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Chromium (III) Ions Were Extracted from Wastewater Effluent Using a Synergistic Green Membrane with a Binary Combination of D2EHPA and Kerosene

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Abstract: This study used a supported liquid membrane system (SLM) using Celgard 2400 polypropylene as the support, di(2-ethylhexyl) phosphoric acid (D2EHPA) as the carrier, and kerosene as the diluent. To obtain the best carrier concentration, D2EHPA concentrations between 0.04 and 0.6 M were used. The Cr (III) solutions used in the feed phase had various ionic strengths and were adjusted with NaCl at concentrations ranging from 0.25 to 1.75 M. To maintain a constant pH (4) in the feed phase, a 0.2 M acetic acid–sodium acetate buffer was utilized. Because the rate of Cr (III)-carrier complex formation at the interface of the feed solution and membrane increased up to 20×10^{-4} mol/L, it was discovered that transport of Cr (III) rose with an increase in chromium content in the feeding phase. For the optimization of the various stripping agents, HCl concentration was employed, from 0.25 M to 1.75 M. It was observed that Cr (III) transport increased with the increase in HCl concentration because the transport was at a pH gradient, which was the main driving force. Because of the fact that at the feed phase-membrane contact, D2EHPA combined with chromium ions to form the Cr (III)-carrier complex and released H⁺ protons, in the feed phase, the Cr (III)-carrier complex was diffused into a stripping phase, wherein Cr (III) ions were stripped and the carrier was reversibly protonated again.

Keywords: heavy metal toxicity; bis(2-ethylhexyl) phosphoric acid; Cr (III) extraction; supported liquid membrane; transportation efficiency

1. Introduction

Heavy metals, because of their tremendous toxicity, are regarded as one of the most harmful environmental contaminants, being five times denser than water heavy metals and posing toxicity to organisms even if present in trace amounts. However, some heavy

metals are necessary for proper growth and development in the human body [1–3]. Aquifer systems are exposed to these heavy metals through industrial discharges and agricultural runoff [4]. One of the major causes of the occurrence and accumulation of heavy metals in the environment is untreated industrial effluents [5]. These industrial toxic discharges contaminate groundwater resources through soil percolation [5].

To help lessen the detrimental impacts of heavy metals on human, animal, and environmental health, a variety of remediation techniques are available. Chemical precipitation is the traditional and most widely used method for treating industrial wastewater that contains heavy metals because it is straightforward and less expensive [6]. The precipitation process produces sludge, which must be dewatered before being disposed of in landfills. This adds to the treatment process' overall cost [7]. Coagulation and flocculation are additional techniques for removing heavy metal ions from aqueous media. In coagulation, charged particles neutralize and destabilize colloids, causing sedimentation and then filtering to take place [8,9]. However, these methods do not eliminate heavy metal ions [10]. Because of its enormous capacity, quick kinetics, and higher effectiveness, ion exchange removal is considered to be a superior technique for treating water [11]. In the ion-exchange technique, cations of resins substitute heavy metal ions effectively [12]. However, ion-exchange systems have several drawbacks, such as resins being harmed by oxidants in water, necessitating additional water treatment, and contaminants being transferred to another media that must once again be disposed of.

Studies of the literature reveal that liquid membrane, a more advanced adaptation and fusion of solvent extraction and membrane separation methods, was shown to be capable of recovering metal ions from diluted metal aqueous solutions. Diverse membrane types, including reverse osmosis, ultrafiltration, nanofiltration, and electrolysis, have been used in water treatment because they have several advantages over earlier methods [13–17]. The pH, polymer-metal type, and polymer-metal ratio all play a role. Despite being extremely efficient and selective, it has no industrial uses. Reverse osmosis (RO) uses a membrane to separate dissolved species from wastewater and enables only specific molecules to diffuse; however, it is expensive in terms of electricity and membrane stability consumption [18–20]. An easy-to-use water treatment method is nanofiltration. In terms of dependability and power, it is effective [21–23].

The creation of liquid membranes for different liquid–liquid and gas–liquid separation processes has been an exciting area of study during the last several years. Supported ionic liquid membranes (SILMs), a kind of modified supported liquid membrane, stand out as a leading contender in this area [24–26]. It is a type of solvent–solvent extraction technique, but it is a three-phase system. In liquid membrane, thin support or film that acts as a semi-permeable membrane has been used. It relies on ion charge density and size. It has been found to be highly effective and efficient in recent times [26,27]. An alternative to solvent extraction is a supported liquid membrane (SLM), which operates with much less solvent and stages. Because liquids have a greater solute diffusion coefficient than solid polymeric membranes, the transport flow of metal ions via SLM may be higher. Using an appropriate extractant and adjusting the chemistry of the feed and stripping phases, selective recovery of metal ions can be accomplished, just as with solvent extraction [28].

In this study, stripping extraction experiments were conducted to ascertain and then understand the ideal chemical conditions that could be used to the supported liquid membrane for chromium (III) separation. This work is a component of a larger study that uses selective stripping to separate heavy metals that can coextract using a single kind of extractant. As far as we are aware, selective stripping in an SLM system has not yet been thoroughly explored. The current results can serve as a foundation for modeling and supplying stripping performance under various experimental setups.

2. Materials and Methods

2.1. Chemicals and Reagents

In the present study, bis(2-ethylhexyl) phosphoric acid (97% pure, Fluka) was employed in kerosene (analytical grade, Fluka, Darmstadt, Germany) as diluent. Feed solution of chromium (III) was prepared by adding salt $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (>96% pure, Riedel de Haen, Darmstadt, Germany) and NaCl (>99% pure, Fluka, Darmstadt, Germany) in buffer solution. The buffer solution was prepared by the addition of glacial acetic acid (99%, Fluka, Darmstadt, Germany) and sodium acetate ($\geq 99.0\%$, Fluka, Darmstadt, Germany) in RO water. HCl (37%, Sigma Aldrich, Darmstadt, Germany) solution was used as a stripping agent. All the solutions were prepared with RO water. Weighing balance with ± 0.01 g accuracy was used.

2.2. Membrane Phase in SLM

Micro-porous polypropylene support (Celgard 2400, Sigma Aldrich, Darmstadt, Germany) in the membrane phase was employed for the SLM experiment. Its features, color, thickness, pore diameter, and porosity were white, 25 μm , 0.043 μm , and 40%, respectively. Support (Celgard 2400, Sigma Aldrich, Darmstadt, Germany) for the membrane phase was submerged, to saturate membrane pores by capillary action, in diluent (kerosene) possessing various concentrations of the carrier (D2EHPA, Sigma Aldrich, Darmstadt, Germany). Following the impregnation of support for different soaking times, it was isolated from carrier solutions. Before employing it in a supported liquid membrane cell, it was drained off for 10 min [29].

2.3. Supported Liquid Membrane Cell

All experiments were conducted in a supported liquid membrane cell at 25 ± 1 °C. The SLM cell was composed of acrylic material and consisted of two compartments. The membrane was held between chambers with the help of clamps [30]. The compartment's volume for solutions was 180 cm^3 each. The membrane interfacial area was 16.56 cm^2 .

