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Carrier-mediated transport of Cr(III) across Lasalocid A-NPOE supported liquid membrane

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Abstract

A weak amount of Cr(III), not exceeding 5%, was transported through a flat sheet supported liquid membrane (FSSLM) using Lasalocid A as carrier and nitric acid as stripping agent. This inefficient transport was mainly due to a driving force disappearance caused by a nitric acid leakage through the flat sheet membrane and then a feed pH decrease. Three experimental solutions have been proposed to overcome, at least partially, this hindrance. Firstly, Cr(III) was transported across a hollow-fiber supported liquid membrane (HFSLM) working as a column system, i.e., by recirculating the feed solution and the stripping solution separately and successively. A transport rate of 19% has been found when each solution was recirculated for 24 h. Secondly, tributyl phosphate (TBP) was used as modifier of the organic membrane solution to accelerate reaction kinetics to interfaces. The addition of TBP permits the transport of 17% of the initial Cr(III) amount in feed after 79 h of the transport process. Thirdly, the feed pH was kept constant by the addition of concentrated NaOH solution. This addition led to a complete Cr(III) transport and an initial flux of $4.1 \times 10^{-7} \text{ mol.m}^{-2}.\text{s}^{-1}$ was obtained.

Keywords: Supported liquid membrane (SLM); Facilitated transport; Lasalocid A; Tributylphosphate; Cr(III)

1. Introduction

Chromium exists in natural waters mostly in two oxidation states, Cr(III) and Cr(VI). The toxic-

ity of their compounds differs widely: the hexavalent chromium is more toxic than the trivalent one. Chromium is a common pollutant released to the subsurface at numerous sites of several industrial wastewaters such as leather tanning,

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electroplating, metallurgy and metal finishing industries [1]. The metal may also enter tap water supply systems from the corrosion inhibitors used in water pipes and container [2].

Some different techniques for the treatment of chromium(III)-containing effluents have been described, such as liquid–liquid extraction [3], ion exchange [4] and adsorption [5]. Chromium has also been recovered by membrane techniques in the past years, like, for example, micellar enhanced ultrafiltration (MEUF) [6] and nanofiltration [7]. Among membrane techniques, supported liquid membranes (SLMs) can be considered as very competitive when the species used for separation and concentration are ions in aqueous solutions [8,9]. An SLM is expected to be an efficient membrane process since higher fluxes and simplicity of implementation are shown [10].

In the majority of cases, chromium has been transported and recovered through an SLM under its hexavalent oxidation state. The carriers incorporated in SLMs can include quaternary ammonium salts [11,12], amines [13,14] and also phosphine oxides [15]. Chaudry et al. [14] have even transported Cr(VI) through an SLM containing tri-*n*-octylamine (TOA) diluted with toluene via a prior oxidation of Cr(III) tannery wastewaters by H₂O₂ and NaOH. Cr(III) probably exists in natural waters in the form of many different species: hydrolysed (Cr(OH)₂ (H₂O)₄⁺), complexed and some even adsorbed on colloidal matter. This metallic cation was chosen because it is an important environmental pollutant and is present in high amounts in tannery wastewaters. In a few works chromium has been transported across an

SLM under its trivalent oxidation state. Molinari et al. [16] recovered Cr(III) using a flat-sheet supported liquid membrane (FSSLM) impregnated with an organic solution composed of dinonylnaphthalene sulfonic acid (DNNSA) diluted in *o*-xylene, whereas the feed aqueous solution was 0.1 g L⁻¹ Cr(III) solution buffered at pH 4.2, and the receiving aqueous solution was H₂SO₄ solution at pH 0. On the other hand, Djane et al. [17] succeeded to transport Cr(III) through a di-(2-ethylhexyl) phosphoric acid (D2EHPA) SLM. The optimised conditions for Cr(III) transport were as follows: feed solution was kept at pH 3, stripping solution 0.1 M HNO₃ and organic membrane solution 10% (w/w) D2EHPA in kerosene.

Some previous studies already showed the capacity of the carboxylic polyether Lasalocid A to extract various monovalent and divalent metallic cations [18–20]. Based on liquid–liquid extraction studies, a recent work done in our laboratory proved that Cr(III) is extractable using the carboxylic polyether Lasalocid A as extractant [21]. The chemical formula of this ionophore is given in Fig. 1. A maximum of extraction of 92% has been obtained using an aqueous 10⁻³ M Cr(III) solution buffered at pH 5.5 (2-[N-morpholino] ethane sulfonic acid (MES) and NaOH), whereas a maximum of release of 89% has been reached using HNO₃ at pH 0 as stripping agent. The liquid–liquid results obtained show the feasibility of the process of transport of Cr(III) across an SLM containing Lasalocid A as ionophore dissolved in 2-nitrophenyl octyl ether (NPOE) and using nitric acid as stripping acid.

