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RESEARCH ARTICLE

REMOVAL OF HEAVY METAL FROM AQUEOUS WASTEWATER BY EMULSION LIQUID MEMBRANE.

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Abstract

Extraction and recovery of heavy metal from waste water using Liquid Membrane technology is more efficient than methods such as precipitation that form sludge that needs to be disposed in landfills. A green emulsion liquid membrane (ELM) has been formulated in this work using an environmental-friendly refined palm oil as the main diluent of ELM to recover zinc ions from aqueous waste solution using di-(2-ethylhexyl) phosphoric acid (D2EHPA) as a highly selective carrier with double Water-Oil-Water emulsion. This system promotes many advantages including simple operation, high selectivity, low energy requirement, and single stage extraction and stripping process. In this study ELM process was used to transport zinc metal ion from aqueous feed phase to stripping phase which was prepared by using H_2SO_4, HCl, and HNO3. This extraction was done in a Batch-type stirred tank at room temperature with different types of vegetable oils green solvent. For green ELM process the various vegetable oils have been studied as diluents, such as palm oil, sesame oil, coconut oil, soyabean oil and for further studies we found that palm oil is more effective vegetable oil which gives more recovery of zinc ion from wastewater. The effect of various parameters such as, pH of the feed solution, concentration of the stripping phase, surfactant concentration, carrier concentration, F/M phase ratio, O/I phase ratio, contact time of the double emulsion etc. were studied. After determining the optimum conditions it was possible to extract zinc metal ion up to 62% from aqueous feed phase in a single stage extraction.

Introduction:-

A major problem worldwide is excessive release of heavy metals into the environment due to wastewater and industrial effluent. Unlike organic pollutants, the heavy metal ion pollutants do not degrade into harmless end products. The presence of heavy metals in the environment is a major concern to many life forms such as aquatic life, plants and ecology due to their toxicity. [1] Heavy metals are generally considered as those whose density is greater than 5 kg per cubic meter. Most of the elements falling into this category are highly water soluble, well-known toxins and carcinogenic agents. Following elements are considered to be Heavy metals: Copper, Silver, Zinc, Cadmium, Gold, Mercury, Lead, Chromium, Iron, Nickel, Tin, Arsenic, Selenium, Molybdenum, Cobalt, Manganese and Aluminum. In human body these can be absorbed and accumulated and this can cause serious health effects like cancer, organ damage, nervous system damage, and in extreme cases, death. Also increasing metal concentration in the body reduces growth and development. Removal of heavy metals from wastewater has recently

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become the subject of considerable interest owing to strict legislations because even low amounts of these metals are highly toxic. [2] The US EPA maintains list of primary pollutants which result in imposed limit on heavy metal contaminants in industrial wastewaters that are discharged to the surface including a lake, river or stream and Publically Owned Treatment works (POTWs).

There are several methods for removal of heavy metal contaminants from aqueous wastewater such as chemical oxidation and advance oxidation, chemical precipitation, chemical coagulation, chemical stabilization, Ion Exchange, Filtration such as microfiltration, Nano filtration , Ultrafiltration etc. [3]

Nowadays, many publications presenting studies on effectiveness of metal removal in wastewater treatment processes are available. Liquid membrane technology is widely used for metal ions separation from aqueous wastewater. In recent years a lot of study has been done on Liquid membrane separation. ELM process is an alternative technique for conventional liquid-liquid extraction. It provides high interfacial area and the system is able to selectively recover solute. [4] Liquid membrane is literally a membrane made of liquid. It consist of liquid phase that serves as a membrane barrier between two phases of aqueous solution or gas mixtures existing either in supported or unsupported form. The most common driving force used in liquid membrane process is concentration gradients. [5] There are the three types of liquid membranes:
1. Emulsion Liquid membrane
2. Supported Liquid membrane
3. Bulk Liquid membrane

