Paulina ŁOBODZIN
Institute for Sustainable Technologies – National Research Institute, Radom
paulina.lobodzin@itee.radom.pl
Jakub RAJEWSKI
Warsaw University of Technology, Warszawa
j.rajewski@ichip.wp.edu.pl

THE SYNERGISTIC EFFECT ON Cr(III) IONS TRANSPORT THROUGH SLM WITH CARRIER MIXTURES

Key words

SLM, synergistic effect, Cr(III), D2EHPA, Cyanex272.

Abstract

Transport of Cr(III) ions through a mix carrier supported liquid membrane (SLM) was studied. A mixture of D2EHPA and Cyanex272 was used as a carrier. It was observed that the effectiveness of the process depends on the concentration ratio of carriers in the liquid phase. There is a threshold concentration of the carriers in the membrane phase, above which the efficiency was decreased. The threshold concentration of carriers mixtures for Cr(III) ions transport was obtained when 30% of D2EHPA was added to the 5% of Cyanex272. This composition allows one to shorten the time from 5 to 1.5 hours and to remove ~98% of Cr(III). The value of flux increased 3-fold and the effectiveness also increased.

Introduction

Among the worse contaminations that occur in the water are heavy metals and their compounds. They accumulate in the sediments and are toxic for living organisms. Chromium is one of the heavy metals. The highest oxidation state of chromium is +6, whereas the lowest is -2. Nevertheless, the +3 and +6 states most commonly occurred in chromium compounds. It is still problematic to remove chromium from wastewater efficiently. Some hope is seen in using liquid membranes, mainly immobilized – SLM (supported liquid membrane). In the SLM, the pores of the polymer matrix fill the membrane phase. Typically the polymer support is made of polypropylene, polyethylene, Teflon, polyamide, etc. Due to the facilitated carrier transport, the liquid membrane comprises the most effective techniques for the selective separation of metals from aqueous solutions. The most popular types of ion metal carriers are crown ethers, organophosphorus compounds, and primary, secondary, tertiary, and quaternary ammonium salts [1].

Ochromowicz K., Apostoluk W. [2] found that, for a defined initial concentration of a carried substance, there exists a determined carrier concentration in SLM to obtain the highest flux.

There is a little known [3, 4] concerning the use of mix carriers in the liquid membranes, until now. The data indicates that the membrane match with suitably carriers shows significantly better transport properties than the membrane with one carrier. It can be propose that using a mixture of carriers allows achieving greater speed, efficiency, and selectivity of chromium ion transport through the liquid membrane.

The aim of the study was to investigate Cr(III) ions transport through the supported liquid membrane with two carriers. The influence of the carrier mixtures of di(2-ethylhexyl) phosphoric acid (D2EHPA, Aldrich) and bis(2,4,4-methylpentyl) phosphinic acid (Cyanex272, Cytec) on the effectiveness of Cr(III) ion transport in the SLM system was carried out.

1. Experimental

According to the published data [1-3], carriers with good transport properties of Cr(III) ions through SLM were chosen. The SLM was formed by immobilization of the organic solution of the carrier mixture, o-xylene (Fluka) and kerosene (Dragon) in the microporous polymeric film PTFE (Sartorius). The ratio of kerosene to the o-xylene was 1:1 v/v. The PTFE filter was soaked in organic phase for 24 h. The excess of the organic phase was removed and the finished membrane was placed between the vessel’s chambers. In previous studies [5], the concentration of carriers where the transport of chromium occurred with the greatest efficiency was determined. The tests were conducted with the system showed in the works [5, 6]. Transport experiments were carried out in a tank consisting of two cylindrical chambers. The volume of both chambers was equal 130 cm^3. The solutions, feed with a Cr(III) concentration equal 0.1 g/dm^3 (aqueous chromium(III) chloride solution, $CrCl_3 \cdot 6H_2O$) and stripping (6 mol/dm^3 HCl) was separated by SLM. The active membrane area was equal to 15.2 cm^2. The initial pH of the feed phase was equal to 5. The whole process was termostatted to ambient temperature (T=25±0.5°C). The solutions were mixed in both chambers by mechanical stirrers (1200 rpm).

Cyanex272 (Cytec) and D2EHPA (Aldrich), which have shown good properties in respect to the Cr(III) ions extraction, were used as carriers [5-9].

