WASTE MANAGEMENT OF ARSENIC ACCUMULATED PLANTS AT RON PHIBUN DISTRICT, NAKORN SI THAMMARAT PROVINCE, THAILAND

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ABSTRACT

The efficiencies of soil phytoremediation (SP) and constructed wetlands (CW) to remove arsenic from contaminated tap water at hot spots in the Ron Phibun District obtained in this study were high (79-85%). Arsenic accumulated plants and other residues were managed by burning them in a crematorium, degrading them in freshwater, utilizing arsenic accumulated banana stem fibres in the production of paper and paper products, performing solidification and stabilization (S/S) of high arsenic residues such as marigold ash and sediment sludge. Arsenic leaching tests were also performed on S/S samples with a result of 0.007-0.73 mg L^{-1}. Arsenic concentrations in tap water (influents) and effluents from the CW and SP were in the ranges of 0.09-0.45 and 0.05-0.08 mg L^{-1}, respectively. As a result, it could be reported that these plants were efficient in arsenic cleanup. The effluents could be discharged into a natural reservoir because arsenic levels were lower than the regulatory limit of 0.25 mg L^{-1}. Therefore, the residuals had been managed properly. Marigold burning and S/S of its ash were simple and suitable processes. Plant waste degradation, the production of banana paper, and S/S of contaminated soils and sludge all proved to be beneficial to human health and the environment.

KEY WORDS: ARSENIC ACCUMULATED PLANT / WASTE MANAGEMENT / PHYTOREMEDIATION / SOLIDIFICATION/STABILIZATION / UTILIZATION

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การจัดการพืชที่สะสมสารหนูจากอำเภอร่อนพิบูลย์ จังหวัดนครศรีธรรมราช ประเทศไทย
WASTE MANAGEMENT OF ARSENIC ACCUMULATED PLANTS AT RON PHIBUN DISTRICT, NAKORN SI THAMMARAT PROVINCE, THAILAND

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บทคัดย่อ

ประสิทธิภาพของแปลงทดลองไฟโตรีมิดีเอชั่นซึ่งประกอบด้วยสองระบบคือการใช้พืชที่ทนน้ำขังและพืชที่ปลูกบนดิน ผลปรากฏว่าพืชที่ใช้สามารถดูดสารหนูที่ปนเปื้อนในน้ำประปาภูเขาให้ลดลงได้คือลดค่าความเข้มข้น ของสารหนูในน้ำ ระหว่าง 0.09-0.45 มิลลิกรัมต่อลิตร เหลือเพียง 0.05-0.08 มิลลิกรัมต่อลิตรหรือคิดเป็น 79-85% พืชที่ใช้ดูดสารหนูเสร็จแล้ว เช่น ต้นกก บอน ดาวเรือง กล้วยน้ำว้า กล้วยหอม กล้วยเล็บมือนาง ดินหรือของเหลือ ทิ้งจากระบบ เช่น กากตะกอน เถ้าจากการเผาต้นดาวเรืองได้นำมาหาวิธีบำบัดให้เหมาะสมกับสภาพพื้นที่ซึ่งใช้ต้นทุนต่ำ ในการศึกษาครั้งนี้ใช้วิธีเผาต้นดาวเรือง การย่อยสลายในน้ำจืดของต้นบอน กล้วย ดาวเรือง การนำต้นกล้วยมาผลิตกระดาษแล้วแปรรูปกระดาษเป็นดอกไม้จันท์ใช้ในงานศพ พัดลมประดิษฐ์ ดอกไม้ประดับแจกัน ส่วนของเหลือทิ้งที่เป็นกากตะกอน เถ้าดาวเรือง ดินที่ใช้ปลูกพืชนั้น ได้นำมาศึกษาด้วยวิธีการละลายออกจากแหล่งเดิมด้วยสารละลายกรดอะซิติกและน้ำไม่มีประจุ ผลการศึกษาพบว่า ในกากตะกอน ดินปลูกพืช เถ้าดาวเรืองจะมีค่า สารหนูสูงกว่าค่ามาตรฐาน (50 มิลลิกรัมต่อกิโลกรัม) เช่น 5,740-23,438; 75-173; 158 มิลลิกรัมต่อกิโลกรัม ตามลำดับ แต่เมื่อทดสอบการละลายด้วยวิธีมาตรฐาน ระดับความเป็นพิษ (TCLP) พบว่ามีค่าต่ำกว่าค่ามาตรฐานคือไม่เกิน 5 มิลลิกรัมต่อลิตร ค่าที่ได้อยู่ในช่วง 0.02-1.86 มิลลิกรัมต่อลิตร เท่านั้น แสดงว่าของเหลือทิ้งดังกล่าวไม่เป็นของเหลือทิ้งชนิดอันตราย และเมื่อ นำมาผสมกับซิเมนต์เพื่อ ทดสอบการเป็นแท่งแข็งและเสถียร (S/S) ค่าการละลายของสารหนูยิ่งลดต่ำลงไปอีกคือต่ำกว่า 0.73 มิลลิกรัมต่อลิตร เท่านั้น จากผลดังกล่าวพิสูจน์ว่าการจัดการพืชที่สะสมสารหนูโดยการเผา การสลายตัวในน้ำจืด การนำมาผลิตกระดาษและการกักให้สารหนูเสถียรอยู่ในแท่งซิเมนต์ทำได้โดยไม่ทำความเสียหายต่อสุขภาพของคนและสิ่งแวดล้อม

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LIST OF ABBREVIATIONS

AA	activated alumina
As	arsenic
As (III)	arsenite
As (V)	arsenate
^{o}C	degree Celsius
CCA	chromated copper arsenate
cm	centimeter
CW	constructed wetland
d	day, days
DIW	deionized water
DW	dry weight
EC	electrical conductivity
EDTA	ethylenediaminetetraacetic acid
EfW	energy from waste
e.g.	example gratia
et al.,	et alii
EXAFS	extended X-ray absorption fine structure spectroscopy
Fe	iron
FeAsS	arsenopyrite
FMBO	Fe-Mn binary oxide
FTIR	Fourier transform infrared spectroscopy
g	gram
GFH	granular ferric hydroxide
h	hour, hours
HFO	hydrous ferric oxides
HGAAS	hydride generation atomic absorption spectrophotometer
H_2O_2	hydrogen peroxide

LIST OF ABBREVIATIONS (cont.)

i.d.	inner/inside/internal diameter
i.e.	id est
K	potassium
kg	kilogram
L	liter
m	meter
M	molarity
MΏ	megaohm
MCL	maximum contaminant level
MF	microfiltration
mg	milligram
min	minute, minutes
mL	milliliter
mm	millimeter
mM	milimolar
mol	mole
MW	magawatt
NF	nanofiltration
NTA	nitrilotriacetic acid
PA	phenylarsonic acid
PC	phytochelatins
PCC	pulverized cement concrete
Q	quantity
RO	reverse osmosis
rpm	round per minute
SD	standard deviation
SE	standard error
Sig.	significance

LIST OF ABBREVIATIONS (cont.)

SP	soil phytoremediation
spp.	species
S/S	solidification/stabilization
SS-EDDS	S,S-ethylenediaminedisuccinic acid
TCLP	toxicity characteristic leaching procedure
TDS	total dissolved solids
TSS	total suspended solids
U.S.EPA	the United States of America, Environmental Protection Agency
UF	ultrafiltration
v/v	volume per volume
WHO	the world health organization
wk	week, weeks
w/v	weight per volume
µg	microgram
µL	microliter
µm	micrometer
%	percent
[As]	arsenic concentration

CHAPTER I
INTRODUCTION

1.1 Arsenic contaminated water

Tin mining was operated for many years at Ron Phibun District, Nakorn Si Thammarat Province, southern of Thailand before the year 1987. This arsenic (As) anthropogenic source of arsenopyrite (FeAsS) released As into the environment of soil, surface and underground waters. Arsenic contaminated water from the canals of waterfall which originates from the hot spot area of arsenic source was measured in this study at the level of 0.34 mg L^{-1}. Arsenic released from this tin mining has contaminated widespread water and soil in the area. Natural surface water contained arsenic up to 0.50 mg L^{-1} (Visoottiviseth, 2006). It was reported that inorganic arsenic forms, As (III) and As (V), were the major cause of skin cancer for people living in Ron Phibun District. Ron Phibun District has 7 Sub-districts. Ron Phibun Sub-district has 16 villages. This Ron Phibun Sub-district had the highest cancer risk in Thailand (Intharapanit, 2004; Paijitprapapon, 2006). Health problems from arsenic contamination in drinking water were first discovered in 1987 following the diagnosis of a case of arsenical skin cancer at Ron Phibun District.

After the first arsenic poisoning patient was revealed in the local hospital in 1987, the detail clinical surveys were carried out by both regional and central public health authorities. The Public Health Office of Ron Phibun District revealed that there were 1,049 patients (Paijitprapapon, 2005) suffering from arsenic poisoning (called Blackfoot disease), or skin disorders diagnosed as hyperpigmentation, keratosis and skin cancer. Their ages varied from 4 months to 85 years and the incidence was 6.6% of total population at that time. Most patients, over 75%, were diagnosed with pigment changes showing spotty dermal melanosis and pinheaded dermal papules on palms and soles (Chuprapawan, 1994; Paijitprapapon, 2005; Visoottiviseth, 2006). The cancers of the skin and other internal organs (bladder, kidney, liver, and lung) have been reported to increase at the final stage of the disease (Intharapanit, 2004;

Paijitprapapon, 2005). The risk of cancers in Thai people at the age of 70 years old was one to ten (Chulalongkorn University, 2005). These manifestations and symptoms were related to chronic arsenic poisoning. The patients had been exposed to arsenic toxicity through drinking arsenic contaminated water from shallow dug wells over a long period of time. At present, people at the hot spot area of Ron Phibun District still use arsenic contaminated tap water which its original sources contact and contain arsenic higher than the maximum contaminant level (MCL) of 0.01 mg L^{-1}.

1.2 The arsenic removal experiments by constructed wetland and soil phytoremediation

Drinking arsenic-free water could reduce symptoms of arsenic toxicity. The World Health Organization (WHO) and the Thai drinking water standards for arsenic are set at 0.01 mg L^{-1} (Cairncross, 1999; Thai Industrial Standards Institute, 2006; Westbrook, 2006). This study was conducted in order to remove arsenic out from the arsenic contaminated tap water by constructed wetland and soil phytoremediation.

1.3 Phytoremediation and arsenic accumulated plants

Phytoremediation, a plant based green technology, means using plants to clean up toxicants in contaminated soils and waters by plant uptake toxic elements from roots transferred into stems and leaves. Chinese Brake fern (*Pteris vittata*) and silver fern (*Pityrogramma calomelanos*) have been discovered to be an arsenic hyperaccumulator (Ma et al., 2001; Francesconi et al., 2002; Visoottiviseth et al., 2002; Daus et al., 2005; Sridokchan et al., 2005). This technique is a cost-effective and environmentally friendly approach for field operation, especially suitable in Thailand, a tropical country.

Arsenic contaminated water was treated by the constructed wetland (CW) and soil phytoremediation (SP) plants. Plants used of the CW were *C. alternifolius* and *C. esculenta* (Elephant ear), while marigolds and bananas were used for removing arsenic in the SP. *C. alternifolius* and *C. esculenta* were selected for the CW because

C. esculenta was the best plant that removed arsenic from the solution of 1 mg L^{-1} for a 28 day exposure period as evidenced by the studying results on comparison among other plants of *Typha spp*., *Canna spp*., *H. psittacorum* and *T. dealbato* J. Fraser (Aksorn and Visoottiviseth, 2004; Jampanil, 2000). *Cyperus* spp. was grown at 10 plants m^{-2} in the water treatment with sand filter in Viet Nam (Proter and Cat, 2006). The authors reported that arsenic was removed to the level below the WHO standard. Marigold was also proved to have high efficiency to remove arsenic from contaminated soils at the high arsenic contaminated area in Ron Phibun District (Visoottiviseth, 2006; Chintakovid et al., 2008). Banana is the common name for the herbaceous plants of the genus Musa. It was also reported to be a potential plant used for soil phytoremediation (Tock et al., 2010).

1.4 Waste management of arsenic accumulated plants

Arsenic can be converted into different forms or transformed into insoluble compounds in combination with other elements, such as iron (Fe), but it cannot be destroyed (Leist et al., 2000). Arsenic in the form of pentavalent arsenate (As (V)) is most effectively removed or stabilized (Fuessle and Taylor, 2000; Leist et al., 2003). It was reported that As (V) was much more removable at 90% efficiency, while only 30% for As (III) during coagulation with ferric chloride (Hering et al., 1997). Three options are available for dealing with arsenic wastes. The first option is concentrating and containment; the second is diluting and dispersion; and the third is encapsulation of the material. The first option is limited by the issues of cost and safety. The second option causes serious health problems according to enhanced risks for cancers of skin and various internal carcinomas by long-term exposure and low concentration of arsenic. The most attractive option lies in encapsulating the contaminated material through solidification/stabilization technique and disposing of the treated wastes in secure landfills (Leist et al., 2000).

The biomass of arsenic accumulated plants needs proper disposal and management. Therefore, the objectives of this study were three techniques in order to manage these plant wastes. The first technique was weight reduction by drying and burning. This technique was applied with marigold biomass. Also marigold ash was studied by solidification/stabilization (S/S) before disposal. The S/S, encapsulation, or fixation is a technology used to transform hazardous liquid or solid wastes into less hazardous solids. The second technique was degradation in freshwater. This was explored with biomass of *C. esculenta*, banana and marigolds. The last technique was utilization as commercial products, i.e., making benefit from selling as ornamental plants of *Cyperus* spp. and making paper and its products from pseudostems of banana residuals.

CHAPTER II

OBJECTIVES

This work was performed to study the appropriate management techniques for arsenic accumulated wastes from the arsenic phytoremediation project at Ron Phibun District, Nakorn Si Thammarat Province. The objectives of this study were as follows:

1. To determine efficiency of plants used in constructed wetland and soil phytoremediation for arsenic removal from arsenic contaminated water.
2. To investigate arsenic accumulated plants by degradation in freshwater.
3. To manage marigold biomass by burning.
4. To study utilization of arsenic accumulated plants by making papers and their products and selling as ornamental plants.
5. To perform solidification/stabilization and leaching test for arsenic contaminated waste.
6. To study the suitable methods for management of arsenic accumulated plants, sludge, soil, and bottom ash of marigolds.

CHAPTER III
LITERATURE REVIEWS

3.1 Arsenic

Arsenic (As), toxic metalloid, is the third element in Group 15 (formerly named subgroup VA) of the Periodic Table, it has the atomic number of 33, atomic mass of 74.92, melting point of 817 ºC, oxidation states of -3, 0, +3, and +5, and its chemical properties are similar to those of phosphorus. Arsenite, As (III), is the dominant form under reducing conditions (less oxygen, underground water); while arsenate, As (V), is the stable form in oxygenated conditions such as surface waters. Both forms interconvert readily and their ratio varies depending on redox chemistry and biological activity. It is colorless, odorless, and tasteless.

Arsenic mobility, since arsenic is a redox-sensitive element, its chemical speciation is dependent on changes in system redox parameters that are driven by biotic and abiotic processes. The mobility of arsenic is tied to the cycling of major elements such as carbon, iron, and sulfur between the solution and solid phase in natural and engineered systems (U.S. EPA, 2003).

3.1.1 Arsenic in the environment and its sources

Elevated arsenic concentrations are found in groundwater due to anthropogenic activities and natural processes. Anthropogenic activities include mining and smelting, using of arsenical pesticides, herbicides and crop desiccants, releasing of industrial effluents, and disposing of chemical waste (Bang et al., 2005). The release of arsenic from natural processes can be caused by the reduction of iron hydroxides and the oxidation of pyrite minerals including orpiment (As_2S_3) and realgar (As_2S_2). Naturally occurring arsenic in drinking water supplies may affect more than 100 million people worldwide, including countries like Bangladesh, India, China, Chile, Argentina, Mexico, Hungary, Taiwan, Vietnam, Japan, New Zealand, Germany, and the United States (Ng, 2005).

Arsenic occurs in crustal rock at an average concentration of 2-3 mg kg^{-1}; arsenopyrite (FeAsS) is the most abundant arsenic-containing mineral (Francesconi, 2005). Weathering of rocks leads to the soluble oxoanions, arsenite (As^{+3}) and arsenate (As^{+5}) and they are the dominant forms of arsenic in freshwater and in seawater. Arsenate is favored over arsenite under usual environmental oxygen levels.

Figure 3.1 Arsenic rocks from Ron Phibun District, Nakorn Si Thammarat Province

The presence of arsenic in natural water is related to the process of leaching from the arsenic containing source rocks and sediments. It is generally associated with the geochemical environments such as basin-filled deposits of alluvial acustrine origin, volcanic deposits, inputs from geothermal sources, mining wastes (Figure 3.1) and landfills. Arsenic is a constituent of over 300 minerals and is commonly found in non-ferrous ores such as copper, lead, zinc, gold, and uranium. Arsenic is a primary constituent of certain ores (e.g. the copper mineral enargite) and occurs as a trace impurity in others.

Uncontrolled anthropogenic activities such as smelting of metal ores, using of arsenical pesticides and wood preservatives agents may also release arsenic directly to the environment. Presently, arsenic has been used for a variety of purposes such as treatment of ulcers, tuberculosis, syphilis, and many other ailments. Arsenic trioxide is a very effective treatment for certain types of leukaemia (Francesconi, 2005). More recently, arsenic has been used as an insecticide, fungicide, rodenticide, and wood preservatives. The common applications of arsenic are in the manufacture of pesticides, dessicants, glass, alloys, electronic components (semiconductors), pigments, pharmaceuticals (Yokel et al., 2002). Also, burning fuels (petroleum, coal, and wood), waste incineration, cattle and sheep dips, feed additives and dye stuffs are generated of arsenic released into the environment. Figure 3.2 showed that the estimated end-use of arsenic in the United States of America (USA) was 70% in wood preservatives, 22% in agricultural chemicals, 4% in glass, 2% in nonferrous alloys, and 2% in other uses (Ng, 2005).

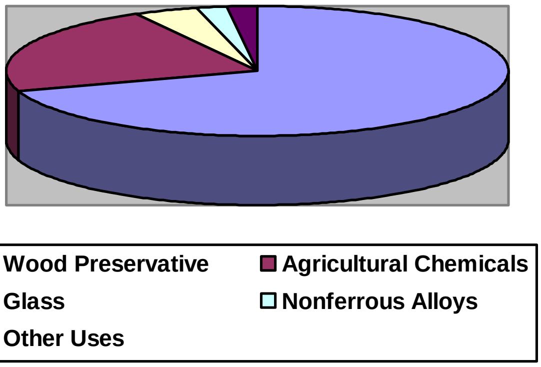


Figure 3.2 Sources of anthropogenic activities for arsenic toxicants in the USA

3.1.2 Arsenic toxicity and impact on human health in Thailand

Most natural waters contain inorganic species; As (III) is predominant in ground waters (H_3AsO_3) and As (V) is released in surface waters as H_2AsO_4 (pH 3-7) and $HAsO_4^{2-}$ (pH7-11) (Abernathy; Clesceri, 1998). Arsenite is the most toxic inorganic arsenic (Michon et al., 2010) and 25-60 times more mobile than arsenate (Moon et al., 2007). For organic arsenicals are less toxic than inorganic arsenic (Choi et al., 2010); arsenobetaine (quick decay in the environment) in seafoods is excreted unchanged in the urine of humans consuming it and toxicity tests have indicated that arsenobetaine has no measurable toxicity (Francesconi, 2005). In marine waters, algae take up arsenate and transform it into a group of arsenosugars. Inorganic arsenic generally exists in two predominant oxidation states, arsenite ($NaAsO_2$) and arsenate (Na_2HAsO_4), both are toxic to man and plants. Inorganic arsenic is always considered a potential human carcinogen, associated with increased risk for cancer of the skin, lungs, urinary bladder, liver and kidney. Arsenic commonly present in water are pH dependant species of the arsenic (H_3AsO_4) and arsenous (H_3AsO_3) acids, respectively. These anions have acidic characteristics, the stability and dominance of a specific species depend on the pH of the solution. Arsenates are stable under aerobic or oxidizing conditions, while arsenites are stable under anaerobic or reducing conditions.

Arsenic is toxic and carcinogenic. It has been classified in Group I (carcinogenic for human). The toxicity of arsenic is reported to be in the order of arsine, followed by arsenites and arsenates and the least, organic arsenic compounds. The acute (high-dose) and chronic (low-dose) effects of arsenic exposure are different. Lethal doses in human range from 1.50 mg kg^{-1} (diarsenic trioxide) to 500 mg kg^{-1} of body weight (dimethyl arsenate). The symptoms of acute toxicity occur within 30 minutes of exposure but may be delayed for several hours if it is solid or taken with a meal. In the first edition of the guidelines for drinking water quality, The WHO recommended a guideline value of 0.05 mg L^{-1}, it has been reduced to 0.01 mg L^{-1} in 1993 and was expected to reinforce in the USA in 2006. The present recommended value of arsenic in drinking water was the value of total arsenic. The toxicity of inorganic arsenic was more higher than organic arsenic with very low LD$_{50}$; chemical form and LD$_{50}$ were shown in the table 3.1.

Table 3.1 Arsenic toxicity and the LD$_{50}$

Chemical form	Structure	Abbreviation	LD$_{50}$ (mg kg^{-1})
Inorganic arsenic			
Arsenous acid (arsenite)	H_3AsO_3	As (III)	14.0
Arsenic acid (arsenate)	H_3AsO_4	As (V)	20.0
Organic arsenic			
Monomethyl arsenic acid	CH_3AsO_n	MMA	700-1,600
Dimethyl arsenic acid	$(CH_3)_33AsO_n$	DMA	700-2,000
Arsenocholine	$(CH_3)_3AsCH_2CH_2$	AsC	6,500
Arsenobetaine	$(CH_3)_33AsCH_2COO$	AsB	> 10,000

Source: Visoottiviseth, 2006.

3.1.3 Arsenic contamination and population at risk

People about 100 million were estimated to be at risk of exposing to excessive levels of arsenic globally, such as Bangladesh, China, Argentina, West Bengal of India, Nepal, Chili, Mexico, Peru, Taiwan (Table 3.2). The people at risk about 200-50,000 thousand from these countries have ingested drinking water containing arsenic from less than 0.01 to 8 mg L^{-1} (Ng, 2005). Although Thailand had a number of people at risk only 1,049 since 1980s (Chuprapawan, 1994; Paijitprapapon, 2005); but, arsenic concentration in drinking water was high at 5 mg L^{-1}. Regulation for arsenic in drinking water of the WHO, US EPA, Taiwan, Vietnam, Hungary, Romania, and Australia was limited for $\leq$ 0.01 mg L^{-1} (Bhattacharya et al., 2007). The maximum contaminant level of arsenic in drinking water for Thailand was 0.01 mg L^{-1} (Ministry of Science Technology and Environment, 1994; Ministry of Natural Resources and Environment, 2000; Thai Industrial Standards Institute, 2006).

Arsenic in water cannot be seen, tasted, or smelled. Arsenic may cause neurological damage to those who drink arsenic contaminated water with slightly greater than 0.10 mg L^{-1}. Arsenicosis may lead to a very painful death. Arsenic tends not to accumulate in the body but is excreted naturally through feces, urine, sweat, milk, hair and skin. If arsenic is ingested faster than it can be excreted; it will be accumulated in hair and fingernails and is stored in the liver, the kidney, the heart and the lungs. Arsenic readily crosses the placental barrier and fetal damage has been reported. Toxicity of arsenic depends on its accumulation in the body. It may take 5-20 years to develop symptoms in human beings, depending on the exposure, body defense mechanism and nutritional status. Early symptoms can range from the development of dark spots on the skin, to a hardening of the skin into nodules, often on palms and soles. Advanced skin lesions on the palms and soles can be very painful. Skin cancer (squamous cell carcinoma, or Bowen’s disease and basal cell carcinoma) can be occurred in the severe case of chronic toxicity (Chuprapawan, 1994; Visoottiviseth, 2006). The only efficient way to reduce chronic global exposure to arsenic and to avoid further human losses is the inactivation of important sources of anthropogenic arsenic such as hard rock mining and burning of fossil fuels (Dani, 2010).

Table 3.2 Countries of arsenic contamination and population at risk

Country	Population at risk (thousands)	As concentration (mg L^{-1})	Discovery date
Bangladesh	50,000	0.001-4.70	1980s
China	5,630	0.001-8.00	1980s
Argentina	2,000	0.10-1.00	1981
West Bengal (India)	1,000	< 0.01-3.90	1980s
Nepal	550	0.008-2.62	2001
Chili	437	0.90-1.04	1971
Mexico	400	0.01-4.10	1983
Peru	250	0.50	1984
Hungary	220	0.01-0.18	1974
Taiwan	200	0.01-1.82	1950s
Romania	36.0	0.01-0.18	2001
Bolivia	25.0	-	1997
Vietnam	Millions	0.001-3.05	2001
Western USA	-	0.01-48.0	1988
Thailand (Ron Phi Bun)	1.00	0.001-5.00	1980s

Source: (Visoottiviseth, 2006)

Choong and colleagues (2007) reviewed that there are four recognized stages of arsenicosis, or chronic arsenic poisoning:

1. Preclinical: the patient shows no symptoms, but arsenic can be detected in urine or body tissue samples.
2. Clinical: various effects can be seen on the skin at this stage. Darkening of the skin (melanosis) is the most common symptom, often observed on the palms. Dark spots on the chest, back, limbs or gums have also been reported. Oedema (swelling of hands and feet) is often seen. A more serious symptom is keratosis, or hardening of skin into nodules, often on palms and soles. WHO estimates that this stage requires 5–10 years of exposure to arsenic.

3. Complications: clinical symptoms become more pronounced and internal organ are affected. Enlargement of liver, kidneys and spleen have been reported. Some research indicates that conjunctivitis (pinkeye), bronchitis and diabetes may be linked to arsenic exposure at this stage.

4. Malignancy: tumors or cancers (carcinoma) affect skin or other organs. The affected person may develop gangrene or skin, lung or bladder cancer.

3.1.4 Arsenic and health problems in Thailand

Cases of chronic arsenic poisoning to people in Ron Phibun District were first diagnosed in 1987. Investigations by the Department of Public Health have confirmed that the main cause of exposure was the consumption of high arsenic contaminated water. In 1988, the estimated population “at risk” was 15,000; and more than 1,000 people aged between 18 months to 85 years were found suffering from chronic arsenic poisoning (Williams, 1996). The different stages according to the Thai diagnosis standard was shown in the Table 3.3. Most patients, over 75%, were diagnosed with pigment changes showing spotty dermal melanosis and pinheaded dermal papules on palms and soles (Chuprapawan, 1994; Paijitprapapon, 2005). These manifestations and symptoms were related to chronic arsenic poisoning. The patients had been exposed to arsenic toxicity through drinking arsenic contaminated shallow groundwater from dug wells over a long period of time. Some died with skin cancer 10 years ago (Figure 3.3).

Arsenic poisoning: blackfoot disease and skin cancer

melanosis or depigmentation

rain-drop like

nodular keratosis

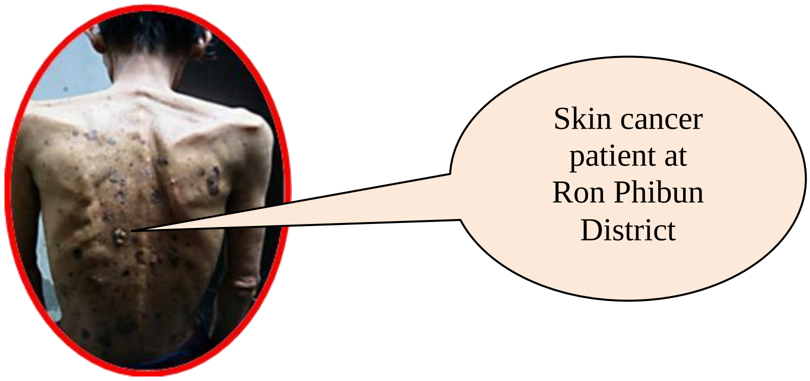


Figure 3.3 Showing the symptoms of arsenic poisoning patients at Ron Phibun (Visoottiviseth, 2006).

Table 3.3 Classification of chronic arsenic poisoning in Thailand

Level	Symptom
0	No skin lesion, high arsenic level in blood, urine, hair or nail
1a	Spotty dermal melanosis of palm and sole
1b	Pin-headed dermal less than 5 papules of palm and sole
2	Pin-headed dermal more than 5 papules of palm and sole
3	Pin-headed dermal papules with keratosis papules with crater size more than 0.5 cm
4	Scaly erythematous or brownish patches of Bowen's disease, basal cell epithelioma and squamous cell carcinoma, usually generalize

Source: (Chuprapawan, 1994; Visoottiviseth, 2006)

3.2 Arsenic contamination in the study area of Ron Phibun

3.2.1 The study area of Ron Phibun Sub-district

The Ron Phibun Sub-district consists of 3 Moo (village) of 2, 12, and 13 that people at risk have been living in many more than other villages (Figure 3.4 and 3.5). Most people stay in their houses along roads, or paths; also water supply systems like tap water, big tanks, etc. have been setup for them. Arsenic concentration in the water was shown in higher than the Thai water drinking standard of 0.01 mg L^{-1}, so this means that they are at risk for chronic symptom of arsenic. The experimental site was located at the begin of mountain tap water pipe lines (Figure 3.6).

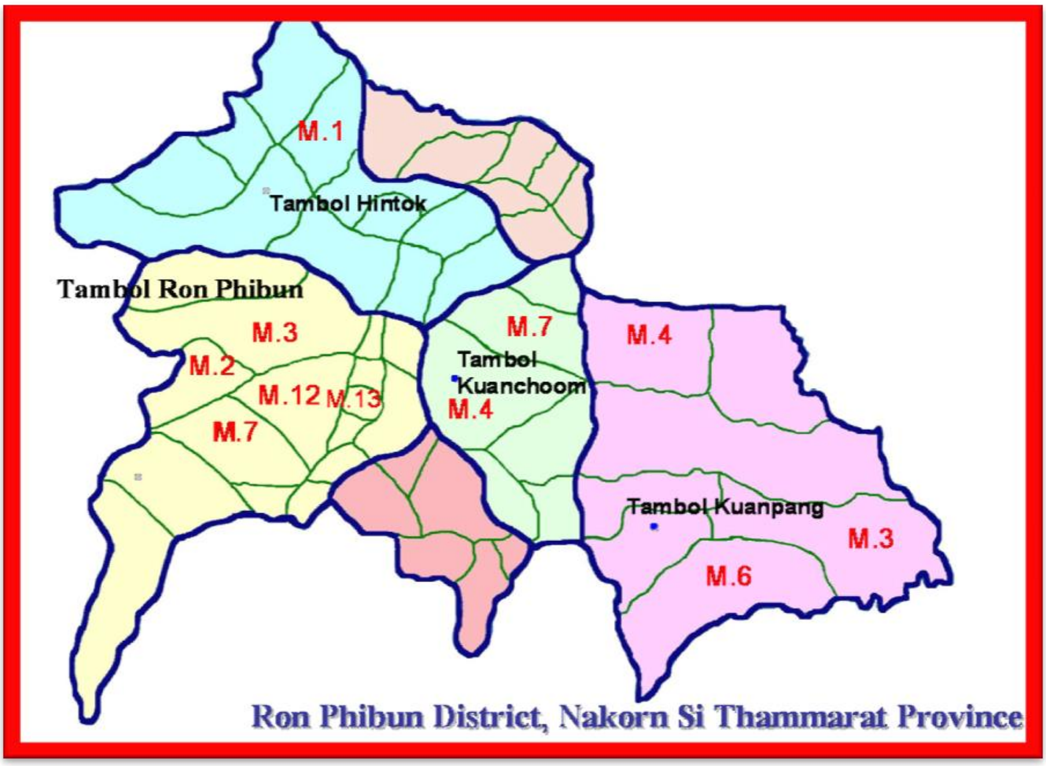


Figure 3.4 Map of Ron Phibun District : high risk arsenicals area

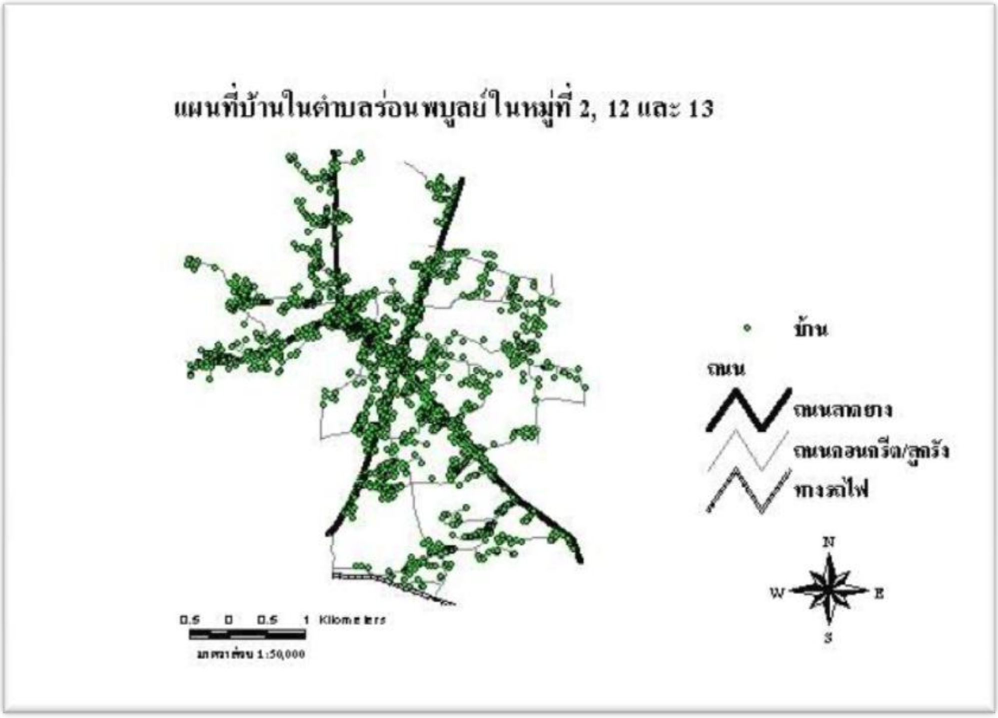


Figure 3.5 Community at high risk of arsenicosis: Moo 2, 12, and 13, Ron Phibun Sub-district

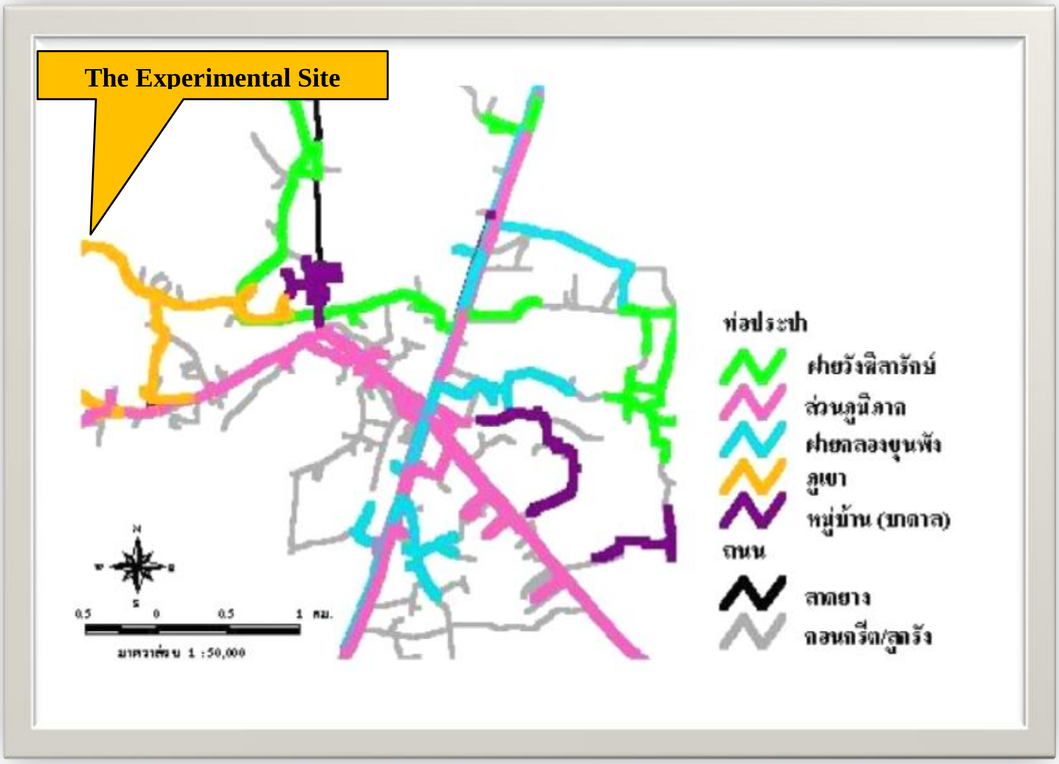


Figure 3.6 Pipelines of water supply in Moo 2, 12, and 13, Ron Phibun Sub-district

3.2.2 Arsenic contamination in Ron Phibun District

Tin mining had been an economic activity in the area for more than a century and it was concluded that mining and mineral processing was the cause of arsenic contamination. Arsenopyrite (FeAsS) concentrations (around 1%) are associated with economic mineral concentrations of the tin and tungsten minerals, cassiterite and wolframite, that occurred in pegmatite and quartz veins throughout the granite mountain. The mining technique in the area was open pit mining which caused exposure of the mineralized layers to the atmosphere and stimulated the oxidization processes (Figure 3.7). Mining wastes in Ron Phibun were determined for arsenic concentration in the range of 21-11,100 mg kg^{-1} (Warzke, 2006). Arsenic contained in the disseminated arsenopyrite was liberated into the environment as inorganic arsenic of arsenite and arsenate (Paijitprapapon, 2006).

