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สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

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MODIFICATION OF SLUDGE FROM TAP WATER PRODUCTION BY IRON FOR ARSENIC
IONS ADSORPTION FOLLOWED BY SOLIDIFICATION USING CEMENT

Mr. Porndanai Sarntanayoot

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry

Department of Chemistry

Faculty of Science

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By	Mr. Porndanai Sarntanayoot
Field of Study	Chemistry
Thesis Advisor	Assistant Professor Apichat Imyim, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial
Fulfillment of the Requirements for the Master's Degree

.....Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

.....Chairman
(Associate Professor Vudhichai Parasuk, Ph.D.)

.....Thesis Advisor
(Assistant Professor Apichat Imyim, Ph.D.)

.....Examiner
(Assistant Professor Narong Praphairaksit, Ph.D.)

.....External Examiner
(Woravith Chansuvarn, Ph.D.)

พรตัญญู สารธนาบุตร : การดัดแปรกากตะกอนจากการผลิตน้ำประปาด้วยเหล็กสำหรับการดูดซับไอออนอาร์เซนิกตามด้วยการทำให้เป็นก้อนแข็งด้วยซีเมนต์ (MODIFICATION OF SLUDGE FROM TAP WATER PRODUCTION BY IRON FOR ARSENIC IONS ADSORPTION FOLLOWED BY SOLIDIFICATION USING CEMENT) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.อภิชาติ อ๋มยิ้ม, 95 หน้า.

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ภาควิชา เคมี ลายมือชื่อนิสิต

สาขาวิชา เคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก

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PORNANAI SARNTANAYOOT: MODIFICATION OF SLUDGE FROM TAP WATER PRODUCTION BY IRON FOR ARSENIC IONS ADSORPTION FOLLOWED BY SOLIDIFICATION USING CEMENT. ADVISOR: ASST. PROF. APICHAT IMYIM, Ph.D., 95 pp.

Sludge of tap water production from the Metropolitan Waterworks Authority (Bangkhen, Thailand) was modified by iron via borohydride reduction of ferric chloride. The modified sludge with 10% (w/w) iron was used as an adsorbent for arsenic removal from arsenic-contaminated water. The modified sludge was characterized by inductively coupled plasma-optical emission spectrometry (ICP-OES), x-ray fluorescence spectrometry (XRF), x-ray diffraction spectrometry (XRD), scanning electron microscopy with energy dispersive x-ray spectrometry (SEM-EDS), transmission electron microscopy (TEM) and surface area analysis. Then, factors affecting the adsorption of arsenite and arsenate were studied. The optimal pH was 3.0. The equilibrium adsorption of both arsenite and arsenate was reached within 1 hour. The maximum adsorption capacity was found to be 24.15 and 35.71 mg/g for arsenite and arsenate, respectively. High concentrations of phosphate, sulfate and humic acid caused a decrease in arsenite and arsenate removal efficiency. Moreover, the iron(0)-modified sludge was applied to remove arsenic from wastewater, surface water and ground water samples. All results showed that the iron(0)-modified sludge was effective for arsenite and arsenate removal from water. Furthermore, the sludge obtained after arsenic removal process was stabilized/solidified using a mix proportion of 60% (w/w) cement. The leaching characteristic of arsenic studied by dynamic monolithic leaching test (DMLT) showed that arsenic was hardly leached from the solidified waste. Its leaching mechanism was controlled by diffusion at the beginning and the depletion had occurred at the end of leaching process.

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CONTENTS

	Page
THAI ABSTRACT	iv
ENGLISH ABSTRACT	v
ACKNOWLEDGEMENTS	vi
CONTENTS	vii
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF ABBREATIONS.....	xv
CHAPTER I INTRODUCTION.....	1
1.1 Statement of problem	1
1.2 Objectives and scope of the research.....	3
1.3 Benefits of this research	3
CHAPTER II THEORY AND LITERATURE REVIEW	4
2.1 Arsenic	4
2.1.1 Chemistry of arsenic and its toxicity.....	4
2.1.2 Methods for arsenic removal	7
2.2 Adsorption at the liquid-solid interface.....	12
2.2.1 Type of adsorption	12
2.2.2 Type of adsorbents	13
2.2.3 Adsorption kinetics	14
2.2.3.1 Pseudo first-order model.....	14
2.2.3.2 Pseudo second-order model.....	15
2.2.4 Adsorption isotherms.....	16

	Page
2.2.4.1 Langmuir isotherm	17
2.2.4.2 Freundlich isotherm.....	18
2.3 Tap water production and tap water production sludge	19
2.4 Zero-valent iron.....	22
2.5 Management of contaminated sludge.....	23
2.6 Literature review.....	25
2.6.1 Removal of arsenic from water by using low cost adsorbent.....	25
2.6.2 Removal of arsenic from water by using zero-valent iron and zero-valent iron supported materials.....	28
CHAPTER III EXPERIMENTAL.....	32
3.1 Instruments.....	32
3.2 Chemicals.....	33
3.3 Preparation of tap water production sludge	34
3.4 Modification of tap water production sludge.....	34
3.5 Characterization of the modified tap water production sludge.....	35
3.5.1 Elemental composition using ICP-OES	36
3.5.2 Characterization of iron particles in modified tap water sludge.....	36
3.5.3 Determination of the point of zero charge	37
3.6 Batch experiment for arsenic adsorption	37
3.6.1 Effect of pH.....	38
3.6.2 Effect of contact time	38
3.6.3 Investigation of arsenic adsorption mechanism onto the adsorbent	38
3.6.4 Adsorption isotherms.....	39

	Page
3.6.5 Effect of interfering ions	39
3.7 Application in real contaminated water samples	40
3.7.1 Batch system	40
3.7.2 Column system	40
3.8 Stabilization/solidification of the modified tap water sludge after arsenic removal using cement as binder	41
3.8.1 Solidified waste preparation.....	41
3.8.2 Leaching characteristics of arsenic by dynamic monolithic leaching test (DMLT).....	43
3.8.3 Total dissolved solids	45
CHAPTER IV RESULTS AND DISCUSSION	46
4.1 Modification of tap water production sludge by iron.....	46
4.2 Characterization of the modified tap water production sludge.....	46
4.2.1 Elemental composition	47
4.2.1.1 ICP-OES	47
4.2.1.2 XRF	47
4.2.2 Structural information by XRD	48
4.2.3 Morphology	50
4.2.3.1 SEM-EDS.....	50
4.2.3.2 TEM.....	52
4.2.4 Characterization of iron particles in modified tap water sludge.....	53
4.2.5 Surface area	54
4.2.6 Determination of the point of zero charge (pH_{pzc})	55
4.3 Batch experiments for arsenic adsorption	56

	Page
4.3.1 Effect of pH	56
4.3.2 Effect of contact time	58
4.3.2.1 Adsorption kinetics	58
4.3.3 Adsorption isotherms	61
4.3.4 Investigation of arsenic adsorption mechanism onto the adsorbent	69
4.3.5 Effect of interfering ions	71
4.4 Application in real contaminated water samples	72
4.4.1 Batch system	72
4.4.2 Column system	73
4.4.3 Arsenic removal from surface water and ground water samples	74
4.5 Stabilization/solidification of the modified tap water sludge after arsenic removal using cement as binder	76
4.5.1 Solidified waste preparation	76
4.5.2 Leaching characteristics of arsenic by dynamic monolithic leaching test (DMLT)	77
4.5.3 Total dissolved solid	80
CHAPTER V CONCLUSION	82
5.1 Conclusion	82
5.2 Suggestion for the future work	85
REFERENCES	86
VITA	95

LIST OF TABLES

Table	Page
2.1 List of various arsenic species	5
2.2 Acute toxicity of arsenic on human organ systems.....	6
2.3 Summary of common arsenic removal methods	10
2.4 Typical applications of some commercial adsorbents	13
3.1 List of instruments	32
3.2 Conditions of ICP-OES for arsenic determination.....	33
3.3 List of chemicals	34
3.4 List of the amounts chemicals used in the modification of tap water production sludge.....	35
3.5 Techniques for characterization of the modified tap water sludge.....	36
3.6 List of amounts of the adsorbent	39
3.7 Time intervals for water collection.....	44
4.1 The amount of element using ICP-OES technique.....	47
4.2 The amount of elements using XRF technique	48
4.3 BET surface area value.....	55
4.4 Adsorption kinetic parameters for arsenic adsorption onto the modified tap water sludge.....	60
4.5 Adsorption isotherm parameters for arsenite adsorption onto the modified tap water sludge	65
4.6 Adsorption isotherm parameters for arsenate adsorption onto the modified tap water sludge	66
4.7 Comparison of adsorption capacity for arsenic onto some adsorbents	67

Table	Page
4.8 The arsenic removal from the wastewater samples (TK-80 and TK-81) in batch system	73
4.9 The arsenic removal from the wastewater sample (TK-81) with different types of column system.....	74
4.10 The arsenic removal from natural water samples spiked with arsenite	75
4.11 The arsenic removal from natural water samples spiked with arsenate	75
4.12 Compressive strength of solidified waste cured for 14 days.....	77
4.13 The arsenic and iron leaching concentration of each times in leaching process	79
4.14 TDS values of each times in leaching process.....	81
5.1 The optimal conditions for arsenic removal in batch system.....	83

LIST OF FIGURES

Figure	Page
2.1 Distribution diagram of (a) arsenite and (b) arsenate.	6
2.2 Pseudo first-order kinetic plot.....	15
2.3 Pseudo second-order kinetic.....	16
2.4 (a) Langmuir adsorption isotherm and (b) Langmuir linearized equation plot.	18
2.5 (a) Freundlich adsorption isotherm and (b) Freundlich linearized equation plot.	19
2.6 Tap water treatment diagram.	20
2.7 The interaction of arsenite on nano zero-valent iron.....	23
3.1 Plastic cylindrical container.	43
4.1 Pictures of tap water production sludge and the modified sludge with different iron:sludge ratios.	46
4.2 XRD pattern of sludge.....	49
4.3 XRD pattern of iron prepared from the borohydride reduction of Fe(III).	49
4.4 XRD pattern of modified tap water sludge (Fe:sludge 10:90).	50
4.5 SEM images of (a) sludge, (b) iron and (c) Fe:sludge 10:90 under magnification of 200x (left images) and 7500x (right images).....	51
4.6 Elemental mapping images of (a) sludge, (b) Fe:sludge 2:98, (c) Fe:sludge 4:96, (d) Fe:sludge 6:94, (e) Fe:sludge 8:92 and (f) Fe:sludge 10:90.	52
4.7 TEM images of (a) sludge and (b) Fe:sludge 10:90.....	53
4.8 Photographs of (1) copper(II) chloride solution and the reaction of copper(II) chloride with (2) tap water sludge, (3) the modified tap water sludge (Fe:sludge 10:90), (4) iron particles (via sodium borohydride reduction) and (5) purchased iron(0) powder.	54

Figure	Page
4.9 Experimental mass titration curve of the modified tap water sludge (Fe:sludge 10:90).	55
4.10 Effect of pH on arsenite adsorption.....	57
4.11 Effect of contact time on adsorption of (a) arsenite (b) arsenate.....	58
4.12 (a) Pseudo first-order kinetic plot of arsenite and (b) Pseudo second-order kinetic plot of arsenite.....	60
4.13 (a) Pseudo first-order kinetic plot of arsenate and (b) Pseudo second-order kinetic plot of arsenate.....	60
4.14 Adsorption isotherms of arsenite of iron:sludge (a) 2:98, (b) 4:96, (c) 5:95, (d) 6:94, (e) 8:92 and (f) 10:90.	62
4.15 Langmuir plots (left image) of iron:sludge (a) 2:98, (c) 4:96, (e) 5:95, (g) 6:94, (i) 8:92, (k) 10:90 and Freundlich plots of iron:sludge (right image) (b) 2:98, (d) 4:96, (f) 5:95, (h) 6:94, (j) 8:92 and (l) 10:90.	64
4.16 Adsorption isotherm of arsenate of iron:sludge 10:90.....	66
4.17 (a) Langmuir isotherm plot and (b) Freundlich isotherm plot.	66
4.18 Comparison of adsorption amount for arsenite and arsenate onto some adsorbent.	70
4.19 Effect of sulfate and phosphate on (a) arsenite and (b) arsenate adsorption..	71
4.20 Effect of humic acid on arsenite and arsenate adsorption.....	72
4.21 (a) photograph of column system and (b) the scheme of different types of column system.....	74
4.22 Solidified waste sample (6:4 of cement to contaminated sludge ratio).....	77
4.23 Photograph of test portion in leaching process.	78
4.24 Graph between cumulative release correlated with time of (a) the protocol proposed by CEN/TS 15863:2012 and (b) this work.	80

LIST OF ABBREATIONS

$\mu\text{g/L}$	Microgram per liter
mg/L	Milligram per liter
$\mu\text{g/g}$	Microgram per gram
mg/g	Milligram per gram
m^2/g	Square meter per gram
$^{\circ}\text{C}$	Degree Celsius
w/w	Weigh by weigh
v/v	Volume by volume
w/v	Weight by volume
mol/L	Molar
nm	Nanometer
μm	Micrometer
ΔG^0	Standard Gibbs free energy change in a chemical process
W	Watt
rpm	Revolutions per minute
V	Volt
psi	Pound per square inch
kg/cm^2	Kilogram per square centimeter
MPa	Mega Pascal

CHAPTER I

INTRODUCTION

1.1 Statement of problem

Nowadays, growing technology and industry brings about one of major critical environmental problems. One of the most important environmental and human concerns is the contamination of heavy metals in water. Arsenic is a well-known toxic element which is metalloid in the periodic table [1]. It can contaminate in water from natural and anthropogenic activities such as industrial smelting of metals, mining, power generation with coal and applications of arsenic-containing pesticides in agriculture [2]. In natural water, arsenic is mostly found in trivalent (arsenite) and pentavalent (arsenate) states. Arsenite remains as neutral species (H_3AsO_3) below a pH of 9.2 while arsenate exists as negative species (H_2AsO_4^- , HAsO_4^{2-}) in a pH range of 2-12 [3]. From the previous research, it showed that arsenite is more difficult to be removed from water and more lethal around 60 times than arsenate [4]. The consumption of water contaminating arsenic in high level causes serious effects on human health include skin damage, cancers in multiple tissues, cardiovascular diseases, pulmonary effects and neurological disorders [5]. The World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) have set a value of 10 $\mu\text{g/L}$ for the arsenic concentration in drinking water [6]. Hence, the removal of arsenic from water by effective techniques is very important.

There are common arsenic removal techniques, such as, coagulation/flocculation, oxidation, membrane filtration, electrochemical methods and adsorption. Many of these techniques require the optimal conditions such as pH of solution and some of which require an oxidation step as pre-treatment to convert

arsenite to arsenate [7]. Adsorption is one of the most popular techniques which can reduce arsenic in water due to the fact that it is easy, safe and inexpensive [8].

Tap water production sludge is a by-product of water treatment process. This sludge contains mainly aluminium and iron hydroxides remaining from coagulation process during water treatment. Remaining aluminium and iron hydroxides in sludge can strongly adsorb some anion species such as phosphate and arsenate [9]. Therefore, tap water production sludge is an alternative low-cost adsorbent for arsenic removal process. Tap water sludge obtained from the Metropolitan Waterworks Authority, Bangkok, Thailand was used as an adsorbent in arsenic removal process. This sludge showed a capability to adsorb arsenate ions but it had low capacity for arsenite adsorption [10].

Recently, nano zero-valent iron has been used for the arsenic removal process owing to its large active surface area and high arsenic adsorption capacity [11]. However, the direct utilization of nano zero-valent iron for field scale application seems to be limited by tiny particle size that causes high-pressure drop in a fixed bed column. Loading of nano zero-valent iron onto a supporting larger-sized material is potential method to overcome such mentioned problem [12]. Thus, zero valent iron was chosen to modify the tap water production sludge with the purpose to increase a capability to adsorb arsenite which is more toxic and difficult to be removed than arsenate and to reduce the limitation of small particle size of zero-valent iron.

Furthermore, the sludge obtained after arsenic removal process is a toxic waste. This solid waste must be safeguarded to reduce the risk in toxicity of waste before landfill. The stabilization/solidification using cement is commonly used for reducing the potential hazard of waste due to its simplicity, inexpensiveness, and effectiveness [13]. Moreover, studying of leaching characteristic of arsenic is necessary

to evaluate the environmental assessment of solidified and stabilized (S/S) hazardous wastes. For this reason, cement was chosen in this research as a binder in the stabilization/solidification of the modified tap water sludge after arsenic removal process and the leaching characteristic of arsenic was studied by dynamic monolithic leaching test (DMLT).

1.2 Objectives and scope of the research

The objectives of this research include the modification of a low-cost adsorbent from tap water production residue by iron via sodium borohydride reduction of ferric chloride. The modified sludge was used as an adsorbent for the removal of arsenite and arsenate ions from water. Factors affecting the arsenic removal including pH of solution, contact time, adsorption isotherms and the effect of interfering ions on arsenic removal process were studied. Moreover, the removal efficiency using the modified sludge for real arsenic-contaminated water samples was evaluated. Furthermore, the modified sludge after arsenic adsorption process was stabilized/solidified using cement-based binder and the leaching characteristics of arsenic by using dynamic monolithic leaching test (DMLT) was studied to evaluate the environmental assessment of the remedial measures of the solidified/stabilized waste.

1.3 Benefits of this research

The modified tap water sludge by iron being effective for arsenite and arsenate adsorption was obtained. Also, the leaching characteristic of arsenic after stabilizing/solidifying process was achieved.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Arsenic

2.1.1 Chemistry of arsenic and its toxicity

Arsenic is a metalloid element in the periodic table of the elements. It is well-known as the king of poisons which has effect on environmental and human health. Utilization of arsenic in human activities included industrial smelting of metal, mining, power generation with coal and applications of arsenic-containing agriculture and pesticides may cause the contamination of arsenic in natural water. Arsenic occurs in the environment in different oxidation states such as +5, +3, 0 and -3 depending on redox potential and pH conditions [14]. They can be found in organic and inorganic forms as displayed in Table 2.1. In general, arsenic is mostly found in oxyanions of trivalent arsenic (arsenite) and pentavalent arsenic (arsenate). Arsenite is predominant species under reducing conditions and it exists as neutral species (H_3AsO_3) at a pH less than 9.2, while arsenate become dominating species under oxidizing conditions at a pH range of 2-12, the negative species (H_2AsO_4^- , HAsO_4^{2-}) exist. The distribution of arsenite and arsenate species under different pH conditions is shown in Figure 2.1a and Figure 2.1b [15], respectively. The dissociation reactions and corresponding equilibrium constants of arsenite and arsenate are shown in the following equations [16],

Arsenite or As(III):



Arsenate or As(V):

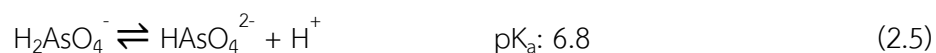


Table 2.1 List of various arsenic species [6]

Name	Abbreviation	Chemical Formula
Arsenite, arsenous acid	As ^(III)	As(OH) ₃
Arsenate, arsenic acid	As ^(V)	AsO(OH) ₃
Monomethylarsonic acid	MMA ^V	CH ₃ AsO(OH) ₂
Monomethylarsonous acid	MMA ^{III}	CH ₃ As(OH) ₂
Dimethylarsinic acid	DMA ^V	(CH ₃) ₂ AsO(OH)
Dimethylarsinous acid	DMA ^{III}	(CH ₃) ₂ AsOH
Trimethylarsine oxide	TMAO	(CH ₃) ₃ AsOH
Trimethylarsine	TMA ^{III}	(CH ₃) ₃ As
Arsenobetaine	AsB	(CH ₃) ₃ As ⁺ CH ₂ COO ⁻
Arsenocholine	AsC	(CH ₃) ₃ As ⁺ CH ₂ CH ₂ OH
Tetramethylarsonium ion	Me ₄ As ⁺	(CHM ₃) ₄ As ⁺
Dimethylarsinoyl ethanol	DMAE	(CHM ₃) ₂ AsOCH ₂ CH ₂ OH

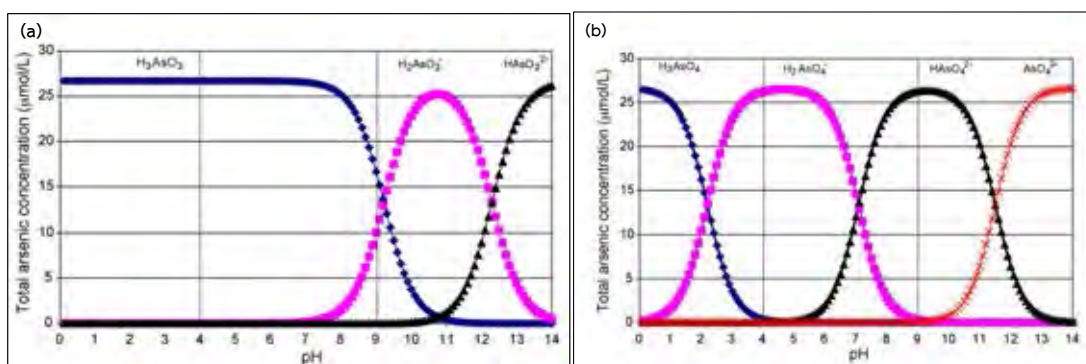


Figure 2.1 Distribution diagram of (a) arsenite and (b) arsenate [15].

