ARSENIC REMOVAL OF SAND FILTRATION FOR POTABLE WATER IN RURAL NEWFOUNDLAND AND LABRADOR

DANIAL BIN ROHAIL

Arsenic Removal by Sand Filtration for Potable Water in Rural Newfoundland and Labrador

By

Danial Bin Rohail ©

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Abstract

The high concentration of arsenic in groundwater sources of Newfoundland has been reported by governmental departments and individual researchers. Arsenic uptake by human beings can cause the cancer of lungs, kidneys and skin. The National Health and Medical Research Council (2003), NHMRC, of Australia has set the maximum acceptable concentration (MAC) for arsenic in drinking water at 7 μg/L. The main objective of this research was to find an economical and sustainable water treatment method for rural Newfoundland. The locally available sand was used as a filter media to treat the groundwater without the aid of chemicals. Leaching column studies were conducted to determine the ability of sand to treat the water without exceeding the arsenic levels of 7 μg/L. 1400 mL of high strength Wabana water (As: 62.91 μg/L and Fe: 11825.84 μg/L) could easily be treated using a small sand filled column (6.7 cm x 6.7 cm (dia. x length)) as compared to the 4,000 mL and 10,500 mL for mixtures of the high strength and normal Wabana waters in the ratios of 1:1 and 1:3, respectively. Combining aeration and dilution, 9,000 mL and 18,000 mL of 1:1 and 1:3 mixtures, respectively, were treated without exceeding the arsenic limit of 7 μg/L. The Fe/As ratio was a major factor affecting arsenic adsorption and column tests were conducted with the high strength Wabana water mixed with Freshwater water in 1:10 (Mix-1), 2:10 (Mix-2) and 3:10 (Mix-3) proportions. The 2:10 mixture performed better than the Mix-1 or Mix-3 mixtures. The arsenic concentration after treating 39,000 ml was 8.735 μg/L for the Mix-2 water and 23.93 μg/L and 12.315 μg/L for the Mix-1 and Mix-3 waters, respectively.

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List of Symbols

^{o}C	Degree Celsius
cm	Centimeters
cfm	Cubic foot per minute
d*f*	Degree of Freedom
µg	Micrograms
µg/L	Micrograms per liter
g	Grams
H^+	Hydrogen Ion
in-Hg	Vacuum (inches of mercury)
Ka	Dissociation Constant
L	Liter
mg	Milligram
mL	Milliliter
mL/min	Milliliter per minute
mL/hr	Milliliter per hour
mol	Moles

mmol	millimoles
OH^-	Hydroxyl Ions
pH	$-\log[H^+]$
pKa	-log Ka
[]	Concentration

List of Abbreviations and Acronyms

AA	Activated Alumina
AAS	Atomic Adsorption Spectrometer
AC	AC
Al	Aluminum
As	Arsenic
As (III)	Arsenite, trivalent arsenic
As (V)	Arsenate, pentavalent arsenic
AsS	Realgar
As_2S_3	Orpiment
Be	Beryllium
C_o	Initial concentration of Solute
Ca	Calcium
CC	Char Carbon
C_i	Concentration of Solute at 'i'
CoAsS	Cobbalite
Cr	Chromium

Cu	**Copper**
Cl	**Chlorine**
Fe	**Iron**
Fe^{2+}	**Iron (II) Oxide**
Fe^{3+}	**Iron (III) Oxide**
FeAsS	**Arsenopyrite**
FM	**Finesse Modulus**
FMBO	**Ferric and manganese binary oxides**
GAC	**Granular AC**
GFAA	**Graphite furnace Atomic Adsorption**
HFOs	**Hydrous Ferrous Oxide**
IARC	**International Agency for Research on Cancer**
ICP-ES	**Inductively Coupled Plasma emission spectroscopy**
ICP-MS	**Inductively Coupled Plasma mass spectrometry**

Li	**Lithium**
Mg	**Magnesium**
Mn	**Manganese**
NF	**NF**
Ni	**Nickel**
NiAs	**Niccolite**
P	**Phosphorous**
Pb	**Lead**
POE	**Point of Entry**
POU	**Point of Use**
ppb	**parts per billion**
ppm	**parts per million**
PZC	**Point of Zero Charge**
RO	**RO**
S	**Sulfur**
Se	**Selenium**
Sb	**Antimony**
UF	**Ultra filtration**

U.S. EPA	**United States Environmental Protection Agency**
V	**Vanadium**
WHO	**World Health Organization**
UC	**Uniformity Coefficient**
Zn	**Zinc**

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Chapter One

Introduction

1.1. The Problem of Arsenic in Newfoundland

The problem of groundwater contamination by arsenic is documented in various regions including USA, China, Chile, Bangladesh, Taiwan, Mexico, Poland, Vietnam, Japan, India and Canada (Berg et al. 2006; Wang and Mulligan 2006; Leupin and Hug, 2005; Mohan & Pittman, 2007). Arsenic is a known carcinogen and its uptake by humans through drinking water is a growing concern among the nations. Through epidemiological studies, arsenic has been verified as one of the most carcinogenic and toxic substances found in surface and groundwater sources (Jiang, 2001). Mondal et al. (2007) referred to arsenic as the “world’s most hazardous chemical”. As per recent estimates, approximately 140 million people all over the world and possibly more are affected by arsenic contamination (Bagchi, 2007). The current situation regarding the arsenic contamination of groundwater sources in Canada appears also to be alarming (Wang and Mulligan, 2006). The arsenic concentrations in surface water in Canada range from 1 to 2 μg/L, while arsenic concentrations in groundwater are often higher than those measured for surface waters. Fifty percent of the water sources in the Newfoundland and Labrador (NL) are groundwater resources which are fulfilling the potable water requirement of the people residing in the rural parts of the province (Rageh, 2008). The analysis of water wells conducted by the Department of Energy and Department of Mines and Energy revealed that many of them exhibited high arsenic contents. The wells that have high arsenic contents could either be abandoned or they could be treated to protect the consumer from the carcinogenic effects of arsenic. The selection is based entirely on the cost of each available alternative. Digging new wells may not be a feasible alternative as there is always a risk of contamination in the new source (Rageh, 2008).

The recent research by Rageh et al. (2007) reported that only 3 wells out of 52 tested in NL had an arsenic concentration below the 10 μg/L limit, which is very alarming. Further, the paper stated that the majority of arsenic contaminated wells were located on the Avalon Peninsula, where the majority of the province's population resides. This situation stresses the need for an economical treatment method for arsenic removal.

Sources of arsenic in groundwater are both natural and anthropogenic. Natural sources of arsenic in water have been attributed to the weathering of rocks, oxidation of arsenic bearing sulfides, release of arsenic from geothermal water, leaching of arsenic from sulfides by carbonate, and volcanic eruptions (Piver, 1983; Wang and Mulligan, 2006). Arsenic in the environment from natural enrichment is strengthened by anthropogenic activities (Wang and Mulligan, 2006). The anthropogenic sources include pesticides production and application, herbicides, non ferrous metals mining and smelting, fossil fuels processing and combustion, zinc production, industrial wastes and wood preservatives (Piver, 1983; Wang and Mulligan, 2006).

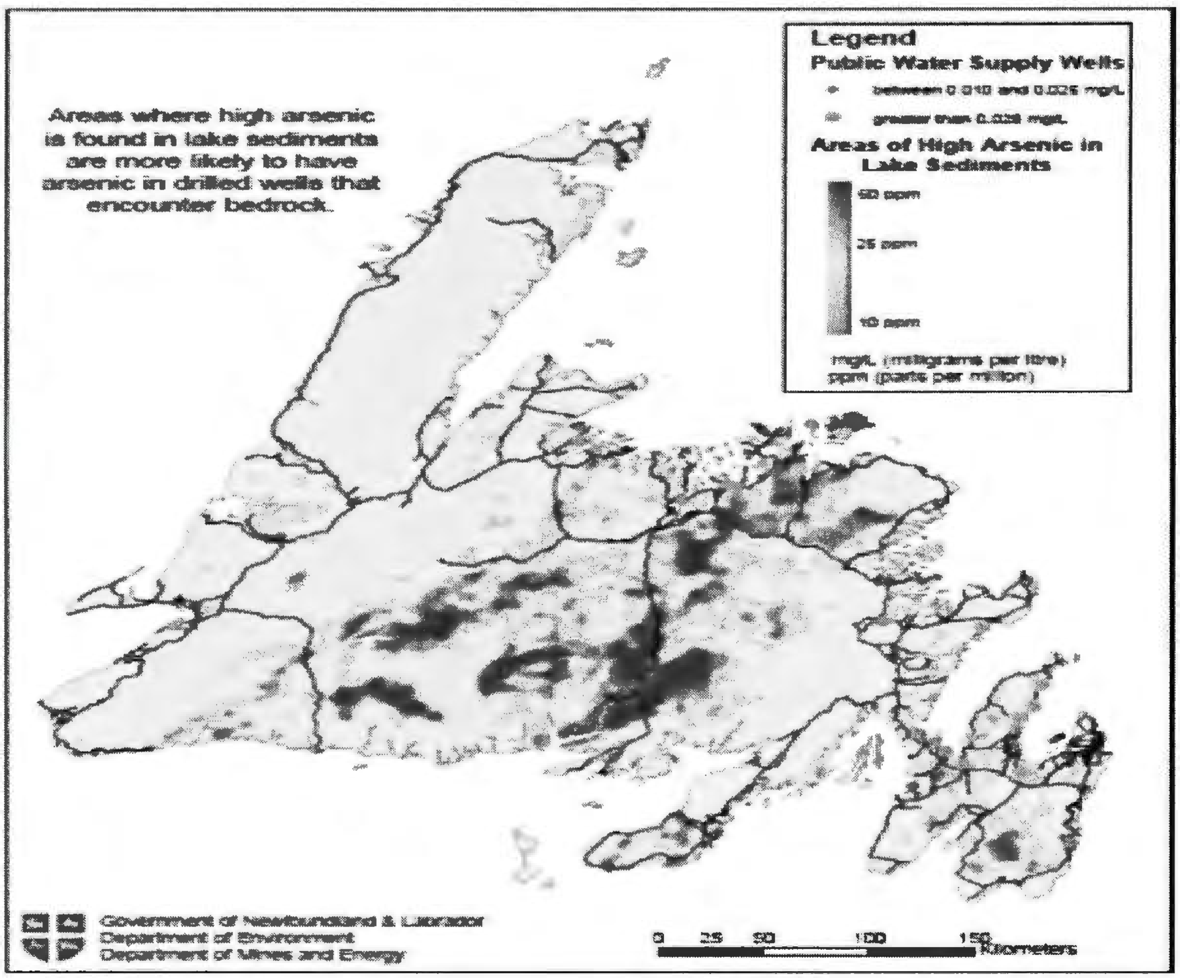

Figure1.1 Areas of potential Arsenic concentrations in well water

(Source: Department of Environment and Department of Mines and Energy)

Arsenic exists naturally in the sedimentary rocks and weathering of these formations results in its release into the environment. The two main types of rocks that exist in NL are igneous and sedimentary. The arsenic concentration in igneous rocks ranges from 0.2-13.8 mg/kg while sedimentary rocks have higher arsenic contents such as 0.3-500 mg/kg (shale), 0.1-20 mg/kg (limestone) and 0.6-120 mg/kg (sandstone) (Salbu and Steinnes, 1995)

Swinden (1988) mentioned that the sulfide minerals are the main arsenic bearing formations. In NL, the main source of arsenic is "arsenopyrite (FeAsS), realgar (AsS), orpiment (As_2S_3), niccolite (NiAs) and cobbalite (CoAsS)" (Rageh et al., 2007). The arsenic that accumulates in the soils and sediments can be released as a result of weathering of rocks and under reducing conditions and thus can pollute the groundwater reservoir (Robinson and Ayotte, 2006).

Arsenic is found mostly in water wells that are drilled into the geological formations containing high levels of arsenic. The contact between groundwater and arsenic rich sediments and rocks results in the dissolution of arsenic bearing minerals and ores due to the weathering. As a result of the slow movement of groundwater, the contact time increases and the probability of arsenic contamination of groundwater increases (Department of Environment and Conservation and Department of Mines and Energy).

1.2. Background

Arsenic is toxic and is a known human carcinogen. It has therefore been included in Group 1 (carcinogenic to humans) both by Health Canada (2006) and the International Agency for Research on Cancer (IARC, 2004). Arsenic may be consumed by drinking water, eating food and through inhalation. Arsenic is the 20th most abundant element in the earth's crust (Mandal and Suzuki, 2002). The two most common form of inorganic arsenic are As III (trivalent) and As V (pentavalent). Arsenic occurs as a metastable species in the +III oxidation state under oxic water conditions and As (III) is more mobile and is less efficiently removed as compared to As (V) (Chiu and Hering, 2000). In trivalent form it is found as arsenic trioxide and sodium arsenite, while common pentavalent forms include arsenic pentoxide and various arsenates (Report on Carcinogens, Eleventh Edition).

As listed in the First Annual Report on Carcinogens (1980). The maximum acceptable concentration (MAC) of arsenic in drinking water is 50μg/L for most developing countries; while the World Health Organization (WHO) guideline is 10μg/L. Inorganic arsenic compounds are notorious for increasing the risk of cancer of the skin, lung, liver, bladder, kidney and digestive tract (Kapaj et al., 2006). Because of its marked negative effects on human health, there is an urgent need for the development of a simple, efficient and cost effective solution to remove arsenic from groundwater at the household level.

1.2.1. Comparison of Arsenic Removal Techniques

Ion-exchange, activated alumina, reverse osmosis (RO) and membrane filtration are some of the methods recommended by United States Environment Protection Agency (USEPA) for the removal of arsenic (Berg, et al., 2006). Although they can remove arsenic to below 10μg/L, they are not suitable for the small water systems with limited resources (Gu et al., 2005). The focus should be given to the removal of arsenic using sand filtration as this system can be simple, easy to operate and inexpensive.

The selection of the appropriate arsenic removal technique depends primarily on the constituents dissolved in the water, the pH, the oxidation state of arsenic and its concentration, and the concentration of iron, and the other ions (excluding As (III) and As (V)) in the water competing for adsorption (Gu et al., 2005). Moreover, the cost of treatment and the population of the community are other important factors that influence the selection of a suitable water treatment technique. The tests conducted by the Research and Productivity Council (RPC), Fredericton, New Brunswick, in September 2002 revealed that the dominating species in the groundwater wells of the Avalon Peninsula was As(V) (Rageh, 2008).

Activated carbon (AC) based adsorbents for arsenic removals have been widely studied. Adsorption depends on the properties of the AC, the pH, the temperature and properties of the adsorbate (Mohan and Pittman, 2007). Various AC adsorbents are synthesized commercially such as iron containing-granular AC adsorbents, char carbon (CC) derived from fly-ash, iron-oxide impregnated AC, and zirconium loaded AC (Mohan and Pittman, 2007). The AC based adsorbents are widely used for the treatment of groundwater and wastewater but these adsorbents are expensive. A typical granular AC (GAC) tank can be seen in the Figure 1.2.

Oxide based adsorbents are most commonly used for arsenic removal. They include Activated Alumina (AA), porous granular ferric hydroxide, ferrihydrite/iron oxides, hydroxide/iron oxides, and zirconium oxide. The mechanism of arsenic retention by these adsorbents is based on the

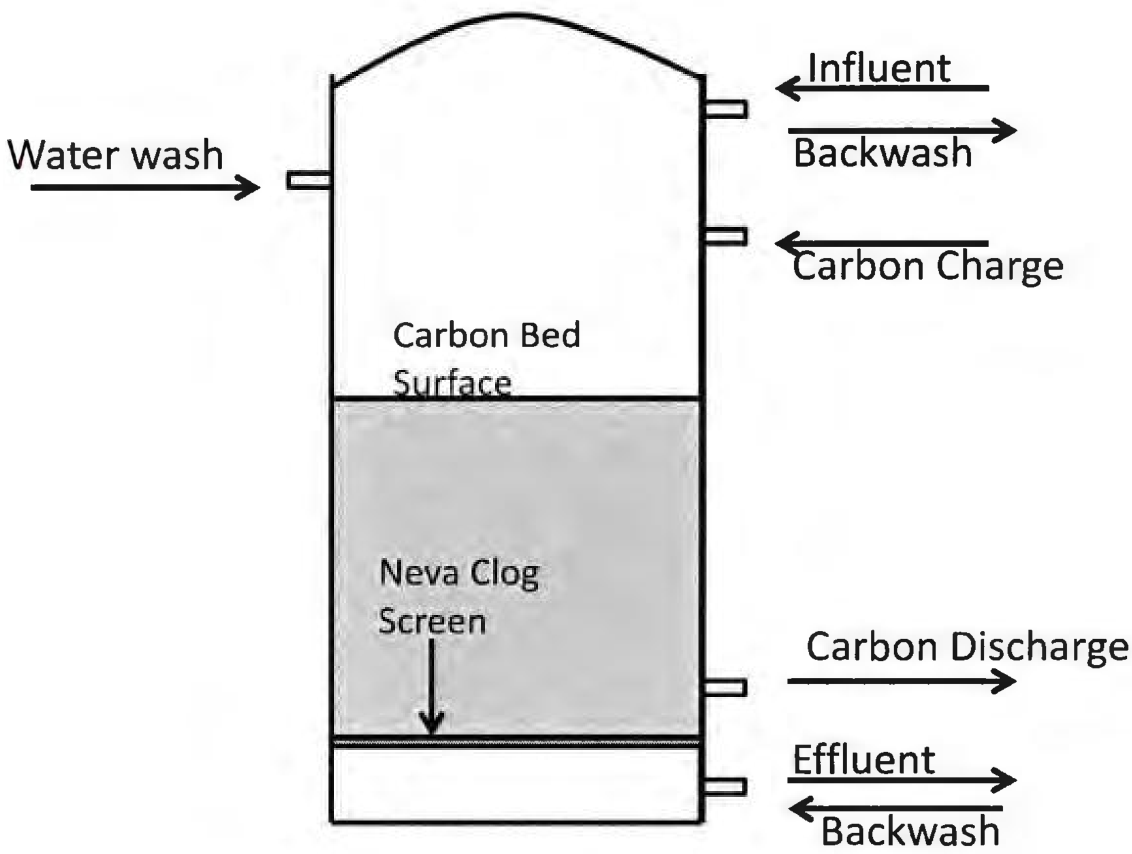

Figure 1.2 Schematic of the typical GAC tank (modified from Metcalf and Eddy Inc, 1979)

process called ligand exchange. A ligand is an ion, atom or molecule that forms a coordination complex with a central metal atom or ion by sharing one or more of its electrons through a covalent bond. It is a complexing group (ligand) in coordination chemistry that stabilizes and determines the reactivity of central metal atom. The coordination complex consists of a metal atom or ion surrounded by a ligand or complexing agent. The AA based adsorbents need replacement after four to five regenerations (Mohan and Pittman, 2007).

Arsenic can be removed by co-precipitation with iron (III) hydroxide, aluminum sulfate and manganese salts. In the precipitation process coagulants are added to the wastewater in the presence of lime to flocculate and settle small particles which would remain suspended otherwise (Rageh, 2008). The addition of the coagulants to the water containing arsenic causes the coagulant to hydrolyze. A complexes form between the metal oxide and arsenic and they settle to the bottom of the tank. As (V) is more readily removed as compared to As (III). 95% of As(V) was removed from the water containing 0.09 mmol/L of Fe(III) and 300 μg/L of As (V), however, only 50-60% of As(III) was removed (Bissen and Frimmel, 2003). The effectiveness of arsenic removal by precipitation is lower when alum is employed instead of $FeCl_3$. Water containing 20 μg/L of arsenic, when treated with 4.9 mg/L of $FeCl_3$ removed 80% of the arsenic, while; 40 mg/L of alum was required to achieve the same removal (Bissen and Frimmel, 2003).

Ultra-filtration (UF), Nano-filtration (NF) and Reverse Osmosis (RO) can also be used for arsenic removal. UF is not suitable in removing dissolved arsenic, but, NF and RO can be used to remove the dissolved matter. The typical schematics of NF and RO can be seen in the Figures 1.3 and 1.4. RO and NF can effectively reduce the arsenic levels in the water by up to 95% (Bissen and Frimmel, 2003).

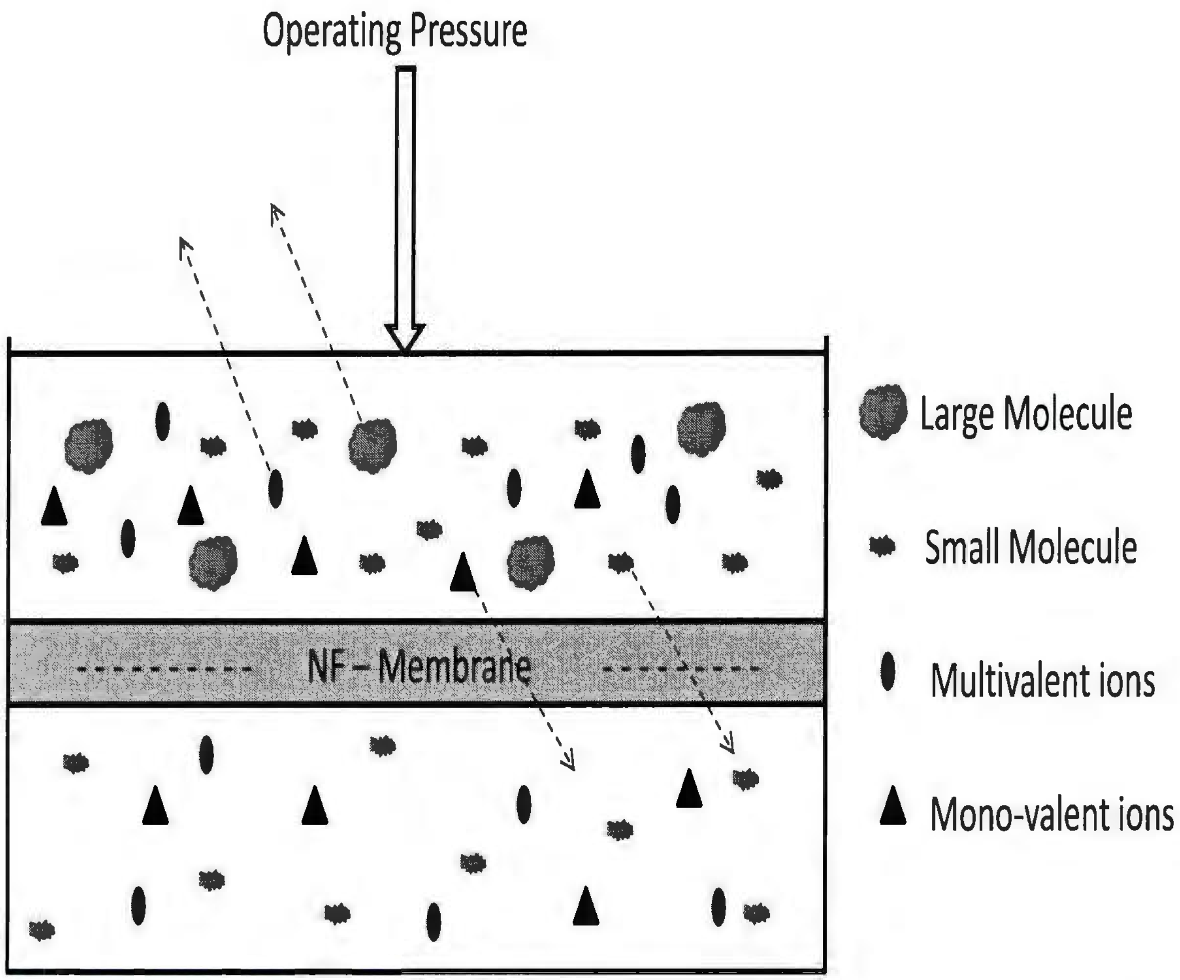

Figure 1.3 Schematic of the typical NF Process (modified from Zhaoa et al., 2011)

A combination of precipitation, adsorption and filtration can be economical for arsenic removal. The cost associated with the in-situ precipitated ferric and manganese binary oxides (FMBO) adsorption, sand filtration and UF combined for arsenic removal is 0.056 US$/$m^3$ (Ruiping et al. 2009).

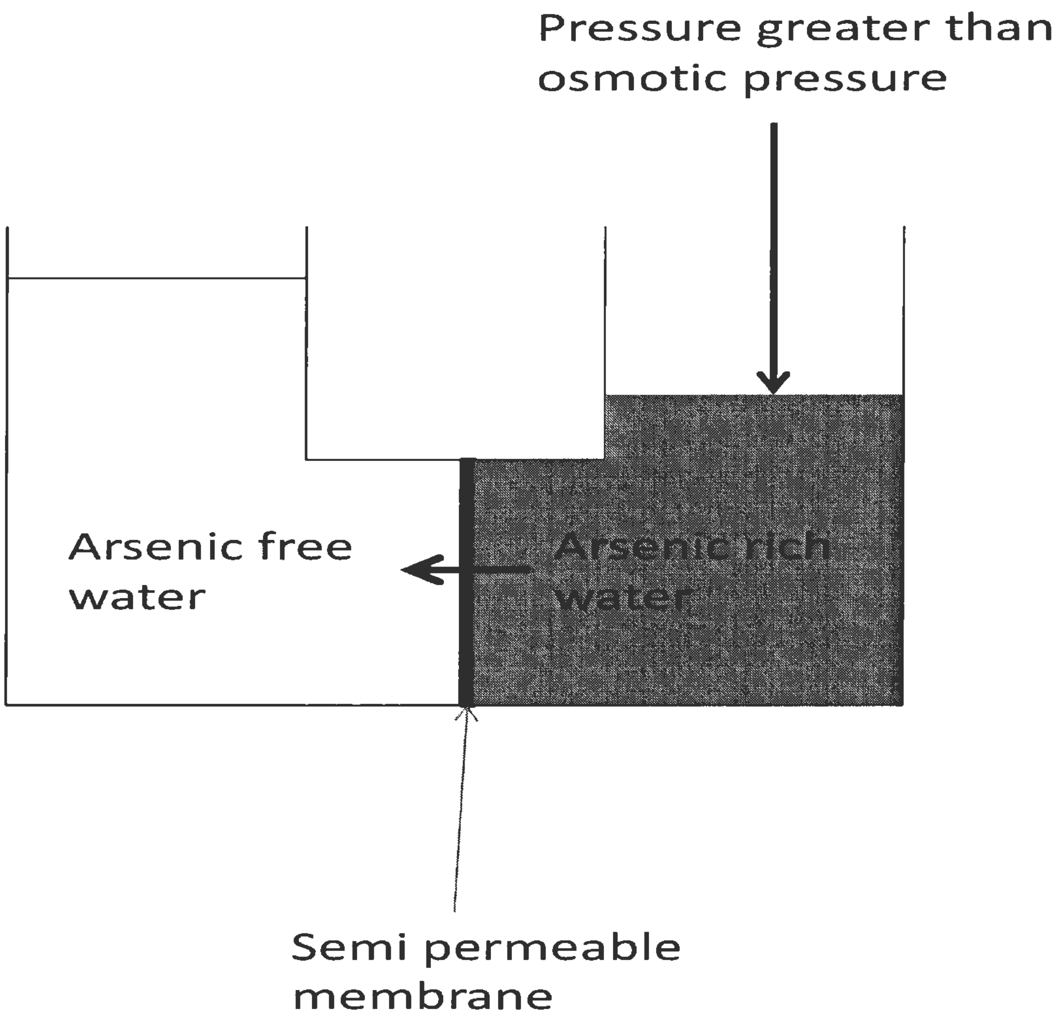

Figure 1.4 Schematic of the typical RO Process

Ruiping et al. (2009) found that sand could remove more than 90% of arsenic and the main operating cost associated with this system was acceptable for arsenic removal in rural areas. The cost could further be reduced by removing the UF. Similarly, the study conducted by Leupin and Hug (2005) concluded that As(V) could be removed by the oxidation of Fe(II) and subsequesnt adsorption of As(V) onto hydrous ferric oxide which was then removed by filtration. Further, the growing concern of arsenic uptake through water for smaller communities, where a centralized system is not viable, can be minimized by the application of point of use (POU) or point of entry (POE) devices. In NL, where the tax-base is low, POE devices with sand filtration systems could prove to be very effective. These devices are based on the combination of filtration, precipitation and adsorption technologies and can easily be installed at the taps and points of entry. The adsorbent can either be dipped in the water or placed in the water supply pipelines (Rageh, 2008). The arsenic removal efficiencies for the various techniques that have been discussed were reported by the Government of NL in 2006 and are presented in Table 1.1. Table 1.1 also presents the costs associated with the different available techniques for arsenic mitigation. The NF and RO techniques require high initial investment and their corresponding operational costs are also high. Further, the operation of NF and RO equipment is complex and requires skillful operator and maintenance personnel. The techniques such as GAC, AA and sand filtration are easy to operate and require low setup costs. Sand filtration equipment, is simple to operate, is inexpensive and can provide arsenic free water at the household level.

