REMOVAL OF ARSENITES FROM INDUSTRIAL EFFLUENTS USING TRIDODECYLAMINE SUPPORTED LIQUID MEMBRANE

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Acknowledgement

All praise is due to Allah, whose worth cannot be described by speakers Whose claim to obedience cannot be satisfied by those who attempt to do so, and Whom the height of intellectual courage cannot appreciate; He for Whose description no limit has been laid down, no eulogy exist, no time is ordained and no duration is fixed. After Almighty Allah, praises are due his Prophet Muhammad (S.A.W), the most exalted who is forever a source of guidance and knowledge for the whole mankind.

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Finally, without the endless support and love of my parents I would be unable to reach this excellence where I stand today.

Sunbul Azeem

Summary

The current work is based on the extraction of arsenic(III) ions from industrial effluents through supported liquid membrane. Tridodecylamine was used as a mobile carrier supported on polypropylene membrane. The transport of arsenic was studied at various parameters such as concentration of carrier, feed, acid, strip reagent, and pH. The aqueous solution of arsenic and hydrochloric acid was used as feed phase and sodium hydroxide as receiving phase. The maximum transfer of arsenic was obtained at 0.1 mol/L of TDDA, 1.0 mol/L of HCl in feed phase, 1.0 mol/L 0f NaOH, at optimum pH 1. The stability of membrane was studied under the optimized conditions. The system was applied for real samples collected from pesticide industry, glass industry, paint industry, wood preservatives, and pharmaceutical industry.

CHAPTER-1

INTRODUCTION

The industrial operations are the major sources which are responsible for the various environmental problems such as air pollution, water pollution, and soil contamination. The industrial wastes are rich in harmful substances that contain heavy metals such as arsenic, mercury, chromium, nickel, zinc, copper, lead, cadmium, etc. The disposal of the industrial wastes to the environment has hazardous effects on the living organisms as these contaminants can cause serious health problems. Arsenic is highly toxic although it has a wide range of industrial applications. Therefore, the removal of arsenic has become a subject of immediate attention.

1. Arsenic

Arsenic is derived from a Greek word *arsenikon,* meaning “potent” [1] or “yellow orpiment” [2]. Arsenic is a toxic element which is extensively used in number of industrial processes. It is used in the power plants of coal and oil. In the production of glass, the arsenic is used as a decoloring agent. In the electronic industry, it is used as a mixture in the production of semiconductors. Arsenide is used as a laser material for the conversion of electrical energy into coherent light. Arsenic is used in many metallurgical operations such as smelting and roasting of ores. It is also used in the process of galvanizing, the production of bronze, and alloys of copper and lead. In ammunition industries, arsenic is used for the hardening of projectiles and to improve their flight characteristics. Arsenic is also used in chemical industries such as dyes, pesticides, wood preservatives, drying agent and in pharmaceutical industry [3]. Arsenic in the

form of trioxide is used in the glass industry as a fining agent. It is mixed with other compounds in order to remove air bubbles from glass and lighten glass [4].

1.1 Arsenic in the environment

1.1.1 Sources of arsenic

Arsenic occurs in soil, rock sediments, groundwater, and is also present in some food such as poultry, fish, meat, cereals and grains [5, 6]. The element is found in more than 200 minerals which mainly contain 60% arsenates, 20% arsenites, arsenides, and elemental arsenic, and the 20% of sulfides. These minerals include proustite (Ag_3AsS_3), smaltite ($CoAs_2$), orpiment (As_2S_3), energite (Cu_3AsS_4), domeykite (Cu_3As), loellingite ($FeAs_2$). Adamite, arsenolite, claudetite, scorodite, tennantite, safflorite, and hoernesite are also found in nature [7, 8]. Some other minerals such as realgar (AsS), arsenopyrite (FeAsS), niccolite (NiAs) [9], cobaltite (CoAsS), mimetesite ($Pb_5[Cl/(AsO4)_3]$) are also known [3, 7]. Arsenopyrite is the most abundant mineral followed by realgar and orpiment, which are formed in the earth's crust at high temperature [8].

The mobilization of arsenic in the environment is natural such as volcanic emissions, weathering, and biological activities. However, arsenic through anthropogenic sources such as mining, wood preservation, and burning of fossil fuels also has an important role in poisoning the environment [8, 10]. The release of industrial effluents and using arsenical herbicides and pesticides such as sodium arsenate, lead arsenate, and calcium arsenate have remarkable effects in the pollution of air, soil, and the water [11].

1.1.2 Chemistry of arsenic

Arsenic exists in the environment in a different of oxidation states e.g., arsenates (III), arsenates (V), arsine (-III) and arsenic (0) [2, 12]. Normally it is found in the combined form with oxygen (i.e. As_2O_3, As_2O_5), sulfur (i.e. As_2S_3, AsS, $HAsS_2$, $HAsS_2^{3-}$), and iron. Arsenic exists in both organic and inorganic forms. Some of the common inorganic arsenical species present in the environment include arsenous acids (H_3AsO_3, $H_3AsO_3^{2-}$), arsine (AsH_3), arsenic acids (H_3AsO_4, H_3AsO^{4-}, $H_3AsO_4^{2-}$), and the organic arsenic as methylarsenic acids (CH_5AsO_3) and dimethylarsenic acid ($C_2H_7AsO_2$) [2, 9]. The organic arsenicals (methylarsonic acid (MMA) and dimethylarsinic acid (DMA)) are found in seawater and marine organisms. Inorganic arsenic generally found in water as arsenites and arsenates. The toxicity of arsenic depends on the oxidation state of the element. The trivalent arsenic (arsenites) are considered 60 times more toxic than the pentavalent arsenic (arsenates). The organic compounds of arsenic are reported to be 100 times less toxic than inorganic arsenic [12-14]. It has been reported that pentavalent arsenic exists predominantly in an aerobic environment where sufficient of oxygen is present under natural pH conditions, whereas, the trivalent arsenic is found mostly in reducing conditions. The arsenates exist in the form of monovalent or divalent anions such as ($H_2AsO_4^-$) and ($HAsO_4^{2-}$) while the trivalent arsenic (arsenites) is present as anionic species ($H_3AsO_3^0$) or as uncharged species ($H_2AsO_3^-$) [6, 10].

1.1.3 Toxicity of arsenic

The presence of arsenic in the environment is a serious health issue of significant concern worldwide. Arsenic compounds are notorious as poisons which are used as suicidal and homicidal substances. It is believed that the death of Napoleon Bonaparte was due to the

poisoning of arsenic [7]. The toxicity of arsenic is classified as acute and chronic poisoning. The ingestion of arsenic contaminated food or drink causes acute poisoning. The symptoms of acute poisoning are vomiting, abdominal pain, dryness of throat and mouth, dysphasia, and diarrhea. Chronic poisoning mainly includes gastro-intestinal, cardiovascular, hematopoietic, respiratory, and nervous system disorder. Nausea, loss of appetite, erythema, hair fall, shivering of hands and feet, darken skin, and eczema. Exposure to arsenic may also cause skin lesions, hyperkeratosis, conjunctivitis, hyperpigmentation, leucomelonisis, and gangrene [13, 15]. Inorganic arsenic has been reported as a carcinogen to humans. It may cause cancer of brain, liver, skin, lungs, and kidney [6, 12, 16]. The adverse effects due to long-term arsenic exposure include renal, immunologic, neurological, genotoxic, reproductive, and mutagenic effects [7].

1.1.4 Arsenic in water

Arsenic contamination in groundwater has been investigated many parts of the world like China, Nepal, Bangladesh, India, Taiwan, Vietnam and Chile where groundwater is the source of drinking water. Millions of people in India and Bangladesh have been reported at risk due to drinking arsenic-contaminated water and food [1, 17, 18]. Traces of arsenic in water has also been reported in USA, Canada, Argentina, Mexico, Hungary, Poland and Japan [1, 13].

The World Health Organization (WHO) recommended value for the maximum arsenic concentration in drinking water is 10µg/l. However, in many developing countries the permissible limit is 50 µg/l arsenic concentrations in drinking water [8, 11, 12, 17]. The arsenic contamination in drinking water is mainly associated with the geochemical process, hydrology, manmade sources such as using arsenical pesticides, mining, and disposal of industrial effluents into water [11, 19]. Arsenic contamination of water corresponds to the discharge of wastes from industrial operations, using arsenical pesticides [6, 7], the process of leaching from rocks and

sediments that contain arsenic. It is also associated with the hydrological, geological and geochemical properties of aquifer [13]. When the presence of arsenic in water is detected, the two main options are to find a new safe source which is free of harmful chemicals and other bacteriological contaminants or to find some effective arsenic removal techniques [20].

1.2 Water treatment technologies

The industrial wastes are discharged into the environment which needs purification and separation process. It is challenging for researchers to remove and recover arsenic and other precious metal from contaminated water. Several methods and technologies have been introduced in order to remove toxic elements from water, which mainly includes adsorption, ion exchange, reverse osmosis, coagulation, lime softening, precipitation, and liquid membrane process [6, 21]. Although each method has some advantages, however, these also have some technical problems.

Adsorption was supposed to be an effective treatment for the removal of various toxic substances. The adsorption process using activated carbon shows excellent efficiency for the removal of both arsenates and arsenites but with the production of toxic wastes and also offers high cost [2]. It was discovered in the 1970s by Bellack that activated alumina can be used for the removal of arsenic from water. The finely granulated form of aluminum oxide (Al_2O_3) is used as activated alumina with the high internal surface area that provides a greater number of active sites for adsorption. The similar mechanism is followed to that of ion exchange resins, therefore, they are sometimes collectively known as ‘adsorption’. However, ion exchange is considered as a separate process. Arsenic is efficiently removed through activated alumina but kinetics for removal of arsenic are slower than ion exchange resins. Sometimes it has also been

noticed that arsenic is leaked in the activated alumina. Moreover, the system meets with the problems of regeneration and the possibilities to be clogged, as well as a long time for contact is required.

Ion-exchange involves the displacement of adsorbed ions from the solid surface by dissolved ions similar to that of the adsorption process. However, unlike the other forms of adsorption where the stronger bonds are formed and the process is irreversible, ion exchange has the reversible displacement of ions. Synthetic ion exchange resins are used for the treatment of water to remove many unwanted dissolved particles consisting of cross-linked polymer framework which is called 'matrix'. The most commonly used matrix is polystyrene cross-linking divinylbenzene. The resins may be acidic or basic, acidic resins being negatively charged are treated with cations which are used for the removal of other positively charged species are called cation exchange resins. The basic resins are called anion exchange resins which are positively charged and are used for the removal of negatively charged particles during the treatment of water. Different anion exchange resins are used for the removal of arsenic which shows effective results for arsenates. However, arsenites are not removed because they are uncharged species, but an additional step of oxidation will be required for arsenites. Usually, sulfate or nitrate-selective resins are used for the removal of arsenates [20]. In ion-exchange process, toxic chemical reagents used for the regeneration of resin are released in the environment.

