



Pseudo-emulsion based hollow fibre strip dispersion (PEHFSD) technique for permeation of Cr(VI) using Cyanex-923 as carrier

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ABSTRACT

Pseudo-emulsion based hollow fibre strip dispersion (PEHFSD) technique is investigated for the permeation–separation of chromium from hydrochloric acid media. The permeation of Cr(VI) is investigated in relation to various experimental variables: hydrodynamic conditions, the concentration of Cr(VI) and HCl in the feed phase, Cyanex-923 concentration, hydrazine sulphate as the stripping agent in the pseudo-emulsion phase. The performance of the PEHFSD was analyzed and optimum conditions are suggested for chromium separation from simulated industrial waste in a hydrochloric acid media.

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1. Introduction

The major users of chromium are the metal plating, leather tanning and metal alloy manufacturing industries [1–4]. Some of these industries are major producers of chromium waste. Chromium(VI) is a toxic element and has been shown to be mutagenic, carcinogenic [5,6] and a strong oxidant [7]. In contrast, chromium(III) is significantly less toxic than chromium(VI) [8], but it appears in higher concentrations in tannery wastewater, for example, a great volume of wastewater is produced during the rinsing step of electroplating processes, which is the main problem faced by metal-finishing industries [9]. As far as the concentration of chromium in these effluents is concerned, only broad generalizations can be made because of the great variability of these types of industries and types of baths. In general terms, it can be said that rinse waters have a concentration of between 50 and 500 mg L⁻¹ of chromium(VI), which makes it necessary to treat them before discharging them into natural streams [10]. Although the standard technologies employed for the treatment of these effluents,

such as reduction, precipitation, ion exchange and reverse osmosis, reduce the chromium concentration in the waste effluents to low levels, these techniques create additional sludge and/or are costly [11]. Thus, research has been undertaken to develop cleaner technologies that would make it possible to remove and make concentrations of chromium compounds for their reuse.

In recent years, membrane-based processes have attracted considerable attention as a valuable technology for many industries. This significant gain in momentum is driven in part by spectacular advances in membrane development, a wider acceptance of the technology as opposed to conventional separation processes, increased environmental awareness and, most of all, stricter environmental regulations and legislation. Solvent extraction processes that employ hollow-fibre (HF) modules have been used for the removal and/or concentration of different metallic elements, anions, organic compounds, and other substances [12–17]. In view of this, a more stable technique was sought that was able to utilize the merits of LM techniques and that would also be suitable for industrial use; the PEHFSD fulfils these criteria. A newly introduced PEHFSD technique has the following merits as compared to conventional liquid–liquid extraction: extraction and stripping in one module, no flooding limitations, no density difference requirements, high throughput, more modular systems and easy scale-up [18,19]. Several research groups have carried out work in the field of copper, cadmium, actinide extraction–separation and other hazardous metals using the PEHFSD [20–25]. To date, no systematic research has been done using the PEHFSD for the separation

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Nomenclature

C	metal concentration (g/cm ³)
d	diameter of one fibre (cm)
d_a	thickness of the aqueous feed boundary layer (cm)
d_i and d_o	inner and outer fibre diameter, respectively (cm)
D_r	partition coefficient of chromium
D_{eff}	effective membrane diffusion coefficient of the chromium-containing species (cm ² /s)
J	flux of the metal-carrier species (mol/cm ² s)
k_i	aqueous mass transfer coefficient (cm/s)
k_m	membrane mass transfer coefficient (cm/s)
L	fibre length (cm)
n_f	number of fibres
Q	flow rate (cm ³ /s)
r_i and r_o	inner and outer hollow fibre radius (cm)
P_{Cr}	overall permeability coefficient (cm/s)
$[R_{org}]$	Cyanex-923 (mol/L)
R_m	denotes Cyanex-923 in pseudo-emulsion membrane
t_m	thickness of the fibre membrane (cm)
V	tank volume (cm ³)
V_m	volume of hollow fibres (cm ³)

Subscripts

f and s	refer to feed and stripping solutions, respectively
in	inside the fibre
out	along the outside of the fibre
i	for inner radii
o	for outer radii

Superscripts

m and T	refer to membrane module and phase tank
o	refers to concentration at time zero

Greek letters

τ	tortuosity of the membrane.
v_f and v_s	velocity of liquid inside fibre and shell side (cm/s)

of chromium from hydrochloric acid media using Cyanex-923. Cyanex-923 was selected for this piece of research based on published work on chromium and other metals by several researchers [26–28].

