

Removal of Chromium(VI) from Industrial Effluents Through Supported Liquid Membrane Using Trioctylphosphine Oxide as a Carrier

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The present study describes extraction of chromium(VI) through supported liquid membrane (SLM), Celgard 2400, which was impregnated with trioctylphosphine oxide (TOPO) dissolved in toluene. The stripping phase was comprised of diphenylcarbazine (DPC) in sulfuric acid (H_2SO_4) whereas the feed phase consists of potassium dichromate ($K_2Cr_2O_7$) and hydrogen peroxide (H_2O_2). The effects of concentrations of chromium, TOPO, DPC, and H_2SO_4 have been studied in order to evaluate the transport efficiency of chromium(VI) ion. The optimum experimental conditions for the chromium(VI) extraction were established as follows: $19.2 \times 10^{-4} \text{ mol L}^{-1}$ chromium ion, $1.5 \text{ mol L}^{-1} H_2O_2$ concentration in the feed phase, 0.1 mol L^{-1} TOPO concentration in the membrane phase and 0.001 mol L^{-1} DPC and $1.5 \text{ mol L}^{-1} H_2SO_4$ as stripping phase. The measurements of percent recovery, distribution coefficient, flux and permeability were made at the given optimized conditions. The extraction time and membrane stability were also investigated. Extraction efficiency of 80% was recorded in 180 min and the SLM system was found stable up to 10 days. The optimized SLM system was then applied on the paint industry wastewater; about 80% of chromium(VI) was successfully removed from the wastewater.

Keywords: supported liquid membrane, trioctylphosphine oxide, diphenylcarbazine, Cr^{VI} extraction, transport efficiency

Introduction

The extensive industrialization has caused environmental pollution at alarming level. The water near industrial sites is generally polluted by mixture of metals and organic compounds. Among many other metal pollutants chromium is one of the most serious threats to the living organisms. The total worldwide chromium production is about 16.4 million tons, while 15.38 million tons are produced in South Africa, India, Kazakhstan, Zimbabwe, Finland, Brazil and Turkey.¹ Chromium compounds are mainly used in industrial processes, such as corrosion control, oxidation process, leather tanning process, electroplating, metallurgy, cement, textile dyeing, paper making, ink, paints and pigments, and photographic industry.² Due to extensive use of chromium, various industries are discharging a significant concentration of chromium without prior treatment of the waste. Chromium concentration of 0.25 mg L^{-1} is responsible for the serious threats to aquatic as well as human life.¹

Generally, chromium occurs in the form of chromate and dichromate anions³ and their major oxidation states

are Cr^{III} and Cr^{VI} . The hazardous effect and reactivity of chromium depend on its chemical form and oxidation state. The trace amount of Cr^{III} is essential for humans and animals to maintain the tolerance factor of the glucose and other metabolism processes.¹ Cr^{VI} however, has comparatively high toxicity due to its solubility and high oxidation potential. Nickens *et al.*⁴ have reported the carcinogenesis and DNA damage effects by Cr^{VI} . Due to these health hazardous effects, various conventional techniques are used for the removal of Cr^{VI} from ground and surface water such as precipitation,⁵ extraction,⁶ ion exchange,⁷ electrochemical treatment,⁸ reverse osmosis,⁹ and membrane separation processes,^{10,11} but these techniques have their own limitations such as less efficiency, high capital and operating cost, secondary sludge formation, complex and sensitive operating conditions.¹² Therefore, more effective and efficient methods are required to seek out these difficulties. Among these techniques, the removal of Cr^{VI} by membrane technique is getting popular nowadays. The different kinds of membranes used in this technique include bulk liquid membrane (BLM), emulsion liquid membrane (ELM), supported liquid membrane (SLM), activated

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composites membrane (ACM) and polymer inclusion membrane (PIM).¹³⁻¹⁷

Among these, SLM technique is easy, involves low inventory of solvents, has low capital and operating cost as well as low energy consumption¹⁸ and allows the high amount of pollutants recovery. The use of supported liquid membrane technology helps to remove the toxic metal ions from the industrial effluents. Supported liquid membrane is very simple in operation and flexible. It can also minimize the use of chemicals and energy consumption, high interfacial area *per* unit volume which results in increased process efficiency,¹⁹ low solvent requirement as compared to conventional solvent extraction systems,²⁰ high selectivity and effective separation of target metal ions. Hence, it has a strong impact on the capital cost of the process due to less operating parts involved in the extraction process and influences the economic feasibility. Another great advantage of SLM technology is that the extraction, stripping and regeneration processes combine in a single step process.²¹⁻²⁴

SLM has attractive applications in the analytical field, chemical and pharmaceutical industry as well as in hydrometallurgy. SLM has been extensively used for the treatment of wastewater to remove the toxic heavy metal ions²⁵⁻²⁷ and other hazardous chemicals such as phenols and ammonia, from different sources.^{28,29} SLM has also been reported for the separation and recovery of precious metals,^{30,31} alkali metals,³² and rare earth elements.^{33,34}

Removal of Cr^{VI} through supported liquid membrane using various synthetic carriers has been widely reported by the scientific community. Kozłowski and Walkowiak³⁵ studied the Cr^{VI} transport across SLM with tertiary amines and quaternary ammonium salt (Aliquat 336) from acidic aqueous solution. Ashrafi *et al.*³⁶ have reported the selective separation of Cr^{VI} with Alamine 336 carrier through flat and hollow fiber SLM. Winston Ho and Poddar³⁷ have studied the removal of Cr^{VI} from wastewater by SLM with strip dispersion method. The secondary amine was used as a carrier in the membrane and sodium hydroxide as a stripping solution to remove the Cr^{VI} from acidic aqueous solution. Methyl tricaprylammonium chloride (Aliquat 336) with kerosene impregnated in SLM was reported for the extraction of Cr^{VI} from a biological sample like urine while sodium nitrate was used as a stripping phase.³⁸ Venkateswaran and Palanivelu³⁹ reported the recovery of Cr^{VI} from chromium plating wastewater by using tri-*n*-butylphosphate based flat-SLM. Park *et al.*⁴⁰ studied the facilitated transport of Cr^{VI} through an SLM consisting of trioctylmethylammonium chloride as a carrier in the hydrophobic microporous polytetrafluoroethylene membrane, using potassium dichromate in the feed side, and sodium hydroxide in

