

CHEMICAL-FREE ARSENIC REMOVAL FROM POTABLE WATER
WITH A ZVI-AMENDED BIOFILTER

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by

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Abstract

With a reduction in the maximum allowable concentration (MAC) from 25 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ in Canada, arsenic in potable water is of growing concern. Many of the currently available arsenic removal technologies require considerable capital investment that is not feasible for small to medium-sized communities. These technologies also have associated operating costs and skill requirements that make them unsuitable for many small-scale utilities. As a result several small communities in Western Canada do not currently meet the new arsenic MAC and will require innovative potable water treatment solutions to do so.

This research project examined the use of a zero valent iron (ZVI)/sand column to remove arsenic from potable water. Batch studies were conducted using both arsenic-spiked reverse osmosis (RO) water and naturally arsenic-laden groundwater from two Saskatchewan communities (Kannata Valley and Buena Vista, Saskatchewan). The Langmuir isotherm best described the adsorption of arsenic onto ZVI for all samples. The maximum loading capacity (Langmuir constant q_{max}) was found to be 833, 2 000 and 5 000mg As/kg ZVI for arsenic-spiked RO, Buena Vista water and Kannata Valley water, respectively.

Continuous column studies with nutrient-enhanced RO water showed no statistical difference in arsenic removal performance of various mixtures (v/v) of filtration sand and ZVI provided the mixture consisted of at least 30% ZVI filings. Column studies with Kannata Valley and Buena Vista raw water indicated that columns containing 50/50 and 40/60 ZVI/filtration sand (v/v) could effectively remove arsenic to well below 10 $\mu\text{g/L}$. Arsenic removal efficiency of the ZVI/sand columns was greater than 95% and 88% for Buena Vista and Kannata Valley water, respectively, using both 50/50 and 40/60 media mixtures. Arsenic speciation tests of raw and treated water indicated that the ZVI filings were equally adept for removing As(III) and As(V). No significant amount of iron was leached from the ZVI/sand columns under the conditions tested.

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Dedication

To MBT, thank you for believing in me and encouraging me to believe in myself.

Nomenclature

a	Langmuir empirical constant; related to binding energy (L/mg)
AA	Activated alumina
As	Arsenic
As(III)	Trivalent arsenic (arsenite)
As(V)	Pentavalent arsenic (arsenate)
b	Langmuir empirical constant; maximum amount of adsorbate that can be adsorbed (mg/kg)
BAT	Best available technology
BET	Brunauer-Emmet-Teller
BOM	Biodegradable organic matter
BRP	Biomass Respiration Potential
BV	Bed volume
C_e	Equilibrium concentration of adsorbate in liquid phase after adsorption (mg/L)
C_0	Initial concentration of adsorbate in solution
\emptyset	Diameter
d_{10}	Effective size; 10% of the media grain are smaller by weight
DO	Dissolved oxygen
EBCT	Empty bed contact time
EPA	Environmental Protection Agency
ft	Foot
Fe	Iron

FeAC	Iron-impregnated activated carbon
g	Gram
GFAA	Graphite furnace atomic adsorption spectrometry
GFH	Granular ferric hydroxide
GFO	Granular ferric oxide
gpd	gallon/day
gpm/ft ²	gallon/minute/square foot
HDPE	High density polyethylene
HFO	Hydrous ferric oxide
HIX	Hybrid ion exchange
hp	horse power
ICPMS	Inductively coupled plasma mass spectrometry
IOCS	Iron-oxide coated sand
K _f	Freundlich capacity factor [L/mg]
kg	Kilogram
L	Litre
MAC	Maximum acceptable concentration
MCL	Maximum contaminant level
MCT	Modified conventional treatment
m	meter
mg	milligram
mm	millimeter
m/h	meters/hour

mV	millivolt
n	Freundlich intensity parameter
NOM	Natural organic matter
1/n	Freundlich intensity parameter (unitless)
O ³	Ozone
ORP	Oxidation reduction potential
PLE	Polymeric ligand exchanger
q _e	Mass of adsorbate adsorbed per unit mass of adsorbent (mg/g)
q _{max}	Langmuir empirical constant; maximum amount of adsorbate that can be adsorbed (mg/kg)
r	Correlation coefficient
R	Langmuir equilibrium parameter
RO	Reverse osmosis
rpm	Revolutions per minute
SD	Standard deviation
SMI	Sulfur-modified iron
SMIOCS	Sulfate modified iron-oxide coated sand
SFBW	Spent filter backwash waste
TCLP	Toxic Characteristics Leaching Procedure
TOC	Total organic carbon
μg	Microgram
U.S. EPA	United States Environmental Protection Agency
UV	Ultra violet

v/v	volume/volume
x/m	Amount of solute adsorbed (x) per unit mass of adsorbent (m) (q_e)
ZVI	Zero valent iron (Fe^0)

Table of Contents

1	List of Tables	xi
	List of Figures	xii
	List of Appendices	xiii
1.	INTRODUCTION	1
1.1	Background	1
1.2	Exposure and Health Effects	2
1.3	Treatment Technologies for Arsenic Removal	2
1.3.1	Best Available Technologies (BAT)	2
1.3.2	Alternative Technologies	6
1.3.2.1	Biological Removal Methods	10
1.3.2.2	Zero-Valent Iron (ZVI)	10
1.4	Rationale for Using ZVI and a Modified Slow Sand Filter System for Arsenic Removal	12
1.5	Objectives and Scope of the Study	13
2.	REVIEW OF LITERATURE	14
2.1	Geochemistry of Arsenic in the Natural Environment	14
2.1.1	Redox Conditions and pH	15
2.1.2	Interaction with Other Chemical Elements in Ground Water	16
2.2	Fundamentals of Adsorption	19
2.3	Arsenic Removal via Adsorption and Co-precipitation with ZVI	21
2.3.1	pH and Eh	21
2.3.2	Oxidation of Arsenic	22
2.3.3	Interaction with Iron and Fe/As Ratio	23
2.3.3.1	Iron Oxidation and Complexation with Arsenic	23
2.3.3.2	Fe/As Ratio	24
2.3.4	Reactions with Other Constituents in the Water Matrix	25
2.3.5	Reaction Kinetics	26
3.	MATERIALS AND METHODS	28
3.1	Water Sources and Study Area	28
3.2	Chemicals, equipment and analytical methods	29
3.2.1	Biomass Respiration Potential	31
3.3	Batch Isotherm Studies	31
3.4	Column Studies	32
3.4.1	Phase I: RO Water	32
3.4.2	Phase II: Kannata Valley and Buena Vista Ground Water	34
4.	RESULTS AND DISCUSSION	37
4.1	Water Quality	37
4.1.1	Nutrient-Enhanced RO Water Quality	37
4.1.2	Ground Water Quality	37
4.2	Batch Isotherm Studies	41
4.2.1	Batch Adsorption Study with RO Water	41

4.2.2	Batch Study with Buena Vista and Kannata Valley Water.....	43
4.3	Continuous Column Studies.....	48
4.3.1	Column Study with RO Water.....	48
4.3.2	Column Study with Buena Vista and Kannata Valley Water.....	50
4.3.2.1	Arsenic removal efficiency.....	51
4.3.2.2	Arsenic Speciation.....	52
4.3.2.3	Filtrate water quality.....	53
4.3.2.4	Biomass Activity.....	53
4.4	Feasibility of ZVI/sand column for arsenic removal for municipal potable water utilities.....	54
4.4.1	Conceptual scale-up design.....	55
4.4.2	Disposal.....	55
4.4.3	Economic considerations.....	56
5.	CONCLUSIONS AND RECOMMENDATIONS.....	58
5.1	Conclusions.....	58
5.2	Further Research.....	59

List of Tables

Table 1-1: Reported efficiencies of various experimental adsorbents to remove As	9
Table 1-2: Examples of commercially available adsorbents for arsenic removal	10
Table 2-1: Results of laboratory study of oxidants used to oxidize As(III) to As(V)	23
Table 2-2: Fe:As ratios required to achieve desired levels of arsenic removal	25
Table 2-3: Competitive interactions noted by researchers.....	26
Table 3-1: Composition and Phase I conditions of ZVI/sand columns testing in continuous-flow column study with nutrient-enhanced RO water	32
Table 4-1: Nutrient-enhanced RO water characteristics.....	38
Table 4-2: Kannata Valley ground water characteristics.....	39
Table 4-3: Buena Vista ground water characteristics	40
Table 4-4: Freundlich and Langmuir isotherm equations and parameters for the adsorption of arsenic onto ZVI filings for RO water.....	42
Table 4-5: Freundlich and Langmuir isotherm equations and parameters for the adsorption of arsenic onto ZVI filings in Buena Vista and Kannata Valley ground water	44
Table 4-6: Summary of results from nutrient-enhanced RO water experiment.....	48
Table 4-7: Dissolved Fe (mg/L) in influent and effluent from Phase I column study.....	50
Table 4-8: Continuous-flow column performance on Kannata Valley water.....	50
Table 4-9: Continuous-flow column performance on Buena Vista water	51
Table 4-10: Total dissolved Fe (mg/L) influent and effluent concentrations for Kannata Valley and Buena Vista water filtration run.....	53
Table 4-11: Biomass Respiration Potential test results for Buena Vista and Kannata Valley columns	54
Table 4-12: Specifications of a conceptual design for a full-scale municipal water treatment plant	55
Table 4-13: Treatment costs and media replacement frequency for comparable adsorptive media	56
Table A-1: Nutrient, trace minerals and vitamin solution for RO-enhanced water for column study.....	71
Table B-1: RO water batch experimental data.....	73
Table B-2: Kannata Valley batch experimental data	74
Table B-3: Buena Vista batch experimental data	75
Table B-4: Nutrient-enhanced RO water filtration run (bed volumes treated and arsenic removal capacity)	76
Table B-5: Summary of results from Kannata Valley and Buena Vista filtration runs....	77
Table B-6: Quality of raw water and effluent from 50/50 columns for Buena Vista and Kannata Valley.....	78

List of Figures

Figure 2-1: The Eh-pH diagram for As at 25°C and 101.3kPa (Wange and Mulligan, 2006)	16
Figure 3-1: Location of Kannata Valley and Buena Vista, Saskatchewan.....	29
Figure 3-2: Column apparatus design for Phase I (RO water).....	34
Figure 3-3: Column apparatus design for Phase II.....	35
Figure 4-1: Langmuir adsorption isotherm for RO water.....	41
Figure 4-2: Freundlich adsorption isotherm for RO water	42
Figure 4-3: Langmuir adsorption isotherm for Buena Vista ground water	44
Figure 4-4: Freundlich adsorption isotherm for Buena Vista ground water	45
Figure 4-5: Langmuir adsorption isotherm for Kannata Valley ground water	45
Figure 4-6: Freundlich adsorption isotherm for Kannata Valley ground water.....	46

List of Appendices

Appendix A: Nutrient Solution.....	71
Appendix B: Experimental Data.....	72
Appendix C: Statistical analysis	79

1. INTRODUCTION

1.1 Background

Until recently low concentrations of arsenic (lower than 25µg/L) in water have been of limited concern. However, since the maximum allowable concentration (MAC) of arsenic has been reduced from 25 to 10µg/L in the new Saskatchewan potable water quality guidelines, there is significantly more awareness about arsenic and the treatment options available for the removal of arsenic from water.

Many of the currently available arsenic removal technologies require a considerable capital investment for small to medium-sized communities. These treatment methods also have associated operating costs such as chemical addition for co-precipitation, replacement of expensive media, or contaminated sludge removal that also requires a skilled operator. Other treatments such as membrane filtration require investments in operator training and maintenance that may be unaffordable for smaller towns and villages.

A small-market assessment was conducted by an independent third party in conjunction with this project. The purpose of the assessment was to enumerate and identify communities in rural, remote and resort areas having smaller populations (<5000) in need of potable water arsenic removal technology. The study identified at least 63 small communities in the three Western Canadian provinces that do not meet the new arsenic MAC and will require innovative potable water treatment solutions to do so (Thomas, 2007). Private ground water wells and water supplies, such as farm and some rural community resources were not included in the market analysis. From the data collected and the need for treatment identified, a Regina company, Mainstream Water Solutions Inc., initiated a project to develop an arsenic removal technology suitable for small communities. The present study constitutes the bulk of the initial research, identification of options, and engineering optimization to develop that proprietary technology using chemical-free methods of treatment.

1.2 Exposure and Health Effects

The impact of arsenic exposure on human health is dependent on the arsenical involved, the extent of the exposure and the individual's response (Gorby, 1994; Morton and Dunnette, 1994). A fatal dose of arsenic trioxide (As_2O_3) is considered to be within the range of 200 to 300mg (Gorby, 1994). Smaller doses produce negative health effects due to repeated chronic exposure; symptoms typically appear gradually and it is difficult to develop a dose-response measurement (Morton and Dunnette, 1994). Chronic arsenic exposure may manifest in general symptoms such as weakness and fatigue. However, the symptoms may gradually worsen involving several organ systems most vulnerable to arsenic poisoning (Morton and Dunnette, 1994). Arsenic ingestion has been linked to negative effects on the nervous, dermatologic, gastrointestinal, renal, hematological, cardiovascular and respiratory systems (Gorby, 1994).

Because arsenic is a carcinogen, as classified by the International Agency for Research in Cancer and United States Environmental Protection Agency (U.S. EPA), even low level arsenic ingestion in drinking water is cause for concern. Exposure to inorganic arsenic at concentrations of less than $50\mu\text{g/L}$ has been linked to bladder, liver, skin and kidney cancer as well as to skin diseases and neurological and cardiovascular problems (U.S. EPA, 2000).

1.3 Treatment Technologies for Arsenic Removal

1.3.1 Best Available Technologies (BAT)

The U.S. EPA (2005) has identified ion exchange, activated alumina, membrane filtration (reverse osmosis, nanofiltration, electrodialysis), modified coagulation/filtration and modified softening as the best available technologies (BATs) for arsenic (As) removal. However, the latter two technologies are not considered as BAT for communities with fewer than 500 service connections since these are unlikely to have access to appropriate operation and maintenance services. Membrane filtration technologies are similarly

encumbered, making these unsuitable for most small communities and, thus, not BAT in those circumstances.

Modified conventional treatment (MCT) refers to the addition of various coagulants to enhance arsenic removal in a conventional water treatment plant. Because the removal of arsenic to concentrations below the standard is challenging through the addition of coagulant alone, further treatment such as microfiltration must often be added to conventional plants (An *et al.*, 2005). By exploiting the relationship between arsenic and other metals, particularly iron, existing iron and manganese removal plants can be optimized to affect arsenic removal (Chen *et al.*, 2002).

Coagulation with alum or ferric salts has the potential to achieve both highly economical and efficient arsenic removal (Meng *et al.*, 2001; Edwards, 1994). Coagulation is used particularly in situations where dissolved (ferrous) iron is not present in the raw water source. The addition of ferric salts promotes the formation of iron hydroxides that have a high adsorption capacity for arsenate (As(V)). Arsenite (As(III)) can be oxidized to As(V) by oxidizers such as ozone, hypochlorite or permanganate. The extent of removal is related to specific water quality conditions with particular dependence on pH, coagulant dose and arsenic concentration. The coagulant itself is also a significant factor for the efficiency and extent of arsenic removal in the treatment system. Cheng *et al.* (1994) observed that ferric coagulants (FeCl_3) perform more effectively than alum for arsenic removal on an equal-weight dosage basis. Typically, ferric salts are more widely used for more efficient for As(III) removal and stronger bonds formed with As. The stronger bond results in reduced susceptibility to competition from background electrolytes. Despite some of the positive results using coagulation for larger potable water treatment plants, the handling of excess sludge can make this process challenging to manage, particularly in smaller communities (Vaishya and Gupta, 2006). Typically, coagulation-precipitation techniques are costly and not considered suitable for small utilities (Zeng, 2003).

Modified coagulation methods such as microsand-ballasted coagulation and coagulation-assisted microfiltration have been evaluated for arsenic removal with good results observed at near-neutral pH. Smith and Edwards (2002) concluded that microsand-ballasted coagulation with the addition of an appropriate polymer can remove arsenic adequately at pH 7.5 with no filtration step.

Activated alumina (AA) has a long history of use as an adsorptive media for arsenic removal. AA is effective for arsenic adsorption in many cases, but is a highly pH dependent process often requiring chemical pH adjustment. Additionally, AA tends to form a very strong bond with As limiting its regeneration capacity. The use of AA also requires oxidation to produce As(V) that is more readily adsorbed than As(III) (Zeng, 2003). For these reason the use of AA has been supplanted by emerging adsorbents that have fewer operational inputs. Preliminary studies of a iron-modified AA media called FS-50 indicate that it performs slightly better than AA throughout the pH scale (Westerhoff *et al.*, 2006; Singh and Pant, 2006). Kuriakose *et al.* (2004) concluded that iron-impregnated AA effectively removes As(III), with greatly enhanced overall removal compared to unmodified AA.

Softening is considered an effective method for achieving a greater than 90% reduction of As(V) (Garelick *et al.*, 2005). Lime softening can be effectively adapted for arsenic removal through the precipitation of calcium arsenates at high pH (Robins *et al.*, 2000). Arsenate is significantly more readily removed through softening processes than is arsenite. The addition of iron improves removal while the presence of carbonate and orthophosphate at certain pH levels can suppress removal (Garelick *et al.*, 2005).

