Possibilities of chromium (III) separation from acid solution using the double-carrier supported liquid membrane (DCSLM)

Jakub Rajewski and Paulina Rajewska

ABSTRACT

This paper describes the problem of recovery and reusing chromium from aqueous solutions. The authors studied a novel double-carrier supported liquid membrane system (DCSLM) with di(2-ethylhexyl) phosphoric acid (D2EHPA) and bis(2,4,4-trimethyl) phosphinic acid (Cyanex272) as a carrier of Cr(III) ions as a method to separate chromium (III) from acid solutions. As a result, they confirmed that the presence of two carriers in the DCSLM with the most effective carrier concentration ratios, leads to approximately three times shorter pertraction, compared to a process conducted with the D2EHPA only. It was found that synergistic effect is independent of the initial concentration of chromium in the feed solution. Higher initial concentrations of Cr(III) cause high ‘exhaustion’ of active carrier molecules at the interface. Moreover, the authors observed the increase in viscosity in the membrane phase and process inhibition. It was found that efficiency of separation of chromium ions from aqueous solutions using a liquid membrane depends on the transport rate for these ions in the membrane (ions pertraction). Therefore, it was concluded that the pertraction stage of the Cr(III) ions limits the efficiency of the whole separation process.

Key words | chromium (III) separation, Cyanex272, D2EHPA, supported liquid membrane

INTRODUCTION

Chromium issues

Chromium is a heavy metal commonly applied in all major industries. Due to its features, like high hardness, resistance to abrasion and corrosive factors (e.g. acidic environment, high temperature and pressure, salinity), and attractive appearance (it is glossy and makes covered elements look more elegant), chromium compounds have been widely used in industries listed in Table 1.

In spite of many advantages of using chromium and its compounds, industrial waste solutions pose a threat to the environment because of the large amounts of chromium, characterized by high toxicity (Table 2).

Accordingly, it is necessary to monitor the Cr concentration isolated from waste and to reduce waste streams to lower their regulation value before they are released to the environment. In addition, on 26 May 2014, the European Commission published a Communication to the Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on reviewing the list of critical raw materials for the European Union and the implementation of the Raw Materials Initiative (Report On Critical Raw Materials For The EU). The document reports the specific situation of raw materials in Europe and lists of elements and minerals necessary for further development of the European countries. These elements were described as ‘critical’ because their lack in the market could pose a serious threat to the EU economy. This list includes the following elements: antimony, beryllium, chromium, cobalt, indium, gallium, germanium, magnesium, niobium, tantalum, wolfram, platinum group metals (platinum, palladium, iridium, rhodium, ruthenium, osmium), and the rare Earth metals.

Annex to the Communication indicated that 11 elements listed in the document (Table 3) are the ‘critical’ raw materials. This means that there is a significant risk of their resource depletion. The negative effects the scarcity of these ‘critical’ raw materials might have on the economy of EU countries (Poland included) are higher than for other raw materials. Table 3 shows the replacement rate of the
elements. The replacement rate is a measure of the difficulty in replacing the raw material, calculated and weighted in relation to all applications. The values are in the range of 0 to 1, with 1 being the lowest degree of replacement.

According to the Regulations of the European Commission, chromium is a critical raw material with the lowest degree of replacement. Taking into account the above factors, it is necessary to search for and develop new effective methods of recovery and reuse of chromium from waste streams.

**Classical methods of treatment of industrial waste chromium**

The conventional methods for removing chromium from aqueous solutions include precipitation, biological treatment, ion exchange, adsorption, and extraction. They are summarized in Table 4.

Since the choice of a method depends on the type and composition of the wastewater and the required degree of cleaning, each method is characterized by the high recovery of chromium (approximately 99%), but this is highly dependent on the process conditions and the characteristics of wastewater. The most common treatments of chromium acid wastewater are chemical precipitation of chromium hydroxide (III), and its separation from liquid by means of filtration (Hintermeyer et al. 2008; Kanagaraj et al. 2008). However, chrome bath recovered that way also contains

### Table 1 | Areas of application of various chromium compounds (Akbal & Camci 2011; Religa et al. 2011; Verma et al. 2013; Hussain et al. 2004)

