A Study of Removal Techniques for Arsenic Species in Landfill Gas Condensate

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Abstract

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Arsenic is a highly toxic contaminant of concern to many entities, notably for a landfill utility within King County (KC), where its high concentrations have been observed in landfill gas (LFG) condensate, a byproduct of the process of purifying landfill gas, and landfill leachate. This thesis focuses on the removal of arsenic from LFG condensate using micro-electrolysis (ME) implemented in fixed bed column and batch column reactor configurations.

The fixed bed column experiments were conducted using a 1 L clear PVC column and a 3D printed module with detachable layers made of polylactic acid (PLA). The experiments consisted of a comparison of material of adsorbent used for treatment, height of individual treatment beds, pH of LFG condensate influent, and pretreatment of LFG condensate with granular activated

carbon (GAC). These experiments showed that using either of a combination of GAC and zero valence iron (ZVI) or powder activated carbon (PAC) coated nano-ZVI resulted in a relatively high removal of arsenic within the fixed bed column, but only for a limited number of bed volumes. The pretreatment of LFG condensate using GAC had little effect on arsenic removal within fixed bed column. The fixed bed column experiments were halted in this study due to hydraulic blockages in the system albeit they may be continued at a later time.

Micro electrolysis (ME) batch column treatment examined a wide variety of operating conditions, including pH of solution, adsorbent dose and composition, counterflow gas conditions, and filtration conditions. The experiments testing adsorbent conditions cover different adsorbent concentrations, always held constant at a ratio of 2:1 Fe:C, varied adsorbent addition methods, and staggered adsorbent addition times. These experiments were conducted to determine the combination of factors that would lead to the most effective removal of arsenic. Counterflow conditions included varying the method of flow in which the counterflow gas was added and whether the flow was constant or intermittent. The other important factor being tested was the filtration method. Testing whether or not samples needed to be filtered post-treatment, during treatment, or not at all could be an important factor when determining technology treatment efficiency.

These experiments are ongoing and are in the process of being upscaled to treat more LFG condensate at once. The data showed a more effective treatment at a lower pH and a higher concentration, or dose, of adsorbent material. A flow through the solution during treatment of CO_2 gas is necessary for arsenic removal, and experiments are ongoing to determine whether N_2 is also an acceptable carrier gas for these experiments.

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on the project, I would like to thank you for your knowledge of the engineering industry and unending help.

Abbreviations

AC – Activated Carbon

As (III) – Arsenite

As (V) – Arsenate

ASARCO – American Smelting and Refining Corporation

BV – Bed Volume

CDC – Center for Disease Control

DMA – Dimethylarsinic Acid

EBCT – Empty Bed Contact Time

EPA – Environmental Protection Agency

FDA – Food and Drug Administration

GAC – Granular Activated Carbon

GHG – Greenhouse Gas

KC – King County

LFG – Landfill Gas

LFL – Landfill Leachate

LNAPL – Light Non-Aqueous Phase Liquid

LPM – Liters per minute

LRPC - Landfill Gas/Renewable Natural Gas Process Condensate

ME – Micro Electrolysis

MF – Microfiltration

MMA – Monomethylarsonic Acid

MSWLF - Municipal Solid Waste Landfill

NF – Nanofiltration

NIOSH – National Institute for Occupational Safety & Health

NZVI – Nano Zero Valent Iron

PAC – Powder Activated Carbon

RNG - Renewable Natural Gas

RO – Reverse Osmosis

SR – Sampling Round

TMA – Trimethyl Arsine Gas

TMAO – Trimethyl Arsine Oxide

UF – Ultrafiltration

WHO – World Health Organization

ZVI – Zero Valent Iron

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Introduction

Arsenic, atomic number 33, is a toxic element found in both geogenic and anthropologic sources. It is present in a variety of mineral ores, as various solutes in water, and in the gaseous phase in forms of arsines. Given the high toxicity levels of arsenic, it is important to the health of the environment and general public to develop treatment technologies and solutions to capture arsenic species with the highest efficiency possible to limit exposure.

Landfills are an important utility that keep society functioning properly; however, they can contain toxic and dangerous materials that need to be captured and treated properly. This thesis will discuss and examine possible treatment methods for arsenic species found in a landfill utility operated within KC. The two approaches used for arsenic treatment to be discussed in this thesis are based on fixed bed column experiments and micro electrolysis experiments. Both of these experiment types examine the effect of varying pH levels, volumes, contact times/absorbent dose (fixed bed/ME experiments respectively), and CO_2 counterflow levels.

The purpose of these experiments is to identify the arsenic species found within the landfill leachate and, more importantly, in landfill gas condensates, determine the most effective treatment technology for a larger scale operation, and ultimately implement, with the collaboration of our colleagues at the landfill site, and consulting companies involved on the project, such technology for pilot-scale and ultimately full-scale arsenic removal operations. In the work described in this thesis as well as in other experiments carried out by our research group, a number of As-containing samples from the KC site were received and used in assessing our treatment technologies. All told, up to 13 sampling rounds have been carried at the KC site since 2019. Since I joined the project during the middle-phase development in 2021, the

sampling rounds (SR) used in the experiments reported here are SR8 through to SR13. The ultimate goal of this thesis is to present the experimental information, as well as a general background of arsenic chemistry, pertinent to the development of novel methods to remove arsenic from very challenging matrixes. This study also reports effects of different operational parameters and other aspects of the novel treatment technologies on the effectiveness of arsenic removal.

Literature Review

Arsenic Speciation

Wherever it is present in the world, arsenic takes many chemical forms. Because of its ability to readily speciate into solids, solute, and volatile forms with varying toxicities, it poses many types of danger to humans and the environment. In its inorganic form, the main oxidation states of As are As III, primarily existing as arsenite and As V, also referred to as arsenate. In its organic forms, arsenic has a broad range of species, notably monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAO) that occur widely in the environment, and many other solutes. Lastly, in sufficiently reducing conditions, arsenic readily forms arsine gases, for instance AsH_3 and its methylated forms, leading to a potential increase in air pollution and potential health hazard for those who live near a source of arsine gas.

Arsenic has a unique ability among other heavy metals, to which class it is conventionally ascribed, despite its being a metalloid rather than a metal. In its reduced form (arsenite) that is prevalent in anoxic conditions, arsenic may become mobile in the pH range of 6.5 to 8.5, the range for most groundwater. That, with its presence in many subsurface minerals, makes it a common groundwater contaminant in many countries that use groundwater that interacts with

arsenic-bearing subsurface minerals (Smeldley and Kinniburgh 2001). Inorganic arsenic has a higher toxicity for humans than organic arsenic, making studying its environmental chemistry and treatment options a necessity. Because of this, most of the research done into arsenic removal has focused on removal techniques tailored for the removal or inorganic arsenic. According to Xuexia et al. 2008, arsenite has been reported to be 25-60 times more toxic and mobile than arsenate under most environmental conditions. For environments that are likely to be contaminated with arsenite, it is important and reasonably achievable to carry out water treatment to oxidize arsenite to arsenate.

Organic forms of arsenic, including MMA and DMA, may be less toxic and relatively less common albeit still ubiquitous in environmental systems. However, this does not mean that they can be ignored both in terms of arsenic mobility and its toxic effects. Although MMA, DMA and related methylated As species occur in groundwater and associated environments at lower concentrations than those of arsenite and arsenate solutes, they often occur in water sources affected by industrial pollution, by landfill leachates or by naturally occurring biochemical processes in soils and sediments (Smeldley and Kinninburgh 2001). In surface waters, MMA and DMA can be formed, or advected from soils and sediments, as a result of reactions of arsenic catalyzed by microorganisms. The review paper by Smeldley and Kinninburgh 2001 summarizes results of multiple studies showing that there is an increase of the MMA and DMA forms of arsenic in summer due to the larger amounts of microbial activity during this time. Mandal and Suzuki, 2002, also show that use of MMA and DMA salts as herbicides led to a reduction of these As solutes by microbes to highly volatile methylated arsines.

The formation of arsines is notably promoted in acidic and reductive environments ("CDC | Facts About Arsine" n.d.). According to the CDC, the toxicity of inorganic arsine, AsH_3, is one of the

highest among the various arsenic species. The toxic effects of AsH_3 depends on the exposure time and the concentration during the exposure. The exposure level, set in the United States at 0.05 (0.2 mg/m^3), is set by NIOSH and regulated by the CDC ("CDC | Facts About Arsine" n.d.).

Arsenic Volatilization

One of the unique properties of arsenic is the volatility of many of its reduced species, specifically inorganic arsine (AsH_3) in which the arsenic oxidation state is -3. Arsenic volatilization is also relevant for organic, typically methylated arsines. A chemical's volatilization presents a potential challenge since this can make it harder to treat, albeit several actionable options may be available as well. As was mentioned above, several organic forms of arsenic solutes, notably MMA, DMA and trimethyl arsine oxide (TMAO) are typical for many environmental systems. All these species are formed through the biomethylation of As(III) and As(V) compounds. MMA, DMA, TMAO and their reduced analogues can be deemed to be precursors of their corresponding volatile arsines, notably monomethyl arsine (CH_3AsH_2), dimethyl arsine ($(CH_3)_2AsH$) and trimethyl arsine, TMA ($(CH_3)_3As$). When designing treatment technologies, it is important to look for the environmental conditions and specific species of arsenic that are prevalent in any specific environmental system, for instance groundwater or landfill leachate, in order to apply the correct forms of treatment.

Reducing conditions in both natural and engineered combined with biological activity can promote volatilization of arsenic. Certain bacteria, such as *Staphylococcus aureus* and *Escherichia coli* have been demonstrated to volatilize arsenic under aerobic conditions. As far back as the 1800s, fungi were shown to have the capacity to transform inorganic and organic arsenic species into volatile methylarsines. People who lived in rooms with arsenic containing

wallpaper where fungi grew and produced toxic trimethyl arsine gas, had pronounced effects of arsenic poisoning (Frankenberger 2002).

The presence of vegetation and soil organic matter leads to increased microbial activity, which has been shown to increase volatilization. Cellulose addition enhances microbial activity, and addition of amino acids such as phenylamine, isoleucine, and glutamine has been shown to enhance TMA production. Redox conditions in the soil can also have a strong effect on the different speciation and volatilization of arsenic within soil samples. Lowering a soil's redox potential tends to increase As (III) production and promote the methylation of arsenic. In a study mentioned by Frankenberger 2002, low levels of oxygen were also shown to lead to the release of volatile arsenic species.

Arsenic is common in landfill leachate and (as emerging evidence demonstrates) landfill gas condensate. In the mid-1990s in the UK, landfill waste contained between 1.8-10 mg/kg of arsenic, leading to an annual flow of 31-88 tons of arsenic to landfill sites. Within landfill leachate in the UK, arsenic concentrations range from 5-15 ug/L, depending on whether the contents of the landfill contain some hazardous material. Those sites that only contain hazardous materials can contain up to 17,000 ug/L of arsenic in the waste (Zevenhoven et al. 2007). In addition to being present within landfill leachate, arsenic can also be present in landfill gas (LFG) condensate. When landfill gas is collected from wells, condensate forms and is collected for treatment before being released to the environment. This condensate can be made up an aqueous phase, organic phase, and contain heavy metal contamination. According to a study by Zhao et. al published in 2013, a preliminary test in a Pennsylvania landfill showed between 7-40 mg/L of arsenic in the LFG condensate, a much higher than acceptable level for release to the water treatment plant. According to speciation studies reported to have been performed at this

site, the arsenic species present was most likely an organic form. This was believed to be a byproduct of the weathering process of As-bearing minerals in soils and sediments (Zhao et al. 2013). The speciation of As, mentioned in a previous section, is important to understand because treatment technologies must be developed differently depending on the forms of arsenic found in any waste stream.

Landfills, Landfill Gas, and Leachate

Landfills

Landfills are locations where a city or county's trash and refuse are taken and stored. In the United States, each state deals with the material at the landfill according to that state's environmental regulations. Modern landfills need to be designed to prevent refuse from leaking into the environment and causing further environmental issues. The landfills relevant to the focus of this thesis are Municipal Solid Waste Landfills (MSWLFs). MSWLFs are designed to process everyday nonhazardous material from household waste. In 2009, there were about 1,908 MSWLFs in the continental United States ("Municipal Solid Waste Landfills" n.d.).

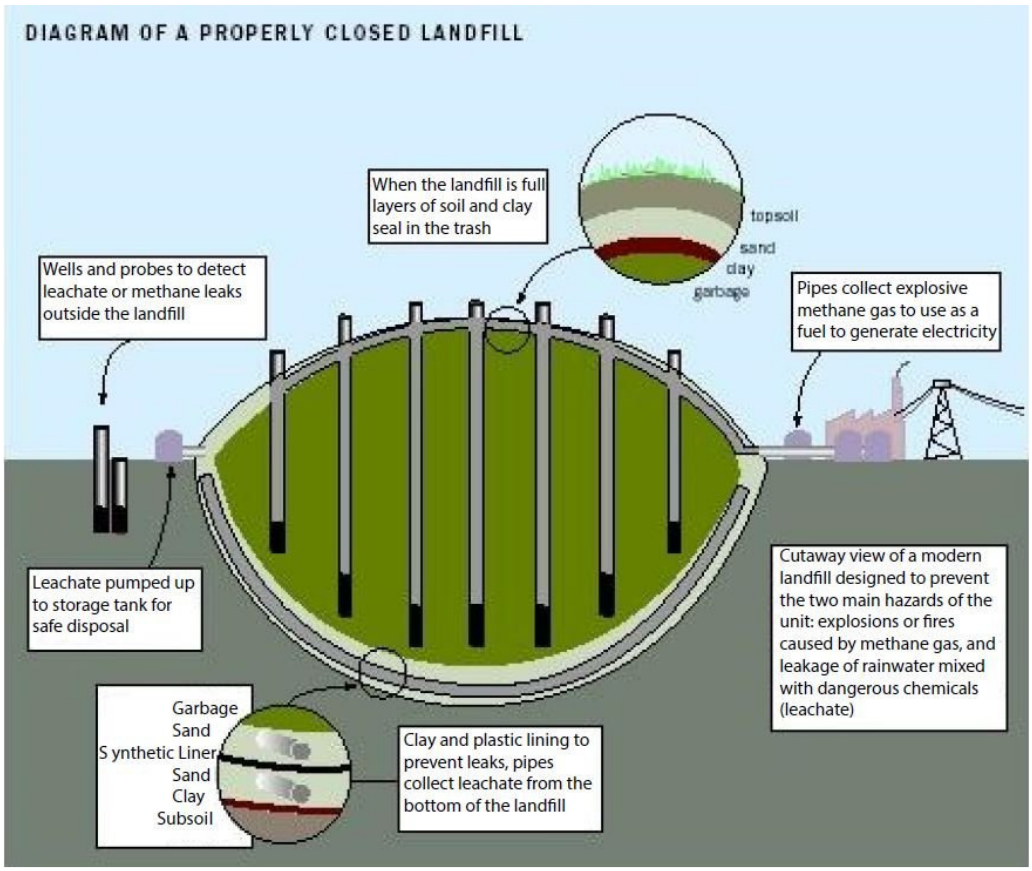

Figure 1 – Diagram of a properly closed landfill (adapted from US EPA 2021)

With the increasing temperatures and rising greenhouse gas emissions (GHG), it is becoming ever so important to monitor emissions from landfills, improve technology for recycling programs, and focus on landfill gas recovery to use the methane found in much of the solid waste we produce. According to a 2011 study that tracked GHG from the previous 25 years, active management of municipal waste locations has reduced potential GHG emissions "despite an almost 2-fold increase in waste generation" (Weitz et al. 2011). In 1997, the million metric ton carbon equivalent (MMTCE) of GHG emissions was 8, compared to 36 in 1974.

While state environmental agencies are responsible for overseeing their own landfills, there are regulations and codes implemented by the EPA, which address major components of a

successfully run MSWLF. These components include location restrictions, liner requirements, leachate collection systems, operating practices, groundwater monitoring requirements, closure and post closure care requirements, corrective action in the case of an accident, and financial assurance that funding will not be lost during the middle of a project ("Municipal Solid Waste Landfills" n.d.). Within all of these regulations are what types of materials are allowed to be brought to a municipal landfill. Many landfills exclude certain paints, oils, batteries, and household cleaners. These require hazardous waste landfill sites, however this issue will not be covered further, as it is not the focus of the thesis.

Landfill Gas

Methane gas is a ubiquitous byproduct of MSWLF operations. Approximately 50% LFG is methane (CH_4), 45% is carbon dioxide (CO_2), 5% is nitrogen (N_2), and < 1% is other non-methane organic compounds (NMOC) (Themelis and Ulloa 2006). In 2019, the EPA reported that approximately 15% of the human sourced methane emissions were from MSWLFs ("Basic Information about Landfill Gas n.d.).

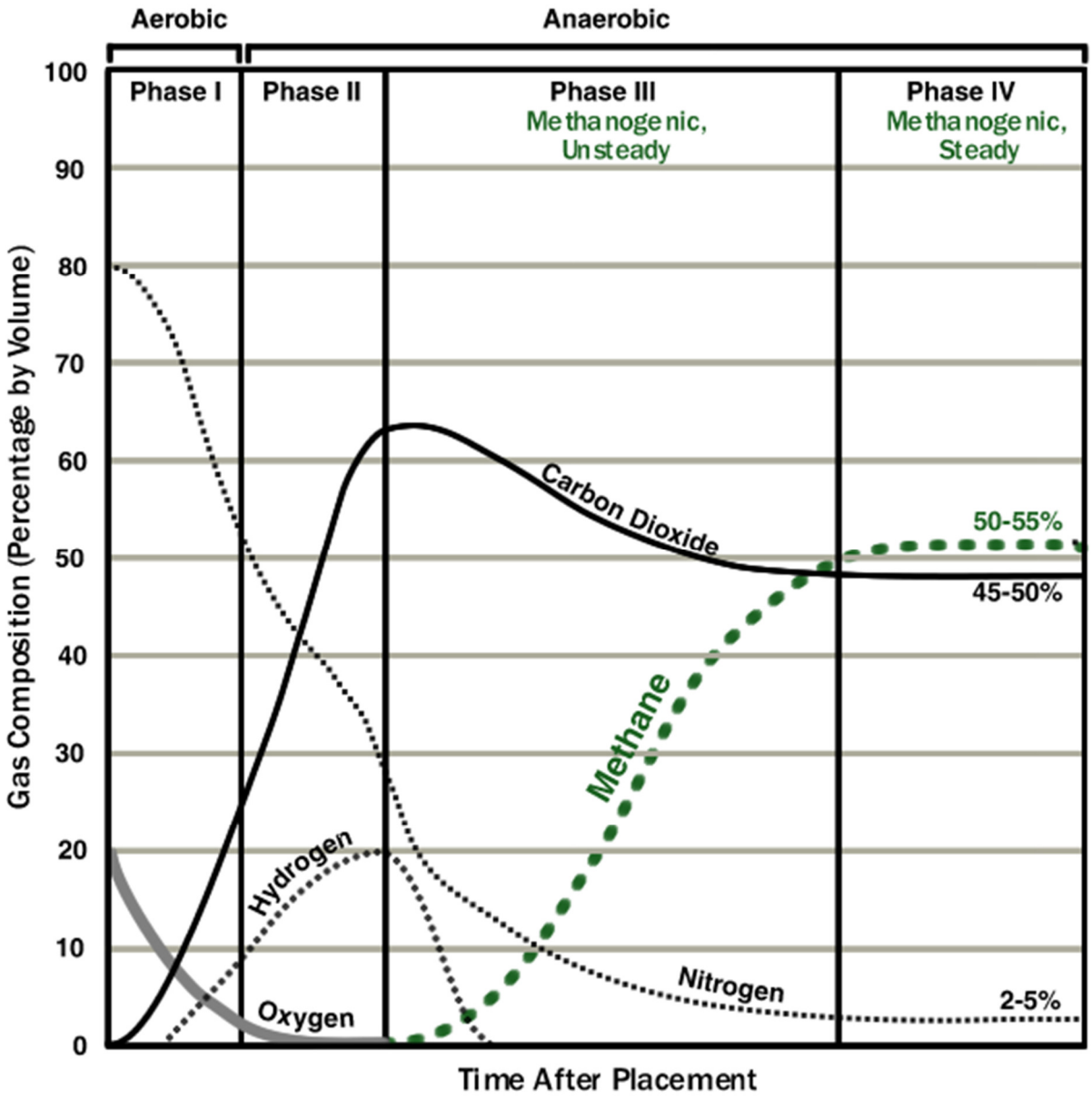

Figure 2 – Gas composition change in a landfill over time (adapted from US EPA 2008).

Figure 2 demonstrates how the composition of LFG changes over municipal waste's time from the moment of its initial disposal. While the first two phases yield little to no methane, the third and fourth phases allow for methane generation and stabilization. When treating landfill leachate and condensate, it is important to know the composition of the material whose degradation causes the leachate and LFG to from.

The majority of solid waste worldwide is left in unregulated landfills or piles, leading to copious quantities of methane escaping into the atmosphere on a regular basis. This is changing, as many countries are trying to find ways to utilize the methane in solid waste for heat generation and electricity. In 2001, there were about one thousand landfills collecting and utilizing the trapped methane worldwide. According to a paper published in 2006, in the United States, 70% of the annually captured 2.6 million tons of landfill-generated methane was being used to generate heat or electricity (Themelis and Ulloa 2006). The United States topped the charts with 325 plants recovering energy from landfills, with Germany and the United Kingdom coming in second and third with 150 and 135 plants, respectively.

Once the gas has been recovered, it can be used for a multitude of applications.

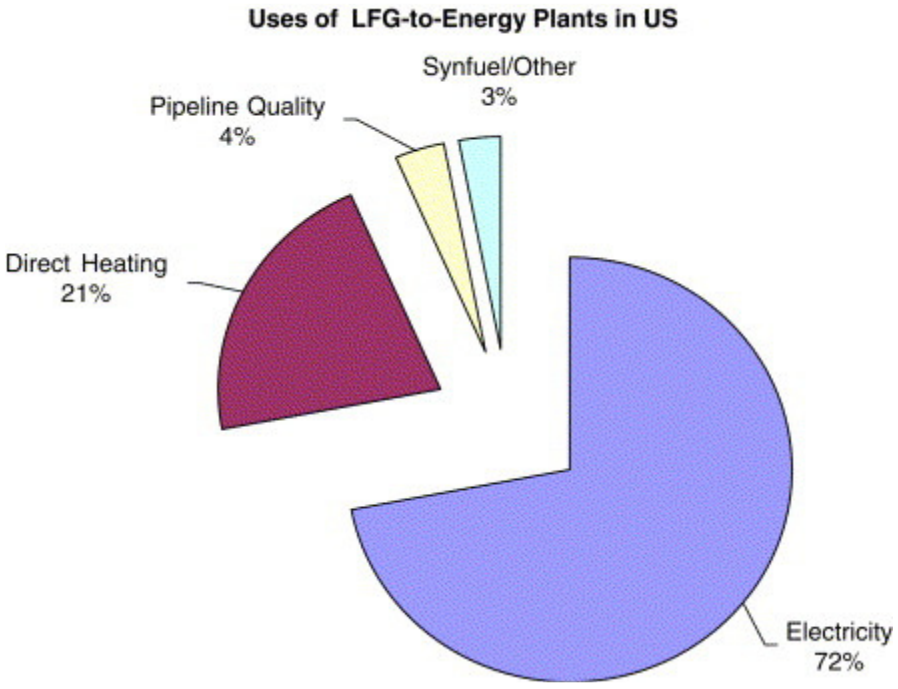

Figure 3 – Uses of LFG-to-energy plants in the US (adapted from Themelis and Ulloa 2006).

According to Figure 3, 72% of LFG-to-Energy Plants use the methane captured for electricity. This can include turbines operation, processing and use in fuel cells, and processing and use in

reciprocal internal combustion engines. 21% of the capture goes toward direct heating through processes such as industrial boilers and industrial heating and cooling. The other 7% goes toward pipeline quality, synthetic fuel, and other applications.

Landfill Leachate

Leachate is defined as "the aqueous effluent generated as a consequence of rainwater percolation through wastes, biochemical processes in waste's cells and the inherent water content of wastes themselves" (Renou et al. 2007). Landfill leachate (LFL) can contain large amounts of organic material, salts, and heavy metals. Since landfill leachate is linked to rainfall levels and surface runoff, it is important to have a well-built landfill that can withstand substantial amounts of rainfall, especially in the Pacific Northwest. Without a durable foundation, landfills can leak or fail in other structural manners, causing contamination of groundwater with the aforementioned chemicals.

Heavy metals pose a risk to the exposed environment through uncontrolled LFL release. Common heavy metal elements found in LFL include Cd, Cr, Pb, Hg, Ni, Cu, Zn, Fe, Se, and As. For instance, an assessment of heavy metal contamination in LFL was performed at Kham Bon Landfill in Khon Kaen Province in NE Thailand (Chuangcham et al. 2008). The study used soil samples collected at separate times of the year and showed that the soil at the landfill was contaminated by different heavy metals carried due to leachate percolation and migration within 2000 meters of the landfill. The contamination leaked as far as 90 m into the subsurface and followed the drainage patterns of the area. The other major find of the study was that the concentrations were determined by different precipitation levels due to seasonal variation (Chuangcham et al. 2008).