2.4. Instruments

Agilent's 700 (Santa Clara, CA, USA) series model of the inductively coupled plasma-optical emission spectrometer was used to measure the presence of Cr (III) ions in the feed solution and strip solution ($\lambda = \text{nm}$, carrier gas = argon).

2.5. Transport Studies

Firstly, a supported liquid membrane cell was set up and rinsed with RO water. The membrane phase was mounted in the SLM cell with clamps after impregnation with carrier solutions and different soaking times. Feeding solution and stripping solution were added to compartments of SLM cells. The electric stirrer (1000 rpm) was employed to prevent the accumulation of ions concentration at the solution–membrane interface.

Secondly, for the optimization of the different parameters for effective metal ion transport in the SLM system, the following ranges were employed: carrier concentration, 0.04 mol/L to 0.6 mol/L; membrane soaking time, 6 h to 32 h; feed solution concentration, 10×10^{-4} mol/L to 50×10^{-4} mol/L; and stripping solution concentration 0.25 mol/L to 1.75 mol/L. Inductively coupled plasma was used to evaluate samples from the feed solution and stripping solution that was obtained after predefined time intervals.

2.6. Calculations

The distribution coefficient for Cr (III) transport in the supported liquid membrane was determined as follows [30]:

$$K_D = \frac{K_{Df}}{K_{Ds}} \quad (1)$$

where K_{Df} and K_{Ds} stand for the distribution co-efficient for the feed phase and stripping phase, respectively.

$$K_{Df} = \frac{[Cr(III)]_M}{[Cr(III)]_F} \quad (2)$$

$$K_{Ds} = \frac{[Cr(III)]_M}{[Cr(III)]_S} \quad (3)$$

Permeability coefficient calculations were conducted to optimize various parameters for Cr (III) transport in the SLM system as follows [31]:

$$\ln\left(\frac{C_t}{C_0}\right) = -\varepsilon \frac{S}{V} Pt \quad (4)$$

where C_t , C_0 , ε , S , V , P , and t represent Cr (III) concentration at elapse “t” time, initial Cr (III) concentration, membrane porosity, membrane area, feed phase volume, and elapsed time, respectively.

Flux was calculated to realize Cr (III) transport through the membrane in SLM cells quantitatively as follows [31]:

$$J = \frac{dC_{(f)}}{dt} \frac{V_{(f)}}{A_{(m)}} \quad (5)$$

where J is the flux (mol/cm² s), $V_{(f)}$ (cm³) is the feed phase volume, A is the effective membrane area, and $dC_{(f)}/dt$ is the slope of the straight-line graph. $V_{(f)}$ was 180 cm³, and the effective membrane area was 5.024 cm².

The recovery (%) of Cr (III) was calculated as follows [30]:

$$\text{Recovery \%} = 100 \frac{C_{(t)}}{C_0} \quad (6)$$

where $C_{(t)}$ and C_0 represent Cr (III) concentration at the elapsed time and the beginning of the feeding phase or stripping phase, respectively.

3. Results and Discussion

Following this, parameter conditions and their ranges were optimized for Cr (III) ion transport through SLM studies (Table 1).

Table 1. The concentrations of various components for the optimization of parameters in SLM.

Parameter	Membrane Phase Concentration	Membrane Soaking Time	Feed Phase Concentration	Stripping Phase Concentration
Optimization range	0.02–0.6 M D2EHPA	6–32 h	10–50 × 10 ^{−4} mol/L Cr (III)	0.4–1.75 M HCl

3.1. D2EHPA Effects on Cr (III) Extraction

As shown in Table 1, the impact of D2EHPA concentration on Cr (III) extraction was examined. Different concentrations of D2EHPA, ranging from 0.02 to 0.6 mol/L, were used. It is clear from the curves of Figure 1a,b that Cr (III) concentration was decreased in the feeding phase and that Cr (III) concentration gradually increased in the stripping phase over time. With an increase in D2EHPA concentration, the trend of Cr (III) transportation arose. It was shown that the formation of the Cr (III)-D2EHPA complex increased with D2EHPA concentration and that ultimately the rate of transport of Cr (III) increased. However, beyond the 0.3 M D2EHPA concentration, Cr (III) transport trend was decreased. This observation was found to be in agreement with the literature studies that revealed that the transport of metal ions in SLM decreased with the increasing concentration of D2EHPA, and thus the concentration effect was tested up to 0.6 M D2EHPA [29].

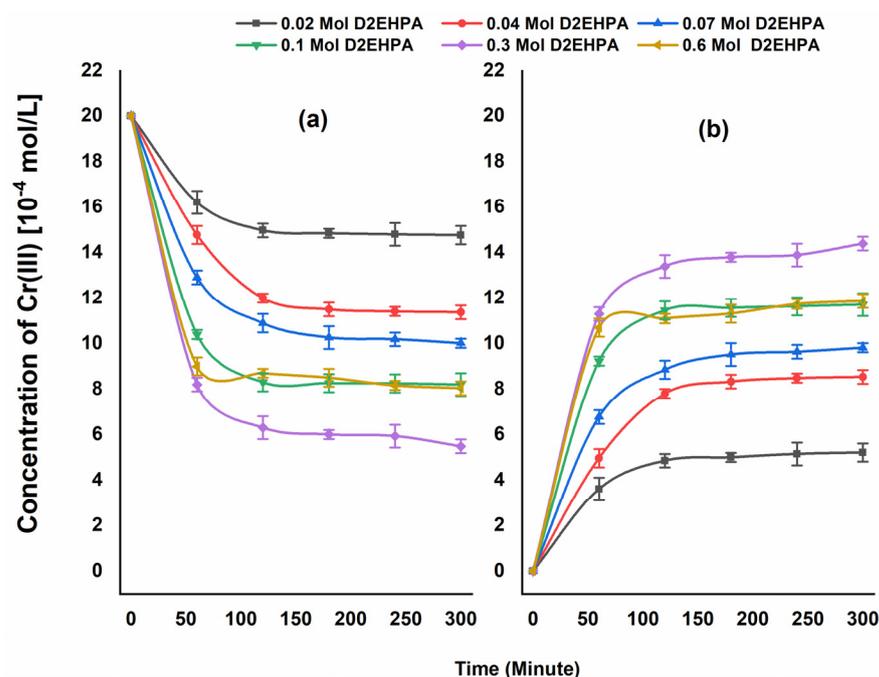


Figure 1. Cr (III) concentration at different D2EHPA concentrations in the feed phase (a) and stripping phase (b); $[\text{Cr(III)}] = 20 \times 10^{-4}$ mol/L, $[\text{HCl}] = 1.25$ mol/L.