The consumption of water containing arsenic in high concentration produces serious effects on human health. The symptoms of the acute toxicity of arsenic on human organ systems are listed in Table 2.2. Arsenic does not show only acute toxicity on human organ systems but also, has chronic toxicity effect on multiorgan systems such as hyperpigmentation with depigmentation, hearing loss and diabetes mellitus [14]. Moreover, it is well known that arsenite is more lethal around 60 times than arsenate and it also more difficult to be removed from water due to its neutral form at a wild range of pH [4]. Therefore, the removal of arsenic by effective methods is necessary. The various techniques for arsenic removal are provided in the next subsection.

Table 2.2 Acute toxicity of arsenic on human organ systems

Organ System	Symptoms
Gastrointestinal	Nausea, vomiting, thirst, anorexia, heartburn, abdominal pain, diarrhea with bloody stool
Dermal	Dermatitis, vesiculation, melanosis
Neural	Encephalopathy (hyperpyrexia, convulsion, tremor, coma, disorientation), neuritis, peripheral neuropathy (primarily sensory type, paresthesia, hyperesthesia, numbness of extremities, neuralgia, muscular cramp, and weakness)

Table 2.2 (cont.) Acute toxicity of arsenic on human organ systems

Organ System	Symptoms
Renal	Cortical necrosis, leukocyturia, glycosuria, hematuria, oliguria, uremia
Hepatic	Congestion, fatty infiltration, central necrosis, acute yellow atrophy, cholangitis, cholecystitis
Hematological	Anemia, thrombocytopenia, leukopenia, bone marrow suppression
Cardiovascular	Cardiac abnormality (ventricular fibrillation and atypical tachycardia), prolonged Q-T interval, abnormal T wave; congestive heart failure, hypotension
Respiratory	Irritation of nasal mucosa, pharynx, larynx and bronchi, pulmonary edema, tracheobronchitis, bronchial pneumonia, nasal septum perforation
Ophthalmic	Conjunctivitis

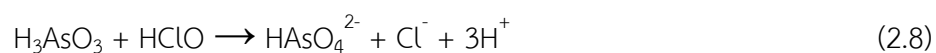
2.1.2 Methods for arsenic removal

Currently, there are many methods available for the removal of arsenic from water including oxidation, co-precipitation, ion exchange, membrane filtration and adsorption methods. A detail of these techniques is roughly described in the following subsections.

i) Oxidation method

It is well known that arsenite is more difficult to be removed from water than arsenate. Therefore, the oxidization of arsenite to arsenate is the way to improve the efficiency of arsenic removal process. However, oxidation alone does not remove arsenic from water, and it must be combined with other techniques such as coagulation or adsorption. Arsenite can be oxidized by various oxidizing agents,

including oxygen, hypochlorous and potassium permanganate as shown in Equations 2.7, 2.8 and 2.9, respectively [17]. Moreover, some solids such as manganese oxides and iron oxides can also oxidize arsenite to arsenate [18]. Beside chemical oxidation, there are other types of oxidation that have been used as a pre-treatment step such as biological oxidation by micro-organisms, air oxidation and solar oxidation. Nevertheless, these techniques are very slow and can take more weeks for oxidation while chemicals can rapidly oxidize arsenite to arsenate [7].



ii) Co-precipitation method

Co-precipitation is a method which has been widely used for arsenic removal. It can remove not only arsenic but also many suspended and dissolved matters from water by using coagulants such as alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), ferric chloride (FeCl_3) and ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$). The mechanism for arsenic removal by co-precipitation method, including firstly, the precipitation of insoluble compounds of arsenic and alum or iron salts such as $\text{Al}(\text{AsO}_4)$ and $\text{Fe}(\text{AsO}_4)$, secondly, the attachment of arsenic species into a growing metal hydroxide phase. This process is called co-precipitation. Finally, the adsorption of arsenic species on the surfaces of the insoluble metal hydroxides occurs via electrostatic forces. All these three mechanisms can independently occur. However, this method requires a filtration step after the co-precipitation step to ensure a complete removal of all particles [7, 18].

iii) Ion exchange method

Ion exchange is one of the methods for arsenic removal in which ions are swapped between a solution phase and a solid resin phase. The solid phase is based on a cross-linked polymer skeleton containing a large number of ionizable groups electrostatically bound to the resin. Ion exchange resins can be divided into four types including,

- Strongly acidic (cation exchange) : sulfonate, $-\text{SO}_3^-$
- Weakly acidic (cation exchange): carboxylate, $-\text{COO}^-$
- Strongly basic (anion exchange): quaternary amine, $-\text{N}^+(\text{CH}_3)_3$
- Weakly basic (anion exchange): tertiary amine, $-\text{N}(\text{CH}_3)_2$

Arsenate can be removed from water by using strong-base anion exchange resin while arsenite is not removed by this resin. Therefore, the oxidation step of arsenite to arsenate as a pre-treatment is necessary for improving the efficiency of ion exchange process. However, the excess of oxidant often needs to be removed before the ion exchange in order to avoid the damage of sensitive resins. Moreover, pH, concentration of other anions and total dissolved solid of the solution can strongly affect the efficiency of the ion exchange for arsenic removal [18].

iv) Membrane filtration method

Membrane filtration method can remove many contaminants from water such as bacteria, salts and heavy metals. The method is carried out by passing water through special filter media which physically retain the impurities presented in water. The membrane filtration method can be categorized by the pore size of membrane including, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). All of these categories are pressure driven. However, this method is

usually expensive than other arsenic treatment methods. Therefore, it is not commonly used for arsenic removal [7].

v) Adsorption method

Adsorption is a widely used method for arsenic removal from water due to the fact that it is easy to operate, safe and economical. It involves the partition of adsorbates in liquid phase to the surface of solid phase adsorbent. The adsorbent is generally packed into a column. During adsorption process, contaminants are adsorbed on adsorbent surfaces. When adsorption sites become filled, the contaminated adsorbent might be regenerated or appropriately managed. The efficiency of arsenic removal depends on the properties of the adsorbent. Moreover, to increase the adsorption efficiency, a pretreatment step such as oxidation prior adsorption process might be done [7].

All of methods for arsenic removal which are mentioned above can conclude in Table 2.3 [17].

Table 2.3 Summary of common arsenic removal methods

Method	Chemical	Benefits	Drawbacks
Oxidation	O ₂	Relative simple	The process is only pretreatment step
	HClO	Relative low-cost	
	KMnO ₄	Relative rapid	does not remove
	Biological oxidation	process (some	arsenic from water
	Air oxidation	oxidize)	
	Solar oxidation		

Table 2.3 (cont.) Summary of common arsenic removal methods

Method	Chemical	Benefits	Drawbacks
Co-precipitation	Alum	Relatively low-cost	Produces toxic
	Iron salt	Relatively simple operation Common chemicals available	sludge Low removal of arsnite Pre-oxidation may be required
Membrane filtration	Microfiltration (MF)	High removal efficiency	Very high-cost
	Ultrafiltration (UF)		High tech operation and maintenance
	Nanofiltration (NF)	Not produces toxic solid waste	Produces toxic wastewater
	Reverse osmosis (RO).	Capable for removal of other contaminants	
Sorption	Activated carbon	Relatively well known and commercially available	Produces toxic solid waste
	Activated alumina		Replacement/regeneration required
	Sludge		
	Ion exchange resin		
	Other sorbents	Relatively low-cost (depending on type of adsorbent) Plenty possibilities and scope of development	High tech operation and maintenance

2.2 Adsorption at the liquid-solid interface

Adsorption at the liquid-solid interface is a surface phenomenon occurring when a liquid solute (adsorbate) accumulates on a surface of solid (adsorbent). The adsorption process is generally explained by 3 steps as follows [19];

i) External mass transfer: adsorbates from bulk solution transport to the surface of an adsorbent.

ii) Intraparticle mass transfer: adsorbates from the surface of an adsorbent transfer to the intra-particle active sites.

iii) Adsorption: adsorbates are uptaken on the active site of an adsorbent through physisorption or chemisorption.

The efficiency of adsorption process depends on the physical and chemical properties of adsorbate and adsorbent and the conditions that are used in the adsorption process such as pH of solution, contact time and initial concentration of adsorbate.

2.2.1 Type of adsorption

The interaction between an adsorbate and an adsorbent depends on chemical properties of the species involved. The adsorption process is generally divided into 2 types including physisorption and chemisorption.

i) Physisorption

Physisorption or physical adsorption is the interaction of adsorbate and adsorbent in which an adsorbate attracts to the surface of adsorbent via Van der Waals forces or electrostatic forces which are weak forces. Physisorption occurs quickly and may be multilayer of adsorbate on adsorbent surfaces. The maximum adsorption capacity of this process depends on the pore volume and surface area of adsorbent [20, 21].

ii) Chemisorption

In contrast to physisorption, chemisorption or chemical adsorption involves the formation of chemical bonds such as covalent bonding (sharing of electron) between adsorbates and functional groups on the surface of adsorbent. Therefore, the interaction as chemisorption is stronger than the other one. The adsorption of this process occurs only as monolayer [20, 21].

2.2.2 Type of adsorbents

Adsorbents are very important in the adsorption process due to the fact that it affects the efficiency of the process. Adsorbents must have strength, resistance and good kinetic properties and good capacity for analyte adsorption which refers to high number of active sites on their surface. Moreover, the adsorbents must ultimately be inexpensive. The typical applications of some commercial adsorbents are concluded in Table 2.4 [22].

Table 2.4 Typical applications of some commercial adsorbents

Type	Typical applications
Silica gel	Removal of moisture
Activated alumina	Drying of gases, organic solvents Removal of arsenic, fluoride, uranium, and selenium
Zeolites	Drying of gases Removal of water from azeotropes Removal of acetylene, propane and butane from air Catalysts for several important reactions involving organic molecules Separation of ammonia and hydrogen

Table 2.4 (cont.) Typical applications of some commercial adsorbents

Type	Typical applications
Clays (acid treated and pillared)	Removal of organic pigments Refining of mineral oils Removal of polychlorinated biphenyls (PCBs)
Drinking water treatment sludge	Removal of phosphate and arsenic

2.2.3 Adsorption kinetics

The rate of the analyte adsorb on the surface of the adsorbent is important to investigate so as to design the adsorption process. The pseudo first-order and the pseudo second-order models are commonly used for describing the adsorption kinetics.

2.2.3.1 Pseudo first-order model

The pseudo first-order can be generally expressed in Equation 2.10. It appropriates for low concentrations of analyte [23].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2.10)$$

Integrating Equation 2.10 by applying the initial conditions $q_t = 0$ to $q_t = q_t$ and $t = 0$ to $t = t$, the equation becomes as follows [23],

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2.11)$$

Where q_e is the adsorption amount of the adsorbate at equilibrium (mg/g)

q_t is the adsorption amount of the adsorbate at time (mg/g)

t is time (min)

k_1 is the adsorption rate constant of the pseudo first-order kinetic model (min^{-1})

The plot of $\ln(q_e - q_t)$ against t gives a linear line with a slope of $-k_1$ and intercept $\ln q_e$ as shown as Figure 2.2.

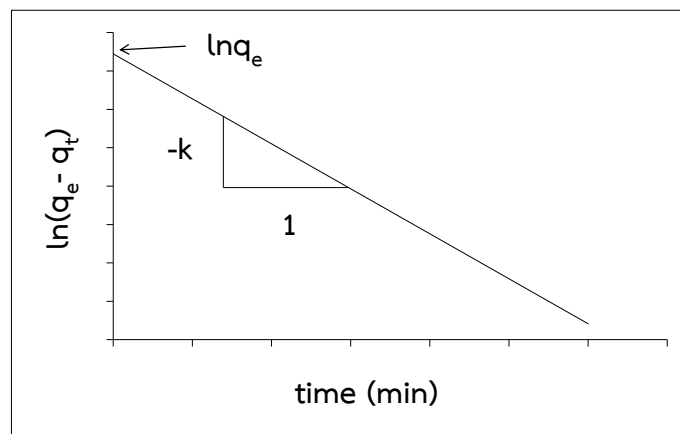


Figure 2.2 Pseudo first-order kinetic plot [24].

2.2.3.2 Pseudo second-order model

The pseudo second-order model is represented in Equation 2.12. It is assumed that the rate of reaction is reliant on the amount of analyte adsorbed on the surface of adsorbent and the amount adsorbed at equilibrium [23].

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2.12)$$

Integrating Equation 2.12 by applying the initial conditions $q_t = 0$ to $q_t = q_t$ and $t = 0$ to $t = t$, gives as follows [23],

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2.13)$$

Where q_e is the adsorption amount of the adsorbate at equilibrium (mg/g)

q_t is the adsorption amount of the adsorbate at time (mg/g)

t is time (min)

k_2 is the adsorption rate constant of the pseudo second-order kinetic model (g/mg·min)

The plot of t/q_t versus t gives linear line with slope $1/q_e$ and intercept $1/k_2q_e^2$ is shown in Figure 2.3.

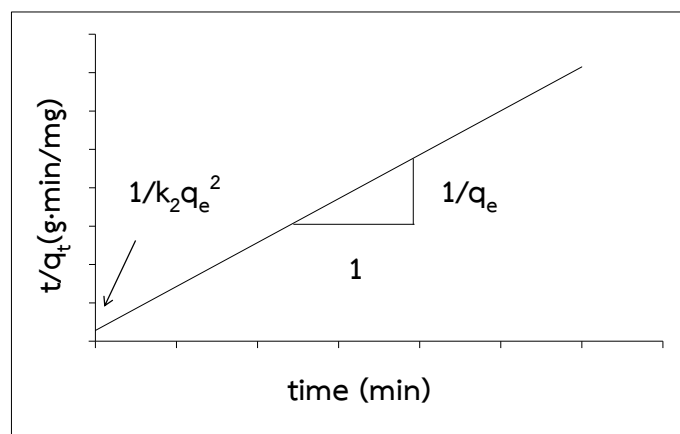


Figure 2.3 Pseudo second-order kinetic [24].

2.2.4 Adsorption isotherms

Adsorption isotherms define as the sorption of adsorbate on the surface of adsorbent at equilibrium under constant temperature. It can display as a function of the equilibrium concentration of adsorbate and the adsorption capacity. The common models which are widely used for determination of the adsorption process include Langmuir isotherm and Freundlich isotherm.

2.2.4.1 Langmuir isotherm

The Langmuir isotherm was proposed by Irving Langmuir in 1918. It appropriates for the description of the chemisorption which is assumed that the adsorption of an adsorbate on the surface of adsorbent is monolayer and is limited by the available number of active sites [22, 25]. The Langmuir isotherm equation and its linearized equation are shown in Equations 2.14 and 2.15, respectively.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2.14)$$

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (2.15)$$

Where

- C_e is the equilibrium concentration of adsorbate (mg/L)
- q_e is the equilibrium adsorption capacity of adsorbent (mg/g)
- q_m is the maximum adsorption capacity of adsorbent (mg/g)
- b is the constant related to the affinity of binding sites (L/mg)

The theoretical curve of Langmuir isotherm between the adsorption capacity of adsorbent (q_e) with the equilibrium concentration of adsorbate (C_e) and the curve is demonstrated from its linearized equation are shown in Figure 2.4a and Figure 2.4b, respectively.

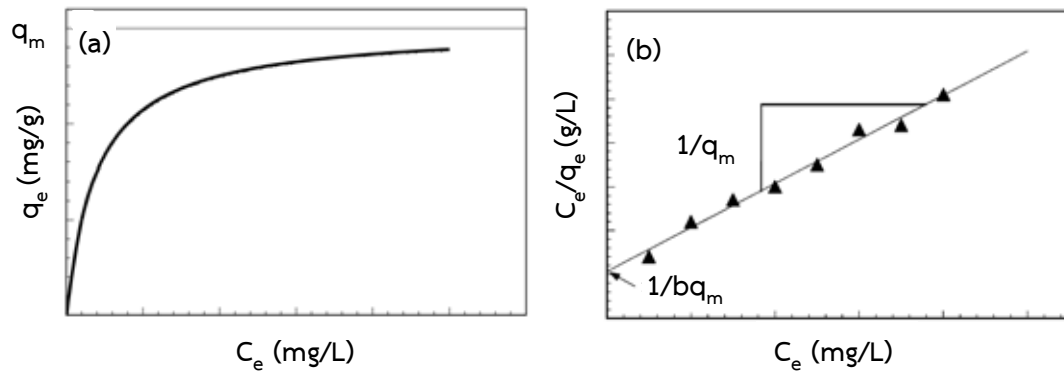


Figure 2.4 (a) Langmuir adsorption isotherm and (b) Langmuir linearized equation plot [24].

2.2.4.2 Freundlich isotherm

The alternative isotherm was developed by Herbert F. Freundlich. It is presumed that the adsorption of an adsorbate on the heterogeneous surface of adsorbent is chemisorption in multilayer [25]. The Freundlich isotherm equation and its linearized equation can be represented in Equations 2.16 and 2.17, respectively.

$$q_e = K_f C_e^{1/n} \quad (2.16)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2.17)$$

Where K_f is the constant related to adsorption capacity (mg/g)
 n is the Freundlich constant related to adsorption intensity
 C_e is the equilibrium concentration of adsorbate (mg/L)
 q_e is the equilibrium adsorption capacity of adsorbent (mg/g)

The theoretical curve of Freundlich isotherm between the adsorption capacity of adsorbent (q_e) with the equilibrium concentration of adsorbate (C_e) and the curve is demonstrated from its linearized equation are shown in Figure 2.5a and Figure 2.5b, respectively.

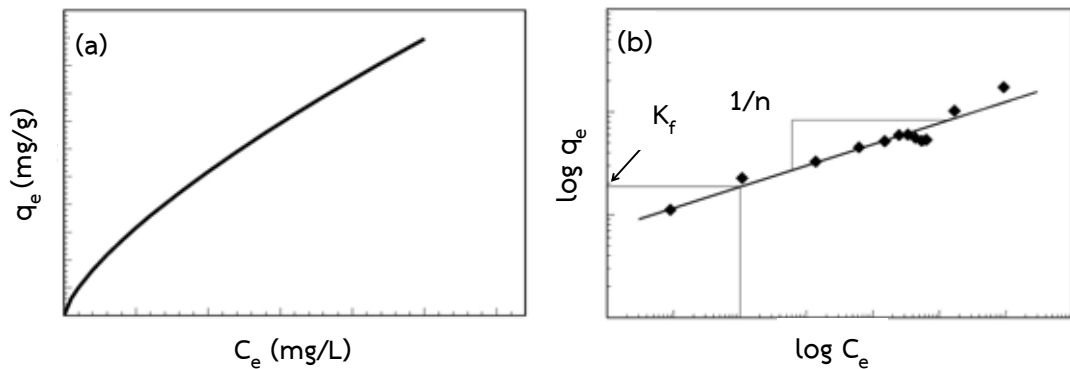


Figure 2.5 (a) Freundlich adsorption isotherm and (b) Freundlich linearized equation plot [24].

2.3 Tap water production and tap water production sludge

Water is necessary in human life. Human consume water in living activities such as drinking, cleaning and the other. Therefore, water with high quality is required to ensure safety for human being. Tap water production was established to produce the quality water for people. Tap water is produced from natural water which is called as raw water. Raw water is treated by the appropriate processes as follows [26],

i) Raw water quality improvements: Raw water from natural water is flowed through a canal. When it passes canals, some natural precipitates will occur. Then the raw water is pumped through coarse and fine screens before being transmitted to the next water treatment process.

ii) Clarification: Lime ($\text{Ca}(\text{OH})_2$), alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) and chlorine (Cl_2) are added into the filtered raw water to adjust the pH, stimulate the sedimentation and stop the growth of algae and moss, respectively.

iii) Sedimentation: After adding chemical agents such as alum and iron salts under alkaline conditions, colloidal particles in the water are precipitated together with the precipitation of alum and iron salts as shown in Equations 2.18 and 2.19,

[27] respectively. These particles agglomerate and form flocs then settle at the bottom of the tank. These solids are called as sludge.



iv) Filtration: The water after sedimentation process is passed through filters including sand/anthracite coal filters and other filters in order to filter small particles or dissolved matters remaining in the pretreated water.

v) Water storage: The filtered water is collected in a reservoir. In this process chlorine and lime are more added in an appropriate amount to improve the water quality.

vi) Transmission and distribution: The treated water is distributed to the household by transmission and distribution pumping stations through water tunnels and conduits. The tap water treatment process diagram is shown in Figure 2.6.

