Cadmium Removal Using Hollow Fiber Membrane with Organic Extractant

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Abstract−Removal of cadmium ion by using a hollow fiber module is investigated experimentally, and organic extractant is applied to enhance the removal rate. The roles of pH, flow rates of the aqueous phase and the organic phase, initial concentration of cadmium ion and coexisting metals are investigated to find an optimum operating condition of the module. The experimental outcome indicates that the best performance is yielded with pH of 4 and the flow rate of aqueous phase in tube side flow controls mass transfer rate. In addition, the initial concentration of 100 ppm gives the best removal. Effect of coexisting component is negligible except Zn and Cu when both of them are present at the same time.

Key words: Cadmium Removal, Hollow Fiber Membrane, Solvent Extraction, D2EHPA, Heavy Metal Separation

INTRODUCTION

Heavy metals, such as chromium, cadmium, copper, zinc and nickel, are contained in industrial waste water, which pollutes the environment and strongly affects human health; the prevention of environmental pollution has actively been studied. Techniques to separate heavy metals from the industrial waste water include precipitation, ion exchange, adsorption electro-dialysis and filtration, but these have limitations on selective separation and heavy cost of investment and operation of equipment. In order to solve theses problems, membrane separation has been widely investigated recently. Though the membrane process has difficulty of solid removal, membrane fouling and separation efficiency drop for long time application, the structural characteristic that two different flows are totally separated prevents channeling and loading. In addition, the physical and chemical stability of membranes is high, and treatment of membrane solution is simple. Because of high interfacial area per unit volume, mass transfer rate is high-more than ten times as fast as that of a direct contact liquid extraction process. Therefore, room temperature operation is available to handle heat-sensitive material. Also, the equipment is simple so investment and operation costs are reduced. Recently, the practical utilization in the fields of ultra-pure water, waste water treatment, heavy metal removal, gas separation and concentration, pharmaceutical purification, bio-medical application and metal refining has been widely studied.

The removal of cadmium by using a modified activated carbon fiber was investigated by Rangel-Mendez and Streat [2002]. Electrochemical oxidation was applied to the surface of the fiber, and a significant increase of cadmium uptake was yielded. Unlike other surface oxidation techniques, the electrochemical treatment does not deteriorate the physical property of the fiber for prolonged implementation. Instead of membranes, a strong-base anion exchange resin was utilized in the removal of cadmium and cyanide complexes from synthetic wastewater [Kim et al., 2001].

Hollow fiber modules have widely been applied to remove phenol, precious metals and heavy metals. Cichy and Szymanowski [2002] studied the recovery of phenol using extractants of Cyanex 923, Amberlite LA-2 and trioctylamine (TOA) in the module and found that Cyanex 923 gives the best performance. Palladium, platinum and rhodium were recovered from spent automotive catalytic converters using the hollow fiber module and Cyanex 471 and Aliquat 336 as carriers [Fontas et al., 2002]. In another study, mercury, copper, lead and cadmium were extracted from phosphoric acid with the module and the carrier of Cyanex 302 [Koopman and Witkamp, 2002]. The hollow fiber was also implemented in the separation of gas [Park et al., 1999].

In this study, the extractive separation of cadmium from mixed solution containing various heavy metals is investigated. The extractant used here is di-(2-ethyl hexyl) phosphoric acid (D2EHPA) with organic solvent of n-heptane. Flow rates of organic and water phases, pH and concentration of solution are varied to find an optimal operation condition. In addition, the effect of coexisting metal components on the removal of cadmium is examined.

