

Removal of Cr³⁺ from Waste Solution by a Bulk Liquid Membrane and Ion-Exchange Membrane Nafion 117

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In this paper the removal efficiency of chromium trivalent ions by a bulk liquid membrane (BLM) and polymeric membrane has been investigated. Transport of Cr³⁺ ions has been performed using bulk liquid membrane containing D2EHPA (di-(2-ethylhexyl)phosphoric acid) as carrier and polymeric membrane (Nafion 117). The pH of feed solution was maintained at 2, while 1 M H₂SO₄ served as stripping phase in the received compartment of the permeation cell for BLM. The concentration of chromium in the feed and stripping phase vs the contact time were measured by AAS. The best removal efficiency (68 %) was observed for chromium ions when the membrane Nafion 117 was used. The recovery factor in BLM for chromium concentration 0.005M and 0.001 M was 20 %, respectively 24 %, that means the recovery factor depends on the feed solution concentration which influences the transport of chromium ions.

Keywords: trivalent chromium, bulk liquid membrane, ion-exchange membrane, Donnan dialysis

Removal of Cr(III) from wastewater is very important for protection of human health and environment. Trivalent chromium is an essential component having an important role in the glucose (Cr(III) is one of the component in GTF (Glucose Tolerance Factor) potentiating the action of insulin), lipid and protein metabolism. Toxicity of trivalent chromium is less than hexavalent chromium, which is recognized as a human carcinogen, especially via inhalation. However, some *in vitro* data show that chromium (III) has the potential to react with DNA and to cause DNA damage [1]. Moreover, the relation between Cr(III) and Cr(VI) strongly depends on pH and oxidative properties of the solution i.e. under oxidizing conditions, Cr(VI) is thermodynamically favoured and exists as relatively soluble oxyanions [2,3].

Many methods has been developed for the removal of trivalent chromium ions from waste water based on the ion exchange process [4], electrocoagulation [5], precipitation [6,7], ultrafiltration [8], adsorption [7,9,10], electrodialysis [11], nanofiltration and reverse osmosis [12]; however the membrane transport is the most efficient technique in the separation.

A typical liquid membrane system is an organic liquid phase which separates two other liquid phases (feed and stripping phases) with which it is immiscible [13]. Liquid membranes offer several advantages such as low cost, the highly selective separation, the ability to conduct simultaneously an extraction and a stripping processes as well as due to small amounts of carriers (extractants) required in the transport, the possibility of using expensive extractants and their continuous regeneration [13]. However, liquid membranes are not widely used in industrial applications because of low membrane stability and short lifetime. It has been investigated a number of papers dealing with Cr(III) transport through different liquid membrane configurations using various type of carriers. The choosing of the type of carrier is important in the design of metal separation. Among carriers used for Cr(III) transport most studied are: di-(2-ethylhexyl)phosphoric acid (D2EHPA); bis(2,4,4-trimethylpentyl) monothio-

phosphinic acid (CYANEX 302); tri-n-octylamine (TOA); Aliquat 336 [14]. Two papers [15,16] deal with applications of BLMs for Cr(III) removal using di-(2-ethylhexyl) phosphoric acid (D2EHPA) and as the ion carrier.

Donnan dialysis may be considered as an alternative method for Cr(III) removal from aqueous solution. For instance, the concentration and separation of Cr(III) with cation exchange membrane (Nafion 117) was reported by J. Lambert et al. (2005) [17-19].

Donnan dialysis (DD) is an ion exchange membrane process especially useful for treatment of diluted solutions. In the case of this membrane process, a chemical potential difference between two compartments separated by an ion exchange membrane is the driving force for the transport [20]. In Donnan dialysis, metal ions move across an ion-selective membrane based on the Donnan equilibrium principle [21,22]. Donnan dialysis is used in analytical fields when the preconcentration of various cations and anions are performed [23,24].

In this paper, the removal of trivalent chromium ions from a nitric aqueous solution using a bulk liquid membrane (BLM) was investigated. The results were compared with the experiment of Donnan dialysis.

