

## Efficient transport and selective extraction of Cr(VI) from waste pickling solution of the stainless steel-cold rolled plate process using Aliquat 336 via HFSLM

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**Abstract**—The selective extraction of Cr(VI) from waste pickling solution of the stainless steel-cold rolled plate process by hydrophobic hollow fiber supported liquid membrane (HFSLM) was investigated. The effects of various parameters—types of organic extractants, i.e., methyl trioctylammonium chloride (Aliquat 336), tri-n-octylamine (TOA), tri-n-butyl phosphate (TBP) and the mixture of Aliquat 336 and TBP, concentration of the selected extractant, types of stripping solutions (NaCl and NaOH), pH and concentration of the selected stripping solution, and the operating temperature—were studied. The feed and stripping solutions flowed countercurrently. The results showed that the co-existing contamination in spent pickling solution of Fe(II) and Ni(II) ions had no significant effect on Cr(VI) extraction. Among the extractants used in this study, Aliquat 336 was a specific carrier to attain the highest percentage of Cr(VI) extraction. About 70% extraction was achieved by using 0.11 M Aliquat 336 and 0.5 M NaCl at pH 7. The percentage of stripping slightly increased when the concentration of NaCl increased. In addition, it was found that the operating temperature of 20, 30, 40, and 50 °C had almost no influence on the percentages of extraction and stripping of Cr(VI). The calculated diffusion energy of Cr(VI) extraction was 15.14 kJ/mol.

Key words: Extraction, Cr(VI), Hollow Fiber, Methyl Trioctylammonium Chloride, Pickling

### INTRODUCTION

Chromium is extensively used for industrial applications in alloying and plating elements on metal and plastic substrates for corrosion resistance, chromium-containing and stainless steels, protective coatings for automotive and equipment accessories, nuclear and high-temperature research and constituents of inorganic pigments. It is commonly a reactive metal and exists in different oxidation states of Cr(II), Cr(III) and Cr(VI). Cr(II) and Cr(VI) are unstable forms and can be changed to Cr(III). Hexavalent chromium Cr(VI) compounds are known to be highly toxic, having mutagenic and carcinogenic effects and corrosive on tissue, resulting in ulcers and dermatitis on prolonged contact more than Cr(III) [1-3]. In a stainless steel-cold rolled plate process, chromium is used to produce a hard and beautiful surface of stainless steel to prevent corrosion. Chromium is found as Cr(VI) with Fe(II) and Ni(II) in a pickling bath of the stainless-steel making process using H<sub>2</sub>SO<sub>4</sub> and HF/HNO<sub>3</sub>. Normally, Cr(VI) ions exist in the anion forms, i.e., Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup> and HCrO<sub>4</sub><sup>-</sup>. In highly acidic aqueous solution (pH<1), Cr(VI) ion exists mostly as H<sub>2</sub>CrO<sub>4</sub>. In pH between 2 and 6, the aqueous solution is in equilibrium between Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and HCrO<sub>4</sub><sup>-</sup> ions, while under alkaline condition (pH>8), it exists predominantly as chromate ion [4]. In the spent pickling solution (pH 2-3) in our work, Cr(VI) ions are mostly Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and HCrO<sub>4</sub><sup>-</sup> ions. To comply with legislation, chromium concentration in liquid effluent from the pro-

cess must meet the standard permissible concentration before discharge to the environment. Therefore, the removal of chromium ions from industrial wastewater has received considerable attention. The extensive studies on metal separations including Cr(VI) have been examined by several methods [4-29]. In practice, separation techniques of Cr(VI) from industrial wastewater include reduction-precipitation, which transfers Cr(VI) to a less toxic form Cr(III), ion exchange, adsorption, electro-dialysis and filtration. However, these techniques have limitation in selective separation, high investment and operating costs. Hollow fiber supported liquid membrane (HFSLM) has been considered as a potential technique for heavy metal separation due to its outstanding characteristic of simultaneous extraction and stripping or recovery steps for the feed of dilute concentration. It does not require phase mixing for high mass transfer. Despite the fact that membrane fouling restricts long time application of the membrane, the structural characteristics of two separated flows in the membrane process prevent channeling and loading at extraction operation and less energy consumption compared with other conventional separation processes.

Among a number of previous works, various extractants such as Aliquat 336, D2EHPA, TOA, TBP, Lix 79, Cyanex 921 for the selective of removal and recovery of Cr(VI) were applied. From ref. [18], it was reported that TBP was an efficient carrier to extract and recover Cr(VI) from plating wastewater through supported liquid membrane (SLM). In addition, TBP can mix with either basic or acidic extractant for an investigation of the synergistic effect as it is a neutral extractant [16,29]. It was found that the mixture of D2EHPA and TBP enhanced the extraction efficiency of Cr(VI) [16]. How-

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ever, for anion forms of Cr(VI), the basic extractant is likely to be appropriate. Thus, in this current work Aliquat 336 and TOA were used to compare with TBP and the mixture of Aliquat 336 and TBP for the extraction of Cr(VI) from the spent pickling solution of the stainless steel-cold rolled plate process. In case of the stripping solution, most researchers used NaCl and NaOH [8-10,12,14-19] so both NaCl and NaOH were experimented. The optimum condition using the selected extractant and stripping solution will be finally identified in this work.

