

Simultaneous Removal of Cyanide and Copper Ions in a Semi-Fluidized Ion Exchanger Bed

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Abstract—Simultaneous removal of cyanide and copper ions from electroplating wastewater was studied in a liquid-solid semi-fluidized ion exchanger bed. The diameter and the height of column are 20 mm and 600 mm, respectively. Strong-base anion exchange resin particles (Dowex1X8-50) were contacted with synthetic solutions containing copper and cyanide ions. Cyanide and copper ions in the solution were analyzed by a cyanide electrode and ICP (inductively coupled plasma), respectively. The ion exchange equilibrium data of Cu⁺ removed as cyanide-copper complexes on Dowex1X8-50 at 25 °C can be fitted with the Langmuir equation. Early leakage of cyanide from experimental loading profile data results in not only lower selectivity of free cyanide but also different selectivities of CN-Cu complexes due to the size and the structure of complexes. The optimum molar ratio (Q) between cyanide and copper ions is about 3 to obtain a reasonable removal rate of cyanide in this experiment.

Key words : Simultaneous Removal, Cyanide, Copper, Ion-exchange, Semi-fluidized Bed

INTRODUCTION

There are high levels of cyanide and toxic heavy metals such as lead, nickel, chromium, cadmium, and copper in industrial waste effluents from chemical syntheses, electroplating, and steel industries [Tchobanoglous and Burton, 1991; Lee and Hong, 1995]. In general, heavy metal-cyanide complexes could be formed under the pH of wastewater. In particular, the presence of copper-cyanide complexes in wastewater has presented a significant problem in several operations so far [Jae et al., 1988; Hsu et al., 1991; Fagan et al., 1997]. The removal and recovery of metal-cyanide complexes are very important not only for environmental protection but also because they are valuable materials.

The classical and most common method for eliminating cyanide ions from wastewater is alkaline chlorination where cyanide can be totally oxidized to cyanate and then to CO₂ and N₂ (1). Such oxidative processes using chloride, hydrogen peroxide, and ozone can possibly create toxic gases (ClCN, CNO) and other chemicals (cyanate, chlorinated phenol) as by-products. Furthermore, these methods are ineffective for complexed cyanides because of an inability to destroy metal complexes [Avery and Fries, 1975]. Several other methods have been suggested in the literature for treating wastewater containing cyanide ions. These include evaporation, reverse osmosis, electrodialysis, activated carbon adsorption, and ion exchange [Gupta, 1985; Goncalves et al., 1998].

Ion exchange operation has been applied in heavy metal treatment because of the following advantages: (1) no secondary pollutants, (2) very compact, (3) easy recovery of metals,

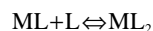
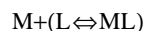
and (4) more versatile than other methods. One often cited problem, the disposal of waste regeneration solution, has been solved by a combination with other methods [Goto and Goto, 1987; Short et al., 1997; Brewer et al., 1997].

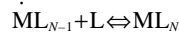
In general, most ion exchange operations for removing metal ions from wastewater have been studied in packed bed reactors. However, packed bed operation has some disadvantages, such as channeling and high pressure drop, though ion exchange operation is usually used for advanced treatment. Ion exchange in fluidized or spouted beds can effectively eliminate these problems, particularly when resin particles are mobile.

In this work, mass transfer between liquid and ion exchange resin particles was studied experimentally in a semi-fluidized bed reactor. Ion exchange characteristics in simultaneous removal of copper and cyanide ions from synthetic solutions containing Cu-CN complexes using a strong-base anion exchanger were experimentally studied. In addition the optimum value of Q was experimentally determined to give a reasonable removal rate.

THEORY

Heavy metals in electroplating baths form very stable complexes with cyanide ions.



$$\vdots$$


$$K_i = \frac{[ML_i]}{[ML_{i-1}][L]} \quad (1)$$

$$\beta_i = \frac{[ML_i]}{[M][L]^i} \quad (2)$$

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where K_i =the stepwise formation constants

β_i =the overall formation constants

$[L]$ =free liquid concentration

$[M]$ =free metal concentration

$[ML_i]$ =concentration of complex ML_i

$\beta_0=K_0=1$.

