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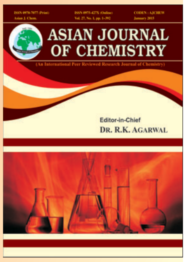

Liquid Emulsion Membrane Stabitiy Studies for Removal of Nickel from Liquid Aqueous Waste

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Stability of the liquid emulsion membrane (LEM) is a measure of its leakage during the operation of metals extraction in liquid emulsion membrane process. As liquid emulsion membrane stability decreases, the permeation of metal ions decreases due to release of the internal stripping aqueous phase containing the extracted metals to the external aqueous phase, which reverses some of the metal already extracted. Liquid- liquid extraction of nickel ions from acetate media was first investigated using di-2-ethylhexylphosphoric acid as an extractant diluted with cyclohexane as a diluent. The results showed that the optimum conditions for extraction of nickel ions from acetate media were as follows, pH 8 at the feed solution containing 0.01 M ammonium acetate, 6 % di-2-ethylhexylphosphoric acid as a carrier, 0.1 M sulfuric acid as a stripper and cyclohexane as a diluent. The different parameters affecting the stability of the prepared liquid emulsion membrane were studied; pH values at the feed solution; surfactant types and concentrations; emulsification time and speed; volume ratios of emulsion to feed solution; and ammonium acetate concentration in the feed solution. The result obtained well be used to prepare a stable membrane to study the permeation and removal of nickel from aqueous waste solution.

Keywords: Liquid emulsion membrane, Nickel(II), Membrane stability.

INTRODUCTION

Over the last decades, there are increasing concerns about hazardous waste disposal due to the problem of environmental pollution. One of the challenging problems in the radioactive waste management is the cleanup of aqueous waste effluents from hazardous elements before re-use or discharge to the environment. Hazardous elements could be radioactive elements or heavy metals which may have toxic behaviours. According to IAEA recommendations, radioactive waste containing heavy metals (mixed waste), it is recommended to remove such heavy metals before solidification because these types of metals have no half life time and could be present for ever at the disposal site[1]. Many radioactivity measurements were carried out on the reactor coolant concerned with detection of the fission products[2-5] where nickel was found to be present in reactor water and spent fuel pool water as radioactive Ni-63.The fresh fuels which are burned-up inside the reactor core are transferred to be stored under deionized water which should be controlled to suppress conditions that might lead to a corrosive environment for the spent fuel and related components[6]. Nickel and its compounds have many industrial and commercial uses. Most nickel is used for the production of stainless steel and other nickel alloys with high corrosion and temperature resistance. Nickel salts of greatest commercial importance are nickel chloride, sulphate, nitrate, carbonate, hydroxide, acetate and oxide[7,8]. Plating is an electrochemical process having advantages of simple apparatus and an economical process. Electroless nickel plating process is a source of stable nickel and is widely used in the automobile and electronic industries[9]. Although nickel is universal and is vital for the function of many organisms, concentrations in some areas from both anthropogenic release and naturally varying levels may be toxic to living organisms[10-12]. Inhalation exposure in occupational settings is a primary route for nickel-induced toxicity and may cause toxic effects in the respiratory tract and immune system[9]. The exposure of the general population to nickel mainly concerned oral intake, primarily through water and food, as a contaminant in drinking water or as both a constituent and contaminant of food[13,14].

Liquid emulsion membranes (LEMs) are improved solvent extraction technique that found different applications in liquid aqueous waste treatment and hydrometallurgy[15-23]. The present work is directed to prepare stable liquid emulsion membrane system for removal of nickel to clean up liquid waste effluents produced from nuclear activities as well as other industrial processes. In this concern, a liquid emulsion membrane system was developed based on di-2-ethylhexyl phosphoric acid (HDEHP) as a carrier, cyclohexane as organic diluents and Span-80 as emulsifier. The optimum conditions for preparing stable liquid emulsion membranes containing the above mentioned carrier were elaborated to obtain suitable efficient and stable liquid emulsion membrane system.

EXPERIMENTAL

All reagents used were of analytical grade. All aqueous solutions were prepared with deionized water. The extractant di-2-ethylhexyl phosphoric acid (HDEHP) was obtained from Merck and was used without any further purification. The surfactants used were obtained from Fluka (Span-80, Arlacel-A, Tween-20, Tween-80 and Span-85). H_2SO_4 was obtained from Sdfci. The diluents were purchased from Poch.

Liquid-liquid extraction preparations and investigations: The aqueous solutions containing nickel were prepared by dissolving its nitrate salt in deionized water. Liquid-liquid extraction was carried out at 1:1 phase ratio aqueous to organic. The two phases are shaked well till equilibrium and then the aqueous phase was separated by centrifugation and analyzed for nickel using spectrophotometer (Shimadzu model 160A double beam UV spectrophotometer) using PAR reagent[24]. The distribution ratio (D) and the extraction percentage (E, %) were calculated by the relations:

$$D = \frac{(C_0 - C_e)}{C_e} \tag{1}$$

$$E\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

where C_0 is the initial concentration of metal ions in the feed solution and C_e is the metal ion concentration in the feed solution at the equilibrium time.

