ARSENIC ADSORPTION IN AQUEOUS SOLUTION AND IMMOBILIZATION IN SOILS AND USING HAND WARMERS

by

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Abstract

Adsorption is a commonly used method for arsenic remediation. The adsorption and immobilization effectiveness of arsenic by soil particles and used hand warmers was studied. The adsorption effectiveness at equilibrium of soil particles in 10 ppm As(III) solution was: clay (77.70%) > silt (69.24%) > sand (41.35%). In 1000 ppm As(III) solution, 17.02 mg As(III) was adsorbed onto each gram of hand warmers at equilibrium, which was significantly higher than other adsorbents. For As(III) adsorption from aqueous solution, soil samples and hand warmers were well fitted to the pseudo second-order model and the Freundlich model. After 8 weeks of soil incubation, the sequential extraction procedure data indicated the labile fractions of arsenic (F1 and F2) decreased with the addition of hand warmers. Meanwhile, the percentage of the most stable fraction, F5, increased. These results are valuable for the future application of used hand warmers as an adsorbent/amendment for arsenic decontamination.

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Glossary

As(V)	Arsenate
As(III)	Arsenite
Available P	Available phosphorus
CCME	Canadian Council of Ministers of the Environment
CEC	Cation exchange capacity
Eh	Redox potential
U.S. EPA	United States Environmental Protection Agency
F1	Fraction 1, non-specifically sorbed arsenic
F2	Fraction 2, specifically sorbed arsenic
F3	Fraction 3, arsenic bound to amorphous Fe oxides
F4	Fraction 4, arsenic bound to crystalline Fe oxides
F5	Fraction 5, residual arsenic
HW	Hand warmer(s)
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectrometry
MMA	Monomethylarsonate
SD	Standard deviation(s)
SEP	Sequential extraction procedure
WHO	World Health Organization
XRD	X-ray diffraction

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Chapter 1 Literature Review

1.1 Arsenic contamination and standards

Arsenic, a metalloid, is ubiquitous in the environment around the world. Its abundance in the earth's crust ranks 20th out of all the elements (Mohan and Pittman, 2007). Arsenic contamination is a worldwide concern; it has drawn increasing attention due to the wide range of arsenic pollution and the toxicity of arsenic and its compounds to humans and other organisms.

Arsenic in the environment is a result of natural sources, such as volcanism, rock weathering and biological activity. It can also be released into the environment as a result of anthropogenic sources, such as agricultural practices (e.g., the use of herbicides/pesticides/insecticides containing arsenic) and industrial activities (e.g., wood preservation, mining, smelting, and tanning processes) (Bissen and Frimmel, 2003; Jain and Ali, 2000).

The soils near the cooperative gold mines in Bolivia, for example, have mean arsenic concentrations ranging from 13 to 64 ppm due to the presence of arsenopyrite as well as anthropogenic mining activities (Acosta et al., 2015). Arsenic concentrations in soils from Minas Gerais, Brazil, range from 200 to 860 ppm, while arsenic concentrations of the highly-polluted area in Lower Silesia, Poland, reach a level of 18,100 ppm due to human intervention (Rahman et al., 2014). In China, the concentrations of arsenic in soils from the Dexing copper mine areas range from an acceptable 2.2 ppm far from the mine site to as high as 899 ppm near the Dexing and Leping mining activities area (Teng et al., 2010; Teng et al., 2014). These levels exceed acceptable international arsenic concentration standards.

Furthermore, many groundwater sources have been observed to have arsenic

concentrations over 1000 μ g/L in many countries, including Argentina, Bangladesh, China, Greece, India, and United States (Rahman et al., 2014). This concentration of arsenic is far higher than the World Health Organization (WHO) guideline value of 10 μ g/L which is the level acceptable for human consumption (WHO, 2011). In addition, the United States Environmental Protection Agency (U.S. EPA) has reduced the permissible limit of arsenic in drinking water from 50 μ g/L to 10 μ g/L (U.S. EPA, 2001), while the cleanup guidelines for arsenic in soil vary from State to State (Teaf et al., 2010).

According to the Chinese Environmental Quality Standard for Soils, the permissible limit of arsenic is between 15 and 40 mg/kg, varying with soil characteristics (Table 1), while the Canadian maximum limit of inorganic arsenic in soils for the protection of environmental and human health is 12 mg/kg (CCME, 1997).

Table 1. Chinese Environmental Quality Standard for Soils (mg/kg) (Ministry of
Environmental Protection of the People's Republic of China, 1995)

Element	Level	Level one	Level two		Level three	
	рН	Background values	<6.5	6.5 - 7.5	>7.5	>6.5
Arsenic	Paddy fields	15	30	25	20	30
	Dry land	15	40	30	25	40

Note: Drinking water sources, pastures, protection zones, etc. must comply with level one; normal farmlands, vegetable fields, orchards, pastures etc. must comply with level two; forests, soils with high background value, farmlands near mines etc. must comply with level three.

1.2 Chemical characteristics of arsenic

Arsenic, being a pnictogen, can commonly occur in four oxidation states: -3, 0, +3,

and +5. It is found in various organic and inorganic compounds, with inorganic

compounds predominating in environmental media. Arsenite (As(III)) and arsenate

(As(V)) are the main inorganic forms in soils and water supplies and As(V) is the more common as well as less mobile species (Adriano, 2001; Guan et al., 2008). The toxicity of arsenic species to humans conforms to the following order: As(III) (e.g., H₃AsO₃) > As(V) (e.g., H₃AsO₄) > organic arsenicals (e.g., methylated species: CH₃AsO(OH)₂) (Fitz and Wenzel, 2002).

The speciation, mobility and (bio)availability of arsenic in soils are affected by many environmental factors such as the redox potential (Eh), the pH, the mineral presence such as phyllosilicates, iron, manganese and aluminum oxides (Masscheleyn et al., 1991; Adriano, 2001; Komárek et al., 2013).

Arsenic speciation is complex, as illustrated by a Pourbaix diagram (Figure 1), but inherently relies on both Eh value and pH value. A decrease in Eh value results in a shift to lower oxidation states for arsenic as these are reducing conditions. As(V) exists as H_3AsO_4 at pH below 2.3, whereas As(III) exists as H_3AsO_3 at pH < 9.5 within a certain range of Eh. With the increase of pH value, H_3AsO_4 and H_3AsO_3 undergo deprotonation and dissociation to form mobile and negatively-charged anionic species (Wang and Zhao, 2009).



Figure 1. The Eh-pH diagram for arsenic at 25 $^{\rm o}{\rm C}$ and 101.3 kPa (Mohan and Pittman, 2007)

1.3 Adverse effects of arsenic

In terms of ecological effects, for example, rice grown in monomethylarsonate (MMA) rich soils in the U.S. exhibited symptoms of straighthead disease due to the MMA accumulation (Meharg and Hartley, 2002). Also, the exposure of plants to As(V) may inhibit root growth or cause plant death (Meharg and Hartley, 2002). In experimental studies, hamsters treated with sodium arsenite(NaAsO₂) showed an increase in maternal mortality or prenatal mortality to varying degrees or a decrease in fetal weights (Golub et al., 1998).

Arsenic is one of the top 10 chemicals of significant concern to WHO because of its adverse effects on public health (WHO, 2014). Acute arsenic poisoning may cause vomiting, abdominal pain, diarrhea, or may even be lethal (Bissen and Frimmel, 2003).

Chronic arsenic poisoning may induce pigmentations, hyperkeratosis, cardiovascular diseases, neurological, and organic disorders, any of which may be a precursor to cancer.

In fact, arsenic and its compounds are classified as carcinogenic to humans by the U.S. EPA and the International Agency for Research on Cancer (U.S. EPA, 2012; IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 2012). As early as 1879, the high ratios of lung cancer in miners in Germany were attributed to the inhalation of arsenic (Smith et al., 2002). Wiencke et al. (1997) reported that As(III) can trigger mutation in human cells through the genetic modification.

In the early 1990s, a research study investigated 9202 people in Xinren Country, Guizhou Province, China, and found 16.80% of those individuals were affected by arsenicosis. The approximate average daily intake of arsenic by each person who lives in the affected area was 2.4 mg (87.92% from food, 5.53% from air and 6.55% from water) (Mandal and Suzuki, 2002).

1.4 Arsenic remediation

Various methods can be applied to mitigate arsenic contamination in environmental media, such as adsorption, oxidation, phytoremediation, and the use of membrane technologies.

