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# Minimization of Toxic Ions in Waste Water Using Emulsion Liquid Membrane Technique

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## Abstract

*In the present study, the removal of zinc from synthetic waste water using emulsion liquid membrane extraction technique was investigated. Synthetic surfactant solution is used as the emulsifying agent. Diphenylthiocarbazon (ditizone) was used as the extracting agent dissolved in carbon tetrachloride as the organic solvent and sulfuric acid is used as the stripping agent. The parameters that influence the extraction percentage of* $Zn^{+2}$ *were studied. These are the ratio of volume of organic solvent to volume of aqueous feed (0.5-4), ratio of volume of surfactant solution to volume of aqueous feed (0.2-1.6), pH of the aqueous feed solution (5-10), mixing intensity (100-1000) rpm, concentration of extracting agent (20-400) ppm, surfactant concentration (0.2-2) wt.%, contact time (3-30) min, and concentration of strip phase (0.25-2) M . It was found that 87.4% of* $Zn^{+2}$ *can be removed from the aqueous feed solution at the optimum operating conditions. Further studies were carried out on extraction percentages of other toxic metal ions (*$As^{+3}$, $Hg^{+2}$, $Pb^{+2}$, $Cd^{+2}$*) by using the same optimum conditions which were obtained for zinc ions except for the pH of the feed solutions. The pH values for best extraction percentages of arsenic, lead, and cadmium were (1, 10, 10) respectively. Maximum extraction percentage of (98.5, 95.5 and 93.8) was obtained for arsenic, lead, and cadmium respectively, while mercury was completely removed from the aqueous feed solution within the acidic pH range.*

***Keywords*:** Emulsion liquid membrane, Waste water, Removal of toxic ions, Surfactant

## Introduction

The heightened concern for reduction of environmental pollution that has been occurring over the past 20 – 25 years has stimulated active continuing research on the toxicology of heavy metals. While the toxic effects of these substances is a widespread concern in the modern industrial context [1], many industries, such as the electroplating and mining companies, produce large amounts of mercury, lead, cadmium, silver, copper, and zinc ions. These industries are required by law to reduce the concentration of these toxic metals in their waste water before it is discharged into sewers, lakes, and streams [2].

Virtually all metals can produce toxicity when ingested in sufficient quantities, but there are several which are especially important because either they are so pervasive, or produce toxicity at such low concentrations [1].

A broadly defined group of elements classified as heavy metals contain a number of members that are toxic. This toxicity may by virtue of their interaction with enzymes, their tendency to bind strongly with sulfhydryl (-SH) groups on proteins, or other in vivo effects [3] poses serious health risks to humans. This threat puts the scientific community under pressure to develop new methods to detect and eliminate toxic contaminants from wastewaters in efficient and economically viable ways [4].

Removal of heavy metal ions from aqueous solutions has traditionally meant the precipitation of the ion, but this practice is now unpopular as it produces a sludge that has to be disposed in a landfill. Electrochemical metal recovery is promising; however, waste streams are often dilute metals and have low plating efficiencies. Solvent extraction of metals has been extensively used in hydrometallurgical operations [5], however the outlay of such equipment can be expensive, large volumes of organic extractants are required and the performance is often limited by hydrodynamic constraints such as flooding and entrainment [6].

Since the invention of the liquid surfactant membrane by Li (1968) the separation technique using liquid membranes has been noted as a novel method for separating and concentrating metal ions. The process is capable of giving higher degree of concentration of metal ion in fewer stages with maintaining the high selectivity of the solvent extraction [7]. Liquid membrane extraction processes have certainly some attractive features like simple operation, high efficiency, extraction and stripping in one stage, larger interfacial area and scope of continuous operation [6]. An emulsion liquid membrane (ELM) is a three-liquid-phase configuration consisting of two phases of the same nature (usually aqueous) separated by a third one, called the liquid membrane, immiscible with the other two. A typical system consists of a water-in-oil emulsion, stabilized by addition of a surfactant, dispersed in an aqueous solution in an agitated contactor. In either form, ELMs are used in separation processes in which a solute is extracted from the continuous phase into the liquid membrane, and from there into the emulsion droplets, by selective solubilization or by chemical reaction [8,9].

This study was set out to find the best operating conditions for the removal of the toxic ions: $Zn^{+2}$, $As^{+3}$, $Hg^{+2}$, $Pb^{+2}$ and $Cd^{+2}$, using ELM extraction for the purpose of waste water treatment.

