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EVALUATION OF A FILTRATION SORBENT FOR REMEDIATION OF ARSENIC IN GROUNDWATER

A Project

Presented to the

Faculty of

California State University,

San Bernardino

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in

Earth and Environmental Sciences:

Professional Science Masters

by

Clement Duvan Do

June 2017

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June 2017

Approved by:

James Noblet, Committee Chair, Chemistry

Brett Stanley, Committee Member

David Maynard, Committee Member

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ABSTRACT

A commercially available product, PURA PhosLock, was identified and evaluated for use as a sorbent to remove dissolved arsenic (As) from drinking water. Although marketed as a product to remove phosphate in aquaria, it is composed of iron oxide hydroxide (i.e., FeO(OH)), which is also known to adsorb dissolved As species from water. Arsenic was measured using standard methods and Graphite Furnace Atomic Absorption Spectroscopy. A first rough filtration test was performed to see if the PhosLock adsorbed As well. About 50 g of PhosLock was used to filter 10 L of tap water containing 100 ppb As. No detectable As was observed in the filtrate. A sorption study was then performed to determine the time required to reach equilibrium, which was attained after seven hours. A second set of sorption studies were performed using different As concentrations and the data was evaluated using the Langmuir adsorption model. The model predicted a maximum adsorption capacity of 457 to 636 μg/g. A final flowing water column breakthrough experiment was performed. Tap water spiked with 50 ppb was filtered through 0.5 grams of sorbent in a glass chromatography column. The results showed that seven liters of water were filtered before any As was detected. Over 10 L were filtered before the maximum contaminant level (MCL) of 10 ppb was exceeded. The flow through study results showed that the PhosLock has an As adsorption capacity of 700 μg/g. This is consistent with the highest sorption capacity predicted by the Langmuir

model. The results of this study show that PhosLock is a very effective and economical sorbent for the removal of As from drinking water.

ACKNOWLEDGEMENTS

I would like to thank my parents Joseph Do and My-Lien Duvan for their continuous support on my educational endeavors. Without them I would probably be a rock star or something cooler, but I guess this is a good back up plan. I would like to thank my awesome siblings Christine, Steve and Anthony for understanding the struggle of graduate school as you all go through it now. Next on my list is my beautiful wife, Genevieve. Thank you for always being there for me every time I felt like quitting. I love you all and am so glad you are all part of this journey with me.

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CHAPTER ONE

INTRODUCTION

Background

Arsenic is a chemical element that can be located on the periodic table as a metalloid with the symbol of As along with an atomic number of 33 and an atomic mass of 74.92. Arsenic can exist in -3, -1, 0, +3, and +5 oxidation states. Arsenic also occurs in the environment in two allotropic states. Allotropes are forms of an element that has difference chemical and physical properties (Grund et al., 2005). The common form of arsenic is a shiny, metallic silver solid and the less common form is a yellow crystalline solid. The less common form is produced by fast vapor cooling of arsenic gas. When heated arsenic does not readily melt, but instead releases a gas. Therefore, the melting point of arsenic is very high with a melting point of 814°C or 1500°F (Chak et al., 2010). Arsenic can be found naturally in the environment, through industrial processes caused by man, and through everyday use.

Naturally occurring arsenic can be found in abundance in the Earth's crust and about one-third of the arsenic in the Earth's atmosphere comes from natural sources such as volcanoes, which produces a significant amount of arsenic. Elemental arsenic is produced commercially from arsenic trioxide. Arsenic trioxide is a by-product of metal smelting operations (Ng et al., 2012). This occurs when arsenic or an arsenic containing mineral gets oxidized in the air and by

heat. An example of this reaction can be seen in the arsenic sulfide containing mineral orpiment. These minerals are very common in the environment and worldwide. It occurs by sublimation during volcanic activities, in hot springs, and as a byproduct of another arsenic sulfide mineral, realgar (Chak et al., 2010).

Arsenic Formation/Movement in Water

Pure arsenic is insoluble in water, but some arsenic compounds can be easily dissolved in water. Inorganic forms of arsenic mostly exist in water supplies, which are commonly arsenite and arsenate. According to Mohan and Pittman (2007), arsenic is very sensitive to mobilization in the range of pH 6.5-8.5 and under both oxidizing and reducing conditions among heavy metalloids. These arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) ions are formed by the oxidation of arsenic trioxide in the air. This converts the arsenic into oxides that are more soluble in water. Arsenic trioxide dissolves in water to produce arsenous acid (H_3AsO_3). Arsenic pentoxide can be produced by heating arsenic trioxide, which then dissolves in water to produce arsenic acid (H_2AsO_4) (Grund et al., 2005). High concentrations of naturally occurring arsenic can also be found in oxidizing conditions where groundwater pH values are high.

1) $2\ As_2S_3(s) + 9\ O_2(g) \rightarrow 2\ As_2O_3(s) + 6\ SO_2(g)$

2) $As_2S_3(s) + 6H_2O(l) \rightarrow 3H_2S(g) + 2H_3AsO_3(aq)$

Health Risk Associated with Arsenic

Arsenic in groundwater poses a threat to human health when ingested through everyday uses such as cooking and drinking. Ingestion of large doses (70 to 180 mg) may be acutely fatal (Casarett et al., 1991). There are two forms of poisoning related with arsenic. The two forms are chronic and acute poisoning. Chronic poisoning occurs when there is a cumulative effect of intake. Arsenic can be taken into the body everyday by inhaling vapors, drinking water, and being in contact with insecticides containing arsenic.

The accumulation of arsenic through these means can present some mild to severe symptoms. These symptoms include headaches, confusion, and drowsiness. As the poisoning accumulates convulsions and changes in the fingernail pigmentation may occur, as well as breathing and heart difficulties, which then could lead to death. The greatest to least arsenic toxicity (along with their oxidation states) is arsine (-3), organo-arsine compounds, arsenites (+3) and oxides (+3), arsenates (+5), arsonium metals (+1) and native arsenic (0) respectively (Welch et al., 1988).

History of Lowering Arsenic Maximum Contaminant Level in Drinking Water

The first regulation for arsenic in drinking water was in 1942 at 50 ppb, which was set by the United States Public Health Services (USPHS). However, in 1962, the USPHS identified that arsenic in drinking water should not exceed 10 ppb and tries to set that as their goal. In 1988, the Environmental Protection Agency (EPA) estimated that ingestion of 50 ppb arsenic could lead to skin

cancer with a chance of 1 in 400 people. Therefore in 1993, the World Health Organization recommended that the maximum contaminant level (MCL) of arsenic in drinking water should be lowered to 10 ppb. In 1996, Congress then directed the EPA to have a new arsenic drinking water standard by January of 2000. The EPA then proposed a 5 ppb standard, but requested comments on whether to stay with that or look to concentrations of 3, 10, and 20 ppb.

In January 2001, the Clinton administration proposed a 10 ppb arsenic maximum concentration standard for drinking water days before Clinton was out of office. The Bush administration, however, blocked the proposed 10 ppb standard in March 2001. According to the EPA (2012), there was national debate on whether the proposed 10 ppb standard was too low based on the science and cost it would take to have such a standard. So on March 20, 2001 the EPA decided to enlist the help of the National Academy of Sciences to form a panel of scientific experts to review the cost, benefit and science on whether the standard would be plausible. On October 31, 2001, the EPA Administrator announced that the 10 ppb (0.010 mg/L) standard for arsenic would remain stating that, "the 10 ppb protects public health based on the best available science and ensures that the cost of the standard is achievable." (Environmental Protection Agency, 2012)

Areas that have high concentrations of arsenic include western parts of the United States, some parts of Mexico, Chile, and Argentina (Lollar, 2005). These high arsenic groundwater areas are usually in arid or semi-arid regions where groundwater salinity is high. Evaporation has been suggested to be an

important additional cause for arsenic accumulation in some arid areas (Lollar, 2005). Another correlation of high arsenic concentration on groundwater are areas on bedrock and mining activities.