## THEORY

### 1. Transportation Mechanism of Cr(VI) Ions in an HFSLM

The hollow fiber supported liquid membrane process can be divided into three phases, namely feed solution, liquid membrane and stripping solution, as shown in Fig. 1. Liquid membrane is between feed solution and stripping solution to exchange target metal ions. The transportation mechanism of Cr(VI) ions can be described by

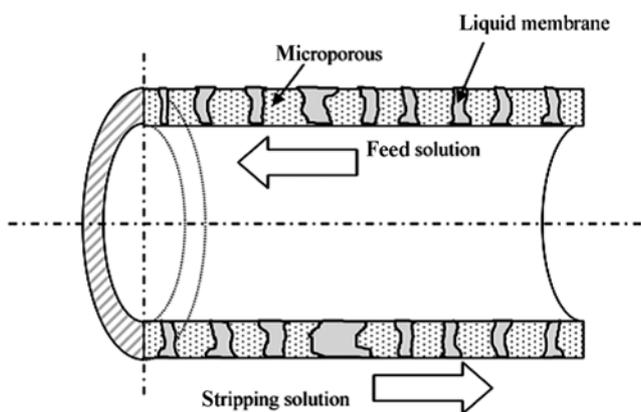
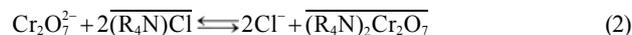


Fig. 1. Counter current flow pattern in hollow fiber supported liquid membrane [14].

Fig. 2.

Step 1: Cr(VI) ion as monovalent  $\text{HCrO}_4^-$  and divalent  $\text{Cr}_2\text{O}_7^{2-}$  in the feed solution are transported to a contact surface between feed solution and liquid membrane. Subsequently,  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions are reacted with the extractant (Aliquat 336) to form complex species as described in Eqs. (1) and (2) [19].



where  $\overline{(\text{R}_4\text{N})\text{Cl}}$  represents the initial extractant form, and the complex species are  $\overline{(\text{R}_4\text{N})\text{HCrO}_4}$  and  $\overline{(\text{R}_4\text{N})_2\text{Cr}_2\text{O}_7}$ .

Step 2: The chromium complex species diffuse to the opposite side of the hollow fiber by the concentration gradient.

Step 3: The chromium complex species react with NaCl solution, a stripping solution, at the contact surface between liquid membrane and the stripping solution, as described in Eqs. (3) and (4):



Step 4:  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions are transferred into the stripping solution while the extractant moves back to liquid membrane and diffuses to the opposite side of hollow fiber by the concentration gradient to react again with  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions in feed solution.

In this current work, the percentages of extraction and stripping were determined by the following equations.

$$\% \text{ Extraction} = \frac{C_{\text{Cr, feed(in)}} - C_{\text{Cr, feed(out)}}}{C_{\text{Cr, feed(in)}}} \times 100 \quad (5)$$

$$\% \text{ Stripping} = \frac{C_{\text{Cr, stripping(out)}}}{C_{\text{Cr, feed(in)}}} \times 100 \quad (6)$$

where  $C_{\text{Cr, feed(in)}}$ ,  $C_{\text{Cr, feed(out)}}$  and  $C_{\text{Cr, stripping(out)}}$  represent the concentra-

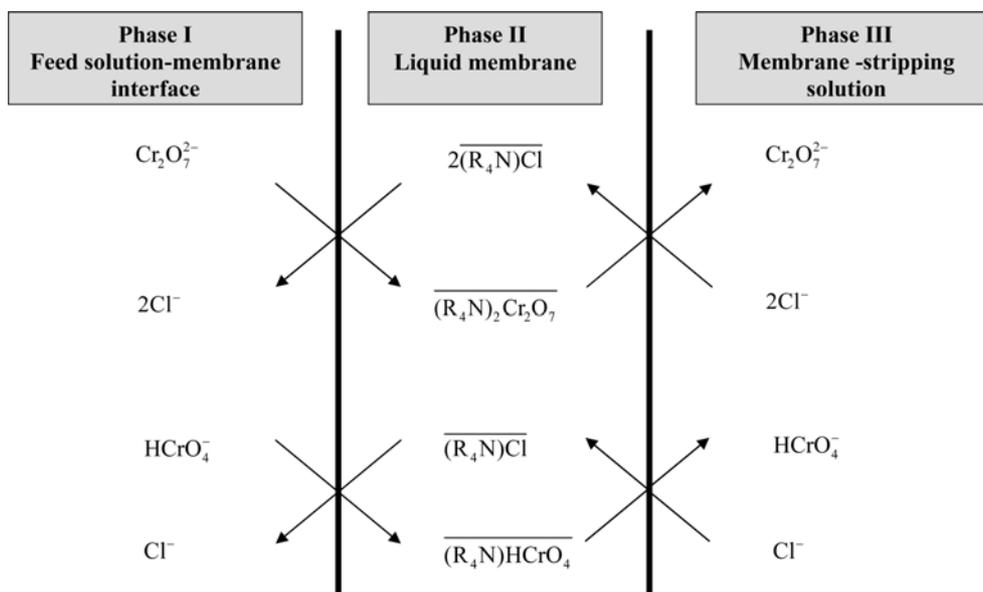


Fig. 2. Scheme for removal of Cr(VI) ions with Aliquat 336 as the extractant and NaCl as the stripping solution.

tion of Cr(VI) ions in the inlet feed, outlet feed and outlet stripping, respectively.

