# Chromium (III) removal from aqueous solution applying bulk liquid membrane using tri-n-butyl phosphate (TBP) as a mobile carrier.

**Prof. Dr. Ahmed A. Mohammed**

**Environmental Engineering Department, University of Baghdad, Iraq.**

**Asst. lect. Ammar A. Saoud,**

**Environmental Engineering Department, University of Baghdad, Iraq.**

## ABSTRACT

The separation of chromium (III) ions from aqueous solutions using bulk liquid membrane (BLM) process has been studied, in this techniques kerosene chosen as organic solvent and tri-n-butyl phosphate (TBP) as mobile carrier. BLM extraction was tested by varying the pH of the feed phase in range (2-6), TBP carrier concentration in range (10-40% (v/v)), $H_2SO_4$ concentration of stripping phase in range (0.25-1M), the initial concentration of the feed phase in range (100-400 mg/l), and agitation speed in range (100-300 rpm) to find the best operating conditions to reach maximum recovery of chromium (III) ions.The transfer kinetics was inspected using a kinetic model including two consecutive irreversible first-order reactions were the maximum extraction (E%) and stripping (S%) efficiencies achieved of chromium (III) ions were 93.6% and 93.2% respectively. The rate constants of the extraction and stripping processes ($k_1$ and $k_2$), transport fluxes of ions across the BLM ($J_f^{max}$, $J_s^{max}$) and time dependency of the process ($t_{max}$) of maximum solute concentrations in membrane ($R_m^{max}$) were determined and discussed. Results proved that the $k_1$ and $k_2$ had increased with the increasing acidity of donor phase and time required to reach steady state ($t_{max}$) decreased. The transport rate of Cr (III) ion had increased with the increasing of TBP concentration, transport rate decreased with increased initial feed phase concentration and was increased with increasing agitation speed.

**Keywords**: **Chromium, liquid membrane, Tri-n-butyl phosphate, stripping agent**

## 1. Introduction.

In the hydrometallurgical and environmental process, selective recovery and removal of metals from industrial and waste solutions are very important and has been extensively studied [8]. The environmental significance of the heavy metal ion decontamination is very essential due to their high persistence, toxicity, represents a major threat to human health. The removal and recovery of heavy metals from wastewater and industrial effluents is economically driven as much as it is a health issue. For these causes, several methods for the removal of hazardous contaminants from wastewater have been studied and implemented for many years. These methods include the adsorption, flotation, biological process, chemical precipitation, coagulation, ions exchange, reverse osmosis and solvent extraction [2], none of these techniques used alone to ensure environmental compliance in all of situations [5]. Therefore, efficient, economic and sustainable methods for this purpose are required. Liquid membranes (LM) are expected to be most appropriate among wastewater treatment techniques, as their applicability outcomes from fundamental studies achieved for over forty years [13]. Liquid membrane technology has been widely used for attaining separations, due to its capability for a very high separation selectivity, simple operation, fast mass transfer can happen on carriers, yields can be extremely concentrated due to facilitated transport mechanism, process costs are quite low, greater interfacial area, extraction and stripping in one stage, and scope of continuous operation [12]. Liquid membrane consisted of liquid film that serve as a barrier between two phases and through which gases, ions and molecule are selectivity transport [3]. The main types of liquid membrane systems include supported liquid membrane (SLM), emulsion liquid membrane (ELM), bulk liquid membrane (BLM). Liquid membrane can be used to remove some heavy metals form positive ions in solution. They have high surface area to volume ratio (100-200 $m^2/m^3$) for solid supported and 3000 $m^2/m^3$ for ELM compared to solid membranes (10 $m^2/m^3$) [4]. The liquid membrane methods can be worked continuously and scalable. The portion of membrane phase to external phase can be very high up to 1:40 [11]. Chromium is one of the heavy metal have a specific toxicological significance, which can be coexist at a degree of oxidation rang from (-II) to (+VI). The world production of chromite ore is several millions of tons per year. Ferro chromite is obtained by direct reduction of ore while chromium produced by chemical reduction (aluminothermy process) or by electrolysis of either $CrO_3$ or chrome alum solutions [9].

## 2. Experimental work

### 2.1 Chemicals

Kerosene organic solvent was used as a membrane (density: 0.8 kg/L, refractivity: 1.440) insoluble in aqueous phase with very low viscosity (0.000115 Pa.s) supplied from Al-Daura petroleum refinery, Tri-n-butyl phosphate (TBP) as a mobile carrier agents with chemical formula $C_{12}H_{27}O_4P$ (Merck) with purity $\geq 99\%$ is shown in Fig. 1. Potassium dichromate ($K_2Cr_2O_7$) with purity > 99.8% (ROMIL), the chemical was used of analytical grade without further purification and. Sulfuric acid $H_2SO_4$ (assay>95.0%) from Sigma Aldrich.

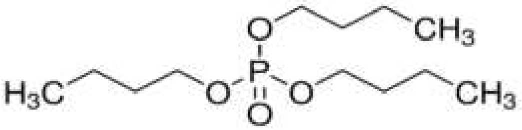


**Fig. 1 Chemical structure of Tri-n-butyl phosphate (TBP).**

## 2.2 Equipment's

Atomic Absorption Spectrometer AAS from (GBC-Germany), Mechanical mixer (IKA, RW 20, Germany), pH meter (WTW, Germany), and micropipette.

## 2.3 Membrane preparation

The membrane prepared by mixing different concentration of carrier tri-n-butyl phosphate (TBP) of (10, 20 and 30 ml) with pure kerosene solvent (90, 80 and 70 ml), respectively, in order to obtain membrane TBP/kerosene volume ratio of (10, 20 and 30% (v/v)) respectively at room temperature (22±2◦C).

