

**EXTRACTION OF TOXIC METAL IONS BY USING DIFFERENT
CARRIERS THROUGH FLAT-SHEET SUPPORTED LIQUID
MEMBRANE TECHNIQUE**



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By

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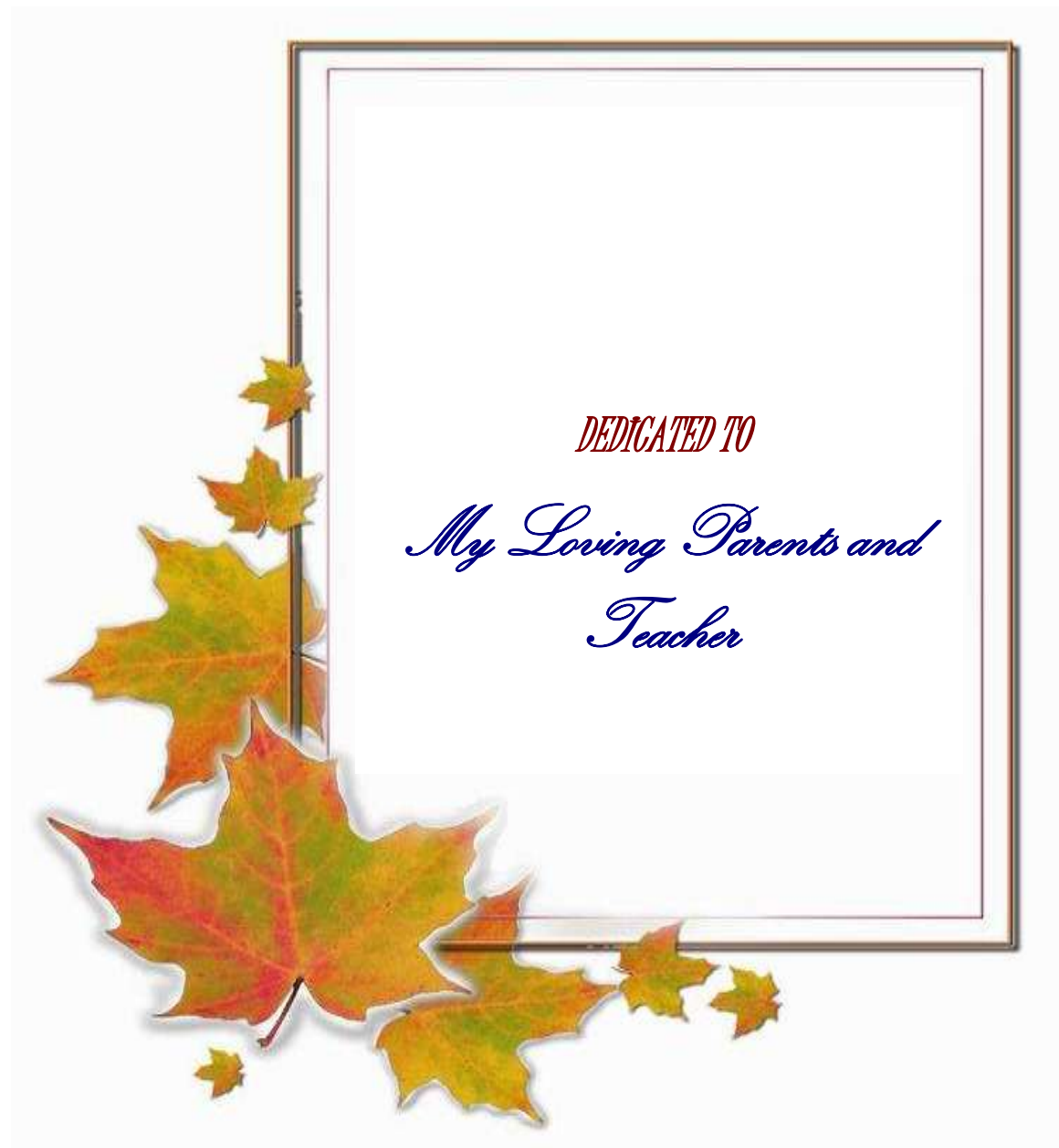
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LIST OF SYMBOLS AND ABBREVIATONS

C_f	Concentration of metal ions in the bulk feed solution (mol L^{-1})
C_s	Concentration of metal ions in the stripping solution (mol L^{-1})
C_{fm}	Metal ions concentration in the membrane phase on feed side of membrane
C_{sm}	Metal ions concentration in the membrane phase on strip side of membrane
D	Diffusion coefficient (ms^{-1})
ELM	Emulsion liquid membrane
BLM	Bulk liquid membrane
J	Flux ($\text{mol m}^{-2} \text{s}^{-1}$)
K	Boltzmann constant
$\acute{k}$	Constant
B	Constant
$\acute{K}$	Constant
$\mathfrak{D}$	Constant
K	Equilibrium constant of metal ion
ℓ	Membrane thickness
$[M]$	Metal ion concentration
LM	Liquid membrane

n	Number of moles of OH^- , TDDA, Cl^- , NH_3 or H^+ associated in the complex
p	Permeability (m s^{-1})
A	Area of the membrane
T	Time (s)
SLM	Supported liquid membrane
T	Absolute temperature (K)
TDDA	Tri-n-dodecylamine
TEA	Tri-ethanolamine
TOPO	Tri-octylphosphine oxide
DPC	Diphenylcarbazine
SEM	Scanning Electron Microscopy

Greek Symbols

η	Viscosity (centipoise)
λ	Distribution coefficient of metal ion
λ_f	Distribution coefficient of the complex into membrane from feed solution
λ_s	Distribution coefficient of the complex into membrane from strip solution
ε	Porosity of membrane

Subscripts

m	membrane
f	feed
s	strip
aq	Aqueous
org	Organic

ABSTRACT

This work elucidates the transport study of toxic heavy metal ions such as Zn (II), Hg (II), Cr (VI), Cu (II), Pb (II), and Cd (II) ions through flat-sheet supported liquid membrane. For the transport of Zn (II) and Cu (II) ions, the triethanolamine (TEA) dissolved in cyclohexanone was used as a carrier, incorporated in microporous polypropylene membrane (Celgard 2400). The Hg (II) and Cr (VI) transport was carried out through tri-octylphosphine oxide (TOPO) dissolved in toluene while tri-n-dodecylamine (TDDA) in xylene was used for the transport of Cd (II) through supported liquid membrane. For the transport of Pb(II), Aliquat 336 dissolved in toluene was used as a carrier. The flux value of the ions through the membrane was used as an index of optimization of different experimental parameters. These optimized parameters were adjusted in a single experiment to find out the flux value of metal ions called hereafter as optimum flux. The optimum conditions for the transport of Zn (II) were found to be: 50% (v/v) TEA in cyclohexanone and 2.30×10^{-4} mol L⁻¹ of zinc ions and 1 mol L⁻¹ HCl was present in the feed phase. While in case of strip phase 0.7 mol L⁻¹ NaOH concentration played an optimum role. Under these optimum conditions, the maximum extraction of zinc ions was achieved with 87% of extraction efficiency in 120 minutes duration of experiment. The optimum flux value obtained was 2.68×10^{-7} mol m⁻² s⁻¹. The stoichiometry of Zn-TEA complex [*TEAH ZnCl₂₊₁*] was evaluated through equilibrium slope method and it was found that 1:1 mole ratio of TEA and H⁺ ion was involved in the complex formation. TEA-cyclohexanone SLM under optimum conditions was found to be stable up to 10 extraction experiments. This SLM was applied to recover Zn (II) from the dry battery waste and about 87% zinc ions were extracted.

For Hg (II) transport, maximum extraction was achieved in 180 minutes at a carrier (TOPO) concentration of 0.1 mol L⁻¹, 4.98×10^{-4} mol L⁻¹ of mercury, and 1 mol L⁻¹ of HCl in the feed phase, 0.05 mol L⁻¹ concentration of hydrazine (N₂H₄) in the stripping phase. The SLM was found to be stable for about 50 hours use. Under optimum conditions, this SLM was employed for the extractions of metal ions from the hospital effluents and approximately 90% Hg (II) ions extraction was achieved.

The maximum chromium extraction was accomplished with 19.2×10^{-4} mol L⁻¹ initial chromium ion concentration and 1.5 mol L⁻¹ H₂O₂ as feed phase, 0.1 mol L⁻¹ TOPO

concentration in membrane phase, while 0.001 mol L^{-1} of DPC, and $1.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ was employed in the stripping phase. The calculations of the percent recovery, distribution coefficient, flux, and permeability were carried out from the data on the optimum conditions. The extraction time for chromium ion transport was found to be 180 minutes and membrane was stable at least up to 10 experiments. This SLM system was applied to remove Cr (VI) from the paint industry wastewater with about 80% extraction efficiency.

For the transport of Cu (II) ions, 3.5 mol L^{-1} TEA concentrations in membrane phase was found to be the optimum concentration. In feed phase $3.17 \times 10^{-3} \text{ mol L}^{-1}$ of copper (II) ions concentration, exhibited the highest extraction in the presence of $1 \text{ mol L}^{-1} \text{ HCl}$ whereas in strip phase, 0.03 mol L^{-1} EDTA was the optimum concentration. Under these optimum experimental conditions, the maximum extraction efficiency of 87% copper (II) ion was obtained in 120 minutes. Equilibrium slope method was used to calculate the stoichiometry of Cu-TEA complex and it was found that 1:1 mole ratio of TEA and H^+ ion was involved in the Cu-TEA complex formation $[(\text{C}_2\text{H}_4\text{OH})_3\text{NHCuCl}_{2+1}]$. The membrane was quite stable up to 10 extraction experiments. These optimized conditions were applied to recover Cu (II) ions from the match industry wastewater and about 87% copper (II) ions were extracted.

The optimum conditions for the extraction of Pb (II) were: $3.61 \times 10^{-4} \text{ mol L}^{-1}$ lead (II) ion and 0.004 mol L^{-1} KI concentrations in the feed, 40% Aliquat 336 concentration in toluene in membrane phase, $1 \text{ mol L}^{-1} \text{ NaOH}$ concentration in stripping phase. The calculations of the percent recovery, distribution coefficient, flux, and permeability were made from the data obtained on the optimum conditions. The extraction time was found to be 180 minutes for lead ions transport and it was found that the membrane was stable at least up to 10 experiments. In the presence of other metal ions like Cd (II), Cu (II), and Zn (II), 90% of lead (II) ions have been selectively removed from the battery wastewater.

For the extraction of Cd^{2+} ion, optimum experimental conditions were $13.3 \times 10^{-5} \text{ mol L}^{-1}$ Cd (II) concentrations, $1 \text{ mol L}^{-1} \text{ HCl}$ in the feed solution, 30% TDDA-xylene in SLM, $6 \text{ mol L}^{-1} \text{ NH}_3$ solutions in the stripping phase. The extraction time for optimum transport of cadmium ions through the supported liquid membrane under the optimum experimental conditions was 120 minutes. The results show that 92% removal of Cd (II) was achieved from the feed solution in

spike experiments while 87 % cadmium was removed from wastewater of paint industry. The present SLM was found to be stable for about 50 hours use.

Chapter No. 1

Introduction

Introduction

With the growing industrial development the use of various metals has been tremendously increased in recent decades. The importance of these metals and environmental pollution problems demand to avoid the wastage of metals, to remove and recover metals from industrial process waste water.

Removing and recovering metals from aqueous solutions can be carried out, *inter alia*, by adsorption [1], ion exchange [2], chemical precipitation [3], solvent extraction [4], and reverse osmosis [5]. Due to the inherent limitations of these techniques, including low efficiency, complex operating conditions, secondary sludge formation, and high cost, etc., more effective method for the removal of toxic metal ions is now under intensive investigation which mainly includes the removal of metals using liquid membrane technology. Some of the important advantages of this technique over the classical separation methods are low capital and operating cost, less energy consumption, and less solvent requirements, high concentration factors, and high fluxes [6-7].

1.3 Membrane Technology

Membrane technology has widely been used nowadays for the wastewater treatment and has great advantages over other conventional separation techniques. The energy efficiency, high separation capacity and selective separation are a few important features of the membrane technology [8-11]. In membrane separation techniques, the membrane used is a thin porous film, which acts as a semi permeable membrane to transport the selective species and retain the others on one side of the membrane. The extractants dissolved in an organic solvent are imbedded in micro porous support (membrane) for the metal ions removal and separation [12-13].

Molecular size, charge, and charge density of the species significantly affect the membrane separation process.

1.4 Liquid Membrane

Liquid membrane (LM) technique has been given significant interest by the researchers for removal of toxic heavy metals ions from different solutions. The membrane is semipermeable in nature and placed in between two aqueous phases. The separation can occur by the transport of solute from source (feed) to strip side through the membrane. The basic properties of the membrane are: simple in structure and operation, easy to scale up, and low energy consumption. Polymeric and inorganic membranes are widely used in the separation of toxic metals, drugs, dyes, and gases etc. They are also widely used commercially in waste water treatment and the separation of macromolecules. Liquid membrane separation technique is very effective techniques among the other membrane extraction technologies and is being widely used in many fields such as inorganic, organic, analytical, biotechnology, chemical engineering, biomedical and waste water treatment.

1.2.1 Types of Liquid Membranes

There are three types of liquid membranes:

- I. Bulk Liquid Membrane (BLM)
- II. Emulsion Liquid Membrane (ELM)
- III. Supported Liquid Membrane (SLM)

1.3.1.1 Bulk Liquid Membrane (BLM)

BLM technique plays a significant role in the selective extraction of cations from the aqueous solution. This technique is widely employed for the toxic metal ion removal. The BLM is a simple technique in which both the aqueous phases (source and receiving phases) are separated by an organic phase. The solute is transported from feed, through organic phase, and released into the receiving phase. The density of the organic phase is different from that of the aqueous phases. However, the large amount of solvent consumption makes the BLM process more costly to be used in industrial field. Therefore, its use was limited to the laboratory level for the kinetic study of various mass transfer processes [14].

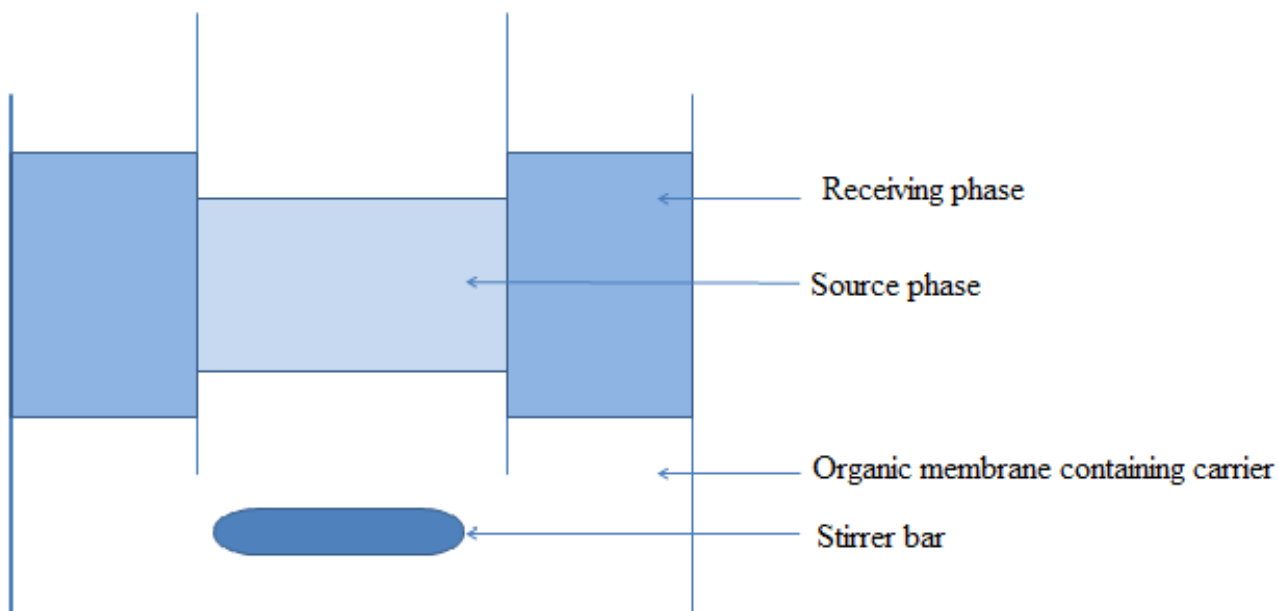


Fig.1. Bulk liquid membrane.

1.3.1.2 Emulsion Liquid Membrane (ELM)

Large interfacial area, simple operation, high extraction efficiency has some of the effective feature of the ELM. Another important feature is that both extraction and strip processes occur in one step. The double emulsion system is of two types: water-oil-water emulsion type and oil-water-oil emulsion type. In water-oil-water system the immiscible oily membrane is in between the two aqueous phases while in the oil-water-oil system the immiscible water phase separates the two organic phases. In ELM, the membrane phase has dual function; it not only permits the selective transport of species from one phase to another phase but also prevents the mixing of two phases. The carrier present in the membrane phase combines with the solute ions and transports it to the strip side [15].

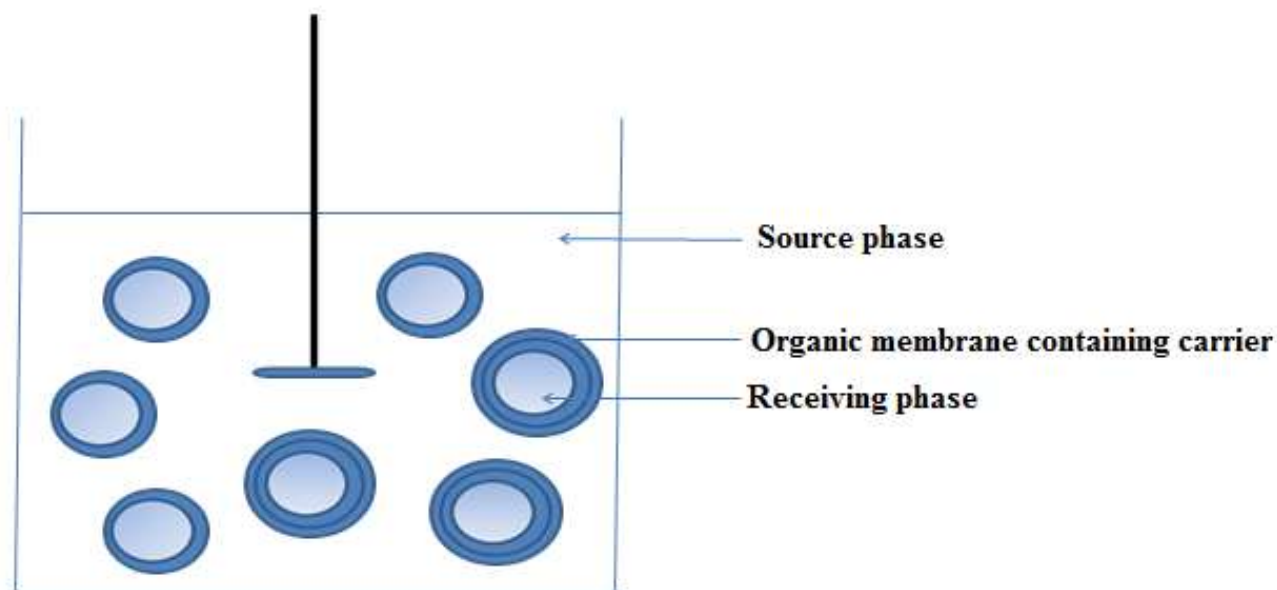


Fig.2. Emulsion liquid membrane.

1.2.1.3 Supported Liquid Membrane

The supported liquid membrane technique (SLM) has recently received considerable attention due to low cost, less solvent and energy consumption, high transport efficiency and flux [16,9]. SLM is an efficient separation technique for extraction and removal of heavy metal ions from different sources. The SLMs find its applications, both in industry and analytical fields.

The supported liquid membrane is a simplified form of liquid membrane in which solid support is impregnated with extractant or carrier. The extractant, dissolved in diluents, is imbedded in the hydrophobic macro porous membrane. The membrane is placed in between the two aqueous phases, feed phase and strip phase [17-18]. In supported liquid membrane both the extraction and stripping processes occur at the same time and is also known as unitary process. The extractant combines with the substance or species to be extracted, present in the feed phase, and transport it towards the strip phase through the membrane under the influence of concentration gradient [19-20].

1.2.1.4 Classification of Supported Liquid Membrane

Based on the shapes and structures, SLM is classified into two types:

- i. Flat-sheet supported liquid membrane
- ii. Hollow fiber supported liquid membrane

i. Flat-Sheet Supported Liquid Membrane

Flat-sheet supported liquid membrane is one of the simplest forms of the SLM in which micro-porous polymer sheet is used as a membrane. The solid support is impregnated with

extractant solution and then it is clamped tightly in between the two compartments (feed and strip sides) of the extraction cell. Each compartment is filled with their respective feed and strip solutions. The mechanical stirrers are used for stirring the solutions to avoid the concentration polarization at the interfaces [21].

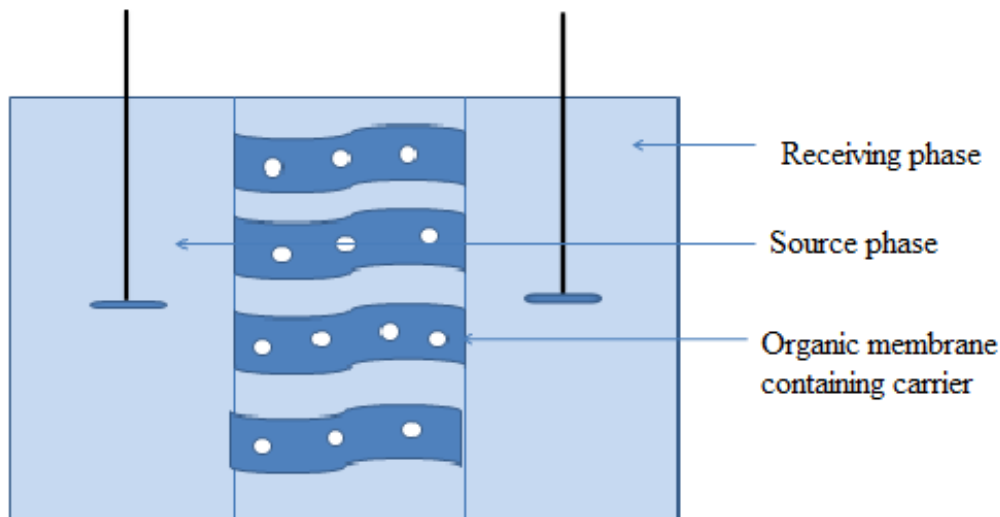


Fig.3. Flat-sheet supported liquid membrane.

ii. Hollow Fiber Supported Liquid Membrane

In hollow fiber supported liquid membrane a special module system, consisting of hollow fibers, is used for the transport of heavy metal ions. The module consists of two shells, outer shell and inner shell. The inner shell is packed with the thin fibers which are arranged in rows. The solute from the source phase passes through the fibers and enters the receiving phase, where it goes outside through the outlet provided in the shell with the help of pumps [22].

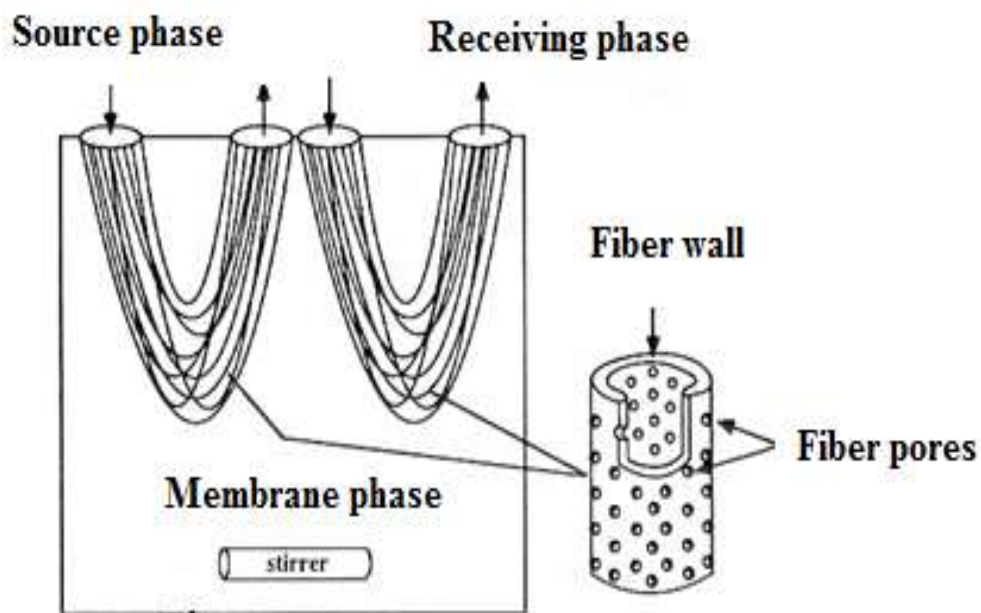


Fig.4. Hollow fiber supported liquid membrane.

1.4 Components of Supported Liquid Membrane

1.3.1 Solid Support

The solid support used in the SLM techniques includes a variety of materials. There are a number of support materials which are commercially available for the preparation of SLM. The materials are hydrophobic/hydrophilic, systematic or unsystematic, homogeneous or heterogeneous in nature. For SLM, the material should be hydrophobic in nature. It should be thermally and chemically stable. The support material is usually a membrane, which are generally polymeric in nature. The membrane is made up of the polymers like polypropylene, poly-sulphones, poly-vinylidene fluoride and poly-tetrafluoroethylene. The solute particle size to be transported across the membrane should lie in the range of 0.1-10 μ m [23]. However, the pore size of the membrane can be varied by a careful process control. The polypropylene films are commercially available under the different trade names. These films are manufactured by various

multistage patent processes which include extrusion, annealing and stretching of polypropylene to form elongated pores. Celgard 2400 and Celgard 2500 most common type of membranes which are widely used for the removal of heavy metal ions from the different sources [24].

The poly-sulphones membranes are prepared by dissolving the polymer in the solvent and then subjected to phase inversion process. In case of hollow fiber, the membrane is cast or spun and the solvent is slowly removed by evaporation, then precipitation and annealing processes are carried out. The fibers obtained are asymmetric with fine pores inside the fiber lumens.

1.3.5 Extractant or Carrier

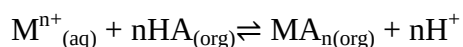
Extractants used in supported liquid membrane for extraction of heavy metal ions like Zn, Mn, Ni, Co, Cu, Fe and Mo etc. are chelating substances or may be acids, which are commonly used in the hydrometallurgical process[23]. The extractants are basically organic in nature and the choice of extractant in SLM is based on the selectivity of the compounds being used for the extraction. The membrane phase is prepared by impregnating the membrane in extractant solution made in suitable solvent. The extractant penetrates into the pores of the membrane by capillary action. The extractants or carriers [25] are usually tertiary amines or quaternary ammonium salts e.g. tri-ethanolamine (TEA), tri-octylamine (TOA), tri-dodecylamine (TDDA), tri-iso-octylamine (TIOA) and triocylmethyllummonium chloride (Aliquat 336) etc.

There are mainly three types of the extractants:

- i. Acidic extractants
- ii. Basic extractants
- iii. Neutral extractants

i. Acidic Extractants

Acidic extractants are organic carrier which possesses acidic functional group mainly used for the extraction of metal ion across SLMs and are also called cation exchangers. The cation exchangers are either acidic or chelating agents. The acidic extractants follow the compound formation extraction mechanism which is given as follows [26].

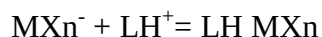
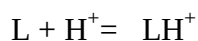


Extraction process by acid extractants is highly pH dependent. The common examples of acidic cation exchanger are organic acid such as sulfonic, phosphoric, carboxylic and phosphinic acids.

The chelating acidic extractants have two functional groups that bind with metal and form bi-dentate complexes [27]. Aromatic β -hydroxyoximes and hydroxyl-benzophenone (with trade code LIX64) are the most common chelating agents used in the extraction process. The acidity of the extractants has remarkable effects on the extraction process which controls the removal of metal ions. D2EHPA, PC88A, LIX84-I, LIX 64N, LIX 62N, Cyanex 272etc. are some of the examples of chelating acidic extractant.

ii. Basic Extractants

The basic compounds having high molecular weight are used as a basic extractants. The process of extraction takes place through the formation of an ion-pair and due to this reason these extractants are also called anion exchanger. In the case of amine based extractants the mechanism of carrier-metal complex formation may be given as follows. The carrier 'L' is protonated to form positive charged specie 'LH⁺' which makes a complex 'LH MX_n' with metal anion specie 'MX_n⁻' [28].

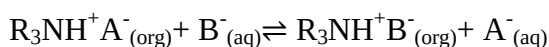
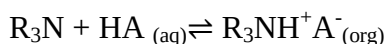


There are two main categories of the basic extractants:

- i. Alamine Series
- ii. Aliquat Series

i. Alamine Series

The reagents of alamine series contain nitrogen, which have capacity to form amine salts with many organic and inorganic acids. The amines, which are generally used in the extraction of metal ions, are tertiary amines having general formula of R_3N where R represents the hydrocarbon chain. The extraction chemistry of alamine series reagents can be represented in the equations given below [29]:



The extent to which B^- exchanges A^- depends on the relative affinity of two anions for the organic cations and their relative stability in the aqueous medium.

The Alamine 300, 308, 336, 310, 304 is some of the most widely used Alamine series reagents. These reagents are commonly used in the hydrometallurgy process for the extraction of different metal ions such as copper, zinc, nickel, cadmium, chromium, uranium, vanadium, and zirconium etc.

In case of amine extractants the reagents used for the stripping of metal ions are Na_2CO_3 , $(\text{NH}_4)_2\text{SO}_4$, NaCl , NaOH etc. The choice of compounds used for the stripping phase depends on the overall extraction process, but the stripping agents which deprotonate the amines exhibit the better stripping results. For example the stripping mode of action of Na_2CO_3 is given below:

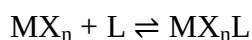


ii. Aliquat Series

Aliquat 336 is a second type of basic extractant. The Aliquat series is based on methyl chloride quarterization of an alamine reagent. The anionic form of metal ion gets associated with positive charged quarterized amine and thus extraction of metal ions takes place. The process of extraction based on Aliquat series reagent is not pH dependent. These reagents are used for the extraction of heavy metal ions from aqueous solution as well as for the purification of inorganic acids and reclaiming of metals from spent catalysts. Aliquat 336 (tri-C8-C10) methyl ammonium chloride) and Aliquat 336 nitrate are commonly used for the extraction process [30].

iii. Neutral Extractants

The extractants of this type are weakly basic in nature. It is an electron rich species (O and S), one of the atoms of extractant has ability to donate an electron pair to a neutral atom. The extraction processes is facilitated by coordination of extractant with metal ions and results in the formation of neutral complexes or adduct [31]. This organo-metallic complex is insoluble in aqueous solution but soluble in organic medium.



Where M is a metal ion, X is its associated anion, and L is a neutral extractant.

The neutral extractants are widely used in the field of hydrometallurgy and industrial waste water treatment. Examples are tri-octylphosphine oxide (TOPO), tri-n-butyl phosphate (TBP), and methyl isobutyl ketone (MISK) etc.

1.3.6 Diluents

In the preparation of extractant solution, different kinds of solvent/diluents are normally used. For the choice of diluent following features must be taken into consideration [32] i.e. the diluent should be:

- i. Cheap
- ii. Hydrophobic
- iii. Low viscosity
- iv. Low surface tension
- v. Low volatility
- vi. Low interfacial tension

Firstly, the diluent should be hydrophobic in nature, so that it becomes immiscible with the aqueous phase. Secondly, the diluent should have low viscosity to ensure high mass transfer across the membrane. The low surface tension and low volatility are other important characteristics of the diluent to keep the extractant molecules in the solid support pores by capillary forces. The interfacial tension between aqueous and organic phase is another essential feature. In the membrane phase the degradation of the organic liquid causes emulsion formation due to low interfacial tension, but it increases the mass transfer by contacting with the aqueous phase. The value of flux is largely affected by the extractant (carrier) concentration in the carrier-mediated transport. The rate of flux depends on the solubility of the carrier in solvent. Due to

high solubility of the carrier in aliphatic and aromatic organic solvents, these are preferred and commonly used in SLM system. Examples of solvents are: toluene, xylene, kerosene, 1-octanol etc.[32].

1.4 Mechanisms of Supported Liquid Membrane

There are two types of mechanisms.

- i. Facilitated coupled counter transport
- ii. Facilitated coupled co-transport

1.7.1 Facilitated coupled counter transport

Figure 5(a) shows the mechanism of SLM based extraction of ions. In this case metal A from the feed solution is selectively extracted by the carrier through an organic membrane. The carrier picks up metal 'A', at the membrane-feed interface, diffuses across the membrane as a complex, and finally exchanges 'A' with the charged specie 'C' on the strip side of the membrane. In this case, 'C' has the same charge as of 'A'. Thus, the carrier acts as a shuttle carrying 'A' and 'C' in the opposite directions. That is why the process is called facilitated coupled counter transport. The typical example of this process is the metal cation exchange with H^+ ions facilitated by acidic carrier [33].

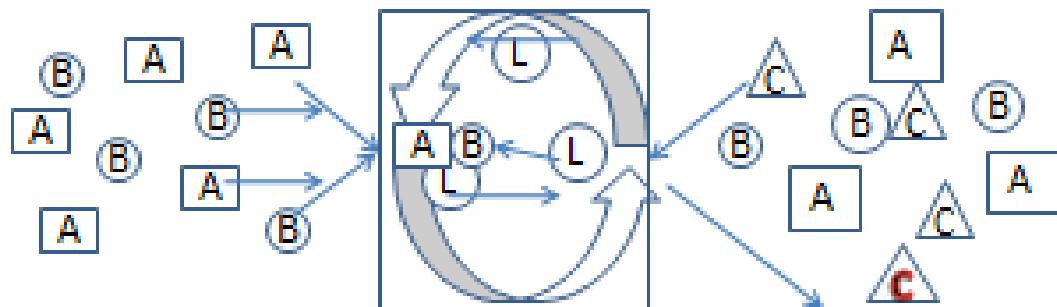
1.4.2 Facilitated coupled co-transport

Basic carrier, for examples amines, can be used to carry H^+ ions together with negatively charged ions, such as Cl^- , in the same direction. This process is called facilitated coupled co-transport shown in Figure. 5(b)[33].

Feed Phase

Membrane Phase

Strip Phase

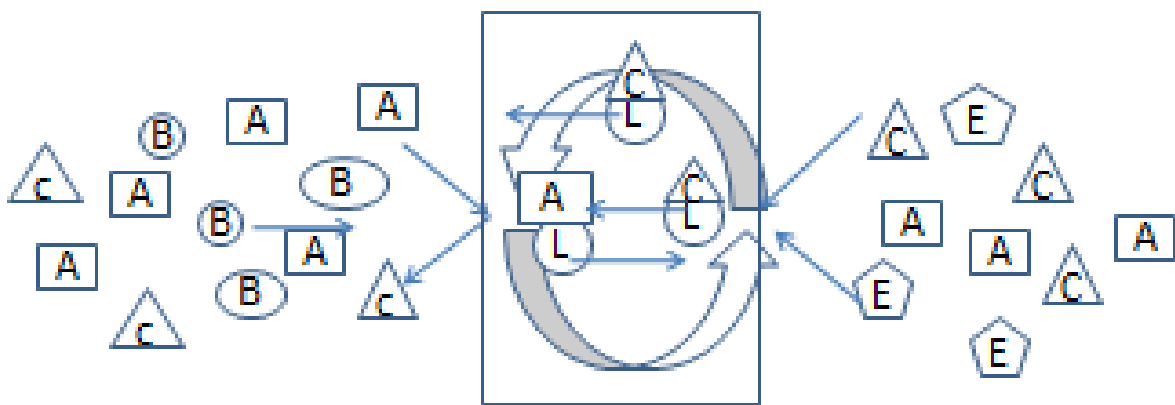


(a)

Feed Phase

Membrane Phase

Strip Phase



(b)

Fig.5. Mechanism of metal ion transport through the SLM (a) Facilitated coupled counter transport (b) Facilitated coupled co-transport.

1.8 Advantages of Supported Liquid Membrane

1.8.1 Extraction and stripping in a single step

One of the significant advantages of the SLM is that both extraction and stripping processes occur simultaneously in a single step. Due to this reason these processes are cheaper, and involve less complexity with less energy consumption and high efficiency [34].

1.8.2 Uphill transport

In conventional process the separation is limited by equilibrium conditions while in SLM the separation is non-equilibrium because both the extraction and stripping processes occur in a single unit. In uphill transport, the desired solute transports from low to high concentration solution [35].

1.8.3 High interfacial area

The SLM system provides a large interfacial contact area per unit volume for extraction and mass transfer than the classic methods. In hollow fiber SLM configuration, the spiral wound hollow fibers provide high interfacial contact area per unit volume which ranges from 1500 to 7000 $\text{m}^2 \text{m}^{-3}$ as compared to flat-sheet SLM where the contact area is very small. The high interfacial area entails in high extraction efficiency and reduction in the volume of the equipment needed [36].

1.8.4 Low solvent inventory

Very little amount of solvent is needed (about 10cm^3) to impregnate the membrane with carrier which reduces the operational cost of the SLM [37].

1.8.5 Wastewater treatment

The SLM technique has been used for the removal of pollutants including toxic heavy metal ions, phenols, ammonia, and other hazardous material from the wastewater [38-40].

1.9 Literature Review of Extraction of Heavy Metal Ions through Supported Liquid Membrane

During the last century, the concentration of heavy metals ions has increased in the environment due to the extension growth of human activities. Removal of heavy metal ions by using different liquid membranes has received great attention due to the higher efficiency of separation, moreover, the toxic heavy metals provoked special interest in this regard [41].

1.9.1 Extraction of Zinc (II)

Zinc is the 24th most abundant element in the earth crust with 0.0075% amount. Soil contains 5-770 ppm of zinc. Seawater has only 30 ppb zinc [42]. After iron, aluminum, and copper, zinc is fourth element which is commonly used. It is extensively used in galvanizing, making alloys and other industrial and everyday used items [43-44].

Due to extensive use of zinc, a significant amount of zinc is being dumped in the lakes and rivers from various industrial wastewaters which cause serious environmental problems.

K. Sarangi et al. [45] have investigated the separation of copper and zinc by using di-2-ethyl hexyl phosphoric acid (TOPS-99) as a carrier while Celgard 2500 was used as a support. The stripping reagent was H_2SO_4 and different parameters have been studied. It was noted that zinc extraction was maximum at pH from 1.5 to 3.5 whereas copper extraction takes place at pH from 3.0 to 4.1. The kinetics of zinc (II) permeation through cyanex 272 in kerosene by using

supported liquid membrane was studied by Kunungo et al. [46]. The separation parameters have been determined and it was found that the zinc metal ion flux was depended on the concentration of Zn (II), H^+ and carrier. In case of Zn (II) ions and carrier concentrations the flux was found to be first order and 0.75 order respectively. M. S. Gasser et al. [47] have carried out the extraction of zinc(II) using cyanex 925 in kerosene through SLM from the sulphate and thiocyanate medium. The ammonia was used as a stripping solution. The effect of concentration of H^+ , carrier, SCN, H_2SO_4 and ammonia was investigated. As the concentration of these reagents increases the extraction of zinc (II) ion increases and the maximum value of flux was obtained. R.S. Juang et al. [48] have studied the simultaneous removal of Zn(II) and Cd(II) from aqueous chloride solution through supported liquid membrane using Aliquat 336 in kerosene. The n-decanol was used as modifier, HCl solution as a stripping phase while the solid support was PVDF membrane. The experiments were carried out at different concentrations of metals and carrier. The concentration ratios of Zn(II) and Cd(II) were also evaluated. The non-ideal equilibrium behavior of the aqueous and membrane phase was expressed by thermodynamic model. A. Urtiaga et al. [49] have investigated the selective separation of zinc(II) and iron(III) from the chromium (III) ions by using galvanic industrial effluent. The combined techniques of Emulsion liquid membrane with hollow fiber membrane contactors were used in this process containing cyanex 272 in 1-decanol as an extractant. The effect of various concentrations of metals, carrier, and acid was determined. The results show that the nature of acidic stripping reagent has remarkable effect on the transport of zinc (II) ions, as the extraction was faster in case of H_2SO_4 as compared to HCl. The permeation study of zinc (II) through PC-88A/kerosene based SLM was employed by A.M. Tarditi et al. [50]. The influence of different experimental parameters such as pH, stirring rate, carrier concentration, and temperature was carried out. The

kinetic modeling was also designed to predict the zinc (II) permeation. The results indicate that the best transport of zinc (II) ions occurs in the pH of 4-2 in feed and strip solution.

1.9.2 Extraction of Mercury(II)

Mercury is a toxic heavy metal and has hazardous effects on human health [51]. In the environment, under aerobic conditions, the soluble mercury compounds are converted to organic compounds like methyl mercury (Me-Hg). Me-Hg is very toxic and accumulates in the organisms through the food chain and disrupts the ecosystem. Mercury is released into the environment through natural as well as anthropogenic processes. Major anthropogenic sources include fuel combustion, coke and lime production, hazardous waste recycling, petroleum refining, mercury cells, chloro-alkali plants, batteries, fertilizers, pulp and paper industries, etc. [52]. Mercury-poisoning is a worldwide concern owing to its high toxicity, carcinogenicity and non-biodegradable nature and placed on top of the list of pollutants by the USEPA [53]. According to European environmental regulations the permissible mercury level in drinking water and wastewater is limited to 1 and $5\mu\text{gL}^{-1}$, respectively [54].

Several studies show pronounced potentials of LM for the extraction of mercury from different solutions. Chakrabarty et al. [55] have studied the separation of mercury through SLM using environment-friendly diluent. Safavi et al. [56] have reported the efficient method for the transport of Hg (II) through SLM using methyl red as a carrier. The arsenic and mercury removal from natural-gas-co-produced water using synergistic extractant via HFSLM is described by Lothangkum et al. [57]. Chakrabarty et al. [58] have investigated the synchronized separation of mercury and lignosulfonate through TOA based SLM. The mercury transport through different types of LM containing calixarene as carriers was evaluated by Ersoz [59]. Fontas et al. [60] have used the benzoylthiourea based SLM for the selective removal of mercury. Shamsipur et

al.[61]have illustrated the SLM system for the concurrent separation of silver (I) and mercury (II) from its aqueous solutions. Suren et al.[62]have applied HFSLM technique for the separation and removal of lead and mercury ions by using different extractants such as D2EHPA, Cyanex 471, Aliquat 336, and TOA.

1.9.3 Extraction of Chromium (VI)

Removal of Cr (VI) through SLM using different synthetic carriers has been widely reported by the scientific community. Kozłowski and Walkowiak studied the tertiary amines and quaternary ammonium salt (Aliquat 336) carriers for the transport of Cr (VI) through SLM from acidic solution [63]. Ashraf et al. have reported the selective separation of Cr (VI) with alamine 336 carrier through flat and hollow fiber SLM [64]. W.S. Winston Ho et al. have studied the removal of Cr (VI) from wastewater rby SLM with strip dispersion method. The secondary amine was used as a carrier in the membrane and sodium hydroxide as a stripping reagent[65]. Methyl tri-capryl-ammonium chloride (Aliquat 336) with kerosene impregnated in SLM was reported to remove Cr (VI) from a biological sample like urine while sodium nitrate was used as a stripping phase [66]. P. Venkateswaran et al. have reported the separation of Cr (VI) from chromium plating wastewater through tri-n-butylphosphate based flat-SLM [67]. Sang-Wook Park et al. have studied the facilitated transport of Cr (VI) through an SLM consisting of tri-octyl-methyl-ammonium chloride as a carrier in the hydrophobic micro-porous polytetrafluoroethylene membrane, using potassium dichromate in the feed side, and sodium hydroxide in the strip side [68]. The removal of Cr(VI) using Cyanex 923 as a carrier and hydrazine sulfate as a strippent has been reported [69]. Imam B. Solangi et al. have described a transport of Cr(VI) across supported liquid membrane containing different p-tert-butylcalix[4]arene diamide derivatives using Celgard 2500 as supported membrane. In the presence of many

other metal cations the selective removal of Cr (VI) has been carried out [70]. A.I. Alonso et al. have presented the removal and recovery of Cr(VI) ions with Aliquat 336 using hollow fiber module [71]. S.Bey et al. have prepared the polyether ether ketone based hollow fiber membrane by using Aliquat 336 as a carrier in kerosene. This membrane was used for the extraction of Cr(VI) from the aqueous solution [72]. Cristina-Veronica Gherasim et al. have reported the removal of chromium (VI) using Aliquat 336 based PVC inclusion membrane [73]. M. Rajasimman et al. have investigated the extraction of chromium (VI) by emulsion liquid membrane from pharmaceutical wastewater. In this process, Aliquat 336 in kerosene was used as a carrier while surfactant is Span-80 and potassium hydroxide as a strippent [74]. Ting Chia huang et al. have investigated the transport of chromium (VI) from aqueous solutions of pH 2-4 through a supported liquid membrane with tri-n-octylphosphine oxide (TOPO) dissolved in kerosene, using the porous membrane poly-vinylidenedifluoride (PVDF) with a mean pore size of 0.45 μ m, porosity of 75%, and thickness of 125 μ m. The HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ species are predominant in the pH range of 2 to 4 [75].

1.9.4 Extraction of Copper(II)

Ren et al. [76] have studied a hollow fiber liquid membrane technique for extraction of the copper metal ions from the wastewater. Takahashi et al. [77] have employed the hybrid type liquid membrane for the transportation study of copper. The LIX65N in kerosene was used as a carrier which extracted copper (II) from an aqueous sulfate feed into a strip solution containing dilute sulfuric acid. Alaguraj et al. [78] have reported the removal of copper (II) ions through an emulsified liquid membrane (ELM). The extractant, Alamine and Span-80 (a surfactant), were used as a membrane phase, dissolved in kerosene. The LIX 984N-C based tubular supported liquid membrane was also used for the extraction of copper ions [79]. The copper extraction was

carried out through the hollow fibers containing Aliquat 336 dissolved in kerosene as a carrier and HCl as a stripping reagent [80]. Alguacil, et al. [81] have employed the MOC-55 TD in Iberfluid for the transport of copper (II) ions through facilitated supported liquid membrane and they further studied the process by using theoretical modelling of mass transfer of the copper ions.

1.9.5 Extraction of Lead (II)

Extensive studies on removal of lead via supported liquid membrane with different carriers as well as solvents are available in the literature. R. Anupama et al. [82] have studied the remediation of lead through supported liquid membrane (SLM) by iodo system with tributyl phosphate as a carrier where they found that the permeability value was higher at low concentration of lead metal ions. Sumeth Khaoya et al. [83] have employed the application of D2EHPA as a carrier in kerosene using HFSLM for the extraction of lead. The results show that the separation of lead from battery industry wastewater using D2EHPA based HFSLM is a more efficient process as compared to the other conventional processes. M. Ulewicz et al. [84] have reported the transport of lead through polymer inclusion membrane with p-tert-butylcalix[4]arene derivatives as a carrier. The results show that lead is effectively removed from the solution. The stability of polymer inclusion membrane (PIM) with p-tert-butylcalix[4]arene derivative was described using Danesi's thermodynamic model. Saeed ur Rehman et al. [85] have investigated the extraction of lead (II) ions through SLM using tri-n-octylamine (TOA) as a carrier. Various parameters such as concentrations of Pb^{2+} ions, HNO_3 , NaOH , and TOA were studied. The $\text{Pb}(\text{NO}_3)_{n+2}(\text{HNR}_3)_n$ complex stoichiometry was studied with the help of flux data. The membrane was found efficient and stable for a consistent use of 10 days. The optimized SLM system was then applied to the paint and industrial effluents for the removal of lead ions.

Yadav et al [86] have studied the use of TBP as a carrier in methyl isobutyl ketone for the removal of lead and noted that TBP, in the presence of iso-butyl ketone exhibits efficient extraction. Wei et al. have reported the extraction of lead by using dithiozone as a carrier with ionic liquids as solvent. The ionic liquid provided more competent SLM system as compared to hydrocarbon [87]. Canet et al. have examined the efficient transport system of lead using lasolocid as carrier in n-nitrophenol octyl ether with polypropylene as support [88].

