Article

The removal of Cr(VI) through polymeric supported liquid membrane by using calix[4]arene as a carrier

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A B S T R A C T

In this work, the transport and removal of Cr(VI) were achieved through supported liquid membrane (SLM) by using a 5,17, di-tert-butyl-11,23-bis[(1,4-dioxa-8-azaspiro [4,5]decanyl)methyl]-25,26,27,28-tetrahydroxy calix [4]arene carrier, dissolved in 2-nitrophenyl octyl ether dichloromethane. The studied parameters are the solvent effect in the membrane phase, the effect of carrier concentration, and the acid type in the donor phase. The Celgard 2500 was used as a membrane support. We used the Danesi mass transfer model to calculate the permeability coefficients for each studied parameter. In addition, AFM and SEM techniques were used to characterize the surface morphology of the prepared Celgard 2500 membrane that included the calix[4]arene carrier.

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1. Introduction

The earth is degraded through environmental pollution due to problems caused by technological advances and industrialization, combined with rapidly increasing populations. Environmental pollution emerged for the first time at the beginning of urban life, and has increased parallel with industrial development. Particularly in the second half of the twentieth century, increasing environmental pollution due to accelerated population growth caused more pollution of living resources, and as a result, the degradation of the ecosystem balance became increasingly more serious. Irregular urbanization, uncontrolled population growth, and unplanned development of the industry cause problems known as pollutant disposal and pollution. These wastes are defined as solid, liquid, and/or gaseous substances, which have physical, chemical, and/or bacteriological characteristics that change the properties of the entrances by altering their properties [1,2].

Certain wastes also fall in the class of hazardous and harmful wastes. This is waste that pollutes underground and surface waters, which have chronic toxicity and carcinogenic effects, and accumulates in the environment; it enters into living organisms through respiration, digestion, or skin absorption, and it cannot be discharged. The main source of toxicity is the heavy metals in this class. Therefore, environmental pollution from these heavy metals is currently one of the most important problems in the world, and it is necessary to clean the industrial wastes containing these metals before they are left to the environment [3].

For these reasons, separation and purification technologies and processes have become very important. Various techniques are used to remove some metals and compounds that cause environmental pollution (especially water pollution) and that are important for industrial applications. Chemical precipitation, electrodialysis, ion exchange, distillation, reverse osmosis, solvent extraction, ultrafiltration, and liquid membranes are some of these techniques [4]. In the separation and purification processes in which these techniques are used, it is very important that the toxic metals be selectively separated and removed [5].

Liquid membrane technology is one alternative method of membrane technology that has recently become very popular [6]. Liquid membranes are crucial in separation technology and purification processes, as they are effective systems for separating substances from diluted solutions. Membrane processes are primarily used for filtration, concentration, and purification purposes. Liquid membranes have a distinctive feature among these processes and have been studied extensively in recent years, in order to develop new, selective, and stable separation systems with special chemical reactions [7]. Liquid membranes normally combine the extraction and stripping processes into a single process. The single-stage liquid membrane process provides maximum driving force for separation of the respective components, and thus provides the best separation and recovery.

In SLMs, the liquid membrane phase is an organic liquid that impregnates in the pores of a microporous support material. When the organic liquid comes into contact with the microporous support, it easily impregnates the pores and forms the SLM [8]. For the extraction of target material, the organic-based SLM is placed between the donor and acceptor solutions. The SLM acts as a semi-permeable membrane for the transport of the target material from the feed solution to the stripping solution. The organic phase in SLM is immiscible with aqueous feed and stripping solutions, and it generally contains an inert organic solvent or extractant [9].

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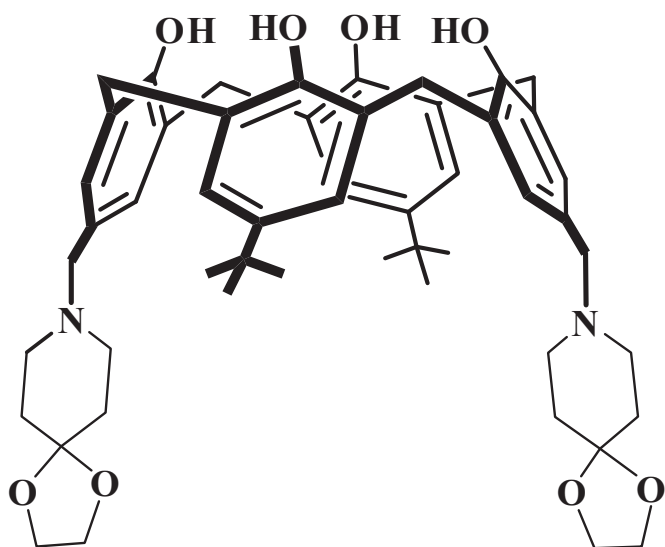E-mail address: hkalpoguz@pau.edu.tr (H.K. Alpoguz).

