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The Elimination of Trace Arsenic via Hollow Fiber Supported Liquid Membrane: Experiment and Mathematical Model

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Abstract

This work presents the elimination of arsenic ions from synthetic produced water via hollow fiber supported liquid membrane (HFSLM). The effects of extractants, pH of feed solution, strippant solutions, and flow rates of feed and strippant solutions are duly investigated. Results demonstrate that arsenic ions in synthetic wastewater could be treated to comply with the standard of wastewater discharged (< 0.25 mg/L) via HFSLM. Percentages of extraction and stripping proved to be 100% and 98%, respectively. Thus, in a single-step operation, arsenic ions are extracted and stripped, using 0.5 M Aliquat 336 as the extractant, at pH of feed solution of 12, with a mixture of thiourea and hydrochloric acid (0.5 M each) as the synergistic strippant solution, and flow rates of both feed and strippant solutions of 100 mL/min. A mathematical model has also been developed to predict the final concentration of arsenic ions in feed and strippant solutions. The results predicted by the mathematical model fit in well with the experimental results.

Keywords: Arsenic; Extraction; Strippant; HFSLM; Mathematical model

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1. Introduction

Arsenic is a highly toxic metal causing chronic or acute poisoning in human beings, depending on the quantity received [1]. It is found in produced water from the offshore oil and gas production in the Gulf of Thailand and is present in the form of H_3AsO_3 , H_3AsO_4 and H_2AsO_4^- [2, 3]. The amount of arsenic exposed to the environment continuously increases with the quantity of produced water. Its concentration from various wells can vary, being between 1 – 4 mg/L (or parts per million, ppm) [4]. Both the Thailand Ministry of Industry and the Ministry of Natural Resources and Environment regulate the discharge limit of arsenic from industrial wastewater so that it is not greater than 250 ppb (0.25 mg/L) [5].

Conventional methods i.e. adsorption, ion exchange, coagulation and precipitation, are introduced to treat arsenic as well as other toxic metals in the produced water. However, sometimes the concentration of toxic metals in wastewater after treatment is over the standard of wastewater discharged [6]. Inbaraj et al. [7] recorded that conventional methods are always ineffective when concentration of the target metal ions is very low, at ppb level. In practice, treated wastewater having toxic metal over the discharge limits is re-injected into the rock formations from where the

oil and gas originated [6]. Nevertheless, reinjecting produced water into rock formations is still risky since toxic metals can spill into the environment. An alternative method is therefore required.

In recent years, new adsorbents for removing toxic metals have been developed [8, 9]. Magnetic MCM-41 nanosorbents, for instance, have been used to selectively remove chromium(VI) oxyanions from various aqueous systems [8]. However, the concentration of chromium(VI) oxyanions that remained in the aqueous solutions proved to be over the standard of wastewater discharged.

According to several researches [10-12], HFSLM has been found to be a favorable method for elimination of target ions from various solutions, at extremely low concentration of ppb levels within a single-step operation. Other advantages of HFSLM over traditional methods involve high selectivity, less consumption of extractant and solvent used, low energy consumption as well as low capital and operating costs. The high surface area of HFSLM provides high mass transfer rate of elimination. Thus, it is clear that HFSLM can be applied in many industries such as water treatment, food processing, and pharmaceutical. Moreover, connecting the hollow fiber modules in series or in parallel can increase the capacity of elimination. After other traditional methods have been carried out, HFSLM is found to be most suitable for use as a secondary process to fulfill their drawbacks.

Elimination of metal ions via HFSLM strongly depends on the types of extractants and strippant solutions used as well as the acidity of feed solution. Hence, these parameters have been reviewed and applied in this work. Pancharoen et al. [3], for instance, highlighted the high extraction (about 90%) and stripping (about 70%) of arsenic ions using Aliquat 336 (tri-octyl methyl ammonium chloride) as the extractant and NaOH as the strippant. However, the process of elimination required 4 circles which took a long time (3 h and 20 min in total) and percentage of

arsenic ions stripping was still low. Jantunen et al. [13] separated arsenic from concentrated sulfuric acid using TBP (tributyl phosphate) as the extractant, extracting 83.7% of arsenic in three-stages. As for the stripping of various metal ions, thiourea has been found to be effective [14-16]. Fábrega and Mansur [17] found that thiourea could strip almost 100 percent of mercury(II) from mercury-Aliquat 336 complex.

HFSLM has attracted the interest of many researchers in its application for the treatment of polluted wastewater. For application on an industrial scale, however, solid mathematical models are required. Such models help to provide an essential guideline for understanding the transport mechanism of target ions across the liquid membrane. Such models can also help to predict elimination time and efficiency. Mathematical models are vital tools for estimating the cost and scaling up of the process of elimination.

Several mathematical models have been applied to explain the transport of metal ions across HFSLM. Yet, only a few models have been generated to report the transport of target ions on both feed and strippant sides. Jagdale et al. [18], for example, developed a mathematical model for predicting the extraction and stripping of neodymium(III) via HFSLM. The model was implemented by considering mass accumulation, convection and diffusion but chemical reaction was ignored. In addition, our previous mathematical model, which evolved in order to predict the extraction and stripping of mercury(II) as well as lead(II) via HFSLM, was based on chemical reactions, mass accumulation and mass convection, though diffusion was ignored [19]. It is noted that the above-mentioned models ignored either the chemical reaction or diffusion. Subsequently, the models could not predict the extraction and stripping of some target ions, which have different chemical and physical properties. Examples of mathematical models for predicting the elimination of target ions via HFSLM are summarized in Table 1.

This work investigates the elimination of arsenic ions from synthetic produced water via HFSLM. The parameters studied are as follows: types of extractants (Aliquat 336, TBP, TOPO, Cyanex 471 and DEHP), concentration of selected extractant, pH of feed solution, types of strippant solutions (NaOH, thiourea and HCl), concentration of selected strippant solution, and flow rates of feed and strippant solutions. Respond surface has also been applied in order to treat arsenic ions at the highest efficiency and the lowest cost of chemicals. Moreover, a mathematical model, based on conservation of mass considering axial convection, diffusion, reactions at the liquid-membrane interfaces, and mass accumulation, has been generated to predict the extraction and stripping of arsenic ions.

Table 1. Mathematical models used for elimination via HFSLM.

Authors	Target ions	Extractants/ strippants	Included parameters				Model predicted /
			CT	DT	MA	R	%deviation
Kandwal et al. [20]	Cs(I)	CNC/ distilled water	✓	✓	-	-	Extraction / n/a
Vernekar et al. [21]	Co(II)	D2EHPA/ H ₂ SO ₄	✓	✓	-	-	Extraction / n/a
Choi et al. [22]	Co(II) and Ni(II)	HEH/ H ₂ SO ₄	✓	✓	✓	-	Extraction / n/a
Yang and Kocherginsky [23]	Cu(II)	LIX54/ H ₂ SO ₄	✓	✓	-	✓	Extraction / n/a
Jagdale et al. [18]	Nd(III)	TODGA/ distilled water	✓	✓	✓	-	Extraction and stripping / n/a
Suren et al. [19]	Hg(II) and Pb(II)	Aliquat 336 for Hg(II), D2EHPA for Pb(II)/ thiourea for Hg(II), HCl for Pb(II)	✓	-	✓	✓	Extraction / 2%, and stripping 5%
This work	As(V)	Aliquat 336/ HCl	✓	✓	✓	✓	Extraction / 2%, and stripping 4%

Note: CT, convection transport; DT, diffusion transport; MA, mass accumulation; R, reaction.

2. Modeling: transport of arsenic ions

2.1 Transport mechanisms of arsenic ions across HFSLM

Arsenic in co-produced water is present in various forms, depending on the pH. At pH lower than 2, arsenic is present in its undissociated form such as H_3AsO_4 . For Arsenic(V), it predominantly exists as anions H_2AsO_4^- at pH between 3 – 6 and exists as AsO_4^{3-} at pH between 12 – 14 [24]. In Fig. 1(a), a schematic diagram of arsenic ions transport across HFSLM is shown. The HFSLM system is comprised of a feed phase (an aqueous solution containing arsenic ions), a strippant phase, and a supported liquid membrane phase embedded with an organic extractant, which separates both feed and strippant phases. As shown in Fig. 1(a), AsO_4^{3-} reacts with $\text{CH}_3\text{R}_3\text{N}^+\text{Cl}^-$ (Aliquat 336) at the feed–liquid-membrane interface forming an arsenic-extractant complex species $\overline{(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})}$. Then, $\overline{(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})}$ diffuses across the liquid membrane to the liquid-membrane–strippant interface to react with the strippant (HCl). Subsequently, arsenic ions are stripped into the strippant phase. Thus, arsenic ions can be simultaneously extracted and stripped in a single-step operation. The rate of transport of arsenic ions is governed by the concentration gradient between feed and strippant phases.

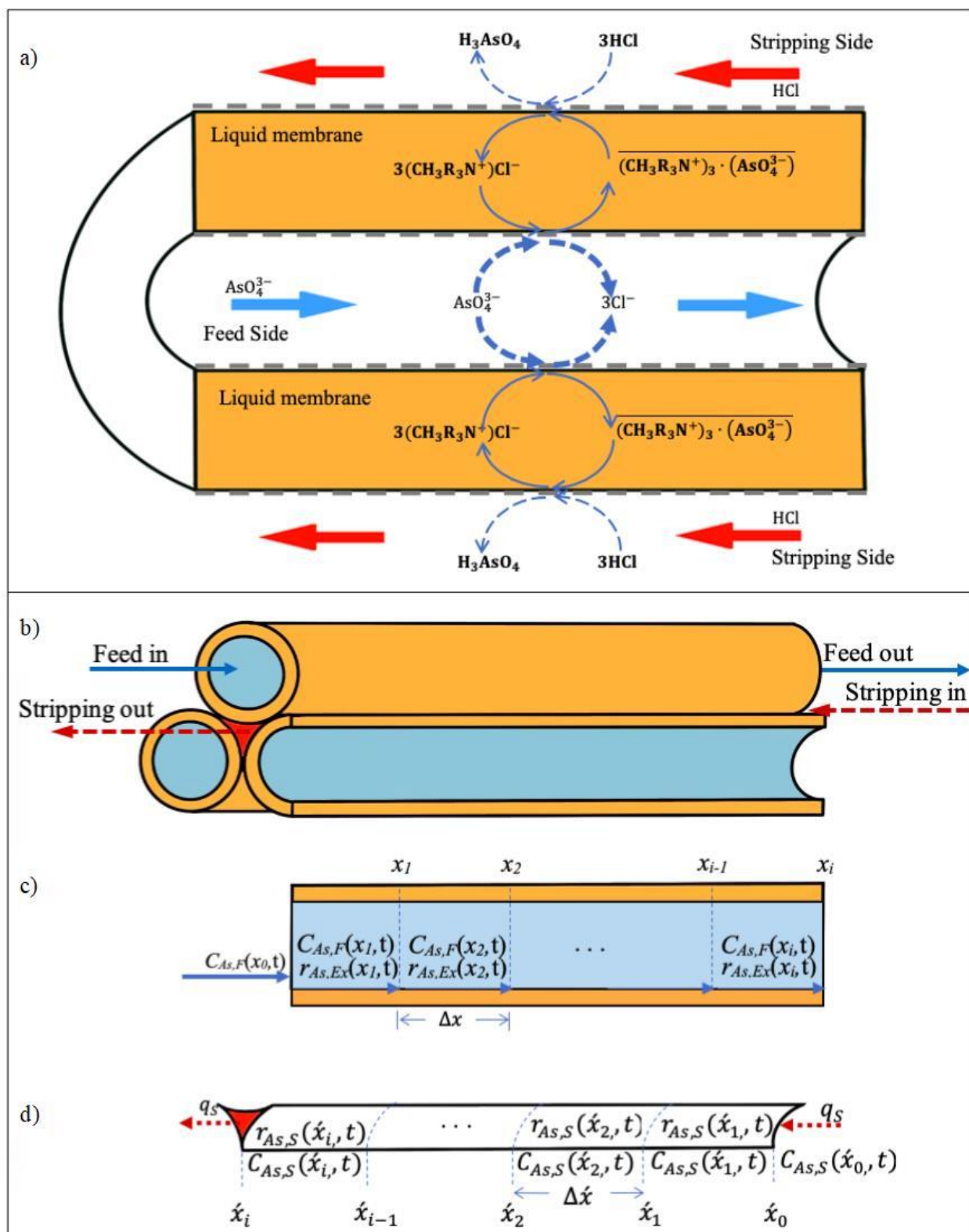
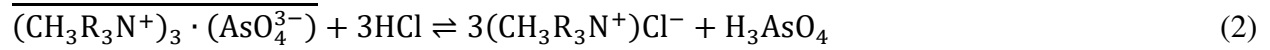


Fig. 1. Schema of arsenic ions transport across HFSLM: a) mechanisms of the extraction and stripping, b) tube and shell sides of the hollow fibers, c) tube side, and d) shell side.

The extraction reaction of AsO_4^{3-} and $\text{CH}_3\text{R}_3\text{N}^+\text{Cl}^-$ can be expressed as in Eq. (1):



The stripping reaction of the arsenic-extractant complex and HCl can be expressed as in Eq. (2):



The reaction rate of arsenic ions extraction ($r_{As,Ex}$) can be expressed:

$$r_{As,Ex}(x, t) = -k_{Ex} C_{As,F}^m(x, t) \quad (3)$$

where x is the longitudinal axis of the hollow fiber in the feed phase, k_{Ex} is the reaction rate constant of extraction, t is the elimination time, $C_{As,F}$ is the concentration of arsenic ions in the feed phase (mg/L) and m is the reaction order of extraction.