1.4.1 Adsorption

Minerals alter the soluble arsenic concentrations in soil solution and/or pore water through adsorption and desorption processes (Sun and Doner, 1998). Surfaces of phyllosilicates (e.g. smectite, kaolinite, and vermiculite) have strong affinity for the adsorption of As(V) and As(III) in soils (Adriano, 2001), with As(V) having a stronger affinity than As(III). This increased affinity is a result of particle edges with positive charges being the preferred sites for the "adsorption of H_3AsO_4 (pK₁=2.20) and $H_2AsO_4^-$ (pK₂=6.97)" compared to H_3AsO_3 (pK₁=9.22) (Lin and Puls, 2000, p. 756).

Iron oxides are the major sinks for arsenic compounds and influence the transport process of arsenic in soils (Adriano, 2001). Arsenic adsorption on iron oxides enhances arsenic retention in soils. Iron oxides such as goethite(α -FeOOH) and hematite(α -Fe₂O₃) are widely used amendments for the *in situ* remediation of arsenic-contaminated soils. The formation of As(V)-Fe(III) inner sphere complexes via ligand exchange mechanism under strong oxidized conditions occur predominantly as bidentate or binuclear surface complexes (Miretzky and Cirelli, 2010).

In addition, granular activated carbon (GAC) has proved to be an effective adsorbent whereas Fe^{3+} modified GAC (GAC-Fe) is a better adsorbent with higher adsorption ability (Jang et al., 2008). Mondal et al. (2007) reported when using GAC, the maximum removal of As(III) and As(V) from an artificially contaminated groundwater were 41% and 71%, respectively. For GAC-Fe, the removal values for As(III) and As(V) increased to 93% and 98%, respectively. It has also been reported that FeSO₄ modified activated carbon shows a higher arsenic removal percentage than four types of FeSO₄ modified zeolites under the same experimental condition (Payne and Abdel-Fattah, 2005).

Many commercially available (modified) activated carbons are expensive. Therefore, researchers have been looking for easily available, readily regenerated, and low-cost substitutes. Recycling and reusing wastes to substitute for expensive adsorbents has received increasing attention. For example, agricultural byproducts such as rice husks have been used for aqueous arsenic remediation (Mohan and Pittman, 2007). Biochar byproducts, created by fast pyrolysis of biomass, have shown various capacities for the

removal of arsenic dependent upon the type of biomass. For instance, pine bark char removed 12.15 μ g As(III) per gram whereas pine wood char only removed 1.20 μ g per gram under the same experimental process (Mohan and Pittman, 2007).

1.4.2 Oxidation

As(III) is easily dissolved and readily available to plant roots compared with As(V). As a consequence, oxidation processes (e.g., chemical oxidation, photooxidation and biological oxidation) have been used to convert As(III) to As(V) as a method to immobilize arsenic. It is an effective technology for arsenic removal, followed by the subsequent adsorption/precipitation of the As(V) because As(V) can be adsorbed more readily on solid surfaces (Singh et al., 2015).

1.4.3 Phytoremediation

Phytoremediation, including phytoextraction, phytostabilization, phytovolatilization, and phytofilteration, is "the use of plants and their associated microbes for environmental cleanup" (Pilon-Smits, 2005, p. 16). Arsenic resistant plants can be classified into arsenic tolerant, accumulator, and hyperaccumulator plants. They can tolerate and grow in moderate to high arsenic containing soils without showing toxic symptoms (Roy et al., 2015).

The first known arsenic hyperaccumulator was *Pteris vittata* (brake fern). It accumulates large amounts of arsenic at concentrations much higher than the surrounding soil in a short time. For example, arsenic concentration in brake fern fronds increased to 15,861 ppm in two weeks, reaching 22,630 ppm after six weeks in soil spiked with 1,500 ppm arsenic, according to Ma et al. (2001).

In terms of arsenic phytovolatilization, Sakakibara et al. (2010) collected vapor samples from fronds of brake fern and were able to show that about 90% of the arsenic uptake amount was volatilized. However, this causes a further problem as arsenic released into the atmosphere results in secondary contamination.

1.4.4 The use of membrane technologies

Membrane technologies are typically very expensive and not particularly robust. They are able to remove arsenic from water systems, through the use of various pressure driver processes. Membrane's function as a selective barrier, rejecting arsenic, and thereby removing it from solution (Singh et al., 2015).

Coagulation and flocculation processes are applied to form arsenic bearing species with a larger particle size prior to microfiltration so as to increase the arsenic removal efficiency (Singh et al., 2015).

Using a reverse osmosis membrane to remove arsenic is the best available method for small water treatment systems (Singh et al., 2015). However, As(III) removal using a reverse osmosis membrane has a low efficiency. Walker et al. (2008) reported that over 95% of total arsenic was removed from wells where arsenic concentration exceeded 10 ppb, while the arsenic rejection efficiency was less than 45% at eight of the nine sites where As(III) was the dominant species.

1.5 Thesis research study

Many materials (e.g., goethite, hematite, and charcoal) have been studied as adsorbents because researchers are seeking new adsorbents that are more effective and more cost efficient than current commercial adsorbent products. In this case, if a waste material could be recycled and reused, not only will it adsorb arsenic from the natural environment, but it will also turn into a beneficial material.

1.5.1 Air activated disposable hand warmers

Worldwide, an increasing number of people, especially hikers, skiers, and other winter recreation enthusiasts, are using hand, foot, and body warmers in cold weather to protect their extremities. These warmers are disposable, light-weight, and low-cost (Sands et al., 2009).

The hand warmers (HW) used in this research study are the air activated disposable type sold under the brand name HotHands by Heatmax Incorporated. According to their Safety Data Sheet for these air-activated heating packs, the product consists of iron powder (50-60%), activated charcoal (5-10%), vermiculite (5-10%), water-adsorbent resin (1-5%), sodium chloride (1-5%), and water (30-40%). When the HW are exposed to air by shaking, there is an exothermic reaction (Fe+O₂ \rightarrow Fe₂O₃) which produces heat with the water acting as a medium and the salt catalyzing the reaction. In addition, the charcoal conducts the heat while vermiculite is an insulator to control the reaction rate (Sands et al., 2009). The hand warmer is a great invention, but a used hand warmer will be thrown out and it contributes to a landfill site.

Based on the background studies reviewed above, the retention of arsenic on adsorbents plays a vital role in arsenic removal in aqueous solutions as well as arsenic immobilization in soils. Phyllosilicates (such as vermiculite), iron oxides, and activated charcoal have been demonstrated to be relatively effective adsorbents for the reduction and immobilization of heavy metals and arsenic. These materials can be used to reduce the exposure of humans to heavy metals and arsenic through food ingestion and/or

through groundwater consumption. Groundwater may also be contaminated by leaching from contaminated soils (Miretzky and Cirelli, 2010; Singh et al., 2015; Mondal et al., 2007; Payne and Abdel-Fattah, 2005; Dixit and Hering, 2003; Malandrino et al., 2006). The literature survey indicates a majority of ingredients in HW are effective adsorbents, therefore, the hand warmer itself might be reused as a new form of adsorbent for arsenic remediation in the environment.

1.5.2 Objectives

Specifically, this research aims to (1) compare As(III) adsorption capacities on goethite, HW and three soils with different properties in aqueous solutions; (2) model As(III) adsorption on HW and three soils using kinetics and isotherm equations; (3) identify the influence of soil mineral components to arsenic adsorption; (4) determine the immobilization capacity of HW in soils for a short period of time; and (5) evaluate the effectiveness of HW for the removal of As(III) from aqueous solutions and for the immobilization of As(III) from soils.

Chapter 2 Materials and Methods

2.1 Materials

2.1.1 Soils

The surface (0 to 20cm) soil samples used in this study were collected from Dawangqiaocun, Taizhou, Zhejiang, China. Three soil samples (soil A, soil B and soil C) were collected on February 6th, 2015 from site 1 (28°30'58.8"N, 121°23'00.7"E), site 2 (28°30'55.9"N, 121°23'14.3"E) and site 3 (28°30'59"N, 121°23'20.5"E), respectively by Professor Hualin Chen at Wenzhou University.

The three sites are surrounded by e-waste dismantling and recycling facilities and other industrial factories. As shown in Figure 2, site 1 is situated in a dry farmland area 50 m from the road and 50 m from a closed factory, while site 2 lies right near an unknown factory. Site 3 is a rice paddy facing a village with several factories.

Half of each sample was stored in field moist condition in polyethylene bag at 4 °C in a refrigerator. The rest of each soil sample was air-dried at room temperature for one week, ground to pass through a 2 mm sieve, homogenized thoroughly, and stored in a polyethylene bag prior to use.



Figure 2. Soil sample collection sites

2.1.2 Chemicals and instruments

Disposable hand warmers (Hot Hands) were procured from Amazon (the Amazon Standard Identification Number of the product is B00D7H9LIA). Used hand warmers were mixed thoroughly, air dried and stored in a polyethylene bag prior to use.

