Emulsion Liquid Membrane for Cadmium Removal: Determination of Liquid Membrane Components

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ABSTRACT: *Removal of cadmium is very important as it is one of several harmful heavy metals commonly found in textile wastewater. This study focused on determination of emulsion liquid membrane (ELM) components for cadmium removal. Carrier, diluent and stripping selection was done by contacting feed phase (150 ppm cadmium) with organic solution at ratio of 1:1. Both solutions were mixed at 500 rpm for 24 h using magnetic stirrer, then the samples were allowed to settle and separate. The results of the study showed that in comparison with acid solution, basic solution containing trioctylamine (TOA), kerosene and NH_3 as the carrier, diluent and stripping agent, respectively provided the best performance for cadmium removal using ELM. In addition, the ordering of the extraction in terms of magnitude for the diluents was highly correlated with the polarity, solubility and viscosity. Low polarity and viscosity, and high solubility of the diluent are preferred.*

Keywords: Emulsion liquid membrane, liquid membrane components, cadmium, extraction, ELM

1. INTRODUCTION

Textile is one of the major industries in Indonesia. Textile industry plays an important role in the economy of Indonesia, growing linearly since 2010. It is the third biggest export after palm oil and rubber products. There are many sectors in

textile processing, i.e., fibre preparation, spinning, fabric making, colouring and finishing. The last two processes involve the use of huge amount of water. Textile finishing processes involve bleaching, dyeing, printing and stiffening of various processing stages (fibre, yarn, fabric, knits and finished items).[1] The finishing process is aimed to improve the look, performance and acceptability of the finished textile products to meet the requirements of the following process. Colouring process can be done through dyeing and printing. Both processes apply many types of textile dyes such as anionic which are direct, acid and reactive dyes, cationic which are basic dyes, non-ionic which are disperse dyes, azo, diazo, anthroquinone based and metal complex dyes.[2] The wastewater from colouring process compose of metals, salt, surfactants, organic processing assistants, cationic materials, colour, biological oxygen demand (BOD), chemical oxygen demand (COD), sulphide, acidity/alkalinity, spent solvents, suspended solids, urea, solvents, colour, heat and foam.[1] The commonly available metals in textile wastewater are Pb, Fe, Cu, Cd, Zn, Ni and Cr.[3,4]

Batik is an industry that involves textile printing and dyeing processes. Indonesia has areas operating batik business. The economy of certain areas, such as Pekalongan, mainly depend on batik industry since there were about 1,115 batik home operators in 2011.[5] Printing and dyeing processes consume about 16 and 300 l water per kg product, respectively. In Pekalongan, about 4500 m^3 textile wastewater is released daily.[1] The capacity of wastewater treatment installation is only about 40%. Considering the harmful effects of the wastewater, a proper action is urgently needed to overcome the problems.

There are many methods offered to solve textile industrial wastewater problem. Some research in textile wastewater treatments have been done by coagulation, adsorption, membrane separation and extraction.[6–14] Those conventional technologies have their own advantages and disadvantages. Emulsion liquid membrane (ELM) as an alternative of solvent extraction provides advantages of combining extraction and stripping process in a single step, thus minimising the equipment as well as processing time. This method also effectively removes low-concentration contaminants usually available in textile wastewater.

The basic process of ELM is the use of a three-phase dispersion system. In this system, primary emulsion that consists of membrane and stripping phase is dispersed in the feed or effluent phase, which is the phase to be treated. Carrier as an organic soluble extractant is used for metal separation even in a very low concentration. The metal and carrier form a complex that is soluble in the membrane phase. Subsequently, this complex will permeate through the membranes from the outer to the inner interface. At the inner interface, the complex decomposes through

reversal of the equilibrium reaction and the metal ion is released into the internal phase and the regenerated free carrier diffuses back into the membrane phase.