Figure 3.7 Open pit mining for tin smelting at Ron Phibun District

Arsenic concentration in water and soil exceeded the national health standard of 0.01 mg L^{-1} for drinking water and the geochemical guideline of 50 mg kg^{-1} for soil (Paijitprapapon, 2005). Monitoring data from 1992-1997 identified that arsenic concentrations in running water around mountainous areas average 0.50 mg L^{-1} whereas those at the downhill alluvial plain measured higher than 1.00 mg L^{-1}. The average concentration of arsenic was around 0.10-0.20 mg L^{-1} with the highest value of 0.90 mg L^{-1} (Paijitprapapon, 2006; Wongsanoon, 2004).

Arsenic contamination in shallow groundwater from dug wells trended to decrease; it could be depended on changing seasons. Shallow well water in 1990 had a relatively high concentration of 0.90 mg L^{-1}. The highest value declined to 0.51 mg L^{-1} in 1994 and to 0.20 mg L^{-1} in 1999 (Paijitprapapon, 2006). However, in 2004 the arsenic concentration in well water increased to 0.31 mg L^{-1} and declined again to 0.20 mg L^{-1} in 2005 (Paijitprapapon, 2005). It was significant that the wells where the highest concentrations of arsenic were found during annual surveys were not always the same. This showed the complexity of the mechanism of dispersion and precipitation of arsenic and its compounds. The chemical form of arsenic in surface and shallow well waters showed a dominance of arsenate (Paijitprapapon, 2006).

Distribution patterns of arsenic concentration in soil and stream sediment of more than 100-5,000 mg kg^{-1} (Visoottiviseth, 2006) corresponded quite closely with those in shallow groundwater. Sources of water supply in this Ron Phibun were high arsenic contained: surface water contained 0.30-0.50 mg L^{-1}, tap water 0.10-0.17 mg L^{-1} (Visoottiviseth, 2006) and 0.29 mg L^{-1} (Warzke, 2006), and in dug well 0.22 mg L^{-1} (Intharapanit, 2004). High arsenic contamination in all media was found concentrated in two Moo of 2 and 12 in Ron Phibun Sub-district covering a small area of 7-10 km^2.

Surface arsenic contaminated water

Dug well arsenic contaminated water

Mountain arsenic contaminated tap water

Figure 3.8 Arsenic containing waters from surface water, shallow dug well and tap water supply at the hot spots of Ron Phibun District

3.3 Treatment and removal of arsenic

Choong and colleagues (2007) had reviewed the results of the studies for arsenic removal and treatment. Dilution and dispersion methods attract the interest of mining and waste disposal operators. The method provides the possibility for combining numerous waste streams together and in a way which dilutes the hazardous contaminants, thus passing any regulatory limits. It helps in reducing human exposure to arsenic. There are several methods for arsenic removal. These methods include coagulation and flocculation, precipitation, adsorption and ion exchange, membrane filtration, ozone oxidation, bioremediation and electrochemical treatments also used in the removal of arsenic.

3.3.1 Coagulation, flocculation, and precipitation

Coagulation and flocculation are used for processes of arsenic removal. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge of the colloids. As a result, the particles collide to form larger particles. Rapid mixing is required to disperse the coagulant throughout the liquid. Flocculation is the action of polymers to form bridges between the larger mass particles or flocs and bind the particles into large agglomerates or clumps. Bridging occurs when segments of the polymer chain adsorb on different particles and help particles aggregate. An anionic flocculant will react against a positively charged suspension, adsorbing on the particles and causing destabilization either by bridging or charge neutralization. Aluminium-based coagulation with disinfection by chlorination is one of the commonly used treatment methods.

Changing forms and concentrations of arsenic through aluminium-based coagulation treatment processes for drinking-water treatment plants were studied. Aluminium-based coagulation with disinfection by chlorination, the form of arsenic most likely to be present in the treated water is soluble As (V) because final chlorination should have converted any remaining As (III) to As (V). This study showed that prechlorination can have an adverse effect on other water quality parameters such as the formation of disinfection by-products and the release of taste and odor compounds from algal cells (Gregor, 2001).

Using limestone as a sorbent, $Ca_3(AsO_4)_2$ was produced by the oxidation of the $Ca(AsO_2)_2$ (Diaz-Somoano et al., 2010).

Altundoğan and Tümen (2003) studied the As (V) removal using neutralization of liquid phase red mud (LPRM) - arsenical solution mixtures with acid solution accompanied with air-agitation and neutralization of those mixtures with CO_2 gas. It was found that As (V) was removed effectively by LPRM with a volumetric

LPRM/As (V) solution ratio of 0.1 from an arsenical solution, in the As (V) concentration of 20 mg dm^{-3}. For an efficient removal, it was found that an Al/As (V) molar ratio of 6–8 was required.

Ferric salts are common in the uses of as a coagulant. A combination system of ferric sulphate coagulation/sand filtration in arsenic removal was studied and showed that it was economic and effective (Yuan et al., 2003). Arsenic removal by applying a modification of a coagulation/flocculation process referred to the introduction of pipe flocculation process in the first stage of the technique, whereas the second step had been performed by direct filtration with sand filters, instead of separation by sedimentation (Zouboulis and Katsoyiannis, 2002). In the system, alum or ferric chloride was used as the coagulant agent enhanced by some organic polymers. The coagulants were found to be efficient regarding arsenic removal and had achieved up to 99% of arsenic removal. However, the actual efficiency of removal is highly dependent on the raw water quality.

Four precipitation processes are useful; alum coagulation, iron coagulation, lime softening, and a combination of iron (and manganese) removal with arsenic.

Alum precipitation is able to remove solids and dissolved metals. For the removal of arsenic, alum is most effective if an oxidizing agent, such as chlorine, is added ahead of the flocculator and clarifier and the pH is reduced to 7 or less. It would probably be necessary to use a number of chemicals in order to treat the arsenic in the drinking water. The arsenic removed from the water would be contained in the alum sludge from tile clarifier (Kartinen and Martin, 1995).

Iron precipitation is simple and low cost. The operator adjusts pH and iron dose to remove the trace elements. In this process, an iron compound, such as a ferric salt, i.e. ferric chloride, ferric sulphate, is added to the untreated water. The arsenic combines with the iron to form a precipitate (iron oxyhydroxide in the form of sludge) that settles out in the clarifier. Following the clarifier, a filter is employed which removes iron/arsenic particles not taken out in the clarifier. The best arsenic removal rates are obtained at pH of less than 8.5 with or without chlorine. Ferric chloride is more frequently used rather than ferric sulfate. Jones and colleaques (1977) studied the removal of arsenate from sulphuric solution. It was found that ferrous iron provides an effective treatment giving residual dissolved arsenic concentrations of below 1 mg L^{-1} over a range of compositions along with 99.9% removal. They also noticed that ferric iron treatment is more effective in conjunction with mixed lime and magnesium hydroxide.

Developments and improvements of remedial technologies are needed to effectively manage arsenic contamination in groundwater at hazardous waste sites. Wilkin and colleaques (2009) built the pilot-scale permeable reactive barrier (PRB) of 9.1-m long, 14-m deep, and 1.8-2.4-m wide (in the direction of groundwater flow) at a former lead smelting facility, located near Helena, Montana (USA). The reactive barrier was designed to treat groundwater contaminated with moderately high concentrations of both As (III) and As (V). The reactive barrier was installed over a 3-day period using bio-polymer slurry methods and modified excavating equipment for deep trenching. The reactive medium was composed of granular iron which was selected based on long-term laboratory column experiments. A monitoring network of approximately 40 groundwater sampling points was installed. Monitoring results indicated arsenic concentrations >25 mg L^{-1} in wells located hydraulically upgradient of the PRB. Collecting 80 groundwater samples from the pilot-PRB, 11 samples exceeded 0.50 mg L^{-1}; 62 samples had concentrations of arsenic at or below 0.50 mg L^{-1}; and, 24 samples were at or below the MCL for arsenic of 0.01 mg L^{-1}. After 2 years of operation, monitoring points located within 1 m of the downgradient edge of the PRB showed significant decreases in arsenic concentrations at depth intervals impacted by the emplaced zero-valent iron. This study indicated that zero-valent iron can be effectively used to treat groundwater contaminated with arsenic given appropriate groundwater geochemistry and hydrology.

Lime softening will remove substances from water other than hardness (calcium and magnesium ions). Arsenic can be removed by lime softening. The produced sludge does not present any added value, and can limit the use of this technology. The suppliers prefer a treatment in two stages: removal of arsenic following with a lime softening. The arsenic removal efficiencies of the lime softening process are significantly affected by the pH and the presence (or absence) of chlorine. Chlorine is required to oxidize the arsenic and acid would probably be necessary to lower the pH of the treated water to acceptable drinking water levels. The arsenic removed from the water will be removed together with the lime sludge produced by the process. Huang and Rong (2001) reported the uses of calcium breach and lime in the treatment of sewage with high arsenic content.

Combined with iron (and manganese) removal, there are a number of processes that are used to remove iron and/or manganese from water by oxidizing the iron and/or manganese from their soluble state (valence of 2+) to a higher valence to form iron and/or manganese precipitates that can be filtered from the water. One of the processes involves a proprietary media. In one variation of this process, chlorine is injected into the raw water containing iron and/or manganese and allowed to react with the iron and/or manganese in a reaction vessel for a short time-a minute or two. Following the chlorine reaction vessel, sulfur dioxide may also be injected into the water and allowed to react for a short period of time. The water is then discharged into one or more filter vessels which contain the proprietary media. Differences exist between media that result in different capabilities. The process in which iron and/or manganese are frequently removed from water using manganese greensand, called “greensand”, which is coated with manganese dioxide.

Kartinen and Martin (1995) reported that arsenic removal rates of 90% obtained from this process. When permanganate is applied intermittently to the greensand during backwash, the process will form a layer of MnO_2 on the filter media that adsorbs multivalent cations. The adsorbed ions are then held until permanganate is applied again during backwash. This adsorbed material is eliminated may be oxidized to insoluble forms that remain in layers on the greensand.

Other precipitation methods, Palfy and colleaques (1999) studied the treatment of arsenic using H_2O_2, calcium oxide, ferric sulphate, Portland cement (Kundu et al., 2004) as the precipitation agents and arsenic waste neutralization. Their findings suggested that a considerable reserve of arsenic solubility was achieved by relatively high excess of additives. From their leachate analysis approved that lime precipitation in combination with cement solidification can provide safe material. The solubility of arsenic was reduced from original value of 6,430 mg L^{-1} to 0.82 mg L^{-1} leachate from the produced solidification.

Leonard and Stegemann (2010) explored the effectiveness of Portland cement (CEM I), with the addition of high carbon fly ash (HCFA), as a novel binder, for the improvement of leachability-related properties of solidified/stabilized (S/S) petroleum drill cuttings. A factorial design experiment was adopted to investigate the effects of waste-to-binder ratio, HCFA addition, and curing time on leachate pH, acid neutralization capacity (ANC), and metal, chloride and hydrocarbon leaching. The leachate pH and ANC of all products suggested successful formation of a calcium-silicate-hydrate-based matrix with good resistance to acid attack, and little detrimental effect from drill cuttings addition. Leaching of amphoteric metals was significantly affected by pH, which was a function of other studied factors. All studied factors also affected leaching of chloride and hydrocarbons. CEM I, without HCFA addition, was more effective in immobilizing chlorides, but the overall chloride immobilization was poor in all runs. HCFA addition significantly reduced the leaching of hydrocarbons. Comparison of milligram of contaminant leached per kilogram of drill cuttings from the S/S products and untreated drill cuttings provided clear evidence of hydrocarbon and chloride immobilization. This work shows that HCFA improved the immobilization of organic contaminants and may represent an inexpensive binder for stabilization/solidification of organic wastes.

3.3.2 Adsorption and ion exchangers

Adsorption is a process that uses solids for removing substances from either gaseous or liquid solutions. Adsorption characteristics are operative in most natural physical, biological, and chemical systems. Adsorption operations employing solids such as activated carbon, metal hydrides and synthetic resins are used widely in industrial applications for purification of waters and wastewaters. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Thus adsorbents are characterized by surface properties such as surface area and polarity.

For arsenic removal, an ion exchange resin, usually loaded with chloride ions at the exchange sites, is placed in vessels. The arsenic containing water is passed through the vessels and the arsenic exchanges for the chloride ions. The water exiting the vessel is lower in arsenic but higher in chloride than the water entering the vessel.

Eventually, the resin becomes exhausted; that is, all or most of the exchange sites that were loaded with chloride ions become loaded with arsenic or other anions. The chloride ions that used to be on the resin were exchanged for the arsenic and other anions that were in the water being treated.

Jackson and Miller (2000) found that sulfate was reported not to influence As (V) sorption by ferrihydrite but resulted in a considerable decrease in As (III) sorption below pH 7, with the largest decrease at the lowest pH. On the contrary, sulfate was found to decrease both As (V) and As (III) sorption on hydrous ferric oxide in the pH range of 4-7 (Wilkie and Hering, 1996). Some of sorbents include zeolites, goethite, clay, kaolinites, activated carbon, chitosan beads, coconut husk, coal, fly ash, ferrous iron, alumina, zirconium oxide, red mud, red earth (Vithanage et al., 2007), petroleum residues, rice husk, human hair, sawdust, manganese greensand, orange juice residues (Ghimire et al., 2003).

Zinc removal from leachate was studied using fly ash, phosphogypsum and red mud. The adsorption capacities and adsorption efficiencies were determined. The results show that addition of fly ash, phosphogypsum and red mud to the zinc leach residue drastically reduces the heavy metal content in the leachate and they could be used as liner materials (Zoruh and Ergun, 2010).

Activated carbon is commonly used as the material in arsenic treatment. The adsorption of As (III) and As (V) using activated carbon was various pH values. The iron oxide impregnated activated carbon has shown higher As (III) and As (V) removals compared with the non-impregnated carbon (Huang and Vane, 1989). Carbon pretreated with Ag^+ or Cu^{2+} ions improved As (III) adsorption but reduced As (V) adsorption (Rajakovic, 1992). Arsenic adsorption can be improved by impregnating carbon with ferric hydroxide or tartaric acid. Lorenzen and colleaques (1995) studied the factors (solution pH, carbon type and carbon pretreatment and elution of the arsenic from loaded carbon) that affect the mechanism of the adsorption of arsenic species on activated carbons. They found that As (V) is more effectively removed from solution by using activated carbon with high ash content and pre-treatment of the carbon with Cu (II) solutions improves its arsenic removal capacity. The use of commercial activated carbon is not suitable for developing countries because of its high cost. The preparation of low cost adsorbent for water purification and wastewater treatment has been reviewed as follows: agricultural wastes like rice husk (Bailey et al., 1999; Khalid et al., 1998; Lee et al., 1999), coconut husk (Manju et al., 1998), amine modified coconut coir (Baes et al., 1997), carbonized wood powder (Pulido et al., 1998), sawdust (Raji and Anirudhan, 1999), orange juice residues (Ghimire et al., 2002) and waste tea fungal biomass (Murugesan et al., 2006).

Adsorption process has been proven one of the best water treatment technologies around the world and activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse types of pollutants from water (Bhatnagar and Sillanpไไ, 2010). But, commercial activated carbon is restricted due to its higher costs. Attempts have been made to develop inexpensive adsorbents utilizing numerous agro-industrial and municipal waste materials. Use of waste materials as low-cost adsorbents is attractive for waste disposal.

Iron oxides also have been widely used, as sorbents to remove contaminants from wastewater and liquid hazardous wastes, compared to activated carbon. Removal has been attributed to ion exchange, specific adsorption to surface hydroxyl groups or co-precipitation. Hydrous ferric oxide (HFO) is an important sorbent in wastewater treatment especially for hazardous chemical. Leupin and Hu (2005) removed arsenic groundwater by filtering the water through sand and zero-valent iron. As (V) sorbed on the forming hydrous ferric oxides (HFO) resulted from the oxidation of iron. Different similar sorbent materials have been used, including amorphous iron hydroxide and ferric hydroxide (Quan et al., 2001). Chlorination enhanced efficiency of the zero-valent iron used to remove arsenite from water (Biterna et al., 2010).

A treatment unit packed by granular adsorbent of Fe-Mn binary oxide incorporated into diatomite (FMBO(1:1)-diatomite) was studied to remove arsenic from anaerobic groundwater without any pre-treatment or post-treatment. The raw anaerobic groundwater containing arsenic was collected from suburb of Beijing. Arsenic (III) constituted roughly 60-80% of the total arsenic content. The final concentrations of iron and manganese in effluents were nearly zero. The treatment units proved that adsorbent FMBO(1:1)-diatomite had high oxidation ability and exhibited strong adsorptive filtration (Chang et al., 2010).

Li and colleaques (2010) used pyrolusite (alpha-MnO_2) to investigate the oxidative transformation of arsenite into arsenate with batch experiments under different reaction conditions. The results showed that arsenite transformation occurred and was accompanied by the adsorption and fixation of both As (III) and As (V) on alpha-MnO_2. About 90% of sodium arsenite (10 mg L^{-1}) were transformed by alpha-MnO_2 under the conditions of 25 ^{o} C and pH 6. It was adsorbed (36.6%) and fixed (28.9%) by alpha-MnO_2. Increased alpha-MnO_2 dosages promoted As (III) transformation rate and adsorption of arsenic species. The transformation rate and adsorption of arsenic species raised with increasing pH values of reaction solution from 4.7 to 8.0. The oxidation rate decreased and adsorbed As (III) and As (V) increased with increasing initial arsenite concentration. The results demonstrated that alpha-MnO_2 has important potential in arsenic transformation and removal as the environmentally friendly natural oxidant in soil and surface water.

Arsenic removal technology by adsorption with a commercial granular ferric hydroxide (GFH) has been developed in the early 1990s (Jekel, 2002). It can be applied in simple fixed bed reactors, similar to those for activated alumina or activated carbon. Simplified operation is a key benefit of the system, which will operate without the need for chemical pre-feed or pH correction. GFH has a high adsorption capacity in natural waters. Jekel and Seith (2000) compared the methods for the precipitation/flocculation by iron (III)-chloride and iron (II)-sulphate as well as adsorption on GFH in a full scale water treatment plant. Their findings showed that adsorption on granulated iron hydroxide has proven to be the method which will provide greater operational reliability with least maintenance and monitoring efforts. Above pH 5, most of the arsenic is removed from the water and deposited with the iron oxy-hydroxide (Pantano, 2001).

Asta and colleaques (2010) determined the role of sedimentary phases in the behavior of arsenic in acid waters and sediments of the Tinto Santa Rosa acid stream (Iberian Pyritic Belt; SW, Spain). Aqueous arsenic and iron concentrations decreased from the adit mouth to 300 m downstream indicating iron minerals precipitation as well as arsenic sorption onto these newly-formed phases. This was confirmed by the high arsenic concentrations observed in bed-stream precipitates, which play a major role in controlling arsenic mobility. The results showed that

(1) arsenic was present predominantly in its pentavalent state; (2) upstream arsenic was sorbed onto the main phase, whereas downstream it was chiefly associated with goethite and jarosite; and (3) changes in arsenic speciation with depth were observed in the consolidated terrace sediments, where arsenic appeared primarily associated with schwertmannite in the upper part of the terraces, but with goethite at depth. Arsenic mobilization was controlled by sorption onto newly formed precipitates (schwertmannite, goethite and jarosite), causing natural arsenic attenuation.

Zeolites have also attracted ever increasing interest from academic and industrial laboratories**.** They represent an important group of materials due to their catalytic, sieve and exchange properties. Other low cost adsorbents include clay (Lin and Puls, 2000), kaolin, goethite, fly ash (Goswami and Das, 2000), red mud (Altundogan et al., 2000), humic acid, human hair, hematite/feldspar and fungal biomass (Loukidou et al., 2003).

3.3.3 Membrane filtration

Membrane separation is a pressure driven process. Pressure driven processes are divided into four overlapping categories of increasing selectivity: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and hyperfiltration or reverse osmosis (RO). MF can be used to remove bacteria and suspended solids with pore sizes of micron. UF (0.0003-0.1 µm) will remove colloids, viruses and certain proteins. NF (0.001-0.003 µm) relies on physical rejection based on molecular size and charge. RO (0.0005 µm) can be used for desalination. High pressures are required to force water to pass across the membrane from a concentrated to dilute solution. In general, driving pressure increases as selectivity increases. Clearly it is desirable to achieve the required degree of separation (rejection) at the maximum specific flux (membrane flux/driving pressure). Separation is accomplished by MF membranes and UF membranes via mechanical sieving, while capillary flow or solution diffusion is responsible for separation in NF membranes and RO membranes. Nanofiltration is considered as one of the methods that can be used to meet regulations for lowered arsenic concentrations in drinking water. Waypa and colleaques (1997) studied the arsenic removal from synthetic freshwater and from surface water sources by NF and RO. The results show that both As (V) and As (III) were effectively removed from the water by RO and NF membranes (NF70, Dow/Filmtec) over a range of operational conditions. Both membranes can achieve rejections of 99%. Removal of As (V) and As (III) was comparable, with no preferential rejection of As (V) over As (III). This suggests that size exclusion governed their separation behavior and not the charge interaction. Saitúa and colleaques (2005) used loose NF membranes to study the difference in rejection between As (V) and As (III). The rejection of As (III) was below 30% and was much lower than the rejection of As (V). The removal of As (V) was varied between 60% and 90%. The performance of nanofiltration for arsenic removal both As (V) and As (III) was not affected by source water chemical compositions. NF membranes could remove over 95% of arsenic. Furthermore, more than 75% of trivalent arsenic, which is toxic form of arsenic (V), could be removed without any chemical additives (Sato et al., 2002).

Reverse osmosis (RO) membranes have been identified as another alternative to remove arsenic in water. The removal of As (V) was much higher than As (III) over the pH range of 3-10. The effect of solution pH on the removal of arsenic using RO membranes was strongly affected by the solution pH, especially As (IlI). Ning (2002) had reviewed the removal mechanism of RO and concluded that arsenic in the commonly high oxidation states of As (V) was very effectively removed by RO.

3.3.4 Oxidation with ozone

Ozone is a type of chemical oxidation process used for disinfecting drinking water in municipal water industry. Since ozone is made of oxygen, it reverts back to pure oxygen after use. After disinfecting harmful bacteria and/or pollutants, it generally leaves behind no by-products. Ozone when added to water which contains arsenic and soluble iron, will oxidize both arsenic and iron, forming sites on the ferric hydroxide for arsenic to adsorb to. Then, the arsenic bearing iron hydroxide is removed by solid-liquid separation processes. Frank and Clifford (1986) showed that under ambient conditions, all the As (III) was completely oxidized with oxygen and chlorine within 61 days. The half-life for As (III) oxidation by ozone was very short, only 4 minutes. The half-life for pure oxygen ranged from 2-5 days, and for air a half-life of 9 days. The findings showed that ozone can be used to remove arsenic from groundwater through oxidation, coprecipitation and adsorption reactions effectively (Papassiopi et al., 2003).

3.3.5 Biological remediation

Biological treatment has been demonstrated to be a useful alternative to conventional treatment systems for the removal of toxic metals from dilute aqueous solution. However, the bioprocesses for treating toxic effluents must compete with existing methods in terms of efficiency and economy (Choong et al., 2007). To its advantages, the biotechnological solution to the problem requires only moderate capital investment, a low energy input, are environmentally safe, do not generate waste in most cases, and are self-sustaining. It is expected that future biotechnological methods of toxic waste treatment will play a key role as a displacement for the existing methods. The treatment of arsenic and other acidic metal (Cu, Zn, Ni, Fe, Al and Mg) and sulfate contaminated waters in a bench-scale up-flow anaerobic packed bed reactor by employing a mixed population of sulfate-reducing bacteria was studied (Jong and Parry, 2003). The initial concentrations of arsenic were removed more than 77.5%. Their findings have agreed well to the work of Simonton and colleaques (2000) who reported consistent removal for arsenic and Cr (>60–80%) from solution using SRB (*Desulfovibrio desulfuricans*) in columns containing silica sand. It is evident that the action of bacterial sulfate reduction has enhanced the arsenic removal rate. Katsoyiannis and Zouboulis (2004) studied the removal of As (III) and As (V) during biological iron oxidation. Their results showed that both forms of arsenic could be efficiently treated for the concentration range of concentration 50-200 mg L^{-1}. The bacteria has found to catalyze the oxidation of trivalent arsenic and enhanced the overall arsenic removal. Papassiopi and colleaques (2003) also reported the use of iron reducing bacteria for the removal of arsenic from contaminated soils.

3.3.6 Electrochemical treatment

The electrochemical reduction of inorganic As (III) and As (V) in aqueous solutions has been studied preoperatively with the objective of maximizing the yield of elemental arsenic at the expense of the highly toxic gas arsine (AsH_3). The method for removal of As (III) from mineral acids by electrochemical reduction to arsenic was deposited on a three-dimensional carbon cathode, using a divided cell and cathode potentials that disfavored over-reduction to arsine (Twardowski, 1987). Bisang and colleaques (2004) studied the feasibility of removing the arsenic from acid electrochemically. They used Cu, Pb, 316 L stainless steel and graphite as cathodic rotating discs. The best results were achieved for copper where the arsenic deposition takes place in a range of potentials without hydrogen evolution.

3.3.7 Solar oxidation technique

Solar oxidation in individual units (SORAS) was explored to treat arsenic from the groundwater. The process is based on photochemical oxidation of As (III) followed by precipitation or filtration of As (V) adsorbed on Fe (III) oxides (García et al., 2004). The findings showed that the underlying chemistry was very complex, and the removal efficiency was affected by the changes in the chemical matrix, or by changes in the operative conditions.

3.4 Generation and disposal of arsenic residuals after treatments

Water treatment systems will produce residuals, arsenic with other production processes. It is the disposal of the treatment arsenic bearing residual and not the treatment technology itself that is the most difficult issue in practice. Restrictions have been placed on the discharge of residuals to water bodies and onto land to prevent further contamination. Residual generation and disposal of five arsenic removal systems was from anion exchange, activated alumina absorption, iron/manganese removal, media adsorption, and membrane processes (Choong et al., 2007).

3.4.1 Anion exchange

A liquid and solid residual may be generated from an anion exchange system. The liquid residual consists of the backwash water, regenerant solution, and rinse water. These waters constitute 1.5 to 10% of the treated water volume depending on the feed water quality and type of ion exchange unit used (U.S.EPA, 1993). The spent regenerant may contain high levels of arsenic or have a corrosive characteristic.

Spent resin will be produced when the resin can no longer be regenerated, or when it becomes poisoned or contaminated. Spent resin for disposal may be subject to hazardous waste regulations depending upon the results of a toxicity characteristic leaching procedure (TCLP) test. Disposal of these solid wastes (spent resin) are via hazardous waste landfill or return to vendor. Liquid effluent will be treated via sanitary sewer or ponds/lagoon (Sorg, 2000).

3.4.2 Activated alumina (AA)

A liquid and/or solid residual may be produced from an AA system depending on the type of operation. If the system is regenerated, a liquid waste is produced from the backwash, caustic regeneration, neutralization, and rinse steps. In some instances, sludge may be generated from the regeneration and neutralization streams because some alumina dissolves during the regeneration step and may be precipitated as aluminum hydroxide. If aluminum based sludge is produced, this sludge will contain a high amount of arsenic. This sludge and the remaining liquid fraction of the solution will require disposal. Both residuals contain arsenic, their disposal may be subject to disposal requirements. The AA has reached the end of its useful life, the media will also become a solid residual that must be disposed. An activated alumina system, high arsenic removal capacity, may be operated on a media throw-away basis rather than a media regeneration basis. When operated on a throw-away basis, the exhausted AA media will be the principal residual produced. This media has the potential of being classified as a hazardous waste because of its high arsenic content. A TCLP test is necessary to determine its classification and ultimate disposal restrictions. The AA media will filter out particulate material in the source water, the media bed will occasionally require backwashing. This backwash water will contain some arsenic attached to either the particulate material. Consequently, the disposal of the backwash water may be subject to the disposal requirements.

3.4.3 Adsorption

Contaminated water is passed through a bed of the specially developed media, where arsenic is adsorbed and removed from the water. Two general types of residuals are potentially generated from media adsorption: spent media and regeneration solutions. Spent media will be generated from systems that use the media on a one-time throw-away basis, or from systems where the media has become exhausted and can no longer be regenerated, or is no longer effective. In some cases, depending on manufacturer policy, spent media may be sent back to the vendor for reactivation, recovery, or disposal. It is assumed that the same steps as for ion exchange will be utilized: backwash, regeneration, and rinse. Each of these steps will generate an aqueous residual which will likely be combined. Some of the new adsorption media have such large arsenic removal capacities. The periodic backwashing (with regeneration) is required to remove the particulate material that is filtered out during its treatment operation. This backwash water will likely contain some arsenic attached to the particulate material or any very fine adsorption media having be removed by the backwashing process. The waste stream is a residual that may be disposed of immediately at the time of backwashing or it may be held and disposed with the regeneration waste water. Depending on the concentration of arsenic in the influent and other factors, the disposal of the regeneration waste and the backwash water may be subject to the disposal requirements.

3.4.4 Iron/manganese removal methods

Iron/manganese removal processes, both the oxidation/filtration and the potassium permanganate greensand techniques, produce a liquid residual from the filter backwashing step. Occasionally, the filter media or greensand needs to be replaced and this material also becomes a residual product that must be disposed. Similar to the backwash and regenerant solution from the ion exchange and activated alumina processes, the filter backwash water will contain arsenic, the concentration dependent upon the amount of arsenic removed and the quantity of backwash water. Although the liquid fraction of the backwash water will contain some soluble arsenic, most of the arsenic will be associated with the iron/manganese solids. Depending on their arsenic concentration, the disposal of the backwash water residual and the spent solid media residual may be subject to the disposal requirements.

3.4.5 Membrane processes

All membrane processes produce a reject waste product containing the materials, including arsenic, rejected by the membrane (U.S.EPA, 1993). The reject water is generally high in total dissolved solids. Depending on the concentration of the arsenic and other contaminants in the reject water, the disposal of this waste may be subject to the disposal requirements. Each treatment technology in arsenic removal differs in residual production and residual management options.

Table 3.4 Residual generation and disposal for the various arsenic treatment methods (Sorg, 2000)

Arsenic treatment method	Form of residual	Residual generation	Disposal
Ion exchange	Liquid	-Regeneration streams -Spent backwash -Spent regenerant -Spent rinse stream	-Sanitary sewer -Discharge -Evaporation ponds/lagoon -Landfill
	Solid	-Spent resins	-Hazardous waste landfill -Return to vendor
Activated alumina	Liquid	-Regeneration streams -Spent backwash -Spent regenerant (caustic) -Spent neutralization (acid) -Spent rinse -Liquid filtrate (when brine streams are precipitated)	-Sanitary sewer -Direct discharge -Evaporation ponds/lagoon
	Solid	-Spent alumina -Sludge (when brine streams are precipitated)	-Landfill -Hazardous waste landfill -Land application

Table 3.4 (cont.) Residual generation and disposal for the various arsenic treatment methods (Sorg, 2000)

Arsenic treatment method	Form of residual	Residual generation	Disposal
Adsorption	Liquid	-Regeneration streams -Spent backwash -Spent regenerant -Spent rinse stream	-Sanitary sewer -Direct discharge -Evaporation ponds/lagoon
Iron and manganese removal processes	Liquid	-Filter backwash	-Direct discharge -Sanitary sewer -Evaporation ponds/lagoons -Sanitary sewer
	Solid	- Sludge (if separated from backwash water) -Spent media	-Land application -Landfill -Hazardous waste landfill
Membrane processes	Liquid	-Brine (reject and backwash streams)	-Direct discharge -Sanitary sewer -Deep well injection -Evaporation ponds/lagoon

To remove arsenic from wastewaters, the most commonly used technologies are adsorption onto activated alumina, and precipitation or adsorption by metals oxides, predominantly Fe (III) and membranes. These technologies are most suited to dealing with relatively low concentrations of arsenic. However, the technique of precipitation, generally using Fe (III) or lime softening is suited to higher concentrations. Adsorption is a method that has been an important method used in arsenic removal. Most studies are focused on the type of adsorbent mediums and the economics of their regeneration. Membrane technology, especially nanofiltration, becomes a promising method in arsenic removal and is also widely considered as the methods that can be used to meet regulations for lowered arsenic concentrations in drinking water. Arsenic removal technology should take into considerations of reducing the treatment cost, simplifying the operational complexity of the technology and disposal of arsenic bearing treatment residual.

3.5 Management of wastewater and solid waste

All arsenic treatment technologies create residuals with concentrated arsenic and other contaminants. Technologies remove other contaminants in addition to arsenic, the residual may have concentrated levels of co-occurring contaminants, such as lead, barium, or radionuclides. The removal of co-occurring contaminants may pose disposal problems even when the arsenic levels in process residuals are not high enough to lead to a hazardous waste classification or interfere with local limits set by publicly owned treatment works (POTWs). Water systems should thoroughly test their wastes prior to making disposal decisions.

3.5.1 Types of residuals

Water systems must legally manage and dispose of residuals in a manner that does not adversely impact human health and the environment. They should seek to reduce the production of residuals if possible and should attempt to manage their treatment processes to avoid the production of hazardous waste. Water treatment plants produce four types of residuals:

1. Liquids, including brines, concentrates, backwash water, rinse water, and filter to waste water.
2. Solids, including spend media, spent membranes, and dewatered sludge.
3. Sludge, which is semi-solid and usually must be dewatered prior to disposal; and, gases.
4. Gaseous residuals, with the exception of radon, are not widely regulated.

All treatment processes will produce one or more types of residuals, the amount of residuals produced is a function of raw water quality, facility design and operating flow, and treatment process employed. Certain raw water characteristics can impact a system’s residual disposal options. One challenge for a system is to optimize treatment while not creating residual disposal problems. Raw water characteristics that may impact disposal alternatives include: excessively high or low pH, high total suspended solids (TSS), high total dissolved solids (TDS), high concentrations of heavy metals, including arsenic, lead, and aluminum; high concentrations of competing ions, including fluoride, sodium, sulfate, chloride, and other salts concentrations; and, high concentrations of radionuclides and daughter products.

3.5.2 Disposal options

Options to manage liquid residual are included: direct discharge to a receiving body, discharge to a POTW, underground injection, land application, and, recycle to facility head works. Intermediate processing may be necessary prior to disposal by some or all of these alternatives. Most intermediate processing concentrates contaminants into a smaller volume for disposal, usually producing two waste streams: a cleaner liquid waste stream and a more concentrated solid waste stream. Economics, disposal alternatives, and regulations will dictate the extent of intermediate treatment. Intermediate processing for liquid wastes may include:

1. Flow equalization - large spikes in flow quantity or contaminant concentration may interfere with POTW treatment. Therefore, detaining and mixing water system wastes may be necessary prior to release to a POTW.
2. Brine recycling - water systems may be able to reuse brine rinse, reducing the total amount of brine that must be disposed. Systems should use caution, however, the reused brine streams may contain higher levels of suspended solids and contaminants, which may limit disposal options.
3. pH neutralization - waste streams with excessively high or low pH may need to adjust the pH before release to a POTW or to receiving bodies.
4. Settling or gravity thickening - settling basins or mechanical presses may be used to remove suspended solids and contaminants from liquid waste streams, resulting in a sludge and a cleaner liquid waste.
5. Evaporation - in hot or dry climates, evaporation can enhance settling basins by removing water and leaving solids and contaminants.
6. Chemical precipitation - coagulants can be added to remove contaminants from liquid waste streams and precipitate them as sludges.

Options to manage solid residual are included: non-hazardous waste landfill, hazardous waste landfill, and land application. Intermediate processing may be necessary prior to disposal by some or all of these alternatives.

1. Mechanical dewatering processes, including centrifugal filter presses, vacuum-assisted dewatering beds, belt filter presses, and plate-and-frame filter presses. Mechanical dewatering techniques can require a large capital and operating investment and therefore may only be an option for larger systems. Filter presses can increase the solids content of lime softening sludges from 3% to 40-70% and can increase the solids content of alum sludges after modification to pH 11 from 1% to 35-50%.
2. Non-mechanical dewatering processes, including lagoons, settling basins, gravity thickening, evaporation ponds, drying beds, etc.
3. Thermal processing, including incineration (aerobic) and pyrolysis (anaerobic). Applicable regulations may include the Resource Conservation and Recovery Act (RCRA) Subtitle C and the Clean Air Act National Emission Standard for Hazardous Airborne Pollutants (NESHAPS) program. These processes may produce an ash that will need further disposal.

3.5.3 Regulations for residual management and disposal

We studied the three federal regulations that provide the requirements applicable to residuals management and disposal include:

1. RCRA, which governs the management of solid and hazardous wastes and covers land disposal and land application.
2. The Clean Water Act (CWA), which covers direct discharge to receiving bodies and discharge to a POTW.
3. The Safe Drinking Water Act (SDWA), which covers underground injection under the Underground Injection Control (UIC) program.

Other federal regulations that may affect WTP residual disposal include:

1. The Atomic Energy Act (AEA), which covers high and low level radioactive waste disposal.
2. The Comprehensive Environmental Response, Compensation and

Liability Act (CERCLA), which established prohibitions and requirements concerning closed and abandoned hazardous waste sites, provided for liability of persons responsible for releases of hazardous waste at these sites, and established a trust fund to provide for cleanup when no responsible party could be identified.

3. The Toxic Substances Control Act (TSCA), which was enacted by Congress to give EPA the ability to track the 75,000 industrial chemicals currently produced or imported into the United States.

4. The Marine Protection, Research, and Sanctuaries Act (MPRSA), which governs permits for and otherwise prohibits (1) transportation of material from the US for the purpose of ocean dumping, (2) transportation of material from anywhere for the purpose of ocean dumping by US agencies or US-flagged vessels, and (3) dumping of material transported from outside the US into the US territorial sea.