Table1.1 Efficiencies and Prices (where applicable) for various arsenic removal techniques (Redrawn from Rageh, 2008 and updated)

Technique	Arsenic removal efficiency (Government of Newfoundland and Labrador, 2006) unless otherwise indicated	Cost	Reference for cost of technique
Activated Alumina (AA)	51%	$1200-1600 for low contamination levels (6-10 gpm)	Arsenic Removal System, 2008
Granular AC (GAC)	96%	$550 for a drum (55US gal) and it should be replaced every 9-12 month (low contamination level).	Omitha Devendra, Customer service representative, Carbon Activated Corp, California, personal communication, 2008.
Iron Oxide Coated Sand (IOCS)	96%	-	-
Ion Exchange Resins	40-49%	-	-
Nanofiltration	95%	$5000 including a storage tank (1850 gallons)	Shaun Segel, MD, Clean Water Products, Arizona, personal communication, 2012.
RO	95%	$13,975 including a storage tank (1000 gpd)	(Rageh, 2008)
Sand		$25 per ton	Boyd Critch, Capital Ready Mi personal communication, 2011

1.2.2. Selected Mechanism and Material

The techniques for arsenic removal such as ion-exchange, activated alumina, RO and membrane filtration are not employed on a large scale due to the sophisticated technology and consequently lofty investment. The removal of arsenic by adsorption using iron oxide based adsorbents is considered to be an environmentally sustainable and cost effective solution. Further, reasonably large amounts of arsenic contaminated water can be treated using slow sand filters due to which this technology has a potential of serving small communities. The use of slow sand filters for the arsenic removal has shown positive results in mitigating the arsenic concern in Bangladesh and Vietnam (Berg et al., 2006 and Meng et al., 2000). Berg et al (2006) reported that removal of Arsenic by adsorption onto a sand surface was not an efficient process unless it was accompanied by the simultaneous precipitation of iron. They reported, however, that sand filters performed better (+12% on average) as compared to the co-precipitation alone. Slow sand filters could be a preferred choice over other available technologies for arsenic removal due to easy maintenance, low operational cost and simple operation (Berg et al., 2006).

The most important parameter in successfully removing arsenic from groundwater to the acceptable limit was the iron to arsenic ratio (wt/wt) (Berg et al. 2006). In this study water sampling locations were narrowed down based on the composition of groundwater provided by the NL Department of Environment and Conservation.

1.3. Objective

The aim of this research project was to use the locally available materials including sand from a local provider to treat groundwater; thus providing arsenic free water, without the addition of chemicals, to the rural population of NL. Slow sand filters are cheap and require little maintenance and hence, can be used as POE devices for households in small communities.

The oxidation of naturally present Fe^{2+} ions in groundwater forming iron oxides to precipitate with adsorbed arsenic is the simplest conceivable water treatment method for arsenic removal (Roberts et al., 2004). However, the arsenic removal efficiency is compromised by the presence of a low iron concentration and competing anions for adsorption in the groundwater. The oxidation of ferrous ions and consequent formation of iron oxides results in a higher sorption capacity that for arsenic (Roberts et al., 2004). The sand itself adsorbs little arsenic but provides the support to iron oxides that adsorb the major portion of the arsenic.

The mechanism of arsenic uptake by iron oxide based metal sorbents is anion exchange as is evident by the decrease in arsenic removal efficiency with the increase in pH (Streat et al., 2008a). Arsenic has a strong affinity for the sorption sites available on the surface of iron (III) hydroxide (Jovanovic et al., 2011). At the pH that is encountered in groundwater 6.5-8.5, the As (III) is mostly present in molecular form; while, the As (V) species are found in ionic form and for this reason most sorbents performed well in removing As (V) but were found to be ineffective in removing As (III). Further, the iron oxides coated material adsorb both molecular and ionic arsenic species which makes it beneficial for water treatment (Jovanovic et al., 2011). Arsenic in NL groundwater resources primarily exists in the form of As (V) (Rageh, 2008). The total arsenic present in groundwater is the sum of As (III) and As (V), whereas, the later is easier to remove using adsorption as it exists in anionic form. Hence, it was anticipated that the treatment of groundwater with sand filtration could be effective in mitigating the arsenic concern in this province.

1.4. General Outline

This thesis consists of five chapters. The first chapter has summarized arsenic uptake release in the environment, various techniques that can be used for arsenic removal and the method that was tested in this research to mitigate arsenic. The second chapter presents a summary of previous studies conducted in this area and their relation to this research. The methods, materials, tools, and equipment that were used in this study are discussed in chapter three. Chapter four describes experiments that were conducted and the results that were obtained. It includes breakthrough analysis curves, statistical analysis of water samples and the effect of water composition on arsenic uptake by sand. Conclusions and recommendations for future research are highlighted in the last chapter.

Chapter Two

Theoretical Background

2.1. Arsenic Removal by Iron-Oxide Based Adsorbents

Arsenic can be removed from groundwater by a variety of adsorbents such as AA, ferric hydroxide, iron oxide coated sand and several other materials. Iron oxides have greater affinity for arsenic as compared to AA (Driehaus et al., 1998).

Iron-oxides are produced in the natural water by the oxidation of ferric salts. The products can vary in chemical structure, compostion and physical characteristics (Streat et al., 2008b). The complexity of iron oxide chemistry is illustrated in the Table 2.1.

Table 2.1 Iron Oxide Materials (Redrawn from Streat et al., 2008b).

Formula	**Mineral**	**Morphology**	**Colour**
α-FeOOH	Goethite	Needles	Yellow
β-FeOOH	Akaganeite	Rods	Brown
γ-FeOOH	Lepidocrocite Plates	Fibrous	Orange
δ'-FeOOH	Feroxyhyte	Non-crystalline	Brown
$Fe_5HO_8.4H_2O$	Ferrihydrite	Spherical	Red
α-Fe_2O_3	Haematite	Cubic, ellipsoidal	Bright red
γ-Fe_2O_3	Maghaemite	Very small	Reddish Brown
Fe_3O_4	Magnetite	Needles, octahedra	Black

Arsenic exists as either arsenate, As(V) or arsenite, As(III) in the groundwater system. The most commom arsenate and arsenite species found in groundwater are (AsO_4^{-3}) and (AsO_3^{-3}), respectively.

Arsenic is strongly attracted to the sorption sites of iron (III) hydroxide. Hydrous Ferric Oxides (HFOs) exists as $FeOH^{+2}$, FeOH and FeO^-on solid surfaces in contact with water depending on the pH as shown in Figure 2.1 (Cumbel and Sengupta, 2005). The HFO is the Fe(III) hydroxide with loosely bounded water. The HFO has a large surface area due to which it could be used as an arsenic adsorption media for groundwater treatment applications.

$$FeOH_2^+ \longleftrightarrow H^+ + FeOH \longleftrightarrow H^+ + FeO^-$$

Figure 2.1 The balance between HFO active surface forms depending on the pH

$FeOH^{+2}$ and FeOH forms of hydrous ferric oxides are the main species found at neutral pH conditions and they are responsible for binding both types of arsenic species (Jovanovic et al., 2011). Under neutral conditions FeOH ions bond the molecular form of As (III) ($HAsO_2$); while, $FeOH_2^+$ sites bond both the ionic forms of As(V) (H_2AsO^{4-} and $HAsO_4^{2-}$) (Jovanovic et al., 2011). As a result of Lewis acid-base reactions, the HFOs have a high sorption affinity towards both As(III) and As(V) (Cumbel and Sengupta, 2005). The ability of HFOs to adsorb both the ionic and molecular forms of arsenic makes them useful in treating groundwater. Water with high iron content can significantly increase the arsenic removal efficiencies of sand.

The dominant form of As (III) in water up to pH 8 is H_3AsO_3 which is a non-ionic species and hence, difficult to adsorb onto the iron oxide sorption sites, due to high mobility. It is necessary to pre-oxidize As (III) to As (V) to aid in its removal (Hug & Leupin, 2003). It has been reported that As (III) is oxidized in parallel with the oxidation of Fe (II) by the dissolved O_2 and when the oxidation of Fe(II) is completed, the oxidation of As (III) is also stopped (Hug & Leupin, 2003).

The dominant arsenic species in NL groundwater sources is As (V) (Rageh, 2008); hence, it is easy to mitigate arsenic in NL due to the better adsoprtion characteristics of the ionic As (V) species ($H_2AsO_4^-$ and $HAsO_4^{-2}$).

2.2. pH and Arsenic Speciation

Speciation includes the formation of complexes of ligands with heavy metals in the aqueous phase and can result in the competition for adsorption of the heavy metals between soil solids and the ligands (Yong et al., 1992). As the pH increases, the adsorption of arsenic decreases which suggests that it is an anion exchange material (Streat et al., 2008b & Driehaus et al., 1998). The isoelectric point (IEP) for hydrous ferric oxide is in the pH range of 7-8. The IEP is defined as "the pH value of the dispersion medium of a colloidal suspension at which the colloidal particles do not move in an electric field" (McGraw-Hill Science and Technology Dictionary). Therefore, at a pH below the IEP, the surface of an adsorbent will remain positively charged and it will attract anions. Stumm & Morgan (1981) suggested the mechanism of ligand exchange for protonated arsenic species for the pH below the IEP with the help of the following equations.

$$FeOH + H_2AsO_4^-(aq) \rightarrow FeH_2AsO_4^- + OH^-(aq) \qquad 2.1$$

$$FeH_2AsO_4^-(aq) \rightarrow FeHAsO_4^{-2} + H^+(aq) \qquad 2.2$$

The release of OH^- ions increases the pH of the solution (Equation 2.1) and hence, decreases the positive surface charge; thus, lowering the forces to attract anionic species. This increase in pH is counterbalanced by the deprotonation of acid ($FeH_2AsO_4^-$) as depicted in Equation 2.2. At a pH greater than the IEP, the arsenic adsorption could still takes place despite the repulsion between the negative surface and the anionic species (Streat et al., 2008b). The adsorption at pH greater than IEP takes place only if the energy gained by the surface in forming bonds with anions is higher than the repulsive forces and the speciation of arsenic changes from $H_2AsO_4^-$ to $HAsO_4^{-2}$ (Streat et al., 2008b). The specific adsorption at a pH higher than the IEP can take place as a result of the release of the proton by an acid ($HAsO_4^{-2}$) to form water (Equation 2.4) after reacting with the OH^- ions released by the FeOH (Equation 2.3). This water molecule bonded with the iron hydroxide surface is displaced by the anionic adsorption species (AsO_4^{3-}) to form an iron-arsenic complex ($FeAsO_4^{-3}$) (Westall, 1980). The anion adsorption capacity of oxides, hydrous oxides, amorphous materials and other variable charge clays is greater than can be measured from the concentration of the anions adsorbed to neutralize the positive charges since adsorption can also takes place through an interaction between ions. Such adsoprtion of anions is knows as specific adsoprtion and it occurs by the displacement of lattice O^{2-} and OH^- groups by anions (Tan, 2010).

$$FeOH + HAsO_4^{-2}(aq) \rightarrow FeHAsO_4^{-2} + OH^- \qquad 2.3$$

$$FeOH + HAsO_4^{-2}(aq) \rightarrow FeAsO_4^{-3} + H_2O\ (aq) \qquad 2.4$$

From Equations 2.3 and 2.4, OH^- ions and H^+ ions are being released, respectively, to form water that bonds itself to FeOH. This water is displaced by an adsorbing anionic arsenic species. Further, change in the arsenic speciation from $H_2AsO_4^-$ to $HAsO_4^{-2}$ keeps the pH from increasing any further, and thus aids in adsorption of arsenic species onto iron oxide surfaces.

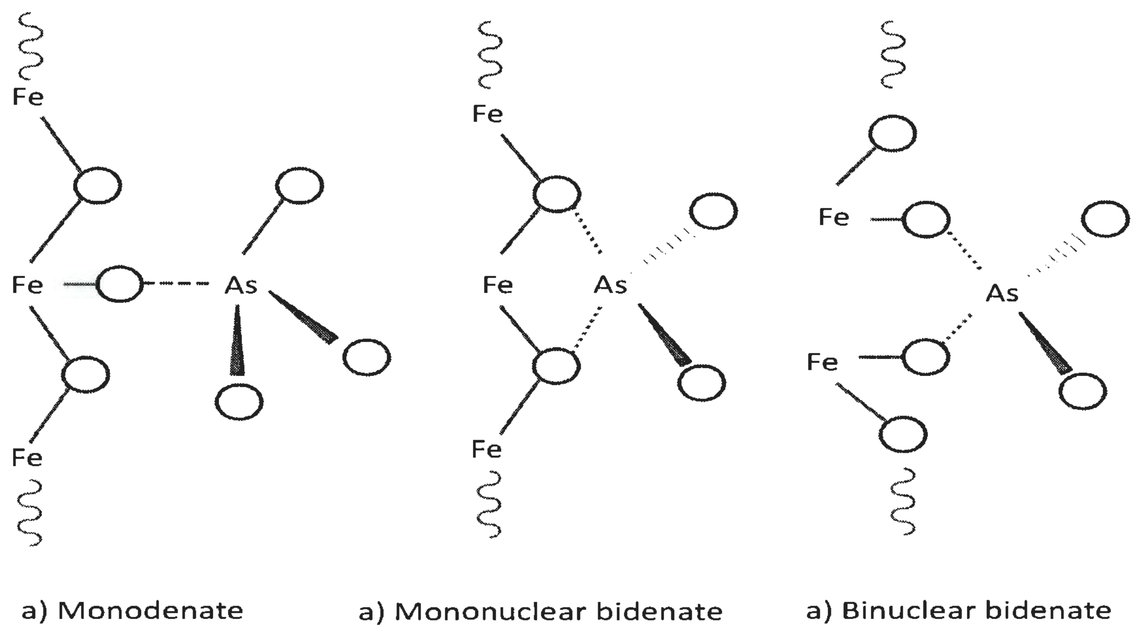

Figure 2.2 Arsenate Surfaces Complexes (Redrawn from Davis et al., 1978)

Figure 2.2 illustrates the monodentate and bidentate bonding using arsenate complexes. Protonated bidentate species occur at low pH as the surface functional groups of hydrous metal oxides are protonated at low pH; while, bidentate and mono-dentate species predominate at the mid pH range and low pH, respectively (Streat et al., 2008b). Table 2.2 lists the various forms of arsenic that are found in groundwater based on pH.

Table 2.2 Speciation of Arsenate and Arsenite (adapted from Streat et al., 2008b)

	Speciation	pH	pKa
Arsenate	H_3AsO_4	<2.24	
	$H_2AsO_4^-$	<7	2.2
	$HAsO_4^{-2}$	7-11	7.08
	AsO_4^{-3}	>11	11.5
Arsenite	H_3AsO_3	2-9	
	$H_2AsO_3^-$	9-12	9.22
	$HAsO_3^{-2}$	>12	12.3

2.3. Effects of Water Composition on Arsenic Removal

2.3.1. Iron

The oxidation of naturally present Fe^{2+} ions in groundwater forms hydrous ferric oxides precipitates that have a high affinity for arsenic adsorption and it could be beneficial for arsenic removal from groundwater containing a high concentration of arsenic (Roberts et al., 2004). The sand itself does not retain much arsenic but provides the support to HFOs that adsorb the major portion of the arsenic. Average removal rates of 80% and 76% were observed in the study conducted by Berg et al (2006) for raw water samples, containing 10-382 μg/L As, treated with sand filtration and co-precipitation experiments, respectively. The mechanism involves the oxidation of Fe^{2+} to Fe^{3+} ions in the presence of an oxidizing agent (atmospheric oxygen or chemicals can also be added) followed by the oxidation of some of As(III) to better adsorbable As(V). Further, arsenites and arsenates are adsorbed on HFO particles followed by the formation of $FeAsO_4$(s) that is precipitated along with the HFOs. One study found that the adsorption affinity of As(V) to HFOs was higher compared to As(III) by a factor of 100 (Roberts et al., 2004). This shows that a positive correlation exists between the arsenic removal and initial iron concentration. Roberts et al. (2004) showed that As(V) removal increased rapidly as the concentration of Fe^{2+} ions was increased in solution from 0-2mg/L (free of P and Si); while, a much larger amount of Fe^{2+} ions were required in the case of As(III) to achieve the same removal rates.

Statistics presented by Berg et al. (2006) showed that the concentration of arsenic in sand filtered water was lowered below the WHO guidelines of 10 μg/L in 40% of the samples collected; while, 90% of the samples had an arsenic concentration below 50 μg/L. A concentration higher than 50μg/L was attributed either to the presence of a low concentration of iron or dissolved competing anions. Hence, it was concluded that the proportion in which iron and arsenic were dissolved in water played a vital role in contributing to the arsenic removal potential. Further, an Fe/As ratio of 50 was required to achieve a residual arsenic concentration of 50 μg/L and in order to comply with WHO guidelines an Fe/As ratio of 250 was required (Berg et al., 2006)

2.3.2. Manganese

The mobility of arsenic in water and its removal efficiency is strongly dependent on its oxidation state. In oxic waters arsenic occurs as a metastable species in the +III oxidation state (Chiu and Hering, 2000) and is more mobile than As (V). The slow mobility of As (V) is attributed to its adsorption capacity on a variety of sorbents such as filter media and mineral components of soils and sediments (Chiu and Hering, 2000). Since, As (III) is less strongly sorbed to a variety of sorbents, it is more mobile in water and hence it is difficult to remove. Oxidation of As (III) to As (V) enhances the immobility of the arsenic in water and concomitantly increases its removal efficiency. Therefore, an oxidative treatment must be employed for the As (III) rich water for enhanced arsenic removal. It is evident from the study conducted by Mohan and Pittman (2007) that manganese dioxide (MnO_2) also enhanced the oxidation of As (III) to As (V) in water bodies.

The oxidation of As (III) with MnO_2 or birnessite is a two step process as explained by Equations. 2.5 and 2.6 (Mohan and Pittman, 2007).

$$2MnO_2 + H_3AsO_3 \rightarrow 2MnOOH + H_3AsO_4 \qquad 2.5$$

MnOOH is the Mn (III) intermediate reaction product. The MnOOH also reacts with As (III) to oxidize it to As (V)

$$2MnOOH + H_3AsO_3 + 4H^+ \rightarrow 2Mn^{2+} + H_3AsO_4 + 3H_2O \qquad 2.6$$

The study conducted by Driehaus et al. (1995) revealed that the concentration of soluble Mn^{2+}, released in the filtrate during the oxidation of As (III) was negligible. This was attributed either to the adsorption capacity of manganese oxides for soluble manganese or the formation of arsenate-manganese ion complexes. The formation of arsenate-manganese complexes is favorable for arsenic removal as it provides adsorption sites for removal of arsenic besides the HFOs. An additional reaction could include the adsorption of As (V) by the MnO_2 surface (Mohan and Pittman, 2007) as shown in Eq. 2.7.

$$2Mn - OH + H_3AsO_3 \rightarrow (Mn^{2+})_2AsOOH + 2H_2O \qquad 2.7$$

Mn-OH is the reactive hydroxyl group on the MnO_2 surface and $(MnO)_2AsOOH$ represents the As (V) surface complex. The formation of arsenate-manganese complexes after the oxidation of As (III) needs to be investigated as very little is known about this reaction. It is believed that oxidation of As (III) causes a surface alteration on MnO_2 which creates the fresh reaction sites for As (V) adsorption (Mohan and Pittman, 2007).

The oxidation of As (III) to As (V) by manganese oxide is favorable in lowering the arsenic concentration in groundwater because the As(V) is immobile and can be easily removed through precipitation with HFOs. Further, the formation of arsenate-manganese complexes increases the adsorption of As (V) which assists in achieving the lower concentration of arsenic in filtered groundwater.

2.3.3. Effects of Anions (Silicates and Phosphates)

The effect of anions on arsenic removal is based on their adsorption affinity for ferric oxide. Further, the adsorption of potential determining anions reduces the surface potential and therefore increases the electrostatic repulsion between arsenic species and negatively charged surface sites (Meng et al., 2000). Potential determining ions are those ions that influences the surface charge of the adsorbent.

2.3.3.1. Silicates

The silicates compete with As (III) and As (V) for the adsorption sites of HFOs and reduce the number of adsorption sites available either for As (III) or As (V) and hence, reduce the arsenic removal efficiency. The adsorption of silicates reduces the surface potential of the adsorbate and subsequently increases the electrostatic repulsion between the negatively charged surface sites and arsenic species, thus, further hampering the arsenic removal (Meng et al., 2000). Silicates significantly decreases the As (III) removal at a concentration higher than 1mg/L and a pH greater than 5, while, that of As (V) is moderately affected (Meng et al., 2000). With increasing pH and silicate concentration, the effect on arsenic adsorption is more severe. The presence of silicates along with the pH higher than 8.6 significantly reduces the arsenic removal due to the interaction of silicate with Fe(III) to form a soluble polymer which reduces the amount of ferric oxide precipitate (Meng et al., 2000). Further, Roberts et al. (2004) also concluded that silicates decreased the removal efficiency of As (III) as compared to As (V) as silicates more effectively competed with As (III) for adsorption sites. The deleterious effects of silicates on As (V) removal can be controlled by maintaining the pH at 6.8 and by adding Ca^{2+} and Mg^{2+} (naturally present in groundwater) into the system to neutralize the negative surface charges (Meng et al., 2000), while the effect of As (III) can be controlled by its oxidation to As (V).

2.3.3.2. Phosphates

The affinity of anions for iron hydroxide adsorption sites based on an apparent adsorption constant decreased in the following order As (V)>Phosphate>As (III)>Silicate>Bicarbonate (Meng et al., 2002). This suggests that the presence of anions such as phosphate, silicate and bicarbonate anions can affect the adsorption of As (III) onto sorption sites due to its low affinity for surface sites and consequently its removal from groundwater. Berg et al. (2006) showed that 25% of the sand filters removed less then 70% of the arsenic and it was attributed to low Fe and/or high phosphate levels (>2.5 mg/L). The As (V) has greater affinity for sorption sites and hence its removal efficiency should only be moderately affected. However, it was also reported that the presence of silicates and bicarbonates enhanced the deleterious effects of phosphorus on the adsorption of As (V) as a result of greater site coverage by the two other anions. The increased coverage of available adsorption sites decreased the removal of As (V) (Meng et al., 2002).

2.4. Column Tests

Column tests are used to assess the performance of adsorbent media to remove heavy metals and other undesired components from surface water or groundwater. The columns are treated as a small scale laboratory filtration system that can be used to determine the potential of a full scale sand filtration system in removing arsenic from the groundwater. Determination of the adsorption characteristics of a soil requires the simulation of the passage of water being studied through a test soil (Yong et al., 1992). When the water sample containing metals is passed through the column filled with soil, the extraction of metals occurs by their retention in the soil by a combination of adsorption, precipitation, and filtration. These tests are designed primarily to gain an insight into the effect of a soil composition on the retention of pollutants in the soil solution (Yong, 2001). Figure 2.3 shows a typical column used for conducting column tests.

When the fluid or leachate is passed through the column filled with soil, the pollutant concentration in the effluent initially decreases. Then it slowly increases with time as more and more fluid is passed through the soil. The point comes when the sorption capacity of the soil is reached and no further partioning of the pollutants takes place and they remain in the fluid as they are transported through the soil (Yong, 2001). The Figure 2.4 shows the characteristic equilibrium sorption curve.

Leaching column tests result in lower sorption capacities compared to batch tests as the entire reactive soil surface is not available for the adsorption. Further, masking by changes in the surface characteristics due to coating by oxides and the formation of peds significantly affects the reactive surface available for adsorption (Yong, 2001).