Although ELM process offers several advantages for various industrial wastewater recoveries including heavy metals, the method needs to be improved to overcome some technical barriers in its application, especially the removal of low-concentration cadmium in the wastewater. The successful application of this method is not only dependent on the selection of suitable emulsification process but also the emulsion formulation in accordance to the solute which is to be recovered. This is obviously related to the emulsion stability that still remains a great challenge for ELM application at industrial scale. It was reported that generally ELM processes suffer emulsion instability of about 8% on average in terms of membrane breakage and emulsion swelling of about 35% on average.[15–20] These figures are interesting when considering the ELM tolerance for membrane breakage and emulsion swelling of 0.1% and 10%, respectively.[21,22]

In order to obtain the liquid membrane with best performance, a detailed study was done to select potential carriers, diluent and stripping solutions which are suitable for cadmium recovery under batch ELM process. The efficiency of extraction process was governed by emulsion formulation including types of carrier. Three parameters namely carrier, stripper and diluent were investigated to screen the most suitable carrier, stripping solution and diluent on extraction efficiency. Several potential carriers and diluents were compared toward their cadmium extraction capacity under emulsion liquid membrane system. Carrier and diluent selections were considered based on their performance in extracting cadmium, with parameter of extraction efficiency.

Carriers were selected based on their capacity to recover cadmium. The suitable carrier must have high tendency in forming complex with cadmium ion. Carrier screening experiment was carried out using two types of carrier, i.e., trioctylamine (TOA) and di-(2-ethylhexyl) phosphoric acid (D2EHPA) which were run under various concentrations. Three types of organic solutions, i.e., kerosene, n-heptane and oxylene were tested. The determination of liquid membrane components was carried out by employing cadmium solvent extraction process, each for extraction and stripping process.

2.   EXPERIMENTAL

2.1   Materials

The non-ionic surfactant of sorbitan monooleate which is commercially known as Span 80 was used as emulsion stabiliser. Kerosene, oxylene (>99%) and n-heptane (>99%) were used as a diluent. Ammonia solution (25%), nitric acid (65%) and acetic acid (96%) were used as internal phase. TOA (>95%) and D2EHPA (95%) were used as carrier. Cadmium chloride (99.99%) was used in the external feed phase. Deionised water was used to prepare all aqueous solutions. The research employed reagents of analytical grade. Span 80, oxylene, n-heptane, ammonia, nitric acid, acetic acid, TOA and D2EHPA were purchased from Merck. Low-odour kerosene and cadmium chloride were obtained from Sigma Aldrich.

2.2   Procedures

Carrier/extractant and diluent selection was done by contacting feed phase (cadmium solution) with organic solution at ratio of 1:1 as given by some studies on cadmium removal using solvent extraction process.[23–29] Cadmium concentration in feed phase was kept constant at 150 ppm. The organic solution consisted of carrier and diluent at various concentrations. Both solutions were mixed at 500 rpm for 24 h using magnetic stirrer, then the samples were allowed to settle and separate. The concentration of cadmium in the feed phase was measured using atomic absorption spectrophotometer (AAS) at wavelength 228.5 nm. The cadmium concentration in loaded organic phase was obtained by mass balance. The obtained value was then used to calculate extraction efficiency as given in the following equation:

$$\text{Extraction efficiency} = \frac{C_{A,III}^{0} - C_{A,III}}{C_{A,III}^{0}} \times 100\% \tag{1}$$

Complete parameters and conditions are presented in Table 1.

Screening for type of stripping solution was done by contacting aqueous phase and organic phase using magnetic stirrer. The aqueous phase consisted of stripping solution either NH_3 HNO_3 or CH_3COOH at fixed concentration of 0.1 M. While the organic phase contained 4 wt% loaded TOA and 96 wt% kerosene. Both of aqueous and loaded organic phases were contacted in the equal volume for 24 h. Afterwards, the samples were allowed to settle and separate. Cadmium concentration in aqueous phase was measured by AAS while cadmium concentration in organic phase was calculated by mass balance. Extraction and stripping efficiency were calculated by Equation 1.