the strip side. The removal of Cr^{VI} through facilitated transport using Cyanex 923 as a carrier and stripping with hydrazine sulfate has been reported.⁴¹ Solangi *et al.*¹ have described a comparative transportation of Cr^{VI} across supported liquid membrane containing different derivatives of *p-tert*-butylcalix[4]arene diamide which were impregnated onto supported membrane (Celgard 2500). They have carried out the selective separation of Cr^{VI} in the presence of many other metal cations. Alonso and Pantelides⁴² have presented the modelling and simulation of a complete plant for the removal and recovery of Cr^{VI} with Aliquat 336 using hollow fiber module. Bey *et al.*⁴³ have prepared the hydrophilic hollow fiber membrane based on a modified polyether ether ketone by using Aliquat 336 as a carrier in kerosene. These prepared membranes were used for the extraction of Cr^{VI} from the aqueous solution. Gherasim and Bourceanu⁴⁴ reported the removal of Cr^{VI} from aqueous solutions using Aliquat 336/polyvinylchloride inclusion membrane. Rajasimman *et al.*⁴⁵ have investigated the statistical optimization of process parameters for the extraction of Cr^{VI} from pharmaceutical wastewater by emulsion liquid membrane. In this process, Aliquat 336 in kerosene was used as a carrier, while Span-80 was used as the surfactant and potassium hydroxide as internal reagent. Huang *et al.*⁴⁶ investigated the transport of Cr^{VI} from aqueous solutions of pH 2-4 through a supported liquid membrane with tri-*n*-octylphosphine oxide (TOPO) dissolved in kerosene, using the porous membrane polyvinylidene fluoride (PVDF) with a mean pore size of 0.45 μm , porosity of 75%, and thickness of 125 μm . In the pH range of 2 to 4 the predominant species of Cr^{VI} are HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. The transport proceeds through membrane diffusion as a series of steps in which the equilibria between $\text{HCrO}_4^-/\text{Cr}_2\text{O}_7^{2-}$ in the aqueous phase and between $\text{H}_2\text{CrO}_4\text{-(TOPO)}/\text{H}_2\text{Cr}_2\text{O}_7\text{-(TOPO)}_3$ in the membrane phase took place.⁴⁶

The scientific community has used various methods for the separation of Cr^{VI} in the field of supported liquid membrane and the literature published has been summarized in Table. 1.

In the present study, we have selected the system consisting of potassium dichromate with hydrogen peroxide in the feed phase whereas diphenylcarbazide was used in stripping phase. The polypropylene membrane (Celgard 2400) was used as a solid support; this system has not been reported previously.

Potassium dichromate is soluble in water and in the dissolution process it ionizes⁶² as



Table 1. Literature review of the extraction of Cr^{VI} through SLM

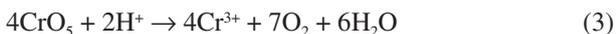
Feed Phase	Membrane/method	Membrane phase	Strip phase	Reference
K ₂ Cr ₂ O ₇	PVDF	Cyanex 921/Solvesso 100	H ₂ N-NH ₂	47
K ₂ Cr ₂ O ₇	HFSLM	Aliquat 336/dodecane	HNO ₃	48
K ₂ Cr ₂ O ₇	PVC-based SLM	Aliquat 336, NPOE/THF	NaCl	49
K ₂ Cr ₂ O ₇ + HCl	Millipore GVHPO4700	CYPHOS IL101/toluene	NaOH	50
K ₂ Cr ₂ O ₇	PTFE membrane	Aliquat 336/kerosene	HNO ₃ /NaNO ₃	51
K ₂ Cr ₂ O ₇	artificial neutral networks	Alamine 336	NaOH	52
K ₂ Cr ₂ O ₇	bulk liquid membrane	dicyclohexano-18-crown-6/dichloromethane	KOH	53
K ₂ Cr ₂ O ₇	polymer inclusion membrane	TOA/ONPPE/dichloromethane	NaOH	54
K ₂ Cr ₂ O ₇	SLM	Alamine 336	NaOH	55
Electroplating/tannery effluents containing Cr ^{VI}	emulsion liquid membrane	bis-(2-ethylhexyl)-phosphate/kerosene	H ₂ SO ₄	56
K ₂ Cr ₂ O ₇	emulsion liquid membrane	Alamine 336/kerosene	NaOH	57
K ₂ Cr ₂ O ₇	PVDF	methylchololate/toluene	HNO ₃	58
Cr ^{VI} from tannery wastewater	SLM	trioctylamine	NaOH	59
K ₂ Cr ₂ O ₇	polymer inclusion membrane	Aliquat 336/tertiary amines	NaOH	60
K ₂ Cr ₂ O ₇	microporous PVDF	Hostarex A327/cumene	NaOH	61

PVDF: polyvinylidene fluoride; HFSLM: hollow fiber supported liquid membrane; PVC: polyvinyl chloride; SLM: supported liquid membrane; NPOE: *o*-nitrophenyloctyl ether; THF: tetrahydrofuran; PTFE: polytetrafluoroethylene; TOA: tri-octylamine; ONPPE: *o*-nitrophenylpentyl ether.

In acidic medium, Cr₂O₇²⁻ reacts with hydrogen peroxide in feed compartment⁶³ as

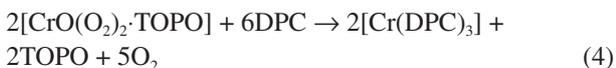


CrO(O₂)₂ or CrO₅ decomposes to chromium(III)⁶⁴ as



TOPO reacts with species CrO(O₂)₂·H₂O at membrane phase⁶³ and stabilizes Cr^{VI} and avoids reduction to Cr^{III}. Since TOPO has no H⁺ for ion exchange with metal ion the extraction of chromium only occurs via a solvating mechanism.⁶⁵

The complex CrO(O₂)₂·TOPO at membrane-strip interface reacts with diphenylcarbazide (DPC) forming complex Cr(DPC)₃.^{66,67} The reaction in the acidic medium in the strip side may be written as



Chemical equation related with extraction process in feed phase is given as follows:



The equilibrium constant for this reaction is as follows:

$$K' = \frac{[\text{CrO}(\text{O}_2)_2 \text{ TOPO}] [\text{H}_2\text{O}]}{[\text{CrO}(\text{O}_2)_2 \text{ H}_2\text{O}] [\text{TOPO}]} \quad (6)$$

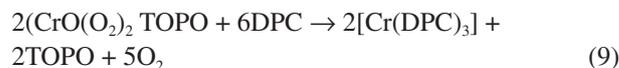
Since concentration of H₂O remains constant, the equilibrium constant is given as:

$$K = \frac{[\text{CrO}(\text{O}_2)_2 \text{ TOPO}]}{[\text{CrO}(\text{O}_2)_2 \text{ H}_2\text{O}] [\text{TOPO}]} \quad (7)$$

The distribution coefficient (K_{Df}) of chromium between aqueous and organic phases (membrane phase) in the feed phase is given by the following relation:

$$K_{Df} = \frac{[\text{CrO}(\text{O}_2)_2 \text{ TOPO}]_{\text{org}}}{[\text{CrO}(\text{O}_2)_2 \text{ H}_2\text{O}]_{\text{aq}}} \quad (8)$$

On the other hand, in the strip side the reaction is as follows:



The distribution coefficient (K_{Ds}) of chromium between membrane and strip phase is given as follows:

$$K_{Ds} = \frac{[\text{CrO}(\text{O}_2)_2 \text{ TOPO}]_{\text{org}}^2}{[\text{Cr}(\text{DPC})_3]_{\text{aq}}^2} \quad (10)$$

The influence of the studied parameters, such as concentration of TOPO, DPC, Cr^{VI} metal ion, and H₂SO₄, on the chromium transport was evaluated by means of the permeability coefficient (P) as described by the mass-transfer model proposed by Danesi.⁶⁸ The permeability coefficient in the feed phase was obtained by using following equation:

$$\ln \frac{C}{C_0} = -\epsilon \frac{S}{V} Pt \quad (11)$$

where P is the permeability coefficient (cm s⁻¹), C₀ is the initial concentration of Cr^{VI} in the feed phase, and C is the concentration of Cr^{VI} in the feed phase at time t (s). S is the effective membrane area (cm²), V (cm³) is the volume of the feed phase and t is the elapsed time.