In the strippant phase, the strippant is kept at an excess concentration. Hence, the total reaction of arsenic stripping in Eq. (2) can be considered as the forward reaction. Thus, the reaction rate of arsenic stripping ($r_{As,S}$) becomes:

$$r_{As,S}(x, t) = k_S C_{As,S}^n(x, t) \quad (4)$$

where x is the longitudinal axis of the hollow fiber in the strippant phase, k_s is the reaction rate constant of stripping, $C_{A_s,S}$ is the concentration of arsenic ions in the strippant phase (mg/L) and n is the reaction order of stripping.

To enhance elimination, resulting from the synergistic effect, a mixture of substances is used. Whether the mixture of substances is the synergistic elimination or not, the synergistic coefficient R , in terms of distribution ratio, is defined as shown in Eq. (5) [25]. The greater the synergistic coefficient of the synergistic system is, the greater the elimination is:

$$R = \frac{D_{max}}{D_A + D_B} \quad (5)$$

where D_{max} refers to the maximum distribution ratio of the synergistic system (using a mixture of the substances A and B) to separate the specified ions. D_A stands for the distribution ratio of elimination using the single substance A, and D_B is the distribution ratio of elimination using the single substance B. If the synergistic coefficient > 1 , it confirms the synergistic elimination.

2.2 Development of the mathematical model

A mathematical model for predicting the extraction and stripping of arsenic ions across HFSLM is generated from the conservation of mass at tiny segments of the hollow fibers, as shown in Fig. 1(b)-(d). Parameters in the model include axial convection, diffusion, reactions at the liquid-membrane interfaces, and mass accumulation.

The mathematical model for the extraction, in the feed side, is generated based on the hypotheses as follows:

1. Temperature, pressure and volume of the feed phase, inside the tube, are constant.
2. The inside radius of the hollow-fiber is tiny. Therefore, the concentration profile of arsenic ions in the radial direction is constant, meaning that the diffusion fluxes of the ions in the feed phase occur only in the axial direction.
3. The extractant in the liquid membrane phase is kept at an excess concentration and arsenic ions are transferred into the strippant solution continuously. Therefore, extraction reaction can be considered as forward reaction.
4. The extraction reaction takes place at the feed–liquid-membrane interface along the length of the hollow fiber.
5. Only the arsenic-extractant complex, which forms due to the extraction reaction, not arsenic ions, can transport into the liquid membrane phase.

In the case of a mathematical model for the stripping of arsenic ions into the strippant phase, a model is generated based on the hypotheses as follows:

1. Temperature, pressure and volume of the strippant phase, in the shell, are constant.
2. The stripping reaction occurs at the liquid-membrane–strippant interface along the length of the hollow fiber.
3. Only the arsenic ions according to the stripping reaction at the interface, not the arsenic-extractant complex, can be stripped into the strippant solution.
4. The strippant is kept at an excess concentration. Therefore, the stripping reaction can be considered as forward reaction.

In the feed phase, the conservation of mass for arsenic ions in each tiny segment (Δx), Fig. 1(c), is defined as:

$$q_F C_{As,F}(x_{i-1}, t) - q_F C_{As,F}(x_i, t) + \frac{A_{c,F} \mathcal{D}_{As,F}}{\Delta x} (C_{As,F}(x_i, t) - C_{As,F}(x_{i-1}, t)) + r_{As,Ex}(x_i, t) V_F = V_F \frac{dC_{As,F}(x_i, t)}{dt} \quad (6)$$

where q_F is the volumetric flow rate of the feed solution, i is the number of tiny segments divided, $A_{c,F}$ is the cross-sectional area of the tube, V_F is the volume of a tiny segment of the hollow fiber in the tube side, and $\mathcal{D}_{As,F}$ is the mass diffusivity of arsenic ions in the feed solution, which can be estimated by Eq. (7) [26]:

$$\mathcal{D}_{As} = \frac{7.4 \times 10^{-8} (\emptyset M)^{1/2} T}{\eta V_A^{0.6}} \quad (7)$$

where \emptyset is the solvent association factor and is equal to 2.6, M is the solvent molecular weight (g/mol), T is the temperature (K), η is the dynamic viscosity of the solvent (cP), and V_A is the molar volume of solute A at its boiling temperature (cm³/mol).

Linearizing reaction rate in Eq. (3), as described in Appendix A in Supplementary Information online, and then substituting in Eq. (6) yields:

$$\frac{V_F}{q_F} \frac{dC_{As,F}(x_i, t)}{dt} = \left(1 - \frac{A_{c,F} \mathcal{D}_{As,F}}{\Delta x}\right) C_{As,F}(x_{i-1}, t) - \left(1 + \frac{V_F \Omega}{q_F} - \frac{A_{c,F} \mathcal{D}_{As,F}}{\Delta x}\right) C_{As,F}(x_i, t) - \frac{V_F \psi}{q_F} \quad (8)$$

where $\Omega = mk_{Ex}C_{As,F}^{m-1}(0,0)$

$$\psi = (1 - m)k_{Ex}C_{As,F}^m(0,0)$$

The conservation of mass of arsenic ions, in the tiny segments 1, 2, 3, ..., i in the feed side, based on Eq (8), is as follows:

$$\frac{V_F}{q_F} \frac{dC_{As,F}(x_1,t)}{dt} = \left(1 - \frac{A_{c,F}\mathcal{D}_{As,F}}{\Delta x}\right) C_{As,F}(x_0, t) - \left(1 + \frac{V_F\Omega}{q_F} - \frac{A_{c,F}\mathcal{D}_{As,F}}{\Delta x}\right) C_{As,F}(x_1, t) - \frac{V_F\psi}{q_F} \quad (9)$$

$$\frac{V_F}{q_F} \frac{dC_{As,F}(x_2,t)}{dt} = \left(1 - \frac{A_{c,F}\mathcal{D}_{As,F}}{\Delta x}\right) C_{As,F}(x_1, t) - \left(1 + \frac{V_F\Omega}{q_F} - \frac{A_{c,F}\mathcal{D}_{As,F}}{\Delta x}\right) C_{As,F}(x_2, t) - \frac{V_F\psi}{q_F} \quad (10)$$

$$\frac{V_F}{q_F} \frac{dC_{As,F}(x_3,t)}{dt} = \left(1 - \frac{A_{c,F}\mathcal{D}_{As,F}}{\Delta x}\right) C_{As,F}(x_3, t) - \left(1 + \frac{V_F\Omega}{q_F} - \frac{A_{c,F}\mathcal{D}_{As,F}}{\Delta x}\right) C_{As,F}(x_3, t) - \frac{V_F\psi}{q_F} \quad (11)$$

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$$\frac{V_F}{q_F} \frac{dC_{As,F}(x_i,t)}{dt} = \left(1 - \frac{A_{c,F}\mathcal{D}_{As,F}}{\Delta x}\right) C_{As,F}(x_{i-1}, t) - \left(1 + \frac{V_F\Omega}{q_F} - \frac{A_{c,F}\mathcal{D}_{As,F}}{\Delta x}\right) C_{As,F}(x_i, t) - \frac{V_F\psi}{q_F} \quad (12)$$

The series of differential equations i.e. Eqs. (9) to (12) can be solved using the concept of the Generating Function, as explained in Appendix A in Supplementary Information online. Thus, Eq. (13) is used to predict the concentration of arsenic ions in the outlet feed solution, $C_{As,F}(x_i, t)$:

$$C_{As,F}(x_i, t) = -C_{As,F}(0,0)e^{-\frac{tq_F}{V_F}} \sum_{k=1}^i \frac{1}{(i-k)!} \left(\frac{1}{\vartheta}\right)^k \left(\frac{tq_F}{V_F}\right)^{i-k} \omega^i + \frac{V_F\psi e^{-\frac{tq_F}{V_F}}}{q_F\vartheta} \sum_{k=1}^i \frac{1}{(i-k)!} \left(\frac{tq_F\omega}{V_F}\right)^{i-k} \sum_{l=1}^k \left(\frac{\omega}{\vartheta}\right)^{l-1} - \frac{V_F\psi \sum_{k=1}^i \omega^{i-k}}{q_F\vartheta^{i-k+1}} + C_{As,F}(0,0) \left(\frac{\omega}{\vartheta}\right)^i \quad (13)$$

where $\omega = 1 - \frac{A_{c,F}\mathcal{D}_{As,F}}{\Delta x}$

$$\vartheta = 1 + \frac{V_F\Omega}{q_F} - \frac{A_{c,F}\mathcal{D}_{As,F}}{\Delta x}$$

$C_{As,F}(0,0)$ stands for the concentration of arsenic ions in the inlet feed solution.

In the stripping phase, the conservation of mass of arsenic ions in the tiny segment ($\Delta\hat{x}$), Fig. 1(d), is written as:

$$q_S C_{As,S}(\hat{x}_{i-1}, t) - q_S C_{As,S}(\hat{x}_i, t) + \frac{A_{c,S}\mathcal{D}_{As,S}}{\Delta\hat{x}_i} (C_{As,S}(\hat{x}_i, t) - C_{As,S}(\hat{x}_{i-1}, t)) + r_{As,S}(\hat{x}_i, t)V_S = V_S \frac{dC_{As,S}(\hat{x}_i, t)}{dt} \quad (14)$$

where q_S is the volumetric flow rate of the stripping solution, $A_{c,S}$ is the cross-sectional area of the shell side of the hollow fiber, V_S is the volume of a tiny segment of the shell side of the hollow fiber, and $\mathcal{D}_{As,S}$ is the mass diffusivity of arsenic ions in the stripping solution, which is calculated using Eq. (7).

Linearizing reaction rate of stripping ($r_{As,S}$) in Eq. (4), using the Taylor series as described in Appendix A in Supplementary Information online, and merging with Eq. (14) achieves:

$$\frac{V_S}{q_S} \frac{dC_{As,S}(\hat{x}_i, t)}{dt} = \left(1 - \frac{A_{c,S}\mathcal{D}_{As,S}}{\Delta x}\right) C_{As,S}(\hat{x}_{i-1}, t) - \left(1 - \frac{V_S\sigma}{q_S} - \frac{A_{c,S}\mathcal{D}_{As,S}}{\Delta\hat{x}}\right) C_{As,S}(\hat{x}_i, t) + \frac{V_S\delta}{q_S} \quad (15)$$

where $\sigma = nk_S C_{As,S}^{n-1}(0,0)$, and $\delta = (1-n)k_S C_{As,S}^m(0,0)$

The conservation of mass of arsenic ions in the tiny segments 1, 2, 3, ..., i based on Eq (15) is as follows:

$$\frac{V_S}{q_S} \frac{dC_{As,S}(\acute{x}_1, t)}{dt} = \left(1 - \frac{A_{c,S} \mathcal{D}_{As,S}}{\Delta \acute{x}}\right) C_{As,S}(\acute{x}_0, t) - \left(1 - \frac{V_S \sigma}{q_S} - \frac{A_{c,S} \mathcal{D}_{As,S}}{\Delta \acute{x}}\right) C_{As,S}(\acute{x}_1, t) + \frac{V_S \delta}{q_S} \quad (16)$$

$$\frac{V_S}{q_S} \frac{dC_{As,S}(\acute{x}_2, t)}{dt} = \left(1 - \frac{A_{c,S} \mathcal{D}_{As,S}}{\Delta \acute{x}}\right) C_{As,S}(\acute{x}_1, t) - \left(1 - \frac{V_S \sigma}{q_S} - \frac{A_{c,S} \mathcal{D}_{As,S}}{\Delta \acute{x}}\right) C_{As,S}(\acute{x}_2, t) + \frac{V_S \delta}{q_S} \quad (17)$$

$$\frac{V_S}{q_S} \frac{dC_{As,S}(\acute{x}_3, t)}{dt} = \left(1 - \frac{A_{c,S} \mathcal{D}_{As,S}}{\Delta \acute{x}}\right) C_{As,S}(\acute{x}_2, t) - \left(1 - \frac{V_S \sigma}{q_S} - \frac{A_{c,S} \mathcal{D}_{As,S}}{\Delta \acute{x}}\right) C_{As,S}(\acute{x}_3, t) + \frac{V_S \delta}{q_S} \quad (18)$$

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$$\frac{V_S}{q_S} \frac{dC_{As,S}(\acute{x}_i, t)}{dt} = \left(1 - \frac{A_{c,S} \mathcal{D}_{As,S}}{\Delta \acute{x}}\right) C_{As,S}(\acute{x}_i, t) - \left(1 - \frac{V_S \sigma}{q_S} - \frac{A_{c,S} \mathcal{D}_{As,S}}{\Delta \acute{x}}\right) C_{As,S}(\acute{x}_i, t) + \frac{V_S \delta}{q_S} \quad (19)$$

Solving the series of differential equations i.e. Eqs. (16) to (19), using the concept of Generating Function, as explained in Appendix A in Supplementary Information online, yields Eq. (20) which is used to determine the concentration of arsenic ions in the outlet strippant solution, $C_{As,S}(x', t)$.

$$C_{As,S}(\acute{x}_i, t) = -C_{As,S}(0,0) e^{-\zeta \frac{tQ_S}{V_S}} \sum_{k=1}^i \frac{1}{(i-k)!} \left(\frac{1}{\zeta}\right)^k \cdot \left(\frac{tQ_S}{V_S}\right)^{i-k} \varpi^i - \frac{\delta V_S e^{-\zeta \frac{V_S}{Q_S}}}{Q_S \lambda} \sum_{k=1}^i \frac{1}{(i-k)} \left(\frac{tQ_S \varpi}{V_S}\right)^{i-k} \sum_{l=1}^k \left(\frac{\varpi}{\zeta}\right)^{l-1} + \frac{\delta V_S}{Q_S} \sum_{k=1}^i \frac{\varpi^{i-k}}{\zeta^{i-k+1}} + C_{As,S}(0,0) \left(\frac{\varpi}{\zeta}\right)^i \quad (20)$$

where $\varpi = 1 - \frac{A_{c,S} \mathcal{D}_{As,S}}{\Delta \dot{x}}$

$$\zeta = \left(1 - \frac{V_S \sigma}{q_S} - \frac{A_{c,S} \mathcal{D}_{As,S}}{\Delta \dot{x}} \right)$$

$C_{As,S}(0,0)$ is the concentration of arsenic ions in the strippant phase at time zero, which can be calculated by Eq. (A.23) [35], see Appendix A in Supplementary Information online.

