

## Application of Poly(Ethyl Eugenyl Oxyacetate) Compounds as the Ions Carrier for Heavy Metals Separation and Separation of Fe and Ni in Ferronickel Using Liquid Membrane Transport Method

La Harimu<sup>1\*</sup>, Sabirin Matsjeh<sup>2</sup>, Dwi Siswanta<sup>2</sup>, Sri Juari Santosa<sup>2</sup>, and Muhamad Jalil Baari<sup>3</sup>

<sup>1</sup>Department of Chemistry Education, Faculty of Teacher Training and Education, Universitas Halu Oleo, Jl. Kampus Hijau Bumi Tridharma, Anduonou, Kendari 93132, Indonesia

<sup>2</sup>Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia

<sup>3</sup>Department of Chemistry, Faculty of Science and Technology, Universitas Sembilanbelas November Kolaka, Jl. Pemuda, Kolaka 93511, Indonesia

\* **Corresponding author:**

email: harim\_1@yahoo.com

Received: January 24, 2022

Accepted: July 19, 2022

DOI: 10.22146/ijc.72486

**Abstract:** Poly(ethyl eugenyl oxyacetate) (PEEOA) had been synthesized for separating heavy metals like Fe(III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) by liquid membrane transport method. The effects of pH, ion carrier volume, stripping concentration, transport time, and metal ion concentration were investigated to obtain optimum conditions. Experimental results showed that optimum pH occurred at pH 4 for Fe(III) ions and pH 5 for others. Carrier volumes were optimum at 8.5 mL for Fe(III) and Pb(II) ions but 7.5 mL for others. The optimum concentrations of the stripping phase were 2 M for Fe(III) and Cu(II) ions, 1 M for Cr(III), Ni(II), Co(II) ions, and 0.5 M for Pb(II) ion. Transport times were optimum at 36 h for Fe(III) and Co(II) ions and 48 h for others. The optimum metal ion concentrations were 0.25 mM for Fe(III) and Cr(III) ions, while other ions were 0.1 mM. The response of PEEOA to Fe(III) ion was the best with selectivity order, Fe(III) > Cr(III) > Pb(II) > Cu(II) > Ni(II) > Co(II). PEEOA also could separate Fe and Ni in a ferronickel sample whose transport percents were 8.87 and 0.92%, respectively. Hence, PEEOA is reasonably effective as an ions carrier for separating metal ions individually or ionic mixture and also in a ferronickel compound.

**Keywords:** poly(ethyl eugenyl oxyacetic acid); metal ion; transport; liquid membrane; ion carrier

### ■ INTRODUCTION

The presence of heavy metals in a water environment and wastewater must be minimized. It directly relates to environmental sustainability and the health of surrounding organisms. The separation of metal ions from a particular mixture is challenging for scientists. It is affected by the similar tendency of metal ions to interact or bind with other substances. Thus, appropriate methods and selective ion carriers are required. A method that can separate and purify specified substances is liquid membrane transport due to its selectivity, efficiency, and relatively simple [1]. Macrocyclic and macromolecular

compounds are mainly concerned by researchers with producing specific host-guest complexations and good separation selectivity.

Several studies in respect of metal ion separation using polymers as ion carriers in liquid membrane transport have been conducted by solvent extraction [2-3]. Chemical reactions among tested metal (solute) in the solvents extraction and liquid membrane transport are similar. However, the basic differences between those separating systems relate to the transport of the tested metal through a liquid membrane directly apart and the presence of the stripping phase. Whereas in

solvent extraction, the tested metal is still being extracted from the organic phase to the aqueous phase.

The phenomenon of the transport process in a liquid membrane shows that complex formation can be influenced by the physicochemical properties (permeability and selectivity) of the targeted ion, ion carrier, and solvent type in the membrane phase. In addition, the chemical composition of the membrane phase in both the source phase solution and the stripping phase also influences the amount of complex formation and transport percent. The selectivity of the membrane and its transport efficiency can be optimized by the macromolecular ion carrier design. It can be conducted through combinations of the ring size and its substituent groups [4-5]. Types of ion carriers lead to different complexation mechanisms. The molecular structure of the ion carrier and the chemical interactions involved in the complexation and transport process are the most decisive factors for membrane selectivity. Hence, it can be adjusted to obtain specific selectivity.

Alkaline and neutral ion carriers show poor selectivity for certain metal ions. Hence, research has been carried out using acidic compounds. Poly(eugenyl oxyacetate) or PEOA could separate Fe(III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) using the solvent extraction method [6]. In the previous study, the PEOA compound also acted as a ligand to separate Fe(III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) ions by transporting liquid membrane method [7].

Meanwhile, Poly(ethyl eugenyl oxyacetate) or PEEOA had been applied as a ligand to separate the Fe(III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) ions using solvent extraction method [8]. The use of PEEOA as an ion carrier through liquid membrane transport for metal ions separation has not been reported. In this study, the performance of PEEOA was tested to separate Fe(III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) ions using the liquid membrane transport method for seeking of a macromolecular compound with good separability and selectivity. The transported propensity of the targeted ion is generally carried out separately. However, this study was conducted in a solution with the presence of interfering ions to adjust the actual condition in the water

environment. Investigations were carried out to analyze optimum pH, carrier/PEEOA volume, stripping concentration, transport time, and concentration of metal ions. In addition, the effectiveness of separating Fe and Ni ions in ferronickel samples was also analyzed.

## ■ EXPERIMENTAL SECTION

### Materials

The materials used in this study are chloroform (Merck), NaOH (Merck), HCl (Merck), HNO<sub>3</sub> (Merck), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck), Cr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Merck), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Merck), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Merck), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (Merck), Pb(NO<sub>3</sub>)<sub>2</sub> (Merck), demineralization water, and poly(ethyl eugenyl oxyacetate) or PEEOA. PEEOA was synthesized from a chemical reaction between polyeugenol and ethyl chloroacetate based on our previous study [8]. Structure characterizations had also conducted in that study. The structure of the PEEOA is displayed in Fig. 1.