Liquid emulsion membrane preparations and stability studies: Liquid emulsion membrane was prepared by mixing 25 mL of the organic carrier diluted in cyclohexane with 1 mL of the surfactant. To this mixture, 25 mL of the stripping aqueous solution was added. The solution was then emulsified with an ultrahigh speed homogenizer. A stirring speed of 11500 rpm was used for 6 min to form the emulsion. The prepared W/O emulsion was then poured into the external aqueous phase. The system was stirred with a magnetic stirrer of variable speeds. Samples were taken at different time's interval from the external aqueous phase for analysis of nickel. The stability of the prepared liquid emulsion membrane was studied in terms of the degree of leakage of a yellow dye as a tracer from the stripping internal aqueous phase to the external aqueous by the following expression[25]:

$$B\ (\%) = \frac{[\text{dye}]_{\text{ext}}}{[\text{dye}]_{\text{in}}} \times 100 \tag{3}$$

where B is the emulsion breakage and the subscripts, ext and in, represents the external and internal aqueous phases, respectively. The operating conditions, unless otherwise stated, were; initial concentration of Ni(II) ion was 100 mg/L in ammonium acetate solution; the organic phase was 4 % HDEHP in cyclohexane and the stripping phase was 0.1 M H_2SO_4.

RESULTS AND DISCUSSION

Liquid-liquid extraction investigation: For the application of liquid membranes (LMs) as a technique for metal ions extraction and separation, liquid-liquid (L-L) extraction is usually carried out as a first step to help in the selection of the approximate conditions for selective permeation of metal ions across the liquid membrane. The liquid-liquid extraction investigations were started by studying the extraction of Ni(II) by HDEHP in cyclohexane. The different parameters affecting the extraction process were studied like; pH values; ionic strength by adding ammonium acetate, extractant concentration; diluents types; stripper types and concentrations and shaking time. The results obtained were analyzed to get the optimum conditions for the removal process.

Effect of hydrogen ion concentration: A liquid-liquid batch extraction of 100 mg/L of Ni(II) ions from neutral media by 4 % HDEHP in cyclohexane at different pH's ranges from 1 to 9 was investigated. The pH of feed solution was adjusted using nitric acid and ammonia solutions. The data obtained is given in Fig. 1. Under these conditions we reached an extraction yield of 35 and 37.8 at pH 8 and 9. This is explained by the fact that the H^+ ions of acid being in excess in the aqueous phase results in equilibrium shift to the left. After pH 9, nickel precipitated as nickel hydroxide[26].

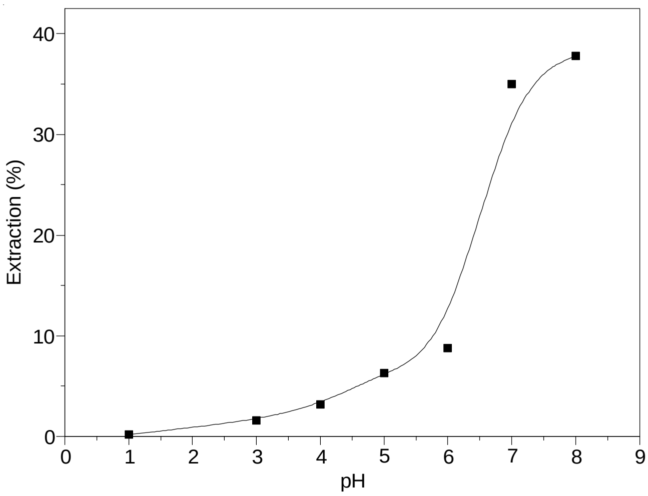

Fig. 1. Effect of pH on the extraction of 100 mg/L Ni(II) by 4 % HDEHP/cyclohexane in absence of ammonium acetate

Influence of the ionic strength on the extraction of nickel: The influence of the ionic strength on the extraction yield has been studied by adding ammonium acetate to the aqueous phase. The previous experiment was rechecked again in presence of 0.01M ammonium acetate in the feed solution. The data obtained is given in Fig. 2. It is clear that, nickel extraction was improved in presence of ammonium acetate with increasing the pH with maximum extraction of 78.5 and 80 % at pH 8 and 9. This is referred to the fact that the cationic exchange being more difficult when the acidity increased because the hydrogen ions compete with nickel ions[27]. For effective extraction of nickel, the pH was controlled at pH 8.