Fig. 1. Structure of calix[4]arene derivative used as carrier (5,17, di-*tert*-butyl-11,23-bis [(1,4-dioxa-8-azaspiro[4,5]decanyl)methyl]-25,26,27,28-tetra-hydroxy calix[4]arene).

The supported liquid membrane technique has become one of the treatment technologies used to remove specific substances from waste water and for recovering valuable substances, and it has considerable advantages over other liquid membrane techniques. The advantages of SLMs are: its use of organic solvent and carrier in small quantities, its mass transfer in one step, its achievement of a high separation factor, its efficient separation of substances, and its low separation cost [10].

Chromium is the most toxic and mutagenic metal ion found in biological systems. Although chromium can be found in many different forms, the most common and stable forms are trivalent chromium(III) and hexavalent chromium(VI) species. Cr(III) is slightly less soluble at neutral and alkaline pH, and less toxic than Cr(VI). Unlike other heavy metals, Cr(VI) oxides or chromates are readily soluble in the liquid phase at almost all pH ranges, and therefore Cr(VI) is one of the most toxic materials that must be urgently controlled.

In this paper, the separation of Cr(VI) metal cation was achieved by using the supported liquid membrane technique, which is an effective separation method. The transport properties of the Cr(VI) metal cation have been investigated, and the removal of Cr(VI) has been effectively carried out by using a calixarene derivative as a carrier. Calixarenes have the ability to complex with cations, anions, and neutral compounds – both in the solid phase and in the solution – as they have cavities in which different guest molecules can be placed. For this reason, they are widely used as a molecule and ion carrier. In this study, the aim was to compare the transport efficiencies of different parameters (carrier ligand concentration, donor phase acid type and concentration, solvent, surface characterization) and then compare them with each other [11–14].

5,17di-*tert*–butyl-11,23-bis[(1,4-dioxa-8-azaspiro[4,5]decanyl) methyl]-25,26,27,28-tetra-hydroxy calix[4]arene is the carrier ligand (Fig. 1), which was synthesized according to the literature method [12, 15]. Celgard 2500 membrane was used as the solid support.

2. Experimental

2.1. Reagents and chemicals

Organic compounds were purchased from Fluka such as 2-NPOE (2-nitrophenyl octyl ether), and dichloromethane (CH_2Cl_2) and used without further purification. Inorganic compounds were purchased from Merck such as potassium dichromate ($K_2Cr_2O_7$), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3), ammonium acetate (CH_3COONH_4), sodium acetate (CH_3COONa), and acetic acid (CH_3COOH) and they were used without further purification too. The polymeric film Celgard 2500 (thickness: 25 μm, porosity 55%) was obtained from Celgard Inc. (Germany).
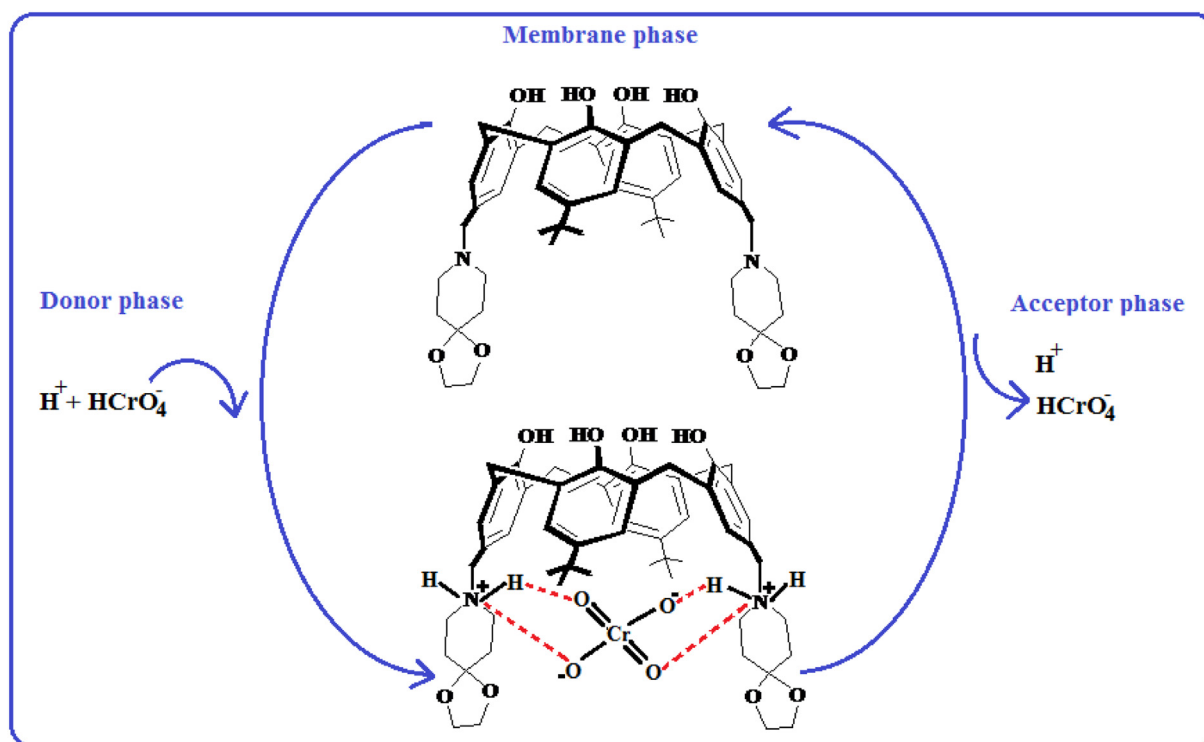

