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Emulsion Liquid Membrane for the Recovery Chromium (VI) from Effluents Using Monosuccimide and Bisuccimide as Surfactant

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ABSTRACT

An emulsion liquid membrane (ELM) process is being developed for application to many industrial waste treatment problems. Using the ELM technique to remove chromium (VI) from electroplating effluent with the objective of reducing levels to below allowable discharge limits was investigated. In this work, tertiary amine N7301 was chosen as a carrier. In establishing a mental recovery process using ELM, the choice of a suitable surfactant is a key factor. Monosuccimide L113A, bissuccimide L113B, and Span 80—three surfactants—were examined. The emulsion made of L113A or L113B had a good efficiency in removal of chromium (VI) from electroplating effluent and were stable, which could still attainted a reasonable result after 60 days of being made.

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The electroplating effluents were treated with the emulsion made of L113A or L113B. A total of 184 mg Cr/L in the effluent decreased to 0.35 mg Cr/L in one run, and 673 mg Cr/L reduced to 0.25 mg Cr/L by using a two-stage process. The concentration of chromium (VI) in internal phase could reached 8 g/L, which could be reused directly.

Key Words: Emulsion liquid membrane; Chromium; Effluent; Monosuccimide 113A; Bissuccimide L113B; Span80; Tertiary amine N7301.

INTRODUCTION

Chromium (VI) has been widely used in industrial applications such as electroplating, metal-finishing, steel making, leather tanning, and corrosion inhibition. It is highly toxic and must be removed from wastewater before it is discharged into the environment.[1,2] Removal of chromate from water can be achieved using reverse osmosis, anionic-exchange resins, or precipitation techniques that are costly and produce additional sludge, which motivated interest in other processes. One such alternative for the treatment of Cr (VI) and other metals in wastewater is the use of liquid membrane.[3]

Since the invention of surfactant-stabilized liquid membrane by Li in 1968,[4] the separation of technique using liquid membrane has been noted as an advanced technique for separating and concentrating metals. During the past 20 years, several pilot plants for the recovery of zinc,[5,6] copper,[7] uranium,[8] and cadmium[6,9] have demonstrated the technical feasibility of this process. Diffusion-limited transport of molecules and ions across liquid membrane represents a powerful tool that exceeds most conventional separation techniques because it combines extraction, scrubbing, and regeneration into a single step.[10] The addition of nonvolatile complex agent to a liquid membrane enhances permeability of solute by several orders of magnitude.[11,12] Liquid membrane possesses such characteristics as expediency of operation, efficiency of energy, lack of side reactions, high functional capacity, high selectivity, and no repollution of the environment.

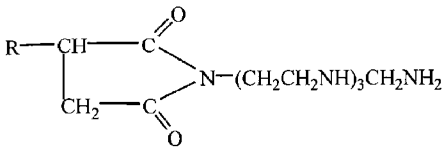
Emulsion liquid membrane (ELM), also called liquid surfactant membrane was the earliest and most popular liquid membrane process.[4] The advantage of this technology is that higher mass transfer rates can be obtained even at low feed concentrations because of larger mass transfer area ($10^6\ m^2/m^3$) within the emulsion drops. Several reviews have been reported.[10,13–16]

In this work, tertiary amine N7301 (C_8—C_{10}, 2.40 mol/L) was chosen as a carrier, which was synthesized by primary alcohol (C_8—C_{10}). Monosuccimide

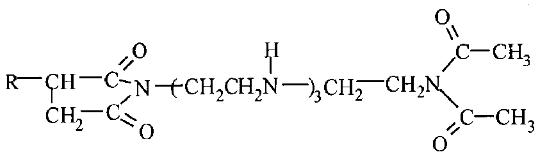
L113A, bissuccimide L113B, and Span80—three surfactants—were investigated. Their structures were shown in Fig. 1.

The separation condition was examined by the method of orthogonal experiment. The effluent of electroplating was treated with this process under the optimum operating conditions.