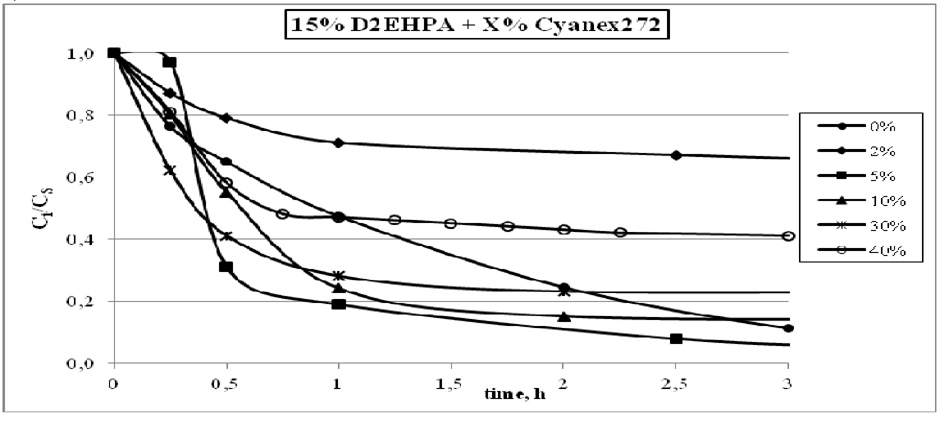
The samples from the feed and stripping phase were collected in order to monitor changes. The analysis of the Cr(III) ion concentrations in both phases was determined with a PN-77/C-04604.02 spectrophotometer UV/VIS using a 1.5 – diphenylcarbazide method with a wavelength of 540nm. The values of the flux (J_0) and penetration coefficient (k) were determined in the way described in [10].

2. Result and discussion

It is known that, in the liquid membranes for the defined ion concentrations, the most efficiency concentrations of the carriers to obtain the highest flux can be found [2, 8, 11]. For the initial Cr(III) ion concentration equal 0.1 g/dm^3 (the concentration of chromium was reported in chrome tanning liquor), the highest flux (J_0= $4.598 x 10^{-5}$ $mol/m^{-2}s^{-1}$) of chromium transport was obtained with 15% D2EHPA. In the first stage of the study, the effect of Cyanex272 concentration, while amount of D2EHPA (15%) was kept constant, was investigated. The results are shown in Figure 1, and the fluxes and coefficient penetrations are summarized in Table 1.

Introduction of Cyanex272 to the membrane with 15% D2EHPA also increases the penetration rate and the release of Cr(III) ions compared to the membrane with only D2EHPA. For the system with one carrier, the velocity process was higher than of the carrier mixture. Moreover, the pH decrease for each type of membrane was observed. Then, after 1.5 h of the process, it was in the range 1.0-1.5. When the pH decreases, the degree of hydrolysis ion transport also decreases (below pH=2 in the aqueous solutions chromium form is Cr^{3+}). Moreover, the decline of pH in the feed solution attends the loss of the gradient of the activity of H^+ ions. It has a significant influence on the number of Cr(III) ions penetrating through the membrane [3]. The work of the membrane is characterized by the flux (J). It determines the multiplicity of the transported metal ions through the unit area per the unit time. Increasing Cyanex272 in the membrane phase corresponds to lower values of the chromium flow through the membrane (Tab. 1). According to the Buonomenna et al, the decrease of flux might be caused by the accumulation of chromium in the membrane and by the viscosity of the membrane phase, which changes with the growth of carrier concentration. The highest flux (J) and penetration coefficient (k) were observed with the SLM containing 5% Cyanex272. In the next stage of the study, the effect of D2EHPA concentration in the range of 5 – 40%, while amount of Cyanex272 (5%) was kept constant, was investigated. Analysing the results (Fig. 2), it can be seen that the mixture of carriers in the membrane, Cyanex272, representing only 5% of the membrane phase volume and 30% of D2EHPA allow one to shortens the time of process to 1.5 h and the efficiency of the process to increase to 98 – 99%. The synergistic effect of the carriers is ensured by selection of the concentrations of carriers in the SLM.

a)



b)

