Effect of Natural Organic Matter and a Biosurfactant on Arsenic Mobilization from Mine Tailings

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ABSTRACT

Effect of Natural Organic Matter and a Biosurfactant on Arsenic Mobilization from Mine Tailings

Suiling Wang, Ph.D., P.Eng.

Concordia University, 2007

Batch and column experiments were conducted to elucidate the mechanisms of arsenic mobilization from the mine tailings in the presence of a natural organic matter (NOM, represented by a Fluka humic acid, HA) and a biosurfactant (represented by JBR425, mixed rhamnolipids), and to evaluate the feasibility of using NOM and biosurfactant in remediating arsenic contaminated mine tailings or soils. It was indicated that HA addition might help retain arsenic and heavy metals in the mine tailings under acidic conditions. Both HA and rhamnolipid were capable of increasing arsenic mobility from the mine tailings under alkaline conditions. It was shown that the introduction of HA at a low mass ratio of HA to mine tailings (below 2 mg/g) under acidic conditions inhibited arsenic mobilization. Generally, arsenic mobilization by HA increased with an increase in mass ratio. When the mass ratio reached 10 mg/g at pH 11, arsenic was mobilized the most after a 24-hour reaction. The mobilization of arsenic in the presence of rhamnolipid increased with the mass ratio and pH. When the mass ratio was 10 mg/g at pH 11, rhamnolipid mobilized the most arsenic after a 24-hour reaction. A desorption isotherm was developed to predict arsenic mobilization from the mine tailings in the presence of the organic additives. The addition of three low-molecular-weight-organic-acids (i.e., aspartic acid, cysteine, and succinic acid) under acidic to neutral conditions inhibited arsenic mobilization and arsenic was mobilized the most at pH above 9. Higher arsenic mobilization was obtained in column experiments. Rhamnolipid was found to be more efficient in mobilizing arsenic, probably due to its efficiency in lowering the interfacial tension and mobilizing other metals. Capillary electrophoresis analyses indicated that arsenic redox reaction might not have a significant effect on arsenic mobilization. The mobilization of co-existing metals might, to some extent, enhance arsenic mobilization by helping incorporate it into soluble complexes in the presence of organic additives. The findings will be important in advancing our understanding of the fate and transport cycle of arsenic in the environment and the cause of arsenic contamination in groundwater. NOM and biosurfactants might be used potentially for the remediation of arsenic contaminated sites.

To my parents, sisters and brothers

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Table of Contents

Table of Contents (Continued)

Table of Contents (Continued)

Table of Contents (Continued)

Table of Contents (Continued)

Table of Contents (Continued)

Table of Contents (Continued)

List of Tables

List of Tables (Continued)

List of Tables (Continued)

List of Figures

List of Figures (Continued)

List of Figures (Continued)

List of Figures (Continued)

List of Figures (Continued)

List of Figures (Continued)

List of Figures (Continued)

List of Figures (Continued)

List of Figures (Continued)

List of Figures (Continued)

List of Figures (Continued)

List of Abbreviations

AAS	atomic absorption spectrophotometer
ASTM	American Society for Testing and Materials
ATR	attenuated total reflectance
CA	citric acid
CE	capillary electrophoresis
CEC	cation exchange capacity, $cmoles^+/kg$
DMAA	dimethylarsinic acid
DOC	dissolved organic carbon
DOM	dissolved organic matter
DTPA	diethylenetriaminepentaacetic acid
EDS	energy dispersive spectrometer
EDTA	ethylenediaminetetraacetic acid
EGME	ethylene glycol monoethyl ether
EM	electrophoretic mobility
EOF	electroosmotic flow
EXAFS	extended X-ray absorption fine structure
FA	fulvic acid
FTIR	Fourier transform infrared

List of Abbreviations (Continued)

HA	humic acid
ICP-MS	inductively coupled plasma mass spectrometry
IMCL	interim maximum concentration level
LMWOA	low molecular weight organic acid
MMAA	monomethylarsonic acid
MSDS	Material Safety Data Sheet
NOM	natural organic matter
NRC	National Research Council
NRCS	Natural Resources Conservation Service
OMC	organic matter content, %
RLITMF	Rabbit Lake in-pit tailings management facility
RWED	Department of Resources, Wildlife and Economic Development
SDS	sodium dodecyl sulphate
SEM	scanning electron microscopy
SG	specific gravity
SSA	specific surface areas, m^2/g
TCA	tricarboxylic acid
USDHHS	US Department of Health and Human Services

List of Symbols

a	empirical constant
b	sorption constant, *mg/g*
D_t	dielectric constant
Eh	redox potential, *mV*
G_s	specific gravity of mine tailings
M_m	mass of dried mine tailing sample, *g*
M_{wm}	mass of a volumetric flask filled with water and mine tailings, *g*
M_w	mass of a 500 ml volumetric flask filled with distilled water, *g*
K_s	distribution coefficient
r	mass ratio of organic additives to mine tailings, *mg/g*
ρ_{water}	density of water, *g/ml*
V_t	viscosity of suspending liquid
W_a	weight of dried mine tailings after ashing, *g*
W_b	weight of dried mine tailings before ashing, *g*
W_{EGME}	weight of EGME, *g*
W_m	weight of mine tailings, *g*
ζ	zeta potential, *mV*

CHAPTER ONE

INTRODUCTION

1.1 General background

Arsenic belongs to Group 15 (formerly Group V) of the Periodic Table below nitrogen and phosphorus. It has an atomic number of 33 and an atomic weight of 74.92. It is a metalloid exhibiting both metallic and nonmetallic properties. It ranks the 20th most abundant element in the earth's crust and is widely distributed throughout the rocks, soils and natural waters. It is present in trace amounts in almost all living matter. In addition to its natural occurrence in soils, arsenic has also historically been used in a variety of commercial applications (Table 1-1). Environmental impacts are incurred from both anthropogenic activities and natural enrichments. The weathering and erosion of arsenic-enriched geological formations present a principal natural source of arsenic in the environment. Anthropogenic arsenic sources mainly include nonferrous metal mining and smelting, fossil fuel processing and combustion, wood preserving, and pesticide production and application, as well as disposal and incineration of municipal and industrial wastes. Particularly, mine tailings with high arsenic and heavy metal contents have been considered as potential contamination sources (Wang and Mulligan, 2006a).

Arsenic exits essentially in the environment in four oxidation states (i.e., +V, +III, 0, -III) and forms various compounds. The valency state of arsenic plays an important role in its behavior in the environment. It has been well established that the physiological and toxicological effects of arsenic are dependent on the chemical form and oxidation state in which it exists, which also determines its sorption behavior and consequently its mobility and bioavailability in the environment (Wang and Mulligan, 2004a). Inorganic arsenic species generally are more toxic and mobile than organoarsenic species, while arsenite [As(III)] is considered to be more toxic and mobile than arsenate [As(V)].

Table 1-1. Main modern uses of arsenic compounds

Sector	Uses
Agriculture	Pesticides, insecticides, defoliants, wood preservatives, debarking trees, soil sterilant
Livestock	Feed additives, disease prevention (swine dysentery, heartworm infection), cattle and sheep dips, algaecides
Medicine	Antisyphilitic drugs, treatment of trypanosomiasis, amebiasis, sleeping sickness
Electronics	Solar cells, optoelectronic devices, semiconductor applications, light-emitting diodes (digital watches)
Industry	Glassware, electrophotography, catalysts, pyrotechnics, antifouling paints, dyes and soaps, ceramics, pharmaceutical substances
Metallurgy	Alloys (automotive body solder and radiators), battery plates (hardening agents)

Adapted from: Nriagu and Azcue (1990)

Arsenic has gained great notoriety historically for the strength of its killing properties since its isolation in 1250 A. D. by Albertus Magnus. Most arsenic compounds are odorless and tasteless and readily dissolve in water, creating a high potential risk associated with exposure to elevated levels. Many cases of acute and chronic arsenic poisoning have now been documented in various parts of the world. Signs of chronic arsenicalism, including dermal lesions, peripheral neuropathy, skin cancer, peripheral vascular disease and other internal cancers such as tumors of the bladder, kidney, lung, liver and prostate, have been reported in populations ingesting arsenic-bearing drinking water in Bangladesh, India, Chile, Mongolia, Vietnam, Argentina, Mexico, Ghana, Canada, China, and the United States (Tseng *et al.*, 1968; WHO, 1993; Schreiber *et al.*, 2003; Wang and Mulligan, 2004a). The case of Bangladesh and West Bengal is the greatest arsenical calamity of the world due to the use of groundwater bearing high arsenic concentrations.

Ingesting food or water containing only 60 mg/L of inorganic arsenic can be fatal, while lower levels can damage nerves (WHO, 1993). It has also been reported that arsenic can cause toxic effects to plants or may accumulate in plants and thereby enter the animal and human food chain. An average toxicity threshold of 40 mg/kg was established for crop plants (Sheppard, 1992). The maximum level recommended for drinking water by the World Health Organization (WHO) is 10 μg/L (WHO, 1993), while the Canadian Interim Maximum Concentration Level (IMCL) was lowered from 25 μg/L to 10 μg/L in 2006. The Canadian federal soil quality guideline suggests that the maximum concentration of arsenic in soil should not exceed 12 mg/kg (CCME, 1999/2002). The Canadian Environmental Protection Act (CEPA) included arsenic and its compounds in Group 1 of the Priority Substances List, a list to identify substances, including chemicals, effluents and wastes, which may be harmful to the environment or constitute a danger to human health.

1.2 Statement of the problem

Knowledge of natural geochemical and biological processes that govern arsenic transportation and transformation in the environment, therefore, is necessary for the protection of the environment and public health. The geochemistry of arsenic can be complex, including a series of reactions such as adsorption-desorption, precipitation-dissolution, oxidation-reduction, and organic/biochemical methylation. Of these, the adsorption-desorption process is of principal significance in determining arsenic mobility and bioavailability. It is a function of various factors such as pH, redox potential, arsenic concentration and speciation, the concentration of competing ions, aquifer mineralogy, reaction kinetics, organic matter, and the presence of microbes and higher plants (Frost and Griffin, 1977; Pierce and Moore, 1982; Bowell, 1994; Manning and Goldberg, 1996; Lin and Puls, 2000; 2003; Saada *et al.*, 2003). A simplified transfer cycle of arsenic is illustrated in Figure 1-1. The estimated fluxes of arsenic transfer among different reservoirs are summarized in Table 1-2.

Table 1-2. Estimated fluxes of arsenic transfer (Mackenzie *et al.*, 1979)

From:	**To:**	**Estimated Fluxes (10^8 g/yr)**
Land	Oceans	3000
	Atmosphere	1000
	Biota	300
Atmosphere	Oceans	2000
	Land	1000
Oceans	Sediments	2500
	Biota	1300
	Dissolved	1000
Sediments	Land	2400
Mining, smelting		500
Terrestrial biota	Land	300
Volcanoes	Land	54
	Sediments	40
	Atmosphere	3

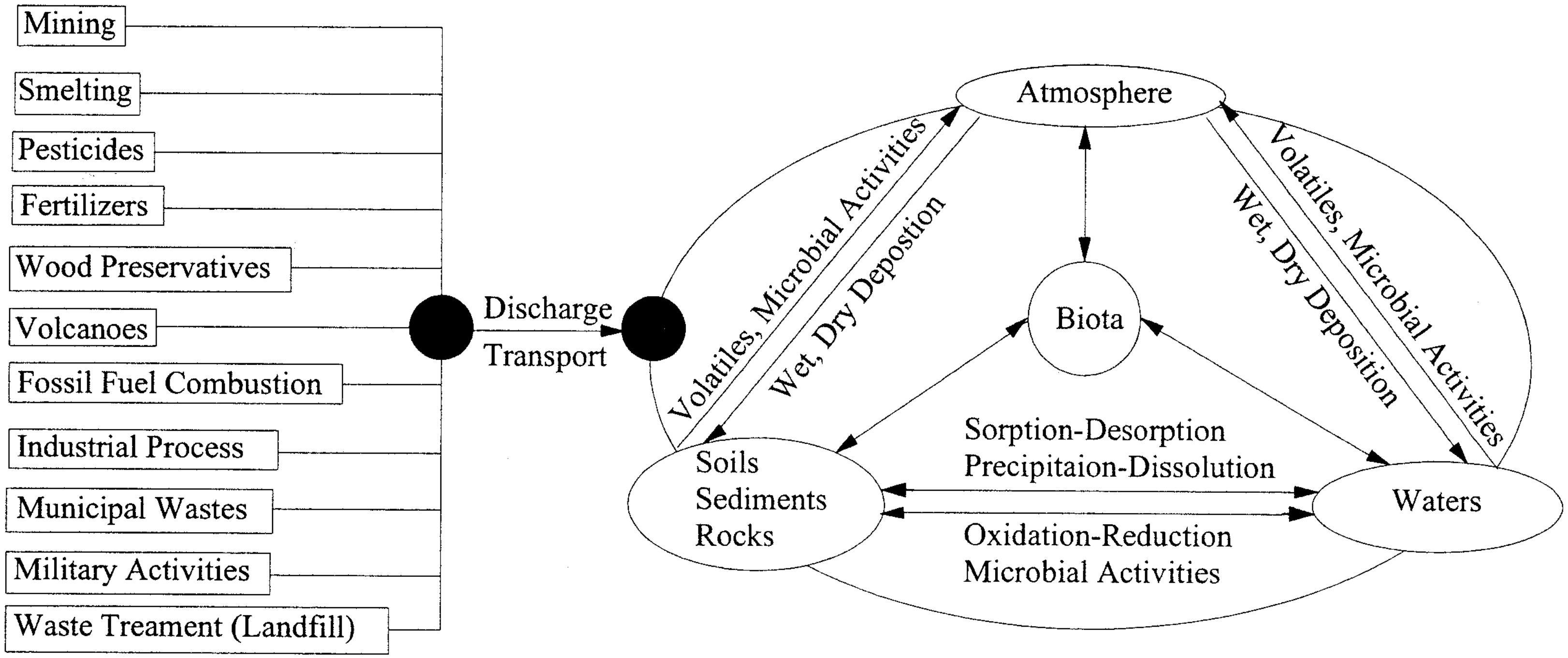


Figure 1-1. A simplified and comprehensive cyclic transfer of arsenic (Wang and Mulligan, 2006a)

There has been increasing interest recently on the role of natural organic matter (NOM) on the sorption behavior of arsenic species. Prevalent in the subsurface, NOM is highly reactive toward both metals and mineral surfaces, and therefore may play an important role in governing the mobility and bioavailability of both organic and inorganic contaminants. Dissolved organic matter (DOM) may complex some heavy metals leading to changes in their mobility. Moreover, organic acids may compete with metal ions, oxyanions and other organic ligands for reactive surfaces sites, which may inhibit or enhance dissolution depending on the type of surface complex formed and the strength of the bond (Eick *et al.*, 1999). Research studies have shown that organic acids could decrease phosphate adsorption on goethite and other surfaces of soil constituents (Fontes *et al.*, 1992). Arsenic behaves as an analog to phosphate (Yong and Mulligan, 2004), which could mean that organic acids could affect arsenic sorption through competition for reactive surface sites. Kalbitz and Wennrich (1998) demonstrated that dissolved organic carbon (DOC) concentration correlated very well with arsenic concentrations in aqueous extracts from soil. Hossain *et al.* (2003) suggested that sedimentary organic matter and peat soils are one of the important materials related to high arsenic concentrations in the sediments of the Bengal delta.

It has been demonstrated that biosurfactants (e.g., rhamnolipids) generated by bacteria and yeasts could be used potentially for the environmental remediation of organic contaminants and heavy metals from soils and sediments (Mulligan *et al.*, 1999; 2001a; 2001b; Wang and Mulligan, 2004b; 2004c; Mulligan, 2005; Mulligan and Wang, 2006). Biosurfactants can enhance the mobility of contaminants by reducing the interfacial tension between the contaminant and soil and forming micelles. One more attractive characteristic is that they are natural products, may be less toxic to biodegrading bacteria and can be degradable themselves. Therefore, they may be effective and nontoxic candidates for the remediation of arsenic contaminated sites.

1.3 Objectives

This research study therefore was focused on elucidating the effect of selected natural organic acids and a biosurfactant on arsenic mobilization from mine tailings to understand the cause of high arsenic concentrations in groundwater. Batch experiments were designed to determine the effects of pH, mass ratio of organic additives to the mine tailings, and reaction time. Comparisons were made between the effect of humic acid (HA) and rhamnolipid and other three low molecular weight organic acids (LMWOAs, i.e., L-cysteine, succinic acid, and L-aspartic acid) with well-defined structures. Based on batch tests, column experiments were run to investigate the feasibility of using NOM and biosurfactant for the remediation of arsenic contaminated soils.

The overall objectives of this research were

- to elucidate the mechanisms of arsenic mobilization from mine tailings in the presence of organic additives; and
- to determine the feasibility of using NOM and biosurfactant for the remediation of arsenic contaminated soils.

The specific objectives were:

- to identify crystallized arsenic mineral phases and particular oxides in the mine tailings;
- to identify arsenic-bearing phases in the mine tailings;
- to investigate the interaction between HA and arsenic on the mine tailings, exploring their implications on the control of arsenic mobility;
- to investigate the effects of rhamnolipid on arsenic mobilization from the mine tailings;
- to compare the effects of HA and rhamnolipid with that of LMWOAs on the mobilization of arsenic;
- to examine the effects of pH, mass ratio of HA and rhamnolipid to the mine tailings, and reaction time on arsenic mobilization;
- to determine the most affected fractions by washing with HA and rhamnolipid through comparing the fractional distribution of arsenic in the mine tailings before and after washing;
- to identify water-soluble arsenic species from the mine tailings, and to examine the effect of HA and rhamnolipid on the oxidation states of arsenic species; and
- to evaluate the feasibility of using NOM and biosurfactant in the remediation of arsenic contaminated soils.

1.4 Thesis contents and structure

This thesis consists of ten chapters and four appendices as follows:

- Chapter One gives an introduction of the extent, context and description of the problem and the objectives as well as the organization of this thesis;

- Chapter Two reviews the literature covering the sources, speciation, and fate of arsenicin the environment; the background of NOM and previous research studies on the interaction between NOM and arsenic; and the background of biosurfactants and their environmental applications as well as the current existing remediation technologies for arsenic contaminated soils;
- Chapter Three describes the materials, methods, and procedures used in the experiments;
- Chapter Four presents the main physicochemical characteristics of the mine tailings;
- Chapter Five summarizes and interprets the results from batch tests, and compares the SSE results of mine tailings before and after washing with HA and rhamnolipid;
- Chapter Six includes the main results from the FTIR tests;
- Chapter Seven presents the main results of arsenic speciation by CE analyses;
- Chapter Eight summarizes and interprets the results from column experiments;
- Chapter Nine discusses the effect of NOM and rhamnolipid on arsenic mobility and exploits the implications on the remediation of arsenic contaminated soils;
- Chapter Ten presents the conclusions, expected scientific contributions, and recommendations for future research;
- Appendix I presents arsenic concentrations of the mine tailings by ICP-MS analysis;
- Appendix II includes the main XRD results for the mine tailings;
- Appendix III summarizes the distribution coefficients of arsenic in the presence of HA and rhamnolipid, and the parameters of the desorption isotherm; and
- Appendix IV includes the electropherograms of standard solutions.

1.5 Scientific contribution of this research study

This research study examined the effects of a HA and a biosurfactant on arsenic mobilization from three Canadian mine tailings. Generally, this study adds to our expanding knowledge of global arsenic issues, and gives implications on the control of arsenic mobility. It helps to advance the knowledge of the sources, fate and transport of arsenic in natural systems and the understanding of the cause of arsenic contamination in groundwater, and provides a possible effective and environmental compatible remedial option for arsenic contaminated mine tailings, soils and sediments to prevent and avoid further contamination therefore helping to protect the environment and public health.

CHAPTER TWO

LITERATURE REVIEW

2.1 Arsenic sources

2.1.1 Natural arsenic sources

Arsenic is a naturally occurring toxic element and is widely distributed in natural ecosystems. Traces of arsenic are almost universal. Arsenic in soils may originate from parent rocks and human activities. The concentrations of arsenic in natural reservoirs with respect to soils have been calculated (Table 2-1). From Table 2-1, it is shown that more than 99% of the total arsenic in the environment is present in rocks (Bhumbla and Keefler, 1994). Of more than 320 known arsenic minerals, fewer than 10 are commonly identified in the environment, with the exception of scorodite ($FeAsO_4 \cdot 2H_2O$). The most commonly reported arsenic minerals are arsenic sulfides such as arsenopyrite (FeAsS), realgar (AsS), and orpiment (As_2S_3). They are often present in the sulfide ores of other metals. Arsenic can be released to the environment from these overburdened materials. It has become a major starting point for introduction of arsenic into the environment. Weathering and erosion of soils and rocks are the principal responsible processes.

The total arsenic in natural soils is evenly distributed with depth, varying with soil type and the nature of parent materials. The average amounts of arsenic in the earth crust and shale are 1.8 and 13 mg/kg, respectively (Iimura, 1981). The mean natural content of arsenic in soils is about 5-6 mg/kg, with a typical range of 0.1-40 mg/kg (Tamaki and Frankenberger, 1992). Soils derived from shales and granites have been shown to contain elevated arsenic concentrations of up to 250 mg/kg (Colbourn *et al.*, 1975). Wang and Mulligan (2006a) reported that arsenic concentrations in uncontaminated soils in Canada are normally below 15 mg/kg, but elevated concentrations up to 172,000 mg/kg were found in soils receiving anthropogenic inputs (Table 2-2).

Table 2-1. Calculated ratios of arsenic concentrations in natural reservoirs with respect to soils

Reservoir	Approximate Ratio with Respect to Soil (wt/wt)
Rocks	25000
Oceans	4
Soil	1
Biota (plants, man, microbial)	0.0005
Atmosphere	0.000001

(Mackenzie *et al.*, 1979; Bhumbla and Keefer, 1994)

The natural occurrence of arsenic contamination in waters has been attributed to several geophysical, geochemical and biological processes, including oxidation of arsenical sulfides, desorption of arsenic from (hydro)oxides, reductive dissolution of arsenic-containing (hydro)oxides, release from geothermal waters, and evaporative concentration, as well as leaching of arsenic from sulfides by carbonates (Kim *et al.*, 2000; Bennett and Dudas, 2003; Schreiber *et al.*, 2003; Wang and Mulligan, 2004a; 2006a; 2006b). Adsorption is the primary control on arsenic mobility in aqueous systems. It is affected by factors such as changes in pH, occurrence of redox reactions, presence of competing ions, and solid-phase structural changes at the atomic level as well.

Table 2-2. Arsenic concentrations in Canadian soils

Location	Arsenic Concentration average (range) (mg/kg)	References
Natural uncontaminated soils	4.8-13.6	CCME (1999/2002); CED (2003)
	11	MacLean and Langille (1981)
Acid sulfate soils, AB	5 (1.5-45)	Dudas and Pawluk (1980); Dudas (1984); Dudas *et al.* (1988); Bennett and Dudas (2003)
Resident garden soil, Ottawa	3.0 (1.7-9.9)	Rasmussen *et al.* (2001)
Surface peat, MB	4-280	Zoltai (1988)
Yellowknife	4-150	ESG (2000)
	32 (4-70)	Ollson (1999)
Sydney, NS	2-157	Lambert and Lane (2004)
Bowen Island, BC	2-172,000	Boyle *et al.* (1998)
Montreal, QC	410 ± 150	Zagury *et al.* (2003)
Elmsdale, NS	262	Bamwoya *et al.* (1991)
Delora, ON	1,023 ± 15	Zheng *et al.* (2003)
Playgrounds, Vancouver	6.4-51.3	CED (2003)
Playgrounds, Edmonton	8.6-52.3	CED (2003)
Playgrounds, Winnipeg	2.8-21.3	CED (2003)
Playgrounds, Toronto	2.6-147.0	CED (2003)
Playgrounds, Ottawa	3.1-17.4	CED (2003)
Playgrounds, Montreal	0.5-104.0	CED (2003)
Playgrounds, Halifax	9.4-69.4	CED (2003)
Giant Mine Townsite, Yellowknife	754-9,580 1,174 ± 519 (crushed rock) 87 ± 89 (clay)	EBA (1998)

Arsenic is found in natural waters in wide ranging amounts, from less than 0.5 μg/L to greater than 12,000 μg/L (Schreiber *et al.*, 2003; Wang and Mulligan, 2006a). Arsenic concentrations in freshwater are typically less than 10 μg/L. High concentrations of arsenic tend to be found more in groundwater than in surface water sources of drinking water. Arsenic concentrations in water samples from wells in a thin, alluvial aquifer of the Madison River Valley, Montana, have been reported to be in the range of 26 to 150 μg/L (Sonderegger and Ohguchi, 1988). Arsenic concentrations up to 12,000 μg/L have been measured in groundwater from a sandstone aquifer in the Fox River valley in eastern Wisconsin, USA (Schreiber *et al.*, 2003).

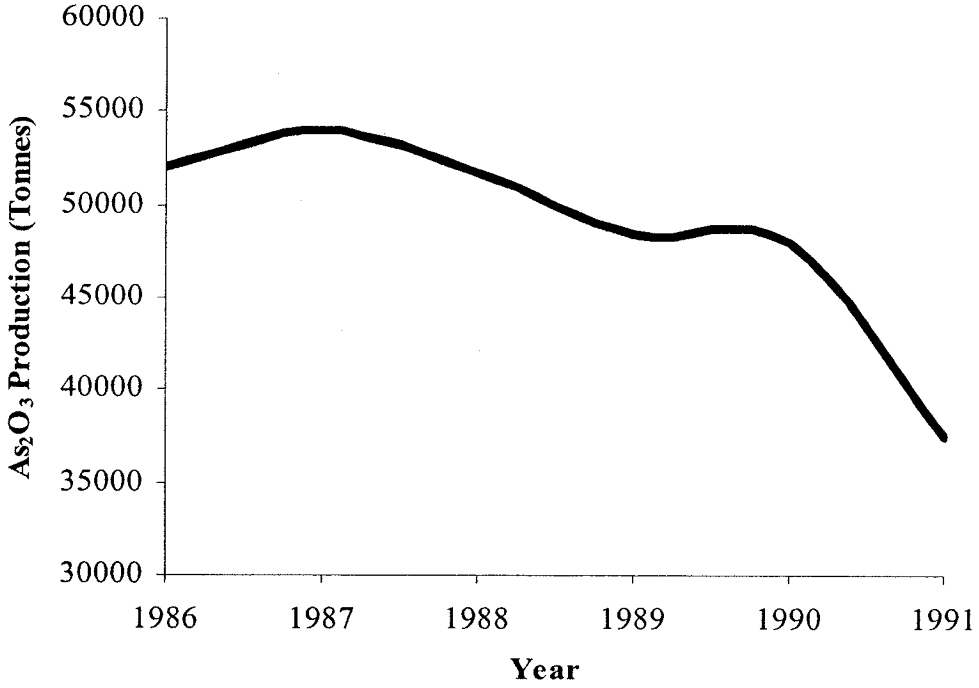


Figure 2-1. World Production of As_2O_3, 1986-1991

(modified from Loebenstein, 1993)

2.1.2 Anthropogenic arsenic sources

Human activities are also important sources of arsenic in the environment. Arsenic trioxide (As_2O_3) is the major form of arsenic that is produced for industry. Limited data on world production of As_2O_3 and Canadian arsenic production is shown in Figures 2-1 and 2-2, respectively. The main anthropogenic activities that may release arsenic into the environment include nonferrous metal mining and smelting, fossil fuel processing and combustion, wood preserving, pesticide production and application, and disposal and incineration of municipal and industrial wastes. Moreover, the contamination in agricultural regions due to irrigation with groundwater with a high arsenic content from natural origin is widely reported (Tanabe *et al.*, 2001). Of the total arsenic added to soils about 41% has come from commercial product wastes, about 23% comes from coal fly ash and bottom ash, 14% from atmospheric fallout, 10% from mine tailings, 7% from smelters, 3% from agriculture, and 2% from manufacturing, urban, and forestry wastes (Figure 2-3, Nriagu and Pacyna, 1988). The on-site, off-site and total releases of arsenic from 1994 to 2001 based on the Environment Canada's National Pollutant Release Inventory (NPRI) are illustrated in Figure 2-4.

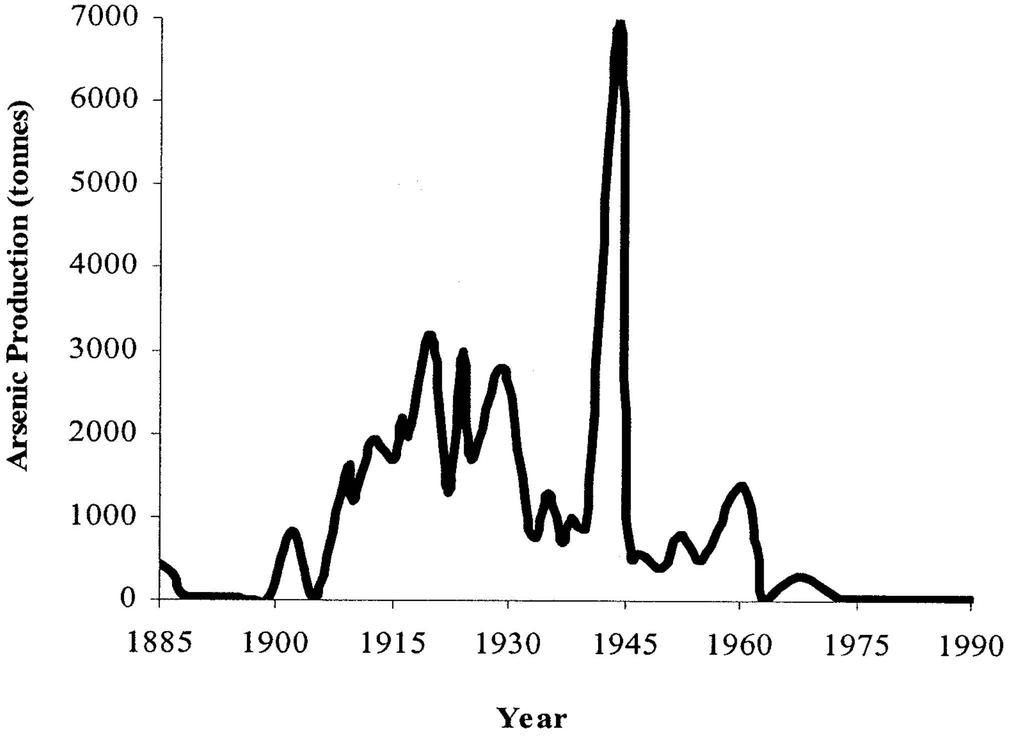


Figure 2-2. Canadian arsenic production, 1885-1990 (modified from Cranstone, 2001)

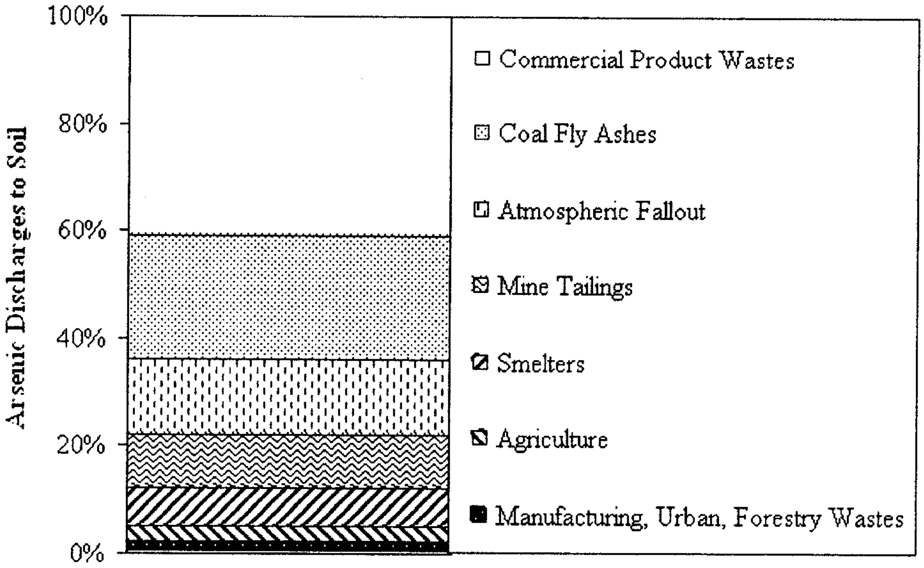


Figure 2-3. Anthropogenic arsenic discharges onto soil

(modified from Nriagu and Pacyna, 1988)

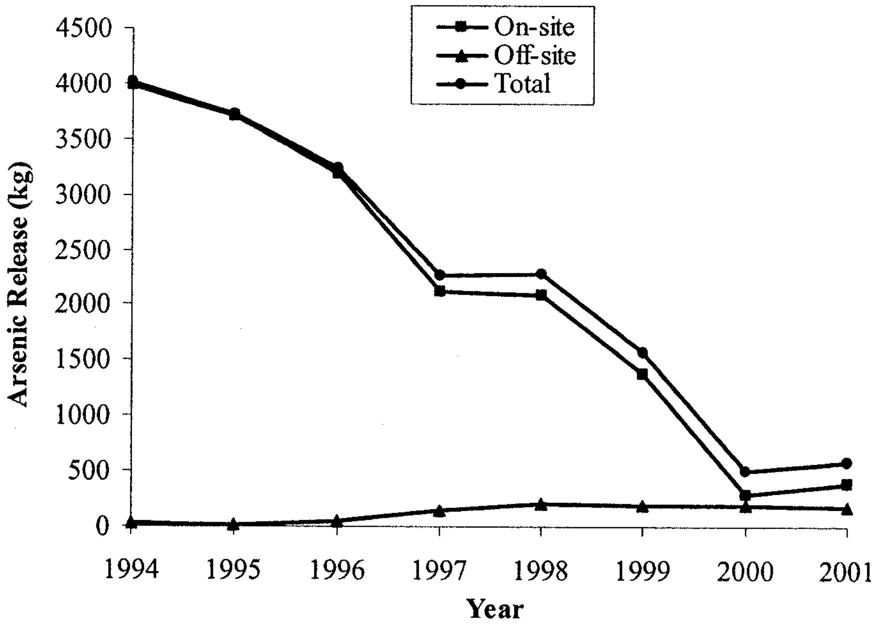


Figure 2-4. Arsenic release from Canadian NPRI Reporting Facilities, 1994-2001

(Wang and Mulligan, 2004a)

The effect of anthropogenic inputs on the level of arsenic contamination is dependent on the intensity of human activity and the distance from the pollution sources as well as the pollutant dispersion pattern. Most anthropogenic releases of arsenic are to land or soil, primarily in the form of pesticides or solid wastes. However, substantial amounts are also released to air and water (USDHHS, 2000). Soluble forms of arsenic are known to leach into groundwater and may enter surface waters from runoff. Slimak and Charles (1984) estimated that 19% of the arsenic follows soil-related pathways via runoff and leaching.

Both historical and recently deposited tailings from mining operations usually contain high levels of arsenic, and are of concern as potential sources of environmental contamination. It was reported that the annual total fluvial input of arsenic to the Moira Lake in Ontario (Canada) was approximately 3.5 tonnes due to local mining and mineral processing (Azcue and Nriagu, 1995). Coumans (2003) estimated that about 220 million tonnes of highly toxic arsenic trioxide were buried underground which threatens ground and surface water for kilometers around the Giant Mine in Yellowknife, NWT.

In mine tailings, arsenic occurs in various forms such as arsenopyrite, arsenian pyrite, arsenates, and arsenic-bearing iron oxyhydroxides. Peterson *et al.* (1979) reported total arsenic concentrations greater than 20,000 mg/kg in grossly contaminated mine spoils of southwest England. The maximum concentration was found at a depth of 20-40 mm, and very high concentrations up to 33,750 mg/kg were detected at the lowest depth sampled (250-300 mm). As(V) and As(III) were the major arsenic species present in the water-soluble soil extracts, and organoarsenic such as dimethylarsine was also detected in surface samples. In Yellowknife, Canada, arsenic concentrations up to 25,000 mg/kg was found in Con Mine tailings, 4,800 mg/kg in Giant Mine tailings, and 12,500 mg/kg in the historical Negus tailings (Ollson, 1999). In northern Saskatchewan (Canada), total arsenic concentrations in the mine tailings and their associated pore fluids from the Rabbit Lake in-pit tailings management facility (RLITMF) ranged from 56 to 9,871 mg/kg and 0.24 to 140 μg/L, respectively (Moldovan *et al.*, 2003). Donahue and Hendry (2003) reported that dissolved arsenic concentrations in 5 monitoring wells installed within the tailings body from RLITMF ranged from 9,600 to 71,000 μg/L.

Elevated arsenic concentrations have been reported in waters near the vicinity of gold-mining or ore-roasting operations. The arsenic contents of the suspended particulates from Gegogan Lake, Nova Scotia near an abandoned gold mine, ranged from 1,500 to 5,000 mg/kg, and the arsenic contents in filtered stream water varied from 30 to 230 μg/L (Wong *et al.*, 1999). In the vicinity of Yellowknife, arsenic concentrations in the water of lakes ranged from 700 to 5,500 μg/L (Wagemann *et al.*, 1978). Coumans (2003) estimated that the surface water in the Kam Lake, Yellowknife, contained up to 1,570,000 μg/L of arsenic. The dominant species were As(V) anions (Ollson, 1999).

2.2 Arsenic speciation

Arsenic speciation has gained its significance since it plays a vital role in determining the mobility and bioavailability of arsenic in the environment. Also it is reported that physiological and toxic effects of arsenic differ dramatically with the wide range of its chemical forms and oxidation states. Arsenic exists essentially in four oxidation states (-

III, 0, +III, and +V) in natural environments. Arsenic metal rarely occurs and the minus III oxidation state is found only in extremely reduced environments. Arsenic forms a variety of inorganic and organic compounds in soils, sediments and natural waters (Figure 2-5), but most of them are in the inorganic form of As(III) and As(V). The As(III) group is characterized with a distinctive pyramidal geometry due to the stereochemically active lone pair of electrons on the As(III) species, whereas the As(V) group shows a tetrahedral coordination (Lee and Harrison, 2004). Methylated arsenic compounds such as monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) can be formed through biomethylation by microorganisms under favorable conditions (Cullen and Reimer, 1989). Moreover, in sulfide concentrated solutions, the dissolved thioarsenic species such as $H_2AsOS_2^-$ and $H_2AsS_3^-$ can be significant (Clarke and Helz, 2000).

2.2.1 Effect of pH and Eh on arsenic speciation

Depending on pH and redox conditions (Eh), As(V) and As(III) are usually the main species present in soil and natural waters, while concentrations of organoarsenic compounds are generally low or negligible (Yong and Mulligan, 2004). As(V) is found mainly in oxic conditions (Eh>200 mV, pH 5-8), whereas As(III) is predominant in reducing conditions (Tamaki and Frankenberger, 1992). Masscheleyn *et al.* (1991) found that As(III) and As(V) could occur together even in oxic conditions because the oxidation of As(III) to As(V) is a kinetically slow process. The ratio of As(III) to As(V), however, increases with Eh decreases caused by water saturation or anoxic conditions. Woolson and Kearney (1973) reported that there is no obvious correlation between Eh and the formation of organoarsenic species presumably due to microbiological transformations.

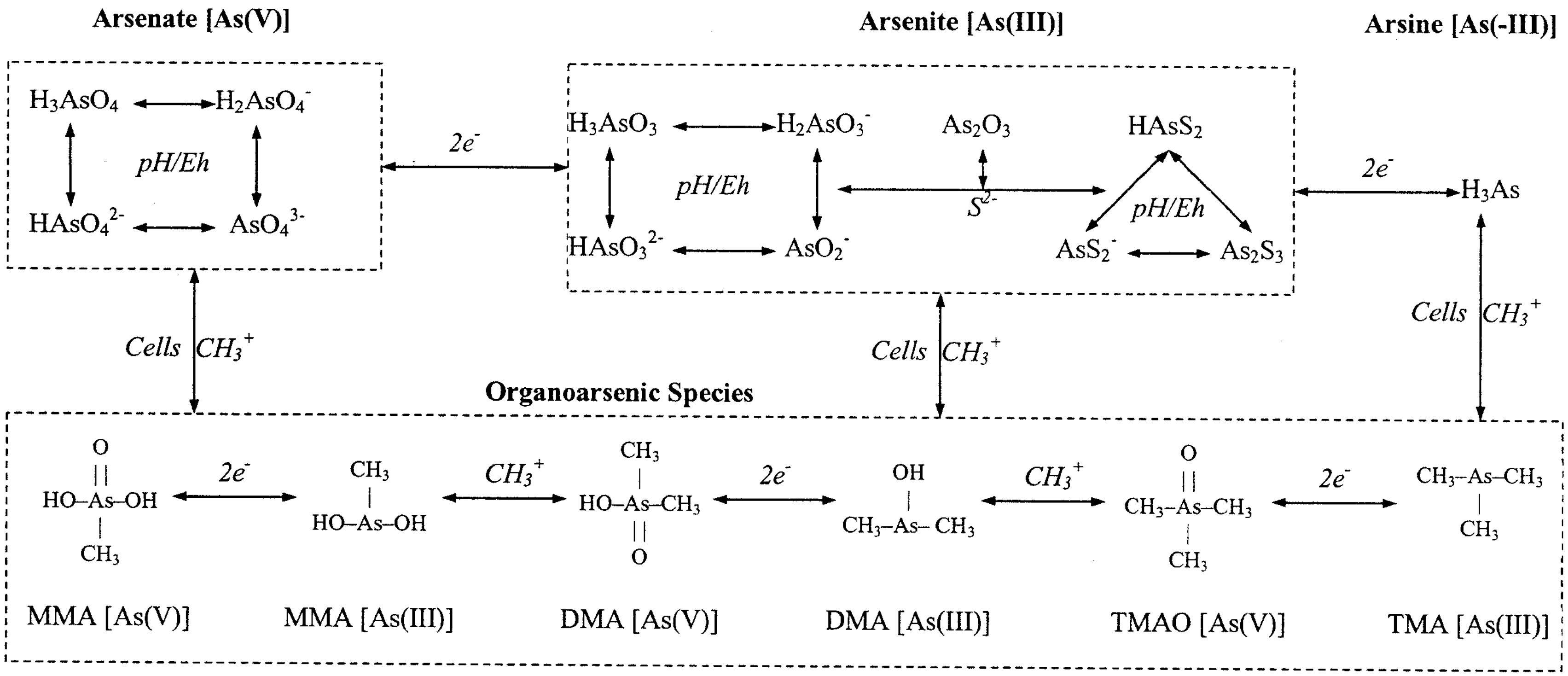


Figure 2-5. Main arsenic species and inter-transformations

(Wang and Mulligan, 2006b)

Both As(III) and As(V) form protonated oxyanions in aqueous solutions, and the degree of protonation increases with pH decrease (Ferguson and Gavis, 1972). The pK_a values for As(III) are $pK_a^1 = 9.2$ and $pK_a^2 = 12.1$, and those for As(V) are $pK_a^1 = 2.2$, $pK_a^2 = 6.9$, and $pK_a^3 = 11.5$ (Figure 2-6; Ferguson and Gavis, 1972). As a consequence, in the low to intermediate pH range of about 3 to 9 commonly found in soil and natural waters, As(III) exists dominantly as the neutral species H_3AsO_3 , whereas As(V) can exist as negatively charged $H_2AsO_4^-$ and $HAsO_4^{2-}$.

2.2.2 Effect of arsenic speciation on its mobility

The chemical form of arsenic is of great importance in determining its sorption behavior to mineral surfaces and further mobilization to the aqueous phase in equilibrium with soil and sediments. Sorption reactions are of most significance in controlling the mobility of As(III) and As(V) in the environment. As(III) is considered more mobile than As(V) in aquatic systems, and inorganic arsenic species are more mobile than organoarsenic species. As(V) is somewhat less mobile because As(V) usually sorbs more strongly than As(III) to minerals (Pierce and Moore, 1982), and the reduction of As(V) to As(III) sometimes may convert sorbent oxides into soluble forms. Gulens *et al.* (1979) reported that As(III) is 5 to 8 times more mobile than As(V) in a non-adsorbing sandy loam. Xu *et al.* (1991) found that the adsorption of arsenic on alumina decreased in the order of As(V) > MMAA = DMAA > As(III) at a pH below 6 and As(V) > As(III) > MMAA = DMAA at a pH above 6. The maximal adsorption achieved around pH 5 for As(V), pH 7 for As(III) and pH 4 for MMAA and DMAA.

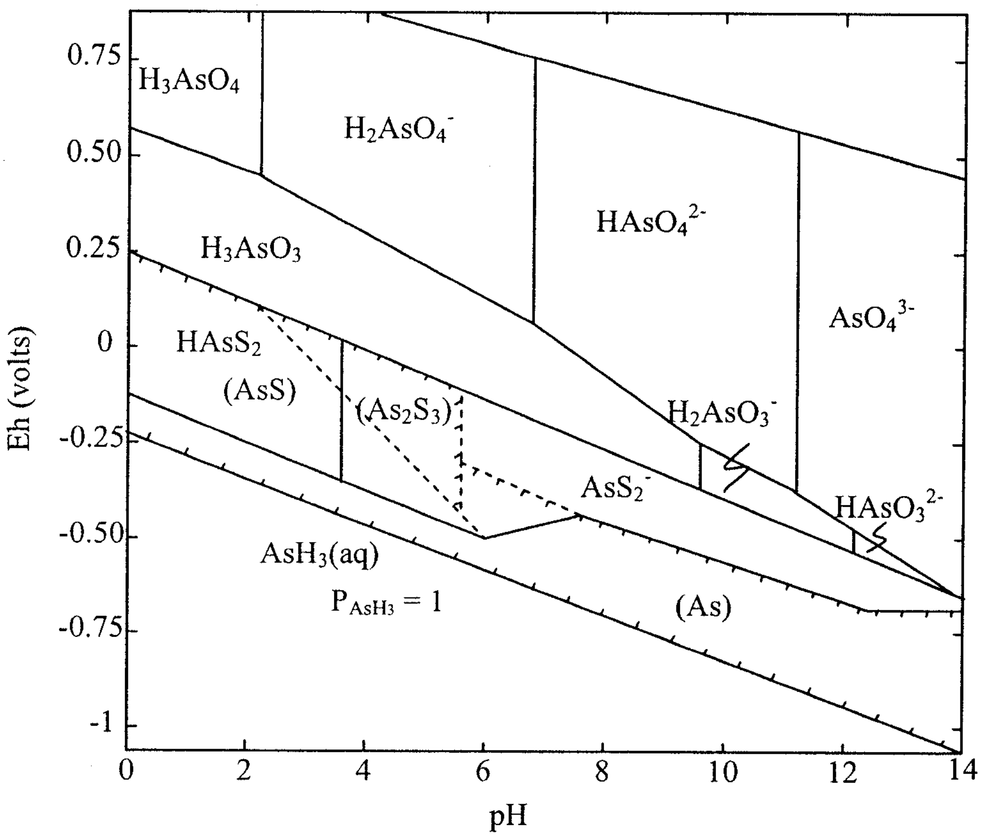


Figure 2-6. *Eh-pH* diagram for arsenic at 25°C and 101.3 kPa with a total concentration of arsenic of 10^{-5} mol/L and a total concentration of sulfur of 10^{-3} mol/L. Solid species with solubilities less than $10^{-5.3}$ mol/L are enclosed in parentheses in the cross-hatched area. The dotted line indicates the lower boundary between the arsenic sulfides and arsenic metal due to a decrease in sulfide activity (after Ferguson and Gavis, 1972).

2.2.3 Effect of arsenic speciation on its toxicity

It is reported that physiological and toxicological effects of arsenic differ dramatically due to the wide range of its chemical forms and oxidation states. The inorganic forms are highly toxic. As(V) acts as an analog of phosphate (PO_4^{3-}) in the glycolytic pathway, whereas As(III) binds strongly to sulfhydryl groups of amino acids such as cysteine in proteins inactivating a wide range of enzymes in intermediate metabolism (Tamaki and Frankenberger, 1992). Therefore, As(III) is more toxic than As(V). However, exposure to both As(III) and As(V) may result in similar toxicological effects since more recent studies have shown that most ingested As(V) can be reduced to As(III) by As(V) reductases (Oden *et al.*, 1994). Although organoarsenic species generally are considered less toxic than inorganic species, some trivalent methylated arsenic species [e.g., MMAA(III) and DMAA(III)] have been found to be more toxic than inorganic arsenic and are more efficient at causing DNA breakdown (Styblo *et al.*, 2000). Whether arsenic is in a dissolved or particulate state may also be very important from an ecotoxicological viewpoint, depending on the uptake mode of the particular organism.

2.3 Transport and fate of arsenic in the environment

The fate and transport of arsenic in natural systems are principally governed by its sorption behavior on the (hydro)oxides of iron (Fe), aluminum (Al) and manganese (Mn), organic matter, and clay minerals (Table 2-3; Wang and Mulligan, 2006d). Ubiquitous in the environment, (hydro)oxides of Fe, Al and Mn are potentially the most important source/sink for arsenic in soil and aquifer sediments. They usually coat other particles. Upon exposure to water, metal ions on the oxide surface complete their coordination shells with OH groups, which can bind or release H^+ when pH changes. The formation of the OH_2^+, OH, and O^- surface functional groups determines the adsorption properties of the oxides (Wang and Mulligan, 2006b). At pH values lower than the isoelectric point, a positive surface charge is formed and the adsorption of arsenic anions is facilitated by coulombic attraction. At pH greater than the isoelectric point, a negative surface charge is formed and arsenic is specifically adsorbed onto the hydroxide surface.

Spectroscopic studies have confirmed that both As(III) and As(V) may form inner-sphere complexes on the surfaces of Fe, Al, and Mn (hydro)oxides and clay minerals through ligand exchange with OH and OH_2^+ surface functional groups, As(III) may also form outer-sphere complexes by simple coloumbic (electrostatic) interactions on the surface of amorphous Al hydroxides and sulfide minerals (Wang and Mulligan, 2006c). Inner-sphere complex bonds are much stronger than outer-sphere complex bonds, resulting in a stronger adsorption. The sorption to mineral surfaces can transfer soluble arsenic to particulate phases, thus immobilizing it. However, the particulate phases may eventually act as an arsenic releasing source due to changes in pH, redox potential, and microbial activity.

The sorption of As(V) on amorphous $Al(OH)_3$, α-Al_2O_3, ferrihydrite and hematite is optimal at acidic pH 3-5, while the sorption of As(III) on ferrihydrite, goethite, kaolinite, illite, montorillonite, and amorphous aluminum oxides increases gradually from pH 3.5 to 8.5 (Wang and Mulligan, 2006b). Under anaerobic conditions, sorbed arsenic may be released due to the reductive dissolution of metal oxides (Nickson *et al.*, 2000). Under anaerobic and strongly reducing conditions the formation of sulfide minerals in the presence of sulfur (S) controls arsenic mobility. In the deeper zone of bottom lake sediments, where SO_4^{2-} reduction to H_2S under very reducing conditions, arsenic can precipitate in the form of secondary sulfides like orpiment, As_2S_3, or arsenic-rich pyrite (Belzile and Tessier, 1990).

Table 2-3. Effects of main adsorbents on arsenic mobility and transformation

Mineral occurrence	Main affecting mechanism	References
Fe hydroxides	As(V), $CH_3AsO_2(OH)^-$ and $(CH_3)_2AsOOH$ adsorption at pH 4-7, maximized at pH 4; As(III) adsorption at pH 7-10, maximized at pH 7; Desorption when pH increases; Amorphous phases of higher adsorption capacity; Releasing sorbed arsenic during chemical and microbial reduction dissolution ; As(III) oxidization	Pierce and Moore (1982) Cox and Ghosh (1994) Lin and Puls (2003)
Al hydroxides	As(V), $CH_3AsO(OH)_2$, and $(CH_3)_2AsOOH$ adsorption up to pH 7 and decreases at higher pH; As(III) adsorption at pH 6-9.5 and decreases at higher pH; Amorphous phases of higher adsorption capacity	Ghosh and Teoh (1985) Xu *et al.* (1988) Cox and Ghosh (1994) Manning and Goldberg (1997)
Mn hydroxides	Negligible As(V) adsorption, but increased in the presence of other divalent cations, forming inner-sphere complexes; Slightly greater As(III) oxidization rate at low pH; Poorly crystalline phases are more efficient	Scott and Morgan (1995) Manning *et al.* (2002)
Clay	As(V) adsorption up to pH 7 and decreases with pH increase; Low As(III) adsorption at low pH and increases with pH; High surface areas showing higher adsorption capacity; As(III) oxidation in the presence of trace amounts of Fe or Mn oxides, iodide, or TiO_2	Frost and Griffin (1977) Manning and Goldberg (1997) Lin and Puls (2000)
Sulfides	Arsenic substitution for S, forming arsenic sulfide precipitates in reduced environment; Releasing arsenic during chemical and microbial oxidation of arsenic-bearing sulfides	Beattie and Poling (1987)
Anions	Competition for active adsorption sites, influenced by pH and mass ratios	Manning and Goldberg (1996) Jain and Loeppert (2000) Meng *et al.* (2000)
Cations	Enhancing arsenic adsorption by increasing the amount of positive charge on the oxide surfaces	Ghosh and Teoh (1985) Meng *et al.* (2000)

The presence of dissolved cations (e.g., Ca^{2+}, Fe^{2+}, and Mg^{2+}) can enhance the sorption of arsenic to minerals by increasing the amount of positive charge on the mineral surface and/or forming a positively charged surface, while the presence of competing anions (e.g., phosphate, sulfate, and carbonate) can inhibit arsenic sorption by competing for active adsorption sites. Experimental results have demonstrated that phosphate can suppress the adsorption of both As(V) and As(III), while As(V) is much more strongly affected than As(III) (Manning and Goldberg, 1996; Jain and Loeppert, 2000). Sulfate has essentially no effect on As(V) adsorption but may compete with As(III) adsorption when pH is below 7 (Jain and Loeppert, 2000). The presence of bicarbonate (HCO_3^-) can facilitate the mobilization of arsenic from arsenic-containing sulfides such as orpiment in both oxic and anoxic environments (Kim *et al.*, 2000). The mobilization of arsenic increases with increasing HCO_3^- concentrations and pH. Meng *et al.* (2000) reported that silicate reduced the adsorption of As(III) and As(V) on ferrihydrite at pH 6.8. Competitive adsorption between As(V) and molybdate (MoO_4^{2-}) was also observed (Roy *et al.*, 1986).

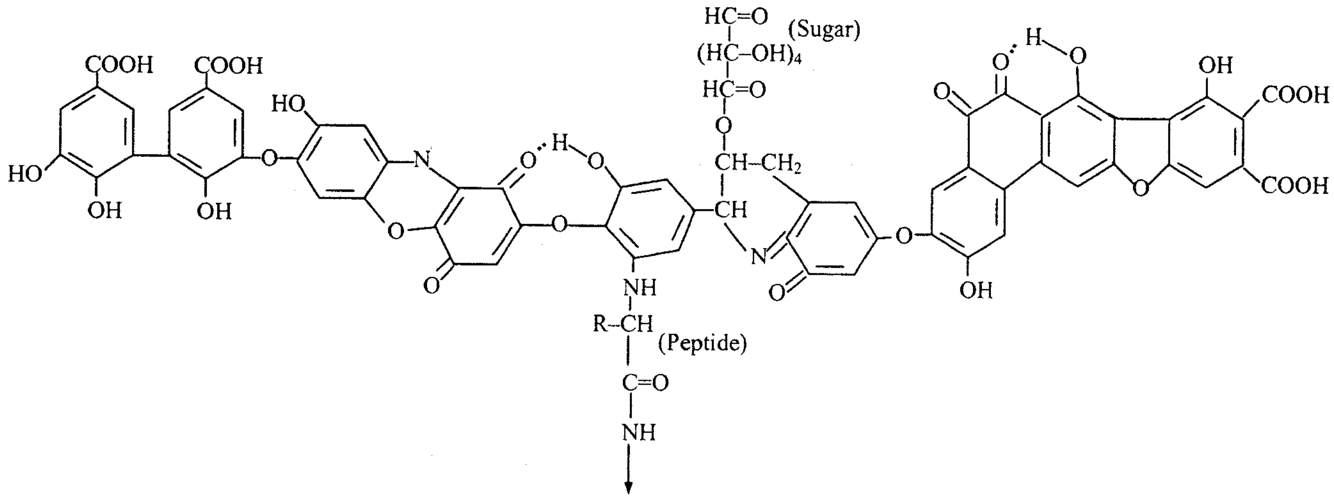
Microorganisms also play a vital role in influencing the redox transformation, detoxification, and mobilization processes of arsenic. Under anaerobic conditions such as in landfills and deep sediments, anaerobic microorganisms can potentially use As(V) as an electron acceptor for the oxidation of organic matter or H_2 gas, yielding energy to support their growth. Zobrist *et al.* (2000) reported that As(V) reduction can lead to the mobilization of arsenic without dissolving the sorbent phase by anaerobically incubating As(V) coprecipitated with Al hydroxide in the presence *Sulforospirillum barnesii.* However, As(V) reduction does not necessarily take place as an energy providing (dissimilatory) process. Macur *et al.* (2001) ascribed the active As(V) to As(III) reduction under oxic conditions in limed mine tailings to a detoxification rather than an energy-producing, respiratory process. Certain chemoautotrophs, such as *Pseudomonas* *arsenitoxidans* NT-26, can oxidize As(III) by using O_2, NO_3^-, or Fe(III) as a terminal electron acceptor and CO_2 or HCO_3^- as the carbon source, providing energy for the microbial growth. It has been reported that *Thermus aquaticus* and *Thermus thermophilus* may catalyze in oxidizing As(III) in thermal environments (Gihring *et al.*, 2001). The Fe and Mn oxidizing bacteria, including sheaths (e.g., *Sphaerotilus*), *Leptothrix* group (e.g., *Leptothrix ochracea*), or spirally twisted stalks (e.g., *Gallionella ferruginea*), are able to accelerate the removal of Fe(II) from groundwater (Mouchet, 1992). These bacteria can cause the oxidation of dissolved Fe(II) cations, resulting in the precipitation of respective Fe oxides, which can enhance arsenic removal from waters by direct adsorption and coprecipitation. On the other hand, other microbially induced reduction reactions may remobilize sorbed arsenic. Cummings *et al.* (1999) reported that the dissimilatory Fe reducing bacterium *Shewanella alga* (strain BrY) could enhance the mobilization of arsenic from a crystalline ferric arsenate (scorodite, $FeAsO_4 \cdot 2H_2O$) as well as from sorption sites within whole sediments. There is evidence that high arsenic concentrations can accumulate in microbes and plants (Ma *et al.*, 2001). The hyperaccumulation of arsenic in plants may reduce arsenic concentrations at the contaminated sites by translocating it into plant tissues.

2.4 Interaction between NOM and arsenic

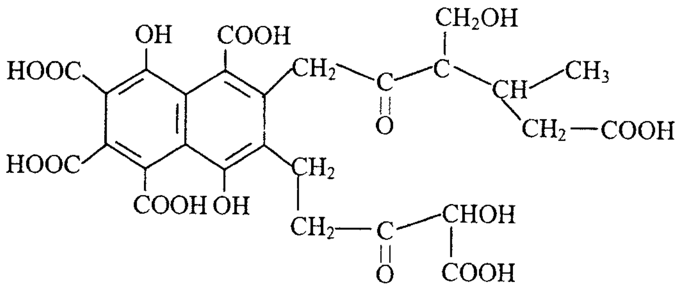
2.4.1 Background on NOM

NOM originates mainly through chemical and microbial decomposition of terrestrial and aquatic animals as well as plants. It is ubiquitously distributed and constitutes the main organic fraction in water, soil, and sediments. Insoluble NOM is a part of soil and sediments. Dissolved organic matter (DOM) in aquatic environments consists of a heterogeneous association of amorphous, poorly defined macromolecular substances with a large number of diverse chemical functionalities. About 20% of DOM consists of carbohydrates, carboxylic acids, amino acids, hydrocarbons and other unidentifiable organic acids (Sposito, 1984). The remaining 80% of DOM consists of humic substances such as humic and fulvic acids (HA; FA; Figure 2-7; Sposito, 1984). They are either truly dissolved or colloidal in form and are distributed throughout the aqueous phase. They can also bind to soil and sediment components.

The reactivity of NOM varies greatly with its physicochemical properties such as molecular weight, elemental composition, aromaticity, and functional group content. As structurally complex products of biomass decomposition, these molecules possess unique combinations of functional groups, including carboxylic, esteric, quinone, amino, nitroso, sulfhydryl, phenolic and alcoholic hydroxyl, and other moieties (Perdue *et al.*, 1980; Redman *et al.*, 2002). These functional groups have different dissociation constants and deprotonate at different pH conditions. The majority of them are negatively charged at neutral pH. At low pH values, they are protonated and uncharged with a tightly coiled and cross-linked conformation, but at higher pH values, they are dissociated and become negatively charged with a more open conformation (Amina *et al.,* 1999). The occurrence of negative charges and open conformation enables NOM to bind dissolved cations and to adsorb to positively-charge reactive sites at the surface of clays and (hydro)oxides (Stevenson, 1982). This phenomenon results in changes in the properties of the sorbent and therefore interferes with the sorption of other ions.



A: Humic acid (Stevenson, 1982)



B: Fulvic acid (Buffle, 1977)

Figure 2-7. Hypothetical model structures of HA and FA

Ligand exchange-surface complexation, between carboxyl/hydroxyl functional groups of NOM and metal (e.g., Al and Fe) (hydro)oxides, has been proposed as the dominant interaction mechanism for the sorption of NOM, especially under acidic or slightly acidic pH conditions (Parfitt *et al.,* 1977; McKnight *et al.*, 1992; Gu *et al.*, 1994). The adsorption occurs with the replacement of the surface hydroxyl groups on oxides by the carboxyl groups of organic acids (Parfitt *et al.*, 1977). Functional groups such as carboxyl, hydroxyl, and amino groups as well as other N- and S-containing groups have the potential to form strong complexes with metal cations (Parfitt *et al.*, 1977; McKnight *et al.*, 1992; Gu *et al.,* 1994). It has been demonstrated that carboxyl and hydroxyl functional groups of HA and FA are able to form very stable complexes with many metal cations or hydroxy metal cations in the order of $Fe^{3+} > Al^{3+} > Pb^{2+} > Ca^{2+} > Mn^{2+} > Mg^{2+}$ (Gu *et al.*, 1994).

This ligand exchange-surface complexation mechanism for NOM sorption to metal (hydro)oxides is similar to that proposed for the sorption of As(III) and As(V). Both HA and FA are negatively charged and show a high affinity for adsorption to the metal (hydro)oxide surfaces. Therefore, they tend to compete with As(V) and As(III) anions for adsorption to the solid surfaces (Xu *et al.,* 1988; Takahashi *et al.*, 1999; Grafe *et al.*, 2001; 2002). On the other hand, the formation of NOM-metal complexes may strongly bind As(III) and As(V) anions through metal-bridging mechanisms (Redman *et al.*, 2002). Both As(III) and As(V) can form aqueous complexes with HA and FA, but As(III) prefers aqueous complexation when compared to As(V) (Ko *et al.,* 2004). Crist and Martin (1999) reported that the complexes of FA generally are more soluble than those of

HA because of their lower molecular weights, higher oxygen content, higher contents of acidic functional groups and higher acidity.

Sorbed NOM usually forms a coat on the mineral surfaces. The surface behavior of the coated minerals therefore (e.g., electrophoretic mobility and colloidal stability) may be dominated by the sorbed NOM (Gu *et al.*, 1994). A major fraction of the sorbed NOM are humic and fulvic acids. HA is polyfunctional and oligoelectrolytic and thus behaves as a heterogeneous ligand, whereas FA is especially active in dissolving minerals and metals when in water (Crist and Martin, 1999). McKnight *et al.* (1992) observed that the adsorption of FA to hydrous Al and Fe oxides increased with the carboxyl acids, N, S, and amino acid contents of the FA. As(III) is known as a potent electrophile and can react strongly with amino and sulfhydryl groups due to their nucleophilic properties. Several studies have demonstrated the significance of amine groups in the adsorption of arsenic onto the organic matter (Thanabalasingam and Pickering, 1986; Cornu *et al.*, 1999; Saada *et al.*, 2003). Moreover, NOM is able to reduce Fe(III) and Mn(III or IV) oxides, leading to the leaching of sorbed arsenic (McArthur *et al.*, 2001; 2004). It may also catalyze the oxidation and reduction reactions between As(III) and As(V) (Welch and Lico, 1997; Redman *et al.*, 2002). However, the transformation of NOM upon reaction with mineral surfaces has not been well documented due to the heterogeneity of NOM.

2.4.2 Previous research studies on interactions between NOM and arsenic

A number of research studies have been performed to elucidate the effect of NOM on the sorption behavior of arsenic species and the consequential influence on their mobility

(Table 2-4). Thanabalasingam and Pickering (1986) found that the adsorption of As(V) and As(III) to two HAs varied with the concentration, pH, and inorganic content of the substrate and valency state.

Xu *et al.* (1988) found that the introduction of FA at low or moderate concentration levels decreased arsenic adsorption on alumina (α-Al_2O_3) greatly. Grafe *et al.* (2001) reported that both a peat HA and a Suwannee River FA decreased As(V) adsorption on goethite (α-FeOOH) but citric acid (CA) had no effect. As(III) adsorption was reduced by all three organic acids in the order of CA>FA≈HA. Both FA and CA reduced As(III) adsorption on ferrihydrite ($Fe_5OH_8 \cdot 4H_2O$) whereas HA had no effect (Grafe *et al.*, 2002). The studies demonstrated the significance of characteristics of solid surface in adsorption processes and functional group composition. COOH groups are likely to be the most involved in the adsorption process while phenol groups are not likely to interact with a ferrihydrite surface as much as they do with a goethite surface (Kaiser *et al.*, 1997).

Redman *et al.* (2002) suggested that the aqueous complexation between NOM and arsenic was sufficiently great, that NOM could substantially increase arsenic mobility whether it were introduced into a system before or after the arsenic. Furthermore, NOM may greatly influence redox as well as complexation speciation of arsenic in freshwater environments. Hematite may act as a surface catalyst or as an electron-transfer intermediate in this process.

