Liquid Membrane-based Extraction of Arsenic: Part 1 - Experimental Study and Mathematical Modelling

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This work focuses on the liquid membrane-based extractive removal of arsenic from water. The entire work has been divided into two parts. The Part 1 presents the experimental studies and mathematical modelling. The reaction mechanism of the transport of arsenic from one aqueous phase to the another one via thin liquid membrane were explored in two-phase liquid-liquid extraction studies and three-phase flat-sheet supported liquid membrane. The experimental studies were conducted in both two-phase (only extraction) and three-phase (extraction and recovery) mode. Various process parameters were varied and their corresponding extraction and recovery results were recorded for further analysis. The crucial process parameters were identified. This study employed a steady-state diffusion-based modelling approach to assess the distribution coefficient and extraction equilibrium constant. Additionally, it conducted a kinetic-controlled investigation to determine the permeability coefficient, from which the mass transfer coefficients were subsequently derived. Arsenic present in the aqueous feed phase binds to the extractant present in the organic phase to form a complex, leading to the transport of arsenic ions from the feed to the organic phase. The extractants may be dissolved in any one of the environmentally benign diluents including vegetable oils such as coconut oil, mustard oil, sesame oil, soybean oil and sunflower oil that has maximum extraction efficiency. Environmental benignity was emphasized in order to reduce the toxicity of the organic phase. Various types of extractants including acidic, basic and neutral were studied to find the one that had better binding affinity toward arsenic ions. As arsenic anions might exist in the solution, depending on the pH, the basic extractants such as trioctylamine (TOA) and methyltrioctylammonium chloride (Aliquat 336®) were included in this work. We studied the extraction of As(III) and As(V) when they were present in water as single components, as well as when they were present in combinations with various ratios such as As(III):As(V)::1:1, As(III):As(V)::1:2, and As(III):As(V)::2:1. The extraction equilibrium constant determined from the distribution coefficient through mathematical modelling showed that As(V) species were favourable for extraction into organic phase, having a value of 8.2 M. Furthermore, it was found that all the species of arsenic form complexes in the organic phase with Aliquat 336® in the stoichiometric ratio of 1:1. The complexes formed between arsenic and Aliquat 336® were $(NR_4Cl)(H_3AsO_3)$ for As(III) and $(NR_4)(H_2AsO_4)$ for As(V), where $R \equiv (C_8H_{17})_3CH_3$ was methyltrioctyl.

Keywords: As(III), As(V), Mathematical modelling, Two-phase liquid-liquid extraction, Supported liquid membrane, Permeability

INTRODUCTION

Arsenic is one of the most hazardous metalloid found in the groundwater that has adverse toxic effects on human

health such as arsenicosis, cancer and failure of major organ systems. According to a report by WHO, the presence of iron-sulphide (arsenopyrite) minerals in sedimentary deposits from volcanic rocks are the major source of arsenic in groundwater [1]. Other geogenic and anthropogenic causes such as burning of fossil fuels, mining [2], smelting plants,

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pesticide application and/or leaching into soil are also potential source of arsenic. As it poses a menace to the society, removal of arsenic is of utmost importance for the well-being of the humankind.

In the environment, arsenic is present in different oxidation states. In the surface waters, biological activity transforms the arsenic into its organic form, while arsenic mostly remains in inorganic forms as oxyanions of trivalent arsenite As(III) or pentavalent arsenate As(V) in the groundwater [3]. Inorganic forms of As(III) has been found to be more harmful and toxic than the organic forms and pentavalent arsenate due to its reactivity with sulphur containing compounds and generation of reactive oxygen species [4]. Several conventional removal techniques of arsenic have been studied by scientists and researchers all over the world. However, liquid membrane based separation technique is the most promising one as it overcomes the limitations of the other conventional techniques such as high operating costs, less efficiency, sensitive operating conditions, production and disposal of secondary sludge.

Two phase liquid-liquid extraction-based study forms the stepping stone towards liquid membrane-based separation technique that is often used because of its simplicity, low cost and selective separation. Liquid-liquid extraction consists of two different immiscible liquids, usually polar and non-polar solvent, for separation of compounds or metal complexes based on the relative solubility. There is a transfer of the analyte from one liquid phase to another, usually from aqueous to organic phase due to difference in their chemical potentials. Liquid-liquid extraction (solvent extraction) is based on the ability of the target species to distribute itself in different ratios between the two immiscible liquid phases. This distribution ratio is the ratio of the concentration of the solute in the organic phase to the concentration of solute in the aqueous phase. This is a common initial separation/extraction technique widely used for the recovery of metal ions such as arsenic [5], copper [6], cobalt, nickel, iron, cadmium, mercury [7] and biomolecules [8]. Similar liquid-liquid extraction-based studies for the removal of arsenic have been carried out to investigate the behaviour of both organic and inorganic arsenic from various systems [9]; this helps to understand the removal of arsenic from sulphuric acid solution [10], and for determination and speciation analysis of inorganic arsenic [11].

Liquid membrane, on the other hand, is an arrangement of two liquid-liquid extraction units in series innovated for the separation of hydrocarbons [12], extraction of copper [13] and a great number of other metal ions and removal of phenolic compounds and organic acids [14]. Polymer inclusion membranes (PIMs) are relatively newer class of membranes [15-22]. The advantages of liquid membrane-based separation process includes selective separation, low capital and operating costs, low energy and solvent consumption, high concentration factors, and high fluxes.

SLM process is one of the promising technologies due to its high selectivity and simultaneous extraction and recovery in one single stage. So, it finds its application in both industrial and analytical fields for extraction, separation and removal of valuable metal ions or other pollutants from various resources. Certain limitations such as bulk aqueous/organic phase ratio, emulsification, phase disengagement, usage of high amount of organic solvent can be easily avoided [23]. Thus, this technology is considered as an attractive alternative over conventional unit operations such as adsorption, membrane filtration, precipitation, oxidation, biological remediation, and electrochemical treatment for separation and concentration of target species. As all these conventional processes require residual management options due to different residual productions.

Flat sheet supported liquid membrane (FSSLM) consists of a porous support impregnated with the organic phase and placed in between the two aqueous phases. The organic phase containing the extractant temporarily binds with the solute (arsenic ions in this study) from the feed aqueous phase and releases it to the receiving phase based on concentration gradient. Thus, the solute or the target element can be extracted and recovered simultaneously in a single step. Separation based on SLM have found its application in the separation of aromatic hydrocarbons [24], removal of heavy metals such as lead, cadmium and chromium [25,26]. Furthermore, transport of textile dyes [27] and phenolic wastewater treatment by extraction of phenols using SLM have also been reported elsewhere [28]. SLM has been used to study the transfer of As(V) ions [29] and in separation of arsenate and arsenite from aqueous media [30].

The aim of this work is to understand the transport mechanism during the extraction and recovery of arsenic ions through two phase liquid-liquid extraction and three phase

SLM process. A complete mathematical modelling of the process was considered in this study. Initially, identification of solvent followed by selection of extractant were carried out through a two-phase study. The chemistry of the reactants was studied. The efficiency of liquid membrane process depends upon various operating parameters such as pH of feed and/or receiving phase(s), concentration of extractant, duration of operation, temperature, and stirring speed. An optimal operating condition was evaluated using the above experimental approach. The transport of arsenic was determined through the evaluation of mass transfer coefficients. Overall, our work provides a framework for an interested reader in working on similar type of metal contaminant in water to experimentally obtain an optimal operating condition along with mass transfer coefficients for the target metal contaminant.
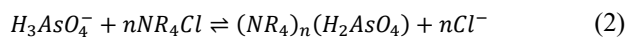
THEORETICAL BACKGROUND

Arsenic present in the aqueous feed phase binds to the extractant present in the organic phase to form a complex, which leads to the transport of arsenic ions from the feed to the organic phase. The extractants may be dissolved in any of the environmentally benign diluents, including vegetable oils such as coconut oil, mustard oil, sesame oil, soybean oil, and sunflower oil that has maximum extraction efficiency. Environmental benignity was emphasized in order to reduce the toxicity of the organic phase. Various types of extractants including acidic, basic and neutral were studied to find the one that shows better binding affinity with arsenic ions. Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is an acidic organophosphoric extractant with a tendency to form dimers. This anionic ligand finds its application in the extraction of divalent metals [31], lanthanide [32] and arsenic [33]. Tributyl phosphate (TBP), a neutral extractant, is efficient in forming complex with arsenic ions. TBP has mostly been applied for the extraction of rare earth elements [34], metals [35] including arsenic [36]. As arsenic anions might exist in the solution, depending on the pH, the basic extractants such as trioctylamine (TOA) and methyltrioctylammonium chloride (Aliquat 336®) were also included in this work.