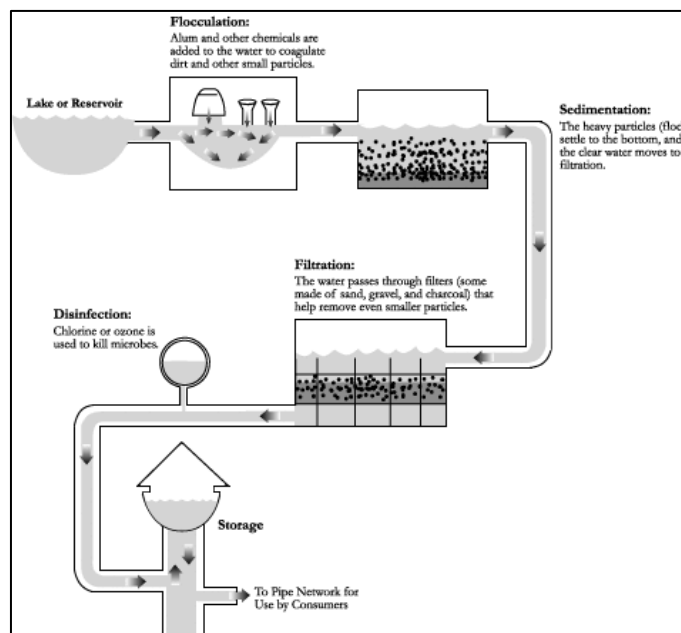
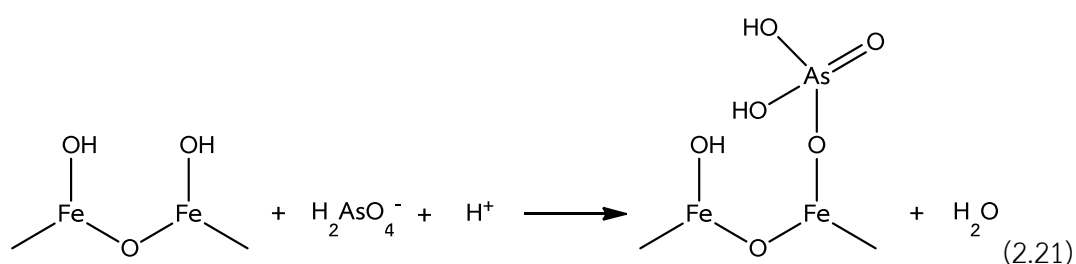
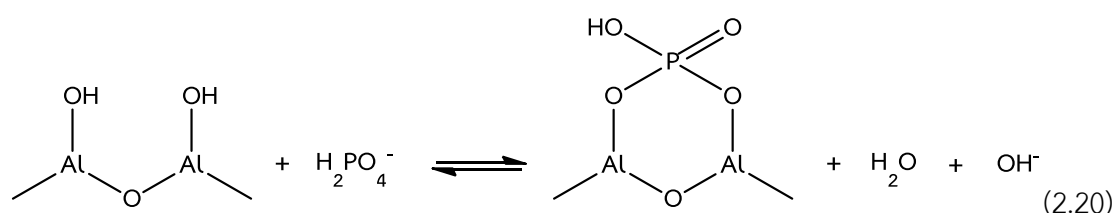


Figure 2.6 Tap water treatment diagram [28].

It can be seen that the tap water production sludge is a by-product resulting from the tap water treatment processes during the sedimentation step. During the clarification process the addition of lime and alum is a source of the production of tap water sludge containing mainly aluminium and iron hydroxide. High content of aluminium and iron hydroxides result in a strong affinity of this sludge to anion species such as phosphate and arsenate [29]. However, the affinity for phosphate or arsenate depends on types of coagulants used in clarification process. Ferric residual solids have stronger affinity for both phosphate and arsenate comparing with alum residual solids. The adsorption mechanisms for phosphate and arsenate on the surface of aluminium hydroxides and ferric hydroxides surface can be described by hydroxide exchange mechanism and surface complexation mechanism [29] as shown as Equations 2.20 and 2.21, respectively.

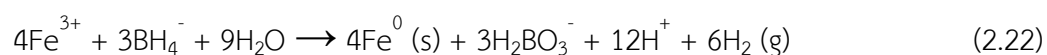


In this research, tap water production sludge was collected from Bangkhen water treatment plant which is the third plant of the Metropolitan Waterworks Authority (MWA), Thailand. This plant produces tap water around 3.6 million m³/day

[26] and generates tap water production sludge with the amount of 100 tons/day [30]. Large quantities of this sludge could be used as an alternative low-cost adsorbent for arsenic removal process. Moreover, this sludge could be modified by iron or the other chemicals to improve its adsorption capacity for arsenic removal. The next subsection deals with zero-valent iron which is one of the most popular adsorbents used for hazardous waste treatment [11].

2.4 Zero-valent iron

Nano zero-valent iron or Fe(0) has been widely used for environmental clean-up such as reductive degradation of halogenated organics and removal of inorganic contaminants including Cr(VI), U(VI), As(III) and As(V). Nano zero-valent iron can be synthesized by various methods. Sodium borohydride reduction of ferric chloride method is one of the most popular methods that has been used in a lab scale [11]. The reaction mechanism is shown in Equation 2.22,



Previous researches showed that nano zero-valent iron exhibited high adsorption capacity for arsenic due to its core-shell structure which consisted of a dense metallic of iron at the center and iron oxide at the surface. The interaction of arsenic and zero-valent iron is revealed that 1) arsenite and arsenate can be adsorbed on the iron oxide surface which is high affinity for both arsenic species; 2) arsenite can be oxidized by iron oxide to arsenate and then adsorbed on its surface and 3) arsenite can diffuse through the oxide layer and be reduced by iron at the core shell then form an As-Fe intermetallic phase adjacent to the iron core. The interaction diagram is shown in Figure 2.7.

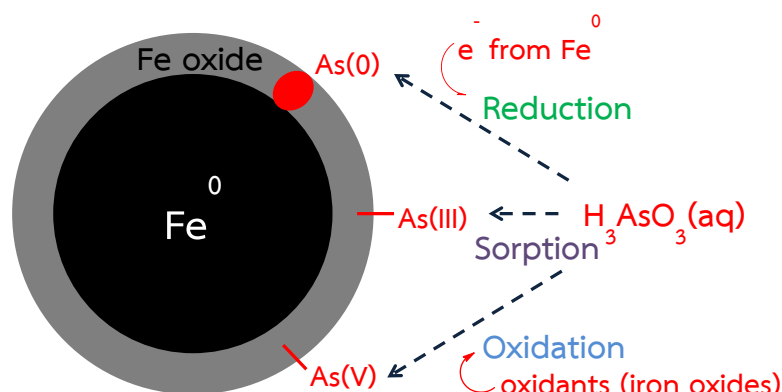


Figure 2.7 The interaction of arsenite on nano zero-valent iron [11].

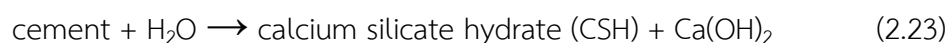
As mentioned above nano zero-valent iron shows high efficiency for arsenic removal. However, the drawback of this material is the limitation for utilization in field applications owing to the tiny particle size that causes high pressure drop in a fixed bed column or any other dynamic flow systems [12]. Loading of nano zero-valent iron onto a supporting larger-sized material is a potential method to overcome such mentioned problem. The modification of zero-valent iron onto the surface of materials such as silica, clay and activated carbon can be done via soaking the solid materials in iron salt solutions followed by borohydride reduction. Examples of research are provided in the last subsection of this chapter.

2.5 Management of contaminated sludge

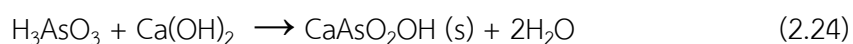
The contaminated sludge after arsenic removal process is a waste material containing arsenic. It is hazardous and has a risk to the environment and human health. The Ministry of Industry, Thailand mandates the ministerial regulations that the contaminated sludge containing arsenic in the amount of 500 mg/kg or more must be treated to reduce the potential hazard of waste before landfill disposal [31]. The stabilization/solidification (S/S) is a technique which can reduce the potential hazard of waste normally used as a pre-landfill disposal of waste material. The process involves mixing the contaminated sludge with cement and water in order to

form a solid. Cement is a binder which is used in the S/S process due to the fact that it can reduce arsenic leaching by transforming arsenic species to its less soluble forms during the hydration of cement; the hydration of cement produces Ca(OH)_2 (as shown in Equation 2.23) which can continually interact with arsenic species to form Ca-As compounds as shown in Equations 2.24 and 2.25. Moreover, the formation of calcite (CaCO_3) in the presence of carbon dioxide (carbonation) as shown in Equation 2.26 can seal pores in the solidified waste resulting in reducing the diffusion of arsenic to the environment [32, 33].

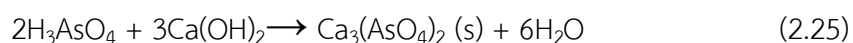
Cement hydration:



Arsenite:



Arsenate:



Carbonation:



In addition, cement used as a binder in S/S process is often a major cost. Therefore, the minimum amount of cement should be employed to allow the solidified waste having satisfied compressive strength and passing leaching regulatory tests before landfill disposal.

2.6 Literature review

Arsenic removal from water was achieved by various techniques as mentioned earlier. Adsorption technique is one of the most popular techniques which is still widely used due to the fact that it is an easy, safe and cost-effective method. An adsorbent is one of the most important factors influencing the efficiency of adsorption process. Some researches demonstrated that adsorbents exhibited good adsorption capacity for arsenic removal. However, these adsorbents still have many preparation steps and causes high cost for using. Recently, many researches have focused on alternative low-cost materials used as adsorbents for arsenic removal process.

2.6.1 Removal of arsenic from water by using low cost adsorbent

There are many researches about arsenic removal by using low-cost adsorbents, some of which are summarized below.

Chakravarty et al. (2001) [34] presented low-cost ferruginous manganese ore (FMO) as an adsorbent in arsenic removal process. The results showed that FMO could adsorb both arsenite and arsenate in the pH range of 2-8 without any pretreatment step. The FMO could remove arsenic from real groundwater containing arsenic in the range of 0.04-0.18 mg/L.

Chio et al. (2009) [35] studied the adsorption of arsenic by using shrimp shell which was obtained from two species including black tiger shrimp (*Penaeus monodon*) and white shrimp (*Litopenaeus vannamei*). The adsorption isotherms of both shrimp shells for arsenite adsorption were fitted to the Langmuir and Freundlich models with $R^2 > 0.90$. The maximum adsorption capacities calculated from the Langmuir and Freundlich models were 0.125-0.126 mg/g and 0.105-0.124 mg/g, respectively. The adsorption kinetics of both black tiger shrimp and white shrimp were best described by the pseudo-second-order model.

Li et al. (2009) [36] modified red mud (RM) which is a by-product during alkaline leaching of bauxite in Bayer process by using ferrous chloride (FeCl_2) with the purpose to be an adsorbent for arsenic removal process. The results showed that ferrous based red mud was effective for removal of arsenic from aqueous solutions with the initial concentration of arsenate of 0.2-0.3 mg/L within 24 hours. The presence of phosphate affected the arsenic removal efficiency while carbonate did not affect the arsenic removal.

Rajapaksha et al. (2011) [37] used Natural Red Earth (NRE) as a low-cost adsorbent for arsenic removal. The equilibrium contact time for both arsenite and arsenate were 90 minutes and the adsorption kinetics were fitted to the pseudo-second order model. The adsorption isotherms of arsenite were fitted to the Langmuir model while that of arsenate was fitted to the Freundlich model. The effect of competitive anions was found in the order of $\text{PO}_4^{3-} > \text{NO}_3^- > \text{SO}_4^{2-}$.

Wang and Tsang (2013) [38] investigated the efficiency of three industrial products including coal fly ash, lignite and green waste compost as low-cost adsorbents for arsenate removal. The results showed that coal fly ash was more efficient for arsenate removal than lignite and green waste compost due to its high content of calcium minerals and amorphous iron and aluminium hydroxides. The presence of humic acid, phosphate and silicate slightly inhibited the adsorption of arsenate.

Wu et al. (2013) [39] studied the composition of iron-based washing sludge which obtained from water treatment plants and used it as an adsorbent for arsenite removal. The results showed that the sludge containing high content of $\gamma\text{-FeOOH}$ and $\text{Fe}(\text{SO}_4)\text{OH}$ which exhibited high affinities for arsenite and arsenate adsorption. The optimal pH for arsenite adsorption was around 8 with the equilibrium contact

time of 18 hours. The maximum adsorption capacity calculated from the Langmuir model for arsenite was 59.7 mg/g.

Ko et al. (2013) [40] used acid mine drainage sludge (AMDS) which was obtained from Hambeak mine in South Korea to adsorb arsenic from water. The results showed that AMDS containing of amorphous particles with the surface area of 251.2 m²/g. The optimal pH for both arsenite and arsenate adsorption was 7. The maximum adsorption capacity for arsenite and arsenate were 58.5 mg/g and 19.7 mg/g, respectively.

Chammui et al. (2013) [41] used a new prepared Leonardite char carbonized at 450°C as an adsorbent for arsenite and arsenate adsorption. Leonardite contains high content of humic substances. The optimal pH and the equilibrium contact time of both arsenite and arsenate were 7 and 3 hours, respectively. The adsorption isotherms for arsenite and arsenate were fitted to both Langmuir and Freundlich models. The maximum adsorption capacities calculated from the Langmuir model for arsenite and arsenate were 4.46 mg/g and 8.40 mg/g, respectively. The effect of competitive anions was found in the order of $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$.

Srechainate (2013) [10] used tap water sludge obtained from the Metropolitan Waterworks Authority (Bangkhen, Thailand) as an adsorbent for arsenite, arsenate and dimethylarsenic acid (DMA) removal. The results showed that the sludge containing high amount of aluminium and iron hydroxides. The optimal pH for arsenite, arsenate and DMA was 2 and the equilibrium contact time was 12 hours. The adsorption kinetics of arsenite, arsenate and DMA was fitted to the pseudo-second order model. The adsorption isotherm of arsenate was better described by the Langmuir model while those of arsenite and DMA were fitted to both Langmuir and Freundlich models. The maximum adsorption capacities for arsenite, arsenate and DMA were

1.89, 8.76 and 1.78 mg/g, respectively. The presence of phosphate affected the efficiency of arsenic removal while sulfate did not affect the arsenic removal.

Yadav et al. (2014) [42] used bagasse fly ash-iron coated (BFA-IC) and sponge iron char (SIC) as an adsorbent for arsenic removal. SIC is a sponge iron industry waste while BFA-IC was treated by soaking bagasse fly ash-iron coated (BFA) which is ash from a biofuel producer in ferric chloride solution and dried at 105°C for 12 hours. The adsorption kinetics for arsenic of both adsorbents was fitted to the pseudo-second order model. The adsorption isotherms were fitted to the Langmuir, Freundlich, Tempkin and Redlich–Peterson models. The maximum adsorption capacities of BFA-IC and SIC for arsenite were 39.53 µg/g and 27.85 µg/g, respectively and that of arsenate was 25.82 µg/g and 28.58 µg/g, respectively.

2.6.2 Removal of arsenic from water by using zero-valent iron and zero-valent iron supported materials

Sun et al. (2006) [43] used zero-valent iron as an adsorbent for arsenite and arsenate removal. Zero-valent iron was purchased from Tian-jin Fuchen Chemical Reagent Co., Inc., China. The results showed that arsenite and arsenate were removed by zero-valent iron under aerobic and relatively anaerobic conditions. It was observed that arsenite was oxidized to arsenate by iron species in aerobic which is an important mechanism in arsenic removal by zero-valent iron. The removal efficiency for arsenite and arsenate decreased as pH of the solution increased. Moreover, the presence of phosphate affected the efficiency of arsenic removal while the presence of sulfate, nitrate and humic acid slightly inhibited the arsenic removal.

Zhu et al. (2009) [44] modified activated carbon by zero-valent iron via sodium borohydride reduction of ferrous sulfate. The iron content of approximately 8.2% (w/w) was loaded onto carbon. The optimal pH for arsenite and arsenate

removal was 6.5 and the equilibrium contact time was 72 hours. The maximum adsorption capacities calculated from the Langmuir model for arsenite and arsenate were 18.2 and 12.0 mg/g, respectively. The presence of phosphate and silicate inhibited both arsenite and arsenate removal while other anions and humic acid did not significantly affect the arsenite and arsenate removal. Moreover, the modified material could be regenerated by an elution with 0.1 mol/L sodium hydroxide.

Mamindy-Pajany et al. (2011) [45] studied the efficacy for arsenate removal by using four commercial adsorbents including hematite, goethite, magnetite and zero-valent iron (ZVI). The results showed that arsenate adsorption decreased as the pH of solution increased. The adsorption capacity of arsenate was proportional to the iron content of adsorbent. The adsorption rate increased in the following order: ZVI>magnetite>hematite>goethite. The adsorption isotherms of all adsorbents were fitted to the Langmuir model and the maximum adsorption capacity of ZVI was higher than other adsorbents.

Huang et al. (2011) [46] synthesized the nanoscale zero-valent iron (NZVI) via sodium borohydride reduction of ferric chloride with the purpose to be an adsorbent for arsenite removal from drinking water. The synthesized NZVI had a surface area of 49.2 m²/g. The adsorption kinetics was better described by the pseudo-first order. The maximum adsorption capacity for arsenite calculated from the Langmuir model was 76.3 mg/g at pH 7. The presence of H₂PO₄⁻ or SiO₃²⁻ inhibited the efficiency of arsenite removal while HCO₃⁻, SO₄²⁻, Br⁻, CO₃²⁻ and NO₃⁻ did not significantly affect the arsenite removal.

Praveen et al. (2013) [47] developed a method for modifying montmorillonite K10 by zero-valent iron via reduction of ferric nitrate using tea liquor which contained phenolic compounds that could act as reducing and capping agents. This method is a green technique. The results showed that the zero valent iron nanoparticles

supported on montmorillonite K10 was able to remove arsenite from water up to the extent of 99% within 30 minutes.

Bhowmick et al. (2013) [12] modified Montmorillonite by nanoscale zero-valent iron (Mt-nZVI) via sodium borohydride reduction of ferric chloride for removal of arsenite and arsenate from water. The results showed that the Mt-nZVI had high affinity for arsenite and arsenate adsorption over a pH range of 4-8. The adsorption kinetics for both arsenite and arsenate was better described by the pseudo-second order model. The maximum adsorption capacities for arsenite and arsenate calculated from the Langmuir model were 59.9 and 45.5 mg/g, respectively at pH 7. The presence of PO_4^{3-} inhibited the efficiency of arsenic removal while SO_4^{2-} , HCO_3^- and NO_3^- did not significantly affect the arsenic removal. Moreover, Mt-nZVI could be regenerated by an elution of 0.1 mol/L sodium hydroxide.

Mosaferi et al. (2014) [48] synthesized nanoscale zero-valent iron (NZVI) via sodium borohydride reduction of ferrous sulfate for arsenite and arsenate removal. The NZVI was stabilized with two different polymers including Starch (S) and Carboxymethyl cellulose (CMC). The results showed that a starch stabilizer particle (S-nZVI) was more effective for arsenite and arsenate removal than CMC stabilized nanoparticles (C-nZVI). The optimal pH for both arsenic species was 5 and the equilibrium contact time was 30 minutes. The adsorption kinetics was better described by the pseudo-second order model. The adsorption isotherms of S-nZVI for both arsenic species adsorption were fitted to the Langmuir model with maximum adsorption capacities of 12.2 and 14 mg/g for arsenite and arsenate, respectively.

