Cu-Fe BIMETALLIC MATERIAL ON ARSENIC REMOVAL UNDER GAS-BUBBLING CONDITIONS

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การกำจัดสารหนูในระบบฟองก๊าซด้วยโลหะคู่ Cu-Fe

นางสาวปิยะเนตร นาคสีดี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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ปิยะเนตร นาคสีดี : การกำจัดสารหนูในระบบฟองก๊าซด้วยโลหะคู่ Cu-Fe (Cu-Fe BIMETALLIC MATERIAL ON ARSENIC REMOVAL UNDER GAS-BUBBLING CONDITIONS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. นุรักษ์ กฤษดานุรักษ์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ศ. ดร. จื้อเฉียง เลียว, รศ. ดร. เจียชิน จู่, 135 หน้า.

การกำจัดสารหนูถูกทดสอบโดยใช้โลหะคู่เหล็กอนุภาคนาโน ทองแดงและนิกเกิลถูกเลือกเพื่อสังเคราะห์ร่วมกับเหล็กศูนย์เพื่อใช้ภายใต้สภาวะในการทดลองแบบกะด้วยความเข้มเข้นของสารหนูเริ่มต้น 5000 ไมโครกรัมต่อลิตร ค่าความเป็นกรดเบสเริ่มต้น 7.0 ผลการศึกษาพบว่าโลหะคู่ทองแดงเหล็กอนุภาคนาโนสามารถกำจัดสารหนูได้ดีกว่าการใช้โลหะคู่นิกเกิลเหล็กและเหล็กศูนย์ วิธีการสังเคราะห์โลหะคู่ทองแดงเหล็กถูกศึกษาเพิ่มเติมโดยเปรียบเทียบสองวิธี วิธีแรกคือวิธีการทำปฏิกิริยาร่วมในแหล่งกำเนิด และวิธีทำให้เหล็กเอิบชุ่มด้วยสารละลายทองแดง คุณสมบัติของโลหะคู่ถูกวิเคราะห์ด้วยเครื่องมือ SEM-EDX, TEM, BET และ XANES หลังจากนั้นการกำจัดสารหนูด้วยโลหะคู่ทองแดงเหล็กอนุภาคนาโนถูกใช้ร่วมกับระบบฟองก๊าซคาร์บอนไดออกไซด์และออกซิเจนที่อัตราการไหลของก๊าซ 300 มิลลิลิตรต่อนาทีซึ่งเป็นสภาวะค่าความเป็นกรดเบสต่ำและปริมาณออกซิเจนละลายในน้ำสูง ปริมาณของทองแดงที่ใช้ในการสังเคราะห์ถูกศึกษาในช่วงร้อยละ 2.5 ถึง 30 โดยพบว่าปริมาณทองแดงร้อยละ 10 ด้วยวิธีการสังเคราะห์แบบเอิบชุ่มให้ผลในการบำบัดสารหนูที่ดีกว่าทั้งอาซีไนท์และอาซีเนท กลไกปฏิกิริยาการกำจัดสารหนูของโลหะคู่ทองแดงเหล็กถูกนำเสนอในการศึกษานี้ เมื่อทำการศึกษาการกำจัดสารหนูที่มีการผสมกันระหว่างอาซีไนท์และอาซีเนท พบว่าการกำจัดสารหนูในรูปอาซีเนทเพียงอย่างเดียวจะเร็วกว่าการกำจัดสารหนูในรูปของอาซีไนท์และอาซีเนทอยู่ร่วมกัน นอกจากนั้นอิออนที่ปนเปื้อนในน้ำใต้ดินมีผลมากต่อการกำจัดสารหนูโดยใช้โละหะคู่ทองแดงเหล็ก และเมื่อพิจารณาจลนพลศาสตร์ของการกำจัดสารหนูด้วยระบบฟองก๊าซร่วมกับโลหะคู่ทองแดงด้วยวิธีเอิบชุ่มพบว่าสอดคล้องกับปฏิกิริยาอันดับสองเทียบเท่าและมีค่าคงที่ปฏิกิริยา 0.0003 $L\cdot(\mu g\cdot min)^{-1}$ สำหรับสารละลายอาซีไนท์ และอันดับหนึ่งเทียบเท่าและมีค่าคงที่ปฏิกิริยา 0.1489 min^{-1} สำหรับสารละลายอาซีเนท เมื่อนำระบบฟองก๊าซร่วมกับโลหะคู่ทองแดงไปประยุกต์ใช้ในการบำบัดสารหนูอย่างต่อเนื่องด้วยการเติมโละหะคู่ทองแดงเหล็กแบบหลายครั้ง พบว่าสามารถลดความเข้มข้นของสารหนูให้อยู่ในระดับที่ต่ำกว่าค่ามาตรฐานของความเข้มข้นสารหนู (10 ไมโครกรัมต่อลิตร) ในน้ำดื่มได้

สาขาวิชา การจัดการสิ่งแวดล้อม

ปีการศึกษา 2557

ลายมือชื่อนิสิต ....

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KEYWORDS: Bimetallic Catalyst / NZVI / gas bubbling system / Arsenic removal

PIYANATE NAKSEEDEE: Cu-Fe BIMETALLIC MATERIAL ON ARSENIC REMOVAL UNDER GAS-BUBBLING CONDITIONS. ADVISOR: ASSOC. PROF. NURAK GRISDANURAK, Ph.D., CO-ADVISOR: PROF. CHIH-HSIANG LIAO, Ph.D., ASSOC. PROF. JIA-CHIN HSU, Ph.D., 135 pp.

Arsenic removal was investigated using nano X-Fe (bimetal) particles. Copper and nickel were selected as additional metals into NZVI. Under a batch condition with an initial concentration of 5000 µg/L of arsenic, pH of 7.0, nanoparticles of Cu-Fe showed higher arsenic treating efficiency over Ni-Fe and NZVI. The synthesis of Cu-Fe was further investigated via two kinds of synthesis techniques. One was an in-situ [$(Cu\text{-}Fe)_{IS}$] and the other was impregnation [$(Cu\text{-}Fe)_{IM}$]. Properties of both materials were characterized by SEM-EDX, TEM, BET, and XANES. The arsenic removal was carried out in CO_2/O_2 gas bubbling under the flow rate of 300 ml/min accommodating low pH and high DO condition. Copper loading varied from 2.5-30.0%wt was studied on both $(Cu\text{-}Fe)_{IS}$ and $(Cu\text{-}Fe)_{IM}$, where 10%Cu loading under impregnation synthesis technique provided highly removal on both As(III) and As(V) in synthetic wastewater. The mechanism of arsenic removal on Cu-Fe was proposed. A mixture of As(III)-As(V) solution was tested and it was found that solution containing As(V) individually showed the faster in arsenic removal. Furthermore, the removal of arsenic species, including As(III) and As(V), in field groundwater and synthetic groundwater by $(Cu\text{-}Fe)_{IM}$ were tested. The presence of background species was observed significantly on arsenic removal. Concerning in kinetics of arsenic removal using $(Cu\text{-}Fe)_{IM}$ in gas bubbling system, it was well fit with pseudo-second order and pseudo-first order for As(III) and As(V), respectively. Rate constants were evaluated to be 0.0003 $L\cdot(\mu g\cdot min)^{-1}$ for As(III), and 0.1489 min^{-1} for As(V). The proposed gas bubbling system was conducted in a continuous system for multiple additions of $(Cu\text{-}Fe)_{IM}$, providing a beneficial outcome of arsenic treatment to meet a standard drinking limitation of 10 µg/L.

Field of Study: Environmental Management Student's Signature ....
Academic Year: 2014 Advisor's Signature ....
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NOMENCLATURE

Cu-Fe	bimetallic copper iron
$(Cu\text{-}Fe)_{IS}$	bimetallic copper iron synthesized by in-situ method
$(Cu\text{-}Fe)_{IM}$	bimetallic copper iron synthesized by impregnation method
Eh	redox potential
Fe–Au	iron gold bimetal
Fe-Ce	iron cerium bimetal oxide
Fe-Co	iron cobalt bimetal
Fe-Ni	iron nickel bimetal
Fe-Sn	iron tin bimetal
Ni-Fe	bimetallic nickel iron

Abbreviation

As(III)	arsenite
As(V)	arsenate
$AsNaO_2$	sodium arsenite
As_2O_3	arsenolite
As_2S_3	orpiment
As_4S_4	realgar
Ca^{2+}	calcium
$CaCl_2$	calcium chloride
Cd^{2+}	cadmium
Co^{2+}	cobalt
Cl^-	chloride
CO_2	carbon dioxide
Cu	copper
$CuCl_2$	copper chloride
DMA	dimethylarsinic acid
Fe	iron
FeAsS	arsenopyrite

$FeAs_2$	loellingite
Fe^0	zero-valent iron
Fe^{2+}	ferrous ion
Fe^{3+}	ferric ion
$FeC1_2$	ferrous chloride
$FeC1_3$	ferric chloride
FMBO	iron manganese binary oxide
FeOOH	goethite
Fe_2O_3	hematite
Fe_3O_4	magnetite
$Fe_2(SO_4)_3$	ferric sulphate
FZBO	iron zirconium binary oxide
GFH	granular ferric hydroxide
H^+	hydrogen ions
HA	humic acid
HCl	hydrochloric acid
HCO_3^-	bicarbonate
H_2SO_4	sulfuric acid
MMA	monomethylarsonic acid
Mn	manganese
Na_2HAsO_4	sodium arsenate
$NaBH_4$	sodium borohydride
NaCl	sodium chloride
$NaHCO_3$	sodium bicarbonate
Na_2PO_4	sodium hydrogen phosphate
Na_2SO_4	sodium sulfate
NH_4	ammonium
NZVI	nano zero-valent iron
Ni	nickel
O_2	oxygen
Pd	palladium
PO_4^{3-}	phosphate ion

Pt	platinum
$SnCl_2$	tin(II) chloride
SO_4^{2-}	sulfate
Zn^{2+}	zinc

CHAPTER 1

INTRODUCTION

1.1 Research rationale

Arsenic and its compounds are especially potential poisons. The European Union classified elemental arsenic and its compounds to be toxic and dangerous for the environment, while the International Agency for Research on Cancer (IARC) and EU, classified arsenic trioxide, arsenic pentoxide, arsenate salts and its compounds as group 1 carcinogens (IARC, 2004). Moreover, highly consuming of arsenic water can cause bladder, lung, kidney and skin cancers, especially black foot diseases (shown in Figure 1.1), which is untreatment disease (Mohan and Pittman, 2007).

Figure 1.1 Black foot diseases symptoms (ATSDR, 2009)

Recently, high arsenic in natural water has become a serious concern in many countries such as Bangladesh, India, China (Li et al., 2010), Chili, USA (Shao et al., 2008), Thailand and Taiwan (Ning, 2002). Figure 1.2 shows the distribution of arsenic affecting water system in the world. Arsenic presents in several oxidation states (-3, 0, +1, +2, +3 and +5), but it is mostly found in inorganic form as oxyanions of trivalent arsenite (As(III)) which is uncharged at neutral pH, or pentavalent arsenate (As(V)) which is predominantly anionic at neutral pH in natural groundwater and surface water environments (Smedley and Kinniburgh, 2002). Many researchers have reported that As(III) is more mobile and toxic than As(V), and As(III) is predominant in many groundwater sources (Cullen and Reimer, 1989; Korte and Fernando, 1991).

There are many technologies for removing arsenic from groundwater such as reverse osmosis (Ning, 2002), coagulation (Song et al., 2006; Wickramasinghe et al., 2004), ion exchange (Korngold et al., 2001), biological process (Katsoyiannis and Zouboulis, 2004), adsorption (Maji et al., 2008; Nikolaidis et al., 2003; Ruiping et al., 2009), etc. Among the processes for arsenic removal from groundwater, adsorption process is the most promising and widely used because of its low cost and high efficiency (Zhang et al., 2010). Nano-scale zero-valent iron (NZVI) has been developed for arsenic removal, due to its ability to remove both As(V) and As(III) simultaneously, without the pre-oxidation step, and the advantages of larger surface area and higher surface reactivity than micro-scale ZVI (Liou et al., 2005; Sun et al., 2006).

In treating arsenic with NZVI, it was reported that its removal is enhanced under lower pH conditions (Bang et al., 2005; Sun et al., 2006). Acidic species such as HCl and H_2SO_4 can be used to lower the pH for the purpose of higher arsenic removal. However, application of these species results in adverse impact of inorganic ions on drinking water quality. According to the studies reported earlier (Tanboonchuy, 2012), the above issue can be resolved by CO_2 bubbling for acidify pH solution condition through hydrogen ions generated from carbonated water. To avoid this problem, the CO_2 bubbling for the solution acidification was employed in many studies (Tanboonchuy et al., 2011a; Watanabe et al., 2009).

In addition, some articles report that an increase in dissolved oxygen will result in higher arsenic removal (Biterna et al., 2010; Leupin and Hug, 2005; Tanboonchuy et al., 2011a). Therefore, the CO_2 for hydrogen ions (H^+) and the O_2 for dissolved oxygen supply in the solution were adopted in this research to create both acidic and oxygenated environment.

According to (Tanboonchuy et al., 2011b), a slight improvement of As(III) removal was found by using NZVI combined with CO_2 gas bubbling system. Since the surface precipitation or adsorption was suggested to be the predominant mechanism for both As(V) and As(III) removal (Lackovic et al., 2000), increasing the pH during the reaction resulting in electrostatic repulsion is the important limitation for arsenic removal using NZVI. To improve the performance and promote reactivity of NZVI, depositing a second metal to a freshly prepared NZVI such as Pd, Pt, Ni and Cu has been widely investigated (Cao et al., 2011; Cwiertny et al., 2006; Elsner et al., 2007; Fennelly and Roberts, 1998). Under an economic circumstance, noble metals were generally excluded. Researches on bimetallic Cu-Fe showed the enhancement of reduction reaction on several pollutants such as chlorinated solvents and nitrate possessed higher efficiency than that of NZVI (Bransfield et al., 2006; Elsner et al., 2007; Fennelly and Roberts, 1998; Liou et al., 2005). Nevertheless, the Cu combined with NZVI as bimetal was rarely investigated for arsenic removal.

Thus, the main objective of this study was to propose the effective process for arsenic removal by combination of bimetallic nanoparticles of Cu-Fe and gas bubbling system. In addition, the effects of synthesis method, percent copper loading, mass ratios of As(III)/As(V), and background species were studied as well.

A continuous system to reduce arsenic by using gases bubbling process was employed. The optimal condition of the continuous system both As(III) and As(V) was examined firstly. Then, effects of influent flow rate and addition step of mixed arsenic solution were also investigated. Finally, arsenic spiked field groundwater was used to test the potential of using Cu-Fe bimetal combined with gas bubbling system for both in batch and continuous system.

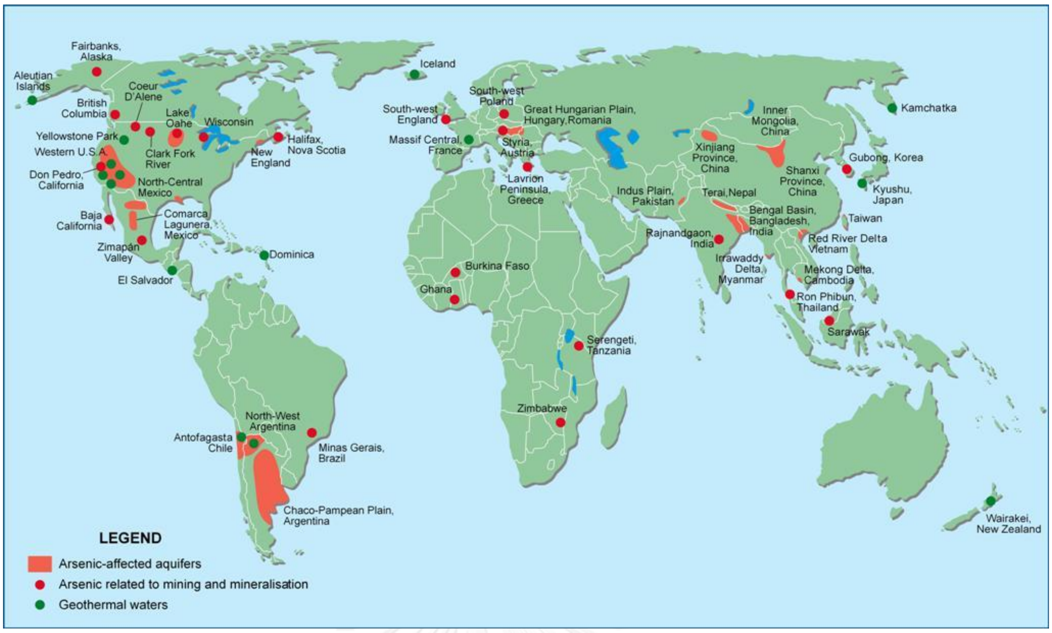

Figure 1.2 Regions affected by arsenic (Soria, 2013)

1.2 Objectives

Main objective: To investigate the performance of arsenic removal, especially As(III) by gases bubbling with NZVI-based bimetals; Cu-Fe bimetal.

Sub-objectives:

1. To compare the effect of synthesis methods of nanoscale Cu-Fe bimetal and their arsenic removal efficiencies.
2. To evaluate the parameters affecting on arsenic removal efficiency. Studied parameters included percent copper loading, ratio of As(III) and As(V), and common ions.
3. To determine kinetic rate of arsenic removal.

   *** The studies above were carried out in a batchwise procedure.
4. To optimize the performance of arsenic removal in continuous system.

1.3 Hypotheses

1. The presence of copper serves to neutralize the negative surface charge of NZVI, which reduces the electrostatic repulsion for negatively charged arsenic, allowing the arsenic to remain on the adsorption site.

2. CO_2 and O_2 bubbling system accelerate the oxidation of nanoparticles surface, resulting in higher As(III) and As(V) uptake with iron corrosion product.

1.4 Scopes of work

Cu-Fe bimetals were synthesized by adopting the method of Mondal et al. (2004) for one-step reaction method, and Mossa Hosseini et al. (2011) for two-step reaction method. NZVI was synthesized by adopting the method of Wang and Zhang (1997). The concentration of arsenic for all studies was fixed at 1000 µg/L except in part of preliminary experiment, which it was prepared at 5000 µg/L. Six species of HA, SO_4^{2-}, PO_4^{3-}, HCO_3^{-}, Ca^{2+}, and Cl^{-} were used to study the effect of background species on arsenic removal. The groundwater used in this study was obtained from groundwater site at Chia Nan University of Pharmacy and Science, Taiwan. Then field groundwater was spiked with arsenic to obtain the removal effect studied further.

1.5 Significance of research work

This research was reported the basic information of using Cu-Fe bimetal on arsenic removal. Currently, there still remains lack of research regarding use of bimetal for arsenic removal. The problem of undesirable species of sulfate and chloride from solution acidification that risk the drinking quality is mitigated by bubbling CO_2 to provide hydrogen ion (H^+) instead of using chemicals. Also, this technique can be operated easily. This process can be applied in groundwater remediation or some wastewaters contaminated with arsenic.

CHAPTER 2

LITERATURE SURVEY

2.1 Properties of arsenic compounds

Arsenic is an element in Group 15, Period 4 of the periodic table which has an atomic number of 33, an atomic mass of 74.91, specific gravity 5.72 (at 27 ºC), boiling point 603 ºC and melting point 808 º C. Arsenic is the heavy metal (metalloid) widely distributed in the earth’s crust with natural abundance of 1.5 ppm. Arsenic and its compounds could be found in rocks, soil, water and air. It exists in four valences; −5, −3, 0, and +5. Elemental arsenic and arsine [As(III)] can exist in strongly reducing environments; trivalent arsenite [As(III)] is a dominant form under moderately reducing environments. The pentavalent arsenate [As(V)] is generally stable in oxidation state and oxygenated environments, but its predominant forms are both As(III) and As(V) in natural water (Smedley and Kinniburgh, 2002).

Considering the toxicity of each arsenic species, As(III) is about 60 times more toxic than As(V), and inorganic arsenic compounds are about 100 times more toxic than organic arsenic compounds (Jain and Ali, 2000). However, the conversion of As(III) to As(V) is dependent on the pH and redox potential (Eh), which are the important factors to control arsenic speciation. At moderate to high Eh and pH less than 6.9, arsenic can be stabilized as a series of arsenate consisting of H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}. Whereas under reducing conditions at pH value less than 9.2, uncharged arsenite species predominate (Vu et al., 2003; Yan et al., 2000), as presented in Table 2.1. These can be indicated that more As(III) than As(V) is found in reducing groundwater conditions, whereas in oxidizing groundwater conditions are converse. A pH and Eh diagram of arsenic is shown in Figure 2.1.

Pure form of arsenic is not found in the environment. It is generally found combined with oxygen, chlorine or sulfur to form inorganic arsenic compounds, while organic arsenic compound is formed by combining arsenic with carbon and nitrogen in animals and plants. Generally, these mineral which is inorganic forms of arsenic are more toxic than its more complex organic compounds that can be found naturally in animal tissues. In many countries, arsenic has been used as a poison; rodent poisons, insecticides, biocides, and weed killers that containing arsenic in both organic and inorganic forms.

Table 2.1 Stability of arsenic species (Vu et al., 2003)

Reducing Conditions		**Oxidizing Conditions**	
pH	As(III)	**pH**	As(V)
0-9	H_3AsO_3	**0-2**	H_3AsO_4
10-12	$H_2AsO_3^-$	**3-6**	$H_2AsO_4^-$
13	$HAsO_3^{2-}$	**7-11**	$HAsO_4^{2-}$
14	AsO_3^{3-}	**12-14**	AsO_4^{3-}

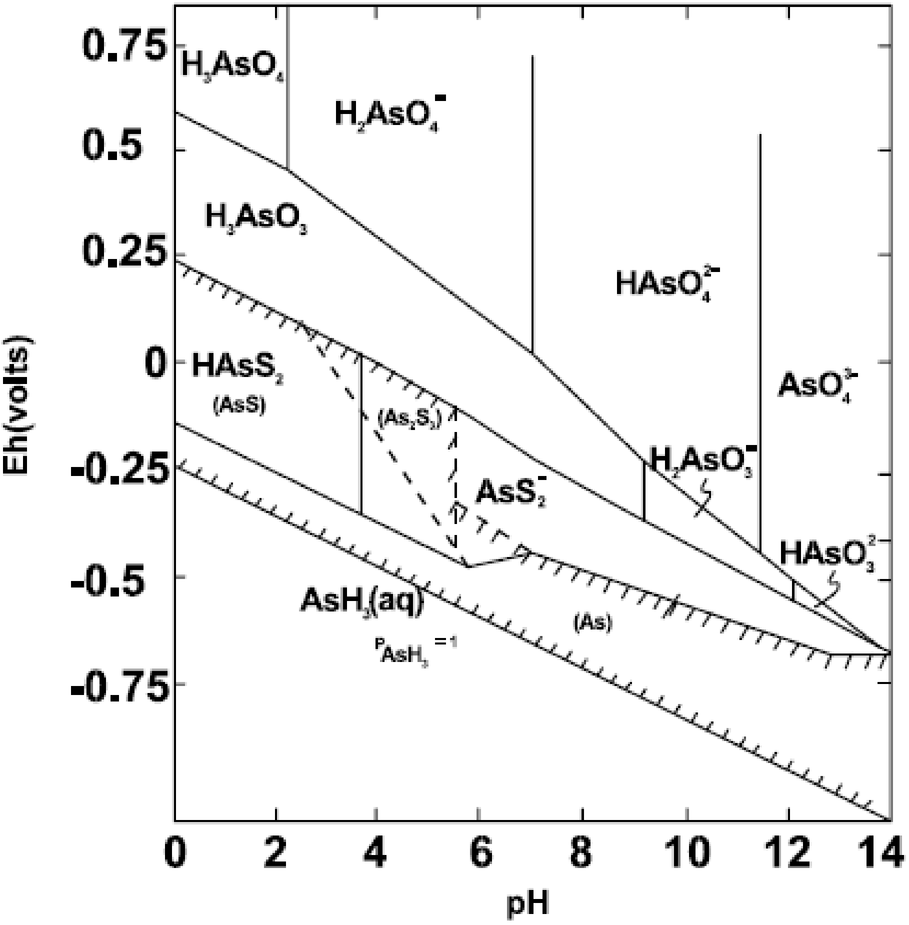

Figure 2.1 Eh-pH diagram for arsenic of arsenic 10^{-5} mol/L at 25 ºC, 1 atm (Ferguson and Gavis, 1972)

2.2 Arsenic issues of concerns

2.2.1 Arsenic in the environment

In natural, arsenic is found mainly in form of mineral arsenicals including orpiment (As_2S_3), arsenolite (As_2O_3), realgar (As_4S_4) and iron minerals, e.g., arsenopyrite (FeAsS) and loellingite ($FeAs_2$). Onishi (1969) reported that there is 60% of arsenate, 20% of sulfide and sulfosalts, and 20% of arsenides, arsenites, oxides and elemental arsenic from more than 200 mineral species that arsenic is constituent. Unless arsenic appears naturally in minerals and soil, it may contaminate in air, land, and water from wind-blown dust, runoff and leaching. Moreover, arsenic is also presented in the environment because of using of many arsenical products, which can affect local soil and water (Banerjee et al., 2008; Farrell et al., 2001).

Arsenic can only change its forms and move around in environment, but it cannot be destroyed. The dissolved forms of arsenic in water include arsenate, arsenite, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) (Braman and Foreback, 1973). The concentrations of arsenic contaminated in surface water and groundwater are typically in ranges of 1-10 µg/L (Azcue and Nriagu, 1995; Tamaki and Frankenberger, 1992). High concentration obviously point sources of arsenic contamination are mainly found in groundwater. If arsenic presented in groundwater sources show the concentration levels over the drinking water standard, it is serious to reduce that arsenic concentration to protect human health from long-term, chronic ingestion of this contaminant.

2.2.2 Health aspect

Arsenic is classified as a Class A human carcinogen by the US Environmental Protection Agency (US EPA, 2000). Human bodies cannot absorb the arsenic element itself, so pure arsenic is much less dangerous than arsenite compounds such as AsH_3 and As_2O_3 which are easily absorbed in organs and are carcinogenic with high toxicity. Arsenic can enter the body by both ingestion and inhalation. Then, it can be absorbed from the digestive tract and from the lung to all parts of the body by the bloodstream. It may also serve a useful function in the body, but only at very low levels. Body system can detoxifies and eliminates arsenic automatically. If amounts of arsenic are absorbed greater than the body can detoxify and eliminate, the body may develop an increasing burden of arsenic.

High dosages of arsenic can cause acute effects including nausea, vomiting, and diarrhea. The Arsenic concentration of 5 mg/m^3 is immediately dangerous to life or health. Ingestion of more than 2 g may be lethal in a very short time. At low doses, arsenic is known to cause skin changes over a long period of time that can lead to skin cancer, even black foot diseases which is untreatment disease (Mohan and Pittman, 2007). Moreover, arsenic has been found to cause other kinds of cancer, e.g., colon, lung and bladder cancers (Astolfi et al., 1981; Hopenhayn-Rich et al., 1996; Nikolaidis et al., 2003). Also, its harmful effects result to the heart and circulatory system.

A chronicle use of water contaminated arsenic for irrigation can result to arsenic level increasing in soil that is harmful to animals, human, and also plants in that area. Although inorganic arsenic is shown serious health effect to humans, but nothing is reported about the effect of organic arsenic compounds in humans. Ohki et al. (1996) investigated the experiment in animals, and the results show that organic arsenic compounds are less toxic than inorganic forms.

Figure 2.2 Symptom of blackfoot disease appeared on legs (Bearden, 2014)

The Department of Health and Human Services (DHHS), the EPA, and The International Agency for Research on Cancer (IARC) have determined that inorganic arsenic is a known human carcinogen.

2.2.3 Regulation for arsenic

Normally, the limit for arsenic was 50 µg/L, but the SDWA required US EPA develops an arsenic research strategy. Then, the US EPA established a mandatory drinking water limit as the Maximum Contaminant Level (MCL) of arsenic at 10 µg/L of water (US EPA, 2001). Moreover, the Occupational Safety and Health Administration (OSHA) have set a permissible exposure limit (PEL) for inorganic arsenic of 10 µg/m^3 for 8 hour shifts and 40 hour work weeks (EASHW, 2005). National Institute for Occupational Safety and Health, Immediately dangerous to life or health (NIOSH/IDLH) limit exposure for all inorganic arsenic compounds of

5 mg of As/m³ (NIOSH, 2009a). In Thailand, the arsenic standard for drinking water and groundwater quality standard has been set at 50 µg/L by Pollution Control Department (PCD, 1978, 2008).

2.3 Arsenic contaminant in groundwater

Fate and transport of arsenic in the environment, especially in groundwater have become the major concern in many countries in the world. As mentioned in previous section, arsenic can be released to ground or surface water through erosion, dissolution, and weathering. Arsenic concentrations increasing in surface water and groundwater up to 100-5000 µg/L can be detected in areas of sulfide mineralization (Ning, 2002; Vu et al., 2003). Although the US EPA set the arsenic concentration limit in drinking water of 10 µg/L, many third world countries still continue with the 50 µg/L because of the financial problem. Many studies have reported about the elevated arsenic concentration in many countries such as China (Kinniburgh and Smedley, 2001; Li et al., 2010), Taiwan (Liu et al., 2003; Ning, 2002), India (Sarkar et al., 2005), North Vietnam (Berg et al., 2001), and Bangladesh (Chakraborti et al., 2002; Tanabe et al., 2001), etc. Moreover, high arsenic concentration as 1000 µg/L has been found in some regions of Bangladesh (Mondal et al., 2007). Taiwan also faces this problem; Wu et al. (1989) reported that arsenic concentrations were in a range of 50–2000 µg/L around the western area of Taiwan foothill. Blackfoot disease was observed in the southwest coast area of Taiwan and continued for a year (Chen et al., 1994).

Although elevation of arsenic can come from anthropogenic activities, most high-arsenic groundwater provinces are the result of natural occurrences (Mariner et al., 1996). In groundwater usually present in two species of arsenic; arsenate As (V) or arsenite As (III), and have high concentrations of Fe, Mn, and NH_4. Arsenic-bearing minerals undergo oxidation and release arsenic to water and subsequent oxidation of arsenic-containing pyrite in the sediment (Meng et al., 2002). Groundwaters contain high concentration of dissolved iron, which is readily oxidized and precipitate to ferric compounds. The auto-oxidation of ferrous ion (Fe^{2+}) to ferric ion (Fe^{3+}) generates surface reactive sites for uncharged arsenite adsorption as well as anionic arsenate species (Joshi and Chaudhuri, 1996).

In South East Asian countries, arsenic contamination in groundwater and drinking water have been a serious problem in such as India, Vietnam, Cambodia and Thailand (Mandal and Suzuki, 2002; Sthiannopkao et al., 2010; Wattanasen et al., 2006). The groundwater surveys have been investigated in Kandal Province, Cambodia, and high arsenic concentrations in groundwater was reported (Buschmann et al., 2007; Buschmann et al., 2008; Kocar et al., 2008; Rowland et al., 2008). Sthiannopkao et al. (2010) studied on the analysis of arsenic levels in human hair samples collected from six villages in the Kandal Province of Cambodia, and they found that As(III) is the dominant species in Kandal's groundwater and arsenic concentration ranged from 5-1543 µg/L. In addition, the modeling approaches for arsenic concentration using on-site measurement data were conducted to quantify the arsenic contamination. Cho et al. (2011) reported the high efficiency of using the principal components combined with an artificial neural network (PC-ANN) to predict arsenic concentration, and propose assessment tools for many countries in Southeast Asian countries, including of Thailand. Wantala et al. (2012) investigated the performance of Fe-RH-MCM-41-immobilized GAC adsorbing As(V) using the Box–Behnken Design (BBD) to evaluate the effects of pH, adsorbent loading, and initial As(V) concentrations.

In Thailand, arsenic contamination has been found in Ron Pibul District of Nakorn Si Thammarat Province, in the southern peninsula area (Williams et al., 1996). Fordyce (1995) exhibited that arsenic can contaminate from both point sources and mobile sources. The arsenic contamination in water and soil from agricultural areas in Ron Pibul was continuously monitored for one year period and found that total arsenic concentration in surface soil were more than that in water (Patarasiriwong et al., 2004). Since arsenic is the composition of arsenopyrite, so it can separate and diffuse into soil, water, and pollutes to the environment. Gold mining at Wangsaphung district of Loei province, Thailand, is one of the mining industry also faced this problem (Weerasiri et al., 2012). The arsenic concentration in water of many areas exceeds the standard concentration 10 µg/L, which was set by US EPA.

Although the levels of contaminant in some sites were less than the MCL specified by US EPA, the effects of arsenic contamination in soil and water still have been addressed.

