Removal of Heavy Metal-Cyanide Complexes by Ion Exchange

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Abstract−Simultaneous removal of heavy metal and cyanide ions in an ion exchange column is studied on the basis of formation of metal-cyanide complexes at high pH range. Strong base anion exchange resin beads were contacted with water containing heavy metal (Cu, Cd, Zn) and cyanide ions in semi-fluidized and fluidized beds. Compositions of the heavy metal-cyanide complexes formed for different heavy metal and cyanide concentrations are used to explain the ion exchange behavior. Ion exchange equilibrium data of this study were fitted well with the Langmuir isotherm. The ion exchange capacity of CN⁻ as metal complexes increased to about three times that of free cyanide due to higher selectivity of metal complexes on the anion exchange resin. The ion exchange efficiency of the three heavy metal-cyanide systems decreases as the concentration ratio of cyanide and heavy metal increases. The regeneration rates of the regenerants used was in the order of NaSCN>NaCN>NaOH, and the regeneration rate of NaOH was substantially lower than other two.

Key words: Ion Exchange, Heavy Metal, Cyanide, Complex, Regeneration

INTRODUCTION

Heavy metals in water have become an ecotoxicological hazard because of their accumulation in living organisms. Toxic heavy metals are released into the environment in a number of different ways [Kuruyama et al., 2000; Jang et al., 2001]. Several metals such as zinc, copper and cadmium are plated out of cyanide baths. These baths contain several metal salts dissolved in sodium cyanide. The pH of these baths can be maintained at about 12 by the addition of sodium hydroxide. Thus, the rinse waters obtained from these plating processes form metal-cyanide complexes [Gupta, 1985]. The conventional techniques for the removal of heavy metal-cyanide complexes are filtration, chemical precipitation, reverse osmosis, solvent extraction and membrane techniques, and the strength and weakness of these techniques are discussed [Eckenfelder, 2000].

Recently, a number of publications have been reported including biosorption method to remove heavy metal ions from waste water [Jeon et al., 2001; Lee et al., 2000, 2001; Kim et al., 2000; Yang et al., 2000].

The Ion exchange method is known as one of the more efficient methods for the removal and recovery of heavy metal ions, and its operational and economic advantages for treating electroplating rinse water have been discussed [Weltrowski et al., 1996]. The Ion exchange method has the following advantages in treating heavy metals in water: 1) no secondary pollutant, 2) very compact facility, 3) easy recovery of metals, and 4) more versatile than the other methods. One problem often cited, the disposal of regeneration solution, has been solved by combination with other methods [Goto and Goto, 1987; Short et al., 1997].

A semi-fluidized bed is a modified fluidized bed which can re-strict bed expansion by a particle retaining grid; the characteristics and applications are discussed [Fan et al., 1959, 1960; Mydlarz, 1987]. A semi-fluidized can be formed by inserting a retaining grid in a fluidized bed and increasing the flowrate above U_{mf}. In this case, the semi-fluidized bed is divided into two sections, namely the lower fluidized bed section and upper packed bed section. The portion of each section varies according to the flowrate, static bed height and retaining grid height. The particles in the upper packed bed section are slightly smaller than those in the fluidized bed section, and most of the bed pressure drop is developed from the upper packed bed section. Since the semi-fluidized bed possesses the features of both fluidized and packed beds, the breakthrough curves of semi-fluidized beds lie between those of fluidized and packed beds [Kim et al., 1999].

In previous works, the authors studied removal of Cu-CN complexes [Kim et al., 1999], and removal of Cd-CN complexes and recovery of Cd by regeneration of resin [Kim et al., 2001]. In this work, simultaneous removal of heavy metal and cyanide ions and recovery heavy metal ions were studied in order to understand the ion exchange behavior of heavy metal-cyanide complexes and compare the removal and recovery rates of various heavy metal ions. The formation of various heavy metal (Cu, Cd, Zn)-cyanide complexes and compositions of heavy metal-cyanide and free cyanide were studied for different molar ratio of heavy metal and cyanide in water. Ion exchange characteristics of the heavy metal-cyanide complexes were studied experimentally in a batch reactor, and the breakthrough curves a semi-fluidized are obtained and the characteristics are discussed. The regeneration rates of the exhausted resins for different regenerants (NaCN, NaSCN, NaOH) were obtained experimentally.
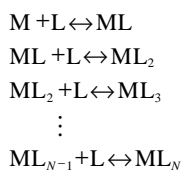
THEORY

Heavy metals in solution form very stable complexes with cyanide ions which act as ligand. These reactions can be represented

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[‡]This paper is dedicated to Professor Dong Sup Doh on the occasion of his retirement from Korea University.

as:

$$M + L \leftrightarrow ML$$
$$ML + L \leftrightarrow ML_2$$
$$ML_2 + L \leftrightarrow ML_3$$
$$\vdots$$
$$ML_{N-1} + L \leftrightarrow ML_N$$

$$K_i = \frac{[ML_i]}{[ML_{i-1}][L]} \tag{1}$$

$$\beta_i = \frac{[ML_i]}{[M][L]^i} \tag{2}$$

where K_i=stepwise formation constants
β_i=overall formation constants
[L]=free ligand 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 be attached to one metal cation.

