Selective chromium III/VI separation in polymer inclusion membrane system

J. Rajewski[1]*, P. Religa[2], M. Wojasiński[1], P. Gierycz[1]

[1] Faculty of Chemical and Process Engineering, Warsaw University of Technology, Waryńskiego 1, 00-645 Warszawa, Poland
[2] Department of Environmental Protection, Kazimierz Pułaski University of Technology and Humanities in Radom, Chrobrego 27, Radom, Poland
*Corresponding author: e-mail: j.rajewski@ichip.pw.edu.pl

Analyze of chromium(III) transport process from mixtures of Cr(III)/Cr(VI) ions with polymer inclusion membrane (PIM) system have been done. Di(2-ethylhexyl) phosphoric acid (D2EHPA) have been used as a carrier. It was found that the transport efficiency in PIM is dependent on the carrier concentration in the membrane. It was found that there is an optimal range of carrier concentration in the membrane, which ensures rapid and efficient transport. In studied system optimal D2EHPA concentration was in range between 0,9- 1,5 mol/dm3. Membrane worked as selective barrier for Cr(VI) ions. However increase of Cr(VI) concentration above 0,0005 mol/dm3 negatively influenced Cr(III) transport. It was caused by degradation of the polymer inclusion membrane made of cellulose triacetate (CTA) . Strongly oxidizing Cr(VI) ions can damage polymer inclusion membrane with CTA matrix. The chemical attack of strongly oxidant Cr(VI) ions could lead either to hydrolysis of the pendant acetyl group or to oxidation of polymer backbone leading to chain scission. Moreover, oxidation is accelerated at high concentration of Cr(VI) ions.
The membrane containing D2EHPA as a carrier can be recommended for selective separation of Cr(III) ions only from diluted Cr(VI)/Cr(III) mixtures. However the polymer inclusion membrane need a change the polymer matrix.

Key words: chromium separation, selectivity, D2EHPA, PIM

Introduction

In some industrial processes, for example: metallurgical, dyeing, textile, tanning, huge quantity of wastewater including chromium ions are generated. The dominant form of chromium occurs in the above-mentioned wastewater is harmful, difficulty water-soluble Cr(III) form but the mobile, toxic for the biocenosis, mutagenic, carcinogenic and teratogenic for the man – Cr(VI) form [1,2] there is either present.

Differences in the biochemical, chemical and environmental activity of different forms of chromium became a reason for investigations concerning Cr(VI) separation from Cr(III)/Cr(VI) mixtures. Such separation can enable, among others, the regeneration of waste streams from the metallurgical, dyeing, textile and others industries as well as can indicate different forms of chromium appearing in environmental samples.

The precipitation [1], the ion exchange [3] and the extraction [4] are most often applied, traditional methods for removal of chromium from wastewater. Unfortunately, these methods are not enough selective for the reason of chromium(III)/(VI) mixtures regeneration. Arthanareeswaran et al. [5] showed that ultrafiltration (UF) assisted by complexation is a promising separation technique applied to purification of effluents containing heavy metals such as chromium. As the chromium ions are too small to be retained by the filter, they had to be first complexed with a water-

soluble macroligand. Moreover the UF membranes had to be modified to ensure high retention of the chromium.

New efficient methods of separation are still being searched. In recent years, a remarkable increase in the applications of liquid membranes especially supported liquid membrane (SLM) and polymer inclusion membrane (PIM) for metal ions separation processes has been found [6-9].

At present, liquid membranes, thank to the carrier-mediated transport, belong to the group of the most effective, selective separation techniques for removal of metals ions from aqueous solution [7-10], including separation of Cr(VI) [11] and Cr(III) ions [12]. The selectivity of liquid membranes allows for separation of different metals ions mixtures [5] or different forms – speciation of the same metal mixtures [13].

The selectivity of liquid membranes allows for separation of different metals ions mixtures [14,15]. In the literature, there is a small number of papers dedicated to separation of Cr(VI)/Cr(III) ions from aqueous solutions by liquid membranes [16-18]. The results shown that the simultaneous maintenance of high efficiency and selectivity of the process is very complicated but still can't find the discussions about the causes of the diagnosed problems.