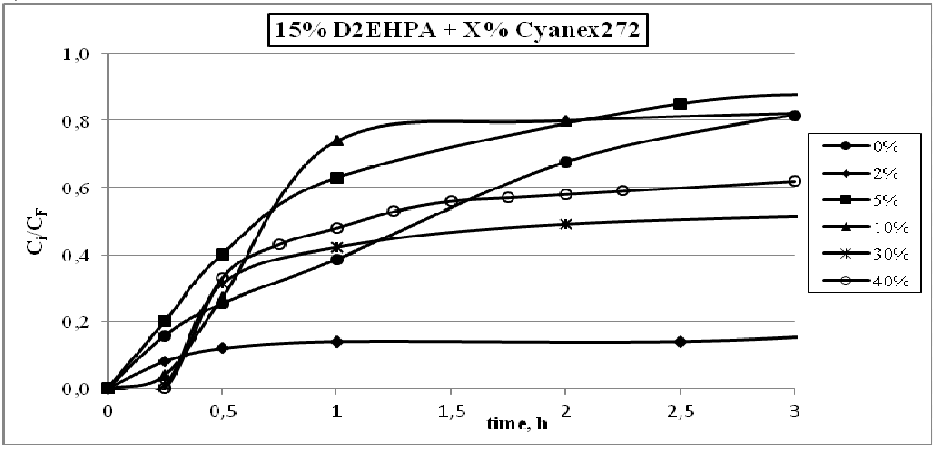


Fig. 1. Variation of chromium(III) concentration vs. time in feed (a) and stripping phase – 6M HCl (b) SLM system: 15% D2EHPA and variable content of Cyanex272. Initial concentration in feed $C_{i(III)}$=0,1 g/dm^3; pH = 5. C_F – concentration of Cr(III) in feed phase; C_S – concentration of Cr(III) in stripping phase

According to the changes in the chromium concentration in time, the fluxes and the penetration coefficients were determined. The flux value for this mix carrier was threefold greater than for the D2EHPA individually (Tables 1, 2).

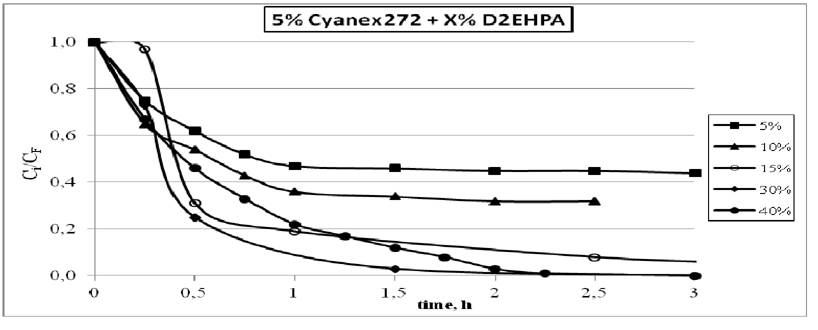
Table 1. The value of the flux and penetration coefficient of Cr(III) transport through the SLM with mixture carriers: 15% D2EHPA + 2-40% Cyanex272. C – carrier concentration in the membrane [%]; k – penetration coefficient [1/h]; J_0 – flux [x10^{-5} mol/m^{2}s]

15% D2EHPA + X% Cyanex272					
C	**2**	**5**	**10**	**30**	**40**
k	0.515	0.846	0.409	0.350	0.359
J₀	0.848	5.761	2.787	2.384	2.446

Table 2. The value of the flux and penetration coefficient of Cr(III) transport through the SLM with mixture carriers: 5% Cyanex272 + 5-40% D2EHPA. C – carrier concentration in the membrane [%]; k – penetration coefficient [1/h]; J_0 – flux [x10^{-5} mol/m^{2}s]

5% Cyanex272 + X% D2EHPA					
C	**5**	**10**	**15**	**30**	**40**
k	0.296	0.445	0.846	2.409	1.587
J₀	2.014	3.028	5.761	16.402	10.804

a)



b)

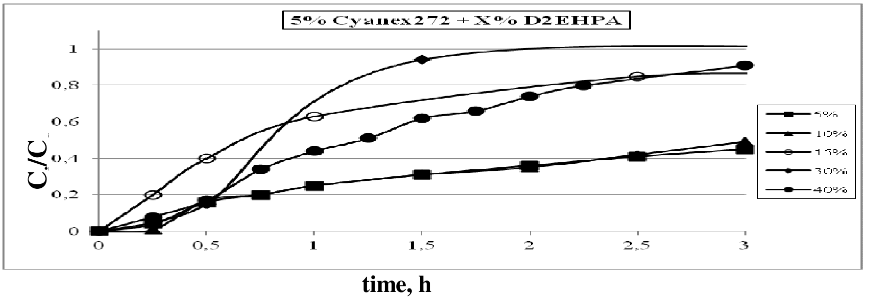


Fig. 2. Variation of chromium(III) concentration vs. time in feed (a) and stripping phase – 6M HCl (b) SLM system: 5% Cyanex272 and variable content of D2EHPA. Initial concentration in feed $C_{i(III)}$ = 0.1 g/dm^3; pH = 5, C_F – concentration of Cr(III) in feed phase; C_S – concentration of Cr(III) in stripping phase