Another study done on heavy metal contamination was focused on the occurrence of heavy metals in anaerobic leachate polluted groundwater samples collected downline from a Danish landfill (Jensen et al. 1999). Groundwater was determined to have varying concentrations of Cd, Ni, Zn, Cu, and Pb. Their speciation was divided into three categories: colloidal, organic, and inorganic species of the heavy metals. The study indicated a strong association between heavy metals in leachate-polluted groundwater and small size colloidal matter and organic molecules.

The focus of this thesis is on arsenic removal from landfill gas condensate that is typically recycled back to the leachate collection system. Research being done in the field of environmental quality has recently shown the presence of arsenic in the leachate in many landfill sites. Some common arsenic containing wastes coming into the landfill are arsenic bearing solid residuals (ABSR) from drinking water facilities, construction debris, and industrial solid waste. Some common ABSRs in landfills are granular ferric oxide, granular ferric hydroxide, activated alumina, and titanium oxide. The concentrations in these ABSRs range from around 500 to 45000 mg/kg of arsenic. Some of the problems with landfill disposal of these materials include groundwater contamination due to arsenic leaching and impact on leachate quality. Additionally, the types of arsenic species vary from site to site (Al-Abed and Jegadeesan 2006).

Previous research from our group within the project has determined that the types of arsenic present in landfill leachate produced at the site in question is not limited to arsenite and arsenate. While the focus of the technology we are developing is the removal of the arsenic from the landfill leachate and LFG condensate, we must know the speciation of the arsenic we are treating. These other species include arsine gases, MMA, DMA, and any other forms of arsenic.

Arsenic Sources

Natural (geogenic) arsenic sources

Arsenic is a naturally occurring element both within the crust of the ore as well as over two hundred different types of mineral species. Arsenic comprises about 0.00005% of the earth's crust and its concentration in uncontaminated mineral matrixes ranges from 0.5 to 2.5 mg/kg. 60% and 20% of the mineral forms are As(V) and sulfur containing minerals, respectively, and the remaining 20% are As(II)-containing solid phases, such as oxides, silicates, and in some cases elemental arsenic. The most common form of arsenic containing ores is arsenopyrite FeAsS. Table 1 (Mandal and Suzuki, 2002) lists some common arsenic ores and As-bearing minerals and where they are typically found.

Table 1 – An abridged list of common arsenic-containing solid phases (adapted from Mandal and Suzuki 2002).

Table 2
Major arsenic minerals occurring in nature [15]

Mineral	Composition	Occurrence
Native arsenic	As	Hydrothermal veins
Proustite	Ag_3AsS_3	Generally one of the late Ag minerals in the sequence of primary deposition
Rammelsbergite	$NiAs_2$	Commonly in mesothermal vein deposits
Safflorite	$(Co,Fe)As_2$	Generally in mesothermal vein deposits
Seligmannite	$PbCuAsS_3$	Occurs in hydrothermal veins
Smaltite	$CoAs_2$	–
Niccolite	NiAs	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs
Orpiment	As_2S_3	Hydrothermal veins, hot springs, volcanic sublimation product
Cobaltite	CoAsS	High-temperature deposits, metamorphic rocks
Arsenopyrite	FeAsS	The most abundant As mineral, dominantly mineral veins
Tennantite	$(Cu,Fe)_{12}As_4S_{13}$	Hydrothermal veins
Enargite	Cu_3AsS_4	Hydrothermal veins
Arsenolite	As_2O_3	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals
Claudetite	As_2O_3	Secondary mineral formed by oxidation of realgar, arsenopyrite and other As minerals
Scorodite	$FeAsO_4{\cdot}2H_2O$	Secondary mineral
Annabergite	$(Ni,Co)_3(AsO_4)_2{\cdot}8H_2O$	Secondary mineral
Hoernesite	$Mg_3(AsO_4)_2{\cdot}8H_2O$	Secondary mineral, smelter wastes
Haematolite	$(Mn,Mg)_4Al(AsO_4)(OH)_8$	–
Conichalcite	$CaCu(AsO_4)(OH)$	Secondary mineral
Adamite	$Zn_2(OH)(AsO_4)$	Secondary mineral
Domeykite	Cu_3As	Found in vein and replacement deposits formed at moderate temperatures
Loellingite	$FeAs_2$	Found in mesothermal vein deposits
Pharmacosiderite	$Fe_3(AsO_4)_2(OH)_3{\cdot}5H_2O$	Oxidation product of arsenopyrite and other As minerals

As well as being present in rocks, arsenic occurs naturally in soils. Depending on the site and geologic conditions, the levels of arsenic in the soil can vary drastically. The climate, other

components of the soil, redox potential and anthropogenic exposures can all have an effect of the amount and type of arsenic in the soil. Some countries have as low as 0.1 mg/kg while others have closer to 40 mg/kg (Mandal and Suzuki, 2002). Peats and bogs can have higher concentrations of arsenic, due to the presence of sulfide rich terrains. In Canadian pyrite rich shales, studies have found up to 45 mg/kg of arsenic (Smeldley and Kinninburgh 2001). They also reported that the majority of arsenic in the soil is geogenic, however industrial sources such as smelting, and mining can lead to elevated As levels.

Arsenic also naturally occurs, typically at low levels, in natural water sources. The normal levels of As in oceanic water range from 0.001-0.008 mg/L of arsenic. While As(III) is found in lower concentrations in soils, sediments, and ores compared to As(V), the ratio is much smaller for arsenic species found in seawater. This is thought to be because of biological reduction occurring within the seawater (Johnson, 1972). In unpolluted fresh water sources, the levels reach between 1-10 µg/L while certain industrial levels could cause levels to reach between 100-5000 µg/L (Mandal and Suzuki, 2002). High concentrations of arsenic found in the groundwater naturally can be associated with As release from oxidizing and reducing aquifers and areas affected by geothermal activity. Another cause of naturally high As concentration in groundwater is associated with evaporation which causes the concentration of As to increase naturally through evaporation of exposed groundwater (Smeldley and Kinninburgh 2001).

Lastly, arsenic occurs naturally in the atmosphere. Through wind erosion, volcanic emissions, and low-temperature volatilization, arsenic levels in the atmosphere can increase in certain areas. However, most of the addition of arsenic to the atmosphere comes from anthropogenic sources such as pollution through smelting and mining. In rain and snow, arsenic levels have been reported to be around levels less than 0.03 ug/L. Previously mentioned anthropogenic sources

have been reported to raise these levels to 0.5 ug/L in certain areas (Smeldley and Kinninburgh 2001). However, the majority of atmospheric precipitation contributes little to groundwater As levels.

Arsenic levels in food

Since arsenic is present in so many types of soils and rocks, it is often found in several types of food, especially in seafood, rice, and fruit juices. Arsenic levels in food are closely watched, especially as it relates to food for infants, such as rice cereal. Impaired intellectual development has been associated with arsenic exposure, however since the removal of arsenic from food entirely is impossible, the FDA has issued guidance for food distributors to not exceed more than 100 ppb of arsenic for rice cereal, 10 ppb for apple juice, and 10 ppb for bottled water (FDA 2020).

Anthropogenic arsenic sources

As is the case with many environmental concerns, humans are the cause of a large amount of the arsenic contamination in groundwater and soils, especially in cities and countries with poor water infrastructure. In Bangladesh, irrigation of vegetable fields with arsenic contaminated groundwater (in this case the initial source of As contamination is geogenic) has become a major health concern. Between 1999 and 2004, more than two thousand water, soil, and vegetable samples were analyzed for arsenic in Bangladesh. Irrigating a rice field with groundwater that had 0.55 mg/L arsenic was shown to result in an increase of 5.5kg of arsenic per ha per year. The consumption of these contaminated foods can have adverse effects on the local population (Huq et al. 2006).

In the 1970s, the use of arsenic containing pesticides began to grow. These chemicals included sodium arsenite (Na_2HAsO_3), calcium meta arsenite ($Ca(AsO_2)_2$), copper acetoarsenite or Paris Green ($Cu(CH_3COO)_2 – 3Cu(AsO_2)_2$), copper pyroarsenite ($Cu_2As_2O_5$), calcium arsenate ($Ca_3(AsO_4)_2$), and sodium arsenate ($Na_2HAsO_4$). In the 1980s, nearly 70% of the wood preservatives used in the workforce contained arsenic species. During the Vietnam War, one of the herbicides used by the military was Agent Blue, which contained a mixture of DMA and its salt form. Although these chemicals are no longer used today, the use of arsenic containing pesticides over the last 50 years has had severe impacts on human health. Exposure to acutely toxic levels of DMA can eventually lead to death over an exposure period of 3-14 days (Bencko and Yan Li Foong 2017).

In the Guizhou province of China, arsenicosis or arsenic poisoning, is a common side effect of coal mining (Liu et al. 2002). The mining operations disturb the already elevated levels of natural arsenic in the soil and rock, leading to unhealthy concentrations in the groundwater. Arsenic species are also released from the coal when burned as a fuel source. Since this region of China relies on coal burning for “cooking, drying of crops, and heating purposes” (Liu et al. 2002).

In 1905 in Tacoma Washington, the American Smelting and Refining Corporation, or ASARCO began operations of a copper smelter, that only recently ended in 1986. In addition to the processing of mined copper ore, the smelter also extracted lead and arsenic for use in pesticides in Eastern Washington. The 546-foot-tall smokestack of ASARCO became an icon in the state. However, it was also the delivery device for substantial amounts of lead and arsenic being pumped into nearby communities (Gilbert n.d.). The site was listed as a superfund site in 1983 and ASARCO filed for bankruptcy in 2005. Four years later they paid Washington State $94.6

million dollars in 2009 to help with the cleanup of the site ("Tacoma Smelter - Washington State Department of Ecology" n.d.). Since the contamination from the site still affects certain areas today, the Washington State Department of Ecology runs a web map service called Dirt Alert, where people can check predicted arsenic concentrations for their area (if that area was affected by the plume) and determine whether they need to get their soil concentrations checked for arsenic levels. Figure 4 is a screenshot taken from the map on October 18, 2021.

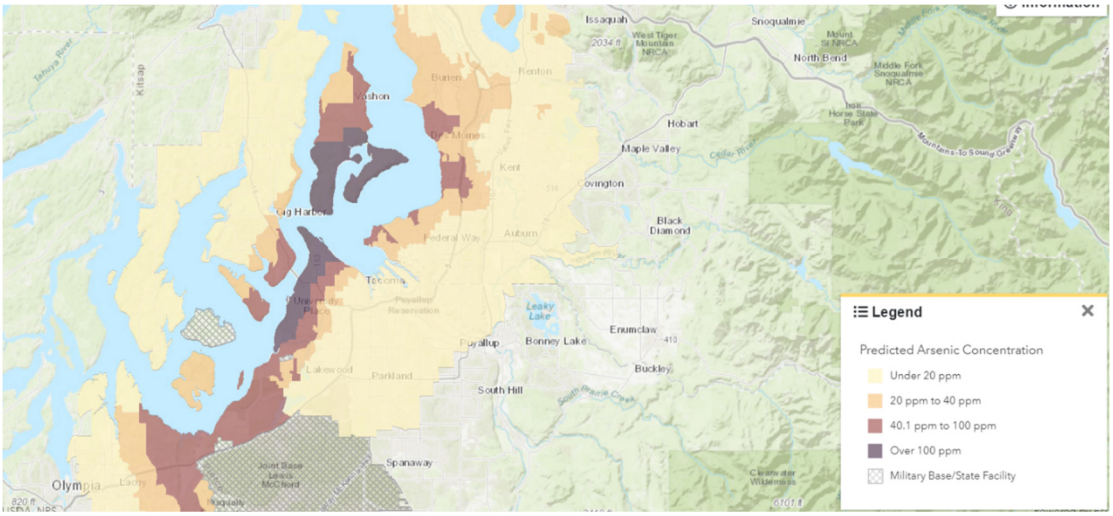

Figure 4 - Dirt Alert screenshot October 18, 2021, Washington State Department of Ecology

Arsenic and its health effects

Arsenic contamination poses a very real threat and ultimately a danger to millions of people around the world. This threat comes from poorly managed drinking water, contaminated groundwater, as well as many industrial operations around the world. According to the WHO, long term exposure to arsenic can lead to cancer, lesions, and severe damage to the bladder and lungs. Exposure to unsafe amounts of arsenic can lead to acute symptoms such as vomiting, abdominal pain, and diarrhea. High enough exposure to arsenic can lead to death. (Howard

2003). A study by Quansah et al. published in 2015 in Environmental Health Perspectives showed an association between adverse pregnancy outcomes and infant mortality and arsenic exposure. In the study that looked at 888 PubMed and Ovid MEDLINE articles published between 1946 and 2013 showed that arsenic concentration in groundwater higher than 50 ppb was connected to an increased risk of spontaneous abortion, neonatal mortality, and infant mortality. This study provided more evidence to support the claim that arsenic contamination continues to be a global health risk and needs to be addressed immediately (Quansah et. al 2015).

Effects of Arsenic on Exposed Biota

Arsenic can have a drastic effect on not only the health of the human body, but the health of the planet and the other organisms living on it. A study published by Osuna-Martínez et al. 2021 looked at arsenic levels in the water, soils, sediments, and biota from Mexico. Since arsenic bioaccumulates within an organism, it is important to understand its effects on biota since it may take a long time for arsenic to be removed from an organism, if at all. This study showed that plants exposed to heavy metals, including As, can show different physiological responses, depending on the species and the environmental conditions of the soil they are grown in. For the continental biota, the highest concentration of As found in animals examined in the study was in birds, ranging from 3.55 mg/kg in shorebirds to 6 mg/kg in ducks from Durango. In the marine and coastal environment, the highest arsenic concentration was found in the central part of Baja California. This can be explained because As bioaccumulation is higher in water areas with higher temperature and low salinity.

Chen et al. 2015 examined the changes in freshwater ecosystems in response to arsenic contamination caused from industrial sources. Sediment records from two contaminated Chinese

lakes show between a 13.9 and 21.4-fold increase in total arsenic levels relative to pre-1950 levels. This is correlated to a more than 10-fold loss of crustacean zooplankton and a more than 5-fold increase of metal tolerant algae. This study also goes as far to say that "such fundamental ecological changes will cascade through the ecosystem, causing potentially catastrophic consequences for ecosystem services in contaminated regions" (Chen et al. 2015).

Removal of Arsenic from Water

With all of the possible arsenic contamination sources, the threat of arsenic to health is profoundly serious. Historically, there have been many different methods for arsenic removal. These include oxidation, membrane technologies, adsorption, ion exchange, and micro electrolysis. All of these techniques work for different types of arsenic species, different scales and treatment sizes, and have different costs. Most of these technologies handle the removal of arsenate, with some handling arsenite. This is because arsenite solutes are predominantly uncharged below a pH of 9.2, so many of these technologies are not effective at removing arsenite (Nicomel et al. 2015). Arsenite, being the more soluble species of the two, is less easily removed through adsorption and precipitation than arsenate, so an oxidation step to convert As (III) to As (V) is often needed. While an enormous amount of research has been to develop technologies suitable for the removal of arsenite and arsenate, very few technologies are currently available to remove organo-As species.

Oxidation

For water treatment technologies, there exists several categories of oxidation combined in some cases with other treatment approaches, for instance oxidation followed by filtration, photochemical oxidation, photocatalytic oxidation, and biological oxidation. Oxidation/filtration

is used for arsenic removal by oxidizing the soluble Fe(II) and As(III). Then, another removal technique is applied, such as adsorption, where the new As(V) adsorbs onto iron hydroxide and is precipitated out of the solution (EPA 2015).

While oxidation can be done with oxygen, the latter oxidant is too slow for most practical applications and more rapidly acting oxidants such as chlorine, chlorine dioxide, ozone, hydrogen peroxide, chloramine, ferrate, and permanganate are used. The oxidation is especially important for anoxic waters, since arsenite is more prevalent than arsenate under neutral pH in these conditions. The reactions that are driven by chlorine, ozone, and permanganate are much faster than those in the case of hydrogen peroxide and chloramine (Singh et. al, 2015).

Photocatalytic oxidation involves using a light activated catalyst for the oxidation process. After the photocatalytic oxidation of arsenite to arsenate, arsenic can be adsorbed onto titanium oxide. Using this process described by Singh et. al in 2015, they were able to reduce the arsenic concentration to below the WHO recommended drinking water levels of 10 ug/L. The study also describes a way to increase the adsorption of arsenic by exposing the solution to UV light. However, a disadvantage to this process is a competition between anions and organic matter normally found in groundwater that leads to an incomplete oxidation of arsenite to arsenate.

Another form of oxidation discussed by Singh et. al in 2015 was biological oxidation. It uses iron and manganese for As removal since groundwater is usually reducing and contains both iron and manganese in their reduced forms. For this treatment, the following reactions occur: oxidation from Mn(II) to Mn(IV) and Fe(II) to Fe(III), oxidation from As(III) to As(V), precipitation of manganese oxides, abiotic oxidation of As(III) by manganese oxides, and As(V) sorption by manganese oxides. The study covered by Singh et. al used the microorganisms *Gallionella ferruginea* and *Leptothrix ochracea* to support biotic oxidation of iron (Katsoyiannis and

Zouboulis 2006). This study also reported that iron oxidizing bacteria remove As from contaminated groundwater faster than manganese oxidizing bacteria.

Membrane Technologies

The four common classes of membrane technologies used in water treatment are reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF). The process that each of these technologies use is similar. It involves using a semipermeable membrane to filter out certain molecules, depending on the size of the filter used. Figure 5 shows the differences in size and the types of molecules and organisms filtered out of water with each treatment technology.

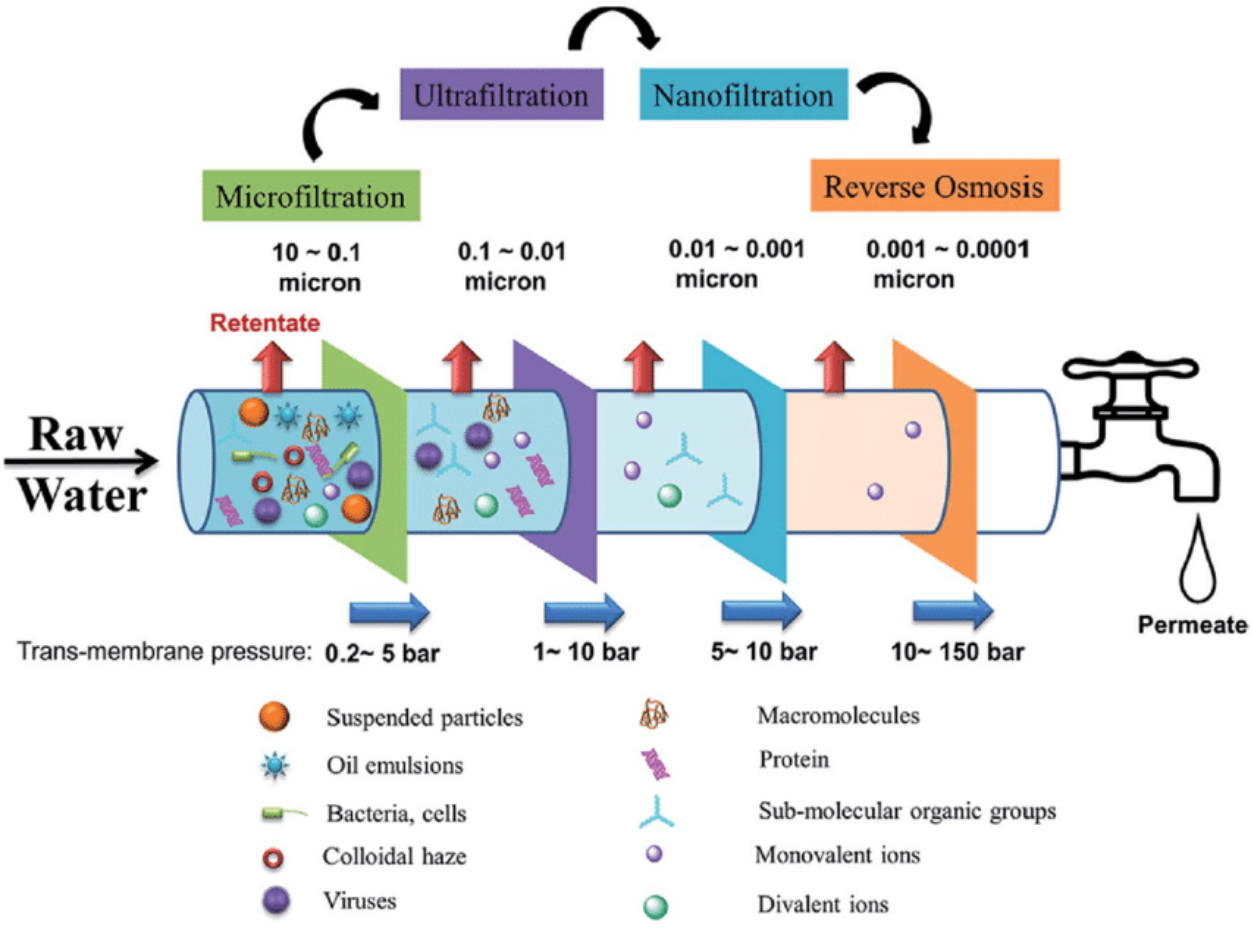

Figure 5 – A general scheme of pressure-driven membrane processes for water treatment technologies (adapted from Elsevier Science Ltd. 2018).

A study published by Worou et al. in 2021 examined the efficacy of using NF to remove arsenate and arsenite ions from water. While NF was used to remove arsenate nearly completely, the removal of arsenite using NF membranes or RO required additional treatment steps. One of the downsides of using membrane technology is membrane fouling, where particles are deposited onto the surface of a membrane over time, leading to decrease in the membrane's performance. The paper covered the replacement of commercial membranes with synthesized NF membranes, which lead to an increase in the removal of arsenate from the water samples. With just a commercial NF membrane, the removal was between 86 and 99 percent, while a synthesized membrane was able to achieve a removal of 99.8%. The paper also covered advantages membrane technologies hold over other treatment technologies. These include ease of operation and no sludge production (Worou et al. 2021).

Adsorption

Adsorption in water treatment is based on the use of certain materials (adsorbents), placed in contact with a solution in order to have molecules attach to the adsorbent in order to remove them from the water source. For water treatment, adsorption has several advantages. These include the frequently low cost of the adsorbents and the low maintenance required during the process. Several different factors can affect the efficacy of the treatment. These include pH of the treatment solution, the material used, the contact time of the solution with the adsorbent, and the use of a opposite flow gas.

Adsorption processes can be implemented in batch or CSTR reactors, or fixed bed column treatment modes. Batch or CSTR treatments are set up by adding adsorbent to a solution and samples are removed at various times to test the best removal time, whereas column experiments

are set up by forming a stationary column, sometimes with layers of different materials, and passing solution through at a constant flow rate depending on the empty bed contact time (EBCT) and bed volume (BV). Empty bed contact time is the time in which the liquid is in contact with an adsorbent in a treatment column, and bed volume is the volume of adsorbent used. Both categories of adsorption treatment options have been used in different studies. The first half of my research focused on fixed bed column flow, while the latter half focused on ME experiments in a batch setup, where a set volume of LFG condensate dosed with a set concentration of adsorbent.

As technologies develop, many different kinds of adsorbents have been tested for arsenic removal from water, albeit the focus of these studies has been overwhelmingly on the removal of inorganic As species. Chammui et al. 2014 used Leonardite char, a waste product found in coal mines, as a low-cost adsorbent. Removal experiments were conducted using batch systems where the optimal contact time and pH for the best removal of arsenite and arsenate was found to be 3 hours and pH 7. The study analyzed the data using both Langmuir and Freundlich isotherms, modeling systems commonly used for reactor systems. A size of 75 µm was used for the char since it had a close to 100% removal for both arsenite and arsenate. The study concluded that the use of Leonardite char was successful for the removal of arsenic species (that were present as arsenite and arsenate) and could be used for future studies as a low-cost adsorbent, since it is a recycled material from the mining industry (Chammui et al. 2014).

Other common adsorbents and/or reactive media used for the removal of arsenic species in water treatment through adsorption are zero valent iron (ZVI) and powdered or granular activated carbon (PAC or GAC, respectively). These are the adsorbents primarily used in the research described in this thesis. Zhu et al. 2009 used nanosized ZVI on activated carbon and found that

this material was particularly effective in removing inorganic As species. The reported results showed a fast removal of arsenite and arsenate onto the nano zero valent iron (NZVI)/activated carbon (AC) within the first 12 hours and equilibrium was achieved at 72 hours. In order to use the same material, the column went through a period of desorption, or regeneration, with 0.1M sodium hydroxide (Zhu et al. 2009). The following table shows the removal of both arsenite and arsenate using this system over 8 cycles of adsorption and desorption.

Table 2 – Removal of inorganic arsenic species (2 mg/L initial As concentration, 1.0 g/L NZVI/AC, and pH 6.5 (Adapted from Zhu et al. 2009).

	Cycle							
	1	2	3	4	5	6	7	8
Arsenic removal (%)								
As(III)	96.4	99.5	97.8	94.0	99.4	96.3	96.1	95.5
As(V)	75.6	82.3	81.8	73.9	79.2	81.4	75.1	72.7

Ion Exchange

Another treatment technology to be briefly discussed here is ion exchange. In this process, contaminants are removed from a solution by replacing certain ions on the surface of the ion exchange resin. A typical use of this technology is in water softening, where calcium and magnesium ions are removed in order to reduce the hardness of the water. For the removal of arsenic from water, ion exchange is often combined with oxidation since arsenate is much easier remove than arsenite.