Wang et al. (2014) [49] modified reduce graphite oxide (RGO) by nanoscale zero-valent iron via sodium borohydride reduction of ferrous sulfate with the purpose to be an adsorbent for arsenite and arsenate removal. The optimal pH of

arsenite and arsenate was 5 and 2, respectively. The equilibrium contact time of both arsenic species was 60 minutes and the adsorption kinetics was fitted to the pseudo-second order model. The adsorption isotherms were better described by the Langmuir model and the maximum adsorption capacities were 35.83 and 29.04 mg/g for arsenite and arsenate at pH 7, respectively.

CHAPTER III

EXPERIMENTAL

3.1 Instruments

The instruments used in this research are shown in Table 3.1.

Table 3.1 List of instruments

Instruments	Model, Manufacturing company
Inductively coupled plasma-optical emission spectrometer (ICP-OES)	iCAP 6500 DUO, Thermo Scientific
Multi-position hotplate stirrer	KIKA-WERKE
Sonicator	Ultrasonic Steri-Cleaner, CHEST
pH meter	MELTER TOLEDO
Conductivity meter	CM-115, KYOTO TOLEDO
Oven	UM500, Memmert
Analytical balance	SI-234, Denver Instrument
Transfer pipet	BRAND
Overhead mixer	Rotax 6.8, VELP scientifica
Vacuum pump	V-700, Buchi
SPE vacuum manifold	Supleco
Scanning electron microscope with energy dispersive x-ray spectrometer (SEM-EDS)	JSM-6400 with Link ISIS series 300, JEOL
X-ray fluorescence spectrometer (XRF)	ED-2000, Oxford
Transmission electron microscope (TEM)	JEM-1400, JEOL TEM
Surface area analyzer (BET)	Autosorb-1, Quantachrome
Centrifuge	CENTAUR 2, Sanyo
X-ray diffraction spectrometer (XRD)	DMAX 2200 Ultimate+, Rigaku

The inductively coupled plasma-optical emission spectrometer (ICP-OES) was used mainly to determine remaining arsenic concentration in the solutions. The conditions operated in this research are shown in Table 3.2.

Table 3.2 Conditions of ICP-OES for arsenic determination

Conditions	Values
Arsenic emission wave length	189.042 (nm)
Radio frequency power	1150 (W)
Auxiliary gas flow	0.5 (L/min)
Nebulizer gas flow	0.6 (L/min)
Coolant gas flow	12 (L/min)
Flush pump rate	50 (rpm)
Pump stabilization time	5 (s)
Plasma view	Axial
Repeatability	3 (replicates)

3.2 Chemicals

Tap water production sludge was obtained from the Metropolitan Waterworks Authority (Bangkhen Water Treatment Plant), Bangkok, Thailand. All chemicals were analytical grade and used without further purification. Deionized water (DI water) was used to prepare all the solution. All chemicals used in this research are listed in Table 3.3.

Table 3.3 List of chemicals

Chemicals	Supplier
Ferric chloride, FeCl ₃	Sigma-Aldrich
Sodium borohydride, NaBH ₄	Sigma-Aldrich
Absolute ethanol 99%, C ₂ H ₅ OH	Merck
Stock solution of arsenate (1000 mg/L As(V)), H ₃ AsO ₄	Merck
Sodium (meta) arsenite, NaAsO ₂	Sigma-Aldrich
Ferric oxide, Fe ₂ O ₃	-
Iron powder	Aldrich
Copper(II) chloride, CuCl ₂	BDH
Sodium hydroxide, NaOH	Merck
Hydrochloric acid 37%, HCl	Merck
Nitric acid 65%, HNO ₃	Merck
Sodium sulfate, Na ₂ SO ₄	Fisher Scientific
Sodium dihydrogen phosphate, NaH ₂ PO ₄	Merck
Purify Humic acid	-
Potassium nitrate, KNO ₃	BDH
Cement (green Tiger brand)	The Siam Cement Public Company Limited (Thailand)

3.3 Preparation of tap water production sludge

The tap water production sludge was dried in an oven at 105°C for 24 hours. Then, the dried sludge was crushed and sieved (less than 500 µm). After that, the obtained sludge was modified by iron in the next step.

3.4 Modification of tap water production sludge

The tap water production sludge modified by iron was prepared via sodium borohydride reduction of ferric chloride [11]. The modified tap water production sludge was synthesized in different amount of iron: the tap water production sludge

ratio from 2:98, 4:96, 5:95, 6:94, 8:92 to 10:90 (w/w). For 10:90 ratio; 10.1 g of the tap water production was added into 30 mL of 0.67 mol/L ferric chloride solution which was prepared by dissolving FeCl_3 into 4:1 (v/v) ethanol:water mixture (24 mL ethanol:6 mL DI water). The mixture was held on a magnetic stirrer to be mixed. Then, 100 mL of 0.80 mol/L sodium borohydride was added dropwise into the mixture. The black solid was produced in the solution. After that, the modified tap water production sludge was filtered (using Whatman No. 1) and washed with DI water and ethanol, respectively. Last step, the modified tap water production sludge was dried in an oven at 50°C overnight and kept in a desiccator to prevent the moisture from the air. In cases of other ratios of iron:tap water production sludge, the preparation protocol was the same as the procedure presented above except that the amounts of chemicals are different. The amounts of chemicals used in the synthesis of the modified tap water production sludge are listed in Table 3.4.

Table 3.4 List of the amounts chemicals used in the modification of tap water production sludge

Iron:sludge	2:98	4:96	5:95	6:94	8:92	10:90
FeCl_3 (g)	0.7566	1.5447	1.9512	3.2440	3.2440	3.2430
NaBH_4 (g)	0.5294	1.0800	1.3653	3.0500	3.0500	3.0500
Sludge (g)	12.7650	12.7650	12.7650	17.4997	12.8455	10.0500

3.5 Characterization of the modified tap water production sludge

The modified tap water sludge was characterized by various techniques as shown in Table 3.5. Moreover, the point of zero charge (pH_{pzc}) of the modified tap water sludge was evaluated by mass titration method.

Table 3.5 Techniques for characterization of the modified tap water sludge

Information	Techniques
Elemental composition	Inductively coupled plasma-optical emission spectrometry (ICP-OES) X-ray fluorescence spectrometry (XRF)
Structural information	X-ray diffraction spectrometry (XRD)
Morphology	Scanning electron microscopy with energy dispersive x-ray spectrometry (SEM-EDS) Transmission electron microscopy (TEM)
Surface area	Surface area analyzer

3.5.1 Elemental composition using ICP-OES

The modified tap water sludge was digested by aqua regia (HCl:HNO₃, 3:1 v/v) in order to transform the solid into a solution before determining the elemental contents using ICP-OES. Briefly, 1.0 g of the modified tap water sludge was added into 40 mL of aqua regia (30 mL conc. HCl:10 mL conc. HNO₃), then the mixture was held on a hotplate. The mixture was refluxed at 95 ± 5 °C for 15 minutes and was filtered (using Whatman No. 1). After that, the filtrate was adjusted to 100 mL by DI water. Finally, the digested sample solution was analyzed by ICP-OES. The whole digestion process was done in a fume hood as the nitrogen dioxide also occurred during experiment.

3.5.2 Characterization of iron particles in modified tap water sludge

In order to investigate the oxidation state of iron dispersed on the surface of the modified tap water sludge, the redox reaction of copper(II) ions and some adsorbents were carried out by soaking approximately 0.5 g of tap water sludge,

modified tap water sludge (Fe:sludge 10:90), iron particles which was synthesized via sodium borohydride reduction of ferric chloride or iron powder into 10.0 mL of approximately 0.5 mol/L CuCl_2 solutions for 24 hours at room temperature and then visually observing the change in color and appearance of the solution.

3.5.3 Determination of the point of zero charge

The point of zero charge of the modified tap water sludge was investigated by mass titration method which was carried out by shaking 10.0 mL of 0.3 KNO_3 solutions with different amounts of the modified tap water sludge within the content range of 1-100 g/L for 24 hours with a shaking speed of 30 rpm. The pH_{pzc} is the value at which a plateau is achieved when plotting equilibrium pH values of the solution versus the sorbent mass.

3.6 Batch experiment for arsenic adsorption

Arsenic adsorption was carried out by shaking 10 mL of arsenic solution with approximately 0.0500 ± 0.0005 g of the modified tap water sludge with a shaking speed of 30 rpm. The equilibrium contact time ranged from 1-24 hours depending on experiments. All the adsorption experiments were conducted at room temperature. The pH of the solution was adjusted using 5% (v/v) of HNO_3 and/or 5% (w/v) of NaOH. After the adsorption period, the sample was filtered through a 0.45 μm membrane and the filtrate was analyzed for remaining arsenic concentration by ICP-OES. The amount of arsenic adsorbed was calculated from the following Equation 3.1,

$$q_e = (C_0 - C_e) \times \frac{V}{1000 \times W} \quad (3.1)$$

Where q_e is the adsorption amount of the adsorbate (mg/g)
 C_0 is the initial concentration of arsenic (mg/L)
 C_e is the equilibrium concentration of arsenic (mg/L)
 V is volume of the solution (mL)
 W is the adsorbent amount (g)

The percentage of arsenic removal was calculated from the following Equation 3.2,

$$\%removal = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3.2)$$

3.6.1 Effect of pH

The effect of pH on arsenite adsorption was investigated in the range of 2-12 with approximately 0.0500 ± 0.0005 g of the modified tap water sludge (using iron:sludge 6:94 w/w) at a fixed initial arsenic concentration of 100 mg/L. The equilibrium contact time was 24 hours for this experiment.

3.6.2 Effect of contact time

The effect of contact time was evaluated in the range of 5-120 minutes by 0.0500 ± 0.0005 g of the modified tap water sludge at a fixed initial arsenic concentration of 100 mg/L with the optimal pH value. The results were fitted with pseudo first order and pseudo second order to evaluate the kinetics of the modified tap water sludge for arsenic removal.

3.6.3 Investigation of arsenic adsorption mechanism onto the adsorbent

The effect of iron and iron oxide (Fe_2O_3) on arsenic adsorption process was studied. An amount of the adsorbent as shown in Table 3.6 was shaken with 10 mL

of 100 mg/L arsenic solution using optimal conditions from previous experiments. The results are shown as an adsorbed amount of arsenic in unit of mg.

Table 3.6 List of amounts of the adsorbent

Adsorbent	Weight (g)
Iron powder	0.0050 ± 0.0005
Iron oxide	0.0050 ± 0.0005
Sludge	0.0450 ± 0.0005
The modified tap water sludge (Fe:sludge 10:90)	0.0500 ± 0.0005

3.6.4 Adsorption isotherms

To evaluate the effect of the amount of iron : tap water production sludge ratio, different amounts of iron to tap water production sludge ratio (2:98, 4:96, 5:95, 6:94, 8:92 and 10:90) were used as adsorbent for arsenic removal process in a batch system. An amount of 0.0500 ± 0.0005 g of adsorbent was shaken with 10 mL of various initial arsenic concentrations of 50, 100, 150, 200 and 250 mg/L using optimal conditions from previous experiments at room temperature. The results were fitted with the Langmuir and Freundlich adsorption models in order to evaluate their adsorption mechanism and the maximum adsorption capacity for arsenic removal.

3.6.5 Effect of interfering ions

The effect of interfering ions on the adsorption of arsenic was examined; PO_4^{3-} and SO_4^{2-} were added such that they contained mole ratio of anions to arsenic of 1:1, 5:1, 10:1, 20:1, 50:1 and 100:1. Moreover, to simulate a real groundwater, humic acid solutions were added in different concentrations in the range of 100-1000 mg/L. All experiment in this part was performed with a fixed initial arsenic concentration of 100 mg/L and the optimal pH value of sample solution from previous experiments.

3.7 Application in real contaminated water samples

TK-80 and TK-81 are the wastewater obtained from PTT Public Company Limited (Thailand). They contain total arsenic in the range of 68-78 mg/L. Firstly, the wastewater was filtered and analyzed for an exact concentration of total arsenic by ICP-OES. Then, the pH of the filtrate was adjusted to the optimal pH. The treatment of wastewater for arsenic removal was divided into 2 systems including batch system and column system.

3.7.1 Batch system

The application for arsenic removal of wastewater in batch system was carried out by shaking 10 mL of wastewater (TK-80, TK-81) with approximately 0.0500 ± 0.0005 g of the modified tap water sludge with shaking speed of 30 rpm. The optimized conditions obtained from previous experiments were used in this section. After the adsorption process, the sample was filtered through a $0.45 \mu\text{m}$ membrane and the filtrate was analyzed for remaining arsenic concentration by ICP-OES.

3.7.2 Column system

The column system for arsenic removal was investigated by using 1.8560 ± 0.0005 g of the modified tap water sludge packed in a syringe and the height of the adsorbent was approximately 2 cm. The volume of wastewater (TK-81) used in this experiment was 25 mL with the optimal pH and a flow rate was 1 mL/min. To evaluate the efficiency of arsenic removal in column system, the different types of column system was set up into 3 types including,

- 25 mL of wastewater was passed through the single column in one cycle.
- 25 mL of wastewater was passed through the first column and then the wastewater effluent from the first column was passed through the second new column.
- 25 mL of wastewater was passed through the single column in two cycles.

Finally, the amount of remaining arsenic in the effluents after passing the column was determined by ICP-OES.

Moreover, a pond water of Chulalongkorn University and groundwater samples were also used to assess the arsenic removal efficiency in batch system using the modified tap water sludge. First of all, a pond water and groundwater were filtered and then they were spiked with arsenite or arsenate in a concentration of 100 mg/L. The removal procedure was similar to the one mention above (see Section 3.7.1).

3.8 Stabilization/solidification of the modified tap water sludge after arsenic removal using cement as binder

The modified sludge being full of adsorbed arsenic is the waste material which obtained from arsenic removal process. It is hazardous to the environment and human health. Therefore, the management of the waste material is necessary. The stabilization/solidification is one of the alternatives techniques that can reduce the potential hazard of waste, converting contaminants into their less soluble forms. Cement is one of the binders which is widely used due to its availability and cheapness. The stabilization/solidification using cement is the result of chemical transformations of contaminants. Leaching test is one important expression in the environmental assessment of the remedial measures of solidified and stabilized (S/S) hazardous wastes. Therefore, this research used cement as a binder in the stabilization/solidification of the modified tap water sludge after arsenic adsorption and studied the leaching characteristics of arsenic by using dynamic monolithic leaching test (DMLT).

3.8.1 Solidified waste preparation

The modified sludge after arsenic adsorption process was dried in an oven at 100°C overnight. The obtained waste product was solidified using cement. The

cement used was the green Tiger brand. The solidified waste preparation was performed by mixing the arsenic contaminated sludge with cement at four different cement:contaminated sludge ratios (6:4, 7:3, 8:2 and 9:1), using a water to dry solid ratio of 1:2.4. Mixing was performed by a manual mixer to homogenize. After that, the homogeneous mixture was placed in plastic cylindrical containers (40 ± 1 mm in height and 43 ± 1 mm in diameter), see Figure 3.1. During the placing of the homogeneous mixture in plastic cylindrical containers, de-airing was necessary to avoid the formation of bubbles in the sample matrix. Plastic wrap was used to seal the containers and the samples were cured at a room temperature for 14 days. The unconfined compressive strength testing was used to determine the suitable proportion of cement to contaminated sludge ratio. The suitable proportion of cement to contaminated sludge ratio of solidified waste was prepared following the procedure above except the curing period changed to 38 days. After the curing period, samples were demolded. Dust and loose particles from the solidified waste were removed by blowing gently using compressive N_2 . Before the leaching test the geometric shape of the solidified waste was determined by measuring the height and diameter then the whole geometric surface area A (cm^2) was calculated from the following Equation 3.3,

$$A = 2\pi r(r + h) \quad (3.3)$$

Where A is the surface area of closed cylinder (cm^2)

r is the radius of closed cylinder (cm)

h is the height of closed cylinder (cm)



Figure 3.1 Plastic cylindrical container.

3.8.2 Leaching characteristics of arsenic by dynamic monolithic leaching test (DMLT)

The dynamic leaching test of solidified waste was done using a standard leaching test of CEN/TS 15863:2012. The procedure was carried out by calculating the leachant (DI water) volume from the following Equation 3.4,

$$V_1 = (8 \pm 0.1) \times A \quad (3.4)$$

Where V_1 is the volume of the leachant (mL)

A is the surface area of the test portion (cm²)

The solidified waste was placed in a container using a support to prevent the solidified waste from touching the inner side of the container then the calculated volume of leachant (V_1) was added. The container was closed with Parafilm and the time as t_0 was recorded. After the leaching period of first step (2 ± 0.1 hours after adding DI water), the solidified waste was removed from the container and the obtained solution (leachate) was filtered through a filter paper. pH and conductivity of the filtrate was measured then the filtrate was analyzed for remaining arsenic concentration by ICP-OES. The calculated volume of leachant was added into the container again. The leaching period of each step was followed the time indicated in Table 3.7.

Table 3.7 Time intervals for water collection

Step/ fraction	Duration of time interval (days)	Duration from the start of the test t_0 (days)
1	$0.08 \pm 5\%$	$0.08 \pm 5\%$
2	$0.92 \pm 5\%$	$1 \pm 5\%$
3	$1.25 \pm 5\%$	$2.25 \pm 5\%$
4	$5.75 \pm 5\%$	$8 \pm 5\%$
5	$6 \pm 5\%$	$14 \pm 5\%$
6	$1 \pm 5\%$	$15 \pm 5\%$
7	$13 \pm 5\%$	$28 \pm 5\%$
8	8 days \pm 1 day	$36 \pm 5\%$
9	28 days \pm 1 day	64 days \pm 0.25 day

At the end of each step the solidified waste was removed from the water and the obtained water was filtered through a filter paper. The pH and conductivity were measured then the filtrate was analyzed for remaining arsenic concentration by ICP-OES. The next step of leaching was continued immediately. The results were showed as the cumulative amount of the constituents released related to the geometric surface area of the solidified waste (mg/m^2) in each step. The measured release of each constituent was calculated from the following Equation 3.5,

$$r_i = \frac{10 \times C_i \times V_1}{A} \quad (3.5)$$

Where r_i is the measured release of a constituent in step i (mg/m^2)

C_i is the measured concentration of that constituent in the water of each step (mg/L)

V_1 is the volume of the leachant (mL)

A is the geometric surface area of the solidified waste (cm^2)

The cumulative release of a constituent over a period of time was calculated from the following Equation 3.6,

$$R_n = \sum_{i=1}^n r_i \text{ (for } n=1 \text{ up to } 9) \quad (3.6)$$

Where R_n is the cumulative release of a constituent over a period of time, running from step 1 until step n (mg/m^2)

r_i is the measured release of a constituent in step i (mg/m^2)

The result was evaluated by plotting the calculated cumulative release of the different constituents as a function of time on a double logarithmic scale.

3.8.3 Total dissolved solids

Total dissolved solids is a value which express the whole of inorganic and organic substances contained in water. The determination of total dissolved solids was carried out by weigh the aluminium foil container and then 25 mL of water after leaching process was added. The water was evaporated in an oven at 105°C for 24 hours (until dried). Then, the aluminium foil container was weighed again. The total dissolved solids was calculated in mg/L unit from the following Equation 3.7,

$$\text{total dissolved solids (mg/L)} = \frac{W_{final} - W_{initial}}{V} \quad (3.7)$$

Where W_{final} is weight of aluminium foil container before evaporation (mg)

$W_{initial}$ is weight of aluminium foil container after evaporation (mg)

V is the volume of water which was added into the aluminium foil container (L)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Modification of tap water production sludge by iron

Iron(0) in the modified tap water production sludge was prepared via sodium borohydride reduction of ferric chloride. The reaction mechanism is shown in Equation 4.1,



The amount ratio of iron to the tap water sludge which was synthesized in this research was theoretically calculated based on Equation 4.1. The color of the modified sludge changed from brown to black and it displayed more darkened black color proportional to the starting amount of ferric chloride used. The pictures of various materials are shown in Figure 4.1.



Figure 4.1 Pictures of tap water production sludge and the modified sludge with different iron:sludge ratios.

4.2 Characterization of the modified tap water production sludge

The modified tap water sludge with the iron to sludge ratio of 10:90 (w/w) was used in all batch experiments to study the effect on arsenic removal. Therefore, some characteristics of the modified tap water sludge were studied by using 10:90

(w/w) iron to tap water sludge ratio. The discussions are provided in the following subsections.

4.2.1 Elemental composition

Inductively coupled plasma-optical emission spectrometry (ICP-OES) and X-ray fluorescence spectrometry (XRF) were used to evaluate the amount of element in the tap water production sludge and the modified tap water production sludge.