The concentration of arsenic in the groundwater will vary widely and regionally (Sorg et al., 2014). The variability of the arsenic concentration in ground waters is attributed to the arsenic content of the aquifer materials and the varying desorption/dissolution processes that release the arsenic from the solid phase into the liquid phase (Hering and Kneebone, 2001; Jain and Ali, 2000; Welch et al., 1988; Welch et al., 2000). According to Sorg (2014), the most common type of arsenic bearing minerals found in the environment are pyrite and arsenic sulfides, and therefore, areas with the highest arsenic concentration in the Western United States are associated with mining.

Another factor that could lead to higher concentrations of arsenic regionally and variance is geothermal waters. Geothermal waters is groundwater that is heated by the Earth's crust. This is due to arsenic's ability to bind and form large concentrations in igneous, metamorphic, and sedimentary rocks. According to Welch et al., (1988), "geothermal water generally has a higher arsenic concentration than non-thermal ground water with the highest concentrations found in brines, such as those found in the Salton Sea." However, it is still not fully understood why arsenic is released into the groundwater in some places more than others.

Areas such as Victorville and Lake Elsinore, California also have problems with arsenic in the groundwater.

Background on the Location of Study

The project areas are located in the cities of Mecca and Thermal in California. According to the City of Coachella website, the 2009 racial and ethnic demographic is roughly 96% Hispanic, 3% White, and 1% other with a population of approximately 41,000 people (Figure 1.).Most of the Hispanic residents are undocumented low income agricultural workers. Coachella is also known as the "City of Eternal Sunshine" and is located in the easternmost city in the region collectively known as the Coachella Valley (or the Palm Springs area). It is located 28 miles east of Palm Springs, 72 miles east of Riverside, and 130 miles east of Los Angeles.

The study will be focused on rural and low income areas. The locations that the samples were taken are in the mobile home parks shown in (Figure 2.). Many residents live in substandard trailers in mobile home parks with limited infrastructure for safe drinking water, wastewater systems, paved roads, sidewalks and storm water drainage (London and Zagofsky, 2013). Some of the mobile home park's water supply were maintained by the city's water department, while some others were not. The study focused on the water taken from residential faucets in homes to determine whether the water was below the EPA arsenic standards. The mobile home parks visited were the Rancho Garcia

Mobile Home Park, Sunbird Mobile Home Park, D&D Oasis Mobile Home Park, and the St. Anthony Mobile Home Park.

According to a 2006 California State-funded economic survey provided by Rural Community Assistance Corporation, Coachella ranks the third lowest in average personal income for any California city. These tough economic conditions make it difficult for public drinking water systems in Coachella to comply with Federal, State, or local regulatory requirements. Many systems are not regulated or permitted. The majority of the residents that live under these conditions are also constrained with language barriers and legal status, limiting their ability to fight these problems. Forcing many families to do their best and live under these circumstances.

To summarize, arsenic in drinking water is a global problem, with contamination stemming from both anthropogenic pollution and naturally elevated arsenic concentrations in some aquifers. Many rural areas of Inland Southern California have naturally elevated levels of As in the groundwater that often exceeding the maximum contaminant level allowable in drinking water of 10 ppb. There is a need to cost-effectively remove arsenic from drinking water for residents of rural areas, especially in low-income agricultural areas where residents are dependent upon well water for their drinking water supply.

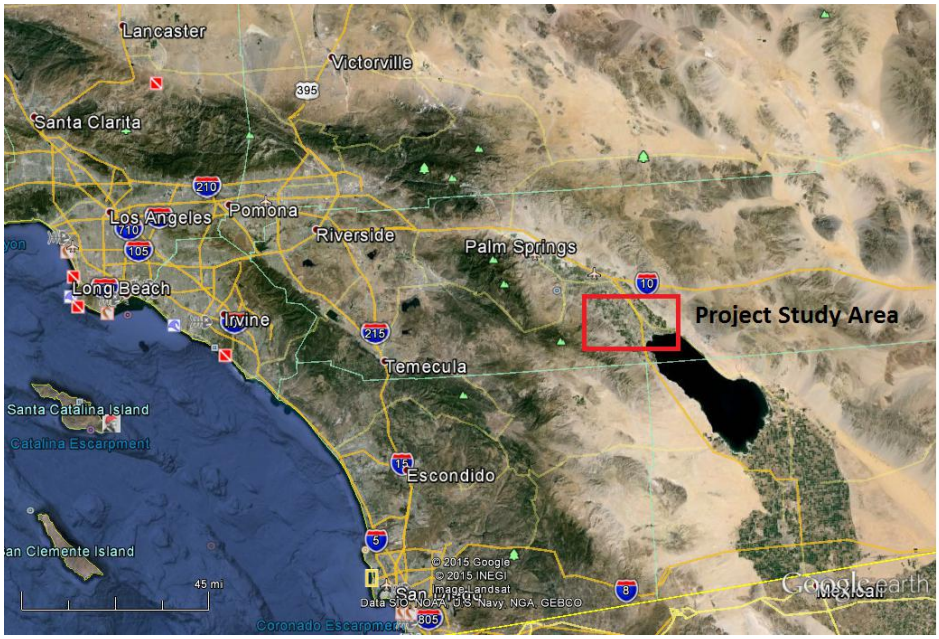


Figure 1. Project Study Area
Map created by C. Do from Google Earth

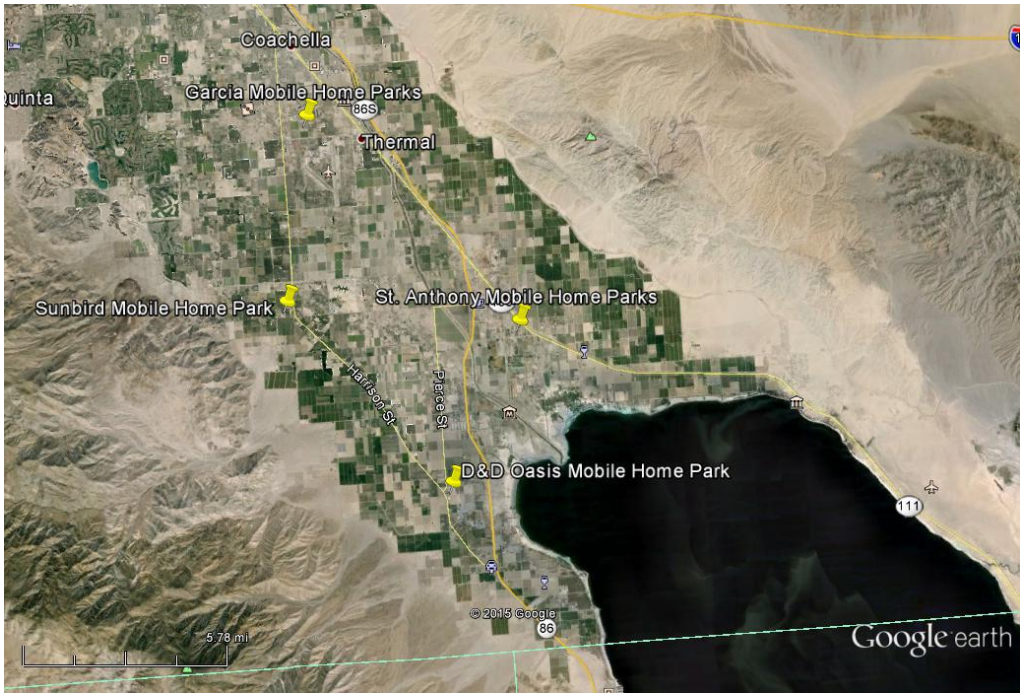


Figure 2. Study Area Sampling Location Map
Map created by C. Do from Google Earth

The SONO Filter

To help address the serious public health problem arsenic poses in Bangladesh and other developing countries, the National Academy of Engineering held an engineering contest in 2007 to find a sustainable and economical water treatment system for arsenic contaminated groundwater. The winner of the system was rewarded with $1,000,000 funded by The Grainger Foundation. However, there were stipulations to the contest, which the inventor must follow. The system had to be robust, affordable, socially acceptable, environmentally friendly, and easy to maintain. Dr. Abul Hussam and his team won the prize with their invention the SONO filter. The filter has been produced and used in Bangladesh to filter out the arsenic. At the time, this filter was called the SONO filter which met WHO and Bangladesh water standards, had no breakthroughs and worked without any pre or post chemical treatment (Hussam and Munir, 2007).