Table 2-4. Summary of previous studies on interaction between NOM and arsenic

Description	Main Observation & Conclusions	References
Experimental investigation of the sorption of As(III) and As(V) by two HAs	Adsorption of arsenic to the HAs varied with concentration, pH, and inorganic content of the substrate and valency state.	Thanabalasingam and Pickering (1986)
Experiments to study the adsorption of As(V) on alumina, hematite, kaolin and quartz, and the effects of pH, arsenic concentration, sulfate and fulvic acids	Low or moderate concentration levels of fulvic acids decreased As(V) adsorption by alumina at pH 3-7.5.	Xu *et al.* (1988)
Batch type distribution experiments to study the effects of acidification on adsorption and potential mobility of various arsenic forms	Both acidification and organic matter addition reduced arsenic mobility with arsenic adsorption reaching a maximum at around pH 5 for As(V).	Xu *et al.* (1991)
Experiments to measure the effects of pH and soil organic acids on sorption of As(V), As(III), MMA and DMA on goethite, hematite and lepidocrocite	Both a drop in pH and an increase in fulvic acid increase arsenic leaching. Amorphous iron oxyhydroxides sorb much more arsenic than crystalline iron oxyhydroxides.	Bowell (1994)
Batch experiments to study the influence of organic matter on As(V) adsorption onto clay minerals	The coat of HA on kaolinite increased significantly the As(V) adsorption at pH 7.	Cornu *et al.* (1999)
Multitracer technique used to compare the adsorption behavior of multiple inorganic ions on kaolinite and silica in the presence of HA	The adsorption of arsenic on kaolinite and silica was prevented by the adsorption of HA.	Takahashi *et al.* (1999)
Adsorption edges and kinetic studies to examine the effects of HA, FA and CA on As(V) and As(III) adsorption on α-FeOOH	Organic acids are capable of decreasing the adsorption of arsenic to a crystalline iron oxide.	Grafe *et al.* (2001)
Adsorption edges and column studies to examine the effects of HA, FA, and CA on As(V) and As(III) adsorption on ferrihydrite	Organic acids are capable of decreasing the adsorption of arsenic to a poorly crystalline Fe oxide. Effect of surface crystallinity was demonstrated.	Grafe *et al.* (2002)

Table 2-4. Summary of previous studies on interactions between NOM and arsenic (Continued)

Description	Main Observation & Conclusions	References
Studies to elucidate the effects of NOM on arsenic speciation and sorption onto hematite	In natural waters, NOM may greatly influence redox and complexation speciation of arsenic, and compete with arsenic for active adsorption surfaces.	Redman *et al.* (2002)
Batch experiments to study adsorption on kaolinite and on kaolinite-HA complexes	The presence of previously adsorbed (HA) increased As(V) adsorption on kaolinite at pH 7. Amine groups play a key role in arsenic adsorption to organic matter.	Saada *et al.* (2003)
Study of the prevalence of skin cancer in an arsenic affected area of Taiwan	Waters tapped from organic black sediments of the lagoons in the endemic area were heavily contaminated with arsenic.	Tseng *et al.* (1968)
Investigation arsenic contamination in groundwater beneath the southern Carson Desert, Nevada	Oxidation-reduction reactions involving metal oxides and sedimentary organic matter accounts for the occurrence of arsenic contamination.	Welch and Lico (1997)
Investigation of the mobility of arsenic and the effects of DOM in the wetland soils of the Mudle river, Germany	DOM concentration correlated very well with arsenic concentration in aqueous extracts from soil.	Kalbitz and Wennrich (1998)
Investigation of the cause of arsenic pollution in the groundwater of the Ganges-Meghna-Brahmaputra delta plain	Microbial FeOOH reduction driven by buried peat release sorbed arsenic to groundwater.	McArthur *et al.* (2001)
Investigation of arsenic mobility and groundwater extraction in southern Bangladesh	Young carbon brought to the depth by recent irrigation pumping drives the reduction of FeOOH	Harvey *et al.* (2002)
Investigation of the occurrence, sources and mobilization of arsenic in groundwater of the Bengal delta plain	Sedimentary organic matter and peat soils are one of the important materials relating to high concentration of arsenic in sediments of the Bengal delta.	Hossain *et al.* (2003)
Investigation of arsenic release to anoxic groundwater in alluvial aquifers in the Bangal Basin	Arsenic mobilization is controlled by the balance between the quantity and biodegradability of organic matter, and the FeOOH buffer ability to sorb arsenic.	McArthur *et al.* (2004)

McArthur *et al.* (2001) postulated that it was the distribution of buried peat deposits, rather than the distribution of arsenic in aquifer sediments, that was responsible for the severity and distribution of arsenic pollution in the groundwater of the Ganges-Meghna-Brahmaputra delta plain. Microbial metabolism of buried peat deposits drives the microbial reduction of FeOOH and therefore leads to the release of sorbed arsenic to groundwater. McArthur *et al.* (2004) further proposed that the extent of arsenic mobilization will be controlled by the balance between the quantity and biodegradability of organic matter, and the size of FeOOH buffer available to sorb arsenic.

These previous research studies have demonstrated that NOM has great potential in influencing arsenic sorption behavior by interacting with mineral surfaces and/or with arsenic itself, and thus may play a substantial role in the release of arsenic from soils and sediments into groundwater. The interactions between NOM and arsenic can be influenced by various factors such as pH, redox potential, arsenic speciation and concentration, other competing ions and complexing ligands, aquifer mineralogical properties, and reaction kinetics.

However, available information is limited and much remains unknown. Most of the research studies were conducted with pure laboratory-produced solid phases under idealized laboratory conditions. More and extensive investigations on various geological materials are required to achieve a thorough understanding. Further research is needed to evaluate the complex role of organic acids on arsenic redox cycling. Moreover, there is a need for further experiments to elucidate the role of other oxyanions or metal cations in the interaction between arsenic species and organic acids.

2.5 Biosurfactants and their environmental applications

2.5.1 Surfactants

Surfactants (surface active agents) are a class of natural and synthetic chemicals that promote the wetting, solubilization, and emulsification of various types of organic and inorganic contaminants. Typically, surfactants are amphiphilic (both loving) molecules, consisting of a strongly hydrophilic (water loving) group (polar group), the "head" of the molecule, and a strongly hydrophobic (water fearing) group (nonpolar group), which is the "tail" (Figure 2-8).

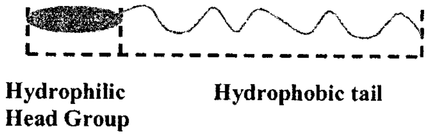


Figure 2-8. Basic molecular structure of surfactants

The most useful chemical classification of surfactants is based on the nature of the hydrophile and subgroups are defined by the nature of the hydrophobe. The general groups of the surfactants are defined as follows (Myers, 1999):

- Anionic, with the hydrophilic group carrying a negative charge such as carboxyl ($RCOO^-M^+$), sulfonate ($RSO_3^-M^+$), or sulfate ($RSO_4^-M^+$) (R: surfactant; M^+: cation);

- Cationic, with the hydrophile bearing a positive charge, as for example, the quaternary ammonium halides ($R_4N^+X^-$) (X^- : anion);
- Nonionic, where the hydrophile has no charge but derives its water solubility from highly polar groups such as polyoxyethylene ($-OCH_2CH_2O-$), sugars or similar groups.
- Amphoteric (and zwitterionic), in which the molecule has, or can have, a negative and a positive charge on the principal chain (as opposed to a counter ion, M^+ or X^-) such as the sulfobetaines, $RN^+(CH_3)_2CH_2CH_2SO_3^-$.

As they are amphiphilic molecules with both hydrophilic and hydrophobic portions (Figure 2-8), many surfactants, depending on concentration and surfactant type, can act as a bridge between the air and liquid interface and can reduce the surface tension of water to approximately 25 ± 5 mN/m (Myers, 1999). As a result, this promotes the mobilization of contaminants from unsaturated soils, and thereby making the contaminant more available for remediation. Also, surfactants have the ability to increase aqueous contaminant concentrations through partitioning the solute into the hydrophobic interior of the micelles and forming spheroid or lamellar structures with organic pseudo-phase interiors (Figure 2-9). The minimum concentration at which this occurs is termed as the critical micelle concentration (CMC).

Cationic, anionic and nonionic surfactants are particularly used for soil washing or flushing (Mulligan, 2005). They can be used in mixtures or with additives such as alcohol and/or salts such as sodium chloride. Polymers or foams can also be added to control the mobility of the contaminants (Mulligan *et al.*, 2001b; Wang and Mulligan, 2004b; 2004c). Addition of surfactants can have two beneficial effects: (1) a decrease in the aqueous activity coefficient for the dissolved nonionic organic compound and (2) formation of micelles in the aqueous phase.

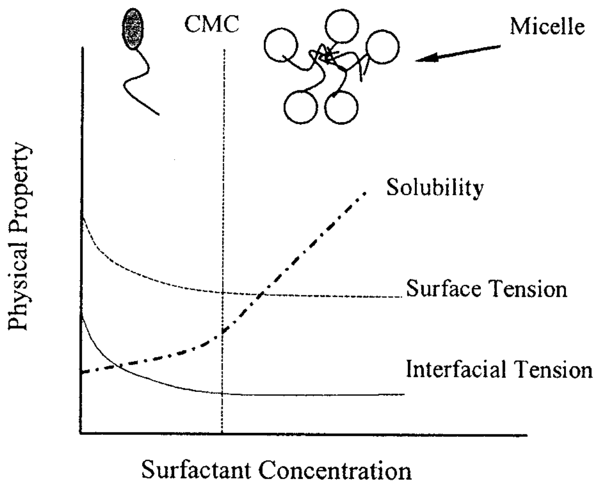


Figure 2-9. Schematic diagram of the variation of surface tension, interfacial and contaminant solubility with surfactant concentration (Mulligan *et al.*, 2001b)

2.5.2 Biosurfactants

Biosurfactants are produced by bacteria or yeast. They include classes of molecular structures quite different from synthetic surfactants, ranging in chemical structure from simply fatty acids (soaps) to complex cyclic peptides, glycolipids, and proteins. Most of them are lipids, which are grouped as glycolipids, lipopeptides, lipopolysaccharides, phospholipids, and fatty acids. Some of the major types and their microbial origin are listed in Table 2-5. Most of these compounds are either anionic or neutral. Only a few are cationic such as those containing amine groups (Mulligan *et al.*, 2001a).

Biosurfactants as a class contribute significantly to the repertoire of available surfactants. Effective physicochemical properties (low interfacial tensions and CMCs) and temperature stability are characteristics of these compounds. The CMC of biosurfactants range from 1 to 2000 mg/L. Surface and interfacial tensions of good biosurfactants are less than 30 and 1 mN/m, respectively (Mulligan and Gibbs, 1993). Other distinct advantages of biosurfactants over synthetic surfactants include higher specificity, lower toxicity, higher biodegradability, better environmental compatibility (Mulligan *et al.*, 2001a), and the ability to be synthesized from renewable feedstocks (Wang and Mulligan, 2004c).

Table 2-5. Classifications and microbial origin of biosurfactants

Surfactant Class	Microorganisms
Rhamnolipids	*Pseudomonas aeruginosa*
Lipopeptides	*Arthrobacter sp.*
	Bacillus pumilis
	Bacillus subtilis
	Bacillus licheniformis
	Pseudomonas fluorescens
Lipopolysaccharides	*Acinetobacter calcoaceticus*
	Pseudomonas sp.
	Candida lipolytica
Phospholipids	*Thiobacillus thiooxidans*
	Corynebacterium alkanolyticum
Fatty acids	*Penicillium spiculisporum*
	Corynebacterium lepus
	Arthrobacter parafineus
	Talaramyces trachyspermus

(Mulligan and Gibbs, 1993; Wang and Mulligan, 2004b)

Biosurfactants exhibit high specificity and are consequently suited to new applications. They are frequently used in detergents and food products to alter the properties of solution interfaces. They also can be added to washing water to assist in the solubilization, dispersion and desorption of contaminants from excavated soils in a washing unit for subsequent return of the cleaned soils to their original site (Mulligan *et al.*, 2001b).

2.5.3 Application of biosurfactants in soil remediation

The use of surfactants to enhance the removal of soil contaminants has been well studied in recent years. Mainly anionic and nonionic surfactants are used for soil washing or flushing (Mulligan *et al.*, 2001a). They can be used in mixtures or with additives such as alcohol and/or salts such as sodium chloride. These agents would be most effective in promoting the mobilization of organic compounds of relative low water solubility and high lipid solubility. They can also be used as extractants to transfer metal ions from an aqueous to an organic phase. The possible mechanisms for the extraction of heavy metals by surfactants are ion exchange, precipitation-dissolution, and counterion binding. Previous batch and bench studies have demonstrated encouraging results for surfactant-enhanced remediation for a variety of contaminants (Mulligan, 2005).

Mulligan (2005) gives a comprehensive and critical review on the applications of biosurfactants (i.e., rhamnolipids, surfactin, and sophorolipids) for soil and water treatment. The author pointed out that biosurfactant applications in environmental industries are promising due to their biodegradability, low toxicity and effectiveness in enhancing biodegradation and solubilization of low solubility compounds. A number of studies have demonstrated the feasibility of biosurfactants enhanced recoveries of hydrophobic organic contaminants (Mulligan and Eftehari, 2003; Mulligan, 2005).

Biosurfactant enhanced remediation of heavy metal contaminated soils has also been demonstrated (Mulligan *et al.*, 1999; 2001b; Wang and Mulligan, 2004b; 2004c; Mulligan and Wang, 2006).

Previous research studies have demonstrated that biosurfactants may be applicable to remediate contaminated soils by increasing the solubilization and mobility of organic or inorganic contaminants. However, the use of biosurfactants in remediating arsenic contaminated soils has not been reported yet. Further research is required to investigate the role of biosurfactants in arsenic mobilization from contaminated soils or other solid wastes.

2.6 Remediation technologies for arsenic contaminated soils

Due to its high toxicity, remediation of arsenic contaminated sites and removal of arsenic from drinking water therefore are necessary for the protection of the environment and public health. Arsenic has been removed from waters by physicochemical technologies including coagulation/sorption, precipitation, polymeric anion exchange, lime softening, membrane separation (reverse osmosis), and solvent extraction as well as electrochemical methods (Edwards, 1994; Kim and Nriangu, 2000; Katsoyiannis *et al.*, 2002). Occasionally, excavation and physical separation were used for arsenic contaminated soils followed by disposal as hazardous materials. However, they are becoming less popular due to the prohibitive cost and lack of disposal space. Alternately, a number of advanced and innovative treatment methods have been investigated at the laboratory and/or field-scale to remediate arsenic contaminated soils (Table 2-6).

Table 2-6. Summary of treatment methods for arsenic contamination in soil and water

Treatment method	Description	Applicable media	Cost (US$)	Main limitation
Oxidation	Chemical or photochemical oxidation of As(III) to As(V)	Drinking water, groundwater and wastewater	\$0.3-30/10 m^3	Sludge problems
Anion exchange	Accumulation of arsenic anions at the surface of anion-exchange resins		\$0.8-2.1/10 m^3	Co-occurring anions may cause the resins exhaust quickly
Membrane separation	Separation arsenic from water by membrane		\$2.5-12/10 m^3	Membrane does not withstand oxidizing agents
Adsorption/precipitation	Formation of insoluble solids to precipitate arsenic		\$0.01-2/10 m^3	Regeneration of adsorbents required
Stabilization/solidification	Containment of arsenic within an inert mass	Soil and solid wastes	\$60-290/t	Increased waste volume
Vitrification	Creation of a vitreous mass by high temperature treatment		\$375-870/t	High energy required
Soil washing	Addition of extraction solutions to solubilize arsenic (ex-situ)		\$30-400/t	Restricted to weakly bound arsenic
Soil flushing	Using of extraction solutions to leach arsenic (in-situ)		\$30-330/m^3	Difficult to control the arsenic migrate in subsurface
Electrokinetics	Application of electric direct current to mobilize arsenic	Saturated soil with low groundwater flow	\$70-883/t	Undesirable products may be formed by redox reactions
Electrocoagulation	Electrically enhanced coagulation	Wastewaters	\$7-23/10 m^3	Anode replacement required
Electrodialysis	Electromembrane to mobilize and separate arsenic anions	Groundwater, wastewaters and soil	\$3.5-15/10 m^3 (water)	Clogging problems may occur
Biological methods	Use of microbial activity to transform, leach, or precipitate arsenic	Waters and soil	\$1.5-6/10 m^3 (water) \$30-100/m^3 (soil)	Biostimulation and bioenhancement required
Phytoremediation	Use of plants to extract arsenic	Soil, surface waters and shallow groundwater	\$5-20/10 m^3 (water) \$0.02-1.0/m^3 (soil)	Arsenic hyperaccumulating capacity of plants is low
Natural attenuation	Arsenic immobilization and transformation by naturally occurring processes	Soil and groundwater	Not available	Long-term continued monitoring required
Enhanced natural attenuation	Use of engineering strategies to enhance the rate and efficiency of natural attenuation processes			

(Mulligan *et al.*, 2001b; USEPA, 2003)

Stabilization/solidification (S/S) method has been demonstrated successfully to contain arsenic in the contaminated soil, sediments and solid wastes. Arsenic immobilization is mainly controlled by the formation of Ca-arsenic precipitates such as $Ca_3(AsO_4)_2$ and $CaHAsO_3$ in contaminated soils treated with cement, lime and pozzolanic material (Dutre and Vandecasteele, 1995). Vitrification is also applicable since arsenic is of low volatility, but may be more cost expensive due to the high energy requirements. Electrochemical methods based on electrokinetics are emerging. Especially, electrokinetics and electrodialysis are suited for fine-grained soils. Chemical extraction, either *in-situ* or *ex-situ*, may be developed as an efficient method to remove bulk arsenic from contaminated soil and solid wastes. Selection of proper extractants is the key to the success of this method.

Bioremediation, phytoremediation, and natural attenuation show great potential for future developments because of their environmental compatibility and cost effectiveness. Biological methods involving microbial activities can be used for the treatment of arsenic contaminated soil and water. Pretreatments may be required to reduce the arsenic concentration to a tolerable level for the microbes. Phytoremediation is to use plants to translocate arsenic from contaminated sites into harvestable plant issues. Genetics-based strategies may be used to improve the engineering tolerance and hyperaccumulating capacity of plants. Natural attenuation processes have potential in immobilizing arsenic and transforming it into less toxic forms. It may be a cost-effective *in-situ* remedial option. Sufficient site characterization is the key to assess the site natural attenuation capacity. Data modeling and long-term continued monitoring are required. Engineering strategies may be employed to improve the attenuation rates (Wang and Mulligan, 2006d).

In general, the basic criterion in selecting a proper remediation strategy for a contaminated site is to choose the least expensive applicable method to comply with the regulatory requirements for the protection of the environment and public health. No technology should be considered a panacea for all contaminated sites. Selection of a specific technology for the treatment of a contamination problem accounts on the contaminant speciation and specific site characteristics. The chosen method should neither add other toxic pollutants nor leave toxic residues, which must be subsequently removed. Combination of existing technologies may provide an efficient and cost-effective treatment alternative. Biodegradable environmentally benign products such as biosurfactants may be used as enhancements for the treatment processes. Naturally occurring organic matter such as humic and fulvic acids has demonstrated a potential in influencing arsenic mobility. Further research is needed to investigate their roles in the remedial strategies for arsenic contamination.

CHAPTER THREE

EXPERIMENTAL MATERIALS AND METHODS

3.1 Scope of work

The scope of work for this study is detailed in Figure 3-1. Batch tests were designed to elucidate the mechanisms of arsenic mobilization from mine tailings in the presence of organic additives, and column experiments were designed to determine the feasibility of using NOM and a biosurfactant for the remediation of arsenic contaminated sites.

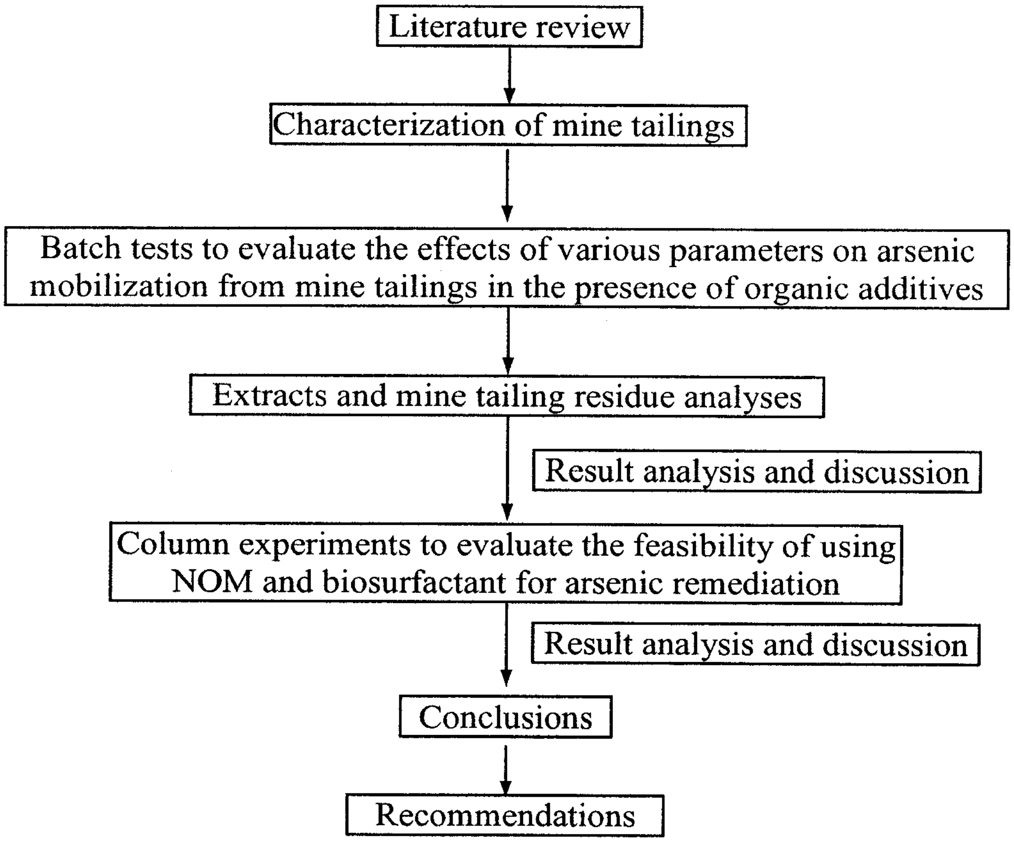


Figure 3-1. Diagram of the scope of work

Fluka HA and rhamnolipid were chosen in this study to evaluate their effects on arsenic mobilization from mine tailings. Batch tests were designed to find out the effect of pH, mass ratio of organic additives to mine tailings, and reaction time. The effect was compared with that of other simple acids, including succinic acid, L-cysteine and L-aspartic acid. Based on the batch tests, column leaching experiments were run to further examine the effect of HA and rhamnolipid on arsenic mobilization by simulating *in-situ* conditions in the environment.

3.2 Experimental materials

3.2.1 Mine tailing samples

Six oxidized mine tailings samples from different locations (Canada) were collected (Table 3-1). Total arsenic concentrations in the mine tailings were determined using ICP-MS analyses by Canada Bodycote Material Testing Inc. (Appendix I). Based on arsenic concentrations and the type of the mine tailings, three samples were selected for further experiments (Table 3-1).

Table 3-1. Arsenic concentrations in the mine tailings measured by ICP-MS

Type of Tailings	Location	Arsenic Concentration (mg/kg)	Reference No. in following experiments
Copper Mine	Murdochville, QC	500	
Gold Mine	Musselwhite, ON	63	1
Copper-zinc Mine	Val d'Or, QC	270	2
Iron Mine	Mont-Wright, QC	<0.70	
Lead-zinc Mine	Bathurst, NB	2200	3
Gold Mine	Marathon, ON	270	

3.2.2 Fluka HA

A commercial and standardized HA (Fluka, Saint-Quentin Fallavier, France) was chosen as a model for NOM. The ash content was 18.8%, as stated by the manufacturer. Table 3-2 shows the results for the elemental analysis, surface area, and acidic groups (Saada *et al.*, 2003; Alvarez-Puebla *et al.*, 2004). The HA was used without any further purification.

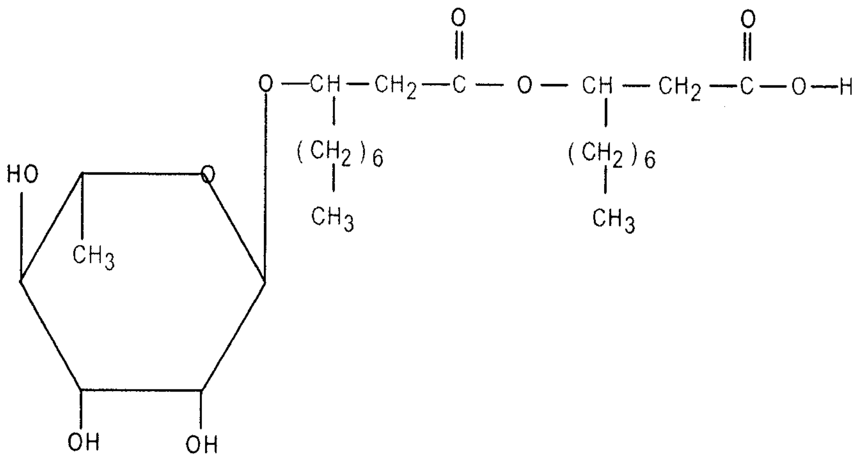
Table 3-2. Physical and chemical characteristics of Fluka HA

Elemental analysis in percentage by weight(1)	
C	55.1 ± 0.6
H	5.14 ± 0.02
O	38.1 ± 0.8
N	0.51 ± 0.01
S	1.20 ± 0.01
Surface area(2)	
As N_2 (77 K) m^2/g	<1
As CO_2 (273 K) m^2/g	42.5
Acid-base properties(2)	
pH (NaCl, 0.05 M, 298 K)	5.77
$C_{strong\ acid\ goups}$ (mol/kg)	4.02 (pK_a = 3.92)
$C_{weak\ acid\ goups}$ (mol/kg)	2.95 (pK_b = 8.22)

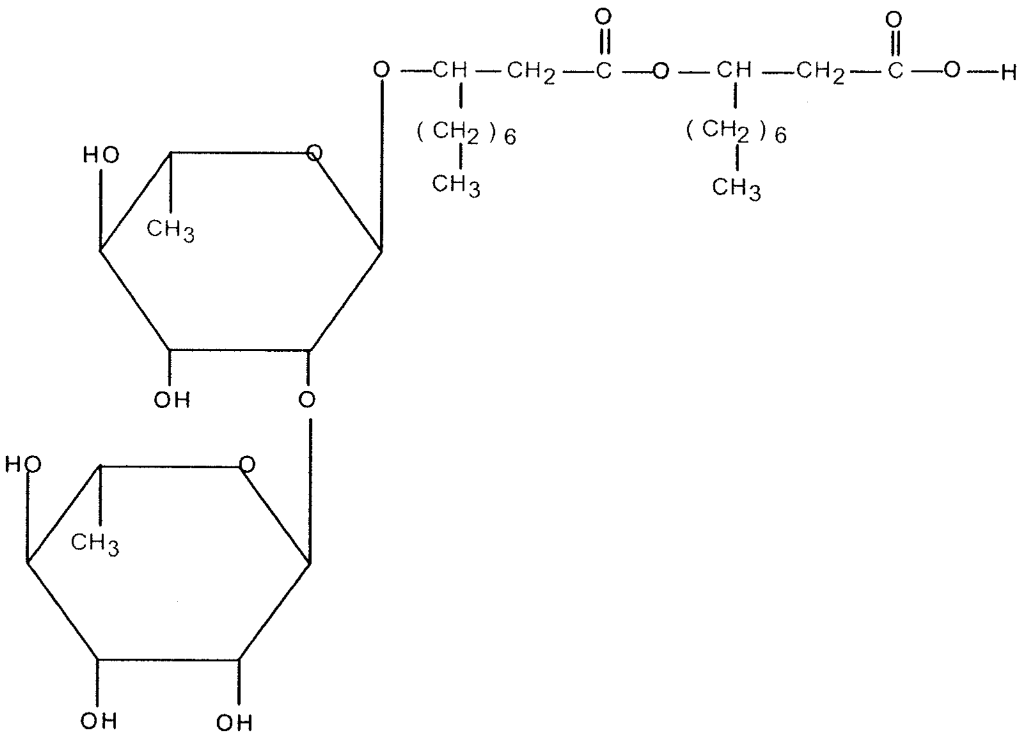
(1) Saada *et al.* (2003); (2) Alvarez-Puebla *et al.* (2004)

3.2.3 Rhamnolipid

The biosurfactant, represented by JBR425 (mixed rhamnolipids), was obtained from JENEIL Biosurfactant Co. (USA). Chemically, rhamnolipids are glycosides of rhamnose (6-deoxymannose) and β-hydroxydecanoic acid. Two rhamnolipids, RLL (R1) and RRLL (R2) (Figure 3-2), are formed during controlled fermentation at a R2/R1 molar ratio of 0.9 to 1 (Jeneil, 2001). The properties of JBR425 on the MSDS (Jeneil, 2001) are listed as Table 3-3.



RLL or R1
α-L-Rhamnopyranosyl-β-hydroxydecanoyl-β-hydroxydecanoate



RRLL or R2
2-O-α-L-Rhamnopyranosyl-α-L-rhamnopyranosyl-β-hydroxydecanoyl-β-hydroxydecanoate

Figure 3-2. Structure and chemical names of JBR425 (Jeneil, 2001)

Table 3-3. Properties of rhamnolipid JBR425

Product name	JBR425
Type	anionic biosurfactant
Formula	$C_{26}H_{48}O_9$, $C_{32}H_{58}O_{13}$
Appearance and odor	Amber, Soapy liquid
Specific gravity @ 25 °C	1.05 - 1.06 mg/ml
pH (1% suspension)	6.5 - 7.5
CMC$^{(1)}$	0.03 g/L
Surface tension $^{(1)}$	26 mN/m

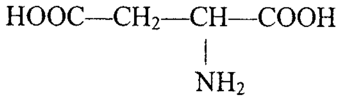
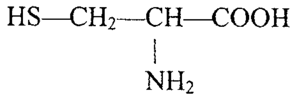
(1) Mulligan *et al.*, 2001b

3.2.4 LMWOAs

Three LMWOAs, including succinic acid, L-aspartic acid and L-cysteine, were chosen to compare the effect on arsenic mobilization with that of HA and rhamnolipid (Table 3-4). All of them were purchased from Fisher Scientific Co. (Canada). The physicochemical properties of the three acids, according to the MSDS, are summarized in Table 3-4.

Succinic acid is a dicarboxylic acid produced as an intermediate of the tricarboxylic acid cycle (TCA) and also as one of the fermentation products of anaerobic metabolism. It can be used for scientific applications such as radiation dosimetry and standard buffer solutions and in food and pharmaceutical industries. Recently, succinic acid has been used for the manufacture of synthetic resins and biodegradable polymers, such as the monomer of polybutylene succinate. It was also reported that the molecule succinic acid is able to chelate bivalent metal ions, affecting their adsorption onto clay minerals by forming metal complexes (Abollino *et al.*, 2003).

Table 3-4. Physicochemical properties of succinic acid, L-cysteine, and L-aspartic acid

Organic acids / Properties	Succinic acid	L-aspartic acid	L-cysteine
Structure	$HOOC—CH_2—CH_2—COOH$	 $HOOC—CH_2—\underset{NH_2}{\underset{\mid}{CH}}—COOH$	 $HS—CH_2—\underset{NH_2}{\underset{\mid}{CH}}—COOH$
Other names	butanedioic acid, ethane-1,2-dicarboxylic acid	asparaginic acid, L-aminosuccinic acid, 1-amino-1,2-carboxyethane	beta-mercaptoalanine, L-2-amino-3-mercaptopropanoic acid, alpha-amino-beta-thiolpropionic acid
Molecular weight	118.09	133.05	121.11
Appearance	White crystals	Colorless to white crystals	Colorless crystals
Odor	Odorless	Odorless	Not available
Solubility	80 g/L @ 20°C	Slightly soluble	Soluble in water
pH	2.7 (0.1 M solution)	2.5-3.5 (10% solution)	Not available
Specific gravity (25 °C)	1.57	1.66	Not available
Reference	Fisher Scientific, 2006a	Fisher Scientific, 2006b	Fisher Scientific, 2006c

L-aspartic acid is an amino acid and chelating agent. It is able to form complexes with almost all metal ions (Gharib *et al.*, 2001), holding a great potential in influencing the mobility of metals. L-cysteine acid is similar to L-aspartic acid by substituting a carboxyl group by a sulfhydryl group. It is a protein amino acid naturally present in the proteins of life forms. It has been mainly used in food industry. Experiments have shown that L-cysteine may increase the mobilization of metals by forming stable complexes (Farrah and Pickering, 1978).

3.3 Mine tailings characterization

The mine tailings samples were air-dried and homogenized in the laboratory. The main physicochemical characteristics of the mine tailings such as particle size distribution, specific gravity (SG), specific surface area (SSA), cation exchange capacity (CEC), and organic matter content (OMC) were measured following standard or well-established methods.

3.3.1 Particle size distribution

The particle size distribution of the three samples was examined following the sieve and hydrometer ASTM method D422 (ASTM, 1970). Approximately 300 g of mine tailings samples were dried at 105 ^{o}C for 24 hours and then cooled to room temperature. Large particles were crushed by mortar and pestle. A set of USA Standard Testing Sieves (Fisher Scientific Company, USA) was used to separate the mine tailing particles. After a 15-minute shaking period, the dry weight retained by each sieve was determined.

3.3.2 Specific gravity (SG)

Specific gravity is defined as the ratio of the density of the mine tailings to the density of water at a specified temperature (20 °C, in this study). In this study the SG of the mine tailings was measured following the ASTM method D854 (ASTM, 1999). The mass of a 500 ml volumetric flask filled with distilled water (M_w) was measured first. The temperature of the water was recorded by inserting a thermometer into the flask with the water (T °C). After the volumetric flask was empty and dried, approximately 75 g air-dried mine tailings was transferred into it and distilled water was added to make it about two-thirds full. The entrapped air was removed by applying a partial vacuum and rolling the volumetric flask for 15 minutes. The volumetric flask then was filled carefully with distilled water until the bottom of the meniscus touches the 500 ml mark. The mass of the volumetric flask filled with water and mine tailings was measured (M_{mw}). The mine tailings and water were poured into an evaporating dish and dried in an oven (LINDERG/BLUE) at 105 °C until the weight of the sample (M_m) did not change over an hour interval. The specific gravity of the mine tailings (G_s) was then calculated using the following equation:

$$G_s = \frac{M_m}{(M_w + M_m) - M_{wm}} \times \frac{\rho_{water\,at\,T\,°C}}{\rho_{water\,at\,20\,°C}} \qquad \textit{Eq.3-1}$$

3.3.3 Specific surface area (SSA)

Specific surface area (SSA, in m^2/g) was measured by ethylene glycol monoethyl ether (EGME) adsorption with 24-hour oven drying (105°C) as a pretreatment (Carter *et al.*, 1986; Tiller and Smith, 1990). This method is based on the assumption that EGME will form a monomolecular layer on all interlayer and external surfaces of the solid. Approximately 1.1 g of dried mine tailings was wetted with approximately 3 ml of EGME and equilibrated. The excess liquid was removed by evaporation under vacuum. This procedure was repeated until a constant mass was obtained, generally after 24 hours. The weight increase of mine tailings samples exposed to EGME was then used to estimate the specific surface areas of mine tailings samples on the basis of the equation:

$$SSA = \frac{W_{EGME}}{0.000286 \times W_m} \qquad \text{Eq. 3-2}$$

where SSA is the specific surface area in m^2/g, W_{EGME} is the weight of EGME in g, W_{m} is the weight of mine tailings in g, and 0.000286 is the weight of EGME required to form a monomolecular layer on a square meter of surface (g/m^2).

3.3.4 Organic matter content (OMC)

OMC was measured from the weight loss after calcination at 550 °C (Wang, 2003). Approximately 10 g of air-dried mine tailings were weighed in pre-weighed crucibles. The samples was dried at 105 °C in an oven (LINDERG/BLUE) for 48 hours, and then heated at 550 °C in a muffle furnace for 2 hours. After cooling the samples overnight in a dessicator, they were weighed. The OMC was calculated based on the difference in weight before and after the calcinations, using the equation:

$$OMC = \frac{W_b - W_a}{W_a} \times 100\% \qquad \text{Eq. 3-3}$$

where OMC is the organic matter content of mine tailings (%), W_b is the weight of dried mine tailings before ashing in g, and W_a is the weight of dried mine tailings after ashing in g.

3.3.5 pH determination

The pH of the mine tailing samples was determined by using 1:2.5 w/v mine tailings with distilled water and 0.01 M $CaCl_2$ (Schofield and Taylor, 1955). Measurements were carried out after stirring the slurry on a magnetic stirrer for 30 minutes. The addition of excess $CaCl_2$ salt in the slurry was to mask the effect of different soluble salt concentrations in individual samples.

3.3.6 Cation exchange capacity (CEC)

CEC refers to the concentration of readily exchangeable cations on a mineral surface and is often used to indicate the affinity of the mineral surfaces for uptaking cations. The CEC was determined by replacement of exchangeable cations by potassium acetate following the method by Wang (2003). 5 g of dried mine tailings was mixed with 20 ml of 1 M potassium acetate first. The slurry was shaken and separated by centrifuge (IEC HN-SII centrifuge, International Equipment Company, USA) at 3000 rpm for 15 minutes. After the steps were repeated, the sample was washed with 20 ml of methyl alcohol twice. Subsequently, the potassium cation was replaced by ammonium cation with 20 ml of 1 M ammonium acetate. The supernatant was then separated from the mine tailings by centrifugation. The steps were repeated and the supernatant was pooled together. The potassium concentration in the supernatant was analyzed by atomic absorption spectrophotometry (AAS, Analyst 100, PerkinElmer Inc., ON, Canada), and it was used to calculate the CEC of the mine tailings in cmol/kg.

3.3.7 Zeta potential measurement

Zeta potential is a physical property exhibited by any particle in suspension. At the particle-water interface, the first few layers of water molecules are stagnant and move along with the particle. The slip plane refers to the boundary between the water molecules moving with the particle and the bulk of water. Zeta potential is the potential at the slip plane and can be calculated from the electrophoretic mobility. The Smoluchowski's equation, the most elementary expression for zeta potential, shows a direct relation between zeta potential (ζ) and electrophoretic mobility (EM),

$$\zeta = \frac{4\pi V_t}{D_t} \times EM \qquad Eq.\ 3\text{-}4$$

where V_t is viscosity of the suspending liquid, D_t is dielectric constant (Zeta-Meter System 3.0 Operating Instructions, Zeta-Meter Inc., USA).

Zeta potential of the mine tailings was determined by a Zeta Meter System 3.0 (Zeta-Meter Inc., USA) with an Automatic Sample Transfer System in this study. A standard Type GT-2 electrophoresis cell along with a molybdenum anode and a platinum cathode was used. The unit automatically calculates the electrophoretic mobility of the particles and converts it to zeta potential via the Smoluchowski's equation.

Approximately 0.2 g of dried mine tailings (passing through a 200 mesh sieve) was added in 250 ml of solution (containing 100 mM NaCl as an indifferent electrolyte to maintain the ionic strength constant). The suspension was stirred on a magnetic stirrer. The pH of the solution was adjusted by 1 N HCl or 1 N NaOH. Measurements were performed 24 hours after preparation of the suspension at room temperature. The applied voltage during the measurements varied in the range of 50 to 200 mV. The average of 10 to 50 measurements was taken to represent the measured zeta potential. From the data of zeta potential versus pH, the isoelectric point (the pH value at which the zeta potential is zero) was determined.

3.3.8 Mineralogical analysis by X-ray diffraction (XRD)

XRD is based on the principle that X-rays can be diffracted from the repeating patterns of atoms that are characteristic of crystalline materials. The constructed diffraction patterns give evidence for the periodically repeating arrangement of atoms in the crystal. The symmetry of the diffraction patterns reflects the symmetry of the atomic packing. Information on the positions of the atoms can be obtained by comparing the calculated intensities of diffracted spots with the experimental diffraction intensity. XRD has been used to characterize crystalline materials and determine their structures.

X-ray powder diffraction was applied in this study to the three mine tailing samples to identify the existence of crystallized arsenic mineral phases and particular oxides including those of Fe, Al, Si, and Mn. A Philip PW1710 diffractometer using $\mathrm{Cu}K_{\alpha}$ radiation (λ = 15,418 Å) was employed (McGill University, Montreal, Canada). XRD patterns were collected over 3 to 60° θ. A step scanning technique with a fixed time of 0.5 s per 0.02° θ was adopted for the measurements.

3.3.9 Scanning electron microscopy (SEM)

SEM generates a beam of electrons in a vacuum. The focused beam of high-energy electrons is raster-scanned across the sample surface. The elements present in the sample are characterized by the electrons ejected from or bounced off of the surface or X-rays produced during the interactions between energetic electron beam and the sample. Energy dispersive X-ray spectrometer (EDS) analyzes the wavelength or energy spectra to measure accurately the nature and quantity of different elements in the material. It is a standard procedure for identifying and quantifying elemental composition of samples.

SEM-EDS analysis provides chemical spectra and elemental line scans and maps that show the spatial distribution of specific chemical elements on a submicron scale. It has been applied for identifying and quantifying arsenic-bearing phases (such as arsenopyrite) in soil, sediments and mine tailings (Matera *et al.*, 2003). SEM-EDS were used to determine arsenic-containing phases in the three mine tailings. The samples were examined at McGill University (Montreal, Canada) on a JEOL-JSM-840A Scanning Electron Microscope (JEOL, Tokyo, Japan) equipped with an Energy Dispersive Spectrometer. Analyses were carried out at an accelerating voltage of 20 keV.

3.4 Selective sequential extraction (SSE) procedure

SSE methods have been developed to fractionate targeted elements in solid materials to evaluate their potential effects. This technique assumes that the different bonding forms of trace elements in soil or sediments can be extracted selectively by applying a series of extraction solutions in the order from the least to the most chemically aggressive. Most of the SSE techniques have been developed to determine the solid phase speciation of cationic species such as heavy metals (Mulligan, 1999; Mulligan and Dahr Azma, 2003; Wang and Mulligan, 2006c). Since arsenic is mainly found in the anionic forms, SSE procedures adopted follow those that have been used for studies of phosphorus retention.

In this study, a SSE procedure was applied on the basis of Yong *et al.* (1992). For each procedure, 2.0 g of dried mine tailing sample was used. Between each successive extraction, separation was made by centrifugation (IEC HN-SII Centrifuge, International Equipment Company, USA) at 3000 rpm for 15 min. The supernatant was collected and the residue was washed with 8 ml of distilled water. Each extract and the rinse water associated were pooled together. Each of the fractions was collected and the concentrations of arsenic were determined. The amounts of arsenic extracted from the mine tailings by each of the extractants were then calculated.

The sequential extraction procedure that was used is as follows:

F1. Water soluble: 8 ml of distilled water or washing solution added, shaking at room temperature for 30 minutes;

F2. Exchangeable: 8 ml of 1 M $MgCl_2$, pH 7, 1-hour shaking at room temperature;

F3. Carbonate associated: 8 ml of 1 M NaOAc, pH adjusted to 5 with acetic acid, 5-hour shaking at room temperature;

F4. Oxide and hydroxide associated: 8 ml of 0.04 M $NH_2OH{\cdot}HCl$ in 25% (v/v) acetic acid, pH 2.5, at 96 °C in a water bath for 6 hours;

F5. Organic matter and sulphide associated: 3 ml of 0.02 M HNO_3 and 5 ml of 30%

H_2O_2 (pH 2) at 85 °C for 2 hours, followed by 3 ml of 30% H_2O_2 (pH 2) at 85 °C for 3 hours, and then 5 ml of 3.2 M NH_4OAc in 20% (v/v) HNO_3 diluted to 20 ml at room temperature for 30 minutes; and

F6. Residual fraction: digestion at 90 °C with 25 ml of dilute aqua regia (50 ml HCl + 200 ml HNO_3 + 750 ml water) for 3 hours.

3.5 Arsenic speciation by capillary electrophoresis (CE)

Quantitative determination methods are necessary to differentiate arsenic species, which can further the understanding of arsenic biogeochemistry, toxicity and metabolism. CE is a powerful separation technique developed in the last decade. This technology allows for rapid separation of charged compounds on the basis of differences in their electrophoretic mobility.

In this study, all CE separations were carried out on a Beckman P/ACE MDQ CE system (Beckman Coulter, Inc., Fullerton, California, USA) equipped with a UV detector. A fused-silica capillary tube (70 cm × 75 μm I.D., effective length was 61 cm) was used. To obtain uniform capillary surface conditions, the capillary was washed with a 100 mM NaOH solution for 10 minutes at the beginning of each workday. Prior to each injection, the capillary tube was rinsed with 100 mM NaOH for 1 minute followed by 5 mM sodium dodecyl sulphate (SDS) for 1 minute and conditioned with separation buffer solution for 2 minutes. The buffer solution consisted of 15 mM Na_2HPO_4 adjusted to pH 6.5 with 1 N NaOH. 10 mM SDS was added as the electroosmotic flow (EOF) modifier.

The buffer solution was filtered through a 0.45 μm filter and degassed by vacuum before using.

Stock solutions (1g/L) were prepared by dissolving the appropriate amount of As(III), As(V), MMAA, and DMAA in water. Arsenic trioxide, sodium metaarsenate and DMAA were purchased from Sigma, USA. MMAA was purchased from Welck, USA. All the reagents were of analytical grade. Distilled water was used throughout all measurements.

The extracts from batch tests were analyzed to examine the effect of organic additives on the speciation of arsenic. Before the separation procedure, the samples were filtered through a 0.45 μm filter and degassed by vacuum. The samples were injected hydrostatically by a pressure of 3.45 kPa for 10 seconds. The capillary temperature was adjusted to 28 ^{o}C. A positive voltage of 25 kV on the injection side was applied for separation. The detection wavelength was 200 nm.

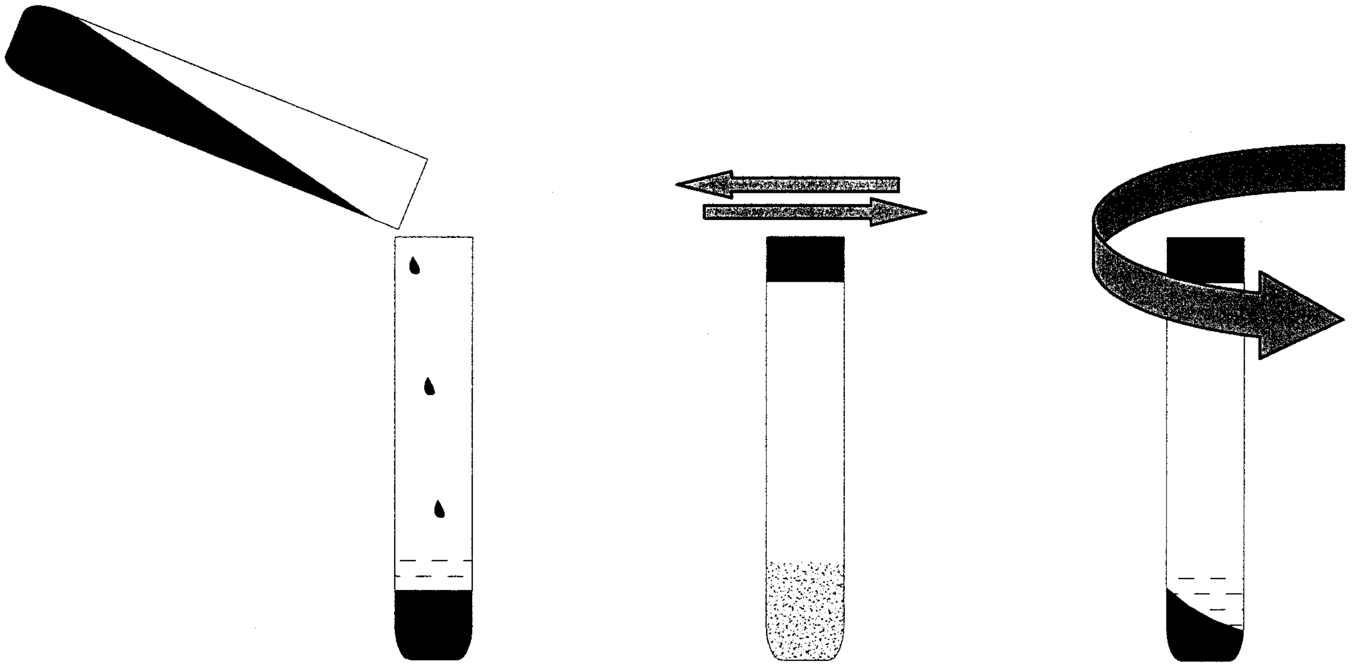
3.6 Batch tests

Batch tests were run to elucidate the effect of HA and rhamnolipid on arsenic mobilization from the three selected mine tailing samples. Batch methods are primarily closed systems. After all the reactants are added and mixed together, no additional amounts of reactants are added and products are allowed to accumulate. The only material removed from the system is that removed for analysis, and that is usually a very small fraction of the total.

In this study, batch tests were designed to determine arsenic mobilization from the mine tailings in the presence of the organic additives (Figure 3-3). The tests were carried out in 50 ml polypropylene centrifuge tubes containing a 10:1 (v/wt) solution to mine tailings ratio (20 ml/2 g), with varying the concentrations of HA and rhamnolipid, pH and reaction time. The mixtures were shaken at 60 rpm for a desired time period. The mixture were then centrifuged at 3000 rpm for 15 minutes to separate the supernatant and the mine tailing residue, and diluted before analysis. All batch tests were conducted at room temperature.

The pH value was adjusted by 1 N NaOH or 1 N HCl solutions with less than 2% of the volume changed. The deviation from the originally adjusted pH values was corrected by re-adjustment after 1 hour equilibration. Five pH values, i.e., 3, 5, 7, 9 and 11, were tested for HA. Since rhamnolipid may precipitate at pH below 6, three pH values above 6, i.e., 7, 9 and 11, were tested in this study.

Based on the test results of HA and rhamnolipid, the other three LMWOAs, including succinic acid, L-aspartic acid and L-cysteine, with a selected concentration (1,000 mg/L) at the pH values (i.e., 3, 5, 7, 9, and 11) were used to evaluate the effects of the LMWOAs on the mobilization of arsenic from the mine tailings. Distilled water alone with pH adjustment was used to account for the mobilization of arsenic by physical mixing and the effect of pH.



Phase I:
Add extractant into mining tailings and adjust pH value

Phase II:
Shake the mixture at 60 rpm

Phase III:
Centrifuge at 3000 rpm for 15 minutes to separate the mining tailings and extracts

Figure 3-3. Main experimental procedure for batch tests

To determine the effect of reaction time, sampling commenced after every 6 or 12 hours shaking of the mixture of mine tailings and HA or rhamnolipid solution until a constant arsenic concentration was reached in the supernatant.

The supernatant and residues were then analyzed to determine the concentrations of arsenic and metals. The mass of dissolved arsenic in solution has been determined by the equation:

$$M_{arsenic-solution}(mg) = \left(\frac{mg\,Arsenic}{L\,solution}\right) \times \left(\frac{1L}{1000\,mL}\right) \times 20\,mL \qquad Eq.\ 3\text{-}5$$

The amount of arsenic extracted was expressed as the percentage of the total mass of arsenic in the mine tailings

$$M_{arsenic-tailings}(mg) = \left(\frac{mg\,Arsenic}{kg\,Tailings}\right) \times \left(\frac{1kg}{1000g}\right) \times 2g \qquad Eq.\ 3\text{-}6$$

$$\%Arsenic\,mobilized = \frac{M_{Arsenic-solution}}{M_{Arsenic-tailings}} \times 100\% \qquad Eq.\ 3\text{-}7$$

or as the part of the total mass of the mine tailings

$$C_{arsenic\,mobilized}(mg/kg) = \frac{M_{Arsenic-solution}}{2g} \times \frac{1000g}{1kg} \qquad Eq.\ 3\text{-}8$$

Mass balances were checked by comparing the sum of arsenic in supernatant and residual arsenic in the mine tailings with the initial amount of arsenic in the mine tailings. The comparisons were done according to the following equations:

$$M_{Arsenic-residue}(mg) = \left(\frac{mg\,Arsenic}{kg\,residue}\right) \times \left(\frac{1kg}{1000g}\right) \times 2g \qquad Eq.\ 3\text{-}9$$

$$Mass\ Balance\,Coefficient = \frac{\left(M_{arsenic-solution} + M_{arsenic-residue}\right)}{M_{arsenic-tailings}} \qquad Eq.\ 3\text{-}10$$

The value of the mass balance coefficient (*Eq. 3-10*) should be around 1.0. All results were the average of duplicate experiments and are presented as percentage of the arsenic dissolved.

3.7 Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy operates through generating an infrared radiation and measuring the absorption caused by infrared active molecules. The obtained spectra are compared to individual standard spectrum to identify and qualify the identities, surrounding environments, and concentrations of the chemical bonds in the sample. The detection limit of FTIR varies from sample to sample, typically, in the range of 0.1-1% wt. (Smith, 1996). It also can provide detection limits in the low ppm (mg/kg) range. FTIR is usually used to study molecules in the interfacial region such as surface hydroxyl groups and arsenic anions on mineral surfaces, and to identify the local environment of arsenic in solids (Voegelin and Hug, 2003). The interaction of arsenic anions with surface hydroxyl groups on mineral surface can be studied through examining changes in the IR signal of arsenic group vibrations and/or surface hydroxyl group vibrations as a function of arsenic sorption.

In this study, FTIR spectra on HA solution (1000 mg/L) and the extracts from mine tailings with 1000 mg/L HA at pH 11 were collected to examine the functional groups of

HA involved in arsenic mobilization and complexation. FTIR spectra were obtained with a Thermo Nicolt Nexus 670 FT-IR E.S.P. spectrometer (Thermo Instruments Inc., Canada). Samples and background were collected on 128 scans at a resolution of 4 cm^{-1}.

3.8 Column experiments

A unique feature of column experiments is that these methods are inherently open systems when compared with batch tests. The solute is continuously added to the system and reaction products are continuously removed. This unique feature produces special attributes for column methods that solve some of the problems associated with batch systems. Perhaps the main advantage of these methods is the continual removal of reaction products that in batch reactors are allowed to accumulate. Furthermore, with these methods, the solid phase will react with a greater mass of solute (concentration × flow rate × time) than in batch reactors (concentration × volume).

Based on the results from batch tests, column experiments were run to further examine the effect of HA and rhamnolipid on arsenic mobilization by simulating *in-situ* conditions in the environment and evaluate the feasibility of using NOM and biosurfactant for the remediation of arsenic-contaminated soils. The experimental setup is illustrated in Figure 3-4. All column experiments were conducted at room temperature.

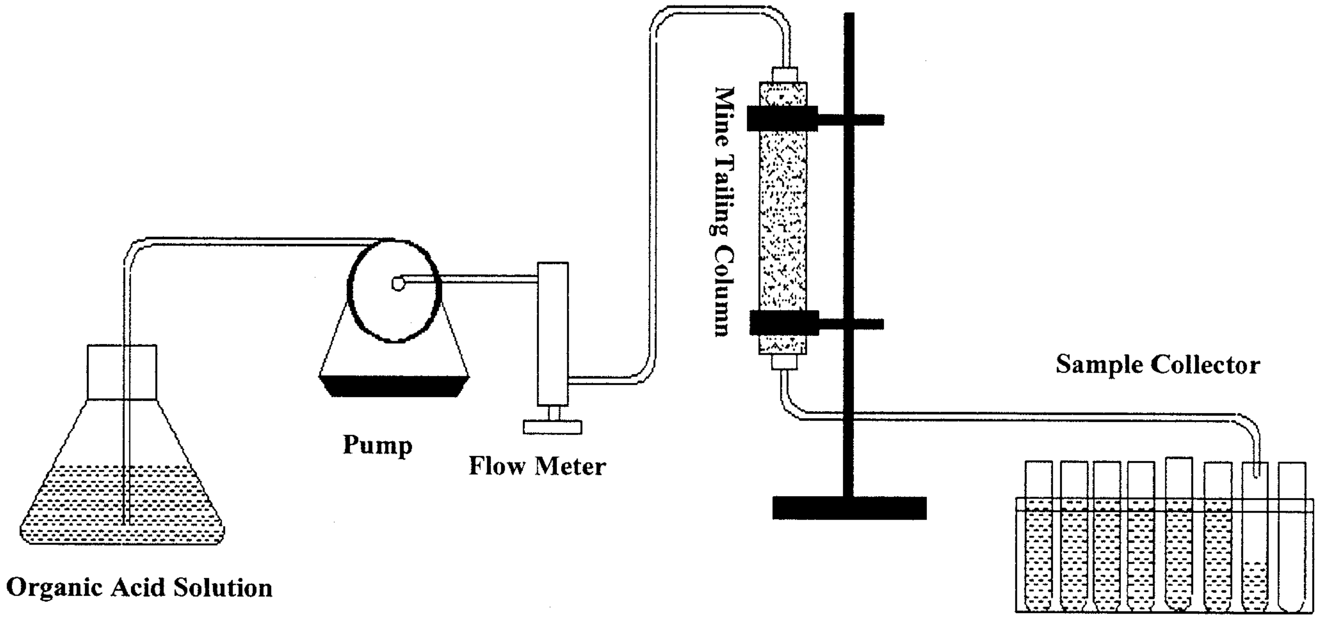


Figure 3-4. Experimental setup for column leaching test (column length: 15 cm, inside diameter: 1.5 cm)

Dried mine tailings (53 ± 2 g) were compacted in the column (length: 15 cm, inside diameter: 1.5 cm). The plastic wall of the column was tapped continuously as the mine tailings were added. The purpose of tapping and compacting was to pack the mine tailings uniformly. The pore volume of the packed column, an important parameter for the following experiments, was measured by saturating the loaded column with distilled water at a pressure gradient close to zero. Distilled water was pumped upward into the column at a flow rate below 0.1 ml/min, and the column was assumed to be saturated when water first appeared at the top of the column. The volume of water that needed to saturate the soil column was used to indicate the pore volume of the column. The tested value of pore volume was compared with that of theoretically calculated pore volume. The latter was calculated from the difference between the column volume and the volume of the mine tailings (calculated by the mass of the loaded dried mine tailings divided by its specific gravity). Good agreement was achieved.

The concentration of HA or rhamnolipid (1000 mg/L) and the pH value of the flushing solution (initial pH adjusted to 11) were selected based on the batch tests. Flow rates were controlled below 0.5 ml/min to prevent heaving and channeling. Distilled water with same adjusted pH value was taken as controls. The pH value was adjusted by 1 N NaOH or 1 N HCl solutions.

Effluents exiting the column were collected according to pore volumes passed through the column, and then were analyzed for concentrations of arsenic and metals. Samples of the mine tailings after flushing were taken at different points along the length of the column. Arsenic concentrations in the effluents and in the residual mine tailings were analyzed to determine the percentage of arsenic leached from the mine tailings and check the mass balances. All experiments were performed in duplicate, and triplicate if required and the average values were presented.

3.9 Arsenic concentration determination

In this study, total arsenic concentration was determined by a visual Hach method. The arsenic detection kit, Hach-28228-00, was purchased from Anachemia Canada Inc. The detection limit of this method is 10 μg/L.

To determine the potential interference of organic matter, standard solutions of known concentrations of As(III), As(V), or mixed As(III) and As(V) in a background of Fluka HA, rhamnolipid, or other organic acids were measured. No significant interference was observed from the presence of the organic matter.

Table 3-5. Comparison of arsenic concentrations in the mine tailings by different measuring methods

Mine tailings	Arsenic concentration (mg/kg)		
	ICP-MS	Hach method	XRF
Sample 1	63	61	Not detectable
Sample 2	270	263	265
Sample 3	2200	2250	2556

To determine arsenic concentration in the mine tailings, the mine tailings were first digested by aqua regia method. The extract was then filtered and diluted before measurement. The results were compared with those from ICP-MS and X-ray fluorescence (XRF, Niton Corporation, MA, USA) analyses (Table 3-5). Good agreements were achieved between the data obtained from ICP-MS and Hach methods. The slight variation of the concentrations by Hach method from those of ICP-MS measurement was predictive and reasonable. Therefore, the Hach method is reliable. Errors were minimized by using the same measuring method during the experiments.

3.10 Metal concentration determination

Metal concentrations were measured by AA analysis with an Atomic Absorption Spectrophotometer (PERKIN ELMER, AAnalyst 100, Perkin Elmer Inc., ON, Canada). Mine tailing samples, supernatants from batch tests, and effluents from column leaching tests were digested and diluted with 12 N or 6 N HNO_3 and shaken at 60 rpm for 24 hours. All the samples were analyzed under the same conditions such as standard solutions, slit, lamp current, and wavelength.

CHAPTER FOUR

CHARACTERIZATION OF THE MINE TAILINGS

4.1 Physicochemical characteristics of the mine tailings

A series of measurements were performed to determine the concentrations of arsenic and other metals in the mine tailings, and the physicochemical properties of the mine tailings (Table 4-1). The specific gravity, specific surface area, organic matter content, cation exchange capacity and pH values of the mine tailings were determined. Isoelectric points of the mine tailings were determined on the basis of zeta potential measurements. High contents of heavy metals such as Cu, Zn and Pb were detected in the mine tailings.

Table 4-1. Main physicochemical properties of the mine tailings

Physicochemical properties	Sample 1	Sample 2	Sample 3
Arsenic concentration (mg/kg)	60	260	2180
Specific gravity (at 20 °C)	3.24	3.32	3.65
Specific surface area (m^2/g)	2.07	2.23	1.84
Organic matter content (%)	0.64	2.83	4.67
Cation exchange capacity (cmol/kg)	6.49	5.79	10.38
pH	8.32	4.83	3.61
Isoelectric point	2.5	2.6	4.3
Pb content (mg/kg)	173	238	12860
Cu content (mg/kg)	310	2525	1100
Zn content (mg/kg)	897	4870	5075
Fe content (%)	21.9	18.1	23.8

4.2 Particle size distribution

The particle size distribution of the mine tailings is illustrated in Figure 4-1. All three samples have a sand content more than 90%. Approximately 75% of sample 1, 60% of sample 2, and 45% of sample 3 were finer than 0.2 mm. These results indicate that all three samples can be classified as sandy soils, according to the particle size definition by the American Society for Testing and Materials (ASTM).

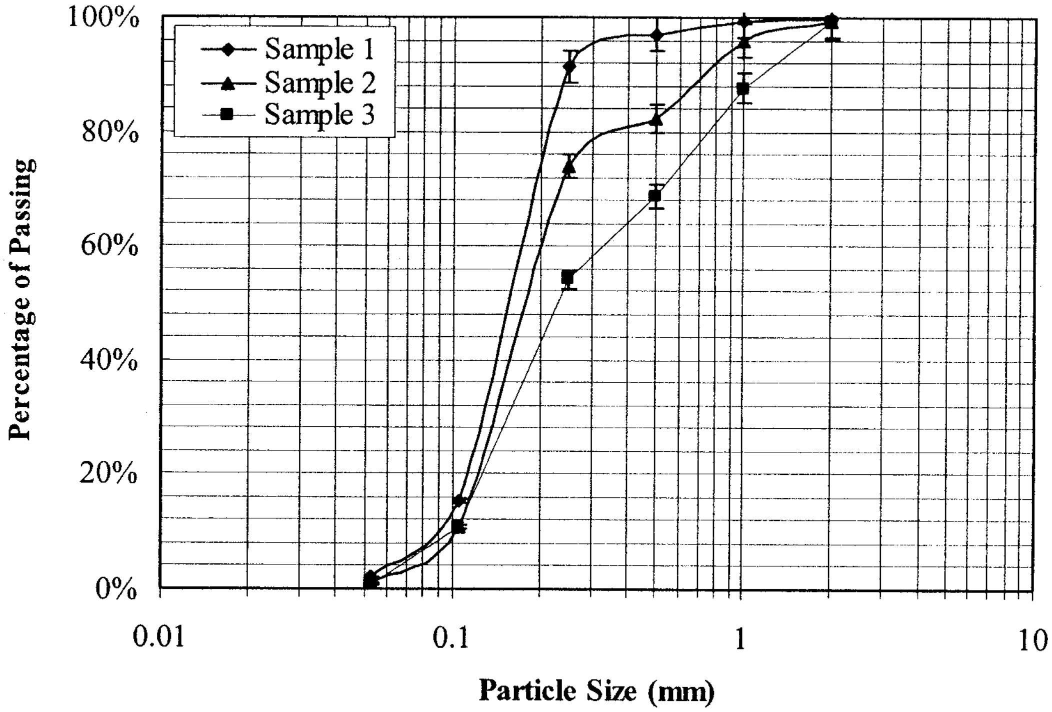


Figure 4-1. Particle size distribution for the three mine tailing samples

4.3 Specific surface area

The surface area of the mine tailings is closely correlated to its physicochemical properties. It is an important factor related to the adsorption capacity of the materials. The measured specific surface areas of the mine tailings ranged from 1.84 to 2.23 m^2/g (Table

4-1), conforming to the typical range of the specific surface areas for fine sandy particles (below 10 m^2/g, Brady and Weil, 2002).

4.4 Organic matter content

Organic matter content in the mine tailings contributes significantly to the retention of contaminants. The organic matter contents of the mine tailings were determined (Table 4-1) and were shown to fall into the range of reported organic matter contents in mine tailings from 0 (Schwab *et al.*, 2006) to 5.8% (Wu *et al.*, 2006) and also the range of the organic matter contents reported in soils (0.5 – 5%, Yong *et al.*, 1992).

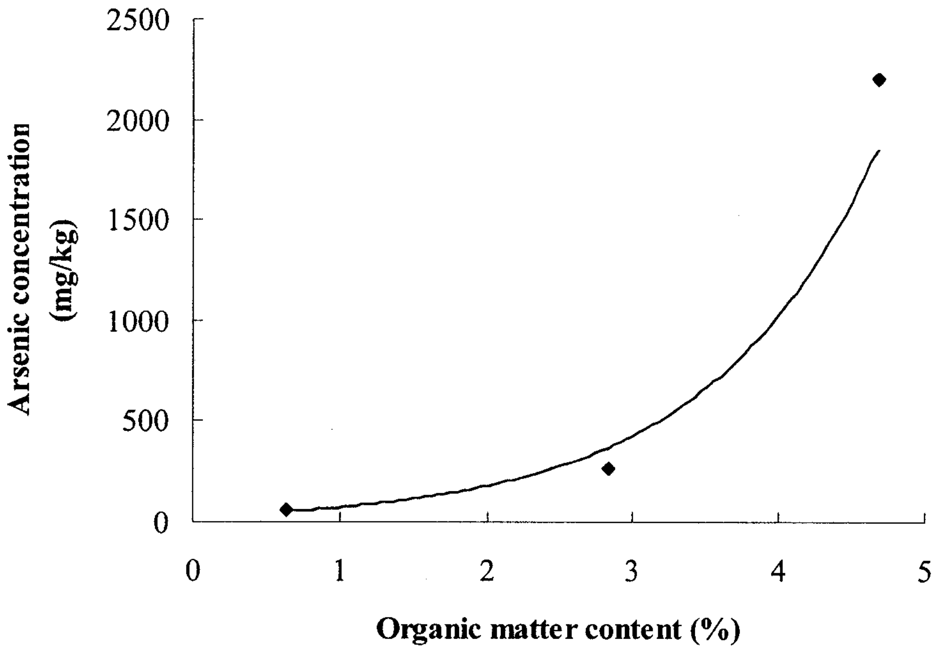


Figure 4-2. Correlation between arsenic concentration and organic matter content in the mine tailings

Although the mine tailing samples were collected from different mine locations in Canada, it can be seen from Table 4-1 that there is a positive statistical correlation between the arsenic concentrations and the organic matter contents in the mine tailings. As plotted in Figure 4-2, arsenic concentration increases exponentially with the organic matter content. This observation is similar to that of Kalbitz and Wennrich (1998), who found that the dissolved organic carbon (DOC) concentration correlated well with the arsenic concentration in aqueous extracts from soil.

