



## Research article

# Application of green solvents for arsenic removal from petroleum produced water: Statistical, DFT and McCabe-Thiele determination

Natthawan Srinam<sup>a</sup>, Vanee Mohdee<sup>a</sup>, Ura Pancharoen<sup>a,\*</sup>, Kasidit Nootong<sup>a,\*\*</sup>,  
 Kreangkrai Maneeintr<sup>b,c</sup>, Wikorn Punyain<sup>d</sup>, Sirikul Chunsawang<sup>e,\*\*\*</sup>

<sup>a</sup> Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Patumwan, Bangkok, 10330, Thailand

<sup>b</sup> Department of Mining and Petroleum Engineering, Faculty of Engineering, Chulalongkorn University, Patumwan, Bangkok, 10330, Thailand

<sup>c</sup> Carbon Dioxide Capture, Transportation, Subsurface Utilization and Storage Research Center, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand

<sup>d</sup> Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok, 65000, Thailand

<sup>e</sup> Department of Chemical Engineering, College of Engineering, Rangsit University, Pathum Thani, 12000, Thailand

## ARTICLE INFO

## Keywords:

Arsenic extraction  
 Petroleum produced water  
 Vegetable oil  
 Mechanism  
 Optimization

## ABSTRACT

This work presents the novel application of green oils to extract arsenic ions from petroleum produced water via liquid-liquid extraction (LLE). In the experiment, the removal of arsenic ions from synthetic petroleum produced water is investigated, using five green oils: canola oil, corn oil, linseed oil, rice bran oil, and sunflower oil, in place of petroleum-based solvents: toluene and kerosene. Both extraction and stripping optimizations are examined. For extractants, Aliquat 336 and Cyanex 921 are implemented. The initial arsenic concentration ( $3.984 \text{ mg L}^{-1}$ ) of petroleum produced water is examined. Results demonstrate that Aliquat 336 in corn oil proved to be most effective for arsenic removal. At optimal conditions via response surface methodology (RSM), the highest extraction and stripping percentages reached 99.95 % and 100.00 %, respectively. In accordance with the World Health Organization (WHO) levels of  $\leq 0.01 \text{ mg L}^{-1}$ , arsenic concentration remaining in the extracted water ( $0.002 \text{ mg L}^{-1}$ ), is seen to fulfill the requirement needed. The extraction and stripping kinetics are of first and second-order. Mechanisms of arsenic removal are evaluated via density functional theory (DFT). Further, selectivity, recycling of the organic phase, and the number of stages via McCabe-Thiele theory are determined under optimal conditions.

## 1. Introduction

Petroleum underground water, also known as petroleum produced water derived from offshore oil and gas production sources, contains salts and toxic heavy metals, such as arsenic (As), other metals, and impurities [1,2]. Before being discharged into the environment, the petroleum produced water has to undergo treatment to get rid of this contamination [3]. It is well known that arsenic

\* Corresponding author.

\*\* Corresponding author.

\*\*\* Corresponding author.

E-mail addresses: [ura.p@chula.ac.th](mailto:ura.p@chula.ac.th) (U. Pancharoen), [kasidit.n@chula.ac.th](mailto:kasidit.n@chula.ac.th) (K. Nootong), [sirikul@rsu.ac.th](mailto:sirikul@rsu.ac.th) (S. Chunsawang).

<https://doi.org/10.1016/j.heliyon.2024.e36072>

Received 6 May 2024; Received in revised form 4 July 2024; Accepted 8 August 2024

Available online 10 August 2024

2405-8440/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC license (<http://creativecommons.org/licenses/by-nc/4.0/>).

is a hazardous metal, which is comprised of As (III) and As (V) species, which contaminate the water [4]. Arsenic can adversely affect both humans as well as other living organisms. Arsenic poisoning can cause a wide range of diseases, including cardiovascular disease [5], diabetes [6], neurological disorders [7] etc. Due to arsenic-contaminated drinking water in Southeast Asian countries, many people suffer from serious health issues, such as skin lesions as well as metabolic and cardiac disorders [8]. Arsenic poisoning in Bangladesh has emerged as a significant environmental, health, and social catastrophe. People who have been exposed to arsenic suffer a range of health issues, including hepatitis, renal failure, gastrointestinal, and reproductive difficulties as well as cancer [9].

Since 1993, under the World Health Organization (WHO) that is responsible for arsenic contamination, drinking water has been improved from  $0.05 \text{ mg L}^{-1}$  to  $0.01 \text{ mg L}^{-1}$ . However, due to the lack of sufficient testing facilities for arsenic contamination, developing countries have had to use former WHO levels [10]. In Thailand,  $0.05 \text{ mg L}^{-1}$  for the arsenic level in underground drinking water is recommended [11]. In addition, in the case of effluents, the arsenic levels in effluents do not exceed  $0.25 \text{ mg L}^{-1}$ , in accordance with Thailand's Ministries of Industry and Natural Resources and Environment levels [12]. Nevertheless, it is found that the concentration of arsenic ions in petroleum produced water still surpasses these levels [1].

To remove arsenic from water, numerous methods have been introduced including adsorption, coagulation, and ion-exchange. Many types of adsorbents have been also developed, such as nanoadsorbents like MXene [13], magnetite nanoparticles [14], and pyroaurite-based green adsorbents [15]. Nonetheless, these methods have vital drawbacks, which include the need for discarding sludge, and required high temperature for recycling adsorbents and resins [16]. Liquid-liquid extraction process (LLE) is a simple and widely used method, which has been found to be most effective in separating very low concentrations of metal ions from water [17]. LLE is low cost, and both extractants and solvents are easily recycled, employing this technique [3,18,19]. For the extractant, ionic liquids (ILs), such as tri-octyl-methylammonium chloride (Aliquat 336) and phosphine oxide (Cyanex) have been accepted for use in the process of arsenic removal from aqueous solutions [1,3,18–24].

Recently, toxic solvents, mostly volatile solvents and petroleum-based solvents have been replaced by green solvents i.e. green oils that are able to eliminate heavy metal ions from water [25]. Green oils are non-polar alternative solvents. Such solvents are non-volatile substances but have a high temperature flash point. Green oils are environmentally friendly and consist of hydrocarbon components mainly triglycerides and fatty acids [26]. Palm oil, for example, has been applied for the separation of nickel (II) from industrial effluent, using a supported liquid membrane extraction process to dilute bis(2-ethylhexyl) phosphate (D2EHPA); extraction and stripping percentages reached 91.0 % and 65.0 % at 299 K, respectively [27]. Besides, sunflower oil has been used to removal mercury (I) ions from water via the LLE process whereby extraction percentage reached 100.0 % at 323 K [26]. Further, sunflower oil has been employed to eliminate mercury (II) ions from water via hollow fiber supported liquid membrane (HFSLM); extraction and stripping percentage attained 98.0 % and 81 % at 323 K, respectively [16]. To remove chromium (VI) from water, rice bran oil has been applied, using emulsion liquid membrane extraction; extraction percentage reached 97.0 % [28].

To date, the application of green oils to remove As (V) ions from water, especially petroleum produced water is still rare. This research presents the novel application of green oils to substitute conventional toxic solvents for the removal of arsenic (V) ions from synthetic petroleum produced water via LLE method. Green oils used have been selected according to their different chemical and physical properties (Table S1) [29–42].

To optimize the experimental conditions in LLE, both response surface methodology (RSM) combined with the Box-Behnken design (BBD) have been applied as a statistically-based mathematical strategy. For BBD, the model required three levels of each parameter to be studied [43–45]. Furthermore, this approach has the capability to predict outcomes and to evaluate the significance of parameters through the analysis of variance analysis (ANOVA) [46]. Moreover, density functional theory (DFT) is employed to determine the characteristics of substances by demonstrating extraction and stripping mechanisms, including thermodynamics of the mechanisms. DFT is a theoretical attempt to describe the electronic structure and properties of substances from the electronic energy of the ground state as a function of electron density [47].

This work aims to find an appropriate new green oil as solvent to replace conventional toxic solvents for the removal of arsenic ions from synthetic petroleum produced water via LLE. Aliquat 336 and Cyanex 921 have been employed as extractants. Canola oil, corn oil, linseed oil, rice bran oil, and sunflower oil have been utilized as green solvents to compare the two toxic solvents: toluene and kerosene. In the investigation, stripping agents, including NaOH, HCl, thiourea, and the synergism of HCl + thiourea have been employed. In the extraction process, the effects of pH, volume of organic and aqueous phases ratio (O/A), and concentration of extractant have been examined via RSM combined with BBD. For the stripping process, the influence of stirring rate, temperature, and volume (A/O) ratio has been studied. Besides, kinetics of the optimal conditions for both extraction and stripping processes have been analyzed in terms of reaction orders and rate constants. Both the selectivity factor and recycling numbers of the organic phase have

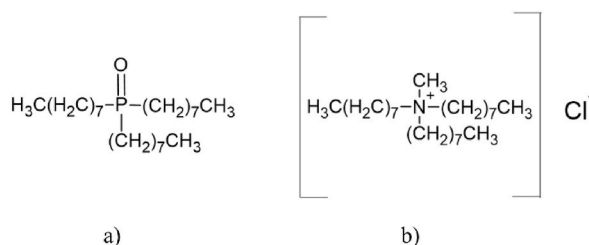


Fig. 1. Chemical structures of extractants: (a) Cyanex 921 and (b) Aliquat 336.

been determined. The number of stages in the column design for extraction and stripping processes has been determined by the McCabe-Thiele theory. Finally, extraction and stripping mechanisms as well as IR characterizations have duly evaluated by DFT.

## 2. Theory

### 2.1. Extraction

#### 2.1.1. Extraction mechanisms

To study the extraction reaction of arsenic ions, the mechanisms for extractants and arsenic species are investigated. In Fig. 1a and b, the chemical structures of the two extractants: Cyanex 921 and Aliquat 336 are shown. The As (V) (arsenate) ions in natural water has been classified into four species i.e.  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{AsO}_4^{3-}$ , depending on the pH of the water [48].

Mechanisms between As (V) ions and Aliquat 336 for dissociated forms:  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{AsO}_4^{3-}$  are shown in Eqs. (1)–(3), respectively [1,20]:



where  $\text{R}_4$  represents the short and long chain of alkyl groups, and  $\text{X}^-$  denotes the  $\text{Cl}^-$  (chloride ion) from the Aliquat 336 structure.

In Cyanex 921, one of the phosphine oxides extractants is seen to react with an undissociated ( $\text{H}_3\text{AsO}_4$ ) species in acid form, as in Eq. (4) [22,49,50]:



#### 2.1.2. Extraction and stripping calculations

For the extraction and stripping processes of arsenic ions, the extraction percentage (%E) and the stripping percentage (%S) are calculated. Eqs. (5) and (6) are defined, as follows [20]:

$$\%E = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (5)$$

$$\%S = \frac{C_s}{(C_0 - C_e)} \times 100\% \quad (6)$$

where  $C_0$  is the initial concentration of arsenic ions ( $\text{mg L}^{-1}$ ),  $C_e$  is the remaining concentration of arsenic ions after extraction ( $\text{mg L}^{-1}$ ), and  $C_s$  represents the remaining concentration of arsenic ions after stripping ( $\text{mg L}^{-1}$ ).

### 2.2. RSM for experimental design

Herein, RSM combined with the BBD model operates at three levels for each parameter ( $-1$ ,  $0$ , and  $+1$ ). For the extraction and stripping of arsenic ions, the three parameters are predicted in random order i.e. 15 runs and 3 duplications. To predict the extraction and stripping percentages of arsenic ions, a quadratic polynomial model is presented as in Eq. (7) [51]:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{1 \leq i < j \leq k} \beta_{ij} x_i x_j + \varepsilon \quad (7)$$

where  $y$  is the predicted required value,  $\beta_0$  is the intercept,  $\beta_i$ ,  $\beta_{ii}$  and  $\beta_{ij}$  are the linear, quadratic, and interaction coefficients of each parameter, respectively.  $x_i$  and  $x_j$  refer to each independent parameter.  $k$  refers to the number of independent parameters:  $k = 3$ , both  $i$  and  $j$  represent 1, 2 or 3. The predicted values of the parameters were analyzed via ANOVA to estimate the statistical values [46].

### 2.3. Synergistic coefficient

Nowadays, synergistic effects are widely used for systems that need to be matched with at least two classes of reagents to encourage the increased potential of the reagents for the systems [49,52–54]. The synergistic coefficient (SC) can be determined in terms of the distribution ratio [53]:

$$d_i = \frac{C_{aq}}{C_{org}} \quad (8)$$

$$SC = \frac{d_{ij}}{d_i + d_j} \quad (9)$$

where  $C_{aq}$  and  $C_{org}$  signify the concentration of arsenic in both the aqueous phase and organic phase of substance  $i$ . Thus,  $d_i$ ,  $d_j$ , and  $d_{ij}$  denote the distribution coefficient of arsenic ions for substance  $i$ , substance  $j$ , and binary interaction between  $i$  and  $j$ , respectively.

Further, if  $SC$  is greater than unity ( $>1$ ) synergism occurs. When  $SC$  is less than unity ( $<1$ ), it signifies an antagonistic effect. When  $SC = 1$ , there is no synergism [53].

#### 2.4. McCabe-Thiele theory

To apply the liquid-liquid extraction data on a commercial scale, a number of stages in both extraction and stripping processes need to be considered. The McCabe-Thiele theory is widely recognized and has been employed to determine the number of stages to achieve a specified separation [55].

To validate the precision of stage numbers derived from the diagram, the following Eqs. (10) and (11) were used [56]:

$$\varphi = \frac{\varepsilon - 1}{\varepsilon^{n+1} - 1} \quad (10)$$

$$\varepsilon = \frac{C_o \cdot V_o}{C_A \cdot V_A} \quad (11)$$

where the ratio of arsenic ions in the aqueous phase to the initial solution is represented by  $\varphi$  to estimate the efficiency of calculation.  $\varepsilon$  implies an extraction factor.  $C_o$  and  $C_A$  represent the concentration of arsenic ions that is held in the organic phase and the aqueous phase, respectively. Both  $V_o$  and  $V_A$  denote the volume between the organic and aqueous phase.  $n$  refers to the number of theoretical stages.

#### 2.5. Density functional theory (DFT)

DFT is arguably the most successful approach for electronic structure calculations [47]. The principle of DFT, based on the electronic energy of the ground state, is a function of electron density. The computational advantage of DFT is due to the fact that electron density has three spatial coordinates, regardless of the number of electrons in a chemical system. DFT enables the calculation of structures and properties of molecules within a couple of hundred atoms. Hence, DFT is directly related to the intensity of a chemical bond, which is proportional to the energy required to break it down. Bond energy decreases as bond length increases, inversely proportional to bond length [57]. In this work, the extraction and stripping mechanisms of arsenic species were calculated via DFT.

