Transport of chromium(III) from mixtures of chromium ions by CTA- and PVC-based inclusion membranes

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ABSTRACT

The author analysed the stability of cellulose triacetate (CTA)- and poly(vinyl chloride) (PVC)-based polymer inclusion membranes (PIMs) containing bis(2-ethylhexyl) phosphoric acid (D2EHPA) as a carrier for chromium(III) separation from mixtures of Cr(III)/Cr(VI) ions. He also studied the influence of carrier (D2EHPA) concentration in PVC- and CTA-based PIMs on chromium(III) ion transport, at different initial concentrations of the Cr(III) ions. Based on the results, the optimum range of carrier concentration in both membranes guaranteeing the fastest process was found. Moreover, PIMs with D2EHPA as the carrier worked as selective barriers for Cr(VI) ions. However, in the case of CTA/PIM, the increase in Cr(VI) concentration above 0.005 mol/dm³ negatively influenced Cr(III) transport, which was caused by the degradation of the polymer matrix. The PVC/PIM was not influenced by the Cr(VI) ions, thus PVC was definitely a better polymer for the synthesis of PIM for the separation of Cr(III)/VI) ions. It was also demonstrated that both membranes were not stable over a long process time. The results reported in this study suggest that the factor that determines the stability of PIMs with D2EHPA is the presence of water in the membrane and the formation of unstable micellar structures.

Key words | chromium (III/VI) separation, CTA, D2EHPA, polymer inclusion membrane, PVC

HIGHLIGHTS

• CTA- and PVC-based PIMs containing D2EHPA are selective barriers for Cr(VI) ions.
• Strong oxidation properties of Cr(VI) caused morphological changes in the CTA/PIM.
• The PVC matrix was not influenced by the Cr(VI) ions.
• Water molecules absorbed by D2EHPA diffuse through the membrane to the stripping phase.
• Stability of PIMs with D2EHPA is limited by the presence of water in the membrane phase.

INTRODUCTION

Depending on the degree of oxidation, the metabolism and availability of chromium forms are different. Under physiological conditions, chromium(VI) occurs in the form of chromates, while chromium(III) is a cation. The difference in charge means that the negatively charged chromium(VI) can easily penetrate the cell membrane using anion channels. The human body does not have a metabolic path allowing chromium(III) oxidation, whereas the reduction of chromium(VI) occurs in many tissues of the body. This process leads to the formation of chromium(III), which has a greater ability to bind to DNA, RNA, proteins and lipids than chromium(VI) (Cohen et al. 1995). Chromium compounds are very dangerous and cause serious damage to the respiratory system, nervous system, and the skin. In addition, they have carcinogenic and mutagenic effects (Levy & Venitt 1986).

Because of the significantly different physiological functions of Cr(III) and Cr(VI), it is important to determine the speciation of chromium in environmental samples (Ying et al. 2011; Rajewski & Rajewska 2017).

Direct determination of the chromium species, including Cr(III) and Cr(VI), by instrumental techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), is not suitable (Memon et al. 2009). These methods can easily detect the total amount of chromium but cannot distinguish...
between Cr(III) and Cr(VI). Total chromium does not provide sufficient information to understand its toxicity, bioavailability, biotransformation and circulation in the environment.

Separation and preconcentration techniques, including solvent extraction (Ying et al. 2011), cloud point extraction (Meeravali & Jiang 2009), solid phase extraction (Lin & Whang 2007) and membrane separation (Kończyk et al. 2010), are available for the separation of Cr(III) and Cr(VI). By using the separation and preconcentration techniques, the detection limit for chromium is improved (Religa et al. 2015). Separation using liquid membranes (LMs), and in particular, polymer inclusion membranes (PIMs), is a very promising technique for the selective separation of metal ions. PIMs consist of a polymer matrix, a carrier/extractant and a plasticizer (if necessary). Due to the excellent ability of PIMs to selectively remove metal ions from dilute solutions, in recent years they have been given considerable attention. The main advantages of PIMs compared to traditional extraction are the higher transport selectivity of the desired metal ion, lower carrier consumption and extraction and re-extraction in one integrated process (Fontas et al. 2007; Almeida et al. 2017).