## 2.4 Extraction and re-extraction experiments

The experimental setup of TBP/kerosene bulk liquid membrane compartment consists of a rectangular glass container (130mm length×65mm width×80mm height) separated into two sections by a 70mm height glass plate of thickness 2mm as shown in Fig. 2. The section is filled with an aqueous feed (F) phase while the other one with an aqueous stripping (S) phase, both are covered with organic solvent of kerosene (M). The aqueous feed phase solution (300 ml) loaded with (100, 200, 300 and 400 ppm) of Cr (III) metal ion. The stripping phase is sulfuric acid ($H_2SO_4$) (300 ml) in concentration range (0.25, 0.5, 0.75 and 1M).

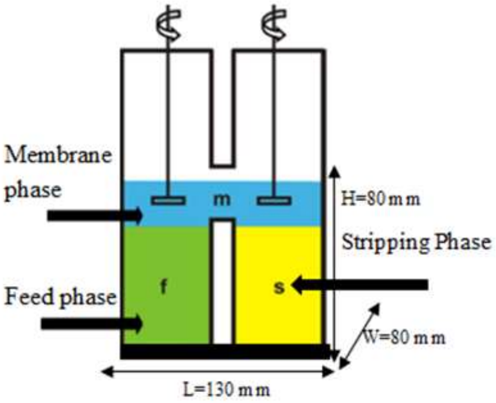


**Fig. 2 Schematic representation of bulk liquid membrane**

## 2.5 Sample analysis

At regular intervals of 1, 2, 3, 4, and 5 hour, samples were taken from the feed and stripping phases by pipetting out the aqueous phases, and after appropriate dilution the samples of both phases were analyzed for Cr (III) metal ion concentrations by a flame atomic absorption spectrophotometer.

## 2.6 Calculus methodology

The percentage extraction (E%) and stripping efficiency (S%) of chromium (III) were calculated according to equations (1), (2) respectively.

$$E\% = \frac{(C_o - C_F)}{C_O} \times 100 \qquad (1)$$

$$S\% = \frac{C_S}{C_O - C_F} \times 100 \qquad (2)$$

Where:

$C_o$: Initial heavy metals ion concentrations in the feed phase (mg/l).

$C_F$ : heavy metals concentration at any time in feed phase (mg/l).

$C_S$ : heavy metals concentration at any time in strip phase (mg/l).

## 3. Kinetic model

ssuming the facilitated transport of Cr (III) metal ions through bulk liquid membranes can be explained by a kinetic law of two consecutive irreversible first-order reactions [15-9-2-10].

This behavior can be described according to:

$$C_F \underset{\text{Extraction}}{\xrightarrow{k_1}} C_M \underset{\text{Stripping}}{\xrightarrow{k_2}} C_S \qquad (3)$$

Where:

$C_M$: concentration of solute in the membrane phase.

$k_1$,$k_2$: are the apparent first order- rate constants of solute extraction and stripping processes .

The dimensionless reduced solute concentrations ($R_i=C_i/C_0$) introduced and the concentrations become:

$$R_F = \frac{C_F}{C_0}\ , R_M = \frac{C_M}{C_0}\ , R_S = \frac{C_S}{C_0} \qquad (4)$$

Then Equation (3) becomes:

$$R_F \xrightarrow{k_1} R_M \xrightarrow{k_2} R_S \qquad (5)$$

Where: $R_F$, $R_M$ and $R_S$ are the instantaneous reduced solute concentrations in feed, membrane and stripping phases, respectively.

$C_0$ : the initial concentration of solute in feed phase.

The relation between the reduced solute concentrations in different phases is found as:

$$R_F + R_M + R_S = 1 \qquad (6)$$

According to Equation (5), the rates of change of solute concentration in different phases are expressed as:

$$\frac{dR_F}{dt} = -k_1 R_F = J_F \qquad (7)$$

$$\frac{dR_M}{dt} = k_1 R_F - k_2 R_M = J_M \qquad (8)$$

$$\frac{dR_s}{dt} = k_2 R_M = J_S \qquad (9)$$

Where: $J_F$ , $J_M$ and $J_S$ are the instantaneous solute fluxes in feed, membrane and stripping phases, respectively.

When $J_M$ (Equation (8) is equal to zero, the maximum fluxes of solute transport across bulk liquid membrane are realized.

$$J_F^{max} = -k_1 e^{-k_1 t_{max}} \qquad (9)$$

$$J_M = \frac{k_1}{(k_2-k_1)}\left[k_2\ e^{-k_2 t_{max}} - k_1 e^{-k_1 t_{max}}\right] = 0 \qquad (10)$$

$$J_S^{max} = \frac{k_1 k_2}{(k_2-k_1)}\left[\ e^{-k_1 t_{max}} - e^{-k_2 t_{max}}\right] \qquad (11)$$

Where: $J_F{}^{max}$ and $J_S{}^{max}$ are the maximum fluxes of solute transport in feed and stripping phases, respectively, while $t_{max}$ is the time at which the maximum fluxes are achieved. From Equation (10), $t_{max}$ is derived as:

$$t_{max} = \frac{\ln(\frac{k_2}{k_1})}{(k_2-k_1)} \qquad (12)$$

Substitution of Eq. (12) into Eq. (11), the value of $R_M$ at $t_{max}$ , i.e. $R_M^{max}$ is found as follows

$$R_M{}^{max} = \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{(k_2-k_1)}} \qquad (13)$$

