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Extraction of Chromium Ion (VI) Using Bulk Liquid Membrane

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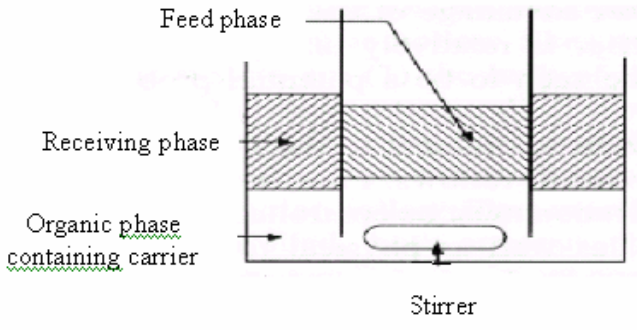
Abstract
Liquid membranes with impressive properties such as high selectivity and efficient consumption of energy in separation processes seem to be more suitable. Other advantages such as variety of configuration and carriers for different applications, simplicity of assembling and high rate of mass transfer are facilitated the implementation of these membranes. Chromium is one of contaminants that exist in waste water of various industries like steel, pigment and leather tanning. In this project separation of Cr (VI) ion by implementation of a bulk liquid membrane using alamine as carrier, kerosene as solvent, sodium hydroxide as stripping product phase, dodecanol for preventing from jellying of inorganic and organic phases have been investigated.Effective parameters on separation of Cr(VI)ion including feed phase pH, stripping phase molarity, mixer rotational rate in feed and stripping phase, volume percentage of carrier in organic phase, presence/absence of surfactant in organic phase have been studied. In the range of designed experimental, the optimum conditions as follow have been found: pH=2, Stripping phase molarity=3, mixer rotational rate in both inorganic phases = 100 rpm, volumetric amount of carrier = 1%, and presence of surfactant.

Keywords: Extraction, Liquid Membrane, Chromium, Alamine (336)

Introduction
Membrane separation is an area deserving special attention because of its great potential for low capital cost and energy efficiency. To date, however, few membrane processes other than reverse osmosis and hydrogen separation have demonstrated any industrial utility primarily because of problems of speed and selectivity in separation [1]

Bulk Liquid Membrane
This set up is useful only for laboratory expriments, and is setup as follows. Following Figure 1, a U tube cell is used, and some type of carrier, perhaps dissolved in CH_2CL_2, is placed in the bottom of the tube. That is the organic membrane phase.
Two aqueous phases are placed in the arms of the U-tube, floating on top of the organic membrane. With a magnetic Stirrer rotating at fairly slow speeds, in the range of 100 to 300 rpm, the transported amounts of materials are determined by the concentrations in the receiving phase. Stability is maintained so long as the stirrer is not spinning too quickly.



Experimental

For doing expriments we used glass cell which divided to 2 compartments by thin sheet of glass. Dimensions of cell were $(10\text{cm} \times 24\text{cm} \times 20\text{cm})$. Volumes of one section were 3 times greater than other section. In bottom of each section and 2cm upper then the bottom- two holes were arranged for sampling. Both holes sealed with plastic caps. Feed phase and stripping phase were pour in greater and little section respectively. Membrane phase was pour over foregoing both phases. Two pirex blades rotated by mixer with constant speed $(15\text{cm} \times 1\text{cm}\,\text{diameter})$. Each one of blades have two paddles. Potassium chromate & NaoH were pouring with determined concentration in grate and little section of cell respectively. Membrane phase was pour over two foregoing phases in two steps. First, Kerosene was added without carrier (for example 350 ml), then 41 ml Kerosene + 5ml Alcohol + 4cc Alamine was added to membrane phase. To avoid, of vaporization of membrane phase top of the cell was covered with foil. Sampling was started step by step up to 24 hours. (1 day).At the beginning of expriments, the color of feed phase was yellow. Membrane phase and stripping phase were color less. Gradually the color of feed phase approached to pale yellow and simultaneously the color of membrane and stripping phases approached to very pale yellow (colorless) and the color of stripping phase approached to dark yellow. This variation in the color of feed and stripping phases showed the process of extraction of chromium ion from feed phase to stripping phase. During the expriments, the pH of feed phase was controlled and sulfuric acid was added to feed phase for maintaining the pH.

