SUPPORTED LIQUID MEMBRANE PROCESS FOR NICKEL REMOVAL FROM ELECTROPLATING WASTEWATER

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This thesis is dedicated to my beloved parents, siblings, friends and those who directly or indirectly assist me in this research for their endless love, prayer and support

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ABSTRACT

Supported liquid membrane (SLM) is one of the potential separation methods in treating wastewater loaded with toxic heavy metal ions owing to several advantages including simultaneous extraction and recovery processes, high separation factor, simple operation and it is easy to scale up. Right formulation, high stability and sustainable predominantly influence the success of the SLM process. Petroleum based diluents are hazardous whereas the single carrier is unable to efficiently extract nickel ion at lower pH. Liquid membrane loss leads to the SLM instability and short lifetime. In this study, a sustainable and stable SLM process using a mixture of carrier and cooking palm oil impregnated in composite membrane support was developed for the extraction and recovery of nickel ion from the electroplating wastewater. Electroplating wastewater was analyzed and SLM components such as carriers (di (2-ethylhexyl) phosphoric acid (D2EHPA), diisooctylthiophosphinic acid (Cyanex 302), tridodecylamine (TDA) and octanol), synergist carriers (Cyanex 302, TDA and octanol), diluents (kerosene and cooking palm oil) and stripping agents (sulfuric acid, hydrochloric acid and nitric acid) for nickel ion extraction were formulated via liquid-liquid extraction process. The formulated liquid membrane containing D2EHPA and octanol in kerosene was impregnated in the membrane support pores of polyvinylidene fluoride (PVDF) with the features of 125μm thickness, 75% porosity and 0.22μm pore size. Parameters affecting SLM extraction of nickel such as carrier, synergist carrier and stripping agent concentrations as well as flow rate of feed and stripping phases were screened and optimized using the response surface methodology method. Several compositions of kerosene and cooking palm oil were studied to determine the feasibility of cooking palm oil in the extraction of nickel in SLM. The stability of SLM was investigated by developing a composite membrane support containing sulfonated poly (ether ether ketone) (SPEEK) and PVDF. Results showed that D2EHPA, octanol, cooking palm oil and sulfuric acid have potential as a carrier, synergist carrier, diluent and stripping agent, respectively. About 90 and 95% of nickel ions were successfully extracted and recovered, respectively under optimized conditions of 1.25M D2EHPA, 15% (v/v) octanol and 1.75M sulfuric acid. Upon applying 100% cooking palm oil as diluent, around 91% of nickel ions were extracted and 65% were recovered. The developed composite membrane support (SPEEK-PVDF) is capable of improving the SLM stability by reducing the liquid membrane loss from 47 to 23% upon applying the SPEEK layer at the feed side of the PVDF membrane support. High permeability (9.26×10^{-4} cms^{-1}) and flux (6.48×10^{-7} $molcm^{-2}s^{-}1$) of nickel were achieved as the thickness of SPEEK was increased from 0.025 to 0.055mm. Recycling of the composite membrane support was found to be satisfactory until the ninth cycles with low weight loss percentage of the impregnated composite membrane support (8%). The findings of this study revealed that a sustainable and stable SLM process was successfully developed for the removal and recovery of nickel ion from the electroplating wastewater.

ABSTRAK

Membran cecair bersokong (SLM) adalah salah satu kaedah pemisahan yang berpotensi untuk merawat air sisa yang mengandungi ion-ion logam berat toksik kerana memiliki beberapa kelebihan termasuklah proses pengekstrakan dan perolehan secara serentak, faktor pemisahan yang tinggi, pengoperasian yang mudah dan ianya mudah untuk peningkatan penskalaan. Rumusan yang betul, tahap kestabilan yang tinggi dan mampan sangat mempengaruhi kejayaan proses SLM. Bahan-bahan pencair berasaskan petroleum adalah berbahaya manakala pembawa tunggal tidak dapat mengekstrak ion nikel secara efektif pada pH yang rendah. Kehilangan membran cecair membawa kepada ketidakstabilan SLM dan jangka hayat yang pendek. Dalam kajian ini, SLM yang mampan dan stabil menggunakan campuran pembawa dan minyak masak sawit yang diimpregnasi dalam komposit membran sokongan telah dibangunkan untuk pengekstrakan dan perolehan ion nikel daripada air sisa penyaduran. Air sisa penyaduran telah dianalisis dan komponen-komponen SLM seperti pembawa-pembawa (di (2-etilheksil) asid fosforik (D2EHPA), asid diisooctiltiofosfinik (Cyanex 302), tridodesilamina (TDA) dan oktanol), pembawa-pembawa sinergis (Cyanex 302, TDA dan oktanol), bahan-bahan pencair (kerosin dan minyak masak sawit) dan agen-agen pelucutan (asid sulfurik, asid hidroklorik dan asid nitrik) untuk pengekstrakan ion nikel telah dirumuskan melalui proses pengekstrakan cecair-cecair. Membran cecair yang telah dirumuskan mengandungi D2EHPA dan oktanol dalam kerosin telah diimpregnasi dalam liang-liang membran sokongan polivinilidena fluorida (PVDF) dengan ciri-ciri seperti ketebalan 125µm, porositi 75% dan saiz liang 0.22µm. Parameter-parameter yang memberi kesan kepada pengekstrakan nikel dalam SLM seperti kepekatan pembawa, kepekatan pembawa sinergis, kepekatan agen pelucutan termasuk kadar aliran fasa suapan dan kadar aliran fasa pelucutan telah disaring dan dioptimumkan dengan menggunakan kaedah gerak balas permukaan. Beberapa komposisi kerosin dan minyak masak sawit telah dikaji untuk menentukan kebolehan minyak masak sawit untuk pengekstrakan ion nikel dalam SLM. Kestabilan SLM telah diselidiki dengan membangunkan komposit membran sokongan yang mengandungi poli (eter eter keton) tersulfonat (SPEEK) dan PVDF. Keputusan menunjukkan bahawa D2EHPA, oktanol, minyak masak sawit dan asid sulfurik masing-masing berpotensi sebagai pembawa, sinergis pembawa, bahan pencair dan agen pelucutan. Sekitar 90 dan 95% ion nikel masing-masing telah berjaya diekstrak dan diperoleh di bawah keadaan optimum 1.25M D2EHPA, 15% (v/v) oktanol dan 1.75M asid sulfurik. Apabila menggunakan 100% minyak masak sawit sebagai bahan pencair, sekitar 91% ion nikel telah diekstrak dan 65% telah diperoleh. Komposit membran sokongan (SPEEK-PVDF) yang telah dibangunkan mampu meningkatkan kestabilan SLM dengan mengurangkan kehilangan membran cecair daripada 47 kepada 23% setelah lapisan SPEEK digunakan di bahagian fasa suapan membran sokongan PVDF. Kebolehtelapan (9.26×10^{-4} cms^{-1}) dan fluks (6.48×10^{-7} $molcm^{-2}s^{-1}$) nikel yang lebih tinggi dicapai apabila ketebalan SPEEK ditingkatkan daripada 0.025 kepada 0.055mm. Kitar semula komposit membran sokongan didapati memuaskan sehingga kitaran yang kesembilan dengan peratusan penurunan berat komposit membran sokongan yang diimpregnasi yang rendah (8%). Penemuan kajian ini telah menunjukkan bahawa proses SLM yang mampan dan stabil telah berjaya dibangunkan untuk penyingkiran dan perolehan ion nikel daripada air sisa penyaduran.

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LIST OF ABBREVIATIONS

AAS	-	Atomic Absorption Spectroscopy
ANOVA	-	Analysis of variance
BBD	-	Box Behnken design
BLM	-	Bulk liquid membrane
DoE	-	Design of experiment
DS	-	Degree of sulfonation
ED	-	Electrodialysis
ELM	-	Emulsion liquid membrane
ENP	-	Electroless nickel plating
FFD	-	Fractional factorial design
FO	-	Forward osmosis
FSSLM	-	Flat sheet supported liquid membrane
HFSLM	-	Hollow fiber supported liquid membrane
H^1NMR	-	Hydrogen nuclear magnetic resonance
HSAB	-	Hard soft acid base
IC	-	Ion Chromatography
IEC	-	Ion exchange capacity
LLE	-	Liquid liquid extraction
LM	-	Liquid membrane
MS	-	Mean square
MWCO	-	Molecular weight cut off
RSM	-	Response surface methodology
SEM	-	scanning electron microscopy
SLM	-	Supported liquid membrane
SSR	-	Sum of square of regression
TFC	-	Thin film composite
W/O	-	Water-in-oil
W/O/W	-	Water-in-oil-in-water

LIST OF SYMBOLS

ppm	-	Part per million
wt %	-	Weight percent
v/v	-	Volume per volume
R^2	-	Coefficient of determination
J	-	Flux
A	-	Effective area of membrane
ε	-	Porosity of the membrane
P	-	Permeability coefficient
τ	-	Tortuosity of the membrane
C_{aq}	-	Final concentration of nickel ions in the feed phase
C_{org}	-	Nickel concentration in organic phase after extraction
C_i	-	Initial concentration of nickel ion in the feed phase
C_s	-	Concentration of the nickel ions in the stripping phase
d_{aq}	-	Thickness of aqueous boundary layer
D_{org}	-	Diffusion coefficient of the nickel-carrier complex across the membrane
$D_{org,b}$	-	Diffusion coefficient of the nickel-carrier complex in the bulk organic phase
$Df_{regression}$	-	Degree of freedom of regression
$Df_{residual}$	-	Degree of freedom of residual
J_{org}	-	Diffusional flux of nickel ion from bulk of feed phase to the aqueous stagnant layer in the membrane phase
J_{aq}	-	Diffusional flux of nickel ion from bulk of feed phase to the aqueous stagnant layer in the feed–membrane interface
K_{eq}	-	Equilibrium constant
K_{aq}	-	Mass transfer coefficient of nickel ion at the feed solution-membrane interface
K_{org}	-	Mass transfer coefficient of nickel ion in the membrane phase
m_0	-	Weights of the dry membrane support
m_1	-	Weights of wet membrane support
m_2	-	Weights of used membrane support

V_F	-	Volume of aqueous feed phase
W_{wet}	-	Weights of wet SPEEK
W_{dry}	-	Weights of dry SPEEK
δ_{eff}	-	Effective thickness of the membrane
Δ_{aq}	-	Transport resistance of the diffusion across aqueous feed boundary layer
Δ_{org}	-	Transport resistance of the diffusion across aqueous membrane phase

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Electroplating process involves a metal surface coating that is performed via electrodeposition or electroless deposition to provide anticorrosion, high mechanical strength, decorative and so forth. Anyhow, electroplating industry is known as one of the heavy metal dischargers to the environment since they are consuming a high volume of water in various steps of the process. Nickel appears as one of the hazardous and toxic heavy metals that which is heavily utilized in the electroplating industry. Through electroless nickel plating (ENP) process, nickel is deposited via chemical reduction by means of certain reducing agent. Commonly, the main components involves during ENP process are nickel sulfate, sodium hypophosphite and ammonium sulfate [1]. As reported by Coman *et al*. [2], about 5000 mg/L of nickel sulfate is added with certain proportions of reducing agents, hypophosphite compounds in the plating bath during the plating process. It is reported that the rinsewater from the nickel plating industries have nickel concentrations from 900 to 1583 mg/L of nickel in the concentrated stream [3-4]. Based on the standard discharge limit of industrial effluents in Malaysia, the allowable discharge concentration of nickel is 1.0 mg/L [5]. Uncontrolled discharge beyond limited concentrations of nickel into the water body may lead to the severe impact since the heavy metal is amongst the pollutants that build up in the food chain which responsible for the adverse effects especially towards aquatic organisms. As for human being, the severe damages can occur to the lungs and kidneys, causing gastrointestinal distress, nausea, vomiting, diarrhoea, pulmonary fibrosis, renal oedema, and skin dermatitis [6-7].

Liquid membrane (LM) technology has been introduced as one of the potential methods to preserve the environment in terms of the removal and recovery of various metal ions. Many researchers found that LM technology offers a great potential with an advanced technique for solutes extraction compared to the solvent extraction method. This technology provides a simple method of operation, fast, energy saving and uses less chemicals [8-11]. The transport mechanism of LM technology is basically the same as that found in solvent extraction, but the transport is governed by kinetic (nonequilibrium mass transfer) rather than equilibrium parameters. Principally, liquid membrane system represents an immiscible liquid that functions as a semipermeable barrier between the two liquid or gas phases which acts as a feed and stripping phases, respectively. Meanwhile, the transport of a targeted solute in LM system considering only diffusional process [12]. The solute ion dissolves in the liquid membrane phase, hence diffusing across the liquid membrane phase due to an imposed concentration gradient. Indeed, the different solute ion favors different solubility and diffusion coefficient in the liquid membrane phase. The efficiency and selectivity can be improved in the presence of the carrier which reacts rapidly and reversibly with the targeted solute. Additionally, liquid membrane technology is a process which occurs due to a chemical potential gradient, not by equilibrium between phases [13]. Theoretically, there are three types of LM technology namely, bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM).

SLM is defined as liquid membrane phase containing carrier and diluent that is immobilized or impregnated in the pores of the thin microporous polymer support [14]. This type of configuration has been extensively employed for the removal and recovery of various organic compounds [15], heavy metals [16] and precious metals [17]. Carrier and diluent are two important components in the liquid membrane phase. The carrier aids the transportation of metal ions from the feed-membrane interface towards membrane-stripping interface by forming complexation with the targeted solute ion. Therefore, the high selectivity of targeted solute in SLM is depending on the selection of the good carrier that is highly chosen based on the type of the desired solute extracted. Apart from that, diluent also another major constituent used in LM formulation since it acts as a medium to reduce the viscosity of the liquid membrane phase. Conventionally, the petroleum based diluent is commonly used in LM phase namely kerosene, hexane, toluene and so forth. This type of diluent is classified as non-renewable, flammable, difficult to handle, easily volatile and hazardous to humans and aquatic life [18-20]. Interestingly, the application of vegetable oils such as sesame oil, coconut oil, palm oil and corn oil in LM technology have been reported by previous researchers [21-25]. This green diluent normally possess low melting point, low specific gravity, high flash point, non-volatile as well as low dielectric constant values (~3) which makes them non-polar [26].

