Chromium(VI) Removal in a Semi-Continuous Process of Hollow Fiber Membrane with Organic Extractants

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Abstract–Chromium(VI) extraction from aqueous metal solution was experimentally studied by using a hollow fiber supported liquid membrane module. Organic extractants of D2EHPA, TBP, Lix79 and TOA were used to investigate the extraction performance. The extraction efficiencies of single and multiple component systems were examined with single or multiple extractants, and the role of multiple extraction operations and the difference between batch and continuous processes were inspected to find the optimum extraction condition. The experimental outcome indicates that the extraction process is controlled by aqueous phase mass transfer and multiple extraction operations do not reduce the extraction efficiency. The coexisting elements give no significant effect on chromium removal, while the mixed extractants of D2EHPA and TBP enhance the extraction efficiency by 84%. The efficiencies of batch and continuous extraction processes are nearly identical.

Key words: Chromium (VI) Removal, Hollow Fiber Membrane, Solvent Extraction, D2EHPA, Heavy Metal Separation

INTRODUCTION

Separation techniques of heavy metals, such as chromium, cadmium, copper, zinc and nickel, from industrial wastewater include precipitation, ion exchange, adsorption, electro-dialysis and filtration, but these techniques have limitations in selective separation and the problems of high investment cost and equipment operation. Recently, membrane separation has widely been considered as a suitable technique for heavy metal separation. Despite the fact that membrane fouling caused by some chemical components and fine solid particles restricts long time application of the membrane, the structural characteristic of two separated flows in the membrane separation process prevents channeling and loading at extraction operation and less energy is required compared with conventional separation processes.

Chromium is known to be highly toxic, and its removal from industrial wastewater has been studied for a long time. Because no metal coating is better than chromium plating in terms of surface polish and durability, chromium has widely been used in metal handling industries. Also, leather tanning consumes chromium-containing chemical to produce large amounts of chromium wastewater. Among a variety of removal techniques, the application of supported liquid membrane technology using hollow fiber was investigated by many researchers [Vincent and Guibal, 2000; Ho and Poddar, 2001; Ho, 2003; Alguacil et al., 2003]. They applied various extractants, such as, TBP, Aliquat 336, Cyanex 921 and alkyl phenylphosphonic acids to find the most efficient extractant for selective removal of chromium. For the chemical analysis of heavy metals, resin extraction was applied to separate and to enrich chromium [Narin et al., 2001]. As an environmentally friendly technique, biosorption with seaweed was implemented in the recovery and recycling of chromium [Aravindhan et al., 2004].

As other applications of supported liquid extraction using hollow fiber, Cichy and Szymanowski [2002] studied the recovery of phenol with extractants of Cyanex 923, Amberlite LA-2 and trioctylamine (TOA). Palladium, platinum and rhodium were recovered from spent automotive catalytic converters by using a hollow fiber module with Cyanex 471 and Aliquat 336 as extractants [Fontas et al., 2002]. Lanthanum, neodymium and palladium were extracted with similar technique [Weerawat et al., 2003; Prakorn and Ura, 2003]. Also, mercury, copper, lead and cadmium were extracted from phosphoric acid with the module and a carrier of Cyanex 302 [Koopman and Witkamp, 2002]. A mixture of copper, chromium and zinc was separated from sulfate media [Prakorn et al., 2004]. The extractive separation of cadmium from a mixed solution containing various heavy metals was investigated by using extractant of di-(2-ethyl hexyl) phosphoric acid (D2EHPA) [Choi and Kim, 2003].

In this study, the extractive removal of chromium(VI) from metal-containing aqueous solution is investigated. The used extractant is di-(2-ethyl hexyl) phosphoric acid (D2EHPA) with organic solvent of n-heptane. Overall mass transfer coefficient is evaluated, and the effects of multiple extraction operations and coexisting metal ions are examined. In addition, the extraction efficiency of semi-continuous process is compared with that of batch extraction.

MASS TRANSFER COEFFICIENT

The overall mass transfer coefficient is evaluated from the concentrations of chromium solution at inlet and outlet by using the following equation for countercurrent operation [Dahuron and Cussler, 1988].

