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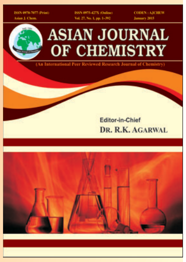

Removal of Lead from Liquid Waste Using Liquid Emulsion Membrane

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Removal of Pb(II) from contaminated aqueous waste using liquid emulsion membrane is of great concern. The liquid membrane is made up of di-2-ethylhexyl phosphoric acid as an extractant, cyclohexane as a diluent, sulfuric acid as a stripper and Span-80 as a surfactant. The extractant and the stripper were selected according to batch extraction experiments. The important parameters affecting the permeation of Pb(II) through the prepared liquid emulsion membrane were investigated. The stability of the prepared membrane which play an important role in the permeation process was studied as a function of surfactant types and concentration.

Keywords: Emulsion liquid membrane, Lead(II), Liquid waste.

INTRODUCTION

Over the last decades, lead is used in different industrial applications as manufacturing of batteries and explosives. Removal of lead from contaminated aqueous waste resulting from its wide applications is of great concern because it has a highly toxic behaviour especially for children. Different methods have been used for the removal of lead from contaminated aqueous waste like chemical precipitation, adsorption, ionic exchange and solvent extraction[1]. Emulsion liquid membrane reported by Li[2] has a great approach for removal, separation and preconcentration of metal ions including heavy metals. Emulsion liquid membrane technique has been widely used to remove dissolved metals due to its high separation efficiency and its potential application variety, studies in this respect being of great interest[3-23]. Tests were carried out to remove radioactive elements like uranium and uranium products from nuclear wastes[24,25] using liquid membranes technique. The components of the emulsion liquid membrane systems are: solvent, emulsifier, receiving aqueous phase, source phase (aqueous phase in which are dissolved the components to be separated) and carrier in the processes with facilitated transport. The three liquid systems are stabilized by an emulsifier at a concentration of 1-5 %, depending on the liquid membrane. Receiving phase is emulsified in an organic solvent under vigorous stirring. The primary emulsion formed is stable, due to a microscopic droplet size of receiving phase (1-10 μm) and due to its high specific emulsifier content. After that, the prepared membrane is mixed with the external aqueous phase containing the metals to be extracted. For this purpose, the emulsion is dispersed in the source phase, under gentle stirring. The mixture is slowly stirred to form larger drops of primary emulsion in the source phase. The diameter of these drops is of the order of 0.1-2 mm. This paper aims at studying the possible retention of lead ions from synthetic aqueous solutions by emulsion type liquid membrane technique (ELM).

EXPERIMENTAL

The reagents used were of high pure analytical reagents. Liquid solutions were prepared using deionized water. The carrier di-2-ethylhexyl phosphoric acid was obtained from Merck. All surfactants used and the stripper H_2SO_4 acid were obtained from SDFCI. The diluents were purchased from Poch. Lead salt was obtained from alpha chemicals and its aqueous solutions were prepared by dissolving its nitrate salt in deionized water. Ammonium acetate was obtained from Honeywell. The hydrogen ion concentration of the different solutions was measured accurately using a digital pH meter of the type (Hanna Instruments 8417, Italy).

Liquid-liquid extraction preparations and investigations: Liquid-liquid extraction of lead was investigated by adding equal volumes (25 mL) of aqueous and organic solutions in thermostatic shaker at 25 °C for 1 h, the aqueous and organic phases have been separated using centrifugation and the aqueous phase was analyzed for lead using spectrophotometer (Shimadzu model 160A double beam UV spectrophotometer) and PAR reagent[26].The distribution ratio (D) and the extraction percentage (% E) were calculated by the relations:

$$D = C_0\text{-}C_e/C_e \quad (1)$$

$$\%E = [(C_0–C_e)/C_0] \times 100 \quad (2)$$

where C_0 is initial lead concentration in the aqueous solution and C_e is lead concentration after equilibrium.