The objective of this study is to investigate Cr(VI)–Cyanex-923 in relation to various experimental variables: hydrodynamic conditions, concentration of Cr(VI) and HCl in the feed phase, Cyanex-923 concentration and hydrazine sulphate as a stripping agent in the pseudo-emulsion phase and the speed of the pseudo-emulsion phase. The transport process includes a stripping step in which Cr(VI) is reduced *in situ* to Cr(III) by the use of hydrazine sulphate as a strippant.

2. Experimental

A stock solution of Cr(VI) was prepared from pure solid Na₂CrO₄ (E. Merck, Darmstadt, Germany). Its average molecular weight was 348 and its density (20 °C) was 880 Kg/m³. The Cyanex-923 extractant was supplied by Cytec Ind., Canada and specification of the reagent is provided elsewhere [27]. The detailed PEHFSD study was carried out by using Cyanex-923/kerosene to check the transport of Cr(VI) as the results obtained were encouraging. The extractants were used as supplied by the manufacturers Exxon Mobil Chem. Iberia, Spain. All other chemicals were of AR grade.

2.1. Partition coefficients of Cr(VI)

The partition coefficient (D_r) of Cr(VI) for extraction and stripping was determined as detailed elsewhere [14]. The Cr(VI) content after stripping the metal ion was analyzed. All the measurements were performed at least in duplicate and the agreement of the D_r values obtained was within $\pm 2\%$, with a good material balance (>95%).

2.2. PEHFSD setup

The hollow-fibre device used for the single step was a commercially available unit that was purchased from Hoechst Celanese (now known as Celgard GmbH), Charlotte, North Carolina (Liqui-cel, 8 × 28 cm 5PCG-259 contactor). Module details and hollow-fibre membrane characteristics are published elsewhere [14].

2.2.1. PEHFSD preparation and methods

The hollow fibre strip dispersion process was comprised of a single membrane module for extraction and stripping. More detailed information on PEHFSD preparation and method is provided elsewhere [17]. The PEHFSD operation was carried out using 10% (0.36 M) Cyanex-923/kerosene in which feed was contacted in chloride form that contained chromium (passed through the tube side) and the pseudo-emulsion of Cyanex-923/kerosene and hydrazine sulphate (10 g/L) passed through the shell side in counter current mode. The stirring rate using the magnetic stirrer was kept at 1200 rpm. It was determined that this stirring speed was best suited to our experiments.

The pseudo-emulsion phase was a 400 mL solution that contained 200 mL of 10% Cyanex-923/kerosene + 200 mL of 10 g/L hydrazine sulphate. A quantity of 1000 mL of aqueous feed solution of the desired Cr(VI) concentration was prepared by taking a suitable aliquot from the stock solution. In addition, the desired feed acidity was adjusted by adding 1 M HCl solution. At a predetermined time during the experimental run, small aliquots of the feed stream and from the pseudo-emulsion tank were taken and analyzed for metal concentration by standard atomic absorption spectrometry (AAS).

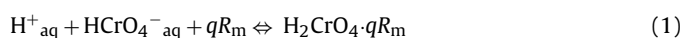
3. Theoretical background

3.1. Extraction equilibrium

The transport of chromium(VI) through the PEHFSD that contained the pseudo-emulsion of Cyanex-923/kerosene + 10 g/L hydrazine sulphate was flowed through the shell side and the feed which contained the Cr(VI) flowed through the tube side.

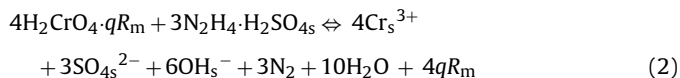
Chromium(VI) in the feed solution diffused towards the feed-membrane interface, in which the complex formation between Cr(VI) and Cyanex-923/kerosene occurred. The organic complex that was in the pseudo-emulsion of 10% Cyanex-923/kerosene and 10 g/L hydrazine sulphate was stripped by hydrazine sulphate, in which Cr(VI) was reduced to Cr(III).

In accordance with the chromium(VI) transport scheme [27], a tentative mechanism that explained the chromium transport through the membrane to the pseudo-emulsion phase can be represented by the following equation:



where q is a stoichiometric coefficient (probably 1) (calculated by standard procedure using liquid–liquid extraction by plotting $\log[\text{extractant}]$ vs. $\log[D]$), and aq and m refer to the feed and membrane pseudo-emulsion phases, respectively. In the stripping

phase, the possible following reaction occurs:



where *s* and *m* refer to the stripping and membrane in the pseudo-emulsion phase, respectively. N_2 liberated in the stripping reaction is in very meagre amount and may not disturb the operation of pseudo-emulsion.

