Removal study of As (V), Pb (II), and Cd (II) metal ions from aqueous solution by emulsion liquid membrane

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Abstract. Emulsion Liquid Membrane (ELM) is a prominent technique for the separation of heavy metal ions from wastewater due to the fast extraction and is a single-stage operation of stripping-extraction. The selection of the components (Surfactant and Carrier) of ELM is a very significant step for its preparation. In the ELM technique, the primary water- in-oil (W/O) emulsion is emulsified in water to produce water-in-oil-in-water (W/O/W) emulsion. The water in oil emulsion was prepared by mixing the membrane phase and internal phase. To prepare the membrane phase, the extractant D2EHPA (di-2-ethylhexylphosphoric acid) was used as a mobile carrier, Span-80 as a surfactant, and Paraffin as a diluent. Moreover, the internal (receiving) phase was prepared by dissolving sulphuric acid in water. Di-(2- ethylhexyl) phosphoric acid such as surfactant concentration, carrier concentration, sulphuric acid concentration in the receiving (internal) phase, agitation time (emulsion phase and feed phase), the volume ratio of the membrane phase to the receiving phase, the volume ratio of the external feed phase to the primary water-in-oil emulsion and pH of feed were studied on the percentage extraction of metal ions at 20°C. The results show that it is possible to remove 78% for As(V), 98% for Cd(II), and 99% for Pb(II).

Emulsion Liquid Membrane (ELM) is a well-known technique for separating heavy metal ions from wastewater due to the fast extraction and is a single-stage operation of stripping-extraction. The selection of ELM components (Surfactant and Carrier) is a very significant step in its preparation. In the ELM technique, the primary water-in-oil (W/O) emulsion is emulsified to produce water-in-oil-in-water (W/O/W) emulsion. The water in the oil emulsion was prepared by mixing the membrane and internal phases. The extractant D2EHPA (di-2-ethylhexylphosphoric acid) was used as a mobile carrier, Span-80 as a surfactant, and Paraffin as a diluent. Moreover, the internal (receiving) phase was prepared by dissolving sulphuric acid in water. Di-(2-ethylhexyl) phosphoric acid such as surfactant concentration, carrier concentration, sulphuric acid concentration in the receiving (internal) phase, agitation time (emulsion phase and feed phase), the volume ratio of the membrane phase to the receiving phase, the volume ratio of the external feed phase to the primary water-in-oil emulsion and pH of feed were studied on the percentage extraction of metal ions at 20°C. The results show that it is possible to remove 78% for As(V), 98% for Cd(II), and 99% for Pb(II).

Keywords: D2EHPA; emulsion liquid membrane; metal ions extraction; paraffin; span 80; wastewater treatment

1. Introduction

Water contamination with harmful heavy metal ions such as arsenic Marino and Figoli (2015), lead, zinc, nickel, iron, and cadmium poses a severe problem for humans and are hazardous to the environment. Due to the presence of these heavy metal ions in drinking water, these cause serious health issues, such as cancer, skin lesions, and metabolic and cardiac disorders. Many methods are offered to solve industrial wastewater problems, such as adsorption, ion-exchange, floatation, coagulation, chemical precipitation, and various membrane processes.

One of the membrane processes growing rapidly is Emulsion Liquid Membrane (ELM) technology San Roman *et al*. (2010). Lohiya *et al*. (2019), Imdad and Dohare (2021) have used ELM to separate the synthetic dye and phenol very efficiently. This process offers the possibility

to operate highly selective separation and recovery of chemical compounds from dilute aqueous solutions, leading to extraction and subsequent stripping operations in a single step Molinari *et al*. (2009). ELM is a relatively effective prospective separation system consisting of a liquid film through which selective mass transfer of gases, ions, or molecules occurs via permeation and transport processes. ELM uses the minimum quantity of expensive organic solvent to separate heavy metal ions from aqueous solution, indicating that this technique is more efficient and economical than the other current separation processes. Ionic liquid membrane is one of the option to remove the heavy metals from the industrial wastewater Dohare and Imdad (2022).

The ELM process is based on the use of liquids impregnated in the pores of membranes; it is not miscible with the feed and product phases. ELMs can be efficiently used for wastewater treatment, biotechnology applications, and chemical/biomedical engineering systems. Furthermore, ELM systems allow us to obtain high permeability, especially compared to solid membranes, due to higher diffusion coefficients in liquids, low operating costs, and

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easy feasibility Kislik (2009), Bartsch and Way (1996). ELM has several advantages over solid membranes and solvent extraction, such as (a) high interfacial area for mass transfer (b) high diffusion rate of the metal ion through the membrane, (c) simultaneous extraction and stripping in the same system, and (d) capable for separation of a wide range of elements and compounds in an industrial setting with greater efficiency Kumbasar (2013). Emulsion liquid membranes (ELMs), also called surfactant liquid membranes or liquid surfactant membranes, are double emulsions formed by emulsifying two immiscible phases (e.g., water droplets in an oil phase and vice versa) and dispersing the resulting emulsion in another external feed (or donor) phase containing solutes to be removed. Therefore, there are two different configurations for the ELM: (1) oil-in-water-in-oil (O/W/O) system and (2) water-in-oil-in-water (W/O/W) system.

