

การแยกอาร์เซนิกสปีชีส์ด้วยเรซินแลกเปลี่ยนไอออนและโลหะออกไซด์ผสมสำหรับการตรวจวัด
ด้วย ICP-OES



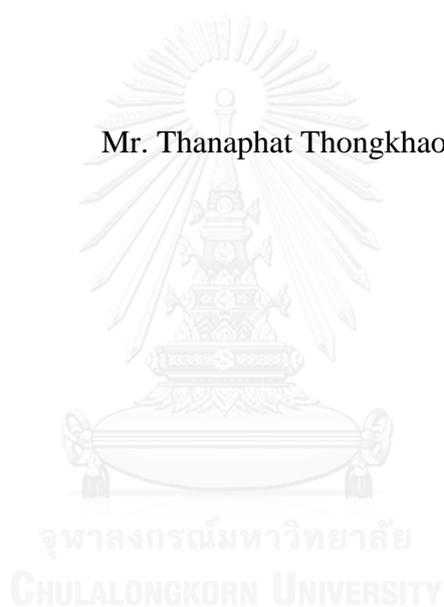
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SEPARATION OF ARSENIC SPECIES BY ION EXCHANGE RESIN
AND MIXED METAL OXIDES FOR DETERMINATION BY ICP-OES

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
Department of Chemistry
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ธณภัทร ทองขาว : การแยกอาร์เซนิกสปีชีส์ด้วยเรซินแลกเปลี่ยนไอออนและโลหะออกไซด์ผสม สำหรับการตรวจวัดด้วย ICP-OES (SEPARATION OF ARSENIC SPECIES BY ION EXCHANGE RESIN AND MIXED METAL OXIDES FOR DETERMINATION BY ICP-OES) อ.ที่ปริกษาวิทยานิพนธ์หลัก: ผศ. ดร. อภิชาติ อิ่มยิ้ม, 63 หน้า.

พัฒนาวิธีการแยกอาร์เซนิกสปีชีส์ ได้แก่ อาร์เซไนต์ [As(III)] อาร์เซเนต [As(V)] และไดเมทิลอาร์เซนิกแอซิด (DMA) ในตัวอย่างน้ำโดยใช้การดูดซับด้วยตัวดูดซับสองชนิด คือ แอนไอออนเอกซ์เชนจ์เรซิน (SBAE) และตัวดูดซับโลหะออกไซด์ผสมของเหล็กและทองแดง จากนั้นตรวจวัดปริมาณอาร์เซนิกด้วยเทคนิคอินดักทีฟลิคัฟเฟิลพลาสมาออฟติคัลอิมิสชันสเปกโทรเมตรี เริ่มจากการสังเคราะห์ตัวดูดซับโลหะออกไซด์ผสมของเหล็กและทองแดงด้วยกระบวนการตกตะกอนร่วม จากนั้นแยกอาร์เซไนต์ อาร์เซเนต และไดเมทิลอาร์เซนิกแอซิด โดยผ่านกระบวนการสกัดด้วยเฟสของแข็ง 2 ขั้นตอน ที่ pH เดียวกัน โดยทำการศึกษาภาวะที่เหมาะสมสำหรับการสกัดแบบเบทซ์ ได้แก่ ค่าพีเอชของสารละลาย ความเข้มข้นของตัวชะ และค่าความจุการดูดซับ พบว่าแอนไอออนเอกซ์เชนจ์เรซินสามารถดูดซับอาร์เซเนตที่พีเอชเท่ากับ 11 ในขณะที่อาร์เซไนต์และไดเมทิลอาร์เซนิกแอซิดถูกดูดซับได้น้อย ส่วนตัวดูดซับโลหะออกไซด์ผสมของเหล็กและทองแดงที่พีเอชเท่ากับ 11 สามารถดูดซับได้ทั้งอาร์เซไนต์และอาร์เซเนต โดยที่ไม่ดูดซับไดเมทิลอาร์เซนิกแอซิด แล้วตรวจวัดปริมาณของอาร์เซนิกทุกสปีชีส์ด้วยเทคนิค ICP-OES โดยค่าความจุการดูดซับสูงสุดที่พีเอชเท่ากับ 11 ของแอนไอออนเอกซ์เชนจ์เรซินสำหรับการดูดซับอาร์เซเนตมีค่าเท่ากับ 10.6 มิลลิกรัมต่อกรัม และส่วนตัวดูดซับโลหะออกไซด์ผสมของเหล็กและทองแดงสำหรับการดูดซับอาร์เซไนต์มีค่าเท่ากับ 36.8 มิลลิกรัมต่อกรัม



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THANAPHAT THONGKHAO: SEPARATION OF ARSENIC SPECIES BY ION EXCHANGE RESIN AND MIXED METAL OXIDES FOR DETERMINATION BY ICP-OES. ADVISOR: ASST. PROF. DR. APICHAT IMYIM, 63 pp.

A novel method for speciation of arsenic (As(III), As(V) and dimethyl arsenic acid (DMA)) in water using solid phase materials including strong base anion exchange (SBAE) resin and iron-copper binary oxide coupled with inductively coupled plasma optical emission spectrometry (ICP-OES) was developed. This study aims to separate and quantitatively determine water-soluble arsenic (As(III) As(V) and dimethyl arsenic acid (DMA)) towards two steps of solid phase extraction at the same pH. In this work, nanostructured iron-copper binary oxide was prepared by using coprecipitation method. The effect of pH of solution and concentration of eluent on adsorption behavior of As(III), As(V) and DMA were investigated. Results concluded that SBAE resin can adsorb As(V) at pH 11 while As(III) and DMA could not be retained. For iron-copper binary oxide material, DMA could not be retained while As(III) and As(V) could be adsorbed at pH 11. The determination of each arsenic species was achieved by ICP-OES. The maximum adsorption capacities of As(V) on SBAE resin and As(III) on iron-copper binary oxide were 10.6 mg g^{-1} and 36.8 mg g^{-1} , respectively.



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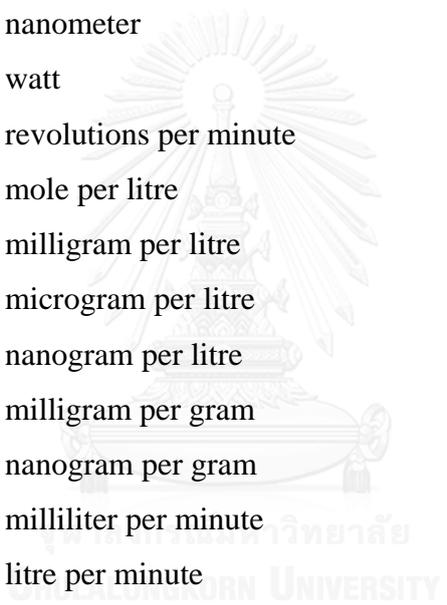
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LIST OF ABBREVIATION

ICP-OES	=	inductively coupled plasma optical emission spectrometry
g	=	gram
mg	=	milligram
mL	=	milliliter
mol	=	mole
hr	=	hour
°C	=	degree Celsius
nm	=	nanometer
W	=	watt
rpm	=	revolutions per minute
mol L ⁻¹	=	mole per litre
mg L ⁻¹	=	milligram per litre
µg L ⁻¹	=	microgram per litre
ng L ⁻¹	=	nanogram per litre
mg g ⁻¹	=	milligram per gram
ng g ⁻¹	=	nanogram per gram
mL min ⁻¹	=	milliliter per minute
L min ⁻¹	=	litre per minute



CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Nowadays, the environmental problem from the metal contamination are highly affect to human health. One of the natural metal that can cause diseases in human is arsenic [1]. According to agricultural and industrial processes, arsenic are released into the environment from natural sources and man-made sources [2]. In natural source, arsenic species can be divided into two groups that are organic and inorganic arsenic species which occurs in four oxidation states: +5, +3, 0, and -3. Normally, the toxicity of inorganic arsenic is higher than organic arsenic. The transformations of arsenic founded in environment are reduction-oxidation, methylation and precipitation processes [3]. The arsenic species including arsenite [As(III)], arsenate [As(V)], monomethyl arsenic acid (MMA) and dimethyl arsenic acid (DMA) can be founded in environment [4].

World Health Organization (WHO) and the US Environmental Protection Agency (USEPA) set the regulation that the maximum As contamination in drinking water is 10 mg/L [5]. It is important to remove and determine of arsenic in the environment due to their extremely harmful to human health. The various techniques used to determine arsenic concentration such as hydride generation atomic absorption spectrometry (HG-AAS) [6], high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) [7], and inductively coupled plasma mass spectrometry (ICP-MS) [8] are mostly used via their high sensitivity for a wide range of analytes, low detection limits, high sample throughput, speed, and wide linear dynamic range.

The speciation of arsenic species is very important because chemical form of each arsenic species lead to the toxicity of arsenic. The speciation of arsenic species cannot used spectrometric method individually. A combination of chromatographic method or non-chromatographic method with appropriate spectrometric detector are frequently employed for arsenic speciation such as high performance liquid

chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS) [9], liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS) [10], high performance liquid chromatography hyphenated to inductively coupled plasma mass spectrometry (HPLC/ICP-DRC-MS) [11], dispersive liquid-liquid microextraction and hydride generation-atomic fluorescence spectrometry (DLLME/HG-AFS) [12], cloud-point extraction and UV-visible spectrometry (CPE-UV-Vis) [13], and CPE-HG-AFS [14]. However, the disadvantages of combination of chromatographic method with spectrometric detector are expensive and complicated process.

Another popular technique used to speciation of arsenic is solid phase extraction (SPE) due to their high efficiency, simple and low cost [15]. In this study, we introduces the speciation of arsenic species (arsenite [As(III)], arsenate [As(V)], and dimethyl arsenic acid (DMA)) by using a solid phase extraction with strong base anion exchange (SBAE) resin and Iron-Copper binary oxide sorbent.

1.2 Objective

The purpose of this research aimed to develop a method for the speciation of arsenic species by using a strong anion exchange column and an iron-copper binary oxide column.

1.3 Scope of the research

Initially, mixed metal oxides was synthesized via co-precipitation method. Then prepared mixed metal oxides and ion exchange resin for separation of arsenite, arsenate and DMA were carried out by the determination of arsenic by inductively coupled plasma optical emission spectrometry (ICP-OES). Several parameters such as amount of sorbent, pH of arsenic solution, sorption time, and concentration of eluent were investigated.

Finally, the optimum condition of this method was validated and applied in the speciation and determination of arsenic in the real industrial wastewater samples.

1.4 Benefits of this research

The separation of arsenic species was achieved by ion exchange resin and mixed metal oxides.



CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Arsenic chemistry

Arsenic is a toxic metalloid element which is quite widespread in the environment. Arsenic contamination in groundwater results from natural sources, such as volcanic activity and erosion of rock, and anthropogenic sources, such as pesticide application and coal combustion [2]. Arsenic is present in the environment in four different oxidation states: As(-III), As(0), As(III) and As(V) depending on the conditions of the environment [16]. Arsenic can be classified into two groups: organic arsenic (oAs) and inorganic arsenic (iAs). The most common arsenic species found in the environment are presented in Table 2.1 [17]. The retention in the body and excretion process of inorganic arsenic are longer than organic arsenic [18]. In general, inorganic arsenic is more toxic than organic arsenic [19]. Generally, the major forms of inorganic arsenics are arsenite (iAs^{III}) and arsenate (iAs^V). The major methylated metabolites are monomethylarsonous acid (MMA^{III}), dimethylarsinous acid (DMA^{III}), monomethylarsonic acid (MMA^V) and dimethylarsinic acid (DMA^V) (Figure 2.1) [20]. Physical and chemical properties of arsenic are shown in Table 2.2 [21].

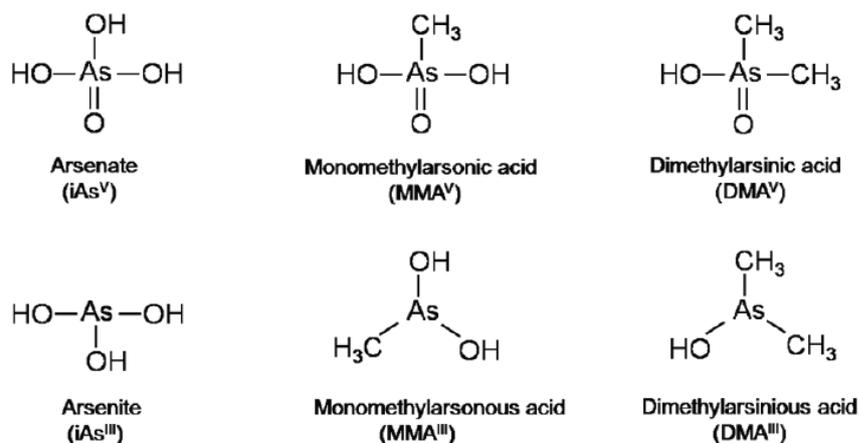


Figure 2.1 The major forms of inorganic arsenics and methylated metabolites.

Table 2.1 The most common arsenic species found in the environment.

Species name	Chemical name	Structures
Mostly determined		
Organic compound		
Arsenocholine	AsC	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{OH}$
Arsenobetaine	AsB	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{COOH}$
Monomethylarsenic acid	MMA(V)	$\text{CH}_3\text{AsO}(\text{OH})_2$
Dimethylarsenic acid	DMA(V)	$(\text{CH}_3)_2\text{AsO}(\text{OH})$
Inorganic compounds		
Arsenite	As(iii)	$\text{As}(\text{OH})_3$
Arsenate	As(v)	$\text{AsO}(\text{OH})_3$
Rarely determined		
p-arsenilic acid	p-ASA	$\text{C}_6\text{H}_8\text{AsNO}_3$
4-Hydroxy-3-nitrobenzene arsonic acid	Roxarsone	$\text{C}_6\text{H}_5\text{As}(\text{O})(\text{OH})_2$
Trimethylarsine oxide	TMAO	$(\text{CH}_3)_3\text{AsO}$
Thioarsenosugar sulphate	Thio-SO ₄	$\text{C}_{10}\text{H}_{16}\text{AsO}_5(\text{S})\text{OSO}_3\text{H}$
Trimethylarsine sulphide	TMAS	$(\text{CH}_3)_3\text{As}(\text{S})$
Thiodimethylarsenate	Thio-DMA	$(\text{CH}_3)_2\text{As}(\text{S})(\text{OH})$
Phenylarsonic acid	PAA	$\text{C}_6\text{H}_5\text{AsO}(\text{OH})_2$
Diphenylarsenic acid	DPAA	$(\text{C}_6\text{H}_5)_2\text{AsO}(\text{OH})$
Tetramethylarsonium ion	TMA	$(\text{CH}_3)_4\text{As}^+$
Dimethylarsinyloethanol	DMAE	$(\text{CH}_3)_2\text{As}(\text{O})\text{CH}_2\text{CH}_2\text{OH}$
Monomethylarsonous acid	MMA(iii)	$(\text{CH}_3)_3\text{As}(\text{OH})_2$
Thioarsenosugar glycerol	Thio-gly	$\text{C}_7\text{H}_{14}\text{AsO}_3(\text{S})\text{OCH}_2\text{CH}$ $(\text{OH})\text{CH}_2\text{OH}$
Trimethylarsenopropionate	TMAP	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{COO}^-$

Table 2.2 Physical and chemical properties of arsenic compounds.