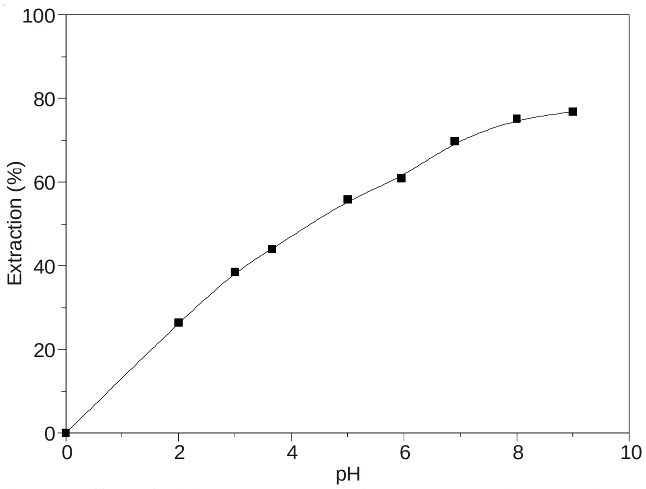

Fig. 2. Effect of adding 0.01M ammonium acetate on the extraction of 100 mg/L Ni(II) by 4 % HDEHP/cyclohexane at different pHs

Effect of ammonium acetate concentrations on the extraction of nickel: Effect of ammonium acetate concentration in the aqueous phase on the extraction yield of 100 mg/L nickel at pH 8 by 4 % HDEHP was investigated in the range from 0.005 to 1 M (Fig. 3). It was observed that the extraction percentage of Ni is greatly improved in presence of ammonium acetate whatever its concentration till 0.1 M. This is because the concentration of H^+ decreases with increasing the acetate concentration leading to oppose the diffusion of nickel to the organic phase[28]. Increasing the concentration of ammonium acetate above 0.1 M shows a decrease in the extraction yield because the ammonium ions begin to compete with nickel ions[29]. According to this result, 0.01 M ammonium acetate was used to enhance the extraction of nickel.

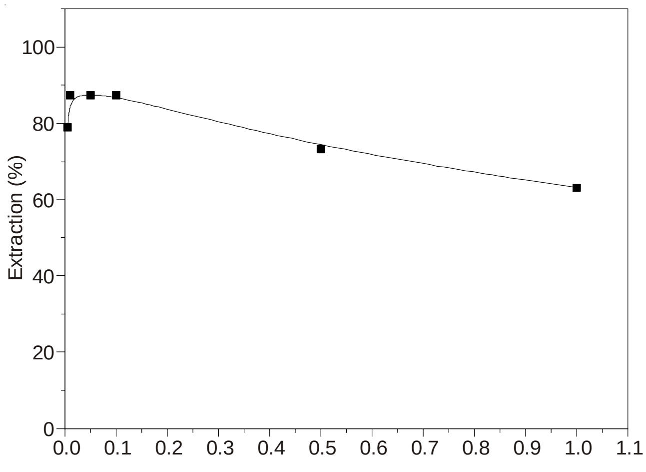

Fig. 3. Effect of different ammonium acetate concentrations on the extraction of 100 mg/L Ni(II) by 4 % HDEHP/cyclohexane at pH 8

Effect of diluents: Different diluents were examined for the extraction of 100 mg/L nickel from 0.01 M ammonium acetate at pH 8 by 4 % HDEHP namely; toluene, cyclohexane and xylene as shown in Table-1. It was found that the extraction of nickel by HDEHP diluted with cyclohexane shows the highest value. This is referred to the dielectric constant, because the extraction of metal ions increases with decreasing of the dielectric constant of diluents[30].

TABLE-1
EFFECT OF DIFFERENT DILUENTS ON THE EXTRACTION OF 100 mg/L Ni(II)/0.01 M AMMONIUM ACETATE BY 4 % HDEHP/CYCLOHEXANE

Diluents type	Extraction (%)
Cyclohexane	87
Toluene	81
Xylene	65

Effect of HDEHP concentration: The carrier HDEHP is known to dimerize in non-polar solvents and it works during the extraction reaction as a cation therefore, the extraction of Ni(II) ions at low acetate concentration may be represented by eqn. 4 as follow:

$$Ni^{2+}_{aq} + Ac^{-} + 2(HR)_{2,\,org} = [Ni(Ac).(HR_2).2HR]_{org} + H^{+}_{aq} \quad (4)$$

To study the effect of carrier concentration, 100 mg/L nickel dissolved in 0.01 M ammonium acetate and adjusted to pH 8 was extracted at various concentrations of HDEHP from 2-10 % (v/v). The data presented in Fig. 4. It can be seen that as HDEHP concentration increased from 2 to 6 % the extraction efficency is higly increaded due to increase the capacity of the carrier. Increasing the concentration above 6 % shows no significant effect on the extration efficiency, therefore, 6 % HDEHP was used as optimum condition.

