Removal of Hg^{2+} ions using tri n-butyl phosphate based supported liquid membrane from aqueous samples

Ayyavoo Saravanan[*1,2], Ramasamy Sankar[2] and Kandasamy Palanivelu[3]

[1]Water Chemical Treatment Plant, TPS II Expansion, NLC India Ltd, Neyveli, Cuddalore-607 801, India
[2]University College of Engineering Villupuram, Anna University, Villupuram-605 103, India
[3]Centre for Environmental Studies, Anna University, Chennai- 600 025, India

Abstract. Mercury is a poisonous heavy metal that causes deleterious effects on public health and the ecosystem, even with a trace level of contamination. Selective separation of mercury ions in an aqueous environment is a challenging task, while supported liquid membrane poses to be a promising tool. In this research work, the removal of mercury ions using a porous PTFE membrane with TBP as a carrier has been studied. Batch experiments were carried out in an SLM reactor with feed phase and strip phase solution on either side of the membrane. Maximum removal of 97% of Hg^{2+} ions occurred under optimum conditions, namely, 0.5 M of HCl (feed), 0.4 M NaOH (strip), 90% of TBP, stirring speed at 300 rpm and 3 h of reaction time. SEM analysis of the membrane confirmed the formation of a complex between TBP and Hg^{2+} ions. SLM was found to be stable for 18 h. The high selectivity of the SLM towards Hg^{2+} ions was unaltered in the presence of Cd^{2+}, Ni^{2+} and Zn^{2+} ions. The proposed SLM was used for the treatment of spiked seawater samples, wastewater from a thermal power plant, and contaminated lake water samples. The results indicated that the SLM system was highly efficient in removing Hg^{2+} ions from real contaminated samples.

Keywords: mercury; removal; supported liquid membrane; transport; tri n-butyl phosphate

1. Introduction

Mercury is a non-biodegradable, toxic, and carcinogenic, polluting heavy metal that exists naturally in the earth's crust. It is present in trace amounts in the atmosphere, and its level is augmented by natural disasters and human activity (Hutchison and Atwood 2003, Jose *et al.* 2010). In water bodies, mercury can be easily transformed as organic mercury by aquatic microorganisms, from which it accumulates in fish (Naidu *et al.* 1983), and it also has a strong tendency to pass through the food chain. Acute mercury exposure may lead to cough, sore throat, shortness of breath, chest pain, vomiting, tasteless mouth, vision problems and kidney damage. Chronic exposure may lead to serious health issues like fatigue, loss of memory, anxiety, changes in vision and hearing, anorexia, and stultification in neurological functioning (WHO 2008). Environmental Protection Agency of United States, 1987 reported mercury as one of the top ten hazardous chemicals which is of serious concern to the health of the public. Its standard limits for drinking water and wastewater discharges are 2 µgL^{-1} and 5 µgL^{-1}, respectively. The highest level of mercury contamination that has been reported in wastewater is about 10 mgL^{-1} (Barron-Zambrano *et al.* 2004). In an aqueous medium, mercury behaves in a complex manner due to its form, oxidation state, pH and interference from other metals (UNEP 2013). Consequently,

the separation of mercury in water and wastewater has received great attention, and it is very essential that it is selective.

There are many conventional separation methods for the removal of heavy metals from wastewater, such as precipitation, coagulation, adsorption, solvent extraction, chemical oxidation and reduction, ion exchange process, liquid-liquid extraction, cementation, liquid membranes, and electrolysis (Dabrowski *et al.* 2004, Sharma *et al.* 2015). Among these techniques, liquid membrane has been identified as a potential tool for efficient and selective separation for trace level of concentration, whereas other methods are less attractive as they are not reliable, generate secondary wastes, and consume large volume of chemicals (Chakrabarty *et al.* 2010a, Raffaele and Pietro 2011).

Supported liquid membrane (SLM) comprises micro-porous solid thin polymer sheets whose pores are filled with a small quantity of liquid carrier, which separates the feed (donor) and strip (acceptor) phases (Kislik 2010). SLM shows a reliable separation of pollutants at trace level contamination for various heavy metals such as arsenic, vanadium, cadmium, uranium, and thorium (Prapasawat *et al.* 2008, Pancharoen *et al.* 2006, Pont *et al.* 2018) and various organic pollutants, namely dyes, phenol, citric acid, lactic acid, ethyl lactate and amino acids (Hajarabeevi *et al.* 2006, Kocherginsky *et al.* 2007).

Research studies aiming at the use of SLM for the transport of mercury ions from aqueous solutions have been reported. Recent studies with the advancements in the removal of mercury ions are as follows. Shamsipur *et al.* (2006) reported simultaneous transport of mercury and

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*Corresponding author, M.Sc , Research Scholar,
E-mail: asakithyan@gmail.com

silver ions with two membranes in three compartments as a flat sheet SLM (FSSLM) reactor. They used tetrathia 12-crown-4 as a carrier for the transport of mercury ions and ethylene diamine tetraacetic acid as a strip for mercury ions and attained 94% removal. Pancharoen *et al*. 2010 attempted the transport of mercury ions from natural gas-produced well water using trioctylamine (TOA) as a carrier by hollow fiber SLM (HFSLM). They achieved about 99% removal using NaOH as strip phase. Chakrabarty *et al*. (2010a) investigated the selective transport of mercury ions using TOA from aqueous solutions with NaOH as the strip phase by FSSLM and achieved about 91% removal. The same research group namely, has reported simultaneous separation of mercury ions with lignosulfonate from aqueous solutions using TOA as a carrier by FSSLM and achieved 53% transport of mercury ions (Chakrabarty *et al*. (2010b)). Lothongkum *et al*. (2011) demonstrated simultaneous separation of mercury and arsenic ions from natural gas co-produced water by a mixture of aliquat 336 and cyanex 471 as a carrier by HFSLM with an achievement of 94% removal of mercury ions using different strip phase solutions including NaOH. Selective separation of mercury ions along with lead ions using various amine carriers by HFSLM with thiourea as a stripping solution was studied by Suren and Pancharoen (2012). They achieved almost 100% removal of mercury from aqueous solutions.

The majority of reported works established the potential of amine carriers for the removal of mercury ions from aqueous solutions. Among them, NaOH is the best strip phase for the separation of mercury ions. Recently, Ren *et al*. (2015) demonstrated that nitrogen-containing carriers like tri n-butyl phosphate (TBP) has greater extraction capacity than amine carriers. TBP is a neutral carrier that is more stable than amines with high flash points and is used extensively for the extraction of a large number of heavy metals owing to the formation of metal complexes (Zhang *et al*. 2009). TBP has been potentially applied for extracting many pollutants, including metal ions (Zhang *et al*. 2015, Seyfi and Abdi 2009) and organic pollutants like textile dyes (Hajarabeevi *et al*. 2007) by both solvent extraction and liquid membranes. Interestingly TBP has also been employed for the extraction of mercury ions from acidic solutions by liquid-liquid extraction (Sato *et al*. 2002). As of date, no reports are available for the removal of Hg^{2+} ions using SLM containing TBP as a carrier.