No.	Chemical name	Molecular weight	Oxidation state	Physical state	Water solubility
1	Arsenic	74.92	0	Solid	Insoluble
2	Arsenic acid	141.95	+5	Solid	Freely soluble
3	Arsenic tri-oxide	197.82	+3	Solid	Slightly soluble
4	Arsenic penta-oxide	229.84	+5	Amorphous solid	Freely soluble
5	Sodium arsenate	85.91	+5	Solid	Very soluble
6	Arsine	85.91	+3	Solid	Freely soluble
		77.93	+3	Gas	Slightly soluble
7	Dimethylarsenic acid	138.01	+5	Solid	Soluble
8	Methanearsonic acid	139.98	+5	Solid	Freely soluble
9	Sodium dimethyl arsenate	159.98	+5	Solid	Readily soluble
10	Sodium methane arsonate	161.96	+5	Solid	Soluble

2.2 Arsenic toxicity

Arsenic is present in both pentavalent (i.e., iAs^V , MMA^V and DMA^V) and trivalent (i.e., iAs^{III} , MMA^{III} and DMA^{III}) forms. The toxicity of arsenic depends on the type of arsenic, concentration of arsenic, age, gender, frequency and duration of exposure [22]. Different forms of arsenic have different toxicity. Pentavalent arsenics are less toxic than trivalent arsenics [3]. World Health Organization (WHO) and the US Environmental Protection Agency (USEPA) set the regulation that the maximum As contamination in drinking water is 10 $\mu\text{g/L}$ [5]. There are generally two kinds of toxicity: acute and chronic. Acute toxicity describes the effect of toxin that occurs at a short time after single exposure or multiple exposures. Chronic toxicity describes the poisonous effect that have produced by long-term exposure. The effects of arsenic on the human body are shown in Figure 2.2 [18].

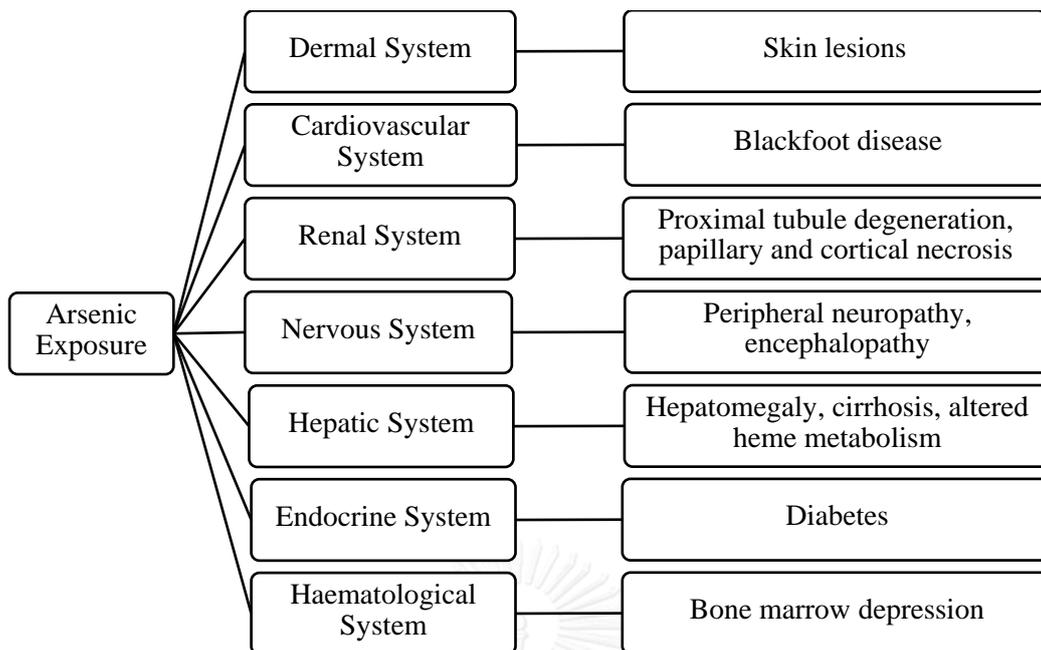


Figure 2.2 The effects of arsenic on the human body.

Short-term exposure

Swallowing or breathing high level of arsenic can result in irritated lungs, stomach ache, diarrhea, pins and needles, muscle weakness, bruising, skin changes, nausea and vomiting.

Long-term exposure

Long-term exposure to low level of arsenic can result in abnormal heart rhythms, darkening of the skin, liver, kidney and central nervous system damage [23].

2.3 Method for arsenic determination

There are several methods used to determine arsenic concentrations such as atomic fluorescence spectrometry (AFS) graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) are widely used for determination of arsenic species due to high sensitivity, speed, low detection limits, and wide linear dynamic range. Advantage and disadvantage of common method for determination of arsenic are shown in Table 2.3 [24].

Table 2.3 Advantages and disadvantages of common method for determination of arsenic.

Instrumentation	Detection limit	Advantages	Disadvantages
GFAAS	Sub-ppb range	<ul style="list-style-type: none"> - Small sample size - Compact - Few spectral interferences 	<ul style="list-style-type: none"> - Slower - Chemical interferences - 1-6 elements/ determination - No screening ability - Limited range
ICP-OES	1-10 ppb range	<ul style="list-style-type: none"> - Multi-element (73) - High productivity - Few chemical interferences - Robust - Excellent screening abilities - High total dissolved solids - Solid or organic samples 	<ul style="list-style-type: none"> - Moderate to low detection limits - Spectral interference - Some element limitations
ICP-MS	ppt range	<ul style="list-style-type: none"> - Multi-element (82) - High productivity - Wide dynamic range - Isotropic measurements - Fast semi-quant screening - Hybrid techniques - Easily interpreted data 	<ul style="list-style-type: none"> - Method development skill required

2.4 Arsenic speciation

Arsenic speciation in the environment is very important because the different oxidation states have different chemical and toxicities. Therefore, speciation of arsenic requires an effective separation method coupling with a sensitive detection method. Hyphenated methods that combine chromatography and atomic spectrometry is widely used for speciation of arsenic such as liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS) [10]. The advantages of hyphenated techniques are short analysis time, accurate analysis, increased automation, high sample throughput, better reproducibility, and reduced contamination. These disadvantages include tedious procedure and require expensive instrumentation. Although hyphenated techniques is preferred for speciation of arsenic, the methods based on non-chromatographic technique is still growing and being hot topic research because simple and inexpensive. There are several non-chromatographic methods based on chemical speciation, for example solid-phase extraction (SPE) [25], liquid-liquid extraction (LLE) [26], hydride generation (HG) [27], cloud-point extraction (CPE) [28], and capillary electrophoresis (CE) [29].

2.5 Solid phase extraction (SPE)

Solid phase extraction (SPE) is one of various techniques used to separate analytes of interest from impurities. SPE is actually liquid-solid chromatography. SPE has been the most often used as a method for speciation of metals and metalloids. The advantages of SPE technique are lower solvent and reagent consumption, shorter lab time, higher concentration factor and lower detection limit [15]. The limitations of SPE are analyte breakthrough, filtered samples and low recoveries. Breakthrough of analytes occurs when the column is overloaded, or when flow rate is too fast. The benefits and limitations of difference type of solid phase extraction are shown in Table 2.4 [30]. SPE has been coupled with another preparation method to enhance separation performance. SPE is more efficient than liquid-liquid extraction (LLE) because easy to achieve, no solvent concentration, automation, increased speed and simplicity. The differences between liquid-liquid extraction and solid phase extraction are shown in Table 2.5 [30].

Table 2.4 The benefits and limitations of difference type of solid phase extraction.

Type of SPE	Benefits	Limitations
Free Discs	<ul style="list-style-type: none"> - can operated with smaller elution volumes - higher flow rates (glass fibre - ticker) - large surface area per unit bed mass - increase in density and uniformity of packing provided by the smaller particles - may be used at fast flow rates without loss of analyte. - cleaner extracts with lower interferences due to optimization of the bed mass to reduce non-specific matrix adsorption. - ability to retain organic compounds even when high flow rates are utilized. 	<ul style="list-style-type: none"> - decrease in breakthrough volume - mainly for more polar compounds - come only in 3 diameters - small samples would be lost - the glassware needs to be cleaned between extractions, and a test tube needs to be placed under the apparatus in the vacuum flask for extraction.

Table 2.4 (Continue) The benefits and limitations of difference type of solid phase extraction.

Type of SPE	Benefits	Limitations
Discs in syringe barrels- Cartridge	- available in a wide range of sizes	- restricted flow rates and plugging of the top frit when handling water containing suspense solid like surface water/ waste mated - cross sectional area is small and sampling processing rates are slow and tolerance to blockage particle - inadequate packing density - channelling reduces the capacity of the cartridge to retain analytes - incomplete reversibility of the sorption of some analytes from active sorbent sites lowers their expected recovery
96-well plates	- reduce handling errors - limit labour outputs - types of plates is fixed and flexible in term of volume and sorbent - shows excellent repeatability - compatibility with small sample volumes. - reduced use of solvents; - clean sample extracts minimizing the potential for ionization suppression	- costly wells - may use a test only a few wells used - due to open-bed configuration, this technique is unsuitable for volatile analytes due to evaporative losses
SPE pipette tips	- conditioning steps necessary for conventional spe is not required - stationary phase is washed only with 1ml of water or buffer - faster extraction time - one extraction method for all analytes - clean extracts - less sample volumes - less solvent waste	

Table 2.5 The differences between liquid-liquid extraction and solid phase extraction.

Differences	Liquid-liquid extraction (LLE)	Solid phase extraction (SPE)
Separation result	Two immiscible liquid phase	Involve partition between a liquid which is sample matrix or solvent with analyze and solid phase as sorbent
Price	Cheaper	Expensive cartridge
Rate of separation	Slower	Faster
Detection of several drugs	Cannot detect most notably, morphine and benzoylecgonine	Can detect most notably, morphine and benzoylecgonine
Handling technique	Too labour intensive	Easier to automate and less manual effort
Solvents	High purity solvents required	Low purity solvents still can give best separation
Selectivity	Limited	High range of immiscible solvents available
“Art of extraction”	More gentle extraction and give high recovery	Easily oxidized during drying
Repeatability	Low	High

2.5.1 The basic steps of solid phase extraction

Solid phase extraction involves four basic steps: conditioning of the adsorbent, sample loading, washing, and eluting (Figure 2.3).

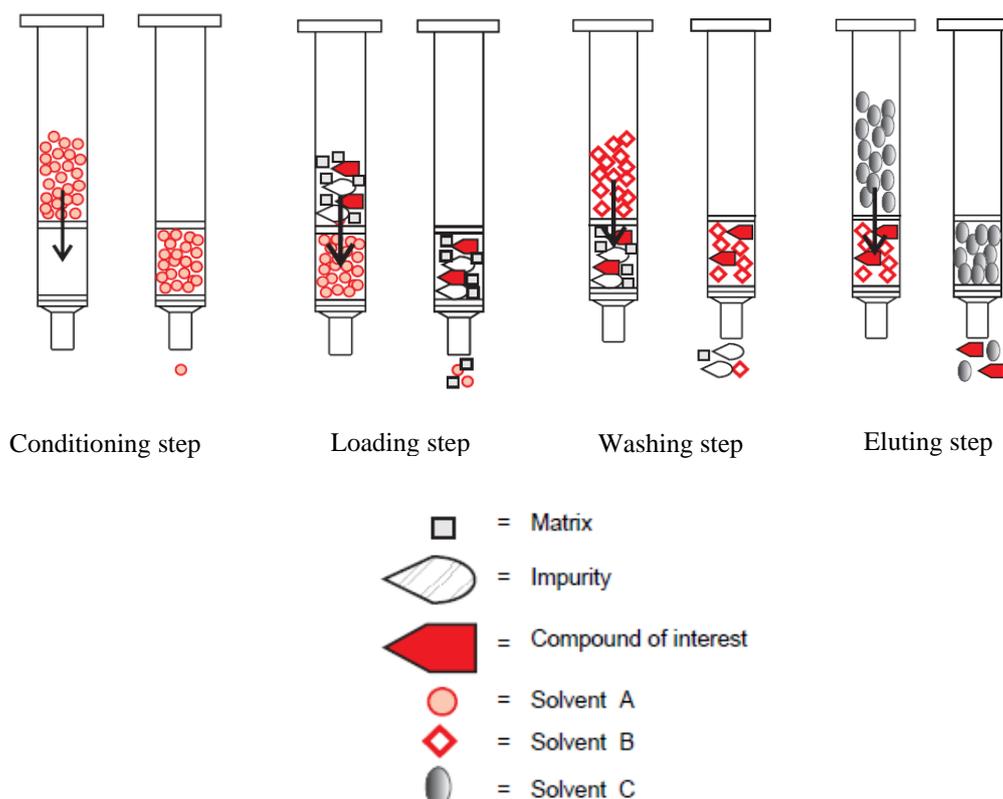


Figure 2.3 The basic steps of solid phase extraction.

2.5.1.1 Conditioning of the adsorbent (solvation)

Solvent is passed through the SPE column resulting in produces surface of sorbent which is suitable for adsorption of the analyte and removing any impurities. Organic solvent such as methanol, isopropanol, or acetonitrile can be used to activate the bonded functional groups. Generally, the volume of the solvent is 5-60 mL. The adsorbent must not be dried after the conditioning step because solvation is destroyed.

2.5.1.2 Sample loading

Liquid sample is passed through the SPE column result in the analytes are retained while matrix components pass through the SPE column. Typically, the volume of sample range from a few milliliters to liters. The sample can be passed through the SPE column by vacuum, applied pressure, or suction. The flow rate depends on the

analytes, the area of column and the particle size of adsorbent. The flow rate generally from 2-50 mL/min.

2.5.1.3 Washing

The aim of this step is to remove interferences while retaining the analytes. The wash solvent should be performed with the strongest solvent that will not elute the analytes of interest. Various parameters affecting the washing step such as pH value, organic constituent and ionic strength.

2.5.1.4 Eluting

The final step in the extraction process is to remove the analytes from SPE column by elution with a suitable solvent and can be collected in the liquid phase. Generally, the volume of the eluent is 200 μ L to 10 mL. The eluent should be performed with the weakest organic solvent that will remove the analytes of interest. There are several eluents such as methanol, acetonitrile, ethylacetate, acetone, and tetrahydrofuran (THF). Characteristics of solvents commonly used in SPE are shown in Table 2.6.

Table 2.6 The differences between liquid-liquid extraction and solid phase extraction.

		Polarity		Solvent
Nonpolar	Strong	Weak		Hexane
	Reversed	Normal		Isooctane
	Phase	Phase		Carbon tetrachloride
				Chloroform
				Methylenechloride(dichloromethane)
				Tetrahydrofuran
				Diethyl ether
				Ethyl acetate
				Acetone
				Acetonitrile
				Isopropanol
	Weak	Strong		Methanol
	Reversed	Normal		Water
	Phase	Phase		Acetic acid
polar				

2.5.2 Separation modes in solid phase extraction

The main modes of separation are reversed phase, normal phase, and ion exchange chromatography.

2.5.2.1 Reversed-phase (R-P) SPE

Reversed phase separation involves nonpolar interaction between the analytes and the adsorbent through van der Waals forces or dispersion forces. Generally, the analyte of interest is mid- to nonpolar. The affinity between the analytes and the R-P adsorbent depend on hydrophobicity. There are several R-P SPE materials such as the alkyl- or aryl-bonded silica. Trifunctional bonding (linked to three oxygen atoms) is more resistant to acid pH (Figure 2.4). C18 and C8 are the most popular type of reversed phase packing. Acetonitrile, ethyl acetate or methanol are the most commonly used eluent in R-P SPE [31].

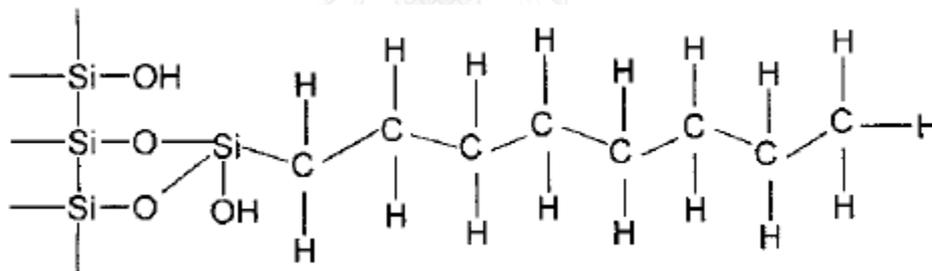


Figure 2.4 Structure of trifunctional bonding.