The relative amounts of various complexes can be calculated from knowledge of the 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:

$$T_M = [M] + [ML] + [ML_2] + [ML_3] + \cdots + [ML_N] = \sum_{i=0}^{N} [ML_i] \tag{3}$$

$$T_L = [L] + [ML] + 2[ML_2] + 3[ML_3] + \cdots + N[ML_N]$$
$$= [L] + \sum_{i=0}^{N} i[ML_i] \tag{4}$$

Using Eq. (2), we get:

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

$$T_L = [L] + [M] \sum_{i=0}^{N} i\beta_i [L]^i \tag{6}$$

The mole fraction of the complex ML_i is given by:

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

The average ligand number is defined as:

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

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

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

Table 1. Properties of ion exchange resin (Dowex1X8-50)

Form*	Cl⁻
Mean diameter [mm]	0.446
Density [kg/m^3]	1250
Moisture content* [%]	43.0
Total capacity* [meq./g]	3.5

*given data from the manufacturer.

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

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 by Eq. (7).

EXPERIMENTS

1. Material, Apparatus and Concentration Measurement

Synthetic wastewater was prepared by dissolving reagent grade sodium cyanide, zinc sulfate, cadmium nitrate and copper cyanide in distilled water. In this work, synthetic solutions of three Q value were used for experiment (Q=3, 4, 5, where Q=T_{CN}/T_M, and T_M= 1.92 mmol/L). The solution pH was adjusted to 12 to get optimum heavy metal cyanide complexes for ion exchange by the addition of sodium hydroxide. The ion exchange resin used in this work was strong-base, gel type, Dowex1X8-50 (Dow Chem. Co.). The properties of Dowex1X8-50 are shown in Table 1.

Concentration of cyanide was measured by using cyanide ion selective electrode (Orion 9606). As an ISA (Ionic Strength Adjuster), 10 mol/L sodium hydroxide solution was added to the sample to adjust the solution pH to 12 and to keep background ionic strength constant. The cyanide electrode does not respond to the total cyanide ions in the presence of heavy metal ions since they form stable heavy metal-cyanide complexes. Therefore, the EDTA procedure was employed to decomplex the heavy metal-cyanide complexes. The cyanide electrode response in the presence of heavy metal-cyanide complexes has been modeled by Gupta [Gupta, 1985].

The EDTA procedure used is,

ⓐ add disodium EDTA at a concentration of 0.05 M,
ⓑ acidify the samples at a pH of 4 with 10% acetic acid,
ⓒ keep the samples at 50 ℃ for 15 minutes in closed flasks,
ⓓ cool the samples to 25 ℃ and adjust the pH and ionic strength.

The concentration of heavy metal ion was measured by ICP (Leeman 010-2106. USA).

2. Ion Exchange Equilibrium and Batch Experiments

The ion exchange equilibrium data were obtained by contacting the resin with the synthetic wastewater for 72 hours. The ion exchange resin (0.05-1.0 g/L) was injected to 100 mL of synthetic wastewater in 300 mL conical flasks, and the solution and ion exchange resin were agitated constantly. During the experiment, pH and temperature of the solution were kept at 12 and 25±1 ℃, respectively.

For batch experiments, 1 g of resin and 1,000 mL synthetic waste-

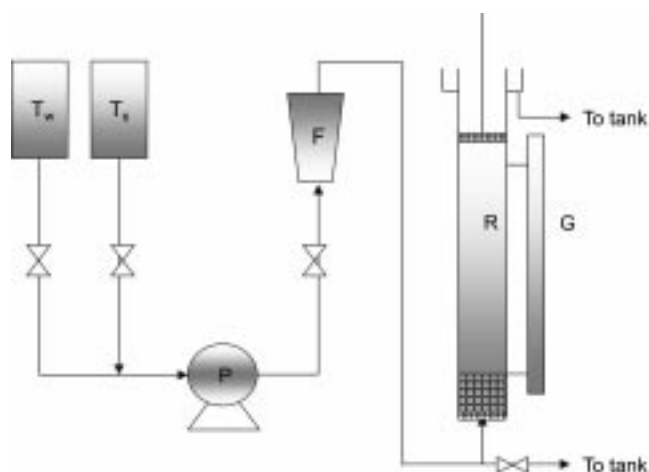**Fig. 1. Schematic diagram of the experimental apparatus.**
  T_W: Water tank T_S: Solution tank   P : Pump
  F: Flow meter   R: Reactor   G: Piezometer tube

water were contacted, and samples were taken periodically and analyzed to obtain the concentration of ions in the liquid phase. Solution pH and temperature were the same as those for the equilibrium experiments.

3. Column Experiments

Fig. 1 shows the schematic diagram of the experimental setup. The bed used for the experiment was made of transparent acrylic resin tube, 20 mm in diameter and 600 mm in height. The pressures along the column axis were measured by using pressure taps attached on the column wall. The lower part of the column was packed with glass beads 4 mm in diameter to distribute the solution uniformly into the ion exchanger bed.