The permeability coefficient can be obtained from the slope of the linear plot of $\ln \frac{C}{C_0}$ vs. time. In order to quantify the transport through the membrane, flux was calculated using equation 12:

$$J_0 = \left(\frac{dC_f}{dt} \right)_0 \left(\frac{V}{S\epsilon} \right) \quad (12)$$

where J₀ is the initial flux (mol cm⁻² s⁻¹), V (cm³) is the volume of the feed phase, ε is porosity of the membrane, C_f is the concentration of chromium (mol L⁻¹) in the feed phase at elapsed time, t is the time (s) and S is the membrane surface area. Flux (J) was determined from the slope of concentration of chromium in feed phase vs. time, i.e. $\frac{dC_f}{dt}$ and putting it in equation 12, while the volume of solution was 250 mL, and the surface area of the membrane was 16.04 cm² and porosity was 30%.

The percent recovery of Cr^{VI} was also calculated as:

$$\text{Recovery \%} = 100 \left(\frac{C_s}{C_0} \right) \quad (13)$$

where C_s and C₀ are the concentrations of chromium at elapsed time and at the beginning, respectively.

Experimental

Chemicals and reagents

Trioctylphosphine oxide (TOPO; Merck, analytical grade (A. G.), 98%) was used as extractant in toluene diluent (99%). Potassium dichromate (Fluka, A. G., 99%), and H₂O₂ (Sigma-Aldrich, A. G., 30%) solutions were used in the

feed phase while diphenylcarbazide (DPC) (Sigma-Aldrich, A. G., 98%), and H₂SO₄ (Riedel de Haen, A. G., 99%) solution were used in the strip phase. Ethylenediamine (Sigma-Aldrich, A. G., 99%) and NaOH (Merck, A. G., 98%) were also used as receiving phase or stripping reagents. All the solutions were prepared in triply distilled water.

Membrane

The support for the membrane was a microporous polypropylene film (Celgard 2400), with thickness of 25 μm, porosity 41% and a mean pore diameter of 0.043 μm.

Membrane cell (permeator)

All ion permeation experiments were performed at 25 ± 1 °C with a simple batch type permeator (cell) shown in Figure 1. The permeator was made of acrylic material having two compartments with flanges to clamp the membrane between these compartments. Each compartment had enough volume capacity to accommodate 250 cm³ of test solutions. The effective membrane contact area was 16.04 cm².

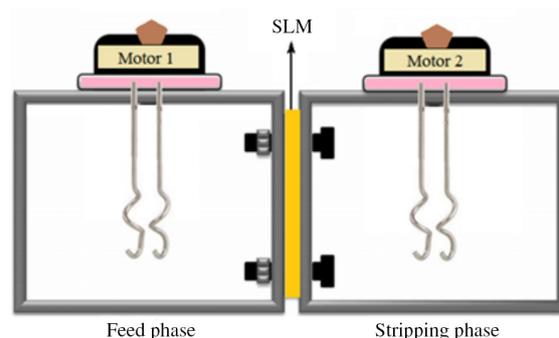


Figure 1. Schematic presentation of liquid membrane permeator cell.

Instruments

The atomic absorption spectrometer Perkin Elmer model 400 was used for determination of total metal ion concentration in the feed and strip solutions ($\lambda = 357.9$ nm, $\Delta\lambda = 0.2$ nm, reducing C₂H₂/air flame). Brookfield viscometer/rheometer LVDV-III was used for viscosity measurement of TOPO in toluene.

Procedure

The supported liquid membranes were prepared by soaking the membrane in a solution of TOPO in toluene for 24 h during which the pores of the membrane are filled with carrier solution by capillary action. Afterwards,

the membrane was taken out of the carrier solution and allowed to drain off for 5 min to remove excess amount of carrier solution from the surface of the membrane. The cell compartments were filled with feed and stripping solutions with the membrane mounted in between the two compartments, such that the two solutions were separated from each other. The solution in each compartment was stirred with an electric stirrer at a speed of 1500 rpm to avoid concentration polarization at the membrane faces. For the permeator experiments, different concentrations of $K_2Cr_2O_7$ (9.6×10^{-4} - 4.81×10^{-4} mol L⁻¹) were used. Different concentrations of DPC (0.0005-0.004 mol L⁻¹) were used in the stripping phase.

Samples from the feed and the stripping solutions were drawn after regular time intervals and analyzed by atomic absorption spectrophotometry.

Results and Discussion

Effect of TOPO concentration on extraction of Cr^{VI}

The effect of TOPO concentration on the extraction of Cr^{VI} has been studied. For this purpose, various concentrations of TOPO were employed in membrane phase. The range of TOPO concentration was from 0.001 to 0.2 mol L⁻¹. It was observed that with the increase in TOPO concentration, the extent of extraction of chromium increases (Figure 2a). However, 0.1 mol L⁻¹ TOPO concentration has exhibited maximum extraction. The same effect is shown in Figure 2b, wherein a decrease in Cr^{VI} in the feed phase can be observed with the increase in TOPO concentration. From Figure 2, it can be concluded

the TOPO concentration of 0.1 mol L⁻¹ is the one which shows the maximum extraction of the chromium ions but beyond 0.1 mol L⁻¹ TOPO concentration the extraction decreases. The limiting value of extraction of chromium at 0.1 mol L⁻¹ TOPO may be attributed to increased viscosity of TOPO solutions which hampers the movement of metal ions through the membrane (the viscosity data has not been included in the text).

The same phenomenon is being reflected in Figure 3, wherein the two curves show the said additive behavior, which is clear from their mirror image nature. By a careful observation, it can be analyzed that a decreasing trend in the concentration of chromium in the feed side is observed, however, the concentration goes to a minimum value at 0.1 mol L⁻¹ TOPO where after, on further increase in the TOPO concentration the transport of chromium towards the strip side is reduced. This might be due to the increase in the viscosity of organic phase of the membrane which hampers the movement of complex through the membrane. This fact can be conversely observed from the strip side where the concentration of chromium increases with the increase of TOPO concentration, reaches a maximum at 0.1 mol L⁻¹ TOPO, and then decreases afterwards. So 0.1 mol L⁻¹ TOPO concentration was an optimum condition for chromium extraction.