Here, we studied the extraction of As(III) and As(V) when they were present in water as single components, as well as when they were present in combinations with various ratios such as As(III):As(V)::1:1, As(III):As(V)::1:2, and As(III):As(V)::2:1.

Reaction Mechanism

The chosen organic phase of this study consists of a mixture of sesame oil and Aliquat 336®. This mixture was selected based on the cited research work [37]. Aliquat 336® was preferred in this study for its ability to react with both dissociated and undissociated arsenic ions present in the feed phase [38]. The interactions between Aliquat 336® and the arsenic ions were studied here due to its ability to react with both dissociated and undissociated arsenic ions [38], as shown below.

$$H_3AsO_3 + nNR_4Cl \rightleftharpoons (NR_4Cl)_n(H_3AsO_3) \qquad (1)$$

$$H_3AsO_4^- + nNR_4Cl \rightleftharpoons (NR_4)_n(H_2AsO_4) + nCl^- \qquad (2)$$
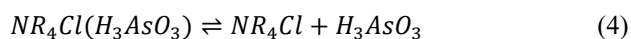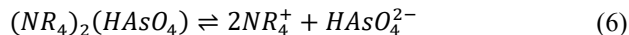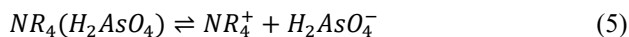
In above equations, $R \equiv (C_8H_{17})_3CH_3$ denotes methyltrioctyl and n denotes the number of Aliquat 336® molecules to be associated with one molecule of arsenic salt to form the desired complex. In addition, the pKa values of inorganic As(III) have been reported as $pKa^1 = 9.23$, $pKa^2 = 12.13$, and $pKa^3 = 13.4$ [39] and that of As(V) are $pKa^1 = 2.2$, $pKa^2 = 7$ and $pKa^3 = 11.5$ [40]. This indicates that As(V) is a stronger acid. Furthermore, H_3AsO_3 and $H_2AsO_4^-$ are the prevalent species of As(III) and As(V), respectively, within the studied pH range of groundwater [41]. From this, it can be inferred that As(III) is thermodynamically stable and most abundant in anoxic conditions or lower pH range; whereas, As(V) is most stable and abundant under oxic conditions. Under suboxic conditions at intermediate pH range, both the arsenic species may possibly coexist; hence, combined As(III) and As(V) in various ratios can be studied [41].

In the three phase SLM, the reactions occurring between arsenic ions and Aliquat 336® at the feed-membrane interface are Eq. (1), Eq. (2) and Eq. (3).

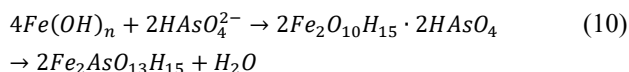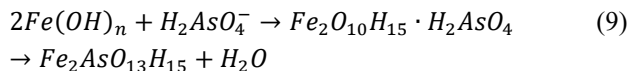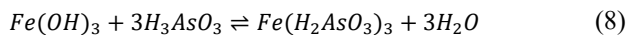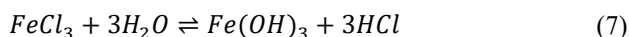$$HAsO_4^{2-} + 2NR_4Cl \rightleftharpoons (NR_4)_2(HAsO_4) + 2Cl^- \qquad (3)$$
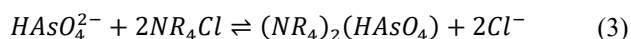
On the other hand, the reactions occurring in the membrane-strip interface are shown below [38].

$$NR_4Cl(H_3AsO_3) \rightleftharpoons NR_4Cl + H_3AsO_3 \qquad (4)$$

$$NR_4(H_2AsO_4) \rightleftharpoons NR_4^+ + H_2AsO_4^- \tag{5}$$

$$(NR_4)_2(HAsO_4) \rightleftharpoons 2NR_4^+ + HAsO_4^{2-} \tag{6}$$

Furthermore, arsenic is naturally found in iron based minerals. Iron is abundant and readily reacts with arsenic, so it finds its application in arsenic remediation. Hence, ferric chloride has often been used as a coagulant for arsenic removal [42]. In this study, ferric chloride solution was used as the strippant. In the receiving phase, iron hydroxides are formed from ferric chloride based on the pH as in Eq. (7), which then reacts with As(III) as in Eq. (8) [43] and As(V) as in Eq. (9) and Eq. (10) [44].

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl \tag{7}$$

$$Fe(OH)_3 + 3H_3AsO_3 \rightleftharpoons Fe(H_2AsO_3)_3 + 3H_2O \tag{8}$$

$$2Fe(OH)_n + H_2AsO_4^- \rightarrow Fe_2O_{10}H_{15} \cdot H_2AsO_4 \tag{9}$$
$$\rightarrow Fe_2AsO_{13}H_{15} + H_2O$$

$$4Fe(OH)_n + 2HAsO_4^{2-} \rightarrow 2Fe_2O_{10}H_{15} \cdot 2HAsO_4 \tag{10}$$
$$\rightarrow 2Fe_2AsO_{13}H_{15} + H_2O$$

Mathematical Modelling

The distribution (partition) coefficient, ($D_{(\cdot)}$), for arsenic ions is the ratio of concentration of arsenic ions in the organic phase (C_{org}) to the concentration of arsenic ions in the aqueous phase (C_{aq}), as shown below.

$$D_{(\cdot)} = \frac{C_{org}}{C_{aq}} \tag{11}$$

whereas the magnitude of extraction (%Extraction) may be expressed as Eq. (12).

$$\%Extraction = \frac{C_0 - C_t}{C_0} \times 100 \tag{12}$$

In above formula, C_t is the concentration of arsenic ions in the feed phase at time t and C_0 is the initial concentration of arsenic ions in the aqueous feed phase. Based on the two-phase equilibrium study, the extraction equilibrium constant and the mole balance of the reacting arsenic species and

Aliquat 336® can be obtained from the Eq. (1) and Eq. (2). The extraction equilibrium constants for As(III) and As(V) can be expressed as follow:

$$K_{III} = \frac{[(NR_4Cl)_n(H_3AsO_3)]_{fm}}{[H_3AsO_3]_{fm}[NR_4Cl]^n} = D_{III}\frac{1}{[NR_4Cl]^n} \tag{13}$$

$$K_V = \frac{[(NR_4)_n(H_2AsO_4)]_{fm}[Cl^-]^n}{[H_2AsO_4^-]_{fm}[NR_4Cl]^n} = D_V\frac{[Cl^-]^n}{[NR_4Cl]^n} \tag{14}$$

Here, the suffix *fm* refers to "feed-membrane interface", and D_{III} and D_V are the distribution coefficients of As(III) and As(V) respectively. The magnitude of $[Cl^-]$ in the Eq. (14) is surmised to be negligible in comparison to $[NR_4Cl]$. Hence, Eq. (13) and Eq. (14) can be re-written as shown in the following.

$$D_i = K_i[NR_4Cl]^n \tag{15}$$

or

$$\ln D_i = n\ln[NR_4Cl] + \ln K_i \tag{16}$$

Here, *i* denotes III and/or V depending on the case. The experimental data may be plotted as per Eq. (16) that slope and the intercept of which can yield the values of *n* and the equilibrium constant. In addition, the rate of complex formation between arsenic ions and Aliquat 336® and the nature of the diffusional process through the membrane may also be modelled through the steady-state diffusion-based modelling approach with the following few assumptions:

• The direction of mass flow of arsenic is from the feed phase to the organic phase in two phase, and additionally from the organic membrane phase to the receiving phase in three phase SLM. So, the molar flux in the feed phase is decreased with time.