2.5.2.2 Normal-phase (N-P) SPE

Normal phase SPE aims to remove polar analytes (e.g. carbonyl, sulfhydryls, amine, aromatics, and hydroxyl) from a mid- to nonpolar matrix (e.g. acetone and hexane). A polar adsorbent (e.g. diol, amino, and bare silica) is used to retain the analytes. The interactions between the analyte and the adsorbent surface are including hydrogen bonding, pi-pi interactions, dipole-dipole interactions, and dipole-induced dipole interactions. Very polar compounds or amino compounds cannot be eluted because bind very strongly to silica and alumina. The eluting solvent is usually more

polar than the sample matrix. The eluting solvent should be a high eluting power such as methanol.

2.5.2.3 Ion exchange SPE

The retention mechanism of ion exchange SPE is based on electrostatic interaction between the charged functional group on the analyte and the charged group on adsorbent surface. The pH of the samples is adjusted before extraction and then the analytes are ionized. After that the analytes are adsorbed on adsorbent surface. Ion-exchangers may be silica- or resin-based. The elution can be achieved by changing the pH and/or increasing the strength of ionic species that displaces the analytes.

2.6 Adsorbents for arsenic adsorption

There are several methods for removal of arsenic such as oxidation, coagulation, membrane separation, precipitation, and filtration. The use of adsorbent serves as low cost and environmentally friendly. The types of materials from conventional adsorbents such as chars and activated carbons, activated alumina, and ion exchange resins. The maximum adsorption capacities (Q_m) of different type of adsorbent materials are shown in Table 2.7 [5].

Table 2.7 Some activated carbons for arsenic adsorption.

Adsorbent	As oxidation state	pH	Q _m (mg/ g)	Ref.
Chars and activated carbons				
Char-carbon (from fly-ash)	As(V)	2.2 - 3.0	34.5	(Pattanayak et al., 2000)
	As(III)	2.2 - 3.1	89.2	
GAC	As(V)	4.7	0.038	(Gu et al., 2005)
GAC-Fe (0.05 M)	As(V)	4.7	2.96	
GAC-Fe-NaClO (0.05 M)	As(V)	4.7	6.57	
AC (from apricot stone)	As(V)	3.0	0.034	(Tuna et al., 2013)
AC-Fe(II)	As(V)	3.0	2.023	(Lodeiro et al., 2013)
AC-Fe(III)	As(V)	3.0	3.009	
AC (from sugar beet pulp)	As(V)	9	0.691	
AC-Fe (from sugar beet pulp)	As(V)	4-9	2.9-17	(Chang et al., 2010)
Fe-GAC (4.22% Fe)	As(V)	7	1.95	
AC (from oat hulls)	As(V)	5	3.08	(Chuang et al., 2005)
Fe ₃ O ₄ -AC (from biomass)	As(V)	8	204	(Liu et al., 2010)
Fe-coated Biochar (from empty fruit bunch)	As(III)	8	31.4	(Chammui et al., 2014)
	As(V)	6	15.2	
Leonardite chars	As(III)	7	4.46	
	As(V)	7	8.40	

Table 2.7 (continue) Some activated carbons for arsenic adsorption.

Adsorbent	As oxidation state	pH	Qm (mg/ g)	Ref.
Activated alumina, oxides and minerals				
AA	As(III)	7.6	0.18	(Singh and Pant, 2004)
AA grains	As(III)	7.0	3.48	(Lin and Wu, 2001)
	As(V)	5.2	15.9	
Iron oxide impregnated AA	As(III)	12	0.73	(Kuriakose et al., 2004)
Al-impregnated AA	As(V)	7	3.0	(Tripathy and Raichur, 2008)
Chitosan-coated AA	As(III)	4	56.5	(Hao et al., 2009)
	As(V)	4	96.5	
Fe-Cu binary oxide	As(III)	7	122	(Zhang et al., 2013)
	As(V)	7	82.7	
Fe-Ti bimetal oxide	As(III)	7	85	(Gupta and Ghosh, 2009)
	As(V)	7	14	
Mn-oxide-doped Al oxide	As(III)	7	142	(Wu et al., 2012b)
	As(V)	7	99.7	
Bimetal oxide magnetic nanomaterials MnFe ₂ O ₄	As(III)	3	94	(Zhang et al., 2010)
	As(V)	7	90	
Bimetal oxide magnetic nanomaterials CoFe ₂ O ₄	As(III)	3	100	(Chen et al., 2013)
	As(V)	7	74	
Mesoporous Ce-Fe bimetal oxide	As(III)	7	97.7	(Basu et al., 2013)
	As(V)	5.5	86.3	
Fe(III)-Ce (IV) oxide nanoparticle agglomerates	As(III)	6.5	0.025	(JimenezCedillo et al., 2011)
	As(V)	6.5	0.11	
Fe-zeolite	As(III)	6	0.060	(Chutia et al., 2009)
	As(V)	6	0.1	
Zeolite (mordenite)	As(V)	6	17.3	(Chutia et al., 2009)
	As(V)	6	9.33	
DTMA- mordenite	As(V)	6	97.3	
HDTMA clinoptilolite	As(V)	6	45.3	
Mixed ferrite and hausmannite nanomaterials	As(III)	3	41.5	(Garcia et al., 2014)
	As(V)	3	13.8	
Resins				
Iron-impregnated ion exchange bead (PWX5)	As(V)	6.5	5.6-7.5	(LeMire et al., 2010)
Nickel/nickel boride nanoparticles coated resin	As(III)	6	23.4	(Çiftçi and Henden, 2015)
	As(V)	6	17.8	

2.6.1 Chars and activated carbons

Activated carbon (AC) is most popular and widely used as commercial adsorbent for wastewater treatment. Virgin activated carbon has shown the minimal adsorption of arsenic. Virgin activated carbon should be treated with various compounds (e.g. iron or copper compounds) [32-34] which resulted in an enhanced arsenic adsorption. The most important parameter of AC for arsenic removal is pH_{PZC} (pH of the point of zero charge). The impregnation of iron causes a shifting pH_{PZC} to higher values (acidic carbons) or lower values (basic carbons) [35]. Some activated carbons for arsenic adsorption are shown in Table 2.7.

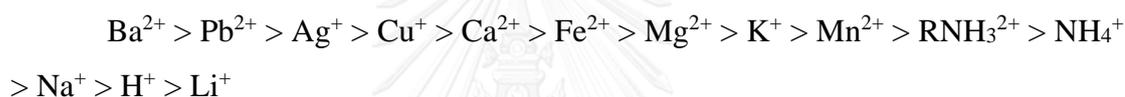
2.6.2 Activated alumina

The United Nations Environmental Program Agency (UNEP) classified activated alumina (AA) adsorption among the best available technologies for arsenic removal from water. AA was prepared by thermal dehydration of aluminum hydroxide. AA is used to remove contaminants from water such as silica, fluoride and arsenic. AA has a high porous structure, high surface area, and abrasion resistance. The regeneration of the activated alumina (AA) is done in three steps: 1) treatment with a strong base (e.g. sodium hydroxide) to desorb impurities ions and displace with hydroxide ions; 2) treatment with a strong acid to remove residual sodium hydroxide; 3) flushing with water. Disadvantages of AA treatment are generated a liquid and/or solid residual and the costs of preparation of AA [36].

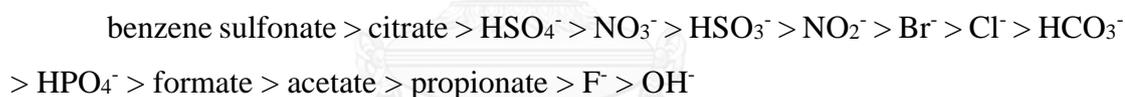
2.6.3 Ion exchange resins

Ion exchange resin can be either synthetic or natural resin. Synthetic resins are preferred because they are mostly to remove the heavy metal [37]. Ion exchange resins divide in two types: strong and weak. Strongly acidic resins with sulfonic acid groups (-SO₃H) and weakly acid resins with carboxylic acid groups (-COOH) are the most commonly used cation exchangers. Strong ion exchangers are often preferred resins because they are unaffected by pH. Moreover, the most commonly used resin for remove heavy metal is natural zeolite. Zeolites shows good cation-exchange capacities for heavy metal ions [38-40]. The relative selectivity of different counterions is shown below.

For Cation Exchangers:



For Anion Exchangers:



2.7 Adsorbent selection

The sorbent chosen for an extraction is dependent on three factors: 1) type of analyte; 2) type of sample matrix; 3) volume of sample. The properties of analyte (e.g. pKa, functional group, and polarity) should be considered. The flow chart of the selection process are shown in Figure 2.5 and 2.6.

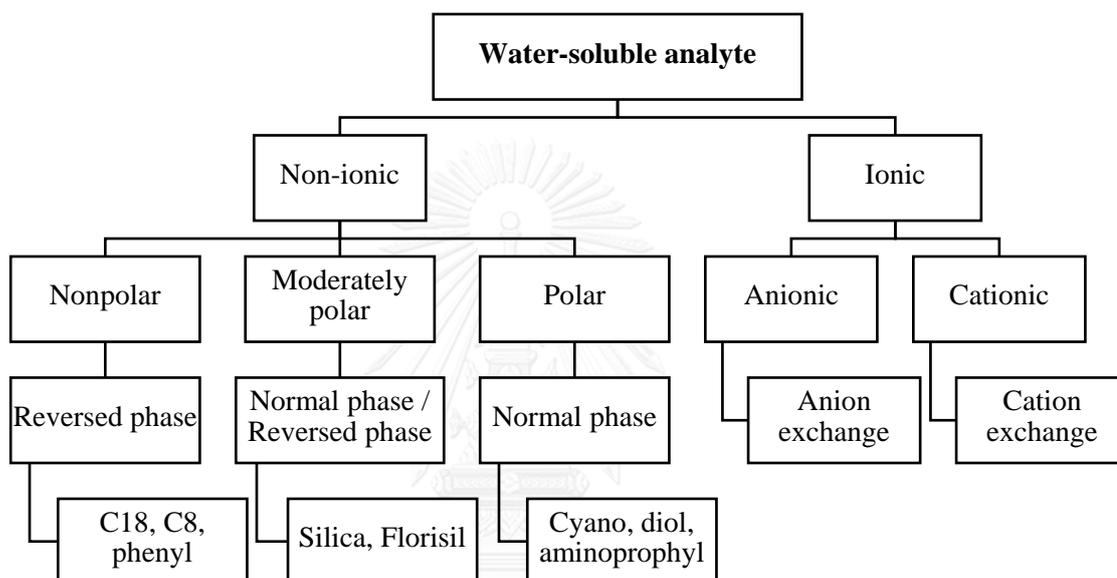


Figure 2.5 The selection of adsorbent process for water-soluble analytes.

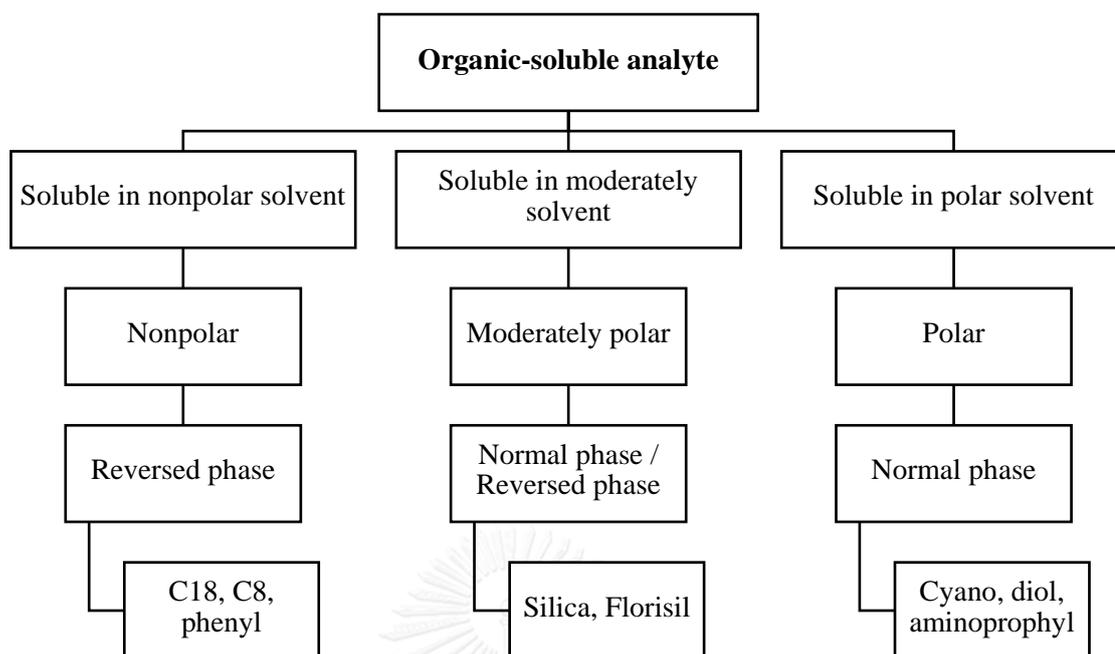


Figure 2.6 The selection of adsorbent process for organic-soluble analytes.

2.8 Literature review

Arsenic is extremely toxic to human health. Therefore it is important to remove and detect arsenic from the environment. Various techniques for determination of arsenic such as hydride generation atomic absorption spectrometry (HG-AAS) [41], high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) [7], and inductively coupled plasma mass spectrometry (ICP-MS) [42] are widely used detector for determination of arsenic species due to high sensitivity for a wide range of analytes, high sample throughput, speed, low detection limits, and wide linear dynamic range.

Because the toxicity of arsenic is related to its chemical form, the speciation of arsenic species is an important. To use of spectrometric method alone do not provide speciation of arsenic species. A combination of chromatographic method or non-chromatographic method with appropriate spectrometric detector are frequently employed for arsenic speciation such as high performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS) [43, 44], liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS) [10],

high performance liquid chromatography hyphenated to inductively coupled plasma mass spectrometry (HPLC/ICP-DRC-MS) [11], dispersive liquid-liquid microextraction and hydride generation-atomic fluorescence spectrometry (DLLME/HG-AFS) [12], cloud-point extraction and UV-visible spectrometry (CPE-UV-Vis) [13], and CPE-HG-AFS [14]. For example, In 2001, Jackson et al. [45] have studied the determination of 4-hydroxy 3-nitrobenzenearsenic acid (Roxarsone, ROX) or 4-aminobenzenearsenic acid (p-arsanilic acid, p-ASA), As(III), As(V), MMA and DMA in poultry waste by using three types of exchange resin column; Dionex AS14, AS16 and AS7 using phosphate, hydroxide and nitric acid as an eluent, respectively and detected analytes by ICP-MS. The detection limit of all arsenic species using three method was less than 0.5 ug L^{-1} . Guerin et al. [46] have studied the separation of As(III), As(V), MMA, DMA and trimethylarsine oxide (TMAO) in wastewater and the comparison between HPLC-ICP-MS and HG-GC-QFAAS. The detection limit of both techniques were 200-400 and 2-10 ng L^{-1} , respectively. The advantages of HG-GC-QFAAS were easy to applied, high sensitivity and low cost although HPLC-ICP-MS was multiple element analysis.