Emulsion Liquid Membrane:-
The extraction of metal ions from aqueous solutions by emulsion liquid membrane (ELM) is one of the promising techniques was 1st investigated by Li. [6] and other scientists. Emulsion liquid membrane separation process is newly found technology with a wide verity of applications, such as removal, recovery and purification of many heavy metal ions from aqueous solutions of industrial waste. [7] Emulsion Liquid membrane is made by preparing water-in-oil (W/O) and oil-in-water (O/W) emulsion and multiple emulsion e.g. water-in-oil-in-water (W/O/W) emulsion also called as double emulsion membrane. In water-in-oil (W/O) emulsion water is present as dispersed phase and oil is present as continuous phase, similarly oil-in-water (O/W) emulsion oil is present as dispersed phase and water is present as continuous phase. Double emulsions may be either of the water-in-oil-in-water type (W/O/W) (with dispersed oil drops containing smaller aqueous droplets) or of the oil-in-water-in-oil type (O/W/O) (with dispersed aqueous globules containing smaller oil dispersed droplets).[8] 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. [9, 10] In ELM mass transfer surface area to volume ratio is very high up to (1000 -3000m^2/m^3) and internal surface area to volume ratio is also lager (106 m^2/m^3). ELM consists of mainly three-phase dispersion systems, such as aqueous stripping phase, aqueous feed phase and organic membrane phase which contains extractant in organic diluents with surfactant, co-surfactant, emulsifier etc. to stabilize emulsion droplets. Therefore ELM process involves extraction and stripping simultaneously in single step. [10] The Fig. 1 shows that the different types of emulsion liquid membrane as we discussed above;

Double emulsions are generally thermodynamically unstable systems and require the presence of two emulsifiers with opposite solubility (hydrophilic and hydrophobic emulsifier) to ensure their kinetic stability. So ELM suffers from poor emulsion stability. [11] Emulsion instability may result in the membrane leakage, coalescence, and emulsion swelling. The lack of stability of the emulsion globules will decrease extraction efficiency. On the other hand, an overly stable emulsion causes problems during its settling and de-emulsification after it extracts the pollutants [12]. There are only a small number of investigations have been made on the stability of (W/O/W)

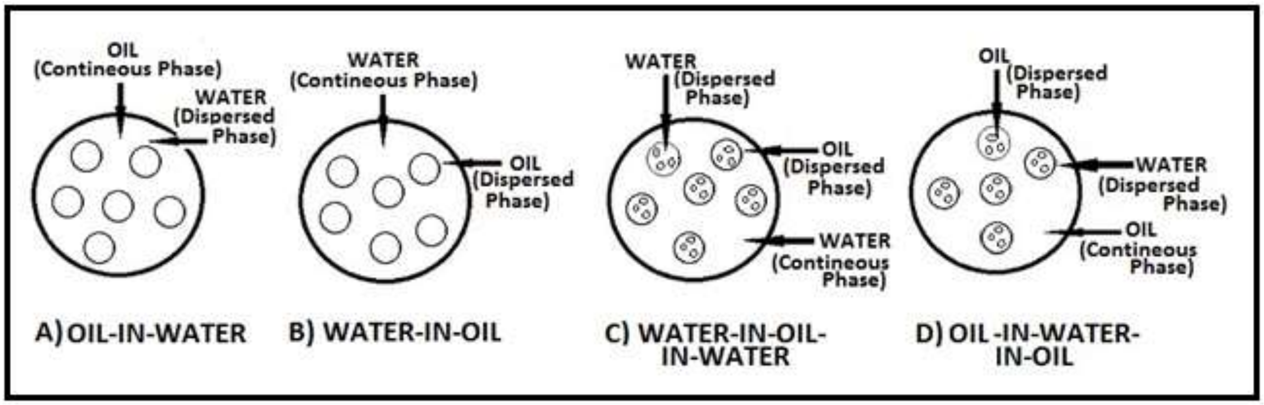

Fig.1 Different Types of Emulsion[8]

emulsion system in stirred vessels.[13] Instability of ELM results in their tendency to undergo swelling and internal phase leakage (breakage). The instability of ELM is normally due to the globule rupture and osmotic swelling. Globule rupture is caused by the excessive interfacial shear between the continuous and membrane phase; the liquid membrane becomes thinner and easier to break. When rupture or breakdown occurs in the membrane, the previously extracted solutes as well as the stripping reagents are leaked and released back into the feed stream and this will decrease the extraction efficiency of the ELM system. Osmotic swelling occurs when water diffuses from the external phase into the internal phase. In practical process, about 10 % emulsion swelling of considered acceptable while about 0.1 % membrane leakage is allowable. Excessive stirring speed of double emulsion leads to coalescence of the dispersed globule and finally ruptures the emulsion.[14]

The present paper aims to study the extraction of zinc metal ions from aqueous sulfate solutions with D2HEPA as extractant and vegetable oil such as refined soya bean oil, palm oil, sunflower oil, sesame oil, coconut oil etc. as a green solvent, instead of using conventional petroleum base diluent. There are very few previous studies available using vegetable oil or palm oil as a solvent in ELM process, so this is the main purpose of this project. Vegetable oil such as palm oil, soyabean oil, coconut oil, sunflower oil etc. are loaded with D2EHPA as carrier and this successfully removes the heavy metal pollutants like Hg(II),Cu(II), methyl violet and rhodamine.[15]