Liquid emulsion membrane preparations and stability studies: Preparation of liquid emulsion membrane was carried out by preparing 25 mL of the extractant dissolved in appropriate solvent mixed with 1 mL of the suitable surfactant. To this solution, another 25 mL of the stripper dissolved in deionized water was added. The solution was then emulsified using ultrahigh speed homogenizer at stirring speed of 11500 rpm for about 6 min to form the emulsion membrane. The prepared membrane was then mixed with the external aqueous phase containing lead and stirred with a magnetic stirrer of variable speeds. Analysis of lead was carried out by following its concentration in the feed solution at different time intervals. The stability of the prepared emulsion liquid membrane was investigated by following the degree of leakage of a tracer (yellow dye) from the internal aqueous phase to the external aqueous phase by the following expression[27]:

$$\%E = ([\text{Tracer}]_{ext} / [\text{Tracer}]_{in}) \times 100 \quad (3)$$

where E is the per cent of 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 Pb(II) ions 100 mg/L in 0.01 M ammonium acetate solution; the organic phase was 6 % di-2-ethylhexyl phosphoric acid (HDEHP) in cyclohexane and the stripping phase was 0.1 M H_2SO_4.

RESULTS AND DISCUSSION

Liquid-liquid extraction investigation: Batch solvent extraction investigations were firstly started to study the extraction of Pb(II) by HDEHP in cyclohexane. The parameters affecting the extraction of lead have been investigated. The general conditions used for such study were as follows unless otherwise stated: the aqueous phase was 100 mg/L of Pb(II) in 0.01 M ammonium acetate and the organic phase was 6 % HDEHP in cyclohexane. The carrier HDEHP is known to dimerize in non-polar solvents as reported by Guezzen and Didi[28] and it works during the extraction reaction as a cation exchange. The extraction of lead ions at low acetate concentration may be represented by eqn. 4 as follow[29]:

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

Effect of hydrogen ion concentration in feed solution: A liquid-liquid batch extraction of 100 mg/L of Pb(II) ions in 0.01 M ammonium acetate media by 6 % HDEHP in cyclohexane at different pH's ranges from 1 to 8 was investigated. The pH of feed solution was adjusted using nitric acid and ammonia solutions. Fig. 1 shown that the extraction yield increases with increasing the pH with maximum extraction of 99 % at pH 5. The increase in the extraction percent of lead with increasing the pH value is referred to the fact that as the acidity decreases the completion of hydrogen ions with the metal ions decreases and the extraction increases[30]. It should be mentioned that, the results obtained at pH higher than 5.0 is not due to lead extraction, but due to its absence in the aqueous phase as a result of its precipitation at pH higher than 5.0. So, pH 5.0 is taken as the best result.

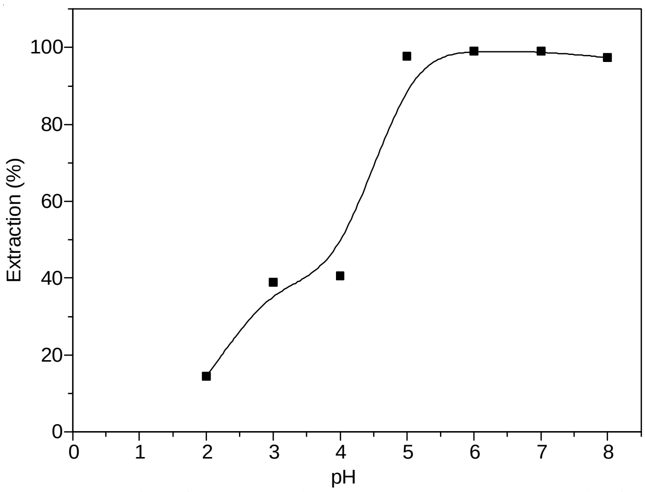

Fig. 1. Extraction of 100 mg/L Pb(II)/0.01 M ammonium acetate by 6 % HDEHP/cyclohexane at different pHs

Effect of di-2-ethylhexyl phosphoric acid concentration: The effect of carrier concentration plays an important role in the extraction process. 100 mg/L lead in 0.01 M ammonium acetate was adjusted to pH 5 and extracted with different concentrations of HDEHP from 2 to 8 % (v/v). The data presented in Fig. 2. It was found that an increase in extractant concentration from 2 to 6 % leads to a high increase in extraction rate as a result of increasing carrier capacity. With increasing HDEHP concentration from 6 to 8 %, there was no effect on the extraction rate, as a result, 6 % HDEHP was used for the optimum results.