Table 1. Specification of hollow fiber module and operation variables

Fiber potting material	polyethylene
I. D.	244 μm
Effective pore size	0.03 μm
Porosity	40%
Area per unit volume	29.3 cm²/cm³
Wall thickness	28 μm
Fiber length	15 cm
Module I. D.	8 cm
Module O. D.	28 cm
Number of fibers	10,000
Volume of aqueous phase	2 L
Volume of organic phase	1 L

$$\ln\frac{\Delta c}{\Delta c_0} = -t\left[Q_w\left(\frac{1}{V_w} + \frac{1}{HV_s}\right)\right]$$

$$\times \left[\frac{1 - \exp(-4K_w L/dv_w(1 - Q_w/HQ_s))}{1 - \frac{Q_w}{HQ_s}\exp(-4K_w L/dv_w(1 - Q_w/HQ_s))}\right] \quad (1)$$

where K_w is the overall mass transfer coefficient, and the ratio of solute concentration difference in the left hand side of Eq. (1) is computed from

$$\ln\frac{\Delta c}{\Delta c_0} = -\ln\left[\frac{c_w\left(1 + \frac{V_w}{HV_s}\right) - \frac{c_w^0 V_w}{HV_s} - \frac{c_s^0}{H}}{c_w^0 - \frac{c_s^0}{H}}\right] \quad (2)$$
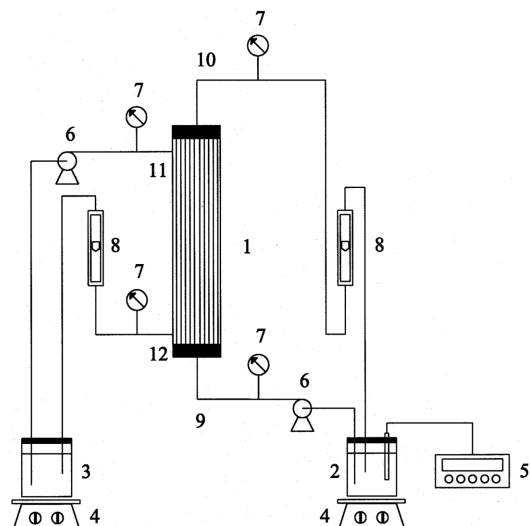
In the evaluation of the overall mass transfer coefficient the values of operational variables are necessary, and the specifications of the hollow fiber module and operational variables are listed in Table 1.

EXPERIMENTAL

A hollow fiber module (Hoechst Celanese, U.S.A., model Liqui-Cel Extra-Flow) having a size of 2.5 inches I. D. and 8 inches O. D. was used in this experiment. The characteristic properties of the module are listed in Table 1. An experimental setup built by Hoechst Celanese (model Lab Liq/Liq Extraction System) was employed here. Aqueous phase was supplied to the tube side of the module with a micro-pump, and the flow rate was adjusted with a valve attached at the pump. Organic phase was provided to the shell side in countercurrent flow. Because the hollow fiber is hydrophobic, inside pressure was set at 5 psi higher than outside in order to prevent dispersion of the organic phase into the aqueous phase. A brief schematic diagram of the experimental setup is described in Fig. 1.

Sodium chromate was dissolved in water and used as aqueous phase solution. Di-(2-ethyl hexyl) phosphoric acid (D2EHPA), 2-hydroxy-5-nonyl-acetophenoneoxime (Lix84), tri-n-octylamine (TOA) and tri-n-butyl phsophate (TBP) were dissolved in n-heptane and used as organic phase extractant.

A semi-continuous extraction was conducted at the conditions of chromium concentration of 100 ppm in aqueous phase, pH of 4 and flow rate of 378 mL/min. The flow rate of organic phase was

Fig. 1. A schematic diagram of 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	

30 mL/min. The concentration of D2EHPA in organic phase was 0.05 mol/L. These operation conditions were used as the base of this study, because the least amount of the extractant extracts the most amount of chromium at the conditions. For multiple extraction operations, the aqueous phase was only replaced, and extra extractant was added to the organic phase every 3 hours for 15 hour continuous operation. Experiments with mixed extractants were carried out with the mixtures of TBP and D2EHPA, TBP and Lix84, and TBP and TOA. Because the TBP is the poorest extraction performance, it was employed in all three groups of mixed extractants and each of the others was added to it for the evaluation of performance enhancement. The concentration of individual extractant is 0.01 mol/L for all, and the mixed one is a mixture of two extractants of 0.01 mol/L each. Batch extraction was conducted in a 500 mL flask with the mixture of aqueous and organic phases in the ratio of 2 to 1. The concentrations of aqueous and organic phases are equal to the continuous process of the base system. The concentration of chromium was determined with an atomic absorption spectrometer (Varian, Inc., U.S.A., model SpectrAA-200HT).