4.5 Cation exchange capacity

CEC indicates how tightly the contaminants are bound to the soil, and soils of lower CEC bind metals less tightly (Yong *et al.*, 1992). Sample 3 has a higher CEC value partially due to its high organic matter content, since organic matter and clay phases contribute extensively to the CEC. The hydroxides or oxides in the mine tailings do not contribute to the CEC. CEC values of 12 to 20 cmol/kg are considered medium and low if below 12 cmol/kg (Cameron, 1992). Based on this criterion, the CEC values of the three samples are all fairly low.

4.6 Zeta potential measurement

Zeta potential was used to determine the electro physicochemical interaction at the mine tailings-liquid interface. The change of the zeta potential of the mine tailings with pH is illustrated in Figure 4-3. The negative charge increases with the increase of pH, due to the continuum ionization of acidic groups on the mineral surface.

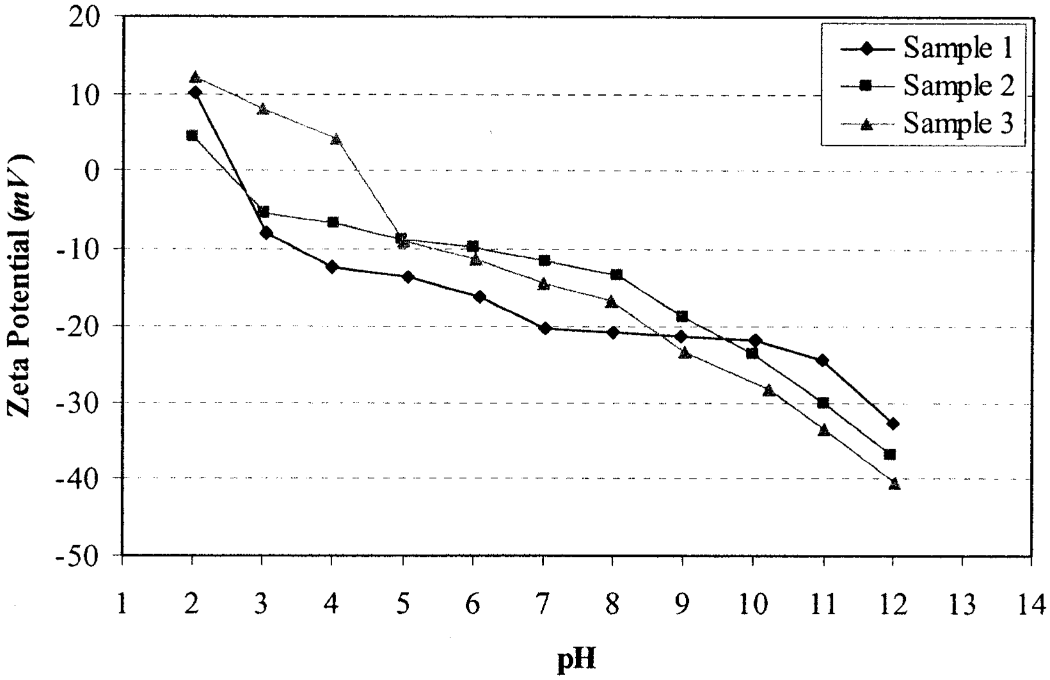


Figure 4-3. Zeta potential of the mine tailings as a function of pH

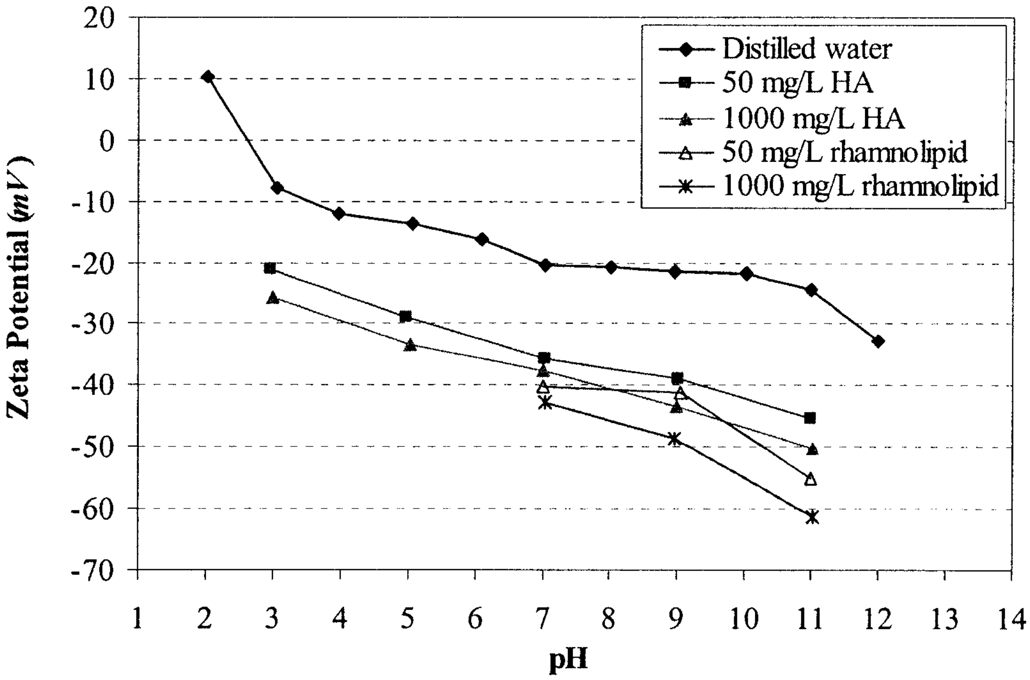


Figure 4-4. Zeta potential of sample 1 in the presence of HA and rhamnolipid

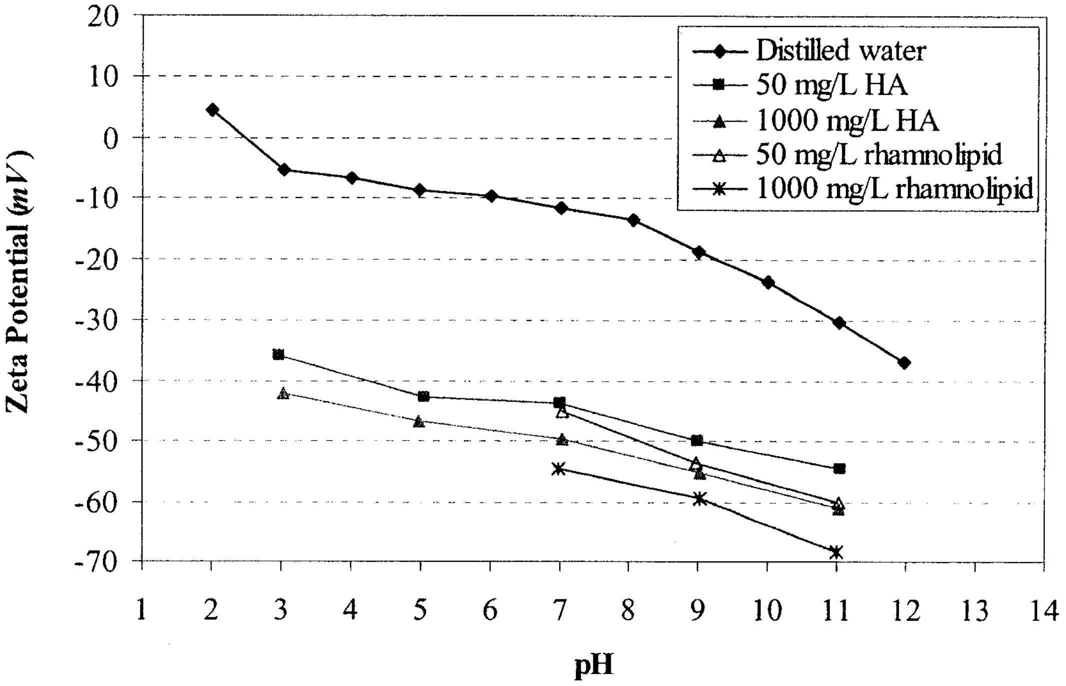


Figure 4-5. Zeta potential of sample 2 in the presence of HA and rhamnolipid

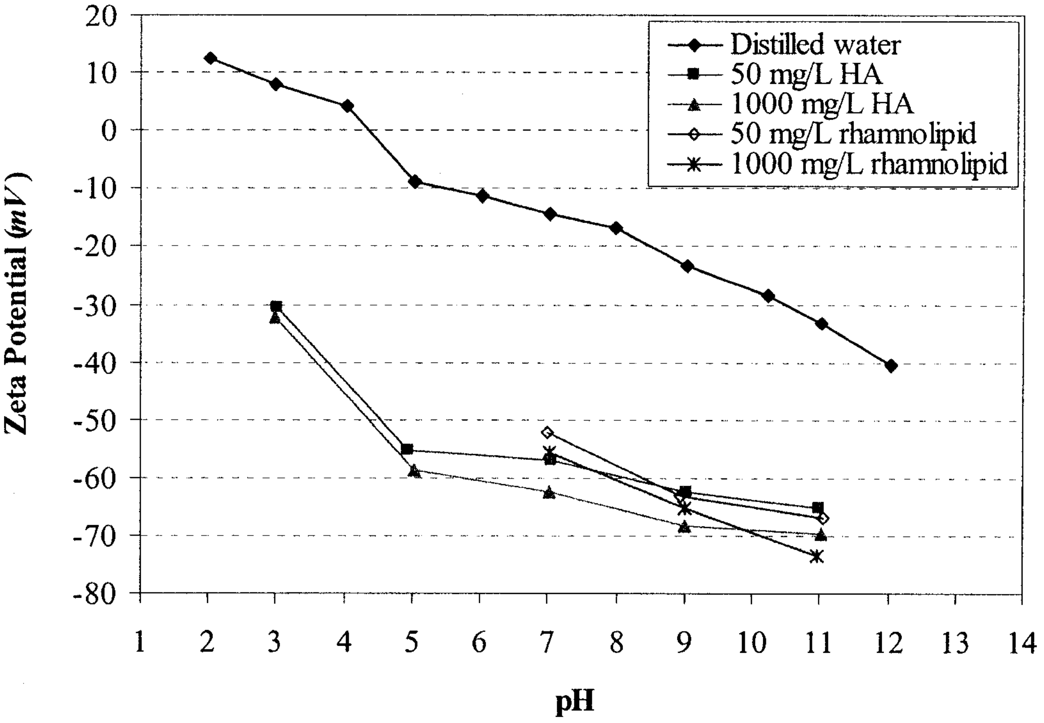


Figure 4-6. Zeta potential of sample 3 in the presence of HA and rhamnolipid

The isoelectric points were determined as the pH value at which the zeta potential is zero. From Figure 4-3, it can be determined that the isoelectric points were around 2.5, 2.6 and 4.3 for samples 1, 2 and 3, respectively. The mineral surfaces will be negatively charged at pH values above the isoelectric point whereas the mineral surfaces will be positively charged at pH values below the isoelectric point. The negatively charged particles tend to repel anions or attract cations in the suspension through electrostatic interactions.

The zeta potential of the mine tailings was then measured in solutions of HA and rhamnolipid to determine the effect of HA and rhamnolipid addition on the zeta potential. The effect of the solution concentration was determined by varying the concentrations of HA or rhamnolipid. The introduction of HA and rhamnolipid decreased the zeta potential significantly (Figures 4-4 to 4-6). The zeta potential of the mine tailings became more negative slightly with the increase of the concentration of HA or rhamnolipid, probably due to the increased sorption of HA or rhamnolipid on the mine tailing surfaces, which increased the density of negatively charged functional groups on the surfaces. The increased density of negative charges with increasing pH favors the mobilization of arsenic anions through repulsive electrostatic interactions.

4.7 pH determination

According to the classification by the US Natural Resources Conservation Service (NSSH 618.47, USNRCS, 2005), the pH of the mine tailing sample 1 (Table 4-1) falls into the moderately alkaline range (pH 7.9 – 8.4), while those of the samples 2 and 3

(Table 4-1) can be categorized into the very strong acidic range (pH 4.5 – 5.0) and the extremely acidic range (pH 3.5 – 4.4), respectively.

By comparing the isoelectric points and the pH values of the samples, it can be postulated that both samples 1 and 2 are of negative zeta potential while sample 3 is of positive zeta potential at the mine sites. This may partially explain why sample 3 contains a higher level of arsenic, since the positively charged surface tends to adsorb the arsenic anions through electrostatic attraction.

4.8 Total metal contents

From Table 4-1, it shows that Fe contents in the mine tailings are quite high. Elevated levels of heavy metals such as copper (Cu), lead (Pb), and zinc (Zn) were also detected. It indicated that the mine tailings could be important pollution sources of heavy metals in the environment. This also raised the issue of whether these metals will be mobilized together with arsenic, or whether they will interfere with arsenic mobilization. This aspect was then examined during the batch and column tests by monitoring the concentrations of these metals in the supernatants and effluents.

4.9 XRD analyses

XRD tests were carried out to identify whether there is crystalline arsenic mineral in the mine tailings. Usually, arsenic in crystalline phases is thought to be not easily mobilized by the addition of organic matter. The main XRD patterns are illustrated in Figures 4-7 to 4-9, and the results are summarized in Table 4-2. The XRD analyses did not show the presence of crystalline arsenic mineral phases. This was probably due to the detection limits of the method (2% - 5% wt.). Crystalline silica oxides were found in all of the samples (Table 4-2). A high proportion of pyrite was found in sample 3. No crystalline Fe (hydro)oxides were detected in all the three samples. It can be explained as: 1) the Fe (hydro)oxides are present mainly in amorphous phases, and/or 2) the crystalline Fe (hydro)oxides might be encapsulated in clayey materials, thus could not be detected.

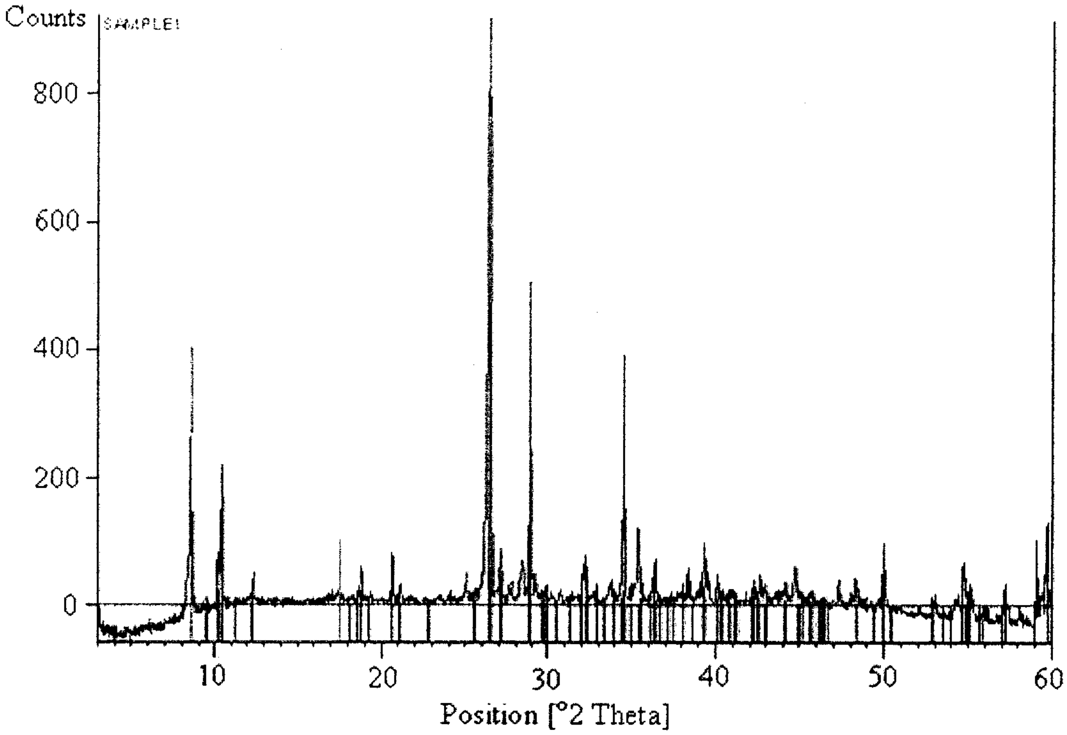


Figure 4-7. XRD patterns of sample 1

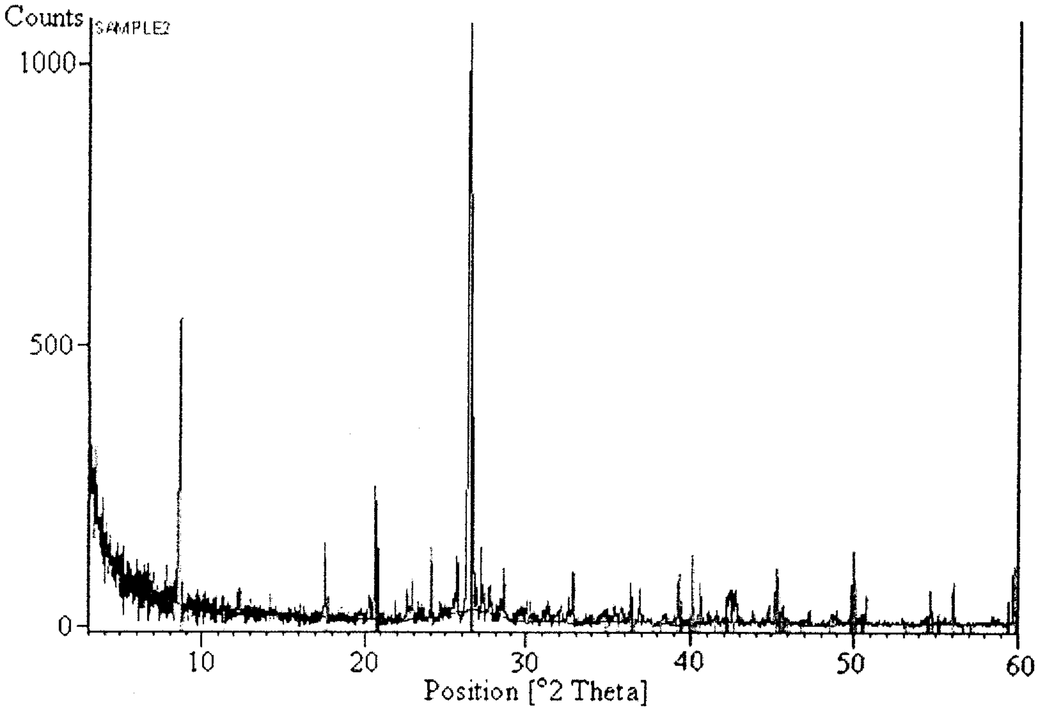


Figure 4-8. XRD patterns of sample 2

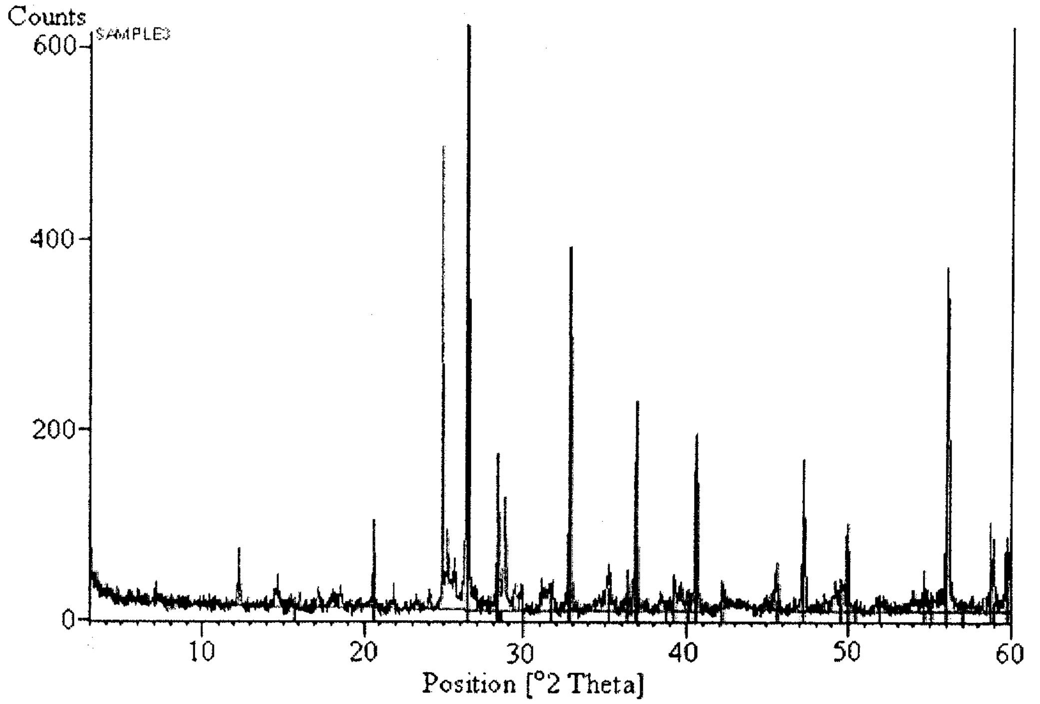


Figure 4-9. XRD patterns of sample 3

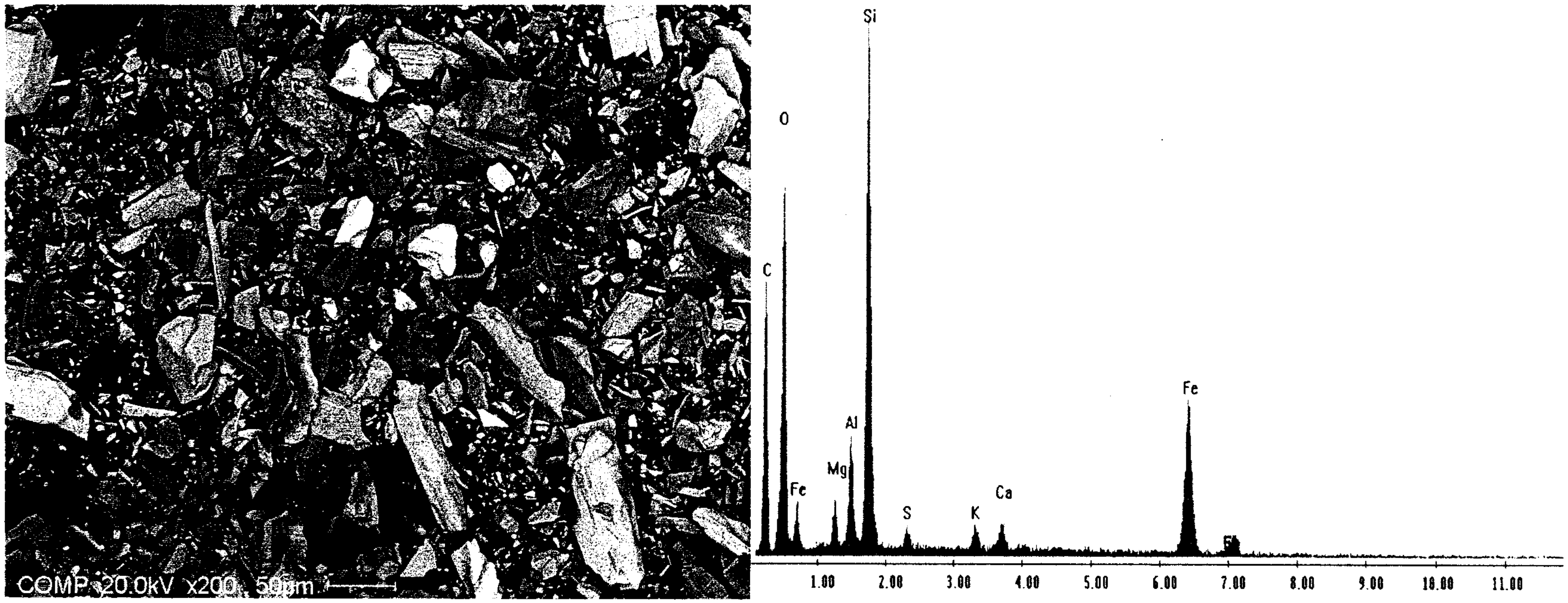


Figure 4-10. SEM image and associated EDS spectrum of sample 1

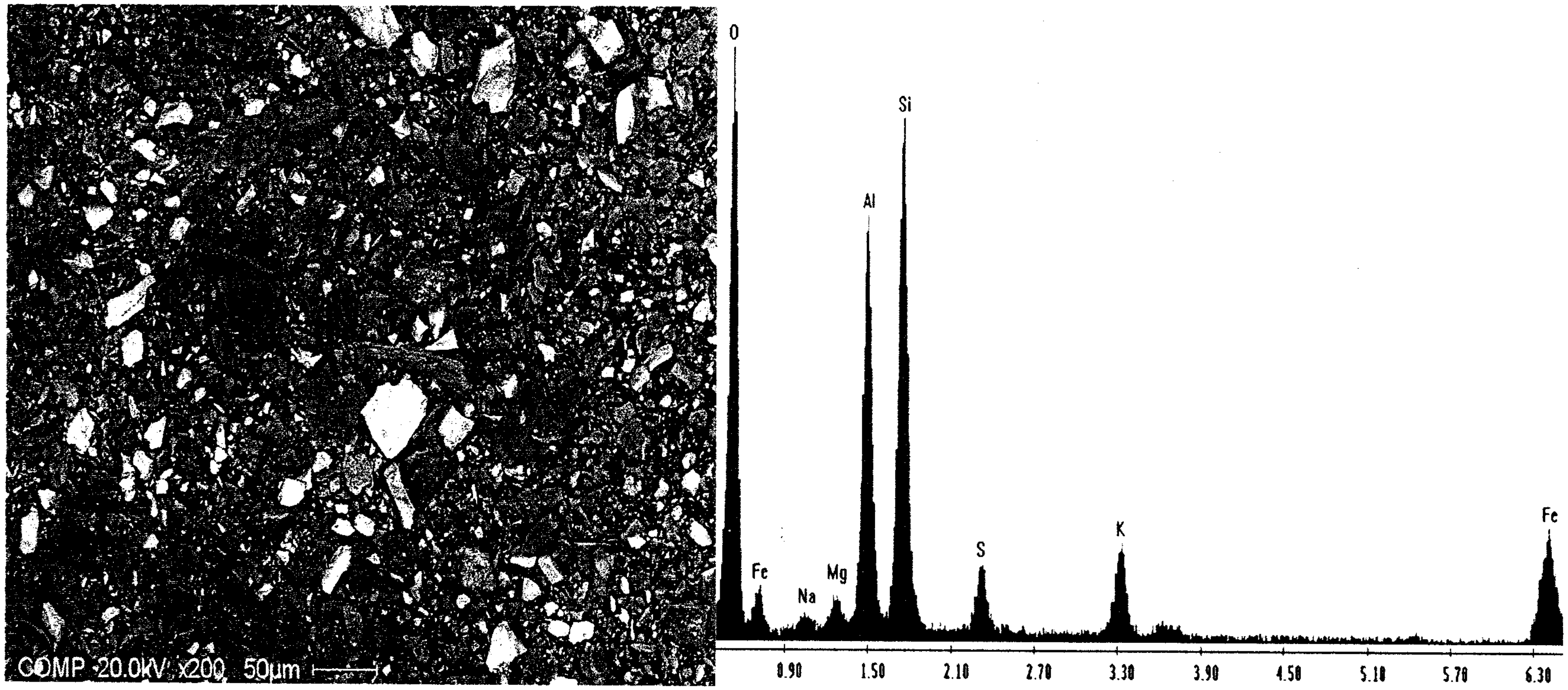


Figure 4-11. SEM image and associated EDS spectrum of sample 2

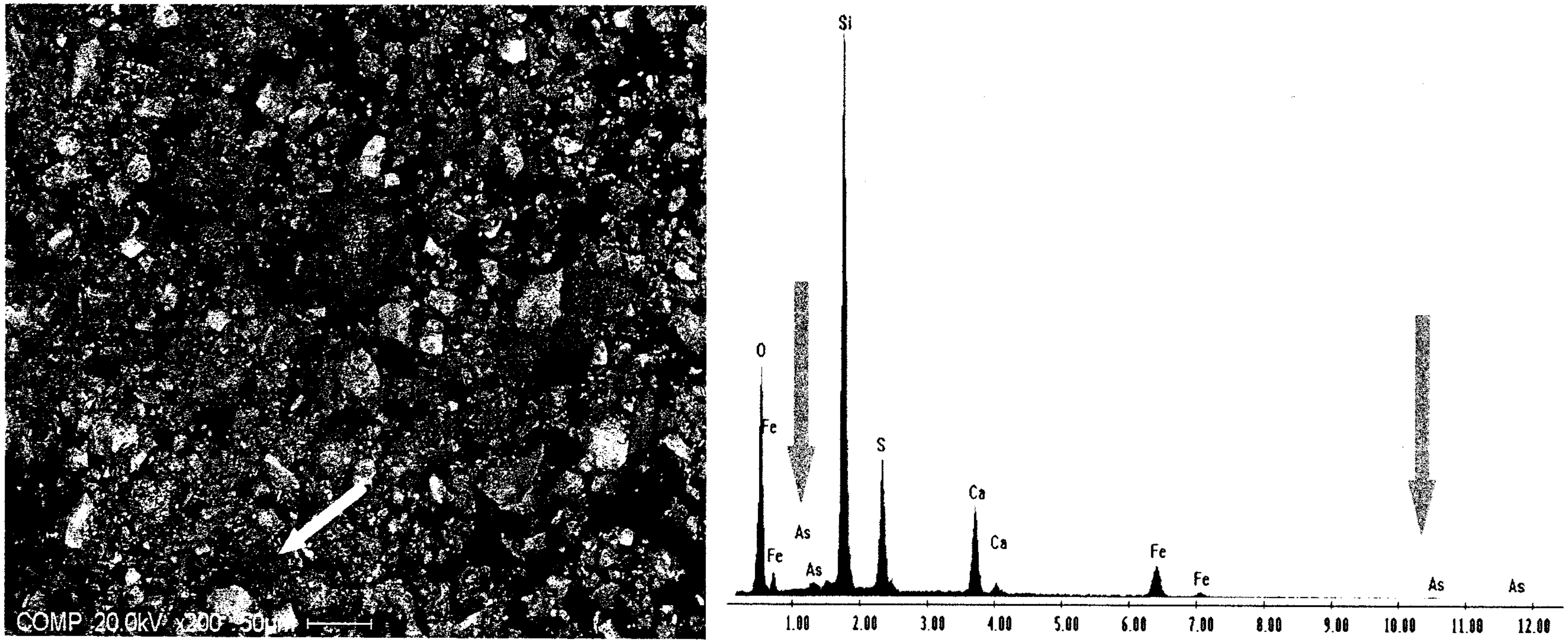


Figure 4-12. SEM image and associated EDS spectrum of sample 3

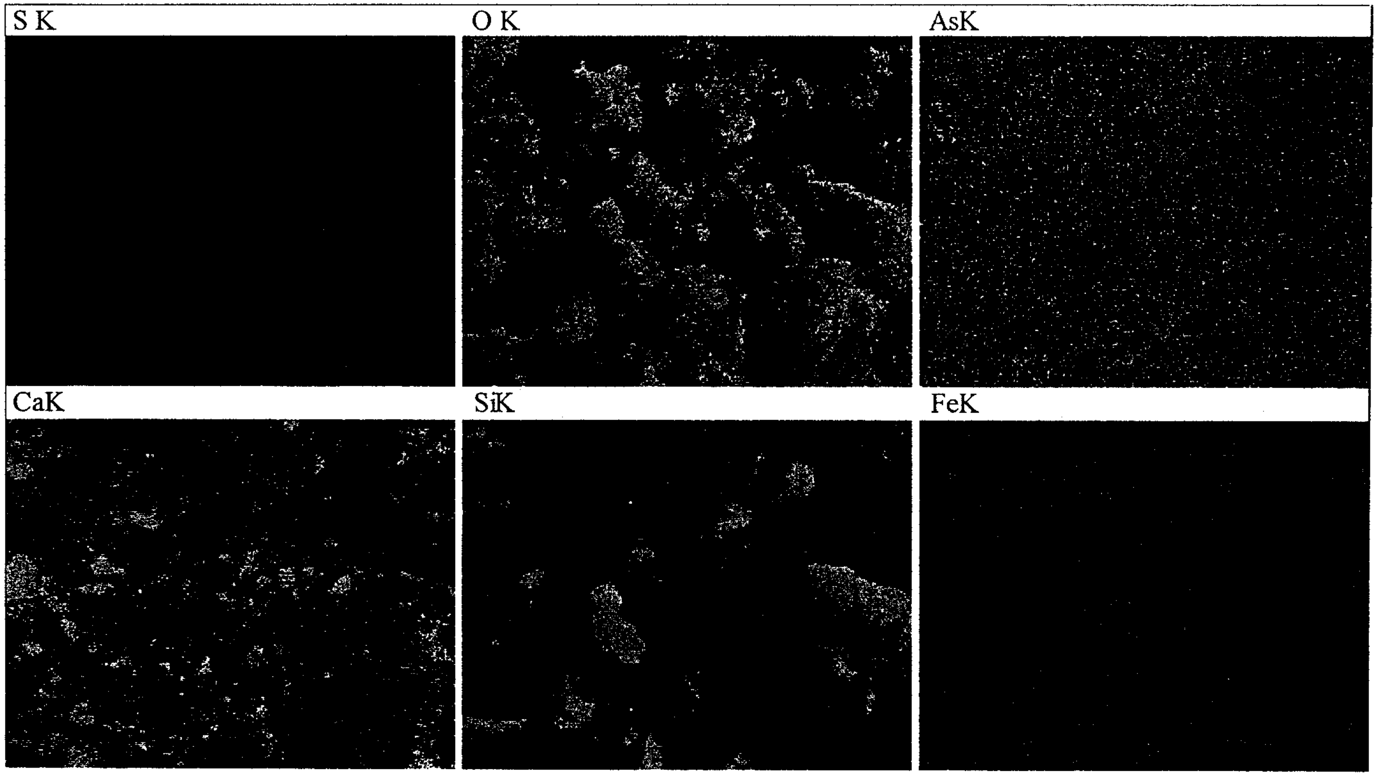


Figure 4-13. SEM-EDS X-ray mapping of sample 3 (1000 ×; KV: 20.0; Tilt: 0)

Table 4-2. Main XRD results for the three mine tailing samples

Sample No.	Main XRD results			
	Compound name	**Displacement [°2 θ]**	**Scale factor**	**Chemical formula**
1	Quartz	-0.192	0.922	SiO_2
	Birnessite-syn	-0.057	0.020	MnO_2
	Calcium manganese oxide hydrate	-0.234	0.292	$Ca_2Mn_{14}O_{27}.xH_2O$
	Dannemorite	-0.080	0.238	$(Fe, Mg, Mn)_7Si_8O_{22}(OH)_2$
2	Quartz, low	-0.090	0.119	SiO_2
	Silicon oxide-alpha	0.084	0.567	SiO_2
	Calcium manganese oxide hydrate	-0.073	0.266	$Ca_2Mn_{14}O_{27}.xH_2O$
3	Quartz	-0.229	0.993	SiO_2
	Pyrite	-0.209	0.613	FeS_2

4.10 SEM-EDS analyses

SEM-EDS analyses of the mine tailing samples were carried out to identify the existence of arsenic concentrated particles in the samples. The SEM images of the samples were illustrated in Figures 4-10 to 4-12. No apparent arsenic concentrated particles were detected in samples 1 and 2, due to the high detection limits (2% wt.) and possibly, the homogeneous distribution of arsenic in these samples. Possible arsenic-enriched particles were found only in sample 3. The arsenic was detected mainly in association with Fe, Ca, Si, and S as well as O (Figures 4-12 and 4-13), which might indicate that the arsenic was largely in association with the clayey phase in the mine tailings.

CHAPTER FIVE

BATCH TEST RESULTS AND DISCUSSION

Batch experiments were carried out to investigate the mobilization of arsenic from the mine tailings in the presence of HA and rhamnolipid. The effects of pH, mass ratio of added HA or rhamnolipid to mine tailings and reaction time on arsenic mobilization were examined. The effects of HA and rhamnolipid on arsenic mobilization were compared with those of three LMWOAs, succinic acid, L-cysteine, and L-aspartic acid. The correlation of metal (e.g., Fe, Cu, Pb, and Zn) mobilization with arsenic mobilization was also monitored. The experimental results from the batch tests are presented and discussed in this chapter.

5.1 Distilled water

Batch tests first began with distilled water to determine the mobilization of arsenic from the three mine tailings without additives. It was used as a control for the following batch tests. The effect of pH was investigated by varying the pH values every two units from 3 to 11 (i.e., 3, 5, 7, 9 and 11). The pH values were adjusted by 1 N NaOH and 1 N HCl. Though pH adjustment introduced HCl or NaOH into the solution at a concentration level of 1×10^{-3} to 1×10^{-11} M, the term "distilled water" was used in the text for convenience. Distilled water at different adjusted pH values without addition of the mine tailings were used as blank controls. No arsenic was detected in the blank controls.

Figure 5-1 shows the concentrations of arsenic mobilized from the mine tailings (2 g) after a 24-hour shaking with distilled water at different pH values. Arsenic was mobilized the most by distilled water at pH 3, 3 mg/kg from sample 1, 3 mg/kg from sample 2 and 43 mg/kg from sample 3. Generally, arsenic mobilization decreased when pH increased. However, in the case of samples 2 and 3, an increase in arsenic mobilization was observed when pH increased from 7 to 9. At pH 11, distilled water alone mobilized 0.5, 2, and 6 mg arsenic/kg, respectively.

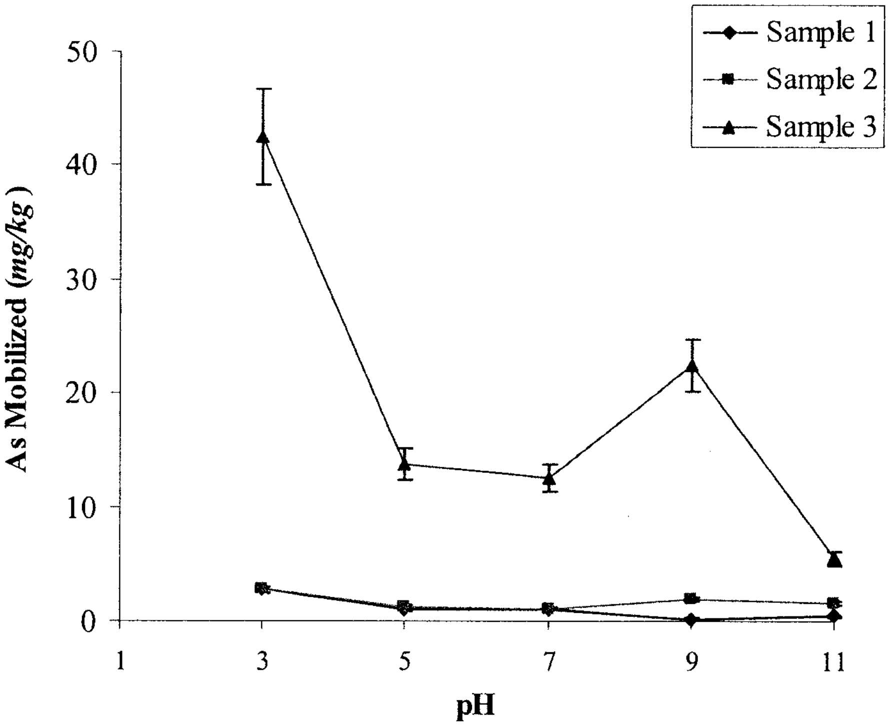


Figure 5-1. Arsenic mobilization from the mine tailings by distilled water

The high mobilization of arsenic at pH 3 from the mine tailings might be due to the dissolution of the components of the mine tailings, such as metal oxides which released the associated arsenic. It was reported that pH incurred Fe oxide dissolution at pH below 3.8 (Ulrich, 1983). High contents of arsenic in the mine tailings and the high mobility of arsenic at low pH suggested that the mine tailings might impose a high risk to the surface- and groundwater quality under acidic conditions.

Previous research studies using pure Fe or Al hydroxides to investigate the pH-dependent arsenic desorption revealed that As(V) solubility increased upon increasing pH in the range of 3 to 8, whereas As(III) tended to follow the opposite pattern (Wang and Mulligan, 2006b). Masscheleyn *et al.* (1991) also observed that soluble arsenic concentration was three times higher at pH 8 than that at pH 5, and the authors contributed the results to the decrease of positive surface charge at high pH. However, in this study, it was observed that arsenic was mobilized the most from all the three samples at the lowest pH value of 3. The discrepancy should be due to different experimental procedures and conditions, and especially, the complex components of the mine tailings, which is greatly different from the pure experimental materials such as Fe hydroxides. Similar results were observed by Shaw (2004) that arsenic was more mobile from sediments under acidic conditions (pH 4). The author explained that the conversion of As(V) to As(III) increased the mobility of arsenic (Shaw, 2004). It was plausible even though there was no further verification of this postulation in that study. At low pH and redox potential, As(V) might be converted to As(III) according to the following equations (Bose and Sharma, 2002):

$$AsO_4^{3-} + 2H^+ + 2e^- \rightarrow AsO_3^{3-} + H_2O \quad \log K = 5.293 \qquad \textit{Eq. 5-1}$$

i.e.,

$$\log K = \log \frac{[AsO_3^{3-}]}{[AsO_4^{3-}]} + 2pH + 2pE \qquad \textit{Eq. 5-2}$$

This is consistent with the Eh-pH diagram for arsenic speciation (Figure 2-6). While pH controls the speciation of arsenic within a particular oxidation state, the Eh controls the distribution of arsenic species between the two oxidation states (Bose and Sharma, 2002). The electron donor could be the Fe(II) or ferrous form of Fe or organic matter (Bose and Sharma, 2002; Redman et al., 2002; Dobran and Zagury, 2006).

5.2 Fluka HA

5.2.1 Effect of mass ratio

The mobilization of arsenic from the mine tailings by Fluka HA at different pH values (from 3 to 11) with different mass ratios of the added HA to the mine tailings (from 0.25 to 12 mg/g) was investigated. Measurements were conducted after 24-hour shaking at room temperature. Arsenic concentrations in the HA solutions without addition of mine tailings at different pH values were also measured, and no arsenic was detected in these blank controls. Results showed that arsenic mobilization from the mine tailings was affected by both the mass ratio and pH.

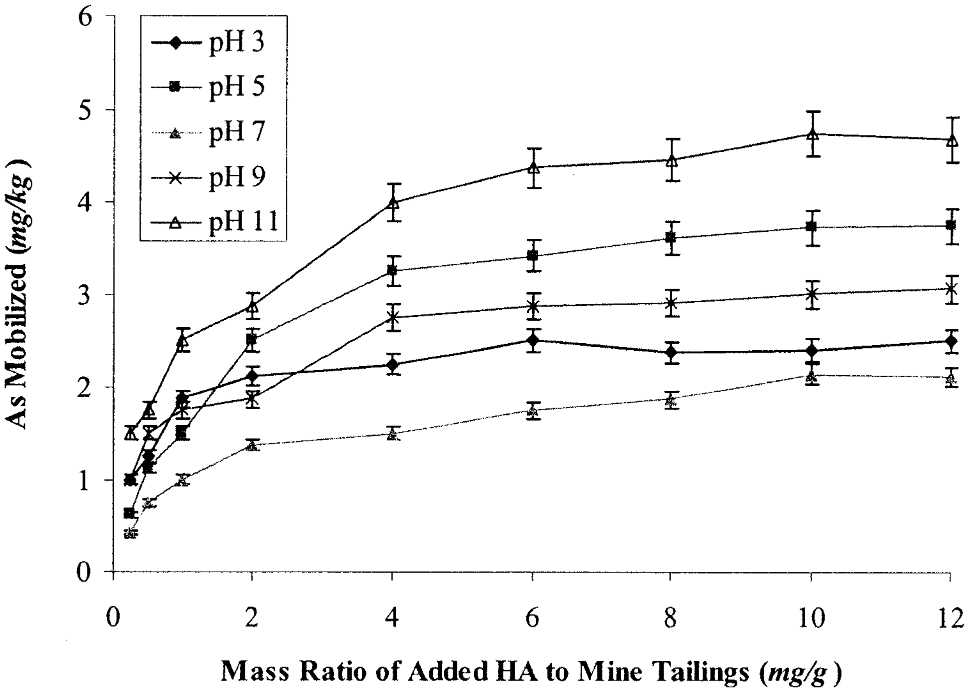


Figure 5-2. Arsenic mobilization by HA from sample 1

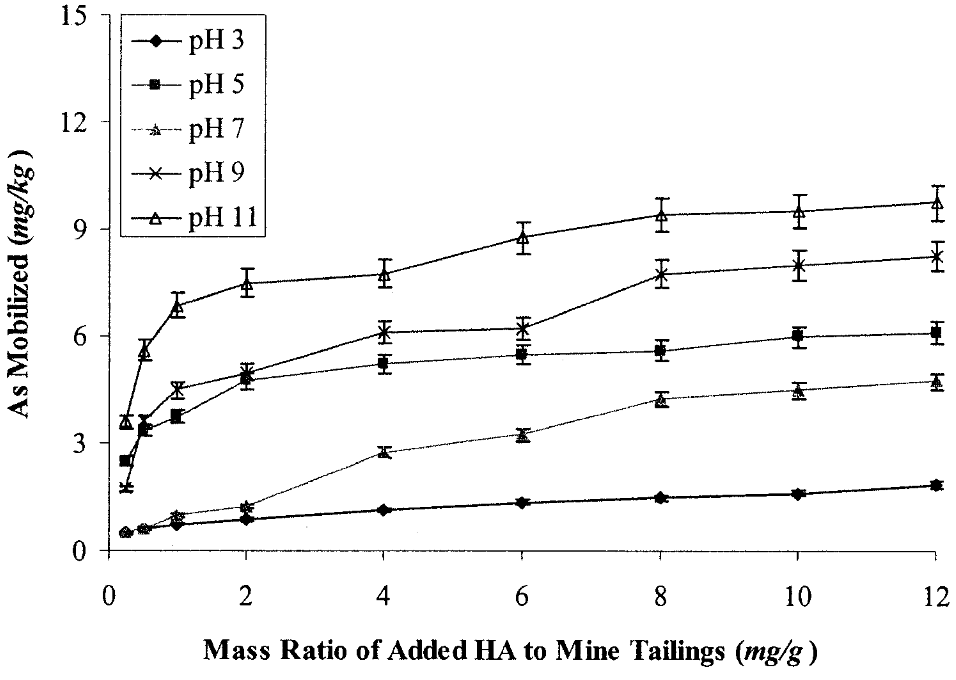


Figure 5-3. Arsenic mobilization by HA from sample 2

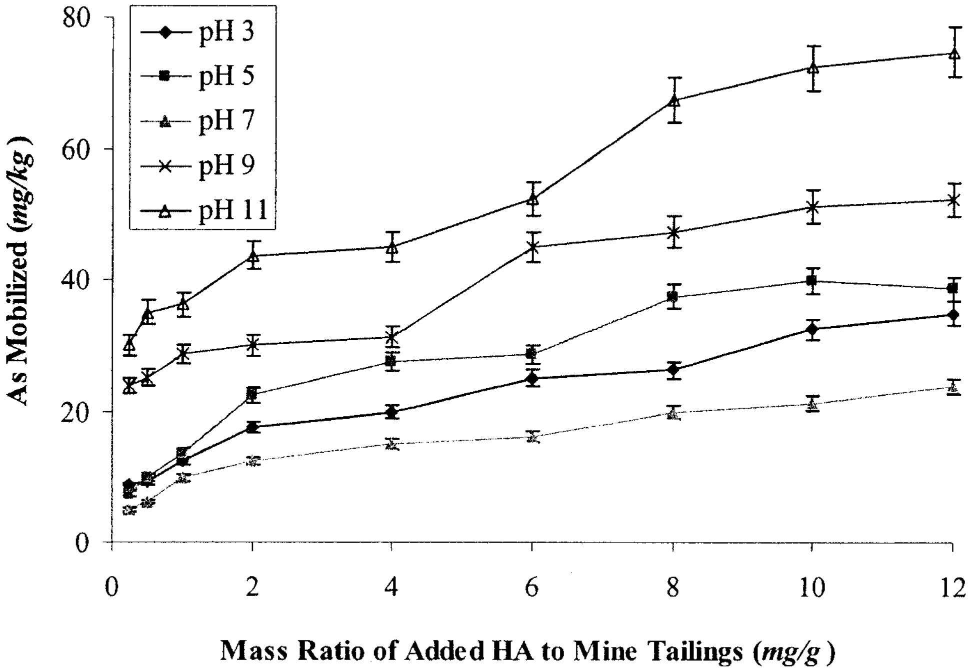


Figure 5-4. Arsenic mobilization by HA from sample 3

Generally, the mobilization of arsenic from the mine tailings increased with the increase of the mass ratio (Figures 5-2 to 5-4). At pH 3 with a mass ratio of 10 mg/g, arsenic mobilization was 2 mg/kg from sample 1, and 1 mg/kg from sample 2 and 33 mg/kg from sample 3, with corresponding concentration ratios (the ratio of arsenic concentration mobilized by HA to that mobilized by distilled water at same pH value) of 0.87, 0.59 and 0.76, respectively. The concentration ratios were below 1.0, which meant that the addition of HA at pH 3 inhibited arsenic mobilization from the mine tailings.

Arsenic was mobilized the most at pH 11. When the mass ratio was 10 mg/g at pH 11, 5 mg arsenic/kg was mobilized from sample 1, 10 mg arsenic/kg from sample 2, and 73 mg arsenic/kg from sample 3. The corresponding concentration ratios were 10.36, 5.85 and 13.18, respectively. The results indicated that arsenic mobilization was significantly enhanced by the addition of HA at pH 11.

Increasing both the mass of mine tailings and added HA while keeping the same mass ratio (2 mg/g) increased the dissolved arsenic concentrations in the supernatants significantly, but had no significant effect on the portion of arsenic mobilized. However, arsenic mobilization was significantly enhanced when the mass ratio of added HA to the mine tailings was increased from 2 to 10 mg/g. This might indicate that arsenic mobilization from mine tailings in the presence of HA was controlled mainly by the interaction between HA to mine tailings. HA sorption to the mine tailings was essential for the mobilization of arsenic.

5.2.2 Effect of pH

Arsenic mobilization in the presence of HA is highly pH-dependent, due to the fact that the distribution of arsenic species and the development of surface charge on the solids are highly pH-dependent (Figures 2-6 and 4-3). The OH groups on mineral surface can either bind or release H^+ with pH changes, leading to the change of the composition of surface functional groups and aqueous arsenic speciation through protonation and deprotonation reactions (Hingston *et al.*, 1972; Ghosh *et al.*, 2006). The presence of the OH_2^+, OH and O^- surface functional groups may have a significant effect on the adsorption of HA to the mine tailing surface and the interaction between arsenic and HA (Sposito, 1984).

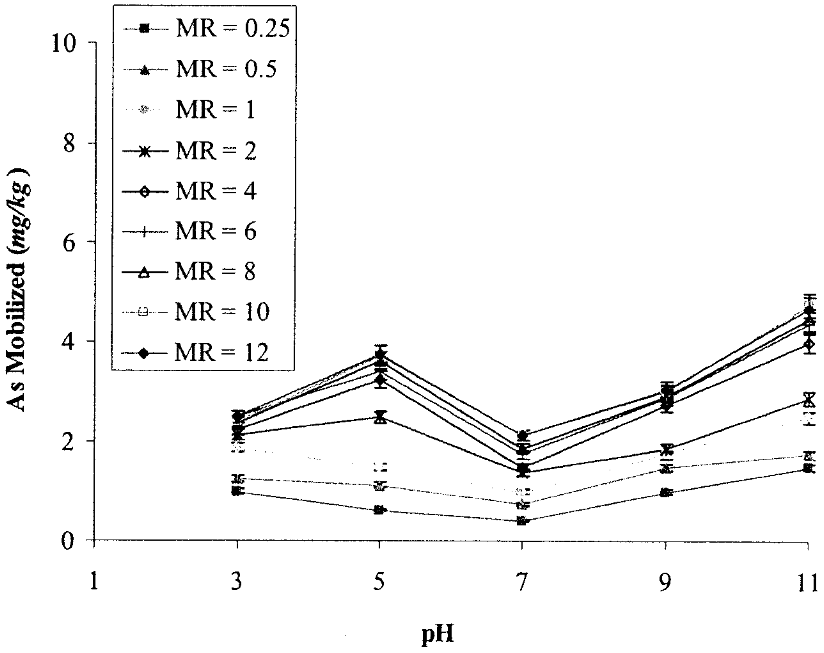


Figure 5-5. Effect of pH on arsenic mobilization from sample 1 by HA (MR: mass ratio of added HA to mine tailings, mg/g)

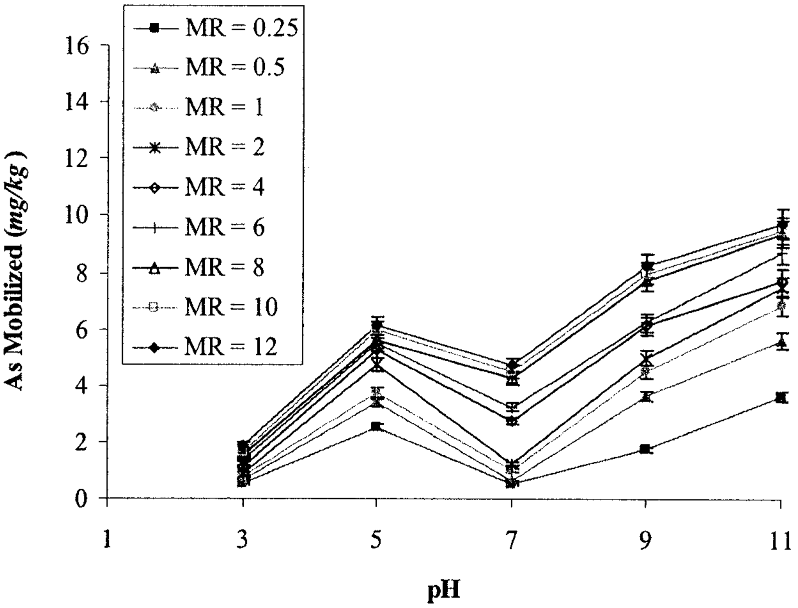


Figure 5-6. Effect of pH on arsenic mobilization from sample 2 by HA (MR: mass ratio of added HA to mine tailings, mg/g)

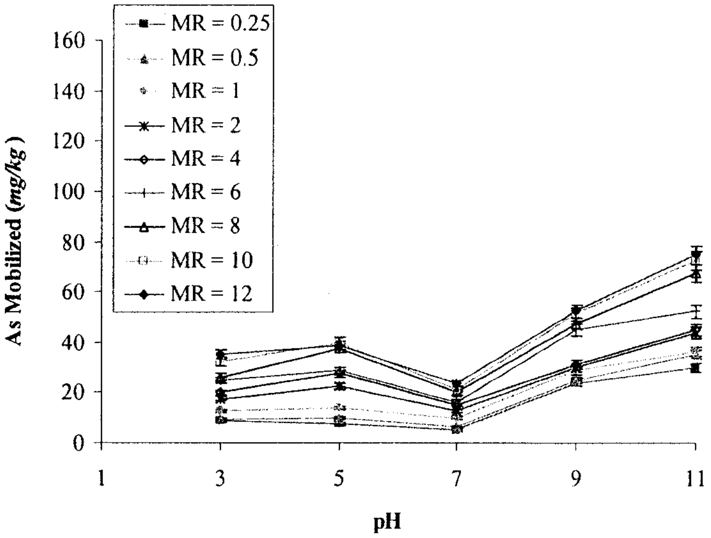


Figure 5-7. Effect of pH on arsenic mobilization from sample 3 by HA (MR: mass ratio of added HA to mine tailings, mg/g)

Figures 5-5 to 5-7 show the effect of pH on arsenic mobilization from the mine tailings in the presence of HA (MR = mass ratio of added HA to mine tailings, mg/g). The mobilization of arsenic from the mine tailings by HA was found to be highly dependent on pH. Low arsenic mobilization at pH 3 in the presence of HA might result from the sorption of HA to the mine tailings and the retention of arsenic to the sorbed HA through metal bridging mechanisms (Redman *et al.*, 2002; Wang and Mulligan, 2006b)

When pH increased from 3 to 5, arsenic mobilization from the mine tailings was increased because the solubility of HA increased and the available metal cations were decreased due to pH increase. The mobilization of arsenic was decreased significantly at pH 7, probably due to the decrease of HA sorption to mine tailings. Grafe *et al.*

(2001) reported that HA adsorption onto ferrihydrite decreased significantly from pH 3 to 6, and leveled off between 6 and 7. These observations further verified that HA adsorption to mine tailings played a significant role in arsenic mobilization from the mine tailings.

High arsenic mobilization was observed when pH was greater than 7. Dissociation of HA and formation of soluble aqueous complexes contributed to the high arsenic mobilization (Redman et al., 2002; Lin et al., 2004). Arsenic was most mobilized by HA at pH 11. Desorption of arsenic from Fe (hydro)oxides and the dissolution of organic matter in the mine tailings at high pH values might release associated arsenic, thus contributing to the high mobility of arsenic. Significant desorption of As(V) from Fe hydroxides was observed at pH values of approximately 8 and higher (Fuller *et al.*, 1993; Lumsdon *et al.*, 2001).

5.2.3 Comparison with distilled water

Compared with distilled water, the addition of HA showed significant influence on arsenic mobilization from the mine tailings (Figures 5-8 to 5-10). The extent of influence varied with pH change. Generally, the addition of HA inhibited arsenic mobilization at a low mass ratio (below 1.0 mg/g) under acidic to neutral conditions, and enhanced arsenic mobilization when the mass ratio was above 2.0 mg/g under alkaline conditions. The results are consistent with the previous observation that HA could contribute more to the retention process of arsenic in acidic environments, but, under alkaline conditions, distribution favors the aqueous phases (Thanabalasingam and Pickering, 1986).

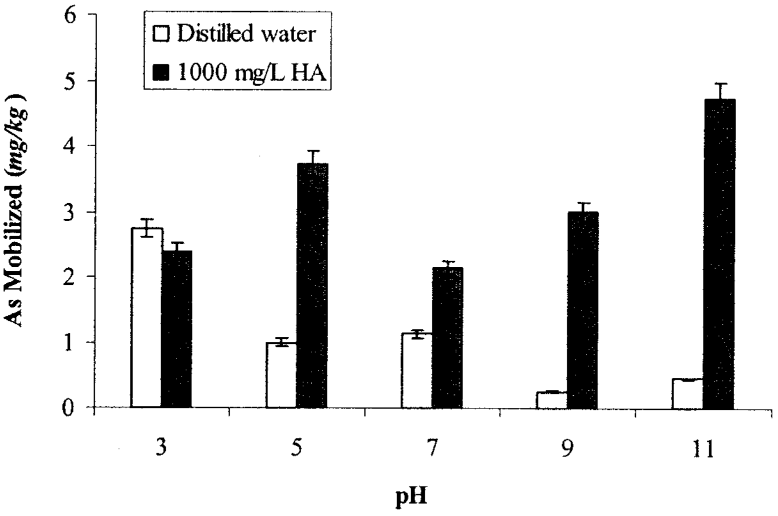


Figure 5-8. Comparison of arsenic mobilization from sample 1 by distilled water and 1000 mg/L HA

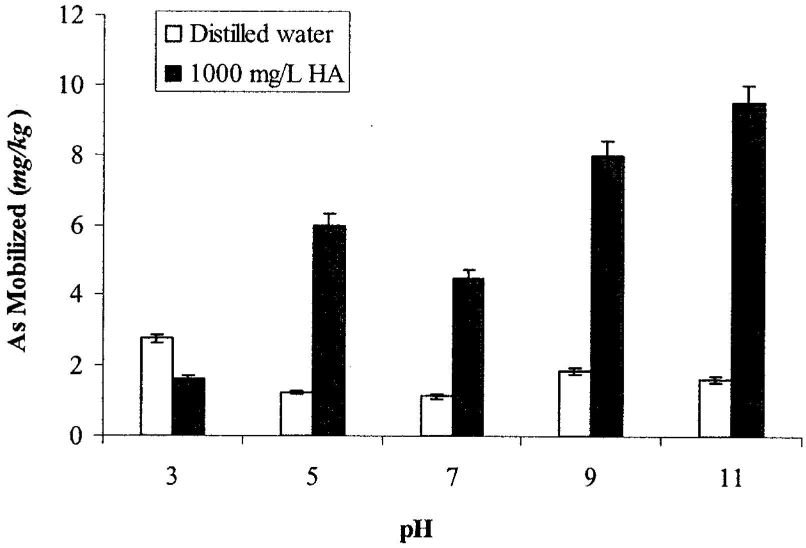


Figure 5-9. Comparison of arsenic mobilization from sample 2 by distilled water and 1000 mg/L HA

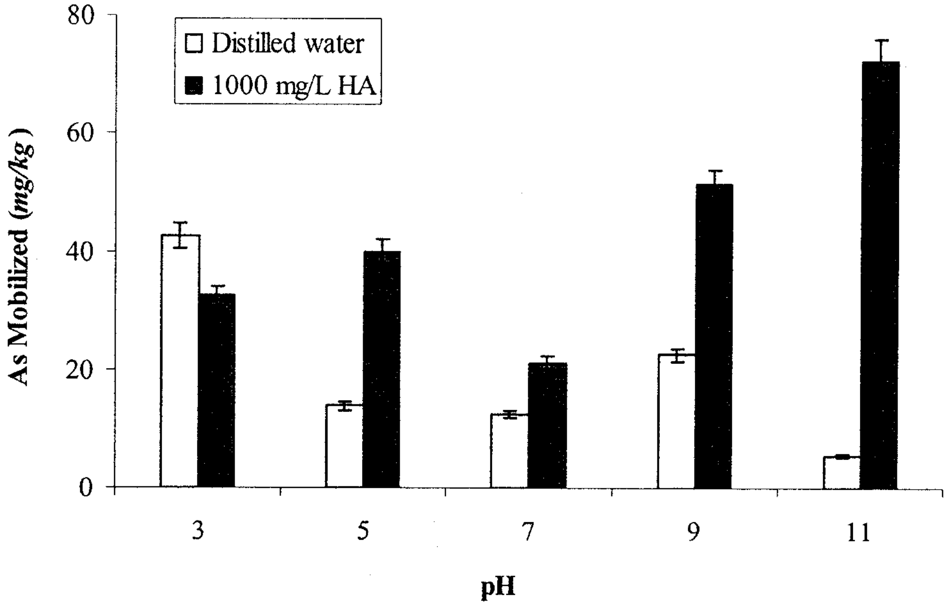


Figure 5-10. Comparison of arsenic mobilization from sample 3 by distilled water and 1000 mg/L HA

At pH 3, the dissolution of the metal oxides in the mine tailings occurred, releasing associated arsenic and metals into the solution. However, it is observed that the addition of HA decreased the dissolved arsenic portion in the solutions at pH 3 (Figure 5-11). This observation is similar to the previous one that showed that acidification and organic matter addition (FA) reduced arsenic mobility (Xu *et al.*, 1991).

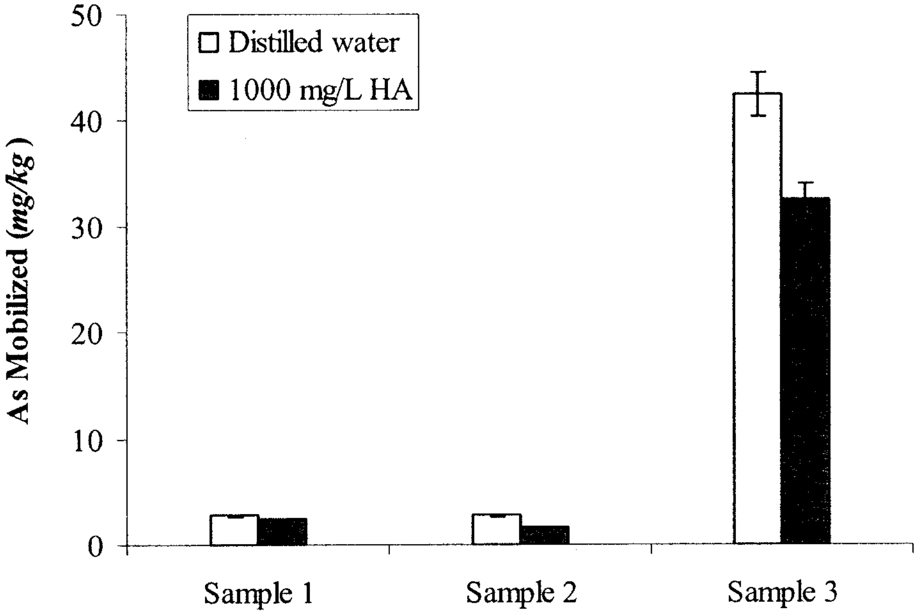


Figure 5-11. Arsenic mobilization by distilled water and 1000 mg/L HA at pH 3

The decreased arsenic mobilization may be a result of a two-phase process. The density of negatively charged sites on the mine tailing surface decreased at pH 3. The mine tailing surface of sample 3 might be even positively charged (Figure 4-3). HA might first be adsorbed to the mineral surfaces through hydrogen bonding and electrostatic interactions (Grafe *et al.*, 2001). The dissolution of metal oxides in the mine tailings under acidic conditions provided more active adsorption sites for HA. Arsenic might also be released in this phase as a result of the dissolution of metal oxides, anion exchange and competition adsorption with HA. Consequentially, the dissolved arsenic was re-adsorbed to the positively charged mineral surface or to the organic matter. The arsenic might be adsorbed to the organic matter by electrostatic interactions or by forming inner-sphere complexes presumably through metal-bridging mechanisms (Figure 5-12).

