resin before and after the adsorption of  $\text{Cu}^{2+}$  ions using scanning electron microscopy. Surface: (A) Before adsorption. (B) After adsorption. Cross section: (C) Before adsorption. (D) After adsorption.

of this measurement. This result suggests that the adsorption of  $\text{Cu}^{2+}$  ion by the spherical resin was caused by physical adsorption based on attractive forces.

#### Adsorption of Heavy-Metal Ions to Packed Resin

Results are shown in Figure 6. Both  $\text{Cr}^{6+}$  and  $\text{Cu}^{2+}$  initially eluted at about 4 L/L-R, after which the concentration of heavy-metal ion in the eluate gradually increased. From these results, we concluded that initially the adsorption of heavy-metal ion by

the spherical tannin occurred at the surface of the resin, after which the surface was covered with adsorbed metal. The metal ion was then able to diffuse into the resin, allowing adsorption to take place. However, when the rate of flow was larger than the rate of diffusion, the metal ion ceased being adsorbed and leaked out. In general, when the velocities of adsorption to smooth surfaces are compared, physical adsorption is rapid, and chemical adsorption is slow. Since the STR is porous, this generalization does not hold. The type of the leakage displayed by this resin was not that seen with commercial ion exchange resins, representative of chemical adsor-



Surface  
(B) After adsorption

5  $\mu$  m

Plate 1 (Continued from the previous page)

bents, but was very similar to the leakage curve of active carbon, which adsorbs physically.

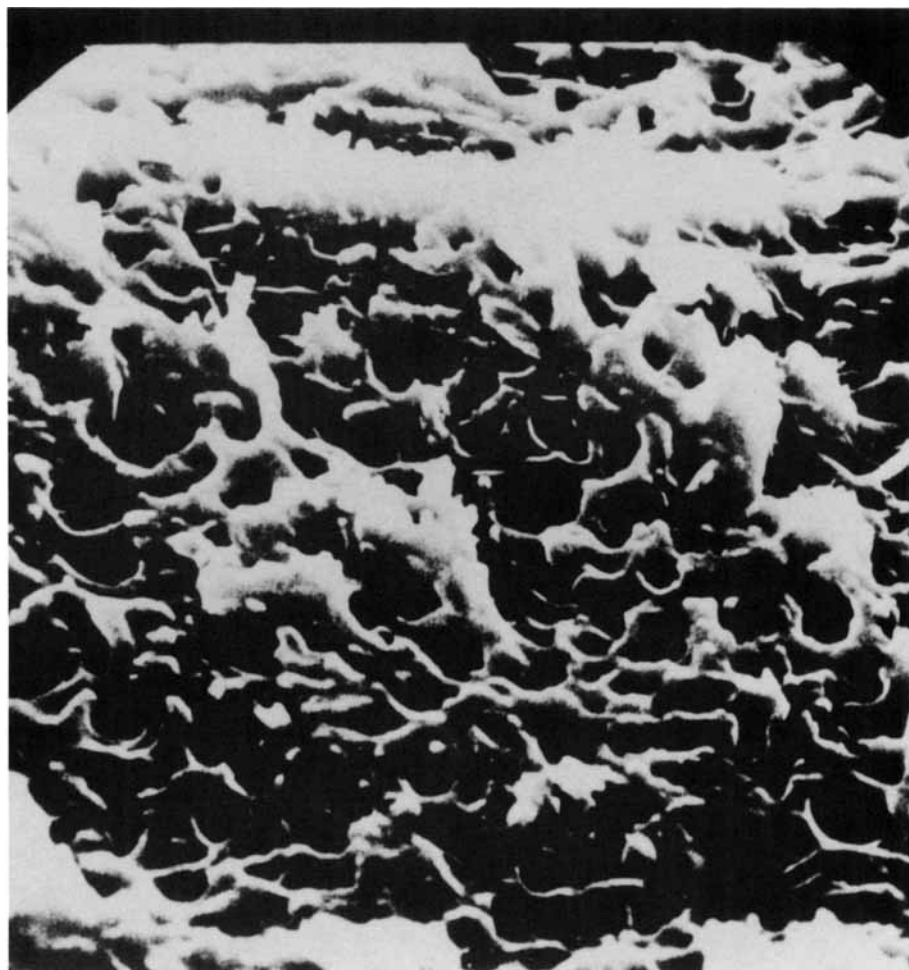
**The Effect of Anion on the Adsorption Rate of  $\text{Cu}^{2+}$  Ion**

The results are shown in Figures 7 and 8. The ratios of initial (one hour) adsorption rate constant were as follows: hydrochloride–nitrate–acetate = 1 : 1.43 : 2.18. Also, the acetate was able to adsorb  $\text{Cu}^{2+}$  ion over a wider concentration range than nitrate and chloride. Comparing the nitrate with chloride, the same concentration of  $\text{Cu}^{2+}$  ion was adsorbed more efficiently from the nitrate solution.

These results indicate that the rate of adsorption was influenced by the hydration state of  $\text{Cu}^{2+}$  ion in the buffer solution or by the diffusion rate of hydrated  $\text{Cu}^{2+}$  ion into the pore of the resin.