2.4 Arsenic remediation technology profiles

Arsenic can be removed from groundwater by various treatment technologies, but it should concern in the expense, and the comfortable of maintenance and monitoring. Current available treatment processes include coagulation process, reverse osmosis, membrane filtration, ion exchange resins, and adsorption process. Each kind of theses treatment technologies are not totally effective, and the single treatment method cannot remove all contaminants from water. Every treatment technologies have different limitations and advantages. Therefore, the information about each treatment should be studied before deciding on treatment of arsenic.

2.4.1 Coagulation

Coagulation process is traditionally process by adding ferrous chloride ($FeC1_3$) and ferric sulphate ($Fe_2(SO_4)_3$), which are the recommended chemicals for coagulation before membrane, but the application of $Fe_2(SO_4)_3$ was more suitable because of less corrosion. For this process, arsenate As(V) or arsenite As(III) will precipitate with the ferric or aluminum ions on the coagulated solid and become the coagulated solid. Then, the coagulated solid can be separated from water by filtration that is arsenic elimination from the water. The coagulant ions can strongly reduce the absolute zeta potential values of the particles. Song et al. (2006) reported that usually coagulation process can be enhanced arsenic removal efficiency, especially As(V) by adjusting pH and electrolyte concentration to reduce zeta potentials values of particles. Moreover, the optimization of coagulation kinetics can also increase the efficiency of arsenic removal.

In the case of As(III) species alone, oxidation to convert As(III) to As(V) is firstly required to coagulation. Although coagulation process shows highly adsorption capacities and less disposal problems, but it requires continuously of chemicals for dosing, and pH adjustment. The effects of important operating parameters in arsenic removal from water by coagulation process depend on initial arsenic concentration in water (Jiang, 2001; Thirunavukkarasu et al., 2005). After that, Lakshmanan et al. (2009) offered electrocoagulation (EC) is a promising technology, which resembles coagulation in term of in-situ production of the hydroxides, but without manual addition of coagulant. Electrocoagulation has provided many advantages including higher adsorption capacity, no manual chemical addition, less area requirement, and no media replacement, requires less coagulant, produces less sludge (Mills, 2000).

In addition, coagulation process can be applied by adding appropriate fine particles in suspensions coat coarse particles in multilayer form. Such coagulated solid consist of fine particles and coarse particles. The coarse particle can be enhanced coagulation of fine particles by reduce particles in suspensions and also increases coagulated solid size. The mechanism of the coarse particle effect might be resulted in the aggregation rate increasing (Song et al., 2006). Although coagulation combining with filtration are an effective arsenic removal technology, but the performance of system will be very dependent on the water quality (Wickramasinghe et al., 2004).

Adjustment of pH may be necessary in order to reduce the ferric ion dose, which a lower pH tend to improve As(V) removal. Hering et al. (1997) reported that in coagulation experiments with $FeC1_3$ at pH 7.0 for both As(III) and As(V) removal were dependent on coagulant dosage and As(V) was completely removed above 5 mg/L $FeC1_3$. Comparing with alum, the average removals were 87% for 10 mg/L $FeC1_3$ and only 67% for 20 mg/L alum at pH greater than 7.6. Edwards (1994) concluded that at significant coagulant dosages for As(V) removal was close to that for both ferric and alum coagulants at about pH 7.6, but the average removals were 87% for 10 mg/L $FeC1_3$ and only 67% for 20 mg/L alum at pH greater than 7.6.

However, further geographical and economical factors for site remediation should be also considered before large-scale testing and design of a facility for arsenic removal. Nevertheless, coagulation process is difficult to achieve on low concentration levels of arsenic treatment.

2.4.2 Membrane technologies

Previously, reverse osmosis has been expected to be a best available technology for arsenic removal, but it has shown high cost in process (Vrijenhoek and Waypa, 2000). The use of membrane filtration has been applied for drinking water treatment (Ballinas et al., 2003; Han et al., 2002; Velizarov et al., 2004). However, the process of coagulation should be required when a microfilter or ultra-filter membrane is used. Since the drawback of multiple chemical treatments, required pre-treatment, high cost for regeneration of medium and handling of sludge in co-precipitation method, reverse osmosis combining with nanofiltration membrane processes has been considered (Richards et al., 2009). Nevertheless, percent of solution product that can be produced from the feed water with this method is still lower than that of using microfilter or ultra-filter membrane (Shih, 2005).

Therefore, new nanofiltration membranes are used mostly for bivalent ions rejection and other contaminants such as arsenic and increased water flux (Floch and Hideg, 2004; Wang et al., 2009). For the nanofiltration, some researcher revealed high removal efficiency of As(V) but very low removal efficiency of As(III) (Brandhuber and Amy, 1998). Then, the hydrophobic membrane process-membrane distillation that include of water vapor transportation through a porous hydrophobic membrane was presented for arsenic removal, and it showed higher removal efficiency (above 99.95%) of both As(III) and As(V) than reverse osmosis and nanofiltration processes (Qu et al., 2009). For the electrodialysis membrane, it is more effective in removing As(V) than As(III), but the injection of an oxidizing agent into the feed water was needed (Ahmed, 2001). However, oxidizing agents may harmful to the conventional ion exchange. Weng et al. (2005) used electro-ultrafiltration membrane with applied voltage to its cell to remove of arsenic and humic substances from water, and more than 90% rejection for As(V) and 71% rejection for As(III) were found.

The rejection of solutes by nanofiltration membranes influenced by two basic membrane characteristics; membrane charge and pore size (Sato et al., 2002). Košutić et al. (2005) reported that the relative contributions of these two mainly mechanisms in the nanofiltration process cannot be assessed easily since all the operating parameters have not been completely understood. Therefore, the influence of various effects and also modeling of the solute transport mechanisms through a nanofiltration membrane should be studied so far.

2.4.3 Ion exchange

The mechanism of ion exchange is the exchanging of ions between two electrolytes or between an electrolyte solution and a complex. Typical ion exchangers compose of exchange resins, zeolites, montmorillonite, clay, and soil humus.

Anion exchange is an effective technology for removing As(V) from drinking water and as well as for removing nitrate since its ability to remove these ions almost quantitatively from solution, the insensitivity of the process to solution pH, and the long effective lifetime of the resins (Awual et al., 2013). Ion exchange seems best suited for small systems. It typically exhibits high arsenic removal efficiencies while allowing a relatively wide range of inlet water quality conditions. The small-scale systems and point-of-entry (POE) systems often use ion exchange to removal arsenic since it is easy to handle and provides sludge free operation (Fox, 1989). Ion exchange processes combined with an oxidation pretreatment step has been reported to reduce total arsenic to low levels but it is limited for water supplies that have low total dissolved solids and sulphate concentration (Clifford, 1999). However, costs of treatment are relatively higher than the large-scale of conventional treatment. Furthermore, ion exchange cannot be used to remove As(III) because it predominantly occurs as neutral complexes in water (H_3AsO) with less than 9.0 of pH value (Quamruzzaman et al., 2003). The predominant species of As(V), H_3AsO_4 and $HAsO_4^{2-}$ show negatively charged, which are removed by ion exchange process. If As(III) is present, the oxidation of As(III) to As(V) should be investigated before removal by ion exchange (Clifford and Lin, 1991).

2.4.4 Adsorption

There are many efforts to study of arsenic removal technologies from wastewater as mentioned earlier. Common methods for removing arsenic from aqueous solution include chemical precipitation, oxidation, reverse osmosis, ion exchange, membrane filtration, and solvent extraction but none of them is widely accepted because of cost or maintenance of the process. Among many techniques, adsorption processes are most promising technique applied for wide range arsenic in groundwater (Sun et al., 2006).

A serious problem in arsenic removal from groundwater is that the speciation of arsenic, which mainly presented in both As(III) and As(V) compounds in water. At normal drinking water pH, As(III) compounds are primarily non-ionic whereas As(V) compounds are ionic (Sarkar et al., 2005). Therefore, The method that are very effective only for removal of As(V), not for As(III) compounds. The pre-oxidation of As(III) to As(V) is of is necessary in order to enhance the efficiency of arsenic removal in drinking water to safe levels. A combination of adsorption media with oxidants may also be used such as manganese compounds to pre-oxidize any presented As(III) to As(V), which can be more adsorbed from the contaminated water. Lackovic et al. (2000) studied about preoxidation step to transform As(III) to As(V) before the process for arsenic removal. However, this method may take more time because it requires a pretreatment step.

The most widely used of adsorptive media are ion exchange resin, iron compounds, activated alumina, organic polymers, red mud, blast furnace, chars, coal, slag, silica sand, and kaolin clay, etc (Genç et al., 2003; Han et al., 2011; Iesan et al., 2008; Kanel et al., 2006b; Lafferty and Loeppert, 2005; Lin et al., 2006; Mohan et al., 2007; Peräniemi et al., 1994; Singh and Pant, 2004; Zhou et al., 2010). Sometimes, a combination of the media mentioned above is used together to increase the adsorption performance. Iron compounds are among the most popular adsorbents being used for the removal of arsenic from aqueous solution (Ferguson and Gavis, 1972; Lafferty and Loeppert, 2005; Lakshmipathiraj et al., 2006). Townsend et al. (1991) reported about batch removal of As(V) and As(III) from water by using iron treated activated carbon and natural zeolite, and they found that activated carbon remove ≈60% of As(V) and As(V) 30% of the As(III). Nevertheless, the adsorption process by using these adsorptive media are mostly effective for As(V) removal.

Arsenic could be adsorbed onto a various forms of iron (hydr)oxides, for examples; hematite (Fe_2O_3), goethite (FeOOH), magnetite (Fe_3O_4), amorphous iron oxide, and mixed valent iron oxides (Dixit and Hering, 2003; Mishra and Farrell, 2005; Redman et al., 2002). The study of As(III) and As(V) adsorption versus pH was investigated on FeOOH, amorphous iron oxide, and clay pillared with titanium(IV), iron(III), and aluminium(III) synthesized from a bentonite. The results indicated that amorphous FeOOH provides the highest capacity of adsorption because of the highest surface area (Lenoble et al., 2002). Most iron oxides are fine powder, which are difficult to separate from solution after treatment process. Therefore, Iron oxide-coated sand filtration was proposed as an emerging technology for arsenic removal (Thirunavukkarasu et al., 2003; US EPA, 1999). Consequently, Swedlund and Webster (1999) studied on the use of ferrihydrite to remove As(III) and As(V) from water, and reported that silicic acid shows a significant effect on oxyanions of arsenic adsorption.

In the comparison of the adsorption behavior of As(III) and As(V) on ferrihydrite, adsorption was almost complete in a few hours and As(III) reacted faster than As(V) with this material. The high As(III) removal efficiency was due to the transformation of ferrihydrite to a ferric arsenite phase, but it was not simply adsorbed at the surface. Driehaus et al. (1998) investigated the use of granular ferric hydroxide (GFH) to remove arsenic from natural water, and it demonstrated high treatment capacity of 30,000-40,000 bed volumes. Adsorption of As(V) in range of concentrations from 100-750 µg/L with pH range of 4-9 by using GFH was carried out (Saha et al., 2005). The efficiency of adsorption decreased due to the pH of solution increased, and the optimal pH in adsorption process was at pH 4. Roberts et al. (2003) studied arsenic removal through the naturally oxidizing by present of Fe(II) or iron(III) (hydr)oxides with aeration. They revealed that the application of Fe(II) over Fe(III) is that the dissolved oxygen used for Fe(II) oxidation can causes partial oxidation of As(III). Therefore, the multiple additions of Fe(II) combined with aeration could further increase As(III) removal. However, a preoxidation step is still required to transform As(III) to As(V).

For the preparation of metals-loaded polymers, variety of polymer, i.e., macroporous polymers, strong cation-exchange resins, biopolymer gels and chelating resins have been used in to adsorb arsenic (Dambies, 2005). The improvement of metal materials become zero-valent iron (ZVI), which is a promising technique for arsenic remediation because it can be remove both As(V) and As(III) simultaneously, without pre-oxidation step. Moreover, it the additional chemical reagents were not required (Sun et al., 2006). The reviews of using ZVI and its development were exhibited in Section 2.4.5.

Table 2.2 Comparison of arsenic removal by various technologies

Main technologies	Advantages	Disadvantages
Coagulation	- Relatively low capital cost and simple in operation - Effective over a wider range of pH - Chemicals are available commercially	- Produces toxic sludges - Pre-oxidation of arsenic species is required - Medium removal of As(III) - Re-adjustment of pH is required
Reverse osmosis	- No toxic of solid waste is produced	- High tech operation and maintenance
Membrane technologies	- Well-defined - High removal efficiency	- Very high capital and running cost - Pre-conditioning; high water rejection
Ion exchange	- Well-defined capacity and medium - No effect on pH change	- High cost medium - Regeneration creates a sludge disposal problem - As(III) is difficult to remove; life of resins
Adsorption	- Well known and cheap - Commercially available - Regeneration is not required - Simultaneously remove both As(III) and As(V)	- Needs replacement after four to five regeneration - Not standardized - Toxic solid waste may be produced

2.4.5 Nano zero valent iron (NZVI)

Previously, zero valent iron (ZVI) filings had been used for about 10 years as a permeable reactive barrier (PBR) for in situ trichloroethene (TCE) treatment of groundwater containing contaminants (Reynolds et al., 1990). It has been the most common metallic reducing agent used for the treatment of environmental contaminants since it is available at low cost and nontoxic. In general, the key factor of ZVI corrosion depends considerably on the solution pH level. ZVI can be used to remove both organic and inorganic contaminants such as halogenated hydrocarbons, anions, and heavy metal (Joo et al., 2004; Lien and Zhang, 1999; Wang and Zhang, 1997). The first report of arsenic removal by using ZVI was revealed by Lackovic et al. (2000), they reported that ZVI show a high capacity for arsenic remediation. However, the use of ZVI still has a problem that is the long reaction time (Jegadeesan et al., 2005).

From above reasons, nano zero valent iron (NZVI) has been developed for more efficient. In recent years, the NZVI has been the widespread attention from many researchers for groundwater treatment and hazardous waste treatment because of small particle size, high surface area, high reactivity, and high mobility in groundwater (Zhang, 2003). Due to the advantages of this material, NZVI can be applied as a colloidal reactive barrier for simulate of in situ groundwater remediation (Furukawa et al., 2002; Kanel et al., 2006a; Wilkin et al., 2003) or ex-situ groundwater treatment as pack bed column treatment process (Westerhoff et al., 2006; Westerhoff and James, 2003).

Various methods have been developed to synthesize NZVI, enhance their surface properties and reactivity such as chemical method (Ponder et al., 2000), microemulsion method (Li et al., 2003), sono-chemical method (Khalil et al., 2004), and thermal decomposition (Amara et al., 2009). Each method of synthesis has limitations and disadvantages, for example, toxic by-product is generated in the sono-chemical method (Choi et al., 2008), NZVI particles tend to aggregate in the thermal decomposition method (Amara et al., 2009). Due to the strong aggregation potential that affects the mobility of NZVI in groundwater, the method for the synthesis of fully dispersed was investigated. Sun et al. (2007) used polyvinyl alcohol-co-vinyl acetate-co-itaconic acid in the synthesis of NZVI and it lead to the significant enhancements in surface chemistry, particle stability and subsurface mobility potential.

Based on the study of both As(III) and As(V) removal by using NZVI by Kanel et al. (2005,2006), they reported that using NZVI shows higher capacity for arsenic removal than microscale of ZVI. In addition, NZVI can remove both As(V) and As(III) simultaneously, without pre-oxidation step, and the use of additional chemical reagents (Kanel et al., 2005; Sun et al., 2006). Removal of arsenic by using NZVI occurs through chemical adsorption and co-precipitation during the formation of iron (hydr)oxides (Bang et al., 2005; Lackovic et al., 2000; Mishra and Farrell, 2005). Firstly, NZVI in the solution, which called reductant, will rapidly oxidize into ferrous ion (Fe^{2+}). Under aerobic conditions, the reaction was illustrated in Eqns. (2.1)-(2.2).

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{2.1}$$

$$2Fe^0 + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^- \tag{2.2}$$

Then, Fe^{2+} will be further oxidized into ferric ion (Fe^{3+}), according to Eqn. (2.3). Both of Fe^{2+} and Fe^{3+} will transform to several forms of iron (hydr)oxides because of the dissolved oxygen in the solution. These mechanisms can be expressed in Eqns. (2.4)-(2.8) (Giasuddin et al., 2007; Huang and Zhang, 2005; Kanel et al., 2006b; Li et al., 2006b). For the analysis of NZVI structure, it provided the strong evidence that the structure of NZVI consisting of a metallic iron core covered by a thin amorphous oxide layer (Yan et al., 2010), as shown in Figure 2.3.

$$4Fe^{2+} + 2H_2O + O_2 \rightarrow 4Fe^{3+} + 4OH^- \tag{2.3}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{2.4}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \tag{2.5}$$

$$6Fe(OH)_2 + O_2 \rightarrow 2Fe_3O_4 + 6H_2O \tag{2.6}$$

$$Fe(OH)_3 + 3H^+ \rightarrow FeOOH + H_2O \tag{2.7}$$

$$FeOOH + Fe^{2+} \rightarrow Fe_3O_4 + 2H^+ \tag{2.8}$$

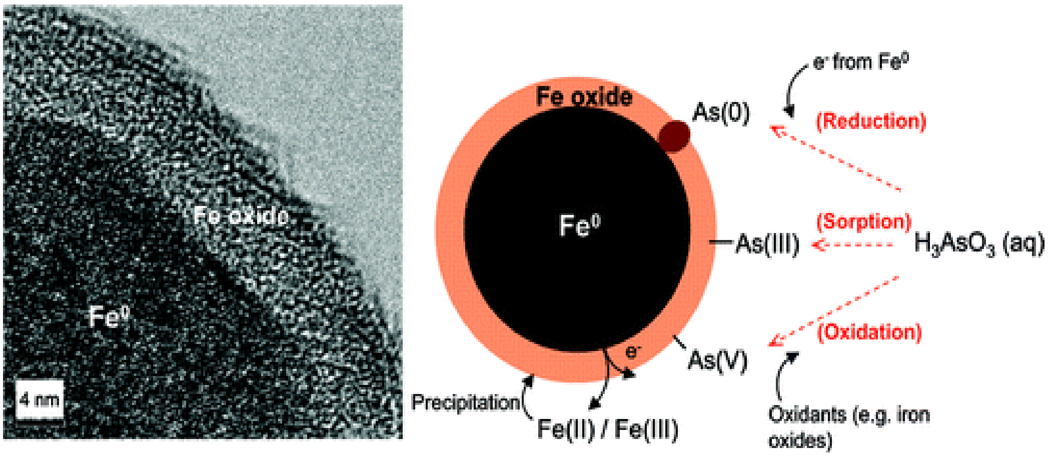

Figure 2.3 Core shell model and schematic of arsenic removal mechanism (Yan et al., 2013)

Due to the corrosion, charge separation will occur to form an electrical double layer on the iron metal surface (Piron, 1991). At initial stage, the concentration of Fe^{2+} in the bulk solution is much smaller than in the metal surface. This creates a concentration gradient, leading to a tendency to expel Fe^{2+} from the metal and then leaving an excess of electrons. However, this chemical driving force will be opposed increasingly as the electrical double layer, an electrical force of attraction, build up, and ultimately an electrochemical equilibrium.

Moreover, There are many researchers reported that arsenic removal by NZVI is more effective in acidic environment (Bang et al., 2005; Sun et al., 2006) and dissolved oxygen will result in higher arsenic removal (Biterna et al., 2010; Leupin and Hug, 2005; Tanboonchuy et al., 2011a). However, using chemical for the pH adjustment may have impact on the water quality since acid-derived alien species. Ruangchainikom et al. (2006) have proposed the alternative for pH adjustment by CO_2 bubbling. The CO_2 bubbling in the NZVI system for arsenic removal was used as a hydrogen ion supplying source since the CO_2 is able to create an acidic environment efficiently (Hsu et al., 2004). This gas bubbling technique is a safe and common practice in water purification industries. According to Tanboonchuy et al. (2011a), high As(V) removal efficiency was observed by using the combination of NZVI and gas bubbling system, there was no significant improvement for As(III). Therefore, the novel material or technology needs to find out to favor the arsenic removal with a high removal performance.

2.4.6 Bimetallic material

In recent years, some researchers have made efforts on developing materials for improving arsenic removal, especially As(III) species. The major problems associated with use of NZVI for arsenic removal is that the requirement of reaction time for complete As(III) removal and the effect of pH increasing during the reaction process. Recent studies indicated that using zero valent iron in conjunction with a noble metal, induces zero valent iron to release electron faster resulting in accelerated galvanic corrosion (Graham and Jovanovic, 1999; Mondal et al., 2004; Odziemkowski et al., 2000). Iron will be oxidized more rapidly when attached to a less active metal. Moreover, the second metals (noble metals) occur in solution as cations (e.g., Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+},Zn^{2+}) which generally become increasingly insoluble as the pH increases. Many studies can confirm the effectiveness of bimetallic materials in the removal of contaminants such as dechlrorination of N-nitrosodimethyl-amine (Odziemkowski et al., 2000), trichloroethylene (Fendorf et al., 1997; Wang and Zhang, 1997; Zhang et al., 1998), and selenite (Mondal et al., 2004).

Currently, there is some researchers study about using bimetallic particles for arsenic removal. Zhang et al. (2005) and Dou et al. (2011) revealed the successful development for As(V) removal by using an iron-cerium bimetal oxide (Fe-Ce). For As(III) removal, Zhang et al. (2007) developed Fe-Mn binary oxide (FMBO) for the simultaneous arsenic removal and found that it effective for As(III) removal. Moreover, the use of nanostructure Fe(III)-Zr(IV) binary mixed oxide (NHICO) and manganese associated nanoparticles agglomerate of Fe(III) oxide (MNFHO), respectively, were developed for As(III) removal (Basu et al., 2010; Gupta et al., 2010). This is agreed with Ren et al. (2011), using Fe-Zr binary oxide (FZBO) to remove the mix of As(III)/As(V) removal and it showed higher As(III) adsorption capacity than using pure Fe oxides. It should be noticed for these bimetallic oxides that iron-based oxides were used as the primary component, and the another metal was acted as the additive material. Although these bimetallic oxides can enhance arsenic adsorption capacity of Fe oxides, but the additive material will changed the surface characteristics and structure of the Fe oxides (Basu et al., 2010; Gupta et al., 2010; Zhang et al., 2007). The most commonly used metallic nanoparticles for contaminant removal is NZVI because of its high reactivity, low cost, easily obtained raw materials, and nontoxicity (Crane and Scott, 2012; Li et al., 2006a; O'Carroll et al., 2013). However, there is little information available regarding NZVI based bimetal materials reported for both As(III) and As(V) adsorption.

Ferrando et al. (2008) reported that bimetallic iron nanoparticles can be occurred in different structure including of core-shell segregated structure, heterostructure, intermetallic structure, and multishell structure as illustrated in Figure 2.4. They found that the key factors of the different structure of bimetallic iron nanoparticles are the natural elements of the primary and the second metal. The strong bonds between the primary and the second metal generally prefer to mix into intermetallic structure, while the weak bonds of those favors to segregate two metals to be a core-shell segregated structure, named as heterostructure, and multishell structure (Liu et al., 2014).

The synthesis of bimetallic nanoparticles can be classified into two types, consisting of physical and chemical methods. Generally, chemical methods (e.g., thermal decomposition, chemical reduction, and electrochemical method) are more widely used than physical method since the advantages of preparation, size controlling (Wang and Li, 2011). Thermal decomposition technique has been used to synthesize many bimetal by using the metal complex as precursor (Ferrando et al., 2008). Among various technologies of chemical methods, chemical reduction is the most common method of synthesizing bimetallic nanoparticles (Wang and Li, 2011). Chou and Schaak (2007) study on shape controlling for Fe-Sn intermetallic nanocrystals synthesize by using $FeCl_3$ and $SnCl_2$ as the precursor materials, and $NaBH_4$ as the reducing agent, they can achieve a well-defined cube shape of that nanoparticles. Apart from strong reducing agent like $NaBH_4$, weak reducing agents can be used but it cannot reduce Fe precursors to zero-valent Fe in liquid phase (Cho et al., 2009; Ma et al., 2010). Fendler (1997) claimed that electrochemical synthesis of bimetal has the advantages of the avoidance of contamination caused by by-products derived from chemical reducing agents and the easy isolation of products from the precipitate, comparing with chemical reduction method. Bimetallic Fe-Co and Fe-Ni nanoparticles synthetized by the electrodeposition technique showed the successful of nanoscale bimetallic clusters forming, which the average size of 2.5-3.0 nm (Reetz et al., 1995). Recently, Chen et al. (2011) have prepared nanoscale Fe–Au particles by electrodeposition of Fe, and they have found that the bimetallic Fe–Au NPs consist of a double-layered shell of Au over layer of Fe. However, the suitable method should be selected for the nanoparticles synthesis based on their applications.

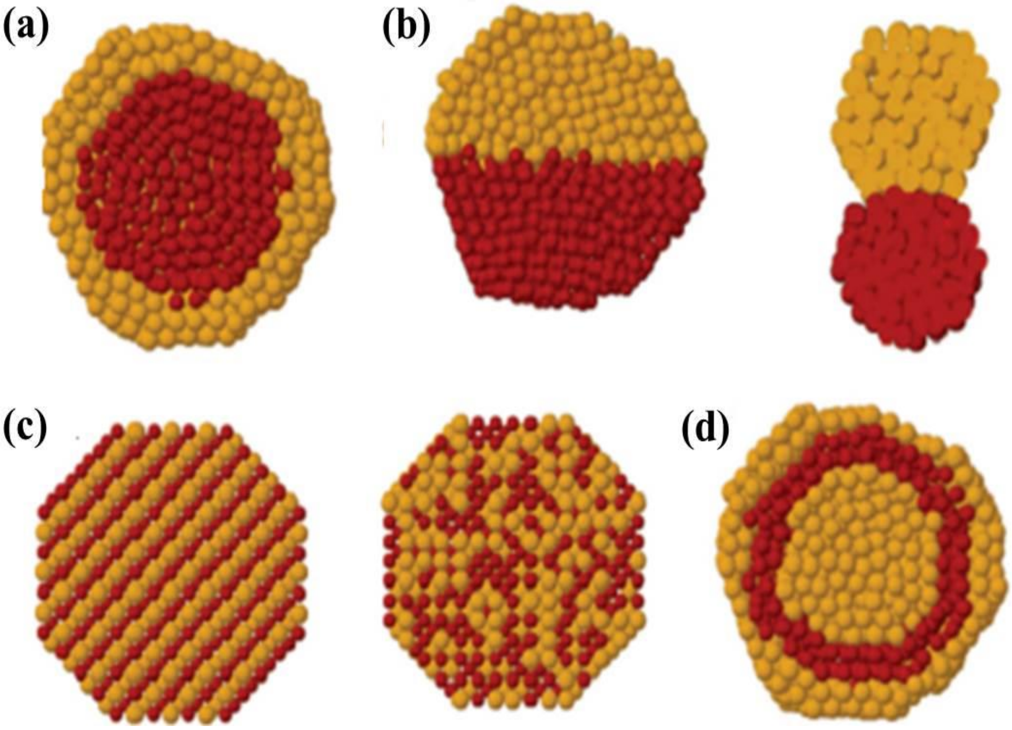

Figure 2.4 Different structures of bimetallic iron nanoparticles; (a) core-shell segregated structure, (b) heterostructure, (c) intermetallic or alloyed structure, and (d) multishell structure (Ferrando et al., 2008)

2.4.7 Arsenic removal mechanism

In general, arsenic removal in NZVI materials may involve many complicated processes, for examples, surface adsorption, precipitation, co-precipitation, and redox reaction (Lackovic et al., 2000; Tyrovola et al., 2006). However, the main mechanism could be surface adsorption involves the binding of arsenic species onto the surface of iron oxides (Lien and Wilkin, 2005). Nikolaidis et al. (2003) assumed that surface adsorption was a fast reaction that reaches equilibrium. According to Figure 2.5, the arsenic removal mechanism can be explained under pathway 1–2–3 and 4. In solution, Fe^0 spontaneously reacts with water and oxygen to produce Fe^{2+} and Fe^{3+}, which can forms a series of iron oxide, hydroxides and oxyhydroxides such as ferrous hydroxide, ferric hydroxide, maghemite, magnetite; depending upon the redox and pH of the solution, as described earlier in Section 2.4.5. Melitas et al. (2002) revealed that As(V) and As(III) could form inner sphere bidentate surface complexes with the surface bonded OH^- (>Fe–OH), then the hydroxyl group at NZVI/H_2O interface formed complexes with aqueous arsenic at the surface, which is the mechanism of arsenic removal from the solution. Moreover, Noubactep (2008) have been indicated that arsenic was trapped on the corrosion product and removed via precipitation and/or co-precipitation process. Following Fenton process, oxidizing intermediate in solution such as H_2O_2, HO^-, O^-, which produced from reaction of Fe2+ forms with water and oxygen, can oxidize As(III) to As(V) (Manning et al., 2002).

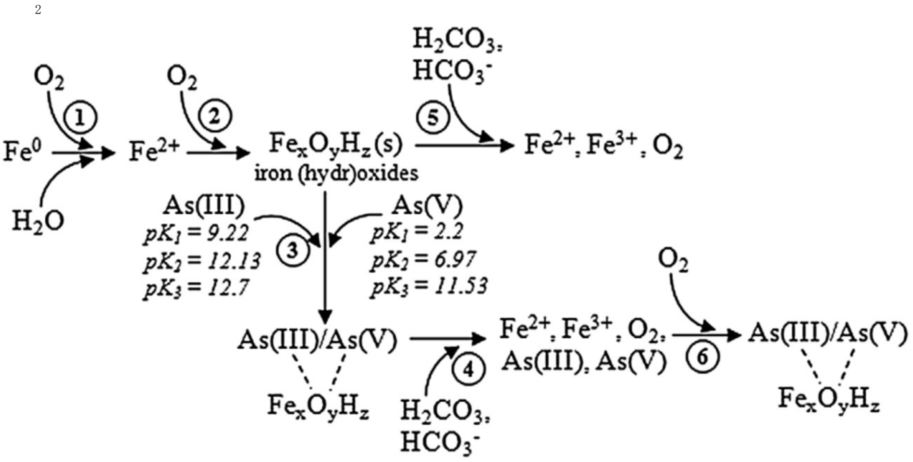

Figure 2.5 Proposed mechanism of arsenic removal using NZVI materials

CHAPTER 3

METHODOLOGY

3.1 Material and reagents

All chemicals used in this research were analytical reagent grade. Chemical solutions are prepared by using deionized water (18.2 MΩ MillQ). Cu-Fe bimetal and NZVI in this study were synthesized from chemicals including $FeCl_3 \cdot 6H_2O$ (99%), $NaBH_4$ (> 96%), (Merck), and $CuCl_2$ (Merck). As(V) solution was prepared from $Na_2HAsO_4 \cdot 7H_2O$ (J.T. Baker) and As(III) solution from $AsNaO_2$ (Fluka). Selected background species were prepared from HA (Acros organics), Na_2SO_4 (Merck), $NaHCO_3$ (Merck), $Na_2PO_4 \cdot 12H_2O$ (Merck), $CaCl_2 \cdot 7H_2O$ (Merck), and NaCl (Merck). CO_2 gas with purity of 99.5% and Air (O_2 21%, N_2 79%) were purchased from a local supplier (Tainan, Taiwan). Arsenic-contaminated groundwater used in this study was pumped from a site located in Chia Nan University of Pharmacy & Science, Taiwan. Chemical characteristics of the groundwater are listed in Table 3.1.

Table 3.1 Chemical characteristics of the field groundwater

Parameter	Value
pH	7.95
Eh (mV)	35
Dissolved oxygen (mg/L)	3.02
Arsenic (µg/L)	42
Calcium (mg/L)	19
Iron (mg/L)	0.8

3.2 Experimental procedures

3.2.1 NZVI synthesis

NZVI was synthesized according to a chemical method as described by (Wang and Zhang, 1997). 40 mL of 0.25 M $NaBH_4$ (<96%; Merch) was added into 40 mL 0.045 M $FeCl_3 \cdot 6H_2O$ (99%), which contained in beaker sealed with aluminum foil through a pumping system (Masterflex L/S) with feeding rate at 4 mL/min and agitating speed of 300 rpm. The solutions were mixed through a revolving propeller (see Figure 3.1). In addition, this preparation was carried out under room temperature condition. Consequently, the NZVI was formed according to Reaction (3.1).

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0 + 3B(OH)_3 + 10.5H_2 \qquad (3.1)$$

Afterwards, NZVI was separated from liquid solution by a magnet. Obtained material was applied to remove arsenic right after.