According to the hazardous waste determination regulations in 40 CFR 262.11, any person who generates a solid waste (as defined in 40 CFR 261.2) must determine if that waste is a hazardous waste. There are two ways that a waste can be considered hazardous. The waste can be, or contain material listed, in Subpart D of 40 CFR 261. This subpart contains several lists that enumerate various hazardous wastes. Note that any mixture or derivative of a listed hazardous waste is considered to be hazardous. Even if the waste is listed, a generator still has an opportunity under 40 CFR 260.22 to demonstrate to the Administrator that the waste from his or her particular facility or operation is not a hazardous waste. The waste can have one or more of the characteristics of hazardous waste: reactivity, corrosivity, toxicity, ignitability. There are specific definitions for each of these in 40 CFR 261.21-261.24.

If the waste is determined to be hazardous, the generator must manage and dispose of the waste in accordance with the stringent regulations of RCRA Subtitle C. However, some types of waste have been excluded and are not considered hazardous even if they are listed or have the characteristics of hazardous waste. Under 40 CFR 261.4, these excluded wastes include:

1. CWA point source discharge
2. Direct discharge or discharge to a POTW
3. Atomic Energy Commission source, special nuclear, or by-product

material

4. WTP waste, if it is determined to be hazardous, is most likely to be considered hazardous under the toxicity characteristic (TC). Wastes that contain high levels of readily leachable arsenic, barium, lead, and other toxic compounds (see 40 CFR 261.24) may be considered hazardous unless accepted by a POTW or covered under a CWA discharge permit. Water systems with extremely high levels of hydrogen sulfide in their source waters may also be considered hazardous under the reactivity characteristic.

RCRA only regulates what it defines as a “solid waste.” Therefore, even if a material meets the criteria for hazardous waste, if it is not first a solid waste, it is not regulated under RCRA. A material is a solid waste under 40 CFR 261.2 if it is:

1. Garbage, refuse, or sludge, irrespective of whether it is discarded, used, reused, recycled, reclaimed, stored, or accumulated; or,
2. Solid, liquid, semi-solid, or contained gaseous material which is discarded, has served its intended purpose, or is a manufacturing or mining by-product.

Under 40 CFR 261.4, some waste is not solid waste by specific exclusion. The exclusions include:

1. Domestic sewage or any mixture of domestic sewage and other wastes that passes through a sewer system to a publicly-owned treatment works for treatment. "Domestic sewage" means untreated sanitary wastes that pass through a sewer system;
2. Industrial wastewater discharges that are point source discharges subject to regulation under section 402 of the CWA, as amended. Note that this exclusion applies only to the actual point source discharge. It does not exclude industrial wastewaters while they are being collected, stored, or treated before discharge, nor does it exclude sludges that are generated by industrial wastewater treatment;
3. Irrigation return flow;
4. Source, special nuclear or by-product material as defined by the AEA of 1954, as amended;
5. Materials subjected to in-situ mining techniques which are not removed from the ground as part of the extraction process;

6. Sludge is defined as “any solid, semi-solid, or liquid waste generated from a water supply treatment plant. Therefore, WTP sludge is a solid waste regulated by RCRA and is not excluded by the 40 CFR 261.4. WTP sludges may also be regulated by section 402 of the CWA.

A variety of technologies can be used to treat arsenic-bearing materials. EPA and other investigators of technologies available to treat wastes and media containing arsenic and their usage reported about technologies are used to stabilize and/or remove arsenic contamination. Recycling uses pyrometallurgical or precipitation techniques that convert arsenic waste to a concentrated arsenic product. The treatments of non-wastewaters are vitrification, incineration, soil flushing, soil washing/acid extraction, electrokinetics, and phytoremediation. The methods of chemical precipitation, ion exchange, carbon adsorption, membrane separation, foam floatation, and permeable reactive barriers are for the treatment of process wastewater, groundwater, and wellhead treatment (Choong et al., 2007).

3.6 Phytoremediation for arsenic removal

Phytoremediation is the use of vegetation and its associated microorganisms, enzymes and water consumption to contain, extract or degrade contaminants from soil and groundwater (Green and Hoffnagle, 2004). It is a plant based green technology, which using plant to clean up toxicants in the environment of contaminated soils and waters. A plant will uptake toxic elements from roots transferred into stems and leaves. Both organic and inorganic contaminants can be successfully contained or degraded using phytoremediation in a variety of media (i.e., soil, sediment, sludge, wastewater, groundwater, leachate and air). The mechanisms of phytoremediation include:

1. Phytoextraction : removal and storage of contaminants from the media into the plant tissue;
2. Phytostabilization : isolation and containment of contaminants within soil through the prevention of erosion and leaching;
3. Phytovoltalization : uptake and transpiration of contaminants from the

media through the plant tissue into the atmosphere;

4. Phytodegradation : degradation of contaminants within the plant tissue
5. Rhizodegradation : degradation of contaminants by microorganisms in the soil zone that surrounds and is influenced by the roots of plants, known as the rhizosphere;
6. Hydraulic control : containment of contaminants within a site by limiting the spread of a contaminant plume through evapotranspiration.

Plants that are suited for arsenic hyperacumulation should have wide distribution, high above-ground biomass, high bioconcentration factors, a short life cycle and high propagation rates (Wang and Mulligan, 2006). Chinese Brake fern (*Pteris vittata*) and silver fern (*Pityrogramma calomelanos*) have been discovered to be an arsenic hyperaccumulator (Daus et al., 2005; Francesconi et al., 2002; Ma et al., 2001; Sridokchan et al., 2005; Visoottiviseth et al., 2002; Wu et al., 2009; Xie et al., 2009). This technique is a cost-effective and environmentally friendly approach for field operation, especially in Thailand. Arsenic contaminated tap water in RonPibun District, Nakorn Si Thammarat Province was treated by the constructed wetland (CW) and soil phytoremediation (SP) plants. Plants used of the CW were *C. alternifolius* and *C. esculenta*, while marigolds and banana were used for removing arsenic in the soil phytoremediation.

3.6.1 Constructed wetland

Constructed wetland pond was designed for degradation, sorption, and filtration followed the studies of Langergrabera and colleaques (2009) who reported the best model for constructed wetland experiments. They used gravel for cover and drainage layers and sand for filter layer (Figure 3.9). Domestic wastewater was treated in wetland by different plant species: *Phragmites australis, Cyperus papyrus, Canna sp., Iris pseudoacorus, Juncus ensifolius,* and *Lythrum salicaria.*

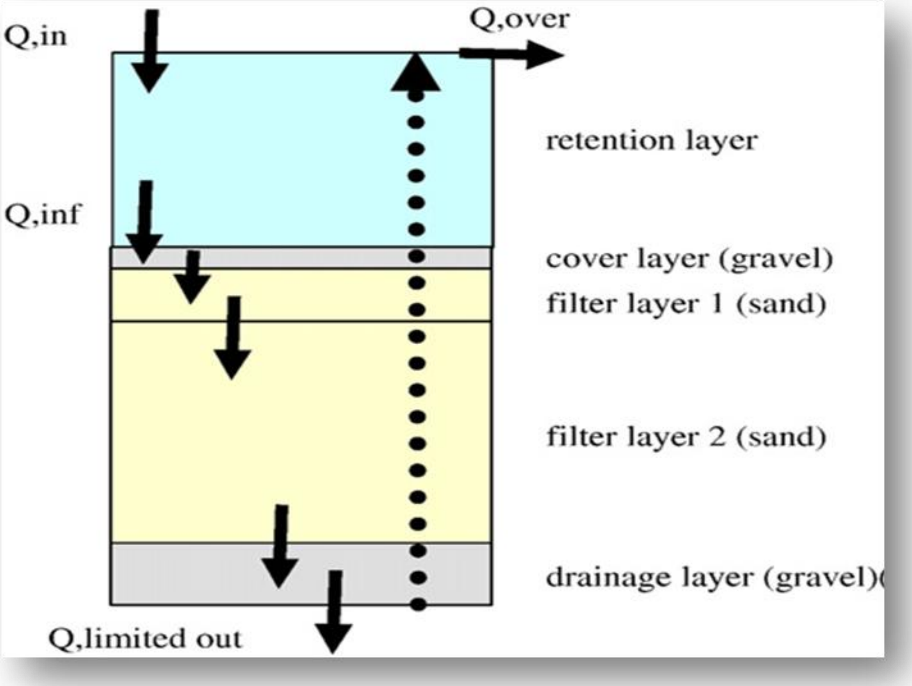


Figure 3.9 Design layers of constructed wetland (Langergrabera et al., 2009)

The studies about wetland experiments were reported as follows:

Lazareva and Pichler (2010) investigated the efficiency of a constructed wetland/filter basin (CW/FB) treatment to improve the chemical composition of waste and surface waters. The system was constructed in closed phosphate mines used for clay settling and sand tailings. Monitoring was carried out for 18 months to evaluate the CW/FB performance under a variety of climatic conditions. The results showed the following changes in water quality between the input and output: (1) strong decrease of water temperature (up to 10 ºC); (2) significant change in pH from 9.0 to 6.5-7.0; (3) negative oxidation-reduction potential (ORP) confirming the reducing conditions of the treatment system; (4) substantial increase of H_2S (up to 1,060 mg L^{-1}); (5) reduction of arsenic from 5 to <2 mg L^{-1}. In general, the performance of the CW/FB treatment showed great potential to improve the water quality of industrial and municipal wastewater. Despite significant seasonal variations to temperature, rainfall and humidity, the chemical/microbiological composition of the wetland output remained relatively constant.

Zhang and colleaques (2009) investigated arsenic accumulation, speciation and tolerance of the rootless duckweed (*Wolffia globosa*) and its potential for arsenic phytofiltration. Duckweed is a common macrophyte in paddy and aquatic environments. *W. globosa* accumulated 2-10 times more arsenic than four other duckweed or *Azolla* species tested. *W. globosa* was able to accumulate > 1000 mg kg^{-1} in frond dry weight, and tolerate up to 400 mg kg^{-1}. At the low concentration range, uptake rate was similar to arsenate and arsenite, but at the high concentration range, arsenite was taken up at a faster rate. Arsenite was the predominant arsenic species (90% of the total extractable arsenic) in both arsenate- and arsenite-exposed duckweed. *W. globosa* was more resistant to external arsenate than arsenite, but showed a similar degree of tolerance internally. *W. globosa* decreased arsenate in solution rapidly, but also effluxed arsenite. *W. globosa* is a strong arsenic accumulator and an interesting model plant to study arsenic uptake and metabolism because of the lack of a root-to-frond translocation barrier. Wang and Mulligan (2006) showed that duckweed (*Lemna gibba*) accumulated arsenic up to 2,000 mg kg^{-1} from the tailings water of abandoned uranium mine sites in Saxony, Germany. The authors suggested that *L. gibba* might be used as an indicator for uptaking arsenic from contaminated waters to plants.

Chiemchaisri and colleaques (2009) reported about the constructed wetland of four concrete ponds (1-m wide, 3-m long, and 1-m depth) used to investigate the removal efficiency of organic and nitrogen from solid waste leachate. The inlet and outlet zones were filled with 30–60 mm gravel of 0.8 m depth; and 1–2 mm sand was used in plantation zone. The water depth was 0.7 m, i.e., 0.1 m below the gravel surface level. Cattail (*Typha augustifolia*) was used as emergent in the system with initial planting density of 40 rhizomes m^{-2}.

Nateewattana and colleagues (2009) investigated to use wetland ponds of aquatic plants to remove arsenic from the wastewater treatment at Mae Moh Power Plant in Thailand. It was showed that the arsenic concentrations in sediment and supernatant were below Thailand National Standard of 0.25 mg L^{-1} for water and 27 mg kg^{-1} for soil. The decrease of dissolved arsenic, especially at some wetland ponds could mainly result from the precipitation of the dissolved arsenic. The arsenic accumulation in plant biomass revealed that 5 species of aquatic plants could absorb arsenic in their vicinity. The order of those accumulation amounts from maximum to minimum was *Echornia crassipes* (Mart.) Solms., *Typha angustifolia* (L.), *Ipomoea aquatica* Forsk., *Canna glauca* (L.), and *Colocasia esculenta* (L.) Schott, respectively. All plants accumulated the highest arsenic content at the root.

Perbangkhem and Polprasert (2010) showed the operation of the pilot-scale free water surface wetland that indicated the feasible use of papyrus (*Cyperus papyrus*) as a potential plant used for domestic wastewater treatment. The papyrus gave the plant biomass of about 2,590 g dry weight m^{-2} with the growth rate constant of 0.04 g d^{-1} and its energy-capturing efficiency of about 4.3%. The optimum period for plant harvesting was about 41–50 days

Arienzo and colleaques (2009) investigated the designing winery wastewater treatment systems involving constructed wetlands. Three macrophyte wetland species (*Phragmites australis*, *Schoenoplectus validus* and *Juncus ingens)* were tested using a pot experiment to study about plant tolerance through biomass production, total chlorophyll and nitrogen, phosphorous and potassium tissue concentrations. The results showed that at greater than 25% wastewater concentration all the macrophytes died and that *Phragmites* was the least hardy species

Khan and colleaques (2009) performed to remove heavy metals from industrial wastewater by constructed wetland in Gadoon Amazai Industrial Estate (GAIE), Swabi, Pakistan. The performance of the CW was efficient to remove the heavy metals of Cd (91.9%), Fe (74.1%), and Cu (89%). The aquatic macrophytes were used of *Typha latifolia, Scirpus cypernius, Carex aquatilis, Phragmites australis, Juncus articulates, Ceratophyllum demersum, Lemna gibba* L., *Echornia cressipes, Polygonum glabrum, Alisma plantago-aquatica, Pistia stratiotes.* It was observed that *T. latifolia, P. stratiotes, P. australis, C. aquatilis* and *A. plantago-aquatica* were more efficient in removal of heavy metals from wastewater

Many studies revealed that different wetland systems performed differently with plant species and productivity variety. Zhang and colleaques (2009) used wetland plants to remove total nitrogen (TN) and total phosphorus (TP). The resulted showed that *Canna indica* Linn., *Pennisetum purpureum* Schum., and *Phragmites communis* Trin. had higher removal rate for TN and TP than other wetland species. Moreover, removal efficiency varied with season and plant growth, e.g., wetlands vegetated by *P. purpureum* significantly outperformed wetlands with other plants in May and June, whereas wetlands vegetated by *Ph. communis* and *C. indica* demonstrated higher removal efficiency from August to December. For removing BOD_5, *Cyperus malaccensis* was the most efficient one. The treatment efficiency in a pilot-scale mangrove wetland in Futian, Shenzhen, China for municipal sewage treatment, *Sonneratia caseolaris* was the most efficient one with all the effluent samples below the discharge standards for COD, BOD_5, and NH_3-N. Investigating the growth vitality and their removal ability of the pollutants in domestic sewage, nine aquatic plant species commonly used in northern China and transplanted in CWs in Beijing region. The report was shown that among the tested plant species, *Iris pseudacorus* (with the capacity of high N & P removal efficiency) ranked first in setting up the constructed wetland, followed by *Typha angustifolia*, *Acorus calamus*, and *Triarrhena sacchariflora*, whereas *Alisma plantago* and *Arundo donax* were not recommended due to their sensitivity in cold winter in northern China.

In hot spot areas in Thailand, *Cyperus alternifolius* and *Colocasia esculenta* were selected plants for the constructed wetland because *C. esculenta* was the best plant that removed arsenic from the solution of 1 mg L^{-1} for a 28 day exposure period, studying compared with other plants of *Typha spp.*, *Canna spp.*, *Heliconia psittacorum* and *Thalia dealbato* J. Fraser (Aksorn and Visoottiviseth, 2004; Jampanil, 2000). In Viet Nam, *Cyperus* spp. were grown at 10 plants m^{-2} in the water treatment with sand filter (Proter and Cat, 2006). The authors reported that arsenic was removed to the level below the WHO standard.

3.6.2 Soil phytoremediation

There are two main strategies in soil phytoremediation, phytostabilization and phytoextraction (Kra¨ mer, 2005). Phytostabilization is used to provide a cover of vegetation for a moderately to heavily contaminated site, thus preventing wind and water erosion. Plants suitable for phytostabilization develop an extensive root system, provide good soil cover, possess tolerance to the contaminant metals, and immobilize the contaminants in the rhizosphere. Phytostabilization is often performed using plant species occurring on local contaminated sites. The most effective but also technically the most difficult phytoremediation strategy is phytoextraction. It involves the cultivation of tolerant plants that concentrate soil contaminants in their above-ground tissues.

Zabludowska and colleaques (2009) evaluated the strategies for coping with arsenic toxicity developed by the mine species (*Calamagrostis arundinacea*, *Fragaria vesca*, *Stachys sylvatica*, and *Epilobium parviflorum*), and to compare results obtained from plants exposed to arsenic in contaminated soil (2,000-3,500 mg kg^{-1}) and in hydroponic solution (2 µM and 12 µM arsenate). *Calamagrostis* had the highest level of arsenic tolerance among the tested species. When grown in soil, it accumulated the highest amount of arsenic in roots and shoots relative to other species. However, it had lower arsenic concentrations when exposed to arsenic in hydroponics. The efficiency of arsenic root-to-shoot translocation was also different, being less effective in soil-grown *Calamagrostis* compared with hydroponics. In *Calamagrostis* exposed to arsenate in liquid medium, As (III) was the predominant arsenic form, in contrast to plants grown in arsenic contaminated soil, in which As (V) predominated. Comparison of the level of phytochelatins (PC) showed that only PC2 was detected in plants from hydroponics, whereas in those from soil, additionally PC3 and PC4 were found. The results showed that the basic components of a plant's response to arsenic, including uptake, accumulation and detoxification, change depending on the experimental conditions (arsenic in liquid medium or contaminated soil).

Yadav and colleaques (2009) performed the remediation of the metalloid and metal contaminated soil by using non-edible and economic plant species (*Jatropha curcas* L.). The experiment was conducted in pots to improve the survival rate, metal tolerance and growth response of the plant on soil; having different concentrations of arsenic, chromium and zinc. The soil was amended with dairy sludge and bacterial inoculum (*Azotobacter chroococcum*) as biofertilizer. The results showed that the bioaccumulation potential was increased with increase in metalloid and metal concentration in soil system. Application of dairy sludge significantly reduced the DTPA-extractable As, Cr and Zn concentration in soil. The application of organic amendment stabilized As, Cr and Zn and reduced their uptake in plant tissues. Plant survival by combined dairy sludge and biofertilizer application improved from 250 to 500 mg kg^{-1} of arsenic.

Metal hyperaccumulator plants are naturally capable of accumulating trace elements, i.e., Ni, Zn, Cd, As or Se, in their above-ground tissues, without developing any toxicity symptoms. The concentrations of these elements in dry leaf biomass were up to 100-fold higher than the concentrations in the soil (McGrath and Zhao, 2003).

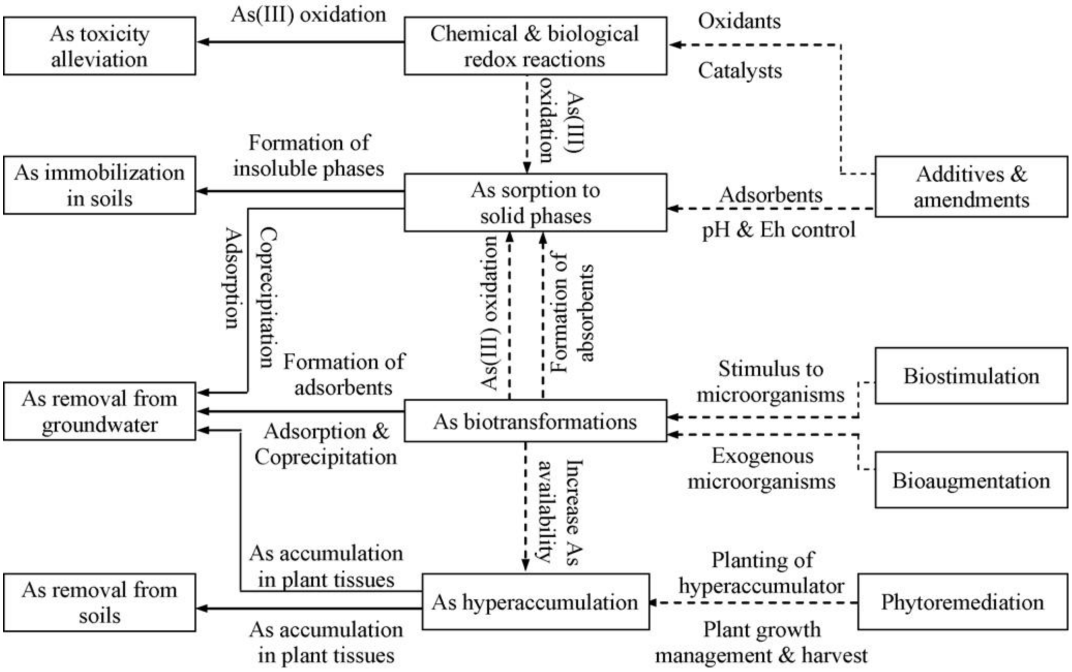


Figure 3.10 Main arsenic processes and enhancement strategies (Wang and Mulligan, 2006)

Arsenic hyperaccumulators are those plants that have the ability to uptake arsenic from soils and waters extraordinarily and transport and accumulate it in their shoots. The ratio of shoot arsenic concentration to soil/water arsenic concentration, defined as bioconcentration factor, should be greater than 10 (Wang, 2006; Mkandawire, 2005; Weber et al., 2004). Chinese brake fern (*Pteris vittata*) accumulated arsenic up to 7,500 mg g^{-1} on a contaminated site without showing toxicity symptoms (Ma et al., 2001). It can accumulate 12-64 mg kg^{-1} in its fronds from uncontaminated soils containing 0.5–7.5 mg kg^{-1} , and up to 22,630 mg kg^{-1} from a soil amended with 1,500 mg kg^{-1} (Mkandawire and Dudel, 2005). Several other fern species, including *Pityrogramma calomelanos, Pteris cretica*, *Pteris longifolia* and *Pteris umbrosa*, have also been reported to be able to hyperaccumulate arsenic

(Sridokchan et al., 2005). However, the uptake and accumulation of arsenic in plants are influenced by the soil properties and the presence of other ions (Figure 3.10). Phosphates have long been reported to suppress plant uptake of As (V) because As (V) uptake through phosphate uptake pathway. Significant reduction in arsenic accumulation in *Lemna gibba* and Indian mustard (*Brassica juncea*) were observed with the addition of phosphate (Mkandawire and Dudel, 2005).

The studies investigated for soil phytoremediation by using plants as follows:

Srivastava and colleaques (2010) evaluated the ability and mechanisms of 19 *Pteris* and non-*Pteris* species to accumulate arsenic in a hydroponic system spiked with 300 [mu]M As. Plants used were four *Pteris vittata* accessions (China, India, Poland, and the United Kingdom), *P. biaurita* and 17 non-*Pteris* species. Among the accessions, *P. vittata* from China and UK were the most and the least efficient in terms of arsenic accumulation. The non-*Pteris* species: *Chielanthes sinuta, Adiantum raddianum, Polystichum acrostichoides, Actiniopteris radiata, Pellaea rotundifolia, and Nephrolepis cordifolia* concentrated arsenic as effectively as the least efficient *P. vittata* ascension. As (III) in the fronds of *P. vittata* accessions ranged from 59% to 89% and for non-*Pteris* species it ranged from 47% to 65%. Maximum arsenic accumulation coincided with highest percentage of As (III) in the fronds. The phosphorus (P) uptake of *P. vittata* accessions was 12-15 and 6-12 times greater than the As-uptake in the roots and fronds, respectively. In contrast, the P-uptake of non-*Pteris* species ranged from 9 to 151 and from 4 to 162 times the As-uptake, in the roots and fronds, respectively.

Fornes and colleaques (2009) investigated the effects of “alperujo” compost on trace element availability and on microbial activity of two contaminated soils. A calcareous soil (S1) with high contents of Pb and Zn, and an acidic soil (S2) with a substantial amount of Al, As, Pb and Zn was reported that compost amendment did not affect S1, but in S2 it increased soil pH, thus reducing Al and Zn bioavailability and toxicity Also, the growth and capacity for contaminant phytoextraction of five *Brassica* species were studied. Compost application also increased microbial population and bioactivity in both soils. *Brassica* plants did not survive in S2, yet they thrived in S1. When compost was applied to S2, *Brassica* *carinata, Brassica napus and Brassica oleracea* grew adequately. Considering both the capacity to accumulate trace elements in the shoot and the ability to grow in the contaminated soils tested, the most efficient phytoextractors were *Brassica juncea* in S1 (particularly for Zn) and *Brassica oleracea* in S2 (for Al, As, Pb and Zn).

Haque and colleaques (2009) showed that the selection of appropriate seeds is essential for the success of phytoremediation/restoration projects. The growth and elements uptake by the offspring of mesquite plants (*Prosopis* spp.) grown in a copper mine tailing (site seeds, SS) and plants derived from vendor seeds (VS) was investigated. Plants were grown in a modified Hoagland solution containing a mixture of Cu, Mo, Zn, As (III) and Cr (VI) at 0, 1, 5 and 10 mg L^{-1} each. After one week, plants were harvested and the concentration of elements was determined by using ICP-OES. At 1 mg L^{-1}, plants originated from SS grew faster and longer than control plants (0 mg L^{-1}); whereas plants grown from VS had opposite response. At 5 mg L^{-1}, 50% of the plants grown from VS did not survive, while plants grown from SS had no toxicity effects on growth. Finally, plants grown from VS did not survive at 10 mg L^{-1} treatment, while 50% of the plants grown from SS survived. The results suggest that SS could be a better source of plants intended to be used for phytoremediation of soil impacted with Cu, Mo, Zn, As and Cr.

Marigolds and banana were also proved to have high efficiency to remove arsenic from contaminated soils at the high arsenic contaminated area in Ron Phibun District (Chintakovid et al., 2008; Visoottiviseth, 2006). Marigold is one of the commercial flowers in Thailand used for decoration in various occasions, and its life is short only for 3-4 months.

Huq and colleaques (2005) applied marigold and ornamental arum. Marigold (*Tagetes patula*) and ornamental arum (*Syngonia spp.*) were grown on arsenic spiked soils up to 10 mg kg^{-1} soil to assess their properties as phytoremediators. At flowering stage, the maximum arsenic concentration in the root, shoot and leaf of marigold were 1,987; 5.45; and 3.50 mg kg^{-1} dry mass, respectively. The maximum arsenic concentrations in root and shoot of ornamental arum after two months were 14.3 and 12.1 mg kg^{-1}, respectively. The arsenic accumulating property of the *Tagetes patula* and *Syngonia spp.* appeared to be good sources to be exploited for phytoremediation of arsenic contaminated soil.

3.7 Waste management technologies for arsenic

Commercial waste encapsulation processes use concretes to incorporate arsenical wastes into claimed environmentally acceptable products. Management of hazardous wastes, such as arsenic, is of major public concern (Leist et al., 2000). Arsenic is an unwanted hazardous waste generated from the processing of a variety of ores including those of copper, gold, nickel, lead and zinc. Arsenic in the past was widely used in many agricultural applications as an active ingredient in many herbicides and insecticides. Safe disposal of arsenic wastes poses several problems:

1. Incineration is limited because of the volatilization of arsenic containing compounds.

2. Recovery of arsenic is of little economic interest because of the limited number of uses for the element.

3.7.1 Waste management concepts

In general, waste management is the collection, transport, processing, recycling or disposal of waste materials. Waste management involves solid, liquid, or gaseous substances with different methods and fields of expertise for each. Waste management for non-hazardous residential and institutional waste in metropolitan areas is the usually the responsibility of local authorities, while management for non-hazardous commercial and industrial waste is done by the generator. Principle options of waste management are operated to be ranked from most to least favored methods of pollution prevention, recycling, resource recovery, and disposal, respectively (Figure 3.11).

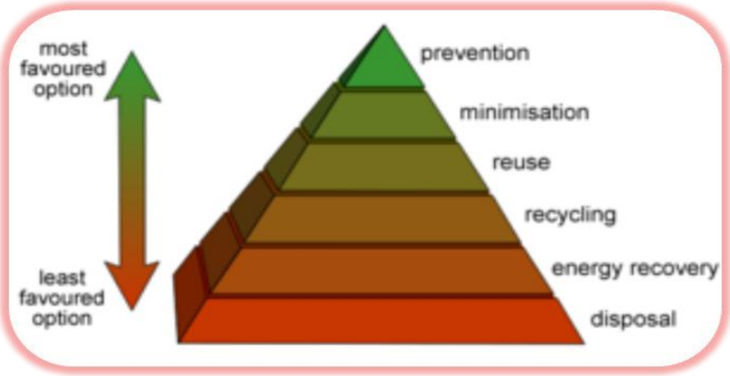


Figure 3.11 Waste management concepts (USEPA online)

3.7.1.1 Pollution prevention, this method applies for the most efficient use of energy and resources. In other word, called reduction at source, zero waste, and waste minimization are the same principal. Source reduction involves efforts to reduce hazardous waste and other materials by modifying industrial production, changing in manufacturing technology, raw material inputs, and product formulation. Reduction at source has many means to use. Ecological design product is one way to follow this pollution prevention.

3.7.1.2 Recycling, it means to recover for other use a material that would otherwise be considered waste. The popular meaning of “recycling” in most developed countries has come to refer to the widespread collection and reuse of various everyday waste materials. They are collected and sorted into common groups; so that the raw materials from these items can be used again.

3.7.1.3 Resource recovery, a recent idea in waste management has been to treat the waste material as a resource to be exploited, instead of simply a challenge to be managed and disposed of. There are a number of different methods by which resources may be extracted from waste. The materials may be extracted and recycled, or the calorific content of the waste may be converted to electricity.

3.7.1.4 Disposal, it is the last option to treat wastes under the regulatory limits. CCA-treated wood was disposed through incineration and ash disposal. During incineration, wood or plant materials can be used for energy recovery purposes or as a fuel in certain industrial operations such as cement kilns.

3.7.2 Hazardous waste

Hazardous waste is the waste that poses substantial or potential threats to public health or the environment and generally exhibits one or more of these characteristics: flammable, ignitable, oxidizing, corrosive, and toxic. Hazardous waste is a hazardous material destined for disposal or recycling with properties that make it dangerous or potentially harmful to human health or the environment. The universe of hazardous wastes is large and diverse. Hazardous wastes can be liquids, solids, contained gases, or sludge. They can be the by-products of manufacturing processes or simply discarded commercial products, like cleaning fluids or pesticides.

Researchers explained about four characteristics of the hazardous wastes: toxicity (acute, chronic and extrinsic), inflammability, reactivity and corrosiveness (Navia and Bezama, 2008). Acute toxicity is mainly related with specific compounds present in wastes that can cause death to human beings in small doses (e.g., arsenic oxides such as As_2O_5 and As_2O_3). Chronic toxicity is related with wastes that contain substances that can cause accumulative toxic effects, carcinogenic effects, mutagenic effects and teratogenic effects in human beings (e.g., 2,4,6-trichlorophenol). Extrinsic toxicity is associated with the leachability of toxic (acute and chronic) compounds present in wastes and is related to the maximum permissible concentration of the compound in the leachate (e.g., lead, 5 mg L^{-1}). Inflammability of a waste is related to four main characteristics: the waste is a liquid with an inflammation point under 61 ºC; the waste is not a liquid and can provoke, under standard pressure and temperature (1 atm and 25 ºC), fire by friction, by water absorption or spontaneous chemical changes. Finally, reactivity is associated with the following waste properties: the waste reacts strongly with water and can cause explosive mixtures with it. The waste contents of cyanides and sulphurs that can produce toxic gases in a pH range between 2 and 12.5. Corrosiveness is mainly attributed to a liquid waste with a pH value less than 2 or more than 12.5, or if the waste can corrode steel (SAE 1020) at a minimum rate of 6.35 mm/year at 55 ◦C.

Hazardous Wastes in the United States, US facility that treats, stores or disposes of hazardous waste must obtain a permit for doing so under the Resource Conservation and Recovery Act (RCRA). A RCRA hazardous waste is a waste that appears on one of the four hazardous wastes lists (F-list, K-list, P-list, or U-list), or exhibits at least one of four characteristics-ignitability, corrosivity, reactivity, or toxicity.

3.7.2.1 Listed wastes, the EPA determined that some specific wastes are hazardous. These wastes are incorporated into lists published by the agency. These lists are organized into three categories:

1. The F-list (non-specific source wastes), this list identifies wastes from common manufacturing and industrial processes, such as solvents that have been used in cleaning or degreasing operations. Because the processes producing

these wastes can occur in different sectors of industry, the F-listed wastes are known as wastes from non-specific sources.

2. The K-list (source-specific wastes), this list includes certain wastes from specific industries, such as petroleum refining or pesticide manufacturing. Certain sludges and wastewaters from treatment and production processes in these industries are examples of source-specific wastes.

3. The P-list and the U-list (discarded commercial chemical products), these lists include specific commercial chemical products in an unused form. Some pesticides and some pharmaceutical products become hazardous waste when discarded.

3.7.2.2 Characteristic wastes, waste that does not meet any of the listings explained above may still be considered a hazardous waste if exhibits one of the four characteristics defined in 40 CFR Part 261 Subpart C - ignitability (D001), corrosivity (D002), reactivity (D003), and toxicity (D004 - D043).

1. Ignitability: Ignitable wastes can create fires under certain conditions, are spontaneously combustible, or have a flash point less than 60 °C (140 °F). Examples include waste oils and used solvents.

2. Corrosivity: Corrosive wastes are acids or bases (pH less than or equal to 2, or greater than or equal to 12.5) that are capable of corroding metal containers, such as storage tanks, drums, and barrels. Battery acid is an example.

3. Reactivity: Reactive wastes are unstable under "normal" conditions. They can cause explosions, toxic fumes, gases, or vapors when heated, compressed, or mixed with water. Examples include lithium-sulfur batteries and explosives.

4. Toxicity: Toxic wastes are harmful or fatal when ingested or absorbed (e.g., containing mercury, lead, arsenic, etc.). When toxic wastes are land disposed, contaminated liquid may leach from the waste and pollute ground water. Toxicity is defined through a laboratory procedure called the Toxicity Characteristic Leaching Procedure (TCLP: Method 1311). The TCLP helps identify wastes likely to leach concentrations of contaminants that may be harmful to human health or the environment.

Arsenic compounds are listed in the Annex II-C8 under the European Union’s hazardous waste directive (91/689/EEC) as a household hazardous waste. Hazardous waste management options must be suitable for fixed and operation costs (Slack et al., 2009).

3.7.3 Management of hazardous waste

Arsenic hazardous waste generated from the processing of a variety of ores including tins, copper, gold, nickel, lead and zinc. Arsenic in the past was widely used in many agricultural applications of herbicides and insecticides. The existing problems of arsenic wastes, there will be an increase in the future production of arsenic wastes as industry begins to process more complicated sulphide ores, such as low-grade gold associated with arsenopyrite and nickel ores with high arsenic contents. There will also be an increase in the global cycling of arsenic due to the progressive industrialization of developing nations.

Arsenic cannot be destroyed; it can only be converted into different forms or transformed into insoluble compounds in combination with other elements, such as iron. Arsenic wastes may contain many impurities such as lead, iron and selenium. These elements can often be uneconomic to remove and the arsenic is stockpiled as waste. In general, there are three options available for dealing with arsenic waste streams:

1. Concentration and containment: There are two major drawbacks associated with the first option: the cost and safety issues. There is little commercial interest in investing in plants and technology to recover arsenic and its compounds when there is a very limited market for the recovered material except where the arsenic is of a relative high purity. Additionally, there are safety concerns associated with the storing of arsenic in a concentrated form and possibly dire consequences associated with any accident at the point of storage.
2. Dilution and dispersion: This option is superficially attractive to the waste disposal and mining industries, because it offers the possibility for combining numerous waste streams together and in a way which dilutes the hazardous contaminants, thus passing any regulatory limits. However, this does not represent any real technical solution to arsenic contamination, but merely a legislative solution.

Long-term exposure to low concentrations of arsenic still poses serious health problems, including enhanced risks of skin cancers and various internal carcinoma.

3. Encapsulation of the material: the most attractive option for dealing with arsenic wastes lies in encapsulating the contaminated material, usually through solidification/stabilization techniques (Leist et al., 2000) and disposing of the treated wastes in secure landfills. The U.S. Environmental Protection also recognizes cementitious solidification as ‘‘the best demonstrated available technology’’-BDAT, for land disposal of most toxic elements (U.S.EPA, 1993).

3.7.4 Waste management technologies for arsenic

Yang and colleaques (2007) reviewed that major technologies currently used for remediation of heavy-metal contaminated soils include excavation and disposal, vitrification, electrokinetic treatment, soil flushing, chemical fixation, and solidification/stabilization.

Excavation and disposal is the most the direct way to remediate heavily contaminated soils. Its applicability varies depending on the characteristics of the contaminated site and the remediation process can be very costly, especially if hand digging is required.

Vitrification involves high temperature treatment of soil and is aimed primarily at the reducing the mobility of metals by their incorporation into a chemically durable, leach resistant, vitreous mass. Because of the difficulties in controlling and treating the volatile emissions produced during this process, so its applicability varies from site to site.

Electrokinetic remediation can be used as an *in situ* remediation technology. The treatment process involves passing a low amperage electrical current between a series of cathodes and anodes imbedded in the contaminated soil. It requires the presence of a conducting pore fluid in the soil mass to be treated and is therefore applicable to soils only under saturated conditions. Moreover, the contaminated species must be solubilized by the introduction of acids or other appropriate chemicals during the treatment process.

Soil flushing is designed to solubilize and extract contaminants in soils by extracting aqueous solutions. Additives can be added into extracting solutions to enhance efficiencies. However, this method mainly focuses on volatile organic compounds and is still quite limited for metal removal.

In situ chemical fixation (ISCF) remediation technology was developed to safe and economically treat the contaminated area. The ISCF treatment was tailored to the soil chemistry of the contaminated sites and designed to promote the formation of more insoluble arsenic-bearing phases by injections of chemical reagents in order to reduce arsenic environmental leachability.