The present study aims to remove Hg^{2+} ions across FSSLM comprising TBP as a carrier under acidic halide conditions with NaOH as strip phase. The objective is to determine the removal efficiency of the SLM system with TBP for the separation of Hg^{2+} ions and to study the effect of various operational parameters such as choice of feed phase, the concentration of feed phase acid, the concentration of strip phase, concentration of carrier, soaking time of membrane in the carrier, stirring speed and concentration of mercury ions in feed phase on removal efficiency. The study also attempts to establish the selectivity of Hg^{2+} ions with other heavy metals. Finally, potential application studies of the present SLM system for the separation of Hg^{2+} ions were also demonstrated.
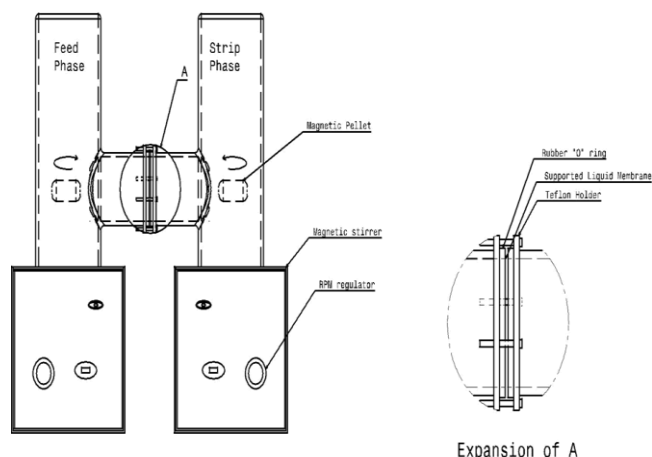

Fig. 1 Schematic diagram of SLM reactor (Anupama and Palanivelu 2005)

2.Experimental

2.1 Materials

All the reagents used in this study were of analytical grade. Mercury chloride ($HgCl_2$), n-hexane, hydrochloric acid (HCl), hydrobromic acid (HBr), and hydroiodic acid (HI) were procured from Merck, India. TBP and stannous chloride ($SnCl_2$) were obtained from the Sisco laboratory, India. Sodium hydroxide (NaOH) and rhodamine B was obtained from Central Drug House, India. Double distilled water was used for the preparation of aqueous solutions. Polytetrafluoroethylene (PTFE) membrane was obtained from Sartorius Bio Lab Products, Germany.

2.2 SLM reactor setup

The SLM reactor consists of two cylindrical tanks of equal volume (200 ml). It is made up of glass and connected by a glass rim, supported with a Teflon holder, held by screws, as shown in Fig. 1. The microporous polymeric sheet containing the carrier was placed between the joints with the support of two rubber o-rings. Experiments were conducted with 150 ml of feed and strip phase solutions on both sides of the reactor. The assembled reactor was placed on a magnetic stirrer (model 841 deep vision limited, India), and stirring was provided with the help of magnetic pellets on both sides of the reactor.

2.3 SLM preparation

PTFE membrane with a thickness of 58 µm, a pore size of 0.45 µm, and 75% of porosity were used to prepare SLM. This membrane was soaked in mixtures of TBP and hexane in a glass plate covered with a cap. Pores of the membrane were occupied by the TBP molecule through capillary forces. The effective contact area of the membrane was determined as 13.2 cm^2. After the definite soaking time, the membrane was taken out and wiped with tissue paper to remove the excess carrier and was then used for further studies.

2.4 Experiments

Batch experiments were performed at room temperature (27 ± 2ºC) for a specified reaction time. Equal volumes of samples were collected at regular intervals of time from both sides of the reactor and taken for analysis. Experiments were carried out to study the influence of the feed phase acid concentration (0.1-1 M HCl), strip phase alkali concentration (0.1-1M NaOH), carrier concentration (90-50% (v/v)), soaking time of membrane in carrier (10 min-16 h) and stirring speed (100-600 rpm). All the experiments were carried out in triplicates.

2.5 Analysis

Samples collected from each experiment were analyzed for mercury concentration in triplicates. The concentration of mercury ions in aqueous samples (range: 1-20 mgL^{-1}) was analyzed with the help of a visible spectrophotometer (Visiscan 167, Systronics, India) by the method described by Loo *et al*. (2012). Cold vapor atomic fluorescence spectrophotometer (CVAFS) (Model: 10.025, Millenium Merlin, PS analytical London) operated with a millennium merlin detector working on the principles of fluorescence was used for the measurement of trace levels of concentrations (0.1-1000 µgL^{-1}). In this method, samples were acidified with 5% HCl and then allowed to react with 20% stannous chloride in 10% HCl. HCl was used as a reductant to transform ionic mercury to metallic mercury vapors. These vapors enter into the detector with the assistance of argon (carrier gas), where they absorb light and fluoresces at their characteristic wavelength of 254nm (PSA 10.025 2010). Scanning electron microscope (SEM) images of the samples were obtained using Carl Zeiss MA15/EVO18 SEM. The concentration of other heavy metals was determined using inductively coupled plasma optical emission spectroscopy, namely, ICAP 6500, supplied by Thermo Fisher Scientific Private Limited, USA. pH was monitored for the entire duration of the experiment using a digital pH meter (model: Li 120) by Elico, India.

2.6 Removal efficiency calculations

The removal efficiency of Hg^{2+} ions by SLM in each experiment was calculated from the concentration of mercury obtained after the analysis as mentioned in the above section using Eq. (1). In this equation, C_o denotes the initial concentration of Hg^{2+} ions present in the feed phase. C_t denotes the concentration of Hg^{2+} ions present in the feed phase that has been extracted and transported through the membrane at time t (Pancharoen *et al*. 2010).

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_t}{C_o} \times 100 \qquad (1)$$

3.Application studies

The SLM system was applied for the treatment of mercury spiked seawater, wastewater, and contaminated lake water.

Table 1 Viscosities of mixture (TBP and n-hexane)

Mixture (%) (TBP + hexane)	Viscosity (mPa.s)
90 + 10	3.28
80 + 20	2.93
70 + 30	2.13
60 + 40	1.67
50 + 50	1.42

3.1 Mercury spiked seawater

Seawater collected from the Chennai coast was taken for the study (Bay of Bengal). 100 mL of seawater was taken in a beaker, which was subjected to evaporation on a hot plate and reduced to a volume of 10 ml. This solution was then digested with 9 ml of HCl for 15 min. It was later diluted to 100 ml with double distilled water. The method proposed by Bhandare and Argekar (2002) was used for spiking mercury ions in seawater. Seawater was spiked with mercury ions, and three concentration sets were used for the study, namely, 10 mgL^{-1}, 5 mgL^{-1}, and 0.1 mgL^{-1}.