Fig. 2. Schematic illustration of mechanism between Cr(VI) and calix[4]arene.

2.2. Experimental procedure

Experimental conditions were prepared the same as in our previous studies [16,17]. Transport experiments were carried out in a permeation cell that consisted of two identical cylindrical compartments. The supported liquid membrane consisted of a thin, microporous polypropylene film that immobilized the solution of calix[4]arene carrier in organic solvents. An aqueous solution of $0.1\ mmol \cdot L^{-1}\ K_2Cr_2O_7$ in $0.1\ mol \cdot L^{-1}$ HCl was used as a feed phase, and $0.1\ mol \cdot L^{-1}$ sodium acetate solution was used as the stripping phase. The soaking time of the Celgard 2500 membrane was 24 h, and the stirring speed was chosen as $500\ r \cdot min^{-1}$ in all transport experiments. The samples taken were analyzed with a UV spectrometer to determine Cr(VI), as in our previous studies. All kinetic results were calculated according to the mass transfer model described by Danesi [15,18].

The permeability coefficient (P) is given in Eq. (1).

$$P = \varepsilon \frac{dC}{C} \frac{1}{dt} \frac{V}{A} \qquad (1)$$

By integrating Eq. (1), the following Eq. (2) was obtained:

$$\ln \frac{C_i}{C} = \varepsilon \frac{A}{V} Pt \qquad (2)$$

where P is the permeability coefficient ($cm \cdot s^{-1}$), C_i 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). ε is the porosity of the supported liquid membrane (55%), A is the effective membrane area (9.08 cm^2), and V is the volume of the feed phase (ml).

The knowledge of P values allows an establishment of the initial membrane flux (J_i) according to Eq. (3).

$$J_i = PC_i \qquad (3)$$

To describe the efficiency of Cr(VI) removal from the feedphase, we calculated the recovery factor (RF) with Eq. (4).

$$RF = \frac{C_i - C}{C_i} \cdot 100\% \qquad (4)$$

The suggested schematic illustration of the mechanism between Cr(VI) and calix[4]arene carrier is presented in Fig. 2.

2.3. Surface characterization

Atomic Force Microscopy (AFM, Veeco di Caliber) and Scanning Electron Microscopy (SEM, Zeiss LS-10) measurements were applied to illuminate both the structure of the calix[4]arene carrier and how the carrier was connected to the Celgard 2500 support layer in the supported liquid membrane transport studies. In surface characterization studies, AFM is the most-used method that obtains topographic images of the membrane surface. For this reason, a surface photograph of the Celgard 2500 membrane with and without carrier was taken under optimal conditions. AFM and SEM images of the carrier-free Celgard 2500 membrane are shown in Figs. 3(a,b) and 4(a,b). The differences are clear between the Celgard 2500 membrane (carrier-free) and the Celgard 2500 membrane with calix[4]arene derivative.