Experimental part

Bulk liquid membrane

All aqueous solutions were prepared using analytical grade chemical reagents (POCh, Gliwice, Chemical Co. Sigma, Chmes, Poland) and without purification. Chromium nitrate solution were prepared by dissolving the Cr(NO₃)₃ · 9H₂O in double distilled water (conductivity - 0.10 μS/cm). The solution pH 2 and was adjusted with 1M nitric acid (HNO₃ analytical grade, Chempur).

Figure 1 shows the scheme of the experimental BLM. The experiments were mixed by a magnetic stirrer (2) at a speed of 200 rpm. The volume of the feed phase (F) was 105 cm³. The initial concentration of Cr(III) was 0.005M and 0.001M. The initial pH (pH=2) was adjusted with 1M HNO₃ (HNO₃ analytical grade, Chempur). As the stripping phase (S), 25 cm³ of 1M H₂SO₄ was applied. All experiments were performed in thermostat (3) at 25 ± 1 °C.

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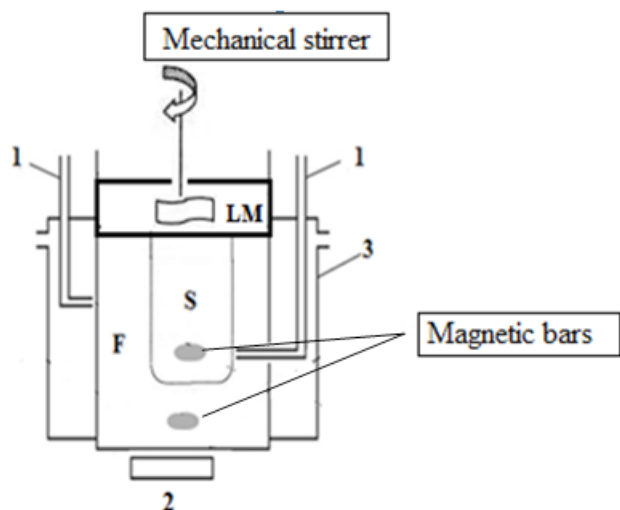


Fig. 1. Scheme of the experimental set-up. (1) sampling tubes, (2) magnetic stirrer, (3) thermostat. LM: liquid membrane, F: feed phase, S: stripping phase

The liquid membrane was composed of 25 cm³ 0.1M di-(2-ethylhexyl)phosphoric acid (D2EHPA, Chemical Co. Sigma, 95% purity) dissolved in kerosene. The membrane phase was mixed by a mechanical stirrer. The surface contact area were as follows: $A_{F/LM} = 16.45 \text{ cm}^2$, $A_{LM/S} = 5.5 \text{ cm}^2$, for feed/LM and LM/stripping phase, respectively. Periodically, the samples (0.5 cm³) from the feed and stripping phases were taken out by sampling tubes (1), and chromium concentration in both phases were determined using a spectrophotometer AA Varian 20ABQ at wave length 357.9 nm.

Donnan Dialysis- Nafion 117

The transport experiments were carried out using a transport cell made of Plexiglas. Between two compartments, a Nafion 117 (DuPont de Nemours, USA) was inserted. The surface contact area of the membrane was 17 cm². The feed and stripping phases were mixed by a magnetic stirrer at 400 rpm and thermostated at 25°C. As the feed phase 0.005 M Cr(NO₃)₃ and the stripping phase 1M HNO₃ were applied. The feed (1000 cm³) and the stripping solutions (100 cm³) were circulated by means of peristaltic pumps through each compartment where the volume was 10 cm³. Samples from the feed (0.5 cm³) and stripping (1 cm³) solutions were taken periodically during 26 h and analyzed using a AA Varian 20ABQ atomic absorption spectrophotometer.

Dalla Costa et al. [27] also studied the diffusion coefficients of Cr³⁺ ions in the Nafion 117 cation-selective membrane, to elucidate the mechanisms of transport of

this ion through these ion-selective membranes, which is an ion exchange membrane process that can be used for the purification and concentration of diluted solutions.