Parameters

Parameters were investigated as follow:
1) PH of feed phase.
2) Percentage of carrier in membrane phase.
3) Presence / absence of Dodecanol in membrane phase
4) Molarity of stripping phase
5) Velocity of mixer in feed phase
6) Velocity of mixer in stripping phase

Where pH was investigated in 3 states like: 2/4/6, Presence of dodecanol in membrane phase was investigated in 3 states like: 0.5%, 1%, 2%, Molarity of stripping phase was investigated in 3 states like :1 / 2 / 3,velocity of mixer in both liquid phases was investigated in 3 states like :80rpm ,100rpm& 120rpm.

Description of model experiment
Feed phase:

Solving 1.94 gr potassium chromate (K_2Cro_4) in 2 lit DM water, (0.005 mol). Adding 5 ml sulfuric acid for approaching to solution with pH=2. Diluting 100 ml of foregoing solution to 1 lit with DM water. 750 ml of final solution was our feed phase.

Stripping phase:

Solving 30 gr NaOH on 250 ml DM water.

Error Analysis

For calculation of ions concentration error formula No 1 was used:

NO1) $\overline{X} \pm \frac{ts}{\sqrt{N}}$ where:

$\overline{X}$: Average of 3 amounts of ion concentration obtained from Calibration curve.
T= 95% safety limit with constant amount = 4.3
N= obtained samples
S= Standard deviation where

$$S = \sqrt{\frac{\sum(\overline{x} - x_i)^2}{N-1}}$$

in standard deviation formula we have $\overline{x}$ & x_i:

$\overline{x}$ and x_i are average of 3 amounts of ion Concentration and ion concentration in each sampling respectively.

Governing equations in transportation of chromium
A) Diffusion of chromium from bulk of feed to interface of feed phase and membrane phase:

$$N_{CrO_4^{2-}} = \frac{D_f}{d_{if}}\left(\left[CrO_4^{2-}\right]_f - \left[CrO_4^{2-}\right]_{if}\right)$$

B) Reaction on the interface of membrane phase & feed phase:

$$Cro_4^{-2}(\text{if}) + 2AlmoH_{(\text{of})} \leftrightarrow Alm_2Cro_4(\text{of}) + 2oH^-(\text{if}) \quad (2)$$

$$K = \frac{[Alm_2Cro_4]_{if}[OH^-]^2_{if}}{[AlmoH]_{of}[Cro_4^{-2}]_{if}} \quad (3)$$

and following reaction:

$$H^+ + OH^- \leftrightarrow H_2O \quad K = \frac{1}{K_w} = 10^{14} \quad (4)$$

C) Diffusion of product complex of up reaction from interface between feed phase and membrane phase to bulk of membrane:

$$N_{Alm_2Cro_4} = \frac{D_o}{\delta_{of}}\left([Alm_2Cro_4]_{of} - [Alm_2Cro_4]_o\right) \quad (5)$$

D) Diffusion of product complex of reaction reaction No (2) from bulk of membrane to interface of membrane and stripping phase:

$$N_{Alm_2}Cro_4 = \frac{Do}{Dos}\left([Alm_2Cro_4]_0 - [Alm_2Cro_4]os\right) (6)$$

E) Reaction in the interface of membrane and stripping phases:

$$Alm_2Cro_4(os) + 2OH^-(is) \leftrightarrow 2AlmOH(os) + Cro_4^{-2}(is) \quad (7)$$

$$K = \frac{[AlmOH]_{os}[Cro_4^{-2}]_{is}}{[Alm_2Cro_4]_{os}[OH^-]_{is}^2} \quad (8)$$

and following reaction:

$$H^+ + OH^- \leftrightarrow H_2O \quad K = \frac{1}{k_w} = 10^{14} (9)$$

F) Diffusion of chromate ion to bulk of stripping phase:

$$Ncro_4^{-2} = \frac{Ds}{Dis}\left([Cro_4^{-2}]_{is} - [Cro_4^{-2}]_s\right) \quad (10)$$

Diphenylcarbazide method

Diphenylcarbazide (*sym*- diphenylcarbazide, diphenylcarbohydrazide) reacts in acid medium with chromium (VI) ions to give a violet solution which is the basis of this sensitive method.