Other than that, in SLM, there are many types of polymeric support are used namely Teflon material [27], polypropylene (PP) [28] and polyvinylidenedifluoride (PVDF) [29-31]. In terms of the stability, the loss of the liquid membrane phase that forced out from the membrane support pores is a common problem encountered by SLM as well as interrupting the lifetime of SLM. Such behaviour can be caused by the solubility of carrier and diluent to the adjacent aqueous phase, blockage of support pores by the carrier, pressure difference over membrane and others [32-34]. Thus, the selection of the suitable membrane support is very crucial in minimizing the instability problem during SLM process. Apart from that, the modification of the membrane support has been paid attention among the researchers to reduce the SLM instability by reducing the liquid membrane phase loss. These consists of the addition of the coating layer on the membrane support [35], ion exchange membrane [36], interfacial polymerization coating [37], and composite membrane with the hydrophilic and hydrophobic layer [38-39].

1.2 Problem Statements

The release behaviour of nickel ion above the standard discharge limit can cause the troublesome to the environment. Hence, prior to discharging, the removal of nickel from the spent electroplating wastewater solutions according to the required standard is extremely recommended. Several potential methods were introduced for the nickel extraction include precipitation, ion exchange, electrochemical, electrolysis and electro winning. Though, these methods come with some drawbacks such as high operational costs of the treatment as well as high disposal of the residual metal sludge [40-45]. Meanwhile, ion exchange and adsorption are limited by the capacity of ion exchange and adsorption, respectively. Normally they are used for low concentration wastewater treatments in the range of 100 to 200 mg/L [2, 3, 46-47]. Additionally, the saturated adsorbents and ion exchange resins are still annoying problems [40].The aforementioned methods introduced mostly focus on the removal part. Hence, SLM with the main advantages of simultaneous removal and recovery is highly favored for the extraction and recovery of nickel from the electroplating wastewater. Mostly, the researchers seem to focus on the simulated wastewater instead of working with the real one [48-49]. Thus, in this current study, the real nickel electroplating wastewater was employed as a feed phase.

The extraction of nickel from weak acidic medium has been widely carried out using organophosphorus and hydroxyoximes carriers but experiences slow kinetic, small loading capacity and slow phase separation [11, 48-50]. Hence, the use of mixed carrier is gaining attention to overcome the problems arises when utilizing the single carrier. The mixture of organophosphorus and hydroxyoximes carrier produces a highly stable nickel-carrier complexes that provides very slow decomplexation for stripping process in SLM [34, 48-49, 57, 72, 173]. The mixture involving both organophosphorus carriers is unsuitable as this mixture might interrupt the dissociation constant of the carrier, hence leading to the nickel extraction inefficiency [53, 57]. The mixture of organophosphorus and basic carrier only improves the stripping kinetic not extraction [61-62]. On the other hand, the mixture of organophosphorus and solvating carrier (alcohol) can improved both extraction and stripping ability as it can modify the structure of the organophosphorus carrier [53]. Thus, a new approach was made in this study regarding the utilization of mixture of carriers containing organophosphorus and alcohol for improving the nickel extraction efficiency. To the best of our knowledge, there is no work reported yet regarding the combination of organophosphorus and alcohol to synergistically increase the nickel ion extraction.

In addition, the common diluents used in the supported liquid membrane process are typically flammable, volatile and toxic, thus leading to environmental and safety risks [25]. Thus, as a way to promote a sustainable SLM process, an environmentally friendly and biodegradable diluent (cooking palm oil) was incorporated into the LM formulation for SLM process since it is capable of reducing the toxicity effects, and non-hazardous. Other sustainable diluents that less viscous as well as providing almost similarities with palm oil such as soybean, canola, sunflower, and corn oil provide higher price compared to the palm oil [54]. Advantageously, palm oil provides high availability due to the large palm oil community in Malaysia. Since palm oil is used in a small volume and recyclable in the SLM process, there is no conflict issue with the food demand.

One of the main problems concerning SLM is their instability due to the loss of carrier solution to the adjacent feed and stripping phases which has an influence on both flux and selectivity of the SLM. Due to this limitation, SLM is quite difficult to be scaled up to industrial level. Several researchers have stabilized SLM using some methods such as gelation, interfacial polymerization coating, and composite membrane using hydrophilic layer [35, 37-39]. However, the flux tends to decrease due the open structure of the gel network while the interfacial polyamine coating layer only allows the free transport of nitrate ions but not for the carrier. Beside the hydrophilic layer is limited by the low mechanical strength. A development of composite membrane support containing SPEEK provides the high permeability and flux of targeted solute since SPEEK rich with fixed negative charges that can improve the permeability and flux of the metal ion through the membrane support [56]. However, the high penetration of SPEEK through some pores of the thin membrane support (25µm thickness) experiences undesired selectivity loss.

Thus, in this present study, a new composite membrane support consisting of SPEEK and PVDF (125µm thickness) was developed. This study was focusing on the use of SPEEK as a stabilization layer to reduce the liquid membrane loss in SLM extraction of nickel. The high thickness of PVDF membrane enable to minimize the deeper penetration of SPEEK into the membrane support as well as reducing the selectivity loss of nickel. Meanwhile, LM containing of palm oil impregnated in the composite membrane support also has the ability to increase the membrane support resistance as well as retaining the liquid membrane from leaching out into the aqueous feed and stripping phase [23,184-186]. The combination of these two features in this present work reduced the liquid membrane loss as well as extending the lifetime of the SLM process and become more reliable for application in the industrial level. To the best of our knowledge, there is no work reported yet regarding the use of composite

SPEEK/PVDF impregnated with palm oil for overcoming liquid membrane loss for SLM extraction of nickel.

In addition, the efficiency of SLM process for nickel extraction was investigated using several parameters such as carrier, synergist carrier and stripping agent concentrations and flow rate of feed and stripping phases. The optimization of these process parameters was carried out using response surface methodology (RSM) method to find the relationship among the parameters towards nickel extraction. In addition, in terms of the economic prospective, the membrane support recycling was also investigated.

1.3 Research Objectives

This research contributes four objectives as below:

a) To formulate the liquid membrane component for nickel ion extraction from electroplating wastewater using liquid-liquid extraction (LLE) process
b) To optimize the parameters influencing the performance of nickel ion extraction using response surface methodology (RSM) method in SLM
c) To investigate the potential of incorporating cooking palm oil as a diluent in SLM process
d) To evaluate the stability of SLM process using composite membrane support

1.4 Research Scopes

The first objective addresses the screening of liquid membrane formulation for the extraction and stripping of nickel ion using LLE process. Several types of carriers such as acidic, basic and solvating carriers (Di (2-ethylhexyl) phosphoric acid

(D2EHPA), Diisooctylthiophosphinic acid (Cyanex 302), Tridodecylamine (TDA) and octanol) and stripping agents (sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3)) were investigated to choose a suitable SLM formulation that can efficiently extract and strip the nickel ion from the nickel electroplating wastewater, respectively. In terms of the carrier selection, acidic carriers (D2EHPA and Cyanex 302) were investigated as they are organophosphorus carriers with high dissociation constant that are widely used for nickel extraction from low pH aqueous solution [53, 57]. Meanwhile, the basic carrier (TDA) was tested since there are works that reported on the utilization of amine based carrier for nickel plating solution [58, 60]. As for solvating carrier, it is reported that they cannot extract nickel from acid solution but helped improving the cation extraction via synergistic effect with the main carrier. The solvating carriers of alcohol group (octanol) was examined to compare the extraction result of using the single solvating (as a reference) with the one using the mixture of acidic-solvating carrier for nickel extraction. On the other hand, the carrier synergism was carried out through the combinations two carrier namely acidic-acidic, acidic-basic, and acidic-solvating carriers. The combination of two acidic phosphorus carriers was performed as both D2EHPA and Cyanex 302 were capable of extracting nickel from slightly acidic wastewater [95, 174]. Then, the mixture of acidic-basic carriers (D2EHPA-TDA) was investigated as some studies reported that the binary extraction systems of acidic-basic carriers have been used to selectively extract nickel in acidic chloride and sulfate solutions to improve the stripping efficiency [61-62]. Besides, the cooperation of acidic-solvating carriers was investigated as it is reported that the binary extraction was also obtained from the mixture of acidic and solvating carriers on the extraction of metal cation [53]. Subsequently, the feasibility of the cooking palm oil as a substitute green solvent was investigated by incorporating the palm oil as diluent in the liquid membrane formulation for nickel extraction.

Next, in order to successfully achieve the second objective, the formulation obtained from LLE was applied in SLM process for the screening and optimization of several significant process parameters influencing nickel ion extraction using response surface methodology (RSM) method which are fractional factorial design (FFD) and Box Behnken design (BBD), respectively. A total of 8 and 27 experimental runs were performed during the screening and optimization process, respectively.

The parameters involve namely carrier concentration (0.5-2.0M), synergist carrier concentration (5-25 % (v/v)), stripping agent concentration (0.50-3.0M) as well as flow rates of feed and stripping phases (50-100 mL/min). The regression model obtained for both screning and optimization were validated using analysis of variance (ANOVA). Through the screening process, the aforementioned parameters were evaluated in terms of the degree of significance effect. Subsequently, for the next optimization study, the selected significant parameters from screening part were optimized to obtain the optimum conditions for the extraction of nickel. Additionally, the individual and interaction effect among parameters also can be evaluated using three dimensional (3D) surface plot. Next, the kinetic permeation of nickel through SLM also was studied for better understanding the mass transfer of nickel through SLM. The experimental results were used to estimate the diffusional parameters involve namely transport resistance of the diffusion across aqueous feed boundary layer (Δ_{aq}) and membrane phase (Δ_{org}), mass transfer coefficient of nickel ion at the feed-membrane interface (K_{aq}) and membrane phase (K_{org}), and diffusion coefficient of the nickel-carrier complex across the membrane (D_{org}). The third objective highlights an initiative to promote a sustainable development in SLM process by investigating the impact of substituting a cooking palm oil in the SLM formulation for nickel extraction. In this part, the ratios of palm oil to kerosene were ranged from 0 to 100%. Also, the variations of permeability, flux and liquid membrane phase loss as a function of different diluent compositions were determined to examine the extraction, recovery and stability performance.

Last but not least, in order to overcome the stability of the membrane support in SLM, the composite membrane containing sulfonated poly (ether ether ketone) (SPEEK) layer has been developed. SPEEK was produced through sulfonation of PEEK polymer using sulfonation conditions from literature [63]. The degree of sulfonation (DS) of SPEEK was determined using Hydrogen Nuclear Magnetic Resonance (H^1NMR) analysis. Meanwhile, the PVDF membrane was pretreated with fuming sulfuric acid to increase the hydrophilicity for better adhesion with SPEEK [56]. The composite membrane was characterized using scanning electron microscopy (SEM). Next, the stability performance of composite membrane support was evaluated by observing several parameters namely configuration types of SPEEK (feed and stripping sides) and different thicknesses of SPEEK layer. Also, the permeability, flux and liquid membrane phase loss were studied to examine the performance of the composite membrane support. Finally, the recycling of the composite membrane support also was carried out to evaluate the SLM lifetime during continuous SLM extraction of nickel ion.

1.5 Significance of Study

The removal of the hazardous nickel ion from the wastewater is highly necessary to reduce the toxicity effect as well as increasing the quality of water. In order to achieve this goal, supported liquid membrane (SLM) appears as one of the promising methods which possesses multiple advantages of single step of extraction and recovery process, simple operation, uses less chemicals and high separation factor with energy and cost saving. Additionally, the utilization of cooking palm oil as a green substitute diluent as well as replacing the petroleum based diluent (kerosene) enable to promote high prospective for sustainable SLM process as well as offering a better insight in the separation process that deals with an environmentally friendly materials in the future. Besides the development of the composite membrane is capable of overcoming the instability problem as well as enhancing the SLM lifetime which make it highly possible for the industrial application.

1.6 Thesis Outline

This thesis composed of five chapters which embodies the research works in a sequential order. Firstly, Chapter one introduces the research background, problem statement, research objectives, research scopes, significant of research as well as thesis outline. Next, Chapter two describes the detailed review of nickel in the electroplating industry, method of nickel extraction, LM technology, SLM technology, SLM configurations, material of membrane support in SLM, liquid membrane loss, improvement of SLM stability, SPEEK, liquid membrane formulation, parameters affecting SLM, and kinetic permeation of metal ion in SLM. Henceforth, Chapter three includes all the materials and reagents used together with the methods involved in the present work. These methods include wastewater characterization, LM formulation, SLM rig set up, screening and optimization of SLM parameters, kinetic permeation study, and approach of green process as well as stability of composite SPEEK-PVDF membrane. Subsequently, Chapter four addresses the results along with the discussion as well as achieving the objectives of this research. Lastly, Chapter 5 draws the conclusions and recommendations for future work.