<table>
<thead>
<tr>
<th>Chromium compound</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium (II) CrCl₂</td>
<td>Preparation of other compounds of chromium and metallic chromium; catalyst in organic chemistry</td>
</tr>
<tr>
<td>Chromium (III) Cr₂O₃</td>
<td>Pigment in paints and varnishes, manufacture of porcelain, ceramic coatings, glass, cement, refractories; chemical industry – as a synthetic intermediate or a catalyst</td>
</tr>
<tr>
<td>Cr(NO₃)₃</td>
<td>Laboratory reagent, for chemical syntheses; electroplating; tanning</td>
</tr>
<tr>
<td>CrCl₃</td>
<td>Impregnant before dyeing fabrics in the textile industry; a chromium plating method, a substrate for the preparation of other compounds of chromium; as a dietary supplement</td>
</tr>
<tr>
<td>Cr(OH)SO₄</td>
<td>The tanning industry; surface treatment including galvanization and passivation</td>
</tr>
<tr>
<td>Chromium (VI) K₂Cr₂O₇</td>
<td>Oxidizer in the chemical industry and preparative laboratory; for the production of dyes, electrolysis, pyrotechnics, manufacture of glass, adhesives, dyes, photography, lithography and ceramic industry. The acidified solution of K₂Cr₂O₇ is an indicator of the presence of reducing properties (e.g. Aldehyde). K₂Cr₂O₇ solution of sulfuric acid is known as chromic-sulfuric acid. This mixture has very strong oxidizing properties and is sometimes used in laboratories as a glass cleaner to remove the residual organic substances</td>
</tr>
<tr>
<td>CrO₃</td>
<td>It is mainly used in the finishing metal plating (e.g. chrome and decorative plating), conversion coatings and brightening; as a fixative of preservatives used to protect driftwood. Other minor uses include: manufacture of dyes and paints, catalysts, production of detergents, as well as an oxidant</td>
</tr>
<tr>
<td>Na₂CrO₄</td>
<td>It is used as an intermediate to produce other compounds of chromium and, to a limited extent, as a laboratory reagent</td>
</tr>
</tbody>
</table>

### Table 2 | Concentration of chromium (III) and chromium (VI) in wastewater from various industries

<table>
<thead>
<tr>
<th>Industry</th>
<th>Concentration of Cr(III) in wastewater, mol (dm⁻³) (g·dm⁻³)</th>
<th>Concentration of Cr (VI) in wastewater, mg/L</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tanning</td>
<td>0.004 (2.1)</td>
<td>0.015 (0.8)</td>
<td>Abdulla et al. (2010)</td>
</tr>
<tr>
<td>Metallurgic</td>
<td>0.003 (1.5)</td>
<td>0.019 (0.9)</td>
<td>Akbal &amp; Camci (2011)</td>
</tr>
<tr>
<td>Textiles</td>
<td>0.002 (0.1)</td>
<td>1.3·10⁻⁴ (0.007)</td>
<td>Hussain et al. (2004)</td>
</tr>
<tr>
<td>Iron and steel</td>
<td>6·10⁻⁷ (&lt;3·10⁻⁵)</td>
<td>1·10⁻⁷ (&lt;5·10⁻⁵)</td>
<td>Beh et al. (2022)</td>
</tr>
</tbody>
</table>

### Table 3 | Replacement rate of critical elements (report on critical raw materials for the EU)

<table>
<thead>
<tr>
<th>Lp.</th>
<th>Critical elements</th>
<th>Replacement rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Antimony</td>
<td>0.62</td>
</tr>
<tr>
<td>2</td>
<td>Beryllium</td>
<td>0.85</td>
</tr>
<tr>
<td>3</td>
<td>Chromium</td>
<td>0.96</td>
</tr>
<tr>
<td>4</td>
<td>Cobalt</td>
<td>0.71</td>
</tr>
<tr>
<td>5</td>
<td>Gallium</td>
<td>0.60</td>
</tr>
<tr>
<td>6</td>
<td>Germanium</td>
<td>0.86</td>
</tr>
<tr>
<td>7</td>
<td>Indium</td>
<td>0.82</td>
</tr>
<tr>
<td>8</td>
<td>Magnesium</td>
<td>0.64</td>
</tr>
<tr>
<td>9</td>
<td>Niobium</td>
<td>0.69</td>
</tr>
<tr>
<td>10</td>
<td>Silicon</td>
<td>0.81</td>
</tr>
<tr>
<td>11</td>
<td>Wolfram</td>
<td>0.70</td>
</tr>
</tbody>
</table>
large amounts of impurities in the form of proteins and fats, and it cannot be re-used in the process. Therefore, the objective of many investigations (Hintermeyer et al. 2008; Akbal & Camci 2011; Jian-Hong et al. 2015; Verma et al. 2015; Fan et al. 2015) is to remove chromium from the wastewater by means of techniques such as biological methods, ion exchange, adsorption on activated carbon or extraction solvent. Biological methods allowed the reduction of chromium (III) up to about 94%, but it is necessary to maintain pH of 6–9 in effluent because the chromium (III) concentration up to 0.002 mol·dm$^{-3}$ is not toxic to activated sludge.