All charges are omitted for the sake of simplicity. i is the number of ligands and N is the maximum number of ligands that can attach to one metal cation. The relative amounts of various complexes can be calculated from the information of formation constants and the free ligand concentration. The total metal concentration, T_M , and the total ligand concentration, T_L , are given by the following mass balances:

$$T_M = [M] + [ML] + [ML_2] + \dots + [ML_N] = \sum_{i=0}^N [ML_i] \quad (3)$$

$$T_L = [L] + [ML] + 2[ML_2] + \dots + N[ML_N] = [L] + \sum_{i=1}^N i[ML_i] \quad (4)$$

Using Eqs. (2), (3) and (4) we get:

$$T_M = [M] \sum_{i=0}^N \beta_i [L]^i \quad (5)$$

$$T_L = [L] + [M] \sum_{i=1}^N i \beta_i [L]^i \quad (6)$$

The mole fraction of the complex ML_i is given by:

$$\alpha_i = \frac{[ML_i]}{T_M} = \frac{\beta_i [L]^i}{\sum_{i=0}^N \beta_i [L]^i} \quad (7)$$

The average ligand number is defined as follows:

$$\bar{n} = \frac{\{T_L - [L]\}}{T_M} = \frac{\sum_{i=1}^N i \beta_i [L]^i}{\sum_{i=0}^N \beta_i [L]^i} \quad (8)$$

Combining Eqs. (5), (6), and (8), we get:

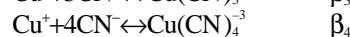
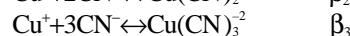
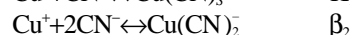
$$T_M = \frac{[L]}{Q - \bar{n}} = \frac{\sum_{i=0}^N \beta_i [L]^{i+1}}{\sum_{i=0}^N (Q - i) \beta_i [L]^i} \quad (9)$$

where $Q = \frac{T_L}{T_M}$

Using Eq. (9), a diagram of $\log T_M$ against $\log [L]$ can be plotted with Q as a parameter. This permits the determination of $\log [L]$ from the knowledge of T_L and T_M . Then, the relative amounts of various complexes can be calculated from Eq. (7).

Copper ions are present in monovalent state in electroplating baths. Copper-cyanide complexes are usually present as monovalent ($Cu(CN)_2^-$), divalent ($Cu(CN)_3^{2-}$), and trivalent

($Cu(CN)_3^-$) species in aqueous solutions and formed by the following complexation reactions:



where K_1 is $10^{19.5}$, β_2 is 10^{24} , β_3 is $10^{28.59}$, and β_4 is $10^{30.3}$ [Gupta, 1985].

Charge balance of aqueous solution in this study is $[Na^+] + [Cu^+] + [H^+] = [CN^-] + [Cu(CN)_2^-] + 2[Cu(CN)_3^{2-}] + 3[Cu(CN)_4^{3-}] + [OH^-] + [Cl^-]$.

EXPERIMENT

Fig. 1 shows the schematic diagram of the experimental apparatus for this study. This column was made of an acrylic tube of 20 mm diameter and 600 mm height. A movable upper retaining grid, which was made of a 60 mesh stainless steel net, was also fixed in the column to adjust it as a fixed bed or a semi-fluidized bed according to its purpose.

The resin used was a strong-base, gel type, ion exchanger, Dowex1X8-50. The physical properties of the resin are shown in Table 1. Synthetic waste solutions were prepared by dissolving reagent grade sodium cyanide and copper (I) cyanide in distilled water. The pH of solution was about 12 to form optimum Cu-CN complexes by the addition of sodium hydroxide and an ionic strength adjustor (ISA). The temperature was kept at $24 \pm 1^\circ C$ during experiments.

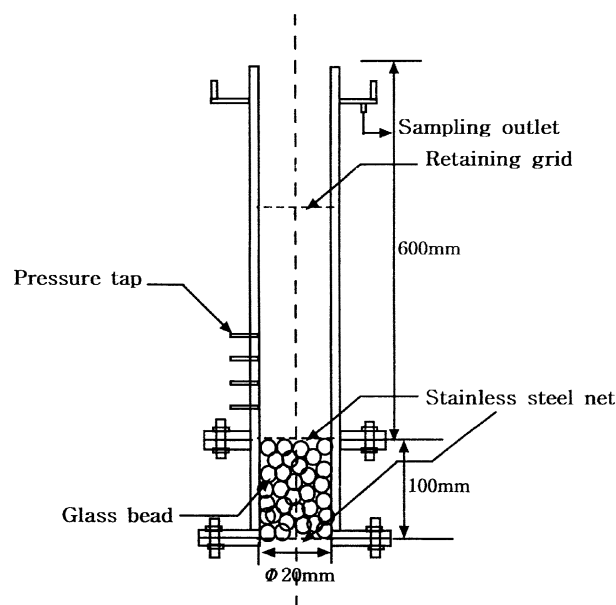


Fig. 1. Schematic diagram of the experimental apparatus.