As can be seen in the AFM images of the Celgard 2500 membrane without carrier, the shaded areas show the highest points, and the darker areas show the pores in the vertical profile. The difference between the membranes in Fig. 3(a) and (b) makes the addition of the calix[4]arene derivative carrier quite apparent. In Fig. 3(b), pores, light colored areas, and roughness of the AFM image were increased by adding the calix[4]arene derivative carrier to the Celgard 2500 membrane.
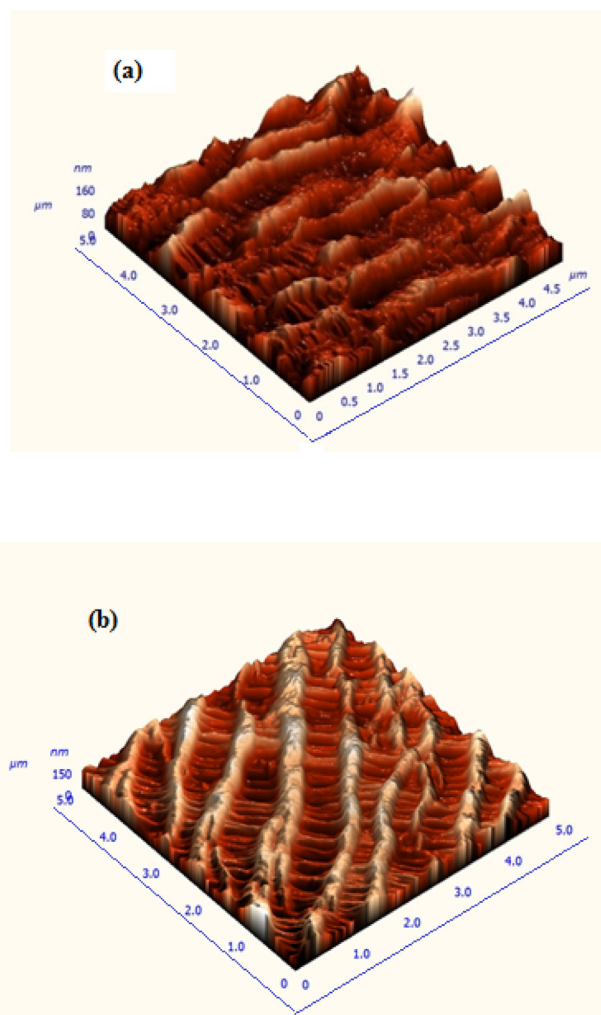
Fig. 3. (a) AFM image of the original Celgard 2500 support layer, (b) AFM image of Calix[4] arene/Celgard 2500/2-NPOE and CH$_2$Cl$_2$ supported liquid membrane.

When SEM images (a) and (b) of the Fig. 4 are compared, the difference between the Celgard 2500 membranes with and without carrier is clearly visible. In the SEM image of the Celgard 2500 membrane without carrier (Fig. 4(a)), gaps can be seen in the pores of support material and the color is light, while the SEM image of the Celgard 2500 with carrier has darker areas and the size of the pores is decreased. This suggests that our carrier is well-connected to the Celgard 2500 membrane.

3. Results and Discussion

3.1. Effect of carrier concentration

In supported liquid membrane transport studies, the effect of transport concentration on the membrane phase is very important. Therefore, the experiments were performed at four different carrier concentrations (0.75×10^{-3}, 1.00×10^{-3}, 1.50×10^{-3} and $2.00 \times 10^{-3}\ mol \cdot L^{-1}$), in order to determine the optimal carrier concentration in membrane composition. While working at different carrier concentrations, other conditions were kept constant. The experimental conditions were $1 \times 10^{-4}\ mol \cdot L^{-1}\ K_2Cr_2O_7$ solution in $0.1\ mol \cdot L^{-1}$ HCl in the donor phase, with 0.75×10^{-3}, 1×10^{-3}, 1.5×10^{-3}, and $2 \times 10^{-3}\ mol \cdot L^{-1}$ calix[4]arene carriers in the membrane composition, which were dissolved in dichloromethane at 5% of 2-NPOE and $0.1\ mol \cdot L^{-1}$ of sodium acetate solution in the acceptor phase.
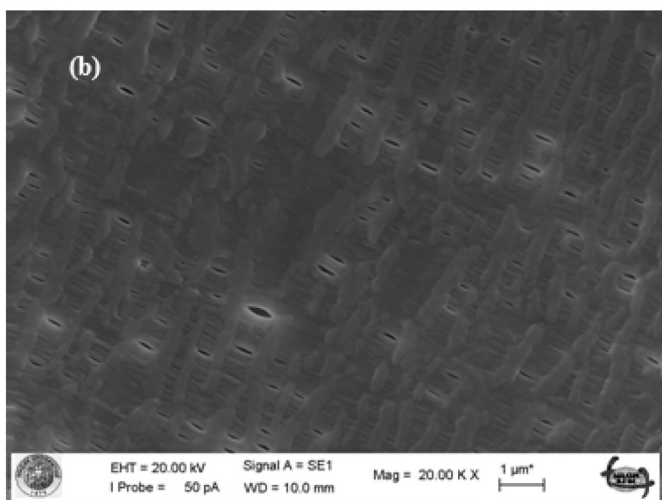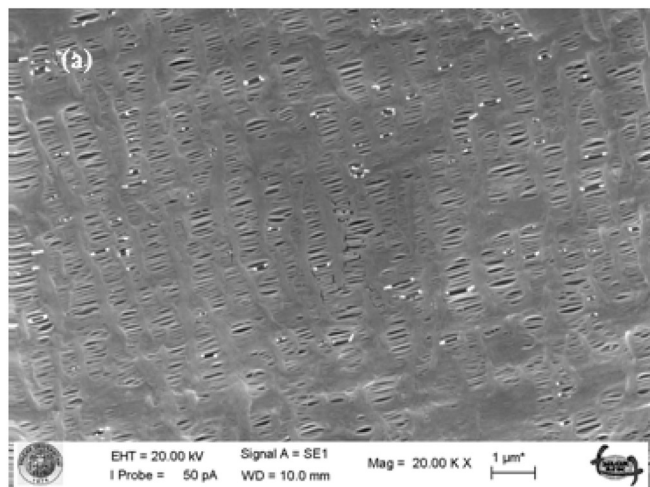
Fig. 5. In $(C/C_i) - t$ graph at different carrier concentrations.

