Article

Not peer-reviewed version

Non-dispersive Extraction of Chromium(VI) by Cyphos IL102/Solvesso 100 Using the Pseudo-Emulsion Based Strip Dispersion Membrane Operation

Francisco Jose Alguacil *

Posted Date: 23 April 2024

doi: 10.20944/preprints202404.1463.v1

Keywords: non-dispersive extraction with strip dispersion; Cyphos IL102; chromium(VI); liquid membrane

doi:10.20944/preprints202404.1463.v1

Article

Non-Dispersive Extraction of Chromium(VI) by Cyphos IL102/Solvesso 100 Using the Pseudo-Emulsion Based Strip Dispersion Membrane Operation

Francisco Jose Alguacil

Centro Nacional de Investigaciones Metalurgicas (CSIC). Avda. Gregorio del Amo 8. 28040 Madrid. Spain; fjalgua@cenim.csic.es

Abstract: The removal of chromium(VI) from acidic (HCl) medium through non-dispersive extraction with strip dispersion (NDXSD) was investigated using a microporous PVDF membrane support in a permeation cell. The ionic liquid Cyphos IL102 (phosphonium salt) in Solvesso 100 was used as organic phase. In NDXSD the stripping phase (NaOH) is dispersed in the organic phase in the cell side with an impeller stirrer adequate to form a strip dispersion. This pseudo-emulsion phase (organic + strip solutions) provides a constant supply of the Cyphos IL102/Solvesso 100 to the membrane phase. Various hydrodynamic and chemical parameters, such as variation in the feed and pseudo-emulsion stirring speeds, HCl and Cr(VI) concentrations in the feed phase, and carrier concentration, were investigated. From the experimental data, several mass transfer coefficients were estimated, as well as it was investigated the performance of the present system against other ionic liquids and the presence of base metals in the feed phase.

Keywords: non-dispersive extraction with strip dispersion; Cyphos IL102; chromium(VI); liquid membrane

---

1. Introduction

Ionic liquids (ILs) are a group of chemicals, which are receiving considerable attention in research and application due to their recognition as green solvents. Due to its specific properties, they are considered as alternatives to the use of some organic or inorganic chemicals, but also the possibility of customization (task-specific ILs) accordingly to special applications, it expanded its usefulness to various fields of interest as protein dissolution, stabilization, extraction, and purification, etc. [1–5].

Chromium and its related compounds are of a wide use in different industries, resulting in the discharge of the element in different environments. This element (as many others) is an essential micronutrient in humans and animals, but it is also a known carcinogenic (especially in the VI oxidation state) when its *ingesta* occurs at high concentrations, thus its removal from generated effluents is of a general concern.

Thus, different technologies had been proposed to remove Cr(VI) from aqueous environments. In solvent extraction studies, Deep Eutectic Solvents combining tetra-n-octyl ammonium bromide and carboxylic acids [6] or amide $C_{14}H_{29}NO$ [7] are used to remove this element. Impregnating resins or polymer materials with DEHPA or ionic liquids (Cyphos IL 101, Cyphos IL 104 [8]) is another technology investigated in the removal of chromium(VI), whereas adsorption using nanocomposites [9], biochar [10] or activated carbon [11] are recent examples of various adsorbents used in this role.

In the case of solvent extraction, some drawbacks related to this technology, especially about to the treatment of diluted metal solutions, lead to the development of alternatives to its use, being supported liquid membrane (SLM) separation technology of interest because it combines the kinetics and selectivity of solvent extraction and the simplicity of the membrane diffusion processes. SLMs

doi:10.20944/preprints202404.1463.v1

belong to the advanced variation of extraction operation [12]. In conventional SLM technology (either in flat-sheet, spiral wound or hollow fiber modules), the extraction and stripping processes are carried out simultaneously. In SLM separations, the feed and stripping or receiving aqueous solutions are separated by a hydrophobic membrane, which has been impregnated with the organic phase (normally comprised by the extractant or carrier and the diluent). This configuration facilitated the transport of the solute from the feed to stripping phase, of further interest is that this operational mode allowed the transport of a solute against its concentration gradient. However, some difficulties resulting from stability or long-term performance of these SLMs led to the development of a more advanced SLM operational mode as being the pseudo-emulsion-based strip dispersion, both in hollow fiber or flat-sheet operational modes [13–17]. Under this operation (see Section 2 for details) a pseudo-emulsion (organic and stripping phases) is formed by their mixing in a vessel, and due to that the membrane support is hydrophobic, the organic phase is immobilized into the membrane pores.

The present work investigates the removal of hazardous chromium(VI) from solutions using the ionic liquid Cyphos IlL02 dissolved in Solvesso 100 as carrier phase. An advanced membrane operation such as non-dispersive extraction with strip dispersion is used to investigate such removal. In this membrane technology, the strip phase is dispersed into the organic phase to form a pseudo-emulsion phase, which disengage at the end of the operation to yield an organic phase and a strip solution containing the transported chromium(VI). Several hydrodynamic and chemical parameters influencing the transport of chromium8VI) are investigated, as well as the use of other ionic liquids and the presence of common base metals in the feed phase. From the strip phase, Cr(VI) was reduced to Cr(III) using hydrazine sulphate to render a less toxic solution with a certain degree of profitability (possible formation of pigments). Some mass transfer parameters are estimated from experimental results.