The mechanism used for the recovery and enrichment of heavy metal ions in the mass transfer is assisted by a carrier present in the membrane phase and ion concentration gradient between the two sides of the membrane phase (Mulder 2012).

ELM system involves the facilitated transport of a solute across the membrane phase by incorporating a carrier agent. In this process, a solute is not soluble in the membrane phase, so it needs a carrier agent to transport the solute from the external feed phase to the internal stripping phase.

The following steps explain the transport mechanism by Ammar and Affat (2012): (1) metal ions diffusion inside the bulk feed solution toward the external interface of the emulsion droplet; (2) occurrence of the interfacial reaction between metal ions and the active species of the carrier extractant at the external interface; (3) diffusion of the metal-extractant complex into the emulsion globule towards the internal aqueous- organic interface of water droplets; and finally (4) a stripping (back-extraction) reaction between the metal complex and the acid stripping agent takes place.

In this study, the emulsion liquid membrane technique was used for the removal of the combination of heavy metal ions like arsenic, cadmium and lead from a synthesized aqueous solution at various operating parameters such as surfactant concentration, carrier concentration, the volume ratio of the membrane to internal phase, the volume ratio of feed to membrane phase, agitation speed for membrane preparation and agitation time for separation. The globules' size of the membrane was measured using optical microscopy. No comparison study of ionic liquid and the organic carrier has been done to remove a mixture of metal ions (arsenic, cadmium and lead) using ELM. The authors also observed the effect of globule size on removal efficiency for the system.

2. Materials and experimental methods

2.1 Materials

To remove the lead from the aqueous solution by emulsion liquid membrane technique, di-(2- ethylhexyl)

phosphoric acid was used as a carrier. Commercial kerosene was used as organic solvent, span 80 as an emulsifying agent, and sulphuric acid as the stripping phase. They found that removing 99–99.5% of the lead after 5 min contact time is possible by using ELM at the optimum operating conditions (Sabry *et al.* 2007).

An emulsion liquid membrane was used to remove cadmium from an aqueous solution using corn oil as a diluent. Ahmad *et al.* (2017) recorded 48.8% emulsion breaking efficiency using ultrasonic power. A comprehensive study on the removal capacity of cadmium and emulsion diameter based on trioctylamine (TOA) as a carrier was studied, and the authors found that the maximum removal capacity was 0.493 mg Cd/ml Ahmad *et al.* (2012). The hybrid liquid membrane was fabricated by Garmsiri and Mortaheb (2015) to remove the cadmium from the ionic feed solution and test the morphology of the fabricated membrane.

Some researchers used 2-Ethylhexyl phosphonic acid mono-2-ehtylhexyl ester (PC-88A) as a carrier, surfactant Span 80 and light paraffin oil as an additive to remove the metal ions by liquid emulsion techniques García, Acosta, and Marchese (2013).

In this study, the salt of Lead, Arsenic, and Cadmium was purchased from Sigma Aldrich in the form of lead nitrate, sodium arsenate, and cadmium chloride. These analytical grade chemicals were used to make the feed phase without further purification. The D2EHPA (Di-(2-ethylhexyl) phosphoric acid) and Aliquat-336 (N-Methyl-N, N, N-trioctylammonium chloride) were used as extractants purchased from LOBA Chemical Pvt. Ltd. Span-80 (Sorbitan-mono-oleate) was used as a surfactant purchased from Sigma Aldrich. Paraffin oil (diluent) and H_2SO_4 (98% pure) were used to prepare the internal stripping phase.

2.2 Apparatus

For the formation of the emulsion phase, an IKA ES-ULTRA-HB18 homogenizer (0-30,000 rpm) was used. The external (feed) phase and emulsion phase were agitated at different agitation speeds to achieve proper dispersion of emulsion globules in the feed phase solution. The solution from the beaker was transferred into a separating funnel, and samples were taken to analyse the metal ions concentration by Atomic Absorption Spectroscopy (AAS) (Make- Thermo Scientific, Modal-ICE 3500 AA system). To measure the emulsion globules Olympus optical microscopy of CX-21i was used.