Table 1. Experimental conditions: $D_c=20$ mm

Size of particle (mesh)	Density of resin (kg/m^3)	U_{mf} (mm/s)	$\epsilon(-)$ of Bed
35-50	1108.30	0.71	0.35

Ion exchange equilibrium amounts of Cu^+ between the resin and liquid phases were experimentally measured in a shaking bath. The shaking bath was kept in a thermostat at 25 °C. In this experiment, the different mass of resin particles (0.1 g, 0.2 g, 0.3 g, 0.4 g, and 0.5 g) was used under the same concentration of the ions. For column tests, synthetic solutions were passed through a column that was packed with about 10 g of the ion exchange resin. The effluent concentrations are monitored to obtain the breakthrough curve. The breakthrough times are defined as the time at which the exit concentration reaches 10% of the inlet concentration. The height of the retaining grid for the semiflu-idized bed was 101.6 mm and operating velocity was $7.71 \cdot U_{mf}$.

A cyanide ion selective electrode (Orion 9606) was used for the analysis of cyanide. The concentration of Cu^+ ions was determined by ICP (Thermo Jarrell Ash IRIS/AP). Cyanide concentration measurements were made in the range $7.69 \times 10^{-5} \text{ M}$ to $2.69 \times 10^{-4} \text{ M}$ with appropriate dilutions. As an ISA (Ionic Strength Adjustor), 10 M sodium hydroxide was added to the solution to adjust the solution pH to the operating range of electrode and keep background ionic strength constant. The cyanide electrode did not respond to the total cyanide in the presence of Cu^+ ions because of stable Cu-CN complexes. Therefore decomplexation was necessary for analysis. These complexes could be broken up by EDTA. Decomplexation procedure by EDTA is outlined as follows :

- (1) Add disodium EDTA at a concentration of $\pm 0.05 \text{ M}$.
- (2) Acidify the samples to a pH of 4 with 10% acetic acid.
- (3) Heat the samples at 50 °C for 15 minutes in closed flasks.
- (4) Cool the samples and adjust the pH and ionic strength.

RESULTS AND DISCUSSION

Fig. 2 shows the effect of copper ions on measurement of total cyanide ions after decomplexation by EDTA. It is shown that analytical error ranges of total cyanide are in $\pm 5\%$, when molar ratio (Q) of the total cyanide to the total copper is over 3. On the other hand, if the amount of copper ions is relatively more than that of total cyanide ions, total cyanide cannot be analyzed completely.

Fig. 3 is a copper-cyanide distribution diagram calculated by the formation constants. The relative amounts of various complexes were calculated from Eq. (7) and shown in Table 2. In the case of a molar ratio of 4 ($T_{\text{CN}}=7.69 \text{ mM}$, $T_{\text{Cu}}=1.92 \text{ mM}$), the copper is present predominantly as the tricyano-complexes, divalent ions, and about 23% of the total cyanide is present as free cyanide at pH 12. On the other hand, for a molar ratio of 3 ($T_{\text{CN}}=7.69 \text{ mM}$, $T_{\text{Cu}}=2.56 \text{ mM}$), the copper is present predominantly as the tricyano-complexes and about 2% of the total

cyanide is present as free cyanide.

Among well-known isotherm equations, the Langmuir equation was applied to fit ion exchange equilibrium data of Cu^+ removed as cyanide complexes on Dowex1X8-50 at 25 °C.

$$\left(\frac{C_e}{X/M}\right) = \frac{1}{ab} + \frac{1}{a} C_e \quad (10)$$

where X/M is the ion exchange capacity per unit mass of resin (mg/g resin)