Ion exchange is identified as a BAT for removal of As(V) by the U.S. EPA (as cited in An *et al.*, 2005). Anionic exchange resins are reasonably effective, however, standard ion exchange resins lack As-selectivity and require frequent regeneration (Johnston and Heijnen, 2000). Further, ion exchange resins are expensive and produce large volumes of arsenic contaminated residuals that produce challenging environmental and economic

costs, particularly for small rural communities (Vaishya and Gupta, 2006; An *et al.*, 2005).

Due to the poor selectivity of traditional ion exchange resins, recent research has focused on identifying innovative resins and processes to provide more effective arsenic removal. One such technology is based on the concept of ligand-exchange-based separation. An *et al.* (2005) described a polymeric ligand exchanger (PLE) prepared by loading a transition metal, in this case Cu^{2+} , to a commercially available chelating ion exchange resin. The metal is firmly bound to the host resin and serves as its terminal functional group. An *et al.* (2005) further noted that the PLE demonstrated enhanced selectivity to arsenate and was therefore able to treat approximately 10 times more bed volumes than common strong-base anion exchangers. They also concluded that the modified resin is effective at neutral pH and can be efficiently regenerated. DeMarco *et al.* (2003) described a hybrid ion exchange (HIX) resin consisting of macroporous cation exchange beads within which agglomerates of nanoscale hydrated iron oxide particles have been dispersed. The resin was shown to selectively remove As(III) and As(V) with no pH adjustment nor any pre- or post-treatment.

Membrane filtration, such as reverse osmosis (RO) and nanofiltration, can remove arsenic from water by exclusionary pore sizes (Johnston and Heijnen, 2000). Nanofiltration is highly effective for reducing As(V) concentrations to below the incoming $10\mu\text{g/L}$ Saskatchewan MAC requirement (Uddin *et al.*, 2007). The same level of efficacy was not observed for the removal of As(III) (Uddin *et al.*, 2007; Sato *et al.*, 2002). Oxidation is often required to achieve effective removal of As(III). However, oxidants can harm RO membranes (Zeng, 2003). The pore size exclusion that renders membrane filtration methods attractive for arsenic removal also promotes the accumulation of organics, particulates, iron, manganese and scale-forming compounds if pretreatment is not employed. Due to the various operational drawbacks, as well as high economic cost of these technologies, membrane filtration systems are generally not considered suitable for small communities (U.S. EPA, as cited in Vaclavikova *et al.*, 2007).

1.3.2 Alternative Technologies

In 2001, the U.S. EPA lowered the maximum contaminant level (MCL) from 50 to 10µg/L affecting approximately 4100 utilities serving more than 13 million people whose potable water treatment plants could not achieve the new MCL (U.S. EPA, 2001b). The cost of compliance was estimated as \$600 million per year in the USA using current treatment technologies. Therefore, there is an urgent need to improve and modify technology to achieve the MCL in the USA, as well as the new MAC levels in Canada, using cost-effective appropriate technologies (An *et al.*, 2005).

In Canada, new arsenic guidelines take effect in provinces such as Saskatchewan between 2008 and 2010 depending on the size of community served. Small utilities are especially challenged to meet these new regulations at a reasonable cost since they don't have the benefit of economies of scale. Most methods for arsenic removal were developed for larger urban utilities and, therefore, are not readily applicable for smaller areas due to high operational and capital costs as well as the significant requirement for skilled operators (Katsoyiannis and Zouboulis, 2006). In these designs, scale-down is often more challenging than the typical engineering design challenge of scaling-up a treatment solution.

There are several techniques in the development stage for application in small communities. However, few innovative and cost-effective treatment processes are immediately available to meet the 2010 deadline for enhanced arsenic removal (Han *et al.*, as cited in An *et al.*, 2005). Because of the lack of appropriate solutions for arsenic removal and provision of high quality potable water in rural areas, adsorbents have been explored by many researchers as a potential alternative (Vaishya and Gupta, 2006). Adsorption is economical and reliable (Kanel *et al.*, 2006) and is a more efficient alternative for removal of complex organic and inorganic metals than conventional treatment (Vaishya and Gupta, 2006).

Activated carbon has been used to treat arsenic contaminated ground water for many years (Yadav *et al.*, 2006; Ng *et al.*, 2004). However, there is limited published research

addressing the cost and technical efficacy and operational optimums. Saha *et al.* (2000) conducted batch and isotherm studies in which 50% removal of As(III) and 65% removal of As(V) were observed. Vaughan and Reed (2005) concluded that removal of As(V) is particularly enhanced by iron oxide impregnated activated carbon (FeAC) at select pHs. Chen *et al.* (2007) further noted that iron-infused activated carbon greatly increases arsenic adsorption capacity resulting in a bed life more than 200 times longer than virgin carbon.

Iron-infused granular media, including iron-oxide coated sand (IOCS) and granular ferric hydroxide (GFH), also offer the benefit of increased iron:arsenic ratio that has been shown to be a requirement for high efficiency sorption-based arsenic removal in water (U.S. EPA, 2005). Iron oxides and hydroxides, such as hydrous ferric oxide, crystalline hydrous ferric oxide, goethite and akaganeite, are promising adsorbents for removing both As(III) and As(V) from water (Vaclavikova *et al.*, 2007). Iron-based adsorbents require fewer chemical pretreatments and have longer operational lives than ion exchange resins or AA (Badruzzaman *et al.*, 2004). Research has proven that IOCS can remove both As(III) and As(V) in batch and column studies to concentrations below 5µg/L (Thirunavukkarasu *et al.*, 2003). Vaishya and Gupta (2006) demonstrated that sulfate modified iron-oxide coated sand (SMIOCS) is effective for As(V) removal in a fixed-bed reactor to concentrations within the incoming Saskatchewan MAC.

Although GFH effectively removes both As(III) and As(V) without pretreatment, the efficiency of targeted arsenic removal is compromised by water matrix constituents including phosphate, sulfate and bicarbonate that compete for sorption sites on the GFH (Manna *et al.*, 2003). Despite this, Thirunavukkarasu *et al.* (2003) established that GFH can be used effectively by small utilities to remove arsenic from ground water to below 5µg/L. Pal (2000) also reported that granular ferric oxide (GFO) can remove very large amounts of arsenic from ground water treating in the range of 40,000 to 60,000 bed volumes before the permissible limit of 10µg/L is exceeded.

The use of nanoscale iron particles is an innovative extension of conventional iron applications that shows promise for arsenic removal in the limited trials conducted to date. The arsenic removal efficiency of iron nanoparticles is again dependent upon both pH and As species (Yuan and Lien, 2006). A modified iron nanoparticle incorporating iron oxide nanoparticles into the pores of zeolite crystals produces a sorbent with magnetic properties that can remove anions (Vaclavikova et al., 2006). In preliminary As(V) removal tests the magnetically modified zeolite proved to be a good adsorbent.

Manganese Greensand has been successfully used to remove arsenic in pilot-scale studies in rural communities including Kelliher, Saskatchewan and Kokomo, Indiana. In those communities, influent As concentrations between 50 and 60µg/L were reduced by 90 to 95% (Subramanian *et al.*, 1997). The researchers further concluded in batch, column and pilot-scale studies that As(III) removal to below 25µg/L was possible provided that As(III) was completely oxidized to As(V) by addition of permanganate before filtration and a sufficient ratio of Fe/As was present. At the laboratory scale, Vu *et al.* (2003) drew similar conclusions at a Fe/As ratio of 20:1.

Examples of further adsorbent materials in literature are provided in Table 1-1 with reported efficiency for each. Commercial adsorbents are also available in response to the need generated by the new arsenic guidelines in both the USA and Canada as shown in Table 1-2. Commercially available media vary by cost, effectiveness and operating parameters, but typically require pH adjustment and chemical regeneration or replacement when spent.

Table 1-1: Reported efficiencies of various experimental adsorbents to remove As

Researchers	Adsorbent	Reported Efficiency
Singh <i>et al.</i> (2002)	Feldspar	Removal of As(III) is feasible, however, retention time, solute concentration, agitation rate and particle size of adsorbent have an effect on adsorption
Nguyen <i>et al.</i> (2006)	Iron-coated Sponge	High capacity for removal of both species. Filtration rate and size of sponge affect adsorption.
Kanel <i>et al.</i> (2006)	Blast Furnace Slag	As(III) can be efficiently removed with pretreatment. Tested for permeable reactive barriers only.
Banerjee <i>et al.</i> (1999)	Waste pickle liquor from a steel mill	With oxidation As can be removed to below 0.05mg/L
Zeng (2003)	Fe-Si binary oxide	Capable of removing both species
Vu <i>et al.</i> (2003)	Iron Sludge	Low efficiency
Ghimire <i>et al.</i> (2003)	Orange waste (chemically modified and loaded with iron)	Can effectively remove both As(V) and As(III)
Vu <i>et al.</i> (2003)	Kimberlite tailings	Good removal in neutral pH range
Manju <i>et al.</i> (1998)	Coconut husk (copper impregnated)	Effective for As(III) removal
Vu <i>et al.</i> (2003)	Wood charcoal	When mixed with appropriate amount of sand showed good removal efficiency
Saha <i>et al.</i> (2000)	Saw dust	Showed removal of 28% and 36% for As(III) and As(V) respectively
Chakravarty <i>et al.</i> (2002)	Ferruginous manganese ore	Adsorbs strongly to As(V) and As(III)
Saha <i>et al.</i> (2000)	Coal fly ash	Reported 20% As(III) removal and 28% As(V) removal Efficient and irreversible adsorption of As(V)
Diamadopoulos <i>et al.</i> (1993)		
Saha <i>et al.</i> (2000)	Spent tea leaf	Showed 25% removal As(III) and 42% As(V)
Shevade and Ford (2004)	Synthetic zeolite	Zeolite NH ₄ ⁺ showed significant arsenate removal capacity
Niu <i>et al.</i> (2007)	Acid-washed crab shells	Very pH sensitive therefore not particularly effective
Maity <i>et al.</i> (2005)	Polymetallic sea nodule	High arsenic loading capacity but not feasible for commercial application
Masih <i>et al.</i> (2007)	Iron-montmorillonites	Highly active in As removal. Exhibited better removal for As(V) than iron oxyhydroxide and comparable performance for As(III)
Thirunavukkarasu <i>et al.</i> (2001)	Ferrihydrite	Effective removal – approximate adsorption capacity of 285µg/g
Pokhrel and Viraraghavan (2006)	Iron-oxide coated fungal biomass	Approximately 95% removal of As(V) with one species

Table 1-2: Examples of commercially available adsorbents for arsenic removal

Adsorbent	Manufacturer	Description	Estimated Cost
E33	Severn Trent Bayoxide and AdEdge	Pelletized ferric oxide	\$0.37/1000gal. (\$5.36/lb for Severn Trent and \$8.75 for AdEdge) with media changeout every 30 months
Metsorb	Hydroglobe	Titanium hydroxide	
Z-33	Water Remediation Technologies (WRT)	Iron-doped zeolite	
G2	ADI Group Inc.	Diatomaceous earth impregnated with iron hydroxide	\$0.75/lb
GFH	US Filter	Granular ferric hydroxide	\$3.03/lb
AAFS50	Kinetico	Iron enhanced AA	\$1.44/lb
Nanocrystalline Media	Eaglepicher	Ferric/lanthanum hydroxide deposited on diatomaceous earth	

1.3.2.1 Biological Removal Methods

Unlike physical and chemical methods for arsenic removal, there is minimal research regarding the biological removal options for As. However, simultaneous removal of both As(III) and As(V) can occur during biological removal of iron and manganese using indigenous ground water microorganisms (Katsoyiannis and Zouboulis, 2006 and 2004). In their 1998 pilot studies of As(III) biological filtration, Lehimans *et al.* (as cited in Sharmin, 2000) noted that for influent concentrations as high as 400µg/L this method could affect a 90% reduction of arsenic and almost complete removal of iron. Jahan *et al.* (2006) conducted studies using common green algae and wastewater bacteria demonstrating that biological activity is capable of significant arsenic removal.

1.3.2.2 Zero-Valent Iron (ZVI)

ZVI (Fe^0) has been used successfully in situ to remove metals and other contaminants from ground water (permeable reactive barriers) (Ahn *et al.*, 2003) and is the focus of much research for potable water treatment (Tyrovola *et al.* 2006; Vu *et al.*, 2003). Several field and laboratory studies attest to the performance of ZVI for arsenic removal

including Nikolaidis and Lackovic (as cited in Ahmed *et al.* 2005) and Nikolaidis *et al.* (2003) who demonstrated a 97% removal efficiency of arsenic through adsorption on a mixture of iron filings and sand.

Incorporating ZVI into sand may provide higher As removal than ZVI alone. Westerhoff *et al.* (2006) observed slightly higher removal of As in a fixed-bed reactor with a ZVI-sand mixture than with ZVI alone at lower pH. Lien and Wilkin (2004) concluded that ZVI alone performed better than a 50-50 mixture of sand and ZVI. Leupin and Hug (2005) found a sand and iron mixture performed well for As(V) removal and that the hydrous ferric oxide formed strongly adsorbed As(V) retained in the sand bed. Incorporating ZVI filings into a sand bed is also important to maintain hydraulic conductivity and avoid filter clogging. Leupin *et al.* (2005) suggest that an iron-to-sand ratio should not be too high. They estimate that 2.5g of Fe(0) contributes 4.78g of Fe(OH)₃ and with a typical pore volume of 40% at least 35cm³ of sand/g of Fe(0) should be used to avoid filling more than a third of the void volume.

Studies on sulfur-modified ZVI (SMI) demonstrate enhanced performance at ambient pH over ZVI alone (Westerhoff *et al.*, 2006). Researchers have also studied the direct addition of sulfate in ZVI removal systems to successfully enhance arsenic removal (Vu *et al.*, 2003; Ramaswami *et al.*, 2001; Nikolaidis as cited in Sharmin, 2000).

Elemental iron is commonly used in household-scale applications in developing countries to remove arsenic from drinking water. The Kanchan filter developed by Massachusetts Institute of Technology and Stanford University using iron nails incorporated into a sand filter; the Sono 3-Kolshi filter consists of brick pieces, cast-iron turnings and sand. Research on both filter configurations indicates that they perform very well for small-scale use.

1.4 Rationale for Using ZVI and a Modified Slow Sand Filter System for Arsenic Removal

Pokhrel *et al.* (2005) evaluated various small water treatment configurations for arsenic removal on Saskatchewan ground water including two slow sand filter systems. The findings indicated that the slow sand systems were highly efficient at 96% arsenic removal capability, outperforming both coagulation and rapid sand filtration. The most effective system analyzed in this research was a Mainstream BAC system consisting of ozone pretreatment, slow sand filtration and biological activated carbon filtration. The mechanism of arsenic removal by biological slow sand filtration was attributed to a combination of chemical and biological oxidation of iron present in the influent water and its co-precipitation with adsorbed arsenic. Pokhrel and Viraraghavan (2009) suggested one major advantage of this system is that it is capable of continuous arsenic removal without exhaustion.

Slow sand filter systems are re-emerging technologies particularly well suited to small communities. They are simplistic in operation, require little process adjustment and, therefore, limited technical expertise, and are economical to install and operate. Several biological systems have been installed to treat municipal water in the Canadian Prairie provinces in recent years including the communities of Craik, Radville and Benson, Saskatchewan.

Slow sand filtration can effectively remove arsenic from ground water. However, its effectiveness is directly dependent on the concentration of iron in the source water. To provide effective treatment a sufficient ratio of iron to arsenic must exist between at least 20:1 (U.S. EPA, 2005). In some ground water, the iron concentration is insufficient to adsorb and co-precipitate with the arsenic. In these instances, iron may be added through such media as ZVI filings, to improve arsenic removal. ZVI filings are a proven and effective media for arsenic removal in permeable reactive barriers, in ZVI iron filings columns or in a mixture with filtration sand in columns. Iron filings are readily available and inexpensive and, therefore, have significant potential as an arsenic removal medium for small-scale potable water systems.

1.5 Objectives and Scope of the Study

The purpose of this project was to identify and quantify an optimized chemical-free potable water treatment method using iron filings for the removal of arsenic from ground water to meet new drinking water standards in Canada.

The specific objectives defined to achieve the purpose of the study were:

- To investigate the use of iron filings for removal of arsenic from ground water;
- To examine the potential of this technology to reduce arsenic concentrations in the source water of two local communities;
- To determine the loading capacity of the iron filings in the source water studied; and
- To examine impact on performance of various ratios of ZVI and sand.

The scope of the study included the design, completion and analyses of:

- Batch studies to elicit adsorption isotherm data indicative of loading capacity and favorability of arsenic adsorption onto the filings with respect to the various source water used in this study and
- Biological sand columns and filtration studies using:
 - Various ratios of iron and sand filtering reverse osmosis (RO) water spiked with a nutrient solution and pentavalent arsenic [As(V)].
 - Raw water over the arsenic MAC of 10µg/L from two local communities

2. REVIEW OF LITERATURE

2.1 Geochemistry of Arsenic in the Natural Environment

Arsenic occurs in natural waters depending on the local hydrology, geology and geochemical characteristics of the aquifer (Bhattacharya, 2006). Stollenwerk (2003) stated that geochemistry of arsenic is unusually complex and partitioning of arsenic between solid and aqueous phases is controlled by:

- Mineral precipitation/dissolution
- Adsorption/desorption
- Oxidation/reduction
- Biological transformation

More specifically, Smith *et al.* (2006) affirms that the presence of natural inorganic aqueous concentrations of arsenic is associated with (but not limited to) four dominant hydrogeochemical processes:

- The oxidation of arsenical pyrite through ground water withdrawal or oxidation
- Reductive dissolution of ferric oxyhydroxides
- Desorption of arsenic from aluminosilicate minerals or aluminum oxides
- Competitive ligand-exchange with phosphate anions

The most common arsenic-containing mineral is arsenopyrite which, upon oxidation, releases arsenic into water (Bhumbla and Keefer, 1994). When oxidized the positively charged metalloid center associates quickly with three or four oxygen atoms forming either arsenite (AsO_3^{3-}) or arsenate (AsO_4^{3-}) depending on pH or redox potential (Grafe and Sparks, 2006).

