

Selective separation of cadmium(II), copper(II) and nickel(II) ions from electroplating wastewater using dual flat sheet supported liquid membrane

Lai Yee Lee, Norhashimah Morad, Norli Ismail, Mohd Rafatullah*

School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia, Tel. +60 4653 2111; Fax: +60 4653 6375; emails: mrafatullah@usm.my/mohd_rafatullah@yahoo.co.in (M. Rafatullah), lly15_tec003@student.usm.my (L.Y. Lee), nhashima@usm.my (N. Morad), norlii@usm.my (N. Ismail)

Received 6 October 2020; Accepted 22 February 2021

ABSTRACT

A dual flat sheet supported liquid membrane (DFSSLM) system was developed based on concurrent extraction, selective separation, and recovery of three metal ions from a mixture in a single process. DFSSLM was made up of a combination of two membranes and three compartments (feed, intermediate and strip) to selectively recover not just one but three types of metal ions at the end of the system. This research aims to study the efficiency of DFSSLM in the selective extraction of cadmium(II) and copper(II) over nickel(II) ions from an aqueous mixture and electroplating wastewater. The first membrane was impregnated with 100 mM di-(2-ethylhexyl)phosphoric acid and 50 mM tributyl phosphate in kerosene, whereas the second membrane was impregnated with 99.64 mM trioctylmethylammonium chloride and 50 mM tributyl phosphate in toluene. After continuous stirring (500 rpm) in all compartments for 48 h, 98.79% of nickel(II) was recovered from the synthetic mixture in feed, 91.32% of copper(II) in intermediate, and 91.04% of cadmium(II) in strip compartment. The flux changes and kinetic studies showed cadmium(II) was preferentially transported over copper(II). The membranes (polymer and extractants) were characterized by Fourier transform infrared spectroscopy and scanning electron microscopy with an energy-dispersive X-ray. In comparison with the treatment of real electroplating effluent, high output/input ratios were obtained for recovered cadmium(II), copper(II) and nickel(II). Most of the other heavy metals were eliminated together with the recovery of 89.09% of cadmium(II) in the strip, 90.87% of copper(II) in intermediate, and 97.61% of nickel(II) in the feed. This study concluded that DFSSLM is efficient for the separation and recovery of cadmium(II), copper(II) and nickel(II) from a complex mixture.

Keywords: Heavy metals; Electroplating effluent; Permeation flux; Selective separation; Supported liquid membrane; Metal recovery

1. Introduction

Electroplating involves using electric currents to deploy electrodeposition to form metallic coatings onto solid substrates to improve their properties, appearance, and durability. Electroplating the solid substrates is done via several water-based solutions containing various chemicals for cleaning, deoxidization, and coating. A huge quantity of water accompanies each succeeding process for rinsing and removing chemicals before each processing step. As a result,

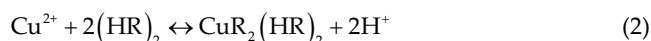
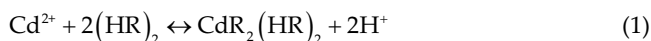
the wastewater produced from washing out the mixtures and massive discharge of used acids usually has a large mass of diffused metallic ions, especially chromium, cadmium, copper, nickel, iron and zinc ions [1]. It is critical to safeguard the environment from heavy metal pollution whilst taking steps to either recoup a part or all of these metals to the process cycle's starting point.

Treating the complex mixture with diverse metals is a complex process due to each waste batch's varying metallic content. As a rule of thumb during the selective extraction

* Corresponding author.

operations, only the precious metals of interest are targeted and recovered whilst ensuring the irrelevant ones are excluded. While this technique of concurrent separation and recovery of heavy metal ions has been dominant in laboratory-scale investigations, it has not progressed towards practical application [2,3]. The solvent extraction technique for removing heavy metals is not economical due to the large consumption of solvent, chemicals, and space. For this study, the supported liquid membrane (SLM) system is highlighted as it gives a broader scope of application that involves a single process of concurrently extracting and stripping metals. SLM is studied widely in whereby immiscible liquid is impregnated in the hydrophobic microporous membrane for the removal of heavy metals [4,5]. SLM also permits metal recovery using low solvent inventory and power utilization, requires less capital and operating cost, is simpler to operate, and easier to scale-up [6].

Di-(2-ethylhexyl)phosphoric acid (D2EHPA), a commercially available cationic extractant has been extensively used for its high loading capacity, high chemical stability and wide range versatility on the extraction of numerous metals such as cadmium(II) [7], chromium(III) [8], cobalt(II) [9], copper(II) [10], iron(III) [11] and zinc(II) [12]. Based on an earlier study [13], D2EHPA showed tangible results in separating cadmium(II) and copper(II) over nickel(II) with kerosene as a diluent and tributyl phosphate as phase modifier. Due to preferential transportation, most nickel(II) remained unextracted. Therefore, D2EHPA was selected as a selective extractant for cadmium(II) and copper(II) due to its high complexation and decomplexation ability. Dimers of D2EHPA, (HR)₂ go through a cation exchange mechanism that involves separating metal ions from aqueous solutions [10]. The pair of cadmium(II) and copper(II) form CdR₂(HR)₂ and CuR₂(HR)₂ complexes with molecules of dimeric D2EHPA as seen in Eqs. (1) and (2). These findings are similar to those reported by [14,15].



Triethylmethylammonium chloride, a water-insoluble quaternary ammonium salt composed of a large organic cation associated with a chloride ion, was brought into focus due to its stability and flexibility in working with aqueous solutions in both acidic and basic pH range [16]. In the search of an extractant to selectively extract cadmium(II) over copper(II), triethylmethylammonium chloride is one of the most widely-used extractants in SLM systems with excellent cadmium(II) extractability [17,18]. Based on the results from the previous study [19], using triethylmethylammonium chloride and tributyl phosphate jointly caused increases in the transport of cadmium(II) over copper(II). Tributyl phosphate showed a greater tendency to improve the separation between cadmium(II) and copper(II) than to enhance the transport efficiency of cadmium(II). The cadmium(II)-complex produced largely arose from reactions involving triethylmethylammonium chloride. Addition reaction mechanism by triethylmethylammonium chloride in the separation of cadmium(II)

was suggested as cadmium(II) was seen to extend its coordination numbers to bond with Cl in the quaternary amine [20]. The separation equilibrium of cadmium(II) out of the sulfate solution using triethylmethylammonium chloride (R₄NCl) is shown below in Eq. (3).



The extraction and separation of heavy metals are largely dependent on the extractant's selectivity properties. Based on their selectivity preferences, incorporation of different extractants onto multiple membranes as separation barriers creates a consolidated multi-compartment system for simultaneous separation of more than two heavy metals. For this research, a prominent SLM-based strategy was proposed to recover three types of metals simultaneously by using two semi-permeable support membranes as partitions to separate three compartments containing three different types of liquid phases. A similar compartmental SLM was applied for the simultaneous separation of copper, cobalt and nickel from ammonia/ammonium chloride solutions using two membranes impregnated with one type of extractant, Acorga M5640 [21]. To the best of our knowledge, there is no reported technique on the immobilization of different extractants into membranes to separate and recover three types of heavy metals. Inspired by the different behaviors of D2EHPA and triethylmethylammonium chloride in extracting cadmium(II), copper(II), and nickel(II), a dual flat sheet supported liquid membrane (DFSSLM) system was proposed. A DFSSLM cell with three compartments separated by two support membranes (immobilized with two different extractants) was designed to study its feasibility to preferentially separate cadmium(II) and copper(II) instead of nickel(II) from aqueous sulfate solution as well as real electroplating wastewater.