Reverse osmosis is an efficient process for the removal of As (V) but having low efficiency for As (III), also the efficiency depends on the pH of the solution and the type of membrane [22, 23]. The consumption of high power because of high pumping pressure as well as is the restoration of the membranes is required in the process of reverse osmosis [24]. It is a high-cost method, as well as toxic wastes are produced in the process. The precipitation or oxidation

process is low-cost, simple but requires a critical pH control and an additional step of oxidation. Coagulation is another simple process that works on a broad range of pH but the drawback is the production of toxic substances and many operational steps [2]. Solvent extraction is another process which is a more established system with high purification properties. However, the process requires a large amount of solvent. Apparatus design, high capital cost, no sufficient kinetic data and loss of extractants are some of the major disadvantages of the solvent extraction process [25].

1.3 Membranes separation technique

Membranes separation processes have been received remarkable attention for the separation of various ions due to its characteristic properties such as easy operation, high selectivity, and low operational cost. A membrane process is a useful tool for separation and purification methods having high functionality with low consumption of energy without any side reactions. The technique has been successfully applied in the analytical, biomedical, and industrial fields as well as in the treatment of wastewater [26, 27].

Membranes separation technique is an auspicious technique for the removal and extraction of ions and molecules. Moreover, no additional steps like oxidation are required. It is a combination of scrubbing, extraction and regeneration process thus making it a single step operation [27]. The process offers an efficient and effective removal of arsenic under moderate conditions without adding toxic wastes to the environment. In membrane separation technique a microporous hydrophobic membrane is used as a barrier between two phases [2]. The membrane process has a wide range of applications which use different kinds of procedures, structures and materials of membrane. On the basis of driving force the membrane process can be categorized as;

(i) Pressure-driven process, which includes ultra-filtration, microfiltration, reverse osmosis, and gas separation.

(ii) Concentration-gradient driven process includes partial pressure driven process, pervaporation, and dialysis.

(iii) Electrical potential-driven process includes electrodialysis and electrolysis.

Membrane separation in combination with conventional process such as membrane contractors, pertraction, and hybrid process are some other processes [28, 29].

1.4 Membrane

Generally, a membrane is considered as a semi permeable barrier between the two aqueous phases that allows the transfer of chemical species and prevents some other species. The movement of species through the membrane normally occurs from higher concentration gradient towards low concentration gradient.

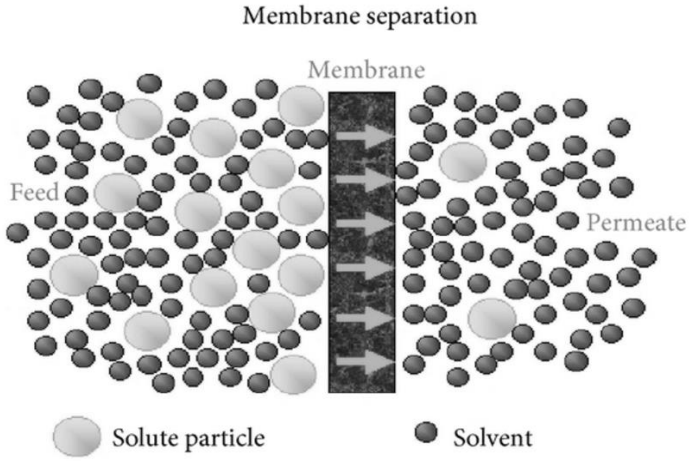


Fig. 1.1. Schematic representation of membrane separation process

It is a diffusion process however; sometimes it has also been observed that ions and molecules can move against their concentration gradient. This is due to presence of the

concentration of second species i.e. coupled transport. The membrane embedded with some extractant or carrier may also facilitate the transport mechanism i.e. facilitated transport. The extractant or carrier are dissolved in an organic solvent supported on microporous surface was first used by Bloch in 1970 for metal ion removal [26].

The properties which determine the performance of the membrane are good thermal stability, chemical and mechanical strength, high fluxes, highly selective, compatibility with the system and cost effectiveness/economy. A membrane may be hollow fibers, tubes, capillaries or flat sheets.

1.5 Types of membrane

The membranes may be liquid films with carrier, porous or dense polymers, ceramic films or metal films, and can be symmetric i.e. the structure is uniform throughout the membrane, asymmetric i.e. the top and bottom sides are different, solid or liquid, homogeneous, heterogeneous, electrically charged or can be neutral. Different types of membranes used may be generally classified as below [28-31]:

- Polymeric membranes
- Microporous membranes
- Nonporous, dense membranes
- Ceramic membranes
- Composite membranes
- Electrically charged membranes
- Anisotropic membranes
- Liquid membranes

Different kinds of membranes are shown in figure 2.

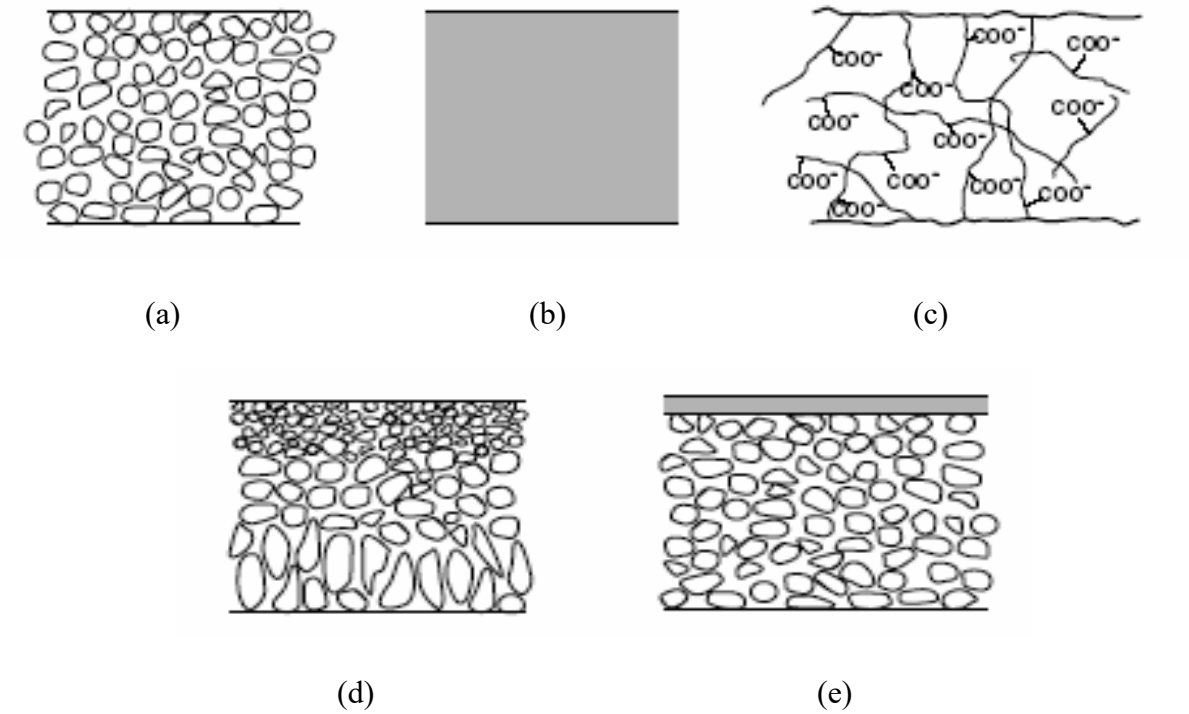


Fig. 1.2. Schematic diagram of principal types of membranes: (a) micro porous membrane (b) non-porous membrane (c) electrically charged membrane (d) anisotropic membrane (e) ceramic membrane

1.5.1 Polymeric membranes

Polymeric membranes are made up of polymers such as polyurethanes, polyvinylidene diflouride, polyvinyl alcohol, and polyacrylic acid. The manufacturing of polymeric membranes is comparatively inexpensive. Another material chitosan is also used for the preparation of membranes having high chemical stability and better film formation. Polymeric membranes are known for high permeation fluxes their perm-selective nature towards water. Polymeric membranes supported with polytetrafluoroethylene (PTFE) and polyacrylonitrile has also been reported. For the dehydration of aqueous system, a polymeric membrane was prepared by Sulzer Chemtech. The membrane has a cross-linked layer of polyvinyl alcohol and a layer of porous

polyacrylonitrile which was directed on polyphenylene sulfide fabric. A cross-linked membrane was developed by Hyder *et al*. by two methods, one is thermally cross-linked and the other is chemically cross-linked. It was experimentally observed that the flux was higher for thermally cross-linked membranes; however, the selectivity was higher for chemically cross-linked membranes. However, the disadvantages of polymeric membranes are the poor temperature stability, insufficient solvent, lower selectivity, and swelling of membranes [29].

1.5.2 Microporous membrane

Microporous membranes are known as the simplest form of membranes. The porous membrane is used as filters and depends upon the pore size as well as on the chemical composition of the system [32]. The choice of material of membrane is determined by the chemical resistant, temperature stability, and fouling [33]. The separation through these membranes is generally based on pore size, ranges from 0.01μm to 10 μm in diameter. Particles which are larger than the largest pore size are restricted. The particles which are smaller than the smallest pore size are allowed to pass through membranes while the particles having size larger than smallest pore but smaller than largest pores are partially restricted [34]. The membranes are applicable in the field of ultra-filtration, electrophoresis, electro-osmosis, and microfiltration.

1.5.3 Dense non-porous membrane

The non-porous membranes are homogeneous in nature. These membranes are applied for gas separation, reverse osmosis and pervaporation. The separation of the species is related to the transport rate and can be determined by concentration and diffusivity in the membrane phase. The membranes are usually a homogenous film supported on a microporous surface [31, 34]. For

non-porous membrane the choice of material is determined by the flux and selectivity of the membrane [33].

1.5.4 Ceramic membranes

Ceramic membranes are also called inorganic membranes. These membranes are made of alumina, silica or zeolite with good resistant properties and high thermal stability, high permeability and high selectivity. Ceramic membranes have a wide range of applications; industrially these membranes are used to produce better quality of products are also used in pervaporation. The porous inorganic membranes have high permeability and high temperature stability as compared to dense membranes and organic membranes respectively. Silica membranes with addition of ZrO_2 and TiO_2 have high resistant and high flux properties. Zeolite membranes with high chemical and mechanical strength as well as biological stability have also been used for separation purposes. Zeolite membranes have many advantages, however, some zeolites show sensitivity towards low pH such as NaA-type zeolite membranes.

1.5.5 Composite membrane

The hydrophilic polymers casting on porous support are known as composite membrane. The porous surface is used as a mechanical support to casting layer. The composite membranes are provided with cross-linked structure which minimizes the swelling of membranes as well as making them highly selective. The organic-inorganic hybrid membranes have good mechanical strength and are thermally and chemically stable. These membranes are provided with the properties of both organic and inorganic membranes to perform ideal separation [29].

1.5.6 Electrically charged membrane

The electrically charged membranes are those types of membranes which has fixed positive or negative charges. These membranes are mostly microporous but can be dense non-porous. The membranes are called anion exchange membranes when it has fixed positively charged ions because these are capable of binding anions from the surroundings. Similarly, when membranes have fixed negative charges and binds negative charges from the surroundings are termed as cation exchange membranes. The separation through electrically charged membranes depends on the concentration and size of ions. These membranes are used mostly in electrodialysis [34].