C_e is the equilibrium ion concentration in the liquid

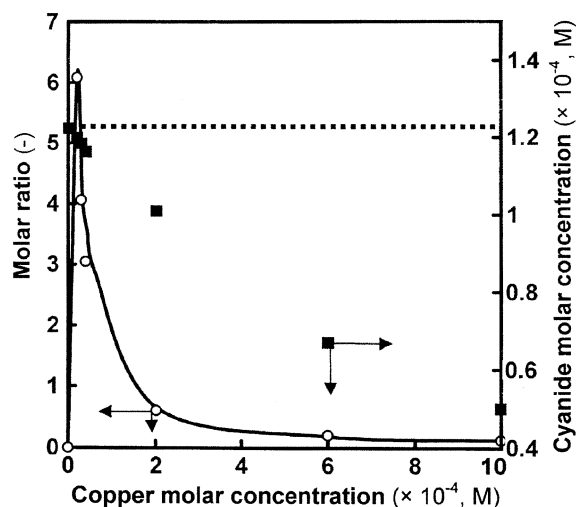


Fig. 2. Effect of Cu^+ ions on measurements of total CN^- ions. ($T_{\text{CN}}=1.22 \times 10^{-4} \text{ M}$)

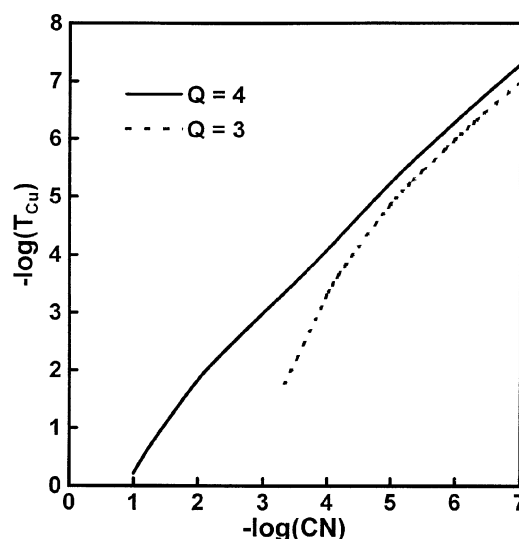


Fig. 3. Copper-cyanide distribution diagram.

Table 2. Detailed compositions of synthetic solutions used for column experiments (pH: 12)

T_{CN}	T_{Cu}	Q	Free cyanide	$\text{Cu}(\text{CN})_2^{-1}$	$\text{Cu}(\text{CN})_3^{-2}$	$\text{Cu}(\text{CN})_4^{-3}$
7.69×10^{-3}	1.92×10^{-3}	4	1.78×10^{-3}	2.52×10^{-5}	1.74×10^{-3}	1.59×10^{-4}
7.69×10^{-3}	2.56×10^{-3}	3	1.49×10^{-4}	3.76×10^{-4}	2.17×10^{-3}	1.65×10^{-5}
5.77×10^{-3}	1.92×10^{-3}	3	1.99×10^{-4}	2.18×10^{-4}	1.69×10^{-3}	1.72×10^{-5}

*All concentrations are in g-mole/L.

phase (mg/L)

a, b are empirical parameters.

Fig. 4 shows the characteristic plot by Eq. (10) and Langmuir constants are determined by slopes and intercepts of lines in Fig. 4. As the results, the following equations are obtained for various ratios.

$$\left(\frac{X}{M}\right)_{Q=3} = \frac{15.1976C_e}{1+0.1094C_e}$$

$$\left(\frac{X}{M}\right)_{Q=4} = \frac{9.033C_e}{1+0.0768C_e}$$

$$\left(\frac{X}{M}\right)_{Q=5} = \frac{7.133C_e}{1+0.0635C_e}$$

Respective synthetic solutions for this batch test were prepared as change of total cyanide concentration at the same concentration of copper. The ion exchange capacity of copper ions decreases with increases in concentration of cyanide ions,

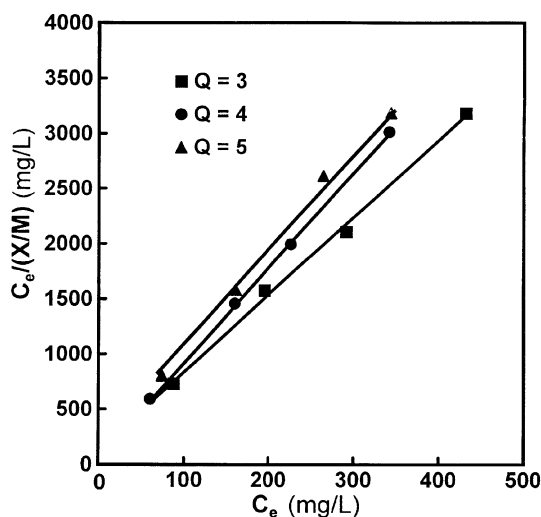


Fig. 4. Ion exchange isotherms of copper ions for value of Q .