Many investigators have studied the reaction [8], offering rather divergent explanations of its mechanism. Pflaum and Howick [9], among others [12, 15, 16], have shown that the cationic chromium (III) and diphenylcarbazone fails to yield a violet color. In all probability, the reaction involves unhydrated chromium (III) ions formed during the oxidation of diphenylcarbazide to diphenylcarbazone.

This explanation is, however, incomplete since, when the colored reaction product is extracted into isoamyl alcohol or chloroform in the presence of perchlorate, the remaining colorless aqueous phase contains half of the chromium [10, 13]. When studing the reactions of diphenylcarbazide and diphenylcarbazone with various metal cations, Balt and van Dalen [18] found that diphenylcarbazide only forms metal chelates after its oxidation to diphenylcarbazone.

According to Allen [17],the molar absorptivity of the colored product of the chromium(VI) reaction with diphenylcarbazide is $4.17*10^4$ (specific absorptivity 0.80) at $l_{max} = 546\,nm$. The color intensity obtained in the reaction is affected by the quality of the diphenylcarbazide reagent used.

Results

Result of feed phase for effect of pH

(Molarity of stripping phase = 3, rotational speed of mixer in all phases = 100rpm. Volumetric percentage of carrier = %1, with presence of dodecanol in membrane phase)

Time (min)	*Concentration(ppm) pH=2*	*Concentration(ppm) pH=4*	*Concentration(ppm) pH=6*
1440	0.1 ± 0.0	0.3 ± 0.1	0.5 ± 0.2

Result of stripping phase for effect of pH

(Molarity of stripping phase = 3, rotational speed of mixer in all phases = 100rpm. volumetric percentage of carrier = %1, with presence of dodecanol in membrane phase)

Time (min)	*Concentration(ppm) pH=2*	*Concentration (ppm) pH=4*	*Concentration (ppm) pH=6*
1440	70.4 ± 0.2	66.4 ± 0.8	58.6 ± 0.6

Result of feed phase for effect of percentage of carrier in membrane phase

(Molarity of stripping phase = 3M, rotational speed of mixer in all phases = 100 rpm, pH=2, with presence of dodecanol in membrane phase)

Time (min)	*Concentration (ppm) % carrier* $\left(\frac{v}{v}\right)$*=0.5*	*Concentration (ppm) % carrier* $\left(\frac{v}{v}\right)$*=1*	*Concentration (ppm) % carrier* $\left(\frac{v}{v}\right)$*=2*
1440	5.6 ± 0.5	0.1 ± 0.0	0

Result of stripping phase for effect of percentage of carrier in membrane phase

(Molarity of stripping phase = 3M, rotational speed of mixer in all phases = 100 rpm, pH=2, with presence of dodecanol in membrane phase)

Time (min)	*Concentration (ppm) % carrier* $\left(\frac{v}{v}\right)$*=0.5*	*Concentration (ppm) % carrier* $\left(\frac{v}{v}\right)$*=1*	*Concentration (ppm) % carrier* $\left(\frac{v}{v}\right)$*=2*
1440	60.3 ± 0.4	70.4 ± 0.2	53.3 ± 0.5

Result of feed phase for effect of presence of dodecanol in membrane phase

(Molarity of stripping phase = 3M, rotational Speed of mixer in all phases =100rpm, pH=2, % Carrier $\left(\frac{v}{v}\right)$ =1)

Time (min)	*Concentration (ppm) with presence of dodecanol in membrane*	*Concentration with out presence of dodecanol in membrane phase*
1440	0.1 ± 0.0	6.4 ± 0.4

Result of stripping phase for effect of presence of dodecanol in membrane phase

(Molarity of stripping phase = 3M, rotational Speed of mixer in all phases =100rpm, pH=2, % Carrier $\left(\frac{v}{v}\right)$ =1)

Time (min)	*Concentration (ppm) with presence of dodecanol in membrane*	*Concentration(ppm) without presence of dodecanol in membrane phase*
1440	70.4 ± 0.2	52.6 ± 0.9