The partition coefficient may be represented as:

$$\log[D] = \log[K_{\text{ex}}] + \log[\text{H}^+] + q \log[R_m] \quad (3)$$

where *q* is a stoichiometric coefficient (probably 1). The value obtained for $K_{\text{ex}} = 36.08$, for 10% Cyanex-923/kerosene, $[\text{H}^+] = 1 \text{ M}$ HCl, $D = 11.27$.

3.2. Model development

3.2.1. PEHFSD extraction

In the case of the PEHFSDs, the calculation of the overall permeability coefficients of the experimental system is based on a first-order mass transfer model with an instantaneous chemical reaction on the stripping side when a recycling mode is employed. The study of the influence of the liquid membrane composition leads to the evaluation of the mass transfer parameters.

Based on five observations related to determination of the permeability values (percent extraction of Cr(VI) at about 90%) under similar experimental conditions exhibits a coefficient of variation of $\pm 1\%$.

As far as the reproducibility of data are concerned, initially several experiments were performed to check the feasibility and consistency of results under the same experimental conditions. Reproducibility was found to be satisfactory for the results obtained for a fixed period of time using three sets of data.

3.3. Permeation definition

For the recycling mode, both the feed solution and the organic carrier solution + stripping solution in the pseudo-emulsion phase were recycled. The similar scheme for other metal ions is published elsewhere [19,29]. To model the recycling mode, in 1984 Danesi [30] proposed a simple model with a constant permeation coefficient. As there are difficulties involved in describing a non-steady state process with variations in the concentration in the axial and radial directions that employ the continuity equation, the macroscopic mass balance of the permeating solute in a certain volume of fibre in a given time interval must be used [31,32]. The model for the transport of Cr(VI) in a hollow fibre supported liquid membrane system that operates in a recycling mode is similar to our previous studies published elsewhere [33,34]. The hollow fibre membrane strip is defined as the strip interface where metal is getting striped in side the dispersed phase (pseudo-emulsion of organic extractant + strippant). When a hydrazine sulphate solution is used as the stripping agent, an instantaneous reaction is assumed to occur on the outside of the fibre in order to strip the metal ion in stripping globules. To evaluate permeability coefficients, the final equations obtained from modelling are presented below in simplified form:

$$V_f \ln \left(\frac{C_{f,t=0}}{C_f} \right) = Q_f \left\{ 1 - \exp \left(\frac{2P_{\text{Cr}}L}{v_f r_i} \right) \right\} t \quad (4)$$

Experimental results can thus be fitted to a first-order kinetic law

$$V_f \ln \left(\frac{C_{A,t=0}^f}{C_A} \right) = St \quad (5)$$

where *S* is the factor dependent on the geometry of the fibres and the module, the linear velocity of the fluids and the overall permeability of the system. The overall permeability coefficient for a system run in a recycling mode can easily be obtained from the experimental value of the slope *S* as follows:

$$P_{\text{Cr}} = \frac{-Q_f}{2n\pi r_i L} \left[\ln \left(1 - \frac{S}{Q_f} \right) \right] \quad (6)$$

The design of PEHFSD for the separation-concentration of chromium using the overall permeability coefficient P_{Cr} centres on three mass transfer resistances, one of which occurs in the liquid that flows through the hollow fibre lumen. The second corresponds to the chromium-complex diffusion across the liquid membrane that is immobilized on the porous wall of the fibre. The third resistance is due to the aqueous interface that is created on the outside of the fibre.

The reciprocal of the overall permeability coefficient is given by:

$$\frac{1}{P_{\text{Cr}}} = \frac{1}{k_i} + \frac{r_i}{r_{\text{lm}}} \frac{1}{P_m} + \frac{r_i}{r_o} \frac{1}{k_o} \quad (7)$$

where r_{lm} is the hollow fibre log mean radius, and k_i and k_o are the interfacial coefficients that correspond to the inner and outer aqueous boundary layers. P_m is the membrane permeability, which is related to the partition coefficient of chromium (denoted as D_f) and (defined as the ratio of $[\text{H}_2\text{CrO}_4 \cdot qR]_{\text{org}}/[\text{HCrO}_4^-]$) obtained with Cyanex-923 ($[R_{\text{org}}]$) [29] by:

$$P_m = D_f k_m = K_{\text{ex}}[\text{H}^+][R]_{\text{org}} k_m \quad (8)$$

By inserting Eq. (8) in Eq. (7) gives P_{Cr} :

$$\frac{1}{P_{\text{Cr}}} = \frac{1}{k_i} + \frac{r_i}{r_{\text{lm}}} \frac{1}{k_m K_{\text{ex}}[\text{H}^+][R_{\text{org}}]} + \frac{r_i}{r_o} \frac{1}{k_o} \quad (9)$$

When the reaction is instantaneous on the stripping side, the contribution of the outer aqueous phase is removed from Eq. (9) and P_{Cr} is determined by:

$$\frac{1}{P_{\text{Cr}}} = \frac{1}{k_i} + \frac{r_i}{r_{\text{lm}}} \frac{1}{k_m K_{\text{ex}}[\text{H}^+][R_{\text{org}}]} \quad (10)$$

This observation is supported by literature as similar behaviour was noted by Pabby and co-workers where author have not considered the resistance due to the contribution of the outer aqueous phase [33,34].