### Procedure

#### **Transport of Fe(III), Cr(III), Ni(II), Co(II), Cu(II), and Pb(II) ions with PEEOA**

The numbers of U tubes were filled with 7.5 mL of PEEOA with a concentration of 0.001 M in chloroform. Then, 10 mL of metal ion solutions were added to a side of the U tube as a source phase with a concentration of 0.1 mM in various pH (3, 4, and 5). Furthermore, as a stripping phase, 10 mL of HNO<sub>3</sub> 1 M solution was poured on another side. U tube was closed and stirred with a magnetic stirrer for 24 h at room temperature. After completing the transport process, the solution on

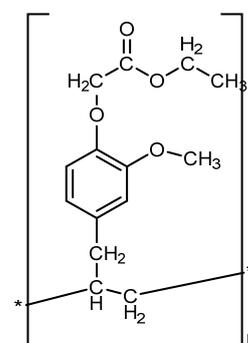


Fig 1. The structure of the PEEOA ion carrier

both sides of the U pipe was separated using a pipette. The concentration of metal ions in the source and stripping phases were analyzed using AAS. The optimum pH was used to optimize the ion carrier volume (7.5, 8.5, and 10 mL), the stripping concentration (0.5, 1, 2, and 4 M), transport time (12, 24, 36, and 48 h), and metal ion concentration (0.075, 0.1, 0.25, 0.5 mM). Transported efficiency or transport percent is calculated based on Eq. (1) as follows.

$$\%T = \frac{C_{Y,S}}{C_{Y,F}} \times 100 \quad (1)$$

where %T is transport percent,  $C_{Y,S}$  is metal ion concentration on the stripping/targeted phase (mM), and  $C_{Y,F}$  is the initial metal ion concentration in the source phase (mM).

### Preparation of ferronickel samples

The ferronickel sample (0.16 g) was dissolved in 5 mL aqua regia (a mixture of concentrated HCl and HNO<sub>3</sub>, 3:1) heated for 1 h. Then, the solution was moved to a room-temperature environment. After that, it was diluted with demineralization water up to 25 mL. The procedure of liquid membrane transport for Fe and Ni ions separation was similar to the treatment of pure metals. Fe and Ni contents before and after transport were measured by Atomic Absorption Spectrometer (AAS) Perkin Elmer 3110.

## RESULTS AND DISCUSSION

PEEOA is a relatively neutral compound. This study uses it as an ion carrier to separate metal ions by liquid membrane transport. Complexation processes occur by forming a neutral complex with metal ions ( $M^{n+}$ ) and anions ( $X^-$ ) in the source phase. This separation takes place by symport mechanism. The transport force in the symport mechanism is the difference in metal ion concentration between the source and the stripping phases. Symport transport mechanism is more effective for metal ions in the form of  $M^+$  and  $X^-$  with neutral ion carriers (I). The Symport mechanism between PEEOA ions carrier and the metal cation is displayed in Fig. 2.

### Transport Parameters with PEEOA as Ions Carrier

The value of the transport percent was calculated from the change in the amount of transported metal ions

that pass the membrane phase and the stripping phase. The performance of PEEOA ions to optimally separate Fe(III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) ions using liquid membrane transport is affected by several parameters as follows.

### Effect of pH

The separation of metal ions using PEEOA as ions carrier through the liquid membrane transport method is related to its capability for accommodating metal ions via interactions with lone pair of electrons on the ester groups. Adjusting pH in the source phase will precisely generate selectivity, and the transport process will take place properly [9]. The influence of pH values on the transport percents is displayed in Fig. 3.

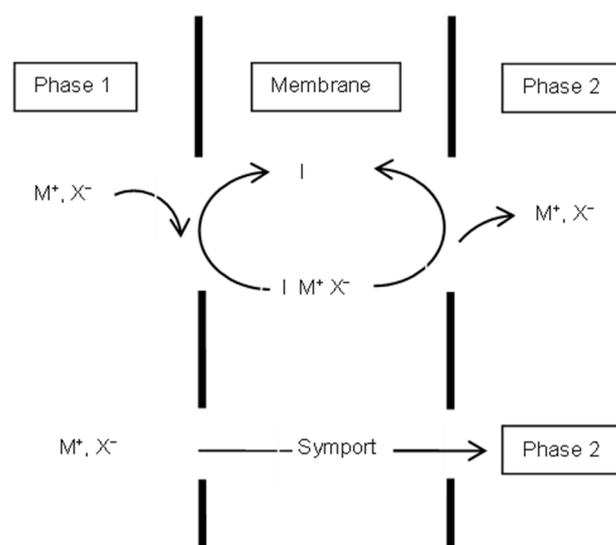


Fig 2. Transport mechanism of cation symport

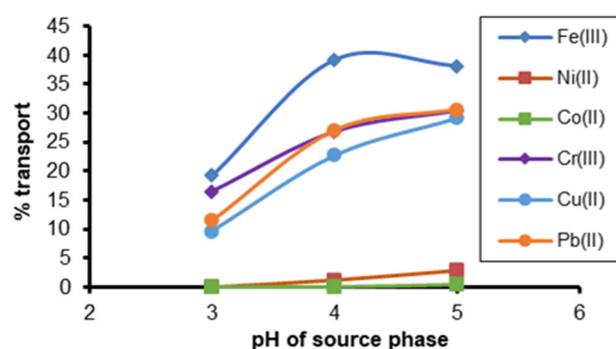


Fig 3. The relationship between the pH variations of the source phase and the transport percent at 0.1 mM of metal ion concentrations, 1 M of HNO<sub>3</sub>, 1 mM of ion carrier concentration, and 36 h of transport time

Fig. 3 shows that the increase in pH generates the increment in the transport percent of metal ions from the source phase to the stripping phase through the membrane containing ion carriers. The highest percentage for transporting Fe(III) ions was 39.20% at pH 4. Then, it decreased at pH 5. This is probably caused by hydrolysis or precipitation of Fe(III) ions. Thus, the number of complexes between PEEOA and metal ions also becomes lower [8]. At pH 3, there is competition between Fe(III) ions with hydrogen ions. Optimum transport percents for Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) are 30.36%, 29.22%, 2.95%, 0.54%, and 30.57%, respectively. These occur at pH 5. In this condition, all metal ions are still predominantly in the ionic state, for instance, Cr(III) as  $\text{Cr}^{3+}$ ,  $\text{Cr}(\text{OH})^{2+}$ , and  $\text{Cr}(\text{OH})_2^+$ , Co(II) as  $\text{Co}^{2+}$ , Ni(II) as  $\text{Ni}^{2+}$ , Cu(II) as  $\text{Cu}^{2+}$ , and Pb(II) as  $\text{Pb}^{2+}$  when form complexes with PEEOA. Those metal ions tend to settle at higher pH [10].