2.3 Procedure

Feed phase consisting of arsenic (25 ppm), cadmium (50 ppm), and lead (200 ppm) ions were prepared by dissolving the salts in deionized water at 20°C. The emulsion phase (100 ml) was prepared by adding stripping solution of aqueous H_2SO_4 at various molarities to the membrane phase solution, which was prepared by paraffin oil, Span- 80, and D2EHPA at various compositions by stirring using the homogenizer for 10 minutes at 8000 rpm to get a stable emulsion phase.

The prepared emulsion was added to the known quantity of feed solution in a predetermined volume ratio of the feed
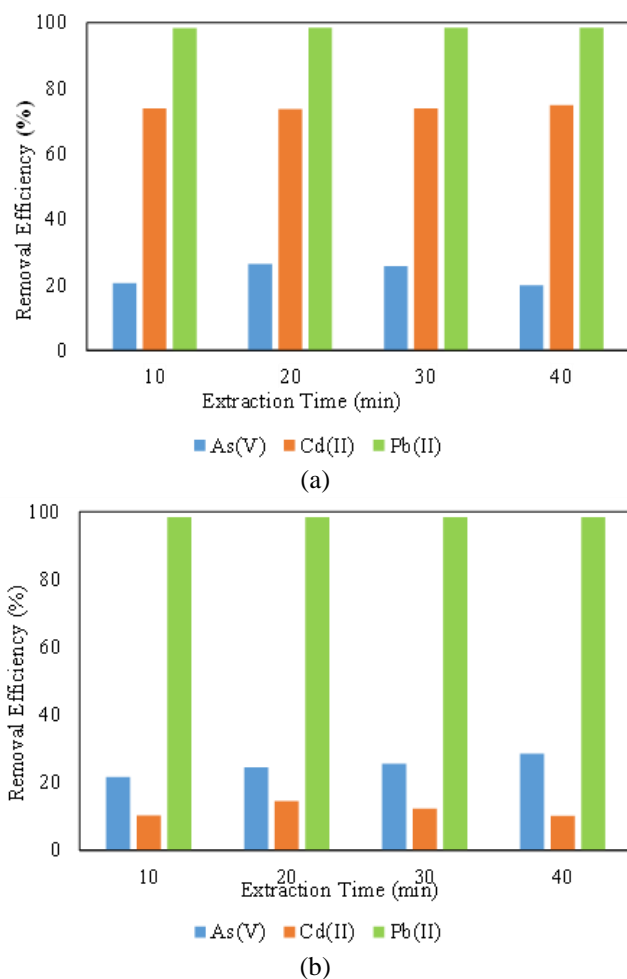
(a)

(b)

Fig. 1 Removal efficiency of heavy metal ions at 4 vol% of Span-80, 4M H_2SO_4 (a) 4 vol% of D2EHPA (b) 4 vol% of Aliquat-336
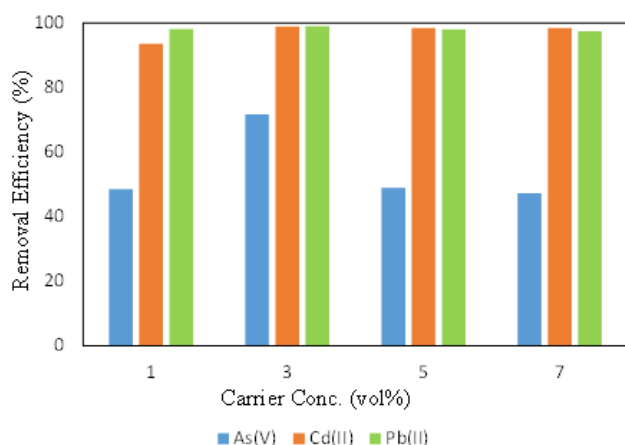

Fig. 2 Effect of D2EHPA carrier concentration on removal efficiency of metals ions

phase to the emulsion phase. The optical CX-21i Olympus Binocular Microscope determined the size of the prepared globules in the membrane at 4X-10X optical zoom. The phases prepared were agitated for different e periods at different agitation speeds using a motor-driven agitator. After proper mixing, the solution was transferred to a

separating funnel from the beaker. After separating the two phases, the sample was taken to determine the concentration of As, Cd, and Pb using Atomic Absorption Spectroscopy (AAS).

3. Result and discussion

3.1 Effect of carriers on percentage removal of metal ions

The selection of carriers is a significant step in forming the liquid membrane Srivastava *et al.* (2017). Two carriers namely D2EHPA and Aliquat-336 were tested at the same composition keeping all other parameters constant to find the suitable membrane phase. The percentage removal of Pb(II), Cd(II), and As(V) are shown in Fig. 1 for different extraction times in the range of 10 to 40 min.

The maximum removal was found to be 98%, 74%, and 26% for Pb(II), Cd(II) and As(V), respectively in case of D2EHPA as shown in Fig. 1(a) and 98%, 10% and 29% in the case of Aliquat-336 as shown in Fig. 1(b).