Rania Sabry et al. [89] have presented the removal of lead through ELM technique. The ELM system consists of di-(2-ethylhexyl) phosphoric acid in kerosene as a carrier, SPAN-80 was used as a surfactant while sulfuric acid as a stripping reagent. The concentration of the carrier, surfactant, stripping reagent, emulsification time, and stirring speed were studied for the ELM stability and transport of lead. At optimum conditions, the ELM system showed effective results for the removal of lead. M. Ulewicz et al. [90] have studied the cellulose triacetate based polymer inclusion membranes (PIM) using calix [4] crown-6 derivatives as a carrier for the selective transport of a mixture of Pb (II), Cd (II), and Zn (II). The influences of the type of calix [4] crown-6 molecule on the selectivity and efficiency of the extraction was studied and it was found that the hydroxamate derived crown molecule shows a high transport of lead (II) ion as compared to zinc and cadmium ions. The ion transport decreases as the concentration of HCl in the stripping phase increases. The effect of the nature of the plasticizers was also evaluated and it was reported that transport increases in the order of DOA < *o*-NPOE < *o*-PPPE.

S.Suren et al [91] have used four types of extractants D2EHPA, Cyanex471, Aliquat336, and TOA with toluene as a diluent. These extractants were selected for the selective transport of lead and mercury ions. The hollow fiber single-module with HCl as stripping reagent was used for the extraction process. The D2EHPA was found to be effective extractant for lead extraction

while Cyanex 471 was efficient extractant for the extraction of mercury ions. Moreover, TOA and Aliquat 336 exhibited a higher selective extraction of mercury ions than Cyanex471 did.

K.K. Bhatluri et al. [92] have studied the extraction of Cd and Pb ions simultaneously. They used the Aliquat 336/ Coconut oil as a carrier and PVDF as a support membrane. The stripping reagent was EDTA. The pH of feed phase was 6.5. The transport time was 10 hours while the transport efficiency was 78% to 84%. In the feed solution HCl transforms into anion (MCl_4^{2-}) from metal chloride (MCl_2). The carrier (Aliquat336) forms a complex with solute at the feed–membrane interface. The solute-carrier complex diffuses through the membrane phase and is released in the stripping solution by reaction with the stripping agent ($\text{Na}_2\text{-EDTA}$) at the strip-membrane interface.

1.9.6 Extraction of Cadmium(II)

Cadmium has a lot of applications such as in the manufacturing of alloys, pigments, batteries, and metal plating. Due to vast industrialization, the water reservoirs are contaminated with cadmium which is highly toxic for the environment as well as to human beings. So, it is necessary to develop an effective method for its removal from wastewater before disposing [93]. Various types of extractants/ carriers (ketoximes, organophosphorus, carboxylic acids) have been used for the removal of cadmium from the different sources. These extractants are of high cost and their long term use is not feasible. Among these the amine based extractants are comparatively low cost. Our aim is to develop low-cost amine based SLM system for the extraction of cadmium from waste water.

A variety of extractants are reported in the literature for the extraction of Cd(II) through SLM. Tripath et al. [94] have studied the cadmium extraction by SLM using organophosphoric

extractant (TOPS-99) as a carrier. It was observed that the maximum cadmium flux was obtained at pH range of 3 to 4 for 8.89 mol/m^3 cadmium ions concentration. The carrier (TOPS-99) concentration has also significant effect on the flux value and gives maximum value at 100 mol/m^3 . Cadmium ions extraction with triaurylamine dissolved in kerosene through FSSLM has been reported. The extraction of cadmium ions takes place from 0.5M chloride solution. The permeability was found to be $1 \times 10^{-6} \text{ m/s}$. The concentration of carrier influences the permeation process of cadmium ions. The carrier crystalized out at 0.2M at the surface of the membrane and thus hampered the extraction process. The effect of solvent was also studied and it was noted that triarylbenzene gives better permeability as compared to other aromatic solvents [95]. The extraction efficiencies of di-(2-ethylhexyl)-phosphoric acid (D2EHPA), 2-ethylhexylphosphonic acid, mono-2-ethylhexyl ester (PC-88A), and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) for cadmium in SLM has been reported by Parthi et al. [96]. Different parameters like, pH, concentrations of feed, strip, and carrier as well as the flow rate were studied. The best efficiency order for the carriers were found to be $\text{D2EHPA} > \text{PC-88A} > \text{Cyanex 272}$. Altin et al. [97] have employed aliquat336 carrier for the transport of cadmium ions through SLM. Toluene was used as a solvent and EDTA as a stripping reagent. Different parameters for the extraction of cadmium were optimized. M. Kazemiet al. [98] have reported the extraction and permeation of cadmium ions through SLM impregnated with mixtures of D2EHPA and M2EHPA. M. Alonso et al. [100] have investigated the extraction of the cadmium ions by using Cyanex 923 as a carrier. The kinetic study of the cadmium ions transport was also studied.

1.10 Aims and Objectives

The objectives of this study are to:

- Investigate the extraction of different metal ions (Zn(II), Hg(II), Cr(VI), Cu(II), Pb(II), and Cd(II)) by using different extractants, i.e. triethanolamine, tridodecylamine, trioctylphosphine oxide, Aliquat 336 etc.
- Study a co-ion transport mechanism for separation of metal ions.
- Find optimum conditions for the separation of metal ions.
- Determine flux at optimum conditions of extraction.
- Determine the chemical stability of supported liquid membrane.
- Study the system for the extraction of heavy metal ions from industrial effluents.

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Chapter No. 2

Experimental

Part I

Selective Removal of Zinc by using Tri-ethanolamine based Supported Liquid Membrane

2.2 Materials and Methods

2.2.1 Chemicals

The TEA (Merck, 98%) in the cyclohexanone diluent (Merck, 99%) (Darmstadt, Germany) was used without further purification. The zinc chloride (98%), HCl (A.G., 35.4%) and NaOH (A.G., 99%) were obtained from Fluka company (Darmstadt, Germany).

The membrane was micro-porous polypropylene film (Celgard 2400); with a thickness of 25 μ m, porosity 41%, and pore size of 0.043 μ m (Celgard LLC, North Carolina, USA).

2.2.2 Analytical Techniques

The atomic absorption spectrometer (Perkin Elmer model 400) (Hopkinton, USA) was used for the measurement of concentration of zinc ions. The pH measurement was carried out by a NeoMet pH meter 200L (Seoul, South Korea). The viscosity measurement of TEA in cyclohexanone was determined by Brookfield Viscometer/Rheometer LV DV-III (Middleboro, USA). The SEM analysis was carried out by using Scanning Electron Microscope model JSM-5910 JEOL (Tokyo, Japan).

2.2.3 Membrane Cell

Extraction experiments were performed at 25 $\pm$ 1 $^{\circ}$ C in the simple batch like permeator (cell). The cell was made of acrylic material having two compartments with flanges to clamp the membrane between these compartments. Each compartment had a volume capacity of 250cm³.

The effective membrane contact area was 24.64 cm². Both the compartments had electrical stirrers to agitate the liquid. The SLM cell (permeator) employed in this endeavor is shown in Fig. 1.

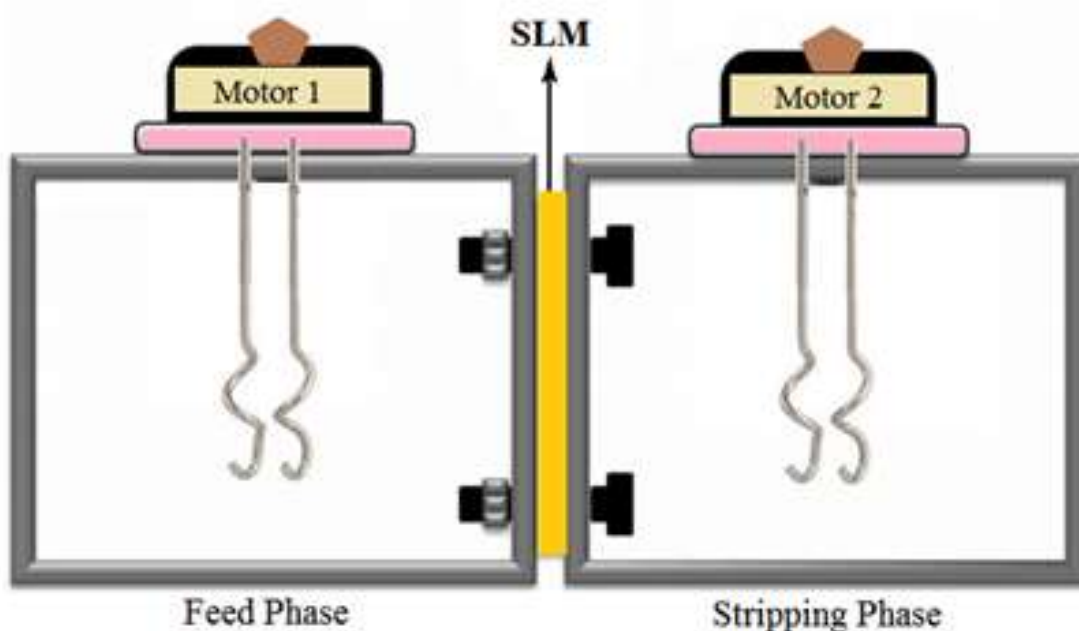


Fig. 1. Schematic presentation of liquid membrane permeator cell.

2.2.4 Procedure

The carrier TEA was dissolved in cyclohexanone to get solutions of various concentrations (10-70%). The liquid membrane was prepared by soaking the polypropylene film for 24 h in a solution that was prepared by diluting triethanolamine in cyclohexanone. For the extraction experiments, different concentrations of zinc $(9.8\text{--}19.6) \times 10^{-4} \text{ mol L}^{-1}$ and HCl (0.1, 0.5, 1, 1.5 and 2 mol L⁻¹) were used as feed solution, NaOH solutions (0.1, 0.3, 0.5, 0.7, 1 and 1.5 mol L⁻¹) were used as stripping solution in strip phase. The feed and strip compartments of the cell were filled with their respective solutions which were separated by the membrane mounted in between the two compartments. The solutions in each compartment were stirred with

an electric stirrer at a speed about 1500 rpm. This was necessary to avoid concentration polarization at the membrane faces. During the trial experiments a two winged stirrer (each wing of 1cm length) was used for stirring but it was causing disturbance and turbulence in the solution. Then the idea of such stirring was changed to rotating rod stirring process and for this purpose the wings of the stirrer were detached and only rod was used for stirring. In this way we could achieve a very smooth and non-turbulent stirring. Samples from the feed and the stripping solutions were taken after regular time intervals and analyzed by atomic absorption spectrophotometer.

2.2.5 Flux Calculation

The flux was calculated using the following equation:

Flux (J)

$$= \frac{\text{Change in the zinc ion concentration (mol } L^{-1}) \times \text{volume of solution in strip or feed (L)}}{\text{membrane area (m}^2) \times \Delta t(\text{s})}$$

Part II

The Recovery of Mercury Engaging TOPO-based Supported Liquid Membrane System

2.7 Materials and Methods

2.7.1 Chemicals and Reagents

All reagents used in this research work were of analytical grade. Aqueous solutions were prepared using double-distilled water. Mercuric chloride was obtained from Fluka (Darmstadt, Germany). Tri-octylphosphine oxide (TOPO) was procured from Sigma-Aldrich (Taufkirchen, Germany). Toluene, hydrochloric acid, and hydrazine were purchased from Merck (Darmstadt, Germany). The stock solution of mercury (II) (10 mg L^{-1}) was made by dissolving 13.54 mg of mercuric chloride, HgCl_2 , in one liter of double-distilled water. The feed phases of various initial concentrations were prepared from this stock solution by dilution method. The concentrations of HCl solutions were prepared in the same way. The receiving (or stripping) solution was aqueous hydrazine.

2.7.2 Membrane

In flat sheet supported liquid membrane, polypropylene film (Celgard 2400), was utilized as support for the organic liquid phase. The physical characteristics of this support material are: 25 μm thickness, 41% porosity and 0.043 μm mean pore diameter (Celgard LLC, North Carolina, USA).

2.7.3 Sampling Area

The effluents from four different hospitals of Peshawar, Pakistan, were taken for different interval of times and the representative sample of each area was selected and analyzed

individually. The sample was filtered in order to remove the suspended particles and subjected to SLM system without any pre-treatment.

2.7.4 Supported Liquid Membrane Cell

.It consists of two equal-volume compartments (made of acrylic sheet) connected to each other (Fig.1). The porous support was impregnated with carrier (TOPO diluted with toluene) and held between the two compartments which act as a medium for solute transport. The respective compartments were filled with 250 mL feed and strip solutions each. The solutions were continuously stirred by mechanical stirrers whose speeds (in rpm) were controlled by voltage regulators. During the process of separation, solute gets transferred through the membrane from the feed phase to the stripping phase. The effective membrane contact area was 0.0016 m^2 .

2.7.5 Analytical Techniques

A UV–Visible spectrophotometer (UV-1602) (Hopkinton, USA) was employed for the measurement of concentration of mercury ions. The detection limit of mercury ion was approximately 0.04 mg L^{-1} . A calibration curve was drawn using known concentrations of mercury within the range of $1\text{--}100 \text{ mg L}^{-1}$ (measured at wavelength of 590 nm) and the pH of solutions was monitored with a NeoMet model 200L digital pH meter (Seoul, South Korea).

2.7.6 Preparation of SLM

The micro-porous polymeric support was impregnated by immersing it in the TOPO solution in toluene for 24h. The pores of the membrane was got filled with the solution by capillary action. After impregnation, it was taken out of the solution and then allowed for a few seconds to drip down the extra solution before placing it in the permeation cell.

2.7.7 Experimental Technique

The SLM transport experiments were carried out in the permeation cell. The volumes of both feed phase and stripping phase were 250 mL each. The solutions were stirred with the speed of 1500 rpm which was essential to ensure uniformity of concentration in aqueous phases. Stirring also minimizes the concentration polarization at the membrane interface. Samples from both the aqueous phases were collected intermittently for the analysis of mercury ions.

2.7.8 Analytical Procedure

Samples were taken out from the feed and strip solutions at selected time intervals. The concentration of mercury in these samples was determined by the Rhodamine B method as follows. An aliquot of 1 cm³ Hg (II) solution was transferred to a 25mL volumetric flask. One milliliter of 10.8 mol/L H₂SO₄, followed by 1 mL of 0.15 mol L⁻¹ KI was added into the solution. After shaking for 1 min, 1 mL of 5 × 10⁻⁴ mol L⁻¹ of Rhodamine B was added to the mixture. Finally, 5 mL of 1% PVAI (polyvinyl alcohol) was mixed with a solution, diluted up to the mark and left for 10 min for stabilization. The absorbance of respective solution was measured against blank at 590 nm.

2.7.9 Flux Calculation

The flux was calculated by the following equation:

Flux (J)

$$= \frac{\text{Change in the mercury(II) ion concentration (molL}^{-1}) \times \text{volume of solution in strip of feed (L)}}{\text{membrane area (m}^2) \times \Delta t(\text{s})}$$

Part III

Removal of Chromium (VI) from Industrial Effluents through Supported Liquid Membrane using Tri-octylphosphine Oxide as a Carrier

2.8 Materials and Methods

2.8.1 Chemicals and Reagents

The trioctylphosphine oxide (TOPO; Mark, A.G., 98%) (Darmstadt, Germany) was used as extractant in toluene diluent (99%). Potassium dichromate (Fluka, A.G., 99%) (Darmstadt, Germany) and H_2O_2 (Sigma-Aldrich, A.G., 30%) solutions were used in the feed phase while Diphenylcarbazide (DPC) (Sigma-Aldrich, A.G., 98%) (Taufkirchen, Germany), and H_2SO_4 (Reidel de Haen, A.G., 99%) (Hanover, Germany) solutions were used in the strip phase. The ethylenediamine (Sigma-Aldrich, A.G., 99%) (Taufkirchen, Germany), and NaOH (Marck, A.G., 98%) (Darmstadt, Germany). were also used as receiving phase or stripping reagents. All the solutions were prepared in triply distilled water.

2.8.2 Membrane

The support for the membrane was a micro-porous polypropylene film (Celgard 2400); with thickness of 25 μm , porosity 41% and a mean pore diameter of 0.043 μm (Celgard LLC, North Carolina, USA).

2.8.3 Membrane Cell (permeator)

All ion permeation experiments were performed at $25\pm 1^\circ\text{C}$ with a simple batch type permeator (cell) shown in Fig.1. The permeator was made of acrylic material having two compartments with flanges to clamp the membrane between these compartments. Each

compartment had enough volume capacity to accommodate 250 cm³ of test solutions. The effective membrane contact area was 16.04 cm².

2.8.4 Instruments

The atomic absorption spectrometer Perkin Elmer model 400 (Hopkinton, USA) was used for determination of total metal ion concentration in the feed and strip solutions ($\lambda=357.9$ nm, $\Delta\lambda= 0.2$ nm, reducing C₂H₂/Air flame). Brookfield Viscometer/Rheometer LVDV-III was used for viscosity measurement of TOPO in toluene (Middleboro, USA).

2.8.5 Procedure

The supported liquid membranes were prepared by soaking the membrane in a solution of TOPO in toluene for 24 hours during which the pores of the membrane are got filled with carrier solution by capillary action. Afterwards the membrane was taken out of the carrier solution and allowed to drain off for 5 min to remove excess amount of carrier solution from the surface of the membrane. The cell compartments were filled with feed and stripping solutions with the membrane mounted in between the two compartments, such that the two solutions were separated from each other. The solution in each compartment was stirred with an electric stirrer at a speed of 1500 RPM to avoid concentration polarization at the membrane faces. For the permeator experiments, different concentrations of K₂Cr₂O₇ ($9.6 - 4.81 \times 10^{-4}$ mol L⁻¹) were used. Different concentrations of DPC (0.0005 - 0.004 mol L⁻¹) were used in the stripping phase.

Samples from the feed and the stripping solutions were drawn after regular time intervals and analyzed by atomic absorption spectrophotometer.

Part IV

Extraction of Copper from Wastewater through Supported Liquid Membrane using Tri-ethanolamine as a Carrier

2.9 Materials and Methods

2.9.1 Reagents

The CuCl_2 monohydrated (99.0%) was obtained from Fluka (Darmstadt, Germany). The TEA (99%) carrier, cyclo-hexanone, EDTA (99%), H_2SO_4 (99%), Oxalic acid (99%), formic acid (98%), HNO_3 (65%), and HCl (37%) were purchased from Merck Company (Darmstadt, Germany). Double distilled water was used for the preparation of solutions.

2.9.2 Membrane

The polypropylene film (Celgard 2400) was used as a solid support with thickness of $25\mu\text{m}$, porosity of 41%, and a mean pore diameter of $0.043\mu\text{m}$ (Celgard LLC, North Carolina, USA).

2.9.3 Permeator Cell

The extraction experiments were carried out in permeator cell which consists of two parts, each with 250 cm^3 volume capacities and equipped with flanges to hold the membrane between the compartments of the cell and agitated with electrical stirrers (Fig. 1). The active membrane contact area with aqueous solution was 0.0016 m^2 .

2.9.4 Instruments

The Perkin Elmer model 400 atomic absorption spectrometer (Hopkinton, USA) was used for determination of copper ion concentration in the feed and strip solutions. The

digital pH meter Neo-Met model 200L (Seoul, South Korea) was used for determination of pH. The viscosity measurement of tri-ethanolamine in cyclohexanone was carried out by Brookfield Viscometer/Rheometer LVDV-III (Middleboro, USA). The Scanning Electron Microscope model JSM-5910 JEOL (Tokyo, Japan) was used to carry out the SEM analysis.

2.9.5 Procedure

The supported liquid membrane was prepared by soaking it, in a solution of tri-ethanolamine (in varied concentrations) in cyclohexanone, for 24 hours during which the pores of the membrane are filled with carrier solution by capillary action. Afterwards the membrane was taken out of the carrier solution and allowed to drain off for 5 min to remove excess amount of carrier solution from the surface of the membrane. The membrane was tightly clamped in between the two compartments of the permeator cell, feed and strip compartments, to be filled with feed and stripping solutions respectively. The electric stirrer was used in each compartment to stir the solution at 1500 rpm to avoid polarization of concentration. In the experiments, various copper (II) ions ($0.79 - 3.97 \times 10^{-3} \text{ mol L}^{-1}$) and EDTA ($0.01 - 0.05 \text{ mol L}^{-1}$) concentrations were used as feed and strip solutions respectively. After every 60 minutes, 1mL of aliquot from the feed and the stripping solutions were withdrawn and analyzed by atomic absorption spectrophotometer.

2.9.6 Flux Calculation

The flux per unit area was determined by the following equation:

Flux(J)

$$= \frac{\text{change in the copper ion concentration in time interval } \Delta t \text{ (mol L}^{-1}\text{) } \times \text{volume of solution in feed (L)}}{\text{membrane area (m}^2\text{) } \times \Delta t \text{ (s)}}$$

2.9.7 % Extraction Efficiency

The % extraction efficiency was calculated by using following equation:

$$\% \text{ Extraction efficiency} = 100 \left(\frac{C}{C_o} \right)$$

Where C is the metal ions concentration in the strip side after the completion of extraction process, and C_o is the initial concentration of metal ions in the feed side.

Part V

Removal of Lead (II) from Battery Industry Waste Water by Supported Liquid Membrane (SLM) with Aliquat 336 as Carrier

2.10 Materials and methods

2.10.1 Chemicals and Reagents

The extractant Aliquat 336 (98%) and toluene (99%) was purchased from Merck (Darmstadt, Germany). The lead nitrate (99%), potassium iodide (99%) and sodium hydroxide (99%) were obtained from Fluka Company (Darmstadt, Germany). All the solutions were prepared in triply distilled water.

2.10.2 Membrane

The support for the membrane was a micro-porous polypropylene film (Celgard 2400); with thickness of 25 μ m, porosity 41% and a mean pore diameter of 0.043 μ m (Celgard LLC, North Carolina, USA).

2.10.3 Membrane Cell

The simple permeator (cell) was used for all the experiments. The acrylic material was used in the preparation of cell having two compartments (Fig.1). Each compartment had enough volume capacity to accommodate 250 cm³ of test solutions. The flanges were used to clutch the compartments together. The membrane contact area was 24.64 cm². The electric stirrers were placed on the top of the compartments to agitate the solutions at a speed of 1500 rpm.

2.10.4 Instruments

The metal ion concentration was determined by atomic absorption spectrometer (Perkin Elmer model 400) (Hopkinton, USA). The pH measurement was carried out by pH meter NeoMet model 200L digital (Seoul, South Korea). The viscosity measurement of Aliquat 336 in toluene was determined by Brookfield Viscometer/rheometer LV DV-III (Middleboro, USA). The SEM analysis was carried out by Scanning Electron Microscope model JSM-5910 JEOL (Tokyo, Japan).

2.10.5 Procedure

The supported liquid membrane was prepared by soaking the membrane in a solution of Aliquat 336 in toluene for 24 hours during which the pores of the membrane are got filled with carrier solution by capillary action. Afterwards the membrane was taken out of the carrier solution and allowed to drain off for 5 minutes to remove excess amount of carrier solution from the surface of the membrane. The cell compartments were filled with feed and stripping solutions with the membrane mounted in between the two compartments, such that the two solutions were separated from each other. The solution in each compartment was stirred with an electric stirrer at a speed of 1500 rpm to avoid concentration polarization at the membrane faces. For the permeator experiments, different concentrations of lead nitrate ($1.21\text{--}4.82 \times 10^{-4} \text{ mol L}^{-1}$) were used. Different concentrations of NaOH ($0.1\text{--}2 \text{ mol L}^{-1}$) were used in the stripping phase.

Samples from the feed and the stripping solutions were drawn after regular time intervals and analyzed by atomic absorption spectrophotometer.

Part VI

Facilitated Transport of Cd (II) through a Supported Liquid Membrane with Tridodecylamine as Carrier

2.11 Materials and Methods

2.11.1 Chemicals and Reagents

The tridodecylamine (TDDA, 98%) and xylene (99%) was purchased from Merck (Darmstadt, Germany). NH_3 solution (33%), $\text{CH}_3\text{COONH}_4$ (98%), NH_4NO_3 (98%) and cadmium chloride (96%) were obtained from Fluka Company (Darmstadt, Germany). The HCl (A.G., 99%) was obtained from Reidel de Haen Company (Hanover, Germany). All the solutions were prepared in triply distilled water.

2.11.2 Membrane

The support for the membrane was a micro-porous polypropylene film (Celgard 2400); with thickness of $25\mu\text{m}$, porosity 41% and a mean pore diameter of $0.043\mu\text{m}$ (Celgard LLC, North Carolina, USA).

2.11.3 Membrane Cell

The simple permeator (cell) was used for all the experiments (Fig.1). The acrylic material was used in the preparation of cell having two compartments. Each compartment had enough volume capacity to accommodate 250 cm^3 of test solutions. The flanges were used to clutch the compartments together. The membrane contact area was 15.89 cm^2 . The electric stirrers were placed on the top of the compartments to agitate the solutions at a speed of 1500 rpm.

2.11.4 Instruments

The metal ion concentration was determined by atomic absorption spectrometer (Perkin Elmer model 400) (Hopkinton, USA). The pH measurement was carried out by pH meter NeoMet model 200L digital (Seoul, South Korea). The viscosity measurement of TDDA in xylene was determined by Brookfield Viscometer/rheometer LVDV-III (Middleboro, USA). The SEM analysis was carried out by Scanning Electron Microscope model JSM-5910 JEOL (Tokyo, Japan).

2.11.5 Procedure

The supported liquid membrane was prepared by soaking the membrane in a solution of tridodecylamine in xylene for 24 hours during which the pores of the membrane are got filled with carrier solution by capillary action. Afterwards the membrane was taken out of the carrier solution and allowed to drain off for 5 minutes to remove excess amount of carrier solution from the surface of the membrane. The cell compartments were filled with feed and stripping solutions with the membrane mounted in between the two compartments, such that the two solutions were separated from each other. The solution in each compartment was stirred with an electric stirrer at a speed of 1500 rpm to avoid concentration polarization at the membrane faces. For the permeator experiments, different concentrations of cadmium chloride ($4.44 - 22.2 \times 10^{-5} \text{ mol L}^{-1}$) were used. Different concentrations of ammonia solution ($1-7 \text{ mol L}^{-1}$) were used in the stripping phase.

Samples from the feed and the stripping solutions were drawn after regular time intervals and analyzed by atomic absorption spectrophotometer.

2.11.6 Flux Calculation

The flux was calculated by using the following equation:

$$Flux (J) = \frac{\text{change in cadmium ion concentration (mol L}^{-1}\text{)} \times \text{volume of the strip or feed (L)}}{\text{membrane area (m}^2\text{)} \times \Delta t (s)}$$

Chapter No. 3

Results and Discussion

Part I

Extraction of Zinc (II)

Selective Removal of Zinc by using Tri-ethanolamine based Supported Liquid Membrane

3.2 Theory

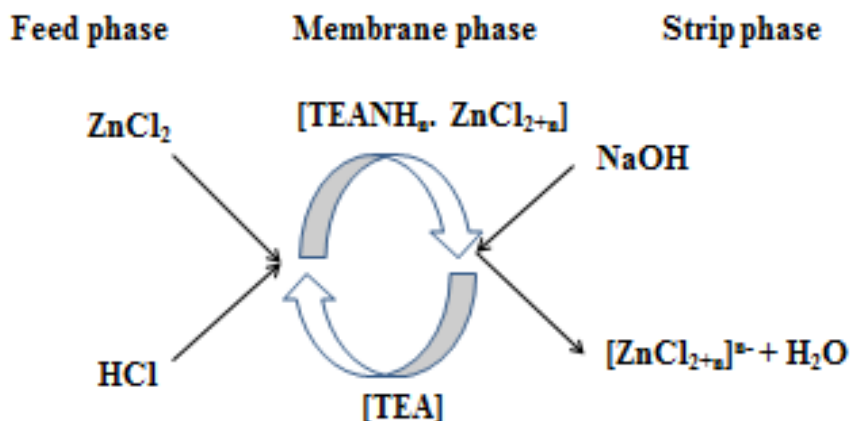


Fig. 1. Schematic representation of transport mechanism of zinc ions.

The chemistry of metal ion transfer through SLM is similar to that of liquid-liquid extraction. The extraction mechanism can be viewed as consisting of extraction by compound formation, ion-pair association, or by solvation. In the present study, the mechanism of extraction involves the ion-pair association. In this process extractant makes an ion-pair complex, which is neutral and can be permeated through a hydrophobic membrane phase. The following possibility of protonation of TEA has been reported [1] in the acidic medium



or in general form



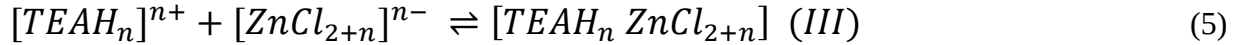
Where ‘n’ may be 1,2,3, or 4, as tri-ethanolamine molecule contains one nitrogen and three oxygen atoms, thus, maximum number of protonation is up to 4. Specie I will associate with a zinc ion in the anionic form associated with chloride.



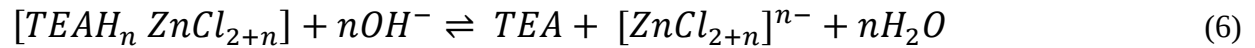
Or in general, depending upon the association number “n”



Anionic species II will associate with a cationic complex of tri-ethanolamine, specie I at the feed-membrane interface.

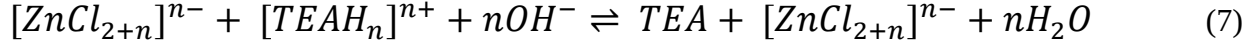


Specie III permeates through the membrane and releases zinc on the strip side at strip-membrane interface, due to reaction of protons with OH^- of the feed solution as follows:



The Zn-TEA complex is unstable in the basic medium as H^+ of the complex spontaneous reacts with OH^- ion, destroying the charge balance, equilibrium of the so-called complex, releasing thus TEA for further transport of zinc ions.

From the aforementioned discussion the overall reaction can be written as



For simplicity and specific mathematical purpose (Eq. 5) can be written as



The equilibrium constant for reaction 8 can be written as

$$K_{Zn} = \frac{[TEAH_n ZnCl_{2+n}]}{[(ZnCl_{2+n})^{n-}][TEA][H^+]^n} \quad (9)$$

If λ_{zn} denotes the distribution coefficient of zinc ions for distribution between the membrane and aqueous phases.

$$\lambda_{zn} = \frac{[TEAH_n ZnCl_{2+n}]}{[(ZnCl_{2+n})^{n-}]} \quad (10)$$

In the light of (Eq. 10), (Eq. 9) can be written as

$$K_{Zn} = \frac{\lambda_{zn}}{[TEA][H^+]^n} \quad (11)$$

On rearranging (Eq. 11), we obtain

$$\lambda_{zn} = K_{Zn}[TEA][H^+]^n \quad (12)$$

According to the Ficks First Law, the rate of diffusion $\frac{dn}{dt}$ of metal ions across an area A, known as diffusion flux and is given the symbol (J) [2].

$$J = \frac{dn}{dt} = -DA \frac{dc}{dx} \quad (13)$$

Where $\frac{dc}{dx}$ is the concentration gradient of the metal ions and dn is the amount of metal ions crossing the area A in time dt .

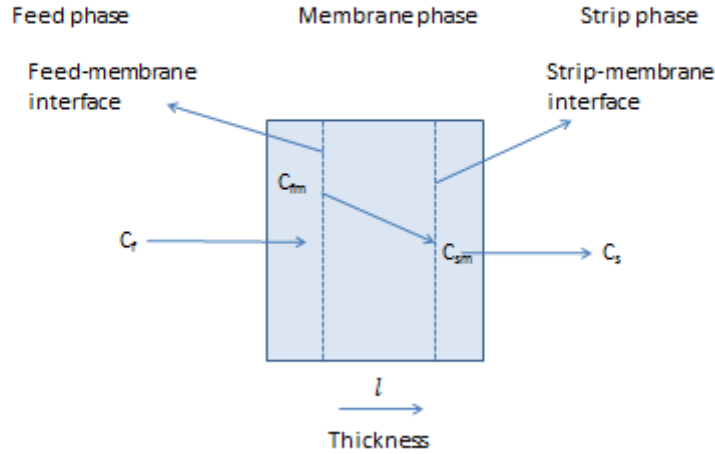


Fig. 2. Concentration gradient of zinc ions at the feed and strip sides of the membrane.

Since solutions are stirred therefore, the concentrations of metal ion in feed and strip phases, C_f and C_s respectively, are maintained at a uniform level. The two solutions are separated by a membrane of thickness ' l ', as shown schematically in Fig. 2. The membrane contains pores filled with extractant dissolved in diluent. At steady state the rate of diffusion does not change with time as long as the concentrations of metal ions at membrane interfaces of feed and strip sides, C_{fm} and C_{sm} respectively, remain constant. In order for there to be a steady state, the concentration gradient must be uniform across the membrane. In other words, the concentration within the membrane must fall linearly, as shown in Fig. 2. The concentration gradient is thus given by

$$-\frac{dc}{dx} = \frac{C_{fm} - C_{sm}}{l} \quad (14)$$

And by the Ficks First Law the rate of flow through the membrane is

$$\frac{dn}{dx} = DA \frac{C_{fm} - C_{sm}}{l} \quad (15)$$

The diffusion coefficient D is therefore, calculated from the measurement of the rate of flow; the area A , thickness l , and concentration difference $C_{fm} - C_{sm}$ are readily determined.

Where D is the diffusion coefficient. Since the distribution coefficient of Zn^{2+} ions at the membrane surface of the feed side and strip side can be given by λ_f and λ_s respectively i.e.

$$\lambda_f = \frac{C_{fm}}{C_f} \text{ and } \lambda_s = \frac{C_{sm}}{C_s} \quad (16)$$

Where C_f and C_s represent feed and strip concentration of Zn^{2+} ions respectively.

From relations (16) we obtain

$$C_{fm} = \lambda_f C_f \text{ and } C_{sm} = \lambda_s C_s \quad (17)$$

and with the help of (Eq. 17), (Eq. 15) becomes

$$J = DA \left(\frac{\lambda_f C_f - \lambda_s C_s}{l} \right) \quad (18)$$

As there is no extraction from the strip to the membrane phase, so $\lambda_s \rightarrow 0$ and as a result, $\lambda_s C_s \approx 0$ and (Eq. 18) transforms to

$$J = DA \left(\frac{\lambda_f C_f}{l} \right) \quad (19)$$

In our case $\lambda_f = \lambda_{Zn}$ as given by (Eq.12), thus (Eq.19) becomes

$$J = DA \frac{K_{Zn}[TEA] [H^+]^n [ZnCl_{2+n}]^{n-} C_f}{l} \quad (20)$$

According to Wilke- Chang relation

$$D = \frac{kT}{\eta} \quad (21)$$

Where T is the absolute temperature, η is the viscosity and k is constant and so

$$J = \frac{kT}{\eta} A \frac{K_{Zn}[TEA] [H^+]^n [ZnCl_{2+n}]^{n-} C_f}{l} \quad (22)$$

Since k , K_{Zn} , T, l and A are constants, combining all these as K (i.e. $K = kK_{Zn}T, l, A$) we obtain

$$J = \frac{K[TEA] [H^+]^n [ZnCl_{2+n}]^{n-} C_f}{\eta} \quad (23)$$

However, if C_f does not change rapidly, then C_f can be taken nearly constant for a short interval of time. Rearranging (Eq. 23)

$$J\eta = K[TEA] [H^+]^n [ZnCl_{2+n}]^{n-} C_f \quad (24)$$

Taking log of (Eq. 24)

$$\log J\eta = \log K + \log[TEA] + n \log [H^+] + \log[(ZnCl_{2+n})^{n-}] + \log C_f \quad (25)$$

Since a specially designed experiment was carried out by keeping K, TEA, $(ZnCl_{2+n})^{n-}$, C_f as constants in order to study the H^+ concentration effect on zinc ions extraction, therefore, the terms involving these parameters in (Eq.26) can be collected in a single parameter as follows:

$$B = \log k + \log TEA + \log[(ZnCl_{2+n})^{n-}] + \log C_f \quad (26)$$

Thus (Eq. 25) become

$$\log J\eta = B + n \log [H^+] \quad (27)$$

The number of H^+ ion 'n' associated with TEA in the form $[TEAH_n]^{n+}$ can be determined by Eq. 27. (Eq. 27) is a straight line equation in which $\log J\eta$ can be plotted on y axis and $\log [H^+]$ on x axis. The value of 'n' is taken from the slope of the curve which gives the number of protons associated with TEA.

3.2.1 Result and Discussion

3.2.1.1 Effect of TEA Concentration on the Extraction of Zinc

In this study, the extraction of zinc ion has been carried out through tertiary amine, triethanolamine (TEA), as a carrier. Different concentrations of TEA in cyclohexanone diluent were employed to study the extraction of zinc metal ion. The concentration range of TEA was from 10 to 70%. Samples from feed and strip phases, in a single run of the experiment, were drawn simultaneously at different interval of time and analyzed for zinc ion by AAS. In this manner seven different experiments were carried out with different concentrations of TEA as mention above. It was found that with an increase in concentration of TEA, extraction of zinc ion increases as shown in (Fig. 3a-b). It is clear from the figures that Zn^{2+} ions concentration decreases in feed while at the same time it increases in strip phase with the passage of time. It can be carefully analyzed that the concentrations of TEA in the feed phase at any particular time supplement that of in the strip phase i.e. it exhibits an additive behavior.

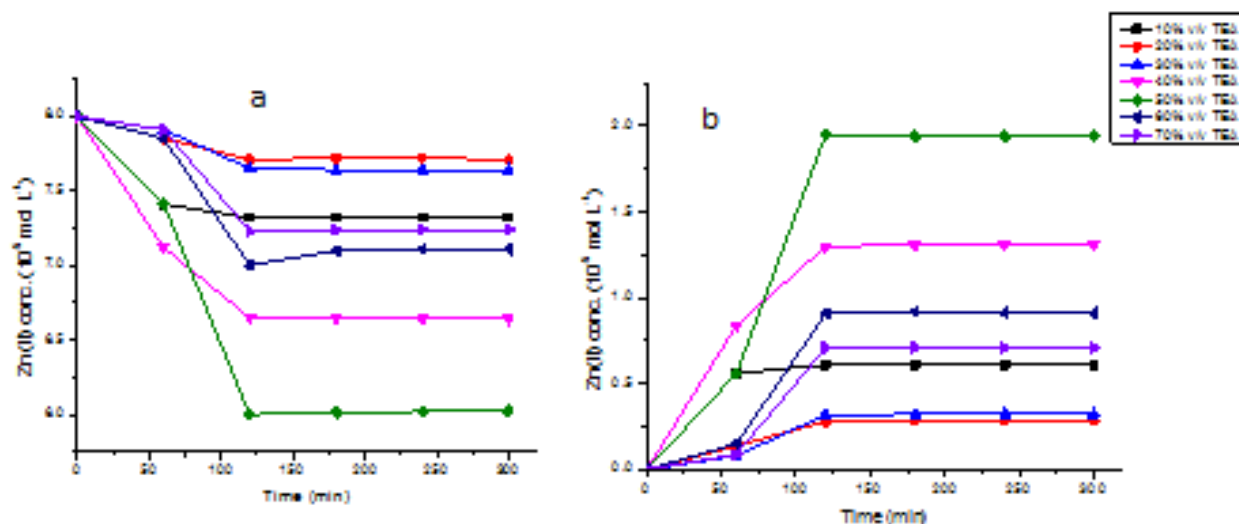


Fig. 3. Variation in Zn^{2+} ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of TEA.

($[\text{Zn}^{2+}] = 8 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NaOH}] = 1 \text{ mol L}^{-1}$, $[\text{TEA}] = 10\text{-}70\%$).

This has been shown in Fig. 4 wherein the two curves show the said additive behavior which is clear from their mirror image nature. By a careful observation, it can be analyzed that a decreasing trend in the concentration of zinc in the feed side is observed, however, the concentration goes to a minimum value at 50% TEA where after, it increases for 60 and 70% concentration which is an indication of smaller transport of zinc towards the strip side. The reason might be that the viscosity of organic phase of the membrane increases with increase in the TEA concentration (Fig. 5), which hampers the movement of complex through the membrane. This fact can conversely observe from the strip side where the concentration of zinc increases as the TEA concentration increases, reaches a maximum at 50% concentration of TEA and then decreases afterwards. So 50% TEA concentration was an optimum condition for zinc extraction.

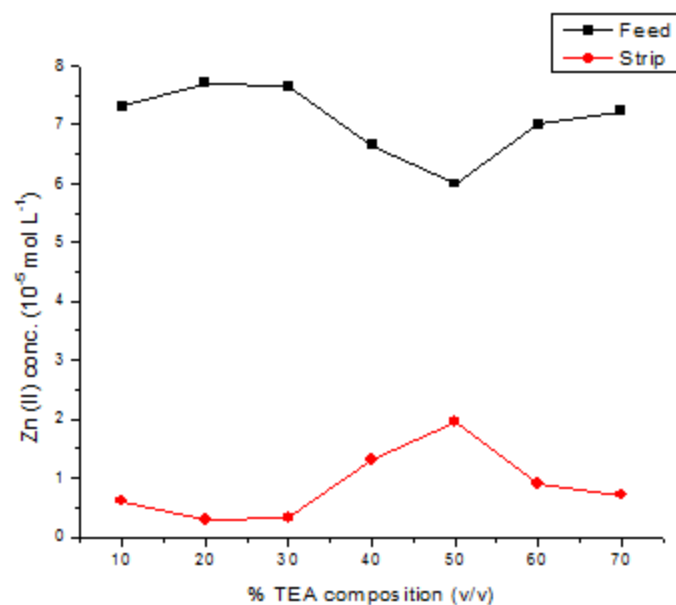


Fig. 4. Concentration of zinc ions versus TEA composition.

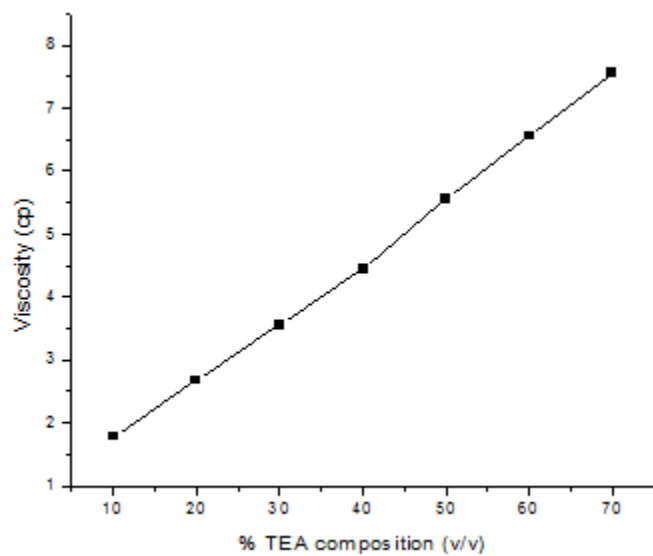


Fig. 5. Viscosity of tri-ethanolamine-cyclohexanone solutions.

3.2.1.2 Flux Study

The flux of zinc ions was calculated using (Eq. 1), and represented in Fig. 6. It can be observed that flux decreases from 10 through 20% TEA concentration and then slightly increase up to 30% and then increases rapidly and goes up to a maximum value of 50%. Where the value of flux was observed as $3.58 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$. Then there is a steep decrease from 60 and 70% TEA concentration. This decrease in flux, as mentioned earlier, is due to increase in viscosity of TEA solution which hampers the transport of zinc ions due to restricted movement of metal-TEA ion complex.

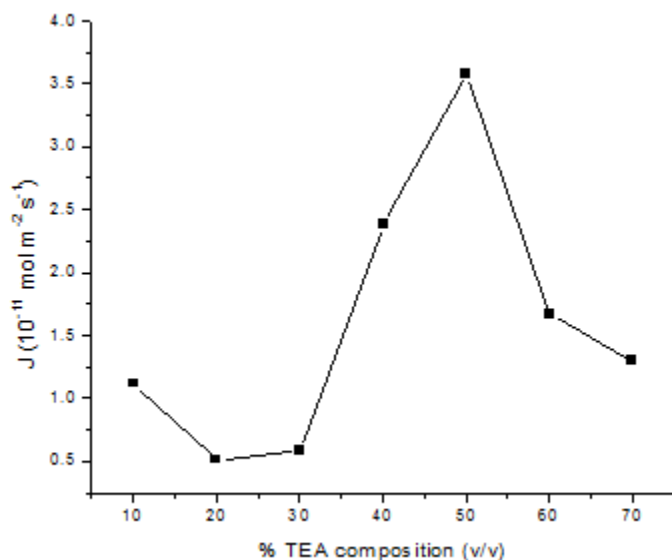


Fig. 6. Effect of TEA concentration on Flux.

($[\text{Zn}^{2+}] = 8 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NaOH}] = 1 \text{ mol L}^{-1}$, $[\text{TEA}] = 10\text{-}70\%$).

3.2.1.3 Effect of NaOH Concentration on the Extraction of Zinc

In transport of metal ions the stripping agents has an important part. They extracts the metal ions from the organic membrane phase to the stripping phase. If the metal complex is not properly stripped the membrane phase becomes saturated with the complex. Otherwise, this will adversely affect the permeation rate. In this work NaOH has been used as a strippent reagent for the extraction of zinc. The concentration range of NaOH from 0.1 mol L^{-1} to 2 mol L^{-1} has been studied.

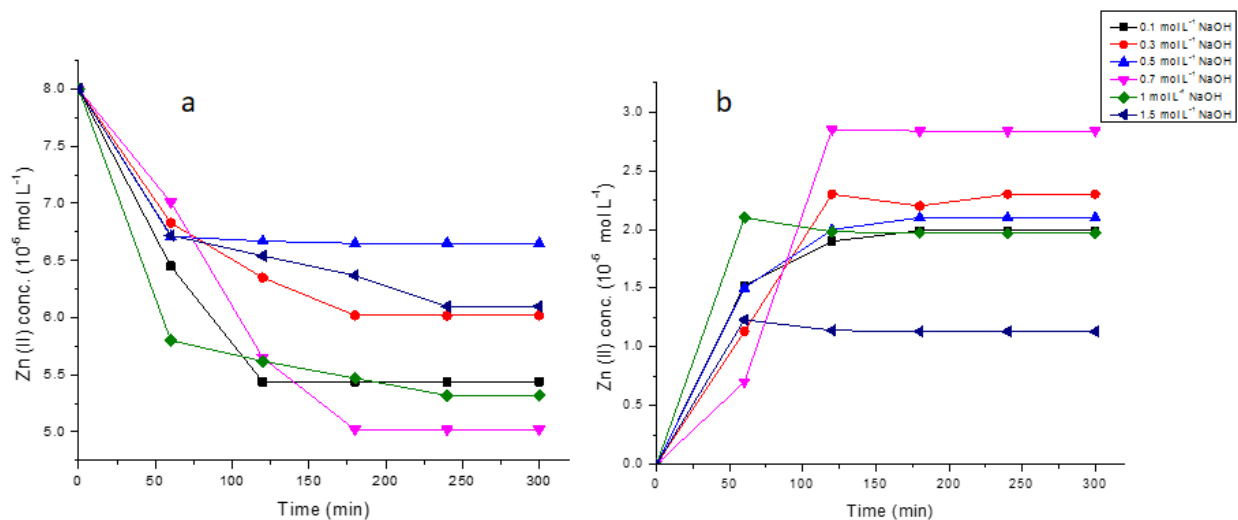
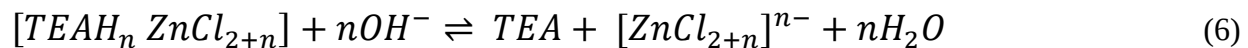


Fig. 7. Variation in Zn^{2+} ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of NaOH.

($[\text{Zn}^{2+}] = 8.0 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NaOH}] = 0.1\text{-}1.5 \text{ mol L}^{-1}$, $[\text{TEA}] = 50\%$).

Indicated in (Fig. 7a-b), as the NaOH concentration increasing the extraction as well as flux value increases with time. Consequently, maximum extraction was noted at 0.7 mol L^{-1} NaOH. On further increase in NaOH concentration, the extraction was decreased abruptly. This could be because at higher concentration of NaOH, precipitation of ZnO at strip-membrane interface may be formed due to excess amount of OH^- ions. This precipitate gets penetrated into

the membrane pores, and affects the transport of zinc due to clogging of pores [3]. Therefore, 0.7 mol L⁻¹ NaOH was an optimum condition for zinc extraction. The Zn-TEA complex immediately dissociates at the strip membrane interface and discharges Zn⁺² and Cl⁻ ions along with H⁺ ions which spontaneously react with OH⁻ to form H₂O into the strip solution.