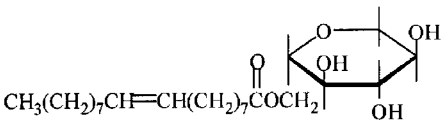
The mechanism for chromium (VI) transport from external phase across the liquid membrane to the internal phase is show in Fig. 2. In these experiments the membrane phase forms a barrier to bulk flow but allows transfer of chromium (VI) and hydrogen ions between an external acidic solution containing chromium and the internal basic solution. The reaction taking place at the interface I follows the mechanism of the complex reaction of organic base (tertiary amine N7301) and inorganic acid. The extraction of chromium (VI) according to Eq. (1) takes place in sulfuric acid solutions of low concentration. In a more concentrated H_2SO_4 solution, the participation



L113A (R= Polyisobutylene, Degree polymerization =20, Molecular weight = 1000)



L113B (R= Polyisobutylene, Degree polymerization <20, Molecular weight = 730-790)



Span80 (Molecular weight = 428)

Figure 1. Molecular structure of surfactants.

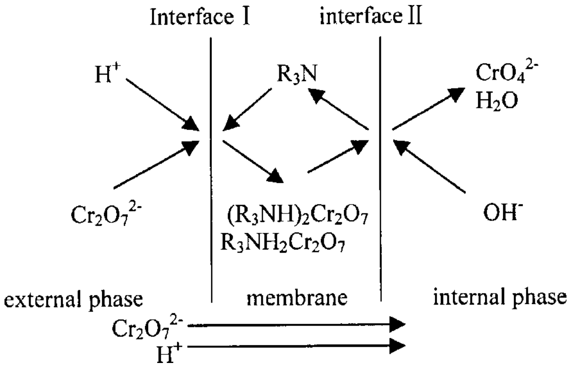


Figure 2. Transport of $Cr_2O_7^{2-}$ and H^+ through the emulsion liquid membrane.

of the reaction of Eq. (2) is considerable. Each $Cr_2O_7^{2-}$ transport from external phase to internal phase accompany by 2 H^+ transport from external phase to internal phase.

The extracting reaction at interface I is:

$$[2R_3N]_{org} + [2H^+ + Cr_2O_7^{2-}]_{feed} \rightleftharpoons [(R_3NH)_2Cr_2O_7]_{org} \tag{1}$$

$$[R_3N]_{org} + [H^+ + HCr_2O_7^{-}]_{feed} \rightleftharpoons [R_3NH_2Cr_2O_7]_{org} \tag{2}$$

The complex $(R_3NH)_2Cr_2O_7$ and $R_3NH_2Cr_2O_7$ diffuse through the organic membrane and reacts with OH^- in the internal phase at interface II releasing the chromate ion into the internal phase and the tertiary amine carrier which diffuse back according to Eq. (3) and Eq. (4).

The stripping reaction at interface II:

$$\begin{aligned}&[(R_3NH)_2Cr_2O_7]_{org} + [4Na^+ + 4OH^-]_{strip}\\ &\rightleftharpoons [2R_3N]_{org} + [4Na^+ + 2CrO_4^{2-} + 3H_2O]_{strip}\end{aligned} \tag{3}$$

$$\begin{aligned}&[R_3NH_2Cr_2O_7]_{org} + [4Na^+ + 4OH^-]_{strip}\\ &\rightleftharpoons [R_3N]_{org} + [4Na^+ + 2CrO_4^{2-} + 3H_2O]_{strip}\end{aligned} \tag{4}$$

The result is a flux of hydrogen ions and chromium (VI) ions from the external phase across the membrane to the internal phase. The difference in hydrogen in concentration between the internal and external phase, as well as the concentration of OH^- in internal mostly influence the transport of chromium (VI).