Table 1: Parameters and conditions for screening of emulsion component.

Component	Condition	
	Extraction	Stripping
Type of carrier	D2EHPA and TOA	TOA
Carrier concentration	4–16 wt% (D2EHPA) 1–6 wt%	4 wt%
Type of diluent	Kerosene, n-heptane, oxylene	Kerosene
Type of internal phase	–	NH_3, HNO_3, CH_3COOH
Feed solution and concentration	150 ppm Cd in 0.1 M HCl	Loaded organic solution
Treat ratio	1:1	1:1
Stirring rate and time	500 rpm for 24 h	500 rpm for 24 h

3.   RESULTS AND DISCUSSION

3.1   Carrier Screening

Theoretically, higher carrier concentration results in higher extraction capacity. However, instead of using excessive concentration of carrier unnecessarily, optimum amounts are required to ensure the economic feasibility. Based on these points of view, a series of experiments had been conducted to determine the most suitable carrier for liquid membrane formulation. The examined carriers were divided into acidic and basic types.

3.1.1   Acidic extractant

D2EHPA was first examined as a carrier for cadmium extraction. For better understanding of the behaviour of the carrier, the effect of carrier concentration on the cadmium efficiency was investigated using solvent extraction experiments. The experimental results are presented in Figure 1. The bar chart given in the figure represents the cadmium extraction efficiency provided from contacting equal volume of feed and organic solutions for 24 h at 500 rpm. Feed solution was 150 ppm cadmium in 0.1 M HCl whilst organic solution was composed of D2EHPA and kerosene as an extractant and diluent, respectively. It can be seen from Figure 1 that the extraction efficiency was highly affected by carrier concentration. Only about 35% cadmium was extracted using 4 wt% D2EHPA. The extraction efficiency enhanced significantly from 4 wt% to 12 wt% of carrier concentration. The result showed that carrier concentration of 12 wt% enhanced the extraction efficiency to about 92%. Expecting higher extraction efficiency,

carrier concentration was further increased 16 wt%, but the increase of extraction efficiency was not significant. At 16 wt%, the system should reach about the same efficiency. This means that D2EHPA has an optimum concentration to extract cadmium from feed solution under the condition investigated. Significant increase of extraction efficiency was within 4 wt% to 12 wt%.
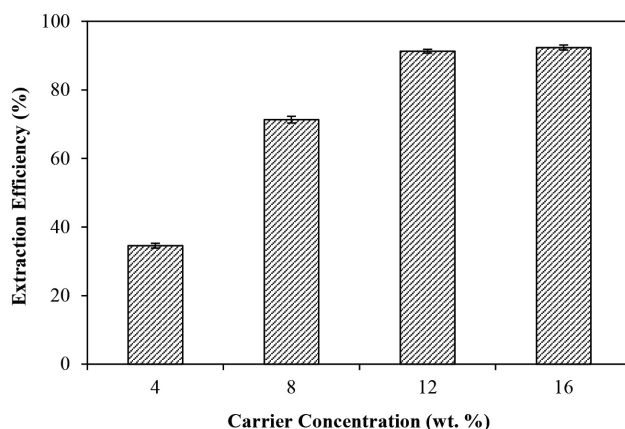

Figure 1: Effect of D2EHPA concentration on extraction efficiency.

The distribution coefficient (K_D) of cadmium prepared by D2EHPA concentration could be obtained from the plot of log (D2EHPA) versus log K_D slope of the line is equal to the number of carrier molecules associated with a metal atom in the extracted species. It was found in Figure 2 that the obtained slope was almost equal to 2, indicating that one mole of cadmium would react with two moles of D2EHPA as mentioned by Basualto et al.[30] Based on these result, the distribution coefficient of various D2EHPA concentration was evaluated by the following equation:

$$K_D = K_D = \frac{C_{A,II}}{C_{A,III}} \tag{2}$$

K_D shows the distribution coefficient, $C_{A,II}$ is organic solution (mg l^{-1}), and $C_{A,III}$ is cadmium-complex concentration in is cadmium concentration in feed phase (mg l^{-1}). Based on the obtained slope value, cadmium reacted with D2EHPA following the reaction as follows:

$$CdCl^4{}_{2-} + 2(HR)_2 \leftrightarrow (CdCl_4R_2).(HR)_2 + 2H^+ \tag{3}$$
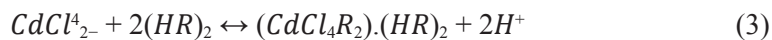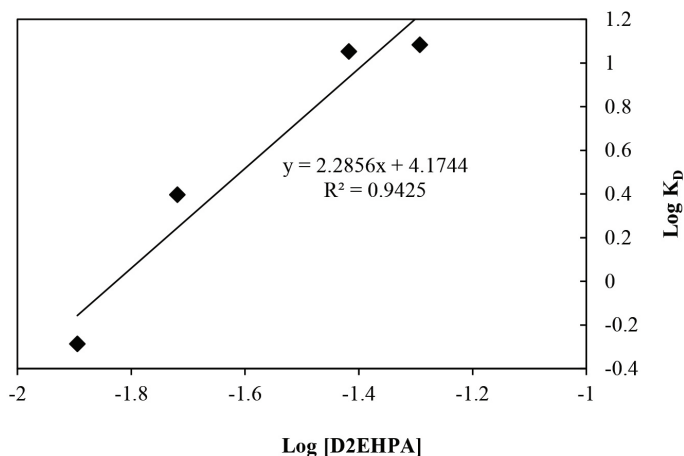
Figure 2: Relationship between D2EHPA concentrations to distribution coefficient.

It should be noted that cadmium in feed solution was available at 150 ppm which is equivalent to 0.0000205 moles. In the meantime, the D2EHPA concentrations employed were 4 wt%, 8 wt%, 12 wt% and 16 wt% which are equivalent to 0.000382, 0.00077, 0.001147 and 0.001537 moles, respectively. Thus, theoretically all the D2EHPA concentrations examined are enough to extract cadmium from feed solution. However, the diffusion of cadmium from aqueous into organic phases is limited due to the existence of mass transfer resistance in the interface of aqueous and organic phases.[31] Thus, higher carrier concentration is preferred as it has higher amount of free D2EHPA for reaction as evidenced by Equation 3. This is consistent with the results obtained above that better cadmium extraction efficiencies were obtained at D2EHPA concentrations of above 8 wt%. Similar observation was also found in previous studies that much more amount of extractant is needed to obtain high extraction efficiency using D2EHPA.[25,26] They found that when toluene was used as the organic phase, high concentration of 0.1 M D2EHPA (equivalent with 3.7 wt%) was needed to obtain 82% extraction efficiency from 5 ppm cadmium in aqueous solution.[26] In another case, when kerosene and mixture of 1% isodecanol with D2EHPA were used as the diluent and extractant respectively, the minimum concentration of 0.15 M D2EHPA (equivalent with 6 wt%) was required to achieve 78% extraction efficiency from 0.00445 M (500 ppm) cadmium in aqueous solution.[26]

3.1.2   Basic extractant

Basic extractant has been known as a promising agent in metal extraction. TOA as a type of basic extractant was chosen and tested in order to study its capability for