Since 0.1 mol L⁻¹ TOPO concentration was optimum concentration exhibiting maximum extraction of chromium, therefore, all subsequent calculations, i.e., percent recovery, distribution coefficient, flux and permeability coefficient, etc., were made at this concentration.

At 0.1 mol L⁻¹ TOPO concentration the chromium concentration was observed at the maximum level, i.e.,

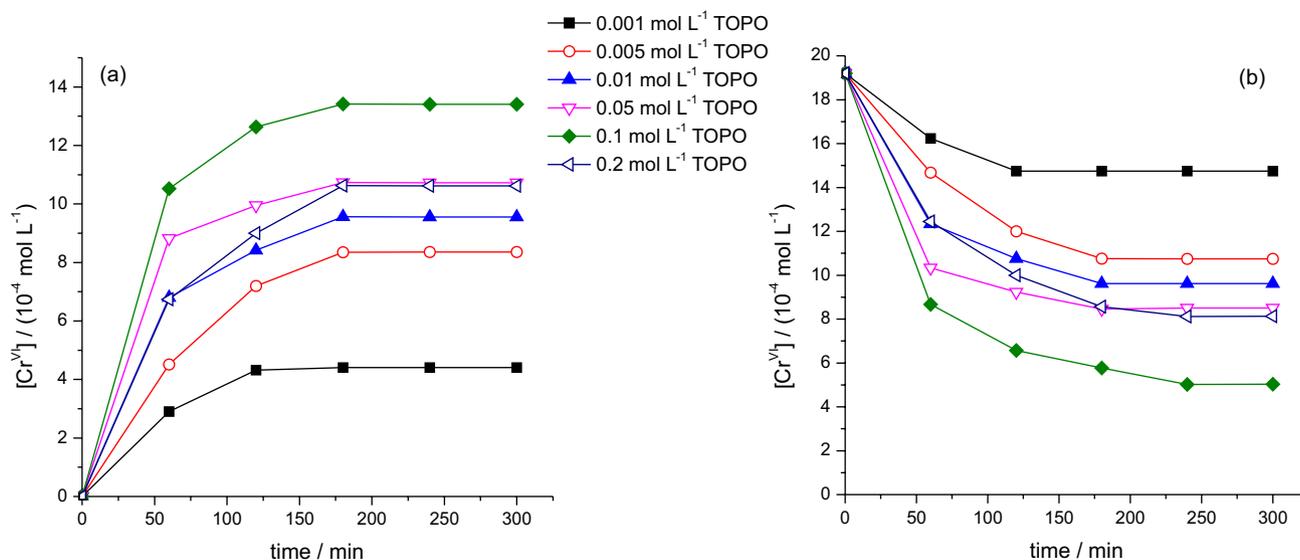


Figure 2. Variation in Cr^{VI} ion concentration with time in the (a) strip and (b) feed solutions at various concentrations of TOPO (initial $[Cr^{VI}] = 19.2 \times 10^{-4}$ mol L⁻¹, $[H_2O_2] = 0.5$ mol L⁻¹, $[DPC] = 0.001$ mol L⁻¹, $[H_2SO_4] = 1$ mol L⁻¹, $[TOPO] = 0.001$ - 0.2 mol L⁻¹).

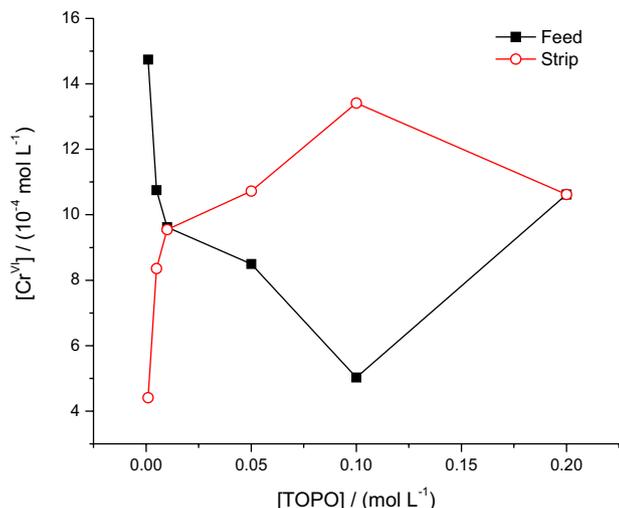


Figure 3. Variation in Cr^{VI} ion concentration in the feed and strip solution at various concentrations of TOPO (initial [Cr^{VI}] = 19.2×10^{-4} mol L⁻¹, [H₂O₂] = 0.5 mol L⁻¹, [DPC] = 0.001 mol L⁻¹, [H₂SO₄] = 1 mol L⁻¹, [TOPO] = 0.001-0.2 mol L⁻¹).

13.42×10^{-4} mol L⁻¹, the percent recovery was found to be 69.84, i.e., almost 70%. The percent recovery decreased by further increase in TOPO concentration. This decrease may be attributed to the reason mentioned above.

The distribution coefficient of chromium between aqueous and the membrane phases (TOPO-toluene) is given by equations 8-10 and were calculated by taking care of mass balance of chromium on the assumption that the total chromium has been distributed among three phases, i.e., feed, membrane, and strip, as shown in Figure 4 and given by the following relation:

$$Cr_{Tot} = Cr_f + Cr_s + Cr_m \quad (14)$$

where Cr_{Tot} is the total chromium concentration and Cr_f , Cr_s , and Cr_m are the chromium concentrations in the feed, strip, and membrane phases, respectively.

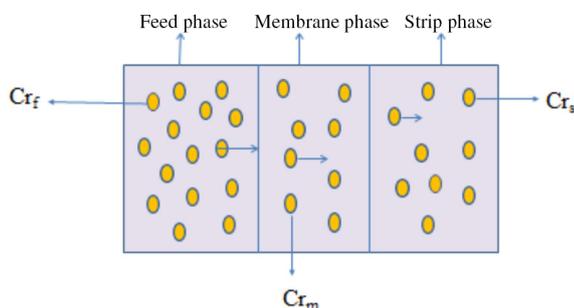


Figure 4. Mass transfer diagram of chromium ions.