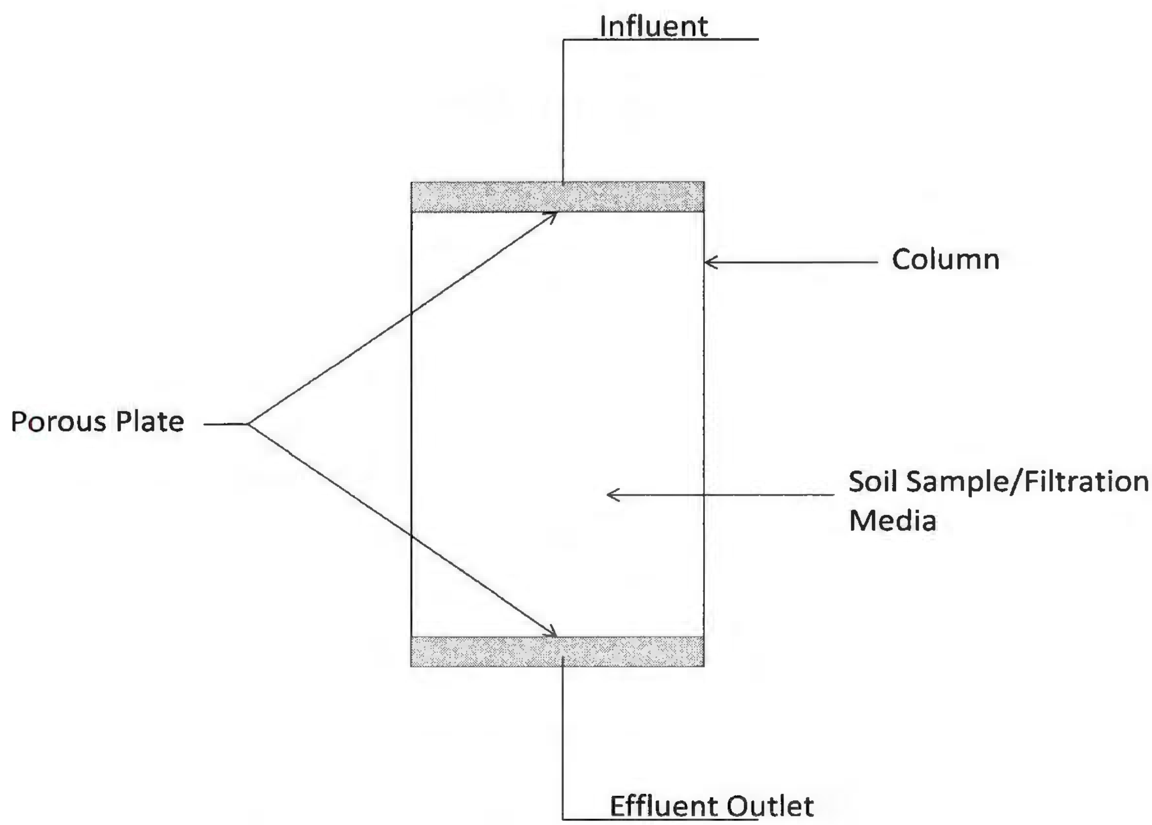

Figure 2.3Typical Column used for conducting column tests

Column based arsenic removal studies for fresh groundwater samples or simulated water are very common and reported in the literature in abundance. Various kinds of adsorbent materials have been tested including, iron fillings, silica (sand), iron oxide coated sand, granulated AC based

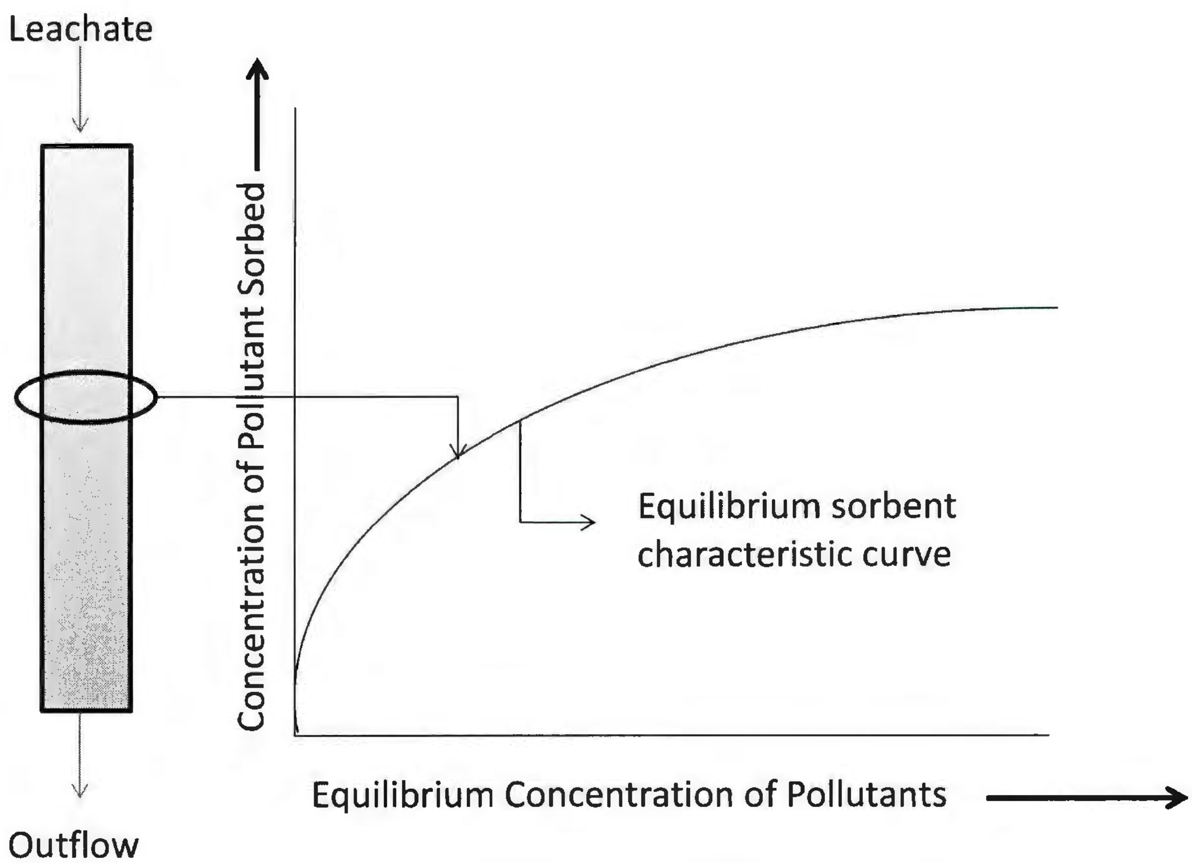

Figure 2.4 Equilibrium sorption characteristic curve from leaching column tests (Modified from Yong, 2001, pp. 161)

iron adsorbents, iron and aluminum based adsorbents and HFOs. (Tyrovolaa et al., 2006; Berg et al., 2006; Rozell, 2010; Streat et al., 2008c ; Jeong et al., 2007; and Gu et al., 2005). The efficiency of arsenic removal depends upon the type of adsorbent used, the oxidation state of arsenic i.e. As(III) or As(V), the iron concentration and the composition of the groundwater. The effect of these factors have already been discussed in detail.

2.5. Breakthrough

A breakthrough curve is an 'S' shaped curve that is generated by plotting the adsorbate concentration against the pore volume or time (U.S. Army Corps of Engineers 2001). Figure 2.5 shows a typical breakthrough curve. The breakthrough point is defined as the point on the breakthrough curve where the concentration of the adsorbate in the effluent reaches to a maximum allowable concentration (U.S. Army Corps of Engineers, 2001) or 50 % of the influent concentration in geo-environmental engineering (Yong, 2001), because at this point the flow is at steady state (Shackelford, 1993). The filter could be taken out of operation for servicing at the breakthrough point.

The water containing the targetted pollutant is passed through the column and the effluent concentration is measured over time with the results being plotted in the form of a solute breakthrough curve showing the concentration in the effluent C_i at time *i*, divided by the concentration in the influent, C_o or $\frac{c_i}{c_o}$, as shown in Figure 2.5. The $\frac{c_i}{c_o}$ of 0.5 in this figure represents the breakthrough point.

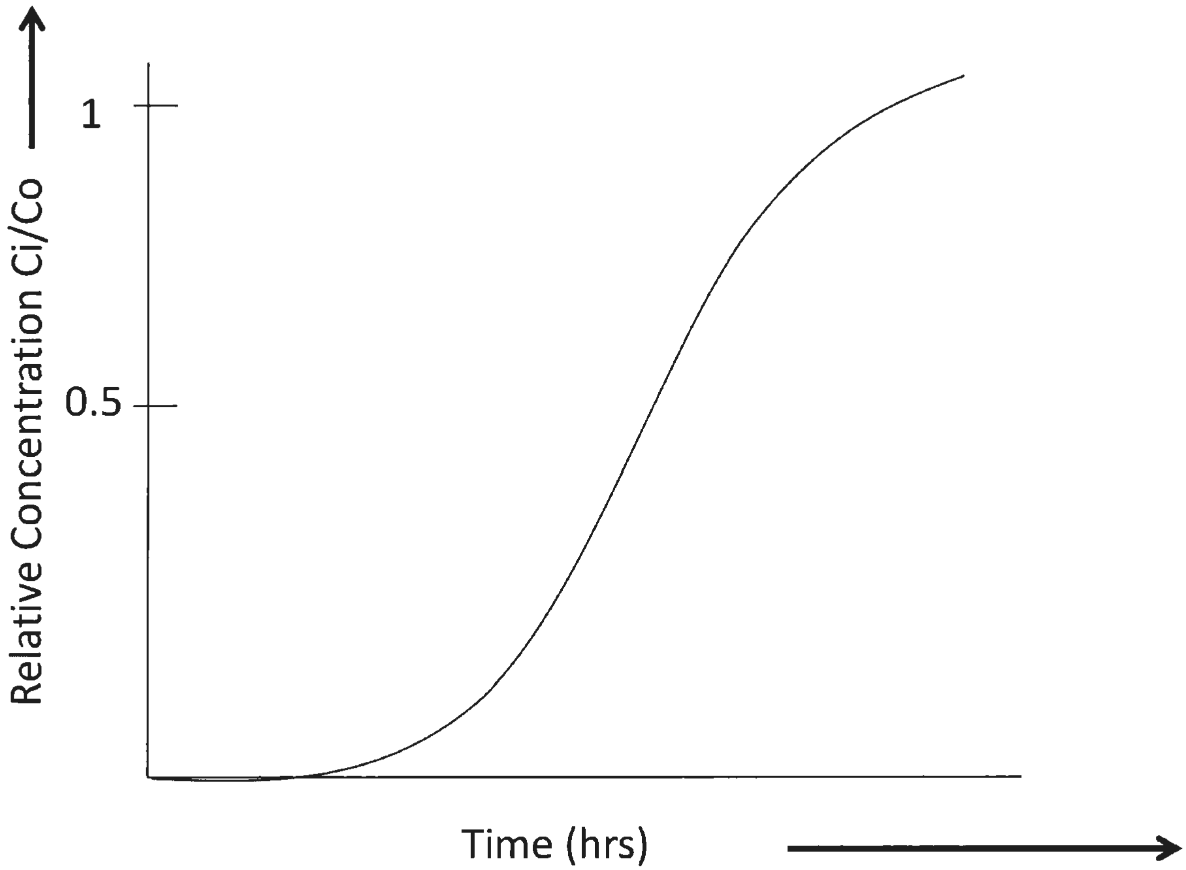

Figure 2.5 Equilibrium sorption characteristic "S" curve

2.6. Minitab

Minitab is a tool that is used for carrying out statistical analysis of simple and complex functions (Zehna, 1992). Minitab was used to statistically analyze the data obtained from the batch column tests. The correlation analysis was performed between the arsenic and all the detected elements present in the effluent of the column tests using inductively coupled plasma mass spectrometry (ICP-MS). The statistical significance of the parameters analyzed by the Minitab was determined using Table 2.3. It consists of four columns and the first column includes the degree of freedom (*df*). The *df* is the value equal to the number of samples minus two. The second, third and forth columns correspond to the Pearson's correlation (r) at three different p-values of 0.1, 0.05 and 0.01 (Rageh et al., 2007). The p-value is the probability of error in a significant correlation (Rageh, 2008). It can be seen from Table 2.3 that as the *df* is increased, the acceptable value of significant correlation is decreased. A positive or negative correlation determines if the correlation between arsenic and the other parameter is either direct or inverse, while, the magnitude of the correlation represents the strength of the correlation (Vincent, 1995).

2.7. Detecting Arsenic Levels

The cost of analyzing the water sample containing arsenic in the commercial laboratories varies from \$15 to \$50. These laboratories use EPA approved methods and equipment such as graphite furnace atomic adsorption (GFAA), inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma emission spectroscopy (ICP-ES) (Rageh, 2008). The ICP-MS analysis was used in this study and the analysis was conducted in the Department of Earth Sciences at the Memorial University of Newfoundland (MUN). The analysis of one water sample cost \$25.5. The ICP-MS analysis method was selected as it provides the concentration of 37 other elements in addition to arsenic. The results obtained from the analysis helped in understanding the effect of water composition on the arsenic removal efficiency of the sand filter media.

Table 2. 3 Pearson's Correlation (adapted from Vincent, 1995)

	P-Value Pearson's correlation		
d*f*	0.1	0.05	0.01
1	0.9877	0.9969	0.9999
2	0.900	0.950	0.990
3	0.805	0.878	0.959
4	0.729	0.811	0.917
5	0.669	0.754	0.875
6	0.621	0.707	0.834
7	0582	0.666	0.798
8	0.549	0.632	0.765
9	0.521	0.602	0.735
10	0.497	0.576	0.708
11	0.476	0.553	0.684
12	0.457	0.532	0.661
13	0.441	0.514	0.641
14	0.426	0.497	0.623
15	0.412	0.482	0.606

Chapter Three

Materials, Methods, Tools, and Equipment

The purpose of this research was to study sand filtration as a treatment technology for drinking water sources in NL, so as to reduce the arsenic concentration to the level of 7 μg/L without using chemicals. Therefore, no chemicals including an iron source, arsenic source or oxidizers were added to the water samples during the course of this study. The research was conducted using the fresh groundwater samples collected from local communities (such as the town of Wabana and the town of Freshwater) facing the issue of arsenic contamination in their groundwater and no experiments were conducted using simulated water.

3.1. Materials

3.1.1. Sand

The aim of this research project was to use locally available materials in order to reduce the dependence on mainland Canada for the materials required for the treatment of arsenic contaminated groundwater using sand filtration. This would help in minimizing the cost of operation and it is highly beneficial for the province of NL where the population is low and spread all over the province. The communities situated in NL have a low tax base and the use of locally available materials would help in reducing the associated cost, hence, making the already economical system much more cost efficient for these communities. Capital Ready Mix, a local sand provider, was contacted to supply the washed sand required for this project. (Please see Appendix A.1 for a sieve analysis of the sand). The washed sand was the sand that was surface mined, washed and screened to remove the silt and clay. The sand had a finesse modulus, FM, of 2.9. The FM is defined as the characteristic coefficient obtained by adding percentages of the sample retained on a specified series of sieves divided by 100. The smaller the value of the FM the finer is the aggregate.

3.1.2. Water Samples

It was concluded with the help of the literature reviewed that the iron to arsenic ratio (wt/wt) was going to be one of the important parameters in successfully removing arsenic from groundwater to the 7 μg/L level defined for this project. Berg et al. (2006) reported that the increase in Fe/As ratio increased the arsenic uptake. Therefore, in this study water sampling locations were narrowed down based on the composition of groundwater provided by Department of Environment and Conservation in NL (courtesy of Mr. Keith Guzzwell). Water samples were collected from two different locations namely, the Town of Wabana on Bell Island and the Town of Freshwater in Carbonear; based on the Fe/As ratios and the ease of access. 120 liters of the groundwater was collected from the town of Wabana that contained 11825.84 μg/L of iron (Fe) and 62.91 μg/L of arsenic; herein after, referred to as the high strength Wabana water. 60 liters of the supply water from the town of Wabana's water distribution network was also collected and it contained 86.327 μg/L of Fe and 4.5 μg/L of arsenic; herein after, referred to as the normal Wabana water. Column tests were conducted for the high strength Wabana water and its mixture with the normal Wabana water in the ratios of 1:1 and 1:3, respectively. The objective of conducting column tests for the mixture of the two water samples from Wabana was to study the effect of dilution on the arsenic uptake by the sand. When the arsenic concentration in the effluent reached the limit of 7 μg/L, intermittent active aeration using the vacuum pump was employed to study its effects on the arsenic uptake by the sand.

The columns were aerated for one hour after passing a batch of 500 ml of the 1:1 and 1:3 mixtures of the high strength Wabana water with normal Wabana water, respectively. Column tests were not conducted for the normal Wabana water as it had only 4.5 μg/L of arsenic or less than the limit of 7 μg/L.

120 liters of water was collected from a groundwater well at the Town of Freshwater in Carbonear that contained 507.52 μg/L and 29.707 μg/L of Fe and arsenic, respectively. The high strength Wabana water was mixed in 1:10 (Mix-1), 2:10 (Mix-2) and 3:10 (Mix-3) ratios with the Freshwater water, respectively, to get the water samples with three different Fe/As ratios. Column tests were conducted for the water collected from the Town of Freshwater and the Mix-1, Mix-2 and Mix-3 water samples. The objective of preparing the mixtures was to investigate the effects of varying the iron and other elemental concentrations on the arsenic uptake by the sand. Breakthrough curves were plotted for the high strength Wabana water and Mix-1, Mix-2 and Mix-3 water samples.

3.2. Sand Characterization Tests

3.2.1. Bulk Density

Bulk density is "the mass per volume in the graduated cylinder including both the particulate volume and the pore volume" (Gad, 2008). The bulk density of the sand was measured using the standard ASTM test method for bulk density measurement i.e. ASTM-D4531-86.

<u>Procedure followed for determining bulk density</u>

1- The beaker of a known volume i.e. 40 cm^3, weighing 26.4422 g, was filled with wet sand.
2- The beaker was then left in an oven for 48 h at 105°C.
3- The sample was taken out of the oven after 48 h and the weight was measured to be 85.5642 g.
4- The sand after drying in oven is known as the dry sand. The weight of the dry sand was 59.122 g and it was calculated by subtracting the weight of beaker, 26.4422 g, from the weight of the beaker containing dry sand, 85.5642 g.
5- Bulk Density was calculated using equation 3.1.

$$\rho_b\left(\frac{g}{cm^3}\right) = m_{sand}(g) \div V_T(cm^3) \qquad \text{Eq-3.1}$$

where, ρb is the bulk density and m_{sand} is the mass of the dry sand. V_T is the total volume and it is defined as the sum of the volume of the solids or sand particles (V_S) and the volume of the voids (V_V).

3.2.2. Pore Volume Measurement

Pore volume or pore space or porosity is "The portion of soil bulk volume occupied by soil pores" (Kirkham, 2005).

Procedure followed for determining pore volume

1- Three containers of known volume (12 cm^3) and mass were used.

2- Sample containers were filled with dry sand and their weights were recorded.

3- The density of the sand was taken as 2.65 g/cm^3.

4- The volume of the sand occupying the container was calculated using equation 3.2.

$$\mathbf{V_s(cm^3) = m_{sand}(g) \div \rho(\frac{g}{cm^3})} \qquad \text{Eq-3.2}$$

Where, m_{sand} is the mass and ρ is the density of the sand.

5- The mass of the sand was calculated using equation 3.3.

$$m_{sand}(g) = m_{sand\ with\ container}(g) - m_{container}(g) \qquad \text{Eq-3.3}$$

6- Pore volume was calculated by subtracting the volume calculated using equation 3.2 and the volume of the cylinder. The pore volume can also be expressed as a percentage of the total volume occupied by the pores.

3.3. Leaching Column Studies

Column tests normally assess the performance of adsorbent media to remove contaminants in surface waters or groundwater. In this study the sand was packed in a column, for lateral confinement, with cotton cloth (Figure 2.5) at the top and bottom ends of the column to allow the passage and uniform distribution of solution over the sand surface and to retain sand particles. Initial tests were carried out with ceramic discs at the top and bottom ends of the column, however, they were found to be interfering with the removal of iron and arsenic. Therefore, ceramic discs were replaced with cotton cloth. Tests were conducted using the water samples of different compositions to determine the amount of contaminated water that could be treated to maintain the arsenic level below 7 μg/L, and to plot breakthrough curves.

Figure 3.1 shows the aspirator bottle on the top right hand side which was filled with the arsenic contaminated water. The aspirator bottle was placed 1.2 m above the column inlet for adequate pressure head. The water flowed through the top of the partially filled sand column and was collected from the bottom end of the column through the hose connected with the valve.

The columns were manufactured by Technical Services in the Faculty of Engineering and Applied Sciences at MUN. Two columns of internal dimensions 6.7 cm x 14 cm (small) and 12.5 cm x 24 cm (large) (Diameter x Length) were fabricated to be used in this research. Figure 3.2 shows the small column.

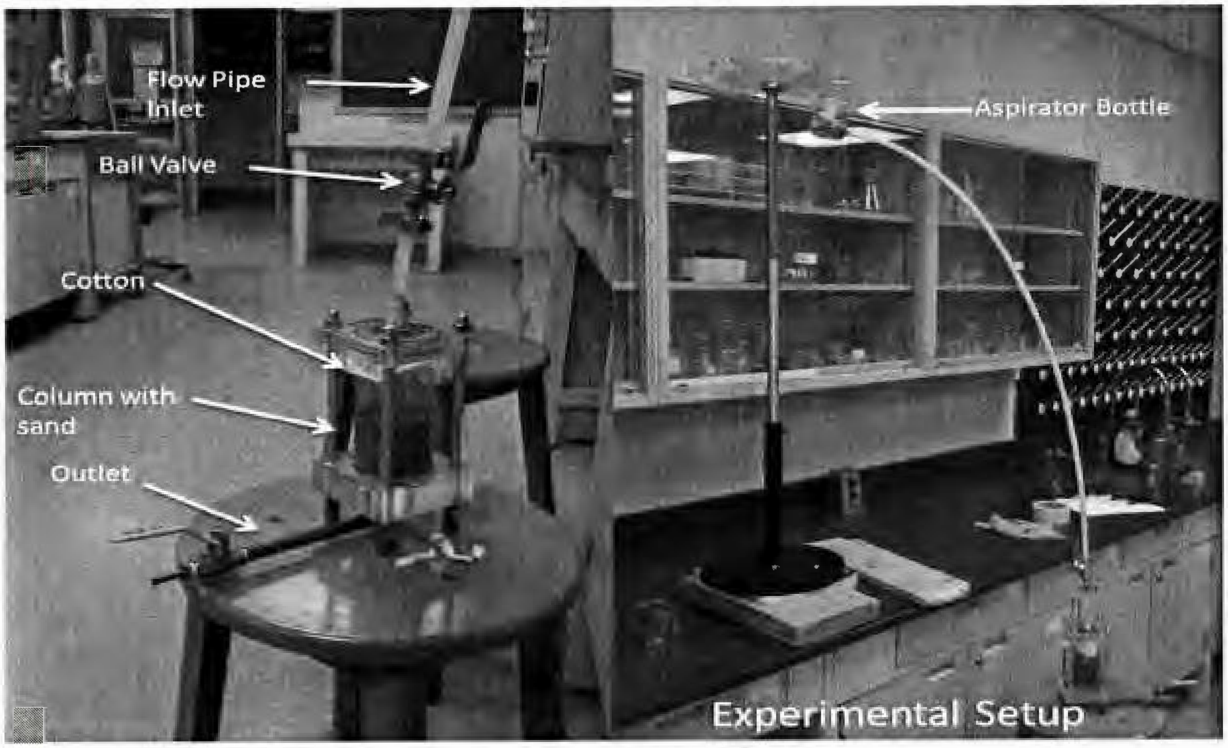

Figure 3.1 Experimental Setup

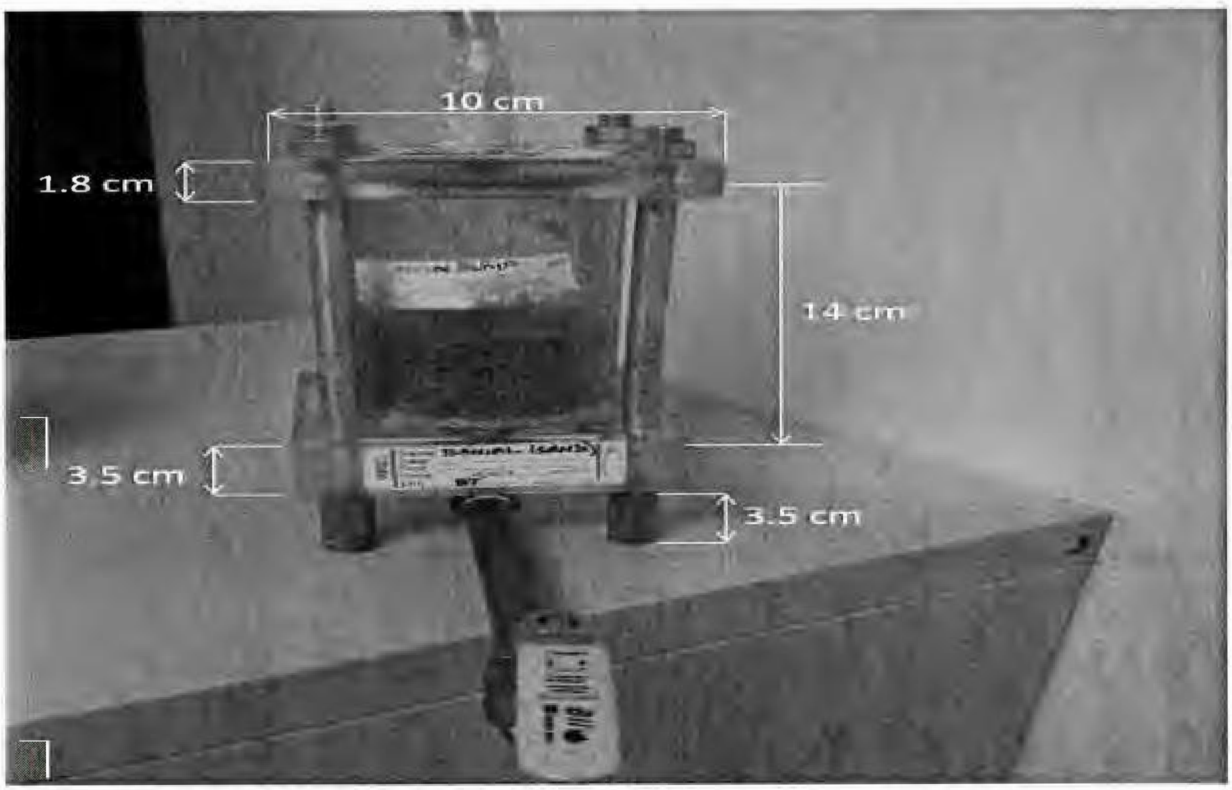

Figure 3.2 Dimensional view of the small Column apparatus

Figure 3.3 shows the various components of the column used which were

1- Hose: used for connecting the aspirator bottle to the column.

2- Nuts: screwed around the threaded bolt to join or split up the column components.

3- Upper Plate that rested over the top of the cylinder. It had a groove that snuggly fitted the upper part of the cylinder. The o-ring was placed inside the grove of the upper plate that sat around the confinement cylinder to stop leakage of water and to make sure that solution passed through the column. It was made of acrylic material which was purchased from E M Plastics.

4- Holes drilled into the upper plate for passage of long threaded bolts.

5- Upper Ceramic Plate or Cotton Cloth to uniformly distribute the water over the entire column cross section and to control the flow of solution into the column. The ceramic disc had an approximate porosity of 50% by volume, pore size of 6 μm, and hydraulic conductivity of 5.11×10^{-5}. The cloth was a mixture of 55% cotton and 45% polyester and had a thread count of 180. One layer of cloth was used at the top to make sure that precipitates, if any, passed through it and should not be retained on the cloth; The plates were purchased from Hoskin Scientific.

6- Aluminum Spacers or long threaded bolts that held together the upper and lower plates and the cylinder. The nuts were screwed on top of the spacer to hold the upper plate in place.

7- Confinement Cylinder used to contain the sand. It was made of acrylic material obtained from E M Plastics.

8- Lower Plate is similar to the upper plate.

9- Lower Ceramic Plate or Cotton Cloth: Its purpose was different than the upper plate/cotton cloth layer as it was used to retain the sand. Three layers of cotton cloth were used in the experiments conducted with the cotton cloth at the bottom to make sure that no sand particles could flow out with the solution.

10- Brass Legs to support the column. They were long enough so that the bottom run out pipe for the treated solution did not touch the bench on which column was placed.

11- Tubing and Valve: Poly-carbon tubing and valves were obtained from Canadian Tire. The valves controlled the flow and the residence time of the solution in the column.

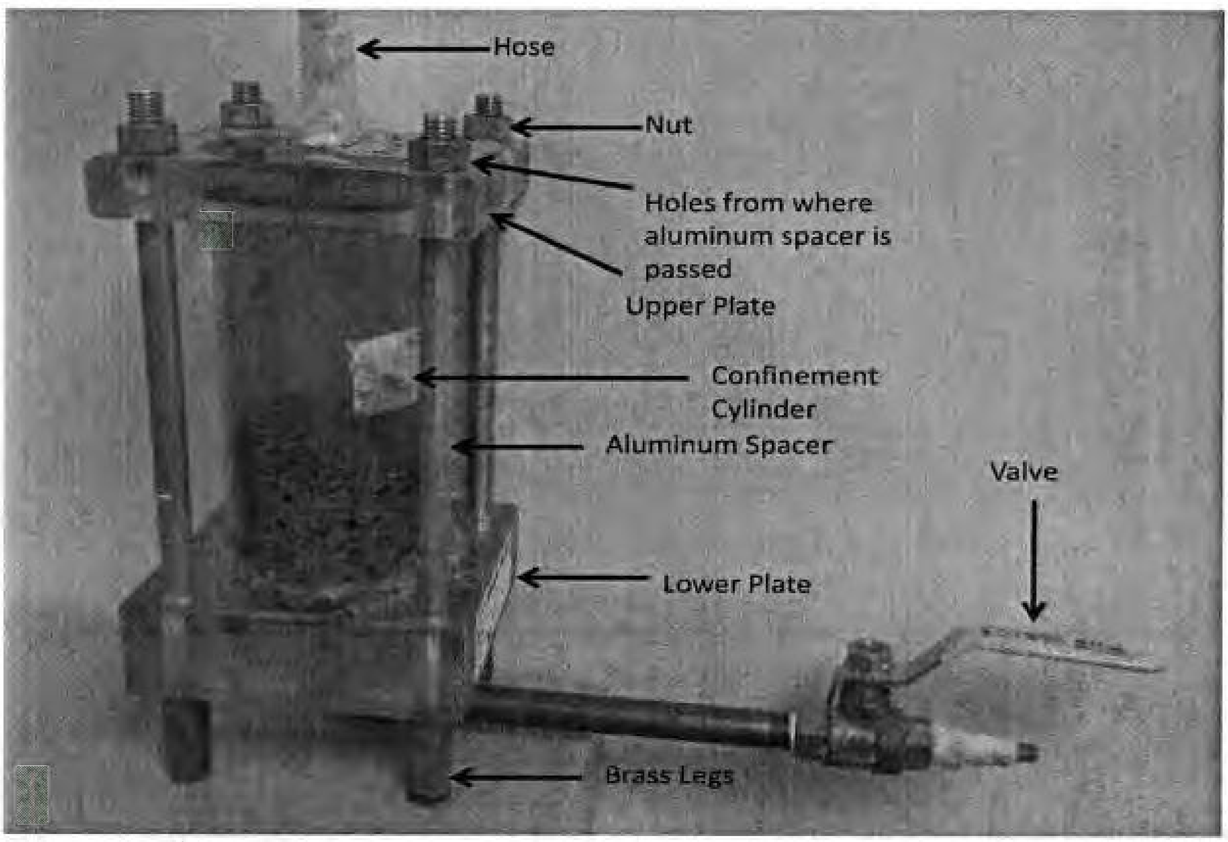

Figure 3.3 Components of the Column apparatus (small and large)

Various tests that were conducted during the course of this study are outlined in Table-3.1. The run-out test is defined as the minimum volume of the water sample that can be treated through the sand filled column without exceeding the limit of 7μg/L of arsenic in the effluent water defined for this study. The column studies are divided into preliminary and detailed experiments.