Result of feed phase for effect of velocity of mixer in stripping phase

(Molarity of stripping phase=3 , rotational speed of mixer in feed phase= 100rpm volumetric percentage of carrier=%1 with presence of dodecanol in membrane phase, pH=2)

Time(min)	*Concentration(ppm) velocity of mixer in stripping phase =80rpm*	*Concentration(ppm) velocity of mixer in stripping phase =100rpm*	*Concentration(ppm) velocity of mixer in stripping phase =120rpm*
1440	5.7 ± 0.5	0.1 ± 0.0	3.7 ± 0.4

Result of stripping phase for effect of velocity of mixer in stripping phase

(Molarity of stripping phase=3 , rotational speed of mixer in feed phase= 100rpm volumetric percentage of carrier=%1 with presence of dodecanol in membrane phase, pH=2)

Time(min)	*Concentration(ppm) velocity of mixer in stripping phase =80rpm*	*Concentration(ppm) velocity of mixer in stripping phase =100rpm*	*Concentration(ppm) velocity of mixer in stripping phase =120rpm*
1440	56.4 ± 0.9	70.4 ± 0.2	60.6 ± 0.9

Result of feed phase for effect of velocity of mixer in feed phase

(Molarity of stripping phase=3 , rotational speed of mixer in stripping phase=100 rpm, pH=2, volumetric percentage of carrier=%1 /with presence of dodecanol in membrane phase.)

Time(min)	*Concentration(ppm) velocity of mixer in stripping phase =80rpm*	*Concentration(ppm) velocity of mixer in stripping phase =100rpm*	*Concentration(ppm) velocity of mixer in stripping phase =120rpm*
1440	6.2 ± 0.4	0.1 ± 0.0	3.0 ± 0.4

Result of stripping phase for effect of velocity of mixer in feed phase

(Molarity of stripping phase=3 rotational speed of mixer in stripping phase=100rpm, pH=2, volumetric percentage of carrier=%1, with presence of dodecanol in membrane phase.)

Time(min)	*Concentration(ppm) velocity of mixer in feed phase =80rpm*	*Concentration(ppm) velocity of mixer in feed phase =100rpm*	*Concentration(ppm) velocity of mixer in feed phase =120rpm*
1440	54.7 ± 0.5	70.4 ± 0.2	57.1 ± 0.7

Result of feed phase for effect of molarity of stripping phase

(rotational speed of mixer in all phases= 100rpm, pH=2 / volumetric percentage of carrier=%1 /with presence of do decanol in membrane phase.)

Time(min)	*Concentration(ppm) 1M Solution*	*Concentration(ppm) 2M Solution*	*Concentration(ppm) 3M Solution*
1440	0.2 ± 0.7	6.2 ± 0.4	6.2 ± 0.4

Result of stripping phase for effect of molarity of stripping phase

(rotational speed of mixer in all phases= 100rpm, pH=2/ volumetric percentage of carrier=%1 /with presence of dodecanol in membrane phase.)

Time(min)	*Concentration(ppm) 1M Solution*	*Concentration(ppm) 2M Solution*	*Concentration(ppm) 3M Solution*
1440	56.5 ± 0.7	66.5 ± 0.6	70.4 ± 0.2

Chromium accumulation % in Membrane phase (C.A) = $= \frac{A-(B-C)}{A}$

A= Initial moles of chromium in feed phase
B= final moles of chromium in feed phase
C= final moles of chromium in stripping phase

Parameter	Amount	C.A
pH of feed phase	2	10.66
	4	14.44
	6	22.44
% Carrier(v/v)	0.5	4.44
	1.0	10.66
	2.0	33.33
Presence / absence of dodecanol in membrane phase	YES	10.66
	NO	8.88
Molarity of stripping phase	1	26.66
	2	14.00
	3	10.66
Velocity of mixer in feed phase	80	4.44
	100	10.66
	120	15.55
Velocity of mixer in stripping phase	80	15.55
	100	10.66
	120	20.88