Goethite-1 and other chemicals were purchased from established commercial sources. Goethite-2 was prepared by mixing a freshly made 1 M Fe(NO₃)₃•9H₂O solution with 5 M KOH solution. Specifically, 180 mL 5 M KOH was added rapidly into a 4 L polyethylene flask containing 100 mL 1 M Fe(NO₃)₃. Precipitated red-brown ferrihydrite appeared at once while stirring; and deionized water was immediately added to bring the total volume to 2 L. The polyethylene flask was sealed and left in an oven at 70 °C for 60 hours. Ferrihydrite was converted to a yellow brown goethite during that time. The supernatant was decanted, and the precipitate (i.e. goethite-2) was collected after being centrifuged, washed to remove any excess ions, and dried (Schwertmann and Cornell, 2008).

All chemicals were of analytical grade or better. Vessels were acid washed.

Samples used to determine the level of As(III) removed from aqueous solutions were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent Technologies 7500 series), while samples to determine the level of As(III) extracted from soils were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) (Agilent Technologies 5100).

All experiments were carried out in triplicate, except the determination of effective cation exchange capacity (CEC), the available phosphorus (available P), and the total element concentrations of soil samples were performed only in duplicate.

2.2 Basic methods

The basic physical and chemical properties of soil samples were measured including moisture content, pH (water), organic matter (loss of ignition), soil texture, total element concentrations, available P (Bray P-1) and effective CEC (0.1 M BaCl₂). Also, the physical and chemical properties of hand warmers were determined including moisture content, pH (water), total element concentrations, available P (Bray P-1) and effective CEC (0.1 M BaCl₂). Also, the CEC (0.1 M BaCl₂). The measurement of CEC and available P (Bray P-1) and effective CEC (0.1 M BaCl₂). The measurement of CEC and available P were conducted by Ministry of Environment in British Columbia (Analytical Chemistry Laboratory).

2.2.1 Moisture content

A field-moist sample (5.00 g) was transferred to a weighed beaker (W1). The beaker containing sample was weighed (W2) and oven dried at 105 °C for at least 24 hours until it had a constant weight. The beaker and sample were then cooled in a desiccator for 30 minutes before weighing (W3) (Kalra and Maynard, 1991).

water content (% by weight) =
$$\frac{W_2 - W_3}{W_3 - W_1} * 100$$
 (1)

2.2.2 рН

The pH was determined in a 1:2 w/v suspension of air-dried soil and water (Kalra and Maynard, 1991). The suspension was stirred every 5 minutes for 30 minutes and settled for 30 minutes at room temperature prior to pH determination using a digital pH meter (Thermo Orion 550A).

2.2.3 Organic matter

The approximate percentage of organic matter is estimated by loss on ignition (Kalra and Maynard, 1991).

Each porcelain crucible was heated at 375 °C for one hour. After the temperature dropped to 150 °C, the crucible was placed in a desiccator for 30 minutes to cool down before weighing (W1). A weighed oven-dried soil sample (about 5.000 g) (W2) was put into each crucible. The crucible was placed in a muffle furnace and heated up slowly to a temperature of 375 °C for 16 hours. After the temperature dropped to 150 °C, the crucible containing the soil sample was placed in a desiccator for 30 minutes and weighed (W3).

loss of ignition (% by weight) =
$$\frac{W_2 - (W_3 - W_1)}{W_2} * 100$$
 (2)

2.2.4 Soil texture

Soil samples were separated into three particle sizes, sand (>50 μ m), silt (2-50 μ m) and clay (<2 μ m), following the pipette method (Kalra and Maynard, 1991).

Each soil sample was mixed and dispersed into deionized water and then pass through a 53 μ m sieve. After wet sieving, the retained sand on the sieve was collected and dried in an oven at 105 °C for at least 24 hours. The remainder (clay and silt suspension) was

placed in a 2 L beaker and deionized water was added to increase the volume to 1.5 L. The beaker was allowed to settle until the silt sank to the bottom and the clay fraction contained in the liquid layer was siphoned and transferred into another beaker using a vacuum suction setup (Figure 3). The silt was washed repeatedly (nine times cycles) to remove all the clay particles until the supernatant was clear.

The clay fraction was then flocculated by adding 20 mL 0.5 M CaCl₂. After flocculating, the supernatant was discarded using the suction setup. The clay fraction was placed in an oven and dried at 105 °C for at least 24 hours. The silt was allowed to settle to the bottom of the 2 L beaker and the supernatant was discarded. The silt was dried at 105°C for at least 24 hours and retained for future analysis.

sand fraction (% by weight) =
$$\frac{\text{sand (g)}}{\text{ovendried soil (g)}} * 100$$
 (3)

clay fraction (% by weight) =
$$\frac{\text{clay (g)}}{\text{ovendried soil (g)}} * 100$$
 (4)

silt fraction (% by weight) = 100 - sand(%) - clay(%) (5)



Figure 3. The vacuum suction setup

2.2.5 Mineral analysis

The Bruker D8 Discover X-ray diffractometer was utilized for X-ray diffraction (XRD) analysis. XRD patterns were used to determine the mineral composition employing EVA software to calculate major XRD pattern peaks to establish the mineral identity of the soil particles.

Each of the sand fraction and silt fraction (about 100 mg each sample) was ground into fine particles with diameter of ~50 μ m using a mortar and pestle respectively. Each ground sample was wetted with deionized water and the resulting paste was spread evenly onto a labelled glass slide before being allowed to air-dry. Full scans (3 to 90° 2 Θ) were carried out at ambient condition to identify mineral composition using the XRD. Ca-saturated clay suspension (~30mL) was added into each of seven 40 mL centrifuge tubes. Tubes were centrifuged at 64 g for 3 minutes and the supernatants were decanted. About 20 mL 1M KCl was added into four of the seven tubes and thoroughly mixed with the clays. The mixtures were centrifuged at 64 g for 3 minutes. This process was repeated three times to ensure the resulting clay was K-saturated. Deionized water (~20mL) was added to each of the seven tubes to remove Cl- through centrifugation (using a centrifuge speed between 2,851 and 6,415 g for 3 minutes). The process was repeated until Cl- was totally removed as indicated by addition of 0.1M AgNO₃.

Each of the Ca-saturated and K-saturated clays was smeared on a glass slide and air dried then subjected to the following seven treatments for XRD analysis: (1) Ca saturated 54% relative humidity (RH) treatment; (2) Ca saturated ethylene glycol treatment; (3) Ca saturated glycerol treatment; (4) K saturated 0% RH treatment; (5) K saturated 54% RH treatment; (6) K saturated 300 °C treatment; (7) K saturated 550 °C treatment (Arocena and Sanborn, 1999). Single scans (3 to 36° 2 Θ) were subsequently conducted at ambient condition.

2.2.6 Elemental content analysis

Total elemental analysis was conducted on microwave digested soil samples using a modified digestion procedure U.S. EPA 3051A (U.S. EPA, 1995). All tubes were acid washed and rinsed with deionized water before they were placed in an oven and dried at 105 °C. The weight of each sample was determined individually (approximately 0.1500 g was used). The sample was placed in a tube. One blank sample and two reference samples (one being a replicate) was prepared for each set of samples prior to digestion. The reference soil sample used was TILL-3 which was collected from O'Brien Mine, near

Cobalt, Ontario. Concentrated HNO₃ (3 mL) and concentrated HCl (1.5 mL) were added to the tube in a fume hood and the tubes were carefully shaken and capped. A set of 15 samples was placed into the microwave digestion chamber at one time and digested using a single reaction chamber microwave digestion system. After digesting, samples were transferred to 15mL tubes and deionized water was added to a total volume of 15 mL each.

A strong magnet was used to separate the magnetic particles from soil A, B and C, respectively, and the remaining residues are non-magnetic soils. Each sample was also microwave digested and its arsenic content was determined by ICP-MS. The magnetic and non-magnetic soil particles were considered as iron-rich and iron-poor soil particles, respectively.

Elemental analysis (ICP-MS and ICP-OES) was performed by the Northern Analytical Laboratory Services at University of Northern British Columbia. The analysis provided total concentrations for each element, regardless of speciation.

2.3 Experimental design

2.3.1 As(III) removal in aqueous solutions

This experiment aimed to determine adsorption equilibration time, adsorption efficiency, and adsorption capacity for the HW, and all three soil types in regard to As(III) removal in aqueous solution. Adsorption experiments were carried out by adding adsorbents (including HW, soil samples and other adsorbents) into aqueous solutions containing As(III). A stock solution containing 1000 ppm As(III) as NaAsO₂ was made and used for all experiments.