All the tests were conducted using the small columns except for the RO-2 test. Gravity filtration was used for all the tests except for the breakthrough tests for which the peristaltic pump was used owing to the large amount of water that was required to pass through the partially filled sand columns. The active aeration of the columns, where required, was conducted using the vacuum pump.

Table 3.1 Types of sand characterization and column tests

	Type of Test	Purpose
Sand Characterization test	Bulk Density and the Pore Volume	To determine the Bulk density and Pore Volume of the sand
	Test conducted using ceramic discs or cotton cloth at the top and bottom of the columns	To determine the effects of ceramic discs and cotton cloth on the arsenic removal
Preliminary Tests	Run Out 1 test (RO-1)	To determine the amount of high strength Wabana water that could be passed through the column while maintaining an effluent limit of 7 μg/L.
	Run Out 2 test (RO-2)	To determine if the larger column (12.5 cm x 24 cm) or the smaller column (6.7 cm x 14 cm) was more efficient
	Run Out 3 test (RO-3)	To study the effect of active sand aeration on the arsenic removal efficiency for the high strength Wabana water
	Run Out 3(b) test (RO-3(b))	To study the effect of the uniformity coefficient of the sand on the arsenic removal efficiency for the high strength Wabana water
	Run Out 5 test (RO-5)	To determine if removing the top layer of the sand, after run-out, would improve the arsenic removal efficiency
Detailed Experimentation	Run Out 4 (RO-4) and Run Out 4(b) (RO-4(b)) test	To study the effects of dilution and active aeration on the arsenic removal efficiency for the Wabana water. RO-4 is the 1:1 ratio of high strength Wabana water to normal Wabana water, while, RO-4(b) is the 1:3 ratio of high strength to normal Wabana water
	Freshwater	A run out test was conducted for the Freshwater water sample to determine the amount of water that could be passed without exceeding the limit of 7μg/L
	Breakthrough Test	Breakthrough test for the Wabana waters, Mix-1, Mix-2 and Mix-3. (see section 3.1.2 for mix descriptions)

3.4. Sand Preparation

The sand for all the experiments was first washed with 60°C distilled water to dissolve all the impurities. The water was then drained to collect the washed sand free of impurities and fine particles that could cause turbidity in the effluent. Further, the sand was dried in the oven at 105°C for 24 h to remove moisture.

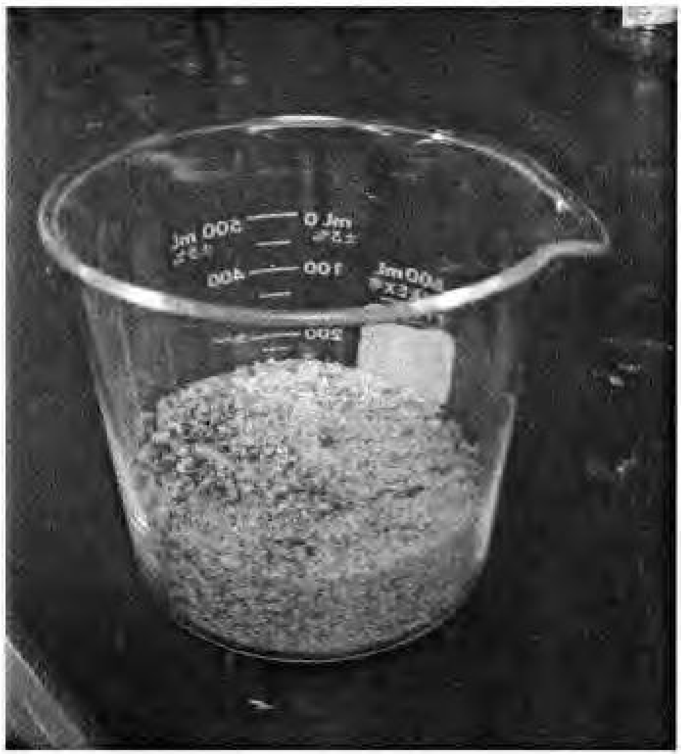

Figure 3.4 Sand Sample

The sand had a high uniformity coefficient (UC) of > 7.5. The UC is defined as the "ratio of the size of grain which has 60 percent of the sample finer than itself to the size which had 10 percent finer than itself" (Dake, 2009). In order to study the effects of UC on the arsenic removal efficiency of the sand, an experiment was conducted with the sand of UC = 4. The details of the experiment are provided in the next chapter. The sand with UC of 4 was prepared as follows:

1- Prior to sieve analysis the sand was washed with a 45 μm screen to remove all the particles finer than 45 μm.
2- The sand was then dried in the oven for 24 h to remove all the moisture at 105°C.
3- A sample of 3 kg was obtained for sieving.
4- Sieves of sizes 850 μm, 595 μm and 212 μm were nested in the proper order, coarsest at the top and a pan at the bottom.
5- The stack was placed on the sieve shaker for 15 minutes.
6- When the shaker was stopped the contents of each sieve were emptied on the paper.
7- The sieve bottom was brushed gently to dislodge any sand grains that were lodged in the mesh.
8- The sand of UC = 4 was prepared by mixing 60% of the sand that was passed through the 850 μm sieve but retained by the 595 μm sieve with 10% of the sand that was passed through 212 μm sieve. The remaining 30% of the sample comprised grain sizes that were passed through the 595 μm sieve but retained by the 292 μm sieve. The ratio of 850 μm to 212 μm was 4.

3.5. Column Preparation

The height of the sand in the columns was kept at 6.7 cm or equivalent to the internal diameter of the small column. The columns were not filled completely with the sand as the total height of the sand column was unnecessary to treat the water and it would have slowed down the filtration process as well. 1000mL of distilled water was passed through the column prior to commencing the leaching column tests in order to remove all the very fine particles that could result in turbidity in the effluent. Once the clear water was collected at the bottom of the column, only then were the tests initiated.

3.6. Vacuum Pump

The vacuum pump was used to aerate the leaching column by drawing air through the column to help oxidize the soluble Fe^{2+} ions to insoluble Fe^{3+} ions that have better adsorption characteristics.

The vacuum pump manufactured by Gast was a non-lubricated diaphragm type pump capable of generating 25.5 in-Hg of vacuum at a pressure of 60 psi with a maximum flow output of 1.90 cfm.

Figure 3.5 Vacuum Pump

3.7. Peristaltic Pump

The peristaltic pump was used to increase the flow rate of the water passed through the leaching column during the breakthrough tests as a large amount of water had to be treated. The precipitates of arsenic adsorbed on to HFOs surfaces also occupied the pore space in the sand and this further slowed the filtration rate. Owing to the slow filtration rate, normal gravity filtration would have taken months to complete the analysis which was completed in weeks using the peristaltic pump.

Figure 3.6 Peristaltic Pump

The pump supplied by Cole-Parmer was a Masterflex variable speed drive pump with a range of 6-600 revolutions per minute (RPM). The flow rate could be adjusted in the range of 0.36 mL/min to 3400 mL/min depending upon the tubing size and the RPM, though the flow rate was not changed throughout the duration of the tests. The outer diameter of the tubing was 1/2 in.

3.8. Arsenic Detection with ICP-MS

Rageh (2008) concluded that the arsenic in water measurement methods such as the La Motte test kit was not accurate in determining low arsenic concentrations (in the range of 29.84 and 62.61 μg/L). Hence, ICP-MS was selected as the sole method for determining arsenic concentrations in the untreated and effluent waters. It was more accurate and it could provide the concentration of 38 different elements in addition to arsenic namely: Lithium (Li), Beryllium (Be), Boron (B), Magnesium (Mg), Aluminum (Al), Silicon (Si), Phosphorus (P), Sulfur (S), Chlorine (Cl), Calcium (Ca), Titanium (Ti). Vanadium (V), Chromium (Cr), Iron (Fe), Manganese (Mn), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Selenium (Se), Bromine (Br), Rubidium (Rb), Strontium (Sr), Molybdenum (Mo), Silver (Ag), Cadmium (Cd), Tin (Sn), Antimony (Sb), Iodine (I), Cesium (Ce), Barium (Ba), Lanthanide (La), Cesium (Ce), Mercury (Hg), Thallium (Tl), Lead (Pb), Bismuth (Bi), and Uranium (U). Hence, ICP-MS was not only beneficial because it was an accurate test method for arsenic measurement but also because it was useful in measuring the concentration of other elements in the effluent that helped in understanding the effect of water composition on the arsenic removal efficiency. The original water samples and the samples collected after passing through the column were filtered using a 0.45 μm filter paper and then acidified with HNO_3 prior to analysis by the Department of Earth Sciences at MUN to determine arsenic and other element concentrations using ICP-MS.

3.9. Minitab

Minitab was used to statistically analyze the results obtained from the ICP-MS analysis of the treated water samples. The correlation analysis was carried out to determine the relationship between arsenic and the rest of the elements found in the effluent water. The correlation was determined based on the relative changes in concentration of arsenic and the concentrations of Li, Be, B, Mg, Al, Si, P, S, Cl, Ca, Ti, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, Se, Br, Rb, Sr, Mo, Ag, Cd, Sn, Sb, I, Ce, Ba, La, Ce, Hg, Tl, Pb, Bi, and U in the effluent. The significance of correlation data obtained from Minitab was verified by consulting Table 2.3 under the column with 0.05 p-values. Minitab uses the 0.05 p-value as a default value. The p-values mentioned in Table 2.3 on page 37 are the minimum accepted values for a significant correlation at a given sample size.

Chapter Four

Results and Discussion

The results of the all the leaching column tests conducted are presented in this chapter. The composition of groundwater samples collected from the towns of Wabana and Freshwater in addition to the mixtures Mix-1 Mix-2 and Mix-3 are included in the Appendix A.2 and A.3 respectively. Correlation analysis between arsenic and other elements present in the effluent of column tests are also included in this chapter. All element concentrations in the effluent of RO-4, RO-4(b), Mix-1, Mix-2 and Mix-3 column tests over time are given in Appendices A.4, A.5, A.6, A.7 and A.8, respectively.

4.1. Preliminary Experiments

4.1.1. Sand Characterization Test

Using equation 3.1 under section 3.2.1, the Bulk Density for the sand was calculated to be 1.47 g/cm^3. The pore volume was calculated by following the procedure described in section 3.2.2 and is outlined in Table 4.1.

Table 4.1 Calculation of Pore Volume

Mass of container (g)	Mass of sand and container (g)	Mass of sand (g)	Volume of sand (cm^3)	Porosity (Fraction or %)	Average Porosity
6.559	27.588	21.029	7.935	0.3387 (33.87%)	
6.661	28.108	21.447	8.093	0.3255 (32.55%)	0.34183 (34.183%)
6.586	29.898	20.312	7.664	0.3612 (36.12 %)	

4.1.2. Compositional Analysis of Water Samples Collected from the Town of Wabana

Two samples were collected from the town of Wabana on Bell Island i.e. one with high Fe and arsenic contents (high strength sample) and one from the normal water supply distribution network. The water samples were tested and the Fe and arsenic contents for the high strength Wabana water were 1825.84 μg/L and 62.91 μg/L, respectively (Figure 4.1). The Fe and arsenic concentrations for the normal (potable) Wabana supply water were 86.33 μg/L and 4.50 μg/L, respectively (Figure 4.1).

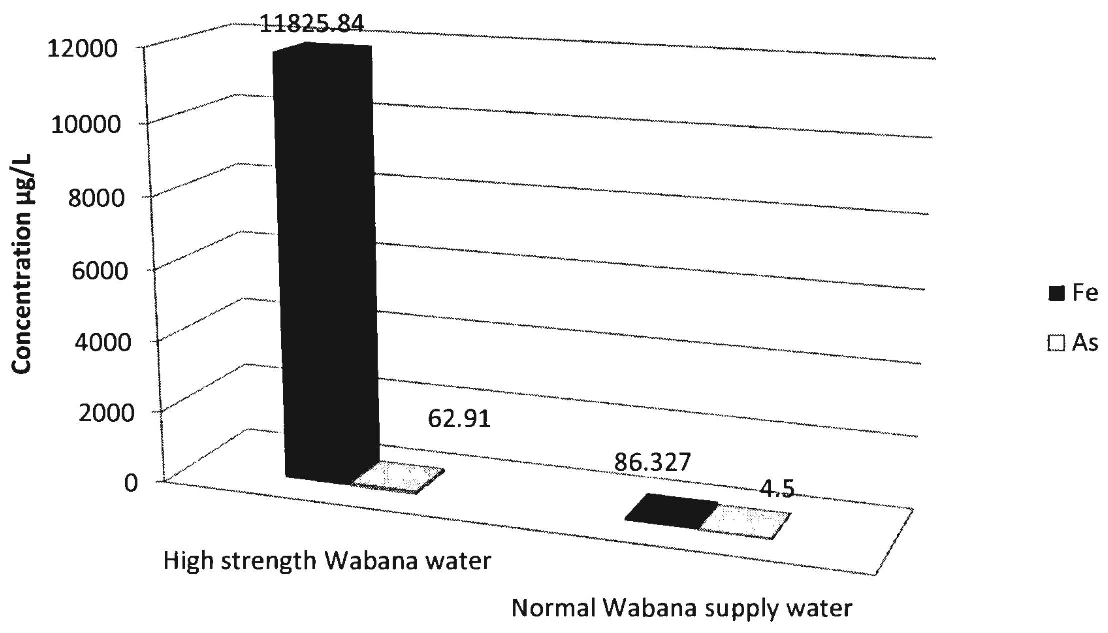

Figure 4. 1 Fe and arsenic concentrations of the high strength Wabana water and the normal Wabana water

4.1.3. Comparison between Ceramic Disc and Cotton Cloth

Two tests were simultaneously carried out with the high strength Wabana water. In one test, the small column was filled with sand and ceramic discs were used as retainers at the top and bottom of the column. In the second test, only ceramic discs were used and the column was not filled with sand. The purpose of this test was to determine if the ceramic discs were interfering with the removal of Fe and arsenic. 200 mL of high strength Wabana water were passed through both the columns and the samples were analyzed. The ceramic discs were found to be interfering with the arsenic uptake as the arsenic concentration for the high strength Wabana water was reduced from 62.91 μg/L to 28.49 μg/L (Figure 4.2) for the column without sand. Although, the result for the column filled with the sand and the ceramic discs was satisfactory as the Fe and arsenic concentrations were reduced to 0 and 0.75 μg/L, respectively (Figure 4.2), the purpose of the study was to use the sand for treatment.

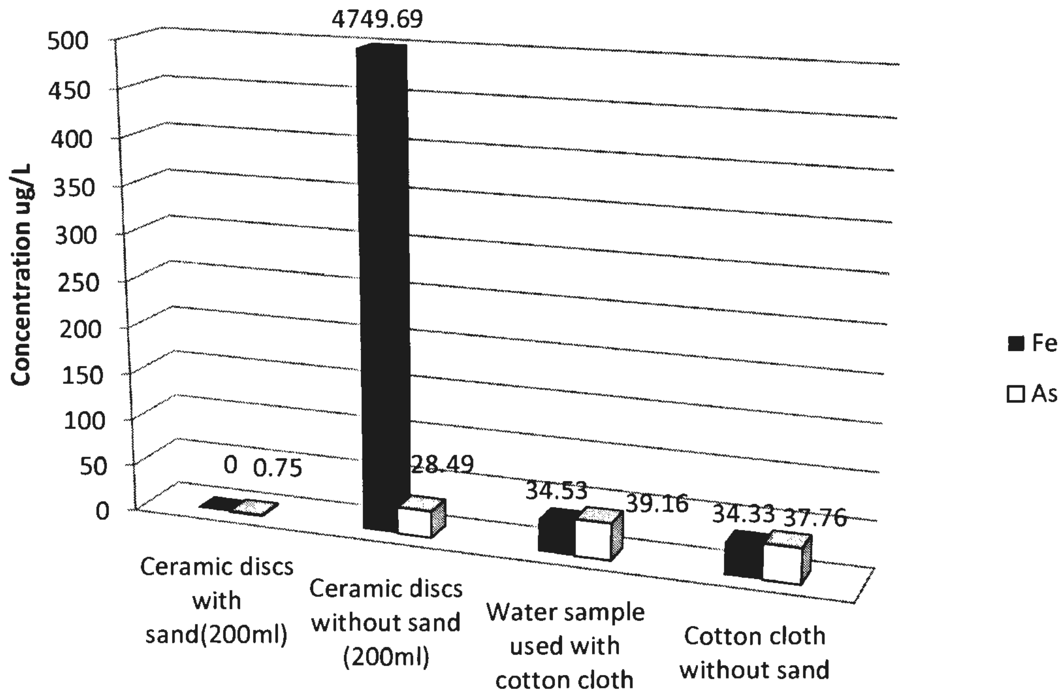

Figure 4.2 Effects of using ceramic discs and cotton cloth on top and bottom of the column as a sand retainer, with and without sand. (200mL of water was passed)

Since the ceramic discs were interfering with the removal of arsenic they were not used in any subsequent column tests. After passing a different sample of high strength Wabana water through the column using cotton cloth as a retainer, the arsenic concentration dropped from 39.16 μg/L to only 37.76 μg/L (Figure 4.2). It was concluded that the effects of the cotton cloth on the removal of arsenic would be negligible for the passage of large volumes of solution. Hence, it was decided to use the cotton cloth (180 Thread Count) in place of ceramic discs as it had a larger pore size and cotton bags filled with sand are commonly found in the water treatment applications.

4.1.4. Run-Out Test – 1

After the issue of interference of ceramic discs with the experimental results was resolved, fresh tests were conducted with the cotton cloth as the flow distributor and sand retainer in the columns. 200 mL of high strength Wabana water was passed through the small column to determine how the sand was aiding in arsenic removal. The arsenic concentration in the effluent after passing 200 mL through the partially filled column (height of sand column was 6.7 cm), was lowered from 62.91 µg/L (Figure 4.1) to 0.607 µg/L (cotton with sand, RO-200, Figure 4.3). The next step was to determine the volume of water that could be treated with the small column that contained 246.91 cm^3 of sand. It was determined that 1400 mL (RO-1400, Figure 4.3) could easily be treated while keeping the arsenic level close to the limit of 7 µg/L. When a total of 2000 mL of water was passed through the small column, the arsenic concentration spiked to 19.73 µg/L (RO-2000, Figure 4.3). The deposition of a high iron content on the top layer of the sand might have restricted the flow of water and water might have passed through the space between the column wall and the sand boundary. Further, the lack of aeration in the column might have restricted the oxidation of Fe^{2+} to Fe^{3+} ions that adsorbed the arsenic (Jovanovic et al., 2011).

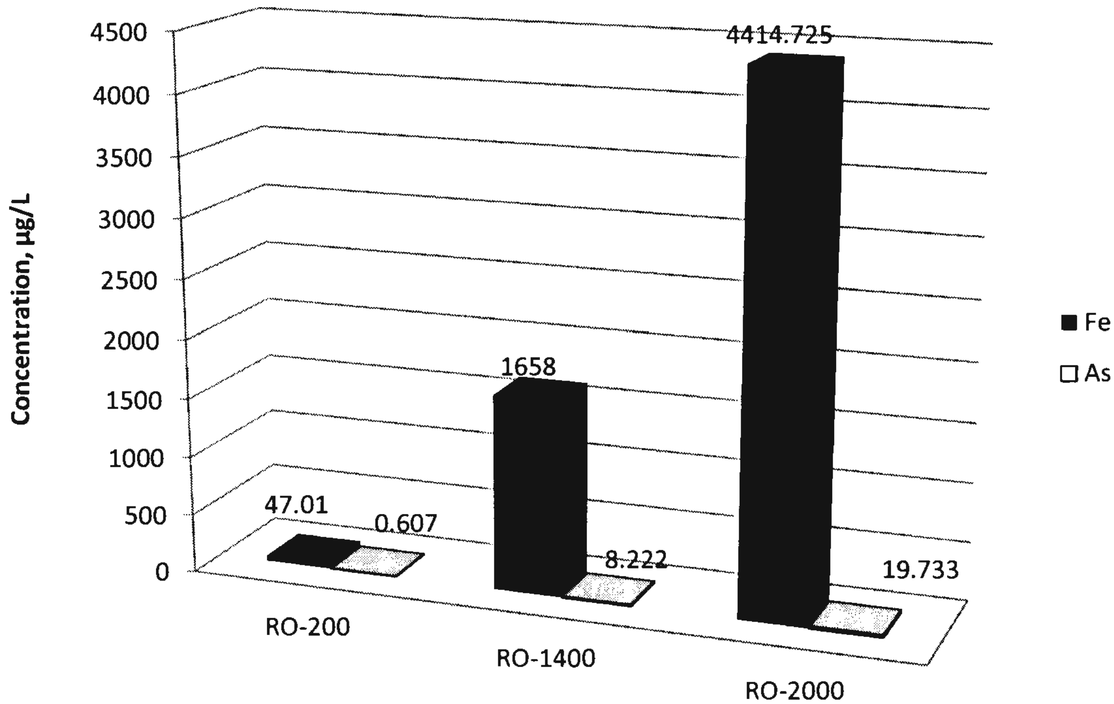

Figure 4.3 Run out Test 1 using cotton as a retainer (RO-200, RO-1400 and RO-2000 represent the Fe and As concentrations in the effluent after passing 200 mL, 1400 mL and 2000mL of the high strength Wabana water containing 11825.84 µg/L of Fe and 62.91 µg/L of As as in Figure 4.1)

4.1.5. Effect of Column Diameter (Run-Out Test – 2)

Next, it was decided to study the effect of the column diameter on the arsenic removal efficiency. Hence, two tests were simultaneously conducted with the small and large diameter columns. Both the columns were filled with sand to the same height i.e. ~6.7

cm. The volume of sand in the large column was 834.33 cm^3 and that in small column was 246.91 cm^3. In order to compare and contrast the results, the liquid to sand ratio was kept the same for both the columns i.e. 5.7:1. It was determined by the preliminary experiments that the small column could treat 1400 mL of high strength Wabana water before the arsenic concentration reached approximately 7 μg/L (RO-1400, Figure 4.3) and this gave the liquid to sand ratio of 5.7:1. So, 4730 mL of high strength Wabana water was passed through the large column. In Figure 4.4, RO2-S1400 corresponds to the volume of 1400 mL for small diameter column and RO2-L4730 corresponds to the volume of 4730 mL for the large column. The small column performed better than the large column as the arsenic concentration was lowered to 4.475 μg/L as compared to 5.827 μg/L. Further, the rate of filtration through the large column was relatively slow. The higher final effluent concentration for the large column could have meant that the solution concentrated around the middle of the column, the full diameter was not utilized, and the accumulation around the centre slowed down the filtration. Hence, it was decided to use a small column with cotton as a retainer for the remainder of the experiments.

It is pertinent to mention here that the difference in Fe and arsenic concentrations in the effluent after treating 1400 mL of water for the RO-1 test (As: 8.22 μg/L, Fe: 1658 μg/L, Figure 4.3) and the RO-2 test (As: 4.475 μg/L and Fe: 1112 μg/L, Figure 4.4) was due in part to the change in composition of the high strength Wabana water sample with time as a result of oxidation of soluble Fe^{2+}ions into insoluble Fe^{3+} ions. These Fe^{3+} ions adsorbed the arsenic and settled at the bottom of the sample container changing the Fe and arsenic concentrations in the sample. In the ground, the prevailing anoxic conditions prevent the oxidation of soluble Fe^{2+} ions to insoluble Fe^{3+} ions. When this water was exposed to oxic conditions, oxidation started taking place. Therefore, the drop in the concentrations of Fe

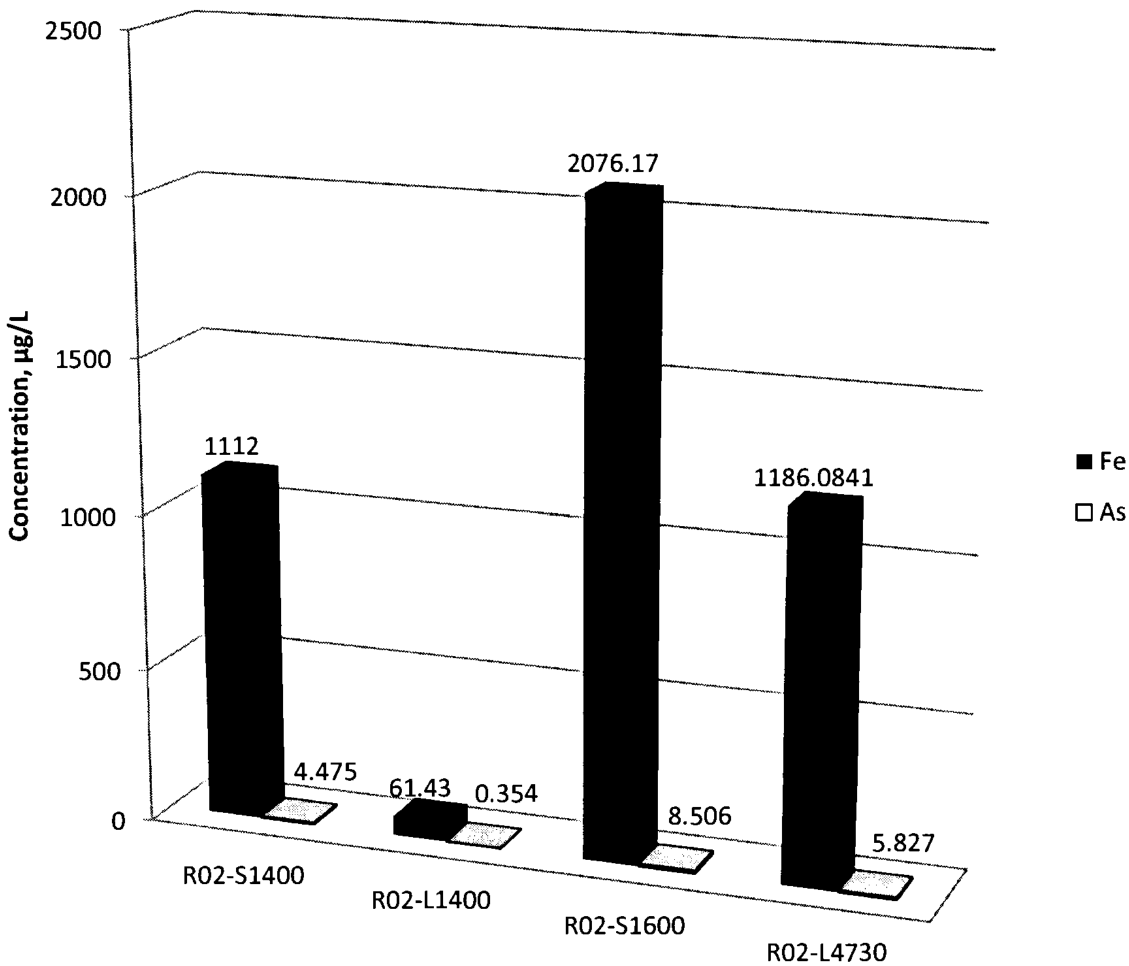

Figure 4.4 Comparison of arsenic removal efficiency between small and large columns (RO2-S1400 and RO2-L1400 represent the effluent concentration after passing 1400mL through the smaller and large columns, respectively, RO2-S1600 for 1600mL through the small column and RO2-L4730 for 4730mL through the large column for water containing 11825.84 µg/L of Fe and 62.91 µg/L of As)

and arsenic were observed. In order to avoid further changes in the concentrations, the water was transferred from the 20 liter capacity gallons to small bottles of two liter capacity. The initial arsenic concentration dropped from 62.91 μg/L for the RO-1 test (Figure 4.3) to 42.906 μg/L for the RO-2 test.