2. Materials and Methods

2.1. Materials

The ionic liquid Cyphos IL102 was obtained from Cytec Ind. (Canada) now Solvay (France), being its active group trihexyl(tetradecyl)phosphonium bromide and it was used without further purification. Cyphos IL101 (trihexyl(tetradecyl)phosphonium chloride) and Aliquat 336 (trioctyl(methyl)ammonium chloride) were obtained from Cytec Ind, and Fluka (Switzerland), respectively. In the experimentation, the ionic liquids were dissolved in Solvesso 100 (99% aromatics, Exxon Chem. Iberia, Spain). Dissolution of the ionic liquid is of interest due to: i) it decreases the viscosity of the organic phase, this is of general importance in separation processes, i.e. solvent extraction, to facilitate phases disengagement, and in the case of membrane operations also to facilitate the transport of a given solute, since the diffusion coefficient of the extractant-solute species in the membrane support is inversely proportional to the viscosity of the organic phase [18], ii) to adequate the range of extractant concentrations to a given system, and iii) in connection to ii), to avoid the use of unnecessary, and thus, unusable extractant in the global inventory of the system.

All the other chemicals in the present work were of AR grade.

The membrane support was Durapore GVHP4700 (Millipore, USA). This PVDF (poly(vinylidenefluoride) support has a diameter of 47 cm diameter, with 0.22 μm nominal pore size, $125 \cdot 10^{-4}$ cm thickness and porosity of 75%.

2.2. Methods

The liquid membrane operation was performed with a flat sheet membrane reactor that comprised two cells (200mL each) provided of impeller stirrers with 2.5 cm diameter. The liquid membrane phase was prepared by soaking the membrane support overnight in a mixture of the ionic liquid and Solvesso 100, and leave to drip during twenty seconds before putting in the cell. In the cell side corresponding to the organic and stripping phases, the impeller was located into the strip phase to provide dispersion of this phase into the continuous organic phase (Figure 1).

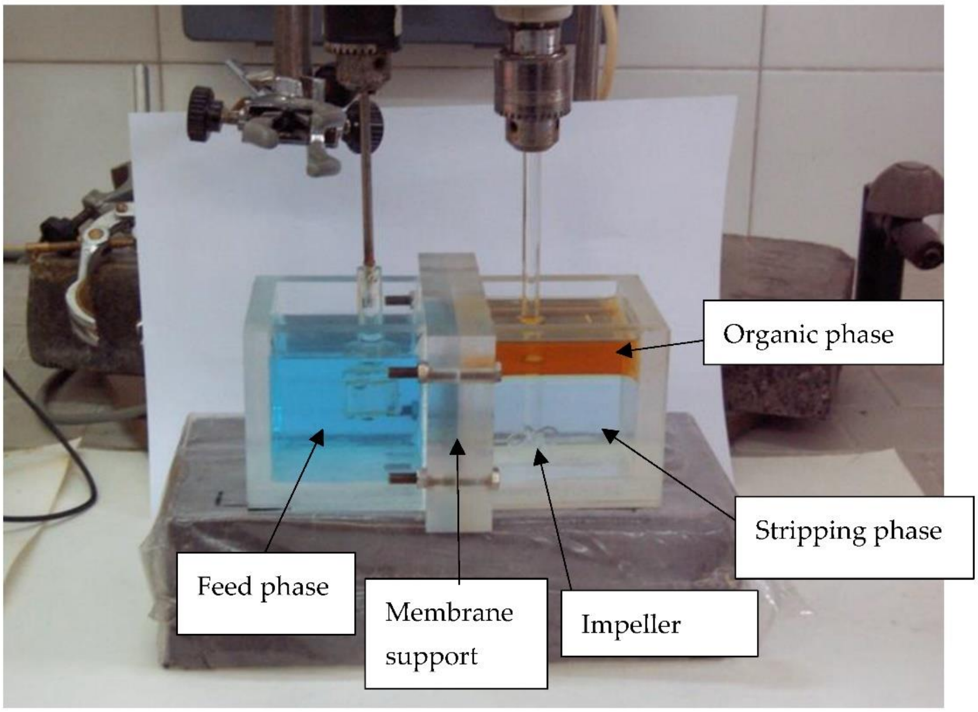

Figure 1. Non-dispersive extraction with strip dispersion. Location of the phases at t= 0.

When the experiment runs, a pseudo-emulsion phase was immediately formed, and the metal was transported from the feed phase to the membrane phase and to the strip phase (Figure 2), mixing of the phases favored the stripping process.

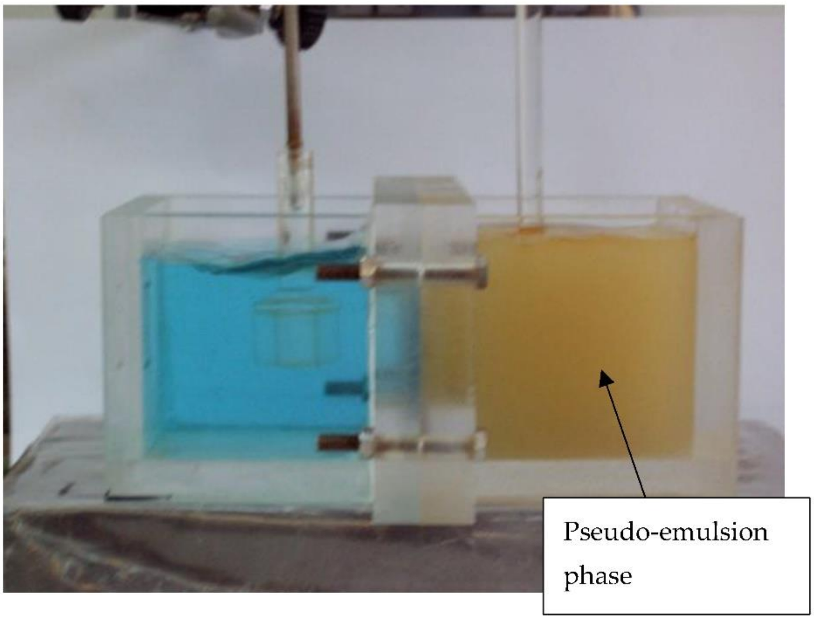

Figure 2. Non-dispersive extraction with strip dispersion. Experiment running at an elapsed time.