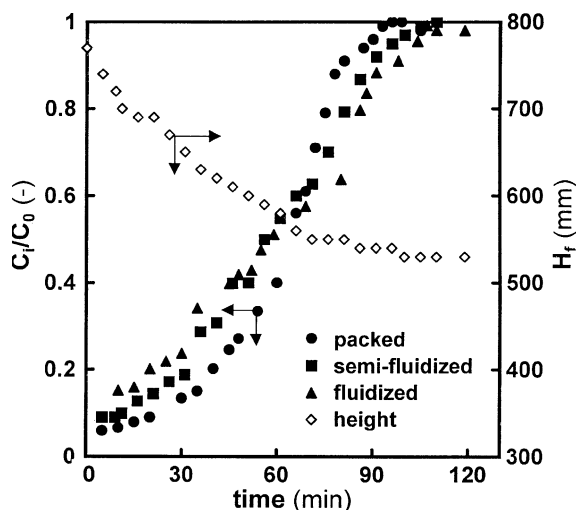


Fig. 5. Breakthrough curves of CN^- ions in the packed, fluidized and semi-fluidized beds.
Resin weight=10 g, $U=7.7 U_{mf}$, $C_{\text{CN}}=7.69 \text{ mM}$, $C_{\text{Cu}}=1.92 \text{ mM}$ ($Q=4$)

though influent copper ions are the same concentration. In turn, simultaneous removal capacity of cyanide and copper ions increases as the value of Q is decreased. This is due to the fact that many complexes are formed as decreases of Q values.

Fig. 5 shows the breakthrough curves of molar ratio of 4 in packed, semi-fluidized, and fluidized beds, respectively. In Fig. 5, it is seen that the breakthrough curve obtained from a semi-fluidized bed lies between those obtained from the packed and fluidized beds, since the semi-fluidized bed possesses the features of both the fluidized and packed beds. Fig. 5 also shows that the shape of the breakthrough curve for the packed bed is steeper than that for the fluidized bed, because mass transfer in the axial direction in a liquid-solid packed bed operation is more a predominant effect than that of the radial direction. On the other hand, because fluidized bed operation has the whole bed as adsorption zone and mass transfer of radial direction prevails in the bed, the breakthrough curve in a fluidized bed is smoother than any other curve.

For fluidized bed operation, the effluent concentrations of the bed exceed the breakthrough concentration ($C_i/C_0=0.1$) immediately after the synthetic solution is introduced into the bed. This result could be expected from the fact that influent synthetic solutions have about 23% of total cyanide as free cyanide form that is poorly removed by the resin [Short et al., 1997]. The profile of total bed height of a fluidized bed is also shown in Fig. 5. The height of the fluidized bed section keeps decreasing, during the exchange process, due to the density difference between Cl^- and Cu-CN complexes. In this figure, the decrease of the height of the fluidized bed section is negligible beyond 100 minutes. This is due to the fact that the resin is saturated completely; thus the density of the resin does not change any more and the bed height is constant.

Fig. 6 shows the breakthrough curves of molar ratio of 3 in a packed, semi-fluidized, and fluidized bed, respectively. Breakthrough curves are clear due to no effect of free cyanide compared with those of Fig. 5.

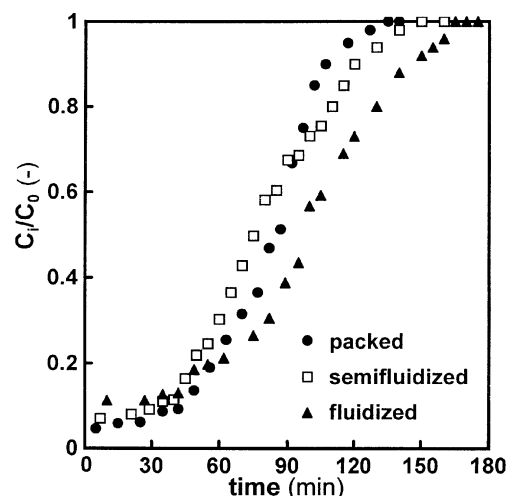


Fig. 6. Breakthrough curves of CN^- ions in the packed, fluidized and semi-fluidized beds.
Resin weight=10 g, $U=7.7 U_{mf}$, $C_{\text{CN}}=7.69 \text{ mM}$, $C_{\text{Cu}}=2.56 \text{ mM}$ ($Q=3$)