## Experimental Work

### Experimental and materials

#### Chemicals

The chemicals used are **c**arbon tetrachloride [$CCl_4$], M.wt 153.82, dithizone [$C_{13}H_{12}N_4S$], M.wt 256.33, sulfuric acid, M.wt 98.08, sodium bicarbonate [$NaHCO_3$], M.wt 84.01, supplied by Merck Ltd. - sodium hydroxide,[NaOH], M.wt 40, zinc sulphate [$ZnSO_4.7H_2O$], M.wt 287.54, , sodium chloride [NaCl], M.wt 58.44, cadmium sulphate [$3CdSO_4.8H_2O$], M.wt 769.56, lead dioxide [$PbO_2$], M.wt 239.19, arsenous oxide[$As_2O_3$], M.wt 197.82, mercuric oxide [HgO], M.wt 216.59, sodium hexametaphosphate $(NaPO_3)_6$, M.wt 611.78, supplied by BDH Chemicals. - sodium carbonate [$Na_2CO_3$], M.wt 105.99, supplied by Thomas Baker Ltd. - sodium alkyl benzene sulphonate [$CH_3(CH_2)nOSO_3Na$], M.wt 288.38, and polyoxyethylene $(O\text{-}CH_2\text{-}CH_2\text{-}O)_{10}$, M.wt 640, supplied by Fluka.

#### Experimental Procedure

Synthetic waste waters were prepared individually for each metal. Specific amounts of metal ions were dissolved in distilled water to obtain the desired solution containing 90 ppm of the targeted metal ions. A green solution was obtained by dissolving a measured amount of the extracting agent (dithizone) in a certain volume of the organic phase of carbon tetrachloride. The volume of aqueous feed was taken as 50 ml. And the ratio of the organic phase to the feed phase was from 0.5 to 4, while that of the surfactant solution to the feed phase was from 0.2 to 1.6. The pH of the aqueous feed solution was adjusted by adding few drops of sodium hydroxide and/or sulfuric acid. A variable steady speed impeller with three blades was used for mixing in a two neck flask used as a container. The organic solvent which was lost during the mixing process due to volatility was recycled by using a condenser. The emulsion was prepared by emulsifying the aqueous solution of the strip phase (sulfuric acid or sodium hydroxide) with the organic phase (membrane phase) containing the carrier (extracting agent) with the aid of a mixer. When the metal ions were extracted from a basic surrounding sulfuric acid was used as the strip phase, while sodium hydroxide was used when the metal ions were extracted from an acidic surrounding. The strip solution of (sulfuric acid or sodium hydroxide) was added drop wise into the two neck flask containing the organic phase with the surfactant solution until 1:1 volume ratio was maintained for the organic phase to the internal phase. The solution was stirred continuously at a stirring speed 1000 rpm for 20 min. until a stable emulsion was formed. The prepared emulsion (organic phase and internal strip phase) was dispersed into the external aqueous feed phase of the waste water from which the targeted metal ions were to be extracted. The surfactant solution used as an emulsifying agent consists of all sodium cations with 50%wt. sodium hexametaphosphate, 10%wt. sodium alkyl benzene sulphonate as anionic surfactant and 0.5%wt. polyethylene as nonionic surfactant; it also contains 39.5% wt. sodium carbonate and sodium bicarbonate as pH buffering agents.

As the system was agitated the targeted metal ions were transported to the interface between the emulsion and the feed phase where these metal ions react**s** with the extracting (chelating) agent (HL) to form soluble metal complexes (MLn). This may be represented by the following equations:

Organic phase

Aqueous phase

The metal complex diffused to the interior of the emulsion droplet until it encountered a micro droplet of the internal phase where the metal ion was stripped by the stripping agent and trapped in the internal phase. The net effect was unidirectional mass transport of the cation (metal ion) from the original feed to the receiving phase with counter transport of hydrogen ions; after contacting the emulsion with the feed phase the dispersion was transported to a separator funnel where it was allowed to separate. The dispersion separated into three layers in the separator funnel. The upper layer contained the feed aqueous solution. The middle layer composed of the emulsion phase of the organic and the enriched internal phase by the metal ions trapped in it. Finally the bottom layer composed of a very small portion of the organic solvent separated from the emulsion.

The recovery of the solvent from the emulsion phase was carried out by applying a physical de-emulsification method including the addition of 0.3 M NaCl which breaks the emulsion into two immiscible phases. The upper layer contained the concentrated strip solution with the targeted ions and the surfactant solution, while the bottom layer comprised of the organic phase containing the carrier (extracting agent). The experiments were carried out at 298 $^{0}$K and the sequence of operations is as shown schematically in figure1.

Atomic adsorption spectrophotometer (Perkin Elmer model 5000) was used to measure the concentration of all metal ions except for mercury where a UV-visible recording spectrometer (Shimadzu model 160 A) was used [10].