2. Experimental

2.1 Chemicals and Reagents:-

The membrane phase consists of a surfactant, co-surfactant, an extractant, diluent and optimal formulation for the stable emulsion and thus extraction to be takes place. The non-ionic span 80 (sorbitanmonooleate) from of Research Lab Fine ChemIndis, Mumbai was used for stabilizing the emulsion. Hydrophilic Tween 80 also product of S. D. Fine Chem Ltd., butanol as a co-surfactant from MERCK Ltd. Mumbai and extractant D2EHPA (di-(2-ethylhexyl) phosphoric acid) of analytical grade from Sigma ALDRICH (USA Product) were used. All the chemicals were used as received. Diluents such as soyabean oil, sesame oil, palm oil and sunflower oil available from the local market were used. Zinc solution was prepared by dissolving requisite amount of zinc sulfate in distilled water. Analytical grade sulfuric acid, obtained from LobaChemie was employed for preparation of aqueous stripping phase.

2.2 Optimization Experiments:-

Experiments were conducted to find the effect of different process conditions on the performance of the system and to obtain optimum conditions for maximum removal efficiency. Following parameters were studied:

1. Effect of External Phase acidity
2. Effect of initial concentration of zinc
3. Effect of surfactant (span 80) concentration
4. Effect of internal phase concentration
5. Effect of feed/membrane phase ratio
6. Effect of carrier (D2EHPA) concentration
7. Optimum conditions

2.3 Preparation of the ELM:-

This is laboratory level batch-type process. The extraction runs were performed in 250 ml glass beaker at room temperature with stirring by a mechanical agitator. ELM used in this work are water-in-oil-in-water emulsion and formed by dissolving extractant (D2EHPA), surfactant span 80, co-surfactant Twee 80 and butanol in vegetable oil diluents (palm oil, sunflower oil, soyabean oil ,sesame oil). H_2SO_4 solution was used as internal/ stripping phase. Primary water-in-oil (W/O) emulsion was made by slowly adding internal phase into the organic membrane phase with high speed of turbine type agitator for 15 min, to obtain stable Primary emulsion membrane.

2.4 Experimental Procedure:-

Firstly aqueous feed phase or waste water was prepared by dissolving the zinc salt in distillated water to obtain the desired solution. The pH of the aqueous feed solution was adjusted by adding few drops of sodium hydroxide and/or sulfuric acid. ELM phase was created by slowly adding prepared stripping solution using pipette into organic phase containing carrier and surfactant while stirring continuously at high speed for 15 min. Created W/O type emulsion membrane and external phase were contacted in 250 ml beaker, new w/o/w double emulsion was formed. In this 'extraction and stripping' of metal ion takes place simultaneously. While contacting phases, samples were taken out within decided time interval by using syringes. De-emulsification of ELM was done by high speed of centrifugation for 20 min. The concentration of zinc in aqueous feed phase was determined by Atomic Absorption Spectroscopy (AAS) and in the stripping phase by taking mass balance at the end of extraction. Fig.2. below describes complete experimental procedure.