Fig. 4. (a) SEM image of original Celgard 2500 support layer, (b) SEM image of Calix[4] arene/Celgard 2500/2-NPOE and CH_2Cl_2 supported liquid membrane.

In Fig. 5, an In (C/C_i) versus time graph was drawn for the different concentrations of calix[4]arene carrier in supported liquid membrane transport experiments. The values of permeability (P), flow rate (J), and recovery factor (RF) were calculated from the values of the rate constant (k). The kinetic results were given in Table 1.

Fig. 6 presents recovery factor percentage (RF) values for each carrier concentration. The transport efficiency increased up to the 1×10^{-3} mol·L^{-1} carrier concentration, and sharply declined after this concentration. Thus, this concentration was kept as an optimum. The recovery factor is a determinative factor for the transport experiments. As seen in Fig. 6, the recovery factors of the supported liquid membrane transport studies performed at 1×10^{-3} and 1.5×10^{-3} mol·L^{-1} carrier concentrations are higher than the results of other carrier concentrations (0.75×10^{-3} and 2×10^{-3} mol·L^{-1}). There was a regular decrease when the concentration was above 1×10^{-3} mol·L^{-1}.

This phenomenon was attributed to the increased carrier concentration, which increased the membrane viscosity. The increased carrier concentration increases the viscosity and so reduces the diffusion constant. Increased membrane viscosity results in a decrease in the transport efficiency. When a certain limit value was exceeded, the kinetic data began to decrease, because the Cr(VI)–carrier complex that occurs at the donor/membrane phase interface was limited in its diffusion.
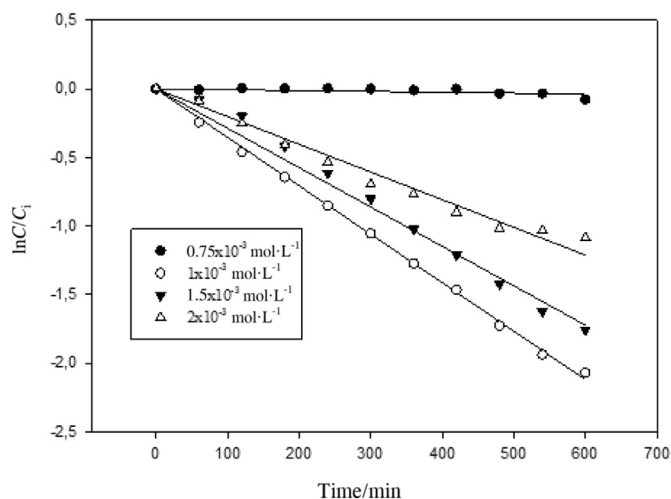
The recovery value was 88.1% in the transport experiment when the 1×10^{-3} mol·L^{-1} carrier concentration was used, whereas it decreased to 66.23% for the 2×10^{-3} mol·L^{-1} carrier concentration. As understood from these kinetic data, the transport of Cr(VI) metal had reached the maximum level when supported liquid membrane experiments were carried out with the 1×10^{-3} mol·L^{-1} calix[4]arene carrier concentration. We used this concentration of 1×10^{-3} mol·L^{-1} – the maximum carrier concentration – as the optimum carrier concentration in our future supported liquid membrane transport studies.

Table 1
Kinetic results at different carrier concentrations

Carrier concentration$\times 10^3$/mol·L^{-1}	$k \times 10^5$ /s^{-1}	$P \times 10^6$ /m·s^{-1}	$J \times 10^6$ /mol·m^{-2}·s^{-1}	RF/%
0.75	0.48	0.62	0.06	7.45
1.00	**5.85**	**7.62**	**0.76**	**88.10**
1.50	5.20	6.76	0.67	82.70
2.00	3.21	4.17	0.41	66.23

Donor phase: 1×10^{-4} mol·L^{-1} $K_2Cr_2O_7$, 0.1 mol·L^{-1} HCl, membrane composition 0.75×10^{-3}, 1×10^{-3}, 1.5×10^{-3} and 2×10^{-3} mol·L^{-1} calix[4]arene containing carriers 5% 2-NPOE, dichloromethane in solution, acceptor phase: 0.1 mol·L^{-1} sodium acetate solution. Boldfaced data represents the optimum carrier concentration.
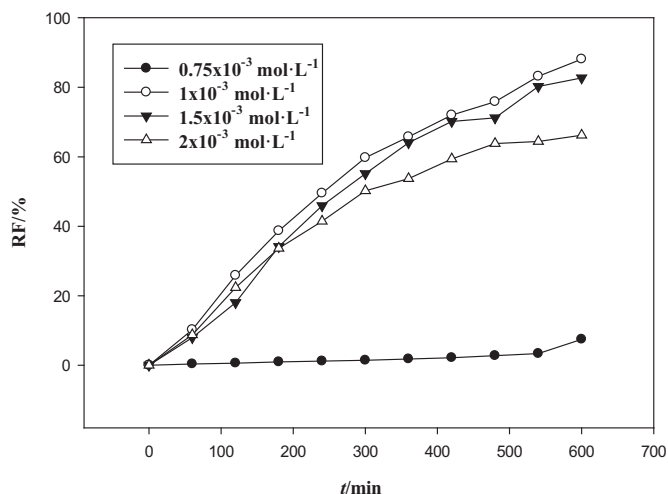