**Table 1**  
Chemical reagents used in the experiments.

Substances	Properties				Source
	MW (g/mol)	Formular	Purity <sup>a, b</sup> (%)	CAS No.	
Aliquat 336	404.2 <sup>a</sup>	C <sub>25</sub> H <sub>54</sub> ClN [59]	90.6	63393-96-4	Acros, Belgium
Cyanex 921	386.6 <sup>a</sup>	C <sub>24</sub> H <sub>51</sub> OP <sup>a</sup>	90.0	78-50-2	Cytec
Toluene	92.1 <sup>a</sup>	C <sub>7</sub> H <sub>8</sub> <sup>a</sup>	99.9	108-88-3	Fisher, U.S.
Kerosene	≈170.0 <sup>a</sup>	C <sub>9</sub> – C <sub>16</sub> <sup>a</sup>	99.0	8008-20-6	Shell, Thailand
Canola oil	≈880.5 [31]	C <sub>14</sub> – C <sub>18</sub> [31]	100.0	120962-03-0	Lam Soon Public
Corn oil	≈872.3 [31]	C <sub>14</sub> – C <sub>18</sub> [30]	100.0	8001-30-7	Thai Vegetable Oil, Thailand
Linseed oil	≈878.3 [36]	C <sub>14</sub> – C <sub>18</sub> [36]	100.0	8001-26-1	ST Art Material
Rice bran oil	≈867.9 [37,60]	C <sub>14</sub> – C <sub>18</sub> [38]	100.0	68553-81-1	King Rice Oil Group, Thailand
Sunflower oil	≈876.2 [40]	C <sub>14</sub> – C <sub>18</sub> [61]	100.0	8001-21-6	Thanakorn Vegetable Oil, Thailand
Hydrochloric acid solution	36.5 <sup>b</sup>	HCl	37.0	7647-01-0	Qrec, Thailand
Sodium hydroxide <sup>c</sup>	40 <sup>a</sup>	NaOH	98.0	1310-73-2	Merck, U.S.
Thiourea <sup>c</sup>	76.12 <sup>a</sup>	(NH <sub>2</sub> ) <sub>2</sub> CS	99.0	62-56-6	Loba Chemie
Sodium chloride <sup>c</sup>	58.4	NaCl	99.5	7647-14-5	Loba Chemie
As standard solution <sup>d</sup>	74.9	As	N/A	7697-37-2	PanReac AppliChem
Hg standard solution <sup>d</sup>	200.6	Hg	N/A	7783-34-8	PanReac AppliChem
Fe standard solution <sup>d</sup>	55.8	Fe	N/A	7439-89-6	PanReac AppliChem
Mg standard solution <sup>d</sup>	24.3	Mg	N/A	7732-18-5	PanReac AppliChem
Ca standard solution <sup>d</sup>	40.0	Ca	N/A	7697-37-2	PanReac AppliChem

<sup>a</sup> Properties from label and sources.

<sup>b</sup> Test by GC technique; MW: average molecular weight.

<sup>c</sup> Solid substance.

<sup>d</sup> The standard concentration 1000 mg L<sup>-1</sup>

## 2.6. Distribution coefficient and selectivity factor

Distribution coefficients ( $D$ ) are employed to estimate the distribution between the organic phase and the aqueous phase.  $D$  values plus a selectivity factor or separation factor ( $S$ ) can be expressed, as in Eqs. (12) and (13) [58]:

$$D_i = \frac{C_{a,org}}{C_{a,aq}} \quad (12)$$

$$S = \frac{D_{As}}{D_j} \quad (13)$$

where  $D$  represents the distribution coefficient of component  $i$  between the organic phase and aqueous phase.  $i$  identifies each component (As, Hg, Fe, Mg, and Ca). Subsequently,  $S$  defines the selectivity factor of component  $i$  versus component  $j$ . If  $D_i$  is greater than one ( $>1$ ), it signifies that the component  $i$  in the organic phase demonstrates a higher capability compared to that in the aqueous phase. If  $S$  is more than one ( $>1$ ), it means that the selectivity of arsenic is higher compared to component  $j$  in the organic phase.

## 3. Experimental

### 3.1. Reagents

All chemicals and materials were commercially available and used without further purification. In Table 1, the chemical reagents used in the experiments are listed. Synthetic petroleum produced water was synthesized from standard arsenic acid solution in the form of H3AsO4 mixed with other metals in the deionized (DI) water. Arsenic and other metals i.e. mercury, iron, magnesium, and calcium were added in the synthetic petroleum produced water. Excess salt was prepared from sodium chloride. HCl and NaOH were applied for pH adjustment. Aliquat 336 and Cyanex921 were employed as extractants. Commercial solvents used included: toluene and kerosene. Green oils are employed as green solvents: namely, canola oil, corn oil, linseed oil, rice bran oil, and sunflower oil. NaOH, HCl, and thiourea were used for the stripping solution. The concentrations of arsenic were detected via inductively coupled plasma optical emission spectrometry analysis (ICP-OES), as used by Agilent 5800 model.

### 3.2. Procedures

#### 3.2.1. Extraction and stripping procedures

The aqueous phase was prepared using 25 ml of synthetic petroleum produced water at pH = 6. In this work, the synthetic petroleum produced water was synthesized following the composition of the produced water from the Gulf of Thailand. In Table 2, the composition of the produced water is shown [3]. The organic phase was prepared using 0.28 M for each extractant, Aliquat 336 and Cyanex921, and each solvent: canola oil, corn oil, linseed oil, rice bran oil, sunflower oil, kerosene, and toluene. Next, both the aqueous phase and organic phase were mixed together in a closed beaker, using O/A ratio (1:1), T = 303.2 K, 0.1 MPa, and 500 rpm for 1 h to ensure the reaction entered the equilibrium state [20].

After that, the mixture was left to rest in a closed separation funnel until two phase layers completely formed via the force of gravity. Consequently, arsenic concentration from the under layer was collected for analysis via ICP-OES technique. As for the stripping, the organic phase for stripping was derived from the top phase after extraction procedures under optimal conditions. The aqueous phase of the stripping process was prepared at 0.5 M for each stripping agent (NaOH, HCl, thiourea, and mixture of HCl + thiourea). Finally, the organic and aqueous phases were mixed together, using the same conditions as in the extraction procedure.

#### 3.2.2. Experimental design via response surface methodology (RSM)

RSM, combined with the BBD model, was developed by Minitab 19 software to predict and optimize experimental conditions for both extraction and stripping procedures. As observed in Figs. S2–S4, preliminary investigations to find a suitable range of parameters i.e. the pH of synthetic petroleum produced water, concentrations of extractant in the solvent, and concentrations of stripping agent, were carried out to find the highest extraction and stripping percentages in the RSM design. In Table 3, three levels of each parameter for the RSM design are shown. RSM experiments were conducted as well as extraction and stripping procedures, using the designed conditions. Optimal conditions, as determined via RSM, were further investigated to study kinetics, mechanisms and characterizations.

### 3.3. DFT simulations

Optimal conditions were used to find the mechanisms for the removal of arsenic ions in both extraction and stripping reactions. To

**Table 2**  
Produced water composition [1].

Composition	As	Hg	Fe	Mg	Ca
Concentration (mg L <sup>-1</sup> )	3.984	0.279	0.169	2.014	15.18

**Table 3**

The BBD level of each parameter for RSM design.

Parameters	Abbreviations	Levels		
		-1	0	1
<b>Extraction process</b>				
pH of synthetic petroleum produced water	$x_1$	6	9	12
O/A ratio	$x_2$	0.5	0.75	1.0
Concentrations of extractant (M)	$x_3$	0.28	0.48	0.68
<b>Stripping process</b>				
Stirring rate (rpm)	$x_4$	300	400	500
Stripping temperatures (K)	$x_5$	303.2	313.2	323.2
A/O ratio	$x_6$	0.5	1.0	1.5

explain the interaction between the extractant and arsenic molecules, quantum chemical calculations were implemented via DFT at B3LYP/LANL2DZ level of theory. Solvation effects were taken into account, applying the conductor-like polarizable continuum model (CPCM). All calculations were completed employing Gaussian09 program package [62]. Molecular geometries were drawn, using the Gabedit and Avogadro program package [63,64].

### 3.4. McCabe-Thiele graphical design

In the McCabe-Thiele experiments, both aqueous and organic phases were combined together in a total volume of 50 ml: O/A ratio varied from 1:8 to 3:1 (for the extraction process), A/O ratio varied from 1:9 to 2:1 (for the stripping process), under stirring (500 rpm), and temperature (303.2 K) in the closed system. Both extraction and stripping procedures were analyzed via ICP-OES. In the organic phase, the concentration of arsenic ions was determined by a mass balance equation, which proved negligible; the change in volume of both the extraction and stripping processes was very small.

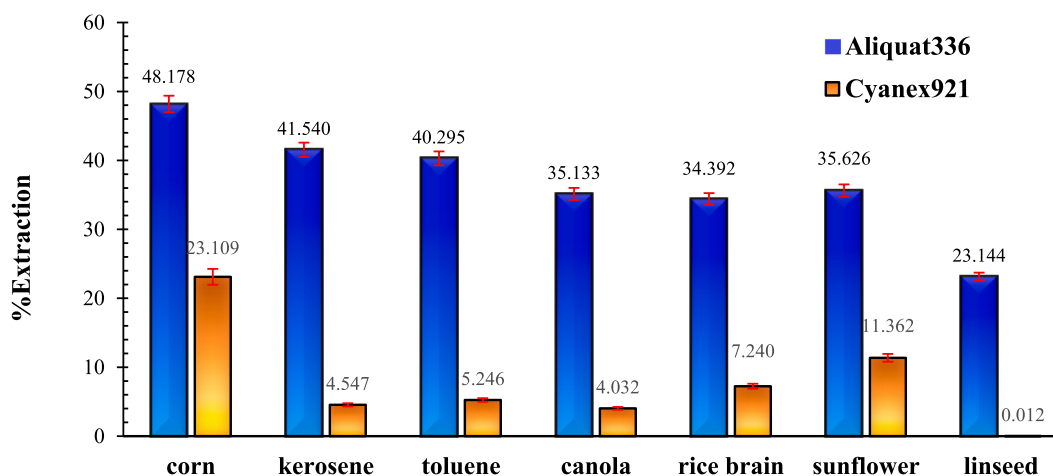
## 4. Results and discussion

### 4.1. Selection of substances in the organic phase

To identify suitable substances in the organic phase, types of extractants and green solvents were investigated for the effective extraction of arsenic ions.

#### 4.1.1. Effect of extractants

In Fig. 2, the effect of extractants and solvent types for arsenic extraction is shown. Results demonstrated that Aliquat 336 provided a better extraction tendency for all organic solvents than Cyanex 921. Herein, at initial pH of synthetic petroleum produced water (pH = 6), it is noted that arsenic forms are favorable to the dissociated forms:  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ . According to the literature, Aliquat 336 is seen to have the ability to extract dissociated forms of arsenic ions through the mechanism of  $\text{Cl}^-$  ion-exchange [3,21,49,65]. It is noted that the  $\text{CH}_3\text{R}_3\text{N}^+$  is attracted to  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  through  $\text{Cl}^-$  ion-exchange and electrostatic attraction. Then, the two complexes:  $\text{CH}_3\text{R}_3\text{N}^+\cdot\text{H}_2\text{AsO}_4^-$  and  $(\text{CH}_3\text{R}_3\text{N}^+)_2\cdot\text{HAsO}_4^{2-}$  appeared and dissolved in the organic phase. Simultaneously, the released  $\text{Cl}^-$



**Fig. 2.** Effect of extractant and solvent types on the extraction of arsenic ions, using 0.28 M for extractant concentrations, synthetic produced water at pH 6, stirring 500 rpm for 1 h, O/A ratio = 1, at 303.2 K and 0.1 MPa.

from Aliquat 336 structures can attract water molecules, dissolved in the aqueous phase [12,20,66]. Cyanex 921 can attach arsenic ions in undissociated form ( $\text{H}_3\text{AsO}_4$ ) only [1,20].

#### 4.1.2. Effect of green solvents

In Fig. 2, it is seen that corn oil has the potential for use as a green solvent greater than kerosene, toluene, sunflower oil, canola oil, rice bran oil, and linseed oil, respectively. Such results arose due to the effects of the physical and chemical properties of the solvents, such as polarity, the mutual solubility for the stability of organic phase, mixed Gibbs free energy of dissolution, and intramolecular interactions between Aliquat 336 and each solvents.

It is acknowledged that the dielectric constant ( $\epsilon$ ) of substances directly relates to their polarity, as high  $\epsilon$  values imply the high polarity of the substances. The near  $\epsilon$  values of the two substances, representing near polarity, dissolve into each other [67]. In this work, the  $\epsilon$  values of Aliquat 336 is closer to water than all solvents [68]. As for the Aliquat 336 structure, it consists of tiny polar and non-polar functional groups of the long chain ternary amine. Aliquat 336 is seen to form a hydrogen bond between water molecules and the nitrogen atom of Aliquat 336, causing a decrease in the stability of the organic phase [68,69]. To prevent such an occurrence from happening, the good properties of the solvents must hold the amount of Aliquat 336 and resist the water soluble in the organic phase.

Within the organic phase, it has been observed that solvents with low  $\epsilon$  values enhance the distribution of Aliquat 336 and resist dissolving in water [67,68,70]. Corn oil expressed the lowest  $\epsilon$  values, as shown in Table S2 [41,42,70–72]. It is significant that water solubility in the mixture of Aliquat 336 and corn oil is the lowest, indicating the good performance of corn oil. Furthermore, thermodynamics behavior and intramolecular interaction of dissolution between Aliquat 336 and corn oil indicates excellent performance and good compatibility [68,70].

Overall, taking into account the solubilities, stability, thermodynamics of dissolutions, and intramolecular interactions, corn oil is regarded as a suitable solvent to dilute Aliquat 336. The application of green oil has been widely used to separate metal ions from water [16,26–28]. However, such application for the removal of arsenic ions is still very rare. It is a novel feature of this work for the investigation of alternate solvents to remove arsenic ions from petroleum produced water. Moreover, one such solvent, i.e. corn oil, proved to be successful. Therefore, corn oil was selected to investigate optimal conditions.