A study published by Oehmen et al. 2011 focused on a hybrid technology combining ion exchange and coagulation. Coagulation is a process in which charged molecules are added to a

solution in order to precipitate other solids out of solution and settle on the bottom of the reactor. This study compared aluminum and iron coagulants for the process, finding that aluminum chloride was more effective than iron chloride due to membrane scaling, a condition in which molecules can deposit onto a membrane and prevent molecules from getting through. Using the ion exchange resin, the group was able to get the arsenic levels to below the drinking water limit of 10 ppb, after the arsenite in the solution was oxidized to arsenate. The membrane chosen for this experiment was Ionics AR204-UZRA, an anion exchange membrane. This hybrid process also avoids possible contamination from coagulants and pH-controlling agents (Oehmen et al. 2011).

Micro electrolysis

Micro electrolysis (ME), while used for other aspects of landfill treatment, has yet to be used in the study of the removal of arsenic from LFG condensate. ME uses zerovalent iron and activated carbon, either powder activated carbon or granular activated carbon as active media for the treatment process. When iron is mixed with activated carbon, galvanic cells are formed between the iron and the carbon. While these cells aid in the flow of electrons within the solution, simultaneous reduction reactions happen between the iron and the activated carbon. This reductive environment converts the arsenic species to easier to remove species, allowing for removal by adsorption or gas treatment of volatile arsine species (Ying et al. 2012).

Removal of Arsenic from Landfill Gas Condensate

General Features of Arsenic Chemistry Expected for Landfill Gas Condensate

In order to better understand the removal of As from LFG condensate, it is important to review the general aspects of the environmental chemistry of arsenic, especially given that As species may exist as volatile gases, true solutes, and solid phases. Figure 6, sourced from a lecture given by Dr. Gregory Korshin at the University of Washington in the class CEE 543 Aquatic Chemistry, shows a simplified scheme of the biogeochemical reactions of arsenic, including arsine gas, arsenous acid, DMA, TMA, and several other forms (Korshin 2021):

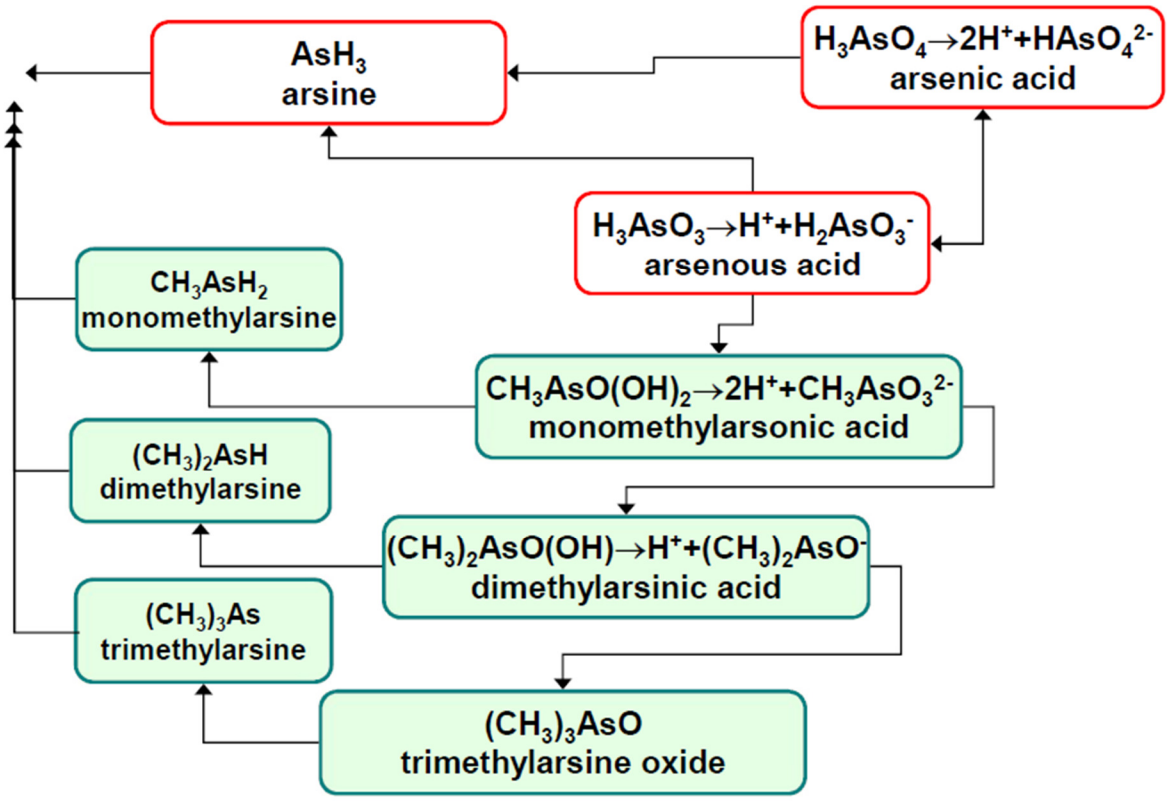

Figure 6 – Basic elements of biogeochemical reactions of arsenic involved in the generation of arsines, Korshin 2021

Figure 6 shows that there are a number of reduction-oxidation reactions that involve both organic and inorganic arsenic species, making the treatment technology potentially difficult in the presence of organic As species. The complexity of this reaction sequence is relevant to the

design of the treatment system that removes As from LFG condensate, as discussed in more detail in the sections that follow.

Prior Studies of As Removal from LFG Condensate

Since this study focuses on removal of arsenic from LFG condensate, it is important to examine the prior research done in the subject and the technology used for treatment of arsenic and arsenic species in LFG condensate. It is also important to study the treatment of arsenic found in process water generated in operations separated methane from LFG to produce renewable natural gas (RNG) which otherwise is frequently referred to as biomethane.

The removal of arsenic species from LFG condensate is a difficult technology to develop, due to the complex chemical nature of LFG condensate and little knowledge about many aspects of the chemistry of this matrix. One of the recent papers concerned with this issue was by Zhao et al. in 2013. This paper described the basic composition of LFG condensate found in a landfill in Pennsylvania, USA and reports arsenic concentrations found in the examined LFG condensate, and the technologies that were used to treat the condensate. The LFG condensate found in the location comprised an aqueous phase and a floating hydrocarbon phase. The arsenic species found in the samples included both inorganic arsenic [As(III) and As(V)], as well as methylated forms of arsenic (MMA, DMA, TMA). Since the forms of arsenic have such diversity within the sample, a technology had to be chosen in order to treat the majority of the arsenic most efficiently.

For treatment, Zhao et. al 2013 considered several different kinds of treatment. These included a sequencing batch reactor, coagulation, permanganate oxidation, Fenton's reagent oxidation, carbon adsorption, and membrane separation (RO). All of these techniques have been briefly

discussed in a previous section, with the exception of Fenton's reagent oxidation. This is a technique covered in Lopez et al., where an advanced oxidation process uses hydroxyl radicals that breakdown molecules unable to be destroyed by other oxidation methods (Lopez et al. 2004). This study also considered the cost of the treatment technology when determining effectiveness.

Each of the treatment options were tested in the study of Zhao et al. 2013 and provided a wide range of results. Biological treatment showed a 26% removal of arsenic from the system, with more than 95% removal of TOCs from the system as well. It was believed that the arsenic removal occurred through adsorption to the biomass and through the removal of activated sludge waste. While this was not the highest removal of arsenic from the system, it showed some level of a biodegradability of organic matter in the LFG condensate. Figure 7, adapted from Zhao et. al 2013, shows the removal arsenic with and without the use of $AlCl_3$:

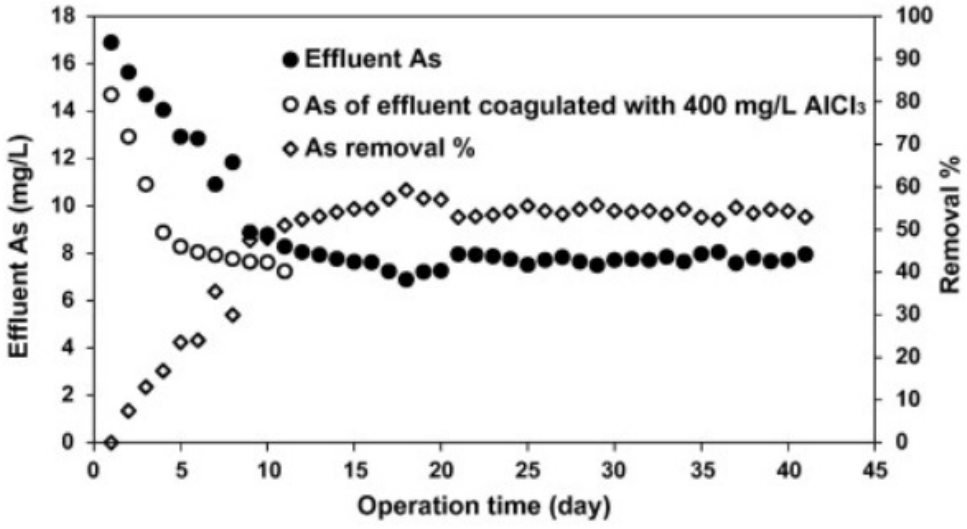

Figure 7 - Removal of arsenic with and without 400 mg/L $AlCl_3$ through biological treatment, Zhao et. al 2013

The next set of treatment technologies that were tested were physio-chemical treatment methods. These included $FeCl_3$ coagulation, $KMnO_4$ oxidation followed by coagulation, Fenton's reagent, and activated carbon. Overall, these technologies proved ineffective for organic arsenic removal from the samples of LFG condensate. The maximum removals were 8.0%, 5.6%, 15.1%, and 6.5%, respectively.

The most successful treatment found for this set LFG condensate samples was reverse osmosis, with a maximum removal of 95.8%. Reverse osmosis has been used historically for treatment of water samples, where the speciation of arsenic is inorganic forms. This study applied RO treatment to SBR treated LFG condensate. This was tested on both diluted and undiluted SBR effluent. The removal is illustrated in Figure 8:

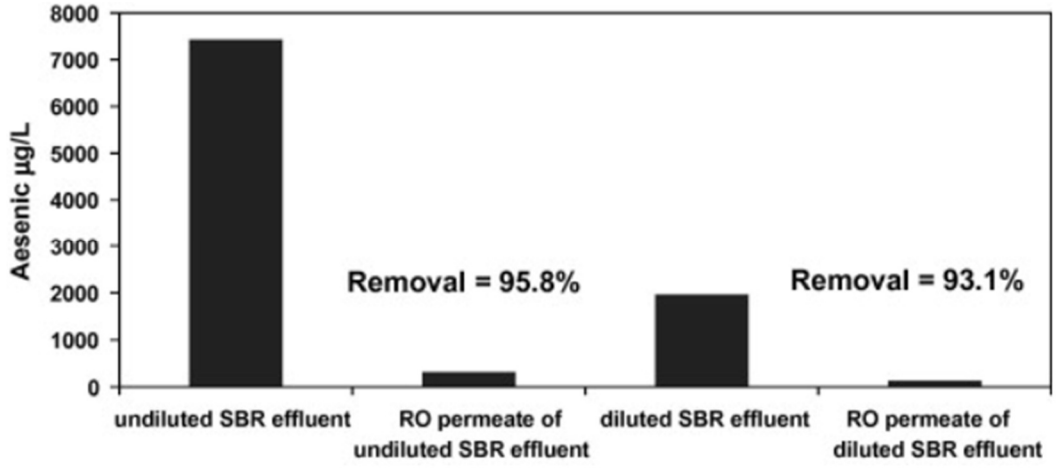

Figure 8 - Removal of arsenic from undiluted and diluted SBR effluent, Zhao et. al 2013

The dilution of the SBR effluent proved important for arsenic removal because although there was 2.7% more removal in the undiluted SBR effluent, the initial starting point of the diluted SBR effluent combined with the removal efficiency reduced the arsenic concentration in the RO permeate to 135 ug/L, below the discharge limit set at 200 ug/L.

While RO was the most successful treatment technology, no data were presented concerning the occurrence of fouling of the RO membrane during the treatment of LFG condensate, and its overall performance during long-term operations. It is also important that RO comes with the highest cost.

Table 9 summarizes treatment method, removal efficiency, arsenic concentration after treatment, conditions needed for treatment, and cost taken as a cost equivalent to the cheapest treatment, coagulation-flocculation by $FeCl_3$:

Table 3 - Treatment summary of landfill gas condensate (adapted from Zhao et. al 2013)

Treatment method	Maximum removal (%)	Effluent As concentration	Condition	Cost level[a]
Coagulation/flocculation ($FeCl_3$)	8.0	6.7 mg/L	500 mg/L $FeCl_3$	1
Oxidation + coagulation ($KMnO_4$ + $FeCl_3$)	5.6	6.8 mg/L	500 mg/L $KMnO_4$ + 600 mg/L $FeCl_3$	4.7
Advanced oxidation (Fenton's reagent)	15.1	5.9 mg/L	1000 mg/L Fe^{2+} + 500 mg/L H_2O_2 pH = 3.49	9.4
Carbon absorption	6.5	6.6 mg/L	20 g/L granular activated carbon contact time = 4 h	43.2
Membrane separation (reverse osmosis)	95.8	311 µg/L	Pressure = 14.5 psig recovery = 9.83%	43.6

Summary of Prior Research and Goals of This Study

The experiments described in this thesis began in in the summer of 2021 when the project was in its 2nd phase. Since then, our research has progressed to the third phase of the project. In the first

and second phases of the project, several treatment options were studied for the treatment of the LFG condensate and RNG process water. The tested treatment methods of arsenic removal included electrochemical pre-oxidation, permanganate oxidation and adsorption via manganese dioxide, pre-treatment using ozonation, adsorption on manganese dioxide, adsorption on AC, reduction and adsorption using ZVI, and reduction and adsorption via ME. Results of these tests were described in the thesis prepared by Surbhi Malik (Malik 2020). Experiments carried out by Gabe Rifkin focused on fixed bed column reactors and landfill gas/renewable natural gas process condensate (LRPC) spent gas treatment solids experiments (Rifkin 2021).

The two foci of my experimental work are on: A) the performance of fixed bed column reactors for arsenic removal (the extent of these tests was limited) and B) detailed tests micro electrolysis (ME) experiments that were largely successful in removing As from LFG condensate and their scaling-up from benchtop sized equipment to (eventually) pilot scale size with the cooperation of the landfill utility of interest. In order to do this, LFG condensate has been collected on a semi-regular interval from a landfill within KC. Each collection time is represented by a different sampling round (SR) and each SR has a unique chemical complexity with varying amounts of arsenic concentration. Additionally, each SR varies in the organic chemical composition, including a variety in the concentrations of oils, colloids, and light non-aqueous phase liquids (LNAPLs).

The first phase of my research took place during the summer and fall of 2021. During this time, I worked on fixed bed column reactor experiments by changing various conditions, including pH, empty bed contact time (EBCT), adsorbent concentration, size of column, and experiment run time. These experiments were put on hold after results were not showing consistent arsenic removal and, more importantly, issues with the rapidly increasing hydraulic resistance of the

fixed bed columns which were causing slowdowns and other difficulties in the treatment efficacy. The group may continue this set of experiments in the future, however for now, these experiments have been halted.

The second phase of my research started in the winter of 2021 and has been focused on the use of ME experimentation with increasing volumes and varied conditions in order to move from benchtop scale to pilot scale field experiments. Continuing off of the experiments which were started before I joined the group in the summer of 2021, these ME experiments are being conducted in batches of 500 mL in 1L acrylic column reactors. The variations of conditions include varying pH, adsorbent dose, carrier gas flow, and experiment time. The pH was held constant using a pH controller at either 4, 5, or 6. The adsorbent dose variation was in dose timing, addition type, and concentration, ranging from 0.5 to 4g/L. The carrier gas flow was carbon dioxide and varied in flow timing, from constant flow to an intermittent pattern the carrier gas in different increments. Lastly, the experiment run time was gradually changed as these experiments progressed. The experiment run times were 24 hours, 8 hours, and 6 hours. Sampling time used in these experiments was also varied, as discussed in the results section of the thesis.

Materials and Equipment

Materials

The complexity of this research project has required the use of many materials in order to find an effective treatment technology for arsenic containing LFG condensate. This includes both common laboratory chemicals as well as samples collected at a landfill utility within KC. Table 3

presents a list of the chemicals and materials used in both the fixed bed column experiments performed during the summer and fall of 2021 as well as the ongoing ME experiments.

Chemicals

Table 4 - Materials used for experiments

Chemical/Material Name	CAS Number	Supplier
LC Plus Fines (Zero Valence Iron)	7439-89-6	Cleanit
Granular Activated Carbon (12-40 mesh)	7440-44-0	Acros Organics
Powder Activated Carbon	7440-44-0	Fisher Chemical
USP Grade Carbon Dioxide	124-38-9	Linde Gas (Formerly Praxair)
Hydrochloric Acid	7647-01-0	Supelco
Sodium Hydroxide	1310-73-2	Fisher Scientific
Nitric Acid, Trace Metal Grade	7697-37-2	Fisher Chemical
Polylactic Acid (PLA)	26100-51-6	Ender
PAC coated nano-ZVI	N/A	Prepared by Po-An Chen (member of Dr. Korshin's group)

LFG Condensate Sampling Rounds (SR)

Multiple rounds of sample collection were carried out to generate LFG condensate samples generated in RNG production and used in the experiments described in this thesis. When I started on the project in the summer of 2021, the group was using Landfill Gas/Renewable Natural Gas Process Condensate (LRPC) samples obtained in the 8th sampling round (SR); correspondingly that sample and those obtained sequentially are is referred to as SR8 and SR with higher numbers. The current SR being used in SR13. The SR specimens have been collected at the

landfill site semi-periodically. This was necessary to gain experience with the highly variable LRPC condensate matrix and also to have sufficiently fresh LRPC samples whose properties may be unstable due to the slow ingress of the atmospheric oxygen as well as due to yet unexplored aspects of the As chemistry in LRPC.

Initially, the process of collecting LRPC samples was difficult due to the inefficiency of the collection setup and unpredictability of LRPC flows. In order to collect a LRPC sample, a tube was lowered into a standpipe to collect a LRPC sample when audio cues informed the team of the coming onset of flow of LRPC condensate. This often led to hours of standing around, waiting for flow to start, since the flow timing was controlled outside of the group. In March of 2022, members of the team located at the landfill utility set up a collection tank for improved and much easier LRPC sampling. This made the collection of SR12 and SR13 a much smoother event and I would like to thank the team at this site for their efforts in making our work easier. Table 4 includes a more detailed summary of the SR properties and other information pertinent to each LRPC sampling event.

Table 5 - Sample information table

Identifier	Use Date	Initial Arsenic concentration (ppm)
SR8	July 2021 – November 2021	11.4
SR9	October 2021	9.6
SR10	September 2021 – October 2021	4.4
SR11	September 2021 – November 2021	4.4
SR12	December 2021 – March 2022	6.5
SR13	March 2022 - Present	8.1

Table 4 shows that there are considerable differences in the As concentrations found in different LRPC samples. This is likely due to the differences in the chemical makeup of the LFG

condensate and LRPC formed as a result of interactions of LFG condensate with LFG treatment solids and other system components at time of collection. Some of the SRs have large amounts of lighter than water organics phase and oils as well as suspended solids that cause the solution to have a darker orange color. However, the presence of non-aqueous phase and suspended solids does not seem to have a critical effect on the treatability of the sample.

As part of the preparation for treatment, each of the SRs are filtered using a 1 µm cartridge filter. A peristaltic pump is connected to the filter cartridge housing and pumps LFG condensate through the filter from the top. The sample flows through the filter into an inner chamber, where the now-filtered material rises back to the top and flows out of the filter cartridge into a secondary container. While some of the SRs can be filtered using just one of the cartridge filters, some of the SRs need multiple filters for effective treatment. This is due to the larger amounts of suspended solids present in these SRs. Even with the variety of the levels of suspended solids in each of the SRs, ME treatment remains an effective treatment for all current SRs. Higher presence of these solids does not seem to have a harmful effect on the removal efficiency of the ME treatment.

Equipment

Analytical Instruments

In order to determine the most effective treatment technique for arsenic removal from the LFG condensate, several different instruments were used. These instruments include a UV-Vis Spectrophotometer, TOC (Total Organic Carbon) analyzer, and ICP-MS (Inductively Coupled Plasma Mass Spectrometer) instrument.

The UV-Vis spectrophotometer used for analysis of samples was a Shimadzu UV-2700 spectrophotometer. A spectrophotometer analyzes the passage of light through a sample and can give an estimation of certain types of light-absorbing chemical groups that may be present in your sample. Each sample was analyzed between a range of 200 and 800 nm in a 5 cm quartz cuvette. The samples were collected from the experimental setups, ran through a 0.45 µm syringe filter, and diluted to 100x in DI water. The UV spectrophotometer was only used for the beginning experiments, as it was determined the higher priority was to analyze the samples for arsenic and antimony using an ICP-MS.

The TOC analyzer previously used is a Shimadzu TOC analyzer that can measure both Dissolved Inorganic Carbon (DIC) and Dissolved Organic Carbon (DOC). A TOC analyzer determines the concentration of organic carbon associated with the organic solutes present in a sample and used for our samples as an ancillary testing method to help confirm the efficiency of certain technology treatment methods. In order to provide accurate results, stock standards were made at 0.5, 1, 2, 5, and 10 ppm of the original premade TOC standard solution from Shimadzu. Samples were first filtered with a 0.45 µm syringe filter and then diluted to 150x in DI water. The Shimadzu TOC stopped functioning in September 2021. As a replacement, a Sievers HPLC-TOC is being operated, however this instrument is limited to DOC analysis only.

A Nexion 2000B ICP-MS used to carry out elemental analyses is owned and operated by the Nanoscience Institute of the University of Washington. ICP-MS works by aerosolizing a liquid sample, transporting the atomized solution into a plasma torch with an argon carrier gas and quantifying the concentrations of various elements based on their mass to charge ratio at a given isotope of elements such As, Sb and others. Samples in the experiments described in this thesis were prepared at first using the 0.45 µm syringe filter after sample collection and later using a

0.45 µm syringe filter built into the collection line system, to help with collection efficiency. Samples generated in the experiments were at first diluted to 400x, with a change to 100x in order to help identify some of the lower concentrations of arsenic and antimony in the analyzed samples. The samples were diluted with DI water, acidified with trace metal-grade nitric acid, and an aliquot from a 1 ppb stock solution of yttrium (used for internal standard). In addition to using the Nexion 2000B ICP-MS in the Nanoscience Institute, select samples were sent to King County Environmental Lab (KCEL). These samples were filtered and preserved with nitric acid before delivery pickup from KCEL.

Testing in Fixed Bed and Batch Reactor Configurations

The experimental results will focus on two specific parts of the project: treatment of LRPC in fixed bed column and batch reactors that use the ME approach. While extensive experiments to explore As removal from landfill leachate and LRPC process water by ME treatment had been done before within the group, the data generated in this study and presented below focus primarily on the ME treatment in 1 L column reactors. The fixed bed column treatment experiments, which constitute a smaller part of this research, took place from June 2021 to December 2021. The second set continued from December 2021 to June 2022, with many variations of the setups along the way.

Both of the treatment experiments included a number of components. The first of the fixed bed column treatment setups used in this study was a 1 L, 2-inch diameter PVC clear cylindrical column. The bottom was secured with a flat plate and a plastic connector was attached to the bottom of the plate in order to collect post-treatment effluent, with a second connector for counterflow gas to carry arsenic species out of the column.

In the fall of 2021, the group purchased an Ender 5 Pro 3D printer which was used to make custom-designed parts for ME reactors. The Ender 5 Pro prints with polylactic acid (PLA), a biodegradable polyester used as a common printing material for 3D printing. Brief tests were run using a custom-built column consisting of removable modules. Figure 10 shows the modular assembly that was 3D printed for these tests. The tests using this column design were brief due to sample flow blockage that rapidly developed within the column and treatment of LFG condensate using ME began soon after the decision was made to temporarily stop experiments using the packed bed column similar to that shown Figure 10.

Figure 9 - 3D Printed Fixed Bed Treatment Column with Removable Cartridges

The next phase of ME treatment experiments utilized a 1 L clear PVC column reactor shown in Figure 11. Initially, the CO_2 carrier gas was injected in the reactor using a flat bottom diffuser attached to the column of the reactor. However, it was discovered that having a flat bottom diffuser of the column resulted in the low arsenic removal efficiency compared to the As removal consistently recorded in the prior phase of ME experiments that utilized small 100 mL

beakers that were continually agitated. To examine effects of the design of the bottom part of the column ME reactor in which the carbon and ZVI phase interact most vigorously, a dome-shaped bottom and a funnel shaped bottom parts (that incorporate the gas diffuser) of the column reactor were 3D printed. Tests were conducted with both, and the results showed the occurrence of consistently better As removal in the experiments that used the funnel shape vs. the dome shape bottom part. Further column ME experiments have continued using only the funnel shape of the bottom reactor part.