From equation (11) Substituted into Equation (12):

$$t_{max} = \frac{\frac{(k_2-k_1)}{k_2} * \ln\left(\frac{1}{R_m{}^{max}}\right)}{(k_2-k_1)}$$

$$k_2 = \ln\left(\frac{1}{R_m{}^{max}}\right) / t_{max}$$

# 4. Results and discussion

## 4.1 Effect of the feed phase pH

The effect of pH was investigated by changing the pH of the donor (Feed) phase in the range (2–6) where experimental conditions involve an aqueous feed phase (F) contained of 100 mg/l (1.9 mM) initial Cr (III) concentration with volume ratio (donor phase-organic phase 3:1), an organic membrane (M) of 90 ml of kerosene loaded with 10 ml (36.8 mM) TBP carrier with volume ratio of 10% (v/v), stripping phase (S) of (0.25 M) $H_2SO_4$ at volume ratio of (stripping phase-membrane phase 3:1), the experiment occur at stirring speed of 100 rpm. The heights extraction efficiency (E%) of Cr (III) ions was achieved at pH 2 of the feed phase as shown in Figs. 3 and 4 where the extraction (E%) and stripping (S%) efficiency is (80%) and (73.4%) respectively, when increase the pH there is a reduction in the transport rate of Cr (III) ions, this is due to of the incomplete protonation and the reducing in complexing ability of TBP carrier in the membrane/donor interface [14]. Fig. 5 show the time variation of reduced concentration Rf, Rm and Rs of Cr (III) at feed phase pH=2. The kinetic analysis of experiment is shown in Table 1 where all kinetic parameters are calculated. The transport rates $k_1$ (extraction rate) and $k_2$ (the average of $k_{2M}$ and $k_{2S}$) where ($k_{2m}$ is membrane diffusion rate controller of complextion of the metal and carrier, $k_{2S}$ is stripping reaction rate) they are clear from all experiments are pH dependence, when the pH increased the value of $k_1$ and $k_2$ decreased and $t_{max}$ increase.

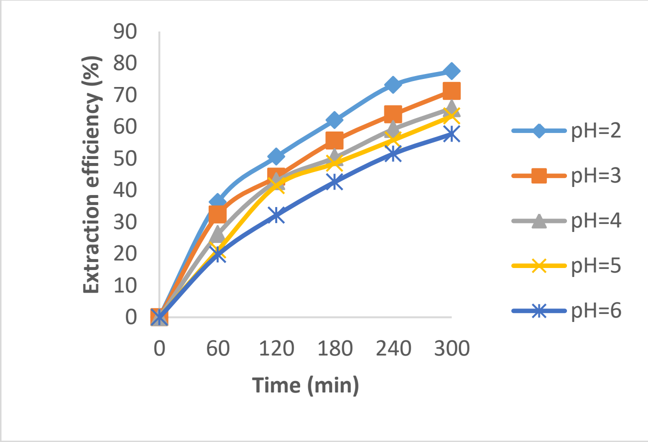


**Fig. 3 Effect of pH on extraction efficiency of Cr (III) (Co: 100 mg/l; TBP:10%(V/V); [$H_2SO_4$]: 0.25M ; stirring speed:100rpm).**

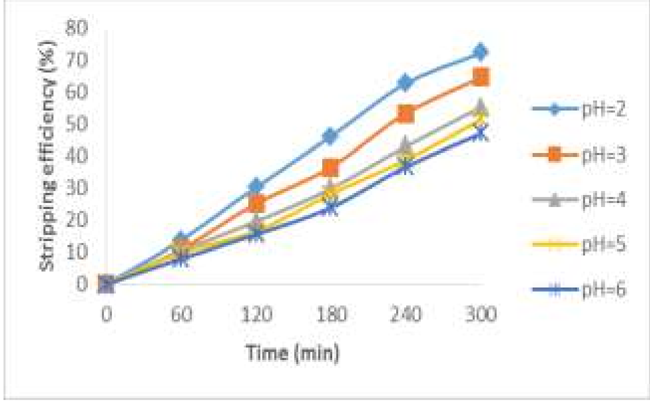


**Fig. 4 Effect pH on the stripping efficiency of Cr (III) (Co:100 mg/l; TBP:10%(V/V); [$H_2SO_4$]:0.25M ;stirring speed:100rpm).**

**Table 1. Kinetic parameters of Cr (III) transport through bulk liquid membrane at feed phase pH range (2-6).**

| | pH | $k_1 \times 10^3$ $(min^{-1})$ | $k_{2S} \times 10^3$ $(min^{-1})$ | $k_{2M} \times 10^3$ $(min^{-1})$ | $k_2 \times 10^3$ $(min^{-1})$ | $t_{max}$ (min) | $R_M^{max}$ | $J_F^{max} \times 10^3$ $(min^{-1})$ | $J_S^{max} \times 10^3$ $(min^{-1})$ |
|---|---|---|---|---|---|---|---|---|---|
| ***Chromium (III)*** | 2 | 6.24 | 6.71 | 7.14 | 6.92 | 152 | 2.86 | -2.42 | 2.42 |
| | 3 | 5.41 | 5.87 | 6.49 | 6.18 | 172.8 | 2.909 | -2.12 | 2.12 |
| | 4 | 4.82 | 6.48 | 6.74 | 6.61 | 176.4 | 3.209 | -2.06 | 2.06 |
| | 5 | 4.78 | 6.64 | 6.96 | 6.8 | 174.4 | 3.275 | -2.08 | 2.008 |
| | 6 | 4.48 | 4.45 | 4.68 | 4.56 | 221.1 | 2.744 | -166 | 1.66 |