PIMs have also proved to be an extremely useful tool in sample pre-treatment for the separation and pre-concentration of a wide range of analytes (Zhang et al. 2011). Good separation from contamination (i.e. selectivity) and increased enrichment factors (i.e. sensitivity) have been reported using different configurations of extraction cells (i.e. conventional two-compartment transport cell, microextraction cell, flow-through cell, and PIM-coated column). Moreover, it has been demonstrated that PIM separation systems can be easily automated to perform both sample pre-treatment and on-line detection and that they can also be miniaturized and designed to be portable and easy to use by non-chemists (Ngäiem et al. 2006).

The selectivity of PIMs allows for the separation of different mixtures of metal ions (Ngäiem et al. 2006; Kończyk et al. 2010) or different forms – speciation of the same metal mixtures, including separation of Cr(VI) and Cr(III) ions (Religa et al. 2014; Almeida et al. 2017). However, 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, especially by PIM systems. Moreover, there is no work where the negative impact of chromium forms on their separation is explained. It is also not possible to find a description of the negative impact of strongly oxidizing Cr(VI) ions on the PIM components (i.e. polymer matrix, carrier, plasticizer) and the physical properties of the membrane. Previous work (Religa et al. 2014) has shown that this is a very important factor in determining the transport efficiency and stability of the supported liquid membrane (SLM) with bis(2-ethylhexyl) phosphoric acid (D2EHPA) as a carrier for chromium(III) separation from mixtures of Cr(III)/Cr(VI) ions. It was shown that an SLM with a D2EHPA carrier was a selective barrier for Cr(VI) ions, but strongly oxidizing Cr(VI) ions can oxidize and partially deactivate the D2EHPA carrier. Moreover, Religa et al. (2015) proved that SLM is unstable in the separation of Cr(III) ions.

By contrast, it has been shown that CTA-based PIM is a much better solution for the separation of Cr(III). It is therefore important to check the possibility of Cr(III/VI) ion separation with a cellulose triacetate (CTA)-based polymer inclusion membrane. However, as reported in Farooque & Al-Amoudi (1999) oxidizing agents such as e.g. Cr(VI) ions may have a degrading effect on the CTA polymer and its derivatives. So, it is also necessary to consider the use of an alternative polymer for PIM synthesis.

As reported by Kolev et al. (2009), polyvinyl chloride (PVC) is a polymer with very good chemical resistance that can be used for the synthesis of polymer inclusion membranes. Kagaya et al. (2012) demonstrated that PVC-based membranes could also be used for metal ion separation and provide better mechanical support for the membrane. Moreover, Kolev et al. (2009) demonstrated that the PVC/D2EHPA membranes do not require the inclusion of an additional plasticizer in their composition as is the case with CTA-based PIMs. This is due to the inherent plasticizing properties of the D2EHPA itself in relation to PVC.

In this paper, the use of PVC- and CTA-based inclusion membranes with D2EHPA for the separation of Cr(III) and Cr(VI) ions from acidic solutions is reported. The process parameters: polymer matrix type, concentration of the carrier, concentration ratio of the chromium(III/VI) ions and their optimum scopes are investigated together with the stability of the systems with CTA/D2EHPA and PVC/D2EHPA membranes. The analyses show that the strong oxidation properties of Cr(VI) ions have an adverse effect on a CTA-based PIM. The author also demonstrates that in the PVC- and CTA-based PIMs with D2EHPA as a carrier the membrane instability is mainly determined by physicochemical properties and amphiphilic nature of D2EHPA. The author proves that this is one of the crucial factors hampering stable transport conditions in the PIM.
MATERIALS AND METHODS

Polymer inclusion membrane preparation

PIMs were formed by being physically immobilized by the carrier D2EHPA (Merck) in a polymer matrix: (1) CTA with plasticizer 2-nitrophenyl octyl ether (2-NPOE; from Fluka); or (2) PVC (Aldrich) without plasticizer. Appropriate amounts of CTA and PVC were dissolved at room temperature in dichloromethane (Merck) and tetrahydrofuran (THF) (Aldrich), respectively. After vigorous stirring, D2EHPA was added and the solutions were stirred to obtain homogeneous solutions. The solvents were allowed to evaporate and the membranes were separated from glass by immersion into cold water. Next, the membranes were conditioned in deionized water. The active membrane surface was equal to 15.2 cm².