The SONO filter is comprised of a two bucket system. The top bucket contains a composite iron matrix (CIM) that is sandwiched between two coarse river sand layers. The CIM is used as the primary source for the removal of arsenic due to the complexation and immobilization of the inorganic arsenic as well as many toxic metal cations. The CIM is manufactured from various iron turnings obtained from machine shops and are washed, dried, and treated with food grade acids (Hussam and Munir, 2007). The coarse river sand is obtained from local rivers and thoroughly washed before use in Bangladesh. They are

used as an inactive material used to filter out coarse particulates and as a flow stabilizer. The coarse river sand has another important function which is the removal of soluble iron (Hussam and Munir, 2007).

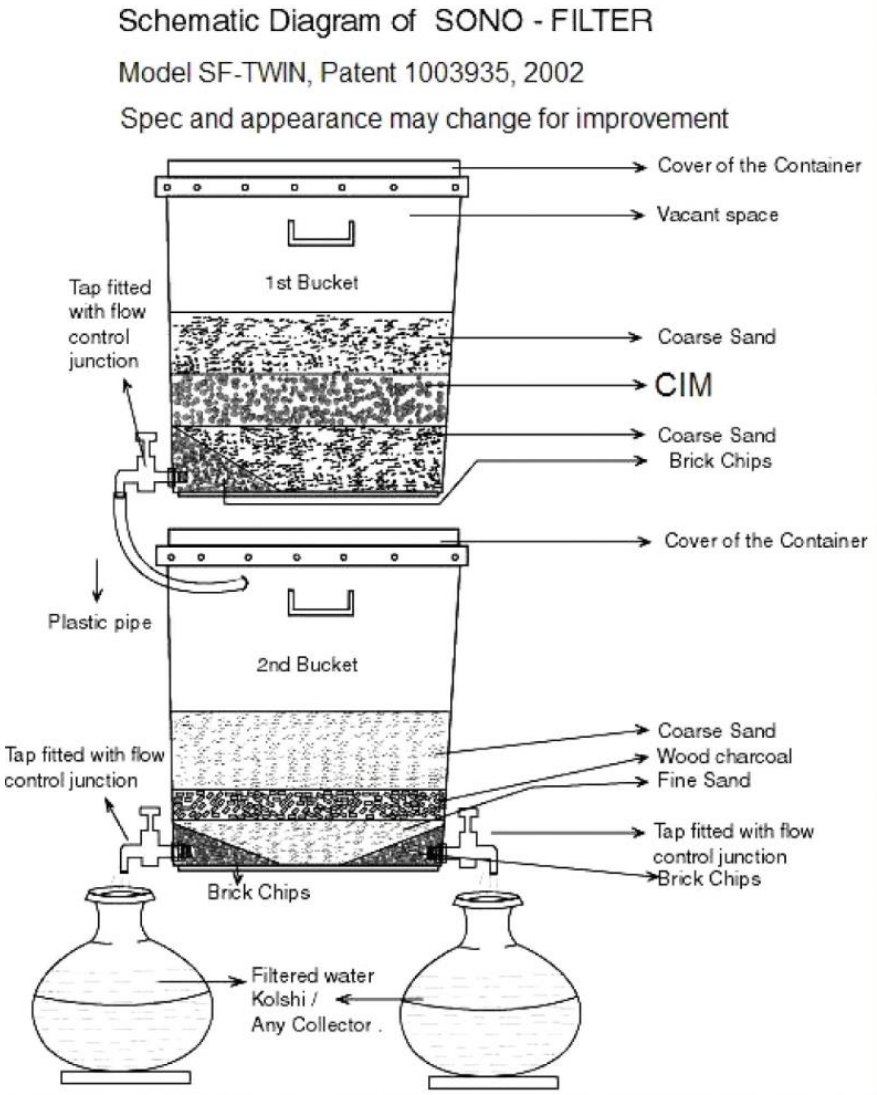


Figure 3. Schematic Diagram of SONO Filter
Source: Hussam, A and Munir, A. A Simple and Effective Arsenic Filter Based on Composite Iron Matrix: Development and Deployment Studies for Groundwater of Bangladesh. *Journal of Environmental Science and Health, Part A* 42.12, **2007**, 1869-878.

The soluble iron becomes oxidized on this media and forms a precipitate. The bottom of the bucket contains a layer of coarse river sand, wood charcoal, fine river sand, and some brick chips. The second bucket is used to clean the water from the top bucket; removing residual iron from the CIM and impurities from the first bucket. The water is then released from a tap that is attached to the second bucket providing drinking water that is within safe drinking limits of arsenic. The “sandwich” of sand layers facilitates compaction, controls flow dispersion, control pore formation, and reduces the production of fine particles. Thus, this configuration has a low probability of clogging and a high probability of long lasting field use without compensating water quality (Hussam et al., 2008).

Arsenate and arsenites form bidentate complexes with =FeOH, =FeOOH, or HFO (hydrous ferric oxide). The arsenate then gets tightly bounded on the iron surface of the composite iron matrix, which removes the arsenic. In order for this filter to function properly inorganic As (III) are oxidized to As (V) by active O_2^-, produced by oxidation of soluble Fe (II) with dissolved oxygen. The Manganese in the CIM also is another process used to oxidize As (III) to As (V). The As (V) species are then removed by surface complexation reactions on the hydrated iron (=FeOH) (Hussam and Munir, 2007).

The research showed the typical test results in which 25,000 L of tube well water containing 1139-1600 µg/L of arsenic was filtered in the SONO filter was able to produce potable drinking water within the range of 2-14 ppb. Not only does the SONO filter remove the toxic arsenic from the groundwater, but it also

removes manganese, which is also a toxic metal in Bangladesh groundwater. Both metals were removed without any chemical treatment.

Purpose of the Study

The purpose of this study was to help reduce arsenic in groundwater in rural areas that are known to have arsenic levels above the MCL standard of 10 parts per billion regulated by the United States Environmental Protection Agency (USEPA). The proposed research was to identify and test a sorbent phase that could be used in a modified filter similar to the SONO filter system discussed above that could help reduce the arsenic levels in drinking water through adsorption.

On September 5, 2012, four different location sites around the city of Thermal and Mecca were investigated. Samples were collected from these sites, which were residential mobile home trailer parks to determine if there were high levels of arsenic in the water.

The results from this study can help produce a possible economical and effective method on reducing arsenic in economically poor and rural areas that have elevated levels of arsenic in groundwater. This project will focus on the removal of arsenic from groundwater with the use of iron oxide hydroxides.

CHAPTER TWO

METHODS AND MATERIALS

Field Site Investigation

Four different location sites near the city of Thermal were investigated in a one day period on September 5, 2012. These sites were residential mobile home trailer parks. The water samples were collected through two procedures. One method was collecting the sample in a 1-liter high density polyethylene (HDPE) bottle from an outdoor faucet and the other procedure was to ask a resident to fill the 1-liter HDPE bottle from their home faucet. The samples were placed in an ice chest and packed on ice until returned to the laboratory. Samples were then taken stored at 4 ºC until analysis.