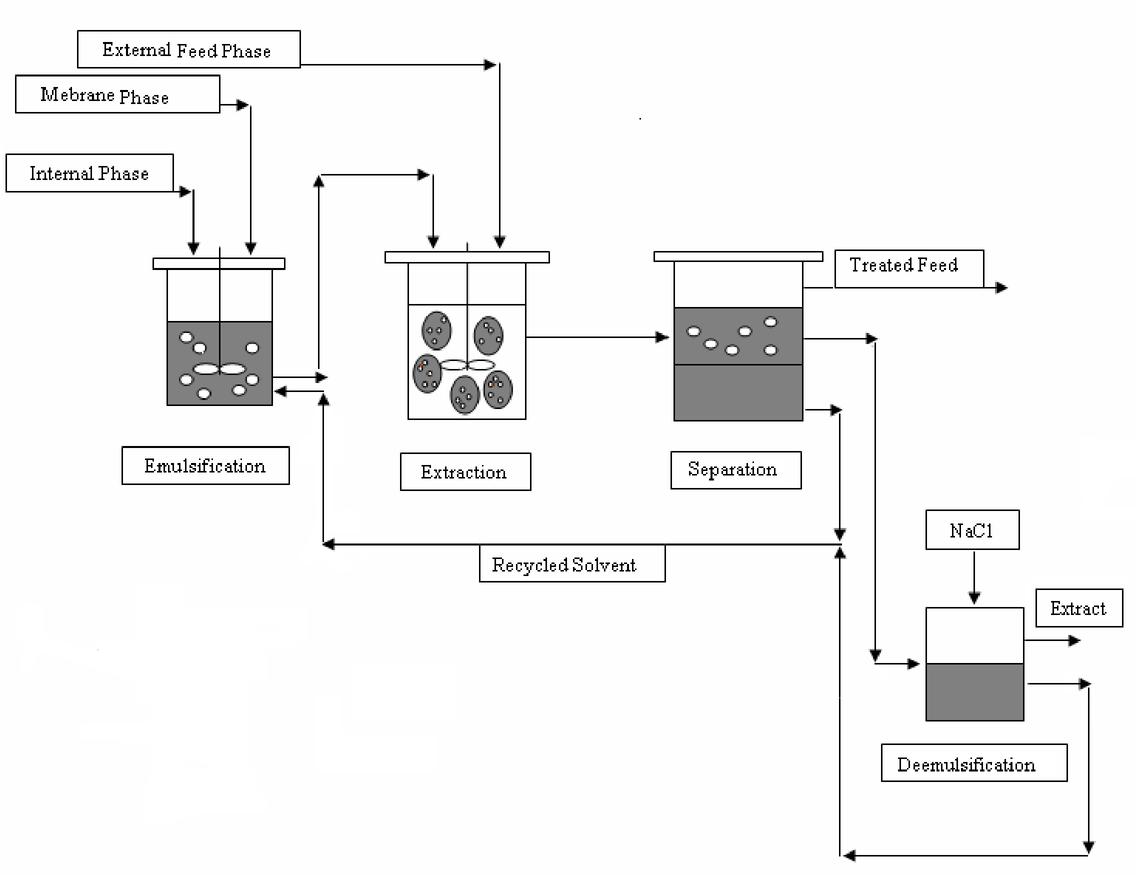

Figure1 Schematic diagram of the operation

## Results and Discussion

The parameters that influence the extraction percentage of $Zn^{+2}$ were studied and are discussed here. These are, ratio of volume of organic solvent to volume of aqueous feed (0.5-4), ratio of volume of surfactant solution to volume of aqueous feed (0.2-1.6), pH of the aqueous feed solution (5-10), mixing intensity (100-1000) rpm, concentration of extracting agent (20-400) ppm, surfactant concentration (0.2-2) wt.%, contact time (3-30) min, and concentration of strip phase (0.25-2) M.

### The Effect of Ratio of Volume of Organic Solvent to Volume of Aqueous Feed

Figure 2 shows the effect of ratio of volume of organic solvent to volume of aqueous feed on extraction percentage of zinc ions when 20 ml of volume of surfactant, the pH of the feed solution adjusted at 7.3, concentration of surfactant 1.0 wt.% , mixing intensity 700 rpm, contact time of 5min., and concentration of strip solution 1M were used. It can be seen that the extraction percentage is low for relatively smaller volumes of solvent. As the relative volume of solvent increases the extraction percentage values increased until it reaches a maximum ratio at (2). The low values of extraction percentage are because when small volume of organic solvent is employed small volume of emulsion is obtained. Therefore, the surface area of mass transfer will decrease due to the formation of a small number of emulsion globules. The increased ratios of organic solvent to aqueous feed also decrease the values of extraction percentage because the globules are close together, therefore, more likely to coalescence leading to a reduction in the total surface of mass transfer.