Additional components of the ME column include a ceramic diffuser, embedded within the 3D printed funnel, used for the injection of CO_2 carrier gas. Purging with CO_2 gas helps carry the volatile arsine species out of solution, so they may be treated in an additional step. The function of a 3D printed cap of the reactor is to limit exposure of the solution being ME treated to the atmosphere. A 3D printed pH probe holder was added to allow for control of pH through the experiment. In addition, the reactor has an intake port for sample collection, and an inflow port for 0.1M HCl for pH control. This low concentration serves only to keep the system at a stable low pH, between 3 and 5. This low pH environment promotes reduction, which allows for the arsenic to be released from solution more easily. After collecting a large amount of data with one column described above, an identical column was created to test for the reproducibility of results and more efficient sample analysis. Shortly after, 2 near identical columns were constructed and commissioned for further testing. These columns, identified from now on as CR1, CR2, CR3, and CR4 have an additional 3D printed probe holder for an electrode used for redox measurements. As the experiments evolve, more columns may be constructed for reproducibility purposes. No control columns were maintained for these experiments, however as reproducibility purposes in future experiments, this would be an advantageous system to have.

Figure 11 shows the entire assembly that incorporated columns reactors (CR) 1 and 2 (columns are numbered in the order they were constructed). Figure 11 also shows that the experimental setups used for ME experiments carried out with CR include additional components. Each of the four columns was equipped with a ISCO carousel autosampler, one or more timer control unit, a Masterflex pump controller, and a Bluelab® pH controller. There are two kinds of timer control units in use at the moment, one by ChronTrol® and three by Nearpow.

Figure 10 - Autosampler, peristaltic pump, timing control unit, pH controller, and column reactors (columns 1 and 2) used for ME experiments

Experimental Data and Discussion

Fixed bed column treatment

The fixed bed column treatment experiments described in this section were conducted between June and November 2021. For these experiments, analyses were carried to yield UV and ICP-MS data. Analyses to yield TOC data were planned, however the Shimadzu TOC instrument was under repair while these experiments were being conducted, so TOC data was not collected on these sets of experiments. As mentioned above, these experiments were halted because of the consistent technical challenges, notably the rapid development of hydraulic blockages within the fixed bed column setup. This halt is considered to be temporary and fixed bed column treatment of LRPC may resume in the future.

ICP-MS data from fixed bed column experiments

The most important set of the experimental data needed to determine arsenic removal efficiency of the fixed bed column experiments was based on ICP-MS analyses. Over the timeframe of the fixed bed column experiments, several variables were changed in order to identify the most effective method of treatment within a fixed bed column reactor. These variables include the adsorbent used, the height of each bed layer of adsorbent material, the pH of incoming LFG condensate sample, and the makeup of incoming LFG condensate sample (filtered or pretreated). All fixed bed column experiments were conducted using SR8 and a counterflow of 0.6LPM of USP Grade carbon dioxide gas.

A second graph displaying antimony removal data from the same experiments will also be included in each of figures displaying data from the ICP-MS, with the exception of experiments

using an arsenite model solution, where no antimony data was collected. While antimony removal is not the primary contaminate focus of the operators of the landfill, its behavior in the treatment of LRPC has been observed in our group's experiments to be frequently similar to that of arsenic and for that reason selected Sb data is included in the results.

ICP-MS data – Effects of fixed bed packing materials

The material combinations used for these sets of experiments were GAC only, ZVI only, alternating layers of GAC and ZVI, and a PAC coated nano-ZVI material manufactured by Po-An Chen (Zhu et al. 2020). Differences in arsenic removal between the first three combinations were tested in July 2021, while the last material was manufactured and tested in October 2021. The experiments for the first three combination used a pH of 3.

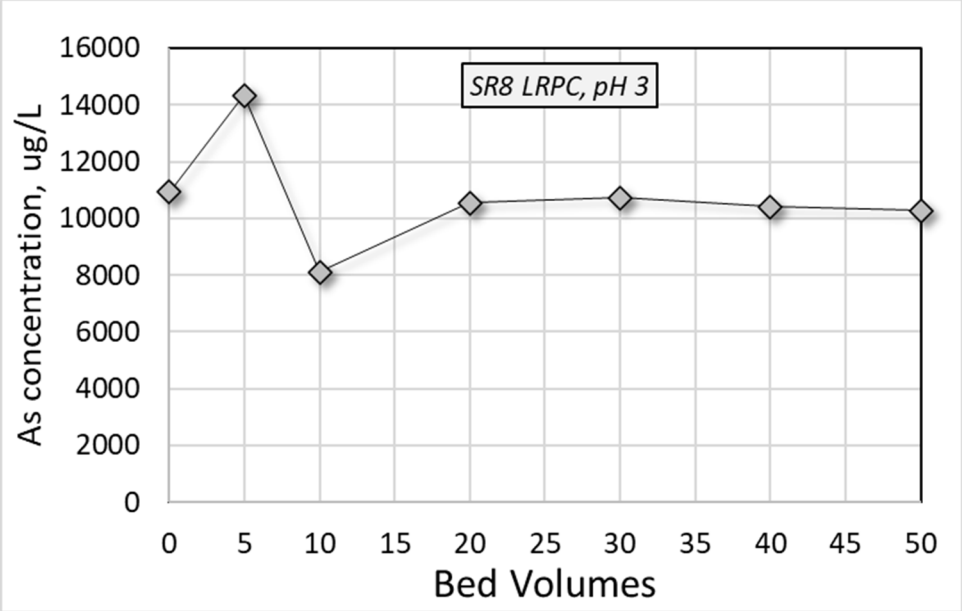

Figure 11 – Arsenic removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC only fixed bed column.

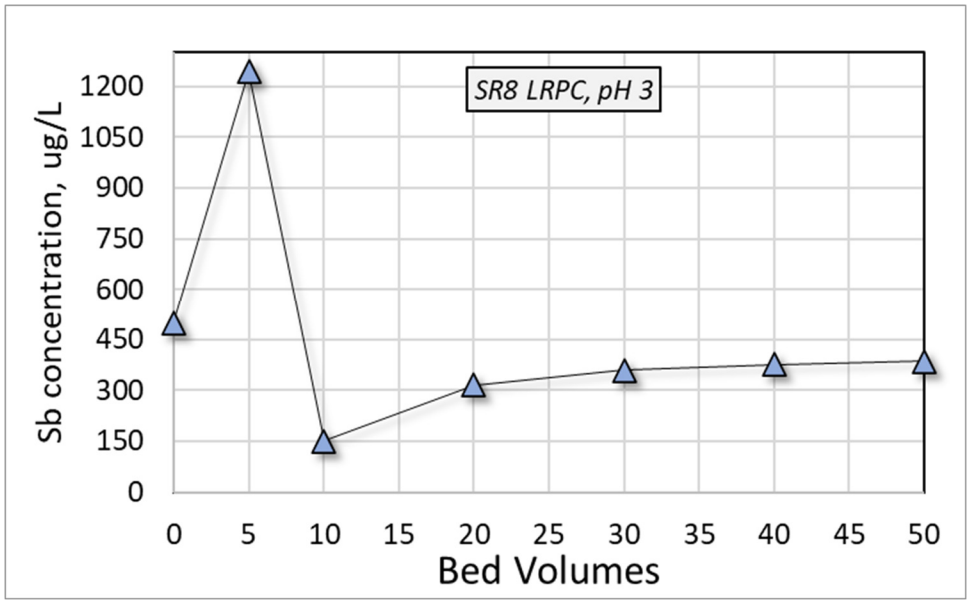

Figure 12 - Antimony removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC only fixed bed column.

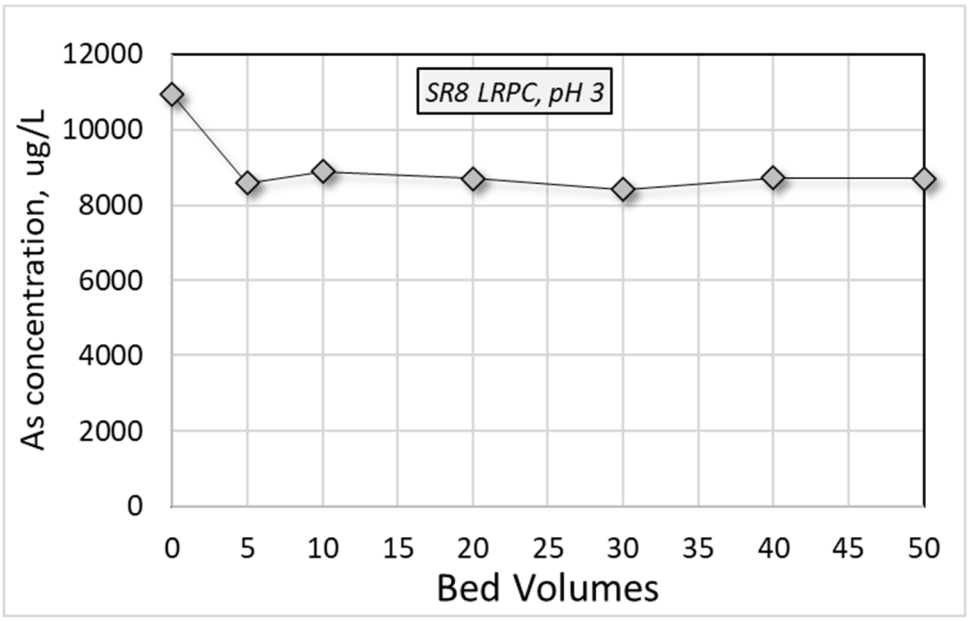

Figure 13 – Arsenic removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, ZVI only fixed bed column.

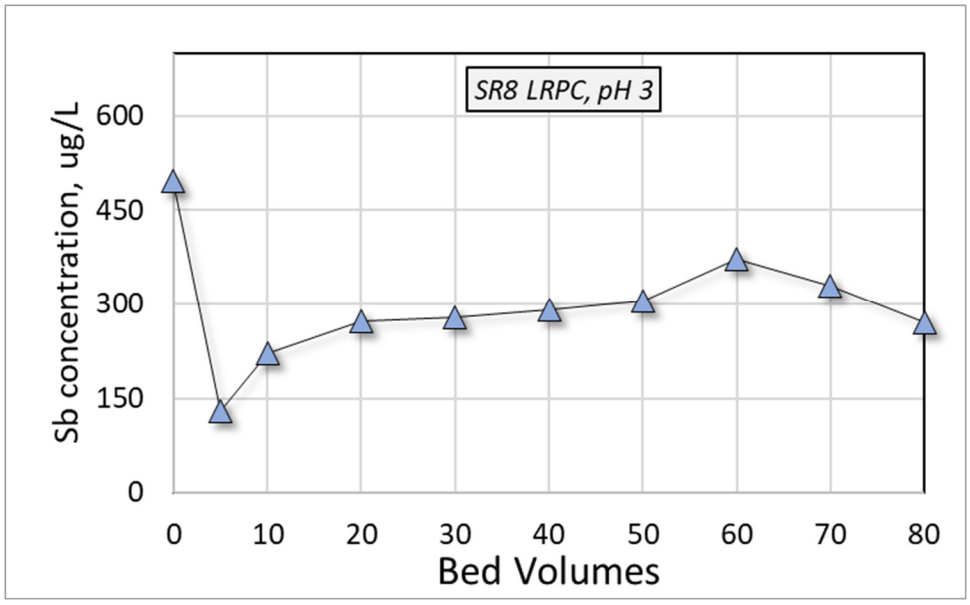

Figure 14 - Antimony removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, ZVI only fixed bed column.

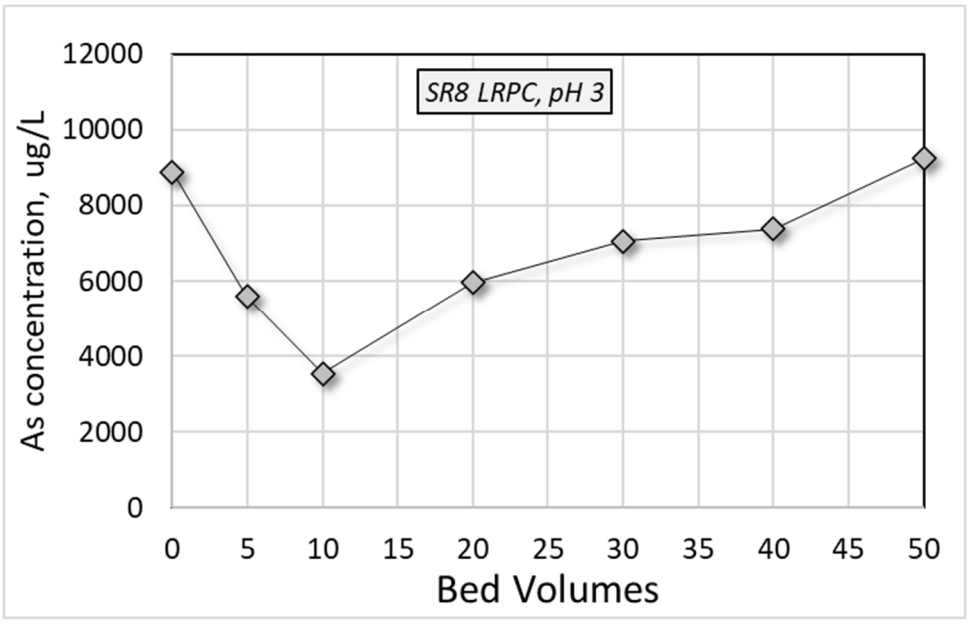

Figure 15 – Arsenic removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers.

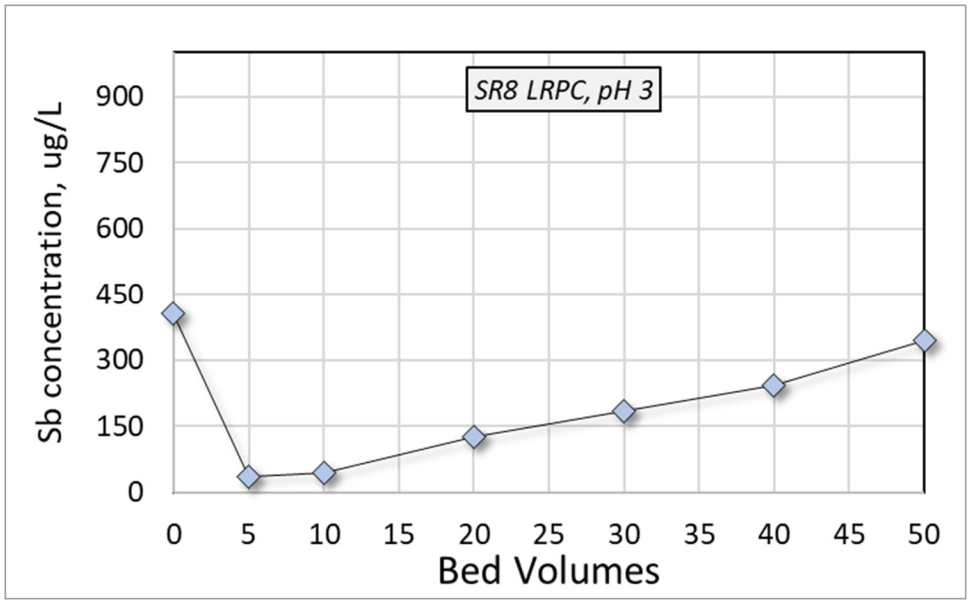

Figure 16 - Antimony removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers.

These data show that the most effective choice out of these three for removal of arsenic, within the first 10 BV is the alternating layers of GAC and ZVI. The use of GAC and ZVI corresponds to ME-type conditions and the use of alternating layers instead of a mixture was to minimize the chance of hydraulic fouling within the column. The increase in arsenic concentration after 10 BV seen in both the alternating layer column packing configuration and the GAC or ZVI only data indicate that GAC only and ZVI only column packing are wholly unsuitable for As removal. In the case of GAC/ZVI packing, As removal is somewhat better but still a rapid breakthrough of arsenic indicates the limited ability of this configuration to remove As.

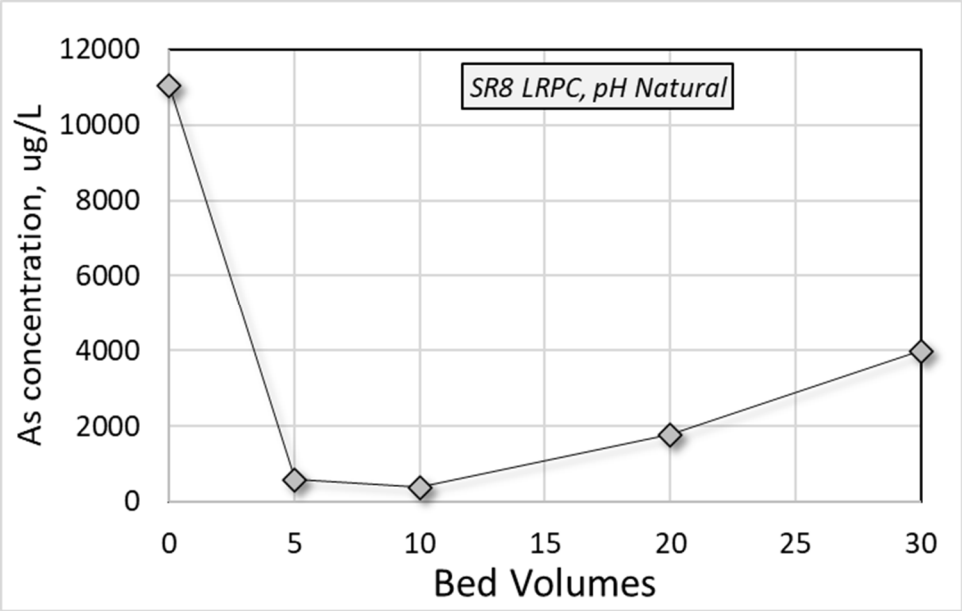

Figure 17 – Arsenic removal from SR8 (filtered), EBCT 10 minutes, natural pH, 0.6 LPM CO_2, PAC coated nano-ZVI.

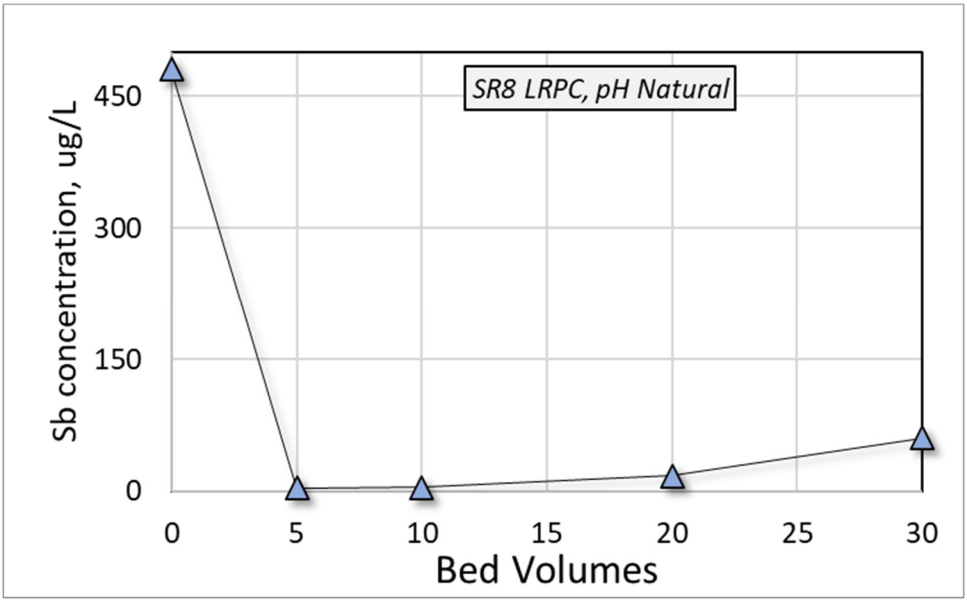

Figure 18 - Antimony removal from SR8 (filtered), EBCT 10 minutes, natural pH, 0.6 LPM CO_2, PAC coated nano-ZVI.

Figure 17 and Figure 18 show that a PAC coated nano-ZVI material, prepared by Po-An Chen performs notably better. This experiment was run without altering the natural pH of SR8 and with the same rate of counterflow gas. PAC was used because GAC granules are too large to coat

the ZVI. The lack of pH adjustment could have had an effect, since the natural pH of SR8 is about 6. This was also run within the 3D printed column unit (a capsule) pictured in Figure 10. While these experiments showed the most effective removal percentage out of all four tests, the test was cut short at 30 BV due to the development of hydraulic blockages mentioned above.

ICP-MS data Effects of GAS/ZVI layer height variations

While using alternating GAC/ZVI layers, it is important to test the differences in arsenic removal using different heights of layers of each adsorbent material. The tested heights of the GAC and ZVI layers were 0.25 cm, 0.5 cm, and 1 cm. The 0.25 and 0.5 cm experiments were run using a pH 5 SR8, while the 1 cm experiment was run using a pH 3 SR8. The lower pH could have aided in the removal of arsenic, since previous research shows a more efficient removal of arsenic species at lower pH. This was done because the 1 cm experiment was part of the previously mentioned experimental group looking at the variation in material combinations.

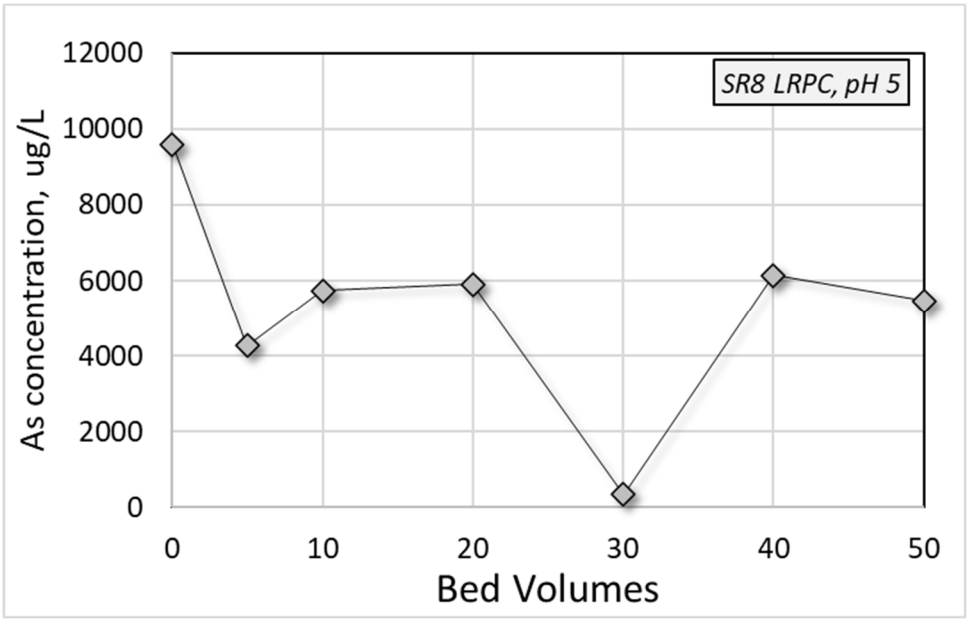

Figure 19 – Arsenic removal from SR8 (filtered), EBCT 10 minutes, pH 5, 0.6 LPM CO_2, GAC and ZVI 0.25 cm alternating layers.

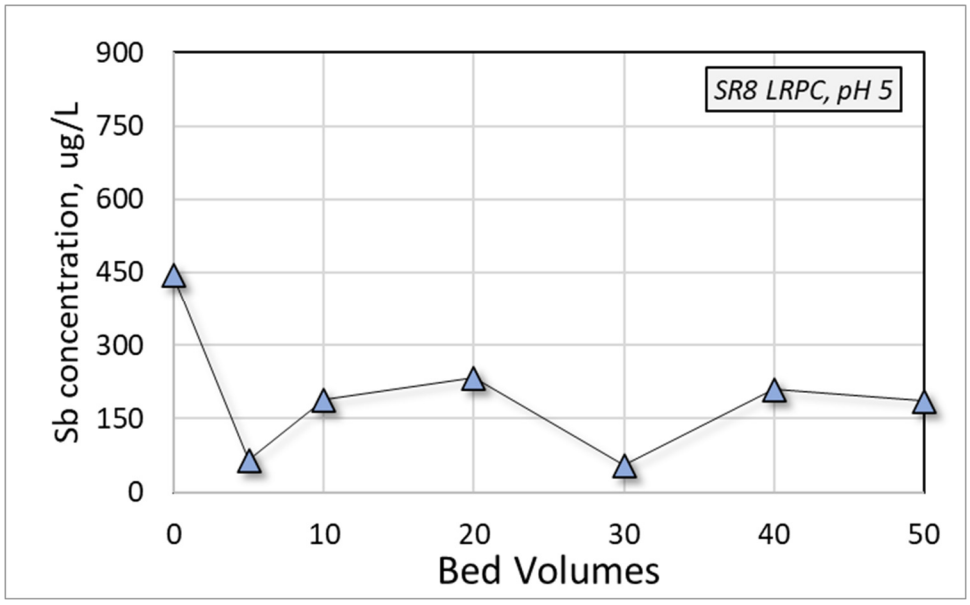

Figure 20 - Antimony removal from SR8 (filtered), EBCT 10 minutes, pH 5, 0.6 LPM CO_2, GAC and ZVI 0.25 cm alternating layers.