The effective diffusion coefficients (D_{eff}) of Cr(VI) extractant complexes through the organic membrane phase were determined through the model [33]. An effective diffusion coefficient (D_{eff}) for the solute in the immobilized organic liquid membrane can be defined as follows:

$$D_{\text{eff}} = k_m t_m \tau \quad (11)$$

4. Results and discussion

The transport of chromium(VI) through the PEHFSD that contained Cyanex-923 as a mobile carrier resulted due to driving force of metal-carrier species across the aqueous-organic interface and further transported to receiving phase due to stripping of species in receiving phase. The similar mechanism with other metal ions are published in detail elsewhere [19]. Chromium(VI) in the feed solution diffuses toward the feed-membrane interface, where the complex formation between Cr(VI) and Cyanex-923 (Eq. (1)) takes place. The complex then diffuses through the membrane toward the membrane-pseudo-emulsion phase, where Cr(VI) is stripped and reduced to Cr(III) by the hydrazine sulphate solution. This reduction is quick and is characterized by the appearance of a greenish colour in the pseudo-emulsion phase. The stripping step regenerates the carrier and then diffuses back to the feed-membrane interface, after which the process is repeated.

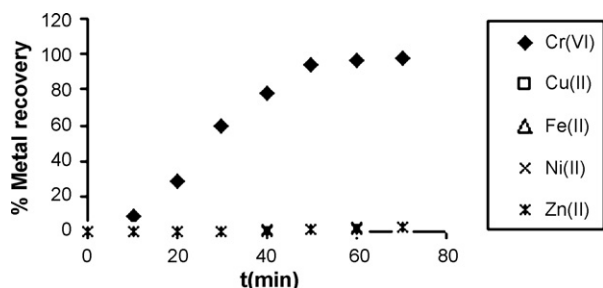


Fig. 1. Separation of Cr(VI) from other metals under standard experimental condition. [Tube side (Feed): 1000 cm³ of 20 mg L⁻¹ Cr(VI), 30 mg L⁻¹ Fe(II), 30 mg L⁻¹ Cu(II), 10 mg L⁻¹ Ni(II), 5 mg L⁻¹ Zn(II) in 1 M HCl solution. Feed flow rate: 20 L/h. Pressure difference (bar): 0.20, Stirring rate: 1200 rpm. Shell side: Pseudo-emulsion phase: 200 cm³ of 10% Cyanex-923/kerosene + 200 cm³ 10 g/L hydrazine sulfate].

In all the transport experiments carried out with Cyanex-923/kerosene, a stirring speed of 1200 rpm (by using a magnetic stirrer) was used to form the pseudo-emulsion of Cyanex-923/kerosene and hydrazine sulphate was used as a strippant (Fig. 1). In a previously published work with Cyanex-921 and Cyanex-923 using the hollow fibre supported liquid membrane (HFSLM) [27], results showed that the percentage of chromium transport becomes virtually independent of the stirring speed in these ranges.

In order to evaluate metal selectivity, a Cyanex-923/kerosene (10% v/v or 0.36 M) system was used to carry out various experiments in a counter current mode in the presence of other metals, as shown in Figs. 1 and 2. In Fig. 2, it can be seen that Cr(VI) ions can be transported against their concentration gradient. As the concentration of Cr(VI) in the feed solution decreased, it was simultaneously found to increase in the stripping phase in the pseudo-emulsion in the same module as time elapsed. Experiments were carried out by taking 1000 cm³ that contained Cr(VI) (20 mg L⁻¹), Fe(II) (30 mg L⁻¹), Cu(II) (30 mg L⁻¹), Ni(II) (10 mg L⁻¹) and Zn(II) (5 mg L⁻¹) in 1 M HCl, which maintained the feed flow rate at 20 L/h. The pseudo-emulsion was prepared by mixing 200 cm³ of 10% Cyanex-923/kerosene and 200 cm³ of 10 g/L hydrazine sulphate (stirred at 1200 rpm), which was passed through the shell side. As seen in Fig. 1, Cr(VI) can be separated from other metal ions. The percentage transport of other metal ions after 120 min is 2.56% (Cu(II)), 3.43% (Fe(II)), 2.98% (Ni(II)) and 2.65% (Zn(II)), while the transport of Cr(VI) over the same time span is >95%. This shows that Cr(VI) can be separated from other metal ions.