In this study, it was found that D2EHPA removes Cd (II) and Pb (II) higher than Aliquat 336 from a mixture of heavy metal ion systems consisting of As(V), Cd (II), and Pb (II). Since D2EHPA is an organo-phosphorus compound that makes better metal complexes than a quaternary ammonium salt i.e., Aliquat 336.

3.2 Effect of carrier concentration on percentage removal of metal ions

The initial concentration of heavy metal ions in an aqueous solution was taken as 25 ppm, 50 ppm and, 200 ppm for As(V), Cd (II), and Pb (II), respectively. The effect of carrier concentration on the removal efficiency of the metal ions is shown in Fig. 2 by varying carrier concentration from 1 to 7 vol %. Increasing the concentration from 1 to 3 vol% increases the percentage removal of heavy metal ions because of increasing mass transfer rates. These data were well explained because, as the concentration of selective carrier increases in the membrane phase, the metal–carrier complex at the membrane–feed interface increases. Due to that, the concentration gradient in the peripheral oil layer is increased, it affects the rate of extraction of metal ions in the forward direction. With a further increase in carrier concentration, the viscosity of the membrane phase increases, which decreases the extraction rate. However, the emulsion stability decreases with a large amount of carrier concentration Saravanan, Begum, and Anantharaman N. (2006) Saravanan, Begum, and Anantharaman N. (2006).

As seen in Fig. 2, maximum extraction was found to be 71.68% for As (V), 98.8% for Cd (II), and 98.95% for Pb (II) at 3 vol% of D2EHPA concentration keeping all other parameters as constant shown in Table 1.

It can also be observed that the extraction of Cd(II) and Pb(II) was not found to vary significantly, however, that for As(V) increases from 48.48% to 71.68% on increasing the carrier concentration from 1 to 3 vol% and then decreases to 47.24% on further increasing the carrier concentration up to

Table 1 Operating parameters for heavy metals removal

Parameter		Value
Temperature		20°C
External Phase Concentration	As(V)	25 ppm
	Cd(II)	50 ppm
	Pb(II)	200 ppm
Span-80 (surfactant) concentration in diluent		3 % vol.
Sulfuric acid concentration in the internal phase		1M
Carrier concentration of D2EHPA		3 vol%
Volume Ratio	Internal Phase (water) to Liquid Membrane (oil) phase	1
	External feed Phase to Primary W/O emulsion	2
pH of the feed phase		2.6
Agitation speed (External phase and emulsion phase)		500 rpm
Agitation speed (Emulsion phase preparation)		8000 rpm
Agitation time		5 min.

7% due to emulsion stability at higher carrier concentration. Emulsion stability decreases with increasing the carrier concentration up to its optimum value. After that, value permeation swelling may occur, which dilutes the stripping phase.

3.3 Effect of surfactant concentration on percentage removal of metal ions

The surfactant concentration (Span-80) was varied from 1 to 7 vol% under operating conditions given in Table 1. The percentage removal of metal ions was observed at 1, 3, 5, and 7 vol. % of Span-80 in the diluent (Paraffin oil) shown in Fig. 3.

To stabilize the emulsion, surfactant concentration plays an important role Park *et al.* (2006). The emulsion formed is highly unstable at 1 vol % of surfactant concentration. As the amount of surfactant increases from 1 to 3 vol % in the membrane phase, the percentage removal of metal ions increases due to the stable emulsion phase.

With the further increase in the amount of surfactant, percentage removal decreases because of the low mass transfer rate and increment in emulsion viscosity and thickness Alaguraj, M.; Palanivelu, K.; Velan (2009) Gasser, El-Hefny, and Daoud (2008).

3.4 Effect of stripping agent (H$_2$SO$_4$) concentration on percentage removal of metal ions

To analyse the effect of stripping agent (sulphuric acid) concentration on the metal ions extraction, its concentration in the internal phase varied from 0.5M to 2M as shown in Fig. 4, keeping all other parameters constant as given in Table 1. From Fig. 4, it can be observed that at low concentration of H$_2$SO$_4$, the percentage extraction is low.