For the fluidization experiment, 20 g of resin beads was loaded into the bed. Distilled water was used for the fluidization experiments to measure the minimum fluidization velocity, pressure drop, and bed expansion. For the ion exchange experiments, synthetic wastewater solutions were used, and effluent concentrations were measured to obtain breakthrough curves. In this work, the breakthrough time is defined as the time at $C/C_0 = 0.1$, and the bed temperature was kept at 25 ± 1 °C.

4. Regeneration of Ion Exchange Resin

Regeneration experiment for the saturated resin was performed in a batch reactor which was kept in thermostat at 25 ± 1 °C. Resin particles, 0.5 g, were contacted with 500 mL synthetic wastewater solution for 72 hours and washed with distilled water. This resin was contacted with 500 mL of regeneration solutions (1.5 mol/L aqueous solutions of NaSCN, NaCN and NaOH) for 48 hours. The concentration of heavy metal in liquid phase was measured and the regeneration rate for each regenerant was obtained.

RESULTS AND DISCUSSION

1. Speciation

There are difficulties in describing ion exchange behavior of heavy metal and cyanide binary system due to the speciation changes of anionic complexes with pH variations and composition changes of the solution as ion exchange proceeds. Kim et al. [1999] studied the relative amounts of Cu-CN complexes formed in the aqueous

Table 2-1. Stepwise formation constants (K_i) and overall formation constants (β_i) for heavy metal-cyanide complexes

Metal ions	The number of ligand (i) Constants	1	2	3	4
Cu$^+$	log β_i	19.50	24.00	28.59	30.30
	log K_i	19.50	4.50	4.59	1.71
Cd^{2+}	log β_i	5.62	10.84	15.72	19.20
	log K_i	5.62	5.22	4.88	3.48
Zn^{2+}	log β_i	5.34	11.03	16.68	21.57
	log K_i	5.34	5.69	5.65	4.89

Table 2-2. Compositions of cyanides (α) calculated from Eq. (7)
(unit: %)

Component	Q	3	4	5
Cu-CN	Free CN	3.5	23.2	37.1
	$Cu(CN)_2^-$	7.6	0.5	0.4
	$Cu(CN)_3^{2-}$	87.9	68.0	52.8
	$Cu(CN)_4^{3-}$	1.0	8.3	9.7
Cd-CN	Free CN	1.0	8.5	22.7
	$CdCN^+$	0.5	0.0	0.0
	$Cd(CN)_2$	9.5	0.0	0.0
	$Cd(CN)_3^-$	70.4	27.8	7.9
	$Cd(CN)_4^{2-}$	18.6	63.7	69.4
Zn-CN	Free CN	0.1	12.0	20.1
	$ZnCN^+$	3.9	0.0	0.0
	$Zn(CN)_2$	14.9	0.1	0.0
	$Zn(CN)_3^-$	50.6	25.0	0.5
	$Zn(CN)_4^{2-}$	30.5	62.9	79.4

solution for different Q values.

Table 2-1 shows the stepwise formation constants (K_i) and overall formation constants (β_i), and Table 2-2 shows the compositions of cyanides form for different Q values in synthetic solution at pH equals 12, calculated from Eq. (7) using the method described by Gupta [1985] and Kim et al. [1999].

1-1. Copper-Cyanide Complexes

For Q of 3, 87.9% of total cyanide is present in the form of Cu$(CN)_3^{2-}$ and only 3.5% is present as free cyanide. On the other hand, for Q of 4, 68.0% of the copper is present as $Cu(CN)_3^{2-}$, and 23.2% of the total cyanide is present as free cyanide in the solution. For Q of 5, the portion of the free cyanide is increased to 37.1% of total cyanide and $Cu(CN)_3^{2-}$ is 52.8%. These show that the portion of free cyanide increases rapidly, while that of copper-cyanide complexes decreases substantially as Q increases from 3 to 5.

1-2. Cadmium-Cyanide Complexes

For Q of 3, 70.4% and 18.6% are present as $Cd(CN)_3^-$ and Cd$(CN)_4^{2-}$, respectively, and only 1.0% as free cyanide. For Q of 4, 27.8% and 63.7% are present as $Cd(CN)_3^-$ and $Cd(CN)_4^{2-}$, respectively, and 8.5% as free cyanide. For Q of 5, 7.9% and 69.4% are present as $Cd(CN)_3^-$ and $Cd(CN)_4^{2-}$, respectively, and 22.7% as free cyanide. These also show that the portions of free cyanide and Cd$(CN)_4^{2-}$ increase rapidly, while that of $Cd(CN)_3^-$ decreases rapidly,

Table 3. Flow and particle properties of ion exchange resin ($D_C = 20$ mm)

d_p (mm)	ρ_p (kg/m^3)	U_{mf} (mm/s)	ε_{mf} (-)	ρ_f (kg/m^3)	$\mu \times 10^3$ (kg/m·s)	U_t (mm/s)
0.446	1,250	0.45	0.42	995.9	0.894	30.8

as Q increases from 3 to 5.