3. Experimental

3.1 Chemicals

H_3AsO_4 was used to synthesize the produced water as feed solution. The initial concentration of H_3AsO_4 in the inlet feed solution was 4.0 mg/L. Both NaOH and HCl were consumed to adjust the pH of the feed solution and to study the types of strippant solutions. Three types of strippant solutions were investigated: NaOH, HCl and thiourea. Types of extractants studied included Aliquat 336 (tri-octyl methyl ammonium chloride), TBP (tributyl phosphate), DEHP (Bis(2-ethylhexyl) phthalate), Cyanex 471 (tri-isobutylphosphine sulphide) and TOPO (tri-n-octylphosphine Oxide). Toluene, as the diluent, was used to dissolve the extractant. All reagents are of AR grade.

3.2 Apparatus

In Table 2, the characteristics of the hollow fiber module used in this work are shown. The hollow fiber module is comprised of 10,000 microporous polypropylene fibers. The HFSLM system is shown in Fig. 2. The concentration of arsenic ions was analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES) (model JY-2000; HORIBA Jobin Yvon, Edison, NJ, USA). The pH of feed solution was measured by pH meter (model EUTECH pH 700).

Table 2. Characteristics of the hollow fiber module.

Characteristics	Description
Module diameter (cm)	6.3
Effective length of hollow fiber (cm)	20.3
Number of hollow fibers (-)	10,000
Inside radius of hollow fiber (cm)	0.012
Outside radius of hollow fiber (cm)	0.015
Contact area (cm ²)	1.4×10^{-4}
Area per unit volume (cm ⁻³)	29.3
Pore size (cm)	3×10^{-6}
Tortuosity	2.6
Porosity (%)	25
Material	Polypropylene

3.3 Procedure

Five potential extractants (Aliquat 336, TBP, DEHP, TOPO, and Cyanex 471) from literature [3, 13, 27-29] were investigated via solvent extraction. All extractants were applied at an excess concentration of 0.28 M to select a suitable extractant for the extraction of arsenic ions for use in the HFSLM system. As for the HFSLM system, the selected extractant mixed with toluene as the liquid membrane was circulated along the tube and shell sides of the hollow fibers simultaneously, until it filled in the hollow-fiber micropores having a total volume of about 52 mL. Then, deionized water was fed through the tube and shell sides of the hollow fibers to purge the excess liquid membrane. After that, 1 L of feed solution (synthetic produced-water) and stripping solution were pumped counter-currently into the tube and shell sides of the hollow fibers,

respectively. The flow pattern of feed and strippant solutions was single-pass. Finally, after an interval of 10 min, outlet feed and strippant solutions were taken (15 mL each) to analyze the concentration of arsenic ions using ICP-OES. A schema of elimination of arsenic ions via HFSLM is shown in Fig. 2 [3].

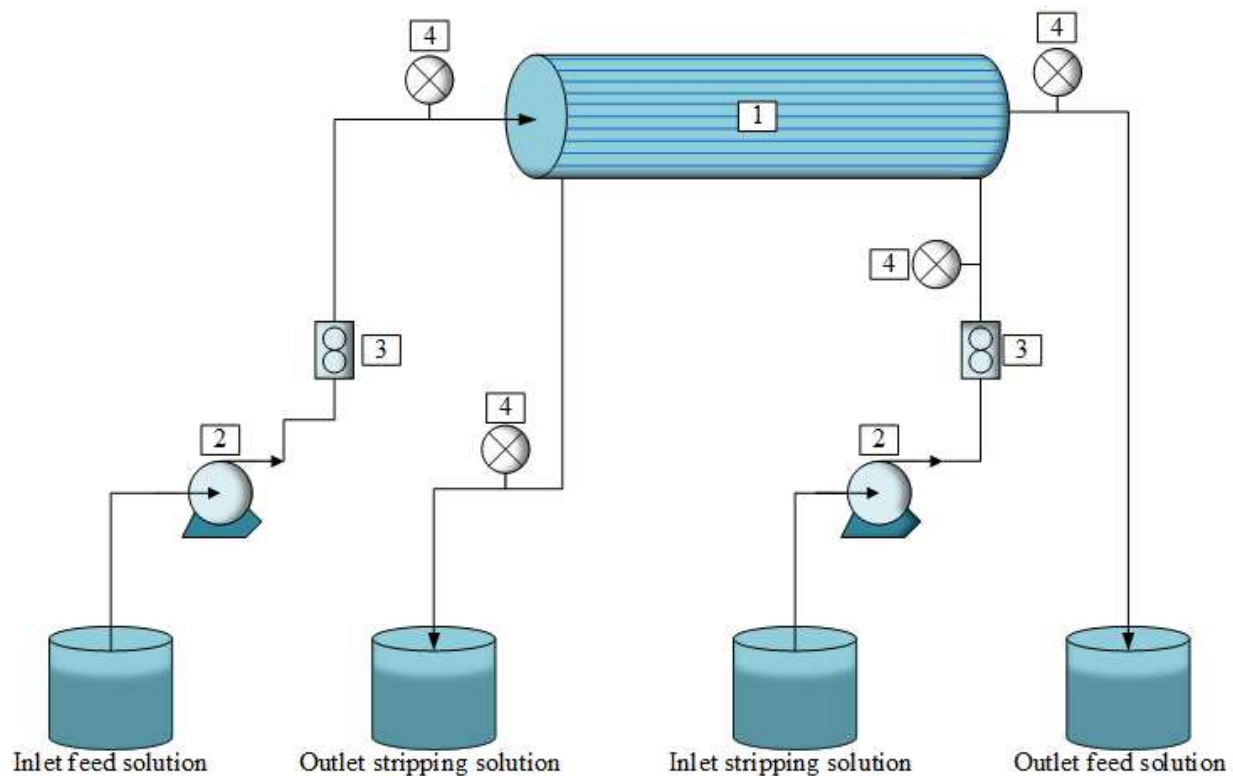


Fig. 2. Schema of elimination of arsenic ions via HFSLM: 1) hollow fiber module, 2) gear pumps, 3) flow meters, and 4) pressure gauges.

Further, the effects of concentration of the selected extractant, pH of feed solution, types of strippant solutions, concentration of the selected strippant solution and flow rates of both feed and strippant solutions were examined. After each experiment, the liquid membrane was removed

from the system by feeding the surfactant into the tube and shell sides of the hollow fibers. Deionized water was then fed into the hollow fibers to eliminate the surfactant.

4 Results and discussion

4.1 Effects of extractants

According to the literature, Aliquat 336 [3] along with the neutral extractants (TBP, DEHP, TOPO, and Cyanex 471) have been found to be the potential extractants for arsenic ions extraction [13, 27-29]. Subsequently, the extraction of arsenic ions by Aliquat 336 and neutral extractants was examined and a comparison of their performance was undertaken. As shown in Fig. 3(a), Aliquat 336 provided the highest extraction of arsenic ions. This result occurred since pH of 6 for feed solution was used in the study. In such a situation, arsenic predominantly exists as dissociated species (anions) [24] and Aliquat 336 is an ionic liquid, which can extract metal ions in various species (cation, neutral and anion) [3], but reacts much better with anions. As observed, the percentages of arsenic ions extraction using the neutral extractants were low because neutral extractants react only with undissociated species [3]. Previous studies have found that extraction of arsenic ions using neutral extractants could be enhanced by adding H_2SO_4 as a co-extractant [28, 29].

In Fig. 3(b), the percentage of arsenic ions extraction versus concentration of Aliquat 336 is depicted. As shown, the extraction of arsenic ions increased as concentration of Aliquat 336 increased. This outcome is in accordance with Le Chatelier's principles that an increase in reactant concentration results in higher fluxes. Percentage of extraction reached maximum at Aliquat 336 concentration of 0.88 M. However, when concentration of Aliquat 336 increased > 0.88 M, the percentage of arsenic ions extraction decreased slightly. In general, when concentration of the

extractant increases, viscosity of the liquid membrane increases, contributing to higher mass transfer resistance [30, 31]. As a consequence, at some point, the extraction does not enhance as the concentration of the extractant increases.

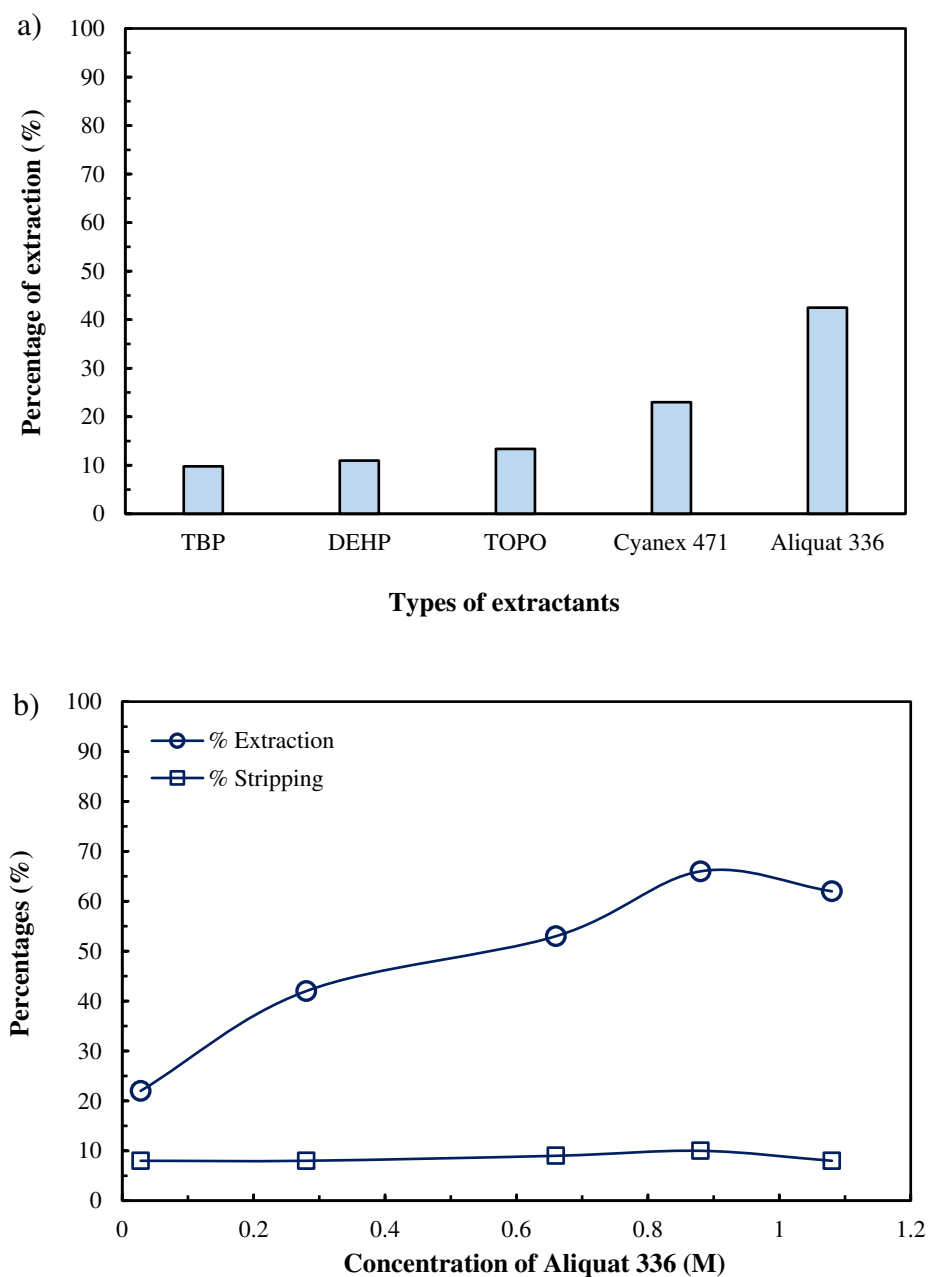


Fig. 3. Percentages of arsenic ions extraction and stripping using pH of 6 for feed solution: a) percentages of extraction against types of extractants (0.28 M each) via solvent extraction, stirring at 500 rpm for 1 hr, b) percentages of extraction and stripping

against concentration of Aliquat 336 via HFSLM, using 0.5 M NaOH as the strippant solution, at flow rates of feed and strippant solutions of 100 mL/min.