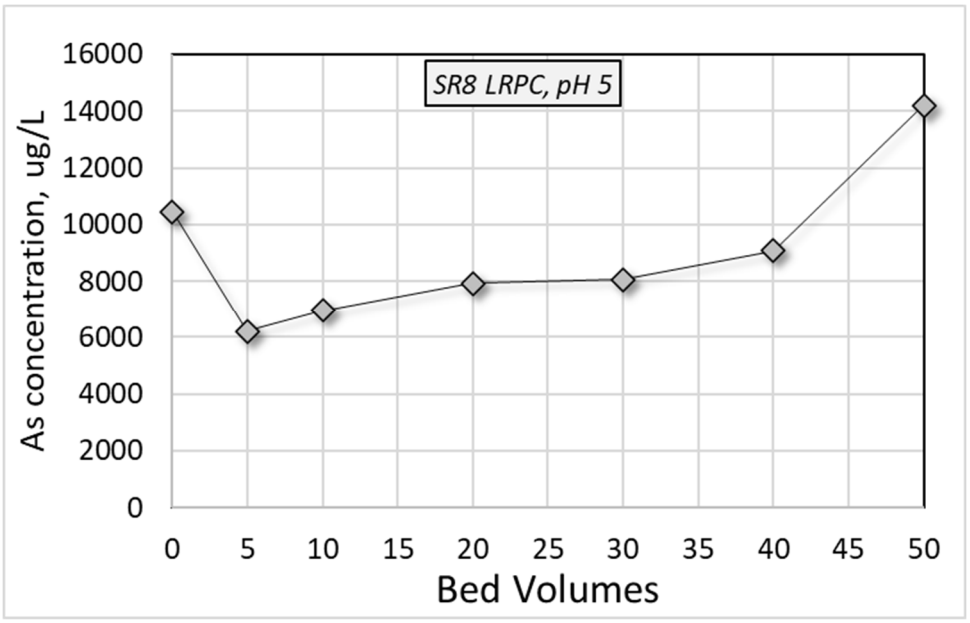

Figure 21 – Arsenic removal from SR8 (filtered), EBCT 10 minutes, pH 5, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers.

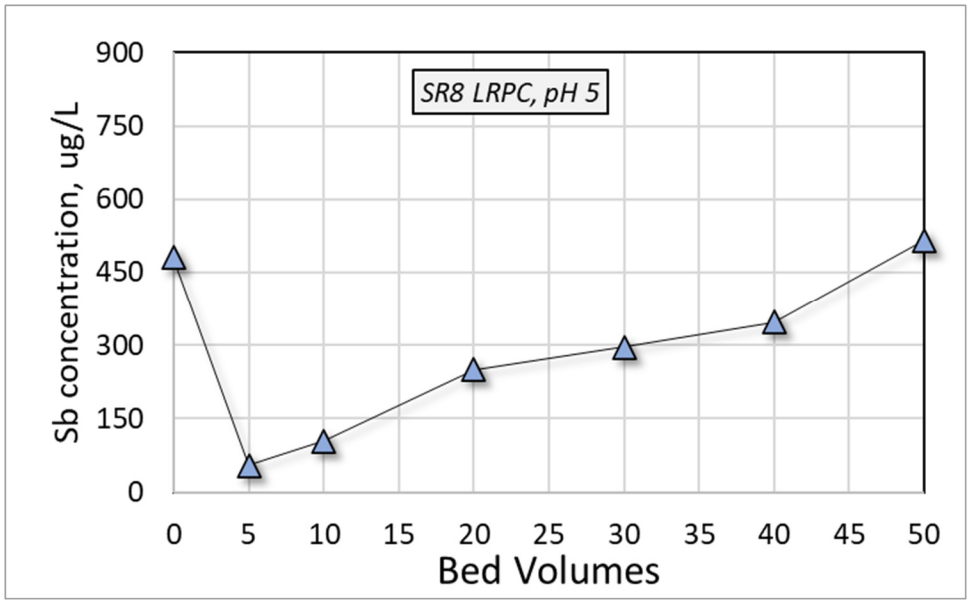

Figure 22 - Antimony removal from SR8 (filtered), EBCT 10 minutes, pH 5, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers.

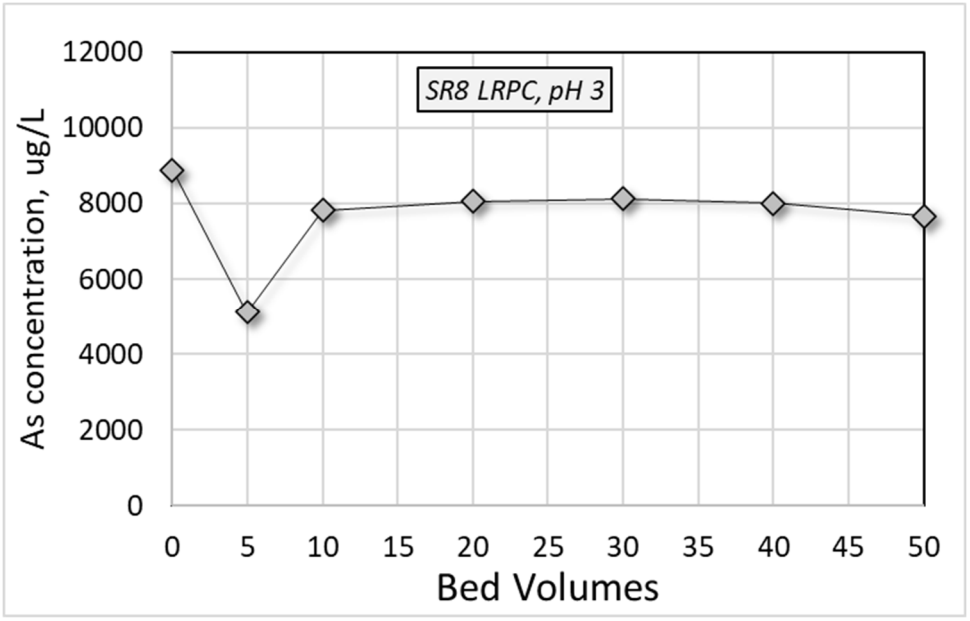

Figure 23 – Arsenic removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 1 cm alternating layers.

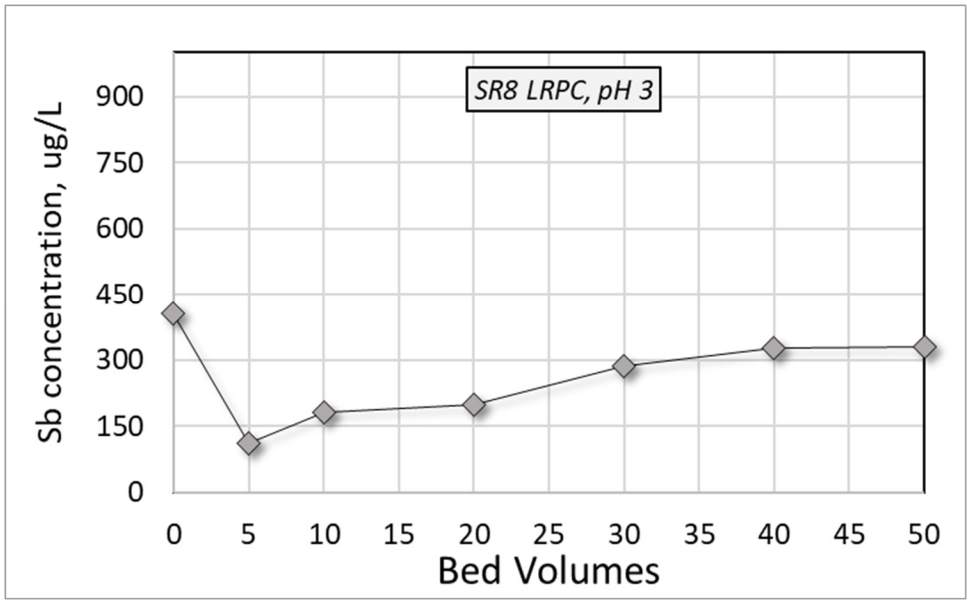

Figure 24 - Antimony removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 1 cm alternating layers.

This set of results was inconclusive, and it was not possible to determine whether alternating the height of the bed layers had a consistent effect on the removal efficiency. In addition, hydraulic resistance developed in all cases. Since the experiments were halted for the time being, future experiments may have more conclusive data.

ICP-MS data –Effects of pH variation of LRPC influent

In order to test whether the pH of the LRPC can affect arsenic removal, a limited experiment was run testing the differences in arsenic removal between a controlled pH of 3 and 5. Both experiments used a GAC and ZVI 0.5 cm alternating layer, and a counterflow of 0.6LPM CO_2.

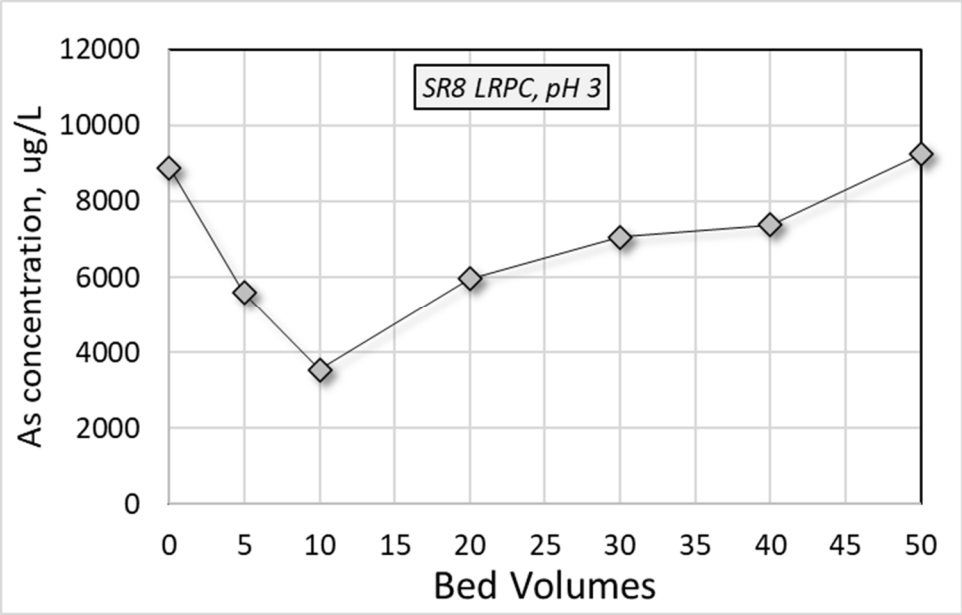

Figure 25 – Arsenic removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers.

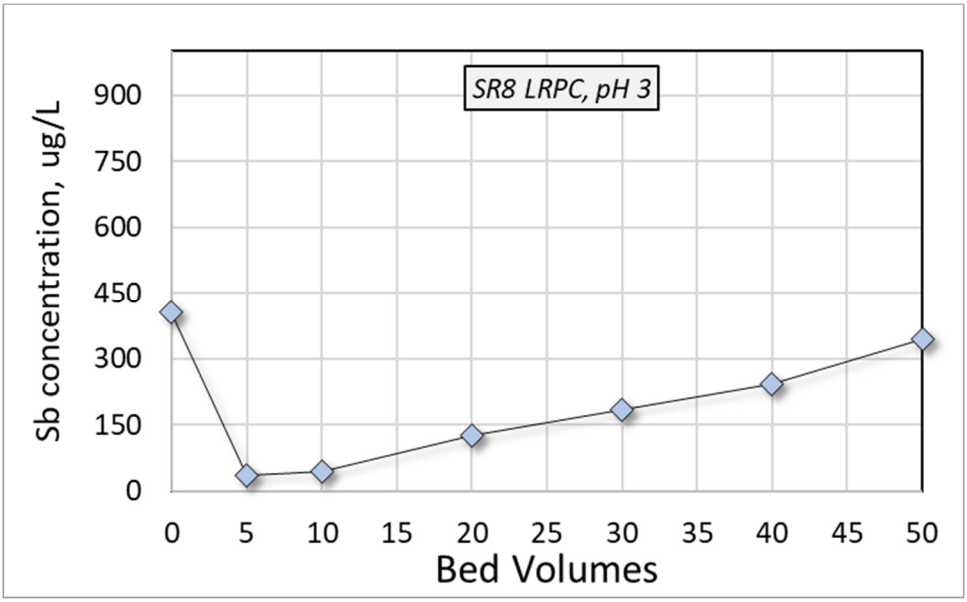

Figure 26 - Antimony removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers.

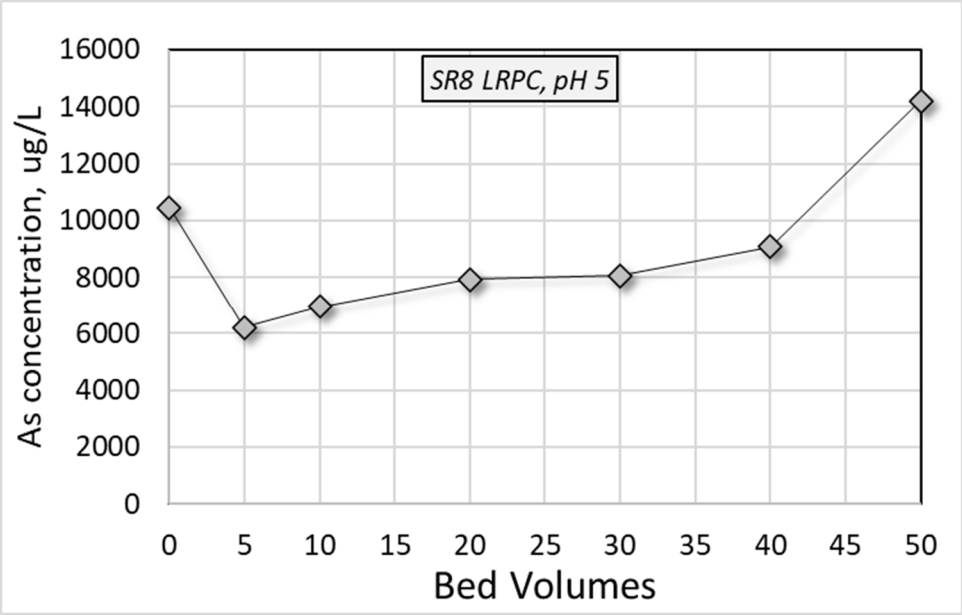

Figure 27 – Arsenic removal from SR8 (filtered), EBCT 10 minutes, pH 5, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers.

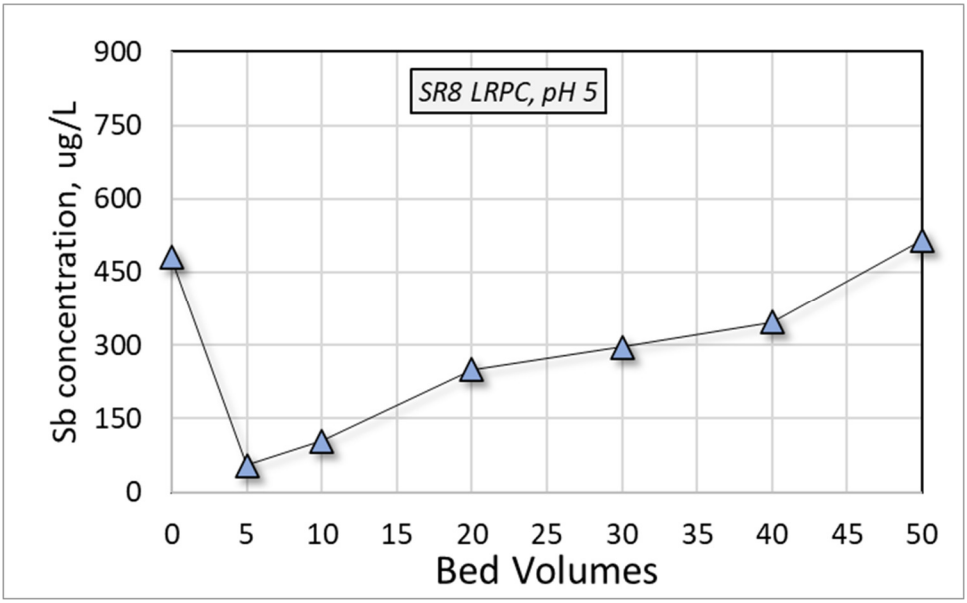

Figure 28 - Antimony removal from SR8 (filtered), EBCT 10 minutes, pH 5, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers.

Comparison of the data generated for pH values of 3 and 5 shows that more initial removal of As and Sb in the case of the column run at pH 3. This matches the hypothesis that since lower pH values increase redox potential of a solution, a lower pH solution would result in a higher

reduction of arsenic species and therefore easier removal of said species from solution. Both of the experiments had an increase in arsenic after 10 BV, however the initial removal is more effective using an LFG condensate controlled at pH 3.

In all, the removal of As in neither of the examined conditions was sufficient, and further tests were halted. Still, this was a limited set of experiments, however, and future experiments using ME treatment may explore further effects of pH variations on As removal from LRPC.

ICP-MS data – Effects of pretreatment of LRPC influent

The last variation to the fixed bed column experiments to be covered in this thesis compares the differences in arsenic removal between filtered SR8, using the 1 µm cartridge filter mentioned above and an LFG condensate sample filtered and then subsequently pretreated with an Aquaboon® GAC cartridge.

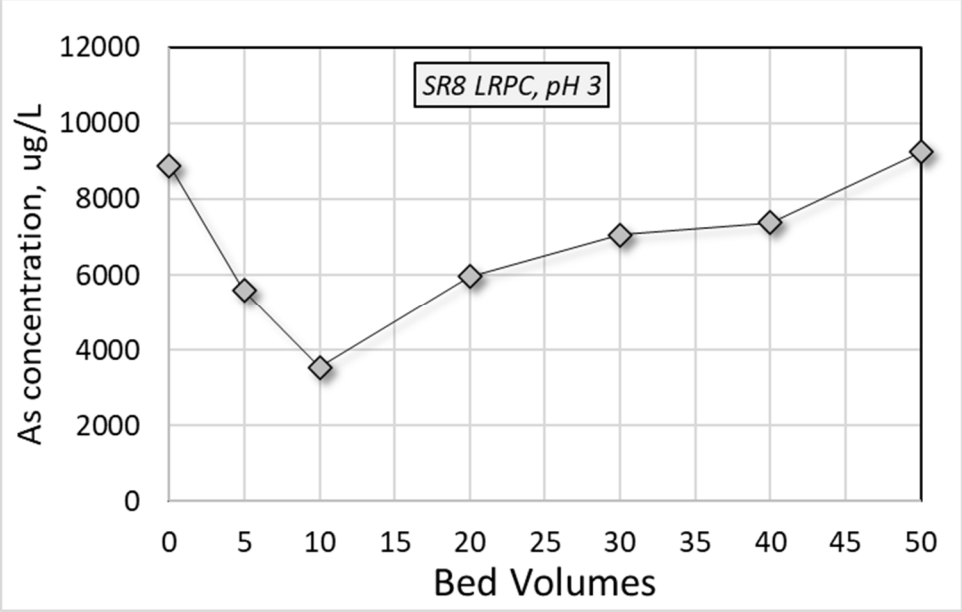

Figure 29 – Arsenic removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers experiment

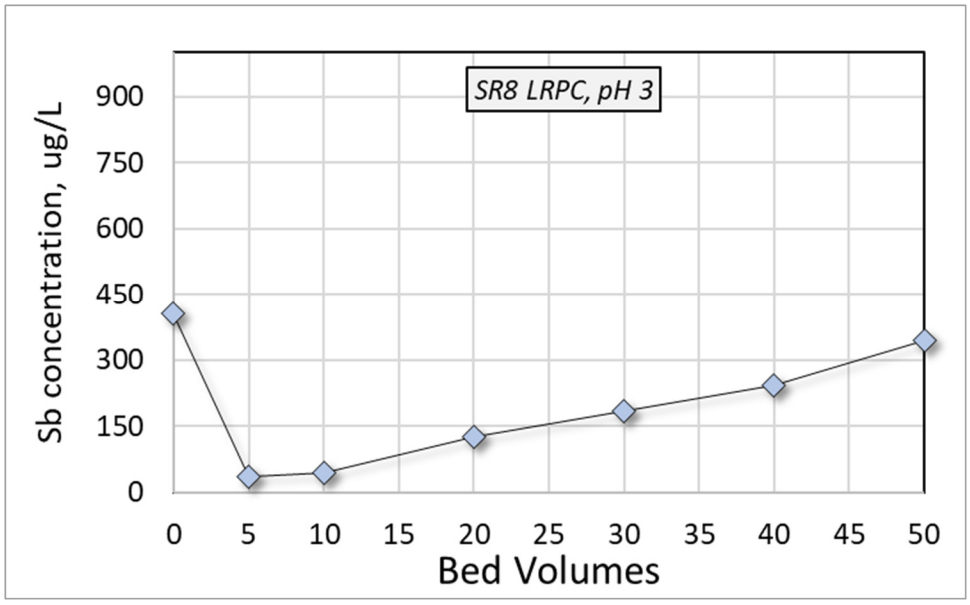

Figure 30 - Antimony removal from SR8 (filtered), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers.

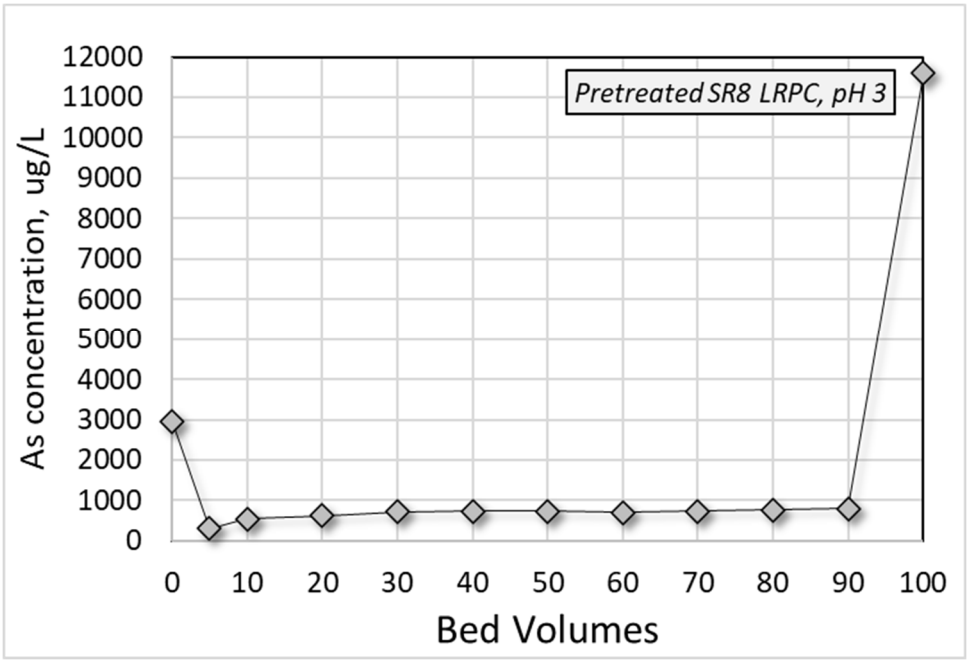

Figure 31 – Arsenic removal from SR8 (filtered and pretreated), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers.

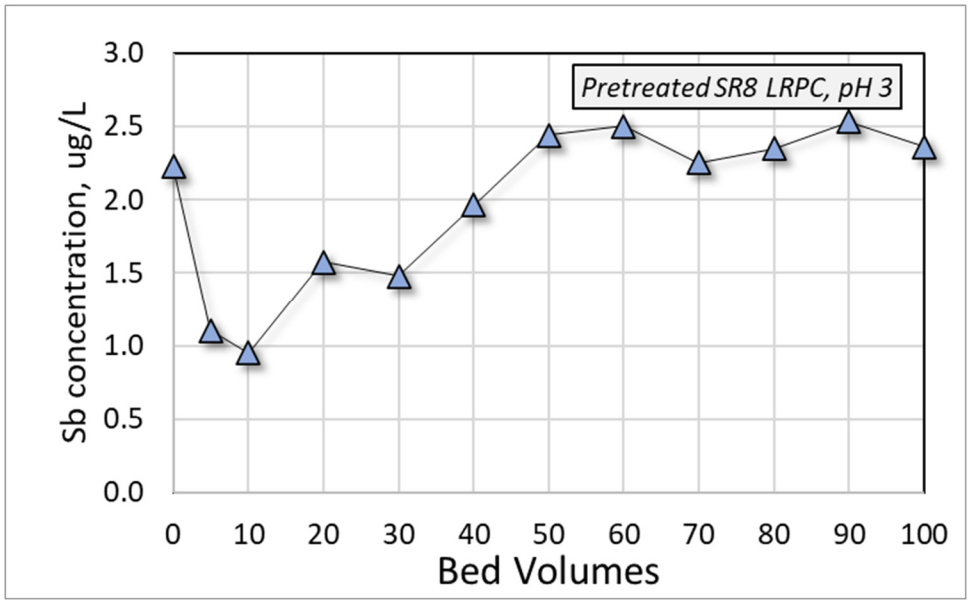

Figure 32 - Antimony removal from SR8 (filtered and pretreated), EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers.