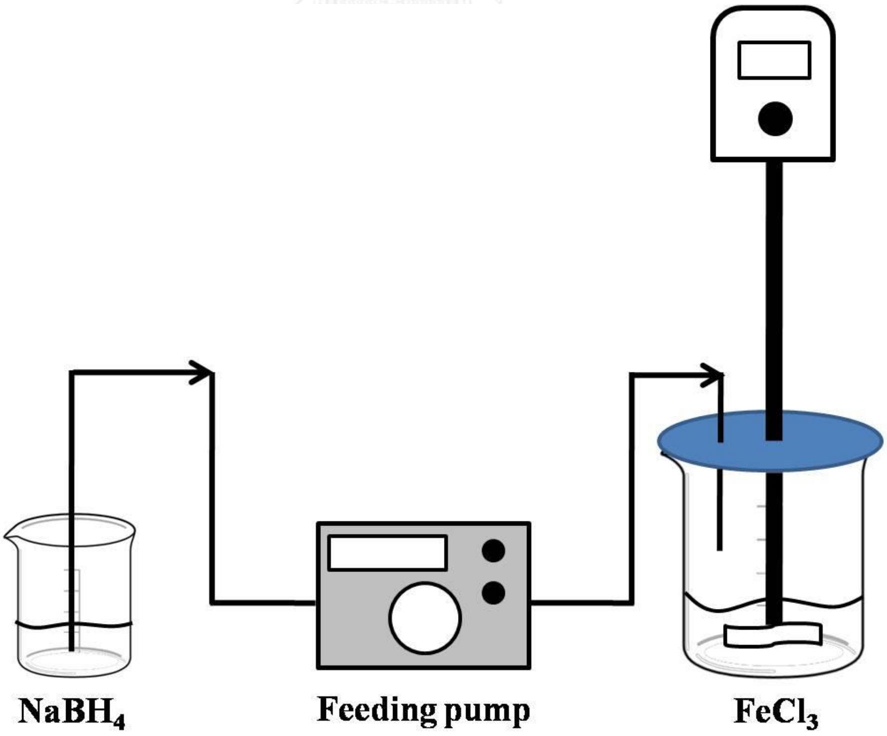

Figure 3.1 Schematic diagram for NZVI synthesis

3.2.2 Bimetal synthesis

3.2.2.1 In-situ method

Cu-Fe nanoparticles were synthesized with $CuCl_2$ mixed with $FeCl_3$ first, according to the same method of NZVI synthesis (Mondal et al., 2004). In this method, Cu will be dispersed onto NZVI particles. Mass ratios of Cu were set as follows; 2.5, 5.0, 10.0, 20.0 and 30.0% (w/w). This method for Cu-Fe synthesis was designated as $(Cu\text{-}Fe)_{IS}$. A redox reaction involving in the synthesis preparation is expressed by Reaction (2):

$$2Fe^{2+} + Cu^{2+} + BH_4^- + 2H_2O \rightarrow 2Fe^0Cu^0 + BO_2^- + 4H^+ + 2H_2 \qquad (3.2)$$

3.2.2.2 Impregnation method

The second metal (either Cu or Ni) will be deposited and distributed on the surface of NZVI particles, which was prepared following by Section 3.2.1. Sample was designated by $(Cu\text{-}Fe)_{IM}$. Such bimetal particles were prepared by mixing the $CuCl_2$ solution for the synthesis of Cu-Fe, and the $NiSO_4$ solution for Ni-Fe (Sun et al., 2006). After the second metal was added for 2 min, the NZVI-based bimetal particles were separated from liquid solution by the use of a magnet. During the synthesis process, $(Cu\text{-}Fe)_{IM}$ was formed according to Reactions (3.3) and (3.4):

$$Fe^0 + Cu^{2+} \rightarrow Fe^{2+} + Cu^0 \qquad (3.3)$$

$$Fe^0 + Ni^{2+} \rightarrow Fe^{2+} + Ni^0 \qquad (3.4)$$

3.2.3 Gas bubbling system

Figure 3.2 presents a dual-function reactor for arsenic removal with a liquid volume of 4.6 L. This reactor provided dual functions consisting of arsenic removal and nanoparticles settling chamber (Anotai et al., 2010). It was the combination of two chambers for reaction (chambers A and B) and one chamber for particles settling (chamber C). It should be noticed that a bottom of chamber A is V-shape, while that of chamber B is U-shape. The V-shape in chamber A will provide an excellent dispersion of nanoparticles, and the U-shape will support the nanoparticles settling from chamber C. The internal- and external-circulating pumps were connected with recirculation rate of 12 L/min and 540 mL/min, respectively. All nanoparticles were settled down at the narrow U-shape bottom of chamber B would be suck up completely through the tube and then discharged into the V-shape bottom of chamber A. Consequently, the solution with suspended nanoparticles would flow back to chamber B and went into the inlet tube due to the drawing force of water pump. The strong turbulent was created because of such high water recirculation and discharge, resulting in homogenous particles in chambers A and B. In addition, the supernatant stream would flow into chamber C and flew out into the outlet tubing line. The solution samples were taken at chamber C.

The solution was first pretreated by bubbling CO_2 of 300 mL/min feed rate for 5 min to adjust the pH to around 4, followed by bubbling air of 300 mL/min feed rate for 10 min to supply oxygen. Then, the solution was treated with the same air flow rate continuously supplied until the end of reaction.

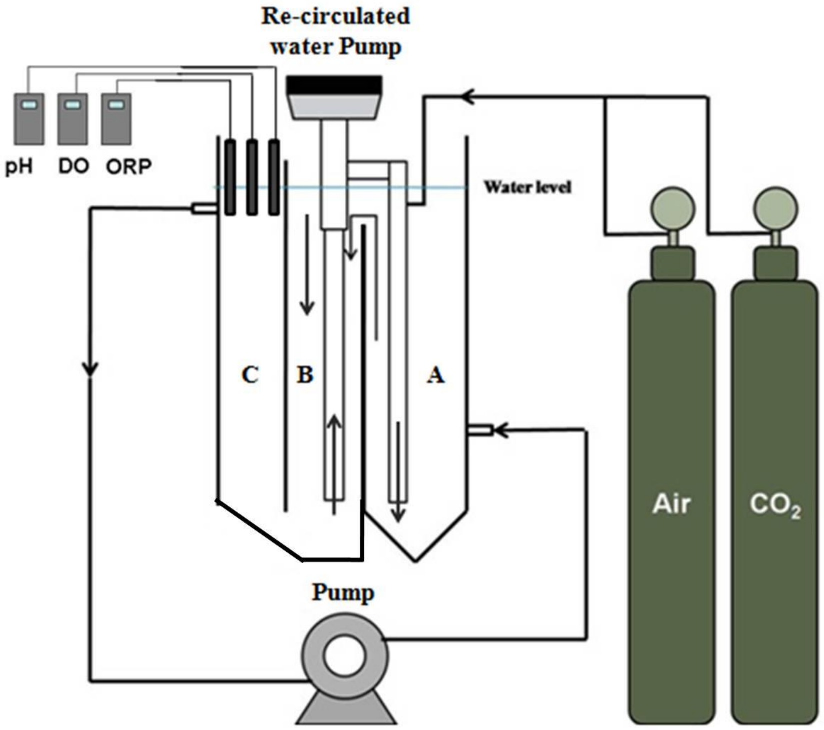

Figure 3.2 Apparatus setup for arsenic removal over nanoparticles

3.3 Research framework

Figure 3.3 shows the experimental framework of the study. The experimental of this study consists of three main parts; preliminary experiments, arsenic removal in batchwise experiment and arsenic removal in continuous system.

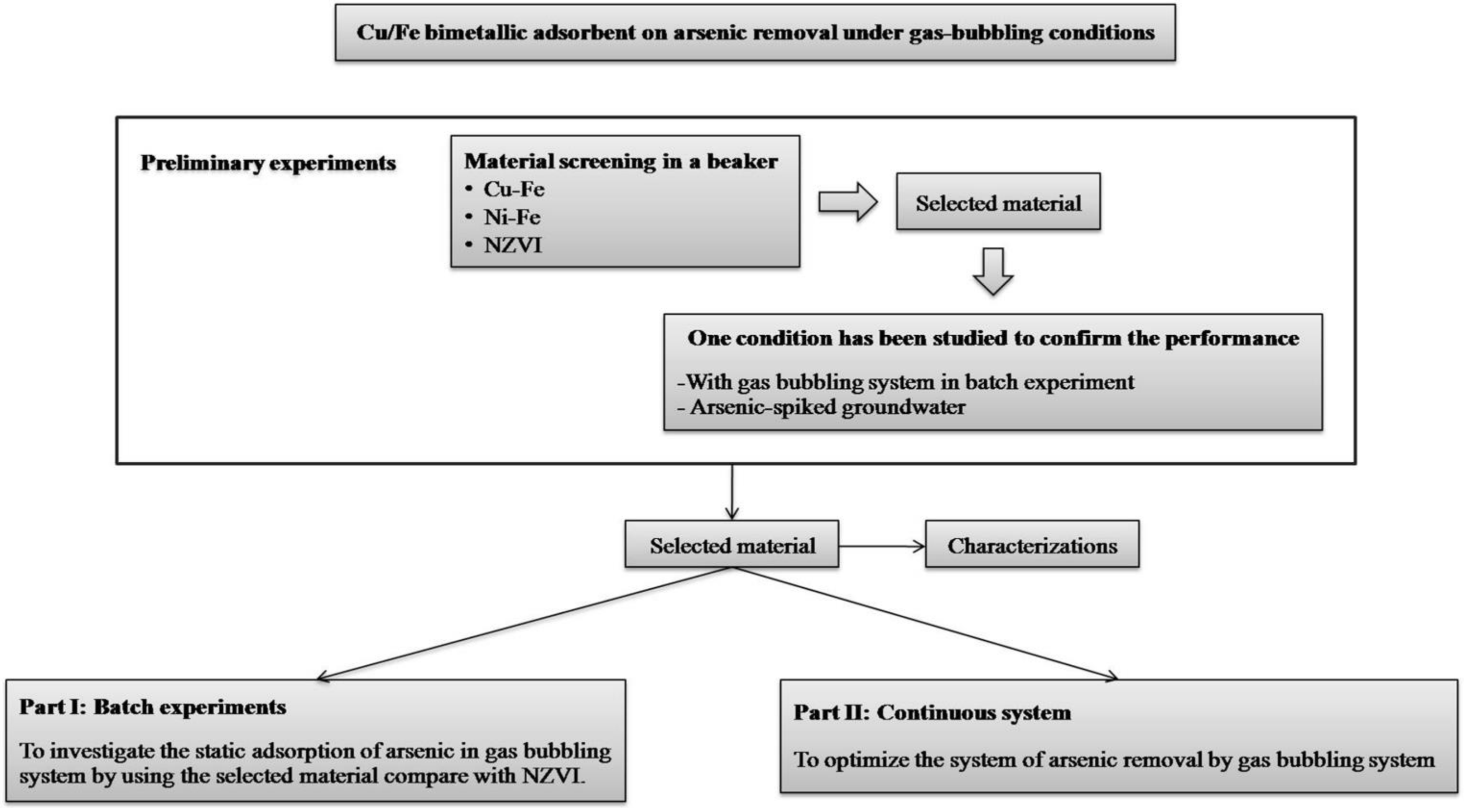

Figure 3.3 Experimental framework

3.4 Preliminary experiments

3.4.1 Comparison of using different types of nanoparticles

This experiment was aimed to evaluate the ability of Cu-Fe bimetal for arsenic removal. Batch experiments were provided in beaker of 1500 mL with As(III) and As(V) concentration of 5000 µg/L. In the study, 0.1 g of nanoparticles (NZVI, 10%Cu-Fe and 10%Ni-Fe) were used separately in each batchwise experiment. Both Cu-Fe and Ni-Fe bimetals were synthesized by the method of impregnation method with 10% of second metal loading.

3.4.2 Arsenic removal at high pH condition

Both arsenic species, As(III) and As(V), was treated in gas bubbling system by using $(\text{Cu-Fe})_{\text{IM}}$ compared with NZVI. The studied pHs were adjusted to 4.0 and 7.0 at the initial stage of reaction. The initial concentration of arsenic was set at 1000 µg/L throughout process.

3.4.3 Field groundwater test

The selected bimetal and NZVI were tested for the removal of As(V) spiked in both deionized water and groundwater, which was taken from the monitoring well at Chia Nan University of Pharmacy and Science, Taiwan. The As(V) solution of 1000 µg/L was spiked into both field groundwater and deionized water. The removal process will be carried out in gas bubbling system as mentioned earlier. The properties of groundwater are described in Table 4.5. The experimental step of preliminary is shown in Figure 3.4.

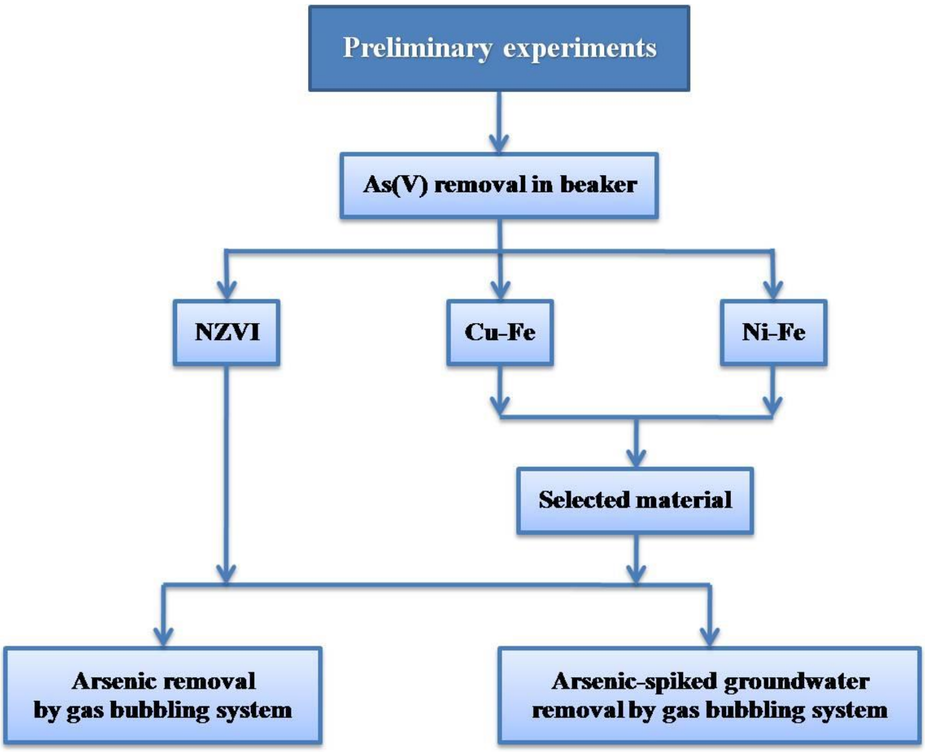

Figure 3.4 Experimental steps for preliminary experiment

3.5 Batch experiments

For the batch experiment, the studies of various effects on arsenic removal were done in gas bubbling system. The effects were study in batch system consisting of different synthesis method, percent copper loading, the ratio of As(III) and As(V), single background ion, and multi-ion system. Also the arsenic spiked field groundwater was carried out. The experimental steps are shown in Figure 3.5.

3.5.1 Effect of synthesis method

The applying only 10% Cu loading on NZVI nanoparticles, which were synthesized with in-situ or impregnation method, was used in arsenic spiked DI water. The initial arsenic concentration applied of 1000 µg/L for both As(III) and As(V).

3.5.2 Effect of copper loading

To study the effect of Cu loading, Cu-Fe nanoparticles, which were synthesized in various percent of Cu contents, was added into a batch reactor for the treatment of both As(III). and As(V). The mass ratios of Cu were as follows: 2.5, 5.0, 10.0, 20.0 and 30.0% (w/w) and the initial arsenic concentration were of 1000 µg/L.

3.5.3 Effect of mixed arsenic species in various As(III) versus As(V) ratio

The impact of different ratios of As(III)/As(V) on arsenic removal is important in the field application. The different mass ratios of As(III)/As(V); 10:0, 7:3, 5:5, 3:7, and 0:10 were investigated. The experiments with As(III) or As(V) alone in the solution were also investigated. The total arsenic concentration was controlled at 1000 µg/L.

3.5.4 Effect of background species

3.5.4.1 Arsenic-spiked field groundwater

The groundwater was taken from the monitoring well at Chia Nan University of Pharmacy and Science, Taiwan. The Cu-Fe prepared by impregnation method and NZVI of 0.1 g will be used coupled with gas bubbling system. The removal of As(III), As(V), and As(III)/As(V) ratio of 1:1 in field groundwater were performed. Arsenic was spiked into this field groundwater sample to obtain its initial arsenic concentration of 1000 µg/L.

3.5.4.2 Single ion system

To study the effect of single background species, 0.1 g of Cu-Fe nanoparticles with impregnation method was added into a batch reactor for the treatment of both As(III) and As(V) comparing with using NZVI. The initial arsenic concentration was prepared at a level as high as 1000 µg/L. Three levels of ion concentrations for each selected species were listed as follows: HA: 0.5, 2, and 5 mg/L; PO_4^{3-}: 1, 3, and 5 mg/L; HCO_3^-: 50, 200, and 500 mg/L; SO_4^{2-}: 50, 200, and 500 mg/L; Ca^{2+}: 50, 200, and 500 mg/L; Cl^-: 50, 200, and 500 mg/L.

3.5.4.3 Multi-ion system

The effect of multi-ions system on arsenic removal was performed in As(III) and As(V) solution. The studied species was varied at low and high concentration, while the others ions were fixed in the middle value from concentration range in the study of effect of single species (Section 3.5.4.1). The initial concentration of arsenic was prepared at the level of 1000 µg/L and 0.1 g of Cu-Fe bimetal prepared by impregnation method was added (0.022 g/L) in each batch. The experiment design of each stated species were given in Table 3.2.

Table 3.2 Concentration of each stated species for study of multi-ion system

Common ion	Low Conc.	Fixed Conc.	High Conc.
HA	0.5 mg/L	2 mg/L	5 mg/L
PO_4^{2-}	1 mg/L	3 mg/L	5 mg/L
HCO_3^-	50 mg/L	200 mg/L	500 mg/L
SO_4^{2-}	50 mg/L	200 mg/L	500 mg/L
Ca^{2+}	50 mg/L	200 mg/L	500 mg/L
Cl^-	50 mg/L	200 mg/L	500 mg/L

3.5.5 Kinetic study

In order to determine kinetic model, the experiments were performed in gas bubbling system at As(III) and As(V) concentration of 1000 µg/L. Then, a series of linearization were presented depending on the reaction order. The best fit should occur with the linearization that is appropriate for the data.

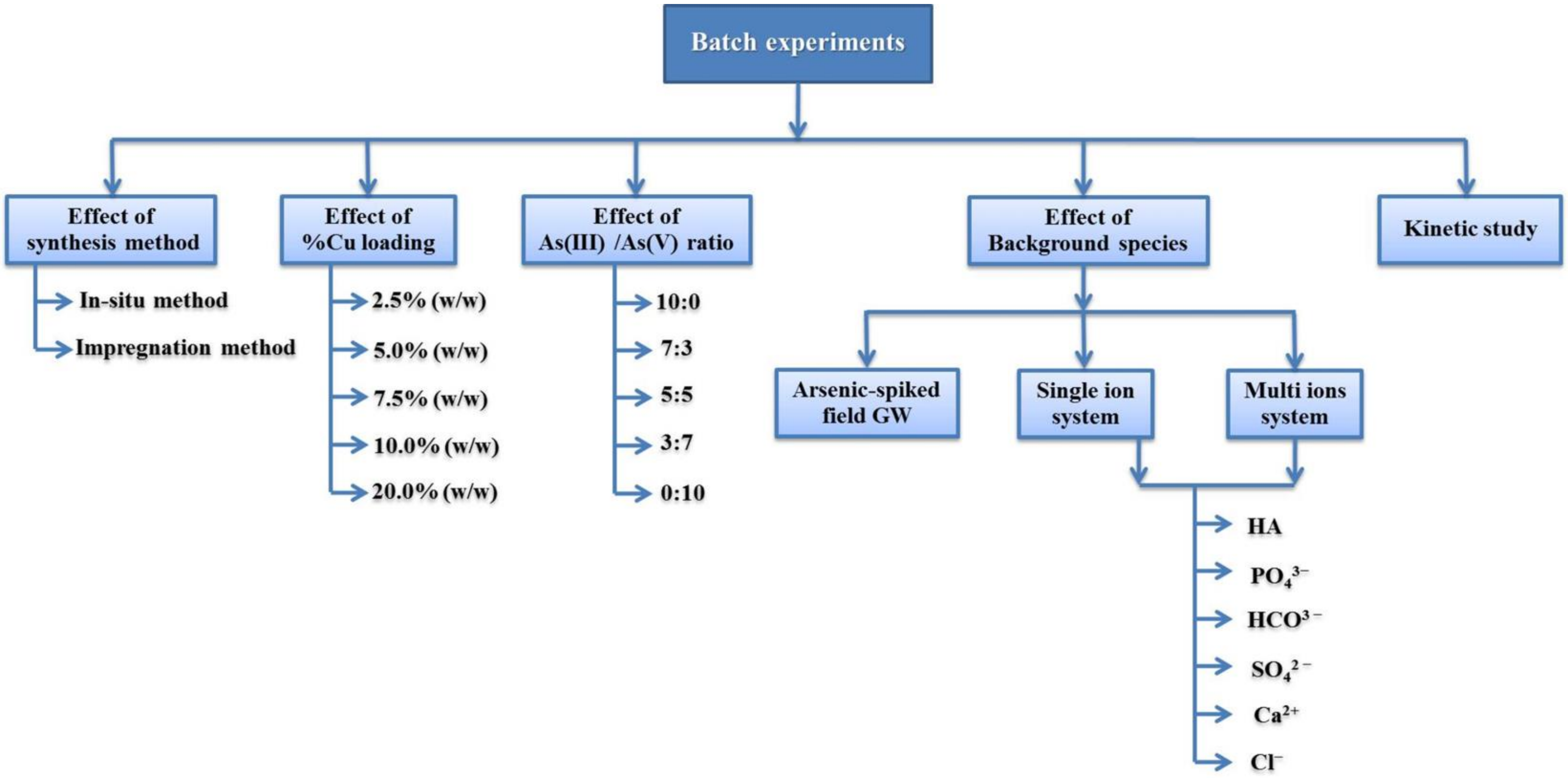

Figure 3.5 Experimental steps for studying the batch experiments

3.4 Continuous system

The use of Cu-Fe coupled with continuous gas bubbling system was developed, according to the application for removing arsenic continuously. The schematic setup of this continuous process was shown in Figure 3.6. For investigating the optimal condition, the effect of influent flow rate and the effect of additional step of bimetal were determined. The initial arsenic concentration of 1000 µg/L were prepared and removed by using 0.1 g of bimetallic material. The experiments of continuous system were carried out for both As(III) and As(V) solution. An outline of this part of experimental is shown in Figure 3.7.

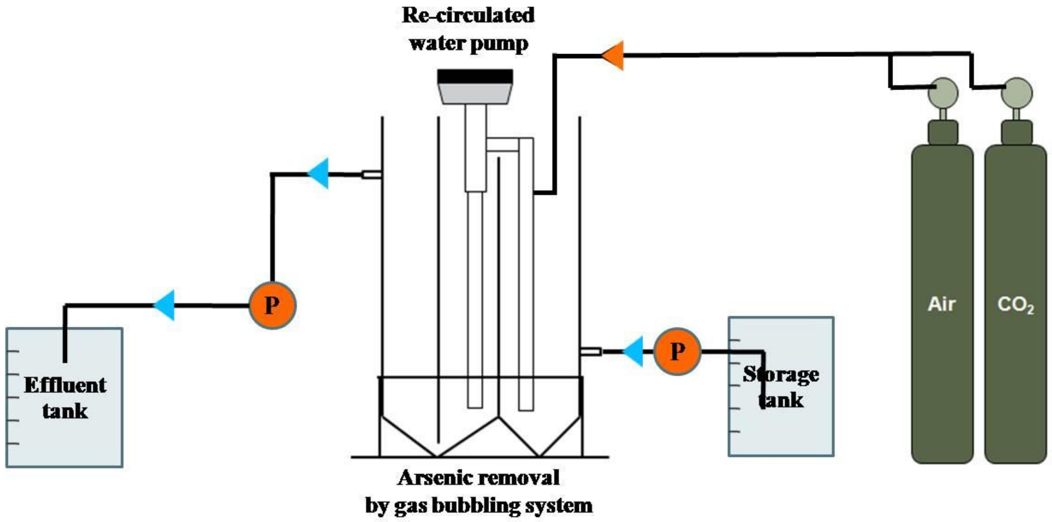

Figure 3.6 Configuration of reactor in continuous process

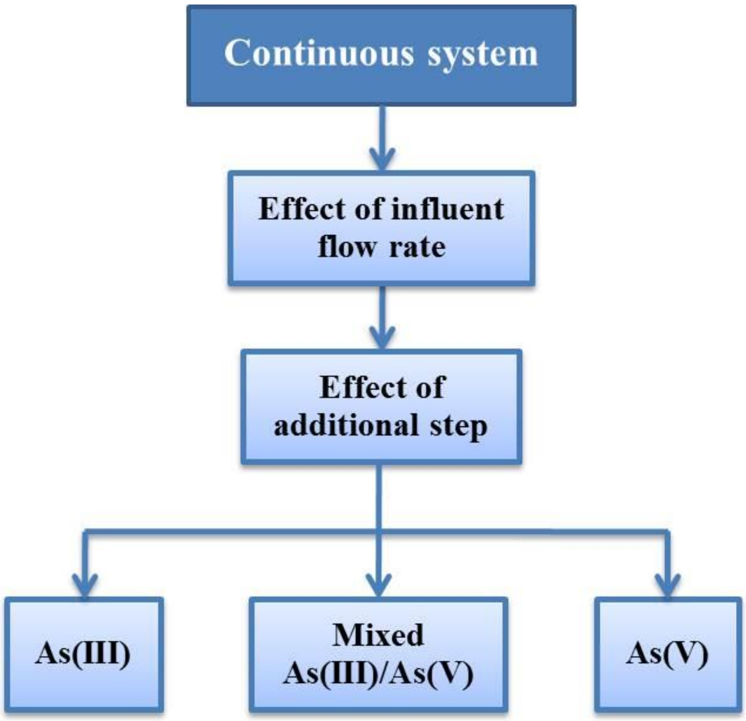

Figure 3.7 Experimental steps for studying continuous system

3.5 Particle characterizations

In order to characterize the size of those metal particles, FEI TECNAI G^2 20 Transmission electron microscopy (TEM) was employed. Moreover, the high resolution images, elemental identification and quantitative compositional were also provided by Scanning Electron Microscopy with Energy Dispersive X-ray (SEM). The surface area of Cu-Fe and NZVI particles was analyzed by Brunanuer-Emmett-Teller (BET) method by N_2 gas adsorption (model : Autosorb-1). The measurement of pH_{PZC} values of the Cu-Fe, Ni-Fe and NZVI was adopted from the technique described by (Mustafa et al., 2002). Fresh and reacted of Cu-Fe were investigated by the X-ray absorption near edge structure (XANES) technique. In addition, Fresh and reacted of NZVI and Cu-Fe were studied with Fourier Transform Infrared Spectroscopy (FTIR) technique.

3.6 Analytical methods

The solution pH and ORP were measured by pH and ORP meter (Suntex TS1), while the dissolved oxygen was measured by DO meter (Oxi 330i). The total arsenic, which is As (V) and As (III), and total dissolved iron are determined by inductively coupled argon plasma (ICP) using Thermo Scientific Model iCAP 6000 series (Thermo Scientific, USA). In addition, the determination of individual arsenic species was conducted by using an anionexchange cartridge, DSC-SAX 500 mg (Supelco) (Ko et al., 2004). The arsenic sampling solution was passed through the cartridge. The As(V) was retained inside, while the As(III) was carried out so As(V) and As(III) was separated from each other. Then, the effluent was analyzed for the As(III) concentration by ICP, and the As(V) concentration was obtained by subtracting the measured As(III) concentration from the total arsenic concentration.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Material characterization

4.1.1 Surface area by BET Analysis

This study used BET liquid nitrogen method to analyze the specific surface area of NZVI and 10% Cu-Fe in both synthesis methods. The results showed that 10%$(\text{Cu-Fe})_{\text{IM}}$ has the highest specific surface area, about 30.14 m^2/g, while 10%$(\text{Cu-Fe})_{\text{IS}}$ and NZVI have the approximate specific surface area of 22.30 m^2/g and 25.63 m^2/g, respectively.

4.1.2 SEM Analysis

The initial survey was conducted on 10%$(\text{Ni-Fe})_{\text{IM}}$, NZVI, 10%$(\text{Cu-Fe})_{\text{IS}}$, and 10%$(\text{Cu-Fe})_{\text{IM}}$ bimetal to determine the major elements and morphology. SEM images exhibited the micron particles of all samples. For the morphology of $(\text{Cu-Fe})_{\text{IS}}$, and $(\text{Cu-Fe})_{\text{IM}}$ bimetal as shown in Figure 4.1(c) and 4.1(d), it shows obviously smaller spherical particles than NZVI and Ni-Fe particles as shown in Figure 4.1(a) and 4.1(b). The comparison between different synthesis methods of Cu-Fe bimetal indicated that the aggregation of $(\text{Cu-Fe})_{\text{IM}}$ (see Figure 4.1(d)) seemed to be less than $(\text{Cu-Fe})_{\text{IS}}$ bimetal (see Figure 4.1(c)). As shown in Figure 4.1, particle size of Ni-Fe was the biggest, the less surface area may effect on arsenic removal performance in further experiments.

Quantitative elemental analysis is shown in Figure 4.2 that the surface of NZVI was predominantly oxygen and iron, while the surface of Cu-Fe and Ni-Fe were additional predominantly copper and nickel, respectively. Besides the SEM images, the difference morphology of two different synthesis method of Cu-Fe were exhibited by EDX profile as shown in Figure 4.2(c) and 4.2(d). This EDX profile evidenced that the major components of Cu-Fe are O, Fe, and Cu, with the following weight percent ratio 5.29: 88.16: 6.55 for $(\text{Cu-Fe})_{\text{IS}}$, and 7.29: 82.22: 10.49 $(\text{Cu-Fe})_{\text{IM}}$.

It can be seen that percent weight of oxygen on the surface of Cu-Fe for both synthesis method were less than that of Ni-Fe, this could result in higher arsenic removal performance. In addition, more weight percent of copper on the surface of $(Cu\text{-}Fe)_{IM}$ can be proved that Cu was deposited on surface of NZVI as a core-shell structure for impregnation synthesis method, while Cu was deposited inside NZVI as an alloyed structure for in-situ synthesis method. In the core-shell structure, metal ions of Fe are reduced to form a metallic inner core firstly, then Cu metal atoms grow around the core and form a shell (Ferrer et al., 2007). For the alloyed structure, a homogenous mixture between Fe and Cu metals might exist in solid solution form (Liu et al., 2005). In addition, the element mapping showed uniform dispersion of Ni and Cu ions on NZVI, as presented in Figure 4.3. This could be confirmed that the preparation technique provides good dispersion of metal loading over supported material.

4.1.3 Zeta potential analysis

The point of zero charge (pzc) of 10%Cu-Fe with both synthesis method and NZVI were measured by Zeta Potential Analyzer. For both synthesis methods of 10%Cu-Fe, the point of zero charge showed higher value than that of NZVI as expected. The point of zero charge of $(Cu\text{-}Fe)_{IS}$, $(Cu\text{-}Fe)_{IM}$, $(Ni\text{-}Fe)_{IM}$, and NZVI were 8.22, 8.73, 8.1, and 7.8, respectively. Such results indicated that 10%Cu-Fe could improve adsorption performance, especially in As(III) solution due to increasing range of positive charge of particles surface.

4.1.4 TEM analysis

Owing to the different methods of preparation and different types of particles, distinct differences in the morphology and particle size among these samples were observed in TEM photomicrograph as seen in Figure 4.4. It was observed from TEM images that almost of diameters of these nanoscale particles were lower than 100 nm, with size of the Cu-Fe particles smaller than the NZVI and Ni-Fe particles. Considering only Cu-Fe bimetals, the $(Cu\text{-}Fe)_{IM}$ was generally smaller than $(Cu\text{-}Fe)_{IS}$. As seen the zoom-in figures, the morphology of these nanoparticles (NZVI, Ni-Fe and Cu-Fe) has two distinct layers. The inside core represents the NZVI itself, while the outer layer covering the NZVI is oxide layer. This is agreed with the report by Yan et al. (2010). Actually, the layer of second metal should be observed in the bimetals particle, but the high resolution was limited by the instrument. The particle size distribution of all nanoparticles that were used in this study, were shown in Figure 4.5. The histogram based on a count of 220 particles shows that the average particle size of NZVI, Ni-Fe, $(Cu\text{-}Fe)_{IS}$, and $(Cu\text{-}Fe)_{IM}$ are 52 nm, 67 nm, 43 nm, and 36 nm, respectively.