1.5.7 Asymmetric membrane

Increasing industrial applications have led to the development of asymmetric membranes. The membranes consist of two layers, a thin upper layer having thickness of 0.1 to 0.5 μm and a porous substructure having thickness of 50 to 150 μm. The surface layer is responsible for high selectivity and high permeation properties while the sub layer provides a mechanical support [33, 34].

1.5.8 Liquid membrane

Liquids can be used as a membrane just like other membranes it also can separate the two phases. The separation in liquid membranes depends upon the diffusivity and solubility of the two phases as in solid membranes. The membranes are often used with carrier which forms a complex with solute and increases the flux of that specific solute. The carrier is mobile in such case and can be soluble in the liquid. However, the carrier may be fixed and less mobile when it is physically or chemically bonded to the solid polymer. The mobile carrier is termed as liquid membrane where the complex between solute and carrier pass over the membrane through

diffusion. The mobile carrier system has higher diffusivity as compared to the fixed carrier system [30].

Liquid membranes play an important role in the field of separation and purification technology. It is a fusion of several steps such as scrubbing, regeneration, extraction making liquid membranes a field of great interest. The hydrometallurgical applications of liquid membranes were first investigated by Li *et. al.* in 1968 for metal ion separation [27]. The liquid membrane process meets several advantages over other methods as it has high selectivity, and requires less solvent and organic carrier with improved characteristics acquired in a single step process [25]. The liquid membranes have been extensively used for the separation and extraction of metals from waste water. They can also be used for the recovery of precious metals from a very low concentration without any secondary wastes production. The uphill transport of solute in liquid membrane occurs when the feed phase and membrane phase has higher solute concentration than the liquid membrane phase and receiving phase. Initially, the liquid membranes used for industrial application was emulsion formation, which is the modified with the formation of bulk liquid membrane for the removal of zinc and copper by Boyadzhiev. Later on, Kralj and his co-workers has made efforts in the field of liquid membranes for selective separation of copper oxalate from a mixture of calcium, cadmium, and copper oxalate with a flat sheet supported liquid membrane [27]. Liquid membranes has a wide range of applications in many fields such as medicines, hydrometallurgy, textile, biotechnology, food industry, and environmental protection etc [35].

1.6 Classification of liquid membrane

Liquid membranes can be classified in different directions such as transport mechanism, module structure, applications, membranes support, and carrier type. Here only the first two classifications are discussed briefly as follows:

1.6.1 Transport mechanism

The liquid membranes of transport mechanism can be classified as simple transport, carrier facilitated transport, coupled co-transport, and active transport.

1.6.1.1 Simple transport

Simple transport mechanism depends on the solubility of the solute in liquid membrane. The transfer of solute is a simple diffusion process occurs through membrane. The transport of solute stops when the concentration reached at equilibrium. The solutes with liquid membrane do not react chemically and is present in the same form as in liquid membrane, receiving phase, and in feed phase.

1.6.1.2 Carrier-mediated transport

Carrier facilitated transport through liquid membranes comprises different modes of transport following partitioning, complex formation, and diffusion. The solute dissolved in feed solution reacts chemically with carrier on the feed phase-liquid membrane surface. The complex is formed which is then dissociated at the liquid membrane-receiving phase interface with the liberation of the solute in the strip solution. The carrier-mediated transport increases the rate of transportation. However, the simple transport also occurs at the same time [36]. The transport mechanism has wide range of applications in removal of ions such as Cu^{++}, Zn^{++}, Hg^{++} as well as nitrates and chromates [30].

1.6.1.3 Coupled counter-transport

The coupled counter transport is an ion-exchange transport where the metal ions are exchanged with H^+ ions is facilitated by acidic carrier. The carrier picks up the metal ions forming complex which diffuses across the membrane. Once again, the exchange of ions occurs on the other side, here the complex exchanging the metal ions with H^+ ions. The metal ions cannot transfer back due to low solubility. The transfer mechanism is similar to that of facilitated transport but the carrier coupling with two species, in which one of the species moves against its concentration gradient allowing the large concentration gradient of the second specie [37, 38].

1.6.1.4 Active Transport

Active transport is a highly selective transport mechanism. The transport of other species is completely restricted. The chemical reactions take place in active transport are irreversible. The active transport has been operated by biochemical conversions, oxidation-reduction reactions, and catalytic reactions [36].

1.6.2 The module design of the system

Liquid membranes can be generally classified as three basic types which are describe as below [26, 30]:

- Emulsion liquid membrane (ELM)
- Bulk liquid membrane (BLM)
- Supported liquid membrane (SLM)

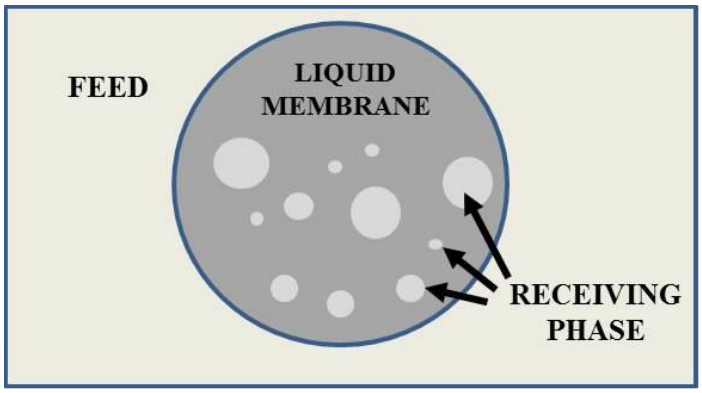
1.6.2.1 Emulsion liquid membrane

The emulsion liquid membrane (ELM) created by Li and his co-workers in 1968, is one of the most widely used liquid membrane type [39]. An emulsion liquid membrane ELM is formed by two immiscible phases, such as water-in-oil emulsion. The resultant emulsion contains carrier

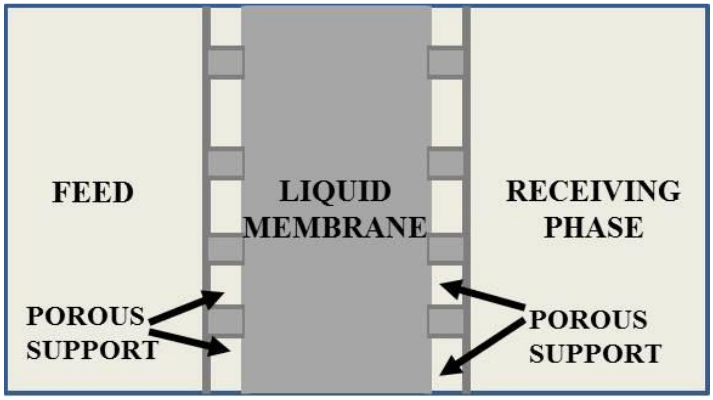
in the membrane solution and the internal aqueous solution with the stripping reagent. [2, 39, 40]. The external phase is an aqueous feed phase containing metal ions. The target species are extracted from feed phase into the emulsion droplet, when sufficient large amount of metal ions has been extracted the emulsion is separated and is broken to liberate the metal ions. The organic phase is then recovered and recycled. The main problem related with ELM is the instability of the liquid membrane. The swelling of emulsion is another disadvantage which can reduce the strip reagent efficiency as well as membrane stability [34, 39].

1.6.2.2 Bulk liquid membrane

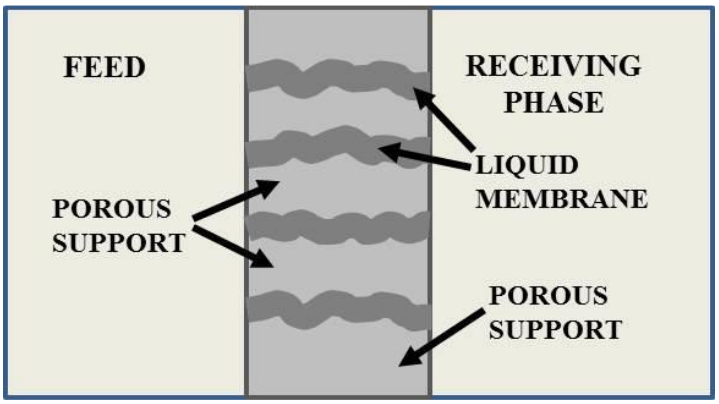
Bulk liquid membrane (BLM) consists of two aqueous phases, the feed phase and the receiving phase. These two phases are separated by a bulk organic phase which is immiscible with water. The BLM is provided with microporous support to separate the two aqueous phases, or it can be without microporous support i.e. layered BLM. There are some other systems that show resemblances with bulk liquid membrane such as hybrid liquid membrane (HLM), hollow fiber liquid membrane (HFLM), flowing liquid membranes (FLM), and multi membrane hybrid system (MHS) [36]. The bulk liquid membrane has a simple set-up which use small amount of solvent and has high degree of separation [35]. The main disadvantage associated with bulk liquid membrane is the smaller surface area of the membrane and rate of mass transfer which limits their practical applications [2, 27].



(a) ELM



(b) BLM



(c) SLM

Fig. 1.3. Comparison of (a) Emulsion Liquid Membrane (ELM), (b) Bulk Liquid Membrane (BLM), (c) Supported Liquid Membrane (SLM).

1.7 Supported liquid membrane

The supported liquid membrane is an interesting technique which is used for the separation, recovery and the removal of contaminants. The technique was studied for various elements such as Copper (II), Cadmium (II), Platinum (IV), Zinc (II), Vanadium (V) and Palladium (II). Supported liquid membrane process has several advantages over other methods as the removal or extractions of species are carried out in a single step. The minimum amount of carrier and organic diluents is used [41]. The process consumes low energy and has low operation cost with high separation efficiency. The supported liquid membrane is a convenient separation process where the carrier is immobilized, also the solutions in the feed and strip side can be removed or added continuously [25].

In the past few years, for the separation and effective removal of ionic and neutral species the supported liquid membrane has been used as an alternative to other membrane process such as electrodialysis, reverse osmosis, etc. The separation of target species from a very dilute solution is possible with SLM. The system is set up with feed phase and receiving phase separated by a microporous film impregnated. The membrane films are used as a support for organic phase. The properties that make a membrane of choice are that it should be highly porous, thin, hydrophobic, small pore size, have good chemical and mechanical stability, and cost effective [42]. The similar process to liquid membrane is solvent extraction process where the striping and extraction of metal ions are carried out simultaneously. The hydrophobic microporous membrane is saturated with organic extractant/carrier and is interposed between the two aqueous phases, the feed and stripping solutions. The membrane at one side is in contact with feed solution while another face of membrane is directed towards stripping solution. The carrier picks up the target species from feed side and is transferred through diffusion to strip side.

However, the ions can also be transport from very low concentration towards high concentration against their concentration gradient [42, 43].