4.2.1.1 ICP-OES

The amount of iron in the tap water production sludge and modified tap water sludge were investigated using ICP-OES which was carried out by an acid digestion of the adsorbents. The results are shown in Table 4.1.

Table 4.1 The amount of element using ICP-OES technique (n=3)

Adsorbent	Fe (mg/g)
Bare sludge	15.5 ± 0.1
Modified tap water sludge (iron:sludge : 10:90)	105.6 ± 1.2

The results show that the modified tap water sludge contained high content of iron comparing with bare sludge and then the calculated content of iron in the modified sludge from the subtraction of the amount of iron in the bare sludge was to be 9% (w/w).

4.2.1.2 XRF

XRF technique can be used for analyzing the elemental composition in a sample. In this research, XRF technique was used to confirm the amount of elements in the modified tap water sludge. The results are presented as weight percentages of elements as shown in Table 4.2.

Table 4.2 The amount of elements using XRF technique

Adsorbent	%SiO ₂	%Al ₂ O ₃	%Fe ₂ O ₃	%K ₂ O	%MgO
Bare sludge	48.1	24.9	7.03	1.75	0.931
Modified tap water sludge (Fe:sludge : 10:90 w/w)	43.8	22.5	20.8	1.46	0.812

The XRF results confirmed that the modified tap water sludge contained higher percentages of iron than the bare sludge similar to the results of elemental content using ICP-OES. Moreover, the amount of %Fe in the modified sludge calculated from the subtraction of %Fe of the bare sludge was 10% (w/w).

These results show the increase of the amount of iron after sludge modification, indicating that the modification of tap water production sludge via sodium borohydride reduction of ferric chloride was successful and the amount of iron that was calculated from ICP-OES and XRF techniques were supposed to be around 10% (w/w) which was relatively closed to the theoretical calculation of iron amount from Equation 4.1.

4.2.2 Structural information by XRD

The structural information of the adsorbent such as crystallographic information and chemical composition was determined by using X-ray diffraction (XRD) technique.

The XRD patterns of the sludge, iron and modified tap water sludge are shown in Figure 4.2, Figure 4.3 and Figure 4.4, respectively. The XRD pattern of sludge shows the characteristic peaks of SiO₂ related to quartz which is predominantly found in the sludge. The pattern of iron which was prepared via sodium borohydride reduction of ferric chloride shows the characteristic peak of zero-valent iron at a two-

theta value of 44.64° and iron oxide at two-theta value of 27.98° , indicating that the obtained iron were in a crystalline phase [50] while no characteristic peak was found in the modified tap water sludge pattern. This reveals that iron particles dispersed on the surface of modified sludge might have been below the detection limit of the XRD technique. Therefore, the characteristic peaks of quartz are mainly found in the XRD pattern of modified tap water sludge.

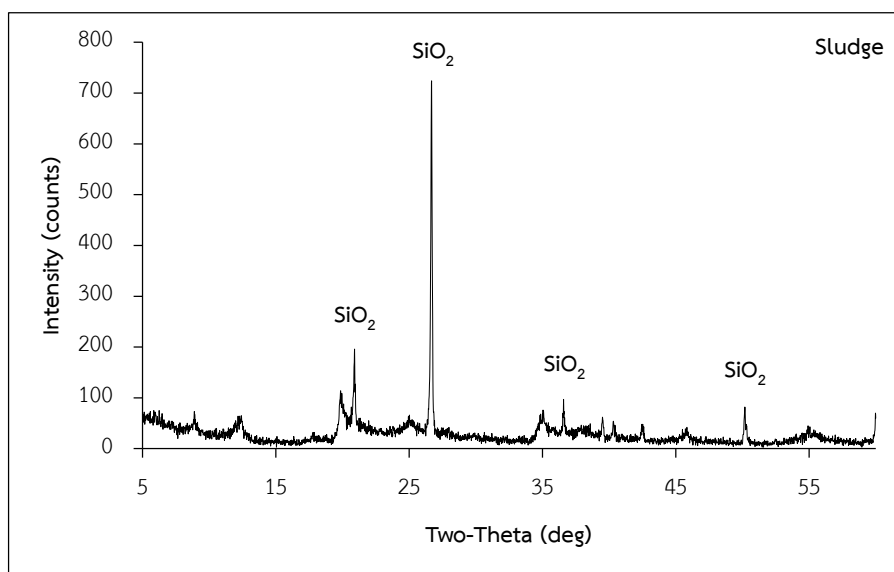


Figure 4.2 XRD pattern of sludge.

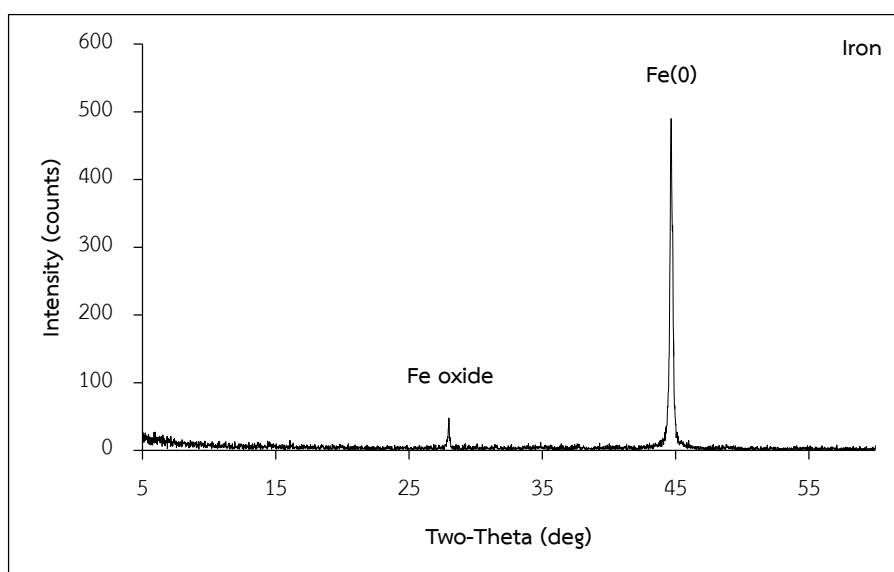


Figure 4.3 XRD pattern of iron prepared from the borohydride reduction of Fe(III).

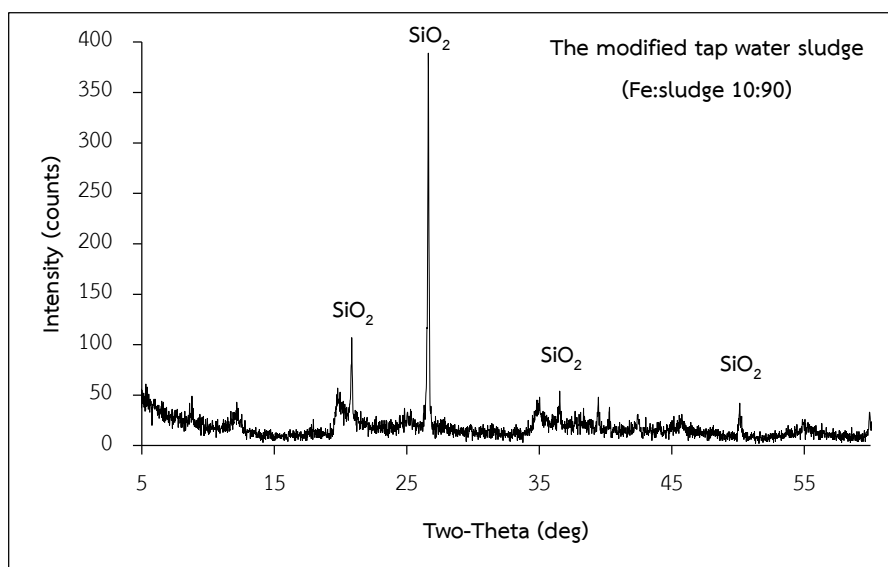


Figure 4.4 XRD pattern of modified tap water sludge (Fe:sludge 10:90).

4.2.3 Morphology

To characterize the surface morphology of the modified tap water sludge, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques were used. Energy dispersive spectrometry (EDS) was applied to determine the quantitative dispersion of iron on the surface.

4.2.3.1 SEM-EDS

The surface morphology of the bare sludge, iron and modified tap water sludge (Fe:sludge 10:90 w/w) were investigated by SEM technique. The SEM image of tap water sludge (Figure 4.5a) shows that the sludge contains small plate particles and form as stratified layers while iron which was prepared via sodium borohydride was spherical particles and form as chain-like structures as shown in Figure 4.5b. The SEM images of sludge modified by iron via the same process are shown in Figure 4.5c. It was found that the morphology of the modified tap water sludge consisted of both characteristics of bare sludge and iron.

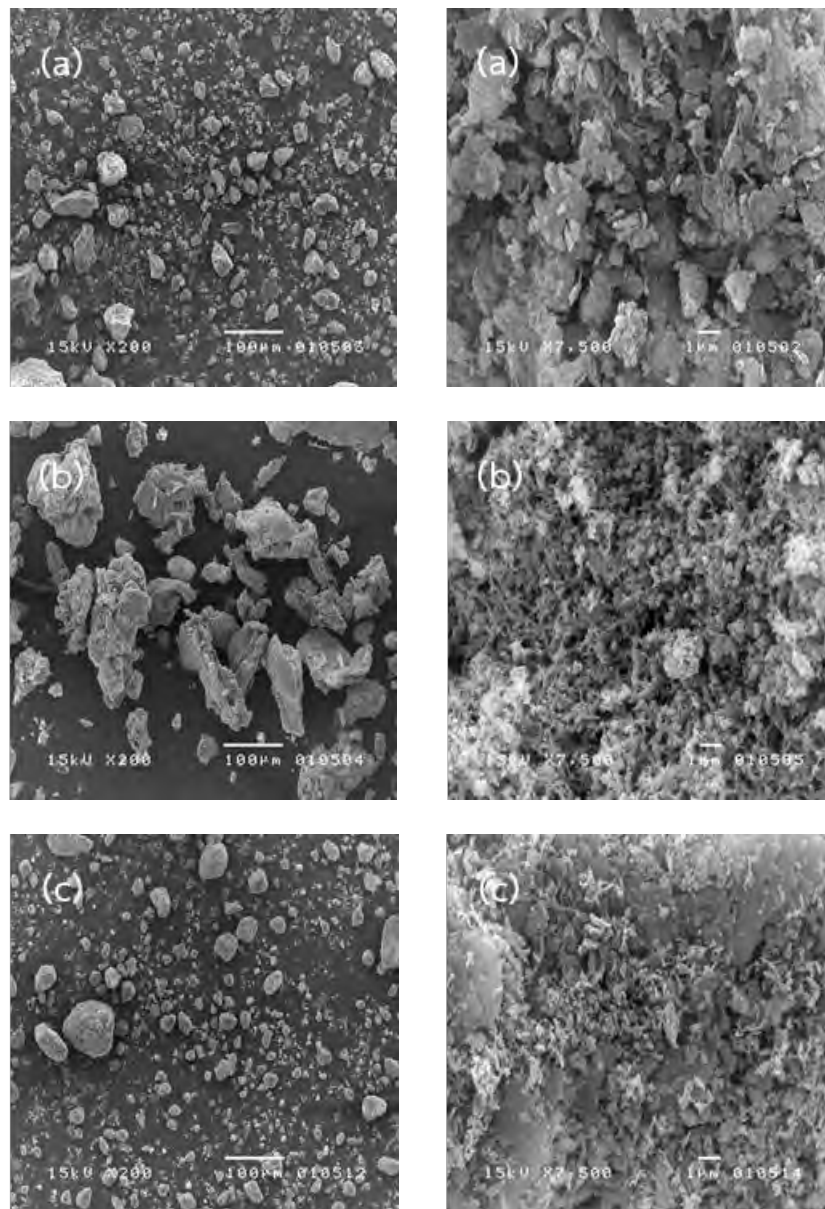


Figure 4.5 SEM images of (a) sludge, (b) iron and (c) Fe:sludge 10:90 under magnification of 200x (left images) and 7500x (right images).

SEM-EDS was used to investigate the dispersion of iron on the surface of the tap water sludge and modified tap water sludge. The mapping EDS images of the tap water sludge and the modified tap water sludge with different iron ratios are shown in Figure 4.6.

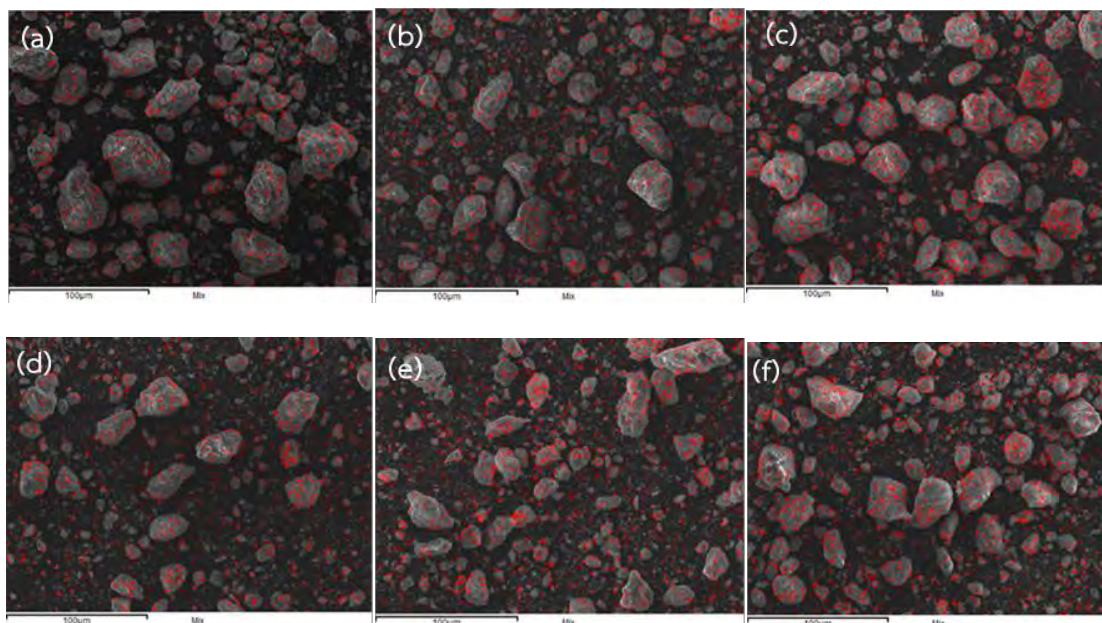


Figure 4.6 Elemental mapping images of (a) sludge, (b) Fe:sludge 2:98, (c) Fe:sludge 4:96, (d) Fe:sludge 6:94, (e) Fe:sludge 8:92 and (f) Fe:sludge 10:90.

It can be seen that the red spots which represent to iron were dispersed well on the surface of the modified sludge and they increased proportional to the amount of iron, indicating that the modified tap water sludge contained iron particles on its surface.

4.2.3.2 TEM

TEM was used to study more detail of the surface of tap water sludge and modified tap water sludge (Fe:sludge 10:90). The TEM images of tap water sludge and modified tap water sludge are shown in Figure 4.7. The black color areas correspond to metallic iron phase while lighter color areas correspond to the sludge. It can be seen that the TEM image of modified tap water sludge has more dark regions than the TEM image of bare sludge, indicating that the modified tap water sludge comprises of iron particles dispersed on its surface after the modification process.

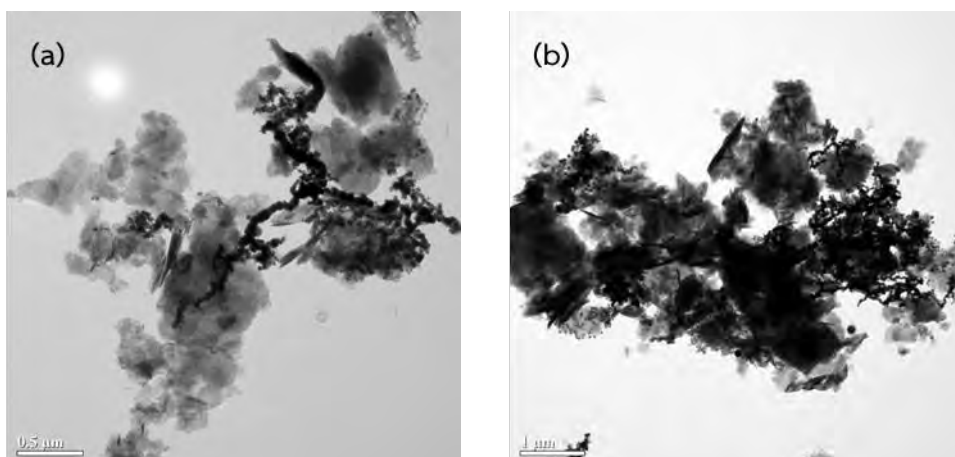


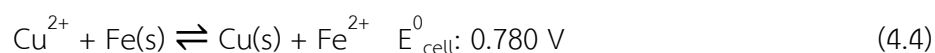
Figure 4.7 TEM images of (a) sludge and (b) Fe:sludge 10:90.

4.2.4 Characterization of iron particles in modified tap water sludge

To identify the oxidation state of iron particles dispersed on the surface of modified tap water sludge, the redox reaction of copper(II) chloride and the modified tap water sludge was carried out by considering the following equations [51],



These reduction potentials show that iron can be oxidized by copper(II) ions and yields iron(II) ions as shown in Equation 4.4. This reaction is spontaneous reaction or galvanic corrosion which has E°_{cell} of 0.780 V.



Therefore, the corrosion of iron(0) to iron(II) ions which displayed a reddish-orange color might be occurred when iron(0) is in contact with copper(II) solution. The photograph of the reaction of some adsorbents in copper(II) chloride solution at room temperature standing for 24 hours was displayed in Figure 4.8. The results show that, copper(II) ions could interact with the modified tap water sludge, iron particles which was synthesized via sodium borohydride reduction of ferric chloride

and purchased iron(0) powder and produced a reddish-orange product (copper(0)) while the tap water sludge did not interact with copper(II) ions. These results indicated that the bare sludge did not contain any zero-valent iron whereas iron particles dispersed on the surface of modified tap water sludge should be zero-valent iron.

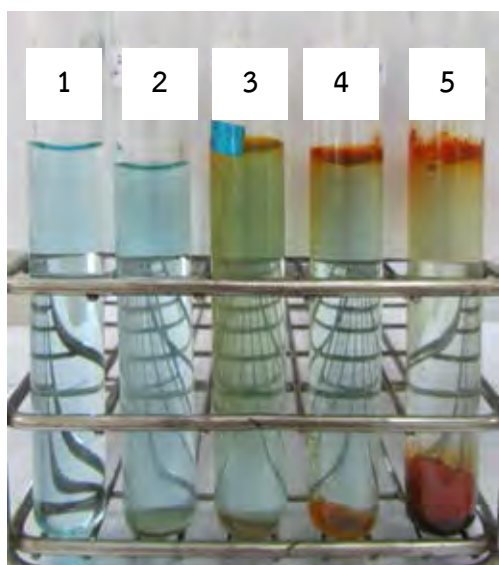


Figure 4.8 Photographs of (1) copper(II) chloride solution and the reaction of copper(II) chloride with (2) tap water sludge, (3) the modified tap water sludge (Fe:sludge 10:90), (4) iron particles (via sodium borohydride reduction) and (5) purchased iron(0) powder.

4.2.5 Surface area

The surface area of the adsorbent was evaluated by BET surface area method. The BET surface area value is shown in Table 4.3. The results show that there is a change in surface area of the modified tap water sludge. The surface area increased when the tap water sludge was modified by iron(0). The increase in surface area might be attributed to the surface of zero-valent iron nanoparticles.