Figure 2's curves, which exhibit additive behavior and are mirror images of one another, demonstrate the same phenomenon. Cr (III) metal ions' concentration in the feed phase was reduced. However, at 0.3 mol/L D2EHPA, the concentration of Cr (III) metal ions dropped to its lowest level. As a result, the transport of Cr (III) metal ions was reduced. Similar to this, the amount of Cr (III) metal ions rose to 0.3 mol/L D2EHPA during the stripping phase.

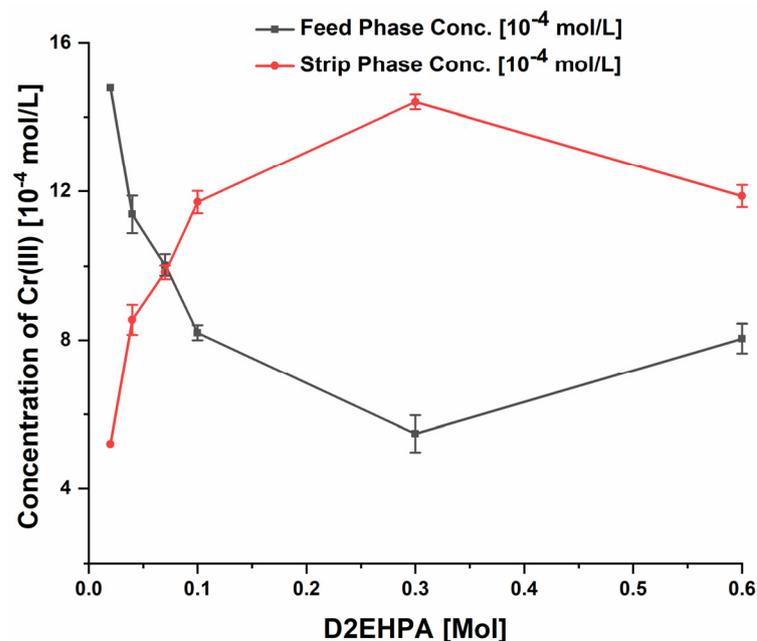


Figure 2. Concentrations of Cr (III) in the feed phase and stripping phase at 0.6 M D2EHPA concentration; $[\text{Cr(III)}] = 20 \times 10^{-4}$ mol/L, $[\text{HCl}] = 1.25$ mol/L.

Reduction in the extraction of Cr (III) may hypothesize a rise in Cr (III)-D2EHPA complex formation at the feed–membrane interface and an increase in its concentration

inside the membrane [29]. However, the viscosity of the D2EHPA concentration increased in the membrane and hampered the Cr (III)-D2EHPA complex in the membrane.

Permeability coefficient was determined by using Equation (4) at different D2EHPA concentrations. It was observed that the permeability coefficient was maximum at the 60th minute of the experiment. The slope of the straight-line graph also showed (Figure 3) that the maximum transportation of Cr (III) ions took place in the first part of the experiment. It is also evident from Figures 1 and 2 that 0.3 mol/L D2EHPA concentration is optimum for Cr (III) metal ions in SLM. Various calculations, such as distribution coefficient (Equation (1)), permeability coefficient (Equation (4)), flux (Equation (5)), and extraction efficiency (Equation (6)), were made at the D2EHPA optimum concentration. The distribution coefficient was calculated by Equation (1) at a 0.3 mol/L D2EHPA concentration. It was assumed that total Cr (III) was distributed between the feed phase, membrane, and strip phase [30], as given as follows.

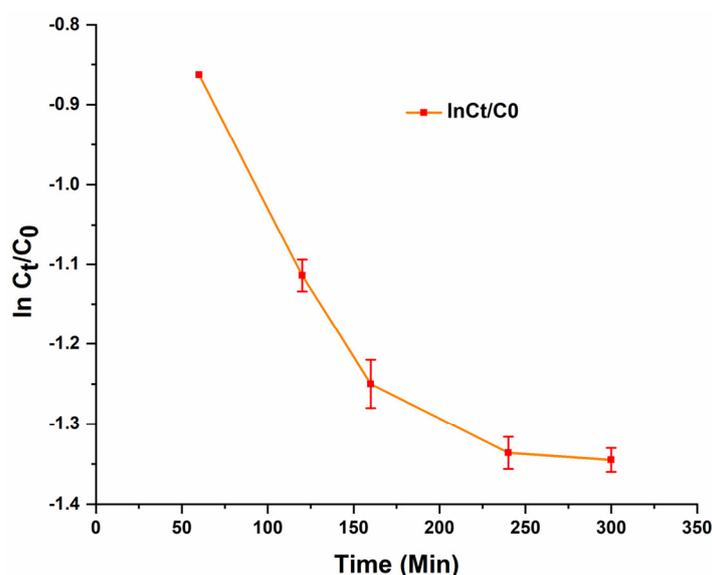


Figure 3. The plot of $\ln C_t/C_0$ vs. time.

$$Cr_{Total} = Cr_{feed} + Cr_{Membrane} + Cr_{strip} \quad (7)$$

As time passes, Cr_{feed} and Cr_{strip} indicate the concentrations of Cr (III) in the feed phase and stripping phase, respectively, while Cr_{Total} represents the starting concentration of the feed phase. By using mass balance, the following formula was used to determine the Cr (III) concentration in the membrane [30]:

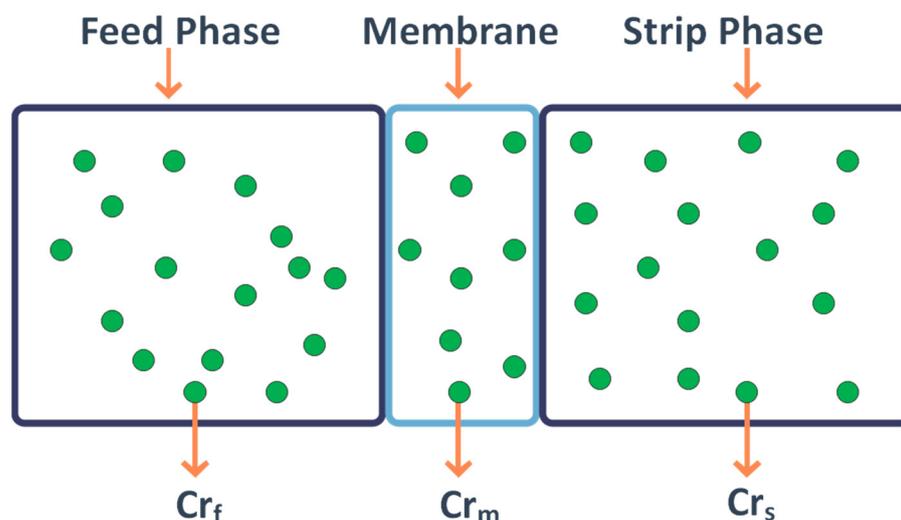
$$Cr_{Membrane} = Cr_{Total} - Cr_{feed} - Cr_{strip} \quad (8)$$

At this point in the experiment, the distribution coefficient for the feed phase was calculated. The first stage is the rising part of the curve (before achieving the equilibrium), and the second stage is the horizontal part of the curve (after attaining the equilibrium), as shown in Figure 1a. The distribution coefficient values at the 60th and 240th minutes of the experiment were 0.061 and 0.029 (Table 2), respectively. This shows that the Cr (III) ion concentration was higher in the membrane phase before the equilibrium than after the equilibrium. The distribution coefficient for the strip phase at the 240th minute was calculated to be 0.012. It was observed that the distribution coefficient of the feed phase was approximately 2.4 times more than that of the strip phase at the 240th minute. It was shown that Cr (III) ions in the feed phase had a higher affinity toward the membrane as compared to Cr (III) in the strip phase. This also acted as a driving force in the SLM and helped in the extraction and de-extraction of Cr (III) ions at the feed phase and strip phase interface, respectively.