4.1. Influence of the HCl concentration in the feed phase

To study the influence of the HCl concentration (0.5–1.5 M) in the source phase, a set of experiments were performed at vari-

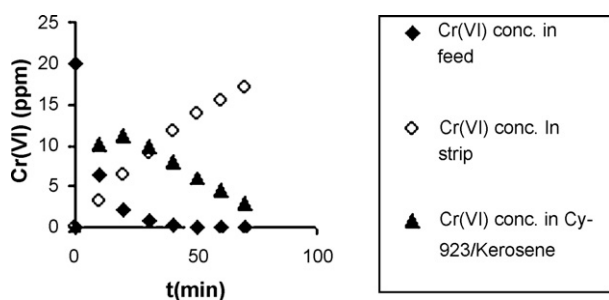


Fig. 2. Concentration courses obtained from the stability study. [Tube side (Feed): 1000 cm³ of 20 mg L⁻¹ Cr(VI), 30 mg L⁻¹ Fe(II), 30 mg L⁻¹ Cu(II), 10 mg L⁻¹ Ni(II), 5 mg L⁻¹ Zn(II) in 1 M HCl solution. Feed flow rate: 20 L/h. Pressure difference (bar): 0.20, Stirring rate: 1200 rpm. Shell side: Pseudo-emulsion phase: 200 cm³ of 10% Cyanex-923/kerosene + 200 cm³ 10 g/L hydrazine sulfate].

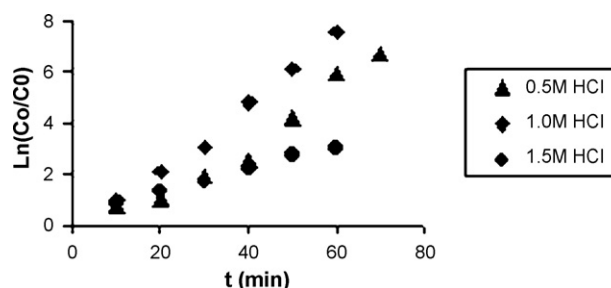


Fig. 3. Influence of the feed acidity on the permeability of Cr(VI) as a function of time in recycle mode.

ous acid concentrations (maintaining fixed carrier concentration in the pseudo-emulsion) in order to optimise HCl concentration in source phase. The pseudo-emulsion of 10 g/L hydrazine sulphate as a strippant and 10% Cyanex-923/kerosene as a carrier was prepared by using a 1200 rpm magnetic stirrer to obtain a continuous flow of the pseudo-emulsion. Fig. 3 shows that the transport of chromium increased as the HCl concentration increased up to 1 M and further tends to stabilize. The permeability coefficient at 1 M HCl was found to be highest, namely, 11.3×10^{-6} cm/s. Hence, further experiments were carried out at 1 M HCl to obtain the best performance. The decrease in permeability of chromium may be due to two reasons. First, it may be due to the existence of less extractable chromium(VI)-chloro-oxo complexes (i.e., CrO_3Cl^-) in the aqueous phase [27] and, second, it may be due to the competition between chromium and HCl. It is known that Cyanex-923 also extracts mineral acids [28].

The experiments were carried out in batch mode using 5 L of 20 ppm of Cr(VI) as a feed and a pseudo-emulsion (made up of 10 g/L of hydrazine sulphate and carrier) to evaluate the concentration factor, which is defined as the ratio of the final concentration of Cr(VI) in the stripping phase to the initial concentration in the feed solution under similar experimental conditions. In this experiment, feed was continuously replaced till 5 batches of fresh feed (25 L) without changing the pseudo-emulsion (in recirculation mode). Thus, metal was allowed to concentrate in the pseudo-emulsion (linear flow velocity 1.25 cm/s). After 25 L had passed through the mixing unit, it was stopped and the pseudo-emulsion was allowed to settle for a few minutes. Finally, the stripping solution (one fifth volume of feed) was checked for metal concentration. This was around 22 times (2210 mg L⁻¹) above the initial metal concentration in the feed. The total time taken for this experiment was around 10 h. The feasibility of concentrating Cr(VI) with the PEHFSM using a pseudo-emulsion of Cyanex-923 in kerosene and 10 g/L of hydrazine sulphate was thus proved.