2. Materials and methods

2.1. Chemicals and reagents

The organic chemicals, D2EHPA ((C₈H₁₇O)₂POOH) (≥95% purity) from Merck, (Germany) and triethylmethylammonium chloride ([CH₃(CH₂)₆CH₂]₃N(Cl)CH₃) (≥99% purity) from Sigma-Aldrich, (Germany) were used as metal ions extractants. Tributyl phosphate ([CH₃(CH₂)₃O]₃PO) (≥99% purity) from Sigma-Aldrich, (Germany) was combined with organic extractants as phase modifier to prevent emulsification and to reduce third phase formation. The dilutions of concentrated D2EHPA and triethylmethylammonium chloride were performed using analytical grade kerosene and toluene from Sigma-Aldrich, (Germany), respectively. The choice of extractants, phase modifiers and diluents were made based on previous experimental studies [13,19].

The inorganic chemicals such as cadmium sulfate hydrate (CdSO₄·H₂O) (≥98% purity), copper sulfate pentahydrate (CuSO₄·5H₂O) (≥99.6% purity) and nickel sulfate hexahydrate (NiSO₄·6H₂O) (≥98% purity) were obtained from Merck, (Germany). Sodium sulfate (Na₂SO₄) (≥99% purity), sodium acetate (CH₃COONa) (≥99% purity), acetic acid (CH₃COOH) (≥99% purity), ethylenediaminetetraacetic acid (EDTA) (≥98% purity), sulfuric acid (H₂SO₄) (≥98%

purity), and sodium hydroxide (NaOH) ($\geq 99\%$ purity) were purchased from Merck, (Germany)

Calibration standards were prepared from single-element standards of 1,000 mg/L cadmium(II), copper(II) and nickel(II), respectively for atomic absorption spectroscopy analysis, TraceCERT® and multielement standard solution IV for inductively coupled plasma analysis, TraceCERT®, purchased from Merck, (Germany).

2.2. Preparation of aqueous and organic mixtures

Equal volumes of 500 mL of working solutions were fixed in each compartment (feed, intermediate and strip) of DFSSLM. The synthetic aqueous mixture in the first compartment (feed) containing 100 mg/L of cadmium(II), copper(II), and nickel(II) was prepared by dissolving the metal salts $\text{CdSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ with 200 mM Na_2SO_4 as inert salt in acetate buffer. To avoid a drastic change in pH in the feed compartment, 0.1 M CH_3COOH and 0.1 M CH_3COONa were used to prepare a 0.1 M acetate buffer solution of pH 4.5. In the second (intermediate) compartment, 1 M H_2SO_4 mixture was added while the third (strip) compartment was filled with 48.86 mM EDTA. The pH adjustment was conducted by adding several drops of 1 M of sulfuric acid (H_2SO_4) ($\geq 98\%$) and 1 M of sodium hydroxide (NaOH) ($\geq 99\%$).

Two types of organic mixtures (100 mM D2EHPA in kerosene and 99.64 mM trioctylmethylammonium chloride in toluene) of equal volumes were prepared to soak the support membranes, PVDF-1 and PVDF-2, respectively. Both organic mixtures were added with 50 mM tributyl phosphate as a phase modifier.

2.3. Preparation of support membranes

The DFSSLM system adopted hydrophobic PVDF membrane filters as its support membranes. PVDF-1 and PVDF-2 were soaked in organic mixtures for 24 h in a vacuum desiccator. Before placing the membranes between compartments of DFSSLM for extraction studies, these membranes were removed from the organic mixtures and left to drip to remove the excess organic mixtures. The physicochemical properties of the membrane filter are described in Table 1.

Table 1
Properties of support membrane used in this study

Properties	Description
Color	White
Surface	Plain
Diameter	90 mm
Thickness	125 μm
Pore size	0.22 μm
Wettability	Hydrophobic
Porosity	75%
Maximum operating temperature	85°C
Bubble point at 23°C	≥ 1.24 bar
Effective membrane surface area	50.27 cm^2

2.4. Instrumentation

Three overhead stirrers (IKA MICROSTAR 7.5 Control, Germany) were employed to stir the mixtures in each component of DFSSLM. A pH meter (Hach Sension+, Sweden) was used to measure the pH changes of the aqueous samples. For extraction studies using synthetic mixtures, concentrations of cadmium(II), copper(II), and nickel(II) ions were examined independently using a flame atomic absorption spectrophotometer FAAS, Shimadzu AA-7000, USA). Determination of metals concentration in real electroplating wastewater before and after DFSSLM studies were conducted using inductively coupled plasma-optical emission spectrometer (ICP-OES) (Perkin Elmer, Optima 7000 DV, USA). Scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) spectroscopy (FEI, Quanta™ 650 FEG, USA) was applied prior to and after the DFSSLM experiment to analyze surface morphology and elemental composition of the support membranes.

2.5. Collection of electroplating effluent

A sampling of effluent was conducted in an electroplating company at Bukit Minyak Industrial Park, Penang, Malaysia. Electroplating effluent was collected from a mixed effluent collection of multistage rinsing system. Effluent samples were transferred immediately into acid-washed 1 L polypropylene bottles. Samples were also collected in 1 L Teflon capped amber glass bottles for determination of oil and grease according to American Public Health Association (APHA) 5520 B method. The identification and analysis of samples were carried out after sampling. The physicochemical parameters such as temperature, pH and color were measured within the same day of sampling. The heavy metals content in the samples was determined by ICP-OES in accordance with APHA 3120 B method. All samples were stored and preserved in the refrigerator until further experimental studies were conducted.

2.6. Use of DFSSLM for separation of cadmium(II), copper(II) and nickel(II) ions

DFSSLM with support membranes PVDF-1 and PVDF-2 impregnated with D2EHPA and trioctylmethylammonium chloride, respectively, was used to study the preferential removal of cadmium(II), copper(II), and nickel(II) from synthetic feed mixture. Fig. 1 shows the DFSSLM setup used in the study. PVDF-1 and PVDF-2 were placed in between compartments, and then bolts were used to hold the corners tightly in place on the individual flange. Three cylindrical 500 mL DFSSLM cell compartments made from borosilicate glass were fabricated, and Teflon flanges were placed between the compartments. Borosilicate glass is preferred than acrylic counterpart because of its transparent nature and higher resistance to chemicals. Clamps and retort stands were used to support the DFSSLM cell.