EXPERIMENTAL

The hollow fiber module (Hoechst Celanese, U. S. A., model: Liqui-Cel Extra-Flow) having size of 2.5 inches I. D. and 8 inches O. D. is used in this experiment, and it is stable in acid, alkali and organic solvent. The characteristic property of the module is listed

Table 1. Specification of hollow fiber module

Fiber potting material	Polyethylene
I. D.	244 μm
Effective pore size	0.03 μm
Porosity	40%
Wall thickness	28 μm
Module I. D.	8 cm
Module O. D.	28 cm
Number of fibers	10000

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in Table 1. An experimental setup built by Hoechst Celanese is utilized here. Because the hollow fiber is hydrophobic, inside pressure is set at 5 psi higher than outside in order to prevent the dispersion of organic phase to aqueous phase. Flows of the organic phase in the shell and that of the water phase containing heavy metal in the tube are countercurrent. A brief schematic of experimental setup is depicted in Fig. 1.
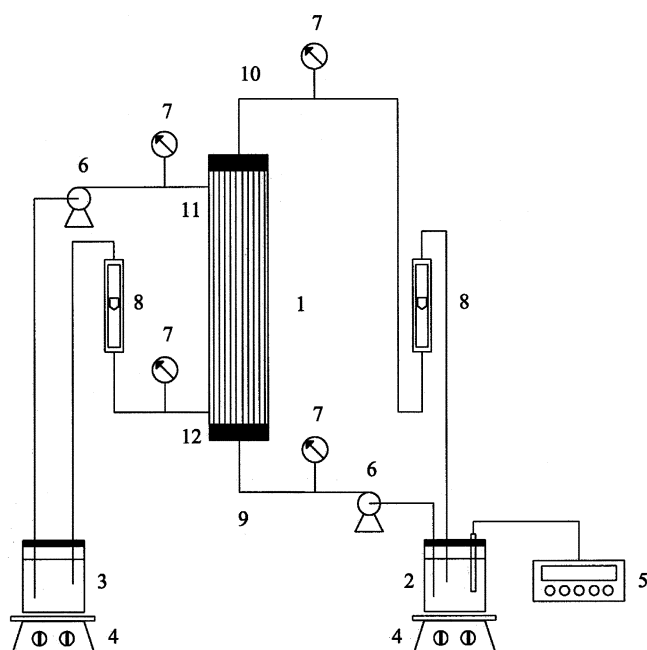
RESULTS AND DISCUSSION

Fig. 1. Experimental setup.

1. Hollow fiber module   7. Pressure gauge
2. Aqueous phase reservoir   8. Rotameter
3. Organic phase reservoir   9. Aqueous phase inlet
4. Stirrer   10. Aqueous phase outlet
5. pH meter   11. Organic phase inlet
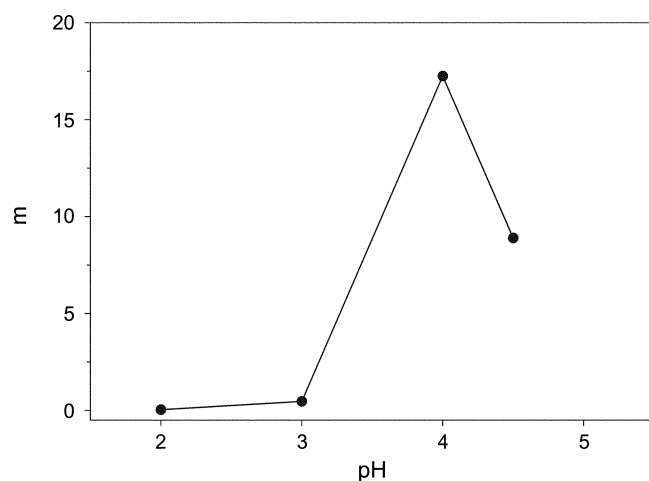6. Pump   12. Organic phase outlet

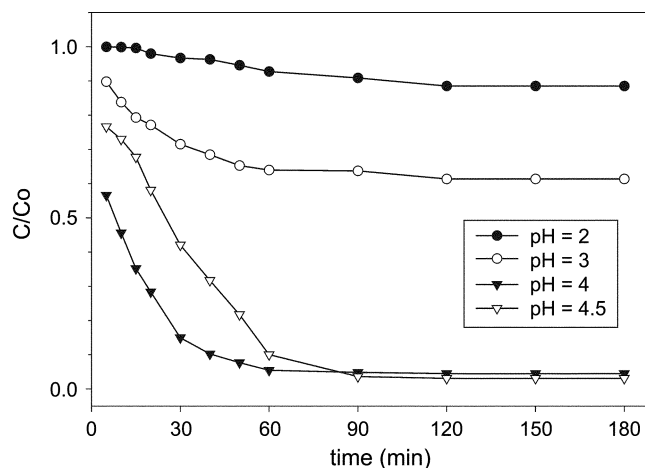Fig. 2. Effect of pH on equilibrium distribution after 60 minute extraction.