There is no works where is explained negative impact of forms of chromium for their separation. It isn't possible also to discern the description of the negative impact of strongly oxidizing Cr(VI) ions on the elements and property of the polymer inclusion membranes.

The aim of this paper was investigation of influence of the membrane composition and process conditions ensuring the selective and effective Cr(III)/Cr(VI) ions separation from the aqueous phase in the polymer inclusion membrane. Such process parameters like: the concentration of the carrier, concentration ratio of the chromium III/VI ions, their optimum scopes have been investigated.

Materials and methods

A two-compartment cell described in our previous papers [18,19] was used in the transport experiments. The membrane was clamped tightly between two compartments of 130cm³. The feed solution was formed by mixing of aqueous chromium(III) chloride solution (CrCl$_3$·6H$_2$O, POCH) at concentration equal to 0,002 mol/dm³ Cr(III) and potassium dichromate (K$_2$Cr$_2$O$_7$, PS PARK) at five different concentrations: 0,0005; 0,001; 0,002; 0,01; 0,02 mol/dm³. Selected concentration of chromium(III) is characteristic for the chromium(III) concentrations of industrial chromium wastewaters after its physico-chemical cleaning [1,6]. Initial pH of the feed phase was equal to 4. Receiving phase consisted of aqueous sulfuric acid solution (96% H$_2$SO$_4$, Lach-Ner) at concentration equal to 4 mol/dm³. Volume of both feed and strip solution was equal to 130 cm³.

PIM was formed by carrier di(2-ethylhexyl) phosphoric acid (D2EHPA) from Merck and plasticizer 2-nitrophenyloctylether (2-NPOE) from Fluka psychical immobilization in cellulose triacetate polymer matrix (CTA) from Fluka. CTA was dissolved in 20cm³ of dichloromethane (Merck) at room temperature. 0,3 cm³ of 2-NPOE in 5cm³ of dichloromethane was then added. After vigorous stirring, D2EHPA was added and the solution was stirred to obtain homogenous solution. Dichloromethane was allowed to evaporate and membrane was separated from glass by immersion into cold water. Next the membrane was conditioning in distilled water. The active membrane surface was equal to 15,2 cm².

The process was termostated (T=25°C±1°C) by the use of Circulator Julabo CF41. The solutions were mixed in both chambers by the use of mechanical stirrers (IKA Yellow Line OST 20 digital). The samples were collected both from the feed and the receiving phase in the defined time intervals. Chromium(VI) concentration was determined with a spectrophotometer (Spectrophotometer NANOCOLOR UV/VIS NUV480) using 1,5-difenylokarbazyde method with wave length λ = 540 nm straight in collected samples. Total chromium was determined with a spectrophotometer using 1,5-difenylokarbazyde method after mineralization of samples. Chromium(III) concentration was calculated from a difference of the total chromium and chromium(VI) concentration.

In order to characterize the cellulose triacetate matrix, scanning electron microscopy (SEM) was used (Phenom FEI Company). First the samples were freeze-dried (Alpha 2-4 LSC Martin Christ lyophilizer). Then, the samples were dusted with a 15nm layer of gold (K550X Quorum Technologies Ltd sputter).

The temporary flux (J$_Z$) of chromium(III) ions transported through the membrane from feed to stripping phase was calculated for initial stage of process, when the process run most quickly. The following formula was used:

$$Jz = \frac{V}{A} \cdot k \cdot Co$$

where J$_Z$ is ions temporary flux [mol/(m²·s)]; V – volume of feed phase [m³]; A – effective membrane area[m²]; Co- initial chromium(III) concentration in the feed phase [mol/m³]; k- penetration coefficient [s].

Results and discussion

Cr(III) transport through PIM

Our own investigations [6,20] and some literature information [12,21] concerning chromium (III) transport through liquid membranes show that for defined initial concentration of a transported substance an optimal carrier concentration in liquid membrane (LM) can be found. In the first stage of the study the optimal concentrations of the investigated carrier (D2EHPA) have been defined for the 0,002 mol/dm³ initial chromium(III) concentration (Fig. 1).