In recent years, solid phase extraction (SPE) is a popular technique for the analysis of arsenic speciation because of high efficiency, simple and low cost. For instances, In 2010, Barakat et al. [47] have studied the separation of As(III) and As(V) from water using strong base anion-chloride. They studied the effect of various parameter (relative arsenic and resin concentrations, retention time, and pH) that effect to the adsorption process. The results show that As(V) was adsorbed on the resin while As(III) was not retained on the resin. The optimum conditions were 1 g of resin for 16 ppm of As(V) at pH 9 for 30 min. the efficiency for removal of As(V) was 99.2%. In 2011, Issa et al. [48] have studied the separation and determination of As(III), As(V), MMA and DMA in drinking, natural and waste water on three types of resins: strong base anion exchange (SBAE) and two hybrid (HY) resins: HY-Fe and HY-AgCl. The results reveal that the adsorption process of arsenic species was depend on solution pH. At pH less than 8, SBAE was adsorbed As(III) while HY-Fe could be adsorbed all arsenic species except DMA. HY-AgCl could be adsorbed As(III) and As(V). The limit of detection of arsenic was 0.2 ugL^{-1} . Their developed method have high precision and accuracy and simple process. In 2016, Ali et al. [49] investigated the speciation of

inorganic arsenic in water using a new polystyrene polydimethyl siloxane polymer in micropipette tip. The factor affected the adsorption of arsenic species were amount of adsorbent, adsorption capacity, pH, pulled and pushed cycles for adsorption and desorption, volume of sample, and eluent type. They were observed that the polystyrene polydimethyl siloxane could be adsorbed arsenate in the pH range of 6-8, while arsenite was passed through the micropipette tip. In 2015, Tunceli et al. [50] investigated the speciation and separation of inorganic species (As(III) and As(V)) in water sample using Amberlite IRA 900 resin. Various parameters such as pH, volume of sample, flow rate, volume and concentration of eluent solution for As(V) were optimized. The adsorption capacity of resin for As(V) was 229.9 mg g⁻¹. The detection limit and quantification limit were 0.126 and 0.420 µg L⁻¹, respectively. In 2015, Pourghazi et al. [51] have studied the speciation of inorganic arsenic species in water and rice samples using 3-mercaptopropionic acid coated 3-aminopropyl triethoxysilane modified Fe₃O₄ nanoparticle. Various parameters affected extraction efficiency of the analyte such as pH, sample volume, amount of adsorbent, extraction time and desorption conditions were optimized. The detection limit of 10 ng L⁻¹ were obtained. In 2014, Chen et al. [52] investigated the speciation of inorganic arsenic in rice using silica-based SAX sorbent followed by hydride-generation atomic fluorescence spectrometry. The arsenic was extracted from rice by microwave-assisted digestion in HNO₃-H₂O₂. The silica-based SAX sorbent were used to separate arsenate from organic forms. The detection of this method was 1.3 ng g⁻¹. The recoveries of As(III) and As(V) were 94 ± 73 % and 93 ± 75 %, respectively. In 2013, Zhang et al. [53] have studied the synthesis and characterization of Fe-Cu binary oxide for adsorption of arsenic. They studied the optimum ratio between copper and iron was 1:2. The maximum adsorption capacity of As(III) and As(V) at pH 7 were 82.7 and 122.3 mg g⁻¹, respectively. Moreover, sulfate and carbonate did not interfere for the adsorption of arsenic while high concentration of phosphate could inhibited the arsenic adsorption. The results indicate that the synthesized Fe-Cu binary oxide have good performance for both As(III) and As(V) removal, low-cost, simple process and easy regeneration.

In this work, SBAE resin and mixed metal oxides were used as sorbents for separation of As(III), As(V) and DMA and arsenic concentration was determined by ICP-OES. The mixed metal oxides was synthesized via co-precipitation method.

CHAPTER III EXPERIMENTAL

3.1 Apparatus

3.1.1 Inductively coupled plasma optical emission spectrometry (ICP-OES)

ICP-spectrometer model iCAP 6500 DUO (Thermo Scientific) was used for determination of arsenic. The ICP-OES conditions for determination of arsenic are shown in Table 3.1.

Table 3.1 ICP-OES conditions for arsenic determination.

Parameter	Conditions
Arsenic wavelength	189.042 nm
RF power	1150 W
Pump rate	50 rpm
Auxiliary gas flow	0.5 L min ⁻¹
Nebulizer gas flow	0.5 L min ⁻¹
Coolant gas flow	12 L min ⁻¹

3.1.2 pH meter

The pH values of the solutions were measured with pH meter (METTLER TOLEDO).

3.1.3 Shaker

A shaker model VELP SCINTIFICA ROTAS68 30 rpm was used for shaking the arsenic solution.

3.1.4 Balance

A balance model DENVERIN STRVMENT (SI-234 max 230 g d = 0.1 mg) was used for weighing solid material.

3.2 Chemical

All chemicals were of analytical reagent grade listed in Table 3.2.

Table 3.2 Chemicals lists.

Chemicals	Supplier
The stock solution of 1000 ppm As(V)	Merck
Sodium (meta)arsenite	Aldrich
Dimethylarsenic acid	Aldrich
Iron(III) chloride	Sigma-Aldrich
Copper(II) sulfate pentahydrate	Merck
Nitric acid	Merck
Sulfuric acid	Merck
Hydrochloric acid	Merck
Sodium hydroxide	Sigma-Aldrich

3.3 Preparation of chemicals and reagents

3.3.1 Arsenic solution

As(III) stock solution (577 mg L^{-1}) and DMA stock solution (543 mg L^{-1}) were prepared from 0.1 g AsNaO_2 in 0.5 M HCl and 0.1 g DMA in 0.5 M HCl, respectively. Standard solution of As(V) (1000 mg L^{-1}) was purchased from Merck. All standards were kept in a refrigerator. Working solutions of As(III), As(V) and DMA were prepared daily from these arsenic stock solutions by dilution with deionized water.

3.3.2 Nitric acid solution

A 1 mol L⁻¹ stock solution of nitric acid was prepared from the concentrated nitric acid (65 %). Dilute solutions of nitric acid (0.1 and 0.5 mol L⁻¹) were prepared using stock solutions. The obtained solution is used in the elution step as an eluent to elute arsenic species from the iron-copper binary oxide sorbents.

3.3.3 Sulfuric acid solution

A 2 mol L⁻¹ stock solution of sulfuric acid was prepared by diluting the concentrated sulfuric acid (95-97 %) with deionized water. The obtained solution is used in the elution step as an eluent to elute arsenic species from the strong base anion exchange resin and the iron-copper binary oxide sorbents.

3.3.4 Hydrochloric acid solution

A 1 mol L⁻¹ stock solution of hydrochloric acid was prepared from the concentrated hydrochloric acid (37 %). Dilute solutions of sulfuric acid (0.1 and 0.5 mol L⁻¹) were prepared by diluting the stock solution of sulfuric acid (1 mol L⁻¹) with deionized water. The obtained solution is used in the elution step as an eluent to elute arsenic species from the strong base anion exchange resin and adjusting pH of solution.

3.3.5 Sodium hydroxide solution

A 1 mol L⁻¹ stock solution of sodium hydroxide was prepared by dissolving the appropriate amount of sodium hydroxide in deionized water. Dilute solutions of sodium hydroxide (0.1 and 0.5 mol L⁻¹) were prepared using stock solutions. The obtained solution is used for adjusting pH of solution.

3.4 Preparation of mixed metal oxides adsorbent

The procedure used to prepare the Fe-Cu binary oxides are as follows [53]; ferric chloride (FeCl_3 , 0.045 mol) and copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.023 mol) were dissolved in 100 mL of deionized water. The solution pH was adjusted to pH 7.5 with sodium hydroxide solution (3 M) under vigorous magnetic stirring. After addition, the solution was continuously stirred for 1 h and then aged at room temperature for 4 hours. The resulting precipitates were washed several times with deionized water and finally filtered and dried at 55°C for 24 h.

3.5 Characterization of mixed metal oxides adsorbent

The mixed metal oxides was characterized by X-ray powder diffraction (XRD) analysis.

3.6 Strong base anion exchange (SBAE) resin

Strong base anion exchange resin (SBAE resin, chloride form, Dowex® Marathon™ A) was obtained from DOW Chemical Company. The physical and chemical properties of Dowex® Marathon™ A resin are shown in Table 3.3. The mechanism of interaction between anionic forms of arsenate and chloride-form SBAE resin as shown in Equation 3.1.

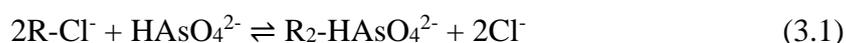


Table 3.3 Physical and chemical properties of Dowex® Marathon™ A resin.

Physical Form		White to amber translucent beads
Matrix		Styrene-DVB, gel
Functional group		Quaternary amine
Ionic form as shipped		Cl⁻ form
Total volume capacity, min	eq/L	1.3
	kgr/ft ³ as CaCO ₃	28.4
Moisture Retention Capacity	%	50-60
Particle size †		
Uniformity coefficient, max		1.1
Harmonic mean diameter	µm	575 ± 50
Whole uncracked beads	%	95-100
Total swelling (Cl ⁻ → OH ⁻)	%	20
Particle density	g/mL	1.08
Shipping density**	g/L	670
	Ibs/ft ³	42

† For additional particle size information, please refer to Particle Size Distribution Cross Reference Chart (Form No. 177-01775).

**As per the backwashed and settled density of the resin, determined by ASTM D-2187

3.7 Investigation of adsorption parameter

3.7.1 Effect of pH

pH is one of the key parameters that affect the adsorption of arsenic species on SBAE resin and mixed metal oxides sorbent. In batch experiments, the adsorbent (10 mg) were added to a test tube containing 10 mL of each As(III), As(V), and DMA (5.8, 10, 5.4 mg L⁻¹, respectively) at various pH values. The arsenic solutions were adjusted pH value at 3-12 by using 1 M NaOH and/or 1 M HCl. The mixed metal oxides sorbent (10 mg) or SBAE resin (10 mg) were mixed with arsenic solutions for 24 hours and 2 hours, respectively. After mixing, the supernatant solutions were filtered through a 0.45

μm Nylon membrane and then arsenic concentrations in the supernatant solutions were measured using ICP-OES.

3.7.2 Effect of eluent concentration

The elution of arsenic species was investigated using different types and concentrations of an eluent. The initial concentration of As(III) and As(V) was 2.32 and 4 mg L^{-1} , respectively. Elution of As(V) was studied using 10 mL of HCl (0.1, 0.5, and 2 mol L^{-1}) and 10 mL of H_2SO_4 (0.1, 0.5, and 2 mol L^{-1}) for 2 hours. For As(III), the elution was studied using 10 mL of HNO_3 (0.1, 0.5, and 2 mol L^{-1}) and 10 mL of H_2SO_4 (0.1, 0.5, and 2 mol L^{-1}) for 2 hours. The amount of arsenic species in the obtained solution was determined by ICP-OES.

3.7.3 Adsorption capacity

The adsorption isotherm was investigated by varying concentration of As(V) (6, 10, 15, and 20 mg L^{-1}) and As(III) (3.5, 5.8, 8.7, and 11.6 mg L^{-1}). The experimental conditions used 10 mg of adsorbent and 10 mL of sample solution. The adsorption capacities of As(V) on SBAE resin and As(III) on mixed metal oxides sorbent were estimated at pH 11 by means of the Langmuir adsorption isotherm as expressed in Equation. (3.3).

$$C_e/q_e = 1/bq_m + C_e/q_m \quad (3.3)$$

where C_e is the residual concentration of arsenic at equilibrium (mg L^{-1})

q_e is the amount of arsenic adsorbed per gram adsorbent (mg g^{-1})

b is the Langmuir constant (L mg^{-1})

q_m is the maximum adsorption capacity (mg g^{-1})

3.8 Adsorption of each arsenic specie

3.8.1 Batch method

3.8.1.1 Strong based anion exchange (SBAE) resin sorbent

An adsorption of each arsenic species was studied by using SBAE resin sorbent. The initial concentration of arsenic in solution of each species (As(III), As(V), and DMA) at pH 11 was 5.8, 10, and 5.4 mg L⁻¹, respectively. Then, 10 mg of SBAE resin sorbent was mixed with the arsenic solution for 2 hours. The concentration of obtained solution was measured by ICP-OES.

3.8.1.2 Mixed metal oxides sorbent

Adsorption of each arsenic species was studied by using mixed metal oxides sorbent. The initial concentration of arsenic in solution of each species (As(III), As(V), and DMA) at pH 11 was 5.8, 10, and 5.4 mg L⁻¹, respectively. Then, 10 mg of mixed metal oxides sorbent was mixed with the arsenic solution for 24 hours. The concentration of obtained solution was measured by ICP-OES.

3.8.2 Column method

3.8.2.1 Strong based anion exchange (SBAE) resin column

An adsorption of each arsenic species was studied by using SBAE resin (100 mg) column. The initial concentration of arsenic in solution of each species (As(III), As(V), and DMA) at pH 11 was 1.74, 3, and 1.62 mg L⁻¹, respectively. Then, the arsenic solution were pass through SBAE resin column at solution flow rate 0.35 mL min⁻¹. The concentration of obtained solution was measured by ICP-OES.

3.8.2.2 Mixed metal oxides column

An adsorption of each arsenic species was studied by using column containing mixed metal oxides 0.01 g and Silica gel 0.09 g. The initial concentration of arsenic in solution of each species (As(III), As(V), and DMA) at pH 11 was 1.74, 3, and 1.62 mg L⁻¹, respectively. Then, the arsenic solution were pass through mixed metal oxides

column at solution flow rate 0.35 mL min^{-1} . The concentration of obtained solution was measured by ICP-OES.

3.9 Speciation of arsenic in mixed arsenic species solution

3.9.1 Batch method

3.9.1.1 Strong base anion exchange (SBAE) resin sorbent

Arsenic speciation was achieved using SBAE resin sorbent. SBAE resin (10 mg) was added to a 10 mL test tube, containing 10 mL of As(III), As(V), and DMA (1.74 , 3.0 and 1.62 mg L^{-1} , respectively) at pH 11. The concentration of obtained solution was measured by ICP-OES.

3.9.1.2 Mixed metal oxides sorbent

Arsenic speciation was achieved using mixed metal oxides sorbent, the solution containing 10 mL of As(III) and DMA (1.74 and 1.62 mg L^{-1} , respectively) at pH 11 was added to 10 mg of mixed metal oxides sorbent in 10 mL test tube. The concentration of arsenic in supernatant solution was measured by ICP-OES.

3.9.2 Column method

3.9.2.1 Strong base anion exchange (SBAE) resin column

Arsenic speciation was achieved using SBAE resin (100 mg) column. The initial concentration of arsenic in solution of each species (As(III), As(V), and DMA) at pH 11 was 1.74 , 3 , and 1.62 mg L^{-1} , respectively. Then, the arsenic solution were pass through SBAE resin column at solution flow rate 0.35 mL min^{-1} .

3.9.2.2 Mixed metal oxides column

Arsenic speciation was achieved using column containing mixed metal oxides 0.01 g and Silica gel 0.09 g . The initial concentration of arsenic in solution of each species (As(III) and DMA) at pH 11 was 1.74 and 1.62 mg L^{-1} , respectively. Then, the

arsenic solution were pass through mixed metal oxides column at solution flow rate 0.35 mL min^{-1} .

3.10 Effect of amount of SBAE resin sorbent on arsenic speciation

In batch experiment, the amount of SBAE resin sorbent was varied from 10-50 mg while mixed metal oxides was fixed at 10 mg. The mixture of arsenic solution containing 10 mL of As(III), As(V), and DMA (0.58 , 1 and 0.54 mg L^{-1} , respectively) at pH 11 were added to a 10 mL test tube, containing SBAE resin (10, 20, and 50 mg). Then the obtain solution was added to mixed metal oxides (10 mg) in a 10 mL test tube.

3.11 Method validation

The method validation was studied under the optimum conditions. Arsenic speciation was achieved using SBAE resin and mixed metal oxides sorbent. SBAE resin (10 mg) was added to a 10 mL test tube, containing 10 mL of As(III), As(V), and DMA (1.74 , 3.0 and 1.62 mg L^{-1} , respectively). Then, the obtain solution was added to mixed metal oxides (10 mg) in a 10 mL test tube. The arsenic species was extracted by SBAE resin and mixed metal oxides sorbent in 3 replicated. Dilute solutions of arsenic were prepared by diluting the stock solution of arsenic with deionized water. The pH of the solution was adjusted to 11 with 1 M NaOH and/or 1 M HCl. After mixing, the supernatant solutions were filtered through a $0.45 \text{ }\mu\text{m}$ Nylon membrane and then arsenic concentrations in the supernatant solutions were measured using ICP-OES. The accuracy and precision of the method were calculated as percent recovery (% recovery) and percent relative standard deviation (% RSD), respectively.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of mixed metal oxides adsorbent

The characterization of the synthesized mixed metal oxides is presented in XRD pattern as shown in Figure 4.1. As a result, the XRD pattern could not be indexed with the reference patterns of any oxides of Cu and Fe and binary oxides of Cu and Fe, this result indicates that the synthesized sorbent was mixed metal oxides. The XRD pattern concludes that the structure of mixed metal oxides was somewhere between the amorphous and crystalline state.