Fig. 3. Effect of pH on outlet concentration of aqueous phase.

The effect of acidity of aqueous phase on cadmium extraction is examined from the experiment of equilibrium distribution, and the outcome is shown in Fig. 2. The distribution coefficient is of organic phase concentration to aqueous phase. The initial cadmium concentration of aqueous phase is 0.1 g/L, organic phase contains 0.05 mol D2EHPA, and the extraction time of 60 minutes is provided. The highest distribution is found at pH of 4, which is the optimum condition. Again, the same outcome is shown in Fig. 3. The outlet concentration of cadmium ion in aqueous phase becomes the lowest with the pH of 4 in the shortest time. The equilibrium distribution affects the capacity of cadmium removal. Though the distribution at 4.5 of pH is smaller than that at 4, the capacity is sufficient enough to remove the cadmium from aqueous phase. Unless the distribution at 5 drops to the level of 2 or 3, the removal capacity is sufficient. After 60 minutes, the concentration remains constant to indicate that the removal is complete.

The role of pH in the equilibrium distribution with D2EHPA is different for various species of ions. For example, silver has the highest distribution between 2 and 3 in pH [Gherrou et al., 2002], cobalt and nickel have above 3.5 and 4.5, respectively [Zhang et al., 1999], copper has at 5 in pH [Juang and Huang, 1999] and manganese has
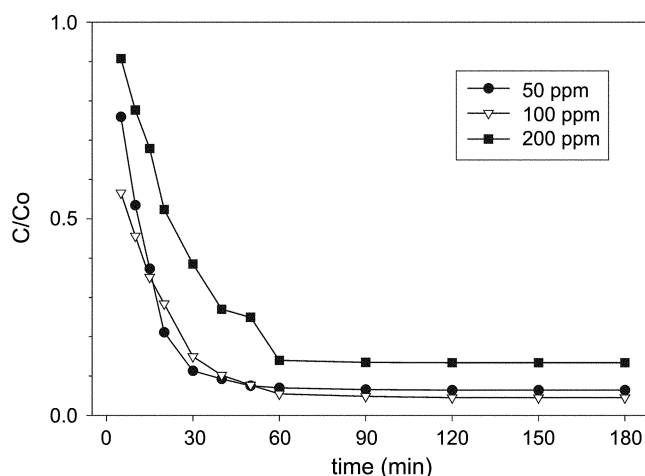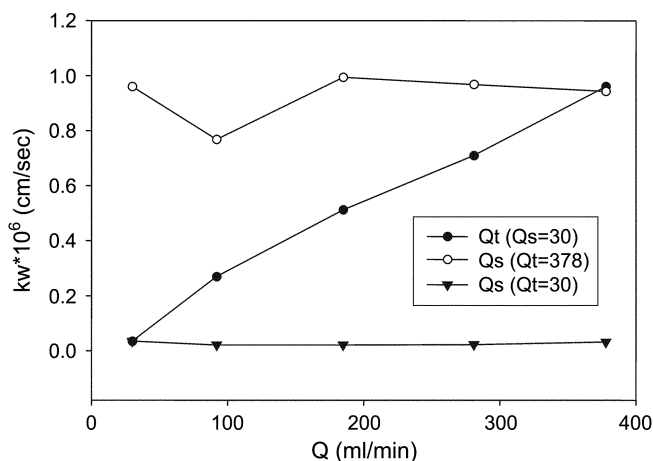
Fig. 4. Effect of initial concentration of cadmium ion.