Here Cr_{Tot} is the original or initial concentration taken for the experiment, and concentrations of chromium in the feed and strip sides, at any elapsed time of the experiment,

were determined by flame atomic absorption spectrometry. The concentration of chromium in membrane phase was calculated by mass balance, i.e.,

$$Cr_m = Cr_{Tot} - Cr_f - Cr_s \quad (15)$$

This calculation was carried out at two different stages of the experiment, i.e., when the system has not attained the equilibrium and secondly when equilibrium has been attained. The first stage corresponds to the rising part of the chromium concentration vs. time curve in the strip phase (as for example in Figure 2a) and second one corresponds to the concentration vs. time curve when it becomes horizontal to x-axis. Mass balance calculation at the 60th min using equation 14 results in:

$$Cr_m = 0.01 \times 10^{-4} \text{ mol L}^{-1} \quad (16)$$

From this data we can calculate $K_{D_{t_1}}$ before equilibrium by using equation 8

$$K_{D_{t_1}} = \frac{0.01 \times 10^{-4}}{8.67 \times 10^{-4}} = 1.15 \quad (17)$$

On similar ground, K_D at equilibrium point (i.e., 240 min), $Cr_{Tot} = 19.2 \times 10^{-4}$, $Cr_f = 5.02 \times 10^{-4}$ and $Cr_s = 13.41 \times 10^{-4}$, which gives

$$Cr_m = 0.77 \times 10^{-4} \quad (18)$$

The $K_{D_{t_2}}$ at equilibrium becomes

$$K_{D_{t_2}} = \frac{0.77 \times 10^{-4}}{5.02 \times 10^{-4}} = 0.15 \quad (19)$$

Thus, distribution coefficient at 0.1 mol L⁻¹ TOPO concentration (optimum concentration) before equilibrium is 1.15 while it is 0.15 after the equilibrium level is reached. This indicates that the distribution of chromium is higher in the membrane phase at the earlier stage of the experiment as compared to at the later stage. It will be instructive if we can compare distribution coefficient at a given time, of feed and strip sides to elaborate this point further.

The concentration of chromium at 240 min in strip side is 13.41×10^{-4} mol L⁻¹ which gives a distribution coefficient of 0.057. Here the distribution coefficient at the feed side is 0.15 which is much greater than that of the corresponding value of 0.057, which is about 2.6 times greater. This comparison implies that there is a greater affinity of chromium for the membrane phase in the feed region and lesser at strip phase. Thus, there is a natural

tendency of chromium flow from feed to strip side through the membrane and a driving force of diffusion exists at SLM together with enhanced chromium de-complexing at the membrane-strip interface.

Flux of chromium through the membrane was calculated using equation 12 in which the volume of the feed solution (V_f) was 250 mL, the effective surface area (S) of the membrane was 16.04 cm² and its porosity (ϵ) was 41%. The factor $\frac{dC_f}{dt}$ was calculated from the slope of the concentration of chromium in the strip region vs. time curve which was taken at the initial time of the experiment, i.e., the initial slope of the concentration vs. time curve. This value was 2.92×10^{-7} mol L⁻¹ s⁻¹ which gives the flux value (J_0 initial flux) of 1.11×10^{-7} mol cm⁻² s⁻¹. Now let us check the status of the flux just before the establishment of equilibrium. The slope at this region is 4.03×10^{-8} mol L⁻¹ s⁻¹, which gives a flux value of 1.53×10^{-8} mol cm⁻² s⁻¹. Here we note that the flux value decreases from 1.11×10^{-7} to 1.53×10^{-8} mol cm⁻² s⁻¹, which is an obvious phenomena, as chromium transport decreases with the passage of time which becomes zero at equilibrium stage, as can easily be predicted from the zero slope where the curve becomes parallel to the x-axis.

The permeability coefficient was calculated using equation 11, which was arranged in straight line form and slope of the $\ln \frac{C}{C_0}$ vs. time curve (Figure 5) is equal to $-\epsilon \frac{S}{V} Pt$; where the porosity ϵ is equal to 41%, S is the effective surface area of the membrane which is 16.04 cm² and V is the volume of feed solution which is 250 cm³. The average slope was calculated to be 3.33×10^{-5} thus P was calculated as 1.26×10^{-5} cm s⁻¹.

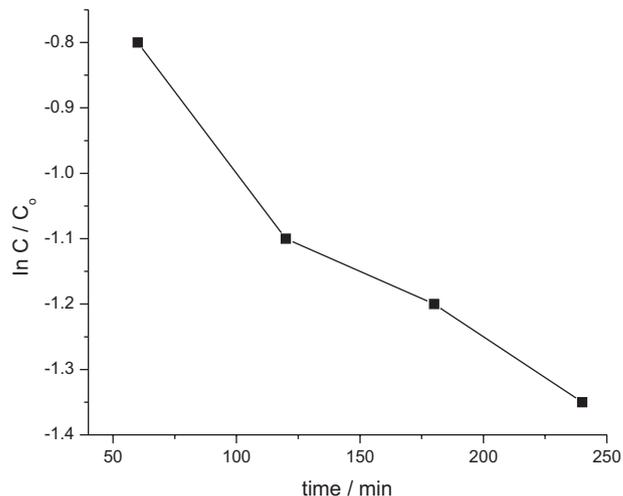


Figure 5. Plot of $\ln C / C_0$ vs. time at 0.1 mol L⁻¹ TOPO concentration.

Effect of diphenylcarbazide (DPC) concentration on extraction of Cr^{VI}

DPC is the common complexing agent for chromium and widely used to extract it.²⁷ In the strip side Cr^{VI} forms a pink complex with DPC. The concentration range of DPC studied in chromium extraction was from 0.0005 to 0.004 mol L⁻¹, shown in Figures 6a and 6b. As indicated in Figures 6a and 6b, with the increase in concentration of DPC the extraction of chromium increases up to 0.001 mol L⁻¹ DPC, beyond which a decrease was observed. DPC forms complex with chromium as Cr(DPC)₃. This indicates that for every one mole of chromium three moles of DPC are required for the complexation. Therefore, initially with the increase in DPC concentration the chromium extraction increases up to 0.001 mol L⁻¹ DPC concentration. Beyond 0.001 mol L⁻¹ DPC concentration the decrease in the extraction of chromium ions has been observed. This might be due to the formation