1.7.1 Types of SLM

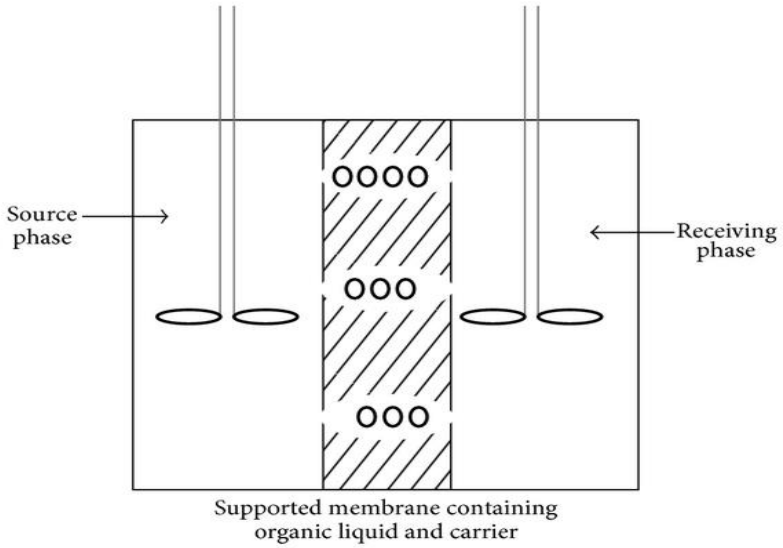
On the basis of shape, size, and surface area the supported liquid membrane are classified as:

1.7.1.1 Flat sheet supported liquid membrane

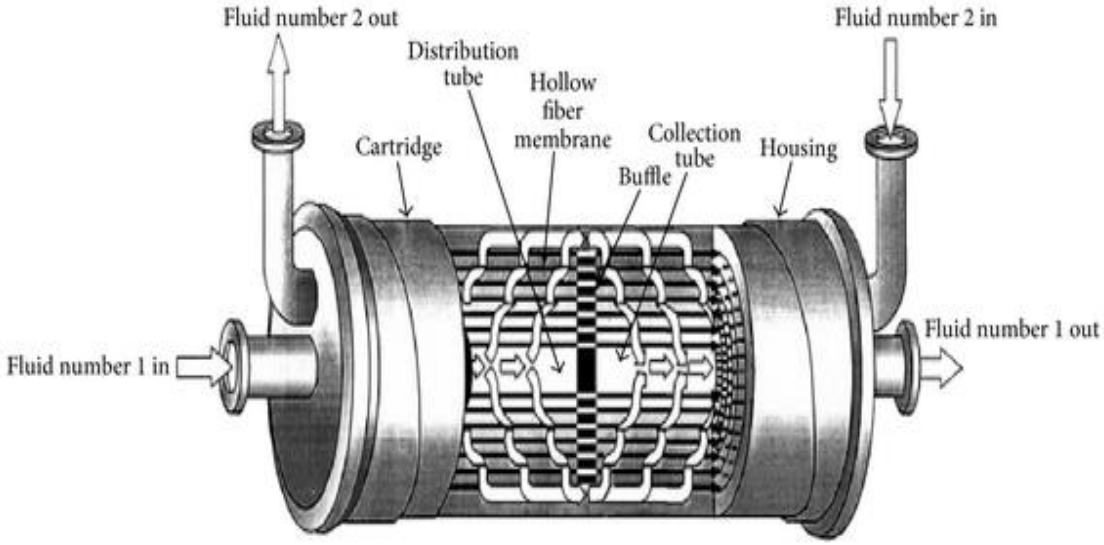
The flat sheet supported liquid membrane (FSSLM) is the simplest form of SLM. In FSSLM a thin microporous solid support is used for liquid membrane. The support is saturated with organic extractant and is placed between the two compartments of the cell i.e. half-cell. One of the half cells contains feed solution while the other has strip solution, stirred with mechanical stirrers.

1.7.1.2 Hollow fiber supported liquid membrane (HFSLM)

The separation of ions is carried out by a hollow fiber module. The outer cell is a nonporous material which restricts the transportation of solution present inside the cell. Internally the cells are nicely packed with thin fibers which allow the source phase to pass through these fibers [44].



(a)



(b)

Fig. 1.4. Schematic representation of (a) flat sheet supported liquid membrane, (b) hollow fiber supported liquid membrane

1.7.2 Mechanism for mass transfer in SLM

The transportation of metals in SLM occurs in various steps.

Step I: In the first step the metal species are diffused in the feed solution and react with carrier at SLM interface forming metal-carrier complex. In case of acidic carrier, the H^+ ions are released in the feed solution (counter-transport) while with basic or neutral carrier the X^- ions are transport with the metal ions (co-transport).

Step 2: The second step involves the dissociation of metal-carrier complex through the membrane due to negative concentration gradient.

Step 3: In third step at the membrane and strip interface the metal ions are released in the strip solution. In case of acidic carrier, the metal ions M^+ are replaced with H ions while X^- ions are released in strip solution in case the basic carrier is used.

Step 4: The carrier after releasing the metal ions are diffused back through the membrane [45].

The metal ions are separated from its aqueous solution by supported liquid membrane. The permeation of ions occurs due to difference between the chemical potential gradient of the two phases of the SLM. If the extractant used is acidic in nature the following reaction takes place:

$$M^{n+} + n\,HX \longrightarrow MX + n\,H^+ \qquad \text{(i)}$$

The chemical potential gradient is achieved by a pH gradient. Here M is the metal ion, HX represent acidic carrier, X^- is anion, and A represent the basic carrier. When a neutral or basic extractant is used the reaction occurs as follows:

$$M^{n+} + nX^- + A \longrightarrow MX_nA \qquad \text{(ii)}$$

The metal ion transportation occurs by the concentration gradient of X^- ions. However, the transport of M^+ and X^- occurs in the same direction [42, 46].

1.8 Carrier

The carrier/extractant is an organic compound which is chosen selectively components of the feed phase. On the basis of metal ion extraction reaction, the carriers are classified as acidic carrier, basic carrier, and neutral carrier.

Acidic extractant are represented by HX, the metal ions are transported by cationic exchange reaction as shown in equation (i). The acidic extractant are further classified as chelating and non-chelating extractants. Chelating extractants are having a proton which easily dissociate. They form the bidentate complex with metal ions. The common types of such extractants used are kelex, salicylaldoximes, ketoximes, or their mixtures. Non-chelating extractants include derivatives of carboxylic acid and phosphorous acid with reactive groups as -SO_3H, -COOH, and >P(O)OH. The most versatile non-chelating extractant is di(2-ethylhexyl) phosphoric acid (D2EHPA), which has good chemical stability, low solubility with water, good stripping properties, and versatility for the extraction of various metals.

The second type of carrier is basic extractant where an anionic exchange reaction takes place. The basic extractants are amines or quaternary ammonium halides. Initially the amines are converted to amine salts by extracting acid from aqueous solution and the exchange the anions with metal ion. The basic extractants used for supported liquid membranes are Alamine 304, Alamine 336, Aliquate 336, etc. The reactions for basic carrier can be represented as follows:

$$R_3N + HA \longrightarrow R_3N^+H\ A^- \qquad \text{(iii)}$$

$$MY^{n-} + n(R_3N^+H\ A^-) \longrightarrow (R_3NH)n\ MY^{n-} + nA^- \qquad \text{(iv)}$$

Here the MY^- represent metal species.

The third type of extractant is called neutral extractant or solvating extractants. These are the organic compounds which have no cationic or anionic groups but the metal species are extracted as neutral complex. The two sub types of such extractants are known as organic compounds in which oxygen is bonded to carbon while the second type have oxygen bonded to sulphur/phosphorous [25, 43, 47].

Aims and Objectives of the work

The extraction of arsenic through supported liquid membrane is studied in the current work. The carrier used is tridodecylamine commercially known as Alamine 304. It is an organic compound having chemical formula $C_{36}H_{75}N$. They are tertiary amines with high molecular weight 521 [48]. The main objectives of the work are as follows:

- To study the transport of arsenic ions through various concentrations of tridodecylamine.
- Investigate the effect of arsenic concentration on the extraction.
- To observe the complex formation during the process.
- To optimize the conditions and study the effects of these parameters on the extraction of arsenic such as acid concentration, stripping reagent concentration, and pH.
- To apply the optimized conditions for real sample collected from industry.
- To determine the flux for the system.
- To investigate the stability of the supported liquid membrane and characterize the membrane by SEM before and after the reaction completion.

CHAPTER-2

EXPERIMENTAL

2.1. Chemical and Reagents

The chemicals and reagents used for the extraction of arsenic are arsenic trioxide (99%), hydrochloric acid (35.5% Merck), sodium hydroxide (99-100% Sigma Aldrich), tridodecylamine (95% Merck) dissolved in tetrahydrofuran (99.99% Scharlau TE0220), was used as a carrier. A polypropylene microporous membrane was used as a support for liquid membrane.

For analysis of samples the reagents used were HCl (35.5% AR grade Merck), potassium iodate (Sigma Aldrich), malachite green dye and acetate buffer.

2.2 Instrumentation

2.2.1. Analytical Instruments

The pH measurements at feed and strip side were carried out with pH meter (resolution 0.001 pH, accuracy ± 0.003 pH), the chemicals and reagents were weighed with Adventurer Ohaus balance (resolution 0.0001 g, accuracy ± 0.0001 g). The samples were analyzed with UV-visible spectrophotometer (UV-1602 BMS), a double beam spectrophotometer with energy-optimizing deuterium and tungsten halogen lamps. The wavelength range of 550-750 nm was set for detection of arsenic in samples.

2.2.2. Membrane Cell

The extraction of arsenic was carried out in a membrane cell which consists of two compartments. Each compartment has a cross sectional area 23.79 cm^2 and the volume capacity was 250 cm^3. The microporous membrane was insert between the two half-cell fitted with clamps on each side of the cell. The solutions in feed and strip sides are continuously agitated with electric stirrers at about 1200-1500 rpm at 25±1 ˚C.

2.3. Preparation of Solutions

The feed solution was prepared by dissolving the requisite amount of arsenic trioxide for different concentration of 1.011×10^{-5} to 5.055×10^{-5} mol/L, and hydrochloric acid solution of 0.1-2 mol/dm^3, and diluted with distilled water. The aqueous solution of sodium hydroxide was prepared as stripping reagent.

For spectrophotometric determination 25 mg of malachite green dye was dissolved in 100 mL of distilled water followed by adding 1.5 mL of 85% phosphoric acid and diluted up to 500 mL in a volumetric flask. HCl of 1M, 1% of potassium iodate, and acetate buffer of pH 4.5 were prepared by dissolving the requisite amount in distilled water [49].

2.4. Permeation Study

The polypropylene membrane celgard 2400 was soaked overnight in tridodecylamine carrier. The membrane cell was set up by placing a membrane film in between the two compartments of the cell. The cells were adjusted with clamps. The feed and strip solutions (250 mL) were transferred to each of the half cell. The cells were covered with lid and were continuously stirred to avoid concentration polarization at membrane interface. The samples (5 mL) were drawn at regular time intervals from both the feed and stripping solutions and were

analyzed by UV-visible spectrophotometer by reported method. The flux was calculated using the formula [50]:

$$\text{Flux} = \frac{\text{Concentration change of metal ion}\left(\text{mol/dm}^3\right) \text{x solution volume in feed or strip}\left(\text{dm}^3\right)}{\text{Effective membrane area}\left(\text{m}^2\right) \text{x dt}} \quad (1)$$

2.5. Optimization of Experimental Conditions for Extraction of Arsenic Ions

For the extraction of arsenic different conditions were optimized by varying concentration of carrier, concentration of arsenic ions, concentration of acid in feed solution, concentration of strip solution, and pH.