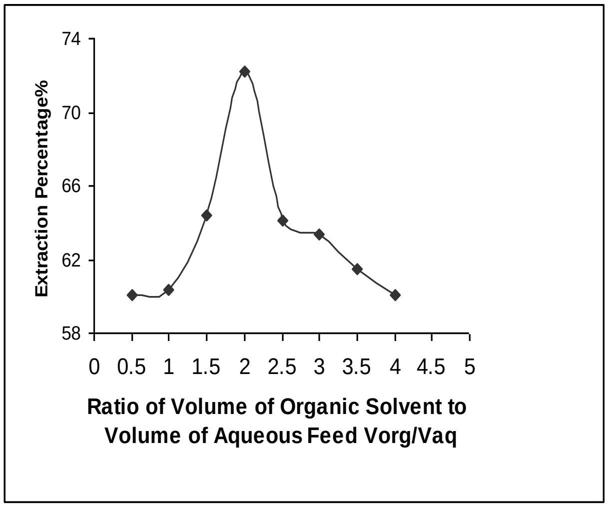

Figure 2 Effect of ratio of organic solvent to aqueous feed on the extraction percentage of $Zn^{+2}$

### Effect of Ratio of Volume of Surfactant Solution to Volume of Aqueous Feed

Effect of ratio of volume of surfactant to volume of aqueous feed on the extraction percentage of zinc ions using ratio of organic solvent to aqueous feed of 2, pH of the feed solution 7.3, concentration of the extracting agent 250 ppm, concentration of surfactant 1.0 wt.% , mixing intensity 700 rpm, contact time of 5min., and concentration of strip solution 1M was investigated. As the volume of surfactant solution is related directly to the droplet size and membrane thickness, the extraction percentage depends on the relative volumes of surfactant solution and the feed. There is a minimum quantity of surfactant solution to obtain a stable emulsion. If the amount of surfactant solution is less than the minimum, the extraction percentage is low because the membrane breaking up reducing the interfacial area for mass transfer. It is expected that for large volumes of surfactant solution, extraction percentage does not change. Figure 3 shows experimental results for this ratio. It can be seen that extraction percentage is constant when the volume ratio approximately 1.4 and this is the minimum amount of surfactant that should be added.

### Effect of pH of The Aqueous Feed

It is observed that the pH of the aqueous feed phase played an important role on the values of extraction percentage of the targeted zinc ions. This is shown in figure 4. The experimental conditions were kept constant at ratio of organic solvent to aqueous feed of 2, ratio of volume of surfactant solution to volume of aqueous feed of 1.4, concentration of the extracting agent 250 ppm, concentration of surfactant 1.0 wt.% , mixing intensity 700 rpm, contact time of 5min., and concentration of strip solution 1M. Higher extraction percentage is obtained as pH was moved towards basic range. This is because the nature of the extracting agent which forms stronger complexes in this range of pH values. At low pH values there is a decrease in the extraction percentage due to the incomplete deprotonation of the extracting agent in the membrane interfaces of the feed phase, thereby decreasing the formation of metal-chelating agent complex. For this same reason the extraction percentage decreases in higher basic range. And it is clear from figure 4 that neutral conditions (pH around 7) gave the highest extraction rate.

### Effect of Mixing Intensity

Figure 5 shows the effect of mixing intensity of emulsion on extraction percentage of zinc ions. The operating parameters were ratio of organic solvent to aqueous feed of 2, ratio of volume of surfactant solution to volume of aqueous feed of 1.4, pH of the feed solution 7.5, concentration of the extracting agent 250 ppm, concentration of surfactant 1.0 wt.% , contact time of 5min., and concentration of strip solution 1M.

It can be seen that the extraction percentage increases with increasing mixing intensity up to 800 rpm where it becomes almost constant. This may be due to the fact that the droplets reach stable drop size that does not change at higher mixing intensity. At low mixing intensity some of the drops might breakup due to rupture of weak membrane; therefore, the extraction percentage decreases. But, when increasing the mixing intensity, gradually, the emulsion becomes more stable because drop diameters of the emulsion decrease. This results in improved permeation rate due to the increase in mass transfer area. However, further studies should be carried out to quantify the effect of the drop size and drop size distribution on the liquid membrane extraction.

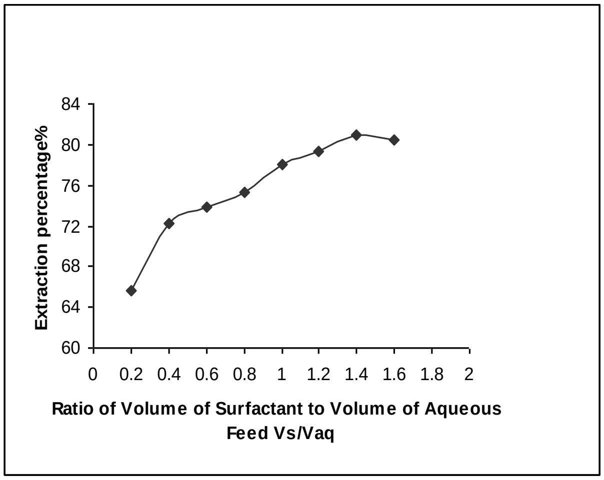

Figure 3 Effect of ratio of volume of surfactant solution to volume of aqueous feed on the extraction percentage of $Zn^{+2}$