At the end of the experiment, and after the stirring was stopped the phases disengage in a very few minutes (Figure 3), and the system reached the initial disposition.

doi:10.20944/preprints202404.1463.v1

Figure 3. Non-dispersive extraction with strip dispersion. Phases at the end of the operation. It can be observed the transport of the metal (blue color) from the feed to the strip phase.

Membrane permeabilities were determined by monitoring chromium or metal concentration by atomic absorption spectrometry (Perkin Elmer 1100 B spectrophotometer, UK) in the feed phase (or the stripping phase at the endo of the experiment) as a function of time. The chromium analysis was found to be reproducible within ±2 %. From the slope of the straight line obtained by plotting the left hand side of the next equation versus time (t), the overall permeation coefficient (P) was estimated:

$$\ln\frac{[\mathrm{Cr}]_{\mathrm{f,t}}}{[\mathrm{Cr}]_{\mathrm{f,0}}} = -\frac{\mathrm{AP}}{\mathrm{V}}\cdot \mathrm{t} \quad (1)$$

where A was the effective membrane area (11.3 cm^2), V was the volume (200 cm^3) of the feed solution, $[Cr]_{f,t}$ and $[Cr]_{f,0}$ were the chromium concentrations in the feed solution at an elapsed time t and time zero, respectively.

The percentage of chromium recovered in the strip phase was determined using the next relationship:

$$\%\mathrm{R} = \frac{[\mathrm{Cr}]_{\mathrm{s,t}}}{\frac{\mathrm{V_f}}{\mathrm{V_s}}([\mathrm{Cr}]_{\mathrm{f,0}}-[\mathrm{Cr}]_{\mathrm{f,t}})}\cdot 100 \quad (2)$$

where $[Cr]_{s,t}$ represented the metal concentration in the strip solution at an elapsed time, $[Cr]_{f,0}$ and $[Cr]_{f,t}$ have the same meaning as in Eq. (1), and V_f and V_s are the volumes of the feed and stripping solutions, respectively.

3. Results and Discussion

3.1. Influence of the Stirring Speed in the Feed and Pseudo-Emulsion Phases on Cr(VI) Transport

The influence of this variable was investigated to optimize uniform mixing of the feed solution and to minimize thickness of aqueous feed boundary layer with feed and pseudo-emulsion conditions maintained as 0.01 g/LCr(VI) in 0.1 M HCl and 10% v/v Cyphos IL102 in Solvesso 100 + 1 M NaOH, respectively. Results derived from these experiments were shown in Figure 4.

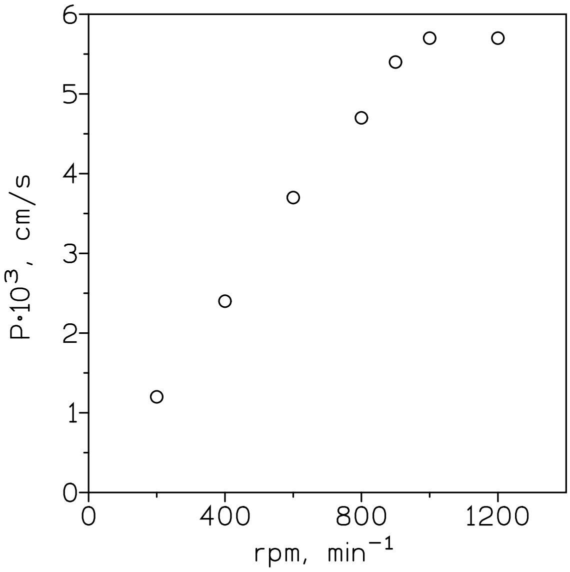

Figure 4. Variation of the permeation coefficient with the stirring speed of the feed phase. Feed phase (200 cm^3). Pseudo-emulsion phase (200 cm^3): 100 cm^3 organic phase + 100 cm^3 stripping phase. Stirring speed pseudo-emulsion phase 400 cm^3. Temperature 20º C.

The permeation coefficient increased from 200 to 1000 min^{-1}indicating a progressive decrease in the boundary layer thickness, and then become independent of the stirring speed above 1000 min^{-1}, thus, a minimum value of thickness is reached in this range of stirring speeds. The appearance of this plateau in the 1000-1200 min^{-1} region does not imply the complete elimination of the aqueous diffusion layer, but the minimization of the resistance due to it [19], resulting in a constant contribution of the diffusion of the chromium(VI) species to the mass transfer phenomena [20]. The stirring speed of 1000 min^{-1} in the feed phase was kept constant throughout the experimentation.

Using the same experimental conditions as above, the influence of the stirring speed in the pseudo-emulsion phase was also investigated. In this case, the speeds were varied in the 400-800 min^{-1}range, and the results indicated that this variation did not influence the metals transport. In consequence, the stirring speed applied on the pseudo-emulsion phase was fixed at 600 min^{-1} in all the experiments.

3.2. Influence of the Stripping Phase Composition on Cr(VI) Transport

It was described elsewhere [21] that NaOH solutions were effective to strip Cr(VI) from loaded Cr(VI)-Cyphos IL102 organic phases. In the strip process, Cr(VI) released to the stripping solution as chromate species, regenerating the ionic liquid. Thus, within the present membrane methodology NaOH solutions were also used as stripping phases. The results of these experiments were summarized in Table 1. The permeation coefficients obtained using the different NaOH concentrations became almost independent of this variable, however, the recovery rate in the strip phase increases with the increase of the alkali concentration though this variation was negligible in the 0.5-1 M NaOH concentrations range. It can be also observed that the chromium concentration in the stripping phase averaging a concentration factor of 1.7 with respect the initial chromium concentration in the feed phase. As result of these experiments, 0.5 M NaOH was used as the stripping phase.