The most common arsenic species of concern in natural waters include As(V) (arsenate) and As(III) (arsenite). Organic species are also found in water, but are not typically present at concentrations above $1\mu\text{g/L}$ and are considered insignificant (Edwards, 1994).

The valence state of arsenic present in solution is important as the solubility, mobility, toxicity and bioavailability are species dependent (Xie and Naidu, 2006).

2.1.1 Redox Conditions and pH

Arsenic speciation is a function of pH and redox potential (Westerhoff *et al.*, 2006; Badruzzaman *et al.*, 2004; Mamtaz and Bache, 2000; Vaclavikova *et al.* 2007). However, in aquatic systems pH is the main controlling factor (Smith *et al.*, 2003). In oxygenated (surface water) conditions As(V) is the dominant species present in the anionic forms of H_2AsO_4^- , HAsO_4^{2-} or AsO_4^{3-} in the pH range of 5-12 (Edwards, 1994). In anoxic ground water conditions As(III) is the predominant species. Below pH 9.22 the nonionic H_3AsO_3 is dominant while below pH 9.22, the anionic H_2AsO_3^- is dominant (Edwards, 1994). In this respect the redox stability of As(III) and As(V) is dependent on the pH and Eh of the solution. An Eh/pH diagram describing the thermodynamic stability for arsenic species is presented in Figure 1-2. Under oxidizing conditions arsenate can be available in four species over a large pH range while arsenite is present as two species over a wide pH range in reducing conditions.

Arsenite is, therefore, present at the typical pH of natural water in a nonionic form. Because it is not ionized it tends to adsorb less strongly, or not at all, to positively charged cations. Therefore, arsenite is more soluble and mobile in aqueous solutions than As(V) and, provided arsenic is present, reducing conditions can lead to increased arsenic concentrations in an aquifer (Nordstrom and Archer, 2003). In addition to solubility and mobility, speciation is important with respect to toxicity of arsenic. The trivalent, inorganic species, As(III), is more toxic than the pentavalent As(V) species (Cheng *et al.*, 1994).

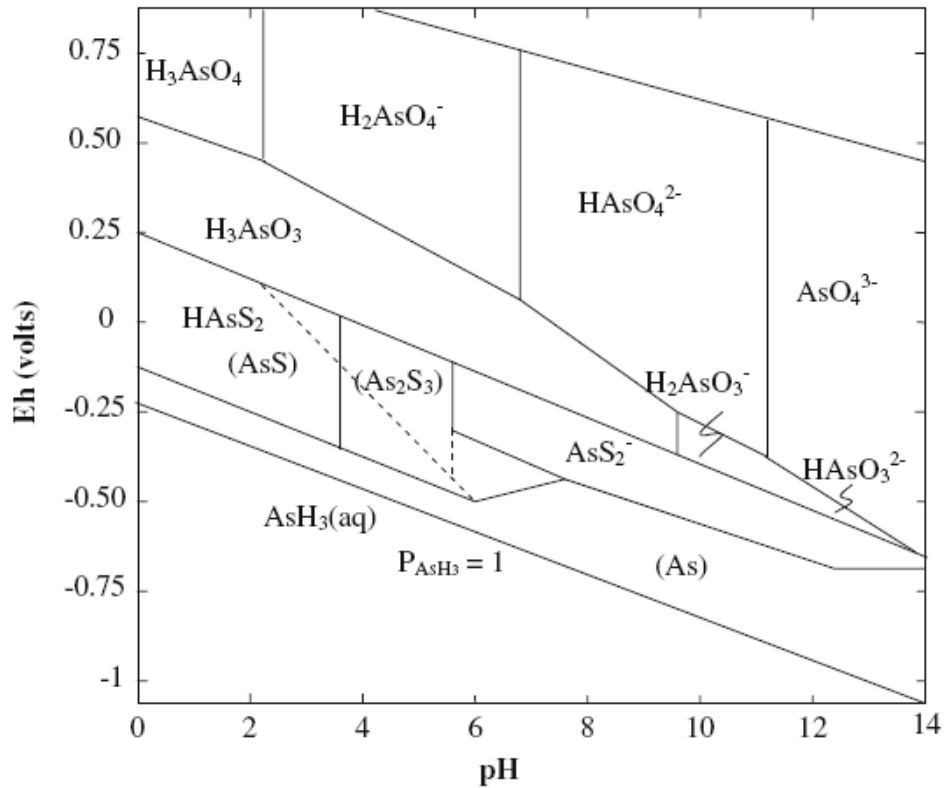


Figure 2-1: The Eh-pH diagram for As at 25°C and 101.3kPa (Wang and Mulligan, 2006)

2.1.2 Interaction with Other Chemical Elements in Ground Water

Many elements and compounds may influence arsenic in ground water particularly through ionic competition and complexation through electrostatic attraction.

Arsenic may be removed from bulk solution by adsorption onto iron oxides or by incorporation into sulfide minerals. Alternatively, it is released by desorption from iron hydroxide and oxidation of arsenic-containing minerals. A reaction between ferrous iron (Fe^{2+}) and sulfide (S^{2-}) eventually forms pyrite (FeS_2) into which arsenic can be incorporated in the presence of sulfur-reducing bacteria (Smith *et al.*, 2006). Correll *et al.* (2006) described the release of arsenic via weathering of pyrite and arsenopyrite. When these minerals are exposed to water and oxygen they are oxidized releasing arsenate and Fe^{3+} , SO_4 and acidity (Correll *et al.* 2006; Smith *et al.*, 2003).

Smith *et al.* (2006) suggested that typically elevated concentrations of arsenic in an aqueous solution are associated with Fe^{2+} and not Fe^{3+} . Therefore, they concluded that arsenic occurrence is associated with reductive dissolution of iron oxyhydroxides to Fe^{2+} . This type of reductive dissolution is common in anoxic ground water where microbial metabolism of organic matter occurs within the aquifer sediment (Nickson; Korte; Korte and Fernando; Matisoff *et al.*, as cited in Smith *et al.*, 2006) and tends to be most rapid under extremes of pH and Eh (Smedley and Kinniburgh, 2002).

Researchers have observed that PO_4^{3-} can displace arsenic in solid phase from iron oxyhydroxide (Charlet *et al.*, 2007), other aquifer mineral, and humic acid sorption sites (Edwards, 1994; Mok and Wai, 1994; Welch *et al.*, Manning and Martens, Peryea and Kammereck, Jackson and Miller as cited in Smith *et al.* 2006). Stollenwerk (2003) states that adsorption experiments show that P(V) has a similar affinity for surface sites as does As(V) and that adsorption of both species decreases with increasing P(V) concentration. This reaction appears to be pH dependent becoming more emphasized with increasing pH for As(V) and with decreasing pH for As(III) (Stollenwerk, 2003). Edwards (1994) and Meng *et al.* (2001) found that orthophosphate can decrease removal of As by co-precipitation.

Smedley and Kinniburgh (as cited in Smith *et al.*, 2006) noted a correlation between calcium and magnesium and arsenic concentrations in ground water. They concluded that the negatively charged As(V) can be adsorbed by cationic Ca^{2+} and Mg^{2+} . Vaishya and Gupta (2006) noted that the reaction of Ca^{2+} and As tends to form $\text{Ca}_3(\text{AsO}_4)_2$.

Carbonate (CO_3^{2-}) may also play a role in the partitioning of arsenic, particularly at high pH (Stollenwerk, 2003). Research by Goldberg and Glaubig (as cited in Stollenwerk, 2003) showed that calcite can adsorb As(V) with concentration adsorbed increasing with pH. Appelo *et al.* (as cited in Charlet *et al.*, 2007) also suggests that As(V) can be desorbed from Fe binding sites by bicarbonate (HCO_3^-) anions.

Edwards (1994) indicated that natural organic matter (NOM) can compete for binding sites with arsenic. NOM can also affect arsenic speciation by forming NOM-As complexes and oxidation-reduction reactions (Welch and Lico, Bradley *et al.*, McArthur *et al.*, Redman *et al.*, as cited in Wang and Mulligan, 2006). NOM has been observed reducing As(V) with metal hydroxides present and complexing with As(V) and As(III) (Redman *et al.*, as cited in Wang and Mulligan, 2006). The formation of NOM-As complexes encourages arsenic mobility from sediment into solution (Berault *et al.*, Redman *et al.*, as cited in Wang and Mulligan, 2006). This reaction is related to pH, humic acid composition and arsenic speciation (Stollenwerk, 2003).

The presence of nitrate (NO_3^-) in ground water may also affect arsenic mobilization through the effect it exerts on the reductive dissolution of arsenopyrite. The microbial reduction of nitrate produces ammonia (NH_4^+), increases pH and releases sulfuric acid (SO_4^{2-}), Fe^{2+} and As into the ground water (Smith *et al.*, 2006).

Arsenate can form stable solids (BaHAsO_4 and $\text{Ba}_3(\text{AsO}_4)_2$) in the presence of barium (Ba^{2+}) (Smith *et al.*, 2003; Vaishya and Gupta, 2006), which can precipitate serving as a sink for arsenic in ground water. Planer-Friedrich *et al.* (as cited in Smith *et al.*, 2006) determined that barium arsenate can precipitate, even at low concentrations of Ba^{2+} and As(V).

Elevated levels of silicate in water may decrease the effectiveness of arsenic removal by co-precipitation. Meng *et al.* (2001) demonstrated that the presence of silicate decreased As(V) removal by ferric chloride addition. They attributed the effect to competition of silicate with As for ferric hydroxide sorption sites. However, the affinity of silicate for ferric hydroxide is much weaker than As(V) and phosphate. Meng *et al.* (as cited in Stollenwerk, 2003) also noted that interference with adsorption of As(III) and As(V) was unaffected at pH values below 8. However, adsorption of As(V) was reduced by 40% when pH was above 8 and silicate was present at 3.1mg/L.

2.2 Fundamentals of Adsorption

For the purposes of this project, adsorption constitutes the mass transfer of an atom or molecule that is in the liquid phase to the solid phase. The *adsorbate* is the substance being transferred, while the *adsorbent* is the liquid or solid that accumulates the adsorbate. Batch adsorption tests can be used to define the amount of a particular substance that can be adsorbed by a specified amount of adsorbent. Typically an adsorbent is placed in a solution with the target solute to be removed. The solution is agitated to provide good contact.

The initial concentration, C_o , of the solute will decrease until an equilibrium value, C_e , is reached. The equilibrium condition is reached when the rate of adsorption is equivalent to the rate of desorption at a particular temperature. Through a series of batch tests a relationship between the equilibrium concentration (C_e) and the amount of solute adsorbed (x) per unit mass of adsorbent (m) can be established.

Adsorption isotherms have been developed to describe the mass of substance adsorbed per unit of adsorbent. Two of the most common isotherms to model adsorption data are the Freundlich and the Langmuir isotherms. The Freundlich isotherm is an empirical equation. It accounts for a heterogeneous surface of the adsorbent where the energy of binding sites may vary.

The Freundlich isotherm is described as follows:

$$q_e = x/m = K_f C_e^{1/n} \quad (2.1)$$

where:

q_e = mass of material adsorbed (x) per unit mass of adsorbent (m) at equilibrium,

K_f = Freundlich capacity factor (units determined by q_e),

C_e = equilibrium concentration of adsorbate in liquid phase after adsorption (mg/L), and

$1/n$ = Freundlich intensity parameter (unitless).

The Freundlich equation can be linearized by taking the log of both sides of the equation:

$$\log q_e = \log K_f + 1/n \log C_e \quad (2.2)$$

The Freundlich intensity parameter ($1/n$) provides insight into the effect of the concentration of the solute on the adsorption capacity or the strength of adsorption. The smaller the value of $1/n$, the stronger is the adsorption bond. The K_f parameter represents the adsorption capacity of the adsorbent. Therefore, a larger K_f corresponds to a greater capacity of the solute for the adsorbent.

The Langmuir isotherm is a theoretical equation that is also used extensively to represent adsorption equilibriums. It includes certain assumptions not part of the Freundlich method, such as (1) that there are limited adsorption sites, (2) that the solute forms a monolayer on the surface of the adsorbent and (3) that adsorption is reversible at equilibrium. It is expressed by the following equation:

$$q_e = q_{max} b C_e / (1 + b C_e) \quad (2.3)$$

where:

q_e = mass of adsorbate adsorbed per unit mass of adsorbent (mg/g)

b = empirical constant; related to binding energy (L/mg)

q_{max} = empirical constant; maximum amount of adsorbate that can be adsorbed (mg/kg)

If a plot of C_e/q_e versus C_e yields a straight line the reciprocal of the slope of the line, the constant q_{max} , is equal to the sorption maximum.

Using the empirical constant, b , the R factor, or equilibrium parameter, can be determined:

$$R = 1/(1 + b C_0) \quad (2.4)$$

The value of R provides insight into the suitability of the adsorbent by using the slope of the linearized isotherm. R values > 1.0 indicate an unfavourable isotherm; $R = 1.0$, linear; $R > 0 < 1.0$, favourable and $R = 0$, irreversible (Phommavong, 1995).

2.3 Arsenic Removal via Adsorption and Co-precipitation with ZVI

Arsenic removal with ZVI from aqueous solution occurs by both adsorption, or retention on an adsorbent, and by co-precipitation, or formation of a complex via covalent or ionic bonding of an ion originating from the adsorbent's surface and the adsorbate. The precipitates may form independent solid phases or may form on the surface of the adsorbent (Grafe and Sparks, 2006).

The adsorption of trivalent (As(III)) and pentavalent (As(V)) arsenic is complex and poorly understood (Jekel, 1994). However, arsenic adsorption is known to be controlled by five factors: pH, redox potential, ionic strength, chemical composition of the water (competing ions), and time (Grafe and Sparks, 2006; Stollenwerk, 2003). All of these factors must be considered to successfully affect removal of arsenic by adsorption/co-precipitation.

2.3.1 pH and Eh

pH is one of the most important controls on adsorption of arsenic as it exerts influence on speciation and composition of surface functional groups through protonation and deprotonation (Stollenwerk, 2003). The pK value of arsenite is greater than arsenate therefore deprotonation (loss of a hydrogen atom) is more difficult from arsenite at neutral pH. Surface complexation efficiency is highly influenced by deprotonation ability. Surface complexation will occur if the undissociated arsenic acid donates a proton to the hydroxyl group present in the hydrous ferric oxide. Because arsenate's deprotonation ability is greater than that of arsenite at a neutral pH it is beneficial to oxidize arsenite to arsenate for removal (Banerjee *et al.*, 1999).

Researchers including Simeoni and Hostetler (2006) and Grafe and Sparks (2006) similarly describe the adsorption properties of As(V) and As(III). Simeoni and Hostetler (2006) state that generally As(III) is adsorbed less strongly at lower pH than is As(V). Above pH 2.2, the charge on As(V) is negative. Therefore, As(V) is electrostatically attracted to the surfaces of the positively charged iron (Grafe and Sparks, 2006). Arsenate

adsorption increases with decreasing pH; however the adsorption maximum for arsenite occurs at or near its first dissociation constant (9.22). Simeoni and Hostetler (2006) agree that As(III) adsorption increases as the pH nears 9 and then declines while As(V) adsorption decreases drastically as pH approaches 7-8. The decreased adsorption is a result of the changing surface charge on the face of the minerals. As pH increases the surface charge becomes zero and then increasingly negative. The negative charge on the surface of the mineral thereby repulses the negatively charged As(V) ions. Correll *et al.* (2006) and Sracek *et al.* (2004) suggest that the adsorption maximum for As(V) and As(III) onto ferric hydroxide is at pH 4.0 and pH 7.0, respectively.

Redox chemistry is an important aspect of removing arsenic from water. The species present determines the treatability as As(III) is a much more soluble and, therefore, mobile form of arsenic.

2.3.2 Oxidation of Arsenic

As(V) is the favored species with respect to removal as As(III) remains uncharged at the pH range of normal water (Ferguson and Gavis as cited in Vaishya and Gupta, 2006). Many oxidizers are capable of oxidizing As(III) to As(V) for removal from water including simple aeration; however, the reaction is slow. The most common oxidizers used for this purpose include chlorine, permanganate, ozone, chlorine dioxide, monochloramine, solid-phase oxidizing media and UV. The U.S. EPA conducted a study on oxidation of As comparing these seven oxidizers (Table 2-1).

The study concluded that ozone, chlorine and permanganate provided effective oxidation of As. However, less than 100% oxidation was obtained with chlorine and permanganate likely due to competition from NOM.

Table 2-1: Results of laboratory study of oxidants used to oxidize As(III) to As(V) (Ghurye and Clifford, 2001).