In the case of ion exchange processes, very good stability and easy regeneration of resin bed exchanger is observed, but it is necessary to oxidate chromium (III) to chromium (VI) before the process, and the bath directed to the ion-exchange column should not contain more than 0.002 mol·dm$^{-3}$ of CrO$_3$ (Fan et al. 2015). On the other hand, chromium (III) adsorption on a column filled with high anionic selectivity of activated carbon allowed the use of solution purification. The solutions probably included anions of sulfate, chloride, or bicarbonate. Unfortunately, the use of this method requires frequent regeneration of activated carbon (Mohan & Pittman 2006).

Solvent extraction allows recovery of 99% of chromium (III) from wastewater (Jian-Hong et al. 2015), but it requires the use of large quantities of extractable organic solvents, which are often toxic and flammable. Therefore, in recent years, researchers pay more attention to more environmentally friendly methods, which allow them to reuse the recovered metal in industrial processes. Membrane processes, including immobilized liquid membranes (supported liquid membrane, SLM) represent an interesting alternative to chemical separation methods. The use of SLMs may significantly improve the quality of recovered chromium which allows its reuse in the technological process.

Works by Religa et al. (2011) and Cassano et al. (1997) show that a nanofiltration process allows chromium to be concentrated at a concurrent removal of salts from tannery effluents, which in turn enables concentrated solution of chromium ions to be obtained and reused. Mungray et al. (2012) shows the possibility of indirect application of low-pressure ultrafiltration assisted surface-active compounds or polymers. The authors show significant improvement in the efficiency of removing chromium (III) from aqueous solutions; however, they also represent that, in this case, it is necessary to introduce additional supply of surfactants. Moreover, the separation efficiency of resulting complexes of Cr(III) is strongly dependent on the pH of the solution. Despite a number of advantages arising from the possibility of applying pressure membrane techniques for extracting chromium (III), there are also disadvantages which limit their practical use in chemical technology (Religa et al. 2011; Mungray et al. 2012). These include the following:

1. On the surfaces of membranes, processes of concentration polarization take place, and in ultra- and nanofiltration processes, additionally, one can also observe the blocking of the membrane surface by a

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Drawback</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation</td>
<td>- the possibility of reducing concentration of chromium (III) in the waste water to 0.38–0.96 mol·dm$^{-3}$ (20–50 g·dm$^{-3}$) - reduction of chromium (III) to about 99.7%</td>
<td>- satisfactory efficiency is the concentration of chromium (III) in the waste water above 0.2 mol·dm$^{-3}$ (10 g·dm$^{-3}$) - poor quality of the obtained chromium (III) resulting from the presence of impurities</td>
</tr>
<tr>
<td>Biological</td>
<td>- reduction of chromium (III) to about 94%</td>
<td>- the need to maintain pH of the effluent in the range of 6–9</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>- very good durability and facility of regeneration resin bed exchanger - reduction of chromium (III) to 99%</td>
<td>- the need to oxidate chromium (III) to chromium (VI) before the process - bath directed to an ion exchange column should contain no more than 0.002 mol·dm$^{-3}$ CrO$_3$ (0.1 g·dm$^{-3}$)</td>
</tr>
<tr>
<td>Adsorption on activated carbon</td>
<td>- high selectivity for anions - reduction of chromium (III) to 99%</td>
<td>- low sorption capacity of the activated carbon and the need for frequent regeneration</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>- recovery of 99% of chromium (III)</td>
<td>- the need to use large quantities of extractable organic solvent, which are often toxic and incendiary</td>
</tr>
</tbody>
</table>
concentrated mass of retained components (often spontaneously gelling), the so-called activated sludge. This reduces the selectivity and capability of filtration and causes the need to replace or regenerate the membranes.