#### Effect of PEEOA volume

The volume of PEEOA in organic solution will affect the number of moles of metal ions as well as the transport percent from the source phase to the stripping phase, as shown in Fig. 4.

Fig. 4 shows that increasing the volume of PEEOA in the organic phase will increase the amount of transported Fe(III) ions at 7.5 and 8.5 mL but decrease at 10 mL. Meanwhile, the optimum PEEOA volume for transporting other metal ions is 7.5 mL. The increasing volume of ions carrier will increase flux and permeability on the liquid membrane [11-12]. Hence, complex formation at the membrane interface is accelerated and increased. After that, it will be extracted to the stripping phase. Further addition of PEEOA volume even increases the thickness (viscosity) and the obstacle of the membrane. Thus, the transport percent of metal ions can decrease due to reducing ion activities at the membrane interface [10,13].

#### Effect of stripping phase concentration ( $\text{HNO}_3$ )

The effect of the stripping phase concentration in the liquid membrane transport was analyzed by varying the concentration of  $\text{HNO}_3$  at ranges of 0.5, 1.0, 2.0, and 4.0 M. It was carried out at the optimum pH and PEEOA

volume. The results show that the concentrations of the stripping phase affect transport percents (% transport), as shown in Fig. 5.

Fig. 5 shows that the optimum transport percent of Fe(III) ions is 43.25% when  $\text{HNO}_3$  concentration is 2 M. While the transport percents of Cr(III), Ni(II), and Co(II) ions are optimum at 1.0 M  $\text{HNO}_3$  with the values 33.42%, 6.87%, and 5.98%, respectively. Then, the optimum transport percents of Pb(II) and Cu(II) ions are 32.24% and 30.15% when the stripping concentration is 0.5 M. The increase in  $\text{HNO}_3$  concentration until optimum concentration produces more hydrogen ions in the solution. These ions can break the complex formed at the interface of the membrane-stripping phase [14].

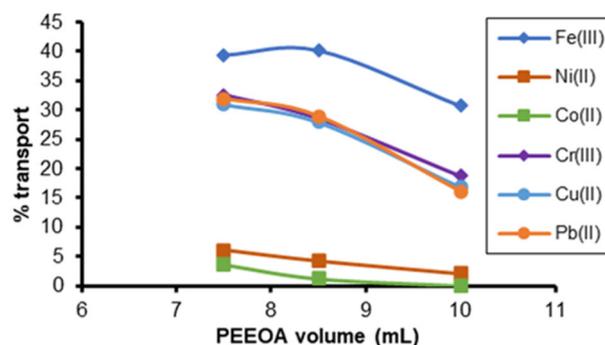


Fig 4. The influence of PEEOA volume on the transport percent at optimum pH, 0.1 mM of metal ion concentrations, 1 M of  $\text{HNO}_3$ , 1 mM of ion carrier concentration, and 36 h of transport time

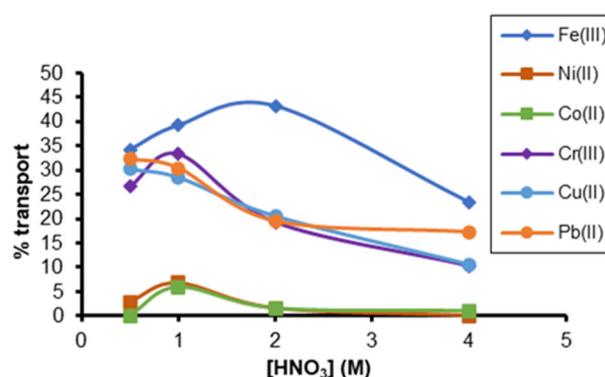


Fig 5. The influence of  $\text{HNO}_3$  concentration on the transport percent (% transport) of metal ions at optimum pH and PEEOA volume, 0.1 mM of metal ion concentrations, 1 mM of ion carrier concentration, and 36 h of transport time

Therefore, ion carriers will return to the membrane-source phase to form complexes faster with metal ions [15]. However, hydrogen ions are significantly increased in the stripping solution after optimum conditions. Thus, the decomplexation process is more challenging to break because the process of releasing cation salts at the membrane-acceptor interface is obstructed. It will decrease the transport percent of metal ions to the stripping phase.

This analysis also informs a larger size of the metal ion needs a lower concentration of the HNO<sub>3</sub> solution. It is probably due to the large metal ion size at the Pb(II) and Cu(II) metal ions having greater decomplexation barriers at the membrane-acceptor interface. Table 1 displays bond energy data from computational simulation between metal ions and PEEOA. It informs that the charge and molecular size of the metal ion also affect the number of metal ions transported.

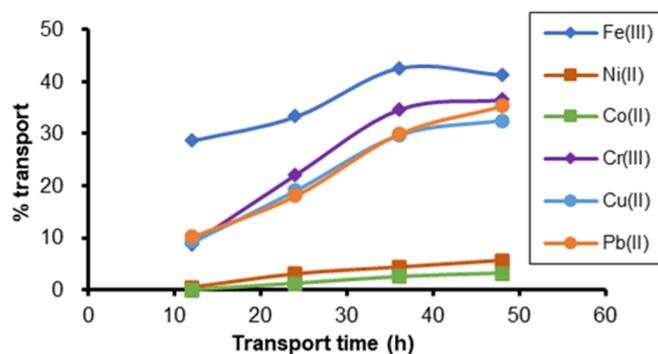
Table 1 shows that the Fe(III) ion has the highest metallic bonding energy, whereas the Pb(II) ion has the lowest energy. Computational simulation results for the reaction between the metal ions and PEEOA show that the highest bonding energy occurs between PEEOA and Cr(III) ions and the lowest bonding energy involves bonds between PEEOA and Co(II) ions. A different phenomenon occurs in Pb(II) ions with PEEOA. There is no stable bond structure between those species. Thus, theoretically, the Pb(II) ion will have a relatively more minor amount transported compared to the other tested metal ions. However, in reality, the transport percent of Pb(II) ions is higher than the Ni(II), Cu(II), and Co(II) ions. Several reasons may cause this. First, the Pb<sup>2+</sup> ion with a larger ion size will be polarized to the PEEOA ion carrier. Hence, it is easier to escape in the stripping phase;

second, small ions will have more water molecules in the hydration layer/cavities than large ions. Meanwhile, the adequate size of the hydrated ion in solution at the larger metal ion size will be small. As a result, the number of Pb(II) ions that may bind to PEEOA is higher; third, this relates to the size conformity between Pb(II) ions and PEEOA for interacting.