HW and soil A, B, and C were applied separately as adsorbents to estimate their adsorption equilibration times. Each adsorbent was weighed (0.500 g) into an acidwashed 40 mL centrifuge tube. The stock NaAsO₂ solution was diluted 100-fold to give a 10 ppm solution and a 25 mL aliquot was added to each centrifuge tube. The tube was shaken (E6010 reciprocating shaker, Eberbach Corporation) at 280 osc/minute at room temperature for a period of time (1, 2, 4, 8, 16 and 24 hours). For the HW sample, additional tubes were shaken to a total of 48 and 72 hours to ensure that an equilibrium was attained. Suspension samples were centrifuged at 713 g for 3 minutes after shaking and filtered through a 0.45 µm nitrocellulose membrane filter using Nalgene filter-ware.

In order to compare the adsorption effectiveness of particles from soils and determine which ingredient from HW is more effective at adsorbing As(III), each component (goethite, sand A, B, and C, silt A, clay A, Fe₂O₃, and activated charcoal) was added individually under the same experimental condition. Fe₂O₃ and activated charcoal were purchased from established commercial sources. These various mixtures were shaken for 24 hours which was determined to be sufficient for equilibration in both soils and HW.

Goethite has been shown to be a useful adsorbent by many other researchers (Antelo et al., 2005) and therefore it was applied in this experiment as a reference to compare with the adsorption effectiveness of the other adsorbents.

HW and soil A, B, and C were applied, respectively, as adsorbents under the same experimental conditions as above except with varying As(III) concentrations in each solution to obtain their adsorption isotherms. As(III) concentrations of 1, 10, 100, 500 and 1000 ppm were used and the resulting solution were shaken for 24 hours.

Experiments were performed in triplicate.

2.3.2 As(III) immobilization in soils

Each soil A, B, and C sample (~200 g) was spiked with As(III) as NaAsO₂ solution to artificially increase the total arsenic concentration in the soil by 100 ppm. Soils were thoroughly mixed with NaAsO₂ solution and stored in mason jars in the dark at room temperature (20 °C), with moisture content at approximately field capacity. The soils were left open to equilibrate for 20 weeks with deionized water being added weekly to maintain a constant moisture content. After 20 weeks of equilibration, the soils were removed from mason jars, air dried, and homogenized by passing through a 2 mm sieve. Total arsenic contents were measured after digestion using the above procedure in triplicate by ICP-OES.

At the end of the 20 weeks of As(III)-spiked soil equilibration, the amendment, HW, was thoroughly mixed with each air-dried arsenic-contaminated soil at 5% w/w ratio (0.150 g HW was mixed with 3.000 g air-dried soil) in a glass vial and a blank control without adding HW was set in triplicate, respectively. All glass vials were stored in the dark at room temperature equilibrating for 1, 2, 4 and 8 weeks, respectively. Deionized water was added weekly to maintain the moisture content at 30% (0.9 mL H₂O per 3.000 g air-dried solids).

This experiment aimed to examine the effect of the addition of HW on the water solubility of arsenic and changes in the arsenic fraction through the water extraction procedure and sequential extraction procedure (SEP). The content of five arsenic fractions was determined following a modified procedure based on Wenzel et al. (2001). The arsenic fractions are shown in Table 2. Fraction 5 (F5) represents the residual arsenic.

Extraction	Fractions	Extractant	Soil: solution	Extraction conditions	Extractable phase
step			ratio (w/v)		
1	Fraction 1 (F1)	0.05 M (NH ₄) ₂ SO ₄	1:25	shaking for 4 hours in the	Non-specifically
				light at room temperature	sorbed arsenic
2	Fraction 2 (F2)	0.05 M (NH4)H ₂ PO ₄	1:25	shaking for 16 hours in the	Specifically sorbed
				light at room temperature	arsenic
3	Fraction 3 (F3)	0.2 M NH ₄ -oxalate	1:25	shaking for 4 hours in the	Bound to
		buffer; pH 3.25		dark at room temperature	amorphous iron
					oxides
4	Fraction 4 (F4)	0.2 M NH ₄ -oxalate	1:25	heating in water bath for 30	Bound to
		buffer; 0.1 M C ₆ H ₈ O ₆ ;		minutes in the light at 96±3	crystalline iron
		рН 3.25		°C	oxides

Table 2. Details of the	sequential extract	ion procedure for	arsenic (Wenzel	et al., 2001)
	Sequential entitaet	fon procedure for		· • • • • • • • • • • • • • • • • • • •

Fraction 5 (F5) represents the residual arsenic.

At five times (0, 1, 2, 4 and 8 weeks) during the experiment, the soil samples were removed from vials and air dried for 24 hours and a 1.000 g of each sample along with 25 mL deionized water was added into a 40 mL centrifuge tube. The tube was shaken for 24 hours and then centrifuged at 713 g for 3 minutes. The supernatant was filtered through a 0.45 µm nitrocellulose membrane filter using Nalgene filter-ware.

For soils without any incubation (0 week) and soils incubated for 8 weeks, 25 mL deionized water was added again and shaken for further 24 hours, followed by repeating subsequent steps. These water sequential batch extractions were repeated a total of five times.

Each of the extracts was transferred to a labelled conical tube for ICP-OES analysis.

The fractionation of arsenic in soils without incubation (0 week) and soils after 8 weeks' incubation was also determined by the modified SEP (Table 2). The arsenic contents of extracts from (NH₄)₂SO₄ and NH₄H₂PO₄ represent weakly (non-specifically) and strongly (specifically) sorbed arsenic contents, respectively. Furthermore, arsenic bound to amorphous iron oxides and arsenic bound to crystalline iron oxides are extracted by the 3rd step and the 4th of SEP. Residual arsenic was calculated by subtracting the sum of the four arsenic fractions from the total arsenic content in soil.

Each homogenized air-dried soil (1.000 g) was mixed with 25 mL of extractant and went through the extraction conditions. A subsequent washing step was carried out after the 3rd and 4th extraction steps in order to collect arsenic trapped in the remaining soil. The washing step was eliminated for the 1st and 2nd extraction steps because the low amount of arsenic carry-over to subsequent extraction steps would hardly affect the results (Wenzel et al., 2001). The washing step involved adding 12.5 mL of 0.2 M NH₄-

oxalate (pH 3.25) to make the soil: solution ratio 1:12.5 (w/v), with 10 minutes of shaking in the dark.

Each sample was centrifuged at 257 g for 15 minutes after each extraction step as well as a washing step. After centrifugation, the supernatant was filtered through a 0.45 µm nitrocellulose membrane filter using Nalgene filter-ware.

Each of the extracts was transferred to a labelled conical tube for ICP-OES analysis.

2.4 Statistical analysis

Analysis of variance (ANOVA) and least significant difference comparison were conducted to compare mean values of the results. Independent-samples T-tests were conducted when needed. Mean values and Standard deviations (SD) are presented in tables and figures. Microsoft Excel and SPSS Statistics software were used to do data analysis. Microsoft Excel was also used for plotting.

Chapter 3 Results and Discussion

3.1 Physicochemical characteristics of soils and hand warmers

The data of physical and chemical properties (Table 3) and element concentrations (Tables 5 and 7) of soils and HW were analyzed and the independent-samples T-tests were applied.

Table 3 shows the differences among three types of soil. Soil A is a relatively neutral soil and soils B and C are acidic soils and the water contents of both soil A (460.9 g/kg) and soil B (489.1 g/kg) are significantly higher than soil C (360.7 g/kg). In addition, the effective CEC of soils follows the order: soil B (14.01 cmol+/kg) > soil C (12.80 cmol+/kg) > soil A (11.14 cmol+/kg). Moreover, the difference in soil particle sizes is indicative of the varying soil textures. Soils A, B, and C exist as loamy sand, silty clay loam, and silt loam, respectively. The arsenic movement in soils is influenced by the soils of different textures.

Soil C has a significantly higher amount of available phosphorus: soil C (92.26 mg/kg) > soil B (27.42 mg/kg) > soil A (2.722 mg/kg). Phosphorus compounds, such as phosphate(PO_4^{3-}), and arsenic compounds, such as AsO_4^{3-} , have the same charge and tetrahedral configuration. Phosphorus anions can compete with arsenic anions for adsorption sites on adsorbents resulting the replacement of absorbed arsenic and arsenic will be released into the environment. The large amount of phosphate is capable of hindering the arsenic remediation process and promoting the desorption of arsenic from OM (e.g., humic acids) and mineral surfaces (Henke, 2009).

Based on the total element concentrations for the soils spiked with 100 ppm As(III) (Table 4) and the original total arsenic concentrations (Table 5), soil A has a significantly

higher contamination level for all the heavy metals and arsenic compared to soils B and C. Therefore, we can surmise the soil A is probably contaminated by the waste dumped by the closed factory nearby or dust produced by the factory. But the increased arsenic concentration could also be a consequence of the adsorption process by iron minerals. The iron concentration in soil A is 85,950 mg/kg. It is more than two times that in soils B and C as well as three times greater than the median iron content (26,000 mg/kg) in soils throughout the U.S. (Shacklette and Boerngen, 1984). Perhaps the higher value of iron concentration in soil A promotes the heavy metals and arsenic adsorption and accumulation in soil A.