(2) According to research conducted by the authors (Religa et al. 2011; Religa et al. 2016), separation of ions chromium (III) from solutions using pressure membrane technology becomes effective and economically justified only for certain ranges of the initial concentrations of Cr(III).

SLM

Unlike the classical solvent extraction, SLM uses a water-immiscible organic phase separating two aqueous phases, whereby a substance is transferred from one aqueous phase (donor) to a second aqueous phase (acceptor) in a one-step process (Figure 1) (Kislik 2010). SLM is a polymer support soaked in the organic/membrane phase. Membrane phase consists of solvents and extractant or mixture of the extractants.

The main advantages of SLM membranes are:

- small amount of organic solvents used as a membrane phase, compared to the extraction;
- relatively large mass flows as a result of a large diffusion coefficient in the liquid phase, greater than in the other phases, for example: polymers;
- good selectivity, resulting from the possibility of using a variety of organic phase;
- the possibility of using selective carriers (despite high prices), due to the small volume of the organic phase. Furthermore, these carriers often allow transport of substances in the opposite direction to the gradient of concentration;
- high separation factors and the possibility of substance concentration;
- low investment and operating costs.

Methods based on liquid membranes are gaining increasing interest, both as a method of separation and concentration. The published works (Bouonomenna et al. 2006; Zaghibani et al. 2009; Ochromowicz & Apostoluk 2010; Religa et al. 2014, 2016) confirm the validity of liquid membranes for extracting ions of chromium (III) in an environmental protection technology. SLM is one of four types of liquid membranes. The great advantage of this type of system is that they provide large interface area, while maintaining a low volume of an organic phase. Another advantage is the good mechanical strength of the polymer supports. Furthermore, high selectivity and effectiveness of the separation process, mean that SLMs give the greatest opportunity for practical use in some technological processes (Kislik 2010).

Research carried out so far (Rajewski & Religa 2016; Religa et al. 2014, 2016) indicates that a type and concentration of the carrier in the membrane phase have the greatest impact on the effectiveness of the separation process. The authors also indicate that modification of SLMs consisting in the introduction of the second carrier to the membrane phase may have a very positive impact on the separation of chromium (III) from acid solutions. In this case, the ratios of both carriers in the membrane phase constitute a very important process parameter as well.

The study presents the influence of the main process parameters (i.e. the concentration of carrier or carriers mixture in the membrane phase and the initial concentration of chromium in the aqueous phase) on the possibility of separation of chromium (III) from acid solutions with a double carrier SLM.

METHODS

Liquid-liquid extraction

The extraction of the Cr(III) ions was carried out in a vessel where equal volumes (15 cm³) of the aqueous and membrane phase were placed. The aqueous phase was a solution of chromium chloride (CrCl₃·6H₂O, Sigma-Aldrich). The initial concentration of the Cr(III) ions was 0.002 and 0.02 mol·dm⁻³, and pH = 4.
The membrane phase was the di (2-ethylhexyl) phosphoric acid (D2EHPA, Merck), and bis (2,4,4-trimethyl) phosphinic acid (Cyanex272, Cytec) with o-xylene (Fluka) and kerosene (Dragon). The ratio of o-xylene to kerosene was 2:1. The aqueous phase was stirred at a constant speed (200 rpm).

**SLM and double-carrier supported liquid membrane system transport experiment**

Transport experiments were carried out in a vessel with two cylindrical chambers separated by an SLM as described in (Religa et al. 2014, 2016). The chambers contained the solutions: the feed phase with Cr(III) concentration: 0.001; 0.002; 0.006; 0.01; 0.02 mol·dm$^{-3}$ (aqueous chromium (III) chloride solution, CrCl$_3$·6H$_2$O) and stripping phase (6 mol·dm$^{-3}$ HCl). The initial pH of the feed phase was 4. The volume of both chambers was 130 cm$^3$. The solutions were mixed in both chambers with mechanical stirrers (IKA, OST20 digital) with a constant speed 600 rpm. The whole process was thermostated to ambient temperature ($T = 25 \pm 0.5$ °C).

At regular time intervals, the samples were taken from both aqueous phases to determine the concentration of chromium.