• The complex formation reactions between arsenic ions and Aliquat 336® are fast and reversible at both the interfaces.

• The complex formation reactions occur at the interface only and not in the bulk aqueous or organic phases.

• The extraction of arsenic ions into the receiving phase is fast after their diffusion through the membrane into the receiving phase.

According to Fick's law of diffusion we have the following equation:

$$J = -D \frac{dC_x}{dx} \tag{17}$$

Here, J is the molar flux of arsenic (in mol m^{-2} s^{-1}), D is the diffusion coefficient (in m^2 s^{-1}), and C_x is the concentration of arsenic (in mol m^{-3}) at a distance x (in m). Upon discretizing Eq. (17) one obtains the following equation:

$$J = -D \frac{\Delta C_x}{\Delta x} \tag{18}$$

Furthermore, the rate of change of arsenic inside the feed cell may be related to the mass flow of arsenic transferred to the receiving phase, as shown below.

$$\frac{d(C_t V)}{dt} = J(A\epsilon) \tag{19}$$

Here, V is the volume (in m^3) of feed phase, A is the membrane area (in m^2), and ϵ is the porosity of the membrane. Using Eq. (18), the Eq. (19) may further be simplified into the following equation:

$$\frac{dC_t}{dt} = -D \frac{A\epsilon}{V} \times \frac{\Delta C_x}{\delta \tau} = -D \frac{\epsilon}{\delta \tau} \times \frac{A}{V} (C_{x,f} - C_{x,s}) \tag{20}$$

In above formula, $C_{x,f}$ and $C_{x,s}$ are the concentration of arsenic at the feed-membrane and membrane-strip interfaces, and τ and δ are the tortuosity of membrane pores and the thickness (in m) of membrane, respectively. The arsenic concentration in the membrane-strip interface is considered to be negligible ($C_{x,s} = 0$), because it is turned into ferric-arsenite coagulation. Furthermore, it is possible to correlate the concentrations of arsenic in membrane/feed interface as shown below.

$$K_x = \frac{C_{x,f}}{C_t C_c} \tag{21}$$

Here, K_x is the equilibrium extractant constant and C_c is the concentration of the carrier element (if any). Combining Eq. (20) and Eq. (21) one obtains the following equation.

$$\frac{dC_t}{dt} = -D \frac{\epsilon}{\delta \tau} \times \frac{A}{V} K_x C_c C_t \tag{22}$$

The Eq. (22) may further be expressed as Eq. 23.

$$\frac{dC_t}{dt} = -P \times \frac{A}{V} C_t \tag{23}$$

Here, $P = D \frac{\epsilon}{\delta \tau} K_x C_c$ is the permeability coefficient (expressed in unit of velocity) and its value refers to the speed that arsenic from the feed phase are transported to the stripping phase. It has been reported [45] that the diffusion coefficient (D) and the viscosity (μ) are the parameters which control the transport through the membranes and they can be related as $D\mu^\alpha = K'$ (constant), where $0.5 < \alpha < 1$ is a coefficient for this kind of liquid media [46]. In the present work with Aliquat 336®, it is observed that $\alpha = 2/3$. Hence, $P = K''\mu^{-2/3}C_c$, where all the constant terms are assimilated into $K'' = K' \frac{\epsilon}{\delta \tau} Kx$. The Eq. (23) may be integrated to obtain Eq. (24).

$$\ln \frac{C_t}{C_0} = \left(-P \times \frac{A}{V} \right) t \tag{24}$$

A simple kinetic study can reveal the value of permeability of the transport process. The mass transfer coefficients for aqueous and organic phases can thereby be calculated from aqueous and organic phase resistances. From Eq. (18) we obtain the following equations:

$$J_{aq} = \frac{1}{\Delta_{aq}} \left\{ [H_3AsO_3]_f - [H_3AsO_3]_{fm} \right\} \tag{25}$$

$$\Delta_{aq}^{-1} = \frac{D_{aq}}{\Delta x_{aq}} \tag{26}$$

Here, the suffixes aq, f, and fm refer to "aqueous", "feed" and "feed-membrane interface", respectively; whereas Δ_{aq} refers to the aqueous phase resistance term and Δx_{aq} refers to the thickness of aqueous film. Similarly, diffusion of Aliquat-Arsenic complex through the membrane phase can be written as the following equations.

$$J_{org} = \frac{1}{\Delta_{org}}\{[(NR_4Cl)_n(H_3AsO_3)]_{fm} \tag{27}$$
$$- [(NR_4Cl)_n(H_3AsO_3)]_{ms}\}$$

$$\Delta_{org}^{-1} = \frac{\epsilon D_{org}}{\delta\tau^2} \tag{28}$$

Here, the suffixes *org* and *ms* refer to "organic" and "membrane-strip interface", respectively; whereas Δ_{org} refers to the membrane phase resistance term. The Aliquat-arsenic complex gets dissociated very fast at the membrane-strip interface and hence its concentration is negligible as compared to that at feed-membrane interface. Therefore, Eq. (27) can be converted to the following equation.

$$J_{org} = \frac{1}{\Delta_{org}}[(NR_4Cl)_n(H_3AsO_3)]_{fm} \tag{29}$$

Moreover, at the steady state we have the following equation:

$$J_{aq} = J_{org} = J \tag{30}$$

Using Eq. (13), Eq. (15), Eq. (25), Eq. (29) and Eq. (30), one can obtain the following equation.

$$J = \frac{D_{III}[H_3AsO_3]_f}{\Delta_{org} + D_{III}\Delta_{aq}}$$

The permeability coefficient can be defined as the flux of solute per unit of its concentration in the feed phase, as shown below.

$$P = \frac{J}{[H_3AsO_3]_f} = \frac{D_{III}}{\Delta_{org} + D_{III}\Delta_{aq}} \tag{31}$$

or

$$\left(\frac{1}{P}\right) = \Delta_{aq} + \left(\frac{1}{D_{III}}\right)\Delta_{org} \tag{32}$$

The above formulation may be extended for As(V) as well. Hence, the Eq. (32) may be re-written for both As(III) and As(V) as shown below.

$$\left(\frac{1}{P}\right) = \Delta_{aq} + \left(\frac{1}{D_i}\right)\Delta_{org} \tag{33}$$

Here, *i* denotes III and/or V depending on the case. The value of D_i is different for the different concentrations of NR_4Cl. By plotting P^{-1} *vs.* D^{-1} of the Eq. (33) for various $[NR_4Cl]$ at constant pH, a straight line with slope Δ_{org} and intercept Δ_{aq} is obtained. The mass transfer coefficients for aqueous and organic phases can thereby be found from Eq. (28) and Eq. (26).

MATERIALS AND METHODS

Chemicals and Reagents

The simulated arsenic contaminated water was prepared by using sodium arsenite and sodium arsenate salts procured from Merck India. The solutions were prepared by dissolving the required amount in Milli-Q® deionized water (Millipore, USA). Refined vegetable oils of good quality (Fortune, Adani Wilmer Limited) such as coconut oil, mustard oil, sunflower oil, soybean oil, and sesame oil were used as green solvents. The extractants used for experimentation includes tributyl phosphate (TBP), trioctylamine (TOA), methyltrioctyl ammonium chloride (Aliquat 336®), and di-2-ethylhexylphosphoric acid (D2EHPA). They were procured from Sigma Aldrich India. The reagents required for analysis by Atomic Absorption Spectrophotometer (AAS) (Make-Varian Model-240FS) and for adjusting pH such as hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium iodide (KI) and sodium borohydride (NaBH₄) were purchased from Merck India. Durapore membrane (0.45 µm PVDF membrane with porosity (ε) 0.7, membrane thickness (δ) 125 µm and tortuosity (τ) 1.19 was impregnated with the organic phase. Ferric chloride salt procured from Merck India were used for preparing the receiving phases. All the chemicals and reagents were of Guaranteed Reagents (GR) grade and used without further purification.