In order to characterize the polymer matrix (PVC or CTA), 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 15 nm layer of gold (K550X Sputter, Quorum Technologies Ltd).

PIM transport experiment

Transport experiments were carried out in a vessel with two cylindrical chambers containing the feed and the stripping aqueous phases described in Religa et al. (2014). The volume of each chamber was 150 cm³. The feed solution was formed by mixing a solution of chromium chloride (CrCl₃·6H₂O) at a concentration equal to 0.002 mol/dm³ Cr(III) and potassium dichromate (K₂Cr₂O₇) at three different concentrations: 0.002, 0.01 and 0.02 mol/dm³ of Cr(VI), based on a composition of environmental and wastewater samples analyzed Bouonomenna et al. (2006); Meeravali & Jiang (2009); Memon et al. (2009) and Kończyk et al. (2010). The stripping solution (6 mol/dm³ HCl) was separated by the PIM. The active membrane area covered 15.2 cm². The initial pH of the feed phase was adjusted to 4. The whole process was carried at ambient temperature (T = 25 ± 0.5 °C). The solutions were mixed in both chambers with mechanical stirrers (IKA, OST20 digital). Separation of chromium(III) and chromium(VI) by liquid membranes is a continuation of previous work. The results obtained were verified and turned out to support the earlier work.

Determination of the chromium ions concentration

Chromium(VI) concentration was determined with a spectrophotometer (NANOCOLOR® UV/vis NUV480 spectrophotometer) using the 1,5-diphenylcarbazide method with wavelength λ = 540 nm directly in the samples collected. Total chromium was determined with a spectrophotometer using the 1,5-diphenylcarbazide method after mineralization of samples. Chromium(III) concentration was calculated from a difference in the total chromium and chromium(VI) concentration. The standard deviation of the measured value determined by statistical methods was ±0.0003. Based on the results, the flux of Cr(III) (J₀) was determined in the way described by Rajewski et al. (2017).

RESULTS AND DISCUSSION

Cr(III) transport through D2EHPA/PVC/PIM

Previous work (Religa et al. 2015; Rajewski et al. 2017) and some literature data (Kebiche-Senhadji & Mansouri 2008; Kończyk et al. 2010) concerning chromium(III) transport through liquid membranes show that the optimum carrier concentration in the membrane can be found for certain initial concentrations of transported ions. In the first stage of the study, the influence of the concentration of carrier D2EHPA in PVC/PIM on chromium(III) ion transport at different initial concentrations of Cr(III) ions was investigated. The results of these studies are shown in Figure 1. The carrier concentration significantly affected the efficiency of the process. There was no transport of chromium(III) ions without the carrier in the membrane. For the low initial concentrations of D2EHPA ≤ 20% (w/w), only a partial extraction and low flux of Cr(III) ions were observed. Increasing the concentration of D2EHPA in a membrane from 50 to 40% (w/w) improved the efficiency of the process. In the case of the high concentration of D2EHPA ≥ 50% (w/w) the membrane lost its physical and transport properties. Visible morphological changes on the surface of the membranes appeared. Similar results were obtained for all initial concentrations of Cr(III). Therefore, in the case of the PVC-based PIM, regardless of the initial concentration of the transported substance, there was a range of D2EHPA concentrations in the membrane that provided the highest efficiency: in the D2EHPA/PVC PIM system studied, this concentration was in the range of 50 to 50% (w/w), in which the extraction of Cr(III) ions was the fastest.
Kebiche-Senhadji & Mansouri (2008) and Kavitha & Palanivelu (2015), who studied the transport of metals through PIMs that included alkyl derivatives of phosphoric acid as a carrier, made a similar observation. The authors also observed that there was a linear increase in the ion flux with an increase in carrier concentration followed by slight decrease. Increase in D2EHPA concentration will lead to more metal ion-D2EHPA complex formation and increase the viscosity in the membrane phase. As a consequence, high viscosity in the membrane limits the diffusivity of the ion–carrier complex in the membrane (Kavitha & Palanivelu 2015). Furthermore, the rate of the process with the PIM with an optimal amount of a carrier, depends on the initial concentration of Cr(III) ions, as illustrated in Figures 1 and 2. Increasing the initial concentration of Cr(III) ions had a negative impact both on the flux of Cr(III) ions and the extraction/re-extraction rate (Figure 2(a) and 2(b)), resulting in slower transport of Cr(III) ions through the membrane (Figure 2(c)).