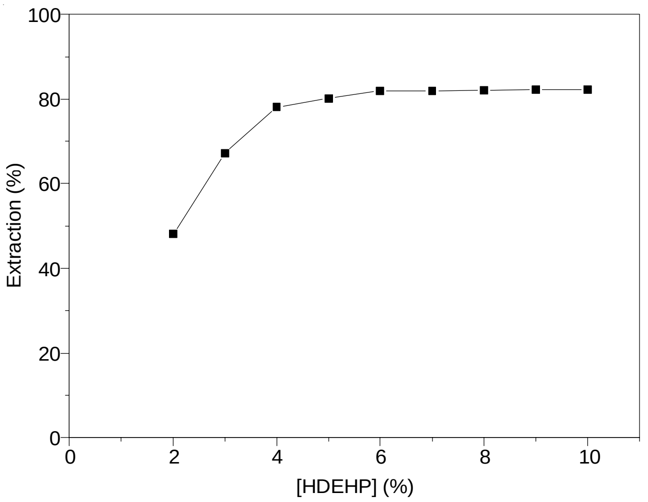

Fig. 4. Effect of HDEHP concentration on the extraction % of 100 mg/L Ni(II) from 0.01M ammonium acetate at pH 8

Stripping investigations: Stripping investigations were carried out to choose an appropriate stripping solution which cans selectively back-extracted Ni(II) from the organic phase to a suitable aqueous solution by chemical means, leaving HDEHP in the organic phase to be recycled. The usual procedure being used is to shake the solvent containing nickel-HDEHP complex with a volume of aqueous containing acids or other reagents under conditions whereby the metal ions are shifted into the aqueous phase. In this concern different stripping agents (0.5 M each) were tested namely; HNO_3, H_2SO_4, HCl, citric acid and EDTA in phase ratio (org.:aqueous) 1:1. The data obtained are given in Table-2. From this data, it is clear that, 2 M H_2SO_4 is the best stripping agent for nickel ions from HDEHP as compared to HCl, HNO_3, citric acid and EDTA.

TABLE-2
EFFECT OF DIFFERENT STRIPPING AGENTS ON THE STRIPPING % OF NICKEL FROM HDEHP IN CYCLOHEXANE

Stripping agent	Stripping efficiency (%)
0.5 M H_2SO_4	91
0.5 M HNO_3	71
0.5 M HCl	70
0.5 M Citric acid	79
0.5 M EDTA	15

Effect of Striping agent concentration: The effect of stripping agent concentration (H_2SO_4) in the range from 0.01 to 2 M on the stripping of Ni(II) from HDEHP/ cyclohexane was studied. Fig. 5 showed that the stripping efficiency of Ni(II) increases rapidly with increasing the concentration of H_2SO_4 from (0.01-0.1 M). This may be due to the increase of hydrogen ion concentrations which enhance the reversible reaction direction. Further increase of stripper concentration from (0.1-2 M) shows no significant effect. Therefore, 0.1 M H_2SO_4 was used as a stripper.

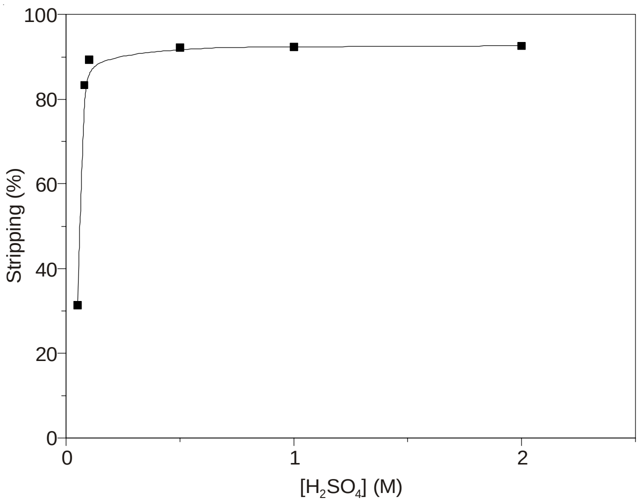

Fig. 5. Effect of different concentration of H_2SO_4 on stripping of Ni(II) from HDEHP/cyclohexane

Effect of shaking time: Kinetic investigation was carried out in order to determine the effect of shaking time (1-60 min) on the extraction efficiency of 100 mg/L nickel from 0.01 M ammonium acetate at pH 8 by %6 HDEHP/cyclohexane. In this concern, the shacking time ranging from 1 to 60 min was tested. From the result represented in Fig. 6 it is clear that the extraction percentage of nickel ions increases with increasing the shaking time and the maximum extraction percent obtained was 80 % after 30 min.