4.1.5 XANES technique

Bimetallic Cu-Fe, before and after react with water, was investigated by the X-ray absorption near edge structure (XANES) technique. The oxidation state of spent $(Cu\text{-}Fe)_{IM}$ was studied using XANES technique. The XANES spectra at the Fe K-edge of the reacted $(Cu\text{-}Fe)_{IM}$ and reference standard materials; including Fe foil, FeO, Fe_2O_3, and Fe_3O_4 are illustrated in Figure 4.6(a). The spectrum of reacted $(Cu\text{-}Fe)_{IM}$ shows the main edge similar to that of Fe foil edge characteristic. Also, it should be noticed that white line of reacted $(Cu\text{-}Fe)_{IM}$ of 7130 eV was close to Fe_3O_4. The results can be suggested that iron species after reaction are possible consisted of Fe^0, Fe^{2+} and Fe^{3+}.

Figure 4.6(b) shows XANES spectra of fresh $(Cu\text{-}Fe)_{IM}$, reacted $(Cu\text{-}Fe)_{IM}$, and copper reference; including Cu foil and CuO. It was found that the XANES feature of fresh $(Cu\text{-}Fe)_{IM}$ is closer to that of Cu-foil while reacted $(Cu\text{-}Fe)_{IM}$ shows the similar XANES feature with CuO rather than Cu metal. The Cu K-edge XANES spectrum of fresh $(Cu\text{-}Fe)_{IM}$ shows a pre-edge peak around 8980-8982 eV similar to Cu(0) reference. As well known, the adsorption edge of Cu K-edge XANES is assigned to main 1s → 4p transition. Cu(0) (Cu foil) with a d^0 configuration have no hole in 3d orbital and Cu(2+) (CuO) is in a d^9 configuration. As a result, Cu(2+) represents a weak pre-edge peak the quadruple allowed 1s → 3d transition and it serves as a significant feature for divalent copper. The Cu K-edge XANES spectrum of fresh Cu-Fe and reacted sample shows a weak pre-edge peak around 8983-8985 eV like that of Cu(2+) reference, indicating that the oxidation state of reacted $(Cu\text{-}Fe)_{IM}$ is divalent. Moreover, it can be observed that the edge position shifted toward higher energy as the oxidation state of material increases. The edge positions for fresh Cu foil, $(Cu\text{-}Fe)_{IM}$, CuO, and reacted $(Cu\text{-}Fe)_{IM}$ obtained from the maximum point of first derivative function were 8981.4, 8981.1, 8984.9, and 8984.3, respectively.

4.1.6 FTIR analysis

The chemical structures of arsenic complexes formed on 2 types of materials have been studied using FTIR. Figure 4.7 shows the FITIR spectra of NZVI and $(Cu\text{-}Fe)_{IM}$ before and after exposed to As(III) and As(V) individually under arsenic concentration of 5000 µg/L for 60 min.

It was difficult to detect the presence of sorbed arsenite on the surface of either Fe oxide. However, the peak at 797 cm^{-1} was found for both NZVI and Cu-Fe after arsenic adsorption as shown in Figure 4.7(a), which may be due to As–O absorption in the AsO_4^{3-} group (Goldberg and Johnston, 2001). This result is in agreement with the earlier study of As(III) sorption to iron oxide-coated sand by Devi et al. (2014). However, no bands were observed in the 750–800 cm^{-1} region in unreacted samples. This observation suggested that the 797 cm^{-1} may result from the formation of an inner-sphere surface complex.

The intensity of the two bands at 875 cm^{-1} and 834 cm^{-1} of reacted NZVI and $(Cu\text{-}Fe)_{IM}$ presented that As(V) species adsorbed on the iron oxide as shown in figure 4.7(b). This could be assigned to the *v*(As–OH) of As–O–Fe groups (Lumsdon et al., 1984). The bands appeared in the 1700–1000 cm^{-1} region of the spectra was assigned to carbonate species adsorbed on the iron oxide film. Comparing the spectra of unreacted and reacted materials, the difference was the strong broad band at 1644 cm^{-1}. This band is characteristics for the stretching carbonyl groups (C=O), which was found as CO_2 bubbling in the removal system. The decrease in the band intensity indicates that arsenic replaced some of carbonate species adsorbed on the surface. The IR spectra of As(V) adsorbed to samples indicates that As(V) is predominantly bound as a surface complex.

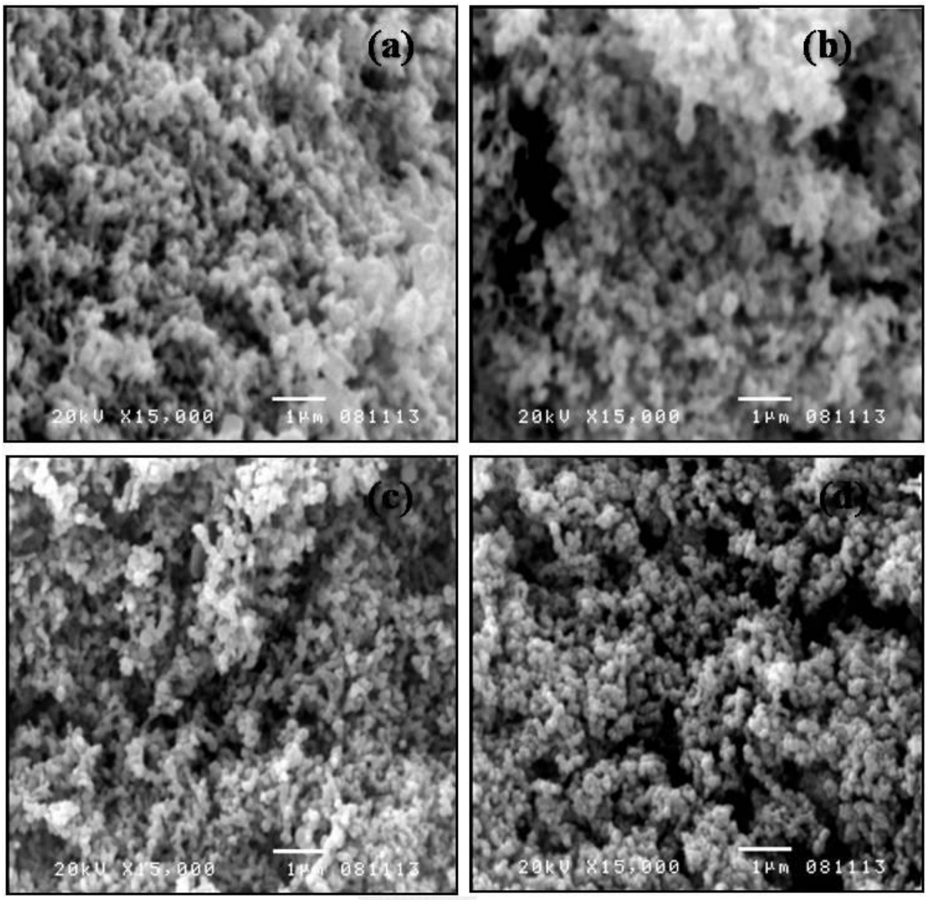

Figure 4.1 SEM images of nanoscale 2 different synthesis methods of Cu-Fe, Ni-Fe and NZVI: (a) NZVI, (b) Ni-Fe, (c) $(Cu\text{-}Fe)_{IS}$, and (d) $(Cu\text{-}Fe)_{IM}$

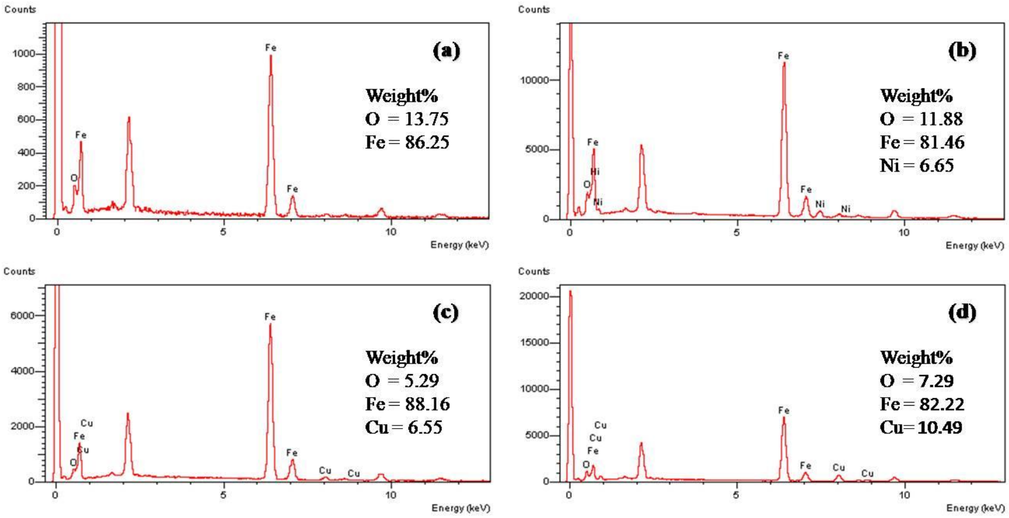

Figure 4.2 EDX profiles of Cu-Fe, Ni-Fe and NZVI:
(a) NZVI, (b) Ni-Fe, (c) $(Cu\text{-}Fe)_{IS}$, and (d) $(Cu\text{-}Fe)_{IM}$

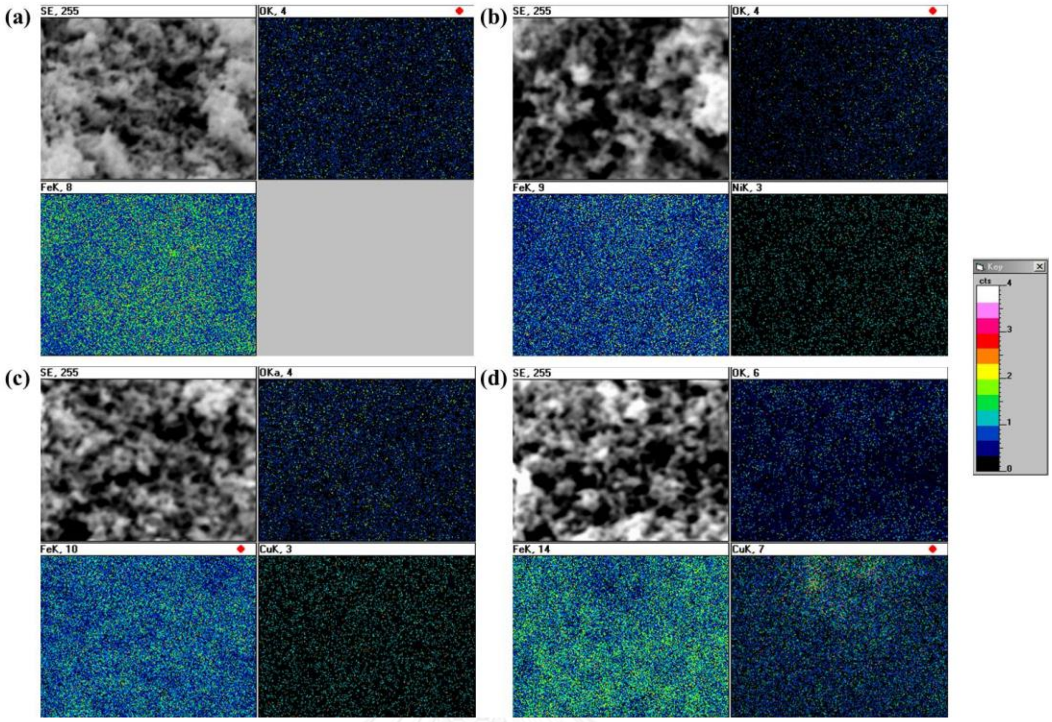

Figure 4.3 Element mappings for nanoparticles of:
(a) NZVI, (b) Ni-Fe, (c) $(Cu\text{-}Fe)_{IS}$, and (d) $(Cu\text{-}Fe)_{IM}$

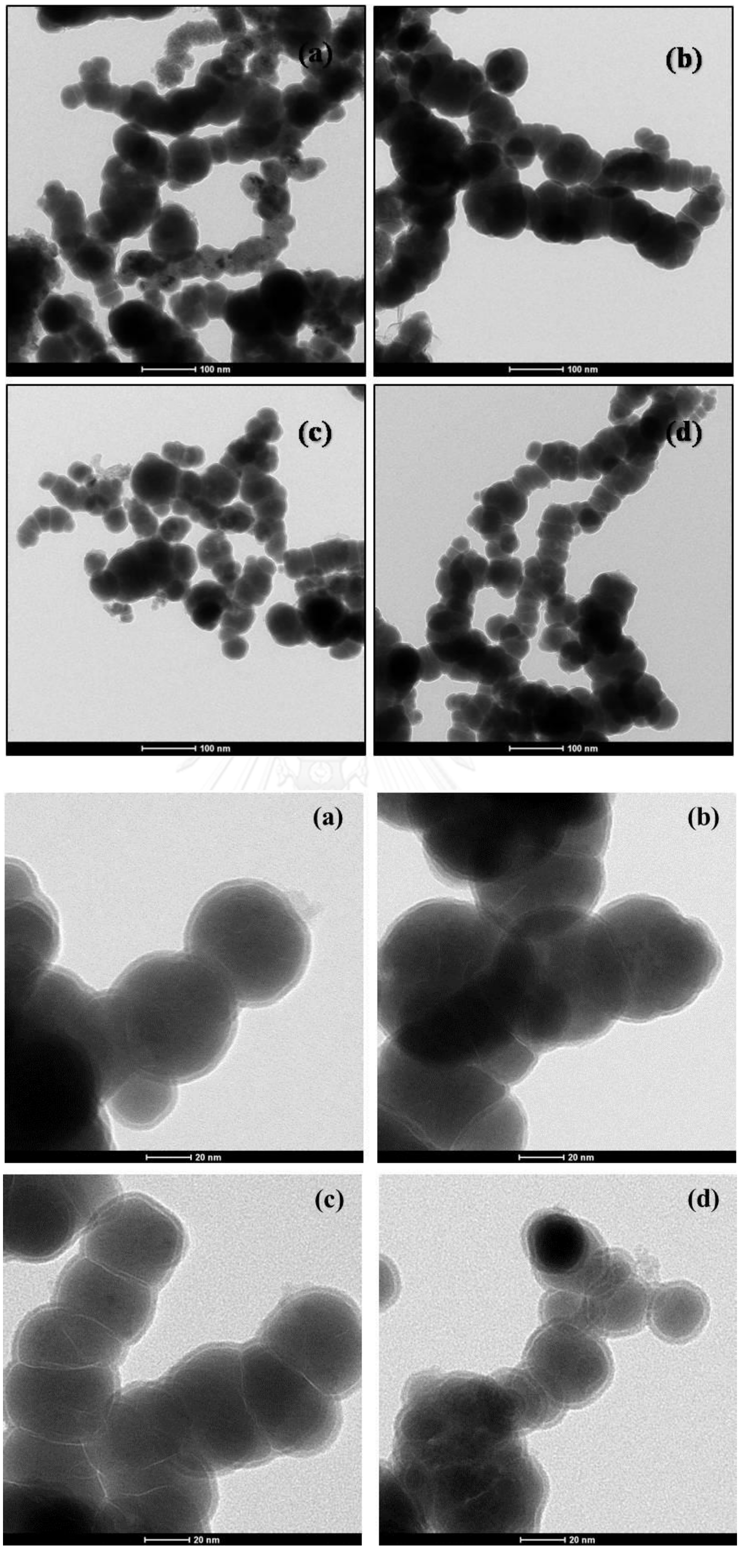

Figure 4.4 TEM and Zoom-in images of nanoscale 2 different synthesis methods of Cu-Fe, Ni-Fe and NZVI: (a) NZVI, (b) Ni-Fe, (c) $(\text{Cu-Fe})_{IS}$, and (d) $(\text{Cu-Fe})_{IM}$

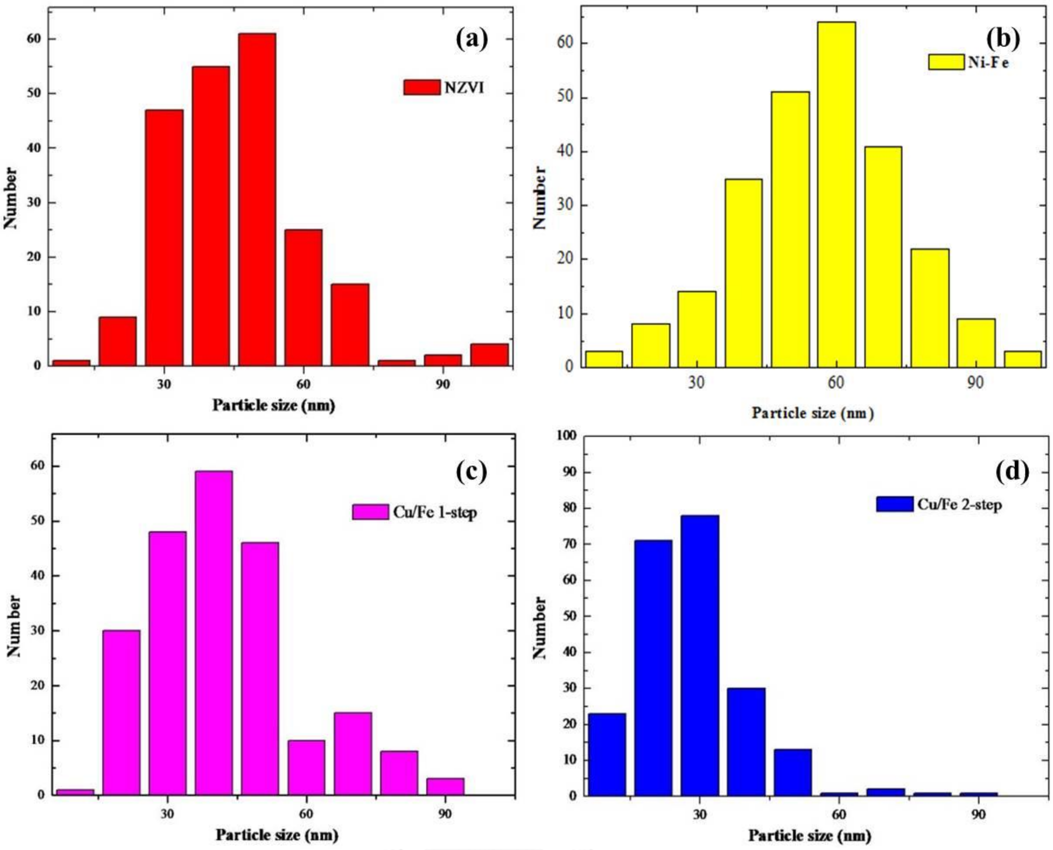

Figure 4.5 Particle size distributions from:

(a) NZVI, (b) Ni-Fe, (c) $(Cu\text{-}Fe)_{IS}$, and (d) $(Cu\text{-}Fe)_{IM}$

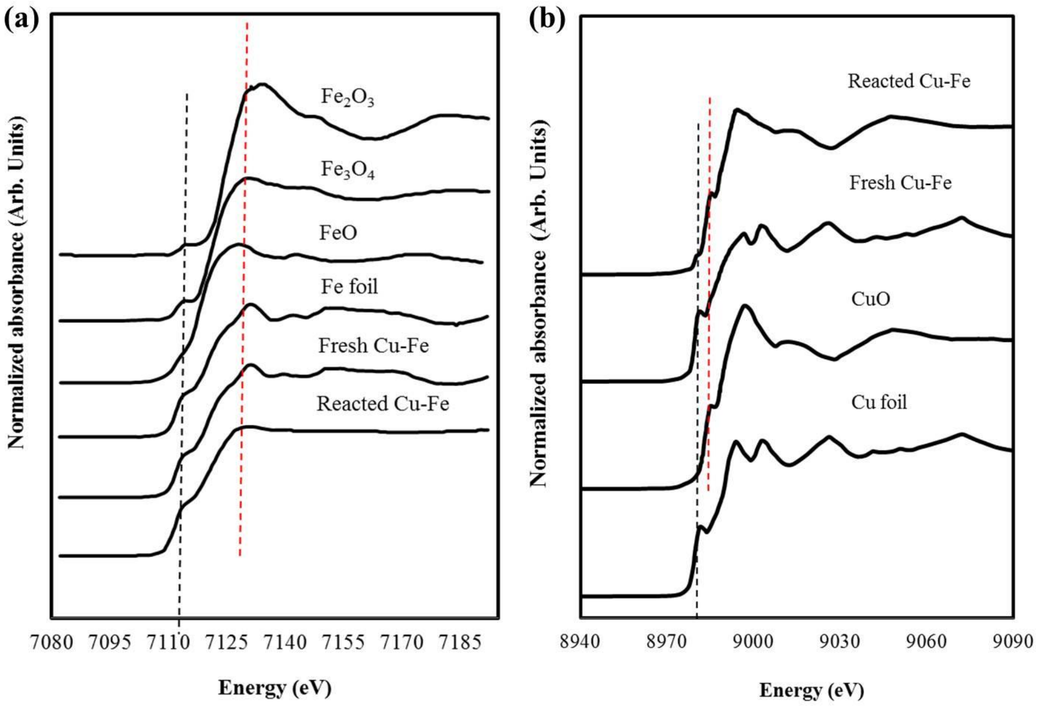

Figure 4.6 (a) Fe K-edge and (b) Cu K-edge XANES spectra of references and synthesized materials

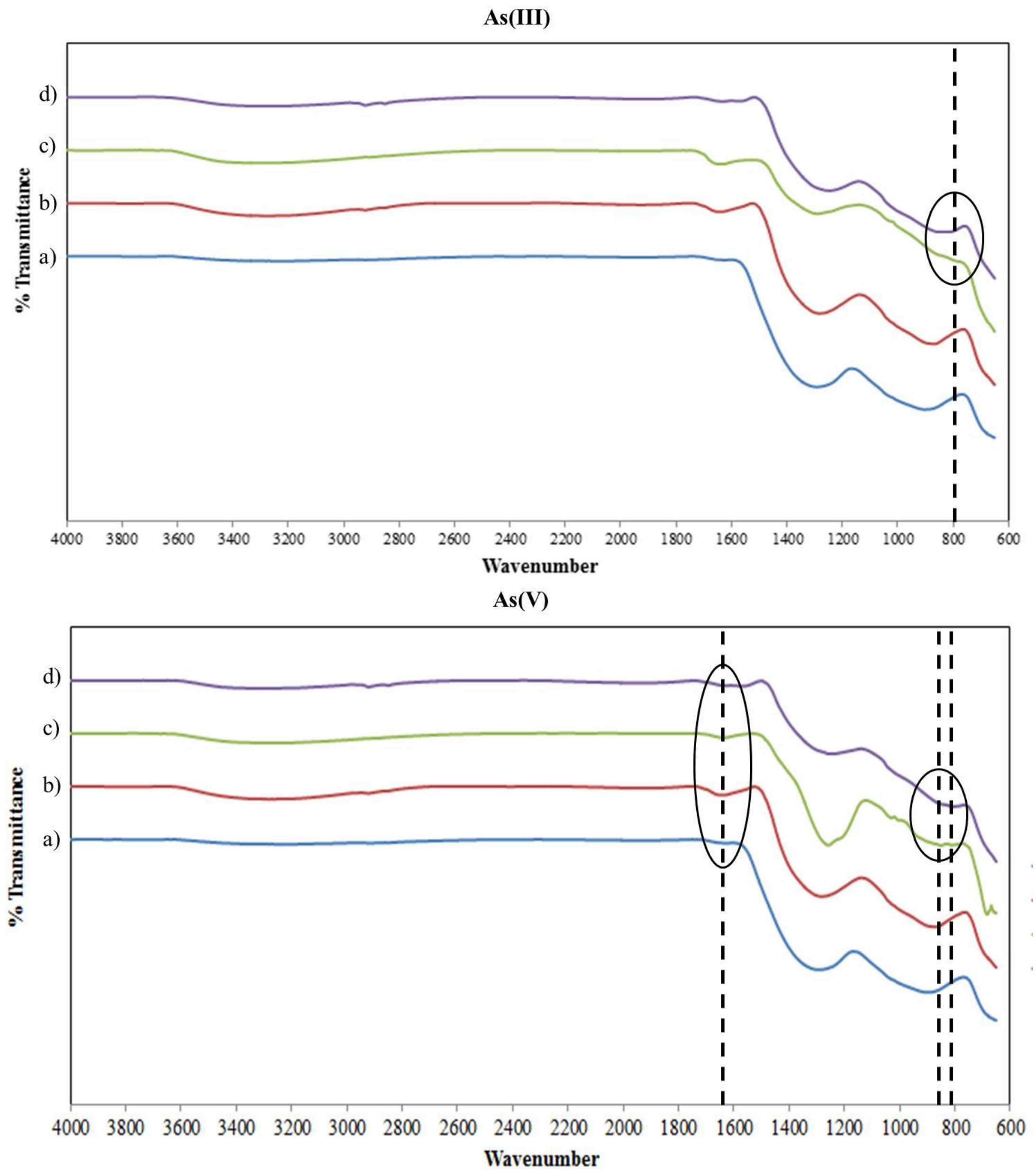

Figure 4.7 FTIR spectra of NZVI and (Cu-Fe)$_{IM}$ before and after arsenic removal for both As(III) and As(V):

a) unreacted NZVI; b) unreacted (Cu-Fe)$_{IM}$; c) reacted NZVI; d) reacted (Cu-Fe)$_{IM}$

4.2 Preliminary experiments

4.2.1 Comparison of using different types of nanoparticles

Preliminary experiments for adsorbent screening were carried out in a beaker. Bimetallic NZVI and bare NZVI were included for the removal tests. In the experiments, 0.1 g of nanoparticles (NZVI, Cu-Fe, and Ni-Fe) was added in the beaker containing 1500 mL of arsenic-spiked DI water at concentration of 5000 µg/L of As(V) and As(III), separately. The initial pH of solution studied was adjusted at pH 7.0. Bimetallic adsorbents used in preliminary part were synthesized by impregnation method [$(\text{Cu-Fe})_{\text{IM}}$ and $(\text{Ni-Fe})_{\text{IM}}$] with 10% (w/w) of 2^{nd} metal. Concentration of As(V) and As(III) were analyzed along the reaction process as shown in Figure 4.8(a) and 4.9(a). The pH of the solution was also monitored as presented in Figure 4.8(b) and 4.9(b) for As(V) and As(III), respectively.

Considering only using bimetal, the $10\%(\text{Cu-Fe})_{\text{IM}}$ appears to outperform the $10\%(\text{Ni-Fe})_{\text{IM}}$ in both removing As(V) and As(III) as seen in Figure 4.8(a) and 4.9(a). The treatment rate of As(V) could be ranked as NZVI > $10\%(\text{Cu-Fe})_{\text{IM}}$ > $10\%(\text{Ni-Fe})_{\text{IM}}$. However, at the end of the experiment (60 min.), the removal of As(V) reached to about 99% on both NZVI and Cu-Fe as shown in Figure 4.8(a). On the other hand, the performance of Ni-Fe in the As(V) removal is only around 80% after 60 min. In the removal of As(III), Cu-Fe performed As(III) removal better than the other two. The removal performance for As(III) was lower compared to that for As(V), accordingly. For example, $10\%(\text{Cu-Fe})_{\text{IM}}$ only removed around 80% of As(III), but almost complete for As(V). In this study, therefore, As(III) removal should be used as a criterion for material screening.

Normally, arsenic can exist in different forms, depending on the pH condition. Based on literature review, the removal of total arsenic was effective in acidic environment (Bang et al., 2005; Sun et al., 2006). The pK_a values of arsenic are summarized as follows: $pK_1 = 9.22$, $pK_2 = 12.13$, and $pK_3 = 12.7$ for As(III); and $pK_1 = 2.2$, $pK_2 = 6.97$, and $pK_3 = 11.53$ for As(V) (Raven et al., 1998), respectively. As mention in Section 4.1.3, the pH_{PZC} values for NZVI, $10\%(\text{Cu-Fe})_{\text{IM}}$ and $10\%(\text{Ni-Fe})_{\text{IM}}$ were determined at 7.8, 8.7 and 8.1, respectively.

For this batch removal experiments, these solutions were initially adjusted to pH of around 7.0. With such an initial pH, the dominant form of As(V) is in negative charge of $H_2AsO_4^-$, and it shows neutrally of H_3AsO_4 for the As(III). In this condition, surface of all adsorbents was found to be positively charged. At low pH condition of initial stage, the opposite charges of arsenic form and all adsorbents led to electrostatic attraction which definitely enhanced the arsenic removal, as shown in Figure 4.8(a) and 4.9(a). When the contact time increased, pH changed to basic condition due to the formation of OH^- from the corrosion process as shown in Eqns. (4.1)-(4.3) (Furukawa et al., 2002; Triszcz et al., 2009).

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{4.1}$$

$$2Fe^0 + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^- \tag{4.2}$$

$$4Fe^{2+} + 2H_2O + O_2 \rightarrow 4Fe^{3+} + 4OH^- \tag{4.3}$$

In basic condition (pH 7-12), the dominant form of As(V) still remains negatively charged ($HAsO_4^{2-}$), while the form of As(III) shifts from neutral to negative charges of $HAsO_3^-$ and $HAsO_3^{2-}$. It is obvious that adsorbent surface presents the charge negatively, when pH stays higher than their pH_{PZC} values. Therefore, a higher value of pH_{PZC} facilitates arsenic removal in higher pH condition.

Considering As(III) removal in basic condition, a profile of solution pH for NZVI falls slightly higher than its pH_{PZC} of 7.8. This resulted in the decrease of arsenic removal by using NZVI due to the electrostatic repulsion force, but not for Cu-Fe. This could be referred to pH profile of Cu-Fe activity was fell into 7.0-7.3, as shown in Figure 4.9(b) while its pH_{PZC} of $10\%(Cu\text{-}Fe)_{IM}$ is 8.7. This caused more positive charge presenting on the surface of Cu-Fe bimetallic adsorbent, resulting in higher As(III) removal. The arsenic removal using Ni-Fe could reach only ≈ 80% in both species of As(V) and As(III). Cu-Fe bimetals also show smaller particles size than NZVI and Ni-Fe as seen in section 4.1.4. This indicated that bimetallic Cu-Fe can be much more reactive per unit weight and migrate much further due to their smaller particles size and larger surface area. Another reason is that the redox potential of Ni was quite similar to Fe, the acceleration of iron corrosion by Ni was insignificantly observed.

In summary, since the Cu-Fe shows an excellent performance for As(V) removal and better performance for As(III) removal than NZVI and Ni-Fe, so Cu-Fe was chosen for the further study in batch experiment part.