RESULTS AND DISCUSSION

The concentration variation of solute in aqueous phase with increasing time gives a linear relation, and the overall mass transfer coefficient is evaluated from the relation using Eq. (1). The coefficients at various flow rates in the base system are shown in Fig. 2. The closed circles are of the varying flow rates in aqueous phase with constant flow of organic phase. The open circles are of organic phase in varying flow rates. While the flow rate of aqueous phase affects the coefficient, that of organic phase does not. This indicates that the overall mass transfer in the hollow fiber module is controlled by the mass transfer in aqueous phase. The outcome is
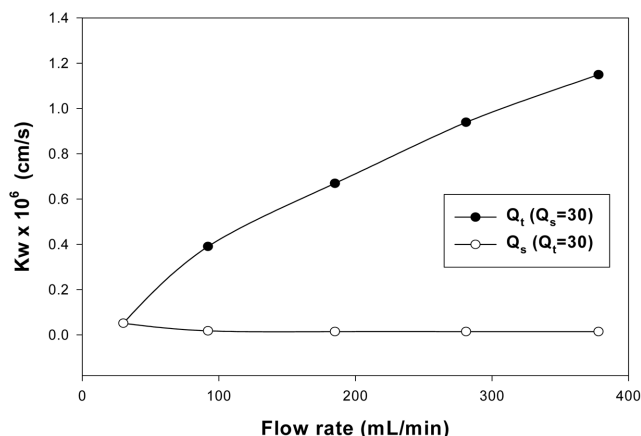
Fig. 2. Effect of stream flow rates on overall mass transfer coefficient. Aqueous phase is denoted with Q_t and organic phase is with Q_s.
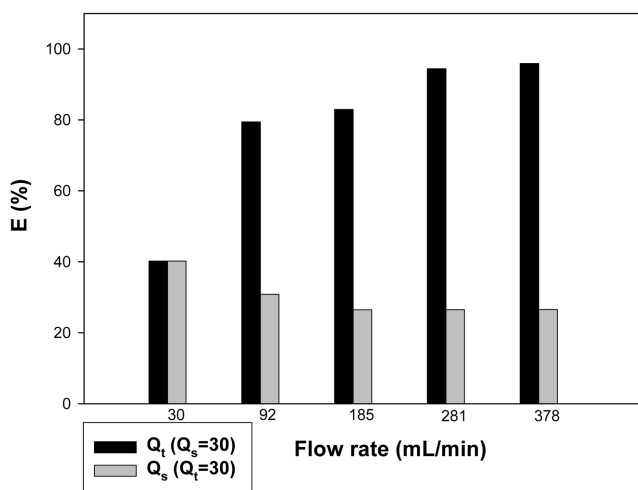

Fig. 3. Effect of stream flow rates on extraction efficiency. Aqueous phase is denoted with Q_t and organic phase is with Q_s.

consistent with the experimental result of cadmium removal by using the same extraction system [Choi and Kim, 2003]. The mechanism of mass transfer is also explained with a comparison of extraction efficiencies, as illustrated Fig. 3. The efficiency is defined as the following equation.

$$E(\%) = \left(1 - \frac{c}{c_0}\right) \times 100 \tag{3}$$

where c is the solute concentration in aqueous phase and the concentration ratio is to the initial concentration. The increase of the efficiency is found from the elevated flow rates in aqueous phase only. This result is identical to the variation of overall mass transfer coefficient, and aqueous phase controlled mass transfer occurs here. Because the extractant in organic phase produces chelate with the extracted chromium ion, the mass transfer in organic phase is enhanced by the reaction. Therefore, the mass transfer in aqueous phase is slower than that in organic phase to be the rate determining process of overall mass transfer.

A preliminary experiment was conducted to determine the opti-

mum pH in aqueous phase, and it was found that the highest equilibrium distribution is given at pH of 4. The pH was implemented in the extraction of this study. 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], manganese has at 5.5 [Devi et al., 2000] and cadmium has at 4 [Choi and Kim, 2003].