EXPERIMENTAL

Instruments and Reagents

We used the following instruments: homogenizer (0–20000 rpm, Sifang Electrify Instument Plant of Railway Ministry, Tianjin); high-voltage electrostatic emulsion breaker (1–10 kv, North East Teacher's College, Changchun); JJ-2 electrical agitator (Jintan Medical Instrument Plant, Jiangsu); Hitachi 220 ultraviolet–visible spectrophotometer (Japan); surfactant monosuccimide L113A and bissuccimide L113B were bought from the Lanzhou Oil Refining Plant; Span80 was manufactured in the Shanghai Dazhong Medical Plant; extractant tertiary amine N7301 (C_8—C_{10}) was synthesized by primary alcohol (C_8—C_{10}) (the Fifth Nucleus Industrial Ministry of Science Academy of China); civilian kerosene was bought in market; and electroplating effluent was taken from Tangshan Bicycle Plant. All solutions were prepared from analytical reagent grade chemicals and distilled water.

Extraction, Stripping, and Analysis Procedure

Emulsion was prepared in the following steps: A solution of the NaOH (80–100 mL) was added by burette to a stirred mixture (in the same volume of internal phase) of surfactant, extractant N7301, and solvent kerosene in a 0.5 L pyramine kettle, and was stirred at 6000 rpm simultaneously at ambient temperatures. All the internal phase was added completely in 2.5 min. The total stirring time was 5 min.

The resulting liquid membrane emulsion was dispersed in external phase. The mixing rate was kept constant at 150 rpm throughout the run. After extraction, the mixture was separated by separatary funnel. The aqueous solution was analyzed by spectrophotometry. A total of 25 mL of this solution in a comparison tube and 1 mL H_2SO_4, 0.5 mL H_3PO_4, and 2 mL color reagent (2% diphenylcarbazide in solvent of acetone: water = 1:1) were added. After 15 min, the absorbance was measured at 540 nm with the reference of distilled water.

RESULTS AND DISCUSSION

Orthogonal Design Experiment

On the basis of many tests, we adopted the method of orthogonal design experiment to examine the optimum conditions for each system. Four independent factors were selected as follows:

1. The amount of surfactant in membrane phase (%(v/v));
2. The amount of carrier in membrane phase (%(v/v));
3. The concentration of sulfuric acid in external phase (mol/L);
4. The concentration of sodium hydrate in internal phase (mol/L).

The level for each factor is shown in Table 1.

Because we have four three-level factors, the orthogonal experiment $L_n(t^m)$ ($n = \text{trial}$, $t = \text{level}$, $m = \text{factor}$) was designed as $L_9(3^4)$. The corresponding level combinations are shown in Table 2.

For each level combination, the experiments were run at 100 mg Cr/L and 200 mg Cr/L in the external phase, respectively; the results are shown in Tables 3 and 4. From Tables 3 and 4, the response results are shown in Tables 5 and 6, respectively.

The values in Tables 5 and 6 were average values of total three values of each level of different factor in Tables 3 and 4. The symbol R was the differential of the maximum and the minimum value of the three levels of each factor. The factor with the biggest R affected the results most. The results in Tables 5 and 6 demonstrated that the acidity in external phase affected the results most. When the acidity in external phase is 0.01 mol/L H_2SO_4, the efficiency of removal of chromium (VI) is the worst, whereas, when the acidity is ≥ 0.1 mol/L H_2SO_4, reasonable results were obtained. That was because H^+ was the driving force of

Table 1. The levels for each factor in experiment.

	Factor			
Level	A	B	C	D
1	3	3	0.1	0.2
2	4	4	0.01	0.8
3	5	5	0.2	0.5

Table 2. The $L_9(3^4)$ and the level combinations.

	Factor				
Trial no.	A	B	C	D	Level combination
1	1	1	3	2	$A_1B_1C_3D_2$
2	2	1	1	1	$A_2B_1C_1D_1$
3	3	1	2	3	$A_3B_1C_2D_3$
4	1	2	2	1	$A_1B_2C_2D_1$
5	2	2	3	3	$A_2B_2C_3D_3$
6	3	2	1	2	$A_3B_2C_1D_2$
7	1	3	1	3	$A_1B_3C_1D_3$
8	2	3	2	2	$A_2B_3C_2D_2$
9	3	3	3	1	$A_3B_3C_3D_1$

the chromium (VI) transfer from the external phase into the internal phase through to the membrane phase (see Eq. 1 and Eq. 2); therefore, a high enough concentration of H^+ is needed.