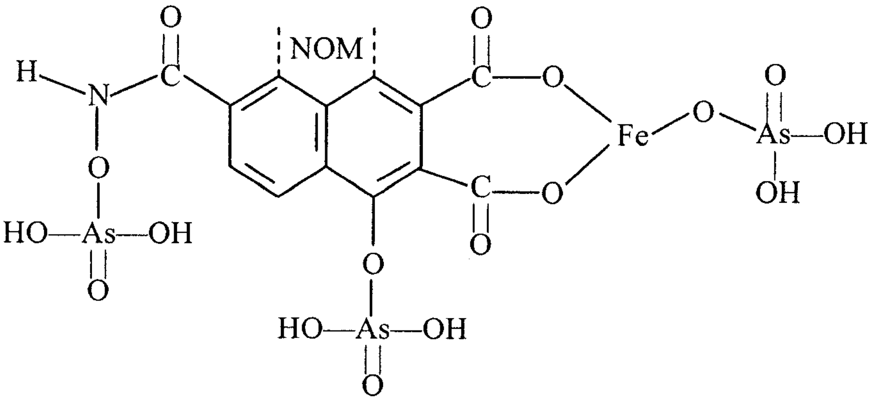


Figure 5-12. Hypothetical model structure of arsenic-NOM complex

(Wang and Mulligan, 2006b)

At higher pH values, the addition of HA enhanced the mobilization of arsenic from the mine tailings (Figures 5-13 to 5-16). Increasing pH increased the negative zeta potential of the surfaces of the mine tailings (Figure 4-3). Both the mine tailing surface and the organic matter are negatively charged. The HA might be adsorbed to the mine tailing surface through ligand exchange reactions and hydrogen bonding between the organic functional groups (mainly COOH and OH) and surface hydroxyls (Gu *et al.*, 1994; Grafe *et al.*, 2001), thus releasing arsenic anions into the solution. The adsorption of organic matter increased the density of negatively charged functional groups on the mineral surfaces. Zeta potential measurements indicated that the negative zeta potential of the mine tailings could increased significantly due to the presence of HA (Figures 4-4 to 4-6), which produced a greater repulsive interaction between the mine tailing surface or the organic matter surface and arsenic anions, thus preventing the re-adsorption of arsenic anions on to the surfaces, leading to the increase of the mobilization of arsenic. Furthermore, increasing pH also might dissolve organic matter in the mine tailings, thus releasing the associated arsenic.

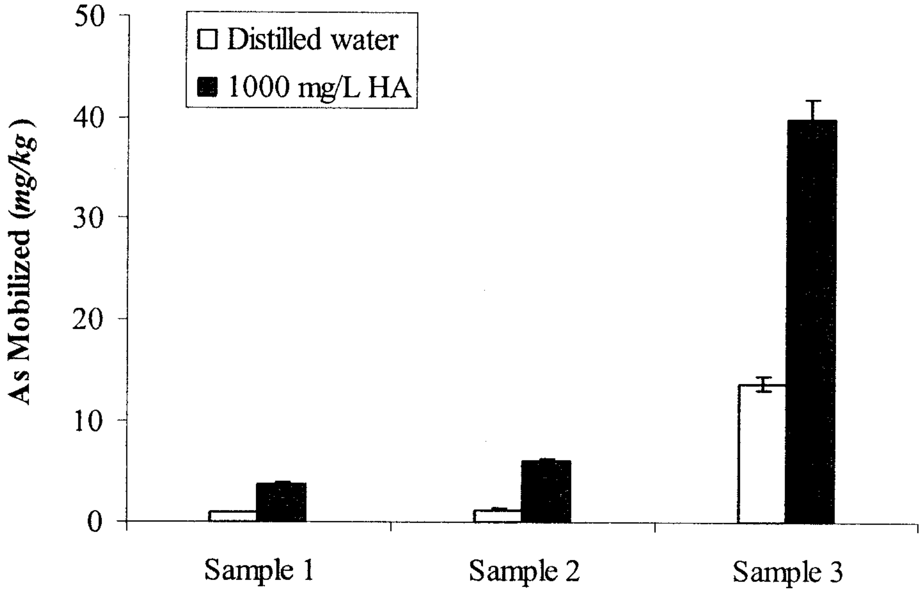


Figure 5-13. Arsenic mobilization by distilled water and 1000 mg/L HA at pH 5

The formation of soluble arsenic-HA and/or arsenic-metal-HA complexes at high pH was another potential mechanism contributing to the high arsenic mobilization from the mine tailings (Redman *et al.*, 2002; Lin *et al.*, 2004; Buschmann *et al.*, 2006; Wang and Mulligan, 2006b). Recent research studies have proposed HA as a supramolecular association, in which many relatively small and chemically diverse organic molecules form clusters linked by hydrogen bonds and hydrophobic interactions (Sutton and Sposito, 2005). The supramolecular association dissociates into low molecular weight organic matter at high pH, which may form soluble complexes with arsenic. Moreover, Spark *et al.* (1997) observed that the interaction between HA and metal cations resulted in the formation of soluble metal-humate species instead of the precipitation of metal hydroxides at high pH, which further prevented the re-precipitation of arsenic by adsorption to and/or coprecipitation with the hydroxides. It was also found that the solubility of the metal-HA complexes increased at high pH. Arsenic can be bound to the complexes through metal bridging mechanisms or form aqueous complex with HA directly, which enhanced arsenic mobilization from the mine tailings.

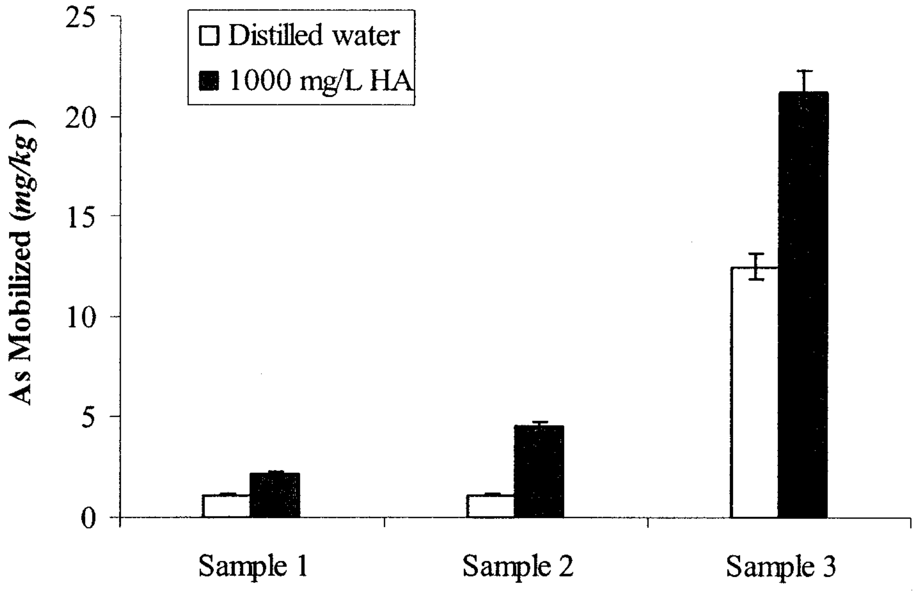


Figure 5-14. Arsenic mobilization by distilled water and 1000 mg/L HA at pH 7

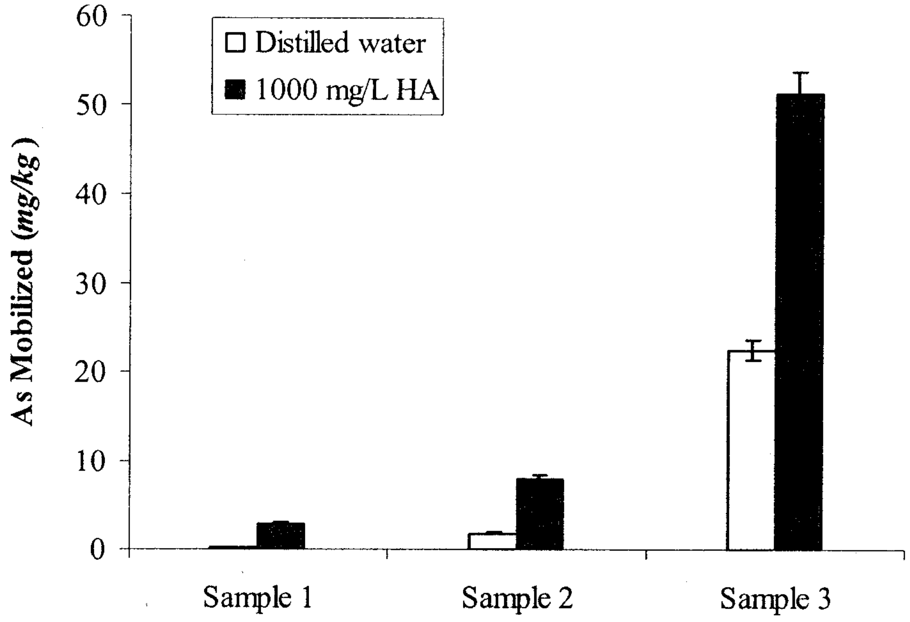


Figure 5-15. Arsenic mobilization by distilled water and 1000 mg/L HA at pH 9

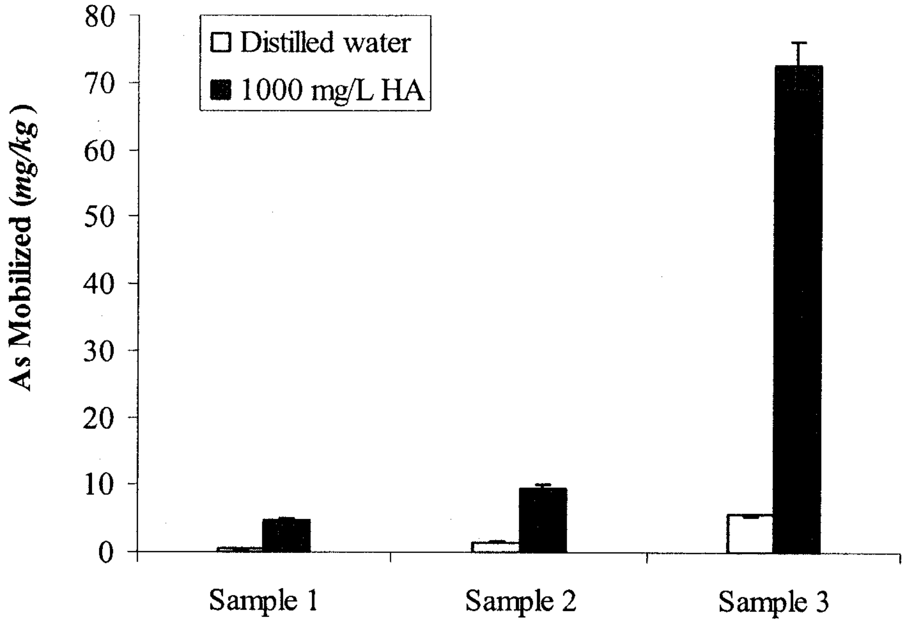


Figure 5-16. Arsenic mobilization by distilled water and 1000 mg/L HA at pH 11

The addition of organic matter might also incur the reductive dissolution of Fe hydroxides in the mine tailings, then releasing the sorbed arsenic into solution. This theory has been applied to explain the occurrence of high arsenic levels in the groundwater in Bangladesh (Nickson *et al.*, 2000; McArthur *et al.*, 2004). However, it might not be a dominant mechanism for arsenic mobilization in this study since the reductive dissolution processes mainly occur under anaerobic conditions.

5.3 Rhamnolipid

The effect of rhamnolipid on arsenic mobilization from the mine tailings was examined by varying the mass ratio of added rhamnolipid to the mine tailings (from 0.25 to 12 mg rhamnolipid/g mine tailings) and pH. Since rhamnolipid may precipitate at pH values below 6, all experiments were carried out at higher pH values (i.e., 7, 9 and 11). Rhamnolipid solutions without addition of the mine tailings at the tested pH values were used as blank controls. No arsenic was detected in these solutions.

5.3.1 Effect of mass ratio

The results of arsenic mobilization by rhamnolipid at different mass ratios (through changing rhamnolipid concentrations) and pH are illustrated in Figures 5-17 to 5-19. The mobilization of arsenic from the mine tailings by rhamnolipid increased with the mass ratio. Variation of pH also showed a significant effect on arsenic mobilization.

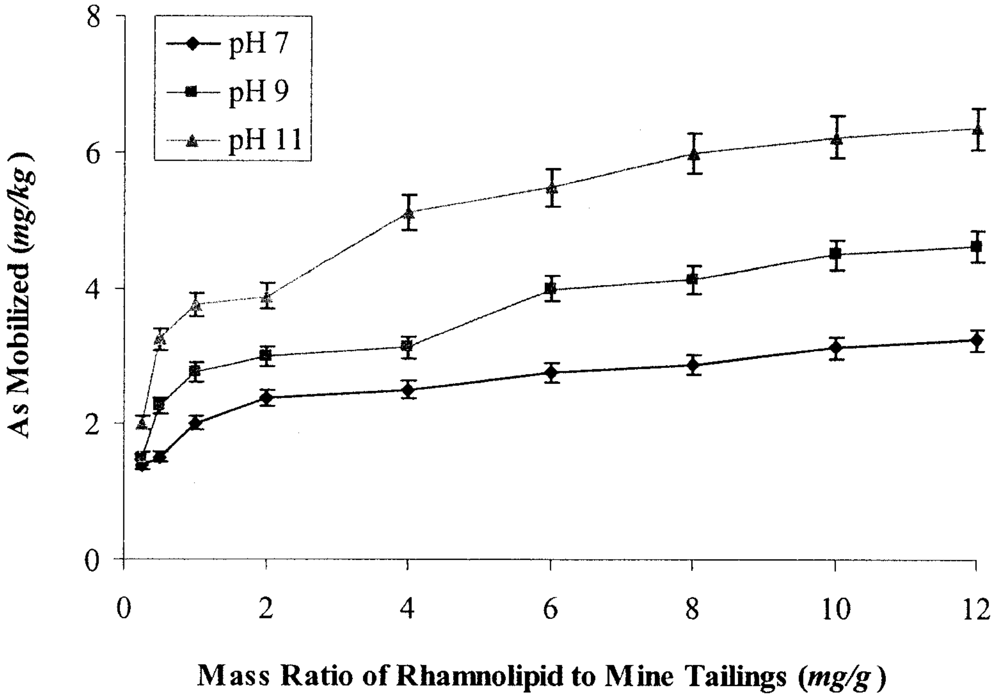


Figure 5-17. Arsenic mobilization from sample 1 in the presence of rhamnolipid

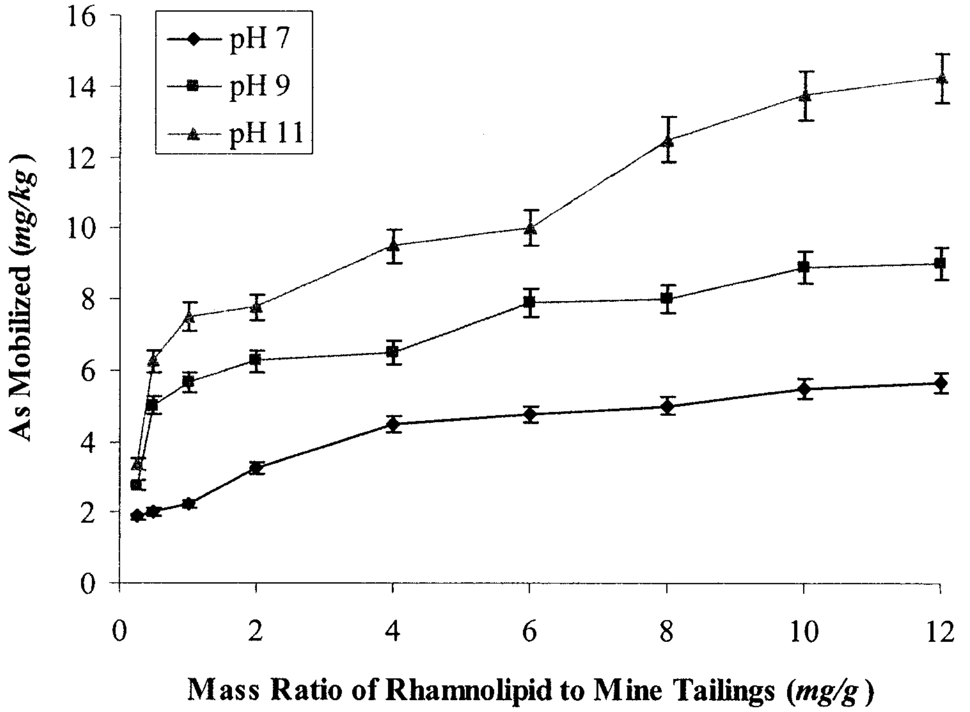


Figure 5-18. Arsenic mobilization from sample 2 in the presence of rhamnolipid

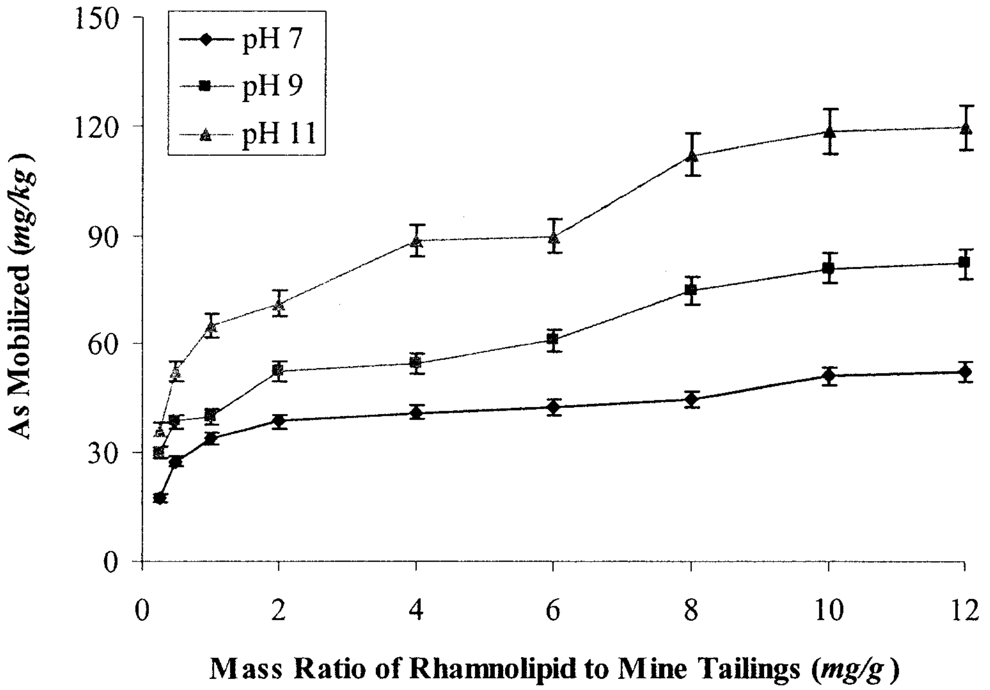


Figure 5-19. Arsenic mobilization from sample 3 in the presence of rhamnolipid

The mobilization of arsenic increased with increasing pH. With a mass ratio of 10 mg/g at pH 11, rhamnolipid mobilized 6 mg arsenic/kg from sample 1, 14 mg arsenic/kg from sample 2, and 119 mg arsenic/kg from sample 3, with corresponding concentration ratios (the ratio of arsenic concentration mobilized by rhamnolipid to that by distilled water at same pH value) of 13.64, 8.46, and 21.59, respectively. The observation that arsenic mobilization increased with increasing mass ratio indicated that rhamnolipid sorption to the mine tailings might be involved in the mobilization of arsenic from the mine tailings. It was similar to the observation in the batch tests with HA.

The mobilization of arsenic from the mine tailings increased with the concentration of rhamnolipid (expressed as the mass ratio of added rhamnolipid to mine tailings) and became relatively stable when the concentrations of the rhamnolipid solution were above 1000 mg/L (at a mass ratio of 10 mg rhamnolipid/g mine tailings). Doong *et al.* (1998) reported that the removal of metals by surfactants increased linearly with increasing surfactant concentration below CMC, and remained relatively constant above the CMC. The CMC of rhamnolipid is around 30 mg/L (Mulligan *et al.*, 2001b). High concentrations of biosurfactant required in this study may be due to the sorption of rhamnolipid to the mine tailings and the dilution and binding effects of the mine tailing particles (Rothmel *et al.*, 1998).

Similar to the observation with HA, increasing the mass of both rhamnolipid and mine tailings without changing the mass ratio (2 mg rhamnolipid/g mine tailings) increased the dissolved arsenic concentrations in the supernatants, but had no significant effect on arsenic mobilization efficiencies. However, increasing the mass ratio from 2 to 10 mg/g increased arsenic mobilization significantly.

5.3.2 Effect of pH

Figures 5-20 to 5-22 show the effect of pH on arsenic mobilization from the mine tailings in the presence of rhamnolipid (MR = mass ratio of the added rhamnolipid to the mine tailings, mg/g). It can be seen that the mobilization of arsenic by rhamnolipid increased dramatically with a pH increase.

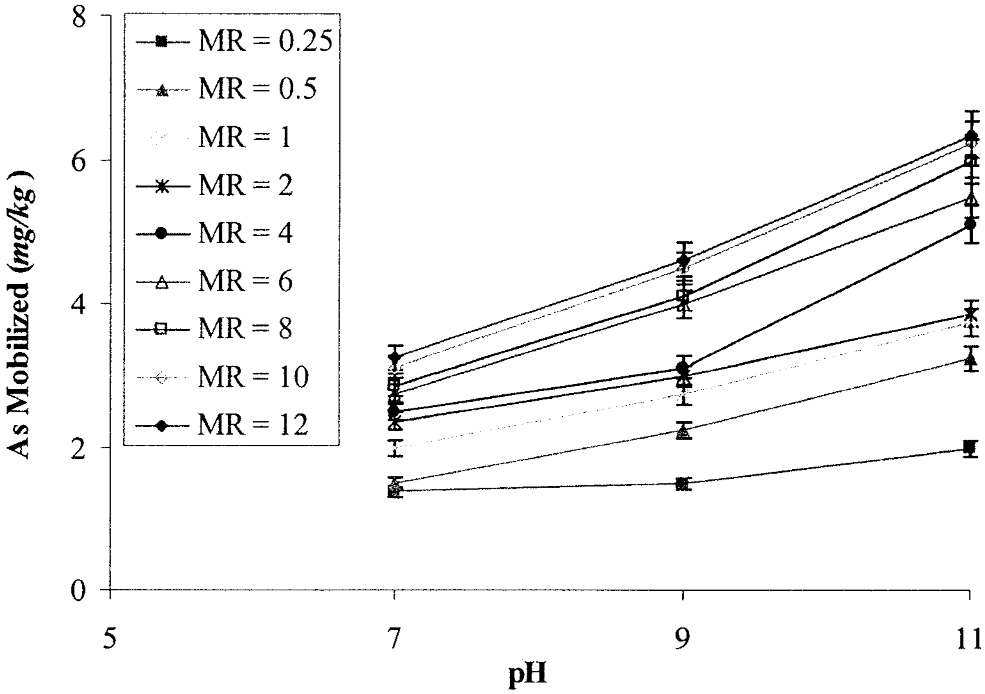


Figure 5-20. Effect of pH on arsenic mobilization from sample 1 by rhamnolipid

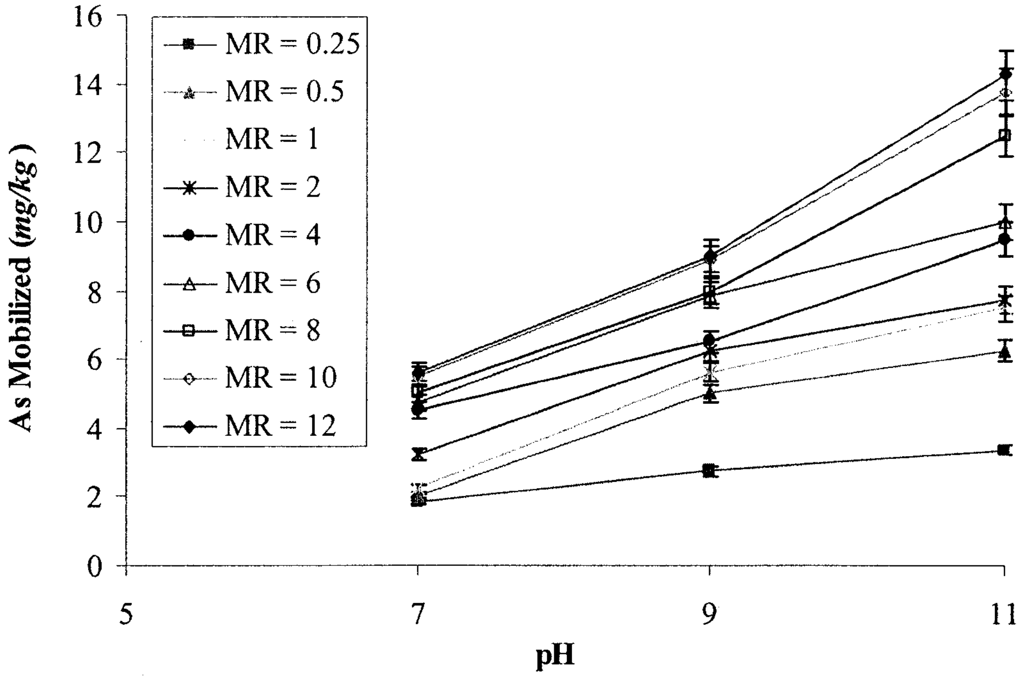


Figure 5-21. Effect of pH on arsenic mobilization from sample 2 by rhamnolipid

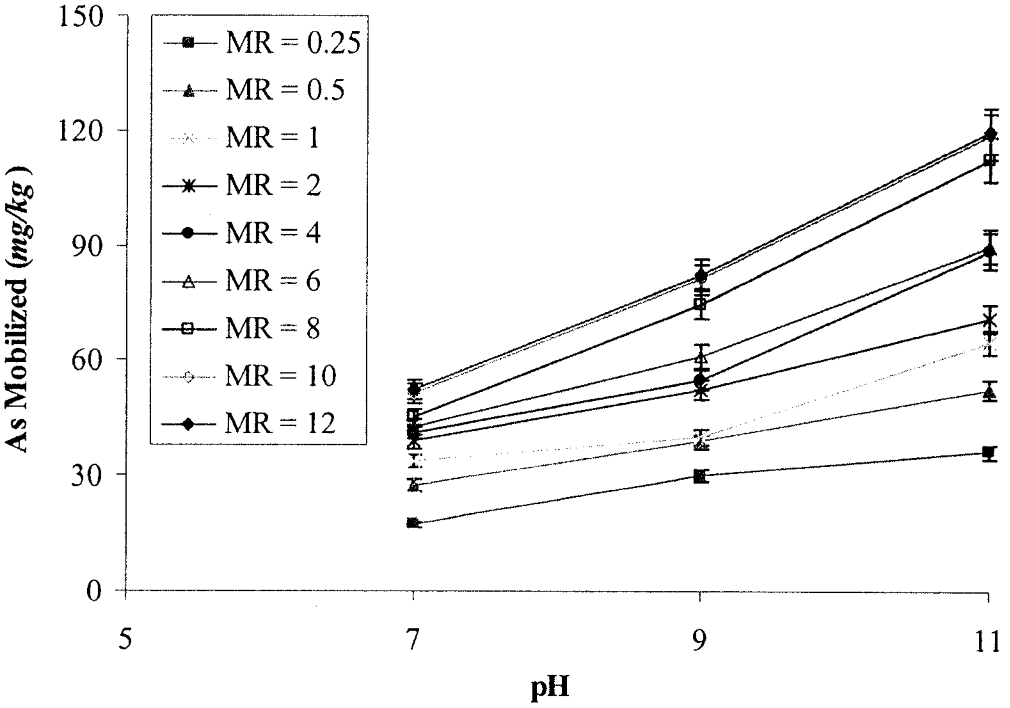


Figure 5-22. Effect of pH on arsenic mobilization from sample 3 by rhamnolipid

The mobilization of arsenic from the mine tailings in the presence of rhamnolipid increased with pH. This could be the result of a combination of the enhanced metal solubility and surfactant activity with the increase of pH (Radha, 1993; Wang and Mulligan, 2004b). Moreover, it has been shown that interfacial tension can be further reduced by increasing the solution pH (Lin *et al.*, 1987). Dissolution of organic matter in the mine tailings at high pH also released the associated arsenic and metals into solution. Similar to that of HA, the addition of rhamnolipid and increasing pH increased the negative zeta potential significantly (Figures 4-4 to 4-6), which produced a greater repulsive electrostatic interaction between arsenic and the mine tailing surfaces, thus enhancing arsenic mobilization.

5.3.3 Comparison with distilled water and HA

Rhamnolipid was more efficient to mobilize arsenic from the mine tailings at all the tested pH values than distilled water (up to 22-fold) and HA (up to 3-fold) (Figures 5-23 to 5-25). Rhamnolipid might enhance arsenic mobilization from the mine tailings by reducing the interfacial tension between arsenic and the mine tailings, thus mobilizing the weakly bound arsenic from the mine tailings. Formation of more soluble complexes or micelles might also contribute to the higher arsenic mobilization, compared to that by distilled water and HA.

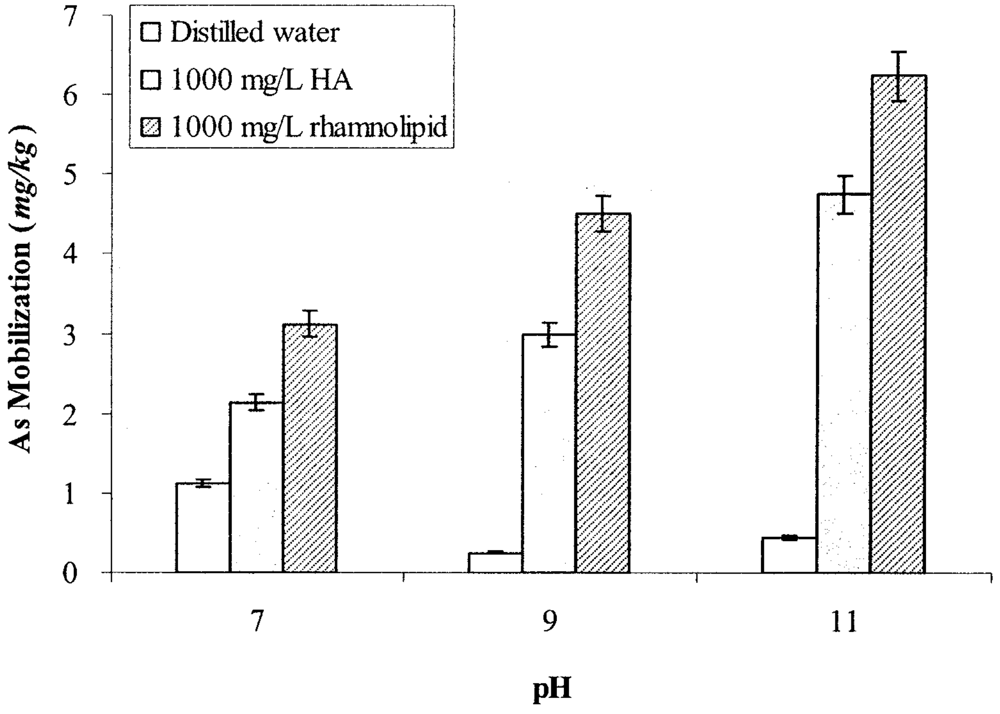


Figure 5-23. Comparison of arsenic mobilization from sample 1

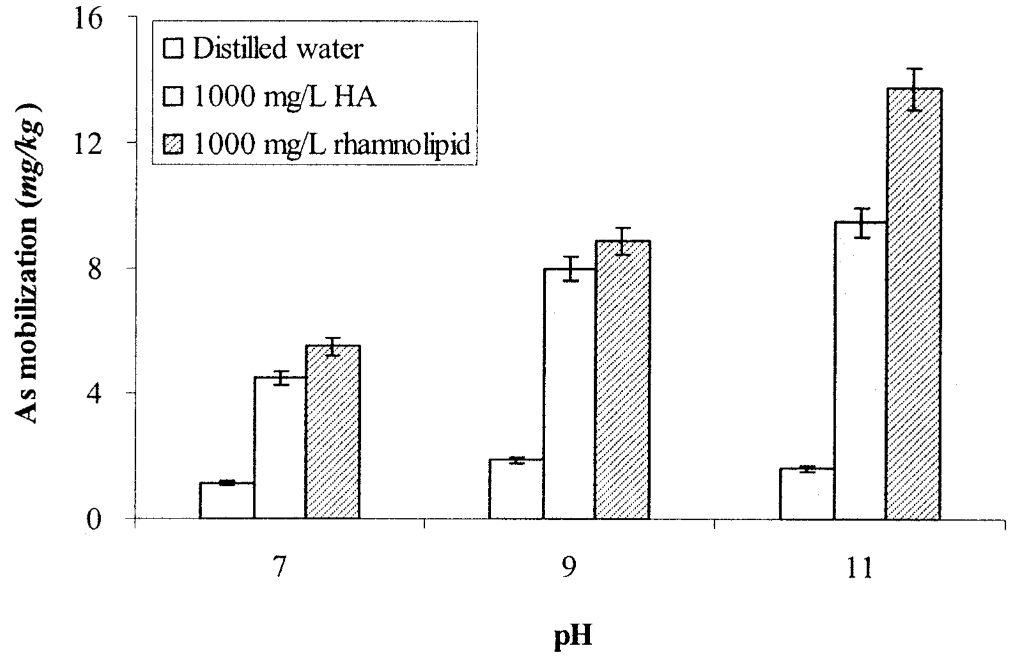


Figure 5-24. Comparison of arsenic mobilization from sample 2

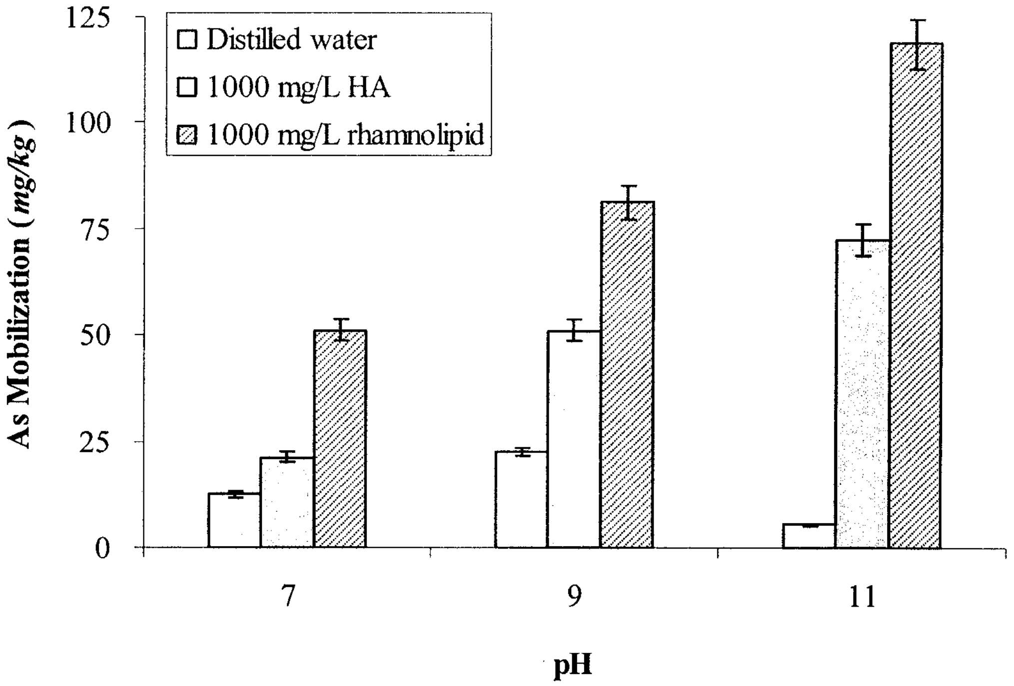


Figure 5-25. Comparison of arsenic mobilization from sample 3

Rhamnolipid might also enhance arsenic mobilization through anion exchange (Nivas *et al.*, 1996). The negatively charged surfactant would replace the negatively charged arsenic anions adsorbed onto the mine tailing surface. Furthermore, similar to that of HA, the addition of rhamnolipid had been shown to be able to increase the negative zeta potential significantly (Figures 4-4 to 4-6), which would produce a greater repulsive interaction, thus preventing the re-adsorption of arsenic to the mine tailings. Moreover, the wettability of the mine tailings could potentially be improved by the rhamnolipid, leading to enhanced arsenic mobilization (Chowdiah *et al.*, 1998).

It has been established that rhamnolipid may mobilize metals by lowering the interfacial tension and forming micelles at concentration above CMC (Mulligan, 2005). Metals might be adsorbed to rhamnolipid first, and the adsorbed metal might then work as a bridge to bind the dissolved arsenic anions, forming arsenic-metal-rhamnolipid complexes or micelles (Figure 5-26). The incorporation of arsenic into the complexes or micelles then prevented the metal and arsenic from re-adsorbing to the mine tailings. Also the formation of micelles prevented the formation of metal-arsenic precipitation, thus enhancing the mobilization of arsenic. The existence of the complexes might be, or at least partially, verified by the co-release of metals and arsenic by rhamnolipid from mine tailings. However, further efforts are required to verify the existence and to determine the structure of the arsenic-metal-rhamnolipid complexes or micelles.

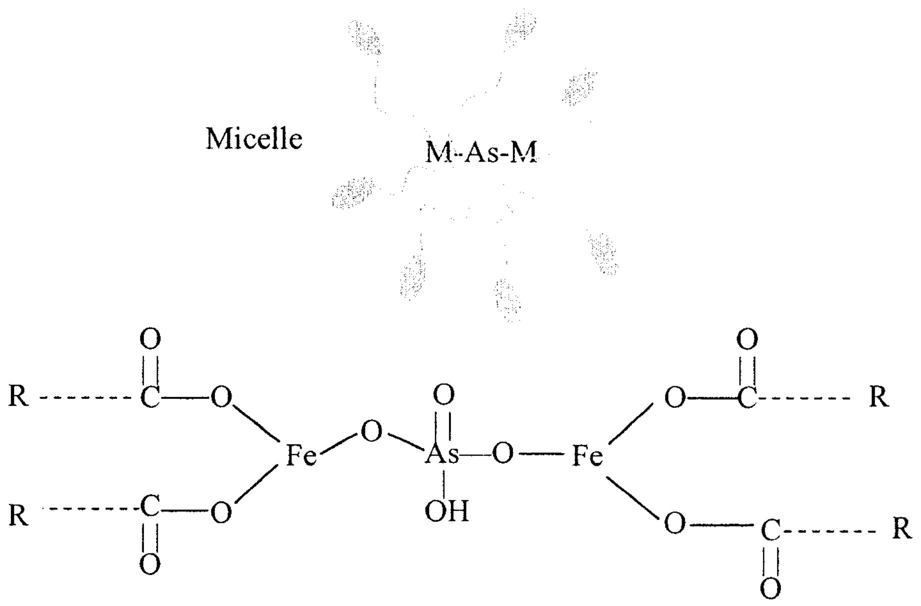


Figure 5-26. Retention of arsenic within surfactant micelles

(M: metal cation; R: rhamnolipid)

Compared to HA, rhamnolipid is characterized by the capacity of lowering the interfacial tension and forming micelles (Johnson and John, 1999). The surface tension of rhamnolipid was estimated to be around 26 mN/m (Mulligan *et al.*, 2001b), whereas that of HA was generally above 65 mN/m (Sierra *et al.*, 2005). Moreover, the formed micelles usually had a higher solubility than the complexes formed between arsenic or metal and HA. Therefore, rhamnolipid worked better than HA to improve the mobilization of arsenic from the mine tailings. Although it has been proposed that HA can form micelle-like aggregates, the aggregates are formed mainly under acidic conditions, and the hydrophobic regions formed will disperse under basic conditions (Sutton and Sposito, 2005).

5.4 Effect of reaction time

The effect of reaction time on arsenic mobilization from the mine tailings was examined with distilled water and HA at pH 3 and 11, and rhamnolipid at pH 11. The equilibrium state is reached when there was no significant effect of reaction time on the dissolved arsenic concentration. The concentrations of rhamnolipid and HA were both 1000 mg/L.

The change of dissolved arsenic concentrations with reaction time by distilled water and HA under acidic conditions (pH 3) is illustrated in Figures 5-27 to 5-29. Under acidic conditions (pH 3), the equilibrium state of the distilled water-mine tailings systems was reached after about 12 to 24 hour reaction. However, for the HA-mine tailings systems, a longer reaction time, more than 48 hours, was required.

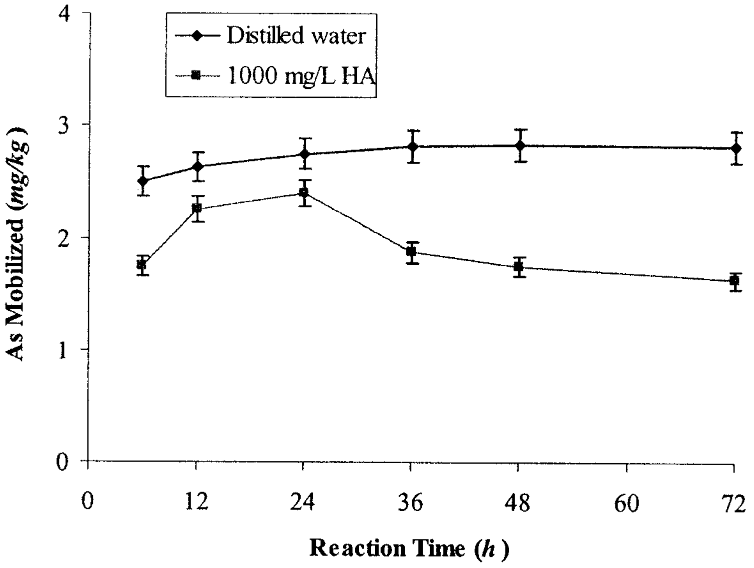


Figure 5-27. Effect of reaction time on arsenic mobilization from the mine tailing sample 1 at pH 3

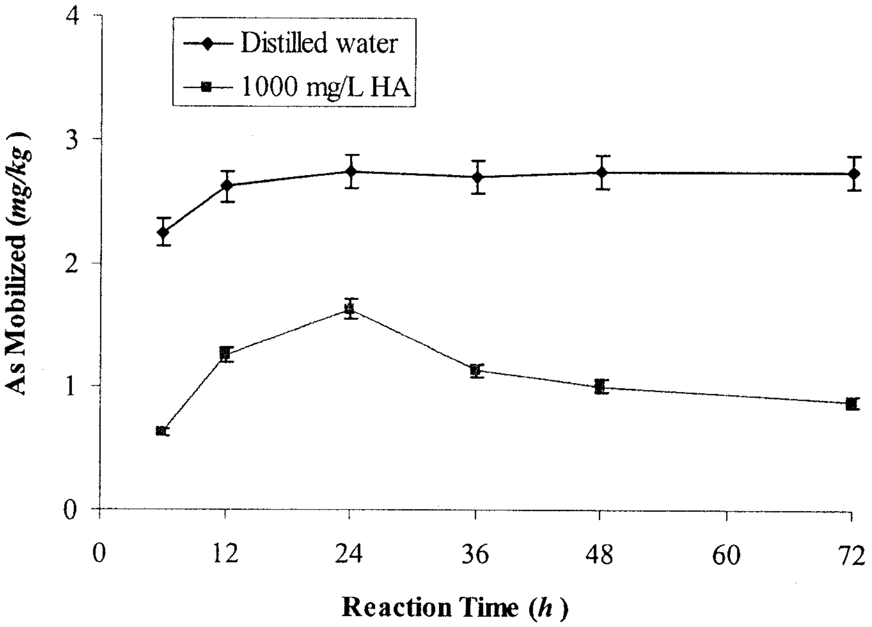


Figure 5-28. Effect of reaction time on arsenic mobilization from the mine tailing sample 2 at pH 3

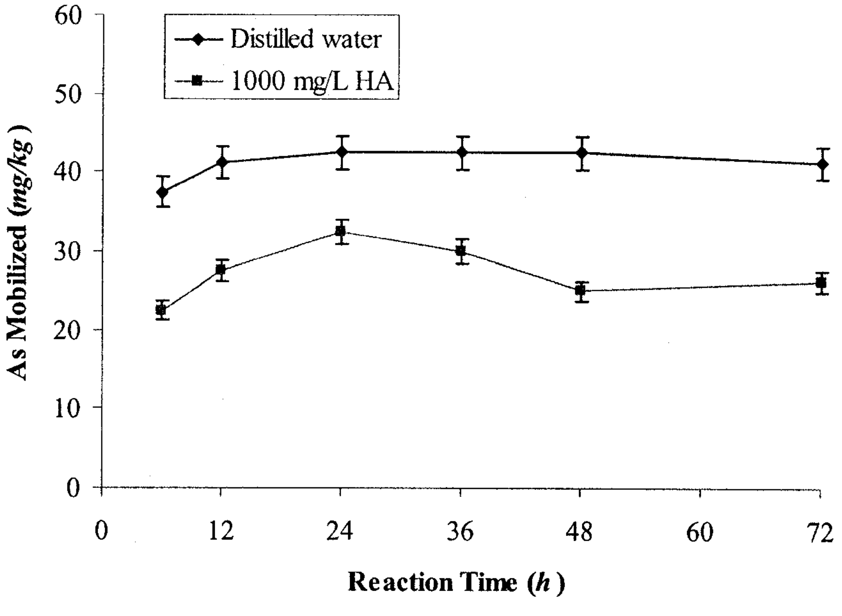


Figure 5-29. Effect of reaction time on arsenic mobilization from the mine tailing sample 3 at pH 3

Under acidic conditions (pH 3), it was observed that the dissolved arsenic concentrations in the HA-mine tailing systems increased with reaction time to 24 hours, and then decreased with reaction time and reached equilibrium after 48 hours or longer (Figures 5-27 to 5-29). This might indicate that the mobilization of arsenic from the mine tailings by HA might involve several intermediate reaction steps.

Ideally, it may be simplified as a two-phase process. The first phase involved the desorption of arsenic from the mine tailings by HA through ligand exchange or competition for active adsorption sites. In the following phase, the dissolved arsenic anions might be re-adsorbed onto the adsorbed HA on the mine tailings surface or to the remaining mine tailing surface. Correspondingly, the desorption rate of arsenic from the mine tailings increased with reaction time and then decreased, and the resorption rate of arsenic to the mine tailings or other solid phases increased with time gradually, until an equilibrium state was reached (Figure 5-30). Furthermore, the arsenic anions might adsorb to HA first and then to the remaining mineral surfaces of the mine tailings. Saada *et al.* (2003) suggested that the adsorption of As(V) anions to kaolinite-HA complexes occurred first on the HA sites and then on the remaining kaolinite sites once the HA sites were saturated.

The change of dissolved arsenic concentrations by distilled water, HA and rhamnolipid with reaction time under alkaline conditions (pH 11) is illustrated in Figures 5-31 to 5-33. The equilibration time was between 12 to 24 hours.

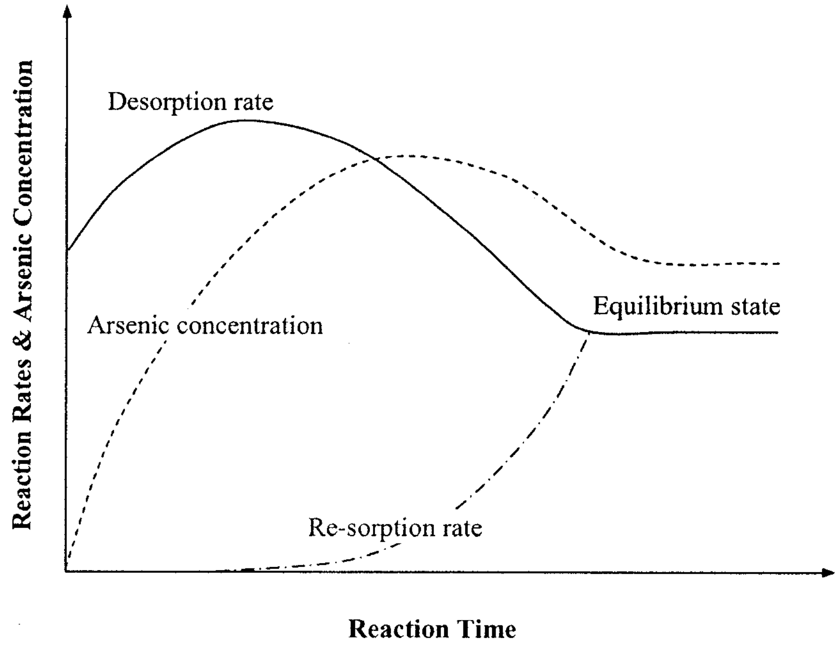


Figure 5-30. Illustration of the change in reaction rates and arsenic concentration with reaction time in the HA-mine tailings system at pH 3

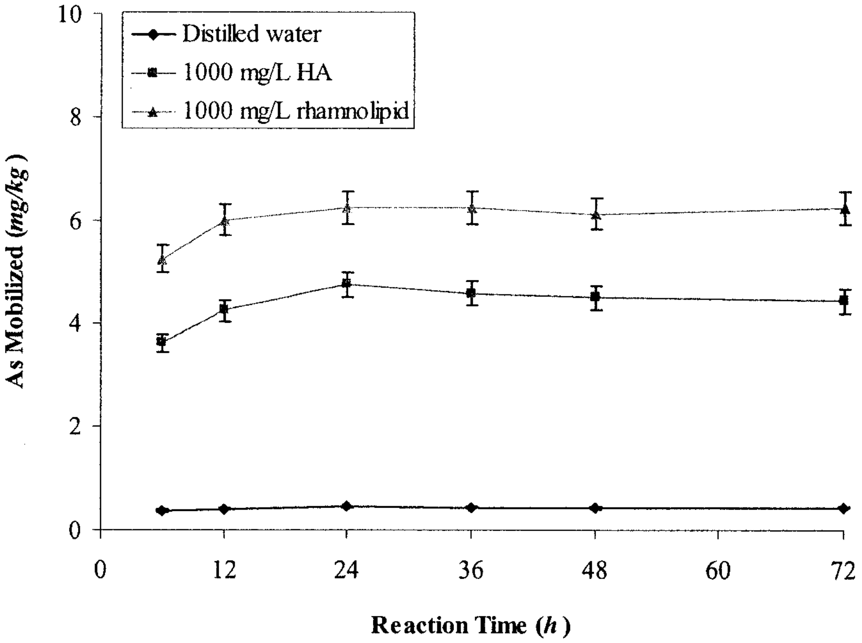


Figure 5-31. Effect of reaction time on arsenic mobilization from the mine tailing sample 1 at pH 11

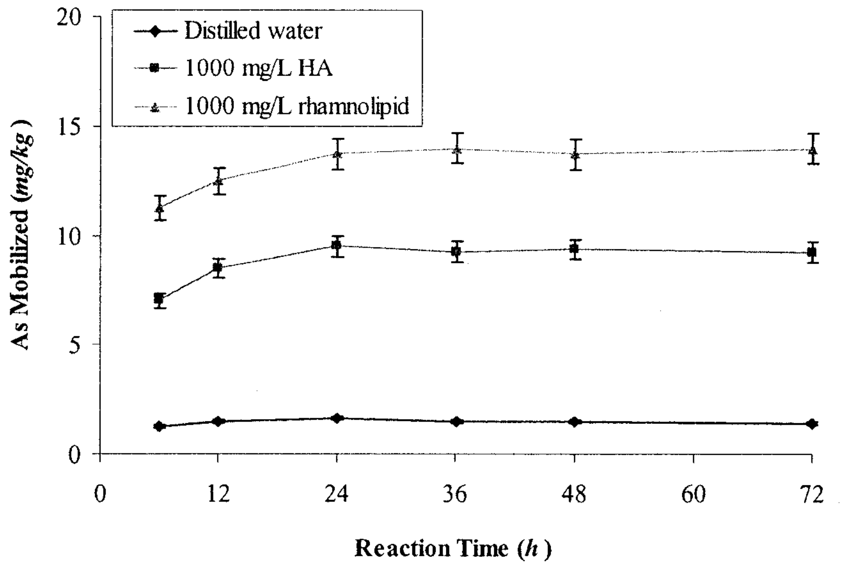


Figure 5-32. Effect of reaction time on arsenic mobilization from the mine tailing sample 2 at pH 11

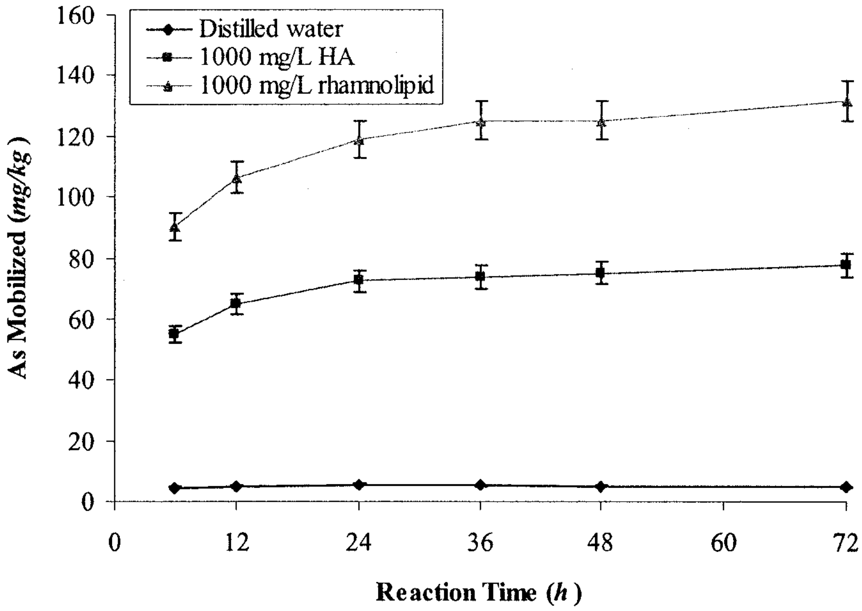


Figure 5-33. Effect of reaction time on arsenic mobilization from the mine tailing sample 3 at pH 11

5.5 Selective sequential extraction

A six-step SSE procedure was used to investigate the fractional distribution of arsenic in the mine tailings before and after washing with HA and rhamnolipid at a mass ratio of 10 mg/g and a pH of 11. Each step targeted a specific solid phase associated with arsenic and could provide useful information on relative liability. The arsenic fractions in the mine tailings before and after washing were compared to determine the most affected fractions.

5.5.1 Arsenic fractions before washing

The arsenic fractions in the mine tailings determined by the SSE procedure are illustrated in Figure 5-34. As shown in Figure 5-34, for all three samples, arsenic was mainly extracted in the fractions associated with the oxides and residual, followed by those associated with the organic matter and sulphide fractions. Water soluble arsenic levels were quite low, accounting only for 0.4% to 1.3% of the total arsenic contents in the mine tailings (Figure 5-34).

The exchangeable arsenic was below 1.0% of the total arsenic contents in the samples (Figure 5-34). Exchangeable arsenic is usually non-specifically sorbed by electrostatic attraction with the amphoteric surfaces of the amorphous compounds present, and also with broken clay edge surfaces (Yong *et al.*, 1992). The arsenic can become mobile under conditions where electrostatic forces of the system alter or where anion exchange reactions occur.

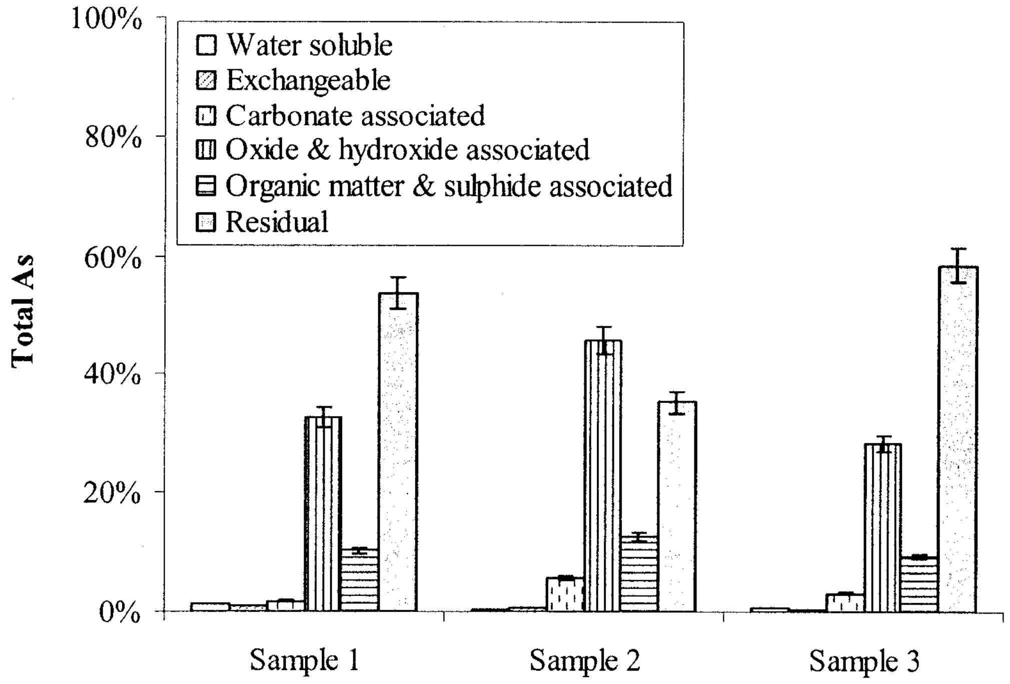


Figure 5-34. Arsenic fractions in the mine tailings before washing

As shown in Figure 5-34, arsenic associated with carbonates accounted for 1.8% to 5.7% of the total arsenic in the three mine tailings, while arsenic associated with the oxides and hydroxides in the mine tailings are quite high, which made up to 28.4% to 45.7% of the total arsenic contents. The oxide and hydroxide associated arsenic are related to the detrital metals. It is the result of ligand exchange of arsenic oxyanions on the mineral surfaces and diffusion of arsenic into the minerals (Yong *et al.*, 1992). Arsenic associated in this fraction is less mobile. Release of arsenic from this fraction would require diffusion of the arsenic out of the mineral structures and/or dissolution of the minerals which would subsequently release the sorbed arsenic to solution. The arsenic in this fraction can be potentially changed to be mobile or bioavailable, depending on the environmental conditions, such as acidification or weathering. This was consistent with the observation in the batch tests that arsenic was more mobile under acidic conditions (pH 3) without organic addition (Figure 5-1).

Arsenic in the oxidable fraction associated to organic matter and sulphide made up around 10% of the total arsenic in all the three tailings. It indicated that the arsenic in the mine tailings might be combined with sulfur to a significant extent. This was in agreement with the XRD and SEM-DES observations. This fraction is fairly stable, but the associated arsenic may be released once the organic matter is decomposed over time. Dissociation of the organic matter at high pH may also release the associated arsenic.

A significant proportion of arsenic was found in the residual fraction, which accounted for 53.9%, 35.4% and 58.7% of the total arsenic in the three mine tailings, respectively (Figure 6-1). This was consistent with the observation of SEM-EDS analyses that arsenic in sample 3 might be mainly associated with the clayey phases. The residual arsenic is assumed to represent arsenic hosted by silicate or sulfide minerals. Significant changes in subsurface chemistry over long periods would be required to allow this fraction of arsenic to become mobile. However, the residual arsenic represents a long-term source of contamination in the case of the weathering and erosion of the minerals.

Generally, the SSE results indicated that arsenic in the mine tailings was of relatively low mobility. The SSE results of the mine tailings before washing indicated that the arsenic was concentrated in the last three fractions. The sum of arsenic extracted in the last three fractions was more than 90% of the total arsenic contents in the samples. The water soluble and exchangeable fractions, however, were low. Similar observation was reported in the mine tailings (abandoned Au-Ag and Au-Ag-Pb-Zn mines) of South Korea (Kim *et al.*, 2003). It was also found that a high portion of the total arsenic present in historically polluted soils was extracted in the residual fractions only (Matera *et al.*, 2003). Shaw (2004) reported that more than 70% of the arsenic in a sediment was retained in the oxide and residual fractions. The low mobility of arsenic in the mine tailings could help reduce the bioavailability and then the toxicity of arsenic in the environment. However, as indicated in the batch tests, the arsenic might be mobilized when the environmental conditions changes.

5.5.2 Arsenic fractions after washing with HA and rhamnolipid

The mine tailings (2 g) washed with 1000 mg/L HA and rhamnolipid solutions at pH 11 were chosen for SSE analyses. The arsenic fractions in the mine tailings after washing with 1000 mg/L HA at pH 11 are illustrated in Figure 5-35. The arsenic fractions in the mine tailings after washing were compared with those before washing. The percentage of arsenic mobilized from each fraction is summarized in Table 5-1. After washing with 1000 mg/L HA solution at pH 11, the fractional distribution of arsenic in the mine tailings was not significantly changed. However, most of the arsenic in the water-soluble and exchangeable fractions was extracted. Arsenic was also extracted from the oxide, carbonate and organic fractions. The residual fractions were not significantly affected by HA washing (Table 5-1).

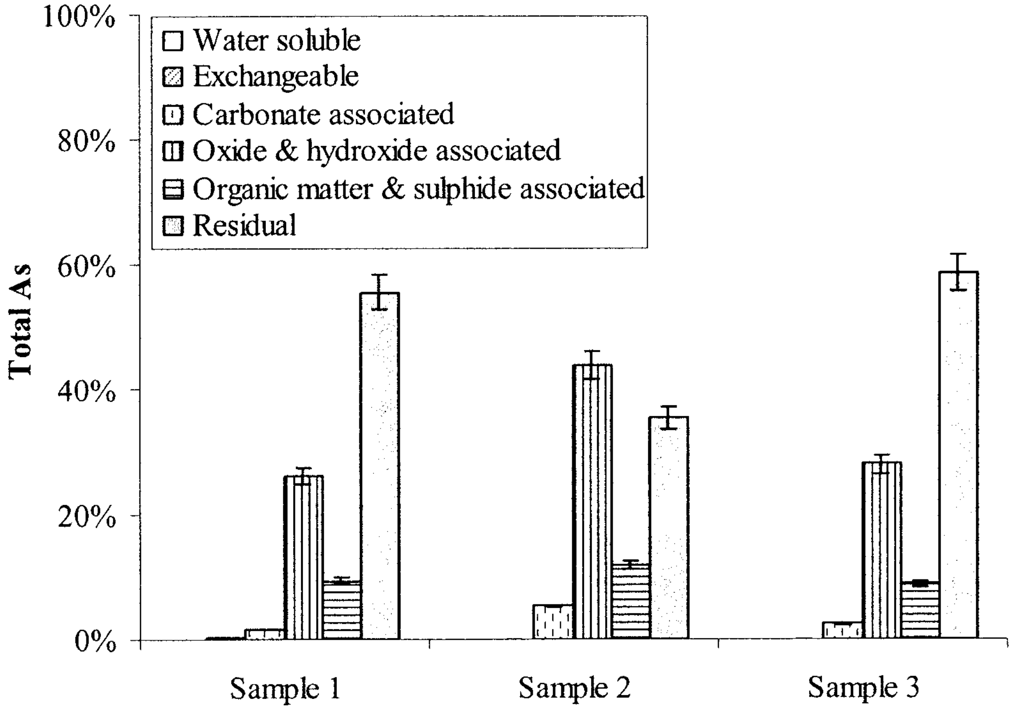


Figure 5-35. Arsenic fractions in the mine tailings after washing with 1000 mg/L HA at pH 11

The SSE results of arsenic fractions in the mine tailings washed with 1000 mg/L rhamnolipid at pH 11 are illustrated in Figure 5-36. After washing with rhamnolipid, the main arsenic-abundant fractions still were the oxide, organic and residual fractions. Arsenic in the water soluble and exchangeable fractions was completely extracted. Rhamnolipid was able to extract the arsenic associated with carbonate, oxide and organic fractions. However, the arsenic associated with the residual fractions remained almost un-changed (Table 5-1).

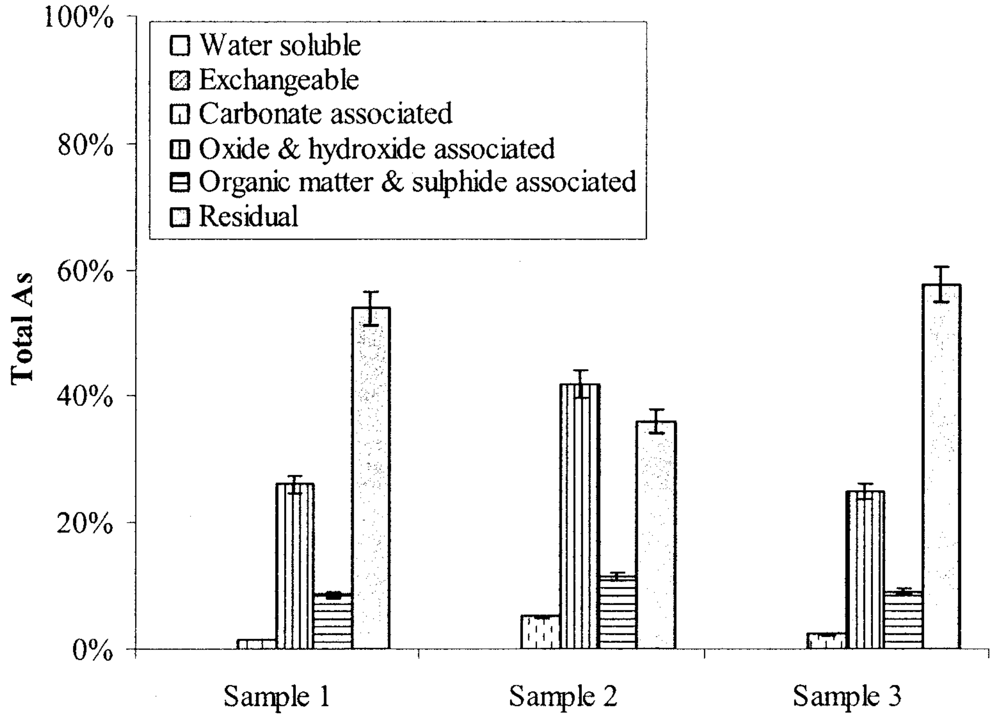


Figure 5-36. Arsenic fractions in the mine tailings after washing with 1000 mg/L rhamnolipid at pH 11

5.5.3 Fractions affected by washing

SSE studies were run to investigate arsenic distribution in the mine tailings among the water soluble, exchangeable, carbonate, oxides, organic and residual fractions, and to determine the most affected fractions during washing with HA and rhamnolipid. Arsenic was easily mobilized from the weakly bound and relatively more mobile fractions by rhamnolipid and HA. Almost all the arsenic in the water soluble and exchangeable fractions were mobilized by HA or rhamnolipid washing. Arsenic in the fraction associated with carbonates was also mobilized by rhamnolipid and HA, due to the competition effect between arsenic and the organic additives, especially, the lowering of interfacial tension in the case of rhamnolipid. Generally, rhamnolipid worked better than HA to mobilize arsenic in this fraction, consistent with the overall arsenic mobilization by HA and rhamnolipid.