2.7. Extraction efficiency of DFSSLM

Optimization of the extraction efficiency was observed for 48 h using DFSSLM. The contents of cadmium(II),

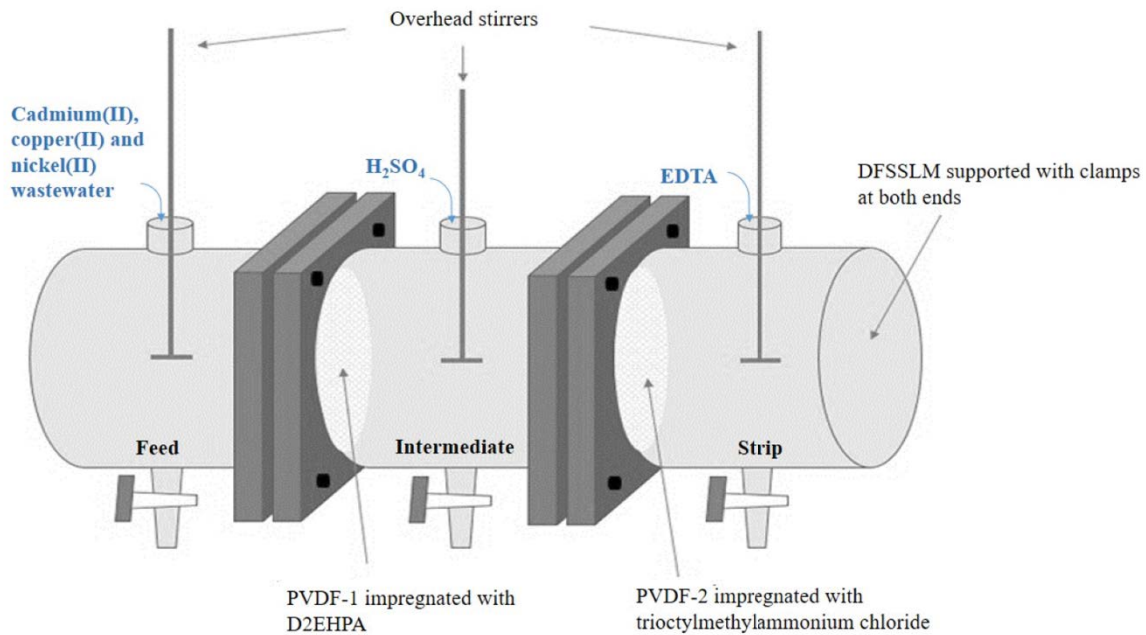


Fig. 1. Schematic diagram of DFSSLM.

copper(II), and nickel(II) were examined by extracting little quantities of raffinates from each DFSSLM component every hour for 48 h. Metal concentrations were analyzed with FAAS after proper dilution, as captured in Table 2.

To quantify the dissimilarity and transformations for 48 h, the changes in the measurement of the metals pre ($[M_o]$) and post DFSSLM extraction ($[M_t]$) at the time, t was shown using mass balance as captured in Eq. (4).

$$\text{Mass(\%)} = \frac{[M_t]}{[M_o]} \times 100 \quad (4)$$

The input/output attributes for the metals being studied was gotten with Eq. (5) after 48 h:

$$\text{Input / Output} = \frac{[M_t]_{\text{feed}} + [M_t]_{\text{intermediate}} + [M_t]_{\text{strip}}}{[M_o]} \quad (5)$$

where $[M_t]$ represents the varying amounts of the metals in each compartment at the end of the study period.

Permeability is what defines the transport efficiency of the membrane, and thus assesses the total effectiveness of the DFSSLM. Permeation flux is the measure at which the metal is transported through the membrane and is accompanied by a concentration gradient that is confined to the

boundaries of the membranes and includes permeability which refers to the thickness of the membrane [22]. Based on Fick's law, the flux (J , mol/m²s) is measured based on Eq. (6):

$$J = \frac{(\Delta C \times V)}{(A \times \Delta t)} \quad (6)$$

where ΔC is the change of metal ion concentration (mol/L), V is the feed volume (m³), A is the effective surface area of membrane (m²) and Δt indicates time duration (s).

Separation is the phenomenon of a large movement of matter invariably altering the make-up of the feed compartment but not to the extent of affecting the form of individual parts [22]. Selectivity is separating a solute within a multi-element complex. Pore proportions of the membrane's support affect selectivity and the movement mechanism inside the membrane [23]. A metal's selectivity as opposed to others and its extraction from the mixture is shown in Eq. (7) and termed as the separation factor, $S_{M1/M2}$:

$$S_{M1/M2} = \frac{D_{M1}}{D_{M2}} \quad (7)$$

where D_{M1} and D_{M2} measure the distribution of metal M_1 and M_2 .

Table 2
Standard conditions for FAAS analysis in this study

Conditions	Cadmium(II)	Copper(II)	Nickel(II)
Wavelength (nm)	228.8	324.8	232.0
Background correction with D ₂ lamp (1% absorbance in ppm)	0.007–0.015	0.02–0.04	0.04–0.07
C ₂ H ₂ flow rate (L/min)	1.8	1.8	1.6

2.8. Characterization of support membranes using SEM-EDX

DFSSLM with support membranes PVDF-1 and PVDF-2 impregnated with D2EHPA and trioctylmethylammonium chloride, respectively, was used to study the preferential removal of cadmium(II), copper(II), and nickel(II). To provide an understanding of membrane performance, the surface properties of support membrane used and their interactions with metal must be studied [24]. SEM analysis on PVDF-1 and PVDF-2 with 10,000 magnifications was used to characterize the support membranes' structures before and after DFSSLM experiments. The changes in pore size and surface morphology of the SEM images were matched against those of the unimpregnated PVDF membrane. SEM images of PVDF-1 and PVDF-2 once DFSSLM was carried out were also captured and analyzed.

The elements of interest as contained in the support membranes of PVDF-1 and PVDF-2 prior to and subsequently after the infusion of organic phases were identified using EDX analysis. At the end of the DFSSLM experiment, the peaks from the EDX spectra belonging to the metals of interest for PVDF-1 and PVDF-2 were analyzed.

3. Results and discussion

3.1. DFSSLM extraction studies using synthetic mixtures

3.1.1. Separation of cadmium(II), copper(II) and nickel(II) using DFSSLM

Results in Table 3 reveal that DFSSLM was capable of dissociating cadmium(II), copper(II) over nickel(II) by taking into cognizance their distribution ratios, separation characteristics in various sections, and how penetrable they are through the sections.

Using operating time under optimum conditions, the variations in the three metals' mass profiles in the main parts of DFSSLM, (feed, intermediate, and strip) were studied, and the output is presented in Fig. 2.

Fig. 2a shows that both cadmium(II) and copper(II) were transported from the mixed sulfate solution in the feed compartment into the 1 M H_2SO_4 in the intermediate compartment across the first SLM had 100 mM D2EHPA and 50 mM tributyl phosphate diluted in kerosene. During the entire transfer process, over 98% of nickel(II) stayed inside the feed section at the end of the 48 h period. Based on Fig. 2b, 91.32% of copper(II) was observed in the intermediate compartment after 48 h, giving it a significant separation factor of 247 more than a nickel(II) and 133 more than cadmium(II). However, cadmium(II) from the intermediate part showed a steady rise till it reached a

maximum at the 24th hour then started to decline. The separation factor shared by cadmium(II) and copper(II) inside the intermediate part was then lowered to 93 because competition between cadmium(II) and copper(II) has a higher tendency of increasing when the available extractant is limited. This competition between cadmium(II) and copper(II) was seen in the 24th hour and gave rise to extraction complexes in PVDF-2 with trioctylmethylammonium chloride and tributyl phosphate. This led to cadmium(II) dropping at the 24 h mark in the intermediate section and ending the experiment with 6.86% as shown in Fig. 2b.