Oxidant	Performance	Interfering Reductants
Chlorine and Permanganate	Rapid oxidation (complete in less than 1 minute) in pH range of 6.3 to 8.3	Dissolved manganese, dissolved iron, sulfide and TOC
Ozone	Rapid oxidation	Sulfide is significant; TOC quelched reaction producing incomplete oxidation at high concentration
Chlorine Dioxide	Limited oxidation	
Preformed monochloramine	Ineffective	
Filox (manganese dioxide-based media)	Effective and complete oxidation	Performance effected by interfering reductants when dissolved oxygen (DO) is reduced
UV	Ineffective when used alone	Requires sulfite addition to perform adequately

2.3.3 Interaction with Iron and Fe/As Ratio

As a strong reducer, Fe⁰ has proven effective for removing both inorganic arsenic species by adsorption and surface precipitation as the hypothesized primary mechanisms (Vu *et al.*, 2003). Due to the number and complexity of potential reactions that may be taking place, these mechanisms remain hypothetical (Leupin and Hug, 2005). To perform well, ZVI must corrode to form the oxides/hydroxides that will adsorb, or otherwise react, with the arsenic to remove it from solution.

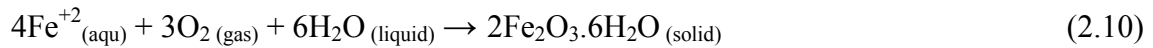
2.3.3.1 Iron Oxidation and Complexation with Arsenic

The oxidation of Fe⁰ leads to the formation of various mixed Fe(II,III)(oxyhydr)oxides that can adsorb As(III) and As(V). The reaction in its most basic form is represented as:

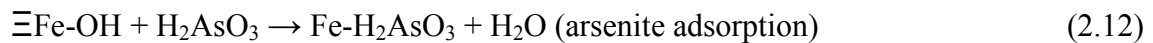
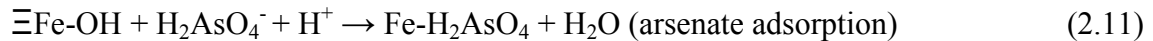
$$\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{+2} + \text{H}_2 + 2\text{OH}^- \quad (2.9)$$

The elemental iron oxidizes to ferrous iron (Fe(II)), oxygen is consumed and a temporal increase in pH is noted (Ahn *et al.*, 2003; Ramaswami *et al.*, 2001). The redox potential of the solution maintains iron in the ferrous form (Nikolaidis *et al.*, 2003).

The Fe²⁺ ions are then oxidized forming hydrous ferric oxide (Fe(OH)₃).



Insoluble reaction products are formed from As(V) and As(III) through adsorption or co-precipitation as defined by the incorporation of the soluble arsenic into a growing hydroxide phase by inclusion, occlusion or adsorption (Edwards, 1994). The reactions may be ($\Xi\text{Fe-OH}$ represents a hydroxide surface site):



2.3.3.2 Fe/As Ratio

The arsenic removal efficiency of iron-based methods is thought to be strongly dependent on the initial iron and arsenic concentrations (U.S. EPA, 2005). The U.S. EPA (2005) suggests that a ratio of iron to arsenic of at least 20:1 (mass Fe:As) is required for removal efficiency greater than 80%. This ratio assumes that 1mg Fe removes 50 μg As. The Fe:As ratio is referred to by many researchers who have examined iron-based methods and it is commonly noted that an increase of the As/Fe ratio increases the As removal (Mamtaz and Bache, 2000; Fuller *et al.*, Pierce and Moore, Waychunas *et al.* as cited in Donahue and Hendry, 2003; Donahue and Hendry, 2003). In many cases the ratio required for adequate removal may be well in excess of 20:1 (Table 2-2).

Meng *et al.* (2001) noted that the applicable Fe:As ratio is a function of more complex water quality parameters including the presence of competing ions.

Table 2-2: Fe:As ratios required to achieve desired levels of arsenic removal

Researchers	Method	Ratio
Subramanian <i>et al.</i> (1997)	Manganese greensand	Fe/As=20 to achieve less than 25µg/L
Banerjee <i>et al.</i> (1999)	Waste pickle liquor (Iron)	Fe/As = 10 to achieve less than 50µg/L
Mamtaz and Bache (2000)		Fe/As > 10 to achieve 50µg/L
Meng <i>et al.</i> (2001)	FeCl coagulation	Fe/As>40 to achieve >85% removal (high ratio thought to be due to phosphate and silicate)
Pokhrel and Viraraghavan (2009)	Biological sand filtration	Fe/As >30:1
USEPA (2005)	All Fe Removal Process	Fe/As >=20:1
Vogels and Johnson (1998)	Ferrate and ferrous ions	Fe/As = 32:1

2.3.4 Reactions with Other Constituents in the Water Matrix

Adsorption of arsenic during water treatment is affected by compounds that compete with arsenic or otherwise affect its adsorption and mobility. Competitive adsorption reactions of arsenic have been observed and modeled for phosphate, sulfate, molybdate and various dissolved organic acids (Grafe and Sparks, 2006). Although the extent of reduction in sorption due to competition depends on the competitor and type of sorbent, the most prolific competitive interaction is observed with phosphate (Tyrovola *et al.*, 2006; Su and Puls, 2001a).

Several researchers have documented these interactions while performing adsorption experiments (Table 2-3). In addition to the compounds noted below chromate, nitrate, borate and humic and fulvic acids can interfere with adsorption of arsenic on ZVI (Su and Puls as cited in Grafe and Sparks, 2006).

Table 2-3: Competitive interactions noted by researchers

Researchers	Removal Method	Constituent and Interaction
McNeill and Edwards, 1997	Metal hydroxide	Competing anions such as sulfate and NOM
Su and Puls, 2001a	ZVI	Phosphate, silicate, chromate, molybdate, carbonate and nitrate caused strong inhibition. Borate and sulfate caused slight inhibition.
Su and Puls, 2004	ZVI	Phosphate at 1mg/L and silicate at 20mg/L showed strong inhibitory effect
Kanel <i>et al.</i> 2006	Blast furnace slag	Nitrate and phosphate reduced adsorption while sulfate and bicarbonate did not
Westerhoff <i>et al.</i> , 2006	ZVI	Silica binds to surface of iron hydroxides, decreasing surface charge and leads to repulsion of anionic As. Vanadium competes for binding sites.
Manna <i>et al.</i> (2003)	Crystalline hydrous ferric oxide	Phosphate, sulfate and bicarbonate interfere negatively
Meng <i>et al.</i> (2001)	FeCl coagulation	Phosphate and silicate reduced removal
Hering <i>et al.</i> (1996) [in Garelick <i>et al.</i> 2005]	FeCl coagulation	Sulfate decreased As(III) removal but had little effect on As(V) removal. At pH>7 calcium increases As(V) removal.
Saha <i>et al.</i> (2001) [in Garelick <i>et al.</i> 2005]	FeCl coagulation	Orthophosphate and carbonate decreased As(V) removal
Garelick <i>et al.</i> (2005)	Lime softening	As(V) removal affected by carbonate at pH 10-10.5 and by orthophosphate at pH<12
Benjamin <i>et al.</i> (1998) [in Garelick <i>et al.</i> 2005]	Activated Alumina	Presence of DOCs reduces removal by 50%
Saha <i>et al.</i> (2000)	Granular Ferric Oxide	Removal efficiency decreased with more than 10mg/L phosphate and 2mg/L fluoride. No effect from nitrate, sulphate, chloride, chromate, calcium, magnesium and iron.
Vogels and Johnson (1998)	Ferrate and ferrous ions	Phosphate decreased removal efficiency while nitrate did not.
Tyrovola <i>et al.</i> (2006)	ZVI filings	Nitrate and phosphate decreased removal
Tipping (1981) [in Bissen and Frimmel, 2003]	Iron oxides(Fe(OH) ₃)	NOM interfered with As(III) removal at pH 4-9

2.3.5 Reaction Kinetics

Adsorption of arsenic by ZVI can be a slower process due to its need to corrode before the surface oxides are available to react with the arsenic (Daus *et al.*, 2004). However, Ramaswami *et al.* (as cited in Vu *et al.*, 2003) observed very high removal efficiency with ZVI within a short contact time (0.5 to 3 hours); longer contact times were observed when phosphate was present. Similarly Krishna *et al.* (as cited in Bissen and Frimmel, 2003) found that removal of As(V) by ZVI filings could be completed in acceptable times for drinking water treatment purposes.

The reaction for arsenic adsorption onto ZVI follows first-order kinetics when arsenic is sufficiently small and zero-order when arsenic is significantly greater than k_0/k_1 (Lien and Wilkin, 2004). Lien and Wilkin hypothesized that at low concentrations there is not competition for reactive sites, which results in first-order kinetics. At higher concentrations the number of reactive sites controls the removal rate. The number of reactive sites may be limited by either their formation by iron corrosion products and/or competition with other arsenic species.

Desorption of arsenic from adsorbents has been observed. However, desorption reaction kinetics are slower than for adsorption (Stollenwerk, 2003). Under aerobic and acid to near-neutral conditions, As(V) adsorbs very strongly onto oxides. However, as pH increases above 8.5 arsenic can desorb (Stollenwerk, 2003; Smedley and Kinniburgh, 2002; Sracek *et al.*, 2004). Desorption of arsenic can also be prompted by the influx of a strongly competing ion (Stollenwerk, 2003). Smedley and Kinniburgh (2002) stated that the onset of strongly reducing conditions that enable Fe(III) and SO₄ reduction can also trigger arsenic desorption. Although the exact mechanism is not known, the change in sorption from strongly adsorbed As(V) to less strongly adsorbed As(III) may be a factor. This weaker adsorption may also allow for stronger competition from interfering ions such as phosphate (Smedley and Kinniburgh, 2002).

3. MATERIALS AND METHODS

3.1 Water Sources and Study Area

Raw water was obtained from the resort villages of Buena Vista and Kannata Valley, Saskatchewan. Both communities are located near the city of Regina in southern Saskatchewan on Last Mountain Lake (Figure 3-1). Buena Vista is located on the south shore of the lake with a permanent resident population of approximately 700. Their current drinking water infrastructure consists of a deep well and a chlorination facility. Kannata Valley, located on the northern shore of Last Mountain Lake, has a permanent population of approximately 100. Raw water is supplied by one deep well which flows under artesian pressure and treatment consists of disinfection with chlorine.

Both water sources are located within the Upper Qu`Appelle River Watershed. The ground water is likely extracted from the Swift Current aquifer, an Empress Group (glacial) aquifer which is formed on top of the local bedrock and composed of stratified gravel, sand, silt and clay (Saskatchewan Watershed Authority, 2007). In a study of arsenic in glacial aquifers in central Illinois, Kelly *et al.* (2005) found that there was no correlation between arsenic concentration and well depth and that arsenic concentrations over 10 μ g/L were associated with TOC concentrations greater than 2mg/L and reduction of Fe oxide.

Raw water was transported from the communities in plastic containers and used in testing within 5 hours. Reverse osmosis (RO) water, supplied by a Vectapure RO unit, was used for all control experiments.



Figure 3-1: Location of Kannata Valley and Buena Vista, Saskatchewan (Google Earth, 2009)

3.2 Chemicals, equipment and analytical methods

Three As(V) stock solutions at 0.2, 2 and 10g/L were prepared by dissolving 0.8329, 8.3289 and 41.6444g, respectively, of sodium arsenate ($\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$, Acros Organics) in deionized water bringing the total volume to 1 litre. Stock solutions were prepared in glass containers and used within 5 hours.

Iron filings used for the batch and column studies were 20-40 mesh (ASTM) iron aggregate (0.45-0.55mm) obtained from Peerless Metals (Detroit, Michigan). BET analysis to determine surface area of the filings was completed but the results were indeterminable likely due to the pore sizes being smaller than 3.5 angstroms. However, it is known that Fe^0 surface area is not a primary factor controlling the adsorption of arsenic (Su and Puls, 2001b).

All glassware was prepared by washing with detergent and rinsing with deionized water. It was then soaked overnight in a weak HNO_3 acid and rinsed again with deionized water.

Eh, pH and temperature were measured using a Hach sensION378 laboratory multi-parameter meter with platinum series pH and ORP electrodes. An Ohaus Explorer Pro balance with draftshield was used for weighing compounds.

Samples were analyzed for total dissolved arsenic and iron using a graphite furnace atomic adsorption spectrometer (GFAAS) at the water quality laboratory in the Centre for Sustainable Infrastructure Research (CSIR), National Research Council (NRC) in Regina, Saskatchewan. A PerkinElmer AA800 was connected to an AS-800 autosampler using Win32 data collection software. Both arsenic and iron analyses were performed using the manufacturer's specified furnace programs for analysis as well as adhering to the methods described in "Standard Methods" (APHA, 1998).

For arsenic determination a mixed modifier of palladium and magnesium nitrate was made by adding 0.5ml Pd(NO₃)₂ (in 15% HNO₃, 10,000mg/L, PerkinElmer) and 0.3mL Mg(NO₃)₂ (10,000mg/L, PerkinElmer) in 4.2ml nanopure (Direct Q – Millipore 18 Ω m²cm) water (0.1% Pd + 0.06% Mg). Standard solutions for calibration were created using H₃AsO₄·1/2H₂O (in 2% HNO₃, PerkinElmer) calibration standard and nanopure water. Nanopure water was used for blanks and diluent. Quality control samples of 10µg/L were made using a 1,000µg/mL arsenic standard (SCP Science).

The spectrometer was calibrated as per manufacturer instructions using the appropriate standards and achieving a correlation coefficient of at least 0.99. A calibration curve from 0-60µg/L was created. A detection limit of 0.5µg/L was determined by using the standard method (3 times the standard deviation (SD) of a blank). Quality control was accomplished by running random samples in triplicate and observing SD and relative SD, and regular analysis of a known concentration standard (10µg/L).

Iron analysis was completed in a similar manner using manufacturer suggested protocols. A 0.3% Mg(NO₃)₂ modifier was used to reduce interference. A similar calibration (0-2mg/L) and quality control procedure to the arsenic method was used.

3.2.1 Biomass Respiration Potential

To determine maintenance of biological activity within the columns throughout the study a procedure developed by Urfer and Huck (2001) was performed. The Biomass Respiration Potential (BRP) test is a respirometric method of determining the biomass activity in a drinking water filter. The advantage of this test is that it determines the extent of biological activity rather than amount of biomass. The method is based on the consumption of DO resulting from the biodegradation of biodegradable organic matter (BOM) by aerobic respiration in a water sample containing a given amount of biomass-laden filter media.

The procedure was adapted to the current situation and performed as follows:

1. Place 8g sample of iron/sand media in 250mL BOD bottle
2. Fill with dechlorinated, ozonated (to sterilize) tap water
3. Measure DO
4. Add a nutrient mixture (The nutrient mix consisted of C:N:P [21:5:1] using sodium nitrate, potassium diphosphate and d-glucose)
5. Fill to no headspace with dechlorinated, ozonated tapwater and cap
6. Place on a platform shaker table for 5 hours
7. Re-measure DO
8. Determine BRP as reduction in O_2 (mg O_2 /L)

3.3 Batch Isotherm Studies

The experiments were accomplished by adding 10g of iron filings to 100ml of water containing between 1 to 500,000 μ g/L As(V). The solutions were agitated on an orbital shaker table (100rpm) for 48 hours after which a sample of water was drawn off, filtered, preserved and analyzed for residual arsenic concentrations.

Adsorption data was fitted to the Freundlich and Langmuir isotherms and equation parameters were tested for significance at the 95% confidence interval using the student's t-test.

3.4 Column Studies

A column study apparatus was designed and built to accurately replicate performance of full-scale slow sand filter operation. The columns comprised 2L HDPE Nalgene carboys with a bottom outlet. Biologically active filtration sand (silica, effective size, d_{10} : 0.45-0.55mm) was obtained from an operating slow sand filter at a local water treatment plant. All experiments were performed in triplicate. Samples were collected by placing 50mL Nalgene bottles below the outlet and allowing them to fill at the set flowrate (4mL/min.). The samples were then filtered with disposable syringe filters using a 0.45 μ m membrane and preserved with nitric acid.

There were two phases of research included in the column studies, namely Phase I with RO water influent and Phase II using authentic water samples collected from Kannata Valley and Buena Vista, Saskatchewan.

3.4.1. Phase I: RO Water

Initially, the column study consisted of running RO water spiked with sodium arsenate and a complex nutrient solution through columns containing varying ratios of biologically-active sand and iron filings (Table 3-1).

Table 3-1: Composition and Phase I conditions of ZVI/sand columns tested in continuous-flow column study with nutrient-enhanced RO water

Column #	% ZVI by volume	% sand by volume
1 – 3	0	0
4 – 6	0	100
7 – 9	50	50
10 - 12	40	60
13 - 15	30	70
16 – 18	20	80

The Phase I columns were assembled by adding a base of gravel (effective size, d_{10} : 3.0-3.5mm) and the media configurations under investigation (Table 3-1). The total volume of media in the columns was $1.17 \times 10^{-2} \text{m}^3$ (0.0414ft³). The series also included blank columns with no media and control columns with sand only (Table 3-1). The columns

were constructed and monitored in triplicate at each desired media configuration. To ensure a homogenized mixture, the media was thoroughly mixed using a motorized blending apparatus.