Table 2. Distribution coefficient (KD) at the 60th and 240th minutes of the experiment.

Time (Min)	Optimized Parameters	Feed Phase Distribution Co-efficient (KD_f)	Stripping Phase Distribution Co-efficient (KD_s)	Distribution Co-efficient (KD)
60	0.3 M D2EHPA	0.061	0.044	1.378
240	0.3 M D2EHPA	0.029	0.012	2.344
60	24 h soaking time	0.030	0.020	2.393
240	24 h soaking time	0.014	0.007	3.028
60	20×10^{-4} mol/L Cr (III)	0.055	0.051	1.077
240	20×10^{-4} mol/L Cr (III)	0.025	0.007	3.440
60	1.25 M HCl	0.062	0.039	1.577
240	1.25 M HCl	0.071	0.012	5.731

The flux of Cr (III) ions was calculated by using Equation (2) at the optimized conditions of the experiment. During the investigation, samples were taken at regular time intervals and subsequently analyzed. It is clear from the graph that the flux of Cr (III) was maximum at the 60th minute of the experiment and decreased with time, becoming almost zero at equilibrium. The relationship between flux and D2EHPA carrier concentration is represented graphically in Figure 4. Finally, extraction efficiency was determined by using Equation (6) at different D2EHPA concentrations. It was shown in Figure 4 that extraction efficiency was increased, indicating that 0.3 mol/L D2EHPA concentration is the optimum for Cr (III) extraction from aqueous media.

**Figure 4.** Mass transfer of chromium (III) ions in SLM.

3.2. Membrane-Soaking Time Effects on Cr (III) Extraction

In SLM extraction, the transport of metal ions relies on the dipping time of the membrane in the diluent. Membrane soaking in carrier-diluent solution is necessary because it allows for the movement of metal ions. It lessens the friction that metal ions experience when moving across the supported liquid membrane from the feed phase to the stripping phase. We studied the effects of membrane soaking times of 6, 12, 18, 24, and 32 h on Cr (III) extraction. As can be seen in Figure 5, it was discovered that Cr (III) transport increased as membrane soaking time increased up to 24 h. However, beyond 24 h soaking time, the extraction of Cr (III) decreased because of the high quantity of kerosene–D2EHPA solution that may be absorbed in SLM support and the subsequent evaporation of the kerosene molecule. Resultantly, the Cr (III) carrier complex was adequately congested, and

the viscosity of the D2EHPA carrier molecule was increased, obstructing the passage of Cr (III) ions.

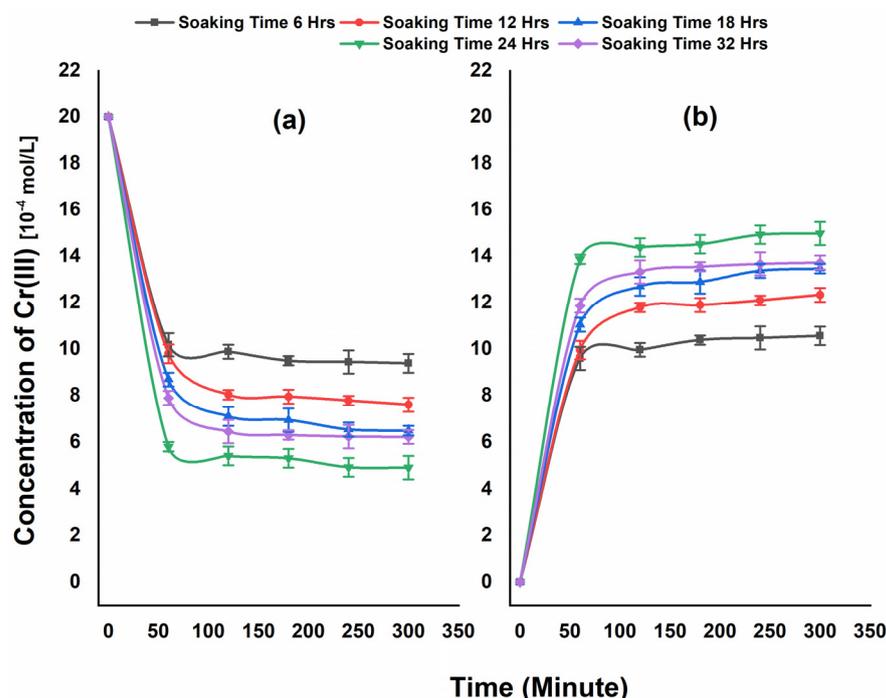


Figure 5. Variation of ion (a) feeding and (b) stripping; $[\text{Cr(III)}] = 20 \times 10^{-4} \text{ mol/L}$, $[\text{D2EHPA}] = 0.3 \text{ mol/L}$, $[\text{HCl}] = 1.25 \text{ mol/L}$.

The distribution coefficient for the feed phase and strip phase was calculated by using the equation at the 240th minute, as shown in the table. The flux of Cr (III) ion extraction was also calculated by Equation (5), with a graphical representation shown in Figure 4. Flux for different membrane soaking times showed that 24 h soaking was the optimum for Cr (III) extraction from aqueous media. Extraction efficiency performed for the soaking times of various membranes (Figure 5) increased with membrane soaking time, but a decrease in extraction was observed beyond 24 h. This behavior can be explained by the fact that membrane support was extremely saturated because excess numbers of carrier molecules were accumulated by the capillary action in the membrane support, which hindered the passage of the Cr (III)-carrier complex through the membrane. The suggested findings were also found to be in agreement with the literature reported on the effect of membrane soaking time on the transport behavior of metal ions [32].

3.3. Feed Phase Concentration Effects on Cr (III) Extraction

Feed phase concentration effects on Cr (III) transport were investigated in the range of 10×10^{-4} to $50 \times 10^{-4} \text{ mol/L}$ in the feed phase solution. Sodium chloride salt was used in the feed phase to maintain ionic strength concerning the stripping phase [33]. Using a 0.2 M acetic acid/sodium acetate buffer, the pH 4 of the feed phase was kept constant. The concentration of the feed phase solution was seen to rise, while the concentration of the stripping feed was seen to fall, as illustrated in Figure 6. The highest transit of the Cr (III) ion occurred, as shown in Figure 6, at a feed solution concentration of $20 \times 10^{-4} \text{ mol/L}$. In this research, however, the transport of Cr (III) ions reduced with time. The high concentration of the Cr (III)-D2EHPA complex in the membrane phase may have been the cause of this. Additionally, a significant amount of Cr (III) may have been adsorbed on the membrane, blocking the pores of the membrane phase and resulting in a reduction in Cr (III) transit over time.