The application of the initial concentration of Cr(III) $\geq 0.002$ mol/dm$^3$, on the one hand, results in a significant reduction in the rate of penetration (Figure 1) and, on the other hand, prevents complete re-extraction (Figure 2(b)). The accumulation of Cr(III) in the membrane is observed (Figure 2(c)). According to the literature, (Bouonomenna et al. 2006; Religa et al. 2014; Baczynska et al. 2016), quick ‘exhaustion’ of active carrier molecules can be observed at the interface of the membrane in the case of SLM systems.

Moreover, as reported by Bouonomenna et al. (2006) the selected carrier has 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 aqueous solution.

It is also likely that the Cr(III)- D2EHPA complexes accumulated in the membrane phase cause an increase in membrane viscosity (Rajewski et al. 2017). The increase in viscosity of the membrane phase causes the accumulation of the chromium(III) ions in the membrane phase. As a consequence, this leads to the inhibition of process. Therefore, as in the case of the SLM, it is preferable for the process to be carried out under low initial concentrations of the transported substance.

It can be concluded that the PVC/PIM with D2EHPA as a carrier facilitates efficient separation of Cr(III) ions only at low initial concentrations. This is an advantage in the case of the application of a PIM in the analysis of environmental samples which are characterized by low chromium concentration (Ying et al. 2011).

The same analysis was performed for the CTA-based PIM system. However, in the case of CTA/PIM, the observed flux values of the Cr(III) ions penetrating the membrane were higher than for PVC (Figure 3). For example, for the initial concentration of Cr(III) $= 0.002$ mol/dm$^3$ the values obtained for the ion fluxes were $J_0 = 1.4 \cdot 10^{-4}$ and $0.28 \cdot 10^{-4}$ mol/(m$^2$·s), for CTA- and PVC-based PIMs respectively.

Kolev et al. (2009) suggested that PVC/D2EHPA membranes do not require the inclusion of plasticizer in their composition due to the inherent plasticizing properties of D2EHPA itself towards the PVC. On that basis, no plasticizer was used for the PVC/D2EHPA membrane preparation in this study. By contrast, in the case of the CTA/D2EHPA, a plasticizer was used, which probably increased the mobility of carrier molecules, and allowed for faster penetration and transport of Cr(III) ions through the membrane.

**Influence of Cr(VI) ions concentration on efficiency of Cr(III)/Cr(VI) ions separation in CTA- and PVC-based PIMs**

The influence of Cr(VI) ion concentration on the competitive transport of Cr(III) and Cr(VI) ions was verified. The investigations were performed for constant initial concentration of Cr(III) ions and different concentrations of Cr(VI) ions. In all experiments, the receiving phase was free...
from chromium(VI). This means that both membranes used with D2EHPA are selective barriers for Cr(VI) ions. According to previous work (Religa et al. 2014) D2EHPA, as a cation carrier, does not complex with any negative ions, and therefore, regardless of the type of liquid membrane, this carrier guarantees high process selectivity.