4.2. Influence of the hydrazine sulphate concentration in the pseudo-emulsion phase

The influence of the addition of various concentrations of hydrazine sulphate (1–20 g/L) as the stripping agent in the pseudo-emulsion on the transport of chromium by Cyanex-923 was evaluated (Table 1). The organic solution of 10% (0.36 M) Cyanex-923 in kerosene and the source phase contained 20 mg L⁻¹ of chromium in 1 M HCl. The permeability coefficient was increased as the hydrazine sulphate concentration increased up to 10 mg L⁻¹ but further increase was not significant as this resulted in a constant permeability value. The maximum permeability coefficient (P_{Cr}) 11.3×10^{-6} cm/s was obtained for 10 g/L of hydrazine sulphate as the strippant. Therefore, to optimize other parameters 10 g/L of hydrazine sulphate is used as the strippant in the pseudo-emulsion phase.

Table 1

Experimental values of the permeability coefficient (P_{Cr}) as a function of strip concentration in pseudo-emulsion phase.

Hydrazine sulphate (g/L)	Feed flow rate Q_f (cm^3/s)	P_{Cr} (cm/s)
1	5.56	5.8×10^{-6}
5	5.56	6.0×10^{-6}
10	5.56	11.3×10^{-6}
20	5.56	11.4×10^{-6}

Experimental conditions: Feed phase: 1000 cm^3 of 20 mg L^{-1} Cr(VI), Pseudo-emulsion phase: 200 cm^3 of 10% Cyanex-923 + 200 cm^3 of different concentration of hydrazine sulphate. Strip linear flow velocity = 1.25 cm/s .

4.3. Effect of the carrier concentration in the pseudo-emulsion phase

The effect of the carrier concentration in the pseudo-emulsion phase on chromium permeation was studied. A pseudo-emulsion phase of Cyanex-923 in kerosene and 10 g/L of hydrazine sulphate, and an aqueous feed of 20 mg L^{-1} of Cr(VI) in 1 M HCl were established as the experimental conditions. The experiments were conducted at a feed flow rate of $5.56 \text{ cm}^3/\text{s}$ and a strip flow rate of $1.25 \text{ cm}^3/\text{s}$. Fig. 4 depicts the percentage transport values for the transport of chromium through the PEHFSD with various solutions of Cyanex-923 (0.072–0.72 M) in kerosene. It can be seen from Fig. 4 that % transport was observed to be increased with Cyanex-923 concentration up to 10% v/v and then levelled off. The higher concentration of Cyanex-923 was attributed to the higher selective extraction of Cr(VI) complexes, as other metals have lower distribution coefficient values and their extraction is less compared to chromium. The optimum concentration of 10% of Cyanex-923 was selected for further experiments.

4.4. Influence of the feed flow rate on the transport of Cr(VI)

The influence of the feed flow rate was studied in order to optimize Cr(VI) transfer on the tube side by maintaining a fix pseudo-emulsion flow rate in recycling mode. The results for testing a 20 mg L^{-1} of Cr(VI) concentration using 10% Cyanex-923/kerosene are shown in Fig. 5, which are plotted as $\text{Ln}(\text{Co}/\text{C})$ vs. time. P_{Cr} ($\times 10^{-6}$) increased from 7.64 to 11.3 as the linear feed flow rate increased from 4.17 to $5.56 \text{ cm}^3/\text{s}$. A decrease was then observed as the feed linear flow rate increased. As was expected, P_{Cr} first increased as the linear flow rate increased and then decreased. The increase of P_{Cr} was caused by a decrease in the thickness of the aqueous boundary layer when the linear feed flow rate in the fibre lumen increased. The other reason for the decrease in the P_{Cr} value may be the shorter residence time at higher flow rates in recirculation mode, which does not give enough time for complexes to form with chromium in Cyanex-923. This resulted in the incomplete loading of Cyanex-923 with chromium, which contributed to the lower P_{Cr} value in recycling mode under similar experimental conditions. In our experimental study, it was necessary to maintain

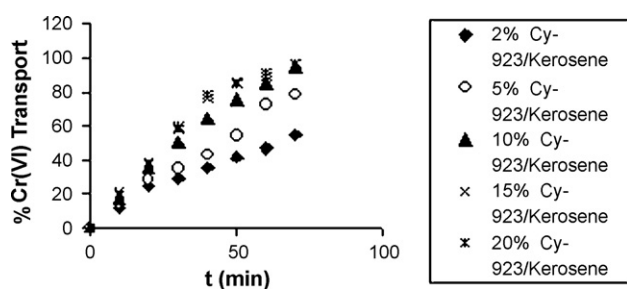


Fig. 4. Influence of the Cyanex-923/kerosene concentration in pseudo-emulsion phase the transport of chromium in recycling mode as function of time.