The nutrient solution was added to the influent water to ensure the biological activity within the columns was sustained throughout the duration of the experiment. The simplified nutrient recipe is available in Appendix A (Table A-1) and in general contained inorganic nutrients, such as nitrate and phosphate, sufficient to promote biological growth in the columns.

A 10 000 μ g/L arsenic stock solution was prepared by dissolving 0.1666g of sodium arsenate in 4L of RO water.

The RO water was produced using a 284L/day (75gpd) VectaPure reverse osmosis unit and then pumped to a mixing tank fitted with a Little Giant $\frac{1}{2}$ hp submersible pump that continuously recirculated the water within the tank.

The RO water in the mixing tank was spiked with nutrient solution plus 50 μ g/L arsenic [As(V)]. Preparation of water was completed within 24 hours of beginning the column experiments. At that time, it was pumped into an adjacent feed tank that supplied the columns. The mixing and supplying of feed water was prepared according to this process in separate tanks to ensure that accurate concentrations of arsenic and nutrients were applied.

The apparatus was built to support 18 columns as shown in Figure 3-2. Water was pumped via a Little Giant $\frac{1}{2}$ hp submersible pump through a 3.175cm (1 $\frac{1}{4}$ ") clear braided hose to the 2.54cm (1") PVC feed line. The feed line was fitted with kynar nipples to connect 0.635cm ($\frac{1}{4}$ ") clear PVC Type 10 tubing. The feed rate into each column was regulated by kynar needle valves. Effluent exited the column by a similar length of 0.635cm clear tubing connected to a kynar needle valve.

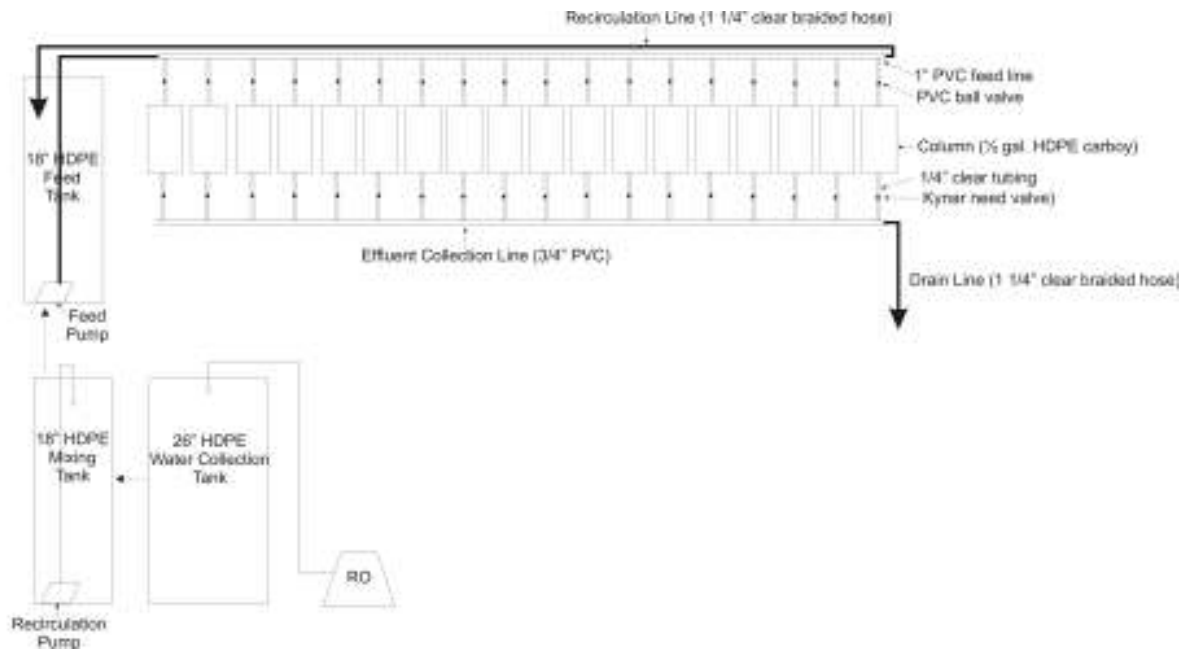


Figure 3-2: Column apparatus design for Phase I (RO water)

Flow through each column was regulated by adjusting the kynar needle valve. The flowrate into each column was monitored and adjusted as necessary. The columns were operated in downflow mode with a hydraulic loading rate of 0.023m/h (0.01gpm/ft²). Column effluent was collected in a 1.905cm (3/4”) PVC pipe connected to a length of 1.905cm PVC hose.

The columns were allowed to acclimatize for 7 days before arsenic was applied. Effluent samples were collected from each column on a regular basis over the 4-week experimental period.

3.4.2 Phase II: Kannata Valley and Buena Vista Ground Water

Clean 2L Nalgene carboys were loaded with fresh media to study the removal efficiency of various media configurations using authentic ground water samples from two rural, resort communities near Regina, SK. In Phase II, two separate column apparatuses (as described in Figure 3-3) were setup to treat Kannata Valley and Buena Vista raw water.

The column trains included triplicate columns of each 50/50 and 40/60 (iron/sand – v/v) and 3 control columns of sand only (0/100, iron/sand [v/v]).

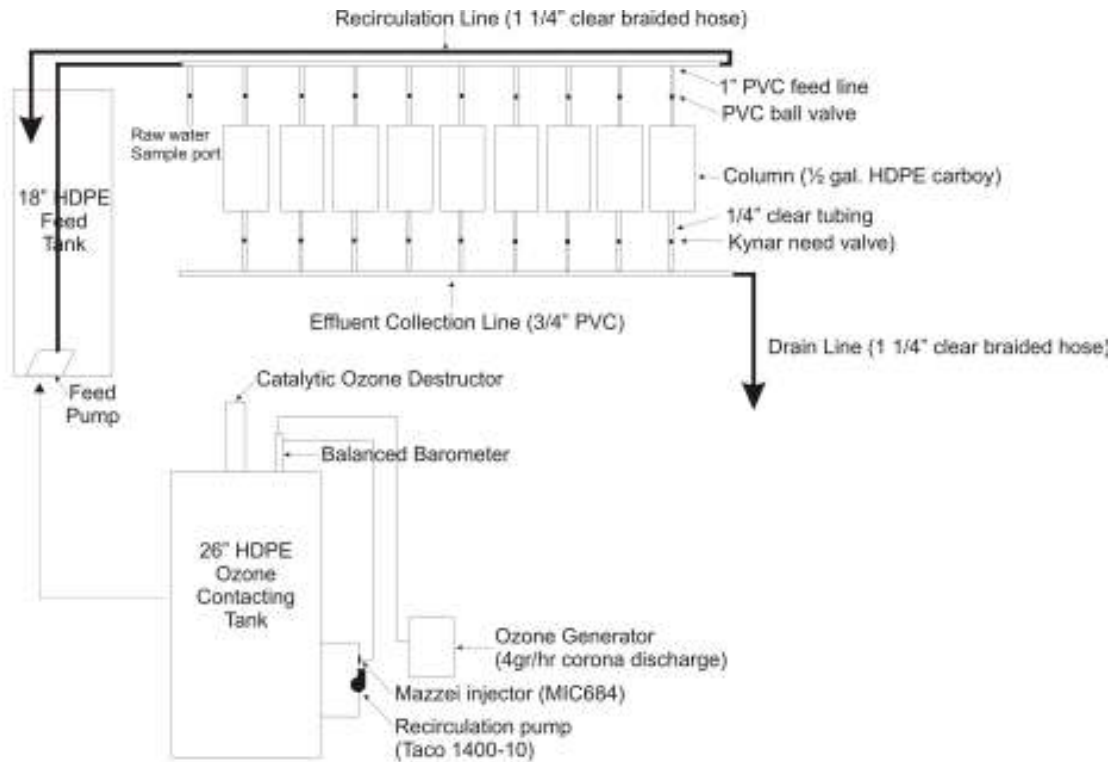


Figure 3-3: Column apparatus design for Phase II*

*diagram represents one of two separate trains

Fresh raw water was collected and transported to the testing site approximately every 4 to 5 days to maintain the experimental flowrates and ensure that samples entering the columns were representative with respect to both chemical and microbiological quality.

In general, column apparatus setup with respect to raw water feed and effluent collection was similar in design to the nutrient-enhanced RO water filtration run.

One required experimental modification included the ozonation of raw water from the resort communities to oxidize As(III) to As(V). Two ozone contacting tanks were required to accommodate the two water sources and were built according to Mainstream Water Solutions standard design. The tank was a 66cm \varnothing (26") HDPE vessel with a

sealed lid fitted with a balanced barometer and catalytic ozone destructor. Ozone was applied via sidestream injection with a Mazzei 684 injector. A Taco 1400 ¼ hp pump recirculated the water in the tank through a sidestream where the injector provided the suction drawing the ozone via the balanced barometer from the ozone generator. The ozone generator was a 4gr/hr corona discharge generator by Azco Industries (VMUS-04). The raw water was ozonated until the oxidation-reduction potential (ORP) reached at least 800mV where arsenic species present should be predominantly As(V).

Similar to Phase I column testing, nutrient-spiked RO was fed through the columns for 6 days to allow for acclimation of the biological communities. On day 7, ozonated Kannata Valley and Buena Vista raw water was applied. Samples were collected and preserved in a similar manner as in the previous filtration run.

Arsenic speciation tests (ion exchange tube/ICP-MS) were completed on ozonated water to determine the arsenic species present after oxidation. The analyses were performed by the Alberta Research Council (ARC) laboratory in Vegreville, AB. Further samples were collected twice for quality control at ALS Laboratories, Saskatoon using ICP-MS analysis. A comprehensive analysis for the raw water as well as the combined effluent from the 50/50 [v/v] Fe/sand columns for each community was also completed by ALS Laboratories toward the end of the study.

4. RESULTS AND DISCUSSION

4.1 Water Quality

4.1.1 Nutrient-Enhanced RO Water Quality

The RO water used for the column study was spiked with sodium arsenate to obtain a concentration of 50 μ g/L. A solution of nutrients, trace minerals and vitamins (Appendix A) was also added to the water to sustain the biological activity in the columns. The addition of the nutrient mixture resulted in the complex water matrix (Table 4-1). The enhanced RO water had an Fe:As ratio of 7:1 and high concentrations of interfering ions particularly nitrate and phosphate.

4.1.2 Ground Water Quality

The ground water quality characteristics for the two sources used in the batch and column studies identify Fe:As ratios between 9:1 and 56:1 (Tables 4-2 and 4-3). Each water source represents a particular challenge to removal of arsenic by conventional methods.

Buena Vista raw water is characterized by an Fe:As ratio of 9:1. Arsenic removal from this water source proved difficult during previous pilot-scale tests and was attributed primarily to an insufficient Fe:As ratio. The ground water also contains interfering compounds in lower concentrations than those present in the Kannata Valley water, but perhaps sufficient to reduce arsenic removal efficiency. The pentavalent As(V) is the predominant species in Buena Vista raw water at 12 to 13 μ g/L; trivalent As(III) concentration is typically between 6 to 7 μ g/L.

Despite an adequate Fe:As ratio of 56:1, pilot-scale testing of ground water treatment at Kannata Valley indicated challenges to arsenic removal. In particular, the Kannata Valley water matrix contains interfering ions including high concentrations of sulfate, bicarbonate, and organic matter that may require a much higher Fe:As ratio to achieve adequate As removal. The majority of the total As is comprised of As(III), which is typically between 30 and 34 μ g/L; As(V) is usually between 4 and 6 μ g/L.

Table 4-1: Nutrient-enhanced RO water characteristics

Parameter	Concentration (mg/L)
Al (Aluminum)	0.13
As (Arsenic)	0.044
Ba (Barium)	0.0083
B (Boron)	2.13
Cd (Cadmium)	<0.0002
Cr (Chromium)	0.0038
Cu (Copper)	0.002
Fe (Iron)	0.313
Pb (Lead)	0.0007
Mn (Manganese)	0.056
Se (Selenium)	<0.0001
U (Uranium)	<0.0001
Zn (Zinc)	0.025
Ammonia-N	0.05
Br (Bromide)	0.5
Colour (TCU)	9
DOC (Dissolved Organic Carbon)	20
PO ₄ -P (Orthophosphate)	1.42
Silica	6.9
TOC (Total Organic Carbon)	22
Alkalinity (Total as CaCO ₃)	27
Bicarbonate	33
Hydroxide	<5
Carbonate	<5
Cl (Chloride)	41
F (Fluoride)	<0.2
Ca (Calcium)	9
K (Potassium)	11.2
Mg (Magnesium)	3.4
Na (Sodium)	49
SO ₄ (Sulfate)	38
Ion Balance (calculated, %)	87.4
TDS (calculated)	237
Hardness (as CaCO ₃)	36
Nitrate-N	9.4
Nitrite-N	6.16
Nitrate+Nitrite	15.6
Turbidity (NTU)	0.34
pH	6.6
Conductivity (EC)	370

Table 4-2: Kannata Valley ground water characteristics

Parameter	Concentration (mg/L)
Al (Aluminum)	<0.02
As (Total dissolved arsenic)	0.037
Ba (Barium)	0.0142
B (Boron)	1.09
Cd (Cadmium)	<0.0002
Cr (Chromium)	0.0026
Cu (Copper)	0.002
Fe (Iron)	2.09
Pb (Lead)	<0.0001
Mn (Manganese)	0.133
Se (Selenium)	0.0023
U (Uranium)	0.0004
Zn (Zinc)	0.005
Ammonia-N	3.37
Br (Bromide)	1.4
Colour (TCU)	6
DOC (Dissolved Organic Carbon)	5
PO ₄ -P (Orthophosphate)	0.26
Silica	24.7
TOC (Total Organic Carbon)	5
Alkalinity (Total as CaCO ₃)	502
Bicarbonate	612
Hydroxide	<5
Carbonate	<5
Cl (Chloride)	174
F (Fluoride)	0.25
Ca (Calcium)	93
K (Potassium)	7.1
Mg (Magnesium)	47.4
Na (Sodium)	531
SO ₄ (Sulfate)	840
Ion Balance (calculated, %)	98.1
TDS (calculated)	1990
Hardness (as CaCO ₃)	427
Nitrate-N	<0.5
Nitrite-N	<0.05
Nitrate+Nitrite	<0.5
Turbidity (NTU)	16.8
pH	7.7
Redox Potential (mV)	199
Conductivity (EC)	3100

Table 4-3: Buena Vista ground water characteristics

Parameter	Concentration (mg/L)
Al (Aluminum)	<0.02
As (Arsenic)	0.017
Ba (Barium)	0.0342
B (Boron)	0.45
Cd (Cadmium)	<0.0002
Cr (Chromium)	<0.0008
Cu (Copper)	0.002
Fe (Iron)	0.159
Pb (Lead)	0.0002
Mn (Manganese)	0.062
Se (Selenium)	<0.0008
U (Uranium)	0.0002
Zn (Zinc)	0.019
Ammonia-N	1.03
Br (Bromide)	<0.1
Colour (TCU)	7
DOC (Dissolved Organic Carbon)	3
PO ₄ -P (Orthophosphate)	0.26
Silica	23.2
TOC (Total Organic Carbon)	3
Alkalinity (Total as CaCO ₃)	358
Bicarbonate	423
Hydroxide	<5
Carbonate	<5
Cl (Chloride)	13
F (Fluoride)	0.4
Ca (Calcium)	23.1
K (Potassium)	3.46
Mg (Magnesium)	10.3
Na (Sodium)	158
SO ₄ (Sulfate)	87.3
Ion Balance (calculated, %)	98.3
TDS (calculated)	510
Hardness (as CaCO ₃)	100
Nitrate-N	<0.5
Nitrite-N	<0.05
Nitrate+Nitrite	<0.5
Turbidity (NTU)	0.78
pH	7.8
Redox Potential (mV)	189
Conductivity (EC)	880

4.2 Batch Isotherm Studies

4.2.1 Batch Adsorption Study with RO Water

The purpose of this study was to examine the adsorption of arsenic by ZVI filings in a solution free of known interfering ions. The results of the batch experiment were fitted to both Langmuir and Freundlich isotherms (Figures 4-1 and 4-2).