Fiedler (2001) found that non-aqueous arsenic hazardous waste of 1.84 million tons was managed offsite; 400,000 tons (22%) were treated via stabilization/chemical fixation using cement or pozzolans. Thermal technologies (incineration, energy recovery, or fuel blending) were used for 36% of the wastes, most likely to address the organic fraction of the waste. An additional 11% were subjected to recovery technologies (high temperature metals recovery or secondary smelting). Based on this information, stabilization was the most common technology for disposing of non-aqueous remediation waste containing arsenic. At least 45 sites were using stabilization to treat arsenic-contaminated soil, sediments, sludge, and other solids. Cement, lime, and phosphate are the most common stabilization binders used at these sites. Other technologies used at contaminated sites include: soil washing (6 sites), chemical treatment (4), acid extraction with hydrochloric acid (2), in situ soil flushing (2), vitrification (3), and electrical separation (1). Chemical treatment agents used include a combination of ferrous iron/lime/potassium permanganate, oxygenated water with an iron catalyst, and phosphate.

Vitrification was selected by EPA as the Best Demonstrated Achievable Technology (BDAT) for characteristic and listed wastes containing arsenic including D004, K031, K084, K101, K102, P10-12, P36, P38, and U36 (Wickramanayake et al., 2001). Vitrification involves the use of a plasma torch, an electrical current, or other heat source to melt the contaminated material into a glass matrix at extremely high temperatures ranging from 2,900 to 3,650 °F. The vitrified material is non-porous, has a high strength, and is much more resistant to leaching than the original feed materials. Although vitrification, as BDAT, would be considered the “conventional” approach to treatment, it is not widely used and has been selected as a treatment option for arsenic-contaminated waste at only one out of twelve Superfund sites identified. The remaining sites with arsenic-impacted soil or other wastes had Record of Decision (ROD) selected remedies that included solidification/stabilization (6), containment/capping (4), and soil washing (1). Vitrification is not used extensively for the following reasons:

1. The cost is prohibitive since the process require complex, capital-intensive equipment
2. Wastes with elevated moisture content, high metal content, and/or inappropriate physical characteristics may be more expensive or difficult to treat; and
3. Significant volatile losses of arsenic can occur unless the waste is properly pre-treated to produce less volatile forms of arsenic.

Solid waste management in developing countries is often unsustainable, relying on uncontrolled disposal in waste dumps. Particular problems arise from the disposal of treatment residues generated by removing arsenic from drinking water because arsenic can be highly mobile and has the potential to leach back to ground and surface waters.

In this study, solid wastes were managed according to their types, solid and liquid wastes. The main wastes were solid wastes of arsenic accumulated plants materials from soil phytoremediation (SP) field experiment and concrete constructed wetland (CW) ponds, sewage sludge from sedimentation ponds, and arsenic contaminated soils; and arsenic containing water discharge from the CW, SP, and paper production experiments.

Arsenic accumulated plant wastes were managed by drying in the sunlight and burning in local incinerator. As well as waste utilization of banana stems has proceeded for paper and paper products. For these sewage sludge, bottom ash from incineration, and arsenic contaminated soils from the CW and SP had been managed before disposal by solidification/stabilization method and leaching tests.

3.8 Waste management of arsenic accumulated plants

At the end of the growth period or suitable time, plant biomass is harvested, dried or incinerated, and the contaminant-enriched material is deposited in a special dump or added into a smelter. The energy gained from burning of the biomass could support the profitability of the technology; if the resultant fumes can be cleaned appropriately (Kra¨ mer, 2005).

The biomass of arsenic accumulated plants needs proper disposal and management (Nakwanit et al., 2009). Three options were performed in order to manage these plant wastes. The first technique was weight reduction by drying and burning. This technique was applied with marigold biomass. The marigold bottom ash was studied by solidification/stabilization (S/S) before disposal. The S/S, encapsulation, or fixation is a technology used to transform hazardous liquid or solid wastes into less hazardous solids. The second technique was degradation in water. This was explored with *C. esculenta*, banana and marigolds. The last technique was making benefit from selling as ornamental plants and making paper. This method was suitable for *Cyperus* spp. (ornamental purpose) and banana stems waste (paper production).

3.8.1 Incineration

Incineration is a waste disposal method that involves the combustion of waste at high temperatures. Incineration and other high temperature waste treatment systems are described as thermal treatment. Incineration of waste materials converts the waste into heat, gaseous emissions, and residual solid ash. Other types of thermal treatment include pyrolysis and gasification. A waste-to-energy plant (WtE) is a modern term for an incinerator that burns wastes in high-efficiency furnace/boilers to produce steam and/or electricity and incorporates modern air pollution control systems and continuous emissions monitors. This type of incinerator is sometimes called an energy-from-waste (EfW) facility. Incineration is popular in countries such as Japan where land is a scarce resource, as they do not consume as much area as a landfill. Sweden has been a leader in using the energy generated from incineration over the past 20 years. Denmark also extensively uses waste-to-energy incineration in combined heat and power facilities supporting district heating schemes (Figure 3.12).

Incineration is carried out both on a small scale by individuals, and on a large scale by industry. It is recognized as a practical method of disposing of certain hazardous waste materials (such as biological medical waste), though it remains a controversial method of waste disposal in many places due to issues such as emission of gaseous pollutants. The disadvantages include potential air emission problems and the high metals concentrations in the waste ash. At temperatures greater than 300 ºC, some arsenic is volatilized (Solo-Gabriele, H and Townsend, 1999). The amounts of arsenic volatilized ranges from 40 to 60 % between temperatures of 500 to 700 ºC.

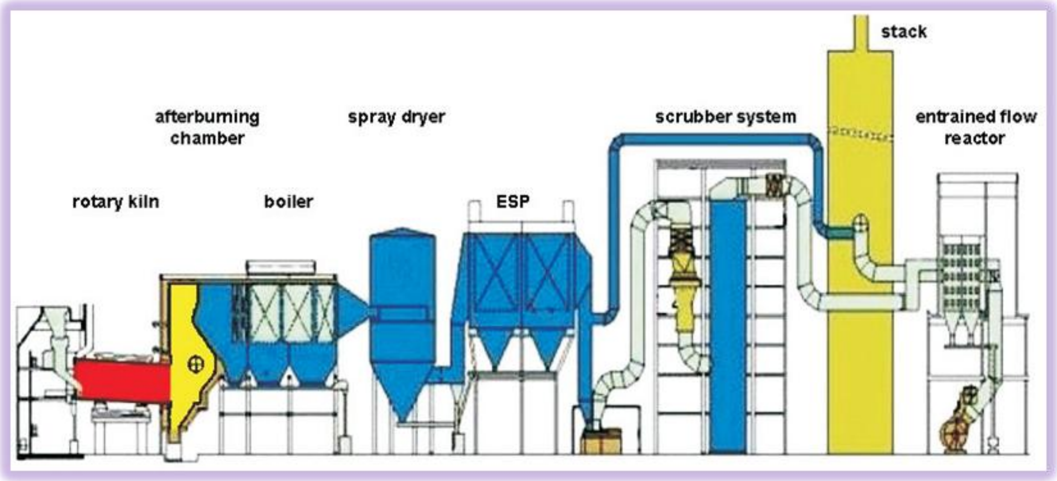


Figure 3.12 The hazardous waste incineration plant at Biebesheim (Reinhardt et al., 2008)

3.8.2 Solidification and stabilization

Arsenic waste disposal generally involves one of four options as follows (Bowell and Parshley, 2001): (1) physical stabilization through the use of engineered disposal facilities and institutional controls; (2) chemical stabilization of arsenic containing waste; (3) chemical treatment of effluents to produce saleable products, such as white arsenic oxides by the El Indio or Warox processes or production of an insoluble arsenate such as ferric arsenate; (4) chemical stabilization of the arsenic waste by fixing it within an inert material such as cement, slag or silica material.

There are several other treatment options for arsenic-contaminated wastes, including the most commonly applied technology, solidification/stabilization (S/S) with cement, fly ash, sodium silicates, or other binders. S/S relies on mobility reduction, resulting from a combination of physical entrapment (e.g., encapsulation) and chemical reaction (e.g., precipitation) mechanisms. Cement, silicate, and other S/S binder materials were evaluated by EPA, but not accepted as BDAT for arsenic wastes due to concerns about long-term stability and waste volume increases. However, EPA did not preclude the use of S/S methods for the treatment of arsenic wastes, but instead recommended site-specific treatability studies. Several studies have demonstrated that S/S can be successfully implemented for the treatment of arsenic-contaminated wastes; if pre-treatment methods are employed first to transform arsenic into the appropriate oxidation stage or species and then to decrease the solubility or availability of the arsenic compounds in the solid matrix prior to binding. The following is a list of alternate or innovative treatment technologies that can be applied to treat arsenic contaminated hazardous wastes:

1. S/S with pretreatment by oxidation using hydrogen peroxide, potassium permanganate, and others
2. S/S with pretreatment by hydrated salt addition including ferric sulfate, ferrous sulfate, ferric chloride, and others
3. S/S with proprietary formulations
4. Slag incorporation
5. Encapsulation with polymer resins

The waste consisted of iron-arsenic sludge and sludge generated from arsenic precipitated with lime. As part of the ROD selected remedy, an estimated 3,800 tons of these arsenic wastes, containing up to 260,000 mg kg^{-1} of arsenic, were removed and treated off-site with S/S before disposal at a RCRA Subtitle C landfill. The treatability study tested a total of 88 mixture designs to determine an effective method of treating the vault wastes.

Solidification/stabilization (S/S) is one of the most effective treatment processes for the remediation of heavy-metal contaminated soils (Moon and Dermatas, 2007). S/S is used as a pre-landfill waste treatment technology that aims to make hazardous industrial wastes safe for disposal. Cement-based S/S technology is widely used because it offers assurance of chemical stabilization in many contaminants and produces a stable form of waste (Singh and Pant, 2006). S/S method involves mixing contaminated soils or residual particulates from other treatment methods with a physical binding agent to form a crystalline, glassy, or polymeric framework surrounding the waste particles. A process that converts contaminants to forms that are less soluble, mobile, or toxic is referred to as stabilization, and the incorporation of contaminants into a monolithic solid with a reduced surface area is known as solidification. Various stabilizing agents, such as cement, hydrated lime, and fly ash, have been used in S/S processes. In soils treated with stabilizing agents, three possible mechanisms may be responsible for the immobilization of As. One mechanism may be precipitation resulting from the formation of insoluble Ca–As precipitates. Another may be inclusion, either by physical encapsulation or chemical inclusion. Physical encapsulation can be achieved by creating a solidified monolith, and chemical inclusion can be achieved through the incorporation of arsenic in binder hydration products, such as calcium silicate hydrates (CSH) by isomorphous substitution. Also, sorption on clays and pozzolanic reaction products may immobilize arsenic.

Sullivan and colleaques (2010) reviewed the disposal of water treatment wastes containing arsenic, with a particular emphasis on S/S technologies. Portland cement/lime mixes are expected to be appropriate for wastes from sorptive filters, but may not be appropriate for precipitative sludges, because ferric flocs often used to sorb arsenic can retard cement hydration. Brine resulting from the regeneration of activated alumina filters is likely to accelerate cement hydration. Portland cement immobilises soluble arsenites and has been successfully used to stabilise arsenic-rich sludges (suitable for treating sludge generated from precipitative removal units). Oxidation of As (III) to As (V) and the formation of calcium-arsenic compounds are important immobilisation mechanisms for arsenic in cements. Geopolymers are alternative binder systems that are effective for treating wastes rich in alumina and metal hydroxides and may have potential for arsenic wastes generated using activated alumina. The long-term stability of cemented, arsenic-bearing wastes is uncertain because they are susceptible to carbonation effects which may result in the subsequent re-release of arsenic.

Arsenic mobility is affected by environmental conditions including acid-base equilibria and overall pH, oxidation-reduction potential and electron activity, the presence of complexing cations and anions (such as sulfides, calcium, and iron), and adsorption/desorption reactions (Fiedler, 2001).

Many papers (Banerjee and Chakraborty, 2005; Jing et al., 2003; Leist et al., 2003) were shown to manage solid waste of arsenic contaminated sludge and bottom ash for concrete production by replacing cement. At present, the most attractive option for dealing with arsenic wastes lies in encapsulating the contaminated material, through solidification/stabilization techniques and disposing of the treated wastes in secure landfills.

The study provided a potential application for the fly ash, as a kind of solid waste from thermal power stations, to be reused to control water pollution. An effective adsorbent for arsenic (V) removal from aqueous system has been successfully developed using high iron containing fly ash as raw material (Li et al., 2009).

Natural zeolites are abundant and low cost resources, which are crystalline hydrated aluminosilicates with a frame work structure containing pores occupied by water, alkali and alkaline earth cations. Natural zeolites have been used as adsorbents in separation and purification processes in water and wastewater treatment because their high cation-exchange ability and the molecular sieve properties. Various natural zeolites around the world have shown varying ion-exchange capacity for cations such as ammonium and heavy metal ions. Some zeolites also show adsorption of anions and organics from aqueous solution. Modification of natural zeolites can be done in several methods such as acid treatment, ion exchange, and surfactant functionalisation, making the modified zeolites achieving higher adsorption capacity for organics and anions (Wang and Peng, 2010).

3.8.3 Leaching test

Treated and untreated soils were subjected to sequential leaching using the leachate solutions described in U.S.EPA (Methods 1311 and 1312) in order to evaluate the effectiveness of each treatment for reducing the mobility of arsenic during long-term leaching. EPA Method 1311 (Al-Abed et al., 2007; U.S.EPA, 1992), toxicity characteristic leaching procedure (TCLP) fluid is an acetic acid solution with a pH of 2.88. While EPA Method 1312 synthetic precipitation leaching procedure (SPLP) fluid is a dilute mixture of sulfuric and nitric acids having a pH of 4.20. The TCLP exceeded the toxicity characteristic limit (5 mg L^{-1} of arsenic), classifying it as a hazardous waste (Jambeck et al., 2007).

Regulatory requirements for the disposal of wastes differ somewhat depending on the country; but in general, solid wastes such as ash must be tested to determine whether they display toxic or hazardous properties sufficient to require special management. In the US the first determination that must be made is whether the ash is hazardous by establishing its toxicity characteristic (TC) which is assessed using the toxicity characteristic leaching procedure. The TCLP involves leaching the ash in a leaching fluid that simulates a domestic waste landfill, and analyzing the leachate for designated constituents. If the leachate concentration of a designated constituent is greater than the TC concentration, the waste is hazardous by the TC. Arsenic and chromium are both designated TC constituents with regulatory limits of 5 mg L^{-1} each (Solo-Gabriele et al., 2002).

Arsenic is co-precipitated with iron hydroxide in an arsenic-removal water plant; a large quantity of sludge is generated which contains an amount of arsenic. Some suitable solutions to disposal of this arsenic-bearing sludge, safe disposal of stabilization processes such as briquette production, cement mortar and concrete making have been attempted in the present investigation. It has been found that in the preparation of briquette, cement-sand mortar and concrete, mixing up to 10, 18 and 40% of arsenic-bearing sludge by volume, respectively with the other common ingredients did not produce a TCLP leachate beyond its permissible direct inland water discharge standards. Also, it was noted that 25% (by volume) of cement could be replaced by fly ash to stabilize arsenic-laden sludge to the tune of 11% by volume of cement-sand (1:3) mortar (Banerjee and Chakraborty, 2005).

Leaching tests, Fourier transform infrared spectroscopy (FTIR), extended X-ray absorption fine structure (EXAFS) spectroscopy, and thermodynamic modeling were performed to investigate arsenate [As (V)] immobilization mechanisms in iron hydroxide sludge stabilized with cement (Jing et al., 2003). The sludge from a groundwater remediation site in Tacoma, WA was mixed and immobilized with premixed cement to reach cement-to-sludge ratios of 2.5, 3.3, 5, 10, and 20 (wt premixed cement/wt dry sludge). The EXAFS analysis determined that As (V) formed bidentate mononuclear complexes on the iron hydroxide surface in the sludge. The adsorbed As (V) had a characteristic FTIR band at 830 cm^{-1}. Cement treatment converted the adsorbed As (V) to calcium arsenate precipitate with a FTIR peak at 860 cm^{-1}. The chemical forms of the As (V) were incorporated in an adsorption triple layer model (TLM) to describe the leaching behavior of As (V) in a pH range between 3 and 12. Leaching of arsenite is found to be more than that of arsenate. Higher leaching of arsenic from CalSCo-sludge take place when pH of the surrounding medium reaches <3, or >11, and also in presence of Cl$^-$ ions (Bang et al., 2005).

Yang and colleaques (2007) reported the results of an experimental study testing a low-cost in situ chemical fixation method designed to reclaim arsenic-contaminated subsurface soils. Subsurface soils from several industrial sites in southeastern USA were contaminated with arsenic through heavy application of herbicide containing arsenic trioxide. The mean concentrations of environmentally available arsenic in soils collected from the two study sites, FW and BH, were 325 mg kg^{-1} and 900 mg kg^{-1}, respectively. Ferrous sulfate, potassium permanganate and calcium carbonate were used as the reagents for the chemical fixation solutions evaluated in three sets of batch experiments: (1) FeSO4; (2) FeSO4 and KMnO4; (3) FeSO4, KMnO4 and CaCO3. The optimum treatment solutions for each soil were identified based on the mobility of arsenic during sequential leaching of treated and untreated soils using the fluids described precipitation leaching procedure (SPLP). Both FW and BH soils showed significant decreases in arsenic leachability for all three treatment solutions, compared to untreated soil. While soils treated with solution (3) showed the best results with subsequent TCLP sequential leaching, SPLP sequential leaching of treated soils indicated that lowest arsenic mobility was obtained using treatment solution (1). Treatment solution (1) with only FeSO4 was considered the best choice for remediation of arsenic contaminated soil because SPLP sequential leaching better simulates natural weathering. Analysis of treated soils produced no evidence of newly-formed arsenic-bearing phases in either soil after treatment. Sequential chemical extractions of treated soils indicate that surface complexation of arsenic on ferric hydroxide is the major mechanism for the fixation process.

Bhunia and colleaques (2007) studied on synthetically prepared arsenic-laden CalSiCo-sludge that was converted to pulverized cement concrete (PCC) using solidification/stabilization technology with cement. Batch leaching experiments were conducted to estimate the leaching of As (III) and As (V) from the CalSiCo-sludge and the PCC. The leaching of As (III) and As (V) was found to be the function of time, pH and concentration of anions such as Cl^{-}, NO_3^{-}, and SO_4^{2-} present in the extraction fluid. It is observed that from the CalSiCo-sludge, the leaching of As (III) is >0.05 mg L^{-1} (which is above the permissible limit for arsenic in drinking water) at any pH. But, in case of As (V) the leaching is >0.05 mg L^{-1} only at pH > 8 and at pH < 4. It is noted that maximum leaching occurs when the extraction liquid contains Cl^{-}. In contrary, NO_3^{-}, and SO_4^{2-} have negligible effect on arsenic leaching from the CalSiCo-sludge. Extraction tests were carried out to determine the maximum leachable concentration under the chosen conditions of leaching medium and leaching time. Leaching of As (III) and As (V) from exhausted arsenic-laden CalSiCo-sludge and from PCC was carried out in both tap water and rain water. It was noticed that tap water has no effect in leaching of arsenic from CalSiCo-sludge but rain water causes significant amount of leaching, which is mostly due to pH effect. However, in all cases the leaching of As (III) was more than that of As (V). When compared with CalSiCo-sludge PCC showed negligible leaching of arsenic.

Scoria (a vesicular pyroclastic rock with basaltic composition) from Jeju Island, Korea, were conducted as an efficient sorbent to remove divalent heavy metals: Pb (II), Cu (II), Zn (II), Cd (II)) and trivalent arsenic of arsenite from aqueous solutions. The removal efficiencies of Pb, Cu, Zn, Cd, and As by the scoria (size = 0.1-0.2 mm, dose = 60 g L^{-1}) were 94, 70, 63, 59, and 14 %, respectively, after a reaction time of 24 h under a sorbate concentration of 1 mM and the solution pH of 5. A careful examination on ionic concentrations in sorption batches suggested that sorption behaviors of heavy metals onto scoria are mainly controlled by cation exchange. On the other hand, arsenic appeared to be sensitive to specific sorption onto hematite (a minor constituent of scoria). The arsenic removal increased with increasing pH of aqueous solutions, which can be attributed to co-precipitation with metal hydroxides (Kwon et al., 2010).

3.8.4 Degradation of arsenic accumulated plants

Ocean disposal is one option for the arsenic-enriched plant biomass. The idea that marine primary producers have evolved an efficient way of living for arsenic by converting potentially toxic inorganic arsenic to apparently innocuous arsenosugars (Francesconi, 2005).

Phenyl substituted arsenic compounds are widely used as feed additives in the poultry industry and have become a serious environmental concern. Phenylarsonic acid (PA) was degraded by TiO_2 photocatalysis. The pH of the solution influenced the adsorption and photocatalytic degradation of PA due to the surface charge of TiO_2 photocatalyst and speciation of PA. Phenol, catechol and hydroquinone were observed as the predominant products during the degradation. The roles of reactive oxygen species, OH, $1O_2$, O_2^- and hVB^+ were probed by adding appropriate scavengers to the reaction medium and the results suggested that OH played a major role in the degradation of PA. By-product studies indicated the surface of the catalyst played a key role in the formation of the primary products and the subsequent oxidation pathways leading to the mineralization to inorganic arsenic. TiO_2 photocatalysis results in the rapid destruction of PA and may be attractive for the remediation of a variety of organoarsenic compounds (Zheng et al., 2010).

Ko and colleaques (2010) investigated the biodegradable chelating agents: S,S-ethylenediaminedisuccinic acid (SS-EDDS) and nitrilotriacetic acid (NTA) as potential alternatives was studied and compared them with ethylenediaminetetraacetic acid (EDTA) for effectiveness. Extraction of heavy metals from chromated copper arsenate (CCA)-treated wood with EDDS, NTA, or EDTA solvent was evaluated at various solvent pH levels and stoichiometric ratios. The extraction conditions of pH 4 and EDDS-CCA stoichiometric ratios of 10 were recommended

Natural biological processes usually occur at a low rate. Substrates can become less bioavailable via interaction with negatively charged clay particles and organic matter. Bioavailability of electron acceptors can influence microbial activity. Solid Fe (III) must be available and in direct contact for the microorganisms. Bioaugmentation and biostimulation can be used to promote local microbial activity. Biostimulation is the process by which a stimulus to the microorganisms that already exist in the site is provided by adding nutrients and other growth substrates, together with electron donors and acceptors. While, bioaugmentation is the process of introducing exogenous microorganisms into the site (Wang and Mulligan, 2006).

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 (Wang and Mulligan, 2006). The As (III) oxidation process provides energy for the microbial growth. It was found that the ecological role of the As (III) oxidation to As (V) by *Thermus* (Gihring et al., 2001). The oxidation of As (III) to As (V) by bacterial colonies attached to macrophytes occurs immediately when the geothermal fluid is exposed to oxygenated conditions. An estimated half-life was around 20 minutes for the oxidation of As (III) to As (V) in Hot Creek, Sierra Nevada Mountains of California.

Arsenic concentrations in the foliar leachate ranged from 0.004-0.52 mg L^{-1}, and the percentages of As (III) with respect to total arsenic in leachate ranged from 5-10% (Yan et al., 2009). A positive linear relationship existed between arsenic concentrations of the foliar leachate and the amounts of arsenic accumulated in the plant. The rate of arsenic leaching from the leaves was accelerated by an increase of rainfall and time in a simulated precipitation experiment. Water-soluble arsenic distributed within the cuticle and apoplast of the plant was speculated as the main source of the leached arsenic.

Tabelin and colleaques (2010) studied the factors affecting arsenic mobility from hydrothermally altered rock under in situ conditions. Four impoundments with rectangular base, truncated-pyramid structures were built on site. Impoundment 1 was composed of the hydrothermally altered rock while impoundments 2-4 were covered with different types of silty covering soil in order to minimize O_2 and water intrusion into the rock. The results indicated that seasonal variations in temperature, O_2 concentration and volumetric water content in the impoundments strongly influenced arsenic leaching. Oxidation of sulfide minerals in the rock was enhanced because of a higher air-water-rock interaction when high temperature and low water content. Arsenic concentration in the porewater increased when it rained after a specific period of dry weather. The use of a silty covering soil influenced the concentrations of arsenic and in the porewater. O_2 and water movement might be the rate controlling step of arsenic leaching. If there is no covering soil on the impoundment, more arsenic will leach out from the rock. The use of a silty covering soil showed the reduction of arsenic leaching from the waste rock, but utilizing it alone was insufficient to effectively prevent arsenic release from the rock. A combination of covering soil and bottom arsenic-adsorption layer to incorporate any arsenic released from the rock is recommended.

3.8.5 Utilization of arsenic accumulated plants

After harvesting the fruit of banana, the pseudostem is normally left in the soil plantation as organic fertilizer or used for making animal feed such as pig feed. Banana leaves are widely used as plates and for wrapping food for cooking or storage. Improved processes have made it possible to utilize banana fiber for many purposes such as paper, rope, table mats and handbags.

Tock and colleaques (2010) reviewed the utilization of banana residuals in the followings. A craft type paper of good strength has been made in India, from crushed, washed and dried banana pseudostems which yield 48-51% of unbleached pulp. This good quality paper is made by combining banana fiber with that of the betel nut husk (*Areca catechu* L.). However, the yield of banana fiber is too low for extraction to be economic. Only 28-113 g can be obtained from 18-36 kg of green pseudostems; 132 tons of green pseudostems would yield only 1 ton of paper. During recent years, banana residue has made into the energy production sector. Successful examples were shown by the banana biogas project by Growcom, Australia and the Compact Biogas Plant. There are two available methods for conversion of banana biomass into energy, thermal and biological conversion. The thermal conversion performs by direct combustion and gasification while biological conversion involves anaerobic digestion. Clarke’s research found that the maximum yield produced were more than 398 L of methane per kilogram of dry banana. With this much amount of methane that is available for energy conversion, 1 ton of banana waste per day can generate around 7.5 kW of electricity (being supplied for 6-8 modern households). The advantage of producing a very clean form of biogas, consisting of just methane and carbon dioxide as compared to the other waste streams such as human sewage, piggery or feedlot waste, with the added attraction of less noxious odors as well as different trace elements. This energy potential generated by banana plant biomass in Malaysia showed a maximum power of 80.52 MW can be obtained from direct combustion and 869.13 MW from anaerobic digestion.

3.9 Standards for arsenic

3.9.1 Arsenic standards for drinking water and food

The World Health Organization (WHO) revised the guideline for arsenic in drinking water from 0.05 to 0.01 mg L^{-1} in 1993 (Leist et al., 2000). As the results, Germany has lowered its permissible limit of arsenic to 0.01 mg L^{-1} in 1996, while the Australian drinking water limits were also lowered to 0.007 mg L^{-1}. The French current standard was 0.015 mg L^{-1}. In the European Union, the arsenic standard level was set to 0.01 mg L^{-1}. The U.S.EPA has also eventually implemented the reduction of permissible values of arsenic in drinking water from 0.05 to 0.01 mg L^{-1}, in light of the epidemiological evidence to support the carcinogenic nature of the ingested arsenic and its connection with liver, lung and kidney diseases and other dermal effects (Thomas et al., 2007). Levels of arsenic in excess of the WHO recommended limit of 0.01 mg L^{-1} can occur naturally in water bodies used as sources of drinking water, but the problem was intensified by the sinking of wells in areas of arsenic-rich geological strata (Gillman, 2006). For Thailand, the maximum contaminant level (MCL) of arsenic was set at 0.01 mg L^{-1} for drinking water (Ministry of Science Technology and Environment, 1996; Thai Industrial Standards Institute, 2006). Guidelines for maximum permissible concentrations of arsenic in foods, where such guidelines existed were set at 1 mg kg^{-1}(The Arsenic in food Regulations, 1959). Total arsenic regulation limit for all foods in Thailand was set at less than 2 mg kg^{-1} (Ministry of Public Health, 2003).

3.9.2 Arsenic standards for wastewater and non-wastewater

A hazardous waste exhibited the toxicity characteristic for arsenic if the arsenic concentration was greater than 5 mg L^{-1} when analyzed using the TCLP (Fiedler, 2001). Hazardous waste in the U.S. is regulated under the RCRA. For 29 listed hazardous wastes, U.S.EPA has identified arsenic as a hazardous element, or has established a land disposal restriction (LDR) standard. The LDR treatment standard for arsenic in wastewater was 1.40 mg L^{-1}, based on the performance achievable by chemical precipitation. The standard for non-wastewaters was 5 mg L^{-1} as measured by the TCLP. The waste was determined to be non-hazardous if its leached concentration was below the toxicity characteristic regulatory limit at 5 mg L^{-1} (García-Ubaque et al., 2007; Shaw et al., 2007; Swash and Monhemius, 2005). This limit wastewater of arsenic in UK regulations was 10 mg L^{-1}; and for safe soil arsenic concentration is not exceeded 50 mg kg^{-1} (Bhattacharya et al., 2007).

Nateewattana and collegues (2009) found that the arsenic concentration in Mae Moh reservoir water was below the Thailand National Standard of 0.25 mg L^{-1} for surface water type II–IV; Notification of the Ministry of Science, Technology and Environment, No.3, 1996 (MOSTE, 1996). The highest arsenic concentration found at the reservoir's bottom sediment was 5,213 mg kg^{-1} which was above the Thailand National Guideline of 27 mg kg^{-1} for soil surface of non-agriculture practice. Thailand Natural Environmental Board (2004) regulates the standard for soil used for agriculture purpose with arsenic concentration less than 3.9 mg kg^{-1}.

The air industrial emission standard for arsenic volatilized was not exceeded 16.0 mg m^{-3} (Notification of Natural Environmental Board, No.25, 2004).

CHAPTER IV

MATERIALS AND METHODS

4.1 Conceptual Framework

This study composed of 5 experiments:

Experiment I : Arsenic removal efficiency by constructed wetland and soil phytoremediation

Experiment II : Waste management of the arsenic accumulated plant biomass by degradation in freshwater

Experiment III : Management of the arsenic accumulated marigold biomass by burning

Experiment IV : Waste management by utilization (as papers and paper products and ornamental plants)

Experiment V : Management of sediment sludge, soils, and marigold bottom ash by solidification/stabilization

Experiment I : Arsenic removal efficiency by constructed wetland and soil phytoremediation

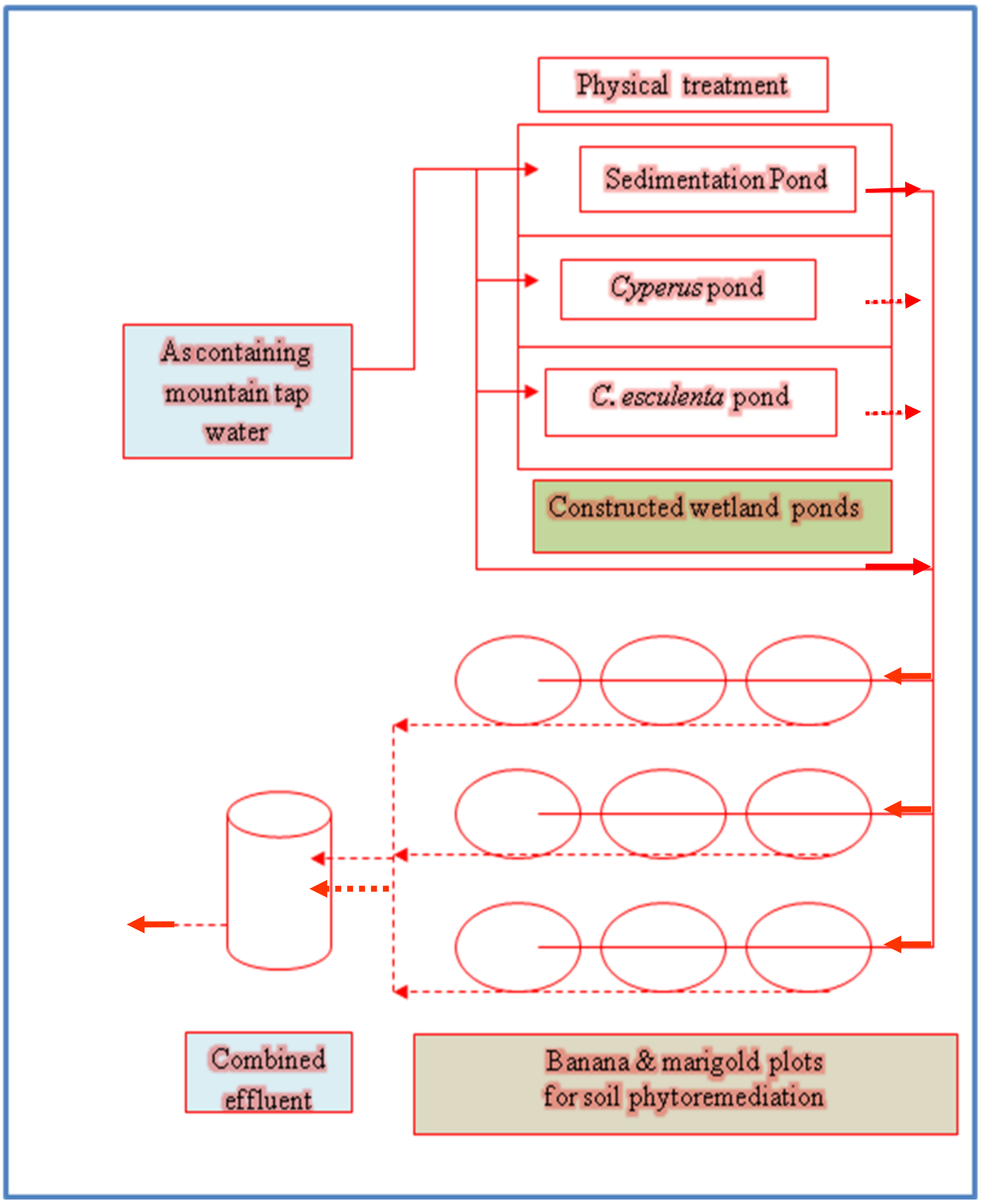
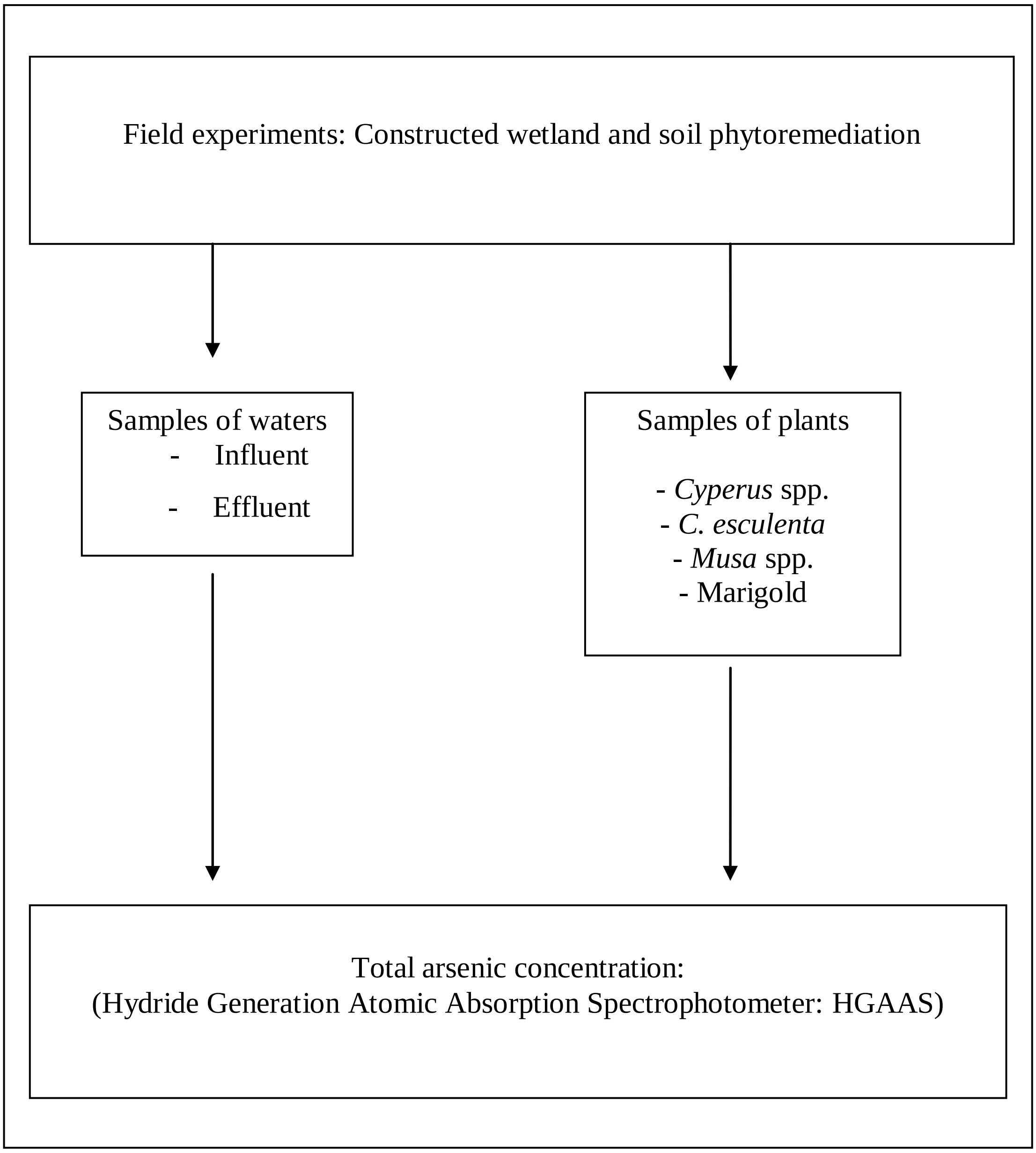
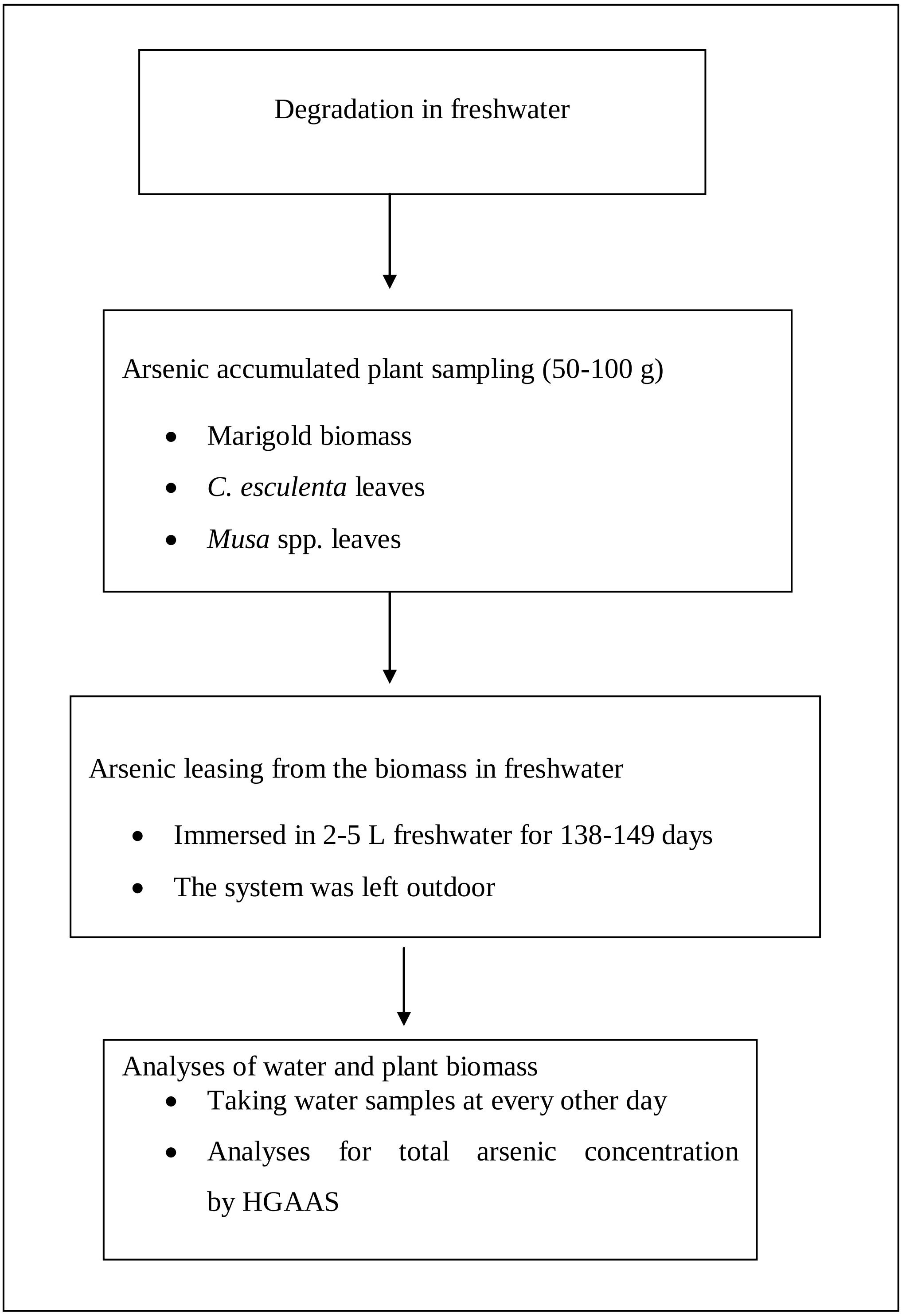


