

Supported liquid membrane system for Cr(III) separation from Cr(III)/Cr(VI) mixtures

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ABSTRACT

This paper presents the results of analyses of the chromium(III) transport process from mixtures of Cr(III)/Cr(VI) ions using supported liquid membranes (SLM), in which dinonylnaphthalene sulfonic acid (DNNSA) and di(2-ethylhexyl) phosphoric acid (D2EHPA) were used as carriers. In both cases the membrane worked as a selective barrier for Cr(VI) ions. The increase in both the time of Cr(VI) ions-carrier interaction and the Cr(VI) concentration in the feed phase negatively influenced the Cr(III) separation. The polarizing layer consisting of Cr(VI) ions prevents the access of Cr(III) ions to the inter phase surface and leads to the deactivation of the carrier, which is the result of the strong oxidation properties of Cr(VI) ions. These factors meant that, in the case of the membrane with DNNSA, the membrane could not be used for the effective separation of Cr(III) from the Cr(III)/Cr(VI) mixture. On the other hand, the membrane with D2EHPA can be used for fast and efficient transport of Cr(III) ions, but only for strictly defined process parameters, i.e. where the level of chromium(VI) concentration is below 10^{-3} M and with intensive feed phase mixing.

Key words | chromium separation, DNNSA, D2EHPA, selectivity, SLM

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INTRODUCTION

During some industrial processes, (e.g. metallurgical, dyeing, textile or tanning processes), huge quantities of wastewater containing chromium ions are generated. The industrial wastewaters produced typically contain Cr(III) ions which are harmful and difficult to dissolve in water; however Cr(VI) ions, displaying mutagenic, carcinogenic and teratogenic properties, are also present in them (Li *et al.* 2011).

Differences in the biochemical, chemical and environmental activity of different forms of chromium are the reason for investigations concerning Cr(III) separation from Cr(III)/Cr(VI) mixtures.

Precipitation (Kongsricharoern & Polprasert 1995), ion exchange (Fernandes *et al.* 2012) and extraction (Wionczyk *et al.* 2006) are the most commonly applied and traditional methods for the removal of chromium from wastewaters. Unfortunately, these methods are not effective when it comes to the regeneration of chromium(III)/(VI) mixtures and therefore new effective separation methods are still sought.

Arthanareeswaran *et al.* (2007) showed that ultrafiltration (UF) assisted by complexation is a promising separation technique for the purification of effluents

containing chromium. However, in such systems, the destruction of the recirculation of complexes and ligands limits the possibility to apply this technique. Moreover, UF membranes, like traditional methods, are not selective enough for the separation of different forms of metal ions. In recent years, a remarkable increase in the application of liquid membranes, particularly supported liquid membranes (SLM), for selective metal ions separation processes has been noticed (Joshi *et al.* 2009).

Currently, due to the carrier-mediated transport, liquid membranes are part of the group of the most effective, selective separation techniques for the removal of metal ions from aqueous solutions (Buonomenna *et al.* 2006). The selectivity of liquid membranes enables separation of different types of metal ions from their mixtures (Joshi *et al.* 2009). The number of publications devoted to the issue of separation of Cr(VI)/Cr(III) ions from aqueous solutions using liquid membranes is not extensive (Djane *et al.* 1999; Gęga & Walkowiak 1999; Kończyk *et al.* 2010); the authors show that the simultaneous maintenance of high efficiency and selectivity of the process is very complicated but they do not define the diagnosed problems.

In this paper, we identify and characterize the process conditions determining selective Cr(III)/Cr(VI) mixture separation with a supported liquid membrane. Process parameters such as the kind and concentration of the carrier, the concentration of the chromium(VI) ions, the stirring speed of the feed phase and their optimum scopes were investigated. The influence of the parameters on selectivity and efficiency of Cr(III)/Cr(VI) ions separation in SLM systems is also discussed.