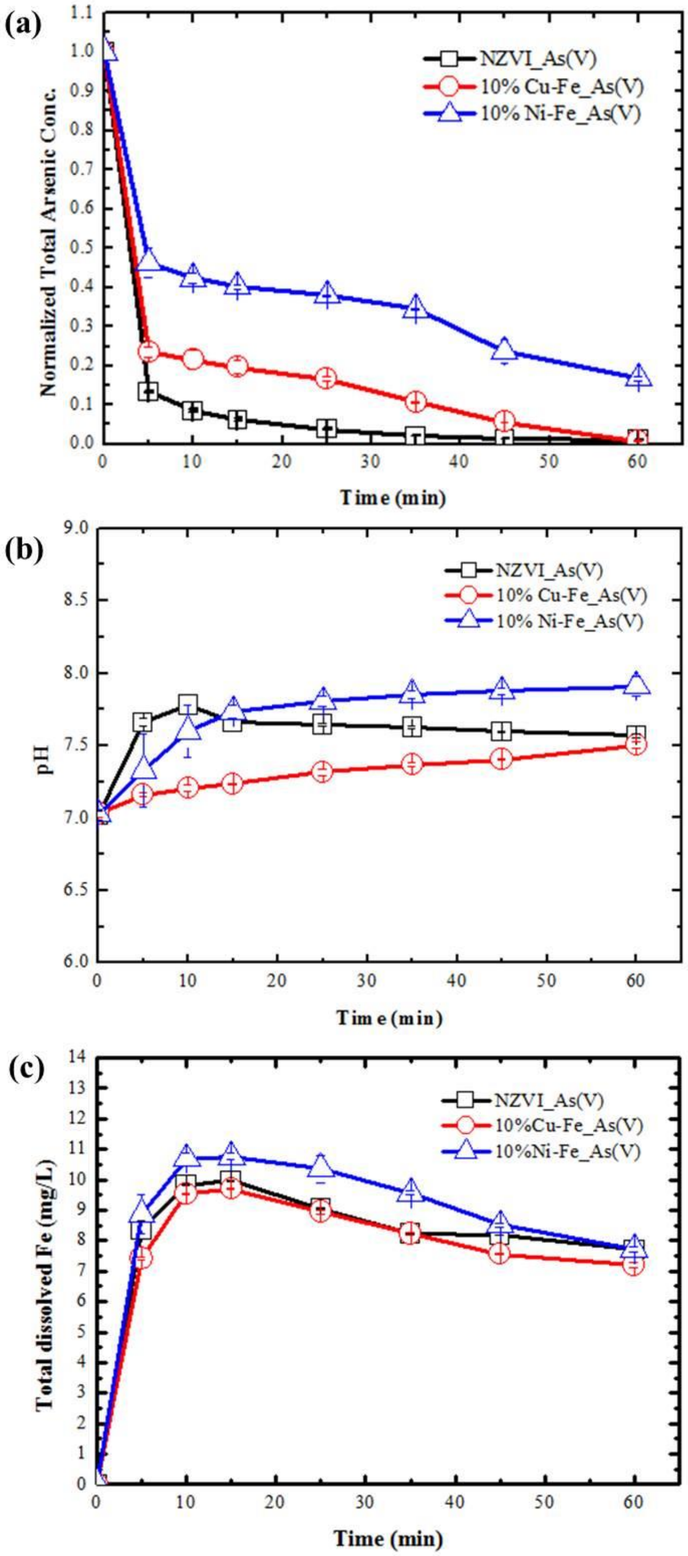

Figure 4.8 Profiles of (a) normalized arsenate concentration, (b) pH, and (c) total dissolved iron in the presence of different bimetals (10%(Cu-Fe)$_{IM}$, 10%(Ni-Fe)$_{IM}$) comparing with NZVI

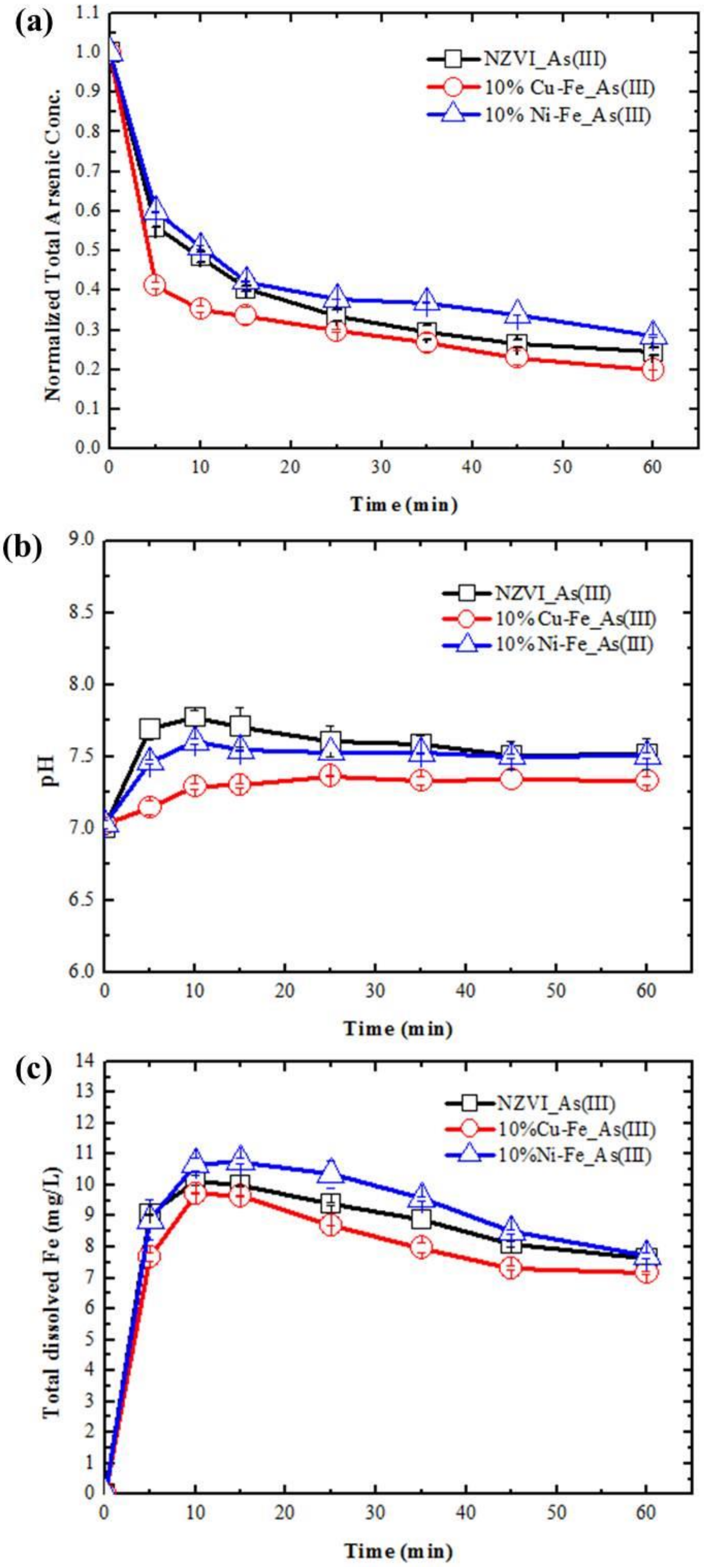

Figure 4.9 Profiles of (a) normalized arsenite concentration, (b) pH, and (c) total dissolved iron in the presence of different bimetals (10%$(Cu\text{-}Fe)_{IM}$, 10%$(Ni\text{-}Fe)_{IM}$) comparing with NZVI

4.2.2 Arsenic removal at high pH condition

Based on high pH_{PZC} of $(Cu\text{-}Fe)_{IM}$, arsenic removal in gas bubbling system by $(Cu\text{-}Fe)_{IM}$ at high and low initial pH were tested compare to using NZVI. The initial arsenic concentration was set of 1000 μg/L, while the initial pH of solution were adjusted at 4.0, and 7.0. Treatment of arsenic in gas bubbling system was carried out by using $(Cu\text{-}Fe)_{IM}$, comparing with NZVI. As presented in Figure 4.10(a), increase of initial pH from 4.0 to 7.0, insignificant reduction of As(III) and As(V) removal was observed using $(Cu\text{-}Fe)_{IM}$. On the other hand, the removal of both As(III) and As(V) by NZVI decreased with increasing of initial pH. The pH profiles along reaction were shown in Figure 4.10(b). This can be seen that pH increased to about 8.5 in the final, which exceed pH_{PZC} of NZVI, resulting in the reduction of arsenic removal by NZVI. For using $(Cu\text{-}Fe)_{IM}$ ($pH_{PZC} = 8.7$), arsenic removal performance at initial pH of 7.0 was 90% and 100% for As(III) and As(V), respectively.

The use of $(Cu\text{-}Fe)_{IM}$ to remove arsenic at high pH was expected to show a greater performance, because of high pH_{PZC} of $(Cu\text{-}Fe)_{IM}$ as mentioned in previous part (≈ 8.7). However, arsenic removal with $(Cu\text{-}Fe)_{IM}$ showed slightly decrease when initial pH was increased. This could be indicated that the opposite charge between arsenic species and material surface is not only one factor affected arsenic removal efficiency.

Concerning iron (hydr)oxides formation as related to total dissolved iron profiles in Figure 4.11. The dissolved iron at initial pH 4.0 was lower than that at initial pH 7.0 due to the higher amount of iron (hydr)oxides formation. The iron (hydr)oxides could also serve as the adsorptive sites for arsenic adsorption, which enhance arsenic removal efficiency. Therefore, the initial pH 4 should be set up as the suitable condition to treat arsenic in gas bubbling system.

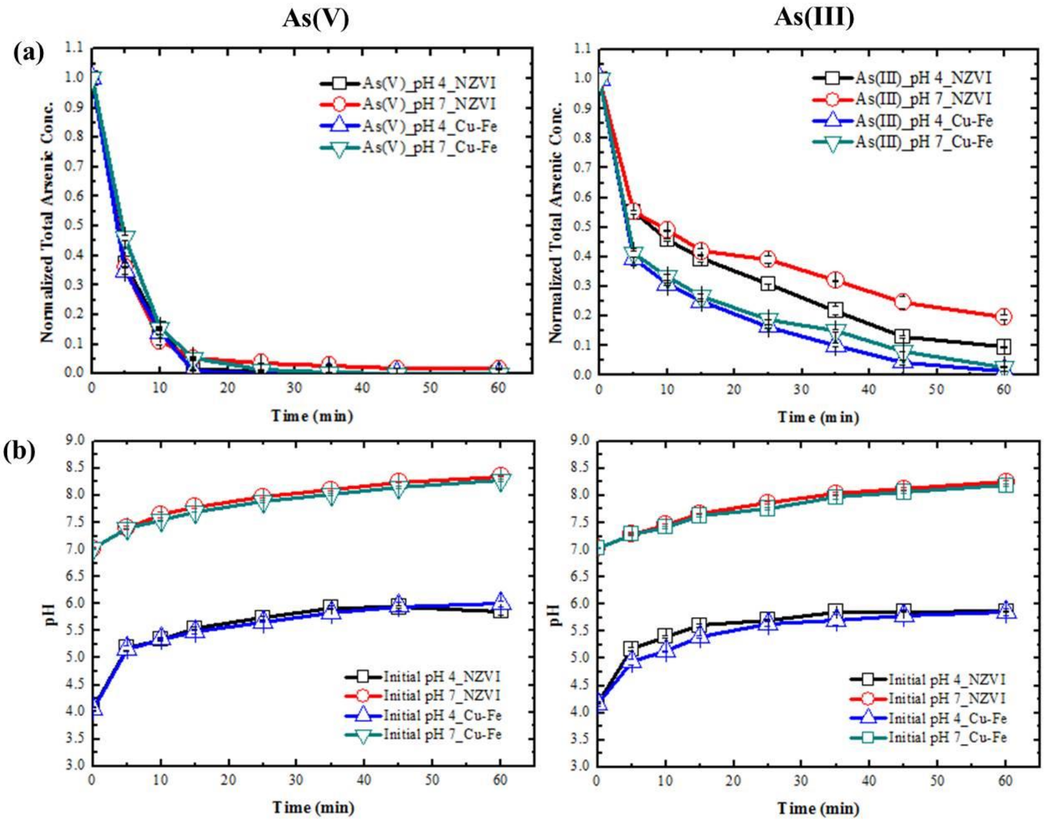

Figure 4.10 Effect of initial pH of 4.0 and 7.0 on:

(a) normalized arsenic concentration, (b) pH

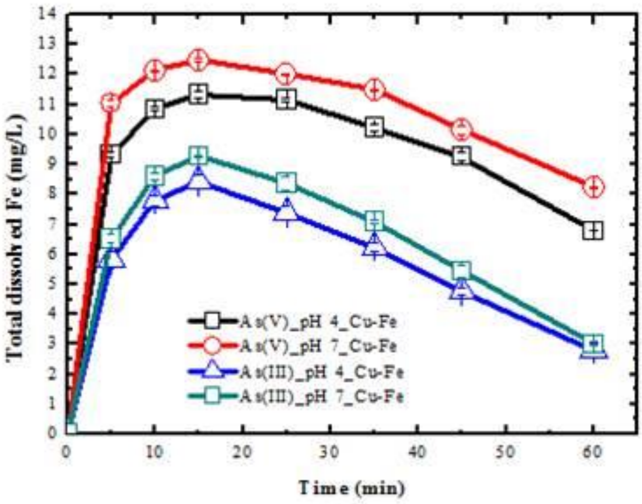

Figure 4.11 Behavior of pH for arsenic removal at different initial pH

4.2.3 Field groundwater test

The 10%$(Cu\text{-}Fe)_{IM}$ and NZVI were tested for the removal of both of As(V) and As(III) in groundwater. The groundwater was taken from the monitoring well at Chia Nan University of Pharmacy and Science, Taiwan. The primary chemical characteristics of the groundwater are listed in Table 3.1. The As(V) and As(III) solution was spiked separately into field groundwater water to obtain its initial arsenic concentration of 1000 µg/L. The removal process was carried out in gas bubbling system, as mentioned earlier. Figure 4.12 presents concentration profiles of As(V) and As(III) on both NZVI and 10%Cu-Fe, and their total dissolved iron. The removal of As(III) on both materials lie on the same trend with reaction progress, while that of As(V) were somewhat different in the beginning of the reaction, which, in the first 10 min, 10%Cu-Fe showed higher removal than bare NZVI.

This can be explained by the total dissolved iron profile, indicating that the total dissolved iron of using 10%Cu-Fe was lower than that of using NZVI. This means that formation of iron (hydr)oxides should be taken into account when using Cu-Fe. It corresponded to lower total dissolved iron shown in Figure 4.12(b).

However, the presence of background species affect on arsenic removal as drop of removal efficiency were observed compared to the removal efficiency in Section 4.2.2. The investigation on background species effect on arsenic removal by this Cu-Fe process will be carried out in further experiments.

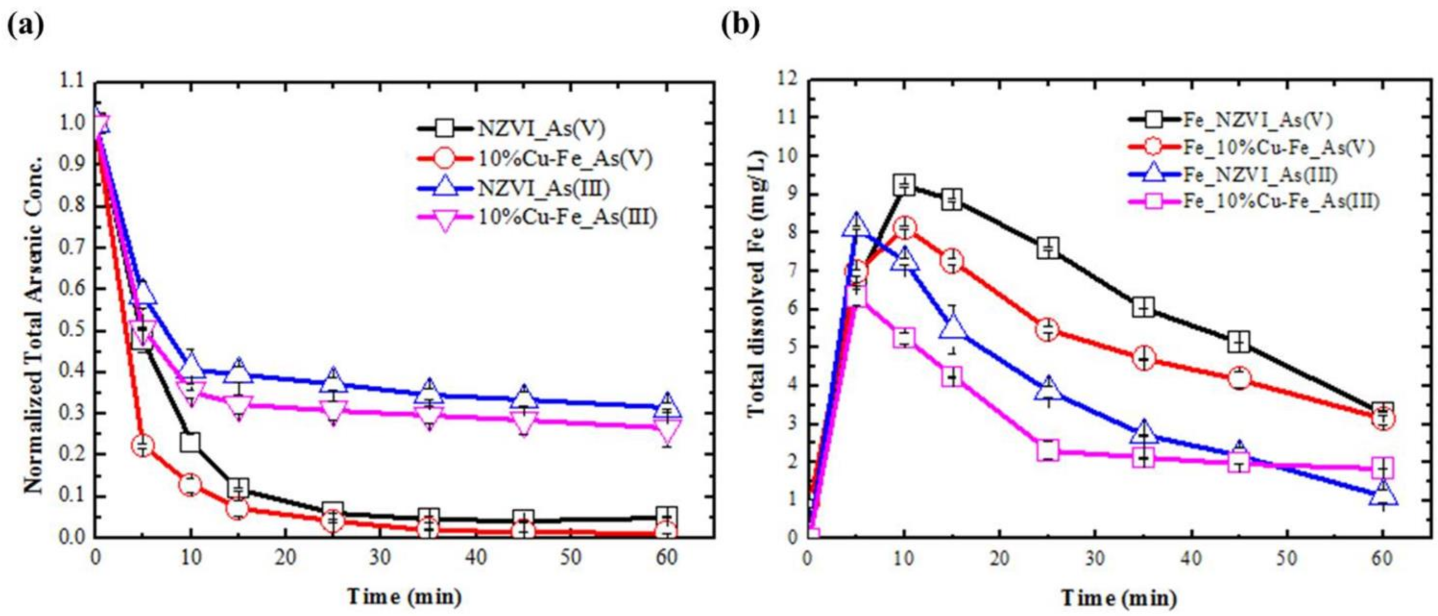

Figure 4.12 Effect of NZVI and 10%Cu-Fe in real groundwater on (a) normalized arsenic concentration and (b) total dissolved iron

4.3 Batch experiments (Part I)

4.3.1 Effect of synthesis method

Based on preliminary experiment, only 10% of Cu loading was selected to describe the effect of synthesis method on arsenic removal. A comparison of arsenic removal was considered under different synthesis methods, in-stu and impregnation techniques. Figure 4.13 presents profiles of normalized total arsenic concentration, pH and total dissolved Fe along with reaction time. The As(III) removal was more than 80% after 25 min of the reaction, with $(Cu\text{-}Fe)_{IM}$ while 60% was removed with $(Cu\text{-}Fe)_{IS}$. Considering As(V) removal, 73% and 90% of total arsenic disappeared after 10 min of reaction, with $(Cu\text{-}Fe)_{IS}$ and $(Cu\text{-}Fe)_{IM}$, respectively. It is obvious that As(V) tends to be removed easier than As(III) due to the different electrostatic attraction of two arsenic species (Tanboonchuy et al., 2011a). This might be due to As(V) shows the opposite charge with Cu-Fe particles, while As(III) acts as neutral charge at the observed pH. In addition, $(Cu\text{-}Fe)_{IM}$ was observed to be more effective than $(Cu\text{-}Fe)_{IS}$ with ≈ 17-20% removal efficiency in removing As(III).

During the reaction, pH and total dissolved iron have been monitored, as presented in Figure 4.13(b) and (c). The pH profiles of solutions were no significant differences when using $(Cu\text{-}Fe)_{IS}$ and $(Cu\text{-}Fe)_{IM}$. This was to confirm that no effect on pH range was observed by using different synthesis method of Cu-Fe. Focusing on total dissolved iron in the system, the profile of total dissolved iron using $(Cu\text{-}Fe)_{IM}$ was less than that of using $(Cu\text{-}Fe)_{IS}$ in both cases of As(III) and As(V) removal. The presence of iron in solution could related to the formation of iron (hydr)oxides from Fe^{2+} and Fe^{3+} according to Equation (4.1)-(4.8) (Giasuddin et al., 2007; Huang and Zhang, 2005; Lackovic et al., 2000; Li et al., 2006b; Mishra and Farrell, 2005). Afterwards, arsenic can absorbed onto those iron (hydr)oxides through inner- and/or outer-sphere complexes (Bang et al., 2005).

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \qquad (4.1)$$

$$2Fe^0 + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^- \qquad (4.2)$$

$$4Fe^{2+} + 2H_2O + O_2 \rightarrow 4Fe^{3+} + 4OH^{-} \quad (4.3)$$

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_{2\downarrow} \quad (4.4)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3\downarrow} + 3H^{+} \quad (4.5)$$

$$6Fe(OH)_{2\downarrow} + O_2 \rightarrow 2Fe_3O_{4\downarrow} + 6H_2O \quad (4.6)$$

$$Fe(OH)_{3\downarrow} + 3H^{+} \rightarrow FeOOH_{\downarrow} + H_2O \quad (4.7)$$

$$FeOOH_{\downarrow} + Fe^{2+} \rightarrow Fe_3O_{4\downarrow} + 2H^{+} \quad (4.8)$$

According to the Standard Redox Potentials as shown in Eqns. (4.9) and (4.10), the standard potential for copper is about 0.34 volts, which was higher than that of iron (-0.44 volts). The greater redox potential of copper, resulting in Cu^{2+} in form of CuO can accelerate the oxidation of Fe^{0} to Fe^{2+}, then it was further oxidized into Fe^{3+} and form iron (hydr)oxides as mentioned earlier. Expected copper species of Cu^{2+} and iron species of Fe^{2+} after apply in the solution were confirmed by XANES spectra (explained in Section 4.1.5).

$$Cu^{2+} + 2e^{-} \rightarrow Cu(s) \qquad E = 0.34\ V \quad (4.9)$$

$$Fe^{2+} + 2e^{-} \rightarrow Fe(s) \qquad E = -0.44\ V \quad (4.10)$$

In addition, it was proven that Cu was formed on the surface for $(Cu\text{-}Fe)_{IM}$ material, as previous explained by SEM-EDX technique in section 4.1.2. As expected, no Cu distribute much on the $(Cu\text{-}Fe)_{IS}$ surface. An intra-particle mass diffusion could be one of the factors of the scarification of Fe using $(Cu\text{-}Fe)_{IS}$. The higher Cu dispersion on the surface led to higher corrosion rate of Fe^{0}. Consequently, dissolved iron readily precipitate in form of iron (hydr)oxides (Jegadeesan et al., 2005), so the faster removal rate of both As(V) and As(III) were observed in the initial stage of using $(Cu\text{-}Fe)_{IM}$. Moreover, arsenic can be removed through co-precipitation with Fe^{2+} and Fe^{3+} ions in the solution (Tyrovola et al., 2007).

The mechanisms of iron oxidation by copper and arsenic removal were proposed in Figure 4.14 and 4.15, respectively. For fresh Cu-Fe, Cu^{0} appears on NZVI surface (see Figure 4.14). When Cu-Fe was induced into removal system, Cu^{0}

will be oxidized to Cu^{2+} as CuO formation. Then, Cu^{2+} act as an electron transfer to accept electron from Fe^0, resulting in Fe^{2+} formation. The reaction goes continuously until the precipitate covers all the copper particles (Hu et al., 2010). Possible mechanism of arsenic removal, including precipitation and co-precipitation is illustrated in Figure 4.15. Since Cu^{2+} can accelerate iron corrosion, more arsenic removal through precipitation and co-precipitation was observed.

To further address the feasibility of the studied bimetallic process, it was applied in the field groundwater for its capacity to remove arsenic. Both $(Cu\text{-}Fe)_{IS}$ and $(Cu\text{-}Fe)_{IM}$ were tested for the removal of both As(V) and As(III) in arsenic-spiked field groundwater. The removal process was carried out in the gas bubbling system. The concentration profiles of As(V) and As(III) and their total dissolved iron are shown in Figure 4.16. Considering arsenic removal profile, the disappearance of both As(III) and As(V) with $(Cu\text{-}Fe)_{IM}$ were observed to be faster than that with $(Cu\text{-}Fe)_{IS}$, especially at the initial stage. This could be confirmed that Cu deposited on NZVI surface in $(Cu\text{-}Fe)_{IM}$ can induce Fe corrosion in the faster rate than $(Cu\text{-}Fe)_{IS}$. Under the removal period of 60 min, the performance of As(III) removal in groundwater was ca. 75%, which was lower than that in arsenic-spiked DI water, due to the presence of background species in groundwater (Tanboonchuy et al., 2012). Similarly, the higher As(III) and As(V) removal with $(Cu\text{-}Fe)_{IM}$ compared with $(Cu\text{-}Fe)_{IS}$, could be explained by total dissolved iron profiles. The total dissolved iron with $(Cu\text{-}Fe)_{IM}$ was lower than that with $(Cu\text{-}Fe)_{IS}$. This implies that arsenic tends to be adsorbed on the iron (hydr)oxide surface dissolved from metallic Cu-Fe, as has been previously explained.

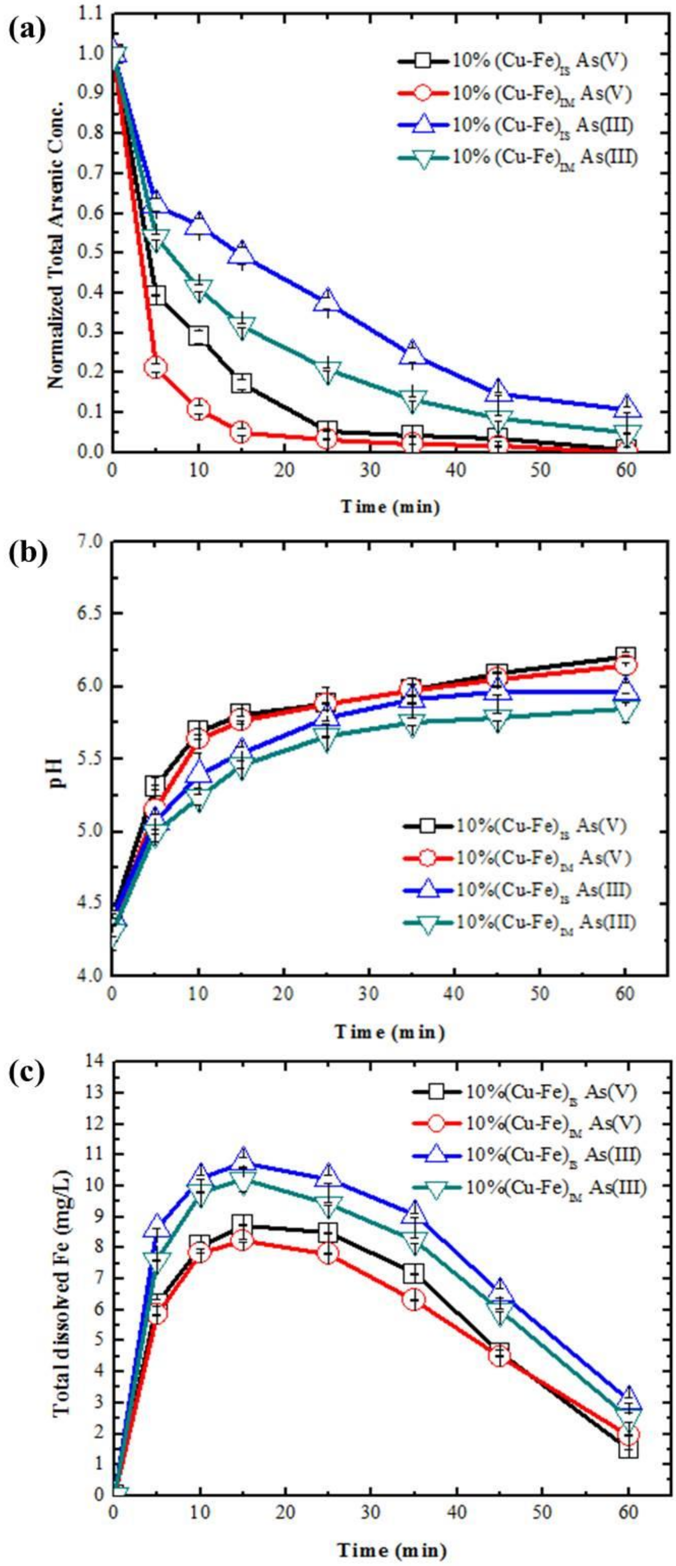

Figure 4.13 Comparison of As(III) and As(V) removal under different synthesis methods (in-situ and impregnation method), pH and total dissolved iron profiles

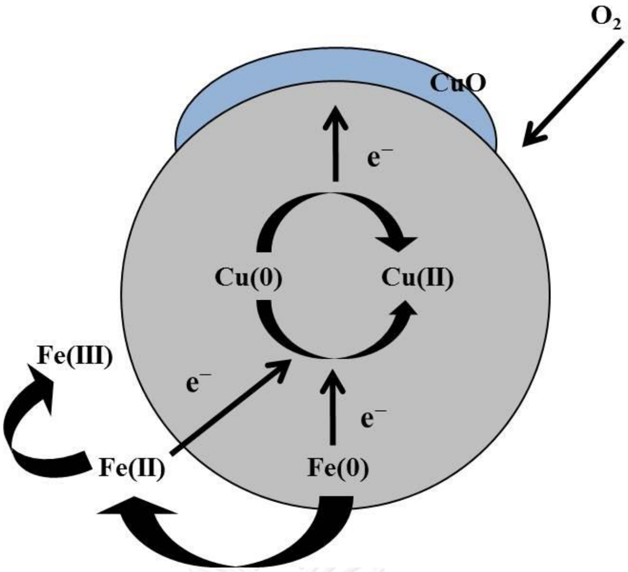

Figure 4.14 Mechanism of Cu-Fe bimetal accelerated Fe oxidation

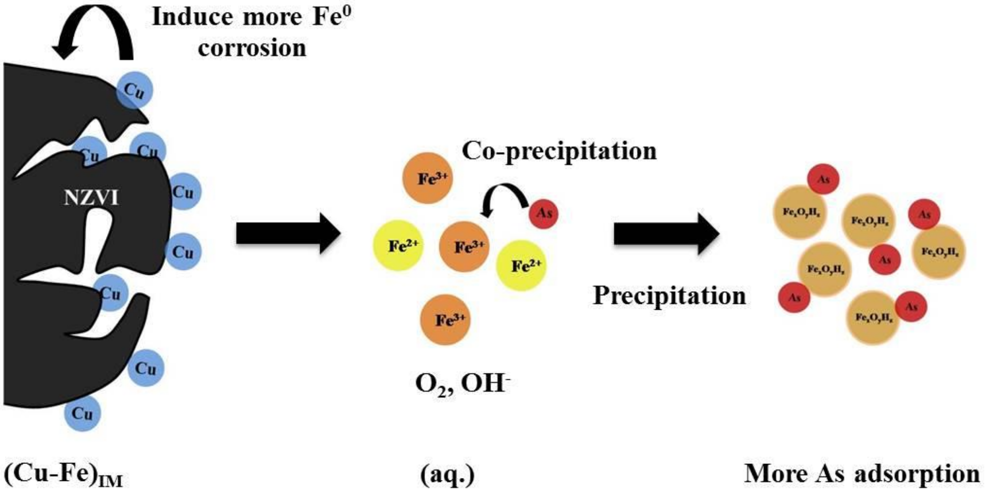

Figure 4.15 Mechanism of As removal by using $(Cu\text{-}Fe)_{IM}$

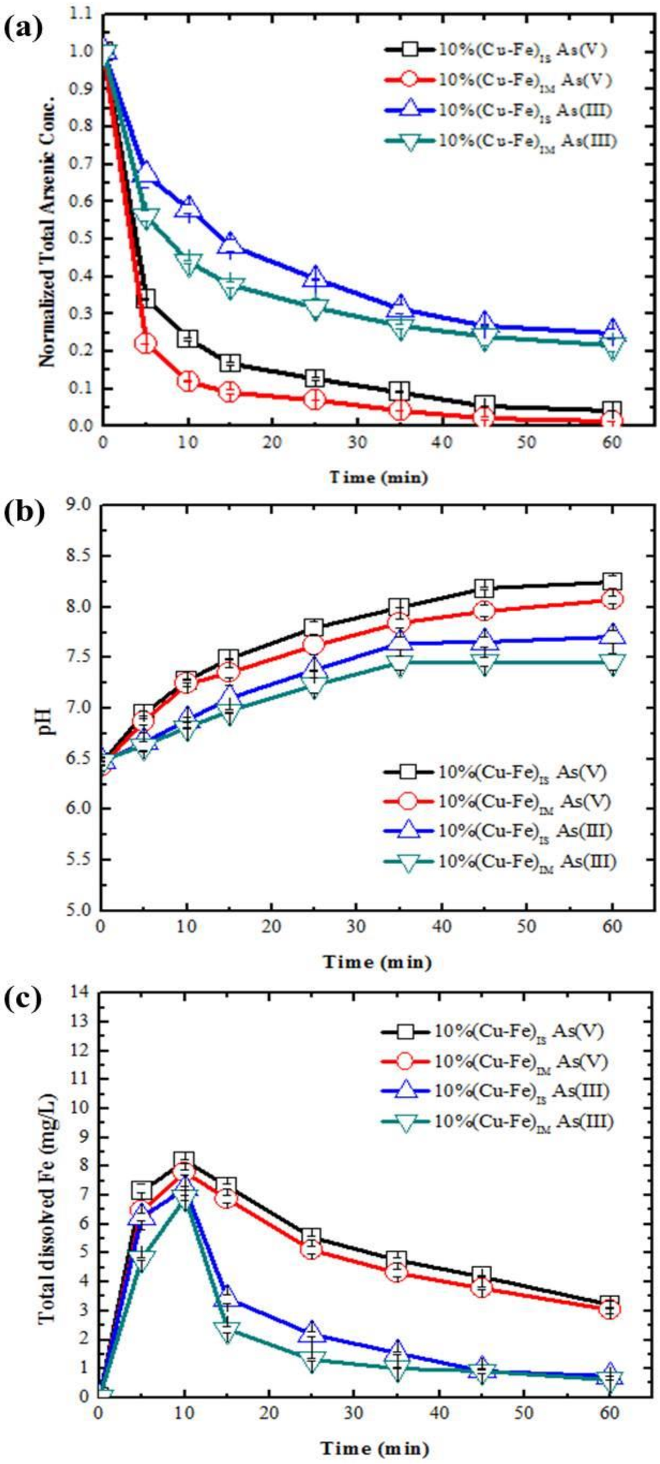

Figure 4.16 Effect of different synthesis methods of Cu-Fe in groundwater condition on: (a) normalized arsenic concentration, (b) pH profile, and (c) total dissolved iron

4.3.2 Effect of percent copper loading

For bimetallic nanoparticles, the ratio of incorporated of two metals is important for its reactivity (Liu et al., 2001). Impregnation method for bimetallic synthesis was proven to enhance arsenic removal significantly. Therefore, (Cu-Fe)$_{IM}$ with various amount of different Cu loadings of 2.5, 5, 10, 20, 30% (w/w) on NZVI was prepared, comparing with pristine NZVI to removal arsenic as shown in Figure 4.17. The As(V) removal using all six different ratio of Cu was quite similar to each other, but arsenic removal seem to be retarded at the initial by using 20% and 30%(Cu-Fe)$_{IM}$. The As(III) removal profiles, shown in Figure 4.17(b), are clearly different from As(V). All loadings of Cu-Fe showed higher performance of arsenic removal (> 90%) than that of NZVI. Arsenic was totally removed in the final when 10%, 20%, and 30%(Cu-Fe)$_{IM}$ were used. Since Cu on NZVI surface affect significantly on Fe corrosion rate as mentioned in Section 4.3.1. According to the results, it can be indicated that the higher content of Cu loading on NZVI may enhance such corrosion mechanism. However, it should be noticed that using 20 and 30%(Cu-Fe)$_{IM}$ showed the higher total dissolved iron than 10%(Cu-Fe)$_{IM}$ as seen in Figure 4.17(c) and (d). It means that the over dosage of Cu loading could act as the protection layer on NZVI, which can inhibit the NZVI corrosion mechanism. This may be due to that excessive Cu loading could cause Cu particles agglomeration, resulting in negative effect on the reactivity of NZVI (Mossa Hosseini et al., 2011). Based on high removal efficiency both of As(III) and As(V), 10% (w/w) of Cu on NZVI was chosen as the best condition for Cu-Fe synthesis.