Liquid emulsion membrane preparation and stability studies: The stability of the prepared liquid emulsion membrane is one of the most important factors that affecting the permeation process. Membrane break-up causes a decrease in the separation efficiency due to the leakage of the separated ions from the internal aqueous phase to the external aqueous phase[31]. Liquid emulsion membrane globules are stabilized by adding suitable surfactant. The stability of liquid emulsion membrane was investigated by tracing the yellow dye which loaded into the internal aqueous phase and detect its leakage in the external aqueous phase. The per cent leakage was determined[25] using eqn. 3. It is important to mention that the yellow dye was examined first to ensure that it is not extracted by the system used. The different factors affecting the stability of liquid emulsion membrane like; surfactant types and concentrations; emulsification time and speed *etc*., were studied. Unless otherwise stated, the general conditions for preparing and examine the stability of liquid emulsion membrane were as follow: the membrane phase was 6 % HDEHP/cyclohexane, 1.8 % v/v Span-80 and 0.1 M H_2SO_4. The external aqueous phase was 0.01 M ammonium acetate adjusted to pH 8.

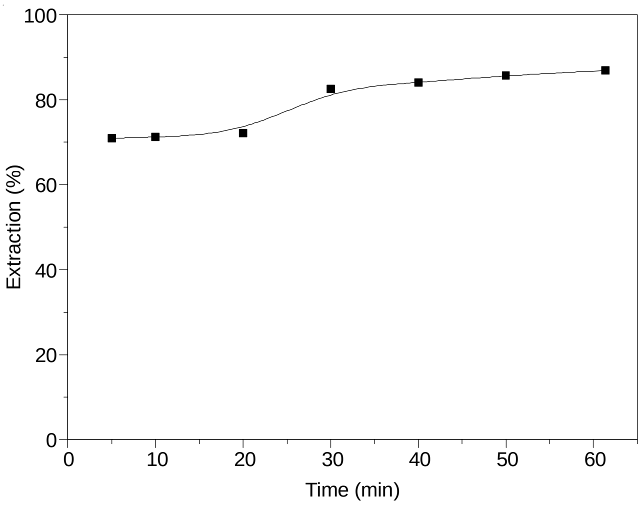

Fig. 6. Effect of shaking time on the extraction of 100 mg/L Ni(II) nickel from 0.01 M ammonium acetate at pH 8 by 6 % HDEHP/ cyclohexane

Effect of surfactant types on liquid emulsion membrane stability: The effect of surfactant types on the amount of yellow dye leaked from the internal aqueous phase to the external aqueous phase as indictor for the prepared membrane stability was studied using different surfactants with constant concentration of 2 % v/v. The different surfactants experimented were Span-80, Arlacel-A and Span-20, Tween-20 and Tween-80. It is to be mentioned that both Tween-20 and Tween-80 showed no emulsification for the used system. The leakage percentage for the other investigated surfactants was studied as a function of time (Fig. 7). It was found that Span-80 showed the highest stability for the prepared emulsion membrane.

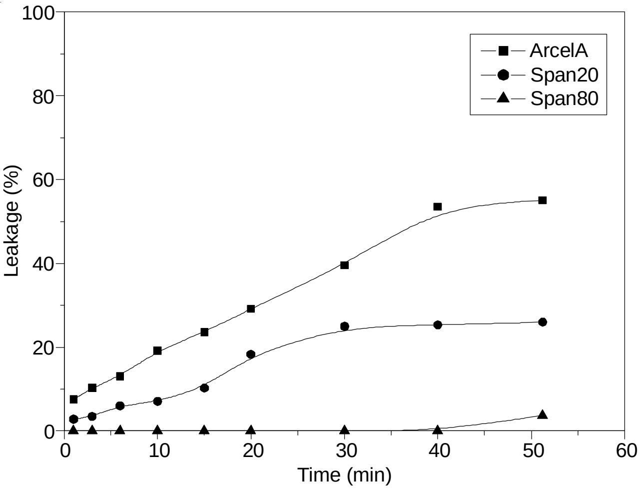

Fig. 7. Effect of different surfactant types on the stability of liquid emulsion membrane

Effect of surfactant concentration on liquid emulsion membrane stability: Since, Span-80 showed the highest stability for the prepared membrane therefore, the effect of its concentration on the amount of yellow dye leaked from the internal aqueous phase to the external aqueous phase was studied as in Fig. 8. It was found that with increasing the surfactant concentration in the range from 0.6 to 1.8 % v/v, the stability of emulsion globules increases. This is due to the fact that; as the concentration of surfactant increases, it will be adsorbed to a greater extent, hence a more compact and more strongly adsorbed interfacial film of surfactant molecules would be formed. Increasing the surfactant concentration to 2 % shows no significant increase in the stability of the membrane. Therefore a concentration of 1.8 % v/v of Span-80 is used in preparing the emulsion membrane.