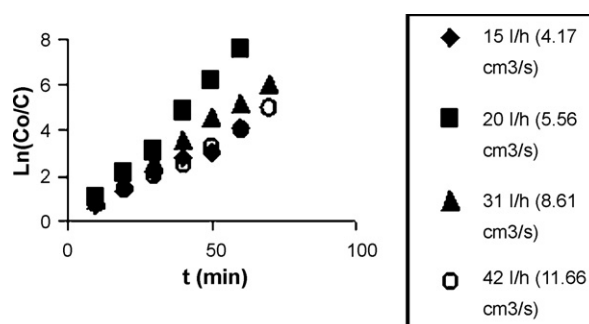


Fig. 5. Influence of the feed linear flow rate on the permeability of Cr(VI) in the feed phase as a function of time in recycle mode by PEHFSD technique [Feed phase: 1000 cm^3 of 20 mg L^{-1} Cr(VI), Pseudo-emulsion phase: 200 cm^3 of 10% Cyanex-923 + 200 cm^3 of different concentration of hydrazine sulphate. Strip linear flow velocity = 1.25 cm/s].

the interface in the pore of the fibre mouth. To avoid the problem of the contamination of the aqueous feed solution by the emulsion at a higher flow rate ($11.66 \text{ cm}^3/\text{s}$), the $5.56 \text{ cm}^3/\text{s}$ linear flow rate was selected throughout the study. The importance of pressure control across the tube and shell side hollow fibre contactor in the PEHFSD is also described in a previous publication in which metal separation from different media was carried out [34–36].

4.5. Effect of Cr(VI) concentration on the feed phase, evaluation of K_m and diffusional parameters, mass transfer resistances and performance analysis

The influence of the initial chromium concentration on the transport of metal by Cyanex-923 was investigated. This study was carried out using feed phases that contained various chromium concentrations in 1 M HCl, and a pseudo-emulsion phase of 10% Cyanex-923 in kerosene and 10 g/L of hydrazine sulphate.

Fig. 6 shows the results for permeability (P_{Cr}), which were calculated by using Eq. (8). The highest percentage of metal transport was obtained when the source phase consisted of an initial concentration of 20 mg L^{-1} of chromium. The decrease in the percentage of metal transport was noted at higher metal concentrations. For higher metal concentrations, the mass transfer of Cr(VI) that crossed the membrane is only described in terms of diffusional parameters. The interfacial transport of Cr(VI) seem to take place at the aqueous feed solution-membrane and aqueous-membrane-pseudo-emulsion phase interfaces. Previous studies [33] suggest that chemical reactions can be considered to occur simultaneously to the diffusion process. Therefore, the Cr(VI) transport rate is determined by the diffusion rate of chromium that contains species through the feed diffusion layer and by the diffusion rate of chromium-Cyanex-923 ($\text{H}_2\text{CrO}_4 \cdot qR_m$) species through the mem-

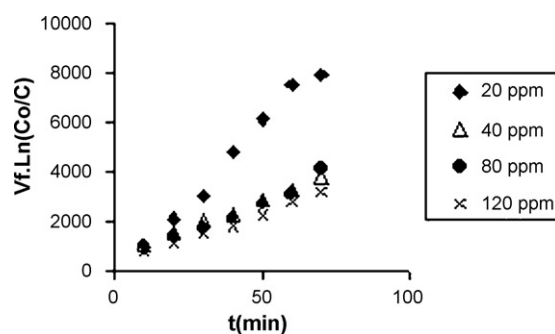


Fig. 6. Influence of the Cr(VI) concentration in feed phase the on transport of chromium in recycling mode as function of time.

brane. The membrane mass transfer coefficient (K_m) and diffusivity that crosses the membrane (D_{eff}) is then calculated by using Eq. (11) [21,30,33]. Although we have tried first-order model in the entire study but this was not fitting when the higher concentration of chromium was used. This is due to the highly loaded aqueous phase interface where stripping of chromium was slow. Similar behaviour was noted by Danesi et al. [21,30] and they have used zeroth order model. In similar direction, we have also tried the zeroth order model as suggested in literature.