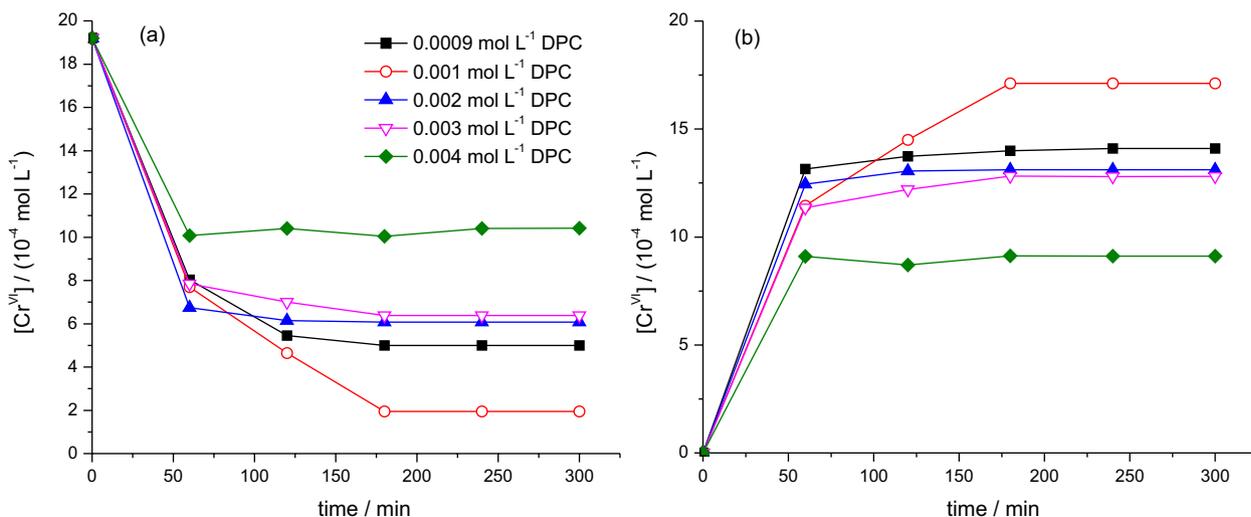


Figure 6. Variation in Cr^{VI} ion concentration with time in the (a) feed and (b) strip solutions at various concentrations of diphenylcarbazide (DPC) (initial [Cr^{VI}] = 19.2×10^{-4} mol L⁻¹, [H₂O₂] = 0.5 mol L⁻¹, [DPC] = 0.0005-0.004 mol L⁻¹, [H₂SO₄] = 1 mol L⁻¹, [TOPO] = 0.1 mol L⁻¹).

of dimer of DPC at elevated concentration which makes it unavailable for complexation.⁶⁹ Thus, 0.001 mol L^{-1} DPC was an optimum concentration for chromium extraction. Therefore, all subsequent calculations were made on this optimum concentration of DPC. The maximum recovery calculated under the mentioned condition was 86%.

Distribution coefficient calculated in the feed region before equilibrium (at 60th min) was 0.008 and at equilibrium (at 240 min) it was 0.072 while corresponding value of strip side was 0.0082. Thus, K_D value at feed side is 8.7 times higher than that of strip side. This suggests that reversal of chromium from strip to feed side is hampered by 8.7 times lower value of K_D in strip side and the higher value of K_D in feed side imposes a so-called pushing effect on chromium transfer towards the feed side.

Flux value was calculated before establishment of equilibrium, i.e., at 60 min which was $1.21 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ while just before establishment of equilibrium, i.e., at 180 min its value was $1.1 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$. The decrease in the flux is obviously due to the decrease in the concentration of chromium ions in the feed region. Permeability coefficient was $7.60 \times 10^{-5} \text{ cm s}^{-1}$.

Effect of Cr^{VI} ion concentration on extraction of Cr^{VI}

The effect of chromium ion concentration on chromium extraction was studied in the range of 9.6×10^{-4} to $48.1 \times 10^{-4} \text{ mol L}^{-1}$ concentration in the feed phase. The concentration of H_2O_2 in feed solution was adjusted to 0.5 mol L^{-1} , DPC in stripping solution at 0.001 mol L^{-1} and

TOPO in membrane phase at 0.1 mol L^{-1} . As indicated in Figures 7a and 7b, the concentration of Cr^{VI} ion decreases in the feed side while at the same time it increases in the strip side. With the increase in Cr^{VI} ion concentration the extraction also increases and gives the maximum value at $19.2 \times 10^{-4} \text{ mol L}^{-1}$ and after that the decrease in the extraction can be observed. This could be attributed to the following reason: as the concentration of metal ions increases, the requirement of H_2O_2 , to make $\text{CrO}(\text{O}_2)_2$ complex, also increases, whereas we have kept H_2O_2 concentration at a constant level which is insufficient to cater for the $\text{CrO}(\text{O}_2)_2$ complex.

Thus, $19.2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cr}^{\text{VI}}$ concentration was the optimum concentration for the extraction of Cr^{VI} ions from the solution and all the relevant calculations were made on this Cr^{VI} concentration. Recovery of 78% was obtained at $19.2 \times 10^{-4} \text{ mol L}^{-1} \text{ Cr}^{\text{VI}}$ concentration.

The distribution coefficient was calculated for both feed and strip sides. It was found that before equilibrium (at 60th min) in the feed side the K_D value was 0.027 while at equilibrium (240th min) it was 0.0195. Similarly, on the strip side, the equilibrium value of K_D was 0.0053. It can be noted that with the passage of time the concentration of chromium increases in the strip side in contrast to the feed side. This is supported by the 3.7 times higher K_D value of feed side.

The flux value before equilibrium was calculated as $8.32 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ while just before the equilibrium the flux value is $3.75 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$. The decrease in flux value was due to the higher concentration of chromium

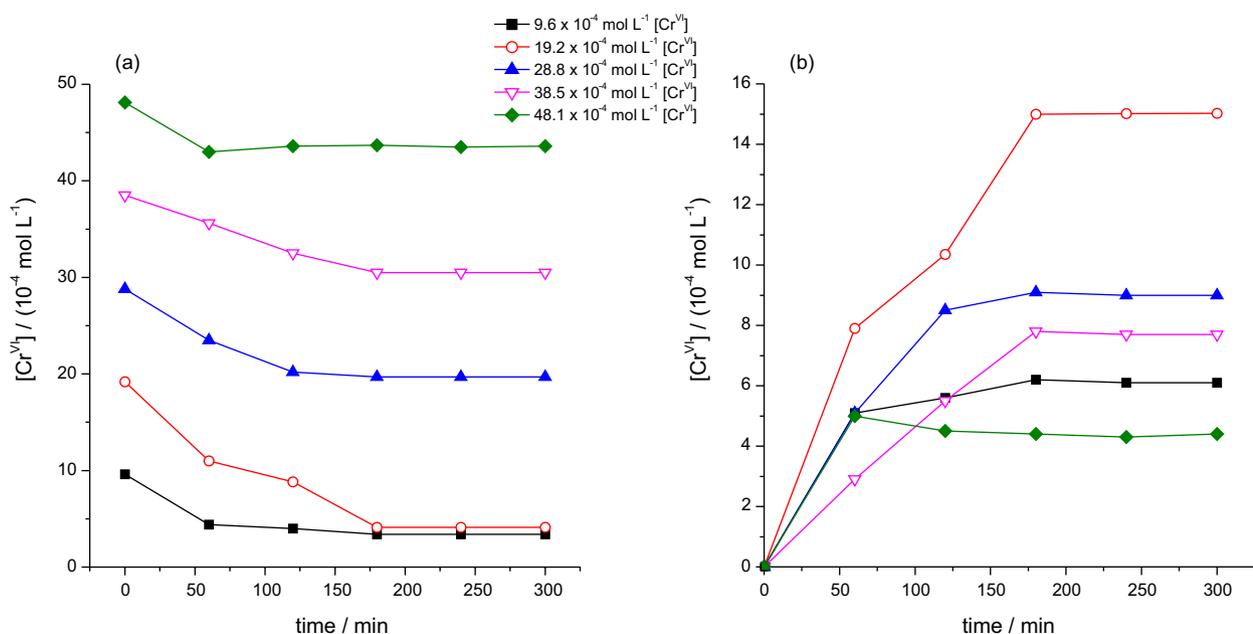


Figure 7. Variation in Cr^{VI} ion concentration with time in the (a) feed and (b) strip solutions at various concentrations of Cr^{VI} ion (initial $[\text{Cr}^{\text{VI}}] = 9.6 \times 10^{-4}$ – $48.1 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] = 0.5 \text{ mol L}^{-1}$, $[\text{DPC}] = 0.001 \text{ mol L}^{-1}$, $[\text{H}_2\text{SO}_4] = 1.5 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.1 \text{ mol L}^{-1}$).