The characteristics of the commercial anion exchange membrane (Nafion 117) are reported on table 2. Their properties can be deduced from measurements of their characteristics. Membranes are non-reinforced films based on chemically stabilized perfluorosulfonic acid/PTFE copolymer in the acid form. The physical properties remain the same for the chemically stabilized membranes, which exhibit substantially lower fluoride ion release compared to the non-stabilized polymer – a sign of improved chemical durability. The polymer is chemical resistant and durable.

Calculus Methodology

The concentration factors (CF) is defined as the ratio of metal concentration in the stripping solution ($C_{S(t)}$) at the time t and the initial feed concentration ($C_{F(t=0)}$) at $t=0$ [25]. CF is calculated from the equation (1):

$$CF = \frac{C_{S(t)}}{C_{F(t=0)}} \quad (1)$$

The concentration factors CF were calculated to demonstrate the transfer of cations from the dilute feed to the concentrate stripping solution [26]. Note that this quantity depends both on the ionic fluxes and volume of the stripping solution.

Up-hill transport (UH) is defined as the ratio of metal concentration in the stripping solution at the time t and the metal concentration in the feed solution at the same time t . The percentage of metal transported (UH) was determined by using the following equation (2):

$$UH = \frac{C_{S(t)}}{C_{F(t)}} \quad (2)$$

where, $C_{S(t)}$ is the metal concentration in the stripping solution at time “ t ” and $C_{F(t)}$ is the metal concentration in the feed solution at time “ t ”.

Recovery factor (RF) [29-32] is defined as the percentage of the total chromium ions that have cross through the membrane to the stripping phase. It was calculated with equation (3):

$$RF = \frac{(C_{F(t=0)} - C_{F(t)})}{C_{F(t=0)}} \times 100 \quad (3)$$

where, $C_{F(t=0)}$ is the initial metal concentration in the feed phase and $C_{F(t)}$ is the metal concentration in the feed solution after the time t .

The flux (J_s) of Cr(III) ions (in mol/cm²s) was calculated by following equation:

| | Thickness[cm] | Ion Exchange capacity [mol/kg dry mb] | Lit. |
|--|---------------|---------------------------------------|------------------------|
| NAFION 117 (DuPont de Nemours, USA) | 0.021 wet | 0.83 | [Koter et al., 1999] |
| | 0.0180 dry | | [Goering et al.,2000] |
| | 0.0178 dry | 0.91 | [Logette et al., 1998] |
| | 0.0178 dry | 0.909 | [Hang et al., 2006] |

Nominal equivalent weight EW = 1100 g/equiv

Tabel 1
CHARACTERISTICS OF THE ANION EXCHANGE MEMBRANES

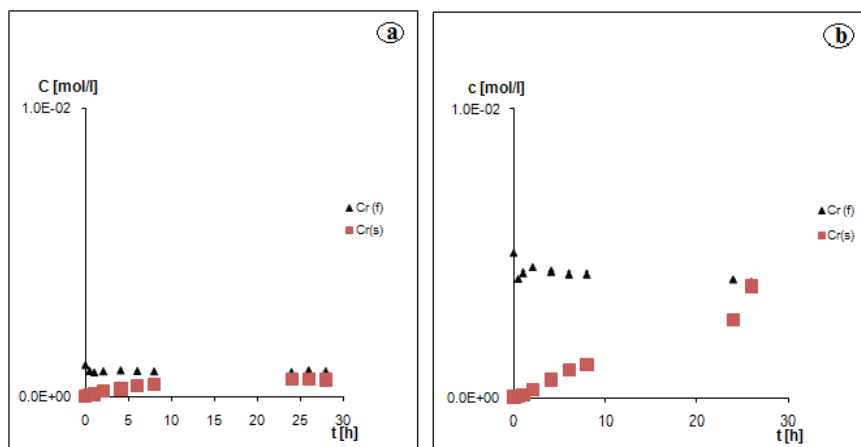


Fig. 2. Variation of chromium concentration in feed and stripping phase in BLM vs. time. (a) Feed phase (▲): 0.001 M Cr³⁺; Strip phase (■): 1 M H₂SO₄; Membrane phase: 0.1 M D2EHPA in kerosene; (b) Feed phase (▲): 0.005 M Cr³⁺; Strip phase (■): 1 M H₂SO₄; Membrane phase: 0.1 M D2EHPA in kerosene