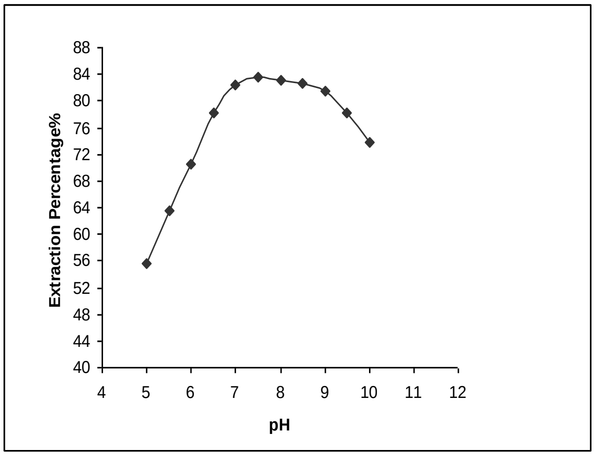

Figure 4 Effect of pH on the extraction percentage of $Zn^{+2}$

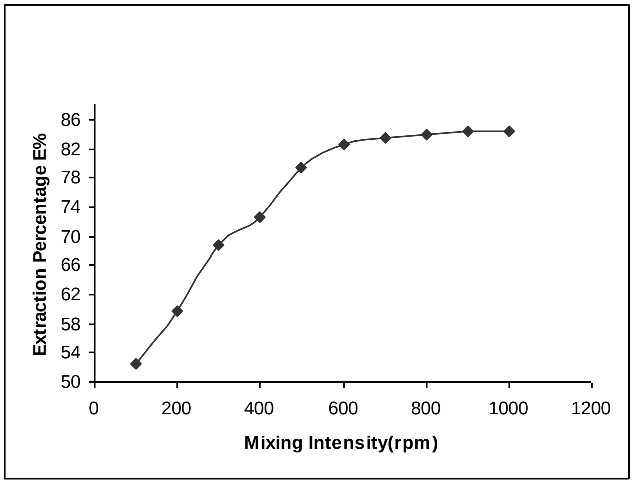

Figure 5 Effect of mixing intensity on the extraction percentage of $Zn^{+2}$

**Effect of Concentration of Extracting Agent**

It is obvious that the concentration of the extracting agent also plays an important role in emulsion liquid membrane (ELM) extraction and on the extraction percentage of the targeted zinc ions. Emulsion liquid membrane (ELM) parameters were kept constant at ratio of organic solvent to aqueous feed of 2, ratio of volume of surfactant solution to volume of aqueous feed of 1.4, pH of the feed solution 7.5, mixing intensity 1000 rpm, concentration of surfactant 1.0 wt.% , contact time of 5min., and concentration of strip solution 1M. The effect of carrier (extracting agent) concentration on the extraction percentage is displayed in figure 6.

The initial extraction percentage increased with the increase in the concentration of extractant, because there would be enough molecules of extractant in the membrane to complex with the zinc ions and carries these metal ions from one side of the membrane to the other side. However, it will be expected that at a very high content of extractant in the membrane the values of extraction percentage decreases. The increasing concentration of extractant promotes swelling of the emulsion, which dilutes the aqueous strip phase and decreases the efficiency of the process. Also when increasing the concentration of the extractant maximum percentage of zinc ions remain in the complex form (in membrane phase) without getting stripped which in turn affected the final recovery by ELM process.

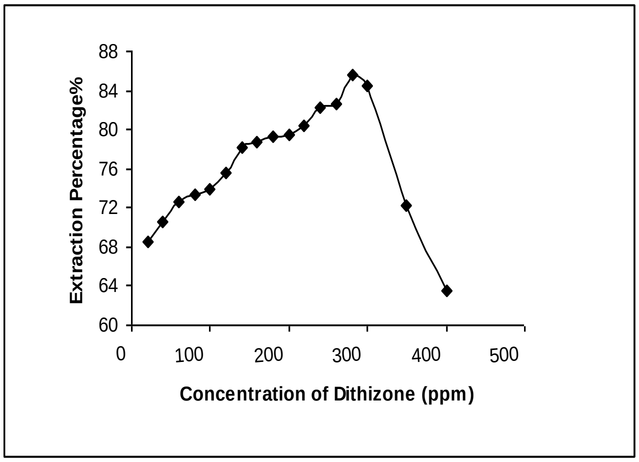

Figure 6 Effect of extracting agent concentration on the extraction percentage of $Zn^{+2}$

### Effect of Surfactant Concentration

Effect of concentration of surfactant on the extraction percentage of zinc ions using ratio of organic solvent to aqueous feed of 2, ratio of volume of surfactant solution to volume of aqueous feed of 1.4, pH of the feed solution 7.5, concentration of the extracting agent 280 ppm, mixing intensity 1000 rpm, contact time of 5min., and concentration of strip solution 1M was investigated.