The separation factor (SF) of Cr(VI) ions compared with other metal ions can be calculated from:

$$SF = \frac{K_{Cr}}{K_M} \quad (7)$$

$K_{Cr}$  and  $K_M$  are the overall mass transfer coefficients of Cr(VI) and other metal ions.

The overall mass transfer coefficient can be evaluated by the following equation [22]:

$$K_{Cr} = \frac{Q_f}{A} \ln \frac{C_{Cr,feed(in)}}{C_{Cr,feed(out)}} \quad (8)$$

where  $Q_f$  is the volumetric flow rate of feed solution,  $A$  is mass transfer area of the hollow fiber.

We selected Aliquat 336, TOA, TBP and the mixture of Aliquat 336 and TBP to find the efficient extractant and the optimum condition for Cr(VI) removal. Both NaCl and NaOH solutions were studied as the stripping solution.

## EXPERIMENTAL

### 1. Reagents

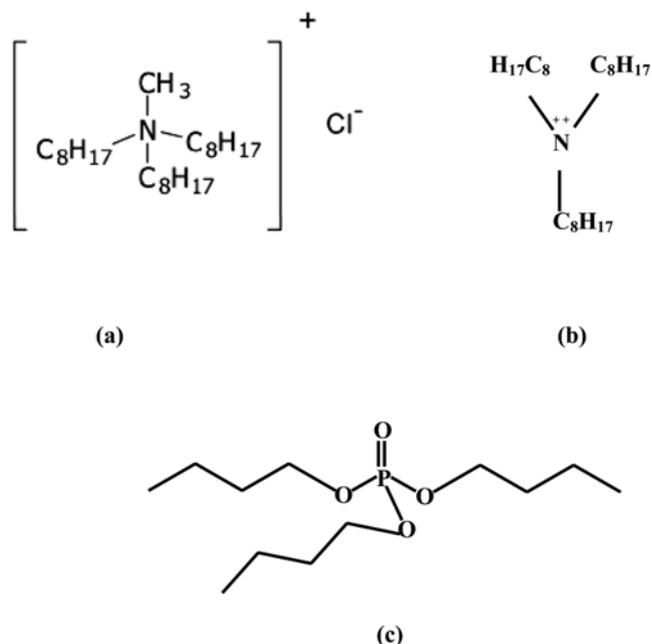
Feed solution containing Cr(VI) ions was the spent pickling solution from the stainless steel-cold rolled plate process. The compositions are shown in Table 1. NaCl and NaOH as the stripping solutions were analytical reagent grade. The extractants, methyl trioctylammonium chloride (Aliquat 336), tri-*n*-octylamine (TOA) and tri-*n*-butyl phosphate (TBP), in liquid membrane were supplied by Merck Ltd. The chemical structures of the extractants are shown in Fig. 3. The extractants were diluted in kerosene, then added with 1-dodecanol to avoid segregation. Kerosene, JPI grade from PTT Public Co., Ltd. without further purification, was selected as an organic solvent for high stability of liquid membrane due to its low solubility in water, high surface tension and low volatility.

### 2. Apparatus

A hollow fiber module, the Liqui-Cel<sup>®</sup> Extra-flow module, by CELGARD LLC (Charlotte, NC; formerly Hoechst Celanese), was used as a supporting material. This module was composed of Celgard<sup>®</sup> microporous polypropylene fibers which were woven into the fiber and wrapped around a central tube feeder to supply the shell side fluid. Woven fabric fibers provided a superior uniform

**Table 1. Physical properties and compositions of feed solution**

| Color                                | Yellow  |
|--------------------------------------|---------|
| pH                                   | 2-3     |
| Fe(II) (mg/L)                        | 180     |
| Mg(II) (mg/L)                        | 14.42   |
| Cr(VI) (mg/L)                        | 300-500 |
| Al(III) (mg/L)                       | 0.88    |
| Cu(II) (mg/L)                        | 2.53    |
| Zn(II) (mg/L)                        | 1.53    |
| Ni(II) (mg/L)                        | 32      |
| SO <sub>4</sub> <sup>2-</sup> (mg/L) | 750     |