4.2 Effect of pH of feed solution

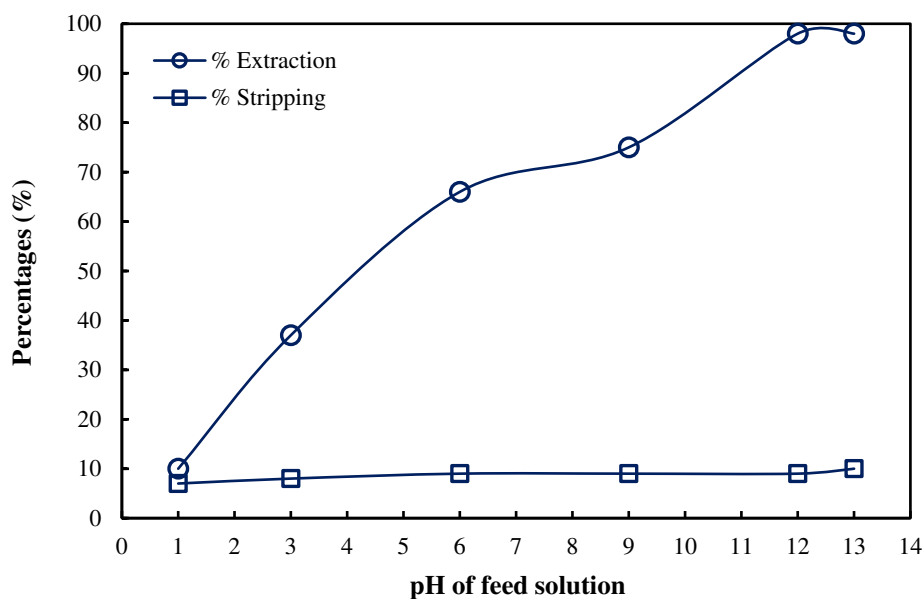


Fig. 4. Percentages of arsenic ions extraction and stripping against pH of feed solution via HFSLM, using 0.88 M Aliquat 336 as the extractant having 0.5 M NaOH as the strippant solution, at flow rates of feed and strippant solutions of 100 mL/min.

It is acknowledged that forms of arsenic species in solution depend on the pH of the solution. As(V) predominantly exists as undissociated H_3AsO_4 at $\text{pH} < 2$ and predominantly appears as dissociated H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-} at pH between 3 to 6, 8 to 11, and 12 to 14, respectively [24]. In Fig. 4, results demonstrate that the extraction of arsenic ions enhanced as pH of feed solution enhanced but remained constant at pH between 12 to 13. This outcome arose due to the fact that the extraction mechanism of Aliquat 336 transpired via an ion-exchange of anion metal ions and Cl^- in Aliquat 336 [11, 32]. Undissociated H_3AsO_4 transforms to anions when pH

of feed solution increases and predominantly appears as AsO_4^{3-} at pH between 12 and 13 [24], resulting in greater arsenic extraction at higher pH of feed solution. At pH 12 to 13, maximum percentage of arsenic extraction was achieved (99.9%), indicating that Aliquat 336 could extract the dissociated species AsO_4^{3-} much better than $\text{H}_2\text{AsO}_4^- > \text{HAsO}_4^{2-}$.

4.3 Respond Surface

Respond surface was applied to evaluate the optimum condition for extraction of arsenic ions using MINITAB 19 software. As shown in Table 3, the concentration of Aliquat 336 (A) and pH of feed solution (B) were coded into 3 levels using ANOVA design. Thus, 13 runs, including 4 repetitions at the center points, were obtained.

According to ANOVA Table 3, the experimental data of arsenic ions extraction were analyzed by MINITAB to generate the correlation for predicting the percentage of arsenic ions extraction, at various concentrations of Aliquat 336 and pH of feed solution. The regression equation obtained from ANOVA analysis is in Eq. (21). Analysis of variance is shown in Table 4.

$$E = 81.1 + 95.2A - 18.68B - 64.9A^2 + 1.284B^2 + 2.29AB \quad (21)$$

where E refers to the percentage of arsenic ions extraction, A is the concentration of Aliquat 336, and B is pH of feed solution, respectively.

Table 3. Experimental designs of two variables: concentration of Aliquat 336 (A) and pH of feed solution (B) with 3 levels (-1, 0 and 1).

Run	Level		Experimental condition		Percentage of arsenic extraction	
	A	B	A	B	Expt. result	Predicted by Eq. (21)
1	-1	-1	0.28	6	42	41
2	-1	0	0.28	9	47	44
3	-1	1	0.28	12	67	71
4	0	-1	0.68	6	53	59
5	0	0	0.68	9	66	66
6	0	1	0.68	12	100	95
7	1	-1	1.08	6	62	57
8	1	0	1.08	9	62	66
9	1	1	1.08	12	98	99
10	0	0	0.68	9	66	66
11	0	0	0.68	9	66	66
12	0	0	0.68	9	66	66
13	0	0	0.68	9	66	66

As portrayed in Table 3, the percentages of arsenic ions extraction predicted by the regression Eq. (21) was compared with those obtained from the experimental results. Thus, the values determined using Eq. (21) were found to be in accordance with the experimental results. The average relative deviation proved to be 3.77%. Therefore, it is seen that the regression equation, as determined by the respond surface analysis, can be used to predict the optimum conditions (optimum concentration of Aliquat 336 and optimum pH of feed solution) for the extraction of arsenic ions.

Table 4. Analysis of variance.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	3181.51	636.30	34.25	0.000
Linear	2	1635.65	817.98	44.03	0.000
A	1	0.7	0.7	0.04	0.851
B	1	1635.25	1635.25	88.02	0.000
Square	2	484.86	242.43	13.05	0.004
A ²	1	298.13	298.13	16.05	0.005
B ²	1	369.11	369.11	19.87	0.003
2-way interaction	1	30.25	30.25	1.63	0.243
A×B	1	30.25	30.25	1.63	0.243
Error	7	130.05	18.58		
Lack-of-fit	3	130.05	43.35		
Pure error	4	0.00	0.00		
Total	12	3311.56			

With regard to extraction of arsenic ions, both concentration of Aliquat 336 and pH of feed solution play a vital role. In Figs. 5(a) and (b), the contour and respond surface plots of arsenic ions extraction against concentration of Aliquat 336 and pH of feed solution are shown. Results show that maximum percentage of arsenic extraction (99.9%) was achieved at 0.68 M Aliquat 336 when pH of feed solution was increased from 6 to 12. Therefore, it is recommended that the pH of feed solution be adjusted to 12 and concentration of Aliquat 336 be reduced from 0.88 to 0.68 M, in order to treat arsenic from wastewater at the highest efficiency and the lowest cost of chemicals. It is evident that the respond surface plot is economically useful as Aliquat 336 is much more expensive than NaOH, which was used to adjust the pH of feed solution.

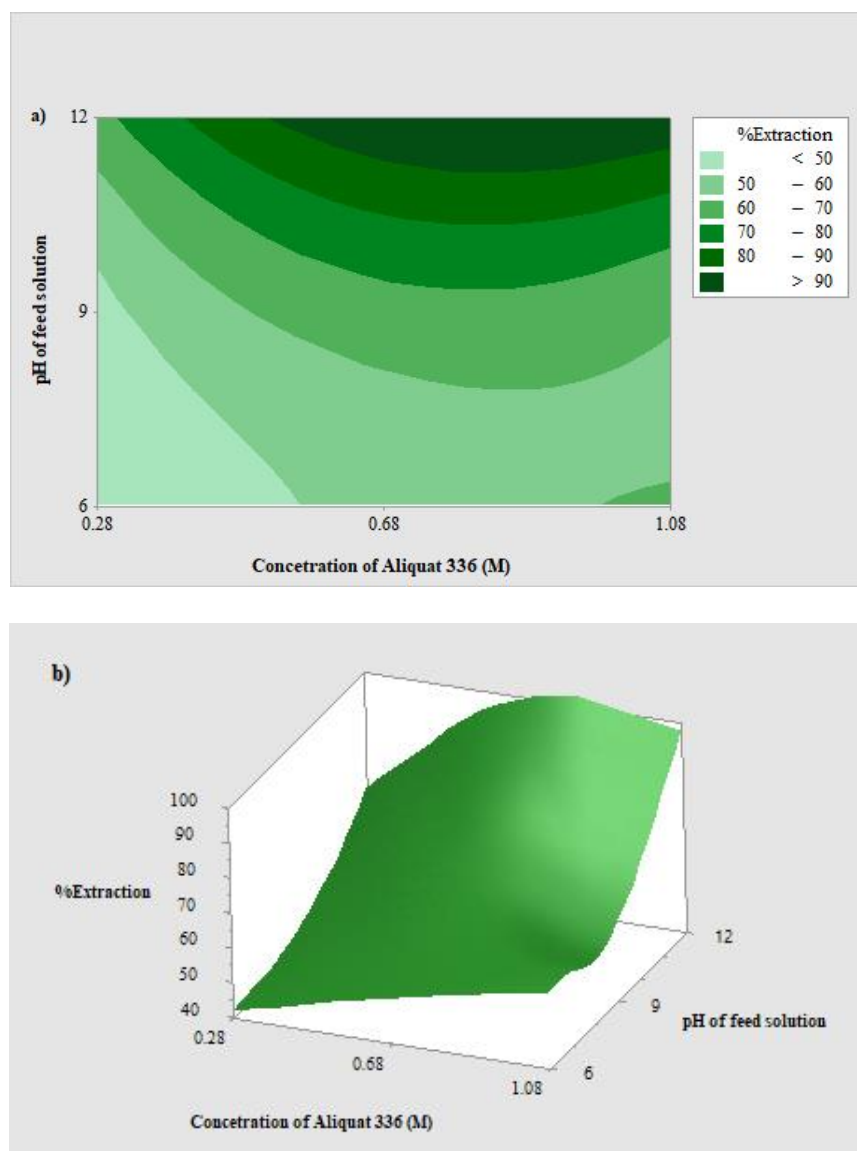


Fig. 5. Percentages of arsenic ions extraction against concentration of Aliquat 336 and pH of feed solution via HFSLM, using 0.5 M NaOH as the strippant solution, at flow rates of feed and strippant solutions of 100 mL/min: a) contour plot, and b) surface plot.

4.4 Effects of strippant solutions

As shown in Fig. 6(a), of all the strippant solutions used in this study: NaOH, thiourea and HCl, HCl was found to be the best strippant solution for the stripping of arsenic ions. Low stripping of arsenic ions using NaOH and thiourea can be explained that once arsenic ions are stripped into these strippant solutions, they are present as anions, which could be extracted back by Aliquat 336. In the case of using HCl as strippant solution, arsenic anions, which are released into the HCl solution, combine with H^+ resulting in H_3AsO_4 which reacts poorly with Aliquat 336 in the liquid membrane phase.

When HCl was mixed with thiourea, the percentage of arsenic stripping increased from 45% to 98%. This was due to the synergistic effect [33]. To confirm the synergistic effect of stripping arsenic ions using the mixture of HCl and thiourea, the distribution ratios of arsenic stripping, using each extractant, were estimated. Results are shown in Table. 5. According to Eq. (5), the synergistic coefficient was found to be 1.57, confirming the synergistic effect of the mixture of the strippant solutions of HCl and thiourea. Therefore, the mixture of HCl and thiourea was used as the strippant solution and their suitable concentrations will be further investigated.

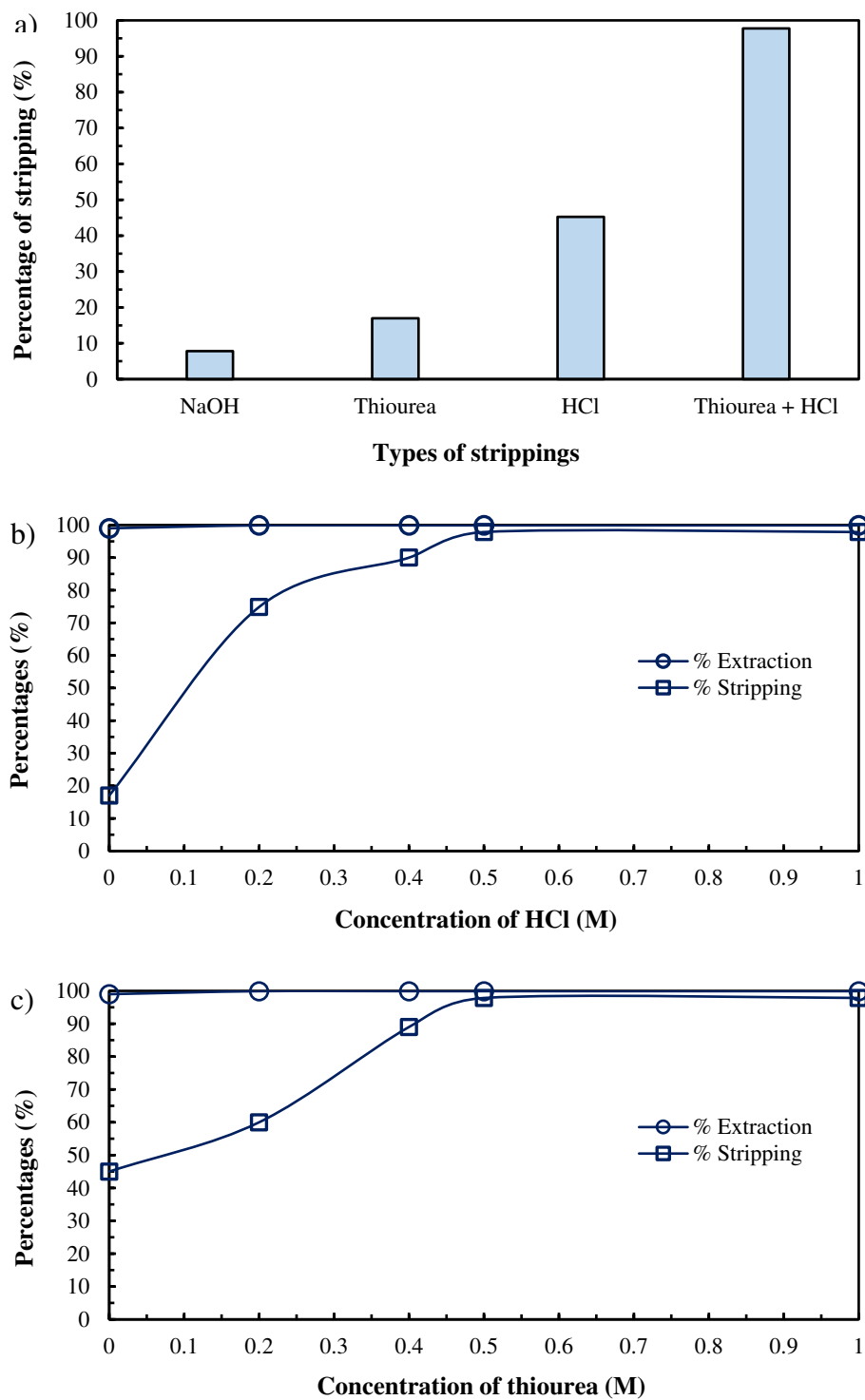


Fig. 6. Percentages of arsenic ions extraction and stripping, using 0.68 M Aliquat 336 as the extractant having pH of feed solution of 12, at flow rates of feed and strippant solutions of 100 mL/min: a) types of strippant solutions (0.5 M each), b) 0.5 M thiourea mixed

with various concentrations of HCl, and c) 0.5 M HCl mixed with various concentrations of thiourea.