4.1.6. Effect of Removal of Top Layer of Sand

Preliminary experiments were also carried out with the removal of a top 1 cm layer of sand to determine if the sand removal improved the arsenic uptake or not. The small diameter column and sand that were used for conducting the RO2-S1600 test (results presented in Figure 4.4) were used for the RO-5 test (to study the effect of sand removal). The sand was removed to expose the fresh surface of sand and 200 mL of the high strength Wabana water was passed through the column making the cumulative volume up to 1800 mL (RO5-1800, Figure 4.5) as 1600 mL had already been passed during the RO-2 test. The arsenic concentration was higher than the level of 7 μg/L; hence, it was decided to remove one more approximately 1 cm thick layer of sand. An additional 200 mL of the same water was passed through the column again to bring the total volume to 2000 mL (RO5-2000, Figure 4.5).

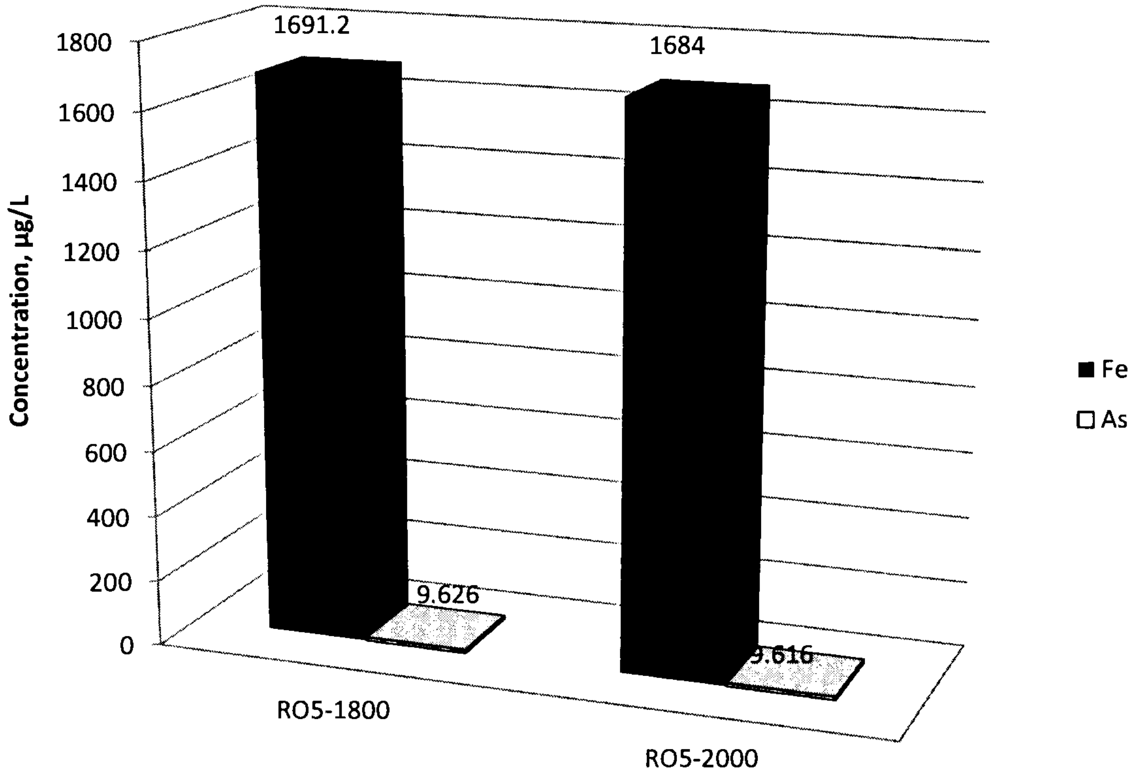

Figure 4. 5 Run Out Test 5 (RO5-1800 and RO5-2000 represents the effluent concentrations after passing 1800 mL and 2000 mL of high Fe and arsenic water, respectively, and after removing some sand).

The results in Figure 4.5 suggested that removing the top layer of sand did actually enhance the arsenic removal efficiency of the sand, when compared with the arsenic concentration recorded in the effluent water for the RO-1 test (Figure 4.3). The spike in the arsenic concentration in the effluent that was observed in the case of RO-1 test between 1400 mL (RO-1400) and 2000 mL (RO-2000) was not observed in this case. In fact, the arsenic concentration stayed at approximately the same level i.e. 9.626 and 9.616

respectively. The reason for the lower arsenic concentration in the effluent when the top layers of sand in the column were removed may have been that there was less pore blockage from the HFO precipitates. Further, the freshly exposed sand had more pore space due to a lower uniformity coefficient that allowed the oxidation of Fe^{2+} ions to Fe^{3+} ions to occur and enhance the arsenic removal. Although, the low uniformity coefficient might have increased oxidation, it might have also decreased the precipitates holding ability of sand due to the larger pore spaces. Since removing the top sand layer did not actually reduce the arsenic concentration in the effluent below the limit of 7 μg/L, more similar experiments were not conducted.

4.1.7. Run-Out Test – 3

It can be seen from the Figure 4.3 that the arsenic concentration in the treated water suddenly increased as the volume of treated water was increased from 1400 mL to 2000 mL. A possible cause could have been lack of aeration which inhibited the oxidation of Fe^{2+} ions to Fe^{3+} ions and hence arsenic removal efficiency started to decrease. In order to study the effect of aeration on arsenic removal efficiency, an experiment was designed to aerate the column for two hours with the vacuum pump after passing each batch of 500 mL of high strength Wabana water. This was achieved by suctioning air through the column. The results were very promising and the sample collected after passing 2400 mL of water i.e. RO3-2400 in Figure 4.6, had Fe and arsenic contents of 14.4 and 1.69 μg/L, respectively. The mechanism of arsenic uptake involved the oxidation of Fe^{2+} ions to Fe^{3+} ions in the presence of an oxidizing agent (atmospheric oxygen or chemicals can also be added) followed by the oxidation of some of As(III) (arsenite) to better adsorbable As(V) (arsenate).

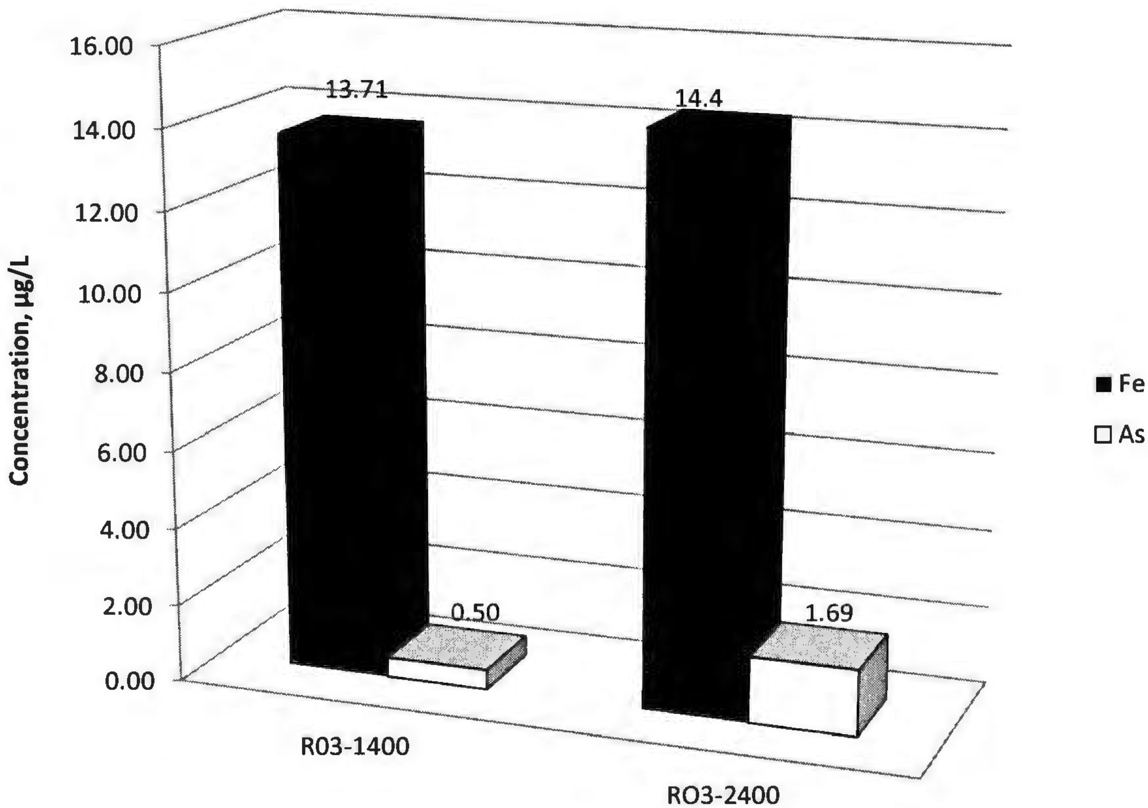

Figure 4.6 Run Out Test 3 with active aeration (RO3-1400 and RO3-2400 represent the effluent concentrations after treating 1400mL and 2400mL of the high strength Wabana water, respectively, containing 11825.84 µg/L of Fe and 62.91 µg/L of As)

It is proposed that arsenites and arsenates were adsorbed on HFO particles followed by the formation of $FeAsO_4(s)$ that was precipitated along with the HFO particles. Roberts et al. (2004) found that the adsorption affinity of As(V) for HFO particles was higher by a factor of 100 compared to the affinity of As(III). Arsenic in NL groundwater resources exists primarily in the form of arsenate, hence, it is comparatively easy to mitigate the arsenic concern in this province due to the better adsorption characteristics of the ionic As (V) species (H_2AsO^{4-} and $HadO_4^{-2}$) (Rageh, 2008).

Berg et al., (2006) suggested that an Fe/As ratio of 50 was required to achieve a residual arsenic concentration of 50 μg/L or less and in order to comply with WHO guidelines (10 μg/L) an Fe/As ratio of 250 was required. In the high strength Wabana water the Fe/As ratio were 187.98. Possibly in this study there were other mechanisms, besides HFO adsorption that aided in achieving the residual arsenic concentration of 7 μg/L. It is believed that the removal of arsenic was not only dependent on the Fe concentration but also on the presence of manganese (Mn). Manganese dioxide (MnO_2) oxidizes the As (III) to better adsorbable As (V) in water bodies (Mohan and Pittman, 2007). The study conducted by Driehaus et al., (1995) concluded that Mn had the ability to form arsenate-manganese ion complexes which are favorable for arsenic removal as they provide adsorption sites for removal of arsenic similarly to the HFOs. Hence, the presence of high Mn content (1561.51 μg/L) along with the high Fe content could have been responsible for achieving the better arsenic removal rates in this study.

The sand had a high uniformity coefficient (UC) of > 7.5 and the iron content of the high strength Wabana water was 11825.84 μg/L. Due to the high UC of the sand and the high Fe content of high strength Wabana water, the fine particles in the sand and the conversion of soluble Fe^{2+} ions to insoluble Fe^{3+} ions greatly occupied the pore space during the vacuum pump operation and over time slowed down the water filtration rate through the column. The operation of this vaccum pump also affected the bulk density of the sand by tightly packing the sand bed which further slowed down the rate of filtration. Hence, it was not feasible to pass more than 2400 mL of the high strength Wabana water through this column and experiments could not be continued further.

4.1.8. Run-Out Test - 3(b)

An experiment was designed to study the effect of a lower UC on the arsenic removal efficiency of the sand. Sand with a UC of 4 was used to facilitate passive aeration in addition to carrying out active aeration, and the results are presented in Figure 4.7. The RO-3(b) test was similar to the RO-3 test with only difference being the UC of the sand. It can be seen from Figure 4.7 that the arsenic concentrations after treating 1500 mL and 2500 mL of the high strength Wabana water were 8.190 μg/L and 8.712 μg/L, respectively. These concentrations were higher than those recorded for the RO-3 test for approximately the same volumes (Figure 4.6). Further, the Fe and arsenic concentrations after passing 2500 mL were found to be 1296 μg/L and 8.712 μg/L, respectively, which were low compared to the Fe and arsenic concentrations recorded for the RO-1 test for 2000 mL i.e. 4414 μg/L and 19.73 μg/L, respectively (Figure 4.3). It was therefore concluded that active aeration aided in reducing the arsenic concentration in the effluent.

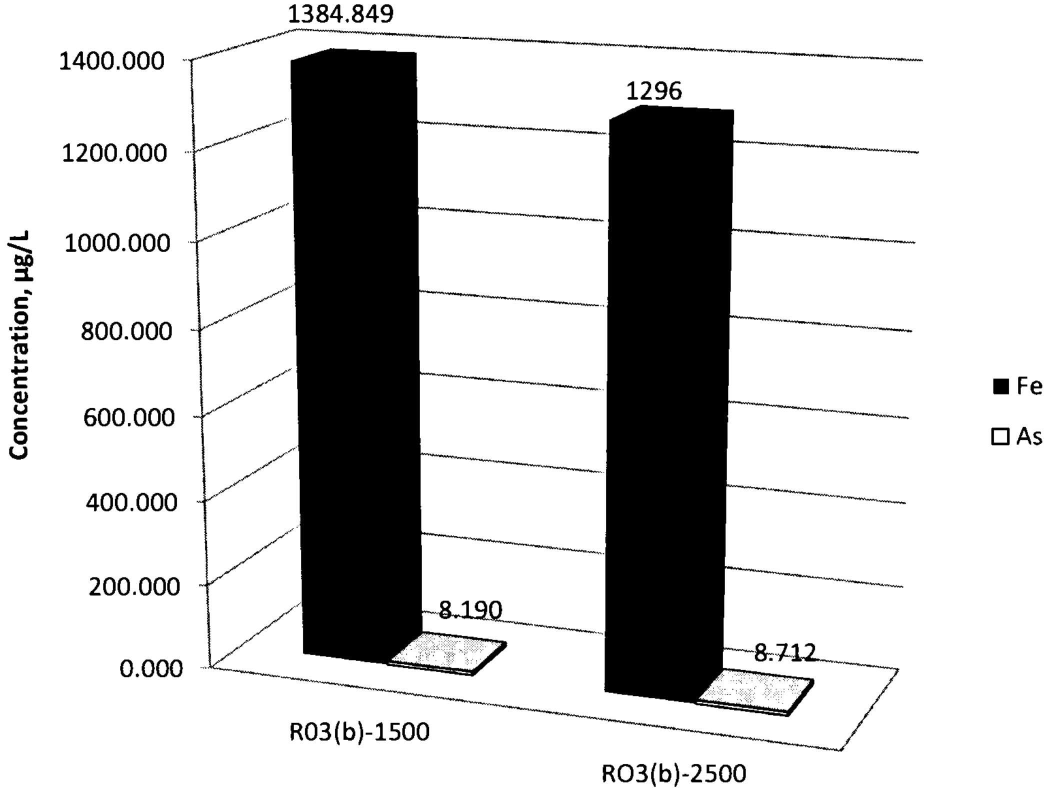

Figure 4.7 Run Out Test 3(b) with active aeration (RO3(b)-1500 and RO3(b)-2500 represents the effluent concentrations after treating 1500 mL and 2500 mL of the high strength Wabana water containing 11825.84 μg/L of Fe and 62.91 μg/L of As using a sand with UC of 4)

It is possible that the efficiency of arsenic removal decreased as a result of the increased pore space with the lower UC which might have reduced the ability of the sand to trap HFO precipitates. The low UC sand mix had less fine particles and as a result the porosity was increased and the capacity of sand to retain HFO particles decreased. In Figure 4.7, the Fe contents were 1384.8 μg/L and 1296 μg/L for the treated volumes of 1500 mL and 2500 mL, respectively for the RO-3(b) tests as compared to the Fe contents of 13.71 μg/L and 14.4 μg/L for the RO-3 tests for the volumes of 1400 mL and 2400 mL, respectively (Figure 4.6). The increased Fe concentration in the water corresponded directly to the increased arsenic concentration as the HFO particles have a high adsorption capacity for the arsenate species (Roberts et al., 2004).

4.2. Detailed Experiments

After conducting preliminary experiments it was decided to use a combination of dilution and aeration to conduct more extensive experiments while limiting the arsenic concentration in the effluent to 7 μg/L. This was in an effort to increase the life of the sand bed by increasing the volume of the water that could be treated i.e. reduced the sand replacement frequency.

4.2.1. Run-Out Test – 4

A combination of dilution and aeration was planned to extend the life of the sand bed. The run-out test was designed entirely for this purpose. The Run out 4 tests involved the dilution of high strength Wabana water with the normal Wabana supply water in a ratio of one to one (1:1). The objective was to study the effect of water dilution on the arsenic removal efficiency of the sand and to determine if this approach could have practical application. If high arsenic concentration groundwater was commingled with water from other groundwater wells, it might result in better conservation of water resources. The Fe and arsenic concentrations of the freshly collected Wabana water were 10045 μg/L and 65.579 μg/L, respectively at the beginning of the test. The water sample was transferred into small containers. To retard the oxidation of Fe^{2+} ions to Fe^{3+} ions the sample containers were filled to zero air space and sealed and water from only one container was used at a time. The results were very promising and suggested that 4000 mL of diluted water sample could be treated (Figure 4.8) without replacing the sand instead of 1400 mL for the high strength Wabana water (Figure 4.3). After treating 4000 mL the arsenic concentration in the treated water approached the mark of 7 μg/L and the Fe concentration was 1133 μg/L.

The waters would have naturally contained approximately the same amounts of oxygen from the air during the experiments, but the diluted sample would have had higher oxygen to arsenic ratio which might have explained the better arsenic removal in the more diluted sample.

Next, the column was aerated for one hour using the vacuum pump to help oxidize the Fe^{2+} ions to Fe^{3+} ions and 200 mL of water was passed through the column. The arsenic concentration in the treated water dropped from 6.96 μg/L for 4000 mL to 6.21 μg/L for 4200 mL (Figure 4.8). Hence, it was decided to aerate the column for one hour after treating every batch of 500 mL of water. After treating 4500 mL, the vacuum pump was taken into the service again and 500 mL of more water was filtered through the column and so on.

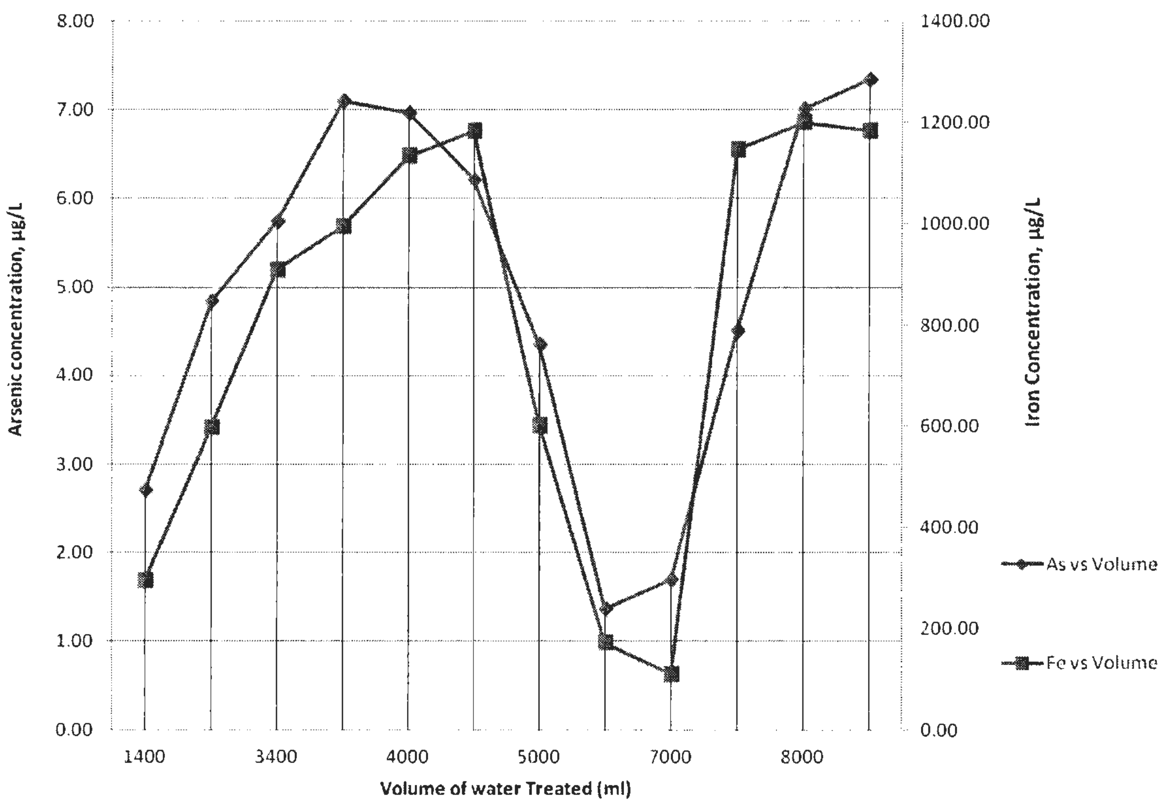

Figure 4.8 Change in Fe and arsenic concentrations in the effluent with volume for the RO-4 test with an Fe:As ratio of 1:1 and active aeration.

The downward trend in the arsenic concentration was observed and it dropped from 6.96 μg/L for 4000 mL to 1.36 μg/L for 6000 mL (Figure 4.8). Moreover, the downward trend in the Fe concentration of the effluent water was also observed from 1133 μg/L for 4000 mL to 110 μg/L for 6000 mL (Figure 4.8). This could be due to the oxidation of Fe^{2+} to insoluble Fe^{3+} ions causing Fe to accumulate in the sand rather than being carried out with the water. The results suggested that the arsenic removal efficiency was enhanced because of the oxidation of Fe^{2+} ions to Fe^{3+} ions. The Fe^{3+} ions have better adsorption characteristics for the arsenite and arsenate species. After treating further water the increasing trend in the arsenic and Fe concentrations was observed. The arsenic concentration was increased to the 7.34 μg/L after treating 9000 mL of this mix (Figure 4.8). Hence, in total 121.58 μg of arsenic was removed by treating 4000 mL of water, while, the input iron concentration was 5065.66 μg/L. The amount of arsenic adsorbed (μg) was calculated using the following formulas and is tabulated in Table 4.2:

$$\boldsymbol{Arsenic\ adsorbed(\mu g)} =$$

$$\sum\left[\left\{\boldsymbol{Influent\ As}\ \left(\frac{\mu g}{L}\right) \times \boldsymbol{Vol}\ (L)\right\} - \{\boldsymbol{Effleuent\ As}\ (\mu g)\}\right] \qquad 4.1$$

The effluent arsenic mass (μg) was calculated using the following relation:

$$\boldsymbol{Effluent\ As\ (\mu g)} =$$

$$\sum_{i=1}^{n}\left[\boldsymbol{Eff.As\ Conc_i}\left(\frac{\mu g}{L}\right) \times \{\boldsymbol{Vol.Treated_i}(L) - \boldsymbol{Vol.Treated_{i-1}}(L)\}\right] \quad 4.2$$

The influent arsenic concentration was calculated by:

$$\boldsymbol{Influent\ Arsenic}\ \left(\frac{\mu g}{L}\right) = \mathbf{0.5} \times \mathbf{65.579}\ \left(\frac{\mu g}{L}\right) + \mathbf{0.5} \times \mathbf{4.5}\ \left(\frac{\mu g}{L}\right) \quad 4.3$$

The constant i.e. 0.5 was the ratio in which the samples were mixed. 65.579 µg/L and 4.5 µg/L were the arsenic concentrations of the high strength Wabana water and normal Wabana water, respectively. The input arsenic concentration was calculated to be 35.0395 µg/L. The effluent arsenic masses (µg) for various analysis intervals are also tabulated in Table 4.2.

Table 4.2 Calculation of effluent arsenic mass (µg) and the total mass of arsenic removed (µg) for RO-4 test

Volume (mL)	Effluent As (µg/L)	Volume (L) (Col.1/1000)	Volume (L) between Successive Intervals	Input As (µg/L)	Influent As (µg) (Col3 x Col5)	Effluent As (µg) (Col2 x Col3)	As Removed (µg) (Col5 - Col6)
1400	2.70	1.4	1.4	35.04	49.06	3.78	45.28
2400	4.84	2.4	1		35.04	4.84	30.20
3400	5.74	3.4	1		35.04	5.74	29.30
3700	7.10	3.7	0.3		10.51	2.13	8.38
4000	6.96	4	0.3		10.51	2.0889	8.42
Cumulative Arsenic Removed (ug)							121.58

Similarly, the influent Fe concentration was calculated using the following equation:

$$\boldsymbol{Influent\ Iron}\left(\frac{\mu g}{L}\right) = \mathbf{0.5} \times \mathbf{10045}\left(\frac{\mu g}{L}\right) + \mathbf{0.5} \times \mathbf{86.327}\left(\frac{\mu g}{L}\right) \quad 4.4$$

The constant i.e. 0.5 is the ratio in which samples were mixed. 10045 μg/L and 86.327 μg/L were the Fe concentrations of high strength Wabana water and normal Wabana water, respectively. The influent Fe was calculated to be 5065.66 μg/L.

Minitab was used to determine the correlation between arsenic and different elements' concentrations. It was found out that arsenic levels were significantly correlated with the iron and chloride contents (Table-4.3). The correlation between Fe and arsenic was positive, while, that of arsenic and chlorine was negative.

Table 4.3 Concentrations of elements significantly correlated with arsenic in the effluent of the RO-4 test

Volume Treated (mL)	As Content (μg/L)	Fe Content (μg/L)	Cl Content (μg/L)
1400	2.70	294.04	41653
2400	4.84	597.20	44073
3400	5.74	910.04	38313
3700	7.10	994.86	55154
4000	6.96	1133.93	36137
4200	6.21	1184.00	50802
5000	4.35	601.50	41741
6000	1.36	171.44	60653
7000	1.70	110.00	106519
7500	4.51	1184.00	35589
8000	7.01	1200	37104
9000	7.34	1146	33418
Correlation with As	1	0.906	-0.597

According to Vincent (1995), for data of 12 different samples, a significant correlation should be of value 0.576 or more. The Fe based adsorbents are widely used in water treatment applications to adsorb the arsenic and the high positive correlation between Fe and arsenic in Table 4.3 is in accordance with the literature (Leupin and Hug 2005, Gu et al. 2005 and Berg, et al. 2006). Further, the chloride anion has the same effect as that of other anions like phosphate, silicate and bicarbonate anion on arsenic adsorption i.e. it competes with arsenic for the iron oxides adsorption sites (Meng, et al. 2002). The effect of chloride is more significant for As (III) than for As (V) (Meng, et al. 2002).

4.2.2. Run-Out Test – 4(b)

The Run out 4(b) test was similar to the Run-out-4 test with only difference being the ratio of the waters used. It involved the dilution of high strength Wabana water with the normal Wabana water in a ratio of one to three (1:3). Like the RO-4 test, the RO-4(b) test was designed to study the combined effect of aeration and dilution on the arsenic removal efficiency of the sand medium and to compare results with the RO-1 test (Figure 4.3).

The results for the RO-4(b) test were very promising and suggested that, before replacing the sand, approximately 11,000 mL of diluted water or 0.25 x 11,000 mL or 2750 mL of the high strength Wabana water could be treated compared to 1400 mL of the high strength Wabana water (Figure 4.3) or 4000 mL of diluted water (or 2000 mL of the high strength Wabana water) in the RO-4 test (Figure 4.8) before any aeration was carried out.