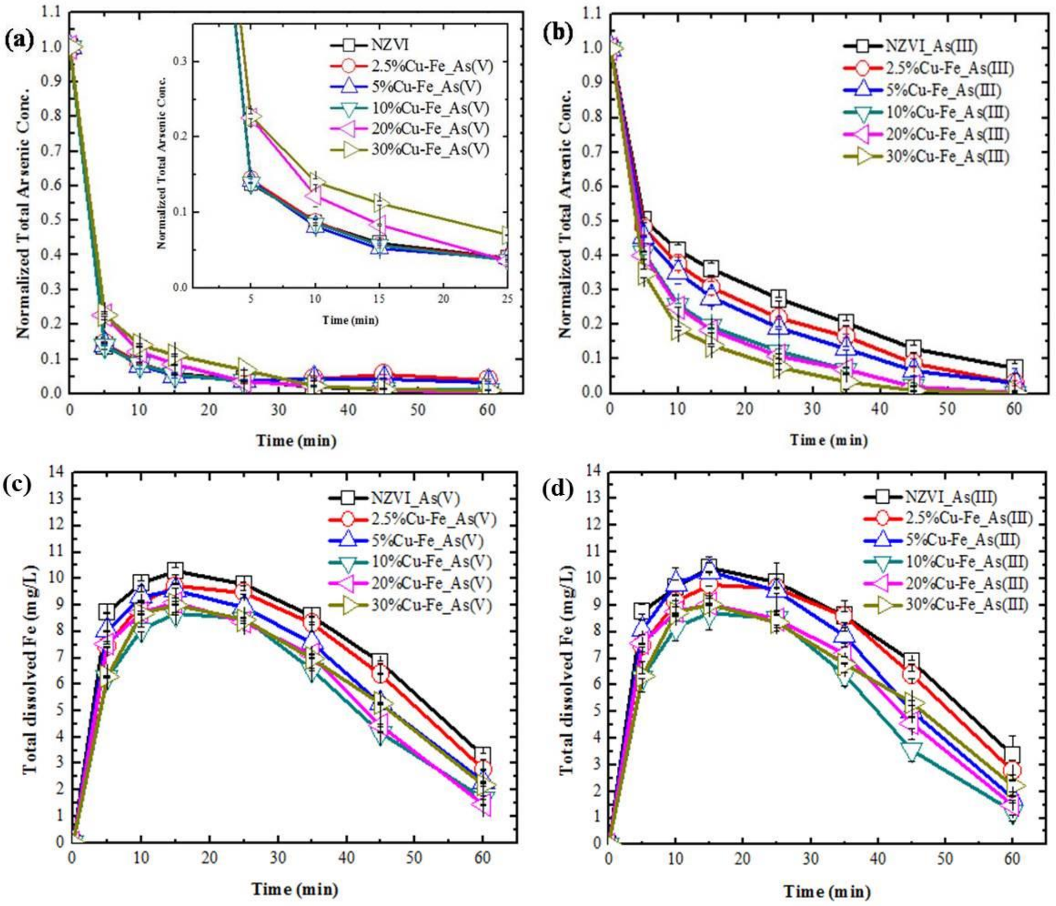

Figure 4.17 Effect of copper loading in bimetallic $(Cu\text{-}Fe)_{IM}$ in the presence of gas bubbling on: (a) As(V) removal, (b) As(III) removal, (c) total dissolved iron in As(V) solution, and (d) total dissolved iron in As(V)

4.3.3 Effect of mixed arsenic species in various As(III) versus As(V) ratio

In this experiment, two different synthesis methods of Cu-Fe bimetal ((Cu-Fe)$_{IS}$ and (Cu-Fe)$_{IM}$) and NZVI were tested in known mixtures of arsenic. As shown in Figure 4.18, the removal efficiencies by using bimetal range from 86 to 97% for (Cu-Fe)$_{IS}$ and 95 to 100% for (Cu-Fe)$_{IM}$. It seems that the removal of As(V) in the solution is easier than the solution blended with As(III). The total arsenic removal from the highest to the lowest is in the following sequence with respect to As(III)/As(V) ratios of 0:10, 3:7, 5:5, 7:3, and 10:0. The results show that using both of (Cu-Fe)$_{IS}$ and (Cu-Fe)$_{IM}$ were observed to remove mixed arsenic in higher capacity than the NZVI. To ensure the previous results, (Cu-Fe)$_{IM}$ shows obviously higher performance of mixed arsenic removal than the (Cu-Fe)$_{IS}$. The removal percentage of different As(III)/As(V) ratios by using (Cu-Fe)$_{IS,}$ (Cu-Fe)$_{IM}$, and NZVI were compared to be seen clearly in Table 4.1.

As mentioned in section 4.3.1, the mechanism of arsenic removal by the NZVI particles involves not only adsorption but also precipitation and co-precipitation (Anotai et al., 2010; Lackovic et al., 2000). The nano zero-valent iron-based copper particles are assumed to have similar mechanism as the NZVI. The reason for easier removal of As(V) than As(III) might because the As(III) was removed by co-precipitation to a lower degree than As(V) since ferric arsenate complex is less water soluble than ferric arsenite complex (Geroni et al., 2009; Hering et al., 1997; Tyrovola et al., 2007). Also, ferric iron co-precipitation of arsenite is less effective due to London Van der Waals bonding (Pierce and Moore, 1982). The removal efficiency of As(V) was always higher than that of As(III) for all cases, as seen in Figure 4.21. In details, the mechanism of co-existence for arsenic removal in both species could be explained by Figure 4.19. In the process of co-precipitation process of ferrous or ferric ion and As(V), it was expected to create the new adsorptive site for As(III). As seen in Figure 4.20, As(V) is readily to precipitate with iron when the Eh/pH conditions are maintained to effect that removal (Vance, 1995). Therefore, the higher the ratio of As(V) in solution, resulting in the higher the total arsenic removal.

The removal of individual profiles of As(III) and As(V) are evidenced the results of total arsenic removal as shown in Figure 4.21. In all cases of different ratio of As(III) and As(V), the removal percentage of As(V) was apparently higher than that of As(III). In addition, it should be noticed that mixed arsenic removal by using $(Cu\text{-}Fe)_{IM}$ shows the higher efficiency than using $(Cu\text{-}Fe)_{IS}$ for both of As(III) and As(V) species. As a result, it can confirm the higher performance of $(Cu\text{-}Fe)_{IM}$ material as mentioned earlier in section 4.3.1.

Table 4.1 Percentage of total arsenic removal of different As(III)/As(V) ratios

Percentage of arsenic removal **As(IIII)/As(V) ratios**	$(Cu\text{-}Fe)_{IS}$	$(Cu\text{-}Fe)_{IM}$	NZVI
10:0	89.3	95.1	88.7
7:3	93.3	95.9	90.7
5:5	93.8	96.1	92.5
3:7	95.7	97.8	93.7
0:10	98.1	100	97.0

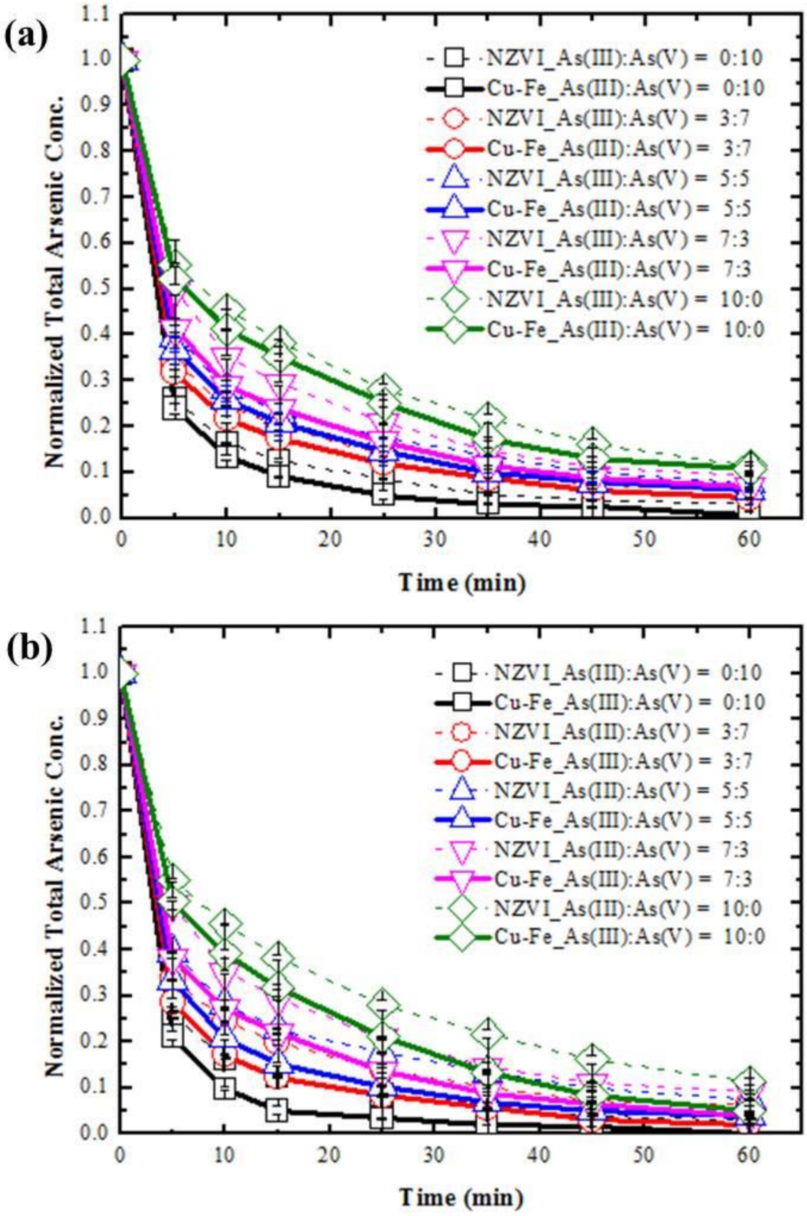

Figure 4.18 Comparison of monometal (NZVI) and bimetal (Cu-Fe) effect on arsenic removal with different As(III)/As(V) ratios: (a) In-situ synthesis; (b) Impregnation synthesis

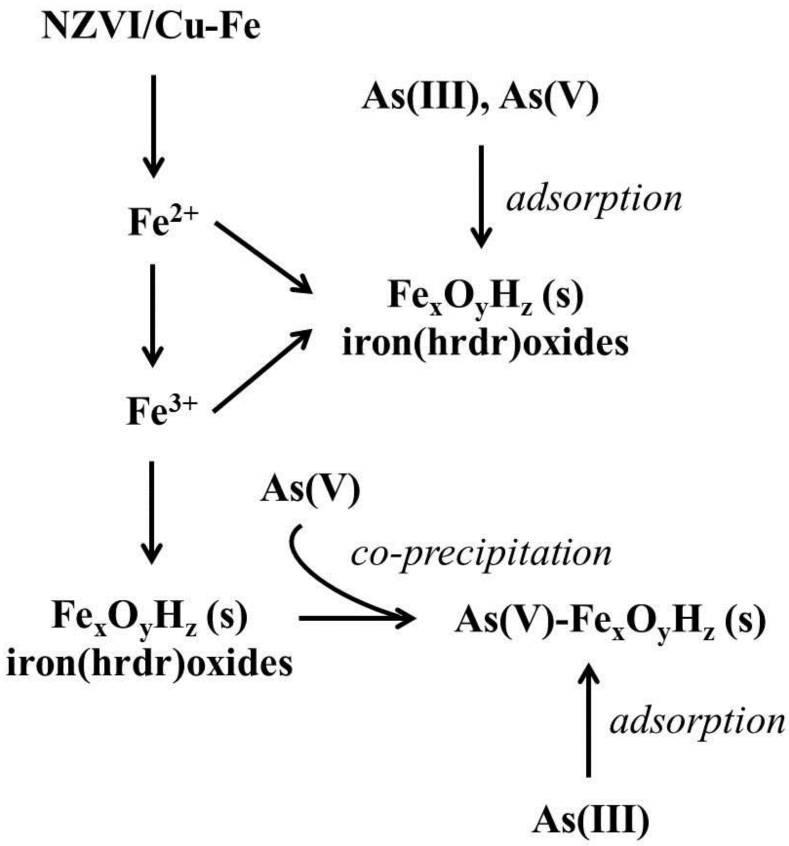

Figure 4.19 Mechanism of arsenic adsorption for As(III) and As(V)

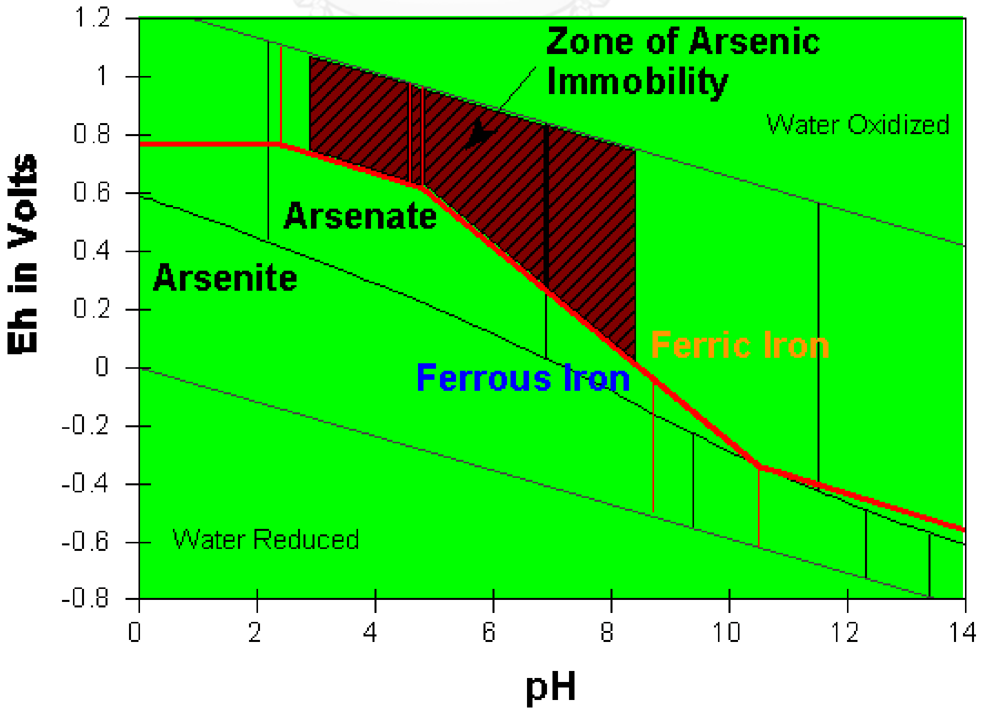

Figure 4.20 Eh/pH relationships for arsenic and iron systems (Vance, 1995)

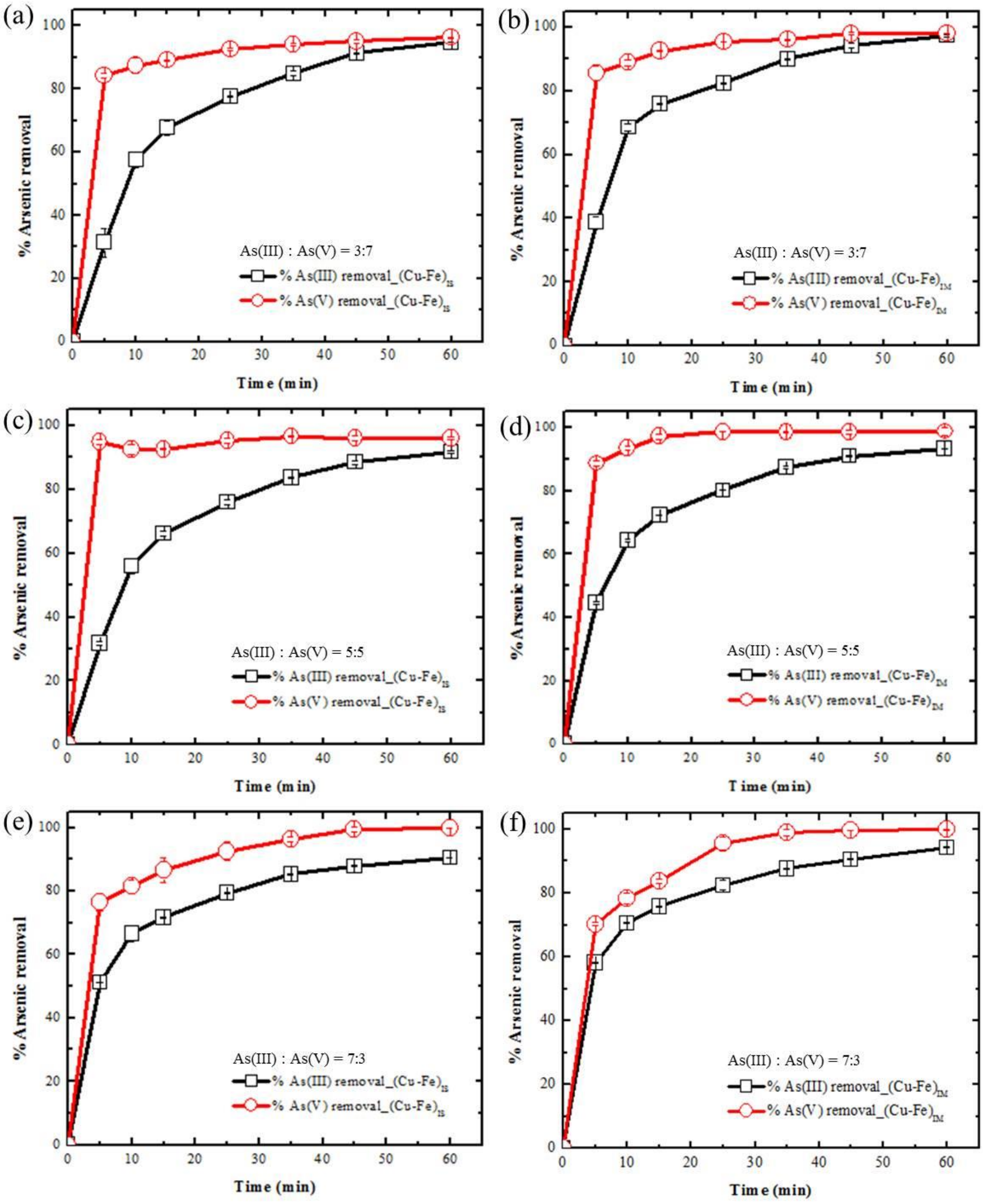

Figure 4.21 Individual profiles of percent removal at different ratio of arsenic species and synthesis method: (a) 3:7 and $(Cu\text{-}Fe)_{IS}$, (b) 3:7 and $(Cu\text{-}Fe)_{IM}$, (c) 5:5 and $(Cu\text{-}Fe)_{IS}$, (d) 5:5 and $(Cu\text{-}Fe)_{IM}$, (e) 7:3 and $(Cu\text{-}Fe)_{IS}$, and (f) 7:3 and $(Cu\text{-}Fe)_{IM}$

4.3.4 Effect of background species

4.3.4.1 Comparison of arsenic removal in DI water and groundwater

The 10% $(Cu\text{-}Fe)_{IM}$ was used to compare the removal efficiency in both deionized water and groundwater. The arsenic was spiked into field groundwater and deionized water sample to obtain its initial arsenic concentration of 1000 µg/L. For both As(III) and As(V) removal in Figure 4.22(a), the arsenic removal performance in deionized water was higher than that in groundwater. This should be the reason of the presence of background species in field groundwater (see Table 4.2). Some background species, which were detected in this field groundwater i.e. humic acid (HA), bicarbonate (HCO_3^-), phosphate (PO_4^{3-}), etc. might inhibit mechanism of arsenic removal (Biterna et al., 2007; Jegadeesan et al., 2005; Mak and Lo, 2011). As reported, humic acid (HA) tend to compete to adsorbed onto the surface of iron (hydr)oxides (Giasuddin et al., 2007; Xie and Shang, 2005). Also phosphate (PO_4^{3-}), it can compete with arsenic for active sites on adsorbent surface (Dong et al., 2012; Meng et al., 2002). In addition, it should be noted that high concentration of bicarbonate (HCO_3^-) and chloride (Cl^-) were found in this field groundwater as can be seen in Table 4.2. The phosphate (PO_4^{3-}), and was reported to reduce performance of arsenic removal (Su and Puls, 2001), while chloride (Cl^-) can enhance arsenic removal capacity (Klausen et al., 2001). As a result of two contrast effect, arsenic removal in groundwater for both As(III) and As(V) species was slightly lower than that in deionized water.

In addition, the initial dissolved oxygen in field groundwater was lower than that in deionized water as seen Figure 4.22(b), resulting in lower oxidizing rate of NZVI to form iron (oxy)hydroxides, which favor adsorptive of arsenic (Farquhar et al., 2002; Manning et al., 2002). Therefore, it can be noted that arsenic removal in field groundwater shows the significant effect on arsenic removal by $(Cu\text{-}Fe)_{IM}$ combined with gas bubbling system. However, gas bubbling system can still be used to remove arsenic in groundwater to low level, especially for As(V). The effect of individual and mixed background species on arsenic removal should be study further.

Table 4.2 Chemical characteristics of the field groundwater used in this study

Ion Species	**Concentration**
Total organic carbon (ppm)	5.04
Calcium (ppm)	25.56
Sulfate (ppm)	40.1
Phosphate (ppm)	1.76
Alkalinity (ppm as $CaCO_3$)	649
Chloride (ppm)	259

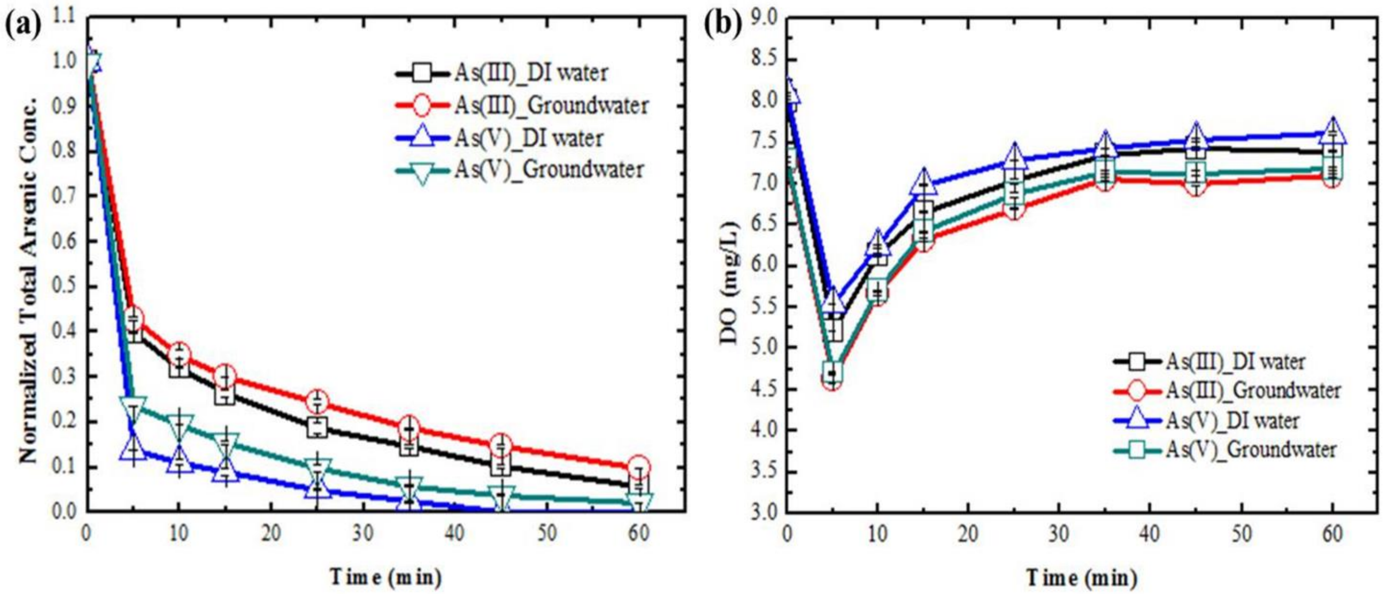

Figure 4.22 Arsenic removal by $(Cu\text{-}Fe)_{IM}$ in deionized water and groundwater

4.3.4.2 Single ion system

According to section 4.3.4.1, arsenic removal in field groundwater was found in low efficiency comparing with DI water due to the competitive of arsenic species and some background for adsorptive sites. It could be indicated that the impact of background species on arsenic removal is important in field application**.** To simulate groundwater environment, several common ions such as humic acid (HA), calcium (Ca^{2+}), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), bicarbonate (HCO_3^-), and chloride (Cl^-) were selected to evaluate their effects on arsenic removal. The spiked background species in arsenic solution were explored by using batch process. The arsenic removal profiles for both As(III) and As(V) in the presence of selected background species with different levels of concentration were shown by divided into promoting effect and inhibiting effect in Figure 4.23 and 4.24, respectively.

Figure 4.23(a) indicates that both of As(III) and As(V) removal efficiency slightly increase in the presence of chloride (Cl^-). No significant of arsenic removal increasing was observed when chloride (Cl^-) concentration was increased. Many researchers reported that the presence of chloride (Cl^-) could be enhanced the arsenic removal performance by inducing pitting corrosion of iron surface, resulting in reactive area for arsenic adsorption increasing (Gotpagar et al., 1999; Kim and Pyun, 1996; Klausen et al., 2001).

As shown in Figure 4.23(b), the presence of calcium (Ca^{2+}) did not affect the removal of arsenic at the initial period. The removal efficiency of both arsenic species increased after 25 min in the presence of calcium (Ca^{2+}), especially for As(III) removal. As well know, the solution pH increased when the reaction was in process. It indicated that arsenic removals in the presence of calcium (Ca^{2+}) were increased when pH increased. Enhancement of arsenic removal by calcium (Ca^{2+}) in adsorption process was observed at high pH in many researches. It can be explained by the fact that the specific adsorption of calcium (Ca^{2+}) can increased the surface positive charge and led to arsenic remained on the adsorptive site for As(V) removal (Smith et al., 2002; Wilkie and Hering, 1996). Moreover, calcium (Ca^{2+}) ion can compress and reduce the thickness of double layer, which can help to reduce charge exclusion and create accessible internal pore (Masue et al., 2006). For As(III) removal, the presence of calcium (Ca^{2+}) could be enhance the arsenic removal performance with more precipitation and surface charge of precipitates increasing (Smith et al., 2002; Wilkie and Hering, 1996). There is another explanation that calcium (Ca^{2+}) can form a complex with surface sites (SS) of iron (oxy)hydroxides, which ready to form the bridge between adsorbent surface and the negatively charged arsenic (Guan et al., 2009; Tanboonchuy et al., 2012), as shown in Eqns. (4.11) and (4.12).

$$Ca^{2+} + 2SS{-}OH \longleftrightarrow (SSO^{-})_2{-}\,Ca^{2+} + 2H^{+} \qquad (4.11)$$

$$Ca^{2+} + 2SS{-}OH + H_2O \longleftrightarrow SSO^{-}{-}\,Ca{-}{}^{\bullet}OH^{+} + 2H^{+} \qquad (4.12)$$

As presented in Figure 4.23(c), the presence of sulfate (SO_4^{2-}) accelerated the removal of As(V), while slightly retarded the removal of As(III) . Within the first 30 min of the removal process, the increase of arsenic removal were observed about 10% for As(V). The presence of relatively high concentration of sulfate (SO_4^{2-}) can increase the arsenic removal by acceleration of As(V) precipitate in FeAsS form according to Eqn. (4.13) (Ramaswami et al., 2001; Sun et al., 2006).

$$14Fe^{2+} + SO_4^{2-} + AsO_3^{-} + 14H^{+} \longleftrightarrow FeAsS + 13Fe^{3+} + 7H_2O \qquad (4.13)$$

Sulfate (SO_4^{2-}) was reported to decrease the As(III) sorption at pH below 7, with the largest decrease at the lowest pH (Su and Puls, 2001; Wilkie and Hering, 1996). This phenomenon might be due to the electrostatic repulsion force between SO_4^{2-} and negatively charge of As(III) species. However, the inhibiting effect of sulfate (SO_4^{2-}) on As(III) removal was observed only slightly at the initial period (first 30 min) since pH increasing belong process.

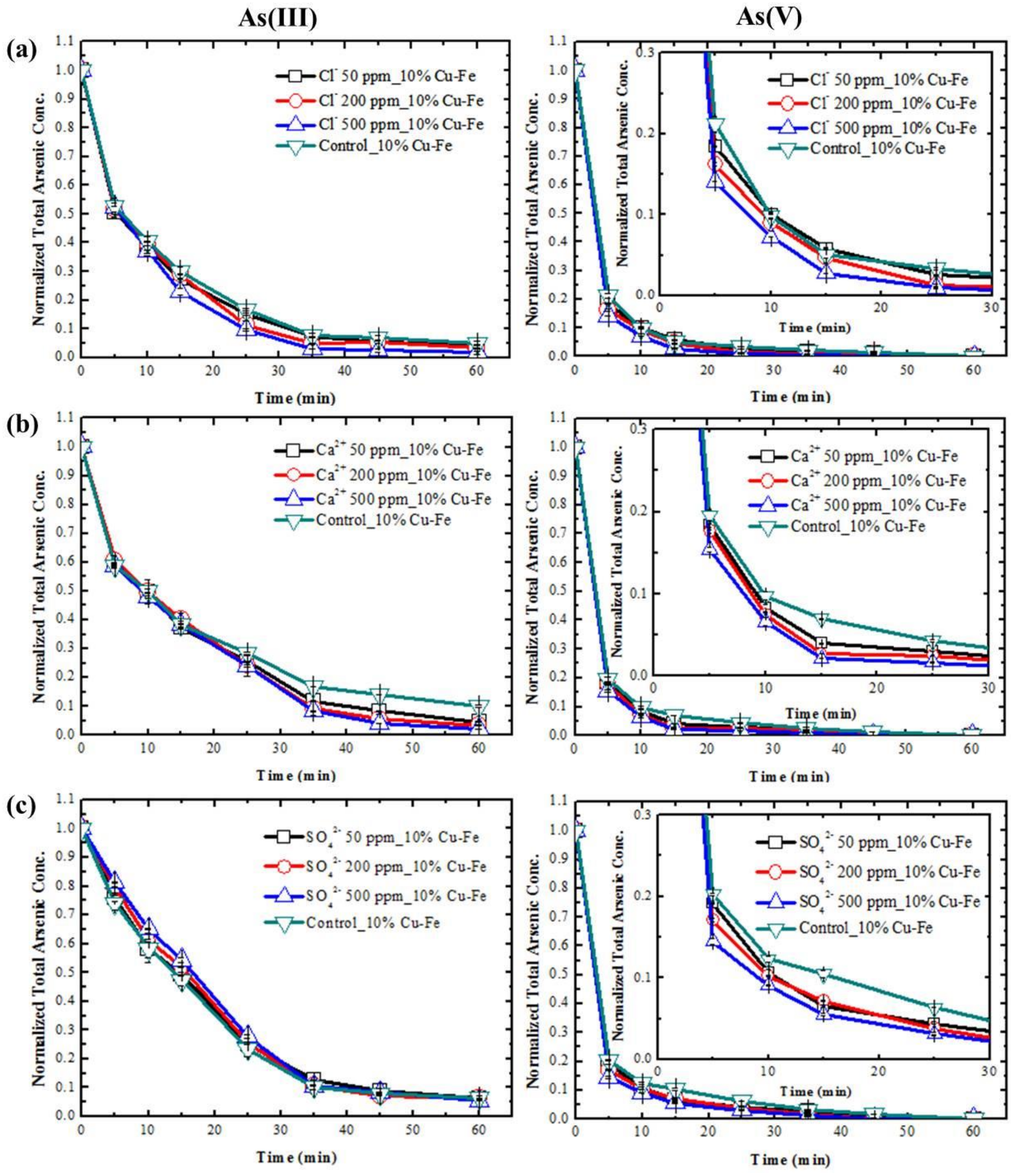

Figure 4.23 Presence of single background species on As(III) and As(V) removal with different level concentration of (a) Cl^-, (b) Ca^{2+}, and (c) SO_4^{2-}

The presence of humic acid (HA) decreased the removal performance of both As(III) and As(V), with the higher degree for As(III) removal. When the concentration of humic acid HA increases from 0.5 to 5 mg/L, the removal efficiencies of arsenic slightly decrease from 96% to 91% for As(III), as illustrated in Figure 4.24(a). In the presence of humic acid (HA), the Fe^{3+} that was oxidized from Fe^{2+} can react with humic acid (HA) to form Fe-humate complex (Giasuddin et al., 2007; Mak and Lo, 2011). Since such complex formation mechanism, the iron (oxy)hydroxides was decreased, leading to arsenic adsorption onto the iron (oxy)hydroxides decreasing. Another reason is that the humic acid, which is a typical natural organic matter (NOM), can bind to iron (oxy)hydroxides surface, resulting in the available of adsorptive surface of iron (oxy)hydroxides for arsenic was decreased (Kong et al., 2014).