In this study, transport of chromium(III)

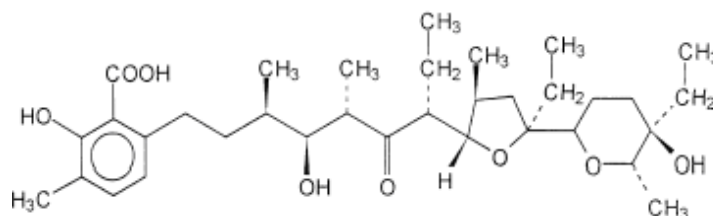


Fig. 1. Lasalocid A chemical formula.

through Lasalocid A-NPOE SLM was described. Three experimental solutions have been proposed to overcome the observed weak Cr(III) transported amount through an FSSLM.

2. Experimental

2.1. Chemicals

2-nitrophenyl octyl ether (NPOE) and chromium(III) salt as chromium(III) chloride hexahydrate $[\text{CrCl}_2(\text{OH}_2)_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ were purchased from Fluka as analytical grade reagent. A buffer solution composed of NaOH (Carlo Erba, min 98%) added to (2-[N-morpholino] ethane sulfonic acid (MES, Sigma, min 99.5%) was used to buffer the feed solution at pH 5.5. Lasalocid A sodium salt (Sigma) was purified and transformed into its acidic form using the protocol described by Juillard et al. [18]. Tributyl phosphate (TBP) is procured from Fluka. Used water was deionized through a MilliQ Plus column (Millipore, USA). A polypropylene film (Accurel[®] PP 2E-HF, Membrana, Germany) with an average pore size of 0.2 μm , a porosity of 75%, and an average thickness of 160 μm was used as an inert support.

2.2. SLM preparation and transport experiment

SLMs were prepared by soaking the inert support with the carrier dissolved in NPOE for at least 48 h. The SLMs obtained were placed in the middle of a two-compartment permeation cell described elsewhere [22,23]. The feed solution (50 cm^3) was $10^{-3} \text{ mol L}^{-1}$ Cr(III) aqueous solution buffered at pH 5.5 (MES buffer). The stripping solution (50 cm^3) was HNO_3 aqueous solution adjusted to pH 0. Both aqueous feed and stripping solutions were magnetically stirred at 25°C. For sampling, 1 mL of feed and stripping solutions was periodically taken, and chromium concentration was determined by flame atomic absorption spectrophotometry (Analytikjena AAS vario 6).

3. Results and discussion

3.1. Cr(III) transport through an FSSLM containing Lasalocid A as carrier

A recent liquid–liquid extraction work done in our laboratory proved that Cr(III) is extractible using the carboxylic polyether Lasalocid A as extractant [21]. The feed solution is composed of aqueous 10^{-3} M Cr(III) solution buffered at pH 5.5, while the stripping solution was nitric acid aqueous solution adjusted at pH 0. The organic solution used to extract trivalent chromium was $5 \cdot 10^{-3} \text{ M}$ Lasalocid A dissolved in NPOE.

The obtained liquid–liquid results are used to study the transport of Cr(III) across an SLM incorporating Lasalocid A as ionophore dissolved in NPOE and nitric acid as stripping acid. Transport experiments of Cr(III) through an FSSLM showed that only a weak amount of initial chromium(III), not exceeding 5%, had been transported. During the transport experiments, a rapid feed pH decrease was observed, bringing feed pH until high acidic values to which Cr(III) complexation by Lasalocid A at feed solution–membrane interface was no longer possible. Taking into account this fact, Cr(III) transport was arrested since the driving force, that is a pH gradient between the feed solution and the receiving solution [19,20], disappeared after a few minutes. This feed pH decrease was due to a HNO_3 leakage through the membrane, confirmed by UV-visible spectra of the feed solution presented in Fig. 2. Indeed, UV spectra of the blank feed solution (no transport experiment) with addition of nitric acid solution at pH 0 (curve 2) and of the feed solution after transport experiment (curve 3) were characterized by an absorption band with a maximum around 300 nm which can be attributed to HNO_3 presence due to nitric acid leakage across the membrane towards the source solution. This nitric acid leakage decreased the feed pH until sufficiently low pH values for which trivalent chromium complexation by Lasalocid A was no longer possible [18].