This reaction was established by monitoring the pH value of the strip solution which was decreased, showing the consumption of the OH⁻ ions in the above reaction.

The flux value increases gradually from 0.1 to 0.5 and then become maximum at 0.7 mol L⁻¹ NaOH, where after the decreasing trend can be seen (Fig. 8) up to 1.5 mol L⁻¹ NaOH concentration.

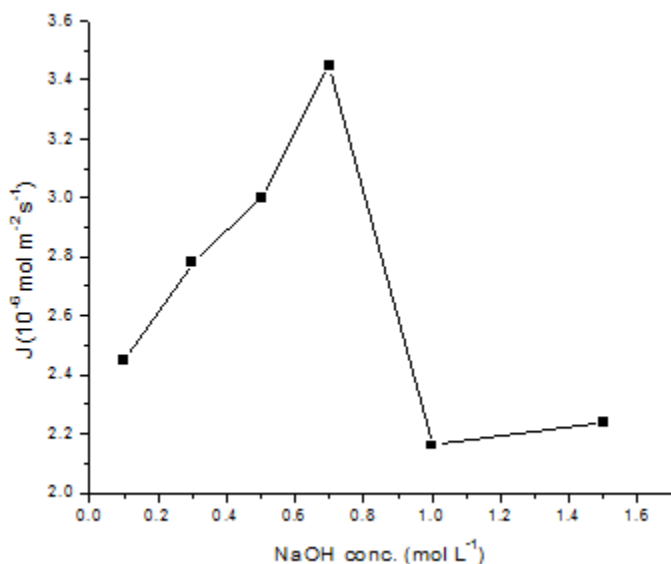


Fig. 8. Effect of NaOH concentration on flux.

([Zn²⁺] = 8.0 × 10⁻⁵ mol L⁻¹, [HCl] = 1 mol L⁻¹, [NaOH] = 0.1-1.5 mol L⁻¹, [TEA] = 50%).

3.2.1.4 SEM Analysis

The SEM images of the membrane before and after the extraction are given in Fig. 9, (a) and (b). It can be observed that before the extraction the membrane was smooth with cracks therein whose approximated length ranges from 0.2 to 6 μm and width of the crack is 0.025 μm in average. A careful examination of the SEM image after the extraction shows a material deposition on the membrane with larger dimension of the cracks. This deposition can be of ZnO which may have been deposited after a number of consistent use of the membrane [4].

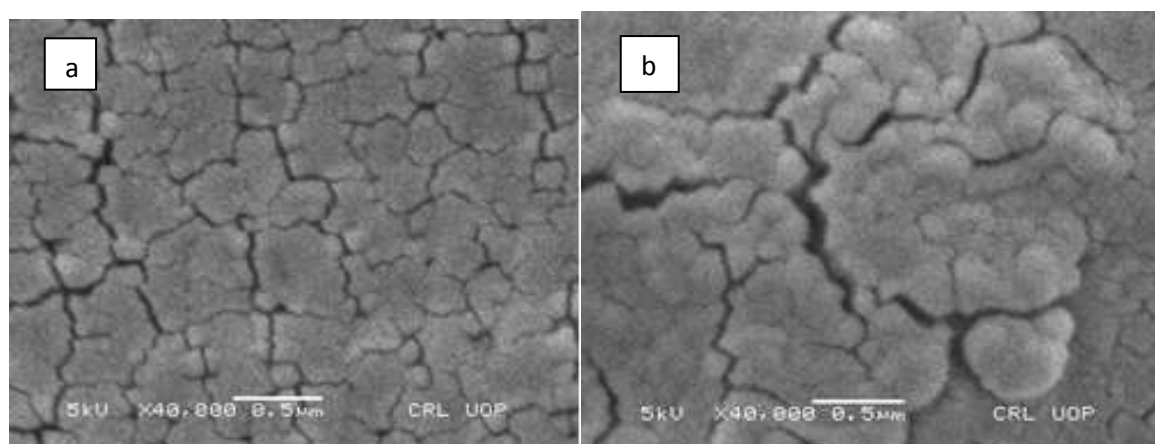


Fig. 9. SEM analysis (a) before Extraction (b)after Extraction.

3.2.1.5 Effect of HCl Concentration on the Extraction of Zinc

Fig. 10(a-b) indicates the effect of concentration of HCl, in the feed side, on transport of zinc ions. The concentration of HCl in the range of 0.1-2mol L⁻¹ was studied by keeping the TEA concentration at 50% in cyclohexanone and NaOH at 0.7 mol L⁻¹ in stripping phase. It was noted that the transport of zinc ion increases with the increase in concentration of HCl, it reaches at its maximum value at 1M HCl where after the extraction decreases. The extraction efficiency was effected by the Cl⁻/Zn²⁺ ratio: fewer amounts of Cl⁻ results in the formation of ZnCl⁺ while

excess of Cl^- leads to the formation of ZnCl_3^- or ZnCl_4^{2-} [3]. At very high concentration common ion effect causes the reaction to go in reverse direction and inhibits the formation of Zn-TEA complex. So, 1 mol L^{-1} HCl concentration was an optimum condition for the extraction of zinc ions.

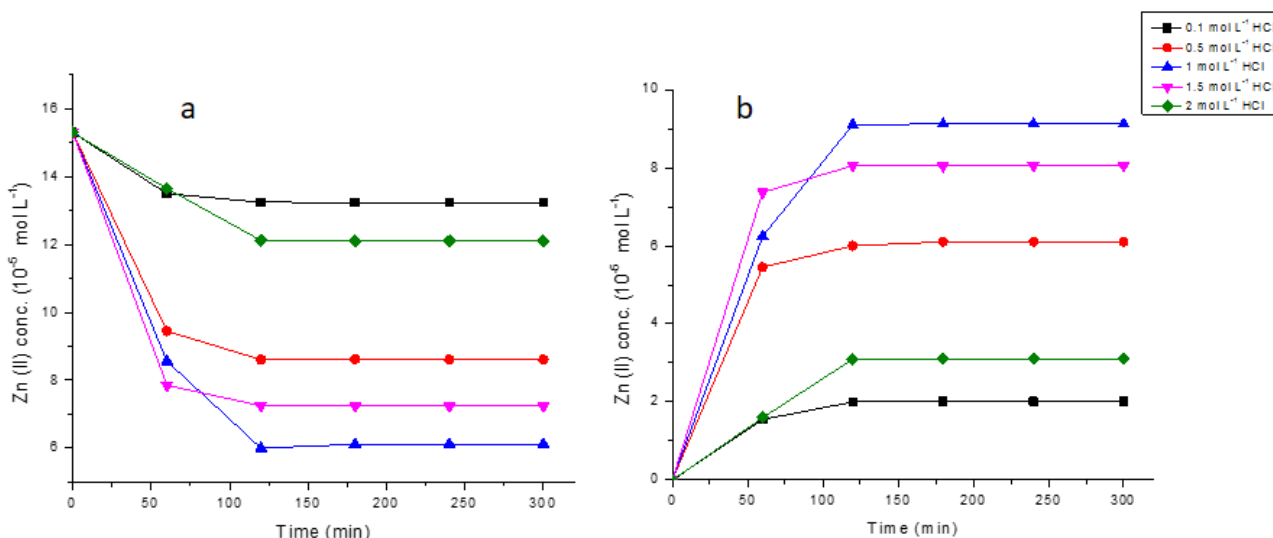


Fig. 10. Variation in Zn^{2+} ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of HCl.

($[\text{Zn}^{2+}] = 15.3 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 0.1\text{--}2 \text{ mol L}^{-1}$, $[\text{NaOH}] = 0.7 \text{ mol L}^{-1}$, $[\text{TEA}] = 50\%$).

The (Fig. 11) shows the pH change of the feed solution with time during a single extraction experiment. The increase in pH is slow at the beginning and rises almost steeply between the 90th and 120th minutes of the experiment. Initially the carrier (TEA) molecules were utilized by the protons of HCl in feed solution to convert it into a charged species by protonation at the feed membrane interface. Further increase in pH may be attributed to the transport of H^+ ion from the feed to the membrane phase and ultimately to the strip phase.

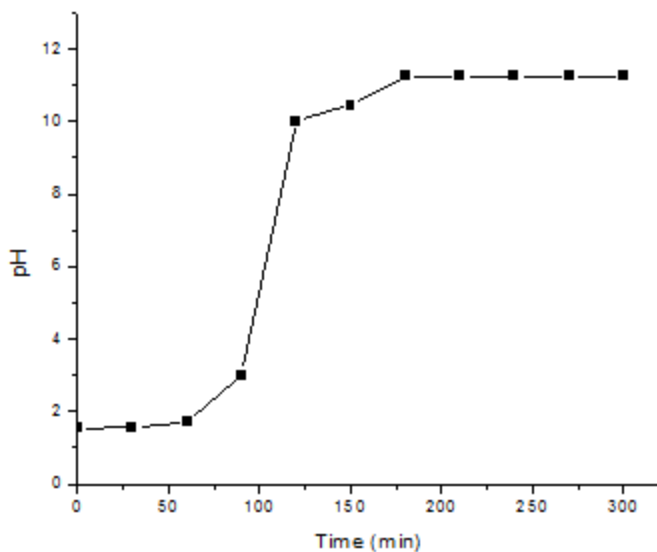


Fig. 11. Variation in pH of feed solution with time.

($[\text{Zn}^{2+}] = 15.3 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 0.1\text{-}2 \text{ mol L}^{-1}$, $[\text{NaOH}] = 0.7 \text{ mol L}^{-1}$, $[\text{TEA}] = 50\%$).

Fig. 12 reveals the flux of Zn^{2+} with the concentration of HCl. The flux increases as the HCl concentration increases and goes to a maximum at 1 mol L^{-1} HCl and then it decreases. The highest flux value of $3.20 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ was noticed at 1 mol L^{-1} HCl. The decrease in the flux beyond 1 mol L^{-1} HCl is due to the excess amount of H^{+} concentration which suppresses the extraction in forward direction.

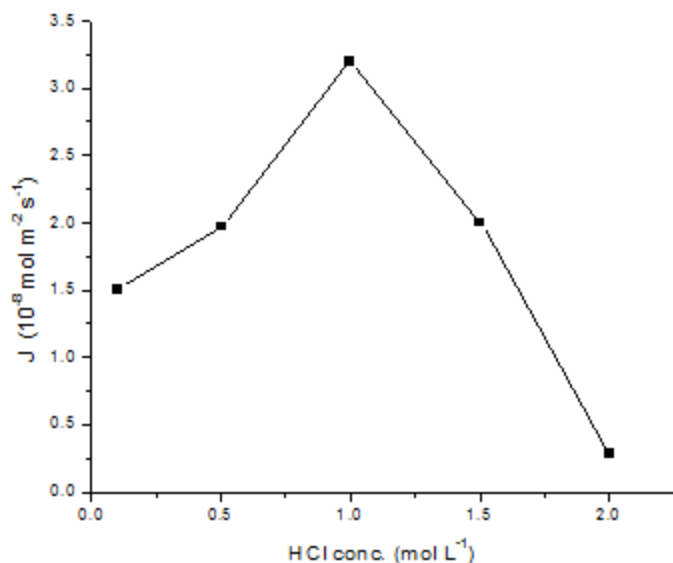


Fig. 12. Effect of HCl concentration on flux.

($[Zn^{2+}] = 15.3 \times 10^{-5} \text{ mol L}^{-1}$, $[HCl] = 0.1-2 \text{ mol L}^{-1}$, $[NaOH] = 0.7 \text{ mol L}^{-1}$, $[TEA] = 50\%$).

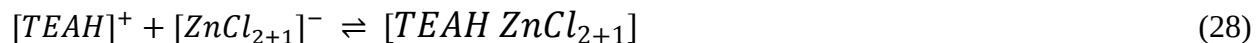
3.2.1.6 Determination of 'n'

The number of H^+ ion 'n' associated with TEA in the form of $[TEAH_n]^{n+}$ can be determined by using (Eq.27) which is a straight line equation where $\log J\eta$ can be plotted on y axis and $\log [H^+]$ on x axis. The slope of this curve will give 'n' which gives the number of protons associated with TEA.

$$\log J\eta = B + n \log [H^+] \quad (27)$$

Fig.13 shows $\log J\eta$ versus $\log [H^+]$. The first three values of the data from Fig. 12 were taken from this plot because these were showing an increasing trend in the flux with increase in concentration of H^+ ions. The slope of the curve is showing a value of 1.098 which can be safely taken as 1. Thus, the complex $[TEAH_n]^{n+}$ can be assumed to be like $[TEAH]^+$ and analogously by intuition we can say that the zinc-chloride anionic complex has the form $[ZnCl_{2+1}]^-$. The

zinc-TEA complex, thus acquire the form $[TEAH_n ZnCl_{2+n}]$. Thus, in the light of the aforementioned discussion (Eq. 5) can be written as



Thus, (Eq. 28) predicts the stoichiometry of the complex.

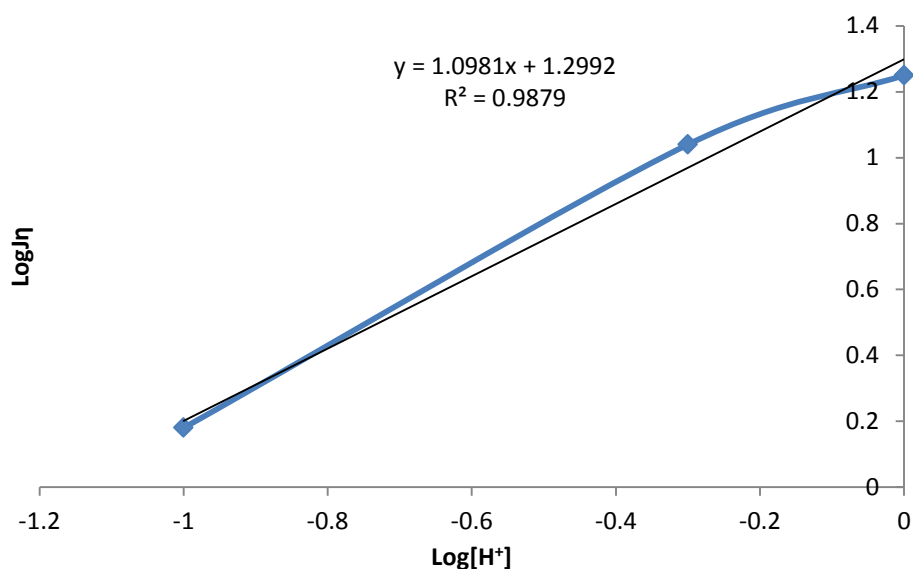


Fig. 13. Plot of $\log J\eta$ versus $\log [H^+]$.

3.2.1.7 Effect of Zinc metal Concentration on the Extraction of Zinc

In order to investigate the effect of zinc ion concentration on the extraction, 0.77 to 3.84×10^{-4} mol L⁻¹ of zinc ions concentration were employed. During this study the other parameters such as, concentration of HCl in feed solution, NaOH in stripping solution, and TEA in membrane phase were kept at optimum levels i.e 1 mol L⁻¹, 0.7 mol L⁻¹, and 50% respectively. Fig. 14a-b shows the change in the concentration of zinc ions with respect to time in the feed and strip phases respectively. It can be noted from Fig. 14a that maximum extraction was obtained with a zinc concentration of 2.30×10^{-4} mol L⁻¹. A decrease in the extraction can be

observed from the same figure by further increases in zinc ion concentration. This might be attributed to the following reason: as the metal ions concentration increases, the requirement of HCl, to make zinc-chloride complex, also increases, whereas we have kept HCl concentration at a constant level which is insufficient to cater for the zinc-chloride complex [5].

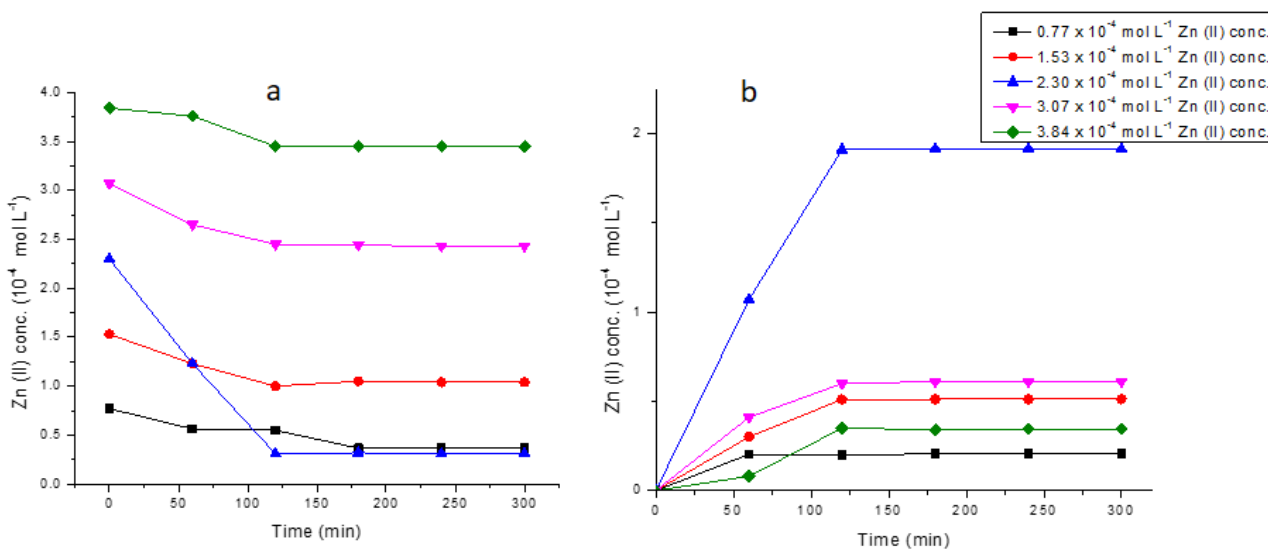


Fig. 14. Variation in Zn^{2+} ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of zinc metal solution.

($[\text{Zn}^{2+}] = 0.77\text{--}3.84 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NaOH}] = 0.7 \text{ mol L}^{-1}$, $[\text{TEA}] = 50\%$).

The flux was also maximum at this concentration and gives the value of $3.51 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$ as shown in (Fig. 15). There was a decrease in the flux beyond the aforementioned concentration of zinc ion due to the reason mentioned above.

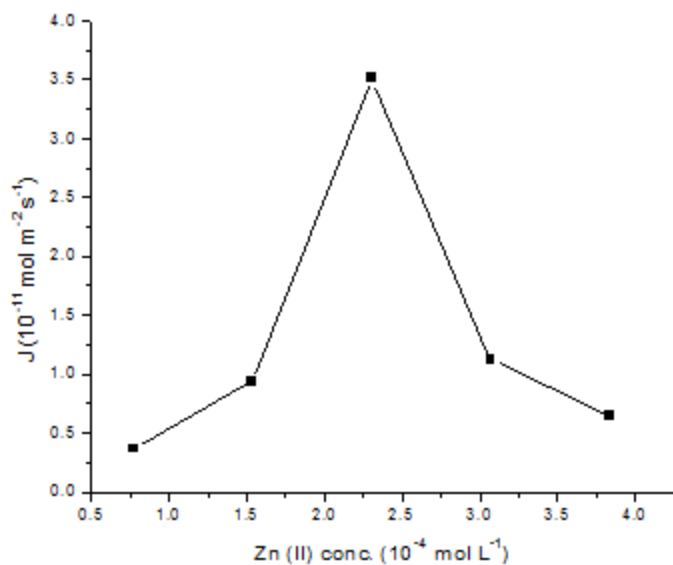


Fig. 15. Effect of Zn^{2+} ion concentration on Flux.

($[\text{Zn}^{2+}] = 0.77\text{--}3.84 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NaOH}] = 0.7 \text{ mol L}^{-1}$, $[\text{TEA}] = 50\%$).

3.2.1.8 Extraction Time

Fig. 16 shows the extraction of zinc against time at optimum conditions of the extraction of zinc ion. It can be noted that the extraction reaches to its maximum level (87%) at 120th minutes where after there is no increases in extraction and it remains constant as indicated by Fig. 16.

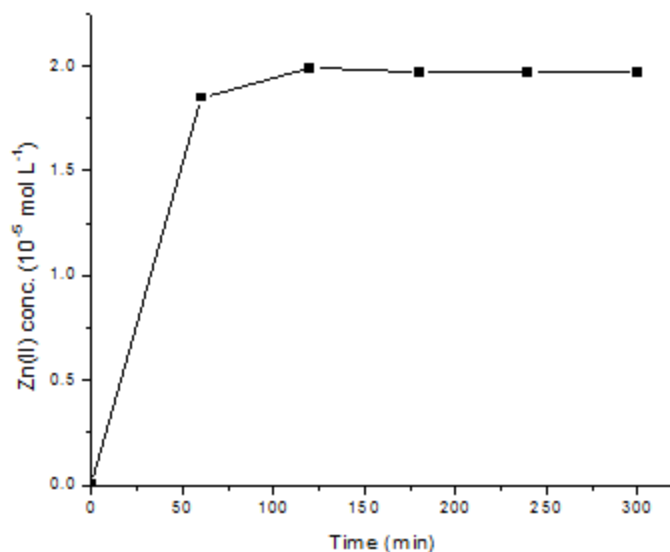


Fig. 16. Variation in Zn^{2+} ion concentration with time in strip phase.

($[\text{Zn}^{2+}] = 2.30 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$ in feed phase, $[\text{NaOH}] = 0.7 \text{ mol L}^{-1}$ in strip phase, $[\text{TEA}] = 50\%$ membrane phase).

3.2.1.9 Membrane Stability

The stability of TEA based SLM was studied for 10 days by carrying out 10 independent extraction experiments at optimum conditions for extraction. These optimum conditions were, in the feed zinc ion concentration at $2.30 \times 10^{-4} \text{ mol L}^{-1}$, 1 mol L^{-1} HCl, 50% TEA concentration in cyclohexanone, 0.7 mol L^{-1} concentration of NaOH in stripping phase, and at the stirring speed of 1500 rpm. Each experiment was of 5 hours duration using the same membrane impregnated only once, while fresh solutions were added into the feed and strip compartments for every experiment. As seen in Fig. 17 that the extraction was not affected and remained at 87% during all the experiments. This shows that despite all deteriorating factors of membrane, what so ever, the efficiency has not decreased during these experiments.

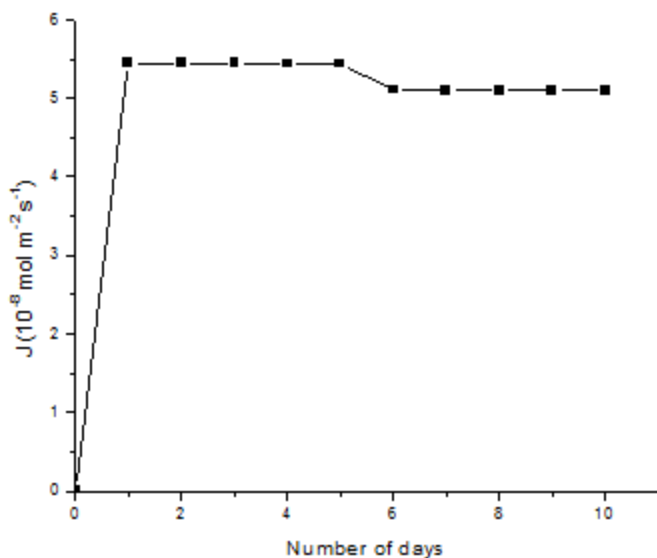


Fig. 17. Flux versus time for stability study of SLM.

($[\text{Zn}^{2+}] = 2.30 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NaOH}] = 0.7 \text{ mol L}^{-1}$, $[\text{TEA}] = 50\%$).

3.1.1.10 Extraction of Zn (II) ion from Dry Battery Waste

Zinc is largely use in the zinc-carbon dry battery [6]. The optimized conditions were then applied for the recovery of zinc from discharged zinc-carbon dry battery. At room temperature the carbon black powder from inside the zinc-carbon dry battery (heavy duty 1.5V, size D), was digested in acid for 4 hours, and filtered through filter paper (Whatman®-41) to remove the residue (carbon powder). This solution was analyzed for zinc, cobalt, nickel and manganese ions by AAS. However, only zinc and manganese ions were found to be present in the solution. The filtrate (80 mL) was diluted with distilled water up to 250 mL and analyzed by AAS before subjecting the sample for extraction. The extraction was carried out at the optimum experimental conditions as described earlier. The study shows that almost 87% zinc ions were recovered (Fig. 18), however, no Mn ions were detected in the strip phase, showing selective behavior of TEA for zinc ions (Table 1).

Table 1 Analysis of Dry Battery Waste Solution

S No	Metal ion	Concentration of metal ions (mol L^{-1})		% Recovery
		B.E (Feed)	A.E (Strip)	
1	Zn	2.68×10^{-3}	2.34×10^{-3}	87
2	Co	0.00	0.00	-
3	Ni	0.00	0.00	-
4	Mn	7.28×10^{-3}	0.00	-

B.E = before extraction

A.E = after extraction

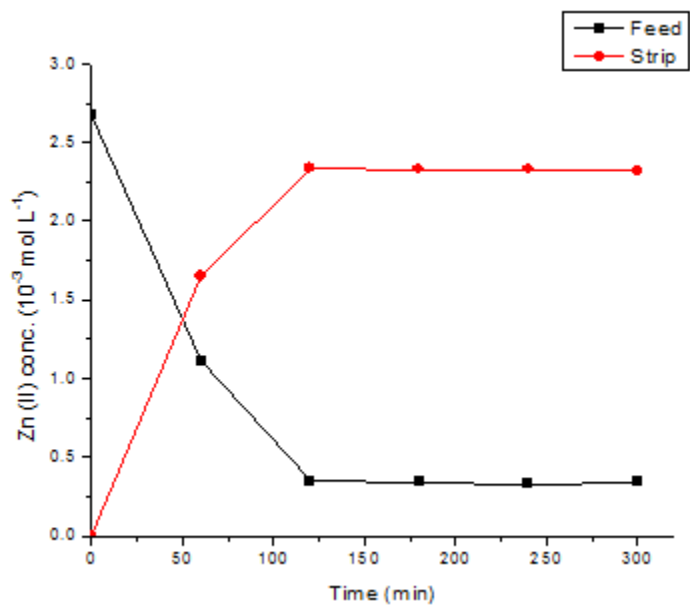


Fig. 18. Variation in Zn^{2+} ion concentration in the feed and strip solution versus time (Dry battery waste solution).

($[\text{Zn}^{2+}] = 2.68 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NaOH}] = 0.7 \text{ mol L}^{-1}$, $[\text{TEA}] = 50\%$).

Conclusion

In the present work, SLM, containing Celgard 2400 as a support, TEA as carrier and cyclohexanone as solvent, in the separation of zinc (II) from their aqueous acidic solution has been investigated. The influence of various parameters on the transport of zinc (II) has been studied to optimize the process. The maximum extraction was obtained at 50% TEA concentration with a flux value of $3.58 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$. In feed phase $2.30 \times 10^{-4} \text{ mol L}^{-1}$ of zinc ions and 1 mol L^{-1} HCl were the optimum conditions for the extraction of zinc ions. The maximum flux value of $3.51 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$ was noticed at $2.30 \times 10^{-4} \text{ mol L}^{-1}$ of zinc ion concentration while $3.20 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ of flux was observed at 1 mol L^{-1} HCl. While in case of strip phase, the 0.7 mol L^{-1} NaOH concentration gives the highest value of flux, i.e. $5.23 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$. Under these optimum conditions, the maximum extraction of zinc ions was achieved and gives 87% of extraction efficiency. The Extraction time for zinc ion transport has been studied. The maximum extraction was found at 120 minutes. The stoichiometry of Zn-TEA complex $[\text{TEAH ZnCl}_{2+1}]$ was evaluated through equilibrium slope method and it was found that 1:1 mole ratio of TEA and H^+ ion was involved in the complex formation. The stability of SLM under optimum conditions was investigated and it was concluded that the membrane was stable for up to 10 extraction experiments. This SLM was applied to recover Zn (II) from the dry battery waste water and about 87% zinc ions were extracted. The whole study was replicated thrice with relative standard deviation of ± 2 .

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Part II

Extraction of Mercury (II)

The Recovery of Mercury engaging Tri-octylphosphine oxide-based Supported Liquid Membrane System

3.3 Transport Mechanism

The feed phase includes mercury chloride and hydrochloric acid while membrane phase consists of TOPO diluted with toluene and strip phase contains aqueous solution of hydrazine. The HCl plays a vital role in extraction by forming a mercury-chloro complex as given by equations 1b, 2a below. Kherfan et al. have reported an enhanced extraction of cadmium using HCl in feed phase along with the TOPO as a carrier [1]. TOPO has a major use in metal extraction due to high polarity. TOPO binds with metal ion due to its high polarity which is a result of dipolar phosphorus-oxygen bond. The octyl group of TOPO renders it soluble in low polar solvent such as kerosene, toluene, etc [2]. Ghazy et al. have used hydrazine derivatives for mercury extraction [3]. Facon et al. have used thiourea-hydrazine-sodium hydroxide as a stripping agent for metal extractant [4].

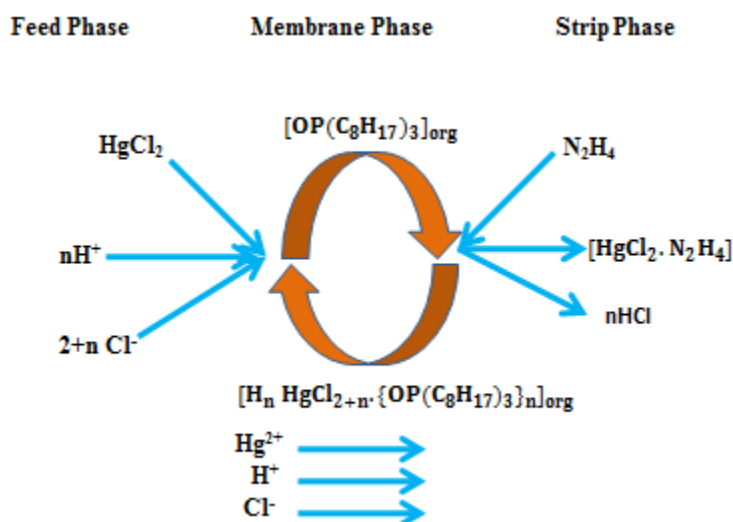
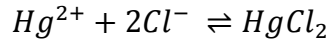


Fig.1. Transport mechanism of Hg(II)ions through supported liquid membrane.

In the extraction process, the solute from the feed phase reacts with carrier to form a complex inside the pores of the support membrane at feed-membrane interface. Due to the concentration gradient, the complex diffuses through the membrane and enters into the stripping phase at strip-membrane interface as shown in Fig.1.

The reaction on the feed side may be given as follows

The reaction of HCl with $HgCl_2$ in aqueous solution results in the formation of complex $[HgCl_{2+n}]^{n-}$ as follows [5].

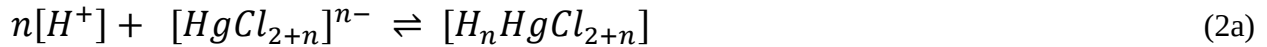


The number of chloride ions attached with $HgCl_2$ cannot be predicted at this stage; therefore, we assume 'n' the chloride ions attached with $HgCl_2$ as follows

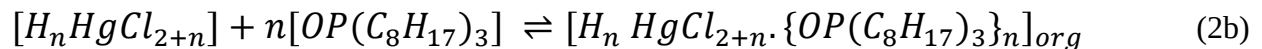


where 'n' can be determined experimentally

$[HgCl_{2+n}]^{n-}$ combines with H^+ to form an acid complex $[H_nHgCl_{2+n}]$ as follows

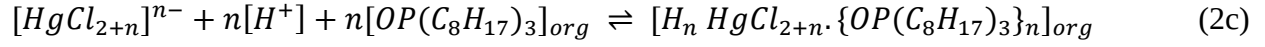


This complex moves towards the feed- membrane interface to react with the carrier molecule, $OP(C_8H_{17})_3$ (Trioctylphosphine oxide, TOPO) [6], at the membrane interface with the following equilibrium reaction:



Where the subscript org denotes the presence of specie in the organic phase.

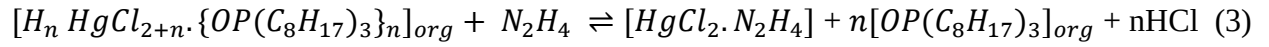
The overall reaction at the feed-membrane interface is as follows:



The transport of $Hg(II)$ ions through SLM, therefore, is supposed to be follows the coupled co-ion transport mechanism in which both H^+ and complex $[HgCl_{2+n}]^{n-}$ are moving towards the stripping phase across the membrane phase.

The reaction on the strip side may be given as follows

The complex $[H_n HgCl_{2+n} \cdot \{OP(C_8H_{17})_3\}_n]_{org}$ is unstable, which immediately dissociates at the strip-membrane interface releasing mercury ions. The $Hg(II)$ ions form complex with hydrazine (N_2H_4) in the stripping phase as follows [7].



3.2.1 Theory

The extraction constant for $Hg(II)$ ion in the feed side is given by K_{Hg} :

$$K_{Hg} = \frac{[H_n HgCl_{2+n} \cdot \{OP(C_8H_{17})_3\}_n]_{org}}{[HgCl_{2+n}]^{n-} [H^+]^n [OP(C_8H_{17})_3]^n} \quad (4)$$

The distribution coefficient of $Hg(II)$ ion, λ_{Hg} , is shown by the following equation:

$$\lambda_{Hg} = \frac{[H_n HgCl_{2+n} \cdot nOP(C_8H_{17})_3]_{org}}{[HgCl_{2+n}]^{n-}]_{aq}} \quad (5)$$

By inserting the value of distribution constant in Eq. (4)

$$K_{Hg} = \frac{\lambda_{Hg}}{[H^+]^n [OP(C_8H_{17})_3]^n} \quad (6a)$$

On rearranging Eq. (6a) we obtain

$$\lambda_{Hg} = K_{Hg} [H^+]^n [OP(C_8H_{17})_3]^n \quad (6b)$$

According to Fick's First Law, the rate of diffusion dn/dt of metal ions across an area A is known as diffusion flux (J) and it is given as follows [5,8].

$$J = \frac{dn}{dt} = -DA \frac{dc}{dx} \quad (7)$$

Where D is the diffusion coefficient, A is the area of the membrane, $\frac{dc}{dx}$ is rate of change of concentration across the membrane per unit distance or thickness of the film x in time dt .

If the distribution constants of metal ion between membrane and aqueous phases at the membrane interfaces of the feed and strip side are λ_f and λ_s , respectively, then:

$$\lambda_f = \frac{C_{mf}}{C_f} \quad (8)$$

$$\lambda_s = \frac{C_{ms}}{C_s} \quad (9)$$

Where C_m is the metal ions concentration in the membrane phase and C is the concentration of the same ion in aqueous phase, f and s denote the feed and strip phases, respectively.

Considering Fig.2 and Fick's First Law, the concentration gradient, dc/dx (or simply $\Delta c/\Delta x$) is negative as Δc is equal to $C_{mf} - C_{ms}$ which is positive since $C_{mf} > C_{ms}$, whereas Δx

is negative as x varies from 0 to x . Since the final value of x is higher than the initial value, i.e. $0 - x = -x$.

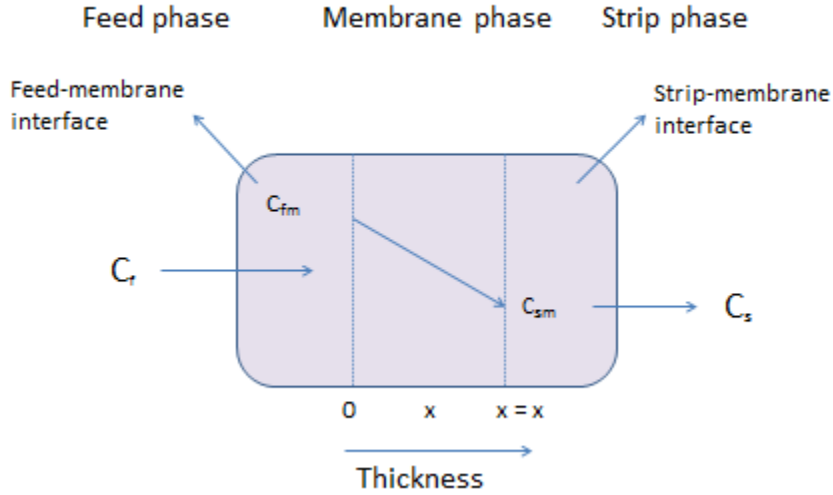


Fig. 2. Concentration gradient of mercury ions at the feed and strip sides of the membrane.

Thus

$$-\frac{dc}{dx} = \frac{\Delta c}{\Delta x} = -\frac{C_{mf} - C_{ms}}{x} \quad (10)$$

By the Fick's First Law, the rate of flow through membrane is

$$\frac{dn}{dx} = DA \frac{C_{mf} - C_{ms}}{x} \quad (11)$$

The diffusion coefficient D is therefore, calculated from the measurement of the rate of flow; the area A , thickness x , and concentration difference $C_{mf} - C_{ms}$ are readily determined.

From Eq. (8) and (9) we obtain

$$C_{mf} = \lambda_f C_f \quad (12)$$

and

$$C_{ms} = \lambda_s C_s \quad (13)$$

In the light of Eq. (12) and (13), Eq. (11), changes to:

$$J = DA \frac{(\lambda_f C_f - \lambda_s C_s)}{x} \quad (14)$$

As there is no extraction from the stripping phase to membrane phase, λ_s is taken as 0 and Eq. (14) reduces to

$$J = DA \frac{(\lambda_f C_f)}{x} \quad (15)$$

And we can consider $\lambda_f = \lambda_{Hg}$, and $C_f = C_{Hg}$ where λ_{Hg} is given by Eq.(6b), therefore Eq.(15) can be written as

$$J = DA \frac{(K_{Hg}[H^+]^n[OP(C_8H_{17})_3]^n C_{Hg})}{x} \quad (16)$$

According to Wilke- Chang relation

$$D = \frac{kT}{\eta} \quad (17)$$

Where T is the absolute temperature, η is the viscosity TOPO solution in toluene and k is constant and so

$$J = \frac{kT}{\eta} A \frac{(K_{Hg}[H^+]^n[OP(C_8H_{17})_3]^n C_{Hg})}{x} \quad (18)$$

Since k , K_{Hg} , T , x and A are constants, moreover, Since flux is concentration dependant, any measurement of flux must be made at a particular constant concentration of the feed, therefore, we consider C_{Hg} in Eq.(18) as constant, combining all these as K i.e.

$$K = \frac{k K_{Hg} T A C_{Hg}}{x} \quad (19)$$

Thus Eq.(18) reduces to

$$J = K \frac{[H^+]^n [OP(C_8H_{17})_3]^n}{\eta} \quad (20)$$

On rearranging Eq.(20) we obtain,

$$J\eta = K[H^+]^n [OP(C_8H_{17})_3]^n \quad (21)$$

Taking log of Eq. (21)

$$\log J\eta = \log K + n \log [H^+] + n \log [OP(C_8H_{17})_3] \quad (22)$$

Since in a specially designed experiment the concentration of TOPO, $OP(C_8H_{17})_3$ was kept constant, thus Eq.(22) reduces to

$$\log J\eta = B + n \log [H^+] \quad (23)$$

Here B includes all the constants as mentioned earlier including $\log K$ and $[OP(C_8H_{17})_3]$.

The number, 'n' of TOPO molecules in the complex $H_n HgCl_{2+n} \cdot \{OP(C_8H_{17})_3\}_n$ can be determined by using the Eq. (23). Eq. (23) is a straight line equation in which $\log J\eta$ can be plotted on y axis and $\log [H^+]$ on x axis. The slope of this curve will give 'n'.

3.2.4 Result and Discussion

3.2.4.1 Effect of HCl Concentration in Feed phase on Extraction of Mercury

In the extraction of Hg^{2+} , HCl plays an important role by not only providing H^+ and Cl^- for the formation of $H_n\text{HgCl}_{2+n}$ and $H_n\text{HgCl}_{2+n}\cdot\{\text{OP}(\text{C}_8\text{H}_{17})_3\}_n$ for the transport of Hg^{2+} ions from the feed phase to stripping phase through a membrane phase. Moreover, Hg^{2+} ions are made soluble by these complexes in the organic membrane phase to diffuse through it for entering into the aqueous stripping solution [9].

The concentration range studied for HCl in feed solution was 0.1-2 mol L^{-1} (Fig. 3a) while the concentrations of TOPO at 0.05 mol L^{-1} in toluene and N_2H_4 at 0.03 mol L^{-1} in stripping phase were kept constant (Fig. 3b) and the results are given in Table 1. Fig. 3 exhibits a decrease in the mercury ions concentration in the feed solution (Fig.3a) while for the same concentration of the HCl corresponding curve shows an increase in the mercury ions concentration in the strip phase with the passage of time (Fig.3b). Moreover, as can be observed from Fig. 3b, that the extraction increases as the HCl, concentration increase up to 1mol L^{-1} HCl while it decreases thereafter. The decrease in the extraction is due to the excess amount of H^+ ions which suppresses the extraction. The $\text{Cl}^-/\text{Hg}^{2+}$ ratio may have a significant effect on extraction efficiency; fewer Cl^- ions result in the formation of HgCl^+ while excess leads to the production of HgCl^{3-} or HgCl_4^{2-} [10]. At very high concentrations, common ion effect steers the reaction in the reverse direction and inhibits the formation of Hg-TOPO complex. Thus, 1mol L^{-1} HCl concentration is optimum for the extraction of mercury ions.

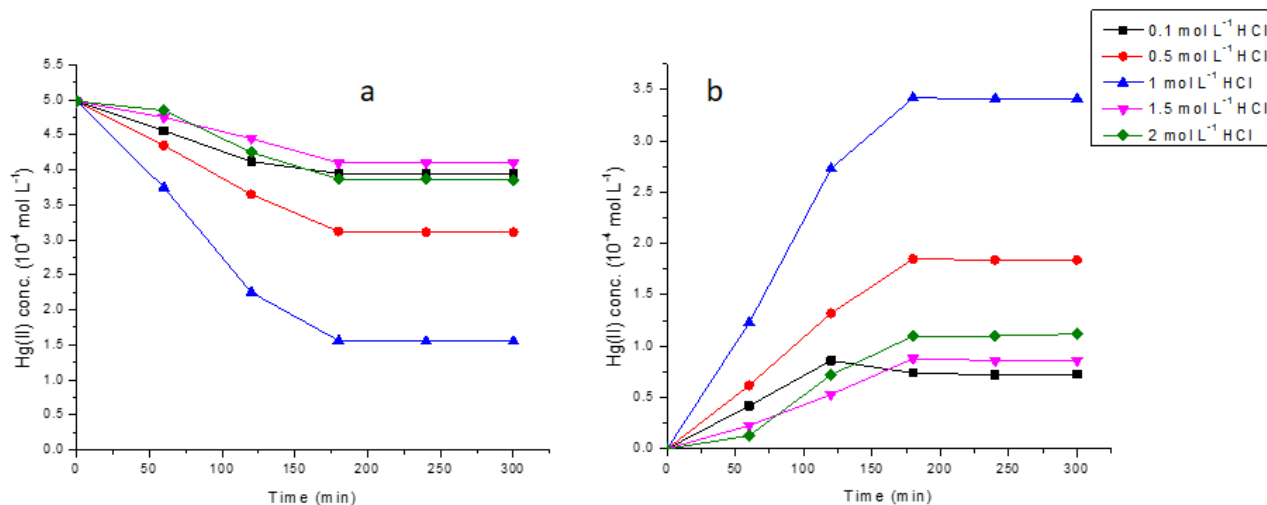


Fig. 3. Variation in Hg (II) ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of HCl.

(Initial $[\text{Hg}^{2+}] = 4.98 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 0.1\text{--}2 \text{ mol L}^{-1}$, $[\text{N}_2\text{H}_4] = 0.03 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.05 \text{ mol L}^{-1}$).

The flux of Hg (II) is directly proportional to the $[\text{H}^+]$ as indicated by Eq. 23 and shown in Fig. 4 and Table 2. The value of flux increases as the HCl concentration increases and reaches to a maximum value at 1 mol L^{-1} HCl and then decreases thereafter. This trend is consistent with the variation in the extraction with concentration of the HCl as discussed earlier in the preceding paragraphs.

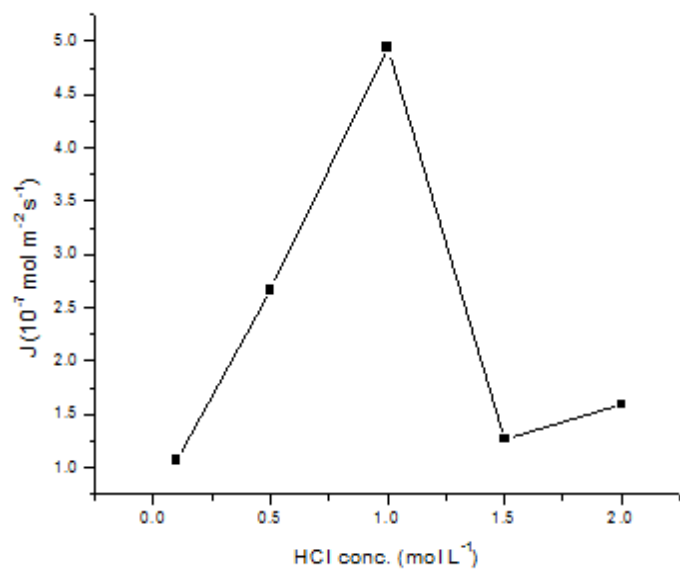


Fig. 4. Effect of HCl concentration on Flux.

(Initial $[\text{Hg}^{2+}] = 4.98 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 0.1\text{-}2 \text{ mol L}^{-1}$, $[\text{N}_2\text{H}_4] = 0.03 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.05 \text{ mol L}^{-1}$).

Table 1. Effect of Hydrochloric Acid Concentration on Extraction of Hg (II)

Time (min)	*0.1 mol L ⁻¹ HCl		0.5mol L ⁻¹ HCl		1 mol L ⁻¹ HCl		1.5 mol L ⁻¹ HCl		2 mol L ⁻¹ HCl	
	Feed	Strip	Feed	Strip	Feed	Strip	Feed	Strip	Feed	Strip
0	99.6±0.42	0	99.6±0.42	0	99.6±0.42	0	99.6±0.42	0	99.6±0.42	0
60	91.2±0.23	8.4±0.35	87±1.4	12.4±0.14	75±0.35	24.6±0.35	95±1.0	4.6±0.40	97±1.2	2.6±0.14
120	82.4±0.14	17.2±0.56	73±1.4	26.4±0.35	45±0.7	54.6±0.35	81±1.4	10.6±0.35	85±1.1	14.4±0.21
180	79±0.7	14.8±0.42	62.4±0.35	37±0.56	31.2±0.98	68.4±0.21	82±1.2	17.6±0.28	77.4±0.14	22±0.35
240	79±0.7	14.4±0.40	62.2±0.32	36.8±0.54	31±0.97	68.2±0.20	82±1.2	17.2±0.27	77.4±0.14	22±0.35
300	79±0.7	14.4±0.40	62.2±0.32	36.8±0.54	31±0.97	68.2±0.20	82±1.2	17.2±0.27	77.2±0.14	22±0.35

*Change conc. of Hg(II) ions (mol L⁻¹)

Table 2. The Effect of Hydrochloric Acid Concentration on Flux

Concentration of HCl (mol L ⁻¹)	Flux value 10 ⁻⁷ J (mol m ⁻² s ⁻¹)
0.1	1.07
0.5	2.67
1	4.94
1.5	1.27
2	1.59

The pH of feed solution was measured, by keeping the HCl concentration at the optimum value i.e. 1 mol L⁻¹, at different time intervals to investigate the behavior of H⁺ ions (Fig. 5). It can be noted from Fig. 5 that an increase in the pH is observed up to 180th min which becomes constant thereafter. The decrease in pH reveals that the carrier (TOPO) molecules were utilized the protons of feed solution and converted into a charged species by protonation at feed-membrane interface.