Furthermore, the level of OM in soil A is 390.1 g/kg, which is six-fold greater than either soil B (63.2 g/kg) or soil C (58.4 g/kg). This could be another reason for the high amount of heavy metals and arsenic. Whether iron minerals or OM, heavy metals and arsenic can be retained in soils through the complexation process of ions (Sparks, 2003).

The iron-rich soil particles separated magnetically demonstrated a much higher arsenic content than the remaining particles (iron-poor) as well as the pre-separated soils (Table 5). This is further indication of the good adsorption capacity of iron minerals.

Compared with the three soil samples, the significantly higher value of CEC (32.43 cmol⁺/kg) of hand warmers is capable of promoting the absorption of metal cations. The HW only have 1.201 mg/kg available phosphorus, and it may reduce the competitive adsorption between phosphorus compounds and arsenic compounds. HW are rich in Fe (492,500 mg/kg), which is significantly higher than any of the soil samples. These characteristics of HW imply that HW have a potential adsorption capacity for heavy metals and arsenic.

Properties	Soil A	Soil B	Soil C	HW
pH (1:2 H ₂ O)	7.66 (0.02)	5.86 (0.02)	4.57 (0.01)	7.70 (0.03)
Water content (g/kg)	460.9 (1.1)	489.1 (14.4)	360.7 (1.9)	60.3 (0.1)
OM (g/kg)	390.1 (1.4)	63.19 (0.20)	58.41 (0.82)	ND
Effective CEC (cmol+/kg)	11.14 (0.08)	14.01 (0.13)	12.80 (0.13)	32.43 (0.13)
Available P (mg/kg)	2.722 (0.668)	27.42 (0.15)	92.26 (1.38)	1.201 (0.052)
Soil texture	loamy sand	silty clay loam	silt loam	ND
Sand (>50 μ m) (% by weight)	74.19	0.97	1.35	ND
Silt (2-50 µm) (% by weight)	21.32	67.52	75.20	ND
Clay (<2 µm) (% by weight)	4.49	31.51	23.45	ND

Table 3. Mean (\pm SD) of physical and chemical properties of soils and HW

ND: not determined

	Soil A	Soil B	Soil C	HW
Arsenic	130.1 (5.7)	114.5 (1.1)	104.1 (3.6)	4.053 (0.025)
Cadmium	103.3 (2.3)	1.656 (0.098)	1.430 (0.069)	7.098 (0.227)
Chromium	377.9 (22.7)	68.54 (1.48)	62.60 (0.14)	126.3 (3.8)
Copper	13,290 (210)	537.7 (15.7)	173.1 (9.1)	129.6 (5.2)
Iron	85,950 (2060)	39,670 (1160)	40230 (80)	492,500 (9800)
Manganese	1,685 (32)	492.1 (7.3)	450.7 (4.4)	1,990 (122)
Lead	2,722 (82)	93.04 (3.17)	64.66 (1.52)	14.70 (0.11)
Zinc	5,616 (81)	739.1 (23.65)	316.3 (4.2)	17.37 (1.18)

Table 4. Mean (±SD) of total element concentration of soils spiked with 100 ppm As(III) and non-spiked HW (mg/kg) (n=3)

ND: not determined
	Soil A	Soil B	Soil C
Arsenic in soils	16.63 (1.94)	3.651 (0.003)	4.664 (0.217)
Arsenic in iron-rich (magnetic) soils	18.64 (1.81)	6.118 (0.346)	7.069 (1.072)
Arsenic in iron-poor (non-magnetic) soils	5.465 (0.072)	ND	ND

Table 5. Mean (±SD) of arsenic concentration of original soils and their magnetic and non-magnetic particles (mg/kg) (n=3)

ND: not determined

3.2 Soil mineral composition

Table 6 shows the major standard d-spacings of minerals that were recognized in the sand and silt samples and they were utilized for identification. The intensity of the actual reflections varies from sample to sample and within the samples, even for the same mineral. The reflections with high intensity of each mineral were obtained in the XRD patterns. Only three reflections of each mineral have been labelled on the sand and silt patterns.

Sand A has quartz, albite, anhydrite and calcite, whereas silt A is a more complex mixture, including quartz, albite, calcite, beyerite and goethite (Figures 4 and 7). In sand B, sand C, silt B, and silt C, quartz, albite and mica(muscovite) were identified (Figures 5, 6, 8 and 9).

Clay minerals give diagnostic d-spacings (interplanar or diffraction spacing) via different treatments at varying temperatures. At high temperatures, certain clay minerals (e.g., kaolinite) will collapse or be unstable (Sparks, 2003). These characteristics help in clay identification. Mica was identified in all three clay samples (A, B, and C) by the 1.0 nm d-spacing observed in all XRD spectra obtained from the seven treatment methods (Figures 10, 11 and 12). Kaolinite was identified in all the three clays by the reflections at 0.71 nm and the doublet reflections at 0.357 nm, but the reflections at 0.71 nm and 0.357 nm disappeared when clays were heated to 550 °C (Figures 10, 11 and 12). Chlorite was recognized in clay B and C by the reflections at 1.4 nm and the doublet reflections at 0.354 nm that were unaffected by any_treatment (Figures 11 and 12).

Isomorphous substitution is "the replacement of one atom by another of similar size in a crystal structure without disrupting or seriously changing the structure" (Soil Science Society of America, 1997, p.59). It plays a vital role in creating negative charge in clays. The isomorphous substitution of Al³⁺ for Si⁴⁺ creates a net negative charge on the structure of mica and chlorite. Furthermore, kaolinite has little isomorphous substitution. The charge on kaolinite is pH dependent, because its CEC is mainly provided by the dissociation of protons from hydroxyl groups (Strawn et al., 2015). In acidic environment, the layer is positively charged due to the formation of R-OH²⁺, while in alkaline environment, the layer forms negatively charged R-O⁻ because of deprotonation. Overall, the types of clay mineral have an effect on CEC in soils.

Mineral name	Major d-spacings (nm)
Albite	0.367, 0.323, 0.322, 0.321, and 0.320
Anhydrite	0.349, 0.285, 0.233, 0.221, and 0.187
Beyerite	0.285, 0.272, 0.214, 0.175, and 0.169
Calcite	0.303, 0.228, 0.209, 0.191, and 0.187
Goethite	0.418, 0.269, 0.258, 0.245, and 0.172
Mica (Muscovite)	0.449, 0.376, 0.352, 0.337, and 0.257
Quartz	0.425, 0.334, 0.245, 0.228, and 0.182

Table 6. Major d-spacings of mineral X-ray diffraction patterns



Figure 4. XRD pattern of the sand fraction from soil A. Quartz, albite, anhydrite, and calcite were detected



Figure 5. XRD pattern of the sand fraction from soil B. Quartz, albite, and muscovite were detected



Figure 6. XRD pattern of the sand fraction from soil C. Quartz, albite, and muscovite were detected



Figure 7. XRD pattern of the silt fraction from soil A. Quartz, albite, calcite, beyerite, and goethite were detected



Figure 8. XRD pattern of the silt fraction from soil B. Quartz, albite, and muscovite were detected



Figure 9. XRD pattern of the silt fraction from soil C. Quartz, albite, and muscovite were detected



Figure 10. XRD patterns under seven treatments of the clay fraction from soil A. Mica and kaolinite were detected



Figure 11. XRD patterns under seven treatments of the clay fraction from soil B. Mica, kaolinite, and chlorite were detected



Figure 12. XRD patterns under seven treatments of the clay fraction from soil C. Mica, kaolinite, chlorite, and smectite were detected

3.3 As(III) removal in aqueous solutions

3.3.1 Effectiveness of soils and hand warmers on As(III) removal

The time dependence curves for As(III) removal efficiency from NaAsO₂ solution by soil samples and HW, with an initial As(III) concentration of 10 ppm, is shown in Figure 13. Initially, it was generally found that the percentage of As(III) increased for each soil type with time. Further, over the time span used in these experiments, it would appear each soil reached adsorption capacity or an equilibrium was established.

The results indicated that 68.12% As(III) was adsorbed on to soil A at an equilibrium time of 24 hours, which is substantially higher than soils B and C with As(III) removal percentage of 32.29% and 24.85% (Figure 13 and Table 7). This result is consistent with the concentration of iron in each soil sample. Iron and its compounds are known as the major sinks for arsenic compounds in soils. Consequently, the high amount of iron

compounds, and specifically goethite, present as effective arsenic adsorbents. Soil A has a higher removal efficiency than soils B and C in an initial As(III) concentration of 10 ppm. It can also be explained by the significantly higher amount of OM in soil A (39.01%) compared to soils B and C.