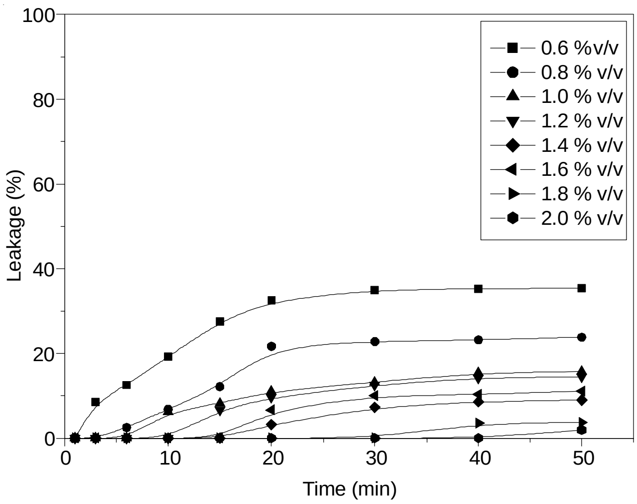

Fig. 8. Effect of Span-80 concentrations on the stability of liquid emulsion membrane

Effect of emulsification speed: The effect of emulsification speed on the stability of the prepared emulsion membrane was investigated. Different speeds from 8000 to 11500 rpm were tested as shown in Fig. 9. It was observed that the emulsion stability increases when the emulsification speed increases from 8000 rpm to 11500 rpm. This is due to the fact that, efficient emulsification gives a good dispersion of the internal aqueous phase into the membrane. Also, as the emulsification speed increases the drops become smaller and they will take much more time to coalesce as well as they shall have large surface area for permeation and hence obtaining a higher fraction of metals recovery[32]. Therefore emulsification speed of 11500 rpm was used for preparation the liquid emulsion membrane.

Effect of emulsification time: The effect of emulsification time (1-8 min) in the emulsion stability was tested as shown in Fig. 10. It is clear that the stability of liquid emulsion membrane increases as the emulsification time increases up to 6 min. This is because as the emulsification time increases; the mixture will be more homogeny; more internal phase will be shrunk and entrapped in the membrane and finer droplets will be produced which take much more time to coalescence. Lower membrane stability was seen for emulsification time less than 6 min because the prepared emulsion globules were had a large size leading to rapid coalescence of these globules. On the other hand, lower membrane stability was also seen for emulsification time over 6 min (8 min) due to high internal shearing leading to a very high number of small droplets by volume unit causing their coalescence[33]. Therefore, emulsification time of 6 min was used to prepare the membrane.

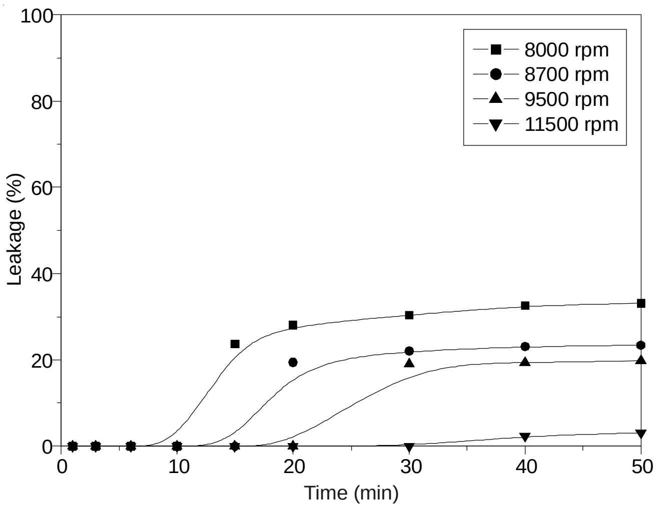

Fig. 9. Effect of emulsification speed on the stability of liquid emulsion membrane

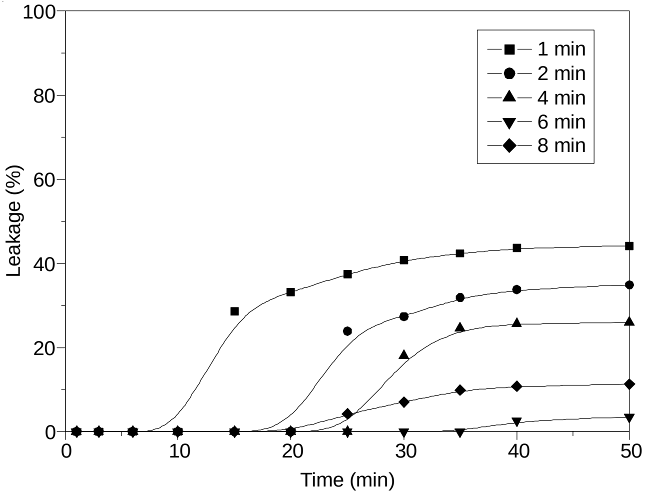

Fig. 10. Effect of emulsification time on the stability of liquid emulsion membrane

Effect of rotating speed of the external aqueous phase and membrane phase: A high stirring speed of the external aqueous phase after pouring the liquid emulsion membrane is required to obtain small globules with larger interface area leading to high mass transfer of the extracted metal ions. Formation of small globules by increasing the stirring rate will also decreasing the coalescence of the emulsion globules. Very high stirring speed could increase the water transfer into the membrane, thus increasing the membrane swelling and hence the leakage per cent[34]. The effect of stirring speed of the external aqueous phase after pouring the liquid emulsion membrane on the membrane stability was studied in the range (200-500) rpm as shown in Fig. 11. It is clear that the stirring speed of 350 rpm gives a lower leakage per cent. Therefore, 350 rpm stirring speed was used for using the prepared emulsion membrane system for removing of nickel ions.