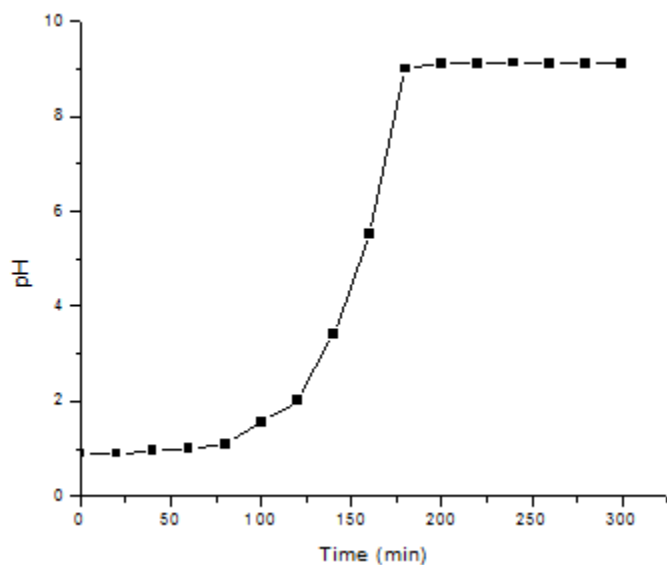


Fig. 5. Variation in pH of feed solution with time.

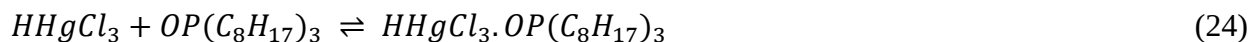
(Initial [Hg²⁺] = 4.98×10⁻⁴ mol L⁻¹, [HCl] = 1 mol L⁻¹, [N₂H₄] = 0.03 mol L⁻¹, [TOPO] = 0.05 mol L⁻¹).

3.2.4.2 Determination of ‘n’

The number of H^+ in the proposed Hg-TOPO complex was determined by using equation 23. Keeping the C_{Hg} and $[TOPO]$ constant, the plot of $\log J\eta$ versus $\log [H^+]$ gives a straight line shown in Fig. 6, which furnishes the value of ‘n’ from its slope. The calculated slope ($0.996 \approx 1$) indicates that one mole of H^+ (Eq. 2a), and Cl^- (Eq. 1b) are involved in the complex formation.

Thus, we can say that the mercury-chloro complex, $[H_nHgCl_{2+n}]$, supposed to be present like $[HHgCl_3]$ and the number of TOPO molecule is also 1 as given in the mercury-TOPO complex $H_nHgCl_{2+n} \cdot \{OP(C_8H_{17})_3\}_n$. Hence, the formula of Hg-TOPO complex can safely be written as $HHgCl_3 \cdot OP(C_8H_{17})_3$.

From above mentioned discussion Eq. (2b) can be written as



Consequently, this equation gives the stoichiometry of the mercury-TOPO complex formation.

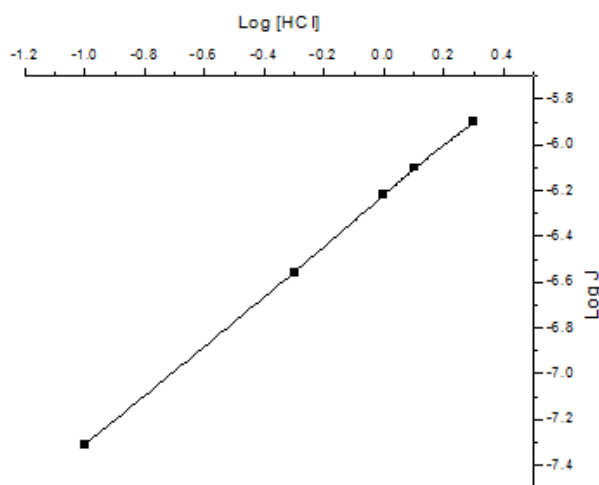


Fig. 6. Plot of $\log J$ versus $\log [HCl]$

3.2.4.3 Effect of Hg (II) ion Concentration on Extraction of Mercury

The concentration range of $1.28 \times 10^{-4} - 2.49 \times 10^{-4} \text{ mol L}^{-1}$ was investigated for extraction of mercury ions in the feed solution. In feed solution the HCl concentration was adjusted at 1 mol L^{-1} , N_2H_4 , in stripping solution at 0.03 mol L^{-1} and TOPO in membrane phase at 0.05 mol L^{-1} . It was noted that with the increase in the Hg (II) ion concentration the extraction increases and a maximum extraction was observed at $4.98 \times 10^{-4} \text{ mol L}^{-1}$ of Hg (II) ion concentration. (Fig. 7(a-b)). Various species taking part in an extraction involved equilibrium reactions between them. Since, the equilibrium constants for these reactions have not been evaluated therefore, the exact concentration of these species are not known. The optimum concentration of mercury i.e. $4.98 \times 10^{-4} \text{ mol L}^{-1}$ can be attributed to the stoichiometric limitation of the concerned reaction, which cannot be specified due to the reason that the value of equilibrium constants are not known. Stoichiometric limitation might have its role in reactions in feed, membrane, or strip phases or interrelated/ interdependent with these phases.

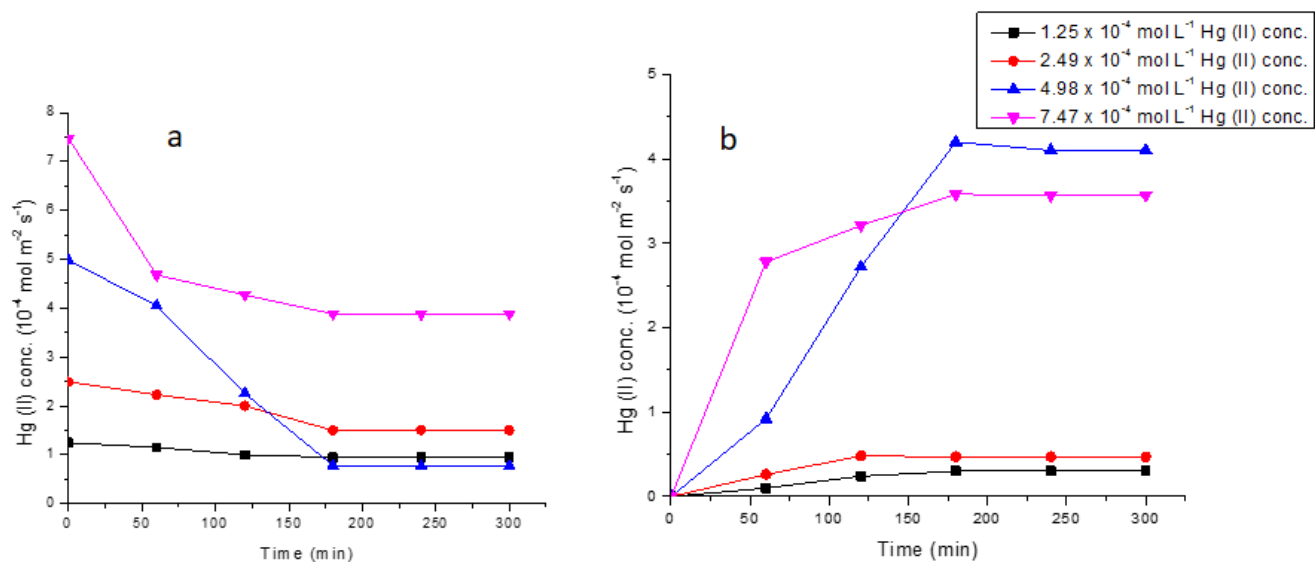


Fig. 7. Variation in Hg (II) ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of Hg (II) ions.

(Initial $[\text{Hg}^{2+}] = 1.25\text{--}7.47 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{N}_2\text{H}_4] = 0.03 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.05 \text{ mol L}^{-1}$).

The flux is directly proportional to feed concentration, so when the mercury ion concentration increases, the flux value also increases and attains a maximum value of $6.07 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ at $4.98 \times 10^{-4} \text{ mol L}^{-1}$ Hg(II) ion concentration, as shown in Fig. 8. However, beyond $4.98 \times 10^{-4} \text{ mol L}^{-1}$, the flux value decreases due to reason as discussed earlier.

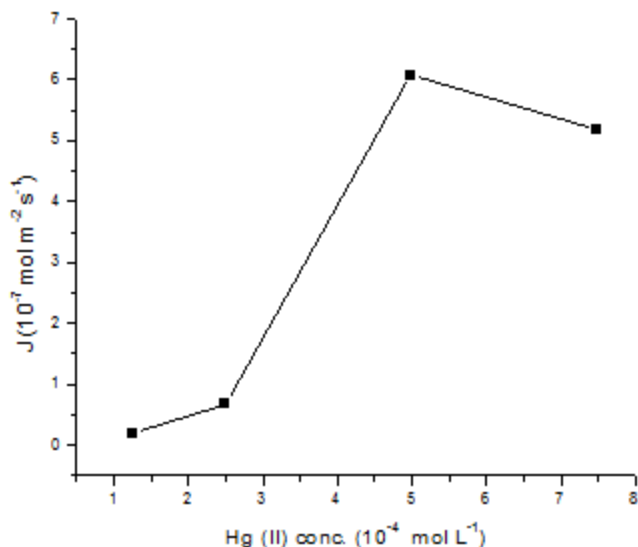


Fig. 8. Effect of Hg (II) ions concentration on Flux.

(Initial $[\text{Hg}^{2+}] = 1.25\text{--}7.47 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{N}_2\text{H}_4] = 0.03 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.05 \text{ mol L}^{-1}$).

3.2.4.4 Effect of TOPO Concentration on the Extraction of Mercury

The effect of concentration of TOPO on extraction of mercury (II) is presented in Fig. 9(a-b). The extraction of mercury (II) ions with the increase in TOPO concentration due to the formation of complex, $H_n \text{HgCl}_{2+n} \cdot \{OP(C_8H_{17})_3\}_n$. The 0.2 mol L^{-1} TOPO is the optimum concentration at which maximum extraction of mercury (II) ions was achieved (Fig. 9b), beyond which a decrease in extraction was observed. The flux value increases with the increase in the concentrations of TOPO, reaches to a maximum at 0.2 mol L^{-1} , and decrease thereafter, as indicated in Fig. 10. This might be due to the following reason: an increasing the TOPO concentration the organic phase viscosity also increases which hampers the transport of the mercury complex through the membrane [11].

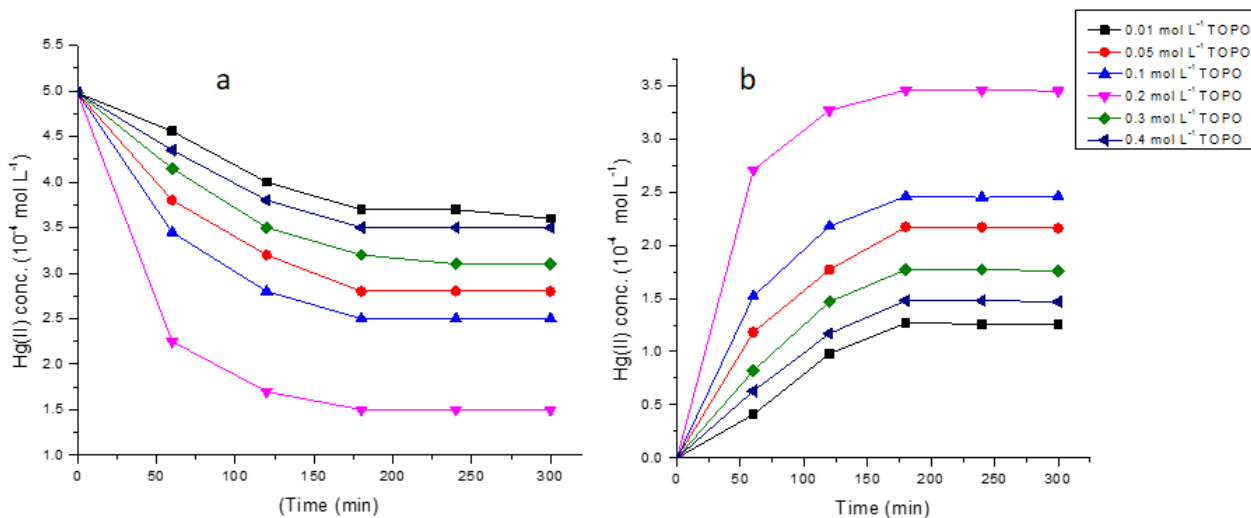


Fig. 9. Variation in Hg (II) ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of HCl.

(Initial [Hg²⁺] = 4.98 × 10⁻⁴ mol L⁻¹, [HCl] = 1 mol L⁻¹, [N₂H₄] = 0.03 mol L⁻¹, [TOPO] = 0.01-0.4 mol L⁻¹).

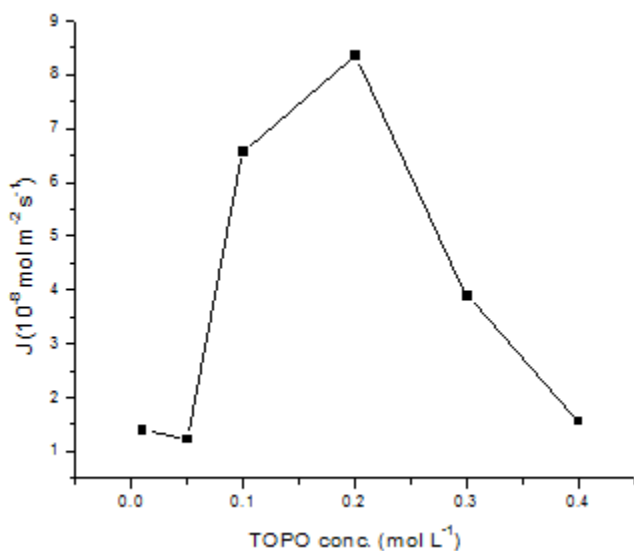


Fig. 10. Effect of TOPO concentration on Flux.

(Initial [Hg²⁺] = 4.98 × 10⁻⁴ mol L⁻¹, [HCl] = 1 mol L⁻¹, [N₂H₄] = 0.03 mol L⁻¹, [TOPO] = 0.01-0.4 mol L⁻¹).

3.2.4.5 Effect of Hydrazine Concentration on the Extraction of Mercury

Hydrazine sulfate is a versatile ligand which reacts with different metal ions and forms a wide range of complexes [12]. In this experiment we have used hydrazine as a stripping agent in the strip phase. To study the effect of hydrazine concentration on the extraction of mercury, different concentration of hydrazine ranging from 0.01 to 0.06 mol L⁻¹ were employed keeping 1mol L⁻¹ HCl and 4.98×10⁻⁴ mol L⁻¹ Hg (II) ions in the feed solution and 0.2 mol L⁻¹ TOPO in membrane constant. The results are illustrated in Figs. 11(a-b).

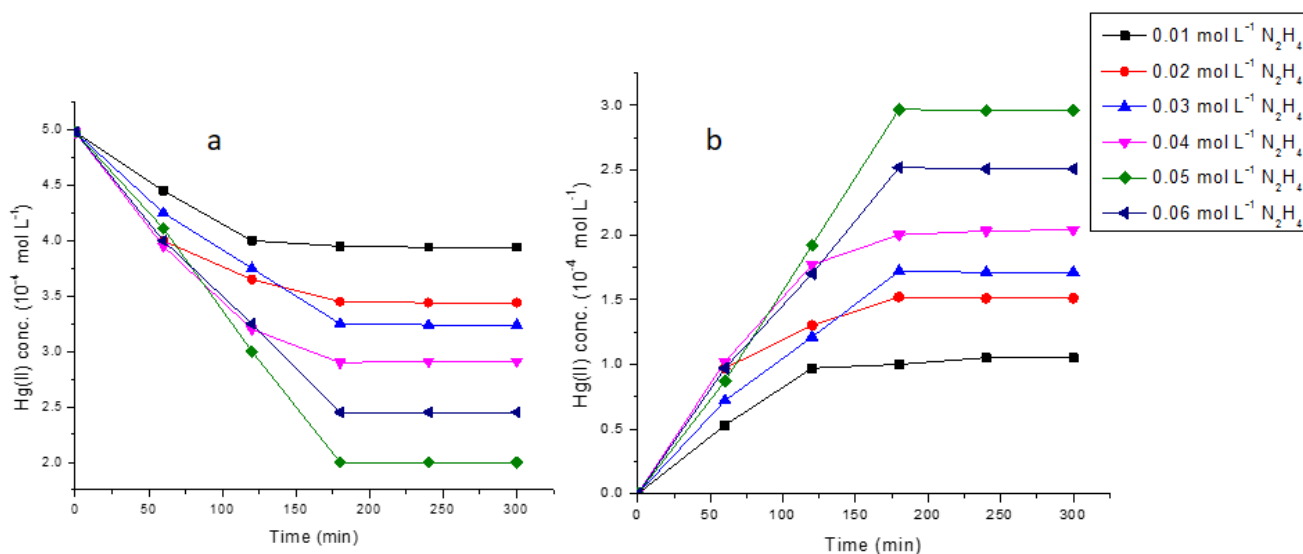


Fig. 11. Variation in Hg (II) ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of HCl.

(Initial [Hg²⁺] = 4.98×10⁻⁴ mol L⁻¹, [HCl] = 1 mol L⁻¹, [N₂H₄] = 0.01-0.06 mol L⁻¹, [TOPO] = 0.2 mol L⁻¹).

It has been observed that on increasing hydrazine concentration, extraction of mercury rises and reaches at maximum value at 0.05 mol L⁻¹ of hydrazine. Below 0.05 mol L⁻¹, fewer hydrazine molecules were available to form a complex with mercury. Above 0.05 mol L⁻¹ hydrazine, the extraction abruptly decreases, which might be due to overcrowding of hydrazine molecules at stripping-membrane interface forming a layer of complex over the membrane

surface, clogging membrane pores and reducing mercury extraction. Consequence, 0.05 mol L⁻¹ hydrazine concentration was considered as optimum for the extraction of mercury. At the strip membrane interface the mercury-TOPO complex dissociates and reacts with hydrazine as follows.

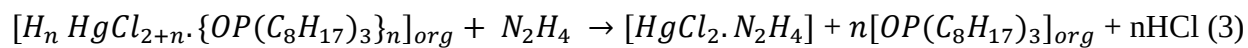


Fig. 12 exhibits the flux profile with hydrazine. At the beginning the flux increases slowly, reach maximum at 0.05 mol L⁻¹ concentration and subsequently declines very sharply. This trend clearly indicates that at higher concentration, more mercury-hydrazine complex are deposited over the membrane surface resulting in the blockage of membrane pores thus flux is decreased.

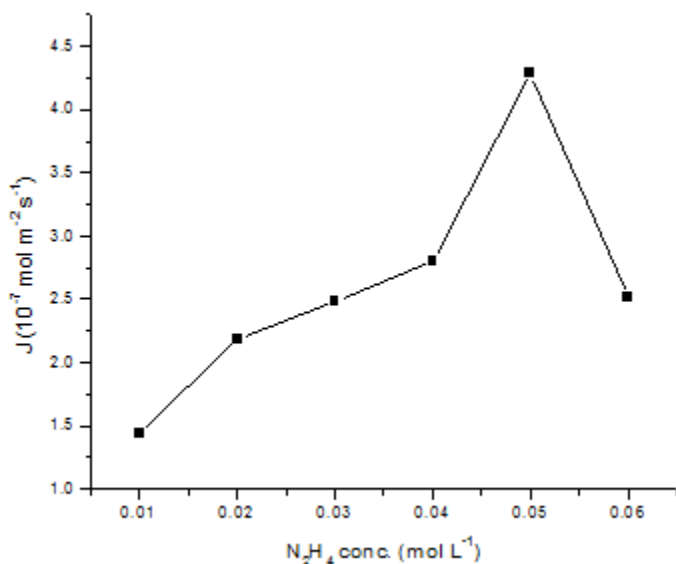


Fig. 12. Effect of N₂H₄ concentration on Flux.

(Initial [Hg²⁺] = 4.98×10⁻⁴ mol L⁻¹, [HCl] = 1 mol L⁻¹, [N₂H₄] = 0.01-0.06 mol L⁻¹, [TOPO] = 0.2 mol L⁻¹).

3.2.4.6 SEM Analysis

Morphology of the supported liquid membrane (Celgard 2400) before and after the extraction is shown in Fig. 13. It is observed that before extraction the surface of membrane is smooth having some irregular cracks as can be seen at 40,000 magnifications (Fig. 13a). After the extraction process, the complex ($\text{Hg-N}_2\text{H}_4$) gets deposited on the membrane surface which entails the blockage of membrane pores as can be seen in Fig.13b even at low magnification of 20,000 [13]. Fig. 13c shows the cross sectional image of the membrane, from which the thickness of the membrane can be calculated and it is found to be 20.36 μm .

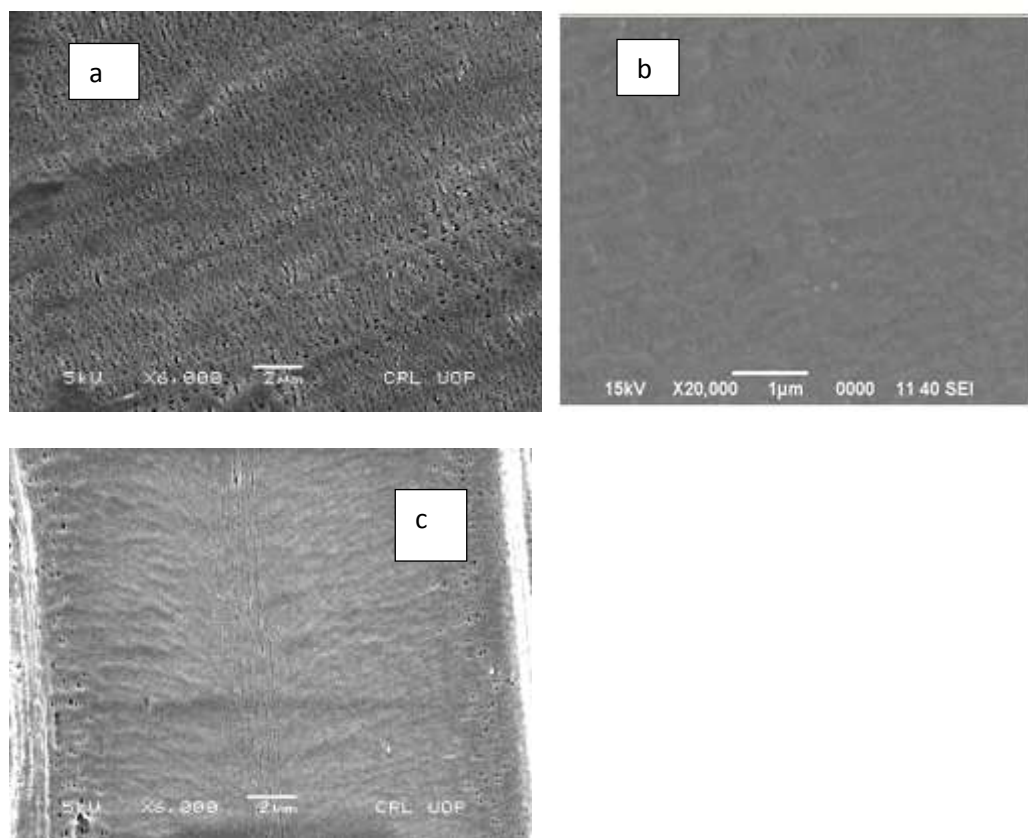


Fig.13. SEM image of the membrane. (a) before extraction (b) after extraction (c) cross section of the membrane.

3.2.4.7 Extraction Time

Fig. 14 depicts the extraction time for mercury ion. At optimum conditions, the mercury ions concentration decreases in the feed phase with the passage of time. As illustrated in the Fig. 14, the concentration of mercury ions increases in the strip phase with the passage of time and reaches at maximum value at 180th min where the extraction was found to be about 90%. Thus, 180 minutes are the optimum extraction time for the transport of mercury ions.

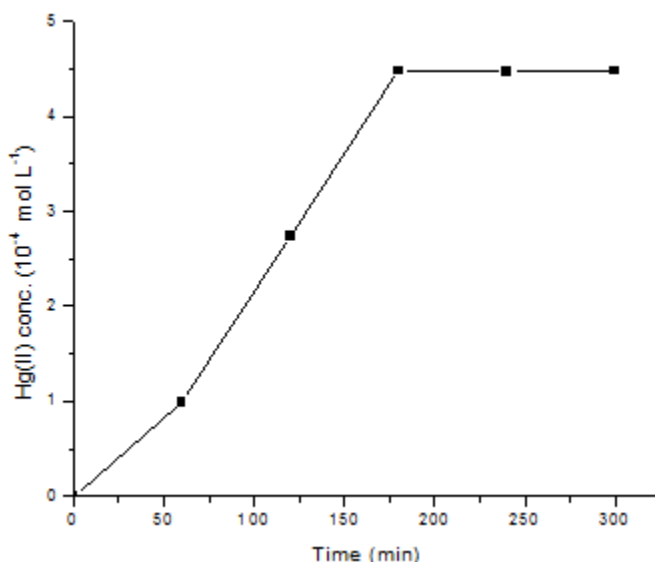


Fig.14. Variation in Hg(II) ions concentration with time.

(Initial $[\text{Hg}^{2+}] = 4.98 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{N}_2\text{H}_4] = 0.05 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.2 \text{ mol L}^{-1}$).

3.2.4.8 Stability of Membrane

The stability of SLM was investigated in terms of carrier loss from the solid support [14]. To observe the stability of polypropylene–TOPO–toluene, SLM, 10 independent extraction experiments (one experiment each day) were carried out at optimum experimental conditions, i.e. concentration of Hg (II) ion at $4.94 \times 10^{-4} \text{ mol L}^{-1}$ along with 1 mol L^{-1} HCl in the feed phase, 0.2 mol L^{-1} of TOPO concentration in the membrane phase while 0.05 mol L^{-1} N_2H_4 was taken in the strip phase while, maintaining at 1500 rpm stirring speed. Each experimental run was of 5h

duration using the same membrane impregnated only once, however, for every experiment, feed and stripping solutions in both the compartments were replaced with fresh ones. Between the successive experiments the cell compartments were filled with distilled water in order to avoid the dryness of the membrane. The results reveal (Fig. 15) that in all these experiments 90% extraction is observed which is an indication of stability of the membrane. Thus, it can be concluded from this series of experiments that the membrane is stable for 50 hours use.

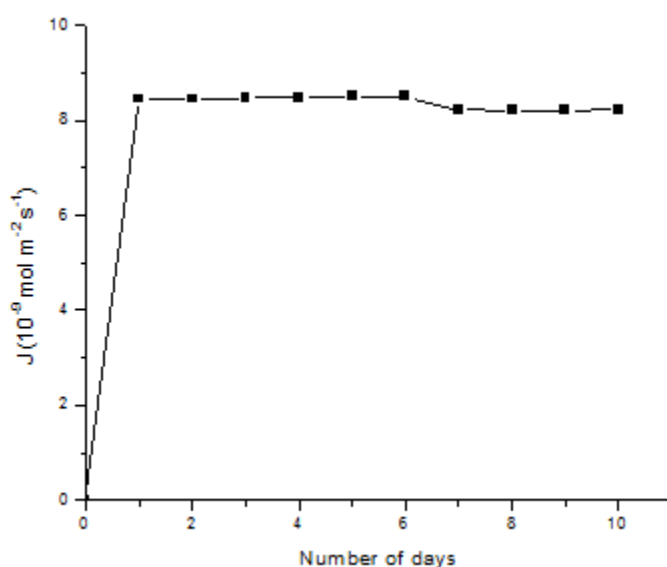


Fig.15. Stability of membrane versus time.

(Initial $[\text{Hg}^{2+}] = 4.98 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{N}_2\text{H}_4] = 0.05 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.2 \text{ mol L}^{-1}$).

3.2.4.9 Extraction of Hg (II) ions from Hospitals Effluent

For Hg (II) ion extraction the SLM was designed which shows the efficient transport of Hg (II) ion. Mercury amalgam is one of the major application of mercury which is used in the hospitals. The optimized SLM was employed for the removal of mercury from four different hospital effluents. The effluent samples from each hospital were first filtered with filter paper (Whatman) in order to remove the suspended particles. The filtrate (80 mL) was diluted with

distilled water up to 250 mL and analyzed spectrophotometrically before subjecting the sample for extraction. The extraction was carried out at the optimum experimental conditions as described earlier. 90% Hg (II) was removed from the effluents samples under these conditions from all the samples. The analytical results of the strip solution of the hospital waste water show that some other metals were also extracted along with the mercury ions (Fig. 16). The data are represented in Tables 3 and 4.

Table 3. Analysis of Hospitals' Effluents

Metal ions	Hospital-I		Hospital-II		Hospital-III		Hospital-IV	
	Original concentration of water sample		Original concentration of water sample		Original concentration of water sample		Original concentration of water sample	
	B.E (mg L ⁻¹)	A.E (mg L ⁻¹)	B.E (mg L ⁻¹)	A.E (mg L ⁻¹)	B.E (mg L ⁻¹)	A.E (mg L ⁻¹)	B.E (mg L ⁻¹)	A.E (mg L ⁻¹)
Hg	291±0.7	27.4±0.7	264±1.4	30±0.35	272±0.7	26±0.35	253±1.1	27±0.21
Co	-	-	0.75±0.04	0.745±0.004	0.94±0.04	0.93±0.04	1.4±0.05	1.38±0.04
Cr	26.6±0.35	25.9±0.63	31±0.35	30.09±0.32	29±0.35	28±0.35	25±0.35	21.25±0.09
Cu	153±0.7	152.9±0.49	212±0.7	211.09±0.68	66±1.1	64.5±1	14±0.49	13.66±0.29
Mn	3.4±0.28	3.37±0.26	0.28±0.01	0.27±0.01	1.7±0.14	1.36±0.01	2.2±0.07	2.14±0.06
Cd	15±1.4	14.93±0.16	16.56±0.21	16.09±0.2	18±0.7	14±0.49	17±0.42	16.56±0.15

B.E = before extraction; A.E = after extraction

Hospital-I: University Town, Hospital-II: University road, Hospital-III: Hayatabad, Hospital-IV: Charsadda road.

Table 4. Percent Extraction of Metal Ions from the Effluents of Various Hospitals'

Metal ion	Hospital- I (% Extraction)	Hospital-II (% Extraction)	Hospital- III (% Extraction)	Hospital -IV (% Extraction)
Co (1)	00	1.6	1.2	1.5
Cr (2)	2.3	2.8	2.2	1.4
Cu (3)	4.9	4.3	2.3	2.4
Mn (4)	1	3.3	2	2.5
Cd (5)	4	2.8	2.2	2.6
Hg (6)	90	89	90	89

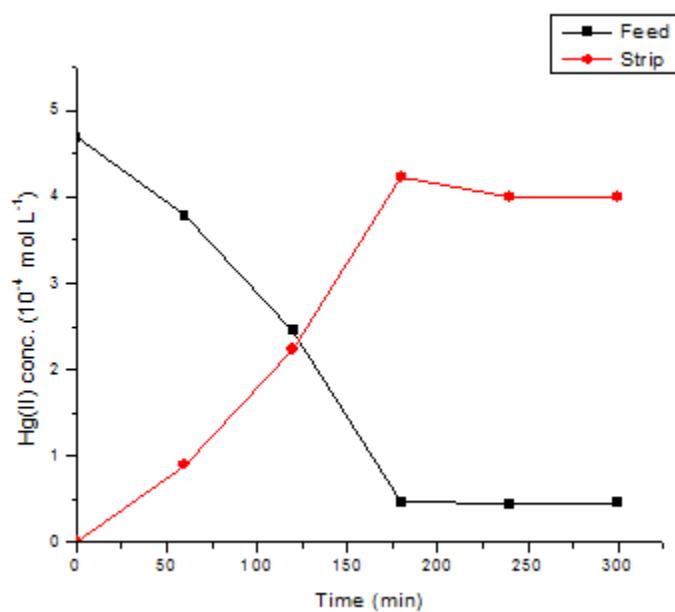


Fig. 16. Variation in Hg (II) ion concentration with time in the feed (a) and strip (b) solutions (Hospital waste water in feed).

(Initial $[\text{Hg}^{2+}] = 4.69 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{N}_2\text{H}_4] = -0.05 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.2 \text{ mol L}^{-1}$).

Conclusion

The TOPO-toluene based flat-sheet supported liquid membrane system was utilized for the transport of Hg (II) ions. The effect of concentration of HCl, TOPO, mercury ions and hydrazine along with extraction time on the extraction of Hg (II) was investigated. The results reveal that maximum extraction of mercury was achieved in 180 minutes at a carrier concentration of 0.1 mol L^{-1} , $4.98 \times 10^{-4} \text{ mol L}^{-1}$ of mercury in the feed concentration, 1 mol L^{-1} of HCl, 0.05 mol L^{-1} concentration of hydrazine (N_2H_4) in the stripping phase and at a stirring speed of 1500 rpm. The present SLM was found to be stable for about 50 hours use. Under optimum conditions, this SLM was employed for the extractions of metal ions from the hospital effluents and approximately 90% Hg (II) ions extraction was achieved.

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Part III

Extraction of Chromium (VI)

Removal of Chromium (VI) from Industrial Effluents through Supported Liquid Membrane using Tri-octylphosphine Oxide as a Carrier

3.4 Theory

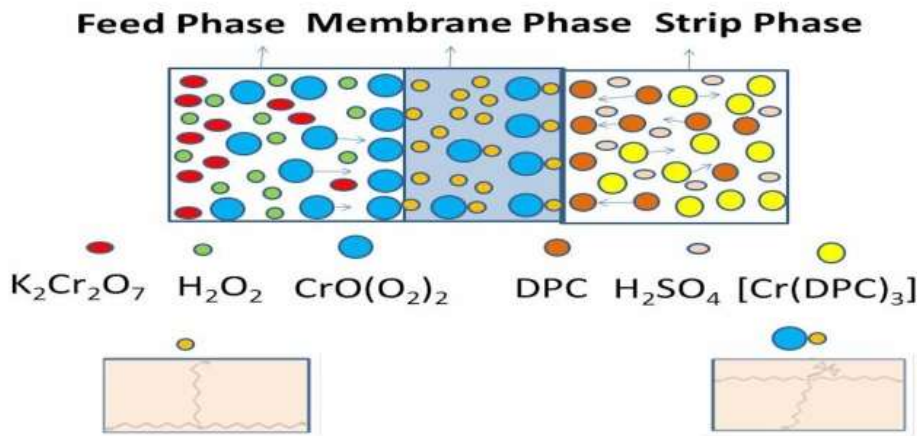
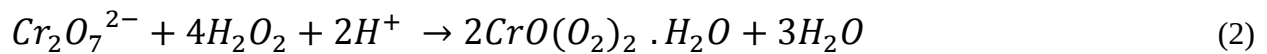


Fig. 1. The SLM design for Cr (VI) extraction shows the transport mechanism of Cr ions in the form of $[CrO(O_2)_2 \cdot TOPO]$ complex from feed to strip phase through membrane phase.

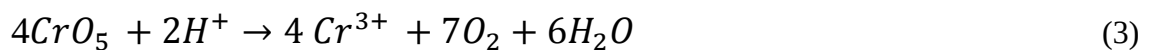
Potassium dichromate is soluble in water and in the dissolution process it ionizes [1] as:



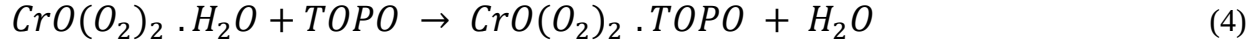
In acidic medium, $Cr_2O_7^{2-}$ reacts with hydrogen peroxide in feed compartment [2] as



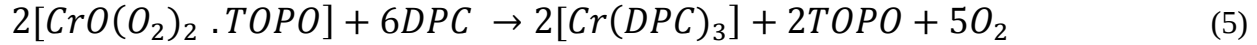
$CrO(O_2)_2$ or CrO_5 decomposes to chromium (III) [3] as



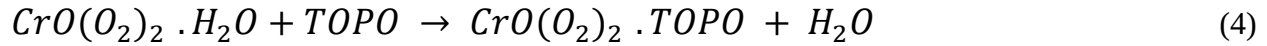
TOPO reacts with specie $CrO(O_2)_2 \cdot H_2O$ at membrane phase [2] and stabilizes Cr (VI) and avoids reduction to Cr (III). Since TOPO has no H^+ for ion exchange with metal ion the extraction of chromium only occurs via a solvating mechanism [4].



The complex $CrO(O_2)_2 \cdot TOPO$ at membrane-strip interface reacts with diphenylcarbazide (DPC) forming a complex $Cr(DPC)_3$ [5-6]. The reaction in the acidic medium in the strip side may be written as



Chemical equation related with extraction process in feed phase is given as follows:



The equilibrium constant for this reaction is as follows:

$$\dot{K} = \frac{[CrO(O_2)_2 \cdot TOPO] [H_2O]}{[CrO(O_2)_2 \cdot H_2O] [TOPO]} \quad (6)$$

Since concentration of H_2O remains constant, so the equilibrium constant is given as:

$$K = \frac{[CrO(O_2)_2 \cdot TOPO]}{[CrO(O_2)_2 \cdot H_2O] [TOPO]} \quad (7)$$

The distribution coefficient (K_{Df}) of chromium between aqueous and organic phases (membrane phase) in the feed phase is given by the following relation

$$K_{Df} = \frac{[CrO(O_2)_2 \cdot TOPO]_{org}}{[CrO(O_2)_2 \cdot H_2O]_{aq}} \quad (8)$$

On the other hand, the reaction on the strip side is as follows:



The distribution coefficient (K_{Ds}) of chromium between membrane and strip phase is given as follows:

$$K_{Ds} = \frac{[\text{CrO}(\text{O}_2)_2 \text{ TOPO}]^2_{org}}{[\text{Cr}(\text{DPC})_3]^2_{aq}} \quad (10)$$

The permeability coefficient (P) was used to evaluate the effect of the different experimental parameters, such as concentration of TOPO, DPC, Cr(VI) metal ion, and H_2SO_4 , on the chromium transport. The mass-transfer model presented by Danesi is used to describe the permeability coefficient [7]. In the feed phase the permeability coefficient was found by the following equation:

$$\ln \frac{C}{C_o} = -\epsilon \frac{S}{V} P t \quad (11)$$

Where the permeability coefficient is denoted by P (cm s^{-1}), C_o and C are the concentrations of Cr(VI) in the feed phase at initial and at time t (s). The effective membrane area (cm^2) is indicated by S while $V(\text{cm}^3)$ is the volume of the feed phase.

From the slope of the linear plot of $\ln \frac{C}{C_o}$ vs time the permeability coefficient can be obtained. In order to calculate the transport through the membrane flux the Eq (12) was used;

$$J_o = \left(\frac{dC_f}{dt} \right)_o \left(\frac{V}{S\epsilon} \right) \quad (12)$$

Where J_o is the initial flux ($\text{mol cm}^{-2} \text{ s}^{-1}$), the volume of the feed phase is denoted by $V(\text{cm}^3)$, porosity of the membrane is represented by ϵ , C_f is the concentration of chromium (mol L^{-1}) in the feed phase at elapsed time and t is the time (s). Flux (J) was determined from the slope of concentration of chromium in feed phase versus time i.e. $\frac{dC_f}{dt}$ and putting it in Eq (12), while the volume of solution was 250 mL, and 'S' the surface area of the membrane was 16.04 cm^2 and porosity ' ϵ' ' was 30%.

The percent recovery of Cr(VI) was also calculated as:

$$\text{Recovery \%} = 100 \left(\frac{C_s}{C_o} \right) \quad (13)$$

While C_s and C_o are the concentrations of chromium at elapsed time and at the beginning respectively.

3.4.1 Result and Discussion

3.4.1.1 Effect of TOPO Concentration on Extraction of Cr (VI)

The effect of concentration of TOPO on the transport of Cr (VI) has been studied. For this purpose, various concentrations of TOPO were employed in membrane phase. The range from 0.001 to 0.2 mol L^{-1} of TOPO concentration was studied. It was found that with the increase in concentration of TOPO, the extent of extraction of chromium increases (Fig. 2a). However, 0.1 mol L^{-1} TOPO concentration has exhibited maximum extraction. The same effect is shown in Fig. 2b, wherein a decrease in Cr (VI) in the feed phase can be observed with the increase in TOPO concentration. From this Fig it can be concluded that the TOPO concentration of 0.1 mol L^{-1} is the one which shows the maximum extraction of the chromium ions but beyond 0.1 mol L^{-1} TOPO concentration the extraction was decreases. The limiting value of extraction of chromium

at 0.1 mol L^{-1} TOPO may be attributed to increased viscosity of TOPO solutions which hampers the movement of metal ions through the membrane (The viscosity data has not been included in the text).

The same phenomenon is being reflected in the Fig. 3, wherein the two curves show the said additive behavior which is clear from their mirror image nature. By a careful observation, it can be analyzed that a decreasing trend in the chromium ions concentration in the feed side is observed, however, the concentration goes to a minimum value at 0.1 mol L^{-1} TOPO where after, the transport of chromium towards the strip side is reduced by further increase in the TOPO concentration. This might be due to the increase in the viscosity of organic phase of the membrane which hampers the movement of complex through the membrane. This fact can conversely observe from the strip side where the concentration of chromium increases with the increase of TOPO concentration, reaches a maximum at 0.1 mol L^{-1} TOPO, and then decreases afterwards. So 0.1 mol L^{-1} TOPO concentration was an optimum condition for chromium extraction.

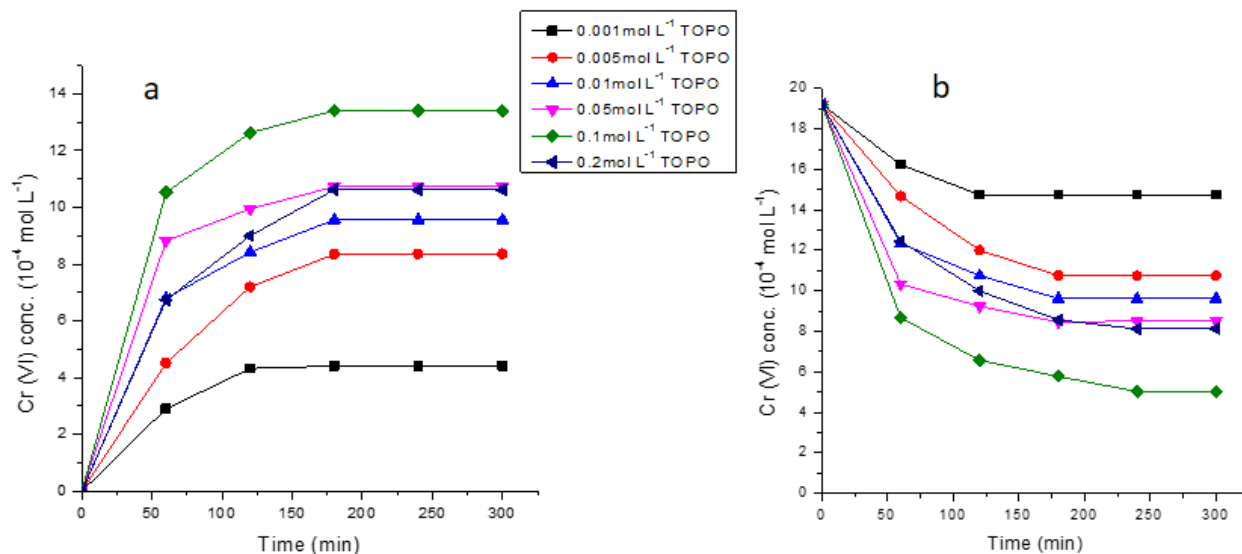


Fig. 2. Variation in Cr (VI) ion concentration with time in the strip (a) and feed (b) solutions at various concentrations of TOPO.

(Initial $[\text{Cr}^{6+}] = 19.2 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] = 0.5 \text{ mol L}^{-1}$, $[\text{DPC}] = 0.001 \text{ mol L}^{-1}$, $[\text{H}_2\text{SO}_4] = 1 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.001\text{-}0.2 \text{ mol L}^{-1}$).

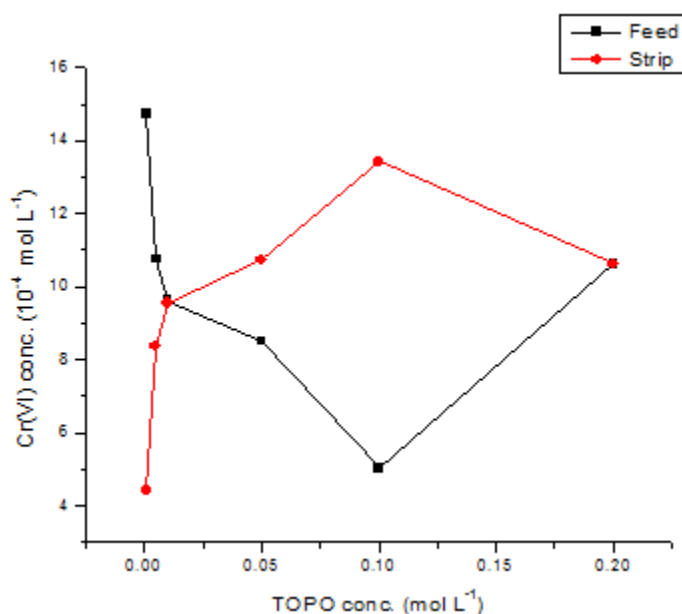


Fig. 3. Variation in Cr (VI) ion concentration in the feed and strip solution at various concentrations of TOPO.

(Initial $[\text{Cr}^{6+}] = 19.2 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] = 0.5 \text{ mol L}^{-1}$, $[\text{DPC}] = 0.001 \text{ mol L}^{-1}$, $[\text{H}_2\text{SO}_4] = 1 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.001\text{-}0.2 \text{ mol L}^{-1}$).

Since 0.1 mol L⁻¹ TOPO concentration was optimum concentration exhibiting maximum extraction of chromium, therefore, all subsequent calculations, i.e. percent recovery, distribution coefficient, flux and permeability coefficient etc., were made at this concentration.

At 0.1 mol L⁻¹ TOPO concentration the chromium concentration was observed at the maximum level i.e. 13.42 x 10⁻⁴ mol L⁻¹, the percent recovery was found to be 69.84 i.e. almost 70%. The percent recovery decreased by further increase in TOPO concentration. This decrease may be attributed to increase in viscosity of TOPO-toluene solution in membrane phase which hampers the transport of chromium (VI) ions across the membrane.

The distribution coefficient of chromium between aqueous and the membrane phases (TOPO-toluene) is given by Eqs.(8,10) and were calculated by taking care of mass balance of chromium on the assumption that the total chromium has been distributed among three phases i.e. feed, membrane, and strip as shown in Figure 4 and given by the following relation

$$Cr_{Tot} = Cr_f + Cr_s + Cr_m \quad (14)$$

Where Cr_{Tot} is the total chromium concentration and Cr_f , Cr_s , and Cr_m are the chromium concentrations in the feed, strip, and membrane phases respectively.

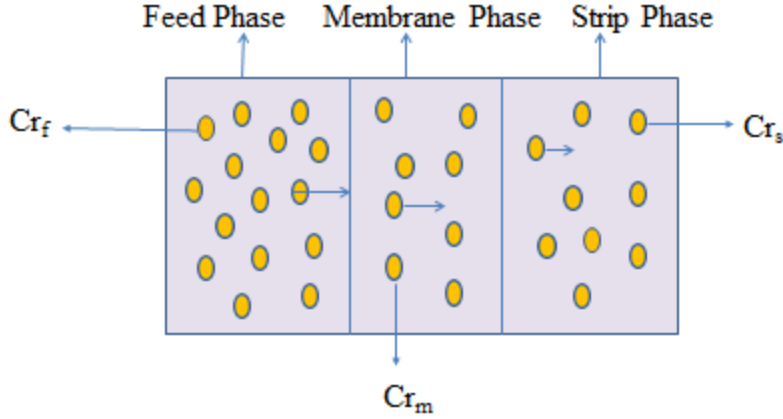


Fig. 4. Mass transfer diagram of chromium ions.