The first location was located on the property of Garcia Mobile Home Park located in the city of Thermal, CA in the East Coachella Valley. The water sample was collected by using an outdoor faucet and the sample was collected in a HDPE bottle and placed on ice in an ice chest. The second water sample location was at the Sunbird Mobile Home Park located in the city of Thermal, CA. The water sample collected from this location required asking permission from a resident to fill up the 1-liter bottle to the top from their indoor sink faucet. The water sample was placed on ice in an ice chest. The third location was D&D Oasis Mobile Home Park located in Thermal, CA. The water sample was taken from an abandoned water pump in a fenced off part of the property. The water

sample was collected in a 1-liter HDPE bottle and placed in ice. The final location was located at the St. Anthony Mobile Home Park in Thermal, California. Two samples were obtained at this location. One sample was collected through a faucet attached to a reverse osmosis pump into a 1-liter HDPE bottle and the other sample was taken from a resident's trailer faucet with permission from the resident. Both samples were placed on ice in an ice chest.

Table 1. Summarization of Field Samples

Location	Location ID	Samples Collected By
Garcia Mobile Home Park	Location 1	Outdoor Faucet
Sunbird Mobile Home Park	Location 2	Resident filling HDPE bottle from indoor faucet
D&D Mobile Home Park	Location 3	Abandoned Water Pump from property
St. Anthony Mobile Home Park	Location 4A	Reverse Osmosis Pump
St. Anthony Mobile Home Park	Location 4B	Resident filling HDPE bottle from indoor faucet.

Analytical Methods

All water samples in this study were analyzed using the appropriate procedures described un EPA Method 200.9, revision 2.2 (1994), “Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption.” All samples were prepared using the acid digestion procedure for Total Recoverable Analysis described in Method 200.9. All prepared water samples were analyzed on a Perkin Elmer AAnalyst 600 Graphite Furnace Atomic Absorption Spectrometer (GFAA). A Perkin Elmer (PE) electrodeless discharge lamp (EDL) was used for all analyses (at 193.7 nm). Instrument parameters were set at the PE recommended values for arsenic analysis. Magnesium and Palladium matrix modifiers were purchased from Perkin Elmer.

Standards Solution Preparation

A 1000 ppm (parts per million) arsenic stock solution was made first by dissolving 0.6608 grams of arsenous oxide (As_2O_3) in 50 mL of Barnstead water (i.e., ultrapure deionized) along with 5 mL of concentrated ammonium hydroxide (NH_4OH) in a 100 mL glass beaker. The solution was gently warmed to effect dissolution. The solution was then acidified with 10 mL of concentrated nitric acid (HNO_3). The solution was then poured into a 500 mL glass bottle and diluted to a volume of 500 mL. Due to the high concentration of the stock arsenic solution an intermediate arsenic stock solution had to be made. A 1 ppm intermediate stock solution was produced by taking 100 µL of the 1000 ppm arsenic stock solution

and pipetting it into a 100 mL volumetric flask and diluting the solution to a volume of 100 mL with Barnstead water. A set of seven standards were produced with concentrations of 2.5 ppb (parts per billion), 5.0 ppb, 10 ppb, 25 ppb, 50 ppb, 100 ppb and 200 ppb. The 2.5 ppb standard was made by pipetting 250 µL of the intermediate stock solution into a 100 mL volumetric flask and diluting the solution to a volume of 100 mL. The 5.0 ppb standard was made by pipetting 500 µL of the intermediate stock solution into a 100 mL volumetric flask and diluting the solution to a volume of 100 mL. The 1.0 ppb standard was made by pipetting 1.0 mL of the intermediate stock solution into a 100 mL volumetric flask and diluting the solution to a volume of 100 mL. The 25 ppb standard was made by pipetting 2.5 mL of the intermediate stock solution into a 100 mL volumetric flask and diluting the solution to a volume of 100 mL. The 50 ppb standard was made by pipetting 5 mL of the intermediate stock solution into a 100 mL volumetric flask and diluting the solution to a volume of 100 mL. The 100 ppb standard was made by pipetting 10 mL of the intermediate stock solution into a 100 mL volumetric flask and diluting the solution to a volume of 100 mL. The 200 ppb standard was made by pipetting 20 mL of the intermediate stock solution into a 100 mL volumetric flask and diluting the solution to a volume of 100 mL. All of the standards were acidified with 200 µL of concentrated nitric acid. Matrix modifiers used were a 1000 ppm magnesium nitrate solution and a 1000 ppm palladium solution were produced by dilution of the 10,000 ppm

solution from PE. The calibration standards and all samples were analyzed in duplicate and the results were averaged.

Preliminary Testing of Sorbent

An experimental filter apparatus was set up as shown in Figure 4, to test the general ability of Pura Phoslock to remove arsenic from water. The filter was made in a layer system to slow the flow of the water through the system, retain the sorbent, and filter the eluate. From bottom to top, the filter was comprised of a 90 mm Whatman GF/F pure glass fiber filter (0.7 μm, acid washed), about 50 grams of Pura Phoslock (β-FeOOH), a layer of glass wool, and a layer of acid washed glass beads (~3 mm in diameter) to keep the layers slightly compressed and in place during the filtration process.



Figure 4. The Experimental Filter Used to Test the Sorbent

A preliminary test for the sorbent was done by preparing ten individual liters of 50 ppb arsenic-spiked tap water and filtering it. The arsenic standards were prepared exactly the same as described before. The 1-liter of arsenic water solution was made by first preparing a 1000 ppm arsenic stock solution. The 1000 ppm arsenic stock solution was prepared the same as before. 50 µL of the stock solution was pipetted into a 1000 mL volumetric flask. Tap water was added to the flask until it reached the 1000 mL mark on the flask. The arsenic-spiked tap water from 10 samples was allowed to flow through the filter apparatus in one liter increments. A flow of one liter per hour of the arsenic spiked water was controlled by the valve of a separatory funnel (Figure 5). The water sample being poured into the filter was added at this rate to cover the top of the acid washed beads. This was done to keep enough water in the filter to prevent the inside of the filter to dry. The filtrate was collected and a 25 mL aliquot from each liter of filtrate was collected and digested with 0.5 mL of 1:1 nitric acid. The standards and the collected filtrate water aliquots were then analyzed by GFAA. The experiment resulted in no detectable arsenic (<~1 ppb) in the collected filtered water.