METHOD

Equipment

Transport experiments were carried out in a reactor with two cylindrical chambers containing the feed and the receiving aqueous phases separated by an immobilized liquid membrane. The base feed solution was formed from the dissolution of chromium(III) chloride ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, POCH) in deionized water with a concentration of 0.002 mol/dm^3 . The selected concentration of chromium(III) is characteristic of the concentrations of chromium(III) in industrial chromium wastewater after its physico-chemical cleaning (Religa *et al.* 2011). The reduced chromium concentration level, although still higher than acceptable, in such wastewater is very problematic for further purification using traditional methods. The initial pH of the feed phase was 4. The receiving phase consisted of the aqueous sulfuric acid solution (96% H_2SO_4 , Lach-Ner) with a concentration of 4 mol/dm^3 . The volume of both the feed and the strip solution was 130 cm^3 .

The SLM membrane used was a standard membrane made from polymer foil PTFE (Sartorius) with pore size of $0.45 \mu\text{m}$, which was soaked in an organic mixture of kerosene (Dragon), *o*-xylene (Fluka) and a carrier for a total of 24 h. The membrane surface was 15.2 cm^2 . The processes were carried out in two reactors simultaneously. In the first of them, dinonylnaphthalene sulfonic acid (DNNSA, Aldrich) was used as a carrier, and its concentration varied between 0.05 and 0.28 mol/dm^3 . In the second system, di(2-ethylhexyl) phosphoric acid (D2EHPA, Merck) was used as a carrier, and its concentration varied between 0.15 and 2.4 mol/dm^3 .

The process was thermostatted ($T = 25 \pm 1 \text{ }^\circ\text{C}$) with a Julabo CF41 Circulator. The solutions were mixed in both chambers and mechanical stirrers (IKA Yellow Line OST 20 digital) were used.

The samples were collected both from the feed and the receiving phase in the defined time intervals. The chromium(III) concentration was determined with a spectrophotometer (NANOCOLOR UV/VIS NUV480) using a 1.5-difenylokarbazyde method with wave length $\lambda = 540 \text{ nm}$, after the mineralization of the samples.

Procedure of the chromium(VI) oxidation tests

The chromium(VI) oxidation tests were carried out in accordance with the following procedure: the membrane or the individual support was soaked in four differently concentrated potassium dichromate aqueous solutions of $\text{K}_2\text{Cr}_2\text{O}_7$, PS PARK (0.001; 0.002; 0.01; 0.02 mol/dm^3) for 1, 2, 5 and 24 hours. Next the membrane was placed in the reactor and the chromium(III) transport experiments were performed in the system with the base feed solution.

Procedure of polarization experiments

In the case of the polarization experiments, the feed solution was prepared by the dissolution of chromium(III) chloride in the deionized water with a concentration of 0.002 mol/dm^3 and 0.001 mol/dm^3 potassium dichromate. The authors investigated the influence of the mixing of the feed phase on the extraction level of Cr(III) ions in the presence of Cr(VI) ions. The tests were conducted for different stirring speeds: 100, 300, 600, 1,200 and 1,700 rpm. The extraction level was also checked for the unmixed solution.

In the process conditions ($\text{pH} \leq 4$) the dominant forms of chromium(III) are Cr^{3+} and $\text{Cr}(\text{OH})^{2+}$, and for chromium(VI) - $\text{Cr}_2\text{O}_7^{2-}$ (Djane *et al.* 1999). According to published data (Buonomenna *et al.* 2006), D2EHPA and DNNSA, as cation carriers, do not complex with any negative ions. To confirm this assumption, the chromium(VI) concentration was determined with a spectrophotometer using a 1.5-difenylokarbazyde method with wave length $\lambda = 540 \text{ nm}$ directly in collected samples of the strip solution. In all the experiments the receiving phase was free of chromium(VI). Chromium(III) concentration was determined using a 1.5-difenylokarbazyde method with wave length $\lambda = 540 \text{ nm}$, after the mineralization of the samples. The results obtained proved that the membranes used, independent of the carrier, are the selective barriers for Cr(VI) ions.