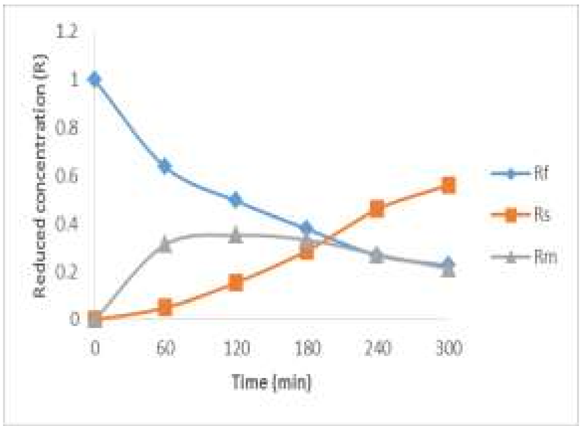


**Fig. 5: Time variation of reduced concentration Rf, Rs and Rm of Cr (III) at feed phase pH=2.**

## 4.2 Effect of carrier concentration

The effect of carrier concentration on the efficiency of BLM extraction/stripping of Cr (III) ions process has been studied. Using four different volume ratio of TBP carrier/kerosene (10-20-30 and 40% v/v). Figs. 6 and 7 show 30% (v/v) of TBP gave maximum level rate of Cr (III) ions transported into the membrane where the extraction and strapping efficiency was 87.7% and 84.8% respectively. The kinetic parameters for extraction of Cr (III) ions are presented in Table 2. The transport rates $k_1$, $k_2$ and $R_m^{max}$ increase and $t_{max}$ decreases with carrier TBP concentration increase from 10 up to 30% (v/v). Fig. 8 show the time variation of reduced concentration Rf, Rs and Rm of Cr (III) at TBP concentration 30% (v/v).

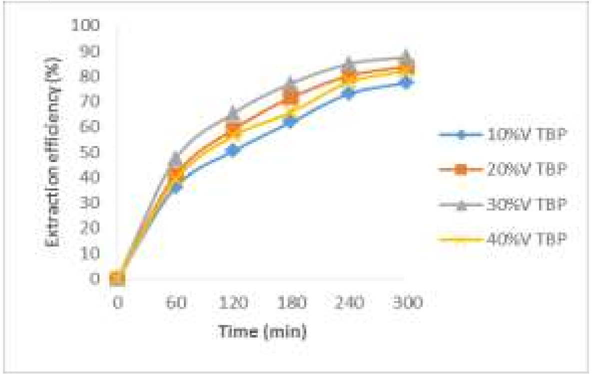


**Fig. 6 Effect of the TBP% (v/v) on extraction efficiency of chromium (III) , ($C_o$: 100 mg/l; pH=2; [$H_2SO_4$]: 0.25M; stirring speed:100rpm).**

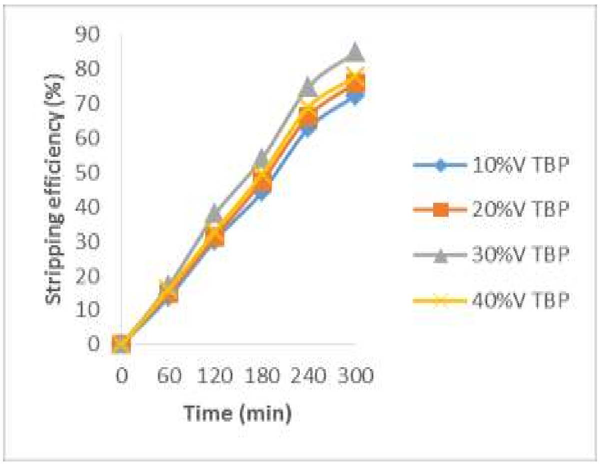


**Fig. 7 Effect of the TBP% (v/v) on stripping efficiency of chromium, ($C_o$: 100 mg/l, pH=2 [$H_2SO_4$]: 0.25M ; stirring speed:100rpm).**

**Table 2. Kinetic parameters of Cr (III) transport through bulk liquid membrane at different TBP concentration.**

| | TBP (v/v) % | $k_1$ ×$10^3$ ($min^{-1}$) | $k_{2S}$ ×$10^3$ ($min^{-1}$) | $k_{2M}$ ×$10^3$ ($min^{-1}$) | $k_2$ ×$10^3$ ($min^{-1}$) | $t_{max}$ (min) | $R_M^{max}$ | $J_F^{max}$ ×$10^3$ ($min^{-1}$) | $J_S^{max}$ ×$10^3$ ($min^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| *Chromium (III)* | 10 | 6.24 | 6.71 | 7.14 | 6.92 | 152 | 2.86 | 2.42 | 2.42 |
| | 20 | 7.21 | 6.98 | 7.42 | 7.2 | 138.7 | 2.716 | -2.65 | 2.65 |
| | 30 | 8.73 | 7.55 | 8.12 | 7.83 | 120.8 | 2.577 | -3.04 | 3.04 |
| | 40 | 7.69 | 7.36 | 7.77 | 7.56 | 131 | 2.696 | -2.81 | 2.8 |

### 4.3 Effect of the strip phase concentration

Sulphur acid ($H_2SO_4$) was used within the concentration range of (0.25-1.0M) as stripping agents. As shown in Figs. 9 and 10, the best Cr (III) transport was achieved at 0.5 M, when the concentration of sulfuric acid in the receiving phase increased from (0.75 to 1 M) there was a reduction in the transport percentage may be due to the imperfect protonation and the reduced complexing ability of TBP based carrier agent in donor/membrane interface. Kinetic parameters are represented in Table 3. The concentration of the stripping phase has low influence on the extraction and stripping efficiency of Cr (III). This may be resulted from the high dissolving capacity or high distribution coefficient of Cr (III) in the LM. Fig. 11 show the time variation of reduced concentration $R_F$, $R_M$ and $R_S$ of Cr (III) transport through the liquid membrane at concentration (0.5 M) $H_2SO_4$ .