After treating 10,500 mL, the arsenic concentration in the effluent was 6.232 μg/L and the column was aerated for one hour using the vacuum pump to help oxidize the Fe^{2+} ions to Fe^{3+} ions. Following aeration 500 mL of water was passed through the column and the arsenic concentration in the effluent decreased from 6.232 μg/L (at 10,500 mL) to 4.751 μg/L (at 11,000 mL) (Figure 4.9). Hence, it was decided to aerate the column for one hour after treating every additional 500 mL of water. After treating 11,500 mL, the vacuum pump was taken into the service again and 500 mL more water was filtered through the column and so on. The downward trend in the arsenic concentration was observed and it dropped from 6.232 μg/L at 10,500 mL to 2.513 μg/L at 14,000 mL (Figure 4.9).

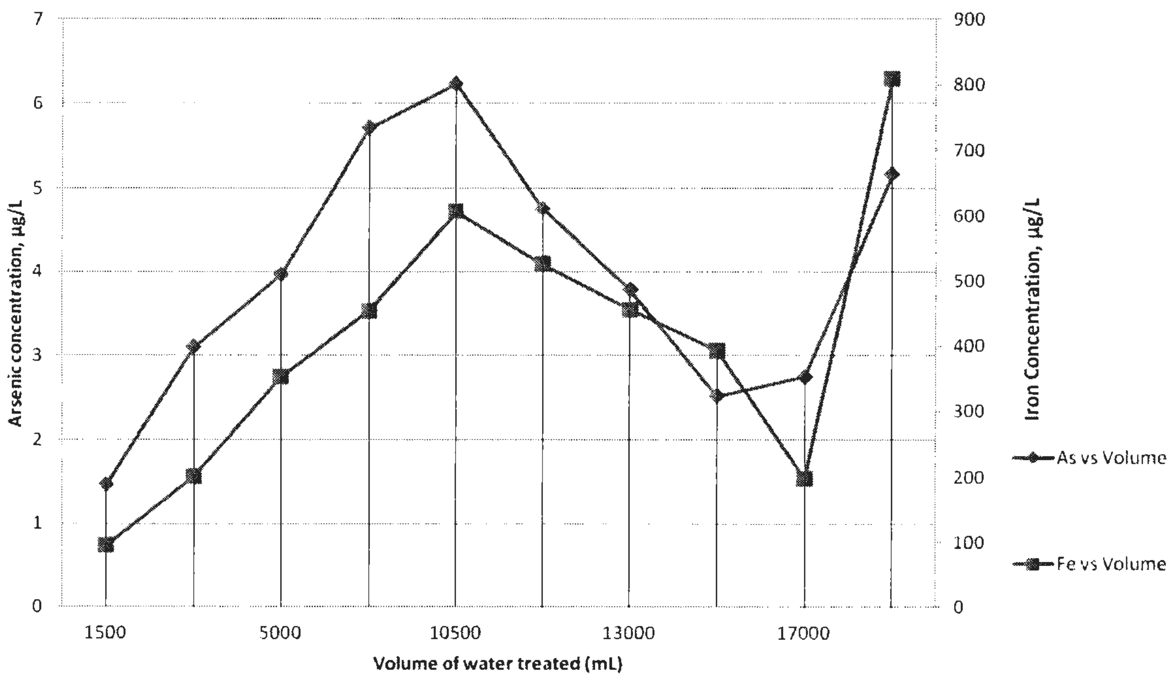

Figure 4.9 Change in iron and arsenic concentration in the effluent with volume for the RO-4(b) test with an Fe:As ratio of 1:3 and active aeration

After treating 17000 mL, an upward trend in arsenic concentration was observed. An arsenic concentration of 2.747 µg/L corresponded with the effluent volume of 17000 mL (Figure 4.9). Moreover, the downward trend in the Fe concentration of the effluent water from 605.99 µg/L at 10,500 mL to 392.14 µg/L at 14000mL was also observed (Figure 4.9). This suggested that oxidation of Fe^{2+} ions to the insoluble Fe^{3+} ions was taking place and Fe was accumulating in the sand rather than being carried out with the water. The results suggested that the arsenic removal efficiency was enhanced because of the oxidation of Fe^{2+} ions to Fe^{3+} ions that had better adsorption characteristics for the arsenite and arsenate species (Roberts et al., 2004). For 18000 mL, the Fe content was raised to 808.2 µg/L (Figure 4.9), while the arsenic concentration increased to 5.157 µg/L (Figure 4.9).

In total 166.50 µg of arsenic were removed by treating 10,500 mL of water before any aeration was carried out, while, the input Fe concentration was only 2576 µg/L. The amount of arsenic adsorbed (µg) was calculated using Equation 4.1 and the effluent arsenic masses (µg) were determined using Equation 4.2 (in section 4.2.1). The masses of arsenic removed (µg) at various analysis intervals are tabulated in Table 4.4.

The input arsenic concentration was calculated as:

$$\boldsymbol{Influent\ Arsenic\ \left(\frac{\mu g}{L}\right) = 0.25 \times 65.579\ \left(\frac{\mu g}{L}\right) + 0.75 \times 4.5\ \left(\frac{\mu g}{L}\right)} \quad 4.5$$

The constants i.e. 0.25, 0.75 are for the ratio in which samples were mixed. 65.579 μg/L and 4.5 μg/L were the arsenic concentrations of high strength Wabana water and normal Wabana water, respectively. The input arsenic concentration was calculated to be 19.770 μg/L.

Table 4.4 Calculation of effluent arsenic mass (μg) and the total mass of arsenic removed (μg) for RO-4(b) test

Volume (mL)	Effluent As (μg/L)	Volume (L) (Col1/1000)	Volume (L) between Successive Intervals	Input As (μg/L)	Influent As (μg) (Col3 x Col5)	Effluent As (μg) (Col2 x Col3)	As Removed (μg) (Col5 - Col6)
1500	1.47	1.5	1.5	19.77	29.65	2.205	27.45
4000	3.093	4	2.5		49.42	7.7325	41.69
5000	3.965	5	1		19.77	3.965	15.80
7500	3.817	7.5	2.5		49.42	9.5425	39.88
9500	5.704	9.5	2		39.54	11.408	28.13
10500	6.232	10.5	1		19.76975	6.232	13.53775
Cumulative Arsenic Removed (ug)							166.50

Similarly, the input Fe concentration was calculated using following equation:

$$\boldsymbol{Influent\ Iron}\ \left(\frac{\mu g}{L}\right) = \mathbf{0.25} \times \mathbf{10045}\left(\frac{\mu g}{L}\right) + \mathbf{0.75} \times \mathbf{86.327}\ \left(\frac{\mu g}{L}\right) \quad 4.6$$

The constants i.e. 0.25 and 0.75 represent the ratio in which samples were mixed. 10045 μg/L and 86.327 μg/L were the Fe concentrations of high strength Wabana water and normal Wabana water, respectively. The influent Fe was calculated to be 2576 μg/L.

Minitab was used to determine the correlation between arsenic and different elements' concentrations. It was found that the arsenic levels were significantly and positively correlated with the Fe and lithium (Li) contents (Table 4.5).

According to Vincent (1995), for data of 10 different samples, a significant correlation should be of value 0.632 or more. The affinity of oxides of Fe for arsenic has been mentioned in the literature and a lot of work has been carried out in this area (Leupin and Hug 2005, Gu, et al. 2005 and Berg, et al. 2006). However, the interaction between Li and arsenic is still unknown and has not yet been mentioned in the literature and still needs to be explored. Although, the correlation observed between Li and arsenic was not very strong, Li could have reduced the adverse effects of anions in inhibiting the arsenic co-precipitation with oxides of Fe either by affecting the surface charge or enhancing the floc aggregation of Fe oxides.

Table 4.5 Concentration of elements significantly correlated to arsenic in effluent of RO-4(b) test.

Volume Treated (mL)	As Content (μg/L)	Fe Content (μg/L)	Li Content (μg/L)
1500	1.470	94.90	2.642
4000	3.093	200.000	13.936
5000	3.965	353.031	12.572
9500	5.704	454	14.416
10500	6.232	605.99	15.758
11000	4.751	525	15.106
13000	3.778	456	11.154
14000	2.513	392	1.906
17000	2.747	198.201	18.100
18000	5.157	808.230	15.426
Correlation with As	1	0.802	0.641

4.2.3. Comparison of RO-1, RO(4) and RO-4(b) Tests

The influent Fe and cumulative arsenic amounts removed for RO-1, RO-4 and RO-4(b) tests are compared in Figure 4.10 to show the effects of diluting the high strength Wabana water with normal Wabana water. It can be concluded from Figure 4.10 that 76.56 μg of arsenic was removed or 1400 mL of high strength Wabana water was treated in sample RO-1400 of the RO-1 test (Figure 4.3). However, after incorporating a 1:1 dilution of the high strength Wabana water and normal Wabana water, 121.58 μg of arsenic was removed or 4000 mL of water was treated for RO-4 test (Figure 8). Similarly, 166.50 μg of arsenic was removed or 10,500 mL of the one to three mixture of Wabana's high strength water with Wabana's normal water could be treated in the RO-4(b) test (Figure 9) test before the arsenic concentration approached the allowable limit of 7 μg/L. It is evident from Figure 4.10 that as the dilution was increased, a greater quantity of water could be filtered and sand replacement frequency could be decreased as the concentration of influent Fe was decreased. The higher the Fe concentration, the more quickly it occupied the pore space in the sand bed limiting the Fe holding capacity of the sand which in turn influenced the arsenic removal efficiency. Hence, it was concluded that if there are one or two wells in the water supply system with high arsenic contents, the water from these wells might be used for potable purposes after sand filtration if the water is diluted with the groundwater wells containing low arsenic concentrations, provided that they have high concentrations of Fe and/or Mn. Further, if dilution is combined with aeration, the efficiency of the filtration system can be further augmented.

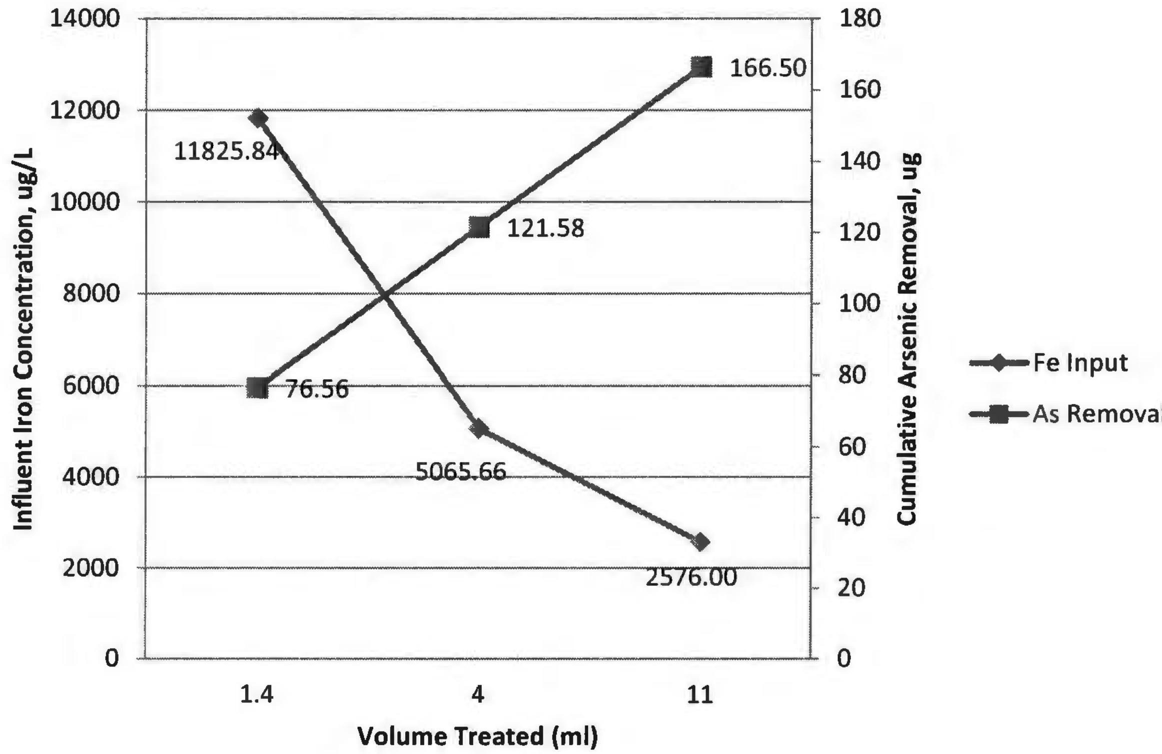

Figure 4.10 Comparison of cumulative arsenic removal versus Fe input for RO-1, RO-4 and RO-4(b) tests without considering the effect of aeration

4.2.4. Run-Out Test for Water Sample Collected from the Town of Freshwater

The water collected from the Town of Freshwater was filtered through the column partially filled with sand to determine the amount of water that could be treated before the arsenic concentration exceeded the level of 7 μg/L. The column and sand were prepared in the same manner as for the other column tests and the results are presented in Figure 4.11.

It can be seen from Figure 4.11 that after treating 1000 mL of water collected from the Town of Freshwater, the Fe and arsenic concentrations dropped from 507.52 μg/L and 29.707 μg/L to 117.46 μg/L and 4.88 μg/L, respectively. As additional water was passed through the column, the arsenic concentration increased to 8.217 μg/L or higher than the limit of 7 μg/L set for this project. It was concluded that the low removal rates were due to the low Fe concentration which is the main source for providing adsorption sites for the arsenic in the form of HFOs.

Therefore, it was decided to conduct more column tests by mixing the high strength Wabana water with the water from the Town of Freshwater in three different Fe/As ratios. Since, the Fe/As ratio was the most important factor in removing the arsenic from the water. The ratios of Wabana to Freshwater waters used were 1:10, 2:10 and 3:10 and were named Mix-1, Mix-2 and Mix-3, respectively.

The elemental composition of these mixes is included in Appendix A.3. The Fe/As ratios (wt/wt) for Mix-1, Mix-2 and Mix-3 were 17.282, 32.227 and 64.957, respectively. The purpose of carrying out these column tests was to determine the minimum Fe/As ratio that could be used to control the arsenic concentration in the effluent.

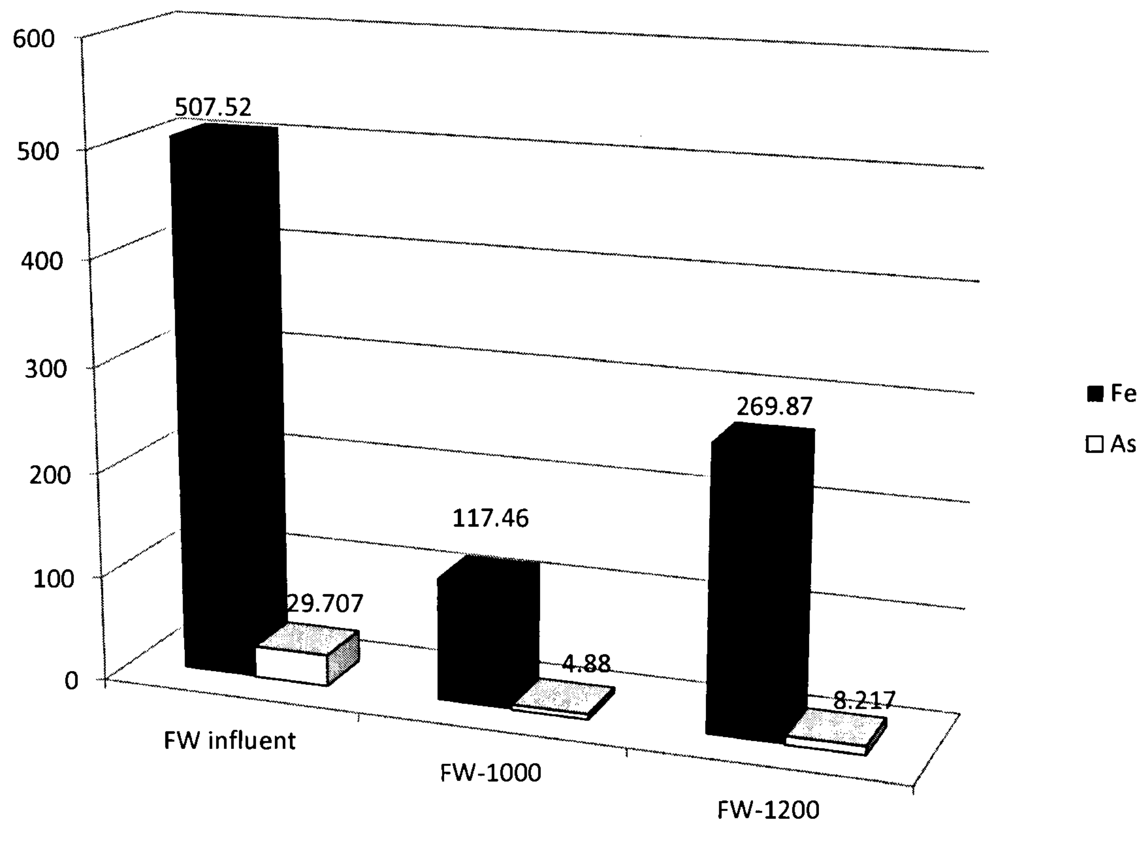

Figure 4.11 Run-Out test for the water collected from the Town of Freshwater (FW influent represents the concentrations of Fe and As in the Freshwater groundwater, whereas, FW-1000 and FW-1200 are the Fe and As concentrations after treating 1000mL and 1200mL of water through the partially filled sand column)

4.3. Breakthrough Curves

Breakthrough curves as explained in section 2.5 were used to show $\frac{Ci}{Co}$ versus time (h) for the arsenic and significantly correlated heavy metals found in the effluent sample. C_i is the effluent concentration of a selected element at time 'i'; while, C_o is the initial concentration of the same element.

4.3.1. High Strength Wabana Water

Breakthrough analysis was conducted for the high strength Wabana water. The concentration of Fe and arsenic in the influent was 8486.688 µg/L and 37.787 µg/L, respectively giving an Fe/As ratio of 224.59. The drop in the Fe and arsenic concentrations from 11825.84 µg/L and 62.91 µg/L, respectively, for the freshly collected water was associated with the instability of this water sample as explained in section 4.1.4.

The column test was allowed to proceed for 150 hours until approximately 11,500 mL of water had passed. The filtration rate at the start of experiment was 125 mL/h which slowly dropped as the test progressed because the pore space in the sand bed quickly filled with the adsorbing species. The average filtration rate was approximately 79.1 mL/h. The peristaltic pump was employed to conduct the breakthrough analysis at a filtration rate higher than the gravity filtration. The parameters such as flow rate of the peristaltic pump were not changed throughout the duration of the test, however, the drop in the rate of filtration was observed due to the filling up of pore space in the sand bed with the adsorbing species. The breakthrough curves were drawn using $\frac{Ci}{Co}$ versus time (h) for As, Fe and Mn. (Figure 4.12).

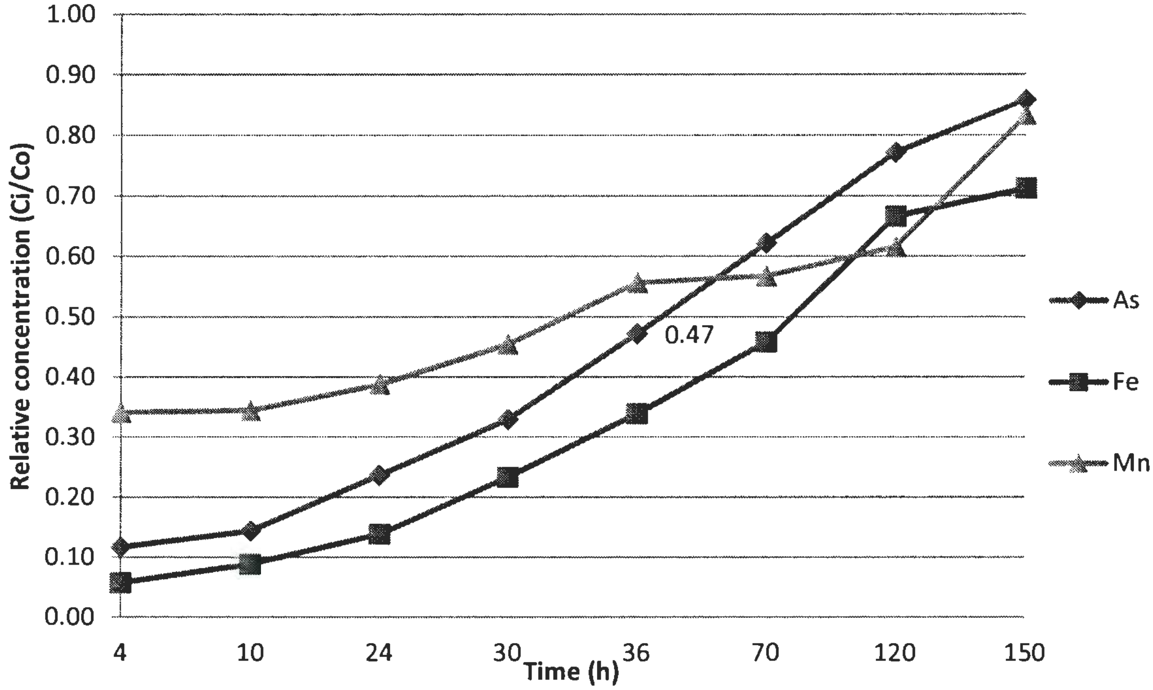

Figure 4.12 Breakthrough curves for As, Fe and Mn when conducting column tests with the high strength Wabana water.

It can be seen from Figure 4.12 that the arsenic concentration dropped from 37.787 μg/L to 4.4 μg/L in the first 4 h and then the uptake rate decreased gradually. After 150 h, the arsenic concentration in the effluent went up to 32.44 μg/L. The breakthrough occurred after approximately 36 h when a value of 17.83 μg/L was obtained (Figure 4.12). Similarly in the first 4 h for the Fe and Mn, the concentrations dropped from 8486.688 μg/L and 3384 μg/L to 483.05 ug/L and 1154 ug/L, respectively. The breakthrough for the Fe occurred after 70 h (3389.4 μg/L), while that of Mn occurred after 36 h (1882.1 μg/L). At the end of the test, the Fe and Mn concentrations were 6046.40 μg/L and 2820.3 μg/L, respectively.

Minitab was used to find the elements that were significantly correlated with the arsenic concentration and they were found to be Be, P, V, Cr, Fe and Mn. The correlation values are shown at the bottom of the Table 4.6. Other than Fe and Mn, the rest of the elements were negatively correlated with arsenic. Iron hydroxide based adsorbents could be used to adsorb SO_4^{-2}, SeO_3^{-2}, PO_4^{-3} and CrO_4^{-2} ions (Meng and Letterman, 1996; Goldberg, 1985, Zachara et al., 1987 and Chowdhury and Yanful 2010). Therefore, in the presence of sulphates, phosphates and chromate ions, the arsenate species competed with them for the HFOs adsorption sites and hence they were found to be negatively correlated with the arsenic. Similarly, it was reported that vanadate anions have the ability to adsorb onto the Fe based adsorbents (Naeem et al., 2007). Most likely they also competed with the arsenic anions for the HFOs adsorption sites. It can be seen from Table 4.6 that as the concentration of the arsenic in the effluent was increased, the concentration of V, P and Cr decreased meaning these anions were negatively correlated with the arsenic.

Table 4.6 Concentration of elements significantly correlated to Arsenic in the effluent of Wabana water

Time (h)	Initial Arsenic (µg/L)	As (µg/L)	Be (µg/L)	P (µg/L)	V (µg/L)	Cr (µg/L)	Fe (µg/L)	Mn (µg/L)
4	37.79	4.4	37.30	358.10	8.03	5.710	483.05	1154.00
10		5.43	37.64	361.30	8.11	5.760	754.68	1165.00
24		8.95	37.65	361.40	8.11	5.770	1172.5	1312.60
30		12.43	3.41	248.50	2.46	4.045	1977.6	1537.32
36		17.83	4.48	326.00	3.24	3.297	2873.6	1882.10
70		23.49	9.91	158.80	2.67	3.255	3889.4	1919.75
120		29.16	3.59	60.323	1.99	1.029	5652.1	2082.96
150		32.44	3.410	34.60	2.17	0.928	6046.4	2820.3
Correlation with Arsenic		1.00	-0.803	-0.942	-0.846	-0.972	0.996	0.954

4.3.2. Mix-1 Test

The sample Mix-1 that had the Fe/As ratio of 17.282 and the initial arsenic concentration of 33.58 µg/L was passed through the small column continuously at a rate of 125 mL/h. The peristaltic pump supplied by Cole-palmer was used for this test. Since, the sample had the Fe concentration of only 580.26 μg/L, no significant drop in the flow rate through the column was observed. A total of 38,500 mL of water was passed through the column in approximately 325 h giving an average flow rate of 118.5 mL/h. The concentration of elements that were present in the effluent and were significantly correlated with the arsenic are tabulated in Table 4.7.

Table 4.7 Concentrations of elements significantly correlated with arsenic in the effluent of Mix-1, the 1:10 mixture of the high strength Wabana and Freshwater waters collected from the Towns of Wabana and Freshwater

Time (h)	Initial As (μg/L)	As (μg/L)	Li (μg/L)	S (μg/L)	Cl (μg/L)	Fe (μg/L)	Ni (μg/L)	Cu (μg/L)	Zn (μg/L)
8	33.58	2	0.95	14318	115175.3	11	47.94	103.82	1069.12
36		4.50	1.93	6247.27	92021.03	18.98	18.91	51.92	595.80
68		6.35	2.94	5437.46	91051.09	21.16	14.14	59.93	665.71
84		5.86	2.48	13509.2	92373.52	13.42	13.59	42.88	291.16
200		11.54	2.84	4370.74	88251.65	16.67	9.07	44.87	328.41
290		16.94	4.67	63426.3	140799.8	3.06	2.82	60.39	397.94
315		20.37	3.69	68199.6	132160.2	66.68	1.51	14.58	117.87
325		23.93	4.31	71532.2	141403.9	203.18	2.26	16.39	98.15
Correlation with Arsenic		1.00	0.879	0.901	0.768	0.777	-0.780	-0.757	-0.805

According to Vincent (1995), for data of 8 different samples, a significant correlation should be of value 0.707 or more. The influent arsenic concentration was 33.58 μg/L and after 8 h the effluent arsenic concentration was 2 μg/L after which the arsenic uptake by the sand gradually decreased. After 325 h, the arsenic concentration in the effluent reached a maximum of 23.93 μg/L. The arsenic concentration limit of 7 μg/L set for this project was exceeded after 84 hours and the breakthrough point was reached after approximately 290 h or at an arsenic concentration of 16.94 μg/L (Figure 4.13).