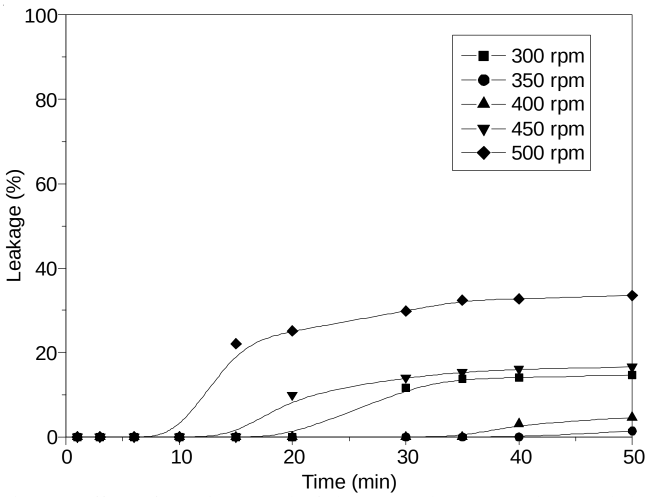

Fig. 11. Effect of rotating speed of the external aqueous phase and the membrane phase

Effect of hydrogen ion concentration in the external aqueous phase: The pH of the external aqueous phase played an important role in the stability of the prepared liquid emulsion membrane. The effect of pH was studied in the range from 3 to 9.0 (Fig. 12). It is clear that the stability of the prepared membrane increases with increases in the pH from 3 to 8. Increasing the pH more than 8 showed a decrease of the stability of the prepared membrane due to the osmotic pressure difference between the external aqueous phase and the inner phase of the prepared emulsion membrane which drives water to the internal phase leading to membrane swelling and breakage[35].

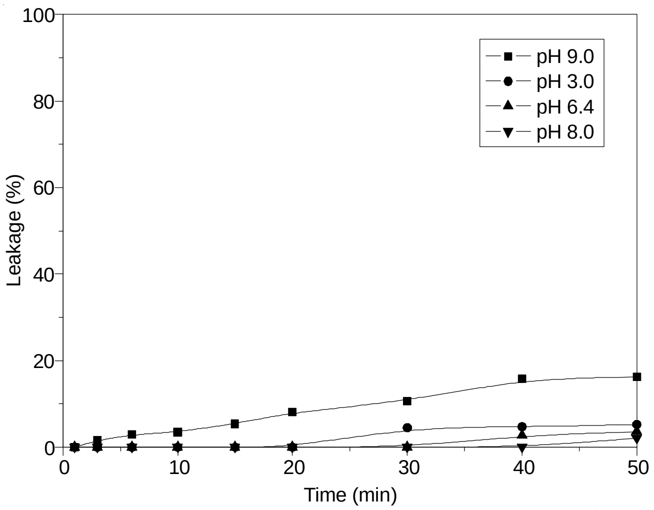

Fig. 12. Effect of pH of the external aqueous phase on the stability of liquid emulsion membrane

Effect of ammonium acetate concentration in the external aqueous phase: In order to evaluate the effect of ammonium acetate concentration in the external aqueous phase on the stability of the prepared membrane, external aqueous phases with different concentrations of ammonium acetate in the range from 0.01 to 1 M were tested (Fig. 13). It is observed that the stability of the membrane decreases with increases the concentration of ammonium acetate in the external aqueous phase from 0.01 to 1 M. Therefore, 0.01 M ammonium acetate was used for the membrane preparation.

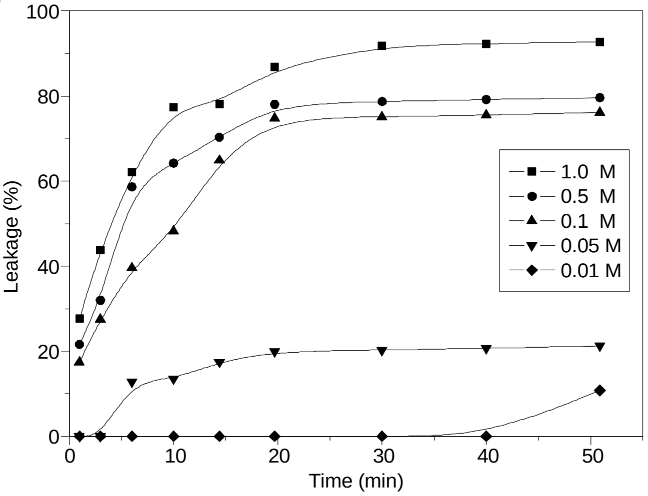

Fig. 13. Effect of ammonium acetate concentration on the stability of liquid emulsion membrane