Fig. 6. RF plotted against time for different carrier concentrations.

3.2. Effect of solvents

The choice of solvent is an important parameter in the transport studies of Cr(VI) metal cations carried out *via* supported liquid membranes. For this purpose, we conducted the experiments with di-octyl terephthalate, tritolyl phosphate, tris(2-butoxy ethyl)phosphate, tris (2-ethylhexyl)phosphate, and 2-NPOE/CH₂Cl₂. The kinetic data obtained from this experiment are given in Table 2.

Table 2
Kinetic results in different solvents

Solvents	$k \times 10^5$ /s^{-1}	$P \times 10^6$ /m·s^{-1}	$J \times 10^6$ /mol·m^{-2}·s^{-1}	RF/%
Di-octyl terephthalate	0.72	0.93	0.09	1.00
Tritolyl phosphate	0.82	1.07	0.11	2.00
Tris(2-butoxy ethyl)phosphate	1.85	1.54	0.15	19.77
Tris(2-ethylhexyl)phosphate	2.10	2.73	0.27	42.86
2-NPOE/CH₂Cl₂	**5.85**	**7.62**	**0.76**	**88.10**

Donor phase: 1×10^{-4} mol·L^{-1} K₂Cr₂O₇, 0.1 mol·L^{-1} HCl, membrane composition, 4.75 ml CH₂Cl₂ and 0.25 ml 2-NPOE, 5 ml di-octyl terephthalate, 5 ml tritolyl phosphate, 5 ml tris(2-ethylhexyl)phosphate, 5 ml tris(2-butoxy ethyl)phosphate; 1×10^{-3} mol·L^{-1} calix[4]arene carrier, acceptor phase: 0.1 mol·L^{-1} sodium acetate solution. Boldfaced data is the optimum solvent type for the membrane.

The maximum kinetic data was reached when 2-NPOE/CH₂Cl₂ was used as a solvent in supported liquid membrane transport experiments, as seen in Table 2. The 2-NPOE solvent is an alternative solvent in SLM work. The extremely low water solubility of nitro phenyl alkyl ethers (NPHE-hexyl, NPOE-octyl) allows the membranes to have a very stable structure. When nitro phenyl alkyl ether solvents are used, the organic solvent–carrier interaction is not likely to diffuse into aqueous phases. For this reason, the membrane is extremely stable. The only disadvantage of using this solvent is its price, as it is more expensive than other organic solvents.

It is apparent from the results that the permeability values are remarkably different in different solvents, as found in the order of 2-NPOE/CH₂Cl₂ > tris(2-ethylhexyl)phosphate > tris(2-butoxy ethyl) phosphate > triethyl phosphate > di-octyl terephthalate. In the case of tris(2-ethylhexyl)phosphate, tris(2-butoxy ethyl)phosphate, triethyl phosphate, and di-octyl terephthalate, the values of the solvents' permeabilities are smaller than 2-NPOE/CH₂Cl₂. Therefore, we used 2-NPOE/CH₂Cl₂ as a membrane solvent in our SLM studies. In addition, the polymeric support materials used are very important to the stability of the membrane [19,20]. A good polymeric support should be have some features such as high porosity, small pore size, good mechanical strength, chemical resistance, thinness, hydrophobicity, and low cost.

Two important features come to the forefront when determining the type of solvent. These are the dielectric constant of the solvent and the viscosity. Table 3 shows the dielectric constants and viscosities of the solvents that we used in our supported membrane transport studies.