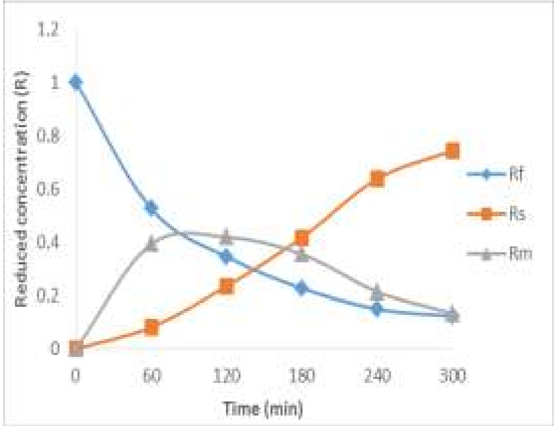


**Fig. 8 Time variation of reduced concentration Rf, Rs and Rm of Cr (III) at TBP concentration 30% (v/v).**

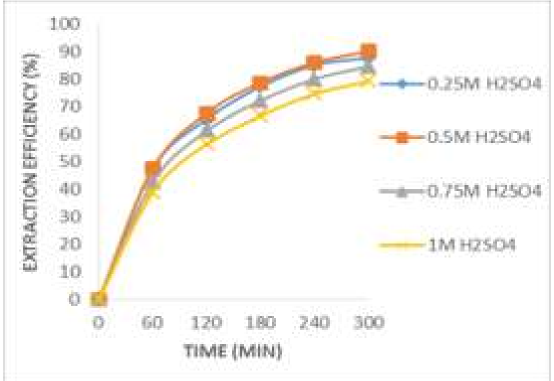
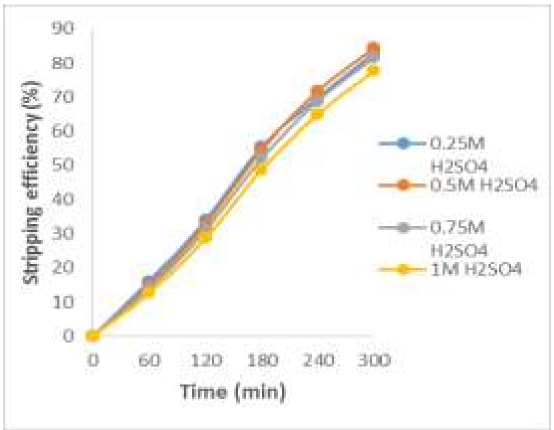


**Fig. 9 Effect of the $H_2SO_4$ concentration on the extraction efficiency of Cr (III), ( Co:100 mg/l, pH=2; TBP=30%(v/v); stirring speed:100rpm).**



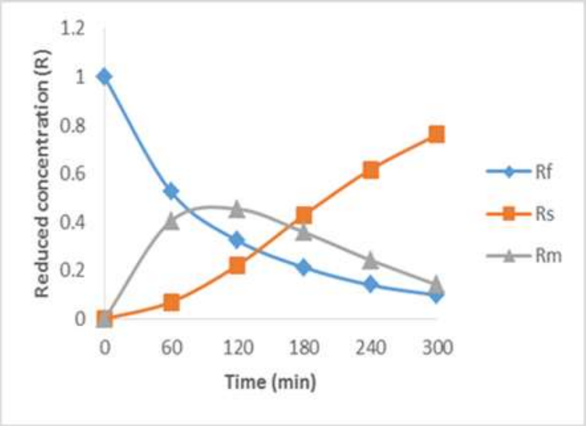


**Fig. 10 Effect of the $H_2SO_4$ concentration on the Stripping efficiency of Cr (III) (Co:100 mg/l, pH=2; TBP=30%(v/v) ; stirring speed=100rpm)**

**Fig. 11 Time variation of reduced concentration Rf, Rs and Rm of Cr (III) at H2SO4 concentration of 0.5 M.**

**Table 3. Kinetic parameters of Cr (III) transport through bulk liquid membrane at (0.25-1M) $H_2SO_4$ concentration.**

| | $H_2SO4$ (M) | $k_1 \times 10^3$ $(min^{-1})$ | $k_{2S} \times 10^3$ $(min^{-1})$ | $k_{2M} \times 10^3$ $(min^{-1})$ | $k_2 \times 10^3$ $(min^{-1})$ | $t_{max}$ (min) | $R_M^{max}$ | $J_F^{max} \times 10^3$ $(min^{-1})$ | $J_S^{max} \times 10^3$ $(min^{-1})$ |
|---|---|---|---|---|---|---|---|---|---|
| *Chromium (III)* | 0.25 | 8.73 | 7.55 | 8.12 | 7.83 | 120.8 | 2.577 | -3.04 | 3.04 |
| | 0.5 | 9.16 | 7.81 | 8.41 | 8.11 | 115.9 | 2.56 | -3.17 | 3.17 |
| | 0.75 | 7.43 | 7.62 | 8.16 | 7.89 | 130.5 | 2.802 | -2.82 | 2.82 |
| | 1 | 6.28 | 6.71 | 7.26 | 6.98 | 150.9 | 2.869 | -2.43 | 2.43 |