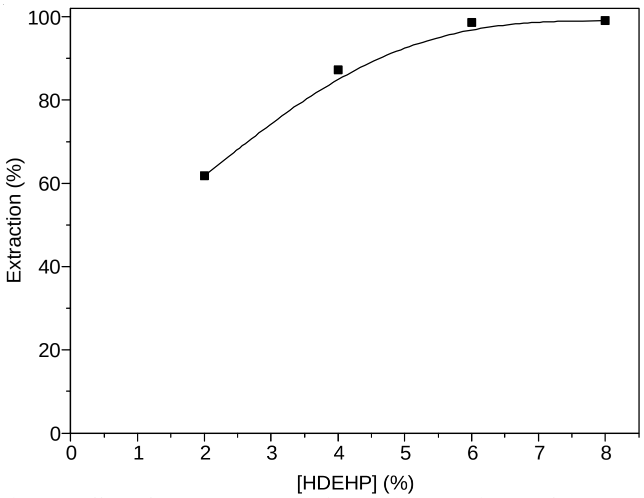

Fig. 2. Effect of HDEHP concentration on the extraction % of 100 mg/L Pb(II) in 0.01 M ammonium acetate at pH 5

Effect of type of stripping agent: Stripping of the extracted lead species from their organic phases was investigated using different stripping agents. The data obtained showed that 71, 86 and 92 % of lead were recovered using 0.5 M aqueous solutions of HCl, HNO_3 and H_2SO_4 respectively. So, H_2SO_4 was chosen as a stripper.

Effect of striping agent concentration: Different H_2SO_4 concentrations were investigated (0.01-2 M) for the recovery of lead from the organic solution as shown in Fig. 3. It is clear that, the stripping efficiency of Pb(II) increases rapidly with increasing the concentration of H_2SO_4 from (0.01-0.1 M) due

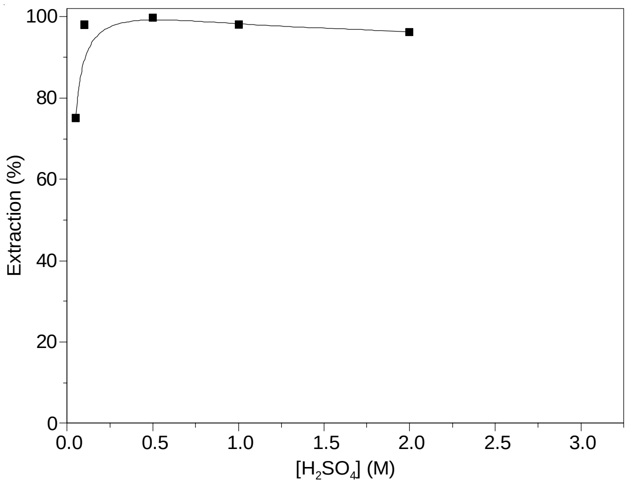

Fig. 3. Effect of different concentration of H_2SO_4 on stripping of Pb(II) from HDEHP/cyclohexane

to the increase of hydrogen ion concentrations which enhance the reversible reaction direction. Further increase in stripper concentration from (0.1-2 M) shows no effect on the stripping efficiency.