**Fig. 3. Chemical structures of the extractants: (a) Aliquat 336 (b) TOA (c) TBP.**

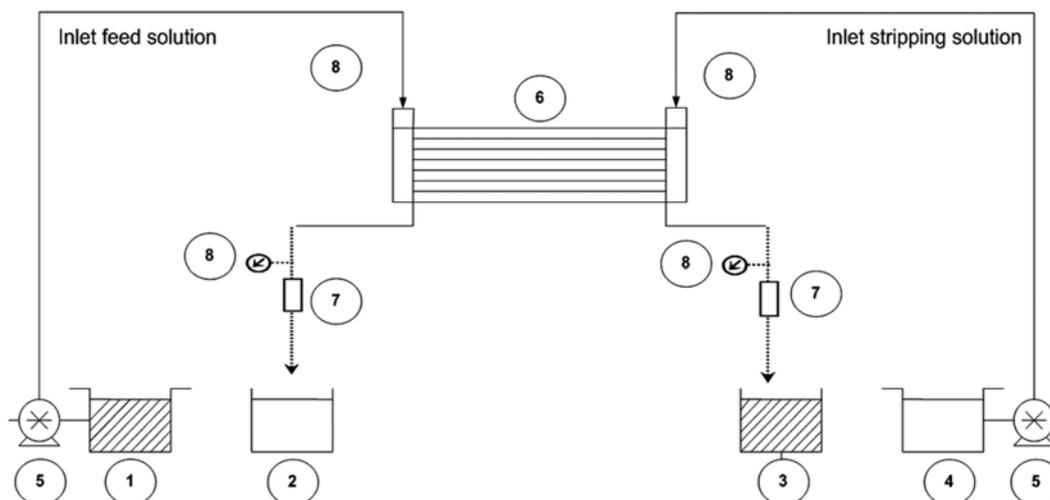
**Table 2. Properties of the hollow fiber module**

| Property                             | Description                           |
|--------------------------------------|---------------------------------------|
| Material                             | Polypropylene                         |
| Inside diameter of the hollow fiber  | 240 $\mu$ m                           |
| Outside diameter of the hollow fiber | 300 $\mu$ m                           |
| Pore size                            | 0.05 $\mu$ m                          |
| Porosity                             | 30%                                   |
| Contact area                         | 1.4 m <sup>2</sup>                    |
| Area per unit volume                 | 29.3 cm <sup>2</sup> /cm <sup>3</sup> |
| Module diameter                      | 6.3 cm                                |
| Module length                        | 20.3 cm                               |
| Number of fibers                     | 240                                   |

fiber spacing leading to higher mass transfer coefficient than that obtained from the individual fiber. The properties of the hollow fiber module are shown in Table 2. The fibers were potted in a solvent-resistant polyethylene tube sheet and shell casing in polyethylene. The concentration of Cr(VI) was measured by atomic absorption spectroscopy (Model AA280FS, Varian, Inc.) The pH of the stripping solution was measured by a pH-meter HI8418A, Hanna Instrument.

### 3. Procedures

First, the organic solution which contained the extractant was pumped into the tube and shell sides then circulated about 30 minutes to make the extractant embedded in micropores of hollow fibers. Thereafter, feed solution (the spent pickling solution from the stainless steel-cold rolled plate process) was pumped through the lumen side (tube side) of the hollow fiber membrane; simultaneously the stripping solution was fed in the shell side in a counter-current flow mode. Feeding solution was the spent pickling solution from the stainless steel-cold rolled plate process and filtered by a filter paper (Whatman No. 42). The schematic diagram is shown in Fig. 4.



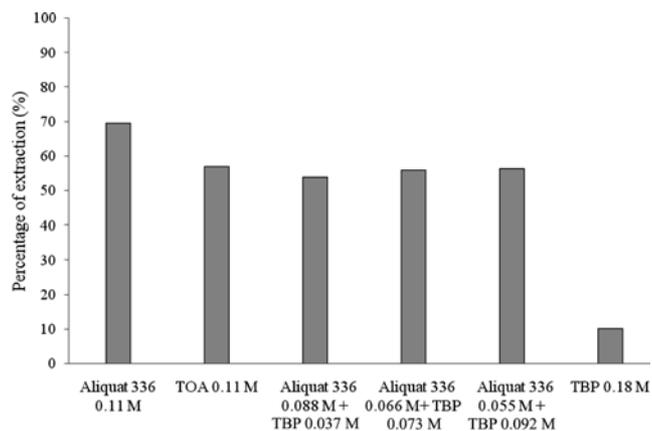
**Fig. 4. Schematic counter-current flow diagram for one-through-mode operation in a hollow fiber supported liquid membrane.**

- |                               |                              |                        |                |
|-------------------------------|------------------------------|------------------------|----------------|
| 1. Inlet feed reservoir       | 3. Outlet feed reservoir     | 5. Gear pumps          | 7. Flow meters |
| 2. Outlet stripping reservoir | 4. Inlet stripping reservoir | 6. Hollow fiber module | 8. Gate valves |

The operating time for 1 cycle was about 50 mins. The outlet feed solution was then supplied as the inlet feed solution for the following cycle as well as at the stripping side. Samples of about 15 cm<sup>3</sup> were taken from feed and stripping reservoirs after 5 cycles and the concentration of metal ions was determined by atomic absorption spectroscopy. The effects of various parameters—types of organic extractants (i.e., Aliquat 336, TOA, TBP and the mixture of Aliquat 336 and TBP), concentration of the selected extractant, types of stripping solutions (NaCl and NaOH), pH and concentration of the selected stripping solution, and the operating temperature—were studied.