1-3. Zinc-Cyanide Complexes

The compositions of cyanide for zinc-cyanides are similar to those of cadmium-cyanides.

2. Bed Height and Pressure Drop

Table 3 shows the flow and particle properties of this experiment. The particle diameter and density of the resin were measured in the swollen state. U_{mf} and ε_{mf} was measured in the fluidized bed. U_t in Table 3 was calculated by using Eq. (10) [Kunii and Levenspiel, 1986] and the density and viscosity of the fluid are those for pure water at 25 °C.

$$U_t = \frac{g(\rho_p - \rho_f)d_p^2}{18\mu} \tag{10}$$

The pressure drop and bed expansion with decreasing flowrate in the fluidized bed showed typical pattern for liquid fluidized bed. But the those for semi-fluidized beds are unique as shown in Fig. 2. The initial height of the packed bed (h_0) was 136 mm, and the height of the retaining grid was 226 mm. As the flowrate increases up to U_{mf}, the pressure drop increases linearly but the bed height is practically constant. As the flowrate increases above U_{mf}, the bed height increases, while the pressure drop is practically constant. As the flowrate increases above 6 U_{mf}, the bed is separated into the two sections: the fluidized bed section in the bottom and the packed bed section in the top as shown in Fig. 2. As the flowrate increases fur-
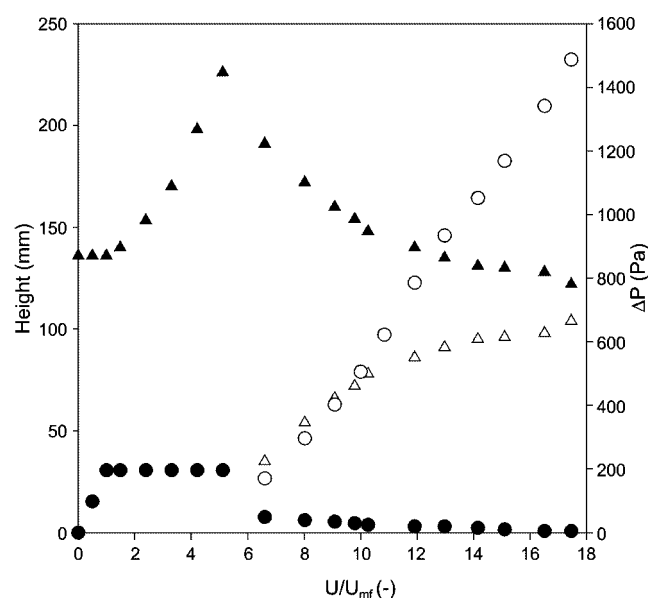
Fig. 2. Variations of bed height and pressure drop in a semi-fluidized bed with flow rate (d_p=0.446 mm, h_0=136 mm, resin weight=20 g, h=226 mm, ●, ○: pressure drop in fluidized bed section and packed bed section, ▲, △: bed heights in fluidized bed section and packed bed section).
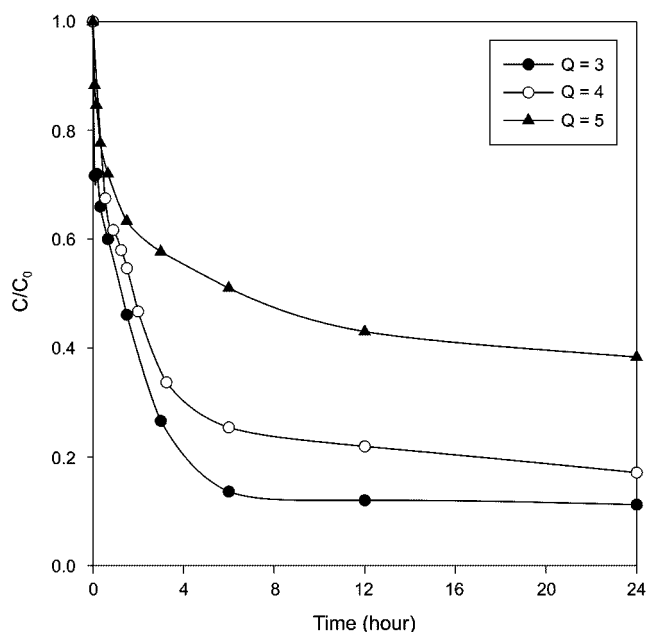
Fig. 3. Concentration of cyanide in solution in a batch reactor.

ther, the height of upper packed bed section increases and the height of the lower fluidized bed section decreases as shown in this figure since small particles are transported to the upper section. However, the height of the each section approaches equilibrium in the flowrate range of this study. The pressure drop in a semi-fluidized bed is also shown in the figure. The figure shows that the pressure drop in the upper packed bed section is dominant, especially for higher flowrate. The pressure drop of the fluidized section decreases slowly as the flowrate increases due to the particle transport from the fluidized section to the upper packed bed section.