By plotting $[\text{Cr(VI)}]_0 - [\text{Cr(VI)}]_{\text{in}}$ vs. time (t) for different Cr(VI) concentrations, one should obtain a straight line with a slope $[\text{Cr(VI)}]_0 - [\text{Cr(VI)}]_{\text{in}}/t$ (at 10% Cyanex-923/kerosene, feed acidity 1 M HCl) (Fig. 7) [21,30]. An ordinate for calculating the value of K_m and D_{eff} should also be obtained. The highest value of chromium complex concentration is equal to total carrier concentration ($[R]_{\text{org}}/n$) and the partition coefficient $D_r = [R]_{\text{org}}/C$ becomes inversely dependent on C . n is the number of carrier molecules per metal ion in the metal carrier complex. Therefore, for large concentration of C , when $1/k_i \ll 1/k_m$, [30].

$$P_{\text{Cr}} = \frac{J}{C} = \frac{[\text{Cyanex} - 923]K_m}{nC} \quad (12)$$

hence, Eq. (6) is no longer valid, therefore the following equation can be used for HFSLM system run in recycling mode [21]. J denotes flux of the metal-carrier species.

$$[\text{Cr(VI)}]_0 - [\text{Cr(VI)}]_{\text{in}} = \frac{[\text{Cyanex} - 923]K_m A}{nV} t \quad (13)$$

The values of $K_m = 1.19 \times 10^{-5}$ cm/s and $D_{\text{eff}} = 1.07 \times 10^{-6}$ cm²/s (Eq. (11)) were obtained from the proposed model under the conditions examined. Tortuosity of HF polypropylene membrane was taken as 3 (supplied by manufacturer).

By plotting $1/P_{\text{Cr}}$ as a function of $1/K_{\text{ex}} \cdot [\text{H}^+] \cdot [\text{Cy-923}]$ for different extractant concentrations of Cyanex-923 (at 1 M HCl concentration) and by varying HCl at 10% Cyanex-923, a straight line with a slope $r_i/r_{\text{im}} \cdot k_m$ and an ordinate $(1/k_i)$ should be obtained. The values of $k_i = 6.6 \times 10^{-2}$ cm/s was calculated from the above calculations.

Eq. (10) indicates that the local value of the total resistance ($1/P_{\text{Cr}}$) is the sum of the local value of the total resistance, which is the sum of the local values of the individual resistances. The overall permeability coefficient was found to be 11.3×10^{-6} cm/s, which means that overall resistance is estimated to be 8850 s/cm. Therefore, the first term (mass transfer resistance due to the aqueous phase) on the right hand side of Eq. (10) is around 675 s/cm, and the second term (mass transfer resistance due to the membrane) is around 8400 s/cm. The overall resistance in the experiments calculated from Eq. (10) and estimated from the model shows that resistance due to the membrane is dominant under the experimental conditions studied, as the second term in Eq. (10) made the maximum contribution.

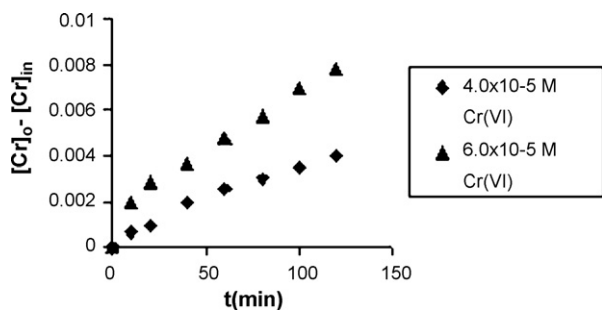


Fig. 7. $[\text{Cr(VI)}]_0 - [\text{Cr(VI)}]_{\text{in}}$ plotted vs. time (t) for the higher concentration of chromium using 10% Cyanex-923.

5. Conclusions

The important finding of the results are as follows:

- (1) The transport of chromium(VI) can be effectively carried out by using Cyanex-923 in kerosene as a carrier across a PEHFSD. By using hydrazine sulphate as a stripping solution in the pseudo-emulsion phase, metal transport is influenced by a number of variables in the feed phase (HCl concentration and metal concentration) and in the pseudo-emulsion phase (carrier concentration, hydrazine sulphate concentration).
- (2) The reduction of chromium(VI) to the less toxic form of chromium(III) is quite fast and effective under used experimental conditions.
- (3) Mass transfer modelling was performed and diffusional parameters including rate controlling steps were evaluated. The values of $K_m = 1.19 \times 10^{-5}$ cm/s, $D_{\text{eff}} = 1.07 \times 10^{-6}$ cm²/s and the value of membrane permeability (P_m) = 1.20×10^{-5} cm/s were obtained from the proposed model under the conditions examined.
- (4) The performance of the PEHFSD was analyzed and separation of chromium was demonstrated against Fe(II) (30 mg L⁻¹), Cu(II) (30 mg L⁻¹), Ni(II) (10 mg L⁻¹) and Zn(II) (5 mg L⁻¹) in hydrochloric acid media.

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