Table 4.3 BET surface area value

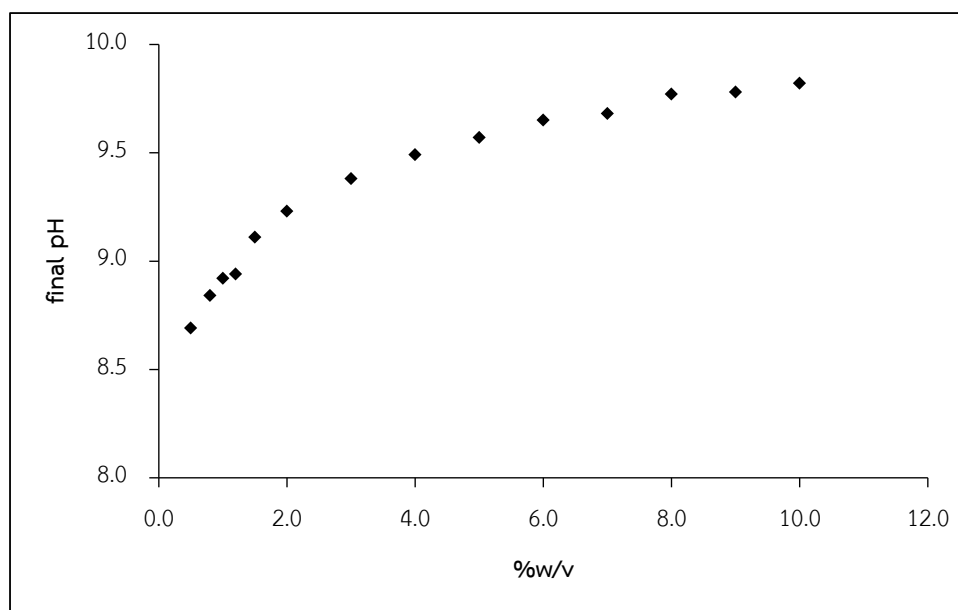
Adsorbent	Surface area value (m ² /g)
Bare sludge	30.82
Modified tap water sludge (Fe:sludge : 10:90 w/w)	73.01

4.2.6 Determination of the point of zero charge (pH_{pzc})

The pH of point of zero charge is the pH where the surface of adsorbent has a net neutral charge. It is utilized for predicting the adsorption mechanism of analyte on the surface of adsorbent. The suggestions of pH_{pzc} include;

- At a pH of solution is more than pH_{pzc}, the net surface charge is negative.
- At a pH of solution is lower than pH_{pzc}, the net surface charge is positive.

To evaluate the pH_{pzc} of the modified tap water sludge, the mass titration method was carried out. The experimental mass titration curve is shown in Figure 4.9. The result indicated that the pH_{pzc} of modified tap water sludge is approximately 9.7.

**Figure 4.9** Experimental mass titration curve of the modified tap water sludge (Fe:sludge 10:90).

All results mentioned above suggest that the modified tap water sludge by iron(0) which was prepared via sodium borohydride reduction of ferric chloride was successful. After that, the factors affecting the arsenic removal process by using the modified tap water sludge as adsorbent in a batch system were studied. The discussions are provided later on.

4.3 Batch experiments for arsenic adsorption

The factors affecting arsenic adsorption using the modified tap water sludge were studied by batch system. The discussions are provided in the following subsections.

4.3.1 Effect of pH

The pH of solution affects dramatically the arsenic adsorption due to the distribution of arsenic species depending on the pH of solution. However, arsenite is well known that it is difficult to be removed from water than arsenate because it forms neutral species under the pH less than 9.2. Therefore, this research aimed to study the effect of pH on arsenite adsorption and the appropriate pH for arsenite adsorption was used in arsenate adsorption. This research was conducted to investigate the effect of pH on arsenite adsorption in the pH range of 2-12. The result is shown in Figure 4.10. The result shows that the highest removal percentage of arsenite is at pH 3 and then the removal percentage of arsenite by the modified tap water sludge decreased when the pH of solution increased. Since arsenite is mostly found in negative forms including H_2AsO_3^- and HAsO_3^{2-} at high pH ($\text{pH} > 9.2$) and at this pH the surface of the modified tap water sludge has a net negative charge due to the fact that the pH of solution is more than the pH_{pzc} (9.7). Hence, the repulsion effect between negatively charged arsenite and the negatively charged surface of modified tap water sludge might be occurred. So, the modified tap water sludge shows less efficiency for arsenite adsorption when the pH of solution increased. The

other reason could be explained by the reaction for the oxidation of arsenite to arsenate by iron oxyhydroxides as shown in Equation 4.5 [52],



Due to iron oxyhydroxides can oxidize arsenite to arsenate and then adsorb on the surfaces of the modified sludge. From the Equation 4.5, the oxidation reaction of arsenite might be favorable in acidic medium so the degree of the oxidation of arsenite to arsenate by oxyhydroxides decreases as the pH increases. Therefore, the adsorption capacity of arsenite might be decreased as pH of solution increased. Thus, the pH of sample solution used in all further experiments was chosen at 3. However, the pH range of 3-9 might be applicable for arsenite adsorption. This observation reveals an advantage that arsenite could be adsorbed on the modified sludge under a wide pH range.

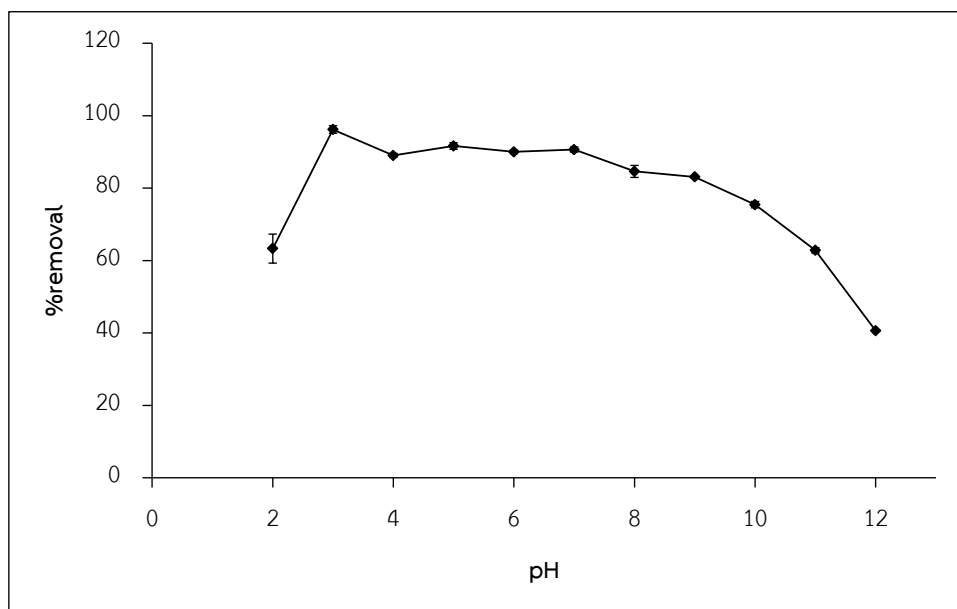


Figure 4.10 Effect of pH on arsenite adsorption (n=3)

(initial arsenic concentration = 100 mg/L, volume = 10 mL, adsorbent = 0.05 g and adsorption time = 24 hours).

4.3.2 Effect of contact time

The equilibrium contact time is one of the important factors for adsorption process. The effect of contact time on arsenic adsorption using the modified tap water sludge was evaluated in the range of 5-120 minutes. The function of adsorption amount of arsenite and arsenate against time are shown in Figure 4.11a and Figure 4.11b, respectively. It can be seen that there were rapid adsorption of arsenite and arsenate in the first 30 minutes and then they continued at a relatively slower rate and finally reached equilibrium after 60-120 minutes. The rapid adsorption in first period can be attributed to the large number of available active sites on the surface of modified tap water sludge. In this research, the contact time of 60 minutes was chosen to use in all future experiments.

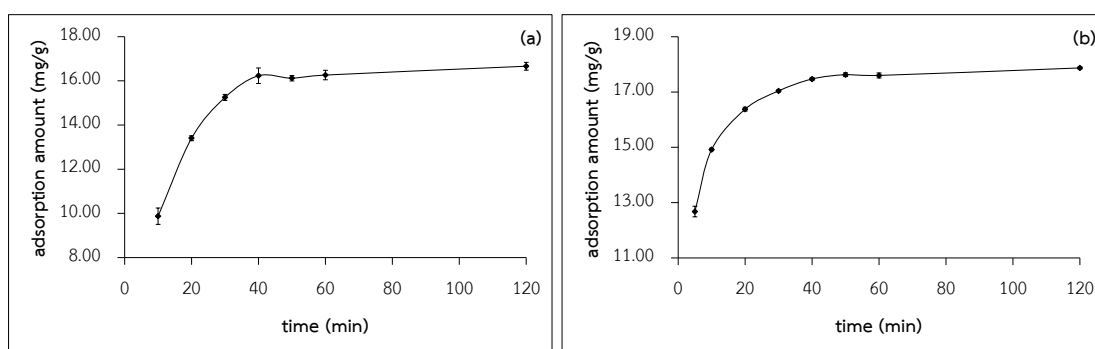


Figure 4.11 Effect of contact time on adsorption of (a) arsenite (b) arsenate (n=3)

(initial arsenic concentration = 100 mg/L, volume = 10 mL, adsorbent = 0.05 g and pH = 3).

4.3.2.1 Adsorption kinetics

To investigate the adsorption kinetics of the adsorption process, the pseudo first-order and the pseudo second-order kinetic models were used to fit the experimental data. The pseudo first-order and the pseudo second-order kinetic models can be expressed in Equations 4.6 and 4.7, respectively [23].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4.6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4.7)$$

Where q_e is the adsorption amount of the adsorbate at equilibrium (mg/g)

q_t is the adsorption amount of the adsorbate at time (mg/g)

t is time (min)

k_1 is the adsorption rate constant of the pseudo first-order kinetic model (min^{-1})

k_2 is the adsorption rate constant of the pseudo second-order kinetic model ($\text{g/mg}\cdot\text{min}$)

The linear regression of both kinetic models of arsenite and arsenate is shown in Figure 4.12 and Figure 4.13, respectively. The kinetic parameters estimated by linear regression are shown in Table 4.4. The results show that the adsorption kinetics of arsenite and arsenate were better described by the pseudo second-order model because the correlation coefficient (R^2) was closer to 1 compared to the R^2 of the pseudo first-order model. The adsorption of arsenite and arsenate on the modified tap water sludge was the pseudo second-order kinetic system which was assumed that the adsorption capacities of the materials were mainly proportional to the number of active sites on their surfaces [53]. Moreover, the rate-limiting step may be chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate [54]. Furthermore, the adsorption rate constant (k_2) of arsenate was higher than that of arsenite, indicating that there was more rapid adsorption of arsenate than arsenite.

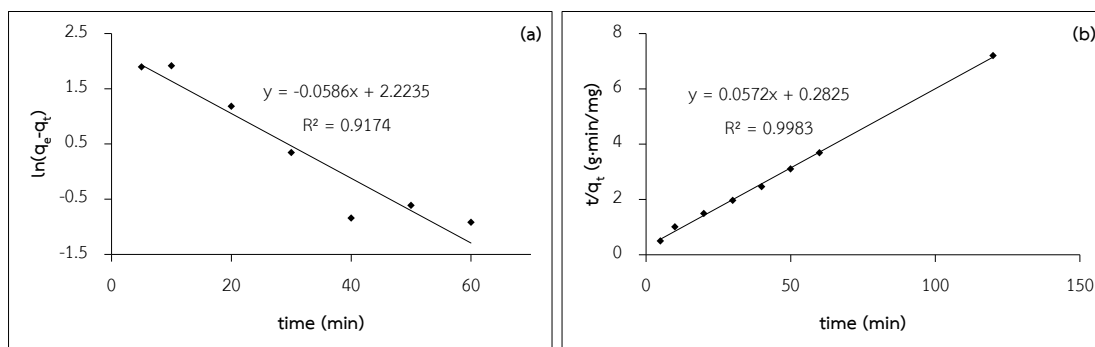


Figure 4.12 (a) Pseudo first-order kinetic plot of arsenite and (b) Pseudo second-order kinetic plot of arsenite.

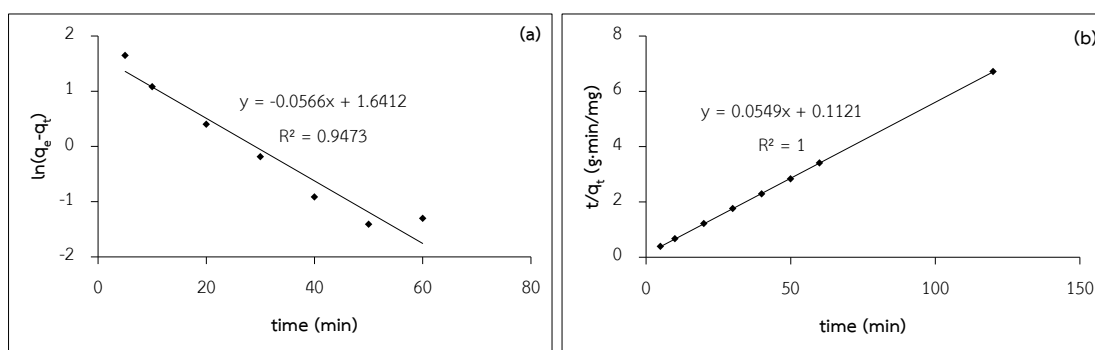


Figure 4.13 (a) Pseudo first-order kinetic plot of arsenate and (b) Pseudo second-order kinetic plot of arsenate.

Table 4.4 Adsorption kinetic parameters for arsenic adsorption onto the modified tap water sludge

Arsenic species	Pseudo first-order kinetic model			Pseudo second-order kinetic model		
	q_e (mg/g)	k_1 (min ⁻¹)	R^2	q_e (mg/g)	k_2 (min ⁻¹)	R^2
arsenite	9.24	0.0586	0.9174	17.48	0.0128	0.9983
arsenate	5.16	0.0566	0.9473	18.21	0.0279	1.0000

4.3.3 Adsorption isotherms

To evaluate the adsorption isotherms of the modified tap water sludge towards arsenite and arsenate, the Langmuir and the Freundlich models were used to describe the experimental data. The linearized equation of the Langmuir and Freundlich models are shown in Equations 4.8 and 4.9, respectively [53].

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4.8)$$

Where C_e is the equilibrium concentration of arsenic (mg/L)
 q_e is the equilibrium adsorption capacity of adsorbent (mg/g)
 q_m is the maximum adsorption capacity of adsorbent (mg/g)
 b is the constant related to the affinity of binding sites (L/mg)

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4.9)$$

Where K_f is the constant related to adsorption capacity (mg/g)
 n is the Freundlich constant related to adsorption intensity
 C_e is the equilibrium concentration of arsenic (mg/L)
 q_e is the equilibrium adsorption capacity of adsorbent (mg/g)

The adsorption isotherms of the modified tap water sludge with different ratios of iron to tap water sludge for arsenite adsorption are shown in Figure 4.14. It can be seen that the arsenic adsorption increased with the increase of arsenic concentrations.

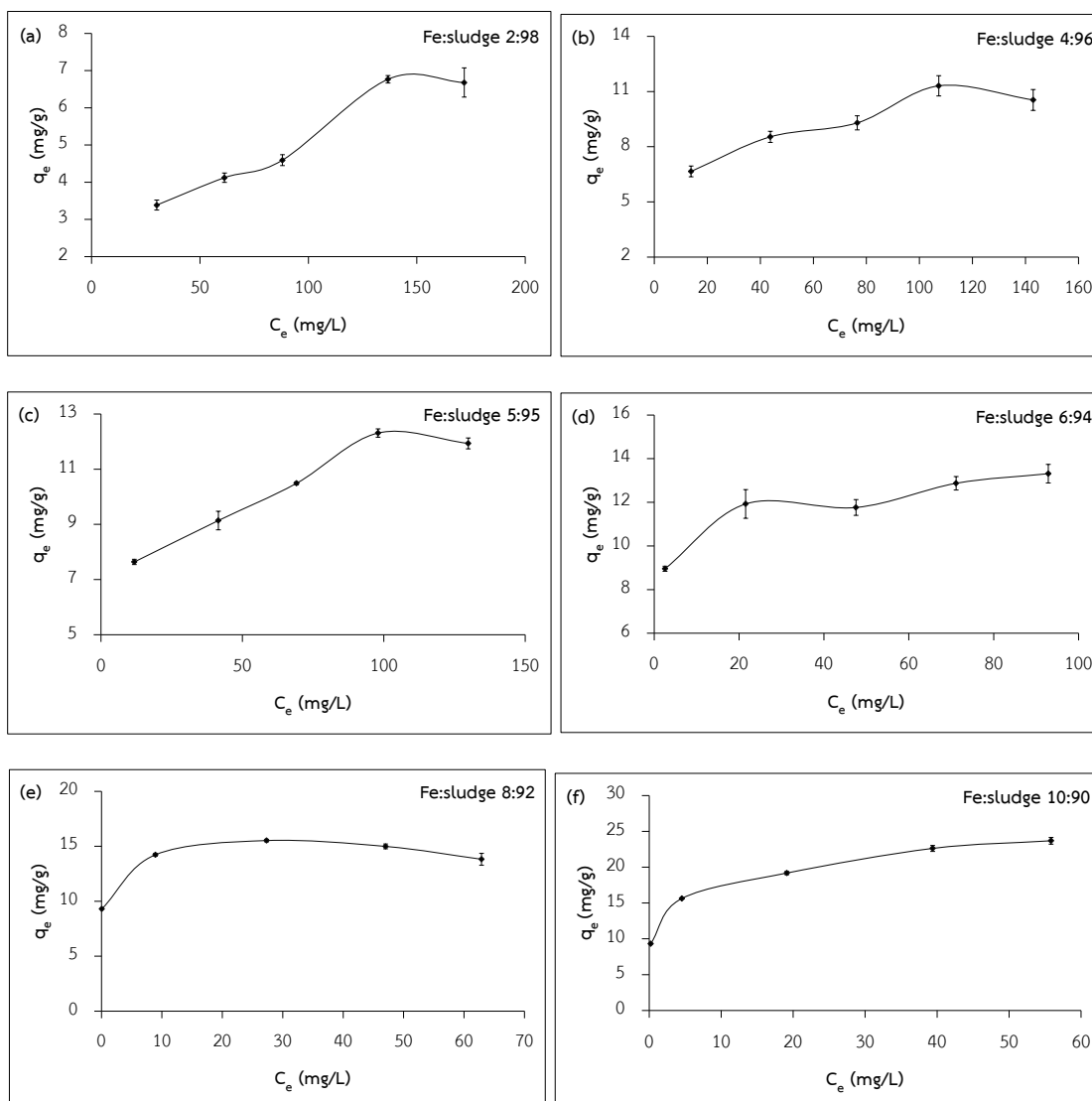
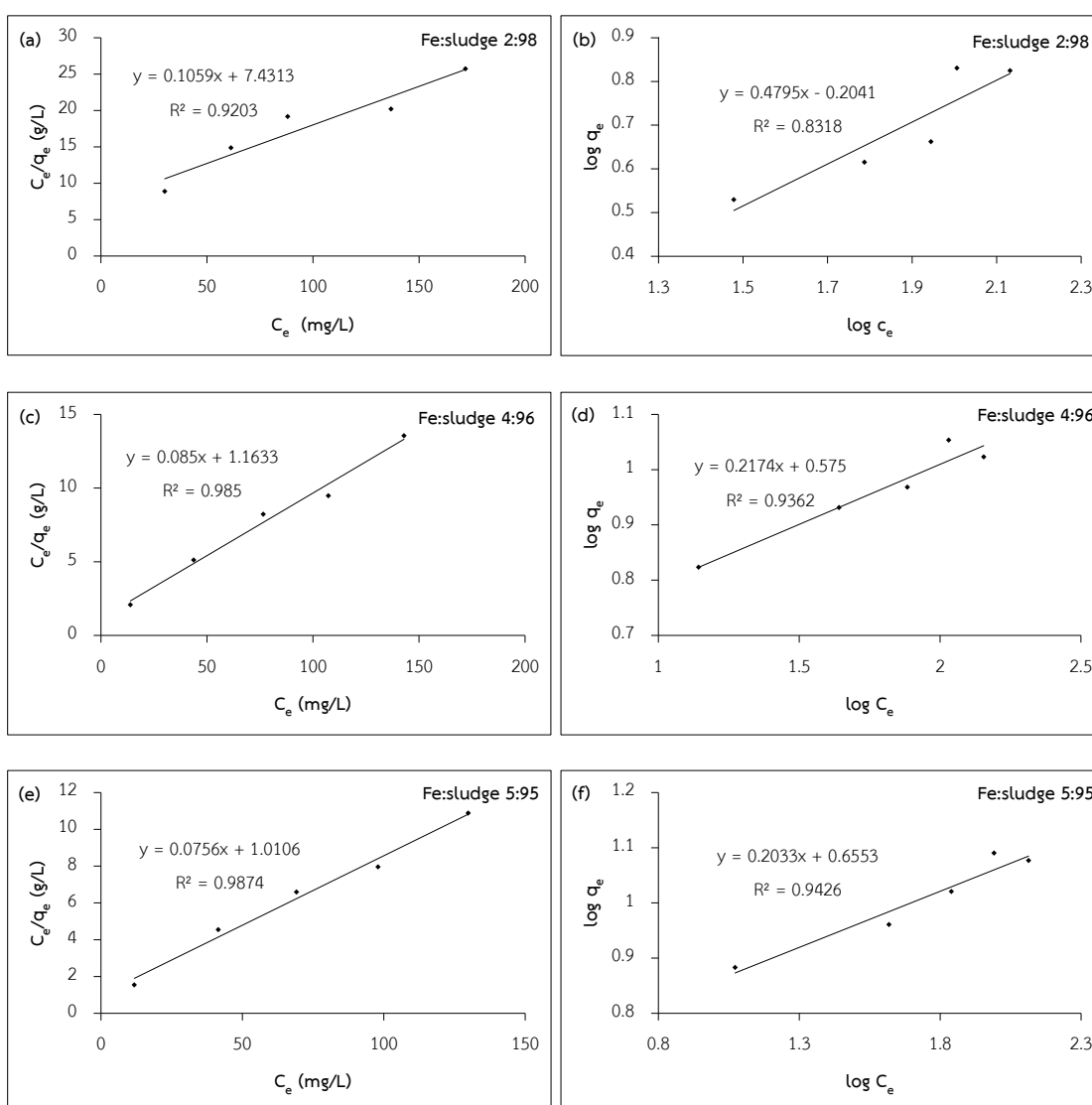


Figure 4.14 Adsorption isotherms of arsenite of iron:sludge (a) 2:98, (b) 4:96, (c) 5:95, (d) 6:94, (e) 8:92 and (f) 10:90 ($n=3$) (initial arsenic concentration = 50-250 mg/L, volume = 10 mL, adsorbent = 0.05 g, time = 2 hours and pH = 3).