As the surfactant concentration increases the values of extraction percentage also increases owing to the increasing in the emulsion stability, but a further increase in the surfactant concentration decreases the values of extraction percentage due to mass transfer resistance caused by surfactant film. Also when the surfactant concentration increases the viscosity of the organic phase increases resulting in lowering the emulsion liquid membrane permeation, and diffusivity of complexes in the organic phase is reduced. Therefore, the amount of the surfactant in the membrane must be minimal but it must be enough to stabilize the emulsion. The effect of concentration of surfactant is showed in the figure 7.

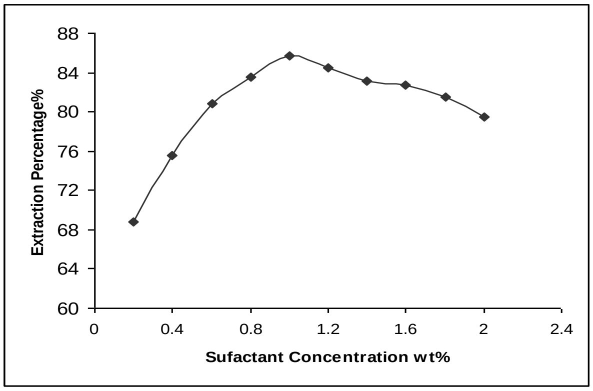

Figure 7 Effect of concentration of surfactant on the extraction percentage of $Zn^{+2}$

### Effect of Contact Time

Figure 8 shows the effect of contact time on extraction percentage of zinc ions. The operating parameters were ratio of organic solvent to aqueous feed of 2, ratio of volume of surfactant solution to volume of aqueous feed of 1.4, pH of the feed solution 7.5, concentration of the extracting agent 280 ppm, mixing intensity 1000 rpm, concentration of surfactant 1.0 wt.% , and concentration of strip solution 1M.

It is observed from the figure that extraction percentage increases with the increase of contact time between the emulsion and the external feed phase until it reaches a maximum value then starts to decrease. At short contact time low values of extraction percentage are obtained. This is because the contact between the external feed phase and the emulsion was not enough to complex zinc ions with the complexing agents to extract them into the membrane phase; thereby the concentration of zinc ions in the external phase remains high. As the contact time increases, the pH of the aqueous feed solution will continue to decrease below the value which promotes the complexation reaction between the metal ions and the complex agents. This is due to the influx of hydrogen ions carried across the membrane from within the emulsion thus increasing water transfer into the internal phase causing the membrane to swell and initiates breakage of the emulsion. This results in the leakage of zinc ions from the internal phase to the external feed, thus decreasing the extraction rate.

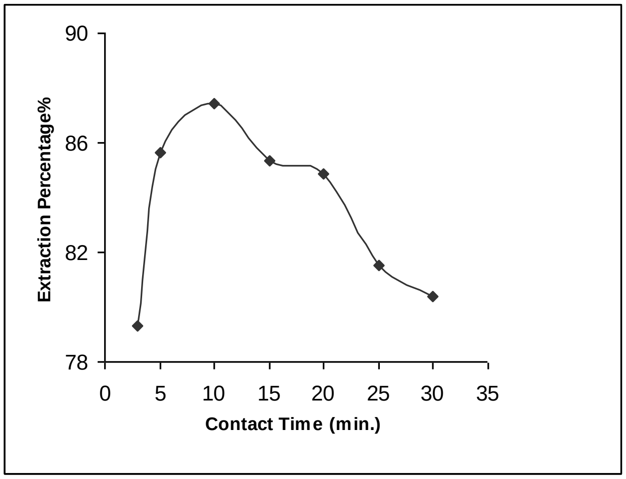

Figure 8 Effect of contact time on the extraction percentage of $Zn^{+2}$

### Effect of Stripping Phase Concentration

Effect of stripping phase concentration on the extraction percentage of zinc ions using ratio of organic solvent to aqueous feed of 2, ratio of volume of surfactant solution to volume of aqueous feed of 1.4, pH of the feed solution 7.5, concentration of the extracting agent 280 ppm, mixing intensity 1000 rpm, concentration of surfactant 1.0 wt. %, contact time of 10 min. was studied.