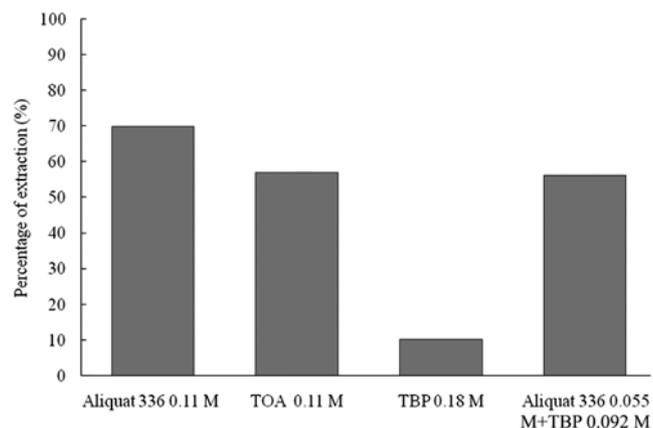
## RESULTS AND DISCUSSION

### 1. Effects of Types of Extractants



**Fig. 5. Effect of the mixture of Aliquat 336 and TBP on the extraction of Cr(VI) by 5-cycle operation: feed solution is the spent pickling solution, stripping solution is NaCl at pH 7 (in case of TOA the stripping solution was NaOH solution) and concentration of 0.5 M, flow rates of feed and stripping solutions are 100 ml/min.**

Figs. 5 and 6 show the effects of types of extractants on the extraction of Cr(VI). It was obviously seen that TBP was a poor extractant to extract Cr(VI) from spent pickling solution. This is because TBP can react with both anions and cations in the spent pickling solution. And the mixture of Aliquat 336 and TBP did not show a significant synergistic extraction. The highest percentage of extraction of Cr(VI) about 70% by 5-cycle operation was obtained by using 0.11 M Aliquat 336. For anion forms of Cr(VI), the basic extractant was approximately the same as the results in [9,12,14,19], and also in our previous works using synthetic feed solution of K<sub>2</sub>CrO<sub>4</sub> that Aliquat 336 gained high extraction of Cr(VI) about 96% and 92% [10, 14]. It was reported that TOA formed strong complexes with HCrO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ions resulting in difficult stripping [20] and NaOH solution had higher stripping performance than NaCl solution [26]; therefore, in case of TOA in Fig. 6, the stripping so-



**Fig. 6. Plot of types of the extractants against the extraction of Cr(VI) by 5-cycle operation: feed solution is the spent pickling solution, stripping solution is NaCl at pH 7 (in case of TOA the stripping solution was NaOH solution) and concentration of 0.5 M, flow rates of feed and stripping solutions are 100 ml/min.**

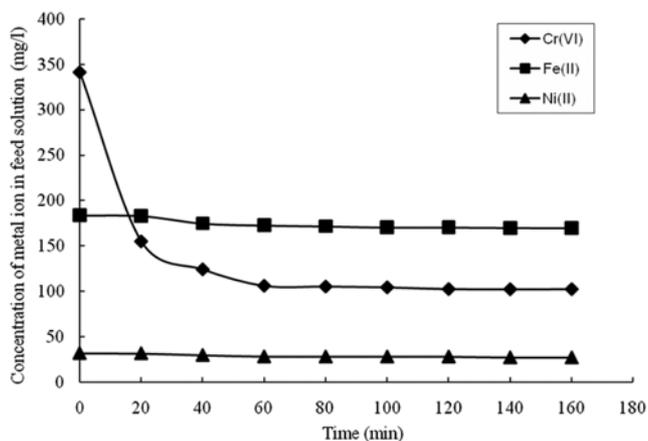


Fig. 7. Concentration of metal ions in the spent pickling solution with time by 0.11 M Aliquat 336, 0.5 M NaCl at pH 7 and flow rates of feed and stripping solutions of 100 ml/min.

lution was NaOH solution instead of NaCl solution.

## 2. The Selective Extraction of Cr(VI) Ions by Aliquat 336

From the results mentioned above, Aliquat 336 was selected. The selective extraction of Cr(VI) ions from spent pickling solution via the HFSLM by using Aliquat 336 as the extractant is shown in Fig. 7. It can be clearly noticed that the concentration of Cr(VI) in the feed solution was abruptly reduced from the initial concentration of 342.2 mg/L to 102.2 mg/L, while no change in Fe(II) and Ni(II) concentrations could be observed. Aliquat 336 had a higher selectivity to extract Cr(VI) from feed solution than Fe(II) and Ni(II). This implies that the coexisting contamination of Fe(II) and Ni(II) ions in spent pickling solution had no significant effect on Cr(VI) extraction by Aliquat 336, which is a basic extractant. In fact, a basic extractant can extract only anion forms of Cr(VI) and is not suitable for cation forms of Fe(II) and Ni(II) contained in feed solution. In addition, the separation factors (SF) of Cr(VI) to Fe(II), and Cr(VI) to Ni(II) were calculated by Eq. (7), accounting for 14.53 and 7.07, respectively. Table 3 compares the percentages of Cr(VI) extraction by Aliquat 336 from previous works [10,14,25] and this work of the spent pickling solution.