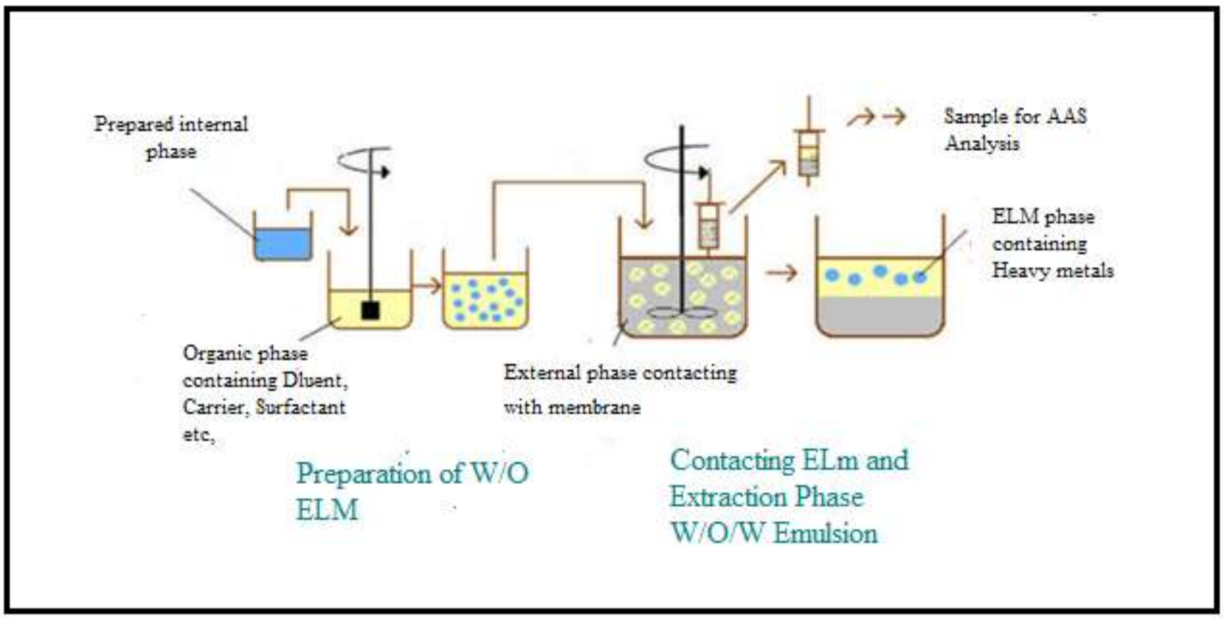

Fig. 2:-The operational steps in the ELM process [15]

2.5 Chemistry and Mechanism of Zinc (II) Solvent Extraction by Using ELM Process:-

The extraction and stripping reactions of Zinc (II) occurring in the ELM process are shown in the equations given below, where RH represents the protonated form of an extractant, which is used as carrier [di-(2-ethylhexyl) phosphoric acid (D2EHPA), in this study]. The carrier D2EHPA is known to dimerise in non-polar aliphatic solvents.

Formation of the complex:

$Zn^{2+} + 2(HR)_2 \rightarrow ZnR_2(HR)_2 + 2H^+$ ……..(1)

Stripping reaction:

$ZnR_2(HR)_2 + 2H \rightarrow Zn^{2+} + 2(HR)_2$ ……..(2)

Equation (1) represents the reaction occurring at the membrane–external/phase interface, the complexation reaction; while Eq. (2) shows the reaction occurring at the membrane–internal/stripping aqueous phase interface stripping of metal ion take place. The overall reaction represents an ion exchange of zinc (II) for two hydrogen ions. A schematic presentation of the liquid membrane globule and simultaneous extraction and stripping mechanism in ELM's is exhibited in Fig.3 below.

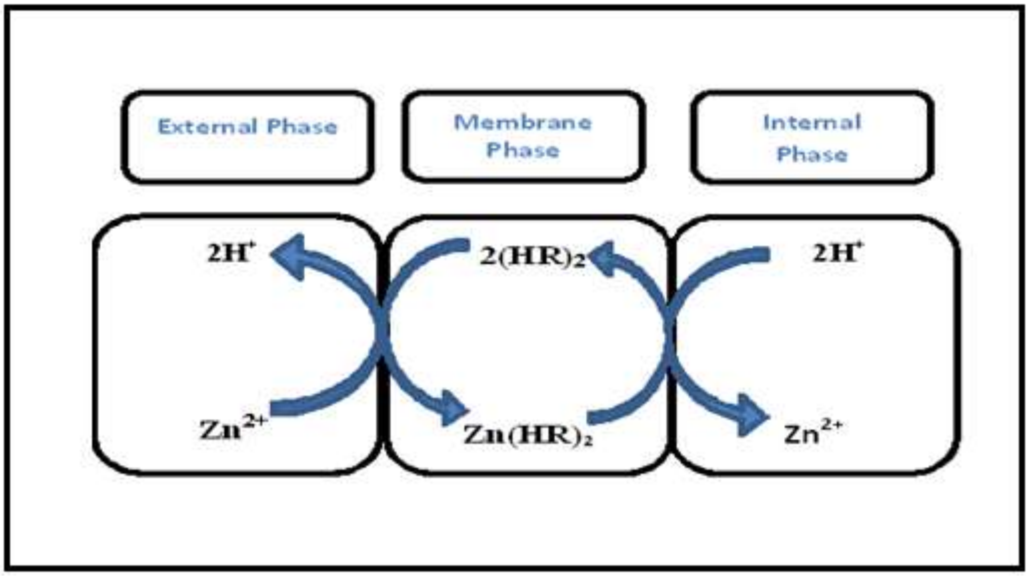

Fig.3 Transport Mechanism of Metal ions Removal by ELM system [10]