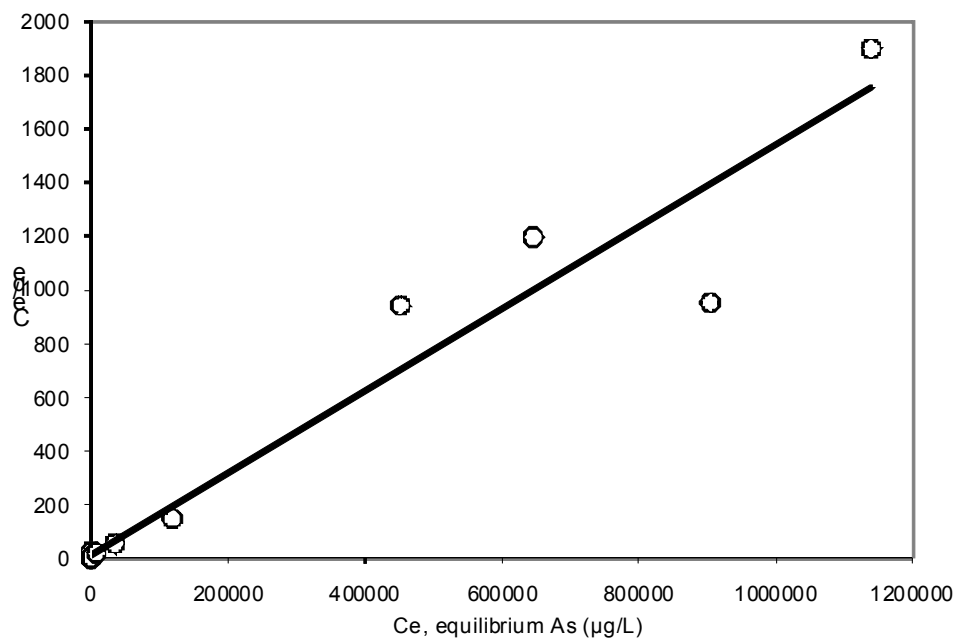


Figure 4-1: Langmuir adsorption isotherm for RO water

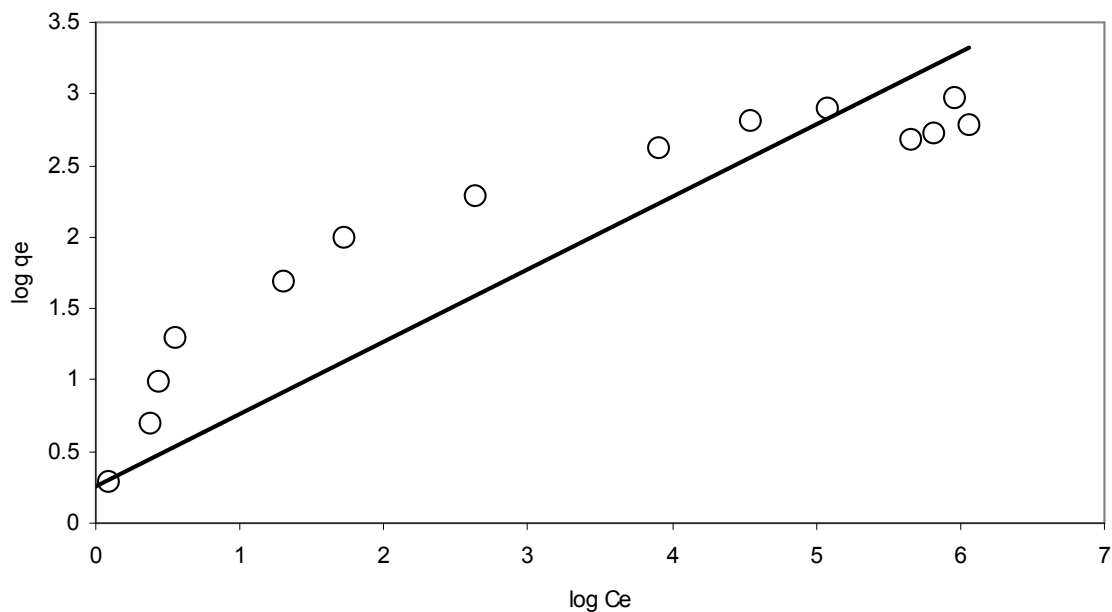


Figure 4-2: Freundlich adsorption isotherm for RO water

All experimental results are summarized in Appendix B (Table B-1) while the isotherm equations and parameters are shown in Table 4-4.

Table 4-4: Freundlich and Langmuir isotherm equations and parameters for the adsorption of arsenic onto ZVI filings for RO water

Model Equation	r	K_f	n	b	qmax	N
Freundlich Isotherm						
$q_e = 0.169C_e^{1/1.5022}$	0.88	0.1690	1.5022			13
Langmuir Isotherm						
$q_e = (833.3333)(0.0003)C_e/(1+0.0003C_e)$	0.99			3.08×10^{-4}	833.333	13

The experimental results of the batch study on RO water show an average arsenic removal capacity of 70.4%. The highest percent removal (99.8%) occurred with an initial arsenic concentration of 2 000 μ g/L.

Testing of the significance of the correlation coefficients was completed using the student's t-test. The results showed that coefficients for both the Freundlich and Langmuir isotherms were significant at the 5% significance level. Therefore, both isotherm equations could be used to describe adsorption of arsenic onto ZVI filings in RO water in this concentration range. However, the Langmuir isotherm has a higher correlation coefficient ($r = 0.99$) indicating it may provide a better description of the adsorption data. The equilibrium parameter, R , for any value of C_0 ranged from 0.01597 to 0.9997 indicating a favourable isotherm.

The Langmuir isotherm yielded a binding energy constant (b) of 3.08×10^{-4} L/mg and adsorption maxima constant (q_{\max}) of 833mg As/kg ZVI. The Freundlich constants, K_f and n , were estimated to be 0.1690 and 1.5022, respectively.

4.2.2 Batch Study with Buena Vista and Kannata Valley Water

Freundlich and Langmuir isotherm equations and parameters obtained using non-linear least squares regression of batch data for both Buena Vista and Kannata Valley ground water are shown in Table 4-5. Parameters for both isotherms were statistically significant at the 95% confidence interval, however the Langmuir isotherm more adequately describes the adsorption of arsenic onto ZVI in Kannata Valley and Buena Vista water. These results are similar to published literature where adsorption of arsenic onto various adsorbents followed the Langmuir isotherm (Guo *et al.* 2007). Values for the equilibrium parameter, R , ranged from 0.0065 to 0.9975 indicating a favourable Langmuir isotherm for the description of both Buena Vista and Kannata Valley water in the particular arsenic concentration range.

Table 4-5: Freundlich and Langmuir isotherm equations and parameters for the adsorption of arsenic onto ZVI filings in Buena Vista and Kannata Valley ground water

Model Equation	r	K_f	n	b	q_{max}	N
Buena Vista						
Freundlich Isotherm						
$q_e = 0.1593C_e^{1/1.2607}$	0.93	0.1593	1.2607			13
Langmuir Isotherm						
$q_e = (2\ 000)(0.0003)C_e/(1 + 0.0003C_e)$	0.76			2.58×10^{-4}	2 000	13
Kannata Valley						
Freundlich Isotherm						
$q_e = 0.4154C_e^{1/1.5473}$	0.93	0.4154	1.5473			17
Langmuir Isotherm						
$q_e = (5\ 000)(0.0003)C_e/(1 + 0.0003C_e)$	0.99			2.75×10^{-4}	5 000	17

Average arsenic removal efficiencies for Buena Vista and Kannata Valley raw water were 95 and 97%, respectively, for the selected range of arsenic concentrations. Arsenic removal was greater than 90% in all samples up to a spiked concentration of 200 000 $\mu\text{g/L}$ or higher.

Figures 4-3 and 4-4 describe the Langmuir and Freundlich isotherms for the Buena Vista ground water. The Langmuir binding energy constant was again found to be low at $2.58 \times 10^{-4} \text{ L}/\mu\text{g}$. The maximum adsorption capacity for this water, determined by the Langmuir q_{max} constant, was 2 000mg As/kg ZVI. The Freundlich adsorption capacity factor, K_f , was found to be 0.1593L/mg while the constant n (intensity factor) was 1.2607.

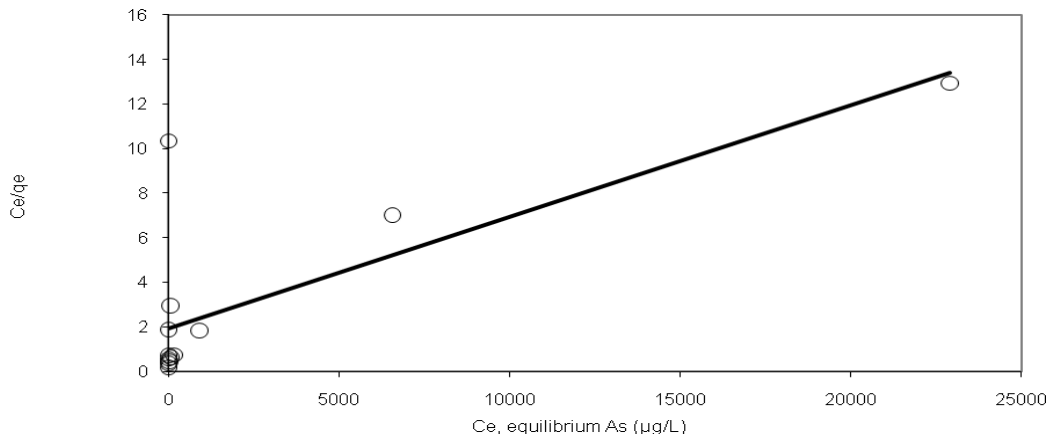


Figure 4-3: Langmuir adsorption isotherm for Buena Vista ground water

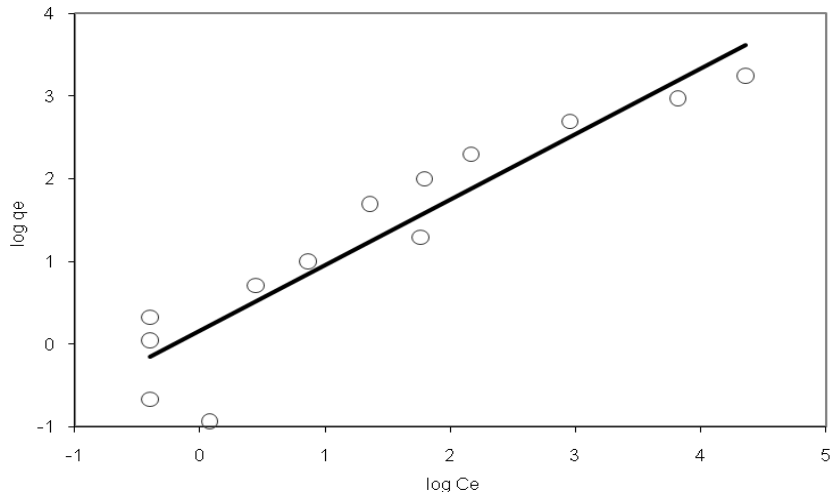


Figure 4-4: Freundlich adsorption isotherm for Buena Vista ground water

Isotherms for Kannata Valley are given in Figures 4-5 and 4-6. By linear analysis the Langmuir constants q_{\max} and b were found to be 5 000 and 2.75×10^{-4} . The adsorption maximum for this particular water would then be determined to be 5 000mg As/kg ZVI. The Langmuir constant b , indicative of binding energy, in this case was very low at 2.75×10^{-4} L/ μ g. The Freundlich constants K_f and n were found to be 0.4154 and 1.5473, respectively.

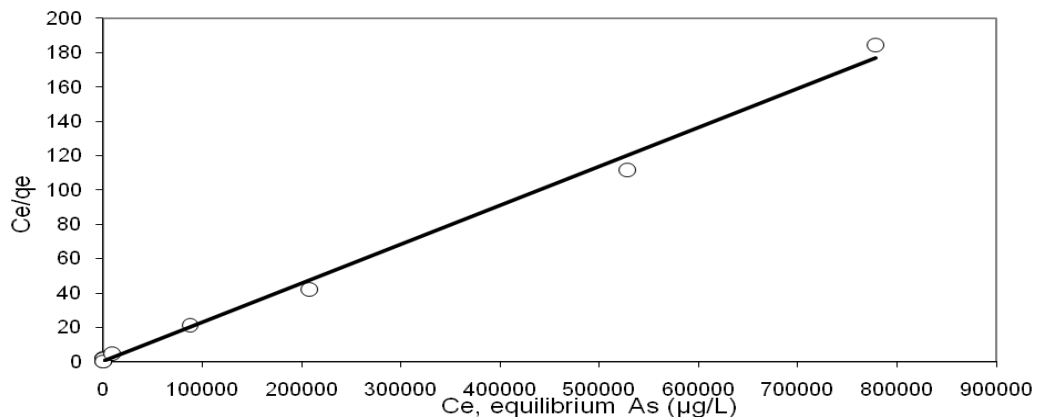


Figure 4-5: Langmuir adsorption isotherm for Kannata Valley ground water

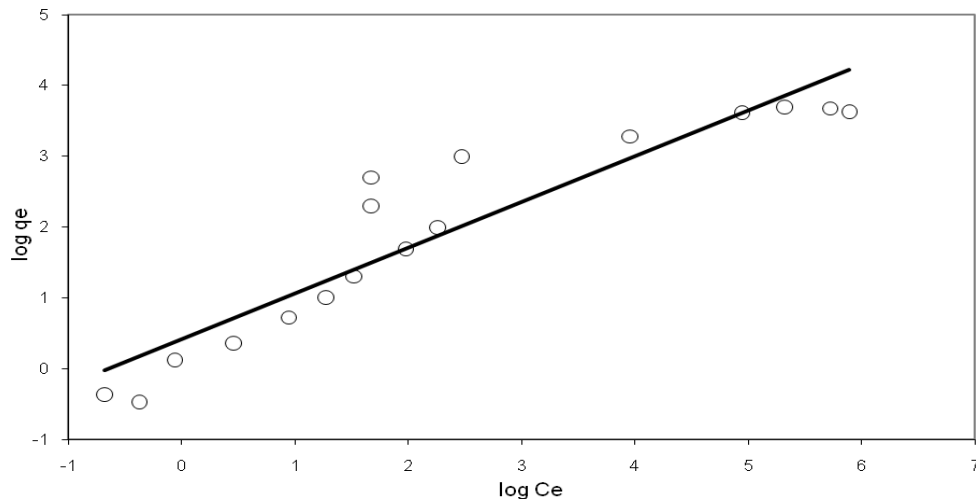


Figure 4-6: Freundlich adsorption isotherm for Kannata Valley ground water

A comparable binding energy constant (b) was observed for both Kannata Valley and Buena Vista water suggesting similar adsorbate-adsorbent interactions. The values of the equilibrium factor (R) for both Buena Vista and Kannata Valley batch results indicate favourable adsorption systems. The adsorption capacities found in this study are within the range of those reported in literature. Arsenic removal capacities of ZVI filings reported in previous published studies include: 4 400mg As/kg ZVI with Connelly GPM, Inc. (Nikolaidis *et al.*, 2003), 7 500mg As/kg ZVI with Peerless (Lien and Wilkin, 2004), 470mg As/kg ZVI with Baker (Lackovic *et al.*, 2000) and 732mg As/kg ZVI (As(V)) and 1 771mg As/kg ZVI (As(III)) with Peerless (Su and Puls, 2001b). These adsorptive capacities of Peerless ZVI filings (20-40 mesh) can be directly used as a design parameter for estimating the amount of reactive media required in field-scale columns for these specific ground waters.

The Eh and pH were determined for each spiked sample before and after the 48-hour equilibrium period. A pattern of decreasing Eh as the spiked arsenic concentration increased was observed for all batch series. The Eh also decreased in all samples after the 48-hour period as the iron was oxidizing consuming the oxygen in the samples.

The pH was noted to increase in conjunction with increasing arsenic concentration in the samples and over the equilibrium time. The pH increase is also due to the decomposition of the ZVI and sorption reactions of the arsenic, which releases OH⁻ groups (Su and Puls, 2001).

Iron corrosion was suppressed at higher arsenic concentration samples. Arsenate adsorption onto ZVI blocks further reduction and therefore lowers the iron corrosion rate. This effect is significant for arsenate concentrations up to 100 µg/L. However, concentrations between 100 and 20 000 µg/L resulted in no further measurable effect on iron corrosion (Melitas *et al.*, 2002).

A desorption reaction may have occurred in the Buena Vista samples as sample pH rose to between 8.95 and 11.28 at the end of the equilibrium period. In contrast, only a few of the RO and Kannata Valley samples reached pH 8.5. As pH increases, particularly above 8.5, arsenic can desorb (Stollenwerk, 2003; Smedley and Kinniburgh, 2002; Sracek *et al.*, 2004). The significant rise in pH in the Buena Vista system was likely due to oxidation of iron in the column and the resulting acid consumption. The lengthy equilibrium time combined with weak binding energy may have allowed for arsenic desorption and stronger competition from other ions. Less Fe⁰ is corroded at higher pH as well resulting in less Fe(II) available for adsorption (Leupin *et al.*, 2005).

The greater concentration of As(III) species in the Kannata Valley water could also have been a minor contributor to the higher loading capacity observed. Su and Puls (2001) and Jain *et al.* (1999) demonstrated greater loading capacity for As(III) onto iron filings than As(V). The lesser affinity for As(V) is likely related to its impact of increasing negative surface charge leading to a decrease in its retention. As(III) does not produce this same reaction (Jain *et al.*, 1999; Melitas *et al.*, 2002). In addition to higher As(III) species, Kannata Valley water also contains a higher background concentration of iron to adsorb and precipitate arsenic.

4.3 Continuous Column Studies

Two phases of column studies were completed using (1) nutrient-enhanced RO water and (2) ozonated Buena Vista and Kannata Valley water. Columns were not operated to achieve breakthrough, but rather to examine arsenic removal performance of ZVI incorporated into a biological sand bed at various volumetric ratios.

4.3.1 Column Study with RO Water

RO water was enhanced with a complex nutrient mixture and spiked to 50µg/L As(V). Five different iron and sand [v/v] mixtures ranging from 0/100 to 50/50 were examined for performance at similar loading rates. The columns operated at 4mL/min (0.023m/h). Total throughput volume for the filtration run was 173L, equivalent to 149 bed volumes.

Results from Phase I of the column study are provided in Table 4-6 and in the Appendix in Table B-4.