Table 1. Influence of the stripping phase composition on Cr(VI) recovery in the strip phase.

Stripping phase	^{a}% Cr(VI) recovery	^{a}[Cr]$_{s,t}$, g/L
0.1 M	90	0.016
0.5 M	96	0.017

1 M	98	0.018

[a]After 2 hours. Experimental conditions as in Section 3.1.

3.3. Influence of the HCl Concentration on Cr(VI) Transport

To asses the significance of the role of HCl concentration in the feed phase during the permeation of chromium(VI), HCl concentration variation investigations in the range 0.1-10 M were carried out in the presence of 0.01 g/l Cr(VI) in the feed phase (200 cm^3), and pseudo-emulsion phase (200 cm^3) of 10% v/v Cyphos IL102 in Solvesso 100 (100 cm^3) + 0.5 M NaOH (100 cm^3). As seen from Figure 5 and Table 2, permeation of Cr(VI) decreased with the increase in the HCl concentration in the feed phase, and thus, with the increase of the aqueous ionic strength which negatively influenced the metal transport within the present system.

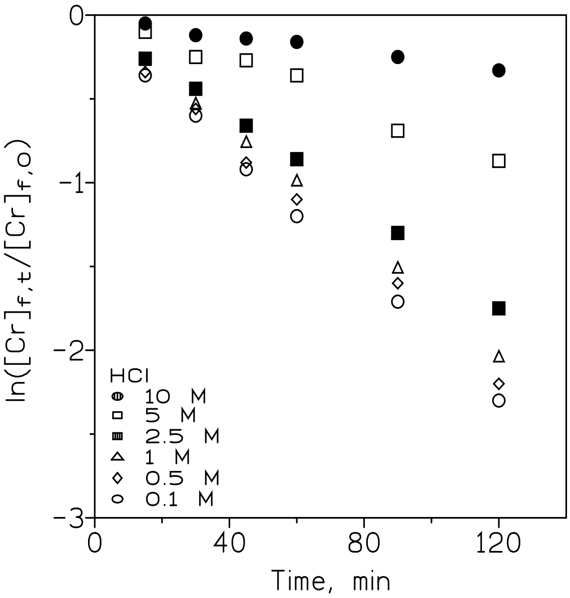

Figure 5. Chromium(VI) transport at various HCl concentrations in the aqueous phase. Temperature: 20º C.

Table 2. Chromium(VI) permeation coefficients at various HCl concentrations in the feed phase.

[HCl], M	**P·10^3, cm/s**
0.1	5.7
0.5	5.5
1	5.0
2.5	4.7
5	2.1
10	0.83

From Figure 5.

3.4. Influence of the Carrier Concentration in the Organic Phase on Cr(VI) Transport

In all the liquid membranes technologies the carrier or extractant plays a key-role in making the transport operation efficient, in fact, the presence of this carrier facilitates the transport of the solute from the feed phase to the stripping phase by forming a specific solute-carrier complex, which also assisted to the selectivity of the process. Moreover, a supported liquid membrane having no carrier immobilized within its pores results in a negligible solute transport. Thus, it is of the utmost importance the evaluation of the influence of Cyphos IL102 concentration in the organic phase on the transport of chromium(VI). The influence of Cyphos IL102 concentration on the permeation of chromium(VI) was studied in the 0.6-10 % v/v (0.01-0,17 M) concentrations range.

As it can be seen from Figure 4, the transport of Cr(VI) increases with the increase of the carrier concentration at 2.5% v/v, with no further increase up to 10% v/v. From these data, the permeation coefficients for chromium(VI) transport at the different carrier concentrations were given in Table 3.

Table 3. Permeation coefficients for Cr(VI) at the different Cyphos IL102 concentrations in the organic phase.

[Cyphos IL 102], % v/v	$P \cdot 10^3$, cm/s
0.6	4.6
1.3	5.0
2.5	5.7
5	5.7
10	5.7

From. Figure 6.

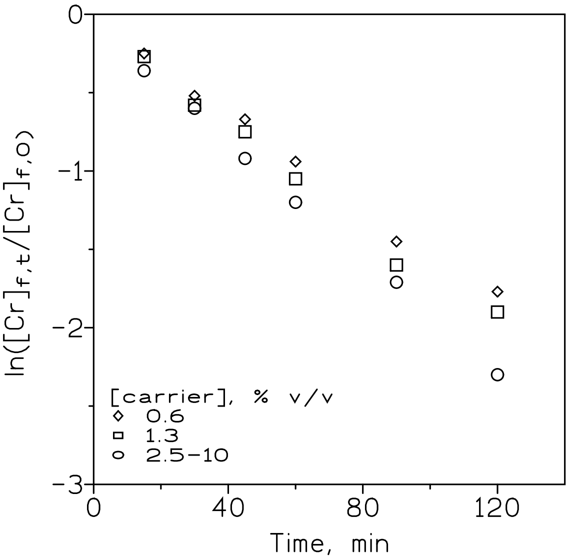

Figure 6. Chromium(VI) transport at various carrier concentrations in the organic phase. Feed phase (200 cm^3): 0.01 g/L Cr(VI) in 0.1 M HCl. Pseudo-emulsion phase (200 cm^3): 100 cm^3 carrier in Solvesso 100 + 100 cm^3 0.5 M NaOH. Temperature: 20º C.