cadmium extraction. In order to obtain a clear interpretation of the effect of basic extractant concentration on cadmium extraction efficiency, the solvent extraction experiment was conducted at various TOA concentrations of 1 wt%, 2 wt%, 4 wt% and 6 wt%. Feed solution was 150 ppm cadmium in 0.1 M HCl whilst organic solution is composed of TOA and kerosene as extractant and diluent, respectively. The result is plotted in Figure 3. It can be seen from the figure that as in the case of D2EHPA, the cadmium extraction efficiency using TOA was also highly affected by the extractant concentration. Very limited amount of cadmium could be extracted using TOA concentration of 1 wt%. However, extraction efficiency improved progressively when the extractant concentration was raised from 1 wt% to 4 wt%. Further increase of extractant concentration beyond 4 wt% resulted in almost the same extraction efficiency, in which more than 90% of cadmium was extracted using 4 wt% and 6 wt% of extractant concentration, respectively. This result indicates that it is more than enough to remove cadmium from feed phase by utilising 4 wt% of extractant concentration. Previous studies pointed out that one of the best extractant to remove cadmium by solvent extraction was TOA in kerosene.[32,33] Cadmium can form anionic chloro complexes in chloride solutions and they could be separated from the organic phase by contacting with organic anion exchanger such as protonated TOA. It can be confirmed that below 10% of TOA was enough to extract cadmium with efficiency of about 90%.[33]
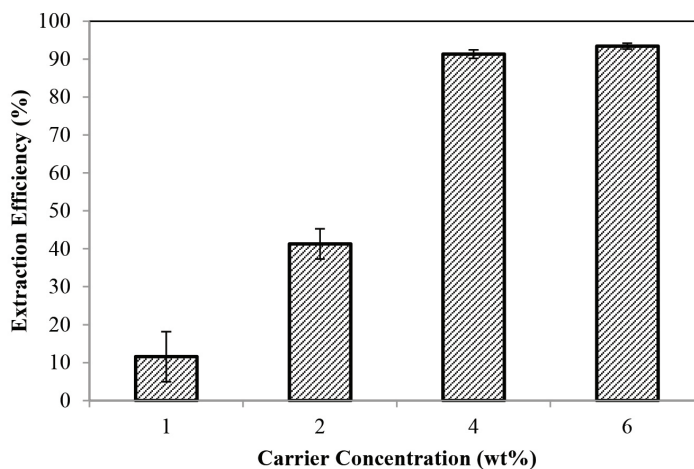

Figure 3: Effect of TOA concentration on extraction efficiency.

The distribution coefficient of cadmium extraction under different TOA concentrations is determined in Figure 4 through the plot of log (TOA) versus log K_D. It could be observed that the obtained slope was about 2, indicating that one mole of cadmium would react with two moles of TOA. Since 4 wt% of extractant

concentration has 0.000346 mole of TOA, it is more than enough to extract 0.0000205 mole of cadmium from 150 ppm cadmium contained in feed phase by considering mass transfer resistance in the interface of aqueous and organic phases. Therefore, 4 wt% of TOA is sufficient.

Based on the obtained slope value, the extraction of cadmium using TOA as extractant was given by the following equation:

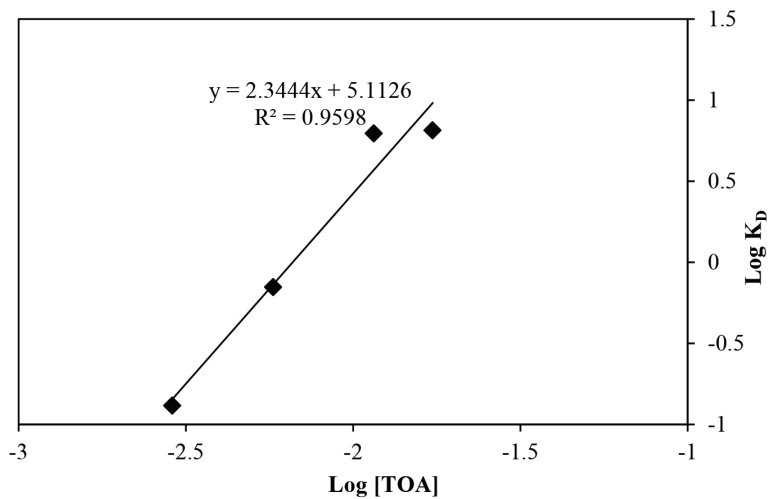$$2H^+ + CdCl^4_{2-} + 2R_3N \leftrightarrow (R_3NH)_2CdCl_4 \tag{4}$$

Figure 4: Relationship between TOA concentrations to distribution coefficient.