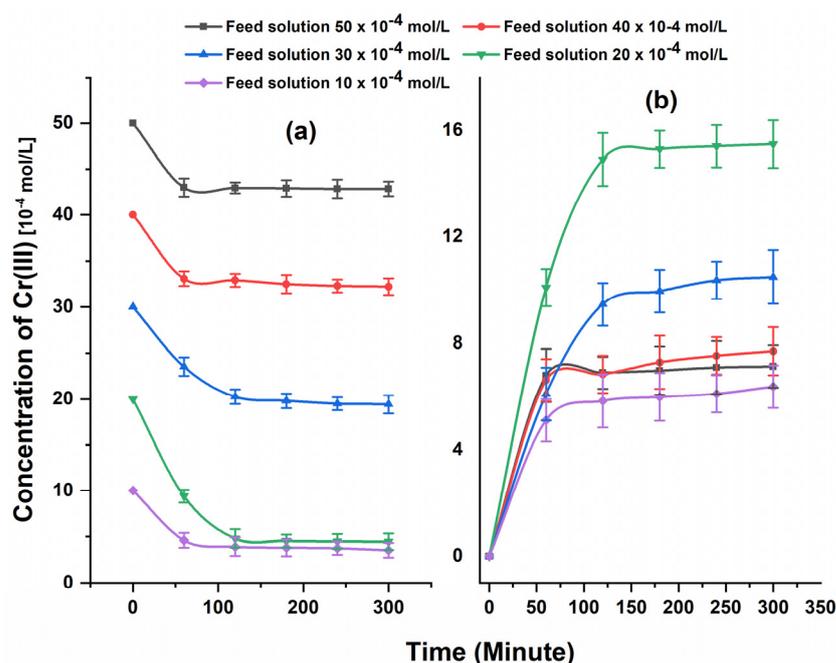


Figure 6. Concentration of Cr (III) in the feed phase (a) and stripping phase (b) at various D2EHPA concentrations; $[\text{Cr(III)}] = 20 \times 10^{-4} \text{ mol/L}$, $[\text{HCl}] = 1.25 \text{ mol/L}$.

To optimize the feed phase starting concentration, the distribution coefficient was determined for the feed phase and the stripping phase and compared with each other. The distribution coefficients for the feed phase before and after the equilibrium were 0.055 and 0.025, respectively, as shown in the table. The distribution coefficient for stripping feed after equilibrium was 0.007. The coefficients for the feed phase and stripping phase were compared, and the results revealed that Cr (III) ions moved more significantly from the feed phase to the stripping phase. Distribution coefficient values showed that the ideal feed phase concentration for extracting Cr (III) was $20 \times 10^{-4} \text{ mol/L}$.

The flux of Cr (III) ion extraction was calculated, and it is shown in Figure 6. It was found that flux increased before equilibrium and decreased after balance, while it became almost zero at equilibrium. A higher concentration of Cr (III) ions in the stripping phase may have been the cause of the reduction in flux; the flow of Cr (III) increased as the feed phase concentration rose. Similarly, the study of extraction efficiency for optimization of the feed phase initial concentration was performed as shown in Figure 6. The optimum concentration of Cr (III) ions in the feed phase in this SLM system was $20 \times 10^{-4} \text{ mol/L}$, according to extraction efficiency.

3.4. The Stripping Phase Concentration Affected Cr (III) Extraction

Re-extraction is necessary on the other side of the supported liquid membrane concurrently where metal is removed, and the carrier is renewed because the extraction takes place at the interface between the supported liquid membrane and the feeding phase. Therefore, constituents in the stripping phase are an essential parameter that influences the efficiency of extraction. For the re-extraction of Cr (III), HCl is used as a stripping agent [34]. In this study, HCl was used as a strip solution, and its concentration effects on Cr (III) transportation were investigated. HCl concentrations ranging from 0.25 to 1.75 M were used in the stripping phase to study the concentration impact. NaCl, ranging from 0.3 to 1 M, was also used to maintain the ionic strength of the feeding phase. The concentration of Cr (III) in the stripping phase rose when the concentration of HCl was raised [33].

Figure 7 illustrates the evaluation of the impacts of stripping phase concentration on Cr (III) ion extraction in the SLM system. The transport of Cr (III) ions was shown to increase when the HCl concentration in the stripping phase rose. At a concentration of 1.25 mol/L

HCl, the highest extraction of Cr (III) ions was achieved. Cr (III) transportation became less efficient at 1.25 mol/L HCl concentration. According to a linked counter transport mechanism, at the interface of the feeding phase of a supported liquid membrane, an acidic carrier molecule releases the proton ion H^+ and removes metal ions. The complex metal carrier diffuses across the supported liquid membrane and dissociates at the interface with the stripping phase, which has a significant proton concentration. To transport metal ions, protons must be available during the stripping phase [35,36]. The transport of Cr (III) ions was shown to increase when the HCl concentration in the stripping phase rose. However, Cr (III) ion transit was reduced at 1.25 mol/L HCl concentration. This occurrence could have resulted from the proton not being available, owing to crowding at the membrane–strip interface, which reduces the amount of the Cr (III)–D2EHPA complex that can be extracted and, as a result, the amount of Cr (III) ions that can be extracted.

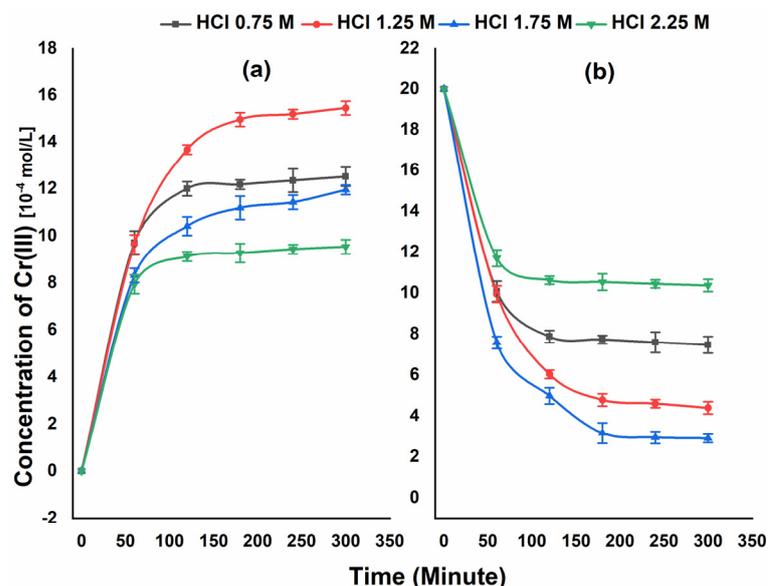


Figure 7. Concentration of Cr (III) in feed phase (a) and stripping phase (b) at various D2EHPA concentrations; $[Cr(III)] = 20 \times 10^{-4}$ mol/L, $[HCl] = 1.25$ mol/L.