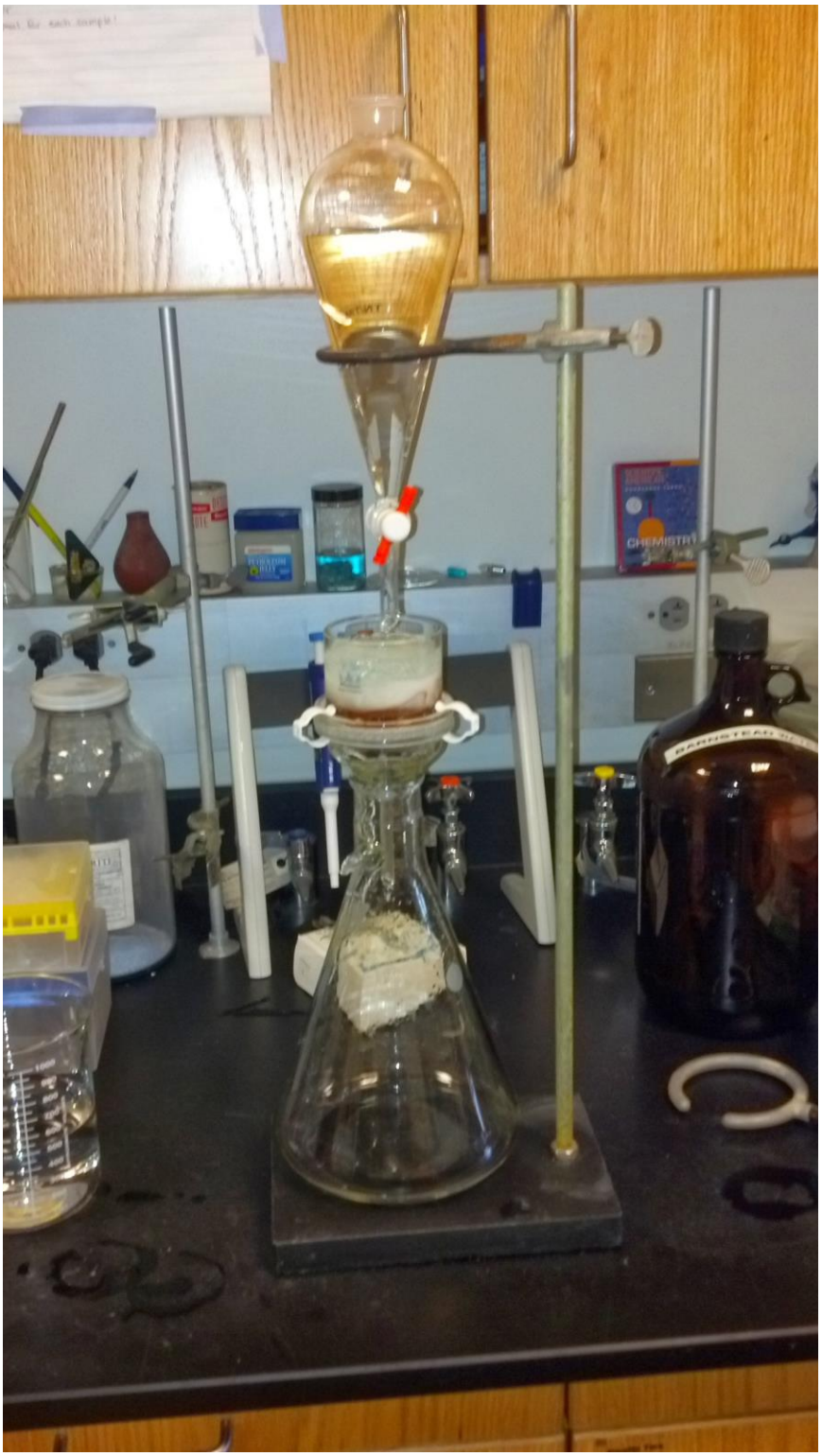


Figure 5. Flow Control of Spiked Water into Filter

Equilibrium Time Study

An equilibration time study was performed to determine the length of time required for the sorption process to reach equilibrium and the concentrations of As in the water sorbent to reach constant values. Six solutions were prepared in acid-washed, I-Chem tall cylindrical 500 ml HDPE bottles, with Teflon-lined caps. One bottle was 500 mL of a 100 ppb As solution with no iron oxide hydroxide sorbent. Four bottles were prepared with 500 mL of 100 ppb As solution with 0.5 grams iron oxide hydroxide. The last solution was a blank, which just consisted of tap water and no sorbent. The 100 ppb As solutions were made by spiking 50 µL of the arsenic stock into 500 mL of tap water. The solutions were then placed on a Wheaton compact 3- deck roller system and rolled slowly for different time intervals of 1, 3, 5, and 7 hours. After the removal of solution from each time interval the solutions were filtered through Whatman GF/F acid washed pure glass fiber filters to remove any colloidal sorbent particles. The filtered solutions were analyzed by GFAA.

Sorption Study to Evaluate Sorbent Properties

Another sorption study was performed by changing the concentration of the arsenic solutions, but with the same amount of adsorbent. The concentrations were 20, 50, 100, 200, 300, 400, and 500 ppb As with 0.5 grams of the adsorbent. The 20 and 50 ppb samples produced dissolved As concentrations below the detection limit (< 1 ppb). So one additional solution was

made at 50 ppb As with a reduced mass of 0.25 grams of the sorbent. The solutions were all left on the roller for 12 hours; thereafter all were filtered, digested and analyzed by GFAA. All samples were filtered using Whatman 47 mm GF/F pure glass filters (0.7 mm, pre-acid washed).

The data obtained from this study was analyzed using the Langmuir Adsorption Model, and the maximum adsorption capacity of the sorbent was calculated. The Langmuir Sorption Model was used because the model is based on the assumption that the adsorbent (PhosLock) surface has a specific number of sites that are capable of binding the adsorbates ($As0_3^{3-}$ or $As0_4^{3-}$), all of the binding sites are assumed to be equivalent, and adsorption is limited to a monolayer of coverage. Moreover, the Langmuir is well-known to accurately describe the binding of ionic species to mineral surfaces.

The Langmuir equation is

$$\frac{C_S}{C_{aq}} = \frac{bC_{sm}}{1+C_{aq}b}$$

C_s= quantity adsorbed by sorbent at equilibrium with C_{aq}, millimoles g^{-1}

C_{aq}= equilibrium aqueous solution concentration, millimoles L^{-1}

C_{sm}= maximum quantity adsorbable per millimoles g^{-1}

b= binding constant per L mol^{-1}

What this equation means is that C_s reaches C_{sm} when all available binding sites have been occupied. This model allows for quick testing and understanding on

the sorption property of the PhosLock. A more useful linearized form of the relation can be obtained from algebraic manipulation to

$$\frac{1}{C_s} = \frac{1}{C_{sm}} + \frac{1}{bC_{aq}C_{sm}}$$

In this form, it is evident that a plot of $1/C_{sm}$ versus $1/C_{aq}$ will give a straight line with a slope of $1/bC_{sm}$ and an intercept of $1/C_{sm}$.

Column Flow Breakthrough Study

A final experiment was performed to test the actual As adsorbing capacity of the sorbent under flowing water conditions as would be the case in an real filter application. About 0.5 g of the PhosLock sorbent was placed in a 250mm x 13 mm glass chromatography column with a 200 mL reservoir. Water was then added to the column and allowed to filter through the sorbent at an ~ 15 mL /min flow rate. A sample was collected for analysis after each 500 mL had been filtered through the column. A total of 22 samples were collected for analysis for a total volume of 10.6 L filtered through the column. The data obtained from this experiment were compared to the theoretical predictions obtained from the Langmuir model, and used to estimate the overall effectiveness of the PhosLock for use in an As removal filtration system.

CHAPTER THREE

RESULTS

Field Sample Results

Four locations were sampled for this project. Some samples were taken from a residential sink faucet and others were taken from an outdoor faucet. The samples were then analyzed by graphite atomic absorption. The table below lists the concentrations of the arsenic standards produced and of arsenic in the water collected after being analyzed in the graphite furnace.

Table 2. Example Calibration Data for Arsenic Standards

Calibration Standard ID	Mean Signal (Abs)	Entered Conc. (µg/L)	Calculated Conc. (µg/L)	Standard Deviation	%RSD
Calibration Blank Standard	0	0	ND	0	20.6
Calibration Standard 1	0.0188	2.5	2.097	0	4.4
Calibration Standard 2	0.0299	5	5.469	0	0.8
Calibration Standard 3	0.0516	10	12.077	0.01	12
Calibration Standard 4	0.0966	25	25.767	0.02	16
Calibration Standard 5	0.1704	50	48.194	0	0.6
Calibration Standard 6	0.3557	100	104.54	0.03	7.1
Calibration Standard 7	0.6630	200	197.98	0.06	9.1
Correlation Coefficient	0.9993				
Slope	0.0033				
Intercept	0.0119				

Table 2 shows the data for the prepared standard solutions were analyzed and calibrated by the graphite furnace. The calculated standard concentrations were very close to the prepared concentrations. The standard deviations were low with the highest at 0.06 ppb. This resulted in a positive correlation coefficient of 0.999. The relative standard deviation ranged from 0.6% to 20.6%.