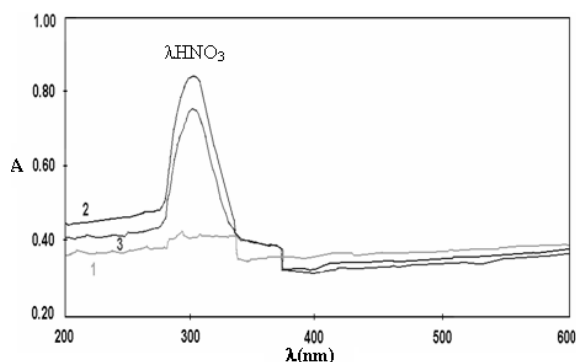


Fig. 2. UV-visible spectra. 1, blank feed solution; 2, blank feed solution with addition of HNO_3 at pH 0; 3, feed solution after transport experiment.

This problem of nitric acid leakage across the SLM led us to study the transport of Cr(III) through a hollow-fibre supported liquid membrane (HFSLM) incorporating Lasalocid A as ionophore to try to overcome this hindrance.

3.2. Cr(III) transport through a HFSLM containing Lasalocid A as carrier

The use of a cell in hollow-fibre configuration (Fig. 3) operating in a column system mode allowed us to surmount the abovementioned problem of feed pH decrease due mainly to nitric acid leakage. In fact, we noted that the simultaneous circulation of the feed phase in the lumen side (inside of the fibre) and of the receiving phase in the shell side (outside of the fibre) lead to an uptake Cr(III) transport rate more or less null. In contrast, a sequential circulation of the source phase and then of the receiving phase (column system) permitted to recover 7% of the initial feed solution Cr(III) amount with a circulation time of 4 h for each of both aqueous phases. This recovery rate increased to 19% for a circulation time of 24 h. In the two cases, the uptake circulation rate of the aqueous feed and receiving solutions was equal to $0.8 \text{ mL}\cdot\text{min}^{-1}$. The fact that the simultaneous circulation of the aqueous phases led to an almost null Cr(III) transport was confirmed by the

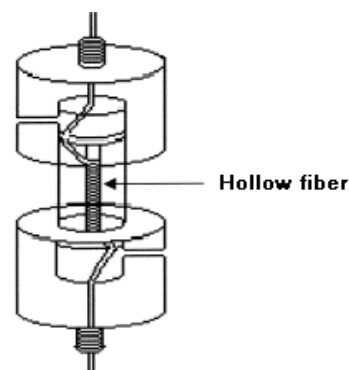


Fig. 3. Scheme of the hollow-fibre module used in the transport experiment.

feed pH decrease as the two phases were in the case of circulation in direct exchange because of the coupling assured by the permeability of the liquid membrane organic phase. On the other hand, in conditions of sequential mode working of the HFSLM, this coupling was not assured anymore, because the liquid membrane was only to the contact with one or the other of the two aqueous phases, but never with the two at the same time, which prevented the HNO_3 leakage towards the source phase. This HFSLM working mode is equivalent to a repetition of the sequence of extraction and stripping steps forming the biphasic exchange experiment.

The use of the HFSLM configuration permits to overcome the obstacle of nitric acid leakage and then the feed pH decrease and an acceptable transport rate was obtained using a 24 h circulation time. The second solution to overcome the observed transport obstruction is the addition of tributyl phosphate (TBP) to the organic membrane phase.

3.3. Effect of the TBP addition on Cr(III) FSSLM transport efficiency

Tributyl phosphate was used in this part as a modifier of the organic membrane phase [25]. Its role is similar to the one of a carrier chelating agent. It can be added to the organic membrane

phase in order to favour the extraction of selected species in a synergetic fashion or to avoid microemulsion or third phase formations [26]. The organic phase was composed, in this case, of $5 \cdot 10^{-3}$ M of Lasalocid A dissolved in 50% NPOE-50% TBP (v/v). Table 1 shows the variations of Cr(III) concentration in the stripping phase and the stripping percentage, i.e., the percentage of transported Cr(III) towards the receiving phase as compared to the initial metallic cations amount as a function of the elapsed transport time.

Table 1 shows that the addition of TBP as modifier of the organic phase improves the efficiency of the transport. It can be seen that after 79 h transport time 17.3% of the initial trivalent chromium has been transported from the source phase to the receiving phase, whereas transported Cr(III) percentage not exceeding 5% has been achieved without TBP addition to the organic membrane phase. When this transport rate was reached, the transport seemed to be inhibited due to a feed pH decrease to values where the complexation step to the interface source solution–membrane was no longer possible. In spite of the improvement of the transport efficiency by the addition of TBP to the organic membrane phase, only 17.3% of the initial trivalent chromium was carried out. This transport disappearance can be explained by the persistence

of the feed pH progressive decrease due to HNO_3 leakage across the FSSLM in the direction of the source phase. The third proposed solution consists of a feed pH correction using concentrated NaOH solution whilst this pH decreases to more or less high acidic values, i.e. less than 4.