#### 4.2. Optimal conditions for arsenic extraction

To determine optimal conditions, the RSM design for optimization of extraction and stripping was investigated. Ranges of parameters were selected through preliminary investigations and reported literature [1,3,20,21,26,29].

As shown in Eq. (14), extraction percentages of arsenic ions can be estimated:

$$\%E = -112.5 + 9.86x_1 + 215.2x_2 + 115.7x_3 - 0.398x_1^2 - 120.2x_2^2 - 123.6x_3^2 - 0.57x_1x_2 + 3.88x_1x_3 + 10.4x_3x_4 \quad (14)$$

where %E is the extraction percentages of arsenic,  $x_1$  represents the concentration of Aliquat 336,  $x_2$  replaces the pH of synthetic petroleum produced water, and  $x_3$  refers to the ratio of O/A.

In Table S3 and Fig. S1, the actual and predicted extraction percentages of arsenic ions via RSM at 303.2 K and 0.1 MPa are illustrated. When the predicted (RSM) values and the actual values of the experiments are compared, the regression equation achieved  $\text{RAD} \leq 0.0507$  and  $R^2$  equaled 0.9897. Such results indicate a low deviation between actual values and predicted values. The predicted extraction results, therefore, are seen to fit in with the experimental results. In Table 4, to analyze the significance of parameters for extraction efficiency, the analysis of variance (ANOVA) was utilized. Consequently, the P-values of individual parameters proved to be

**Table 4**  
ANOVA in the extraction system.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
<b>Model</b>	9	2674.53	297.17	53.48	0.000
<b>Linear</b>	3	2344.93	781.64	140.67	0.000
pH ( $x_1$ )	1	1234.99	1234.99	222.26	0.000
O/A ( $x_2$ )	1	603.26	603.26	108.57	0.000
Conc. ( $x_3$ )	1	506.68	506.68	91.19	0.000
<b>Square</b>	3	306.09	102.03	18.36	0.004
$x_1$ $\times$ $x_1$	1	47.27	47.27	8.51	0.033
$x_2$ $\times$ $x_2$	1	208.31	208.31	37.49	0.002
$x_3$ $\times$ $x_3$	1	90.25	90.25	16.24	0.010
<b>2-Way Interaction</b>	3	23.51	7.84	1.41	0.343
$x_1$ $\times$ $x_2$	1	0.74	0.74	0.13	0.730
$x_1$ $\times$ $x_3$	1	21.69	21.69	3.90	0.105
$x_2$ $\times$ $x_3$	1	1.07	1.07	0.19	0.679
<b>Error</b>	5	27.78	5.56		
<b>Lack-of-Fit</b>	3	27.78	9.26	484051.82	0.000
<b>Pure Error</b>	2	0.00	0.00		
<b>Total</b>	14	2702.31			



< 0.05, signifying that all the parameters were significant [29].

### 4.3. Effect of parameters for arsenic extraction

To select the appropriate pH range for the RSM experiment, the effect of pH was preliminary tested (Fig. S2). Results reveal that the suitable pH levels were 6, 9, and 12 since such pH afford high extraction percentages and cover the three dissociated forms of arsenic ions [48,73]. In Fig. 3, the results of RSM optimization for the extraction of arsenic ions are given. In Fig. 3a, the effect of each parameter on the extraction percentages of arsenic ions is shown. As a result, when pH increased, extraction percentages increased, providing the optimal pH = 12. Due to the extraction mechanisms of Aliquat 336 and arsenic ions through the Cl<sup>-</sup> ion-exchange, Aliquat 336 favorably reacted with the dissociated forms of arsenic ions [74]. In addition, it is seen that when pH increased, the binding distances between arsenic anion and water increased, influencing the decreased strength of the binding interaction energy between arsenic anion and water [75]. It is significant that arsenic ions at pH = 12 (AsO<sub>4</sub><sup>3-</sup>) can react more easily with Aliquat 336 than the dissociated forms: H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> (pH = 6) and HAsO<sub>4</sub><sup>2-</sup> (pH = 9).

To select the range of the extractant, Aliquat 336 concentrations were preliminary tested (Fig. S3). Results indicate that the most suitable range was from 0.28 M to 0.68 M. This range required less extractant to achieve high percentages of arsenic extraction. Thus, such a range was selected for RSM examination. Herein, it is seen that when the concentration of Aliquat 336 in corn oil increased, percentages of arsenic extraction increased, up to the optimal 0.68 M. Such findings proved to be in accordance with Le Chatelier's principle whereby an increase in reactant concentration results in an increased forward reaction. Thus, the increase in Aliquat 336 concentration in corn oil led to the increase in (CH<sub>3</sub>R<sub>3</sub>N<sup>+</sup>)<sub>3</sub> · (AsO<sub>4</sub><sup>3-</sup>) [76].

As for O/A ratio, in the RSM experiment, O/A ratios ranged from 0.5 to 1.0 [1,3,20,21]. Results indicate that when O/A ratio increased, extraction percentages of arsenic ions increased, up to a threshold of 0.9. However, when O/A ratios increased over the 0.9

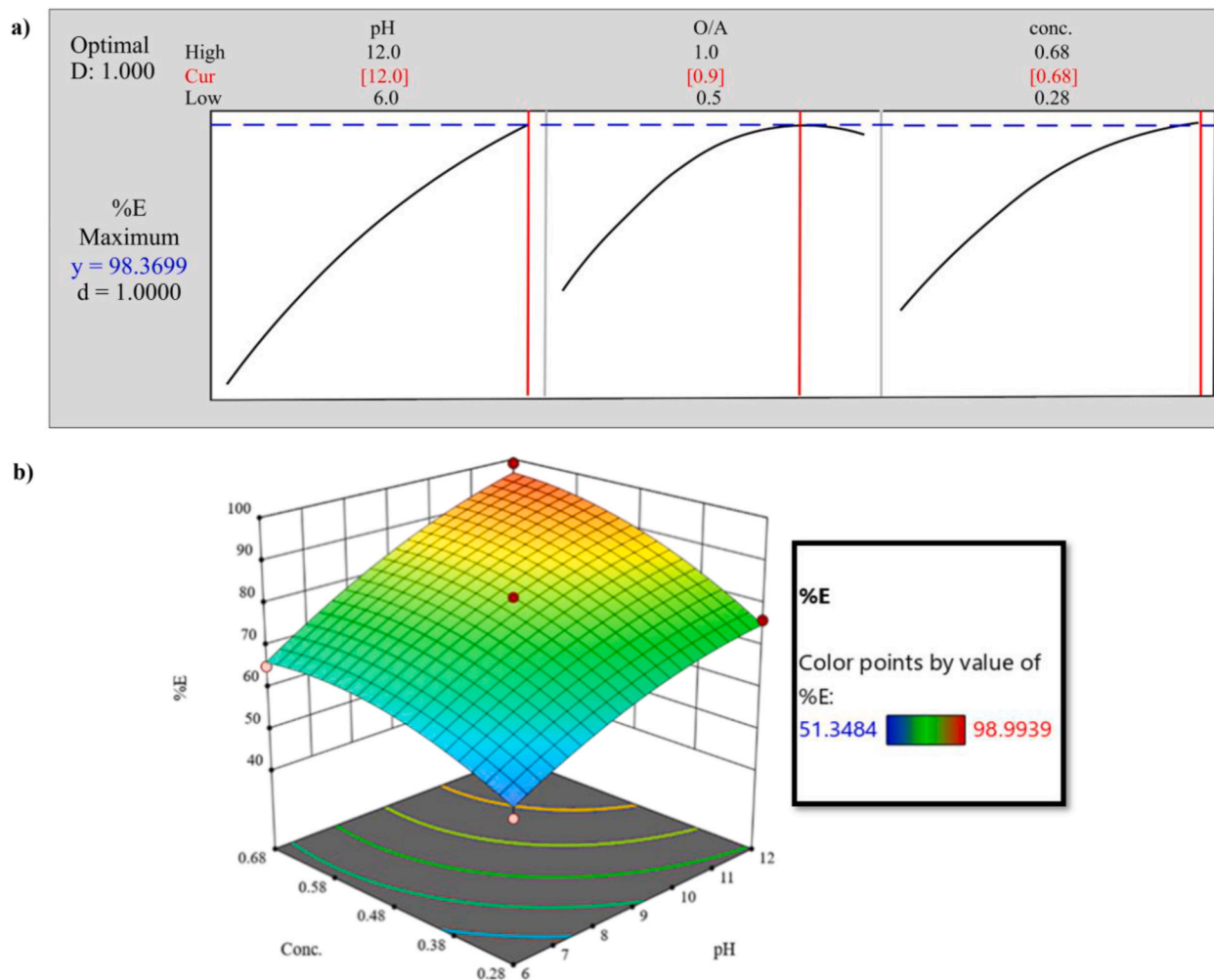


Fig. 3. RSM optimization of the arsenic ions extraction: (a) effect of each parameter regards extraction, and (b) optimized surface plot of the binary interaction between the concentrations of Aliquat 336 in corn oil and pH of synthetic produced water.



threshold, extraction percentages decreased. This outcome came about because equilibrium states were disturbed by changing conditions, leading to reverse reaction [76,77]. In the extraction section, the effect of stirring rate was not investigated because preliminary results indicated that stirring rate hardly influences extraction percentages, as shown in Fig. S4.

In Fig. 3b, the optimized surface plots of the binary interaction between the concentrations of Aliquat 336 in corn oil, and the pH of synthetic petroleum produced water for arsenic extraction, as plotted by Design Expert 13 software are shown. Results demonstrate that optimal conditions reveal maximum extraction of arsenic (99.95 %) at pH 12, O/A ratio = 0.9, and 0.68 M Aliquat 336 in corn oil. In Fig. S5, other optimized surface and contour plots of the binary parameter interaction for arsenic extraction are demonstrated. Results are consistent with the P-values of the individual parameters via ANOVA; the ellipse lines in the contour plots indicate the significance of all parameters for the extraction percentages of arsenic ions [16].

#### 4.4. Effect of stripping agent types

To determine the types of stripping agent, optimal conditions for extraction were investigated. In Fig. 4, the stripping percentages of arsenic ions obtained by various types of stripping solutions, using 0.5 M HCl, 0.5 M thiourea, 0.5 M NaOH, and 0.5 M HCl + 0.5 M thiourea solution, are shown. As observed, in the pure stripping agents, the stripping percentages of HCl proved to be higher than NaOH and thiourea. After the extraction process, the form of arsenic in the organic phase proved to be  $(NR_4^+)_3(AsO_4)^{3-}$  [74]. In the case of HCl solution, the discharged arsenic anions reacted with  $H^+$  to form  $H_3AsO_4$  (undissociated form). It is noted that the ion-exchange phenomena of both  $CH_3R_3N^+$  plus the dissociated forms of arsenic ions i.e.  $H_2AsO_4^-$ ,  $HAsO_4^{2-}$ , and  $AsO_4^{3-}$  facilitated the extraction mechanisms between Aliquat 336 and arsenic. The undissociated form ( $H_3AsO_4$ ) hardly reacted with Aliquat 336, preventing the recovery of arsenic anions into the organic phase [20]. In the case of NaOH solutions, hydroxyl substitution produced  $(NR_4^+ \cdot OH^-)_3$  [78]. However, arsenic ions are still in anion form in the high pH situation, so anions can be recovered back into the organic phase [20]. As for thiourea, it is seen to dissolve in the water wherein the non-charge complex:  $TU-(H_2O)_a$  appeared, where  $a$  represents the number of  $H_2O$  molecules [79]. Such complex hardly reacts with  $(NR_4^+)_3(AsO_4)^{3-}$  [20]. It is observed that the mixture of HCl + thiourea provided the highest stripping percentages of arsenic ions. Such results arose due to the synergistic effect between HCl and the thiourea molecules from the strongly protonated ions of the thiourea molecules via HCl [60]. The synergistic effect is verified by the SC values of system (1.357) [53].

#### 4.5. Optimal conditions. for arsenic stripping

As shown in Eq. (15), the stripping percentage of arsenic ions can be estimated, applying RSM. Thus, a regression equation is derived:

$$\%S = 1119 + 0.37 x_4 - 3.2 x_5 - 971x_6 + 0.000602 x_4^2 + 0.0004 x_5^2 + 54.5 x_6^2 - 0.00214 x_4x_5 - 0.1188 x_4x_6 + 2.797 x_5x_6 \quad (15)$$

where %S is the stripping percentages of arsenic ions,  $x_4$  represents the stirring rate (rpm),  $x_5$  indicates the temperature of the stripping operation (K), and  $x_6$  refers to the ratio of aqueous and organic volume. Table S4 shows the actual and predicted stripping percentages of arsenic ions at 0.1 MPa. It is found that the predicted values proved to be accurate, indicating that RAD was <0.4510 and  $R^2$  equaled 0.9640. As observed in Table 5, in the stripping of arsenic ions, results show that the P-values were below 0.05. It is evident, therefore, that all parameters had a significant effect on the stripping percentages of arsenic ions [29].