The carrier concentration significantly influences transport kinetics of Cr(III). There is no transport of Cr(III) ions through PIM without carrier in investigated system. For low initial concentration of D2EHPA≤ 0,4 mol/dm³ only a partial extraction was observed. Increasing a concen-
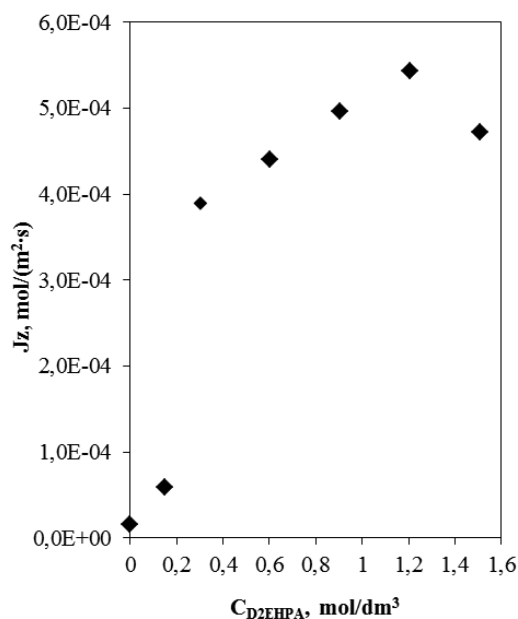

Fig. 1. Effect of carrier concentration on Cr(III) transport with D2EHPA in PIM. Feed phase: CoCr(III) = 0,002 mol/dm³, pH = 4; Stripping phase: 4M H$_2$SO$_4$.
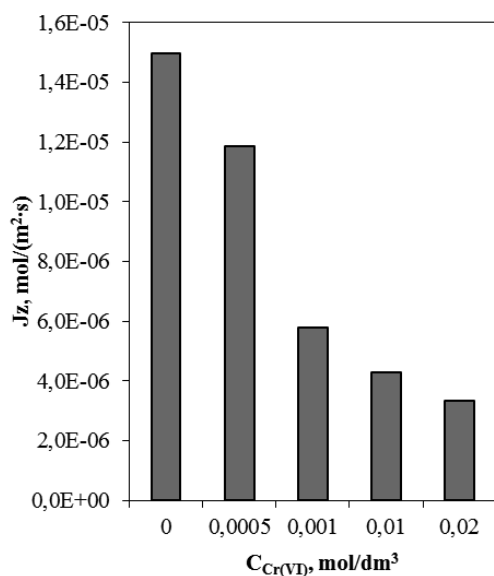
In case of PIM an optimal range of carrier concentration in membrane guaranteeing fastest course of the process was found. In studied system optimal D2EHPA concentration was in range between 0,9-1,5 mol/dm³. In these concentrations range the fastest penetrating of Cr(III) ions to the membrane and their fastest and total re-extraction was found (Fig. 1). The result is comparable with that reported by O. Kebiche-Senhadji et al. [22] and P. Samuel et al. [23], who investigated the transport of metals through PIM containing phosphoric acid derivatives in the role of the carriers.

Influence of Cr(VI) ions concentration on efficiency of Cr(III)/Cr(VI) ions separation

The influence of Cr(VI) ions concentration for the competitive transport of Cr(III) and Cr(VI) ions and their separation has been checked. The investigations have been performed for constant initial concentration of Cr(III) ions and different concentrations of Cr(VI) ions. In all the experiments the receiving phase was free from chromium(VI). This means that the used membrane with D2EHPA is a selective barriers for Cr(VI) ions.

The effect of Cr(VI) ions concentration in feed phase on transport of Cr(III) ions through the PIM with D2EHPA shown in Fig. 2. The result indicate that initial concentration of Cr(VI) ions in the feed phase significantly influences transport efficiency of Cr(III) ions. For low initial concentration of Cr(VI) ≤ 0,0005 mol/ dm³ the chromium (III) flux is decreased of about 20%. Increased the initial concentration of Cr(VI) to 0,001 mol/dm³ additionally decreased the flux of transported ions of even 80%.