Figure 4.1 Diagram of the model system for arsenic removal from mountain tap water by constructed wetland and soil phytoremediation

Sample collection and analysis of arsenic concentration in sample treated with constructed wetland and soil phytoremediation



Experiment II : Waste management of the arsenic accumulated plant biomass by degradation in freshwater



Degradation in freshwater

Arsenic accumulated plant sampling (50-100 g)

- Marigold biomass
- *C. esculenta* leaves
- *Musa* spp. leaves

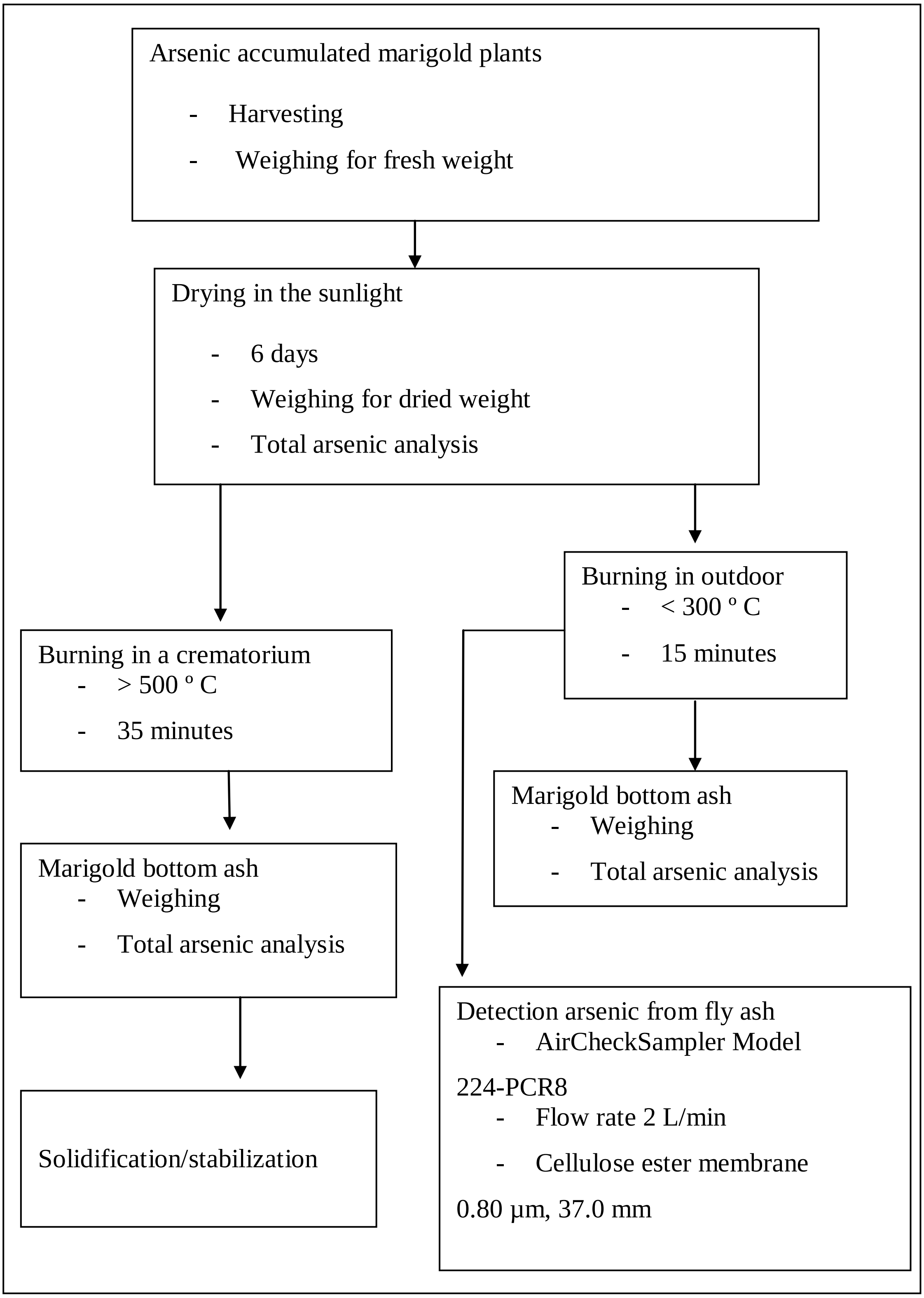
Arsenic leasing from the biomass in freshwater

- Immersed in 2-5 L freshwater for 138-149 days
- The system was left outdoor

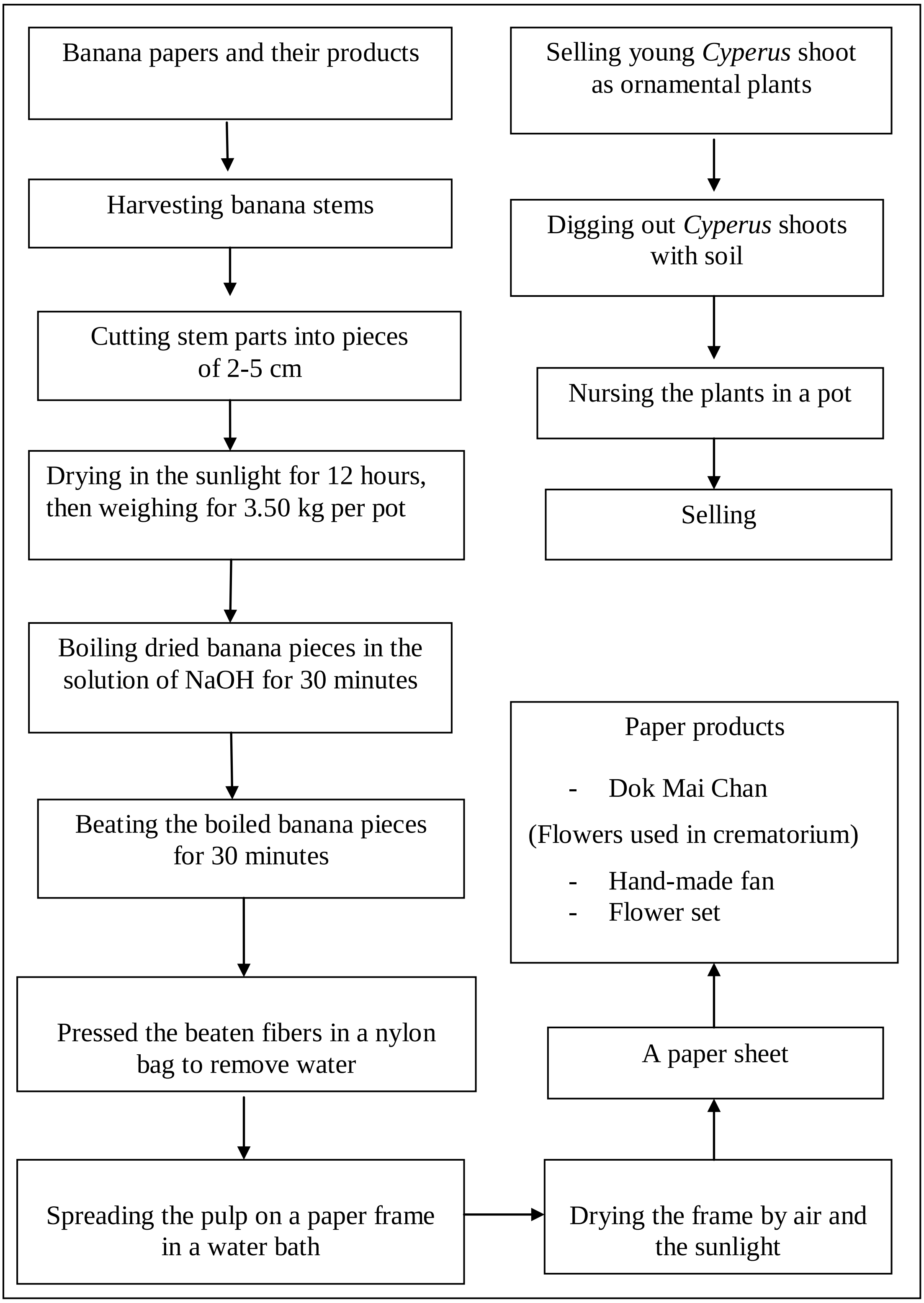
Analyses of water and plant biomass

- Taking water samples at every other day
- Analyses for total arsenic concentration by HGAAS

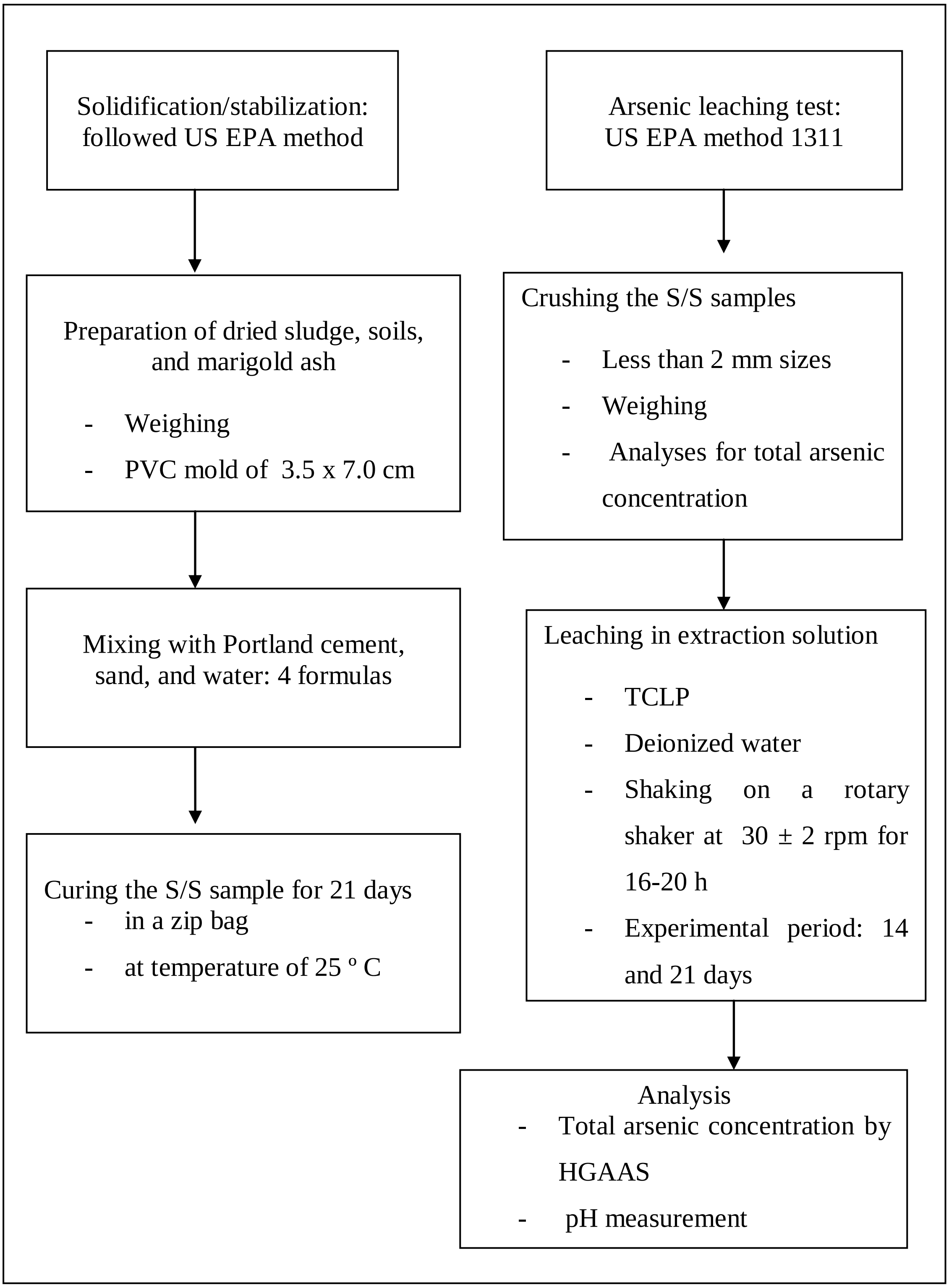
Experiment III : Management of the arsenic accumulated marigold biomass by burning



Experiment IV : Waste management by commercialization (as papers and paper products and ornamental plants)



Experiment V: Management of sediment sludge, soils, and marigold bottom ash by solidification/stabilization



4.2 Arsenic removal efficiency by constructed wetland and soil phytoremediation

4.2.1 Constructed wetland

The first unit of this experiment was the constructed wetland which was built as series of ponds: the sedimentation ponds 1-3, the *Cyperus* pond, and the *Colocasia esculenta*. The unit was located at the yard of Mr. Narong Sriwihok, 187 Moo 2, Ron Phibun District, Nakorn Si Thammarat Province since September, 2007. From Figure 4.1, the arsenic contaminated mountain tap water stored in pond 1 and was overflowed to pond 2 and 3, respectively, before being discharged to the biological treatment of the constructed wetland and the soil phytoremediation. The constructed wetland composed of 2 plant types, i.e., *Cyperus* spp. and *C. esculenta* (elephant ear), growing separately in the 2x7 meters concrete ponds. The plant growing media were as follows: small gravels at the lowest level, sand, and red earth with organic matters as surface soils. The efficiency of each wetland ponds on arsenic removal from water was compared.

4.2.1.1 Sedimentation Pond

The sedimentation pond was built at the size of 2x7x2 meters and divided into 3 small portions (Figure 4.2). The mountain tap water was injected into portion 1, overflowed to portion 2 and 3, respectively. The suspended particles in the water were sedimented to the bottom of the pond. The overflow from the last pond was discharged into the soil phytoremediation plots by mean of distribution pipelines.

Figure 4.2 Sedimentation ponds of series 1-3

4.2.1.2 *Cyperus* pond

Cyperus spp., young shoots, was planted in a pond at 30 cm apart. There were 40 groups; each group composed of 10-15 *Cyperus* plants. Altogether there were about 400-600 plants. The arsenic contaminated water was injected into the pond to the level of 15 cm above the soil. The phosphate fertilizer was added to the plants at 2 and 6 months after planting.

Figure 4.3 Constructed wetland pond with *Cyperus spp.*

4.2.1.3 *Colocasia esculenta* pond

Colocasia esculenta plants were grown for 7 rows and 14 plants for each row, total 98 plants, on May 22, 2007 (7 plants per m^2). After 6.5 months the plants were overgrown in the pond. Thus, half of the plants was harvested by cutting the plants at soil level and it took only 4 months (December 6, 2007-March 6, 2008) for these plants to grow to the same height as the others. The height of the plants was about 1.5 meters (Figure 4.4).

Figure 4.4 Constructed wetland pond with *Colocasia esculenta*

4.2.1.4 Operation of constructed wetland

Each day, the arsenic contaminated water from the sedimentation pond was injected into both of the constructed wetland ponds (*Cyperus* and *C. esculenta*) to the level of 15 cm above the soil in the morning and, then it drained out in the evening. The retention time was about 9 hours (08.00-17.00). The quantity of arsenic contaminated water of 885 L per pond per day was treated. The inlet and the outlet waters from both ponds were taken for arsenic analysis every 3 days during June-December 2007 and only once a week after that.

4.2.2 Soil phytoremediation

Soil phytoremediation plot composed of 120 cement tanks which were divided into 3 groups, 40 tanks for each group. The bottom of each cement tank (1-m diameter, 50-cm height) was filled with small gravels, sand, red earth and regular (black) soil at the top level. The plants used in this experiment were locally grown banana namely, “Namwa”, “Hom Kiau” and “Leb Mu Nang. Namwa banana (*Musa* ABB Group ‘Namwa’) is a hybrid, *Musa acuminata x balbisiana* Colla (ABB Group). Hom kiau banana is *Musa acuminata* Colla (AAA Group) while Leb Mu Nang banana is *Musa acuminata* Colla (AA Group). They were separately grown in each tank.

Six marigolds were also planted in the same cement tanks which grew banana (Figure 4.5). The irrigation system, with water dropping equipments, was set to distribute the arsenic contaminated water to every plant. The outlet pipe was attached at the bottom of the tank so water sample from each tank could be collected. The outlet pipe from each tank was joined together into the main outlet pipe of each group which was then finally combined to the main treated-water cement tanks of about 2 m height Marigold plants were harvested at 2 months aged but the banana plant was allowed to grow until fruiting (1 year).

Figure 4.5 Banana and marigolds in the cement tanks of soil phytoremediation

The arsenic contaminated mountain tap water in the sediment pond no.3 was pumped and irrigated to all 120 banana and marigold cement tanks at every 3 days during June-December 2007, but only once a week during January-April 2008. The samples from the outlets of each banana group and the combined tank were collected for determination of total arsenic concentration.

4.2.3 Soil properties used for constructed wetland and soil phytoremediation

Soil samples were collected from the constructed wetland and phytoremediation plots. They were sent to the Department of Soil Science, Kasetsart University for determination of soil properties.

4.2.4 Sample collection, preparation and analysis

4.2.4.1 Water sample

About 60 mL of water from inlet and outlet of both the *Cyperus* and the *C. esculenta* ponds were separately collected in each bottle. They were then acidified with 10% HNO_3 and stored at 4 ºC until analysis. Water sample was filtered by membrane filter Φ47 mm. Filtrate 1 mL was pipetted into a vial, added with 1 mL of 5% KI and 1 mL HCl (conc.), and then left the solution for 1 h at room temperature. After that, 1 mL 5% ascorbic acid was added and DI water was used to adjust the volume to 10 mL. The standard solutions of arsenic concentrations at 1, 3, 5, 10 µg L^{-1} were prepared in the same way as the water samples.

4.2.2.2 Plant sample

The harvesting times for the arsenic accumulated plants were as follows: *Cyperus* -345 d, *C. esculenta* -345 d, marigold -75 d, and banana -375 d. The plants were collected, washed with tap water and rinsed with deionized distilled water. Fresh plant samples were weighed, oven dried at 60 ºC for 2 d, homogenized by grounding with mortar and pestle, and screened through 2 mm mesh size sieve.

4.2.2.3 Reagents and standards

All chemicals were analytical grade. Milli Q water (18.2 MΏcm) was used for all solution preparations. The procedures for preparing arsenic standard solutions followed Jankong et al. (2007).

4.2.2.4 Determination of total arsenic concentration

After the plants were harvested, separated into parts, washed with tap water, rinsed with distilled water, and weighed for the fresh weight. Samples were oven-dried at 60 °C for 48 h. The dried sample was weighed, ground to a powder (mortar and pestle), and then sieved through 2 mm mesh size filter.

Samples were prepared for analysis using the dry ashing method (Aksorn and Visoottiviseth, 2004) A portion (10-50 mg) of the dry powder was accurately weighed (±0.01 mg) directly into a crucible and mixed with 1.50 mL of freshly prepared slurry from 51.0 g $Mg (NO_3)6H_2O$, 50.0 g MgO and 500 mL of deionized water. The mixture was dried overnight at 80 °C, and digested in a muffle furnace (200 °C for 1 h, 300 °C for 1 h, and 500 °C for 8 h). The residue was dissolved in 2.50 mL 6 M HCl and the solution mixed with 2.50 mL DI water.

Total arsenic concentrations in these solutions were determined by the hydride generation atomic absorption spectrophotometry (HG-AAS) using a Perkin-Elmer MHS-20 mercury/hydride system coupled to a Perkin-Elmer 2380 AAS. Arsenic concentrations in the samples were reported on a dry mass basis. The certified reference material MESS-3: marine sediment (National Research Council Canada, Ottawa, Canada) had been used for quality control. The analysis of MESS-3 (certified [As] = 21.2±1.1 mg kg^{-1}) returned [As] = 18.1±1.4 mg kg^{-1} (mean and standard deviation, n = 3).

4.3 Waste management of the arsenic accumulated plant biomass by degradation in freshwater

This study was performed with 3 types of arsenic accumulated plants biomass, i.e., marigold, banana, and elephant ear. Marigold biomass, 100 g, was immersed in 5.0 L tap water. For the elephant ear and banana, 50.0 g was separately immersed in 2.0 L tap water. There were 3 replicates for each experiment. Both degradation experiments were done outdoor (Figure 4.6). Water samples were collected for 9 times at the start until the end of the experiment to determine for arsenic concentration released into the water from the arsenic accumulated biomass. The duration of the experiments was 138 d for the marigold biomass, and 149 d for the elephant ear and banana biomass. When the water samples were collected, freshwater was added to each experimental container to replace the water lost by evaporation and sampling.

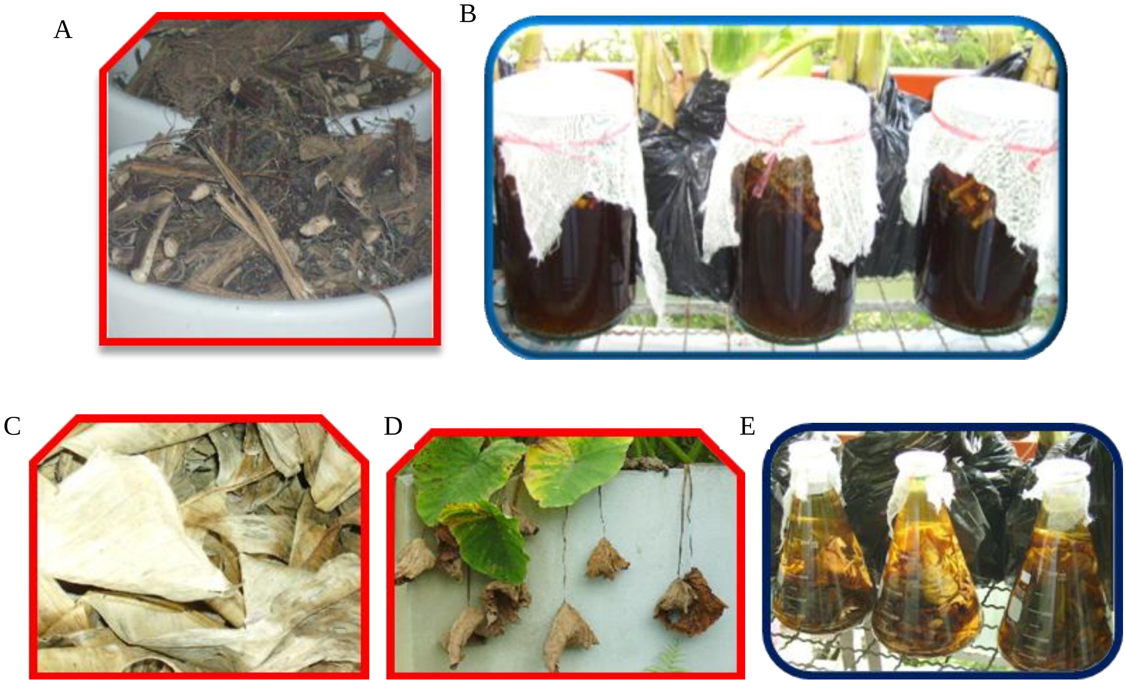


Figure 4.6 Degradation experiments of arsenic accumulated plants in freshwater (A) dried marigold (B) marigold immersed in freshwater (C) dried banana leave (D) dried *C. esculenta* leave (E) banana and *C. esculenta* immersed in freshwater

4.4 Management of the arsenic accumulated marigold biomass by burning

4.4.1 Drying

After the marigold flowers were cut for sale at the flower market, the whole plants, both above ground and underground parts, were collected. The soil was removed from the roots as much as possible before weighing the whole plants for wet weight. After that the plants were dried in the sunlight for 5 days, and then the dry weight was determined (Figure 4.7).

Figure 4.7 Marigold harvesting and drying in the sunlight (A) growing marigolds with banana (B) harvested marigold biomass (C) dried marigold plants

4.4.2 Burning

The dried biomass of arsenic accumulated marigolds was divided into two portions. The first portion was burnt at high temperature (> 500 ºC), while the other was burnt at low temperature (< 300 ºC).

4.4.2.1 High temperature burning

The marigold biomass was burnt at high temperature in the crematorium at Wat KireeKhan, Kao Kaew Sub-district, Lansaka District, Nakorn Si Thammarat Province (Figure 4.8). The bottom ash was collected, weighed, and determined for arsenic concentration as mentioned in Chintakovid et al. (2008).

Figure 4.8 Burning dried marigold biomass at high temperature and bottom ash (A) easily burnt of dried marigold (B) burning in crematorium (C) bottom ash

4.4.2.2 Low temperature burning

The low temperature burning was performed outdoor at the Environmental Research and Training Center, Department of Environmental Quality Promotion, Klong 5, Klong Luang District, Pathumthani Province, in order to collect arsenic dust. Method 7900, issue 2 (NIOSH Manual of Analytical Methods, 4th Edition, 8/15/94) was followed for dust collection of marigold waste burning. The flow rate of personal air pump (AirCheckSampler Model 224-PCXR8), with cellulose ester filter 0.8-µm pore size, 37-mm diameter in cassette filter holder was set at 2 L min^{-1} (Figure 4.9). The filters were stored in a desiccator for 2 h, then weighing to determine the weight before and then after dust collection. Dried marigold plants, 500 g, 500 g, and 382 g, were separately burnt outdoor in a chamber of burning equipment (2 stories of cement tanks, 100 cm diameter). Each burning took 20-30 min with the temperature around 300 ºC. Dried marigold biomass was sampling for arsenic determination before burning. After they were burnt, the ash was collected, weighed and analysed for arsenic.

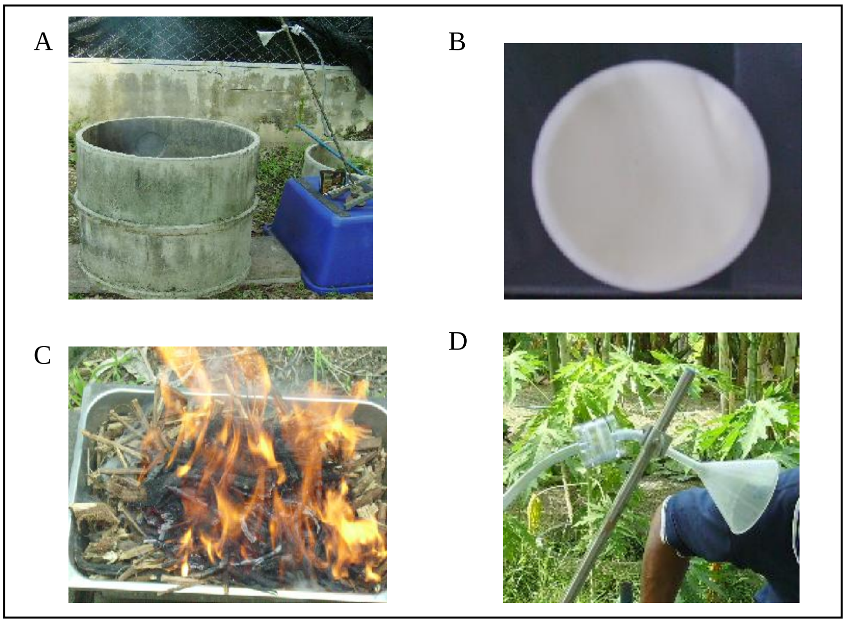


Figure 4.9 Fly ash of dried marigold biomass burning was detected by air sampler (A) Simple burning tanks (B) cellulose ester filter (C) low temperature burning (D) cassette filter holder

4.5 Waste management by utilization (papers and paper products and ornamental plants)

4.5.1 Commercialization of banana stems waste

There were 3 kinds of local banana varieties: Namwa, Hom Kiau, and Leb Mu Nang, these banana plants had grown, since April 12, 2007, separately in cement tanks of 120 plants to remove arsenic from water. Stems of Namwa banana were harvested at 4- and 10- month old for using as raw materials in the production of papers and paper products.

1. Banana stems were harvested, cut into small pieces and dried in the sunlight for 1-2 days, then collected and stored until being used as a raw material of paper production (Figure 4.10).

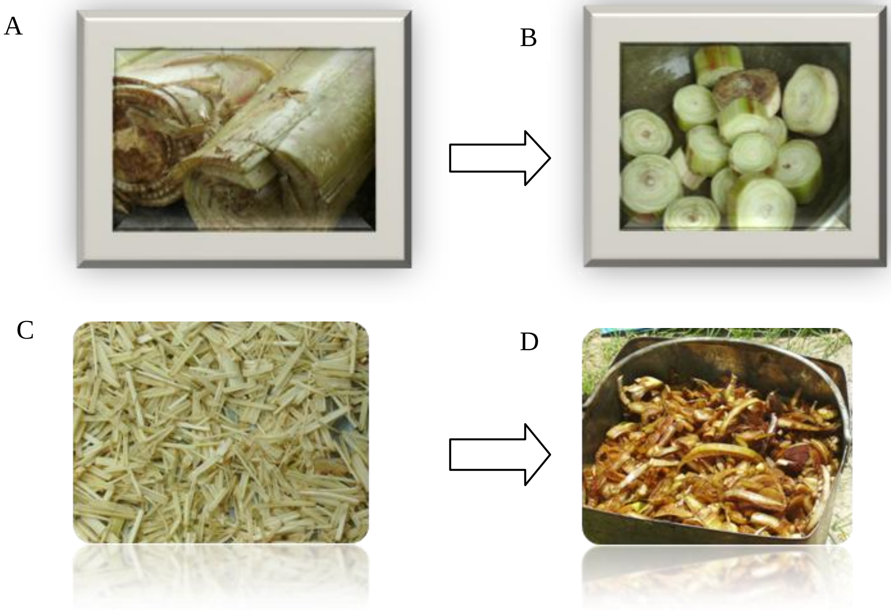


Figure 4.10 Preparation of banana stem pieces from pseudostems (A) wet banana stem waste (B) cutting into small parts (C) dried pieces of stem biomass (D) boiled small dried pieces in pot

2. Training local people at Ron Phibun Sub-district was organized during March 6-7, 2008 to train them to make banana papers and paper products such as hand-made flowers used in crematorium, fans, and flower sets (Figure 4.11). Some of

the banana (stem pieces, pulp) and paper were taken as samples, and determined for arsenic concentration.

Figure 4.11 Training and making papers and paper products (A) training at Ron Phibun Sub-district (B) leader of Ron Phibun Sub-district (C) explaining the program (D) participants attended the training (E) trainers showed the paper (F) participants handed on making papers (G) drying paper

4.5.2 Making papers and paper products

Banana paper production was performed and wastewater discharge from the production was collected and determined foe arsenic concentration. There were three experiments for banana paper production. The first making paper experiment was done at the Woranath KamPangPhet School, Maung District, KamPangPhet Province. The second experiment was performed at the CW and SP experiment site of Ron Phibun District, Nakorn Si Thammarat Province using arsenic contaminated water. The third experiment was performed with arsenic free water at the Faculty of Science, Mahidol University, Bangkok.

Experiment at the CW and SP site of Ron Phibun District, the Namwa banana stems were harvested, cut into pieces of 2x5 cm and dried in the sunlight for 1-2 d. Some dried banana pieces were sampled for use as pulp for making papers.

Dried banana pieces 3.5 kg and NaOH 0.30 kg were boiled in a boiling pot (24x25x27 cm) with 4 L arsenic contaminated mountain tap water (Figure 4.12). They were boiled in 2 pots until the banana pieces were loosely fibered for 35 min. Arsenic contaminated mountain tap water was sampling. Boiled banana fibers were dewatered by draining them in the nylon bag. Wastewater from boiling process was sampling and collected in the waste tank. All dewatered fibers were beaten in 143.6 L arsenic contaminated tap water in a chamber of beating machine (120x57x21 cm). Also additive agents of 30 g rosin (resin), 100 g natural alum, and 100 g used paper (produced from Aungthong) were beaten with the fibers for 30 min. Wastewater from the beating process was sampling before being discharged in the environment. Dewatering beaten fibers was pressed in the nylon bag until the fibers were quite dried. The still moist pulp 500 g was spread by hands of operator on the frame in a bath of 13.9 L tap water (66x105x2 cm). When it was uniformly spread, the paper frame was pull out of water. Wastewater from the washing process was collected for sampling. A frame of banana paper was leaned against each other to be dry in the sunlight for 2 d. Paper sampling was collected by mixing of 5 spots of paper for determination of arsenic.

At the Faculty of Science, Mahidol University, dried pieces of Namwa stem 30 g was boiled in the solution of 5 g NaOH and 900 ml As-free tap water for 2 h. Boiled pieces were beaten in 500 mL tap water for 2 min, then dewatering and weighing wet fibers (85.1 g). When it was uniformly spread, the paper frame was pull out of water (1,500 mL). Washing waste water was collected for sampling. A frame of banana paper was leaned against each other to dry in the sunlight for 2 days. Paper sampling was collected for arsenic determination.

Arsenic leached out from paper by wet hand contact: in order to test for arsenic released from paper when touching papers with wet hands, banana paper 1 g was weighed, cut into pieces of 3x3 cm and immersed in 25 mL tap water in a 50 mL beaker. The samples from the treatment were collected after 10 min. There were 3 replicates samples. The samples and tap water as control were measured for the amount of arsenic released.

Figure 4.12 Process of banana paper production at Ron Phibun Sub-district (A) dried banana stem pieces (B) boiled stem pieces (C) beaten stem pieces (D) dewatered pulp (E) spread pulp on a frame (F) dried banana paper

4.5.3 Selling *Cyperus* as ornamental plants

Cyperus plants were growing in the constructed wetland in order to remove arsenic from the arsenic contaminated water. The plants grew very fast and produced many young shoots. The young shoots were digging out from the constructed wetland and transferred into small pots for selling as ornamental plants (Figure 4.13). They could be harvested and utilized at the age of five months.

Figure 4.13 Utilization of *Cyperus* as ornamental plants

4.6 Waste management of sediment sludge, soils, and marigold bottom ash by solidification/stabilization

4.6.1 Collection and analysis of sediment sludge and soil samples

1. Soil samples were collected to determine the concentration of arsenic accumulated in the soil. There were 3 sites for soil collection, both constructed wetland ponds: *Cyperus* and *C. esculenta* ponds, and banana plot. At each site, 4 soil samples were collected at the level of 10-15 cm below the surface, then, they were combined as 1 sample. The collected soil samples were stored in the sealed containers in the lab refrigerator at 4 °C until being analyses.

The sediment samples from the 3 sedimentation ponds were also collected. The wet sediment was dried in the sunlight for 7 d (Figure 4.14). The dried sediment samples were weighed and then stored separately in each bottle.

2. A portion (125 g) of the samples from each site was placed in an oven at 60 °C for 24 h, homogenized by hand, passed through a 2 mm mesh size sieve to remove stones and plant materials and then ground (mortar/pestle) to a powder at 280-µm size.