The effect of Cr(VI) ion concentration in the feed phase on the transport of Cr(III) ions through the CTA- and PVC-based PIM with D2EHPA is shown in Figure 4. On the one hand, the results indicate that initial concentration of Cr(VI) ions in the feed phase significantly influenced the transport efficiency of Cr(III) ions in CTA/PIM system. For the low initial concentration of Cr(VI) ≤0.005 mol/dm³ the chromium(III) flux decreased by about 15%. An increase in the initial concentration of Cr(VI) to 0.001 mol/dm³, additionally decreased the flux of transported ions by 70%.
On the other hand, the presence and concentration of Cr(VI) ions in the feed phase did not influence the transport efficiency of Cr(III) ions in the PVC/PIM system. For each initial concentration of Cr(VI), the Cr(III) flux had a similar value.

Probably, as reported by Farooque & Al-Amoudi (1999), the degradation of the CTA polymer structure under the influence of strongly oxidizing Cr(VI) ions in the acidic solution was the main reason for the reduced speed and efficiency of the process.

In order to verify this phenomenon in both CTA- and PVC-based PIM systems, the author carried out the following experiments in which the PIMs were soaked in the 0.02 mol/dm³ aqueous chromium(VI) solution for 24 hours.

The results presented in Figure 5 confirm that soaking the CTA/PIM in Cr(VI) solution reduced the efficiency of the extraction process by about 40%. However, in the case of the PVC/PIM, there were no changes in the extraction efficiency after soaking. Moreover, SEM images (Figure 6) consistently indicate a remarkable influence of the Cr(VI) ions on the CTA morphology. Pure CTA and PVC matrices have a smooth surface (Figure 6(a)). Figure 6(b) shows that soaking the CTA matrix in a Cr(VI) solution causes irreversible morphological changes to the surface of the 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 the polymer backbone leading to chain scission (Farooque & Al-Amoudi 1999). However, polymer chain oxidation was established as the major reason for the degradation in the performance of CTA. The effect of oxidation reduced both the molecular weight...
and the mechanical strength of CTA while the PVC matrix was not influenced by the Cr(VI) ions.

If we take into account the chemical resistance of the polymer matrix, it can be concluded that the PVC polymeric matrix is definitely a better solution for the synthesis of PIMs for Cr(III/VI) ion separation. Moreover, the pH also affected the CTA membrane matrix performance. CTA membranes were most stable at pH 4.7 and pH values below or above accelerated the process of hydrolysis of acetyl groups, the pendant to the polymer chain (Farooque & Al-Amoudi 1999).

Comparison of stabilities of CTA- and PVC-based PIM with D2EHPA

The stability of CTA- and PVC-based PIMs containing D2EHPA as a carrier used for selective separation of Cr(III) and Cr(VI) ions from aqueous solutions was investigated by means of the measurement of the change in Cr(III) concentrations as a function of time (over many hours), in water phases, in repeated experiments. The experiment was carried out in the most favorable process conditions. Each cycle was run for 8 hours. The results are shown in Figure 7. The results obtained show that both membranes were not stable during the long process time. In the case of CTA/PIM, a decrease in extraction and re-extraction yield was observed by the third cycle. With each subsequent cycle, gradual decline in the process efficiency was observed. In the seventh and consecutive cycles, the process was completely inhibited (Figure 7(a)).

The membrane worked stably only for five cycles. With each subsequent cycle, a gradual decline in extraction and re-extraction yield was observed.

Most authors (Kolev et al. 2009; Kończyk et al. 2010; Kagaya et al. 2012; Kebiche-Senhadji & Mansouri 2008), who have studied the PVC or CTA/D2EHPA PIM systems claim that the main cause of PIM instability over time is the partial loss of extractant through leaching into the aqueous phases in contact with the membranes. However, those authors carried out measurement cycles only until the first signs of decline in the process efficiency. Therefore, why the transport is completely inhibited in further measurement cycles is not explained.