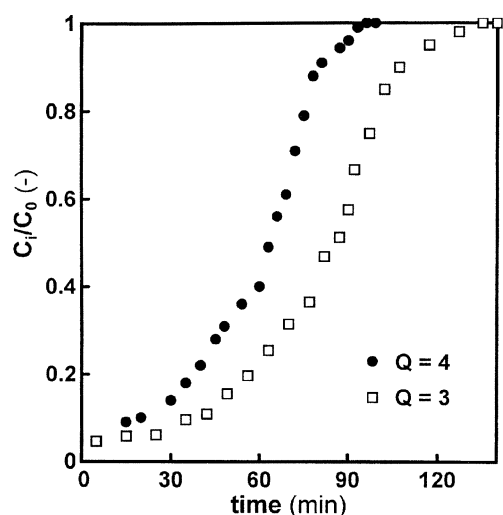


Fig. 7. Effect of the value of Q on the breakthrough curves of CN^- ions.

Resin weight=10 g, $U=7.7 U_{mf}$, $C_{\text{CN}}=7.69 \text{ mM}$, $C_{\text{Cu}}=1.92 \text{ mM}$, 2.56 mM

Fig. 7 shows the effect of Q on the breakthrough curves in the semi-fluidized bed. Synthetic solution was prepared as change of copper concentration at the same concentration of total cyanide. Breakthrough time for the Q of 4 is faster than that of the Q of 3 and is inferior in ion exchange capacity due to free cyanide ions. When the molar ratio of the total cyanide to total copper was 3, a reasonable removal performance is observed from this figure. The following can be expected from the above result. First, for a good removal of cyanide ions, enough copper ions should be present in solution for forming complexes. Second, for the capture of cyanide ions leaked, the proper height of bed is needed. This result is similar to that reported by Short et al. [1997] for Zn-CN system. For a Zn-CN system, the optimum molar ratio between total cyanide and total zinc is 4. If a molar ratio of 4 is exceeded, undesirable free cyanide will be present in solution. When the molar ratio is less than 4, insoluble ZnCN_2 is formed [Short et al., 1997]. Out of consideration for Short's study, it is reasonable that the optimum molar ratio between total cyanide and total copper is 3 in this experiment.

Fig. 8 shows the loading profiles of cyanide and copper for molar ratio of 4 from the semi-fluidized bed. The synthetic solution used in this experiment contains many free cyanide ions. It is shown that cyanide ions exit even if copper ions do not leak in 20 minutes, that is, those are not cyanide as Cu-CN complexes but free cyanide form. As mentioned previously, this is due to lower selectivity of free cyanide on resin used in this experiment.

Fig. 9 shows the loading profiles of cyanide and copper for molar ratio of 3 from the semi-fluidized bed. In the synthetic solution used, the copper is predominantly present as a mixture of tricyano- and tetracyano-complexes and there is negligible amount of free cyanide. In this figure, it is observed that the breakthrough time of copper is about 172 minutes and that of cyanide is about 90 minutes. It is shown that the breakthrough time of copper is much slower than that of cyanide compared

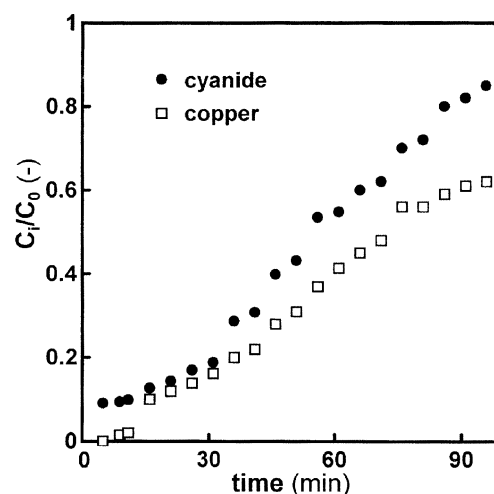


Fig. 8. Loading profiles of Cu^+ and CN^- ions in the semifluidized bed.