It is obvious from figure 9 that the extraction percentage increases with increasing the stripping phase concentration. This is owing to the increase in the capacity of the internal phase. However, for high concentration of the stripping agent the extraction percentage of the targeted zinc ions decreases. This is due to swelling of the emulsion by water transport to the internal phase, thus diluting it and decreasing the emulsion stability.

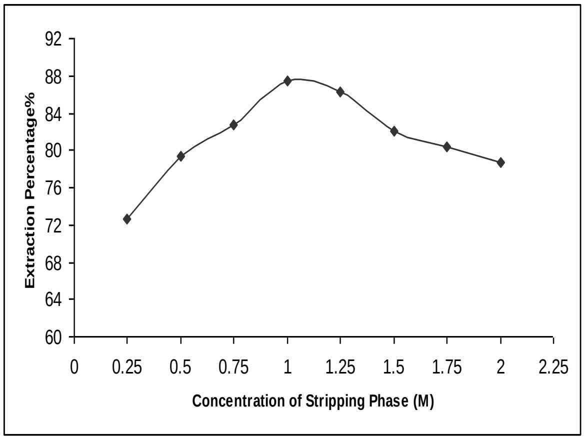

Figure 9 Effect of stripping phase concentration on the extraction percentage of $Zn^{+2}$

**Further Studies**

As the chelating reaction between the chelating agent and the metal ions is very important intermediate step in the emulsion liquid membrane technique which is responsible for the transfer of the metal ion from the external aqueous feed phase to the internal aqueous phase, the effect of pH was investigated for other toxic metal ions ($As^{+3}$, $Hg^{+2}$, $Pb^{+2}$, $Cd^{+2}$). This is done since the nature of the chelating agent (dithizone) is very sensitive to pH values, where it reacts with every metal ion in a definite range of pH values. The same optimum parameters which were obtained for zinc ions (i.e., ratio of volume of organic solvent to volume of aqueous feed of 2, volume of surfactant solution to volume of aqueous feed of 1.4, mixing intensity 1000 rpm, concentration of the extracting agent 280 ppm, surfactant concentration 1wt. %, contact time of 10 min., and concentration of strip phase 1 M) were used for these metal ions since they only affect the effectiveness of the emulsion liquid membrane operation. The effect of pH on extraction for these ions is shown in figure 10.

It is obvious that the pH values of the feed solution slightly affect the extraction percentage of arsenic, however higher extraction percentage is obtained in very high acidic surroundings. This is due to the fact that arsenic possess an ion pair, the nature of which enables it to take part in the chelation reactions and even some of its compounds are used as ion association chelating agents.

It can be seen from this figure that varying the values of pH has no effect on the extraction of Hg ions. This is due to the range of pH values used which is the optimum for the complexing reaction between mercury ions and the chelating agent (dithizone) and very strong metal complexes are formed, thus the metal complexes remain in the membrane phase and it is very difficult to be stripped. This resulted in that the mercury ions are completely removed from the aqueous feed solution and extraction percentage values attend unity.

It is observed that the pH of the aqueous feed phase played an important role on the values of extraction percentage of lead ions. As shown in the above mentioned figure higher extraction percentage is obtained as pH was moved towards more basic range up to a maximum value then it started to decrease. This was due to the nature of the extracting agent which forms strong complexes in this range of pH values. At low pH values there is a decrease in the extraction percentage due to the incomplete deprotonation of the extracting agent in the membrane interfaces of the feed phase, thereby decreasing the formation of metal-chelating agent complex. In very high basic surrounding a significant decrease is observed of the extraction percentage of lead ions. This is due to the nature of the extracting agent which prefers moderate basic surrounding in order to complex with the targeted lead ions.

Higher extraction percentage is obtained as pH was moved towards more basic range up to a maximum value then it started to decrease. This is because the nature of the extracting agent which forms strong complexes with the metals in this range of pH values. At low pH values there is a decrease in the extraction percentage due to the incomplete deprotonation of the extracting agent in the membrane interfaces of the feed phase, thereby decreasing the formation of metal-chelating agent complex. At high pH values there is a slight decrease in extraction percentage this is because of the complexation of the chelating agent with the targeted cadmium ions in a wide range of basic surrounding.