Results and Discussion:-

3.1 Effect of External Phase acidity

The pH of the aqueous feed phase has greater influence on the extraction behavior of zinc metal. The effect of pH of feed phase solution is shown in fig. 4. The zinc extraction from sulfuric acid media was studied using D2EHPA within pH range 2.0-6.0. The operating conditions used were [D2EHPA] = 3 vol. % and with an aqueous/emulsion phase ratio of 3 at room temperature. From this figure it is observed that level of zinc extraction increases with increasing pH up to 5 and then decreases. In the pH range 2-5 effective extraction done from 32 to 56 % and pH 6 had no effect on level of metal extraction. This can be explained in pH range 2-5; extraction is due to cation exchange reaction in which protons are released, whereas beyond 5, an increasing pH leads to formation of other species. The observed difference in extraction shows that the opportunity for maximum separation of zinc from wastewater is at pH 5.

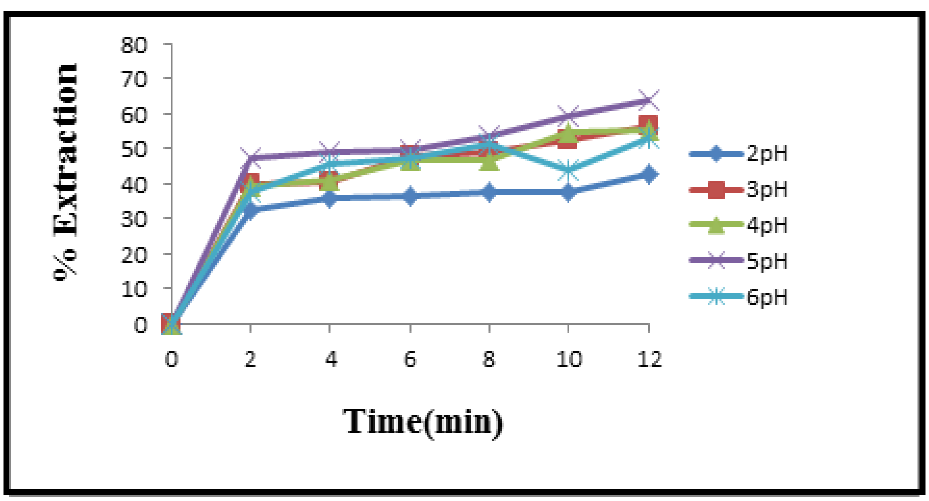

Fig. 4:-Extraction vs. time as a function of acidity of the external phase

3.2 Effect of initial concentration of zinc:-

The effect of initial metal ion concentration on the extraction efficiency was studied in the range of 100 to 250 ppm of Zn. The extraction was performed at pH 3 using stripping sulfuric acid concentration of 1N. The influence of the initial concentration of zinc in the external phase on the percentage extraction is shown in Fig. 5. It is observed that degree of extraction decreases with increasing initial concentration of zinc in the feed solution. At low zinc concentration (100-150ppm), high zinc extraction is obtained about 61%. But for 250 ppm solution, zinc extraction reaches about 48%. This indicates that the process is non-linear with respect to total zinc concentration. This is due to the fact that saturation of the internal droplets in the peripheral region of the emulsion is attained more rapidly for high concentration in the external phase. The zinc complex must diffuse through membrane phase to the inner globule region when the solute concentration is high. This could be conclude that the mass transfer resistance in the emulsion globule i.e. membrane must be very important.