The distribution coefficients for feed phase and stripping phase and their comparison at optimum conditions of D2EHPA concentration, soaking time, and feed phase initial concentration are shown in Figure 8. These calculations were made after the equilibrium. The distribution coefficient indicated that the ready availability of protons was necessary for Cr (III) ion extraction in the SLM system. Flux calculations of Cr (III) ion extraction for stripping optimization were conducted, as shown in Figure 8. It can be observed from Figure 8 that maximum flux took place in the first part of the experiment. This indicates that it was a coupled counter transport mechanism that was governed by the proton gradient. However, the feed phase pH was 4, maintained by acetate buffer, and the strip phase was strongly acidic. The maximum mass transfer occurred before the equilibrium and became almost zero after the equilibrium because the pH gradient vanished. The extraction efficiency for optimization of HCl concentration in the stripping phase was calculated. A graphical representation of extraction efficiency is shown in Figure 9. A maximum of 84% extraction of Cr (III) ions occurred at 1.25 mol/L HCl concentration in the stripping phase. This factor also confirmed that the pH gradient was necessary for Cr (III) ion extraction in the SLM system.

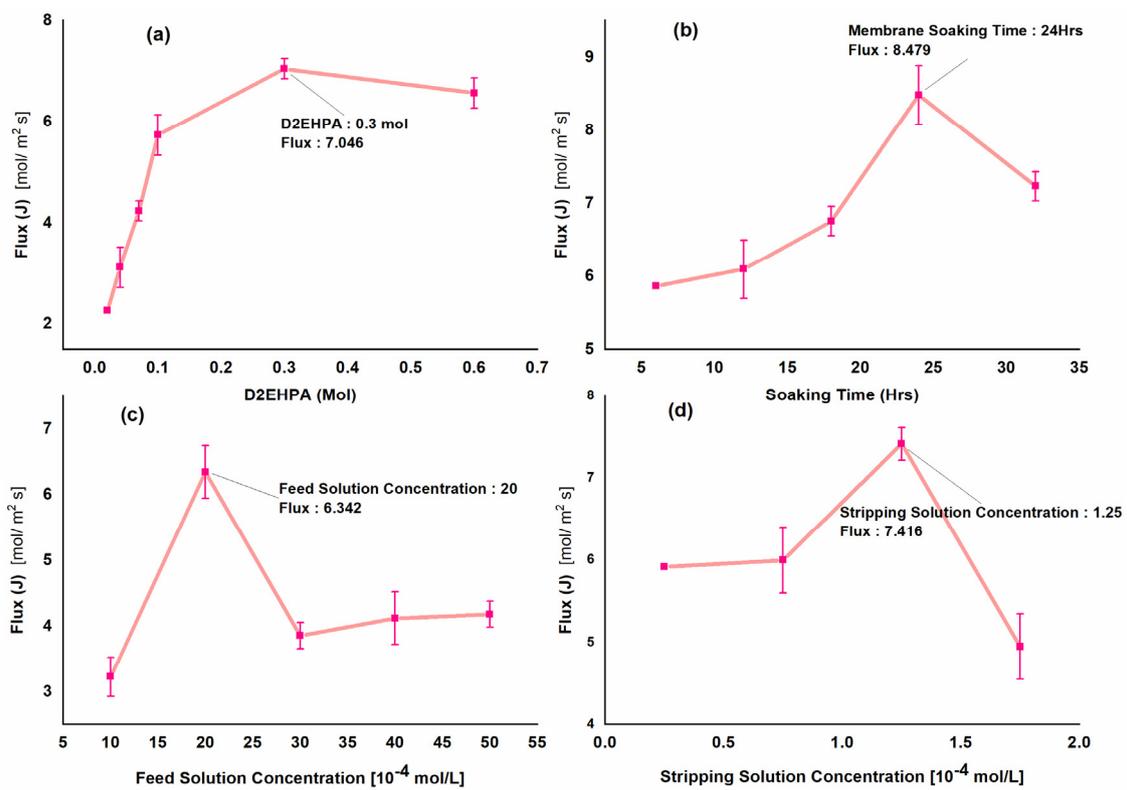


Figure 8. Flux at various concentrations of D2EHPA (a), membrane soaking time (b), initial concentration of feed phase (c), and initial concentration of strip phase (d) for Cr (III) extraction.

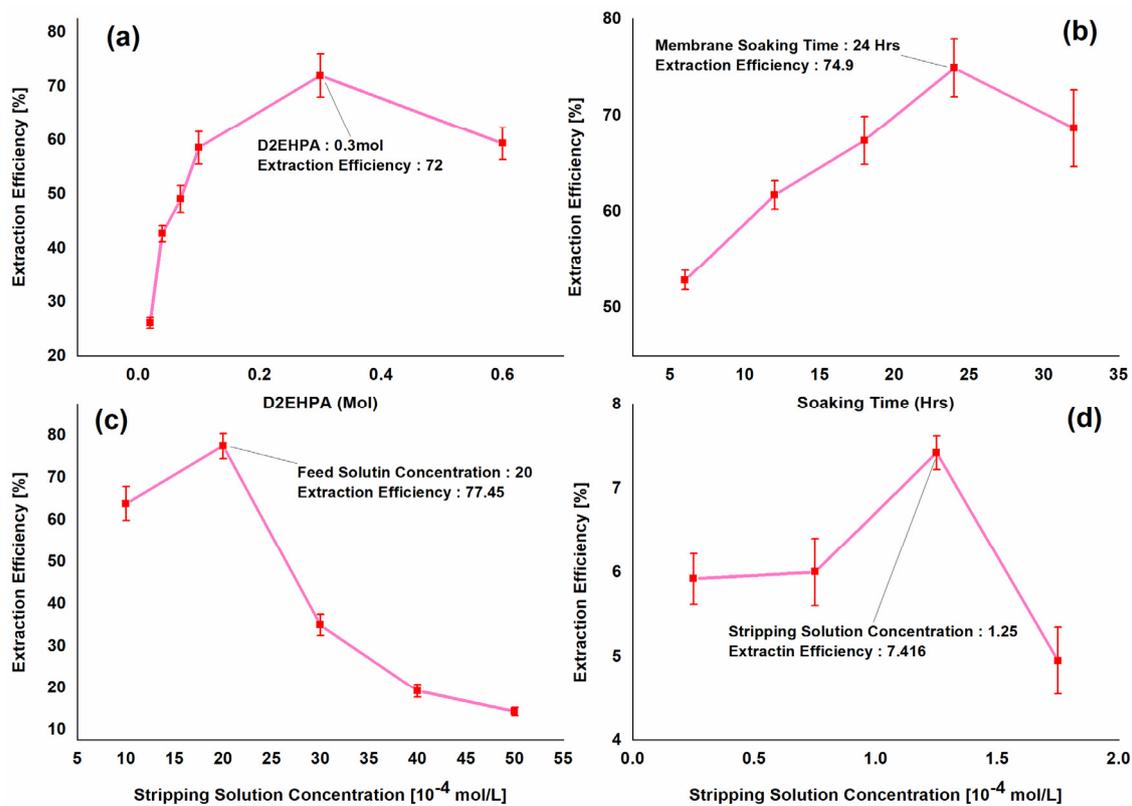


Figure 9. Extraction efficiency at various concentrations of D2EHPA (a), membrane soaking time (b), initial concentration of feed phase (c), and initial concentration of strip phase (d) for Cr (III) extraction.