Design of Experiments

The response surface methodology incorporates a randomly designed group of experiments by varying the parameters simultaneously to generate an empirical model for optimization. This increases the efficiency by doing the least number of experiments for optimization. Design Expert

13 has been used for designing the experiments, plotting the figures and optimization. The number of experiments in this design can be determined by:

$$N = 2^x + 2x + c \qquad (34)$$

Here, N is the total number of experimental runs, x is the number of parameters being optimized, c is the number of centre points. The number of factorial runs is 2^x and the number of axial points is 2x.

It is revealed from the earlier works of our research group [25,26,47] that the extraction in two-phase equilibrium depends mainly on 5 parameters that are shown below.

A: pH of the feed phase
B: %Extractant concentration (vol/vol)
C: Duration (h)
D: Temperature (°C)
E: Stirring speed (rpm)

The parameters studied and their operational range for the arsenic ions are listed in Table 1. Hence, in this study, face-centered design of central composite design was used to conduct 50 experiments each for As(III), As(V), As(III):As(V)::1:1, As(III):As(V)::1:2, As(III):As(V)::2:1, that comprised of $2^5 = 32$ factorial runs, $2 \times 5 = 10$ axial points and 8 centre points, by varying the above 5 parameters to detect the optimum level for maximum extraction of arsenic ions.

In a similar manner the extraction and recovery in three-phase SLM depends mainly on 3 parameters that are shown below.

F: Concentration of the receiving phase
G: pH of the receiving phase
H1: Stirring speed (rpm)
H2: Extractant concentration (%)

It is further revealed from a recent hybrid study of SLM and electrocoagulation by this research group [48], the optimum extractant concentration was obtained for individual arsenic ions in the three-phase SLM study. Assuming that the same concentration was not applied to the combined arsenic study, the extractant concentration (H2) was varied in those cases instead of stirring speed (H1). Furthermore, in most of the experiments conducted, the extractant concentration was turned out to be a significant parameter. The parameters studied and their operational range for both the arsenic ions are listed in Table 1. Hence, in this study, face-centered design of central composite design was used to conduct 15 experiments each for As(III), As(V), As(III):As(V):: 1 : 1, As(III):As(V):: 1 : 2, As(III):As(V):: 2 : 1 , that comprised of $2^3 = 8$ factorial runs, $2 \times 3 = 6$ axial points and 1 centre point, by varying the above 3 parameters to detect the optimum level for maximum extraction and recovery of arsenic ions.

Experimental Procedure

In the two-phase extraction study, the standard arsenic stock solution has been prepared with 1000 ppm

Table 1. Summary of Variable Range Studied for Optimization

Type	Factor	Name	Minimum	Maximum	Mean
	A	pH of feed phase	4	10	7
	B	Extractant concentration (%)	2	10	6
Two phase	C	Duration (hours)	2	12	7
	D	Temperature (°C)	25	55	40
	E	Stirrer speed (rpm)	50	250	150
	F	Concentration of receiving phase (ppm)	1	3	2
	G	pH of receiving phase	3	7	5
Three phase	H1	Stirrer speed (rpm)	200	300	250
	H2	Extractant concentration (%)	10	40	25

concentration. The aqueous feed phase was prepared by diluting the stock solution to make 100 ppb (*i.e.* 1.335 µM) concentration of As(III), As(V) & As(III):As(V)::1:1, and 150 ppb (*i.e.* 2.003 µM) concentration of As(III):As(V)::1: 2 & As(III):As(V)::2:1. The organic phase was prepared by dissolving the desired amount of extractant in the required amount of environmentally benign diluent (*i.e.* vegetable oils). Equal volume (20 ml each) of feed and organic phases were poured cautiously in a conical flask without forming any emulsions. This was placed in the shaking incubator, as shown in Fig. 1, for mixing at a particular stirring rate for the said duration. The mixture was then kept undisturbed for 8 h until the aqueous and organic phases, and got separated into two distinct layers due to the variation in their densities. The samples were collected from the aqueous phase to analyse the total concentration of arsenic ions by atomic absorption spectrometry method. The amount of arsenic ions extracted into the organic phase could then be easily calculated by mass balance. Based on the optimum conditions obtained, the two-phase study was conducted (in triplicate) by varying the extractant concentration to evaluate the distribution coefficient in order to estimate the extraction equilibrium constant.

In the three phase SLM study, the experimental setup was comprised of two cells, an extension connecting the cells and supporting the membrane in between them, as shown in Fig. 2. The membrane phase was prepared by completely immersing the PVDF membrane into the pseudo-binary mixture of sesame oil and Aliquat 336® (v/v) (a.k.a. organic phase) for 24 h. After the pores of the membrane were filled, it was allowed to dry for 2 h to drip off the excess liquid from the surface of the solid membrane. The excess organic phase on the surface was wiped off gently from the surface with a tissue. This solid membrane, impregnated with the organic mixture, acts as the supported liquid membrane (SLM). The SLM was carefully placed between two membrane discs with latex support to prevent any leakage. Equal volume of feed and receiving phases were poured into the setup. The volume of the aqueous phases were 200 ml each. In addition, to avoid the influence of residence interface films, two impellers (Make-REMI Model- RQG 121/D) in both feed and receiving phases were kept in the centre of the SLM cells. The two impellers were placed into each of the aqueous phases for continuous stirring without touching the walls of
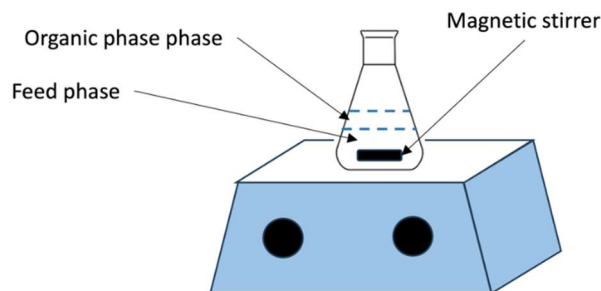

Fig. 1. Schematic of two-phase extraction study.
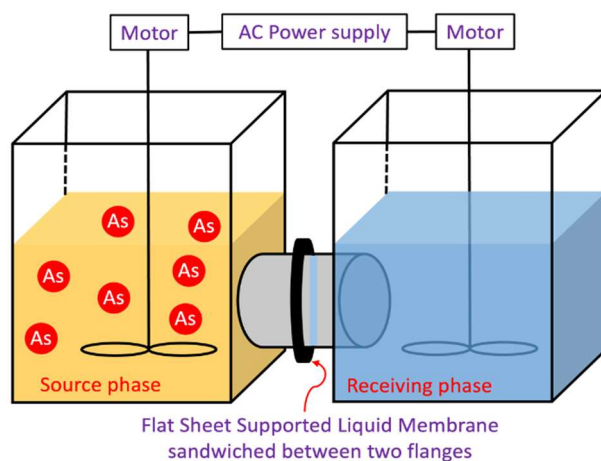

Fig. 2. Schematic of three-phase SLM study.

the setup. Samples were drawn from the feed and receiving phases at time intervals and analysed to measure the concentrations of arsenic ions in both the phases using the vapour generation mode (VGA) of AAS at 193.7 nm wavelength with a slit of 0.7, argon flow 50 ml min^{-1} and pump speed of 120 rpm. The sample preparation procedure for AAS was consisted of standard solution preparation, reductant solution preparation, acid solution preparation and finally sample preparation. The standard solution was prepared by serial dilution from the stock solution of arsenic. The range of standard solutions prepared were 0-100 ppb and to this KI was added followed by HCl. Similarly, for the sample preparation, KI was added along with HCl. The reductant solution was prepared by dissolving 0.6% NaBH$_4$ in 0.5% NaOH solution, and 6M HCl solution was used as the acid solution. This reaction was carried out for 45 min cautiously, as the colour development due to the reaction was time dependent [49].

RESULTS AND DISCUSSION

Selection of the Diluents

Chemical solvents such as benzene, chloroform, decane, dodecanol, kerosene, and toluene are commonly used diluents for liquid membrane based studies. They have been classified as hazardous chemicals. The usage of vegetable oils as diluents in liquid membrane minimizes the level of toxicity. Furthermore, they have other advantages such as being easily and naturally available, low cost and non-hazardous. Figure 3 shows the extraction efficiency of the above-mentioned diluents and extractants. Sesame oil was able to promote the extraction to a maximum value of around 50% for the arsenic species. Mustard oil, that is highly viscous, showed poor extraction efficiency. Though coconut oil shows a good extraction percentage for arsenic ions, it has not been used due to its tendency to change its state with temperature. Sesame, soybean and sunflower oils are highly efficient in extracting arsenic ions. Sesame oil was selected for further studies as it is the most effective environmentally benign diluent for arsenic extraction.