Compared to D2EHPA, TOA has better efficiency in extracting cadmium on the same weight basis. Hence, TOA will be used as the extractant in the subsequent studies. Moreover, this finding is important since in ELM processes the extractant or carrier is the most expensive material for emulsion composition. Therefore, it is expected that by minimising the amount of carrier, the overall ELM processes become economically feasible.

3.2   Diluent Screening

Several types of diluent, namely n-heptane, oxylene and kerosene were tested for dilution of TOA and used for extraction of 150 ppm cadmium in aqueous feed solution. The TOA was completely soluble in all tested diluents. In this study, TOA concentration was fixed at 4 wt%. The cadmium extraction was performed

by contacting equal volume of feed and organic solutions for 24 h at 500 rpm. Extraction efficiency generated by these three diluents is presented in Figure 5.
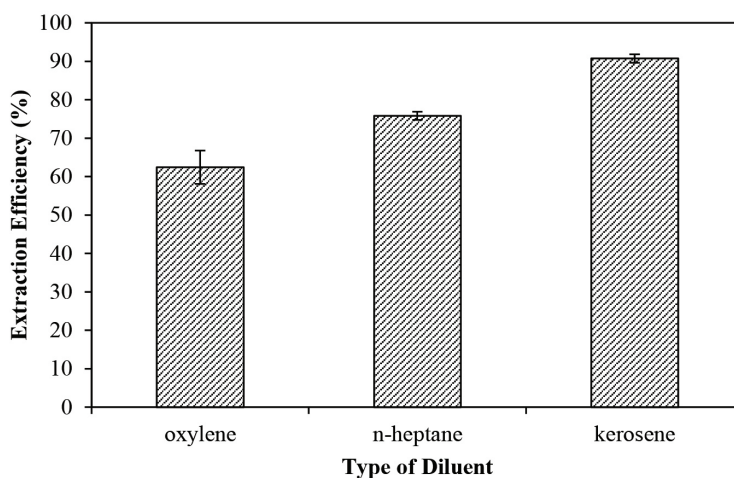

Figure 5: Effect of type of diluents on extraction efficiency.

It can be seen from the figure that the highest extraction efficiency of about 91% was obtained for kerosene, whereas organic solution contained oxylene as the diluent generated the lowest extraction efficiency of about 62%. This result gives an impression of the sequence of extraction ability by different diluents as follows: kerosene > n-heptane > oxylene. Kerosene and n-heptane as aliphatics diluents are generally preferred than oxylene as aromatic diluents because of its low solubility in water.[34,35] Moreover, the ordering of the extraction in terms of magnitude for the diluents is also highly correlated with the polarity or dielectric constant of the diluents. The value of dielectric constant is 1.8 for kerosene, 1.9 for n-heptane, and 2.6 for oxylene. An increase in polarity or dielectric constant of the diluent caused a reduction in extraction efficiency.[36,37]

The evaluation result is given in Table 2. As shown, kerosene as the diluent in organic solution has higher distribution coefficient due to the high cadmium extraction efficiency. Since kerosene provides better extraction performance and distribution coefficient, it was selected as the suitable diluent in the subsequent studies. In addition, kerosene has high boiling point, high solubility of extractant, low toxicity, relatively low viscosity, and it is commercially available with low price, making it more preferred as the diluent. Later, for ELM application, these properties might give better stability, especially in emulsification process aided by a sonicator. Less viscous solution undergoes easier cavitation to form the emulsion, resulting in better emulsion stability.[38] The application of demulsification in the

end of ELM process can minimise the side effect of using this diluent since the used diluent can be recycled.

Table 2: Distribution coefficient of different diluents.