Flux calculation

It was assumed that the transport of Cr(III) ions runs according to the consecutive first-order reaction (Gawroński &

Religa 2007). According to this assumption, the Cr(III) extraction kinetics can be described by the following formula:

$$-\frac{dc_{(f)}}{dt} = k \cdot c_0 \quad (1)$$

where, c_0 is the initial chromium(III) concentration in the feed solution (mol/dm^3), $c_{(f)}$ is the current concentration of chromium(III) in the feed solution (mol/dm^3), t is the elapsed time (h), and k is extraction coefficient (h^{-1}).

The integration of Equation (1) leads to

$$\ln \frac{c_{(f)}}{c_0} = -k \cdot t \quad (2)$$

The extraction coefficient (k) can be determined from the straight line relationship of $\ln(c_{(f)}/c_0)$ against the elapsed time.

The initial flux (J_f) of chromium(III) ions from the feed to membrane phase can be calculated from the following formula:

$$J_f = \frac{V_{(f)}}{A_{(f/m)}} k \cdot c_0 \quad (3)$$

where, $A_{(f/m)}$ is the interfacial area (m^2), and $V_{(f)}$ is the volume of the feed phase (m^3).

RESULTS AND DISCUSSION

Optimal carrier concentration

Our own investigations (Gawroński & Religa 2007) and that from other sources (Buonomenna *et al.* 2006; Kończyk *et al.* 2010) concerning chromium(III) transport through SLM show that, for defined initial concentration of a transported substance, an optimal threshold carrier concentration in SLM can be found. Therefore, at the beginning, the optimal concentrations of the investigated carriers (D2EHPA and DNNSA) were defined for the initial chromium(III) concentration of $0.002 \text{ mol}/\text{dm}^3$.

As shown in Figure 1, the efficiency of transport of Cr(III) in the investigated systems reaches peak values for 0.45 and $0.21 \text{ mol}/\text{dm}^3$ for the D2EHPA and DNNSA carriers, respectively, whereas for low carrier concentration the process rate was rather slow. Once the maximum value is reached, the transport efficiency decreases with further

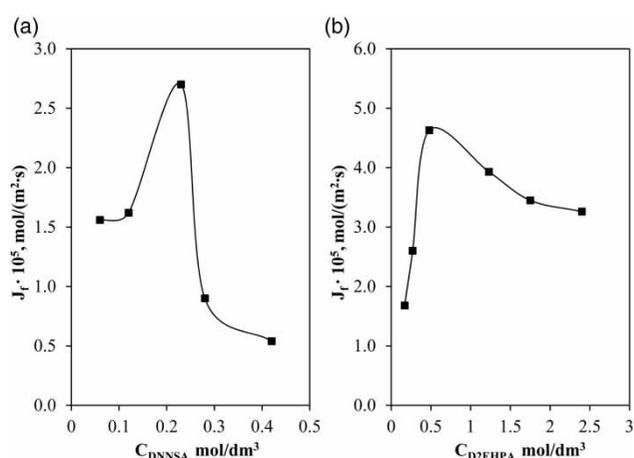


Figure 1 | Effect of carrier concentration on Cr(III) transport with (a) DNNSA, (b) D2EHPA as a carrier in membrane. Feed phase: $C_{\text{Cr(III)}} = 0.002 \text{ mol}/\text{dm}^3$, $\text{pH} = 4$; Stirring speed of the feed phase 300 rpm; Stripping phase: $4 \text{ mol}/\text{dm}^3 \text{ H}_2\text{SO}_4$.

increase in the carrier concentration. The observed effects are in agreement with the results by other authors (e.g. Buonomenna *et al.* 2006) and can be attributed to the viscosity of the organic phase which rises with an increase in the carrier concentration (Kończyk *et al.* 2010). Lower chromium(III) extraction in the case of the DNNSA carrier is probably caused by the formation of large Cr(III)-carrier structures in the membrane phase (Buonomenna *et al.* 2006). The large size and ring structure of DNNSA is responsible for such behaviour.

Based on these results, the concentrations of D2EHPA of $0.45 \text{ mol}/\text{dm}^3$ and DNNSA of $0.21 \text{ mol}/\text{dm}^3$ were selected as optimal for further experiments.