Effect of temperature: Temperature often has indirect effects on emulsification as a result of altering the interfacial tension, adsorption of emulsifier and viscosity. The effect of temperature on the stability of the prepared membrane was studied within the temperature range 15-50 °C (Fig. 14). It is clear that the stability of membrane increases with increases the temperature from 15 to 25 °C. After 25 °C, the stability of liquid emulsion membrane showed a rapid decrease and the most stable membrane was generated at 25 °C. There is some evidence that a sharp increase or decrease of temperature tend to coagulate the particles, thereby causing the deterioration of emulsions[36].

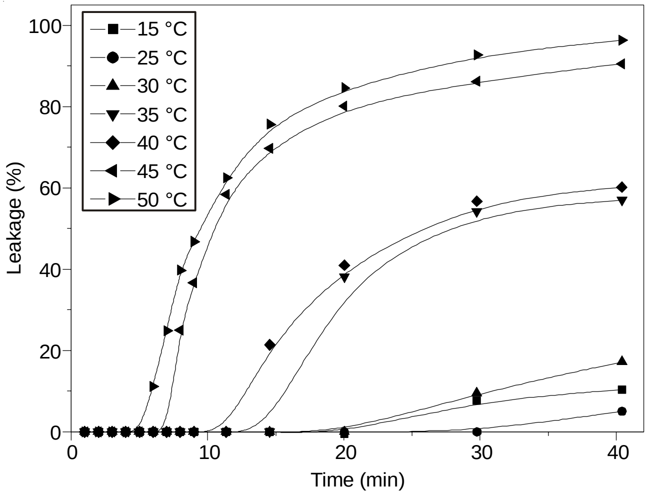

Fig. 14. Effect of temperature on the stability of liquid emulsion membrane

Effect of stripper concentration in the internal aqueous phase: The effect of H_2SO_4 concentration in the internal aqueous phase on the stability of the prepared emulsion membrane was investigated. Different H_2SO_4 concentrations from 0.05 to 0.5 M were tested (Fig. 15). It was observed that the stability of liquid emulsion membrane decreases with increasing the H_2SO_4 concentration. This may be due to the effect of H_2SO_4 concentration on the organic oil layer in the prepared liquid emulsion membrane which responsible for the stability of membrane.

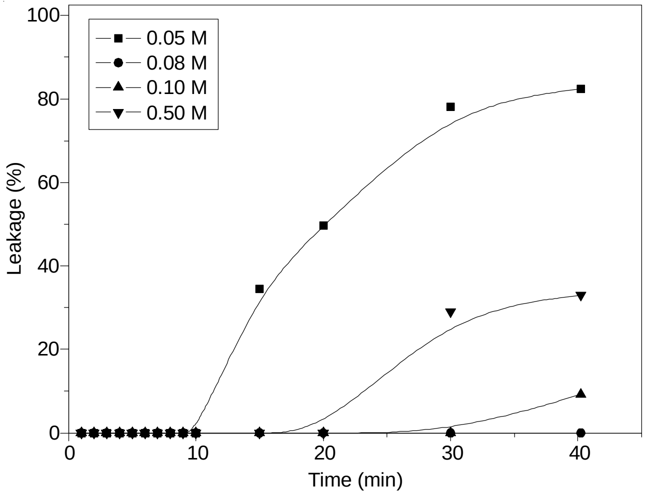

Fig. 15. Effect of stripper concentration in the internal aqueous phase on the stability of liquid emulsion membrane

Conclusion

Removal of nickel from aqueous waste is of great concern due to its hazardous effect both in its radioactive or inactive form. Liquid-liquid extraction and stripping experiments of nickel showed that Ni(II) is extracted from neutral media at pH 8 by 6 % HDEHP in cyclohexane but with low extraction yield (37.5 %). The extraction yield was enhanced by adding 0.01 M ammonium acetate in the aqueous phase which enhances the extraction rate up to 80 % at pH 8.0. Extracted Ni(II) species was stripped by 0.1 M H_2SO_4 solution. These conditions were used to prepare liquid emulsion membrane system for removal of nickel from liquid aqueous waste. Stability studies of the prepared membrane showed that, the prepared liquid emulsion membrane is stable for 30 min when 1.8 % Span-80 is used as a surfactant; emulsification speed of 11500 rpm for 6 min; stirring speed of the external aqueous phase of 350 rpm; pH 8 at the external aqueous phase; 0.01 M ammonium acetate at the external aqueous phase, 0.1 M H_2SO_4 in the internal aqueous phase and temperature of 25 °C. The previous conditions will be used to study the permeation of nickel through the prepared liquid emulsion membrane system.

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