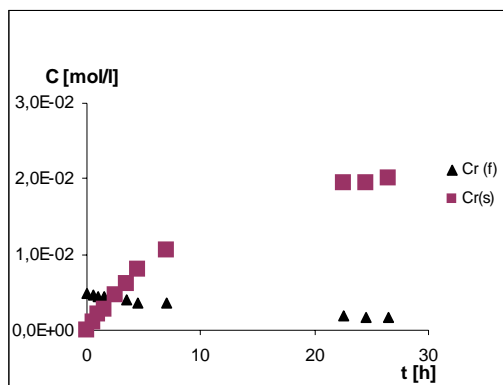


Fig.3. Variation of chromium concentration in feed and stripping phase using Nafion 117 vs. time. Feed phase (▲): 0.005 M Cr³⁺; Strip phase (■): 1 M HNO₃

| Experiment No. | Chromium conc. in feed phase (M) | Concentration Factor, (%) | Up-Hill | Recovery Factor (%) |
|----------------|----------------------------------|---------------------------|---------|---------------------|
| I | 0.001 | 0.563 | 0.717 | 23.60 |
| II | 0.005 | 0.771 | 0.958 | 19.54 |

Table 2
RECOVERY FACTOR OF CHROMIUM TRIVALENT FROM A SYNTHETIC SOLUTION

$$J_s = \frac{\Delta C_{S(t)} \times V_{S(t)}}{1000 \times A_{S/M} \Delta t} \quad (\text{mol/cm}^2\text{s}) \quad (4)$$

where, A is the membrane surface area between the stripping phase and membrane; V is the total volume of the stripping solution and C is a chromium(III) concentration in the stripping solution at time t .

Results and discussions

Transport experiments of Cr³⁺ through BLM and DD- Nafion 117

In order to assess the influence of the chromate concentration on its transport through bulk liquid membrane, the transport experiments were accomplished at two different concentrations: 0.001 and 0.005 M. In case of the transport experiments through Nafion 117, the concentration of feed phase was 0.005M.

The obtained results of chromium trivalent concentration change in a feed and stripping phase with time are shown in figure 2 and 3. We can see that the separation has time intervals: the first period when the separation is very slow observed and the second, when the concentration of chromium ions in the stripping phase increases. During the time interval ions are transported from feed phase to stripping phase through the membrane. As can see the best results were obtained for 0.005 M Cr(III) through Nafion and this concentration has been employed for optimum conditions.

The results of the concentration factor (CF), up-hill (UH) and recovery factor (RF) to the end of the experiment after 28h are presented in table 1. The concentration factors (CF) were calculated to demonstrate possible up-hill-transport phenomena and active transfers of Cr³⁺ in a stripping phase, when CF > 1. As can be seen from table 1, for chromium experiments with D2EHPA the value CF < 1 indicates that up-hill transport does not occur, but CF for DD was 4 which means the up-hill transport occurs. The recovery for both Cr³⁺ concentration through bulk liquid membrane with di(2-ethylhexyl) phosphoric acid (D2EHPA) was calculated to show the percentage amount of chromium removed from the feed phase in stripping phase after a time.

To estimate the removal of chromium ions from solutions by means of Donnan dialysis (DD) and bulk liquid membrane (BLM), the relation (3) was used. RF is the percentage of the chromium ions that have cross through the membrane to the stripping compartment. As can be seen from figure 4 the best recovery for chromium trivalent was observed for DD, 68 %, but the recovery for BLM experiments was very low.