However, when the concentration of As(III) increased to 1000 ppm, 3.70 mg As(III) was absorbed on to each gram of soil A, while 7.05 mg and 8.39 mg As(III) were absorbed on to each gram soil B and soil C, respectively, at saturation (Table 8). The adsorption percentage of soil A decreased dramatically to 7.40%, which is less than either soil B (14.10%) or soil C (16.77%). The reason might be that soil A has limited adsorption sites.

Table 7 indicated that the removal efficiencies of different soil A particles in 10 ppm As(III) solution following the order: clay (77.70%) >silt (69.24%) >sand (41.35%), which is in contrast to the relative size of the particles in each compound. This is consistent with smaller particle size resulting in a higher specific surface area, and the potential for more adsorption sites available for ion exchange and/or adsorption processes.

In the first hour, the As(III) adsorption onto HW rapidly achieved 94.81%. However, over time the total amount of As(III) absorbed continued to drop to a steady state of around 90% (Figure 13). Using a low As(III) concentration (10 ppm), 88.56%, 99.90%, 88.44% and 97.74% of As(III) was adsorbed by HW, goethite, charcoal and Fe₂O₃, respectively, at an equilibrium time of 24 hours.

At lower As(III) concentrations (10 ppm), the adsorption capacity of HW is very close to straight charcoal, although it is also in between its major ingredients (i.e., Fe_2O_3 and charcoal) and lower than goethite. However, when the As(III) concentration was

increased to 1000 ppm, the adsorption percentages of HW, goethite, charcoal and Fe_2O_3 dropped to 34.03%, 19.16%, 10.45% and 14.69%, respectively, (Table 7) where the HW material exhibited the greatest saturation extent. Table 8 demonstrates each gram of HW absorbed as much as 17.02 mg As(III) when exposed to a 1000 ppm As(III) solution at equilibrium. As an adsorbent, although HW do not show any obvious advantage when the As(III) concentration is low, the HW performed far better in the presence of a high As(III) concentration. From this, it can be concluded HW are an effective adsorbent with high As(III) adsorption capacity and worthy further study.



(a)





Figure 13. Effect of shaking time on As(III) adsorption in an initial As(III) concentration of 10 ppm. (a) soils A, B, and C as the adsorbent, respectively; (b) HW as the adsorbent. Symbols represent mean values and error bars are the corresponding SD (n=3)

Adsorbents	10 ppm As(III) removal efficiency of	1000 ppm As(III) removal			
	the adsorbent (%)	efficiency of the adsorbent (%)			
Soil A	68.12 (1.44)	7.40 (0.72)			
Soil B	32.29 (1.63)	14.10 (2.12)			
Soil C	24.85 (0.31)	16.77 (3.25)			
Sand A	41.35 (2.38)	ND			
Sand B	20.61 (1.79)	ND			
Sand C	23.82 (2.26)	ND			
Silt A	69.24 (2.05)	ND			
Clay A	77.70 (1.95)	ND			
HW	88.56 (0.43)	34.03 (2.14)			
Goethite-1	99.04 (0.07)	ND			
Goethite-2	99.90 (0.05)	19.16 (2.64)			
Charcoal	88.44 (0.83)	10.45 (1.67)			
Fe ₂ O ₃	97.74 (1.17)	14.69 (0.57)			

Table 7. As(III) removal efficiency (\pm SD) at a reaction equilibrium time of 24 hours (n=3)

ND: not determined

Adsorbents	Adsorption capacity (mg/g)
Soil A	3.70
Soil B	7.05
Soil C	8.39
HW	17.02
Goethite-2	9.58
Charcoal	5.23
Fe ₂ O ₃	7.35

Table 8. The adsorption capacity of adsorbents in 1000 ppm As(III) solution at a reactionequilibrium time of 24 hours

3.3.2 Adsorption kinetics

Pseudo first-order, pseudo second-order and intra-particle diffusion kinetic models were applied in order to establish the kinetics of arsenic adsorption on soil samples and HW with an initial As(III) solution concentration of 10 ppm. The conformity between experimental data and the predicted values from the model was expressed using the correlation coefficients (\mathbb{R}^2). A model with a relatively high \mathbb{R}^2 indicates the model is able to describe the kinetics of As(III) adsorption, and the dependent variable is predictable by using this model.

The pseudo first-order model equation is expressed as (Oke et al., 2008):

$$\ln(q_e - q_t) = \ln q_e - \frac{k_f}{2.303}t$$
(6)

where q_e and q_t are adsorption capacity at equilibrium (mg/g) and adsorption capacity at time t (mg/g), respectively, t is the reaction time (hour) and k_f is the rate constant of pseudo first-order adsorption. If the adsorption fits the pseudo first-order model, a plot of $\ln(q_e - q_t)$ (dependent variable) versus t (independent variable) should give a linear relationship. From the resulting plot, q_e and k_f can be determined from the slope and intercept, respectively. Figure 14 and Table 9 show the results of the fit of a pseudo first-order model.



Figure 14. Pseudo first-order model of As(III) adsorption on adsorbents. Soil A, soil B, soil C and HW as the adsorbent, respectively.

The pseudo second-order model equation is expressed as (Oke et al., 2008):

$$\frac{t}{q_{t}} = \frac{1}{k_{s}q_{e}^{2}} + \frac{1}{q_{e}}t$$
(7)

where q_e , q_t , and t are as defined above. k_s is the rate constant of pseudo second-

order adsorption.

If the adsorption fits the pseudo second-order model, a plot of $\frac{t}{q_t}$ versus t should result in a linear relationship. The values of q_e and k_s can then be determined from the slope and intercept of the plot, respectively. Figure 15 and Table 9 indicate the results of the fit of a pseudo second-order model.



Figure 15. Pseudo second-order model of As(III) adsorption on adsorbents. Soil A, soil B, soil C and HW as the adsorbent, respectively.

The intra-particle diffusion model equation is expressed as (Wu et al., 2009):

$$q = k_i t^{\frac{1}{2}} + C \tag{8}$$

where q is adsorbed phase concentration (mg/g), t is the reaction time (hour), k_i is the rate constant of intra-particle diffusion and C relates to the boundary layer thickness.

If the adsorption fits the intra-particle diffusion model, a plot of q versus $t^{\frac{1}{2}}$ should have a linear relationship, with a slope of k_i . Figure 16 and Table 9 show the intra-particle diffusion model and values.



Figure 16. Intra-particle diffusion model of As(III) adsorption on adsorbents. Soil A, soil B, soil C and HW as the adsorbent, respectively.

Table 9 shows that the values of correlation coefficient of soils A and B decrease from pseudo second-order model, pseudo first-order model to intra-particle model, while the values of correlation coefficient of soil C decrease from pseudo second-order model, intra-particle model to pseudo first-order model. For HW, the order of correlation coefficient is: pseudo second-order model (0.992)> pseudo first-order model (0.598)> intra-particle model (0.157). This indicates adsorption of As(III) fits into pseudo secondorder kinetics with a correlation coefficient value ranging from 0.978 to 0.998. The values of correlation coefficient are statistically significant at the 95% confidence level. The calculation values of q_e derived from pseudo second-order model are 0.299, 0.142, 0.108 and 0.399 mg/g which is close to experimental values (0.278, 0.129, 0.100 and 0.392 mg/g). Overall, the sorption data are consistent with chemical adsorption reactions.

Adsorbent	pseudo first-order			pseudo	second-o	order	intra-particle		
	k _f	q _e	R ²	k _s	q _e	R ²	ki	С	R^2
Soil A	0.447	0.192	0.987	1.733	0.299	0.998	0.040	0.101	0.942
Soil B	0.250	0.047	0.495	5.506	0.142	0.978	0.015	0.069	0.707
Soil C	0.366	0.063	0.968	4.576	0.108	0.993	0.013	0.039	0.955
HW	0.045	0.039	0.948	2.770	0.399	0.992	0.004	0.356	0.157

Table 9. The adsorption kinetic model rate constants for the NaAsO2 solution containing10 ppm As(III) by using different adsorbents

3.3.3 Adsorption isotherms

Langmuir and Freundlich equations were applied to describe As(III) adsorption on the three different soil samples and HW. The adsorption isotherms for As(III) adsorption were examined by non-linear regression analysis using SPSS statistics software in order to analyze and compare the Langmuir and Freundlich isotherms for each soil type and the HW. The adsorption of As(III) was modelled using the Langmuir isotherm equation and the Freundlich isotherm equation, respectively. The relationship between the adsorbed amount of As(III) on the adsorbent and the amount in the aqueous solution was plotted to calculate the constant values for each isotherm and determine which isotherm fits the measured data better.