### Effect of transport time

The transported rate of metal ions in the liquid membrane was measured by analysis of the transport process at various transport periods from 12, 24, 36, and up to 48 h under optimum pH, PEEOA concentration, and stripping concentration. This parameter also affects the transport percent of metal ions from the source phase to the stripping phase [16]. The results of this analysis are shown in Fig. 6.

Fig. 6 shows that an increase in the transport period will increase the metal ions transported from the



**Fig 6.** The influence of transport time on the transport percent of metal ions at optimum pH, PEEOA volume, and HNO<sub>3</sub> concentration, 0.1 mM of metal ion concentrations, 1 mM of ion carrier concentration, and 36 h of transport time

**Table 1.** Bond energy data from computational simulation between PEEOA and metal ions

No	Bond energy (kcal/mol)		
	Metal ion	PEEOA	PEEOA + metal ion
1	Fe(III)	1811.814	-10609.391
2	Cr(III)	1708.821	-14282.659
3	Ni(II)	1218.846	-10645.808
4	Co(II)	817.319	-10840.483
5	Cu(II)	887.024	-10619.235
6	Pb(II)	457.357	-

-: Cannot be determined

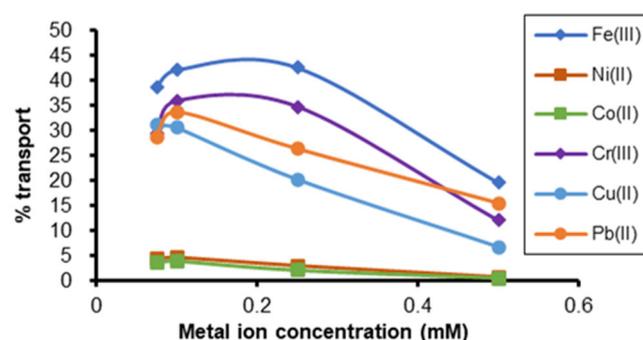
source phase to the stripping phase. This corresponds to the longer contact time between the PEEOA and the metal ion. The metal ions from the aqueous phase can form complexes at the interface of the aqueous phase and membrane phase, which will then be transported to the stripping or target phase. After passing optimum time, complexes slowly form because the equilibrium condition is almost reached [2].

The Fe(III) ion has an optimum transport time of 36 h, while the optimum transport time of Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) ions is over 36 h. The formation rate of complex Fe(III) ions with PEEOA is faster. Fe(III) ions have higher reactivity, greater polarity, and smaller ionic radius to support complex formation with PEEOA ions. Thus, the transport time to the target phase is faster than other metal ions. In addition, there is a compatibility between the cavity size of carrier ions and the Fe(III) ions compared to other tested metal ions.

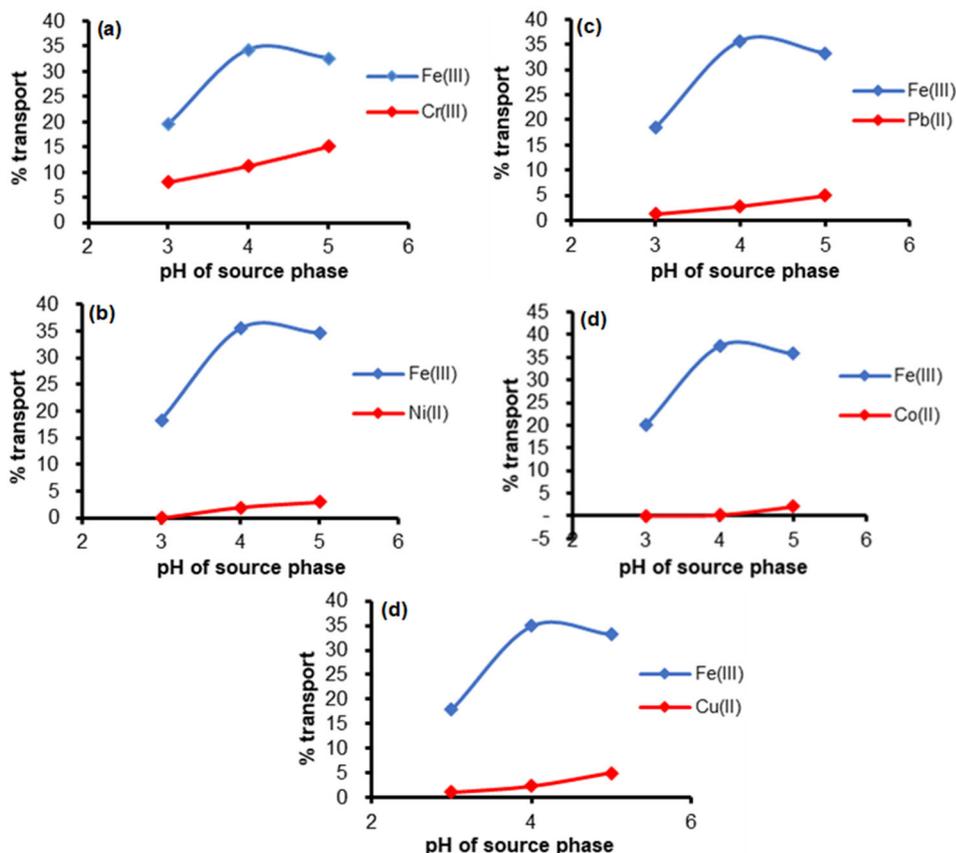
### Effect of metal ion concentration

This analysis applied optimum pH, PEEOA volume, stripping concentration, and transport time from each metal ion which is displayed in Fig. 7.