The fluxes are determined experimentally by the linear regression technique from the decrease of metal concentration in the feed solution expressed by the formula (4).

The figure 5 represents the experimental results for transport Q_s of chromium ions in stripping solution vs. time,

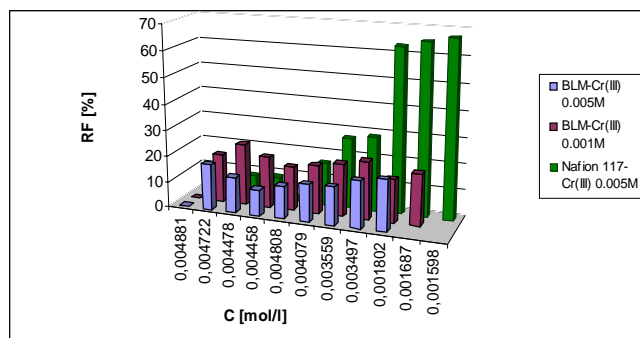


Fig. 4. Recovery factor for BLM with feed phase concentration 0.001M and 0.005M and for donnan dialyses containing 0.005 M Cr³⁺.

where Q was calculated as the amount in moles of cations Cr(III) transported in stripping phase (S) after the time (t) through a cm² of membrane area. Transport Q(s) (mol/cm²) was calculated with equation (5) :

$$Q_s = \frac{C_{S(t)} \times V_{S(t)}}{1000 \times A_{S/M}} \quad (\text{mol/cm}^2) \quad (5)$$

where, $C_{S(t)}$ is the concentration of metal species in stripping phase after transport time t (mol/dm³); $V_{S(t)}$ is the volume of the stripping solution (S) (cm³) after the time t and $A_{S/M}$ (cm²) is the area of the stripping solution/membrane surface area [28].

The results from figure 5 show that the transport Q_s for Cr³⁺ in stripping phase is very low when D2EHPA was used as carriers. In Donnan dialysis using Nafion 117 as membrane the transport Q_s for chromium ions is more efficient after 27 h.

Conclusions

Present work demonstrated that D2EHPA could be used as carrier for the transport of Cr³⁺ across a bulk liquid membrane. Also, it is shown that Donnan dialysis could be an efficient technique to separate chromium trivalent. The advantage of this technique is also the possibility of the recycling of all reactants with a good impact to the environment. However, Donnan dialysis depends greatly on the experimental conditions. The experimental results with D2EHPA in BLM show that the amount of chromium ions transported in stripping phase is dependent on the concentration of chromium in the initial solution of feed phase. The best transport for chromium ions occurred when was used Donnan dialysis with Nafion 117 membrane. The experimental data shows that bulk liquid membrane containing D2EHPA as carrier was not selective and efficient for chromium ions transport.

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References

- EASTMOND D.A., MACGREGOR J.T., SLESINKI R.S., Critical reviews in Toxicology, 2008, **38**(3), p. 173-190.
- RICHARD F.C., BOURG A.C., Water Res., 1991, **25**(7), p. 807-816.
- RAI D., EARY L.E., ZACHARA J.M., Sci. Total Environ., 1987, **86**,1-2, p. 15-23.
- RENGARA J S., JOO C.K., KIM Y., YI J. J., Hazard. Mater., 2003, **102**, p. 257-275.