3. Arsenic determination was done by the HG-AAS followed in 4.2.2.4.

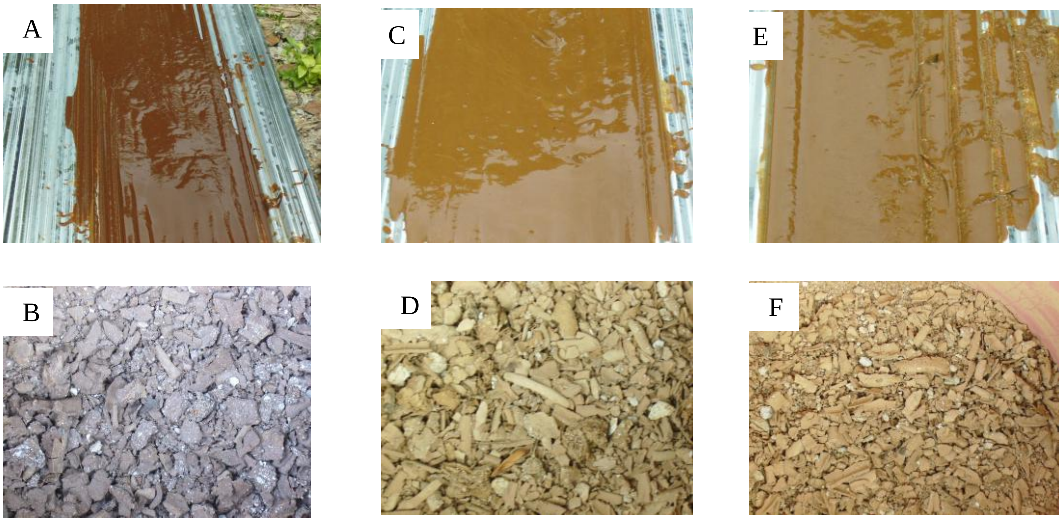


Figure 4.14 Wet and dried sediment sludge from the sedimentation ponds (A) wet sediment sludge no.1 (B) dried sediment sludge no.1 (C) wet sediment sludge no.2 (D) dried sediment sludge no.2 (E) wet sediment sludge no.3 (F) dried sediment sludge no.3

4.6.2 Marigold bottom ash

Since the bottom ash from the high temperature burning and sediment from the sedimentation ponds contained high arsenic concentration, they were further managed by the solidification/stabilization.

4.6.3 Solidification and stabilization (S/S)

The S/S method used in this study was investigated with 4 formulas. The ratio of solid materials and water used in the S/S was 1:0.42. The solid materials used as control in the study were cement mixed with sand at the ratio 1:3. The solid materials were modified (as treatments) by the 4 formulas as follows:

(1) Control: Cement-sand mixture (CSM) 100%

(2) Treatment: CSM 75% + sediment sludge (SS) 25%

(3) Treatment: CSM 75% + marigold ash (MA) 25%

(4) Treatment: CSM 50% + MA 25% + SS 25%

After the solid materials were mixed with water at the ratio (1:0.42), they were then harden in the blocks size 3.5x7 cm^2 and cured at room temperature (25 ^oC) in zipper bags for 21 d (Figure 4.15). At the curing time of 14 and 21 d, these blocks were then subjected for the leaching test by the Toxicity Characteristic Leaching Procedure (TCLP) method followed the Method 1311 (U.S.EPA, 1992) having details in 4.6.4.1. The leaching experiment was also performed using deionized water to compare with the acetic acid leachant used in the TCLP method.

Figure 4.15 Solidification/stabilization of 4 formulas mixed with cement, ash, and sludge of arsenic contaminated wastes

Arsenic concentration was determined for the control (untreated) and treatment samples of sediment and bottom ash by digesting 1 g of the materials with 1 mL concentrated HNO_3 on a hot plate, then 30% H_2O_2 was added and heat until the clear solution was obtained. After cooling, the digested samples were diluted to 100 mL with deionized water for analysis of total arsenic concentration by the hydride generation atomic absorption spectrometry (HGAAS).

4.6.4 Arsenic leaching tests

Two leaching test methods were used to evaluate the arsenic concentration leached out from the untreated and the treated (S/S) samples (Figure 4.16).

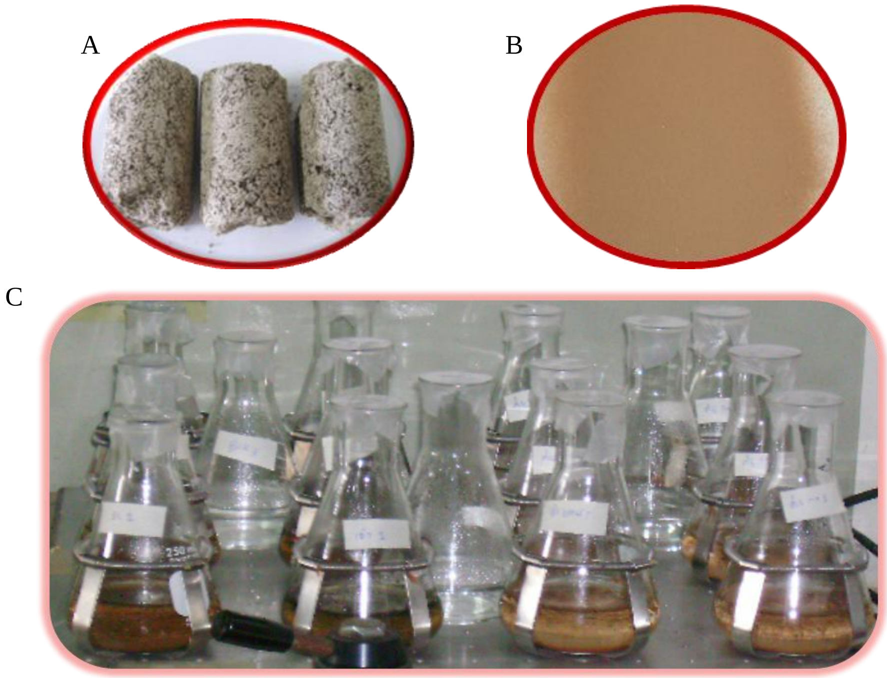


Figure 4.16 Preparation of treated samples and performing arsenic leaching tests (A) S/S treated samples (B) powder of the S/S (C) shaking for arsenic leaching

4.6.4.1 Toxicity Characteristic Leaching Procedure (TCLP): U.S. EPA Method 1311

1. 5 g of sediment sludge with particle size less than 5 mm was extracted with liquid (water or acetic acid) at the ratio (Liquid:Solid) of 1:20.
2. A 0.10 M acetic acid solution (pH 2.88) was used to extract cement-treated samples due to the high alkalinity of the wastes.
3. An extraction solution, 0.10 M acetic acid and 0.0643 M NaOH with a pH of 4.93, was used for the untreated sediment sample.
4. The solid and leachate suspension was placed in a capped polypropylene bottle and tumbled at 30 rpm for 18 h.
5. After the extraction, the final pH of the leachate was measured, and the liquid was separated by filtration through a 0.45 µm membrane fiber filter. The soluble arsenic concentration in the filtrate was analyzed with the AAS.

4.6.4.2 Extraction fluid

1. Extraction fluid for untreated samples: Add 5.70 mL glacial acetic acid to 500 mL of reagent water, add 64.3 mL of 1N NaOH, and dilute to a volume of 1000 mL. When correctly prepared at room temperature, the pH of this fluid will be 4.93±0.05.

2. Extraction fluid for treated samples: Dilute 5.70 mL glacial acetic acid with reagent water to a volume of 1000 mL. When correctly prepared at room temperature, the pH of this fluid will be 2.88 ± 0.05.

4.6.4.3 Deionized water extraction

This method simulated scenarios where a waste was in contact with natural rainwater of very low pH buffer capacity. The extraction procedures were the same as in the TCLP except that deionized (DI) water was used as leachant. Both TCLP and DI water extractions were single point tests without pH adjustment (Singh and Pant, 2006). Leachates were collected after the experiment of curing time at 14 and 21 d.

4.7 Statistical Tests

The program of SPSS 11.5 for Windows was used to test the significances of arsenic contaminated wastewater from the processes of paper production compared between two types of water used. As well as, it was performed to test the differences between S/S formulas, leaching methods, and curing days of arsenic leaching from the TCLP and DIW. Two-WAY Analysis of Variance (2-WAY ANOVA) was calculated to test the hypothesis of more than 2 variables of independent and dependent factors.

For paper production, independent variables were characteristics of water used (free and contaminated arsenic) and the processes of wastewater. Dependent variable was the arsenic concentration from the independents. Arsenic leaching from the S/S, arsenic concentration was dependent variable and independent variables were 4 formulas, 2 methods, and 2 curing times. If the significant value (P-value) is less than 0.05, it is rejected the H_0 and comparisons are checked between and among the variables.

CHAPTER V

RESULTS

5.1 Soil properties used for constructed wetland and soil phytoremediation

Soil properties such as pH, compositions, texture, electric conductivity (EC), iron, arsenic, organic matter (OM), calcium (Ca), magnesium (Mg), phosphorus (P), and potassium (K), were studied. It was found that soil pH (5.2-6.3) and soil texture was suitable for growing plants, i.e., *Cyperus*, *C. esculenta,* in the constructed wetland and bananas and marigolds in soil phytoremediation. Iron in the CW soil was higher than the SP soil. Arsenic concentration in both types of soil was lower than 3.90 mg kg^{-1}, the standard guideline for arsenic in agricultural soil (Ministry of Natural Resources and Environment, 2004). OM, P, K were very high in soil used for Namwa that was very good to increase high plant biomass. P was very high in *Cyperus* soil, while K was very high in *C. esculenta* soil. For all soils, calcium was high and magnesium was medium (Table 5.1).

Table 5.1 Basic soil properties in constructed wetland and soil phytoremediation

Soil property	***Cyperus* soil**	***C. esculenta* soil**	**Namwa soil**
pH	5.6	5.2	6.3
% sand	53	51	63
% silt	11	9	5
% clay	36	40	32
Texture	SiltClay	SiltClay	SiltClayLoam
EC (dS/m)	0.29	0.42	2.15
Fe (mg kg^{-1})	220	188	27.4
As (mg kg^{-1})	0.07	0.05	0.15
% Organic matter	2.1 (Medium)	2.1 (Medium)	9.7 (Very High)
Phosphorus (ppm)	56 (Very High)	16 (Medium)	126 (Very High)
Potassium (ppm)	90 (Medium)	180 (Very High)	800 (Very High)
Calcium (ppm)	960 (High)	840 (High)	2,320 (High)
Magnesium (ppm)	90 (M)	80 (M)	44 (M)

5.2 Arsenic removal efficiency by constructed wetland and soil phytoremediation

Arsenic contaminated mountain tap water has been provided for people in Ron Phibun District. The attempt to reduce arsenic in tap water was performed in this study. The experiment consisted of a series of three sedimentation ponds, two constructed wetland ponds, and the soil phytoremediation plots. Arsenic concentration in the tap water was in the range of 0.09-0.45 mg L^{-1} which was about 45 times over the WHO standard of 0.01 mg L^{-1} (World Health Organization, 2001). Notwithstanding, the concentration of arsenic in the water was increased after it got into the sedimentation pond.

5.2.1 Constructed wetland system

The *Cyperus* shoots were planted in 2 x 7 m^2. There were 40 groups of the average 12 plants/group. For *C. esculenta*, there were 98 plants of 14 plants x 5 rows. Both types of wetland plants, *Cyperus* and *C. esculenta*, showed similar efficiency in removing arsenic in the influent water (0.36 mg L^{-1}) to 0.08 mg L^{-1} in the effluent around 77-79% (Table 5.2). The quantity of the mountain tap water operated by the wetland system was about 885 L per day per pond. In the other word, there was 1,770 L per day of water could be treated by the wetland system. At the end of experiment, the average number of *Cyperus* plants per group was increased from about 12 to 114 of the 40 groups. Therefore, the 0.19 L per plant per day of arsenic contaminated water was treated by *Cyperus*. While, it was 9 L per plant per day for *C. esculenta*. After 345 d, all of the tested plants were harvested. This plant biomass should be treated as solid waste.

Table 5.2 Arsenic removal efficiency of constructed wetland system

Water source	**As concentration (mg L^{-1})**		**Removal efficiency (%)**
	Influent	**Effluent**	
Cyperus pond	0.36±0.07	0.08±0.02	77.0
C. esculenta pond	0.36±0.07	0.08±0.01	78.7

The result of the mass balance (Table 5.3) for the CW plants showed that plant growth (biomass) of *Cyperus* (1,597 g m^{-2} d^{-1}) was better than *C. esculenta* (20 g m^{-2} d^{-1}). Similary, the uptake of arsenic by *Cyperus* was 4.41 (g d^{-1}) was higher than the *C.* esculenta (0.17 g d^{-1}). The height stem and root of *Cyperus* was in the range of 190-200 cm and 20-28 cm, respectively (Figure 5.1). The average dried weight biomass of *Cyperus* was 1.69 kg per plant. The amount of plant growth per group was in the range of 105-125 plants counted at the harvesting day at 345 d. For *C. esculenta*, the height stem and root were 135-150 cm and 10-20 cm, respectively.

The dried weight biomass of *C. esculenta* was 1 kg per plant. Percentage of arsenic removal by the wetland system was in the range of 77-79% (Table 5.2 and 5.3).

Table 5.3 Mass balance for the constructed wetland plants

Factors	**Plant species**	
	Cyperus	***C. esculenta***
Plant growth (g m^{-2} d^{-1})	1,597	20.3
Plant uptake (g d^{-1})	4.41	0.17
Accumulated soil (g d^{-1})	15.2	18.4
Influent water (g d^{-1})	0.92	0.92
Effluent water (g d^{-1})	0.21	0.20
Arsenic removal (%)	77.0	78.7

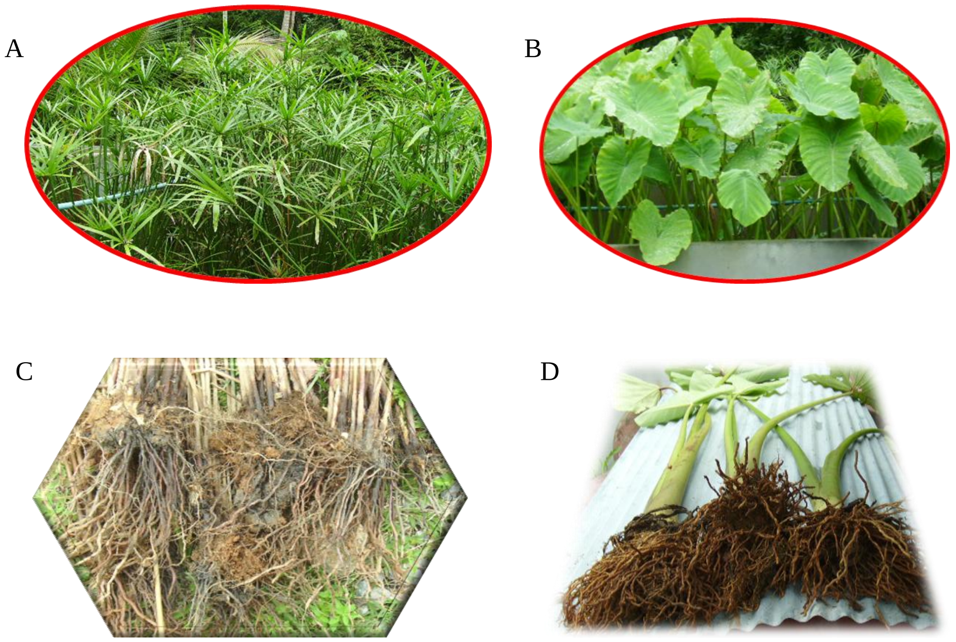


Figure 5.1 Plant growths in the CW ponds of *Cyperus* and *C. esculenta*

(A) *Cyperus* grew for 375 d (B) growing of *C. esculenta* (C) roots of *Cyperus* (D) roots of *C. esculenta*

5.2.2 Soil phytoremediation

There were two experiments for soil phytoremdiation as follows:

Experiment 1: Plant system composed of banana and marigold. Each concrete tank was used to grow 1 banana plant and 6 marigold plants. There were 60 tanks which were divided to 20 tanks for each type of banana (Figure 5.2).

Experiment 2: Plant system composed of only banana. Each tank was used for growing only 1 banana plant. There were 60 tanks; 20 tanks for banana variety, i.e., Namwa, Hom Kiau and Leb Mu Nang.

All of the test plants were irrigated with arsenic containing water at 0.33 mg L^{-1}. The effluents from Namwa, Hom Kiau, and Leb Mu Nang, were 0.14, 0.16, 0.11 mg L^{-1}, respectively. The average efficiency of the banana plants in arsenic removal by the experiment 1 was 58%. The experiment 2 gave was better results; they were 0.13, 0.05, and 0.09 mg L^{-1} for Namwa, Hom Kiau, and Leb Mu Nang, respectively. The ability of plants to remove arsenic in the experiment 2 was 61-85%. The arsenic concentration in the main outlet waters had been collected in the three combined tanks; it was only 0.05 mg L^{-1}, or 85% for arsenic removal efficiency (Table 5.4).

Figure 5.2 Experimental plots of soil phytoremediation

The total quantity of arsenic contaminated water used in irrigating to all plants in the SP was 895 L d^{-1} for 90 d, or 80,550 L. There were 120 banana plants and 720 marigold plants used to uptake arsenic from the water. The areas of the SP experiment were 120 m^2. The duration of the SP experiment was 375 days. Each plant of marigold and banana had treated arsenic containing water of 1.24 and 7.46 L per day, respectively.

Table 5.4 Arsenic removal efficiency of soil phytoremediation

Water source	**As concentration (mg L^{-1})**		**Removal efficiency (%)**
	Influent	**Effluent**	
Experiment 1 (with marigold)			
Namwa	0.33±0.03	0.14±0.07	57.6
Hom Kiau	0.33±0.03	0.16±0.02	51.5
Leb Mu Nang	0.33±0.03	0.11±0.01	66.7
Average	0.33±0.03	0.14±0.03	57.6
Experiment 2 (without marigold)			
Namwa	0.33±0.03	0.13±0.03	60.6
Hom Kiau	0.33±0.03	0.05±0.02	84.9
Leb Mu Nang	0.33±0.03	0.09±0.07	72.7
Average	0.33±0.03	0.09±0.04	72.7
Combined effluent		0.05±0.01	84.9

The mass balance of soil phytoremediation (Table 5.4) shown that the biomass and arsenic uptake of marigold plants was 4 g m^{-2} d^{-1} and 0.02 g d^{-1}, respectively, or about 5.3% for plant uptake (Figure 5.3). The dried plant growth was 0.05 kg per plant. The efficiency of marigold in removing arsenic from the influent was 59%.

Figure 5.3 Plant biomass of marigolds shown for their roots and shoots
(A) Marigold grew in the tank with banana (B) roots of marigold (C) whole plant of marigold harvested

The plant growth for Namwa, Hom Kiau, and Leb Mu Nang was 60.5, 46.9, and 18.7 g m^{-2} d^{-1}, respectively. Plant uptake was in the range of 0.34-0.61 g d^{-1}, or 43-77% (Table 5.5). The plant uptake for Namwa and Leb Mu Nang was similar at 76-77%. At the end of experiment (375 days), the dried weight of Namwa, Hom Kiau, and Leb Mu Nang was 22.7, 17.6, and 7.0 kg per plant, respectively. Efficiency of arsenic removal from the effluent for Namwa, Hom Kiau, and Leb Mu Nang was 62%, 85%, and 74%, respectively.

Figure 5.4 Plant growth of banana and the plant parts in 375 days

(A) Bearing fruits of banana (B) roots of banana (C) Namwa plant parts

Table 5.5 Mass balance for the soil phytoremediation plants

Factors	**Plant species**			
	Marigold	**Namwa**	**Hom kiau**	**Leb Mu Nang**
Plant growth (g m^{-2} d^{-1})	4.00	60.5	46.9	18.7
Plant uptake (g d^{-1})	0.02	0.60	0.34	0.61
Plant uptake (%)	5.29	75.9	42.9	76.5
Accumulated soil (g d^{-1})	323	44.2	32.1	35.9
Influent water (g d^{-1})	3.98	0.80	0.80	0.80
Effluent water (g d^{-1})	1.65	0.30	0.12	0.20
Arsenic removal (%)	58.5	62.1	84.6	74.3

All outlets stored in the combined tanks (Figure 5.5) were less than the MCL of 0.25 mg L^{-1} (Ministry of Science Technology and Environment, 1996). So, they have low potential to harm people and the environment after releasing them to the natural reservoir.

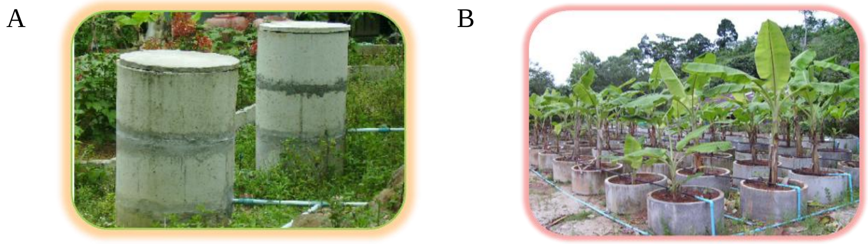


Figure 5.5 Storage tanks of all effluents from marigold and banana tanks

(A) Storage tanks of all effluents (B) irrigation pipeline connected to the collected-treated water

5.2.3 Arsenic accumulated plants

Six types of plants were used in the experiment, i.e., 2 types for the constructed wetland and 4 types for the soil phytoremediation. Average arsenic concentrations per plant were determined. At the start of the experiment, they were 6, 6, 8, 4, 0.7, and 3 mg kg^{-1} for *Cyperus*, *C. esculenta*, marigold, Namwa, Hom kiau, and Leb Mu Nang, respectively. When the experiments ended, they were 198, 619, 24, 24, 19, and 82 mg kg^{-1}, respectively (Table 5.6).

Table 5.6 Arsenic concentration in plants of the constructed wetland and soil phytoremediation during the experiments

Plant	**Arsenic concentration (mg kg^{-1})**	
	2007	**2008**
Cyperus spp.	5.48±1.61	198±58.1
C. esculenta	6.31±0.77	619±38.4
Marigold	8.06±0.78	23.9±8.82
Namwa	4.44±0.44	23.9±12.9
Hom Kiau	0.68±0.59	18.6±7.17
Leb Mu Nang	2.66±0.25	82.4±36.3

Arsenic concentrations in all 6 plant types were found higher in the roots than in the shoot (Figure 5.6 and 5.7). The arsenic concentrations in the roots were 190, 602, 19, 16, 14, and 78 mg kg^{-1} for *Cyperus*, *C. esculenta*, marigold, Namwa, Hom Kiau, and Leb Mu Nang, respectively (Figure 5.6). The range of percentage for arsenic concentration in the roots was 74-98% (Figure 5.7). The banana plants had high biomass, due to their bulbs and stems (Figure 5.1, 5.3, and 5.4). The edible parts of bananas, i.e., fruit and flower, the arsenic concentration was lower than the Thai standard of 2 mg kg^{-1} (Ministry of Public Health, 2003). Thus, they were deemed safe to consume.

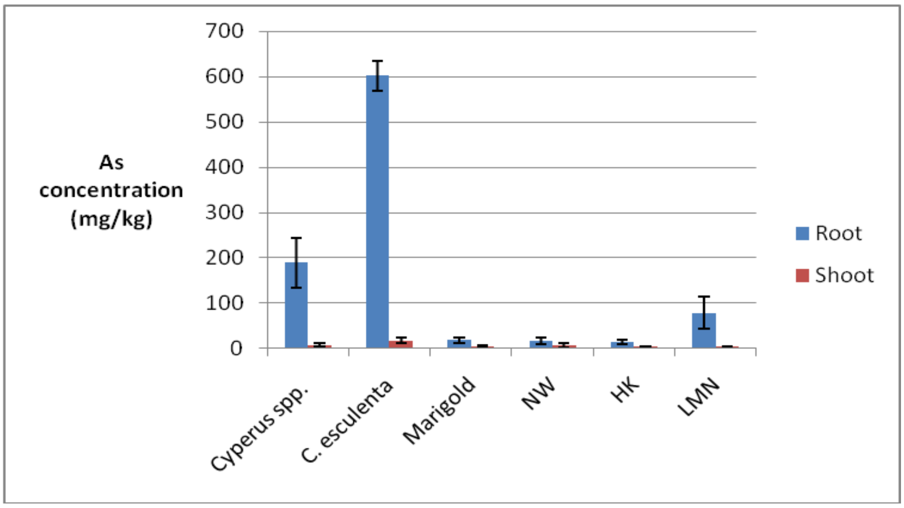


Figure 5.6 Arsenic concentrations in the plant roots and shoots

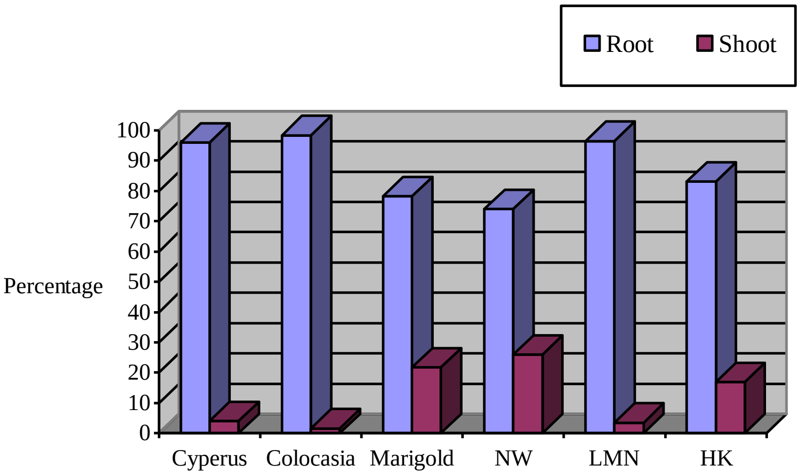


Figure 5.7 Percentage of arsenic accumulated in plant roots and shoots

Table 5.7 Arsenic concentration in plant parts of the constructed wetland and soil phytoremediation

	Arsenic concentration (mg kg^{-1}) in plant					
Plant parts	***Cyperus* spp.**	***C. esculenta***	**Marigold**	**NW**	**HK**	**LMN**
Root	190 ±55.0	602 ±32.1	18.7 ±6.03	16.3 ±7.72	14.3 ±5.18	78.4 ±35.1
Bulb	-	7.40 ±3.35	-	1.36 ±0.55	1.20 ±0.70	1.10 ±0.18
Stem	2.98 ±1.46	5.34 ±1.22	0.81 ±0.67	4.07 ±3.45	1.72 ±0.28	1.36 ±0.37
Leave	5.16 ±1.74	4.63 ±1.74	4.37 ±2.12	1.82 ±1.00	1.32 ±0.90	1.36 ±0.60
Fruit	-	-	-	0.13 ±0.02	0.11 ±0.01	0.18 ±0.004
Flower	-	-	-	0.21 ±0.18	-	-

5.2.4 Arsenic concentration and content in plants

Average plant growth, arsenic concentration, and arsenic content per plant were studied for the wetland system (Table 5.8). During 345 days of the CW performance, *Cyperus* had been growing with higher biomass increase (86%) than the *C. esculenta* (68%). Comparison between the two wetland plant types, the arsenic concentration of *C. esculenta* was 3 times higher; whilst, the arsenic content was 2 times higher than those of the *Cyperus.*

The plants of the SP plots, i.e., marigold, Namwa, Hom Kiau, and Leb Mu Nang, were shown for the dried weight biomass, arsenic concentration and content during the growing period of 75 days for marigold and 375 days for the three bananas. The biomass increase of marigold was 60% (Table 5.8), while the percent arsenic concentration and content increased was 66 and 84, respectively. The increased of the biomass of the 3 banana plants was 89-95% for the growth period of 375 d. The Namwa banana had the highest plant biomass (23 kg per plant per year), while the Leb Mu Nang had the lowest (7 kg per plant per year). The arsenic concentration was 18-82 mg kg^{-1} for marigold and the bananas. The highest arsenic concentration was found in the Leb Mu Nang. The Hom Kiau was the lowest. The increase of arsenic concentration was in the range of 66-97%. The increase of arsenic content was in the range of 84-100%. The Namwa arsenic content per plant (566 mg) was similar with the Leb Mu Nang (571 mg).

Table 5.8 Plant biomass, arsenic concentration, and arsenic content of the CW and SP systems

Plant/Year	**DW biomass** [a] **(kg)**	**As concentration** [b] **(mg kg^{-1})**	**As content** [c] **(mg)**
***Cyperus* spp.**			
May, 2007	0.24	5.48±1.61	1.31±0.39
May, 2008	1.69	198±4.28	335±7.25
Increase (%)	85.8	97.2	99.6
C. esculenta			
May, 2007	0.32	6.31±0.77	2.02±0.24
May, 2008	1.00	619±0.77	619±0.77
Increase (%)	68.0	99.0	99.7
Marigold			
May, 2007	0.02	8.06±0.78	0.16±0.02
July, 2007	0.05	23.9±5.63	1.02±0.28
Increase (%)	60.0	66.3	84.3
Namwa			
May, 2007	1.21	4.44±0.44	5.36±0.53
May, 2008	22.7	25.0±0.43	566±9.75
Increase (%)	94.7	82.2	99.1
Hom Kiau			
May, 2007	1.95	0.68±0.59	1.32±1.15
May, 2008	17.6	18.2±0.49	320±8.61
Increase (%)	88.9	96.3	99.6
Leb Mu Nang			
May, 2007	0.56	2.66±0.25	1.49±0.14
May, 2008	7.00	81.5±1.98	571±13.9
Increase (%)	92	96.7	99.7

[a] Average dried weight per plant

[b] Average arsenic concentration per plant

[c] Average arsenic content per plant

5.3 Waste management of the arsenic accumulated plant biomass by degradation in freshwater

Arsenic accumulated plants chosen for degradation in freshwater were whole plants of marigolds, petioles and leaves of *C. esculenta,* and three types of bananas.

5.3.1 Arsenic released from marigolds in freshwater

Marigolds were grown in the same soils of three types of bananas. Six marigold plants and one banana plant in a tank, there were 720 marigolds had removed arsenic from contaminated tap water. At the exposure times of 38 and 75 days, marigolds could accumulate arsenic at 24 and 44 mg kg^{-1}, respectively. Only 38 days, arsenic accumulated by marigolds was increased at 84%; while arsenic contained in soil increased only 13% (Table 5.9).

Table 5.9 Arsenic accumulation in the marigold roots and shoots

Exposure time (d)	**Arsenic concentration (mg kg^{-1})**			
	Soil [a]	**Marigold**		
		Root	**Shoot**	**Total**
38	74.2 ±7.12	18.7 ±1.29	5.18 ±2.97	23.9 ±0.69
75	84.0 ±14.7	34.1 ±2.45	9.74 ±4.87	43.8 ±7.33
As increase (%)	13.2	82.6	88.1	83.8
As accumulation (%)	-	77.8	22.2	100

[a] Soil pH was in the range of 7.3-7.5.

The whole plants of marigolds could be taken out of the soil easily at harvested time. They were then managed as solid waste because more than 78% of arsenic accumulated in the roots. The management method of marigold was attempted by (1) degradation in freshwater and (2) burning at both low and high temperature. For the degradation in freshwater, 0.10 kg dried marigold plants containing 8.95 mg kg^{-1} of arsenic were immersed in 5 L tap water. The arsenic concentration was released from the marigold biomass into the water during 138 days was in the range of 0.04-0.10 mg L^{-1} (Figure 5.8), or an average of 0.07 mg L^{-1}. The arsenic leached out at the day 5 was the highest; then it came down. After d26 the concentration of arsenic in the water gradually went up again until the end of the experiment; however, it was still lower than that at d5. Notwithstanding, the arsenic concentration leached into the water from the degraded marigold biomass was much lower than the standard guidelines of arsenic in wastewater of 0.25 mg L^{-1}. Thus, it could be released into the natural environment safely.

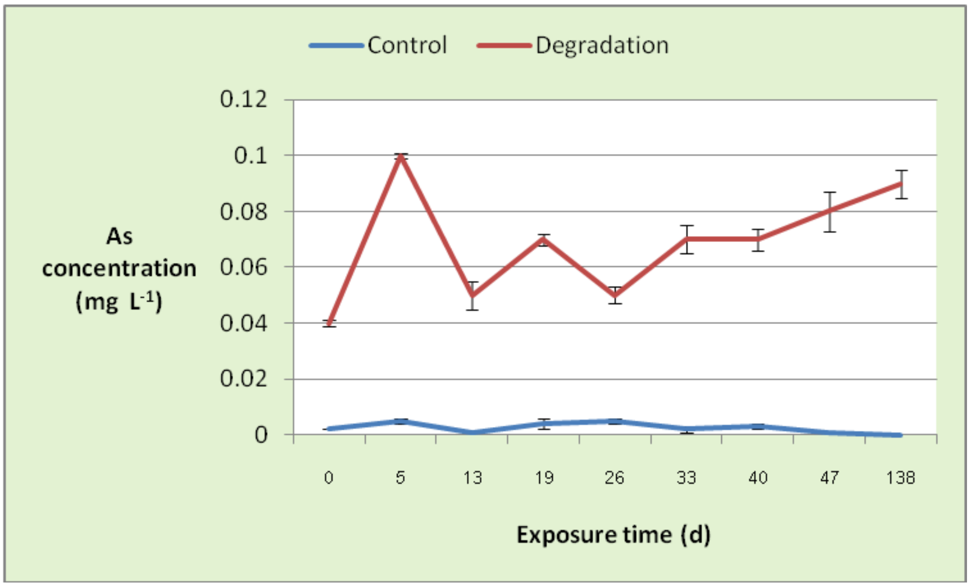


Figure 5.8 Degradation of arsenic accumulated marigold plants in freshwater

At the end of the experiment, the marigold biomass was not completely degraded. There was undegraded biomass left in the tank (Figure 5.9). Since the non-degraded biomass contained arsenic only at 14.4 mg Kg^{-1}, they could not be used as fertilizers for improving quality of soil.

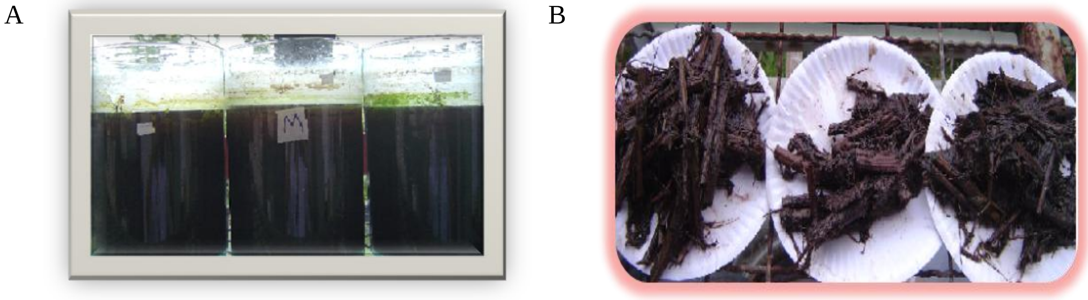


Figure 5.9 Degradation experiment of marigold during 138 days

(A) marigold biomass immersed in the jars (B) undegraded parts marigold

5.3.2 Arsenic released from banana and *Colocasia* leaves

Leaves of each banana type and *C. esculenta* were weighed for 0.05 kg and immersed to degrade in 2 L tap water. The water in the degradation jars was collected separately from each tank for 9 times to determine for the amount of arsenic leached out from the leaves during the 149 days of the experiment (Figure 5.10). At the start of the experiment, the average arsenic concentrations in the leaves of *C. esculenta*, Namwa, Leb Mu Nang, and HomKiau were 1.80, 1.24, 0.91, and 1.22, mg kg^{-1}. The arsenic concentration leached out into the water was in the range of 0.01-0.09 mg L^{-1} for *C. esculenta*, 0.007-0.07 mg L^{-1} for Namwa, 0.003-0.02 mg L^{-1} for Leb Mu Nang, and 0.009-0.03 mg L^{-1} for Hom Kiau. The highest arsenic concentration leached out from the leaves was at d 9, and then it gradually declined until the end of the experiment, d 149. This pattern was true for all plants tested in this experiment. Similar to marigold, the leaves in every tank was not completely degraded. They were some residues left in the tank at the end of the experiment. For *C. esculenta,* the leaf tissues had less fibers, thus, they were better degraded than the banana leaves (Figure 5.11). On the other hand, the high fiber content of banana made it suitable to use in the next experiment.

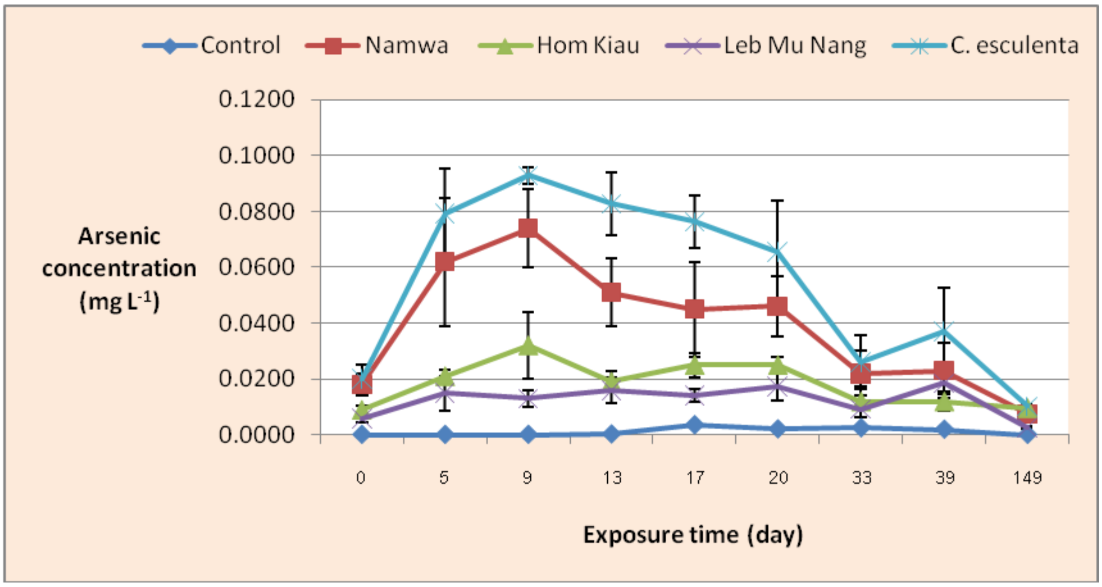


Figure 5.10 *C. esculenta* and banana leaves degraded in freshwater during 149 days

The arsenic concentrations in degraded biomass after the 149 days experiment were 4.51, 2.37, 1.63, and 1.25 mg kg^{-1} for *C. esculenta*, Namwa, Hom Kiau, and Leb Mu Nang, respectively.