Here Cr_{Tot} is the original or initial concentration taken for the experiment, and the atomic absorption spectroscopy was used to determine the chromium (VI) ion concentrations in the feed and strip sides, at any elapsed time of the experiment. The concentration of chromium in membrane phase was calculated by mass balance i.e.

$$Cr_m = Cr_{Tot} - Cr_f - Cr_s \quad (15)$$

This calculation was carried out at two different stages of the experiment i.e. when the system has not attained the equilibrium and secondly when equilibrium has been attained. The first stage corresponds to the rising part of the chromium (VI) ions concentration against time curve in the strip phase (as for example in Fig. 2a) and second one corresponds to the concentration versus time curve when it becomes horizontal to x-axis. Mass balance calculation at 60th minutes using Eq. (14) is as follows.

$$Cr_{Tot} = Cr_f + Cr_s + Cr_m \quad (14)$$

$$Cr_m = 0.01 \times 10^{-4} \text{ mol L}^{-1}$$

From this data we can calculate $K_{D_{f_1}}$ before equilibrium by using Eq (8)

$$K_{D_{f_1}} = \frac{0.01 \times 10^{-4}}{8.67 \times 10^{-4}} = 1.15$$

On similar ground K_D at equilibrium point (i.e. 240 min), $Cr_{Tot} = 19.2 \times 10^{-4}$, $Cr_f = 5.02 \times 10^{-4}$, $Cr_s = 13.41 \times 10^{-4}$ which gives

$$Cr_m = 0.77 \times 10^{-4}$$

The $K_{D_{f_2}}$ at equilibrium becomes

$$K_{D_{f_2}} = \frac{0.77 \times 10^{-4}}{5.02 \times 10^{-4}} = 0.15$$

Thus distribution coefficient at 0.1 mol L⁻¹ TOPO concentration (optimum concentration) before equilibrium is 1.15 while it is 0.15 after the equilibrium level is reached. This indicates that the distribution of chromium is higher in the membrane phase at the earlier stage of the experiment as compared to at the later stage. It will be instructive if we can compare distribution coefficient at a given time, of feed and strip sides to elaborate this point further.

The concentration of chromium at 240 min in strip side is 13.41×10^{-4} mol L⁻¹ which gives a distribution coefficient of 0.057. Here the distribution coefficient at the feed side is 0.15 which is much greater than that of the corresponding value of 0.057 which is about 2.6 times greater. This comparison implies that in the feed region there is a greater affinity of chromium for the membrane phase and lesser at strip phase. Thus, there is a natural tendency of chromium flow from feed to strip side through the membrane and a driving force of diffusion exists at SLM together with enhanced chromium de-complexing at the membrane-strip interface.

Flux of chromium through the membrane was calculated using Eq (12) in which the volume of the feed solution (V_f) was 250 mL, the effective surface area (S) of the membrane was 16.04 cm² and its porosity (ϵ) was 41%. From the concentration of chromium in the strip region versus time curve the slope was used to calculate the factor $\frac{dC_f}{dt}$ which was taken at the initial time of the experiment i.e. the initial slope of the concentration versus time curve. This value was $2.92 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ which gives the flux value (J_0 initial flux) of $1.11 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$. Now let us check the status of the flux just before the establishment of equilibrium. The slope at this region is $4.03 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$, which gives a flux value of $1.53 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$. Here we note that the flux value decreases from 1.11×10^{-7} to $1.53 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$, which is an obvious phenomena that is chromium transport decreases with the passage of time which becomes zero at equilibrium stage as can easily be predicted from the zero slope where the curve becomes parallel to the x-axis.

The permeability coefficient was calculated using Eq (11), which was arranged in straight line form and slope of the $\ln \frac{C}{C_0}$ versus time curve (Figure 4) is equal to $-\epsilon \frac{S}{V} P$. Where ϵ the porosity which is equal to 41 %, S is the effective surface area of the membrane which is 16.04 cm² and V is the volume of feed solution which is 250 cm³. The average slope was calculated to be 3.33×10^{-5} thus P was calculated as $1.26 \times 10^{-5} \text{ cm s}^{-1}$.

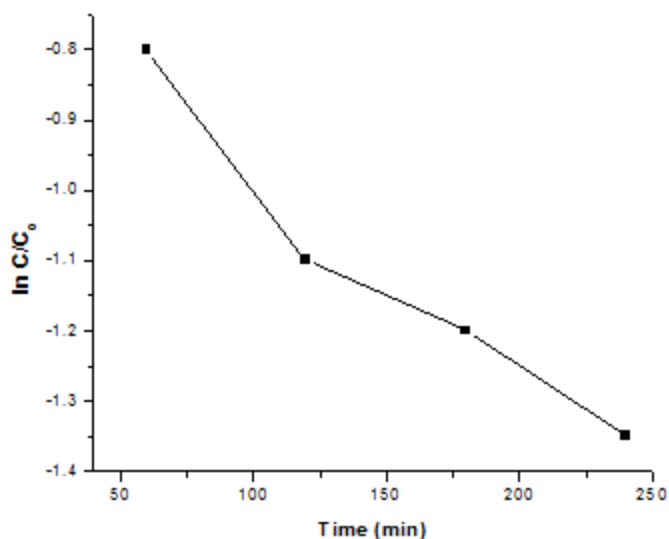


Fig. 5. Plot of $\ln C/C_0$ versus time at 0.1 mol L^{-1} TOPO concentration.

3.4.1.2 Effect of Diphenyl carbazide (DPC) Concentration on Extraction of Cr (VI)

DPC is the common complexing agent for chromium and widely used to extract it [8]. In the strip side Cr (VI) forms a pink complex with DPC. The concentration range of DPC studied in chromium extraction was from 0.0005 to 0.004 mol L^{-1} shown in Fig. 6(a-b). As indicated in Fig. 6(a-b), the extraction of chromium increases with the increase in DPC concentration up to 0.001 mol L^{-1} DPC, beyond which a decrease was observed. DPC forms complex with chromium as $\text{Cr}(\text{DPC})_3$. This indicates that for every one mole of chromium three moles of DPC are required for the complexation. Therefore, initially with the increase in DPC concentration the chromium extraction increases upto 0.001 mol L^{-1} DPC concentration. Beyond which the decrease in the extraction has been observed. This might be due to the formation of dimer of DPC at elevated concentration which makes it unavailable for complexation [9]. Thus, 0.001 mol L^{-1} DPC was an optimum concentration for chromium extraction. Therefore, all subsequent calculations were made on this optimum concentration of DPC. The maximum recovery calculated under the mentioned condition was 86%.

Distribution coefficient calculated in the feed region before equilibrium (at 60th min) was 0.008 and at equilibrium (at 240min) it was 0.072 while corresponding value of strip side was 0.0082. Thus K_D value at feed side is 8.7 times higher than that of strip side. This suggests that reversal of chromium from strip to feed side is hampered by 8.7 time lower value of K_D in strip side and the higher value of K_D in feed side imposes a so called pushing effect on chromium transfer towards the feed side.

Flux value was calculated before establishment of equilibrium i.e.at 60 min which was $1.21 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ while just before establishment of equilibrium i.e. at 180 min its value was $1.1 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$. The decrease in the flux value is obviously due to the decrease in the chromium ions concentration in the feed region. Permeability coefficient was $7.60 \times 10^{-5} \text{ cm s}^{-1}$.

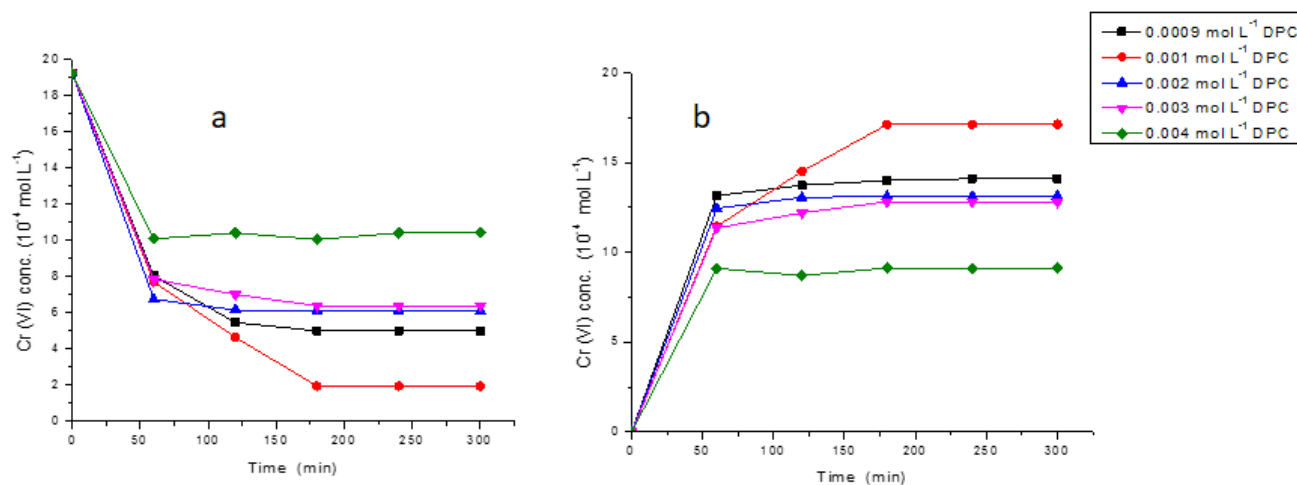


Fig. 6. Variation in Cr (VI) ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of diphenylcarbazide (DPC).

(Initial $[\text{Cr}^{6+}] = 19.2 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] = 0.5 \text{ mol L}^{-1}$, $[\text{DPC}] = 0.0005\text{--}0.004 \text{ mol L}^{-1}$, $[\text{H}_2\text{SO}_4] = 1 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.1 \text{ mol L}^{-1}$).

3.4.1.3 Effect of Cr (VI) ion Concentration on Extraction of Cr (VI)

The chromium (VI) ion concentration effect on chromium extraction was studied in the range of 9.6×10^{-4} to 48.1×10^{-4} mol L⁻¹ concentration in the feed solution. The H₂O₂ concentration in the feed solution was adjusted at 0.5 mol L⁻¹, DPC, in stripping solution at 0.001 mol L⁻¹ and TOPO in membrane phase at 0.1 mol L⁻¹. As shown in Fig. 7(a-b), in the feed side the Cr (VI) ion concentration decreases while at the same time it increases in the strip side. The extraction increases as the Cr (VI) ion concentration increase in feed solution and gives the maximum value at 19.2×10^{-4} mol L⁻¹ and after that the decrease in the extraction can be observed. This might be attributed to the following reason: as the chromium ions concentration increases, the requirement of H₂O₂, to make CrO(O₂)₂ complex, also increases, whereas we have kept H₂O₂ concentration at a constant level which is insufficient to cater for the CrO(O₂)₂ complex.

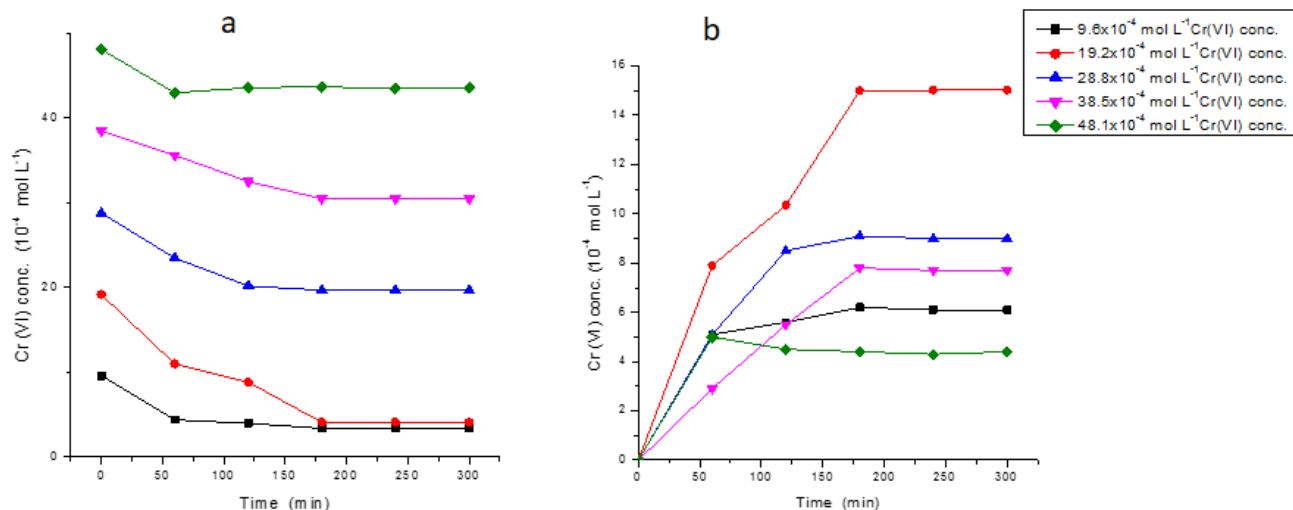


Fig. 7. Variation in Cr (VI) ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of Cr (VI) ion.

(Initial [Cr⁶⁺] = 9.6 - 48.1 $\times 10^{-4}$ mol L⁻¹, [H₂O₂] = 0.5 mol L⁻¹, [DPC] = 0.001 mol L⁻¹, [H₂SO₄] = 1.5 mol L⁻¹, [TOPO] = 0.1 mol L⁻¹).

Thus, $19.2 \times 10^{-4} \text{ mol L}^{-1}$ Cr (VI) concentration was the optimum concentration for the extraction of Cr(VI) ions from the solution and the all the relevant calculations were made on this Cr (VI) concentration. 78% recovery was obtained at $19.2 \times 10^{-4} \text{ mol L}^{-1}$ concentration of Cr (VI) ion.

The distribution coefficient was calculated for both feed and strip sides. It was found that before equilibrium (at 60th min) in the feed side the K_D value was 0.027 while at equilibrium (240th min) it was 0.0195. Similarly, on the strip side, the equilibrium value of K_D was 0.0053. It can be noted that the concentration of chromium increases in the strip side in contrast to the feed side with the passage of time. This is supported by the 3.7 times higher K_D value of feed side.

The flux value before equilibrium was calculated $8.32 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ while just before the equilibrium the flux value of $3.75 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$. The decrease in flux value was due to the higher concentration of chromium in the strip phase than in the feed phase. At equilibrium the flux becomes zero. The value of permeability (P) obtained was $5.28 \times 10^{-5} \text{ cm s}^{-1}$. This indicates the higher chromium (VI) ion transport from feed through membrane to strip side.

3.4.1.4 Effect of H₂SO₄ Concentration on Extraction of Cr (VI)

The presence of H₂SO₄ in the strip solution dissociates the CrO(O₂)₂ complex at the strip-membrane interface and releases Cr (VI) ions which form complex with DPC as Cr (VI)-DPC complex [10].

The effect of H₂SO₄ concentration was studied from 0.5 to 2 mol L⁻¹. Figure 8 indicates the effect of H₂SO₄ concentration on extraction of Cr (VI) ions in the strip side. With the increase in the H₂SO₄ concentration the chromium extraction also increases which reaches at the

maximum value at 1.5 mol L^{-1} of H_2SO_4 concentration. Beyond 1.5 mol L^{-1} concentration the extraction decreases and this phenomena might be that at higher H_2SO_4 concentration, there will be inability of H^+ to dissociate the $[\text{CrO}(\text{O}_2)_2\cdot\text{TOPO}]$ complex due to the overcrowding of H^+ ions at strip-membrane interface [11]. 1.5 mol L^{-1} H_2SO_4 concentration was the optimum concentration for the chromium ions extraction. 84% chromium was recovered at this concentration.

The initial flux value obtained was $7.35 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ at 60min. Similarly, just before the equilibrium the flux value was $2.38 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ and at equilibrium the flux become zero. Initially, there is a rapid mass transfer of chromium from feed to strip side but with passage of time as the equilibrium stage approaches there is a decline in a mass transfer rate and ultimately the value of flux becomes zero at equilibrium. The permeability coefficient calculated was $4.80 \times 10^{-5} \text{ cm s}^{-1}$.

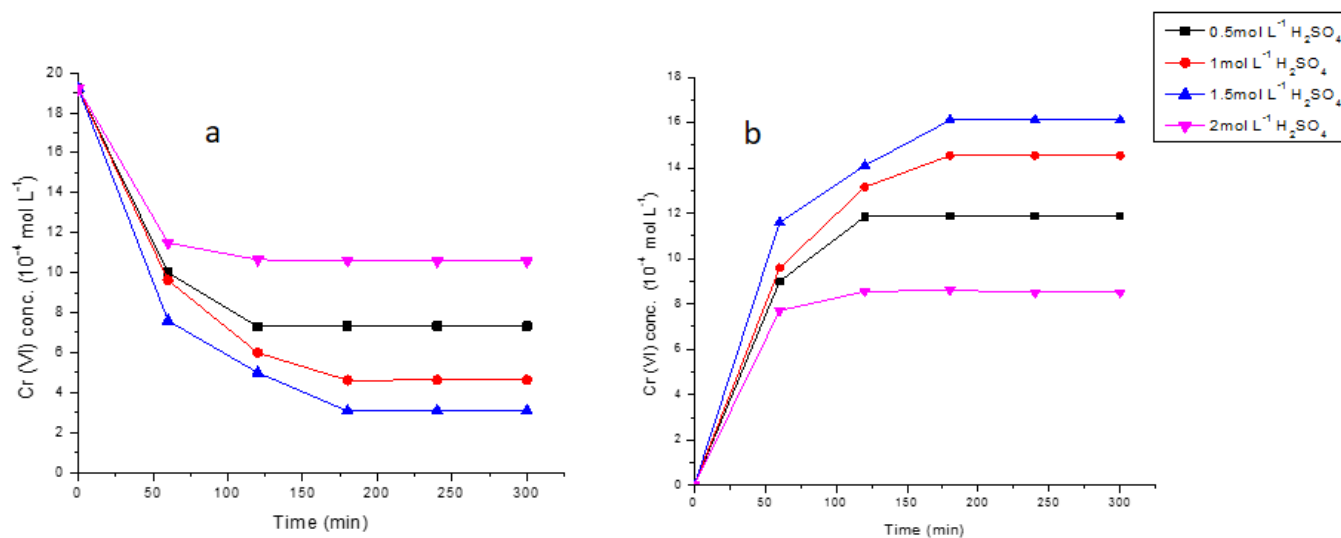


Fig. 8. Variation in Cr (VI) ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of H_2SO_4 .

(Initial $[\text{Cr}^{6+}] = 19.2 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] = 0.5 \text{ mol L}^{-1}$, $[\text{DPC}] = 0.001 \text{ mol L}^{-1}$, $[\text{H}_2\text{SO}_4] = 0.5\text{--}2 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.1 \text{ mol L}^{-1}$).

3.4.1.5 Extraction Time

Fig. 9 shows the extraction time for chromium metal ion. At optimum conditions the extraction of chromium ion increases with time and at 180 min approximately 80% of chromium was extracted, after which no increase in the extraction was observed.

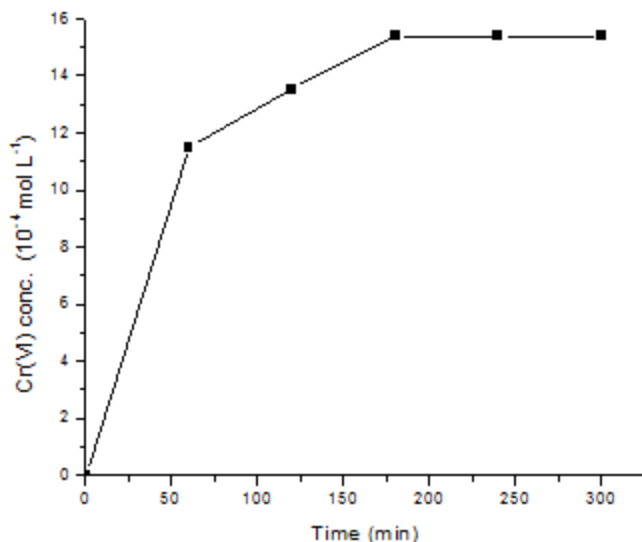


Fig. 9. Variation in Cr (VI) ion concentration with time.

(Initial $[\text{Cr}^{6+}] = 19.2 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] = 1.5 \text{ mol L}^{-1}$, $[\text{DPC}] = 0.001 \text{ mol L}^{-1}$, $[\text{H}_2\text{SO}_4] = 1.5 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.1 \text{ mol L}^{-1}$).

3.4.1.6 Membrane Stability

In spite of their distinguished advantages, SLMs undergo instability with time. The stability of SLMs has great influence on the extraction process in term of flux and selectivity of membrane. The instability of SLMs generally occur due to the loss of solvent or carrier from the membrane support [12]. In this study the SLM was found to be moderately stable for 10 days. To study the long term membrane stability, the extraction experiments were carried out consistently for 10 days (one experimental run per day) made without re-impregnation of the membrane at the optimum conditions, however, the feed and strip solutions were replaced for each run. The cell was kept filled with distilled water, between the successive experiments to prevent the membrane dryness. The optimum experimental conditions were as follows; Cr(VI) concentration in the feed at $19.2 \times 10^{-4} \text{ mol L}^{-1}$ and $1.5 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$, TOPO concentration in SLM at 0.1 mol L^{-1} in toluene, DPC concentration at 0.001 mol L^{-1} and $1.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ in stripping solution and

at 1500 rpm stirring speed. The results show (Fig. 10) that this SLM was quite stable during the investigated time and no decrease in flux and percent recovery of chromium was observed. The study was replicated thrice with relative standard deviation ± 2 .

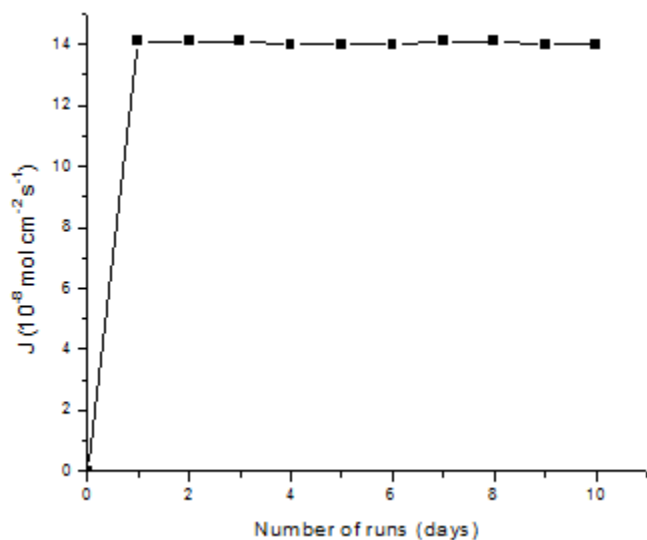


Fig. 10. Stability of SLM, flux versus time.

(Initial $[\text{Cr}^{6+}] = 19.2 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] = 1.5 \text{ mol L}^{-1}$, $[\text{DPC}] = 0.001 \text{ mol L}^{-1}$, $[\text{H}_2\text{SO}_4] = 1 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.1 \text{ mol L}^{-1}$).

3.4.1.7 Extraction of Cr (VI) ions from Paint Industry Wastewater

The SLM designed for Cr (VI) ion extraction shows efficient transport ability. One of the common application of chromium is its use in paint industry [1]. The optimized conditions were employed for the recovery of chromium from paint industry waste water. The waste water was filtered with filter paper (Whatman); 80 mL of filtrate was taken and diluted up to 250 mL with distilled water. In the presence of other metals i.e. Co (II), Cd (II), Cu (II) and Mn (II) the chromium (VI) ion transport through the SLM was carried out. It was noted that only Cr (VI) ions were transported through the membrane. This shows the selectivity of the TOPO towards Cr

(VI) under these experimental conditions. This analysis is shown in Table 1 and it shows that almost 80% Cr (VI) ions were selectively recovered (Fig. 11).

A careful analysis of the Fig. 13 shows that the concentration of chromium (VI) ions in the final solution after the extraction through the membrane contains $0.63 \times 10^{-3} \text{ mol L}^{-1}$ Cr (VI) which corresponds to about 33 ppb chromium concentration. According to WHO recommend maximum allowable concentration in drinking water for Cr (VI) is 50 ppb. In our case the released water has 33 ppb concentration of Cr (VI) which falls under the safer range of chromium. However, if someone is interested in even lower concentration of chromium in the effluent water, the solution in the feed side (having 33ppb Cr concentration) may be subjected to further extraction thus 6.6 ppb chromium will be left un-extracted in the feed side as 80% chromium will be extracted into the strip side.

Table 1. Analysis of Paint Industry Wastewater

S.No	Metal ion	Concentration of metals ions (mol L^{-1})		% Recovery
		B.E (Feed)	A.E (Strip)	
1	Cd	2.45×10^{-3}	0.00	-
2	Co	0.00	0.00	-
3	Cr	3.21×10^{-3}	2.58×10^{-3}	80
4	Cu	2.69×10^{-5}	0.00	-
5	Mn	7.28×10^{-6}	0.00	-

B.E = before extraction

A.E = after extraction

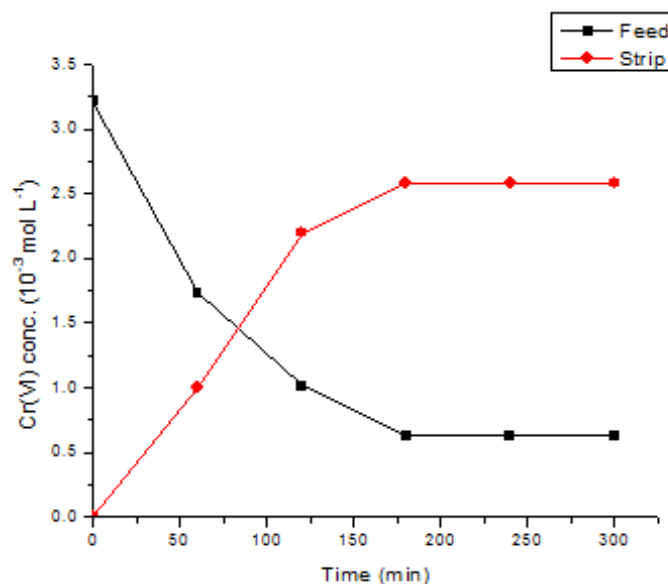


Fig. 11. Variation in Cr (VI) ion concentration in the feed and strip solution versus time (Paint industry waste solution in feed).

(Initial $[\text{Cr}^{6+}] = 3.21 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] = 1.5 \text{ mol L}^{-1}$, $[\text{DPC}] = 0.001 \text{ mol L}^{-1}$, $[\text{H}_2\text{SO}_4] = 1.5 \text{ mol L}^{-1}$, $[\text{TOPO}] = 0.1 \text{ mol L}^{-1}$).

Conclusion

The present study demonstrates that the Cr (VI) can be efficiently and selectively transported through the supported liquid membrane by using TOPO as a carrier. The effects of different parameters, such as concentrations of chromium ion, H_2O_2 , TOPO, DPC, and H_2SO_4 were studied on the extraction of chromium. The experimental results revealed that maximum chromium extraction was achieved with $19.2 \times 10^{-4} \text{ mol L}^{-1}$ initial chromium ion concentration and $1.5 \text{ mol L}^{-1} \text{ H}_2\text{O}_2$ as feed phase; 0.1 mol L^{-1} TOPO concentration in membrane phase, while 0.001 mol L^{-1} of DPC, and $1.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ as stripping phase. The calculations of the percent recovery, distribution coefficient, flux, and permeability were made from the data on the optimum conditions. The extraction time for chromium ion transport was found to be 180

minutes at which the equilibrium has been established. The stability of SLM under optimum conditions was investigated and it was found that the membrane was stable at least up to 10 days. This SLM system was applied to remove Cr (VI) from the paint industry waste water with about 80% efficiency.

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Part IV

Extraction of Copper (II)

Extraction of Copper from Wastewater through Supported Liquid Membrane using Tri-ethanolamine as a Carrier

3.5 Theory

3.5.1 Proposed Mechanism of Copper (II) ions Transport through Supported Liquid Membrane

The extraction chemistry of metal ion through SLM is similar to that of liquid-liquid extraction. In this process, the ion-pair association mechanism is involved in the extraction of copper (II) ion as shown in Fig.1. During the process the carrier makes a neutral ion-pair complex with the metal ions as shown in the proceeding discussion. This complex is transported through hydrophobic membrane phase.

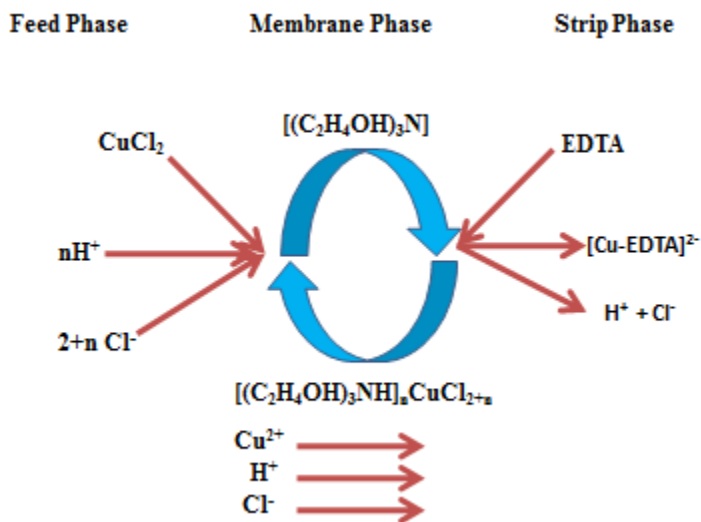


Fig. 1. Transport mechanism of Cu(II) ions through supported liquid membrane.

In acidic medium, the protonation of TEA molecule takes place [1], which is as follows:



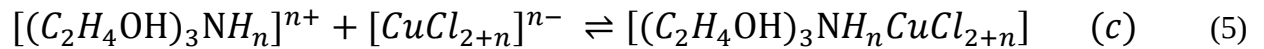
Where 'n' may possibly be 1,2,3, or 4, maximum protonation up to 4 can take place in TEA molecule as it has one nitrogen and three oxygen atoms. The value of 'n' will be determined experimentally. Specie (a) will associate with a copper (II) ion in the anionic form of the copper chloride (b).



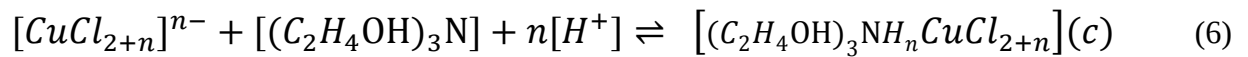
Or in general, depending upon the association number "n"



At the feed-membrane interface, anionic species (b) will associate with cationic specie (a) of tri-ethanolamine.

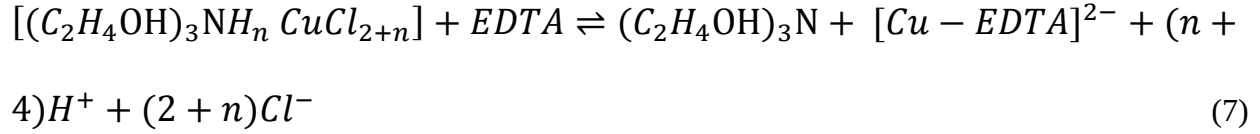


Or Eq. (5), can be written as



Specie (c) is permeated through the membrane phase and discharges copper (II) ions at strip-membrane interface due to reaction of copper (II) ions with EDTA of the strip solution.

This experiment has been carried out at pH 10, at which the EDTA is in the form of $(EDTA)^{4-}$, which associates with the copper ion very effectively as $Cu(EDTA)^{2-}$ as follows:



It may be noted that each molecule of EDTA releases four H^+ ions.

It can also be noted from Eq.(7) that Cu-TEA complex, $[(C_2H_4OH)_3NH_n CuCl_{2+n}]$, becomes unstable in the basic medium, as a result it decomposes into TEA molecules, which remains in the membrane phase, while copper is released into the strip phase as copper-EDTA complex, $[CuEDTA]^{2-}$.

From Eq.(6) the equilibrium constant for copper (II) ion for feed and membrane phase can be given as,

$$K_{Cu} = \frac{[(C_2H_4OH)_3NH_n CuCl_{2+n}]}{[(CuCl_{2+n})^{n-}][(C_2H_4OH)_3N][H^+]^n} \quad (8)$$

The distribution coefficient of copper (II) ions for between the membrane and the aqueous phase is denoted by λ_{Cu} and can be given as

$$\lambda_{Cu} = \frac{[(C_2H_4OH)_3NH_n CuCl_{2+n}]}{[(CuCl_{2+n})^{n-}]} \quad (9)$$

In the light of Eq. (9), Eq. (8), can be written as

$$K_{Cu} = \frac{\lambda_{Cu}}{[(C_2H_4OH)_3N][H^+]^n} \quad (10)$$

On rearranging Eq. (10), we obtain

$$\lambda_{Cu} = K_{Cu}[(C_2H_4OH)_3N] [H^+]^n \quad (11)$$

The Fick's First Law is given as below [2].

$$J = \frac{dn}{dt} = -DA \frac{dc}{dx} \quad (12)$$

where J is the rate of diffusion of solute across an area A, known as diffusion flux.

Where $\frac{dc}{dx}$, is the concentration gradient of the metal ions and dn is the amount of metal ions crossing the area A in time interval dt.

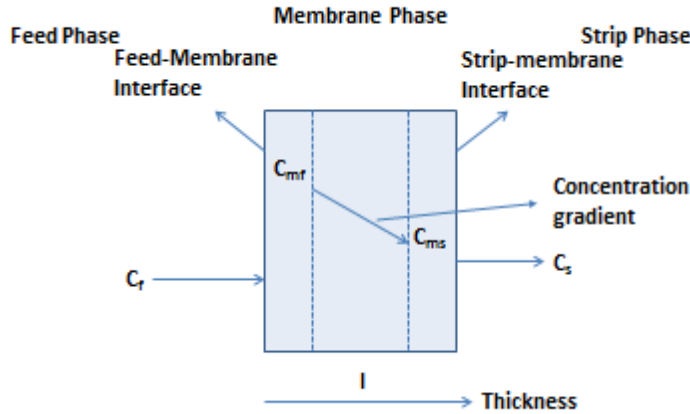


Fig. 2. Concentration gradient of copper (II) ions at the feed and strip sides of the membrane.

Since solutions are stirred therefore, the metal ion concentration in feed and strip phases, C_f and C_s respectively, are maintained at a uniform level throughout the bulk i.e. there is no concentration gradient in the feed and strip phases. The two solutions are separated by a membrane of thickness ' l ', as shown schematically in Fig. 2. The membrane contains pores filled with extractant dissolved in diluent which is responsible for the transport of metal ions. The

concentration of the metal ions falls linearly within the membrane constituting a concentration gradient, as shown in Fig. 2. Which is given as follows

$$-\frac{dc}{dx} = \frac{C_{fm}-C_{sm}}{l} \quad (13)$$

According to the Fick's First Law, the rate of flow through the membrane is

$$\frac{dn}{dt} = DA \frac{C_{fm}-C_{sm}}{l} \quad (14)$$

Since the concentration gradient, $\frac{dc}{dx}$, is negative which cancels out the negative sign in Eq. (12), and hence in Eq. (14)

The diffusion coefficient D can be readily calculated from the measurement of the rate of flow, $\frac{dn}{dt}$; the area A , thickness l , and the concentration difference $C_{fm} - C_{sm}$, where C_{fm} and C_{sm} are concentrations of metal ions at the membrane interfaces of feed and strip sides respectively.

The distribution coefficient of Cu(II) ions at the membrane interfaces of the feed and strip side can be given by λ_f and λ_s respectively i.e.

$$\lambda_f = \frac{C_{fm}}{C_f} \text{ and } \lambda_s = \frac{C_{sm}}{C_s} \quad (15)$$

Where C_f and C_s represent feed and strip phase concentration of Cu(II)ions respectively.

From Eq. (15) we can write

$$C_{fm} = \lambda_f C_f \text{ and } C_{sm} = \lambda_s C_s \quad (16)$$

And with the help of Eq. (16), Eq. (14) becomes

$$J = DA \left(\frac{\lambda_f C_f - \lambda_s C_s}{l} \right) \quad (17)$$

As there is no extraction from the strip to the membrane phase, i.e. there is no back extraction, so $\lambda_s \rightarrow 0$ and as a result, $\lambda_s C_s \approx 0$ and Eq. (17), converts to

$$J = DA \left(\frac{\lambda_f C_f}{l} \right) \quad (18)$$

In our case $\lambda_f = \lambda_{Cu}$, as given by Eq. (11), thus Eq. (18) may be written as

$$J = DA \frac{K_{Cu} [(C_2H_4OH)_3N] [H^+]^n C_f}{l} \quad (19)$$

According to Wilke- Chang relation

$$D = \frac{\dot{k}T}{\eta} \quad (20)$$

Where T is the absolute temperature, η is the viscosity and $\dot{k}$ is constant and so

$$J = \frac{\dot{k}T}{\eta} A \frac{K_{Cu} [(C_2H_4OH)_3N] [H^+]^n C_f}{l} \quad (21)$$

Since $\dot{k}$, K_{Cu} , T, l and A are constants, and if C_f does not change rapidly, then C_f can be taken approximately constant for a short interval of time, combining all these as $\check{K}$ (i.e. $\check{K} = \dot{k}K_{Cu}T C_f A / l$) we obtain

$$J = \frac{\check{K} [(C_2H_4OH)_3N] [H^+]^n}{\eta} \quad (22)$$

Readjusting Eq. (22)

$$J\eta = \check{K}[(C_2H_4OH)_3N] [H^+]^n \quad (23)$$

Taking log of Eq. (23)

$$\log J\eta = \log \check{K} + \log[(C_2H_4OH)_3N] + n \log [H^+] \quad (24)$$

Since a specially designed experiment was carried out by keeping $\check{K}$, $[(C_2H_4OH)_3N]$, C_f as constants in order to study the effect of H^+ concentration on extraction of copper ions, therefore, the terms involving these parameters in Eq.(24) can be collected in a single parameter as follows:

$$L = \log \check{K} + \log[(C_2H_4OH)_3N] \quad (25)$$

Hence Eq. (25), becomes

$$\log J\eta = L + n \log [H^+] \quad (26)$$

From the above Eq. (25) the stoichiometry of the Cu-TEA complex formation can be determined by calculating the number of H^+ ion 'n' associated with the TEA molecule in the form of $[(C_2H_4OH)_3NH_n]^{n+}$. Eq. (25) is a straight line equation in which $\log J\eta$ versus $\log [H^+]$ can be plotted, from the slope of this curve we can calculate the number of protons 'n' associated with the TEA carrier.

3.5.2 Result and Discussion

3.5.2.1 The effect of TEA carrier Concentration on Copper (II) Extraction

The effect of TEA concentration on the extraction of copper has been graphically represented in Fig. 3. The concentration of TEA has been studied in the range from 1 mol L⁻¹ to 4 mol L⁻¹. The transport of Cu (II) ions increases with the increase in the concentration of TEA. From the figure, it is clear that with the passage of time, the concentration of Cu (II) ions decreases in feed (Fig.3a) while at the same time it increases in strip phase (Fig.3b). It can be carefully analyzed that at any particular time, the concentration of copper ions in the feed phase supplements that of in the strip phase i.e. it shows an additive behavior. It can be further noted that with the increase in TEA concentration the extraction of copper increases, reaches at maximum at 3.5 mol L⁻¹ of TEA, beyond that it decreases. The initial increase in the transport of copper with the increasing TEA concentration corresponds to the high transport ability of the carrier which enhances the rate of formation of Cu-TEA complex and facilitates the transport of copper (II) ion and hence the distribution coefficient value of copper (II) ion at the feed-membrane interface increases with increase in the concentration of TEA. The decline in the extraction of copper (II) ion beyond 3.5 mol L⁻¹ concentration of TEA is due to the high viscosity of TEA which renders the complex difficult to diffuse in the membrane phase [2]. Thus, the optimum extraction value was obtained at 3.5 mol L⁻¹ of TEA.

Fig. 4 indicates the influence of TEA concentration on the flux value of Cu (II) ion extraction. The flux per unit area of copper ions was calculated using Eq. (1). There is a gradual increase in the flux value with increasing concentration of TEA, and it reaches to a maximum value of $2.84 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$ at 3.5 mol L⁻¹ TEA. As discuss previously, this tumble in flux

value attributed to increase in TEA solution viscosity which impedes the transport of copper (II) ions due to the limited movement of Cu-TEA complex ion towards the strip side.

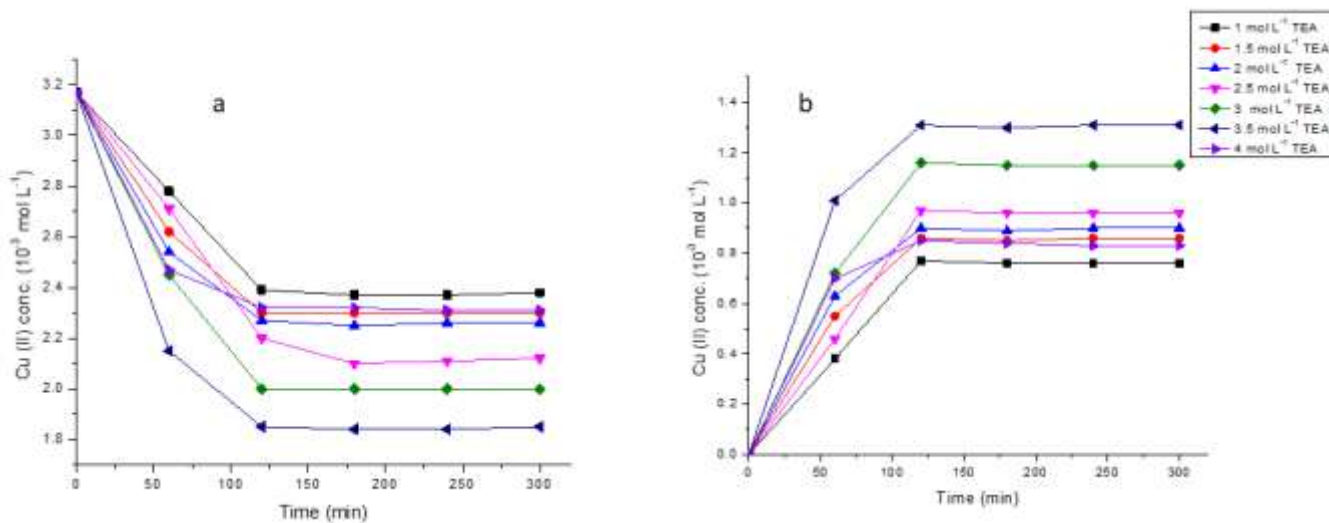


Fig. 3. Variation in Cu(II) ion concentration with time in feed (a) and strip (b) solutions at various concentrations of TEA.

($[\text{Cu}^{2+}] = 3.17 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{EDTA}] = 0.02 \text{ mol L}^{-1}$, $[\text{TEA}] = 1\text{--}4 \text{ mol L}^{-1}$, $\text{pH} = 10$).

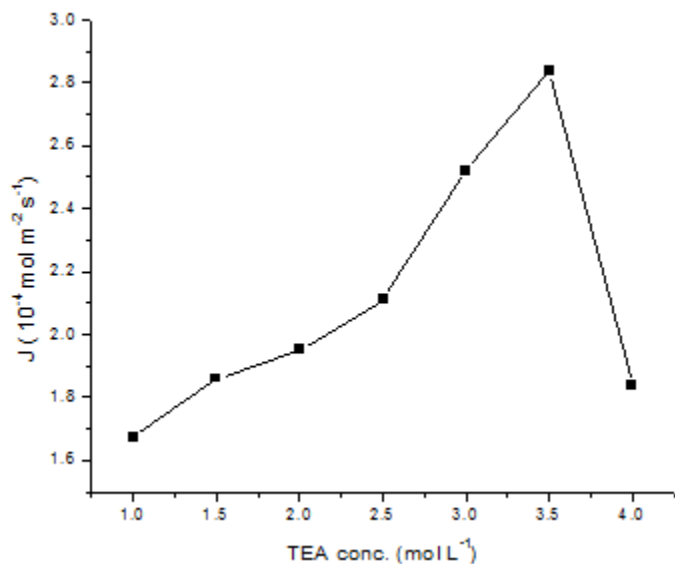


Fig. 4. Effect of TEA concentration on flux.

($[\text{Cu}^{2+}] = 3.17 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{EDTA}] = 0.02 \text{ mol L}^{-1}$, $[\text{TEA}] = 1\text{--}4 \text{ mol L}^{-1}$, $\text{pH} = 10$).

3.5.2.2 The Effect of Concentration of Copper (II) ion on Extraction

In the case of EDTA strippent, the extraction of copper (II) ions is being strongly affected by its own concentration. In the experiment, 1 mol L⁻¹ HCl in the feed and 0.03 mol L⁻¹ EDTA in strip solution at pH 10 were employed. The copper concentration was varied from 0.79 to 3.97×10⁻³ mol L⁻¹. The variation in copper (II) ion concentration with respect to time both for the feed and strip solutions have been represented in Fig. 5. With the passage of time, the copper (II) ion concentration in the feed decreases and increases in strip phase. It can be noted from Fig.5 that the extraction becomes maximum at 3.17×10⁻³ mol L⁻¹ of copper ion concentration beyond which it decreases. This could be attributed to the following reason. As mentioned in Eq.(7) with the associated discussion, copper forms a complex with EDTA which is present in the strip side and plays the role of strippent.



EDTA has a strong affinity for the formation of such complex with copper this is true up to 3.17×10⁻³ mol L⁻¹ copper (II) concentration, in the present case, with the further increase in copper (II) concentration the neutral Cu₂-EDTA complex is formed which is insoluble in aqueous medium and results in the formation of precipitate [3].



The deposition over the surface of the membrane might have clogged the membrane pores and thus, altered the extraction.

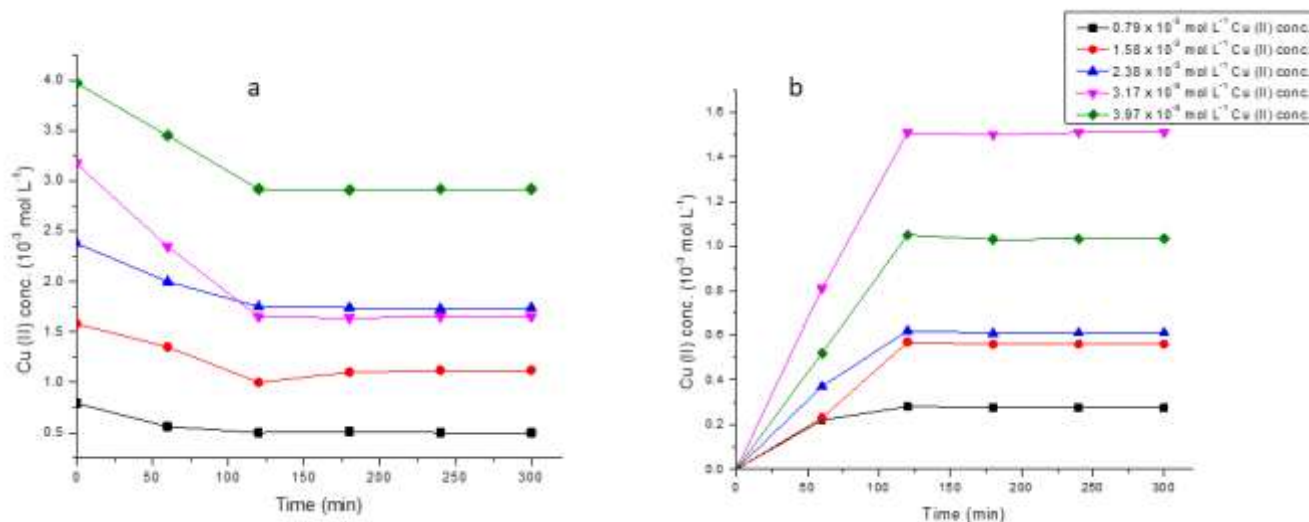


Fig. 5. Variation in Cu (II) ion concentration with time in feed (a) and strip (b) solutions at various concentrations of Cu (II) ions.

$[\text{Cu}^{2+}] = 0.79\text{--}3.97 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{EDTA}] = 0.03 \text{ mol L}^{-1}$, $[\text{TEA}] = 3.5 \text{ mol L}^{-1}$, $\text{pH} = 10$).

Fig. 6 shows the effect of Cu (II) ion concentration on the flux. The flux exhibits the maximum value of $3.28 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$ at $3.17 \times 10^{-3} \text{ mol L}^{-1}$ of copper ion concentration beyond which it shows a decreasing trend. The decrease in the flux value is attributed to the aforementioned reason.