Table 5. Distribution ratios of arsenic ions stripping using various types of strippant solutions.

Strippant solutions	Distribution ratios
0.5 M thiourea	0.17
0.5 M HCl	0.45
0.5 M thiourea + 0.5 M HCl	0.98

In Fig. 6(b) and (c), percentages of arsenic ions stripping against concentration of synergistic strippant solution (mixture of HCl and thiourea) are shown. Fig. 6(a) depicts the percentage of arsenic ions stripping using 0.5 M thiourea having various concentrations of HCl. Percentage of arsenic ions stripping increased as concentration of HCl increased, corresponding to chemical kinetics. Percentage of arsenic stripping reached maximum at 98% at 0.5 M HCl. Then, it remained constant. Fig. 6(b) depicts the percentage of arsenic stripping using 0.5 M HCl having various concentrations of thiourea. Consequently, the percentage of arsenic ions stripping increased as thiourea concentration increased, in accordance with chemical kinetics. When concentration of thiourea was higher than 0.5 M, the percentage of stripping remained constant at 98%. Therefore, 0.5 M thiourea and 0.5 M HCl were used in the study.

4.5 Reaction order and reaction rate constant

Integration and graphical methods, plotted between the integral concentration of arsenic ions versus time, were utilized to estimate the reaction rate constants and reaction orders of arsenic

extraction and stripping. In Table 6, results are given. Reactions, therefore, for both extraction and stripping of arsenic ions from synthetic produced water were of second-order: due to the highest R^2 .

As shown in Fig. 7, according to the plots between the integral concentration of arsenic versus time, the reaction rates of arsenic extraction and stripping were found to be 50.64×10^{-3} and 6.96×10^{-3} L/mg.s, respectively. These values indicate that the rate of stripping is slower than the rate of extraction.

Table 6. Reaction order (m/n) and reaction rate constants of arsenic ions extraction and stripping ($k_{As,Ex}$ and $k_{As,S}$).

m/n	Reaction	Plot	Rate constant	R^2
1	Extraction	$\ln \frac{C_{As,0}}{C_{As}}$ versus t	$28.41 \times 10^{-3} \text{ s}^{-1}$	0.8957
	Stripping	$\ln \frac{C_{As,Org}}{C_{As,Org} - C_{As,S}}$ versus t	$9.90 \times 10^{-3} \text{ s}^{-1}$	0.9669
2	Extraction	$\frac{1}{C_{As}} - \frac{1}{C_{As,0}}$ and t	$50.64 \times 10^{-3} \text{ L/mg.s}$	0.9934
	Stripping	$\frac{1}{C_{As,Org} - C_{As,S}} - \frac{1}{C_{As,Org}}$ versus t	$6.96 \times 10^{-3} \text{ L/mg.s}$	0.9952
3	Extraction	$\frac{1}{2C_{As}^2} - \frac{1}{2C_{As,0}^2}$ and t	$16.67 \times 10^{-2} \text{ L}^2/\text{mg}^2.\text{s}$	0.9893
	Stripping	$\frac{1}{2(C_{As,Org} - C_{As,S})^2} - \frac{1}{2C_{As,Org}^2}$ versus t	$5.52 \times 10^{-2} \text{ L}^2/\text{mg}^2.\text{s}$	0.9895

C_{As} , concentration of arsenic ions in the feed solution at time t ; $C_{As,0}$, concentration of arsenic ions in the inlet feed solution; $C_{As,Org}$, initial concentration of arsenic ions in the organic extractant; $C_{As,S}$, concentration of arsenic ions in the stripping solution at time t .

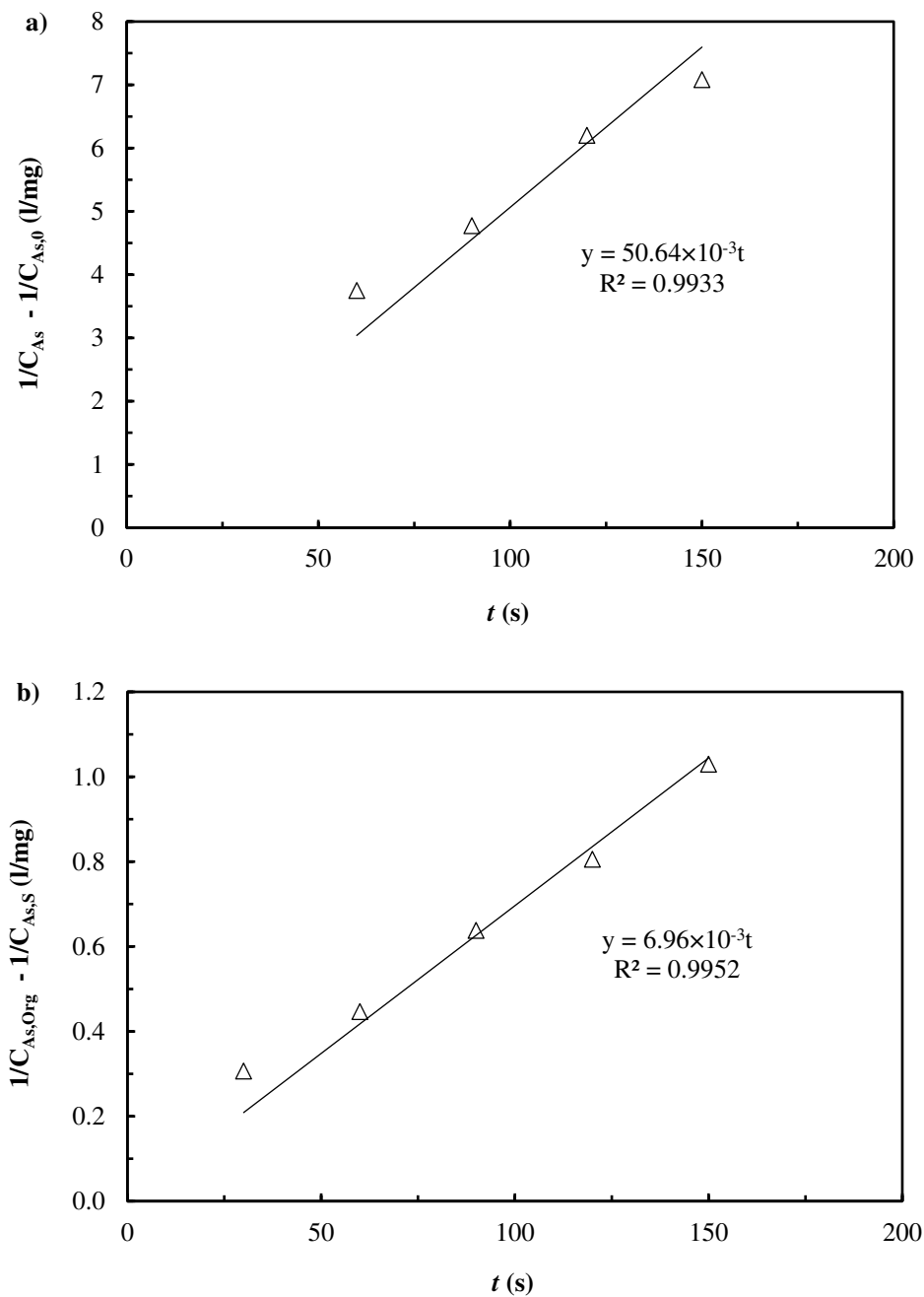


Fig. 7. Graphs plotted between the integral concentration of arsenic ions versus time:
a) extraction reaction, and b) stripping reaction.

4.6 Validation of the mathematical model

Various flow rates of feed and stripping solutions between 50 to 500 mL/min were investigated in order to optimize the elimination of arsenic ions and validate the mathematical model developed in this work. As shown in Fig. 8, at flow rates between 50 to 100 mL/min, the percentages of extraction and stripping of arsenic ions remained constant at 99.9%. The concentration of arsenic ions in the outlet feed solution was found to be 0.003 mg/L, complying with the standard of wastewater discharged, regulated by the Thailand Ministry of Industry and the Ministry of Natural Resources and Environment. Subsequently, due to less residence time [34], percentages of extraction and stripping declined as flow rates increased. Therefore, flow rates of feed and stripping solutions at 100 mL/min were recommended in order to optimize the efficiency and capacity of arsenic ions treatment.

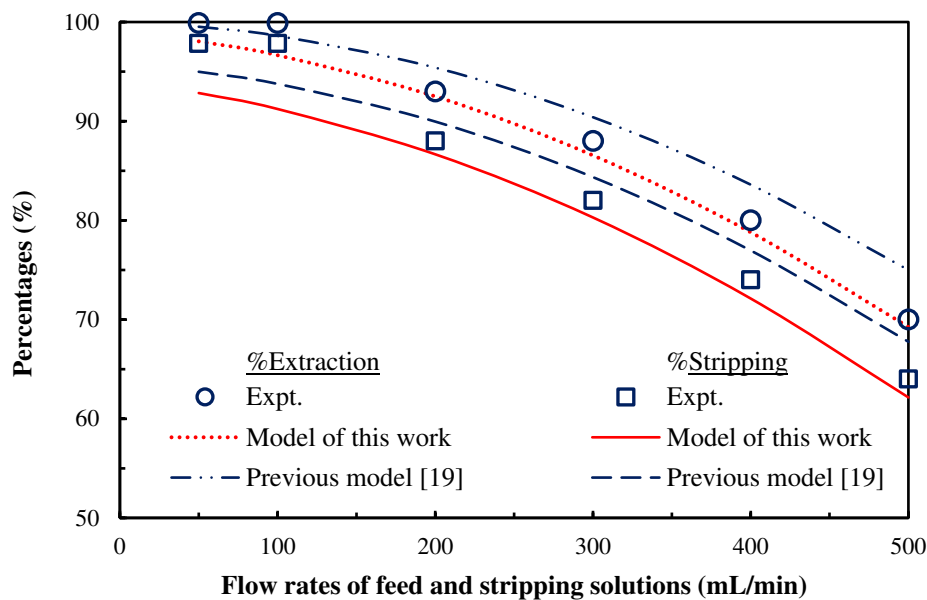


Fig. 8. Percentages of arsenic ions extraction and stripping against flow rates of feed and stripping solutions via HFSLM, using 0.68 M Aliquat 336 as the extractant, at pH of feed solution of 12, having a mixture of HCl and thiourea (0.5 M each) as the stripping solution.

In Fig. 8, percentages of arsenic ions extraction and stripping obtained from the model and experiment are compared. Results clearly show that the mathematical model developed in this work agreed well with the experimental results having an average relative deviation of 2% and 4% for predicting the extraction and stripping, respectively. These values confirm that chemical reactions at the liquid-membrane interfaces as well as diffusion are significant factors governing the rate of arsenic ions transport across the liquid membrane.

Percentages of arsenic ions extraction and stripping obtained from the models developed in this work were compared with those obtained from the models developed previously [19]. As results show in Fig. 8, the mathematical model developed in this work proved to be in agreement with the experimental results more than previous model [19]. This was because previous model was implemented by ignoring the significant factor (diffusion). This reconfirmed that both diffusion and chemical reactions are the key factors controlling the transport rate of arsenic ions across the hollow fibers.

4.7 Adaptability of the mathematical model

To ensure the mathematical model developed in this work can be adapted for use in other metal ions, the model was applied further: to predict the extraction and stripping of neodymium (Nd) and praseodymium (Pr) using HFSLM. As results show in Fig. 9, the concentration of Nd and Pr, in both feed and strippant phases, predicted by the model developed in this work proved to be in good agreement with the experimental results carried out by Ni'am et al. [10]. The results, as in Figs. 8 and 9, indicate that the mathematical model, herein, can predict the extraction and stripping of various metal ions via HFSLM.