The percentage of extraction in this work is lower than in our previous works due to the spent pickling solution containing  $\text{SO}_4^{2-}$  anions which competed with  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions for complex-

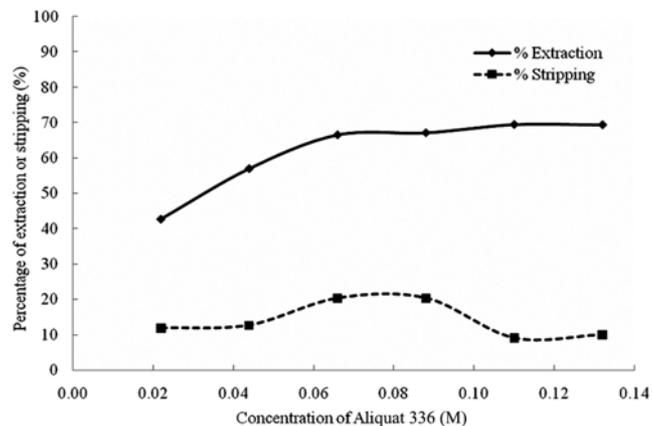


Fig. 8. Plot of extraction and stripping percents by 5-cycle operation against Aliquat 336 concentration: feed solution is the spent pickling solution, stripping solution is NaCl at pH 7 and concentration of 0.5 M, flow rates of feed and stripping solutions are 100 ml/min.

ation in membrane phase with Aliquat 336, which contained a basic nitrogen atom and favored the anionic species. This phenomenon agrees well with the results obtained by Ho et al. using SLM to extract Cr(VI) from synthetic wastewaters containing  $\text{SO}_4^{2-}$  [12]. In case of Guell et al., they used a larger (about double size) HFSLM compared with this work.

## 3. Effect of the Concentration of Aliquat 336

Fig. 8 shows the percentages of extraction and stripping of Cr(VI). As illustrated in the figure, the percentage of extraction increased suddenly when the concentration of Aliquat 336 increased. The percentage of extraction reached the highest value of 70% at a concentration of Aliquat 336 about 0.11 M. It can be explained that the higher the Aliquat 336 concentration was, the more Cr(VI) ions were reacted and converted to complex species in the membrane phase as stated in Eqs. (1) and (2). However, at the concentration higher than 0.11 M, the percentage of extraction was almost constant due to an increase in membrane viscosity, according to the molecular kinetic interpretation by Nernst [6]. The percentage of stripping slightly increased and reached a maximum value at 0.088 M Aliquat 336.

## 4. Effects of NaCl and NaOH as a Stripping Agent

Different stripping solutions of NaCl and NaOH affected the per-

Table 3. Comparison of Cr(VI) removal from different feed solutions by Aliquat 336 via HFSLM

| Year                       | Inlet feed solution (ppm) |  | Outlet feed solution (ppm) |  | Cr(VI) removal (%) |
|----------------------------|---------------------------|--|----------------------------|--|--------------------|
|                            | Cr(VI)                    | Other ions   | Cr(VI)                     | Other ions   |                    |
| 1998 by our group [10]     | 107.1                     | Synthetic wastewater   | 4.1                        | -  | 96                 |
| 2004 by our group [14]     | 100                       | Synthetic wastewater   | 8.3                        | Zn(II) 100<br>Cu(II) 100   | 92                 |
| 2008 by Guell, et al. [25] | 0.12<br>0.15<br>0.0132    | Electroplating rinse water<br>Spiked river water<br>Spiked tap water | 0.0132<br>0.0301<br>0.0029 | Electroplating rinse water<br>Spiked river water<br>Spiked tap water | 89.6               |
| This work                  | 342.2                     | Ni(II) 31.8<br>Fe(II) 183.7  | 102.2                      | Ni(II) 27.0<br>Fe(II) 169.6  | 70                 |

Note:  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  formed cations in feed solution

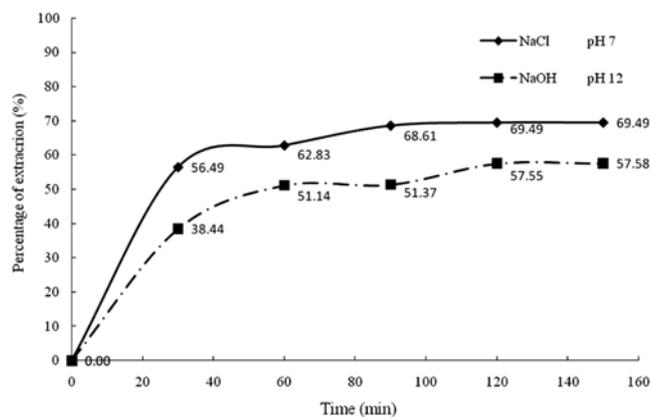


Fig. 9. Plot of percentage of extraction of Cr(VI) from the spent pickling solution by 0.11 M Aliquat 336 against time: stripping solution is NaCl or NaOH solutions at the concentration of 0.5 M, flow rates of feed and stripping solutions are 100 ml/min.

centage of extraction of Cr(VI) from the spent pickling solution, as shown in Fig. 9. The pH used for NaCl was 7 and 12 for NaOH. From the experiment, sodium chloride solution showed better extraction results but very low stripping efficiency. Sodium hydroxide solution achieved the opposite results. At 150 mins, sodium chloride and sodium hydroxide solutions gave percentages of extraction of about 70% and 58%, respectively, and percentages of stripping of about 9% and 50%. The extraction performance of NaCl was superior to that of NaOH because  $(R_4N)OH$  species which were formed in membrane phase could not react as an extractant with  $HCrO_4^-$  and  $Cr_2O_7^{2-}$  ions in the spent pickling solution again, while  $(R_4N)Cl$  could, as illustrated in Eqs. (3) and (4).