Fig. 2. Effect of Cr(VI) ions concentration in feed phase on transport of Cr(III) ions through the PIM membrane with D2EHPA as a carrier. Initial concentration of CoCr(III)=0,002 mol/dm³

tration of D2EHPA in membrane from 0,6 mol/dm³ to 1,5 mol/dm³ increased the efficiency of the process. In the case of the high concentration of D2EHPA≥ 1,6 mol/dm³ the membrane lost physical and transport properties. The visible morphological changes on the surface of the membranes was appeared. This is caused by an excess of carrier crystallization.
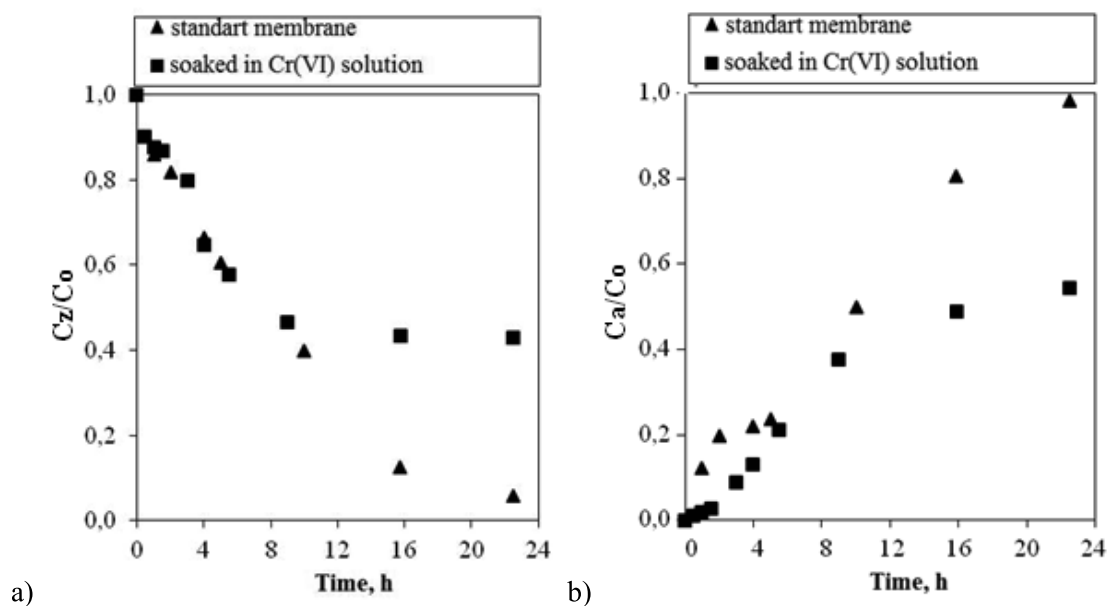
a) b)

Fig. 3. Variation of chromium(III) concentration vs. time in: a) feed phase, b) receiving phase for standard membrane and membrane soaked in Cr(VI) solution= 0,01mol/dm³. Co: initial chromium(III) concentration in feed phase; Cz: current chromium(III) concentration in feed phase; Ca: current chromium(III) concentration in striping phase
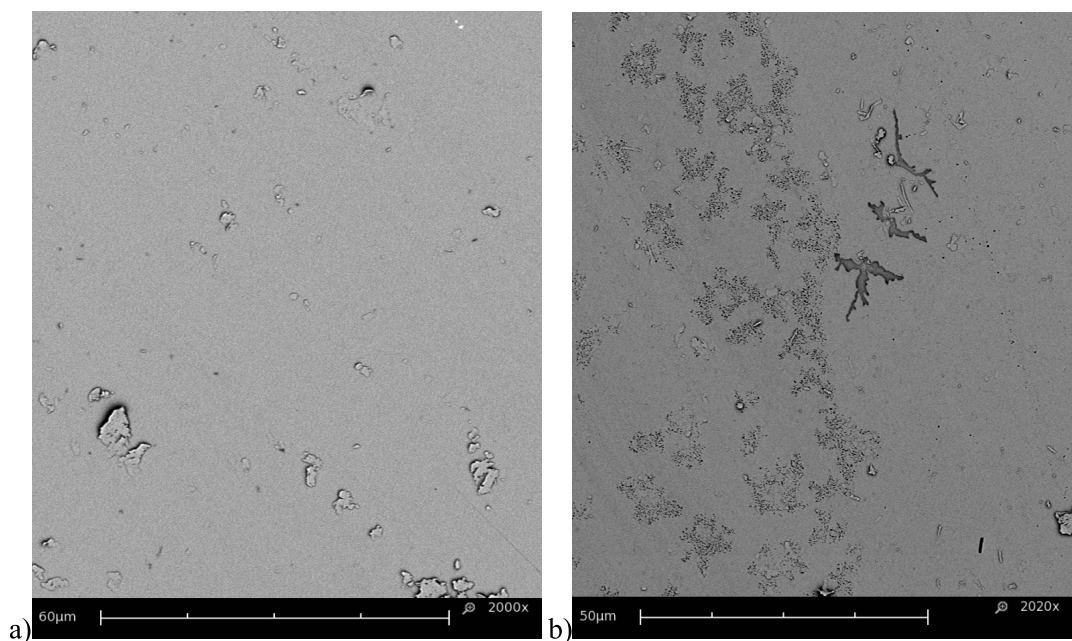
a) b)