The optimized experimental conditions for arsenic ions transportation are:

- The dimension of permeation cell were10 × 8.5 × 8 cm^3 and cross-sectional area was 23.79 cm^2.
- Tridodecylamin 0.6 mol L^{-1} was used as a carrier.
- The arsenic of 5.055×10^{-5}mol L^{-1} in 1 mol L^{-1} of HCl was feed solution.
- Sodium hydroxide of 1 mol/dm^3 was used as strip reagent.
- The analysis was carried out at 617 nm at UV-visible spectrophotometer.

CHAPTER-3

RESULTS AND DISCUSSIONS

3.1. Theory

The transport of arsenic through supported liquid membrane has been studied in the present work. This process of transportation may occur in various steps. In the first step the arsenic ions present in the feed solution form a complex with carrier at feed-membrane interface. In the second step the complex is diffused across the membrane towards the membrane-strip interface. The next step is dissociation step where the metal-carrier complex is dissociated at the strip side. The carrier is then sent back through the membrane phase releasing arsenic ions in the strip solution. A theoretical model is important for the diffusion of complex through the liquid membrane for arsenic ions transportation.

The following possible reactions may take place at feed and strip sides, if the tridodecylamine (TDDA) is represented by L.

3.2. Reactions at Feed-Membrane Interface

In acidic medium provided by HCl, the tridodecylamine may be protonated to form LH^+.

$$L + H^+ \rightleftharpoons LH^+ \qquad (1)$$

In the presence of hydrochloric acid in the feed solution the arsenic trioxide is supposed to convert to arsenic trichloride.

$$As_2O_{3(aq)} + HCl_{(aq)} \longrightarrow [As\,(Cl_3)_{n+1}]^{n-}{}_{(aq)} + H_2O_{(aq)} \qquad (2)$$

The anionic $[As\ (Cl_3)_{n+1}]^{n-}$ then react with cationic LH^+ at feed-membrane interface to form a complex as follows:

$$nLH^+_{(org)} + [As\ (Cl_3)_{n+1}]^{n-}_{(aq)} \longrightarrow (LH)_n.\ As\ (Cl_3)_{n+1(org)} \qquad (3)$$

The subscript 'org' represents organic phase, 'aq' for aqueous phase, and 'n' for the number of molecules of Cl^- and L associated with As(III) ions to form the neutral complex extractable into liquid organic phase.

The contribution of H^+ and Cl^- in Eq. (3) may be represented as:

$$nL_{(org)} + nH^+_{(aq)} + AsCl_{3\ (aq)} + nCl^-_{(aq)} \longrightarrow (LH)_n.\ As(Cl_3)_{n+1(org)} \qquad (4)$$

3.3. Reactions at Membrane-Strip Interface

At feed-membrane interface the neutral complex formed as shown in equation (3) and (4) is extractable in liquid organic phase. The complex is diffused through the liquid membrane from feed solution into strip interface. Here the complex is dissociated by the sodium hydroxide in strip solution.

$$(LH)_n.As(Cl_3)_{n+1} + nNaOH \longrightarrow As\ (III) + 2Cl^- + H_2O + nNaCl + L \qquad (5)$$

The free molecules of tridodecylamine (L) diffuse back to the feed solution across the liquid membrane. These free molecules are once again capable of forming complex with arsenic ions. According to Wilke-Change equation [51], the diffusion coefficient for the forward transportation of carrier molecules should be lesser than the backward transport of free carrier molecules so that the concentration of TDDA will always be higher at feed-membrane interface then the concentration of the complex.

3.4. Effect of Various Parameters on Transport Rate

Different parameters were studied for the extraction of arsenic. These parameters have significant effect on transport rate which are discussed as follows:

3.4.1. Effect of TDDA concentration

The carrier has a momentous effect on the extraction of ions in the supported liquid membrane. To study the effect of tridodecylamine on the transport of arsenic various concentration of TDDA were used from 0.05-0.25 mol/L. Tetrahydofuran was used as a solvent for carrier. The other parameters were kept constant during this study such as the arsenic concentration was kept at 5.055×10^{-5} mol L^{-1} in 1.0 mol L^{-1} of hydrochloric acid, and the sodium hydroxide concentration was constant at 1.0 mol L^{-1}.

The figure 3.5 shows that the concentration of arsenic decreases as the concentration of tridodecylamine increases from 0.05-0.25 mol/L in tetrahydrofuran in membrane phase. The carrier has significant effect on the flux (J) of arsenic (III) in membrane phase at 0.1mol/L of TDDA concentration as shown in the figure 3.6 and 3.7. The flux for arsenic is insignificant beyond 0.1mol/L. This decrease in the transport of arsenic is due to enhanced friction of liquid membrane phase due to high viscosity, as with increasing carrier concentration the viscosity of liquid membrane phase increases. So, the optimum carrier concentration is considered as 0.1 mol/L of tridodecylamine for further studies.

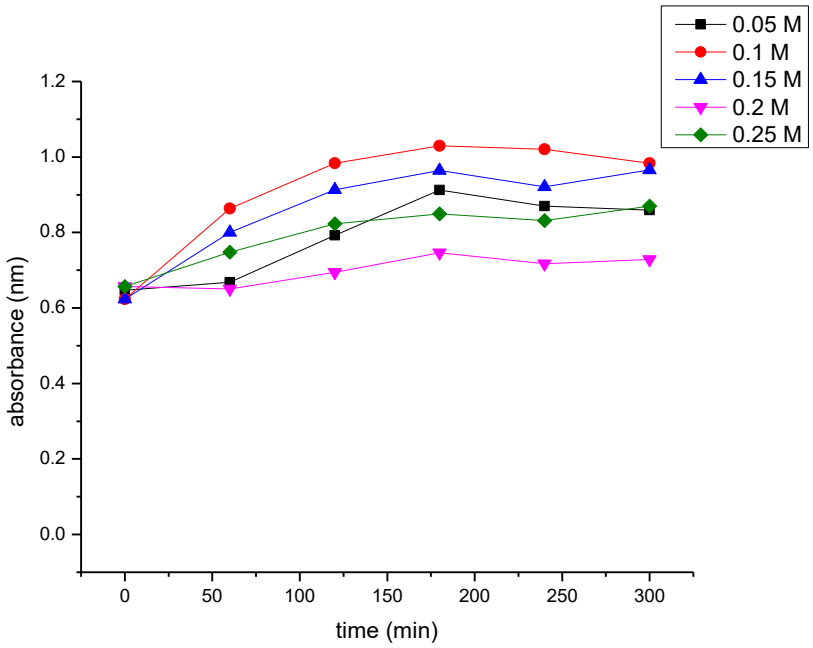


Fig. 3.5. Effect of carrier concentration on transport of As(III) concentration in Feed solution.

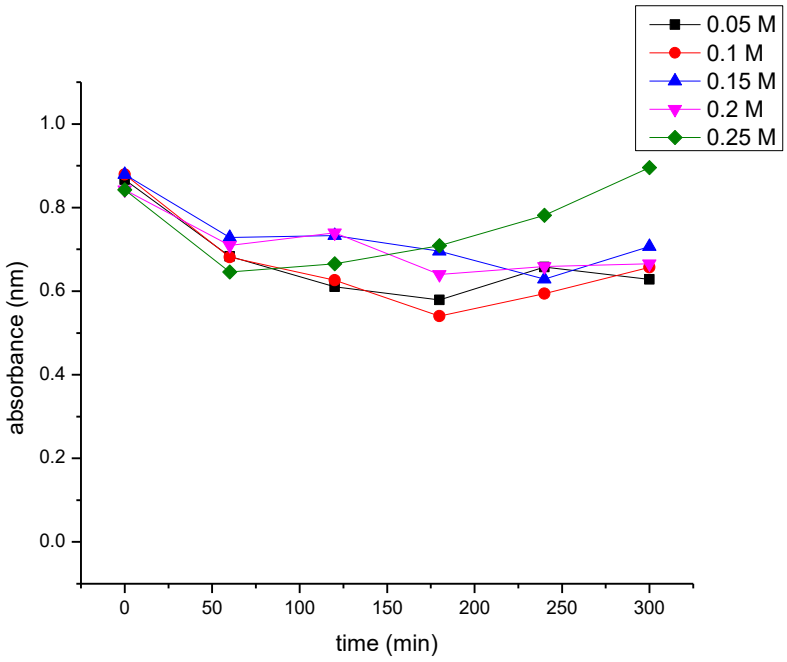


Fig. 3.6. Effect of carrier concentration on transport of As(III) concentration in strip solution.

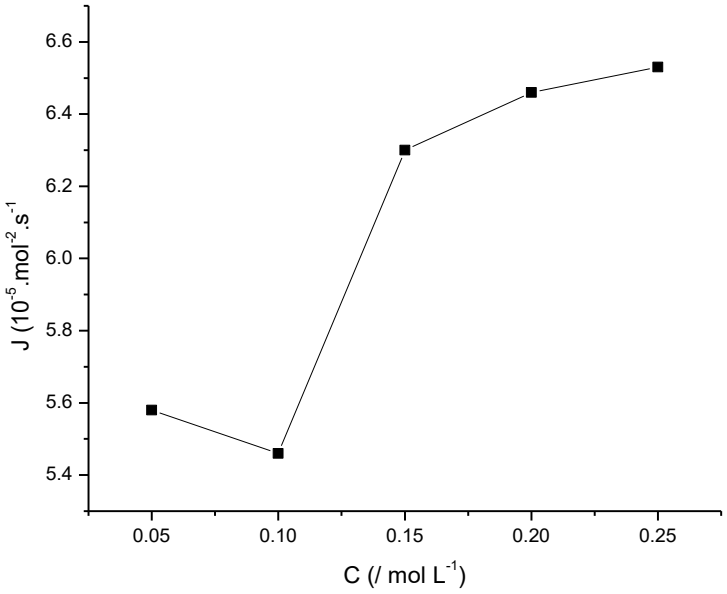


Fig 3.7. Effect of TDDA concentration on transport of As(III) in stripping phase.

3.4.2 Effect of Feed Concentration on Transport

To study the transfer of arsenic through supported liquid membrane various concentration of arsenic was studied. During this study the concentration of arsenic from 1.011×10^{-5} to 5.055×10^{-5} mol/L was observed. While other concentrations such as TDDA at 0.1 mol/L, HCl at 1.0 mol/L, and the sodium hydroxide at 1.0 mol/L was kept constant.

From figures 3.8, 3.9 and 3.10 it is shown that increasing concentration of arsenic from 1.011×10^{-5} to 5.055×10^{-5} mol/L increases the transport of As (III). The reason for this increase in flux is due to the availability of more arsenic ion for complex formation and hence the transport of arsenic increases.