Figures 32 and 33 show an improvement in the collection aspect of the experiment, as 100 BV were able to be collected through the experiment without hydraulic blockages. However, the same issue remains, as previously demonstrated, that the arsenic concentration rises over time. The initial concentration of arsenic is noticeably lower in Figure 32 compared to Figure 30. This is because the sample used for that experiment had been both filtered and pretreated, resulting in a lower starting arsenic concentration. While the addition of a pretreatment step resulted in a decrease in the initial arsenic concentration (this decrease was seen only for the initial one bed volume of the effluent from the GAC column), the removal of As in the ZVI/GAC packed bed column was not consistently improved, as shown in Figure 32 which demonstrates a plateau of arsenic concentration after 10BV, with a large increase of arsenic in the 100 BV collection. This increase could be caused by the release of As that was accumulated over the run time in the column. A similar effect was observed in prior experiments of the UW group (Rifkin 2021). The efficacy of GAC pretreatment of LFG condensate may need to be studied further when the fixed bed column experiments resume.

UV Data from fixed bed experiments

The second set of data discussed here present the results of UV-Vis analysis performed on a portion of the samples collected from the fixed bed column experiments. These analyses were performed between July and September 2021 and illustrate some of the processes quantified based on the ICP-MS data presented in the section above. These variations to the experiment include changes of the material in the fixed bed column, height of bed layer, differences between pretreated and non-treated samples, and differences between two models of GAC pretreatment columns. The peaks in the UV-Vis data represent various organic species within the solution and difference in absorbance curves can lead to a better understanding of what kind of treatments remove light absorbing organics from the LFG condensate. Studying the differences these variations have within the data produced by the UV-Vis can also help better determine the composition of the LFG condensate.

UV-Vis data – Effects of bed packing material

The packing media used for the fixed bed column experiments and examined using the UV-Vis data were GAC only, ZVI only, and alternating GAC and ZVI. The alternating height of bed layers used for comparing the data from these experiments is 0.5 cm. These experiments all use filtered SR8 and a counterflow of 0.6LPM CO_2.

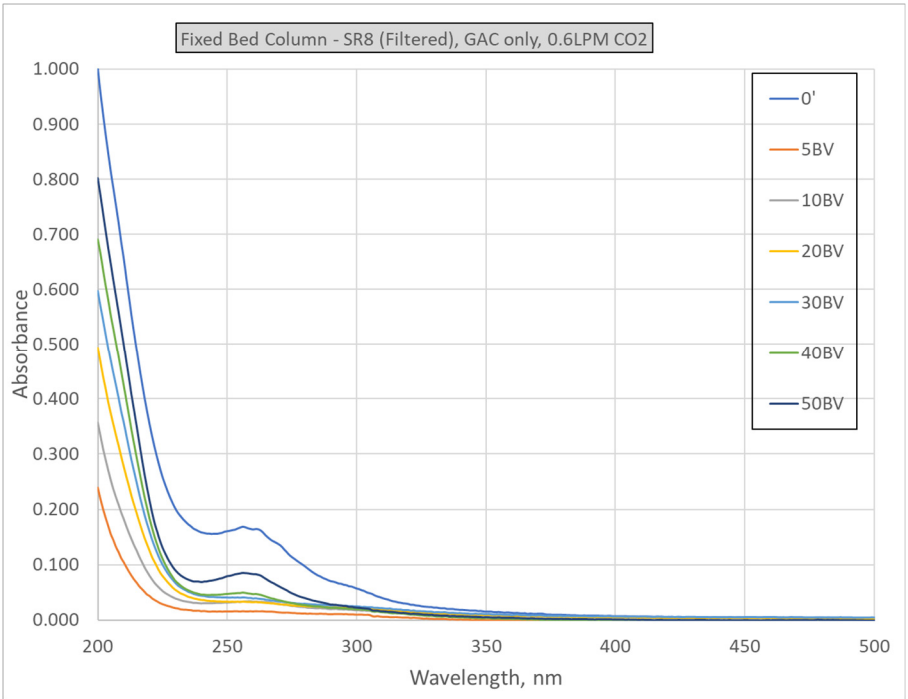

Figure 33 – Absorbance spectra of the SR8 influent (filtered) and selected effluent samples sampled at varying bed volumes. EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC only fixed bed column.

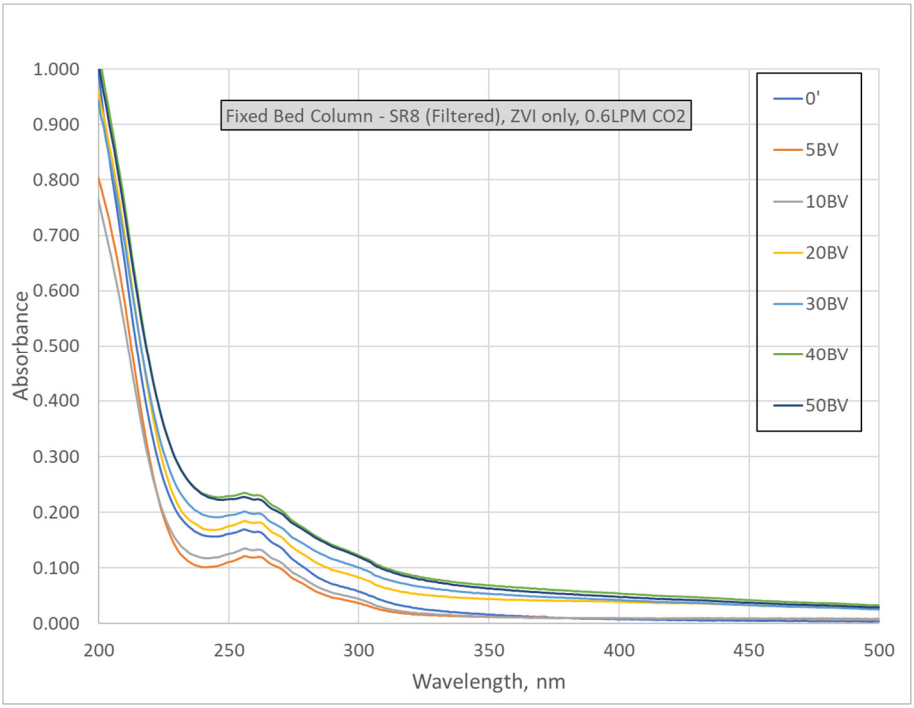

Figure 34 - Absorbance spectra of the SR8 influent (filtered) and selected effluent samples sampled at varying bed volumes. EBCT 10 minutes, pH 3, 0.6 LPM CO_2, ZVI only fixed bed column experiment

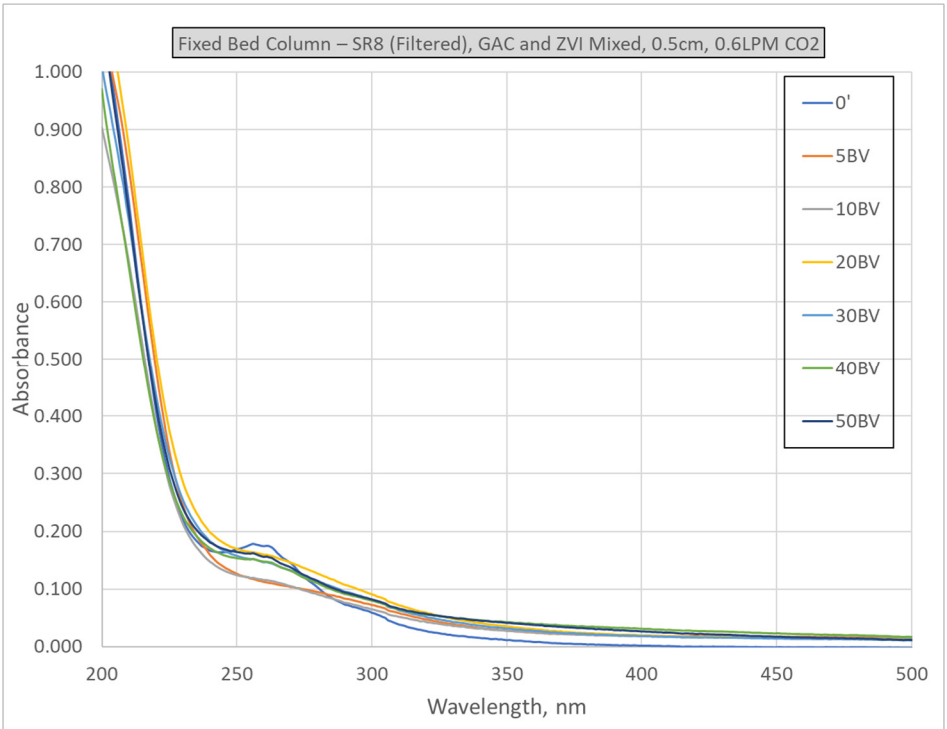

Figure 35 - Absorbance spectra of the SR8 influent (filtered) and selected effluent samples sampled at varying bed volumes. EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers experiment

The experiments show much tighter absorbance spectra fit for the GAC and ZVI alternating layers experiment, however the absorbance on all 3 data sets is relatively low and there does not appear to be major differences in UV-Vis data when the material composition is altered.

UV-Vis data – Effects of the height of alternating GAC/ZVI layers

Similarly compared with ICP-MS analysis, samples were analyzed using the UV-Vis spectrophotometry to identify any differences when the height of an alternating layers experiment was altered. The heights of the layers used in this experiment were 0.25 cm, 0.5 cm, and 1 cm. These experiments also used filtered SR8 and a counterflow of CO_2.

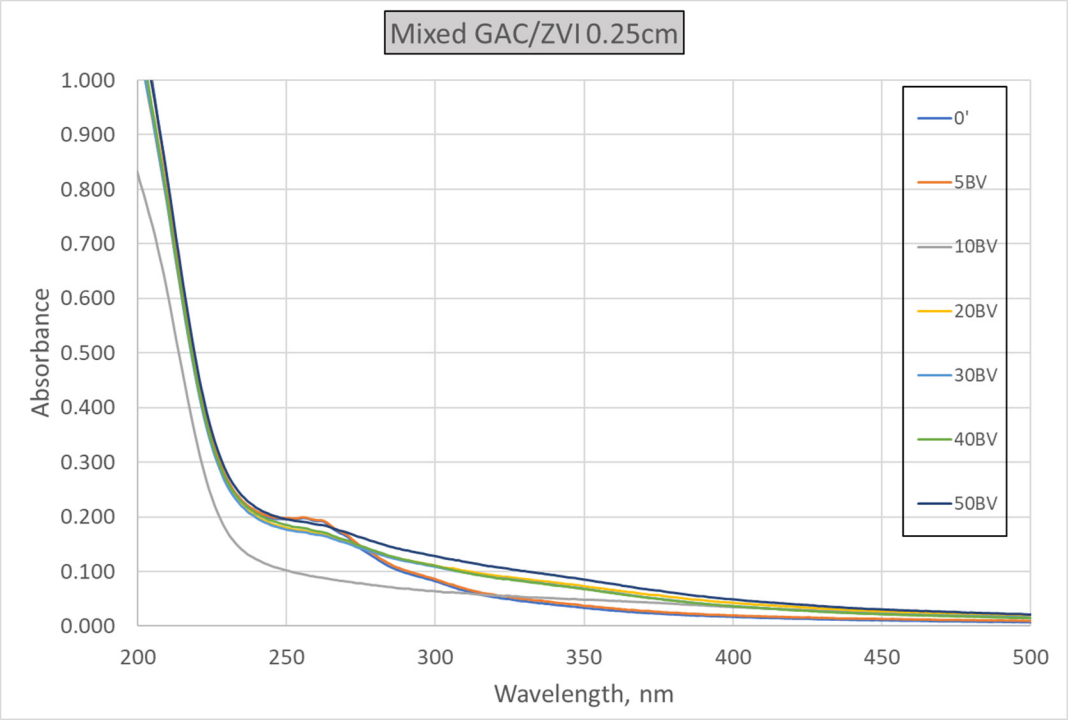

Figure 36 - Absorbance spectra of the SR8 influent (filtered) and selected effluent samples sampled at varying bed volumes. EBCT 10 minutes, pH 5, 0.6 LPM CO_2, GAC and ZVI 0.25 cm alternating layers experiment

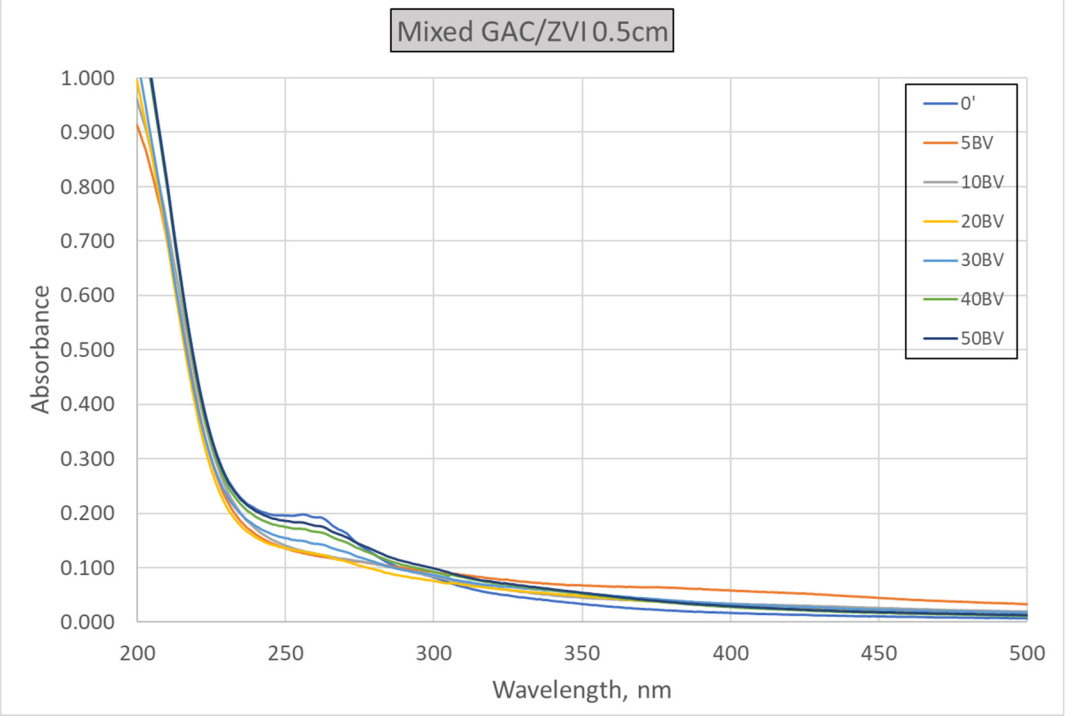

Figure 37 - Absorbance spectra of the SR8 influent (filtered) and selected effluent samples sampled at varying bed volumes. EBCT 10 minutes, pH 5, 0.6 LPM CO_2, GAC and ZVI 0.5 cm alternating layers experiment

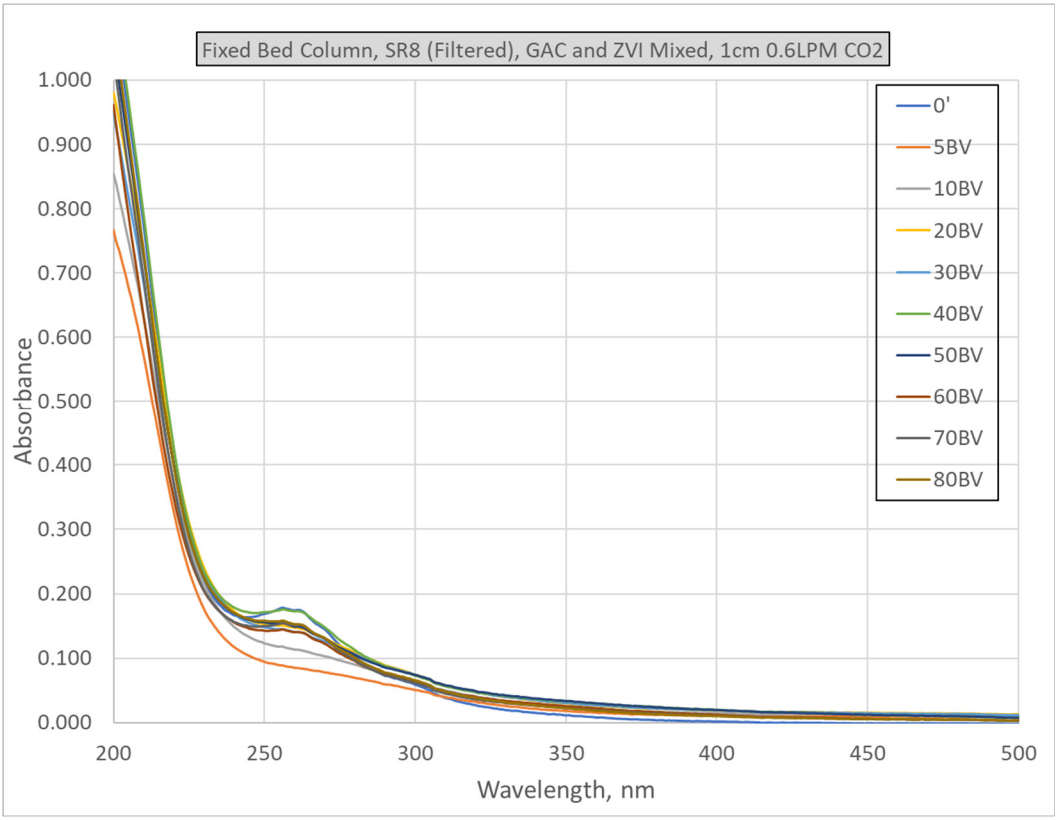

Figure 38 - Absorbance spectra of the SR8 influent (filtered) and selected effluent samples sampled at varying bed volumes. EBCT 10 minutes, pH 3, 0.6 LPM CO_2, GAC and ZVI 1 cm alternating layers experiment

As observed in the above three figures, variations in the height of the bed layer did not seem to have a significant effect on helping identify what light absorbing organics are present in the LFG condensate.

UV-Vis Data – Comparison of the absorbance spectra for pretreated LRPC influent

GAC is known to be a highly effective adsorbent for the removal of organic species, so analysis was performed to analyze the differences between the absorbance curves before and after a SR has been pretreated using a GAC cartridge. The GAC cartridge used for these experiments was a

Barnstead® GAC cartridge and the samples used were taken as part of SR8. Three replicates were analyzed using the UV-Vis before pretreatment, and 3 after. These data are displayed in Figure 40.

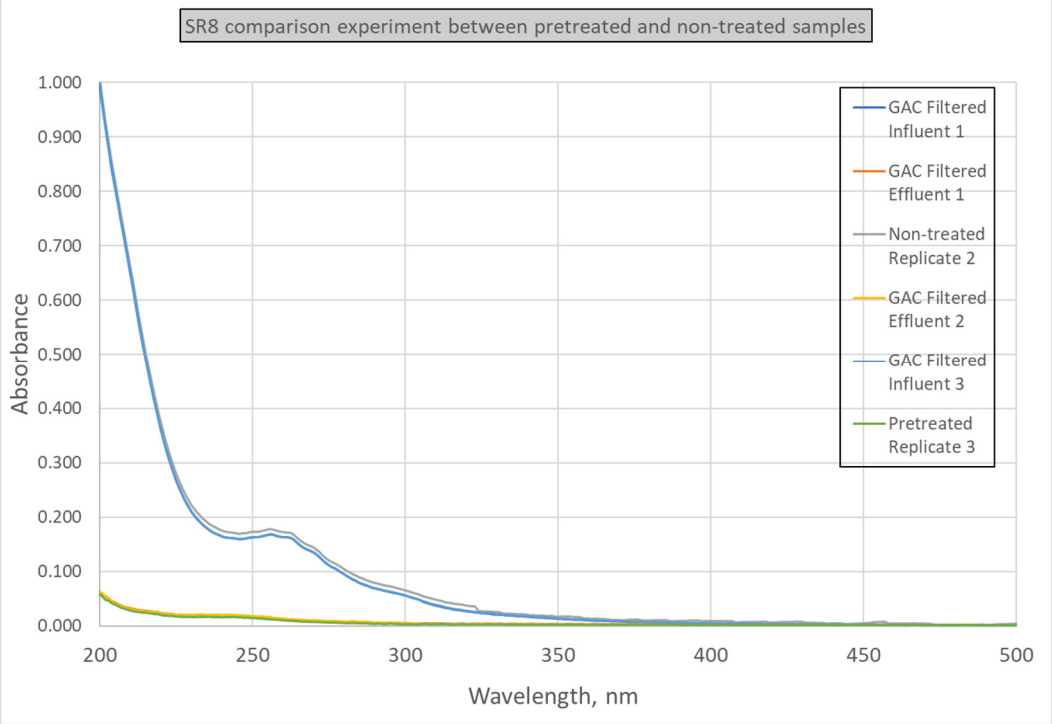

Figure 39 - Absorbance spectra of the SR8 influent (no pretreatment and GAC pretreated). EBCT 10 minutes, natural pH, 0.6 LPM CO_2, filtered vs. filtered and pretreated samples

This analysis showed a massive difference in the absorbance spectra between the non-treated and GAC pretreated samples. After pretreatment with GAC, the absorbance almost fully disappears, compared with the prominent absorbance of the non-treated SR8 LFPC sample. Visually, after pretreatment, the yellow-orange color of the LFG condensate disappears, and the sample becomes clear. The GAC seems to be effective in removing the non-aqueous solutes that provide the LFG condensate with discernible color. However, the removal of organic species, as

indicated by the data shown in Figure 39 did not result in a consistent improvement of the removal of As.

UV-Vis data – Comparison between 2 models of GAC pretreatment cartridges

Two different GAC cartridge models were tested to identify the differences in efficiency of removal of solids between the two manufacturers. The two GAC cartridge manufacturers were Barnstead® and Aquaboon®. The Barnstead® column was older than the Aquaboon® and had a larger bed volume of GAC in the column. Data was collected for 3 replicates of SR8 pretreated using the Aquaboon® and 3 using the Barnstead® Figure 41 illustrates the differences between the two columns.

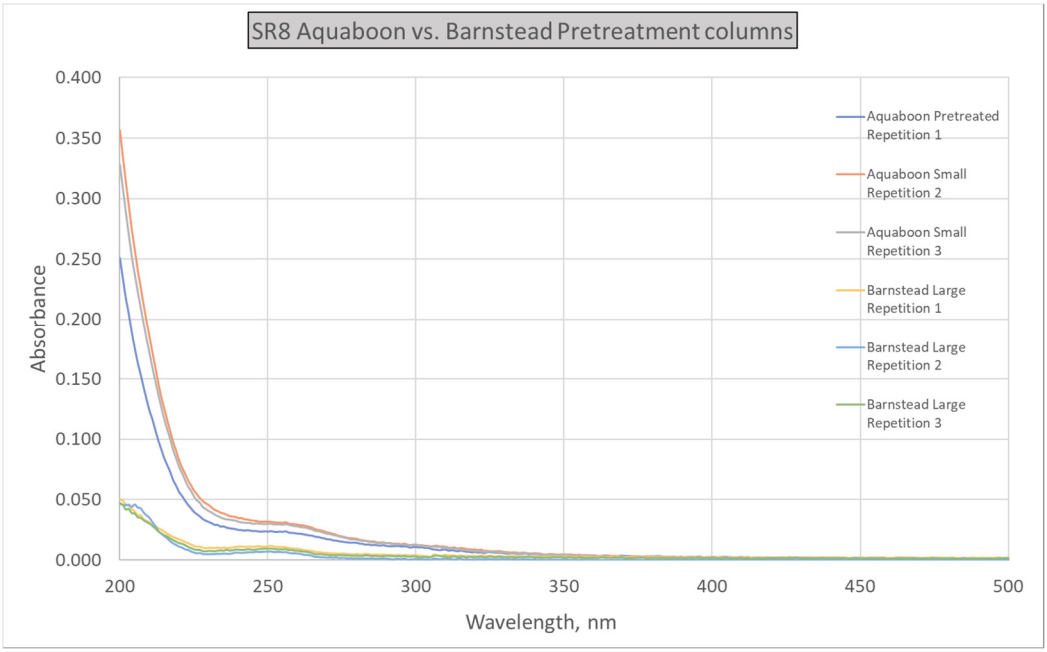

Figure 40 – Absorbance spectra of GAC-pretreated SR8 (filtered), EBCT 10 minutes, natural pH, no CO_2, Aquaboon and Barnstead GAC pretreatment cartridges.

There appears to be a noticeable difference between the two pretreatment columns. The Barnstead® has a much lower absorbance overall and appears to more effective at removing solids.

Summary of the ICP-MS and UV-Vis results for the fixed bed columns

The UV data show that while GAC removes a large fraction of the light absorbing organics within the LRPC water, as exemplified by the data for the SR8 sample. The extent of the removal of absorbance varies somewhat depending on whether the columns were packed with GAC only or GAC/ZVI layers. The notable observation that follows from these measurements is that the extent of the removal of the absorbance of LRPC does not appear to be predictive of the removal of arsenic in the same experiment, as demonstrated by the very low removal of As by the GAC-only packed column and, at the same time, a practically complete removal of the absorbance.

While this observation shows that the removal of absorbance is not predictive of that of arsenic, it also demonstrates that variations of the concentration of light-absorbing organic matter present in LRPC do not significantly affect the performance of the ME approach in the context of As removal. This is an important aspect of ME technology, especially given the wide variability of the properties of LRPC, as was observed in the prior studies of the UW group.