Figure 4.24(b) shows the arsenic removal efficiency in the presence of different concentrations of phosphate (PO_4^{3-}). The presence of phosphate (PO_4^{3-}) significantly decreased arsenic removal, both As(III) and As(V) through the competition for sorption sites at the surface of iron (oxy)hydroxides (Dong et al., 2012; Su and Puls, 2001). As well known that the chemical properties of phosphate (PO_4^{3-}) resembles As(V) since both arsenic and phosphate are in same group of periodic table. The As(III) also is possible displaced by phosphate (PO_4^{3-}). Therefore the ligand exchange mechanism was observed for the displacement of phosphate (PO_4^{3-}) instead of arsenic, resulting in the performance of arsenic adsorption decreasing, apparently in As(V) removal (Antelo et al., 2005). Although As(V) have a relatively strong affinity for iron (oxy)hydroxides surface, but the affinity between phosphate (PO_4^{3-}) and iron (oxy)hydroxides is more stronger (Hingston et al., 1971; Meng et al., 2002). In addition, there is the report that the arsenic adsorption decreases as the pH increases (Antelo et al., 2005).

The effect of bicarbonate (HCO_3^{-}) on arsenic was shown in Figure 4.24(c). The arsenic removal was obviously inhibited in the presence of bicarbonate (HCO_3^{-}), especially in As(III) removal. The decrease of arsenic removal in the presence of bicarbonate (HCO_3^{-}) has been reported by many researchers, possibly due to the formation of protonated and nonprotonated inner-sphere monodentate surface complex with iron (oxy)hydroxides (Biterna et al., 2010; Biterna et al., 2007; Su and Puls, 2001). Furthermore, bicarbonate (HCO_3^-) can directly react with Fe^{2+}, which is the primary product of Cu-Fe oxidation, to form iron carbonate ($FeCO_3$) by the two step process as depicted in Eqs (4.14) and (4.15) (Heuer and Stubbins, 1999). This formed iron carbonate ($FeCO_3$) resulted in the decrease of arsenic adsorption performance.

$$Fe^{2+} + 2HCO_3^- \longleftrightarrow Fe(HCO_3)_2 \qquad (4.14)$$

$$Fe(HCO_3)_2 \longleftrightarrow FeCO_3 + CO_2 + H_2O \qquad (4.15)$$

Therefore, the pre-treatment of humic acid (HA), phosphate (PO_4^{3-}), and bicarbonate (HCO_3^-) in groundwater should be carried out before arsenic treatment to remain the performance of arsenic removal by Cu-Fe bimetal.

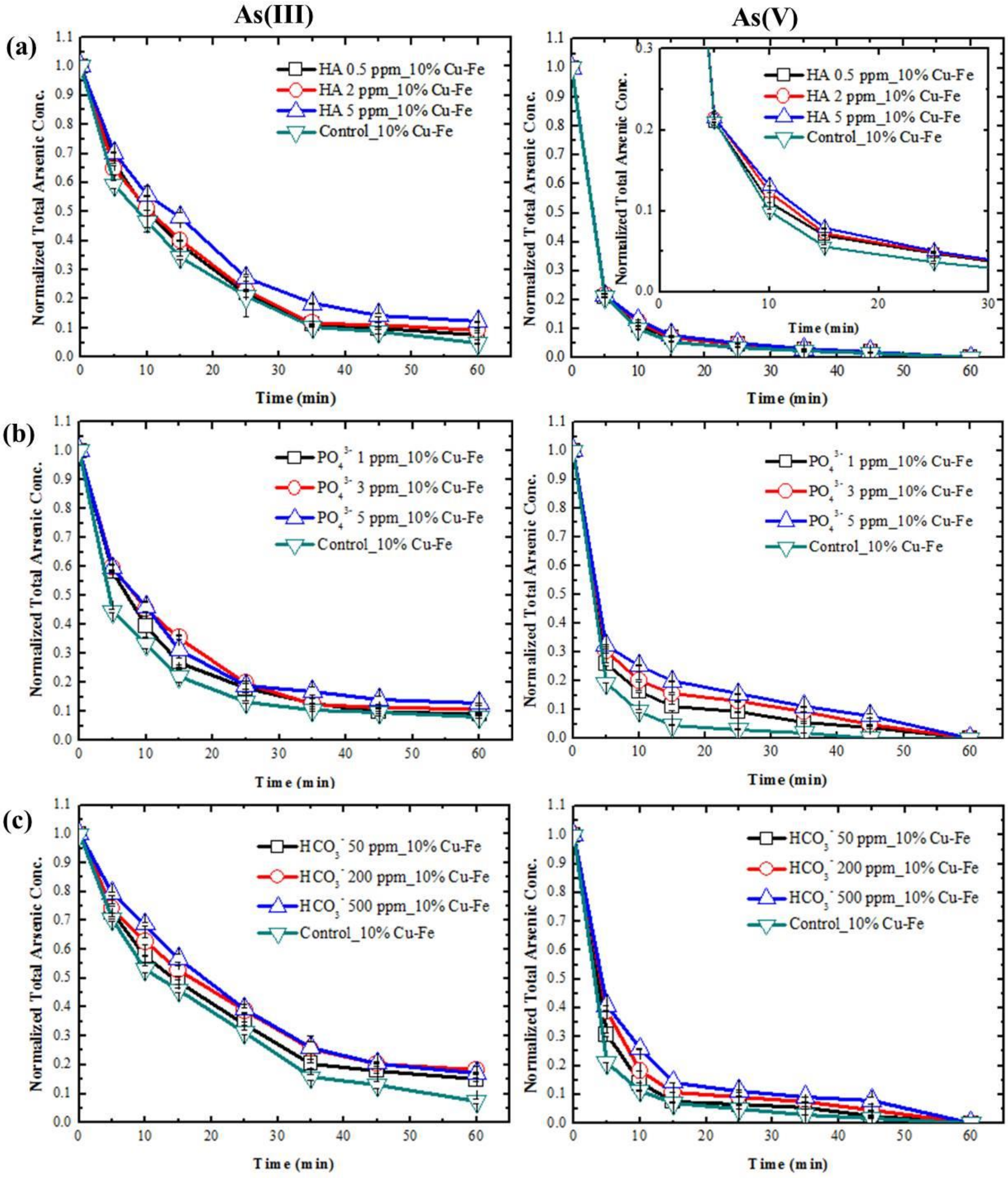

Figure 4.24 Inhibiting effect of single background species on As(III) and As(V) removal with different level concentration of (a) HA, (b) PO_4^{3-}, and (c) HCO_3^-

4.3.4.3 Multi-ion system

The experiment design of each stated species were shown in Section 3.5.4.1 (see Table 3.1). The percentage of arsenic removal performance by using (Cu-Fe)$_{IM}$ in the presence of low and high concentrations of six selected background species were exhibited in Table 4.3. Similar behavior with single ion system in previous experiment was exhibited. For multi-ions system, ion concentration increasing from low to high resulted in inhibition of arsenic removal in the presence of humic acid (HA), phosphate (PO_4^{3-}), and bicarbonate (HCO_3^-), and leading to enhancing of arsenic removal in the presence of chloride (Cl^-), calcium (Ca^{2+}), and sulfate (SO_4^{2-}). The increase of bicarbonate (HCO_3^-) concentration from 50 to 500 ppm can decrease As(III) removal by 3.99%, whereas increasing phosphate (PO_4^{3-}) from 1 to 5 ppm lead to the decrease of As(V) removal by 2.06%. It can be indicated that bicarbonate (HCO_3^-) is the main inhibiting effect for As(III) and phosphate (PO_4^{3-}) is the main inhibiting effect for As(V). These results agree with that in case the single species system, which reveal that arsenic removal obviously decreased in the presence of bicarbonate (HCO_3^-) and phosphate (PO_4^{3-}) for As(III) and As(V) removal, respectively.

Interestingly, arsenic removal in the presence for the single ion system of sulfate (SO_4^{2-}) shows the different results for the muti-ions system. The presence of sulfate (SO_4^{2-}) plays an inhibiting role for both of As(III) and As(V) removal in the single ion system, but the slightly promoting role was observed in the muti-ions system. The main promoting effect could be the effect of calcium (Ca^{2+}), which can increased As(III) removal by 1.23% when calcium (Ca^{2+}) concentration increase from 50 to 500 ppm. For As(V) removal, no significant role was observed since the completely removal in the final period.

In summary, the estimation of the inhibiting effects are in the order as follows: bicarbonate (HCO_3^-) > phosphate (PO_4^{3-}) > humic acid (HA) for As(III) removal, and phosphate (PO_4^{3-}) > bicarbonate (HCO_3^-) > humic acid (HA) for As(V) removal. In addition, the estimation of promoting effects are in the order as follows: calcium (Ca^{2+}) > chloride (Cl^-) > sulfate (SO_4^{2-}) for As(III) removal.

Table 4.3 Percentage of As(III) and As(V) removal in the presence of low and high concentration of selected ion species

Chemical species	**No ion (Batch control)**	**HA**		**PO_4^{3-}**		**HCO_3^-**		**Cl^-**		**Ca^{2+}**		**SO_4^{2-}**	
		Low 0.5 ppm	High 5 ppm	Low 1 ppm	High 5 ppm	Low 50 ppm	High 500 ppm	Low 50 ppm	High 500 ppm	Low 50 ppm	High 500 ppm	Low 50 ppm	High 500 ppm
As(III)	95.27	94.87	92.87	92.60	89.36	91.64	87.65	96.14	97.28	96.98	98.21	95.98	95.81
As(V)	100	98.14	97.83	97.05	94.99	96.32	98.14	100	100	100	100	100	100

4.3.5 Kinetic Study

In order to determine the effect of initial arsenic concentration and kinetic model, the experiments were performed by arsenic concentrations of 1000 µg/L for both As(III) and As(V) species. As shown in Figure 4.25, As(V) removal was decreased faster than As(III) as the reason explained earlier. The final arsenic removal efficiencies of both arsenic species were over 90%.

From this reaction kinetics of arsenic removal by $(Cu\text{-}Fe)_{IM}$, the data presented in Figure 4.25 were further analyzed kinetic order by using the integration method. The linear form of pseudo-first order and pseudo-second order were shown in Eq. (4.16) and (4.17) (Banerjee et al., 2008), respectively.

$$\ln[As]_t = \ln[As]_0 - k_1 t \tag{4.16}$$

$$1/[As]_t = 1/[As]_0 + k_2 t \tag{4.17}$$

where $[As]_0$ and $[As]_t$ are the concentrations of arsenic at initial condition and time of reaction, t; k_1 and k_2 are the specific sorption rate constants for pseudo-first order and pseudo-second order reactions, respectively.

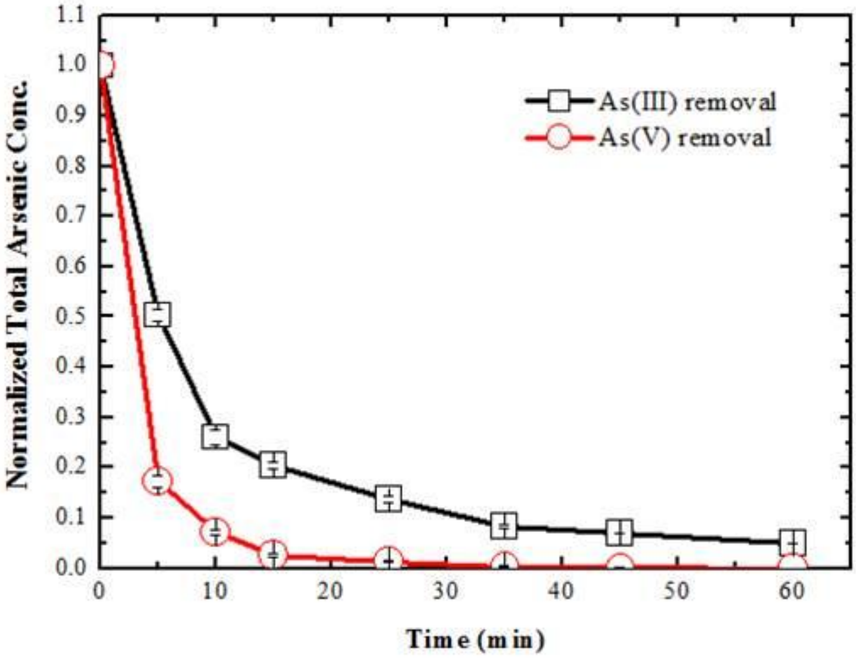

Figure 4.25 Effect of initial concentration on As(III) removal efficiency

In addition, the half-life of reaction ($t_{1/2}$) for pseudo-first order and pseudo-second order reactions can be calculated following to Eq. (4.18) and (4.19), respectively.

$$t_{1/2} = \ln 0.5/(-k_1) \qquad (4.18)$$

$$t_{1/2} = 1/([As]_0 k_2) \qquad (4.19)$$

Fitting the experimental data to these models as shown in Figure 4.26, various parameters were calculated and reported in Table 4.4. Among these models, the criterion for their applicability is based on the respective correlation coefficient (R^2). The results reveal that the removal system followed closely a pseudo-second order kinetic model for As(III), and pseudo-first order kinetic model for As(V). The rate constant (k) as calculated based on pseudo-second order removal kinetic for As(III) was 0.0003 $L\cdot(\mu g\cdot min)^{-1}$ and pseudo-first order removal kinetic for As(V) 0.1489 min^{-1}.

The kinetic constants of arsenic removal of previous studies were compared in different materials, and the information data were depicted in Table 4.5. It is clear that rate constant of pseudo-first order for As(V) and pseudo-second order for As(III) removal by $(Cu\text{-}Fe)_{IM}$ in this study were found to be much faster than that of other materials.

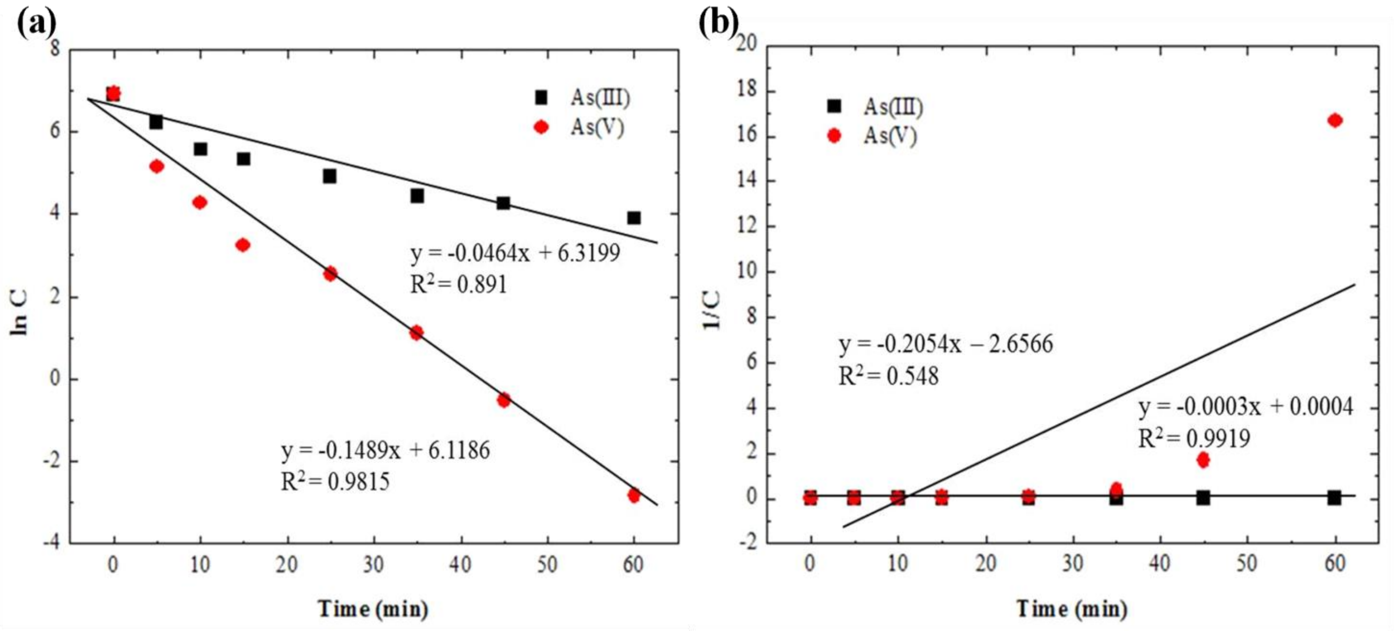

Figure 4.26 Effect of initial concentration on kinetic order;

a) Pseudo first order kinetic b) Pseudo second order kinetic

Table 4.4 Different kinetic model parameters

Model	Parameters	As(III)	As(V)
Pseudo-first order kinetic	k_1 (min^{-1})	0.0464	0.1489
	$t_{1/2}$ (min)	14.94	4.66
	R^2	0.89	0.98
Pseudo-second order kinetic	k_2 (L·(μg·min)$^{-1}$)	3 x 10^{-4}	0.0254
	$t_{1/2}$ (min)	3.33	0.04
	R^2	0.99	0.548

Table 4.5 Rate constants for arsenic removal with different materials

Material	Rate constant (k)		References
	As(III)	As(V)	
ZVI fillings	-	6.94 x 10^{-6} min^{-1}	(Melitas et al., 2002)
Aluminum	0.017 min^{-1}	0.017 min^{-1}	(Balasubramanian et al., 2009)
Mild steel	0.018 min^{-1}	0.018 min^{-1}	(Balasubramanian et al., 2009)
Treated laterite	1.3 x 10^{-7} L·(μg·min)$^{-1}$	1.62 x 10^{-6} L·(μg·min)$^{-1}$	(Maiti et al., 2010)
NZVI	0.07 min^{-1}	-	(Kanel et al., 2005)
Modified alumina	0.215 min^{-1}	-	(Balaji et al., 2000)

4.4 Continuous system (Part II)

4.4.1 Effect of influent flow rate

In this part of experiments, the initial arsenic concentration and bimetal dosage were fixed throughout the experiment at 1000 µg/L and 0.022 g/L, respectively. The influent flow rate of arsenic solution was various from 50 to 300 mL/min. The condition of system was set following bubbling steps in batch experiments part, which was pre-treatment by CO_2 bubbling and then follow by air bubbling. The experiments were conducted to both As(III) and As(V) system, which the results were shown in Figure 4.27.

According to the influent flow rates of 50, 100, 200 and 300 mL/min, hydraulic retention times of continuous system experiment for As(III) and As(V) were referred to 25, 25, 15, 10 min, and 15, 15, 10, 5 min, respectively. Concerning in the initial stage, the arsenic concentrations could decrease for all flow rates, but different removal rate. After retention time, arsenic concentration rebounded gradually depending on the flow rate, as shown in Figure 4.27(a) and (b). The rebound rate was found to be faster in the higher of influent flow rate, they can return to an initial concentration at longer time. For As(V) removal, it was found that the lag phase was shorten, comparing with As(III) removal at the same feeding rate. This could explain by the higher removal rate of As(V) over As(III). Total dissolved iron along the reaction time was also presented in Figure 4.27; it was found that the dissolved iron concentration likely decreased when the retention time increased. This might due to the hydraulic dilution effect. However, arsenic concentration increased when the time increased after the lag phase. Moreover, the concentration of arsenic is still over the standard limitation. This problem should be solved by determine the multiple-step of adding bimetal.

The results in this study can be concluded that the lower influent flow rate of arsenic solution provided sufficient time of removing arsenic to low concentration, and also preparing of Cu-Fe nanoparticles for the next step addition. Therefore, the flow rate of 100 mL/min was chosen to use in continuous further.

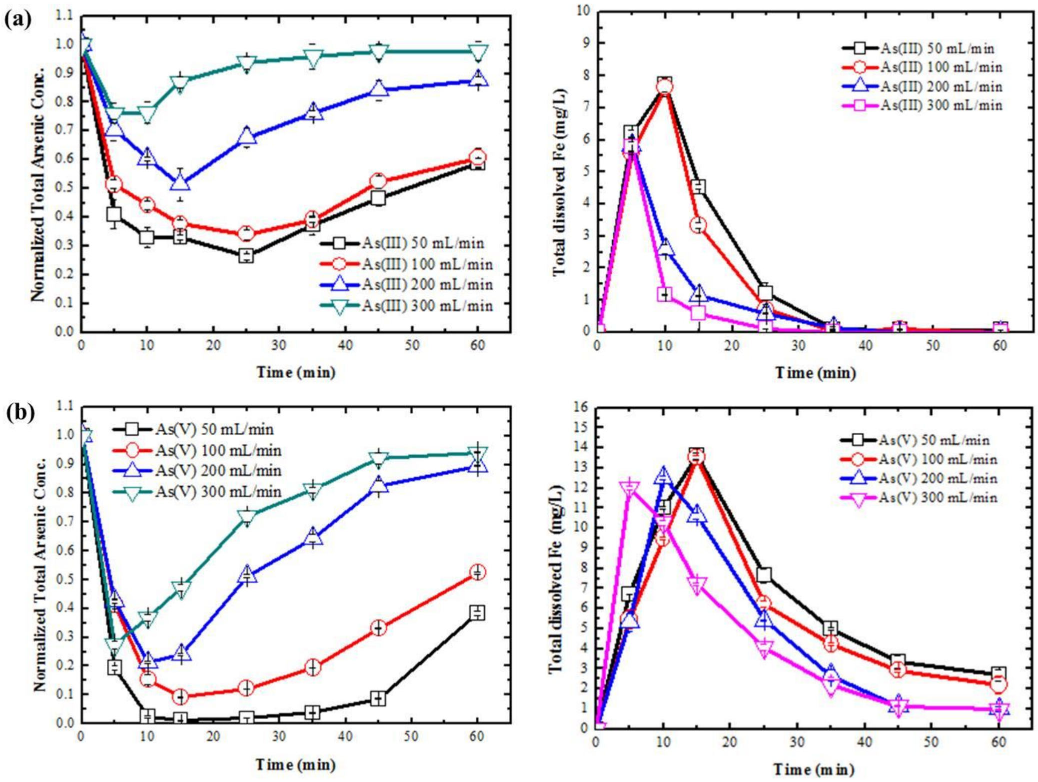

Figure 4.27 Effect of influent flowrate on arsenic removal and total dissolved iron; a) Arsenite removal b) Arsenate removal

4.4.2 Multiple steps of Cu-Fe addition for arsenic removal

In the study of multiple step addition of $(Cu\text{-}Fe)_{IM}$, the addition time interval of Cu-Fe into solution was examined. The reaction times were expanded from 60 min to 120 min to study of multiple step addition. In addition, adding of $(Cu\text{-}Fe)_{IM}$ into solution was expected to economize as much as possible. Firstly, to determine a properly addition time of bimetal, $(Cu\text{-}Fe)_{IM}$ was tested by 1 step addition throughout process until the wash out of $(Cu\text{-}Fe)_{IM}$ supplement was observed. According to Figure 4.28, As(III) removal decreased along the reaction process until 25 min, then gradually rebound to the initial concentration. Such a result indicated that the $(Cu\text{-}Fe)_{IM}$ residual was not sufficient to removal arsenic. In addition, pH was decreased at the initial stage due to iron oxidation process, and it was decreased significantly at ≈ 25 min. This could be due to the hydraulic dilution effect as mention earlier. Concerning in As(V) removal as shown in Figure 4.29, $(Cu\text{-}Fe)_{IM}$ can remove As(V) totally until 35 min before the rebound of arsenic concentration was found.

Therefore, 0.1 g of fresh $(Cu\text{-}Fe)_{IM}$ was decided to add into system at every 35 min to control arsenic to low concentration as shown in Figure4.28 and 4.29. The arsenic removal efficiency increased after $(Cu\text{-}Fe)_{IM}$ was introduced in both As(III) and As(V) system. Arsenic concentration after the 3rd addition of both As(III) and As(V) were observed approximately 100 µg/L and 0 µg/L, respectively. Considering pH and DO profile, a significant increase of pH was found at the supplement of $(Cu\text{-}Fe)_{IM}$ as OH^- released from iron oxidation process while DO was decreased due to DO consumption of $(Cu\text{-}Fe)_{IM}$. In addition, total dissolved iron concentration tend to increase, it should be due to the iron accumulation generated from $(Cu\text{-}Fe)_{IM}$ supplement. Although the efficiency of arsenic removal increased after fresh Cu-Fe was introduced in the system, but the final arsenic concentration was still higher than the standard of arsenic (10 µ/L). Thus, the step addition should be improved to overcome this limitation.

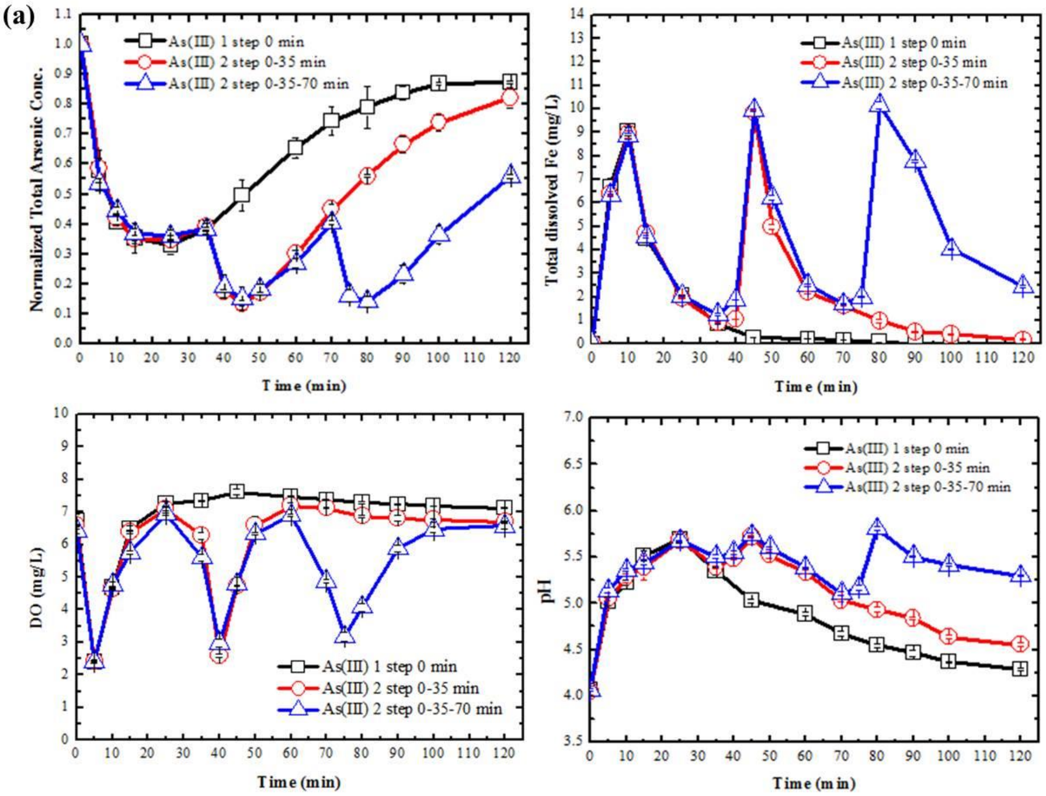

Figure 4.28 Effect of multiple-step of (Cu-Fe)$_{IM}$ supplement for initial As(III) solution on arsenic removal, total dissolved iron, DO, and pH

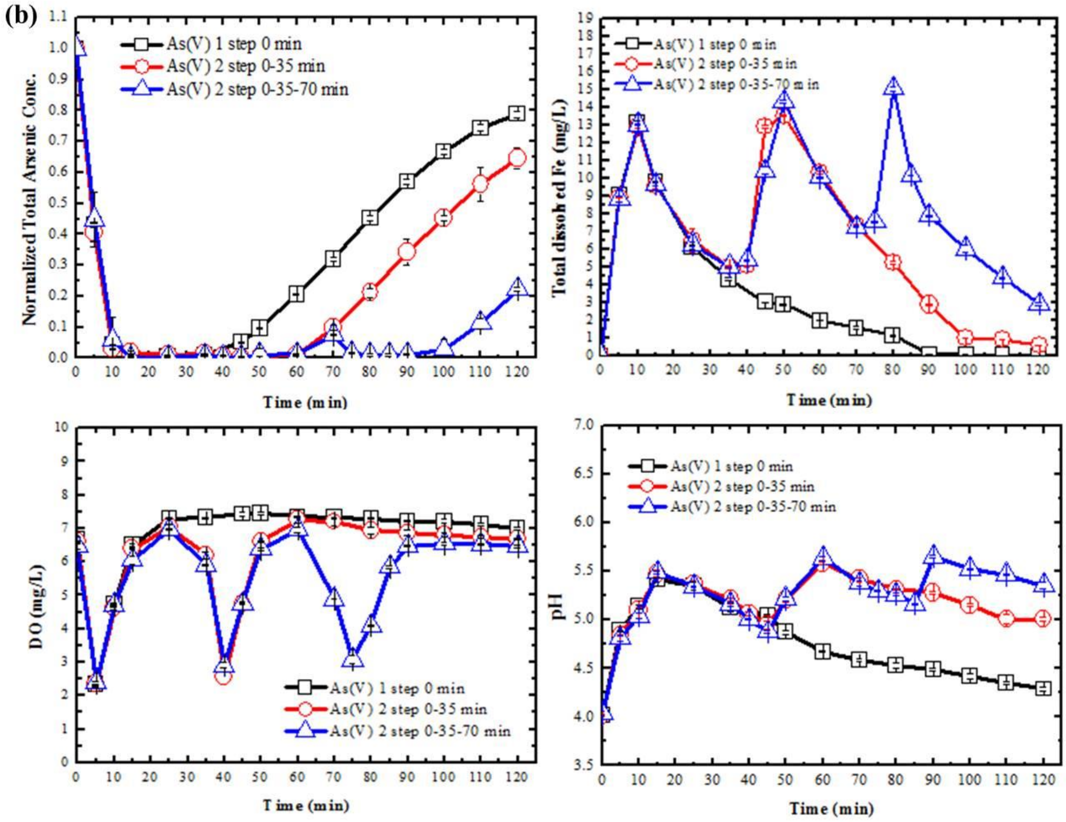

Figure 4.29 Effect of multiple-step of $(Cu\text{-}Fe)_{IM}$ supplement for initial As(V) solution on arsenic removal, total dissolved iron, DO, and pH

4.4.3 Step addition for the improvement

To complete the application of arsenic removal in continuous system, the supplement of $(Cu\text{-}Fe)_{IM}$ was added into the system to control the effluent arsenic concentration to below 10 µg/L throughout process. From 3 step addition, it was improved by changing the time interval. The multiple step addition improvement was tested in As(III), As(V), and mixed As. For As(III) removal, It was found that adding $(Cu\text{-}Fe)_{IM}$ at 0 min, 35 min, and follow by every 15 min, can control the effluent arsenic concentration to lower than 10 µg/L, as shown in Figure 4.30(a).