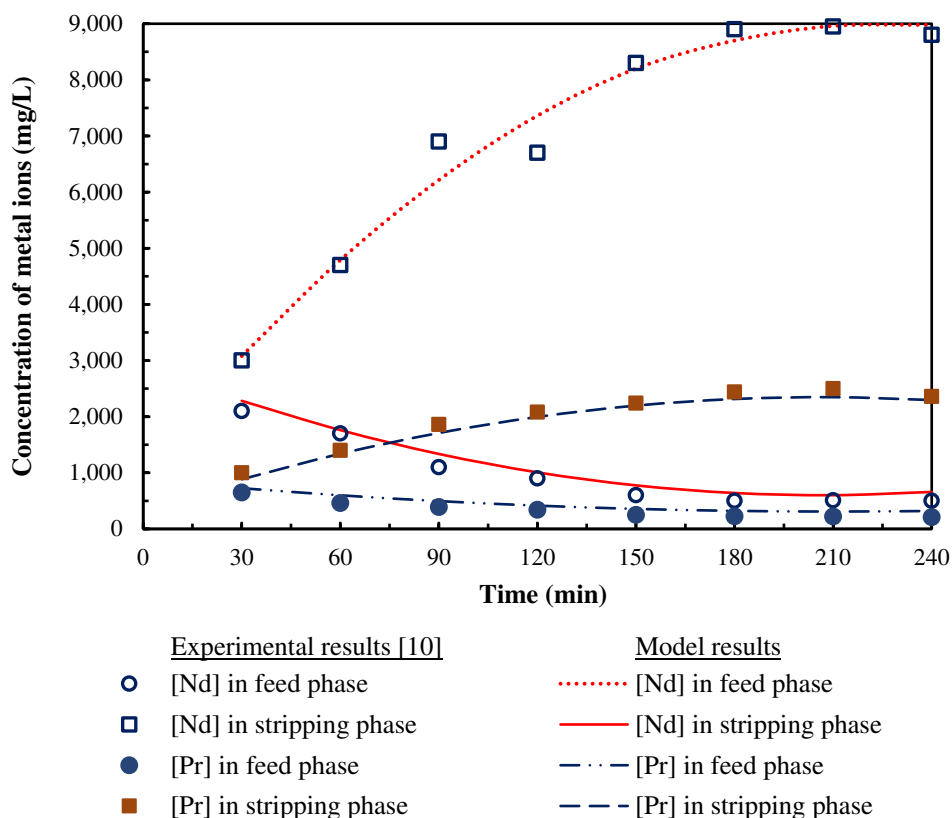


Fig. 9. Adaptability of mathematical model to predict the extraction and stripping of other metal ions via HFSLM.

5. Conclusion

In this paper, results demonstrated that HFSLM could successfully treat arsenic ions in synthetic wastewater to meet the standard of wastewater discharged (< 0.25 mg/L). Arsenic ions were extracted and stripped in a single-step operation. Percentages of arsenic ions extraction and stripping were found to be 99.9% and 98% by using 0.5 M Aliquat 336 as the extractant, pH of feed solution of 12, a mixture of thiourea and hydrochloric acid (0.5 M each) as the synergistic stripping solution, and flow rates of both feed and strippant solutions of 100 mL/min. Extraction and stripping of arsenic ions predicted by the mathematical model fitted in well with the

experimental results. The average relative deviations for the extraction and stripping proved to be 2% and 4%, respectively. This confirms that chemical reactions at the liquid-membrane interfaces and diffusion are the crucial parameters that govern the rate of arsenic ions transport across the liquid membrane.

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Author Contributions

S.S. performed the experiment and wrote the manuscript. W.A. generated figures. U.P. and K.M. reviewed the manuscript.

Competing interests

The authors declare no competing interests.

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Figures

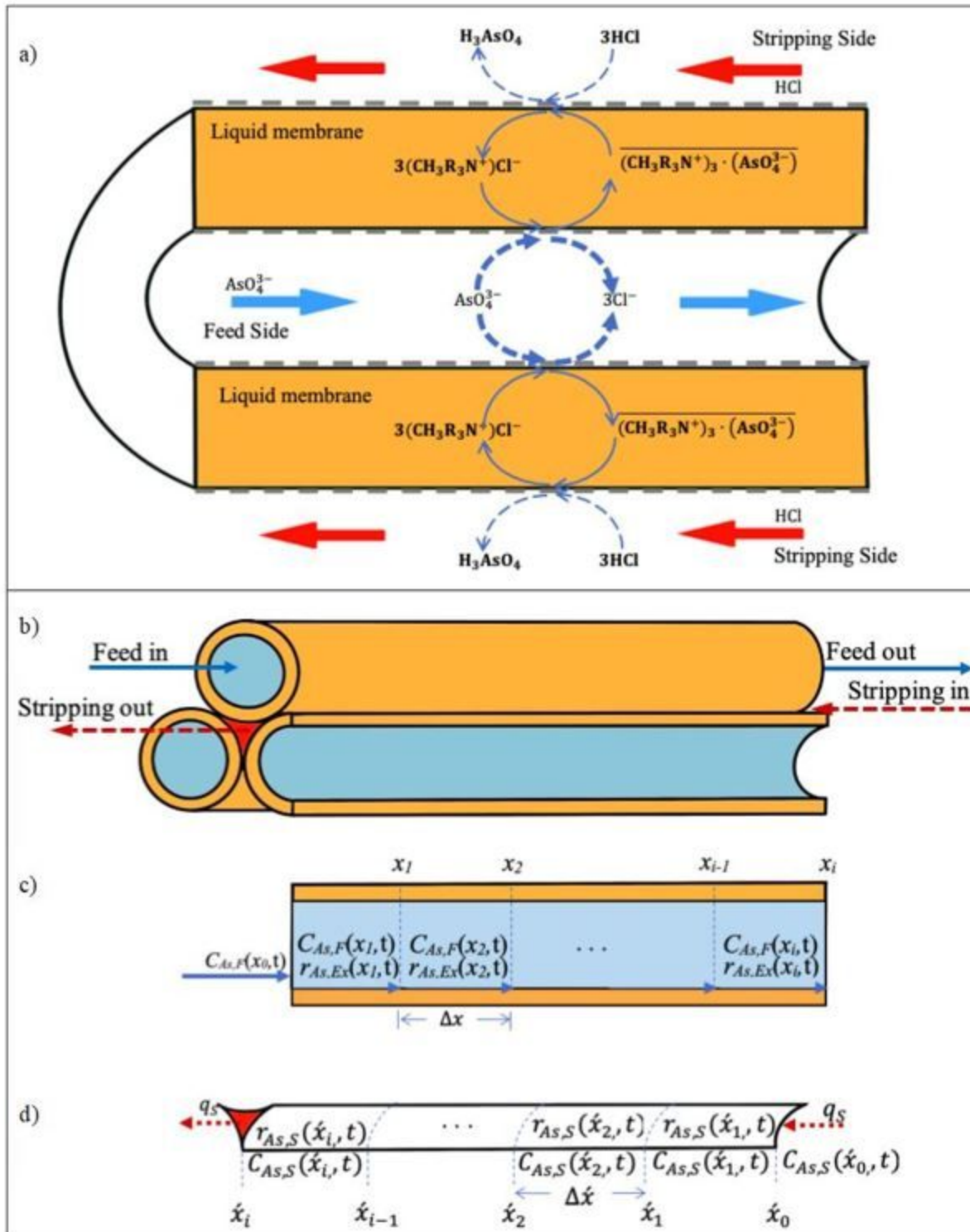


Figure 1

Schematic of arsenic ions transport across HFSLM: a) mechanisms of the extraction and stripping, b) tube and shell sides of the hollow fibers, c) tube side, and d) shell side.

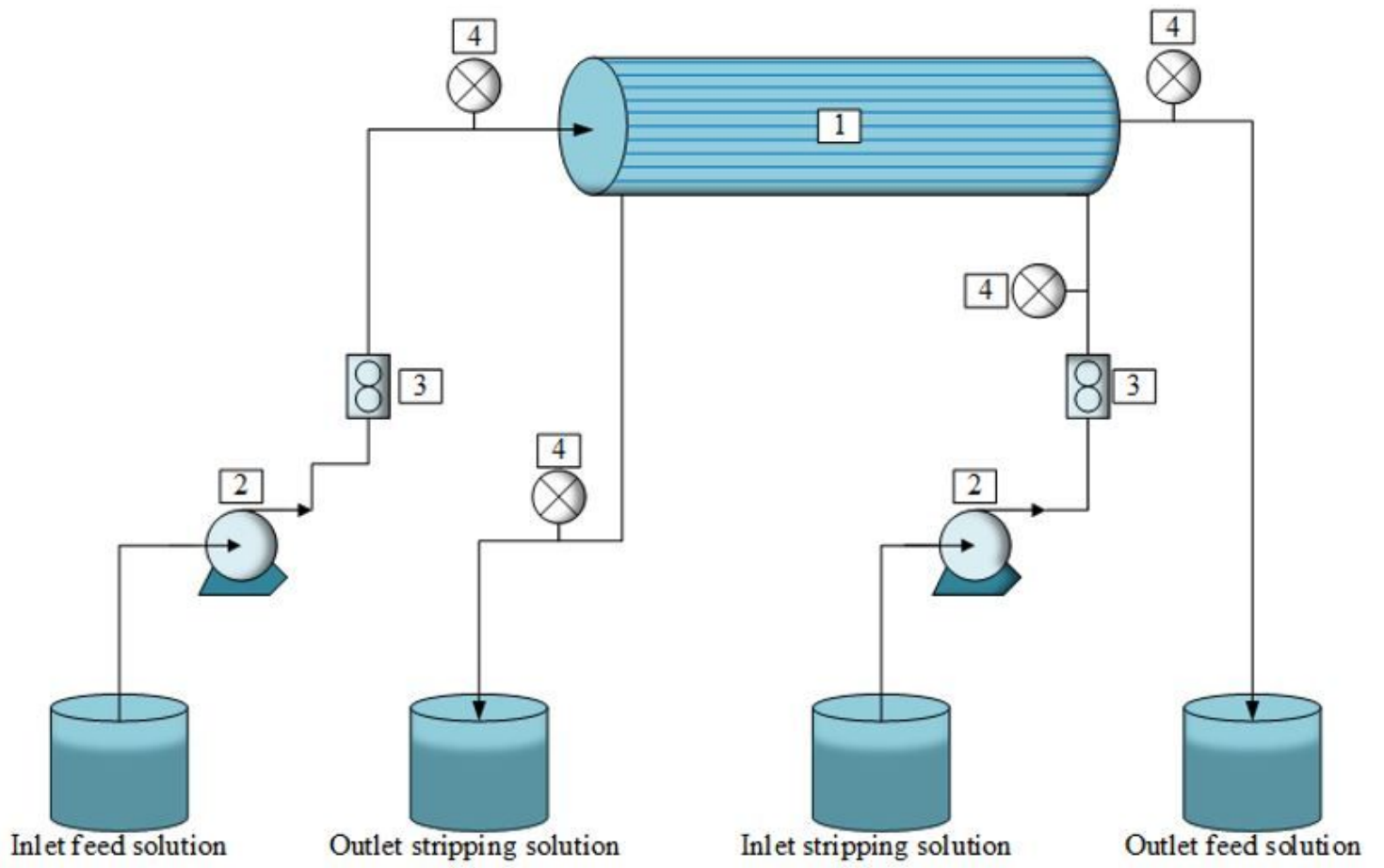


Figure 2

Schema of elimination of arsenic ions via HFSLM: 1) hollow fiber module, 2) gear pumps, 3) flow meters, and 4) pressure gauges.