The data also show that while the removal of As in packed bed columns was not sufficient to implement this approach in practical applications, it may need to be studied and optimized further to find a method to prevent the rapid development of hydraulic resistance observed for the GAC/ZVI columns. The results thus necessitate further development of the treatment in batch

or continuous flow reactors with suspended PAC/ZVI phases. This is discussed in more detail in the sections that follow.

As removal in batch ME column reactor experiments

After the fixed bed reactor operations were halted, operations began on ME column reactor experiments. Following the ME experiments conducted in 100 mL beakers that proved efficient at removing arsenic and antimony, experiments were conducted testing larger 1 L reactor columns. Starting with a single 1 L column, these experiments are currently operating within 5 identical 1 L reactor columns. The purpose of increasing the size is to better understand operating conditions as the final scope of this project is to commission a full-size treatment setup at the landfill utility in question. In order to work toward the most efficient arsenic removal for ME treatment, experiments were run testing different variations to the ME column reactor treatment. The experimental conditions covered in this section are summarized in Table 6:

Table 6 - Experimental conditions for 1 L ME column experiments (batch mode)

Conditions	Individual experiments
Shape of reactor column bottom	Flat (Clear PVC)
	Conical (3D Printed PLA)
	Funnel (3D Printed PLA)
Operating pH	4
	5
	6
Adsorbent concentration	1 g/L (2 : 1 ZVI:PAC ratio)
	2 g/L (2 : 1 ZVI:PAC ratio)
	4 g/L (2 : 1 ZVI:PAC ratio)
Adsorbent timing	Timing 1: Added in full at the beginning of the experiment
	Timing 2: Half and half (beginning, 2 hours in)
	Timing 3: Quarters (beginning, 1 hour in, 2 hours in, 3 hours in)
Adsorbent addition method	Addition Method 1: Top addition for solid mixture

	Addition Method 2: Top addition with assist from 3D printed funnel for solid mixture
	Addition Method 3: Top addition for ZVI, DI water slurry addition for PAC
	Addition Method 4: Top addition for ZVI, premixed with LFG condensate for PAC
Counterflow gas conditions	Gas Timing 1: Constant gas flow throughout experiment
	Gas Timing 2: Gas cycling on/off, 10-minute intervals
	Gas Timing 3: Gas cycling on/off, 20-minute intervals
Filtration methods for collected samples	Not filtered
	Filtered post sample collection
	Inline filtration during experiment

The examined experimental conditions cover changes to the design of the bottom part of the reactor column, variations of operating pH, different adsorbent conditions (varying concentration, addition timing, and addition method), different counterflow gas conditions (continuous flow vs. cycling on/off), filtration methods for collected samples (not filtered, filtered post sample collection, filtered online), and repeatability between different column reactors (CR).

For the ME column reactor experiments, a requisite amount a LRPC sample, or a model solution is held in a batch, typically in a pH-controlled environment. The solution is added to the column through the open top in increments of 100 mL, until a volume of 500 mL is reached. A combination of ZVI (first activated with 0.1M HCl) and PAC at a 2:1 weight ratio (ZVI:PAC) is then added to the solution, typically through the open top of the column (although the most effective method of addition is tested) in varying concentration. A counterflow gas is pumped into the solution from the bottom of the column, either constantly or in a preprogrammed on/off sequence. Samples are collected at varying times, depending on the experimental conditions.

Currently, samples are filtered using a 0.45 µm syringe filter attached online to the system, however samples were previously filtered using the same type of filter post-sample collection.

Only ICP-MS data have been collected from current ME column reactor experiments. Since the UV-Vis data collected from the fixed bed column reactor experiments helped improve the understanding of the makeup of the LRPC and establish that the removal of the absorbance of LRPC is not necessarily predictive of that of arsenic, the primary concern for the ME column reactors is arsenic removal. ICP-MS data for antimony removal is also included, providing similar information to the project as for the fixed bed column reactor experiments.

ICP-MS Data from ME column reactors:

ICP-MS data – Effects of the shape of column reactor bottom parts

This set of experiments was conducted between October and December of 2021. At this time, only one column had been constructed, so all experiments were performed using column reactor 1 (denoted henceforth as CR1). Additionally, all three of the experiments were conducted over a 24-hour time. The first experiment, conducted with filtered SR9, used a flat bottom column reactor. The pH of this sample was not controlled to a certain value, used 1 g/L of the Fe:C ratio described above. The second experiment used a 3D printed dome shaped bottom with a gas inlet hole and the third used a 3D printed funnel shaped bottom with a gas inlet hole. Both the second and third experiment used SR12, a controlled pH of 4, and 2 g/L adsorbent material. The first experiment was conducted in October 2021, with the following two conducted in December 2021.

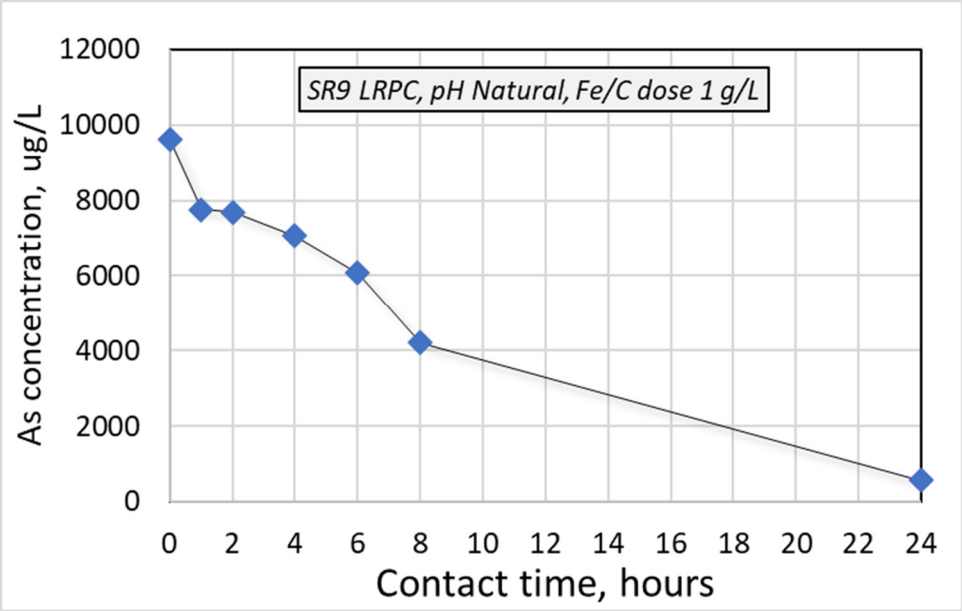

Figure 41 – Changes of arsenic concentrations for CR1, SR9 (filtered), natural pH, 1 g/L Fe/C, 0.6 LPM CO_2, column design experiment (flat bottom)

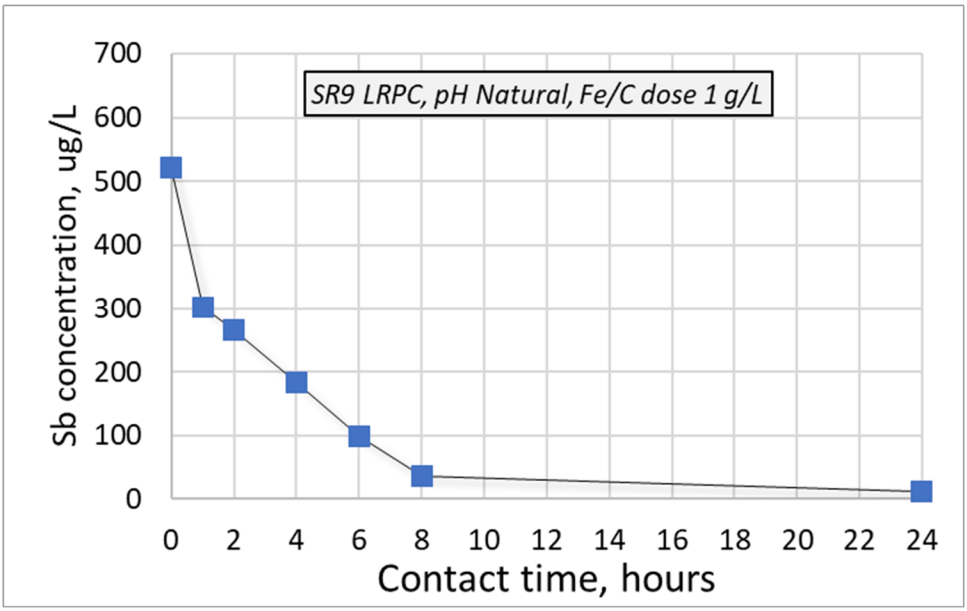

Figure 42 - Changes of antimony concentrations for CR1, SR9 (filtered), natural pH, 1 g/L Fe/C, 0.6 LPM CO_2, column design experiment (flat bottom)

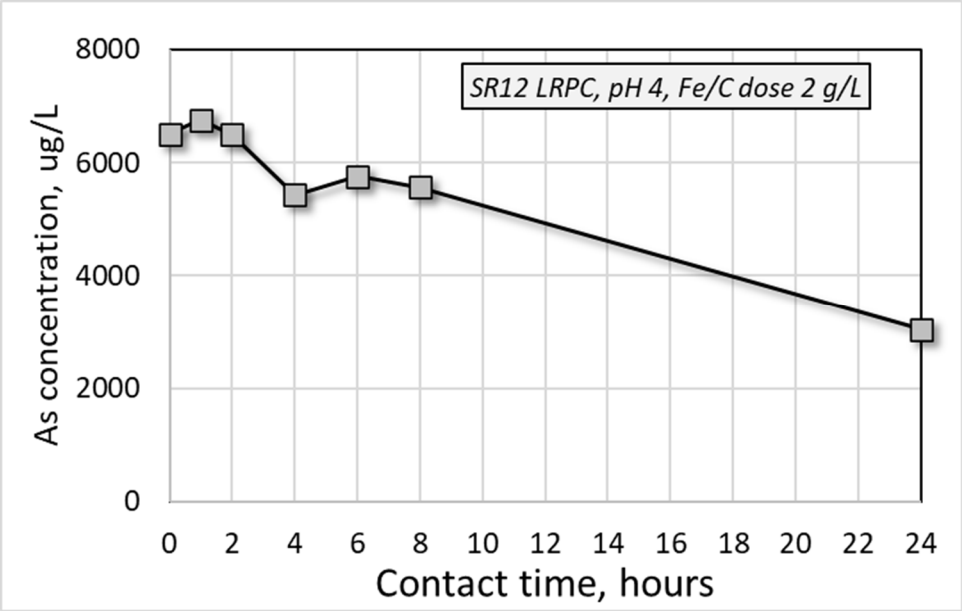

Figure 43 - Changes of arsenic concentrations for CR1, SR12 (filtered), pH 4, 2 g/L Fe/C, 0.6 LPM CO_2, column design experiment (dome bottom)

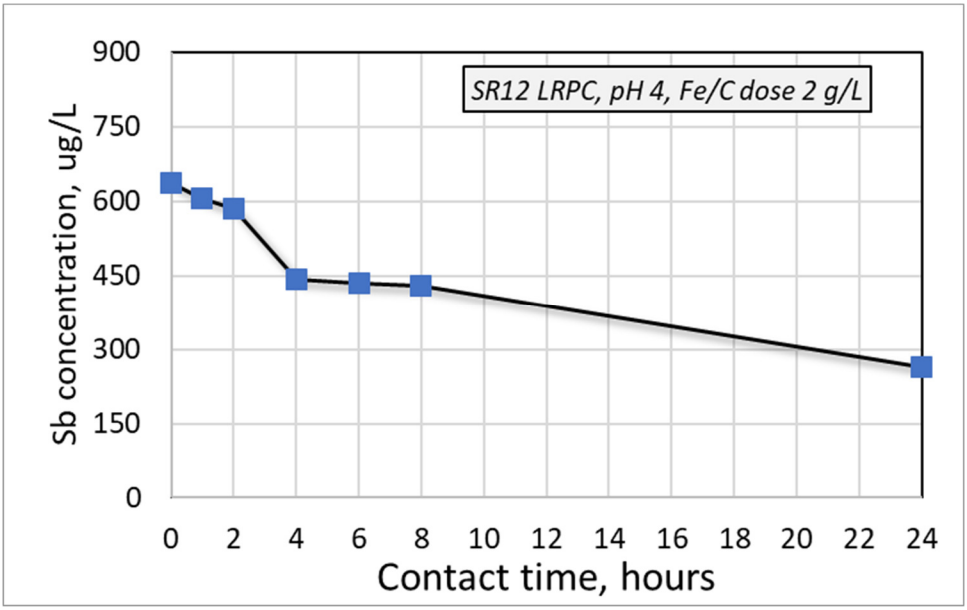

Figure 44 - Changes of antimony concentrations for CR1, SR12 (filtered), pH 4, 2 g/L Fe/C, 0.6 LPM CO_2, column design experiment (dome bottom)

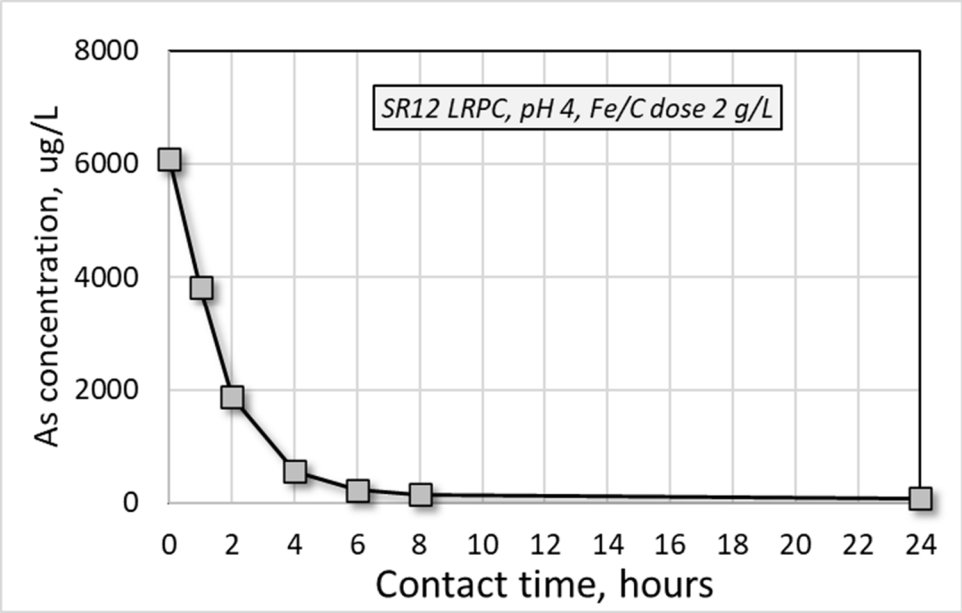

Figure 45 - Changes of arsenic concentrations for CR1, SR12 (filtered), pH 4, 2 g/L Fe/C, 0.6 LPM CO2, column design experiment (funnel bottom)

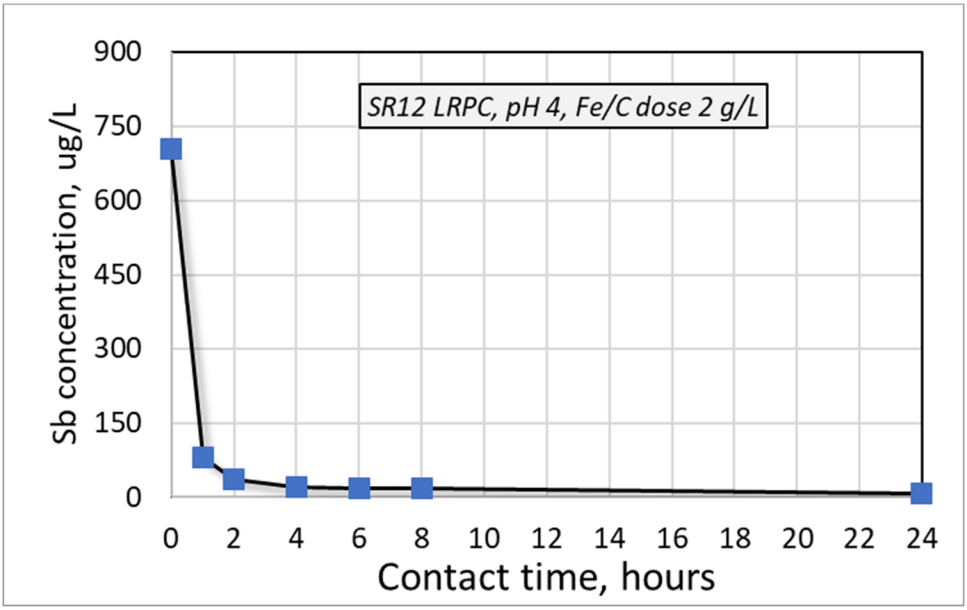

Figure 46 - Changes of antimony concentrations for CR1, SR12 (filtered), pH 4, 2 g/L Fe/C, 0.6 LPM CO2, column design experiment (funnel bottom)

From these data, it is clear that the most efficient removal of arsenic and antimony was achieved through the use of the reactor equipped with the funnel-type bottom part. By the end of the 24-

hour experiment, nearly all of the arsenic and antimony had been removed. The dome reactor column performed the worst, followed by the flat bottom reactor. Using this information, future ME column experiments have been conducted using the funnel design for the bottom part of each of the CRs.

ICP-MS data – Effects of pH

In order to find the most efficient operating condition, the pH of the LFG condensate was tested at several levels. Previously conducted ME experiments had showed increased efficiency of arsenic removal at more acidic conditions, so these experiments cover pH 4, 5 and 6. All of these experiments were conducted using 500 mL of SR12 in CR1 with the funnel bottom component mentioned above, 2 g/L of the adsorbent mix, a constant flow of 0.6 LPM CO_2, and a 24-hour experiment time.

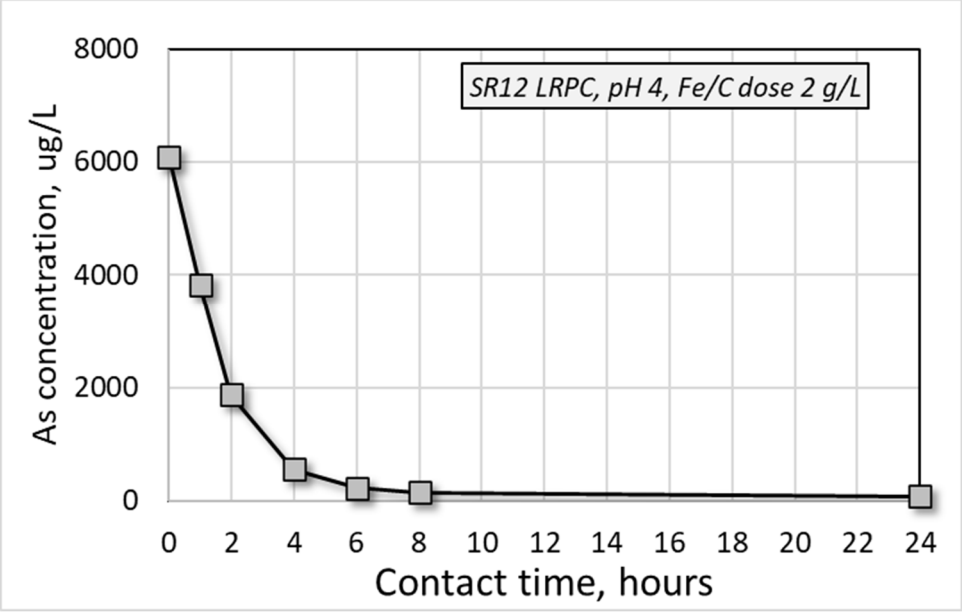

Figure 47 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L Fe:C, pH4, 0.6 LPM CO_2, pH variation experiment.

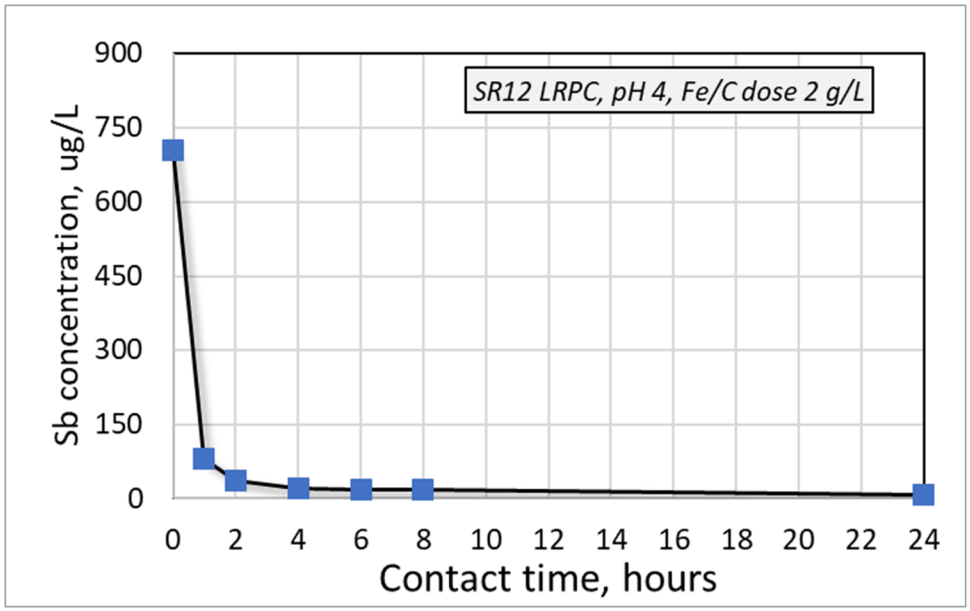

Figure 48 - Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2, pH variation experiment

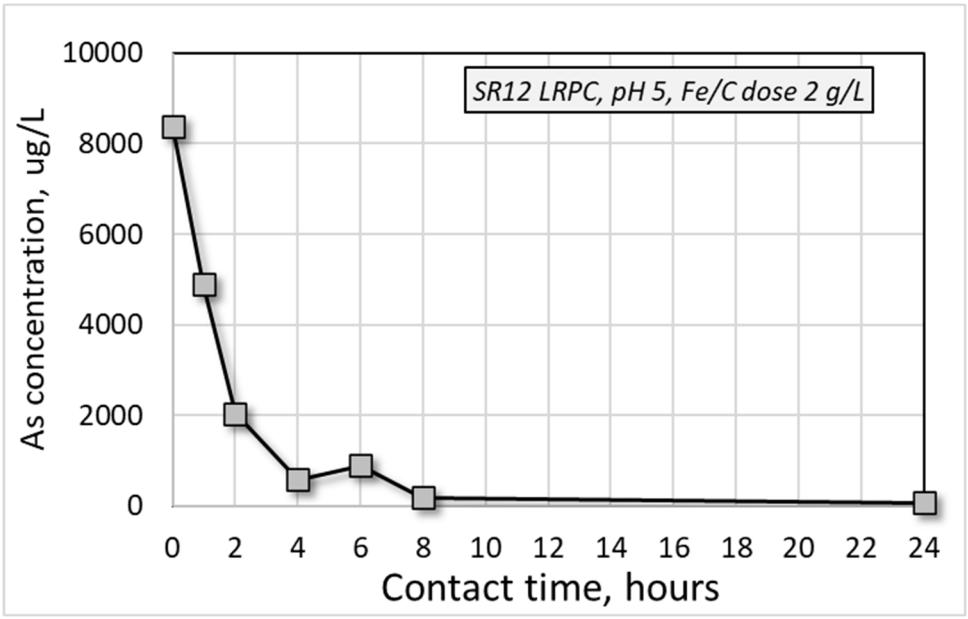

Figure 49 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH5, 0.6 LPM CO_2, pH variation experiment

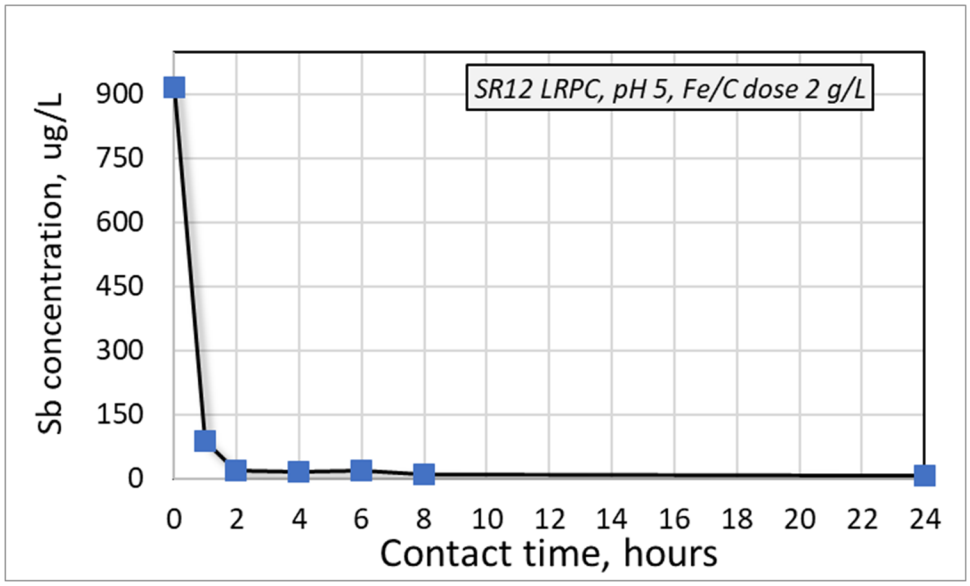

Figure 50 - Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH5, 0.6 LPM CO_2, pH variation experiment