Chromium extraction percentage for each parameter

Extraction%= C/A *100 where

A=Initial moles of chromium in feed phase
C=Final moles of chromium in stripping phase

parameter	amount	Extraction %
pH of feed phase	2	88.88
	4	74.44
	6	71.11
Velocity of mixer in feed phase	80	71.11
	100	88.88
	120	73.33
Velocity of mixer in stripping phase	80	64.44
	100	88.88
	120	77.77
Molarity of stripping phase	1	71.11
	2	84.44
	3	88.88
Presence / absence of dodecanol in membrane phase	YES	88.88
	NO	66.66
% Carrier(v/v)	0.5	75.55
	1.0	88.88
	2.0	66.66

Discussion

Effect of presence / absence of surfactant in membrane phase:
Presence of surfactant in membrane phase decreases surface tension between liquor and organic phases and because of this reason, mass transfer increases. Surfactant should be ineffective, has a high solubility in organic phase and has a polarity in one end. 5 ml dodecanol was used in experiments. Using high amounts of this material create jelling state in surface of liquor & organic phases. Also when high amounts of dodecanol were used, Alamine salts: surrounded by dodecanol and can't react immediately, there fore extraction decreases. As we see in fig No 1; After 24 hours in our experiment with presence of dodecanol, concentration of chromium in feed phase is 0.1 ppm and Concentration of chromium in the experiment without presence of dodecanol after 24 hours is 6.4 ppm. Also in fig No2: Concentration of chromium in stripping phase with presence of dodecanol is 70.4 ppm.

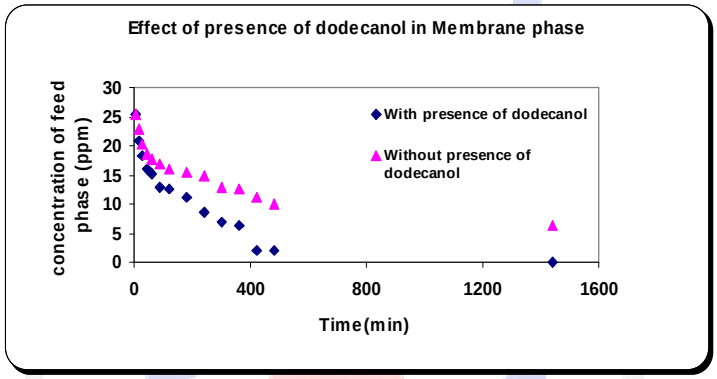


fig No 1

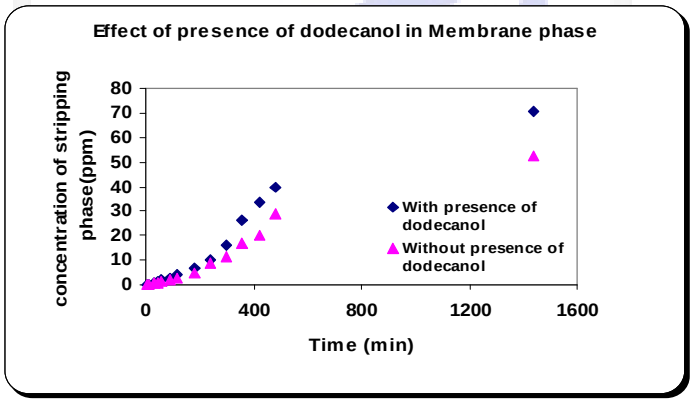


fig No 2

Effect of PH
Decreasing of pH in feed phase cause to neutralize OH^- in formula No 2 and reaction goes to right side: it increases speed of this formula. Therefore if pH was bounded on 2, membrane efficiency increases. If pH was decreased so much may be membrane and carrier was oxidized, because of oxidizing property of chromate.