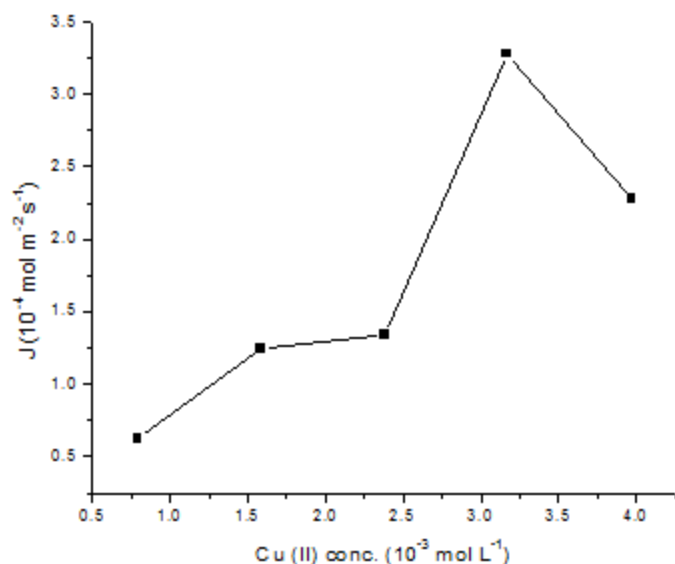


Fig. 6. Effect of Cu (II) ion concentration on flux.

($[\text{Cu}^{2+}] = 0.79\text{--}3.97 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{EDTA}] = 0.03 \text{ mol L}^{-1}$, $[\text{TEA}] = 3.5 \text{ mol L}^{-1}$, $\text{pH} = 10$).

3.5.2.3 The Effect of Concentration of HCl on Copper (II) Extraction

The effect of HCl concentration on the copper transport from feed to strip phase is shown in Fig. 7(a-b). The Cu (II) ions transportation is affected by the presence of HCl in which the Cu(II) ions are converted into CuCl_2 but an excess amount of HCl leads to the formation of $[\text{CuCl}_n]^{2-n}$ complex, while the H^+ ions protonate the TEA molecules. The $[\text{CuCl}_n]^{2-n}$ complex ions associate with the protonated TEA molecules at feed-membrane interface and thus further process of transportation is carried out. A limited chloride ions concentration also have synergetic effect on the transport of copper. The $\text{Cl}^-/\text{Cu}^{2+}$ ratio possibly affects the efficiency of extraction. Insufficient amount of Cl^- ions leads to the formation of CuCl^+ while with the excess of Cl^- ions, CuCl_3^{3-} or CuCl_4^{2-} were mainly formed [4] in these complexes $\text{Cl}^-/\text{Cu}^{2+}$ ratio increases which helps the copper ions transportation. Further increase in the chloride ions concentration inhibits the formation of $[\text{CuCl}_n]^{2-n}$ complex due to common ion effect.

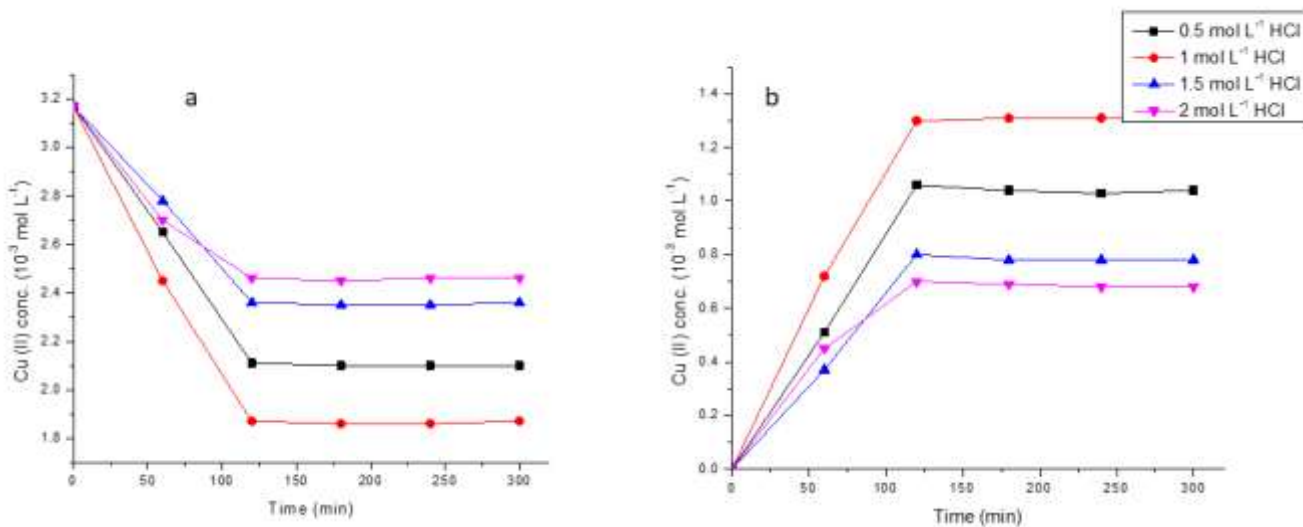


Fig. 7. Variation in Cu(II) ion concentration with time in feed (a) and strip (b) solutions at various concentrations of HCl.

([Cu²⁺] = 3.17 × 10⁻³ mol L⁻¹, [HCl] = 0.5–2 mol L⁻¹, [EDTA] = 0.03 mol L⁻¹, [TEA] = 3.5 mol L⁻¹, pH = 10).

Fig. 8 illustrates the effect of HCl concentration on the flux of copper ions through the membrane. As can be noted from the Fig, the flux value increases as the concentration of HCl increases and gives a highest flux value of 2.80×10^{-4} mol m⁻² s⁻¹ at 1 mol L⁻¹ HCl and then it gradually drops down. The decrease in the flux beyond 1 mol L⁻¹ HCl is due to the excess amount of H⁺ concentration which suppresses the extraction. If the amounts of protons increase beyond 1 mol L⁻¹ HCl, there may be difficulties in dissociating MCl₄²⁻ from H₂MCl₄ in the feed phase [5]. The result causes the decrease of flux.

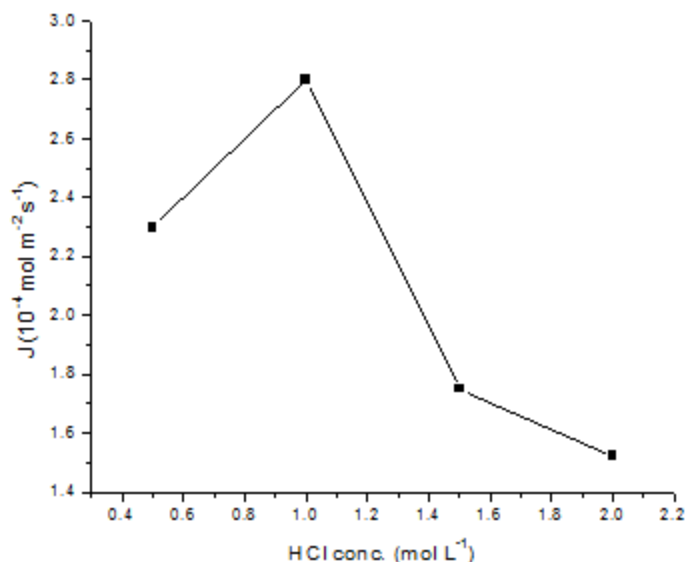


Fig. 8. Effect of HCl concentration on flux of copper ions.

([Cu²⁺] = 3.17×10⁻³ mol L⁻¹, [HCl] = 0.5-2 mol L⁻¹, [EDTA] = 0.03 mol L⁻¹, [TEA] = 3.5 mol L⁻¹, pH = 10).

The pH change of the feed solution, with respect to time, is shown in Fig. 9. During a particular extraction experiment the pH almost remains constant at the beginning and rises gradually and then an abrupt increase is observed between the 80th and 120th minutes of the experiment. The initially increase in the pH may be attributed to the reason that the protons are reacting with carrier (TEA) molecules at the feed membrane interface to convert it into a charged species by protonation. Since protons are transferred towards the strip side, which results in the further increase in pH.

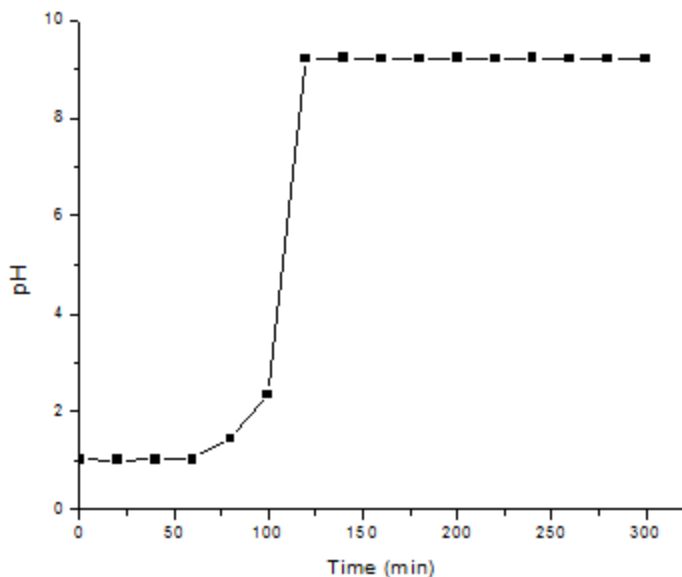


Fig. 9. Variation in pH of feed solution with time.

($[\text{Cu}^{2+}] = 3.17 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{EDTA}] = 0.03 \text{ mol L}^{-1}$, $[\text{TEA}] = 3.5 \text{ mol L}^{-1}$, $\text{pH} = 10$).

3.5.2.4 Determination of 'n'

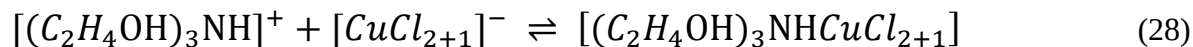
Eq.(25) can be used to determine the number of H^+ ion 'n' associated with TEA in the form of $[(\text{C}_2\text{H}_4\text{OH})_3\text{NH}_n]^{n+}$. This equation is a straight line equation where $\log J\eta$ can be plotted on the y axis and $\log [\text{H}^+]$ on the x axis. The value of 'n' can be determine from the slope of the curve.

$$\log J\eta = D + n \log [\text{H}^+] \quad (25)$$

Fig.10 shows the plot of $\log J\eta$ versus $\log [\text{H}^+]$. The plot shows an increasing trend in the flux with increase in H^+ ion concentration. The slope of the curve gives a value of 1. Thus, one H^+ ion is associated with the complex $[(\text{C}_2\text{H}_4\text{OH})_3\text{NH}_n]^{n+}$ that is, the complex has the form like $[(\text{C}_2\text{H}_4\text{OH})_3\text{NH}]^+$ and further we can say that the copper-chloride anionic complex has the

form of $[CuCl_{2+1}]^-$. The copper-TEA complex, thus attain the form $[(C_2H_4OH)_3NHCuCl_{2+1}]$.

Hence, in the light of this discussion Eq. (5), can be written as



Which predicts the stoichiometry of the complex formation.

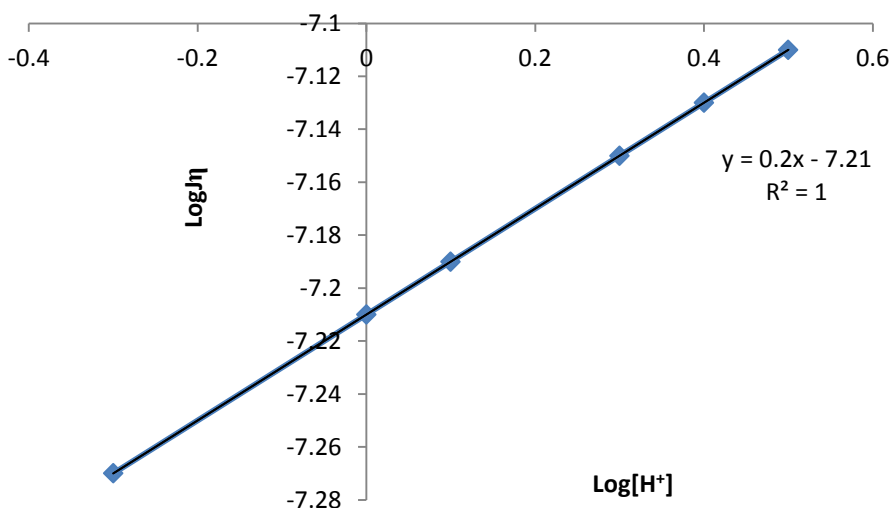


Fig. 10. The Plot of $\text{Log} J\eta$ versus $\text{Log} [H^+]$.

3.5.2.5 The Effect of Nature and Concentration of Stripping Reagent on the Copper (II) Extraction

Effectiveness of various stripping reagents such as, sodium carbonate, nitric acid, oxalic acid, sodium sulphate, and EDTA, were studied for the extraction of copper (II) ions and it was noticed that the EDTA is a best stripping agent among all these reagents as shown in Fig.11. The formation of $Cu-EDTA^{2-}$ complex ion depends on the concentration of the EDTA and pH of the strip solution. It has been observed that the pH has a high influence on the extraction process. Good extraction is achieved at alkaline medium (pH= 10) because in alkaline solution, the formation of $Cu-EDTA^{2-}$ takes place while in acidic medium, the precipitates of Cu_2-EDTA

complex is occur [6]. Thus, the stripping solution should be kept constant at pH 10 by using ammonia buffer solution.

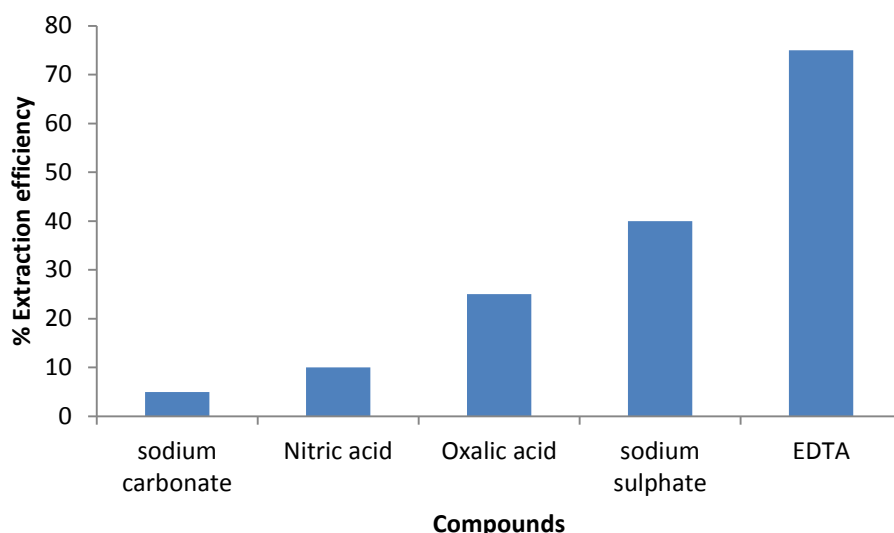


Fig. 11. Effect of different stripping reagents on the extraction of Copper (II).

The effect of EDTA concentration on the Cu (II) ion extraction is shown in Fig. 12. The study was conducted at pH 10 in the strip side keeping other parameters at constant level such as 1 mol L^{-1} HCl concentration and $3.17 \times 10^{-3} \text{ mol L}^{-1}$ Cu (II) ions in the feed phase and 3.5 mol L^{-1} TEA in membrane phase. The concentration of EDTA was investigated in the range of 0.01 mol L^{-1} to 0.05 mol L^{-1} . From the curves in (Fig.12), it can be observed that the extraction of Cu (II) ion increases with the increase in the concentration of EDTA up to 0.03 mol L^{-1} , and then decreases gradually. Beyond 0.03 mol L^{-1} EDTA, the extraction abruptly falls, which might be due to overcrowding of EDTA molecules at strip-membrane interface, which blocks the membrane. Below 0.03 mol L^{-1} , fewer EDTA molecules were available to form a Cu-EDTA^{2-} complex ion [6] and hence extraction of copper is dependent upon the concentration of EDTA. The optimum concentration of EDTA is 0.03 mol L^{-1} .

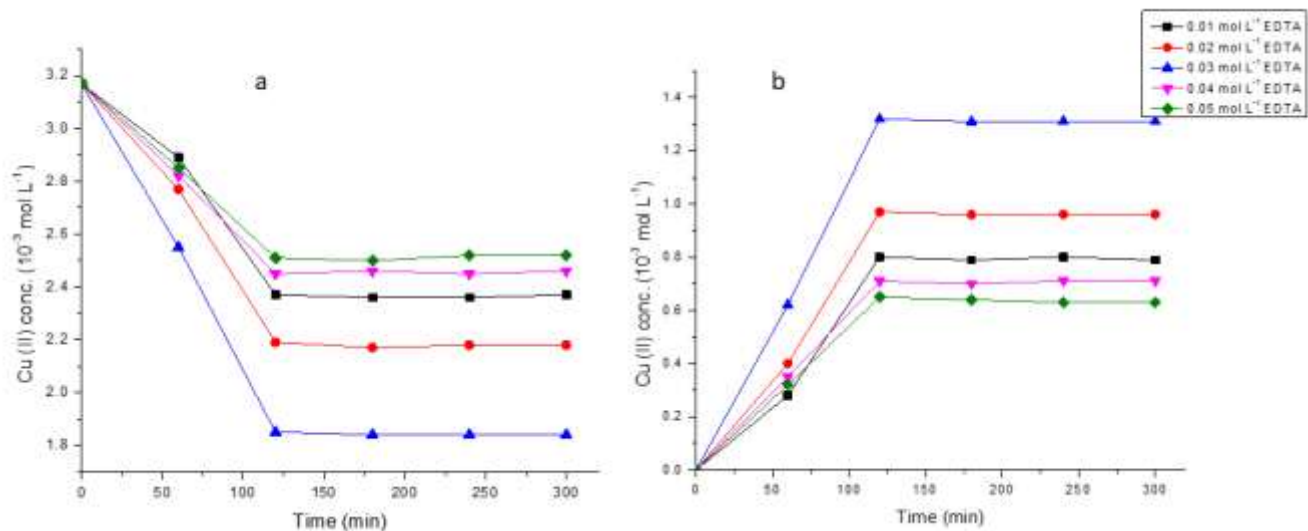
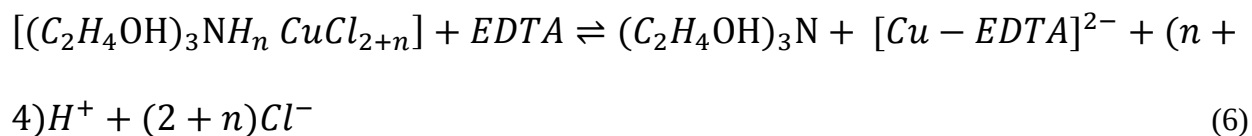


Fig. 12. Variation in Cu(II) ion concentration with time in feed (a) and strip (b) solutions at various concentrations of EDTA.

([Cu²⁺] = 3.17 × 10⁻³ mol L⁻¹, [HCl] = 1 mol L⁻¹, [EDTA] = 0.01-0.05 mol L⁻¹, [TEA] = 3.5 mol L⁻¹, pH = 10).

The flux profile of copper ions is displayed in Fig. 13. Initially the flux value increases somewhat rapidly upto 0.03 mol L⁻¹, where after, it decreases with concentration. From the profile the maximum value of flux can be noted which is 0.03 mol L⁻¹ of EDTA.

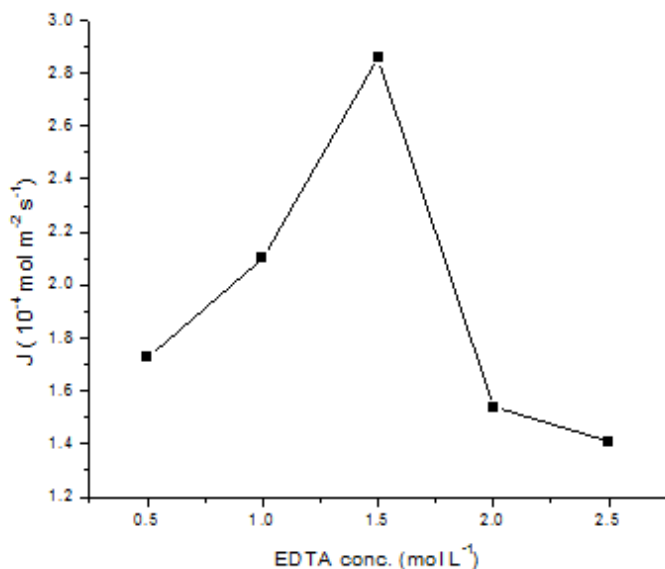


Fig. 13. Effect of EDTA concentration on flux.

([Cu²⁺] = 3.17×10⁻³ mol L⁻¹, [HCl] = 1 mol L⁻¹, [EDTA] = 0.01-0.05 mol L⁻¹, [TEA] = 3.5 mol L⁻¹, pH = 10).

3.5.2.6 SEM Analysis

The membrane is an important part of the SLM technique and influences the transport of metal ions. The surface morphology of the membrane, Celgard 2400, was evaluated by scanning electron microscope images (SEM). The SEM images of the membrane before and after the extraction is given in Fig. 14 (a-b). The porous cracks or grooves in the membrane can be seen before the extraction while some deposits can be seen after the experiment along with the pores and cracks. Fig. 14c shows the cross sectional image of the membrane, from which the thickness of the membrane can be calculated and it is found to be 20.36 μm.

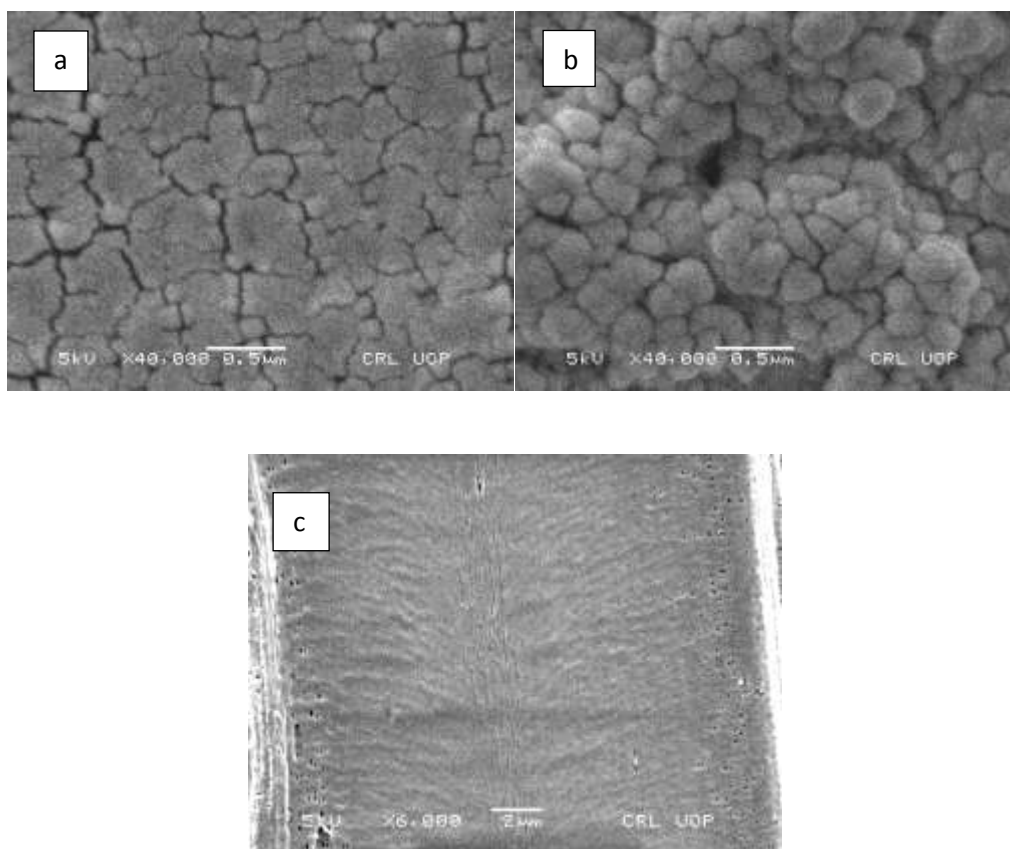


Fig. 14 SEM images of membrane (a) before extraction (b) after extraction (c) cross section image.

3.5.2.7 Extraction Time

The Fig. 15 shows the effect of extraction time on copper ions. At optimum conditions, the extraction of copper (II) ions increases with time and after 120 min about 87% of copper (II) ion has been extracted. The concentration of copper (II) ions become independent of the time after 120 min and further transport of copper ions to strip phase did not occur.

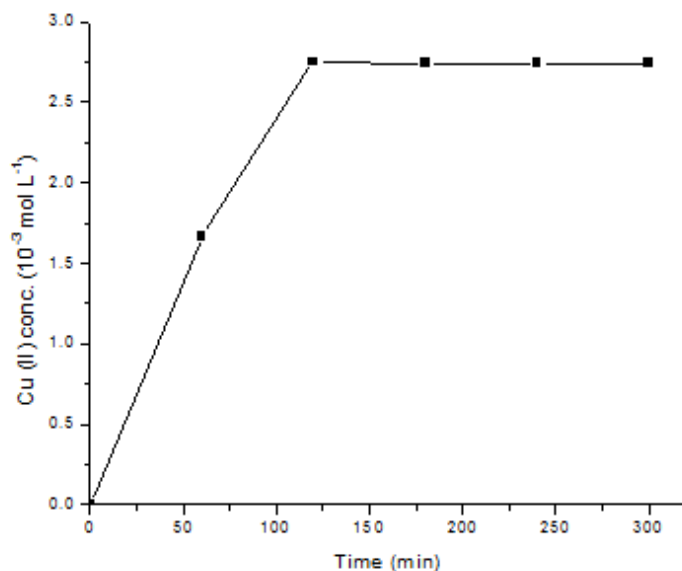


Fig. 15. Variation in Cu(II) ion concentration with time.

($[\text{Cu}^{2+}] = 3.17 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{EDTA}] = 0.03 \text{ mol L}^{-1}$, $[\text{TEA}] = 3.5 \text{ mol L}^{-1}$, $\text{pH} = 10$).

3.5.2.8 Membrane Stability

Low stability of membrane is one of the main drawbacks of the SLM technique. The porous materials are used as supports for SLMs in which the carrier molecules are embedded in membrane pores. After prolonged use, the performance of membrane decreases. This happens due to loss of membrane solvent or carrier, formation of emulsion, chemical degradation, etc. [7-8]. To study the long term membrane stability, the extraction experiments were carried out consistently for 10 days (one experimental run per day) under the optimum conditions. For all these experiments the membrane was impregnated only once, while changing the feed and strip solutions after each run. The cell was kept filled with distilled water, between the successive experiments, in order to prevent the dryness of the membrane. The optimum experimental conditions were as follows; feed Cu (II) ion concentration was at $3.17 \times 10^{-3} \text{ mol L}^{-1}$ and 1 mol L^{-1} HCl, the TEA and EDTA concentrations were kept constant at 3.5 mol L^{-1} in cyclohexanone

and 1 mol L^{-1} respectively, and the stirring speed was at 1500 rpm. The result reveals (Fig. 16) that the efficiency of the membrane has not decreased during these experiments and hence, during all the experiments, the extraction of the copper (II) ion was not affected and stayed at 87%.

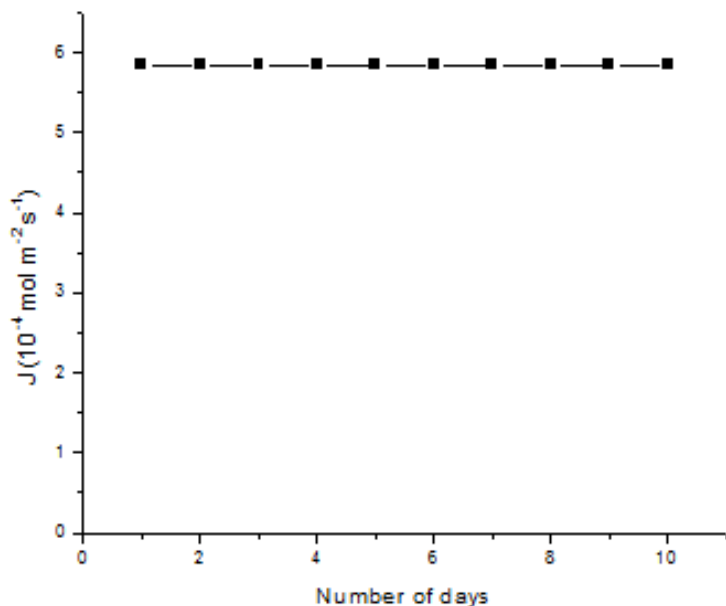


Fig. 16. Stability of SLM, flux versus time.

($[\text{Cu}^{2+}] = 3.17 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{EDTA}] = 0.03 \text{ mol L}^{-1}$, $[\text{TEA}] = 3.5 \text{ mol L}^{-1}$, $\text{pH} = 10$).

3.5.2.9 Extraction of Copper(II) from Industrial Wastewater

The optimized experimental conditions were used for the removal of copper from match industrial waste water. The waste water sample was analyzed for different metal ions, the result is shown in Table 1 (column 2 and 3). The wastewater was filtered with Whattman filter paper; 80 mL of filtrate was diluted up to 250 mL with distilled water and taken as the feed solution. The extraction experiment was performed at optimum conditions as mentioned in section 3. Analysis of wastewater was carried out through AAS and result is shown in Fig. 17-18 and the

data are reproduced in the Table 1. The study demonstrated that about 87% copper (II) ions were recovered. The results also reveal that a little extraction of other ions also takes place.

Table 1 Analysis of Match Industry Wastewater

S. No	Metal ion	Concentration of metals (mol L ⁻¹)		% Recovery
		Before extraction (feed phase)	after extraction (strip phase)	
1	Cu	1.50×10^{-4}	1.31×10^{-4}	87.33
2	Cd	4.45×10^{-6}	0.45×10^{-6}	10.11
3	Pb	6.82×10^{-5}	1.25×10^{-6}	1.83
4	Zn	3.18×10^{-5}	1.10×10^{-6}	3.45

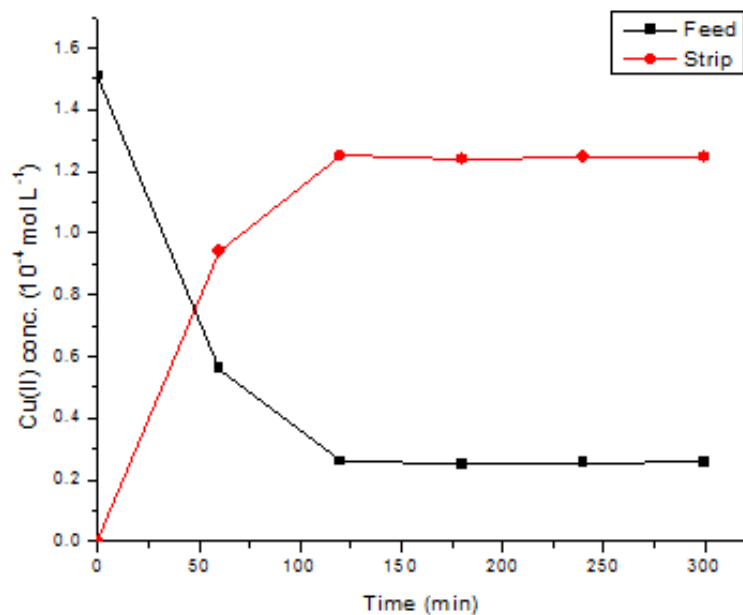


Fig. 17. Variation in Cu (II) ion concentration in feed and strip solution versus time (match industry waste solution in feed).

($[\text{Cu}^{2+}] = 1.50 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{EDTA}] = 0.03 \text{ mol L}^{-1}$, $[\text{TEA}] = 3.5 \text{ mol L}^{-1}$, $\text{pH} = 10$).

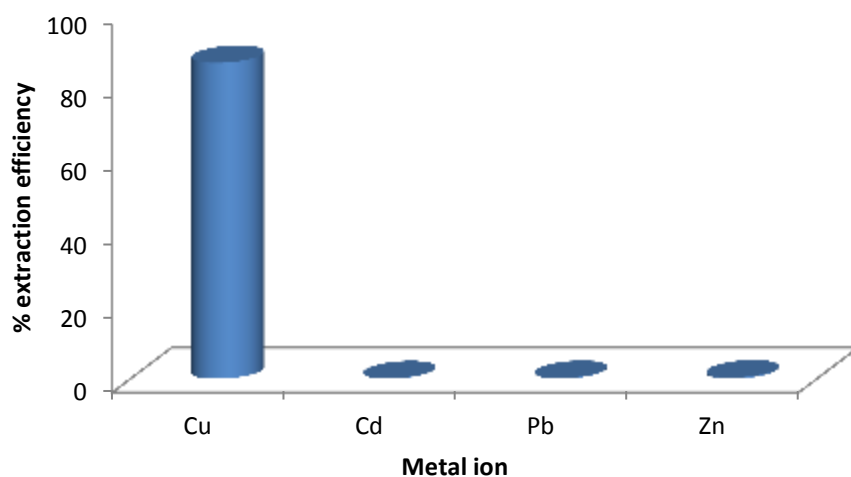


Fig. 18. % Extraction efficiency of different metal ions from match industrial waste water.

Conclusion

The flat-sheet supported liquid membrane technique based on TEA-cyclohexanone has been employed for the transport of Cu (II) ions. The important parameters have been investigated to achieve the best set of the operating conditions for maximum separation of copper (II) ions from aqueous solution through SLM. The maximum extraction was obtained at 3.5 mol L⁻¹ TEA concentration with a flux value of 2.84×10^{-4} mol m⁻² s⁻¹. In the feed phase 3.17×10^{-3} mol L⁻¹ of copper (II) ions concentration exhibited the highest extraction with flux value of 3.28×10^{-4} mol m⁻² s⁻¹, while 1 mol L⁻¹ HCl has delivered the flux value of 2.80×10^{-4} mol m⁻² s⁻¹ for copper (II) ions. Thus, 3.17×10^{-3} mol L⁻¹ of copper (II) ions concentration and 1 mol L⁻¹ HCl are the optimum conditions for the extraction of copper (II) ions. Whereas in strip phase, 0.03 mol L⁻¹ of EDTA concentration gives the highest value of flux of copper (II) ions, i.e. 2.86×10^{-4} mol m⁻² s⁻¹. Under these optimum experimental conditions, the maximum extraction efficiency of (87%) copper (II) ion was achieved. The extraction time for copper (II) ion transport has also been studied. The maximum extraction was found at 120 minutes. The equilibrium slope method was used to calculate the stoichiometry of Cu-TEA complex $[(C_2H_4OH)_3NHCuCl_{2+1}]$ and it was found that 1:1 mole ratio of TEA and H⁺ ion was involved in the Cu-TEA complex formation. The stability of SLM was also investigated under optimum experimental conditions and the result reveals that the membrane was quite stable for up to 10 extraction experiments. These optimized conditions were applied to recover Cu (II) ions from the match industry waste water and about 87% copper (II) ions were extracted. The whole study was replicated thrice with relative standard deviation of ± 2 .

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Part V

Extraction of Lead (II)

Removal of Lead (II) from Battery Industry Waste Water by Supported Liquid Membrane (SLM) with Aliquat 336 as Carrier

3.6 Theory

In the extraction process using supported liquid membrane the metal ion diffuses from the feed to the strip side through the membrane. In this work the extraction of lead has been studied in which $\text{Pb}(\text{NO}_3)_2$ was added in the feed side along with the KI. The membrane was impregnated with Aliquat 336, dissolved in toluene, which was used as a carrier. In the strip side NaOH was used as strippent. The schematic representation of the extraction process of lead is shown in Figure 1.

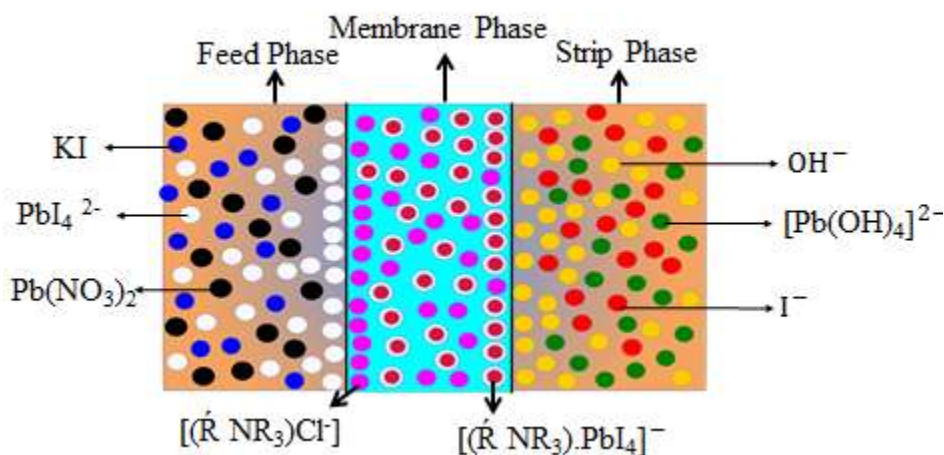


Fig. 1. Schematic Diagram Showing, Transport Mechanism of lead (II) ion.

Various reactions taking place in the three phases i.e. feed, membrane, and strip phases can be given as follows:

Reactions taking place in the feed side are given as under,



The addition of potassium iodide into the lead nitrate solution results in the formation of lead iodide.

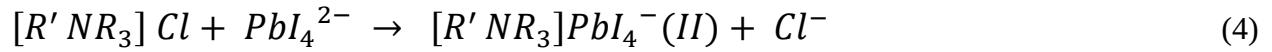


While in the presence of excess amount of the iodide ions lead forms a colorless soluble tetra-iodo plumbate (II) complex ion[1].

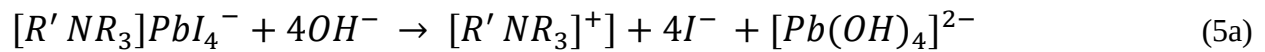


Where complex I is PbI_4^{2-}

At the feed-membrane interface the complex (I) reacts with Aliquat 336 and forms [lead iodo-Aliquat336] complex (II), $[R'NR_3]PbI_4^-$. The extraction mechanism of the Aliquat 336 is based on the anion exchange / ion association of the metals [2]. In case of lead extraction, the chloride ion of the Aliquat 336 is replaced by complex (I).



On the other hand complex (II) dissociates at strip-membrane interface in the presence of sodium hydroxide and Pb (II) is liberated in the form of soluble hydroxide in the stripping solution. The transport is thought to be coupled co-ion transport type, in which both Pb^{2+} and I^- in the complex form $[PbI_4]^{2-}$ are migrated towards the stripping solution(www.public.asu.edu/~jpbirk/qual/qualanal/lead.html) [3].



And Cl^- ions which were released by Aliquat 336 now recombine with $[R'NR_3]$ to regenerate Aliquat 336 again as follows:



The regenerated species act as carrier again.

The distribution coefficient K_{D_f} of lead between aqueous and membrane phase in the feed region is given by

$$K_{D_f} = \frac{[[R'NR_3]PbI_4^-]_{org}}{[PbI_4^{2-}]_{aq}} \quad (6)$$

While the distribution coefficient K_{D_s} in the strip region is given by following relation

$$K_{D_s} = \frac{[[R'NR_3]PbI_4^-]_{org}}{[[Pb(OH)_4]^{2-}]_{aq}} \quad (7)$$

The effects of various parameters, such as concentration of Aliquat 336, NaOH, Pb (II) metal ion, and KI, on the lead transport were investigated and evaluated by means of the permeability coefficient (P) as described by the mass-transfer model proposed by Danesi (1984) [4]. The permeability coefficient in the feed phase was calculated by using following equation:

$$\ln \frac{C}{C_o} = -\epsilon \frac{S}{V} Pt \quad (8)$$

Where P is the permeability coefficient (cm/s), C_o is the initial concentration of Pb (II) in the feed phase, and C is the concentration of Pb (II) in the feed phase at time t (s). S is the effective membrane area (cm²) and V (cm³) is the volume of the feed phase.

From the slope of the linear plot of $\ln \frac{C}{C_o}$ vs time the permeability coefficient can be obtained.

The flux value through the membrane was calculated using Eq. (9).

$$J_o = \left(\frac{dC_f}{dt}\right)_o \left(\frac{V}{S\epsilon}\right) \quad (9)$$

Where J_o is the initial flux (mol/cm².s), ϵ is porosity of the membrane, C_f is the concentration of lead (mol/L) in the feed phase at elapsed time, V (cm³) is the volume of the feed phase, and t is the time (s). Flux (J) was determine from the slope of concentration of lead in the feed phase versus time profile i.e $\frac{dC_f}{dt}$ and placing it in Eq. (9), while the volume of solution was 250 mL, and 'S' the surface area of the membrane was 24.64 cm² and porosity ϵ was 41%.

For the calculation of percent recovery of Pb(II) the following relation was used:

$$Recovery \% = 100 \left(\frac{C_s}{C_o} \right) \quad (10)$$

Where C_s and C_o are the concentrations of lead at elapsed time and at the commencement of the experiment respectively.

3.6.1 Result and Discussion

3.6.1.1 Effect of Concentration of Aliquat 336 on the Extraction of Lead

The concentration effect of Aliquat 336 on the lead (II) ion extraction was examined. For this purpose the membrane was impregnated with different compositions of Aliquat 336 (20-80%, v/v) diluted with toluene. In this experiment, the concentration of Pb(NO₃)₂ and NaOH was kept constant at 1.12×10^{-4} mol L⁻¹ and 1 mol L⁻¹ respectively. Figs. 2a and 2b illustrate the concentration effect of Aliquat 336 on the extraction of Pb²⁺ ion with respect to time. The extraction of Pb²⁺ ion rises as the Aliquat 336 concentration increases from 20-40%, as more Aliquat 336 molecules were available to react with Pb²⁺ ion to form a complex at feed-membrane interface. It can be noted from the Fig. 2b that there is a decrease in the extraction beyond 40% Aliquat 336 concentration where the concentration of the lead in the strip side is 9.16×10^{-5} mol L⁻¹. Further increase in the Aliquat 336 concentration has no effect on the transport of lead (II)

ion rather it decreases and reaches to $4.84 \times 10^{-5} \text{ mol L}^{-1}$ at 80% Aliquat 336 concentration. In the literature similar effect of the carrier concentration on the extraction has already been described [5]. The decrease in extraction can be attributed to the increased viscosity of Aliquat 336 solution which hampers the transport of lead ions. The viscosity versus concentration of aliquat 336 curve is shown in Fig. 3.

The diffusion coefficient is given by Stokes-Einstein equation [6]

$$D = \frac{KT}{6\pi\eta r} \quad (11)$$

This equation illustrates that the diffusion coefficient is inversely proportional to viscosity which hampers the diffusion of lead ion through the membrane and hence a decrease in the extraction is observed. Thus 40% Aliquat 336 composition is the optimum condition for extraction of Pb^{2+} ion for this SLM system, therefore, all subsequent calculations, i.e. percent recovery, distribution coefficient, flux and permeability coefficient etc., were made at this concentration.

At 40% Aliquat 336 concentration in the membrane phase the lead concentration in the strip phase was observed at the maximum level i.e. $9.15 \times 10^{-5} \text{ mol L}^{-1}$, which corresponds to 76% percent recovery. The percent recovery decreases with further increase in Aliquat 336 concentration (Fig.2b). As mentioned earlier this decrease may be attributed to decreased flux due to increase in viscosity of Aliquat 336-toluene solution in membrane phase.

The distribution coefficients of lead between aqueous and the membrane phases (Aliquat 336 -toluene), both for the feed and strip sides, are given by Eqs.(6,7) and the calculations were

made by taking care of mass balance of lead on the assumption that the total lead has been distributed among three phases i.e. feed, membrane, and strip as given by the following relation

$$Pb_{Tot} = Pb_f + Pb_s + Pb_m \quad (12)$$

Where Pb_{Tot} is the total lead concentration in the system and Pb_f , Pb_s , and Pb_m are the lead concentrations in the feed, strip, and membrane phases respectively.

Here Pb_{Tot} is the original or initial concentration taken for the experiment, and concentrations of lead in the feed and strip phases, at any elapsed time of the experiment were determined by atomic absorption spectroscopy. The concentration of lead in membrane phase was calculated by mass balance i.e.

$$Pb_m = Pb_{Tot} - Pb_f - Pb_s \quad (13)$$

This calculation was carried out at two different stages of the experiment i.e. when the system has not attained the equilibrium, the rising part of the concentration of lead versus time curve (Fig.2b), and secondly, when equilibrium has been attained, at the plateau of the same curve. Mass balance calculation at 60th minutes using Eq. (12) is as follows.

$$Pb_m = 0.15 \times 10^{-5} \text{ mol/L}$$

From this data we can calculate $K_{D_{f_1}}$ before equilibrium by using Eq. (6)

$$K_{D_{f_1}} = \frac{0.15 \times 10^{-5}}{5.72 \times 10^{-5}} = 0.026$$

On similar grounds K_D at equilibrium point (i.e. at 240 min), $Pb_{Tot} = 12.1 \times 10^{-5}$, $Pb_f = 2.9 \times 10^{-5}$, $Pb_s = 9.15 \times 10^{-5}$ which gives

$$Pb_m = 0.05 \times 10^{-5}$$

The $K_{D_{f_2}}$ at equilibrium becomes

$$K_{D_{f_2}} = \frac{0.05 \times 10^{-5}}{2.9 \times 10^{-5}} = 0.017$$

Thus distribution coefficient at 40% Aliquat 336 concentration (optimum concentration) before equilibrium is 0.026 while it is 0.017 after the equilibrium level is reached. The decrease in K_{Df} may be attributed to comparatively more decrease in the lead ion concentration in a membrane phase than in the feed phase. This indicates that the distribution of lead is higher in the membrane phase at the earlier stage of the experiment as compared to at the later stage. It will be instructive if we can compare distribution coefficient at a given time, of the feed and strip sides to elaborate this point further.

The concentration of lead at 240 min in strip side is $9.15 \times 10^{-5} \text{ mol L}^{-1}$ which gives a distribution coefficient of 0.006. Here the distribution coefficient at the feed side is 0.017 which is much greater than that of the corresponding value of 0.006 in the strip side which is about 3.1 times greater than that of the feed side. This comparison implies that there is a greater affinity of lead for the membrane phase in the feed region and lesser at strip phase. Thus, there is a natural tendency of lead flow from feed to strip side through the membrane and a driving force of diffusion exists at SLM together with enhanced lead de-complexing at the membrane-strip interface.

Flux of lead through the membrane was calculated using Eq. (9) in which the volume of the feed solution (V_f) was 250 cm^3 , the effective surface area (S) of the membrane was 24.64 cm^2 and its porosity (ϵ) was 41%. The factor $\frac{dC_f}{dt}$ was calculated from the slope of the concentration of lead in the strip region versus time curve which was taken at the initial time of the experiment i.e. the initial slope of the concentration versus time curve. This value was $1.73 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$ which gives the flux value (J_0 initial flux) of $4.3 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$. If we analyze the status of the flux just before the establishment of equilibrium, the slope at this region is $4.1 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$, which gives a flux value of $1.0 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$. Here we note that the flux value decreases from 4.3×10^{-9} to $1.0 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, which is an obvious phenomena that is lead transport decreases with the passage of time which becomes zero at equilibrium stage as can easily be predicted from the zero slope where the curve becomes parallel to the x-axis.

The permeability coefficient was calculated using Eq. (8), which was arranged in straight line form and slope of $\ln \frac{C}{C_0}$ versus time curve (Fig. 4) is equal to $-\epsilon \frac{S}{V} P$. The average slope was calculated to be 3.03×10^{-4} thus P was calculated as $7.57 \times 10^{-5} \text{ cm s}^{-1}$.