3.4. Effect of feed pH correction into transport efficiency

The hindrance of arrested Cr(III) transport through FSSLM due to nitric acid leakage can be also surmounted by maintaining the feed pH in the range of 4–5 during the entire transport experiment by adding concentrated NaOH solution to the source phase [27,28]. The concentrated NaOH addition intervenes each time when the feed pH decreases less than pH 4. Accordingly, this addition changes the source phase volume only slightly, while keeping the feed pH in the range of 4–5. Table 2 shows the variations of the stripping percentage of transported trivalent chromium and of the feed pH as a function of the elapsed transport time.

Table 2 demonstrates net improvement of Cr(III) transported rate which reached a stripping

Table 1
Variations of Cr(III) concentration in the receiving phase and stripping percentage as a function of elapsed transport time

Time (h)	[Cr(III)] _R (10^{-4} mol.L ⁻¹)	Stripping percentage (%)
1.5	0.23	2.3
4	0.25	2.5
22	0.33	3.3
29	0.38	3.8
47	0.83	8.3
54	1.01	10.1
72	1.46	14.6
79	1.73	17.3

Table 2
Variations of Cr(III) stripped percentage and the feed pH corrected using concentrated NaOH as a function of transport time

Time (h)	pH _{feed}	Stripping percentage (%)
0.5	5.0	0.5
1	4.8	0.9
3	4.5	2.7
5	4.9	4.7
23	4.2	20.1
27	4.5	26.7
46	4.4	41.7
49	4.4	46.4
53	5.0	50.8
65	4.9	63.1

rate of 63% after 65 h of transport experiment. The observed improvement can be explained by the fact that the driving force, i.e., the pH gradient between the source phase and the receiving phase, was maintained and then extraction and stripping steps to interfaces took place continuously during the transport experiment time [19,20].

Fig. 4 shows the variation of Cr(III) concentration in the receiving phase as a function of transport time.

Using the linearity obtained between the Cr(III) concentration in the stripping phase and the transport elapsed time, the initial transport flux can be calculated according the following equation:

$$J = \left(\frac{V}{S} \right) \left(\frac{dC}{dt} \right)$$

where V is the stripping solution volume in L, S the exposed membrane area in m^2 , C the molar concentration of Cr(III) ions in the stripping solution in $molL^{-1}$ and t the elapsed transport time in s.

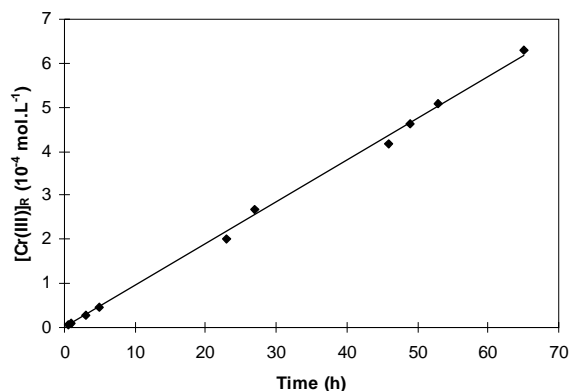


Fig. 4. Variation of Cr(III) concentration in the receiving phase as a function of transport time. Experimental conditions: feed phase, 10^{-3} M aqueous Cr(III) solution buffered at pH 5.5 and corrected using concentrated NaOH; stripping phase, aqueous HNO_3 solution at pH 0; membrane phase, polypropylene film impregnated by 5×10^{-3} M Lasalocid A solution dissolved in 50% NPOE-50% TBP (v/v).

The initial flux, J , is found to be equal to $4.2 \times 10^{-7} mol m^{-2} s^{-1}$, under the experimental conditions mentioned. The acceptable obtained flux value is comparable to the one obtained by Aouad et al. [19] when studying Cd(II) ion transport across an FSSLM containing Lasalocid A as ionophore.

4. Conclusion

This study shows that Cr(III) transport through an FSSLM incorporating Lasalocid A as carrier and nitric acid as stripping agent is inhibited after a few hours due to HNO_3 leakage through the membrane towards the feed solution provoking a driving force disappearance. The use of a HFSSLM operating as a column system, the addition of TBP as a modifier to the organic membrane phase and the correction of the feed pH were three experimental solutions proposed to surmount this hindrance. An almost complete Cr(III) transport can be achieved across an FSSLM-containing Lasalocid A as carrier dissolved in NPOE and incorporating TBP as a modifier when the feed pH is corrected using a concentrated NaOH solution leading to a possible use of such process for Cr(III) wastewater treatment.

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