These results show that the permeation coefficient reached a maximum or limiting value ($5.7 \cdot 10^{-3}$M) at the carrier concentration of 2.5 % v/v and levels off. This limiting value also represented the value of the mass transfer coefficient in the feed phase (Δ_f^{-1}) and :

$$\mathbf{P_{lim}} = \frac{\mathbf{D_f}}{\mathbf{d_f}} \tag{3}$$

where D_f is the metal diffusion coefficient in the feed phase (averaging 10^{-5} cm^2/s [22], and d_f is the minimum thickness of the aqueous boundary layer. Thus, this d_f for the present system is estimated as $1.8 \cdot 10^{-3}$ cm. The above results indicated that at low carrier concentrations in the membrane phase, diffusion of the Cr(VI)-Cyphos IL102 complex across the liquid membrane is the rate-determining step, whereas in the 2.5-10% v/v concentrations range diffusion of the metal species across the aqueous boundary layer governed the transport process.

Assuming that the carrier concentration in the membrane phase is constant [23], the next equation allowed to estimate the value of the diffusion coefficient of the chromium-carrier species in the membrane phase [24,25]:

$$\mathbf{D_m} = \frac{\mathbf{J d_m}}{[\mathbf{Cyphos\ IL102}]} \tag{4}$$

doi:10.20944/preprints202404.1463.v1

where d_m is the membrane thickness ($125\cdot10^{-4}$ cm), and J is the metal flux, calculated as:

$$\mathbf{J} = \mathbf{P}[\mathbf{Cr}]_{\mathbf{f,0}} \qquad (5)$$

Thus, using a carrier concentration of 10% v/v (0.17 M), an initial chromium(VI) concentration in the feed phase of 0.01 g/L, and taking the correspondent value of the permeation coefficient (Table 3), the value of the flux is calculated as $1.1\cdot10^{-9}$ mol/cm²s. Substituting this value in eq.(4), the value of D_m is estimated as $8.2\cdot10^{-8}$ cm²/s.

3.5. Influence of the Chromium(VI) Concentration in the Feed Phase on Metal Transport

Figure 7 shows the variation in chromium(VI) transport with the variation of the initial metal concentration in the feed phase ranging from 0.01 to 0.075 g/L. Within this range of metal concentrations, the transport decreases with the increase of the metal concentration. Results in Figure 4 also indicated that an induction period was not observed which makes eq.(19 valid during all the experiments.

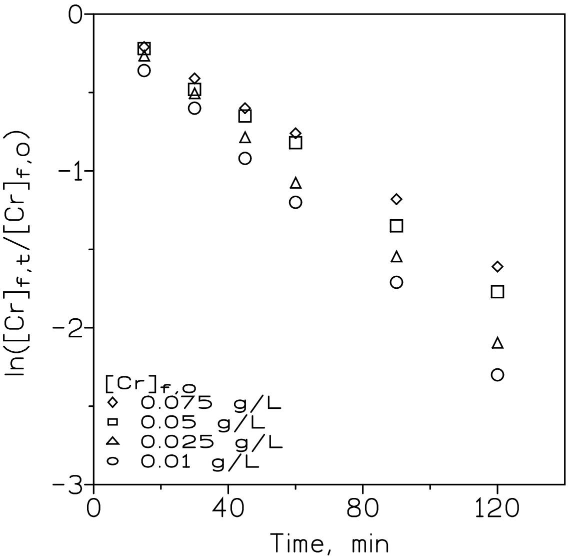

Figure 7. Chromium(VI) transport at various initial metal concentrations in the feed phase. Feed phase (200cm³): Cr(VI) in 0.1 M HCl. Pseudo-emulsion phase (200 cm³): 100 cm³ 10% v/v Cyphos IL102 in Solvesso 100 + 100cm³ 0.5 M NaOH. Temperature: 20º C.

Accordingly with the above, the permeation coefficients decreased with the increase of the chromium(VI) concentration in the feed phase (Table 4).

Table 4. Cr(VI) permeation coefficients, fluxes and recoveries in the strip phase at various initial metal concentrations in the feed phase.

$[Cr]_{f,0}$, g/L	$P\cdot10^3$, cm/s	$J\cdot10^9$, mol/cm²s	ᵃ% Cr recovery ($[Cr]_{s,t}$, mg/L)	Concentration factor
0.01	5.7	1.1	96 (17)	1.7
0.025	5.1	2.4	91(40)	1.6
0.05	4.4	4.2	70(58)	1.2
0.075	3.7	5.2	50(60)	0.8

From Fig.7. ᵃAt time 2 hours.

In this same Table 4 it can observed that the metal flux (J), calculated as in eq.(5) increases with the increase of the initial chromium(VI) concentration, thus, within the present experimental conditions the transport of chromium(VI) is controlled by diffusion of metal species ($HCrO_4^-$ accordingly with the range of metal concentrations used in this work [21]). Metal recoveries in the stripping phase decreased with the increase of the initial metal concentration. After 2 hours of reaction time, metal concentrated in the stripping phase except in the case of the feed solution containing 0.075 g/L Cr(VI), being this probably attributed to the low recovery rate derived with the use of this metal concentration.

It is worth to note that chromium(VI) was transported against its concentration gradient, however, the time to occur these phenomena is dependent on the initial metal concentration in the feed phase (Table 5). As it is seen, this period time increased with the initial chromium(VI) concentration.

Table 5. Estimated time from which Cr(VI) is transported against its concentration gradient.

$[Cr]_{f,0}$, g/L	Time, min
0.01	22
0.025	24
0.05	33
0.075	51

From Figure 7.