REFERENCES

1. Bulasara, V. K., Abhimanyu, M. S., Pravav, T., Uppaluri, R. and Purkait, M. K. Performance characteristics of hydrothermal and sonication assisted electroless plating baths for nickel-ceramic composite membrane fabrication. *Desalination*. 2012. 284:77-85.
2. Coman, V., Robotin, B. and Ilea, P. Nickel recovery/removal from industrial wastes: A review. *Resources, Conservation and Recycling*. 2013.73: 229-238.
3. Priya, P. G., Basha, C. A., Ramamurthi, V. and Begum, S. N. Recovery and reuse of Ni (II) from rinsewater of electroplating industries. *Journal of Hazardous Materials*. 2009.163:899-909.
4. Lu, H., Wang, Y. and Wang, J. Recovery of Ni^{2+} and pure water from electroplating rinse wastewater by an integrated two-stage electrodeionization process. *Journal of Cleaner Production*. 2015. 92:257-266.
5. Department of Environment. *Environmental Quality Report (Industrial Effluent) Regulations*. Malaysia, P.U. (A) 434. 2009.
6. Lu, H., Wang, Y. and Wang, J. Removal and recovery of Ni^{2+} from electroplating rinse water using electrodeionization reversal. *Desalination*. 2014. 348:74-81.
7. Agrawal, A. and Sahu, K. K. An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries. *Journal of Hazardous Materials*. 2009. 171: 61-75.
8. Kumbasar, R. A. Selective extraction of cobalt from strong acidic solutions containing cobalt and nickel through emulsion liquid membrane using TIOA as carrier. *Journal of Industrial and Engineering Chemistry*. 2012.18: 2076-2082.
9. Surucu, A., Eyupoglu, V. and Tutkun, O. Selective separation of cobalt and nickel by flat sheet supported liquid membrane using Alamine 300 as carrier. *Journal of Industrial and Engineering Chemistry*. 2012.18: 629-634.
10. Ahmad, A. L., Shah Buddin, M. M. H. and Ooi, B. S. Extraction of Cd (II) ions by emulsion liquid membrane (ELM) using Aliquat 336 as carrier. *American Journal of Chemistry*. 2015. 5(3A):1-6.

11. Eyupoglu, V. and Kumbasar, R. A. Extraction of Ni (II) from spent Cr-Ni electroplating bath solutions using LIX 63 and 2BDA as carriers by emulsion liquid membrane technique. *Journal of Industrial and Engineering Chemistry*. 2015. 21:303-310.
12. Alguacil, F. J., Alonso, M., Lopez, F.A. and Lopez-Delgado, A. Active transport of cobalt (II) through a supported liquid membrane using the mixture DP8R and Acorga M5640 as extractant. *Desalinatio*n. 2011.281:221-225.
13. Kislik, V. S. *Liquid membrane: principles and applications in chemical separations and wastewater treatment*. 1st edn. Amsterdam: Elsevier.2010
14. Azzoug, S., Arous, O. and Kerdjoudj, H. Metallic ions extraction and transport in supported liquid membrane using organo-phosphoric compounds as mobile carriers. *Journal of Environmental Chemical Engineering*. 2014. 2:154-162.
15. Harruddin, N., Othman, N., Lim Ee Sin, A. and Sulaiman, R.N.R. Selective removal and recovery of Black B reactive dye from simulated textile wastewater using the supported liquid membrane process. *Environmental Technology*. 2015. 36(3): 271-280.
16. Religa, P., Rajewski, J., Gierycz, P. and Swietlik, R. Supported liquid membrane system for Cr (III) separation from Cr (III)/Cr (VI) mixtures. *Water Science Technology*. 2014. 69(12): 2476-2481.
17. Ruhela, R., Panjab, S., Sharma, J. N., Tomar, B. S., Tripathi, S. C., Hubli, R. C. and Suri, A. K. Facilitated transport of Pd (II) through a supported liquid membrane (SLM) containing N-N-N-N-tetra-(2-ethylhexyl) thiodiglycolamide T(2EH)TDGA: a novel carrier. *Journal of Hazardous Materials*. 2012. 229-230: 66-71.
18. Zidi, C., Tayeb, R. and Dhahbi, M. Extraction of phenol from aqueous solutions by means of supported liquid membrane (MLS) containing tri-n-octyl phosphine oxide (TOPO). *Journal of Hazardous Materials*. 2011.194, 62-68.
19. Mahmoud, M. H. H. Effective separation of iron from titanium by transport through TOA supported liquid membrane. *Separation and Purification Technology*. 2012. 84: 63-71.
20. Othman, N., Harruddin, N., Idris, A., Ooi, Z. Y., Fatiha, N. and Sulaiman, R. N. R. Fabrication of polypropylene membrane via thermally induced phase separation as a support matrix of tridodecylamine supported liquid membrane

for Red 3BS dye removal. *Desalination and Water Treatment*. 2016. 57:12287-12301.

21. Bhatluri, K. K., Manna, M. S., Saha, P. K. and Ghoshal, A. K. Supported liquid membrane-based simultaneous separation of cadmium and lead from wastewater. *Journal of Membrane Science*. 2014. 459:256-263.
22. Ahmad, A. L., Shah Buddin, M. M. H., Ooi, B. S. and Kusumastuti, A. Cadmium removal using vegetable oil based emulsion liquid membrane (ELM): Membrane breakage investigation. *Jurnal Teknologi (Sciences & Engineering)* 2015. 5(1): 39-46.
23. Chakrabarty, K., Saha, P. and Ghoshal, A. K. Separation of mercury from its aqueous solution through supported liquid membrane using environmentally benign diluent. *Journal of Membrane Science*. 2010. 350: 395-401.
24. Björkegren, S., Karimi, R. F., Martinelli, A., Jayakumar, N. S. and Hashim, M. A. A new emulsion liquid membrane based on a palm oil for the extraction of heavy metals. *Membranes*. 2015. 5:168-179.
25. Kazemi, P., Peydayesh, M., Bandegi, A., Mohammadi, T. and Bakhtiari, O. Stability and extraction study of phenolic waste water treatment by supported liquid membrane using tributhylphosphate and sesame oil as liquid membrane. *Chemical Engineering Research and Design*. 2014. 92: 375-383.
26. Chang, S. H. Vegetable oil as organic solvent for wastewater treatment in liquid membrane processes. *Desalination and Water Treatment*. 2014. 52: 88-101.
27. Altin, S., Yildirim, Y. and Altin, A. Transport of silver ions through a flat-sheet supported liquid membrane. *Hydrometallurgy*. 2010.103: 144-149.
28. Rehman, S., Akhtar, G. and Chaudry, M. A. Coupled transport of Tl^{3+} through triethanolamine-xylene-polypropylene supported liquid membranes. *Journal of Industrial and Engineering Chemistry*. 2012. 18: 492-498.
29. Raut, D. R., Mohapatra, P. K. and Manchanda, V. K. A highly efficient supported liquid membrane system for selective strontium separation leading to radioactive waste remediation. *Journal of Membrane Science*. 2012. 390-391: 76-83.
30. Alguacil, F. J., Diaz, I. G. and Lopez, F. Transport of Cr (VI) using an advanced membrane technology and ($PJMTH^+NO_3^-$) ionic liquid derived from amine

Primene JMT as green chemicals. *Desalination and Water Treatment*. 2013. 51: 7201-7207.

31. Miguel, E. R., Vital, X. and Gyves, J. Cr (VI) transport via a supported ionic liquid membrane containing CYPHOS IL101 as carrier: System analysis and optimization through experimental design strategies. *Journal of Hazardous Materials*. 2014. 273:253-262.
32. Kemperman, A. J. B., Bargeman, D., Van Den Boomgaard, T. and Strathmann, H. Stability of supported liquid membranes: State of the art. *Separation Science and Technology*. 1996. 31: 2733-2762.
33. Zhao, W., He, G., Nie, F., Zhang, L., Feng, H. and Liu, H. Membrane liquid loss mechanism of supported ionic liquid membrane for gas separation. *Journal of Membrane Science*. 2012. 411-412: 73- 80.
34. Zhang, P., Yokoyama, T., Suzuki, T. M. and Inoue, K. The synergistic extraction of nickel and cobalt with a mixture of di-2-ethylhexyl-phosphoric acid and 5-dodecylsalicylaldoxime. *Hydrometallurgy*. 2001. 37: 223-227.
35. Neplenbroek. A. M., Bargeman, D. and Smolders, C.A. Supported liquid membranes: stabilization by gelation. *Journal of Membrane Science*. 1992. 67: 149-165.
36. Kedem, O. and Bromberg, L. Ion-exchange membranes in extraction processes. *Journal of Membrane Science*. 1993.78: 255-264.
37. Kemperman, A. J. B., Rolevink, H. H. M., Bargeman, D., Boomgaard, T. and Strathmann, H. Stabilization of supported liquid membranes by interfacial polymerization top layers. *Journal of Membrane Science*. 1998. 138: 43-55.
38. Song, J., Mei Li, X., Bi, J., Li, Z., Zhang, M., Yin, Y., Zhao, B., Kong, D., Chen, G. and He, T. Stabilization of composite hollow fiber nanofiltration membranes with a sulfonated poly (ether ether ketone) coating. *Desalination*. 2015. 355, 83-90.
39. Song, J., Niu, X., Lia, X. and He, T. Selective separation of copper and nickel by membrane extraction using hydrophilic nanoporous ion-exchange barrier membranes. *Process Safety and Environmental Protection*. 2018. 113:1-9.
40. Li, L., Takahashi, N., Kaneko, K., Shimizu, T. and Takarada, T. A novel method for nickel recovery and phosphorus removal from spent electroless nickel-plating solution. *Separation and Purification Technology*. 2015.147: 237-244.

41. Mubarok, M. Z. and Lieberto, J. Precipitation of nickel hydroxide from simulated and atmospheric-leach solution of nickel laterite ore. *Procedia Earth and Planetary Science*. 2013. 6: 457-464.
42. Han, H., Sun, W., Hu, Y., Cao, X., Liu, R. and Yue, T. Magnetite precipitation for iron removal from nickel-rich solutions in hydrometallurgy process. *Hydrometallurgy*. 2016.165: 318-322.
43. Peng, C., Jin, R., Li, G., Li, F. and Gu, Q. Recovery of nickel and water from wastewater with electrochemical combination process. *Separation and Purification Technology*. 2014. 136: 42-49.
44. Pinto, I. S. S., Sadeghi, S. M. and Soares, H. M. V. M. Separation and recovery of nickel, as a salt, from an EDTA leachate of spent hydrodesulphurization catalyst using precipitation methods. *Chemical Engineering Science*. 215. 122: 130-137.
45. Yun, X., Liansheng, X., Jiying, T., Zhaoyang, L. and Li, Z. Recovery of rare earths from acid leach solutions of spent nickel-metal hydride batteries using solvent extraction. *Journal of Rare Earths*. 2015. 33(12):1348-1354.
46. Hui, T. S. and Zaini, M. A. A. Isotherm studies of methylene blue adsorption onto potassium salts-modified textile sludge. *Jurnal Teknologi (Sciences & Engineering)*. 2015. 74(7): 57-63
47. Tang, S. H. and Zaini, M. A. A. Malachite green adsorption by potassium salts-activated carbons derived from textile sludge: Equilibrium, kinetics and thermodynamics studies. *Asia-Pacific Journal of Chemical Engineering*. 2017.12:159-172.
48. Eyupoglu, V. and Kumbasar, R. A. Selective and synergistic extraction of nickel from simulated Cr-Ni electroplating bath solutions using LIX 63 and D2EHPA as carriers. *Separation Science and Technology*. 2014. 49, 2485-2494.
49. Eyupoglu, V., Kumbasar, R. A. and Isik, M. Performance evaluation of nickel separation and extraction process from simulated spent Cr/Ni electroplating bath solutions by ELM process using LIX63 and PC88A. *Journal of Dispersion Science and Technology*. 2015. 36:1309-1319.
50. Begum, N., Bari, F., Jamaludin, S. B. and Hussin, K. Solvent extraction of copper, nickel and zinc by Cyanex 272. *International Journal of Physical Sciences*. 2012. 7(22): 2905-2910.

51. Park, K. H., Reddy, B. R., Jung, S. H. and Mohapatra, D. Transfer of cobalt and nickel from sulphate solutions to spent electrolyte through solvent extraction and stripping. *Separation and Purification Technology*. 2006. 51: 265-271.
52. Liu, Y. and Lee, M. Separation of Co and Ni from a chloride leach solutions of laterite ore by solvent extraction with extractant mixtures. *Journal of Industrial and Engineering Chemistry*. 2015. 28:322-327.
53. Zhang, G., Chen, D., Zhao, W., Zhao, H., Wang, L., Wang, W. and Qi, T. A novel D2EHPA-based synergistic extraction system for the recovery of chromium (III). *Chemical Engineering Journal*. 2016. 302: 233-238.
54. Abdullah, R. An analysis of trends of vegetable oil price and some factor affecting CPO price. *Oil Palm Industry Economic Jurnal*. 2013.13:1-14.
55. Auimviriyavat, J., Changkhamchom, S. and Sirivat, A. Development of poly (ether ether ketone) (PEEK) with inorganic filler for direct methanol fuel cells (DMFCS). *Industrial and Engineering Chemistry Research*. 2011. 50: 12527-12533.
56. Wijers, M. C., Jin, M., Wessling, M. and Strathmann, H. Supported liquid membranes modification with sulphonated poly (ether ether ketone): Permeability, selectivity and stability. *Journal of Membrane Science*. 1998. 147: 117-130.
57. Chauhan, S. and Patel, T. A review on solvent extraction of nickel. *International Journal of Engineering Research & Technology*. 2014. 3(9): 1315-1322.
58. Bukhari, N., Chaudry, M. A. and Mazhar, M. Triethanolamine-cyclohexanone supported liquid membranes study for extraction and removal of nickel ions from nickel plating wastes. *Journal of Membrane Science*. 2006. 283: 182-189.
59. Mubeena, K. and Muthuraman, G. Solvent extraction technique for removal and recovery of nickel from effluent by Trimethylamine as a carrier. *International Journal of Science, Engineering and Technology Research* (IJSETR). 2015. 4(1): 128-137.
60. Jung, M. J., Venkateswaran, P. and Lee, Y. S. Solvent extraction of nickel(II) ions from aqueous solutions using triethylamine as extractant, *Journal of Industrial and Engineering Chemistry*. 2008. 14:110-115.