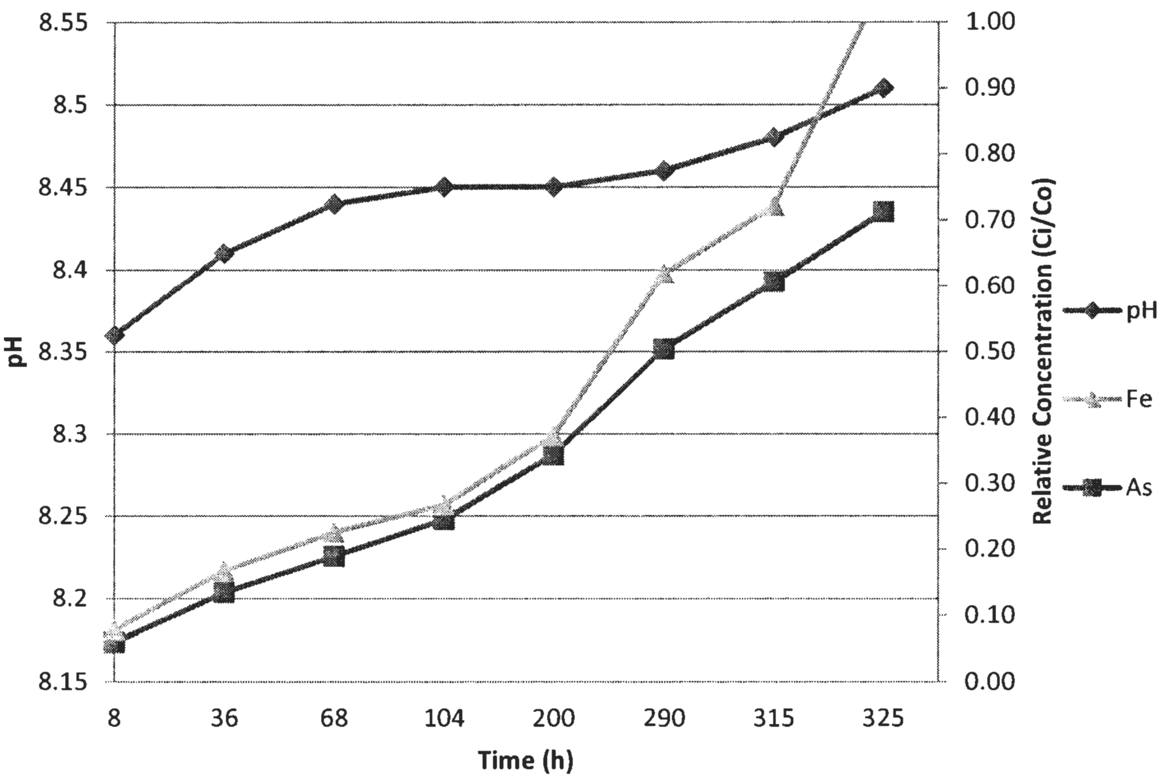

Figure 4.13 Breakthrough curve for Mix-1 test showing Fe, arsenic and pH trends

For an anion exchange material such as arsenic the adsorption normally decreases as the pH increases (Streat et al., 2008b & Driehaus et al., 1998) and this can be seen in Table 4.8. The isoelectric point (IEP) for HFOs is in the pH 7-8 range. The IEP is "the pH value of the dispersion medium of a colloidal suspension at which the colloidal particles do not move in an electric field" (McGraw-Hill Science and Technology Dictionary).

Table 4.8 Change in pH with time in relation to the Fe and arsenic concentrations in the effluent during the Mix-1 test.

Time (h)	pH	As (μg/L)	Fe (μg/L)
0	7.97	33.58	580.26
8	8.36	2	11
36	8.41	4.50	18.98
68	8.44	6.35	21.16
84	8.45	5.86	13.42
200	8.45	11.54	16.67
290	8.46	16.94	3.06
315	8.48	20.37	66.68
325	8.51	23.93	203.18

Therefore, below this pH, the surface of the adsorbent remained positively charged and it attracted anions. Stumm & Morgan (1981) suggested the mechanism of ligand exchange for protonated arsenic species for the pH below the IEP with the help of following equations.

$$FeOH + H_2AsO_4^-(aq) \longleftrightarrow FeH_2AsO_4^- + OH^-(aq) \qquad 4.7$$

$$FeH_2AsO_4^-(aq) \longleftrightarrow FeHAsO_4^{-2} + H^+(aq) \qquad 4.8$$

The release of OH^- ions from HFOs (FeOH, Equation 4.7) increased the pH of the solution and decreased the positive surface charge, lowering the forces to attract anionic species. The proton was dissociated from the acid surface to balance the OH^- ions. (Equation 4.8). Qian, et al. (2009) reported that the higher pH leads to the higher adsorption of copper ions in an aqueous solution with Fe based adsorbents. The increase in the pH, created more metal binding sites that resulted in the high metal ion adsorption. Hence, it may be suggested that the change in pH increased the adsorption of Cu, Ni and Zn ions onto the HFO adsorption sites and the adsorption of arsenic along with the other anionic species (S and Cl) was decreased. Further, Boujelben et al., (2009), studied the adsorption of nickel onto the iron oxide coated sand from aqueous solution in the pH 2 to 9 range. The optimum adsoprtion took place at pH 7 but the adsoprtion was also reported to take place between pH 7 and 9. Moreover, Srivastava and Srivastava (1990) studied the adsorption of Zn(II) on to the Fe(III) hydroxide sites at pHs of 5.5, 6.85 and 8.2. They concluded that adsorption of the Zn(II) increased with the increase in pH. Hence, it could be concluded that HFO adsorption sites were not only capable of adsorbing anionic species but cationic species as well provided that the suitable conditons were met. The decrease in effluent concentrations of the Cu, Ni and Zn with the increase in pH suggested that under these conditons Cu, Ni and Zn ions were more favorably adsorbed onto HFOs sites than arsenic. This is reflected in Table 4.7, where it can be seen that the arsenic concentration was increasing and Cu, Ni and Zn concentrations were decreasing with the rise in pH.

4.3.3. Mix-2 and Mix-3 Tests

The Mix-2 and Mix-3 samples that had the Fe/As ratios of 32.227 and 64.957 and the initial arsenic concentrations of 34.336 μg/L and 34.322, respectively, were passed through the column continuously at a filtration rate of 125 mL/h. The peristaltic pump supplied by Cole-Palmer was used to carry out the tests. The Mix-2 and Mix-3 samples had Fe concentrations of 1106.53 μg/L and 2229.43 μg/L, respectively. A total of 39,000 mL of water was passed through the column with each sample and within 315 h and with an average flow rate of 123.8 mL/h.

According to Vincent (1995), for data of 9 different samples, a significant correlation should be of a value of 0.666 or more. It can be seen from Table 4.9 that arsenic was significantly and positively correlated with Fe and significantly and negatively correlated with Be, V, Ni, Zn and Se for the Mix-2 test. The mechanism suggested to be occurring for the Mix-1 sample related to the Ni and Zn adsorption on the Fe adsorption sites could very well be responsible in this case as well. Similarly, it was reported that vanadate anions have the ability to adsorb onto the iron based adsorbents (Naeem et al., 2007). Further, Jeong, et al. (2007) reported that the adsorption of As(V) onto Fe adsorption sites was affected by the presence of Se(IV) and V(V) which was exactly in accordance with the results presented in the Table 4.9.

Table 4.9 Concentrations of elements significantly correlated with arsenic in the effluent of the 2:10 mixture of the waters from the towns of Wabana and Freshwater (Mix-2)

Time (h)	Initial As (µg/L)	As (µg/L)	Fe (µg/L)	Be (µg/L)	V (µg/L)	Ni (µg/L)	Zn (µg/L)	Se (µg/L)
8	34.34	1.910	23.00	10.020	14.17	153.800	2037	31.350
40		3.399	17.90	3.32	3.200	56.110	901.948	7.140
56		5.709	18.50	3.09	3.020	5.678	283.038	6.770
80		10.97	717.07	1.790	1	2.633	107.261	4.460
120		7.005	122.00	3.17	3.050	23.05	145.094	4.560
160		9.556	156.71	3.180	3.02	12.534	135.257	4.570
280		6.559	137.35	3.60	2.140	18.02	161.906	7.830
296		8.382	180.62	3.28	1.950	20.44	238.983	7.130
315		8.735	87.08	3.46	2.050	37.13	119.374	7.520
Correlation with As		1.00	0.693	-0.722	-0.729	-0.766	-0.828	-0.699

The pH values recorded at different instances during the test are listed in Table 4.10. The arsenic concentration remained below the level of 10 μg/L even after treating 39,000 mL. The arsenic concentration at 80 h increased briefly to 10.965 μg/L, but then dropped and after 315 h the arsenic concentration was still only 8.735 μg/L. The Fe concentration dropped from 717 μg/L at 80 h to 87.08 μg/L at 315 h. The aeration of the small column with the peristaltic pump may have been oxidizing the soluble Fe^{2+} ions to insoluble Fe^{3+} ions as the water reservoir was exposed to air and the operation of pump allowed the air to pass through the column.

Table 4.10 Changes in effluent pH and Fe and arsenic concentrations during the Mix-2 column test.

Time (h)	pH	As (μg/L)	Fe (μg/L)
0	7.91	34.34	1106.53
8	8.32	1.910	23.00
40	8.41	3.399	17.90
56	8.41	5.709	18.50
80	8.44	10.965	717.07
120	8.42	7.005	122.00
160	8.43	9.556	156.71
280	8.45	6.559	137.35
296	8.33	8.382	180.62
315	8.25	8.735	87.08

The formation of Fe^{3+} ions might have provided increased adsorption sites and been responsible for the improved adsorption of arsenic and hence the lower arsenic concentration that was recorded in the effluent. Changes in the effluent pH and iron and arsenic concentrations are depicted in Figure 4.14. Breakthrough did not occur for arsenic even after treating 39,000 mL of water for Mix-2 as it only reached 8.735 μg/L.

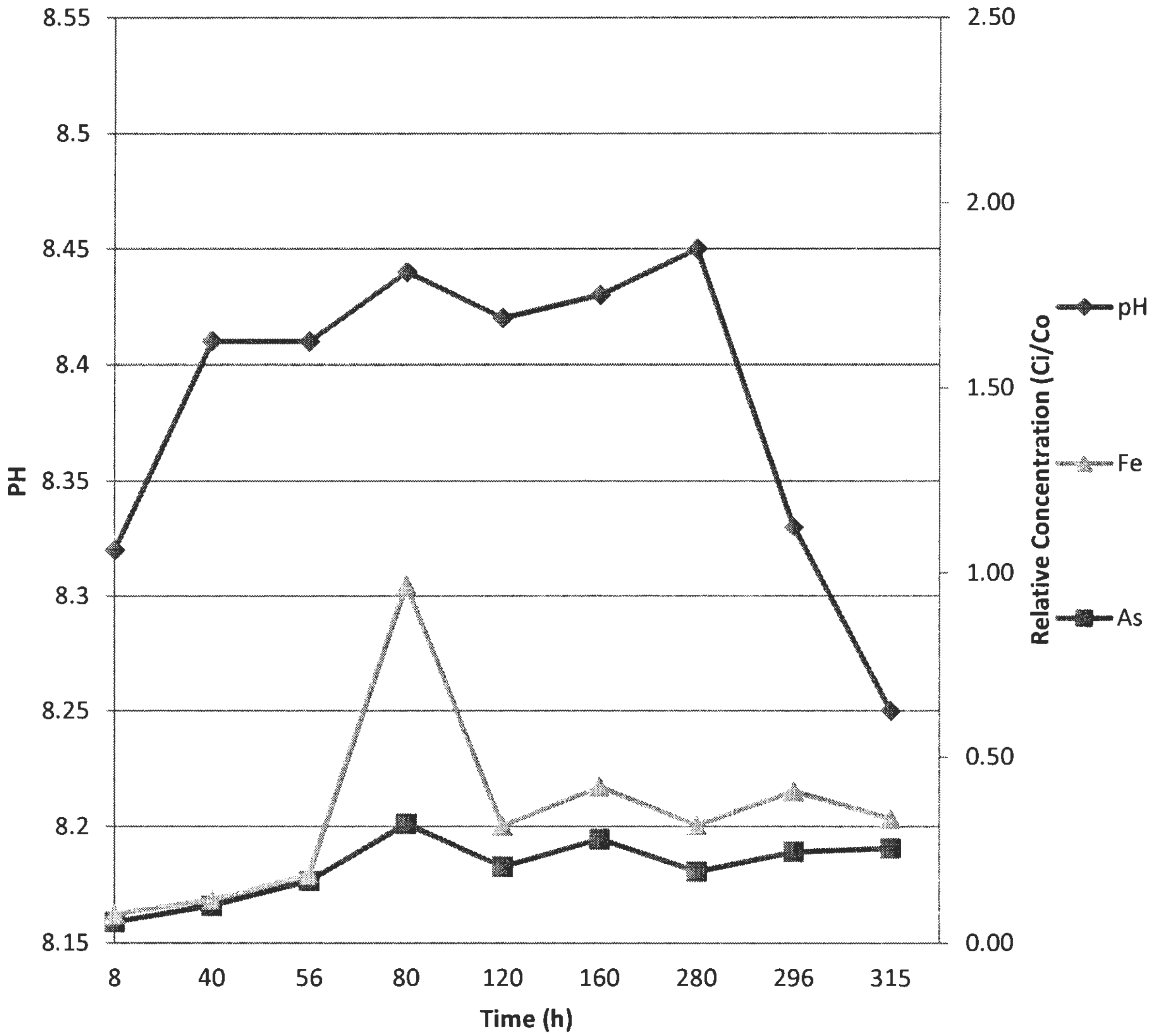

Figure 4.14 Mix-2 column test results showing Fe, arsenic and pH trends until 315 h.

The drop in the pH noted in Table 4.10 and Figure 4.14 between 280 h and 315 h could have been due to the release of proton by acids (see Equation 2.4, section 2.2). The protons reacted with OH^- ions released as a result of a ligand exchange reactions for the protonated arsenic species by the FeOH (see Equation 2.3, section 2.2). The Fe^{3+} ions were released as a result of oxidation of Fe^{2+} ions as discussed under the section Mix-1 (Figure 4.14). The increasing trend observed in the arsenic concentration during this time interval, although small, could be due to the competition provided by the V, Ni, Zn and Se for the HFOs adsorption sites. The change in pH can change the selectivity or the relative affinity preferences among various species (Rageh, 2008). It would have been interesting to continue the column test for the Mix-2 sample to see what reactions would have followed the drop in pH, but time did not permit this. This could be undertaken in the future.

According to the Vincent (1995), for 9 different samples, a significant correlation should be of value 0.666 or more. It can be seen from Table 4.11 that arsenic was significantly correlated with Fe and aluminum (Al) for the Mix-3 test. A similar response was noted for the Mix-2 sample. The arsenic concentration in the effluent at 160 h increased to 14.338 μg/L and decreased to 12.315 μg/L after 315 h. Similarly, the Fe concentration dropped from 1086.34 μg/L to 518.16 μg/L during the same period. The oxidation of soluble Fe^{2+} ions to the insoluble Fe^{3+} ions as a result of operation of the pump could be the main reason for this drop in arsenic concentration. Further, aluminum oxides are known to have a positive effect in mitigating the arsenic concern (Jeong, et al. 2007 and

Giles, et al. 2011), although, these authors reported that the iron oxides are better suited in adsorbing As(V). Therefore, the positive correlation between Al and arsenic in this study is in accordance with the literature. Changes in the Fe and arsenic concentrations and in the effluent pH for the Mix-3 test are depicted in Figure 4.15. Arsenic breakthrough did not occur as the arsenic level even after treating 39,000 mL of water for Mix-3 reached only 12.315 μg/L. The pH values taken during the course of experiment for Mix-3 are also listed in the Table-4.12.

Table 4.11 Concentration of elements significantly correlated with arsenic in the effluent of 3:10 mixture of Wabana and Freshwater waters (Mix-3)

Time (h)	Initial As (μg/L)	As (μg/L)	Al (μg/L)	Fe (μg/L)
8	34.32	1.540	8.563	100.00
40		2.677	5.076	17.180
56		5.781	16.338	86.659
80		10.944	23.02	588.169
120		11.457	34.274	665.795
160		14.338	35.631	1086.34
280		7.677	15.274	164.30
296		13.270	30.207	690.039
315		12.315	21.529	518.16
Correlation with Arsenic		1.000	0.907	0.915

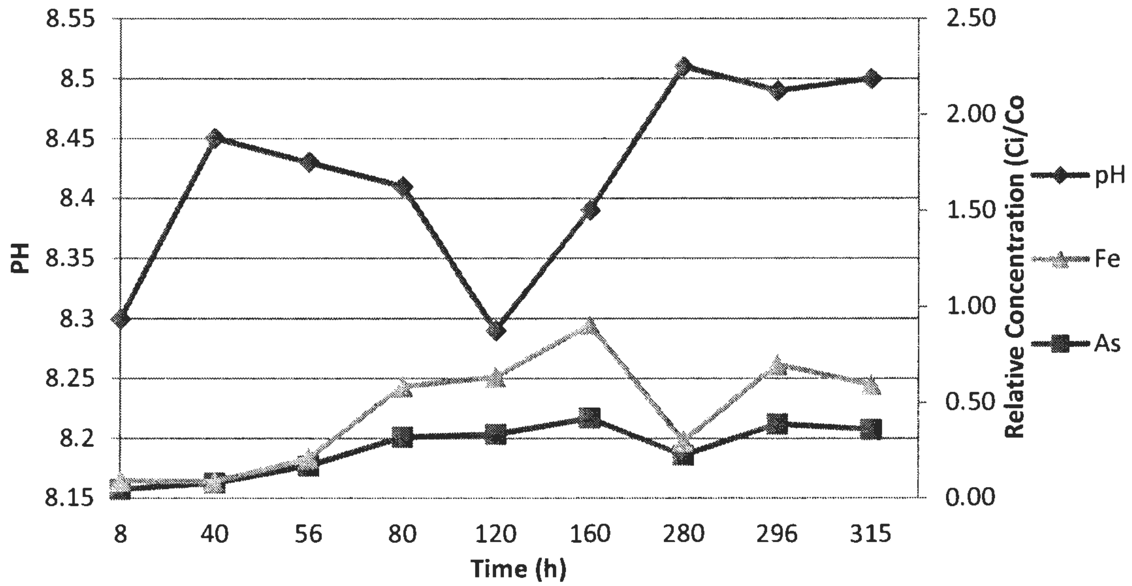

Figure 4. 15 Mix-3 column test results showing Fe, arsenic and pH trends until 315 h.

Table 4.12 Change in effluent pH, Fe and arsenic concentrations during the Mix-3 column test.

Time (h)	pH	As (µg/L)	Fe (µg/L)
0	7.80	34.32	2229.43
8	8.30	1.540	100.00
40	8.45	2.677	17.180
56	8.43	5.781	86.659
80	8.41	10.944	588.169
120	8.29	11.457	665.795
160	8.39	14.338	1086.34
280	8.51	7.677	164.30
296	8.49	13.270	690.039
315	8.50	12.315	518.16

4.3.4. Comparisons between Mix-1, Mix-2 and Mix-3

It is concluded from the preceding discussion that the Mix-2 sample performed the best. After running the experiments for approximately 325h for Mix-1 and 315 h for each of the Mix-2 and Mix-3 tests and passing 38,500 mL for Mix-1 and 39,000 mL for each of the Mix-2 and Mix-3 tests, it was concluded that the Fe/As ratio (wt/wt) of 32.227 in the case of Mix-2 test gave the most desired results. The Mix-1 test was low in Fe concentration and the competition between arsenic ions and Cu, Ni, and Zn ions for the few HFOs adsorption sites appeared to hamper the efficiency of arsenic removal. Moreover, the Fe concentration in the Mix-3 test was on the higher end and it resulted in a rapid filling of the pore spaces in the sand bed that consequently decreased the arsenic adsorption. The drop in pH between 80 h and 160 h for Mix-3 (Table 4.12 and Figure 4.14) did not improve the arsenic removal and the Fe concentration in the effluent was also found to be increased (Table 4.11). After 160 h the pH increased and both the Fe and arsenic in the effluent decreased temporarily.

The higher the Fe content recorded in the effluent, the higher the arsenic concentration reported. On the other hand, the best combination of Fe and arsenic concentrations was found in the Mix-2 test and the results presented in Table 4.9 reflected that even after running the experiments for 315 h the arsenic concentration, although above the 7 μg/L limit set for this study, still stayed below the 10 μg/L limit acceptable to Health Canada.

The comparison between the cumulative arsenic removed based on the influent Fe contents for the Mix-1, Mix-2 and Mix-3 tests is presented in Figure 4.16. It can be seen from Figure 4.16 that with influent Fe concentration of 1106.53 μg/L for the Mix-2 test, a total of 960.73 μg of arsenic was removed. Similarly, 900.48 μg of arsenic was removed with the influent Fe concentration of 2229.43 μg/L for the Mix-3 test. Moreover, with the Mix-1 test, a total of 783.62 μg of arsenic was removed with an Fe input of 580.26 μg/L. The comparison was made for the treated volume of 35,000 mL for each of the Mix-1, Mix-2 and Mix-3 tests. The amount of arsenic removed was calculated in the same way as described under sections 4.2.1 and 4.2.2 for the RO-4 and RO-4(b) tests. The Mix-2 performed better than either of the Mix-1 or Mix-3 water samples. Further, the effluent arsenic concentration in Mix-2 (8.74 μg/L) for the treated volume of 39,000 mL was lower than either the Mix-1 (23.93 μg/L) or Mix-3 (12.32 μg/L) for the treated volumes of 38,500 mL and 39,000 mL, respectively. Therefore, the Mix-2 water sample had the most ideal composition and a greater arsenic adsorption than either of the Mix-1 or Mix-3 waters. The combination of the elements and their respective concentrations were most likely responsible for this remarked behavior, but, there was insufficient data to attribute it to any specific ions and their concentrations.

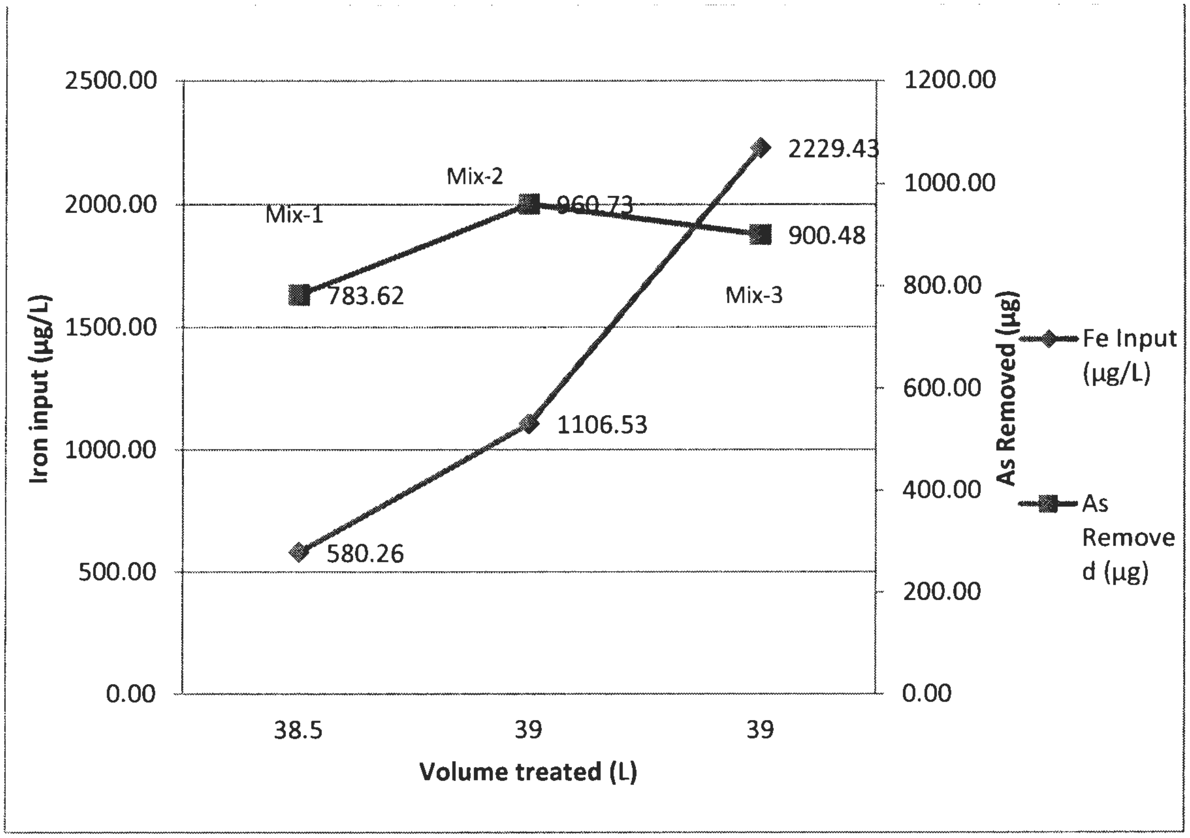

Figure 4. 16 Comparison of Cumulative arsenic removal vs Iron Input for Mix-1, Mix-2 and Mix-3 water sample

Chapter Five

Conclusions and Recommendations

5.1. Conclusions

This research studied sand filtration to remove arsenic from drinking water sources in NL to a level of 7μg/L without the use of chemicals and studied the effect of various ions present in groundwater on the arsenic removal. The iron to arsenic (Fe:As) ratio (wt/wt) was an important parameter in the arsenic removal.

Water sampling locations were chosen based on groundwater data provided by the NL Department of Environment and Conservation (courtesy of Mr. Keith Guzzwell). Two water samples were collected from the town of Wabana on Bell Island; one with high arsenic and iron concentrations (As: 62.91 μg/L and Fe: 11825.84 μg/L) and the second was the Wabana normal supply water (4.5 μg/L As and 86.327 μg/L Fe). One groundwater sample was also collected from Freshwater, Carbonear (29.707 μg/L As and 507.52 μg/L). A local sand provider, Capital Ready Mix, supplied the washed sand with a finesse modulus of 2.9.

Columns of two dimensions 6.7cm x 14cm (small) and 12.5cm x 24cm (large) (diameter X length) were fabricated to be used in this research. The high strength Wabana water was passed through both the columns and the liquid to sand ratio was maintained at 5.7:1 for both the columns. The arsenic concentrations in the effluent were 4.475 μg/L and 5.827 ug/L for small and large column, respectively. It was evident that the small column performed better and all later tests were conducted using the small columns.

The main mechanism for the arsenic removal using sand filled columns may have involved the oxidation of Fe^{2+} ions to Fe^{3+} ions in the presence of atmospheric oxygen as an oxidizing agent (atmospheric oxygen or chemicals can also be added) followed by the oxidation of some of As(III) (arsenite) to better adsorbable As(V) (arsenate). Further, arsenites and arsenates were adsorbed on HFO particles followed by the formation of $FeAsO_4(s)$ that was precipitated along with the HFOs. The HFOs are the Fe (III) hydroxides with loosely bonded water. The large surface area of HFO particles makes them a suitable adsorption media for arsenic.

1400 mL of the high strength Wabana water was filtered without exceeding the effluent arsenic limit of 7 μg/L, as compared to the 4,000 mL and 10,500 mL for mixtures of the high strength and normal Wabana waters in the ratios of 1:1 and 1:3, respectively. Combining aeration and dilution, 9,000 mL and 18,000 mL of 1:1 and 1:3 mixtures, respectively, were treated without exceeding the arsenic limit of 7 μg/L. At greater dilution, more water could be filtered with less sand replacement frequency since the Fe concentrations in the influent were less. At greater Fe concentrations the sand's pore space filled more quickly, retarding the sand's Fe holding capacity and reducing the arsenic removal. The maximum total amount of arsenic removed was 76.56 μg by filtering 1,400mL of the high strength Wabana water, while, 121.58 μg and 166.50 μg were removed for the 1:1 and 1:3 aerated mixtures, respectively.

Breakthrough analysis was conducted for the high strength Wabana water (As: 37.787ug/L and Fe: 8486.688ug/L) and breakthrough occurred after 36 hours when 17.83 μg/L (or 50%) of the initial arsenic occurred in the effluent. Using Minitab to conduct correlation analysis between arsenic and other elements in the effluent revealed that arsenic was significantly positively correlated with Fe and Mn and significantly negatively correlated with P, Be, V and Cr. The results suggested that arsenic removal was dependent upon both the Fe and Mn concentrations. Manganese dioxide (MnO_2) oxidizes the As (III) to better adsorbable As(V) in water bodies and has the ability to form arsenate-manganese ion complexes which can precipitate out (Driehaus et al., 1995) as the HFOs do. Both the high Mn (1561.51 μg/L) and Fe contents could have been responsible for the high arsenic removal rates. The P, Cr and V might have been competing with arsenic for the HFO adsorption sites.