3.6. Diffusional Parameters and Contribution of Mass Transfer Resistances to the Overall Chromium(VI) Transport Process

As it was mentioned in subsection 3.4., the mass transfer coefficient in the feed phase is estimated as $5.7 \cdot 10^{-3}$ cm/s. The membrane mass transfer coefficient was estimated as [26]:

$$\mathbf{k_m} = \frac{\mathbf{D_m \varepsilon}}{\mathbf{\tau d_m}} \tag{6}$$

where the tortuosity (τ) is 1.67, the porosity (ε) 0.75, and dm of 125×10^{-4} cm. Thus, taking the value of 8.2×10^{-8} cm^2/s for the membrane diffusion coefficient, see Eq. (4), for the chromium-carrier species in the organic solution, an estimated value of 2.9×10^{-6} cm/s is obtained for the present membrane system.

Furthermore, an effective membrane diffusion coefficient ($D_{eff,m}$) of the chromium-ionic liquid species flowing across the membrane can be defined as [27]:

$$\mathbf{D_{eff,m} d_m \tau} \tag{7}$$

and $D_{eff,m}$ is estimated as 6.1×10^{-8} cm^2/s, which is of the same magnitude order than the value of the membrane diffusion coefficient.

The diffusion coefficient of the chromium(VI) species in the bulk membrane phase ($D_{m,b}$) can be also estimated as [28]:

$$\mathbf{D_{m,b}} = \frac{\mathbf{D_m \tau^2}}{\mathbf{\varepsilon}} \tag{8}$$

thus, the value of $D_{m,b}$ is 3.1×10^{-7} cm^2/s. The comparison of D_m and $D_{m,b}$ values for the present system shows that D_m value is lower than that of $D_{m,b}$, this being attributable to the diffusional resistance caused by the membrane.

It was described in the literature [29], that the equilibrium and diffusional parameters involved in the transport process, can be combined in an equation of the form:

$$\frac{\mathbf{1}}{\mathbf{P}} = \Delta_\mathbf{f} + \frac{\Delta_\mathbf{m}}{\mathbf{C}} \tag{9}$$

where C is a parameter, involved in the extraction or transport process, which considered the extraction equilibrium constant or constants and the concentration of the species which participated within the process. 1/P was the overall resistance and Δ_f and Δ_m were the transport resistances in relation to diffusion by the feed boundary layer and the membrane, respectively.

In a transport process, the overall mass transfer resistance was the sum of the different resistances participating in the process, and thus, eq. (9) was rewritten as:

$$\mathbf{R} = \mathbf{R_f} + \mathbf{R_m} \quad (10)$$

Table 6 showed the contribution, $\%R_f^0$ and $\%R_m^0$, of these various resistances to the overall resistance.

Table 6. Contribution of R_f and R_m to the overall chromium(VI) transport process.

Experimental condition	R, s/cm	R_f, min/cm	$\%R_f^0$	$\%R_m^0$
Stirring speed	175-833	175	100-21	0-79
[a]HCl concentration	1204-175	175	15-100	85-0
Cr(VI) concentration	175-217	175	100-81	0-71
Carrier concentration	175-270	175	100-65	0-35

[a]The influence of the aqueous ionic strength should also be considered (Section).

It was concluded that the diffusion by the aqueous feed boundary layer contributed in a major extend to the overall transport process. A mixed contribution of both aqueous and membrane diffusion under certain experimental conditions it was also found.

3.7. Treatment of the Cr(VI)-Bearing Strip Phase

The recovery of chromium(VI) from the strip phase was investigated by treatment of this phase with solid hydrazine sulphate in order to reduce Cr(VI) to the Cr(III) oxidation state [30]. The redox reaction can be described as:

$$\mathbf{4CrO_4^{2-} + 7H_2O + \frac{3}{2}N_2H_6^{2-} \rightarrow 4Cr(OH)_4^- + 7OH^- + \frac{3}{2}N_2} \quad (11)$$

This reduction is an instant reaction, and allows obtaining a potential pigment.

3.8. Comparison of the Performance of Cyphos IL102 against Other Ionic Liquids (Cyphos IL101 and Aliquat 336)

This investigation was performed using feed solutions of 0.01 g/L Cr(VI) in 0.1 M HCl and pseudo-emulsion phases containing 0.17 M of the single ionic liquid in Solvesso 100 + 0.5 M NaOH. The results of these experiments were shown in Table 7.

Table 7. Chromium(VI) transport using different ionic liquids.

Ionic liquid	$P \cdot 10^3$, cm/s	[a]%Cr recovery
Cyphos IL101	5.8	80
Cyphos IL102	5.7	96
Aliquat 336	6.0	77

[a]At time 2 hours. Temperature 20º C.

Results indicated that the performance of the three ionic liquids can be considered in similar terms, since if the permeability coefficient is somewhat greater in the case of Aliquat 336, the recovery of chromium(VI) in the strip phase is better in the case of Cyphos IL102.

3.9. Transport of Chromium(VI) in the Presence of Base Metals

It was investigated the transport of chromium(VI) in the presence of various base metals (Cu(II), Fe(III), Zn(II), Co(II)). These experiments were carried out using binary solutions of Cr(VI) and each base metal at initial metal concentrations (each) of $1.9 \cdot 10^{-4}$ M (roughly 0.01 g/L) in 0.1 M HCl. The pseudo-emulsion phase contained 10% v/v Cyphos Il102 in Solvesso 100 + 0.5 M NaOH. The results indicated that none of the investigated base metals permeates, thus, chromium(VI) can be selectively separate from these elements. However, it was found that the value of the chromium(VI) permeation coefficient decreased from $5.7 \cdot 10^{-3}$ cm/s, using single Cr(VI) solutions, to an average value of $4.2 \cdot 10^{-3}$

cm/s for the binary systems. This decrease can be attributable to the crowding or population effect due to the presence of these ions in the feed solution [31].