Influence of Cr(VI) ions concentration on transport kinetics of Cr(III) ions

Before the next stage of experiments, the SLM membranes with separated carriers were soaked for 1 or 24 hours in aqueous solutions with different chromium(VI) concentrations, i.e. 0.02 and $0.002 \text{ mol}/\text{dm}^3$. Next, each membrane was placed in the reactor and the chromium(III) transport experiments were carried out with the base feed solution. The experiment results presented in Figure 2(a) indicate that, in the case of membrane with DNNSA, the process efficiency sharply decreased even after the short time of the membrane contact with chromium(VI) solution. After a 1 hour bath in the chromium(VI) solution, a decrease in the flux was observed for the membrane, which amounted to 65% for the $0.002 \text{ mol}/\text{dm}^3$ Cr(VI) and 76% for the Cr(VI) concentration of $0.02 \text{ mol}/\text{dm}^3$. In the case of a 24 hour bath in chromium(VI) solution, the flux decrease

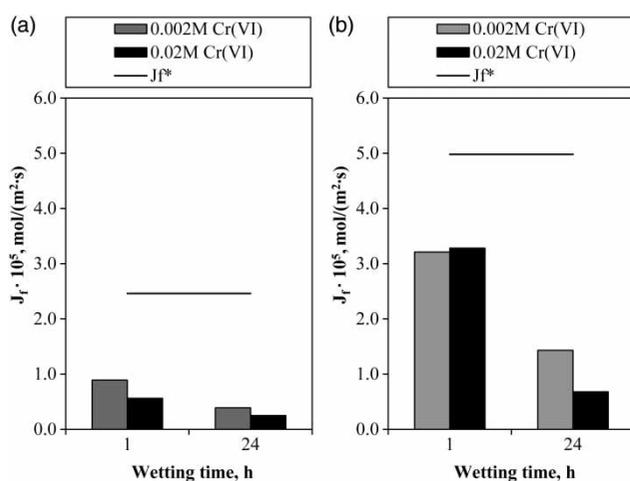


Figure 2 | Transport of chromium(III) through the membrane with (a) DNNSA and (b) D2EHPA as a carrier submerged in a solution consisting of differently concentrated Cr(VI) ions before the pertraction process. Initial concentration of $C_{Cr(III)} = 0.002 \text{ mol/dm}^3$. Stirring speed of the feed phase 300 rpm. J_f^* – chromium(III) flux for a standard prepared membrane.

amounted to 92%. The obtained results show that Cr(VI) ions can partially deactivate the DNNSA carrier. The carrier deactivation level is strongly dependent on both chromium(VI) concentration (the higher the Cr(VI) ions concentration, the higher the carrier deactivation level) and the carrier–Cr(VI) ions interaction time (the longer the interaction time, the higher the carrier deactivation level). A large decrease in both the efficiency and the speed of the process of selective Cr(III) ion separation can be observed for the membrane with DNNSA, as the carrier prevents its effective application. Therefore the authors did not consider such membranes for further analysis.

For membranes with D2EHPA the process efficiency also decreased but these changes were lower than in the case of the membrane with DNNSA. In this case, after a 1 hour bath in the Cr(VI) solution, a flux decrease of 35% was observed, regardless of the Cr(VI) concentration in the aqueous solution (Figure 2(b)). Strong oxidizing properties of Cr(VI) ions lead to the oxidation and partial deactivation of the D2EHPA carrier. Organophosphates, such as di(2-ethylhexyl) phosphate, can be partially oxidized by oxidizing agents (for example $\text{Cr}_2\text{O}_7^{2-}$ ions) which may result in the release of phosphorus oxides (Biswas *et al.* 2003). So far, the impact of this phenomenon on the effectiveness of the selective separation of the Cr(III)/Cr(VI) mixture in the SLM system has not been described in the literature. In spite of this fact, the pertraction of chromium(III) through the membrane, in the investigated system, was on a satisfactory level. Such results indicated that the extent of the carrier oxidation–membrane deactivation

could be determined by the carrier mobility in the membrane. As discussed elsewhere (Gawroński & Religa 2007; Joshi *et al.* 2009), at the threshold concentration of the carrier in the membrane, the carrier molecules are regularly immobilized in the viscous membrane forming a characteristic transport structure. When some oxidizing agents enter the membrane system, the deactivation of the carriers on the feed/membrane surface is initiated. At the same time, the non-active carrier molecules are constantly ‘exchanging’ by active carrier molecules, which stabilize the membrane transport structure. D2EHPA molecules are more mobile than DNNSA molecules, and therefore the process of their exchange within the inter phase surface of the membrane is more effective. As a consequence, for chromium(VI) concentration over 0.002 mol/dm^3 , the transport efficiency in the membrane with D2EHPA as the carrier is high but only for a short time.