SLM was formed from polymer foil polytetrafluoroethylene (PTFE) (Sartorius) with pore size of 0.45 μm, which was submerged for 24 h in an organic phase with a carrier or a carrier mixture (as in the liquid–liquid extraction section). The active membrane surface equaled 15.2 cm$^2$. The process was conducted in two systems. In the first one, only D2EHPA was used as a carrier and its concentration was changed in the range of 0.15–2.4 mol·dm$^{-3}$. In the second system, for some of the initial concentrations of chromium (0.002, 0.006, 0.01 mol·dm$^{-3}$), the double carrier system with the most effective concentrations of the D2EHPA and with different concentrations of Cyanex272 in the range of 0.15–2.4 mol·dm$^{-3}$ was investigated. Then, the influence of the D2EHPA concentration in the range of 0.15–2.4 mol·dm$^{-3}$ for the optimal concentration of Cyanex272 in the double-carrier supported liquid membrane system (D2SLM) (determined on the basis of the above experiment) was analysed.

**Determination of the chromium (III) ions concentration**

The analysis of the Cr(III) ion concentration in water phase was determined with a spectrophotometer (NANOCOLOR UV/VIS NUV480 Spectrophotometer) using a 1.5-difenylkarbazide method with wave length $\lambda = 540$ nm after mineralization of samples. Each measurement was repeated three times, and the standard deviation was between ±0.0003.

**Calculation of the penetration coefficient ($k_Z$)**

The extraction coefficient of Cr(III) ($k_Z$) was determined based on the calculation listed in the previous study (Religa et al. 2014). It was assumed that the transport of Cr(III) ions runs according to the consecutive first-order reaction (Religa et al. 2014). Based on this assumption, the Cr(III) extraction kinetics can be described by the following formula:

$$\frac{dc_Z}{dt} = k_Z \cdot c_P$$

(1)

The integration of Equation (1) leads to:

$$\ln \frac{c_Z}{c_P} = -k_Z \cdot t$$

(2)

where: $c_P$ – the initial chromium (III) concentration in the feed solution (mol·dm$^{-3}$), $c_Z$ – the current concentration of chromium (III) in the feed solution (mol·dm$^{-3}$), $t$ – the elapsed time (h), $k_Z$ – penetration coefficient (h$^{-1}$).

The reaction constant rate ($k_Z$) can be determined from the linear relationship of ln($C_Z/C_0$) vs. the elapsed time.

To compare the transport kinetics in the feed and stripping phases, the reduced concentrations ($C_{\text{reduced}}$) were used:

Feed phase: $C_{\text{reduced}} = \frac{C_Z}{C_P}$

(3)

Stripping phase: $C_{\text{reduced}} = \frac{C_O}{C_P}$

(4)

The reduced concentration of Cr(III) in the membrane phase ($C_M$) was determined from the difference in concentration of Cr(III) in the feed ($C_Z$) and stripping phases ($C_O$).

**Scanning electron microscopy**

The scanning electron microscope was used to characterize the microstructure of the membranes. Photos of the membrane surfaces were recorded using the Phenom G2 microscope by FEI. The membrane samples were sprayed...
with a 2 nm layer of gold using the K550x Sputter Coater by Quorum Technologies.

**Selecting the chromium (III) carriers**

Based on previous experience (Rajewski & Religa 2016; Religa et al. 2014, 2016) and literature data (Zaghbani et al. 2013), it has been established that in acid aqueous solutions <4, chromium occurs mainly in the form of Cr$^{3+}$ (Figure 2).

![Figure 2](image-url)  
*Figure 2 | Eh-pH dependence for chromium (Mollik et al. 2004).*

![Figure 3](image-url)  
*Figure 3 | The dependence of the Cr(III) ions penetration coefficient ($k_z$) to the membrane vs. the concentration of D2EHPA in the membrane for different initial concentrations of Cr(III) in the feed phase. The pH in the feed phase was 4; the stripping phase was 6 mol·dm$^{-3}$ HCl.*

![Figure 4](image-url)  
*Figure 4 | Variations of Cr(III) concentrations in the membrane phase vs. different initial Cr(III) concentrations for different initial concentrations of Cr(III) in the feed phase (0.001 M, 0.002 M, 0.006 M, 0.01 M and 0.02 M). $C_0$ - the initial concentration of chromium(III) in the feed solution; $C_m$ - concentration of Cr(III) in the membrane phase. The pH in the feed phase was 4; the stripping phase was 6 mol·dm$^{-3}$ HCl.*