Fig. 7 informs that the Fe(III) and Cu(II) ions are



**Fig 7.** Effect of metal ion concentration (0.075, 0.1, 0.25, and 0.5 mM) on source phase to transport percent at optimum pH, PEEOA volume, HNO<sub>3</sub> concentration, and transport time



**Fig 8.** The effect of pH on transport percent in a mixture of Fe(III) + Cr(III) (a), Fe(III) + Ni(II) (b), Fe(III) + Pb(II) (c), Fe(III) + Co(II) (d), and Fe(III) + Cu(II) (e). Metal ion concentration was 0.1 mM, [HNO<sub>3</sub>] = 2 M, ion carrier volume and concentration = 8.5 mL and 0.001 M, and transport time = 36 h

optimally transported at a concentration of 0.25 and 0.075 mM, respectively. The transport percentages are 42.64 and 31.20%. Meanwhile, the optimum concentration of Cr(III), Ni(II), Co(II), and Pb(II) ions is 0.1 mM with transport percents of 35.91, 4.74, 3.96, and 33.73%, respectively. Increasing metal ion concentration increases the number of metal ions transported in the target phase first. However, it even decreases above optimum concentration because equilibrium conditions have been reached [14]. In this condition, PEEOA cannot accommodate metal ions for the further transport process. The increase of metal ion concentration in solution after optimum conditions will reduce the diffusion permeability in the membrane [17].

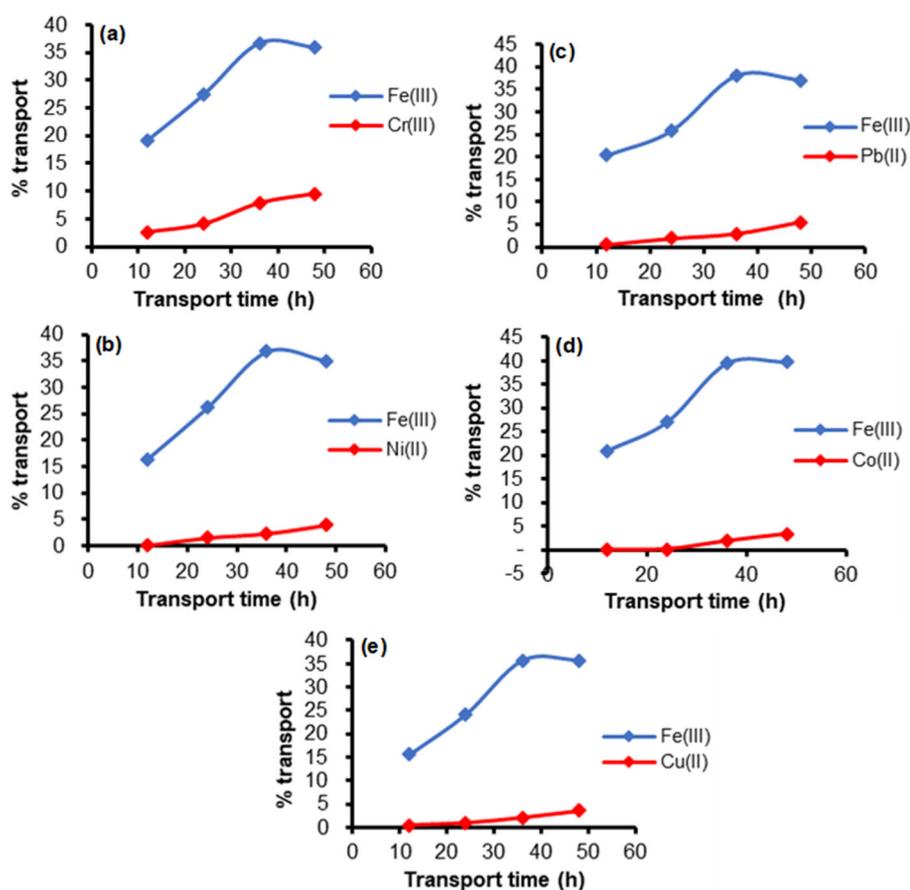
### Transport Competitions of Metal Ions

The selectivity and reactivity of PEEOA as Fe(III),

Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) ions carrier were analyzed from the mixture of two, three, and all-metal ions. Based on the optimization results of each metal ion separately, the Fe(III) ion has the best transport percent compared to the other tested metal ions. Therefore, Fe(III) ion was used as the main ion in the competition tests of metal transport.

### Competition of Two Metals

These experiments compete Fe(III) ions with other metal ions that were conducted in various pH and transport times. The percent transport of metal ions depends on the type of metal ion and the used ion carrier [18]. Several simulations consist of Fe(III)-Cr(III), Fe(III)-Pb(II), Fe(III)-Ni(II), Fe(III)-Co(II), and Fe(III)-Cu(II). The amount of transported metal ions in various pH is presented in Fig. 8.



**Fig 9.** The effect of transport time on the transport percent in a mixture of Fe(III) + Cr(III) (a), Fe(III) + Ni(II) (b), Fe(III) + Pb(II) (c), Fe(III) + Co(II) (d), and Fe(III) + Cu(II) (e). Metal ion concentration = 0.1 mM,  $[\text{HNO}_3] = 2 \text{ M}$ , ion carrier volume and concentration = 8.5 mL and 0.001 M, and transport time = 36 h

Fig. 8 shows that the presence of other metal ions in the solution sufficiently disrupts the ability of Fe(III) ions to be transported. The optimum condition for transporting Fe(III) ions occurs at pH 4 for all combinations. The amount of Fe(III) ions transported varies depending on the metal ion pair in the solution. The smallest percentage (34.26%) of transported Fe(III) ions occurred in the mixture of Fe(III) and Cr(III) ions. This is related to the acidity and polarity of Cr(III), which is almost identical to the Fe(III) ion. Thus, the ability to form complexes is also similar. Meanwhile, the velocity of each metal ion transported to the stripping phase in a mixture of two metal ions can be determined by variations of transport time using the optimum pH for Fe(III) ions transport. The results are shown in Fig. 9.