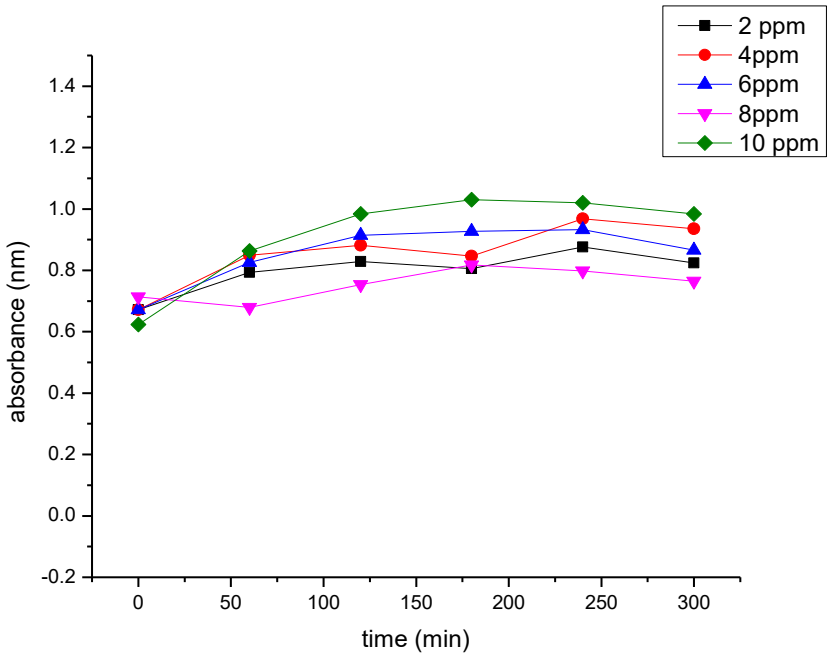


Fig. 3.8. Effect of feed concentration on transport of As(III) in feed solution.

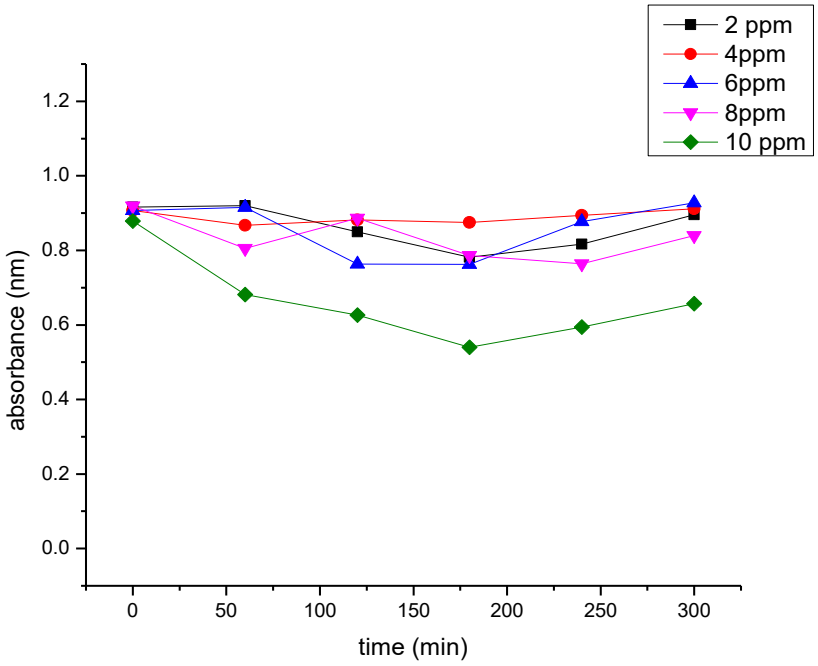


Fig. 3.9. Effect of feed concentration on transport of As(III) in strip solution.

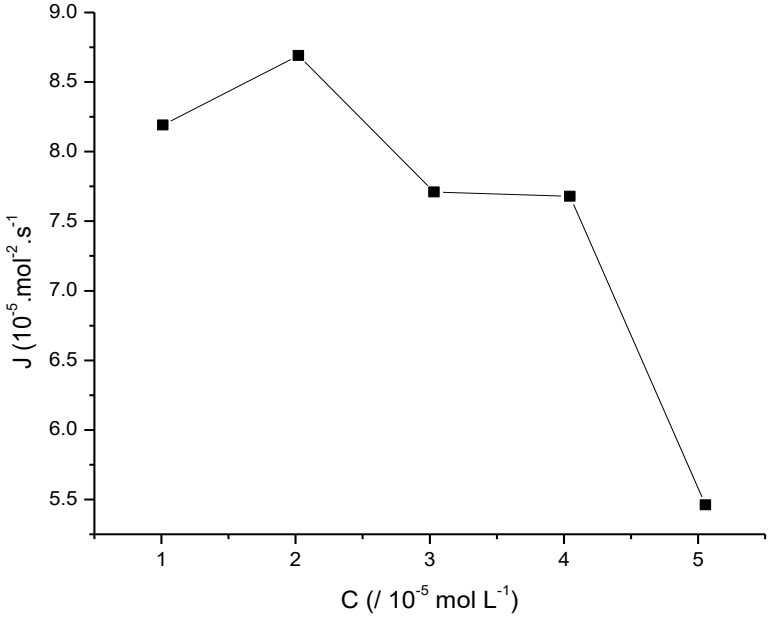


Fig. 3.10. Effect of arsenic concentration on the flux of As(III).

3.4.3. Effect of Acid concentration in Feed Phase

In the transport of As (III) the acid has a significant role in the feed solution, as the H^+ and Cl^- for the complex formation $[(LH)_n . As(Cl_3)_{n+1}]$ is provided by HCl as shown in equation (4). The effect of HCl concentration was studied by varying concentration of acid in the range of 0.1 mol/L to 2 mol/L keeping the concentration of tridodecylamine constant at 0.1 mol/L, and the NaOH concentration at 1.0 mol/L.

It can be seen in figure 3.11 that the concentration of arsenic decreases as the concentration of HCl increases from 0.1mol/L to 1.0 mol/L. This may be due to the formation of H^+ and Cl^- ions at the feed side which in turn increases the formation of complex $[(LH)_n.As(Cl_3)_{n+1}]$ and hence increases the rate of transportation of arsenic. Figure 3.12 and 3.13 shows that the flux of

arsenic increases as the concentration of HCl increases from 0.1mol/L to 1.0 mol/L. However, when the concentration of HCl is further increased from 1.0 mol/L to 2.0 mol/L the flux is decreased. This decreased in the transport of arsenic with increasing HCl concentration may be due to the excessive quantity of H^+ and Cl^- ions which can lead the formation of $H_n.As(Cl_3)_n$ type species in feed phase. Thus, the optimum concentration of HCl was considered as 1.0 mol/L and further studies was carried out with 1.0 mol/L of HCl to evaluate other parameters.

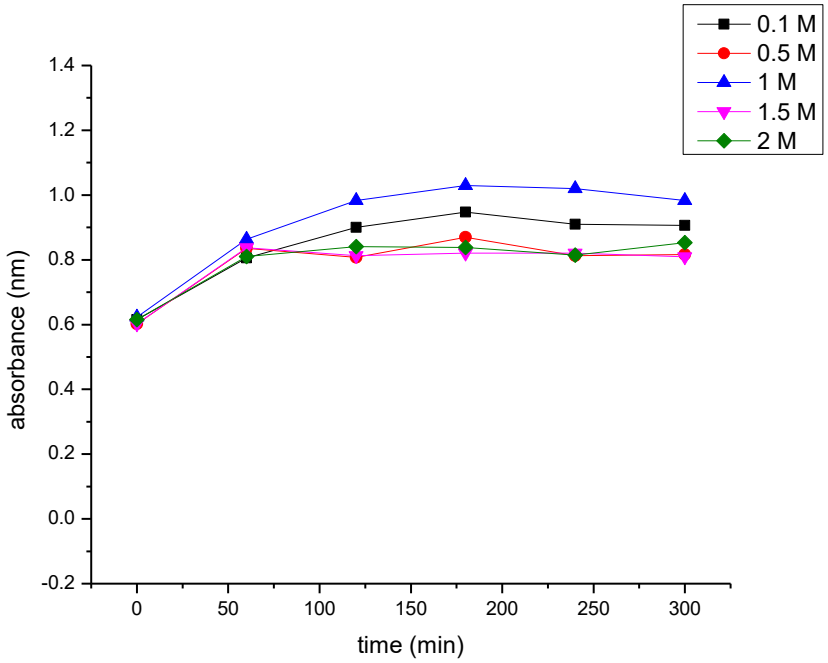


Fig. 3.11. Effect of HCl concentration on transport of As(III) in Feed solution.

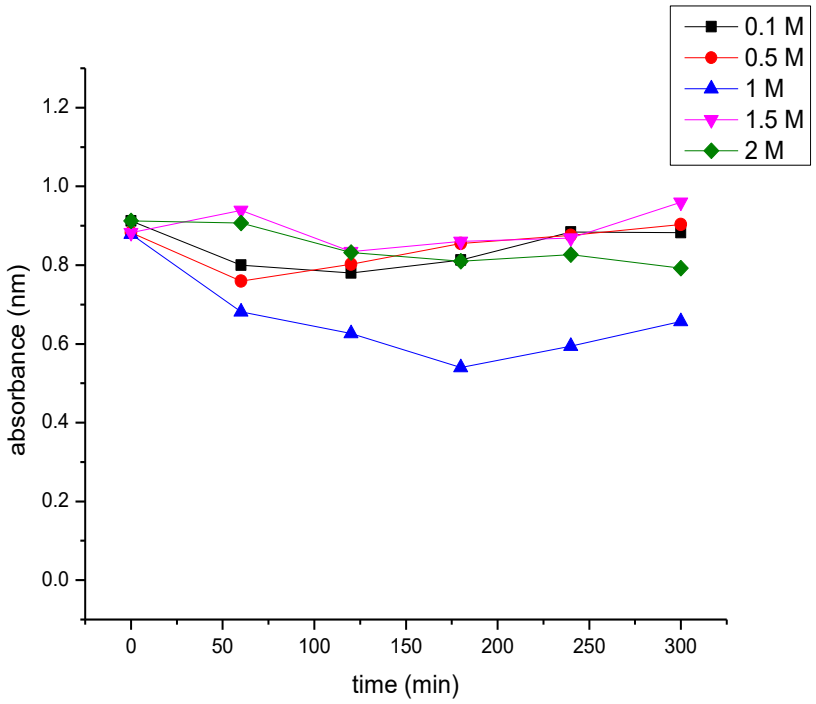


Fig. 3.12. Effect of HCl concentration on transport of As(III) concentration in strip phase.

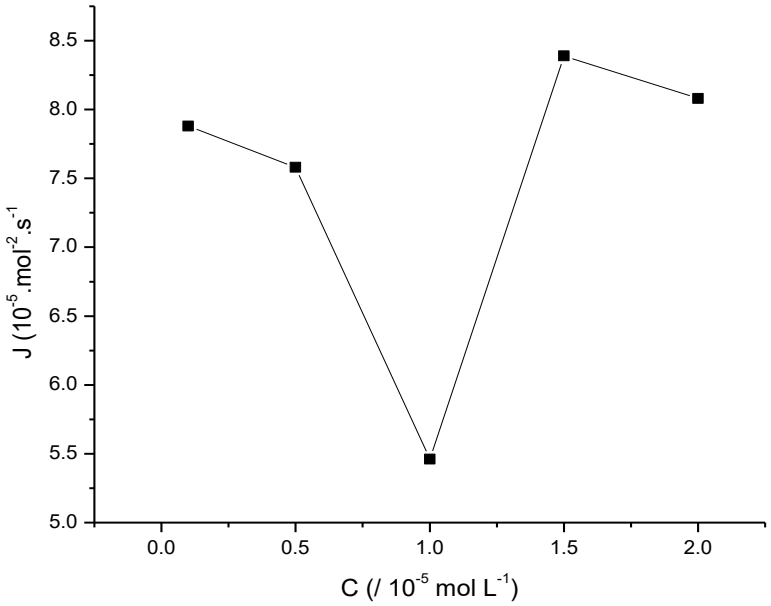


Fig. 3.13. Effect of HCl concentration on the flux of As(III).