3.2 Wastewater from thermal power plant

Wastewater from a thermal power plant situated in Chennai, India was collected from its direct discharge point for the study, and was filtered using a filter paper (pore size- 0.44 µm). 100 ml of the filtrate was acidified with 2 ml of HCl. Transport studies were carried out with the wastewater as the feed phase solution under optimized parameters.

3.3 Mercury contaminated lake water

Water collected from a lake that was contaminated due to the discharge of pollutants from a thermometer factory in Kodaikanal, India (Karunasagar *et al*. 2006) was used for the study. The lake water was filtered using a filter paper (pore size- 0.44 µm). The water sample was directly taken as feed phase in the SLM reactor system, and the removal efficiency was determined.

4.Results and discussion

4.1 Choice of carrier

Pure TBP did not result in a homogeneous organic membrane phase even after soaking for 48 h due to its highly viscous nature (viscosity of 3.46 mPa.S). A high level of viscosity may hinder the transport efficiency of a metal ion complex across SLM (Chaudry *et al*. 2007). Hence, the viscosity of TBP was reduced by adding an organic solvent, namely, n-hexane (viscosity of 0.297 mPa.S), which is an inexpensive, relatively harmless, inert, and volatile non-polar organic solvent (EPA 1987). Various proportions of TBP with n-hexane were used to prepare SLM for the transport of Hg^{2+} ions as given in Table 1. The
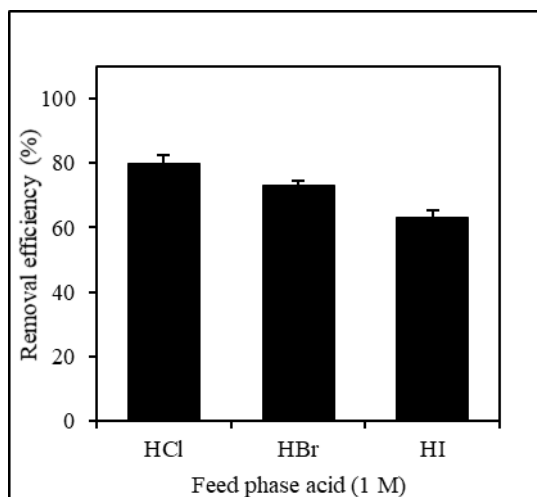
Fig. 2. Effect of various feed phase acid on removal efficiency (%) (NaOH- 1 M, initial concentration of Hg^{2+} ions- 10 mgL^{-1}, TBP- 90%, stirring speed- 200 rpm, soaking time- 12 h, reaction time- 3 h)
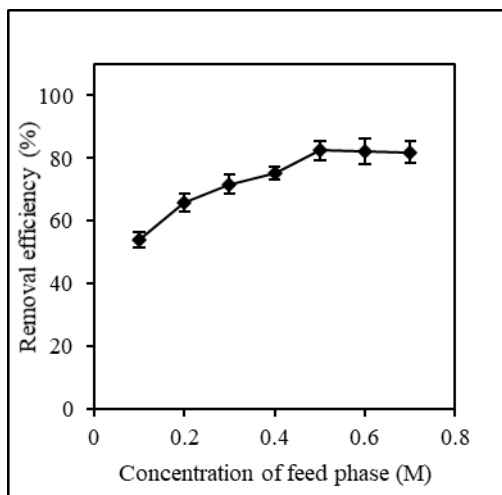

Fig. 3. Effect of the concentration of feed phase (HCl) on removal efficiency (%) (NaOH- 1 M, initial concentration of Hg^{2+} ions- 10 mgL^{-1}, TBP- 90%, stirring speed- 200 rpm, soaking time- 12 h, reaction time- 3 h)

viscosity of the mixture was determined by a modular compact rheometer supplied by Anton-Paar, Austria (Model: MCR 102) at room temperature (27 $\pm$ 2 °C). All the membranes obtained using the mixture of TBP and hexane resulted in the formation of a homogenous phase. A mixture containing 90% of TBP and 10% of hexane was taken for further studies.

4.2 Choice of feed phase acid

Mercury ion forms halogen compounds in aqueous solutions readily, as shown in Eq. (2). Investigations with Cl$^-$, Br$^-$ and I$^-$ were performed to find out the best feed phase, which is liable to form a complex with Hg^{2+} ions. Individual experiments were carried out using 1 M of the acid (HCl, HBr, HI) containing 10 mgL^{-1} of mercury ions as

feed phase and 1 M NaOH as strip phase. Membrane soaking time, carrier concentration, and stirring speed were maintained constant at 12 h, 90% TBP, and 200 rpm, respectively. Fig. 2 shows that under the conditions mentioned above, Cl$^-$ ions showed 80 $\pm$ 2.6% removal of mercury ions whereas with Br$^-$ and I$^-$ ions, removal was about 73+1.5% and 63+2.4%, correspondingly.

$$Hg^{2+} + 4X^- \leftrightarrow HgX_4^{2-} \tag{2}$$
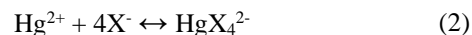
The superior behavior of HCl may be attributed to lower values of interatomic distance between Hg and chloride ions (2.28 Å) than iodide (2.42 Å) and bromide (2.63 Å) ions. This observation could have led to the formation of chloride complexes with mercury ions, which transported readily with TBP over other halogen ions under acidic conditions (Maron et al. 2008).

The stability or formation constant of HgCl$_4^{2-}$, HgBr$_4^{2-}$ and HgI$_4^{2-}$ are 1.3×10^{15}, 9.2×10^{20} and 5.6×10^{29}, respectively. Based on these values, the formation of mercury-iodo complex is comparatively better than either mercury-bromo complex or mercury-chloro complex in the feed phase under an acidic medium. Also, the stability constant is inversely related to the dissociation constant (Clever et al. 1985). Dissociation of iodide ion-pair complex in the strip phase is less when compared with bromide and chloride ion-pair complex under alkaline medium. From Fig. 2, chloride ions in the feed phase show better transport (%) of Hg^{2+} ions across SLM. Hence hydrochloric acid was selected as feed phase acid for the removal of Hg^{2+} ions by TBP based SLM from aqueous solutions, and it provides H$^+$ ions to form TBP cation species and Cl$^-$ ions to form the tetrachloro complex of mercury anion.

4.3 Effect of the concentration of feed phase (HCl)

Feed phase, acid (HCl) concentration was varied from 0.1 to 1 M. NaOH concentration, TBP concentration, membrane soaking time in carrier, stirring speed, feed phase Hg^{2+} ions concentrations were maintained as 1 M, 90%, 12 h, 200 rpm, and 10 mgL^{-1}, respectively, for a reaction time of 3 h. Fig. 3 indicates increasing acid concentration leads to increase in the removal of Hg^{2+} ions which is comparable to the result observed with the transport behavior using Aliquat 336 as a carrier by SLM reported by Chaturabul et al. (2015).