On increasing the concentration of the stripping agent from 0.5 to 1M H$_2$SO$_4$ Ahmad *et al.* (2017), the percentage extraction of As(V) increases from 32.52 to 71.68%, and on
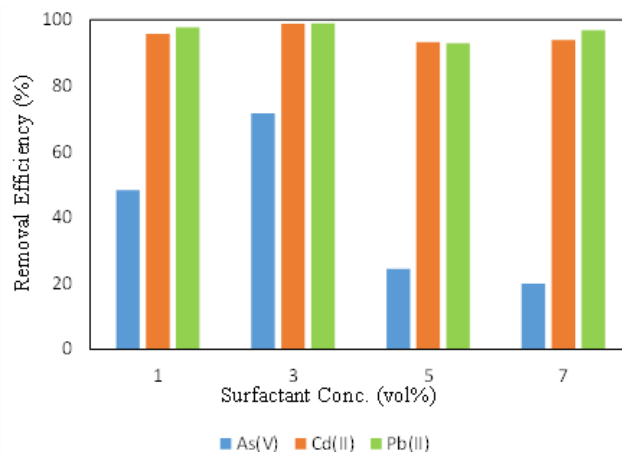

Fig. 3 Effect of Span-80 concentration on removal efficiency of metal ions
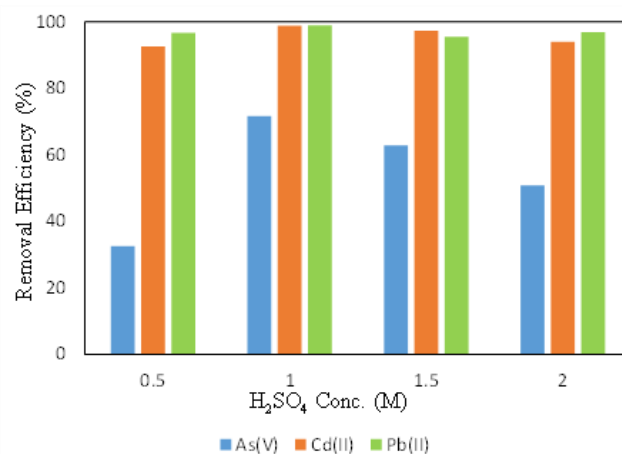

Fig. 4 Effect of stripping agent concentration on removal efficiency of metal ions

composite NF membrane had good oxidation resistance. further increase up to 2M H$_2$SO$_4$, the percentage extraction decreases up to 50.8%. However, there is no remarkable change in the removal efficiency of Cd(II) and Pb(II). Since the driving force in the ELM process is the chemical potential difference of H+ ions between the internal and external phase, therefore, the larger concentration of H$_2$SO$_4$ leads to larger removal efficiency. However, beyond 1M H$_2$SO$_4$ concentration, the membrane starts getting destabilized, causing the removal efficiency lower Norasikin Othman, Kit Hie Chan, Masahiro Goto (2006).

3.5 Effect of volume ratio of internal phase to membrane phase on percentage removal of metal ions

The volume ratio of the internal phase to the membrane phase is also one of the important factors, which was studied to analyse the extraction efficiency of metal ions by ELM. The ratio was varied from 1 to 4 keeping all the other operating parameters constant given in Table 1. The removal efficiency of the three metals As(V), Cd(II), and Pb(II) are shown in Fig. 5 for the volume ratio of 1, 2, 3, and 4. It is observed that removal efficiency decreases significantly from 71.68% to 12.28% for As(V) and 98.8%
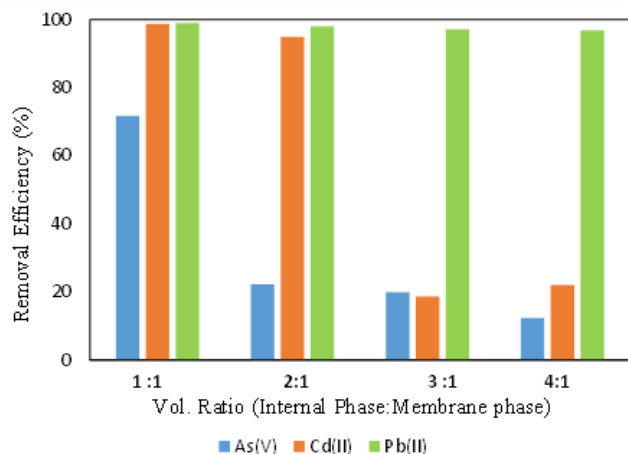
Fig. 5 Effect of volume ratio of internal phase to membrane phase
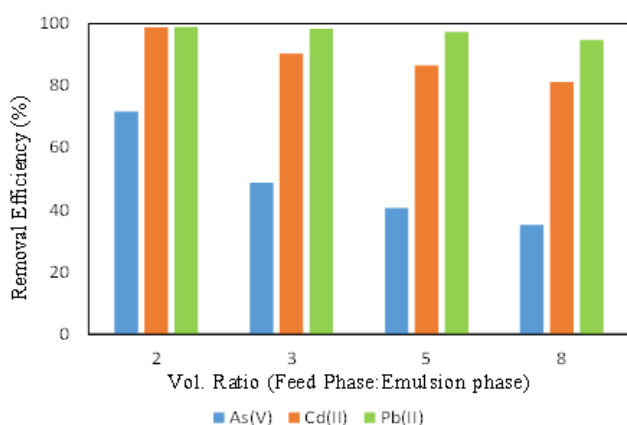