3.4.4. Effect of Strip Reagent concentration

The complex $[(LH)_n.As(Cl_3)_{n+1}]$ is dissociated at the strip membrane interface. The transport of arsenic was studied at different concentrations of sodium hydroxide at strip side. The tridodecylamine concentration was kept constant as 0.1 mol/L, and HCl concentration as 1.0 mol/L. The concentration of sodium hydroxide as stripping reagent was studied from 0.1 mol/L to 1.5 mol/L.

Figure 3.14 shows that the concentration of As(III) decreases as the sodium hydroxide concentration increases. The increase in the flux of arsenic with increase in concentration of NaOH from 0.1 mol/L to 1.0 mol/L is shown in figure 3.15 and 3.16. The reason for increase in flux may be due to the higher concentration of OH^- ions with increasing concentration of NaOH. The OH^- ions enhances the dissociation of complex at strip membrane interface thus the transport of arsenic increases. As the concentration of sodium hydroxide further increases, beyond 1.0 mol/L the transport of arsenic is decreased. This may be due to the formation of some other compounds which are insoluble in the excess of sodium hydroxide. Also, the transport of arsenic is restricted due to the blockage of pores of polypropylene microporous film in the higher concentration of NaOH.

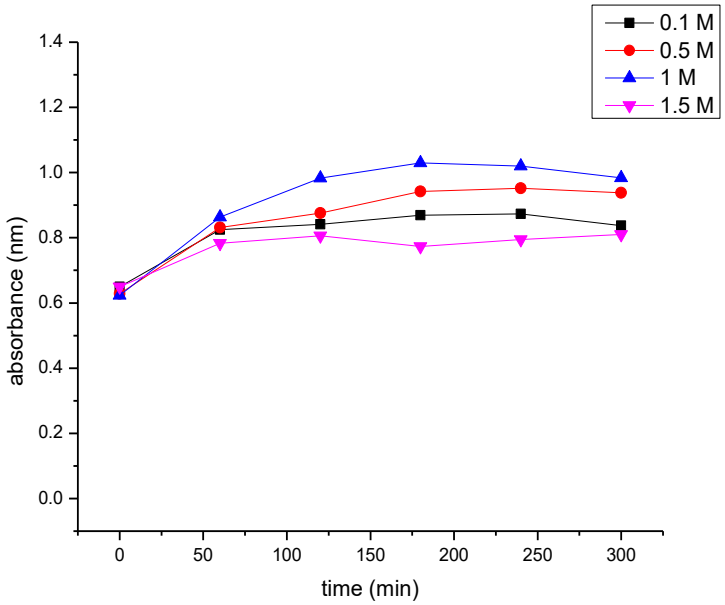


Fig. 3.14. Effect of NaOH concentration on transport of As(III) concentration in feed phase.

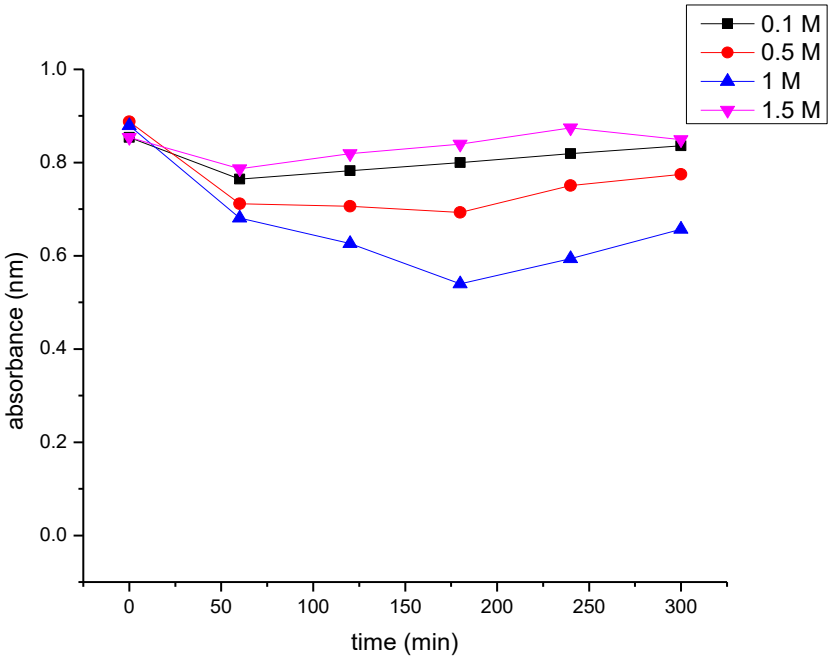


Fig. 3.15. Effect of NaOH concentration on transport of As(III) concentration in strip phase.

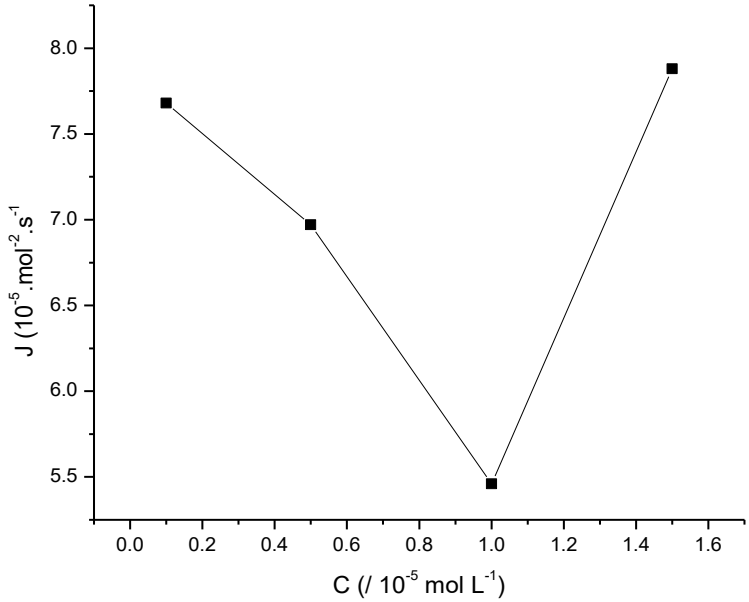


Fig. 3.16. Effect of NaOH concentration on the flux of As(III).

3.4.5. Effect of pH

The significant role of pH in the feed phase was studied with pH variations in the range 1.0-4.0, at constant concentration of 0.1 mol/L TDDA, 1.0 mol/L of sodium hydroxide, and 5.055×10^{-5} mol/L of feed phase concentration.

The figures 3.17 and 3.18 shows that the transport of arsenic(III) is maximum at pH 1.0, as the pH of the system is increased the transport of arsenic(III) decreases. The influence of pH on the flux of As(III) is shown in figure 3.19.

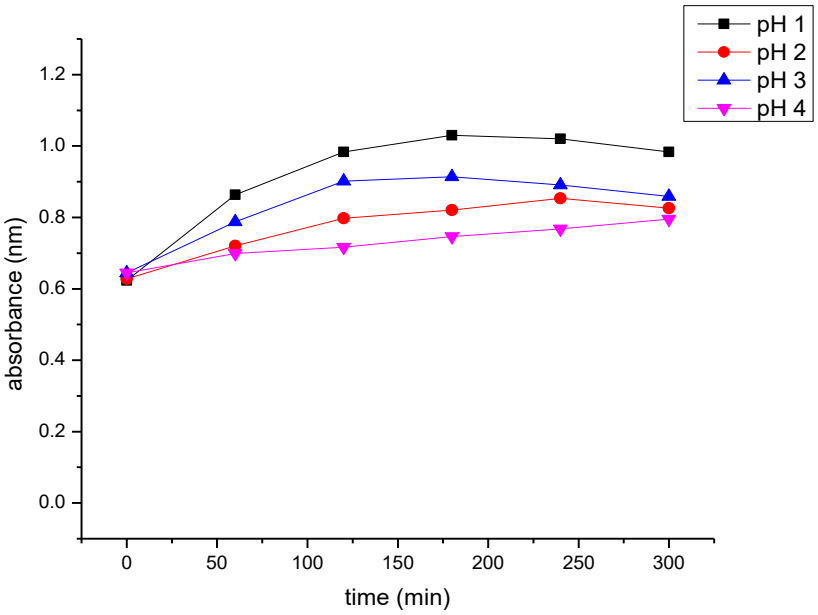


Fig. 3.17. Effect of pH on transport of As(III) concentration in feed phase.

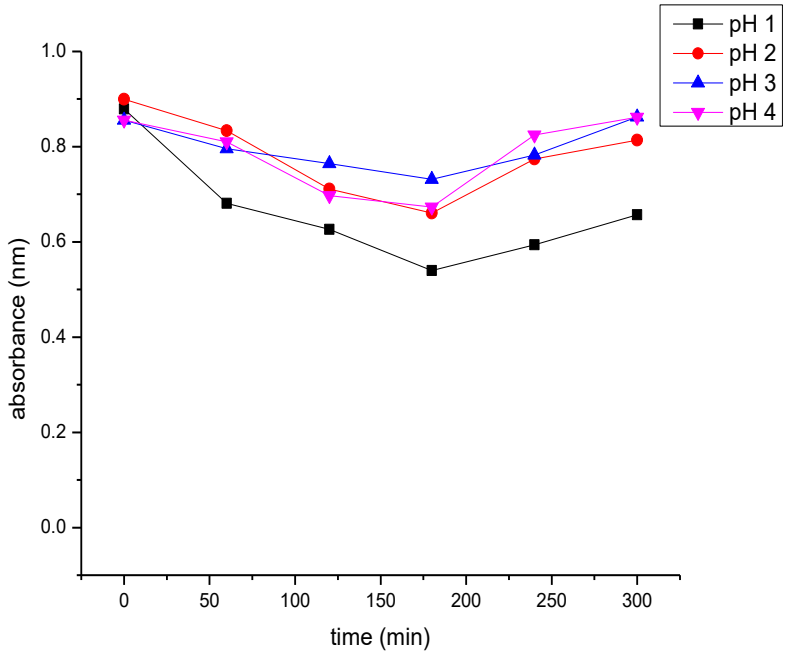


Fig. 3.18. Effect of pH on transport of As(III) concentration in strip phase.