There is a clear gap in the literature regarding the extraction and recovery of chromium ions utilizing the D2EHPA carrier in SLM extraction, as shown in Table 3's summary of various metal ions extracted using the D2EHPA carrier phase.

Table 3. Literature review on D2EHPA as the carrier in the supported liquid membrane.

Carrier	Diluent	Feed Phase	Strip Phase	Ion	Reference
D2EHPA	Kerosene	Na ₂ SO ₄	H ₂ SO ₄	Zn (II)	[37]
D2EHPA	Coconut oil	HCl	Na ₂ CO ₃	Pb (II)	[38]
D2EHPA	Xylene	HNO ₃	Distilled water	V (II)	[39]
D2EHPA	Kerosene	Synthetic wastewater	H ₂ SO ₄	Ni (II)	[40]
D2EHPA	Kerosene	Synthetic wastewater	HNO ₃	Nd (III)	[41]
D2EHPA	Hexane	Synthetic wastewater	HCl	Lu (III)	[42]
D2EHPA	n-Dodecane	H ₃ PO ₄	H ₃ PO ₄	Cu (II)	[43]
D2EHPA	Coconut oil	H ₂ SO ₄	H ₂ SO ₄	Cu (II)	[44]
D2EHPA	n-Dodecane	H ₃ PO ₄	H ₃ PO ₄	Fe (II)	[45]
D2EHPA	Kerosene	HNO ₃	Distilled water	Cd (II)	[46]

Extraction time: Approximately 80% of Cr (III) ions were extracted until the 180th minute of the experiment at optimized experimental conditions, and no significant extraction took place beyond the 180th minute of the experiment, as shown in Figure 10.

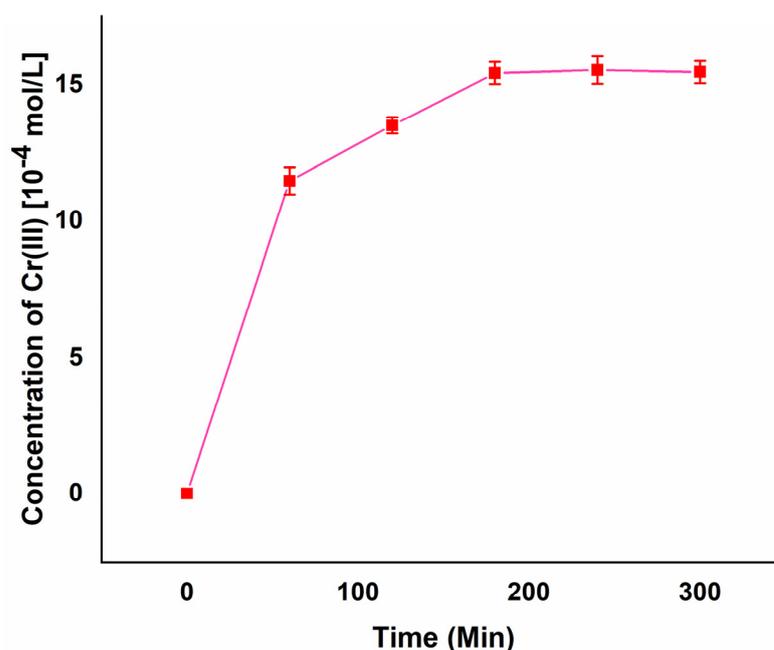


Figure 10. Extraction time.

Stability of the membrane: Membrane stability was studied for the successive experiment at optimum experimental conditions in the SLM system. Successive tests were performed without membrane dipping in extractant-diluent solution. Only the feed phase and strip phase solution were replaced, and the compartment of the SLM cell was filled with RO water to prevent the dryness of the membrane. It was observed that the membrane phase was almost stable for 10 experiments or runs, as shown in Figure 11.

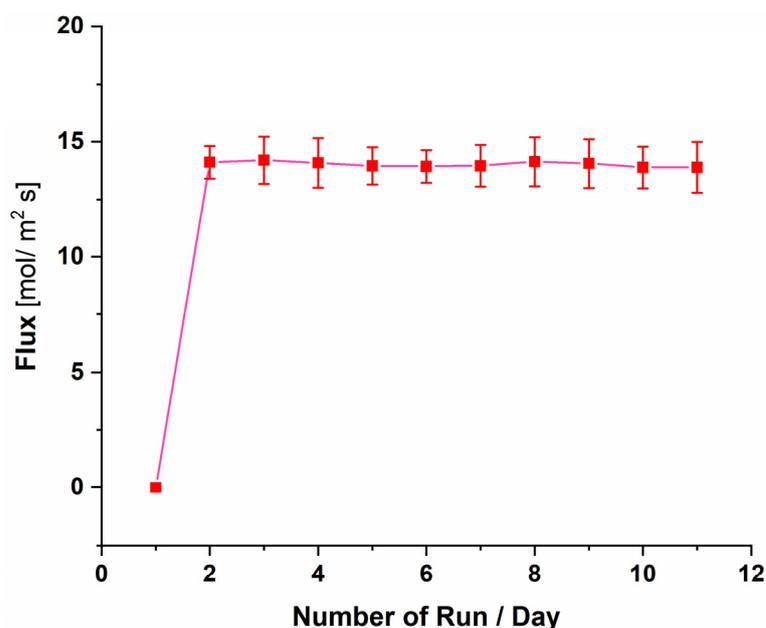
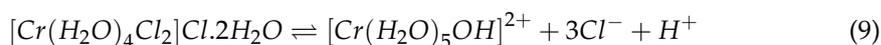


Figure 11. Stability of the membrane.

Proposed Mechanism of Cr (III) Transport in SLM:

In the present study, chromium salt ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) was employed, which is found as $(\text{trans-}[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O})$ naturally [47]. This salt is easily hydrolyzable in water. According to the Pourbaix diagram for the Cr- H_2O system, chromium cation of this salt exists $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ at pH 4 [48]:

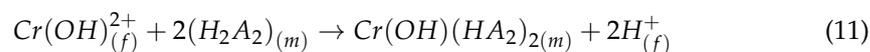


Five water molecules in the coordination sphere can be omitted and denoted as $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$. Bis(2-ethylhexyl) phosphoric acid is an acidic extractant that extracts metal ions by the compound formation mechanism [49–52].