Fig. 9 shows that the increase in the transport time is accompanied by an increase in the transport percent of metal ions. This relates to the number of contacts between the metal ions in the source phase and the ion carriers at the membrane phase through the interface area. Then, complexes were formed. After that, these complexes diffuse across the membrane and are removed at the stripping phase. The presence of other ions as interference in the Fe(III) ion solution also affects the decrease in transport percent of Fe(III) ion in the stripping phase. The

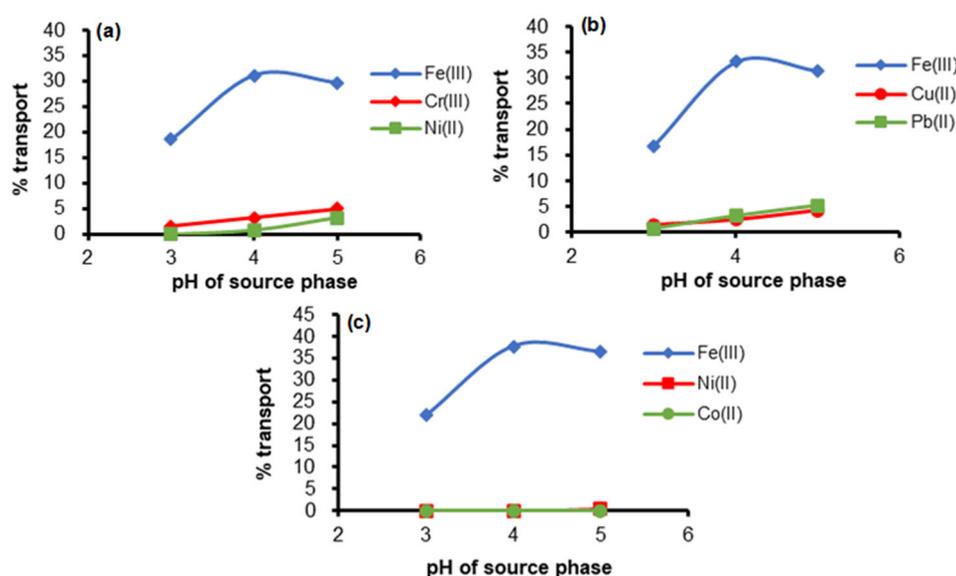
reduction of this transport percent is related to some active groups in the membrane phase forming complexes with interference ions [19].

### Three Metals Competition

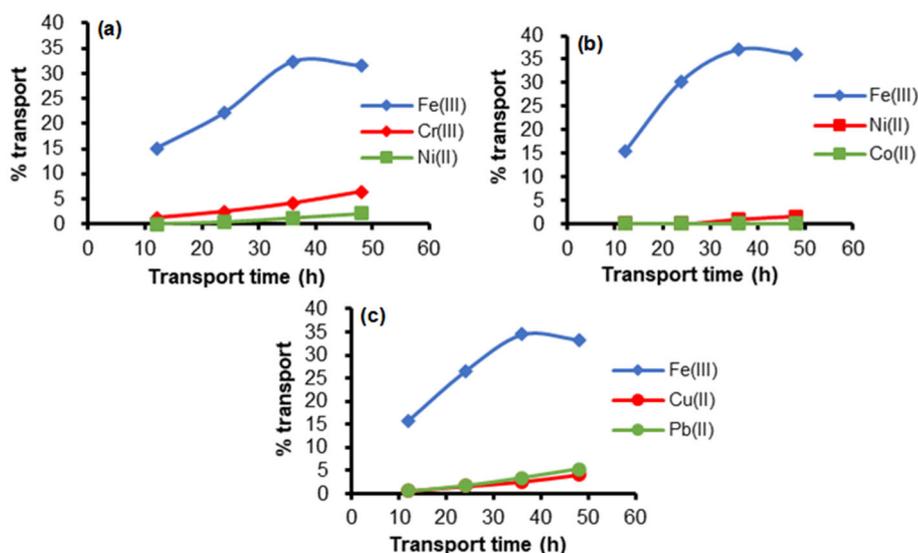
A competition analysis of three metals was carried out for three mixtures. It consists of Fe(III)-Cr(III)-Ni(II), Fe(III)-Cu(II)-Pb(II), and Fe(III)-Ni(II)-Co(II). The transport percents of Fe(III) ions in the stripping phase that are influenced by pH are shown in Fig. 10.

Fig. 10 shows the three types of simulated metal ions. The optimum Fe(III) ion transport percent occurred at pH 4. The most significant disturbance for transporting Fe(III) ions was found in the Fe(III)-Cr(III)-Ni(II) mixture. Cr(III) ions which are classified as hard acids, almost have similar acidity to Fe(III) ions which inflicts competition for complex formations. Besides that, increasing the number of metal ions will require more active sites to complex all metal ions in solution, while the number of active sites does not change. Therefore, the active site has a limited ability to complex all metal ions in solution.

Furthermore, competition of three metals in a system can retard the transport process of all metal ions, including Fe(III) ions. Fig. 11 shows that Fe(III) ions act



**Fig 10.** Transport percent of the system contained three metal ions in various pH. Fe(III) + Cr(III) + Ni(II) (a), Fe(III) + Cu(II) + Pb(II) (b), Fe(III) + Ni(II) + Co(II) (c). Metal ion concentration = 0.1 mM,  $[\text{HNO}_3]$  = 2 M, ion carrier volume and concentration = 8.5 mL and 0.001 M, and transport time = 36 h



**Fig 11.** Transport percent of the system contained three metals in various transport times. Fe(III) + Cr(III) + Ni(II) (a), Fe(III) + Ni(II) + Co(II) (b), Fe(III) + Cu(II) + Pb(II) (c). Metal ion concentration = 0.1 mM,  $[\text{HNO}_3] = 2 \text{ M}$ , ion carrier volume and concentration = 8.5 mL and 0.001 M

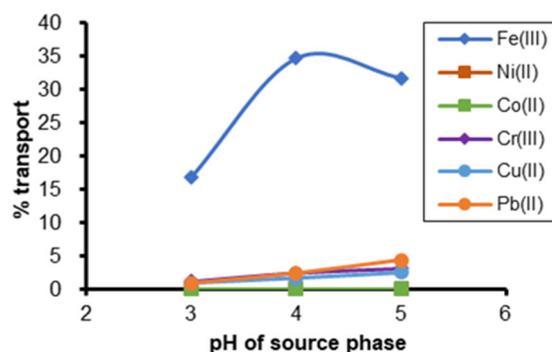
as the primary ion, while other metal ions act as interference. Adding metal ions in the source phase can reduce the number of transported Fe(III) ions in the stripping phase.