#### 4.6. Effect of parameters for arsenic stripping

As shown in Fig. S6, results reveal that the suitable stripping concentration was 0.5 M HCl + 0.5 M thiourea. For the stripping of arsenic ions, parameters (stirring rate, temperature, and A/O ratio) were implemented. In Fig. 5, RSM optimization regards the

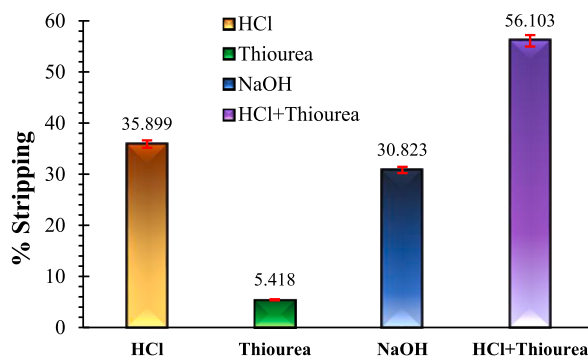
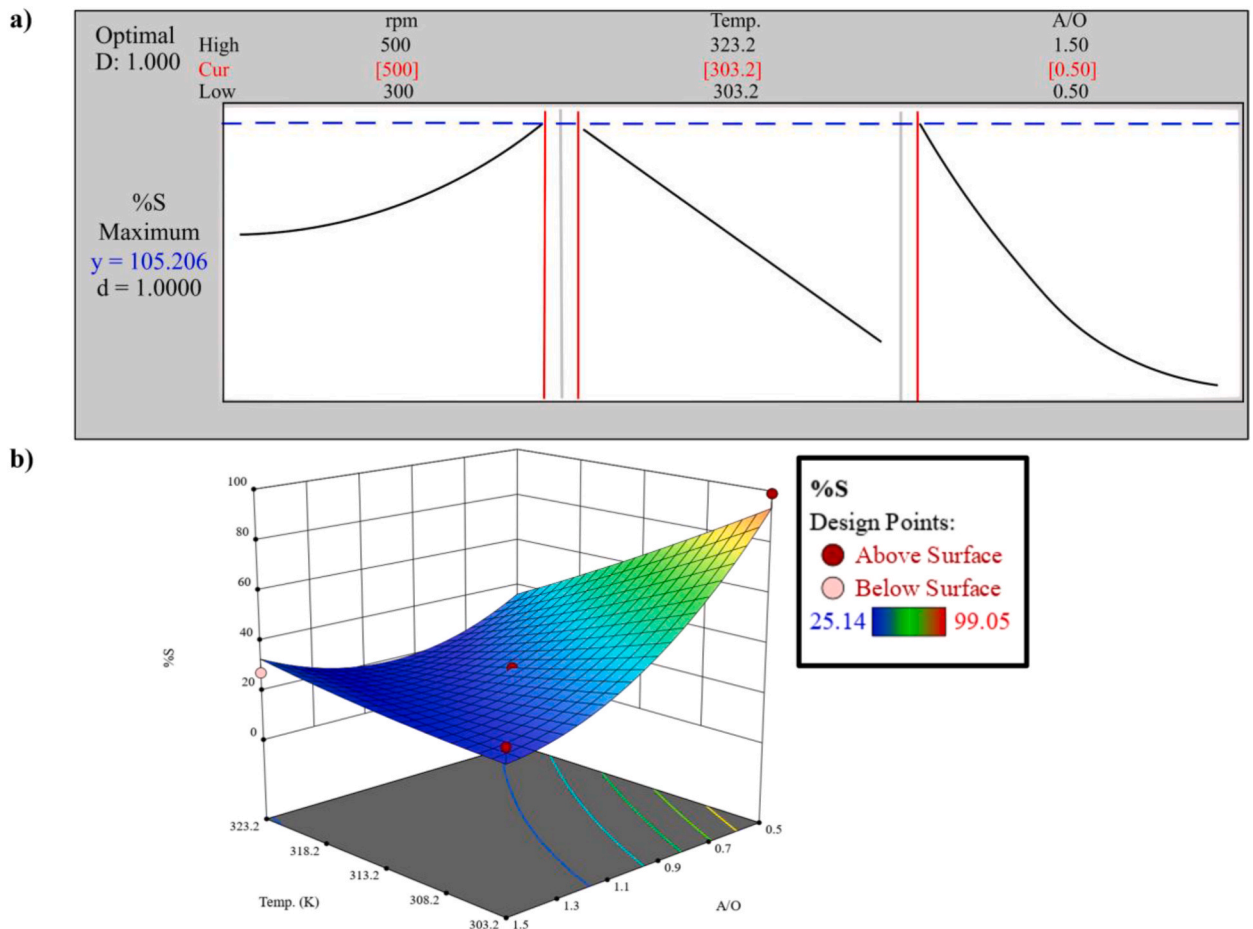


Fig. 4. Effect of types of stripping agents regards the stripping percentages of arsenic ions, using 0.5 M for each stripping concentration, 500 rpm, 1 h, O/A ratio = 1, 303.2 K, and 0.1 MPa.

**Table 5**  
ANOVA in the stripping system.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
<b>Model</b>	9	5195.03	577.23	14.89	0.004
<b>Linear</b>	3	3469.08	1156.36	29.83	0.001
Stirring rate ( $x_4$ )	1	283.82	283.82	7.32	0.042
Temperatures ( $x_5$ )	1	882.95	882.95	22.78	0.005
A/O ( $x_6$ )	1	2302.32	2302.32	59.39	0.001
<b>Square</b>	3	784.36	261.45	6.74	0.033
$x_4 \times x_4$	1	133.82	133.82	3.45	0.122
$x_5 \times x_5$	1	0.01	0.01	0.00	0.991
$x_6 \times x_6$	1	685.59	685.59	17.69	0.008
<b>2-Way Interaction</b>	3	941.59	313.86	8.10	0.023
$x_4 \times x_5$	1	18.28	18.28	0.47	0.523
$x_4 \times x_6$	1	141.13	141.13	3.64	0.115
$x_5 \times x_6$	1	782.18	782.18	20.18	0.006
<b>Error</b>	5	193.83	38.77		
<b>Lack-of-Fit</b>	3	193.83	64.61	102014.00	0.000
<b>Pure Error</b>	2	0.00	0.00		
<b>Total</b>	14	5388.86			



**Fig. 5.** RSM optimization for the stripping of arsenic ions: (a) effect of each parameter on the stripping, and (b) optimized surface plot of the binary interaction between temperature and A/O ratio.

stripping of arsenic ions is shown. In Fig. 5a, the effect of each parameter on the stripping percentages of arsenic ions is illustrated. The stirring rate was examined in the range from 300 to 500 rpm [26,29]. Results demonstrated that the highest stripping percentages occurred at 500 rpm, indicating that this was the optimal stirring rate. Temperature and A/O ratio were investigated in ranges from 303.2 K to 323.2 K and 0.5 to 1.0, respectively [1,3,20,21]. It is noted that when the parameters increased, stripping percentages

decreased. Therefore, 500 rpm, 303.2 K, and 0.5 A/O ratio were chosen for the optimal condition for the stripping.

In Fig. 5b, the optimized surface plots of the binary interaction between temperature and A/O ratio on the stripping of arsenic ions are exhibited, revealing that the stripping percentages of arsenic ions reached 100.00 %. In Fig. S7, other optimized surface and contour plots of the binary parameters for arsenic stripping are illustrated. As observed, the ellipse lines from the contour plots indicate the significance of all the parameters on the stripping percentages of arsenic ions [16].

#### 4.7. Characterization

To verify the validity of DFT calculations, B3LYP/LANL2DZ level IR vibrational spectrum calculations were carried out for optimal extraction and optimal stripping conditions, comparing them to the experimental IR vibrational spectrum.

##### 4.7.1. IR vibrational spectra of arsenic extraction

In Table 6, wavenumbers of the experimental spectra versus predicted spectra of the organic phase via DFT [80–84] are shown. In Fig. 6, experimental and predicted IR spectra in the organic phase (Aliquat 336 in corn oil) before and after the extraction process, are displayed. It can be seen that the vibrational peaks of the organic phase after extraction were quite similar to those before extraction. The four main peaks were derived from the vibration of C–H bonding in the Aliquat 336 molecule, fatty acid molecules, and  $(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})$  supramolecular complex.

As observed, the peaks around  $400\text{--}800\text{ cm}^{-1}$  are attributed to the As–O bond and the rocking vibration of  $\text{CH}_2$  due to  $(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})$  supramolecular complex, which appeared in the IR spectra of the organic phase after extraction [80–84]. This outcome confirmed that the extraction of arsenic ions occurred. In addition, after extraction, the peaks of the  $\text{Cl-H}_2\text{O}$  molecule around  $3300\text{--}3405\text{ cm}^{-1}$  (blue line) appeared because the chloride-water molecule slightly dissolved in the organic phase, through electrostatic attraction by the  $\text{CH}_3\text{R}_3\text{N}^+$  combining with the H atom of the water molecule. When water dissolves in the organic phase,  $\text{Cl}^-$  from  $(\text{CH}_3\text{R}_3\text{N}^+)\text{Cl}^-$  molecule can also be attracted to the water molecule [69,85]. As a result, it was found that the wavenumber of the experimental spectra was close to the wavenumber of the predicted spectra. This outcome proved that the experimental spectra fitted in well with the predicted spectra via DFT.

##### 4.7.2. IR vibrational spectra of arsenic stripping

In Table 7, wavenumbers of the experimental spectra versus predicted spectra of the aqueous phase via DFT are shown [80,86–88]. In Fig. 7, the experimental IR spectra and predicted IR spectra in the aqueous phase before and after the stripping of arsenic ions are displayed. It was found that the experimental IR spectra followed the same trend as the predicted IR spectra. This outcome proved that the experimental spectra fitted in well with the predicted spectra via DFT. The peaks in the aqueous phase occurred through the vibration of thiourea ( $\text{NH}_2\text{CSNH}_2$ ), HCl, and water molecules. Moreover, the wavenumbers around  $641\text{--}707\text{ cm}^{-1}$ , due to the As–O vibration in the experimental spectra, disappeared. This outcome came about because of the very low amount of arsenic in the aqueous phase, based on the amount of thiourea, HCl, and water molecules. Thus, the experimental spectra only exhibited the dominant peaks of thiourea, HCl, and water molecules [89].

#### 4.8. Kinetics

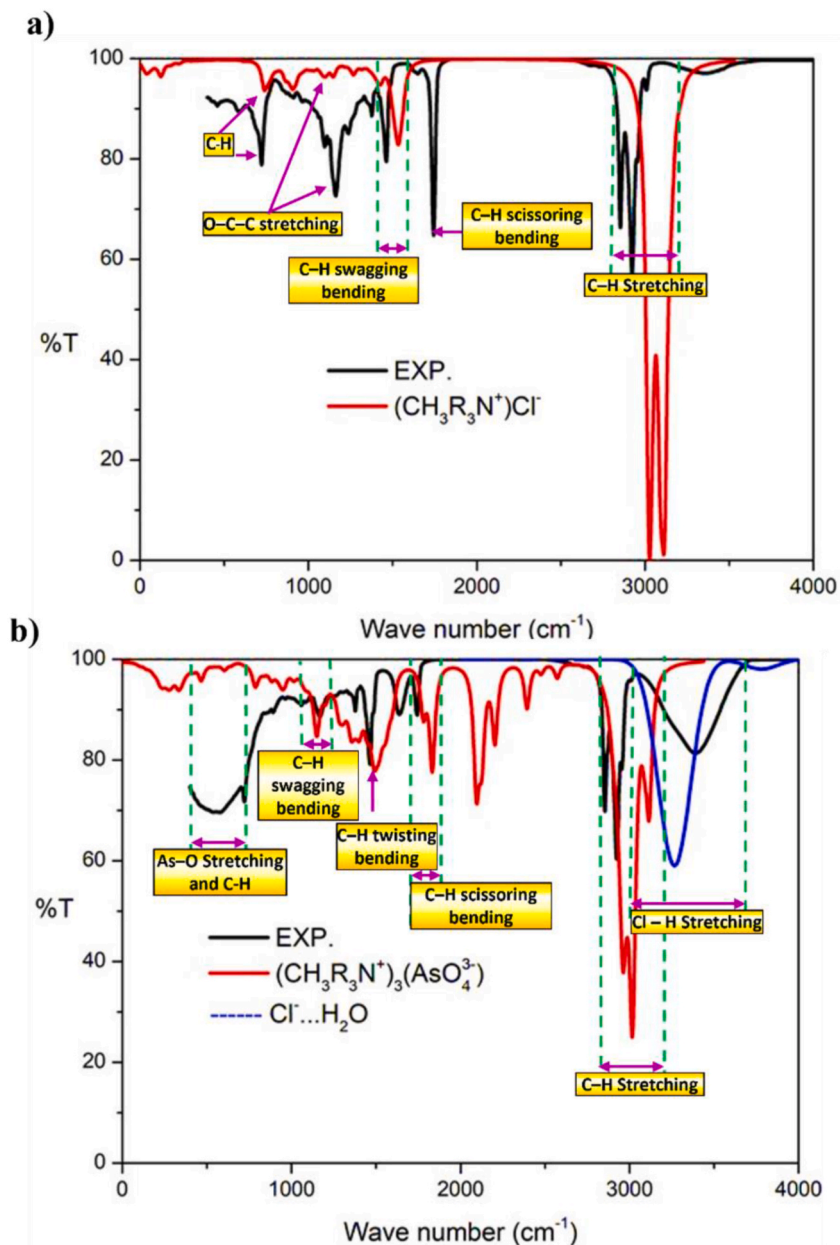
In Fig. 8a and b, equilibrium times of arsenic extraction reaction and arsenic stripping reaction are demonstrated. It is noted that for both extraction and stripping reactions, the concentration of arsenic remained constant over 120 s and 250 s, respectively. Reactions of extraction and stripping were caused due to the rate-limiting reaction and concentration gradient until equilibrium was reached [76]. Therefore, the operating times of 120 s and 250 s were selected for both extraction and stripping reactions, for reaction orders and rate

**Table 6**

Wavenumbers of the experimental spectra versus predicted spectra in the organic phase for arsenic extraction via DFT.

Wavenumber ( $\text{cm}^{-1}$ )		Functional group assigned by	Ref
Experimental (black line)	Predicted (red line)		
<b>Before extraction</b>			
723	730–735	$\text{CH}_2$ in $(\text{CH}_3\text{R}_3\text{N}^+)\text{Cl}^-$ and fatty acid molecules	[81–83]
1162	1150–1200	O–C–C stretching	[82]
1463 and 1544	1470 and 1744	The bending of C–H wagging and C–H scissoring in $(\text{CH}_3\text{R}_3\text{N}^+)\text{Cl}^-$ and corn oil molecules	[82,83]
1742	None	C–H scissoring in the $(\text{CH}_3\text{R}_3\text{N}^+)\text{Cl}^-$ molecule	[84]
2853–2923	3000–3200	The stretching of C–H bonds in the $(\text{CH}_3\text{R}_3\text{N}^+)\text{Cl}^-$ molecule	[82,83]
<b>After extraction</b>			
400–800	500–820	As–O bond and $\text{CH}_2$ rocking from $(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})$ supramolecular complex.	[80–84]
1069–1137		The twisting of C–H bending	[81–83]
1464	None	The wagging of C–H bending	[84]
1641–1742	1700–1800	C–H scissoring	[84]
2853–2923	2900–3000	C–H stretching	[84]
3405	3250–3350 <sup>a</sup>	Cl–H bonded stretching from $\text{Cl}^-$ and $\text{H}^+$ in the water molecule dissolved in organic phase	[84]

<sup>a</sup> The data on blue line in Fig. 6.



**Fig. 6.** The experimental IR spectra and predicted IR spectra in the organic phase: (a) before extraction, and (b) after extraction, at B3LYP/LANL2DZ level of theory.

constants. Reaction orders for extraction and stripping of arsenic ions were found by plotting the integral concentration of arsenic ions versus time. In Table 8, both Y and X axes for plotting the integral concentration of arsenic ions versus times are shown.  $k_E$  and  $k_S$  are the rate constants for both extraction and stripping reactions.  $C_0$  and  $C_{s,0}$  indicate arsenic concentration at initial extraction and stripping reactions.  $C_t$  and  $C_{s,t}$  demonstrate the arsenic concentration at time ( $t$ ) for both extraction and stripping reactions, respectively [16].