Multiple operations of the extraction were conducted to examine the availability of extraction module for cycling use, which eliminates time and efforts of module cleaning, drying and reassembling. In this experiment, the aqueous phase of 100 ppm chromium solution was replaced and the extractant of D2EHPA in the concentration of 0.05 mol/L was added to the organic phase at each cycle of extraction operation in five cycle repetition. The outcomes of extraction rate and efficiency are demonstrated in Figs. 4 and 5. All five runs were conducted for 3 hours each. Though the extraction efficiencies of all runs are similar, the extraction rate in the early stage of runs 2 through 5 is faster than the first. The additional amount of extractant for the repetitive operations helps the extraction to raise
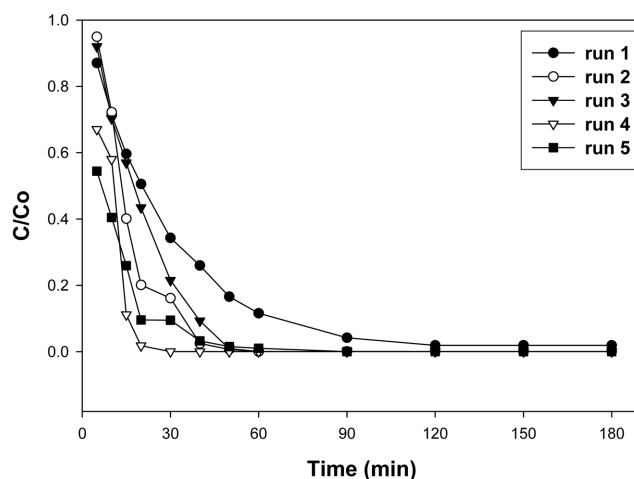

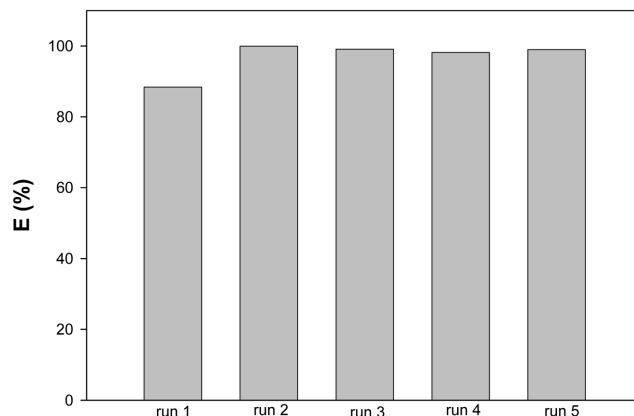Fig. 4. Variation of aqueous phase concentration in multiple operations of base system.

Fig. 5. Effect of multiple operations on extraction efficiency of base system.
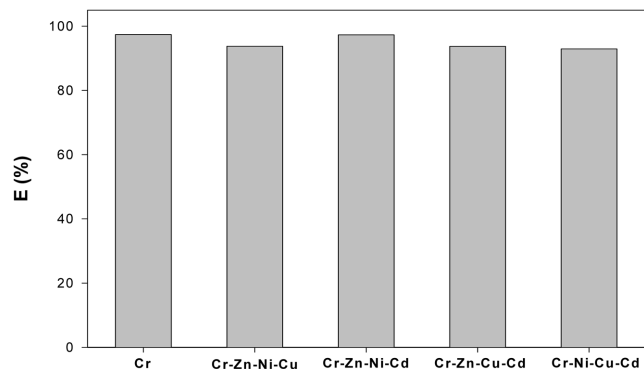
Fig. 6. Effect of coexisting elements on extraction efficiency.

Fig. 8. Variation of aqueous phase concentration in batch and continuous operations.

the extraction rate. In the multiple operations, 1 L of heptane as solvent is saved due to the continuous use and about 90 minutes of module handling time is reduced from each additional operation.

The effect of coexisting elements on the removal of chromium is illustrated in Fig. 6. Several combinations of metal components of zinc, copper, cadmium and nickel were tested with the extractant D2EHPA, and the extraction efficiency from the solutions containing various coexisting metal components ranges between 93% and 96%. The experimental outcome indicates that the coexisting metal components do not affect the extraction efficiency of chromium. Because the amount of extractant is sufficient to extract the coexisting components, the chromium extraction is not affected from the components. The role of the coexisting element was studied in cadmium removal to show the same outcome [Choi and Kim, 2003].