The Langmuir and Freundlich models of these adsorbents are shown in Figure 4.15 and the parameters estimated by the linear regression of both isotherms are summarized in Table 4.5. The results show that the adsorption isotherms of the modified tap water sludge for arsenite were fitted to the Langmuir model because the correlation coefficient (R^2) was closer to 1 compared to the R^2 of another model. The adsorption of arsenite on modified tap water sludge obeyed the Langmuir

isotherm which was assumed that the adsorption of adsorbate on a solid surface is chemisorption in a single layer. It was found that the maximum adsorption capacity of arsenite calculated by the Langmuir adsorption isotherm increased proportionally to the amount of iron ratio. The modified tap water production sludge with 10:90 iron to sludge ratio which had the maximum adsorption capacity for arsenite calculated by the Langmuir isotherm of 24.15 mg/g was chosen to study in this research.



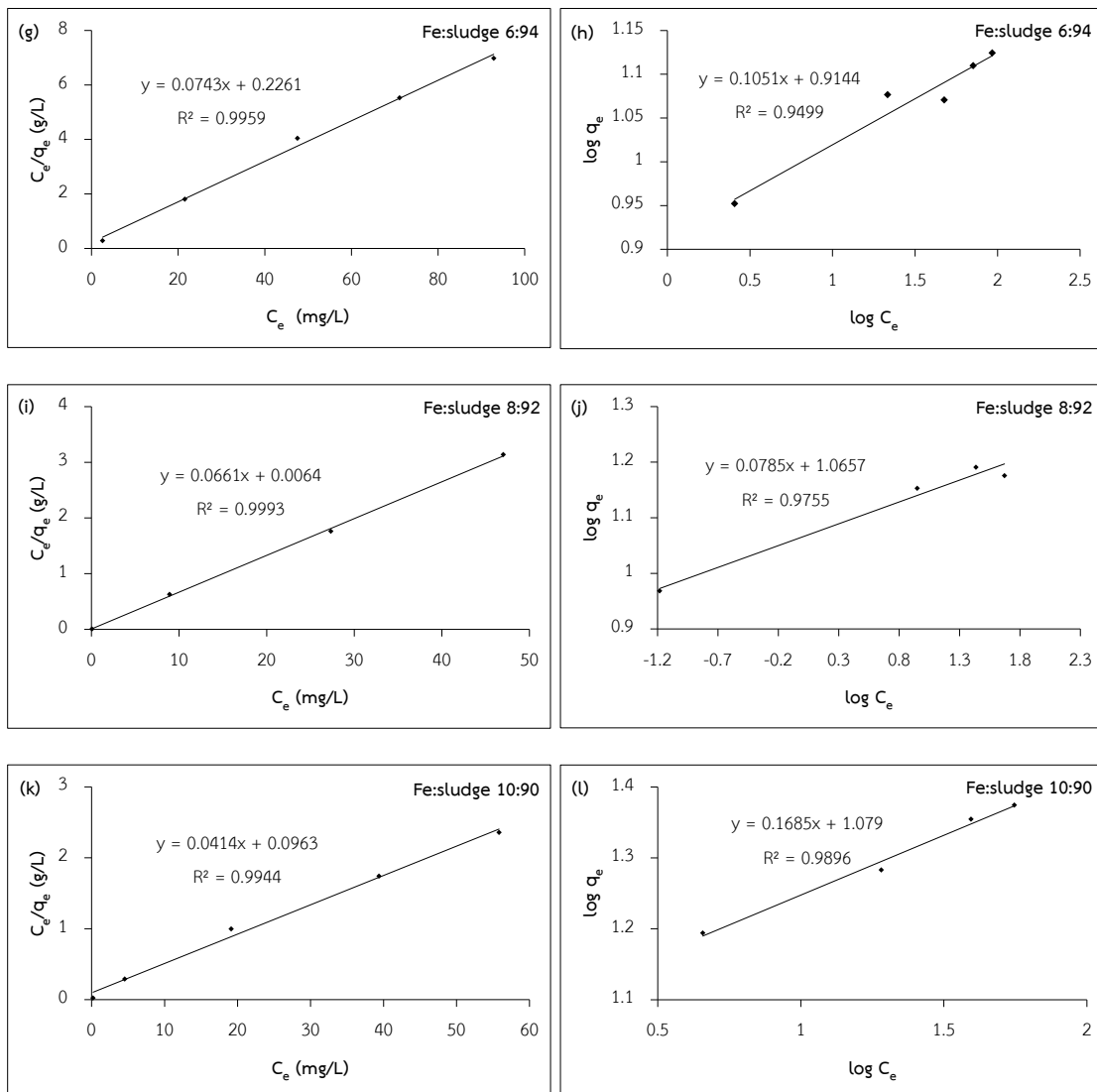


Figure 4.15 Langmuir plots (left image) of iron:sludge (a) 2:98, (c) 4:96, (e) 5:95, (g) 6:94, (i) 8:92, (k) 10:90 and Freundlich plots of iron:sludge (right image) (b) 2:98, (d) 4:96, (f) 5:95, (h) 6:94, (j) 8:92 and (l) 10:90.

Table 4.5 Adsorption isotherm parameters for arsenite adsorption onto the modified tap water sludge

Iron:sludge ratio (w/w)	Langmuir isotherm model			Freundlich isotherm model		
	q_m (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2
2:98	9.44	0.0143	0.9203	0.63	2.0855	0.8318
4:96	11.76	0.0731	0.9850	3.76	4.5998	0.9362
5:95	13.23	0.0748	0.9874	4.52	4.9188	0.9426
6:94	13.46	0.3286	0.9959	8.21	9.5147	0.9499
8:92	15.13	10.327	0.9993	11.63	12.739	0.9755
10:90	24.15	0.4300	0.9944	11.99	5.9347	0.9896

Moreover, the adsorption isotherms of the modified tap water sludge (Fe:sludge 10:90) for arsenate was studied. The adsorption of arsenate increased from 9.57 to 29.10 mg/g with the increase of arsenate concentrations as shown in Figure 4.16. The Langmuir and Freundlich models were used to describe the adsorption process as shown in Figure 4.17a and Figure 4.17b, respectively. The parameters calculated by the linear regression of these isotherms are included in Table 4.6. The results show that the correlation coefficient (R^2) of the Langmuir isotherms is closer to 1 than the Freundlich isotherm. Therefore, the arsenate adsorption on the modified tap water sludge was better described by the Langmuir isotherms model. The maximum adsorption capacity of arsenate calculated by the Langmuir isotherm was 35.71 mg/g.

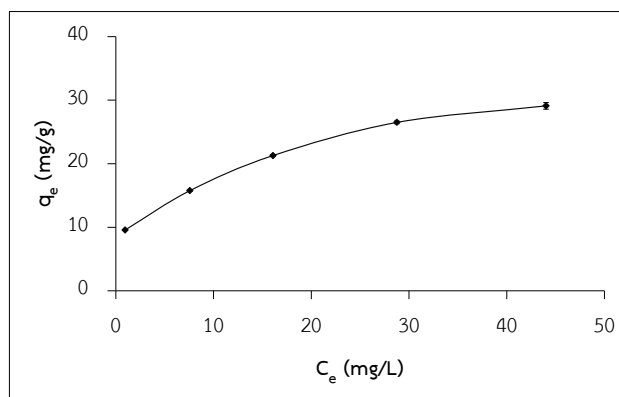


Figure 4.16 Adsorption isotherm of arsenate of iron:sludge 10:90 ($n=3$) (initial arsenic concentration = 50-250 mg/L, volume = 10 mL, adsorbent = 0.05 g, time = 2 hours and pH = 3).

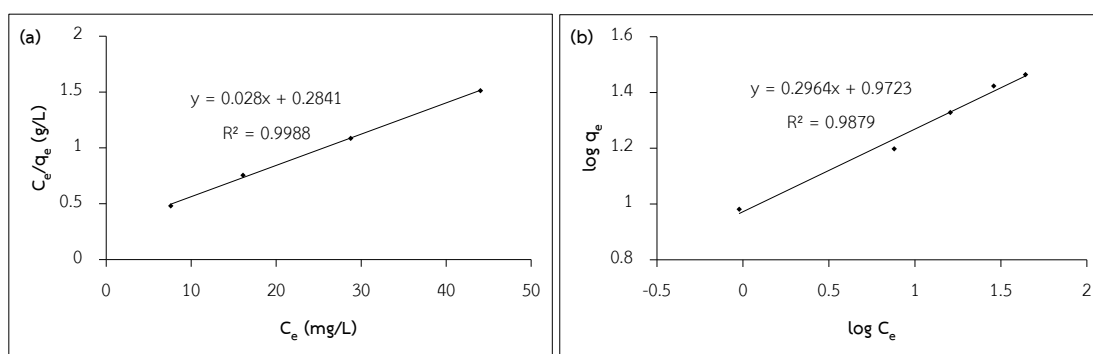


Figure 4.17 (a) Langmuir isotherm plot and (b) Freundlich isotherm plot.

Table 4.6 Adsorption isotherm parameters for arsenate adsorption onto the modified tap water sludge

Iron:sludge ratio (w/w)	Langmuir isotherm model			Freundlich isotherm model		
	q_m (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2
10:90	35.71	0.0986	0.9988	9.3821	3.3738	0.9879

Furthermore, the comparison of the maximum adsorption capacity of various adsorbents for arsenite and arsenate adsorption is shown in Table 4.7. It can be seen that the modified tap water sludge by iron(0) in this research had relatively higher adsorption capacity and more rapid equilibrium contact time for arsenite and arsenate adsorption comparing with other adsorbents.

Table 4.7 Comparison of adsorption capacity for arsenic onto some adsorbents

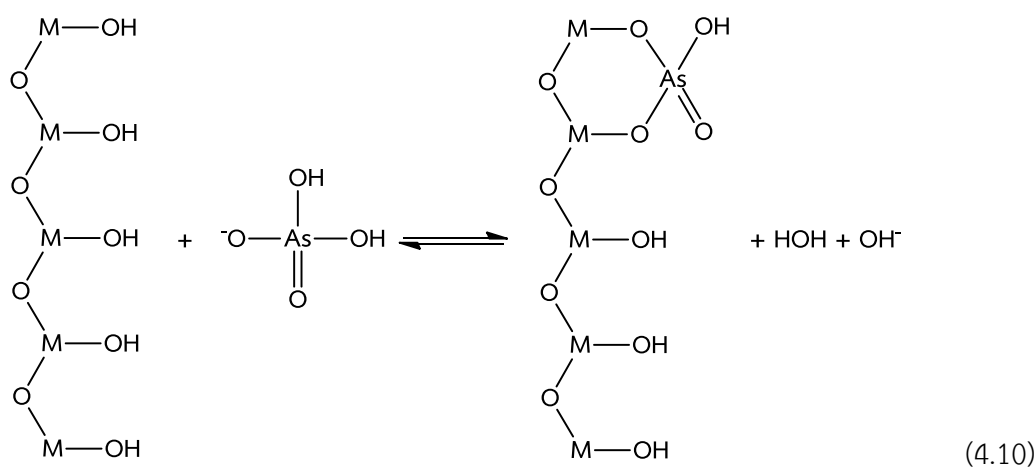
Adsorbents	Adsorption capacity		Equilibrium contact time (hours)	Refs.
	(mg/g)			
	arsenite	arsenate		
Innovative coal-based activated carbon (M-NCPAC)	1.634	1.701	1 (arsenite) 0.5 (arsenate)	[55]
Ferric-based layered double hydroxide with α -alanine intercalation (Mg-Fe-Ala-LDH)	49.8	23.6	6	[53]
- Potassium hydroxide activated carbon based apricot stone (C)	-	27	0.5	[56]
- Calcium alginate beads (G)	-	42.4	0.5	
- Calcium alginate/activated carbon composite beads (GC)	-	66.7	1	
- Sulphuric acid acidified laterite (ALS)	0.3012	0.9236	48	[57]
- Laterite	0.1278	0.1717	48	
- Montmorillonite modified with Fe polycations (Fe-M)	16.58	15.15	0.3	[58]
- Montmorillonite modified with Fe polycations and cethyltrimethylammonium bromide	11.36	8.85	0.3	

Table 4.7 (cont.) Comparison of adsorption capacity for arsenic onto some adsorbents

Adsorbents	Adsorption capacity (mg/g)		Equilibrium contact time (hours)	Refs.
	arsenite	arsenate		
Novel fabricated copper ferrite	-	45.66	5	[59]
Fe-based backwashing sludge (FBBS)	59.7	-	18	[39]
Acid mine drainage sludge (AMDS)	58.5	19.7	0.3	[40]
Leonardite	4.46	8.40	3	[41]
Clay-supported zero-valent iron nanoparticles synthesized with the help of tea liquor	0.495	-	0.5	[47]
Supported nano zero-valent iron on activated carbon	18.2	12.0	72	[44]
Supported nano zero-valent iron on reduce graphite oxide (RGO)	35.83	29.04	1	[49]
Iron(III) loaded zein based adsorbent	-	1.95	8	[60]
Tap water sludge (obtained from the Metropolitan Waterworks Authority, Bangkok, Thailand)	1.89	8.76	12	[10]
Modified tap water sludge (obtained from the Metropolitan Waterworks Authority, Bangkok, Thailand) by iron	24.15	35.71	1	This study

4.3.4 Investigation of arsenic adsorption mechanism onto the adsorbent

The XRD results presented in section 4.2.2.1 indicated that iron particles synthesized via sodium borohydride reduction of ferric chloride consisted of zero-valent iron and iron oxides. Additionally, the results of characterization of iron on the modified tap water sludge as mentioned above (section 4.2.4) indicated that the modified tap water sludge might be comprised of zero-valent iron and iron oxides. Recently, many researchers proposed mechanisms of arsenic onto the surface of zero-valent iron using surface chemical analysis or X-ray absorption spectroscopic techniques. The study showed that zero-valent iron exhibited core-shell structure which consisted of a zero-valent core and an oxide shell. The occurred reaction, included the oxidation of arsenite by iron oxides at the shell, the reduction of arsenic species by iron via diffusion of arsenic through the oxide layer to form As-Fe intermetallic phase and the adsorption [11]. Hence, the reaction that might be occurred between arsenic species and the modified tap water sludge in the adsorption process included the oxidation of arsenite to arsenate (under acidic condition as mentioned above) and then arsenate was adsorbed onto aluminium and iron hydroxides on the surface of sludge by ligand exchange mechanism as shown in Equation 4.10 [61].



(M represent to Fe and Al)

Moreover, to investigate the effect of iron and iron oxide on arsenic adsorption process, commercial iron powder and iron oxide (Fe_2O_3) powder (the amount of these adsorbents used in this experiment was similar to the amount of the added iron in the modified tap water sludge of 10:90 iron to tap water sludge ratio) being used to an adsorbent for arsenite and arsenate adsorption under the optimal conditions. The amounts of arsenite and arsenate which were adsorbed by these adsorbents are shown in Figure 4.18.

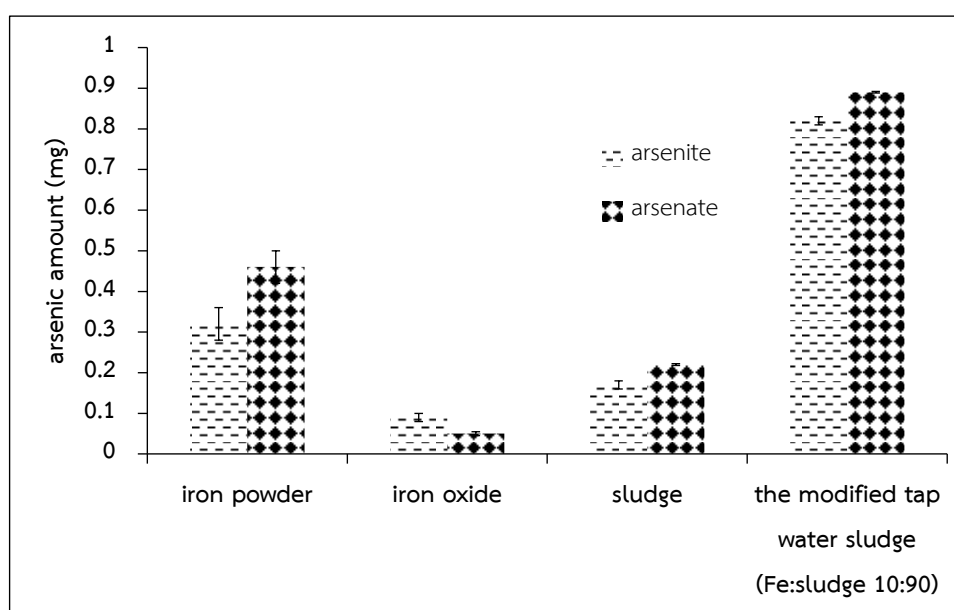


Figure 4.18 Comparison of adsorption amount for arsenite and arsenate onto some adsorbents (n=3).

The results show that iron(0) powder was more effective for both arsenite and arsenate adsorption comparing with iron oxide and sludge. Therefore, the crucial mechanism might be occurred through iron(0). However, the adsorption properties of the modified tap water sludge might be owing to the combination of iron(0), iron oxide and sludge properties.

4.3.5 Effect of interfering ions

Sulfate and phosphate anions are commonly found in natural water. The effect of these ions on the adsorption of arsenite and arsenate are shown in Figure 4.19a and Figure 4.19b, respectively. The results show that phosphate dramatically inhibited the adsorption of both arsenite and arsenate due to its similar chemical properties and structure to arsenic species while sulfate did not have any significant effect on arsenate adsorption but it slightly inhibited the adsorption of arsenite at high concentrations.

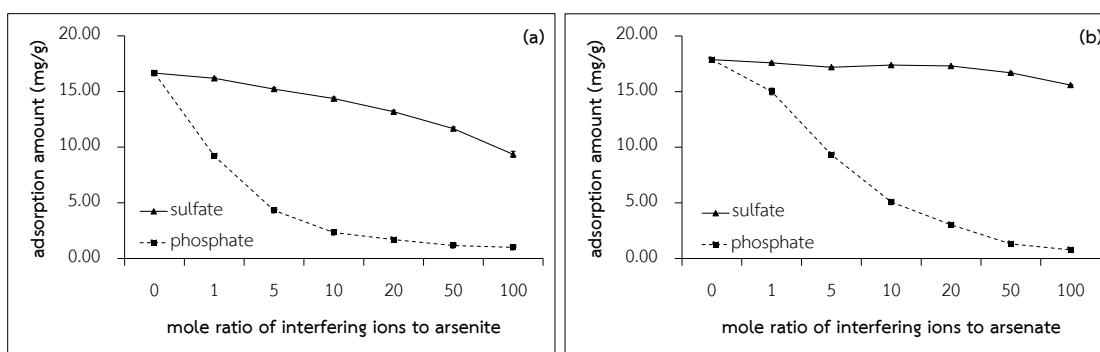


Figure 4.19 Effect of sulfate and phosphate on (a) arsenite and (b) arsenate adsorption (n=3).