The results of the three systems showed the amount of surfactant and N7301 affected the results little. When the concentration of NaOH in internal phase reached 0.8 mol/L, the efficiency of removal of chromium (VI) decreased and the phenomenon of breakage of emulsion was observed in the course of separation. The extensive basicity caused the deterioration of the membrane (large quantities of OH^- will effect with surfactant and carrier). On the other hand, the extensive basicity made

Table 3. The results of orthogonal experiment (100 mg/L Cr (VI)).

	Factor				Remains of chromium (VI) (mg/L)		
Trial no.	A	B	C	D	L113A	L113B	Span80
1	1	1	3	2	0.30	0.32	1.23
2	2	1	1	1	0.28	0.23	0.89
3	3	1	2	3	1.88	2.29	7.39
4	1	2	2	1	1.73	1.78	7.86
5	2	2	3	3	0.14	0.20	0.67
6	3	2	1	2	0.32	0.46	0.58
7	1	3	1	3	0.25	0.23	1.03
8	2	3	2	2	2.10	2.50	9.58
9	3	3	3	1	0.24	0.56	0.68

Table 4. The results of orthogonal experiment (200 mg/L Cr (VI)).

	Factor				Remains of chromium (VI) (mg/L)		
Trial no.	A	B	C	D	L113A	L113B	Span80
1	1	1	3	2	0.60	0.77	9.82
2	2	1	1	1	0.66	0.66	6.74
3	3	1	2	3	5.75	6.34	41.31
4	1	2	2	1	5.28	6.68	46.62
5	2	2	3	3	0.69	0.62	7.78
6	3	2	1	2	0.57	0.85	6.02
7	1	3	1	3	0.83	0.63	8.26
8	2	3	2	2	6.25	6.81	54.22
9	3	3	3	1	0.54	0.98	6.23

the specific weight of internal phase much bigger than that of external phase, which would cause the leakage of internal phase that also deteriorated the emulsion. A total of 0.5 mol/L NaOH was enough to react with chromium (VI) and H^+.

In the liquid surfactant membranes process, the following capabilities are required of a suitable surfactant[15]:

Table 5. The response results of Table 3 (100 mg/L Cr (VI)).

		Factor				
System	Level	A	B	C	D	Optimal level combination
L113A	1	0.76	0.82	0.28	0.75	$A_1B_2C_3D_1$
	2	0.84	0.73	1.90	0.91	
	3	0.81	0.86	0.23	0.76	
	R	0.08	0.13	1.67	0.16	
L113B	1	0.78	0.95	0.31	0.86	$A_1B_2C_1D_1$
	2	0.98	0.81	2.19	1.09	
	3	1.10	1.10	0.36	0.91	
	R	0.32	0.29	1.88	0.23	
Span80	1	3.37	3.17	0.83	3.14	$A_3B_2C_1D_3$
	2	3.71	3.04	8.28	3.80	
	3	2.88	3.76	0.86	3.03	
	R	0.83	0.72	7.45	0.77	

Table 6. The response results of Table 3 (200 mg/L Cr (VI)).

		Factor				
System	Level	A	B	C	D	Optimal level combination
L113A	1	2.24	2.34	0.69	2.16	$A_1B_2C_3D_1$
	2	2.53	2.18	5.76	2.47	
	3	2.29	2.54	0.61	2.42	
	R	0.29	0.36	5.15	0.31	
L113B	1	2.69	2.59	0.71	2.77	$A_1B_1C_1D_3$
	2	2.70	2.66	6.61	2.81	
	3	2.72	2.81	0.79	2.53	
	R	0.03	0.22	5.90	0.28	
Span80	1	21.57	19.29	7.01	19.86	$A_3B_1C_1D_3$
	2	22.91	20.14	47.38	23.35	
	3	17.85	22.90	7.94	19.12	
	R	5.06	3.61	40.37	4.23	

- lowering of the break-up rate of the emulsion globules in a mixer;
- lowering of the swelling rate of the emulsion globules resulting from osmotic pressure;
- enhancement of the extraction rate of metal by ELM, keeping high selectivity for the metal to be separated;
- ease of demulsification of the emulsion prepared by an electrical coalescer; and
- chemical stability and safety of surfactant, which must also be easily and cheaply synthesized.