Fig. 4. SEM pictures of cellulose triacetate matrix: a) pure CTA, b) pure CTA soaked in Cr(VI) solution= 0,01mol/dm³

Degradation of polymer inclusion membrane

The primary investigations concerning transport kinetics of Cr(III) from the Cr(III)/Cr(VI) mixture in a system with PIM show that the reason causing reduction of a speed and effectiveness of the process can be connected with degradation of polymer structure of the membrane. Furthermore studies [24] indicated that cellulose triacetate (CTA) matrix of PIM is prone to chemical attack mainly by oxidizing agents. Probably strongly oxidizing Cr(VI) ions can damage polymer inclusion membrane with CTA matrix.

In order to confirm this assumption the following experiments have been done. The PIM was soaked in 0,01 mol/dm³ aqueous chromium(VI) solution for 24 hours. The results presented in Fig. 3 show that soaking the membrane in Cr(VI) solution caused reduction of about 40% efficiency of the extraction and re-extraction process. The results indicate that the highly oxidizing Cr(VI) ions, as was assumed, can destroy the membrane.

In order to confirm the adverse effects of strongly oxidant Cr(VI) ions for CTA, scanning electron microscopy (SEM) was used. Results obtained from SEM (Fig. 4) consistently indicate a remarkable influence of the Cr(VI) ions on the CTA morphology.

As you can see in the fig. 4a, pure CTA matrix have a smooth surface. Fig. 4b shows that soaking the CTA matrix in a Cr(VI) solution causes irreversible morphological changes on the surface of polymer matrix. The chemical attack of strongly oxidant Cr(VI) ions could lead either to hydrolysis of the pendant acetyl group or to oxidation of polymer backbone leading to chain scission [25,26]. However, polymer chain oxidation was established as the major degradation in performance of CTA. The effect of oxida-

tion reducing both its molecular weight as well as mechanical strength resulting in a decline of efficiency of the process. Oxidation is accelerated at high concentration of oxidizing agents [27] what is compatible with our observations (Fig. 1).

Our investigations and SEM characteristic confirm that Cr(VI) ions can damage polymer inclusion membranes and cause the reduction of a speed and effectiveness of the process

Moreover also pH influence on CTA membrane matrix performance. CTA membranes are most stable at pH 4.7 and the extreme pH, less or above this value, will accelerate the process of hydrolysis of acetyl groups, pendant to the polymer chain [25].

Conclusions

The polymer inclusion membrane containing D2EHPA as carrier is a selective barrier for Cr(VI) ions. Optimal range of carrier concentration in membrane guaranteeing fastest course of the process was found. In studied system optimal D2EHPA concentration was in range between 0,9-1,5 mol/dm³. In these concentrations range the fastest penetrating of Cr(III) ions to the membrane and their fastest and total re-extraction was found.

Strong oxidation properties of Cr(VI) ions caused irreversible morphological changes on the surface of cellulose triacetate (CTA) matrix. Polymer chain oxidation was established as the major degradation in performance of CTA. The effect of oxidation is mainly through the scission of a membrane polymer chain, thus reducing both its molecular weight as well as mechanical strength resulting in a decline

of efficiency of the process. Oxidation is accelerated at high concentration of Cr(VI) ions.

The polymer inclusion membrane need a change the polymer matrix to one that provides chemical resistance. Therefore the membrane containing D2EHPA as a carrier can be used for selective separation of Cr(III) ions from diluted Cr(VI)/Cr(III) mixtures for strictly defined process parameter.

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