61. Bourget, C., Jakovljevic, B. and Nucciarone, D. Cyanex(R) 301 binary extractant systems in cobalt/nickel recovery from acidic sulphate solutions, *Hydrometallurgy*. 2005 77(3): 203-218.
62. Jakovljevic, B., Bourget, C. and Nucciarone, D. Cyanex(R) 301 binary extractant systems in cobalt/nickel recovery from acidic chloride solutions, *Hydrometallurgy*. 2004. 75(1): 25-36.
63. Awang, N., Jaafar, J., Ismail, A. F., Othman, M. H. D., Rahman, M. A., Yusof, N., Aziz, F., Salleh, W. N. W., Suradi, S. S., Ilbeygi, H., Wan Mohd Noral Azman, W. N. E. and Arthanareeswaran, G. Development of dense void-free electrospun SPEEK-Cloisite15A membrane for direct methanol fuel cell application: Optimization using response surface methodology. *International Journal of Hydrogen Energy*. 2017. 42: 26496-26510.
64. Babu, B. R., Bhanu, S. U. and Meera, S. Waste minimization in electroplating industries: a review. *Journal of Environmental Science and Health Part C*. 2009. 27: 155-177.
65. Hosseini, S. S., Bringas, E., Tan, N. R., Ortiz, I., Ghahramania, M. and Shahmirzadi, M. A. A. Recent progress in development of high performance polymeric membranes and materials for metal plating wastewater treatment: a review. *Journal of Water Process Engineering*. 2016. 9: 78-110.
66. Qin, J. J., Oo, M. H., Wai, M. N., Ang, C. M., Wong, F. S. and Lee, H. A dual membrane UF/RO process for reclamation of spent rinses from a nickel-plating operation-a case study. *Water Research*. 2003.37: 3269-3278.
67. Singh, V., Ram, C. and Kumar, A. Physico-chemical characterization of electroplating industrial effluents of Chandigarh and Haryana region. *Journal of Civil and Environmental Engineering*. 2016. 2(4): 1-6.
68. Sivakumar, D., Nouri, J., Modhini, T.M. and Deepalakshmi, K. Nickel removal from electroplating industry wastewater: A bamboo activated carbon. *Global J. Environ. Sci. Manage*. 2018. 4(3): 325-338.
69. Salem, N. M. and Awwad, A. M. Biosorption of Ni(II) from electroplating wastewater by modified (Eriobotrya japonica) loquat bark. *Journal of Saudi Chemical Society*. 2014. 18: 379-386.
70. Wijers, M. C., Jin, M., Wessling, M. and Strathmann, H. Limitations of the lifetime stabilization of supported liquid membrane by polyamides layers. *Separation and Purification Technology*. 1999. 17: 147-157.

71. Chen, C. S., Shih, Y., Huang, Y. and Huang, G. Recovery of nickel with the addition of boric acid using an electrodeposition reactor TOPO. *Desalination and Water Treatment*. 2011.32:345-350.
72. Cheng, C. Y., Barnad, K. R., Zhang, W., Zhu, Z. and Pranolo, Y. Recovery of nickel, cobalt, copper and zinc in sulphate and chloride solutions using synergistic solvent extraction. *Chinese Journal of Chemical Engineering*. 2016. 24:237-248.
73. Ruiz, A. F. J., Caballero, F., Cruz-Díaz, M. R., Rivero, E. P., Vazquez-Arenas, J. and Gonzalez, I. Nickel recovery from an electroplating rinsing effluent using RCE bench scale and RCE pilot plant reactors: the influence of pH control. *Chemical Engineering Research and Design*. 2015. 97:18- 27.
74. Kwon, T. and Jeon, C. Adsorption characteristics of sericite for nickel ions from industrial waste water. *Journal of Industrial and Engineering Chemistry*. 2013. 19(1): 68-72.
75. Benvenuti, T., Krapf, R. S., Rodrigues, M. A. S., Bernardes, A. M. and Ferreira, Z. Recovery of nickel and water from nickel electroplating wastewater by electrodialysis. *Separation and Purification Technology*. 2014.129:106-112.
76. Kumbasar, R. A. Selective transport of cobalt (II) from ammoniacal solutions containing cobalt (II) and nickel (II) by emulsion liquid membranes using 8-hydroxyquinoline. *Journal of Industrial and Engineering Chemistry*. 2012.18: 145-151.
77. Othman, N., Noah, N. F. M., Shu, L. Y., Ooi, Z. Y., Jusoh, N., Idroas, M. and Goto, M. Easy removing of phenol from wastewater using vegetable oil-based organic solvent in emulsion liquid membrane process. *Chinese Journal of Chemical Engineering*. 2017. 25(1): 45-52.
78. Kocherginsky, N.M., Yang, Q. and Seelam, L. Recent advances in supported liquid membrane technology. Separation and Purification Technology.2007. 53 171-177.
79. Muthuraman, G. and Ibrahim, M. Use of bulk liquid membrane for the removal of Cibacron Red FN-R from aqueous solution using TBAB as a carrier. *Journal of Industrial and Engineering Chemistry*. 2013. 19, 444-449.
80. Soniya, M. and Muthuraman, G. Comparative study between liquid–liquid extraction and bulk liquid membrane for the removal and recovery of

methylene blue from wastewater. *Journal of Industrial and Engineering Chemistry*. 2015.30: 266-273.

81. Zhao, L., Fei, D., Dang, Y., Zhou, X. and Xiao, J. Studies on the extraction of chromium (III) by emulsion liquid membrane. *Journal of Hazardous Materials*. 2010. 178: 130-135.
82. Othman, N., Yi, O. Z., Zailani, S. N., Zulkifli, E. Z. and Subramaniam, S. Extraction of Rhodamine 6G Dye from liquid waste solution: study on emulsion liquid membrane stability performance and recovery. *Separation Science and Technology*. 2013. 48: 1177-1183.
83. Bhattacharyya, A., Mohapatra, P. K., Gadly, T., Raut, D. R., Ghosh, S. K. and Manchanda, V. K. Liquid–liquid extraction and flat sheet supported liquid membrane studies on Am(III) and Eu(III) separation using 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine as the extractant. *Journal of Hazardous Materials*. 2011. 195: 238-244.
84. Kumbasar, R. A. Selective extraction and concentration of chromium (VI) from acidic solutions containing various metal ions through emulsion liquid membranes using Amberlite LA-2. *Journal of Industrial and Engineering Chemistry*. 2010. 16: 829-836.
85. Kumbasar, R. A. Selective separation of chromium (VI) from acidic solutions containing various metal ions through emulsion liquid membrane using Trioctylamine as extractant. *Separation and Purification Technology*. 2008. 64: 56-62.
86. Eyupoglu, V., Surucu, A. and Kunduracioglu, A. Synergistic extraction of Cr (VI) from Ni (II) and Co (II) by flat sheet supported liquid membranes using TIOA and TBP as carriers. *Polish Journal of Chemical Technology*. 2015.17(2): 34-42.
87. Han, A., Zhang, H., Sun, J., Chuah, S. K. and Jaenicke, S. Investigation into bulk liquid membranes for removal of chromium (VI) from simulated wastewater. *Journal of Water Process Engineering*. 2017. 17: 63-69.
88. Nawaz, R., Ali, K., Ali, N. and Khaliq, A. Removal of chromium (VI) from industrial effluents through supported liquid membrane using Trioctylphosphine oxide as a carrier membrane process. *Journal of the Brazilian Chemical Society*. 2016. 27(1): 209-220.

89. Kumbasar, R. A. Extraction of cadmium from solutions containing various heavy metal ions by Amberlite LA-2. *Journal of Industrial and Engineering Chemistry*. 2010. 16: 207-213.
90. Mortaheb, H. R., Kosuge, H., Mokhtarani, B., Amini, M. H. and Banihashemi, H. R. Study on removal of cadmium from wastewater by emulsion liquid membrane. *Journal of Hazardous Materials*. 2009. 165: 630-636.
91. Koter, S., Szczepan'ski, P., Mateescu, M., Nechifor, G., Badalau, L. and Koter, I. Modelling of the cadmium transport through a bulk liquid membrane. *Separation and Purification Technology*. 2013. 107:135-143.
92. Kumbasar, R. A. Separation and concentration of cobalt from zinc plant acidic thiocyanate leach solutions containing cobalt and nickel by an emulsion liquid membrane using triisooctylamine as carrier. *Journal of Membrane Science*. 2009. 333:118-124.
93. Jafari, S., Yaftian, M. R. and Parinejad. M. Facilitated transport of cadmium as anionic iodo-complexes through bulk liquid membrane containing hexadecyltrimethylammonium bromide. *Separation and Purification Technology*. 2009.70: 118-122.
94. Kumbasar, R. A. Selective extraction of nickel from ammoniacal solutions containing nickel and cobalt by emulsion liquid membrane using 5, 7-dibromo-8-hydroxyquinoline (DBHQ) as extractant. *Minerals Engineering*. 2009. 22: 530-536.
95. Talebi, A., Teng, T. T., Alkarkhi, A. F. M. and Ismail, N. Nickel ion coupled counter complexation and decomplexation through a modified supported liquid membrane system. *Royal Society Chemistry Advance*. 2015.5: 38424-38434.
96. Kargari, A., Kaghazchi, T., Sohrabi, M. and Soleimani, M. Batch extraction of gold (III) ions from aqueous emulsion liquid membrane via facilitated carrier transport. *Journal of Membrane Science*. 2004. 233: 1-10.
97. Noah, N. F. M., Othman, N. and Jusoh, N. Highly selective transport of palladium from electroplating wastewater using emulsion liquid membrane process. *Journal of the Taiwan Institute of Chemical Engineers*. 2016. 64: 134-141.
98. Sulaiman, R. N. R., Othman, N. and Amin, N. A. S. Emulsion liquid membrane stability in the extraction of ionized nanosilver from wash water. *Journal of Industrial and Engineering Chemistry*. 2014. 20: 3243-3250.

99. Rehman, S., Akhtar, G. and Chaudry, M. A., Ali, K. and Ullah, N. Transport of Ag^{+} through tri-n-dodecylamine supported liquid membranes. *Journal of Membrane Science*. 2012. 389: 287-293.

100. Madaeni, S. S., Jamali, Z. and Islami, N. Highly efficient and selective transport of methylene blue through a bulk liquid membrane containing Cyanex 301 as carrier. *Separation and Purification Technology*. 2011.81:116-123.

101. Manzak, A. and Sonmezoglu, M. Extraction of acetic acid from aqueous solutions by emulsion type liquid membranes using Alamine 300 as a carrier. *Indian Journal of Chemical Technology*. 2010.17: 441-445.

102. Othman, N., Zailani, S. N. and Mili, N. Recovery of synthetic dye from simulated wastewater using emulsion liquid membrane process containing Tri-dodecyl amine as a mobile carrier. *Journal of Hazardous Materials*. 2011. 198, 103-112.

103. Daas, A. and Hamdaoui, O. Extraction of anionic dye from aqueous solutions by emulsion liquid membrane. *Journal of Hazardous Materials*. 2010. 178: 973-981

104. Lee, S. C. Extraction of succinic acid from simulated media by emulsion liquid membranes. *Journal of Membrane Science*. 2011.381: 237-243.

105. Lee, S. C. and Kim, H. C. Batch and continuous separation of acetic acid from succinic acid in a feed solution with high concentrations of carboxylic acids by emulsion liquid membranes. *Journal of Membrane Science*. 2011. 367:190-196.

106. Chanukya, B. S. and Rastogi, N. K. Extraction of alcohol from wine and color extracts using liquid emulsion membrane. *Separation and Purification Technology*. 2013.105: 41-47.

107. Wieczorek, P., Jonsson, J. A. and Mathiasson, L. Concentration of amino acids using supported liquid membranes with di-2-ethylhexyl phosphoric acid as a carrier. *Analytica Chimica Acta*. 1997. 346:191-197.

108. Chakrabarty, K., Saha, P. and Ghoshal, A. K. Separation of lignosulfonate from its aqueous solution using emulsion liquid membrane. *Journal of Membrane Science*. 2010. 360: 34-39.

109. Drapala, A. and Wieczorek, P. Extraction of short peptides using supported liquid membranes. *Desalination*. 2002. 148: 235-239.

110. Agarwal, S., Teresa, M., Reis, A., Rosinda, M., Ismael, C. and Calvalho, J. M. R. Extraction of sulphuric acid with Alamine 308 using pseudo-emulsion based hollow fiber strip dispersion technique. *Separation and Purification Technology*. 2016. 165: 10-17.
111. Lin, C. C. and Long, R. L. Removal of nitric acid by emulsion liquid membrane: experimental results and model prediction. *Journal of Membrane Science*. 1997. 134: 33- 45.
112. Nosrati, S., Jayakumar, N. S. and Hashim, M. A. Performance evaluation of supported ionic liquid membrane for removal of phenol. *Journal of Hazardous Materials*. 2011. 192: 1283-1290.
113. Alguacil, F. J., Alonso, M. and Sastre, A. M. Modelling of mass transfer in facilitated supported liquid membrane transport of copper (II) using MOC-55 TD in Iberfluid. *Journal of Membrane Science*. 2001. 184: 117-121.
114. Yang, X., Duan, H., Shi, D., Yang, R., Wang, S. and Guo, H. Facilitated transport of phenol through supported liquid membrane containing bis (2-ethylhexyl) sulfoxide (BESO) as the carrier. *Chemical Engineering and Processing*. 2015. 93: 79-86.
115. Nosrati, S., Jayakumar, N. S., Hashim, M. A. and Mukhopadhyay, S. Performance evaluation of vanadium (IV) transport through supported ionic liquid membrane. *Journal of the Taiwan Institute of Chemical Engineers*. 2013. 44: 337-342.
116. Panja, S., Mohapatra, P. K., Tripathia, S. C., Gandhia, P. M. and Janardana, P. Supported liquid membrane transport studies on Am (III), Pu (IV), U (VI) and Sr (II) using irradiated TODGA. *Journal of Hazardous Materials*. 2012. 237-238: 339-346.
117. Liang, P., Liming, W. and Guoqiang, Y. Study on a novel flat renewal supported liquid membrane with D2EHPA and hydrogen nitrate for neodymium extraction. *Journal of Rare Earths*. 2012. 30(1): 63-68.
118. Rehman, S., Akhtar, G. and Chaudry, M. A. Coupled transport of Pb^{2+} through Tri-n-octylamine–xylene–polypropylene supported liquid membranes. *The Canadian Journal of Chemical Engineering*. 2013. 91: 1140-1152.
119. Manna, M. S., Bhatluri, K. K., Saha, P. K. and Ghoshal, A. K. Transportation of bioactive (+) catechin from its aqueous solution using flat sheet supported liquid membrane. *Journal of Membrane Science*. 2013. 447: 325-334.