Cadmium(II) was preferentially transported across PVDF-2 to the strip section with a permeability coefficient of $1.46 \times 10^{-6} \text{ ms}^{-1}$. At 48 h, the strip compartment had $\leq 1.09\%$ copper(II) and 91.04% of cadmium(II) which is captured in Fig. 2c. This proves that the selective separation of metals of interest is possible in either of the components of the DFSSLM.

3.1.2. Competitive transportation and separation of cadmium(II) and copper(II)

At the 24th hour, cadmium(II) and copper(II) had started making complexes with trioctylmethylammonium chloride in the intermediate section while the feed section showed a greater proportion of cadmium(II) and copper(II) was extracted. Fig. 3 carries the comparison of the variations in the chemical activity of trioctylmethylammonium chloride that played a role in hiding the outcome of EDTA on cadmium(II) and copper(II), the fluxes (J) which were hinged on the concentration differences of cadmium(II) and copper(II) in the intermediate section. For reference purposes, feed solutions with either 100 mg/L cadmium(II) or copper(II) were applied in obtaining data on the movement of the metal when other metals were excluded for a time frame of 48 h. The findings were matched against those of the movement of cadmium(II) and copper(II) in the feed solutions that contained 100 mg/L of cadmium(II), copper(II) and nickel(II).

The flux of cadmium(II) showed a slight difference when other metals were excluded from the feed. A great difference of $1.60 \times 10^{-6} \text{ mol/m}^2$ of copper(II) flux was obtained after the introduction of different metals, causing a drop to $3.22 \times 10^{-6} \text{ mol/m}^2$ leading to the restrained permeation of copper(II), resulting the majority of copper(II) were left in the intermediate section. While copper(II) ions were restricted to be transported across PVDF-2, trioctylmethylammonium chloride allowed the selective transportation of cadmium(II) ions into the EDTA solution in the strip section. Cadmium(II) ions extraction was favored due to their high affinity for trioctylmethylammonium chloride

Table 3
Distribution ratios, permeabilities and separation factors of cadmium(II), copper(II) and nickel(II) in DFSSLM after 48 h

	Distribution ratio, D			Permeability ($\times 10^{-6} \text{ ms}^{-1}$)			Separation factor		
	Cd(II)	Cu(II)	Ni(II)	Cd(II)	Cu(II)	Ni(II)	$S_{\text{Cd/Cu}}$	$S_{\text{Cd/Ni}}$	$S_{\text{Cu/Ni}}$
Feed	0.0056	0.0063	0.9879	–	–	–	2	176	157
Intermediate	0.0693	0.9227	0.0038	1.97	1.95	–	93	18	243
Strip	0.9876	0.0115	0.0007	1.46	–	–	217	395	1

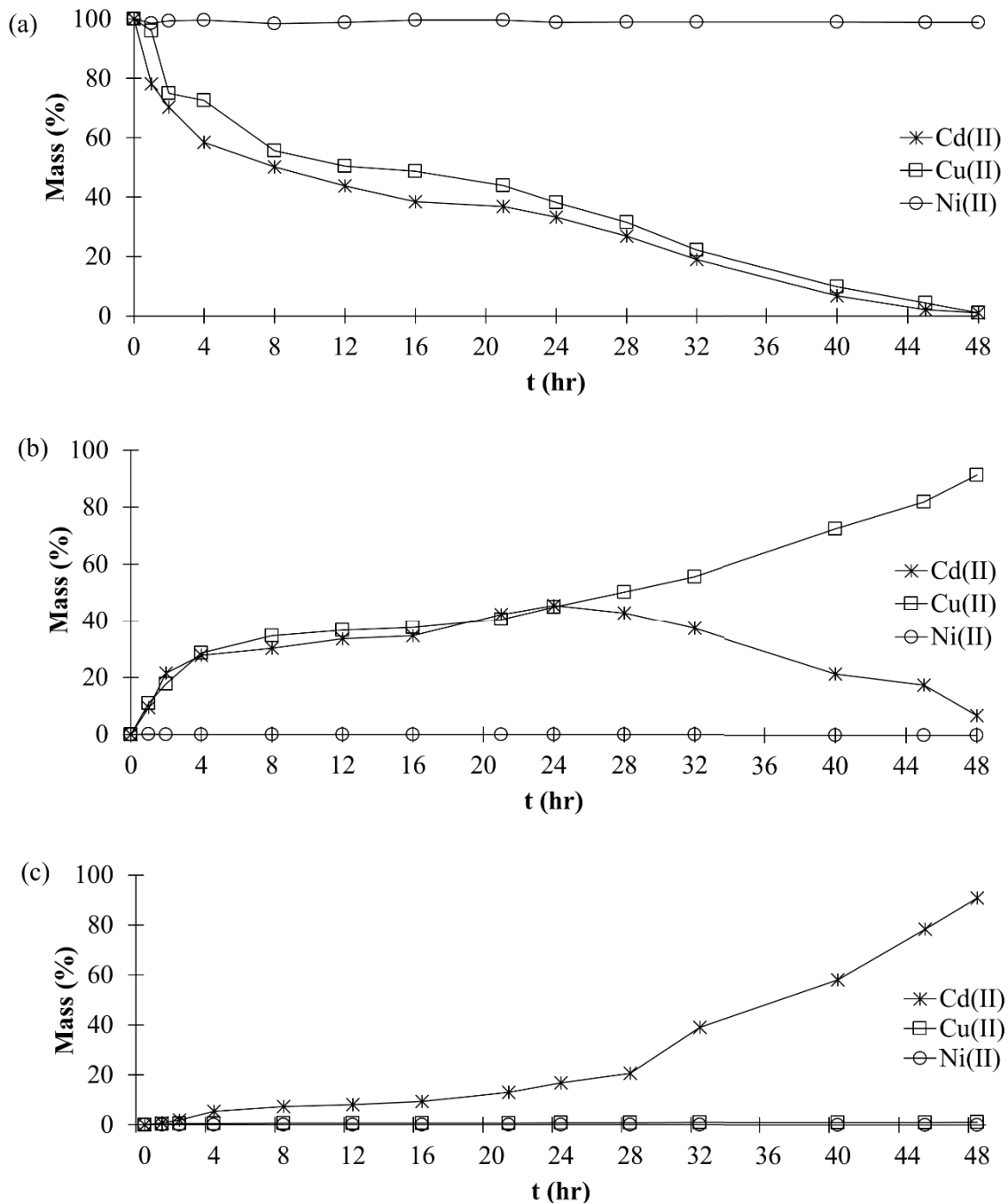


Fig. 2. Variation of mass profiles of cadmium(II), copper(II) and nickel(II) in DFSSLM compartments: (a) feed, (b) intermediate, and (c) strip compartments.

when compared to copper(II) ions. This can be explained that copper(II) tends to have a lower flux due to the crowding effect of cadmium(II) onto copper(II) transport. The crowding effect also accounts for the decline of metal fluxes [25].