3. Ion Exchange Characteristics of Heavy Metal-cyanide Complexes

Fig. 3 shows the variation of cyanide concentration in solution with reaction time for Zn-CN system. The dimensionless concentration decreases rapidly and approaches equilibrium in 24 hours, and the cyanide concentration in solution decreases as Q decreases. Since we used the same amount of ion exchange resin (1 g) for the same volume of synthetic wastewater (1,000 mL) with different cyanide concentration at pH of 12, the removal rate of cyanide by ion exchange was lower for higher cyanide concentration (Note Q= 3 means cyanide concentration of 5.76 mmol/L and Q=5 means cyanide concentration of 9.60 mmol/L). The variations of cyanide concentration in solution with reaction time for Cd-CN and Cu-CN systems are similar to those of Zn-CN system.

Fig. 4 shows the variation of zinc concentration in solution with reaction time for Zn-CN system. The dimensionless concentration decreases rapidly and approaches equilibrium similar to that of cyanide concentration, and the zinc concentration in solution also decreases as Q decreases. The variations of copper and cadmium concentrations with reaction time for Cu-CN and Cd-CN systems are similar to that of Zn-CN system.

The ion exchange capacity of free cyanide for the anion exchange resin contacting with 7.68 mmol/L cyanide solution at pH of 12 is 1.98 CN$^-$ meq./g resin. But the ion exchange capacities of the same
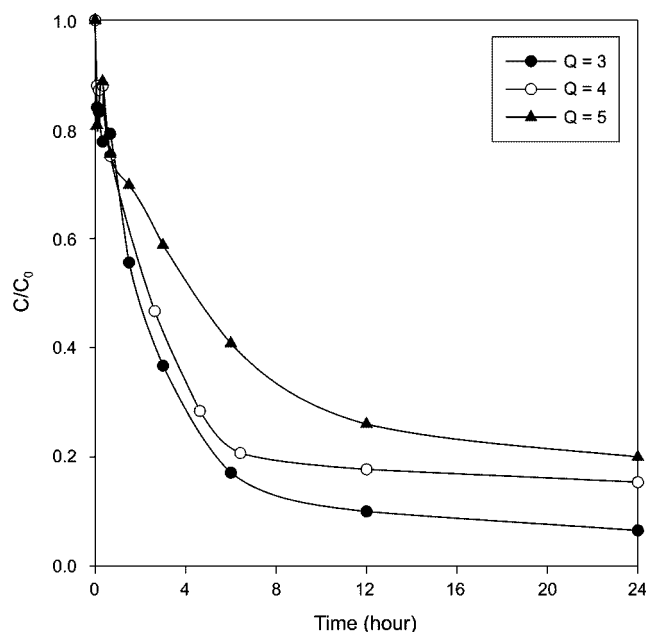
Fig. 4. Concentration of zinc in solution in batch reactor.

resin increase to 2.5, 3.2 and 3.3 times of that of free cyanide [1.98 CN^- meq./g resin] when the cyanide-heavy metal complexes (Q=4 and pH=12) are contacted with the resin. Since Q of 4 means cyanide concentration of 7.68 mmol/L, the ion exchange capacity of CN^- by heavy metal-cyanide complexes is about 3 times of that by free cyanide at the same cyanide concentration in the solution. This could be explained by the difference in selectivity. The free cyanide has a lower selectivity than the heavy metal-cyanide complexes on the anion exchange resin which is explained by the size of the ions, ion pairing and site competition of the complexes [Kim et al., 2001].
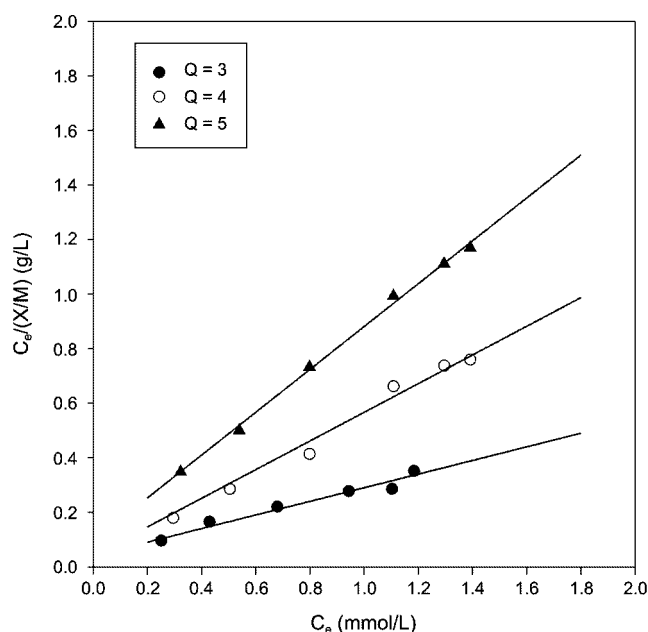

Fig. 5. Ion exchange isotherms of zinc ions.