120. Solangi, I. B., Ozcan, F., Arslan, G. and Ersoz, M. Transportation of Cr (VI) through calix [4] arene based supported liquid membrane. *Separation and Purification Technology*. 2013.118: 470-478.

121. Wannachod, T., Leepipatpiboon, N., Pancharoen, U. and Phatanasri, S. Mass transfer and selective separation of neodymium ions via a hollow fiber supported liquid membrane using PC88A as extractant. *Journal of Industrial and Engineering Chemistry*. 2015. 21: 535-541.

122. Vernekar, P. V., Jagdale, Y. D., Patwardhan, A. W., Patwardhan, A. V., Ansari, A. A., Mohapatra, P. K. and Manchanda, V. K. Transport of cobalt (II) through a hollow fiber supported liquid membrane containing di-(2-ethylhexyl) phosphoric acid (D2EHPA) as the carrier. *Chemical Engineering Research and Design*. 2013. 91: 141-157.

123. Gupta, S., Chakraborty, M. and Murthy, Z. W. P. Performance study of hollow fiber supported liquid membrane system for the separation of Bisphenol A from aqueous solutions. *Journal of Industrial and Engineering Chemistry*. 2014. 20: 2138-2145.

124. Rout, P. C. and Sarangi, K. Separation of vanadium using both hollow fiber membrane and solvent extraction technique- A comparative study. *Separation and Purification Technology*. 2014.122: 270-277.

125. Huidong, Z., Jingjing, C., Biyu, W. and Suying, Z. Recovery of copper ions from wastewater by hollow fiber supported emulsion liquid membrane. *Chinese Journal of Chemical Engineering*. 2013. 21(8): 827-834.

126. Yang, Q. and Kocherginsky, N. M. Copper removal from ammoniacal wastewater through a hollow fiber supported liquid membrane system: Modelling and experimental verification. *Journal of Membrane Science*. 2007. 297:121-129.

127. Jagdale, Y.D., Patwardhan, A. W., Shah, K. A., Chaurasia, S., Patwardhan, A. V., Ansari, S. A. and Mohapatra, P. K. Transport of strontium through a hollow fibre supported liquid membrane containing N, N, N′, N′-tetraoctyl diglycolamide as the carrier. *Desalination*. 2013. 325:104-112.

128. Parhi, P. K. Supported liquid membrane principle and its practices: A short review. *Journal of Chemistry*. 2013. 2013: 1-11.

129. Takeuchi, H., Takahashi, K. and Goto, W. Some observations on the stability of supported liquid membranes. *Journal of Membrane Science*. 1987.34:19-31.

130. Takeuchi, H. and Nakano, M. Progressive wetting of supported liquid membranes by aqueous solutions. *Journal of Membrane Science*. 1987. 42: 183-188.

131. Takigawa, D. The effect of porous support composition and operating parameters on the performance of supported liquid membranes. *Separation Science and Technology*. 1992. 27(3): 325-339.

132. Drioli, E. and Giorno, L. Comprehensive membrane science and engineering. Amsterdam. Elsevier. 2010.

133. Minhas, F. T., Memon, S., Qureshi, I., Mujahid, M. and Bhanger, M. I. Facilitated kinetic transport of Cu (II) through a supported liquid membrane with calix [4] arene as a carrier. *Compted Rendus Chimie*.2013.16: 742-751.

134. Zaheri, P., Abolghasemi, H., Maraghe, M. G. and Mohammadi, T. Intensification of europium extraction through a supported liquid membrane using mixture of D2EHPA and Cyanex 272 as carrier. *Chemical Engineering and Processing*. 2015. 92: 18-24.

135. Shamsudin, N.N., Othman, N. and Sulaiman, R. N. R. Stability of composite SPEEK-PVDF on chromium extraction using supported liquid membrane. *Undergraduate Research Conference (Proceeding)*. 2019:1-6.

136. Coll, M. T., Fortuny, A. and Sastre, A. M. Boron reduction by supported liquid membranes using ALiCY and ALiDEC ionic liquids as carriers. *Chemical Engineering Research and Design*. 2014. 92: 758-763.

137. Venkateswaran, P., Gopalakrishnan, A. N. and Palanivelu, K. Di (2-ethylhexyl) phosphoric acid-coconut oil supported liquid membrane for the separation of copper ions from copper plating wastewater. *Journal of Environmental Sciences*. 2007.19: 1446-1453.

138. Fabiani, C., Merigiola, M., Scibona. S. and Casagnola, A. Degradation of supported liquid membranes under an osmotic pressure gradient. *Journal of Membrane Science*. 1987. 30: 97-104.

139. Neplenbroek, A. M., Bargeman, D. and Smolders, C. A. Supported liquid membranes: instability effects. *Journal of Membrane Science*. 1992. 67: 121-132.

140. Zha, F. F., Fane, A. G. and Fell, C. J. D. Instability mechanisms of supported liquid membranes in phenol transport process. *Journal of Membrane Science*.1995. 107: 59-74.

141. Zheng, H., Wang, B., Wu, Y. and Ren, Q. Instability mechanisms of supported liquid membrane for phenol transport, *Chinese Journal of Chemical Engineering*. 2009. 17:750-755.
142. Neplenbroek, A. M., Bargeman, D. and Smolders, C. A. Mechanism of supported liquid membrane degradation: emulsion formation. *Journal of Membrane Science*. 1992. 67: 133-148.
143. Lozanoa, L. J., Godíneza, C., Ríosa, A. P., Fernándeza, F. J. H., Segadoa, S. S. and Alguacil, F. J. Recent advances in supported ionic liquid membrane technology. *Journal of Membrane Science*. 2011. 376:1-14.
144. Avila, M., Zougagh, M., Escarpa, A. and Rios, A. Supported liquid membrane modified piezoelectric flow sensor with molecularly imprinted polymer for the determination of vanillin in food samples. *Talanta*. 2007. 72:1362-1369.
145. Luque, M., Luque-Perez, E., Rios, M. and Valcarcel, M. Supported liquid membranes for the determination of vanillin in food samples with amperometric detection. *Analytica Chimica Acta*. 2000. 140:127-134.
146. Liang, P., Binghua, P. and Xinglong, F. Study on transport of Dy (III) by dispersion supported liquid membrane. *Journal of Rare Earths*. 2009. 27(3):447-456.
147. Yang, X., Zhang, Q., Wang, Z., Li, S., Xie, Q., Huang, Z and Wang, S. Synergistic extraction of gold (I) from aurocyanide solution with the mixture of primary amine N1923 and bis (2-ethylhexyl) sulfoxide in supported liquid membrane. *Journal of Membrane Science*. 2017.540: 174-182.
148. Bloch, R., Finkelstein, A., Kedem, O. and Vofsi, D. Metal-ion separations by dialysis through solvent membranes**.** *Industrial & Engineering Chemistry Process Design and Development*. 1967. *6* (2): 231-237.
149. Neplenbroek, A. M., Bargeman, D. and Smolders, C. A. The stability of supported liquid membranes. *Desalination*. 1990. 79: 303-312.
150. Wang, Y., Thio, Y. S. and Doyle, F. M. Formation of semi-permeable polyamide skin layers on the surface of supported liquid membranes. *Journal of Membrane Science*.1998. 147:109-116.
151. Wang, Y. and Doyle, F. M. Formation of epoxy skin layers on the surface of supported liquid membranes containing polyamines. *Journal of Membrane Science*. 1999. 159: 167-175.

152. Yang, X. J., Fane, A. G., Bi, J. and Griesser, H. J. Stabilization of supported liquid membranes by plasma polymerization surface coating. *Journal of Membrane Science*. 2000. 168: 29-37.
153. Ho, S.V., Sheridan, P.W., Krupetsky, E. Supported polymeric liquid membranes for removing organics from aqueous solutions I. Transport characteristics of polyglycol liquid membranes. *Journal of Membrane Science*. 1996. 112: 13–27.
154. Dastgir, M. G., Peeva, L. D. and Livingston, A. G. The performance of composite supported polymeric liquid membranes in the membrane aromatic recovery system (MARS). *Chemical Engineering Science*. 2005. 60: 7034-7044.
155. Sonpingkam, S. and Pattavarakorn, D. Mechanical properties of sulfonated Poly (ether ether ketone) nanocomposite membranes (DMFCS). *International Journal of Chemical Engineering and Applications*. 2014. 5(2): 181-185.
156. Jaafar, J., Ismail, A. F. and Matsuura, T. Preparation and barrier properties of SPEEK/Cloisite 15A®/TAP nanocomposite membrane for DMFC application. *Journal of Membrane Science*. 2009. 345: 119-127.
157. Othman, M.H.D., Ismail, A.F., Mustafa, A. Physico-chemical study of sulfonated poly (ether ether ketone) membranes for direct methanol fuel cell application. *Malaysian Polymer Journal*. 2007. 2(1): 10 -28.
158. Yee, R. S. L., Zhang, K. and Ladewig, B. P. The effects of sulfonated poly (ether ether ketone) ion exchange preparation conditions on membrane properties. *Membranes*. 2013. 3:182-195.
159. Xing, P., Robertson, G. P., Guiver, M. D., Mikhailenko, S. D., Wang, K. and Kaliaguine, S. Synthesis and characterization of sulfonated poly (ether ether ketone) for proton exchange membranes. *Journal of Membrane Science*. 2004. 229: 95-106.
160. Jung, H. Y. and Park, J. K. Long-term performance of DMFC based on the blend membrane of sulfonated poly (ether ether ketone) and poly (vinylidene fluoride). *International Journal of Hydrogen Energy*. 2009. 34: 3915-3921.
161. Corvilain, M., Klaysom, C., Szymczyk, A., and Vankelecom, I. F. J. Formation mechanism of SPEEK hydrophilized PES supports for forward osmosis. *Desalination*. 2017. 419: 29-38.

162. He, T., Frank, M., Mulder, M.H.V. and Wessling, M. Preparation and characterization of nanofiltration membranes by coating polyethersulfone hollow fibers with sulfonated poly (ether ether ketone) (SPEEK). *Journal of Membrane Science*. 2008. 307: 62-72.
163. He, T. Preparation and characterization of polysulfone support and sulfonated poly (ether ether ketone) coated composite hollow fiber membranes. *Desalination*. 2008. 225: 82-94.
164. Nayl, A. A. and Aly, H. F. Solvent extraction of V (V) and Cr (III) from acidic leach liquors of ilmenite using Aliquat 336. *Transaction of Nonferrous Metals Society of China*. 2005.25: 4183-4191.
165. Sarkar, R., Ray, S. and Basu, S. Synergism in solvent extraction and solvent extraction kinetics. *Journal of Chemical, Biological and Physical Sciences*. 2014. 4(4): 3156-3181.
166. Voorde, I. K. V., Pinoy, L. and Ketelaere, R. F. D. Recovery of nickel ions by supported liquid membrane (SLM) extraction. *Journal of Membrane Science*. 2004. 234: 11-21.
167. Liang, P., Liming, W., Wei, G. and Nan, Z. Study on a novel disphase supplying supported liquid membrane for transport behavior of divalent nickel ions. *Chinese Journal of Chemical Engineering*. 2012. 20(4):633-640.
168. Singh, R., Kliwaja, A.R., Gupta, B. and Tandon, S. N. Extraction and separation of nickel (H) using Bis (2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) and its recovery from spent catalyst and electroplating bath residue. *Solvent Extraction and Ion Exchange*.1999.17 (2):367-390.
169. Tanaka, M. and Alam, S. Solvent extraction equilibria of nickel from ammonium nitrate solution with LIX84I. *Hydrometallurgy*. 2010. 105: 134-139.
170. Gonzalez, R., Cerpa, A. and Alguacil, F. J. Nickel (II) removal by mixtures of Acorga M5640 and DP8R in pseudo-emulsion based hollow fiber with strip dispersion technology. *Chemosphere*. 2010. 81:1164-1169.
171. Rajewski, J. and Religa, P. Synergistic extraction and separation of chromium (III) from acidic solution with a double-carrier supported liquid membrane. *Journal of Molecular Liquids*. 2016. 218: 309-315.

172. Narita, H., Tanaka, M. and Sato, Y. Structure of the extracted complex in the Ni (II)-LIX84I system and the effect of D2EHPA addition. *Solvent Extraction and Ion Exchange*. 2006. 24: 693-702.
173. Reddy, B. R. and Priya, N. D. Solvent extraction of Ni (II) from sulfate solutions with LIX84I: Flow-sheet for the separation of Cu (II), Ni (II) and Zn (II). *Analytical science.* 2004. 20: 1737-1740.
174. Dimitrov, K., Rollet, V., Saboni, A. and Alexandrova, S. Recovery of nickel from sulphate media by batch pertraction in a rotating film contactor using Cyanex 302 as a carrier. *Chemical Engineering and Processing*. 2008. 47: 1562-1566.
175. Agreda, D. D., Garcia-Diaz, I., Lopez, F. A. and Alguacil, F. J. Supported liquid membranes technologies in metals removal from liquid effluents. *Revision Metal*. 2011. 47(2):146-168.
176. Swain, B., Mishra, C., Jeong, J., Lee, J. C., Hong, H. S. and Pandey, B. D. Separation of Co (II) and Li (I) with Cyanex 272 using hollow fiber supported liquid membrane: A comparison with flat sheet supported liquid membrane and dispersive solvent extraction process. *Chemical Engineering Journal*. 2015. 271: 61-70.
177. Chang, S. H., Teng, T. T., and Norli, I. Screening of factors influencing Cu (II) extraction by soybean oil-based organic solvents using fractional factorial design. *Journal of Environmental Management*. 2011. 92: 2580-2585.
178. Yıldız, Y., Manzak, A. and Tutkun, O. Synergistic extraction of cobalt and nickel ions by supported liquid membranes with a mixture of TIOA and TBP. *Desalination and Water Treatment*. 2015.53: 1246-1253.
179. Lee, S. C. and Kim, H. C. Batch and continuous separation of acetic acid from succinic acid in a feed solution with high concentration of carboxylic acids by emulsion liquid membranes. *Journal of Membrane Science*. 2011. 367: 190-196.
180. Kumbasar, R. A. and Kasap, S. Selective separation of nickel from cobalt in ammoniacal solutions by emulsion type liquid membranes using 8-hydroxyquinoline (8-HQ) as mobile carrier. *Hydrometallurgy*. 2009.95: 121-126.
181. Malik, M. A., Hashim, M. A. and Nabi, F. Ionic liquids in supported liquid membrane technology. *Chemical Engineering Journal*. 2011. 171: 242-254.