Liquid emulsion membrane preparation and stability measurements: One of the most important factors which affect the extraction of metal ions by emulsion liquid membrane is the membrane stability. Membrane leakage decreases the extraction efficiency due to release the extracted metal ions from the internal aqueous phase to the feed solution (external aqueous phase)[31]. It was found that, surfactants play an important role in stabilization of emulsion liquid membranes to give an good emulsion stability during metals transferring stage. Therefore, studying the role of surfactants types and concentration on the membrane stability is of main concern

Effect of surfactant types on the stability of liquid emulsion membrane: Different surfactants with constant concentration of 2 % v/v namely; Span-80, Arlacel-A and Span-20 were used for this investigation. The amount of yellow dye leaked from the internal aqueous phase to the feed solution as indictor for membrane stability was studied as a function of time as mentioned before. From Fig. 4, Span-80 was chosen as a surfactant because it gives the most stable emulsion liquid membrane.

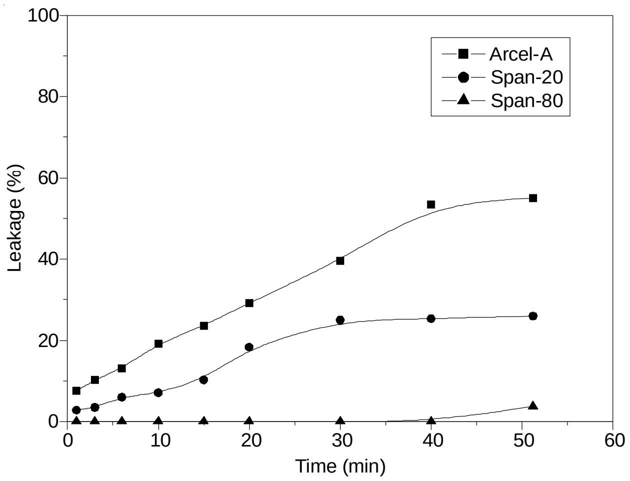

Fig. 4. Effect of different surfactant types on the stability of emulsion liquid membrane

Effect of surfactant concentration on liquid emulsion membrane stability: Different Span-80 concentrations were tested in the range from 0.6 to 2 % for the stability of liquid emulsion membrane. It is clear that the stability of liquid emulsion membrane increases by increases the concentration of Span-80 (Fig. 5). This is because the adsorption of surfactant to a greater extents which form more compact and more strongly adsorbed interfacial film of surfactant molecules. It should be mentioned that, increasing the surfactant concentration to 2 % shows no significant increase in the stability of the membrane.

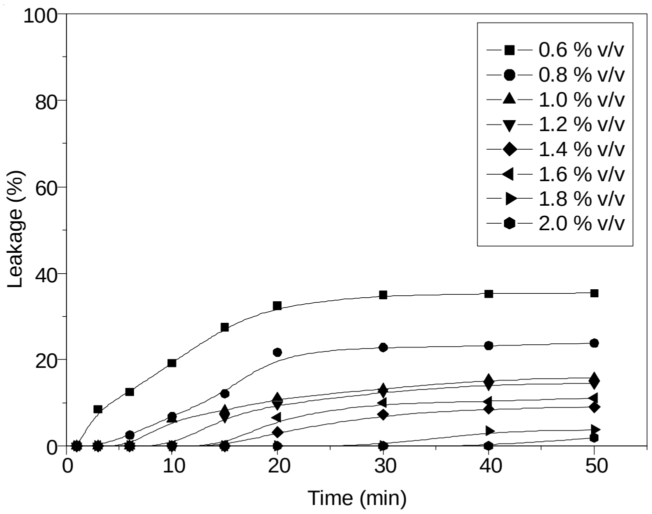

Fig. 5. Effect of Span-80 concentrations on the stability of emulsion liquid membrane

Permeation of lead through the prepared emulsion liquid membrane: The results obtained from both the batch solvent extraction and membrane stability studies were used to prepare stable liquid emulsion membrane systems for studying the removal of lead from aqueous waste solutions. The general conditions used for such study were as follows unless otherwise stated: a 100 mL of a feed solution of 0.01 M ammonium acetate containing 100 mg/L lead adjusted to pH 5, 10 mL of emulsion liquid membrane prepared from 6 % HDEHP and 1.8 % v/v of Span-80 in cyclohexane together with 0.1 M H_2SO_4. All experiments were carried out at 25 °C. The main factors affecting the permeation of lead through emulsion liquid membrane were studied. All the data obtained were illustrated as plots of the permeation % *vs.* time.