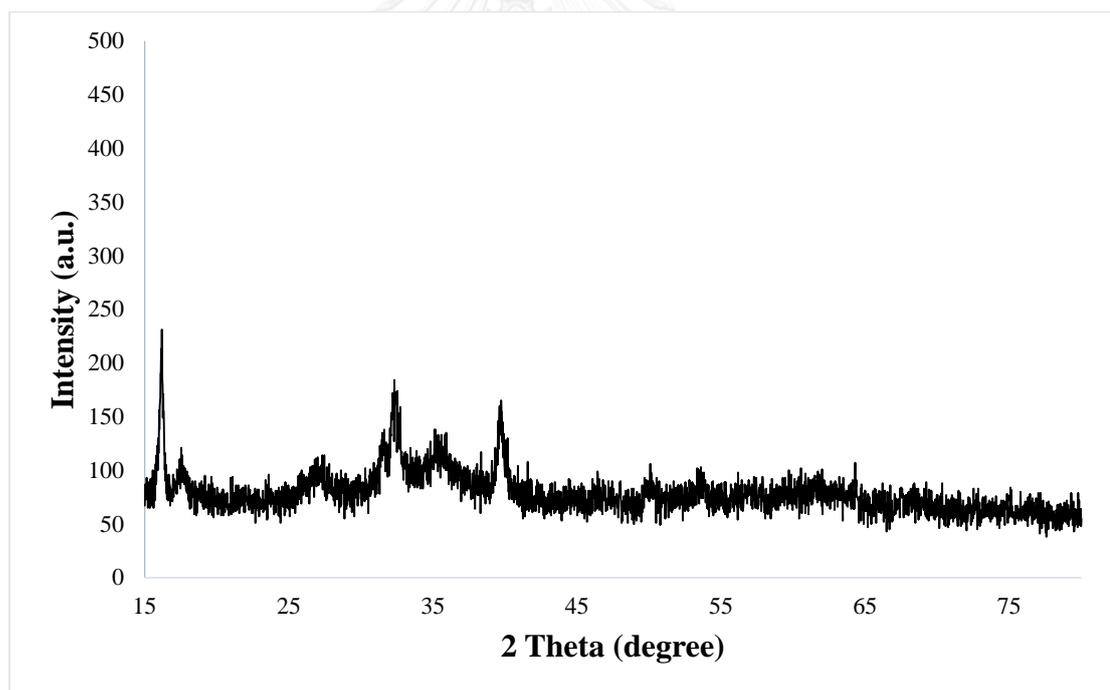


Figure 4.1 XRD pattern of mixed metal oxides.

4.2 Investigation of adsorption parameter

In batch experiment, the various parameters influencing the adsorption of arsenic species such as pH of solution and concentration of eluent were investigated.

4.2.1 Effect of pH

The adsorption efficiency of arsenic on the adsorbent was presented in term of percent adsorption which is calculated by Equation 4.1.

$$\text{Adsorption (\%)} = [(N_i - N_f) / N_i] \times 100 \quad (4.1)$$

where N_i is the initial concentration of arsenic before adsorption (mg L^{-1})
 N_f is the final concentration of arsenic after adsorption (mg L^{-1})

4.2.1.1 Strong base anion exchange (SBAE) resin

The adsorption behavior of arsenic species was investigated at various pH values between 3 and 12. The result of adsorption of arsenic species on SBAE resin were illustrated in Figure 4.2.

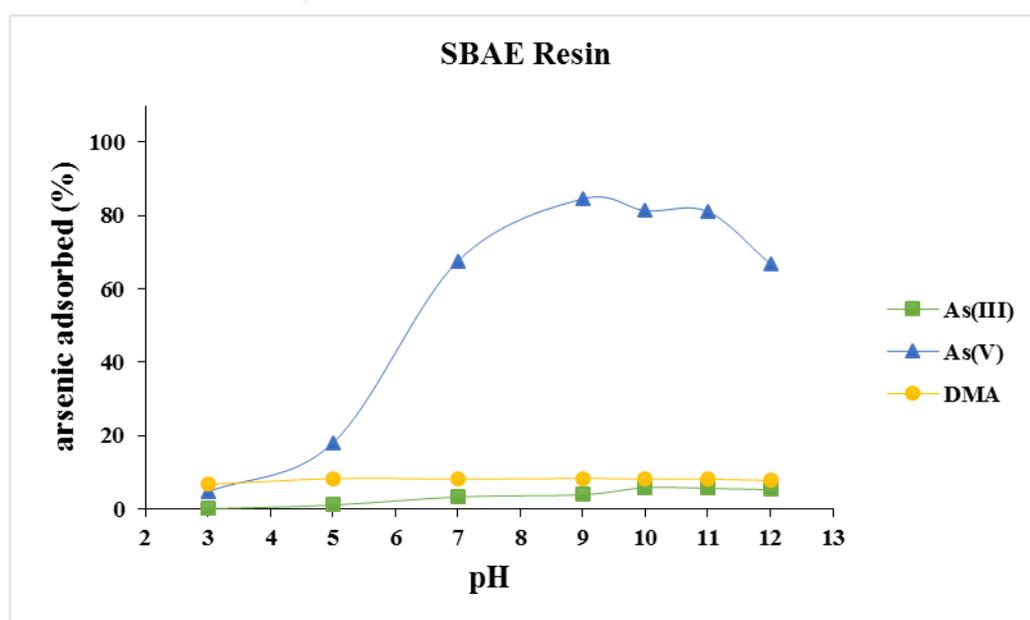
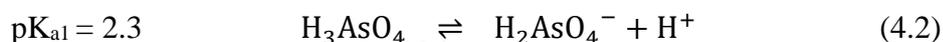
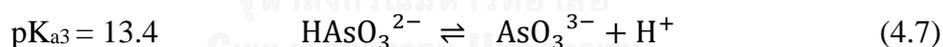
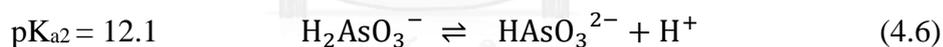
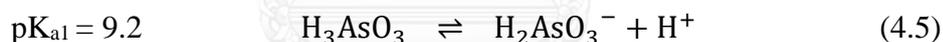


Figure 4.2 Effect of pH on As(III), As(V) and DMA adsorption on SBAE.

In case of As(V), the percent adsorption of As(V) on SBAE increased from pH 3 to 9 and the adsorption reached a maximum point at pH between 9 and 11. As(V) is present as anionic species in the form of H_2AsO_4^- at pH between 2.3 and 7.0, HAsO_4^{2-} at pH s between 7.0 and 11.5, AsO_3^{3-} at pH exceeds 11.5 (Figure 4.3). The maximum adsorption of As(V) was obtained between pH 9 and 11 because HAsO_4^{2-} greater interacts with chloride on SBAE resin than H_2AsO_4^- . The adsorption rapidly decreased at pH 12 due to the competitive effect of hydroxide ions in solution. As(V) is a triprotic acid with $\text{pK}_{a1} = 2.3$, $\text{pK}_{a2} = 7.0$, and $\text{pK}_{a3} = 11.5$, as shown in Equations 4.2-4.4 [48].



For As(III) and DMA, the percent adsorption were low at pH between 3 and 12. As(III) exists as a neutral species ($\text{pH} < 9.2$) or anionic species ($\text{pH} > 9.2$). The pK_a values of As(III) are 9.2, 12.1, and 13.4, as shown in Equations 4.5-4.7 [48].



DMA exists as a neutral species ($\text{pH} < 6.2$) or as anionic species ($\text{pH} > 6.2$). The pK_a value of DMA is 6.2, as shown in Figure 4.3.

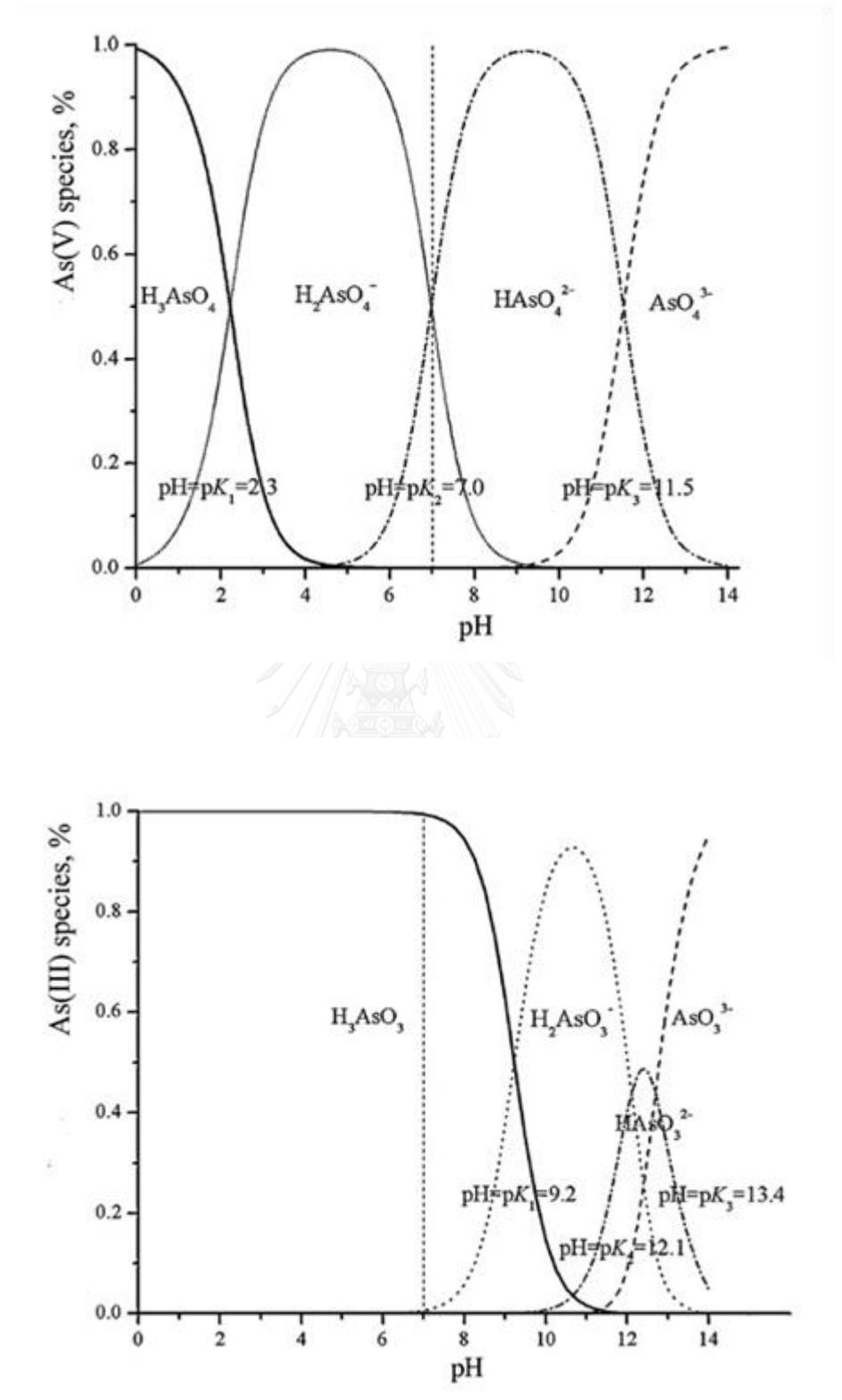


Figure 4.3 As(III), As(V), and DMA speciation as a function of pH.

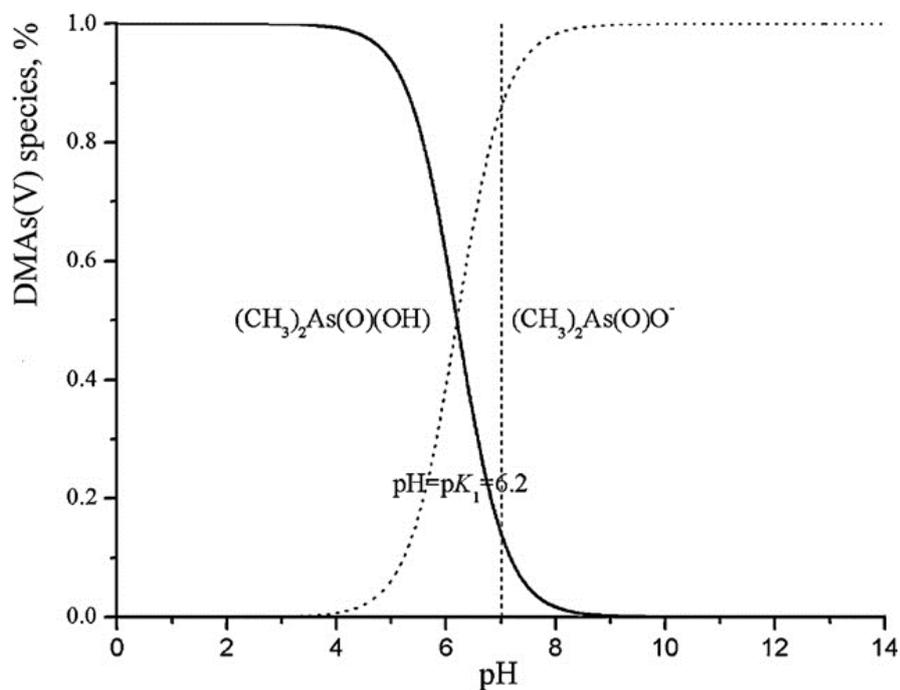


Figure 4.3 (continue) As(III), As(V), and DMA speciation as a function of pH.

4.2.1.2 Mixed metal oxides

The adsorption behavior of arsenic species was investigated at various pH between 3 and 12. The results of adsorption of arsenic species on mixed metal oxides were illustrated in Figure 4.4.

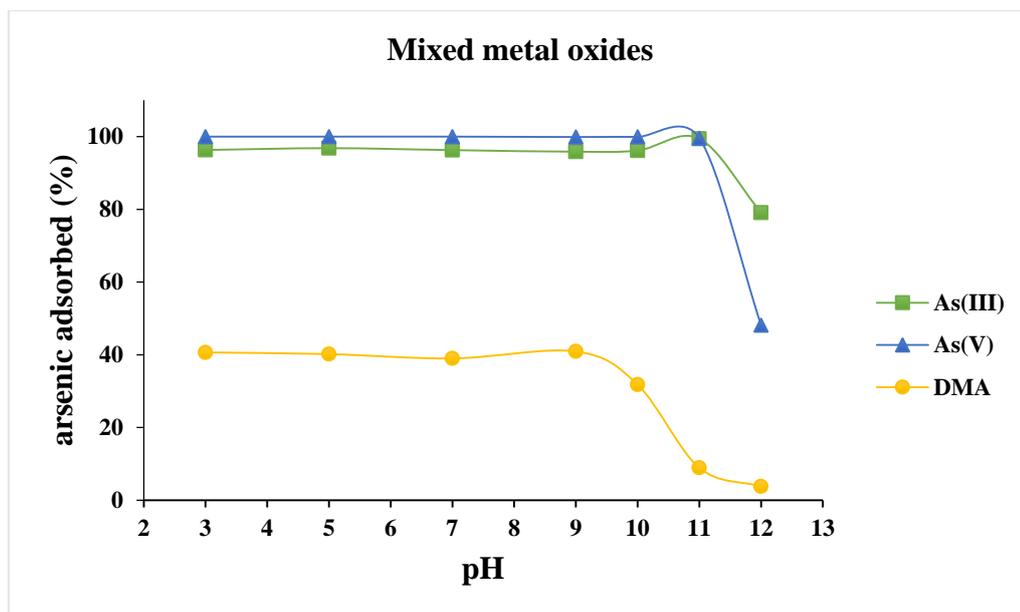


Figure 4.4 Effect of pH on As(III), As(V) and DMA adsorption on mixed metal oxides

In case of As(III) and As(V), the adsorption of As(III) and As(V) on mixed metal oxides shows maximum adsorption at pH from 3 to 11. However, at pH higher than 11 the adsorption percentages of As(V) and As(III) dramatically decreased according to in alkaline condition, the surface of mixed metal oxides becomes negatively charged sites [54] and dominates the repulsion between As(V) in form of AsO_4^{3-} , As(III) in form of AsO_3^{3-} and mixed metal oxides as showed in Figure 4.4.