Resin weight=10 g, $U=7.7 U_{mf}$, $C_{\text{CN}}=7.69 \text{ mM}$, $C_{\text{Cu}}=1.92 \text{ mM}$ ($Q=4$)

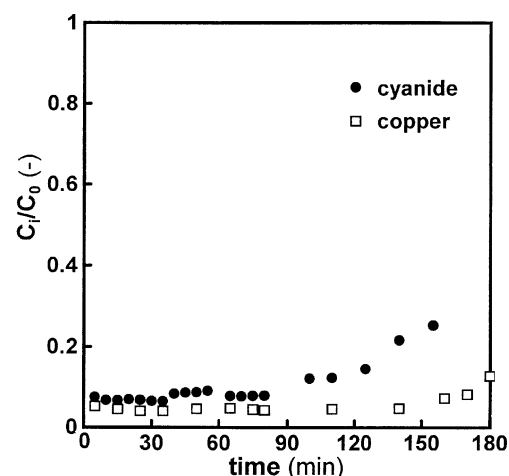


Fig. 9. Loading profiles of Cu^+ and CN^- ions in the semifluidized bed.

Resin weight=10 g, $U=7.7 U_{mf}$, $C_{\text{CN}}=5.77 \text{ mM}$, $C_{\text{Cu}}=1.92 \text{ mM}$ ($Q=3$)

with Fig. 8, though there is negligible amount of free cyanide. This phenomenon indicates that the copper-cyanide complexes present on the resin are different from those in the contacting solution. The molar ratio (Q) of total cyanide to total copper on the loaded resin is deduced by calculating the areas under the loading profiles. The molar ratio of total cyanide to total copper on the resin was about 2, even though the contacting solution contained the tricyano-complexes. This means that $\text{Cu}(\text{CN})_2^-$ is the complex that has a better selectivity than $\text{Cu}(\text{CN})_3^{2-}$ on the anion exchanger used. This can be explained from the size and the structure of complexes. The size of the monovalent CN-Cu complex has a range of 5.57-6.14 Å in the aqueous solution and exhibits angular and linear geometry and divalent complex exhibits distorted tetrahedral shape or plane triangular structure [Lee et al., 1998]. On the other hand, the average distance between the two functional sites on the dry resin used in this experiment is about 11.2 Å. Because divalent and trivalent com-

plexes must occupy two or three sites and the size of monovalent complex is shorter than the distance of two functional sites on the resin, monovalent ($\text{Cu}(\text{CN})_2^-$) has a better selectivity than divalent ($\text{Cu}(\text{CN})_3^{2-}$) on a strong base anion exchanger.

CONCLUSIONS

Experiments are performed to study simultaneous removal of cyanide and copper ions in a liquid-solid semi-fluidized ion exchanger bed. The ion exchange equilibrium data of Cu^+ removed as cyanide-copper complexes on Dowex1X8-50 at 25 °C are obtained experimentally for respective molar ratios. The experimental data can be fitted well with the Langmuir equation. The breakthrough curve in the semi-fluidized bed lies between those obtained from the packed and fluidized beds.

Early leakage of cyanide from experimental loading profile data results in not only lower selectivity of free cyanide but also different selectivities of Cu-CN complexes due to the size and the structure of complexes. $\text{Cu}(\text{CN})_2^-$ is the complex that has a better selectivity than $\text{Cu}(\text{CN})_3^{2-}$ on this strong-base anion exchanger. It is suggested that free cyanide should be controlled by adjusting a total cyanide to total copper molar ratio of about 3 to remove cyanide effectively for the treatment of electroplating wastewater containing cyanide and copper ions.

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NOMENCLATURE

C_i	: effluent concentration of reactant [mg/L]
C_e	: equilibrium copper ion concentration in the liquid phase [mg/L]
C_0	: inlet concentration of reactant [mg/L]
D_c	: diameter of column [mm]
H_f	: height of the fluidized bed section [mm]
K_i	: the stepwise formation constants [-]
[L]	: free liquid concentration [g-mole/L]
[M]	: free metal concentration [g-mole/L]
$[\text{ML}_i]$: concentration of complex ML_i [g-mole/L]
M	: molar concentration [g-mole/L]
T_{Cu}	: total copper concentration [g-mole/L]
T_{CN}	: total cyanide concentration [g-mole/L]
U	: superficial fluid velocity in axial direction [mm/s]
U_{mf}	: minimum fluidization velocity [mm/s]

Q : total cyanide ions to total copper ions molar ratio [-]

Greek Letters

α_i	: the mole fraction of the complex ML_i
β_i	: the overall formation constants [-]
ϵ	: bed voidage [-]

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