### 5. Effect of the pH of NaCl Solution

The pH of NaCl solution, the selected stripping solution, was examined from 9-12 and adjusted by adding NaOH solution. As illustrated in Fig. 10, the pH of NaCl solution had an effect on the percentage of Cr(VI) stripping; about 30% was obtained at the pH of 11. Due to NaOH solution being superb in stripping, by adding NaOH solution the reactions move forward (Eqs. (9) and (10)). Therefore, the percentage of stripping increased. Nevertheless, above pH 11

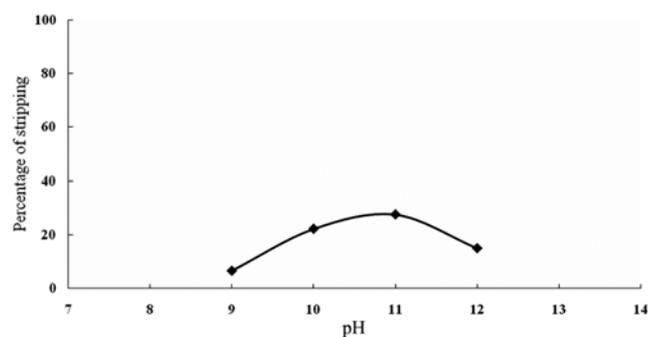


Fig. 10. Percentage of stripping of Cr(VI) from the spent pickling solution by one-through operation using 0.5 M NaCl as the stripping solution at different pH: extractant is 0.11 M Aliquat 336, flow rates of feed and stripping solutions are 100 ml/min.

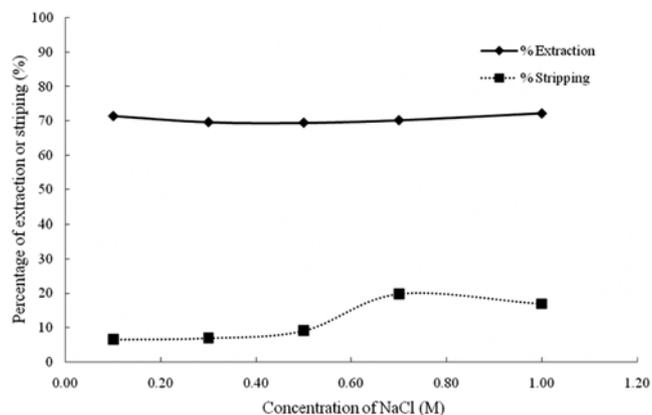
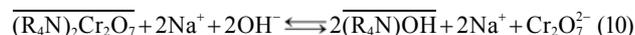
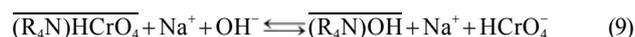


Fig. 11. Percentages of extraction and stripping of Cr(VI) by 5-cycle operation against different NaCl concentrations at pH 7, feed solution is the spent pickling solution, extractant is 0.11 M Aliquat 336, flow rates of feed and stripping solutions are 100 ml/min.

the percentage of stripping decreased due to the excess amounts of  $(R_4N)OH$  to drive the reverse reaction of the stripping.



From Fig. 10, although at the pH of NaCl of 11, high stripping of Cr(VI) was achieved but only 52% extraction. Thus, in this work, the suitable pH of NaCl solution should be at 7 because the percentage of extraction was 70% as seen in Fig. 9.

### 6. Effect of Concentration NaCl Solution

As shown in Fig. 11, the concentration of NaCl solution had no influence on the percentage of extraction. However, the percentage of stripping increased a little at 0.7 M of NaCl. This can be explained by Le Chatelier's principle. The higher concentration of the stripping solution caused more complex species  $(R_4N)HCrO_4$  and  $(R_4N)_2$