The competitive transportation and separation of cadmium(II) and copper(II) after 24 h are captured in Fig. 4, which shows the plots of transport kinetics against time. Similar results were discussed on the effect of competition between metals in a combinatorial separation study [21,26].

A decrease in cadmium(II) concentration with time is visible from the results, and the first-order kinetics with $R^2 = 0.9976$ help to explain it further. Clearly, only cadmium(II) is moved into the third part of the DFSSLM after the 48th hour.

3.1.3. Mass balance for the treatment of a synthetic mixture

A synthetic sulfate feed was prepared with equal concentrations (100 mg/L) of metals. Mass balances of cadmium(II), copper(II) and nickel(II) were constructed and

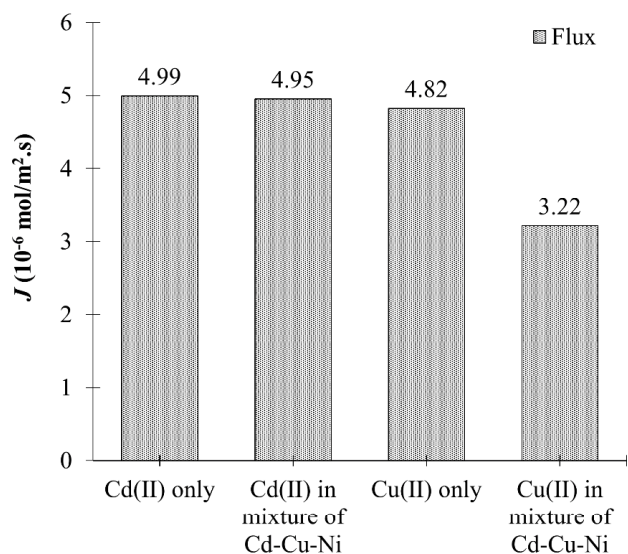


Fig. 3. Competitive transport of cadmium(II) and copper(II) from the intermediate to strip compartment.

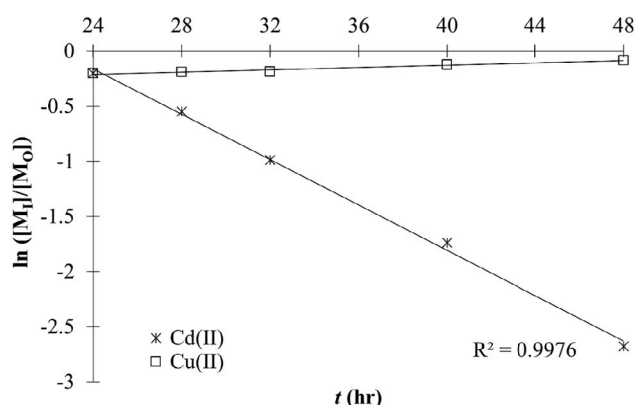


Fig. 4. Kinetic plots of transport for cadmium(II) and copper(II) in the intermediate; $[M_t]$: concentration of metal ion at time, t ; $[M_0]$: initial concentration of metal ion.

outlined in Table 4 in terms of concentration due to the constant volume of working solutions in each compartment of DFSSLM. If most of the metals extracted from the feed compartment were transported to the strip, the reduction of their concentration in one compartment should resemble a similar rise in the other compartment.

From Table 4, 98.79% was recorded as the largest build-up of nickel(II) in the raffinate from the feed. The selective removal by D2EHPA contributed to the majority transfer of cadmium(II) and copper(II) ions to the intermediate, leaving behind approximately 1% of their residues in the feed at the end of the experiment. It is evident that copper(II) achieved the largest recovery of 91.32% during the separation process in the intermediate. Although 7% of cadmium(II) remained in the intermediate, most of the cadmium(II) ions (91.04%) were being recovered in the strip compartment. The result is justified with the reactivity preference of trioctylmethylammonium chloride

towards cadmium. At the end of DFSSLM studies, it was found that none of the copper(II) and nickel(II) ions were transported from the intermediate to the strip. The high input/output ratios in Table 4 had proven the extractants in DFSSLM possessed high loading capacities for the maximum recovery of these three metals.

3.1.4. Characterization of support membranes by SEM-EDX

The pore size of the support membrane has a significant role in defining the liquid membrane system [27]. Fig. 5a captures the SEM image of the PVDF membrane prior to DFSSLM showing visibly porous make-up.

Figs. 5b and d show PVDF-1 and PVDF-2 respectively and reveal the reduction in pore size due to carrier immobilization. Carrier immobilization caused the polymer and carrier complex to be cross-linked, followed by the formation of chemical bonds between them. This invariably led to the reduction in pore size.

The exterior of PVDF-1 and PVDF-2 at the end of the DFSSLM process is seen in Figs. 5c and e respectively. The membranes' surfaces had been altered, thus confirming the membrane was loaded following the 48 h period of the DFSSLM operation. This is similar to a study of Kır et al. [28], whereby significant changes in the morphologies of the macroporous structure of PVDF membranes were observed after coating with extractants.

It is important to study the variations in the elemental properties of PVDF-1 and PVDF-2 using EDX. Fig. 6a represents the original PVDF membrane's elemental characteristics before immobilization with the extractants. Fig. 6 captures the spectra, C and F were identified from the PVDF membrane, composed of fluorosurfactant perfluorononanoic acid [29]. Fig. 6b shows P and O, which is derived from D2EHPA, which comprised organophosphorus. Fig. 6c captures the negligible accumulation of cadmium(II) and copper(II) with less than 0.5% in the PVDF-1, while nickel(II) had 1.2%. P and O peaks prove that the extractant stayed PVDF-1 pores for the entire 48 h. Cl peaks from trioctylmethylammonium chloride are captured in Fig. 6d; whereas Fig. 6e reveals no presence of nickel(II) in PVDF-2, but $\leq 0.2\%$ of cadmium(II) and copper(II) at the end of the 48 h experiment. Similar results were identified from the distribution of the elements of interest on the surface of liquid-based membranes [30].

3.2. DFSSLM extraction studies using electroplating effluent

3.2.1. Characterization of electroplating effluent

Table 5 presents the physical and chemical properties of the rinse electroplating effluent. Quantitative analysis of metal ions was conducted before and after the DFSSLM experiment to determine the change in compositions of the complex and highly variable actual electroplating effluent.