In Fig. 9a and b, results are seen to fit in well, revealing first and second - order for extraction and stripping reactions of arsenic ions. As for other orders, the outcomes are illustrated in Figs. S8 and S9. The findings reveal that rate constants are  $0.0270 \text{ s}^{-1}$  and  $0.0010 \text{ mg L}^{-1} \text{ s}^{-1}$  for the extraction and stripping reactions, respectively [50]. As for the characteristics of reaction orders, it is noted that the conversion of the rate of reaction in the first - order directly depends on the concentration of a single reactant. In the second - order, the rate is proportional to the square of the concentration of a single reactant or the concentration of two reactants [90]. Therefore, the concentrations of  $(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})$  depended on the concentrations of Aliquat 336 in corn oil. Likewise, the conversion of the  $\text{H}_3\text{AsO}_4 \cdot (\text{NH}_2\text{CSNH}_2)_3$  was attained due to the concentrations of both  $(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})$  and protonated thiourea.

**Table 7**  
Wavenumbers of the experimental spectra versus predicted spectra in the aqueous phase for arsenic stripping via DFT.

Wavenumber (cm <sup>-1</sup> )		Functional group assigned by	Ref
Experimental (black line)	Predicted (red line)		
<b>Before stripping</b>			
None	399–514	N–H out-of-plane bending from the NH <sub>2</sub> CSNH <sub>2</sub> molecule	[87]
1095 and 1480	1095 and 1480	Symmetric and asymmetric stretching of C–N	[87]
1393	1393	C=S stretching	[87]
1650	1690	N–H in-plane bending	[87]
2002	2,702 <sup>a</sup>	H–Cl stretching of HCl	[87,88]
3235	None	N–H stretching and O–H stretching	[87]
None	3574 and 3749	N–H symmetric and asymmetric stretching	[87]
<b>After stripping</b>			
None	154–256	O–H vibration	[80,86]
None	500–600	N–H out-of-plane bending	[87]
None	641–707	As–O stretching vibration	[80,86]
1419	1419	C=S stretching	[87]
1600	1650–1700	N–H in-plane bending	[87]
2829	2802	N–H stretching	[87]
3235	None	N–H stretching, and O–H stretching	[87,88]
None	3500–3700	N–H symmetric and asymmetric stretching	[87]

<sup>a</sup> The data on blue line in Fig. 7.

#### 4.9. Effect of organic phase recycling

To reuse both Aliquat 336 and corn oil, the effect of the number of cycles on the extraction percentages of arsenic ions was investigated. In Fig. 10, the effect of the number of cycles on extraction percentages and stripping percentages of arsenic ions is displayed. It is seen that when the number of cycles increased, the extraction of arsenic ions decreased, but the stripping of arsenic ions remained constant. The extraction percentages of arsenic decreased due to the tiny dissolution between Aliquat 336 and water [68,69].

As observed during the first cycle, the remaining concentration of arsenic ions in the extracted eater was 0.002 mg L<sup>-1</sup>, permitted in accordance with the WHO levels ( $\leq 0.01$  mg L<sup>-1</sup>). After two cycles, the remaining concentration of arsenic ions was 0.046 mg L<sup>-1</sup>, permitted as arsenic levels in underground water in Thailand ( $\leq 0.05$  mg L<sup>-1</sup>) [11]. In three cycles, the concentration of arsenic still remained 0.239 mg L<sup>-1</sup>, consistent with the effluent level in Thailand ( $\leq 0.25$  mg L<sup>-1</sup>) [12]. After the 4th cycle, the remaining concentration of arsenic ions (0.321 mg L<sup>-1</sup>) exceeded the levels mentioned previously. Thus, the appropriate number of recycles for the organic phase is twice that for underground drinking water levels or three times for the effluent level in Thailand.

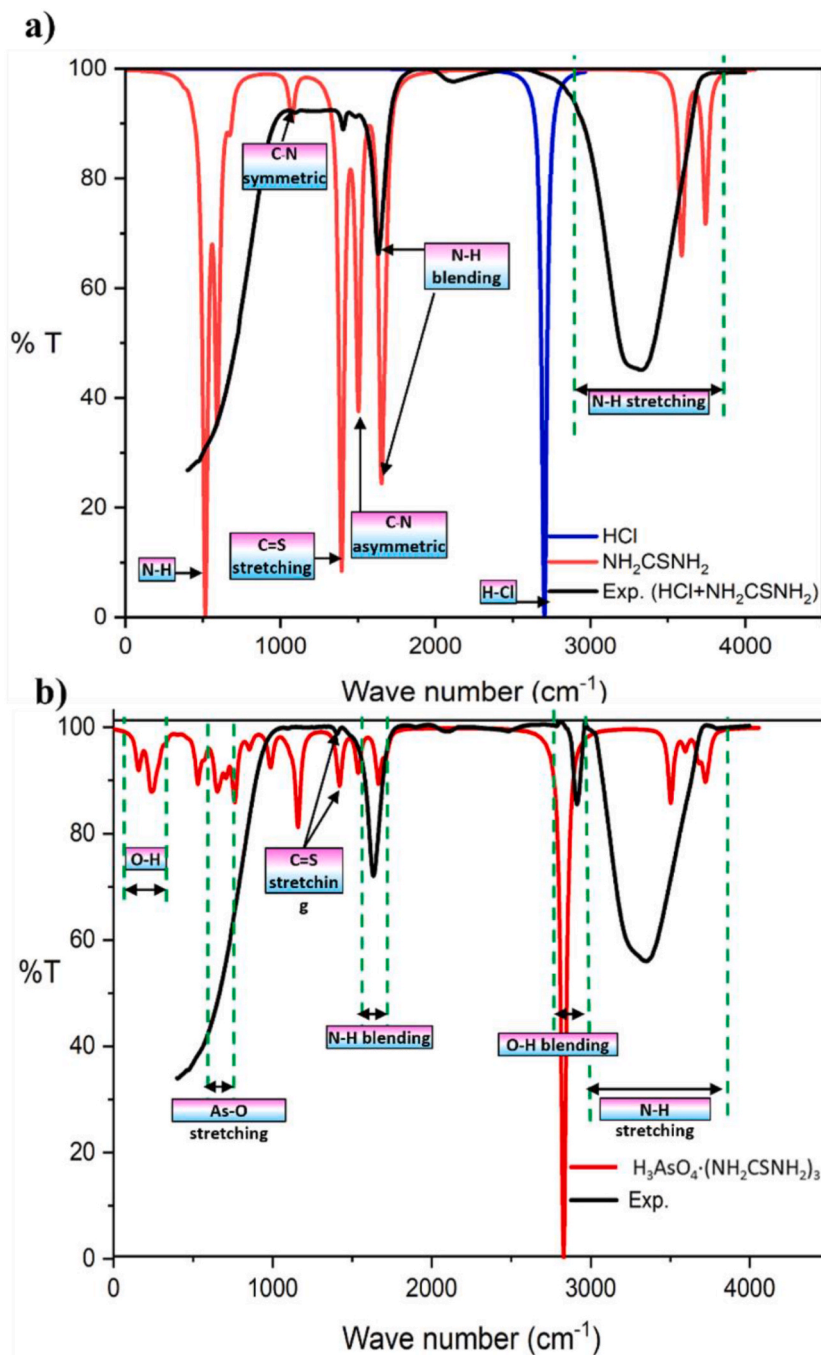
#### 4.10. Selectivity

To investigate the influence of metal ions on extraction selectivity at optimal condition, concentration before and after extraction of individual ions needs to be analyzed. In the Gulf of Thailand, produced water is comprised of heavy metals: arsenic, mercury, and iron, magnesium, and calcium [3]. Such metals can affect the extraction selectivity of the extraction process. In Fig. 11, the concentration of metal ions in the synthetic petroleum produced water, before and after extraction, is presented. In Table 9, to estimate the extractable metal ions of the organic phase from the aqueous phase, both *D* and *S* values are given. Only arsenic obtained *D* > 1 and *S* values of all others were > 1. These findings confirm that corn oil was a good solvent to dilute Aliquat 336 for the removal of arsenic ions via selective extraction [58]. According to the literature, mercury ions in the water can be extracted at acidic pH ( $\approx 6$ ), using Aliquat 336 as extractant. In the aqueous phase, mercury was deprotonated to HgCl<sub>4</sub><sup>2-</sup> in order to react with Aliquat 336 [3,91]. In the case of iron, it is found that high concentration of HCl improved the efficiency of extraction, when Aliquat 336 was used [92]. Thus, the extraction of such metals was poor because the aqueous phase was carried out at pH 12.

#### 4.11. McCabe-Thiele study

To predict the number of extraction stages, the McCabe-Thiele theory was used. For the investigation, optimum conditions were employed. In Figs. S10a and b, the effect of phase ratios (O/A and A/O) on extraction and stripping percentages is demonstrated. Herein, when organic volume ratio increased, extraction percentage increased. This outcome is in line with the Le Chatelier's principle [76]. However, when O/A increased more than 1:1, extraction percentages remained the same since the system reached equilibrium [56]. Likewise, when aqueous volume ratio increased, stripping percentage increased, thus equilibrium was achieved. However, when A/O increased more than 1:2, the stripping system reached equilibrium. These results are quite consistent with the optimal condition via RSM (O/A = 0.9 and A/O = 0.5).

In Fig. 12a and b, the McCabe-Thiele diagram for the extraction and stripping of arsenic ions is presented. In Fig. 12a, it is seen that the distance between the equilibrium line (green line) and the operating lines (blue line and brown line) indicates the quantity of mass transfer driving force. When the mass transfer driving force increased, the number of stages decreased and the distance between the equilibrium line and the operating lines increased, which is a result of the increase in concentration gradient [56]. The number of



**Fig. 7.** The experimental IR spectra and predicted IR spectra in the aqueous phase: (a) Before stripping, and (b) After stripping, at B3LYP/LANL2DZ level of theory.

stages needed for the extraction of arsenic ions was three for operation at O/A = 0.9 and 1.0. In Fig. 12b, the result of the operating line (purple line) at A/O equal to 0.5 shows that the number of stages was four. Likewise, the mass transfer driving force was attained due to the concentration gradient, which is the same as in the case of extraction. It is noted that the number of stages for both extraction and stripping of arsenic ions, as plotted and calculated, was found to be equal [56].

#### 4.12. Mechanism study via DFT analysis

Herein, DFT calculations were used at B3LYP/LANL2DZ level of theory, including the conductor-like polarizable continuum



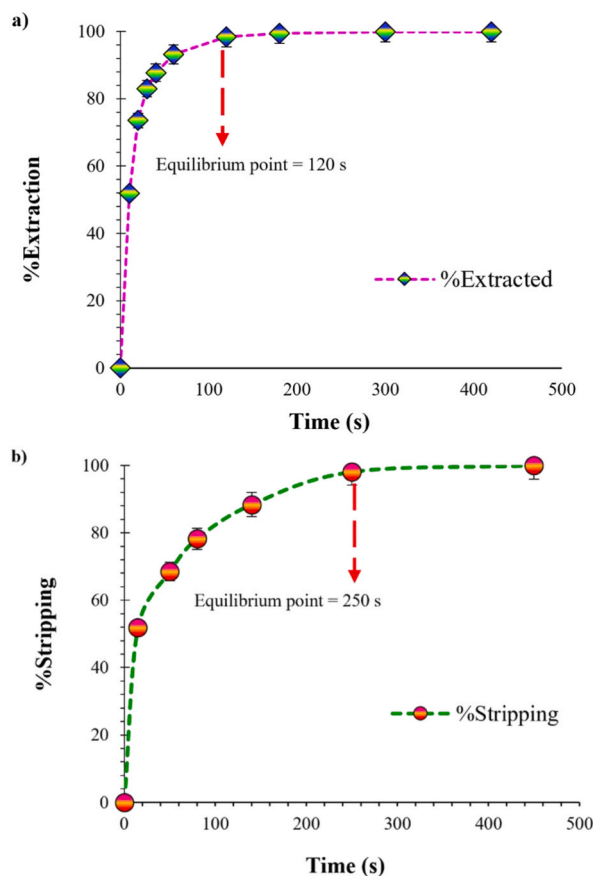


Fig. 8. Equilibrium points: (a) extraction reaction and (b) stripping reaction.

Table 8

Y and X axes to plot the integral concentration of arsenic ions versus time.

Orders	Y axis	X axis	Intercept	Reactions	Rate constants ( $k_E$ and $k_S$ )	Rate constant units	$R^2$
zero	$C_t$	$t$	$C_0$	Extraction	0.0133	$\text{mg L}^{-1} \text{s}$	0.6682
	$C_{s,t}$	$t$	$C_{s,0}$	Stripping	0.1579	$\text{mg L}^{-1} \text{s}$	0.9533
1st	$\ln(C_t)$	$t$	$\ln(C_0)$	Extraction	0.0270	$\text{s}^{-1}$	0.9877
	$\ln(C_{s,t})$	$t$	$\ln(C_{s,0})$	Stripping	0.0027	$\text{s}^{-1}$	0.9065
2nd	$\frac{1}{C_t}$	$t$	$\frac{1}{C_0}$	Extraction	0.2635	$\text{L mg}^{-1} \text{s}^{-1}$	0.8986
	$\frac{1}{C_{s,t}}$	$t$	$\frac{1}{C_{s,0}}$	Stripping	0.0010	$\text{L mg}^{-1} \text{s}^{-1}$	0.9972

solvation model (CPCM). DFT was conducted to investigate both optimal extraction and optimal stripping mechanisms for arsenic ions.

#### 4.12.1. Extraction mechanism

In Fig. 13, the reaction mechanism for the extraction of arsenic ions from the synthetic petroleum produced water is shown.  $\text{AsO}_4^{3-}$  is seen to have a negative charge (red color). In the  $(\text{CH}_3\text{R}_3\text{N}^+)\text{Cl}^-$  molecule, the  $\text{CH}_3\text{R}_3\text{N}^+$  species had a positive charge on the nitrogen atom (blue color) and a negative charge on the chloride atom (red color). Subsequently, when the  $(\text{CH}_3\text{R}_3\text{N}^+)\text{Cl}^-$  molecules reacted with the  $\text{AsO}_4^{3-}$  molecule, the intermolecular force between the cations and anion of  $(\text{CH}_3\text{R}_3\text{N}^+)\text{Cl}^-$  molecules broke and the chloride anion was lost. Then, the released chloride anion formed micro-solvation with water in the aqueous phase [1,20]. Moreover, three cations of  $\text{CH}_3\text{R}_3\text{N}^+$  are seen to connect with the  $\text{AsO}_4^{3-}$  anion through electrostatic attraction. Thus, the supramolecular complex structure of  $(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})$  occurred and dissolved in the organic phase [1,12]. Both the binding distance and interaction energy between O in  $\text{AsO}_4^{3-}$  molecule with H in  $\text{CH}_3\text{R}_3\text{N}^+$  molecules were found to be 1.7 Å and  $-2833.69 \text{ kJ mol}^{-1}$ , indicating that the extraction reaction is an endothermic reaction with  $138.09 \text{ kJ mol}^{-1}$  of the standard reaction energy.