For DMA the percent adsorption were low at pH between 3 and 9 due to the hydrodynamic size of DMA was large when compared with arsenite and arsenate. In alkaline condition, the mixed metal oxides could not adsorb DMA that was in form of $(\text{CH}_3)_2\text{As}(\text{O})\text{O}^-$ via the repulsion of negatively charge site of mixed metal oxides and DMA.

4.2.2 Effect of concentration of eluent

The elution efficiency of arsenic on the adsorbent was presented in term of percent elution which is calculated by Equation 4.8.

$$\text{Elution (\%)} = (C_f/C_i) \times 100 \quad (4.8)$$

where C_f is the concentration of arsenic in the eluted solution (mg L^{-1})

C_i is the concentration of arsenic absorbed into the sorbent (mg L^{-1})

4.2.2.1 Strong base anion exchange (SBAE) resin

The percent elution of As(V) was studied using HCl (0.1, 0.5, and 2 mol L^{-1}) and H_2SO_4 (0.1, 0.5, and 2 mol L^{-1}) for 2 hours. The initial concentration of As(V) was 4 mg L^{-1} . The results of percent elution of As(V) were illustrated in Figure 4.5.

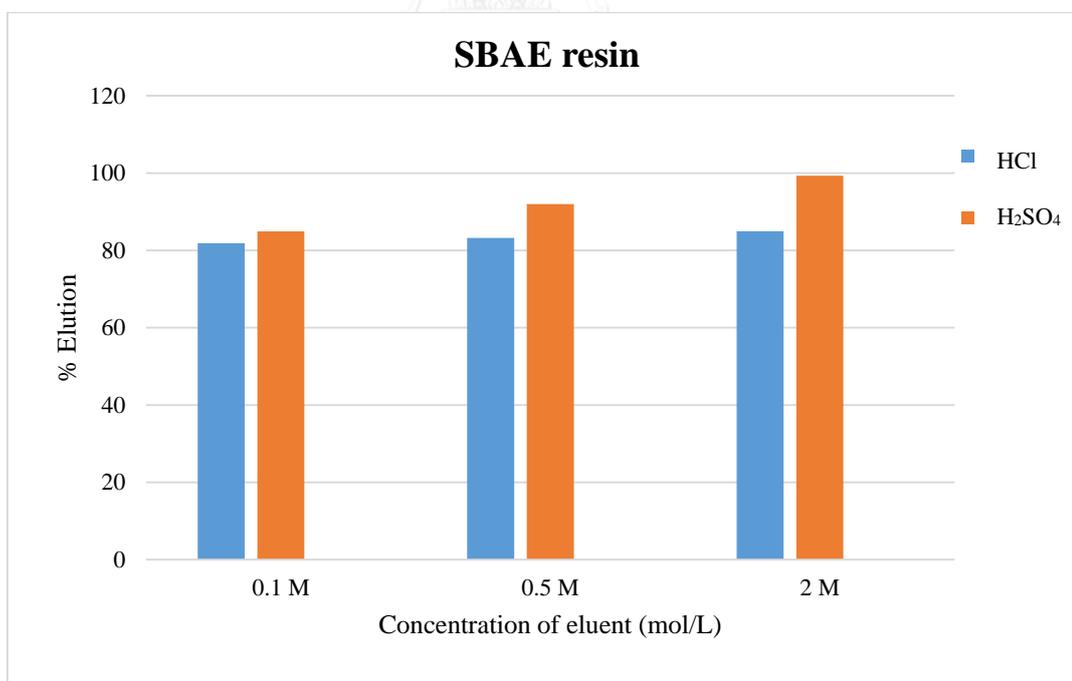


Figure 4.5 Effect of concentration of eluent on % Elution of As(V) using the SBAE resin.

As shown in Figure 4.5, the mean percent elution of 0.1 M, 0.5 M, and 2 M of HCl were 81.86 ± 1.6 , 82.23 ± 1.56 , and 84.96 ± 0.98 , respectively. This result indicated that the elution efficiency of three concentrations of hydrochloric acid were similar for the elution of As(V) on SBAE resin. For H₂SO₄ 0.1, 0.5 and 2 M, the mean percent elution was 84.91 ± 1.42 , 91.97 ± 0.71 and 99.32 ± 0.64 , respectively. Result indicated that sulfuric acid has higher percent elution than hydrochloric acid. Sulfuric acid has higher acid strength towards the resin than hydrochloric acid. As a result, sulfuric acid has higher efficiency than hydrochloric acid. The sulfuric acid concentration of 2 mol L⁻¹ was selected for the elution of As(V) on SBAE resin.

4.2.2.2 Mixed metal oxides

The percent elution of As(III) was studied using HNO₃ (0.1, 0.5, and 2 mol L⁻¹) and H₂SO₄ (0.1, 0.5 and 2 mol L⁻¹) for 2 hours. The initial concentration of As(III) was 2.32 mg L⁻¹. The results of percent elution of As(III) were illustrated in Figure 4.6.

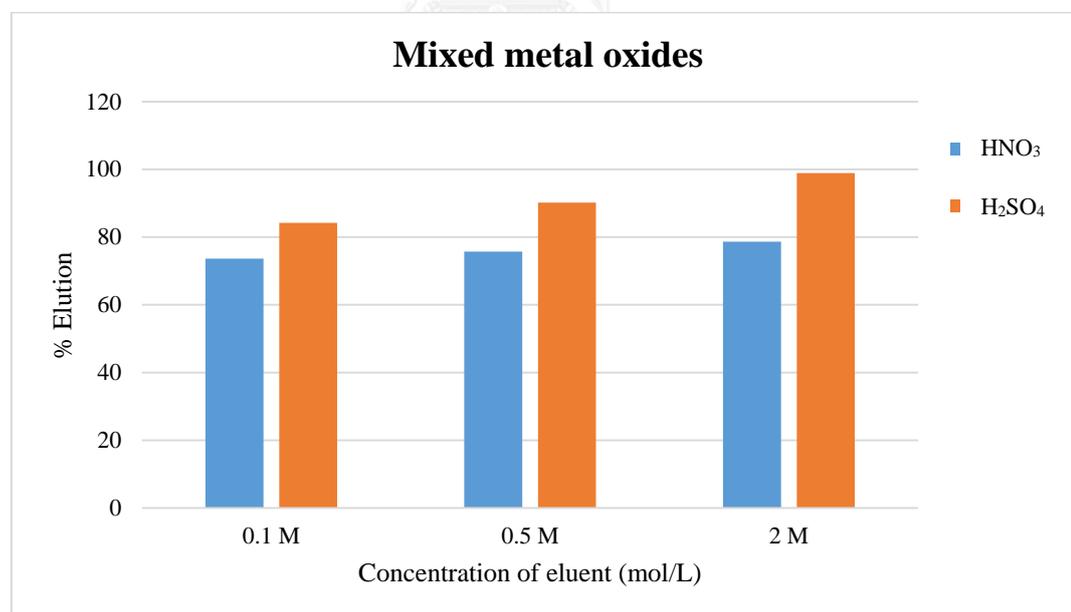


Figure 4.6 Effect of concentration of eluent on % Elution of As(III) using the mixed metal oxides.

As shown in Figure 4.6, the mean percent elution of 0.1 M, 0.5 M, and 2 M of HNO_3 were 73.64 ± 0.41 , 75.72 ± 1.02 , and 78.63 ± 1.04 , respectively. This result indicated that the elution efficiency of three concentrations of nitric acid were similar for the elution of As(III) on mixed metal oxides. For H_2SO_4 0.1, 0.5 and 2 M, the mean percent elution was 84.21 ± 0.75 , 90.17 ± 0.52 and 98.89 ± 0.68 , respectively. Result indicated that sulfuric acid has higher percent elution than nitric acid. Sulfuric acid is a strong acid than nitric acid, and sulfuric acid could destroy mixed metal oxides, as a result the sorbent and arsenic could dissolve. The sulfuric acid concentration of 2 mol L^{-1} was selected for the elution of As(III) on mixed metal oxides.

4.3 Adsorption capacity

The adsorption isotherm was investigated by varying concentration of arsenic species (6, 10, 15, and 20 mg L^{-1}). The experimental conditions used 10 mg of adsorbent and 10 mL of sample solution. The adsorption capacities of As(V) on SBAE resin and As(III) on mixed metal oxides sorbent were estimated at pH 11 by means of the Langmuir adsorption isotherm as expressed in Equation. (4.9) [55].

$$C_e/q_e = 1/bq_m + C_e/q_m \quad (4.9)$$

where C_e is the residual concentration of arsenic at equilibrium (mg L^{-1})

q_e is the amount of arsenic adsorbed per gram adsorbent (mg g^{-1})

b is the Langmuir constant (L mg^{-1})

q_m is the maximum adsorption capacity (mg g^{-1})

4.3.1 Strong base anion exchange (SBAE) resin

According to adsorption isotherm as shown in Figure 4.7, adsorption capacity is constant over the residual concentration of arsenic at equilibrium (C_e) was 6 mg L^{-1} .

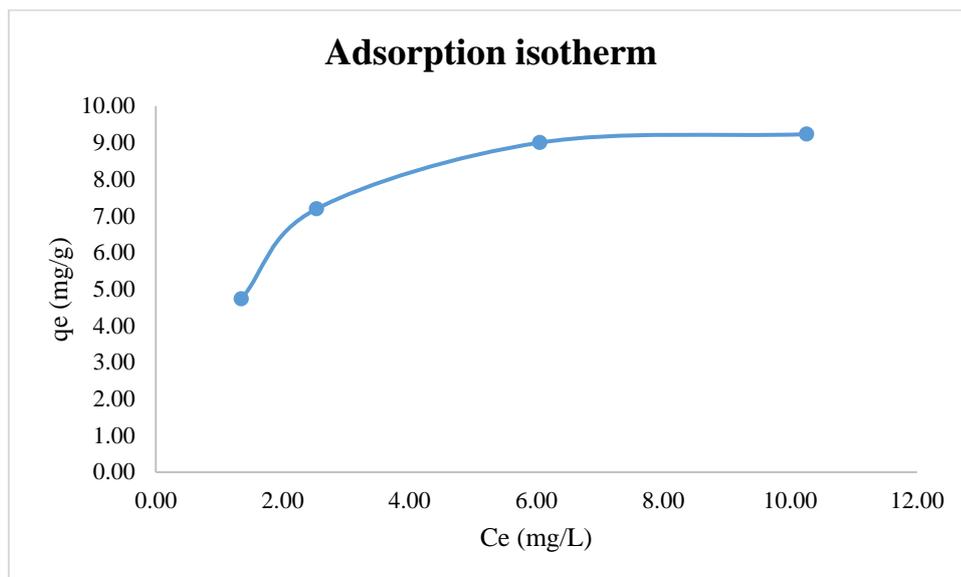


Figure 4.7 Adsorption isotherm of As(V) on SBAE resin.

According to the linear Langmuir plot (C_e versus C_e/q_e) as shown in Figure 4.8, the linear line was obtained with the R^2 of 0.9952 and slope of 0.094. The maximum sorption capacity of As(V) was 10.6 mg g^{-1} .

From the result based on the Langmuir model, the characteristic of As(V) behavior on SBAE resin was monolayer adsorption process due to chemisorption.

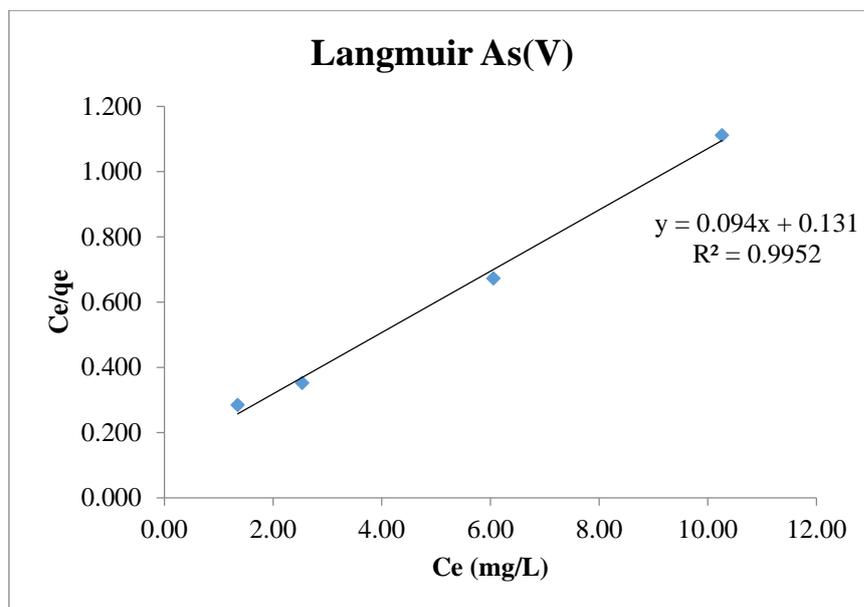


Figure 4.8 Langmuir isotherm plot of As(V) on SBAE resin.

4.3.2 Mixed metal oxides

According to the linear Langmuir plot (C_e versus C_e/q_e) as shown in Figure 4.10, the linear line was obtained with the R^2 of 0.879 and slope of 0.0272. The maximum sorption capacity of As(III) was 36.8 mg g^{-1} .

From the result based on the Langmuir model, the characteristic of As(III) behavior on mixed metal oxides was monolayer adsorption process due to chemisorption.

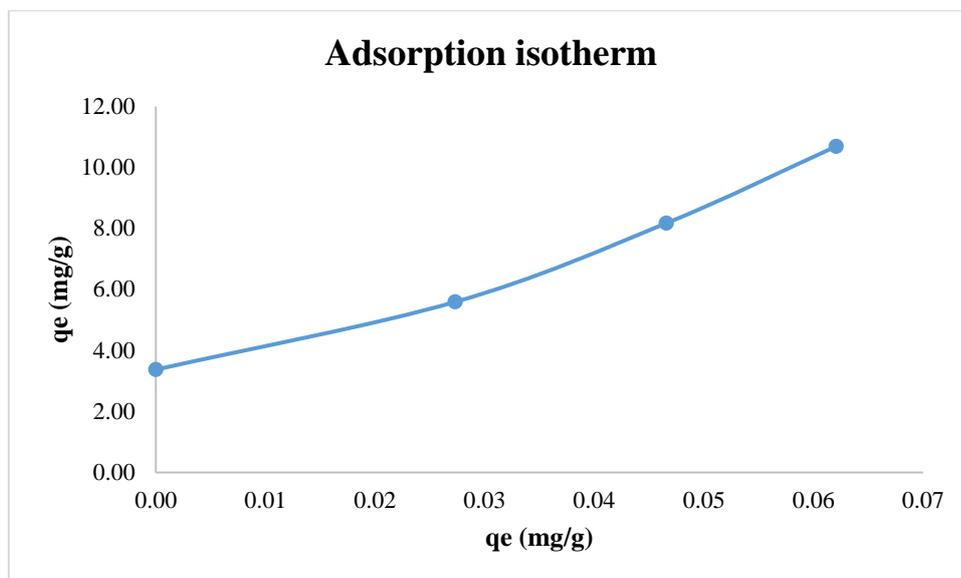


Figure 4.9 Adsorption isotherm of As(III) on mixed metal oxides.