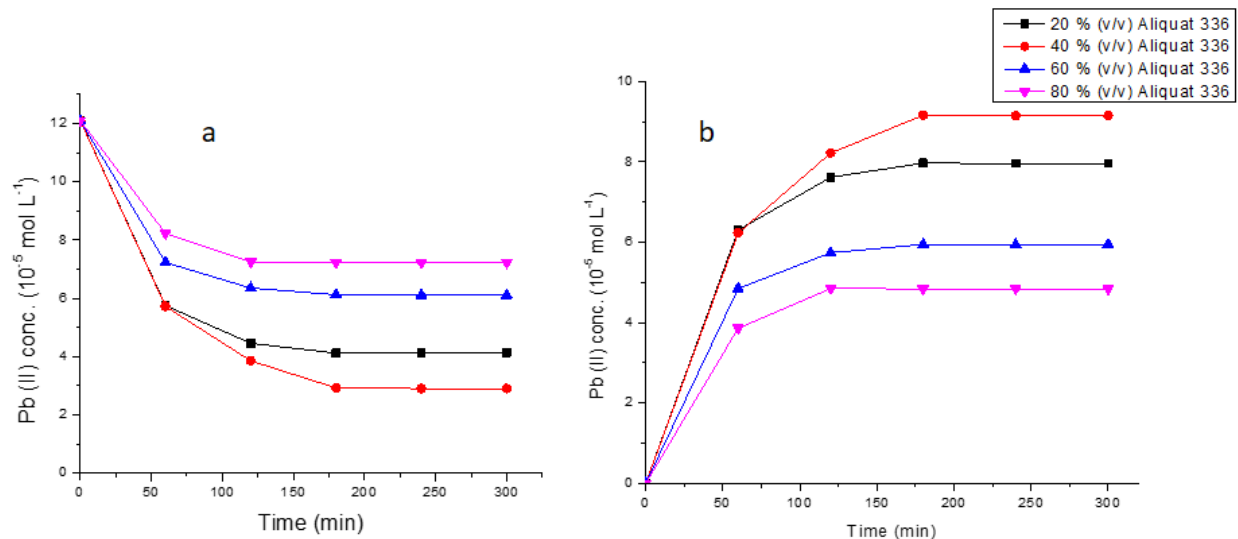


Fig. 2. Variation in Pb^{2+} ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of Aliquat 336.

(Initial $[\text{Pb}^{2+}] = 12.1 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{KI}] = 0.002 \text{ mol L}^{-1}$, $[\text{NaOH}] = 1 \text{ mol L}^{-1}$, $[\text{Aliquat 336}] = 20\text{-}80\%$).

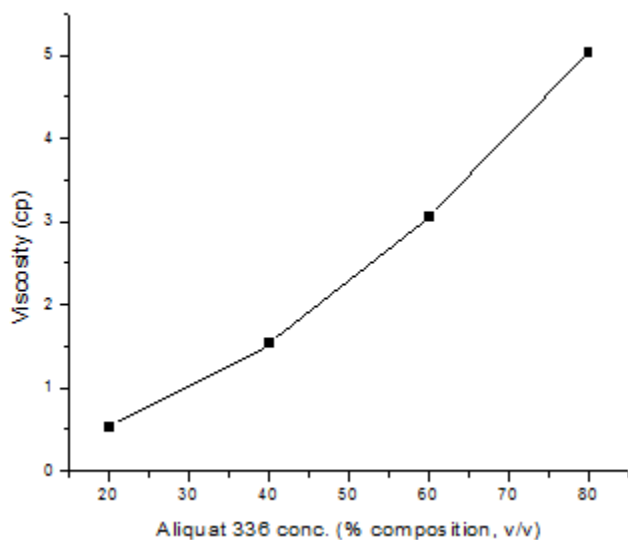


Fig. 3. Viscosity of Aliquat 336-Toulene Solutions.

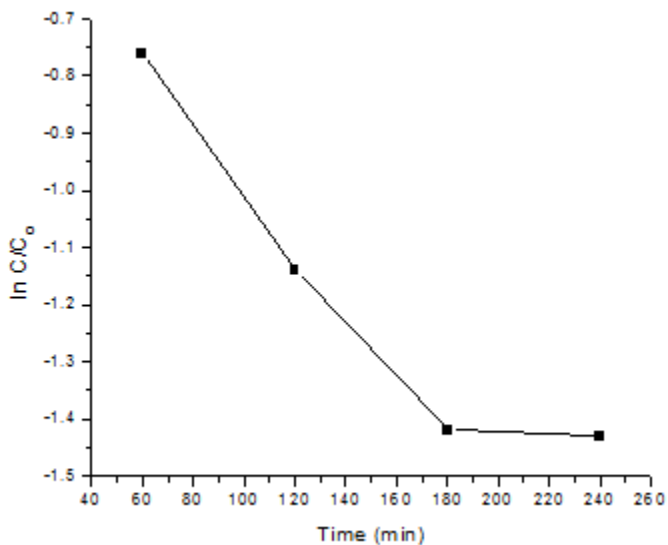


Fig. 4. Plot of $\ln C/C_0$ versus time.

(Initial $[\text{Pb}^{2+}] = 12.1 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{KI}] = 0.002 \text{ mol L}^{-1}$, $[\text{NaOH}] = 1 \text{ mol L}^{-1}$, $[\text{Aliquat 336}] = 40\%$).

3.6.1.2 The pH Effect on the Extraction of Lead

The driving force for the transfer of lead ion between the feed and stripping phases, inter alia, may be attributed to a pH difference between the two phases. The solvent extraction studies exhibit that the system is very efficient in acidic medium hence, the pH plays a significant role in the extraction of lead [7]. In order to investigate the effect of pH on the extraction the pH in the feed phase was varied from 1 to 4. Buffers of pH 1- 4 were used to sustain the feed phase pH. The Figs. 5a and 5b show the pH effect on the extraction of lead, and it is observed that pH 2 yields the maximum extraction. The mechanism of co-transport of lead (II) ion is presented in the Fig. 1. Here iodide and lead, in the form of PbI_4^{2-} ion, transport in the direction of membrane phase. An acidic medium is required to convert the PbI_2 to PbI_4^{2-} . Above pH 2, the existence of iodide ion is not sufficient to convert the PbI_2 to PbI_4^{2-} and therefore, the lead transport drops down [8]. The lesser amount of extraction of lead at pH 1 could be attributed to the kinetic effect as more time is required for conversion of PbI_2 to PbI_4^{2-} . So the pH of the feed side was kept constant at 2 for the rest of the extraction studies and all the relevant calculations were made on this pH. 95% recovery was obtained at pH 2.

The distribution coefficient at 60th min cannot be calculated because on the basis of mass balance principle the concentration of lead in the membrane phase is zero indicating that the flow of lead ion through the membrane is not of the transient nature i.e. the lead ions do not stay at the membrane phase and immediately pass through it. This argument is also supported by forthcoming discussion on the flux value at 60th min where it is $1.93 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ at 60th min; greater than at 180th min. At equilibrium (240th min) it was 0.030. Similarly, on the strip side, the equilibrium value of K_D was 0.0017. It can be noted that with the passage of time the

concentration of lead increases in the strip side in contrast to the feed side. This is supported by the 17.7 times higher K_D value of feed side.

The flux value before equilibrium at (60th min) was calculated $1.42 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ while just before the equilibrium (180th min) the flux value of $9.57 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$. The decrease in flux value was due to the lower concentration of lead in the feed phase than in the strip phase. At equilibrium the flux becomes zero. The value of permeability (P) obtained was $4.2 \times 10^{-5} \text{ cm s}^{-1}$.

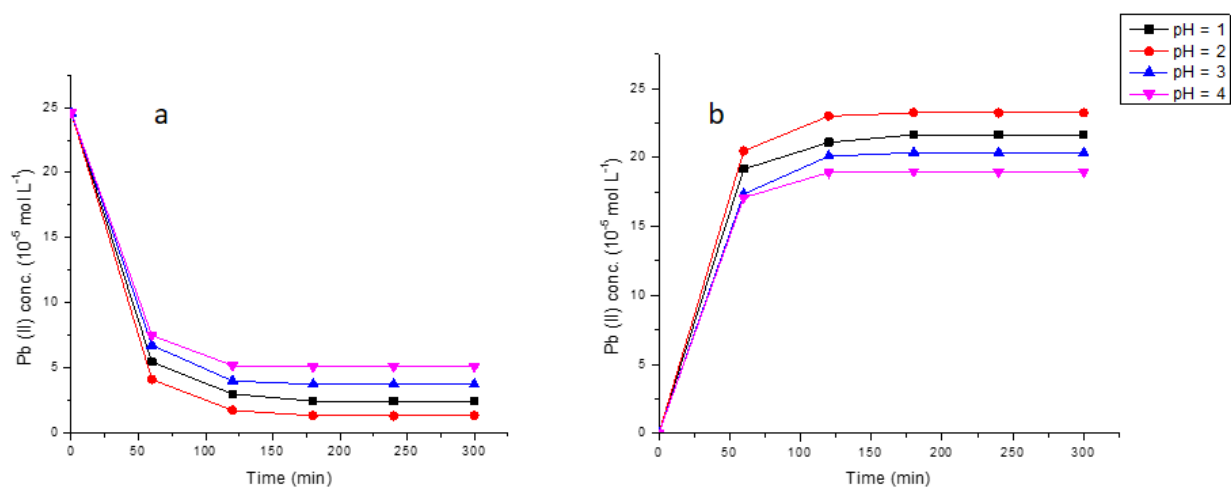


Fig. 5. Variation in Pb^{2+} ion concentration with time in the feed (a) and strip (b) solutions at various pH.

(Initial $[\text{Pb}^{2+}] = 24.1 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{KI}] = 0.003 \text{ mol L}^{-1}$, $[\text{NaOH}] = 1 \text{ mol L}^{-1}$, $[\text{Aliquat 336}] = 40\%$, $\text{pH} = 1-4$).

3.6.1.3 Effect of KI Concentration on the Extraction of Lead

The transport efficiency is affected by the concentration of iodide ion. The concentration of KI was optimized by studying the extraction of lead in the concentration range of 0.001-0.005 mol L^{-1} , and 0.004 mol L^{-1} KI concentrations was found to be the optimum concentration. Figs.6a and

6b exhibit the effect of KI concentration on the extraction of lead. It can be noted that with increase in KI concentration from 0.001 to 0.004 mol L⁻¹ the extraction increases where after it decreases. It can be explained on the following grounds. At low concentration of iodide ions the lead ions are in the form of PbI₂ while at higher concentration the principal species is [PbI₄]²⁻ and hence, this species is responsible for the transport of lead (II) ions from feed to strip solution across the membrane phase [1]. But above 0.004 mol L⁻¹ concentration KI prevents the formation of [PbI₄]²⁻ and inhibits the reaction in the forward direction (www.chem.mun.ca/homes/fmkhome/notes/solubility) [9]. In the feed phase the lead nitrate and potassium iodide were added which results in the formation of [PbI₄]²⁻ due to its relatively higher value of formation constant i.e. 3.0×10⁴ (www.vaxasoftware.com). The solubility of PbI₂ is very small i.e. K_{sp} value is 7.1×10⁻⁹. However, the formation constant of [PbI₄]²⁻ is 3.0×10⁴, therefore, due to high value of formation constant [PbI₄]²⁻ is formed which circumvents the low solubility product of PbI₂.

With increase in the concentration of I⁻ ions in the feed phase the extraction of Pb(II) ions increases which were found to be linear as shown in Fig. 7 i.e. Pb(II) ions concentration in the strip phase versus iodide ions concentration in the feed phase. The mathematical relationship between these two parameters was found to be

$$[\text{Pb}^{2+}]_{\text{strip}} = 0.013 [\text{I}^-] + 1.60 \times 10^{-4}$$

In the case of relationship between Pb²⁺ ion concentration in the feed phase and that of in strip phase, the mathematical relationship was found to be

$$[\text{Pb}^{2+}]_{\text{strip}} = 0.287 [\text{Pb}^{2+}]_{\text{feed}} + 0.17$$

The percent recovery, flux, permeability, distribution coefficient at 60th min and 240th min, calculated at optimum concentration of KI, are given in the Table

Table 1 Values of different Parameters at Optimum level of pH, Concentration of KI, Pb(II) and NaOH

S.No	Parameter	Optimum level	% recovery	Distribution coefficient (K _D) at			Flux (J) (mol cm ⁻² s ⁻¹)		Permeability (P) (cm s ⁻¹)
				60 th min	240 th min		60 th min	240 th min	
				K _{Df(1)} ^a	K _{Df(2)} ^b	K _{Ds} ^c			
1	pH	2	95	-	0.030	0.0017	1.42×10 ⁻⁸	9.57×10 ⁻¹⁰	4.2×10 ⁻⁵
2	[KI]	0.003 mol L ⁻¹	91	0.093	0.490	0.034	1.28×10 ⁻⁸	1.38×10 ⁻⁸	4.6×10 ⁻⁶
3	[Pb(II)]	3.61×10 ⁻⁴ mol L ⁻¹	89	-	0.182	0.019	7.3×10 ⁻⁹	7.5×10 ⁻⁹	5.5×10 ⁻⁵
4	[NaOH]	1 mol L ⁻¹	92	0.0097	0.05	0.0045	1.3×10 ⁻⁸	1.1×10 ⁻⁹	3.3×10 ⁻⁵

^a $K_{Df(1)}$ = distribution coefficient of the Pb (II) ions in the feed side at 60th min

^b $K_{Df(2)}$ = distribution coefficient of the Pb (II) ions in the feed side at 240th min

^c K_{Ds} = distribution coefficient of the Pb (II) ions in the strip side at 240th m

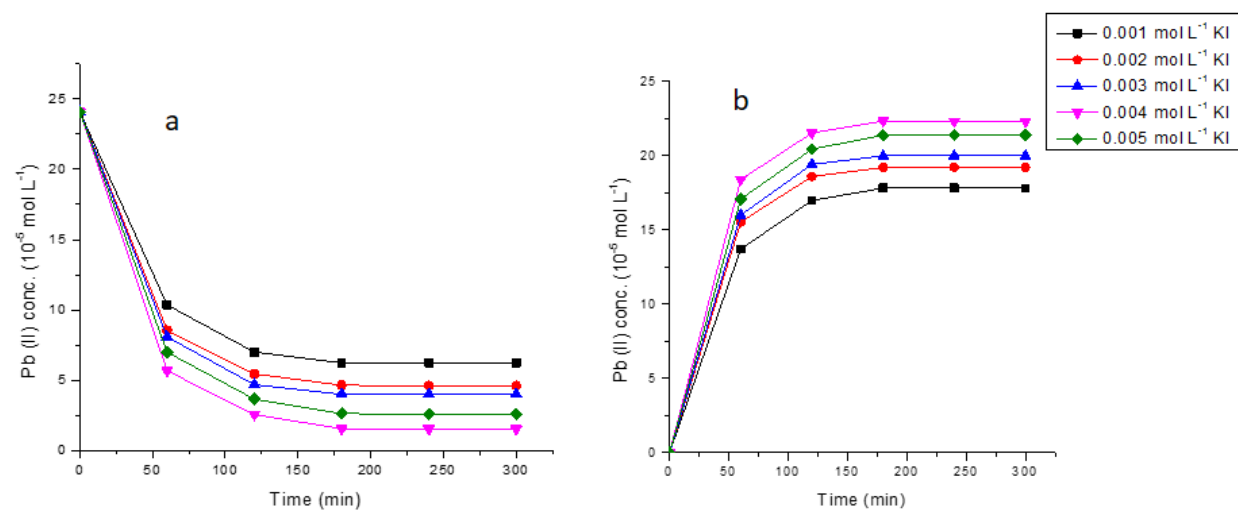


Fig. 6. Variation in Pb^{2+} ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of KI.

(Initial $[Pb^{2+}] = 24.1 \times 10^{-5} \text{ mol L}^{-1}$, $[KI] = 0.001-0.005 \text{ mol L}^{-1}$, $[NaOH] = 1 \text{ mol L}^{-1}$, $[Aliquat 336] = 40\%$, $pH=2$).

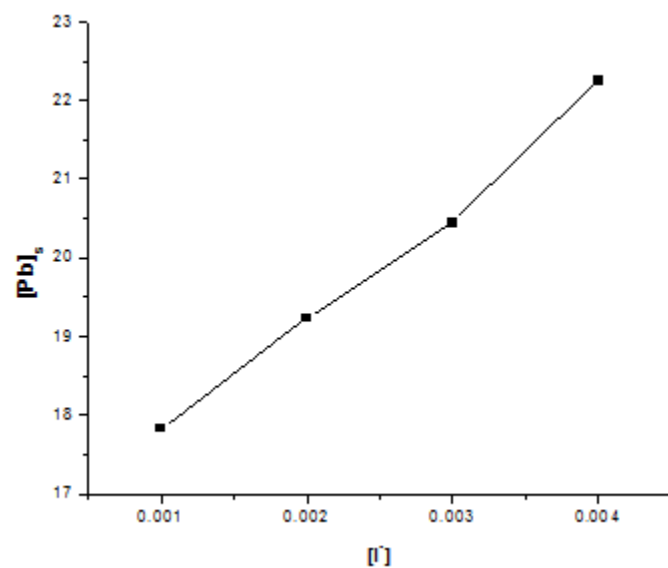


Fig.7. Plot of $[Pb]_s$ versus $[I^-]$.

3.6.1.4 Effect of Lead (II) ions Concentration on the Extraction of Lead

In order to study the effect of lead ion concentration on the extraction of lead, the concentration range of 1.21×10^{-4} to 4.82×10^{-4} mol L⁻¹ of lead metal ion was used in the feed phase. As Pb(II) ion concentration increases the extraction also increases and gives the maximum value at 3.61×10^{-4} mol L⁻¹ lead (II) ions after 3 hours of operation as shown in Fig.8a and 8b for the feed and strip phases respectively. Further increase in the concentration of lead ion results in a decrease in the extraction of Pb²⁺ ions. This decrease may be attributed to the reason that the membrane might be clogged or congested due to PbI₂ and complex ion PbI₄²⁻ [10]. Thus, 3.61×10^{-4} mol L⁻¹ lead concentration was the optimum condition for the extraction of lead.

Therefore, the calculations of different parameters, such as percent recovery, distribution coefficient, flux, and permeability were made on this concentration and shown in Table 1.

The trend of flux is shown in Fig. 9, it can be noted that up to 60th min the flux value increases as the lead (II) ions concentration increases and a maximum value of flux can be observed at 3.61×10^{-4} mol L⁻¹ Pb²⁺ ions, beyond which it decreases. This is because of overcrowding of Pb²⁺ ions at feed-membrane interface, due to the limited diffusion of the lead-carrier complex through the membrane phase, thus carrier molecules were not available for all the Pb²⁺ ions to interact with them and therefore the mass transfer was dropped down [11].

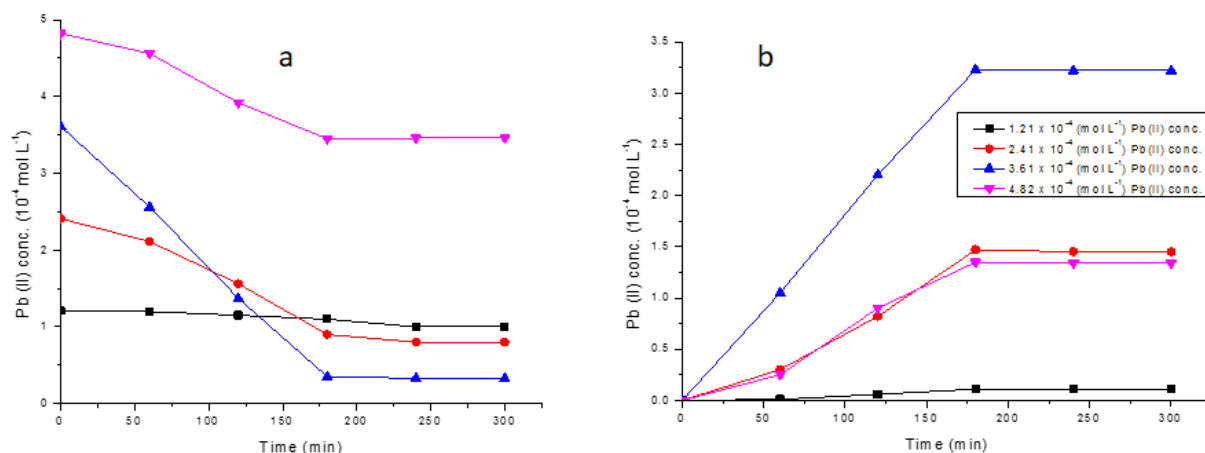


Fig. 8. Variation in Pb $^{2+}$ ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of Pb $^{2+}$ ions.

(Initial [Pb $^{2+}$] = 1.21- 4.82 $\times 10^{-4}$ mol L $^{-1}$, [KI] = 0.004 mol L $^{-1}$, [NaOH] = 1 mol L $^{-1}$, [Aliquat 336] = 40%, pH= 2).

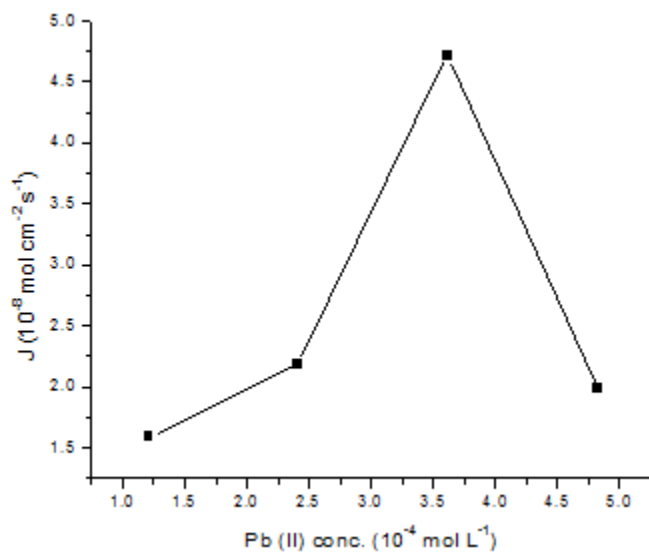
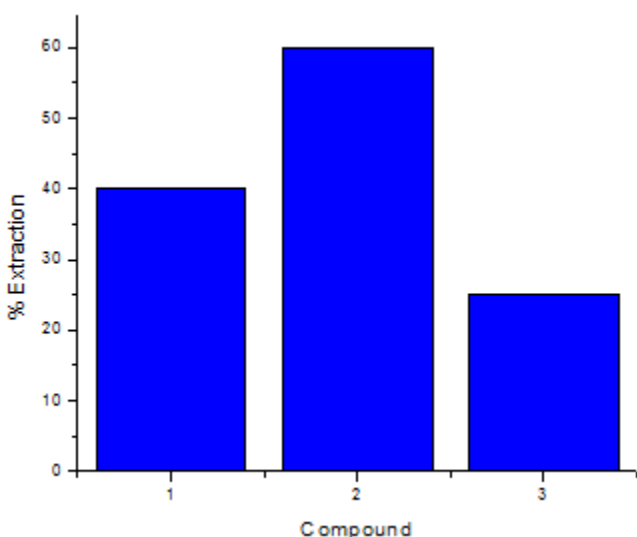


Fig. 9. Effect of Pb $^{2+}$ ion concentration on flux.

(Initial [Pb $^{2+}$] = 1.21- 4.82 $\times 10^{-4}$ mol L $^{-1}$, [KI] = 0.004 mol L $^{-1}$, [NaOH] = 1 mol L $^{-1}$, [Aliquat 336] = 40%, pH= 2).

3.6.1.5 Effect of Nature of Stripping Reagent

The stripping agent in the stripping phase shows a dynamic role in transport of metal ions from the organic membrane phase to the aqueous strip solution. So the influence of different chemicals as a stripping agent in the lead (II) ion extraction was investigated. The initial lead (II) ion concentration in the feed phase, KI concentration, Aliquat 336 concentrations, pH value and stripping solution were adjusted at $3.61 \times 10^{-4} \text{ mol L}^{-1}$, 0.003 mol L^{-1} , 40%, 2.0, 0.1 mol L^{-1} respectively. The experiments were performed using different types of stripping agents such as, sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), and sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_7$). The percent extraction observed by using various stripping agents is illustrated in Fig. 10, which exhibits that NaOH solution shows the highest % extraction as compared to other reagents.

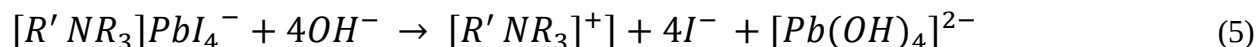


1= Na_2CO_3 , 2= NaOH , 3= $\text{Na}_2\text{S}_2\text{O}_7$

Fig. 10. Effect of different stripping reagents on the extraction of lead (II).

3.6.1.6 Effect of Concentration of NaOH on the Extraction of Lead

To study the effect of NaOH concentration on the extraction of lead, different concentrations of NaOH ranging from 0.1 to 2 mol L⁻¹ were used, whereas 3.61×10⁻⁴ mol L⁻¹ of lead ion and 0.004 mol L⁻¹ KI concentration in the feed solution at pH 2 and 40% Aliquat 336 in the membrane were used. As indicated, by Fig.11a and 11b, by increasing the concentration of NaOH the extraction also increases. The maximum extraction was observed at 1 mol L⁻¹ NaOH and then it decreases on further increase in NaOH concentration. It has been reported [10] that above 1M NaOH concentration the Pb(OH)₂ forms the PbO.H₂O (hydrated Pb oxide). So as we increases the NaOH concentration above 1M the extraction of Pb²⁺ ion decreases which might be due the reason that at high NaOH concentration instead of forming Pb(OH)₄ hydrated PbO is formed which clogs the membrane pores and stops the extraction of Pb²⁺ ions [10]. Therefore, 1 mol L⁻¹ NaOH is an optimum concentration for lead extraction. At the strip membrane interface the complex dissociates and releases Pb⁺² ions and iodide ions in the strip solution.



All subsequent calculations were made on optimum concentration of NaOH. The maximum recovery calculated under the mentioned condition was 92% and rests of the parameters are given in Table 1.

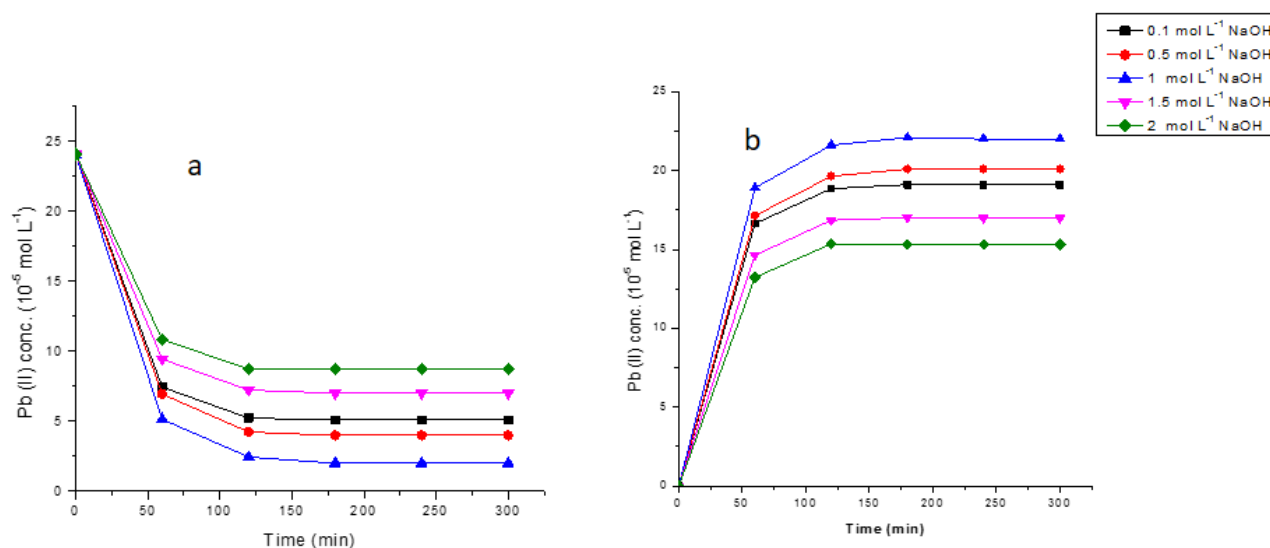


Fig.11. Variation in Pb^{2+} ion concentration with time in the feed (a) and strip (b) solutions at various concentrations of NaOH.

(Initial $[Pb^{2+}] = 3.61 \times 10^{-5} \text{ mol L}^{-1}$, $[KI] = 0.004 \text{ mol L}^{-1}$, $[NaOH] = 0.1\text{-}2 \text{ mol L}^{-1}$, $[Aliquat 336] = 40\%$, $pH = 2$).

3.6.1.7 SEM Analysis

The surface morphology of the membrane, Celgard 2400, was evaluated by SEM images. The SEM images of the membrane before and after impregnation are shown in Fig. 12a-c. The magnification of these images is 6,000. The micro-pores in the virgin membrane (before impregnation) can easily be seen (Fig.12a). However, after impregnation, with Aliquat 336 in toluene, most of these pores are observed to be filled with the carrier solution (Fig 11b). Fig. 12c shows the cross sectional image of the membrane, from which the thickness of the membrane can be calculated and it is found to be 20.36 μm .

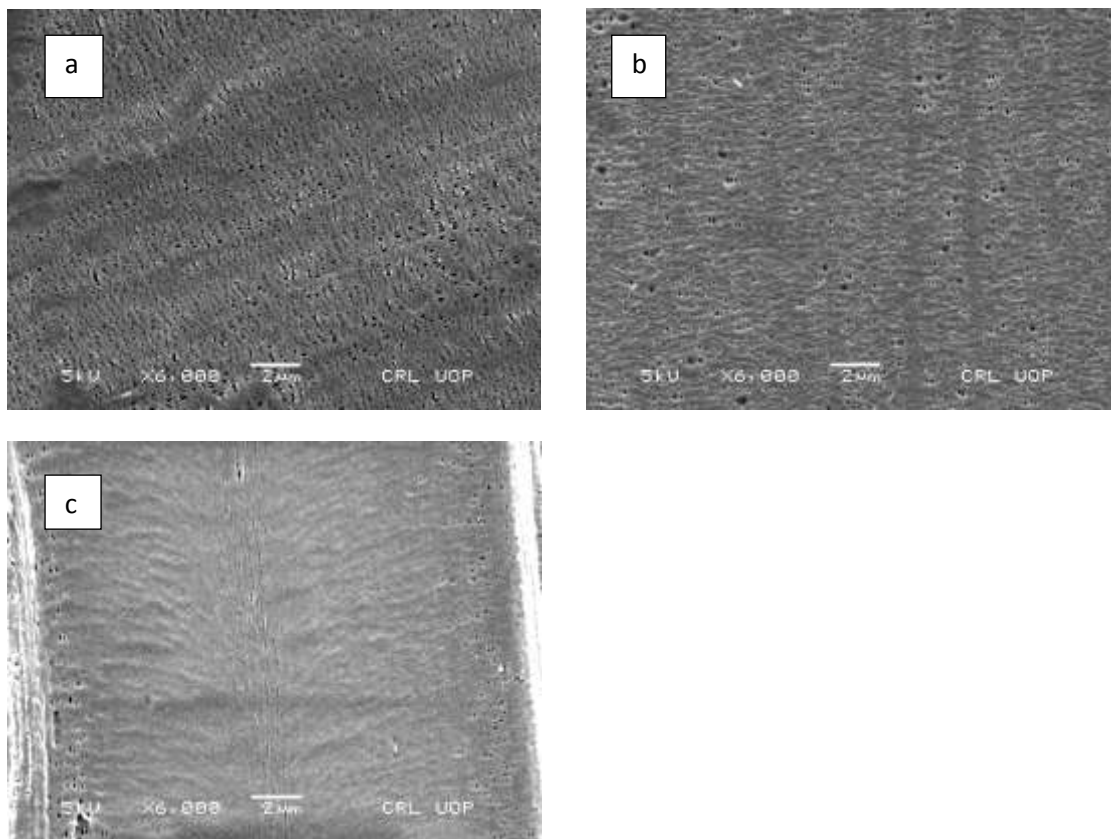


Fig. 12. Scanning Electron microscopy of membrane before extraction (a) and after impregnated with carrier (b) and cross-section of the membrane (c).

3.6.1.8 Extraction Time

Fig. 13 illustrates the concentration of lead ions versus time profile at optimum experimental conditions already established. It can be noted from the Fig. 13 that the concentration reaches to a limiting value of 90% after about 180 min.

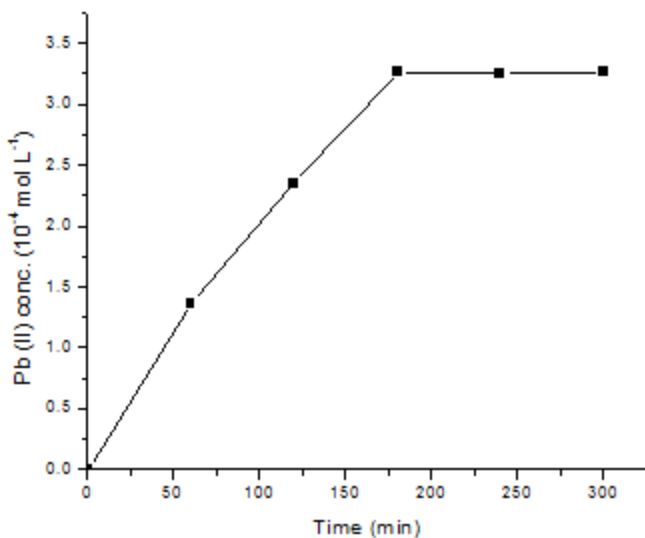


Fig. 13. Variation in Pb^{2+} ion concentration with time.

(Initial $[\text{Pb}^{2+}] = 3.61 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{KI}] = 0.004 \text{ mol L}^{-1}$, $[\text{NaOH}] = 1 \text{ mol L}^{-1}$, $[\text{Aliquat 336}] = 40\%$, $\text{pH} = 2$).

3.6.1.9 Suggested Transport Mechanism

The lead (II) ion transport, by means of Aliquat 336, is a facilitated co-transport type. The lead (II) ion forms a PbI_4^{2-} charge complex with iodide ion. The resulting lead-iodo complex moves towards the feed-membrane interface, reacts with Aliquat 336 forming $[\text{R}'\text{NR}_3]\text{PbI}_4^-$ complex and then diffuses through the membrane phase to the membrane-strip interface by solvation mechanism. The stripping of the lead (II) ion is carried out via formation of a soluble lead hydroxide $[\text{Pb}(\text{OH})_4]^{2-}$ with NaOH. Then the free carrier diffuses back across the liquid membrane and the cycle starts again. The net result is the transport of lead ion from the source phase to the receiving phase across the membrane as shown in Fig.1.

3.6.1.10 Membrane Stability

To study the long term membrane stability, the extraction experiments were carried out consistently for 10 days (one experimental run per day) made under the optimum conditions without re-impregnation of the membrane however, the feed and strip solutions were replaced for each run. The cell was kept filled with distilled water, between the successive experiments, in order to prevent the dryness of the membrane. The optimum experimental conditions were as follows; lead ion concentration in the feed at $3.61 \times 10^{-4} \text{ mol L}^{-1}$ and 0.003 mol L^{-1} KI, Aliquat 336 concentrations in SLM of 40% in toluene, NaOH concentration at 1 mol L^{-1} in stripping phase and stirring speed at 1500 rpm. The results show (Fig. 14) that this SLM was quite stable during the investigated time and no decrease in flux and percent recovery of lead was observed up to 10 days. The study was replicated thrice with relative standard deviation ± 2 .

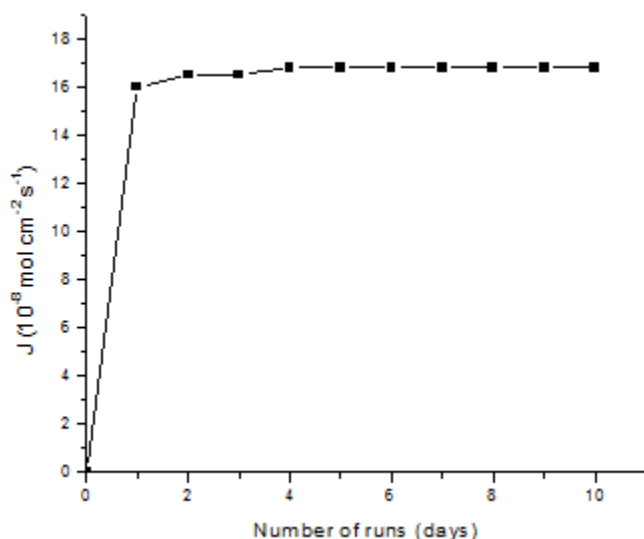


Fig. 14. Stability of SLM, flux versus time.

(Initial $[\text{Pb}^{2+}] = 3.61 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{KI}] = 0.004 \text{ mol L}^{-1}$, $[\text{NaOH}] = 1 \text{ mol L}^{-1}$, $[\text{Aliquat 336}] = 40\%$, $\text{pH} = 2$).

3.5.1.11 Extraction of Pb (II) from Lead Battery Wastewater

One of the major uses of lead is in the battery industry. The optimized conditions of SLM system were used for recovery of lead from battery industry waste water. The waste water was filtered with Whatman filter paper; 80 mL of filtrate was diluted up to 250 mL with distilled water. The test sample was analyzed for other metals i.e. Co (II), Cd (II), Cu (II), Ni (II), and Zn (II) along with lead (II) ion. Only Cd (II), Cu (II), and Zn (II) were present in the test sample along with the Pb (II) (Table 2). The test sample was subjected to extraction process under the optimum experimental conditions as mentioned earlier. The strip solution was again analyzed by AAS and it was noted that along with the lead (II) ions, a minute amount of Zn (II) ions ($2.4 \times 10^{-6} \text{ mol L}^{-1}$) was also extracted through the membrane. However, there was no effect in terms of percent recovery of lead ions due to the presence and transport of zinc ion. The analysis data are shown in Table 1 and it shows that almost 90% Pb (II) ions were recovered as achieved in the controlled experiments (Fig. 15). Interestingly, only 0.75% zinc was extracted along with the lead ions which are a negligible amount as compared to lead ion and secondly, zinc and other metals have no effect on the extraction of lead ions. Thus our system of extraction can be regarded as efficient selective system for the extraction of lead.

Table 2 Analysis of Battery Industry Wastewater

S.No	Metal ion	Concentration of metals ions	Concentration of metals ions	% Recovery
		B.E (mol L ⁻¹)	A.E (mol L ⁻¹)	
1	Pb	3.17×10^{-4}	2.87×10^{-4}	90.5
2	Cd	4.45×10^{-6}	Nil	-
3	Cu	6.82×10^{-5}	Nil	-
4	Zn	3.18×10^{-4}	2.4×10^{-6}	0.75
5	Ni	Nil	Nil	-
6	Co	Nil	Nil	-

B.E= before extraction

A.E= after extraction

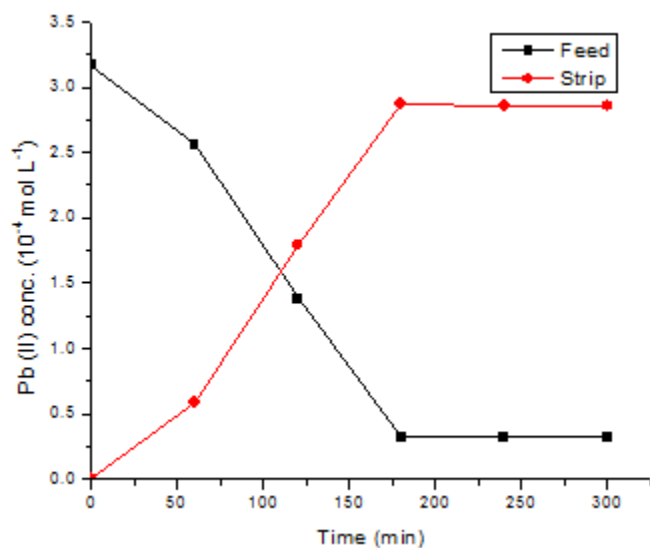


Fig. 15. Variation in Pb^{2+} ions concentration in the feed and strip solution versus time (Lead battery industry waste solution in feed).

(Initial $[\text{Pb}^{2+}] = 3.17 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{KI}] = 0.004 \text{ mol L}^{-1}$, $[\text{NaOH}] = 1 \text{ mol L}^{-1}$, $[\text{Aliquat 336}] = 40\%$, $\text{pH} = 2$).

Conclusion

The supported liquid membrane consisting of Aliquat 336 based on iodo system is very effective for the extraction of lead ions. The influences of various parameters on the transport of lead (II) were studied to obtain the optimum conditions. The optimum conditions for the extraction were; 3.61×10^{-4} mol L⁻¹ lead (II) ion and 0.004 mol L⁻¹ KI concentrations in the feed, 40% Aliquat 336 concentration in SLM in toluene, 1 mol L⁻¹ NaOH concentration in stripping phase and stirring speed at 1500 rpm. The calculations of the percent recovery, distribution coefficient, flux, and permeability were made from the data obtained on the optimum conditions. The extraction time was found to be 180 minutes for lead ion transport at which the equilibrium has been established. Under optimum conditions the stability of SLM was investigated and it was found that the membrane was stable at least up to 10 days. In the presence of other metal ions like Cd (II), Cu (II), and Zn (II), 90% of lead (II) ions have been selectively removed from the battery waste water. Thus this system of extraction can be regarded as efficient selective system for the extraction of lead.

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Part VI

Extraction of Cadmium (II)

Facilitated Transport of Cadmium (II) through a Supported Liquid Membrane with Tridodecylamine as Carrier

3.7 Transport Mechanism

In the extraction process, the solute from aqueous feed side reacts with carrier molecules to form a complex inside the pores of the solid support membrane at feed-membrane interface. The transport of cadmium ions follows the co-ion mechanism as shown in Fig. 1. At strip-membrane interface, the complex diffuses through the membrane to stripping phase due to the concentration gradient.

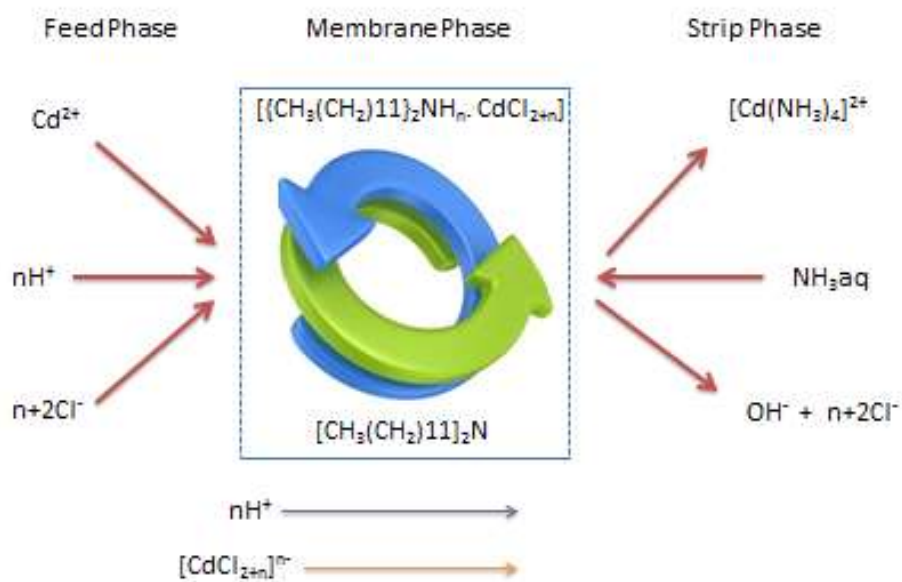
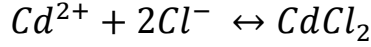


Fig. 1. Coupled co-ion transport mechanism of Cd (II) ions.

The reaction on the feed side may be given as follows

The reaction of HCl with $CdCl_2$ in aqueous solution results in the formation of complex $[CdCl_{2+n}]^{n-}$ as follows [1].



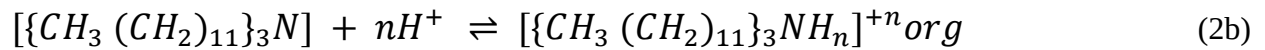
The number of chloride ions attached with $CdCl_2$ cannot be predicted at this stage; therefore, we assume 'n' the chloride ions attached with $CdCl_2$ as follows



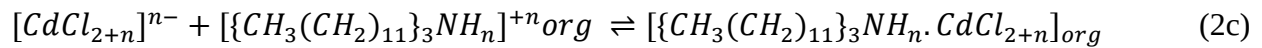
The protonation of TDDA molecule, under the acidic condition, takes place as follows [2];



If there is 'n' number of H^+ ions associated with $[\{CH_3(CH_2)_{11}\}_3N]$ then we can write

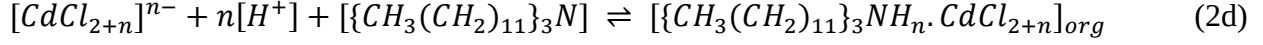


The complex $[CdCl_{2+n}]^{n-}$ moves towards the feed- membrane interface to react with the protonated carrier molecule, $[\{CH_3(CH_2)_{11}\}_3NH_n]^{+n}_{org}$ at the membrane interface with the following equilibrium reaction:



Where the subscript 'org' denotes the presence of specie in the organic phase.

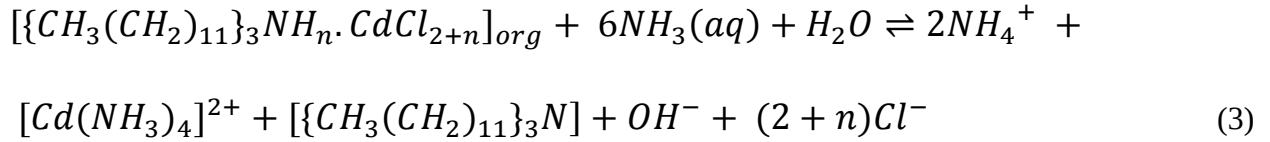
The overall reaction at the feed-membrane interface is as follows:



The coupled co-ion transport mechanism is proposed for the $Cd(II)$ ions transport in which both H^+ and complex $[CdCl_{2+n}]^{n-}$ are on the way to stripping side across the membrane phase.

The reaction on the strip side may be given as follows

The complex $[\{CH_3(CH_2)_{11}\}_3NH_n \cdot CdCl_{2+n}]_{org}$ is unstable, which immediately dissociates at the strip-membrane interface releasing cadmium ions. The $Cd(II)$ ions react with ammonia solution in the stripping phase as follows.



3.7.1 Theory

The extraction constant for $Cd(II)$ ion in the feed side is given by K_{Cd} :

$$K_{Cd} = \frac{[\{CH_3(CH_2)_{11}\}_3NH_n \cdot CdCl_{2+n}]_{org}}{[CdCl_{2+n}]^{n-} [H^+]^n [\{CH_3(CH_2)_{11}\}_3N]} \quad (4)$$

The distribution coefficient of $Cd(II)$ ion, λ_{Cd} , is shown by the following equation:

$$\lambda_{Cd} = \frac{[\{CH_3(CH_2)_{11}\}_3NH_n \cdot CdCl_{2+n}]_{org}}{[CdCl_{2+n}]^{n-}]_{aq}} \quad (5)$$

By inserting the value of distribution constant in Eq. (4)

$$K_{Cd} = \frac{\lambda_{Cd}}{[H^+]^n [\{CH_3(CH_2)_{11}\}_3N]} \quad (6a)$$

On rearranging Eq. (6a) we obtain

$$\lambda_{Cd} = K_{Cd}[H^+]^n [\{CH_3(CH_2)_{11}\}_3N] \quad (6b)$$

According to Fick's First Law, the rate of diffusion dn/dt of metal ions across an area A is known as diffusion flux (J) and it is given as follows [1,2]

$$J = \frac{dn}{dt} = -DA \frac{dc}{dx} \quad (7)$$

Where D is denoted diffusion coefficient, A indicated the area of the membrane, $\frac{dc}{dx}$ is rate of change of concentration across the membrane per unit distance or thickness of the film x in time dt .

If the distribution constants of metal ion between organic and aqueous phases at the membrane face in the feed and strip side are λ_f and λ_s , respectively, then:

$$\lambda_f = \frac{C_{mf}}{C_f} \quad (8)$$

$$\lambda_s = \frac{C_{ms}}{C_s} \quad (9)$$

Where C_m is the metal ions concentration in the membrane phase and C is the concentration of the same ion in aqueous phase, f and s denote the feed and strip phases, respectively.

Considering Fig.2 and Fick's First Law, the concentration gradient, dc/dx (or simply $\Delta c/\Delta x$) is negative as Δc is equal to $C_{mf} - C_{ms}$ which is positive since $C_{mf} > C_{ms}$, whereas Δx

is negative as x varies from 0 to x . Since the final value of x is higher than the initial value, i.e. 0-
 $x = -x$.