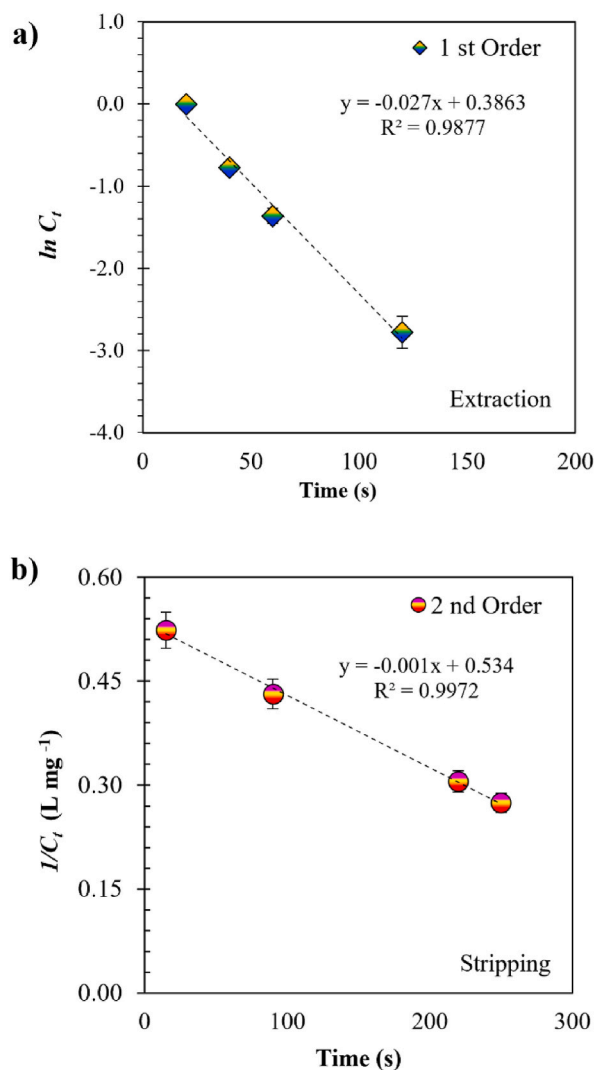


Fig. 9. Plots of the integral concentration of arsenic ions versus time for (a) Arsenic extraction (first order), and (b) Arsenic stripping (second order).

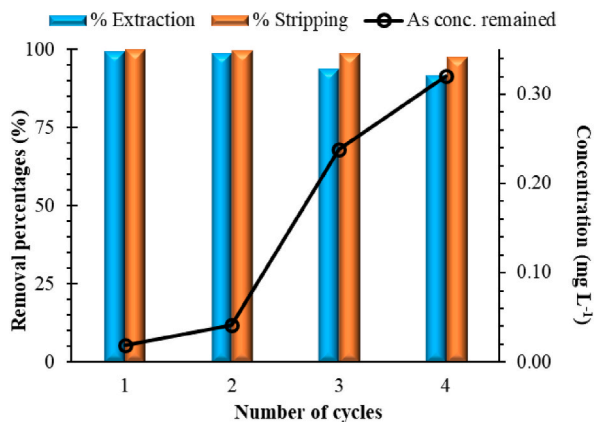


Fig. 10. Effect of the number of cycles on the extraction percentages and stripping percentages of arsenic ions under optimum conditions, 303.2 K, and 0.1 MPa.

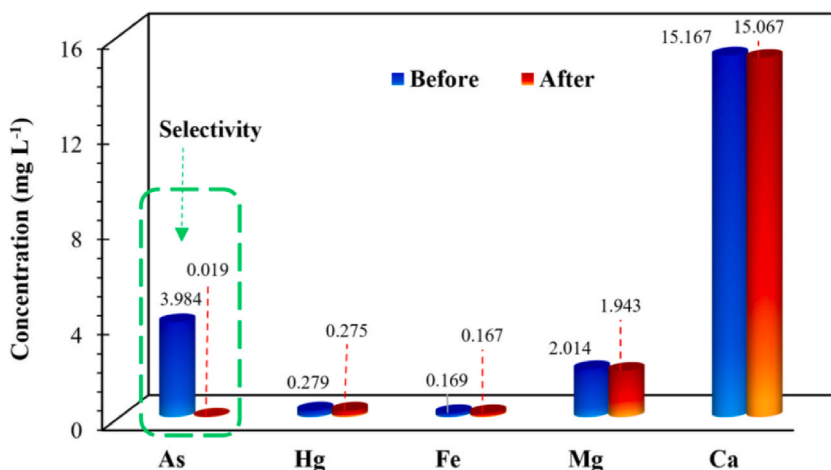


Fig. 11. Concentrations of metal ions in the synthetic petroleum produced water (■): before extraction and (■) after extraction.

Table 9

Distribution coefficient and selectivity factor for the removal of arsenic versus other metals.

metal component ( $i,j$ )	$D_i$	$S \times (10^{-4})$
As	211.141	–
Hg	0.014	1.508
Fe	0.012	1.760
Mg	0.037	0.571
Ca	0.007	3.016

#### 4.12.2. Stripping mechanism

In Eq. (16), the mechanism of the synergistic stripping to strip the  $(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})$  molecule is shown:



In Fig. 14a, the reaction mechanism for the stripping of arsenic from the organic phase is presented. Herein, HCl and thiourea molecules attached to the  $(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})$  complex, at the position of the oxygen atoms of the  $\text{AsO}_4^{3-}$  anion, led to the electrostatic attraction between the  $\text{AsO}_4^{3-}$  anion and three  $\text{CH}_3\text{R}_3\text{N}^+$  cations being broken [76]. Consequently, the covalent bond in the HCl molecule broke, yielding proton ( $\text{H}^+$ ) and chloride anion ( $\text{Cl}^-$ ). Next, the direction of the  $\text{H}^+$  atom points to the sulfur atom, inducing the protonated thiourea form:  $(\text{NH}_2)_2\text{CSH}^+$  to occur. Thus, three  $(\text{NH}_2)_2\text{CSH}^+$  molecules are attracted to the  $\text{AsO}_4^{3-}$  anion at O atoms through both the breaking of the H–S in the thiourea molecule and the forming of covalent bonds between O atoms of  $\text{AsO}_4^{3-}$  and the broken H atom. Suddenly, electrostatic attractions between the sulfur atom in the thiourea molecule and the H atom of O–H covalent bonds occurred. At the same time, the hydrogen bonds between the O atoms in the  $\text{AsO}_4^{3-}$  molecules and the H atoms of the N–H group in the thiourea molecules occurred, giving rise to the  $\text{H}_3\text{AsO}_4 \cdot (\text{NH}_2\text{CSNH}_2)_3$  molecule, which then dissolved in the aqueous phase [12, 16].

In Fig. 14b, it is seen that the total interaction energy in the  $\text{H}_3\text{AsO}_4 \cdot (\text{NH}_2\text{CSNH}_2)_3$  molecule was found to be  $-232.49 \text{ kJ mol}^{-1}$ , which was achieved through the binding distances around  $1.9 \text{ \AA}$  and  $2.1 \text{ \AA}$  for the hydrogen bond and the electrostatic attraction, respectively. Subsequently, the  $\text{CH}_3\text{R}_3\text{N}^+$  cation attracted the  $\text{Cl}^-$  anion, forming  $(\text{CH}_3\text{R}_3\text{N}^+)\text{Cl}^-$  in the organic phase, comprising  $(\text{CH}_3\text{R}_3\text{N}^+)\text{Cl}^-$  in corn oil [12]. The stripping reaction, therefore, is an exothermic reaction, attaining  $-1788.25 \text{ kJ mol}^{-1}$  of the standard reaction energy.

## 5. Conclusions

In this paper, for the removal of arsenic ions from the synthetic petroleum produced water, corn oil proved to be most effective in diluting Aliquat 336. Applying optimal conditions via RSM, percentages of extraction and stripping of arsenic ions reached 99.52 % and 100.00 %, as shown in RAD values ( $\leq 0.0507$  and  $\leq 0.4510$ ) and  $R^2$  values (0.9897 and 0.9640). Besides, optimal condition of extraction was obtained at pH = 12, 0.68 M Aliquat 336 in corn oil, and O/A ratio = 0.9. Optimal stripping condition proved to be 0.5 M HCl + 0.5 M thiourea, 500 rpm, 303.2 K, and A/O ratio = 0.5. In the DFT method, the extraction mechanism of arsenic ions attained  $(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})$  molecules through the chloride ion-exchange of Aliquat 336 molecules. Stripping mechanism occurred through the protonated thiourea and  $(\text{CH}_3\text{R}_3\text{N}^+)_3 \cdot (\text{AsO}_4^{3-})$  molecules, forming  $\text{H}_3\text{AsO}_4 \cdot (\text{NH}_2\text{CSNH}_2)_3$ . The kinetics of both extraction and stripping reactions were found to be  $k_E = 0.0275 \text{ s}^{-1}$  and  $k_S = 0.001 \text{ mg L}^{-1} \text{ s}^{-1}$ . Besides, the selectivity factor for the removal of

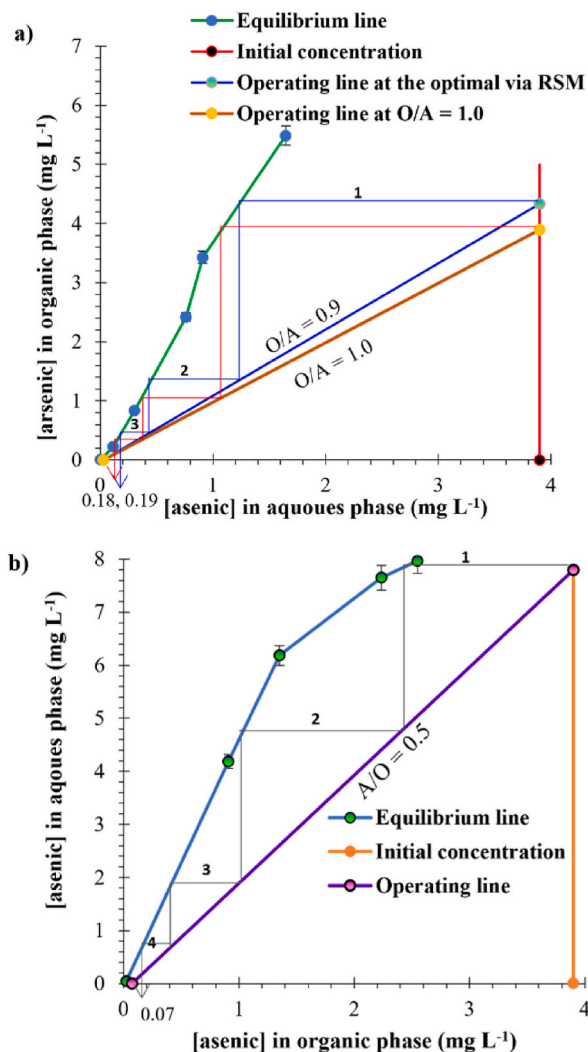


Fig. 12. The McCabe-Thiele diagram: (a) arsenic extraction and (b) arsenic stripping.

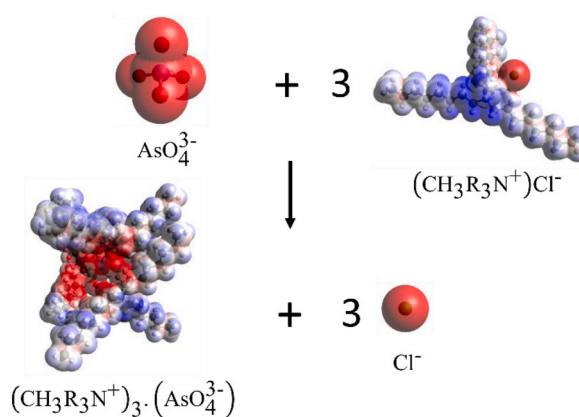
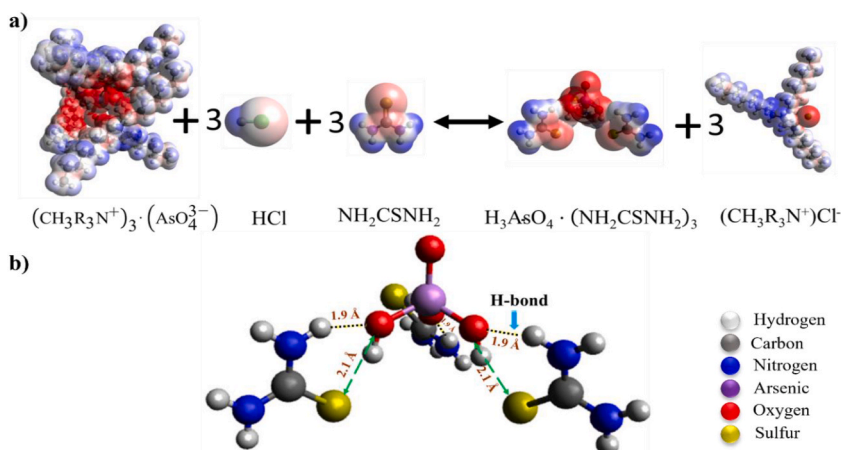


Fig. 13. Reaction mechanism for the extraction of arsenic ions from the synthetic petroleum produced water at B3LYP/LANL2DZ level of theory.



**Fig. 14.** Reaction mechanism for the stripping of arsenic complex from the organic phase at B3LYP/LANL2DZ level of theory: (a) the stripping reaction and (b) the inside interaction of the  $\text{H}_3\text{AsO}_4 \cdot (\text{NH}_2\text{CSNH}_2)_3$  molecule.

arsenic versus other metals was found to be  $\geq 1$ . The number of stages for extraction and stripping of arsenic was found to be three and four stages. To summarize, therefore, corn oil could successfully be used as a green solvent to dilute Aliquat 336 in the water treatment process. This work opens up new directions in the research for green technology that can extract and strip at the same time for industrial wastewater applications.