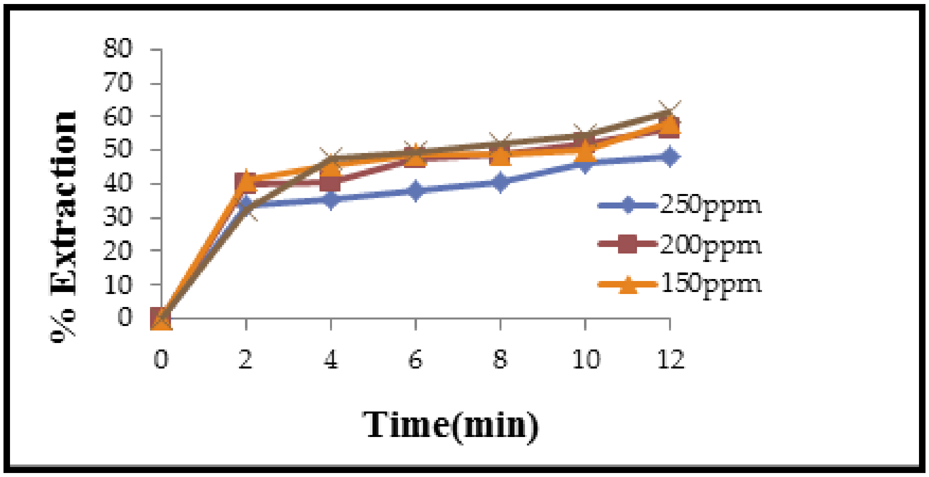

Fig. 5:-Extraction vs. time as a function of initial zinc concentration

3.3 Effect of surfactant (span 80) concentration:-

Surfactant concentration mostly maintains the stability of ELM. Surfactant concentration effect on the emulsion properties i.e. viscosity, interfacial tension between emulsion and aqueous feed phase producing droplets of smaller size which must effect on the removal efficiency of zinc by an ELM. Fig.6 shows the data on varying surfactant concentration using 3 vol.-% D2EHPA dissolved in palm oil diluent. When span80 concentration was increased from 1 to 4 vol.-% , the removal efficiency of zinc metal ion also increased. This is because due to increasing surfactant concentration viscosity of the emulsion membrane therefore emulsion stability as well as mass transfer coefficient increased. Further increasing the surfactant concentration high interfacial resistance to mass transfer would originate which lowered the extraction rate. Below span 80 concentration 2 vol.-%, no emulsion was formed owing to a lack of the surfactant adsorbing the organic/aqueous interface. The surfactant concentration chosen for this work to obtain efficient stabilized membrane was 4 vol.-%.

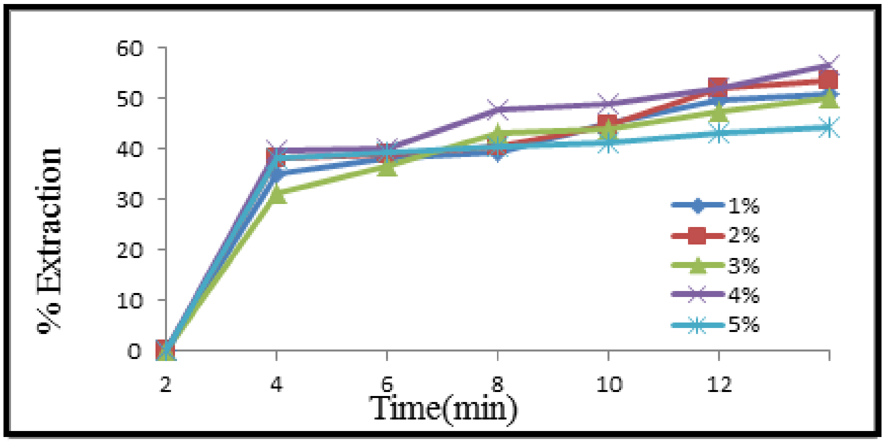

Fig. 6:-Extraction vs. time as a function of surfactant concentration

3.4 Effect of internal phase concentration:-

The role of internal phase concentration (0.5 to 3 N H_2SO_4) in zinc extraction is studied and data obtained using 3 vol.-% D2EHPA dissolved in palm oil diluent at pH 3 are represented in Fig. 7. As shown in this Figure, the % extraction is approximately same that means the final zinc ion concentration in the aqueous phase are nearly the same at different concentration of H_2SO_4.The main driving force in the ELM is difference of hydrogen ion chemical potentials between two aqueous phases. Thus increasing H_2SO_4 concentration from 0.5 – 2 N, the extraction rate increased because the capacity of receiving phase increased. It was expected that emulsion viscosity increases by increasing amount of H_2SO_4 in the internal phase thus decreasing the difference of densities and increased emulsion viscosity. The increasing viscosity of membrane resulted in increasing droplet size.