Figure 5.11 Degradation experiment of *C. esculenta* and banana leaves

(A) leave of banana degraded in flasks (B) undegraded banana leave

(C) undegraded *C. esculenta* leave

Considering the MCL under the Thai regulation, arsenic contaminated leachates from both experiments had lower arsenic concentration than the regulation guideline of 0.25 mg L^{-1} (Ministry of Science Technology and Environment, 1996). Therefore, we could discard the leachates and the residues of the arsenic accumulated marigolds, *C. esculenta*, Namwa, Leb Mu Nang, and Hom Kiau bananas directly into the environment as they were classified as non-hazardous solid wastes.

5.4 Management of the arsenic accumulated marigold biomass by burning

At d 75, all of the whole marigold plants were harvested, weighed, and dried in the sunlight for 5 days. The wet weight of marigolds was 138 kg; the dried weight was 56.5 kg or 59% weight decreased by drying in the sunlight (Table 5.10).

5.4.1 High temperature burning

The dried arsenic-accumulated marigolds were burnt in the crematorium at Wat Keerikhan, KaoKaew Sub-district, Lansaka District, Nakorn Si Thammarat Province. The crematorium was operated at the temperature >500 °C to burn the 52.7 kg of dried marigolds for 39 minutes. The bottom ash was collected; the weight of the ash was 4.20 kg, or weight decreased at 92%. Arsenic concentrations of marigold biomass and the ash were 37.8 and 298 mg kg^{-1}, respectively. From the calculation, 37% of arsenic content was lost (Table 5.11). Unfortunately, we did not collect fly ash and determined for arsenic content.

Table 5.10 Weight reduction of marigold biomass by drying and burning

Biomass reduction	**Biomass weight (kg)**	**Ash weight (kg)**	**Reduction (%)**
Drying			
Day 0	138	-	-
Day 5	56.5	-	59.1
Burning			
High temperature	52.7	4.20	92.0
Low temperature	1.38	0.25	81.9

5.4.2 Low temperature burning

Another 1.38 kg of the marigold biomass was burnt at the low temperature (<300 ºC) to simulate the outdoor burning by the local people. The air sampler was set for 15 min to collect arsenic in the fly ash. The bottom ash weighed 0.25 kg or weight reduced at 82%. The bottom ash contained arsenic at 33.7 mg kg^{-1} but we could not detect arsenic in the dust from the burning. The lost of arsenic content (83%) from the low temperature burning was higher than the high temperature burning (37.3%) (Table 5.11).

Table 5.11 Arsenic concentration and content in biomass and ash after burning at two temperature levels

Burning	**High temperature**	**Low temperature**
Arsenic concentration (mg kg^{-1})		
Biomass	37.8	35.0
Ash	298	33.7
Arsenic dust	-	ND
Arsenic content (mg)		
Biomass	1,994	48.2
Ash	1,249	8.42
Loss	744	39.8
% Loss	37.3	82.6

5.5 Utilization as papers and paper products and ornamental plants

5.5.1 Utilization of banana stems biomass

Since Namwa banana was a big plant, it was difficult to discard the arsenic accumulated stem. It would be a great advantage if we could manage these Namwa plant wastes by utilization. The banana stem has high fiber content and could be used for producing papers and its products. It was reported by Tock et al. (2010) that they could produce 48–51 % yield of unbleached banana pulp.

5.5.1.1 Banana paper production

Arsenic accumulated banana plants was determined for arsenic concentration. It was 23.9 mg kg^{-1} for total arsenic and 4.07 mg kg^{-1} for stem parts. Since a Namwa stem weighed about 16-19 kg, thus, there were a lot of arsenic accumulated plant wastes that needed to be managed. Utilization is a useful and low cost method for disposal as well as income generated. The banana papers were made from the arsenic accumulated banana stem obtained from the experimental plot. The processes of making banana papers were performed locally, at Ron Phibun District, by a group of locally trained people. The banana pulps from the same source were also sent for paper made at the well known banana paper business group in other Provinces. This aimed to compare of arsenic concentration in the papers made from the banana pulps from Ron Phibun District and the locally grown banana pulps (referred to as control in the Table 5.12).

Table 5.12 showed the results of arsenic concentrations in banana stems and the papers. The 4 months banana stems from the experimental plot at Ron Phibun District contained arsenic at 1.30 mg kg^{-1}. These banana pulps were sent to WoranathKamPhangPhet School to make papers. The unbleached and bleached papers, respectively, contained arsenic at 0.98 and 0.82 mg kg^{-1}. The chlorine was used to bleach paper, so the arsenic concentration was lower than unbleached paper. Unexpectedly, the arsenic concentrations of unbleached and bleached control banana papers (0.96 and 0.84 mg kg^{-1}, respectively) were in the same level as those made from Ron Phibun pulps. For dyed paper, the arsenic concentration was higher than unbleached paper almost two times (1.69 mg kg^{-1}). This was resulted from the arsenic contaminated in the pigment used in the dying process. So we concluded that arsenic concentrations in the papers from Kampangpeth and Ron Phibun were not significantly different ($P < 0.05$) in both bleached and unbleached papers made from 4-month banana stems.

The banana stems at aged 12 months contained higher concentration of arsenic (4.07 mg kg^{-1}) than those at 4 months aged. The unbleached papers were made from these pulps in Ron Phibun District and were found to contain arsenic at 6.86 mg kg^{-1}. While they were 0.12 and 0.42 mg kg^{-1}, respectively, for the control pulps and papers from the Veerathai group, AungTong Province. The arsenic concentration of the AungTong paper was higher than the pulp used.

Table 5.12 Arsenic concentrations in the banana stem and banana paper

Banana stem / paper type	**Arsenic concentration (mg kg^{-1})**	
	Control	**Arsenic contamination**
Banana stem		
4-months harvested	not available	1.30±0.23
12-months harvested	0.12±0.002	4.07±3.45
Banana paper		
Made from 4-months stems		
Unbleached paper	0.96±0.16 [a]	0.98±0.43 [b]
Bleached paper	0.84±0.07 [a]	0.82±0.02 [b]
Dyed paper	1.69±0.61 [a]	
Made from 12-months stems		
Unbleached paper	0.42±0.08 [c]	6.86±1.00 [d]
Unbleached paper		0.11±0.002 [e]

[a] Paper samples taken from Woranath KamPhangPet School

[b] Banana stems from Ron Phibun, arsenic hotspot area was performed at Woranath KamPhangPet School

[c] Paper samples taken from Veerathai Group, Aungthong using arsenic free water in the paper processing

[d] Paper proceeded by using arsenic contaminated raw water at Ron Phibun

[e] Paper proceeded by using arsenic free raw water at Mahidol University

5.5.1.2 Arsenic leached out from the paper production

The banana paper processes performed at Ron Phibun District: the arsenic contaminated tap water was used in boiling, beating, cleaning, and framing. Arsenic concentration in the tap water was 0.12 mg L^{-1}; total volume of 166 L arsenic containing tap water was used for making papers from 7 kg banana pulps. Arsenic leached out at boiling, beating, and cleaning were 0.21, 0.14, and 0.12 mg L^{-1}, respectively. Comparing the results obtained from the paper making process using arsenic free tap water performed at the Faculty of Science, Mahidol University, Bangkok, the arsenic concentrations leached out from the processes were in the range of 0.001-0.004 mg L^{-1}; they were lower than those from the processing with arsenic contaminated water around five folds (Table 5.13). The statistical test ($P < 0.05$) showed that arsenic leached out concentrations were significantly different among the processes of boiling, beating, and cleaning. But, arsenic concentrations from the processes of pulp beating and pulp cleaning were the same. Similarly, there was significantly different in arsenic contamination between the water in Ron Phibun and Bangkok. In case that the arsenic contaminated papers were used, it was interesting to know how much arsenic we would expose if our hands were wet. Fortunately, it was only 0.009 mg L^{-1} leached out from the papers. This was lower than the standard of arsenic in drinking water (0.01 mg L^{-1}).

Table 5.13 Arsenic concentrations leached out from the paper production

Banana paper process	**Arsenic leaching (mg L^{-1})**	**Remarks**
Arsenic contaminated water used [a]	0.12±0.009	166 L total water used
Stem boiling	0.21±0.006	Stem pieces 7 kg/ 8 L water
Pulp beating	0.15±0.007	144 L water used
Pulp cleaning	0.13±0.004	13.9 L water used
Arsenic free water used [b]	non detection	2.90 L total water used
Stem boiling	0.04±0.002	stem 0.03 kg/ 0.90 L water
Pulp beating	0.016±0.001	0.50 L water used
Pulp cleaning	0.001±0.0002	1.50 L water used
Safety test [b]		
Wet hand contact	0.009±0.001	0.001 kg (3x3cm pieces) leached out in 0.03 L water for 10 min.

[a] Performed and used arsenic contaminated water at Ron Phibun District

[b] Performed and used arsenic free water at Faculty of Science, Mahidol University

5.5.2 Design for hand-made banana paper products

Mrs. Bunloom Aurubsuk, the leader of Veerathai Group located at Wisethchaichan District, AungTong Province, had trained 50 local people for hand on banana papers and the paper products during a 2-days course. There were many types of products that could be made from the banana papers such as DokMaiChan (flowers used in cremation), hand-made fans, and flowers sets for decoration works (Figure 5.12). After the training end, the trained local people formed a Group doing business in Banana Papers and Products; they invested a beating machine and other tools for making banana paper and the paper products.

Figure 5.12 (A) Making DokMaiChan (B) flowers sets for decoration works

5.5.3 Utilization by selling *Cyperus* as an ornamental plant

Cyperus plants were growing in the constructed wetland in order to remove arsenic from the arsenic contaminated water. The plants grew very fast and produced many young shoots. The young shoots were digging out from the constructed wetland pond and transferred into small pots for selling as ornamental plants. A pot of 10-15 plants with 60-90 cm high could be sold about 80-120 baht at the local market. Some people at the hot spot areas who are interested in growing *Cyperus* plants could both do phytoremediation and gained benefits at the same time.

Figure 5.13 Big decorated container of *Cyperus* as ornamental plants

5.6 Waste management of sediment sludge, soils, and marigold bottom ash by solidification/stabilization

5.6.1 Arsenic concentration in the soils

The soils at the beginning of the experiments, May 2007, were determined for arsenic concentrations; they were in the range of 36-83 mg kg^{-1}; the highest and the lowest were soils for planting Namwa and *C. esculenta* (Table 5.14). One year later, they were increased at 43-60%; the highest % increased was the soil of *C. esculenta* (60%); the lowest increased was the soil of Hom Kiau (42.6%). Although, it was increased at 52% for Namwa, but it contained the highest arsenic concentration of 173 mg kg^{-1} (Figure 5.14).

Table 5.14 Arsenic concentrations in the soils of CW and SP experiments

Source of soil	**Arsenic concentration (mg kg^{-1})**		
	May 2007	**May 2008**	**% Increasing**
Cyperus spp.	41.2±15.1	74.7±20.2	44.9
C. esculenta	35.8±6.37	90.4±23.3	60.4
Namwa	83.0±16.1	173±62.6	51.9
Hom Kiau	71.9±39.3	125±42.3	42.6
Leb Mu Nang	69.2±40.9	140±8.72	50.6

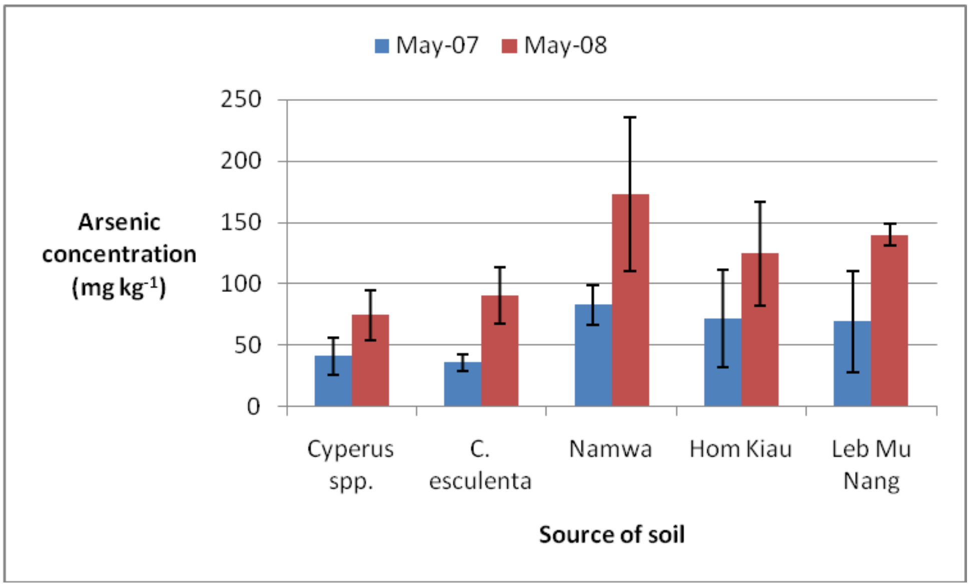


Figure 5.14 Arsenic concentration in the soils used for the CW and SP experiments

5.6.2 Arsenic concentration in the sediments

After three months operation of the CW experiment, the arsenic concentrations in three sediment sludge ponds were determined; the first sludge pond was the highest, then decreasing as follows: 23,438; 14,754; 5,740 mg kg^{-1}, respectively (Table 5.15). The arsenic content in the sediment pond 1 was the highest at 25,782 mg. The quantity of the dried sediment sludge in the pond 1, 2, and 3 was 1.10, 0.45, and 0.50 kg, respectively. The percent decreasing of arsenic concentration after the arsenic contaminated water precipitated in the pond 1 and 2 was 37% and 61%, respectively (Figure 5.15).

Table 5.15 Arsenic concentrations in the sediment ponds

Sediment pond	**Arsenic concentration (mg kg^{-1})**	**Arsenic content (mg)**
No.1	23,438±892	25,782
No.2	14,754±2,613	6,639
No.3	5,740±610	2,870

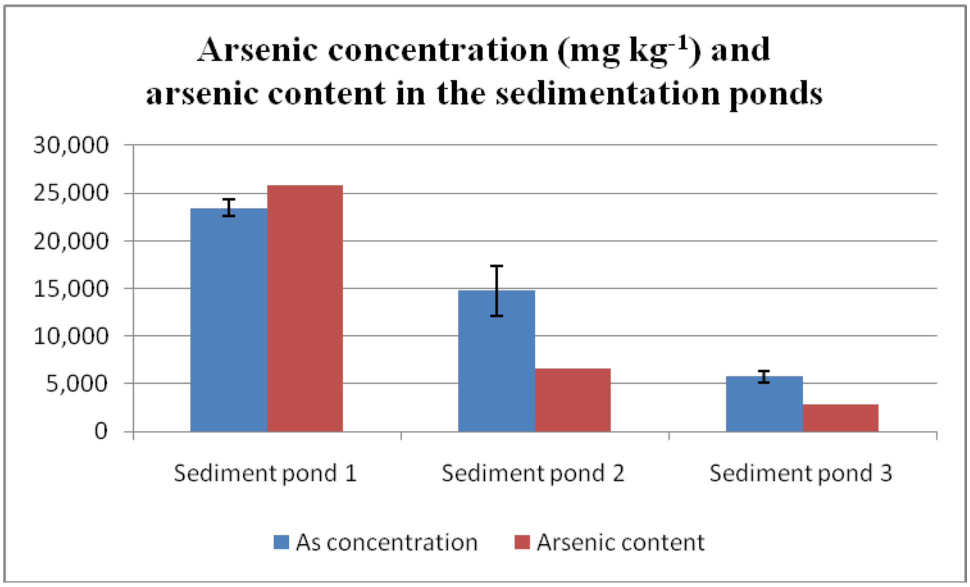


Figure 5.15 Arsenic concentrations in the sediments of the CW

All arsenic concentrations in the ponds were very much higher than the MCL of the United Kingdom of England at 50 mg kg^{-1} (Bhattacharya et al., 2007) and at 3.9 mg kg^{-1} for agricultural soil in Thailand (Ministry of Natural Resources and Environment, 2004). So the sediment must be managed by the methods of arsenic leaching and solidification/stabilization before performing in the secured landfill.

5.6.3 Arsenic leaching tests for untreated waste samples

The methods performed for arsenic leaching of untreated samples were 2 extraction solutions, deionized water (DIW) and Toxicity Characteristic Leaching Procedure (TCLP). Arsenic concentrations of the TCLP were higher than the DIW.

Arsenic leaching by the TCLP from bottom marigold ash, sediment from pond no.1, *Cyperus* soil, and *Colocasia* soil were 1.86, 0.09, 0.02, and 0.016 mg L^{-1}, respectively (Table 5.16). Although, the untreated samples of soils, sediment, and marigold ash had very high arsenic contamination, i.e., sediment : 5,069 mg kg^{-1}. However, the arsenic was leached out in the amount that less than the regulatory limit of 5 mg L^{-1}.

Table 5.16 Leaching tests of untreated waste samples from sludge, soils, and ash

Untreated sample (As-mg kg^{-1})	**TCLP**		**DIW**	
	pH	**As (mg kg^{-1})**	**pH**	**As (mg kg^{-1})**
Cyperus soil	4.90	0.02	9.80	0.003
(74.7 ± 20.2)	± 0.01	±0.004	±0.93	±0.0003
C. esculenta soil	4.90	0.016	8.60	0.003
(90.4 ± 23.3)	± 0.04	±0.003	±0.10	±0.0002
Namwa soil [a]	-	-	8.30	0.12
(138.5 ± 27.9)			±0.06	±0.005
Marigold ash	10.5	1.86	13.4	1.09
(158 ±19.7)	± 0.12	±0.03	±0.12	±0.02
Sludge no.1	6.10	0.09	9.10	0.05
(5,069 ± 282.1)	± 0.19	±0.005	±0.32	±0.004

[a] Arsenic concentration in the soils of Namwa was in the range of the arsenic concentrations for Hom Kiau (149±12.3 mg kg^{-1}) and Leb Mu Nang (140±8.72 mg kg^{-1}).

5.6.4 Solidification and stabilization

Although, the arsenic leached out from the Table 5.16 was shown lower than the standard, but the S/S experiment was also designed and studied for the marigold bottom ash (158 mg kg^{-1}) and sediment no.1 (5,069 mg kg^{-1}) before burying them in a secured landfill.

The ratio of solid materials and water used in the S/S was 1:0.42. The solid materials used in the study were cement mixed with sand at the ratio of 1:3. The solid part was modified by the 4 formulas as follows: (1) Cement-sand mixture (CSM) 100%, (2) CSM 75% + sediment sludge (SS) 25%, (3) CSM 75% + marigold ash (MA) 25%, (4) CSM 50% + MA 25% + SS 25% (Figure 5.16). The arsenic concentrations in the S/S formula 1-4 were 7, 579, 29, and 592 mg kg^{-1}, respectively (Table 5.17).

Figure 5.16 The 4 formulas of solidification/stabilization for arsenic

5.6.5 Arsenic leaching from solidification/stabilization

Treated samples of S/S were taken twice for the experiments of two arsenic leaching tests, DIW and TCLP (Figure 5.17). The first time at 14 d after curing the S/S in the zipper bags at room temperature was performed; the formula 2 (75% cement + 25% sediment) showed the highest arsenic leached out by the TCLP at 0.73 mg L^{-1}. Formula 4 of the TCLP was lower, at 0.38 mg L^{-1}. Then, the second time the data from Table 5.17 of 21d after curing treated samples were revealed the lower arsenic leached out from the formula 2 at 0.61 mg L^{-1} (TCLP), while the formula 4 was at the same level as the formula 2. The arsenic leached out from the formula 3 (mixed with marigold ash 25%) was very low at 0.032 and 0.019 mg L^{-1} (TCLP) for 14 and 21 d, respectively. The study was given the reasonable results; it meant that all treated S/S were safe and did not need to be buried in the secured landfill.

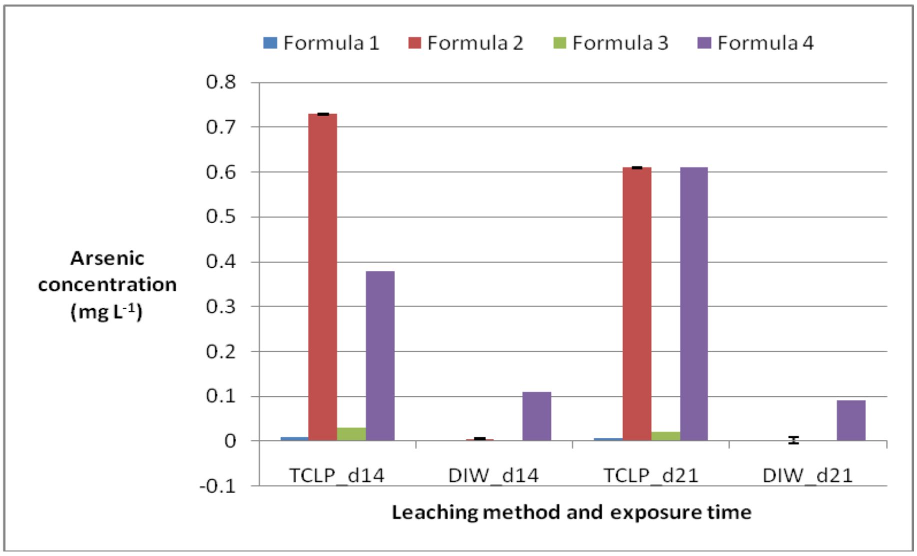


Figure 5.17 Arsenic concentration leached out from the S/S at d14 and d21

Table 5.17 Leaching tests for treated samples of solidification/stabilization

Formula [a]	**DIW**		**TCLP**	
	pH	**As (mg L^{-1})**	**pH**	**As (mg L^{-1})**
Day 14				
1	12.4±0.06	ND	5.60±0.06	0.01±0.001
2	12.6±0.10	0.004±0.001	5.50±0.12	0.73±0.002
3	13.1±0.06	ND	5.60±0.06	0.03±0.002
4	12.8±0.00	0.11±0.004	5.50±0.06	0.38±0.007
Day 21				
1	12.4±0.15	ND	5.50±0.00	0.007±0.001
2	12.5±0.12	0.002±0.001	5.40±0.06	0.61±0.02
3	13.1±0.06	ND	5.50±0.06	0.02±0.004
4	12.7±0.12	0.09±0.005	5.30±0.17	0.61±0.01
Regulatory limit				5.00

[a] Formula 1: CSM 100% = 6.90 ± 1.86 mg As kg^{-1}
Formula 2: CSM 75% + SS 25% = 579 ± 206 mg As kg^{-1}
Formula 3: CSM 75% + MA 25% = 28.6 ± 5.98 mg As kg^{-1}
Formula 4: CSM 50% + SS 25% + MA 25% = 592 ± 22.9 mg As kg^{-1}

5.6.6 The statistical tests for arsenic leaching

We set the variables of arsenic concentration, formula, method of leaching, and curing time in order to see the result comparisions. The data and results of 2-WAY ANOVA was shown in the Appendex B. They were disclosed as followed:

1. Hypothesis testing

<u>S/S formula</u>

H_0 : Mean arsenic concentrations leached out from different 4 formulas were the same.

H_1 : Mean arsenic concentration leached out from each formula was not the same (formula 1 ≠ formula 2 ≠ formula 3 ≠ formula 4).

Arsenic leaching test methods from S/S formula

H_0 : Mean arsenic concentrations leached out from different methods were the same.

H_1 : Mean arsenic concentration leached out from different methods was not the same (TCLP $\neq$ DW).

Arsenic leaching from different curing times of S/S formula

H_0 : Mean arsenic concentrations leached out from different curing times were the same.

H_1 : Mean arsenic concentration leached out from different curing times was not the same (curing time at 14 d $\neq$ 21 d).

2. Rejection zone, reject H_0 : Sig. < 0.05
3. Arsenic concentration leached out from S/S of 4 formulas, sig. of arsenic leached out from formula = 0.00 < 0.05, it meant that arsenic leached out from each formula was significantly different.
4. Arsenic concentration leached out from two leaching test methods of S/S formulas, Sig. of arsenic leached out from leaching test method = 0.00 < 0.05, it meant that arsenic leached out from each method was significantly different.
5. Arsenic concentration leached out at different curing time, Sig. of arsenic leached out from leaching test method = 0.75 > 0.05, it meant that arsenic leached out from curing time of 14 d was the same as 21d.

At the alpha of 0.05, arsenic concentrations were significantly different for each S/S formula and methods of arsenic leaching test. Arsenic leached out from the formula 1 and 2; formula 1 and 4 were significantly different (Sig. = 0.00). While, the arsenic from the formula 1 and 3 (Sig. = 0.84); formula 2 and 4 (Sig. = 0.33) were the same. Arsenic leaching method of TCLP was given the results to be different from the method of DIW. But, the curing times of 14 d and 21 d were the same arsenic leached out.

Interactions of formula, method, and curing time were reported that only the arsenic concentrations leached out from the formula and method were significantly different. In contrast, the formula and curing time (Sig. = 0.26); method and curing time (Sig. = 0.63); and formula, method, and curing time (Sig. = 0.18) were not different.

CHAPTER VI
DISCUSSION

6.1 Efficiency of arsenic removal by constructed wetland and soil phytoremediation

6.1.1 Constructed wetland

Both types of wetland plants, *Cyperus* and *C. esculenta,* showed similar efficiency in removing arsenic from the influent water at 0.36 mg L^{-1} to 0.08 mg L^{-1} in the effluent or 77-79% removal efficiency. The quantity of arsenic contaminated water that was treated by each pond was 885 L d^{-1}. Yang and colleaques (2006) used wetland plants to remove heavy metals from wastewater; the result showed the removal rate of arsenic at 79%. *Cyperus* had better growth (1,597 g m^{-2} d^{-1}) than *C. esculenta* (20 g m^{-2} d^{-1}); therefore, the uptake of arsenic by *Cyperus* at 4.41 g d^{-1} was higher than the *C. esculenta* (0.17 g d^{-1}). The plant biomass and arsenic uptake of *Cyperus* in this study agreed with the study of Perbangkhem and Polprasert (2010). They grew *Cyperus papyrus* in the constructed wetland to treat domestic wastewater. They could obtain 2,590 g m^{-2} of the plant biomass.

The arsenic was found to accumulate at the highest arsenic concentration (96-98%) in the roots of both plants. Sundberg-Jones and Hassan (2007) also found that most arsenic was accumulated in the root tissues of *Schoenoplectus californicus* and *Typha angustifolia*. However, the result of arsenic accumulation in plant parts was different from the study of Zhang et al. (2009). They investigated arsenic accumulation, speciation and tolerance of the duckweed (*Wolffia globosa*) to arsenic and found that *W. globosa* was able to accumulate more than 1,000 mg kg^{-1} in frond dry weight, and could tolerate arsenic up to 400 mg kg^{-1}.

Nateewattana and colleagues (2009) used wetland ponds of aquatic plants to remove arsenic from the wastewater treatment at Mae Moh Power Plant in Thailand. It was shown that the arsenic concentrations in sediment and supernatant were below the Thailand National Standard of 0.25 mg L^{-1} for water and 27 mg kg^{-1} for soil. The decrease of dissolved arsenic in the wetland ponds could mainly result from the precipitation of the dissolved arsenic. The arsenic accumulation in plant biomass revealed that 5 species of aquatic plants could absorb arsenic in their plant parts. The order of the accumulation from maximum to minimum was *Echornia crassipes* (Mart.) Solms., *Typha angustifolia* (L.), *Ipomoea aquatica* Forsk., *Canna glauca* (L.), and *Colocasia esculenta* (L.) Schott, respectively. All plants accumulated the highest arsenic content at the root.

This constructed wetland result could suggest that *Cyperus* and *C. esculenta* had high efficiency to remove arsenic. *Cyperus* was higher plant growth and plant uptake than *C. esculenta*.

6.1.2 Soil phytoremediation

There were two experiments for soil phytoremediation, experiment 1: plant system composed of banana and marigold and experiment 2: plant system composed of only banana. Each experiment, there were 60 tanks; 20 tanks for each of the 3 banana varieties, i.e., Namwa, Hom Kiau and Leb Mu Nang. The total quantity of arsenic contaminated water used in irrigating all plants in the SP was 895 L d^{-1}. Each plant of marigold and banana could treat arsenic containing water at 1.24 and 7.46 L d^{-1}, respectively. After all of the test plants were irrigated with arsenic containing water at 0.33 mg L^{-1}; the effluents in the experiment 2 from Namwa, Hom Kiau, and Leb Mu Nang, were 0.13, 0.05, 0.09 mg L^{-1}, respectively. The ability of plants to remove arsenic in the experiment was 61-85%. The arsenic concentration in the main outlets had been stored in the combined tanks; it was 0.05 mg L^{-1}, or 85% for arsenic removal efficiency. Efficiency of arsenic removal by this SP was high.

The mass balance of SP was shown that the biomass and arsenic uptake of the marigold plants was 4 g m^{-2} d^{-1} and 0.02 g d^{-1}, respectively, or 5.3% for plant uptake. The dried plant growth was 0.05 kg per plant. The efficiency of marigold in removing arsenic from the influent was 59%.

Even though the plant growth per d per m^2 for Namwa was the highest, the % uptake of arsenic was similar to Leb Mu Nang, i.e., 76-77%. At the end of experiment, the dried weight of Namwa, Hom Kiau, and Leb Mu Nang was 23, 18, and 7 kg per plant, respectively. The arsenic accumulated Namwa biomass was managed by utilization as papers and paper products. Whilst Leb Mu Nang had the highest arsenic concentration but the lowest plant biomass, thus, it was suitable to remove arsenic with less solid waste to be managed.

Arsenic concentrations in the roots were higher than that in the shoots. For *Cyperus*, *C. esculenta*, marigold, Namwa, Hom Kiau, and Leb Mu Nang, they were 190, 602, 19, 16, 14, and 78 mg kg^{-1}, respectively. The range of percentage for arsenic concentration in the roots was 74-98%. The results correspond with the study of Huq et al. (2005) who reported that arsenic accumulated at the highest concentration (1,987 mg kg^{-1}) in the marigold roots while arsenic in the shoots was lower than 5.45 mg kg^{-1}. However, Chintakovid et al. (2008) found that Nugget marigold, a triploid hybrid between American (*Tagetes erecta* L.) and French (*Tagetes patula*) marigolds, grew in an arsenic-polluted area in Thailand had accumulated arsenic most in the leaves (46%). Kumar et al. (2008) also reported that marigold plants could grow in soil containing anaerobic digested ferric coagulated sludge of wastewater treatment containing arsenic and irrigated the plants with treated wastewater. They claimed that this digested sludge was an excellent soil conditioner for the marigolds.

Srivastava and colleaques (2010) evaluated the ability and mechanisms of 19 *Pteris* and non-*Pteris* species to accumulate arsenic in a hydroponic system spiked with 300 µM As. The arsenic accumulation for the Pteris species ranged from 59% to 89% and from 47% to 65% for the non-*Pteris* species. The maximum accumulation of As (III) was in the fronds.

6.2 Waste management of the arsenic accumulated plant biomass by degradation in freshwater

There were 2 experiments for degradation of plant biomass in freshwater. The dried marigold plants containing arsenic of 8.95 mg kg^{-1} were immersed in 5 L tap water. The arsenic concentration was released from the marigold biomass into the water during 138 d was in the range of 0.04-0.10 mg L^{-1}, or an average of 0.07 mg L^{-1}. The marigold biomass was not completely degraded in the water. The non-degraded part contained arsenic at 14.4 mg kg^{-1}.

Another experiment was degradation of leaves of banana and *C. esculenta* in 2 L tap water. At starting experiment, arsenic concentrations of *C. esculenta*, Namwa, Leb Mu Nang, and HomKiau were 1.80, 1.24, 1.22, and 0.91 mg kg^{-1}, respectively. The average arsenic concentrations released out into the water were 0.05, 0.04, 0.02, and 0.01 mg L^{-1} for *C. esculenta*, Namwa, Hom Kiau, and Leb Mu Nang, respectively. Under the MCL of Thai regulation, all arsenic contaminated water in both experiments were lower than the regulation of 0.25 mg L^{-1} (MOSTE, 1996). These results confirmed that it was possible to release the leachate from the degradation of the arsenic accumulated plant biomass, i.e., marigolds, *C. esculenta*, Namwa, Leb Mu Nang, and Hom Kiau into the environment. After the 149 d experiment, the arsenic concentrations in degraded biomass were 4.51, 2.37, 1.63, and 1.25 mg kg^{-1} for *C. esculenta*, Namwa, Hom Kiau, and Leb Mu Nang, respectively. All degraded biomass excluded for *C. esculenta* could be left in agriculture land because their concentrations of arsenic lower the Thai soil standard of 3.9 mg kg^{-1} (Ministry of Natural Resources and Environment, 2004).

Rate of biodegradation depends on pH, temperature, oxygen, microbial population, degree of acclimation, accessibility of nutrients, chemical structure of the compound, cellular transport properties, and chemical partitioning in growth medium (Haritash and Kaushik, 2009). Yan and colleaques (2009) studied the factors of rainfall and time for arsenic leaching of plant biomass. Arsenic concentrations in the foliar leachate ranged from 0.004-0.52 mg L^{-1}, and the total arsenic in leachate ranged from 5-10%. The arsenic leaching rate from the leaves was accelerated by an increase of rainfall and time in a simulated precipitation experiment. Water-soluble arsenic distributed within the cuticle and apoplast of the plant was speculated as the main source of the leached arsenic.

Tabelin and colleaques (2010) studied the factors affecting arsenic mobility from hydrothermally altered rock under in situ conditions. Four impoundments with rectangular base, truncated-pyramid structures were built on site. Impoundment 1 was composed of the hydrothermally altered rock while impoundments 2-4 were covered with different types of silty covering soil in order to minimize O_2 and water intrusion into the rock. The results indicated that seasonal variations in temperature, O_2 concentration and volumetric water content in the impoundments strongly influenced arsenic leaching. Oxidation of sulfide minerals in the rock was enhanced because of a higher air-water-rock interaction when high temperature and low water content. Arsenic concentration in the porewater increased when it rained after a specific period of dry weather. The use of a silty covering soil influenced the concentrations of arsenic and in the porewater. O_2 and water movement might be the rate controlling step of arsenic leaching. If there is no covering soil on the impoundment, more arsenic will leach out from the rock. The use of a silty covering soil showed the reduction of arsenic leaching from the waste rock, but utilizing it alone was insufficient to effectively prevent arsenic release from the rock.

6.3 Management of the arsenic accumulated marigold biomass by burning

After the whole marigold plants were harvested, weighed, and dried in the sunlight for 5 d. The dried weight was decreased for 59%. Then, arsenic dried-accumulated marigolds plants were burnt in two temperature levels, high and low.

6.3.1 High temperature burning

The high temperature burning could reduce the weight of dried marigold biomass to the bottom ash at 92%. Arsenic concentration of the ash (298 mg kg^{-1}) increased 8 times from the dried marigold biomass. Arsenic content was lost at 37%. The management of dried marigold biomass by high temperature burning of crematorium in the temple was conducted. In this case, a phytoremediator must have an area to store dried biomass before burning. After that, the bottom ash should be collected and managed by the solidification/stabilization because its arsenic concentration was so high.

Clini and colleaques (2008) found that direct burning at high temperature could convert chemical energy stored in plants into heat and electricity. Tock et al. (2010) reported that the banana plant biomass should be used as source of thermal energy and biogas due to its availability, high growth rates, carbon neutrality and the fact that it bore fruits only once a lifetime.

6.3.2 Low temperature burning

Low temperature burning for dried marigold biomass was easily performed outdoor. The weight reduction was 82% from biomass to ash. We could not detect arsenic in the dust. This is a simply way to manage the marigold biomass at low cost.

6.4 Utilization by making papers and paper products and ornamental plants

6.4.1 Utilization by making papers from arsenic banana stems

The arsenic concentration of the 4-month banana stem at the Ron Phibun site was 1.30 mg kg^{-1}. The paper made from this stem contained arsenic at 0.98 and 0.82 mg kg^{-1} for the unbleached and bleached, respectively. Free arsenic tap water was used to make these papers. After 1 year growing, arsenic concentration in the banana stem biomass was 4.07 mg kg^{-1}. A lot of banana stem biomass was ready to be managed by making papers. The arsenic concentration in the unbleached paper was 6.86 mg kg^{-1}. The very high arsenic concentration in the paper indicated that the banana pulp could some how adsorb arsenic from the arsenic contaminated water used at the Ron Phibun. Tock and colleaques (2010) reviewed that utilization of banana residuals in the followings. A craft type paper of good strength has been made in India, from crushed, washed and dried banana pseudostems which yield 48-51% of unbleached pulp. This good quality paper is made by combining banana fiber with that of the betel nut husk (*Areca catechu* L.). However, the Australian investigators hold that the yield of banana fiber was too low for extraction to be economical. Only 28-113 g can be obtained from 18-36 kg of green pseudostems; 132 tons of green pseudostems would yield only 1 ton of paper.