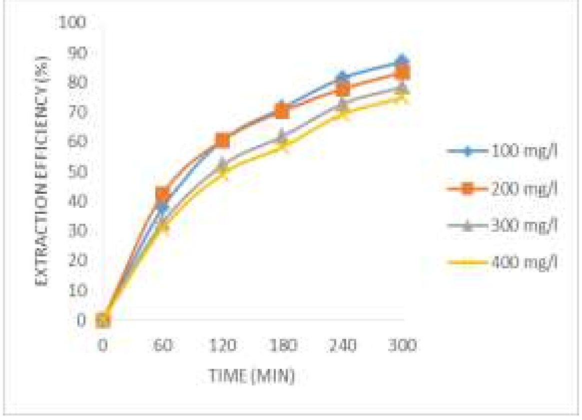


**Fig. 12 Effect of feed concentration on the extraction efficiency of Cr (III) (pH=2; $H_2SO_4$=0.5 M; TBP=30%(v/v) ; stirring speed=100rpm).**

## 4.4 Effect of initial concentration

The feed-phase concentration act as an important factor, therefor to examine the effect of concentration of feed-phase on the Cr (III) transport across bulk liquid membrane, experiments were investigated at various metal ion concentrations in range (100–400 mg/l). Figs. 12 and 13 clearly show a reduction in the removal percentage of Cr (III) with increase the Cr (III) metal concentration in the feed phase. The saturation of the LM at higher concentration Cr (III) may be causing this behavior [16]. From the results in table 4, it can be conclude that the interface between the membrane and donor phase isn't saturated by the chromium (III) in small concentrations but flooded at higher concentrations. Fig. 14 gave time variation of reduced concentration ($R_F$), ($R_M$) and ($R_S$) of Cr (III) transport through a bulk liquid membrane.

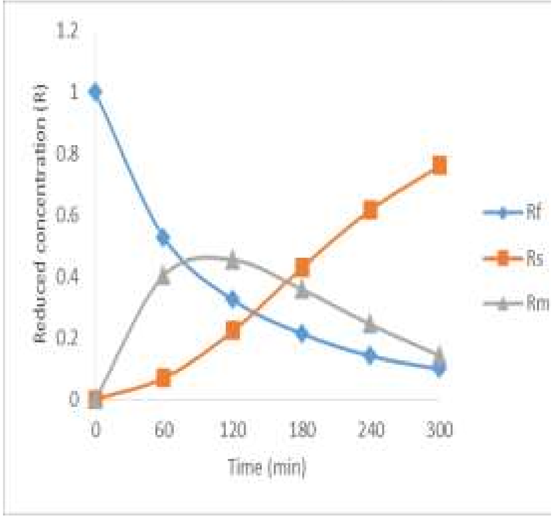


**Fig. 14: Time variation of reduced concentration of Cr (III) Rf, Rs and Rm at feed phase concentration of 100 mg/l**

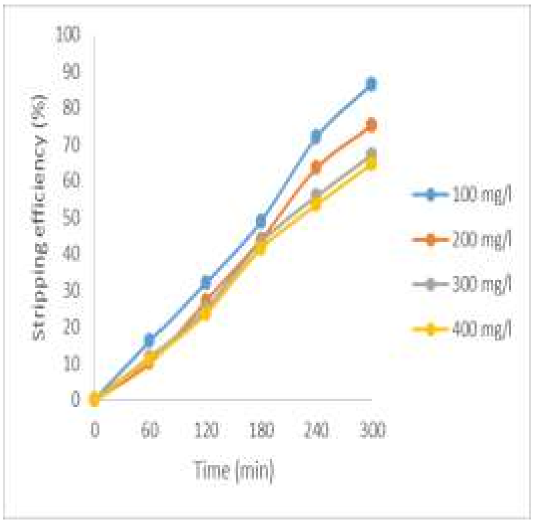


**Fig. 13 Effect of feed concentration on stripping efficiency of Cr (III), (pH=2; $H_2SO_4$=0.5 M; TBP=30%(v/v) ; stirring speed=100rpm)**

**Table 4 Kinetic parameters of chromium (III) transport through bulk liquid membrane at different concentration of feed phase.**

| | $C_o$ (ppm) | $k_1 \times 10^3$ ($min^{-1}$) | $k_{2S} \times 10^3$ ($min^{-1}$) | $k_{2M} \times 10^3$ ($min^{-1}$) | $k_2 \times 10^3$ ($min^{-1}$) | $t_{max}$ (min) | $R_M^{max}$ | $J_F^{max} \times 10^3$ ($min^{-1}$) | $J_S^{max} \times 10^3$ ($min^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| ***Chromium (III)*** | 100 | 9.16 | 7.81 | 8.41 | 8.11 | 115.9 | 2.56 | -3.17 | 3.17 |
| | 200 | 7.37 | 7.97 | 8.5 | 8.23 | 128.2 | 2.876 | -2.86 | 2.86 |
| | 300 | 5.63 | 11.4 | 11.7 | 115.5 | 121.3 | 4.036 | -2.84 | 2.84 |
| | 400 | 5.09 | 12.2 | 12.4 | 12.3 | 122.3 | 4.504 | -2.73 | 2.73 |

## 4.5 Effect of stirring speed

the mixing speed were studied in order to find the best identical mixing and minimize the boundary layer thickness in the feed phase and the striping phase for an effective transport that allows effective transport of Cr (III) in the BLM system. The extraction efficiencies in the range of speed (100–200–300 rpm) were 90.2%, 92.6% and 93.6% respectively and stripping efficiencies were 84.4%, 90.5% and 93.2% as shown in Figs. 15 and 16 that confirm that the extraction efficiency and stripping efficiency enhanced with increasing stirring speed of aqueous phase from 100 to 300 rpm. It is noted that a stronger agitation promotes the interfacial interaction at the feed-membrane and membrane stripping interfaces, and through decreasing the thickness of boundary thickness layer eventually increases the kinetic rate of chemical reaction on the interface [6]. Table 5 summarizes the kinetic parameters and Fig. 17 give time variation of reduced concentration ($R_F$), ($R_M$) and ($R_S$) of Cr (III) in transport through a liquid membrane at string speed of 300 rpm.