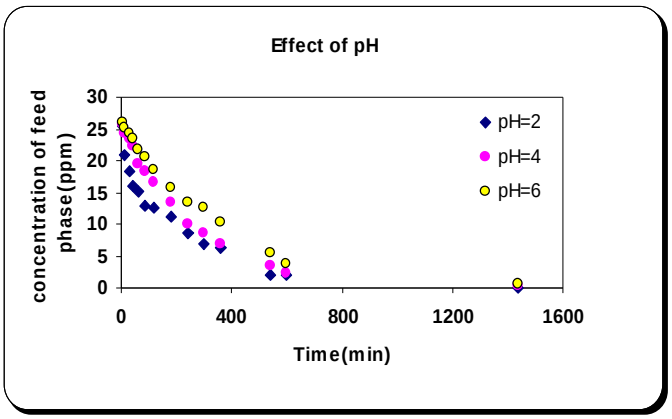


fig No 3

Effect of volumetric percentage of carrier

With increasing of % carrier in membrane phase, extraction increases and in definite concentration of carrier (1%) Maximum percentage of extraction was obtained. But after that, because of increasing in amount, in membrane phase and also increasing of carrier, extraction decreases. Then optimum amount of carrier should be defined. With increasing of % carrier in membrane phase, extraction was operated successfully but because of increasing of chromium in membrane phase, back extraction (extraction from organic phase to stripping phase) was operated slowly. As we considered % carrier was played important role in extraction process. Reaction No 2; is faster than reaction No 7; therefore amount of entering chromium to membrane phase is more than amount of balcony chromium from membrane phase. Since chromium decreases in feed phase in one an exact time speed of entering & balconing chromium equal to each other and amount of chromium in membrane phase goes maximum. Then optimum carrier percentage is so important in extraction processes, and in our expriments it was 1% (V/V).

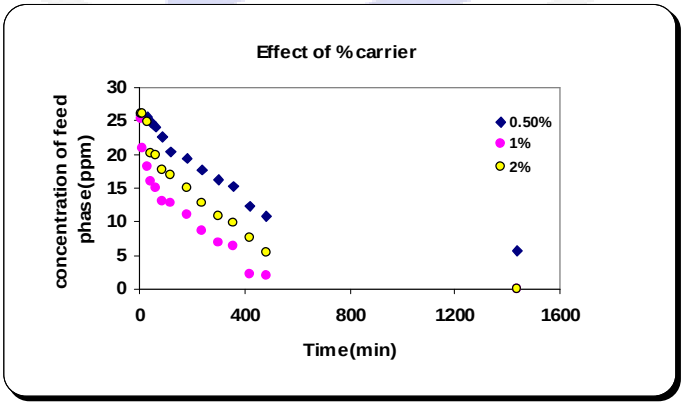


fig No 4

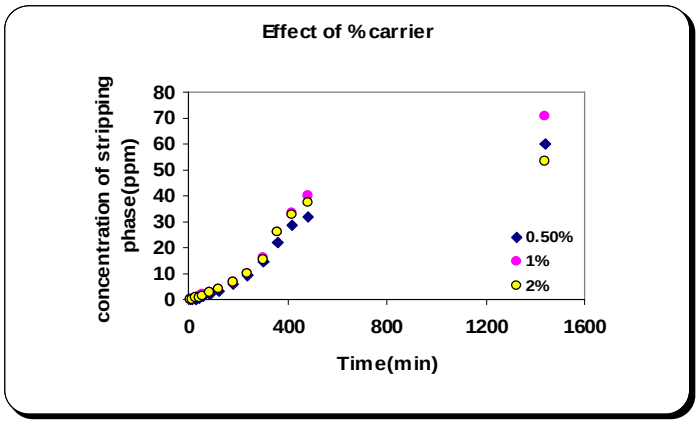


fig No 5

Effect of mixing

The speed of mixing of phases is so important that the fastest speed of mixing of phases lead to smallest thickness of films in equations 1,5,6,10 and because of this reason, mass transfer decreases. As we see in diagrams, the optimum speed of mixing is 100 rpm. Because in some other speed like 80rpm, flow is laminar and it's so silent and phases can't mix together as they can, and mass transfer don't operate successfully.

Because of these reason extraction decreases. The next speed of mixing of phases that we investigated was 120 rpm.In 120rpm, flow is turbulent and because of this reason, fine bubbles of feed and stripping phases enter to membrane phase and because of high velocity of mixers these bubbles can't operate inter facial reactions and go straight to the other liquor phase and extraction decreases. As we see in diagram No6. Concentration of feed phase after 24 hr, in 100,80 and 120 rpm approaches to o.1 ppm, 6.2ppm and 3ppm respectively . Also ,in diagram No7, extraction in 100rpm , is higher than the others. And after 24hr Concentration of stripping phase in 100 rpm,80rpm and 120rpm is 70.4ppm ,56.4ppm and 60.6 ppm respectively.