<table>
<thead>
<tr>
<th>Initial concentration of Cr(III), mol·dm$^{-3}$</th>
<th>Concentration ratio of D2EHPA/Cyanex272, mol·dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>0.9/0.15</td>
</tr>
<tr>
<td>0.006</td>
<td>0.6/0.15</td>
</tr>
<tr>
<td>0.01</td>
<td>1.2/0.06</td>
</tr>
</tbody>
</table>

Table 5 | The optimum ratio of D2EHPA/Cyanex272 in DCSLM at selected initial concentrations of Cr(III)
Therefore, the cationic extractants, derivatives of phosphoric alkyl acid: D2EHPA and/or bis (2,4,4-trimethyl) phosphinic acid (Cyanex272) were selected as carriers. Both extractants have a great ability to bind with the cationic form of chromium (i.e. Cr\(^{3+}\)) (Ochromowicz & Apostoluk 2014).

RESULTS AND DISCUSSION

Chromium transport through SLM

Previous experience (Rajewski & Religa 2016; Religa et al. 2014) and a study conducted in the system with SLM (Figures 3

![Figure 5](https://iwaponline.com/wst/article-pdf/75/10/2358/452287/wst075102358.pdf)

**Figure 5** | The kinetics of chromium (III) transportation in the feed, stripping and membrane at different initial concentrations of Cr(III) of 0.002 mol dm\(^{-3}\) (a), 0.006 mol dm\(^{-3}\) (b) and 0.01 mol dm\(^{-3}\) (c) were conducted using two kinds of membranes containing D2EHPA only and D2EHPA/Cyanex272. \(C_{\text{reduced}}\) - the reduced concentration of chromium(III) in the feed, stripping and membrane phases in SLM or DCSLM system. The pH in the feed phase was 4; the stripping phase was 6 mol dm\(^{-3}\) HCl.
and 4) confirm that D2EHPA has a high capacity for the transport of Cr(III) from acid solutions and its concentration in the membrane has a very high effects on process efficiency. The use of the most effective threshold concentration of D2EHPA causes the fastest penetration of Cr(III) to the membrane, regardless of the initial concentration.

Results presented in Figure 4 indicate that at higher initial concentrations of chromium in the feed phase, the pertraction time of the Cr(III) ions through the membrane is extended. Efficiency of the whole separation process depends on the speed of the Cr(III) ions pertraction through the membrane. Therefore, it can be concluded that the pertraction of Cr(III) in the membrane is the step limiting the efficiency of the SLM transport system.

The initial concentration of chromium is very important for the separation of the SLM. The application of the initial concentration of Cr(III) ≥ 0.006 mol dm⁻³, on the one hand, results in a significant reduction in the rate of penetration, and on the other hand prevents the complete re-extraction. The cumulation of Cr(III) in the membrane is observed (Figure 4). According to literature reports (Bouonomenna et al. 2006; Zaghbani et al. 2009), quick ‘exhaustion’ of active molecules can be observed at the interface of the carrier.

It can be concluded that the SLM with D2EHPA as a carrier facilitates efficient separation of Cr(III) ions only at low initial concentrations, the same as the pressure membrane techniques (mainly nanofiltration, reverse osmosis). Cyanex272 used as second carrier in the membrane could significantly improve the efficiency of the Cr(III) transport (Rajewski & Religa 2016; Religa et al. 2016). Therefore, in the next stage of the study, the effect of the initial concentration of Cr(III) on the concentration of Cr(III) ≥ 0.006 mol dm⁻³, on the one hand, results in a significant reduction in the rate of penetration, and on the other hand prevents the complete re-extraction. The cumulation of Cr(III) in the membrane is observed (Figure 4). According to literature reports (Bouonomenna et al. 2006; Zaghbani et al. 2009), quick ‘exhaustion’ of active molecules can be observed at the interface of the carrier.

It can be concluded that the SLM with D2EHPA as a carrier facilitates efficient separation of Cr(III) ions only at low initial concentrations, the same as the pressure membrane techniques (mainly nanofiltration, reverse osmosis). Cyanex272 used as second carrier in the membrane could significantly improve the efficiency of the Cr(III) transport (Rajewski & Religa 2016; Religa et al. 2016). Therefore, in the next stage of the study, the effect of the initial concentration of Cr(III) on the
the kinetics of the transport system of the double-carrier SLM was examined.