Fig. 6 Effect of volume ratio of Feed phase to emulsion phase
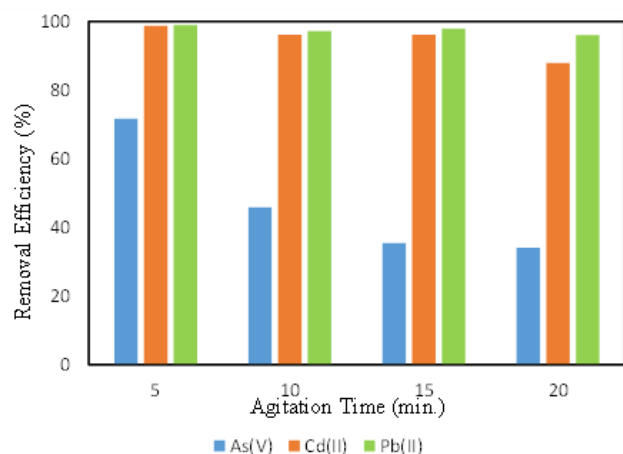

Fig. 7 Effect of agitation time on removal efficiency of metal ions

to 22% for Cd(II), however for Pb(II) the reduction in efficiency is not remarkable, i.e., it is 98.95% to 96.85% only. The viscosity of the membrane decreases by increasing the volume ratio of the internal phase to the membrane phase, which results in the formation of larger emulsion globules., Therefore, the interfacial area of the membrane decreases, which in turn decreases the

percentage extraction Ohtake *et al*. (1988). Moreover, increasing the stripping phase's volume ratio decreases the membrane's viscosity and leads to larger emulsion globules, which causes a decrease in interfacial area between emulsion and feed solution. Moreover, the membrane wall's strength is also reduced, which may enhance the changes of barrier breakage.

3.6 Effect of volume ratio of feed phase to emulsion phase on percentage removal of metal ions

To optimize the ratio of feed volume to membrane volume, various combinations were tried in the range of 2 to 8. The removal efficiency for a volume ratio of 2, 3, 5, and 8 are shown in Fig. 6 for As(V), Cd (II), and Pb(II). It can be observed that the removal efficiency gradually decreases on increasing the volume ratio as expected. The extraction of metal ions decreased slightly as the metal content in the external aqueous feeding phase increased, which is coherent with the necessary carrier to transport a larger quantity of metals. The optimum volume ratio for the maximum extraction for all three metals is 2 Basualto *et al*. (2006), i.e., it is 71.6%, 98.8%, and 98.95% for As (V), Cd(II) and Pb (II), respectively. Such extraction behavior is due to the larger membrane volume and hence the larger interfacial area available for removing metal ions compared to other volume ratios of 3, 5, and 8. The other operating parameters are constant, given in Table 1.

3.7 Effect of agitation time on percentage removal

To analyse the effect of agitation time on the percentage removal of the metal ions, various experiments were performed for agitation time of 3 min, 5 min, 10 min, 15 min, and 20 min as shown in Fig. 7. Other operating parameters are constant except for the agitation time in Table 1. As the agitation time of the emulsion phase and external phase increases at fixed emulsification speed, i.e., 8000 rpm, the removal of As(V) metal ions from aqueous solution decreases remarkably from 71.68% to 34.04% on increasing agitation time from 5 min to 20 min due to coalescence of emulsion droplets which leads to a reduction in the interfacial surface area resulting in a decrease of emulsion efficiency. However, there was no measurable change in Cd(II) and Pb(II) removal efficiency. Therefore, 5 min agitation time gives the maximum removal efficiency of all three metals, i.e., 71.68% for As(V), 98.8% for Cd(II), and 98.95% for Pb(II).