### All Tested Metal Ion Competition

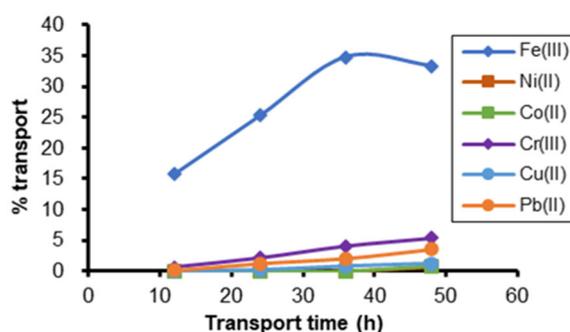
Competition of all tested metal ions was also conducted in optimum pH and transport time. The transport percents of each ion in the mixture at various pH are shown in Fig. 12.

Fig. 12 shows that the optimum conditions for Fe(III) metal ions in the mixture occurred at pH 4. This condition is similar to the system with two and three metal ions but has a lower transport percent. The presence of six metal ions will increase the viscosity of the solution and the concentration polarization. Thus, the activity of each metal ion is limited. As a result, the flux of ions in the ion-carrying solution is reduced [20]. In addition, the limited ion-carrying active site inflicts not all metal ions in the solution forming a complex. The ions' speed can be described by varying the transport time. The transport percent of each ion using PEEOA in different transport times is presented in Fig. 13.

Fig.13 shows that increasing the transport times increases the number of metal ions transported even though the percentage of each metal ion decreases with the



**Fig 12.** The effect of pH on the transport percent in the system contained all tested metals



**Fig 13.** The effect of transport time on the transport percent in the system contained all tested metals

increasing the number of metal ions in the mixture. The expanding number of metal ions in the mixed solution decreases the activity of each metal ion. In this

condition, the number of active sites carrying ions remains, whereas the number of metal ions increases. Consequently, not all metal ions in the solution form complexes such as Ni(II) and Co(II) ions. Besides that, the transport percent of Pb(II) ion also significantly decreased after being in the mixture of metal. This probably relates to the size of Pb(II) ions which are relatively larger than other metal ions. As a result, its ability to form complexes with ion carriers reduces due to competition among metal ions in the solution. The presence of other metal ions in a solution containing Fe(III) ions (two, three, and a mixture of all tested metal ions) did not change the selectivity for the Fe(III) ion. But, it only reduced the amount of transported Fe(III) ions in the stripping phase.

#### Separation of Fe Ion from Ni Ion in Ferronickel Sample

In this study, PEEOA was also tested on a ferronickel sample from PT Aneka Tambang Pomalaa, Kolaka, Southeast Sulawesi. The main content of this ferronickel is Fe and Ni. It also contains chromium, cobalt, and some anions such as sulfide and phosphate.

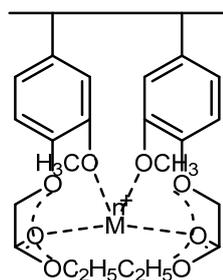
The experiment was conducted to separate Fe(III) and Ni(II) ions in the ferronickel sample using a liquid

membrane transport method under optimum conditions for transporting Fe(III) ions. The solution used was prepared from ferronickel concentrate, which has been diluted 50, 100, and 200 times respectively. The concentration of the ion carrier is 0.001 mM at pH 4. Then, ion carrier volume, stripping concentration, and transport time are 8.5 mL, 2.0 M, and 36 h, respectively. The transport efficiencies of the Fe(III) and Ni(II) ions before and after the transport process are presented in Table 2.

Table 2 shows that separating iron and nickel from ferronickel at different concentrations using PEEOA ion carriers with a concentration of 0.001 mM also has different transportability. A higher concentration of iron and nickel in ferronickel reduces the ability of PEEOA to transport Fe(III), while the Ni(II) ion is not transported for all concentrations. Concentrations of Fe(III) and Ni(II) ions in the stripping phase reduce compared to pure metals due to the presence of other ions as the mixtures in the ferronickel sample. The presence of phosphate and sulfur in ferronickel will compete with PEEOA ion carriers to bind Fe(III) or Ni(II) ions. Reactivity parameters explain phosphate is more reactive compared to PEEOA. Thus, it will reduce the ability of PEEOA to form complexes with Fe(III) and Ni(II) ions.

**Table 2.** The transport efficiency of liquid membrane on the separation of Fe and Ni from ferronickel concentrate using PEEOA as ion carrier

Metal ion	Concentration in source phase before transported ( $\times 10^{-4}$ M)	Concentration in source phase (Cfs) after transported ( $\times 10^{-4}$ M)	Concentration in the stripping phase (Cfp) after transport ( $\times 10^{-4}$ M)	% Cfs	% Cfp
Fe	4.93	4.42	0.09	89.76	1.79
	2.60	1.85	0.11	85.42	5.27
	1.26	1.03	0.11	81.63	8.87
Ni	3.80	3.49	0	91.87	0
	1.66	1.61	0	96.70	0
	1.04	0.99	0.01	95.55	0.92
Metal ion concentration after transported (blank)					
Fe	4.93	4.59	0.022	93.17	0.46
	2.16	2.10	0	97.08	0
	1.26	1.26	0	100	0
Ni	3.80	3.63	0	95.67	0
	1.66	1.61	0	96.91	0
	1.04	1.03	0	99.01	0



**Fig 14.** Approximation of complexed shape of PEEOA with metal ions (M = Fe(III), Cr(III), Ni(II), Co(II), Cu(II), and Pb(II) ions)

Separation of Fe(III) ion from Ni(II) ion in ferronickel using PEEOA shall be carried out at a ferronickel concentration of 0.126 mM for Fe(III) and 0.104 mM for Ni(II) (200 times of dilutions). Fe(III) and Ni(II) ions transport percentages are 8.87 and 0.92%, respectively. The ability of Fe(III) and Ni(II) to be transported in the stripping phase is affected by PEEOA as a carrier ion. This can be displayed from the experimental transport data with blanks or without ion carriers, but only using chloroform as a membrane phase that acts as an ion carrier. The results showed that both Fe(III) and Ni(II) ions are not transported in the stripping phase at all concentrations tested ( $\approx 0\%$ ). Complex formation between the metal ion and the PEEOA involves oxygen in the ether and carbonyl groups. Hence, the complex structure between the PEEOA and the metal ions is approximated in Fig. 14.