At 0.5 M of HCl, the maximum removal of 82.5 $\pm$ 3.2% of Hg^{2+} ions was achieved in 3 h. The removal efficiency of Hg^{2+} ions through SLM in the presence of a neutral carrier TBP is driven by the concentration gradient of the available hydrogen ions in the feed phase. Mercury forms chloro complexes readily in aqueous solutions under strongly acidic conditions due to the availability of excess chloride ions (Bohrer 1983). After attaining the maximum removal efficiency (82.5%) at 0.5 M of HCl, further increase of chloride concentration did not make any considerable impact on the removal of Hg^{2+} ions.

4.4 Effect of the concentration of strip phase (NaOH)

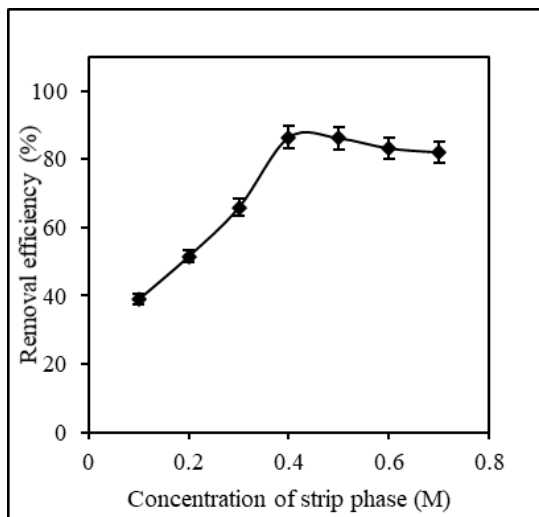The influence of the concentration of strip phase (NaOH) on the removal of Hg^{2+} ions across SLM was

Fig. 4 Effect of concentration of strip phase (NaOH) on removal efficiency (%) (HCl- 0.5 M, initial concentration of Hg^{2+} ions- 10 mgL^{-1}, TBP- 90%, stirring speed- 200 rpm, soaking time- 12 h, reaction time- 3 h)
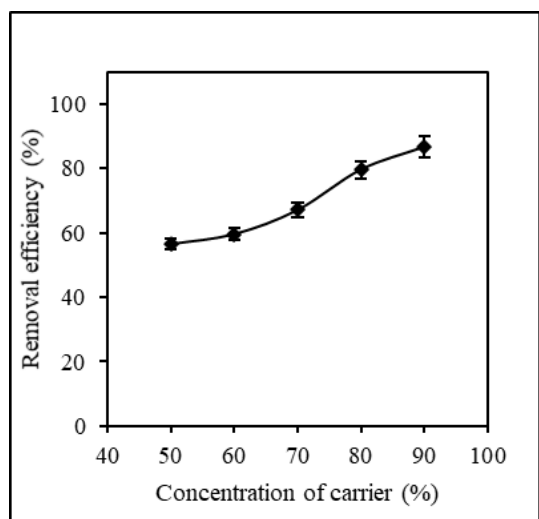

Fig. 5 Effect of concentration of carrier (TBP) on removal efficiency (%) (HCl- 0.5 M, NaOH- 0.4 M, initial concentration of Hg^{2+} ions- 10 mgL^{-1}, stirring speed- 200 rpm, soaking time- 12 h, reaction time- 3 h)

studied by varying it in the range between 0.1-1 M. Results obtained are presented in Fig. 4, from which it can be inferred that the concentration of strip phase plays a significant role in the removal of mercury ions from feed to strip side of the reactor. Increasing the concentration increases the removal efficiency of Hg^{2+} ions gradually. A maximum of about 86.5 ± 3.3% as removal was achieved with a concentration of 0.4 M NaOH.

Pancharoen *et al.* (2010) used 0.5 M NaOH as a strip and TOA as a catalyst in the SLM system to transport Hg^{2+} ions and achieved a maximum transport of about 79%. Increasing strip phase concentration led to excess availability of OH$^-$ ions with a likelihood of forming HgO precipitate. Hence, the transport of mercury ions diminishes
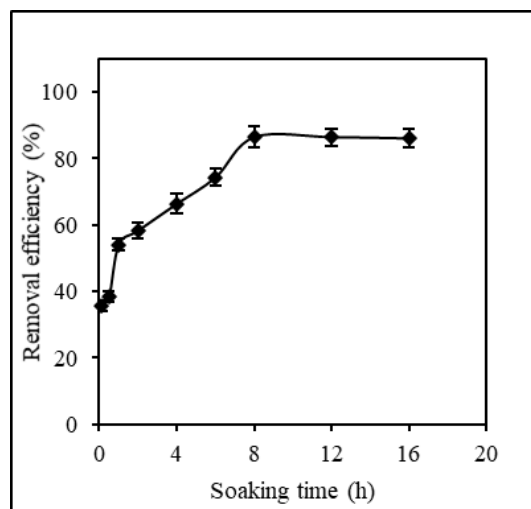

Fig. 6 Effect of soaking time on removal efficiency (%) (HCl- 0.5 M, NaOH- 0.4 M, initial concentration of Hg^{2+} ions- 10 mgL^{-1}, TBP- 90%, stirring speed- 200 rpm, reaction time- 3 h)

slightly at high concentration levels due to this precipitate which could get clogged in the pores of the membrane (Chakrabarty *et al.* 2010a).

4.5 Effect of the concentration of carrier (TBP)

The concentration of the carrier plays a crucial role in the removal of mercury ions through SLM. The concentration of TBP (50-90%) and hexane mixture was varied as indicated in Table 1, and its effect on removal efficiency was determined. Fig. 5 indicates that at higher concentrations, there exists a greater possibility for the formation of an ion-pair complex. A mixture of 90% TBP and 10% hexane showed better performance and removal of 86.5 ± 3.3% was obtained in 3 h.

4.6 Effect of soaking time

The duration of soaking PTFE membrane in TBP was varied from 10 min to 24 h, and its influence on the removal efficiency of Hg^{2+} ions was studied. Fig. 6 indicates that soaking time plays a vital role in the transport and removal of Hg^{2+} ions. PTFE membrane soaked for 10 min showed a removal efficiency of only 45%, and it gradually increased with increasing soaking time.

The maximum removal efficiency of Hg^{2+} ions (86.5 ± 3.3%) was obtained with the membrane soaked for 8 h in the carrier. After 8 h, no variation was observed in the removal efficiency till 24 h. Bhandare and Argekar (2002) have reported similar observations with the carrier tri-isobutyl phosphine sulfide based SLM for the recovery of mercury ions. The removal efficiency increased with the soaking time of the polyvinylidene difluoride membrane in tributyl phosphine sulfide, and the maximum removal of Hg^{2+} ions occurred at 6 h.