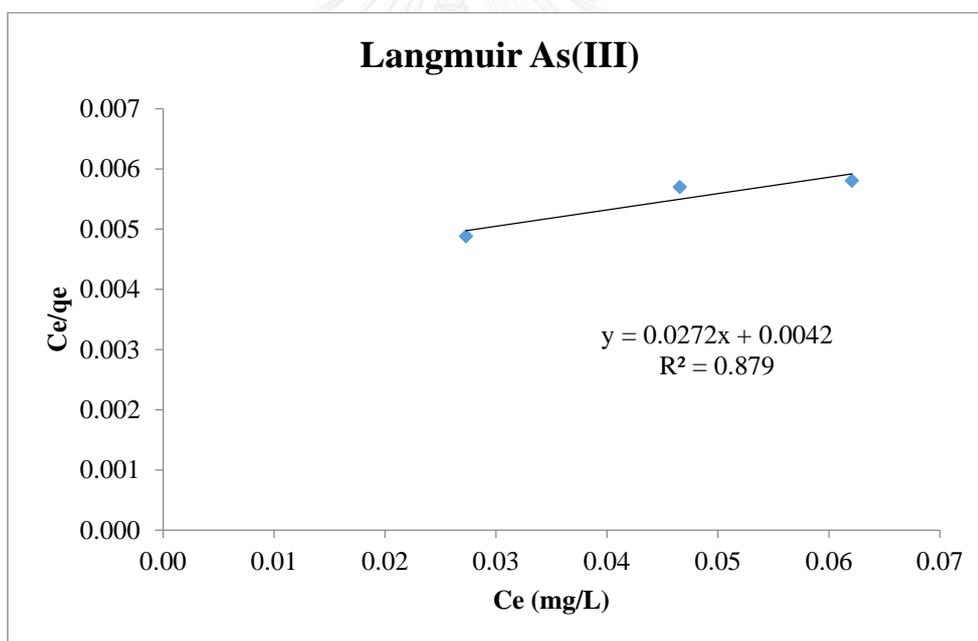


Figure 4.10 Langmuir isotherm plot of As(III) on mixed metal oxides.

4.4 Adsorption of each arsenic specie

4.4.1 Batch method

4.4.1.1 Strong base anion exchange (SBAE) resin sorbent

An adsorption of each arsenic species was studied by using SBAE resin sorbent. The initial concentration of arsenic in solution of each species (As(III), As(V), and DMA) at pH 11 was 5.8, 10, and 5.4 mg L⁻¹, respectively. Then, 10 mg of SBAE resin sorbent was added into the arsenic solution. The concentration of obtained solution was measured by ICP-OES.

The results as shown in Figure 4.11 indicated that the percent adsorption of As(III), As(V), and DMA on the SBAE resin, calculated by equation (4.1), were 5.67 ± 0.05 , 81.09 ± 0.82 and 8.16 ± 0.46 %, respectively. The results conclude that SBAE resin sorbent could be used for adsorption of As(V).

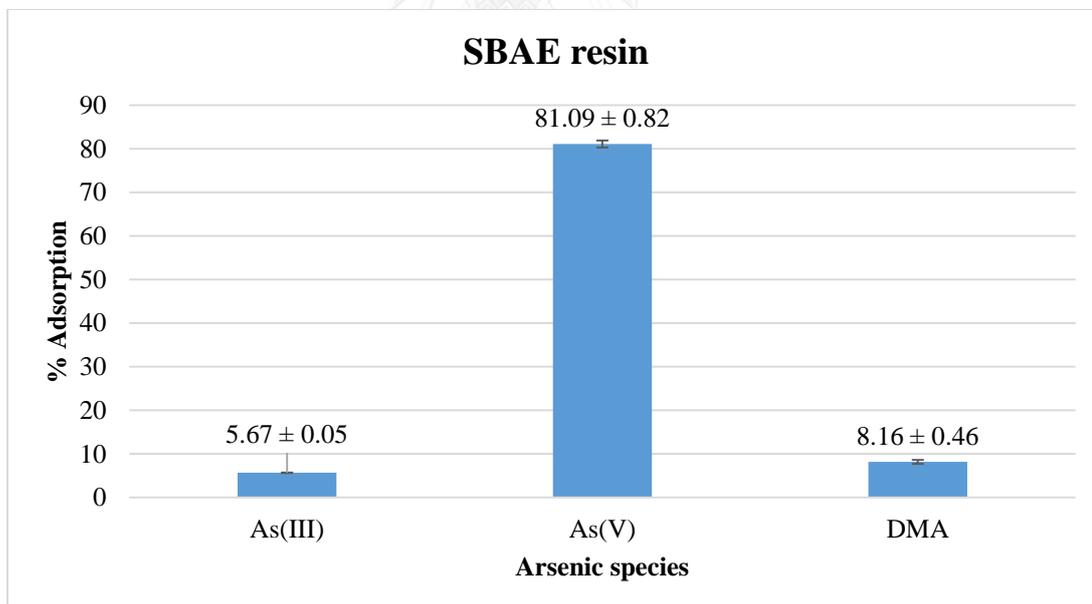


Figure 4.11 The percent adsorption of each arsenic species on SBAE resin sorbent.

4.4.1.2 Mixed metal oxides sorbent

Adsorption of each arsenic species was studied by using mixed metal oxides sorbent. The initial concentration of arsenic in solution of each species (As(III), As(V), and DMA) at pH 11 was 5.8, 10, and 5.4 mg L⁻¹, respectively. Then, 10 mg of mixed metal oxides sorbent was added into the arsenic solution. The concentration of obtained solution was measured by ICP-OES.

According to the results shown in Figure 4.12, the percent adsorption of As(III), As(V), and DMA on mixed metal oxides sorbent, calculated by equation (4.1), were 99.41 ± 0.01 , 99.56 ± 0.39 and 8.93 ± 1.13 %, respectively. The results conclude that mixed metal oxides sorbent could be used for adsorption of As(V) and As(III).

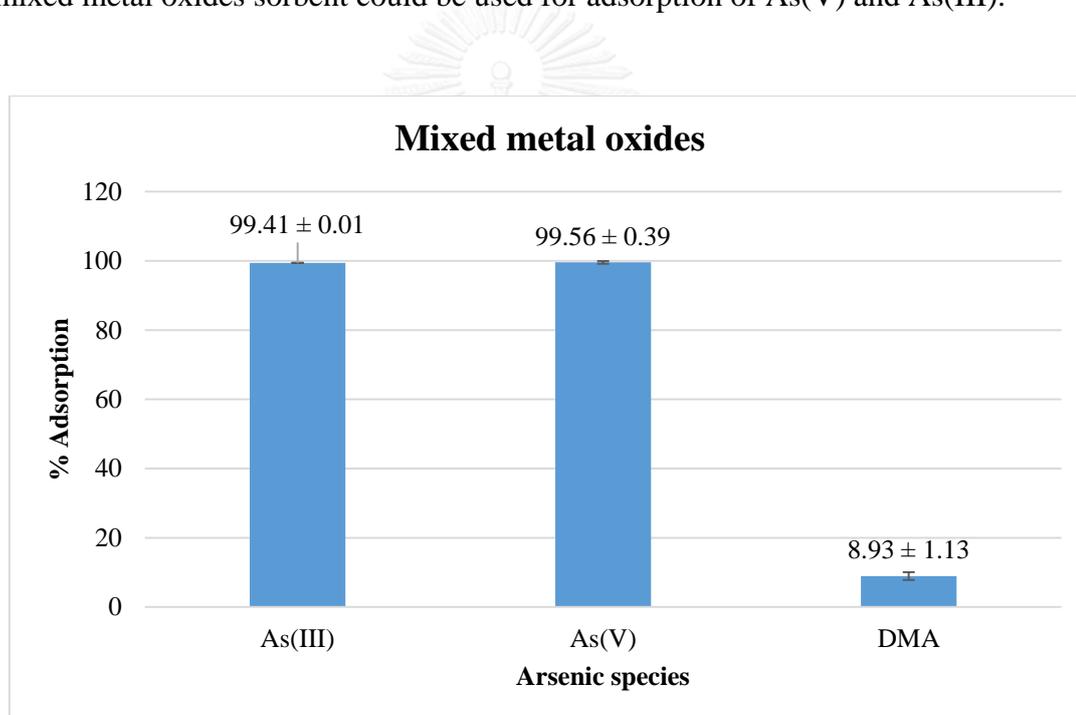


Figure 4.12 The percent adsorption of each arsenic species on mixed metal oxides sorbent.

4.4.2 Column method

4.4.2.1 Strong base anion exchange (SBAE) resin column

An adsorption of each arsenic species was studied by using SBAE resin column. The initial concentration of arsenic in solution of each species (As(III), As(V), and DMA) at pH 11 was 1.74, 3, and 1.62 mg L⁻¹, respectively. Then, the arsenic solution were pass through SBAE resin column. The concentration of obtained solution was measured by ICP-OES.

The results as shown in Figure 4.13 indicated that the percent adsorption of As(III), As(V), and DMA on the SBAE resin, calculated by equation (4.1), were 75.66 ± 0.32 , 83.23 ± 1.82 and 40.34 ± 1.04 %, respectively. When compared with batch method, As(III), As(V) and DMA could be adsorbed increasingly on SBAE resin column due to increasing of SBAE resin sorbent.

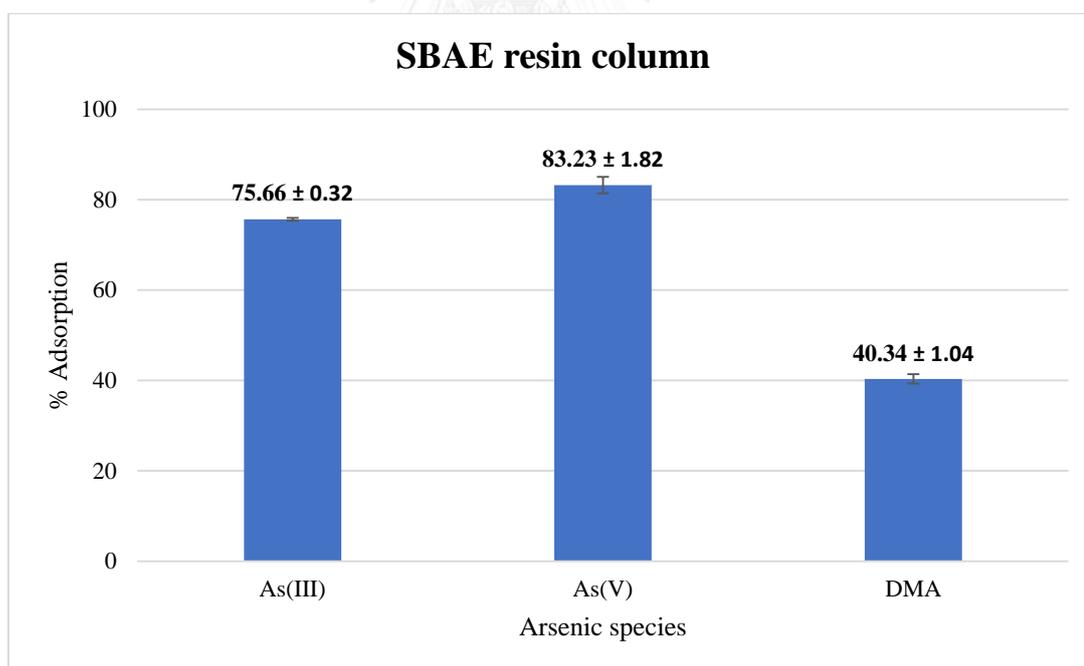


Figure 4.13 The percent adsorption of arsenic species on SBAE resin column.

4.4.2.2 Mixed metal oxides column

An adsorption of each arsenic species was studied by using mixed metal oxides column. The initial concentration of arsenic in solution of each species (As(III), As(V), and DMA) at pH 11 was 1.74, 3, and 1.62 mg L⁻¹, respectively. Then, the arsenic solution were pass through mixed metal oxides column. The concentration of obtained solution was measured by ICP-OES.

The results as shown in Figure 4.14 indicated that the percent adsorption of As(III), As(V), and DMA on mixed metal oxides column, calculated by equation (4.1), were 100, 100 and 30.62 ± 0.66 %, respectively. When compared with batch method, DMA could be adsorbed increasingly on mixed metal oxides column due to the error of pH value.

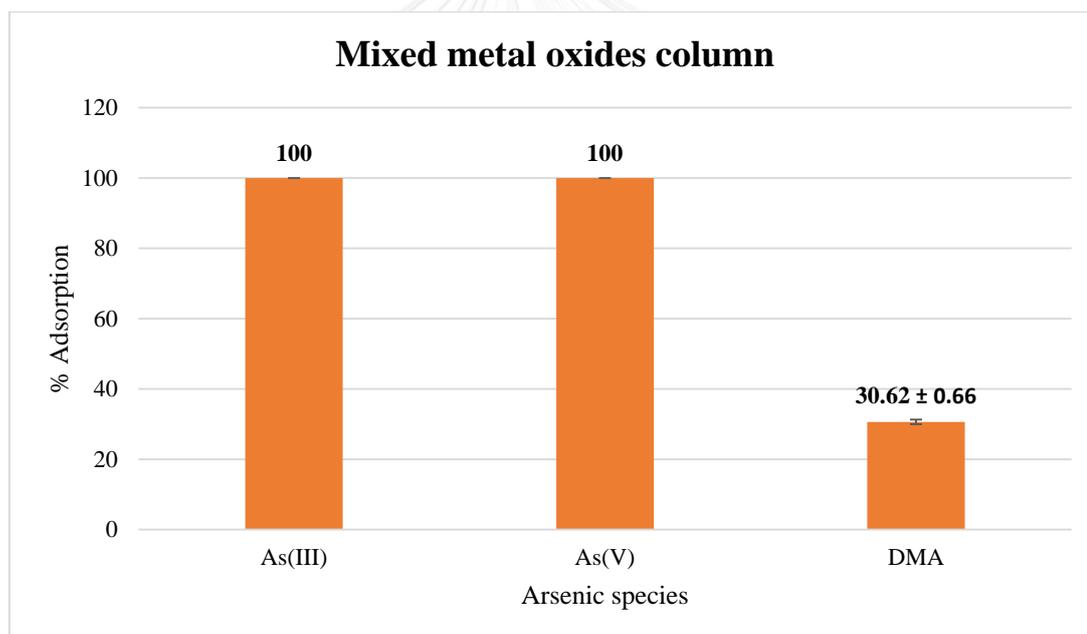


Figure 4.14 The percent adsorption of arsenic species on mixed metal oxides column.

4.5 Speciation of arsenic in mixed arsenic species solution

4.5.1 Batch method

4.5.1.1 Strong base anion exchange (SBAE) resin sorbent

Arsenic speciation was achieved using SBAE resin sorbent. SBAE resin (10 mg) was added to a 10 mL test tube, containing 10 mL of As(III), As(V), and DMA (1.74, 3.0 and 1.62 mg L⁻¹, respectively) at pH 11. After adsorption, the concentration of arsenic in solution was 3.40 ± 0.03 mg L⁻¹. This result shows that the percent adsorption of As(V) was 101 ± 1 when using SBAE resin sorbent under optimal condition.

4.5.1.2 Mixed metal oxides sorbent

Arsenic speciation was achieved using mixed metal oxides sorbent, the solution containing 10 mL of As(III) and DMA (1.74 and 1.62 mg L⁻¹, respectively) at pH 11 was added to 10 mg of mixed metal oxides sorbent in 10 mL test tube. The concentration of arsenic in supernatant solution was 1.61 ± 0.07 mg L⁻¹. Under optimal condition, the percent adsorption of As(III) was 108 ± 4.

As the results shown above, SBAE resin sorbent and mixed metal oxides sorbent could be used for speciation of As(V) and As(III), respectively.

Table 4.1 Arsenic speciation using batch method.

Sorbent	Before adsorption			After adsorption (mean ± SD, n=3)			
	Arsenic (mg L ⁻¹)			Arsenic (mg L ⁻¹)		Adsorption (%)	
	As(III)	As(V)	DMA	As(III)+ DMA	DMA	As(V)	As(III)
SBAE resin	1.74	3.0	1.62	3.40 ± 0.03	-	101 ± 1	-
Mixed metal oxides	1.74	-	1.62	-	1.61 ± 0.07	-	108 ± 4

4.5.2 Column method

4.5.2.1 Strong base anion exchange (SBAE) resin column

Arsenic speciation was achieved using SBAE resin column. The initial concentration of arsenic in solution of each species (As(III), As(V), and DMA) at pH 11 was 1.74, 3, and 1.62 mg L⁻¹, respectively. Then, the arsenic solution were pass through SBAE resin column. After adsorption, the concentration of arsenic in solution was 2.70 ± 0.06 mg L⁻¹. This result shows that the percent adsorption of As(V) was 121 ± 2 . As(III), As(V) and DMA could be adsorbed increasingly on SBAE resin column due to increasing of SBAE resin sorbent.