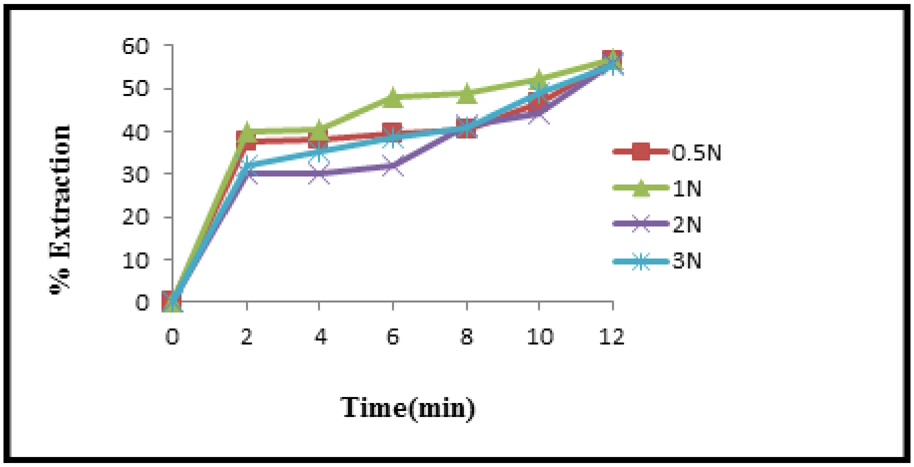

Fig. 7:-Extraction vs. time as a function of internal phase concentration

3.5 Effect of feed/membrane phase ratio:-

It is known as volume ratio or treat ratio of the feed aqueous solution to the W/O emulsion membrane that controls interfacial mass transfer across ELMs. This ratio is also known as Treat ratio. The influence of feed to emulsion volume ratio in the range from 5/2 to 5 on the extraction of zinc are shown in fig. 8. Examined ratio values show that, zinc ion extraction increases with increased about phase ratio 3 and decreased beyond 3 because increase of the emulsion coagulation. Indeed, with increasing volume ratio swelling of emulsion occurs that results increasing internal droplets which reduced the overall metal extraction efficiency. Therefore, it seems that the optimum volume ratio of feed to membrane phase is 3 to obtain the uniform extraction efficiency.

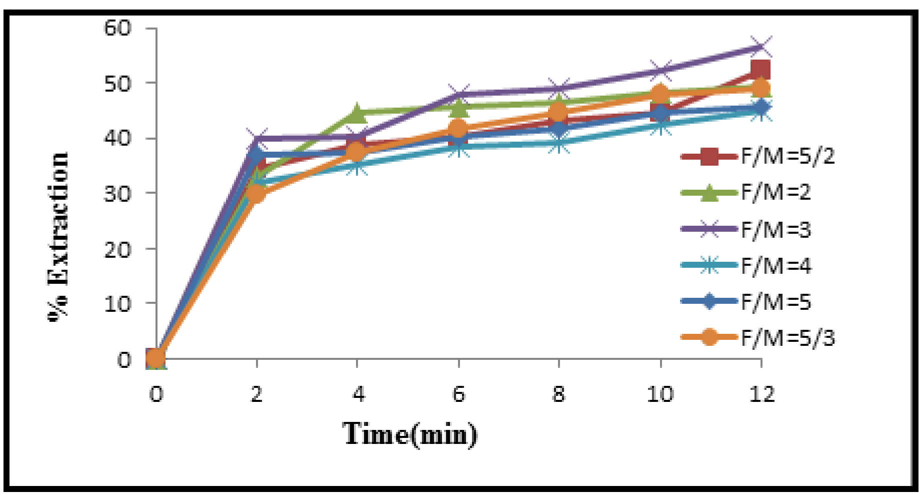

Fig.8:-Effect of feed/membrane phase ratio

3.6 Effect of carrier (D2EHPA) concentration:-

The concentration of D2EHPA was varied in the range from 2-8 vol.-% to determine the effect of organic phase composition on the extraction of zinc. It is conceivable that the increase of the carrier concentration in the membrane phase and hence at the membrane-external aqueous interface enhances the formation of zinc-carrier complexes, resulting in increasing diffusion of zinc from the external aqueous phase to the membrane surface, and the formed complexes through the membrane to the internal aqueous phase. The extraction of zinc ions is represented by;

$$Zn^{2+} + 3(HR)_2 \rightarrow ZnR_2(HR)_2 + 2H^+ \quad (3)$$

From the above equation it seems clear that increasing $(HR)_2$ results in increased extraction of zinc.

From the graph shown in fig. 9 it is observed that removal efficiency of zinc increased with increasing concentration of carrier about 3 vol. %, increasing the carrier concentration further has no effect on the zinc extraction. From 4vol.-% to 8vol.-% the extraction is approximately constant.