Langmuir equation is built on the assumptions that the surface is homogeneous and there is a fixed number of identical adsorption sites that only allow monolayer coverage. Langmuir isotherm equation is expressed as (Sparks, 2003):

$$Q_e = \frac{Q_{\max} * K_l * C_e}{1 + K_l * C_e}$$
(9)

where Q_e and C_e are the amount of adsorption at equilibrium (adsorbate per unit mass of adsorbent) (mg/g) and arsenic concentration in solution at equilibrium (mg/L), respectively. Q_{max} is the maximum amount of the adsorbate that can be adsorbed on to the adsorbent (mg/g) and K₁ is the Langmuir isotherm constant related to binding strength.

Freundlich isotherm equation is a purely empirical model. It assumes the adsorption capacity is infinite which means it does not provide an adsorption maximum. The Freundlich isotherm is given as follows (Sparks, 2003):

$$Q_e = K_f * C_e^{\frac{1}{n}}$$
(10)

where Q_e and C_e are as defined above. K_f is a Freundlich isotherm constant known as the distribution coefficient and n is a correction factor.

The plots of C_e and Q_e for each soil type and HW are given in Figures 17, 18, 19, and 20, respectively. The predicted curves were created by measured experimental results by fitting both Langmuir and Freundlich isotherm models.



Figure 17. Langmuir and Freundlich isotherm models of As(III) adsorption on soil A



Figure 18. Langmuir and Freundlich isotherm models of As(III) adsorption on soil B



Figure 19. Langmuir and Freundlich isotherm models of As(III) adsorption on soil C



Figure 20. Langmuir and Freundlich isotherm models of As(III) adsorption on HW Table 10. Langmuir and Freundlich constants and coefficients of determination (R²) for the fit of As(III) adsorption

Adsorbents	Langmuir			Freundlich			
	Q _{max}	Kı	R ²	n	K _f	R ²	
Soil A	3.734	0.014	0.996	3.067	0.406	0.964	
Soil B	2.280	-0.058	0.173	0.483	6.60*10 ⁻⁶	0.977	
Soil C	2.712	-0.055	0.165	0.596	1.12*10 ⁻⁴	0.994	
HW	16.507	0.015	0.991	2.557	1.310	0.989	

Table 10 provides the constants and correlation coefficients (R²) from Langmuir and Freundlich equations. Correlation coefficients were applied to demonstrate the conformity between experimental data and the predicted values.

Based on the 95% confidence level, only the data of soil A and HW were well fitted with Langmuir model, while all the data were well fitted with Freundlich model. The R^2

in Langmuir model followed the order: soil A (0.996)> HW (0.991)> soil B (0.173)> soil C (0.165). The R² in Freundlich model followed the order: soil C (0.994)> HW (0.989)> soil B (0.977)> soil A (0.964). Therefore, Freundlich model is ideal for HW and soils A, B and C, whereas Langmuir model has a slight advantage for soil A and HW.

Table 10 indicated the Q_{max} values of soil A and HW are 3.73 and 16.51 mg/g, respectively. The values are close to the corresponding values (3.70 and 17.02 mg/g) shown in Table 8, which means all the available adsorption sites were occupied by arsenic once soil A and HW were added to the 1000 ppm As(III) solution and shaken for 24 hours, respectively. The parameters, n and K_f, in Freundlich equations from soil A and HW were greater than soils B and C, which reflects that soil A and HW have better adsorption property. The values of n from soil A and HW is over two, therefore, the concentration of As(III) can hardly influence the adsorption capacity.

Overall, HW are better at adsorbing As(III) in aqueous solution. This could be attributed to the combination of iron compounds, charcoal and vermiculite in HW and their higher CEC value.

3.4 As(III) immobilization in soils

Through a series of adsorption experiments in solutions, HW can be defined as an effective adsorbent for arsenic adsorption in aqueous environment. Also, the usefulness of HW in stabilization of As(III) in soils has been evaluated.

It is not enough to simply compare total arsenic concentrations in soils with government soil quality standards, because arsenic toxicity varies with its valence and chemical forms. For instance, water soluble arsenic is more toxic because it can easily permeate into groundwater and/or be absorbed by plant roots and/or accumulate through trophic levels by direct adsorption. All of these routes can eventually lead to arsenic absorption by humans. Total arsenic concentration does not express the (bio)availability and (phyto)toxicity of arsenic. Consequently, the influence of HW addition on As(III) immobilization in soils was studied based on the determination of water soluble arsenic, non-specifically sorbed arsenic, specifically sorbed arsenic, arsenic bound to amorphous iron oxides, arsenic bound to crystalline iron oxides, and residual arsenic using water extraction procedure and SEP. This provided a better indication of arsenic toxicity compared with the total arsenic concentration which provides a better assessment from arsenic. In addition, to assess the recovery of contaminated soils, the influence of soil properties on arsenic immobilization was considered.

3.4.1 Water extraction

Table 11 and Table 12 indicate the difference in water soluble arsenic concentration with time (before and after 8 weeks of HW incubation, but following 20 weeks of aging of spiked As(III) in soils) through five-sequential water batch extractions. Although the total arsenic concentration is over 100 mg/kg in each soil, water soluble arsenic concentrations are quite low with many of them under the detection limit by ICP-OES (0.1 mg/L which translates to 2.5 mg/kg in soil). Overall, the trend is water soluble arsenic is reduced with the repeated water extraction. Combining these results with Table 13 shows a general trend of water soluble arsenic reduction with time, while the addition of HW does not show any trend with arsenic compared to the blank control.

Table 11. Mean (±SD) of water soluble arsenic concentration (ppm) in each of the five-sequential water batch extraction solution from

Soils	1 st	2 nd	3 rd	4 th	5 th
Soil A	<0.1	<0.1	<0.1	<0.1	<0.1
Soil B	0.120	0.120	0.106	<0.1	<0.1
	(0.009)	(0.004)	(0.019)		
Soil C	0.135	0.149	0.141	0.100	<0.1
	(0.020)	(0.016)	(0.014)	(0.008)	

the soils at 0 week (n=3)

Note: the effective detection limit is 0.1 ppm

Table 12. Mean (±SD) of water soluble arsenic concentration (ppm) in each of the five-sequential water batch extraction solution from the soils at 8 weeks (n=3)

Soils [*]	1^{st}		2 nd		3 rd		4 th		5 th	
	HW treat	Blank	HW treat	Blank	HW treat	Blank	HW treat	Blank	HW treat	Blank
Soil A	<0.1	<0.1	<0.1	<0.1	<0.1	< 0.1	<0.1	<0.1	<0.1	< 0.1
Soil B	0.117 (0.011)	0.100 (0.006)	0.092 (0.005)	0.093 (0.011)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Soil C	0.113 (0.005)	0.107 (0.005)	0.118 (0.020)	0.122 (0.006)	<0.1	0.095 (0.014)	<0.1	<0.1	<0.1	<0.1

Note: the effective detection limit is 0.1 ppm

* The soils had been previously spiked and allowed to incubate for 20 weeks prior to the addition of HW

Table 13. Mean (±SD) of water soluble arsenic concentration (ppm) in each of the water extraction solution from the soils at various length of incubation time after the addition of HW (n=3)

Soils [*]	0 week	1 week		2 weeks	2 weeks 4 week		4 weeks		8 weeks	
		HW treat	Blank							
Soil A	<0.1	<0.1	<0.1	< 0.1	<0.1	< 0.1	< 0.1	< 0.1	<0.1	
Soil B	0.120 (0.009)	0.104 (0.020)	0.112 (0.010)	0.137 (0.037)	0.115 (0.004)	<0.1	0.092 (0.011)	0.117 (0.011)	0.100 (0.006)	
Soil C	0.135 (0.020)	0.097 (0.019)	0.115 (0.020)	0.114 (0.011)	0.116 (0.011)	0.099 (0.003)	0.128 (0.004)	0.113 (0.005)	0.107 (0.005)	

Note: the effective detection limit is 0.1 ppm * The soils had been previously spiked and allowed to incubate for 20 weeks prior to the addition of HW

3.4.2 SEP

The SEP experiment focused on the influence of HW and soil property variation on the fractionation of arsenic in soils over time. It can be useful in predicting the alterations in the arsenic lability in various solid phases for soil remediation. The soil A samples which went through five-sequential water batch extractions at 8 weeks were continued to be used for the SEP experiment to assess the influence of water extraction.