Table 5-1. Percentage of arsenic mobilized from each fraction by washing

Fractions	1000 mg/L HA			1000 mg/L rhamnolipid		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Water soluble	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
Exchangeable	66.7%	76.5%	94.7%	100.0%	88.2%	100.0%
Carbonate	9.1%	6.7%	21.4%	18.2%	10.0%	24.3%
Oxide & hydroxide	20.0%	4.2%	1.6%	20.0%	8.3%	12.5%
Organic matter & sulphide	8.3%	5.3%	4.2%	16.7%	10.5%	2.5%
Residual	-3.1%	0.0%	0.0%	0.0%	-2.2%	1.6%

These results showed that HA and rhamnolipid were able to mobilize arsenic in the oxide and hydroxide associated fraction. Arsenic in this fraction may be mobilized through competition for adsorption sites and/or anion exchange between humate, rhamnolipid and arsenic, which might be the main mechanisms for the organic addition to mobilize arsenic from the mine tailings. Generally, the rhamnolipid performance was better than that of HA. The surface tension of rhamnolipid was estimated to be around 26 mN/m (Mulligan *et al.*, 2001b), whereas that of HA was generally above 65 mN/m (Sierra *et al.*, 2005). Johnson and John (1999) reported that surfactants could be more efficient than HA to depress the interfacial tension. The greater efficiency in lowering the interfacial tension enabled rhamnolipid to be more efficient in mobilizing arsenic and other metals. The mobilization of the metals, in turn, may further enhance arsenic mobilization by help incorporate it into aqueous complexes or micelles. It can be verified partially by the good correlation between the mobilization of arsenic and the metals (e.g., Fe, Cu, Pb and Zn).

As shown in Table 5-1, HA mobilized 4.2% to 8.3% of the arsenic in the fraction associated with organic matter and sulfate, while rhamnolipid mobilized 2.5% to 16.7% of the arsenic in this fraction. This was consistent with the previous SSE experiments, that rhamnolipid might able to mobilize metals (e.g. Cu) from the organic fraction (Mulligan *et al.*, 1999). Also, the mobilization of arsenic from this fraction might also be partially due to the dissolution of organic matter at the high pH value (pH 11), thus releasing the associated arsenic.

Arsenic in the residual fraction in the mine tailings was negligibly attacked by the organic additives. This could be expected, since arsenic in this fraction was of the most stable nature compared to that in other fractions. The negative percentage numbers in Table 5-1 might be due to the experimental errors and measurement variability or the limitations of the SSE methods itself. The determination of arsenic fractions in mine tailings or soils by SSE analyses is strongly dependent on the extractants and the extraction procedure applied (Gruebel et al. 1988; Yong and Mulligan, 2004). The extractability of any given extractant is a function of experimental factors such as extractant concentration, pH, temperature, interaction duration, mixing mode, particle size, matrix composition, and competing chemical reactions (Yong and Mulligan, 2004). Even a small modification of the sequential extraction procedure can result in significant variability of results among laboratories (Davidson et al., 1999).

5.6 LMWOAs

The mobilization of arsenic from the mine tailings by aspartic acid, cysteine, and succinic acid with a concentration of 1000 mg/L was studied and the results are shown in Figures 5-37 to 5-39. The testing pH was evaluated between 3 and 11. The concentration ratios of arsenic mobilization by the organic additives to that by distilled water are summarized in Table 5-2.

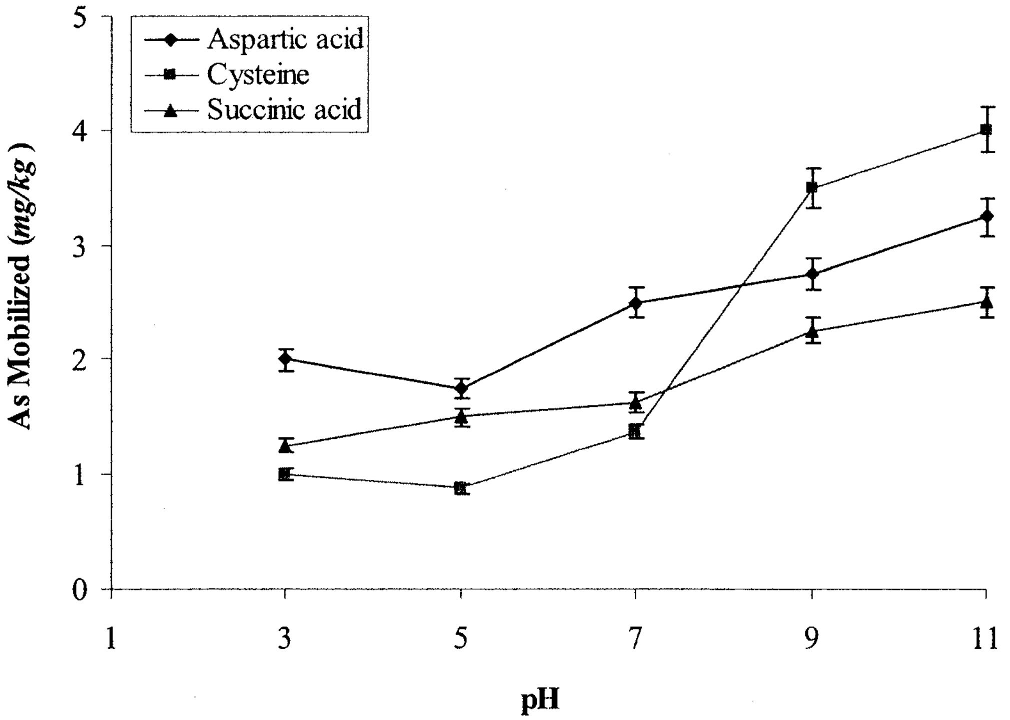


Figure 5-37. Arsenic mobilization from sample 1 by LMWOAs

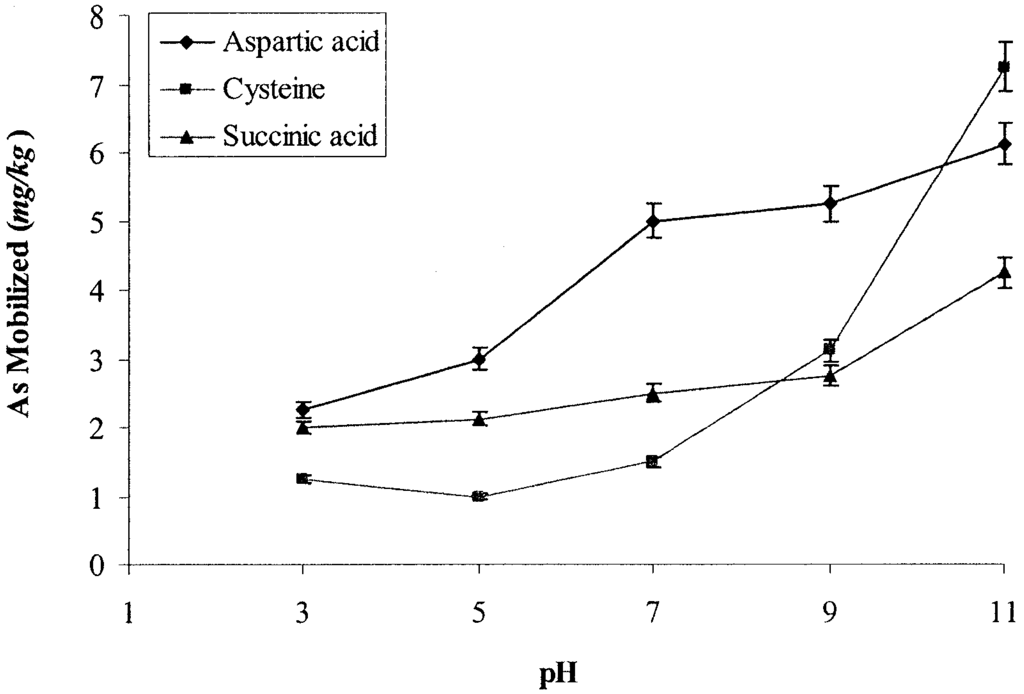


Figure 5-38. Arsenic mobilization from sample 2 by LMWOAs

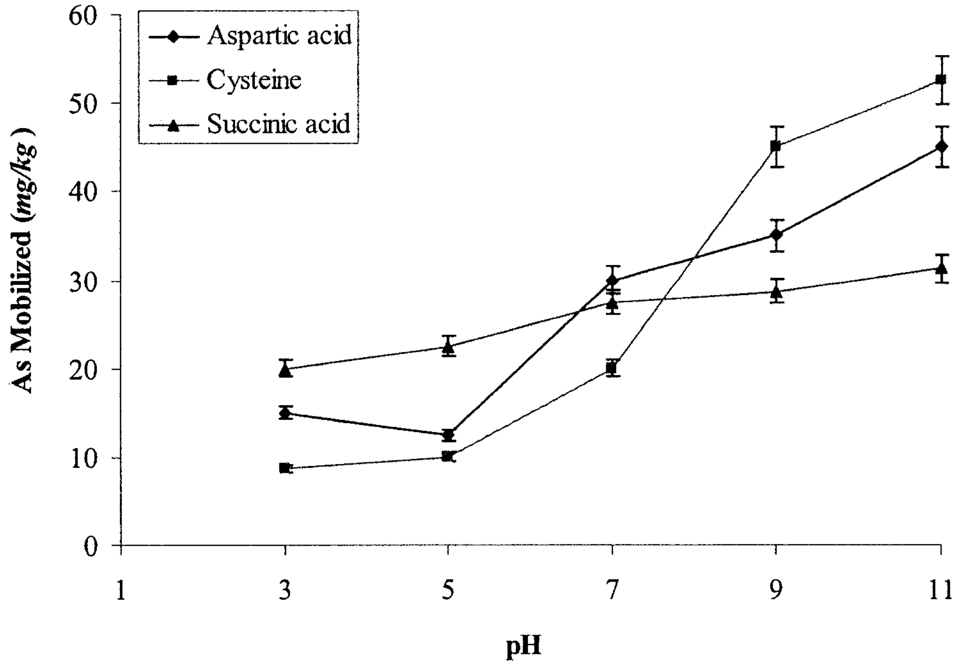


Figure 5-39. Arsenic mobilization from sample 3 by LMWOAs

Table 5-2. Concentration ratios of arsenic mobilization by organic additives to that of distilled water from mine tailings at different pH values

Organic addition	Sample 1					Sample 2					Sample 3				
	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11
Distilled water	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
HA[a]	0.87	3.73	1.91	12.00	10.36	0.59	4.80	4.00	4.27	5.85	0.76	2.91	1.70	2.28	13.18
Rhamnolipid[a]	---	---	2.78	18.00	13.64	---	---	4.89	4.73	8.46	---	---	4.10	3.61	21.59
Aspartic acid[a]	0.73	1.75	2.22	11.00	7.09	0.82	2.40	4.44	2.80	3.77	0.35	0.91	2.40	1.56	8.18
Cysteine[a]	0.36	0.88	1.22	14.00	8.73	0.45	0.80	1.33	1.67	4.46	0.21	0.73	1.60	2.00	9.55
Succinic acid[a]	0.45	1.50	1.44	9.00	5.45	0.73	1.70	2.22	1.47	2.62	0.47	1.64	2.20	1.28	5.68

[a]: mass ratio of 10 mg organic additive/g mine tailings

The pH showed a significant effect on arsenic mobilization by the organic acids. Generally, arsenic mobilization increased with pH. At pH 3, the addition of the organic acids decreased arsenic mobilization from the mine tailings. The concentration ratios varied from 0.21 to 0.82. At pH above 7, the addition of the LMWOAs enhanced the mobilization of arsenic. The highest arsenic mobilization by the LMWOAs was obtained at pH 11. The concentration ratios varied from 2.62 to 9.55. Rhamnolipid and HA were observed to be more efficient for mobilizing arsenic than the LMWOAs at pH 11.

5.7 Metal mobilization

It has been established that arsenic mobility in soils is mostly controlled by surface complexation reaction with the Fe (hydro)oxides (Wang and Mulligan, 2006c). Besides Fe, high concentrations of Cu, Pb and Zn were also detected in the mine tailings. Therefore, the co-mobilization of Fe, Cu, Pb and Zn was investigated in this study to examine the correlation between the mobilization of arsenic and the metals (Figures 5-40 to 5-51). The concentration ratios of metal mobilization by the organic additives to that by distilled water are summarized in Tables 5-3 to 5-6. Generally, both the organic addition and pH showed significant effect on metal mobilization from the mine tailings. Metals were mobilized the most at pH 3 in the case of distilled water, but at pH 11 in the presence of all the organic additives.

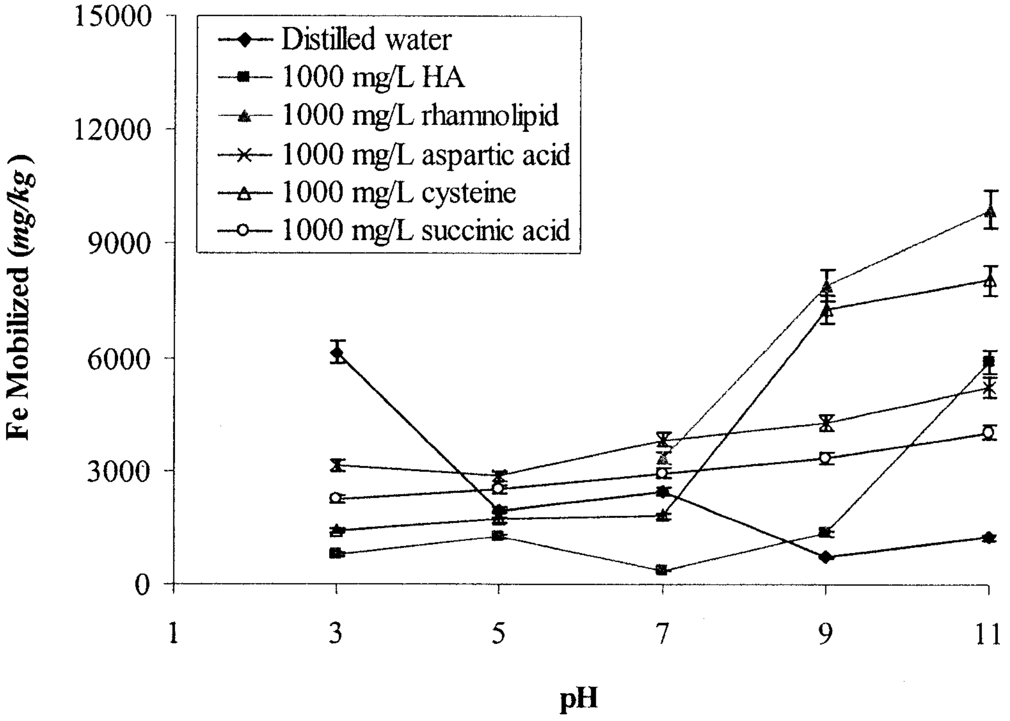


Figure 5-40. Fe mobilization from sample 1

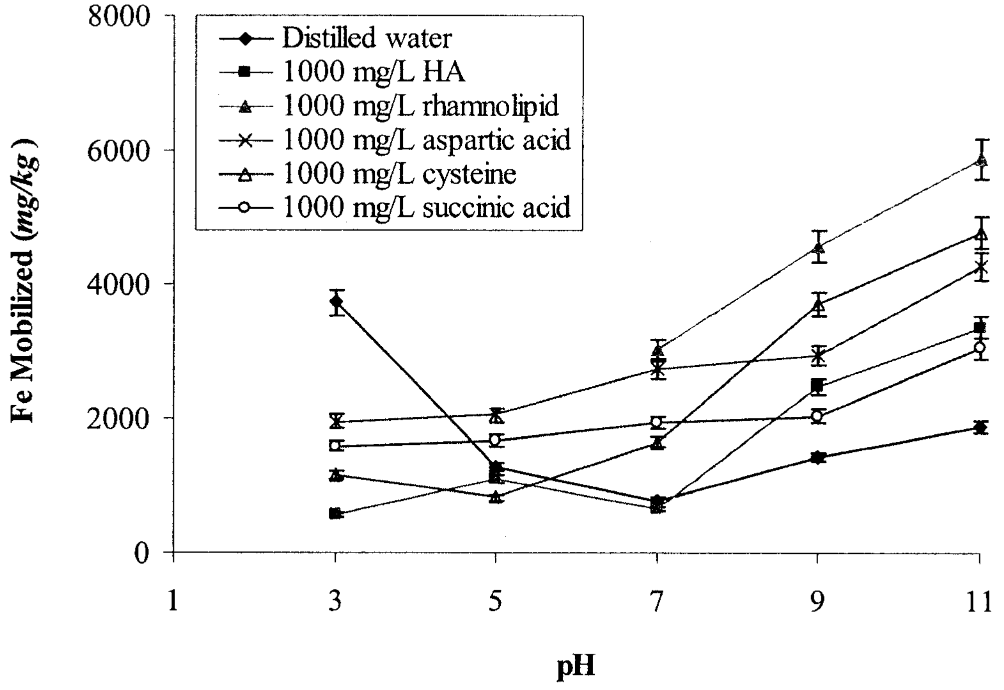


Figure 5-41. Fe mobilization from sample 2

Table 5-3. Ratios of concentrations of Fe mobilization by organic additives to that of distilled water from mine tailings at different pH values

Organic addition	Sample 1					Sample 2					Sample 3				
	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11
Distilled water	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
HA[a]	0.13	0.64	0.15	1.86	4.77	0.15	0.86	0.85	1.73	1.81	0.25	0.79	0.65	0.93	5.29
Rhamnolipid[a]	---	---	1.37	11.00	8.00	---	---	3.87	3.21	3.15	---	---	2.22	1.77	6.30
Aspartic acid[a]	0.51	1.46	1.56	5.97	4.23	0.52	1.59	3.49	2.07	2.29	0.37	0.62	1.12	1.86	4.37
Cysteine[a]	0.23	0.88	0.74	10.14	6.50	0.31	0.64	2.10	2.61	2.57	0.18	0.36	1.36	1.54	4.07
Succinic acid[a]	0.36	1.29	1.20	4.67	3.27	0.42	1.30	2.46	1.42	1.63	0.54	1.34	1.70	1.33	3.31

[a]: with a mass ratio of 10 mg organic additive/g mine tailings

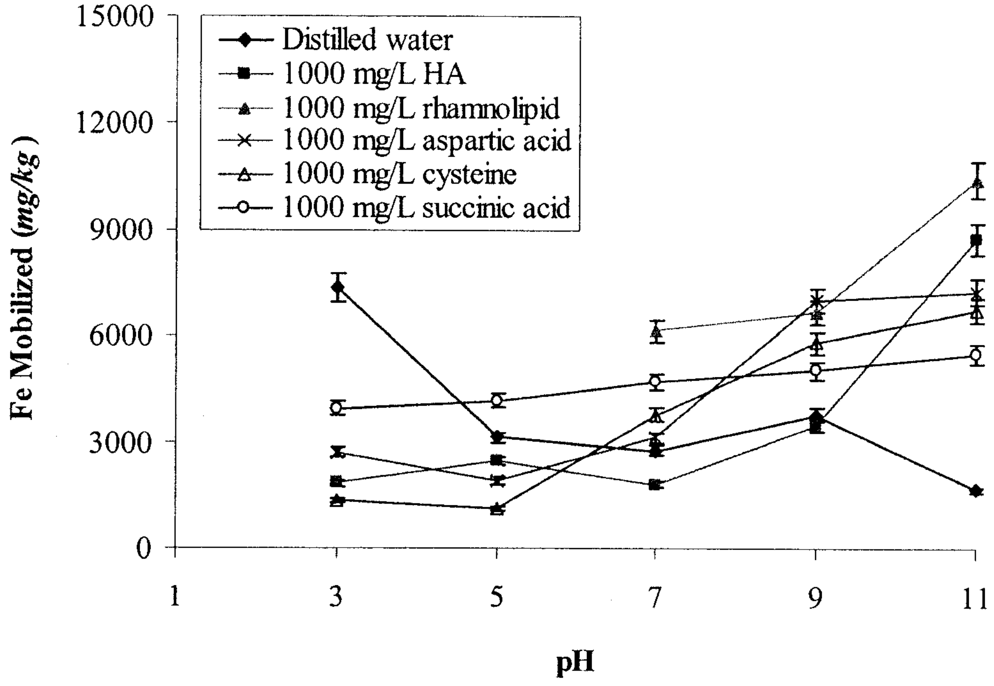


Figure 5-42. Fe mobilization from sample 3

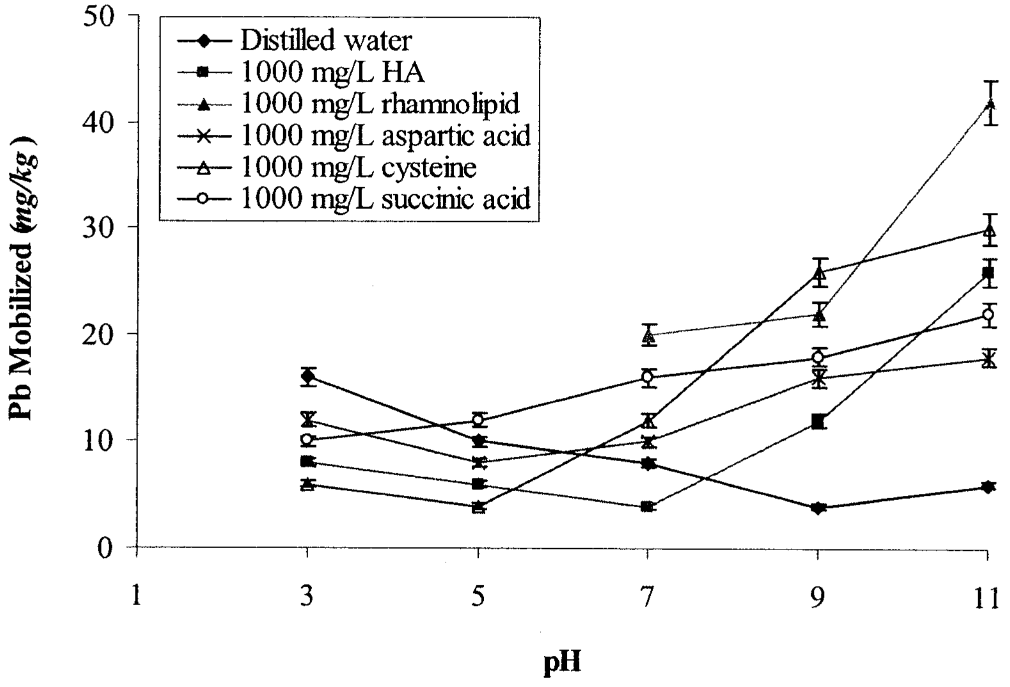


Figure 5-43. Pb mobilization from sample 1

Table 5-4. Ratios of concentrations of Pb mobilization by organic additives to that of distilled water from mine tailings at different pH values

Organic addition	Sample 1					Sample 2					Sample 3				
	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11
Distilled water	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
HA[a]	0.50	0.60	0.50	3.00	4.33	0.22	0.80	0.33	1.50	1.33	0.57	0.85	1.25	1.00	2.46
Rhamnolipid[a]	---	---	2.50	5.50	7.00	---	---	1.67	3.25	2.67	---	---	6.00	6.00	8.69
Aspartic acid[a]	0.75	0.80	1.25	4.00	3.00	0.56	1.20	2.67	2.25	1.83	0.43	1.00	3.50	3.92	6.38
Cysteine[a]	0.38	0.40	1.50	6.50	5.00	0.11	0.00	0.67	2.75	2.17	0.21	0.31	2.00	6.67	7.77
Succinic acid[a]	0.63	1.20	2.00	4.50	3.67	0.67	1.40	2.33	2.00	1.50	0.79	1.23	4.50	3.42	4.00

[a]: with a mass ratio of 10 mg organic additive/g mine tailings

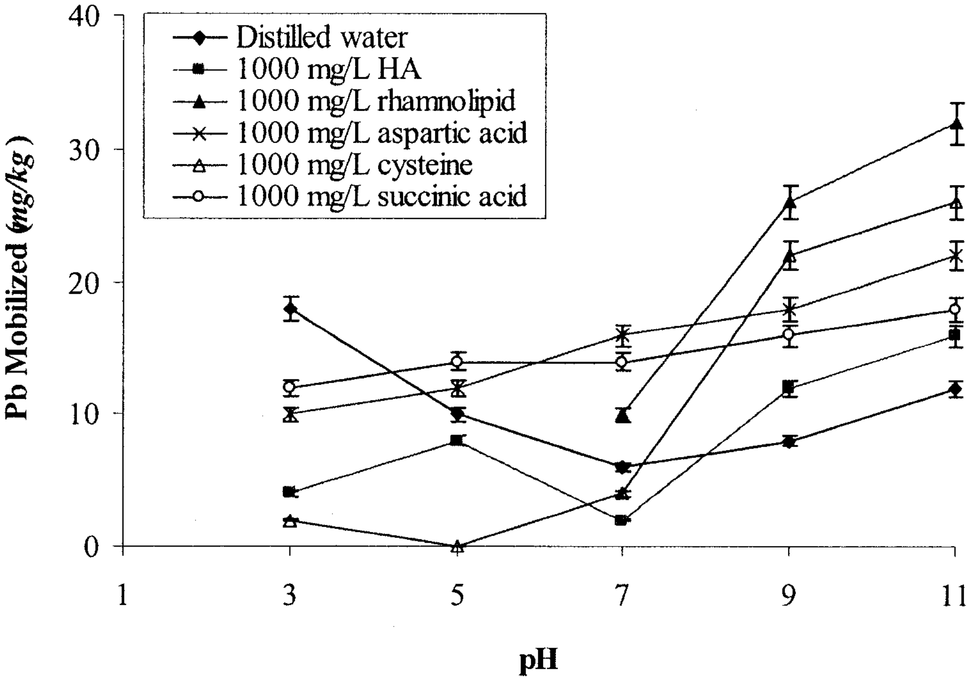


Figure 5-44. Pb mobilization from sample 2

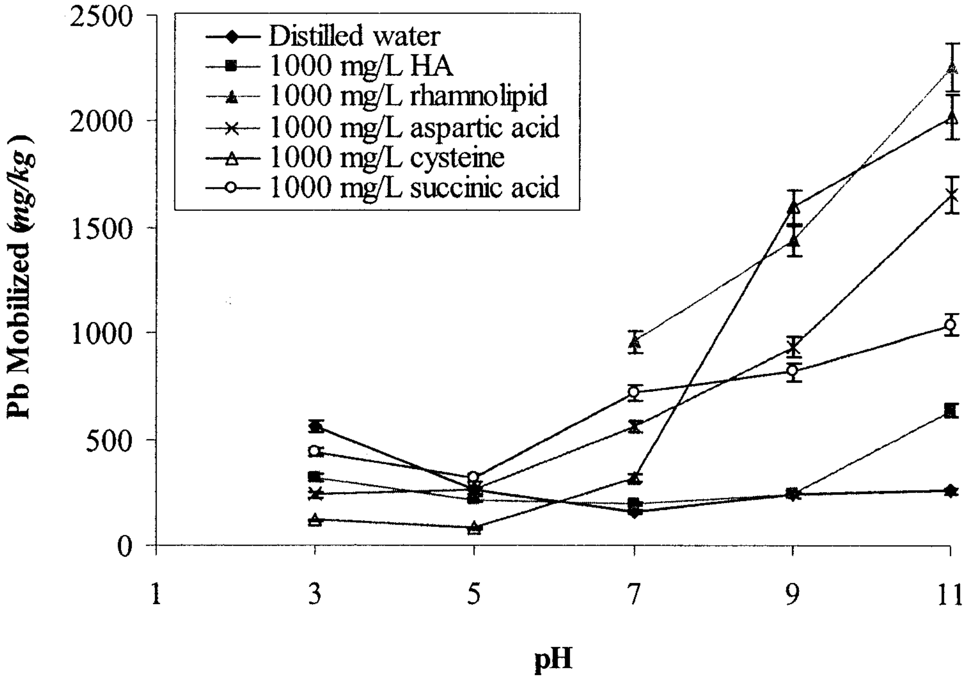


Figure 5-45. Pb mobilization from sample 3

Table 5-6. Ratios of concentrations of Cu mobilization by organic additives to that of by distilled water from mine tailings at different pH values

Organic addition	Sample 1					Sample 2					Sample 3				
	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11
Distilled water	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
HA[a]	0.00	1.50	2.00	3.00	3.50	0.50	0.83	0.60	1.71	2.00	0.31	0.43	1.20	1.43	3.13
Rhamnolipid[a]	---	---	3.00	8.00	5.00	---	---	3.20	6.43	6.63	---	---	2.60	2.86	3.63
Aspartic acid[a]	0.50	2.00	5.00	7.00	4.00	0.67	2.50	5.60	4.57	5.63	1.08	1.29	1.60	2.57	2.88
Cysteine[a]	0.00	0.00	0.00	4.00	2.50	0.08	0.17	0.40	1.43	4.50	0.15	0.14	0.60	2.00	2.38
Succinic acid[a]	0.00	0.50	1.00	2.00	2.00	1.25	2.00	2.00	2.14	3.25	0.69	1.14	2.20	1.71	1.75

[a]: with a mass ratio of 10 mg organic additive/g mine tailings

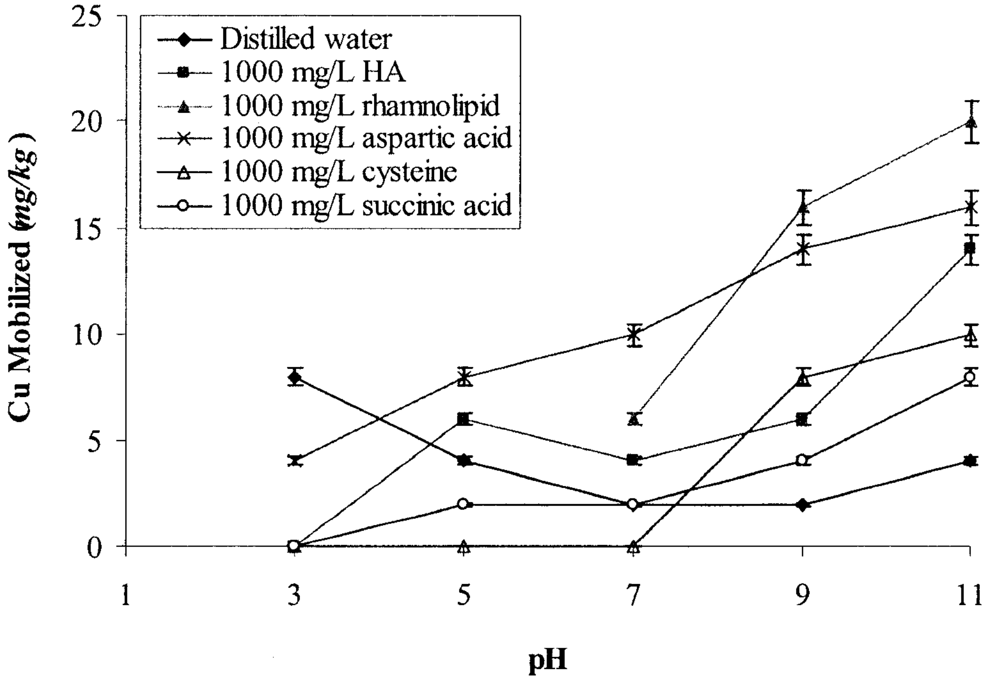


Figure 5-46. Cu mobilization from sample 1

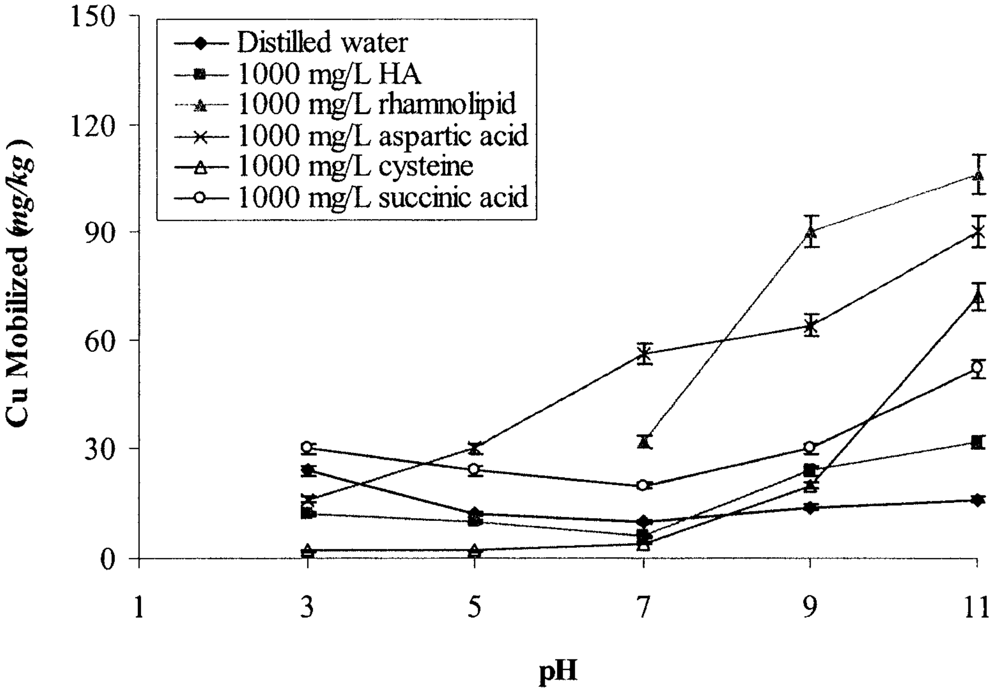


Figure 5-47. Cu mobilization from sample 2

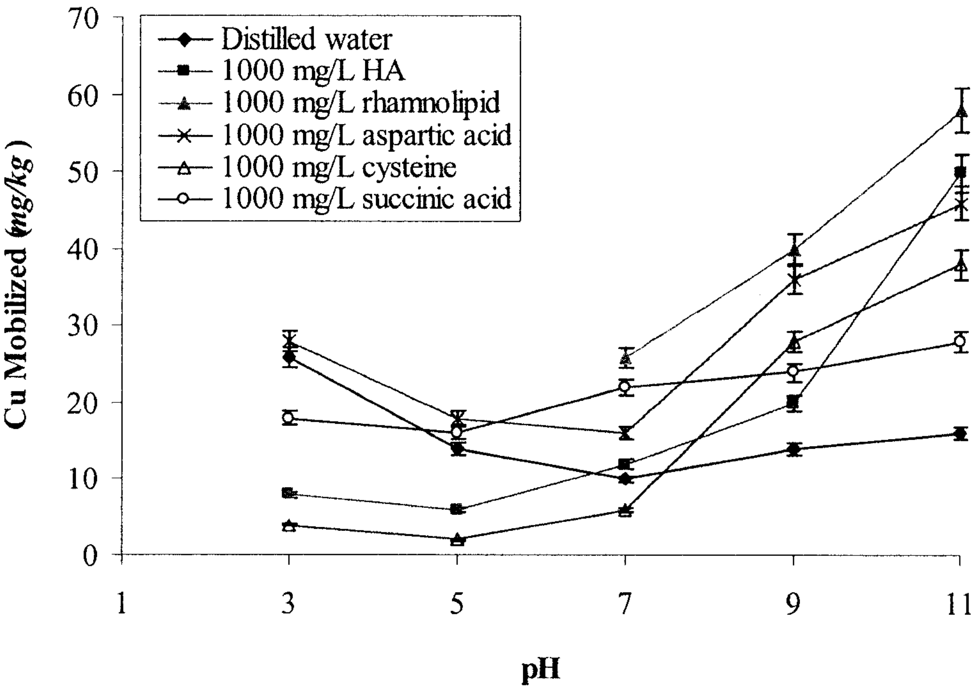


Figure 5-48. Cu mobilization from sample 3

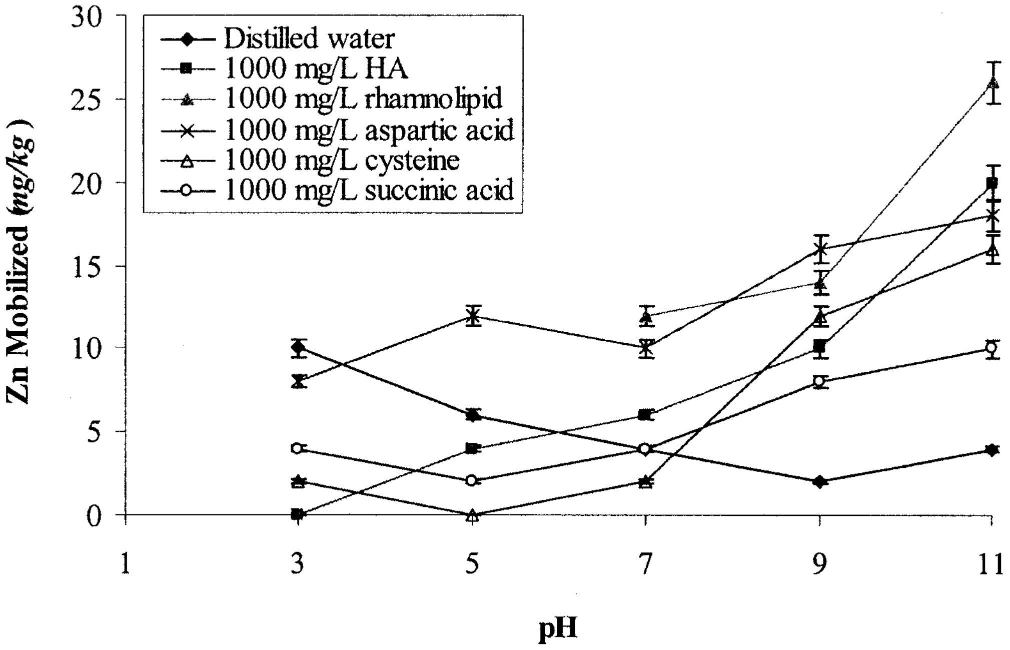


Figure 5-49. Zn mobilization from sample 1

Table 5-6. Ratios of concentrations of Zn mobilization by organic additives to that of distilled water from mine tailings at different pH values

Organic addition	Sample 1					Sample 2					Sample 3				
	3	5	7	9	11	3	5	7	9	11	3	5	7	9	11
Distilled water	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
HA[a]	0.00	0.67	1.50	5.00	3.33	0.34	0.94	1.31	3.88	8.39	0.44	0.75	0.86	1.57	3.54
Rhamnolipid[a]	---	---	3.00	7.00	4.33	---	---	6.00	5.12	11.65	---	---	2.71	2.96	4.46
Aspartic acid[a]	0.80	2.00	2.50	8.00	3.00	0.82	1.50	5.19	4.24	5.61	0.83	1.31	2.57	2.57	2.46
Cysteine[a]	0.20	0.00	0.50	6.00	2.67	0.16	0.24	2.13	6.60	8.96	0.56	0.84	1.52	2.74	2.88
Succinic acid[a]	0.40	0.33	1.00	4.00	1.67	0.74	1.26	2.81	3.16	4.13	0.68	1.41	2.43	2.30	2.15

[a]: with a mass ratio of 10 mg organic additive/g mine tailings

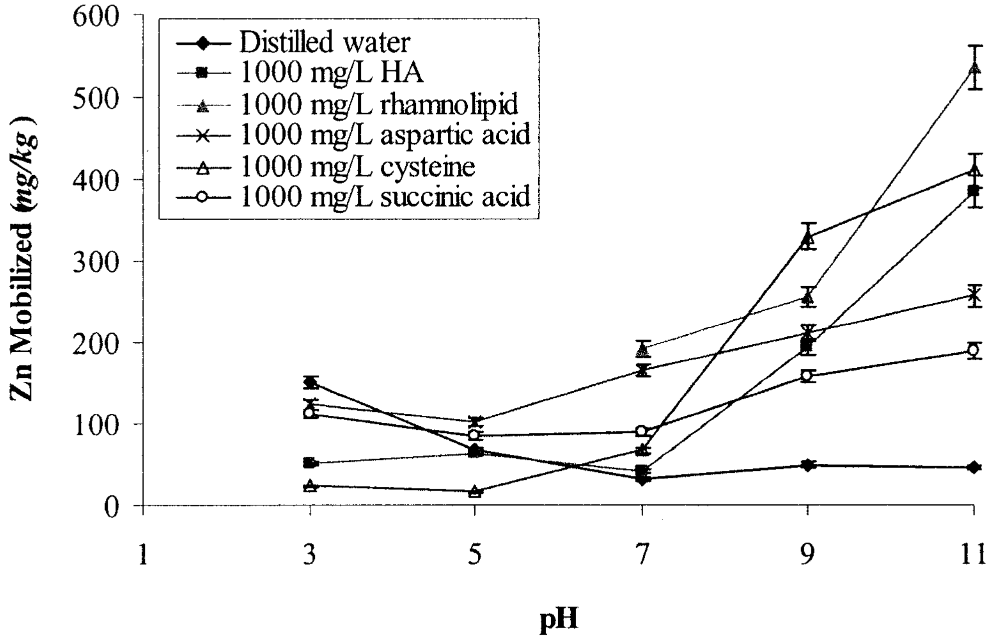


Figure 5-50. Zn mobilization from sample 2

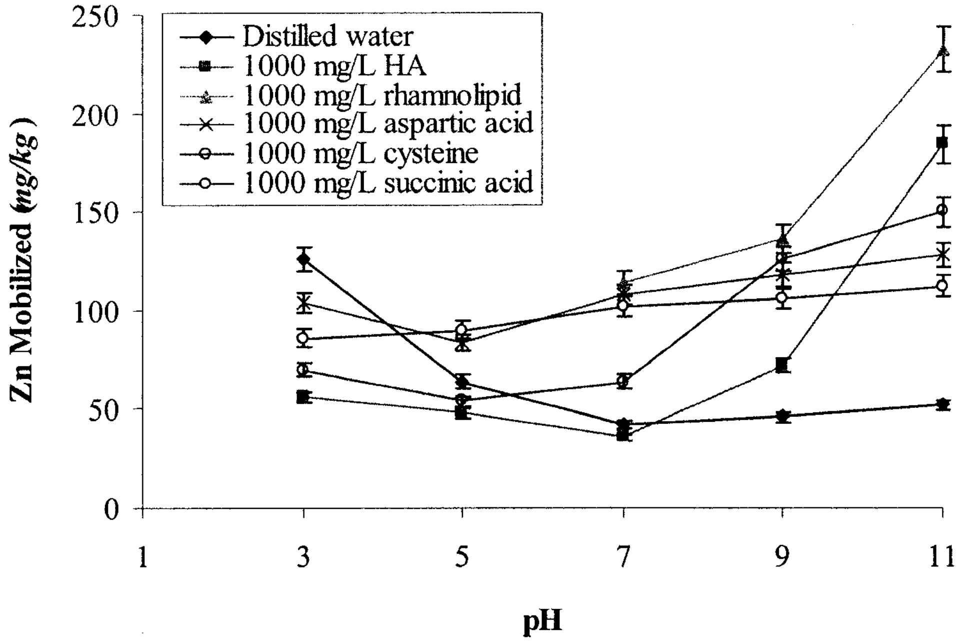


Figure 5-51. Zn mobilization from sample 3

Cation binding to HA is recognized to be mainly due to the presence of acidic functional groups such as carboxylic and phenolic groups. The COOH and phenolic OH groups account for the total acidity of HA, while the alcoholic OH group is only weakly acidic and reacts minimally with metals (Yong *et al.*, 1992; Coles and Yong, 2006). The carboxyl group reacts readily with metals and gradually dissociates between pH 2.5 to 7 to form the carboxylate group (COO^-). The phenolic hydroxyl (OH) group dissociates between pH 8 and pH 13.5. It reacts less with metals, but may play a role in direct arsenic binding (Buschmann *et al.*, 2006).

At low pH, the cations bind initially to carboxylate groups on the insoluble fraction of the HA. The addition of HA decreased the mobilization of all the metals at pH 3. When the pH increased from 3 to 7, the effect of HA on the mobilization of the metals varied from sample to sample and metal to metal. When the pH value was below 7 (included), the addition of HA decreased Fe mobilization compared with that by distilled water at same conditions. Under acidic conditions, HA decreased Pb mobilization from all the samples. For samples 1 and 2, Pb mobilization was even decreased by HA addition at pH 7. The addition of HA slightly increased Pb mobilization from sample 3 at pH 7. There was even no detectable Cu mobilization from sample 1 at pH 3. At pH 5, the addition of HA increased Cu mobilization from sample 1, but decreased Cu mobilization from samples 2 and 3. At pH 7, the addition of HA increased Cu mobilization from samples 1 and 3 but decreased Cu mobilization from sample 2. The introduction of HA at pH 3 decreased Zn mobilization significantly. No Zn mobilization was measured from sample 1 at pH 3. The Zn mobilization then was increased by HA under neutral and alkaline conditions. When pH increased from 9 to 11, the mobilization of the metals was enhanced by HA significantly. The only exception was that the mobilization of Fe from sample 3 was inhibited by the addition of HA.

When pH increased, more carboxyl groups dissociated, allowing a greater extent of binding, and the metal-humate complexes also became more soluble. Sparks *et al.* (1997) reported that the sorption of metals to HA occurred at pH values significantly lower than those associated with the formation of insoluble metal hydroxides, with a maximum occurring in the pH region of 5.5 to 7.5, and involved the solid state fraction of HA. At high pH, the presence of HA significantly reduced metal precipitation, probably due to the formation of soluble metal-humate species. It contributed to the high mobilization of arsenic and metal by HA at high pH. Moreover, the stability of the complexes of HA with metal cations followed the order Cu > Pb > Zn and the complexing capacity order was Pb > Cu > Zn (Abate and Masini, 2001).

The main functional groups of rhamnolipid that interacts with metal probably were the carboxylic and hydroxyl groups. The introduction of rhamnolipid enhanced the mobilization of the metals significantly, and the mobilization of the metals increased radically with pH increase. At pH 11, rhamnolipid was the best extractant for metal mobilization. The unique ability of rhamnolipid to decrease the interfacial tension efficiently and form micelles/complexes to incorporate the dissolved metal cations and arsenic makes it more effective in mobilizing arsenic and metals from the mine tailings.

The introduction of the LMWOAs decreased the mobilization of the metals at pH 3, except that Cu mobilization was slightly increased by succinic acid from sample 2 and by aspartic acid from sample 3. There was no detectable Cu mobilization from sample 1 by cysteine at pH 3 to 7 and by succinic acid at pH 3. The mobilization of the metals by the LMWOAs generally increased with pH increase. The metals were mobilized the most by the LMWOAs at pH 11.

Succinic acid can bind metals with carboxylic groups, aspartic acid can bind metal with amino ($-NH_2$) and carboxylic groups, whereas for cysteine an additional functional group, the thiol group (-SH), can bind metals, and then binds arsenic directly or through the metal-bridging mechanism. It was reported that aspartic acid could form soluble complexes with Pb and Zn at pH above 6 but form soluble Cu complexes from pH 4 (Ikhsan *et al.*, 2004). The acid dissociation values for cysteine are of the order of 8 (NH_3^+) and 10 (SH^+, Farrah and Pickering, 1978). It can form stable complexes with the metal cations under alkaline conditions. Under acidic conditions, the oxidation of cysteine by Cu^{2+} produces a precipitation of cystine and cuprous cysteine (Farrah and Pickering, 1978). This explains the observations in this study that this acid inhibited or did not greatly enhance the mobilization of arsenic and metal mobilization under acidic to neutral conditions, but worked well under alkaline conditions.

Ochs *et al.* (1993) proposed that the release of an element depends on the complexing properties and the stability of the complexes which it forms in organic acid systems. The results from this study showed that the mobilization of the metals by the LMWOAs was generally in the order of the stability constants (logK, the logarithms of equilibrium quotients) of the metal-organic ligand complexes (Table 5-7). Generally, the stability constants were in the order of cysteine > aspartic acid > succinic acid. The mobilization of arsenic by the three organic acids was also consistent with the order of stability of Fe-, Cu-, Pb-, and Zn-organic ligand complexes. It indicated that arsenic mobilization from the mine tailings was mainly accomplished by binding to the metal-organic complexes.

Table 5-7. Stability constants of organic acid-metal complexes

(Martell and Smith, 1976-1989)

Metal cation	L-cysteine	Aspartic acid	Succinic acid
Fe^{3+}	14.01[a]	11.4	6.88
Cu^{2+}	11.38[a,b]	8.57	2.6
Zn^{2+}	9.17	5.84	1.76
Pb^{2+}	11.6	6.67	2.8

[a]: Berthon (1995); [b]: Cu(II) reduction

5.8 Correlation between arsenic and metal mobilization

The correlation between arsenic and metal mobilization from the mine tailings were examined through linear least-squares regression analyses. The correlation coefficients (R^2) were summarized in Table 5-8. The mobilization of arsenic was found to be not only closely correlated with the mobilization of Fe but also correlated well to the mobilization of the heavy metals Cu, Pb and Zn from the mine tailings. The correlation coefficients varied from 0.5834 to 0.9999 (Table 5-8).

Table 5-8. Correlation coefficients of co-released elements from the mine tailing samples

Organic addition	Correlation Coefficients (R^2)									
	As-Fe	As-Cu	As-Pb	As-Zn	Cu-Fe	Pb-Fe	Zn-Fe	Cu-Pb	Cu-Zn	Pb-Zn
Sample 1										
Distilled water	0.9926	0.7336	0.9467	0.8975	0.7549	0.9139	0.8766	0.7862	0.8877	0.9764
1000 mg/L HA	0.7916	0.8022	0.6588	0.5834	0.8256	0.9376	0.8008	0.7194	0.9078	0.8040
1000 mg/L rhamnolipid	0.9178	0.9059	0.8678	0.8999	0.9996	0.6213	0.6692	0.6008	0.6494	0.9975
1000 mg/L aspartic acid	0.9906	0.7849	0.7720	0.6048	0.8024	0.7943	0.6640	0.5436	0.8822	0.5890
1000 mg/L cysteine	0.9866	0.9841	0.9837	0.9848	0.9943	0.9447	0.9681	0.9373	0.9835	0.9583
1000 mg/L succinic acid	0.9428	0.8941	0.9178	0.8523	0.9384	0.9874	0.8192	0.8818	0.7444	0.7734
Sample 2										
Distilled water	0.8899	0.9212	0.7209	0.7529	0.9882	0.9420	0.8794	0.9150	0.8102	0.8284
1000 mg/L HA	0.8432	0.6229	0.7954	0.6970	0.9349	0.9367	0.9390	0.8933	0.9278	0.8539
1000 mg/L rhamnolipid	0.9767	0.8328	0.8751	0.9420	0.9299	0.9574	0.8508	0.9964	0.6198	0.6770
1000 mg/L aspartic acid	0.8193	0.9648	0.9548	0.8385	0.9290	0.9341	0.9072	0.9969	0.8911	0.9163
1000 mg/L cysteine	0.8625	0.9937	0.7883	0.8193	0.8073	0.9854	0.9899	0.7280	0.7640	0.9966
1000 mg/L succinic acid	0.9984	0.7765	0.8512	0.7390	0.7715	0.8298	0.7090	0.5431	0.7962	0.6902
Sample 3										
Distilled water	0.9860	0.6554	0.7472	0.7377	0.6891	0.7928	0.8134	0.9797	0.9029	0.9645
1000 mg/L HA	0.8581	0.7592	0.6701	0.8423	0.9586	0.8668	0.9802	0.8283	0.9430	0.9377
1000 mg/L rhamnolipid	0.8834	0.9999	0.9927	0.9219	0.8884	0.9326	0.9958	0.9940	0.9261	0.9615
1000 mg/L aspartic acid	0.8082	0.5196	0.8925	0.8519	0.7855	0.8174	0.7997	0.7192	0.6707	0.7545
1000 mg/L cysteine	0.9560	0.9693	0.9841	0.9345	0.8806	0.8995	0.8364	0.9957	0.9886	0.9785
1000 mg/L succinic acid	0.9697	0.8611	0.8778	0.9945	0.9257	0.9242	0.9842	0.9963	0.9052	0.9183

The co-mobilization of arsenic and metals from the mine tailings indicated that the co-precipitation of arsenic and metals did not occur or, at least, was minimized. Aqueous arsenic and metals existed simultaneously in the supernatants. Therefore, the dissolved arsenic or metals must be incorporated into either soluble arsenic-organic complexes, or metal-organic complexes, or arsenic-metal-organic complexes. In the case of rhamnolipid, arsenic or metals or both might be incorporated into micelles. This can be verified from the good correlation coefficients between the mobilized arsenic and metals, which also implicated that the mobilization of arsenic from the mine tailings in the presence of organic additives was enhanced, to some extent, by the co-mobilization of the metals. The metals helped arsenic mobilization by acting as bridging agents to incorporate it into soluble organic complexes.

The mobilization of the heavy metals Cu, Pb and Zn was also correlated to Fe mobilization from the mine tailings (Table 5-8). The correlation coefficients between the heavy metals (Cu, Pb and Zn) and Fe ranged from 0.6213 to 0.9996. The correlations between the mobilized heavy metals Cu, Pb and Zn were also examined, and the coefficients ranged from 0.5436 to 0.9975.

5.9 Mass balance check

Batch tests with 1000 mg/L HA and rhamnolipid at pH 11 were selected for a mass balance check. The residual arsenic concentrations in the mine tailings after the batch tests were determined and the mass balance coefficients were calculated, which are summarized in Table 5-9.

Table 5-9. Mass balance coefficients of the selected batch tests

Organic additive	Mass Balance Coefficients		
	Sample 1	Sample 2	Sample 3
HA	1.008	1.003	1.013
Rhamnolipid	1.002	0.998	0.994

From Table 5-9, it can be seen that the mass balances were maintained during the batch experiments, even there was a little variation of the mass balance coefficient from 1.0. This may be caused by the analytical and operational errors, which were unavoidable but were expected during the experiments.

5.10 Summary of batch tests and preliminary discussion

Batch tests with distilled water indicated that the arsenic in the mine tailings was most mobile under acidic conditions due to the dissolution of metal oxides or hydroxides in the mine tailings, which released the associated arsenic. The equilibrium state of the distilled water-mine tailings systems reached after about a 12 to 24 hour reaction.

The addition of HA under acidic to neutral conditions with a low mass ratio inhibited arsenic mobilization. Compared to distilled water, even at pH 5 or 7, arsenic mobilization was inhibited by the addition of HA at a mass ratio of 0.25 to 1 mg/g, and arsenic mobilization was enhanced when the mass ratio was above 2 mg/g. The addition of Fluka HA at pH 3 inhibited arsenic mobilization from the mine tailings significantly. When the mass ratio was 10 mg added HA/g mine tailings at pH 3, the concentration ratios varied were 0.87, 0.59 and 0.76 for samples 1, 2 and 3, respectively. The decrease in arsenic mobilization by HA under acidic conditions involved the sorption of HA to the mine tailings and the re-sorption of arsenic to the sorbed HA and to the remaining mine tailing surfaces. This was verified partially by examining the change of arsenic concentrations in the supernatants with reaction time, which increased gradually up to 24 hours and then decreased and was relatively stable after 48 hours. The re-sorption of arsenic to the HA might occur through a metal-bridging mechanism (Figure 5-12).

The mobilization of arsenic increased with the mass ratio of added HA to the mine tailings. Especially, under alkaline conditions, the addition of HA could enhance arsenic mobilization. When the mass ratio was 10 mg/g at pH 11, arsenic was most mobilized from the mine tailings, with corresponding concentration ratio of 10.36, 5.85 and 13.18, respectively. Increasing both the mass of mine tailings and HA added while keeping the same mass ratio increased the dissolved arsenic concentrations in the supernatants significantly, but had no significant effect on the portion of arsenic mobilized. At pH 11, arsenic concentrations in the supernatants increased gradually before 24 hours and then kept relatively stable with the reaction time. SSE results showed that HA was able to mobilize the weakly-bound arsenic completely. Arsenic associated with carbonates, oxides and hydroxides was also mobilized by HA, probably through the competition adsorption and anion exchange mechanisms. HA also might be able to mobilize the arsenic associated organic matter and sulfate. The dissolution of organic matter at high pH might also release associated arsenic, contributing to arsenic mobilization. Arsenic in the residual fraction was almost not attacked by the organic additions.

Generally, HA might help retain arsenic in the mine tailings under acidic conditions by providing more active binding sites and forming insoluble complexes with arsenic. However, HA may enhance the mobility of arsenic under alkaline conditions mainly through competition for adsorption, formation of aqueous soluble complexes and electrostatic interaction. Formation of soluble arsenic-HA and/or arsenic-metal-HA complexes at high pH probably was the domain mechanism that mobilized arsenic from the mine tailings. The co-mobilization of metals (i.e., Fe, Cu, Pb and Zn) could enhance arsenic mobilization through forming aqueous metal-bridging complexes. Zeta potential measurements indicated that the presence of HA could increase the negative charge density on the mine tailing surface significantly, which resulted in a greater repulsive interaction to enhance arsenic mobility.

One approach to determine the degree to which the arsenic was mobilized is to determine the distribution of arsenic in the solid and aqueous states. It can be described by a distribution coefficient (K_s), which can be defined as:

$$K_s = \frac{residual\ mass\ of\ arsenic\ in\ the\ \min e\ tailings\ (mg/kg)}{mass\ of\ arsenic\ in\ the\ aqueous\ phase\ (mg/kg)} \qquad Eq.\ 5\text{-}3$$

The K_s, similar to the soil distribution coefficient in contaminant sorption studies (Yong and Mulligan, 2004), could be a more general expression, because it takes the residual arsenic concentrations in the mine tailings into consideration, which eliminates the effect of initial arsenic concentrations in the mine tailings, thereby making it a useful predictor of the mobilization of arsenic. The distribution coefficients of arsenic in the presence of HA and rhamnolipid are summarized in Table AIII-1 (Appendix III).

By examining the experimental data from batch tests with HA, it was found that K_s fell into a linear relationship with the reciprocal of the mass ratio of added HA to mine tailings (r, mg/g) (Figures 5-52 to 5-54). It can be expressed as:

$$K_s = \frac{b}{r} + a \qquad \textit{Eq. 5-4}$$

where $r > 0$, a is a dimensionless constant, and b is a sorption coefficient (mg/g). The coefficient b reflects the sorption extent of organic additives to the mine tailings, which is a function of the physicochemical properties of the mine tailings such as surface area and CEC, the nature of the organic matter, and ambient environment conditions such as pH (Gu *et al.*, 1994; Kaiser *et al.*, 1997; Filius *et al.*, 2000; Grafe *et al.*, 2001).

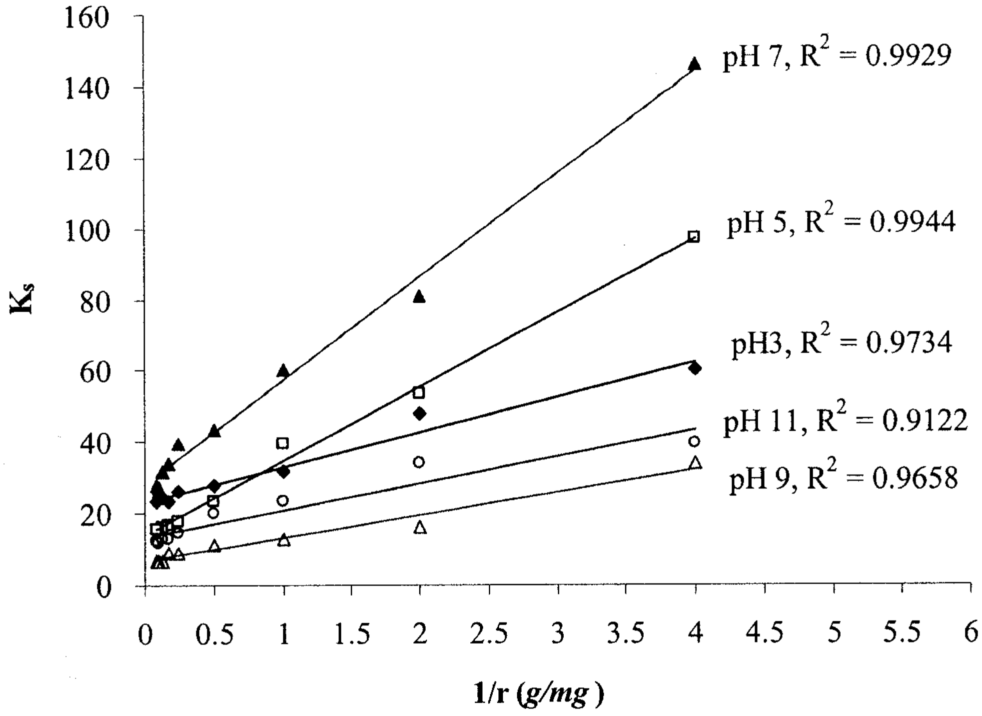


Figure 5-52. Fit of experimental data with the desorption isotherm (HA, sample 1)

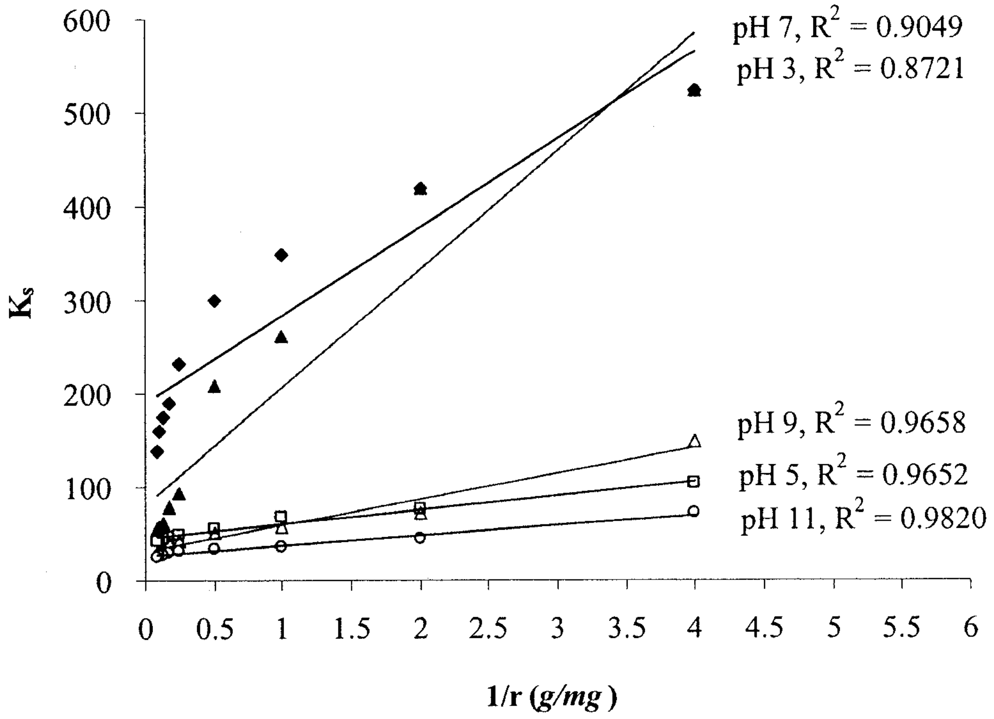


Figure 5-53. Fit of experimental data with the desorption isotherm (HA, sample 2)

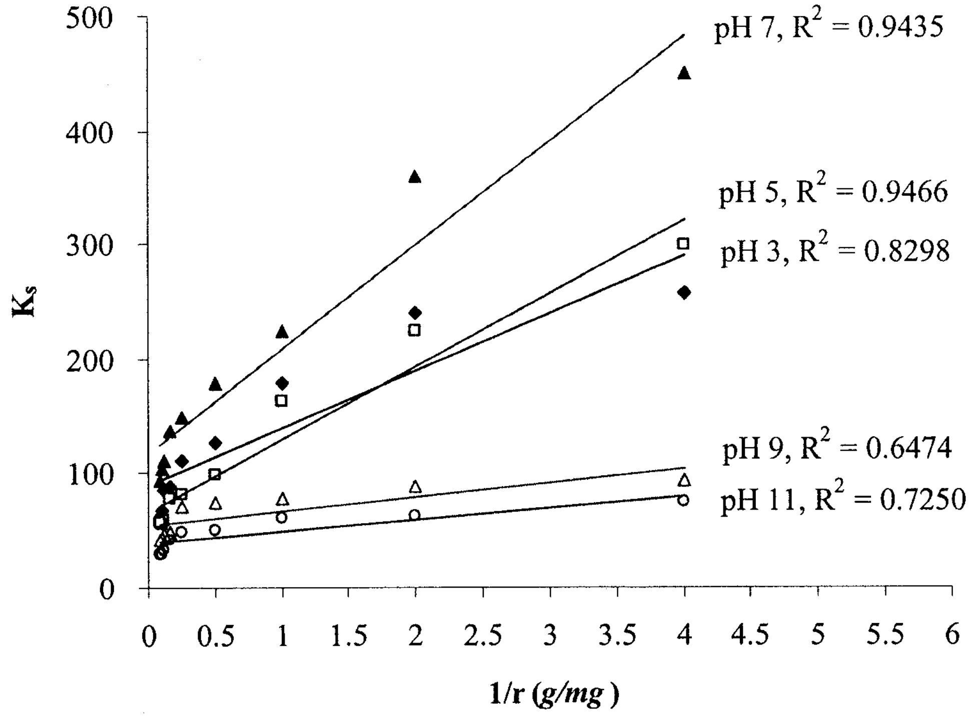


Figure 5-54. Fit of experimental data with the desorption isotherm (HA, sample 3)

The desorption isotherm can be used to predict arsenic mobilization in the presence of humic acid. Based on experimental data, the coefficients of *a* and *b* can be determined by plotting K_s as a function of the reciprocal *r*. Using linear regression, *a* is the y-intercept *and b* is the slope (Table AIII-2, Appendix III).

From the isotherm, it can be seen that arsenic mobilization was mainly determined by the mass ratio of added HA to mine tailings and the sorption extent of HA to the mine tailings. It explains the observation that increasing the mass of both HA and mine tailings without changing mass ratio did not significantly affect the portion of arsenic mobilized from the mine tailings.

The addition of rhamnolipid greatly enhanced the mobilization of arsenic from the mine tailings, which increased with the mass ratio of added rhamnolipid to the mine tailings and pH. When the mass ratio was 10 mg/g (rhamnolipid/mine tailings) at pH 11, arsenic was mobilized the most from the mine tailings. The corresponding concentration ratios were 13.64, 8.46 and 21.59 for samples 1, 2 and 3, respectively. Similar to the observation of distilled water and HA, increasing the mass of added rhamnolipid and mine tailings without changing the mass ratio increased the dissolved arsenic concentrations in the supernatants, but had no significant effect on arsenic mobilization efficiencies. The equilibration time for the rhamnolipid-mine tailings systems was between 12 to 24 hours. The mobilization of arsenic was found to be closely correlated to that mobilization of the metals. The co-mobilized metals might enhance arsenic mobilization by help incorporate arsenic into soluble complexes or micelles.