4. Ion Exchange Isotherms of Heavy Metal Ions

Among the well-known isotherm equations, Langmuir equation (Eq. (11)) was fitted well with ion exchange equilibrium data this study.

$$\frac{X}{M} = \frac{abC_e}{1+bC_e} \tag{11}$$

Here, X/M is the ion exchange capacity per unit mass of resin (mmol/g), C_e is the equilibrium concentration of heavy metal or cyanide ion in liquid phase (mmol/L). Since the heavy metal-cyanide complexes are decomplexed by the EDTA process before the concentration measurement, C_e in Eq. (11) is the total concentration of heavy metal or cyanide in the solution.

Fig. 5 shows Langmuir plots for zinc ions in Zn-CN system. The constants for the isotherms are determined from the slopes and intercepts, and are listed in Table 4. The figure shows that the equilibrium ion exchange rate of zinc ion decrease as Q is increased. This

Table 4. Parameters of Langmuir isotherms

Metal ions	Q	a	b	R^2
Cu^+	3	2.65	4.88	0.992
	4	2.07	5.46	0.993
	5	1.78	5.42	0.999
Cd^{2+}	3	5.04	4.09	0.913
	4	2.04	8.23	0.985
	5	1.46	4.81	0.987
Zn^{2+}	3	4.01	6.10	0.974
	4	1.90	12.75	0.984
	5	1.27	8.22	0.998

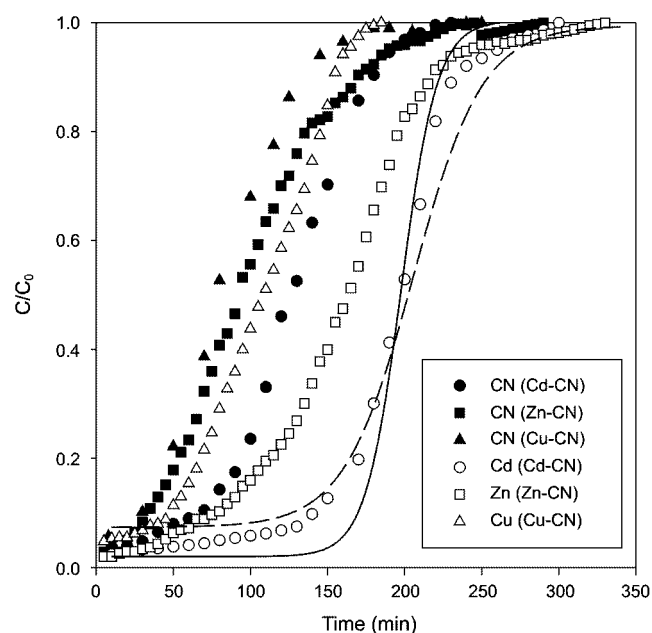**Fig. 6. Comparisons of breakthrough data for Cd-CN, Zn-CN and Cu-CN systems in semi-fluidized bed reactors (U=3.03 mm/ s (6.73 U_{mf}), Q=4, T_{CN}=7.69 mmol/L, h=226 mm)**
—: packed bed for Cd(Cd-CN), ----: fluidized bed for Cd(Cd-CN)

can be explained from the fact that the portion of free cyanide, which has lower selectivity than complexes, increases as Q increases (see Table 2).

The Langmuir isotherm plots for Cu and Cd ions, using the parameters in Table 4, are similar to that of Zn.

5. Breakthrough Curves

Fig. 6 shows the breakthrough data for CN, Cd, Zn and Cu in Cd-CN, Zn-CN and Cu-CN systems, respectively. The bed is in semi-fluidized state with the retaining grid height at 226 mm, and the fluid velocity is 6.73 U_{mf}. For Q of 4, this figure shows that the breakthrough times of heavy metal ions are longer than those of cyanide ions. The breakthrough curves of Cd in a packed bed and a fluidized bed at the same condition are also shown in the figure for comparison. The breakthrough curve for the semi-fluidized bed is located between those of fluidized and packed beds.

6. Regeneration of Resin

The regeneration experiments were conducted by contacting 0.5 g of saturated resin with 500 mL of regeneration solutions (NaSCN, NaCN, NaOH) in a batch for 48 hours. Table 5 shows the results of batch experiment for various regenerants. Although NaOH is commonly used as a regenerant for anion exchange resin, the regeneration rates of the resins saturated with the metal-cyanide ions are low for all three metals. NaSCN gives higher regeneration rate than NaCN for all metal complexes of this work. It is reasoned that the resin saturated with heavy metal-cyanide complexes has higher affinity for the thiocyanate ion than the hydroxide ion. In other words, thiocyanate has a higher polarizability.

CONCLUSIONS

The basic ion exchange characteristics of heavy metal cyanide complexes are studied experimentally in batch and column reactors. The ion exchange equilibrium data of the three heavy metal ions were fitted well with the Langmuir isotherm. The ion exchange capacity of free cyanide at pH of 12 was 1.98 CN$^-$ meq./g resin. But the ion exchange capacity of CN$^-$ as metal complexes increased to about three times that of free cyanide. Ion exchange efficiency of the three heavy metal-cyanide systems decreases as Q increase since the portion of free cyanide, which has lower selectivity, is increased. The regeneration rate of the regenerants used was in the order of NaSCN>NaCN>NaOH, and the regeneration rate of NaOH was substantially lower than other two.