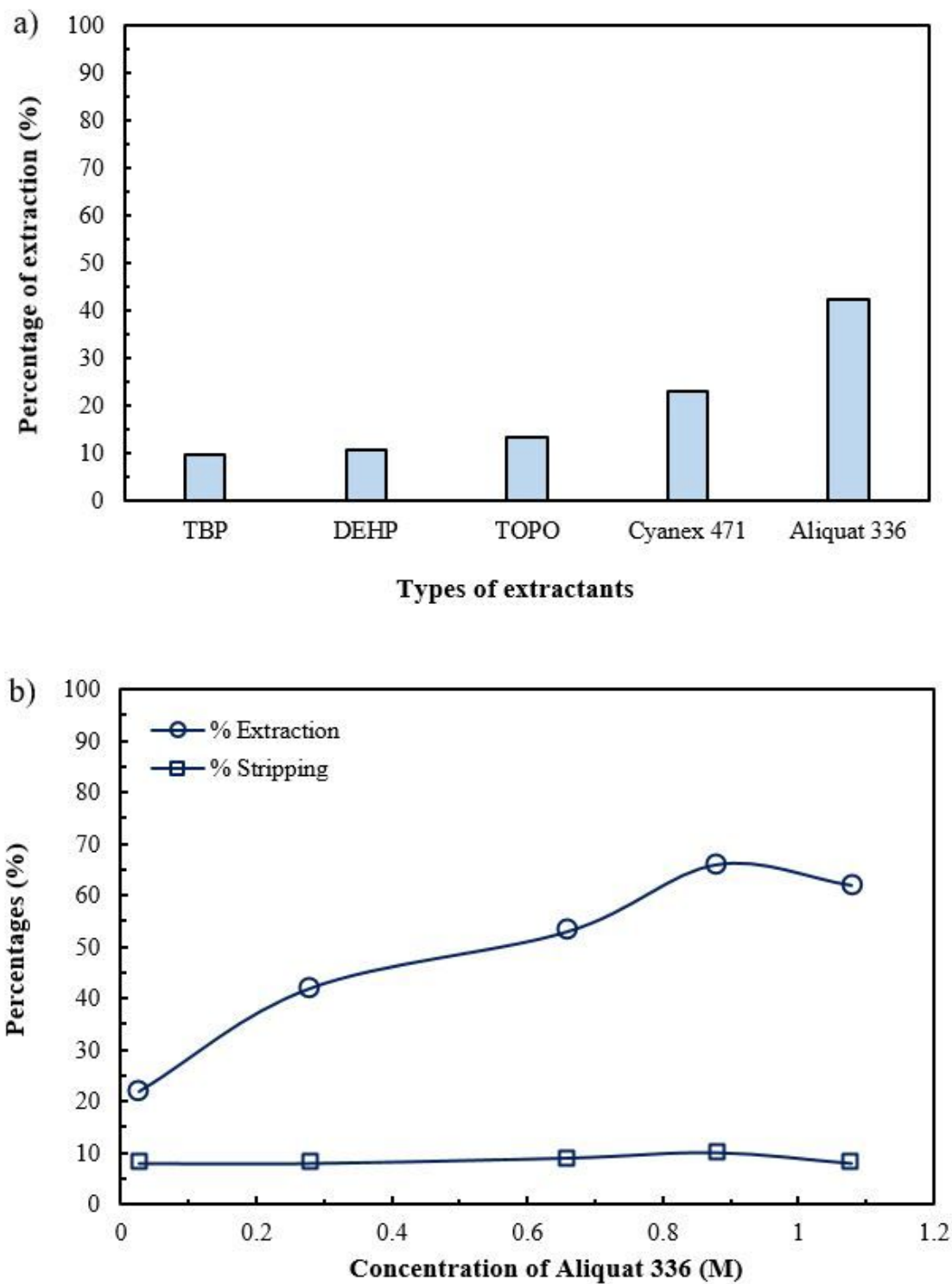


Figure 3

Percentages of arsenic ions extraction and stripping using pH of 6 for feed solution: a) percentages of extraction against types of extractants (0.28 M each) via solvent extraction, stirring at 500 rpm for 1 hr, b) percentages of extraction and stripping against concentration of Aliquat 336 via HFSLM, using 0.5 M NaOH as the strippant solution, at flow rates of feed and strippant solutions of 100 mL/min.

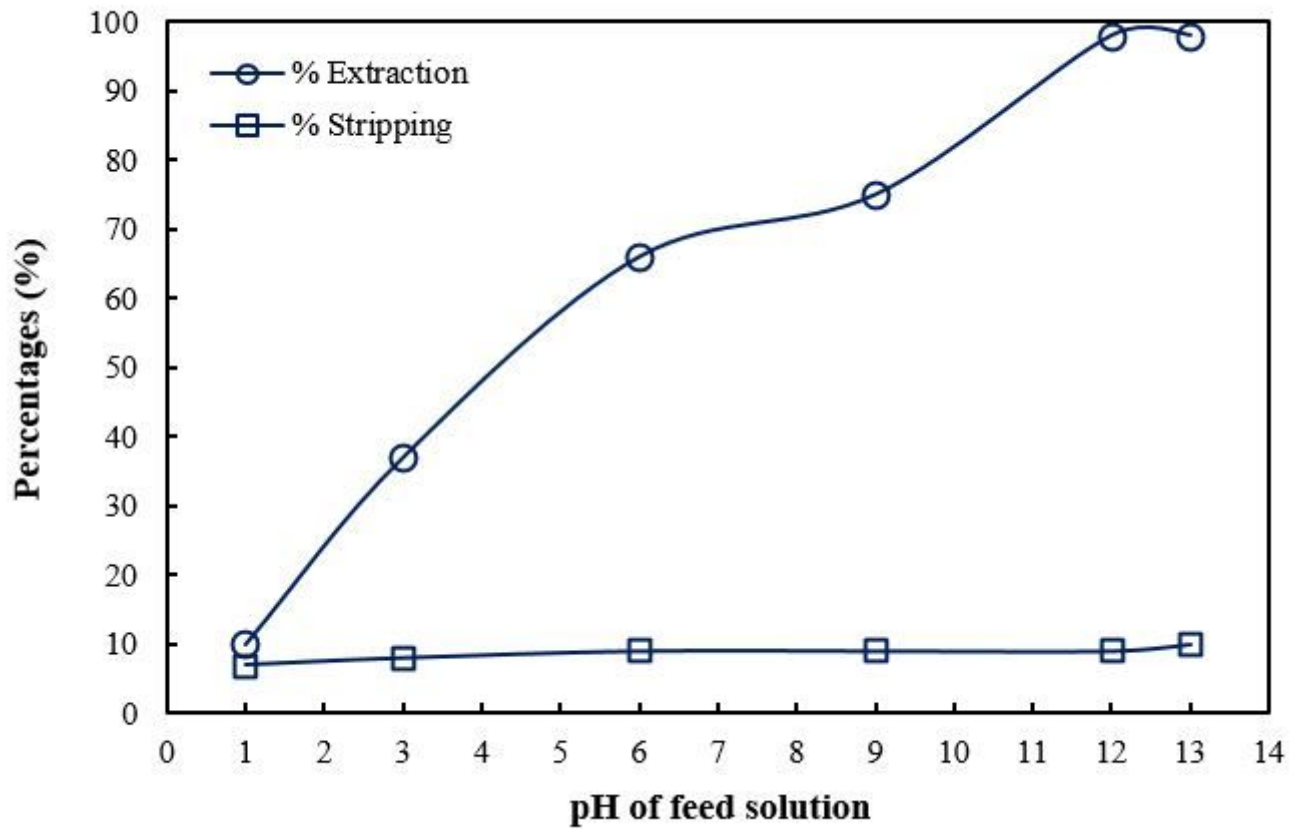


Figure 4

Percentages of arsenic ions extraction and stripping against pH of feed solution via HFSLM, using 0.88 M Aliquat 336 as the extractant having 0.5 M NaOH as the strippant solution, at flow rates of feed and strippant solutions of 100 mL/min.

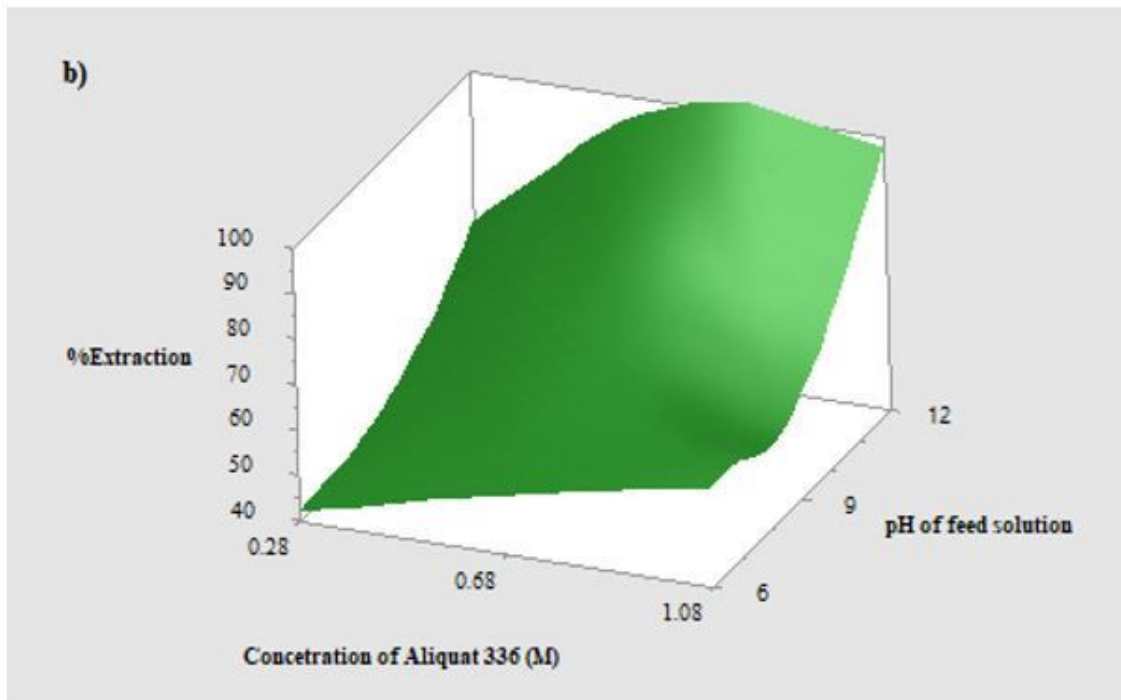
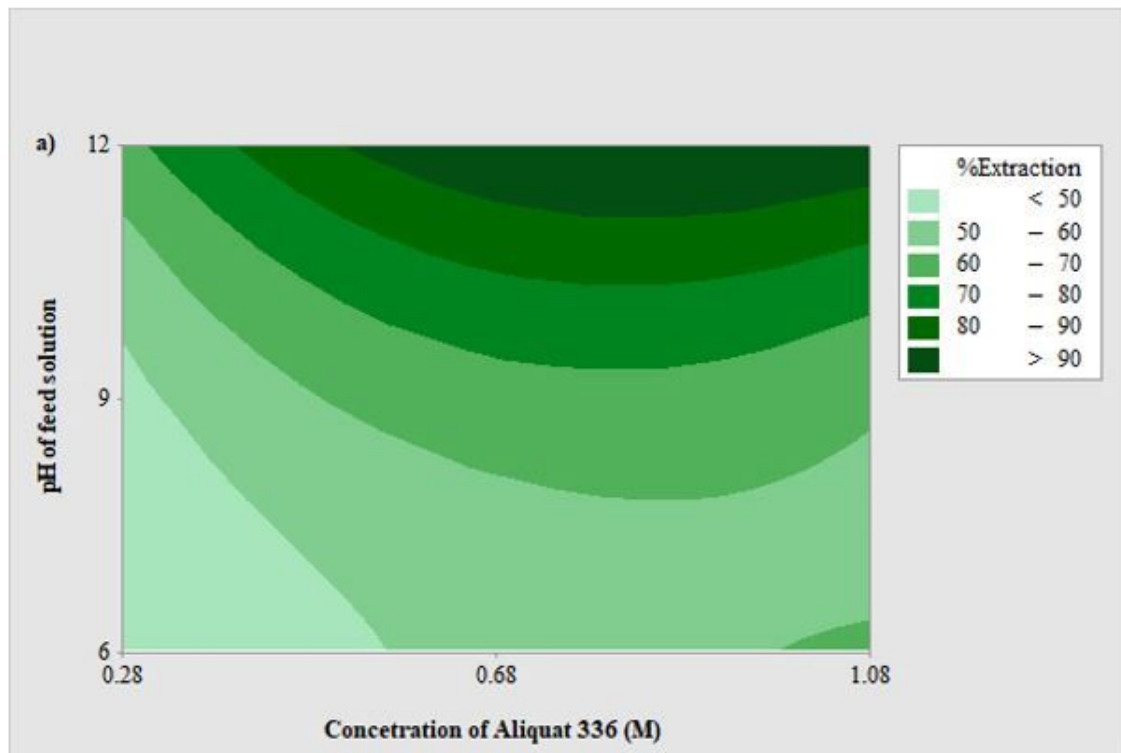


Figure 5

Percentages of arsenic ions extraction against concentration of Aliquat 336 and pH of feed solution via HFSLM, using 0.5 M NaOH as the strippant solution, at flow rates of feed and strippant solutions of 100 mL/min: a) contour plot, and b) surface plot.