In the case of a 24 hour membrane bath in the chromium(VI) solution, the flux decrease amounted to 72% for the Cr(VI) concentration of 0.002 mol/dm^3 and to 86% for the Cr(VI) concentration of 0.02 mol/dm^3 . Based on the results, we assumed that the growth of the non-active carrier molecules caused gradual reduction of ion transport; indeed, a decrease in transport efficiency was noticed. All the above clearly suggests that the process time of Cr(III)/Cr(VI) ions separation should be as short as possible, particularly when the concentration of chromium(VI) ions is high.

The total Cr(III) ion extraction time for the D2EHPA carrier is equal to about 5 hours. Before further experiments, the membrane was soaked in solutions with different Cr(VI) ion concentration for a total of 1, 2 or 5 hours. The obtained results presented in Figure 3(a) show that under the assumed short period of time the transport properties of the investigated membrane with D2EHPA were stable. Moreover, as was expected, the membrane properties were also independent of the level of the Cr(VI) concentration in the solutions tested.

To explain the influence of the Cr(VI) concentration on the membrane system efficiency, additional transport experiments were run for the membrane soaked in the Cr(VI) solution with a concentration of 0.001 mol/dm^3 (different soaking time analyzed). As shown in Figure 3(b), the reduction of Cr(VI) ion concentration has favourable influence on the transport efficiency. In this case, the process efficiency was nearly stable for each of the tested time periods.

The results presented clearly indicate that strong oxidation properties of Cr(VI) ions present in the system partially oxidize and deactivate the carriers used. The deactivation level strongly depends on the time interaction between

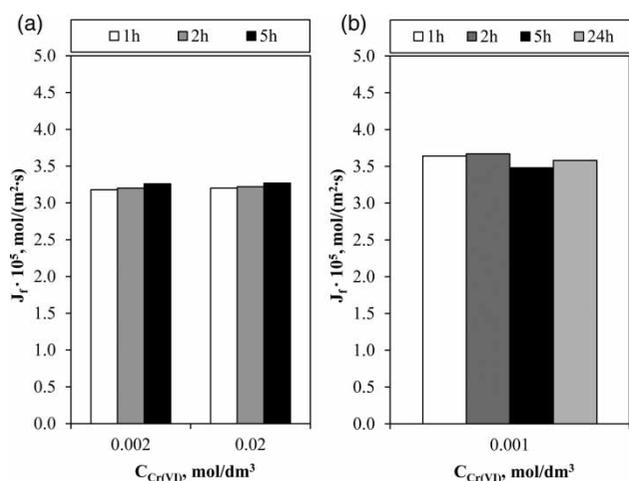


Figure 3 | Transport efficiency of chromium(III) through a previously soaked membrane, before the pertraction process, in solutions containing various concentrations of chromium(VI), in different time periods. Initial concentration of $C_{\text{Cr(III)}} = 0.002 \text{ mol}/\text{dm}^3$. Stirring speed of the feed phase: 300 rpm.

Cr(VI) and the carrier. A short time of interaction, less than a couple of hours, strongly reduces the negative influence of chromium(VI) on the membrane transport properties. The second factor improving effectiveness of the process is the reduction of Cr(VI) concentration. Therefore, high efficiency of the process can be obtained when the chromium(VI) concentration is kept below 10^{-3} M . Similar dependence was observed by Gęga & Walkowiak (1999).