Table 4-6: Summary of results from nutrient-enhanced RO water experiment

ZVI/ Sand [v/v]	Mass gravel [g]	Mass sand [g]	Mass ZVI [g]	Total volume of media [m ³]	Through put volume [L]	Specific through put [L/gZVI]	Column capacity (As removed/volume of media) [kg/m ³]*
0/100	300	1 750	0	0.001172	173	0	3.65 x 10 ⁻⁴
50/50	300	875	1,400	0.001172	173	0.12	6.06
40/60	300	1 050	1,120	0.001172	173	0.15	6.03
30/70	300	1 225	840	0.001172	173	0.21	6.07
20/80	300	1 400	560	0.001172	173	0.31	5.96

*Does not represent capacity at breakthrough

The addition of the nutrient solution resulted in a complex water matrix. A complete analysis was performed on this water (Table 4-1). The nutrient-enhanced RO water contained 22mg/L TOC and 1.42mg/L PO₄³⁻P that may interfere with arsenic adsorption.

The columns containing sand only provided minimal arsenic removal (maximum 11%) from the influent water, as anticipated. In the Phase I sand-only columns, the average

arsenic removal capability was 2.27 μ g/L and the capacity was 3.65 x 10⁻⁴ kg As removed/m³. Both results are well below those from columns containing ZVI within the same amount of bed volumes.

A Tukey multiple comparison test was completed on the performance data (Appendix C) of the ZVI/sand columns of varying ratios. Analysis at the 95% confidence interval indicates that the arsenic removal performance of the 20/80 column was statistically different with poorer removal rates from the other ZVI/sand columns. The remaining columns containing mixtures of 50, 40 and 30% Fe by volume performed similarly to each other. The column capacities ranged from 5.96 to 6.07kg As removed/m³ for the duration of the filtration run (149 bed volumes). Although the 20/80 columns were capable of removing arsenic to below 10 μ g/L, they did not achieve the same level of performance as the columns with larger amounts of ZVI. Less ZVI in the column bed may have resulted in dissolved arsenic passing through the column via “null” paths without reacting with the iron (Lien and Wilkin, 2004).

Arsenic removal efficiency improved with time in all mixed media columns with the exception of the 20/80 columns (Table B-4). Over time the iron in the columns was oxidized into the various ferric oxides that complex with the influent arsenic.

Random effluent samples were collected from the Phase I columns and analyzed for total dissolved iron to determine whether the addition of ZVI to the columns leached significant amounts of dissolved iron into the effluent. The results indicate that, on average, there was less iron in the product water than in the influent water (Table 4-7). The influent water contained an average background concentration of iron of 0.084mg/L (due to nutrient solution addition).

Operationally, it was difficult to maintain a constant flowrate through the columns over the full experimental period as the hydraulic resistance changed. Variations in the hydraulic resistance were due primarily to plugging of pore spaces likely by the

formation of iron oxyhydroxides, which occurs mainly at the influent of the filter where there are greater oxygen concentrations (Johnson *et al.*, 2005).

Table 4-7: Dissolved Fe (mg/L) in influent and effluent from Phase I column study

Water source	Average (mg/L)	Maximum (mg/L)	Minimum (mg/L)
Raw water	0.084	0.178	0.023
0/100	0.060	0.125	0.009
50/50	0.075	0.102	0.023
40/60	0.068	0.147	0.014
30/70	0.146	0.261	0.100
20/80	0.074	0.146	0.019

4.3.2 Column Study with Buena Vista and Kannata Valley Water

Triplicate sand-only columns, as well as those containing ZVI/sand (v/v) mixtures of 50/50 and 40/60 were assembled to treat ozonated Buena Vista and Kannata Valley water. The columns operated at 0.023m/h and treated 184L equating to 154 bed volumes without breakthrough.

The results for this filtration run are summarized in Tables 4-8, 4-9 and B-5.

Table 4-8: Continuous-flow column performance on Kannata Valley water

BV (bed volumes treated)	Initial As (µg/L)	0/100 (Fe/Sand) [v/v]		50/50 (Fe/Sand) [v/v]		40/60 (Fe/Sand) [v/v]	
		Final As (µg/L)	% As Removed	Final As (µg/L)	% As Removed	Final As (µg/L)	% As Removed
20	27.82	29.41	-5.72	2.81	89.90	2.70	90.29
45	22.87	21.62	5.47	2.75	87.98	2.82	87.67
60	23.65	23.48	0.72	2.35	90.06	2.42	89.77
75	21.04	29.20	-38.78	2.31	89.02	2.60	87.64
90	24.38	24.58	-0.82	2.38	90.24	2.56	89.50
110	21.09	19.78	6.21	2.32	89.00	2.57	87.81
125	24.65	26.05	-5.68	2.51	89.82	2.43	90.14
145	25.32	30.88	-21.96	2.82	88.86	2.45	90.32
148	22.05	26.71	-21.13	2.55	88.44	2.16	90.20
151	22.09	22.45	-1.63	2.31	89.54	2.45	88.91
154	26.92	26.77	0.56	2.21	91.79	2.28	91.53

Table 4-9: Continuous-flow column performance on Buena Vista water

BV (bed volumes treated)	Initial As (µg/L)	0/100 (Fe/Sand) [v/v]		50/50 (Fe/Sand) [v/v]		40/60 (Fe/Sand) [v/v]	
		Final As (µg/L)	% As Removed	Final As (µg/L)	% As Removed	Final As (µg/L)	% As Removed
20	16.36	17.68	-7.47	<0.5	>96.94	0.68	95.84
45	17.11	17.14	-0.18	<0.5	>97.08	<0.5	>97.08
60	16.71	16.67	0.24	<0.5	>97.01	<0.5	>97.01
75	16.32	16.97	-3.83	<0.5	>96.94	<0.5	>96.94
90	15.11	16.81	-10.11	<0.5	>96.69	<0.5	>96.69
110	16.13	12.75	26.51	<0.5	>96.90	<0.5	>96.90
125	16.24	16.80	-3.33	<0.5	>96.92	<0.5	>96.92
145	16.98	16.62	2.17	<0.5	>97.06	<0.5	>97.06
148	16.65	16.63	0.12	<0.5	>97.00	<0.5	>97.00
151	16.23	16.67	-2.64	<0.5	>96.92	<0.5	>96.92
154	16.97	15.95	6.39	<0.5	>97.05	<0.5	>97.05

4.3.2.1 Arsenic removal efficiency

The columns containing sand only did not perform well and were not capable of removing arsenic to below 10µg/L. These columns appear to have leached arsenic during the treatment of both Kannata Valley and Buena Vista ground waters.

The arsenic removal efficiency of the ZVI/sand columns was greater than 95% and 87% for water samples from Buena Vista and Kannata Valley, respectively. A 2-sample t-test indicated that within the 95% confidence interval there was no significant performance difference between the 50/50 and 40/60 columns.

The Kannata Valley columns consistently removed influent arsenic to below 3µg/L with an average capacity of 3.35mg As removed/m³ (Table B-5). The Buena Vista columns reduced influent arsenic to less than 0.5µg/L and achieved an average capacity of 2.51 mg As removed/m³.

The higher removal rate of the Buena Vista columns is likely related to a greater ratio of As(V) species in that water. Although oxidation resulted in a higher concentration of

arsenate in the Kannata Valley water approximately half the influent arsenic was As(III). Comparatively, the majority of the arsenic species in the Buena Vista raw water is in the +5 form (Section 4.1.2). Arsenate tends to react much quicker with iron oxides than arsenite due to the easy formation of ferric arsenate (Joshi and Chaudhuri, 1996; Raven *et al.*, 1998).

The greater complexity of the Kannata Valley water may also have contributed to less complete arsenic removal in comparison to the Buena Vista columns. The slow filtration rate combined with compounds, particularly bicarbonate, in the water may have allowed scale formation on the iron filings limiting corrosion (Leupin and Hug, 2005; Leupin *et al.* 2005). There also may have been some blocking of sorption sites through deposition of particles in the columns. This ground water was rather turbid and the columns were removing approximately 65% of that turbidity (Table B-6). The columns were not backflushed during the study.

4.3.2.2 Arsenic Speciation

To achieve oxidation of As(III) and promote oxidation of ZVI in the columns, water was ozonated in batches to reach an ORP of 800mV. Continuous ozonation controlled by a desired ORP was not technically possible with the column apparatus setup. Kannata Valley water in particular displayed a high ozone demand and achieving the desired redox potential took several hours. Once the target ORP was reached ozonation ceased.

Arsenic speciation tests were completed on Kannata Valley water directly after ozonation. The results indicated that excessive ozone application (>33mg O³/L) was only capable of oxidizing 40 to 60% of the As(III) to As(V). In general, half of the total influent arsenic was As(III) after Kannata Valley water ozonation. An arsenic speciation of the effluent from the 50/50 columns showed that As(III) also constituted half the residual concentration after treatment.

Based on limited testing, removal efficiency for both arsenic species was 99.5%. The ZVI in the columns was therefore, proficient at removing As(III) and As(V) equally well. The ability of ZVI to remove both species has been noted in other research including a study by Su and Puls (2004) in which it was noted that As(III) was partially oxidized to As(V) by iron corrosion byproducts. Iron oxides can be an effective oxidant of As(III).

4.3.2.3 Filtrate water quality

Complete water analyses were conducted to determine whether or not mobilization of other elements from the ZVI/sand media occurred and also to characterize the effluent after a ZVI/sand filtration unit. Appendix Table B-6 describes Buena Vista and Kannata Valley raw water characteristics as well as effluent water from 50/50 columns. The results show good arsenic removal and no significant leaching of other elements from the columns. Random samples of column effluent were collected for analysis of iron concentration and potential sloughing into the produced water. The results indicate that there was typically a lower concentration of iron in the effluent than in the raw water (Table 4-10).

Table 4-10: Total dissolved Fe (mg/L) influent and effluent concentration for Kannata Valley and Buena Vista water filtration run

Water Source	Kannata Valley		Buena Vista	
Raw water	1.61		0.20	
	Min.	Max.	Min.	Max.
0/100	0.005	0.053	0.004	0.088
40/60	0.003	0.011	0.006	0.201
50/50	0.005	0.027	0.004	0.150

4.3.2.4 Biomass Activity

A Biomass Respiration Potential test to determine extent of biological activity was completed on two columns of each triplicate set of both the Kannata Valley and Buena Vista columns. Theoretically, if all of the carbon added to the sample were degraded within the 5 hour agitation period the stoichiometric decrease in O₂ would be 5.6mg/L (Urfer and Huck, 2001). Typically, the results of this test fall within the range of 0.2 to

4.0 mg O₂/L. The results from the various columns (Table 4-11) indicate biomass respiration occurred in all the columns, with varying degrees of biological activity.

Table 4-11: Biomass Respiration Potential test results for Buena Vista and Kannata Valley columns

Column*	Initial DO(mg/L)	Remaining DO(mg/L)	Δ DO (mg/L)
Buena Vista			
0/100	7.22	6.75	0.47
40/60	6.48	4.41	2.07
50/50			2.24
Kannata Valley			
0/100	7.59	6.96	0.63
40/60	6.47	4.75	1.72
50/50	6.95	4.91	2.05

*Values represent the average of two selected columns

The columns containing sand only are perhaps the best indicator of biological activity as the DO reduction in the columns containing iron may be in part due to oxidation of the iron.

The significance of biological activity to arsenic removal is related to the production of iron oxides by microbial functions. The micro-organisms are thought to oxidize iron and deposit iron oxides in the filter media which adsorb arsenic. The extent to which this mechanism may have contributed to column performance in this study has not been quantified. However, through the use of biologically-ripened sand from a well-seasoned slow sand filter and the addition of a nutrient solution during column startup biological activity was promoted.

4.4 Feasibility of ZVI/sand column for arsenic removal for municipal potable water utilities

The recommended ratio of sand and ZVI for an adsorption column is 70/30 (% v/v). The advantage of this ratio is that it can achieve comparable arsenic removal to columns with higher Fe content while being less likely to experience filter clogging issues due to Fe

oxide formation blocking pore spaces. This media has since been NSF Standard 61 approved for use in potable water systems.

4.4.1 Conceptual scale-up design

The following scale-up design was based on a subsequent project at Kannata Valley where a pilot scale biofiltration system with a ZVI/sand filter removed arsenic as well as other contaminants resulting in potable quality water (Table 4-12).

Table 4-12: Specifications of a conceptual design for full-scale municipal water treatment plant

Parameter	Design Specification
Plant capacity	720m ³
Number of ZVI/sand filters	6
Size of ZVI/sand filter	3.49mØ x 2.59m high
Filtration rate of ZVI/sand filter	0.68m/h
Total depth of filter media	107cm (30cm pea gravel base, 76cm bed of ZVI/sand)
EBCT	67 minutes
ZVI/sand filter composition	30/70, %, v/v
Mass of Fe per filter	4 487kg

ZVI/sand filters require backwash on a routine basis, approximately every 10 days, to restore flow. Little water is wasted as filtered backwash water required is estimated to be 0.4% of filter production. The backwash is a simple manual process that can be completed in approximately an hour, therefore the operator commitment and expertise required is minimal. The filters are gravity-fed requiring no electricity for pumps other than for the backwash cycle.

4.4.2 Disposal

All arsenic removal methods generate some type of arsenic-rich waste, in this instance a spent arsenic-contaminated adsorption media will have to be appropriately disposed of. Ali *et al.* (2003) evaluated arsenic leaching from various arsenic removal media including iron-coated brick chips, iron-coated sand and GFO. They found that the results obtained

using the U.S. EPA’s Toxic Characteristics Leaching Procedure (TCLP) showed negligible leaching and that the waste from these arsenic removal units are not “hazardous” as defined by the U.S. EPA. However, column tests were also performed to examine long-term leaching using distilled, arsenic-free groundwater, rainwater and pond water. The results indicated that long-term leaching from these spent media would be a significant concern.

When spent, arsenic-contaminated ZVI/sand media will have to be removed from the filter. The most likely method is to create a slurry and remove via vacuum pump truck. According to the Saskatchewan Government Hazardous Substances and Waste Dangerous Good Regulations (2002) arsenic is considered an environmental persistent or chronic hazardous substance. Storage, transport and disposal of this media will have to subscribe to this regulatory framework. Local environmental management companies are available that can provide removal, transportation and disposal of contaminated media.

4.4.3 Economic considerations

A comparison of adsorptive media reveals that ZVI/sand is economical with respect to media and treatment cost and has a satisfactory estimated life (Table 4-13). ZVI filings can be obtained for under \$1.50/kg and the cost of manufacturing this filter is comparable to a biological activated carbon filter making it a feasible technology for Mainstream Water Solutions to utilize.

Table 4-13: Treatment costs and media replacement frequency for comparable adsorptive media

Media	BV Treated	Media density (kg/m ³)	Media cost (m ³)	Treatment cost (\$/L)	Change-out frequency (months)
E33 ^a	54 700	454	5 377	0.10	28.6
GFH ^a	18 300	1 281	7 769	0.42	9.6
Z33 ^a	3 300	881	486	0.15	1.7
ZVI/sand ^b	25 900	1 929	1 305	<0.01	40

^aCalculations based on 1 284m³/day and 45.4m³ of media (Westerhoff *et al.* 2006)

^bEstimates for Kannata Valley conceptual full-scale plant design based on bench-scale and pilot studies

Based on the loading capacity observed in the batch isotherm study and assuming a maximum of 25% of the Fe is available for adsorption (Leupin *et al.*, 2005), the life of the media in the six ZVI/sand filters (based on the conceptual full-scale plant design) is estimated to be approximately 40 months assuming maximum plant design capacity. The treatment cost is estimated to be <\$0.01/L and includes filter installation, media, operation and maintenance, and disposal costs. Comparatively, ZVI/sand as an adsorptive media represents an economically feasible option for arsenic removal for small-scale utilities.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions can be drawn from this study:

(1) Both the Langmuir and Freundlich adsorption isotherms can adequately describe the adsorption of arsenic onto ZVI filings at the 95% confidence interval. Batch adsorption experiments with RO, Kannata Valley and Buena Vista water indicate a favourable reaction with an adsorption maximum (Langmuir constant q_{\max}) of 833; 5 000 and 2 000mg As/kg ZVI respectively.

(2) Batch isotherm studies of arsenic-spiked Buena Vista and Kannata Valley ground waters showed that the average arsenic removal efficiency of ZVI was 97 and 95% respectively. Arsenic removal was greater than 90% in all samples until spiked to a concentration of 200 000 μ g/L or higher.

(3) Continuous column studies with a complex nutrient-enhanced RO water indicated that columns containing filtration sand only were not efficient at arsenic removal. Columns containing 50/50, 40/60, 30/70 and 20/80 (iron/sand, v/v) were capable of removing arsenic from an influent concentration of 50 μ g/L to well below 10 μ g/L. All iron/sand columns achieved greater than 92% removal of influent arsenic.

(4) A Tukey multiple comparison test showed that at the 95% confidence interval there was no difference in arsenic removal performance between the 50/50, 40/60 and 30/70 media mixtures. These columns achieved over 98% arsenic removal. The performance of the 20/80 column was statistically different than the other mixtures. This column removed less arsenic due to less ZVI. However the column still achieved 92% removal of influent arsenic.

(5) Columns containing sand only exhibited poor arsenic removal. Media mixtures of 50/50 and 40/60 were capable of removing arsenic to well below 10 μ g/L. All ZVI/sand

columns achieved greater than 87% removal during the Buena Vista and Kannata Valley ground water filtration run.