Humic acid is a principal component of humic substances, which is the major organic constituent of soil. It is produced by biodegradation of dead organic matter. The graph described the influence of humic acid on the removal of arsenite and arsenate using the modified tap water sludge is shown in Figure 4.20. It showed that the presence of humic acid at high concentrations had slight effect on the adsorption of arsenite and arsenate. The phenomenon of humic and sulfate on arsenite adsorption can be described to the competitive binding effect by substances, which occupy the reactive surface sites of the modified tap water sludge.

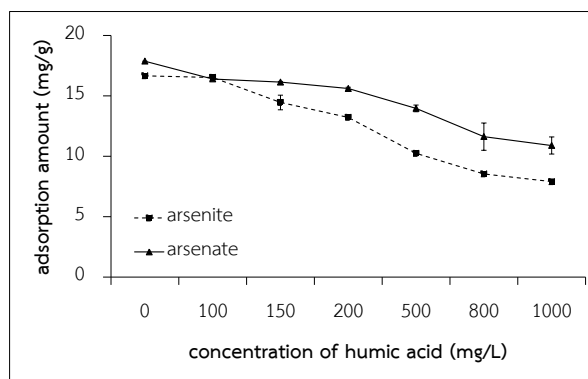


Figure 4.20 Effect of humic acid on arsenite and arsenate adsorption (n=3).

4.4 Application in real contaminated water samples

To evaluate the efficiency of the modified tap water sludge for arsenic removal process in real samples, TK-80 and TK-81 were used. TK-80 and TK-81 are the wastewater obtained from PTT Public Company Limited, Thailand. They contain total arsenic in the range of 68-78 mg/L. The treatment of these wastewater samples for arsenic removal was divided into 2 systems including batch system and column system. Moreover, pond water of Chulalongkorn University and groundwater samples were also used to assess the arsenic removal efficiency in batch system using the modified tap water sludge. The discussions are provided in the following subsections.

4.4.1 Batch system

The results of arsenic removal from wastewater in batch system are shown in Table 4.8. The results showed that the percentage of arsenic removal for TK-80 and TK-81 were 75.82% and 68.38%, respectively. It showed that the percentage of arsenic removal using the modified tap water sludge was higher compared to the percentage of arsenic removal using the bare sludge (17.58% and 11.21% for TK-80 and TK-81, respectively) [10]. However, the percentage of arsenic removal was relatively low comparing with the previous experiment due to the fact that the wastewater are not only composed of inorganic arsenic species but also composed

of organic arsenic species such as dimethylarsinic acid (unpublished results). Moreover, interfering ions might be presented in the wastewater which were suppressed the adsorption of arsenic. All of these might be the main cause that the percentage of arsenic removal in real wastewaters was not met the expectation of removal efficiency. Nevertheless, this method can be improved by increasing the adsorbent amount to increase the active sites for arsenic adsorption.

Table 4.8 The arsenic removal from the wastewater samples (TK-80 and TK-81) in batch system (n=3)

Type of real wastewater	Initial concentration of total arsenic (mg/L)	Adsorption amount (mg/g)	%removal
TK-80	68.44	10.34 ± 0.10	75.82 ± 0.93
TK-81	77.94	10.60 ± 0.27	68.38 ± 1.60

4.4.2 Column system

To evaluate the efficiency of arsenic removal in column system, the different types of column system was set up into 3 types. The scheme of the three column systems for arsenic removal process was operated and shown in the following Figure 4.21.

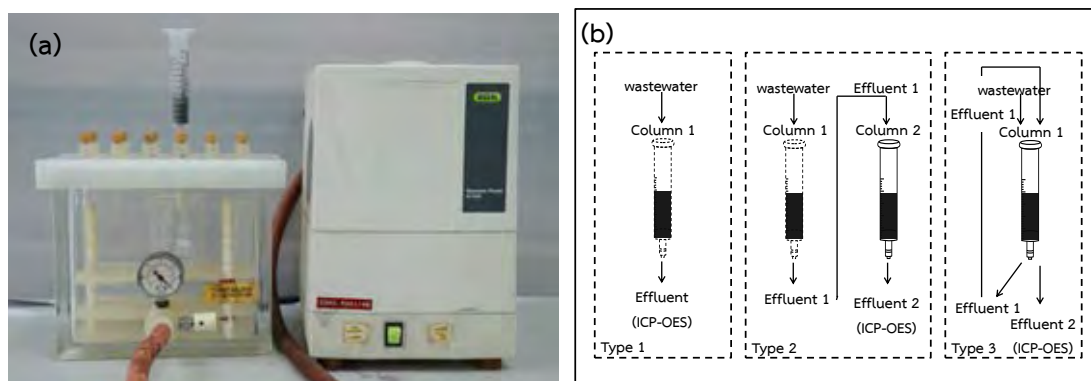


Figure 4.21 (a) photograph of column system and (b) the scheme of different types of column system.

The results of the column system are shown in Table 4.9. It can be seen that the amount of remaining arsenic could not be detected in the effluents obtained from all three column systems. The percentage of arsenic removal for TK-81 was almost 100% in all column systems. This suggests that the column system was effective for arsenic removal and the different types of column system showed the similar efficiency for arsenic removal.

Table 4.9 The arsenic removal from the wastewater sample (TK-81) with different types of column system

Type of column system	Remaining of arsenic concentration (mg/L)	%removal
Single column in one cycle	n.d.	~ 100
Two columns	n.d.	~ 100
Single column in two cycles	n.d.	~ 100

n.d. : not detectable (LOD of arsenic determination by ICP-OES ~ 0.05 mg/L)

4.4.3 Arsenic removal from surface water and ground water samples

To simulate the real surface water and ground water samples, arsenic-free pond water and groundwater samples were used. These water samples were spiked

with arsenite or arsenate in a concentration of 100 mg/L. The results were concluded in Table 4.10 and Table 4.11 for spiked arsenite and arsenate samples, respectively. The results show that the modified tap water sludge had high efficiency for arsenate removal with a removal percentage of almost 100%. Lower adsorption efficiency of the modified tap water sludge for arsenite might be caused by the chemical property of arsenite which forms neutral form in a wide range of pH thus it is difficult to be removed from water. Moreover, lower removal percentage of spiked ground water comparing with spiked pond water might be described that ground water normally contains relatively high level of mineral ions then some of which could probably inhibit the adsorption of arsenite.

Table 4.10 The arsenic removal from natural water samples spiked with arsenite (n=3)

Type of water	Adsorption amount (mg/g)	%removal
Pond water of Chulalongkorn University	13.81 ± 0.07	84.31 ± 0.44
Ground water	11.96 ± 0.21	75.09 ± 1.51

Table 4.11 The arsenic removal from natural water samples spiked with arsenate (n=3)

Type of water	Remaining of arsenic concentration (mg/L)	%removal
Pond water of Chulalongkorn University	n.d.	~ 100
Ground water	n.d.	~ 100

n.d. : not detectable (LOD of arsenic determination by ICP-OES ~ 0.05 mg/L)

All of the results mentioned above show that the modified tap water sludge has potential for arsenic removal from real water samples. Although some of the

cases showed relatively low percentage of arsenic removal, it could be improved by increasing of the adsorbent amount.

4.5 Stabilization/solidification of the modified tap water sludge after arsenic removal using cement as binder

The amount of arsenic in the modified tap water sludge after arsenic adsorption process was determined using ICP-OES after acid digestion. The result shows that the contaminated sludge contained high content of total arsenic in the amount of 19.12 mg/g which is classified as hazardous waste [31]. Therefore, it is necessary to be managed of the contaminated sludge before landfill disposal.

Stabilization/solidification of the modified tap water sludge after arsenic removal process is a technique that can reduce the potential hazard of waste. In this research, cement was used as a binder in stabilization/solidification process and the arsenic leaching characteristic of the solidified waste was studied by dynamic monolithic leaching test (DMLT). The discussions are provided in the following subsections.

4.5.1 Solidified waste preparation

The unconfined compressive strength (USC) testing is primarily used to determine the suitable proportion of cement to contaminated sludge ratio. The USC of solidified waste at different amounts of cement to contaminated sludge ratio is concluded in Table 4.12. The results of USC tested after 14 day- curing show that the USC value increased with the increase amount of cement used. This phenomenon can be described by the property of cement which is able to set and harden in the presence of water and transform the physical properties such as strength and compressibility of the solidified waste. Considering the USEPA criteria for hazardous waste landfill disposal, a minimal UCS value of 0.35 MPa is required [62]. From the results, the solidified with 6:4 of cement to contaminated sludge ratio is adequate in

terms of quality acceptance. So this amount ratio was selected to study the arsenic leaching characteristic which is proposed in the next subsections. The photograph of the solidified waste with 6:4 of cement to contaminated sludge ratio is shown in Figure 4.22.

Table 4.12 Compressive strength of solidified waste cured for 14 days

Cement:sludge ratio	Measured (psi)	Corrected measured (psi)	Corrected measured (kg/cm ²)	Corrected UCS (kg/cm ²)	Corrected UCS (MPa)
6:4	230	200	16.2	14.1	1.38
7:3	400	348	28.1	24.5	2.40
8:2	1,070	931	75.2	65.5	6.42
9:1	1,800	1,566	126.6	110.1	10.80



Figure 4.22 Solidified waste sample (6:4 of cement to contaminated sludge ratio).

4.5.2 Leaching characteristics of arsenic by dynamic monolithic leaching test (DMLT)

In order to evaluate the arsenic leaching characteristic of the contaminated sludge after management, the solidified waste samples (6:4 cement:sludge ratio)

were subject to the standard leaching test of CEN/TS 15863:2012 [63]. The test portion of leaching process is displayed in Figure 4.23.



Figure 4.23 Photograph of test portion in leaching process.

The concentration of arsenic and iron which were leached from the solidified waste sample of each time interval is listed in Table 4.13. It can be seen that the concentrations of arsenic leached from the solidified waste of each steps did not exceed 5 mg/L which was the toxicity characteristic leaching procedure (TCLP) regulatory limit value proposed by the Resource Conservation and Recovery Act (RCRA) and Universal Treatment Standard (UTS) [64]. Meanwhile, the leached concentration of iron which is not toxic element was also very low. Moreover, the calculated percentage of arsenic amount leached from the solidified waste since first step to the end of the leaching process comparing with the whole amount of arsenic contained in the solidified waste was 0.96%. This indicates that the management of the contaminated sludge by stabilization/solidification using cement as a binder was effective for reducing the potential hazard of waste due to the reaction between cement and arsenic species producing less soluble forms of arsenic. The result of chemical transformations of arsenic using cement has been reported by many researches. The formation of calcium arsenite (Ca-As-O), $\text{NaCaAsO}_4 \cdot 7.5\text{H}_2\text{O}$, $\text{Ca}_3(\text{AsO}_4)_2$

and CaAsO_2OH (as described in section 2.5) might be occurred which were the key compounds to immobilize arsenite and arsenate [13, 32].

Table 4.13 The arsenic and iron leaching concentration of each times in leaching process (n = 3)

Duration from the start of the test t_0 (days)	The arsenic leaching concentration (mg/L)	The iron leaching concentration (mg/L)
0.08	0.25 ± 0.05	0.20 ± 0.03
1	1.51 ± 0.03	0.40 ± 0.02
2.25	1.15 ± 0.11	0.34 ± 0.05
8	1.81 ± 0.19	0.39 ± 0.03
14	1.31 ± 0.15	0.24 ± 0.01
15	0.32 ± 0.03	0.16 ± 0.01
28	1.00 ± 0.19	0.20 ± 0.01
36	0.72 ± 0.07	0.162 ± 0.001
64	0.64 ± 0.12	0.167 ± 0.003

The arsenic leaching characteristic of the solidified waste was evaluated by plotting the calculated cumulative release of the different constituents which mentioned in section 3.8.2 as a function of time on a double logarithmic scale. The graphs illustrating the calculated cumulative release correlated with time of the protocol and our experiment are shown in Figure 4.24a and Figure 4.24b, respectively. The graph consists of the cross-sign and the line with a slope of 0.5 which represents the cumulative release and the release by diffusion, respectively. It is shown that the cumulative release of arsenic was fixed to the line of 0.5 slope at the beginning and started to drop gradually in the end of leaching process. The obtained result was similar to the graph of the protocol which was proposed by CEN/TS 15863:2012 indicating that the constituents of solidified waste were highly

soluble. Therefore, at short period time of leaching process arsenic leached from the solidified waste as diffusion control and then it depleted at the end.

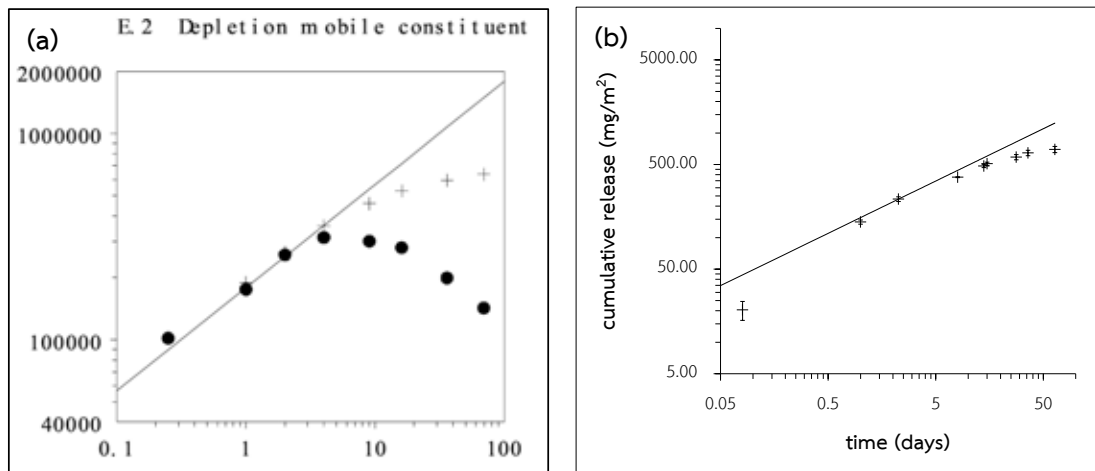


Figure 4.24 Graph between cumulative release correlated with time of (a) the protocol proposed by CEN/TS 15863:2012 and (b) this work.

4.5.3 Total dissolved solid

Total dissolved solid (TDS) is a value which describes the total of inorganic salt, organic salts and small amounts of organic matter contained in water. The TDS values of water which were obtained from leaching process are concluded in Table 4.14. The results show that the TDS values of each time interval did not exceed 3,000 mg/L which was a regulatory limit value of wastewater proposed by the Pollution Control Department (PCD), Ministry of Natural Resources and Environment, Thailand [65]. Therefore, this leachate quality conforms to is the acceptable value for water pollution regulation.

Table 4.14 TDS values of each times in leaching process (n=3)

Duration from the start of the test t_0 (days)	TDS value (mg/L)
0.08	253 ± 27
1	229 ± 16
2.25	200 ± 29
8	506 ± 182
14	477 ± 125
15	118 ± 22
28	526 ± 174
36	466 ± 197
64	757 ± 19

CHAPTER V

CONCLUSION

5.1 Conclusion

In this research, the tap water production sludge obtained from the Metropolitan Waterworks Authority (Bangkhen, Thailand) was modified by iron(0) via sodium borohydride reduction of ferric chloride method under atmospheric conditions with the purpose to enhance the arsenic removal efficiency of the material in environmental applications. The modified tap water sludge with the iron to sludge ratio of 10:90 (w/w) was used in this study. The characteristic of the modified tap water sludge was investigated by using ICP-OES, XRF, XRD, SEM-EDS, TEM and surface area analyzer.

From the results of elemental composition by ICP-OES and XRF, it can be seen that the modified tap water sludge contained high content of iron comparing with the unmodified tap water sludge and the calculated amount of iron by both techniques were supposed to be 10% (w/w), indicating that the modified tap water sludge via sodium borohydride reduction of ferric chloride method was successful. The XRD pattern of the modified tap water sludge shows the characteristic peaks of quartz which was predominantly constituent of sludge while the XRD pattern of iron which was synthesized via the same method was observed the characteristic peaks of zero-valent iron and iron oxides, indicating that the modified tap water sludge might be consisted of zero-valent iron and iron oxides. The SEM images show that the morphology of the modified tap water sludge consisted of sludge and iron characteristic including small plates with spherical particle form. The mapping SEM-EDS and TEM images show that the iron particles was dispersed very well on the

surface of modified tap water sludge. The BET surface area of the bare sludge was a value of $30.82 \text{ m}^2/\text{g}$ and increased to $73.01 \text{ m}^2/\text{g}$ after being modified by iron(0). The pH_{pzc} of the modified tap water sludge evaluated from a mass titration method was 9.7.

The factors affecting arsenic adsorption using the modified tap water sludge were studied by batch system. The optimal conditions for arsenite and arsenate removal are concluded in Table 5.1.

Table 5.1 The optimal conditions for arsenic removal in batch system

Factor	Optimal condition
pH	3
contact time	1-2 hours

(initial arsenic concentration = 100 mg/L, volume = 10 mL, adsorbent = $0.0500 \pm 0.0005 \text{ g}$)

The adsorption kinetics of arsenite and arsenate were better described by the pseudo second-order model. The adsorption isotherms of the modified tap water sludge for both arsenite and arsenate were fitted to the Langmuir model. The maximum adsorption capacity of arsenite and arsenate calculated by Langmuir adsorption isotherms were 24.15 and 35.71 mg/g, respectively. Moreover, the modified tap water sludge by iron(0) in this research had relatively higher adsorption capacity and more rapid equilibrium contact time for arsenite and arsenate adsorption comparing with other adsorbents. Furthermore, the presence of phosphate inhibited the adsorption of arsenite and arsenate while sulfate and humic acid affected the efficiency of arsenite and arsenate adsorption only at high concentrations.

In addition, the modified tap water sludge was applied to arsenic removal in real wastewater samples under optimal conditions in batch and column systems. In

batch system, the percentages of arsenic removal for industrial wastewater samples were 75.82% and 68.38%. The column system showed higher percentage of arsenic removal with a value of almost 100%. Moreover, the results of arsenic adsorption from artificial arsenic-contaminated surface and ground water samples show that the modified tap water sludge had high efficiency for arsenate removal with a removal percentage of almost 100% while relatively high efficiency for arsenite removal (84.31% for surface water sample and 75.09% for ground water sample). All results suggested that the modified tap water sludge by iron(0) was applicable for arsenite and arsenate removal in water with high efficiency.

Finally, the contaminated sludge after the arsenic removal process was managed by stabilization/solidification method using cement as a binder. The solidified with 6:4 of cement to contaminated sludge ratio which was USC value of 1.39 MPa (adequate in terms of quality acceptance using USEPA criteria for hazardous waste landfill disposal). The arsenic leaching characteristic of the contaminated sludge was carried out following the standard leaching test of CEN/TS 15863:2012. The results show that the concentration of arsenic leached from the solidified waste of each steps did not exceed the toxicity characteristic leaching procedure (TCLP) regulatory limit value). The leaching characteristic of the solidified waste exhibited as a diffusion control in short period of time at the beginning and then it depleted at the end of the leaching process. This suggested that the management of the contaminated sludge by stabilization/solidification using cement as a binder was effective for reducing the potential hazard of waste due to the reaction between cement and arsenic species producing less soluble forms of arsenic.

5.2 Suggestion for the future work

- The modified tap water sludge by iron via sodium borohydride reduction of ferric chloride method should be developed to synthesize in large-scale system for wastewater treatment plant applications.
- Adsorption models for column system should be designed in laboratory scale and applied to large-scale for wastewater treatment plant applications.

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APPENDIX

Pressure converting

$$1 \text{ psi} = 14.22 \text{ kg/cm}^2$$

$$1 \text{ psi} = 6.89475729 \times 10^{-3} \text{ MPa}$$

$$\text{corrected pressure} = \text{measure pressure} \times 0.87$$

VITA

Mr. Porndanai Sarntanayoot was born on November 26th, 1990 in Suratthani, Thailand. He graduated from Chulalongkorn University with a Bachelor's degree of Science in Chemistry (2nd Class Honours) in 2013. After that, he continued his study with a Master's degree of Science in Analytical Chemistry at the Department of Chemistry, Chulalongkorn University and became one of the members of the Environmental Analysis Research Unit (EARU). He finished his postgraduate in 2015. His permanent address is 94/12 Ratbumrung Road, Thakham Sub-district, Phunphin District, Suratthani, Thailand, 84130. Contact number is 08-4051-9059. E-mail: p.sarntanayoot@gmail.com.