182. Lozano, L. J., Godinez, C., Rios, A. P. D., Fernandez, F. J. H., Segado, S. S. and Alguacil, F. J. Recent advances in supported ionic liquid membrane technology. *Journal of Membrane Science*. 2011. 376:1-14.

183. Rios, A. P. D., Fernandez, F., Lozano, L. J., Segado, S. S., Anzola, A. G., Godinez, C., Alonso, F. T. and Medina, J. Q. On the selective separation of metal ions from hydrochloride aqueous solution by pertraction through supported ionic liquid membranes. *Journal of Membrane Science*. 2013.444: 469-481.

184. Muthuraman, G. and Palanivelu, K. Transport of textile dye in vegetable oils based supported liquid membrane. *Dyes and Pigments*. 2006.70:99-104.

185. Muthuraman, G. and Teng, T. T. Use of vegetable oil in supported liquid membrane for the transport of Rhodamine B. *Desalination*. 2009.249:1062-1066.

186. Venkateswaran, P. and Palanivelu, K. Recovery of phenol from aqueous solution by supported liquid membrane using vegetable oils as liquid membrane. *Journal of Hazardous Materials*. 2006. 131:146–152.

187. Alguacil, F. J. and Navarro, P. Permeation of cadmium through a supported liquid membrane impregnated with CYANEX 923. *Hydrometallurgy*. 2001. 61: 137-142.

188. Singh, S. K., Misra, S. K., Tripathi, S. C. and Singh, D. K. Studies on permeation of uranium (VI) from phosphoric acid medium through supported liquid membrane comprising a binary mixture of PC88A and Cyanex 923 in n-dodecane as carrier. *Desalination*. 2010. 250: 19-25.

189. Pei, L., Yao, B. and Zhang, C. Transport of Tm (III) through dispersion supported liquid membrane containing PC-88A in kerosene as the carrier. *Separation and Purification Technology*. 2009. 65: 220-227.

190. Chaturabul, S., Srirachat, W., Wannachod, T., Ramakul, P., Pancharoen, U. and Kheawhom, S. Separation of mercury (II) from petroleum produced water via hollow fiber supported liquid membrane and mass transfer modeling. *Chemical Engineering Journal*. 2015. 265: 34-46.

191. Vijayalakshmi, R., Chaudry, S., Anitha, M., Singh, D. K., Aggarwal, S. K. and Singh, H. Studies on yttrium permeation through hollow fibre supported liquid membrane from nitrate medium using di-nonyl phenyl phosphoric acid

as the carrier phase. *International Journal of Mineral Processing*. 2015. 135: 52-56.

192. PEI, L., Wang, L. and Yu, G. Separation of Eu (III) with supported dispersion liquid membrane system containing D2EHPA as carrier and HNO_3 solution as stripping solution. *Journal of Rare Earths*.2011. 29(1): 7-14.
193. Kedari, C. S., Pandit, S. S. and Ramanujam, A. Selective permeation of plutonium (IV) through supported liquid membrane containing 2-ethylhexyl 2-ethylhexyl phosphonic acid as ion carrier. *Journal of Membrane* Science.1999.156 (2):187-196.
194. Othman, N., Sulaiman, R. N. R. and Daud, M. H. A. D2EHPA-Sulfuric acid system for simultaneous extraction and recovery of nickel ions via supported liquid membrane process. *International Journal of Engineering.*2018. 31(8): 1373-1380.
195. Wongkaew, K., Mohdee, V., Pancharoen, U., Arpornwichano, A. and Lothongkum, A. W. Separation of platinum (IV) across hollow fiber supported liquid membrane using non-toxic diluents: Mass transfer and thermodynamics. *Journal of Industrial and Engineering Chemistry*.2017.54:278-289.
196. Chanukya, B. S., Prakash, M. and Rastogi, N. K. Extraction of citric acid from fruit juices using supported liquid membrane. *Journal of Food Processing and Preservation*. 2017. 41(1): e12790.
197. Altin, S. and Gemici, B. T. Separation performances of supported liquid membrane and electrodialysis processes at removal of Cd (II) from dilute solutions. *Fresenius Environmental Bulletin*.2017. 26(11): 6438-6446.
198. Djunaidi, M. C., Lusiana, R. A. and Rahayu, M. D. Recovery of chromium Metal (VI) using supported liquid membrane (SLM) method, a study of influence of NaCl and pH in receiving phase on transport. *2nd International Conference on Materials Engineering and Nanotechnology (ICMEN)*. 2017. 205. 012010.
199. Altin, S., Alemdar, S., Altin, A. and Yildirim, Y. Facilitated transport of Cd (II) through a supported liquid membrane with Aliquat 336 as a Carrier. *Separation Science and Technology*. 2011. 46(5): 754-764.
200. Lu, S. B. and Pei, L. A study of zinc borne waste water treatment with dispersion supported liquid membrane. *International Journal of Hydrogen Energy*. 2016.41(35): 15717-15723.

201. Taoualit, N., Azzazi, F. Z., Benkadi, N. E. and Hadj-Boussaad, D. E. Extraction and transport of humic acid using supported liquid-membrane containing trioctyl phosphine oxide (TOPO) as the carrier. *Acta Physica Polonica A*. 2016. 130(1): 115-121.
202. Ali, K., Nawaz, R., Ali, N., Khaliq, A. and Ullah, R. Selective removal of zinc using tri-ethanolamine-based supported liquid membrane. 2016. 57(18): 8549-8560.
203. Chan, N. Y., Othman, N. and Ooi, Z.Y. Prediction of Kraft lignin extraction performance using emulsion liquid membrane carrier-diffusion model. *Jurnal Teknologi*. 2014.67(2): 17-21.
204. Balasubramanian, A. and Venkatesan, S. Optimization of process parameters using response surface methodology for the removal of phenol by emulsion liquid membrane. *Polish Journal of Chemical Technology*. 2012. 14(1):46-49.
205. Park, H. J. and Chung, T. S. Removal of phenol from aqueous solution by liquid emulsion membrane. *Korean Journal Chemical Engineering*. 2003.20(4): 731-735.
206. Badgujar, V. and Rastogi, N. K. Extraction of phenol from aqueous effluent using triglycerides in supported liquid membrane. *Desalination and Water Treatment.* 2011. 36: 187-196.
207. Leon, G., Martinez, G., Guzman, M. A., Moreno, J. I., Miguel, B. and Lopez, J. A. F. Increasing stability and transport efficiency of supported liquid membranes through a novel ultrasound-assisted preparation method: Its application to cobalt (II) removal. *Ultrasonic Sonochemistry*. 2013.20: 650-654.
208. Sastre, A., Madi, A., Cortina, J. L. and Miralles, N. Modelling of mass transfer in facilitated supported liquid membrane transport of gold (III) using phospholene derivatives as carriers. *Journal of Membrane Science*. 1998. 139: 57-65.
209. Perez, M. E. M., Reyes-Aguilera, J. A., Saucedo T. I., Gonzalez, M. P., Navarro, R. and Avila-Rodriguez, M. Study of As (V) transfer through a supported liquid membrane impregnated with Trioctylphosphine oxide (Cyanex 921). *Journal of Membrane Science*. 2007.302: 119-126.

210. Chang, S. H., Teng, T. T., and Norli, I. Cu (II) transport through soybean oil-based bulk liquid membrane: Kinetic study. *Chemical Engineering Journal*. 2011.173: 352-360.
211. Omar, W. N. N. W. and Amin, N. A. S. Multi response optimization of oil palm frond pretreatment by ozonolysis. *Industrial Crops and Products*. 2016. 85: 389-402.
212. Barbara, J., Russel, J. P. and Walsh, A. An atomic-absorption spectrophotometer and its application to the analysis of solutions. *Spectrochimica Acta*. 1957.8(6): 317-318.
213. Martinez, M., Miralle, N. and Sastre, A. Dissociation constants of organophosphinic acid compounds. *Talanta*. 1993. 40(9):1339-1343.
214. Diawara, C. K., Paugam, L., Pontie, M., Schlumpf, J. P., Jaouen, P. and Quéméneur, F. Influence of chloride, nitrate, and sulphate on the removal of fluoride ions by using nanofiltration membranes. *Separation Science and Technology*. 2005. 40: 3339-3347.
215. Ochromowicz, K. and Apostoluk, W. Modelling of carrier mediated transport of chromium(III) in the supported liquid membrane system with D2EHPA. *Separation and Purification Technology*. 2010. 72:112-117.
216. Vafaei, F., Torkaman, R., Moosavian, M. A. and Zaheri, P. Optimization of extraction conditions using central composite design for the removal of Co (II) from chloride solution by supported liquid membrane. *Chemical Engineering Research and Design*. 2018. 133: 126-136.
217. Chang, S. H., Teng, T. T., and Norli, I. Extraction of Cu (II) from aqueous solutions by vegetable oil-based organic solvents. *Journal of Hazardous Materials*. 2010. 181: 868-872.
218. Jiang, Y., Zhang, Y., Banks, C., Heaven, S. and Longhurst, P. Investigation of the impact of trace elements on anaerobic volatile fatty acid degradation using a fractional factorial experimental design. *Water Research*. 2017.125: 458-465.
219. Samad, K.A. and Zainol, N. The use of factorial design for ferulic acid production by co-culture. *Industrial Crops and Products*. 2017. 95: 202-206.
220. Zidi, C., Tayeb, R., Ali, M. B. S. and Dhahbi, M. Liquid–liquid extraction and transport across supported liquid membrane of phenol using tributyl phosphate. *Journal of Membrane Science*. 2010. 360: 334-340.

221. Kumar, A., Manna, M.S., Ghoshal, A.K. and Saha, P. Study of the supported liquid membrane for the estimation of the synergistic effects of influential parameters on its stability. *Journal of Environmental Chemical Engineering*. 2016. 4: 943-949.
222. Biswas, S., Pathak, P. N. and Roy, S. B. Kinetic modeling of uranium permeation across a supported liquid membrane employing dinonyl phenyl phosphoric acid (DNPPA) as the carrier. *Journal of Industrial and Engineering Chemistry*. 2013.19: 547-553.
223. Kandwal, P., Dixit, S., Mukhopadhyay, S., Mohapatra, P. K. and Manchanda, V. K. Mathematical modeling of Cs (I) transport through flat sheet supported liquid membrane using calix-[4]-bis (2, 3-naptho)-18-crown-6 as the mobile carrier. *Desalination*. 2011. 278: 405-411.
224. Duan, H., Wang, Z., Yuan, X., Wang, S., Guo, H. and Yang, X. A novel sandwich supported liquid membrane system for simultaneous separation of copper, nickel and cobalt in ammoniacal solution. *Separation and Purification Technology*. 2017. 173:323-329.
225. Alonso, M., Lopez-Delgado, A., Sastre, A. M. and Alguacil, F. J. Kinetic modelling of the facilitated transport of cadmium (II) using Cyanex 923 as ionophore. *Chemical Engineering Journal*. 2006.118: 213-219.
226. Tarditi, A. M., Marchese, J. and Campderrós, M. E. Modelling of zinc (II) transport through a PC-88A supported liquid membrane. *Desalination*. 2008. 228: 226-236.
227. Hickey, A.S. and Peppas, N.A. Mesh size and diffusive characteristics of semycrystalline poly (vinyl alcohol) membranes prepared by freezing/thawing techniques. *Journal of Membrane Science*. 1995. 107: 229-237.
228. Kojima, T., Furusaki, S., Takao, K. and Miyauchi, T. A Fundamental Study on recovery of copper with a cation exchange membrane Part 1- Ion exchange equilibria between cupric and hydrogen ions. *The Canadian Journal of Chemical Engineering*. 1982. 60: 642-649.