Fig. 5. Effect of stream flow rates. Aqueous phase is denoted with Q_t and organic phase is with Q_s.

at 5.5 [Devi et al., 2000]. The result of this study with cadmium ion giving the highest distribution at 4 in pH shows a comparable outcome to the previous studies.

The effect of cadmium concentration in aqueous phase is examined, and the result is shown in Fig. 4. In the cases of 50 ppm and 100 ppm of the initial concentration, the removal performance is similar for the organic extractant concentration of 0.05 mol/L. However, the higher concentration of 100 ppm is adopted here because it gives higher amount of throughput. With 200 ppm, the removal is incomplete because of the lack of removal capacity.

The effect of stream flow rate on mass transfer is given in Fig. 5. Aqueous phase is denoted with Q_t and organic phase is with Q_s. The closed circles indicate the increase of mass transfer rate with raised flow rate of aqueous phase while organic phase maintains at the flow rate of 30 mL per minute. The open circles and closed triangles are of varying flow of organic phase with the constant aqueous phase flow indicated in the figure. While the flow rate of organic phase does not affect the transfer, higher aqueous flow induces the increase of mass transfer. From the fact that the equilibrium distribution shows higher concentration at organic phase, it is known that mass transfer at the aqueous phase is much slower than the or-
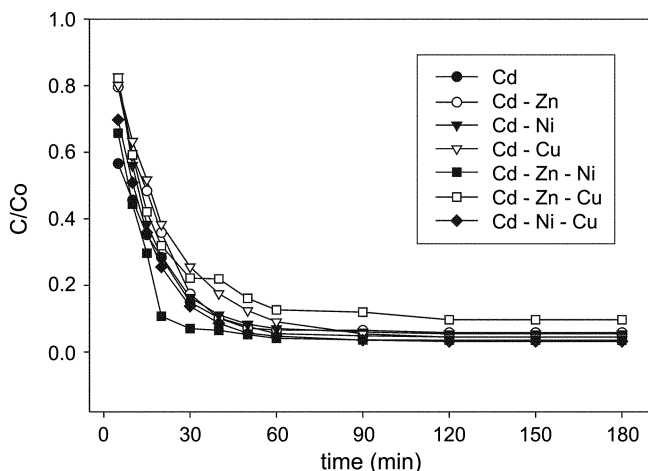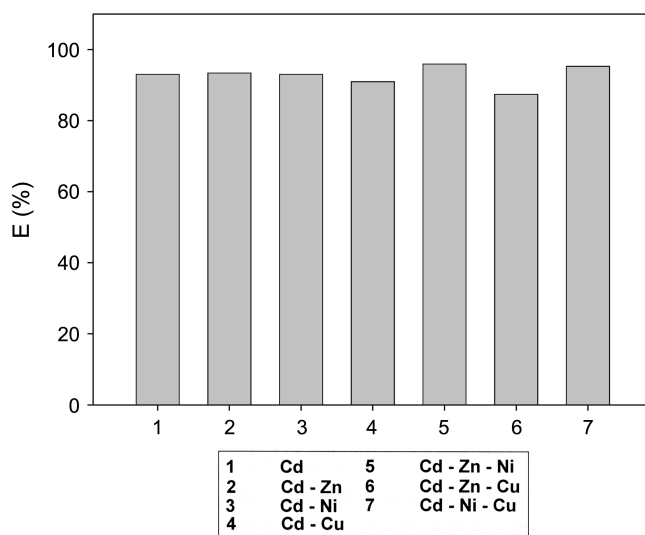

Fig. 7. Removal efficiency in various mixed solutions.

ganic phase and the overall mass transfer is controlled by the transfer at the aqueous phase. Therefore, the flow rate of aqueous phase affects the overall mass transfer rate while that of organic phase does not. The mass transfer coefficient displayed in the figure is calculated from the estimation equation for hollow fibers [Dahuron and Cussler, 1988].

The role of coexisting metal ions in the removal of cadmium ion is investigated as shown in Fig. 6. Except the case of zinc and copper coexisting with cadmium, the completeness of removal is almost the same. With zinc and nickel ions the removal rate is the highest, but the completeness is similar to others. The outcome of the figure indicates that the effect of coexisting metal ions is not notable in the cadmium removal.