We examined the emulsion formed by surfactants Span80, L113A, and L113B. The system formed by L113A or L113B had a better efficiency of removal of chromium (VI) than that of Span80. The external phase of the former two systems after separation are clear, with no sign of swelling of the emulsion. However, the external phase of the system formed by Span80 became a little cloudy, and the swelling of the emulsion was obvious (the volume of emulsion after separation was bigger than the initial volume of the emulsion). We further examined the stability of the emulsion in the following section.

From Tables 5 and 6, we saw the optimal level combination did not appear in $L_9(3^4)$, so a confirmation experiment needed to be run. The confirmation experiment results are shown in Table 7. The efficiency of

Table 7. Confirmation experiment results.

Chromium in external phase	100 mg/L Cr (VI)			200 mg/L Cr (VI)		
Surfactant	L113A	L113B	Span80	L113A	L113B	Span80
Optimal level combination	$A_1B_2C_3D_3$	$A_1B_2C_1D_1$	$A_3B_2C_1D_3$	$A_1B_2C_3D_1$	$A_1B_1C_1D_3$	$A_3B_1C_1D_3$
Remained chromium (mg/L)	0.12	0.15	0.53	0.51	0.55	6.00

removal chromium at the optimal level combination was higher than that of $L_9(3^4)$ by comparing the results in Tables 3, 4, and 7.

Influence of Contact Time and Ratio of Emulsion to External Phase

The contact time of each system was examined at different concentration of chromium (VI). The results are shown in Figs. 3 through 5. Because it was indicated that the transfer rate of chromium (VI) in the systems formed by Span80 was faster than the other two systems formed by L113A and L113B, the concentration of chromium (VI) in external phase reached the lowest value in 3 min for Span80 systems. But as the separation time increased, the concentration of chromium (VI) in external phase increased, which showed the breakage of emulsion was serious. The concentration of chromium (VI) in the external phase of L113A or L113B systems reached the lowest in 5 min, and was unchanged until 10 min, and a high efficiency of removal of concentration of chromium (VI) was attained.

A different ratio of emulsion to external phase (R_{ow}) was examined for each system (Table 8). For the systems made of L113A or L113B, 1:10 was reasonable for the concentration of chromium (VI) below 100 mg/L, and 1:5 was better for higher concentration of chromium (VI). For Span80, 1:5 was acceptable.

Evaluation of the Stability of Emulsion

The separation of 200 mg Cr/L was carried out in a different time after the emulsion was made (Table 9). After 8 hours, the emulsion made of Span80 was

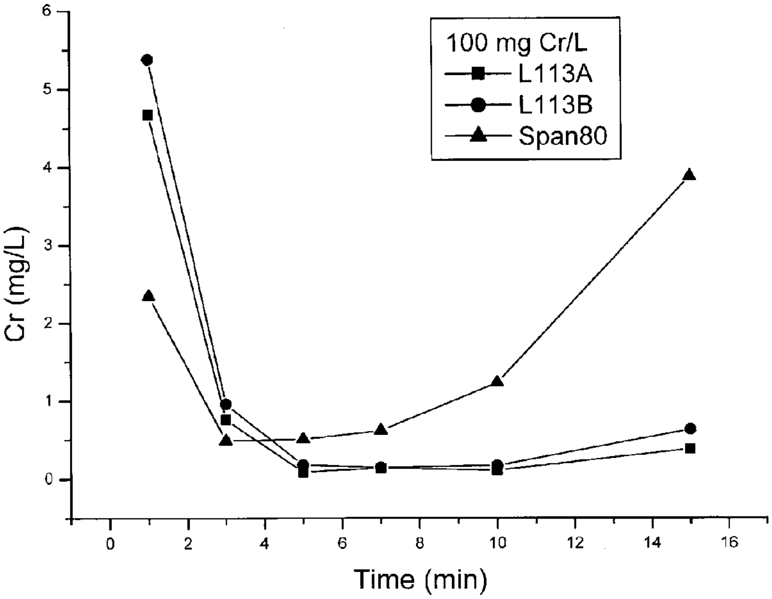


Figure 3. Influence of contact time for 100 mg/L Cr (VI) in external phase.