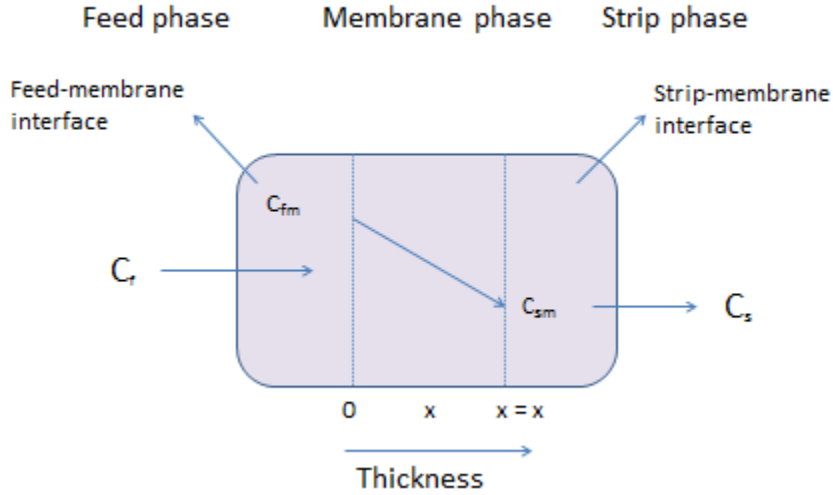


Fig. 2. Concentration gradient of cadmium ions at the feed and strip sides of the membrane.

Thus

$$-\frac{dc}{dx} = \frac{\Delta c}{\Delta x} = -\frac{C_{mf}-C_{ms}}{x} \quad (10)$$

By the Fick's First Law, the rate of flow through membrane is

$$\frac{dn}{dx} = DA \frac{C_{mf}-C_{ms}}{x} \quad (11)$$

The diffusion coefficient D is therefore, calculated from the measurement of the rate of flow; the area A , thickness x , and concentration difference $C_{mf} - C_{ms}$ are readily determined.

From Eq. (8) and (9) we obtain

$$C_{mf} = \lambda_f C_f \quad (12)$$

and

$$C_{ms} = \lambda_s C_s \quad (13)$$

In the light of Eq. (12) and (13), Eq. (11), changes to:

$$J = DA \frac{(\lambda_f C_f - \lambda_s C_s)}{x} \quad (14)$$

As there is no transport of metal ions from the stripping phase to membrane phase, λ_s is taken as 0 and Eq. (14) reduces to

$$J = DA \frac{(\lambda_f C_f)}{x} \quad (15)$$

And we can consider $\lambda_f = \lambda_{cd}$, and $C_f = C_{cd}$ where λ_{cd} is given by Eq.(6b), therefore Eq.(15) can be written as

$$J = DA \frac{K_{cd}[H^+]^n [\{CH_3(CH_2)_{11}\}_3N]}{x} \quad (16)$$

According to Wilke- Chang relation

$$D = \frac{kT}{\eta} \quad (17)$$

Where T indicates the absolute temperature, η shows the viscosity of the TDDA solution in toluene and k is constant and so

$$J = \frac{kT}{\eta} A \frac{(K_{cd}[H^+]^n [\{CH_3(CH_2)_{11}\}_3N] C_{cd})}{x} \quad (18)$$

Since k , K_{Cd} , T , x and A are constants, moreover, Since flux is concentration dependent, any measurement of flux must be made at a particular constant concentration of the feed, therefore, we consider C_{Cd} in Eq.(18) as constant, combining all these as K i.e.

$$K = \frac{k K_{Cd} T A C_{Cd}}{x} \quad (19)$$

Thus Eq.(18) reduces to

$$J = K \frac{[H^+]^n [\{CH_3(CH_2)_{11}\}_3 N]}{\eta} \quad (20)$$

On rearranging Eq.(20) we obtain,

$$J\eta = K[H^+]^n [\{CH_3(CH_2)_{11}\}_3 N] \quad (21)$$

Taking log of Eq. (21)

$$\log J\eta = \log K + n \log [H^+] + \log [\{CH_3(CH_2)_{11}\}_3 N] \quad (22)$$

Since in a specially designed experiment the concentration of TDDA, $\{CH_3(CH_2)_{11}\}_3 N$ was kept constant, thus Eq.(22) reduces to

$$\log J\eta = B + n \log [H^+] \quad (23)$$

Here B includes all the constants as mentioned earlier including $\log K$ and $[\{CH_3(CH_2)_{11}\}_3 N]$.

The 'n' represent the number of TDDA molecules associated with Cd^{2+} ion in the form $[\{CH_3(CH_2)_{11}\}_3 NH_n \cdot CdCl_{2+n}]_{org}$ and its value can be determined by using Eq. (23). Eq.

(23) is a straight line equation in which $\log J\eta$ can be plotted on y axis and $\log [H^+]$ on x axis.

The value of 'n' can be obtained from slope of this curve.

3.7.2 Result and Discussion

3.7.2.1 Effect of HCl Concentration on Extraction of Cadmium

In the extraction of Cd(II), HCl plays dual role by providing H^+ for the protonation of TDDA to produce $[CH_3(CH_2)_{11}_3NH_n]^{n+}$ and Cl^- ions for the formation of $[CdCl_{2+n}]^{n-}$, respectively, and provides the driving force to transport Cd^{2+} ions from feed side to the strip side. The HCl concentration effect on the extraction of Cd^{2+} ions is shown in Fig. 3a and 3b. From this figure it is clear that maximum extraction of Cd^{2+} ions is achieved at 1 mol L^{-1} of HCl concentration. Similarly, the effect of HCl concentration on the flux of Cd^{2+} is depicted in Fig. 3, which shows optimum flux of Cd^{2+} ions in 1 mol L^{-1} HCl. It can be observed that the flux is directly proportional to $[H^+]$ which is in agreement with the Eq. (23)vide supra. HCl provides Cl^- ions to the $CdCl_2$ which is converted to $[CdCl_{2+n}]^{n-}$ species and TDDA is protonated by H^+ ions provided by HCl. The protonated TDDA and $[CdCl_{2+n}]^{n-}$ combine with one another at the feed-membrane interface to form an adduct which releases Cd^{2+} ions in the strip phase. The decrease in extraction and flux beyond 1 mol L^{-1} HCl can be attributed to the common ion effect which plays its role in the presence of excess amount of H^+ ions [3].

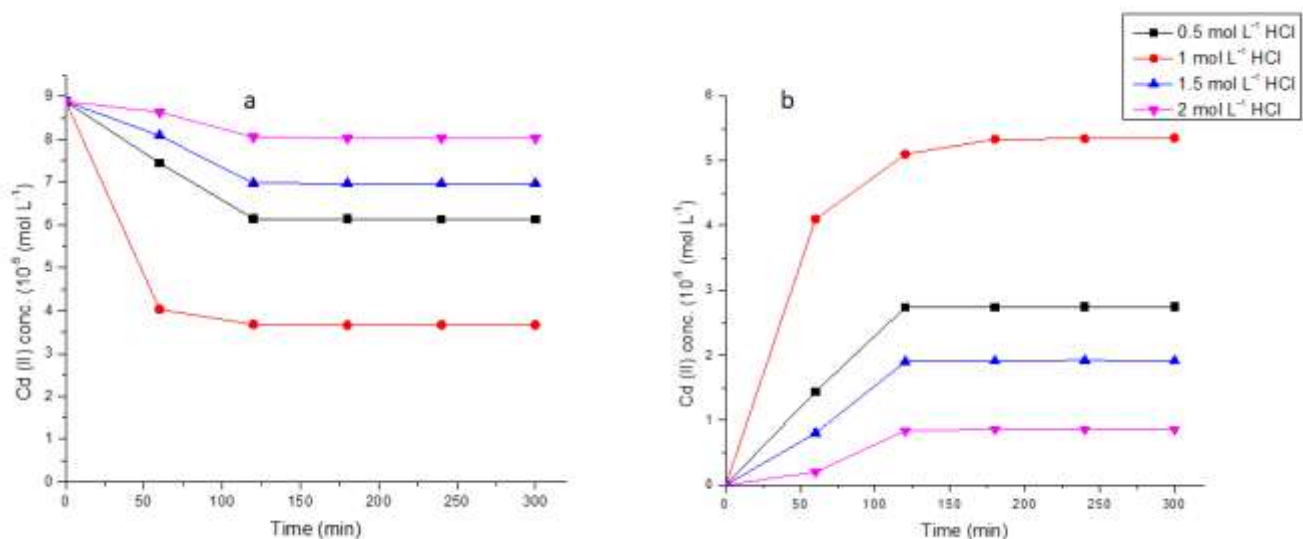


Fig. 3. Variation in Cd^{2+} ion concentration with time in feed (a) and strip (b) solutions at various concentrations of HCl.

(Initial $[\text{Cd}^{2+}] = 8.89 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 0.5\text{-}2 \text{ mol L}^{-1}$, $[\text{NH}_3] = 3 \text{ mol L}^{-1}$, $[\text{TDDA}] = 20\%$).

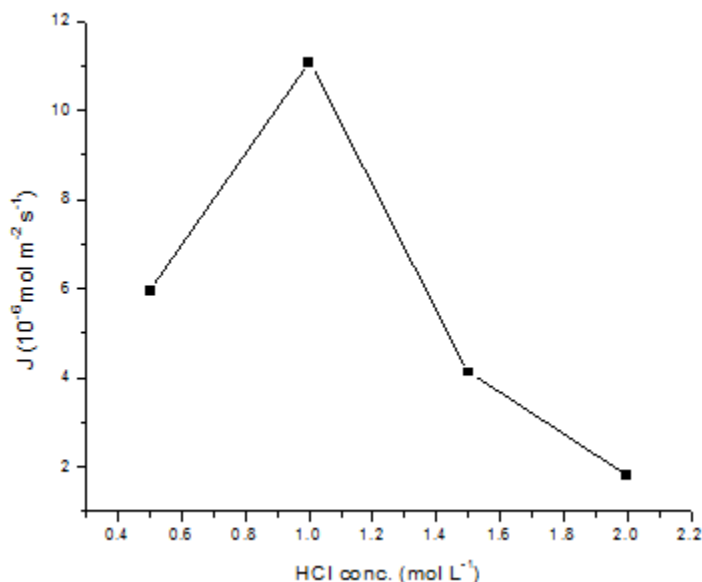


Fig.4. Effect of HCl concentration on Flux.

(Initial $[\text{Cd}^{2+}] = 8.89 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 0.5\text{-}2 \text{ mol L}^{-1}$, $[\text{NH}_3] = 3 \text{ mol L}^{-1}$, $[\text{TDDA}] = 20\%$).

Fig. 5 shows the pH of feed solution at different intervals of time. An increase in the pH was observed at the initial stage of the extraction process owing to decrease in concentration of H^+ ions which renders the transfer of protons towards the strip side. At about 120th minutes the pH value becomes constant indicating the completion of the extraction process [4]. The plot of $\log J\eta$ against $\log[\text{H}^+]$ gives a straight line and the slope was calculated to be 0.97 which can be taken as 1 shown in Fig. 6. As indicated by Eq (23) 'n' gives the number of protons associated with Cd-TDDA complex $[\{\text{CH}_3(\text{CH}_2)_{11}\}_3\text{NH}_n \cdot \text{CdCl}_{2+n}]_{org}$ [4]. Thus, in the light of present calculation of 'n' the Cd-TDDA complex may be written as $[\{\text{CH}_3(\text{CH}_2)_{11}\}_3\text{NH} \cdot \text{CdCl}_3]_{org}$.

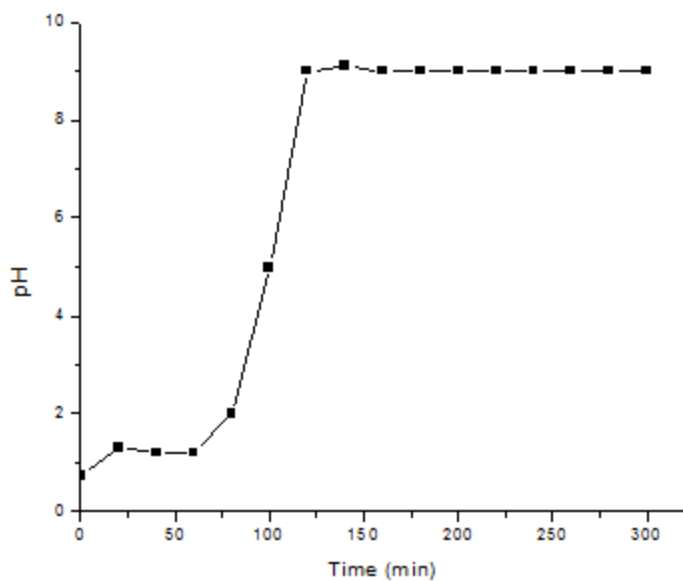


Fig.5. Variation in pH of feed solution with time.

(Initial $[\text{Cd}^{2+}] = 8.89 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NH}_3] = 6 \text{ mol L}^{-1}$, $[\text{TDDA}] = 20\%$).

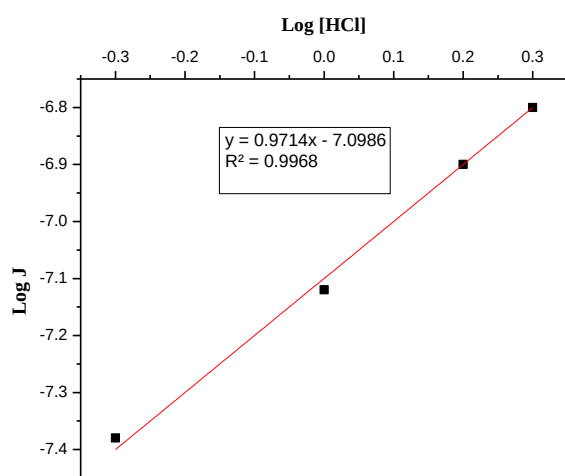


Fig.6. $\log J_\eta$ versus $\log [\text{HCl}]$.

(Initial $[\text{Cd}^{2+}] = 8.89 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NH}_3] = 6 \text{ mol L}^{-1}$, $[\text{TDDA}] = 20\%$).

3.7.2.2 Effect of TDDA Concentration on Extraction of Cadmium

The concentration of carrier has an important part on the metal ions transport across the membrane. Various TDDA concentration ranging from 10 -50% were used to study the effect of concentration of the TDDA and the results are presented in Fig. 7 (a-b) for the feed and strip sides respectively on the extraction of Cd^{2+} ions. Fig. 9 shows maximum extraction of Cd^{2+} ions at 30% TDDA where after a decrease in extraction can be noted. This decrease can be attributed to the high viscosity of TDDA-xylene solution (Fig. 9) which hampers and block the movement of Cd-TDDA complex across the membrane [5].

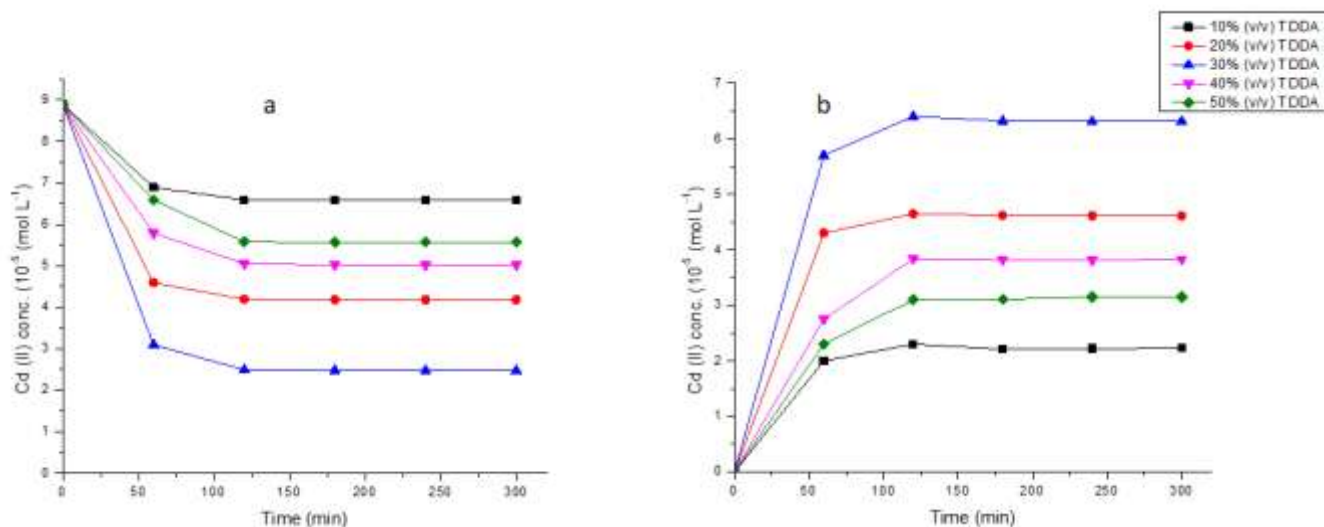


Fig.7. Variation in Cd^{2+} ion concentration with time in feed (a) and strip (b) solutions at various concentrations of TDDA.

(Initial $[\text{Cd}^{2+}] = 8.89 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NH}_3] = 3 \text{ mol L}^{-1}$, $[\text{TDDA}] = 10\text{-}50\%$).

The effect of TDDA concentration on the flux is shown in Fig. 8. An increase in the flux was observed from 1-30% TDDA solution giving maximum value at 30%, however beyond 30%

the value of flux decreases. This decrease in flux may be due to the high viscosity of TDDA solution as discussed earlier.

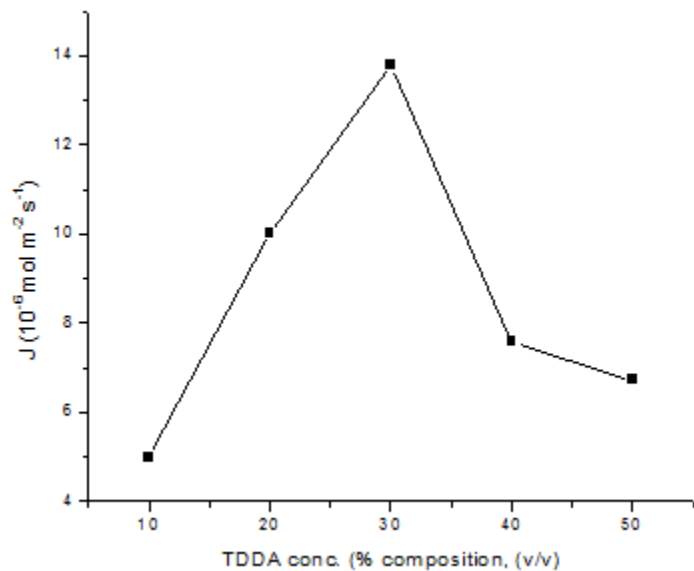


Fig. 8. Effect of TDDA concentration on Flux.

(Initial $[\text{Cd}^{2+}] = 8.89 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NH}_3] = 3 \text{ mol L}^{-1}$, $[\text{TDDA}] = 10\text{-}50\%$).

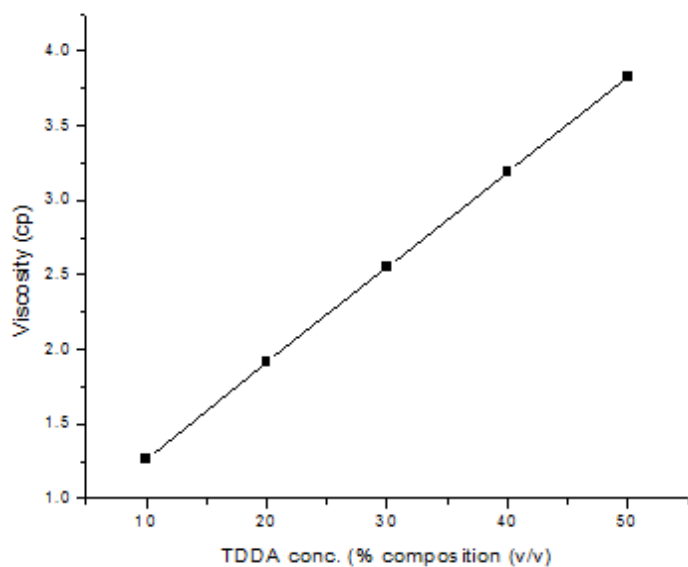
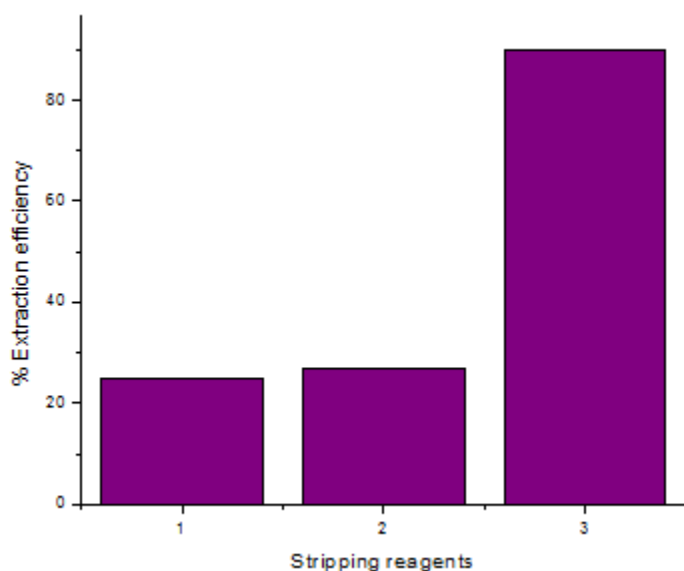


Fig. 9. Viscosity of Tridodecylamine-xylene solutions.

3.7.2.3 Effect of Nature of Stripping Reagent

The stripping reagent has a significant role in the transportation of metal ions from the organic membrane phase to the stripping phase. Regarding the extraction of Cd^{2+} ions different stripping reagents such as ammonium nitrate, ammonium acetate and ammonia solution were evaluated for their stripping ability at same condition of temperature, stripping reagent concentration, and extraction time. The results are shown in Fig.10 which shows that the Cd (II) ions extraction through NH_3 solution as a stripping reagent is better than ammonium nitrate and ammonium acetate. Therefore, NH_3 solution was selected as a stripping reagent for further extraction experiments.

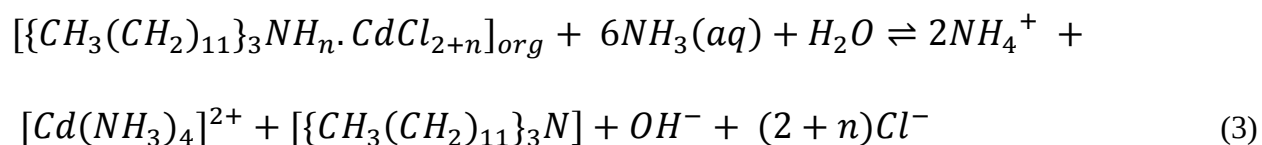


1 = NH_4CO_3 , 2 = $\text{CH}_3\text{COONH}_4$, 3 = $\text{NH}_3(\text{aq})$

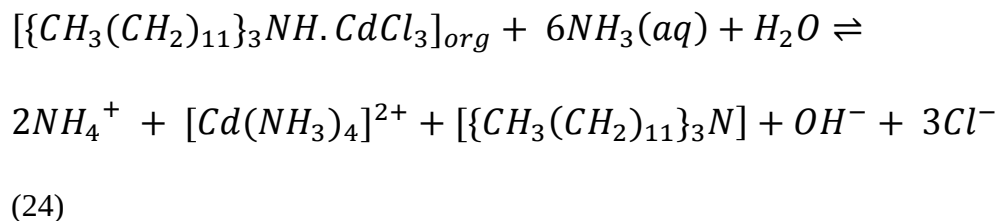
Fig.10. Effect of different stripping reagents on the extraction of cadmium.

3.7.2.4 Effect of NH₃ Concentration on Extraction of Cadmium

To investigate the effect of NH_{3(aq)} concentration on the cadmium ions extraction, different (1-7 mol L⁻¹) NH_{3(aq)} concentrations were used. 1 mol L⁻¹ HCl and 13.3×10⁻⁵ mol L⁻¹ of Cd²⁺ ion in feed solution and 30% TDDA in membrane were kept constant during the experiment. Fig. 11a and b show the effect of NH₃ concentration in the feed and strip phases respectively. It is observed that maximum extraction of Cd²⁺ ion is achieved at 6 mol L⁻¹ NH_{3(aq)} as shown in Fig. 11 (a-b). Beyond 6 mol L⁻¹ NH_{3(aq)}, a decrease in the extraction of the cadmium ion was observed which could be attributed to the precipitation of cadmium oxides or hydroxides at the strip-membrane interface which results in the clogging of the membrane pores, which adversely affects the extraction of Cd²⁺ ion [6]. The reaction is given as follows.



For n = 1 Eq (3) becomes



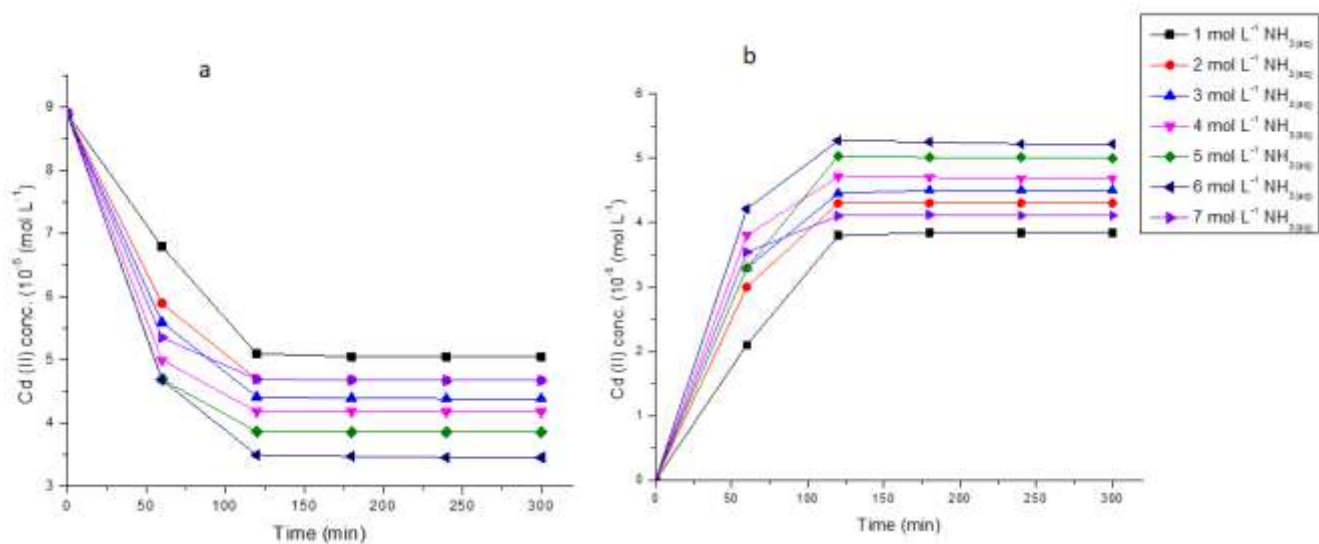


Fig.11. Variation in Cd²⁺ ion concentration with time in feed (a) and strip (b) solutions at various concentration of NH_{3(aq)}.

(Initial [Cd²⁺] = 8.89 × 10⁻⁵ mol L⁻¹, [HCl] = 1 mol L⁻¹, [NH₃] = 1-6 mol L⁻¹, [TDDA] = 30%).

Fig. 12 shows the profile of flux at different concentrations of NH₃ solution. A slightly gradual increase in the flux can be observed up to 6 mol L⁻¹ NH₃, which decreases at next higher NH₃(aq) concentration.

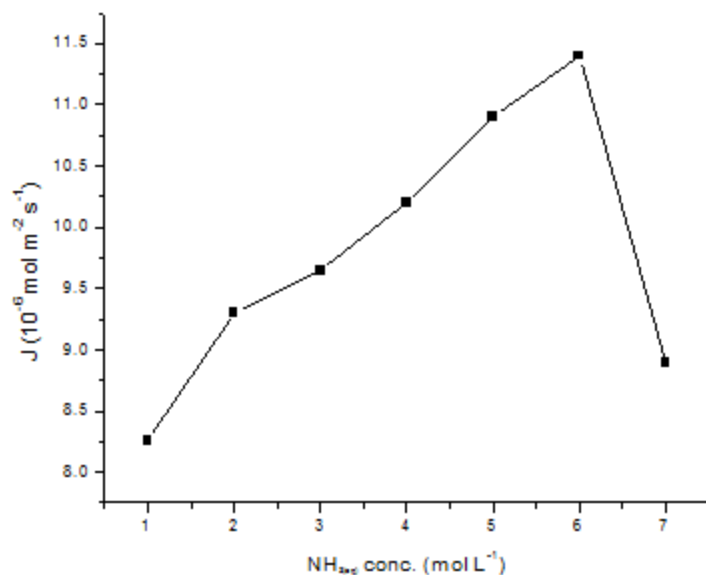


Fig.12. Effect of NH₃ concentration on Flux.

(Initial [Cd²⁺] = 8.89×10^{-5} mol L⁻¹, [HCl] = 1 mol L⁻¹, [NH₃] = 1-6 mol L⁻¹, [TDDA] = 30%).

3.7.2.5 Effect of Cd²⁺ ions Concentration on Extraction

Different concentration of Cd²⁺ ions (4.44×10^{-5} to 22.2×10^{-5} mol L⁻¹), in the feed phase was studied for extraction. Cd (II) ion concentration versus time profile is indicated in Fig. 13 (a-b) for feed and strip phases respectively. Extraction of Cd (II) ion increases as the initial concentration of cadmium ions increases and reaches up to a maximum value at 13.3×10^{-5} mol L⁻¹ of initial concentration of cadmium. The Cd(II) ion concentration also affects the flux value (Fig. 14). The flux value increases gradually to a maximum value of 22.5×10^{-8} mol m⁻² s⁻¹, and then abruptly declines. This decrease may be explained on the basis of following facts. Firstly, with increase in the initial concentration of cadmium salt the membrane becomes overcrowded with metal-carrier complex which results in lower effective membrane area [7]. Secondly, at low initial concentration of cadmium ions the transport of metal ions depends on the activity of the metal ions which is same as the concentration since activity coefficient is unity at low

concentration but at high concentration activity coefficient decreases due to long range columbic force of interaction between anion and cation (Debye-Hackel Limiting Law) and due to increasing ionic strength. This results in low activity of the salt thus, extraction decreases [8].

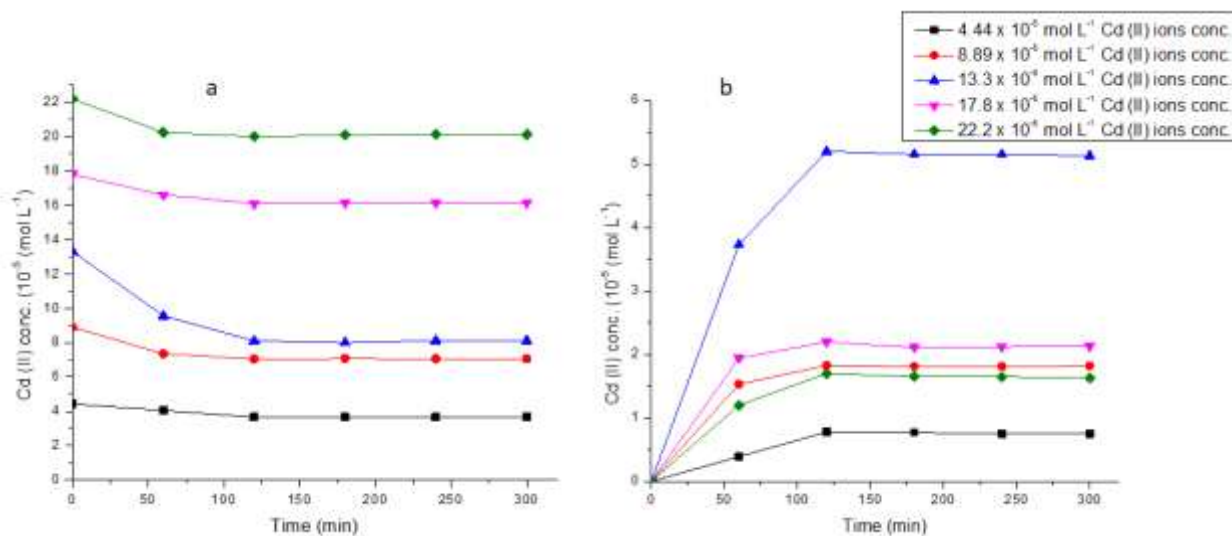


Fig.13. Variation in Cd^{2+} ion concentration with time in the feed (a) and strip (b) solutions at various concentration of Cd^{2+} ions.

(Initial $[\text{Cd}^{2+}] = 4.44 - 22.2 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NH}_3] = 6 \text{ mol L}^{-1}$, $[\text{TDDA}] = 30\%$).

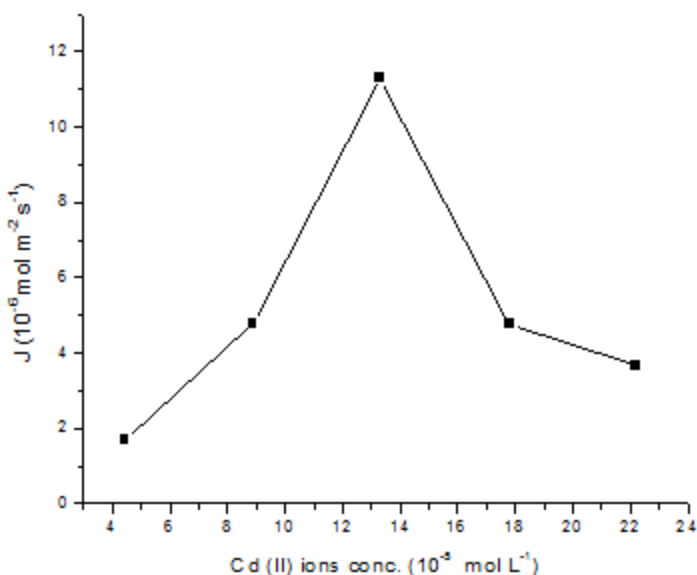


Fig.14. Effect of Cd (II) concentration on Flux.

(Initial $[\text{Cd}^{2+}] = 4.44 - 22.2 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NH}_3] = 6 \text{ mol L}^{-1}$, $[\text{TDDA}] = 30\%$).

3.7.2.6 SEM Analysis

Membrane morphology and surface chemistry are very important in the separation processes. Membrane morphology includes pore size and pore distribution, while membrane surface chemistry refers to the chemical nature and its composition. The nature of the solid support used in SLM should be hydrophobic so, that the organic solvent can retain in the membrane pores by capillary action. It must also be chemically and thermally stable on contact with the feed, receiving phases and the impregnating solvents [9]. The SEM images of polypropylene membrane (2400 Celgard) before and after extraction of cadmium ions are shown in Fig 15(a) and (b), respectively. A smooth surface with uniform pore distribution can be observed from the SEM image of membrane before the extraction while a granular morphology can be noted for the membrane after the extraction of cadmium ions [10]. The irregular morphology is maybe due to the fact that incorporation of Cd-TDDA adduct on the surface of

membrane. The membrane pores then become saturated and blocked, thus diminishing the effective membrane area [11].

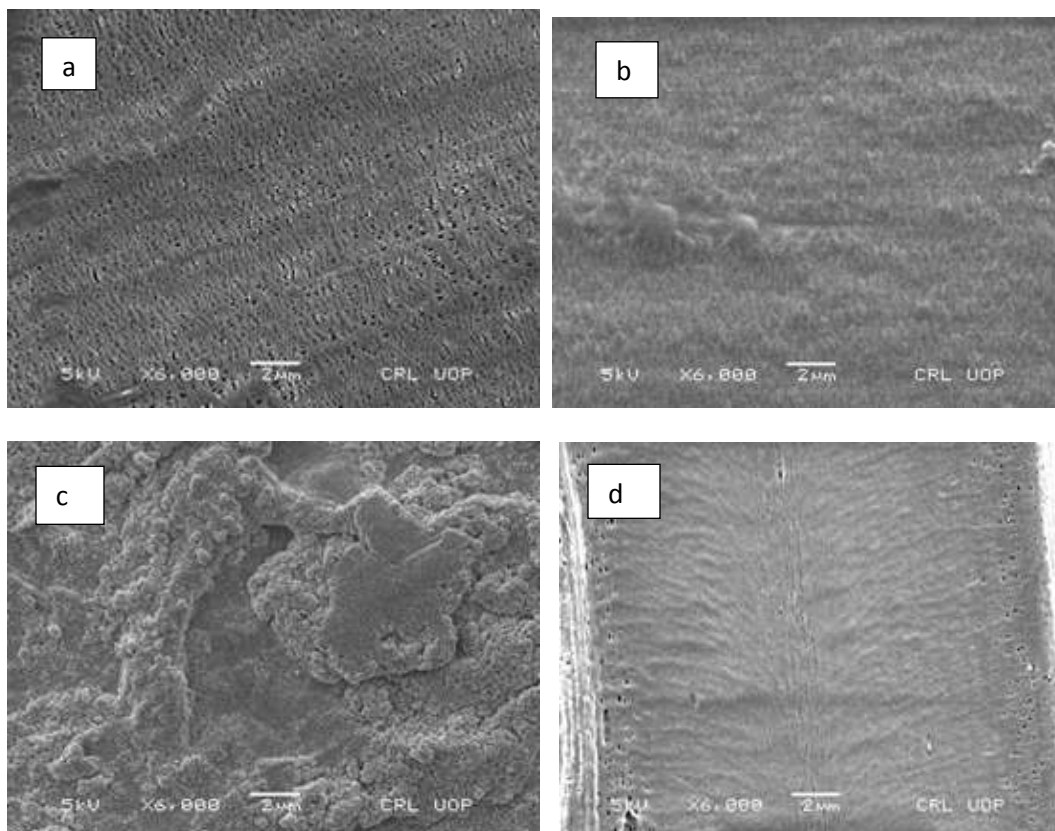


Fig.15. SEM image of membrane (a) before extraction (b) after impregnated with carrier (c) after extraction (d) cross section.

3.7.2.7 Extraction Time

Under the optimum experimental conditions the cadmium ions transport with time through supported liquid membrane was investigated. Fig. 16 shows the Cd^{+2} ions concentration after various intervals of time in the feed solution. Maximum amount of Cd^{+2} ions was removed in 120 minutes from the feed solution. About 92% of cadmium ion was extracted in the spike experiment in 120 minutes.

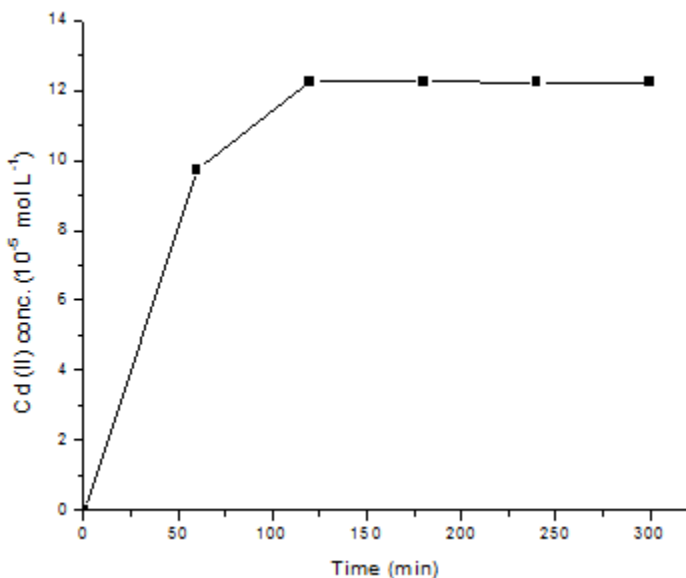


Fig. 16. Variation in Cd^{2+} ion concentration with time.

(Initial $[\text{Cd}^{2+}] = 13.3 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NH}_3] = 6 \text{ mol L}^{-1}$, $[\text{TDDA}] = 30\%$).

3.7.2.8 Membrane Stability

The stability of SLM was investigated in terms of carrier loss from the solid support [12]. To observe the stability of polypropylene–TDDA–xylene, SLM, at optimum conditions, 10 independent extraction experiments (one experiment each day) were carried out, i.e. concentration of Cd (II) ion at $13.3 \times 10^{-5} \text{ mol L}^{-1}$ along with 1 mol L^{-1} HCl in the feed solution, 30% TDDA in the membrane phase while $6 \text{ mol L}^{-1} \text{ NH}_{3(\text{aq})}$ was taken in the strip phase, maintaining at 1500 rpm stirring speed. Each experimental run was of 5h duration using the same membrane impregnated only once, however, for every experiment the solutions in each compartment of the cell were replaced with fresh feed and strip solutions. Between the successive experiments the cell compartments were filled with distilled water in order to avoid the dryness of the membrane. The results reveal (Fig. 17) that in all these experiments 92% extraction is

observed which an indication of stability of the membrane. Thus, it can be concluded from this series of experiments that the membrane is stable for 50 hours use.

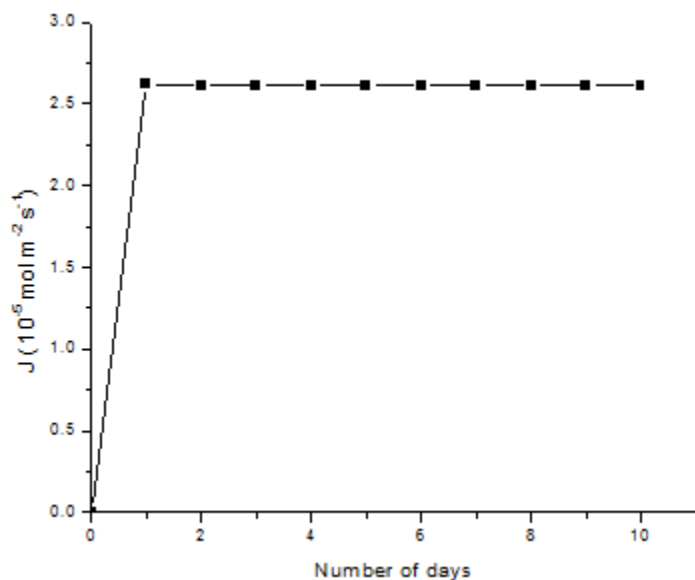


Fig. 17. Stability of SLM, flux versus time.

(Initial $[\text{Cd}^{2+}] = 13.3 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NH}_3] = 6 \text{ mol L}^{-1}$, $[\text{TDDA}] = 30\%$).

3.7.2.9 Extraction of Cd (II) ion from Paint Industry Wastewater

One of the major applications of cadmium is its use in the paint industry. The optimized SLM was used for the removal of cadmium from the waste water of paint industry. The paint waste water was filtered with Whatman filter paper; 80mL of filtrate was diluted up to 250 mL with distilled water. The optimum conditions were applied for the extraction as discussed earlier. The transport of cadmium through the SLM was evaluated in the presence of other toxic metal ions, such as, Cr(III), Cu(II), and Mn(II). The selectivity of carrier in a solid supported membrane system, using paint industry waste water as feed solution was investigated.

The stability constants of the metal ions play an important role in the extraction process. In the present system, the selectivity of the metal ions for extraction can be explained on the basis

of stability constants of the metal ions. The formation constants of $[\text{CdCl}_3]^-$, $[\text{CrCl}_3]$, $[\text{CuCl}_3]^-$, and $[\text{MnCl}_3]^-$ are 2.0, 0.74, 0.04, and 1.9 respectively [13-14]. Due to higher formation constant the chances of formation of cadmium-chloro complex are the highest which results in the higher concentration of cadmium-chloro complex in the feed phase and the higher value of distribution coefficient of Cd^{2+} ions in aqueous feed and organic membrane phases. Hence, more extraction of Cd^{2+} ions takes place.

The study shows that almost 87% of Cd(II) ions were recovered as given in Fig.18, whereas the spike results shows that 92% of cadmium was extracted under these optimized conditions. This might be due to the slight interferences of other metal ions present in the wastewater of paint industry. Detailed analysis of wastewater has been shown in Table 1.

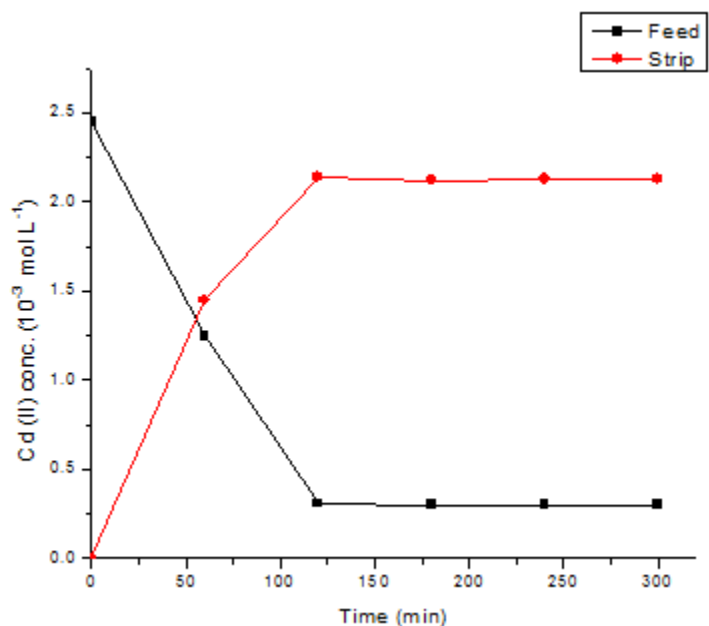


Fig. 18. Variation in Cd^{2+} ions concentration in feed and strip solution versus time (Paint industry waste solution in feed).

(Initial $[\text{Cd}^{2+}] = 2.45 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{HCl}] = 1 \text{ mol L}^{-1}$, $[\text{NH}_3] = 6 \text{ mol L}^{-1}$, $[\text{TDDA}] = 30\%$).

Table 1. Analysis of Paint Industry Waste Solution

S.No	Metal ion	Concentration of metal ions (mol L^{-1})		% Recovery
		B.E (Feed)	A.E (Strip)	
1	Cd(II)	2.45×10^{-3}	2.14×10^{-3}	87
2	Cr(III)	3.21×10^{-3}	1.0×10^{-4}	0.03
3	Cu(II)	2.69×10^{-5}	0.30×10^{-5}	1.1
4	Mn(II)	7.28×10^{-6}	0.12×10^{-6}	0.16

B.E = before extraction

A.E = after extraction

Conclusion

The TDDA-xylene based flat-sheet supported liquid membrane technique was used for the transport and extraction of Cd^{2+} ions. The parameters affecting the transport of cadmium through SLM were investigated to obtain the best operating conditions for the maximum separation of Cd^{2+} ion from aqueous solution. For the extraction of Cd^{2+} ion, optimum experimental conditions were $13.3 \times 10^{-5} \text{ mol L}^{-1}$ Cd (II) concentration, 1 mol L^{-1} HCl in the feed solution, 30% TDDA-xylene in SLM, 6 mol L^{-1} NH_3 solution in the stripping phase, and 1500 rpm stripping speed. The extraction time for optimum transport of cadmium ions through the supported liquid membrane under the optimum experimental conditions is 120 minutes. The SLM was found to be stable for 10 days.

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LIST OF PUBLICATIONS

The following publications have been made out of this thesis:

1. Khurshid Ali, **Robila Nawaz**, Nauman Ali, Alia Khaliq & Rizwan Ullah, Selective Removal of Zinc using Tri-ethanolamine-based Supported Liquid Membrane, Desalination and Water Treatment, 57(18), 2015, 8549-8560.
2. **Robila Nawaz**, Khurshid Ali, Nauman Ali and Alia Khaliq, Removal of Chromium(VI) from Industrial Effluents Through Supported Liquid Membrane Using Tri-octylphosphine Oxide as a Carrier, Journal of Brazilian Chemical Society, 27(1), 2015, 209-220.
3. **Robila Nawaz**, Khurshid Ali, and Muhammad Arshad, Recovery of Mercury Using a Trioctylphosphine Oxide-Based Supported Liquid Membrane System, Environmental Engineering Science, 32 (11), 2015, 948-959.
4. **Robila Nawaz**, Khurshid Ali, and Maria, Extraction of Copper from Wastewater through Supported Liquid Membrane using Tri-ethanolamine as a Carrier, Desalination and Water Treatment, 57(46), 2016, 21827-21841.