**Observation of the Resin with the Scanning Electron Microscope**

The surface of the resin before adsorbing  $\text{Cu}^{2+}$  ion is shown in Plate 1(A), with the surface after adsorption being shown in Plate 1(B). The cross section of the resin before adsorption of  $\text{Cu}^{2+}$  ion is shown in Plate 1(C), and the cross section after adsorption in Plate 1(D). The initial roughness of the



Cross section  
(c) Before adsorption

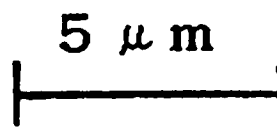


Plate 1 (Continued from the previous page)

surface was smoothed by the adsorption of  $\text{Cu}^{2+}$  ions. Since the adsorption of  $\text{Cu}^{2+}$  ion was so abundant that rough resin faces were made smooth, it was thought that the copper adsorption made a number of layers. When materials form multilayer adsorption, it has been shown that the adsorption occurs physically.<sup>11</sup> The above data confirmed visually that the adsorption of  $\text{Cu}^{2+}$  ions by STR was by physical rather than chemical means.

## CONCLUSIONS

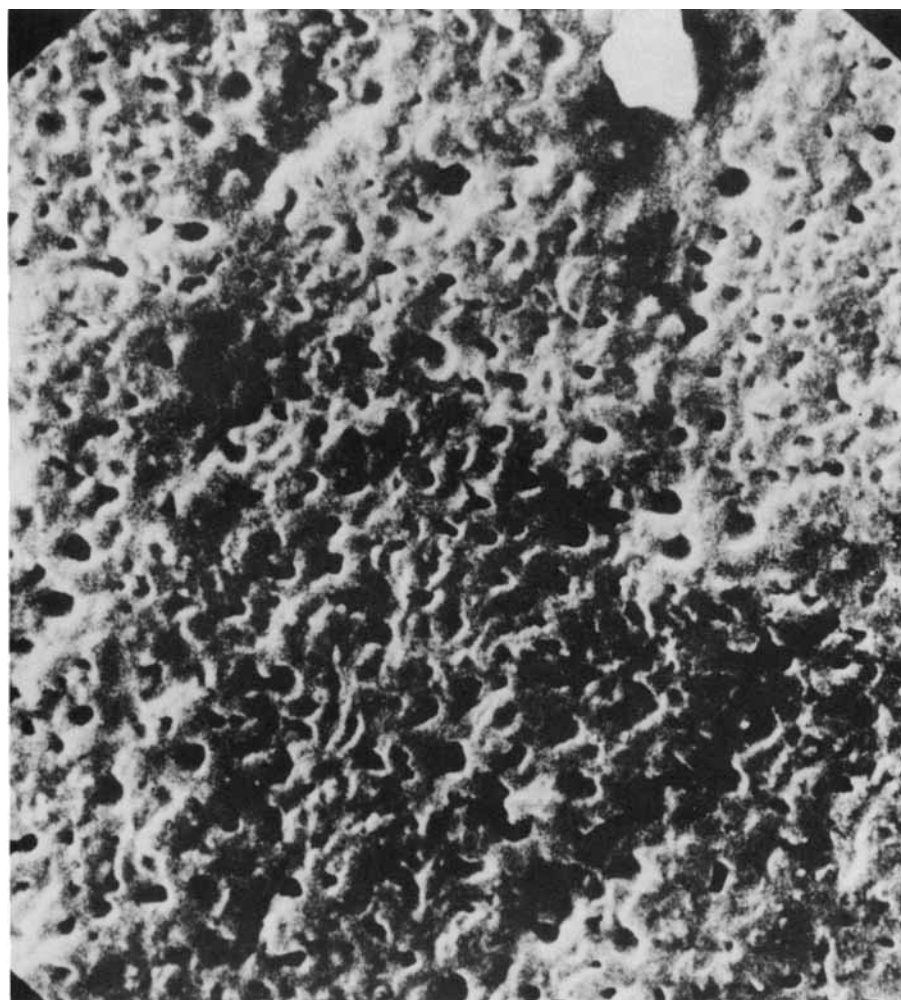
1. The spherical tannin resins are porous spherical adsorbents whose porosity is controllable by

changing the tannin concentration used when the spherical tannin resin is prepared. However, the results of the  $\text{Cu}^{2+}$  ion adsorption experiments showed that the porosity of the resin is not necessarily correlated with the amount of adsorption it displays. In particular, the resins prepared from tannin solutions below 45% concentration showed similar adsorption isotherms. Large differences were not found in the behavior of adsorption.

2. Apparent activation energies were small, the adsorption of heavy-metal ions by this resin being little influenced by the adsorption temperature.

3. The heat of adsorption for  $\text{Cu}^{2+}$  ion adsorption by STR was 1.6 kcal/mol at room temperature. Because the heat of adsorption was very low, it was





Cross section  
(D) After adsorption

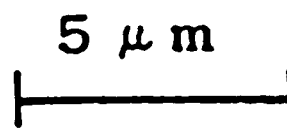


Plate 1 (Continued from the previous page)

thought that the adsorption of  $\text{Cu}^{2+}$  ion by STR occurred by physical adsorption. The possibility that the adsorption of heavy-metal ion by STR occurred by physical adsorption was suggested by the heats of adsorption values, the elution profile of adsorption to packed resin, and the observation with the scanning electron microscope. Also, since during physical adsorption, heavy-metal ions are reduced by the reductive action of tannin,<sup>12</sup> it was thought that the heavy metals were adsorbed during the formation of a number of layers.

4.  $\text{Cu}^{2+}$  ions were best adsorbed when their anions were acetate, nitrate, or chloride in descending order. It was thought that this order was dependent

on the hydration state of  $\text{Cu}^{2+}$  ions. However, there is need for further study of this phenomenon.

5. In the observation, with the scanning electron microscope, of the resin after the adsorption of  $\text{Cu}^{2+}$  ions, it was thought that the copper adsorption made a number of layers. This data confirmed visually that the adsorption of copper ions by this resin was by physical rather than chemical means.

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