LIST OF PUBLICATIONS

Journal with Impact Factor

1. **Sulaiman, R. N. R.,** & Othman, N. (2018). Synergetic facilitated transport of nickel via supported liquid membrane process by a mixture of Di (2-ethylhexyl) phosphoric acid and *n*-octanol: Kinetic permeation study and approach for a green process, *Chemical Engineering and Processing: Process Intensification,* 134, 9-19. https://doi.org/10.1016/j.cep.2018.10.006. **(Q2, IF:2.826)**

2. **Sulaiman, R. N. R.,** Othman, N., Noah, N.F.M., & Jusoh, N. (2018). Removal of nickel from industrial effluent using a synergistic mixtures of acidic and solvating carriers via green supported liquid membrane process, *Chemical Engineering Research and Design, 137,* 360-375. https://doi.org/10.1016/j.cherd.2018.07.034. **(Q2, IF:2.795)**

3. **Sulaiman, R. N. R.,** & Othman, N. (2017). Synergistic green extraction of nickel ions from electroplating waste via mixtures of chelating and organophosphorus carrier, *Journal of Hazardous Materials*, *340*, 77–84. https://doi.org/10.1016/j.jhazmat.2017.06.060. **(Q1, IF:6.434)**

Indexed Journal

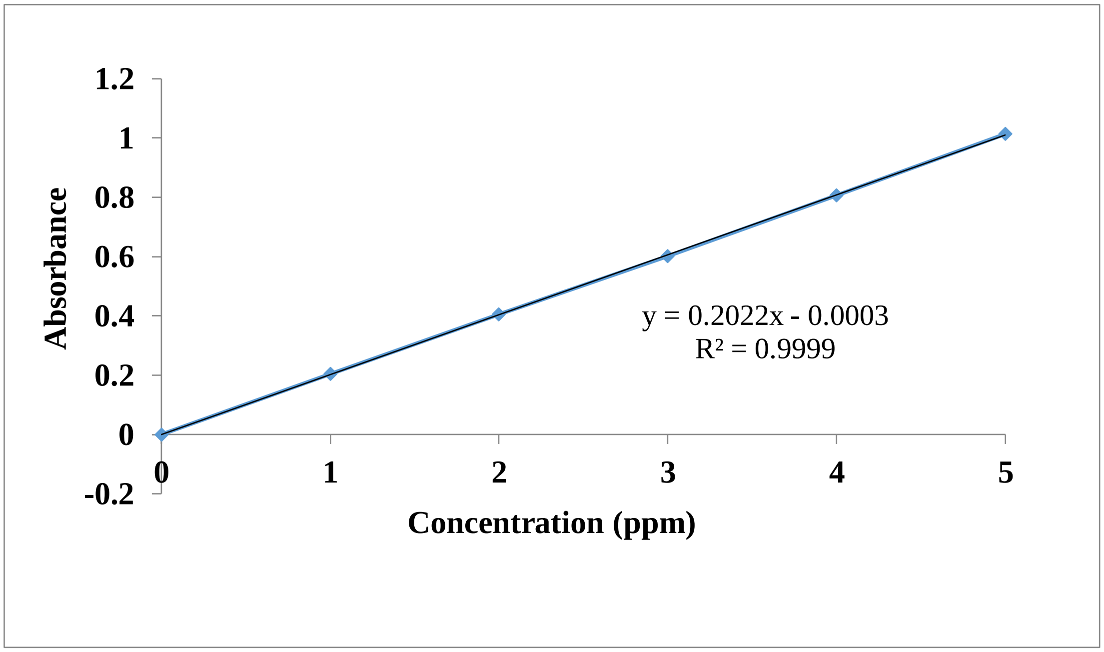
1. **Sulaiman, R. N. R.,** & Othman, N. (2018). Solvent extraction of nickel ions from electroless nickel plating wastewater using synergistic green binary mixture of D2EHPA-octanol system, *Journal of Environmental Chemical Engineering*, *6*(2), 1814-1820**.** https://doi.org/10.1016/j.jece.2018.02.035. **(Indexed by ISI and Scopus)**

2. Othman, N. **Sulaiman, R. N. R.,** & Daud, M. H. A. (2018). D2EHPA-sulfuric acid system for simultaneous extraction and recovery of nickel ions via supported liquid membrane process. *International Journal of Engineering Transactions B: Application, 31*(8), 1373-1380. http://www.ije.ir/Vol31/No8/B/28-2787.pdf. **(Indexed by Scopus)**

Patent

Liquid Membrane Process for Recovery of Metal Ions. PI 2018 00135

STANDARD CURVE AAS FOR NICKEL



Wavelength of nickel: 232 nm

SLM COMPONENT SELECTION

The extraction, stripping, recovery, and distribution ratio for nickel extraction were determined using Equations (C.1) to (C.4) respectively:

$$\text{Extraction (\%)} = \frac{[Ni]_i - [Ni]_{aq}}{[Ni]_i} \ x\ 10 \quad \text{(C.1)}$$

$$\text{Stripping (\%)} = \frac{[Ni]_s}{[Ni]_{org}} \ x\ 100 \quad \text{(C.2)}$$

$$\text{Recovery (\%)} = \frac{[Ni]_s}{[Ni]_i} \ x\ 100 \quad \text{(C.3)}$$

$$\text{Distribution ratio, D} = \frac{[Ni]_{org}}{[Ni]_{aq}} \quad \text{(C.4)}$$

Where, $[Ni]_i$ is the initial nickel concentration in aqueous feed phase (mg/L), $[Ni]_{aq}$ is the nickel concentration in aqueous feed phase after extraction (mg/L), $[Ni]_s$ is the nickel concentration in aqueous stripping phase after extraction (mg/L), and $[Ni]_{org}$ is the nickel concentration in liquid membrane phase after extraction (mg/L).

Table C1 Effect types of carrier towards nickel ion extraction (Experimental conditions: [Ni]: 466 mg/L; pH: 4.8; [carrier]: 1.0M; diluent: kerosene; aqueous wastewater volume: 10 mL; organic volume: 10 mL; temperature: 25±1ºC; duration time: 18 h; agitation speed: 320 rpm.

Carrier	**Type**	**$[Ni]_{aq}$ (mg/L)**	**Extraction (%)**
D2EHPA	Phosphoric acidic	186	60
LIX63	Chelating acidic	256	45
Cyanex 302	Phosphinic acidic	447	4
TDA	Basic	504	0
Octanol	Solvating	501	0
TBP	Solvating	502	0

Table C2 Effect several types of synergist towards nickel extraction (Experimental conditions: [Ni]: 465 mg/L; pH: 4.8; [D2EHPA]: 1.0M; [octanol]: 10% (v/v); diluent: kerosene; aqueous wastewater volume: 10 mL; organic volume: 10 mL; temperature: 25±1ºC; duration time: 18 h; agitation speed: 320 rpm.

Type of synergist	**$[Ni]_{aq}$ (mg/L)**	**Extraction (%)**	**Distribution ratio (D)**
Single D2EHPA	186	60	1.5
D2EHPA+ Cyanex 302	239	49	0.9
D2EHPA+TDA	242	48	0.9
D2EHPA + Octanol	95	80	3.9

Table C3 Effect types of stripping agent towards nickel extraction (Experimental conditions: [Ni]: 466 mg/L; pH: 4.8; [D2EHPA]: 1M; [octanol]: 10% (v/v); aqueous nickel: 10 mL; organic volume: 10 mL; temperature: 25±1ºC; duration time: 18 h; agitation speed: 320 rpm; diluent: kerosene.

Stripping agent	**$[Ni]_{org}$ (mg/L)**	**$[Ni]_{aq, strip}$ (mg/L)**	**Extraction (%)**
HCl	371	489	100
H_2SO_4	371	368	99
HNO_3	371	431	100

Table C4 Effect of composition palm oil to kerosene towards nickel extraction (Experimental conditions: [Ni]: 466 mg/L; pH: 4.8; [D2EHPA]: 1.0M; [octanol]: 10% (v/v); diluent: palm oil and kerosene; aqueous wastewater volume: 10 mL; organic volume: 10 mL; temperature: 25±1ºC; duration time: 18 h; agitation speed: 320 rpm.

Palm oil: kerosene (%)	**$[Ni]_{aq}$ (mg/L)**	**Extraction (%)**
0:100	95	80
10:90	76	84
30:70	78	83
50:50	71	85
70:30	82	82
90:10	83	82
100:0	85	82

Table C5 Effect of carrier concentration towards nickel extraction (Experimental conditions: [Ni]: 465 mg/L; pH: 4.8; [octanol]: 10% (v/v); diluent: palm oil; aqueous wastewater volume: 10 mL; organic volume: 10 mL; temperature: 25±1ºC; duration time: 18 h; agitation speed: 320 rpm.

D2EHPA[mol/L]	**$[Ni]_{aq}$ (mg/L)**	**Extraction (%)**
0.05	280	40
0.30	110	76
0.50	96	79
0.70	73	84
1.00	85	82

Table C6 Effect of synergist concentration towards nickel extraction (Experimental conditions: [Ni]: 466 mg/L; pH: 4.8; [D2EHPA]: 0.7M; diluent: palm oil; aqueous wastewater volume: 10 mL; organic volume: 10 mL; temperature: 25±1ºC; duration time: 18 h; agitation speed: 320 rpm.

[Octanol] (% v/v)	**$[Ni]_{aq}$ (mg/L)**	**$[Ni]_{org}$ (mg/L)**	**Extraction (%)**	**Distribution ratio (D)**
5	112	354	76	3.1
10	73	393	84	5.4
15	47	418	90	8.8
20	47	418	90	8.8

Table C7 Effect of sulfuric acid concentration towards nickel extraction (Experimental conditions: $[Ni]_{org}$: 506 mg/L; pH: 4.8; [D2EHPA]: 0.7M; [octanol]: 15% (v/v); diluent: palm oil; aqueous wastewater volume: 10 mL; organic volume: 10 mL; temperature: 25±1ºC; duration time: 18 h; agitation speed: 320 rpm.

Stripping conc (M)	**$[Ni]_{aq, strip}$ (mg/L)**
0.01	3
0.03	45
0.05	95
0.07	100
0.1	100
0.5	100

SLM EXTRACTION OF NICKEL

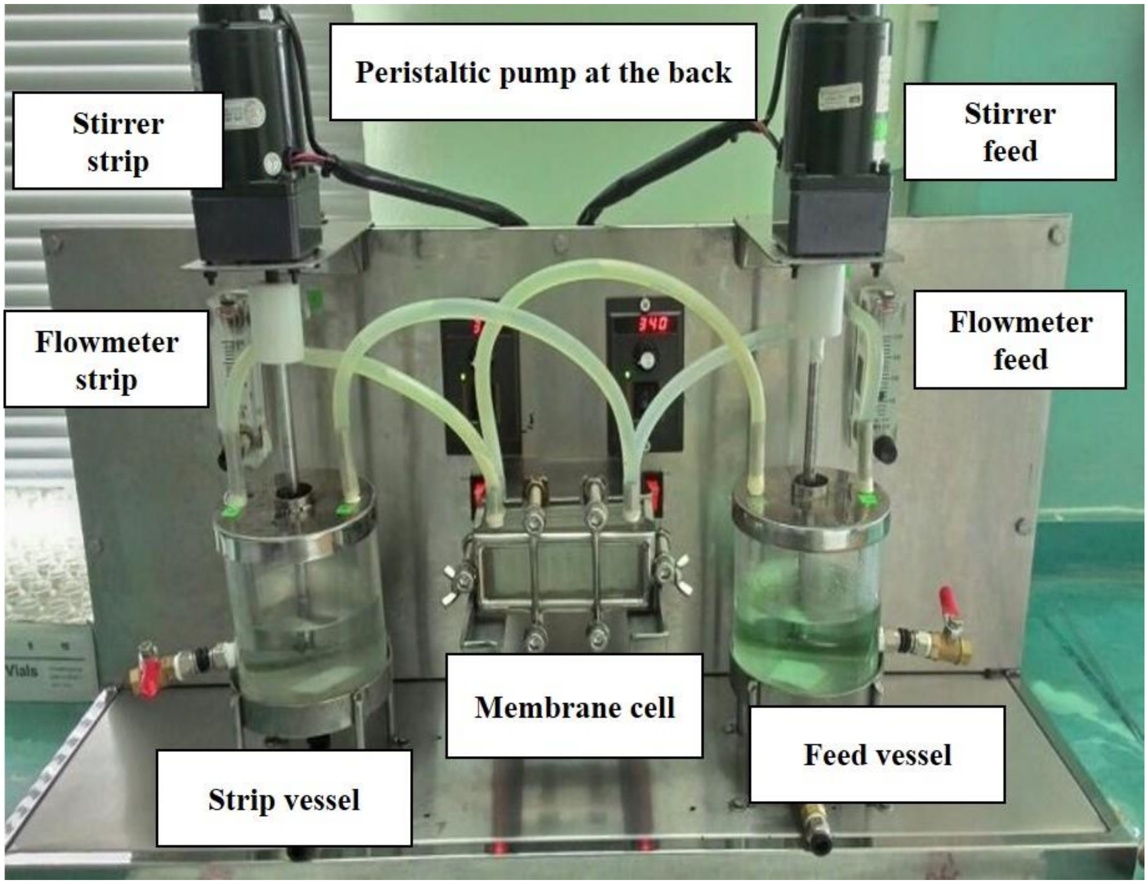


Figure D1 SLM Rig Set UP

Table D1 Effect of initial nickel concentration (130 mg/L) towards nickel extraction and recovery after 6 h of SLM experiment (Experimental condition: [D2EHPA] =0.7M; [octanol] =10% (v/v); [H_2SO_4] =2.0M; diluent= kerosene; feed and stripping phase flowrate=50 ml/min).

Time (min)	**[Ni] (mg/L)**		**Extraction (%)**	**Recovery (%)**
	Feed Phase	**Stripping Phase**		
0	130	0	0	0
60	98	25	32	23
120	89	32	41	30
180	65	50	65	63
240	54	58	76	68
300	41	68	89	75
360	33	75	97	85

Table D2 Effect of initial nickel concentration (206 mg/L) towards nickel extraction and recovery after 6 h of SLM experiment (Experimental condition: [D2EHPA] =0.7M; [octanol] =10% (v/v); [H_2SO_4] =2.0M; diluent= kerosene; feed and stripping phase flowrate=50 ml/min).

Time (min)	**[Ni] (mg/L)**		**Extraction (%)**	**Recovery (%)**
	Feed Phase	**Stripping Phase**		
0	206	0	0	0
60	175	42	24	20
120	147	59	29	29
180	105	124	49	61
240	96	133	53	65
300	84	152	59	74
360	75	164	64	80

Table D3 Effect of initial nickel concentration (278 mg/L) towards nickel extraction and recovery after 6 h of SLM experiment (Experimental condition: [D2EHPA] =0.7M; [octanol] =10% (v/v); [H_2SO_4] =2.0M; diluent= kerosene; feed and stripping phase flowrate=50 ml/min).

Time (min)	[Ni] (mg/L)		Extraction (%)	Recovery (%)
	Feed Phase	Stripping Phase		
0	278	0	0	0
60	250	50	10	18
120	202	69	27	25
180	180	80	35	30
240	159	120	43	43
300	135	135	51	49
360	124	154	55	55

Table D4 Effect of initial nickel concentration (370 mg/L) towards nickel extraction and recovery after 6 h of SLM experiment (Experimental condition: [D2EHPA] =0.7M; [octanol] =10% (v/v); [H_2SO_4] =2.0M; diluent= kerosene; feed and stripping phase flowrate=50 ml/min).