Membrane polarization

The primary investigations concerning transport kinetics of Cr(III) from the Cr(III)/Cr(VI) mixture in a system with SLM show that factors causing the reduction of the speed and the effectiveness of the process can be connected with the issue of membrane polarization (Fontàs *et al.* 2007). As a result of selective membrane properties, the negative ions and Cr(VI) ions present in the solution are stopped in the feed phase. Because of the presence of the high concentration of both negative and positive ions in solution, a diffusive ion layer is formed, which prevents Cr(III) ions having access to the inter phase surface between the feed and the membrane phase. To prevent the formation of the membrane polarizing layer, the turbulence near the membrane surface can be increased (Deon *et al.* 2007). This can be achieved for instance, by an increased stirring speed for the feed phase; therefore, the transport kinetics of the Cr(III) from the Cr(III)/Cr(VI) mixture for different mixing speeds of the feed phase were measured. The results are summarized in Figure 4. Increasing the mixing speed

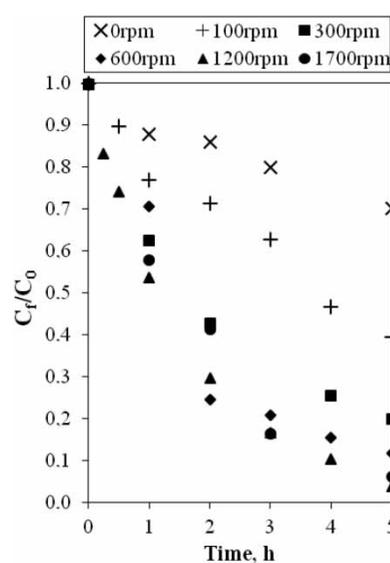


Figure 4 | Influence of stirring speed on extraction of Cr(III) ions in liquid membrane system with D2EHPA. Feed phase: $C_{\text{Cr(III)}} = 0.002 \text{ mol}/\text{dm}^3$, $C_{\text{Cr(VI)}} = 0.001 \text{ mol}/\text{dm}^3$, pH = 4.

of the feed phase clearly reduces the negative influence of the presence of Cr(VI) ions on the Cr(III) extraction level. The obtained results confirmed the formation of a polarizing layer near the membrane surface. Increasing the solution's turbulence reduces the thickness of the polarizing diffusion layers. As a result, an increase in Cr(III) extraction kinetics was observed. The system achieves dynamic equilibrium for a mixing speed of 1,200 rpm. Further increase in the mixing speed has no influence on the transport kinetics of Cr(III) ions. Zheng *et al.* (2009) indicated that too intensive mixing can lead to the leaching of the membrane phase from polymeric support. As a consequence, a decrease in the system stability is observed. Thus, although a moderate mixing speed in the aqueous phases does not prevent the formation of a polarizing layer at the membrane surface, it ensures satisfactory efficiency of the process, and a good stability of the system. For this reason, a mixing speed of the feed solution of 300 rpm was selected as optimal.

CONCLUSION

Both membranes with D2EHPA and DNNSA as a carrier could be used for selective Cr(III) ion separation from a mixture of Cr(III)/Cr(VI) ions.

For the initial concentration of Cr(III) ions of $0.002 \text{ mol}/\text{dm}^3$, the optimal carrier concentrations in SLM selected were 0.45 and $0.21 \text{ mol}/\text{dm}^3$ for D2EHPA and DNNSA, respectively.

Due to the high DNNSA carrier deactivation under strong oxidation of Cr(VI) ions, the practical use of a DNNSA membrane for Cr(III) ion separation from Cr(III)/Cr(VI) ion mixture is impossible.

On the other hand, a membrane with D2EHPA ensures both high selectivity and efficiency of Cr(III) ion separation, but only from a diluted Cr(III)/Cr(VI) ion mixture. Even an increase in the initial Cr(VI) concentration exceeding 10^{-3} M negatively influences the Cr(III) transport in the system. Moreover, a higher concentration of Cr(VI) ions in the feed phase enables the formation of polarizing layers near the membrane, preventing Cr(III) ion access to the inter phase – membrane/feed phase – surface. The decrease in the chromium(VI) concentration and the increase in the mixing speed reduce the negative effect of Cr(VI) ion accumulation near the membrane surface.

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