Selection of the Extractant

Mainly, three types of extractants were studied that are neutral (TBP), acidic (D2EHPA), and basic extractants (TOA and Aliquat 336®). The application of extractants reduces the duration of the process by increasing the mass transfer of arsenic ions, which in turn improves the extraction efficiency. Aliquat 336® showed the maximum extraction of approximately 80% for both the arsenic ions, as shown in Fig. 3. Though TOA is a basic extractant, it cannot bind with neutral arsenic species and requires protonation to be able to bind with anions [50]. TBP and D2EHPA have a tendency to form dimers and transform from α to β multimers, causing low extraction efficiency of arsenic species. However, TBP showed better extraction than D2EHPA owing to its small hydrocarbon chain in comparison to the long branched chain of D2EHPA molecule [37]. The arsenic ions transport in case of TOA, TBP and D2EHPA is due to concentration gradient across the two phases. Aliquat 336® is an ionic liquid, comprising of quaternary ammonium cation and chloride anion, that is capable of interacting with both the arsenic species [37]. Thus, Aliquat 336® was preferred for this study due to its ability to react with both dissociated and

(a) Environmentally benign diluents

(b) Chemical extractants
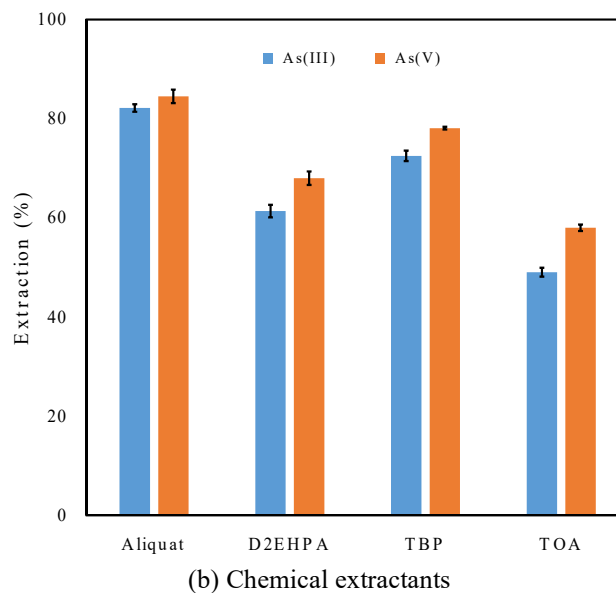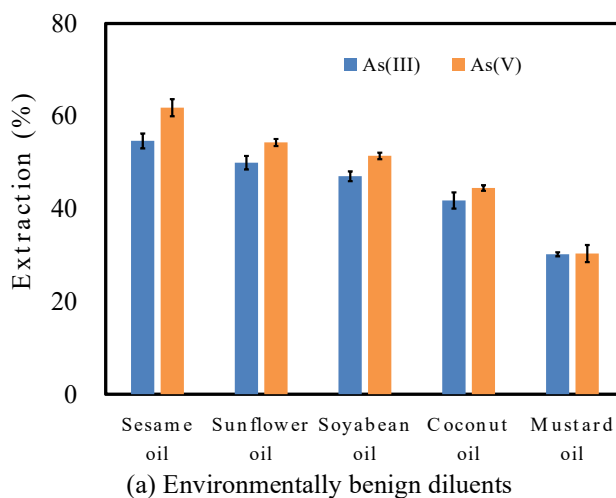
Fig. 3. Extraction efficiency of various extractants and solvents.

undissociated ions of arsenic. The interaction between arsenic and Aliquat 336® at the aqueous-organic interface is given in the equations Eq. (1) and Eq. (2). The diluent binds to the extractant helping to immobilize the extractant in the organic phase; this intermolecular interaction was further explained in our previous research work [37]. The increased lipophilicity could be attributed to the longer hydrocarbon chain, leading to reduced leakage of the extractant into the aqueous phases, ultimately resulting in higher extraction efficiencies.

Two Phase Extraction Equilibrium Studies

The experiments were carried out for each design of experiment stated in Sec.3.2, and the results are shown in Table 2. All the 5 factors, which are feed phase pH, extractant concentration, duration of experiment, temperature, and stirring speed were varied in the same manner for 5 cases that are As(III),As(V), As(III):As(V)::1:1, As(III):As(V)::1:2 and As(III):As(V)::2:1, and the corresponding %extraction was also reported.

Experimental observations and inferences. The experimental observations and their related inferences are shown in Table 2. The arsenic ions present in the feed phase are either in the dissociated state such as $H_2AsO_3^-$ (in case of As(III)), $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-} (in case of As(V)), or in the undissociated forms of H_3AsO_3 (in case of As(III)) and H_3AsO_4 (in case of As(V)), depending on the pH of the feed phase [51]. In the explored pH range for this study, As(III) is present in the undissociated form of H_3AsO_3, and As(V) in

Table 2. Experimental Design with Factors and Response for Two-phase Extraction of Arsenic

| Run | Factors | | | | | Extraction (%) of | | | | |
	A	B	C	D	E	As(III)	As(V)	As(III):As(V):1:1	As(III):As(V):1:2	As(III):As(V):2:1
1	4	2	2	25	250	50.74	45	63.1	64.58	60.11
2	7	6	7	40	150	62.98	73	77.18	81.15	75.39
3	7	6	2	40	150	60.22	70	69.16	79.56	72.83
4	10	10	12	25	250	57.47	50	60.61	63.39	70.67
5	7	6	7	40	50	51.65	72	70.71	78.49	74.9
6	7	6	7	40	250	75.05	78	82.13	83.47	79.84
7	7	6	7	40	150	72.9	74	79.69	80.45	78.98
8	4	2	12	55	50	53.28	53	65.93	68.22	66.74
9	4	2	2	25	50	48.88	43	62.39	64.2	63.61
10	7	6	7	40	150	70.65	75	85.12	79.65	77.95
11	10	2	12	25	250	48.42	41	54.43	56.98	54.12
12	7	6	12	40	150	78.19	81	82.6	83.91	80.71
13	4	10	12	25	50	59.98	63	72.67	77.21	73.65
14	4	10	2	55	50	58.36	60	68.41	71.45	70.96
15	10	10	12	25	50	54.22	49	60.32	61.47	60.42
16	10	2	12	55	50	46.51	42	48.64	58.02	54.6
17	7	6	7	55	150	80.56	79	83.78	85.17	81.38
18	4	2	12	55	250	54.39	55	66.4	68.65	67.87
19	10	2	2	25	50	25.49	30	25.94	41.51	36.93
20	4	2	2	55	250	51.21	49	65.3	65.25	64.73
21	4	10	12	55	50	60.13	67	73.97	77.91	74.57
22	7	6	7	40	150	75.78	76	80.34	82.64	78.63
23	4	2	12	25	250	53.82	51	65.8	66.85	65.29
24	10	2	2	55	50	29.47	36	30.65	47.05	40.31