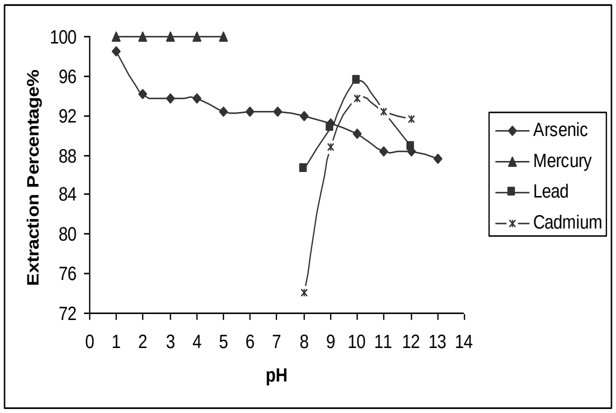

Figure 10 Effect of pH on extraction percentage of some toxic metal ions

## Conclusions

**For the removal of $Zn^{+2}$, the following conclusions are arrived at:**

1. The increase in ratio of volume of organic solvent to aqueous feed caused an increase in extraction percentage up to ratio 2, and then the extraction percentage started to decrease with the increase of the ratio.
2. The extraction percentage increases as the ratio of volume of surfactant solution to volume of aqueous feed increased up to ratio 1.4, then the extraction percentage is essentially constant.
3. As pH of the aqueous feed increased the extraction percentage also increased up to pH value of 7.5, then the extraction percentage started to decrease with the increase in the pH value of the aqueous feed.
4. The increase in mixing intensity caused an increase in extraction percentage up to 1000 rpm, and then the extraction percentage is approximately constant.
5. The increase in extracting agent concentration caused an increase in extraction percentage up to 280 ppm, and then the extraction percentage started to decrease with the increase in the extracting agent amount.
6. As the surfactant concentration increased the extraction percentage increased up to concentration of 1.0 wt %, then the extraction percentage decreases with the increase in surfactant concentration.
7. The extraction percentage increases as contact time increased up to about 10 min., and then the extraction percentage decreases with increasing time of contact.
8. The increase in the concentration of internal aqueous phase caused an increase in the extraction percentage up to concentration of 1 M, and then the extraction percentage started to decrease with the increase of the concentration of internal aqueous phase.

**For the other ions the conclusion is:**

As pH of the aqueous feed increased the extraction percentage of both lead and cadmium also increased up to pH value of 10, then the extraction percentage started to decrease with the increase in the pH value of the aqueous feed. While for arsenic, as the pH values increased the extraction percentage is slightly decreased, maximum value of extraction percentage was achieved at pH value of 1. And the extraction of mercury was not effected by the change in pH of the aqueous feed in the examined pH range, and the extraction percentage is close to unity.

## References

1. Theodore B. Hoekman, **"heavy metal toxicology",** http://www.hbci.com/~wenonah/hydro/heavmet.htm. 5/12/2007.

2. Warren H. Philipp, Jr. and Kenneth W. Street, Jr., "**A new martial for removing metals from water**" http://www.P2 pays.org/ref%5co2/01107.pdf, 25/7/2007.

3. D. Max Roundhill (2001) **"Extraction of metals from soils and waters"**, Springer, http://books.google.com/books, 12/6/2007.

4. Rey Juan Carlos (2007) **"New wastewater treatment system removes heavy metals"**,ScienceDaily, http://www.sciencedaily.com/releases/2007/10/071020110548.htm, 12/6/2007.

5. Bhavani Raghuraman, Neena Trmizi, and John Wienick (1994) **"Emulsion liquid membrane for waste water treatment"**, Environ. Sci. Technol., vol.28, p.p. (1090-1098), http://pubs.acs.org.connector.ivsl.org/cgi-bin/arichive.cgi 12/6/2007.

6. Norasikin Othman, Masahiro Goto, Hanapi Mat (2000) **"Liquid membrane technology for precious metal recovery from industrial waste"**, Engineering University Technology Malaysia, http://www.science direct.com.connector.ivsl.org/science, 25/7/2007.

7. Masahiro Goto, Takahiko Kakoi, Naoya Yoshii, Kazuo Kondo, and Fumiyuki Nakashio (1993) " **Effect of synthesized surfactants in the separation of rare earth metals by liquid surfactant membrane"**, Ind. Eng. Chem. Res., vol. 32, p.p.(1681-1685), published by American Chemical Society, http://pubs.acs.org.connector.ivsl.org/cgi-bin/arichive.cgi, 11/8/2007.

8. Josefine de Gyves and Edwardo Rodriguez de San Miguel (1999) **“Metal ion separation by supported liquid membranes”**, Ind. Eng. Chem. Res., vol.38, p.p. (2182-2202), published by American Chemical Society, http://pubs.acs.org.connector.ivsl.org/cgi-bin/arichive.cgi, 11/8/2007.

9. Tatiana Gallego-Lizon and E. Susana Perez de Ortiz (2000) **“Drop sizes in liquid membrane dispersion”**, Ind. Eng. Chem. Res., vol.39, p.p. (5020-5026), published by American Chemical Society, http://pubs.acs.org.connector.ivsl.org/cgi-bin/arichive.cgi, 11/8/2007.

10. Mahmoud, H. E., (Oct./2007) **“Minimization of Toxic Ions in Waste Water Using Emulsion Liquid Membrane Technique”**, M.Sc. Thesis,Chem.Eng.Dept., Baghdad University.