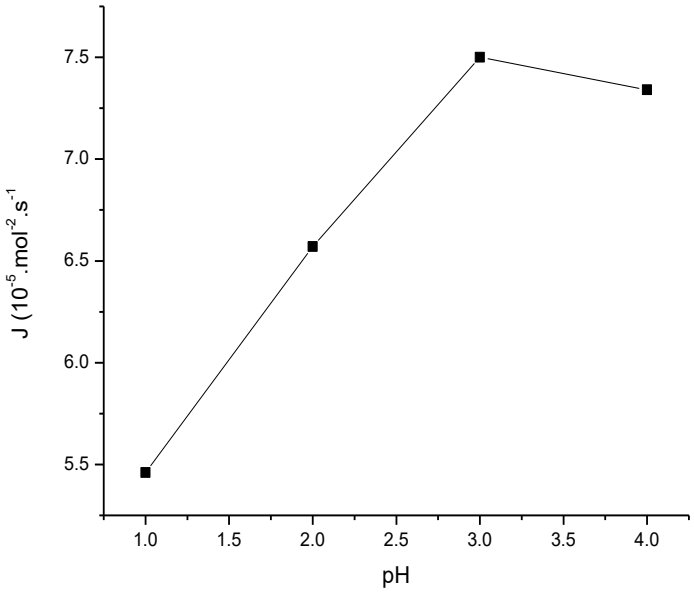


Fig. 3.19. Effect of pH on the flux of As(III).

3.4.6. Membrane stability

The supported liquid membrane is a useful technique for the extraction and removal of metals. The stability and durability of the membrane is thus of great concern, as the pores of the membrane may block due to precipitation reactions.

The stability of the membrane was studied at of 0.1 mol/L of tridodecylamine concentration. The strip reagent concentration was 1.0 mol/L and that of feed phase concentration was 5.055×10^{-5} mol/L at a pH 1.0. The polypropylene membrane was soaked once in carrier for 24 hours and then the transportation of arsenic(III) was studied for 5 days, of about 3-4 hours per day. It is clear from the figure 3.20 and 3.21 that the transport of arsenic(III) ions is feasible in first two days and is comparatively high. The gradual decrease was observed from third to fifth day, this may due to the formation of sodium chloride on the membrane surface at strip-membrane interface resulting the blockage of pore and hence the transfer of ions is restricted.

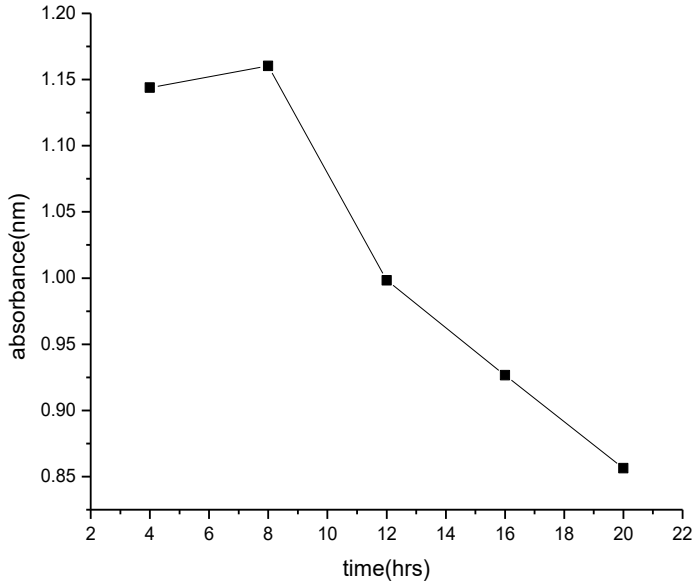


Fig. 3.20. Stability of membrane in feed phase.

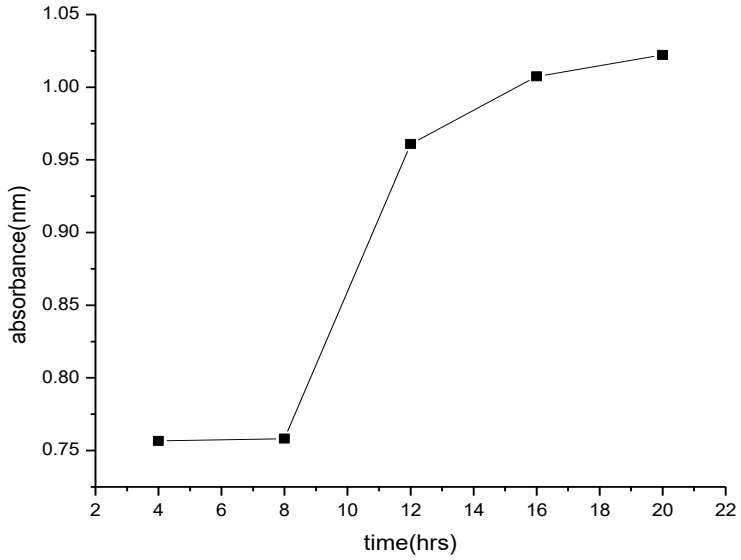


Fig. 3.21. Stability of membrane in strip phase.

3.5. Scanning Electron Microscopic Analysis

To study the morphology of supported liquid membrane under the optimized conditions, the scanning electron microscopic analysis was carried out. Different images obtained are given as:

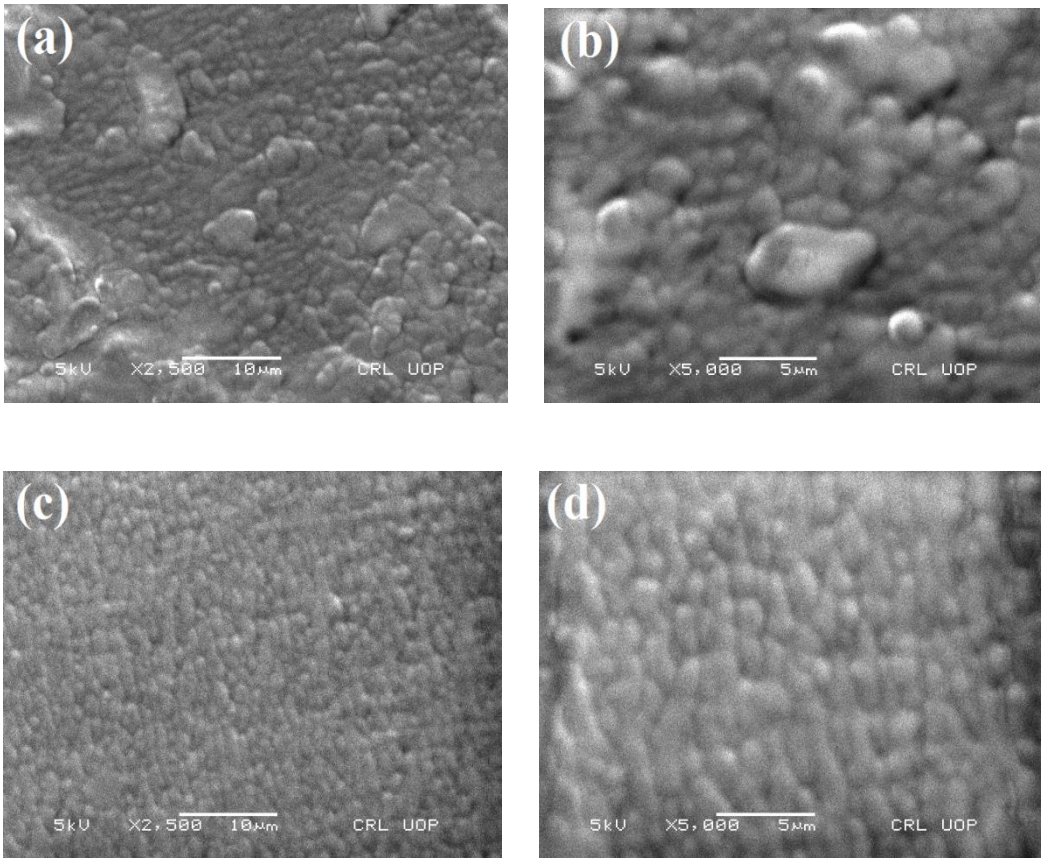


Fig. 3.22. SEM images of supported liquid membrane after extraction of As(III).

3.6. Industrial applications of the system

The optimized conditions for carrier concentration, feed concentration, strip reagent concentration, and pH was applied for real samples collected from different industries located in Hattar, Pakistan. Table 1. shows the various concentration and flux for the corresponding industry. The flux of the system is shown in figure 3.23.

Table 1. Concentration of arsenic in different industrial samples.

Industrial Samples	Concentration (mg/L)	Flux $J(mol^{-2}.s^{-1})$
Pesticides	5.8	2.93×10^{-5}
Glass	4.2	2.12×10^{-5}
Paint	3.46	1.74×10^{-5}
wood preservatives	3.01	1.52×10^{-5}
Pharmaceuticals	2.3	1.193×10^{-5}

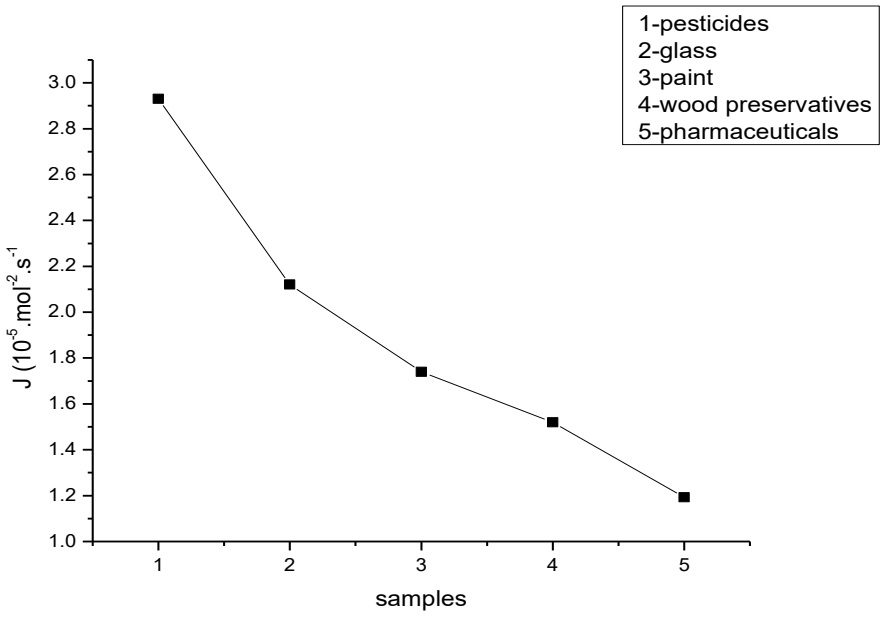


Fig. 3.23. flux for transport of As(III) in real samples collected from industries.

Conclusions

1. The extraction of arsenic(III) was studied by supported liquid membrane with various factors affecting the system.
2. Tridodecylammin was used as a carrier for the transfer of arsenic ions.
3. Hydrochloric acid and sodium hydroxide was studied as a feed and receiving phase, respectively.
4. The optimum conditions for the extraction of arsenic was found to be 0.1 mol/L of TDDA, 1.0 mol/L of HCl, 1.0 mol/L of sodium hydroxide.
5. An increase in the extraction was examined as the concentration of TDDA carrier is increases 0.05 to 0.1 mol/L and a slight decrease in extraction was observed beyond 0.1 mol/L.
6. The maximum extraction was observed when the concentration of arsenic ions was increased to 5.055×10^{-5}.
7. The system was examined at various pH but the best results for extraction was observed at pH 1.
8. The durability and stability for microporous polypropylene film used as a supported liquid membrane was studied and was concluded that the membrane is stable at these conditions with good efficiency.
9. The system was studied for real samples and the arsenic concentration was observed in industrial samples.

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