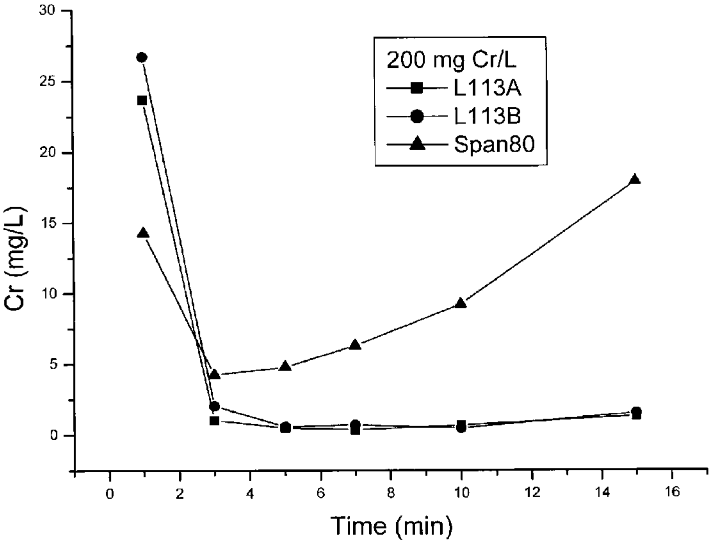


Figure 4. Influence of contact time for 200 mg/L Cr (VI) in external phase.

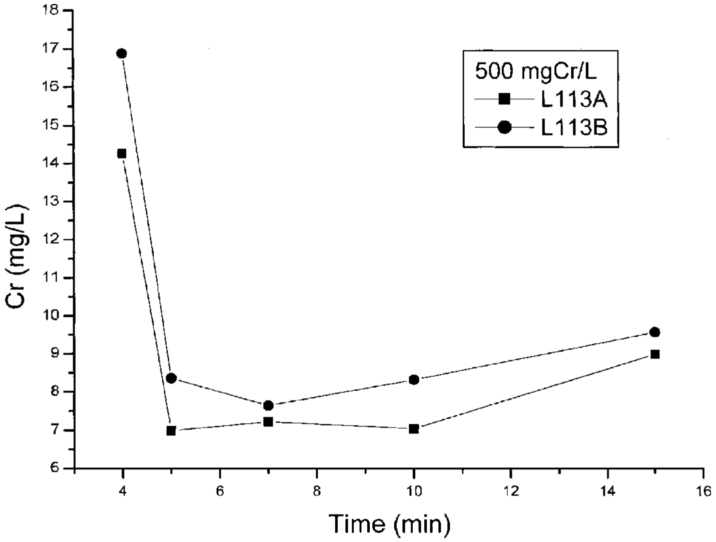


Figure 5. Influence of contact time for 500 mg/L Cr (VI) in external phase.

observed to form two layers of oil and water, and could not be used in separation. A thin layer of oil on the surface of the emulsion made of L113A and L113B appeared 10 hours after it was made, but mixing it uniformly by shaking it slightly could also attain reasonable results after 60 days. This result further confirmed that the emulsion made of L113A or L113B is much better than that of Span80, either in efficiency of removal of chromium (VI) or in stability.

The results in Table 9 could be explained by the molecular structure of these three surfactants (see Fig. 1). The ratio of oxygen to the whole molecular of Span80 is higher than that of L113A and L113B (the ratio of oxygen and nitrogen to the whole molecular of Span80, L113A, and L113B is 22.4%, 10.2%, and 17.0–18.4%, respectively), especially the three OH^- contained in Span80. In addition, the electronegativity of oxygen is bigger than that of

Table 8. Influence of different ratio of emulsion to external phase (200 mg/L Cr (VI)).