3.8 Effect of feed phase pH on percentage removal of metal ions

The pH of the feed phase plays an important role in the extraction of metal ions. The effect of feed phase pH on the percentage extraction of heavy metal ions from an aqueous solution is shown in Fig. 8. The initial pH of the aqueous solution varied from 2.5 to 8.5 using Sodium Hydroxide (NaOH) of 1M concentration while keeping other parameters constant in Table 1. An increase in the pH value of the external phase increases the driving force caused by the concentration gradient. When the pH value of the feed
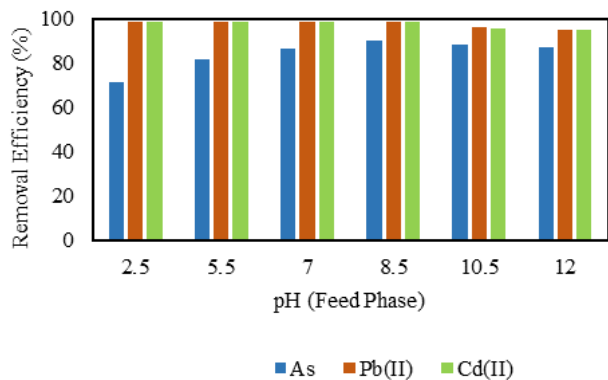
Fig. 8 Effect of pH of feed phase on the removal efficiency of metal ions
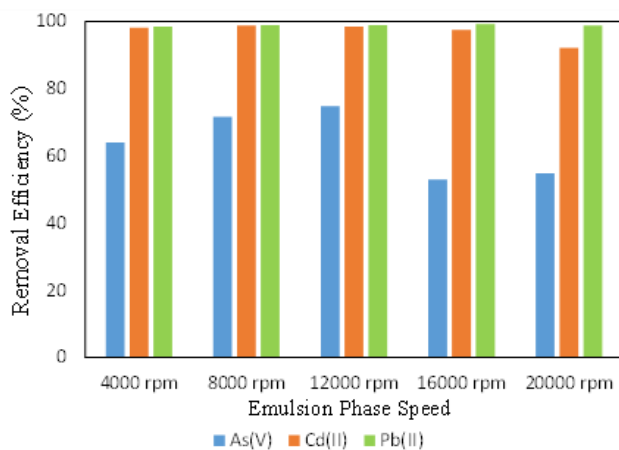

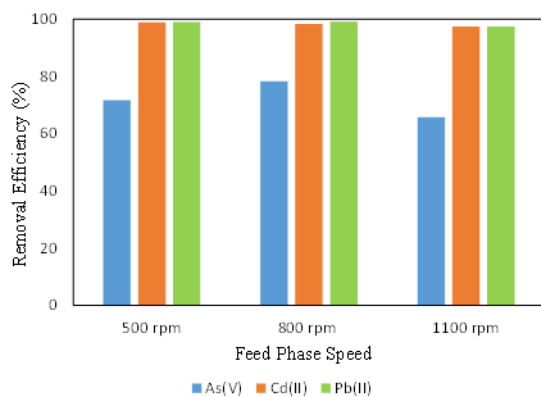Fig. 9 Effect of Emulsion phase preparation speed on removal efficiency of metal ions

Fig. 10 Effect of mixing speed of feed phase and emulsion phase on metal ion removal

phase is high, the carrier (D2EHPA) efficiency also increases. From Fig. 8, it can be seen that the percentage extraction of As(V) increases from 71.68% to 90.4% on increasing the pH from 2.5 to 8.5 because HASO4-2 is dominating species at higher pH. Binnal and Hiremath (2013) have also reported that HASO4-2 has higher mobility among other forms of arsenate through ELM, which leads to higher removal of arsenic at higher pH. HAsO4 -2 ion pairs, dissociate to a considerable extent due to the high polarity of the liquid membrane phase compared

to the Pb++ and Cd++, leading to faster transport based on the ''hopping mechanism'' Güell *et al.* (2011). The percentage extraction was found to be maximum in the basic range (>7). This may be because of metal complex formation with OH- ions. The percentage removal of Cd(II) and Pb(II) is not affected much and is more than 98% for all values of pH.

3.9 Effect of agitation speed during emulsion phase preparation on percentage removal of metal ions

The emulsion phase preparation significantly affects the percentage extraction of heavy metal ions from the external phase. The effect of emulsion preparation agitation speed is shown in Fig. 9 by varying it in the range of 4000–20000 rpm. As(V) extraction increases from 64% to 74.76% on increasing the agitation speed from 4000 to 12000 rpm while keeping other parameters constant, as shown in Table 1. The above variation may be due to the carrier-arsenic complex's instability at a higher emulsification speed On further increase in the agitation speed up to 20000 rpm, the extraction of As(V) decreases up to 54.78%. It is the reason that the interfacial area increases on increasing the emulsification speed because of more number of smaller globules. However, beyond 12000 rpm, the emulsion stability starts deteriorating because of globules coalescence and hence membrane rupture Kaghazchi *et al.* (2006). The same phenomenon was observed by Bourenane et. al. Bouranene, El-Hadi Samar, and Abbaci Faculté (2003). At 12000 rpm, it was observed that the maximum extraction efficiency is 74.76% for As(V), 98.54% for Cd(II), and 99% for Pb(II).

3.10 Effect of agitation speed during emulsion phase preparation on percentage removal of metal ions

The agitation speed plays a major role in the extraction rate through the emulsion liquid membrane process [15]. The mixing speed of external and emulsion phases was varied from 500 to 1100 rpm to observe the effect on the percentage removal of heavy metal ions from aqueous solution, as shown in Fig. 10. The other operating conditions were kept constant, as shown in Table 1. As the mixing speed increases from 500 rpm to 800 rpm, the percentage removal increases from 71.68% to 78.2% for As (V) and decreases thereafter. This may be caused by the swelling effect of emulsion.