Time (min)	[Ni] (mg/L)		Extraction (%)	Recovery (%)
	Feed Phase	Stripping Phase		
0	370	0	0	0
60	350	40	5	11
120	337	72	9	19
180	325	84	12	23
240	310	112	16	30
300	295	135	20	36
360	289	142	22	38

Table D5 Design matrix screening for 2^{5-2} fractional factorial design and extraction efficiency

Run Order	[D2EHPA] (M), x_1	[H_2SO_4] (M), x_2	[Octanol] (% v/v), x_3	Feed phase flowrate (ml/min), x_4	Strip phase flow rate (ml/min), x_5	[Ni]$_{aq}$ (mg/L)	Extraction (%)
1	0.5	0.5	20	50	100	54	59
2	1.5	0.5	5	50	50	40	69
3	0.5	2.0	20	50	50	43	67
4	1.5	2.0	5	50	100	38	71
5	0.5	0.5	5	100	100	44	66
6	1.5	0.5	20	100	50	22	83
7	0.5	2.0	5	100	50	37	72
8	1.5	2.0	20	100	100	19	85

[Ni]$_{initial}$: 131 mg/L

Table D6 Design of experiment for nickel extraction using BBD

4 factor Box-Behnken design, 3 blocks, 27 runs (Spreadsheet1)						$[Ni]_{aq}$ (mg/l)	Extraction (%)
	Block	**[D2EHPA] (M)**	**Feed flowrate (mL/min)**	**$[H_2SO_4]$ (M)**	**[Octanol] (% v/v)**		
1	1	0.5	50	1.75	15	22	85
2	1	2.0	50	1.75	15	22	85
3	1	0.5	150	1.75	15	17	88
4	1	2.0	150	1.75	15	12	92
5	1	1.25	100	0.5	5	24	84
6	1	1.25	100	3.0	5	12	92
7	1	1.25	100	0.5	25	24	84
8	1	1.25	100	3.0	25	16	89
9	1	1.25	100	1.75	15	17	88
10	2	0.5	100	1.75	5	25	83
11	2	2.0	100	1.75	5	14	90
12	2	0.5	100	1.75	25	6	96
13	2	2.0	100	1.75	25	10	93
14	2	1.25	50	0.5	15	31	79
15	2	1.25	150	0.5	15	19	87
16	2	1.25	50	3.0	15	24	84
17	2	1.25	150	3.0	15	13	91
18	2	1.25	100	1.75	15	14	90
19	3	0.5	100	0.5	15	24	84
20	3	2.0	100	0.5	15	22	85
21	3	0.5	100	3.0	15	20	86
22	3	2.0	100	3.0	15	17	88
23	3	1.25	50	1.75	5	28	81
24	3	1.25	150	1.75	5	114	22
25	3	1.25	50	1.75	25	22	85
26	3	1.25	150	1.75	25	11	92
27	3	1.25	100	1.75	15	11	92

$[Ni]_{initial}$: 146 mg/L

Table E1 Extraction and recovery efficiency of nickel ion with respect to the different diluent composition after 8 h experiement (Condition: Feed phase: 100 ppm; Membrane support: PVDF membrane; [D2EHPA]: 1.25M; [octanol]; (15%, v/v); diluent: 100% kerosene; Stripping phase: 1.75M H_2SO_4.

Time (min)	[Ni] (mg/L)		Extraction (%)	Recovery (%)
	Feed Phase	Stripping Phase		
0	138	0	0	0
120	85	78	42	19
240	45	111	69	30
360	15	138	90	38
480	0.50	146	100	100

Table E2 Extraction and recovery efficiency of nickel ion with respect to the different diluent composition after 8 h experiement (Condition: Feed phase: 100 ppm; Membrane support: PVDF membrane; [D2EHPA]: 1.25M; [octanol]; (15%, v/v); diluent: 20% palm oil + 80% kerosene; Stripping phase: 1.75M H_2SO_4.

Time (min)	[Ni] (mg/L)		Extraction (%)	Recovery (%)
	Feed Phase	Stripping Phase		
0	138	0	0	0
120	61	56	56	41
240	30	64	78	46
360	12	111	91	80
480	7	131	95	95

Table E3 Extraction and recovery efficiency of nickel ion with respect to the different diluent composition after 8 h experiement (Condition: Feed phase: 100 ppm; Membrane support: PVDF membrane; [D2EHPA]: 1.25M; [octanol]; (15%, v/v); diluent: 40% palm oil + 60% kerosene; Stripping phase: 1.75M H_2SO_4.

Time (min)	[Ni] (mg/L)		Extraction (%)	Recovery (%)
	Feed Phase	Stripping Phase		
0	138	0	0	0
120	65	43	53	34
240	36	74	74	54
360	18	93	87	67
480	7	128	95	95

Table E4 Extraction and recovery efficiency of nickel ion with respect to the different diluent composition after 8 h experiement (Condition: Feed phase: 100 ppm; Membrane support: PVDF membrane; [D2EHPA]: 1.25M; [octanol]; (15%, v/v); diluent: 60% palm oil + 40% kerosene; Stripping phase: 1.75M H_2SO_4.

Time (min)	[Ni] (mg/L)		Extraction (%)	Recovery (%)
	Feed Phase	Stripping Phase		
0	128	0	0	0
120	56	55	56	39
240	33	77	74	60
360	17	91	87	71
480	8	100	94	78

Table E5 Extraction and recovery efficiency of nickel ion with respect to the different diluent composition after 8 h experiement (Condition: Feed phase: 100 ppm; Membrane support: PVDF membrane; [D2EHPA]: 1.25M; [octanol]; (15%, v/v); diluent: 80% palm oil + 20% kerosene; Stripping phase: 1.75M H_2SO_4.

Time (min)	**[Ni] (mg/L)**		**Extraction (%)**	**Recovery (%)**	**ln (C_t/C_o)**
	Feed Phase	**Stripping Phase**			
0	128	0	0	0	
120	64	27	50	21	-0.6931
240	31	68	76	53	-1.4180
360	15	88	88	69	-2.1440
480	9	93	93	73	-2.6548

Table E6 Extraction and recovery efficiency of nickel ion with respect to the different diluent composition after 8 h experiement (Condition: Feed phase: 100 ppm; Membrane support: PVDF membrane; [D2EHPA]: 1.25M; [octanol]; (15%, v/v); diluent: 100% palm oil; Stripping phase: 1.75M H_2SO_4.

Time (min)	**[Ni] (mg/L)**		**Extraction (%)**	**Recovery (%)**	**ln (C_t/C_o)**
	Feed Phase	**Stripping Phase**			
0	128	0	0	0	
120	46	33	64	26	-1.0234
240	28	55	78	43	-1.5198
360	21	63	84	49	-1.8075
480	11	88	91	69	-2.4541

Table E7 Liquid membrane loss calculation study

Composition diluent	Weight of membrane (wt)		Mean , m_2'				m_2	m_1-m_2	m_1-m_0	Liquid membrane loss (%)
	Dry, m_o	Wet, m_1	1	2	3	m_2'				
100%K	0.3000	0.7966	0.1183	0.1247	0.1278	0.1236	0.5069	0.2897	0.4966	58
20%PO +80%K	0.3000	0.6835	0.1144	0.1094	0.1177	0.1138	0.4668	0.2167	0.3835	57
40% PO+60%K	0.3000	0.684	0.1397	0.1330	0.1395	0.1374	0.5636	0.1204	0.3840	55
60% PO+40%K	0.2997	0.7458	0.1220	0.1254	0.126	0.1245	0.5106	0.2352	0.4461	53
80% PO+20%K	0.3043	0.7151	0.1345	0.1357	0.1345	0.1349	0.5533	0.1618	0.4108	47
100% PO	0.3000	0.897	0.1471	0.1520	0.1521	0.1504	0.6169	0.2801	0.5970	47

Calculation of m_2:

m_2 **=** **(**Total area of membrane / Area of the pieces) **X** mean weight of the pieces (m_2'

SLM STABILITY USING COMPOSITE MEMBRANE

(a) Sulfonation reaction of PEEK polymer for 3 hour under controlled temperature of 50-60°C

(b) The sulfonated PEEK polymer was stopped by precipitating the acid polymer solution into an excessive amount of ice water.

(c) The blended of dry SPEEK was ready for casting. Dimethylformamide will be used as a solvent during casting.

Figure F1 Preparation of SPEEK

Table F1 Extraction and recovery efficiency of nickel ion using composite membrane containing SPEEK at the feed side (Condition: Feed phase: 100 ppm; Membrane support: PVDF membrane; [D2EHPA]: 1.25M; [octanol]; (15%, v/v); diluent: 100% palm oil; Stripping phase: 1.75M H_2SO_4.

SPEEK at feed layer	**Sample Conc (mg/L)**		**Extraction (%)**	**Recovery (%)**	**ln (ci/co)**
Time (Min)	**Feed Phase**	**Stripping Phase**			
60	89	11	16	15	-0.1748
120	78	18	26	17	-0.3067
180	66	49	38	46	-0.4738
240	66	59	38	56	-0.4738
300	40	69	62	65	-0.9746
360	34	72	68	68	-1.1371
420	23	75	78	71	-1.5279
480	13	78	88	74	-2.0985

Initial: 106 ppm

Table F2 Extraction and recovery efficiency of nickel ion using composite membrane containing SPEEK at the stripping side (Condition: Feed phase: 100 ppm; Membrane support: PVDF membrane; [D2EHPA]: 1.25M; [octanol]; (15%, v/v); diluent: 100% palm oil; Stripping phase: 1.75M H_2SO_4.

SPEEK at strip layer	**Sample Conc (mg/L)**		**Extraction (%)**	**Recovery (%)**	**ln (ci/co)**
Time (Min)	**Feed Phase**	**Stripping Phase**			
60	102	18	22	14	-0.25
120	83	43	37	33	-0.456
180	76	64	42	49	-0.544
240	49	100	63	76	-0.983
300	43	119	67	91	-1.114
360	34	139	74	100	-1.349
420	22	172	83	100	-1.784
480	19	188	85	100	-1.93

Initial: 131 ppm

Table F3 Extraction and recovery efficiency of nickel ion using composite membrane with SPEEK thickness of 0.055mm (Condition: Feed phase: 100 ppm; Membrane support: PVDF membrane; [D2EHPA]: 1.25M; [octanol]; (15%, v/v); diluent: 100% palm oil; Stripping phase: 1.75M H_2SO_4.

0.055 mm	**Sample Conc (mg/L)**		**Extraction (%)**	**Recovery (%)**	**ln (ci/co)**
Time (Min)	**Feed Phase**	**Stripping Phase**			
0	**0**	**0**	**0**	**0**	
60	73	85	44	65	-0.577
120	52	125	60	96	-0.916
180	30	170	77	100	-1.466
240	19	183	85	100	-1.923
300	12	213	91	100	-2.383
360	9	228	93	100	-2.67
420	7	276	95	100	-2.922
480	5	299	96	100	-3.258

Initial: 130 ppm

Table F4 Extraction and recovery efficiency of nickel ion using composite membrane with SPEEK thickness of 0.075mm (Condition: Feed phase: 100 ppm; Membrane support: PVDF membrane; [D2EHPA]: 1.25M; [octanol]; (15%, v/v); diluent: 100% palm oil; Stripping phase: 1.75M H_2SO_4.

0.075 mm	**Sample Conc (mg/L)**		**Extraction (%)**	**Recovery (%)**	**ln (ci/co)**
Time (Min)	**Feed Phase**	**Stripping Phase**			
0	**0**	**0**	**0**	**0**	**0**
60	88	49	32	38	-0.39
120	69	83	47	64	-0.633
180	51	116	61	89	-0.936
240	42	144	68	100	-1.13
300	33	171	75	100	-1.371
360	26	191	80	100	-1.609
420	21	256	84	100	-1.823
480	17	300	87	100	-2.034

Initial: 130 ppm

Table F5 Extraction efficiency of nickel ion using PVDF membrane containing nickel (Condition: Feed phase: 100 ppm; Membrane support: PVDF membrane; [D2EHPA]: 1.25M; [octanol]; (15%, v/v); diluent: 100% kerosene; Stripping phase: 1.75M H_2SO_4.

Run	Extraction (%)	Mass of impregnated membrane (g)	Weight loss of impregnated PVDF support (%)
0	100	0.272	11
1	100	0.259	15
2	100	0.243	15
3	100	0.257	15
4	100	0.251	17
5	100	0.250	18
6	100	0.246	19
7	100	0.249	19
8	100	0.243	19
9	100	0.245	19
10	100	0.235	23

Initial Impregnation weight =0.304g

Table F6 Extraction efficiency of nickel ion using recycled composite membrane with SPEEK

Run No	Extraction (%)	Mass of impregnated membrane (g)	Weight loss of impregnated composite PVDF support (%)
0	88	0.272	0
1	85	0.264	3
2	89	0.260	4
3	88	0.259	5
4	86	0.255	6
5	88	0.249	8
6	84	0.250	8
7	91	0.250	8
8	90	0.249	8
9	81	0.246	8
10	20	0.246	8

Initial Impregnation weight =0.237g

Table F7 Liquid membrane loss calculation for composite membrane

Type of composite membrane	Weight of membrane (wt)		Mean , m_2'				m_2	m_1-m_2	m_1-m_0	Liquid membrane loss (%)
	Dry, m_o	Wet,m_1	1	2	3	m_2'				
Composite F (0.025mm)	0.769	0.942	0.302	0.297	0.303	0.301	0.903	0.039	0.173	23
Composite S (0.025mm)	0.775	1.033	0.302	0.290	0.320	0.304	0.912	0.121	0.258	47
Composite F (0.055mm)	0.796	0.991	0.304	0.307	0.313	0.308	0.924	0.067	0.195	34
Composite F (0.075mm)	0.836	1.000	0.332	0.318	0.294	0.315	0.945	0.055	0.164	34