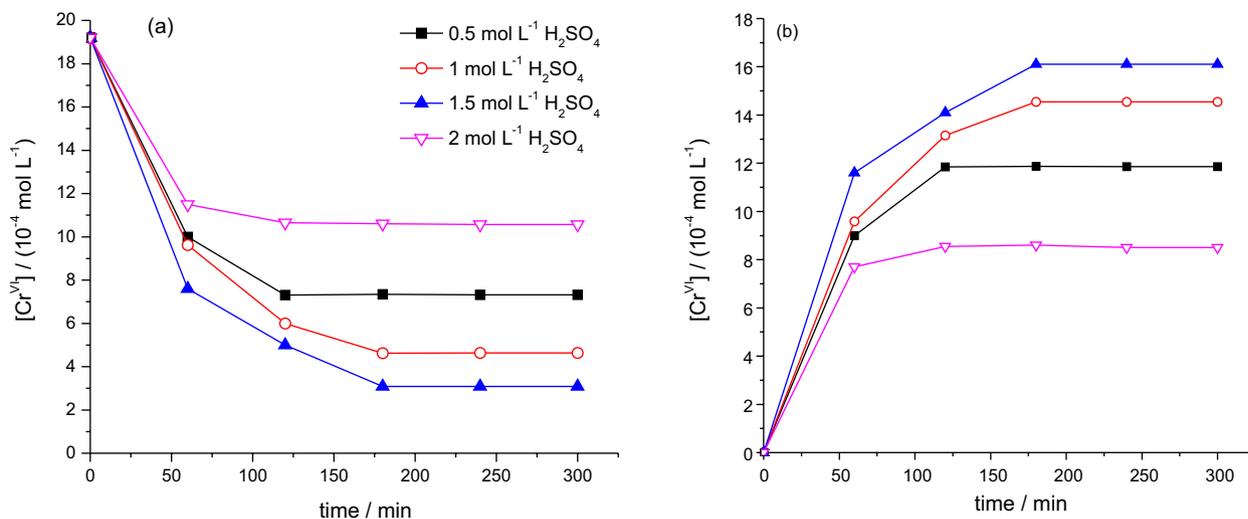


Figure 8. Variation in Cr^{VI} ion concentration with time in the (a) feed and (b) strip solutions at various concentrations of H₂SO₄ (initial [Cr^{VI}] = 19.2 × 10⁻⁴ mol L⁻¹, [H₂O₂] = 0.5 mol L⁻¹, [DPC] = 0.001 mol L⁻¹, [H₂SO₄] = 0.5-2 mol L⁻¹, [TOPO] = 0.1 mol L⁻¹).

in the strip phase than in the feed phase. At equilibrium the flux becomes zero. The value of permeability (P) obtained was 5.28 × 10⁻⁵ cm s⁻¹. This indicates the higher transport of chromium from feed to strip side through membrane.

Effect of H₂SO₄ concentration on extraction of Cr^{VI}

The presence of H₂SO₄ in the strip solution dissociates the CrO(O₂)₂ complex at the strip-membrane interface and releases Cr^{VI} ions which form complex with DPC as Cr^{VI}-DPC complex.²⁶

The effect of H₂SO₄ concentration was studied from 0.5 to 2 mol L⁻¹. Figure 8 indicates the effect of H₂SO₄ concentration on extraction of Cr^{VI} ions in the strip side. The chromium extraction increases with the increase in the H₂SO₄ concentration, which reaches the maximum value at 1.5 mol L⁻¹ of H₂SO₄ concentration. Beyond 1.5 mol L⁻¹ concentration the extraction decreases and this phenomenon might be due to the fact that at higher concentration of H₂SO₄, there will be inability of H⁺ to dissociate the [CrO(O₂)₂.TOPO] complex due to the overcrowding of H⁺ ions at strip-membrane interface.⁷⁰ A concentration of 1.5 mol L⁻¹ H₂SO₄ was the optimum concentration for the extraction of chromium ions, in which 84% chromium was recovered.

The initial flux value obtained was 7.35 × 10⁻⁶ mol cm⁻² s⁻¹ at 60 min. Similarly, just before the equilibrium the flux value was 2.38 × 10⁻⁸ mol cm⁻² s⁻¹ and at equilibrium the flux become zero. Initially, there is a rapid mass transfer of chromium from feed to strip side but, as time passes, as the equilibrium stage approaches there is a decline in a mass transfer rate and ultimately the value of flux becomes zero at equilibrium. The permeability coefficient calculated was 4.80 × 10⁻⁵ cm s⁻¹.

Extraction time

Figure 9 shows the extraction time for chromium metal ion. At optimum conditions the extraction of chromium ion increases with time and at 180 min approximately 80% of chromium was extracted, after which no increase in the extraction was observed.

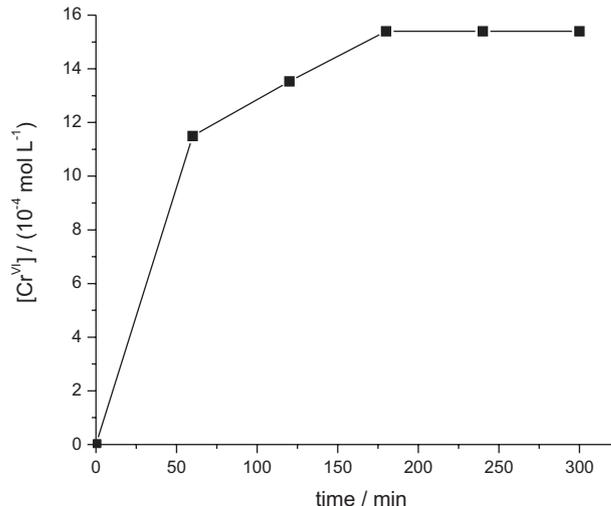


Figure 9. Variation in Cr^{VI} ion concentration with time (initial [Cr^{VI}] = 19.2 × 10⁻⁴ mol L⁻¹, [H₂O₂] = 1.5 mol L⁻¹, [DPC] = 0.001 mol L⁻¹, [H₂SO₄] = 1.5 mol L⁻¹, [TOPO] = 0.1 mol L⁻¹).