## ■ CONCLUSION

PEEOA has been used as an ions carrier to separate Fe(III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) ions by liquid membrane transport method. Besides that, it could also separate Fe and Ni in the ferronickel sample. The best conditions for separating Fe(III) ions were pH 4 (single, mixed metal ions, and ferronickel sample). Increasing the volume of the ion carrier up to 8.5 mL will increase the number of transported Fe(III) ions. Meanwhile, other metal ions have been optimum at 7.5 mL. Optimum stripping concentration ( $\text{HNO}_3$ ), transport time, and concentration of Fe(III) are 2 M, 36 h, and 0.075-0.25 mM, respectively. The order of metal selectivity is Fe(III) > Cr(III) > Pb(II) > Cu(II) > Ni(II) > Co(II). This

propensity was almost similar to the extraction method. However, the transport percentages of metals are relatively lower than the extraction percentages in the solvent extraction method. Complex formations between Fe(III) ions and PEEOA in the transport process occur through interactions among oxygen atoms in the ether and carbonyl groups.

## ■ REFERENCES

- [1] Minhas, F.T., Memon, S., Qureshi, I., Mujahid, M., and Bhanger, M.I., 2013, Facilitated kinetic transport of Cu(II) through a supported liquid membrane with calix[4]arene as a carrier, *C. R. Chim.*, 16 (8), 742–751.
- [2] Cay, S., Sayin, S., and Engin, M.S., 2020, Calix[4]arene embedded polyamide supported liquid membrane for separation of heavy metals from aqueous solutions, *Turk. J. Agric. Food Sci. Technol.*, 8 (2), 387–391.
- [3] El Batouti, M., Al-Harby, N.F., and Elewa, M.M., 2021, A review on promising membrane technology approaches for heavy metal removal from water and wastewater to solve water crisis, *Water*, 13 (22), 3241.
- [4] Parhi, P.K., 2013, Supported liquid membrane principle and its practices: A short review, *J. Chem.*, 2013, 618236.
- [5] Nguyen, B.N.T., Thoburn, J.D., Grommet, A.B., Howe, D.J., Ronson, T.K., Ryan, H.P., Bolliger, J.L., and Nitschke, J.R., 2021, Coordination cages selectively transport molecular cargoes across liquid membranes, *J. Am. Chem. Soc.*, 143 (31), 12175–12180.
- [6] Harimu, L., Matsjeh, S., Siswanta, D., and Santosa, S.J., 2009, Synthesis Polieugenyl oxiacetic acid as a carrier to separate heavy metal ion Fe(III), Cr(III), Cu(II), Ni(II), Co(II) and Pb(II) using the extraction method, *Indones. J. Chem.*, 9 (2), 261–266.
- [7] Harimu, L., Matsjeh, S., Siswanta, D., and Santosa, S.J., 2010, Separation of Fe(III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) metal ions using poly(eugenyl oxyacetic acid) as an ion carrier by a

- liquid membrane transport method, *Indones. J. Chem.*, 10 (1), 69–74.
- [8] Harimu, L., Matsjeh, S., Siswanta, D., Santosa, S.J., and Sutapa, I.W., 2019, Synthesis of poly(ethyl eugenyl oxyacetate) as carrier for separation of heavy metal ions Fe(III), Cr(III), Cu(II), Ni(II), Co(II), and Pb(II) using liquid-liquid extraction method, *J. Phys.: Conf. Ser.*, 1341, 032003.
- [9] Arous, O., Saoud, F., Amara, M., and Kerdjoudj, H., 2011, Efficient facilitated transport of lead and cadmium across a plasticized triacetate membrane mediated by D2EHPA and TOPO, *Mater. Sci. Appl.*, 2 (6), 615–623.
- [10] Amini, M., Rahbar-Kelishami, A., Alipour, M., and Vahidi, O., 2018, Supported liquid membrane in metal ion separation: An overview, *J. Membr. Sci. Res.*, 4 (3), 121–135.
- [11] Ferencz, A., Grosu, A.R., Al-Ani, H.N.A., Nechifor, A.C., Tanczos, S.K., Albu, P.C., Crăciun, M.E., Ioan, M.R., Grosu, V.A., and Nechifor, G., 2022, Operational limits of the bulk hybrid liquid membranes based on dispersion systems, *Membranes*, 12 (2), 190.
- [12] Abejón, R., Rabadán, J., Garea, A., and Irabien, A., 2020, Comparison of supported ionic liquid membranes and polymeric ultrafiltration and nanofiltration membranes for separation of lignin and monosaccharides, *Membranes*, 10 (2), 29.
- [13] Mohebbi, S., Nazari, M., Rahbar-Kelishami, A., and Davoodi-Nasab, P., 2017, Performance of sunflower oil as green solvent for Cr(VI) extraction using supported liquid membrane, *Desalin. Water Treat.*, 64, 173–178.
- [14] Mirea, C.M., Diaconu, I., Ruse, E., Serban, E.A., Clej, D.D., Popa, G.A., Popa, D.F., and Nechifor, G., 2016, The removal of heavy metals using the bulk liquid membrane technique, *Prog. Cryog. Isot. Sep.*, 19 (1), 45–54.
- [15] Alguacil, F.J., 2019, Facilitated chromium(VI) transport across an ionic liquid membrane impregnated with Cyphos IL102, *Molecules*, 24 (13), 2437.
- [16] Manikandan, G.N., Bogeshwaran, K., Jamuna, P., and Sandhya, S., 2014, A review on emulsion liquid membranes on heavy metal separation, *Int. J. ChemTech Res.*, 6 (9), 4328–4332.
- [17] Albaraka, Z., 2019, Use of D2EHPA-mediated liquid membranes for heavy metal ions separation: A review, *Rev. Roum. Chim.*, 64 (2), 113–124.
- [18] Verma, B., Balomajumder, C., Sabapathy, M., and Gumfekar, S.P., 2021, Pressure-driven membrane process: A review of advanced technique for heavy metals remediation, *Processes*, 9 (5), 752.
- [19] Gubari, M.Q., Abdulkarim, A.A., and Alekseeva, N.V., 2021, Diffusion permeability of cation-exchange membrane in different solutions, *J. Ecol. Eng.*, 22 (8), 140–145.
- [20] Nielen, W.M., Willott, J.D., Galicia, J.A.R., and de Vos, W.M., 2021, Effect of solution viscosity on the precipitation of PSaMA in aqueous phase separation-based membrane formation, *Polymers*, 13 (11), 1775.