Physically, the rinse effluent appeared as a light blueish green solution and this is attributed to the high concentration of nickel and copper in the effluent. The rinse wastewater was slightly acidic with pH 4.52. Without adjusting the wastewater's pH or diluting it, it

Table 4
Mass balance of cadmium(II), copper(II) and nickel(II) for treatment of synthetic mixture using DFSSLM after 48 h

Metals (mg/L)	Input	Output (metals present in raffinate)			Output/Input ratio
		Feed	Intermediate	Strip	
Cadmium(II)	100	0.96	6.86	91.04	0.99
Copper(II)	100	1.03	91.32	1.09	0.93
Nickel(II)	100	98.79	0	0	0.99

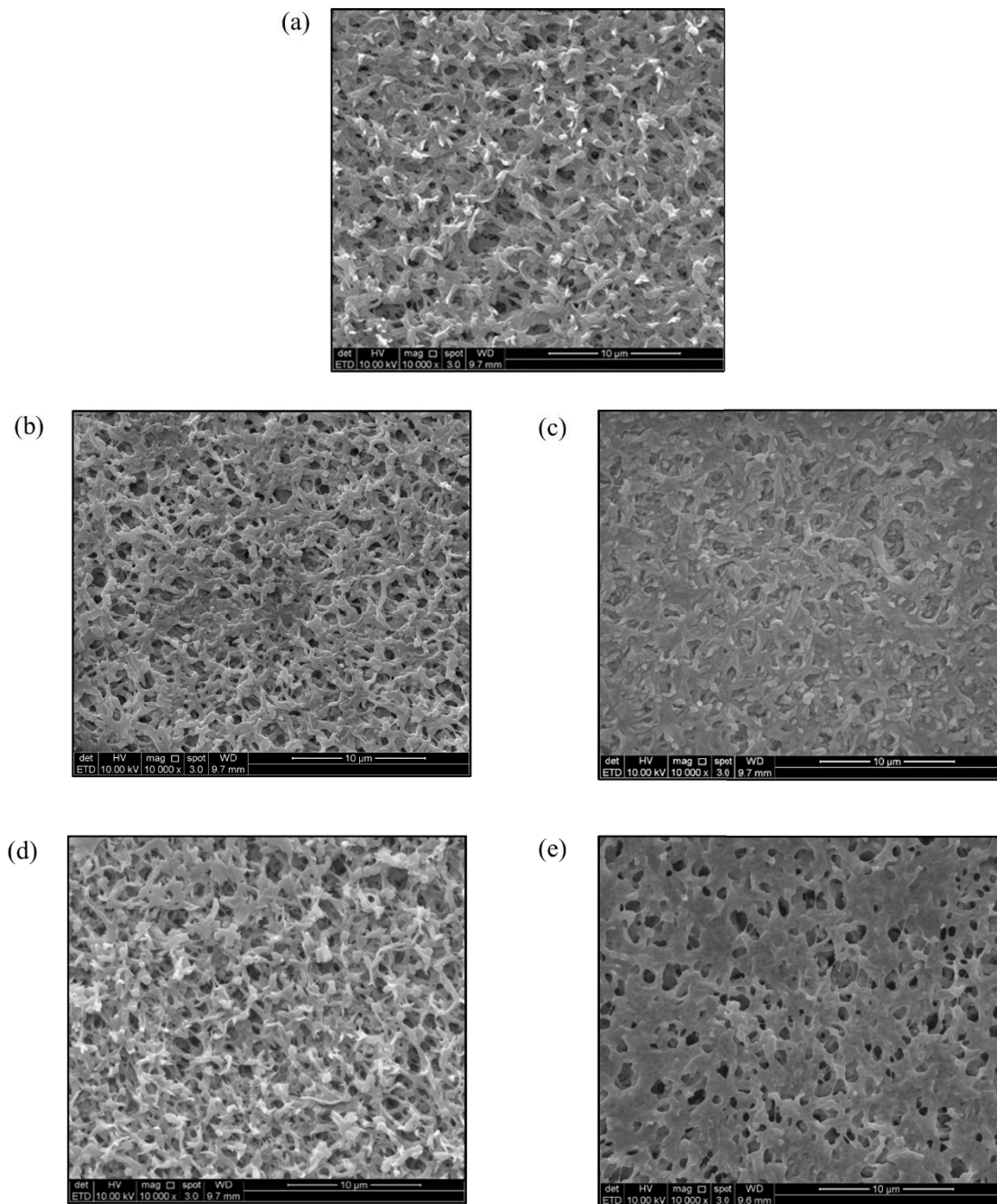


Fig. 5. SEM images of PVDF membranes with 10,000 times magnification: (a) before DFSSLM experiment, (b) PVDF-1 immobilized with D2EHPA, (c) PVDF-1 after experiment, (d) PVDF-2 immobilized with triethylmethylammonium chloride, and (e) PVDF-2 after experiment.

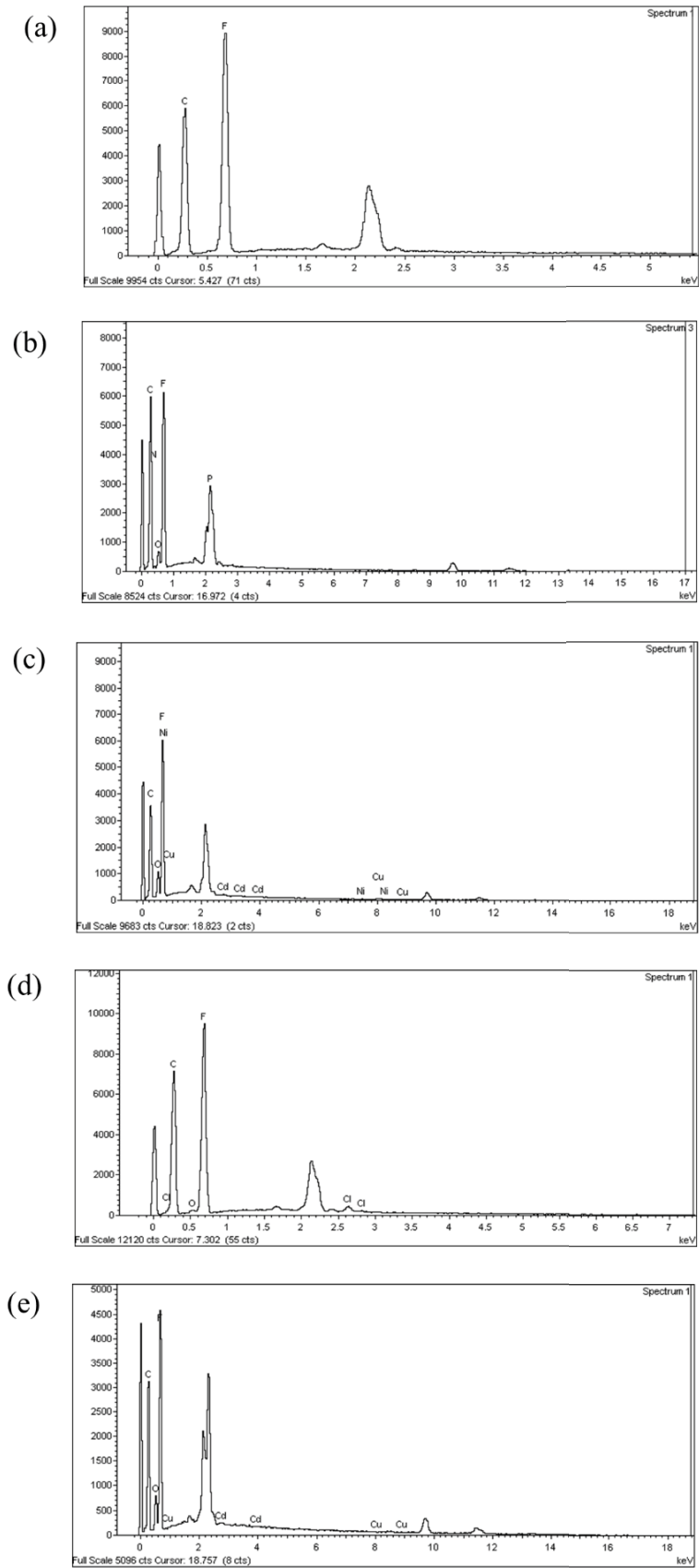


Fig. 6. EDX spectra of PVDF membrane: (a) before experiment, (b) PVDF-1 immobilized with D2EHPA, (c) PVDF-1 after experiment, (d) PVDF-2 immobilized with triethylmethylammonium chloride, and (e) PVDF-2 after experiment.