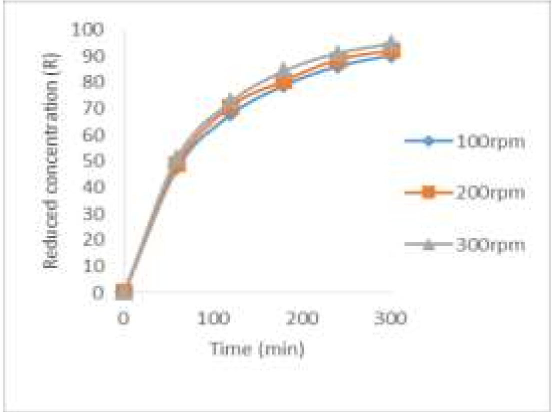


**Fig. 15: Effect of stirring speed (rpm) on the extraction efficiency of Cr (III) ($C_o$.: 100 mg/l, pH=2; $H_2SO_4$=0.5 M; TBP=30%(v/v)).**

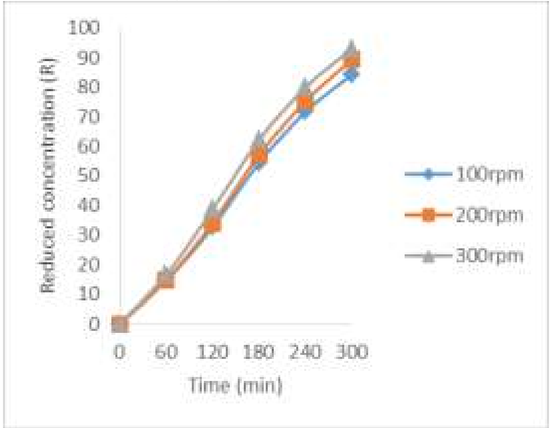


**Fig. 16: Effect of stirring speed (rpm) on the stripping efficiency of Cr (III), (Co: 100 mg/l, pH:2; H2SO4:0.5 M; TBP:30%(v/v).**

**Table 5. Kinetic parameters of chromium (III) transport through bulk liquid membrane at different string speed of feed phase.**

| | string (rpm) | $k_1 \times 10^3$ ($min^{-1}$) | $k_{2S} \times 10^3$ ($min^{-1}$) | $k_{2M} \times 10^3$ ($min^{-1}$) | $k_2 \times 10^3$ ($min^{-1}$) | $t_{max}$ (min) | $R_M^{max}$ | $J_F^{max} \times 10^3$ ($min^{-1}$) | $J_S^{max} \times 10^3$ ($min^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| ***Chromium (III)*** | **100** | **9.17** | **10.7** | **10.1** | **10.4** | **102.3** | **2.898** | **-3.58** | **3.58** |
| | **200** | **9.51** | **9.16** | **9.42** | **9.29** | **106.3** | **2.686** | **-3.45** | **3.45** |
| | **300** | **10.4** | **9.62** | **9.77** | **9.69** | **99.5** | **2.625** | **-3.69** | **3.69** |

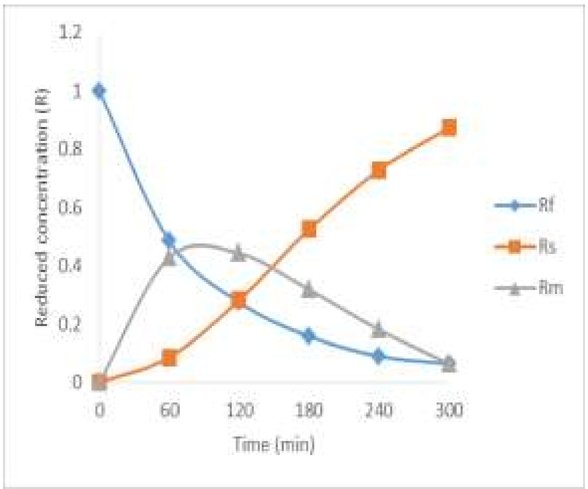


**Fig. 17: Time variation of reduced concentration Rf,Rs and Rm of chromium (III) at stirring speed of 300 rpm**

## 5. Conclusions

the bulk liquid membrane methods used for the separation of Cr (III) ions from wastewater using TBP as carrier based/ kerosene as organic solvent and sulfuric acid in the receiving phase have been approved to be effective processes, where the gradient between the pH of donor and the acceptor phases is the force for the transport of ion across the LM. Membrane interfacial transport fluxes of extraction ($J_F^{max}$) and re-extraction ($J_S^{max}$) were determined to label the mass transfer process successfully reached to $3.69 \times 10^{-3}$ $min^{-1}$ , Cr (III) can be extracted quantitatively from acidic solution at pH 2 using 30 % (v/v) TBP as an extractant and stripped quantitatively with 0.5 M $H_2SO_4$ solution from the loaded organic solvent. The pH-extraction isotherms highly effected, where at the lower pH of the feed (donor phase) there was an increase in the transport of Cr (III) metal ion because high availability of ($H^+$) at the interface that promotes the transport while the transport highly decreased with increasing pH.