#### CRediT authorship contribution statement

**Nathawan Srinam:** Investigation. **Vanee Mohdee:** Methodology. **Ura Pancharoen:** Supervision, Funding acquisition. **Kasidit Nootong:** Supervision. **Kreangkrai Maneeintr:** Methodology. **Wikorn Punyain:** Methodology. **Sirikul Chunsawang:** Writing – original draft, Methodology.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

This research project is supported by Second Century Fund (C2F), Chulalongkorn University. The authors acknowledge the financial support by Thailand Science Research and Innovation Fund Chulalongkorn University (IND66210015). Sincere thanks also the Separation Laboratory (Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University) for their kind support and the National e-Science Infrastructure Consortium (NECTEC) for providing computing resources that have contributed to the research results reported within this paper.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e36072>.

#### References

- [1] U. Pancharoen, W. Poonkum, A.W. Lothongkum, Treatment of arsenic ions from produced water through hollow fiber supported liquid membrane, *J. Alloys Compd.* 482 (2009) 328–334, <https://doi.org/10.1016/j.jallcom.2009.04.006>.
- [2] U. Pancharoen, S. Somboonpanya, S. Chaturabul, A.W. Lothongkum, Selective removal of mercury as  $\text{HgCl}_2$ – from natural gas well produced water by TOA via HFSLM, *J. Alloys Compd.* 489 (2010) 72–79, <https://doi.org/10.1016/j.jallcom.2009.08.145>.
- [3] A.W. Lothongkum, S. Suren, S. Chaturabul, N. Thamphiphit, U. Pancharoen, Simultaneous removal of arsenic and mercury from natural-gas-co-produced water from the Gulf of Thailand using synergistic extractant via HFSLM, *J. Membr. Sci.* 369 (2011) 350–358, <https://doi.org/10.1016/j.memsci.2010.12.013>.
- [4] M.F. Hughes, Arsenic toxicity and potential mechanisms of action, *Toxicol. Lett.* 133 (2002) 1–16, [https://doi.org/10.1016/S0378-4274\(02\)00084-X](https://doi.org/10.1016/S0378-4274(02)00084-X).
- [5] A. Navas-Acien, A.R. Sharrett, E.K. Silbergeld, B.S. Schwartz, K.E. Nachman, T.A. Burke, E. Guallar, Arsenic exposure and cardiovascular disease: a systematic review of the epidemiologic evidence, *Am. J. Epidemiol.* 162 (2005) 1037–1049, <https://doi.org/10.1093/aje/kwi330>.
- [6] A. Díaz-Villasenor, A.L. Burns, M. Hiriart, M.E. Cebrián, P. Ostrosky-Wegman, Arsenic-induced alteration in the expression of genes related to type 2 diabetes mellitus, *Toxicol. Appl. Pharmacol.* 225 (2007) 123–133, <https://doi.org/10.1016/j.taap.2007.08.019>.

- [7] A. Vahidnia, G. Van der Voet, F. De Wolff, Arsenic neurotoxicity—a review, *Hum. Exp. Toxicol.* 26 (2007) 823–832, <https://doi.org/10.1177/0960327107084539>.
- [8] R. Tuli, D. Chakrabarty, P.K. Trivedi, R.D. Tripathi, Recent advances in arsenic accumulation and metabolism in rice, *Mol. Breed.* 26 (2010) 307–323, <https://doi.org/10.1007/s11032-010-9412-6>.
- [9] J. Brinkel, M.H. Khan, A. Kraemer, A systematic review of arsenic exposure and its social and mental health effects with special reference to Bangladesh, *Int. J. Environ. Res. Publ. Health* 6 (2009) 1609–1619, <https://doi.org/10.3390/ijerph6051609>.
- [10] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, *Appl. Geochem.* 17 (2002) 517–568, [https://doi.org/10.1016/S0883-2927\(02\)00018-5](https://doi.org/10.1016/S0883-2927(02)00018-5).
- [11] N. Santha, S. Sangkajjan, S. Saenton, Arsenic contamination in groundwater and potential health risk in Western Lampang Basin, Northern Thailand, *Water* 14 (2022) 465, <https://doi.org/10.3390/w14030465>.
- [12] S. Suren, W. Punyain, K. Maneeintr, K. Nootong, U. Pancharoen, The simultaneous elimination of arsenic and mercury ions via hollow fiber supported liquid membrane and their reaction mechanisms: experimental and modeling based on DFT and generating function, *Arab. J. Chem.* 16 (2023) 104501, <https://doi.org/10.1016/j.arabjc.2022.104501>.
- [13] A.K. Fard, T. Rhadfi, G. McKay, Y. Manawi, V. Kochkodan, O.S. Lee, M.A. Atieh, Two-dimensional MXene for efficient arsenic removal from aqueous solutions: experimental and molecular dynamics simulation, *Desalination Water Treat.* 211 (2021) 280–295, <https://doi.org/10.5004/dwt.2021.26607>.
- [14] J. Nikić, A. Tubić, M. Watson, S. Maletić, M. Solić, T. Majkić, J. Agbaba, Arsenic removal from water by green synthesized magnetic nanoparticles, *Water* 11 (2019) 2520, <https://doi.org/10.3390/w11122520>.
- [15] M.K. Yadav, A.K. Gupta, P.S. Ghosal, A. Mukherjee, Remediation of carcinogenic arsenic by pyroaurite-based green adsorbent: isotherm, kinetic, mechanistic study, and applicability in real-life groundwater, *Environ. Sci. Pollut. Res.* 27 (2020) 24982–24998, pyroaurite-based green adsorbent.
- [16] N. Traiwongsa, S. Suren, U. Pancharoen, K. Nootong, K. Maneeintr, W. Punyain, A.W. Lothongkum, Mechanisms of mercury ions separation by non-toxic organic liquid membrane via DFT, thermodynamics, kinetics and mass transfer model, *J. Ind. Eng. Chem.* 117 (2023) 522–537, <https://doi.org/10.1016/j.jiec.2022.10.041>.
- [17] J. Guo, S. Luo, Z. Liu, T. Luo, Direct arsenic removal from water using non-membrane, low-temperature directional solvent extraction, *J. Chem. Eng. Data* 65 (2020) 2938–2946, <https://doi.org/10.1021/acs.jced.9b00936>.
- [18] S. Kalyanaraman, S. Khopkar, Liquid–liquid extraction of arsenic (III) with diluted tributyl phosphate, *Talanta* 24 (1977) 63–65, [https://doi.org/10.1016/0039-9140\(77\)80191-4](https://doi.org/10.1016/0039-9140(77)80191-4).
- [19] L. Iberhan, M. Wiśniewski, Removal of arsenic (III) and arsenic (V) from sulfuric acid solution by liquid–liquid extraction, *J. Chem. Technol. Biotechnol.* 78 (2003) 659–665, <https://doi.org/10.1002/jctb.843>.
- [20] S. Suren, W. Ampronpong, U. Pancharoen, K. Maneeintr, The elimination of trace arsenic via hollow fiber supported liquid membrane: experiment and mathematical model, *Sci. Rep.* 11 (2021) 1–16, <https://doi.org/10.1038/s41598-021-91326-9>.
- [21] D. Buachuang, P. Ramakul, N. Leepipatpiboon, U. Pancharoen, Mass transfer modeling on the separation of tantalum and niobium from dilute hydrofluoric media through a hollow fiber supported liquid membrane, *J. Alloys Compd.* 509 (2011) 9549–9557, <https://doi.org/10.1016/j.jallcom.2011.07.078>.
- [22] M.M. Perez, J. Reyes-Aguilera, T. Saucedo, M. Gonzalez, R. Navarro, M. Avila-Rodríguez, Study of as (V) transfer through a supported liquid membrane impregnated with triocetylphosphine oxide (Cyanex 921), *J. Membr. Sci.* 302 (2007) 119–126, <https://doi.org/10.1016/j.memsci.2007.06.037>.
- [23] M. Avila-Rodríguez, J. Barron-Zambrano, R. Navarro-Mendoza, T. Saucedo-Medina, Thermodynamic study of liquid–liquid extraction of arsenic (V) by NMPL from H<sub>2</sub>SO<sub>4</sub> medium. Solvent Extr. Ion Exch. 19 (2001) 457–472, <https://doi.org/10.1081/SEI-100103280>.
- [24] M. Wisniewski, Extraction of arsenic from sulphuric acid solutions by Cyanex 923, *Hydrometallurgy* 46 (1997) 235–241, [https://doi.org/10.1016/S0304-386X\(97\)90003-7](https://doi.org/10.1016/S0304-386X(97)90003-7).
- [25] D.R. Joshi, N. Adhikari, An overview on common organic solvents and their toxicity, *Journal of Pharmaceutical Research International* 28 (2019) 1–18, <https://doi.org/10.9734/jpri/2019/v28i330203>.
- [26] T. Wongsawa, W. Ampronpong, N. Traiwongsa, U. Pancharoen, W. Punyain, S. Phatanasri, New and green extraction of mercury (I) by pure sunflower oil: mechanism, kinetics and thermodynamics, *J. Taiwan Inst. Chem. Eng.* 122 (2021) 40–50, <https://doi.org/10.1016/j.jtice.2021.04.056>.
- [27] R.N.R. Sulaiman, N. Othman, N.F.M. Noah, N. Jusoh, Removal of nickel from industrial effluent using a synergistic mixtures of acidic and solvating carriers in palm oil-based diluent via supported liquid membrane process, *Chem. Eng. Res. Des.* 137 (2018) 360–375, <https://doi.org/10.1016/j.cherd.2018.07.034>.
- [28] A. Kumar, A. Thakur, P.S. Panesar, Extraction of hexavalent chromium by environmentally benign green emulsion liquid membrane using tridodecylamine as an extractant, *J. Ind. Eng. Chem.* 70 (2019) 394–401, <https://doi.org/10.1016/j.jiec.2018.11.002>.
- [29] K. Duangchan, V. Mohdee, W. Punyain, U. Pancharoen, Mercury elimination from synthetic petroleum produced water using green solvent via liquid–liquid extraction: experimental, effective solubility behaviors and DFT investigation, *J. Environ. Chem. Eng.* (2023) 109296, <https://doi.org/10.1016/j.jece.2023.109296>.
- [30] D. Barrera-Arellano, A.P. Badan-Ribeiro, S.O. Serna-Saldivar, *Corn, third ed., Elsevier, Amsterdam, 2019.*
- [31] C.A. da Silva, G. Sanaïotti, M. Lanza, L.A. Follegatti-Romero, A.J. Meirelles, E.A. Batista, Mutual solubility for systems composed of vegetable oil+ ethanol+ water at different temperatures, *J. Chem. Eng. Data* 55 (2010) 440–447, <https://doi.org/10.1021/jc900409p>.
- [32] A. Strocchi, Fatty acid composition and triglyceride structure of corn oil, hydrogenated corn oil, and corn oil margarine, *J. Food Sci.* 47 (1982) 36–39, <https://doi.org/10.1111/j.1365-2621.1982.tb11021.x>.
- [33] Y. Cong, W. Zhang, C. Liu, F. Huang, Composition and oil-water interfacial tension studies in different vegetable oils, *Food Biophys.* 15 (2020) 229–239, <https://doi.org/10.1007/s11483-019-09617-8>.
- [34] I. Niță, A. Neagu, S. Geacai, A. Dumitru, A. Sterpu, Study of the behavior of some vegetable oils during the thermal treatment, *Ovidius Univ. Ann. Chem.* 2 (2010) 5–8.
- [35] S.N. Sahasrabudhe, V. Rodriguez-Martinez, M. O'Meara, B.E. Farkas, Density, viscosity, and surface tension of five vegetable oils at elevated temperatures: measurement and modeling, *Int. J. Food Prop.* 20 (2017) 1965–1981, <https://doi.org/10.1080/10942912.2017.1360905>.
- [36] A. Vereshchagin, G.V. Novitskaya, The triglyceride composition of linseed oil, *J. Am. Oil Chem. Soc.* 42 (1965) 970–974, <https://doi.org/10.1007/BF02632457>.
- [37] Y.X. Li, J.W. Yang, F.L. Hui, W.W. Fan, Y. Yang, Optimization of biodiesel production from rice bran oil via immobilized lipase catalysis, *Afr. J. Adv. Biotechnol.* 10 (2011) 16314–16324, <https://doi.org/10.5897/AJB11.2338>.
- [38] F.T. Orthofer, J. Eastman, Rice bran oil, F.T. Orthofer (Eds.), *Bailey's Industrial Oil and Fat Products*, John Wiley & Sons, Ltd., New Jersey, 2020, pp. 1–25.
- [39] L.M. Diamante, T. Lan, Absolute viscosities of vegetable oils at different temperatures and shear rate range of 64.5 to 4835 s<sup>-1</sup>. *J. Food Process.* 2014. <https://doi.org/10.1155/2014/234583>, 2014.
- [40] A. Sánchez, R. Maceiras, A. Cancela, M. Rodríguez, Influence of n-hexane on in situ transesterification of marine macroalgae, *Energies* 5 (2012) 243–257, <https://doi.org/10.3390/en5020243>.
- [41] R. Peñaloza-Delgado, J.L. Olvera-Cervantes, M.E. Sosa-Morales, T.K. Kataria, A. Corona-Chávez, Dielectric characterization of vegetable oils during a heating cycle, *J. Food Sci. Technol.* 58 (2021) 1480–1487, <https://doi.org/10.1007/s13197-020-04660-7>.
- [42] S. Agrawal, D. Bhatnagar, Dielectric study of binary mixtures of edible unsaturated oils, *Indian J. Pure Appl. Phys.* 43 (8) (2005) 624–629.
- [43] G.I. Danmaliki, T.A. Saleh, A.A. Shamsuddeen, Response surface methodology optimization of adsorptive desulfurization on nickel/activated carbon, *Chem. Eng. J.* 313 (2017) 993–1003, <https://doi.org/10.1016/j.cje.2016.10.141>.
- [44] W. Bi, M. Tian, K.H. Row, Evaluation of alcohol-based deep eutectic solvent in extraction and determination of flavonoids with response surface methodology optimization, *J. Chromatogr. A* 1285 (2013) 22–30, <https://doi.org/10.1016/j.chroma.2013.02.041>.
- [45] M. Roosta, M. Ghaedi, A. Daneshfar, R. Sahraei, Experimental design based response surface methodology optimization of ultrasonic assisted adsorption of safranin O by tin sulfide nanoparticle loaded on activated carbon, *Spectrochim. Acta: Mol. Biomol. Spectrosc.* 122 (2014) 223–231, <https://doi.org/10.1016/j.saa.2013.10.116>.
- [46] L. St, S. Wold, Analysis of variance (ANOVA), *Chemometrics Intellig. Lab. Syst.* 6 (1989) 259–272, [https://doi.org/10.1016/0169-7439\(89\)80095-4](https://doi.org/10.1016/0169-7439(89)80095-4).