(6) Arsenic speciation tests indicate that the ZVI/sand columns were capable of removing As(III) and As(V) equally well. Removal efficiency for both species was 99.5%.

(7) No significant amount of iron was leached from the ZVI/sand columns in either the nutrient-enhanced RO water or the Kannata Valley and Buena Vista ground water filtration runs.

(8) ZVI/sand as an adsorptive media represents an economically viable method for arsenic removal for small-scale water treatment utilities.

5.2 Further Research

Recommendations for further study include:

(1) Examine kinetics of arsenic adsorption in a ZVI/sand column to determine minimum contact time required for adequate removal.

(2) Examine hydraulic conductivity of columns composed of various ratios of sand and ZVI to determine a suitable mixture that balances performance and operational problems related to back pressure in the column due to iron oxyhydroxide formation and pore space clogging.

(3) Conduct studies to determine the effect of the primary interfering compounds including phosphate, NOM, sulphate and silicate on arsenic removal using a ZVI/sand column.

(4) Conduct continuous column studies at various loading rates to determine the performance of a ZVI/sand column to remove arsenic.

(5) Conduct pilot studies to determine the effectiveness of a small-scale ZVI/sand column in field operation.

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Appendix A: Nutrient Solution

Table A-1: Nutrient, trace mineral and vitamin solution for RO-enhanced water for column study

Nutrients	mg/L
CaCl ₂ · 6H ₂ O (calcium chloride hexahydrate)	55
MgSO ₄ · 7H ₂ O (magnesium sulphate heptahydrate)	37
Na ₂ SiO ₃ · 9H ₂ O (disodium trioxosilicate nonahydrate)	42.5
NaNO ₃ (sodium nitrate)	42.5
NH ₄ Cl (ammonium chloride)	27
NaHCO ₃ (sodium hydrogen carbonate)	202
KCl (potassium chloride)	11
KH ₂ PO ₄ (potassium dihydrogen phosphate)	9
4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES)	126
Trace Metals	
CuSO ₄ · 6H ₂ O (copper (II) sulfate hexahydrate)	0.00125
NaMoO ₄ · 2H ₂ O (sodium molybdenum oxide dehydrate)	0.00181
CoCl ₂ · 6H ₂ O (cobalt chloride hexahydrate)	0.00298
MnCl ₂ · 4H ₂ O (manganese chloride tetrahydrate)	0.02275
ZnSO ₄ · 7H ₂ O (zinc sulfate heptahydrate)	0.00575
C ₆ H ₉ NO ₆ (nitriloacetic acid)	5.14
FeCl ₃ (iron (III) chloride)	0.61
H ₃ BO ₃ (boric acid)	12.36
Vitamins	
C ₁₀ H ₁₆ N ₂ O ₃ S (biotin – vitamin B ₇)	0.05
C ₆₃ H ₈₈ CoN ₁₄ O ₁₄ P (cyanocobalamin – vitamin B ₁₂)	0.05
C ₁₂ H ₁₇ ClN ₄ OS (thiamine – vitamin B ₁)	105

Appendix B: Experimental Data

Table B-1: RO water batch experimental data

Initial As ($\mu\text{g/L}$) (C_0)	m (g ZVI)	Mass As (μg) in 100ml	Equilibrium As ($\mu\text{g/L}$) concentration (C_e)	Final mass (μg) As in solution	Mass As sorbed (μg)	Mass of As adsorbed per unit of adsorbent (q_e) (mg/kg)	% As adsorbed	C_e/q_e	Log C_e	Log q_e
1	10	0.100	0.189	0.0189	0.0811	0.0081	81.10	23.30	-0.72	-2.09
10	10	1	0.106	0.0106	0.9894	0.0989	98.94	1.07	-0.97	-1.00
100	10	10	0.414	0.0414	9.9586	0.9959	99.59	0.42	-0.38	-0.00
200	10	20	1.224	0.1224	19.8776	1.9878	99.39	0.62	0.09	0.30
500	10	50	2.340	0.2340	49.7660	4.9766	99.53	0.47	0.37	0.70
1 000	10	100	2.700	0.2700	99.7300	9.9730	99.73	0.27	0.43	1.00
2 000	10	200	3.500	0.3500	199.6500	19.9650	99.83	0.18	0.54	1.30
5 000	10	500	19.800	1.9800	498.0200	49.8020	99.60	0.40	1.30	1.70
10 000*	10	1 000	52.300	5.2300	994.7700	99.4770	99.48	0.53	1.72	2.00
20 000	10	2 000	430.000	43.0000	1 957.0000	195.7000	97.85	2.20	2.63	2.29
50 000	10	5 000	8 000.000	800.0000	4 200.0000	420.0000	84.00	19.05	3.90	2.62
100 000	10	10 000	35 000.000	3 500.0000	6 500.0000	650.0000	65.00	53.85	4.54	2.81
200 000	10	20 000	119 000.000	11 900.0000	8 100.0000	810.0000	40.50	146.90	5.08	2.91

*Represents the average of two samples

Table B-2: Kannata Valley batch experimental data

Raw As	Spiked As	Initial As (µg/L) (C ₀)	m (g ZVI)	Mass As (µg) in 100ml	Equil. As (µg/L) (C _e)	Final mass (µg) As in solution	Mass As sorbed (µg)	Mass of As adsorbed per unit of adsorbent (q _e) (mg/kg)	% As adsorbed	C _e /q _e	Log C _e	Log q _e
33.35	1	34.35	10	3.435	0.427	0.043	3.392	0.3392	98.76	1.26	-0.37	-0.47
33.35	10	43.35	10	4.335	0.208	0.021	4.314	0.4314	99.52	0.48	-0.68	0.37
33.35	100	133.35	10	13.335	0.870	0.087	13.248	1.3248	99.35	0.66	-0.06	0.12
33.35	200	233.35	10	23.335	2.888	0.289	23.046	2.3046	98.76	1.25	0.46	0.36
33.35	500	533.35	10	53.335	8.79	0.879	52.456	5.2456	98.35	1.68	0.94	0.72
33.35	1 000	1033.35	10	103.335	18.7	1.870	101.465	10.1465	98.19	1.84	1.27	1.01
33.35	2 000	2033.35	10	203.335	33.24	3.324	200.011	20.0011	98.37	1.66	1.52	1.30
33.35	5 000	5033.35	10	503.335	95.5	9.550	493.785	49.3785	98.10	1.93	1.98	1.69
33.35	10 000*	10 033.35	10	1 003.335	181.4	18.140	985.195	98.5195	98.19	1.84	2.26	1.99
33.35	20 000	20 033.35	10	2 003.335	47	4.700	1 998.635	199.8635	99.77	0.24	1.67	2.30
33.35	50 000	50 033.35	10	5 003.335	47	4.700	4 998.635	499.8635	99.91	0.09	1.67	2.70
33.35	100 000	100 033.35	10	10 003.335	296	29.600	9 973.735	997.3785	99.70	0.30	2.47	3.00
33.35	200 000	200 033.35	10	20 003.335	9 000	900	19103.335	1 910.3335	95.50	4.70	3.95	3.28
33.35	500 000	500 033.35	10	50 003.335	88 000	8 800	41203.335	4 120.3335	82.40	21	4.94	3.61
33.35	700 000	700 033.35	10	70 003.335	208 000	20 800	49203.335	4 920.3335	70.29	42	5.32	3.69
33.35	1 000 000	1000033.35	10	100003.335	528 000	52 800	47203.335	4 720.335	47.20	112	5.72	3.67
33.35	1 200 000	1200033.35	10	120003.335	778 000	77 800	42203.335	4 220.335	35.17	184	5.89	3.63

*Represents the average of two samples

Table B-3: Buena Vista batch experimental data

Raw As	Spiked As	Initial As (µg/L) (C ₀)	m (g ZVI)	Mass As (µg) in 100ml	Equil. As (µg/L) (C _e)	Final mass (µg) As in solution	Mass As sorbed (µg)	Mass of As adsorbed per unit of adsorbent (q _e) (mg/kg)	% As adsorbed	C _e /q _e	Log C _e	Log q _e
11.8	1	12.8	10	1.28	1.2	0.12	1.16	0.116	90.63	10.34	-0.08	-0.94
11.8	10	21.8	10	2.18	<0.4	0.04	2.14	0.214	98.17	1.87	-0.40	-0.67
11.8	100	111.8	10	11.18	<0.4	0.04	11.14	1.114	99.64	0.35	-0.40	0.05
11.8	200	211.8	10	21.18	<0.4	0.04	21.14	2.114	99.81	0.19	-0.40	0.33
11.8	500	511.8	10	51.18	2.8	0.28	50.90	5.090	99.45	0.55	0.44	0.71
11.8	1 000	1011.8	10	101.18	7.3	0.73	100.45	10.045	99.28	0.73	0.86	1.00
11.8	2 000	2011.8	10	201.18	57.5	5.75	195.43	19.543	97.14	2.94	1.76	1.29
11.8	5 000	5011.8	10	501.18	22.8	2.28	498.90	49.890	99.55	0.46	1.36	1.70
11.8	10 000*	10 011.8	10	1 001.18	62	6.20	994.98	99.498	99.38	0.62	1.79	2.00
11.8	20 000	20 011.8	10	2 001.18	147	14.70	1 986.48	198.648	99.27	0.74	2.16	2.30
11.8	50 000	50 011.8	10	5 001.18	903	90.30	4 910.88	491.088	98.19	1.84	2.96	2.69
11.8	100 000	100 011.8	10	10 001.18	6 560	656	9 345.18	935.518	93.44	7.02	3.82	2.97
11.8	200 000	200 011.8	10	20 001.18	22 900	2 290	17 711.18	1 771.118	88.55	12.93	4.36	3.25

*Represents the average of two samples

Table B-4: Nutrient-enhanced RO water filtration run (bed volumes treated and arsenic removal capacity)

BV (bed volumes treated)	0/100 (Fe/Sand [v/v])			50/50 (Fe/Sand [v/v])			40/60 (Fe/Sand [v/v])			30/70 (Fe/Sand [v/v])			20/80 (Fe/Sand [v/v])		
	Initial As (µg/L)	Final As (µg/L)	% As Removed	Initial As (µg/L)	Final As (µg/L)	% As Removed	Initial As (µg/L)	Final As (µg/L)	% As Removed	Initial As (µg/L)	Final As (µg/L)	% As Removed	Initial As (µg/L)	Final As (µg/L)	% As Removed
34	41.61	39.83	4.28	41.61	<0.5	>98.80	41.61	0.90	97.84	41.61	<0.5	>98.80	41.61	0.94	92.79
54	42.70	41.69	2.37	42.70	0.76	98.22	42.70	1.09	97.45	42.70	<0.5	>98.83	42.70	1.36	92.97
74	42.98	38.71	9.93	42.98	0.90	97.91	42.98	0.91	97.88	42.98	0.79	98.16	42.98	1.51	93.02
89	41.88	37.48	10.51	41.88	0.75	98.21	41.88	0.92	97.80	41.88	<0.5	>98.81	41.88	1.44	92.84
109	40.81	40.37	1.08	40.81	0.88	97.84	40.81	1.26	96.91	40.81	0.73	98.21	40.81	1.76	92.65
124	41.05	40.45	1.46	41.05	<0.5	>98.78	41.05	0.59	98.56	41.05	<0.5	>98.78	41.05	1.58	92.69
134	41.47	40.33	2.75	41.47	<0.5	>98.79	41.47	<0.5	>98.79	41.47	<0.5	>98.79	41.47	1.00	92.77
139	41.41	39.25	5.22	41.41	<0.5	>98.79	41.41	<0.5	>98.79	41.41	<0.5	>98.79	41.29	0.88	92.73
149	41.29	36.66	11.21	41.29	<0.5	>98.79	41.29	<0.5	>98.79	41.29	<0.5	>98.79	41.29	1.11	92.73

Table B-5: Summary of results from Kannata Valley and Buena Vista filtration run

ZVI/Sand [v/v]	Mass gravel [g]	Mass sand [g]	Mass ZVI [g]	Total volume of media [m ³]	Throughput volume [L]	Specific throughput [L/g ZVI]	Column capacity (As removed/volume of media) [kg/m ³]*
Kannata Valley							
0/100	300	1 750	0	0.001172	184	0	0.25
50/50	300	875	1 400	0.001172	184	0.13	3.35
40/60	300	1 050	1 120	0.001172	184	0.16	3.35
Buena Vista							
0/100	300	1 750	0	0.001172	184	0	0.01
50/50	300	875	1 400	0.001172	184	0.13	2.51
40/60	300	1 050	1 120	0.001172	184	0.16	2.51

*Does not represent capacity at breakthrough

Table B-6: Quality of raw water and effluent from 50/50 columns for Buena Vista and Kannata Valley

Parameter (mg/L)	Kannata Valley		Buena Vista	
	Raw	Treated	Raw	Treated
Al	<0.02	<0.02	<0.02	<0.02
As	0.037	0.001	0.017	<0.001
Ba	0.0142	0.0077	0.0342	0.0264
B	1.09	1.11	0.45	0.45
Cd	<0.0002	<0.0002	<0.0002	<0.0002
Cr	0.0026	0.0023	<0.0008	<0.0008
Fe	2.09	1.17	0.159	1.33
Pb	<0.0001	<0.0001	0.0002	<0.0001
Mn	0.133	0.062	0.062	0.081
Se	0.0023	0.0023	<0.0008	<0.0008
U	0.0004	<0.0001	0.0002	<0.0001
Zn	0.005	<0.004	0.019	<0.004
Ammonia-N	3.37	0.51	1.03	0.45
Bromide	1.4	1.7	<0.1	<0.1
Colour (TCU)	6	<3	7	9
DOC	5	5	3	3
PO ₄ -P	0.26	<0.02	0.26	<0.02
Silica	24.7	0.4	23.2	2.8
TOC	5	5	3	3
Alkalinity (Total as CaCO ₃)	502	324	358	377
Bicarbonate	612	357	423	428
Hydroxide	<5	<5	<5	<5
Carbonate	<5	19	<5	7
Chloride	174	187	13	14
Fluoride	0.2	0.2	0.4	0.5
Calcium	93	24	23.1	20.5
Potassium	7.1	7.5	3.46	3.8
Magnesium	47.4	43	10.3	10.7
Sodium	531	562	158	167
Sulfate	840	885	87.3	94.2
Ion Balance (calculated, %)	98.1	97.3	98.3	96.5
TDS (calculated)	1990	1900	510	536
Hardness (as CaCO ₃)	427	237	100	95
Nitrate-N	<0.5	<0.5	<0.50	<0.5
Nitrite-N	<0.05	<0.05	<0.05	<0.05
Turbidity (NTU)	16.8	5.8	0.78	9.7
pH	7.7	8.6	7.8	8.5
Conductivity (EC)	3100	3040	880	910

Appendix C: Statistical analysis

D.1 Tukey multiple comparison test for performance of columns related to iron/sand ratio

$$H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4$$

$$H_A: \mu_1 \neq \mu_2 \neq \mu_3 \neq \mu_4$$

$$\alpha = 0.05$$

Arsenic removal performance ($\mu\text{g/L As removed}$) of various columns (sand/iron – v/v)

50/50	40/60	30/70	20/80
0.50	0.90	0.50	0.94
0.76	1.09	0.50	1.36
0.90	0.91	0.79	1.51
0.75	0.92	0.50	1.44
0.88	1.26	0.73	1.76
0.50	0.59	0.50	1.58
0.50	0.50	0.50	1.00
0.50	0.50	0.50	0.88
0.50	0.50	0.50	1.11
$X_1 = 0.64$	$X_2 = 0.80$	$X_3 = 0.56$	$X_4 = 1.29$
$n_1 = 9$	$n_2 = 9$	$n_3 = 9$	$n_4 = 9$

Source of variation	SS	DF	MS
Total	4.67	34	1.021
Groups	2.90	3	0.9657
Error	1.77	32	0.0553

$$F\text{-statistic} = MS_{\text{groups}}/MS_{\text{error}} = 17.46$$

$$F\text{-critical} = F_{0.05(1), 3, 32} = 2.92$$

F-statistic > F-critical, therefore H_0 is rejected. Because a significant F resulted from the analysis the Tukey test is applied on the means ranked in order of magnitude.

Samples ranked by mean: $X_3 = 0.56$, $X_1 = 0.64$, $X_2 = 0.80$, $X_4 = 1.29$

To test each $H_0: \mu_B = \mu_A$

$$SE = \sqrt{0.0553125/9}$$

Comparison (B vs A)	Difference ($X_A - X_B$)	SE	q ($(X_A - X_B)/SE$)	$q_{0.05, 32, 4}$	Conclusion
X_4 vs X_2	0.49	0.078	6.28	3.845	Reject $H_0: X_4 \neq X_2$
X_4 vs X_1	0.65	0.078	8.33	3.845	Reject $H_0: X_4 \neq X_1$
X_4 vs X_3	0.73	0.078	9.36	3.845	Reject $H_0: X_4 \neq X_3$
X_2 vs X_1	0.16	0.078	2.05	3.845	Accept $H_0: X_2 = X_1$
X_2 vs X_3	0.24	0.078	3.08	3.845	Accept $H_0: X_2 = X_3$
X_1 vs X_3	0.08	0.078	1.06	3.845	Accept $H_0: X_1 = X_3$

Overall conclusion: $X_4 \neq X_3 = X_2 = X_1$