4.7 Effect of relative centrifugal force (stirring speed)

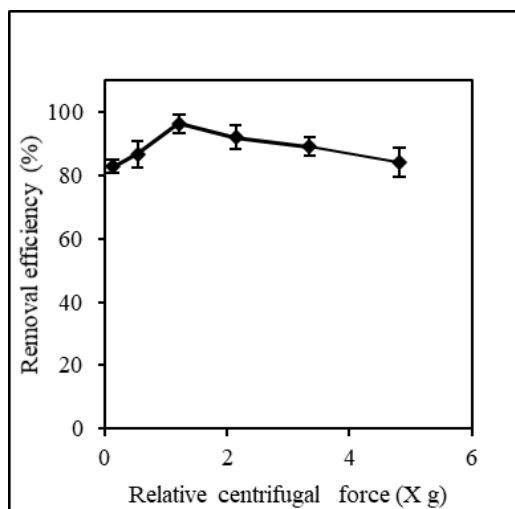It is necessary to study the effectiveness of the diffusion

Fig. 7 Effect of relative centrifugal force on removal efficiency (%) (HCl- 0.5 M, NaOH- 0.4 M, initial concentration of Hg^{2+} ions- 10 mgL^{-1}, TBP- 90%, soaking time- 8 h, reaction time- 3h)
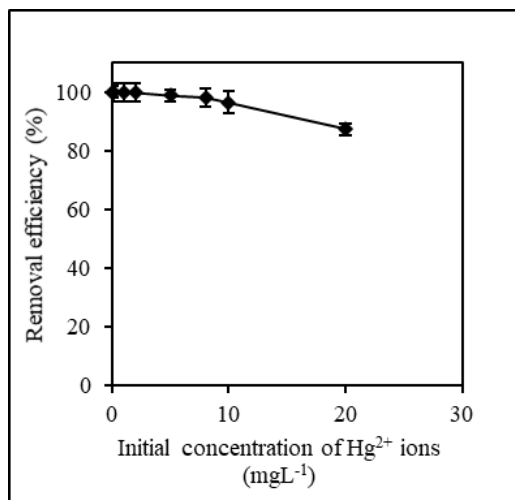

Fig. 8 Effect of initial concentration of Hg^{2+} ions in feed phase (HCl- 0.5 M, NaOH- 0.4 M, TBP- 90%, soaking time- 8 h, stirring speed- 300 rpm, reaction time- 3 h)
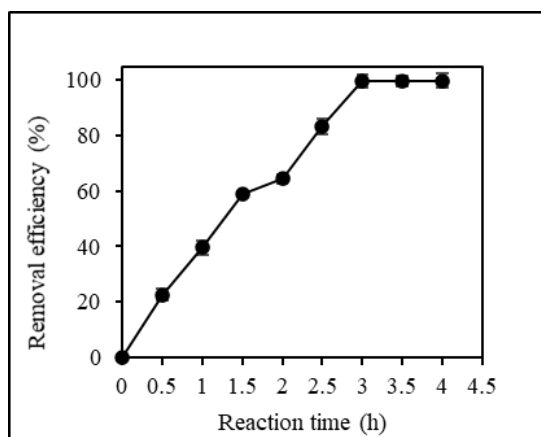

Fig. 9 Effect of reaction time (HCl- 0.5 M, NaOH- 0.4 M, TBP- 90%, soaking time- 8 h, stirring speed- 300 rpm, initial concentration of Hg^{2+} ions- 10 mgL^{-1})

Table 2 Summary of optimum conditions obtained in this study

S.No	Parameters	Range studied	Recommended value
1	Feed phase HCl concentration (M)	0.1-1	0.5
2	Strip phase NaOH concentration (M)	0.1-1	0.4
3	TBP concentration (%)	50-90	90
4	Soaking time of membrane in carrier (h)	0.08-24	6
5	Stirring speed (rpm)	0-600	300
6	Reaction time (h)	0-4	3

process on the transport of ions, to investigate the effect of stirring speed on the removal efficiency of Hg^{2+} ions through SLM. Resistance in the diffusion of metal ions through SLM may be due to the resistance in the liquid boundary layer or the membrane (Bohrer 1983). So, exploration of the effect of stirring speed is necessary, and in the present study, it was varied in the range of 0.13-4.82 Xg (100-600 rpm) in both the feed and strip sides. Fig. 7 indicated that by increasing the stirring speed from (0.13-1.21 Xg) 100 to 300 rpm, the removal efficiency of Hg^{2+} ions also increased owing to the decrease in the thickness of the diffusion layer.

Maximum transport of 96.5 ± 3.3% at (1.21 Xg) 300 rpm under optimized conditions of feed phase acid concentration, strip phase concentration, carrier concentration, and soaking time of the membrane was achieved. Further increase of stirring speed led to a decrease in the removal efficiency due to high turbulence caused by stirring, which possibly replaced some carrier molecules from the pores of the membrane (Chaturabul *et al.* 2015). At static mode that is in the absence of stirring, about 58% Hg^{2+} ions was removed from the feed phase.

4.8 Effect of initial concentration of Hg^{2+} ions in feed phase

The effect of the initial concentration of Hg^{2+} ions in the feed phase was studied by varying it in the range between 0.01-25 mgL^{-1}. Fig. 8 points out that the initial concentration of Hg^{2+} ions plays an important role in the transport across SLM. Transport of Hg^{2+} ions was obtained in an appreciable percentage for the solutions with concentrations varying from 0.01 to 10 mgL^{-1}. Under optimized conditions, almost 100% removal of Hg^{2+} ions was obtained for the samples having an initial concentration of 0.01 to 8 mgL^{-1}. For 10 mgL^{-1}, 96.5% of Hg^{2+} ions in the feed phase were removed in 3 h. Further increase in the concentration of Hg^{2+} ions led to a decrease in the removal efficiency, and only 85% of Hg^{2+} ions were removed for 20 mgL^{-1}.

4.9 Effect of reaction time

The effect of the operating reaction time for the removal of Hg^{2+} ions was studied under optimized conditions for a

Table 3 Recent research on removal of Hg^{2+} ions by SLM

Type of feed	Carrier/ Extractant	Hg^{2+} ions (ppm)	Strip phase	Removal efficiency (%)	Reference
Synthetic solution, sea water	N-benzoyl, N,N-diheptadecyl thiourea	10.0	thiourea	Almost 100	Fontas *et al*. 2005
Synthetic solution	tetrathia12-crown-4	2.0	EDTA	94	Kocherginsky *et al.* 2007
Synthetic solution	TOA	20.0	NaOH	Almost 100	Sangtumrong *et al.* 2007
Natural gas produced well water	TOA	2.4	NaOH	99	Shamsipur *et al.*2006
Aqueous solutions	TOA	10.0	NaOH	91	Sharma *et al.* 2015
Synthetic solution	TOA	10.0	NaOH	53	Pancharoen *et al.* 2010
Natural gas coproduced water	aliquat 336 and cyanex 471	4.0	NaOH	94	Chakrabarty *et al.* 2010b
Synthetic solution	various amine carriers	10.0	thiourea	Almost 100	Lothongkum *et al.* 2011
Petroleum produced water	Aliquat 336	0.5	thiourea	Almost 100	Maron *et al.* 2008
Synthetic solution	TBP	10.0	NaOH	97	Present study

reaction volume of 150 mL, and the result is shown in Fig. 9. Around 30 min, the removal efficiency of Hg^{2+} ions was about 22%. As time increases, the removal efficiency of Hg^{2+} ions from feed to strip phase increased gradually and attained the maximum (100%) efficiency around 3 h. The result is comparable to the study reported by Bhandare and Argekar (2002). They achieved 100% removal of Hg^{2+} ions through SLM with Cyanex 471 as a carrier at 6 h whereas, in this study, the same was achieved within 3 h.