The completeness is described as removal efficiency and demonstrated in Fig. 7. Because the efficiency is not affected from the coexisting metal ions, it is noticed that the cadmium can be separated from a mixed heavy metal solution with hollow fiber system. In case of coexisting zinc and copper ions the removal efficiency is the lowest, though the difference among various combinations of coexisting ions is not significant.

CONCLUSION

Hydrophobic hollow fiber module is implemented in the separation of cadmium ion from various heavy metal solutions. An organic extractant of D2EHPA and a solvent of n-heptane are utilized to form the organic phase of the system. The effects of hydrogen ion concentration, stream flow rates and coexisting metal were experimentally examined with the following outcome.

The hydrogen ion concentration at pH of 4 gives the best removal performance. The flow rate of aqueous phase controls the mass transfer while organic phase flow does not show difference. The effect of coexisting metal ions is not so significant that the proposed system is useful to separate the cadmium from a mixed heavy metal solution.

Fig. 6. Effect of coexisting metal ions.

ACKNOWLEDGMENT

NOMENCLATURE

c   : solute concentration [mol/L]
E   : recovery ratio [%]
k   : overall mass transfer coefficient [cm/s]
m   : equilibrium distribution coefficient [-]
Q   : volumetric flow rate [mL/min]

Subscripts

o   : initial
s   : organic phase
t   : aqueous phase
w   : aqueous side

REFERENCES

Cichy, W. and Szymanoski, J., "Recovery of Phenol from Aqueous Streams in Hollow Fiber Modules," *Envir. Sci. Tech.*, **36**(9), 2088 (2002).

Dahuron, L. and Cussler, E. L., "Protein Extractions with Hollow Fibers," *AIChE J.*, **34**(1), 130 (1988).

Devi, N. B., Nathsarma, K. C. and Chakravortty, V., "Separation of Divalent Manganese and Cobalt Ions from Sulphate Solutions Using Sodium Salts of D2EHPA, PC 88A and Cyanex 272," *Hydrometallurgy*, **54**(2-3), 117 (2000).

Fontas, C., Salvado, V. and Hidalgo, M., "Separation and Concentration of Pd, Pt, and Rh from Automotive Catalytic Converters by Combining Two Hollow Fiber Liquid Membrane Systems," *Ind. Eng. Chem. Res.*, **41**(6), 1616 (2002).

Gherrou, A., Kerdjoudi, H., Molinari, R. and Drioli, E., "Removal of Silver and Copper Ions from Acidic Thiourea Solutions with a Supported Liquid Membrane Containing D2EHPA as Carrier," *Sep. Pur. Tech.*, **28**(3), 235 (2002).

Juang, R.-S. and Huang, H.-C., "Non-Dispersive Extraction Separation of Metals Using Hydrophilic Microporous and Cation Exchange Membranes," *J. Memb. Sci.*, **156**(2), 179 (1999).

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).

Koopman, C. and Witkamp, G. J., "Extraction of Heavy Metals from Industrial Phosphoric Acid in a Transverse Flow Hollow Fiber Membrane Contactor," *Sep. Sci. Tech.*, **37**(6), 1273 (2002).

Park, S. W., Sohn, I. J., Suh, D. S. and Kumazawa, H., "Separation of CO_2 by 2-Amino-2-Methyl-1-Propanol Aqueous Solution in Microporous Hydrophobic Hollow Fiber Contained Liquid Membrane," *Korean J. Chem. Eng.*, **16**, 549 (1999).

Rangel-Mendez, J. R. and Streat, M., "Adsorption of Cadmium by Activated Carbon Cloth: Influence of Surface Oxidation and Solution pH," *Wat. Res.*, **36**(5), 1244 (2002).

Zhang, P., Yokoyama, T., Itabashi, O., Wakui, Y., Suzuki, T. M. and Inoue, K., "Recovery of Metal Values from Spent Nickel-Metal Hydride Rechargeable Batteries," *J. Power Sources*, **77**(2), 116 (1999).