NOMENCLATURE

C : concentration of ion in the liquid phase [mg/L]
C_e : equilibrium heavy metal ion concentration in the liquid phase [mmol/L]
C_0 : inlet concentration of reactant [mg/L]
D_c : bed diameter [mm]
d_p : particle diameter [mm]
h_0 : packed bed height [mm]
h : total bed height in semi-fluidized bed [mm]
K_i : stepwise formation constants [-]
[L] : free ligand concentration or free cyanide concentration [mmol/L]
[M] : free metal concentration [mmol/L]
[ML$_i$]: concentration of complex ML$_i$ [mmol/L]
$\bar{n}$: average ligand number
Q : molar ratio between cyanide and heavy metal [-]
ΔP : bed pressure drop [Pa]
T_{CN} : total cyanide concentration [mmol/L]
T_M : total heavy metal concentration [mmol/L]
T_L : total ligand concentration [mmol/L]
U : superficial liquid velocity in axial direction [mm/s]
U_{mf} : minimum fluidizing velocity [mm/s]
U_t : terminal velocity [mm/s]
α_i : mole fraction of the complex [-]
ε_{mf} : minimum fluidization voidage [-]
ρ_p : particle density [kg/m^3]
ρ_f : water density [kg/m^3]
μ : viscosity [kg/m·s]

Table 5. Regeneration rate in batch reactors for various regenerants (Resin weight=0.5 g, Volume of solution=500 mL, pH=12)

Regenerants	Cadmium loaded [mg/g resin]	Cadmium regenerated [mg/g resin]	Regeneration rate [%]
NaOH	174	107	61.5
NaCN	174	127	73.0
NaSCN	174	152	87.4

Regenerants	Zinc loaded [mg/g resin]	Zinc regenerated [mg/g resin]	Regeneration rate [%]
NaOH	126	87	69.0
NaCN	126	106	84.1
NaSCN	126	118	93.7

Regenerants	Copper loaded [mg/g resin]	Copper regenerated [mg/g resin]	Regeneration rate [%]
NaOH	110	74	67.3
NaCN	110	96	87.3
NaSCN	110	108	98.2

REFERENCES

Akretche, D. E. and Kerdjouj, H., "Donna Dialysis of Copper, Gold, and Silver Cyanides with Various Anion Exchange Membranes," *Talanta*, **51**, 281 (2000).

Avery, N. L. and Fries, W., "Selective Removal of Cyanide from Industrial Waste Effluent with Ion-Exchange Resins," *Ind. Eng. Chem. Prod. Res. Dev.*, **14**, 102 (1975).

Bhakta, D., Shukkla, S. S. and Margrave, L. J., "A Novel Photocata-

lytic Method for Detoxification of Cyanide Wastes," *Environ. Sci., Technol.*, **26**, 625 (1992).

Chi, G., Fuerstenau, M. C. and Marsden, J. O., "Study of Merrill-Crowe Processing. Part I: Solubility of Zinc in Alkaline Cyanide Solution," *Int. J. Miner. Process*, **49**, 171 (1997).

Cho, S. H. and Jeong, W. J., "Treatment of Electroplating Wastewater Containing Heavy Metal-Cyanide Complex," *J. KSEE*, **21**, 1095 (1999).

Eckenfelder, W. W. Jr., "Industrial Water Pollution Control," 3rd. Ed., McGraw-Hill Co. (2000).

Fan, L. T., Yang, Y. C. and Wen, C. Y., "Semi-fluidization: Mass Transfer in Semi-fluidized Beds," *AIChE J.*, **5**, 407 (1959).

Fan, L. T., Yang, Y. C. and Wen, C. Y., "Mass Transfer in Semi-fluidized Beds for Solid-Liquid System," *AIChE J.*, **6**, 482 (1960).

Geol, M., Agrawal, V., Kulkarni, A. K., Cramer, S. M. and Gill, W. N., "Stability and Transport Characteristics of Reverse Osmosis Membranes Using Cyanide Rinse Waters," *J. Membranes Sci.*, **141**, 245 (1998).

Goldblatt, E., "Recovery of Cyanide from Waste Cyanide Solutions by Ion Exchange," *Ind. Eng. Chem.*, **48**, 2107 (1956).

Goncalves, M. M. M., Pinto, A. F. and Granato, M., "Biodegradation of Free Cyanide, Thiocynide and Metal Complexed Cyanides in Solutions with Different Compositions," *Environmental Technology*, **19**, 133 (1998).

Goto, M. and Goto, S., "Removal and Recovery of Heavy Metal by Ion Exchange Fiber," *J. Chem. Eng. Japan*, **20**, 467 (1987).

Gupta, A., "Recovery of Metal-Cyanide Complexes from Electroplating Wastewaters by Ion Exchange," Ph. D. Thesis, The Faculty of Princeton University, U.S.A. (1985).

Hassan, S. O., Vitello, M. P. and Kupferle, M. J., "Treatment Technology Evaluation for Aqueous Metal and Cyanide," *J. Air Waste Manage Assoc.*, **47**, 710 (1991).