The effect of mixed extractants on the chromium removal was examined, and the results are shown in Fig. 7. In a gold recovery process [Kumar et al., 2000], the same hollow fiber supported liquid membrane process as used in this study was implemented with the mixed extractants of TOPO and Lix79, and it was found that the mixed extractants enhance the recovery more than 50 times in comparison with the process with TOPO only. A similar increase of the efficiency was observed in this experiment. Among three groups
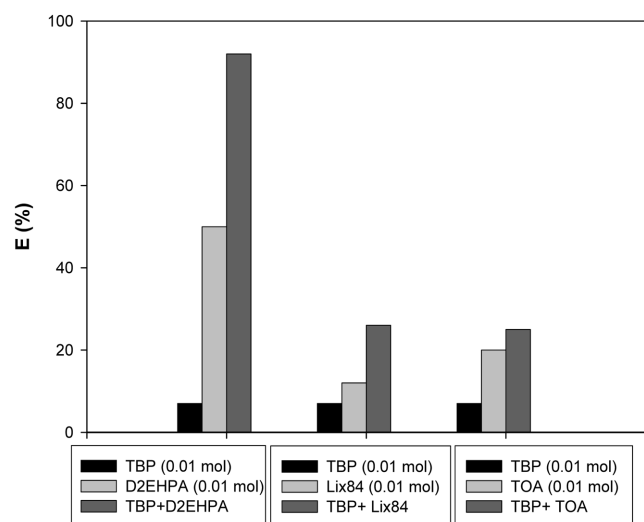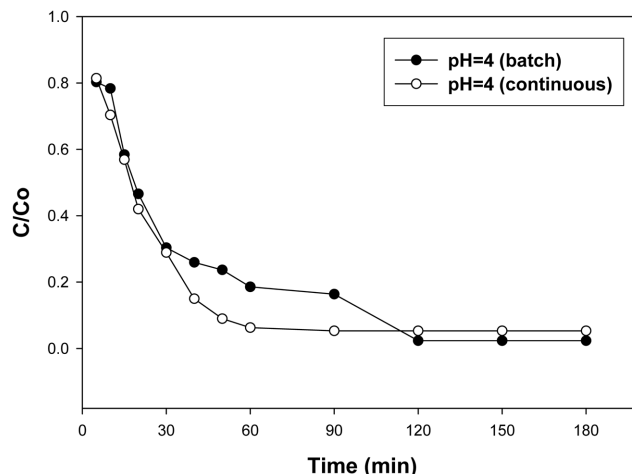
of mixed extractants of TBP+D2EHPA, TBP+Lix84 and TBP+TOA, the first group gives the highest efficiency, and the extraction is enhanced by 84% compared with the D2EHPA only extraction. The second and the third groups improve the extraction by 116% and 25% from the next highest ones, respectively. But the efficiency improvement is not significant compared with the first mixed extractants. Because the mixed extractants are a mixture of each extractant, its minimum efficiency is the sum of individual efficiencies; in this regard the improvement of the first group is only noticeable. Finally, the continuous and batch extractions were compared, and the experimental results are given in Fig. 8. The batch extraction was carried out in a 500 mL flask, while the continuous extraction was conducted with the base system. The extraction efficiency is examined with the chromium content in aqueous phase. In general, the two operations lead to similar performance except the interval between 30 minutes and 2 hours when the batch operation shows higher efficiency due to higher mass transfer rate from better mixing. Yet the difference is not significant. Because the aqueous phase controls the extraction, mixing effects in both processes are nearly the same due to low viscosity of the phase to result in a negligent difference of performance.

CONCLUSION

Chromium(VI) was extracted by using a hollow fiber supported liquid membrane module, and the extraction performance was experimentally evaluated by employing the extractants of D2EHPA, TBP, Lix79 and TOA as organic phase. The role of coexisting elements and mixed extractants was investigated, and also the effect of a multiple cycling operation and the performance difference between batch and continuous operations were examined.

The experimental results indicate that overall extraction is controlled by aqueous phase mass transfer and multiple extraction operations do not affect the extraction efficiency. Coexisting metal ions give no significant effect on chromium removal, and the mixed extractants of D2EHPA and TBP enhance extraction efficiency by 84%. No significant difference between batch and continuous processes was observed.

Fig. 7. Efficiency comparison of mixed extractants.

ACKNOWLEDGMENTS

NOMENCLATURE

c   : solute concentration [mol/L]
d   : fiber diameter [cm]
E   : recovery ratio [%]
H   : partition coefficient [-]
L   : fiber length [cm]
K   : overall mass transfer coefficient [cm/s]
m   : equilibrium distribution coefficient [-]
Q   : volumetric flow rate [mL/s]
V   : reservoir volume [mL]
v   : velocity [mL/s]

Subscripts
o   : initial
s   : organic phase
w   : aqueous phase

Superscript
o   : initial

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