**Chromium transport in DCSLM system**

In accordance with the procedure described in our previous works (Religa et al. 2016), the most effective proportions of D2EHPA/Cyanex272 in DCSLM for some of the initial concentrations of Cr(III) were selected and summarized in Table 5. Then, the kinetics of Cr(III) ions transportation referred to the initial concentration were shown in Figure 5. The results confirmed that the modification of the SLM in the form of an addition of the second carrier has a very beneficial effect on the rate of Cr(III) ions transport with acid solutions. D2EHPA/Cyanex272 membrane (the optimum ratio showed in Table 5) shortened the permeation time by approximately three times, in comparison with a membrane with D2EHPA only. This effect is independent of the initial concentration of chromium.

Analyzing the kinetics of transport of Cr(III) in the membrane, it can be said that, like in the case of SLMs, initial concentration of Cr(III) ≥ 0.006 mol·dm⁻³ results in an accumulation of Cr(III). The time of extraction and re-extraction becomes longer. After 5 h of the process, the extraction was approximately 55% and the re-extraction was approximately 45% (Figure 5(c)), while for initial chromium concentration of 0.002 mol·dm⁻³, approximately 99% of extraction and re-extraction was observed. Chromium accumulated in the membrane also clogs the pores of the membrane and reduces the rate of the process.

As reported by Bouonomenna et al. (2006) and Ochrowicz & Apostoluk (2010), there are several reasons for this behaviour of the system. First of all, the selected carriers have a much better binding properties for the hydrolyzed form of Cr(III). The hydrolysis degree of Cr(III) ions decreases with increasing initial concentration of Cr(III) in a water solution. Therefore, the decrease in the rate of extraction and re-extraction at higher initial concentrations of Cr(III) was observed.

Moreover, the dependence on the viscosity of the membrane phase and the concentration of D2EHPA before and after the extraction at Cr(III) concentrations: 0.002 and 0.02 mol·dm⁻³ is shown in Figure 7. The results of the extraction system indicate that the complexes accumulated in the membrane phase, cause an increase in viscosity. The viscosity is higher at higher initial concentrations of Cr(III). Thus, it can be concluded that the increase in viscosity of the membrane phase causes the accumulation of the Cr(III) ions in the membrane phase. As a consequence, this leads to the inhibition of the process. Therefore, most preferably, similarly as in the case of the SLM, the process is carried out under low initial concentrations of the transported substance.

**CONCLUSIONS**

Based on the review of literature presented in the publication, it can be concluded that the problem of chromium wastewater requires immediate attention. This is mainly
caused by large amounts and toxicity of chromium wastewater. Therefore, the necessity of the recovery and reuse of chromium is a very important environmental and economical aspect. An alternative method to the classical separation can be the system with immobilized liquid membrane. The results of transport of Cr(III) in the studies with the SLM showed that the effectiveness of the process depends on the concentration of the carrier in the membrane. The results of transport of Cr(III) in the studies with immobilized liquid membranes. The results of transport of Cr(III) in the studies with immobilized liquid membranes showed that the effectiveness of the process depends on the concentration of the carrier in the membrane. It was found that there is a ‘threshold’ carrier concentration in the membrane phase, which ensures the highest efficiency of the Cr(III) transport process. This ‘threshold’ carrier concentration is dependent on the initial Cr(III) concentration in the feed phase. It was also shown that the introduction of the second carrier to the membrane considerably improves the speed of the process.

It has been found that the initial concentration of Cr(III) has the greatest impact on the efficiency of both the SLM and DCSLM. It is advised to carry out the process in the range of the initial concentration of Cr(III) ≤ 0.006 mol·dm⁻³. Higher initial concentrations of Cr(III) cause high ‘exhaustion’ of active carrier molecules at the interface. In addition, the increase in viscosity in the membrane phase generated by the accumulation of chromium ions inhibits the process. Therefore, it was concluded that the transport of Cr(III) in the membrane is the step that limits the efficiency of the process in the SLM system.

Separation of Cr(III) from acidic solutions with SLM system required the authors to perform additional experiments, in particular, the analysis of the stability of the membrane.

REFERENCES


Religa, P., Rajewski, J. & Lobodzin, P. 2016 Kinetic of chromium (III) transport through the double-carrier supported liquid


First received 17 May 2016; accepted in revised form 6 February 2017. Available online 27 February 2017