	Span80			L1113A			L113B		
R_{ow}	1:5	1:10	1:15	1:5	1:10	1:15	1:5	1:10	1:15
Cr (mg/L)	0.52	1.83	5.36	0.33	0.85	2.94	0.39	1.05	2.88

Table 9. Separating results at different time of the emulsion made (Cr (VI) [mg/L]).

Time (days)	0	1	5	10	15	23	30	60
L113A	0.50	0.64	0.76	0.78	0.93	0.98	1.12	2.10
L113B	0.61	0.65	0.81	0.85	0.98	1.04	1.23	2.66
Span80	5.98							

nitrogen. All of these made Span80 more easily form hydrogen band with water, so the hydrophilic property was increased, thus resulting in the swelling and eventual leakage of the strip phase from the primary emulsion.

Optimal Experimental Conditions

The sum of the optimal operating experimental condition is reported in Table 10. Emulsion made under the optimal operating experimental condition of 200 mg Cr/L being used to separate solution containing 500 mg Cr/L twice. For L113A and L113B systems, after the second separation, the external phase was still clear, and the concentration of chromium in internal phase was 8.6 mg/L and 8.1 mg/L, respectively. We know from the transport mechanism that two molecular H^+ in external phase and two molecular OH^- in internal phase were needed to transport one molecular chromium (VI). If Roi = 1:1 and Row = 1:5, 8 g Cr/L in internal phase will consume about 0.3 mol OH^-/L in the internal and 0.015 mol H^+/L in the external phase, So 0.1 mol/L H^+ in the external phase and 0.5 mol/L OH^- in the internal phase were enough for chromium transport.

Treatment of Electroplating Effluent

The electroplating effluent taken from the Tanshan Bicycle Plant was treated with the emulsion made of L113A or L113B. A total of 184 mg Cr/L in the effluent decreased to 0.35 mg Cr/L in one run, and 673 mg Cr/L reduced to 0.25 mg Cr/L by using a two-stage process.

Table 10. Optimal experimental conditions for the extraction of chromium.

	Span80		L113A		L113B	
Initial chromium concentration (mg/L)	100	200	100	200	100	200
Initial NaOH concentration (mol/L)	0.5	0.5	0.2	0.2	0.2	0.5
Initial H_2SO_4 concentration in the external phase (mol/L)	0.1	0.1	0.2	0.2	0.1	0.1
Ratio of membrane phase to internal phase Row (v/v)	1:1	1:1	1:1	1:1	1:1	1:1
Ratio of emulsion to external phase Row (v/v)	1:5	1:5	1:10	1:5	1:10	1:5
Complexing carrier N7301 (%(v/v))	4	3	4	4	4	3
Surfactant (% (v/v))	5	5	3	3	3	3
Solvent	Kerosene					
Emulsion time (min)	5					
Rotation per minute of emulsion (rpm)	6000					
Contact time (min)	7					
Rotation per minute of separation (rpm)	150					
Temperature	Ambient					

CONCLUSION

Tertiary amine N7301 as a carrier had a good efficiency in transfer of chromium (VI). A total of 0.5 mol/L NaOH was adopted as internal phase, which was enough to react with chromium (VI) and the accompanying H^+ at the interface of membrane and internal phase, and kept the emulsion stable enough. The emulsion formed by Span80, L113A, and L113B was systematically investigated. It was shown in the results that the emulsion made of L113A or L113B was good enough in removal of chromium (VI) and had good stability. A reasonable separation result could be attained after 60 days after the emulsion was made. The concentration of chromium (VI) in electroplating effluent could reduced from 184 mg/L to below 0.5 mg/L. The effluents with higher concentration of chromium (VI) could reach a reasonable result by using a two-stage ELM process. A total of 8 g Cr/L could be attained in an internal phase, which could be reused directly.

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