## Refrences

1. Ahalya N., Ramachandrl T.V. and Kanamadi RD., Biosorption of Heavy Metal Research Journal of Chemistry and Environment, Vol.7 pp4, Dec. 2003.
2. Alpaydin S., Yilmaz M., Ersoz M., Kinetic study of Hg(II) transport through a bulk liquid membrane containing ester derivative of bis-calix[4]arene, Sep. Sci.Technol. 39 (9) 2189–2206 (2004).
3. Araki T., Tsukube H.,"liquid membrane:chemical application", CRC press Boca Raton (1990).
4. Cahn, R.P. and Li, N.N.,"Separation of phenol from wastewater by the liquid membrane". Sep. Sci. Technol., 9, 505-19 (1974).
5. Cooley A.C., Silver Recovery for Environmental Compliance in Photographic Processing,J. Imaging Science & Technol. 37~374-379 (1993).
6. Fozia, T. Shahabuddin M., and Bhanger M,. "Transport of Hg (II) through bulk liquid membrane containing calix [4] arene thioalkyl derivative as a carrier " Desalination, 262, 215-220 (2010).
7. Ghinwa M. Naja and Bohumil Volesky. Heavy Metals in the Environment. CRC Press, Jun 23, 2009 - Technology & Engineering.
8. Gupta C.K., Mukherjee T.K, Hydrometallurgy in Extraction Processes. CRC Press. 1990.
9. He D.S., Ma M., Kinetics of cadmium(II) transport through a liquid membrane containing

tricapryl amine in xylene, Sep. Sci. Technol. 35 (10) (2000).

10. Léon G., Guzman M.A., Facilitated transport of copper through bulk liquid membranes containing different carriers: compared kinetic study, Desalination 223 (2008) 330–336.
11. Marr, R. and Kopp, A.. Liquid membrane technology – A survey of phenomena, mechanisms, and models. Int. Chem. Eng., 22, 44-60 (1982).
12. Norasikin O., Masahiro G., Hanapi M., Liquid Membrane Technology for Precious Metals Recovery from Industrial Waste, (2004).
13. Piotr S. ski , Szidonia K. Tanczos , Lucian D. Ghindeanu , Romuald Wódzki "Transport of p-nitrophenol in an agitated bulk liquid membrane system–Experimental and theoretical study by network analysis" Separation and Purification Technology 132 (2014) 616–626.
14. Sabri Alpaydin, Ahmet. Saf, Selahattin Bozkurt, Abdulkadir Sirit."Kinetic study on removal of toxic metal Cr(VI) through a bulk liquid membrane containing p-tert-butylcalix[4]arene derivative" Desalination 275 (2011) 166–171.
15. Szpakowska M., Nagy O.B., Chemical kinetic approach to the mechanism of coupled transport of Cu(II) ions through bulk liquid membrane, J. Phys. Chem.A 103 (11) (1999) 1553–1559.
16. Venkatesan S. and Meera K.M., "Emulsion liquid membrane petraction of imidazol from dilute aqueous solutions by Aliquat-336 mobile carrier", J. Desalination, Vol. 236, pp.65-77 (2007).

# ازالة الكروم (الثلاثي) من المحاليل المائيه بتطبيق السوائل الغشائيه وباستخدام (ثلاثي –ن- بيوتيل الفوسفات) كحامل متحرك

**الاستاذ الدكتور: احمد عبد محمد (قسم الهندسة البيئيه/جامعة بغداد)**

**الدكتور: محمد سعدي حميد (قسم الهندسه الكيمياوية/ جامعة النهرين)**

**مدرس مساعد: عمار عبدالله سعود (قسم الهندسة المدنية/جامعة النهرين)**

## الخلاصه

تم دراسة فصل ايونات الكروم (الثلاثيه) من المحاليل المائية باستخدام السوائل الغشائيه, في هذه التقنيه تم اختيارغشاء الكيروسين كمذيب عضوي و(ثلاثي –ن- بيوتيل الفوسفات) كحامل متحرك. ان الاستخلاص بواسطه كتلة السوائل الغشائيه تم اختباره من خلال تغيير الرقم الهيدروجيني للتغذيه في الحدود من(2-6)، وتركيز الناقل المتحرك (ثلاثي –ن- بيوتيل الفوسفات) في حدود (10-40٪(حجم/حجم))، وتركيز حامض الكبريتيك في طور الانتزاع قي الحدود (0.25-1مول)، والتركيز الابتدائي لطور التغذيه ضمن الحدود (100-400 مل غرام/لتر)، وسرعة الخلط في حدود (100-300 دورة في الدقيقة) لايجاد افضل ظروف تشغيليه والوصول إلى الحد الاقصى لاستخلاص واسترجاع الايونات. تم فحص الحركية الانتقاليه باستخدام النموذج الحركي (تفاعلين متتاليتين غير انعكساي من الدرجة الأولى) حيث كان حد الكفاءة الأقصى لاستخلاص ايون الكروم (الثلاثي) من محلولها المائي واستعادته في طور الانتزاع هو 93.6٪ و 93.2 ٪ على التوالي. تم تحديد ثوابت معدل الاستخلاص والانتزاع للعمليات (K1 و K2) و تحديد أعلى تدفق لانتقال

ايونات الكروم في جميع أنحاء السائل الغشائي ($Jf^{max}$، $Js^{max}$) وايجاد الزمن اللازم ($t^{max}$) للتراكيز القصوى للمذاب في السائل الغشائى ($Rm^{max}$) . النتائج اثبتت أن K1 و K2 ترتفع مع زيادة الحامضيه في الطورالمانح و أن الوقت اللازم للوصول إلى حالة مستقرة يقل. ان معدل انتقال ايونات الكروم الثلاثي تزداد مع زيادة تركيز الناقل، وتقل عند زيادة التركيز الابتدائى في طور التغذيه و تزداد عند زيادة سرعة الخلط.