Since the Fe/As ratio was a major factor affecting arsenic adsorption, column tests were conducted with the high strength Wabana water mixed with the Freshwater water in 1:10 (Mix-1), 2:10 (Mix-2) and 3:10 (Mix-3) proportions giving Fe/As ratios of 17.282, 32.227 and 64.957, respectively. After approximately 325 h for the Mix-1 test, 315 h for the Mix-2 test and 315 h for the Mix-3 test and passing 38,500 mL, 39,000 mL and 39,000 mL respectively, the Mix-2 test was observed to perform the best. Mix-1 was low in Fe and competition between arsenic and Cu, Ni, and Zn for HFO adsorption sites may have hampered its removal. The Fe concentration in the Mix-3 test was high and this could have filled up the sand's pore spaces too quickly and limited the arsenic uptake. Mix-2 performed the best and after 315 h the arsenic concentration in the Mix-2 effluent was still below the 10 μg/L limit considered acceptable to Health Canada.

In summary, an elevated iron concentration increased arsenic removal but with time could slow the filtration rate and ultimately increase the sand filter replacement frequency. Aeration during filtration significantly enhanced the arsenic uptake as did dilution of the high strength Wabana water with the Freshwater water. An ideal mix would neither be too lean nor too rich in Fe concentration as both negatively impacted the arsenic uptake. It is therefore suggested that sand filtration in combination with aeration and dilution, and possibly by mixing water from different sources could deal with the arsenic concern in NL.

5.2. Recommendations

HFO particles can play a very vital role in mitigating the arsenic concern in the groundwater of NL. The higher the Fe content, the greater will be the arsenic removal but the sand filter replacement frequency may increase. As a result of the deposition of iron oxides in the pore spaces, the filtration rate decreases along with the filtration efficiency. Further, the incorporation of aeration in the filtration system can significantly enhance the arsenic adsorption. Moreover, the dilution of the high strength Wabana water sample with the low Fe and arsenic containing water can significantly improve the arsenic uptake. The mixture should neither be too lean nor too rich in the Fe concentration as both have a negative impact on arsenic adsorption. Further, the presence of Mn also aids in the removal of arsenic as Mn provides additional adsorption sites for arsenic species. It is therefore suggested to use sand filtration in combination with aeration and dilution to deal with the growing arsenic concern in NL.

5.3. Future Research

The results obtained from this research suggest that sand could be an inexpensive and effective material for mitigating the arsenic concern. However, more research is required in understanding the effect of sand composition on arsenic uptake. Lithium was found to be statistically correlated with arsenic uptake and the exact mechanism is still unknown. Moreover, the effect of temperature and pH on arsenic uptake also needs to be explored. For this study the samples were selected based on the Fe/As ratio. The sand filtration effectiveness also needs to be investigated for the communities in rural NL which do not have high Fe/As ratios but have high concentrations of Mn in their groundwater sources. Since the column test with Mix-2 and Mix-3 waters did not reach breakthrough within the available time frame, similar but longer duration column tests need to be conducted to get a better understanding of the uptake mechanism and the selection of ideal water characteristics.

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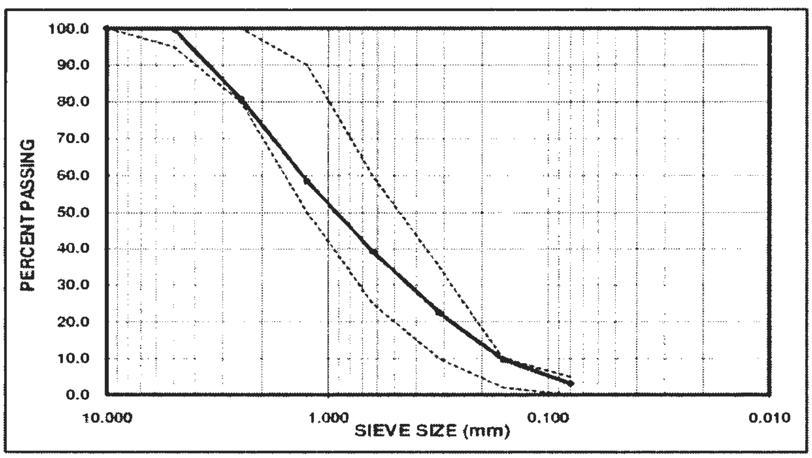
Appendix

A.1 Sieve Analysis of Sand

GRADATION ANALYSIS REPORT

Project No:	TF1030119	**Lab ID:**	3516
Project:	Aggregate Gradation Analysis Foxtrap, NL	**Sample Type:**	Washed Concrete Sand
		Date Sampled:	10-Jun-11
Client:	Capital Ready Mix		
Sampled By:	M. Lynch of AMEC	**Date Tested:**	10-Jun-11
Location:	Loading Face of Working Stockpile	**Sample Source:**	Black Mountain



SIEVE SIZE (mm)	PERCENT PASSING	GRADING LIMITS	
10.000	100.0	100	100
5.000	99.8	95	100
2.500	80.8	80	100
1.250	58.5	50	90
0.630	39.2	25	60
0.315	22.5	10	35
0.160	9.7	2	10
0.080	3.1	0	5

Comments: *The sample gradation meets the project specifications.*

The FM has been determined to be 2.9; CSA standard requires an FM between 2.3 and 3.1.

Reporting of these test results constitutes a testing service only.
Engineering interpretation or evaluation of the test results is provided only on written request.

AMEC Earth & Environmental

Per: [signature]

AMEC Earth & Environmental
133 Crosbie Road
P.O. Box 13216, St John's NL
Canada, A1B 4A5
Tel. (709) 722-7023
Fax. (709) 722-7353

Construction Materials Laboratory
36 Pippy Place
P.O. Box 13216, St. John's NL
Canada, A1B 4A5
Tel. (709) 722-5062
Fax. (709) 722-5025

FM-MAT-57-03

A.2 Composition of Freshwater and Wabana Water Samples

S/N	Sample	Units	Wabana	Freshwater	Wabana Normal
1	**Li 7**	µg/L	7.31	4.13	27.16
2	**Be**	µg/L	<5.26	0.28	<1.55
3	**B**	µg/L	21.02	18.19	37.12
4	**Mg**	µg/L	3151.95	7894.09	5352.69
5	**Al**	µg/L	34.69	5.64	<2.3
6	**Si**	µg/L	5986.58	<12165.6	4932.59
7	**P**	µg/L	78.94	<909.5	18.20
8	**S**	µg/L	<7235	11979.47	10655.62
9	**Cl**	µg/L	37387.19	100101.95	36489.57
10	**Ca 43**	µg/L	25516.55	36224.42	38389.71
11	**Ti**	µg/L	7.31	2.11	13.20
12	**V**	µg/L	0.46	<16.94	<0.64
13	**Cr 52**	µg/L	2.02	6.05	1.39
14	**Fe 54**	µg/L	11436.92	<507.52	86.33
15	**Mn**	µg/L	2819.01	26.05	179.60
16	**Co**	µg/L	6.04	0.33	<0.21
17	**Ni**	µg/L	11.64	1.88	<1.68
18	**Cu**	µg/L	9.55	9.25	<0.57
19	**Zn**	µg/L	95.74	25.63	4.45
20	**As**	µg/L	62.70	29.71	4.50
21	**Se**	µg/L	12.82	<105.65	<6.23
22	**Br**	µg/L	68.19	131.69	89.15
23	**Rb**	µg/L	2.25	9.55	2.46
24	**Sr**	µg/L	157.55	203.08	425.45
25	**Mo**	µg/L	0.86	2.98	0.23
26	**Ag**	µg/L	<0.05	<0.75	<0.05
27	**Cd**	µg/L	<0.36	<3.31	0.15
28	**Sn**	µg/L	<0.23	<1.14	<0.20
29	**Sb**	µg/L	<0.09	4.90	<0.05
30	**I**	µg/L	24.57	8.39	14.49
31	**Cs**	µg/L	0.05	0.12	0.07
32	**Ba**	µg/L	162.18	45.07	91.57
33	**La**	µg/L	0.23	1.32	0.02
34	**Ce**	µg/L	1.09	0.01	0.01
35	**Hg**	µg/L	<0.13	<2.01	<0.07
36	**Tl**	µg/L	0.03	0.03	0.00
37	**Pb**	µg/L	3.35	22.03	0.03
38	**Bi**	µg/L	<0.03	<0.17	<0.01
39	**U**	µg/L	0.08	0.48	0.02

A.3 Composition of Mix-1, Mix-2 and Mix-3

S/N	Sample	Units	Mix-1	Mix-2	Mix-3
1	**Li 7**	µg/L	3.53	3.79	4.43
2	**Be**	µg/L	<3.41	<3.62	<3.24
3	**B**	µg/L	13.45	12.76	15.87
4	**Mg**	µg/L	8754.15	8229.46	7324.02
5	**Al**	µg/L	5.77	7.48	14.72
6	**Si**	µg/L	3704.35	4218.99	3794.10
7	**P**	µg/L	<64.9	<68.9	<61.7
8	**S**	µg/L	<66807.7	<70919.3	<63484.1
9	**Cl**	µg/L	129649.26	121401.90	107490.37
10	**Ca 43**	µg/L	47306.64	46486.27	43786.58
11	**Ti**	µg/L	<16.64	<17.67	<15.81
12	**V**	µg/L	<2.02	<2.15	<1.92
13	**Cr 52**	µg/L	0.71	<2.96	<2.65
14	**Fe 54**	µg/L	580.26	1106.53	2229.43
15	**Mn**	µg/L	195.92	375.47	607.32
16	**Co**	µg/L	3.62	1.65	0.28
17	**Ni**	µg/L	2.10	4.18	3.90
18	**Cu**	µg/L	8.26	7.44	9.81
19	**Zn**	µg/L	54.92	119.69	173.81
20	**As**	µg/L	33.58	34.34	34.32
21	**Se**	µg/L	<7.40	<7.86	<7.03
22	**Br**	µg/L	163.07	164.08	137.46
23	**Rb**	µg/L	0.93	1.24	1.46
24	**Sr**	µg/L	273.53	270.59	254.22
25	**Mo**	µg/L	3.10	2.93	2.50
26	**Ag**	µg/L	<0.04	0.04	<0.04
27	**Cd**	µg/L	<0.46	<0.49	<0.44
28	**Sn**	µg/L	<0.37	<0.39	0.39
29	**Sb**	µg/L	2.53	2.27	2.03
30	**I**	µg/L	10.41	<11.37	12.00
31	**Cs**	µg/L	0.11	0.12	0.13
32	**Ba**	µg/L	14.60	27.03	44.30
33	**La**	µg/L	0.04	0.07	0.10
34	**Ce**	µg/L	0.10	0.15	0.22
35	**Hg**	µg/L	<0.25	<0.27	<0.24
36	**Tl**	µg/L	0.03	0.02	0.04
37	**Pb**	µg/L	2.00	4.72	1.79
38	**Bi**	µg/L	<0.03	<0.03	<0.03
39	**U**	µg/L	0.65	0.73	0.50

A.4 Water Composition at Different Volumes Recorded for RO-4 Test

Element	Volume (mL)										
	1400	2400	3400	3700	4000	4200	5000	6000	7000	7500	8000	
Li 7	4.1	6.6	4.6	4.6	6.5	7.4	7.2	10.1	2.9	1.5	4.9	
Be	9.9	1.6	2.2	1.1	1.1	0.8	0.3	0.1	8.9	38.3	4.0	
B	38.8	65.6	33.4	26.2	20.8	32.0	25.9	36.0	38.8	66.6	17.3	
Mg	3456.6	3791.1	3230.9	3682.3	3643.1	4721.5	4284.5	6115.4	4249.1	4276.8	4474.9	4
Al	27.0	25.7	88.8	19.3	19.2	295.5	67.4	22.5	88.1	56.3	69.9	
Si	3535.6	5210.6	4312.6	4707.7	4916.0	6786.1	5231.8	11321.2	645.0	7235.8	4778.5	8
P	700.0	477.1	341.6	10.1	13.7	19.4	18.7	846.3	143.0	482.6	293.0	3
S	6149.1	3917.5	2522.0	6146.6	5641.7	8187.3	1486.0	6736.9	14090.0	29868.0	11578.0	18
Cl	41652.8	44072.7	38312.6	55154.2	36137.4	50802.2	41740.8	60653.0	106518.9	35588.8	37103.8	33
Ca 43	22589.7	36259.9	26138.5	34531.0	32309.4	39503.2	34650.5	48387.1	2198.5	25792.1	32052.3	30
Ti	4.8	2.0	4.7	5.1	5.0	15.5	3.2	1.3	25.0	143.6	34.6	1
V	0.5	1.8	0.0	18.0	16.2	0.6	0.3	15.8	15.8	8.2	3.4	
Cr 52	2.7	1.5	3.6	2.2	0.7	1.4	0.8	1.4	131.3	5.9	3.5	
Fe 54	294.0	597.2	910.0	994.9	1133.9	1183.6	601.5	171.4	110.0	1184.0	1200.0	1
Mn	79.7	24.4	15.8	1.3	1.0	27.4	5.4	1.9	41.6	1168.3	399.4	1
Co	4.7	8.7	7.7	6.6	3.2	8.9	3.5	5.4	2.9	4.1	3.0	
Ni	2.3	5.9	2.8	5.7	2.2	5.2	2.4	5.3	783.6	2.3	-	
Cu	280.7	367.6	458.0	509.7	514.8	572.3	538.3	365.8	1048.1	171.2	95.8	1
Zn	347.1	514.1	411.4	790.1	587.5	1096.5	667.9	735.7	2594.3	98.9	252.6	1
As	2.7	4.8	5.7	7.1	7.0	6.2	4.4	1.4	1.7	4.5	7.0	
Se	23.1	3.8	3.8	6.7	6.2	1.6	2.1	98.3	28.0	31.2	7.9	
Br	90.1	75.0	87.1	97.8	82.9	98.9	79.9	121.2	15.9	83.6	76.6	
Rb	59.1	10.0	12.8	5.5	6.1	8.0	4.7	6.8	3.0	27.0	2.8	
Sr	153.0	241.5	219.2	282.5	285.0	353.7	296.9	450.2	6.0	159.6	273.0	2
Mo	0.8	0.7	0.7	0.6	0.4	1.0	0.5	1.0	10.4	1.0	1.9	
Ag	0.2	0.1	0.0	0.7	0.3	0.2	0.0	0.7	0.6	1.2	0.3	
Cd	0.9	1.2	0.5	0.2	0.1	0.3	0.2	3.1	1.2	3.3	1.4	
Sn	0.3	0.1	0.7	0.5	0.2	0.2	0.3	1.1	0.7	1.0	1.6	
Sb	0.1	1.0	0.3	0.3	0.1	0.3	0.3	0.3	1.8	0.6	0.4	
I	16.3	13.1	12.5	157.4	129.7	15.0	9.5	20.7	4.0	17.1	13.2	
Cs	2.5	0.2	0.2	0.2	0.2	0.3	0.2	0.3	0.1	0.2	0.2	
Ba	22.1	20.0	20.7	23.8	50.5	47.1	42.8	68.6	6.4	28.2	37.9	
La	11.3	1.4	2.2	2.0	2.9	5.3	1.8	0.2	0.2	1.0	1.3	
Ce	0.2	0.2	0.3	0.2	0.3	2.3	0.6	0.1	0.1	0.8	1.1	
Pb	12.2	18.0	18.7	27.1	51.3	30.4	24.7	9.0	209.8	5.5	10.1	
U	0.9	0.3	0.7	1.2	0.6	1.6	0.7	1.0	0.1	1.6	1.1	

All the concentrations are in μg/L

A.5 Water Composition at Different Volumes Recorded for RO-4(b) Test

Element	Volume (mL)									
	1500	4000	5000	9500	10500	11000	13000	14000	17000	18000
Li 7	2.6	13.9	12.6	14.4	15.8	15.1	11.2	1.9	18.1	15.4
Be	2.2	1.2	0.4	7.8	3.2	11.1	37.3	8.4	22.1	21.7
B	26.2	27.5	27.9	26.6	31.7	65.2	65.0	16.3	22.6	16.2
Mg	3669.7	4265.1	4364.7	4731.9	4639.2	4387.4	4158.6	3554.0	3479.1	3290.2
Al	21.7	48.8	29.7	24.8	39.9	32.1	37.1	45.2	33.8	46.3
Si	3797.0	4920.3	4684.3	3863.3	4436.6	6782.2	6323.3	5268.6	9537.0	9434.1
P	73.7	28.4	18.7	125.6	231.0	146.1	358.5	133.8	155.0	152.0
S	372.7	7172.2	2164.6	12343.0	4716.3	184266.6	183604.0	4332.3	99724.8	98164.0
Cl	34878.8	35598.5	36528.0	34767.4	34453.0	34302.0	33040.7	37630.0	32959.7	31885.4
Ca 43	30395.6	36675.1	35326.3	34270.2	33240.8	35203.2	33909.0	30680.2	32029.9	30824.7
Ti	2.1	5.3	0.7	21.9	27.3	140.7	140.2	3.5	37.6	37.0
V	1.0	17.7	0.5	2.2	2.8	8.1	8.0	2.3	3.4	3.4
Cr 52	1.6	1.6	1.3	4.0	3.4	5.7	5.7	1.3	1.8	1.3
Fe 54	94.9	200.0	353.0	454.4	606.0	525.0	456.0	392.1	198.2	808.2
Mn	13.0	6.5	4.2	18.0	6.9	4.9	1.7	1188.8	4.1	5.3
Co	3.4	1.8	1.5	1.7	1.9	1.5	1.5	0.5	2.1	1.5
Ni	2.8	2.6	2.6	172.1	1719.8	1.2	2.8	49.3	1.4	1.5
Cu	120.4	126.4	53.2	147.2	92.6	168.2	104.0	396.3	90.8	84.9
Zn	213.5	154.0	126.4	198.5	248.6	236.3	176.1	2236.9	172.8	88.5
As	1.5	3.1	4.0	5.7	6.2	4.8	3.8	2.5	2.7	5.2
Se	4.9	7.0	2.1	24.5	6.2	30.5	30.4	26.1	40.0	38.9
Br	72.6	74.4	71.2	71.8	53.7	74.4	81.5	69.8	39.4	48.0
Rb	10.1	5.5	4.4	3.4	3.2	2.6	2.9	4.5	4.5	4.2
Sr	242.8	355.6	340.6	371.0	359.5	329.4	321.1	176.0	679.6	652.6
Mo	0.6	0.5	0.4	0.5	1.5	0.6	1.0	1.5	0.6	0.6
Ag	0.0	0.2	0.0	0.4	0.3	1.2	1.2	0.2	0.6	0.6
Cd	0.3	0.2	0.2	1.0	1.1	3.3	3.3	1.1	2.1	2.1
Sn	0.2	0.2	0.2	0.6	1.5	0.9	1.1	0.6	1.3	0.4
Sb	0.1	0.1	0.1	0.2	0.2	0.5	0.5	0.5	0.0	0.1
I	13.4	143.1	10.4	10.8	12.9	16.7	16.6	6.6	8.4	8.3
Cs	0.2	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.2	0.2
Ba	24.0	24.4	23.2	30.6	29.8	31.4	36.2	27.4	65.0	64.9
La	4.0	1.3	0.7	0.7	0.9	0.7	0.4	2.8	0.4	1.4
Ce	0.2	0.3	0.2	0.2	0.2	0.2	0.2	1.1	0.1	0.4
Pb	8.4	11.2	11.6	7.5	15.5	11.5	7.0	83.6	11.0	7.6
U	1.5	0.4	0.5	0.4	0.3	0.2	0.2	1.0	0.1	0.1

All the concentrations are in µg/L

A.6 Water Composition at Different Times Recorded for Mix-1 Test

Element	Time (h)							
	8	36	68	84	200	290	315	325
Li 7	1.0	1.9	2.5	2.9	2.8	4.7	3.7	4.3
Be	9.1	3.2	2.2	3.5	2.8	3.2	3.5	3.7
B	10.5	14.3	13.4	16.3	13.6	16.0	11.7	18.2
Mg	765.1	7369.2	8081.1	7362.6	7171.6	9541.1	8857.3	9588.4
Al	7.7	13.8	19.6	49.6	17.8	19.3	20.8	21.5
Si	1019.1	3659.5	3602.3	3650.9	3641.1	4591.9	3919.1	4425.5
P	146.0	32.2	27.0	35.8	28.0	61.6	66.2	69.5
S	14318.0	6247.3	13509.2	5437.5	4370.7	63426.3	68199.6	71532.2
Cl	115175.3	92021.0	92373.5	91051.1	88251.7	140799.8	132160.2	141403.9
Ca 43	1625.1	41167.7	39608.4	41386.8	39711.1	52327.0	48201.6	51316.4
Ti	25.4	5.3	6.0	5.9	4.7	15.8	17.0	17.8
V	34.8	3.2	1.0	3.4	2.9	1.9	2.1	2.2
Cr 52	1.1	0.3	1.2	1.9	2.2	1.3	0.9	3.0
Fe 54	11.0	19.0	13.4	21.2	16.7	30.1	66.7	203.2
Mn	21.3	117.9	249.2	219.1	218.3	204.3	173.2	177.9
Ni	47.9	18.9	14.1	13.6	9.1	2.8	1.5	2.3
Cu	103.8	51.9	59.9	42.9	44.9	60.4	14.6	16.4
Zn	1069.1	595.8	665.7	291.2	328.4	397.9	117.9	98.2
As	2.0	4.5	6.3	5.9	11.5	16.9	20.4	23.9
Se	28.4	4.6	5.6	7.6	4.0	7.0	7.6	7.9
Br	20.3	115.3	110.5	119.6	120.3	181.5	172.5	180.8
Rb	1.2	1.9	1.6	1.6	1.2	1.1	1.0	1.0
Sr	7.5	225.0	226.9	224.5	220.0	302.7	279.0	294.8
Mo	8.6	2.9	3.0	2.9	2.6	3.6	3.0	3.4
Ag	2.7	0.1	0.1	0.1	0.1	0.0	0.0	0.1
Cd	1.2	0.2	0.3	0.2	0.2	0.4	0.1	0.5
Sn	0.7	0.3	0.1	0.3	0.2	0.4	0.4	0.4
Sb	0.4	2.7	2.6	2.7	2.4	2.6	2.5	2.7
Cs	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ba	2.0	24.1	22.6	22.4	22.2	20.5	17.0	17.0
La	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.4
Ce	0.1	0.0	0.0	0.0	0.1	0.1	0.1	0.1
Tl	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pb	2.7	1.4	1.8	4.9	1.6	5.5	3.2	3.4
Bi	0.1	0.0	0.1	0.1	0.2	0.6	0.5	0.5
U	0.1	0.9	0.7	0.6	0.6	0.8	0.8	0.9

All the concentrations are in µg/L

A.7 Water Composition at Different Times Recorded for Mix-2 Test

Element	Time (h)								
	8	40	56	88	120	160	280	298	315
Li 7	3.2	3.0	3.7	4.1	3.4	2.4	3.9	3.0	4.1
Be	10.0	3.3	3.1	1.8	3.2	3.2	3.6	3.3	3.5
B	11.1	15.7	15.8	14.9	13.4	10.5	14.0	10.4	14.3
Mg	1125.4	6993.3	6704.5	6762.1	6659.9	6450.3	8310.0	6985.3	8184.9
Al	33.6	6.7	12.6	24.6	15.8	21.1	10.6	21.1	28.2
Si	870.3	4073.3	3900.8	4160.1	4000.3	3703.8	4192.1	3550.8	4191.3
P	97.4	33.7	31.3	21.0	32.2	32.0	68.6	62.5	65.9
S	15798.0	2860.8	5523.0	10841.0	7419.4	710.3	70687.1	64338.1	67860.8
Cl	112945.5	85835.2	84755.5	76852.2	81813.9	78521.9	124771.9	118573.9	123135.6
Ca 43	784.0	41218.4	39485.6	35684.2	38552.2	37112.1	46421.0	39387.6	47049.9
Ti	28.1	5.6	5.2	5.0	5.3	5.3	17.6	16.0	16.9
V	14.2	3.2	3.0	1.0	3.1	3.0	2.1	2.0	2.1
Cr 52	12.9	0.8	1.8	1.9	2.1	1.9	0.6	0.6	0.8
Fe 54	23.0	17.9	18.5	717.1	122.0	156.7	137.4	180.6	87.1
Mn	10.4	205.3	346.5	944.5	357.7	243.7	251.6	161.4	296.7
Co	1.1	1.6	0.2	1.3	0.1	0.7	1.9	0.1	0.6
Ni	153.8	56.1	5.7	2.6	23.0	12.5	18.0	20.4	37.1
Cu	663.9	40.3	43.7	40.2	36.7	36.6	24.3	32.9	37.7
Zn	2037.1	901.9	283.0	107.3	145.1	155.3	161.9	239.0	119.4
As	1.9	3.4	5.7	11.0	7.0	9.6	6.6	8.4	8.7
Se	31.4	7.1	6.8	4.5	4.6	4.0	7.8	7.1	7.5
Br	17.2	112.5	108.9	105.2	105.7	111.4	161.0	137.0	160.5
Rb	1.0	2.1	1.8	1.5	1.4	1.2	1.2	1.0	1.1
Sr	2.0	225.7	217.0	213.4	218.5	203.4	268.9	232.2	269.9
Mo	11.9	2.4	2.8	2.2	2.5	2.3	2.9	3.1	2.8

All the concentrations are in µg/L

A.8 Water Composition at Different Times Recorded for Mix-3 Test

Element	Time (h)								
	8	40	56	80	120	160	280	296	318
Li 7	2.6	3.5	3.4	4.4	3.4	3.7	5.6	3.6	4.5
Be	2.5	2.9	3.0	2.0	3.1	2.8	3.4	3.6	3.7
B	11.1	13.6	14.2	10.8	16.8	13.8	18.0	17.9	19.9
Mg	823.6	6622.5	6182.1	7000.7	5628.1	5791.9	7963.6	6595.3	7563.9
Al	8.6	5.1	16.3	23.0	34.3	35.6	15.3	30.2	21.5
Si	608.1	4292.1	4138.6	4230.0	3801.6	3937.9	4191.0	3637.4	4240.0
P	130.0	29.1	30.0	24.0	31.8	29.0	64.1	68.1	70.1
S	3444.1	3352.1	5066.4	12114.0	10856.1	4576.2	65981.4	70077.4	72212.7
Cl	113607.5	82988.9	77755.6	80392.9	87843.0	78674.3	118484.0	115274.5	111405.0
Ca 43	2101.1	40513.1	37534.8	36840.3	32991.2	34486.8	46201.8	38543.2	44377.4
Ti	22.8	4.8	5.0	5.1	5.2	4.7	16.4	17.5	18.0
V	81.6	2.9	2.9	0.8	3.1	2.8	2.0	2.1	2.2
Cr 52	3.1	1.6	1.8	1.8	1.9	1.9	2.8	2.9	3.0
Fe 54	100.0	17.2	86.7	588.2	665.8	1086.3	164.3	690.0	518.2
Mn	8.8	892.3	775.3	920.9	374.9	415.0	598.4	406.2	493.7
Co	0.6	3.4	0.2	0.6	1.7	0.8	1.1	1.0	0.3
Ni	56.6	6.8	3.1	3.1	8.8	10.3	3.1	3.7	2.3
Cu	316.6	29.1	33.4	49.5	43.2	166.2	39.9	64.5	36.4
Zn	3442.7	57.3	91.8	110.9	236.9	346.3	182.4	265.1	139.7
As	1.5	2.7	5.8	10.9	11.5	14.5	7.7	13.3	12.3
Se	25.4	6.4	6.4	5.0	4.5	4.1	7.3	7.8	8.0
Br	22.1	112.2	104.6	104.1	119.0	113.4	150.7	153.4	139.4
Rb	1.0	1.8	1.6	1.6	1.4	1.8	1.4	1.3	1.2
Sr	6.3	226.2	213.6	221.1	185.9	194.2	273.9	224.8	252.8
Mo	29.5	2.9	1.4	2.5	3.0	2.6	2.5	3.0	2.7
Ba	1.6	38.2	33.6	39.8	47.8	40.3	44.4	35.2	39.0

All the concentrations are in µg/L