4. Conclusions

The transport of chromium(VI) from HCl medium through a supported liquid membrane containing a Solvesso 100 solution of Cyphos IL102 was investigated. A microporous PVDF film, Durapore GVHP4700, was used as a solid support, whereas the pseudo-emulsion with strip dispersion membrane technology was used as advanced membrane operational mode. Chromium(VI) transport depends on a series of hydrodynamic and chemical variables. The aqueous boundary layer minimizes (d_{aq}= 1.8·10^{-3} cm) at stirring speeds in the 1000-1200 min^{-1} range, and carrier concentration in the membrane phase in the 2.5-10% v/v (4.3·10^{-2}-1.7·10^{-1} M) range. An increase of the initial metal concentration in the feed phase produced adecrease of the permeation coefficient, but the metal flux increased, indicating an aqueous diffusion controlled transport. The mass transfer coefficient in the aqueous film, the diffusivity of the Cr(VI)-Cyphos IL102 complex in the bulk organic membrane solution, and in the membrane are also determined. The present system compares well with the use of other ionic liquids, being Cr(VI) transported selectively from a series of base metals. From the strip solution and by the use of hydrazine sulphate, chromium(VI) was effectively reduced to the lesser toxic Cr(III) state, opening the possibility of obtaining a valuable pigment.

Funding: This research received no external funding and the APC was funded by Membranes Editorial Office.

Acknowledgments: To the CSIC (Spain) for support. To Martin Ian Maher for English supervision.

Conflicts of Interest: The author declares no conflicts of interest.

References

1. Bharmoria, P.; Tietze, A.A.; Mondal, D.; Kang, T.S.; Kumar, A.; Freire, M.G. Do ionic liquids exhibit the required characteristics to dissolve, extract, stabilize, and purify proteins?. Past-present-future assessment. *Chem. Rev.* **2024,** *124,* 3037-3084. DOI: 0.1021/acs.chemrev.3c00551
2. El-Nagar, R.A.; Khalil N.A.; Atef Y.; Nessim, M.I.; Ghanem, A. Evaluation of ionic liquids based imidazolium salts as an environmentally friendly corrosion inhibitors for carbon steel in HCl solutions. *Sci. Rep.* **2024,** *14,* 1889. DOI: 10.1038/s41598-024-52174-5
3. Hemmati, A.; Asadollahzadeh, M.; Torkaman, R. Assessment of metal extraction from e-waste using supported IL membrane with reliable comparison between RSM regression and ANN framework. *Sci. Rep.* **2024,** *14,* 3882. DOI: 10.1038/s41598-024-54591-y
4. Yaghoubi, S.; Sadjadi, S.; Zhong, X.; Yuan, P.; Heravi, M.M. Clay-supported bio-based Lewis acid ionic liquid as a potent catalyst for the dehydration of fructose to 5-hydroxymthylfurfural. *Sci. Rep.* **2024,** *14,* 82. DOI: 10.1038/s41598-023-50773-2
5. Li, J.; Zhao, Y.; Zhan, G.; Xing, L.; Huang, Z.; Chen, Z.; Deng, Y.; Li, J. Integration of physical solution and ionic liquid toward efficient phase splitting for energy-saving CO2 capture. *Sep. Purif. Technol.* **2024,** *343,* 127096. DOI: 10.1016/j.seppur.2024.127096
6. Dong, H.; Ci, E.; Zhao T.; Chen P.; Liu, F.; Hu G.; Yang, L. Hydrophobic deep eutectic solvents as the green media for highly efficient extraction of Cr(VI) over a broad pH range and low oil-water ratio. *Sep. Purif. Technol.* **2024,** *334,* 126104. DOI: 10.1016/j.seppur.2023.126104
7. Ying, Z.; Liu, S.; Wei Q.; Ren, X. A pilot scale test study with theoretical justification of reaction mechanism for the recovery of chromium(VI) based on solvent extraction using novel centrifugal extractors. *Hydrometallurgy* **2024,** *223,* 106210. DOI: 10.1016/j.hydromet.2023.106210
8. Witt K.; Kaczorowska, M.A.; Bożejewicz, D. Efficient, fast, simple, and eco-friendly methods for separation of toxic chromium(VI) ions based on ion exchangers and polymer materials impregnated with Cyphos IL 101, Cyphos IL 104, or D2EHPA. *Environ. Sci. Poll. Res.* **2024,** *31,* 7977-7993. DOI: 10.1007/s11356-023-31648-5
9. Saad E.M.; Abd-Elhafiz, M.F.; Ahmed, E.M.; Markeb, A.A. Hexavalent chromium ion removal from wastewater using novel nanocomposite based on the impregnation of zero-valent iron nanoparticles into polyurethane foam. *Sci. Rep.* **2024,** *14,* 5387. DOI: 10.1038/s41598-024-55803-1
10. Su, K.; Hu, G.; Zhao, T.; Dong, H.; Yang, Y.; Pan, H.; Lin, Q. The ultramicropore biochar derived from waste distiller's grains for wet-process phosphoric acid purification: removal performance and mechanisms of Cr(VI). *Chemosphere* **2024,** *349,* 140877. DOI: 10.1016/j.chemosphere.2023.140877