Table 2. Continued

25	10	6	7	40	150	53.99	43	60.12	61.6	60.89
26	10	10	2	55	50	53.09	47	57.52	60.6	59.48
27	7	6	7	40	150	76.71	75	80.85	83.52	77.13
28	7	6	7	40	150	68	73	81.59	80.23	76.71
29	10	2	2	55	250	35.67	37	40.23	49.24	45.54
30	10	10	12	55	250	57.6	52	62.21	63.45	62.6
31	10	10	2	25	50	52.11	45	55.7	59.47	56.19
32	4	10	12	55	250	65.67	68	75.21	78.15	74.76
33	10	2	2	25	250	32.58	31	35.98	46.66	38.15
34	7	2	7	40	150	71.17	65	75.24	78.39	74.82
35	4	10	2	25	50	58.59	58	66.67	68.85	68.63
36	7	6	7	40	150	72.4	73	81.94	80.82	79.15
37	10	2	12	55	250	51.97	44	55.68	58.96	52.85
38	7	6	7	40	150	73.94	72	82.97	83.82	80.83
39	10	10	2	25	250	52.94	46	55.97	60.27	56.89
40	7	6	7	25	150	51.15	72	78.83	79.17	75.03
41	4	6	7	40	150	61.78	62	68.09	69.96	70.3
42	7	10	7	40	150	80.86	84	84.89	85.13	84.1
43	4	10	12	25	250	60.64	66	73.27	77.83	73.8
44	10	10	12	55	50	54.63	51	62.19	61.68	60.93
45	4	10	2	55	250	62.95	61	71.15	72.1	70.47
46	4	2	2	55	50	49.59	47	63.88	65.05	64.17
47	4	10	2	25	250	59.38	59	67.84	69.65	68.96
48	10	2	12	25	50	39.43	39	43.14	53.41	54.11
49	4	2	12	25	50	51.96	50	65.7	65.39	64.93
50	10	10	2	55	250	56.5	48	58.76	60.61	59.73

dissociated species of $H_2AsO_4^-$, and they are abundant compared to other ions. It should be noted that H_3AsO_3 is the predominant form of As(III) in the pH range of 2-9. Any change in pH within this range does not affect the extraction of As(III). $H_2AsO_4^-$ is the dominant form of As(V) in the pH range of 2-7. An increase in the pH beyond 7 leads to the formation and presence of $HAsO_4^{2-}$. In that case, the stoichiometric ratio of arsenic-Aliquat 336® is also changed for the two phase study. However, negligible change in initial feed-phase pH was observed in two-phase study. The

measured optimum values are based on the experiments conducted for following the response surface methodology. However, they are better understood through comparison with the statistical modelling performed in Part 2 of this series. Interested readers are referred to the Part II for more details.

Effect of pH of the feed phase: The pH of the feed phase was varied from 4 to 10 based on the pH reported for contaminated waters in Digboi [52] and Kamrup district of Assam [53]. The optimum pH for As(III) is 6.8 for an

extraction of 84%. As(III) exists as H_3AsO_3 at pH < 9 [54]. Aliquat 336® is an ionic liquid comprising of quaternary ammonium cation and chloride anion that interacts with both undissociated and dissociated forms of arsenic ions favouring the removal of arsenic within this pH range. The optimum pH for As(V) is ~6.7 for an extraction of 86% and in this pH, As(V) is present in the form of $H_2AsO_4^-$ dissociated ions. The optimum pH for combined As(III)-As(V) lies in the range of 6.3-6.65 indicating the presence of both H_3AsO_3 and $H_2AsO_4^-$ at intermediate pH range.

Effect of extractant concentration: Aliquat 336® is a highly viscous cationic surfactant forming structural micelle aggregates owing to its long hydrocarbon chain. The bulk amount of organic phase utilized in this two-phase study further increases the viscosity. So, the extractant concentration in the organic phase was varied from 2 to 10% (v/v) based on the viscosity of the organic phase, because extractant concentration more than 10% (v/v) could increase the viscosity of the organic phase, causing intense emulsification. The optimum extractant concentration for both the arsenic ions and combined species was ~10% (v/v).

Effect of duration of extraction: The duration of this study was varied from 2 to 12 h [27]. The optimum duration for combined As(III)-As(V) was in the range of 7-12 h; for As(III), it was 9 h to obtain an extraction of 84%. The optimum duration for As(V) was 12 h for an extraction of 86%. This difference of three hours could be attributed to the presence of uncharged and charged ions in case of As(III) and As(V), respectively.

Effect of temperature: The variation in temperature was studied over the range of 25 °C to 55 °C [55]. The optimum temperature for As(III) is 37 °C for an extraction of 84% and 55 °C for 86% extraction of As(V). This could possibly be due to the presence of H_3AsO_3 in case of As(III) that interacted by disrupting the strong ionic interactions between Aliquat 336® and sesame oil at 37 °C. The $H_2AsO_4^-$ anion required higher temperature of 55 °C to interact with the ionic interactions of the extractant and diluent. Thus, intermediate temperature range lying between 35 °C-47 °C was found as optimum temperature for combined arsenic species, indicating synergistic interactions between the arsenic species.

Effect of stirring speed: The variation in stirring speed was observed over a range of 50 to 250 rpm [26], and the optimum stirring speed for both the arsenic species was found to be ~170 rpm. The stirring speed varied from 143-196 rpm for different ratios of As(III)-As(V).

Mathematical Modelling

The extraction equilibrium and the moles of extractant reacting with arsenic species were determined from the distribution data of distribution coefficient versus extractant concentration for single and mixed species of arsenic, as shown in Table 3. A very dilute concentration of Aliquat 336® (2-10% vol/vol) was employed for this study.

Therefore, it can be assumed that a monomer form of the extractant predominates in the organic phase instead of micellar aggregates. The graphical representation of distribution coefficient (D_i) against the Aliquat 336® concentration in logarithmic scale is given in Fig. 4. A linear relationship was obtained for all the arsenic species.

Table 4 shows the model parameters (n and K) as referred in Eq. (16). The slope, n, is in the range of 0.8-1.4 for all the arsenic species; the minimum value was 0.8 for As(III) and the maximum value was 1.4 for As(V), while for the mixed species the values were in this range. This implies that the formation of Arsenic-Aliquat 336® complex in the organic phase follows the stoichiometric ratio of 1 : 1. On the other hand, the maximum value of K stipulates that the extraction of As(V) into the organic phase is more favourable in comparison to As(III) and combined arsenic species.
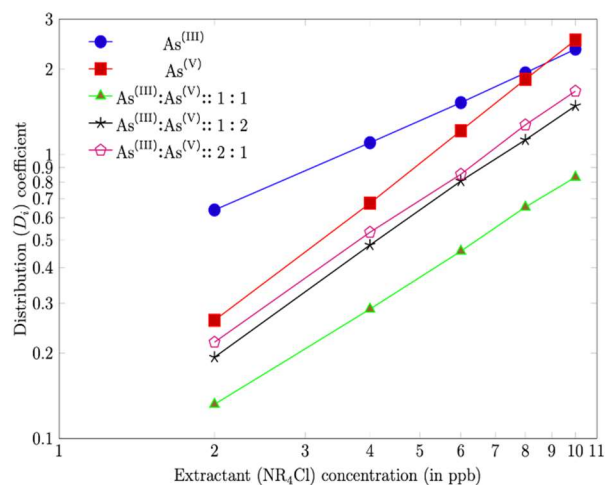

Fig. 4. Distribution coefficient vs. extractant concentration for single and mixed arsenic species in two-phase extraction study.

Table 3. Experimentally-obtained Distribution Coefficients of Various Arsenic Species and/or their Combinations in Two-phase Studies

Arsenic species/combinations	Extractant concentration (%)	Distribution coefficient		
		Run I	Run II	Run III
As(III)	2	0.647	0.638	0.63
	4	1.146	1.065	1.092
	6	1.536	1.614	1.423
	8	1.935	1.923	1.963
	10	2.231	2.393	2.433
As(V)	2	0.235	0.266	0.282
	4	0.658	0.633	0.731
	6	1.19	1.21	1.241
	8	1.827	1.878	1.817
	10	2.533	2.581	2.483
As(III):As(V)::1:1	2	0.149	0.119	0.129
	4	0.296	0.286	0.276
	6	0.446	0.459	0.466
	8	0.63	0.66	0.67
	10	0.831	0.842	0.824
As(III):As(V)::1:2	2	0.175	0.193	0.212
	4	0.5	0.475	0.466
	6	0.852	0.814	0.755
	8	1.125	1.143	1.112
	10	1.491	1.471	1.492
As(III):As(V)::2:1	2	0.189	0.229	0.237
	4	0.577	0.528	0.493
	6	0.879	0.844	0.836
	8	1.25	1.275	1.292
	10	1.708	1.69	1.621

Table 4. Extraction Equilibrium Model Parameters for Various Arsenic Species and/or their Combinations in Two-phase Study

Arsenic species/combinations	Model parameters	
	n	K
As(III)	0.8	4.5
As(V)	1.4	8.2
As(III):As(V)::1:1	1.15	2.16
As(III):As(V)::1:2	1.27	4.31
As(III):As(V)::2:1	1.26	4.76

Three Phase SLM Studies

The experiments were carried out as per the design of experiment stated in Sec.3.2 and the results are reported in Tables 5 and Table 6.