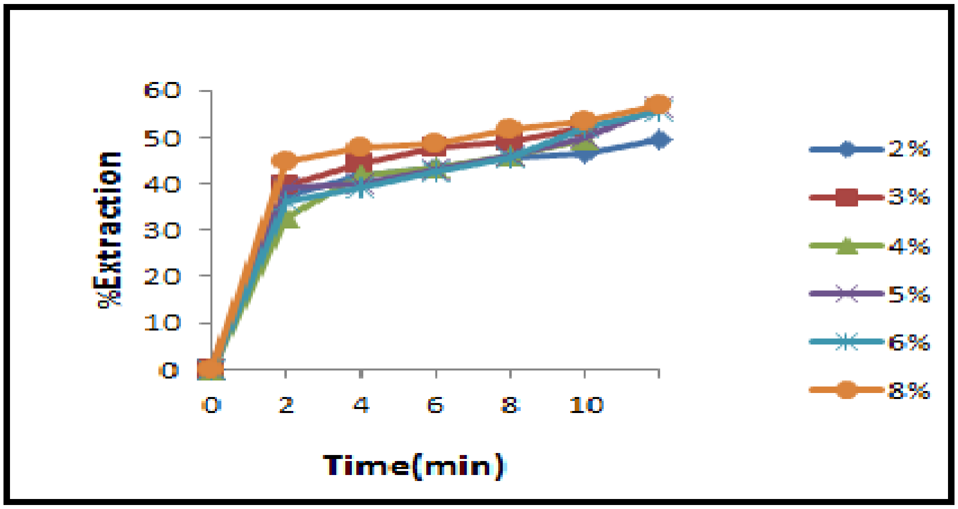

Fig.9:-Effect of carrier (D2EHPA) concentration

3.7 Optimum operating conditions

Optimum operating condition for the recovery of zinc ion is shown in the table below. They indicates that the pH of feed phase in between 4-5 is found to be most effective to recover the zinc ion in presence of carrier about 3vol.% carrier and 4 vol.% surfactant (span80) concentration into the organic phase at an Ephase/Mphase ratio of 6:2 and organic to internal phase ratio of 1. The effect of various parameters concentrations in organic phase at optimum condition such as carrier, surfactant span 80, tween 80, Butanol are studied at low intermediate stirring speed during primary emulsion and high speed stirring achieved at double emulsion time. Primary emulsion is prepared by contacting the organic and internal phases for 15 minutes, that combined phase is known as membrane phase. Similarly double emulsion (w/o/w) obtained by contacting the feed phase and the membrane phase for 12 minutes.

For green ELM process the various vegetable oils have been studied as diluents, such as palm oil, sesame oil, coconut oil, soyabean oil and for further studies we found that palm oil is more effective vegetable oil which gives more recovery of zinc ion from wastewater. Effective extraction is obtained when H2SO4 is used in the internal phase of 1 molarity. At these operating condition 62.76% recovery of zinc ion was achieved. The summary of the operating conditions for the ELM is presented in Table. 1.

Table 1:-Optimum conditions

External Phase		**Organic Phase**	
pH	5	Volume(ml)	10
Volume(ml)	100	Diluent	Palm oil
Zn Conc.(ppm)	60	[D2EHPA](vol. %)	3
		Span80 (vol. %)	4
Internal Phase		Tween80 (vol. %)	0.5
Volume(ml)	10	Butanol (vol. %)	2.5
$[H_2SO_4]$(M)	1	Primary Emulsion Time	15 min
		Secondary (Double) Emulsion Time	12min

Conclusion:-

Emulsion Liquid Membrane extraction of zinc from aqueous phase by using vegetable oil as solvent for extraction of zinc in the presence of D2EHPA was successfully carried out. About 62% zinc extraction is possible at optimum conditions. The effect of various parameters such as, external phase acidity, concentration of feed phase, carrier concentration, surfactant concentration, concentration of stripping phase, different vegetable oil, treat ratio, organic to internal phase ratio, contact time, using Span 20 instead of span 80 surfactant, different stripping phase solution was studied and optimum conditions suggested.

Zinc extraction started from pH 2 to 6pH, efficient extraction was obtained in between pH 4-5. Other optimum conditions obtained was 100ppm feed solution, 4 vol.-% surfactant concentrations and 3vol.-% carrier concentration by volumes %, treat ratio: 3, contact time of feed phase to ELM phase was 12 min in the presence of palm oil as solvent and sulfuric acid as stripping phase.

Future research will concentrate on the stability of ELM and the deemulsification of spent emulsion phase to recover the loaded internal phase and organic phase.

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