Table 3. Field Sample Data from Calibrated Arsenic Standard

Sample Location ID	Mean Signal (Abs)	Mean Sample Concentration (µg/L)	Standard Deviation	%RSD
Location 1	0.0502	11.65	0.0031	6.25
Location 2	0.0087	< 1	0.0082	93.74
Location 3	0.2326	67.1	1.228	1.83
Location 4A	0.0024	< 1	0.0007	28.49
Location 4B	0.111	30.12	0.0051	4.62

The analysis showed that only two of the five locations were below the U.S. E.P.A safe drinking water limit or maximum contaminant level of 10 ppb. Locations 1, 3, and 4B had an arsenic concentration greater than the MCL. Location 1 was taken from a water faucet outside of the trailer park. Location 3 was taken from an abandoned water pump that is no longer in service. Location 4B was taken from an indoor water faucet. Sample 4A was taken from the single

common outdoor faucet of the reverse osmosis treatment system installed at St. Anthony's trailer park. The < 1 ppb ("not detected," ND) results shows that the RO system is effectively removing As from the water. Although inconvenient, this RO system is providing As-free drinking water for the residents.

Adsorption of Arsenic to β-Iron Oxide Hydroxide

The results of the equilibrium time study are given in Table 4 and show the concentration of dissolved As in contact with the sorbent as a function of time. Initially, the concentration of arsenic greatly decreases over time when exposed to the β-iron oxide hydroxide. However, here is little further reduction in dissolved arsenic from five to seven hours, and the system apparently reached equilibrium after about seven hours (Figure 6).

Table 4. Arsenic Equilibrium Time Study

Time (hrs)	Dissolved As (ppb)
0	107
1	74.62
3	43.16
5	21.92
7	18.6

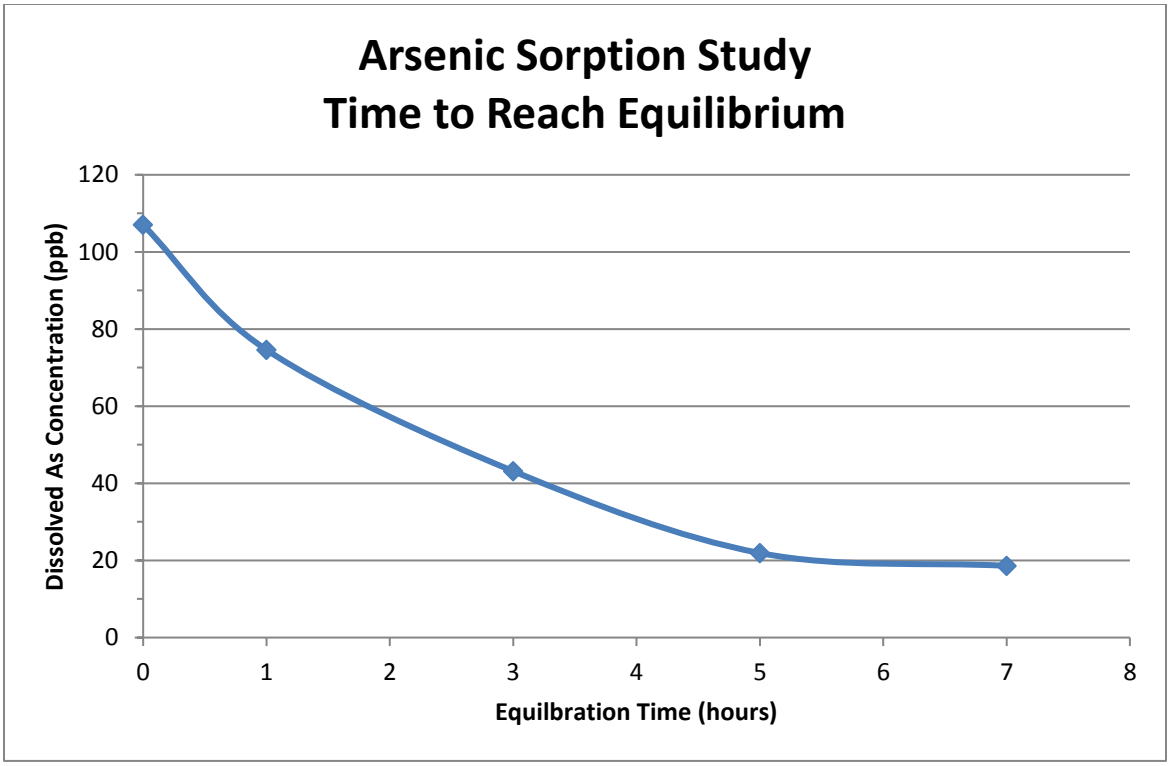


Figure 6. Arsenic Time to Equilibrium Study Graph

The results of the equilibrium sorption study are shown in Table 5. The C_{aq}' and C_s' are the aqueous and sorbent As concentrations calculated on a mass basis (mg/L and mg/g, respectively) directly from the analytical data. The C_{aq} and the C_s are the aqueous and sorbent concentrations converted to a millimolar basis (mmol/L and mmol/g) for use in the Langmuir analysis. The Langmuir model was plotted in Figure 7 using the data from Table 5 to show that adsorption continues until it reaches equilibrium.

Table 5. Sorption Study Analytical Results and Langmuir Model Calculated Data

Spike Conc.	Water	Sorbent	C_{aq}'	C_s'	C_{aq}	C_s	$1/C_{aq}$	$1/C_s$
ug/L	Vol. (mL)	Mass (g)	ug/L	ug/g	mmol/L	mmol/g	L/mmol	g/mmol
50	500	0.25	4.95	90.10	6.60E-05	1.20E-03	15141	831
100	500	0.50	3.64	96.36	4.86E-05	1.29E-03	20577	778
200	500	0.50	11.52	188.48	1.54E-04	2.52E-03	6503	397
300	500	0.50	19.19	280.81	2.56E-04	3.75E-03	3904	267
400	500	0.50	50.20	349.80	6.70E-04	4.67E-03	1492	214
500	500	0.50	74.29	425.71	9.92E-04	5.68E-03	1008	176

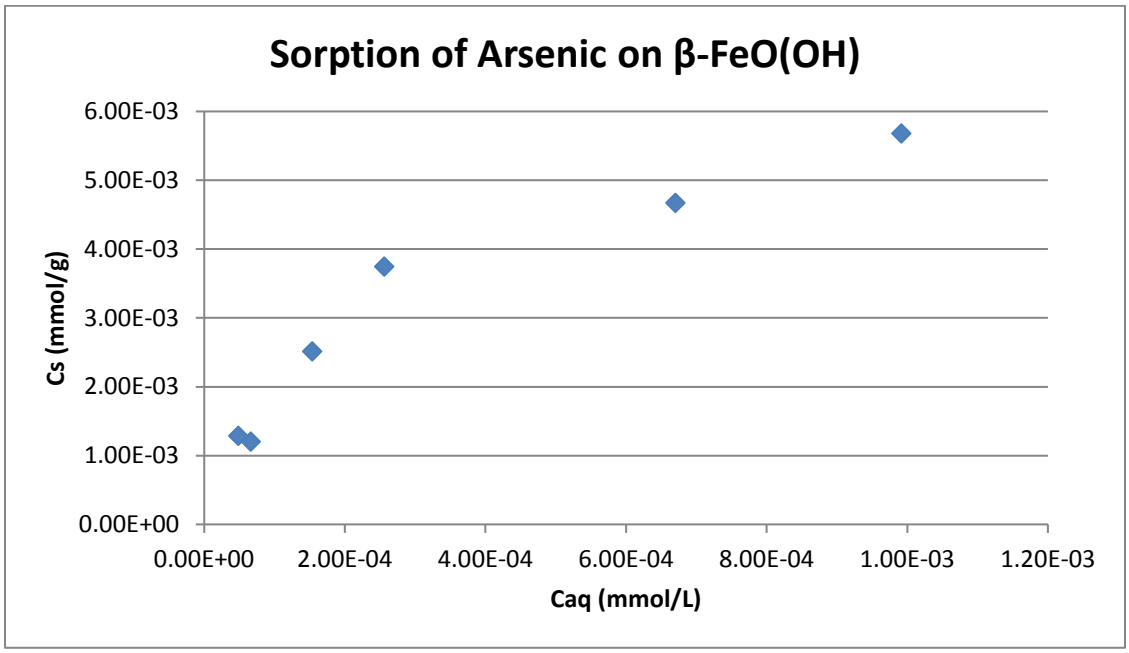


Figure 7. Equilibrium Sorption Data for Arsenic on β-FeO(OH)

In Figure 8, by using the linearized Langmuir model to plot a single linear line, the y-intercept is used to determine the maximum concentration that can be adsorbed (C_{sm}) which is when all the binding sites are occupied, which was 0.0062 mmol/g. Calculations for C_{sm} can be seen in Appendix A.