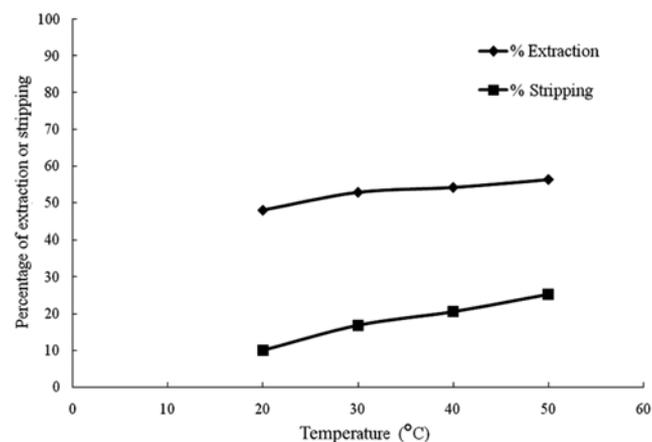
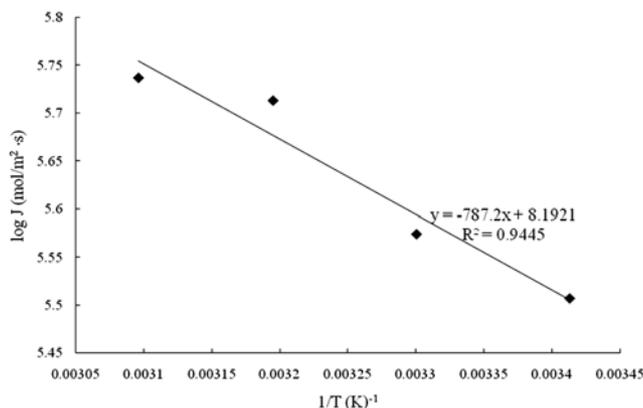


Fig. 12. Percentages of extraction and stripping of Cr(VI) by one-through operation at different operating temperatures: feed solution is the spent pickling solution, extractant is 0.11 M Aliquat 336, stripping solution is NaCl at pH 7 and concentration of 0.5 M, flow rates of feed and stripping solutions are 100 ml/min.



**Fig. 13. Plot of Cr(VI) flux against 1/T: feed solution is the spent pickling solution, extractant is 0.11 M Aliquat 336, stripping solution is NaCl at pH 7 and concentration of 0.5 M, flow rates of feed and stripping solutions are 100 ml/min.**

$\text{Cr}_2\text{O}_7$  in the membrane phase to be able react with  $\text{Cl}^-$  ions, yielding the  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions in the stripping solution (Eqs. (3) and (4)).

### 7. Effect of the Operating Temperature

The effect of temperature on the transport of Cr(VI) ions through HFSLM is shown in Fig. 12. The results are consistent with the kinetic theory that the Cr(VI) ions in feed solution as well as in stripping solution moved faster with higher temperature [9], resulting in high percentages of extraction and stripping. The result of this work was in accordance with the previous works which extracted Cr(VI) ions using Aliquat 336 at a temperature of 20-50 °C [9,19]. However, it must be noted that polypropylene fibers can withstand a temperature higher than 40 °C but not for long operation [30].

In addition, the diffusion energy was studied as follows [9]:

$$\log J = \frac{-E}{2.303RT} + B \quad (11)$$

where E=Diffusion energy (kJ/mol)

T=Absolute temperature (K)

B=Constant

R=Gas constant

From the plot of Cr(VI) flux in Fig. 13, the diffusion energy in this work of 15.14 kJ/mol could be obtained from the slope of the graph. According to the previous study by Chaudry et al. [9], the diffusion energy of Cr(VI) extraction from wastewater by TOA was 30.64 kJ/mol. These numbers show that Cr(VI) ions can diffuse in Aliquat 336 with lower energy than TOA. In short, Aliquat 336 is more favorable for extracting Cr(VI) ions than TOA.

### CONCLUSIONS

The hollow fiber supported liquid membrane is applicable for the extraction of Cr(VI) ions from the spent pickling solution. Aliquat 336 is a selective extractant in this case. The coexisting contamination of Fe(II) and Ni(II) ions in the spent pickling solution had no significant effect on Cr(VI) extraction. It was found that the percentage of extraction was highly dependent on the concentra-

tion of Aliquat 336. The extraction performance of NaCl solution was superior to that of NaOH solution. The concentration of NaCl stripping solution had no significant effect on the percentage of extraction. The suitable pH of NaCl stripping solution was likely at 7 yielding the highest Cr(VI) extraction. The percentages of extraction and stripping were increased with the operating temperature. The percentages of extraction and stripping of 70% and 20% were obtained at 0.11 M Aliquat 336, 0.5 M NaCl solution at pH 7 and the operating temperature of 50 °C.

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### NOMENCLATURE

A : membrane surface area [m<sup>2</sup>]

B : constant

$C_{Cr,feed(in)}$  : concentration of Cr(VI) in inlet feed solution [ppm]

$C_{Cr,feed(out)}$  : concentration of Cr(VI) in outlet feed solution [ppm]

$C_{Cr,stripping(out)}$  : concentration of Cr(VI) in outlet stripping solution [ppm]

E : activation energy [kJ/mol]

J : Cr(VI) flux in the extraction [mol/m<sup>2</sup>·s]

K : overall mass transfer coefficient [cm/s]

$Q_f$  : volumetric flow rate of feed solution [mL/min]

T : absolute temperature [K]

$(R_4N)Cl$  : complex specie from extractant reacted with NaCl solution, Aliquat 336 extractant in membrane phase

$(R_4N)OH$  : complex specie from extractant reacted with NaOH solution

$(R_4N)HCrO_4$  : complex specie of  $HCrO_4^-$  ion in membrane phase

$(R_4N)_2Cr_2O_7$  : complex specie of  $Cr_2O_7^{2-}$  in membrane phase

SF : separation factor

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