4.5.2.2 Mixed metal oxides column

Arsenic speciation was achieved using mixed metal oxides column. The initial concentration of arsenic in solution of each species (As(III) and DMA) at pH 11 was 1.74 and 1.62 mg L⁻¹, respectively. Then, the arsenic solution were pass through mixed metal oxides column. The concentration of arsenic in supernatant solution was 0.83 ± 0.06 mg L⁻¹. Under optimal condition, the percent adsorption of As(III) was 140 ± 4 due to the error of pH value.

As the results shown above, SBAE resin column and mixed metal oxides column could not be used for speciation of As(V) and As(III), respectively.

Table 4.2 Arsenic speciation using column method.

Sorbent	Before adsorption			After adsorption (mean \pm SD, n=3)			
	Arsenic (mg L ⁻¹)			Arsenic (mg L ⁻¹)		Adsorption (%)	
	As(III)	As(V)	DMA	As(III)+ DMA	DMA	As(V)	As(III)
SBAE resin	1.74	3.0	1.62	2.70 ± 0.06	-	121 ± 2	-
Mixed metal oxides	1.74	-	1.62	-	0.83 ± 0.06	-	140 ± 4

4.6 Effect of amount of SBAE resin sorbent on arsenic speciation

In batch experiment, the amount of SBAE resin sorbent was varied from 10-50 mg while mixed metal oxides was fixed at 10 mg. The mixture of arsenic solution containing 10 mL of As(III), As(V), and DMA ($0.58, 1$ and 0.54 mg L^{-1} , respectively) at pH 11 were added to a 10 mL test tube, containing SBAE resin (10, 20, and 50 mg). Then the obtain solution was added to mixed metal oxides (10 mg) in a 10 mL test tube. The result is shown in Figure 4.15, 4.16 and 4.17.

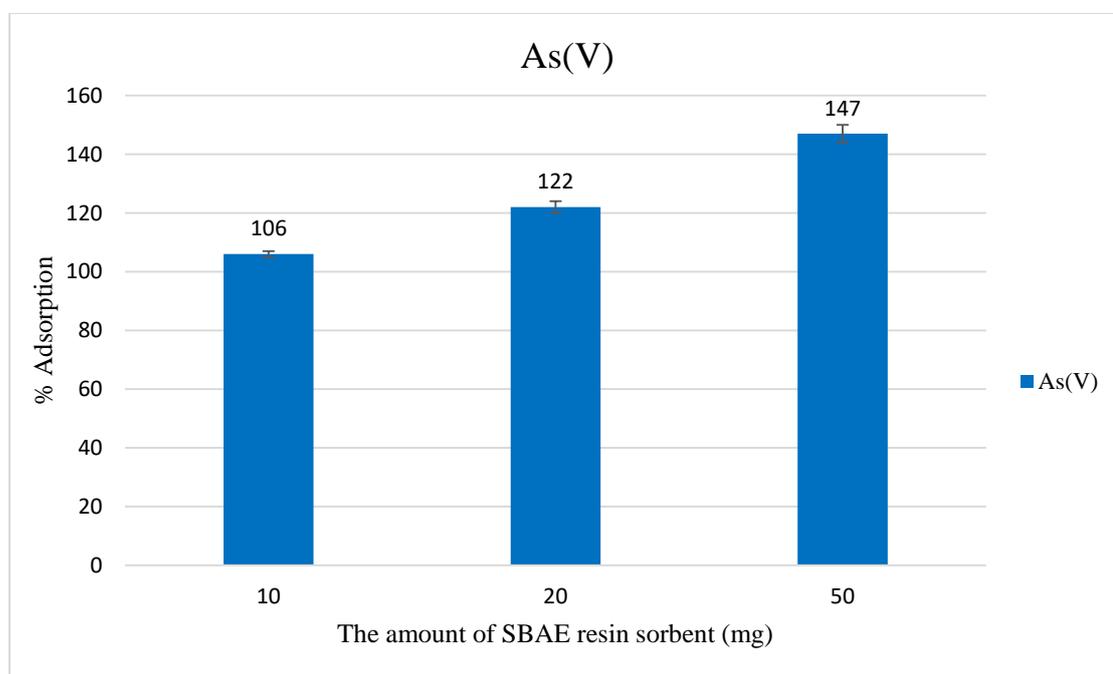


Figure 4.15 The percent adsorption of As(V) on SBAE resin sorbent with various amount of SBAE resin sorbent.

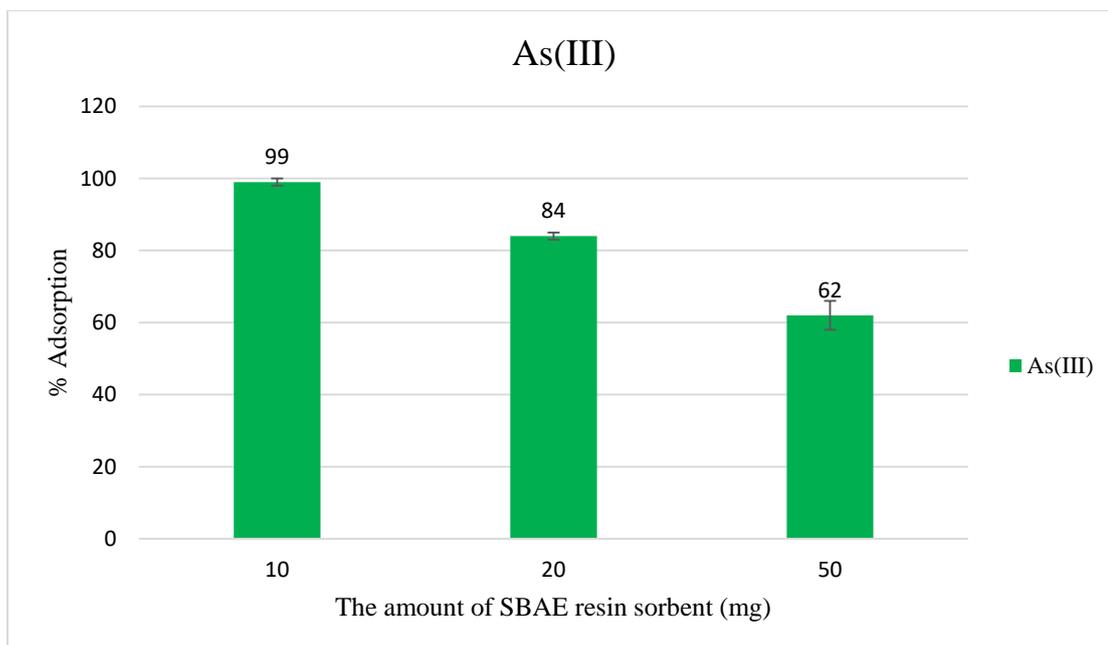


Figure 4.16 The percent adsorption of As(III) on mixed metal oxides with various amount of SBAE resin sorbent.

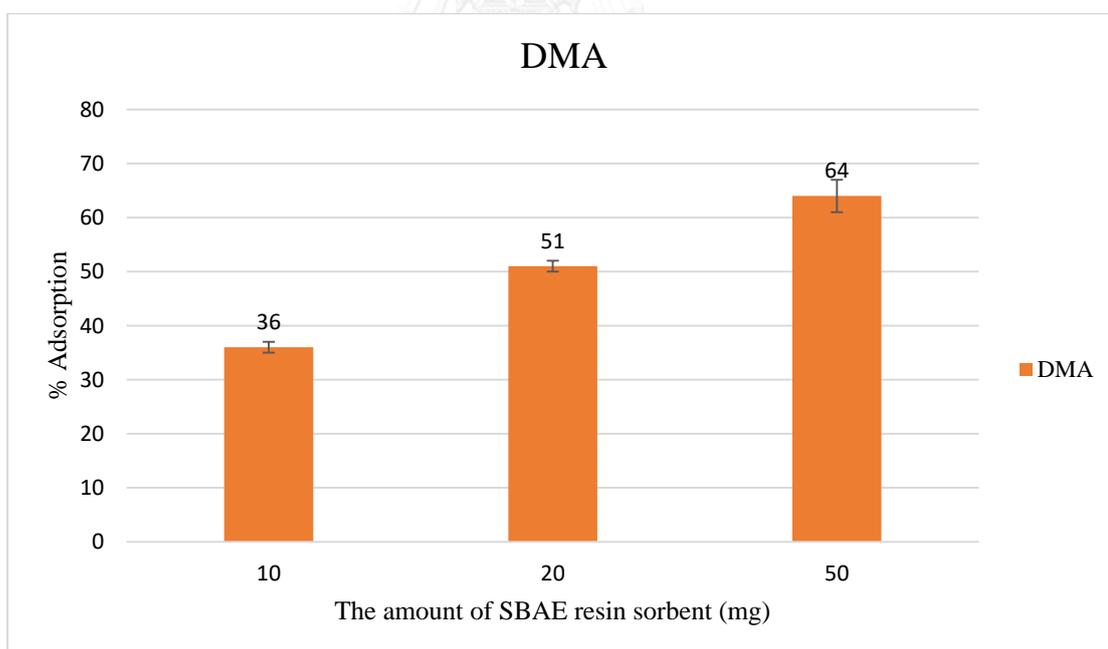


Figure 4.17 The percent adsorption of DMA on SBAE resin sorbent and mixed metal oxides with various amount of SBAE resin sorbent.

The results reveals that when increasing the amount of SBAE resin sorbent, the percent adsorption of As(V) and DMA were increased while the percent adsorption of As(III) was decreased due to As(III), As(V) and DMA could be adsorbed increasingly on SBAE resin sorbent when increasing of SBAE resin sorbent.

4.7 Method validation

Arsenic speciation was achieved using SBAE resin and mixed metal oxides sorbent. SBAE resin (10 mg) was added to a 10 mL test tube, containing 10 mL of As(III), As(V), and DMA (1.74, 3.0 and 1.62 mg L⁻¹, respectively). Then the obtain solution was added to mixed metal oxides (10 mg) in a 10 mL test tube as shown in Figure 4.16.

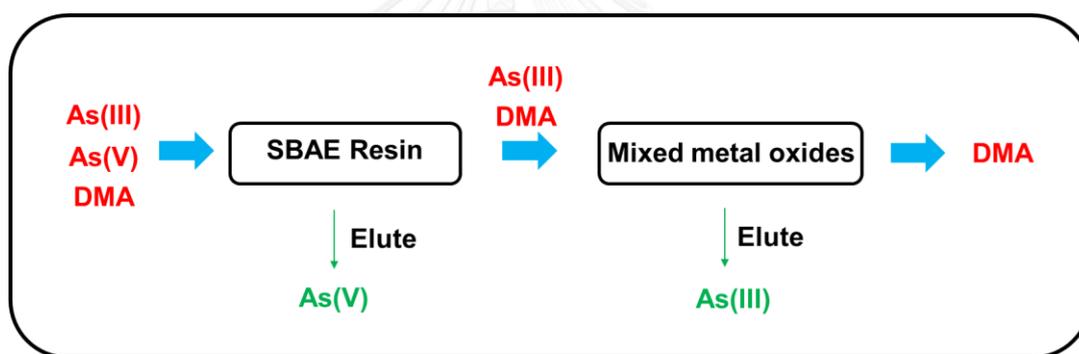


Figure 4.18 Concept of arsenic speciation using SBAE resin and mixed metal oxides sorbents.

The accuracy and precision of speciation of arsenic method was presented in term of %recovery which is calculated by Equation 4.10.

$$\% \text{ recovery} = [C_f/C_i] \times 100 \quad (4.10)$$

where C_f is the concentration of arsenic in the eluted solution (mg L⁻¹)
 C_i is the theoretical initial concentration of arsenic before adsorption (mg L⁻¹)

After adsorption by SBAE resin sorbent, the concentration of As(V) in eluted solution was $2.75 \pm 0.08 \text{ mg L}^{-1}$. This result shows that the % recovery of As(V) was 92 ± 3 under optimal condition. Then, the supernatant solution containing As(III) and DMA was added to mixed metal oxides (10 mg) in a 10 mL test tube. The concentration of As(III) in eluted solution was $1.75 \pm 0.08 \text{ mg L}^{-1}$. Under optimal condition, the % recovery of As(III) was 101 ± 5 . Finally, the concentration of DMA in solution after using SBAE resin sorbent and mixed metal oxides sorbent was $1.34 \pm 0.01 \text{ mg L}^{-1}$ and % recovery was 83 ± 1 .

Table 4.3 Accuracy and precision of the proposed method (n=3).

Arsenic species	%recovery	%RSD
As(III)	101 ± 5	4.83
As(V)	92 ± 3	2.79
DMA	83 ± 1	1.11

As the results shown above, the % recovery and % relative standard deviation of As(III), As(V) and DMA were in the range of 83 - 101 and 1.11 - 4.83, respectively.

CHAPTER V

CONCLUSION

5.1 Conclusion

A novel method for speciation of arsenic (As(III), As(V) and dimethyl arsenic acid (DMA)) in waste water using solid phase materials including strong base anion exchange (SBAE) resin and mixed metal oxides coupled with inductively coupled plasma optical emission spectrometry (ICP-OES) was developed. The mixed metal oxides was synthesized and characterized by XRD analysis. The structure of mixed metal oxides was somewhere between the amorphous and crystalline state. In batch experiment, various parameters influencing the adsorption of arsenic species such as pH of solution and concentration of eluent were investigated. The optimum operating conditions for extraction of arsenic species with the strong based anion exchange resin and mixed metal oxides were shown in Table 5.1.

Table 5.1 The optimum operating conditions for extraction with the strong based anion exchange resin and mixed metal oxides.

Factor	SBAE resin	Mixed metal oxides
Amount of adsorbent	10 mg	10 mg
Solution pH	11	11
Sample volume	10 mL	10 mL
Eluent solution	2 mol L ⁻¹ H ₂ SO ₄	2 mol L ⁻¹ H ₂ SO ₄
Eluent volume	10 mL	10 mL

For investigation of the effect of pH on As(III), As(V) and DMA adsorption with SBAE resin and mixed metal oxides sorbent, As(V) could be adsorbed on SBAE resin while As(III) and DMA could not be retained on the sorbent at pH 11. DMA could not be retained on mixed metal oxides while As(III) and As(V) could be adsorbed at pH 11. For H₂SO₄ 2 M, the mean percent elution of As(V) and As(III) was 99.32 ± 0.64 % and 98.89 ± 0.68 %, respectively. Therefore The sulfuric acid concentration of 2 mol L⁻¹ was selected for the elution of As(V) on SBAE resin and As(III) on mixed metal oxides. From the result based on the Langmuir model, the characteristic of As(V) behavior on SBAE resin and As(III) behavior on mixed metal oxides were monolayer adsorption process. The maximum adsorption capacities of As(V) on SBAE resin and As(III) on mixed metal oxides were 10.6 mg g⁻¹ and 36.8 mg g⁻¹, respectively.

Arsenic speciation was achieved using the batch method. After adsorption, the percent adsorption of As(V) and As(III) in arsenic solution when using SBAE resin sorbent 10 mg and mixed metal oxides sorbent 10 mg under optimal conditions were 101 ± 1 and 108 ± 4 , respectively.

The speciation of arsenic under optimal conditions by the presented method indicates that the % recovery and % relative standard deviation of As(III), As(V) and DMA are in the range of 83 - 101 and 1.11 - 4.83, respectively, showing good accuracy and precision of the method in speciation of arsenic solution.

5.2 Suggestion for future work

The proposed method should be applied to the speciation and determination of arsenic species in industrial wastewater. The influence of coexisting ion should be studied further.

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