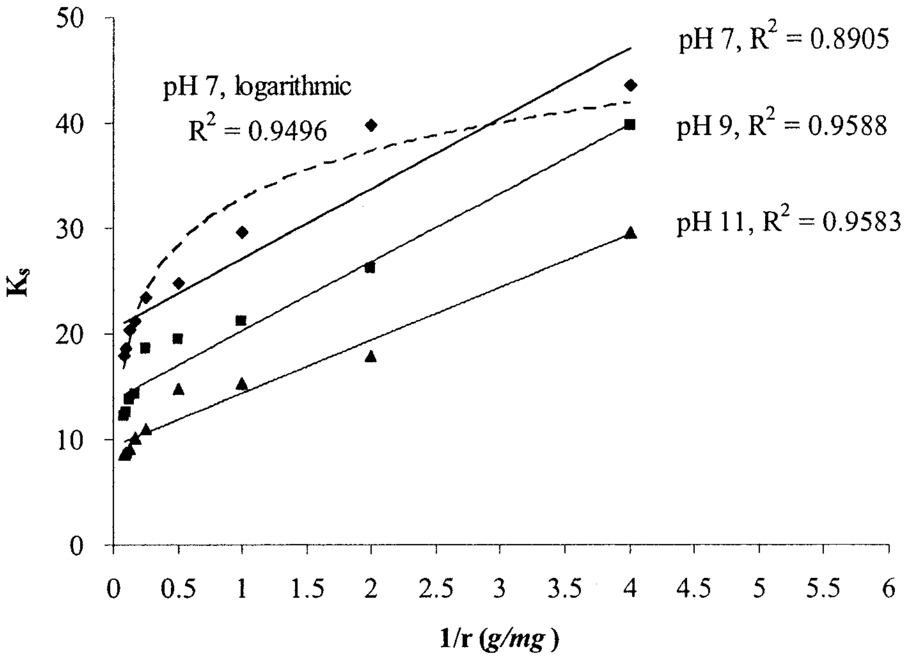


Figure 5-55. Fit of experimental data with the desorption isotherm (rhamnolipid, sample 1)

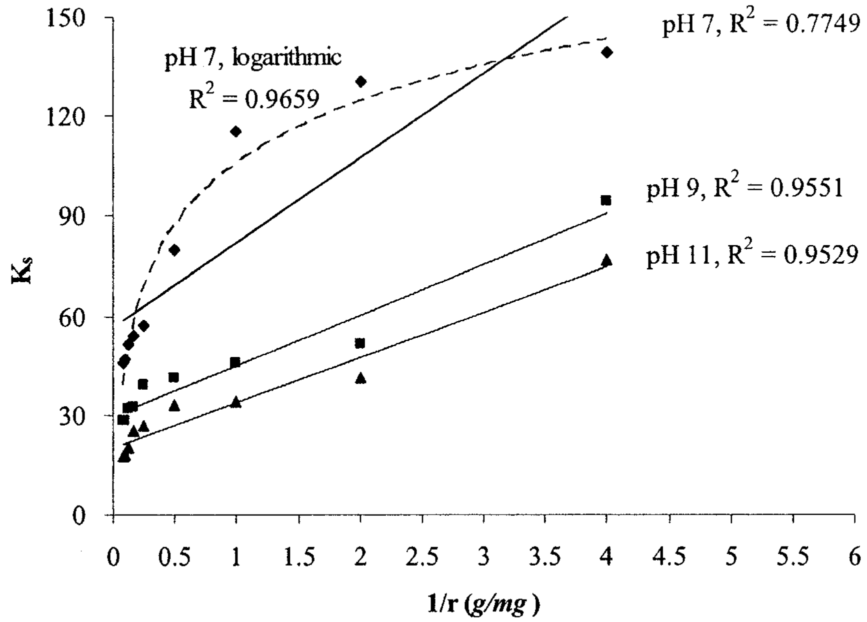


Figure 5-56. Fit of experimental data with the desorption isotherm (rhamnolipid, sample 2)

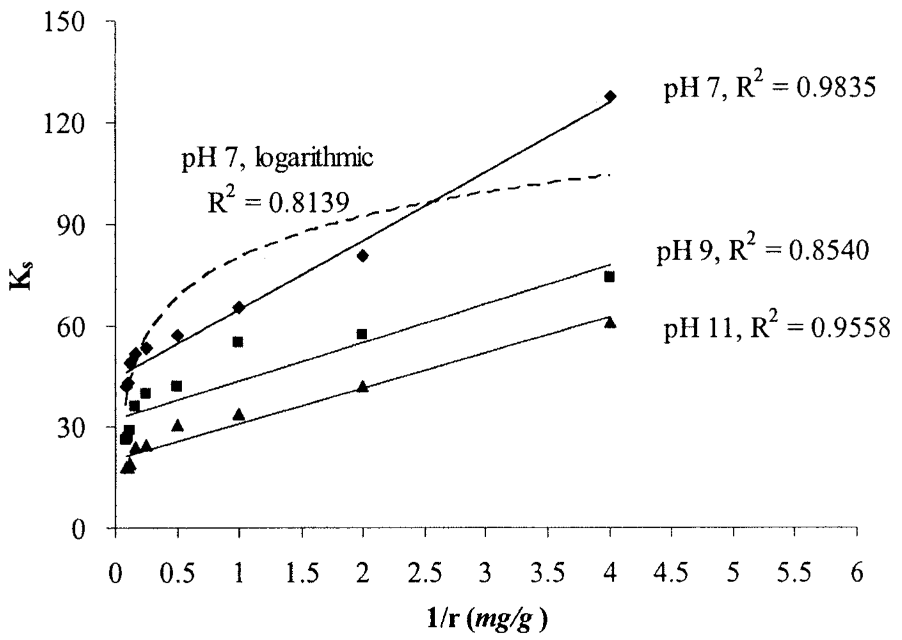


Figure 5-57. Fit of experimental data with the desorption isotherm (rhamnolipid, sample 3)

The desorption isotherm was also applicable to predict arsenic mobilization from the mine tailings in the presence of rhamnolipid (Figures 5-55 to 5-57). The regression coefficients (R^2) varied from 0.7749 to 0.9835. However, at pH 7, a logarithmic regression (dash line in Figures 5-55 to 5-56) fit better for the mobilization of arsenic mobilization from the mine tailings samples 1 and 2 in the presence of rhamnolipid. The logarithmic R^2 values were 0.9496 and 0.9695, compared the linear R^2 values of 0.8905 and 0.7749 for samples 1 and 2, respectively. But for sample 3 at pH 7, the linear relationship fit better, as shown in Figure 5-57. These discrepancies indicated that the properties of the mine tailings might influence the interaction between the mine tailings and rhamnolipids, which further influencing the mobilization of arsenic from the mine tailings.

Rhamnolipid may increase arsenic mobility from the mine tailings through reducing the interfacial tension, formation of soluble complexes or micelles, competition for adsorption and anion exchange, electrostatic interaction and increasing the wettability of the mine tailings. As indicated in the experimental results, these interactions can be affected by the physicochemical characteristics of the mine tailings, pH and the co-mobilized metals from the mine tailings. Similar results were obtained from SSE analyses of the mine tailings washed with HA and rhamnolipid. Generally, rhamnolipid performance is better than that of HA to mobilize arsenic associated with carbonates, oxides and hydroxides, and organic matter and sulfate fractions. This was consistent with the overall mobilization efficiencies of HA and rhamnolipid.

The addition of the LMWOAs inhibited arsenic mobilization from the mine tailings under acidic to neutral conditions, but enhanced arsenic mobilization under alkaline conditions. The addition of LMWOAs at pH 3 inhibited arsenic mobilization from the mine tailings and the concentration ratios varied from 0.21 to 0.73. The mobilization of arsenic generally increased with pH increase. Arsenic was most mobilized at pH 11 and the concentration ratios varied from 2.62 to 9.55. The mobilization of arsenic was closely correlated to that of the metals. Moreover, the mobilization of arsenic by the three LMWOAs was found to be consistent with the order of the stability of Fe-, Cu-, Pb-, and Zn-organic ligand complexes. It further verified that arsenic mobilization from the mine tailings was mainly accomplished by binding to the metal-organic complexes.

At pH 11, arsenic mobilization by the organic additives was in the order of rhamnolipid > HA > cysteine > aspartic acid > succinic acid. Rhamnolipid was found to be more efficient to mobilize arsenic from the mine tailings, probably due to its efficiency in lowering the interfacial tension and capability to form micelles. These capacities also enable rhamnolipid to be more efficient in mobilizing other metals, which may further enhance arsenic mobilization by helping incorporate arsenic into soluble complexes or micelles.

CHAPTER SIX

ROLE OF HA FUNCTIONAL GROUPS IN ARSENIC MOBILIZATION

To investigate the functional groups of HA involved in arsenic mobilization and complexation, FTIR spectra were collected from the 1000 mg/L HA solution (pH 11) and the supernatants from batch tests of the mine tailings with HA at a mass ratio of 10 mg/g with pH 11. The samples were diluted 10 times with 0.001 M NaOH before testing. The FTIR results are analyzed and compared in this chapter.

6.1 FTIR spectrum of the Fluka HA solution

The collected FTIR spectrum of the Fluka HA solution (1000 mg/L, pH 11) is illustrated in Figure 6-1. The spectrum was collected over the 500 to 4000 cm^{-1} range. The spectrum showed three broad bands. According to Nakanishi and Solomon (1977), a broad band at 1550 – 1840 cm^{-1} corresponds to carboxylic acids and derivatives, alkenes, aldehydes and ketones, N=O nitroso and C=N stretches; a broad band at 1950 – 2620 cm^{-1} corresponds to alkynes, S-H thiols, P-H phosphine, Si-H silane and nitriles; and a peak at 2700 – 3810 cm^{-1} corresponds to alcohols and phenols, amines, and C-H stretching of alkyl structures. Especially, the broad band at 3200 – 3600 cm^{-1} characterizes H-bonded OH groups of alcohols, phenols, as well as H-bonded N-H groups (Amir *et al.*, 2004), and it was off-scale because the concentration of solution was chosen to make the features in other regions of the spectrum more intense.

The spectrum also showed a high intensity for two bands, 1670 and 2160 cm^{-1}. The first corresponds to alkenes, benzoic compounds and carboxylic C=O amide I band, and the second arises mainly from alkynes (Nakanishi and Solomon, 1977).

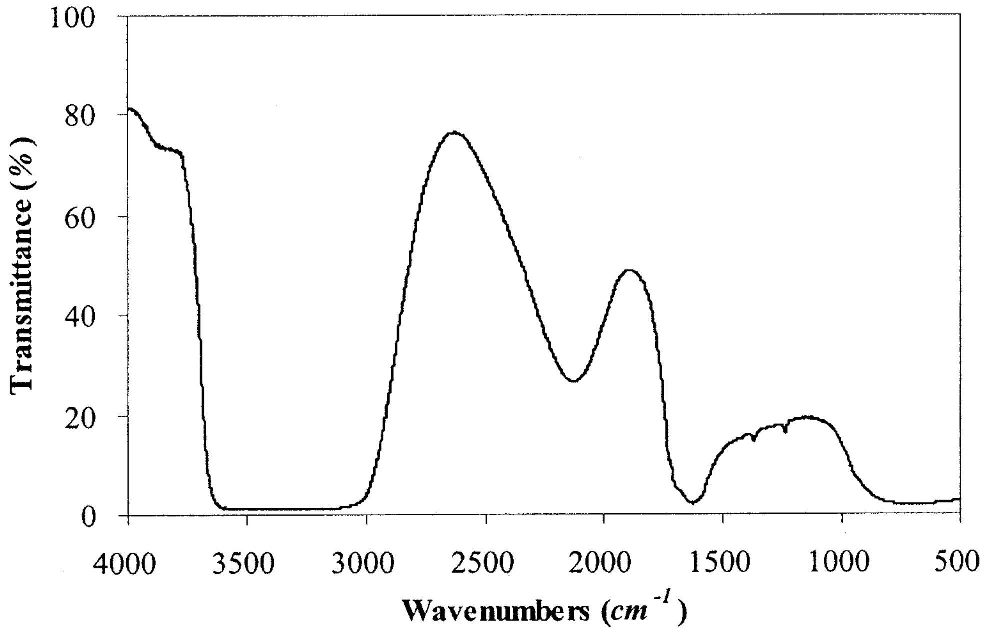


Figure 6-1. FTIR spectrum of Fluka HA solution

6.2 FTIR spectra of supernatants from batch tests with HA

The collected FTIR spectra from the supernatants in batch tests with the mine tailings and HA are illustrated in Figures 6-2 to 6-4. Compared to the spectrum of the HA solution, similar peaks were obtained with the extracts. However, the peaks at 1670 and 2160 cm^{-1} of the extracts showed to be much sharper compared to those of the spectrum of HA solution. Higher transmittance was obtained with the extracts. Both of the observations indicated that the corresponding functional groups were sorbed to the mine tailings (Huang *et al.*, 2006). It might occur through ligand exchange reactions and hydrogen bonding between the organic functional groups and surface hydroxyls (Kaiser *et al.*, 1997). As discussed in Chapter Five, the sorption of HA could enhance arsenic mobilization through competition of adsorption sites. Furthermore, based on the zeta potential measurement, the HA sorption could potentially increase the density of the negative charge on the mineral surfaces, which produced a greater repulsive interaction between the mine tailings surface or the organic matter surface and arsenic anions, thus preventing the re-adsorption of arsenic anions to the surfaces, leading to the increase in arsenic mobilization.

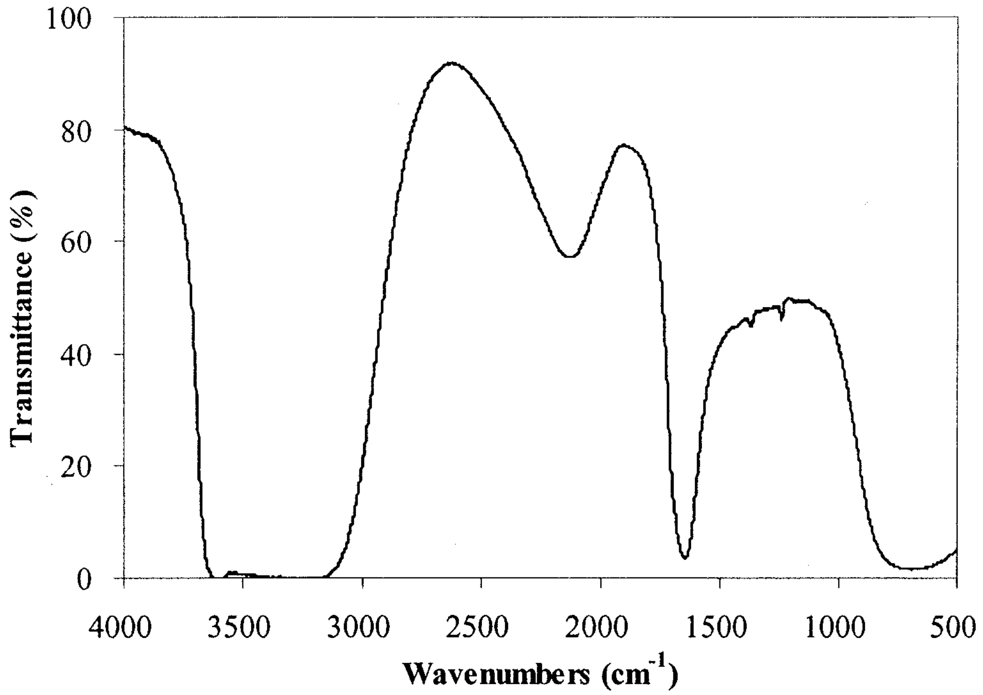


Figure 6-2. FTIR spectrum of the supernatant from sample 1

IR spectroscopy has been used to study the interaction and complexation between organic matter and metals (Gu *et al.*, 1994; Kaiser *et al.*, 1997). The formation of complexes can be evidenced by the shifts in the bands (Yost *et al.*, 1990; Kaiser *et al.*, 1997). Gu *et al.* (1994) indicated that carboxylic groups in HA play a predominant role in the complexing of metal ions. Saada *et al.* (2003) proposed that amino groups might be involved in arsenic complexation by HA. The mobilization of arsenic could be enhanced by forming soluble aqueous complexes with HA directly or through metal-bridging mechanisms.

However, no significant band shifts was observed in this study, though the spectra differed in the relative intensity of some bands. It might be due to the low sensitivity of FTIR and/or the possible overlaps of bonds, since the mine tailings and humic acid are very complex materials. There might be some free HA in the supernatant. A portion of the organic contents might also be solubilized from the mine tailings at pH 11.

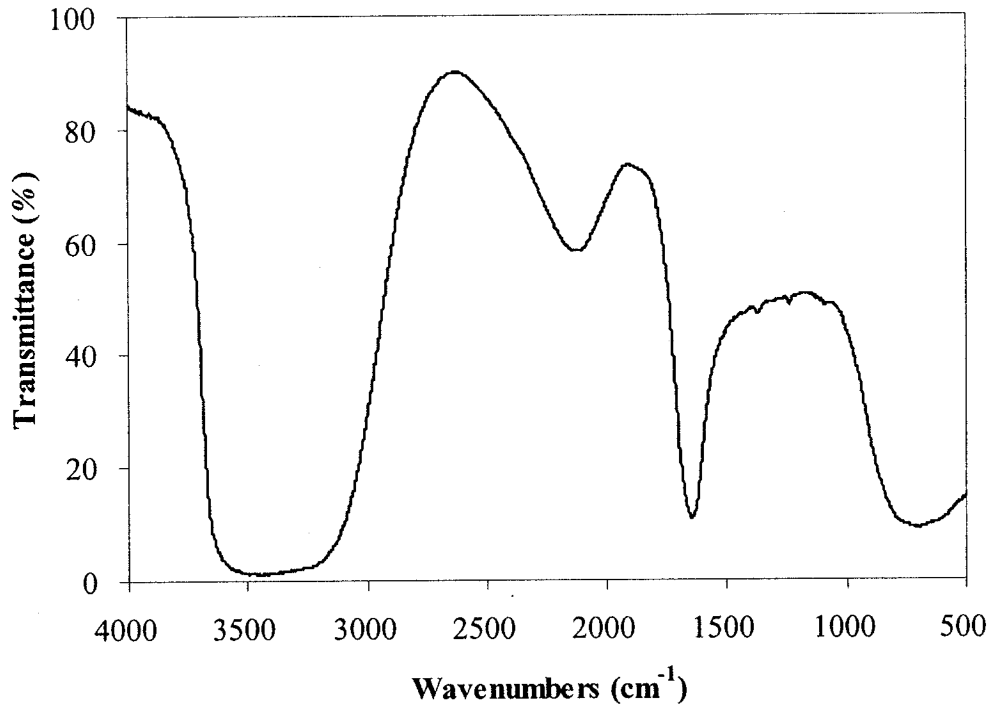


Figure 6-3. FTIR spectrum of the supernatant from sample 2

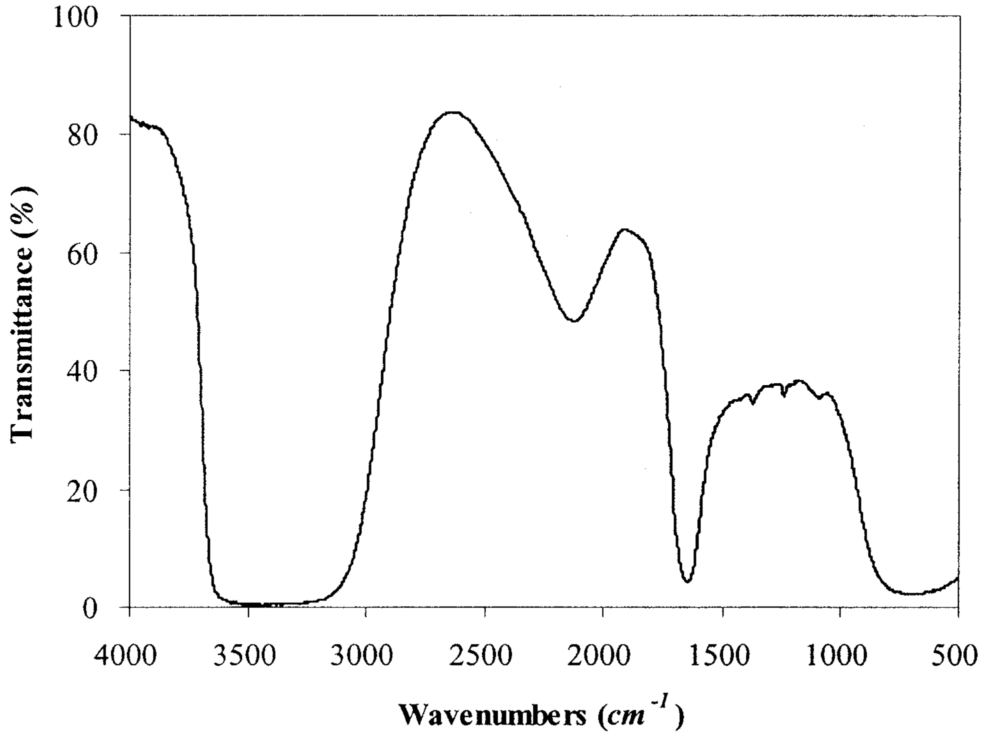


Figure 6-4. FTIR spectrum of the supernatant from sample 3

FTIR results indicated that a portion of the HA was sorbed onto the mine tailings during the interaction processes. However, the results were insufficient to determine the main functional groups of HA involved in arsenic complexation and mobilization, probably due to complexity of the testing material and the low sensitivity of the testing method itself.

CHAPTER SEVEN

ARSENIC SPECIATION

Arsenic speciation is of environmental significance since it plays an important role in its mobility and toxicity behavior in natural systems. In this study, arsenic species in the extracts from the mine tailings by distilled water, HA and rhamnolipid at pH 3 and 11 was determined by capillary electrophoresis (CE) analyses. The results from CE analyses are presented and discussed in this chapter.

7.1 Mine tailing extracts by distilled water

The electropherograms of the extracts from the mine tailings by distilled water at pH 3 and 11 are illustrated in Figure 7-1. By comparing with the electropherogram of a standard solution (Figure AIV-1), only As(V) was detected in the extracts. No arsenic species were detected in the extract from sample 1 at pH 11, probably due to the detection limits. The detection limits for the individual analytes were estimated to be 0.1 mg/L for As(V) and As(III), and 0.8 mg/L for MMAA and DMAA.

As(III) was not detected probably due to two reasons: (1) there was no As(III) in the extractants or (2) the As(III) concentration was below the detection limit. Similar explanations were also applicable to methylated arsenic species. It was also consistent to the previous reported data that the concentrations of methylated arsenic species are usually low or negligible (Wang and Mulligan, 2006a).

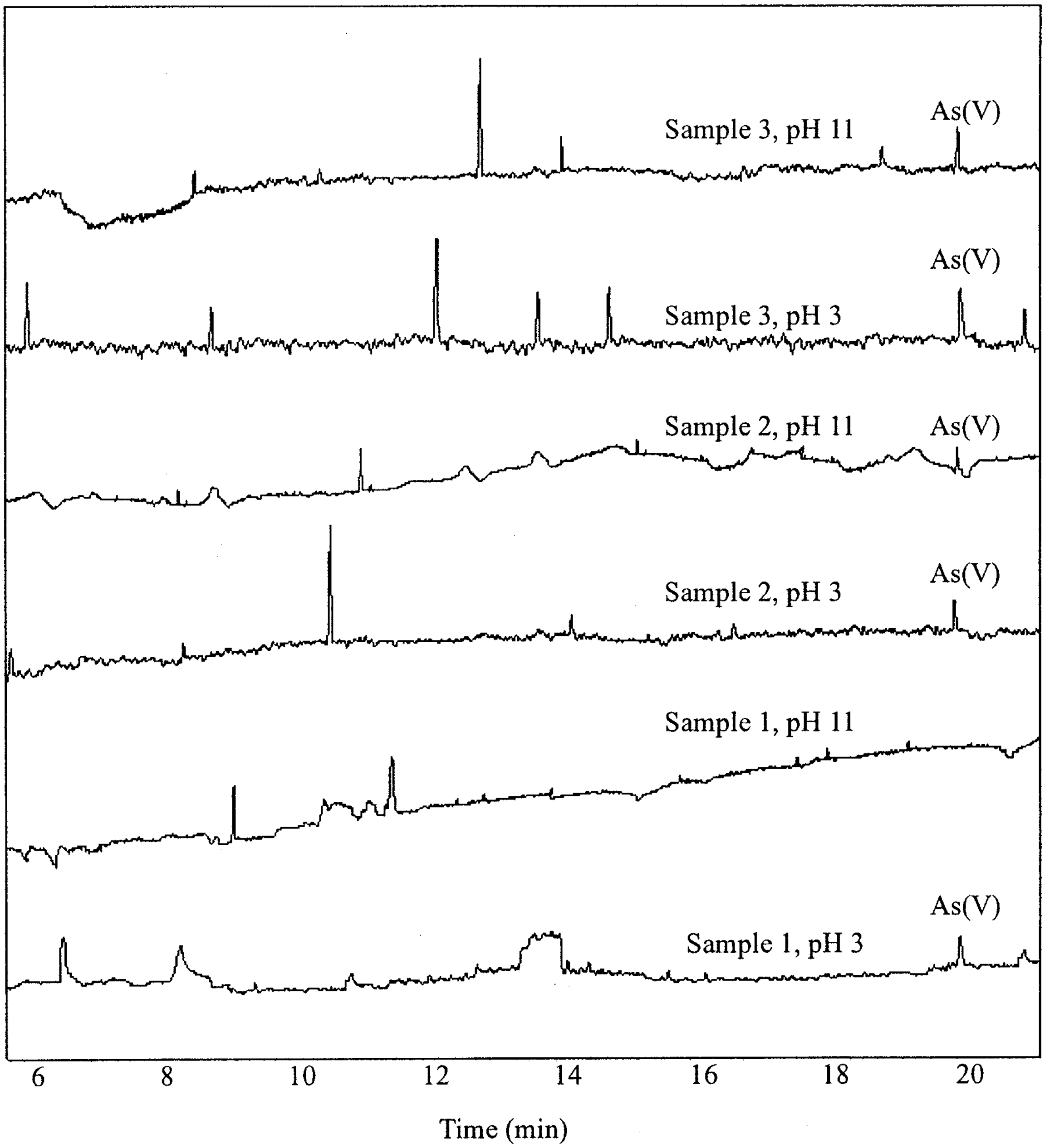


Figure 7-1. Electropherograms of the mine tailing extracted by distilled water

7.2 Mine tailing extracts by HA and rhamnolipid

CE analyses with a standard solution of the four arsenic species and HA showed that the introduction of HA did not have a significant effect on the migration time of the arsenic species (Figure AIV-2). The electropherograms of the extracts after tailings treatment by

HA at pH 3 and 11 are illustrated in Figure 7-2. As(V) was the only detected arsenic species in the extracts. No arsenic was detected in the extract from sample 2 by HA at pH 3, due to the detection limit (0.1 mg/L for As(V) and As(III), and 0.8 mg/L for MMAA and DMAA).

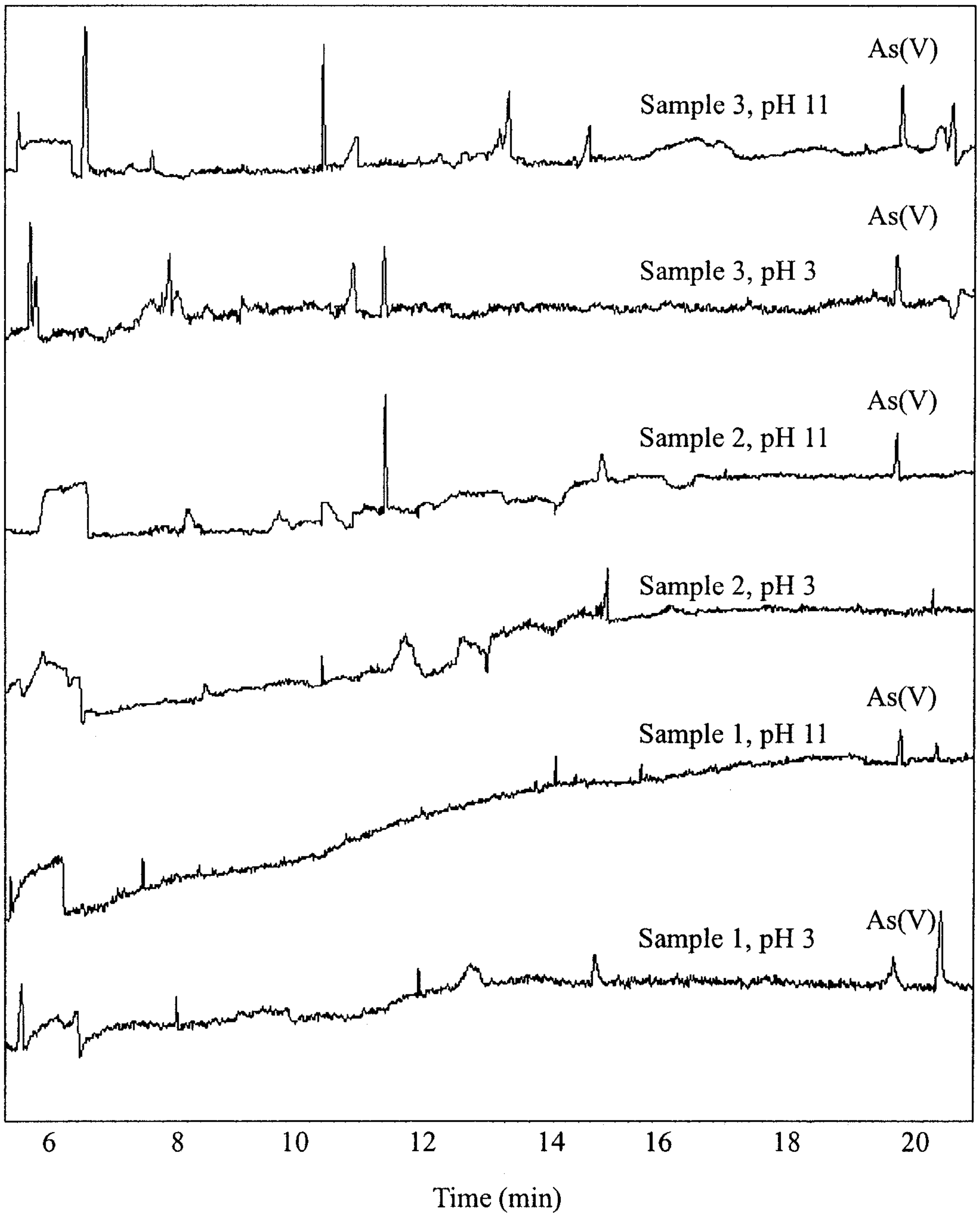


Figure 7-2. Electropherograms of the mine tailing extracted by HA

The electropherograms of the extracts from rhamnolipid treatment at pH 11 from the mine tailings are illustrated in Figure 7-3. Only As(V) was detected in the extracts.

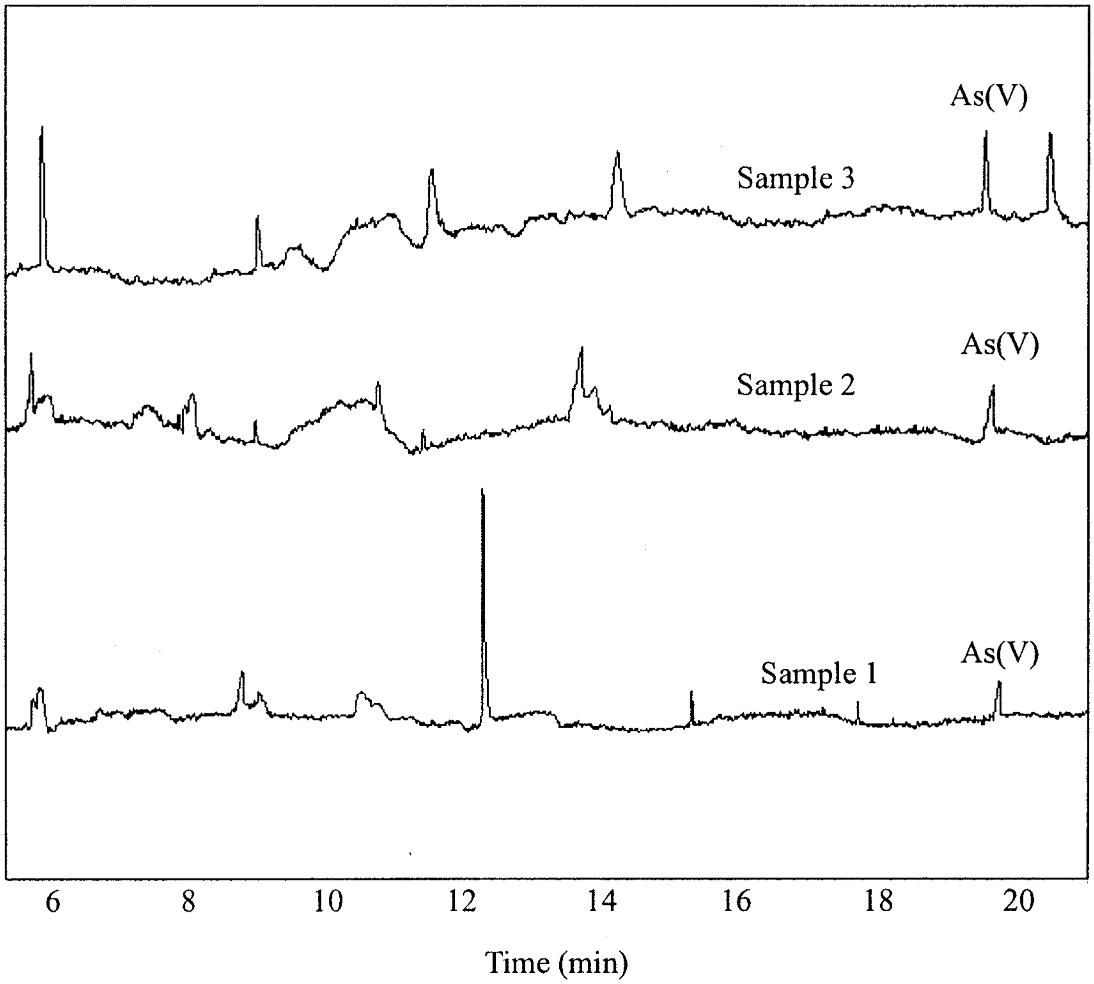


Figure 7-3. Electropherograms of the mine tailing extracted by rhamnolipid

7.3 Summary and preliminary discussion

CE analyses indicated that As(V) was the only water-soluble arsenic species from the mine tailings. This could be explained for either or both of the following reasons: (1) the extractable arsenic in the mine tailings has been oxidized completely and stabilized to

As(V) due to the long-term on-site disposal and (2) the concentrations of As(III) and methylated arsenic species in the extracts were below the detection limits. This was consistent with the previous observation that As(V) was the dominant oxidation state of arsenic in mine tailings (Paktunc *et al.*, 2003).

Similarly, only As(V) was detected in the extracts by HA or rhamnolipid from the mine tailings. It indicated that the HA or rhamnolipid did not incur the reduction of As(V) to As(III) or at least, the reduction reaction did produce a detectable level of As(III) in the extracts. Therefore, arsenic oxidation-reduction reactions might not play a significant role in arsenic mobilization from the mine tailings in the presence of HA and rhamnolipid in this study. This is different from the previous observation that an Inangahua River NOM could reduce As(V) to free As(III) in the presence of hematite (Redman *et al.*, 2002). It may be mainly due to the different properties of the NOM and laboratory conditions.

CHAPTER EIGHT

COLUMN EXPERIMENT RESULTS AND DISCUSSION

Based on the results from batch tests, column experiments were run with HA and rhamnolipid solutions (1000 mg/L) as the flushing solutions to mobilize arsenic from the mine tailings. Distilled water was flushed through the columns as a control. All the initial pH values of the flushing solutions were adjusted to 11. The pore volume of the compacted columns was measured to be around 10.5 to 11.8 ml, and the porosity of the columns was estimated in the range of 38% to 45%. A pore volume of 12 ml was adopted for all the column tests. The hydraulic conductivity with water was measured to be in the range of 1.8 to 3.2 × 10^{-3} cm/s.

To avoid heaving and channeling, the flow rate of flushing solution was controlled below 0.5 ml/min. Effluents from the columns were collected according to pore volumes. Collection of effluents was stopped when there was no detectable arsenic. The effluent pH became relatively stable after 5 to 12 pore volume flushing. Concentrations of arsenic, Fe, Cu Pb and Zn in the effluents were measured and the accumulative mobilization of these elements was then determined. The results were compared with those from batch tests. Correlations of the co-released elements were analyzed. The results from the column experiments are presented and discussed in this chapter.

8.1 Arsenic mobilization

When distilled water along was flushed through the column loaded with the mine tailing sample 1, the average arsenic concentrations in effluent increased gradually with pore volumes to 175 μg/L after 10 pore volumes, and then decreased (Figure 8-1). The accumulative arsenic mobilization reached 0.6 mg/kg (1.0%) after a 40-pore-volume-flushing. When the HA solution was used as the flushing solution, more pore volumes were required. The highest arsenic concentration in the effluents was 1,375 μg/L after 12 pore volume flushing (Figure 8-1). The accumulative arsenic mobilization reached a relatively stable level after a 40-pore-volume-flushing, even though there was still arsenic detectable in the effluents after that. After a 60-pore-volume-flushing arsenic mobilization reached 6 mg/kg (9.1%).

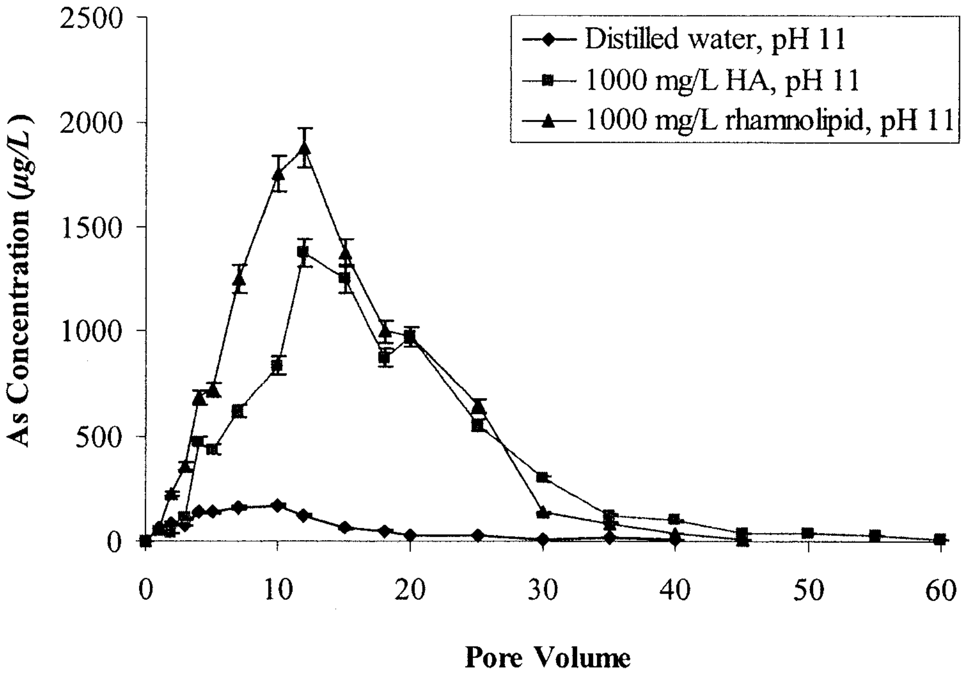


Figure 8-1. Average arsenic concentrations in the effluent from sample 1

In the case of the rhamnolipid solution, totally 45 pore volumes was flushed through the column. The highest arsenic concentration in the effluents was 1,875 μg/L after a 12-pore-volume-flushing (Figure 8-1). The mobilization of arsenic was relatively stable after about a 30-pore-volume-flushing. Final arsenic mobilization reached 8 mg/kg (12.3%) from the mine tailings after a 45-pore-volume-flushing.

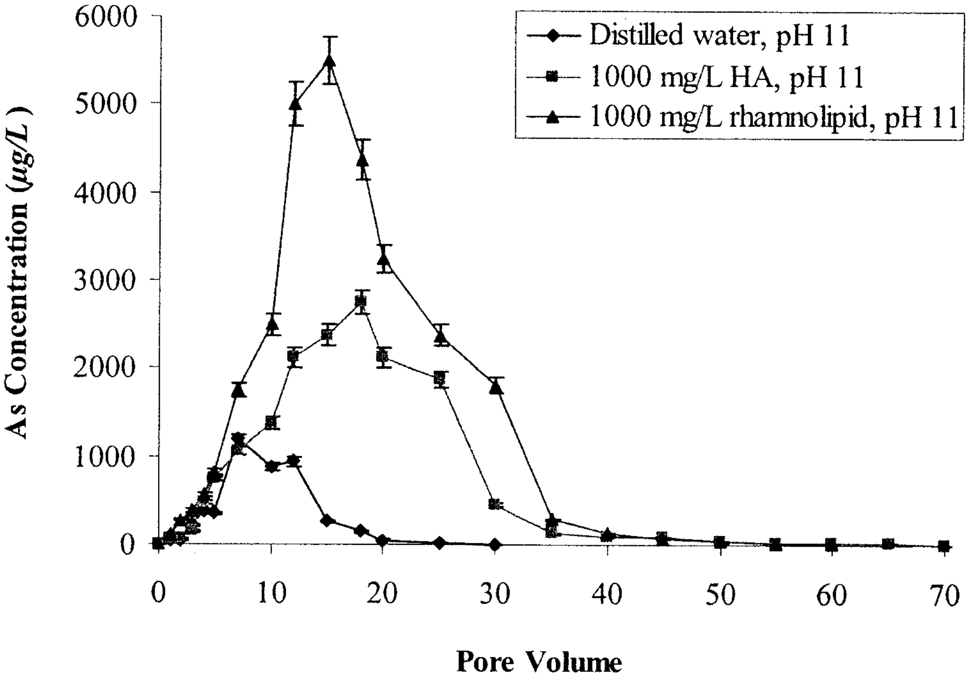


Figure 8-2. Average arsenic concentrations in the effluent from sample 2

For sample 2, when distilled water was the flushing solution, the highest average arsenic concentration in the effluents was around 1,188 μg/L after a 7 pore volume flushing (Figure 8-2). The accumulative arsenic mobilization reached 2 mg/kg (0.9%) after a 30-pore-volume-flushing. When the solution of 1000 mg/L HA was flushed through the column, the highest arsenic concentration in the effluent of 2,750 μg/L occurred after a

18-pore-volume-flushing (Figure 8-2). Arsenic mobilization became relatively stable after a 30-pore-volume-flushing, and reached 11 mg/kg (4.3%) after a 70-pore-volume-flushing. While the rhamnolipid solution was flushed through the column, the highest arsenic concentration in the effluent, around 5,500 µg/L, occurred after a 15-pore-volume-flushing (Figure 8-2), and arsenic mobilization became relatively stable after a 35-pore-volume-flushing and reached 21 mg/kg (7.9%) after 60 pore volumes.

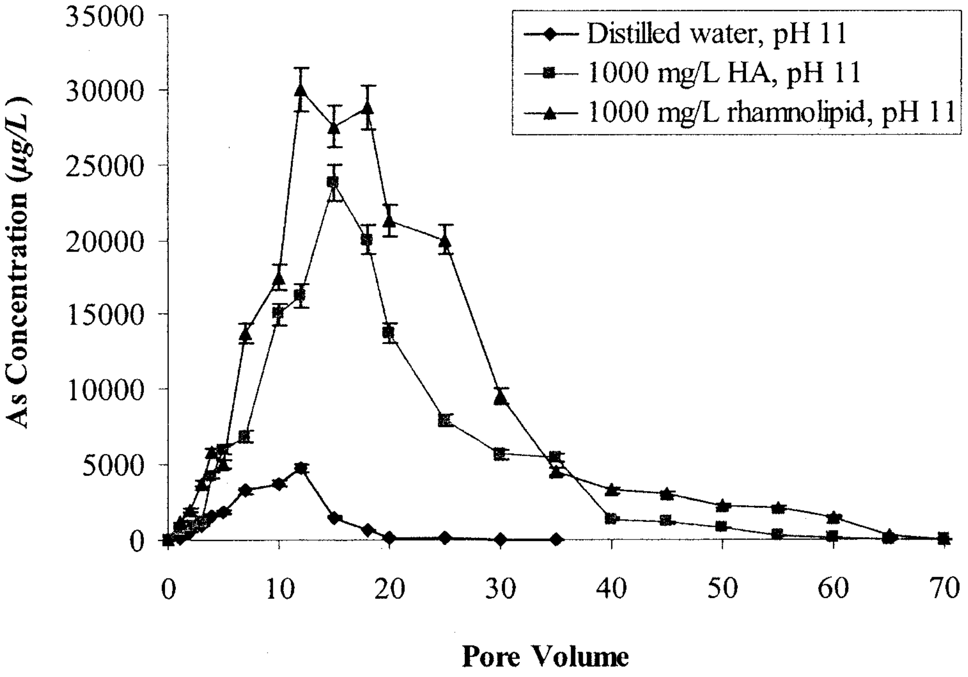


Figure 8-3. Average arsenic concentrations in the effluent from sample 3

The average arsenic concentration in the effluent from the mine tailing sample 3 by the different flushing solutions is illustrated in Figures 8-3. When distilled water was flushed through the column, the highest arsenic concentration in the effluent reached 4,750 µg/L after a 12-pore-volume-flushing, arsenic mobilization reached 10 mg/kg (0.4%) after a

35-pore-volume-flushing. After 45 pore volumes of the 1000 mg/L HA solution was flushed through the column, the highest arsenic concentration in the effluents was about 23,750 µg/L after a 15-pore-volume-flushing (Figure 8-3). The accumulative arsenic mobilization became relatively stable and reached 97 mg/kg (4.3%) after 70 pore volumes. In the case of the rhamnolipid solution, the highest arsenic concentration in the effluents, 30,000 µg/L, occurred after a 12 pore volume flushing (Figure 8-3), and the accumulative arsenic mobilization became relatively stable after a 55-pore-volume-flushing, and reached 148 mg/kg (6.6%) after a 70-pore-volume-flushing.

8.2 Metal mobilization

From the results of batch tests, it can be seen that arsenic mobilization from the mine tailings was closely correlated to the mobilization of metals. Therefore, the mobilization of the metals, Fe, Cu, Pb and Zn, during the column tests was also monitored, and the correlation between arsenic and metal mobilization was examined.

8.2.1 Fe mobilization

As shown in Figure 8-4, the highest average Fe concentrations in the effluents from sample 1 were 960 mg/L after 10 pore volumes of distilled water, 2,255 mg/L after 12 pore volumes of 1000 mg/L HA, and 3,690 mg/L after 12 pore volumes of 1000 mg/L rhamnolipid. The accumulative Fe mobilization reached 2,817 mg/kg (1.3%) after a 40-pore-volume-flushing with distilled water, 9,163 mg/kg (4.2%) after a 60-pore-volume-flushing with 1000 mg/L HA, and 13,676 mg/kg (6.3%) after a 45-pore-volume-flushing-with 1000 mg/L rhamnolipid, respectively.

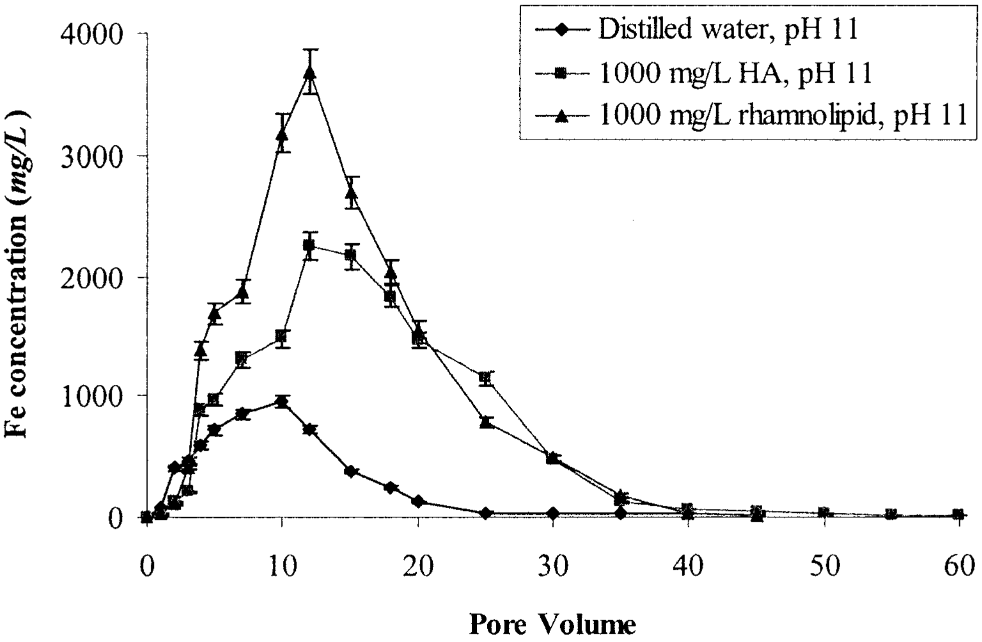


Figure 8-4. Average Fe concentrations in the effluent from sample 1

As for sample 2, the highest average Fe concentration in the effluents by distilled water reached 1,610 mg/L after a 7-pore-volume-flushing (Figure 8-5), and the accumulative Fe mobilization became relatively stable after 20 pore volumes, and reached 2,904 mg/kg (1.6%) after a 30-pore-volume-flushing. When the HA solution was flushed through the column, the highest Fe concentration in the effluents reached 2,285 mg/L after a 18-pore-volume-flushing (Figure 8-5), and the accumulative Fe mobilization became relatively stable after 35 pore volumes and reached 6,650 mg/kg (3.7%) after 70 pore volumes. When the rhamnolipid solution was used as a flushing agent, the highest average Fe concentration in the effluents was 2,193 mg/L after a 18-pore-volume-flushing (Figure 8-5), and the accumulative Fe mobilization became stable after 35 pore volumes and reached 8,729 mg/kg (4.8%) after 60 pore volumes.

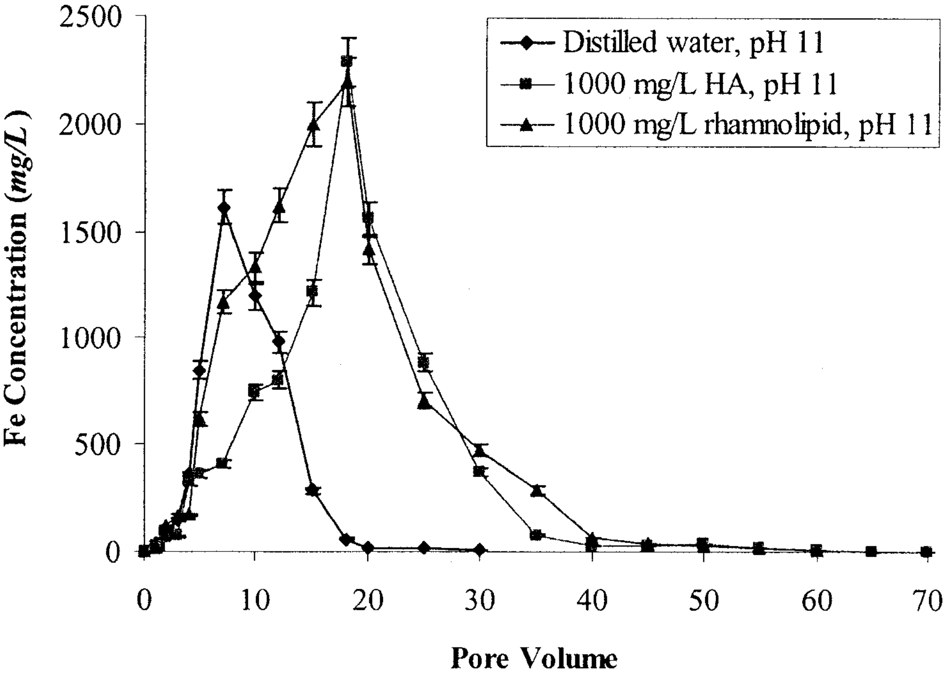


Figure 8-5. Average Fe concentrations in the effluent from sample 2

In the case of sample 3, when distilled water was flushed through the column, the highest average Fe concentration in the effluents was 1,925 mg/L after 12 pore volumes (Figure 8-6), and the accumulative Fe mobilization reached 4,089 mg/kg (1.7%) after a 35-pore-volume-flushing. When the 1000 mg/L HA solution was flushed through the column, the highest average Fe concentration in the effluent was 2,730 mg/L after a 15-pore-volume-flushing (Figure 8-6), and the accumulative Fe mobilization became relatively stable after 55 pore volumes and reached 10,219 mg/kg (4.3%) after 70 pore volumes. In the case of the flushing solution of 1000 mg/L rhamnolipid, the highest average Fe concentration in the effluents reached 2,520 mg/L after an 18-pore-volume-flushing (Figure 8-6). The accumulative Fe mobilization increased with pore volume numbers and became relatively stable after 60 pore volumes. Final mobilization reached to 13,461 mg/kg (5.7%) after a 70-pore-volume-flushing.

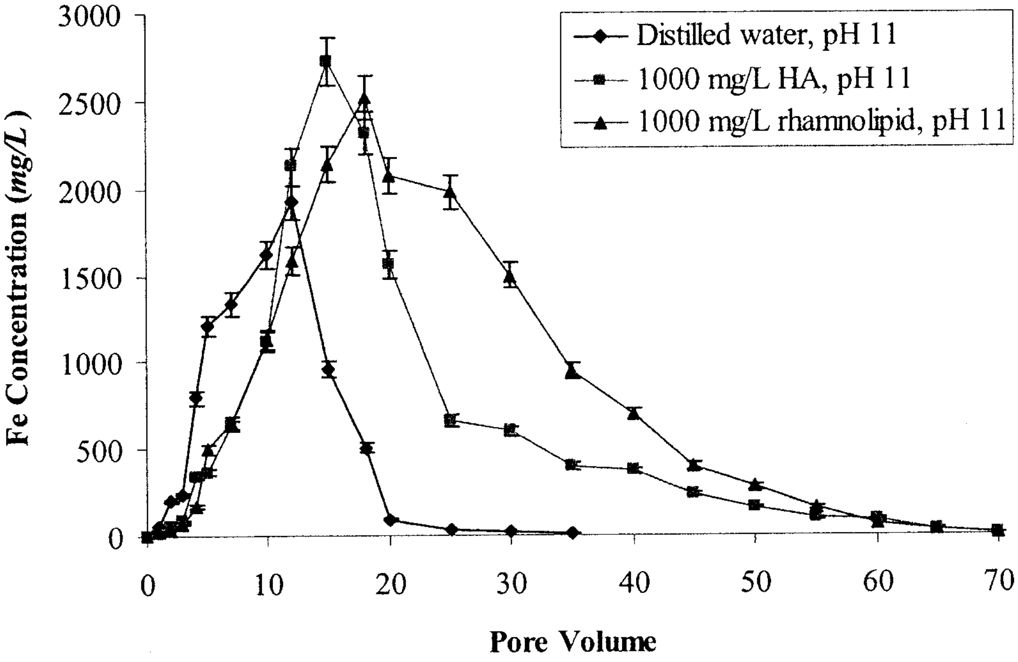


Figure 8-6. Average Fe concentrations in the effluent from sample 3

Similar to the observation in batch tests, arsenic mobilization from the mine tailings was closely related to Fe mobilization. The correlation between arsenic and Fe concentrations in the effluents is illustrated in Figures 8-7 to 8-9. The correlation coefficients (R^2) between arsenic and Fe concentrations in the effluents varied from 0.8226 to 0.9716.

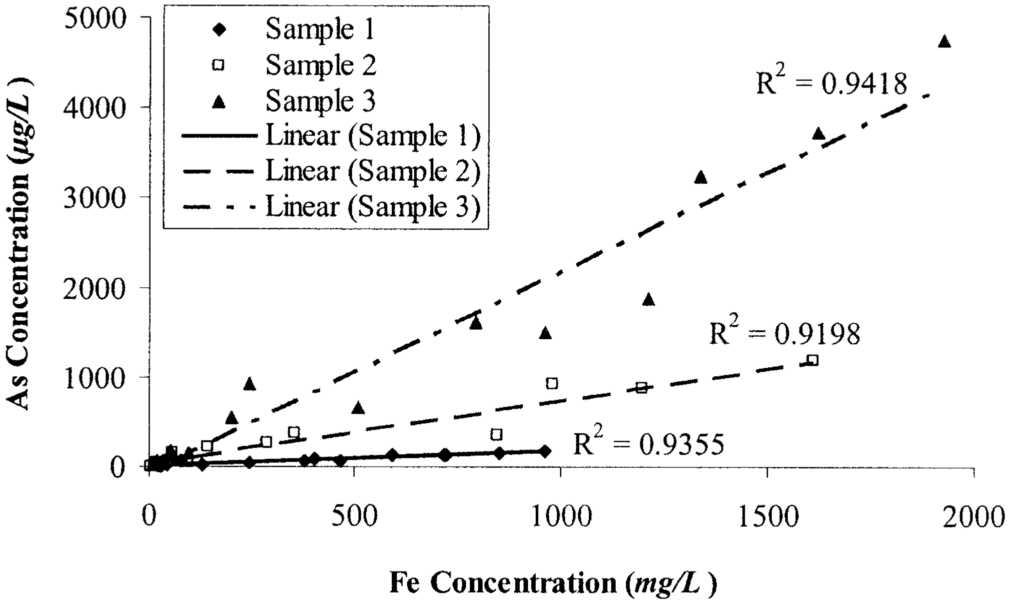


Figure 8-7. Correlation between arsenic and Fe concentrations in the effluents by distilled water (pH adjusted to 11)

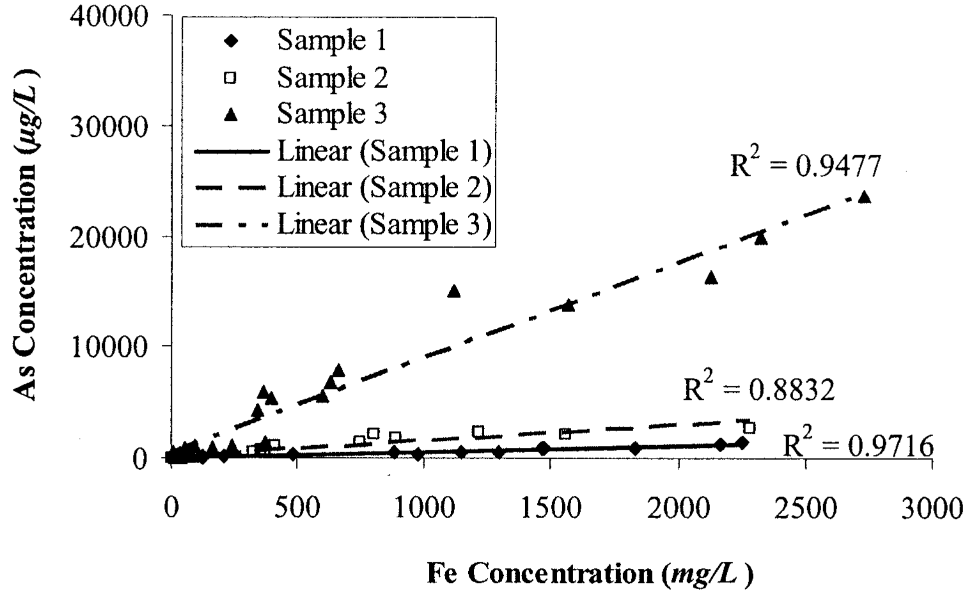


Figure 8-8. Correlation between arsenic and Fe concentrations in the effluents by 1000 mg/L HA (pH adjusted to 11)

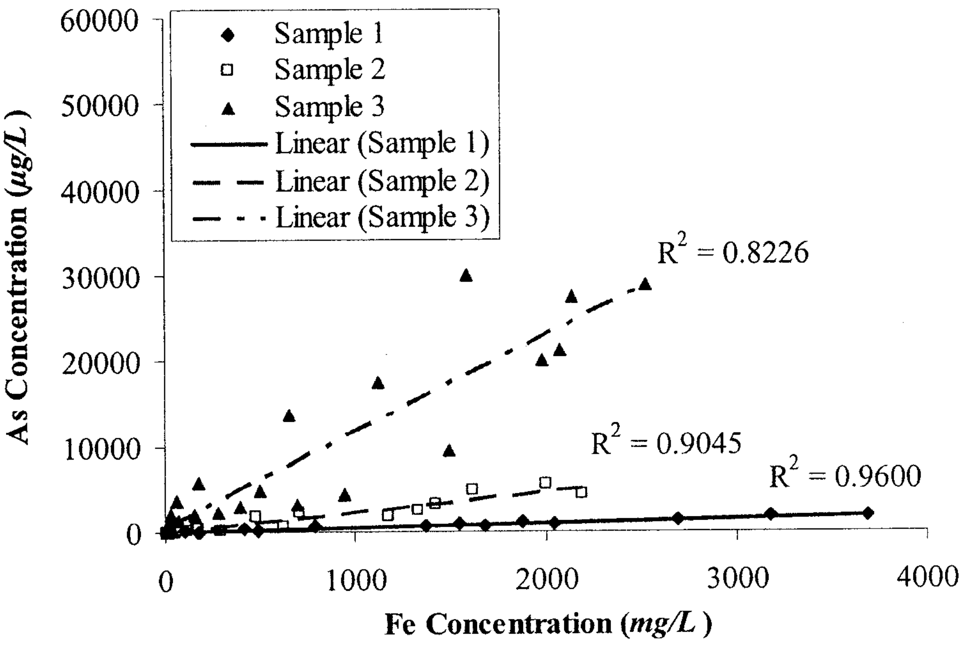


Figure 8-9. Correlation between arsenic and Fe concentrations in the effluents by 1000 mg/L rhamnolipid (pH adjusted to 11)

8.2.2 Pb mobilization

The average Pb concentrations in the effluents from sample 1 by the different flushing solutions are illustrated in Figure 8-10. When distilled water was used as the flushing solution, the highest average Pb concentration in the effluents was 2 mg/L after a 7- pore-volume-flushing, and those for the 1000 mg/L HA and rhamnolipid were 4 mg/L after a 12-pore-volume-flushing and 11 mg/L after a 15-pore-volume-flushing, respectively (Figure 8-10). The accumulative Pb mobilization by distilled water increased with pore volume numbers and became relatively stable after 18 pore volumes and reached 5 mg/kg (3.1%) after 40 pore volumes. Pb mobilization by the 1000 mg/L HA solution with an initial pH of 11 became relatively stable after 50 pore volumes and reached 18 mg/kg (10.6%). In the case of the flushing solution of 1000 mg/L rhamnolipid (pH 11), the accumulative Pb mobilization reached 43 mg/kg (25.3%) after a 40-pore-volume-flushing.

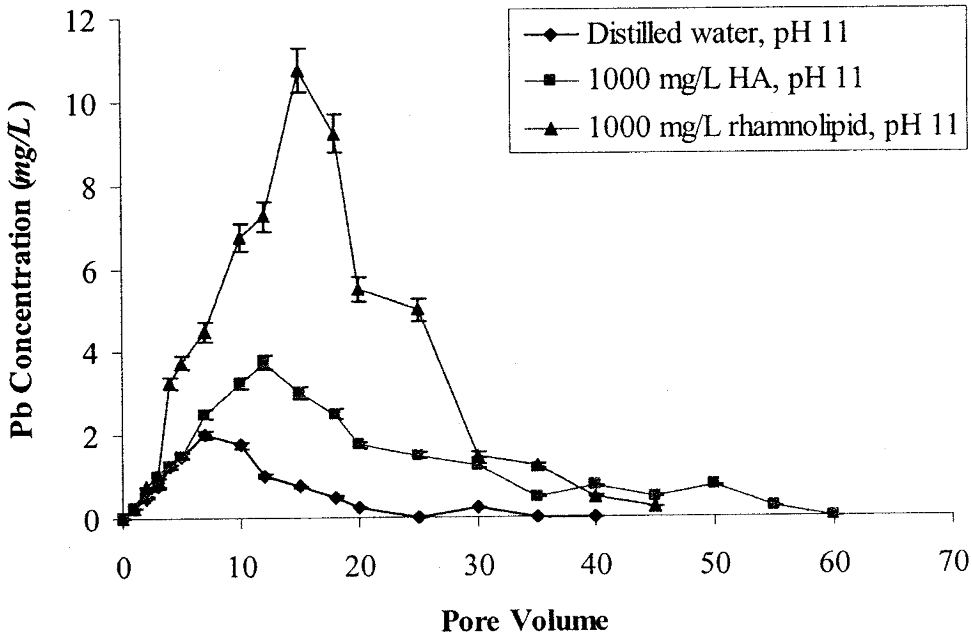


Figure 8-10. Average Pb concentrations in the effluent from sample 1

As for sample 2, when distilled water was flushed through the column, the highest average Pb concentration in the effluents reached 4.8 mg/L after a 7- pore-volume-flushing (Figure 8-11), and the accumulative Pb mobilization reached 13 mg/kg (6.0%) after a 30-pore-volume-flushing. When the solution of 1000 mg/L HA was used as the flushing solution, the highest average effluent Pb concentration was 6 mg/L after a 18-pore-volume-flushing (Figure 8-11), and the accumulative Pb mobilization increased gradually and became relatively stable after a 60-pore-volume-flushing. Final Pb mobilization reached 27 mg/kg (11.9%) after a 70-pore-volume-flushing. When the solution of 1000 mg/L rhamnolipid was flushed through the column, the highest average

Pb concentration in the effluents was around 9 mg/L after a 18-pore-volume-flushing (Figure 8-11), and the accumulative Pb mobilization reached 34 mg/kg (15.2%) after a 60-pore-volume-flushing.

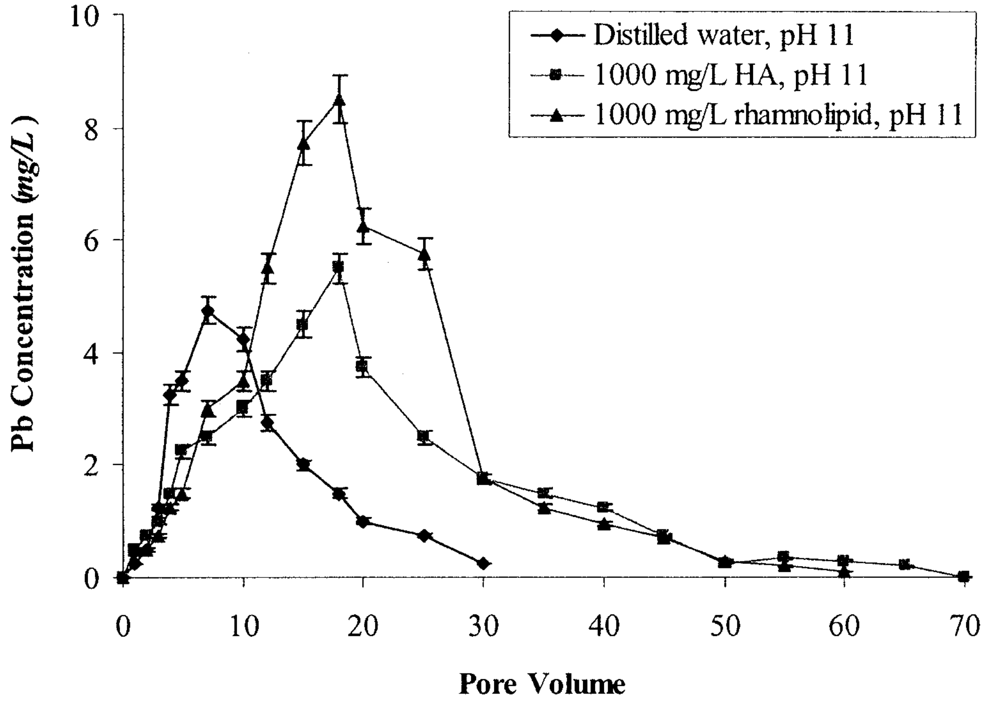


Figure 8-11. Average Pb concentrations in the effluent from sample 2

In the case of sample 3, when distilled water was flushed through the column, the highest average Pb concentration in the effluents was 116 mg/L after a 12-pore-volume-flushing (Figure 8-12), and the accumulative Pb mobilization reached 280 mg/kg (2.2%) after a 35-pore-volume-flushing. The accumulative Pb mobilization by the 1000 mg/L HA solution increased gradually with pore volume numbers and became relative stable after 55 pore volumes. Final Pb mobilization reached 838 mg/kg (6.5%) after 70 pore volumes. The highest Pb concentration in the effluents was 144 mg/L after a 15 pore volume flushing (Figure 8-12). When the solution of 1000 mg/L rhamnolipid was flushed through the column, the highest average Pb concentration in the effluents was 441 mg/L after a 18-pore-volume-flushing, and the accumulative Pb mobilization increased gradually and reached 2,379 mg/kg (18.5%) after a 70-pore-volume-flushing.