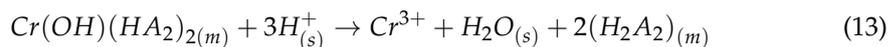
where M is the metal, RH is the extractant, and \overline{MR} is the membrane phase.

The reaction at the feed-membrane interface is as follows:



$\text{D2EHPA} = \text{H}_2\text{A}_2$, because D2EHPA is found as a dimer because of its low polarity.

The reaction at the membrane-strip interface is as follows:



where subscript “ f ” is the feed phase, the subscript “ m ” is the membrane phase, and the subscript “ s ” is the stripping phase.

In this type of transport, extraction and de-extraction of Cr (III) metal ions takes place at the feed-membrane and membrane-strip interfaces simultaneously, respectively, due to pH gradient force. The feed phase pH was 4, which was maintained by the buffer solution. Due to its acidic nature, the extractant released proton at the interface of the membrane-feed phase and extract $\text{Cr}(\text{OH})^{2+}_{(f)}$ by the compound formation, and this shifted the equilibrium to the right, known as the extraction mechanism. Following the formation of the complex $\text{Cr}(\text{OH})(\text{HA}_2)_{2(m)}$, it moved across the membrane. Strip phases have a high concentration

of acids or protons. Due to the high pH gradient, the complex $\text{Cr}(\text{OH})(\text{HA}_2)_{2(m)}$ dissociates and releases Cr (III) in the strip phase [53]. The extractant becomes protonated at the membrane-strip phase interface. The release of Cr (III) and protonation of the extractant in the strip phase took place simultaneously, and ultimately the equilibrium was shifted towards the left. The cycle started with the extraction and de-extraction of Cr (III) metal ions in the SLM system again (Figure 12).

The extraction constant (K_{Ex}) can be represented as follows:

$$K_{Ex} = \frac{\text{Cr}(\text{OH})(\text{HA}_2)_{2(m)} + 2\text{H}_{(f)}^+}{\text{Cr}(\text{OH})_{(f)}^{2+} + 2(\text{H}_2\text{A}_2)_{(m)}} \quad (14)$$

where D = distribution ratio

$$D = \frac{[\text{Cr}(\text{OH})(\text{HA}_2)_{2(m)}]}{[\text{Cr}(\text{OH})_{(f)}^{2+}]} \quad (15)$$

$$K_{Ex} = D \frac{[2\text{H}_{(f)}^+]}{[2(\text{H}_2\text{A}_2)_{(m)}]} \quad (16)$$

The extraction constant (K_{Ex}) shows the transport of Cr (III) metal ions in the supported liquid membrane pH gradient process, known as facilitated coupled counter-transport. The transport behavior of Cr (III) metal ions may be represented in the following way:

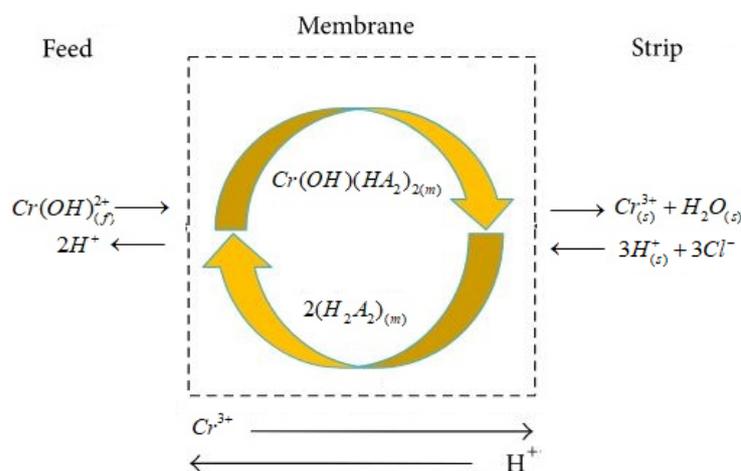


Figure 12. Transport mechanism in Cr (III) extraction.

4. Conclusions

Currently, a cutting-edge technique for removing heavy metal ions from wastewater is membrane technology. In this work, an extractant called bis(2-ethylhexyl) phosphoric acid (D2EHPA) was used to remove Cr (III) ions from synthetic waste. Kerosene was used as a diluent for the reduction of friction in the membrane phase. Celgard 2400, a polypropylene polymer, was employed as support in the membrane phase. To keep the feed phase's pH at 4, a 0.2 M acetic acid-sodium acetate buffer was utilized. NaCl was also used to keep the feed phase's ionic strength constant. The SLM system underwent an adjustment of several parameters, including D2EHPA concentration, membrane soaking period, Cr (III) ion concentration in the feed phase, and HCl concentration in strip solution. Following experimental studies, various factors such as the distribution coefficient, permeability coefficient, flux, and extraction efficiency were calculated. Approximately 64% extraction of Cr (III) ion from synthetic water was observed at optimum conditions; 0.3 M D2EHPA, 24 h membrane soaking time, and 20×10^{-4} mol/L Cr (III) in feed solution and 0.5 mol/L

HCl in strip solution. In this work, it was shown that the rate of extraction in the SLM system from the feed phase to the stripping phase was exponential before the pH reached equilibrium. The removal of heavy metal cations from wastewater and other aqueous media is well-suited for bis(2-ethylhexyl)phosphoric acid. This is because it is acidic, and the pH gradient is what propels counter-current transport. This study reveals that the pH of feed phase solutions has a crucial role in metal cation transport in the SLM system. A supported liquid membrane has advantages over other separation methods such as solvent-solvent extraction, adsorption, and ion exchange because extraction and de-extraction of metal cations occur simultaneously. Its attributes are its low cost, less energy consumption, high selectivity, and dynamic transfer.

5. Future Work

The future and ongoing work include systematic investigation of other heavy metal ion (zinc and nickel) removal via SLM transport behavior under similar conditions. In addition to this, a comparison of the transport behavior of metal ions is under investigation using cyclohexyl amine as the carrier.

Author Contributions: S.S.: Conception, performed metal extraction experiments, visualization of data, writing reviewing, and editing. A.J.A.: Material synthesis, visualization of data, writing reviewing, and editing. M.J.: Conception, design of the study, writing—original draft preparation and critical revision, supervision. S.I.: Design of study, performed major experimental works, writing—original draft preparation. S.O.A.: Methodology, reviewed the original manuscript, and critical revision. M.Z.: Conducted metal extraction experiments, acquisition of data, and writing—original draft preparation. H.A.: Analysis and/or interpretation of data, performed FTIR analysis. E.B.E. and H.H.S.: Visualization of data, reviewed the original manuscript and critical revision. R.A.P.: Drafting the revised manuscript, acquisition of data, and critical revision. E.A.: Analysis and/or interpretation of data, performed FTIR analysis. A.-E.F.: Drafting the revised manuscript, performed adsorption analysis and critical revision. All authors have read and agreed to the published version of the manuscript.

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