Three factors including the concentration, pH of receiving phase, and stirring speed were varied in the same manner for As(III) and As(V), whereas three factors including concentration, pH of receiving phase, and extractant concentration (%) were varied in the same manner for the three cases of As(III):As(V)::1:1, As(III):As(V)::1:2 and As(III):As(V)::2:1, and the corresponding %extraction and %recovery were also reported.

Table 5. Experimental Design with Factors and Response for Three-phase Extraction and Recovery of As(III) and As(V) Individually

Run	Factors			As(III)		As(V)	
	F	G	H1	Extraction (%)	Recovery (%)	Extraction (%)	Recovery (%)
1	1	3	200	35	26	35	25
2	1	3	300	32	22	31	15
3	1	5	250	53	44	40	26
4	1	7	200	44	30	35	20
5	1	7	300	42	29	32	18
6	2	3	250	40	33	53	44
7	2	5	200	55	43	58	43
8	2	5	250	62	50	65.5	48.5
9	2	5	300	51	37	55	39
10	2	7	250	48	39	69	40
11	3	3	200	37	29	55	30
12	3	3	300	35	24	49	24
13	3	5	250	55	45	60	35
14	3	7	200	47	36	54	30
15	3	7	300	43	34	52	28

Table 6. Experimental Design with Factors and Response for Three-phase Extraction and Recovery of Various Combinations of As(III) and As(V)

Run	Factors			As(III):As(V)::1:1		As(III):As(V)::1:2		As(III):As(V)::2:1	
	F	G	H2	Ext (%)	Rec (%)	Ext (%)	Rec (%)	Ext (%)	Rec (%)
1	1	3	10	29.8	11.81	31.8	14.1	24.8	6.9
2	1	3	40	45.39	26.93	47.4	28.8	40.4	21.9
3	1	5	25	40.1	21.4	42.1	23.4	35.6	16.4
4	1	7	10	36.4	14.63	38.4	16.6	31.6	9.6
5	1	7	40	48.89	29.98	50.8	31.9	43.8	24.3
6	2	3	25	52.9	30.91	54.9	32.8	47.9	25.9
7	2	5	10	49.9	28.93	52.3	30.7	44.9	23.9
8	2	5	25	53.32	33.31	55.23	35.35	48.4	28.3
9	2	5	40	57.87	38.77	59.8	40.7	52.8	33.8
10	2	7	25	57.56	35.76	59.6	37.9	52.6	30.8
11	3	3	10	54.2	34.62	56.3	36.6	49.2	29.6
12	3	3	40	63.91	44.19	64.9	46.2	58.9	39.2
13	3	5	25	62.12	43.21	64.2	45.5	57.3	38.2
14	3	7	10	57.5	35.7	59.5	37.7	52.5	30.7
15	3	7	40	65.66	46.56	67.7	48.5	60.7	41.6

Experimental observations and inferences. The experimental observations and their related inferences are shown in Tables 5 and Table 6. However, they can be better understood through the statistical modelling performed in Part II of this series. Interested readers are referred to the Part 2 for more details.

Effect of strippant concentration: The concentration of ferric chloride solution was varied from 1-3 ppm. The ratio of iron and arsenic was varied from 10:1 to 30:1. The ratio of iron and arsenic ≥ 50 was reported for the arsenic removal from groundwater using sand filters [56]. Such high content of iron was required due to the presence of other anions/contaminants that interfered with the iron-arsenic interactions in the groundwater. Furthermore, iron-arsenic ratio of 10 was found to be optimum for removal of arsenic [57]. In this study, the removal process included the anoxic stage, followed by aeration and sand filtration. In comparison to the literature, the 30:1 ratio was found to be the optimum for combined arsenic species in the present study (in between 10 and 50), which was attributed to the absence of additional oxygen supply and other interfering anions.

Effect of pH of the strip phase: It has been reported that $FeCl_3$ shows poor adsorption capacity at pH ≥ 8; so, the studied pH range was 3-7 for this work. However, pH range of 5-7 was found to be optimum for removal of arsenic ions [58]. In the present work, we obtained the optimum pH of 5 in the receiving phase in case of single-species experimentation, and the optimum pH of 7 in case of combined species of arsenic salts. These are in accordance with the reported pH range [58]. As it is evident from the Pearson's correlational analysis in the Part II of this series, the recovery of arsenic ions is directly correlated to their extraction (%). Thus for both extraction and recovery of arsenic species, the pH values of 5 & 7 in the receiving phases were found to be the optimum in cases of single feed and mixed feed, respectively.

Effect of extractant concentration: Based on the previous research works by the same research group [48], the extractant concentration for As(III) and As(V) was found to be 10% (v/v) and 30% (v/v), respectively. However, this parameter was studied for the combined arsenic species by varying from 10-40% (v/v) to find the optimum concentration for maximizing extraction and recovery. The extractant concentration is one of the significant parameters

for removal of all the single and mixed arsenic species. 40% of the pseudo binary mixture (aliquat336®-sesame oil) was found to yield the maximum extraction and recovery for the three different ratios of As(III) and As(V).

Mathematical Modelling

The value of permeability of the transport process was computed from the experimental results using Eq. (24), which is graphically shown in Fig. 5.

It is observed that the permeability coefficients for the processes involving As(III), As(V), As(III):As(V)::1:1, As(III):As(V)::1:2, and As(III):As(V)::2:1 are 0.8991, 1.025, 0.9396, 0.978, and 0.8205, respectively. It was obvious that permeation was favoured towards As(V), as opposed to As(III). Pentavalent arsenic had greater ionic size than trivalent one. As a result, As(V) fits more easily into the crystal lattice of a material. Moreover, higher positive charge of As(V) tends to enhance the mobility of ions. The above reasons facilitate faster diffusion through the crystal structure of the material. The values of permeability, that are used in Eq. (31) to obtain the rate of flux of solute of transfer, are shown in Fig. 6.

It was observed that the flux is higher for the cases where unequal combinations of mixed solutes were used. When there is an unequal proportion of As(V) and As(III) ions, the presence of one type of ion in higher concentration creates
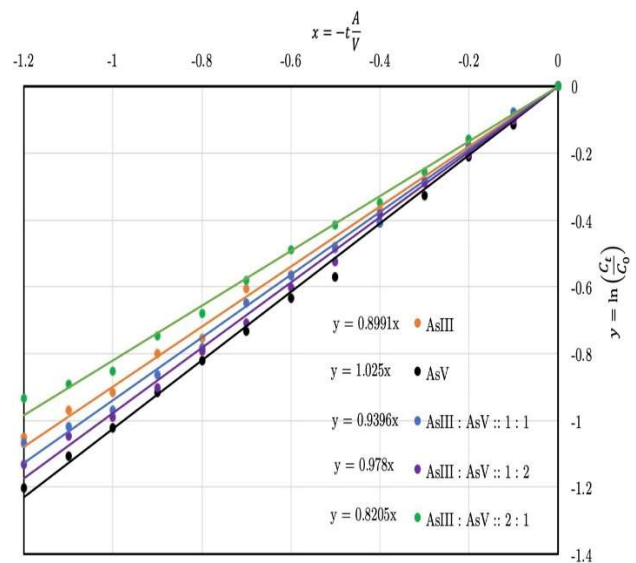
Fig. 5. Graphical method of finding permeability coefficient as per Eq. (24).
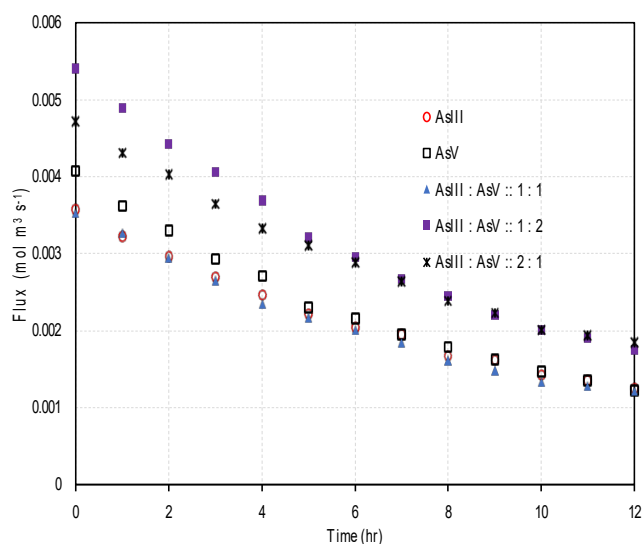
Fig. 6. Rate of flux of solute as per Eq. (31).