Membrane stability

Despite their well-known advantages, SLMs suffer from instability with time. This is mainly due to the loss of carrier and/or membrane solvent from the membrane support which has an influence on both flux and selectivity of membrane.⁷¹ The SLM used in this study was found to be quite stable for 10 days. To study the long term

membrane stability, the extraction experiments were carried out consistently for 10 days (one experimental run *per day*) made under the optimum conditions without re-impregnation of the membrane; however, the feed and strip solutions were replaced for each run. The cell was kept filled with distilled water, between the successive experiments, in order to prevent the dryness of the membrane. The optimum experimental conditions were as follows; Cr^{VI} concentration in the feed of $19.2 \times 10^{-4} \text{ mol L}^{-1}$, $1.5 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$, TOPO concentration in SLM of 0.1 mol L^{-1} in toluene, DPC concentration of 0.001 mol L^{-1} , and $1.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ in stripping phase and stirring speed at 1500 rpm. The results show (Figure 10) that this SLM was quite stable during the investigated time and no decrease in flux and percent recovery of chromium was observed. The study was replicated thrice with relative standard deviation of $\pm 2\%$.

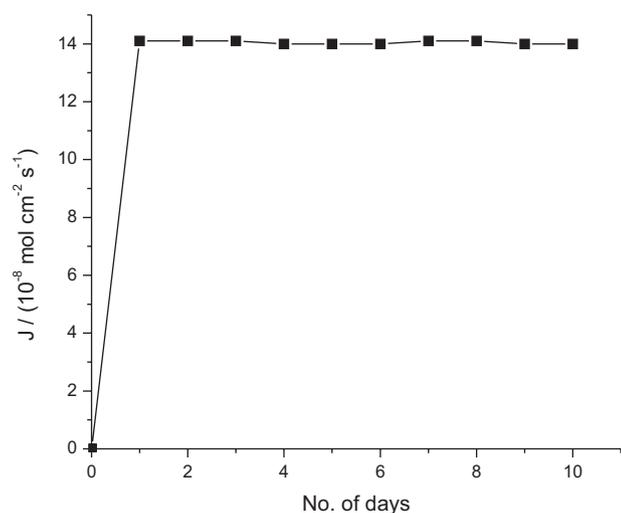


Figure 10. Stability of SLM, flux vs. time (initial $[\text{Cr}^{\text{VI}}] = 19.2 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] = 1.5 \text{ mol L}^{-1}$, $[\text{DPC}] = 0.001 \text{ mol L}^{-1}$, $[\text{H}_2\text{SO}_4] = 1.5 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.1 \text{ mol L}^{-1}$).

Extraction of Cr^{VI} ion from paint industry waste

The SLM designed for Cr^{VI} ion extraction shows efficient transport ability. One of the major applications of chromium is its use in paint industry.¹ The optimized conditions were employed for the recovery of chromium from paint industry wastewater. The wastewater was filtered with Whatman filter paper; 80 mL of filtrate was taken and diluted up to 250 mL with distilled water. The transport of chromium through the SLM was carried out in the presence of other metals, i.e., Co^{II}, Cd^{II}, Cu^{II} and Mn^{II}. It was noted that only Cr^{VI} was transported through the membrane. This shows the selectivity of the TOPO towards Cr^{VI} under these experimental conditions. This analysis is shown in Table 2 and it shows that almost 80% of Cr^{VI} ions were selectively recovered (Figure 11).

Table 2. Analysis of paint industry wastewater

Sample No.	Metal ion	Metal ion concentration / (mol L ⁻¹)	
		Before extraction	After extraction
1	Cd	2.45×10^{-3}	< LOD
2	Co	0.00	< LOD
3	Cr	3.21×10^{-3}	2.58×10^{-3}
4	Cu	2.69×10^{-5}	< LOD
5	Mn	7.28×10^{-6}	< LOD

LOD: limit of detection.

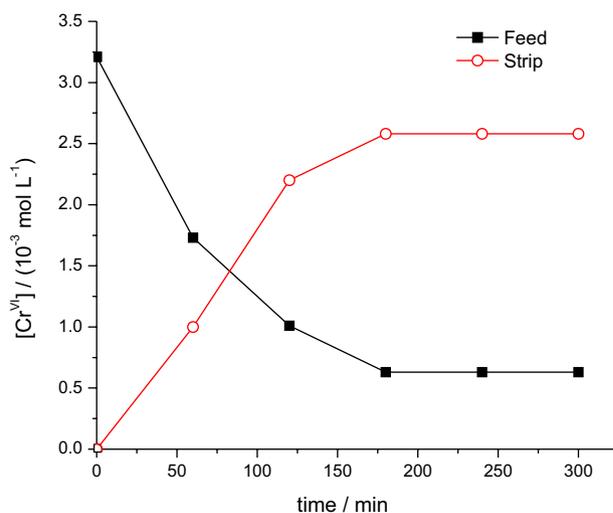


Figure 11. Variation in Cr^{VI} ion concentration in the feed and strip solution vs. time (paint industry waste solution in feed) (initial $[\text{Cr}^{\text{VI}}] = 3.21 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] = 1.5 \text{ mol L}^{-1}$, $[\text{DPC}] = 0.001 \text{ mol L}^{-1}$, $[\text{H}_2\text{SO}_4] = 1.5 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.1 \text{ mol L}^{-1}$).

A careful analysis of Figure 11 shows that the chromium concentration in the final solution after the extraction through the membrane contains $0.63 \times 10^{-3} \text{ mol L}^{-1} \text{ Cr}^{\text{VI}}$ which corresponds to about 33 ppb chromium concentration. According to the World Health Organization (WHO) the recommended maximum allowable concentration in drinking water for Cr^{VI} is 50 ppb. In our case, the released water has 33 ppb concentration of Cr^{VI}, which falls under the safer range of chromium. However, if someone is interested in even lower concentration of chromium in the effluent water, the solution in the feed side (having 33 ppb Cr concentration) may be subjected to further extraction, thus, 6.6 ppb chromium will be left unextracted in the feed side, as 80% chromium will be extracted into the strip side.

Conclusions

The present study demonstrates that Cr^{VI} can be efficiently and selectively transported through the supported liquid membrane by using TOPO as a carrier.

The effects of different parameters, such as concentrations of chromium ion, H₂O₂, TOPO, DPC, and H₂SO₄ were studied on the extraction of chromium. The experimental results revealed that maximum chromium extraction was achieved with 19.2×10^{-4} mol L⁻¹ initial chromium ion concentration, 1.5 mol L⁻¹ H₂O₂ as feed phase, 0.1 mol L⁻¹ TOPO concentration in membrane phase, 0.001 mol L⁻¹ of DPC, and 1.5 mol L⁻¹ H₂SO₄ as stripping phase. The calculations of the percent recovery, distribution coefficient, flux, and permeability were made from the data on the optimum conditions. The extraction time for chromium ion transport was found to be 180 min at which the equilibrium has been established. The stability of SLM under optimum conditions was investigated and it was found that the membrane was stable at least up to 10 days. This SLM system was applied to remove Cr^{VI} from the paint industry wastewater with about 80% efficiency.

Supplementary Information

Supplementary data (details of other parameters and their graphical presentations) are available free of charge at <http://jbcbs.sbgq.org.br> as PDF file.

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