When there is a mixture of carriers in the SLM, the advantageous influence on the rate and the capacity of the Cr(III) ion transport was observed. The surface activity of the Cyanex272 is greater than D2EHPA [13]. Polar groups of Cyanex272 activity will be directed towards the aqueous phase, in turn, the hydrophobic hydrocarbons chains are anchored in organic phase [13, 14]. Therefore, Cyanex272 will take place on the layer on the aqueous/organic phase boundary [14] (Fig. 3), and the complex reaction with Cr(III) ions will occur with a higher rate than with D2EHPA alone. The reduction of Cyanex272 activity by the Cr(III)-Cyanex272 complex formed causes a complex phase transition into an organic phase. The end result the second carrier will be establishing the configuration of spatial molecules and D2EHPA, and the less active surface [13] will be responsible for the transport inside the membrane and the reextraction of ions to the stripping phase (Fig. 3).

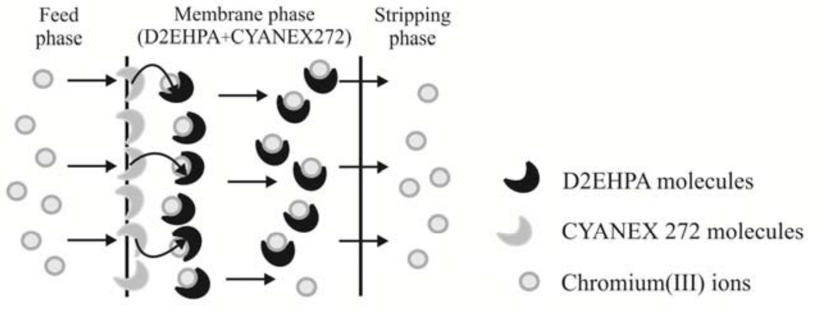


Fig. 3. Transport mechanism of Cr(III) ions through SLM with carriers mixture

2. Conclusion

The synergistic effect of carriers is ensured by the selection of the concentration of carries in the SLM. The introduction of Cyanex272 into the membrane with D2EHPA (at constant values) also caused the penetration rate and release of Cr(III) ions to increase, compared to the membrane with D2EHPA alone. When the pH decreases, the degree of hydrolysis ion transport also decreases. Moreover, when the concentration of carriers in the membrane phase increased, lower values of the flux were observed. The decreased of the chromium flow was caused by the accumulation of chromium in the membrane and the higher viscosity of the membrane phase. However, the effectiveness of the transport of Cr(III) ions with both carriers in the membrane phase increased but only to the threshold concentration of the second carrier, which decreased above the yield of the process. The threshold concentration of mixtures of carriers was obtained when 30% of D2EHPA was added to the 5% of Cyanex272. A SLM of this composition allows a 3-fold increase in the flux, enhancing the effectiveness of the process. It is a step toward working out effective methods of extracting Cr(III) ions from aqueous solutions.

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Transport Cr(III) przez immobilizowaną membranę ciekłą

Słowa kluczowe

SLM, efekt synergistyczny, Cr(III), D2EHPA, Cyanex272.

Streszczenie

Przeprowadzono badania transportu jonów Cr(III) przez dwuprzenośnikową immobilizowaną membranę ciekłą. Do transportu jonów Cr(III) zastosowano mieszaninę przenośników Cyanex272 i D2EHPA. Stwierdzono, że efektywność procesu zależy od stosunku stężeń przenośników w fazie membranowej. Zaobserwowano wzrost efektywności przenoszenia jonów Cr(III), jednak do pewnego progowego stężenia drugiego przenośnika w membranie, po przekroczeniu którego wydajność spadała. W układzie z Cyanex272 i D2EHPA dla transportu Cr(III) przez SLM ich progowe stężenia to odpowiednio 5% i 30%. Membrana o takim składzie umożliwia trzykrotne zwiększenie strumienia, a tym samym zwiększa się efektywność procesu. Czas trwania procesu został skrócony z 5 h (dla samego D2EHPA) do 1,5 h, co umożliwiło usunięcie ~98% chromu z roztworu.