Effect of rotating speed of mixing the two phases: The effect of the rotating speed of mixing the feed solution with the membrane phase on the permeation of lead through the emulsion liquid membrane was studied at 300, 350 and 400 rpm. The permeation % of lead was found to be increase with increasing the stirring speed from 300 to 350 rpm (Fig. 6). This could be explained by formation of small globules with larger interface area leading to high mass transfer of the extracted metal ions. Maximum permeation was achieved at the speed of 350 rpm after 6 min. When the stirring speed was raised to 400 rpm, the permeation of lead was decreased. This may be due to, high stirring speed could increase the water transfer into the membrane, thus increasing the membrane swelling and hence the leakage per cent[32].

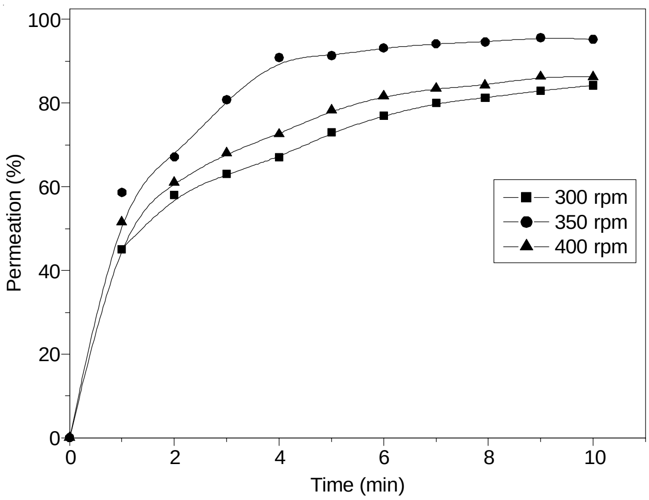

Fig. 6. Effect of rotating speed of mixing the two phases

Effect of hydrogen ions concentrations in the feed solution: The effect of hydrogen ions concentrations in the feed solution (from 2 to 5) on the permeation % of lead through liquid emulsion membrane was studied (Fig. 7). The data showed that the permeation % of Pb(II) increases with the increase in pH from 2 to 5. This is because at low pH (high H^+), the hydrogen ions compete with the lead ions at the membrane-feed interface which decrease the permeation rate of lead[25].

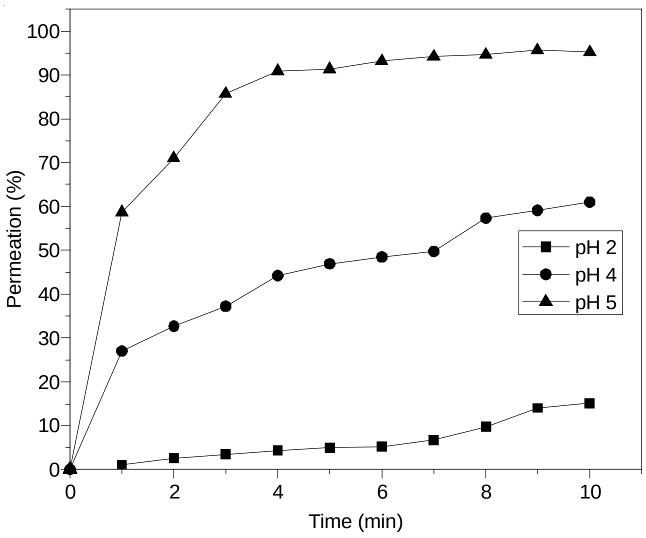

Fig. 7. Effect of hydrogen ion concentrations at the external aqueous phase

Effect of ammonium acetate concentration in the external aqueous phase: The effect of ionic strength was investigated by studying the effect of ammonium acetate concentrations in the ranges from 0.01 to 0.1M on the permeation of Pb(II) through the emulsion liquid membrane (Fig. 8). It is clear that, the permeation % of lead decreases with increases the concentration of ammonium acetate from 0.01 to 0.1M. This is because increasing the concentration of ammonium acetate in the feed solution may increase the competition of ammonium ions with lead ions; hence decrease its permeation[33].