As seen in Table 3, the highest transport of Cr(VI) was obtained with 2-NPOE, which has the highest dielectric constant and the lowest

Table 3
Dielectric constants and viscosities of solvents used in supported liquid membrane transport studies

Solvent type	εr	$\eta \times 10^3$/Pa·s
2-Nitrophenyl octyl ether (2-NPOE)	24	12.35
Tris(2-ethylhexyl)phosphate (T2EHP)	4.8	13.1
Tris(2-butoxy ethyl)phosphate (TBEP)	4.2	13.8
Di-octyl terephthalate (DOPT)	(4–5)	54.77
Tritolyl phosphate	2.78	34

viscosity. Ion pairs are more easily dissociated with a high dielectric constant. Each ion has a higher diffusion coefficient than their neutral form; the target solutes and carriers complex easily with these ion pairs. Thus, ions are located more easily between the active sites of neighboring groups of solvents and the carrier [21]. As can be understood from Table 3, kinetic data were significantly reduced when tritolyl phosphate was used, as it has the lowest dielectric constant as well as di-octyl terephthalate, which has the highest viscosity. This is an expected result according to the Stokes–Einstein equation (Eq. (5)).

$$D = \frac{k_B T}{6\pi\eta r} \tag{5}$$

In Eq. (5), D is the diffusion constant, k_B is the Boltzmann constant, η is the viscosity of the solvent, r is the radius of the spherical particle, and T is the temperature in Kelvin. The diffusion coefficient of viscosity and the Stokes–Einstein equation vary with inverse proportions [19]: an increase in viscosity results in a reduction in diffusion, which leads to a reduction permeability of the membrane. Fig. 7 presents the permeability, flux, and rate constant values for each solvent (1: di-octyl terephthalate, 2: tritolyl phosphate, 3: tris(2-butoxy ethyl)phosphate, 4: tris(2-ethylhexyl)phosphate and 5: a solution of 5% of 2-NPOE in dichloromethane).
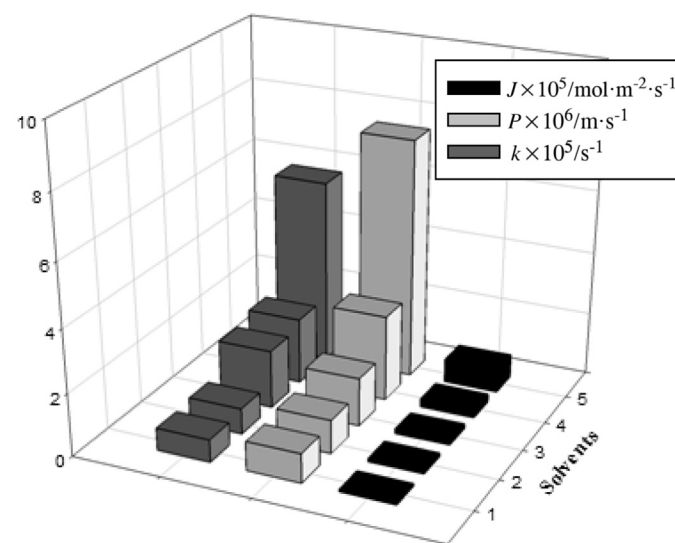
Fig. 7. The effect of solvent type (1: di-octyl terephthalate, 2: triethyl phosphate, 3: tris(2-butoxy ethyl)phosphate, 4: tris(2-ethylhexyl)phosphate, 5: 2-NPOE/CH₂Cl₂).

3.3. Effect of acid type and concentration in donor phase

It is crucial to determine the acid type effect in the donor phase, to provide the Cr(VI) cations in the form of dichromate ions. For this reason, three different kinds of acid species were used to ensure the acidity of the aqueous solution in the donor phase. The concentration of HCl, HNO₃, and H₂SO₄ acids in the donor phase was arranged at 0.1 mol·L^{-1}; the other experimental conditions were kept same. The best kinetic data was obtained when HCl was used in the donor phase in supported liquid membrane transport experiments. The calculated kinetic data were very low when the other two acid types (nitric acid and sulfuric acid) were used. The obtained kinetic data (k, P, J and RF) are given in Table 4.

The most important factor in the selection of donor phase acid type is the complexation reaction between chromate anions and acid type. No complex between Cr(VI) and nitric acid occurred like the complex

Table 4
Kinetic results for different acid species in the donor phase

Donor phase acid type	$k \times 10^5/s^{-1}$	$P \times 10^6/m \cdot s^{-1}$	$J \times 10^6/mol \cdot m^{-2} \cdot s^{-1}$	RF/%
HNO$_3$	0.29	0.39	0.04	0.48
H$_2$SO$_4$	0.24	0.31	0.03	1.34
HCl	**5.85**	**7.62**	**0.76**	**88.10**

Donor phase: 1×10^{-4} mol·L^{-1} K$_2$Cr$_2$O$_7$, 0.1 mol·L^{-1} HCl, HNO$_3$ and in H$_2$SO$_4$, membrane composition: solution of 5% 2-NPOE in dichloromethane containing 1×10^{-3} mol·L^{-1} calix[4]arene carrier, acceptor phase: 0.1 mol·L^{-1} sodium acetate solution. Boldfaced data represents the optimum acid type in the donor phase.

according to Eqs. (6) and (7). Parallel to this situation, the transport efficiency is much lower when nitric acid is used as an acid type in the donor phase. The complex between sulfate anions and chromate cations limits the diffusion and transport of the donor/membrane interfaces, because the sulfuric acid diameter is larger than hydrochloric acid. As a result, it is expected that the highest transport efficiency is achieved in supported liquid membrane experiments in which the donor phase acid type is selected as HCl.