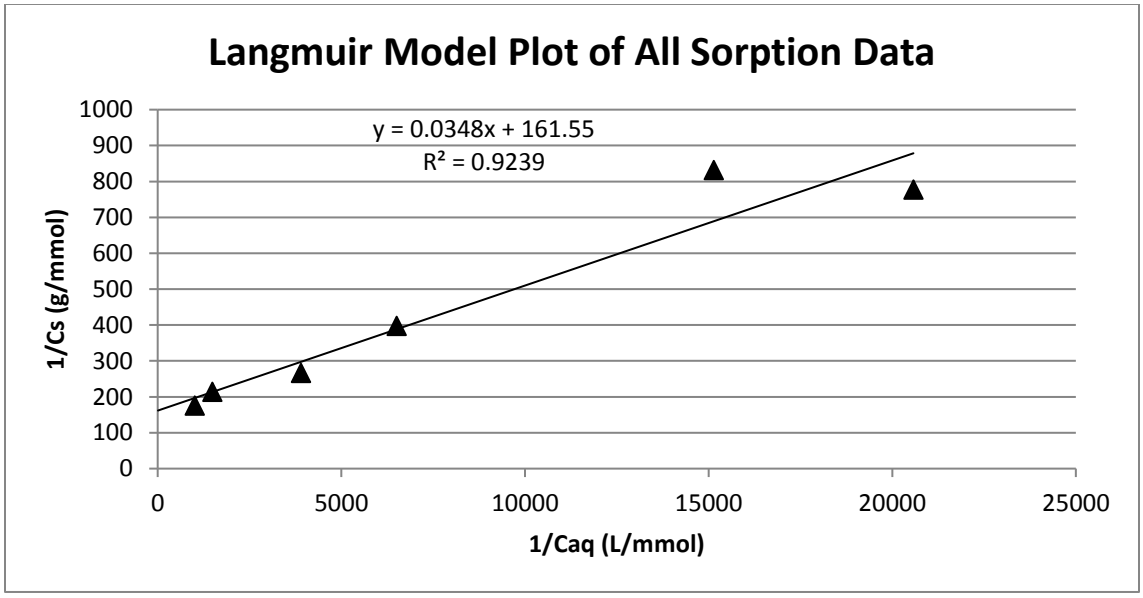


Figure 8. Langmuir Model Plot of All Sorption Data

Another Langmuir model plot in Figure 9, explores the possibility of two alternative interpretations of the experimental results. Better linear relationships can be obtained by either omitting the data for the 50 ppb sample or the 100 ppb sample. The resulting lines give better correlations and different resulting C_{sm} values. The results of the Langmuir model analysis are given in Table 6.

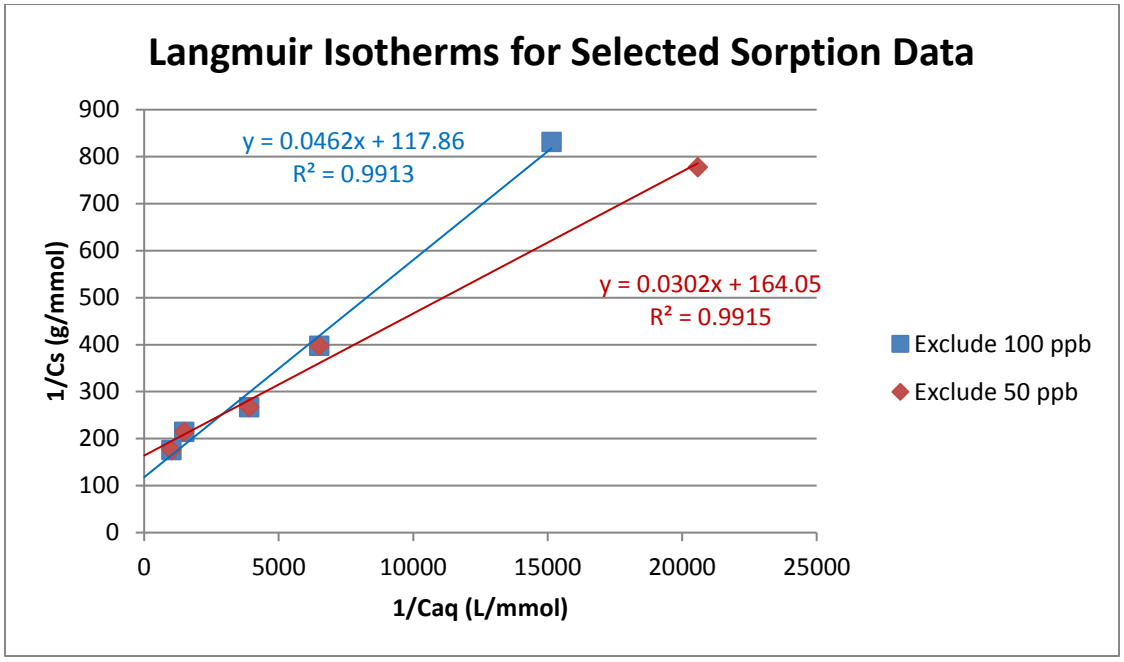


Figure 9. Langmuir Model Plot for Selected Sorption Data

Table 6. Results of the Langmuir Sorption Study

Data	$1/C_{sm}$	C_{sm} (mmol/g)	b	Max As (μg/g)
ALL	161.55	0.0062	4642	464
exclude 50 ppb	164.05	0.0061	5432	457
exclude 100 ppb	117.86	0.0085	2551	636

The results from the As sorption breakthrough study are given in Table 7. The results from Table 7 indicates that about 7 liters of water spiked at 50 ppb was passed through 0.5 grams of sorbent in a column before any detectable arsenic was detected in the water. Moreover, it took more than 10 L of As spiked water to exceed the MCL of 10 ppb and can be seen in Figure 10. This

corresponds to an adsorptive capacity of about 700 μg As /g sorbent. This is slightly above the adsorption maximum predicted by the Langmuir model (636 μg/g). Thus, in a realistic flowing water (15 mL/min or about 1 L per hour) filtration application, one pound of PhosLock could remove the As (at 50 ppb) from over 6000 L of water, which corresponds to about 16 L per day for a whole year.