Diluent	K_D
Oxylene	2.99
n-Heptane	5.21
Kerosene	15.17

3.3   Stripping Agent Screening

Another component of liquid membrane is the stripping agent. The stripping agent must be able to strip off the complex of extractant/carrier and metal ion. Using TOA as selected carrier and kerosene as selected diluent for cadmium extraction, study was continued in screening the suitable stripping agent. An acid was employed as stripping solution namely nitric acid (HNO_3), while for the basic solution, ammonia (NH_3) and acetic acid (CH_3COOH) were chosen.

The experiments were performed by contacting the aqueous and loaded organic phases in the equal volume for 24 h. The aqueous phase consisted of stripping solution either NH_3 HNO_3 or CH_3COOH at a fixed concentration of 0.1 M, while the organic phase contained 96 wt% kerosene and 4 wt% loaded TOA obtained from previous diluent screening experiment. Figure 6 shows the capability of NH_3, HNO_3 and CH_3COOH to strip cadmium from loaded organic phase. It was found that NH_3 solution gave the highest extraction efficiency whilst the system using HNO_3 gave the lowest. This shows that under the investigated condition, basic solution is more suitable to strip the cadmium from organic phase containing TOA as the extractant compared to acid solution. This condition is possible because in the stripping reaction, cadmium ion was released from the complex by the OH^- anion contained in the basic stripping solution.[39] On the contrary, the use of acid stripping agents formed a species of H_2CdCl_4 which is not completely ionised, thus reducing the amount of H^+ in the stripping solution. Consequently, further stripping reaction would decrease due to the less availability of proton.[40]
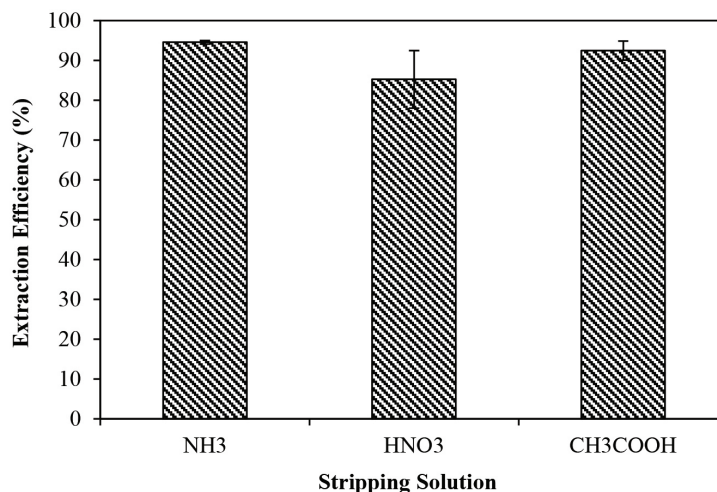
Figure 6: Extraction efficiency for different types of stripping solution.

Based on the result above, the distribution coefficient of different types of stripping solution was also evaluated. The evaluation result is given in Table 3. As shown, NH_3 as the stripping agent has higher distribution coefficient. This is not surprising as it provides high cadmium extraction efficiency. Since NH_3 provides better extraction performance and distribution coefficient, it was chosen as the suitable internal phase solution for further study in ELM system.

Table 3: Distribution coefficient of different stripping phase solutions.

Diluent	K_D
NH_3	13.98
HNO_3	5.02
CH_3COOH	10.36

4.   CONCLUSION

Determination of emulsion liquid membrane components for cadmium removal has been carried out. The screening components consist of carrier, diluent and stripping materials. D2EHPA and TOA as acidic and basic carrier respectively were found to have good performance for cadmium removal. In the meantime, TOA was more efficient compared to D2EHPA as it provided similar extraction efficiency even at low concentration. Among the diluents tested, kerosene was preferred as it gave better ELM performance. The sequence of extraction ability by different

diluents as follows: kerosene > n-heptane > oxylene. This study also found that NH_3 as the stripping agent of ELM gave the highest extraction efficiency, followed by CH_3COOH.

5. ACKNOWLEDGEMENTS

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