Effect of di-2-ethylhexyl phosphoric acid (HDEHP) concentration: The effect of HDEHP concentration in the range of 3-7 % on the permeation rate of Pb(II) through emulsion liquid membrane had been studied (Fig. 9). It was found that the permeation rate of lead through the emulsion liquid membrane increases with increases the carrier concentration due to increase the lead-carrier complex at the feed-membrane interface which will cause an increase in the concentration gradient in the peripheral oil layer, hence, the rate of permeation of lead increases.

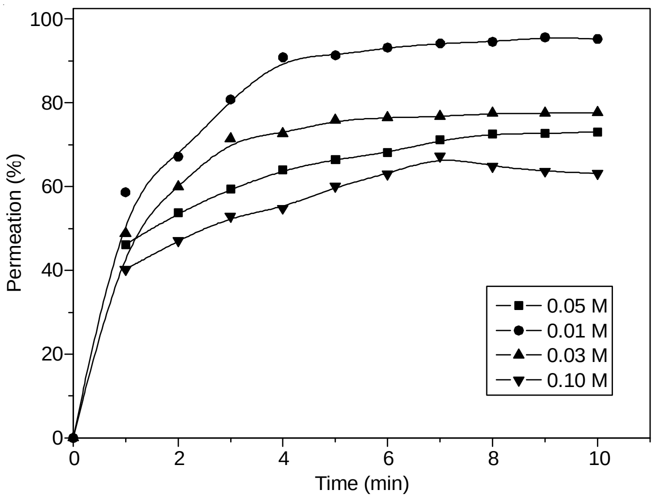

Fig. 8. Effect of ammonium acetate concentrations at the external aqueous phase

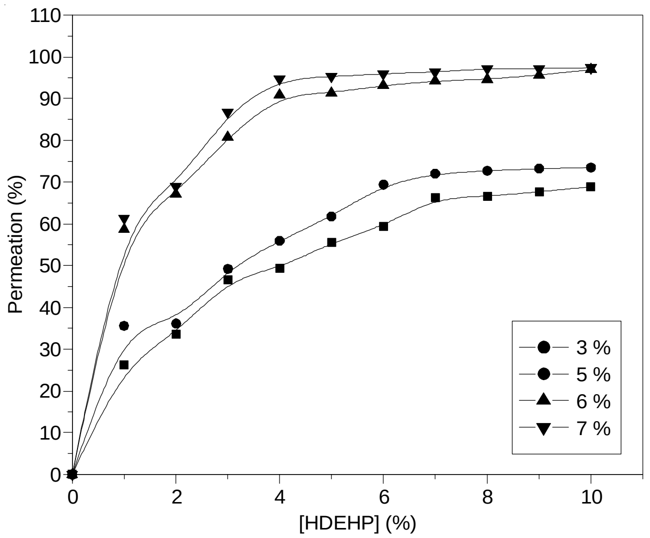

Fig. 9. Effect of HDEHP concentration

Effect of sulfuric acid concentration (stripping agent) in the internal aqueous phase: The effect of H_2SO_4 concentration in the internal aqueous phase in the range 0.05-0.5 M on the permeation % of Pb(II) through emulsion liquid membrane is given in Fig. 10. It is clear that the permeation of lead increases with the increase of H_2SO_4 concentration from 0.05 to 0.5 M due to increasing the capacity of the internal aqueous phase by increasing its concentration, which delays the accumulation of lead-carrier complex in the peripheral oil layer. Hence the concentration gradient of the complex in the membrane increases leading to increase in the rate of permeation of lead[34]. Since the permeation rate was nearly the same at 0.1 and 0.5 M H_2SO_4, 0.1 M H_2SO_4 was chosen as the best concentration for lead permeation.