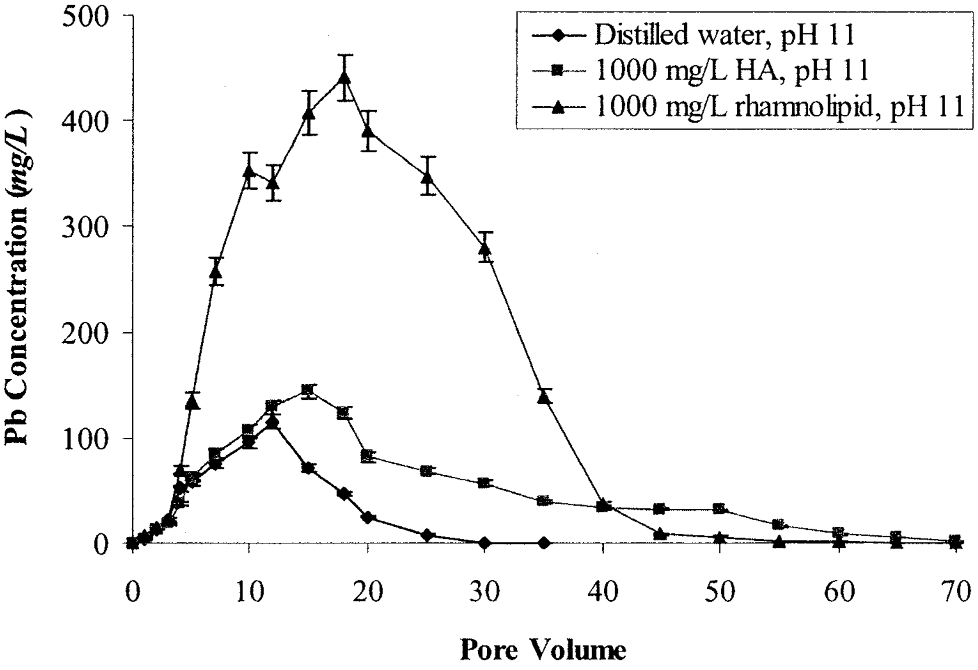


Figure 8-12. Average Pb concentrations in the effluent from sample 3

The correlation between arsenic and Pb mobilization from the mine tailing by the different flushing solutions is illustrated in Figures 8-13 to 8-15. The correlation coefficients varied from 0.7180 to 0.9261.

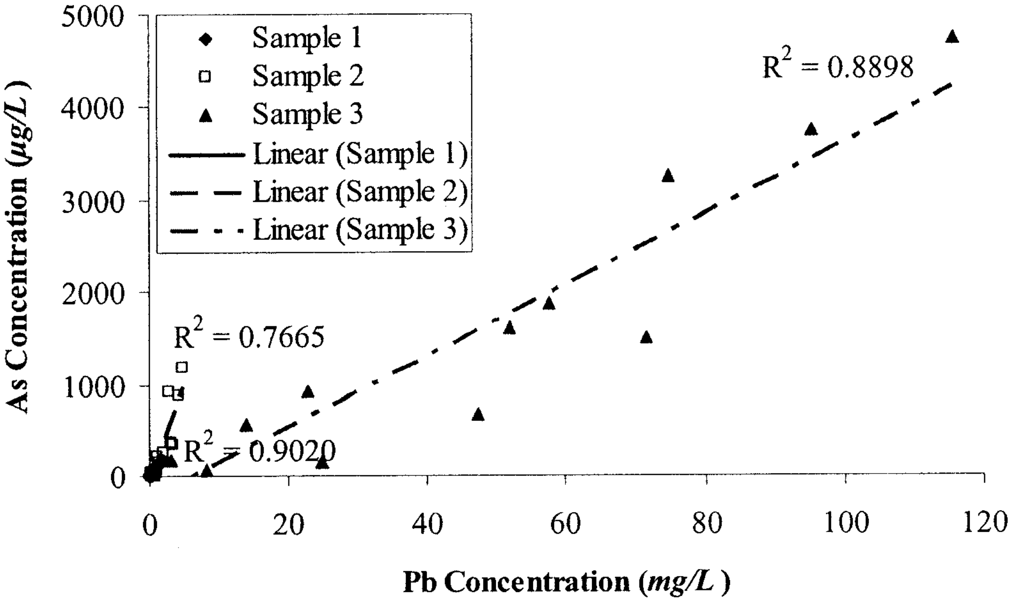


Figure 8-13. Correlation between arsenic and Pb concentrations in the effluents by distilled water (pH adjusted to 11)

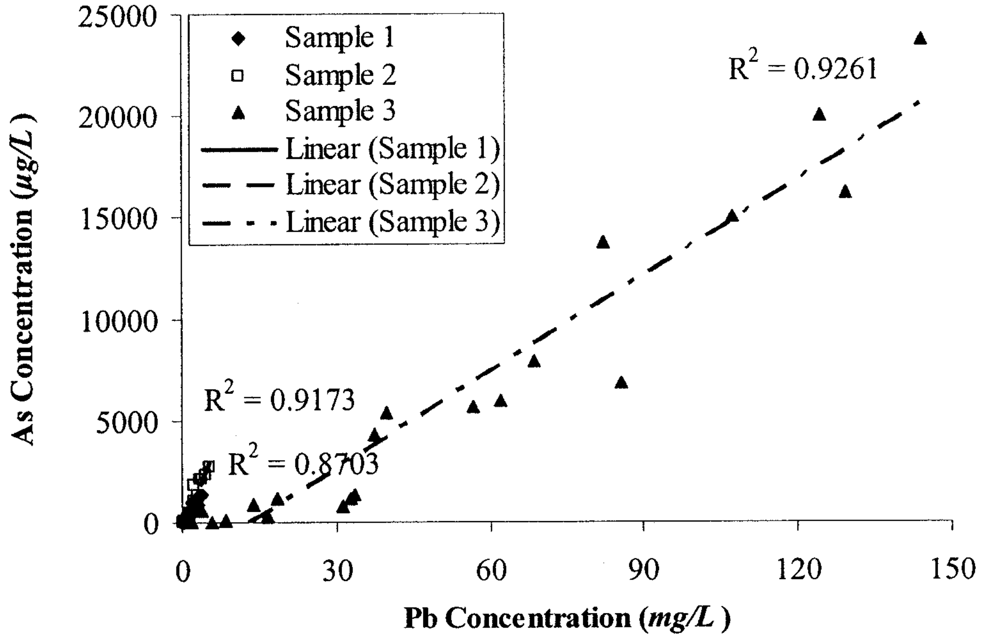


Figure 8-14. Correlation between arsenic and Pb concentrations in the effluents by 1000 mg/L HA (pH adjusted to 11)

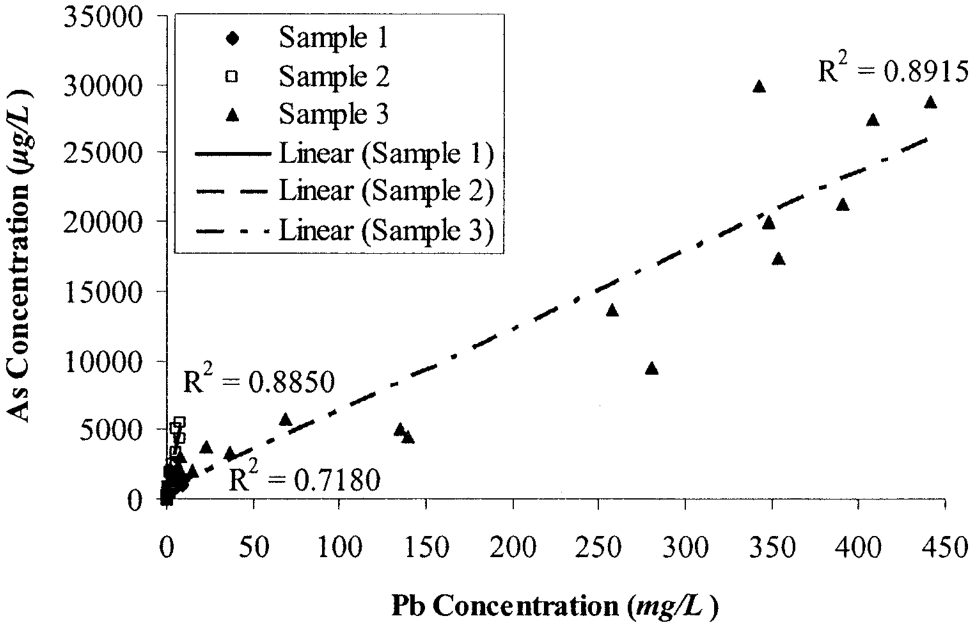


Figure 8-15. Correlation between arsenic and Pb concentrations in the effluents by 1000 mg/L rhamnolipid (pH adjusted to 11)

8.2.3 Cu mobilization

The average Cu concentrations in the effluent from the mine tailing sample 1 by the different flushing solutions are illustrated in Figure 8-16. Distilled water alone mobilized 4 mg Cu/kg (3.3%) after a 40-pore-volume-flushing. The highest average Cu concentration in the effluents was 1 mg/L after a 12-pore-volume-flushing (Figure 8-16). When the solution of 1000 mg/L HA was flushed through the column, the highest average Cu concentration in the effluents reached 4 mg/L after a 15-pore-volume-flushing (Figure 8-16), and the accumulative Cu mobilization increased gradually to 18 mg/kg (14.2%) after a 70-pore-volume-flushing. When the solution of 1000 mg/L rhamnolipid was used as the flushing solution, the highest Cu concentration in the effluents was 5 mg/L after a 12-pore-volume-flushing (Figure 8-16), and Cu mobilization increased gradually with pore volume numbers and reached 20 mg/kg (16.1%) after a 45-pore-volume-flushing.

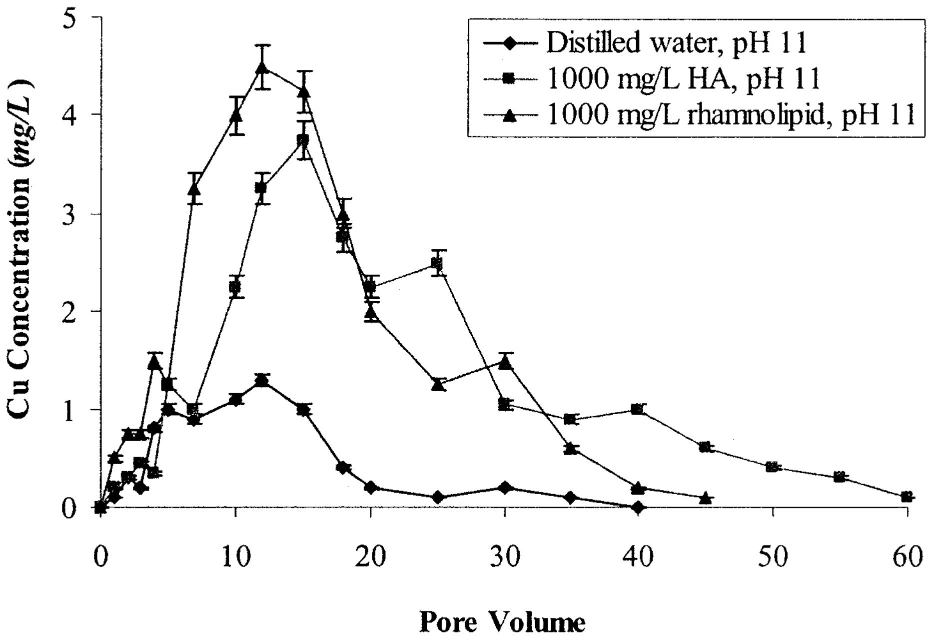


Figure 8-16. Average Cu concentrations in the effluent from sample 1

The average Cu concentrations in the effluent from sample 2 by the different flushing solutions are illustrated in Figure 8-17. Cu mobilization by distilled water increased gradually with the flushed pore volume numbers and was 13 mg/kg (1.9%) after a 30-pore-volume-flushing. The highest average Cu concentration in the effluents was 4 mg/L after 7 pore volume flushing (Figure 8-17). When the solution of 1000 mg/L HA was flushed through the column, the highest Cu concentration in the effluents was 6 mg/L after a 7-pore-volume-flushing (Figure 8-17). The accumulative Cu mobilization increased with pore volume numbers and became relatively stable after a 50-pore-volume-flushing, and final Cu mobilization reached 36 mg/kg (5.4%) after a 70-pore-volume-flushing. When the solution of 1000 mg/L rhamnolipid was used as the flushing solution, the highest average Cu concentration in the effluents was 29 mg/L after a 12-pore-volume-flushing (Figure 8-17), and the accumulative Cu mobilization increased gradually to 142 mg/kg (21.5%) after a 60-pore-volume-flushing.

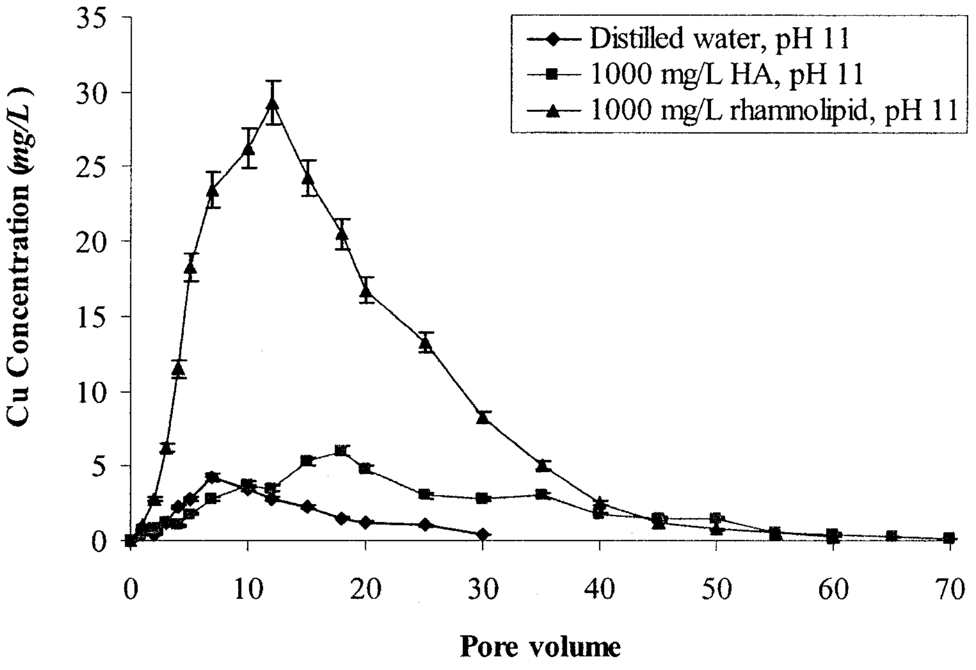


Figure 8-17. Average Cu concentrations in the effluent from sample 2

In the case of sample 3, distilled water mobilized 15 mg Cu/kg (2.8%) after a 35-pore-volume-flushing. The highest average Cu concentration in the effluents was 6 mg/L after a 12-pore-volume-flushing (Figure 8-18). When the HA solution was flushed through the column, the highest Cu concentration in the effluents was 8 mg/L after a 15-pore-volume-flushing (Figure 8-18), and Cu mobilization became relatively stable after a 45-pore-volume-flushing and reached 35 mg/kg (6.5%) after a 70-pore-volume-flushing. When the rhamnolipid solution was used as the flushing solution, the highest Cu concentration in the effluents reached 14 mg/L after a 18-pore-volume-flushing (Figure 8-18), and the accumulative Cu mobilization increased gradually with pore volume and became relatively after a 35-pore-volume-flushing and reached 74 mg/kg (13.9%) after a 70-pore-volume-flushing.

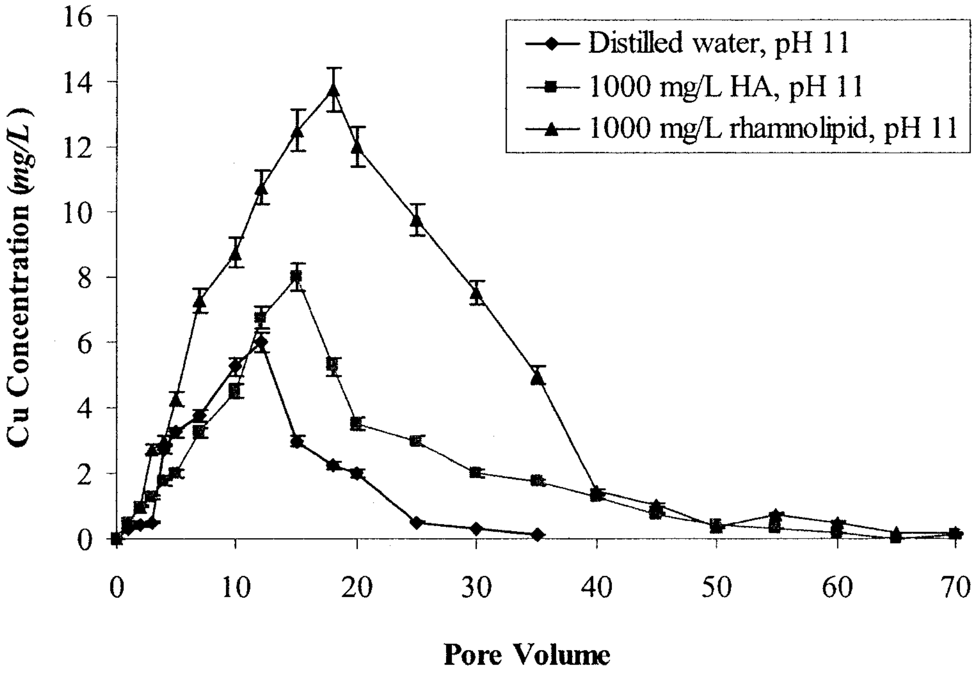


Figure 8-18. Average Cu concentrations in the effluent from sample 3

The correlations between arsenic and Cu mobilization from the mine tailings by the different flushing solutions are illustrated in Figures 8-19 to 8-21. The correlation coefficients were 0.6704 to 0.9336.

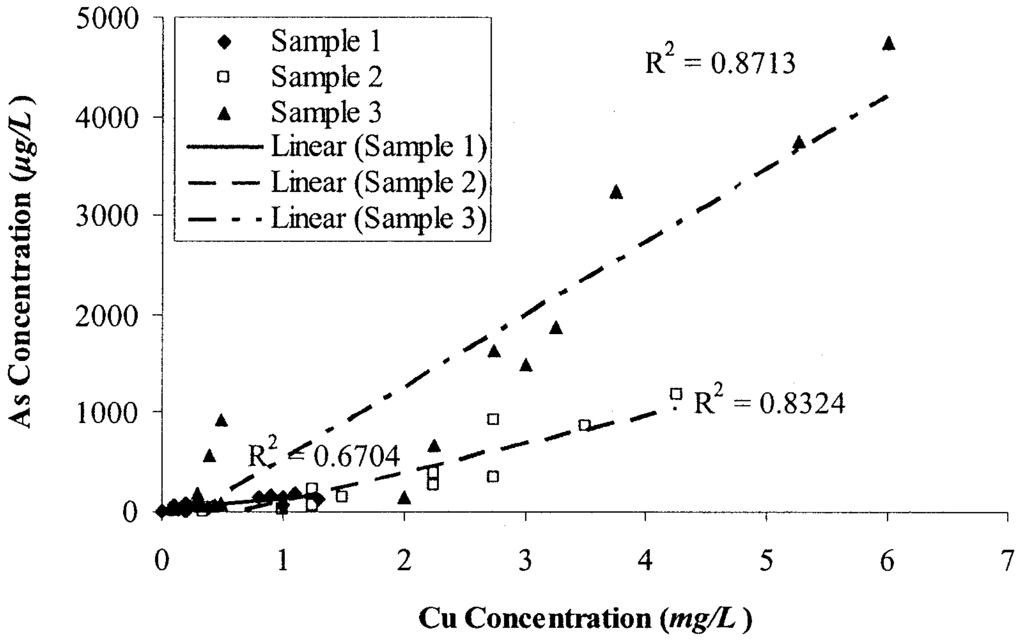


Figure 8-19. Correlation between arsenic and Cu concentrations in the effluents by distilled water (pH adjusted to 11)

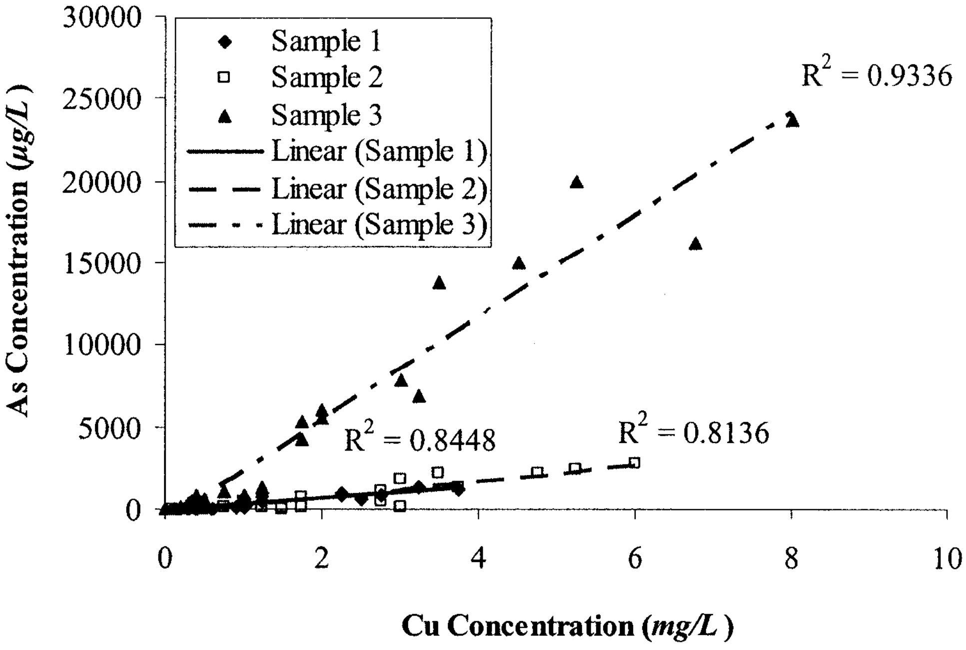


Figure 8-20. Correlation between arsenic and Cu concentrations in the effluents by 1000 mg/L HA (pH adjusted to 11)

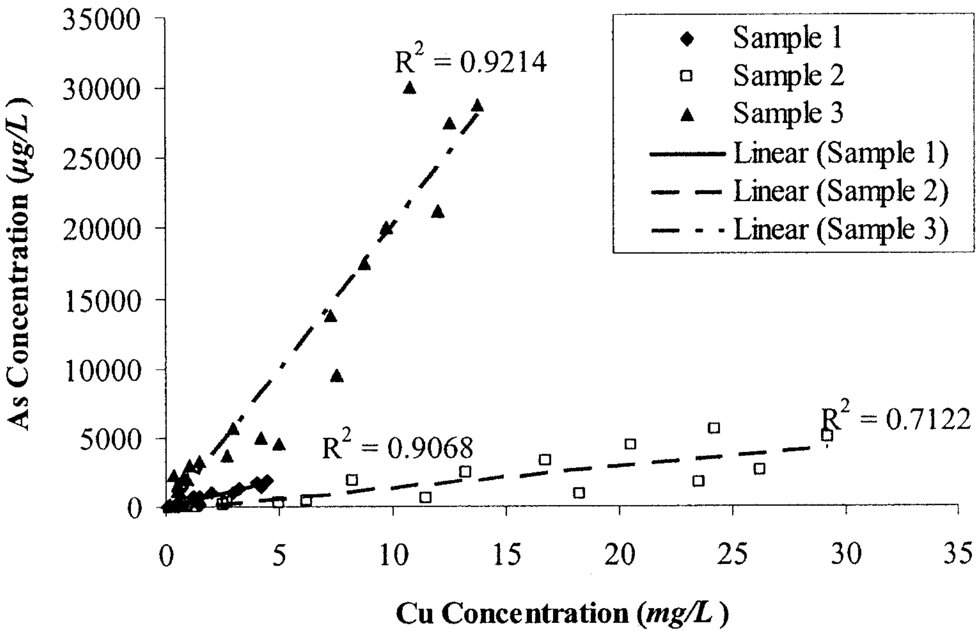


Figure 8-21. Correlation between arsenic and Cu concentrations in the effluents by 1000 mg/L rhamnolipid (pH adjusted to 11)

8.2.4 Zn mobilization

The average Zn concentrations in the effluents from sample 1 are illustrated in Figure 8-22. Distilled water mobilized 6 mg Zn/kg (4.8%) after a 40-pore-volume-flushing. The highest average Zn concentration in the effluents was 2 mg/L after a 10-pore-volume-flushing (Figure 8-22). When the HA solution was flushed through the column, the highest average Zn concentration in the effluents was 4 mg/L after a 12-pore-volume-flushing (Figure 8-22), and the accumulative Zn mobilization increased gradually and became relatively after a 40-pore-volume-flushing, and final Zn mobilization reached 15 mg/kg (12.9%) after a 60-pore-volume-flushing. When the rhamnolipid solution was used as the flushing solution, the highest average Zn concentration in the effluents was 7 mg/L after a 7-pore-volume-flushing (Figure 8-22), and the accumulative Zn mobilization increased gradually and reached 29 mg/kg (24.9%) after a 45-pore-volume-flushing.

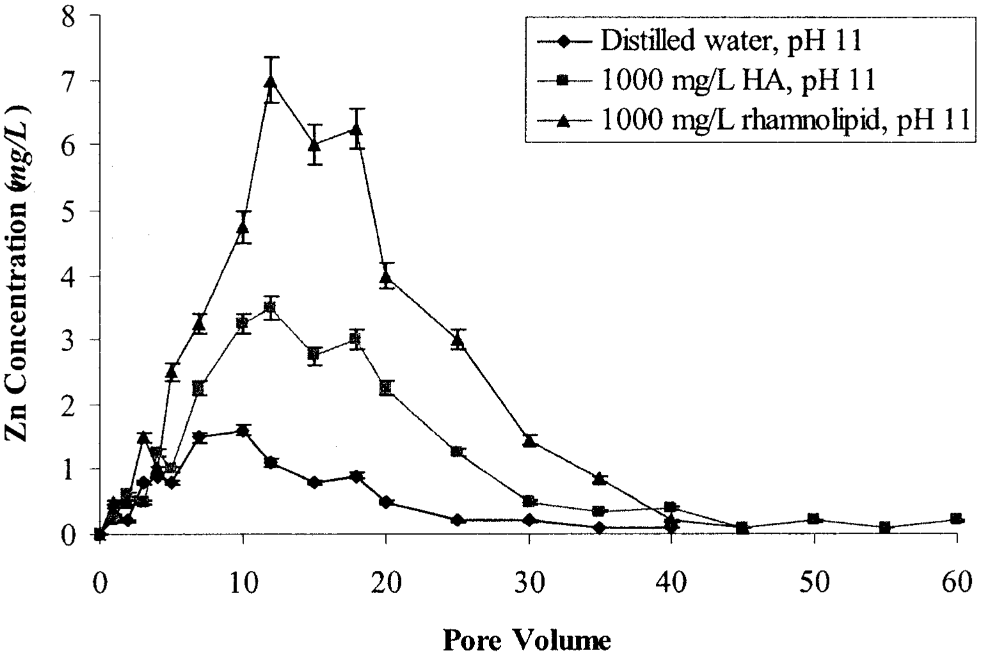


Figure 8-22. Average Zn concentrations in the effluent from sample 1

When distilled water was flushed through the column loaded with the mine tailing sample 2, the highest average Zn concentration in the effluents was 26 mg/L after a 7-pore-volume-flushing (Figure 8-23), and the accumulative Zn mobilization reached 56 mg/kg (2.2%) after a 30-pore-volume-flushing. When the HA solution was used as the flushing solution, the highest average Zn concentration in the effluents reached 87 mg/L after a 18-pore-volume-flushing (Figure 8-23), and the accumulative Zn mobilization increased gradually and became relatively stable after a 40-pore-volume-flushing, and reached 438 mg/kg (17.4%) after a 70-pore-volume-flushing. In the case that the rhamnolipid solution was flushed through the column, the highest Zn concentration in the effluents was 122 mg/L after a 15-pore-volume-flushing (Figure 8-23), and the accumulative Zn mobilization increased gradually and became relatively after a 30-pore-volume-flushing, and reached 561 mg/kg (22.3%) after a 60-pore-volume-flushing.

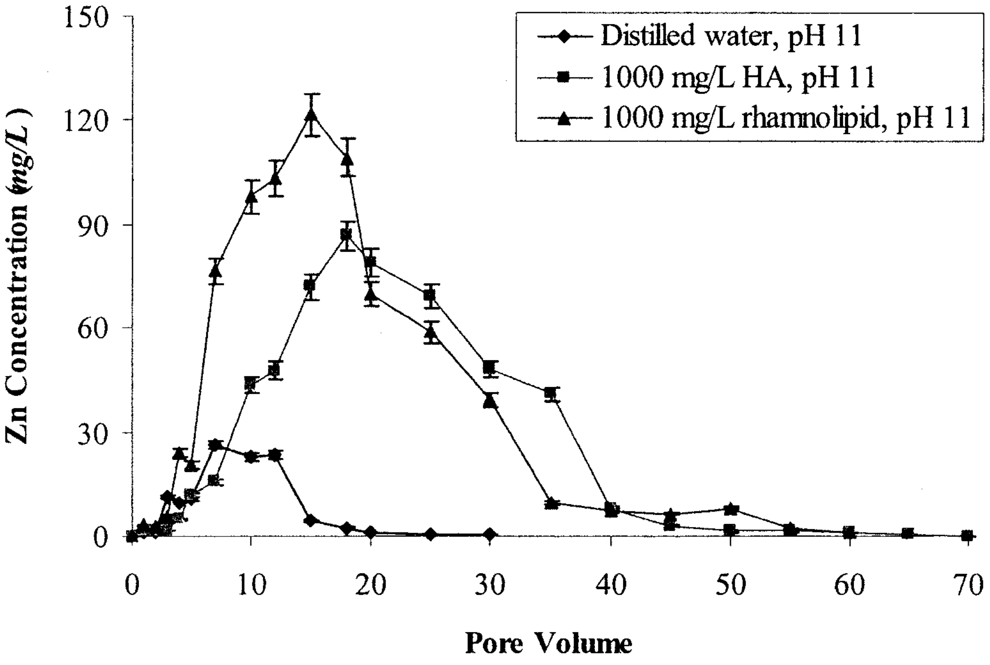


Figure 8-23. Average Zn concentrations in the effluent from sample 2

In the case of sample 3, distilled water mobilized 63 mg Zn/kg (3.5%) after a 35-pore-volume-flushing. The highest average Zn concentration in the effluents was 25 mg/L after a 12-pore-volume-flushing (Figure 8-24). When the HA solution was flushed through the column, the highest average Zn concentration in the effluents reached 42 mg/L after a 15-pore-volume-flushing (Figure 8-24), and the accumulative Zn mobilization increased gradually, became relatively stable after a 50-pore-volume-flushing, and reached 224 mg/kg (12.4%) after a 70-pore-volume-flushing. When the rhamnolipid solution was used as the flushing solution, the highest average Zn concentration in the effluents was 54 mg/L after a 18-pore-volume-flushing (Figure 8-24), and the accumulative Zn mobilization increased gradually and became relatively stable after a 30-pore-volume-flushing. Final Zn mobilization reached 259 mg/kg (14.4%) after a 70-pore-volume-flushing.

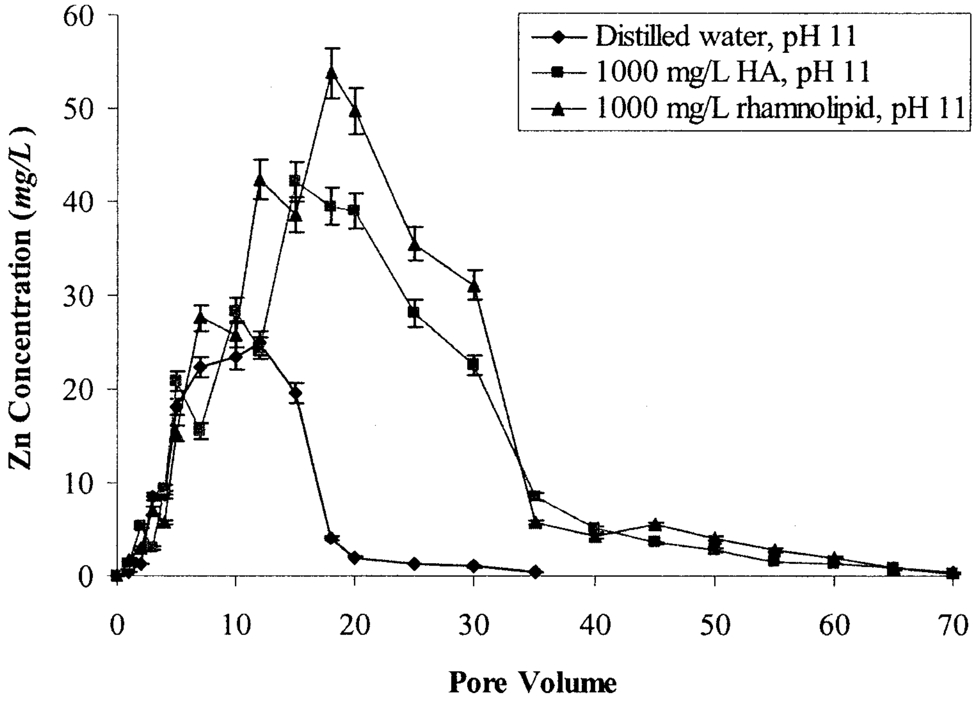


Figure 8-24. Average Zn concentrations in the effluent from sample 3

The correlations between arsenic and Zn concentrations in the effluents by the different flushing solutions are illustrated in Figures 8-25 to 8-27. The correlation coefficients between arsenic and Zn concentrations in the effluents ranged between 0.7202 and 0.9538.

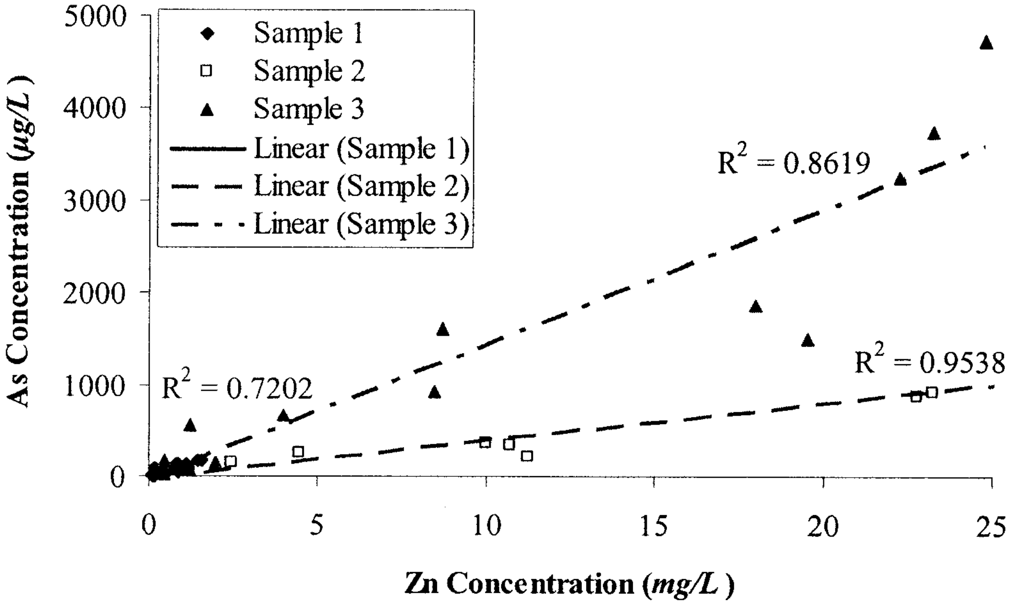


Figure 8-25. Correlation between arsenic and Zn concentrations in the effluents from by distilled water (pH adjusted to 11)

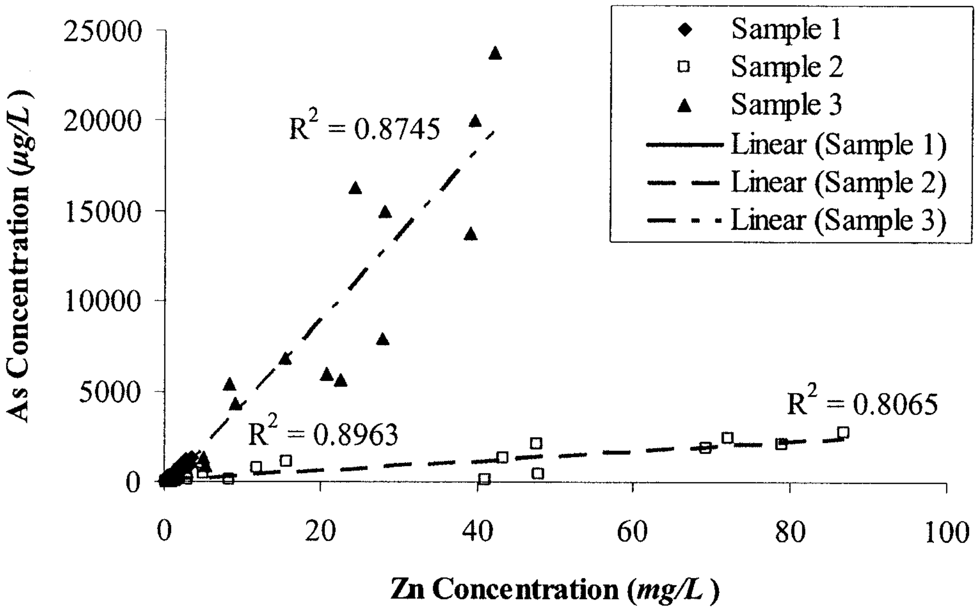


Figure 8-26. Correlation between arsenic and Zn concentrations in the effluents by 1000 mg/L HA (pH adjusted to 11)

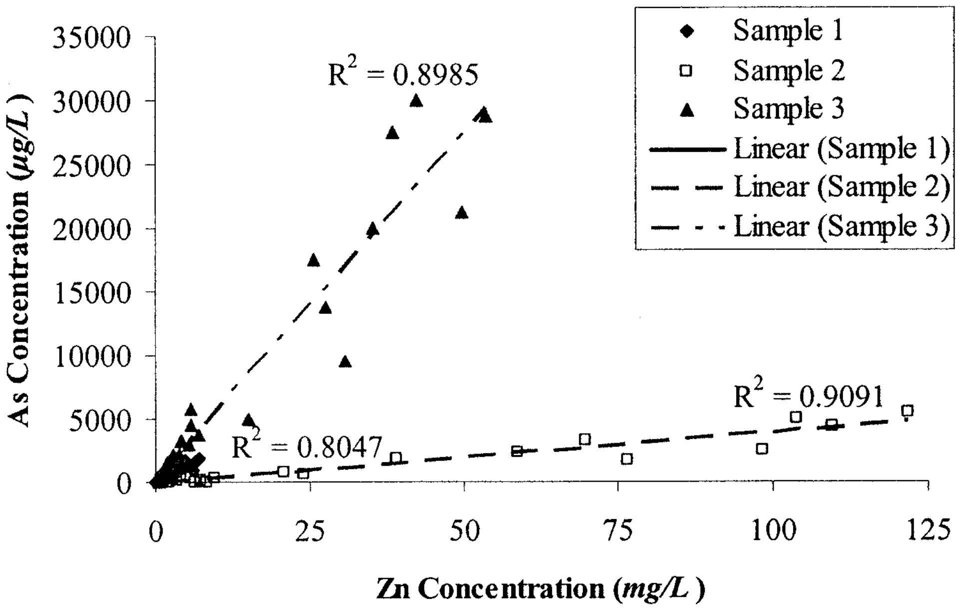


Figure 8-27. Correlation between arsenic and Zn concentrations in the effluents by 1000 mg/L rhamnolipid (pH adjusted to 11)

8.2.5 Correlations between metal mobilizations

The correlation coefficients between the concentrations of the heavy metals and Fe in the effluents by different flushing solutions from the mine tailings are summarized in Table 8-1. The mobilization of the heavy metals from the mine tailings is closely related to the mobilization of Fe and a good correlation was found between the concentrations of the heavy metals (Cu, Pb and Zn) mobilized in the effluents.

Moreover, the correlation coefficients between the mobilized heavy metals (Cu, Pb, and Zn) concentrations in the effluents by the different flushing solutions ranged from 0.5922 to 0.9785 (Table 8-1). The correlation may give some indications on the interaction among the heavy metals during the mobilization processes.

Table 8-1. Correlation coefficients between the co-mobilized elements from the mine tailings during column experiments

Flushing solution	Correlation coefficients (R^2)									
	As-Fe	As-Cu	As-Pb	As-Zn	Cu-Fe	Pb-Fe	Zn-Fe	Cu-Pb	Cu-Zn	Pb-Zn
	Sample 1									
Distilled water	0.9355	0.6704	0.9020	0.7202	0.7556	0.9206	0.8506	0.6832	0.6659	0.8160
1000 mg/L HA	0.9716	0.8448	0.8703	0.8963	0.8296	0.8879	0.9135	0.7238	0.7180	0.9227
1000 mg/L rhamnolipid	0.9600	0.9068	0.7180	0.8047	0.9076	0.7390	0.8231	0.7774	0.8424	0.8935
	Sample 2									
Distilled water	0.9198	0.8324	0.7665	0.9538	0.8683	0.8396	0.8811	0.9525	0.7832	0.7514
1000 mg/L HA	0.8832	0.8136	0.9173	0.8065	0.8078	0.8734	0.8063	0.9094	0.8736	0.7912
1000 mg/L rhamnolipid	0.9045	0.7122	0.8850	0.9091	0.7899	0.8810	0.9394	0.5922	0.8359	0.8321
	Sample 3									
Distilled water	0.9418	0.8713	0.8898	0.8619	0.9305	0.9495	0.9220	0.9613	0.8170	0.8796
1000 mg/L HA	0.9477	0.9336	0.9261	0.8745	0.9124	0.8755	0.7865	0.9386	0.7584	0.8202
1000 mg/L rhamnolipid	0.8226	0.9214	0.8915	0.8985	0.9018	0.8874	0.8799	0.9785	0.9452	0.9295

8.3 Residual arsenic concentrations

After the column tests, the columns flushed by the solutions of 1000 mg/L HA and rhamnolipid (pH 11) were chosen to analyze the residual arsenic concentrations in the mine tailings. From the influent to the effluent end, the mine tailings in the column were divided equally into five layers numbered from 1 to 5. Samples were taken from each of the layers (depth: 3 cm; D: 1.5 cm) and a total of five samples were taken. The residual arsenic concentrations in the samples were then determined.

The average arsenic concentrations in the mine tailing sample 1 along the column length after flushing with 1000 mg/L HA and rhamnolipid are illustrated in Figure 8-28. In the column flushed with the 1000 mg/L HA solution, the residual arsenic concentrations in the five samples in the mine tailings varied from 50 mg/kg to 60 mg/kg. The average arsenic concentration in the mine tailings was 55 mg/kg. In the column flushed with the 1000 mg/L rhamnolipid solution, the arsenic concentrations were in the range of 47 mg/kg to 58 mg/kg in the five samples. The average arsenic concentration in the mine tailings was 54 mg/kg.

The average residual arsenic concentrations in the mine tailing sample 2 along the column depth after flushed with the 1000 mg/L HA and rhamnolipid solutions are illustrated in Figure 8-29. In the column flushed with the 1000 mg/L HA solution, the arsenic concentrations in the five samples ranged from 237 mg/kg to 260 mg/kg. The average arsenic concentration in the mine tailings was 251 mg/kg. In the column flushed with the 1000 mg/L rhamnolipid solution, the arsenic concentrations in the five samples ranged from 212 mg/kg to 255 mg/kg, with an average of 241 mg/kg.

The average residual arsenic concentrations in the mine tailing sample 3 along the column depth after flushed with the 1000 mg/L HA and rhamnolipid solutions are illustrated in Figure 8-30. In the column flushed with the 1000 mg/L HA solution, the arsenic concentrations in the five samples ranged from 2025 mg/kg to 2225 mg/kg, with an average arsenic concentration of 2145 mg/kg in the mine tailings. In the column flushed with the 1000 mg/L rhamnolipid solution, the arsenic concentrations in the five samples ranged from 2000 mg/kg to 2200 mg/kg, with an average arsenic concentration of 2105 mg/kg in the mine tailings.

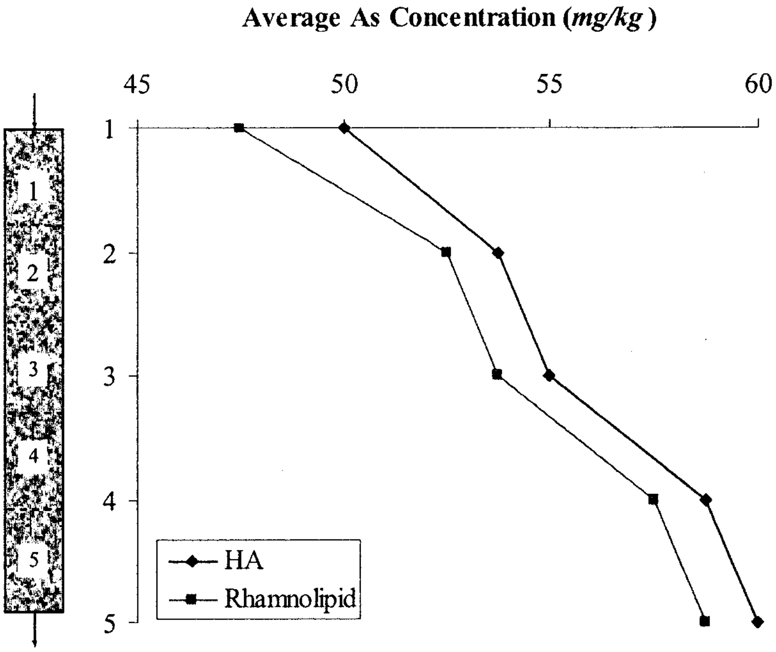


Figure 8-28. Average residual arsenic concentrations in sample 1 after flushing

[Sample cylinder size: 3 cm (depth) ×1.5 cm (diameter)]

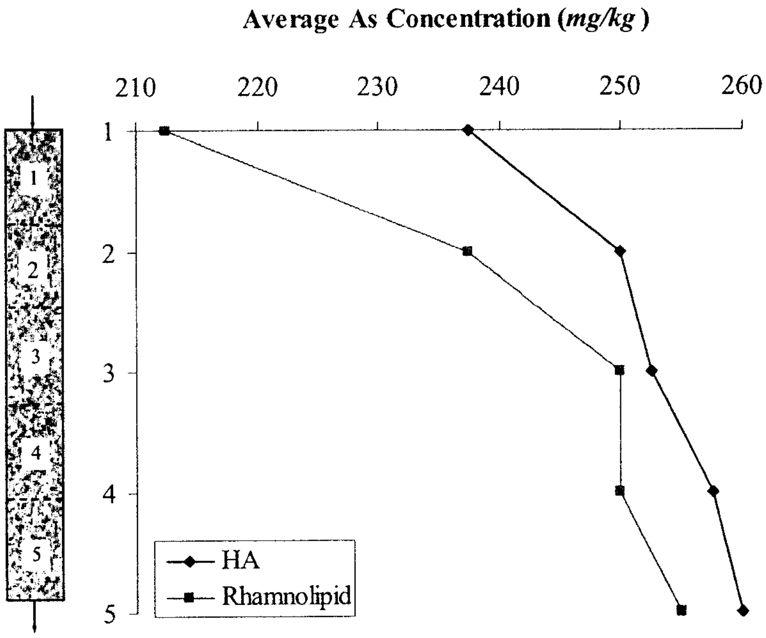


Figure 8-29. Average residual arsenic concentrations in sample 2 after flushing

[Sample cylinder size: 3 cm (depth) ×1.5 cm (diameter)]

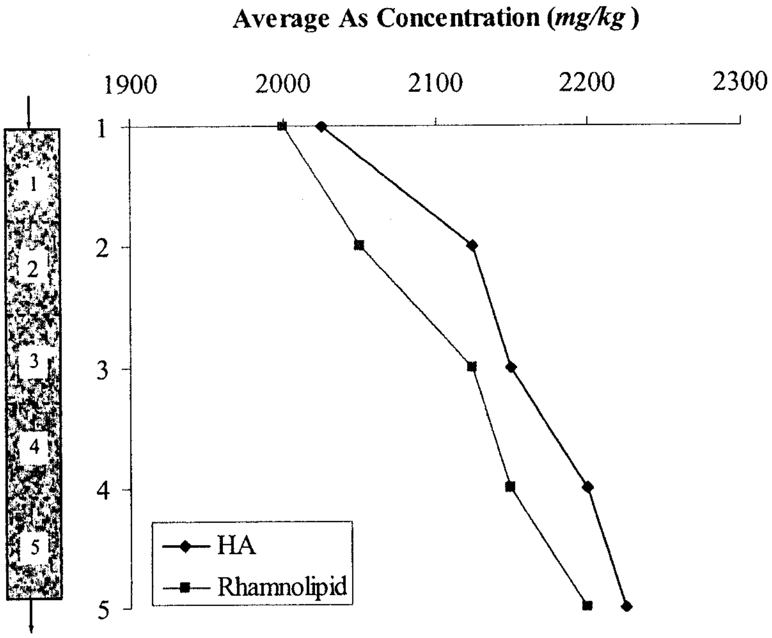


Figure 8-30. Average residual arsenic concentrations in sample 3 after flushing

[Sample cylinder size: 3 cm (depth) ×1.5 cm (diameter)]

Generally, the residual arsenic concentrations increased with depth in the column. This may be due to the re-adsorption of arsenic during the moving process along with the column length, though the re-adsorption might be partially minimized by the continuous flushing process.

8.4 Mass balance check

Based on the average arsenic concentrations in the mine tailings after flushing, the mass balances during the flushing experiments were checked. The mass balance coefficients are summarized in Table 8-2. It can be seen that the mass balances were maintained during the column experiments.

Table 8-2. Mass balance coefficients for the chosen column experiments

Flushing solutions	Mass balance coefficients		
	Sample 1	Sample 2	Sample 3
HA	0.997	1.001	0.996
Rhamnolipid	1.004	0.997	1.001

8.5 Summary of column experiments and preliminary discussion

The mobilization of arsenic and other metals in the column experiments is summarized in Table 8-3. The use of HA and rhamnolipid in column experiments enhanced arsenic mobilization greatly compared to that by distilled water. It indicated that HA and rhamnolipid might be used potentially to enhance the removal of arsenic and heavy metals from contaminated mine tailings or soils.

Table 8-3. Summary of the mobilization of arsenic, Fe, Cu, Pb and Zn from the mine tailings

Flushing solution	As		Fe		Cu		Pb		Zn	
	Mass mobilized (mg/kg)	Percentage	Mass mobilized (mg/kg)	Percentage	Mass mobilized (mg/kg)	Percentage	Mass mobilized (mg/kg)	Percentage	Mass mobilized (mg/kg)	Percentage
Sample 1										
Distilled water	0.6	1.0	2,817	1.3	4	3.3	5	3.1	6	4.8
1000 mg/L HA	6	9.1	9,163	4.2	18	14.2	18	10.6	15	12.9
1000 mg/L rhamnolipid	8	12.3	13,676	6.3	20	16.1	43	25.3	29	24.9
Sample 2										
Distilled water	2	0.9	2,904	1.6	13	1.9	13	6.0	56	2.2
1000 mg/L HA	11	4.3	6,650	3.7	36	5.4	27	11.9	438	17.4
1000 mg/L rhamnolipid	21	7.9	8,729	4.8	142	21.5	34	15.2	561	22.3
Sample 3										
Distilled water	10	0.4	4,089	1.7	15	2.8	280	2.2	63	3.5
1000 mg/L HA	97	4.3	10,219	4.3	35	6.5	838	6.5	224	12.4
1000 mg/L rhamnolipid	148	6.6	13,461	5.7	74	13.9	2379	18.5	259	14.4

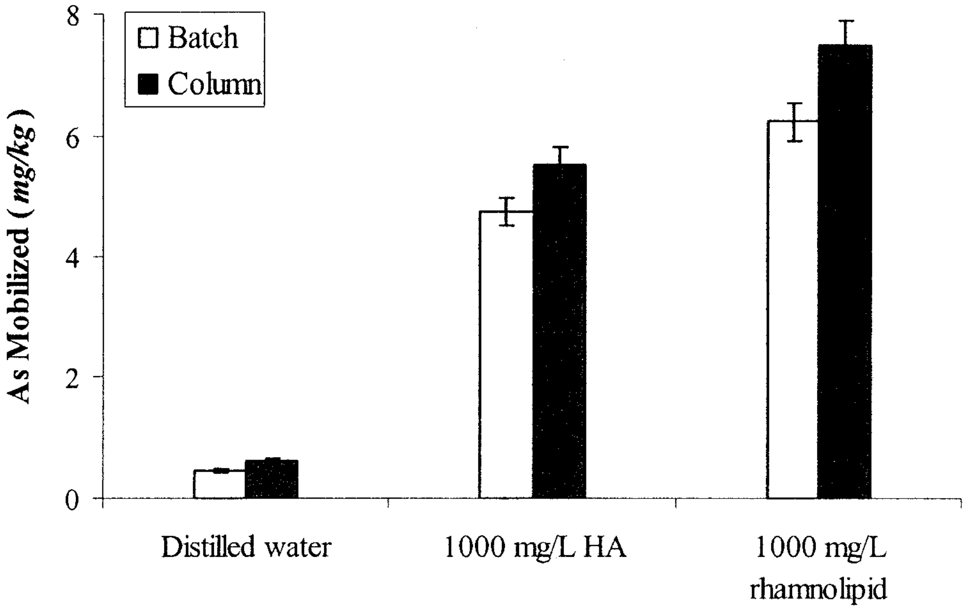


Figure 8-31. Arsenic mobilization from sample 1 in batch and column experiments

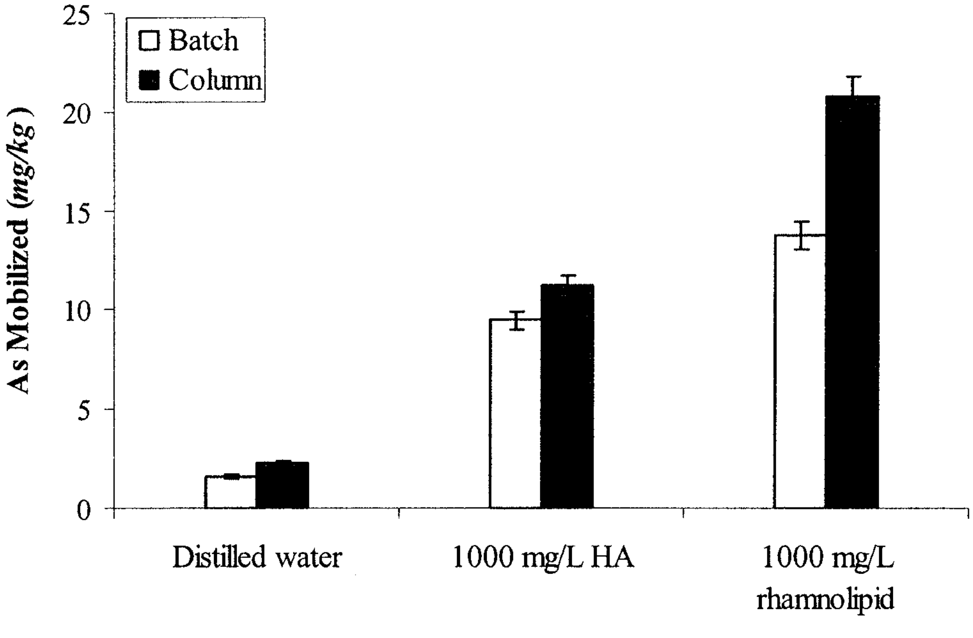


Figure 8-32. Arsenic mobilization from sample 2 in batch and column experiments

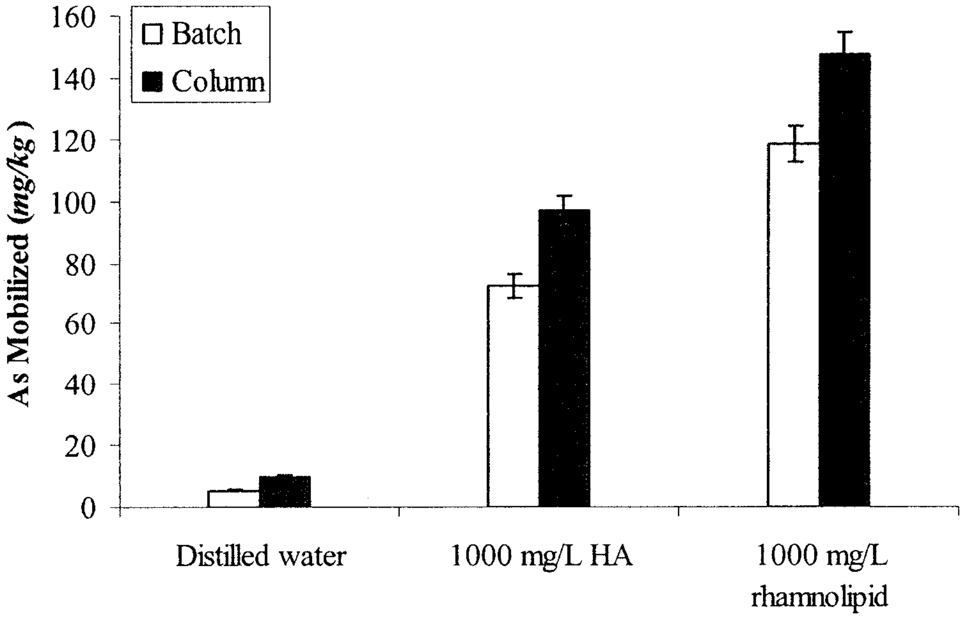


Figure 8-33. Arsenic mobilization from sample 3 in batch and column experiments

Consistent to the observation in batch tests, rhamnolipid was more efficient than HA to remove arsenic and heavy metals, due to its efficiency to lower interfacial tension, formation of more soluble complexes or micelles, and greater capacity to mobilize metals. The mobilization of arsenic was closely related to the mobilization of the metals (e.g., Fe, Cu, Pb and Zn). Once again, it indicated that arsenic mobilization by HA and rhamnolipid was enhanced by the co-mobilization of the metals, which helped transfer arsenic into aqueous phases.

Particularly, it is the first demonstration that biosurfactant can be used in arsenic removal, though a number of studies have been performed to use biosurfactant for the removal of heavy metals and/or organic contaminants (Mulligan, 2005). It was also found that less pore volumes of rhamnolipid solution were required than HA solution to obtain a certain removal efficiency. It could reduce the treatment time and material cost greatly, which indicated that rhamnolipid could be more effective and cost-efficient than HA in the remediation of arsenic contaminated mine tailings or soils.

As shown in Figures 8-31 to 8-33, arsenic mobilization during the column tests by all the flushing solutions were a little higher than that in the batch tests. It might be due to the immediate arsenic mobilization with the flushing solution once it was desorbed, which might, at least partially, prevent the re-adsorption of arsenic back to the mine tailings. However, as indicated by the residual arsenic concentrations the mine tailings along the column length (Figures 8-28 to 8-30), a portion of the mobilized arsenic might be re-adsorbed during the moving process along the column.

CHAPTER NINE

IMPLICATIONS ON ARSENIC MOBILITY AND REMEDIATION OF ARSENIC CONTAMINATED SOILS

The experimental results in this research study indicated that organic additives such as HA and rhamnolipid can have significant effects on the mobilization of arsenic from the mine tailings. In this chapter, the experimental results from batch and column tests, SSE studies, FTIR analyses, and arsenic oxidation state analyses are discussed together to elucidate the mechanisms that HA and rhamnolipid influence arsenic mobilization from the mine tailings. Observations from other previous research studies are also included to explain the mechanisms. The implications on using of NOM and biosurfactants for remediation of arsenic contaminated soils are also indicated. It will be helpful for the proper management of arsenic contamination to reduce and avoid risks.

9.1 Effect of NOM on arsenic mobility

The effect of NOM on arsenic mobility is a complicated process of several interactions between the mine tailings, NOM and arsenic (Figure 9-1). Generally, NOM may affect the mobility of arsenic through electrostatic interaction, competition for adsorption, formation of soluble or insoluble complexes and oxidation-reduction reactions. Moreover, it may influence microbial activity and consequentially indirectly influencing arsenic mobility, though it is beyond the topic of this research study. The interaction between HA and arsenic is influenced by pH, physicochemical characteristics of the mine tailings, the nature of HA, and the co-released metals.

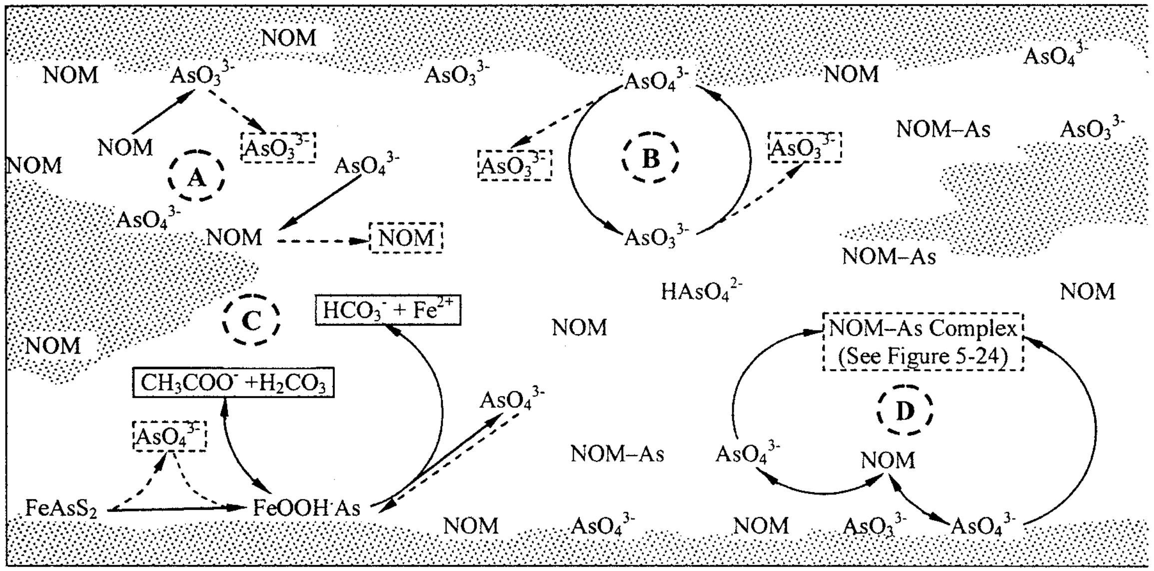


Figure 9-1. Model for the mechanisms of the effect of NOM on arsenic mobilization

A: Competition adsorption between NOM and arsenic; B: Redox transformation between arsenic species, in which NOM may serve as an electron shuttle and mineral oxides may act as a surface catalyst or an electron-transfer intermediate; C: Oxidation of FeS$_2$ and microbial driven reduction of FeOOH, which may release the adsorbed arsenic; D: Complexation between NOM and arsenic, which may enhance arsenic mobility by forming soluble NOM-arsenic complexes.

According to the experimental results from this study, under acidic conditions, the addition of HA may help the retention of arsenic and other heavy metals in the mine tailings. Under acidic conditions, the dissolution of the metal oxides or hydroxides in the mine tailings may release the associated arsenic, providing free arsenic in solution. At the same time, the dissolution of these components provides more active adsorption sites for HA. Sorption of HA onto the mine tailing surface may bind cations in solution and then re-adsorb arsenic back to the solid phases through metal bridging mechanism. A direct result is the observation of decreased arsenic mobilization from the mine tailings at pH 3 in this study. Cornu *et al.* (1999) also reported that the presence of previously adsorbed HA on kaolinite had the effect of increasing As(V) adsorption at pH 7, as compared to crude kaolinite. Xu *et al.* (1991) reported that acidification and organic matter addition reduced arsenic mobility with arsenic adsorption reaching a maximum at around pH 5 for As(V). The variation in pH may be due to the difference between pure laboratory made-materials and natural geologic materials.

HA may increase arsenic mobility under alkaline conditions, and arsenic mobility increases with an increase of the mass ratio of added HA to the mine tailings and an increase of pH, and greater mobilization occurred at pH above 9. A good correlation was observed between arsenic and metal mobilization. The co-mobilized metals, to some extent, can enhance the mobility of arsenic by helping to incorporate it into soluble complexes with the organic additives through metal-bridging mechanisms.

The competition between HA and arsenic for adsorption sites on the mine tailing surface increases with a pH increase, thus leading to enhanced arsenic mobilization. The adsorption of HA increases the density of negative charges on the solid surface (Figures 4-4 to 4-6), which results in a greater electrostatic repulsion to prevent the re-adsorption of arsenic. Similar observations have been reported in laboratory experiments with pure hydroxides and clay minerals (Xu *et al.*, 1988; Takahashi *et al.*, 1999; Grafe *et al.*, 2001). Xu *et al.* (1988) observed that FA reduced As(V) adsorption on alumina as result of a predominantly negatively charged surface created by its adsorption. Takahashi *et al.* (1999) reported that the adsorption of arsenic on kaolinite and silica was prevented by the adsorption of HA. Grafe *et al.* (2001) indicated that direct competitive sorption as well as indirect electrostatic effects might be responsible for the observed effect on As(V) adsorption on α-FeOOH in the presence of humic and fulvic acids.