11. Yazid H.; Bouzid T.; El Mouchtari, El Mountassir; Bahsis, L.; El Himri M.; Rafqah S.; El Haddad, M. Insights into the adsorption of Cr(VI) on activated carbon prepared from walnut shells: combining response surface methodology with computational calculation. *Clean Technol.* **2024,** *6,* 199-220. DOI: 10.3390/cleantechnol6010012
12. Saik, S.G.; Morad, N.; Ismail, N.; Rafatullah, M. Developments in supported liquid membranes for treatment of metalbearing wastewater. *Sep. Purif. Rev.* **2022,** *51,* 38–56. DOI: 10.1080/15422119.2020.1828100
13.] Hu, S.-Y.B.; Wienceck, J.M. Emulsion-liquid-membrane extraction of copper using a hollow-fiber contactor. *AIChE J.* **1998,** *44,* 570-581. DOI: 10.1002/aic.690440308
14. Urtiaga, A.; Abellán, M.J.; Irabien J.A.; Ortiz I. Membrane contactors for the recovery of metallic compounds: modelling of copper recovery from WPO processes. *J. Membr, Sci.* **2005,** *257,* 161 – 170. DOI: 10.1016/j.memsci.2004.10.046
15. Ho, W.S.W.; Bang, W. Strontium removal by new alkyl phenylphosphonic acids in supported liquid membranes with strip dispersion. *Ind. Eng. Chem. Res.* **2002,** *41,* 381-388. DOI: 10.1021/ie0101339
16. Sonawane, J.V.; Kumar Pabby, A.; Sastre, A.M. Au(I) extraction by LIX-79/n-heptane using pseudo-emulsion-based hollow-fiber strip dispersión (PEHFSD) technique. *J. Membr. Sci.* **2007,** *300,* 147-155. DOI: 10.1016/j.memsci.2007.05.016
17. Comesaña, A.; Rodriguez-Monsalve, J.; Cerpa, A.; Alguacil, F.J. Non-dispersive solvent extraction with strip dispersion (NDSXSD) pertraction of Cd(II) in HCl medium using ionic liquid CYPHOS IL101. *Chem. Eng. J.* **2011,** *175,* 228-232. DOI: 10.1016/j.cej.2011.09.099
18. Gupta, S.K.; Rathore, N.S.; Sonawane, J.V.; Pabby, A.K.; Janardan, P.; Changrani, R.D.; Dey, P.K. Dispersion-free solvent extraction of U(VI) in macro amount from nitric acid solutions using hollow fiber contactors. *J. Membr. Sci.* **2007,** *300,* 131-136. DOI: 10.1016/j.memsci.2007.05.018
19. Mahapatra, R.; Kanungo, S.B.; Sarma, P.V.R.B. Kinetics of the transport of Co(II) from aqueous sulfate solutions through a supported liquid membrane containing di(2-ethylhexyl) phosphoric acid. *Sep. Sci. Technol.* 1992, *27,* 765-781. DOI: 10.1080/01496399208019723
20. Alguacil, F.J. Martinez, S. Permeation of iron(III) by an immobilized liquid membrane using Cyanex 923 as mobile carrier. *J. Membr. Sci.* **2000,** *176,* 249-255. DOI: 10.1016/j.memsci. S0376-7388(00)00442-7
21. Alguacil F.J. Facilitated chromium(VI) transport across an ionic liquid membrane impregnated with Cyphos IL102. *Molecules* **2019,** *24,* 2437. DOI: 10.3390/molecules24132437
22. Alguacil, F.J.; Alonso, M.; Lopez, F.; Lopez-Delgado, A. Uphill permeation of Cr(VI) using Hostarex A327 as ionophore in membrane-solvent extraction processing. *Chemosphere* **2008,** *72,* 684-689. DOI: 10.1016/j.chemosphere.2008.02.030
23. El Aamrani, F.Z.; Kumar, A.; Sastre, A.M. Kinetic modelling of the active transport of copper(II) across liquid membranes using thiourea dervatives immobilized on microporous hydrophobic support. *New J. Chem.* **1999,** *23,* 517-523. DOI: 10.1039/a901203f
24. Mahapatra, R.; Kanungo, S.B.; Sarma, P.V.R.B. Kinetics of the transport of Co(II) from aqueous sulfate solution through a aupported liquid membrane containing di(2-ethylhexyl) phosphoric acid in kerosene. *Sep. Sci. Technol.* **1992,** *27,* 765-781. DOI: 10.1080/01496399208019723
25. Bromberg, L.; Levin, G.; Libman, J.; Shanzer, A. A novel tetradentate hydroxamate as ion carrier in liquid membranes. *J. Membr. Sci.* **1992,** *69,* 143-153. DOI: 10.1016/0376-7388(92)80175-J
26. Prasad, R.; Kiana, A.; Bhave, R.R.; Sirkar; K.K. Further studies on solvent extraction with immobilized interfaces in a microporous hydrophobic membrane. *J. Membr. Sci.* **1986,** *26,* 79-97. DOI: 10.1016/S0376-7388(00)80114-3
27. Kumar, A.; Sastre, A.M. Hollow fiber supported liquid membrane for the separation/concentration of gold(I) from aqueous cyanide media: modeling and mass transfer evaluation. *Ind. Eng. Chem. Res.* **2000,** *39,* 146-154. DOI: 10.1021/ie990267a
28. Huang, T.C.; Juang, R.S. Rate and mechanism of divalent metal transport through supported liquid membrane containing di(2-ethylhexyl) phosphoric acid as a mobile carrier. *J. Chem. Technol. Biotechnol.* **1988,** *42,* 3-17. DOI: 10.1002/jctb.280420103
29. Sastre, A.M.; Madi, A., Cortina, J.L.; Miralles, N. Modelling of mass transfer in facili-tated supported liquid membrane transport of gold(III) using phospholene derivatives as carriers. *J. Membr. Sci.* **1998,** *139,* 57-65. DOI: S0376-7388(97)00243-3
30. Alguacil, F.J.; Alonso, M. Chromium(VI) removal through facilitated transport using CYANEX 923 as carrier and reducing stripping with hydrazine sulfate. *Environ. Sci. Technol.* **2003,** *37,* 1043-1047. DOI: 10.1021/es020585s
31. De Gyves, J.; San Miguel, E.R. Metal ion separations by supported liquid membranes. *Ind. Eng. Chem. Res.* **1999,** *38,* 2182-2202. DOI: 10.1021/ie980374p