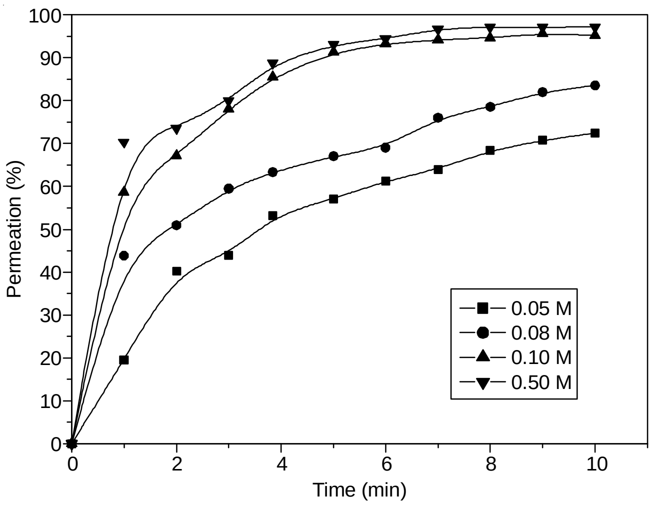

Fig. 10. Effect of sulfuric acid concentrations at the internal aqueous phase

Effect of membrane volume at constant feed volume: The effect of the membrane volume at constant feed volume of 100 mL on the permeation rate of lead through emulsion liquid membrane is given in Fig. 11. The ratios taken were 5:100, 10:100 and 15:100 v/v. It is clear that the permeation rate of Pb(II) increases with increasing the membrane volume. This could be explained on the basis of increasing the carrier concentration as a result of increasing the membrane volume which increases the total surface area available of the membrane globules.

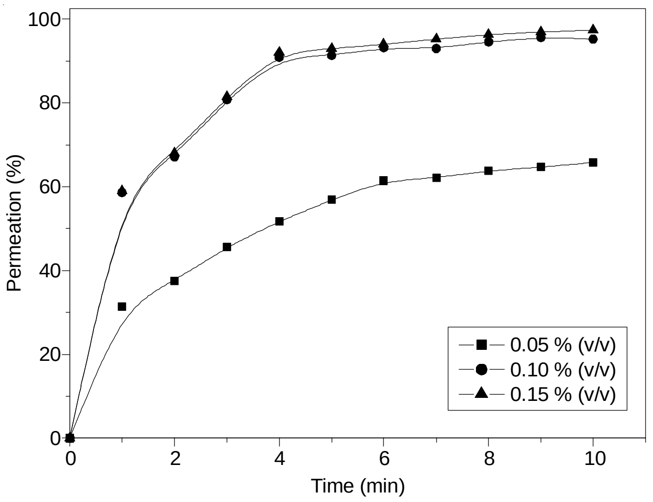

Fig. 11. Effect of membrane volume at constant feed volume

Effect of initial lead concentration in the feed solution: The effect of lead concentration in the feed solution on its permeation through the membrane is given in Fig. 12. The concentration of lead was changed from 50 to 300 mg/L. The result obtained showed that the rate of permeation of lead through the emulsion liquid membrane decreases with the increase in its concentration. This is due to the rapid saturation of the internal aqueous phase with lead as a result of increasing its concentration in the feed solution, which causes a slowdown in its permeation rate through the emulsion liquid membrane.

Effect of preloading the internal aqueous phase with lead: Generally in a pilot plant of extraction and separation by emulsion liquid membrane process, the emulsion is not demulsifying unless it was saturated completely with the permeated metal. The used membrane is brought into contact with a new feed solution till complete saturation. A series of experiments were carried out using an emulsion previously preloaded with lead ions (50-200 mg/L) in the internal aqueous phase (Fig. 13). The result obtained showed that the permeation % of lead decreases with the increase of lead concentration in the internal aqueous phase. This is due to saturation of the internal aqueous phase with lead which decreases its permeation rate.