Fig. 7. Plot for finding organic and aqueous phase resistances as per Eq. (33).

vacancies in the crystal lattice to accommodate the other type of ion. Vacancies act as diffusion paths, facilitating the movement of ions. This increased vacancy formation leads to a higher flux of mass transfer. In certain cases, the presence of both As(V) and As(III) ions together may create synergistic effects, influencing the overall diffusivity. This could be due to complex interactions between the two ions and the material's crystal lattice, resulting in enhanced diffusion properties. As mentioned before, As(V) ions are larger and carry a higher positive charge compared to As(III) ions. When these ions are mixed in unequal proportions, the larger As(V) ions tend to create more vacancies and provide more space for diffusion. Additionally, the higher charge of As(V) ions enhances their mobility, leading to increased mass transfer flux.

The values of mass transfer resistances were obtained from the plot of 1/P *vs*. 1/D at various extractant concentrations, as given by equation Eq. (33). The slope and intercept gives the values of Δ_{org} and Δ_{aq}, respectively. The permeability, P, and the distribution coefficient, D, were tabulated for different concentrations of extractant in Table 7. From the Fig. 7, Δ_{org} and Δ_{aq} for As(III), As(V), As(III):As(V)::1:1, As(III):As(V)::1:2, and As(III):As(V):: 2:1 are {5.77,0.16}, {15.31,0.91}, {40.84,0.69}, {33.32,0.77}, and {11.77,1.20}, respectively. It was observed that the resistances in the phases (both organic and
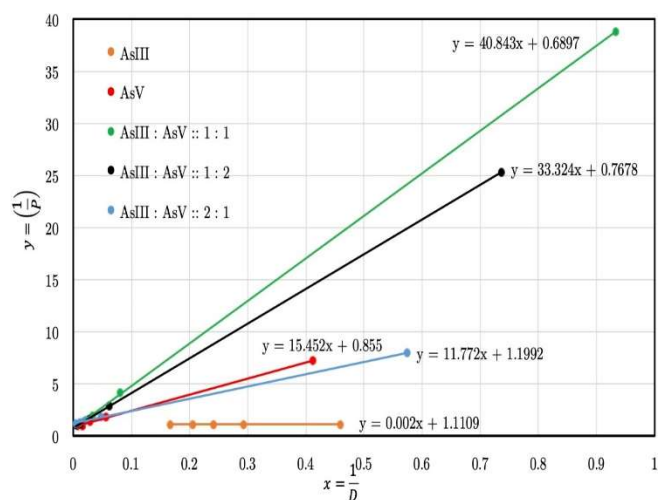
aqueous) were low for As(III) than that for As(V). In case of combined salts of As(III) and As(V), the said resistances decreased with an increase in ratio of As(III).

The opposite phenomenon was observed by an increase in As(V) ratio. As resistances are inversely proportional to the diffusion coefficients, it may be argued that diffusion coefficients are lower for As(V) than that of As(III). These were calculated as follows: the mass transfer coefficients in aqueous phase (Δ_{aq}^{-1}) and organic phase (Δ_{org}^{-1}) for As^{III-V} were calculated as 4.03×10^{-6} and 6.8×10^{-8} m s^{-1} for (1:1), 3.61×10^{-6} and 8.34×10^{-8} m s^{-1} for (1:2), and 2.33×10^{-6} and 2.36×10^{-7} m s^{-1} for (2:1), respectively.

CONCLUSION

Sesame oil is the most effective environmentally benign diluent for arsenic extraction, while Aliquat 336® is the preferred extractant due to its ability to react with both dissociated and undissociated ions of arsenic. The extractant concentration of 10% (v/v) was found to be the optimum parameter for the extraction of individual and combined arsenic ions in two-phase extraction study. The optimum extraction for As(III) was obtained at pH 6.8, temperature 37 °C , stirring speed of 176 rpm, and with 9 h duration of two-phase extraction study. In case of As(V), the optimum conditions were pH 6.7, temperature 55 °C, stirring speed of

Table 7. Experimentally-obtained Distribution Coefficients and Permeability of Various Arsenic Species and/or their Combinations in Three-phase Studies

Arsenic species/ combinations	Extractant concentration (%)	Distribution coefficient	Permeability
As(III)	10	2.178	0.8994
	20	3.42	0.8996
	25	4.145	0.8997
	30	4.886	0.8998
	40	6.001	0.8999
As(V)	10	2.43	0.1388
	20	18.01	0.5588
	25	35.322	0.7436
	30	62.082	1.0242
	40	136.037	1.0242
As(III):As(V)::1:1	10	1.073	0.0258
	20	12.368	0.2421
	25	30.207	0.5213
	30	54.026	0.7536
	40	154.952	0.9406
As(III):As(V)::1:2	10	1.358	0.0395
	20	16.132	0.3536
	25	35.742	0.6294
	30	74.125	0.823
	40	236.5	0.9768
As(III):As(V)::2:1	10	1.744	0.1258
	20	20.726	0.5612
	25	44.982	0.6631
	30	87.44	0.7643
	40	225.984	0.8215

170 rpm, and 12 h duration. The optimum conditions for the extraction of combined arsenic species had values in this mentioned range. It was revealed that the formation of Arsenic-Aliquat 336® complex in the organic phase followed the stoichiometric ratio of 1:1, whereas the extraction of As(V) into the organic phase was more favourable in comparison to As(III) and combined arsenic species. In three-phase study, the extraction and/or recovery was optimum at 30:1 ratio of iron and arsenic, pH between 5 and 7, and 40% of the pseudo binary mixture of Aliquat 336® and sesame oil. Mass transfer resistances were more during the transport of As(V) than that of As(III). The results of current work were compared to other recently-published works, as shown in Table 8.

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Table 8. Comparative Results of this Work with other Recently-published Works

Process	Arsenic species	Diluent	Extractant	Receiving phase	Extraction%	Recovery%	Ref.
2 phase	As(III) and As(V) 30 mg/kg each	L64, Na₂SO₄	APDC		As(III) 98%, As(V) 18%	-	[20]
2 phase	As(III), As(V) & DMA 15 mg/kg each	Triton X 100/165, choline chloride	APDC		As(III) 69.02%, As(V) 92.99%, DMA 90.05%	-	[18]
Liquid-liquid extraction	As(III), As(V) & As(III):As(V):: 1:1 100 ppb each, As(III):As(V):: 1:2 & As(III):As(V):: 2:1 150 ppb each	Sesame oil	10% (v/v) Aliquat 336®		As(III) 84%, As(V) 86%, As(III):As(V)::1: 1 85.5%, As(III):As(V)::1:2 86%, As(III):As(V)::2:1 84.5%	-	This work
FSSLM	As(V) 10 mg l⁻¹	Dodecane modified with 4% dodecanol	0.5 M Aliquat 336® in PVDF	0.1 M NaCl	95%	95%%	[32]
FSSLM	As(III), As(V) & As(III):As(V):: 1:1 100 ppb each, As(III):As(V):: 1:2 & As(III):As(V):: 2:1 150 ppb each	Sesame oil	10%-40% (v/v) Aliquat 336® in PVDF	2-3 ppm FeCl₃	As(III) 60%, As(V) 66.7%, As(III):As(V)::1:1 65%, As(III):As(V)::1:2 66.5%, As(III):As(V)::2:1 59%	As(III) 48%, As(V) 47%, As(III):As(V)::1: 1 46.5%, As(III):As(V)::1:2 48.5%, As(III) :As(V)::2:1 41%	This work

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