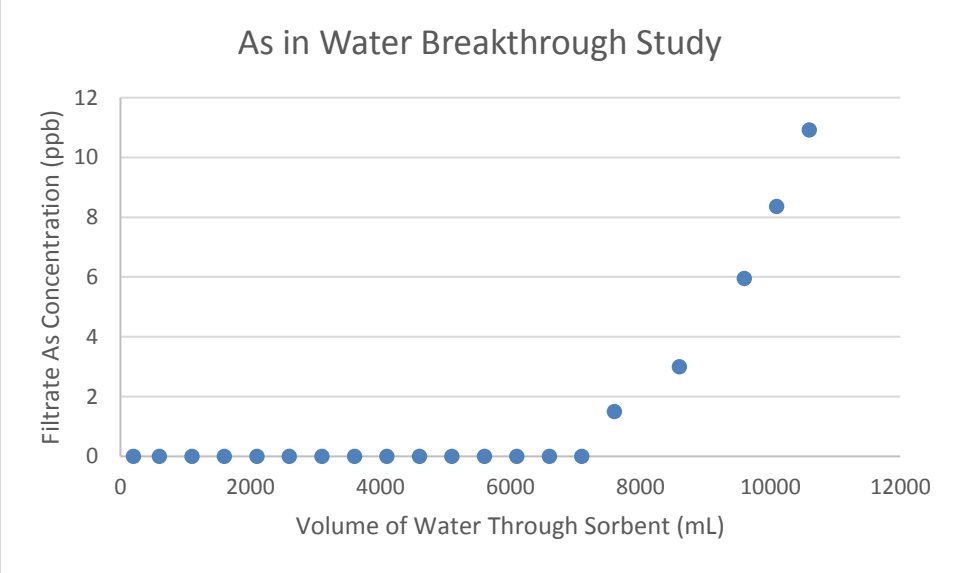


Figure 10. Arsenic in Water Breakthrough Study Graph

Table 7. Arsenic Breakthrough Study Data

Sample No.	All Volume (mL)	All Conc (ug/L)	Used Volume (mL)	Used Conc (ug/L)
A	200	0	200	0
B	600	0	600	0
1	1100	0	1100	0
2	1600	0	1600	0
3	2100	0	2100	0
4	2600	0	2600	0
5	3100	0	3100	0
6	3600	0	3600	0
7	4100	0	4100	0
8	4600	0	4600	0
9	5100	0	5100	0
10	5600	0	5600	0
11	6100	0	6100	0
12	6600	0	6600	0
13	7100	0	7100	0
14	7600	1.5	7600	1.5
15*	8100	3.47	8600	2.995
16	8600	2.995	9600	5.955
17*	9100	2.708	10100	8.355
18	9600	5.955	10600	10.92
19	10100	8.355		
20	10600	10.92		

* Questionable data, poor precision on replicate analyses

CHAPTER FOUR

DISCUSSION

The U.S. EPA does have methods on the removal of arsenic in groundwater, which includes: ion exchange and coagulation filtration and iron removal. These methods are very similar to the method on removing arsenic as the SONO filter. The coagulation filtration method is a precipitative process that uses iron complexation to help remove arsenic. In the process the As (III) is oxidized to As (V) by Cl_2. A coagulant ($FeCl_3$) is added to As (V) to form As (V)-Fe (OH_3). The arsenic-iron complex is then filtered out of the water (Environmental Protection Agency, 2012). The second method is ion exchange which is a physical chemical process in which ions are swapped between a solution phase and solid resin phase. If As (III) is present, it must be oxidized to As (V) in order for ion exchange to be effective (Environmental Protection Agency, 2012). Arsenic removal is accomplished by continuously passing water under pressure through one or more columns packed with strong-base anion (SBA) exchange resin. Anion exchange resins also remove other anions such as sulfate and nitrate. When the resin becomes saturated with arsenate and other anions, it must be regenerated. In the regeneration step, sodium chloride brine is flushed through the resin where the adsorbed arsenate and other anions are replaced with chloride ions (Environmental Protection Agency, 2012).

The methods used by the U.S. EPA are effective in large systems, but for small water systems such as the St. Anthony mobile home park it would not be beneficial to the property. The issue associated with the coagulation filtration system is that it costs a lot of money to maintain. The maintenance of the system requires well trained operators to operate the system. Another dilemma is the disposal of waste. The waste is released as a sludge that may use mechanical or non-mechanical techniques to be properly disposed. As for the ion exchange issues, the resin plays a significant importance on the removal of arsenic. Efficiency of the anion exchange process for As (V) removal depends strongly on the concentration of other anions, most notably sulfates and nitrates. These sulfates and nitrates and other anions compete for sites on the exchange resin. This means that other anions can take up space on the resin, which may not remove the arsenic effectively. The resin, in this case will have to be regenerated in order to work effectively again.

The results of this study show that Pura PhosLock is a viable sorbent for the removal of As in drinking water. It is commercially available and cost effective It could be used in small personal filtration systems (e.g., like a Britta Filter) by residents in rural areas. A one pound jar of PhosLock currently costs around $30 with shipping on Amazon.com. This would be sufficient to remove the arsenic at a concentration of 50 ppb in over 6000 liters of water, which would be about 16 liters a day for one year.

CHAPTER FIVE

CONCLUSION

Five sample locations were collected to analyze the concentration of arsenic that residents use on a daily basis. Out of the five samples, three were detected to be higher than the MCL. The experimental sorbent and filter inspired by these locations yielded good results. The data from this study shows that the concentration of arsenic is reduced to non-detectable levels when filtered through the β-iron oxide hydroxide. Based on the results of the Langmuir model the sorbent Pura PhosLock is an economical and effective sorbent for removing arsenic from drinking water.

The Langmuir isotherm model allowed the estimation of the maximum quantity of As adsorbable which was calculated to be between 457 µg/g and 636 µg/g based on the experimental equilibrium sorption data. The results of the flowing water column breakthrough study were even more encouraging. It required 7 liters of water As-spiked at 50 ppb to be filtered through 0.5 g of sorbent before any detectable concentration of As was observed. And it took over 10 L of As-spiked water to exceed the MCL of 10 ppb. This corresponds to a adsorptive capacity of about 700 µg As /g sorbent. Thus, in a realistic flowing water (15 mL/min or about 1 L per hour) filtration application, one pound of PhosLock could remove the As (at 50 ppb) from over 6000 L of water, which corresponds to over 16 L per day for a whole year.

APPENDIX A

CALCULATIONS

Calculations for $C_{s'}$,C_{aq} and C_s at 50 ppb Spike Arsenic Concentration

C_s'= (spike concentration – C_{aq}')(volume water (L) / sorbent mass (g))

C_s'= (50 µg/L – 4.95 µg/L) (0.5 L / 0.25 g)

C_s'= 90.10 µg/g

C_{aq}= C_{aq}'(1 mg/1000 µg) (1 mmol/74.92 mg)

C_{aq}= 4.95 µg/L (1 mg/1000 µg) (1 mmol/ 74.92 mg)

C_{aq}= 6.60 x 10^{-5} mmol/L

C_s= C_s' (1 mg/1000 µg)(1 mmol/74.92 mg)

C_s= 90.10 µg/g (1 mg/1000 µg)(1 mmol/ 74.92 mg)

C_s= 1.2 x 10^{-3} mmol/g

Deriving Linearized form of the Langmuir Model to obtain C_{sm}

$$\frac{C_s}{C_{aq}} = \frac{bC_{sm}}{1 + C_{aq}b}$$

$$C_s = \frac{bC_{aq}C_{sm}}{1 + bC_{aq}}$$

$$\frac{1}{C_s} = \frac{1 + bC_{aq}}{bC_{aq}C_{sm}}$$

$$\frac{1}{C_s} = \frac{1}{bC_{aq}C_{sm}} + \frac{bC_{aq}}{bC_{aq}C_{sm}}$$

$$\frac{1}{C_s} = \frac{1}{C_{sm}} + \frac{1}{bC_{aq}C_{sm}}$$

From Plot using the most conservative data (excluding 50 ppb), the y-intercept is 164

164 = $1/C_{sm}$, so C_{sm} = 1/164 = 0.0061 mmol/g

0.0061 mmol/g * 74.92mg/mmol=0.457 mg/g * 1000 µg/mg = 457 µg/g

Volume of water at 50 ppb As that can be treated with one gram of sorbent

457 µg/g * 1L/50 µg = 9.14L

For the breakthrough study, it took 7 liters to have a detectable amount of As breakthrough the sorbent into the filtrate,

So, 7 L * 50 µg/ L = 350 mg of As that was adsorbed by 0.5 g of sorbent, so the maximum adsorptive capacity is 350 µg As/0.5 g sorbent =

700 µg As/g sorbent.

So for water contaminated at 50 µg/L, this would mean that 1 lb of PhosLock (454 g) could remove the As from

700 µg/g * 454 g * 1L/50µg = 6356 L or about 6000 L.

6000 L/365 day $year^{-1}$ = 16.5 L per day per year.

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