Banana paper production at Ron Phibun District, the processes were used arsenic contaminated tap water in steps of boiling, beating, cleaning, and framing. Arsenic concentration in the tap water used was 0.12 mg L^{-1}. Arsenic released from the processes was in the range of 0.12-0.21 mg L^{-1}. This wastewater from the paper production process was lower than the MCL of 0.25 mg L^{-1}. The paper was proved to be safe when using it; because the concentration of arsenic leached out was lower than the standard guidelines of drinking water.

6.4.2 Products of banana papers

After training local people of Ron Phibun District to make papers and paper products from banana stems biomass, the Ron Phibun Group of Banana Paper and Products has been cooperated; they invested a beating machine and tools for banana paper and the paper products. They have designed and made DokMaiChan (flowers used in crematorium), hand-made fans, and showed flowers sets for decoration works. They make the products by direct orders.

6.4.3 Utilization as ornamental plants

Cyperus plants grew very fast and produced many young shoots in the constructed wetland. After growing about 5 months, we had managed these arsenic accumulated plants by digging out the young plants from the constructed wetland and transferred into small pots for selling as ornamental plants. A pot of 10-15 plants with 60-90 cm high is sold about 80-120 baht at the local market. Some people at the hot spot areas who are interested in growing *Cyperus* plants can both do phytoremediation and get benefic of income in the same time.

To promote phytoremediation, local people should participate, cooperate, and get some benefit or increase their income. Utilization of banana biomass as papers and their products was agreed by local people. They got benefit from the experiment.

6.5 Management of sediment sludge, soils, and marigold bottom ash by solidification/stabilization

U.S.EPA recommended to use the solidification and stabilization (S/S) method to manage with solid hazardous waste (U.S. EPA, 2003).

6.5.1 Leaching test for untreated soils, sediment sludge and ash

Arsenic concentrations in the soils of the CW and SP at the beginning and at the end of the experiments were in the ranges of 36-83 and 75-173 mg kg^{-1}, respectively or 43-60 % increasing. All soils had the arsenic concentrations higher than the MCL for soil at 3.9 mg kg^{-1} for residential and agricultural soil and at 27 mg kg^{-1} for non-agricultural soil in Thailand (Ministry of Natural Resources and Environment, 2004). The arsenic concentration in Namwa soil was the highest at 173 mg kg^{-1}. However, the arsenic leaching from this soil was only at 0.12 mg L^{-1} which was lower than the MCL of 5 mg L^{-1} for toxicity characteristic of hazardous waste (García-Ubaque et al., 2007). These arsenic contaminated soils could then be managed as non-hazardous waste.

The arsenic concentrations were very high for all 3 sediment ponds but the arsenic leaching concentrations were less than 0.09 mg L^{-1} by the TCLP and 0.05 mg L^{-1} by the DIW. Precipitation of arsenic in the sediment pond no.3 was decreased at 61%. However, arsenic concentration of leaching test from untreated marigold ash was the highest value of 1.86 mg L^{-1}. Although, the untreated soils, sediment sludge, and marigold ash had very high arsenic contamination; but, all the arsenic leaching was in the lower amount than the regulatory limit of 5 mg L^{-1}.

6.5.2 Leaching test for the treated sediment sludge and marigold ash

Due to their high arsenic concentrations in sediment and marigold ash, waste management by solidification/stabilization was applied for these wastes. Cement sand mixture formulas with both wastes having at least 25% each were studied. To decide whether S/S formula was managed as hazardous waste, the leaching test methods of the TCLP and the DIW were determined for arsenic concentration from those S/S formulas. The results of arsenic concentrations leached out from the S/S formula 2 (75% CSM + 25% SS) and 4 (50% CSM + 25% SS + 25% MA) were higher than formula 3 (75% CSM + 25% MA) at both d14 and d21 by the TCLP. This confirmed that marigold ash could be used by replacing the Portland cement at 25% with the same result of arsenic leaching. However, all leachates were lower than the MCL of 5 mg L^{-1}. It meant that all treated S/S did not have to be buried in the secured landfill. Some suitable solutions to disposal of this arsenic-bearing sludge, safe disposal of stabilization processes such as briquette production, cement mortar and concrete making have been attempted to investigate. It has been found that 25% of cement could be replaced by fly ash to stabilize arsenic-laden sludge to the tune of 11% by volume of cement-sand (1:3) mortar (Banerjee and Chakraborty, 2005).

Bottom ash was used as an adsorbent. Since the major chemical compound contained in ash is aluminosilicate; efforts to utilize this material as an adsorbent have been investigated. Malik and colleaques (2009) studied the fly ash obtained from coal power stations to examine for As (V) removal from water and to restrict As (V) migration in the solid wastes. The removal efficiency by the fly ash was higher at pH 4 than that at pH 7 or 10. Rahman and colleaques (2004) utilized maple wood ash to remediate As (III) and As (V) from contaminated aqueous streams in low concentrations. They found that the arsenic concentration was reduced from 0.50 to <0.005 mg L^{-1} in dynamic column experiments. Li and colleaques (2009) found that high iron-containing fly ash developed to remove effectively As (V) from aqueous system has been successfully. The adsorbent was in porous structure with specific surface area of 140 m^2 g^{-1}, which was 22 times of the raw ash.

Solidification/stabilization is one of the most effective treatment processes for the remediation of heavy-metal contaminated soils (Moon and Dermatas, 2007). S/S is used as a pre-landfill waste treatment technology that aims to make hazardous industrial wastes safe for disposal. Cement-based S/S technology is widely used because it offers assurance of chemical stabilization in many contaminants and produces a stable form of waste (Singh and Pant, 2006). S/S method involves mixing contaminated soils or residual particulates from other treatment methods with a physical binding agent to form a crystalline, glassy, or polymeric framework surrounding the waste particles. A process that converts contaminants to forms that is less soluble, mobile, or toxic. It is referred to arsenic stabilization, and the incorporation of contaminants into a monolithic solid with a reduced surface area is known as solidification. Various stabilizing agents, such as cement, hydrated lime, and fly ash, have been used in S/S process.

In soils treated with stabilizing agents, three possible mechanisms may be responsible for the immobilization of arsenic. One mechanism may be precipitation resulting from the formation of insoluble Ca–As precipitates. The others were inclusion, either by physical encapsulation or chemical inclusion. Physical encapsulation could be achieved by creating a solidified monolith, and chemical inclusion could be achieved through the incorporation of arsenic in binder hydration products, such as calcium silicate hydrates (CSH) by isomorphous substitution. Also, sorption on clays and pozzolanic reaction products immobilize arsenic.

Sullivan and colleaques (2010) reviewed the disposal of water treatment wastes containing arsenic, with S/S technologies. Portland cement/lime mixes are expected to be appropriate for wastes from sorptive filters, but may not be appropriate for precipitative sludges, because ferric flocs often used to sorb arsenic can retard cement hydration. Brine resulting from the regeneration of activated alumina filters is likely to accelerate cement hydration. Portland cement immobilises soluble arsenites and has been successfully used to stabilise arsenic-rich sludges (suitable for treating sludge generated from precipitative removal units). Oxidation of As (III) to As (V) and the formation of calcium-arsenic compounds are important immobilisation mechanisms for arsenic in cements. Geopolymers are alternative binder systems that are effective for treating wastes rich in alumina and metal hydroxides and may have potential for arsenic wastes generated using activated alumina. The long-term stability of cemented, arsenic-bearing wastes is uncertain because they are susceptible to carbonation effects which may result in the subsequent re-release of arsenic.

Banerjee and Chakraborty (2005) found that preparation of briquette, cement-sand mortar and concrete, mixing up to 10, 18 and 40% of arsenic-bearing sludge by volume, with the other common ingredients did not produce a TCLP leachate beyond its permissible direct inland water discharge standards.

CHAPTER VII

CONCLUSIONS

7.1 Efficiency of arsenic removal by constructed wetland and soil phytoremediation

Arsenic removing from tap water of the Ron Phibun District was successful performed by the constructed wetland and soil phytoremediation. Efficiency of the CW and SP was for 79-85%. *Cyperus* was the best plant (79%) to decrease arsenic from the treated system of the CW for arsenic contaminated water. However, *C. esculenta* was still high efficiency (77%) to remove arsenic from the water which was not different from *Cyperus* plant.

Marigold and banana plants were shown high efficiency of removing arsenic at 85%. Both plants were suggested to remediate arsenic from the SP at the hot spot sites of arsenic contamination. The best increasing biomass for banana was Namwa. Namwa could be chosen to remove arsenic from contaminated soil and plant biomass could be utilized as papers and paper products. As well as, marigold plants could be grown to remove arsenic and to sell their flowers in the local markets.

7.2 Waste management of the arsenic accumulated plant biomass by degradation in freshwater

Suppose that the arsenic accumulated plant biomass were leaved in the agriculture land without performing any technique. Degradation by freshwater or rainwater could be proceeded naturally by microorganisms. The degradation results from marigold, banana, and *C. esculenta* biomass was revealed that arsenic concentrations in the leaching freshwater were lower than the MCL of 0.25 mg L^{-1}.

7.3 Management of the arsenic accumulated marigold biomass by burning

Dried plant biomass in the sunlight was the firstly easy to reduce its weight. Then, burning the dried biomass also could be managed simply at the phyroremediated areas. Dried marigold plants can be burnt both low and high temperatures. Marigold bottom ash from high temperature in crematorium could be used as part of solidification/stabilization, replacing the composition of Portland cement.

7.4 Commercialization by making papers and paper products and selling as ornamental plants

There were 120 banana stems biomass left after removing arsenic by soil phytoremediation. After they gave fruits and being harvested; these arsenic accumulated plants biomass had been taken for the paper production. These plants had been performed following the management option by resource recovery or utilization by making papers and paper products. Arsenic concentration in this banana paper was higher than the concentration of plant biomass; it meant that pulp from banana paper could be as adsorbent to remove arsenic from the contaminated water.

In the same time, wastewater from the paper production process was under the regulatory limit of 0.25 mg L^{-1}. They were no problems to discharge into the environment.

After, local people about 50 persons attended the training of making paper and paper products; some of them about 15 members had set up “The Ron Phibun Banana Paper Cooperation Group”. They had made papers from banana stems biomass and designed many kinds of paper products such as a bunch of flowers used in crematorium, personal hand-made fan, tabled set bunch of flowers.

Other easy management option by utilization plant biomass of *Cyperus* was selling the pots of young plants to local people or tourists visited that area.

7.5 Management of sediment sludge, soils, and marigold bottom ash by solidification/stabilization

Untreated soils, sediment sludge, and marigold ash were shown for lower arsenic leaching than the regulation limit of hazardous solid waste. From this arsenic leaching result, sediment sludge no.1 and marigold bottom ash were treated by S/S technique. The treated S/S samples were mixed with cement-sand mixture and the values of arsenic leaching test showed to be lower the MCL of 5 mg L^{-1}. Finally, we can manage these solid wastes as the simple way of the S/S and kept them in unsecured landfill.

This management investigation of plant biomass and other residuals from the phytoremediations both in constructed wetland and soil phytoremediation was chosen the methods that are concerned with the study by Roussat and colleagues (2009). They reported that waste management to be sustainable must be made decision from methods with having good points from multicriteria aspects of economic, social, and environment. Firstly, economic perspectives are concerned of cost for waste management and local economic activities. Secondly, social aspects are quality of life for local people and local employment. Lastly, environment issues of energy consumption, global warming, a biotic depletion, and dispersion of contaminants in to the environment are taken into consideration. Utilization of plant biomass by making papers and paper products was accepted from local people. Selling flowers of marigold at least 3 times per crop was also interested at Ron Phibun District, arsenic hot spot areas. Due to lower arsenic leaching from soil growing *Cyperus*, digging the young plants was taken into pots for selling. Phytoremediation will be success with the local people participation.

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APPENDICES

APPENDEX A
THE STATISTICAL RESULTS

1. Arsenic released in wastewater from the paper production processes

1. Hypothesis testing

H_0 : Mean arsenic concentration in wastewater from boiling = beating = cleaning

H_1 : Mean arsenic concentration in wastewater from boiling ≠ beating ≠ cleaning

Univariate Analysis of Variance

Between-Subjects Factors

		Value Label	N
Paper process	1	Boiling	6
	2	Beating	6
	3	Cleaning	6
Water used	1	Arsenic containing water	9
	2	Arsenic free water	9

Levene's Test of Equality of Error Variances[a]

Dependent Variable: Arsenic concentration

F	df1	df2	Sig.
6.704	5	12	.003

Tests the null hypothesis that the error variance of the dependent variable is equal across groups.

a. Design: Intercept+PROCESS+WATER+PROCESS * WATER

Descriptive Statistics

Dependent Variable: Arsenic concentration

Paper process	Water used	Mean	Std. Deviation	N
Boiling	Arsenic containing water	210.2667	26.14237	3
	Arsenic free water	39.4233	7.31579	3
	Total	124.8450	95.13680	6
Beating	Arsenic containing water	144.8333	23.17333	3
	Arsenic free water	15.5733	1.15846	3
	Total	80.2033	72.30341	6
Cleaning	Arsenic containing water	124.6667	15.04305	3
	Arsenic free water	1.3267	.30139	3
	Total	62.9967	68.22302	6
Total	Arsenic containing water	159.9222	43.16975	9
	Arsenic free water	18.7744	17.07723	9
	Total	89.3483	79.29624	18

Tests of Between-Subjects Effects

Dependent Variable: Arsenic concentration

Source	Type III Sum of Squares	df	Mean Square	F	Sig.	Noncent. Parameter	Observed Power[a]
Corrected Model	103890.850[b]	5	20778.170	83.020	.000	415.100	1.000
Intercept	143696.244	1	143696.244	574.144	.000	574.144	1.000
PROCESS	12228.328	2	6114.164	24.429	.000	48.859	1.000
WATER	89652.128	1	89652.128	358.209	.000	358.209	1.000
PROCESS * WATER	2010.393	2	1005.197	4.016	.046	8.033	.601
Error	3003.347	12	250.279				
Total	250590.441	18					
Corrected Total	106894.197	17					

a. Computed using alpha = .05

b. R Squared = .972 (Adjusted R Squared = .960)

2. Rejection zone

Reject H_0 : Sig. < 0.05

3. Arsenic concentration in wastewater from paper production processes

Sig. of As in process = 0.000 < 0.05, it meant that arsenic in wastewater from each process was significantly different.

4. Arsenic concentration in wastewater using free and arsenic contaminated water in the production

Sig. of As in wastewater used different raw water = 0.000 < 0.05, it meant that arsenic in wastewater used different raw water was significantly different.

5. Arsenic concentration both process and used raw water

Sig. of As in wastewater from different process and used different raw water = 0.046 < 0.05, it meant that arsenic in wastewater used different raw water and each process was significantly different.

Estimated Marginal Means

1. Paper process

Estimates

Dependent Variable: Arsenic concentration

Paper process	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
Boiling	124.845	6.459	110.773	138.917
Beating	80.203	6.459	66.131	94.275
Cleaning	62.997	6.459	48.925	77.069

Pairwise Comparisons

Dependent Variable: Arsenic concentration

(I) Paper process	(J) Paper process	Mean Difference (I-J)	Std. Error	Sig.[a]	95% Confidence Interval for Difference[a]	
					Lower Bound	Upper Bound
Boiling	Beating	44.642*	9.134	.000	24.741	64.543
	Cleaning	61.848*	9.134	.000	41.947	81.749
Beating	Boiling	-44.642*	9.134	.000	-64.543	-24.741
	Cleaning	17.207	9.134	.084	-2.694	37.108
Cleaning	Boiling	-61.848*	9.134	.000	-81.749	-41.947
	Beating	-17.207	9.134	.084	-37.108	2.694

Based on estimated marginal means

*. The mean difference is significant at the .05 level.

a. Adjustment for multiple comparisons: Least Significant Difference (equivalent to no adjustments).

Univariate Tests

Dependent Variable: Arsenic concentration

	Sum of Squares	df	Mean Square	F	Sig.	Noncent. Parameter	Observed Power[a]
Contrast	12228.33	2	6114.164	24.429	.000	48.859	1.000
Error	3003.347	12	250.279				

The F tests the effect of Paper process. This test is based on the linearly independent pairwise comparisons among the estimated marginal means.

a. Computed using alpha = .05

2. Water used

Estimates

Dependent Variable: Arsenic concentration

Water used	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
Arsenic containing water	159.922	5.273	148.432	171.412
Arsenic free water	18.774	5.273	7.285	30.264

Pairwise Comparisons

Dependent Variable: Arsenic concentration

(I) Water used	(J) Water used	Mean Difference (I-J)	Std. Error	Sig.[a]	95% Confidence Interval for Difference[a]	
					Lower Bound	Upper Bound
Arsenic containing water	Arsenic free water	141.148*	7.458	.000	124.899	157.397
Arsenic free water	Arsenic containing water	-141.148*	7.458	.000	-157.397	-124.899

Based on estimated marginal means

*. The mean difference is significant at the .05 level.

a. Adjustment for multiple comparisons: Least Significant Difference (equivalent to no adjustments).

Univariate Tests

Dependent Variable: Arsenic concentration

	Sum of Squares	df	Mean Square	F	Sig.	Noncent. Parameter	Observed Power[a]
Contrast	89652.13	1	89652.128	358.209	.000	358.209	1.000
Error	3003.347	12	250.279				

The F tests the effect of Water used. This test is based on the linearly independent pairwise comparisons among the estimated marginal means.

a. Computed using alpha = .05

Post Hoc Tests

Paper process

Multiple Comparisons

Dependent Variable: Arsenic concentration

	(I) Paper process	(J) Paper process	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Scheffe	Boiling	Beating	44.6417*	9.13380	.001	19.1805	70.1028
		Cleaning	61.8483*	9.13380	.000	36.3872	87.3095
	Beating	Boiling	-44.6417*	9.13380	.001	-70.1028	-19.1805
		Cleaning	17.2067	9.13380	.211	-8.2545	42.6678
	Cleaning	Boiling	-61.8483*	9.13380	.000	-87.3095	-36.3872
		Beating	-17.2067	9.13380	.211	-42.6678	8.2545
LSD	Boiling	Beating	44.6417*	9.13380	.000	24.7408	64.5425
		Cleaning	61.8483*	9.13380	.000	41.9475	81.7492
	Beating	Boiling	-44.6417*	9.13380	.000	-64.5425	-24.7408
		Cleaning	17.2067	9.13380	.084	-2.6942	37.1075
	Cleaning	Boiling	-61.8483*	9.13380	.000	-81.7492	-41.9475
		Beating	-17.2067	9.13380	.084	-37.1075	2.6942

Based on observed means.

*. The mean difference is significant at the .05 level.

2. Arsenic concentration difference in paper between control and arsenic contamination raw material used

1. Paper made from 4 months banana stems
2. Arsenic concentrations in papers from Kampangpeth and Ron Phibun were not different in both bleached and unbleached papers at significance level of 0.05.

Univariate Analysis of Variance

Between-Subjects Factors

		Value Label	N
Paper source	1	Kampangpeth	4
	2	Ronpibun	12
Paper type	1	Unbleached paper	8
	2	Bleached paper	8

Descriptive Statistics

Dependent Variable: AS_CONC

Paper source	Paper type	Mean	Std. Deviation	N
Kampangpeth	Unbleached paper	961.1800	160.40010	2
	Bleached paper	838.4400	70.31470	2
	Total	899.8100	123.47396	4
Ronpibun	Unbleached paper	975.1667	433.85136	6
	Bleached paper	818.7067	154.33032	6
	Total	896.9367	321.03008	12
Total	Unbleached paper	971.6700	371.70584	8
	Bleached paper	823.6400	133.42601	8
	Total	897.6550	280.40752	16

Levene's Test of Equality of Error Variances[a]

Dependent Variable: AS_CONC

F	df1	df2	Sig.
2.441	3	12	.115

Tests the null hypothesis that the error variance of the dependent variable is equal across groups.

a. Design: Intercept+P_SOURCE+P_TYPE+P_SOURCE * P_TYPE

Tests of Between-Subjects Effects

Dependent Variable: AS_CONC

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	88529.071[a]	3	29509.690	.325	.808
Intercept	9684895.753	1	9684895.753	106.535	.000
P_SOURCE	24.768	1	24.768	.000	.987
P_TYPE	58464.480	1	58464.480	.643	.438
P_SOURCE * P_TYPE	852.779	1	852.779	.009	.924
Error	1090896.603	12	90908.050		
Total	14071977.658	16			
Corrected Total	1179425.673	15			

a. R Squared = .075 (Adjusted R Squared = -.156)

APPENDIX B

THE STATISTICAL TEST FOR ARSENIC LEACHING TEST FROM 4 S/S FORMULAS

Univariate Analysis of Variance

Between-Subjects Factors

		Value Label	N
FORMULA	1	FORMULA1	12
	2	FORMUAL2	12
	3	FORMUAL3	12
	4	FORMUAL4	12
METHOD	1	TCLP	24
	2	DW	24
CURING TIME	1	D14	24
	2	D21	24

1. **Hypothesis testing**

S/S formula

H_0 : Mean arsenic concentrations leached out from different 4 formulas were the same.

H_1 : Mean arsenic concentration leached out from each formula was not the same (formula 1 $\neq$ formula 2 $\neq$ formula 3 $\neq$ formula 4).

Arsenic leaching test methods from S/S formula

H_0 : Mean arsenic concentrations leached out from different methods were the same.

H_1 : Mean arsenic concentration leached out from different methods was not the same (TCLP $\neq$ DW).

Arsenic leaching from different curing times of S/S formula

H_0 : Mean arsenic concentrations leached out from different curing times were the same.

H_1 : Mean arsenic concentration leached out from different curing times was not the same (curing time at 14 d $\neq$ 21 d).

2. **Rejection zone**

   Reject H_0 : Sig. (P) $<$ 0.05

3. **Arsenic concentration leached out from S/S of 4 formulas**

   Sig. of arsenic leached out from formula = 0.000 $<$ 0.05, it meant that arsenic leached out from each formula was significantly different.

4. **Arsenic concentration leached out from two leaching test methods of S/S formulas**

   Sig. of arsenic leached out from leaching test method = 0.000 $<$ 0.05, it meant that arsenic leached out from each method was significantly different.

5. **Arsenic concentration leached out at different curing time**

   Sig. of arsenic leached out from leaching test method = 0.752 > 0.05, it meant that arsenic leached out from curing time of 14 d was not significantly different with 21d.

Descriptive Statistics

Dependent Variable: ARSENIC CONCENTRATION

FORMULA	METHOD	CURING TIME	Mean	Std. Deviation	N
FORMULA1	TCLP	D14	9.4967	1.03549	3
		D21	6.7867	1.33061	3
		Total	8.1417	1.82766	6
	DW	D14	.9867	.35921	3
		D21	.9200	.33645	3
		Total	.9533	.31341	6
	Total	D14	5.2417	4.71238	6
		D21	3.8533	3.32849	6
		Total	4.5475	3.95669	12
FORMUAL2	TCLP	D14	726.9000	276.00703	3
		D21	608.8700	89.84631	3
		Total	667.8850	194.62841	6
	DW	D14	3.7600	.27221	3
		D21	1.9700	.51118	3
		Total	2.8650	1.04661	6
	Total	D14	365.3300	432.84110	6
		D21	305.4200	337.23483	6
		Total	335.3750	371.25847	12
FORMUAL3	TCLP	D14	32.4033	11.50359	3
		D21	19.2333	5.60833	3
		Total	25.8183	10.84200	6
	DW	D14	.8000	.32741	3
		D21	.0000	.00000	3
		Total	.4000	.48464	6
	Total	D14	16.6017	18.77784	6
		D21	9.6167	11.11565	6
		Total	13.1092	15.15734	12
FORMUAL4	TCLP	D14	376.9000	58.15694	3
		D21	604.8000	275.41353	3
		Total	490.8500	217.42920	6
	DW	D14	105.6667	19.77633	3
		D21	88.9767	6.03028	3
		Total	97.3217	15.95474	6
	Total	D14	241.2833	153.55647	6
		D21	346.8883	331.93027	6
		Total	294.0858	252.66645	12
Total	TCLP	D14	286.4250	328.86192	12
		D21	309.9225	333.85598	12
		Total	298.1738	324.30679	24
	DW	D14	27.8033	47.72088	12
		D21	22.9667	39.89599	12
		Total	25.3850	43.08690	24
	Total	D14	157.1142	265.06873	24
		D21	166.4446	274.86190	24
		Total	161.7794	267.16343	48

Tests of Between-Subjects Effects

Dependent Variable: ARSENIC CONCENTRATION

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3026522.372[a]	15	201768.158	19.675	.000
Intercept	1256283.176	1	1256283.176	122.503	.000
FORMULA	1133581.600	3	377860.533	36.846	.000
METHOD	892964.426	1	892964.426	87.075	.000
TIME	1044.680	1	1044.680	.102	.752
FORMULA * METHOD	900477.315	3	300159.105	29.269	.000
FORMULA * TIME	43332.345	3	14444.115	1.408	.258
METHOD * TIME	2408.475	1	2408.475	.235	.631
FORMULA * METHOD * TIME	52713.532	3	17571.177	1.713	.184
Error	328163.720	32	10255.116		
Total	4610969.268	48			
Corrected Total	3354686.092	47			

a. R Squared = .902 (Adjusted R Squared = .856)

Estimated Marginal Means

1. FORMULA

Estimates

Dependent Variable: ARSENIC CONCENTRATION

FORMULA	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
FORMULA1	4.548	29.233	-54.999	64.094
FORMUAL2	335.375	29.233	275.828	394.922
FORMUAL3	13.109	29.233	-46.437	72.656
FORMUAL4	294.086	29.233	234.539	353.632

Pairwise Comparisons

Dependent Variable: ARSENIC CONCENTRATION

(I) FORMULA	(J) FORMULA	Mean Difference (I-J)	Std. Error	Sig.[a]	95% Confidence Interval for Difference[a]	
					Lower Bound	Upper Bound
FORMULA1	FORMUAL2	-330.827*	41.342	.000	-415.039	-246.616
	FORMUAL3	-8.562	41.342	.837	-92.773	75.650
	FORMUAL4	-289.538*	41.342	.000	-373.750	-205.327
FORMUAL2	FORMULA1	330.827*	41.342	.000	246.616	415.039
	FORMUAL3	322.266*	41.342	.000	238.054	406.477
	FORMUAL4	41.289	41.342	.325	-42.922	125.501
FORMUAL3	FORMULA1	8.562	41.342	.837	-75.650	92.773
	FORMUAL2	-322.266*	41.342	.000	-406.477	-238.054
	FORMUAL4	-280.977*	41.342	.000	-365.188	-196.765
FORMUAL4	FORMULA1	289.538*	41.342	.000	205.327	373.750
	FORMUAL2	-41.289	41.342	.325	-125.501	42.922
	FORMUAL3	280.977*	41.342	.000	196.765	365.188

Based on estimated marginal means

*. The mean difference is significant at the .05 level.

a. Adjustment for multiple comparisons: Least Significant Difference (equivalent to no adjustments).

Univariate Tests

Dependent Variable: ARSENIC CONCENTRATION

	Sum of Squares	df	Mean Square	F	Sig.
Contrast	1133582	3	377860.533	36.846	.000
Error	328163.7	32	10255.116		

The F tests the effect of FORMULA. This test is based on the linearly independent pairwise comparisons among the estimated marginal means.

2. METHOD

Estimates

Dependent Variable: ARSENIC CONCENTRATION

METHOD	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
TCLP	298.174	20.671	256.068	340.280
DW	25.385	20.671	-16.721	67.491

Pairwise Comparisons

Dependent Variable: ARSENIC CONCENTRATION

(I) METHOD	(J) METHOD	Mean Difference (I-J)	Std. Error	Sig.[a]	95% Confidence Interval for Difference[a]	
					Lower Bound	Upper Bound
TCLP	DW	272.789*	29.233	.000	213.242	332.335
DW	TCLP	-272.789*	29.233	.000	-332.335	-213.242

Based on estimated marginal means

*. The mean difference is significant at the .05 level.

a. Adjustment for multiple comparisons: Least Significant Difference (equivalent to no adjustments).

Univariate Tests

Dependent Variable: ARSENIC CONCENTRATION

	Sum of Squares	df	Mean Square	F	Sig.
Contrast	892964.4	1	892964.426	87.075	.000
Error	328163.7	32	10255.116		

The F tests the effect of METHOD. This test is based on the linearly independent pairwise comparisons among the estimated marginal means.

3. CURING TIME

Estimates

Dependent Variable: ARSENIC CONCENTRATION

CURING TIME	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
D14	157.114	20.671	115.008	199.220
D21	166.445	20.671	124.339	208.550

Pairwise Comparisons

Dependent Variable: ARSENIC CONCENTRATION

(I) CURING TIME	(J) CURING TIME	Mean Difference (I-J)	Std. Error	Sig.[a]	95% Confidence Interval for Difference[a]	
					Lower Bound	Upper Bound
D14	D21	-9.330	29.233	.752	-68.877	50.216
D21	D14	9.330	29.233	.752	-50.216	68.877

Based on estimated marginal means

a. Adjustment for multiple comparisons: Least Significant Difference (equivalent to no adjustments).

Univariate Tests

Dependent Variable: ARSENIC CONCENTRATION

	Sum of Squares	df	Mean Square	F	Sig.
Contrast	1044.680	1	1044.680	.102	.752
Error	328163.7	32	10255.116		

The F tests the effect of CURING TIME. This test is based on the linearly independent pairwise comparisons among the estimated marginal means.

4. FORMULA * METHOD

Dependent Variable: ARSENIC CONCENTRATION

				95% Confidence Interval	
FORMULA	METHOD	Mean	Std. Error	Lower Bound	Upper Bound
FORMULA1	TCLP	8.142	41.342	-76.070	92.353
	DW	.953	41.342	-83.258	85.165
FORMUAL2	TCLP	667.885	41.342	583.673	752.097
	DW	2.865	41.342	-81.347	87.077
FORMUAL3	TCLP	25.818	41.342	-58.393	110.030
	DW	.400	41.342	-83.812	84.612
FORMUAL4	TCLP	490.850	41.342	406.638	575.062
	DW	97.322	41.342	13.110	181.533

5. FORMULA * CURING TIME

Dependent Variable: ARSENIC CONCENTRATION

				95% Confidence Interval	
FORMULA	CURING TIME	Mean	Std. Error	Lower Bound	Upper Bound
FORMULA1	D14	5.242	41.342	-78.970	89.453
	D21	3.853	41.342	-80.358	88.065
FORMUAL2	D14	365.330	41.342	281.118	449.542
	D21	305.420	41.342	221.208	389.632
FORMUAL3	D14	16.602	41.342	-67.610	100.813
	D21	9.617	41.342	-74.595	93.828
FORMUAL4	D14	241.283	41.342	157.072	325.495
	D21	346.888	41.342	262.677	431.100

6. METHOD * CURING TIME

Dependent Variable: ARSENIC CONCENTRATION

				95% Confidence Interval	
METHOD	CURING TIME	Mean	Std. Error	Lower Bound	Upper Bound
TCLP	D14	286.425	29.233	226.878	345.972
	D21	309.922	29.233	250.376	369.469
DW	D14	27.803	29.233	-31.743	87.350
	D21	22.967	29.233	-36.580	82.513

7. FORMULA * METHOD * CURING TIME

Dependent Variable: ARSENIC CONCENTRATION

					95% Confidence Interval	
FORMULA	METHOD	CURING TIME	Mean	Std. Error	Lower Bound	Upper Bound
FORMULA1	TCLP	D14	9.497	58.467	-109.596	128.590
		D21	6.787	58.467	-112.306	125.880
	DW	D14	.987	58.467	-118.106	120.080
		D21	.920	58.467	-118.173	120.013
FORMUAL2	TCLP	D14	726.900	58.467	607.807	845.993
		D21	608.870	58.467	489.777	727.963
	DW	D14	3.760	58.467	-115.333	122.853
		D21	1.970	58.467	-117.123	121.063
FORMUAL3	TCLP	D14	32.403	58.467	-86.690	151.496
		D21	19.233	58.467	-99.860	138.326
	DW	D14	.800	58.467	-118.293	119.893
		D21	-1.42E-14	58.467	-119.093	119.093
FORMUAL4	TCLP	D14	376.900	58.467	257.807	495.993
		D21	604.800	58.467	485.707	723.893
	DW	D14	105.667	58.467	-13.426	224.760
		D21	88.977	58.467	-30.116	208.070

Post Hoc Tests

FORMULA

Multiple Comparisons

Dependent Variable: ARSENIC CONCENTRATION

	(I) FORMULA	(J) FORMULA	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Scheffe	FORMULA1	FORMUAL2	-330.8275*	41.34230	.000	-452.7933	-208.8617
		FORMUAL3	-8.5617	41.34230	.998	-130.5275	113.4041
		FORMUAL4	-289.5383*	41.34230	.000	-411.5041	-167.5725
	FORMUAL2	FORMULA1	330.8275*	41.34230	.000	208.8617	452.7933
		FORMUAL3	322.2658*	41.34230	.000	200.3000	444.2316
		FORMUAL4	41.2892	41.34230	.802	-80.6766	163.2550
	FORMUAL3	FORMULA1	8.5617	41.34230	.998	-113.4041	130.5275
		FORMUAL2	-322.2658*	41.34230	.000	-444.2316	-200.3000
		FORMUAL4	-280.9767*	41.34230	.000	-402.9425	-159.0109
	FORMUAL4	FORMULA1	289.5383*	41.34230	.000	167.5725	411.5041
		FORMUAL2	-41.2892	41.34230	.802	-163.2550	80.6766
		FORMUAL3	280.9767*	41.34230	.000	159.0109	402.9425
LSD	FORMULA1	FORMUAL2	-330.8275*	41.34230	.000	-415.0390	-246.6160
		FORMUAL3	-8.5617	41.34230	.837	-92.7732	75.6498
		FORMUAL4	-289.5383*	41.34230	.000	-373.7498	-205.3268
	FORMUAL2	FORMULA1	330.8275*	41.34230	.000	246.6160	415.0390
		FORMUAL3	322.2658*	41.34230	.000	238.0543	406.4773
		FORMUAL4	41.2892	41.34230	.325	-42.9223	125.5007
	FORMUAL3	FORMULA1	8.5617	41.34230	.837	-75.6498	92.7732
		FORMUAL2	-322.2658*	41.34230	.000	-406.4773	-238.0543
		FORMUAL4	-280.9767*	41.34230	.000	-365.1882	-196.7652
	FORMUAL4	FORMULA1	289.5383*	41.34230	.000	205.3268	373.7498
		FORMUAL2	-41.2892	41.34230	.325	-125.5007	42.9223
		FORMUAL3	280.9767*	41.34230	.000	196.7652	365.1882

Based on observed means.

*. The mean difference is significant at the .05 level.

Homogeneous Subsets

ARSENIC CONCENTRATION

	FORMULA	N	Subset	
			1	2
Scheffe[a,b]	FORMULA1	12	4.5475	
	FORMUAL3	12	13.1092	
	FORMUAL4	12		294.0858
	FORMUAL2	12		335.3750
	Sig.		.998	.802

Means for groups in homogeneous subsets are displayed.
Based on Type III Sum of Squares
The error term is Mean Square(Error) = 10255.116.

a. Uses Harmonic Mean Sample Size = 12.000.

b. Alpha = .05.

APPENDEX C

ARSENIC CONCENTRATION RELEASED FROM PLANTS IN FRESHWATER BY DEGRADATION

Table 1 Arsenic concentration in the freshwater leached out from marigold biomass

Time (d)	**Arsenic concentration (mg L^{-1})**	
	Control	**Marigold degradation** [a]
0	0.002±0.0004	0.04±0.01
5	0.005±0.001	0.10±0.01
13	0.001±0.0004	0.05±0.005
19	0.004±0.002	0.07±0.02
26	0.005±0.001	0.05±0.003
33	0.002±0.0005	0.07±0.005
40	0.003±0.0001	0.07±0.004
47	0.001±0.0002	0.08±0.007
138	ND	0.09±0.005
Mean	0.003±0.001	0.07±0.008
Range	0.001-0.005	0.04-0.10

[a] Arsenic concentration of dried marigold biomass at the beginning was 8.95±0.35 mg kg^{-1}.

Table 2 Arsenic concentration in the freshwater leached out from plant biomass of *C.* esculenta, Namwa, Hom kiau, and Leb Mu Nang

Time (d)	**Arsenic concentration (mg L^{-1})**				
	Control	***C. esculenta***	**Namwa**	**Hom Kiau**	**LMN** [a]
0	ND	0.02±0.005	0.02±0.004	0.01±0.001	0.01±0.001
5	ND	0.08±0.016	0.06±0.023	0.02±0.002	0.02±0.006
9	ND	0.09±0.003	0.07±0.014	0.03±0.012	0.01±0.003
13	0.0002	0.08±0.011	0.05±0.012	0.02±0.004	0.02±0.005
17	0.0035	0.08±0.010	0.05±0.017	0.03±0.004	0.01±0.002
20	0.0020	0.07±0.019	0.05±0.011	0.03±0.003	0.02±0.005
33	0.0024	0.03±0.010	0.02±0.008	0.01±0.005	0.01±0.003
39	0.0019	0.04±0.015	0.02±0.012	0.01±0.004	0.02±0.004
149	ND	0.01±0.019	0.01±0.003	0.01±0.005	0.003±0.0004
Mean	0.001	0.05±0.010	0.04±0.011	0.02±0.004	0.01±0.003
Range	0.000-0.004	0.01-0.09	0.01-0.07	0.01-0.03	0.00-0.02

[a] Stand for Leb Mu Nang

[b] Arsenic concentration of dried plant biomass at the beginning was 1.80±0.53 (*C. esculenta*), 1.24±0.35 (Namwa), 1.22±0.25 (Hom Kiau), and 0.91±0.14 (Leb Mu Nang) mg kg^{-1}.

[c] Arsenic concentration of degraded plant biomass at the day 149 was 4.51±1.27 (*C. esculenta*), 2.37±0.60 (Namwa), 1.63±0.94 (Hom Kiau), and 1.25±0.41 (Leb Mu Nang) mg kg^{-1}.

BIOGRAPHY

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