$$HCrO_4^- + HSO_4^- \rightleftharpoons CrO_3SO_4^{-2} + H_2O \tag{6}$$

$$HCrO_4^- + H^+ + Cl^- \rightleftharpoons CrO_3Cl^- + H_2O \tag{7}$$

Another important parameter in the supported liquid membrane transport experiments is the donor phase acid concentration effect. For this purpose, we carried out liquid membrane transport studies with different donor phase concentrations (0.025, 0.050, 0.100, 0.250 and 0.500 mol·L^{-1}), to determine the optimal donor phase acid concentration.

Table 5 presents k, P, J, and RF kinetic values. The flux and other kinetic results increased by increasing the acid concentration of the donor phase from 0.025 mol·L^{-1} to 0.1 mol·L^{-1}. The highest result was achieved at 0.1 mol·L^{-1}, and results began to decrease after this concentration value.

Table 5
Kinetic results at different donor phase acid concentrations

Donor phase acid concentration/mol·L^{-1}	$k \times 10^5/s^{-1}$	$P \times 10^6/m \cdot s^{-1}$	$J \times 10^6/mol \cdot m^{-2} \cdot s^{-1}$	RF/%
0.025	0.77	1.01	0.10	25.58
0.050	3.12	4.06	0.41	45.23
0.100	**5.85**	**7.62**	**0.76**	**88.10**
0.250	3.56	4.63	0.46	52.35
0.500	1.20	1.57	0.16	15.39

Donor phase: $1 \times 10{-4}$ mol·L^{-1} K$_2$Cr$_2$O$_7$, 0.025, 0.05, 0.1, 0.25 and 0.5 mol·L^{-1} HCl, membrane composition: solution of 5% 2-NPOE containing 1×10^{-3} mol·L^{-1} calix[4]arene carrier in dichloromethane, acceptor phase: 0.1 mol·L^{-1} sodium acetate solution. Boldfaced data is the optimum acid concentration in the donor phase.

The pH difference between the donor and acceptor phases is the most important driving force in supported liquid membrane studies. Dichromate anions bind to the calix[4]arene derivative carrier at low pH values and are removed at higher pH values. Therefore, the pH value of the donor phase should be kept lower than the pH value of the acceptor phase, in order to achieve efficient and effective transport of dichromate ions.

Fig. 8 presents the RF values *versus* the different acid concentration values. These results indicate that the maximum transport efficiency was achieved when 0.1 mol·L^{-1} hydrochloric acid concentration was used in the donor phase. For this reason, 0.1 mol·L^{-1} was used as an optimal donor phase acid concentration in supported liquid membrane transport studies.
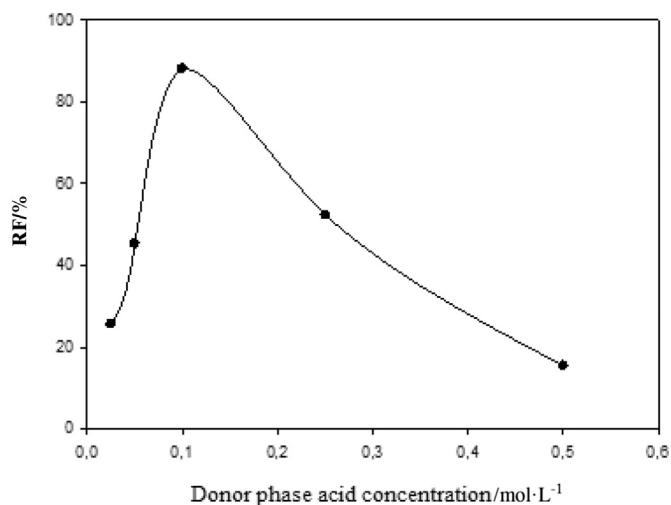

Fig. 8. RF graph against different donor phase acid concentrations.

4. Conclusions

In this study, the separation of Cr(VI) metal cations was achieved by using the supported liquid membrane technique, which is an effective separation method with 88.1% recovery factor. The experiments were performed at different parameters, and the concentration values of the samples were taken at specific time intervals and determined in the UV spectrophotometer. The kinetic values of rate constant (k), flow (J), permeability coefficient (P), and recovery factor (RF) were calculated. As a result of the experiments, it was seen that the flow rate changed linearly with the studied parameters for the transport of the Cr(VI) metal cation. In addition, all other parameters (carrier ligand concentration, donor phase acid species and concentration, solvent effect) were found to be important factors for the transport of the Cr(VI) metal cation.

AFM and SEM pictures demonstrated that the carrier had a good connection with membrane. The experimental results showed that the calix[4]arene had a great selectivity to Cr(VI) metal cation.

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