4.10 Optimum conditions

From all the above experiments, the parameters optimized for the transport of Hg^{2+} ions across SLM for a single cycle (feed and strip each 150 ml) are summarized in Table 2. A comparison of the results obtained in this study with the recent works reported by other researchers is presented in Table 3.

4.11 Transport mechanism

In the extraction process of metal ions across SLM, solute molecules dissolve in the feed phase and diffuse through the liquid boundary layer. They finally react with the carrier, which is filled in the pores of the membrane and form a complex. This complex species diffuses through the membrane phase to the strip phase due to the concentration gradient (Malik *et al.* 2011). Therefore, a study of the transport of Hg^{2+} ions through SLM requires consideration of the diffusion of solute through aqueous feed phase, reversible chemical reaction at membrane phase, diffusion of metal complex species, and chemical reaction at the strip phase.

4.11.1 Reaction at feed phase

The addition of HCl to the feed phase increases the availability of excess chloride ions and protons. The chloride ions in the feed phase react with Hg^{2+} ions and form $HgCl_4^{2-}$ under acidic conditions, which are given in

Eq. (3). The carrier, TBP of the membrane phase initially gets protonated by HCl at the feed phase in an acidic environment which is represented in Eq. (4).

$$Hg^{2+}+ 4\ Cl^- \leftrightarrow HgCl_4^{2-} \tag{3}$$

$$RO)_3PO + H^+ \leftrightarrow ((RO)_3PO)\ H^+ \tag{4}$$
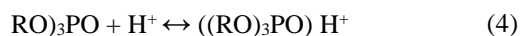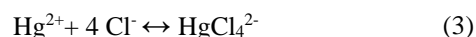
4.11.2 Reaction at membrane phase

Protonated TBP combines with $HgCl_4^{2-}$ and forms an ion pair complex of TBP and Hg, which is represented in Eq. (5) (Sato *et al.* 2002, Xiao *et al.* 2016)

$$HgCl_4^{2-}+ 2\ ((RO)_3PO)\ H^+ \leftrightarrow HgCl_4^{2-}.2((RO)_3PO)H^+ \tag{5}$$
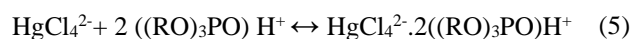
4.11.3 Reaction at strip phase

The ion-pair complex of $TBP.HgCl_4^{2-}$ diffuses through the membrane due to concentration gradient and reaches the strip phase, where NaOH reacts with the ion-pair complex to recover mercury as indicated in Eq. (6).

$$HgCl_4^{2-}.2((RO)_3PO)H^+ +2\ OH^- \leftrightarrow \\ HgCl_4^{2-} + 2\ (RO)_3PO + 2\ H_2O \tag{6}$$
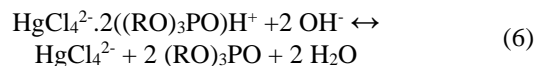
TBP diffuses back to the membrane phase. The above transport mechanism of Hg^{2+} ions through SLM is classified under the principle of co-transport mechanism, represented schematically in Fig. 10.

The concentration-time profile of the transport of Hg^{2+} ions through SLM at optimum conditions over a time period of 3 h was studied, and the results are shown in Fig. 11. The figure depicts the concentration profile of Hg^{2+} ions in the feed phase and strip phase as a function of time. The feed phase concentration of Hg^{2+} ions decrease sharply as time progresses, whereas the strip phase concentration increases at the same time. Thus, increasing the membrane exposure area influences the removal efficiency. The concentration gradient of the ion-pair complex formed in the membrane
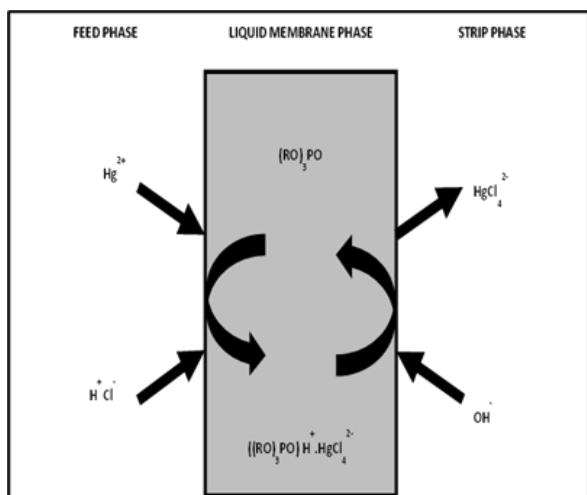
Fig. 10 Schematic representation of co-transport mechanism of Hg^{2+} ion through SLM
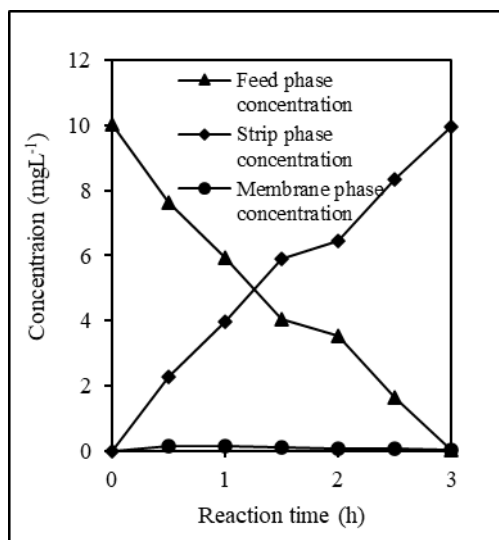
Table 4 Mass transfer co-efficient of various carriers

Carrier	Mass transfer coefficient (k) m/s
Cyanex 471 + cyanex 336 (Chakrabarty *et al*. 2010b)	1.27×10^{-7}
TOA (Shamsipur *et al*.2006)	1.1×10^{-14}
TBP (this work)	8.53×10^{-3}

phase (Fig. 11), is the driving force of the transport. As shown in the figure, the membrane phase concentration of Hg^{2+} ions increases initially and reaches a maximum (1%) around 30 min of the transport. After which, the membrane phase concentration was found to decline steadily owing to the transport of Hg^{2+} ions from the feed phase to the strip phase. This observation is similar to that reported by Venkateswaran and Palanivelu (2005) and Kazemi *et al*. (2014). Venkateswaran and Palanivelu (2005) reported the transport of Cr (IV) ions using a TBP based SLM system in which almost all the feed phase metal ions were transferred to the strip phase at optimum conditions. Transport of phenol by TBP based SLM system was studied by Kazemi *et al*. 2014, wherein the feed phase concentration of phenol was observed to decrease sharply with a corresponding increase in the strip phase within the initial stage of transport.