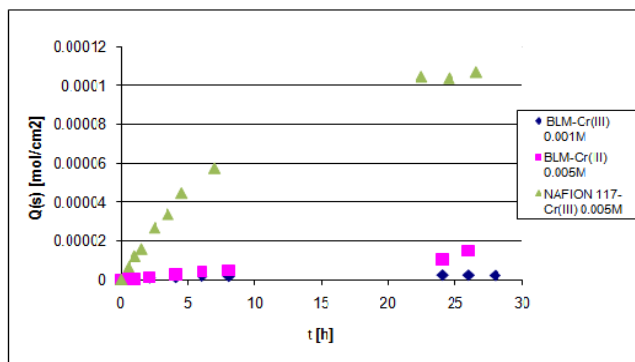


Fig. 5. The transport Q_s of chromium ions through BLM and Nafion 117

- REUSSARD S., PhD thesis, INPT, France, 1994.
- ESMAEILI A., MEDDAGHINIA A., VAZIRINEJAD R., Am. J. Appl. Sci., 2005, **2**, p. 1471-1473.
- HINTERMEYER B.H., LACOUR N.A., PÉREZ PADILLA A., TAVANI E.L., Lat. Am. Appl. Res., 2008, **38**, p. 63-71.
- PUGAZHENTHI G., SACHAN S., KISHORE N., KUMAR A., J. Membr. Sci., 2005, **254**, p. 229-239.
- HASSANIEN M.M., KENAWY I.M., EL-MENSHAWY A.M., EL-ASMY, A.A., J. Hazard. Mater., 2008, **158**, p. 170-176.
- LACH J., OKONIEWSKA E., NECZAJ E., KACPRZAK M., Desalination, 2007, **206**, p. 259-269.
- FRENZEL I., HOLDIK H., STAMATIALIS D.F., POURCELLEY G., WESSLING M., J. Membr. Sci., 2005, **261**, p. 49-57.
- DAS C., DASGUPTA S., DE S., Desalination, 2007, **206**, p. 160-173
- FOURNIER-SALAÜN M. C., SALAÜN P., Desalination 2009, **249**, p. 549-553.
- HO W.S., PODDAR T.K., Environ. Prog., 2001, **20** (1), p. 44-52.
- WALKOWIAK W., KOZŁOWSKI C.A., Desalination, 2009, **240**, p. 186-197.
- RAVANCHI M. T., KAGHAZCHIA T., KARGARI A., Desalination, 2009, **235**, p.199-244
- VAN STADEN, FRESENIUS J. F., J. Anal. Chem. 1995, **352**, p. 271.
- MIRO M., FRENZEL W., Trends Anal. Chem. 2004, **23**, p. 624.
- TAKY M., POURCELLEY G., GAVACH C., ELMIDAOU I.A., Desalination, 1996, **105**, p. 219.
- AKRETCHÉ D.E., KERDJOUJ J. H., Talanta, 2000, **51**, p. 281-289.
- DONNAN F.G., Chem. Rev. 1924, **1**, p. 73.
- PYRZYŃSKA K., Microchim. Acta., 2006, **153**, p. 117-126.
- WÓDZKI R., SIONKOWSKI G., HUDZIK-PIETA T., Polish Journal of Environmental Studies, 1996, **5** (4), p. 45-50.
- SIONKOWSKI G., WÓDZKI R., Sep. Sci. Technol., 1995, **30** (5), p.805-820.
- WÓDZKI R., SZCZEPANSKI P., Polish Journal of Environmental Studies, 2001, **10** (2), p. 101-111.
- WÓDZKI R., SZCZEPANSKI P., Sep. Sci. Technol., 2005, **41**, p. 289
- DALLA COSTA R.F., DESLOUIS C., ZOPPAS FERREIRA J., Proc. 50th ISE Meeting, Pavia, Italy, 1999, 5-10 September.
- WÓDZKI R., SZCZEPANSKI P., PAWŁOWSKI, M. Polish Journal of Environmental Studies, 1999, **8** (2), p. 111-124.
- NECHIFOR G., VOICU S.I., NECHIFOR A.C., GAREA S., Desalination, **241**, (2009), p. 342-348.
- VOICU S. I., ALDEA F., NECHIFOR A. C., Rev. Chim. (Bucharest), **61**, no. 9, 2010, p. 817
- VOICU S.I., STANCIU N.D., NECHIFOR A.C., VAIREANU D.I., NECHIFOR G., Romanian Journal of Information Science and Technology, **12**(3), 2009, p. 410-422.
- CUCIUREANU A., BATRINESCU G., BADEA N.N., RADU D. A., NECHIFOR G., Mat. Plast., **47**, no. 4, 2010, p.416

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