In the study of 3 step addition in As(V) solution, $(Cu\text{-}Fe)_{IM}$ can keep in low As concentration to less than 10 µg/L. However, arsenic concentration can increase up after the 3^{rd} addition at 70 min (see Figure 4.30 (b)). According to the results in multiple step addition, the retention time for As(V) removal was observed to be longer than that for As(III) system. Thus, no necessary to add $(Cu\text{-}Fe)_{IM}$ as fast as time interval of As(III) system. To control arsenic concentration constantly to below 10 µg/L, arsenic removal efficiency for As(V) system can be improve by adding $(Cu\text{-}Fe)_{IM}$ at 35 min and then at every 25 min, resulting in arsenic concentration below the standard for all process.

Since there are both As(III) and As(V) in natural water, the removal improvement for mixed arsenic should be also studied. In this experiment, the ratio of As(III) to As(V) was adjusted at ratio 1:1. The effect of multiple step addition for mixed arsenic was presented in Figure 4.30(c). When 0.1 g of fresh $(Cu\text{-}Fe)_{IM}$ was added into system at 0-35-70 min, the arsenic concentration increased to more than 10 µg/L after 10 min of $(Cu\text{-}Fe)_{IM}$ supplement. Then, $(Cu\text{-}Fe)_{IM}$ was designed to add in the same step addition of As(III) system, which is 0 min, 35 min, and after that at every 15 min in order to reduce arsenic concentration to below 10 µg/L.

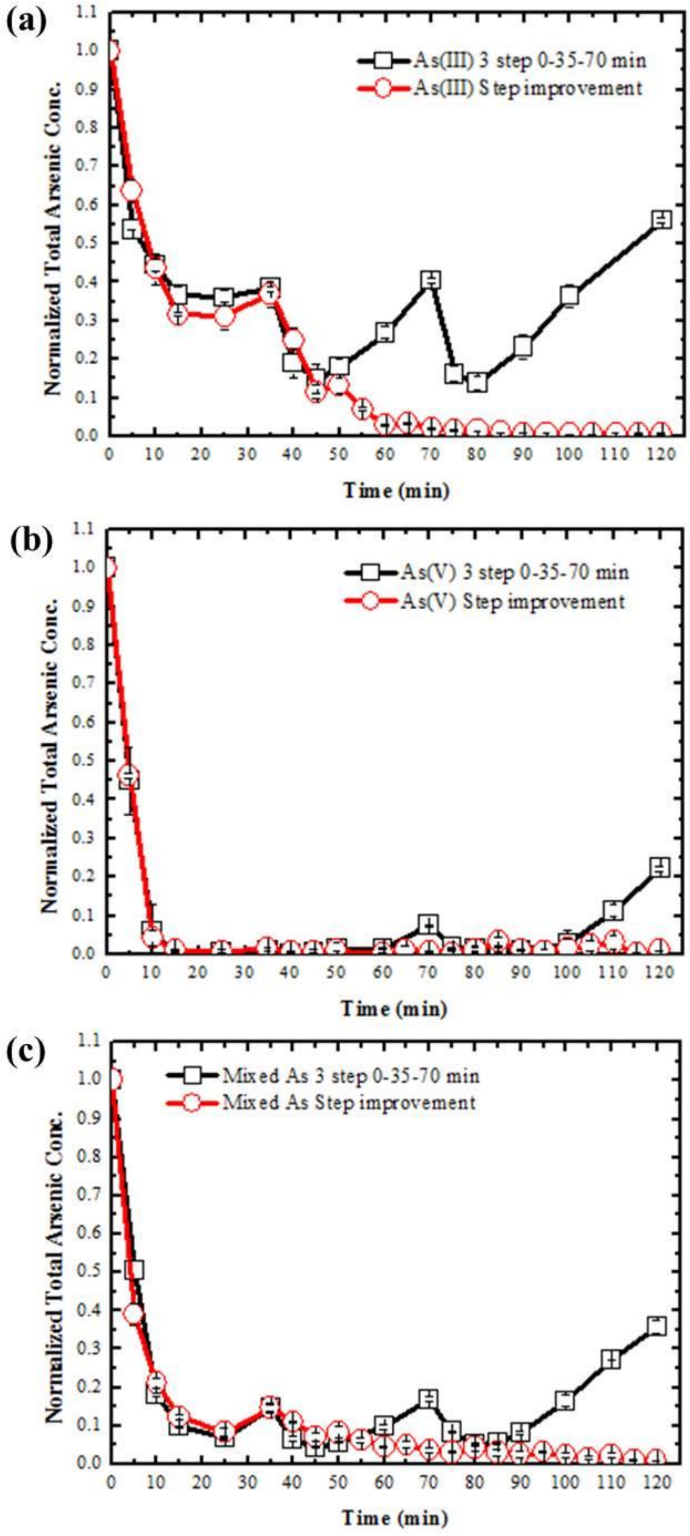

Figure 4.30 Multiple step improvements of (Cu-Fe)$_{IM}$ supplement for (a) As(III), (b) As(V), and (c) mixed As solution

CHAPTER 5

CONCLUSIONS AND RECCOMENDATIONS

5.1 Conclusions

The thesis aimed to study the performance of arsenic removal by gases bubbling coupled with NZVI-based bimetals; Cu-Fe bimetal. Bimetallic was synthesized by both in-stu [(Cu-Fe)$_{\mathrm{IS}}$] and impregnation [(Cu-Fe)$_{\mathrm{IM}}$] method. Under several factors in the study, it could be concluded as follows;

1. The use of Cu combined with NZVI as bimetal resulted in higher removal efficiency in both arsenic spiked DI water and groundwater over using NZVI and Ni-Fe. Among two synthesis methods for Cu-Fe, an impregnation method gave higher potential in arsenic removal than an in-situ technique. The removal efficiency of arsenic increased when Cu loading on NZVI increased, and an optimal loading of Cu was of 10% (w/w).

2. Based on the characterizations by SEM, TEM, and BET, spherical shape of nanoparticles were observed for (Cu-Fe)$_{\mathrm{IM,}}$ (Cu-Fe)$_{\mathrm{IS}}$, (Ni-Fe)$_{\mathrm{IM}}$, and NZVI. (Cu-Fe)$_{\mathrm{IM}}$ possessed smaller size with larger surface area. XANES spectra indicated that the apparent valence states of fresh (Cu-Fe)$_{\mathrm{IM}}$ and reacted (Cu-Fe)$_{\mathrm{IM}}$ are 0 and +2 matching with Cu foil and CuO. It could confirm an ability of Cu to accelerate Fe oxidation. In addition, Cu-Fe showed the higher pH$_{\mathrm{pzc}}$ than NZVI for both (Cu-Fe)$_{\mathrm{IM}}$ and (Cu-Fe)$_{\mathrm{IS}}$. pH$_{\mathrm{pzc}}$ of (Cu-Fe)$_{\mathrm{IM;}}$ was ca 8.7, which provided a wider range for the utilization.

3. Arsenate, As(V), was removed easier than arsenite, As(III) at any studied pH conditions. In the studied conditions, the reduction and oxidation between two species did not taken place. The presence of background ions, Cl^{-}, Ca^{2+}, and SO_4^{2-} enhanced arsenic removal efficiency by (Cu-Fe)$_{\mathrm{IM}}$ while HA, PO_4^{3-}, and HCO_3^{-} inhibited arsenic removal efficiency for both arsenic species. In addition, the results based on

multi-ions system study indicated that decreasing of HCO_3^- and PO_4^{3-} may create the better condition to removal arsenic for both As(III) and As(V).

4. CO_2 bubbling provided the suitable environment of low pH around 4 for arsenic removal, while O_2 bubbling raised DO to enhance the performance of Cu-Fe through acceleration of corrosion rate of NZVI. Arsenic in gas bubbling system coupled with $(Cu\text{-}Fe)_{IM}$ was successfully removed and showed the high performance for both As and As(V). Furthermore, multiple-step addition of $(Cu\text{-}Fe)_{IM}$ in continuous gas bubbling system reduced arsenic concentration to below the standard concentration of 10 µg/L throughout process.

5.2 Recommendations

1. NZVI preparation method was found some limitation in term of amount produced. Approximately 0.1 g could be generally produced for each batch. The preparation in high amount was found characteristic uncertainty. Therefore, the scale-up synthesis condition for Cu-Fe should be investigated.

2. In this study, all materials were employed in the tests right after the synthesis. An effect of storage life of sample was excluded. It was recommended to characterize and experiment the removal regarding to storage period effect.

3. The detailed chemical mechanisms of arsenic removal are not understood in detail, the operative parameters should be characterized sufficiently to describe further.

4. The filtering system to separate toxic precipitates of arsenic before expose to natural water should be provided in removal system.

5. Based on the analysis of the spent Cu-Fe by FTIR, some peaks were observed. However, an exact explanation of precipitation was not clear in the removal mechanism. The analysis using XPS should be conducted. The results are expected to clarify over mechanism in more detail.

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APPENDICES

APPENDIX A

Preliminary experiment of arsenic removal in gas bubbling system

The profiles of As(V) and As(III) removal, carried out in the CO_2-O_2 gas bubbling system using 10%$(Cu\text{-}Fe)_{IM}$ comparing with pristine NZVI as shown in Figure A1(a) and (b). The As(V) removal using two kind of materials seem similar to each other. The 10%Cu-Fe outperform NZVI, especially in As(III) removal. To understand the behavior of these metals more in the reaction solution, the pH and total dissolved iron are also illustrated in Figure A1(a) and (b). The results showed similar trend of pH profiles for both NZVI and 10%Cu-Fe.

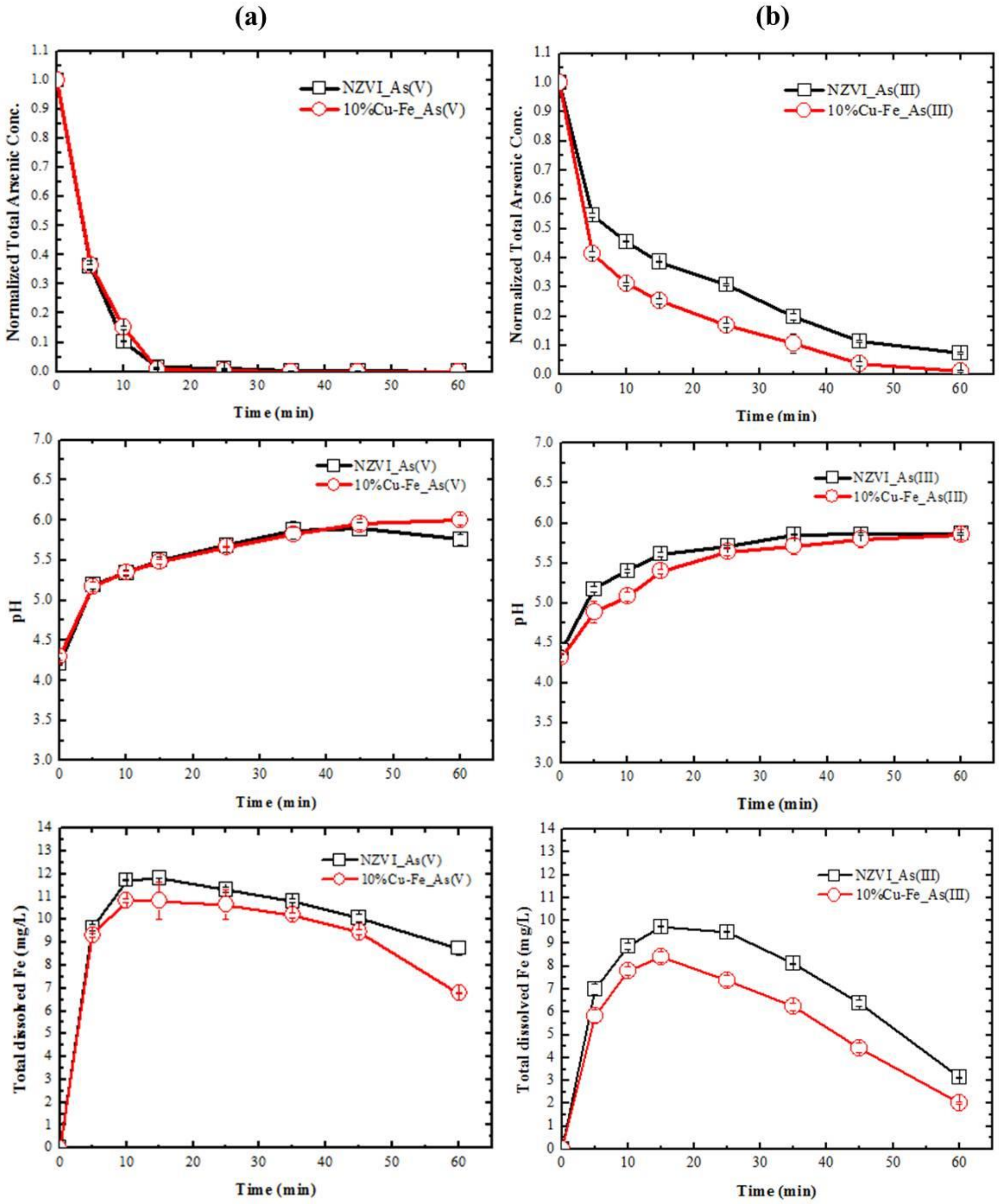

Figure A 1 Comparison of using different materials (NZVI and Cu-Fe) in the gas bubbling system on: arsenate removal and (b) arsenite removal

APPENDIX B

Supplemental data for gas bubbling system

In arsenic removal process, the factor affected in the partition of arsenic and iron is Eh values. Besides a function of pH changes, Eh profiles in the part of effect of synthesis method were shown in Figure B1 for As(III) and As(V), respectively. Considering Eh profile with pH profiles could be confirmed that dissolved iron (Fe^{2+}) tend to precipitates to Fe_3O_4, and ready to co-precipitate with arsenic.

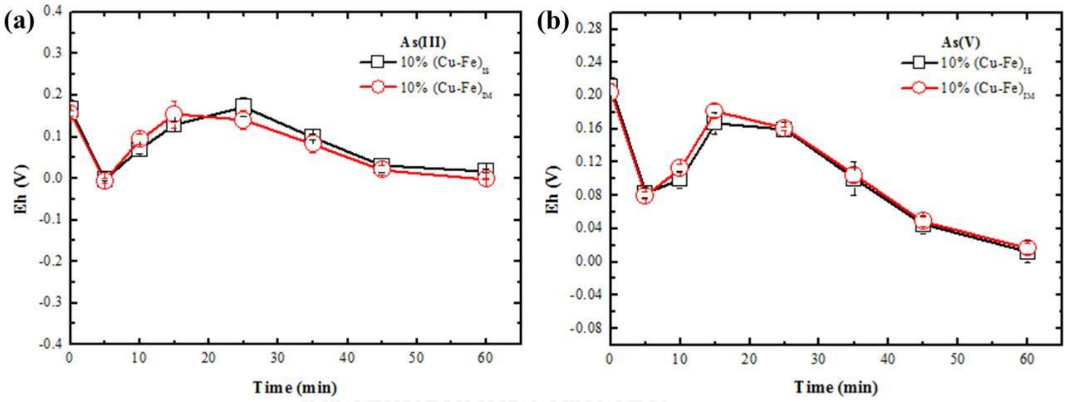

Figure B 1 Eh profiles for the study of different synthesis method;

a) As(III) b) As(V)

APPENDIX C

Mass balance of arsenic concentration for arsenic removal by using (Cu-Fe)$_{\text{IM}}$

To confirm that arsenic was removed by mechanism of (Cu-Cu)$_{\text{IM}}$, mass balance of arsenic concentration along removal process were carried out. The short experiment was set up in 500 mL beaker with 1000 µg/L of As(V) concentration as shown in Figure C 1. After 60 min of removal process, all precipitate was filtrated and measured As(V) uptake by Atomic Absorption Spectrometer (AAS). Capability of (Cu-Fe)$_{\text{IM}}$ and its precipitates to uptake arsenic were demonstrated in Table C 1.

Table C 1 Concentration of remaining arsenic for arsenic removal by (Cu-Fe)$_{\text{IM}}$

Arsenic In	**Arsenic Accumulation**	**Arsenic Out**
1000 µg/L	622 µg/L	228 µg/L
1000 µg/L	625 µg/L	217 µg/L

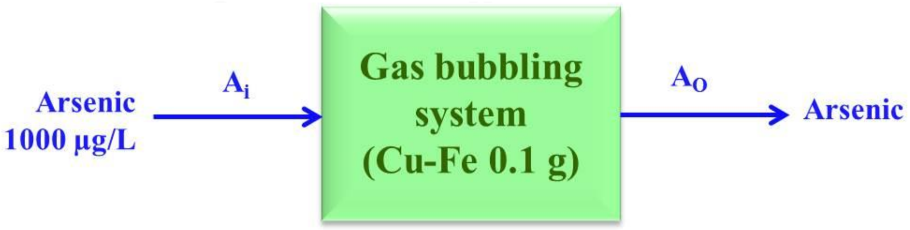

Figure C 1 Flow diagram of mass balance for arsenic removal system, 1000 µg/L for 60 min, with (Cu-Fe)$_{\text{IM}}$

APPENDIX D

Statistic for the study of percent copper loadings don arsenic removal efficiency

For the study of percent copper loading on arsenic removal efficiency, 20% and 30% of copper loadings provided closely results of arsenic removal efficiency with 10% copper loading. To observe the differences between the groups, the F-ratio were examined. Furthermore, t-test was used to examine the differences between the means of two groups. The step of hypothesis test was depicted in Figure D1, and the results of the hypothesis test for variation of T-test and F-test was shown in Table D1 and D2, respectively. As a result, the arsenic removal efficiency using 10%(Cu-Fe)$_{IM}$ was significantly difference with using 20% and 30%(Cu-Fe)$_{IM}$.

Table D 1 Data for F-test

F-Test Two-Sample for Variances					
Variable	**20%Cu**	**10%Cu**		**30%Cu**	**10%Cu**
Mean	0.254416	0.258828		0.22509	0.258828
Variance	0.107896	0.10772		0.111131	0.10772
Observations	8	8		8	8
df	7	7		7	7
F	1.001629			1.031663	
P(F<=f) one-tail	0.499171			0.484129	
F Critical one-tail	6.992833			6.992833	

Table D 2 Data for T-test

T-Test: Two-Sample Assuming Equal Variances					
Variable	**20%Cu**	**10%Cu**		**30%Cu**	**10%Cu**
Mean	0.254416	0.258828		0.22509	0.258828
Variance	0.107896	0.10772		0.111131	0.10772
Observations	8	8		8	8
Pooled Variance	7	7		7	7
Hypothesized Mean Difference	0.107808			0.109426	
df	0			0	
t Stat	14			14	
P(T<=t) one-tail	-0.02687			-0.20398	
t Critical one-tail	0.489471			0.420653	

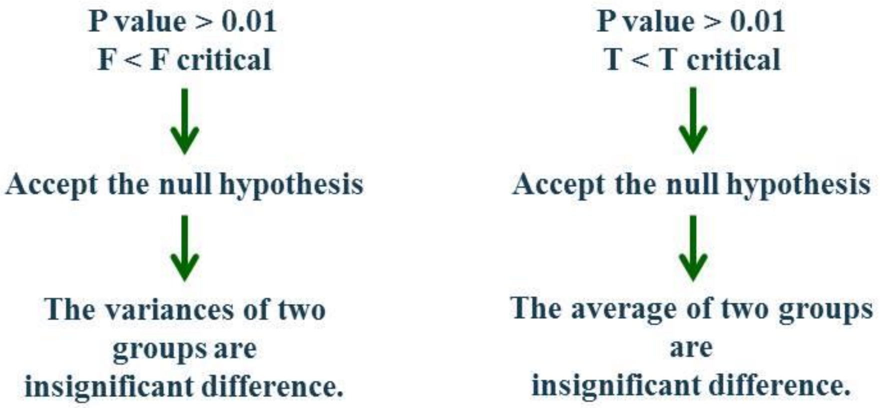

Figure D 1 Hypothesis test for variances

APPENDIX E

Mass balance of arsenic species in mixed arsenic removal in gas bubbling system

Based on the study of effect of As(III)/As(V) ratio, it is of interest to provide information on arsenic speciation. The individual arsenic species was determined by using an anion-exchange cartridge, DSC-SAX 500 mg (Supelco) to filter arsenic samples. According to this technique, As(V) was retained inside, while As(III) was carried out, then concentration of As(III) concentration was analyzed by ICP. Afterthat, As(V) concentration was obtained by subtracting measured As(III) concentration from the total arsenic concentration. Total and individual arsenic removal profiles are shown in Figure E1. There’s no significant oxidation of various ratio of As(III) into As(V) in the arsenic removal by $(Cu\text{-}Fe)_{IM}$ with gas bubbling. In addition, reduction of As(V) was not found possibly due to that As(V) has been removed almost completely within the initial time period.

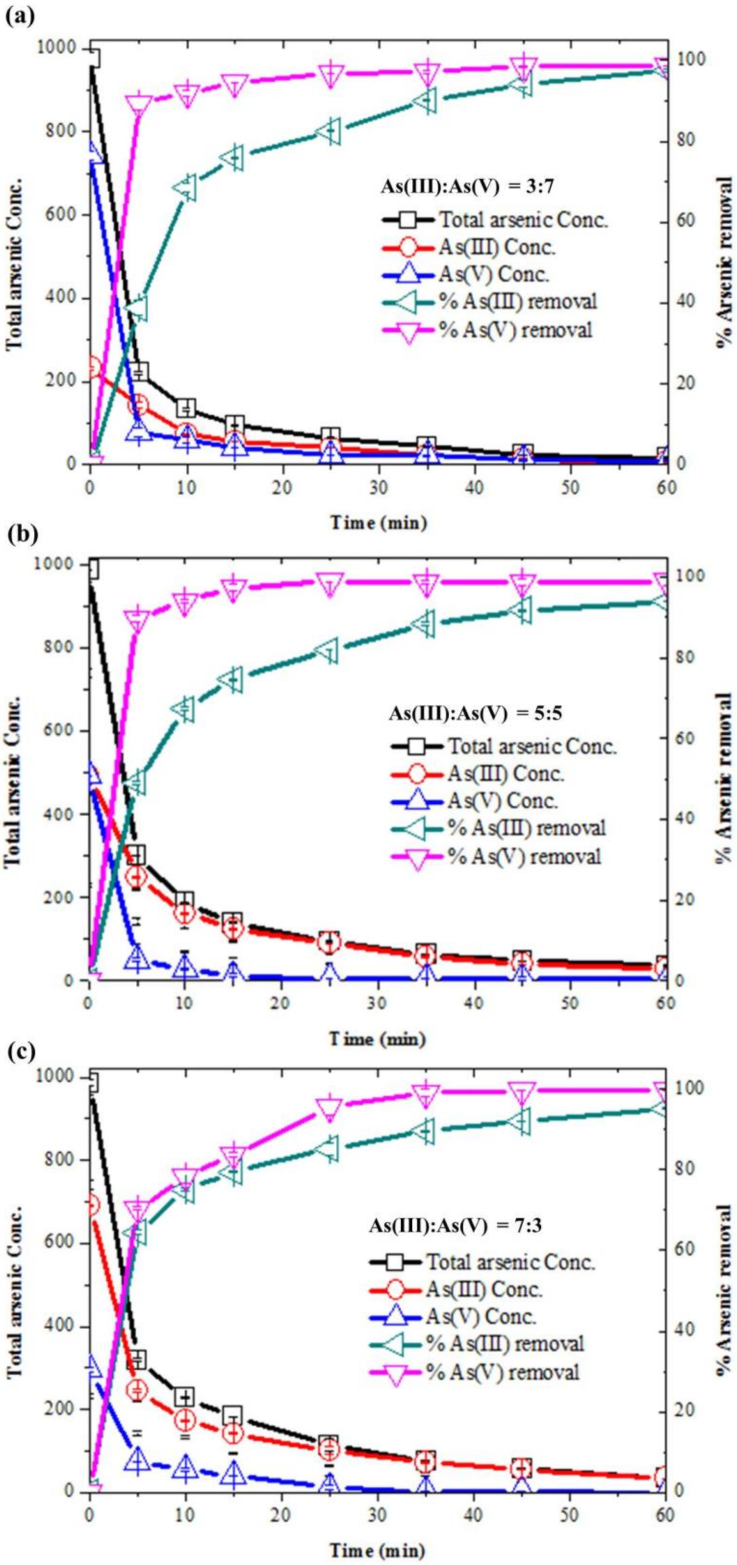

Figure E 1 Total arsenic concentration and the individual profiles of remaining concentration at various ratios of As(III) versus As(V); a) 3:7, b) 5:5, and c) 7:3

APPENDIX F

Multiple step addition tests in continuous system

In the study of multiple-step addition of Cu-Fe in arsenic solution, 3 step additions of Cu-Fe was found increase of arsenic concentration after the 3rd addition. To improve the step addition to control arsenic concentration constantly to below 10 µg/L, 3 step additions was varied to find the removal trends. Figure F1 shows the study of different multiple-step addition of Cu-Fe in arsenic solutions.

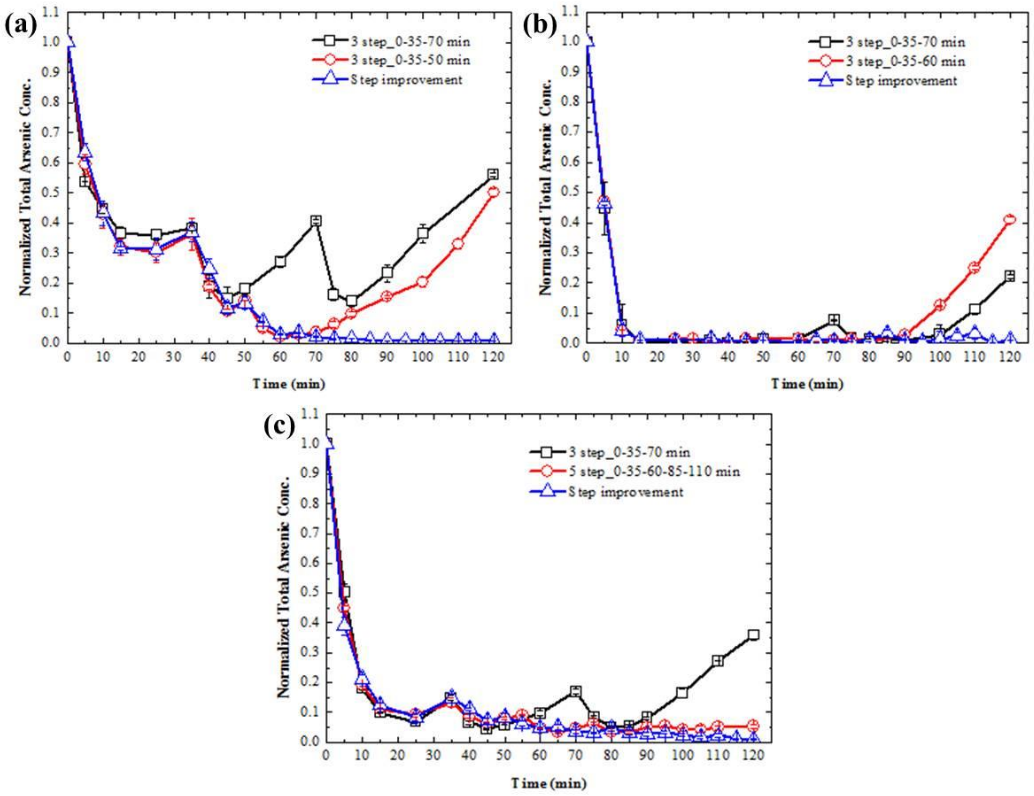

Figure F 1 Study of step addition improvement on;

b) As(III) b) As(V) c) Mixed As solution

APPENDIX G

Experimental raw data

Table G 1 Comparison of using different types of nanoparticles: materials dosage = 0.022 g/L, initial As concentration = 5000 μg/L, initial solution pH = 7

Time (min)	**Normalized total arsenic Concentration**					
	As(III)			**As(V)**		
	Cu-Fe	**Ni-Fe**	**NZVI**	**Cu-Fe**	**Ni-Fe**	**NZVI**
0	1	1	1	1	1	1
5	0.412	0.560	0.559	0.236	0.463	0.133
10	0.353	0.510	0.485	0.216	0.423	0.084
15	0.336	0.422	0.405	0.197	0.402	0.061
25	0.298	0.378	0.335	0.166	0.379	0.038
35	0.268	0.369	0.294	0.107	0.344	0.020
45	0.230	0.338	0.264	0.055	0.237	0.012
60	0.199	0.285	0.244	0.008	0.168	0.010

Table G 2 Effect of different synthesis method of Cu-Fe on As(III) removal in DI water and groundwater: materials dosage = 0.022 g/L, initial As concentration = 1000 µg/L, initial solution pH = 4

Time (min)	**Normalized total arsenic Concentration**			
	DI water		**Groundwater**	
	(Cu-Fe)$_{IS}$	**(Cu-Fe)$_{IM}$**	**(Cu-Fe)$_{IS}$**	**(Cu-Fe)$_{IM}$**
0	1	1	1	1
5	0.55	0.54	0.57	0.56
10	0.45	0.41	0.48	0.44
15	0.38	0.32	0.42	0.38
25	0.27	0.21	0.40	0.35
35	0.17	0.13	0.37	0.33
45	0.13	0.09	0.36	0.32
60	0.11	0.05	0.35	0.29

Table G 3 Effect of different synthesis method of Cu-Fe on As(V) removal in DI water and groundwater: materials dosage = 0.022 g/L, initial As concentration = 1000 μg/L, initial solution pH = 4

Time (min)	**Normalized total arsenic Concentration**			
	DI water		**Groundwater**	
	(Cu-Fe)$_{IS}$	**(Cu-Fe)$_{IM}$**	**(Cu-Fe)$_{IS}$**	**(Cu-Fe)$_{IM}$**
0	1	1	1	1
5	0.25	0.21	0.24	0.22
10	0.15	0.11	0.20	0.12
15	0.11	0.05	0.17	0.09
25	0.05	0.03	0.13	0.07
35	0.04	0.02	0.09	0.04
45	0.03	0.02	0.06	0.02
60	0.01	0	0.04	0.01

Table G 4 Effect of initial concentration of As(III) and As(V) on arsenic removal: materials dosage = 0.022 g/L, initial As concentration = 1000 μg/L, initial solution pH = 4

Time (min)	**Arsenic concentration (μg/L)**							
	Initial concentration of As(III)				**Initial concentration of As(V)**			
	500	**1000**	**1500**	**2000**	**500**	**1000**	**1500**	**2000**
0	500	1004.5	1501.5	1996.5	501	999.5	1500	1999
5	218.15	505.6	829.65	1170.6	76.85	173.05	507.8	951.5
10	119.71	261.65	600.1	862.4	29.15	71.95	201.15	345.65
15	96.77	205.4	476.75	693.4	14	25.55	119.3	203.9
25	61.67	136.67	309.55	440.75	5.15	12.75	77.05	109.15
35	40.08	83.61	217.9	319.75	2.15	3.05	44.35	63.95
45	29.91	70.23	164.89	256.45	0.15	0.6	26.6	39.65
60	17.34	49.3	105.4	172.65	0	0.06	8.15	16.3

Table G 5 Total arsenic removal at different ratios of As(III) versus As(V): (Cu-Fe)$_{IS}$ = 0.022 g/L, initial As concentration = 1000 µg/L, initial solution pH = 4

Time (min)	Normalized total arsenic Concentration				
	As(III):As(V)				
	10:0	**7:3**	**5:5**	**3:7**	**0:10**
0	1	1	1	1	1
5	0.52	0.41	0.37	0.32	0.24
10	0.41	0.29	0.26	0.22	0.13
15	0.35	0.24	0.21	0.17	0.09
25	0.249	0.17	0.14	0.12	0.05
35	0.17	0.11	0.10	0.09	0.03
45	0.13	0.09	0.08	0.06	0.02
60	0.11	0.07	0.06	0.04	0.01

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MANUSCRIPT

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CONFERENCES

- Oral presentation on “Arsenic removal by Cu/Fe bimetal in the gas bubbling system” at “2011 International Conference on Environmental Quality Concern, Control and Conservation”, May 20-21, 2011, Kaohsiung, Taiwan ROC.

- Oral presentation on “Effect of As(III)/As(V) ratio and background species on arsenic removal by Cu/Fe bimetal” at “2012 International Conference On Sustainable Environmental Technologies (ICSET)”, May 26-27, 2012, Bangkok, Thailand.