4.12 Transport kinetics

Kinetics for the transport of Hg^{2+} ions across SLM can be described by the first-order equation. The rate constant and mass transfer coefficient using Eq. 7. Here, C_i is the initial concentration, C_t is the concentration of metal ions as a function of time t, V is the volume of the feed solution, and A is the effective area of the membrane (Tor *et al*. 2009). The relationship of $\ln(C_i/C_t)$ against time was used to plot the data obtained in this work and was found to be linear, as shown in Fig. 12.

The linearity was confirmed by a high value of the correlation coefficient (R^2) ≥ 0.96. The developed system thus followed first-order rate kinetics, which mainly depends on the concentration gradient of the ion-pair complex formed in the membrane. It is the driving force of the transport process across the membrane. Similar results were observed in the transport of phenol using TBP by Kazemi *et al*. 2014. According to which the membrane phase concentration of mercury is considered to be negligible. Mass transport coefficient (k) was 8.53×10^{-3} m/s calculated using Danesi Model Eq. (7) (Danesi 1984). A comparison with other carriers, as indicated in Table 4, shows that TBP is a superior carrier for the removal of mercury ions from aqueous solutions.

Fig. 11 Effect of reaction time on concentration of Hg^{2+} ions (10 mgL^{-1}) (HCl- 0.5 M, NaOH- 0.4 M, TBP- 90%, soaking time- 8 h, stirring speed- 300 rpm)
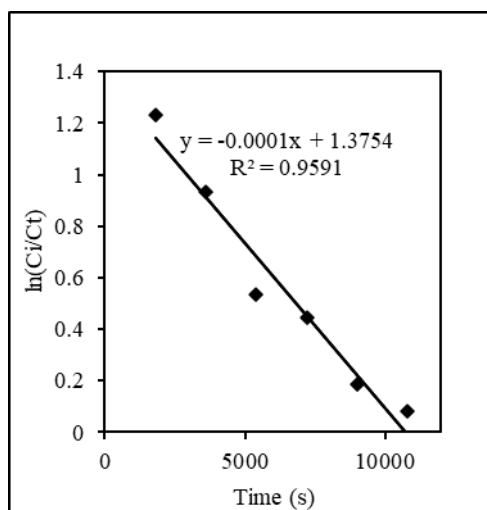
$$-ln\left(\frac{Ci}{Ct}\right) = -\frac{Ak}{V}t \qquad (7)$$

Flux (J) is the number of moles of Hg^{2+} ions diffusing per unit time and effective contact area of the membrane, which can be calculated using Eq. (8) (Amiri *et al*. 2008). Here, V indicates the volume of strip solution, A indicates the contact area of the membrane, dC is the concentration of

Fig. 12 Kinetic plot for the transport of Hg^{2+} ions through SLM

Hg^{2+} ions, and dt is the time interval. The flux value was determined for the removal of Hg^{2+} ions through SLM using 4.5×10^{-9} mol/m^2.s.

$$J = \frac{V}{A} \frac{dC}{dt} \qquad (8)$$

4.13 Morphology studies

The surface morphology of the carrier impregnated PTFE membrane was determined using SEM, and the images are shown in Fig. 13. Fig. 13 (a) shows the SEM image of the membrane before impregnation of the carrier. The porous nature of the membrane could be seen from the SEM image. A membrane was soaked in the carrier for 6 h and was used for the study. After the impregnation of the carrier onto the membrane, the surface morphology was found to be entirely altered, i.e. all the pores were filled by the carrier (Fig. 13 (b & c)). Fig. 13 (d & e) shows the SEM image of SLM after the transport of Hg^{2+} under optimized conditions. On comparing Fig. 13 (b & c) with Fig. 13 (d & e), it could be inferred that the surface morphology of the membrane has changed completely owing to the transport of Hg^{2+} ions. Occurrence of a few complex structures could be observed on the membrane that may be attributed to the ion-pair complex of Hg^{2+} and TBP.

4.14 Selectivity of Hg²⁺ ions

Mercury cells are used for the production of caustic soda in Chlor-alkali industries, which are the major sources of mercury witnessed during the past two decades. Though mercury cells have been replaced by eco-friendly membrane systems, mercury still persists in soil and groundwater around industries (Blue *et al*. 2008). In this study, selective separation of mercury from a binary mixture of metals which are mentioned above was carried out with two different concentrations (10 and 50 mgL^{-1}) of metal ions. Cd, Zn, and Ni were added along with Hg ions (10 mgL^{-1}) in the feed phase of the SLM reactor, and the concentration of the metal ions was analyzed, from which removal efficiency (%) was evaluated at optimum operational conditions as tabulated in Table 5. The results indicated that the metal ions studied did not affect the transport efficiency of Hg^{2+} ions. Also, increasing the concentration of added metal ions by about five times (50 mgL^{-1}) than the mercury ions (10 mgL^{-1}) did not affect the removal efficiency of Hg^{2+} ions across SLM (Table 5). Zn^{2+} and Cd^{2+} ions were used in a binary mixture while studying the selective removal of Hg^{2+} ions. Though Zn^{2+} and Cd^{2+} are known to form tetrahedral MX$_4^{2-}$ ions, it was not stabilized by the large cation such as (RO)$_3$POH$^+$ under similar conditions of extraction. Thus, the transport of mercury ions using SLM was highly selective over the other metals in Chlor-alkali industrial waste.