The observations of both systems showed that in the ninth and tenth measurement cycles, there was a simultaneous decline in the feed phase volume and increase in the strip phase volume. The difference in the volume of the aqueous phases increased in subsequent measurement cycles. It was observed that in the final ninth and tenth cycles, approximately 15% of the initial volume of the feed phase was lost, and at the same time the initial volume of the receiving phase increased.

As reported by (Rajewski & Religa 2016), in the liquid membrane systems the D2EHPA carrier extracts chromium(III) ions from the aqueous phase but also water molecules by means of hydrogen bonds. Moreover, hydrated Cr(III) ions introduce water molecules into the membrane phase. These factors cause favorable conditions in the membrane for the formation of micellar structures, in which the polar ends of the amphiphilic carrier molecules, together with the transported hydrolyzed ions, are inside the micelle, while the non-polar parts of the carrier are outside the micelle. Probably the
same situation takes place in CTA- and PVC-based PIM systems with D2EHPA.

Taking into account the fact that there is a large difference in chemical potential (concentration of Cr and H ions) in the aqueous phases separated by the PIM, the osmotic pressure occurs on the side of the stripping phase. As a result, water molecules absorbed by D2EHPA and introduced by chromium in the membrane (Rajewski & Religa 2016) diffuse through the membrane in micellar structures to the stripping phase. Because it is observed only in later cycles (eighth, ninth, and tenth), it can be concluded that the destabilization of the PIM is mainly caused by the progressive increase in the polar phase inside the D2EHPA micellar structures. As visible in Figure 8, a pH decrease was observed in each cycle. Moreover, in each cycle the pH drop was sharper. In cycles 1 to 5, the pH decreased from 4.00 to about 2.45 after 8 hours and about 48% of Cr(III) was extracted (Figure 7). In the following cycles the pH decreased from 4.00 to 1.5 after 15 min of the process, and only about 8% of Cr(III) was extracted. Facilitated transport of H\textsuperscript{+} ions through the membrane into the feed phase takes place. This phenomenon causes a rapid decrease in the driving force of the process. The highest decrease in process efficiency was observed in the sixth cycle (Figure 7(b)); the unused membrane was kept in distilled water for a weekend (after five cycles), thus the said decrease in the process efficiency in the sixth cycle is mainly caused by water insertion into the membrane phase from the distilled water storage solution.

Based on the above statements, it can be concluded that eliminating problems such as leaching of extractant into the
aqueous phases and degradation of the polymer matrix will not solve the PIM instability problem. The factor that determines the stability of the PIM with D2EHPA is the presence of water in the membrane and the formation of unstable micellar structures.

CONCLUSIONS
Selective separation of Cr(III) and Cr(VI) ions from acid solutions was successfully demonstrated using PIMs with CTA or PVC as the base polymers and D2EHPA as the extractant.

The main system parameters affecting the rate of transport (i.e. the type of the polymer matrix; the composition of the membrane and the initial concentration of the Cr(III)/VI) ions) were investigated and compared.

It was found that in the case of the PIM with D2EHPA, the presence of D2EHPA as the extractant was a selective barrier for Cr(VI) ions. In the case of the CTA/PIM, the presence of Cr(VI) ions caused irreversible morphological changes on the surface of the CTA matrix and a decline in the efficiency of the process.

The PVC matrix was not influenced by the Cr(VI) ions and the process was also efficient, so it was definitely a better base polymer for the PIM synthesis for Cr(III)/VI ion separation from acid solution. However, both CTA- and PVC-based PIMs were not stable over the long process time. PIMs remained selective for Cr(VI) ions, but a decrease in process efficiency was observed.

Water molecules were probably absorbed by the D2EHPA and introduced by chromium to the membrane diffused through the membrane to the stripping phase. This phenomenon caused a rapid decrease in the driving force of the process and the complete inhibition of the Cr(III) ion extraction. Based on these results and those of results of previous work, it can be concluded that the presence of water in the membrane and the formation of unstable micellar structures is the factor that most limits the stability of a PIM with the D2EHPA carrier.

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