- [47] A.L. Parrill, K.B. Lipkowitz, *Reviews in Computational Chemistry*, vol. 29, Wiley Online Library, 2016.
- [48] D. Wilson, W.R. Kelly, T.R. Holm, L. Talbott, Arsenic removal in water treatment facilities: Survey of geochemical factors and pilot plant experiments, Illinois Department of Natural Resource, Illinois State Water Survey, 2004. <https://www.ideals.illinois.edu/items/108226/bitstreams/353280/object>. (Accessed 20 September 2023).
- [49] V. Mohdee, C. Woraboot, K. Maneintr, K. Nootong, U. Pancharoen, Synergistic interplay between Aliquat 336 and organophosphorus extractants towards non-dispersive extraction of arsenic from petroleum produced water via hollow fiber membrane contactor, *Sep. Purif. Technol.* 286 (2022) 120431, <https://doi.org/10.1016/j.seppur.2021.120431>.
- [50] T. Prapasawat, P. Ramakul, C. Satayaprasert, U. Pancharoen, A.W. Lothongkum, Separation of as (III) and as (V) by hollow fiber supported liquid membrane based on the mass transfer theory, *Kor. J. Chem. Eng.* 25 (2008) 158–163, <https://doi.org/10.1007/s11814-008-0029-y>.
- [51] M.A. Bezerra, R.E. Santelli, E.P. Oliveira, L.S. Villar, L.A. Escalera, Response surface methodology (RSM) as a tool for optimization in analytical chemistry, *Talanta* 76 (2008) 965–977, <https://doi.org/10.1016/j.talanta.2008.05.019>.
- [52] C. Homsirikamol, N. Sunsandee, U. Pancharoen, K. Nootong, Synergistic extraction of amoxicillin from aqueous solution by using binary mixtures of Aliquat 336, D2EHPA and TBP, *Sep. Purif. Technol.* 162 (2016) 30–36, <https://doi.org/10.1016/j.seppur.2016.02.003>.
- [53] F. Luo, D. Li, P. Wei, Synergistic extraction of zinc (II) and cadmium (II) with mixtures of primary amine N1923 and neutral organophosphorous derivatives, *Hydrometallurgy* 73 (2004) 31–40, <https://doi.org/10.1016/j.hydromet.2003.07.006>.
- [54] B. Swain, J. Jeong, K. Yoo, J.-c. Lee, Synergistic separation of Co (II)/Li (I) for the recycling of LIB industry wastes by supported liquid membrane using Cyanex 272 and DR-8R, *Hydrometallurgy* 101 (2010) 20–27, <https://doi.org/10.1016/j.hydromet.2009.11.012>.
- [55] X. Zhang, X. Li, H. Cao, Y. Zhang, Separation of copper, iron (III), zinc and nickel from nitrate solution by solvent extraction using LK-C2, *Sep. Purif. Technol.* 70 (2010) 306–313, <https://doi.org/10.1016/j.seppur.2009.10.012>.
- [56] J. Yao, Y. Li, C. Srinivasakannan, J. Ran, S. Li, S. Yin, L. Zhang, Extraction of chloride from slag flush wastewater using solvent N235, *Hydrometallurgy* 213 (2022) 105934, <https://doi.org/10.1016/j.hydromet.2022.105934>.
- [57] W. Ampronpong, S. Suren, V. Mohdee, K. Maneintr, S. Ekgasit, T. Prapasawat, W. Punyain, U. Pancharoen, Experimental and DFT investigations on the supramolecular mechanism of Ni (II) extraction via D2EHPA blended 1-octanol extractant: application of vegetable oils as diluents, *Kor. J. Chem. Eng.* 40 (2023) 594–611, <https://doi.org/10.1007/s11814-022-1322-x>.
- [58] K. Rezaei, H. Nedjate, Diluent effect on the distribution ratio and separation factor of Ni (II) in the liquid–liquid extraction from aqueous acidic solutions using dibutylthiophosphoric acid, *Hydrometallurgy* 68 (2003) 11–21, [https://doi.org/10.1016/S0304-386X\(02\)00168-8](https://doi.org/10.1016/S0304-386X(02)00168-8).
- [59] Y. Litaïem, M. Dhahbi, Measurements and correlations of viscosity, conductivity and density of an hydrophobic ionic liquid (Aliquat 336) mixtures with a non-associated dipolar aprotic solvent (DMC), *J. Mol. Liq.* 169 (2012) 54–62, <https://doi.org/10.1016/j.molliq.2012.02.019>.
- [60] C.M. Oliveira, B.R. Garavazo, C.E. Rodrigues, Liquid–liquid equilibria for systems composed of rice bran oil and alcohol-rich solvents: application to extraction and deacidification of oil, *J. Food Eng.* 110 (2012) 418–427, <https://doi.org/10.1016/j.jfoodeng.2011.12.027>.
- [61] R. Garcías, E. Martínez-Force, J.J. Salas, M. Venegas-Calerón, Current advances in sunflower oil and its applications, *Lipid Technol.* 21 (2009) 79–82, <https://doi.org/10.1002/lite.200900016>.
- [62] M. Frisch, F. Clemente, in: G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zhe (Eds.), *Gaussian 09, Revision a. 01*, Mj Frisch, Gw Trucks, Hb Schlegel, Ge Scuseria, Ma Robb, Jr Cheeseman, 2009, pp. 20–44.
- [63] A.R. Allouche, Gabedit—a graphical user interface for computational chemistry softwares, *J. Comput. Chem.* 32 (2011) 174–182, <https://doi.org/10.1002/jcc.21600>.
- [64] M.D. Hanwell, D.E. Curtis, D.C. Lonie, T. Vandermeersch, E. Zurek, G.R. Hutchison, Avogadro: an advanced semantic chemical editor, visualization, and analysis platform, *J. Cheminf.* 4 (2012) 1–17, <https://doi.org/10.1186/1758-2946-4-17>.
- [65] S. Bey, H. Semghouni, A. Criscuoli, M. Benamor, E. Drioli, A. Figoli, Extraction kinetics of as (V) by Aliquat-336 using asymmetric PVDF hollow-fiber membrane contactors, *Membranes* 8 (2018) 53, <https://doi.org/10.3390/membranes8030053>.
- [66] R. Güell, C. Fontàs, V. Salvadó, E. Anticó, Modelling of liquid–liquid extraction and liquid membrane separation of arsenic species in environmental matrices, *Sep. Purif. Technol.* 72 (2010) 319–325.
- [67] W. Srirachat, T. Wongsawa, N. Sunsandee, U. Pancharoen, S. Kheawhom, Phase equilibrium for ternary liquid systems of water+ di-(2-ethylhexyl) phosphoric acid+ organic diluents: thermodynamic study, *Fluid Phase Equil.* 401 (2015) 34–47, <https://doi.org/10.1016/j.fluid.2015.05.017>.
- [68] T. Koonsang, K. Aunnankat, K. Maneintr, U. Pancharoen, T. Wongsawa, The mutual solubility of organic-liquid membrane and aqueous phases at different water pH for the stability of SLM using Aliquat 336 as an ionic-liquid extractant, *J. Mol. Liq.* 292 (2019) 111363, <https://doi.org/10.1016/j.molliq.2019.111363>.
- [69] X. Liu, *Organic Chemistry I*, Kwantlen Polytechnic University, Minnesota, 2021.
- [70] N. Srinam, V. Mohdee, N. Traiwongsa, U. Pancharoen, K. Maneintr, W. Punyain, S. Chunsawang, Liquid-liquid equilibria of Aliquat 336+ green solvents+ water for replacement of petroleum-based solvents: intramolecular analysis and thermodynamic behavior, *J. Ind. Eng. Chem.* 134 (2024) 244–259, <https://doi.org/10.1016/j.jiec.2023.12.055>.
- [71] M. Uematsu, E. Franck, Static dielectric constant of water and steam, *J. Phys. Chem. Ref. Data* 9 (1980) 1291–1306, <https://doi.org/10.1063/1.555632>.
- [72] T.T.N. Nguyen, V.N.H. Nguyen, Y. Liu, M.S. Lee, Analysis of the interaction in the mixture of organophosphorus acids and Aliquat 336 through the measurement of dielectric constant and viscosity, *J. Mol. Liq.* 315 (2020) 113738, <https://doi.org/10.1016/j.molliq.2020.113738>.
- [73] S.D. Wilson, W.R. Kelly, T.R. Holm, J.L. Talbott, *Arsenic Removal in Water Treatment Facilities: Survey of Geochemical Factors and Pilot Plant Experiments*, 2004. MTAC TR04-03.
- [74] R. Güell, E. Anticó, V. Salvadó, C. Fontàs, Efficient hollow fiber supported liquid membrane system for the removal and preconcentration of Cr (VI) at trace levels, *Sep. Purif. Technol.* 62 (2008) 389–393, <https://doi.org/10.1016/j.seppur.2008.02.015>.
- [75] S.W. Park, C.W. Kim, J.H. Lee, G. Shim, K.S. Kim, Comparison of arsenic acid with phosphoric acid in the interaction with a water molecule and an alkali/alkaline-earth metal cation, *J. Phys. Chem. A* 115 (2011) 11355–11361, <https://doi.org/10.1021/jp2051245>.
- [76] W. Poolkaew, V. Mohdee, K. Purkhitmanont, U. Pancharoen, W. Punyain, A.W. Lothongkum, New upstream solution for mercury removal from petroleum condensate via HFMC: thermodynamics, kinetics, DFT and mass transport, *Hydrometallurgy* 221 (2023) 106135, <https://doi.org/10.1016/j.hydromet.2023.106135>.
- [77] D. Cheung, The adverse effects of Le Chatelier’s principle on teacher understanding of chemical equilibrium, *J. Chem. Educ.* 86 (2009) 514, <https://doi.org/10.1021/ed086p514>.
- [78] B. Galan, A.M. Uriaga, A.I. Alonso, J.A. Iribien, M.I. Ortiz, Extraction of anions with Aliquat 336: chemical equilibrium modeling, *Ind. Eng. Chem. Res.* 33 (1994) 1765–1770, <https://doi.org/10.1021/ie00031a015>.
- [79] Z. Weiqun, Y. Wen, Q. Lihua, Structure and stability of thiourea with water, DFT and MP2 calculations, *J. Mol. Struct.* 730 (2005) 133–141, <https://doi.org/10.1016/j.theochem.2005.06.012>.
- [80] T. Pirom, B. Rojanasiraprapa, W. Punyain, U. Pancharoen, The elimination of arsenic from natural gas condensate via pulse sieve-plate column: experimental and application of DFT for chemical structure, *Arab. J. Chem.* 16 (2023) 104756, <https://doi.org/10.1016/j.arabjc.2023.104756>.
- [81] J.W. Rawlins, M. Pramanik, S.K. Mendon, Synthesis and characterization of soyamide ferulate, *J. Am. Oil Chem. Soc.* 85 (2008) 783–789, <https://doi.org/10.1007/s11746-008-1260-8>.
- [82] E.A.J. Al-Mulla, W.M.Z.W. Yunus, N.A.B. Ibrahim, M.Z.A. Rahman, Difatty acyl urea from corn oil: synthesis and characterization, *J. Oleo Sci.* 59 (2010) 157–160, <https://doi.org/10.5650/jos.59.157>.
- [83] L.Y. Lee, N. Morad, N. Ismail, A. Talebi, M. Rafatullah, Optimization for liquid-liquid extraction of Cd (II) over Cu (II) ions from aqueous solutions using ionic liquid aliquat 336 with tributyl phosphate, *Int. J. Mol. Sci.* 21 (2020) 6860, <https://doi.org/10.3390/ijms21186860>.
- [84] W. Punyain, K. Takahashi, Evaluation of Ar tagging toward the vibrational spectra and zero point energy of X– HOH, X– DOH, and X– HOD, for X= F, Cl, Br, *Phys. Chem. Chem. Phys.* 23 (2021) 9492–9499, <https://doi.org/10.1039/D0CP06339H>.



- [85] S.S. Xantheas, Quantitative description of hydrogen bonding in chloride– water clusters, *J. Phys. Chem. A* 100 (1996) 9703–9713, <https://doi.org/10.1021/jp960779s>.
- [86] R.C. Lucacel, I. Ardelean, Comparative structural investigation of B~ 2 $\bar{O}$  3-MO-CuO glasses (MO→ Te $\bar{O}$  2 or As~ 2 $\bar{O}$  3) by FTIR and Raman spectroscopies, *J. Optoelectron. Adv. Mater.* 8 (2006) 1124.
- [87] V. Mohdee, V. Parasuk, U. Pancharoen, Synergistic effect of Thiourea and HCl on Palladium (II) recovery: an investigation on Chemical structures and thermodynamic stability via DFT, *Arab. J. Chem.* 14 (2021) 103196, <https://doi.org/10.1016/j.arabjc.2021.103196>.
- [88] I. Xueref, F. Dominé, FTIR spectroscopic studies of the simultaneous condensation of HCl and H<sub>2</sub>O at 190 K–Atmospheric applications, *Atmos. Chem. Phys.* 3 (2003) 1779–1789, <https://doi.org/10.5194/acp-3-1779-2003>, 2003.
- [89] Y. Weiss, I. Kiflawi, O. Navon, IR spectroscopy: quantitative determination of the mineralogy and bulk composition of fluid microinclusions in diamonds, *Chem. Geol.* 275 (2010) 26–34, <https://doi.org/10.1016/j.chemgeo.2010.04.010>.
- [90] K.A. Connors, *Chemical Kinetics: the Study of Reaction Rates in Solution*, Wiley-VCH Verlag GmbH, 1990.
- [91] S. Chaturabul, T. Wannachod, N. Leepipatiboon, U. Pancharoen, S. Kheawhom, Mass transfer resistance of simultaneous extraction and stripping of mercury (II) from petroleum produced water via HFSLM, *J. Ind. Eng. Chem.* 21 (2015) 1020–1028, <https://doi.org/10.1016/j.jiec.2014.05.011>.
- [92] R. Mishra, P. Rout, K. Sarangi, K. Nathsarma, Solvent extraction of Fe (III) from the chloride leach liquor of low grade iron ore tailings using Aliquat 336, *Hydrometallurgy* 108 (2011) 93–99, <https://doi.org/10.1016/j.hydromet.2011.03.003>.