Herzorg, A. D., "Cyanide leach Technology and Its Applicability to Alaskan Conditions," Open File Report, U. S. Department of the Interior, Bureau of Mines, 89 (1996).

Hsu, T. L., Tran, T. and Young, D., "Modeling of the Chemical Speciation of Cyanide Species Application to Effluent Treatment," Ausimm Extractive Metal Con., 133 (1991).

Jang, J. G., Kim, W. H. and Kim M. R., "Prediction of Gaseous Pollutants and Heavy metals during Fiuidized Bed Incineration of Dye Sludge," *Korean J. Chem. Eng.*, **18**, 506 (2001)

Jeon, C., Park, J. Y. and Yoo, Y. J., "Removal of Heavy Metals in Plating Wastewater Using Carboxylated Alginic Acid," *Korean J. Chem. Eng.*, **18**, 955 (2001).

Karabulut, S., Karabakan, A., Denizli, A. and Yurum, Y., "Batch Removal of Copper(II) and Zinc(II) from Aqueous Solutions with Low-rank Turkish Coals," *Separation and Purification Technol*, **18**, 177 (2000).

Kim, J. B., Sohn, J. E., Lee, S. S. and Lee, N. W., "Adsorption Characteristics of Cyanide Complex Anion of Heavy Metal on Activated

Carbon," *HWAHAK KONGHAK*, **24**, 1 (1986).

Kim, J. S., Chah, S. and Yi, H., "Preperation of Modified Silica for Heavy Metal Removal," *Korean J. Chem. Eng.*, **17**, 118 (2000).

Kim, S. J., Lim, K. H., Park, Y. G., Kim, J. H. and Cho, S. Y., "Simultaneous Removal and Recovery of Cadmium and Cyanide Ions in Synthetic Wastewater by Ion Exchange," *Korean J. Chem. Eng.*, **18**, 686 (2001).

Kim, S. J., Hwang, K. R. and Cho, S. Y., "Study on Ion-Exchange Behavior of Cu-CN Complexes," *J. Chem. Eng. Japan*, **34**, 193 (2001).

Kim, S. J., Hwang, K. R., Cho, S. Y. and Moon, H., "Simultaneous Removal of Cyanide and Copper Ions in a Semi-Fluidized Ion Exchanger Bed," *Korean J. Chem. Eng.*, **16**, 664 (1999).

Kunii, D. and Levenspiel, O., "Fluidization Engineering," Willy, U.S.A. (1986).

Kuruyama, H. and Catalsarik, T., "Removal of Zinc Cyanide from a Leach Solution by an Anionic Ion-Exchange Resin," *Desalination*, **129**, 1 (2000).

Lee, D. H. and Moon, H., "Adsorption Equillibrium of Heavy Metals on Natural Zeolites," *Korean J. Chem. Eng.*, **18**, 247 (2001).

Lee, H. S. and Suh, J. H., "Interference of Aluminium in Heavy metal Biosorption by a Seaweed Biosorbent," *Korean J. Chem. Eng.*, **18**, 692 (2001).

Lee, H. S. and Suh, J. H., "Continuous Biosorption of Heavy Metal Ions by Ca-loaded laminaria japonica in Fixed Bed Column," *Korean J. Chem. Eng.*, **17**, 477 (2000).

Lee, M. G., Yi, G. and Ahn, B. J., "Conversion of Coal Fly Ash into Zeolite and Heavy Metal Removal Charateristics of the Products," *Korean J. Chem. Eng.*, **17**, 325 (2000).

Lin, S. H. and Juang, R. S., "Heavy Metal Removal from Water by Sorption Using Surfactant-Modified Montmorillonite," *J. of Hazardous Materials*, **92**, 315 (2002).

Lucky, G. C., Van Deventer, J. and Shallcross, D. C., "Equilibrium Model for the Sorption of Gold Cyanide and Copper Cyanide on Trimethylamine Ion Exchange Resin in Saline Solution," *Hydrometallurgy*, **59**, 101 (2001).

Mydlarz, J., "Prediction of Packed Bed Height in Liquid-Solid Semifluidization of Homogeneous Mixtures," *Chem. Eng. J.*, **34**, 155 (1987).

Short, A. E., Haselmann, S. F. and Semmend, M. J., "The GM-IX Process-A Pilot Study for Recovering Zinc Cyanide," *J. Environmental Science & Health*, Part A, **32**, 216 (1997).

Weltrowski, M., Martel, B. and Morcellet, M., "Chitosan N-benzyl Sulfonate Derivatives as Sorbents for Removal of Metal Ions in an Acidic Medium," *J. Appl. Polym. Sci.*, **59**, 647 (1996).

Yang, H. C., Yun, J. S. and Kang, M. G., "Mechanisms and Kinetics of Cadmium and Lead Capture by Calcined Kaolin at High Temperatures," *Korean J. Chem. Eng.*, **18**, 499 (2001).

Zhou, C. and Chin, D. T., "Copper Recovery and Cyanide Destruction with a Plating B13arrel Cathode and a Packed-Bed Anode," *Plat. Surf. Finish*, **80**, 69 (1993).