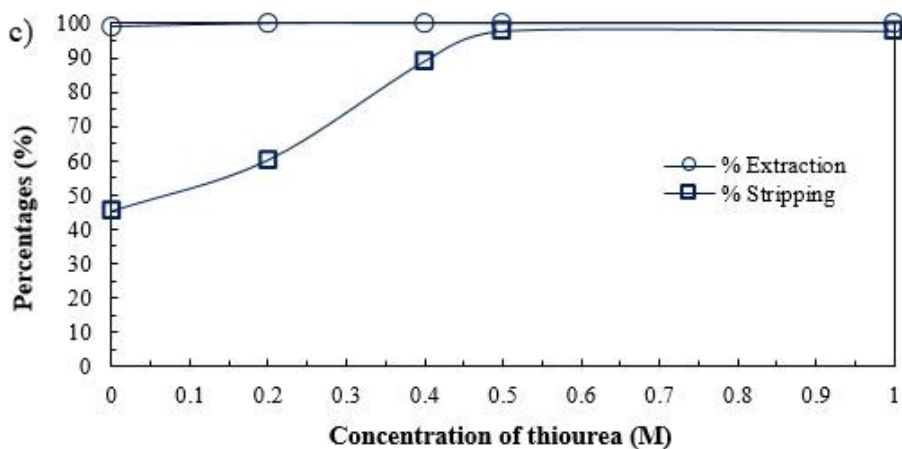
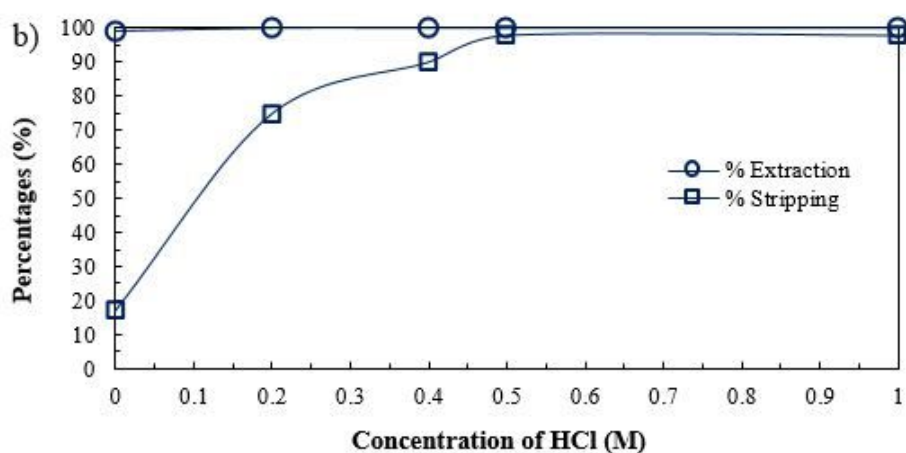
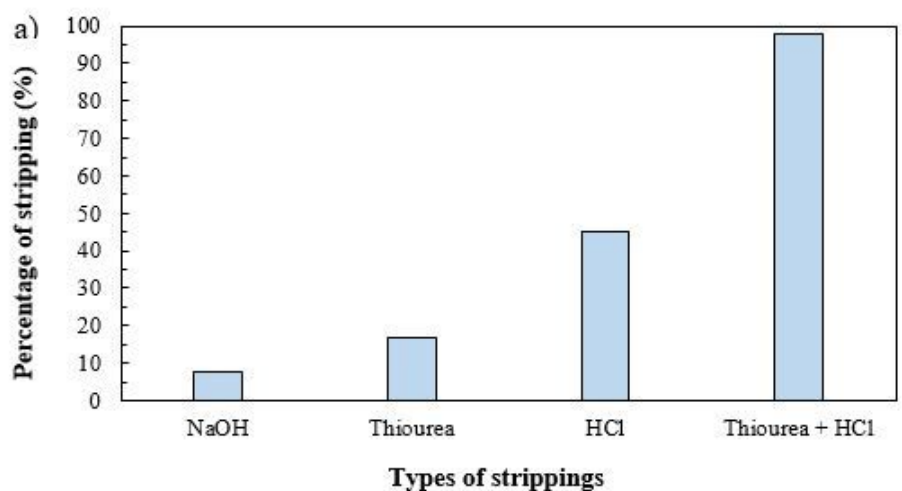


Figure 6

Percentages of arsenic ions extraction and stripping, using 0.68 M Aliquat 336 as the extractant having pH of feed solution of 12, at flow rates of feed and strippant solutions of 100 mL/min: a) types of strippant solutions (0.5 M each), b) 0.5 M thiourea mixed with various concentrations of HCl, and c) 0.5 M HCl mixed with various concentrations of thiourea.

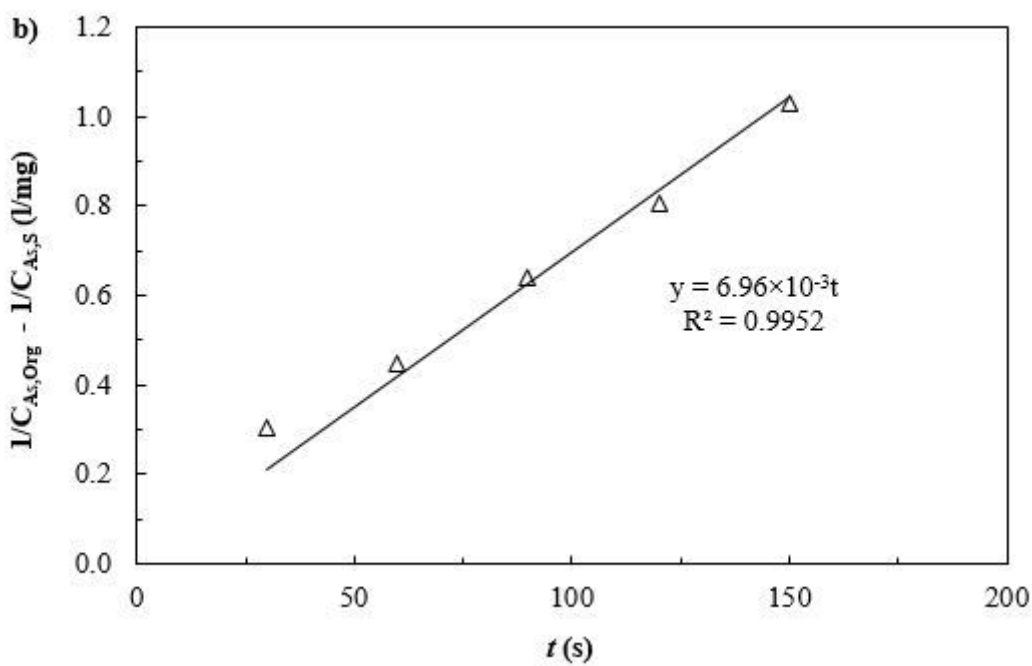
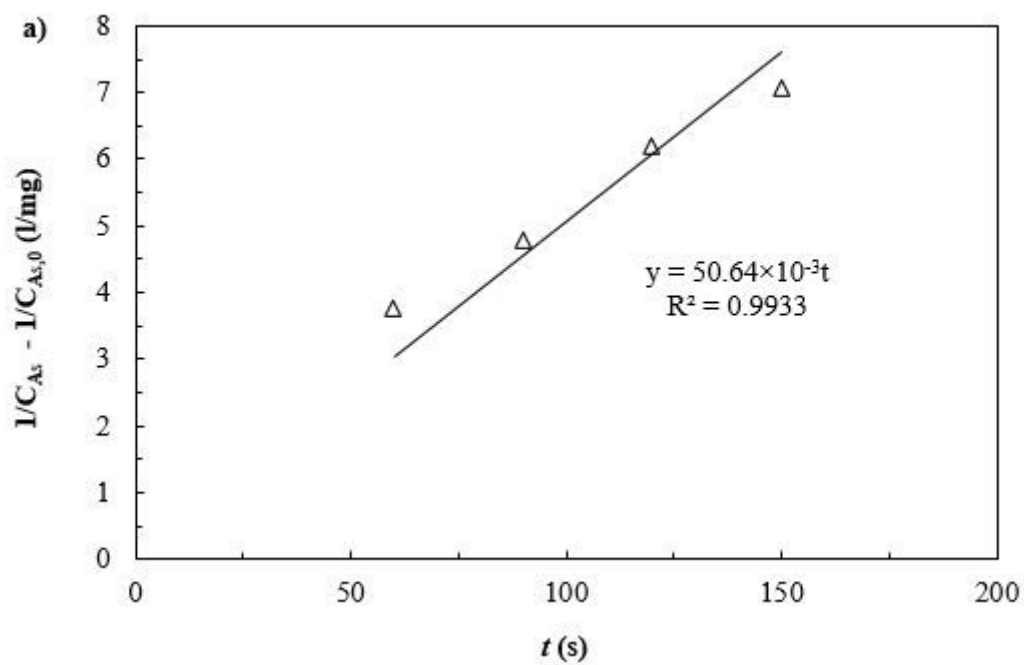


Figure 7

Graphs plotted between the integral concentration of arsenic ions versus time: a) extraction reaction, and b) stripping reaction.

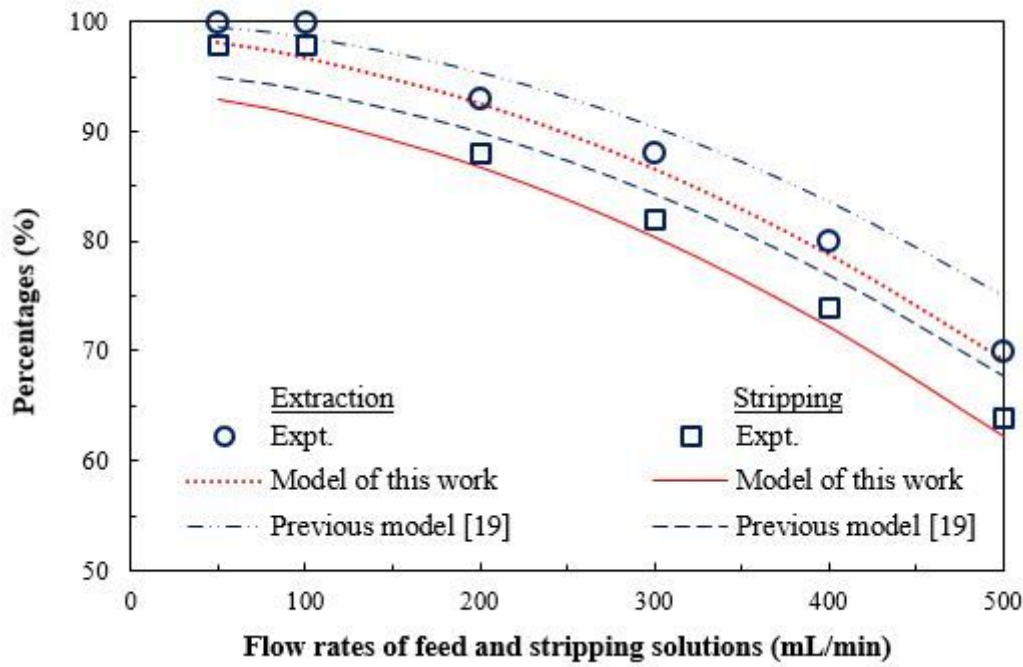


Figure 8

Percentages of arsenic ions extraction and stripping against flow rates of feed and strippant solutions via HFSLM, using 0.68 M Aliquat 336 as the extractant, at pH of feed solution of 12, having a mixture of HCl and thiourea (0.5 M each) as the strippant solution.

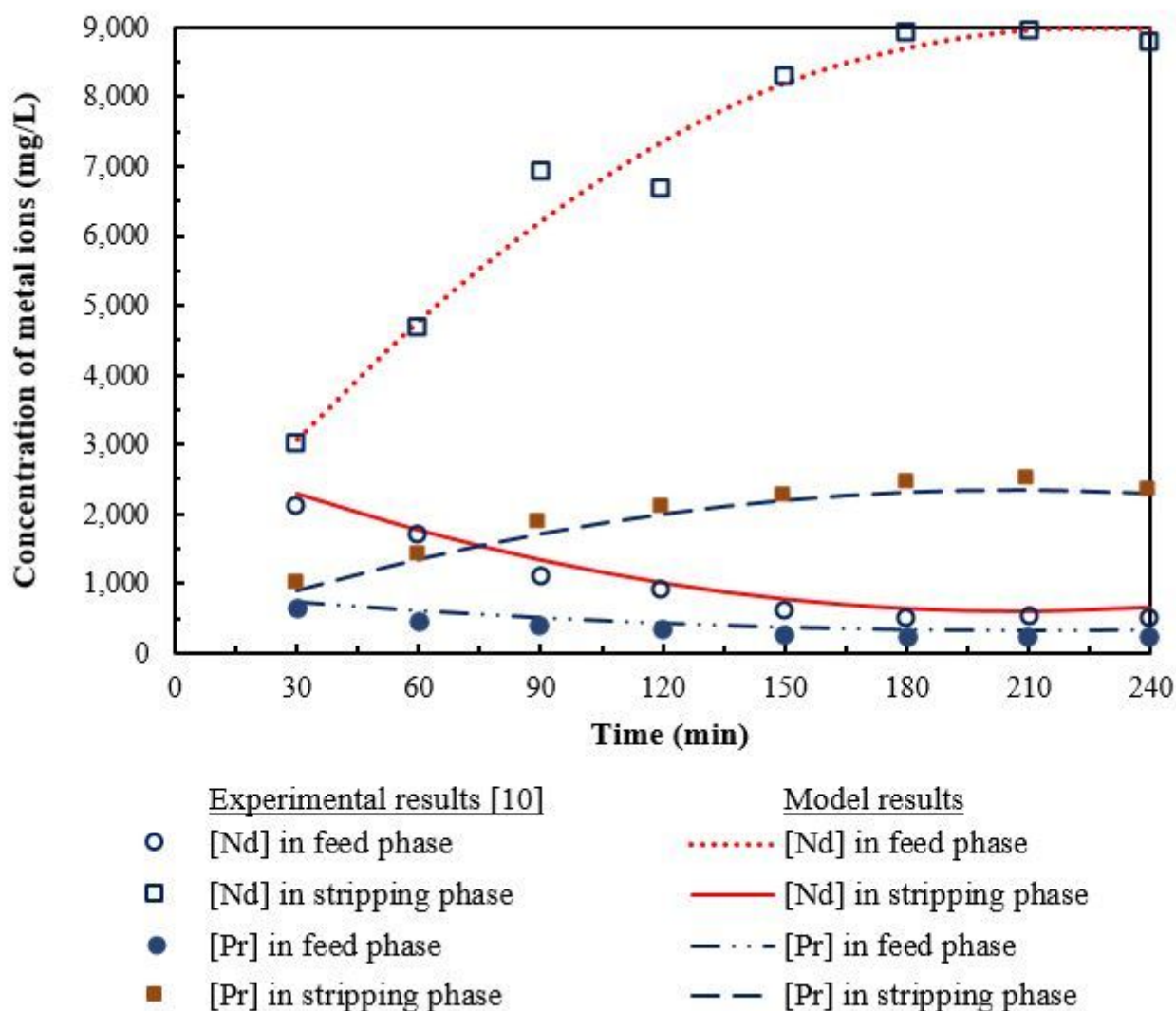


Figure 9

Adaptability of mathematical model to predict the extraction and stripping of other metal ions via HFSLM.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Appendix.pdf](#)