was poured into the DFSSLM directly as a feed solution because of the similar operating pH used in the earlier study. Cadmium(II), copper(II) and nickel(II) ions found in the untreated effluent were mainly from their sulfate solutions used for the electroplating process. Results showed that copper predominated in the highest concentration (131 mg/L) and was followed by nickel (50 mg/L). Cadmium, iron and zinc existed in low concentrations (<6 mg/L) while other metal ions such as aluminum, boron, chromium, manganese and tin appeared almost negligible with concentrations less than 1 mg/L.

Meanwhile, most of the metals were observed in reduced quantities or were absent once the DFSSLM process was completed. After the DFSSLM process, cadmium(II) was removed completely and 96.2% of copper(II) was extracted from the effluent. There was a slight discoloration in the bluish-green color of the effluent due to copper removal. However, 97.5% of nickel(II) was found in the effluent at the end of the DFSSLM process, and thus, nickel has to be responsible for the color value in Table 5. The decrease in pH of effluent to pH 2 after the DFSSLM process indicated the saturation of feed-membrane interface after 48 h and, hence, the transport of nickel(II) ions were refrained.

Table 5
Characteristics of electroplating wastewater. Heavy metal analysis method was based on APHA^a 3120B

Characterization	Before DFSSLM	After DFSSLM
pH	4.52	2.04
Temperature (°C)	29	29
Color ADMI ^b	7	5
Oil and grease (mg/L)	13.2	8
Metal concentration (mg/L)		
Cadmium	5.5	Not detected
Chromium trivalent	0.26	Not detected
Copper	131	4.94
Manganese	0.03	Not detected
Nickel	50.13	48.9
Tin	0.51	0.10
Zinc	1.43	0.20
Boron	0.10	0.09
Iron	3.54	1.21
Aluminum	0.75	0.38

^aAPHA: American Public Health Association, Standard Method for Examination of Water and Wastewater, 23rd ed., 2017;

^bADMI: American Dye Manufacturers' Institute.

Table 6
Mass balance of cadmium(II), copper(II) and nickel(II) for treatment of electroplating wastewater using DFSSLM after 48 h

Metals (mg/L)	Input	Output (metals present in raffinate)			Output/Input ratio
		Feed	Intermediate	Strip	
Cadmium(II)	5.5	0.004	0.18	4.9	0.91
Copper(II)	131	4.94	119.04	0	0.95
Nickel(II)	50.13	48.93	0.035	0	0.98

Due to the selectivity preference of D2EHPA, no nickel transport was observed and nearly all nickel was left unextracted within the 48 h and hence, explained the similar results with the DFSSLM studies using synthetic wastewater.

3.2.2. Mass balance for treatment of electroplating effluent

Table 6 shows the mass balance measurement of the targeted metals at the end of the DFSSLM process. The overall outputs were inclusive of the presence/build-up of metals in each component (feed, intermediate and strip), which made up to the initial metal compositions in the wastewater.

From Table 6, nickel(II) in the raffinate from the feed achieved the highest output/input ratio of 0.98 as the largest build-up in feed after 48 h run of DFSSLM experiment, which is agreeable with previous findings. The selective removal by D2EHPA results in the majority of cadmium(II) and copper(II) ions being moved to the intermediate leaving behind residues of 0.07% and 3.77%, respectively, in the feed at the end of the experiment. copper(II) recorded the largest build-up of 95% during the separation process in the intermediate. Since the initial copper(II) load was the highest among other metals, it resulted in greater extraction and accumulation than other targeted metals. The minimal load of cadmium(II) caused 91% of it being moved to the strip. At the end of extraction studies, copper(II) and nickel(II) was not transported from the intermediate to the strip.

The effects of impurities such as chromium(III), zinc(II), iron(III), aluminum(III), and tin(II) found in the effluent are capable of lowering the effectiveness of the DFSSLM to obtain the desired metal ions. The different loads of metal components in wastewater caused the DFSSLM efficiency to drop when looked at in comparison to the same number of components in a synthetic setup. Other sources of metal-bearing wastewater consist of different combinations of metal components. Different compositions of metals would require the setup of DFSSLM with different extractants based on the extractant's selectivity in order to achieve maximum recovery. Thus, further research on selectively extracting other types of metals from complex mixtures using DFSSLM can be studied.

4. Conclusions

Separation and recovery of cadmium(II), copper(II), and nickel(II) from the synthetic mixture and electroplating wastewater using DFSSLM were investigated and compared. In DFSSLM, selective preferences of the extractants, D2EHPA (towards cadmium and copper), and trioctylmethylammonium chloride (specifically cadmium) have proven to be capable of selectively separating copper(II)

and cadmium(II) over nickel(II). Separation of the synthetic mixture showed 98.79% of nickel(II), 91.32% of copper(II), and 91.04% of cadmium(II) were recovered in three different compartments respectively after a period of 48 h. Despite other metals that exist in the electroplating wastewater being capable of impeding the functionality of the DFSSLM, the output/input ratios for cadmium(II), copper(II), and nickel(II) from each compartment were significant at 0.91, 0.95 and 0.98. SEM-EDX analysis showed significant permeation of organic mixtures onto the PVDF support membranes and validated that the membrane was packed at the 48th-hour mark. The results obtained suggest that the selective separation of cadmium and copper from nickel using DFSSLM provides a good chance for the advancement of metal separation, purification and recovery operation in the future of electroplating wastewater treatment.

Acknowledgment

The authors are grateful to the Universiti Sains Malaysia, Fundamental Research Grant Scheme (FRGS) grant number (203/PTEKIND/6711822) for supporting and providing the research facilities.