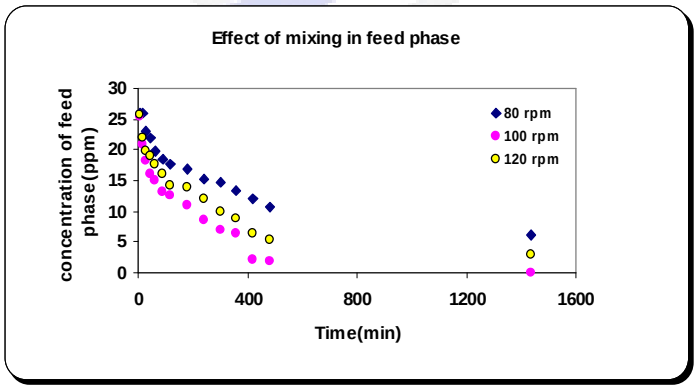


fig No 6

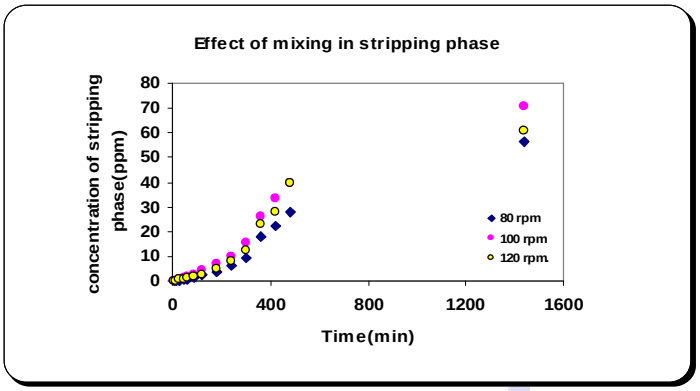


fig No 7

Effect of molarity of stripping phase

Because of low concentration of chromium in feed phase and pay attention to this point that with each chromate ion, two H^+ ions were transferred from feed phase to stripping phase variation of pH in stripping phase is negligible. Therefore most basic stripping phase lead to operate extraction easily . And we see this point in the diagram and results.

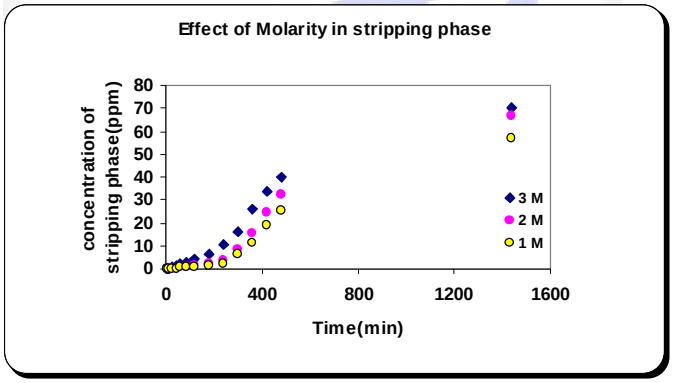


fig No 8

Conclusions

- Presence of surfactant in membrane phase increased extraction process.
- Optimum amount of carrier percentage in our expriments was 1% (V/V). In this measure, maximum extraction was obtained.
- Optimum amount of pH for feed in our expriments was pH=2. In this pH, extractions are increased and Alm_2CrO_4 complexes are generated faster than the other conditions that we did.
- Optimum velocity of mixer for both liquor phases (feed phase and stripping phase) in our expriments is 100rpm. Because extraction and back extraction are operated successfully.
- Best molarity for stripping phase in our expriments is Molarity=3 because under this condition back extraction are operated successfully and AlmoH Complexes are generated faster than the other Conditions that we did.

Symbols

if	Liquid environment near the feed phase
of	Organic environment near the feed phase
os	Organic environment near the stripping phase
is	Liquid environment near the stripping phase
o	Organic phase
i	Liquid phase
δ	Thickness of Mass transfer film
D	Mass transfer diffusion coefficient
N	Mass transfer diffusion

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