As the mixing speed increases beyond 800 rpm, it not only decreases the extraction rate but also affects the stability of the emulsion and makes the emulsion inconsistent. At a higher agitation rate, hydrodynamic shear and swelling work together causing a decrease in percentage extraction Kaghazchi *et al.* (2006).
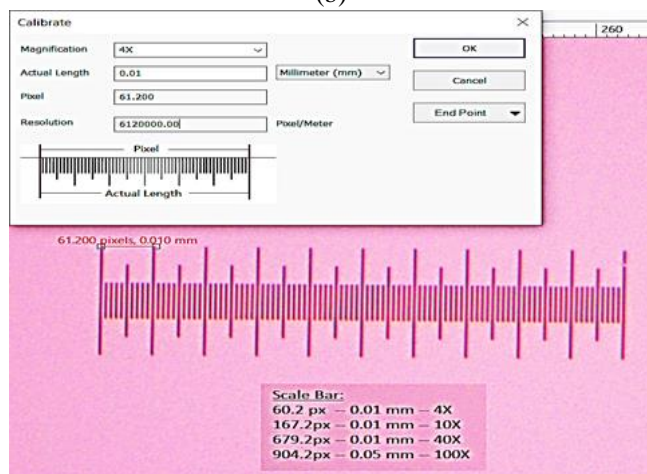
4. Optical microscopy images

The typical microscopic image of the emulsion phase is given in Fig. 11. Measurement of droplets was done by CX-21i Olympus Binocular Microscope. The microscope
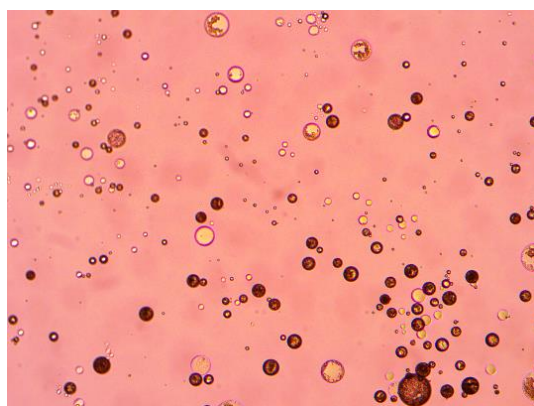
(a)
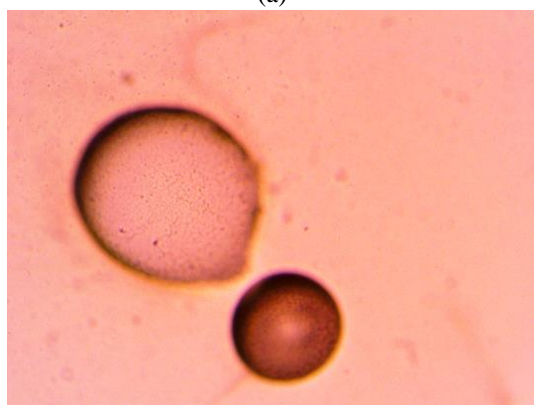
(b)

(c)

Fig. 11 Microscopic image (a) globules in the emulsion phase, (b) zoomed image of globules (c) scale bar

calibration was carried out by fixing the magnification at 4X and measuring the known length of 0.01 mm which was 61.2 pixels. The average size of the globules was found to be 9-10 µm, as shown in Fig. 11 (a). Fig. 11(b) shows the 40X zoomed image of the globules, whereas Fig. 11(c) pixel to µm.

5. Conclusions

In this study, the removal of heavy metal ions such as As(V), Pb(II), and Cd(II) from wastewater was studied

considering various parameters such as type of carrier, surfactant and carrier concentrations, internal phase (stripping agent) normality, external phase pH, the volume ratio of stripping to membrane phase, volume ratio of feed phase to emulsion phase, agitation speed and time. The comparative study of carriers between D2EHPA and Aliquat-336 found that D2EHPA was the better carrier over Aliquat-336. It was found that the optimum parameters are 3% (v/v) concentration of Span-80, 3% (v/v) concentration of D2EHPA, 1M sulphuric acid, external phase pH of 8.5, 1:1 volume ratio of internal phase to membrane phase, 2:1 volume ratio of feed phase to emulsion phase. At these optimum conditions, the percentage extraction was found to be 78% for As(V), 98% for Cd(II), and 99% for Pb(II). It was also analysed by optical microscopy that the average size of the emulsion globules is 9-10 µm. Therefore, the ELM technique is one of the promising alternatives to the conventional methods to separate the mixed metal ions from the aqueous solution.

Acknowledgments

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