4.15 Stability of SLM

In SLM, the organic carrier is impregnated on the membrane by capillary forces. The instability of SLM is
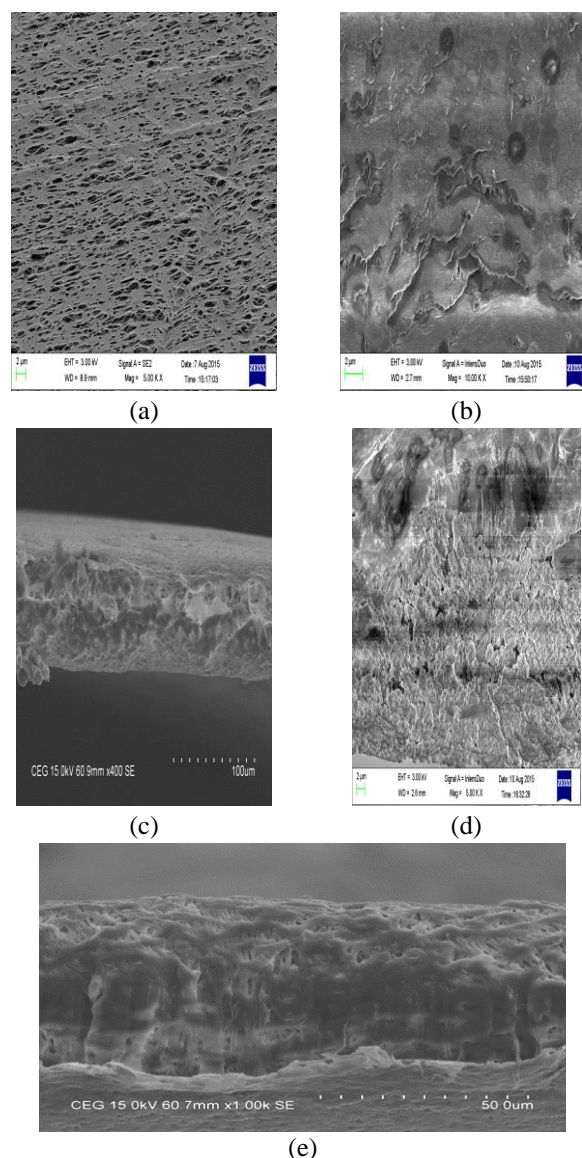

(a)

(b)

(c)

(d)

(e)

Fig. 13 SEM image of PTFE membrane (a) before impregnation of carrier (b) after impregnation of carrier (c) cross section after impregnation of carrier (d) surface after removal of Hg^{2+} ions (e) cross section after removal of Hg^{2+} ions

due to the removal of liquid extractant from the pores in the membrane (Zhang *et al*. 2009). Loss of liquid from the membrane can be used to estimate the stability of the membrane. Serious leakage and direct channelling between feed and strip occur when the membrane liquid is almost lost (Kazemi *et al*. 2014). The stability of SLM varies for time and usage. Prolonged usage of SLM leads to deterioration in the removal efficiency, mainly due to the loss of carrier from the membrane (Clever *et al*. 1985). Experiments were carried out under optimized conditions for finding out the stability of the membrane. The feed and the strip solutions were changed after achieving a maximum removal of Hg^{2+} ions in every single run. Fig. 14 represents the stability of the membrane in terms of removal efficiency across SLM for the system mentioned above. 97% of the Hg^{2+} ions were removed during the first three runs. The

Table 5 Selectivity of mercury ions in binary mixtures

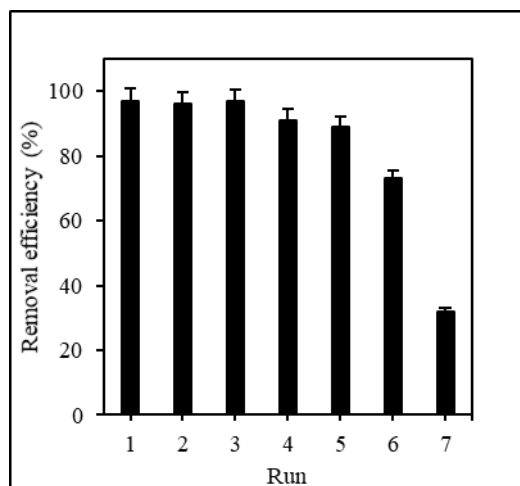| Composition of binary mixtures	Concentration (mgL^{-1}) in feed phase		Relative standard deviation (%)	Removal efficiency (%)	
	Mercury	metal ions		mercury	metal ions
Hg + Cd	10.12	10.02	0.40	96.56	<0.01
Hg + Zn	10.10	9.95	0.64	97.24	<0.01
Hg + Ni	9.99	10.41	0.51	96.24	<0.01
Hg + Cd	10.12	48.23	0.48	95.56	<0.01
Hg + Zn	10.10	50.12	0.55	96.24	<0.01
Hg + Ni	9.99	49.80	0.52	95.24	<0.01

Fig. 14 Stability of SLM (HCl- 0.5 M, NaOH- 0.4 M, TBP- 90%, soaking time- 8 h, stirring speed- 300 rpm, initial concentration of Hg^{2+} ions- 10 mgL^{-1}, reaction time- 3 h)

efficiency was reduced later by 6% for the fourth run with further reductions for consecutive runs, and finally, for the seventh run, the removal efficiency was only 32 $\pm$ 1.1%. Henceforth, from the above investigation, the SLM used in this study was stable for about 18 h.

4.16 Applications

The SLM system was used for the treatment of mercury spiked seawater, wastewater, and contaminated lake water. The results obtained with each study are discussed as follows. Removal of Hg^{2+} ions from seawater was approximately 94% for 10 mgL^{-1}, and 100% removal was achieved with 5 mgL^{-1} and 0.1 mgL^{-1} solutions of mercury. The time taken for 94% of removal of mercury ions from seawater (10 mgL^{-1}) was 3 h. Though 100% removal was attained with 5 mgL^{-1} and 0.1 mgL^{-1} concentration solutions, the time taken for complete removal with 5 mgL^{-1} was 2 h, and 0.1 mgL^{-1} was 30 min. Bhandare and Argekar (2002) demonstrated the removal of almost 100% of mercury ions from spiked seawater with 0.3 and 0.5 mgL^{-1} of mercury in 6 h with SLM and Cyanex 471X as a carrier.

The initial concentration of mercury ions in the wastewater collected from the power plant was determined by CVAFS and was found to be 18 µgL^{-1}. In the case of the contaminated lake water, the initial concentration of mercury

was found to be 42 µgL^{-1}. The level of mercury in these contaminated water sources was above the permissible standards (5 µgL^{-1}), these solutions were then subjected to separation by SLM under optimized conditions. Using the present study, complete removal of Hg^{2+} ions from the wastewater occurred within 10 min of reaction time. In the case of lake water, removal of Hg^{2+} ions occurred within 20 min of reaction time with the SLM reactor. These studies clearly show that the proposed SLM with TBP as a carrier is effective for the treatment of real contaminated water samples.

5. Conclusions

The present laboratory study shows the selective removal of Hg^{2+} ions by a TBP based SLM system. The removal efficiency of about 97% has been attained under the optimum conditions. This study ascertains the co-transport mechanism involved in the separation by SLM, and the membrane was found to be stable for 18 h. The experimental data fitted well with the first-order rate equation. Selectivity studies with Cd, Ni, and Zn indicate the highly selective nature of the developed SLM system for mercury ions. Application studies were successfully carried out for spiked seawater, wastewater from a thermal power plant, and contaminated lake water. Thus, the efficacy of TBP based SLM system for selective removal and separation of mercury ions from aqueous solutions in both synthetic as well as real contaminated water has been successfully demonstrated.

Acknowledgement

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