References

- [1] S.-Y. Tang, Y.-R. Qiu, Selective separation and recovery of heavy metals from electroplating effluent using shear-induced dissociation coupling with ultrafiltration, *Chemosphere*, 236 (2019) 124330, 10.1016/j.chemosphere.2019.07.061.
- [2] L.Y. Lee, N. Morad, N. Ismail, M. Rafatullah, Opportunities and challenges in supported liquid membrane technology for heavy metal extraction and recovery: a review, *Int. J. Environ. Eng.*, 9 (2018) 324–354.
- [3] L. Fang, L. Li, Z. Qu, H.M. Xu, J.F. Xu, N.Q. Yan, A novel method for the sequential removal and separation of multiple heavy metals from wastewater, *J. Hazard. Mater.*, 342 (2018) 617–624.
- [4] K. Ali, R. Nawaz, N. Ali, A. Khaliq, R. Ullah, Selective removal of zinc using tri-ethanolamine-based supported liquid membrane, *Desal. Water Treat.*, 57 (2016) 8549–8560.
- [5] A. Kaya, T. Kutlu, A. Hol, A. Surucu, H.K. Alpoguz, Transport of Pb(II) by supported liquid membrane containing p-tert-butyl calix[4]amine derivative as carrier, *Desal. Water Treat.*, 52 (2014) 3219–3225.
- [6] M. Amini, A. Rahbar-Kelishami, M. Alipour, O. Vahidi, Supported liquid membrane in metal ion separation: an overview, *J. Membr. Sci. Res.*, 4 (2018) 121–135.
- [7] D. Sribudda, N. Sunsandee, P. Ramakul, U. Pancharoen, S. Phatanasri, Separation of Cd(II) from industrial wastewater via HFSLM: equilibrium, kinetic and thermodynamic investigation, *J. Ind. Eng. Chem.*, 25 (2015) 22–28.
- [8] G. Zhang, D.S. Chen, W. Zhao, H.X. Zhao, L. Wang, W.J. Wang, T. Qi, A novel D2EHPA-based synergistic extraction system for the recovery of chromium(III), *Chem. Eng. J.*, 302 (2016) 233–238.
- [9] P. Amani, J. Asadi, E. Mohammadi, S. Akhgar, M. Esmaili, Cooperative influence of D2EHPA and TBP on the reactive extraction of cobalt from sulfuric acid leach solution in a horizontal semi-industrial column, *J. Environ. Chem. Eng.*, 5 (2017) 4716–4727.
- [10] A. Ghosh, D. Datta, H. Uslu, H.S. Bamufleh, S. Kumar, Separation of copper ion (Cu^{2+}) from aqueous solution using tri-n-butyl phosphate and di-2-ethylhexyl phosphoric acid as extractants, *J. Mol. Liq.*, 258 (2018) 147–154.
- [11] D.K. Singh, K.K. Yadav, H. Singh, Extraction and stripping behavior of iron(III) from phosphoric acid medium by D2EHPA alone and its mixtures with TBP/TOPO, *Sep. Sci. Technol.*, 48 (2013) 1556–1564.
- [12] A. Azizitorghabeh, F. Rashchi, A. Babakhani, Stoichiometry and structural studies of Fe(III) and Zn(II) solvent extraction using D2EHPA/TBP, *Sep. Purif. Technol.*, 171 (2016) 197–205.
- [13] L.Y. Lee, N. Morad, N. Ismail, M. Rafatullah, Synergistic extraction of Cd, Cu and Ni with D2EHPA/TBP: screening of factors by fractional factorial design, *Int. J. Chem. Eng. Appl.*, 10 (2019) 114–120.
- [14] J. Gega, P. Otremska, Separation of Ni(II) and Cd(II) ions with supported liquid membranes (SLM) using D2EHPA as a carrier, *Sep. Sci. Technol.*, 49 (2014) 1756–1760.
- [15] S.H. Chang, T.T. Teng, N. Ismail, Efficiency, stoichiometry and structural studies of Cu(II) removal from aqueous solutions using di-2-ethylhexylphosphoric acid and tributylphosphate diluted in soybean oil, *Chem. Eng. J.*, 166 (2011) 249–255.
- [16] T. Koonsang, K. Aunnankat, K. Maneeintr, U. Pancharoen, T. Wongsawa, The mutual solubility of organic-liquid membrane and aqueous phases at different water pH for the stability of SLM using Aliquat 336 as an ionic-liquid extractant, *J. Mol. Liq.*, 292 (2019) 111363, doi: 10.1016/j.molliq.2019.111363.
- [17] S. Altin, S. Alemdar, A. Altin, Y. Yildirim, Facilitated transport of Cd(II) through a supported liquid membrane with Aliquat 336 as a carrier, *Sep. Sci. Technol.*, 46 (2011) 754–764.
- [18] N. Pont, V. Salvadó, C. Fontás, Applicability of a supported liquid membrane in the enrichment and determination of cadmium from complex aqueous samples, *Membranes*, 8 (2018) 21, doi: 10.3390/membranes8020021.
- [19] L.Y. Lee, N. Morad, N. Ismail, A. Talebi, M. Rafatullah, Optimization for liquid-liquid extraction of Cd(II) over Cu(II) ions from aqueous solutions using ionic liquid Aliquat 336 with tributyl phosphate, *Int. J. Mol. Sci.*, 21 (2020) 6860, doi: 10.3390/ijms21186860.
- [20] A.A. Nayl, Extraction and separation of Co(II) and Ni(II) from acidic sulfate solutions using Aliquat 336, *J. Hazard. Mater.*, 173 (2010) 223–230.
- [21] H.P. Duan, Z.Y. Wang, X.H. Yuan, S.X. Wang, H. Guo, X.J. Yang, A novel sandwich supported liquid membrane system for simultaneous separation of copper, nickel and cobalt in ammoniacal solution, *Sep. Purif. Technol.*, 173 (2017) 323–329.
- [22] K.W. Böddeker, An Introduction to Barrier Separation, in: *Liquid Separations with Membranes: An Introduction to Barrier Interference*, Springer International Publishing, Cham, 2018, pp. 1–12.
- [23] P. Dzygiel, P.P. Wiczorek, Chapter 3 – Supported Liquid Membranes and Their Modifications: Definition, Classification, Theory, Stability, Application and Perspectives, in: *Liquid Membranes*, Elsevier, Amsterdam, 2010, pp. 73–140.
- [24] A. Lee, J.W. Elam, S.B. Darling, Membrane materials for water purification: design, development, and application, *Environ. Sci.: Water Res. Technol.*, 2 (2016) 17–42.
- [25] A.M. Sastre, J. Szymanowski, Discussion of the physicochemical effects of modifiers on the extraction properties of hydroxyoximes. A review, *Solvent Extr. Ion Exch.*, 22 (2004) 737–759.
- [26] K.K. Bhatluri, M.S. Manna, P. Saha, A.K. Ghoshal, Supported liquid membrane-based simultaneous separation of cadmium and lead from wastewater, *J. Membr. Sci.*, 459 (2014) 256–263.
- [27] M.S. Manna, P. Saha, A.K. Ghoshal, Studies on the stability of a supported liquid membrane and its cleaning protocol, *RSC Adv.*, 5 (2015) 71999–72008.
- [28] E. Kır, Ş. Yalımlı, S. Kurtulmuş, A. Aydın, H. Yılmaz, Facilitated transport of Ni(II) through supported liquid membranes containing dithiophosphonates as ion carrier, *Phosphorus, Sulfur Silicon Relat. Elem.*, 190 (2015) 178–190.
- [29] S.R. Pilli, T. Banerjee, K. Mohanty, Performance of different ionic liquids to remove phenol from aqueous solutions using supported liquid membrane, *Desal. Water Treat.*, 54 (2014) 3062–3072.
- [30] Z. Baicha, M.J. Salar-García, V.M. Ortiz-Martínez, F.J. Hernández-Fernández, A.P. de los Ríos, D.P. Maqueda Marín, J.A. Collado, F. Tomás-Alonso, M. El Mahi, On the selective transport of nutrients through polymer inclusion membranes based on ionic liquids, *Processes*, 7 (2019) 544, doi: doi.org/10.3390/pr7080544.