NOM may influence arsenic mobility through forming either insoluble or soluble aqueous surface inner-sphere complexes with arsenic species, due to their strong affinity to metal ions and metal oxides. Formation of insoluble complexes may occur mainly under acidic conditions, due to the low solubility of HA. When pH increases, HA dissociates and its solubility increased. Soluble aqueous complexes are becoming predominant. The formation of aqueous complexes may, in turn, associate strongly with other dissolved arsenic, presumably through metal-bridging mechanisms, diminishing the tendencies of arsenic to be re-adsorbed back to solid phases. Moreover, the formation of aqueous humate-metal complexes masks the formation of metal hydroxide effectively under alkaline conditions, which further prevents the adsorption and coprecipitation of arsenic onto and with the hydroxides, thus increasing arsenic mobility. This and the metal-bridging complexion mechanism can be verified partially by the good correlation between arsenic and metal mobilization from the mine tailings in the presence of organic additives in this study. Buschmann *et al.* (2006) reported that phenolates in HA might bind As(III) and As(V) directly to form aqueous complexes. However, it is difficult to determine sound physicochemical parameters to characterize this kind of complexation because of the inherent physicochemical complexity of NOM.

Previous studies have shown that NOM may catalyze both the oxidation and reduction reactions among chemical species, in part by the quinone-mediated formation of free radicals (Scott *et al.*, 1998; Redman *et al.*, 2002). They may serve as an electron shuttle between kinetically inert redox species or between microorganisms and arsenic species (Scott *et al.*, 1998). Mineral oxides may act as a surface catalyst or as an electron-transfer intermediate. Arsenic mobility may therefore be enhanced by the formation of more mobile arsenic ions. Redman *et al.* (2002) observed the reduction of As(V) to free As(III) by an Inangahua River NOM and the oxidation of As(III) to free As(V) by all the experimental NOM samples. Dobran and Zagury (2006) reported that a high organic matter content was able to induce the reduction of As(V) to As(III) even in oxidizing conditions. The theory of oxidation-reduction reactions involving metal oxides and sedimentary organic matter have been employed to explain the occurrence of arsenic contamination in groundwater beneath the southern Carson Desert, Nevada (Welch and Lico, 1997). However, in this study, only As(V) was detected in the extractants, which meant that the oxidation and reduction of arsenic species might not play a significant role in arsenic mobilization from the mine tailings in the presence of NOM.

9.2 Effect of rhamnolipid on arsenic mobility

The introduction of rhamnolipid could increase arsenic mobilization from the mine tailings significantly. The influence increased with increasing rhamnolipid concentration and pH. Compared to HA and the LMWOAs, rhamnolipid was more effective in mobilizing arsenic from the mine tailings.

The effect of rhamnolipid on arsenic mobilization from the mine tailings can result from a series of interactions (Figure 9-2). Rhamnolipid might increase arsenic mobility from the mine tailings through reducing the interfacial tension, electrostatic interaction, formation of soluble complexes or micelles, anion exchange and competition for adsorption, and increasing the wettability of the mine tailings. As indicated in the experimental results, these interactions can be affected by the physicochemical characteristics of the mine tailings, pH and the co-mobilized metals from the mine tailings. Previous study with rhamnolipid indicated that it could inhibit Cr mobility by reducing aqueous Cr(VI) to Cr(III) precipitate in the presence of kaolinite (Massara *et al.*, 2007). However, as indicated by CE analyses in this study, rhamnolipid might not influence the oxidation state of arsenic. The oxidation-reduction interactions, therefore, might not be a significant mechanism that was involved in the mobilization of arsenic from the mine tailings by the rhamnolipid.

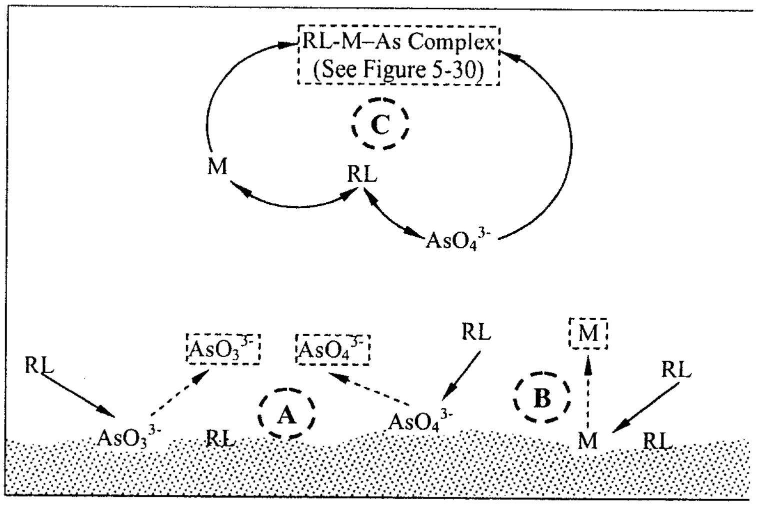


Figure 9-2. Model for the mechanisms of the effect of rhamnolipid on arsenic mobilization A: Arsenic mobilization through competition, electrostatic interaction, and interfacial tension reduction; B: Metal mobilization through interfacial tension reduction; C: Formation of micelles and metal-bridging complexes

According to Mulligan *et al.* (1999), rhamnolipid adsorption is essential for metal mobilization from soil and sediments. This could occur in the case of arsenic mobilization from the mine tailings. Since rhamnolipid is negatively charged, it may compete with arsenic for adsorption sites, therefore suppressing the sorbed arsenic and mobilizing it. Massara *et al.* (2007) indicated competition sorption between rhamnolipid and hexavalent chromium anions [Cr(VI)] to be the main mechanism involved in Cr(VI) mobilization from kaolinite in the presence of rhamnolipid. Anion exchange between arsenic anions and rhamnolipid may be another possible mechanism for explaining arsenic mobilization by rhamnolipid. Furthermore, the introduction of rhamnolipid can further increase the negative charge density of the solid surface, therefore, preventing arsenic re-adsorption by producing a higher repulsive interaction (Figures 4-4 to 4-6).

As indicated in previous studies (Mulligan *et al.*, 1999; 2001a; Wang and Mulligan, 2004b), the addition of rhamnolipid can effectively decrease the interfacial tension between solid surface and contaminants, therefore increasing contaminant mobility. This may also be applicable for explaining the desorption of weakly bound arsenic from the mine tailing surfaces. Increasing pH can further help to reduce the interfacial tension (Wang and Mulligan, 2004b), thus partially contribute to the mobilization of arsenic at high pH values.

Rhamnolipid is known to form micelles at concentrations above the CMC, therefore, increasing the mobilization metal or organic contaminants from soil and sediments (Mulligan *et al.*, 1999; Mulligan, 2005). The good correlation between arsenic and metal mobilization in the batch and column experiments indicated that arsenic might be mobilized together with the metals, by incorporating it into soluble complexes or micelles instead of forming metal-arsenic precipitation. Arsenic might be incorporated into the micelles, analogous to that of the HA-arsenic complexes, directly or through the metal bridging mechanism (Figure 5-30; Figure 9-2). The main functional groups involved should be the carboxylic and hydroxyl groups in rhamnolipid. Moreover, rhamnolipid might improve the wettability of the mine tailings. A direct result is that the particles of the mine tailings become more accessible for washing, then mobilizing the associated arsenic.

9.3 Implications on arsenic release from soil and sediments into groundwater

This study demonstrated that HA showed great potential in influencing arsenic sorption behavior by interacting with mine tailings and with arsenic itself. Similarly, due to its ubiquity in the environment, HA may also play an important role in the release of arsenic from soil and sediments into groundwater. The presence of HA may enhance arsenic release mainly through competition for available adsorption sites, formation of aqueous complexes and electrostatic interaction. Although it was not demonstrated in this study, other researchers also proposed that NOM could enhance arsenic release into groundwater through changing the redox chemistry of solid surfaces and arsenic species (Welch and Lico, 1997; Scott *et al.*, 1998; Redman *et al.*, 2002; Dobran and Zagury, 2006).

On the other hand, under acidic conditions, HA could help immobilizing arsenic in soil and sediments by serving as a binding agent and forming insoluble complexes. It may also reduce arsenic concentration in groundwater by transferring it into particulate phase. However, desorption and remobilization of the sorbed arsenic may occur when the site biological or physicochemical conditions such as pH and Eh change with time, thus releasing arsenic into groundwater.

It was also indicated in this study that the presence of biosurfactants could enhance arsenic mobilization from the mine tailings. Although a commercial biosurfactant was used in the study, the biosurfactants could be present in soil and sediments naturally due to the presence of microbial origins such as the bacteria *Pseudomonas sp.* for rhamnolipid. It has also been demonstrated that surfactants may be present naturally *in-situ* as the excretion products of plants (Kommalapati *et al.*, 1998). Therefore, the naturally occurring surfactants/biosurfactants may play an important role in mobilizing arsenic from soil and sediments into groundwater. Arsenic release into groundwater may be enhance by surfactants through reducing the interfacial tension, formation of soluble complexes or micelles, anion exchange and competition for adsorption, electrostatic interaction and increasing the wettability of the solid phases.

9.4 Implications on remediation of arsenic contaminated soils

The results from this research study indicated that NOM and biosurfactants might be used potentially in the remediation of arsenic contaminated mine tailings or soils. HA and rhamnolipid could be used effectively to extract arsenic from soils under alkaline conditions. Chemical extraction using NOM or biosurfactant solutions, either *in-situ* or *ex-situ*, may be developed as a promising method to remove the bulk of arsenic from soils to reduce environmental risk. It can also be used as a pretreatment for continuing treatment methods such as stabilization/solidification, bioremediation, or natural attenuation processes. Further separation of NOM or biosurfactant and arsenic or heavy metals in the effluents for recycle and reuse might improve the cost-effectiveness of this technology greatly. Surfactants can be recovered by precipitation using mono- or multivalent counterions (i. e. the ions of opposite charge to those of the surfactant) from the micellar-enhanced ultrafiltration (MEUF) (Wang and Mulligan, 2004c). Further efforts are required to develop applicable technologies for NOM recovery and recycle.

NOM and biosurfactants may also be used as an enhancement in electrokinetic remediation technologies. Previous research studies have demonstrated that the addition of surfactant solution in the electrokinetic processes could enhance the mobility of organic contaminants and heavy metals (Saichek and Reddy, 2005). Sawada *et al.* (2003) also reported that HA could be used in electrokinetic remediation successfully to enhance the mobilization of Cu(II)-oxinate from contaminated clayey soils. As discussed in Section 2.6, electrokinetic methods are emerging for the treatment of arsenic contaminated soils. This study indicated the addition of HA and rhamnolipid might be used to enhance the mobilization of arsenic from the mine tailings. Therefore, the introduction of HA and biosurfactant solutions in electrokinetic methods might greatly increase the performance and cost-effectiveness of this technology. Moreover, the HA and biosurfactant used in the flushing process may be recycled and reused.

NOM and biosurfactants also have potential in the bioremediation of contaminated soils. Biological methods rely on microbial activities to remediate arsenic contaminated soils. Bioavailability of electron acceptors can influence microbial activity. Solid Fe(III) must be available and in direct contact for the microorganisms. Biosurfactant foam technology can be used to deliver nutrients or microbial populations into the subsurface (Wang and Mulligan, 2004b; 2004c; Mulligan and Wang, 2006). The use of biosurfactants may increase the availability of Fe(III) and arsenic to the microorganisms due to the decrease in interfacial tension and formation of micelles. An aerobic or anaerobic environment can be created by changing the foaming gas. Aerobic conditions can be created by using air or oxygen as foaming gas. Anaerobic biological processes can proceed with the addition of nitrates, Fe(III) oxides, Mn(IV) oxides, sulfate and CO_2. Addition of NOM such as HA can provide electron acceptors since HA can chelate Fe. The presence of HA can significantly increase Fe bioavailability and arsenic mobility. A preferred pH range can also be achieved with addition of different pH buffers.

Natural attenuation may be a cost-effective *in-situ* remedial option to immobilize arsenic and transform it into less toxic forms. The natural attenuation of arsenic contamination mainly involves processes such as immobilization by sorption to solid phases such as (hydro)oxides of Fe, Mn and Al, organic matter, and clay minerals, the intra-conversion between As(III) and As(V) induced by the Fe and Mn (hydro)oxides and clay phases or NOM, biotransformation, and hyperaccumulation of arsenic in plants (Wang and Mulligan, 2006d). However, natural attenuation generally is subject to hydrological changes and may take substantial periods of time. It alone may not be sufficient for the remediation of contaminated sites in a reasonable time frame. As discussed above, NOM may play a vital role in the adsorption-desorption, reduction-oxidation, and biotransformation processes of arsenic natural attenuation. Therefore, organic matter can be used as engineering enhancements to improve the attenuation rates. Biosurfactants or biosurfactant foam may also be used to enhance arsenic natural attenuation by increasing arsenic and nutrient bioavailability to microbes or plants. However, the role of biosurfactants in arsenic natural attenuation has not been completely elucidated.

CHAPTER TEN

CONCLUSIONS, SCIENTIFIC CONTRIBUTIONS AND RECOMMENDATIONS

Batch and column experiments were carried out in this research study to investigate the effect of NOM and biosurfactants on the mobilization of arsenic from the mine tailings and to evaluate the feasibility of using NOM and biosurfactants in the remediation of arsenic contaminated soils. The effect of pH, mass ratio, and reaction time was examined. The effect of HA and rhamnolipid on arsenic mobilization was compared with that of three LMWOAs. The correlation between the mobilization of co-existing metals and arsenic was also examined. A six-step SSE procedure was employed to determine the fractional distribution of arsenic in the mine tailings before and after washing with HA and rhamnolipid. FITR spectra were collected from 1000 mg/L HA at pH 11 and the extracts from the mine tailings. CE analyses were conducted to identify arsenic species in the extracts and examine the effect of rhamnolipid and HA on arsenic oxidation state. This chapter presents the main conclusions, expected scientific contributions and recommendations for future research.

10.1 Conclusions

Batch tests with distilled water indicated that the arsenic in the mine tailings was most mobile under acidic conditions, which could present a high risk to the environment. The addition of Fluka HA under acidic conditions with a low mass ratio (below 2.0 mg HA/g mine tailings) inhibited arsenic mobilization from the mine tailings significantly. The decrease in arsenic mobilization might be a result from the desorption of arsenic from the mine tailings by HA first and the sequential re-sorption of the dissolved arsenic to the adsorbed HA on the mine tailings or to the remaining mine tailing surface. The mobilization of arsenic increased with the mass ratio of added HA to the mine tailings. Especially, under alkaline conditions, the introduction of HA significantly enhanced arsenic mobilization. A desorption isotherm was developed to predict the mobilization of arsenic in the presence of HA. It indicated that arsenic mobilization was mainly controlled by the sorption interaction between HA and the mine tailings and the balance of arsenic concentrations between the solid and aqueous states. The sorption of HA is essential for the mobilization of arsenic from the mine tailings. Generally, HA may inhibit arsenic mobilization under acidic conditions by working as a binding agent and formation of insoluble complexes. Under alkaline conditions, HA may enhance the mobility of arsenic through competition for adsorption and formation of soluble complexes and electrostatic interaction. CE analyses did not show any evidence of As(III) oxidation or As(V) reduction in this study, which indicated that arsenic redox reactions might not have a significant effect on arsenic mobilization from the mine tailings in the presence of HA.

The desorption isotherm was also applicable for the prediction of arsenic mobilization in the presence of rhamnolipid. The mobilization of arsenic from the mine tailings by rhamnolipid increased with both the mass ratio and pH. Rhamnolipid may increase arsenic mobility from the mine tailings through reducing the interfacial tension, formation of soluble complexes or micelles, competition for adsorption, anion exchange, electrostatic interaction and increasing the wettability of the mine tailings. CE analyses indicated that arsenic oxidation-reduction reactions might not be a significant mechanism that involved in the mobilization of arsenic from the mine tailings by the rhamnolipid in this study.

The addition of LMWOAs under acidic conditions inhibited arsenic mobilization from the mine tailings. The mobilization of arsenic generally increased with pH increase. Under alkaline conditions, arsenic mobilization was enhanced by the organic additives. The mobilization of arsenic by the three LMWOAs was found to be consistent with the order of the stability of Fe-, Cu-, Pb-, and Zn-organic ligand complexes. It further verified that arsenic mobilization from the mine tailings was mainly accomplished by binding to the metal-organic complexes. At pH 11, rhamnolipid was found to be the most efficient to mobilize arsenic from the mine tailings, probably due to its efficiency in lowering the interfacial tension and mobilizing other metals, which may further enhance arsenic mobilization since the mobilization of arsenic is closely correlated to the co-mobilization of metals.

Higher arsenic mobilization was achieved from column tests compared to batch tests, partially due to the immediate mobilization of arsenic with the flushing solution once it was mobilized. Results from the column experiments indicated that HA and rhamnolipid might be used potentially to remove bulk arsenic and heavy metals together from contaminated soils. The introduction of HA and rhamnolipid could increase the mobility of arsenic and heavy metals greatly. It can be applied independently or as an enhancement for other existing or emerging technologies such as bioremediation, electrokinetic technology and natural attenuation processes, to improve the treatment performance and cost-efficiencies.

The mobilization of arsenic was found to be positively correlated with the mobilization of Fe and other heavy metals (e.g., Cu, Pb and Zn) from the mine tailings in both the batch and column tests. It was found that the organic additives could remove arsenic and co-existing heavy metals simultaneously from contaminated mine tailings at high pH, while it might help to retain arsenic and heavy metals at acidic conditions. Arsenic mobilization to some extent might be enhanced by the mobilization of co-existing metals in the presence of organic additives under alkaline conditions, by helping to incorporate arsenic into soluble aqueous organic complexes or micelles in the case of rhamnolipid through metal-bridging mechanisms.

10.2 Scientific contributions

In general, the findings of this research study will be important in advancing our understanding of the fate and transport cycle of arsenic in the environment and the cause of arsenic contamination in groundwater, giving implications on the control of arsenic mobility. Use of NOM and biosurfactant in arsenic remediation may be developed as an environmentally benign and possible cost-effective remedial option to reduce and avoid further contamination.

Specifically, this research contributes to scientific knowledge in the following aspects:

- Investigation of the interaction between NOM, biosurfactant, and arsenic using geological materials, which is different from previous research studies that using pure laboratory-produced or artificially contaminated materials;
- Elucidation of the mechanisms that NOM may influence arsenic mobility;
- Evaluation of the feasibility of using NOM in remediation of arsenic contaminated soils;
- First demonstration that biosurfactants may be used potentially in remediating arsenic contaminated soils, providing an environmentally benign, efficient and possible cost-effective remedial option;
- Development of a desorption isotherm to predict the mobilization of arsenic in the presence of organic additives; and
- Identification of the role of co-existing metals in arsenic mobilization from mine tailings. The mobilization of co-existing metals in mine tailings may enhance arsenic mobilization in the presence of organic additives.

10.3 Recommendations

The following aspects are recommended for future research work:

- Examination of the effect of other HAs or FAs and other biosurfactants on arsenic mobilization;
- Investigation of the role of NOM and biosurfactant in the biological processes of arsenic in natural systems and its influence on further mobility and bioavailability of arsenic.

- Evaluation of the feasibility of using NOM and biosurfactants in combination with other existing remediation technologies;
- Field demonstration to evaluate in-field performance and cost-effectiveness of using NOM or biosurfactant in remediation of arsenic contaminated sites; and
- Development of applicable technologies for the treatment of the effluents containing NOM/biosurfactant, arsenic and heavy metals. Recovery and recycle of NOM and biosurfactant are mandatory for cost considerations.

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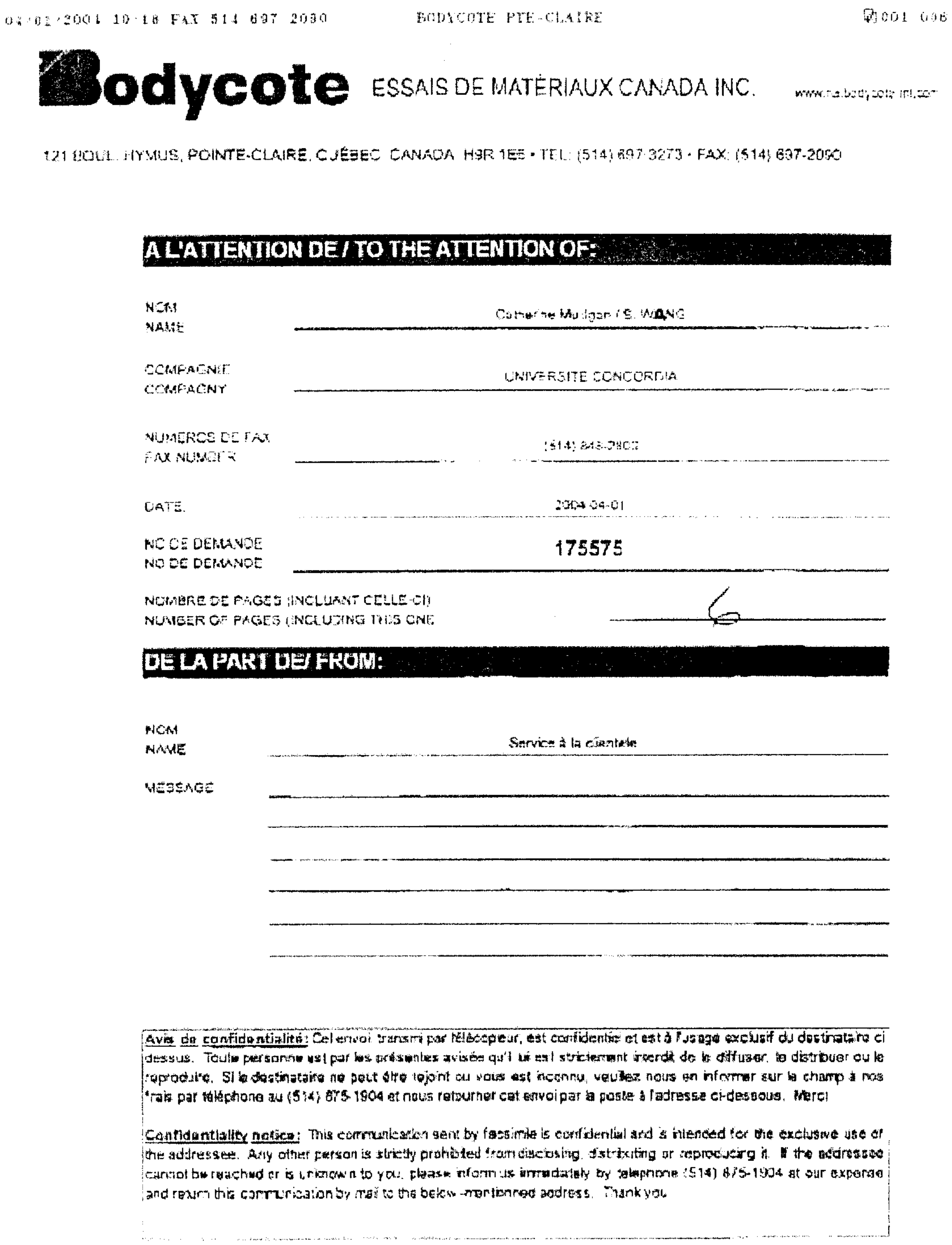
APPENDICES

APPENDIX I

ICP-MS ANALYSIS OF ARSENIC CONCENTRATIONS IN THE MINE TAILINGS



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NOM
NAME Catherine Mulligan / S. WANG

COMPAGNIE
COMPAGNY UNIVERSITE CONCORDIA

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DATE 2004-04-01

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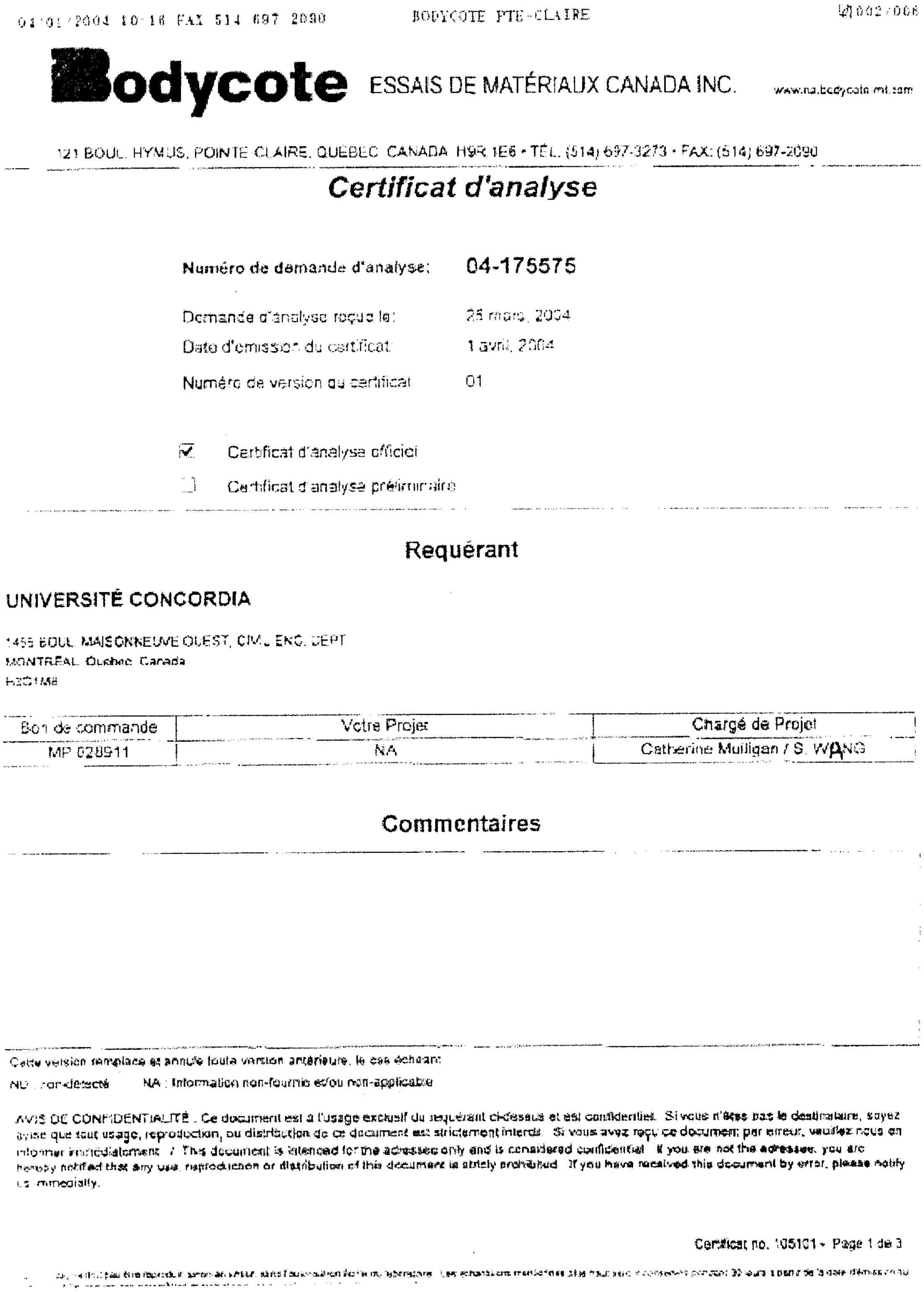

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Demande d'analyse reçue le: 25 mars, 2004
Date d'émission du certificat: 1 avril, 2004
Numéro de version du certificat: 01

☑ Certificat d'analyse officiel
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Requérant

UNIVERSITÉ CONCORDIA

1455 BOUL. MAISONNEUVE OUEST, CIVIL ENG. DEPT
MONTRÉAL, Québec, Canada
H3G1M8

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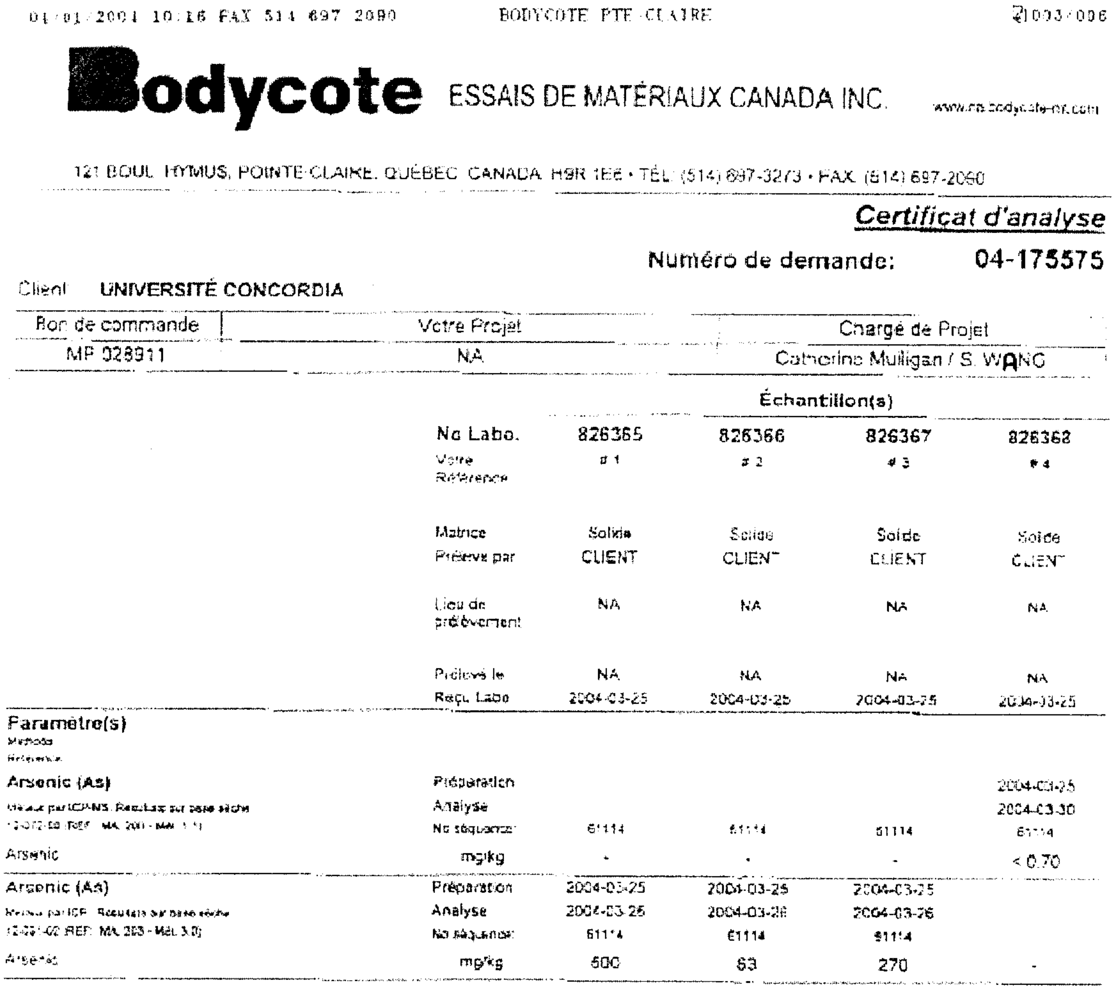

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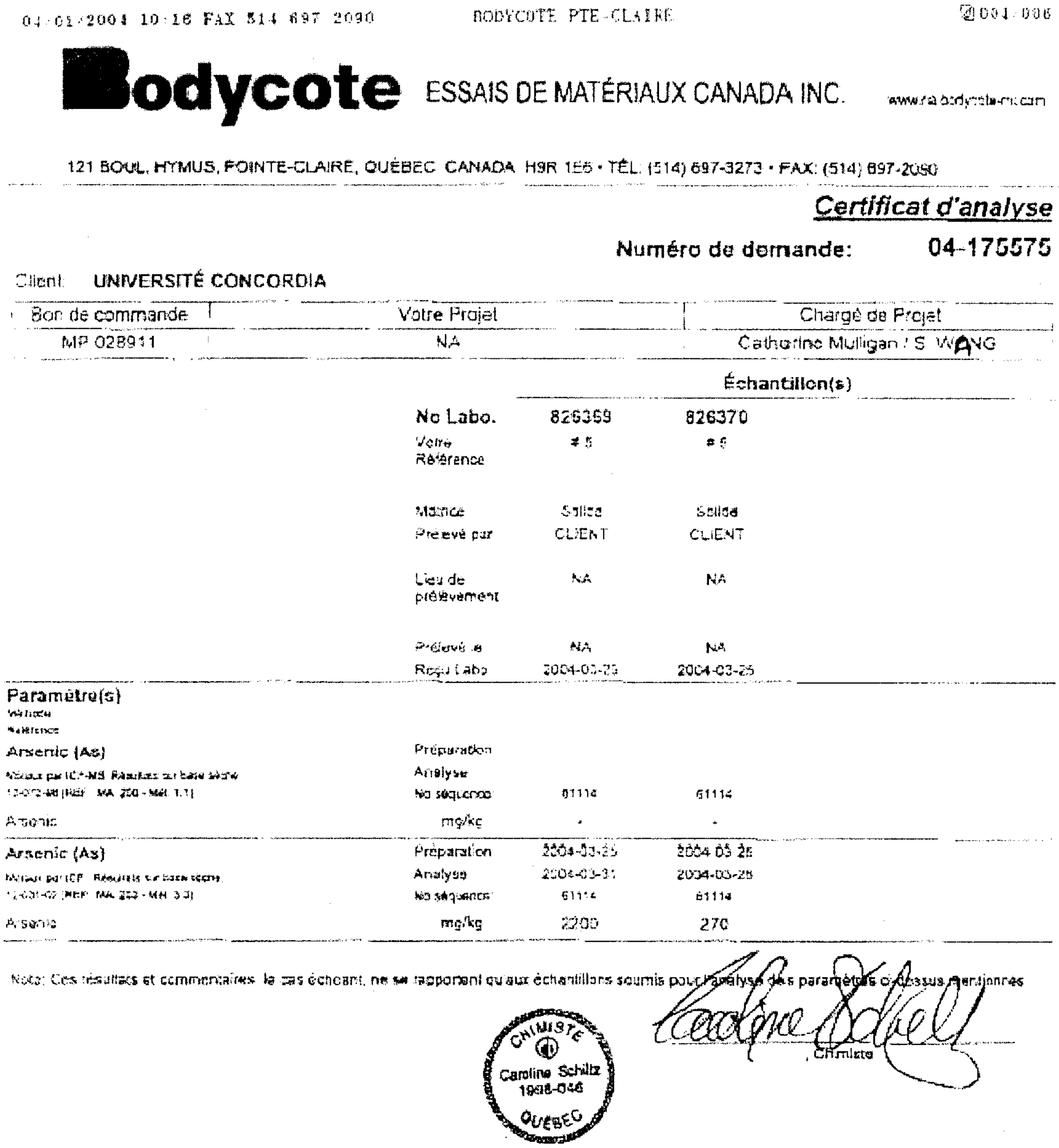
		Échantillon(s)			
	No Labo.	826365	826366	826367	826368
	Votre Référence	# 1	# 2	# 3	# 4
	Matrice	Solide	Solide	Solide	Solide
	Prélevé par	CLIENT	CLIENT	CLIENT	CLIENT
	Lieu de prélèvement	NA	NA	NA	NA
	Prélevé le	NA	NA	NA	NA
	Reçu Labo	2004-03-25	2004-03-25	2004-03-25	2004-03-25
Paramètre(s) Méthode Référence					
Arsenic (As)	Préparation				2004-03-25
Dosage par ICP/MS. Résultats sur base sèche	Analyse				2004-03-30
[illegible]	No séquence	61114	61114	61114	61114
Arsenic	mg/kg	-	-	-	< 0.70
Arsenic (As)	Préparation	2004-03-25	2004-03-25	2004-03-25	
Dosage par ICP. Résultats sur base sèche	Analyse	2004-03-26	2004-03-26	2004-03-26	
(2-031-02 REF: MA. 203 - Mét. 3.0)	No séquence	61114	61114	61114	
Arsenic	mg/kg	500	63	270	-



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Bon de commande	Votre Projet	Chargé de Projet
MP 028911	NA	Catherine Mulligan / S. WANG

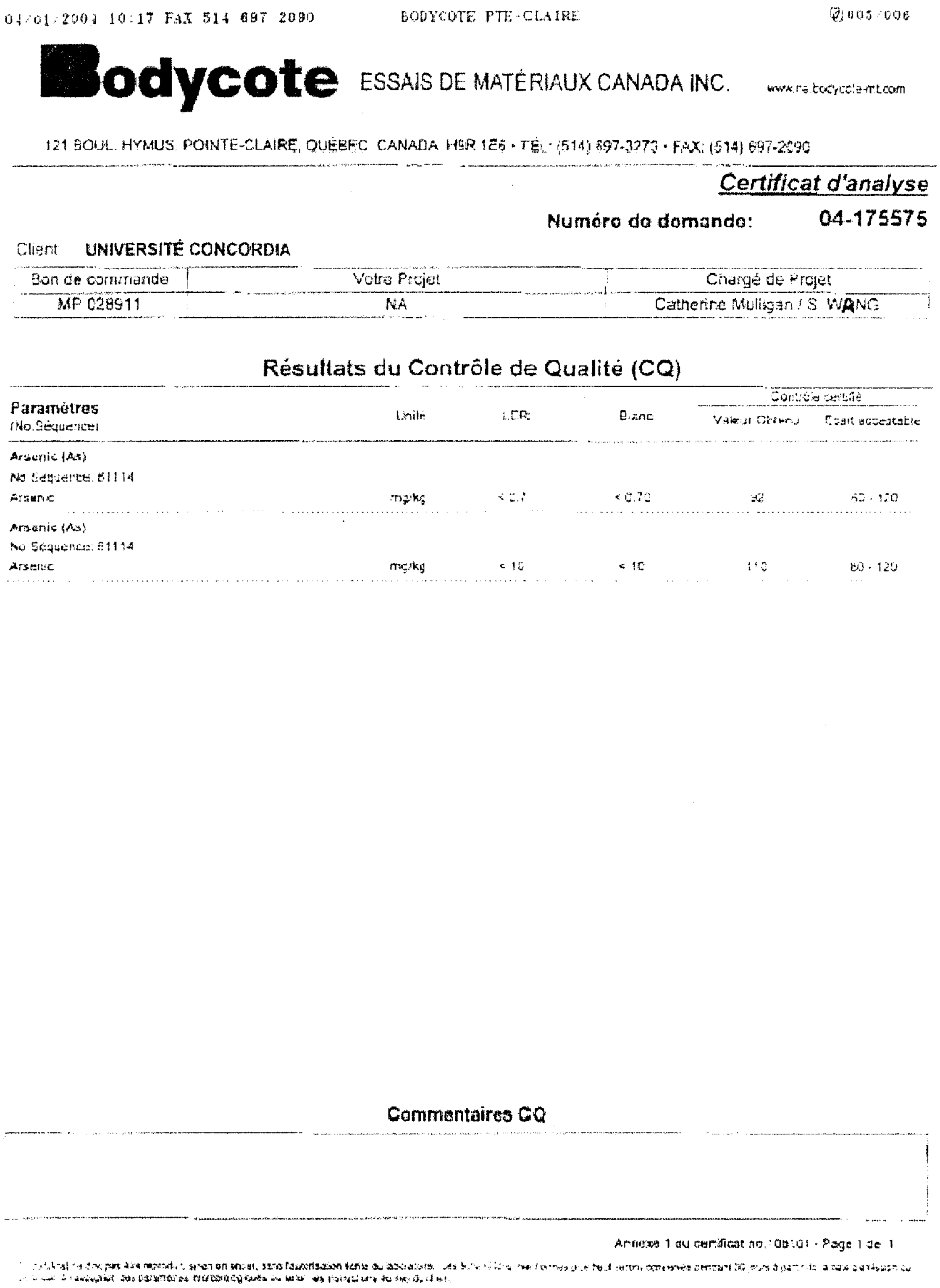
	Échantillon(s)	
No Labo.	826369	826370
Votre Référence	# 5	# 6
Matrice	Solide	Solide
Prélevé par	CLIENT	CLIENT
Lieu de prélèvement	NA	NA
Prélevé le	NA	NA
Reçu Labo	2004-03-25	2004-03-25

Paramètre(s) Méthode Référence			
Arsenic (As) Niveaux par ICP-MS. Résultats sur base sèche 12-012-48 (REF : MA. 200 - Mét. 1.1)	Préparation Analyse No séquence	 61114	 61114
Arsenic	mg/kg	-	-
Arsenic (As) Niveaux par ICP. Résultats sur base sèche. 12-001-02 (REF : MA. 200 - Mét. 3.3)	Préparation Analyse No séquence	2004-03-25 2004-03-31 61114	2004-03-25 2004-03-25 61114
Arsenic	mg/kg	2200	270

Note: Ces résultats et commentaires, le cas échéant, ne se rapportent qu'aux échantillons soumis pour l'analyse des paramètres ci-dessus mentionnés

Caroline Schiltz
1998-046

Caroline Schiltz, Chimiste



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Résultats du Contrôle de Qualité (CQ)

Paramètres (No.Séquence)	Unité	LDR	Blanc	Contrôle certifié Valeur Obtenu	Contrôle certifié Écart acceptable
Arsenic (As)					
No Séquence: 61114					
Arsenic	mg/kg	< 0.7	< 0.70	92	60 - 120
Arsenic (As)					
No Séquence: 61114					
Arsenic	mg/kg	< 10	< 10	110	60 - 120

Commentaires CQ

Annexe 1 du certificat no.108101 - Page 1 de 1

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Numéro de demande: 04-175575

Client **UNIVERSITÉ CONCORDIA**

Bon de commande	Votre Projet	Chargé de Projet
MP 028911	NA	Catherine Mulligan / S. WANG

Résultats du Contrôle de Qualité (CQ) - 2e partie

Paramètres		Duplicata			Ajout Dosé	
(No Séquence)	Unité	Valeur 1	Valeur 2	écart %	Valeur éch.	éch. fortifié
Arsenic (As)						
No Séquence 61114	(No éch)		(825365)			
Arsenic	mg/kg	500	430	15.1		

Commentaires CQ

APPENDIX II

XRD ANALYSIS RESULTS OF THE MINE TAILINGS

```
: SAMPLE1.DI                                                 13-Sep-2004 11:07
===============================================================================
McGill Mining & Metallurgy                         PC-APD, Diffraction software

                        Sample identification: sample1
                             Data measured at: 13-Sep-2004 10:36:00

                           Diffractometer type: PW1710 BASED
                                   Tube anode: Cu
                        Generator tension [kV]: 40
                        Generator current [mA]: 20
                         Wavelength Alpha1 [Å]: 1.54060
                         Wavelength Alpha2 [Å]: 1.54439
              Intensity ratio (alpha2/alpha1): 0.500
                             Divergence slit: AUTOMATIC
                        Irradiated length [mm]: 12
                               Receiving slit: 0.2
                           Monochromator used: YES

                            Start angle [°2θ]:   3.000
                              End angle [°2θ]:  60.000
                              Step size [°2θ]:   0.020
                            Maximum intensity: 1383.840
                            Time per step [s]:   0.500
                                 Type of scan: STEP
                      Intensities converted to: FIXED

                     Peak positions defined by: Minimum of 2nd derivative of peak
                        Minimum peak tip width:    0.00
                        Maximum peak tip width:    1.00
                               Peak base width:    2.00
                         Minimum significance:    0.75
                              Number of peaks:      51


 Angle   d-value   d-value   Peak width   Peak int   Back. int   Rel. int   Signif.
 [°2θ]   α1   [Å]  α2   [Å]    [°2θ]     [counts]   [counts]      [%]

  8.585  10.2915   10.3168      0.140       1384         62       100.0       9.42
 10.165   8.6951    8.7165      0.060        246         48        17.8       2.62
 10.445   8.4626    8.4835      0.080        620         46        44.8       2.06
 12.390   7.1382    7.1557      0.060        104         34         7.5       1.76
 17.430   5.0838    5.0963      0.240         21         19         1.5       1.00
 18.830   4.7089    4.7205      0.080         74         18         5.3       0.99
 20.630   4.3019    4.3125      0.120        106         16         7.7       3.01
 21.205   4.1865    4.1968      0.160         30         16         2.2       1.46
 23.460   3.7890    3.7983      0.240          5         14         0.4       0.75
 25.050   3.5520    3.5607      0.080         48         13         3.4       0.92
 26.460   3.3658    3.3741      0.120       1005         12        72.6       7.87
 27.130   3.2842    3.2923      0.160         71         12         5.1       2.10
 27.815   3.2048    3.2127      0.100         27         12         2.0       0.83
 28.375   3.1429    3.1506      0.060         67         11         4.9       1.15
 28.935   3.0833    3.0909      0.100        493         11        35.6       6.25
 29.875   2.9884    2.9957      0.200         17         11         1.2       1.30
 30.730   2.9072    2.9143      0.160         15         10         1.1       1.27
 32.220   2.7760    2.7829      0.240         58          9         4.2       4.87
 32.795   2.7287    2.7354      0.240          8          9         0.6       1.09
```

```
File: SAMPLE1.DI                                                   13-Sep-2004 11:07
=====================================================================================
McGill Mining & Metallurgy                              PC-APD, Diffraction software

  Angle   d-value   d-value   Peak width   Peak int   Back. int   Rel. int   Signif.
  [°2θ]   α1  [Å]   α2  [Å]     [°2θ]      [counts]   [counts]      [%]

 34.530    2.5954    2.6018      0.060         313          8        22.6        1.54
 34.635    2.5878    2.5942      0.040         123          8         8.9        1.87
 35.305    2.5402    2.5465      0.100          74          8         5.3        1.22
 36.380    2.4676    2.4736      0.100          48          8         3.4        1.82
 38.345    2.3455    2.3513      0.040          41          8         3.0        2.58
 38.460    2.3388    2.3445      0.040          24          8         1.7        0.96
 39.350    2.2879    2.2935      0.120          45          7         3.2        0.80
 40.135    2.2449    2.2505      0.100          26          7         1.9        1.00
 40.840    2.2078    2.2132      0.200          10          7         0.7        1.01
 42.280    2.1359    2.1411      0.080          20          7         1.5        0.96
 42.660    2.1177    2.1229      0.060          27          7         2.0        1.03
 44.200    2.0474    2.0525      0.160          12          6         0.8        1.61
 44.735    2.0242    2.0292      0.120          35          6         2.5        1.61
 45.655    1.9855    1.9904      0.240          10          6         0.7        1.10
 47.300    1.9202    1.9250      0.120          14          6         1.0        2.04
 48.295    1.8830    1.8876      0.080          24          6         1.7        0.75
 48.900    1.8611    1.8657      0.120           8          5         0.6        0.79
 49.975    1.8235    1.8280      0.120          53          5         3.9        2.53
 50.105    1.8191    1.8236      0.060          34          5         2.4        1.09
 53.025    1.7256    1.7299      0.160          14          5         1.0        0.89
 54.285    1.6885    1.6926      0.160          14          5         1.0        1.56
 54.705    1.6765    1.6806      0.140          37          5         2.7        2.37
 55.160    1.6638    1.6679      0.080          29          5         2.1        0.79
 55.945    1.6423    1.6463      0.400          10          5         0.7        2.30
 57.265    1.6075    1.6115      0.080          32          5         2.3        1.20
 58.100    1.5864    1.5903      0.060          16          5         1.2        0.81
 59.105    1.5618    1.5656      0.060          71          4         5.1        1.39
 59.270    1.5578    1.5617      0.060          40          4         2.9        0.82
 59.455    1.5534    1.5572      0.060          27          4         2.0        1.33
 59.640    1.5490    1.5528      0.060          81          4         5.9        0.75
 59.815    1.5449    1.5487      0.060          83          4         6.0        0.90
```

```
: SAMPLE2.DI                                                   13-Sep-2004 11:45
================================================================================
McGill Mining & Metallurgy                          PC-APD, Diffraction software

                      Sample identification: sample2
                           Data measured at: 13-Sep-2004 11:14:00

                         Diffractometer type: PW1710 BASED
                                  Tube anode: Cu
                      Generator tension [kV]: 40
                      Generator current [mA]: 20
                       Wavelength Alpha1 [Å]: 1.54060
                       Wavelength Alpha2 [Å]: 1.54439
             Intensity ratio (alpha2/alpha1): 0.500
                            Divergence slit: AUTOMATIC
                      Irradiated length [mm]: 12
                              Receiving slit: 0.2
                          Monochromator used: YES

                         Start angle [°2θ]:   3.000
                           End angle [°2θ]:  60.000
                           Step size [°2θ]:   0.020
                         Maximum intensity: 1406.250
                         Time per step [s]:   0.500
                              Type of scan: STEP
                   Intensities converted to: FIXED

                  Peak positions defined by: Minimum of 2nd derivative of peak
                    Minimum peak tip width:   0.00
                    Maximum peak tip width:   1.00
                           Peak base width:   2.00
                      Minimum significance:   0.75
                           Number of peaks:     64


 Angle   d-value   d-value   Peak width  Peak int   Back. int   Rel. int   Signif.
 [°2θ]   α1  [Å]   α2  [Å]     [°2θ]     [counts]   [counts]     [%]

  8.690  10.1674   10.1924     0.100        718         56        51.1       2.76
 12.335   7.1699    7.1875     0.160         45         36         3.2       1.00
 14.240   6.2147    6.2300     0.160         28         28         2.0       0.78
 17.610   5.0323    5.0446     0.120        137         18         9.7       3.64
 18.560   4.7768    4.7885     0.240         15         17         1.1       0.90
 19.840   4.4714    4.4824     0.240         23         16         1.6       1.47
 20.305   4.3700    4.3808     0.060         56         15         4.0       0.97
 20.690   4.2896    4.3001     0.100        289         15        20.6       4.01
 22.635   3.9252    3.9348     0.120         62         14         4.4       1.77
 22.910   3.8787    3.8882     0.080         53         14         3.8       0.93
 23.345   3.8074    3.8168     0.200         27         14         1.9       1.41
 24.085   3.6921    3.7011     0.120        149         13        10.6       4.71
 24.720   3.5986    3.6075     0.100         42         13         3.0       0.79
 25.710   3.4623    3.4708     0.080        142         12        10.1       1.32
 26.470   3.3646    3.3728     0.120       1406         12       100.0      12.38
 26.660   3.3410    3.3492     0.060        445         12        31.7       3.51
 27.145   3.2824    3.2905     0.060        128         12         9.1       0.86
 27.710   3.2167    3.2247     0.200         76         12         5.4       3.09
 28.120   3.1708    3.1786     0.080         31         12         2.2       1.47
```

```
File: SAMPLE2.DI                                                  13-Sep-2004 11:45
===================================================================================
McGill Mining & Metallurgy                         PC-APD, Diffraction software

  Angle   d-value   d-value  Peak width  Peak int  Back. int  Rel. int  Signif.
  [°2θ]   α1  [Å]   α2  [Å]    [°2θ]     [counts]   [counts]    [%]

 29.685   3.0071    3.0145     0.120         32         11        2.3       0.99
 30.055   2.9709    2.9782     0.080         38         11        2.7       0.81
 30.285   2.9488    2.9561     0.060         38         10        2.7       1.18
 30.615   2.9178    2.9250     0.200         14         10        1.0       0.89
 31.395   2.8471    2.8541     0.200         37         10        2.6       2.23
 31.925   2.8010    2.8079     0.100         25         10        1.8       0.75
 32.150   2.7819    2.7888     0.120         26         10        1.8       2.44
 32.870   2.7226    2.7293     0.080        106         10        7.5       1.37
 33.670   2.6597    2.6663     0.120         12         10        0.8       1.05
 34.850   2.5723    2.5786     0.320         25          9        1.8       1.74
 35.410   2.5329    2.5391     0.160         30          9        2.2       0.99
 35.840   2.5035    2.5097     0.140         32          9        2.3       1.22
 36.360   2.4689    2.4750     0.060         79          9        5.6       0.77
 36.925   2.4324    2.4384     0.160         55          8        3.9       3.03
 38.435   2.3402    2.3460     0.320         17          8        1.2       1.53
 39.305   2.2904    2.2960     0.060        100          8        7.1       0.94
 39.420   2.2840    2.2896     0.040         55          8        3.9       1.23
 40.140   2.2447    2.2502     0.060        128          8        9.1       1.46
 40.250   2.2388    2.2443     0.040         74          8        5.3       3.05
 40.595   2.2206    2.2260     0.060         79          8        5.6       2.49
 41.115   2.1937    2.1991     0.060         27          8        1.9       1.28
 41.610   2.1687    2.1740     0.160         19          8        1.4       1.06
 42.480   2.1263    2.1315     0.120         77          8        5.5       1.75
 42.790   2.1116    2.1168     0.200         66          7        4.7       2.63
 43.855   2.0628    2.0678     0.160         21          7        1.5       1.02
 44.775   2.0225    2.0275     0.060         37          7        2.6       1.08
 45.270   2.0015    2.0064     0.100        112          7        8.0       1.40
 45.650   1.9857    1.9906     0.060         42          7        3.0       0.98
 46.845   1.9378    1.9426     0.160          9          7        0.6       0.98
 47.275   1.9212    1.9259     0.080         26          7        1.8       0.79
 48.755   1.8663    1.8709     0.480         16          7        1.1       4.16
 49.965   1.8239    1.8284     0.100        132          6        9.4       2.99
 50.140   1.8179    1.8224     0.060         74          6        5.3       2.31
 50.490   1.8061    1.8106     0.120         23          6        1.6       0.79
 50.700   1.7991    1.8036     0.040         58          6        4.1       6.25
 50.840   1.7945    1.7989     0.040         27          6        1.9       1.59
 51.960   1.7584    1.7628     0.480          7          6        0.5       1.02
 52.955   1.7277    1.7320     0.240          7          6        0.5       0.87
 54.665   1.6777    1.6818     0.080         66          6        4.7       1.38
 54.825   1.6731    1.6773     0.080         35          6        2.5       0.78
 56.090   1.6384    1.6424     0.060         74          6        5.3       1.05
 56.245   1.6342    1.6382     0.060         45          6        3.2       0.91
 58.850   1.5679    1.5718     0.240         12          6        0.8       1.22
 59.775   1.5459    1.5497     0.080        108          5        7.7       2.26
```

```
: SAMPLE3.DI                                                      13-Sep-2004 12:18
====================================================================================
McGill Mining & Metallurgy                          PC-APD, Diffraction software

                     Sample identification: sample3
                          Data measured at: 13-Sep-2004 11:47:00

                        Diffractometer type: PW1710 BASED
                                Tube anode: Cu
                     Generator tension [kV]: 40
                     Generator current [mA]: 20
                     Wavelength Alpha1 [Å]: 1.54060
                     Wavelength Alpha2 [Å]: 1.54439
          Intensity ratio (alpha2/alpha1): 0.500
                          Divergence slit: AUTOMATIC
                    Irradiated length [mm]: 12
                            Receiving slit: 0.2
                       Monochromator used: YES

                        Start angle [°2θ]:   3.000
                          End angle [°2θ]:  60.000
                          Step size [°2θ]:   0.030
                       Maximum intensity: 610.0900
                        Time per step [s]:   0.500
                             Type of scan: STEP
               Intensities converted to: FIXED

              Peak positions defined by: Minimum of 2nd derivative of peak
                  Minimum peak tip width:    0.00
                  Maximum peak tip width:    1.00
                        Peak base width:    2.00
                    Minimum significance:    0.75
                         Number of peaks:      44


 Angle   d-value   d-value   Peak width  Peak int  Back. int  Rel. int  Signif.
 [°2θ]   α1  [Å]   α2  [Å]     [°2θ]     [counts]  [counts]     [%]

 6.165   14.3248   14.3601     0.960         12        90        2.0      1.06
12.275    7.2048    7.2225     0.080         90        32       14.8      0.75
14.685    6.0274    6.0422     0.240         49        26        8.0      1.40
15.485    5.7177    5.7318     0.200         18        24        2.9      0.84
17.215    5.1468    5.1595     0.120         31        20        5.1      1.96
18.580    4.7717    4.7834     0.120         30        19        5.0      1.46
20.645    4.2988    4.3094     0.100        123        16       20.2      2.60
21.855    4.0635    4.0735     0.200         22        15        3.6      1.51
24.085    3.6921    3.7011     0.200         20        13        3.3      1.50
24.865    3.5780    3.5868     0.060        552        13       90.5      1.42
25.215    3.5291    3.5378     0.080         86        12       14.2      0.83
25.635    3.4722    3.4808     0.160         58        12        9.5      1.12
26.435    3.3689    3.3772     0.140        610        12      100.0     11.03
28.300    3.1510    3.1588     0.120        108        10       17.7      2.85
28.830    3.0943    3.1019     0.120         92        10       15.1      2.14
29.495    3.0260    3.0335     0.160         27        10        4.4      0.83
29.870    2.9889    2.9962     0.120         21        10        3.5      2.60
31.190    2.8653    2.8724     0.240         18         9        2.9      0.75
31.705    2.8199    2.8269     0.240         23         9        3.8      2.40
```

```
File: SAMPLE3.DI                                        13-Sep-2004 12:18
=========================================================================
McGill Mining & Metallurgy                   PC-APD, Diffraction software

 Angle   d-value  d-value  Peak width  Peak int  Back. int  Rel. int  Signif.
 [°2θ]   α1  [Å]  α2  [Å]     [°2θ]    [counts]  [counts]    [%]

 35.235   2.5451   2.5514     0.200        29          8       4.8      1.64
 36.355   2.4692   2.4753     0.100        27          8       4.4      1.38
 36.845   2.4375   2.4435     0.080       125          8      20.6      1.42
 38.400   2.3423   2.3480     0.160        14          8       2.2      1.05
 39.260   2.2929   2.2986     0.160        23          8       3.8      1.47
 40.115   2.2460   2.2515     0.160        12          7       2.0      0.90
 40.540   2.2234   2.2289     0.060       137          7      22.4      0.77
 40.655   2.2174   2.2229     0.060        81          7      13.3      1.34
 42.245   2.1376   2.1428     0.160        18          8       2.9      1.04
 45.585   1.9884   1.9933     0.200        27          7       4.4      2.30
 47.205   1.9239   1.9286     0.080        92          6      15.1      1.83
 47.355   1.9181   1.9229     0.060        46          6       7.6      1.50
 48.505   1.8753   1.8799     0.200         7          6       1.1      1.23
 49.555   1.8380   1.8425     0.240        18          6       2.9      1.95
 49.915   1.8256   1.8301     0.080        52          6       8.5      1.18
 50.075   1.8201   1.8246     0.060        37          6       6.1      1.09
 51.985   1.7577   1.7620     0.480         5          5       0.8      0.78
 54.055   1.6951   1.6993     0.320         7          5       1.2      0.91
 54.665   1.6777   1.6818     0.080        14          5       2.4      0.88
 56.055   1.6393   1.6433     0.100       193          5      31.7      3.99
 56.235   1.6345   1.6385     0.060        92          5      15.1      2.22
 58.805   1.5690   1.5729     0.080        49          5       8.0      1.29
 58.950   1.5655   1.5694     0.060        37          5       6.1      1.26
 59.745   1.5466   1.5504     0.100        32          5       5.3      1.13
```

APPENDIX III

ARSENIC DISTRIBUTION COEFFICIENTS IN THE PRESENCE OF HA AND RHAMNOLIPID AND THE PARAMETERS OF THE DESORPTION ISOTHERM

Table AIII-1. Summary of the distribution coefficients of arsenic in the presence of HA and rhamnolipid

Humic acid															
r	Sample 1					Sample 2					Sample 3				
(mg/g)	pH 3	pH 5	pH 7	pH 9	pH 11	pH 3	pH 5	pH 7	pH 9	pH 11	pH 3	pH 5	pH 7	pH 9	pH 11
0.25	60.3	97.0	146.0	34.0	39.8	524.0	104.0	524.0	149.0	71.4	256.1	299.0	449.0	93.7	74.0
0.50	48.0	53.4	80.7	15.9	34.0	419.0	76.8	419.0	71.4	45.7	239.0	224.0	359.0	89.0	63.3
1.0	31.7	39.8	60.3	12.6	23.5	349.0	69.0	261.5	57.3	37.2	179.0	162.6	224.0	77.3	61.1
2.0	27.8	23.5	43.5	11.3	20.3	299.0	54.3	209.0	51.5	34.0	127.6	99.0	179.0	74.0	50.4
4.0	26.2	17.8	39.8	9.0	14.3	232.3	49.0	94.5	41.9	32.9	111.5	80.8	149.0	71.0	49.0
6.0	23.5	16.9	34.0	8.8	13.0	189.9	46.7	79.8	41.0	29.0	89.0	77.3	137.5	49.0	41.9
8.0	24.8	15.9	31.7	6.9	12.7	174.0	45.7	60.8	32.9	27.0	84.7	59.0	111.5	46.4	32.3
10.0	24.6	15.4	27.5	6.7	11.9	160.5	42.8	57.3	31.8	26.6	68.2	55.3	104.9	42.9	30.0
12.0	23.5	15.3	27.8	6.4	12.1	139.0	41.9	54.3	30.8	25.9	63.3	57.1	93.7	41.9	29.0
Rhamnolipid															
r	Sample 1					Sample 2					Sample 3				
(mg/g)			pH 7	pH 9	pH 11			pH 7	pH 9	pH 11			pH 7	pH 9	pH 11
0.25			43.5	39.8	29.6			139.0	94.5	76.8			127.6	74.0	61.1
0.5			39.8	26.2	17.8			130.3	51.5	41.0			80.8	57.1	41.9
1.0			29.6	21.3	15.3			115.7	45.7	34.0			65.7	55.3	33.6
2.0			24.8	19.4	14.8			79.8	41.0	32.9			57.1	41.9	30.6
4.0			23.5	18.6	11.0			57.3	39.4	26.6			53.5	39.9	24.4
6.0			21.3	14.3	10.1			54.3	32.3	25.3			51.9	35.7	24.0
8.0			20.3	13.8	9.2			51.5	31.8	20.0			49.0	29.0	19.0
10.0			18.6	12.6	8.8			46.7	28.6	18.1			42.9	26.7	17.9
12.0			17.8	12.2	8.6			45.7	28.2	17.4			41.9	26.3	17.8

Table AIII-2. Parameters for the desorption isotherm

Humic acid									
pH	Sample 1			Sample 2			Sample 3		
	a	*b*	R^2	*a*	*b*	R^2	*a*	*b*	R^2
3	23.01	10.16	0.9984	133.96	240.08	0.9612	59.24	125.07	0.9464
5	13.38	21.18	0.9983	40.72	25.76	0.9973	48.69	101.50	0.9754
7	25.31	38.09	0.9873	36.80	219.67	0.8783	88.16	167.03	0.9667
9	5.95	8.78	0.9872	28.78	37.62	0.9828	39.45	49.74	0.9633
11	10.99	12.35	0.9956	25.11	16.26	0.9960	27.58	39.97	0.9484
Rhamnolipid									
pH	Sample 1			Sample 2			Sample 3		
	a	*b*	R^2	*a*	*b*	R^2	*a*	*b*	R^2
7	17.46	14.47	0.9911	42.14	57.06	0.9899	41.20	33.22	0.9871
9	11.68	12.94	0.9820	27.08	24.68	0.9884	24.86	31.84	0.9695
11	8.09	8.53	0.9922	16.43	25.40	0.9613	16.60	21.18	0.9770

APPENDIX IV

ELECTROPHEROGRAMS OF STANDARD SOLUTIONS

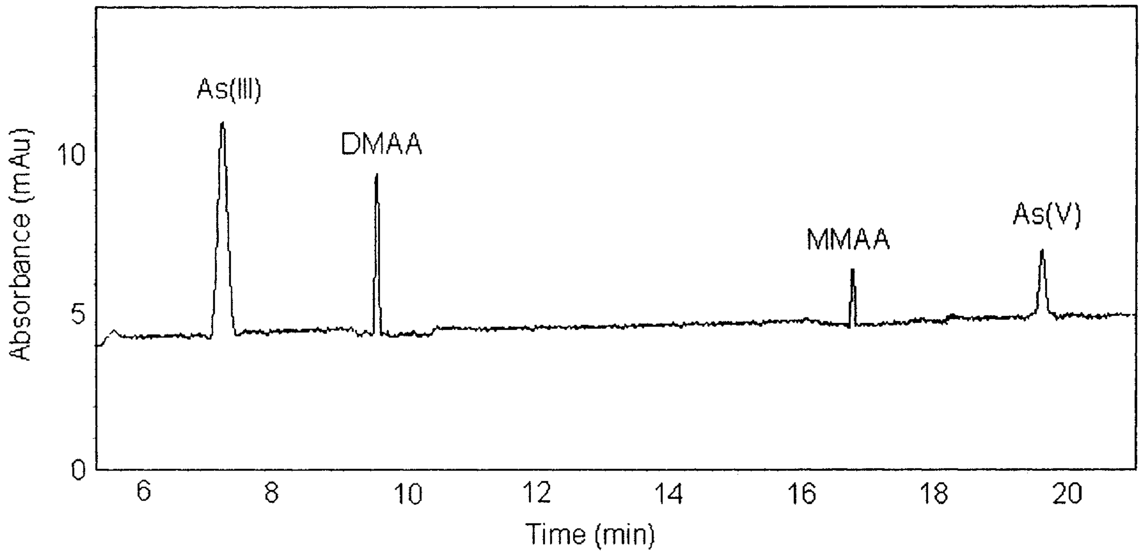

Figure AIV-1. Electropherogram of a standard solution containing As(III), As(V), MMAA and DMAA (25 mg arsenic/L each)

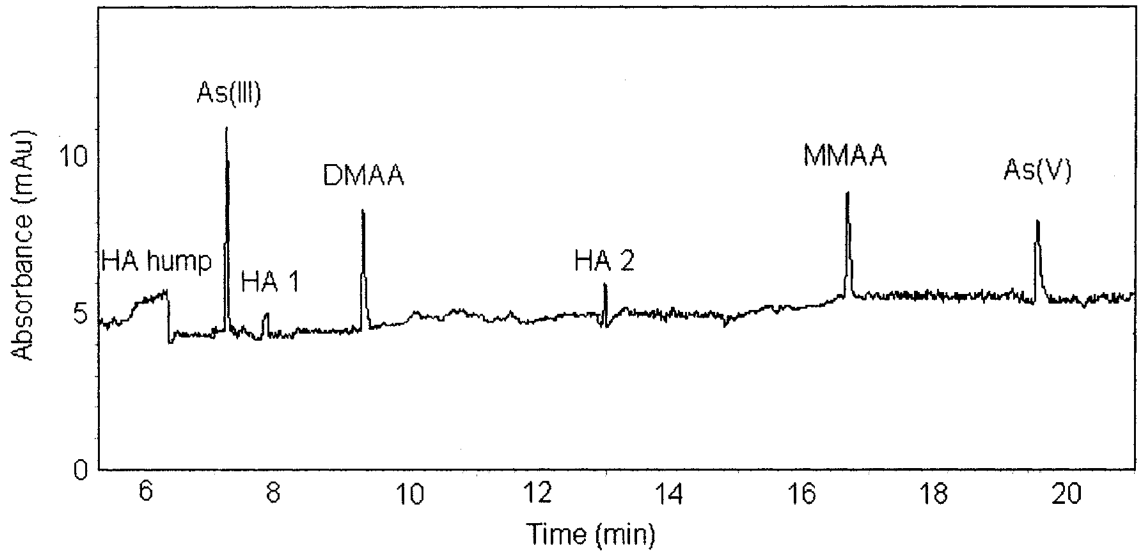

Figure AIV-2. Electropherogram of a standard solution containing four As compounds (25 mg arsenic/L each) and HA (25 mg/L)