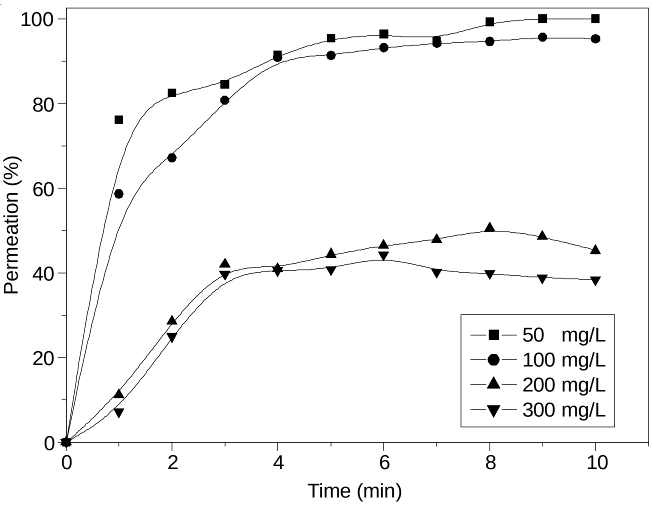

Fig. 12. Effect of initial lead concentration in the external aqueous phase

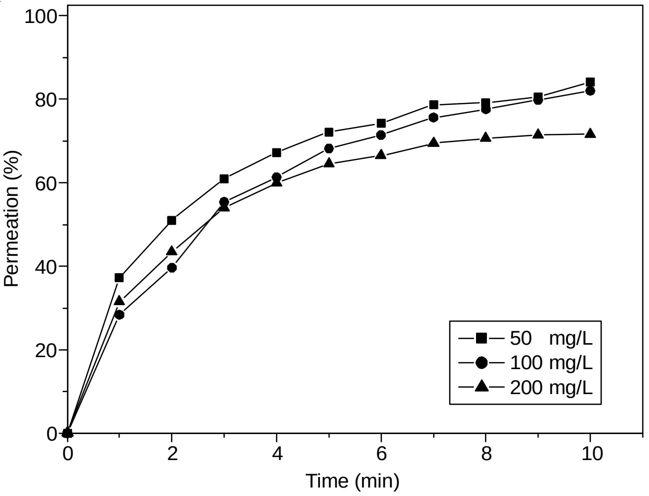

Fig. 13. Effect of preloading the internal aqueous phase with lead

Conclusion

Removal of lead from aqueous waste is of great concern due to its hazardous effect. Liquid-liquid extraction and stripping experiments of lead showed that Pb(II) is extracted from 0.01 M ammonium acetate media at pH 5 by 6 % HDEHP in cyclohexane with an extraction yield of 99 %. Extracted Pb(II) species was stripped by 0.1 M H_2SO_4 solution. These conditions were used as the basis to prepare emulsion liquid membrane system for removal of lead from liquid waste. Stability studies for the prepared membrane showed that the prepared emulsion liquid membrane is stable for 30 min when 1.8 % Span-80 is used as a surfactant; emulsification speed of 11500 rpm for 6 min; at 25 °C. The previous conditions were used to study the permeation of lead through the prepared liquid emulsion membrane system. The different parameters affecting the permeation rate of lead through the emulsion liquid membrane system were studied. The optimum conditions for permeation of lead ions were as follows; 6 % HDEHP as a carrier diluted with cyclohexane, 0.1 M H_2SO_4 as an internal aqueous phase, 1.8 % v/v Span-80 as a surfactant and 0.01 M ammonium acetate at the external aqueous phase adjusted to pH 5. Using the best conditions 10 mL of prepared emulsion liquid membrane can extract about 99 % of 100 mg/L of lead from its dilute acetate solution after 10 min.

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