The partitioning of arsenic in the soils A, B, and C into the five fractions was carried out using SEP. The percentage of total arsenic (including both native and added arsenic) that was extracted by five different extractants varied widely. The data (Figure 23) clearly indicated that F3 is the largest fraction ranging from 45.77% to 56.22% of all the soil samples. F2 and F5 are either the second or the third largest fraction with F2 ranging from 14.05% to 25.40% and F5 ranging from 12.06% to 29.41%, followed by F4 (4.62% to 8.79%) and F1 (0.96% to 1.20%) successively.

The most labile fraction, F1, accounts for only around 1.00% of the total without showing any noteworthy change over time or upon the addition of HW or with sequential water extraction. Furthermore, F1 in soil A was determined to be at a lower level compared with soils B and C.

F2 is also a labile fraction but did not indicate a changing trend with time. However, a tendency to reduce the percentage of F2 can be seen 8 weeks after the addition of HW. Similarly, a decreasing tendency can also be seen after sequential water extraction. Initially, soil A has the lowest F2 (18.66%), while after 8 weeks the trend followed the order: soil C (25.40%) > soil A (22.84%) > soil B (21.96%).

With time, the F3 in soil A and soil B increased from 45.77% to 55.95% and from 47.38% to 54.81%, while the F3 in soil C slightly decreased from 47.89% to 47.60%. Furthermore, F3 in soil A fell off, whereas F3 in both soil B and soil C increased following the HW addition. Similar to F2, the amount of F3 also reduced after sequential water extraction. The order of F3 after 8 weeks of incubation is: soil A >soil B > soil C.

From initial time to 8 weeks, the percentage of F4 increased by anywhere from 0.01% to 1.85%. Following the HW addition, the F3 in soils A and C reduced by 0.31% and 1.82%, respectively, while the F3 in soil B slightly increased by 0.16%. Sequential water extraction did not show a clear trend for F4. Furthermore, the percentage of F4 in soils at both initially and 8 weeks follow the same order: soil C> soil A> soil B.

From 0 to 8 weeks, the percentage of F5 decreased by 16.36%, 4.64% and 1.51% in soils A, B, and C, respectively. The addition of HW increased the percentage of F5 in all soils, with the largest increase occurring for soil A, from 12.06% to 20.53%. The sequential water extraction markedly raised the F5 percentage as well. Initially, the F5 in soil A (28.42%) is higher than the F5 in soils B and C (22.08% and 19.03%), while after 8 weeks without adding HW, soil A has the lowest F5 (12.06%) among three soils with the F5 in soils B and C are 17.44% and 17.52%. In contrast, after 8 weeks following the HW addition, the F5 value (20.53%) for soil A remained relatively higher than soils B and C (17.52% and 19.09%).



Figure 21. Fractionation of arsenic in soils by SEP (F1: non-specifically sorbed; F2: specifically sorbed; F3: bound to amorphous iron oxides; F4: Bound to crystalline iron oxides; F5: residual)

In all soils, the labile fractions, F1 and F2, decreased after all the sequential water extractions and also with the addition of HW. Only a negligible amount of arsenic being washed out through the sequential water extractions, therefore, the transformation from labile fractions to immobile fractions of arsenic in soils was mainly promoted by the extraction procedure. In addition, HW is an effective amendment for arsenic adsorption in soils. Adding HW improved the percentage of the most stable fraction, F5, in all soils. The percentage of F3 also increased except in soil A, because the F3 from soil A was partly transformed to a more stable fraction (F5).

Even though soil A retained arsenic in stable condition very well in the beginning, it released immobilized arsenic faster than soils B and C after 8 weeks. This situation might be attributed to the large amount of OM (39.01%) in soil A. Perhaps some OM occluding arsenic were decomposed during the 8 weeks of incubation, which release the arsenic into the environment. Compared with soil A, soils B and C contain more mobile arsenic initially, but the transformation of arsenic fractions are more stable and have less influence by time.

Arsenic availability generally reduces over time as a result of increased binding/adsorption of arsenic to soil particles (Song et al., 2006). However, this study did not express the same trend. It probably because the binding/adsorption reactions occurred during the 20 weeks of aging were not monitored. Song et al. (2006) indicated that arsenic aging in soils occurred mostly in the first 12 weeks of incubation. Therefore, due to earlier stabilization process during the 20 weeks of aging after arsenic spiking, the percentage of F1 in soils was quite stable over the 8 weeks, which is consistent with the

results from Huang et al. (2016). They showed that water soluble arsenic decreased rapidly within the first 10 days following the addition of arsenic.

Chapter 4 Conclusions

4.1 Research summary

Based on the results and discussion, the following conclusions can be made.

Classification systems for soils indicate there are several hundred different types with varying levels of sand, silt, and clay along with mineral content and composition. These various types of soils exhibit widely different arsenic adsorption capacities depending upon individual properties. In particular, the three soil samples collected from Shuitou, China, could be magnetically separated into two components, the iron-rich particles with a higher arsenic content and the remaining (iron-poor particles) with lower arsenic content. Further, the iron-rich particles of each soil exhibited higher arsenic concentrations than the soil as a whole.

The size of the soil particles exhibited a strong influence on the adsorption as a result of specific surface area, providing more available adsorption sites. For soil A, the adsorption capacity follows the order: clay > silt > sand. Further, soil A adsorbed a higher percentage of arsenic than either soil B or C at equilibrium in a solution with an initial As(III) concentration of 10 ppm. These results are consistent with the concentration of iron in each soil sample. However, soil A exhibited the lowest absorption levels for arsenic when the concentration of As(III) was increased to 1000 ppm. This is likely the result of limited absorption sites with soil A and the sites reaching saturation long before all of the arsenic has been bound. In other words, the sites within soil A absorb arsenic much more readily than in either soil B or C but there are fewer sites so the overall amount of arsenic that can be bound is lower.

In a low As(III) concentration (10 ppm), the As(III) was adsorbed onto the hand warmers rapidly to achieve a maximum of 95.22% in the first two hours and dropped to a steady state of around 90%. HW are not the optimum choice compared to other adsorbents (goethite, charcoal and Fe₂O₃) used in this experiment because of its relative lower adsorption capacity, but it indicated a remarkable adsorption advantage in aqueous solutions with an initial As(III) concentration of 1000 ppm. A total of 17.02 mg As(III) was absorbed onto each gram of HW when exposed to a 1000 ppm As(III) solution. From this, it can be concluded HW are a reasonably effective adsorbent with high As(III) adsorption capacity in aqueous solution.

The pseudo second-order kinetic model was statistically significant at the 95% confidence level in all soils and HW. Furthermore, all soils and HW were well fitted with the Freundlich isotherm model, whereas Langmuir isotherm model has a slight advantage for soil A and HW at the 95% confidence level. To sum up, it indicated both soil A and HW have good adsorption capacity and can hardly influenced by the concentration of As(III).

The water soluble arsenic in soils is quite low with many of measurements below the detection limit for arsenic. Overall, the water extraction procedure showed a general trend of water soluble arsenic reduction with time and the repeated water extraction.

The partitioning of arsenic in soils was carried out using SEP with the result that Fraction 3 exhibited the highest concentrations ranging from 45.77% to 56.22% and Fraction 1 with the lowest ranging from 0.96% to 1.20% of all the soil samples. SEP also indicated that the number of labile fractions (F1 and F2) decreased after sequential water extractions and with the addition of HW, which means arsenic was immobilized. Arsenic

was transformed from labile fractions to immobile fractions through adsorption process due to the water extractions and HW. Adding HW improved the percentage of the most stable fraction, F5, in all soils.

Soil A retained arsenic initially, but it released more immobilized arsenic than other soils after 8 weeks of incubation. It may be assumed the OM occluding arsenic decomposed with time and released accompanying arsenic into the soils. The transformation of arsenic fractions in soils B and C is more stable and are less influenced by time.

In a word, the aging, soil properties, and water extraction effects should be taken into account during soil risk assessment. This study showed that arsenic could be removed by an inexpensive waste product (hand warmers) in aqueous solution and arsenic could be transformed to a more immobile fraction in soils with the addition of hand warmers. We conclude HW can be regarded as an environmentally friendly, economically feasible and promising adsorbent to remediate arsenic contaminated water and soils.

4.2 Limitations and future research

In this research study, the chemical valence of arsenic was not determined. Further study could focus on the transformation of As(III) to As(V) during the adsorption process in aqueous solution and soils. The long-term impact of using hand warmers for arsenic immobilization remains unclear and therefore this should be studied. Furthermore, the adsorption capacity of HW for heavy metals, such as chromium, cadmium and manganese, is worth studying to see if HW is a useful adsorbent that can absorb multiple pollutants. Also, the effectiveness of HW in other soils with various properties should be

evaluated and the effect of temperature should be tested. As for HW application *in situ*, the practical effectiveness should also be examined in the future.

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