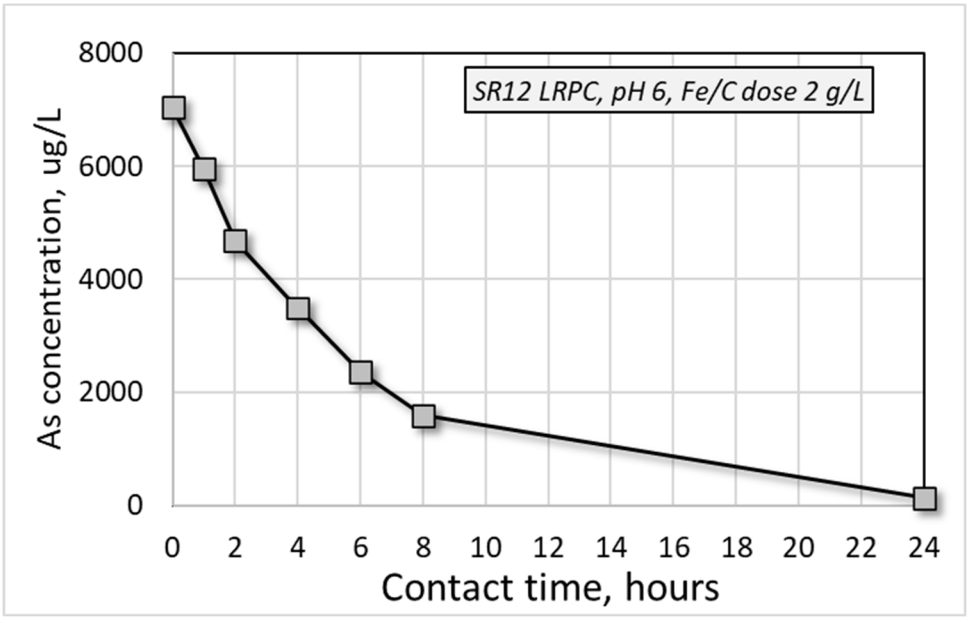

Figure 51 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH6, 0.6 LPM CO_2, pH variation experiment

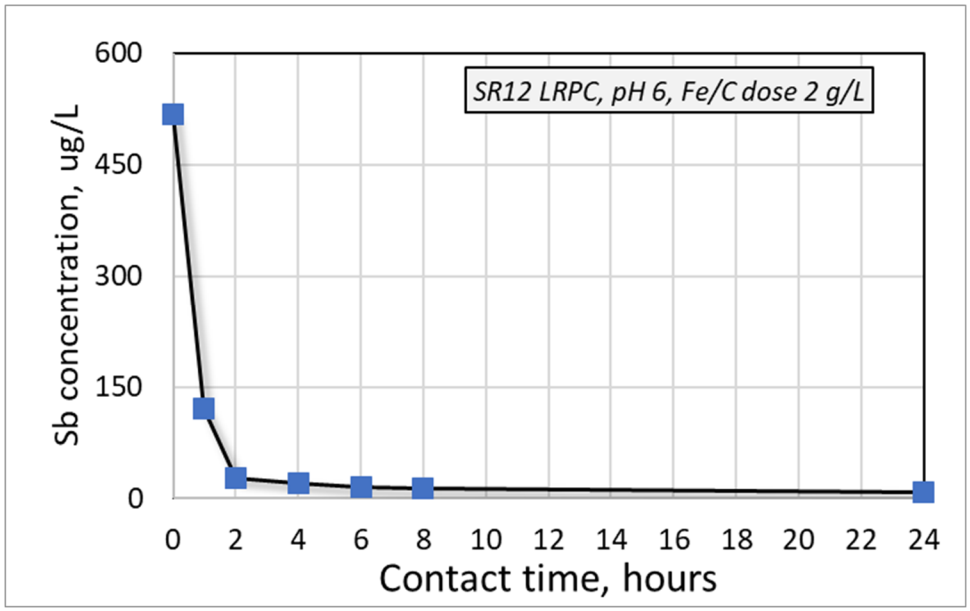

Figure 52 - Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH6, 0.6 LPM CO_2, pH variation experiment

For all three experiments, the arsenic removal by 24 hours was nearly 100%. Figure 48 shows a steady removal of arsenic, with a stable decline over each sampling period. Figure 50 shows a similar removal of arsenic with a slightly less consistent behavior. The slight increase of arsenic concentration at the six-hour mark is most likely due to an experimental error and is not related to the pH during the experiment. The final experiment, represented by Figure 52, shows a much slower removal of arsenic compared to pH 4 or pH 5. The antimony removal, however, seems unaffected by a pH change, at least within the pH range of 4 to 6. With this data, we can confirm data from earlier experiments that showed an increase in the efficiency of arsenic and antimony removal when the experiment is controlled at a lower pH.

ICP-MS Analysis – Effects of variations of PAC/ZVI adsorbent concentration

Total adsorbent concentration controls how quickly the arsenic level decreases within an ME column experiment. Larger concentrations of ZVI and PAC may result in a quicker decrease in

arsenic, shortening the experiment time. Larger concentrations are also more expensive, so these experiments were run to compare doses to find an optimal concentration of adsorbent. All three experiments were ran using LFG condensate from SR12, controlled to a pH of 4, and used a constant CO_2 gas counterflow of 0.6 LPM.

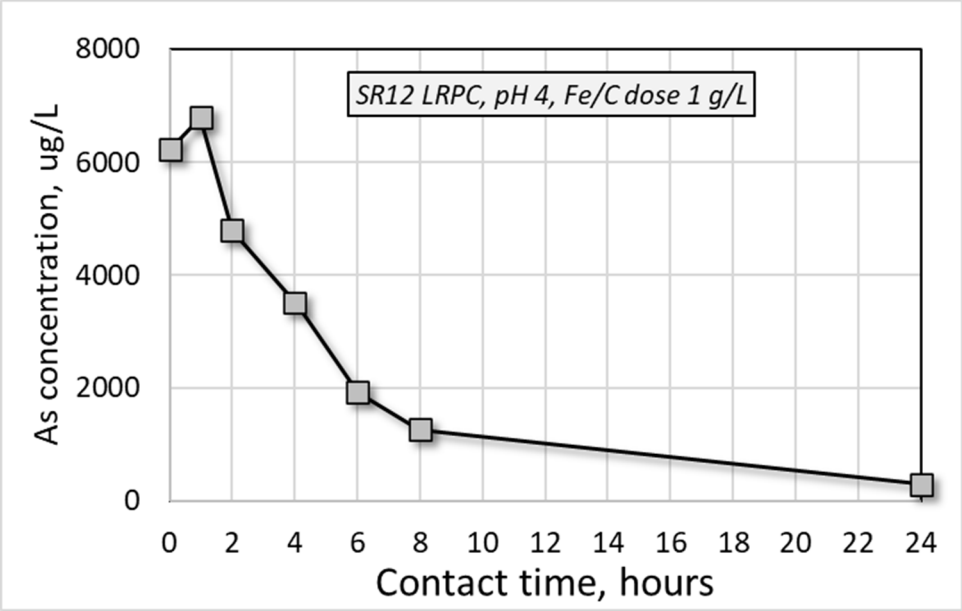

Figure 53 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 1 g/L FeC, pH4, 0.6 LPM CO_2, adsorbent dose variation experiments

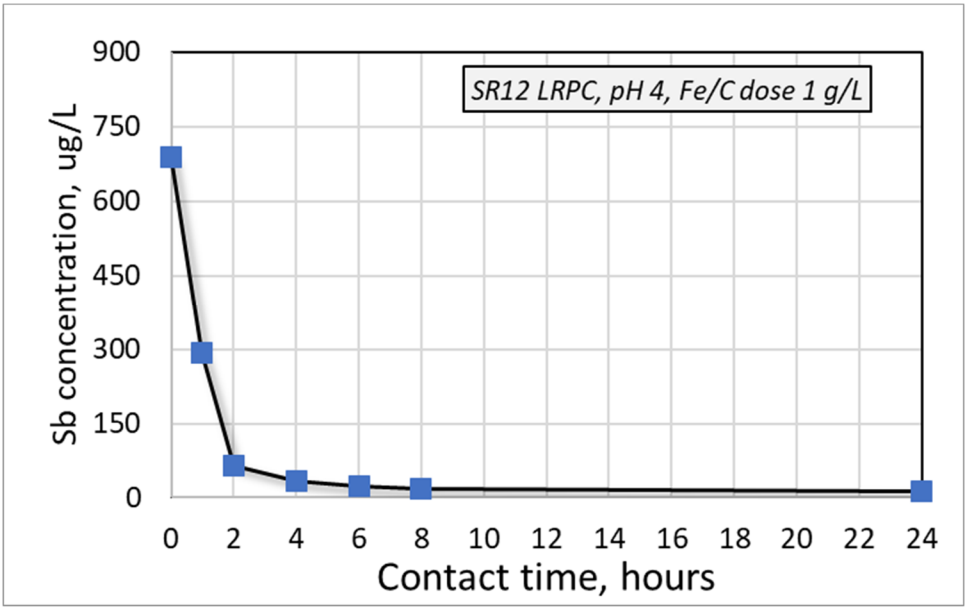

Figure 54 - Changes of antimony concentrations in ME batch reactor, SR12 (filtered), 1 g/L FeC, pH4, 0.6 LPM CO2, adsorbent dose variation experiments

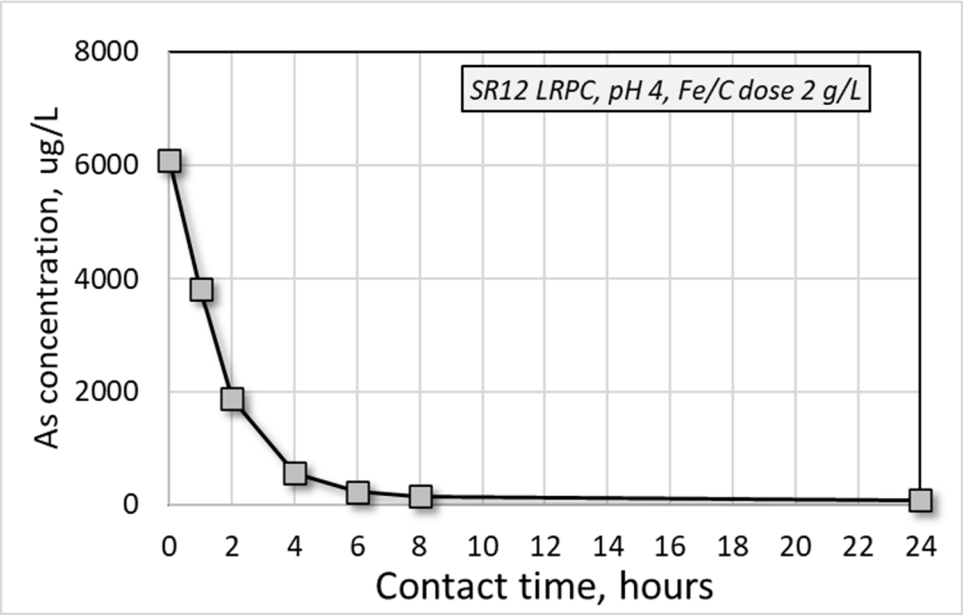

Figure 55 - Changes of arsenic concentrations in ME batch reactor, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO2, adsorbent dose variation experiments

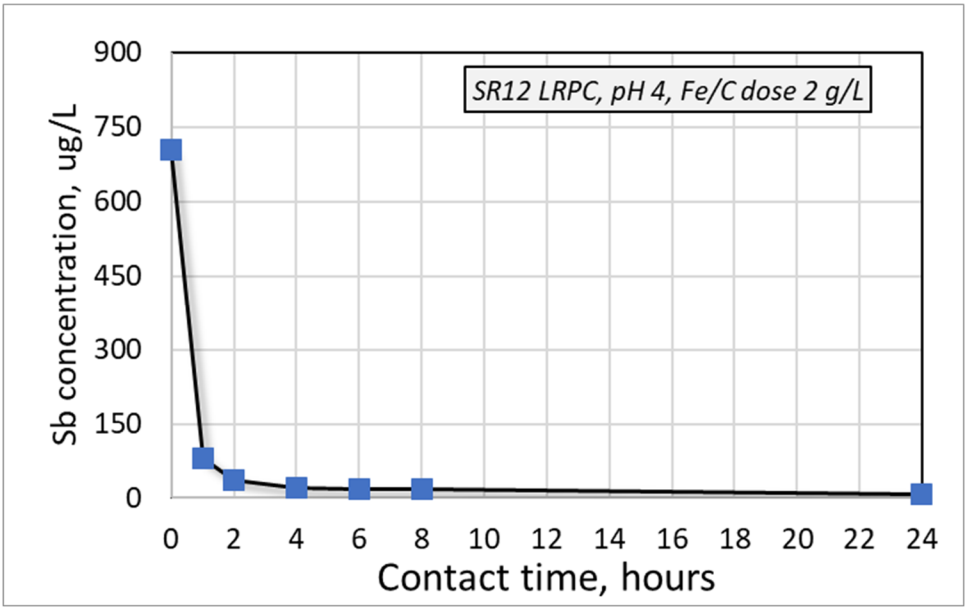

Figure 56 - Changes of antimony concentrations in ME batch reactor, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO2, adsorbent dose variation experiments

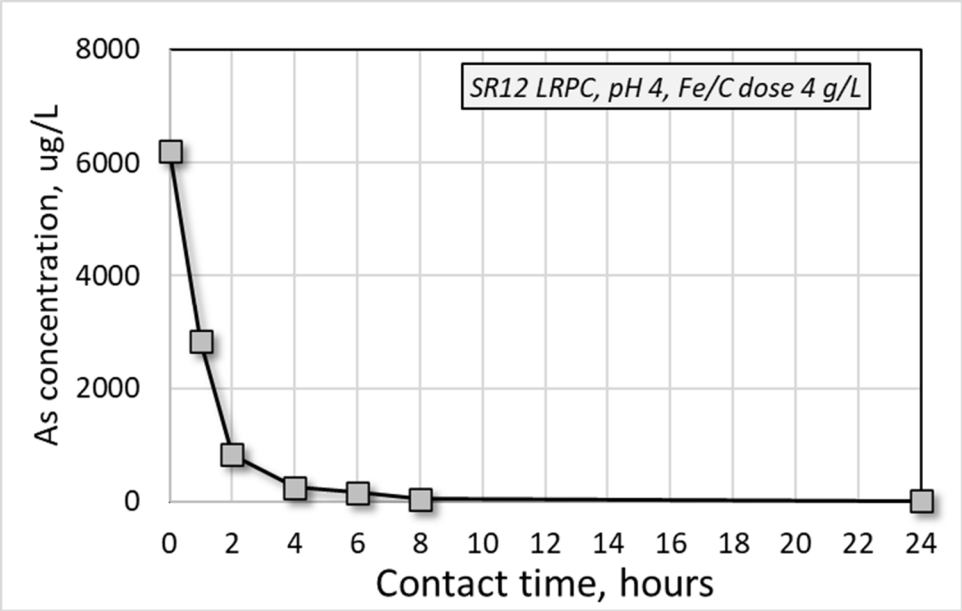

Figure 57 - Changes of arsenic concentrations in ME batch reactor, SR12 (Filtered), 4 g/L FeC, pH4, 0.6 LPM CO2, adsorbent dose variation experiments

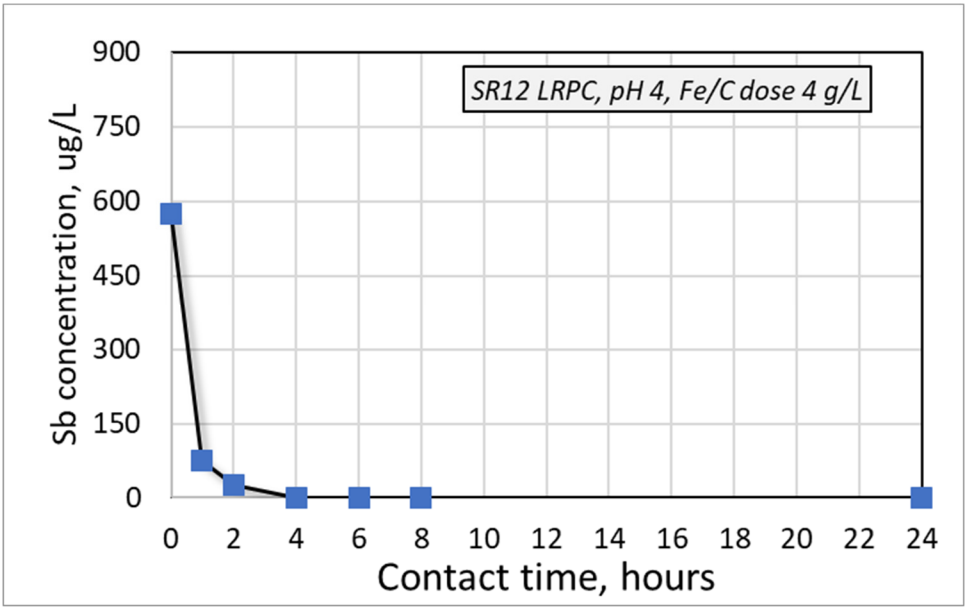

Figure 58 - Changes of antimony concentrations in ME batch reactorCR1, SR12 (filtered), 4 g/L FeC, pH4, 0.6 LPM CO2, adsorbent dose variation experiments

Figure 58 shows the data for the experiment that was run using the largest dose of adsorbent. It demonstrates the clear advantage of using 4 g/L over 1 g/L. By 2 hours into the experiment, the 4

g/L sample had 50% of the arsenic level in the 2 g/L experiment and more than 75% less arsenic than the 1 g/L experiment. To normalize this data, Figure 54 shows a removal of 1431 ppb arsenic per 1 g/L active media, Figure 56 shows a removal of 2103 ppb arsenic per 1 g/L active media, and Figure 58 shows a removal of 1345 ppb arsenic per 1 g/L active media. This normalization shows that over a 2-hour period, the 2 g/L had removed the most arsenic per g/L of active media. Although nearly all the arsenic had been removed by 24 hours, the experiment using 4 g/L adsorbent dose was able to do so in much less of a contact time. However, based on the normalization, the 2 g/L was the most efficient at removing the arsenic compared to the amount of active media used.

ICP-MS data – Effects of timing of additions of Fe/C active media

Another important variation to the ME column experiments to understand is the relationship between arsenic and antimony concentrations and the timing in which adsorbent is added to the LFG condensate. In previously mentioned experiments, the adsorbent had been added only once, with the entire dose added to the solution being treated after collecting the zero-minute sample. To test the affect the timing has on the arsenic and antimony concentrations, experiments were run using three adsorbent timing methods, listed in Table 5. The three experiments were run using filtered LFG condensate from SR12, a controlled pH of 4, an adsorbent dose of 2 g/L, and a constant gas flow of 0.6 LPM CO_2. Figures 60 through 65 illustrate the relationship between arsenic and antimony concentrations and adsorbent dose timings.

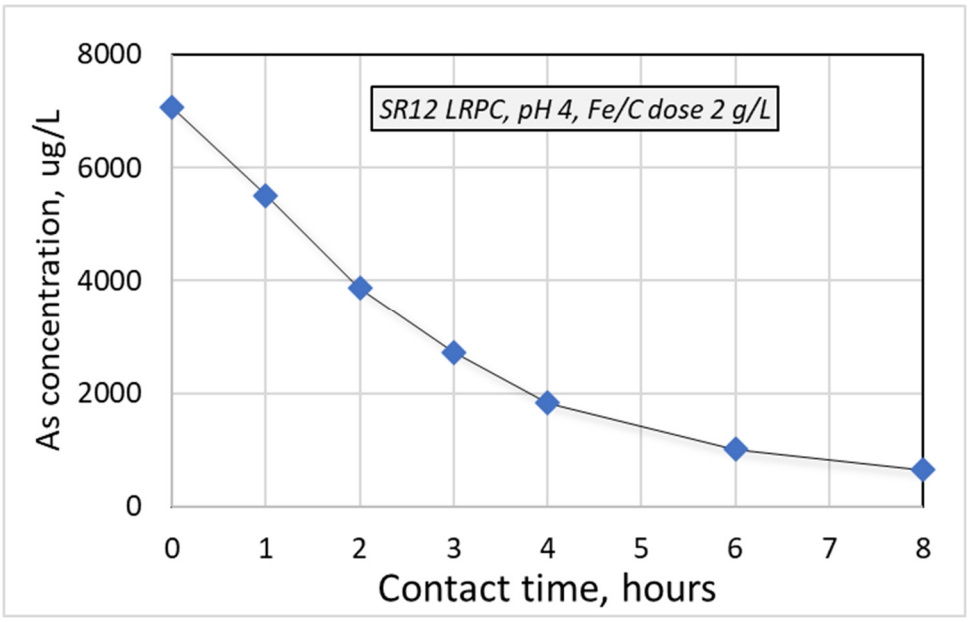

Figure 59 - Changes of arsenic concentrations in ME batch reactorCR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO2, adsorbent timing variations (all Fe/C dose added at zero minute only)

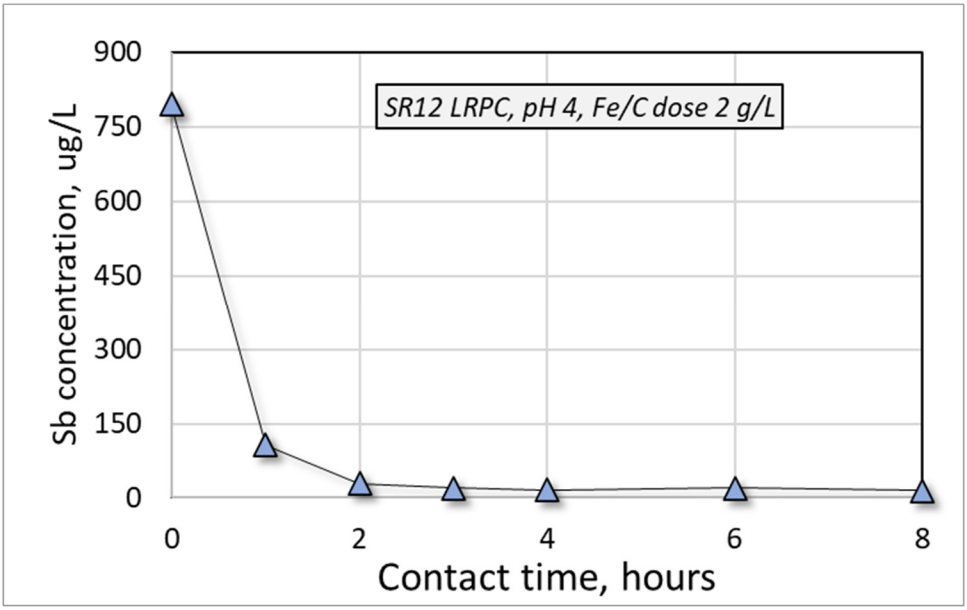

Figure 60 - Changes of antimony concentrations in ME batch reactorCR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO2, adsorbent timing variations (all Fe/C dose added at zero minute only)

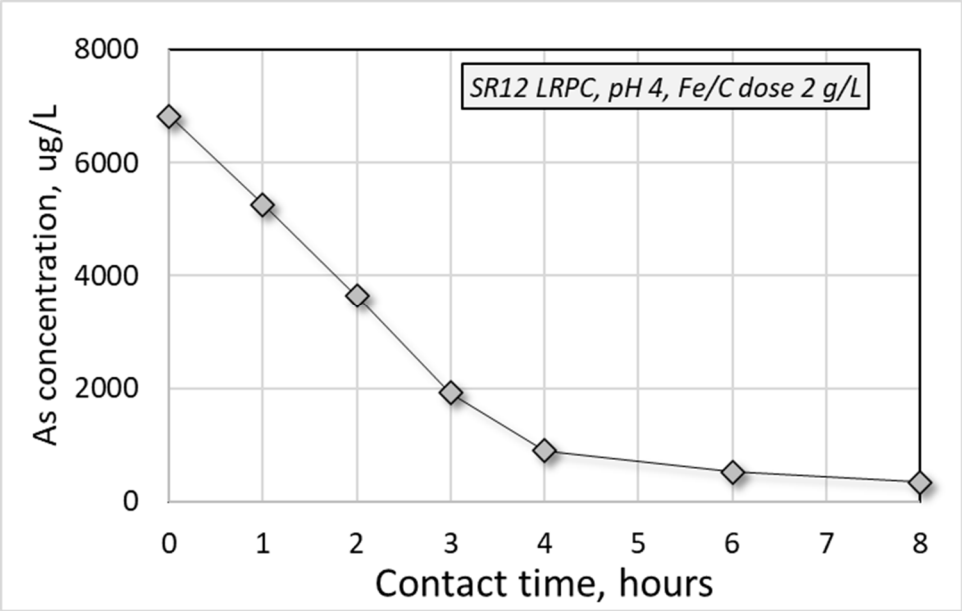

Figure 61 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2, adsorbent timing variations (equal Fe/C amounts added at zero and 2-hour treatment time)

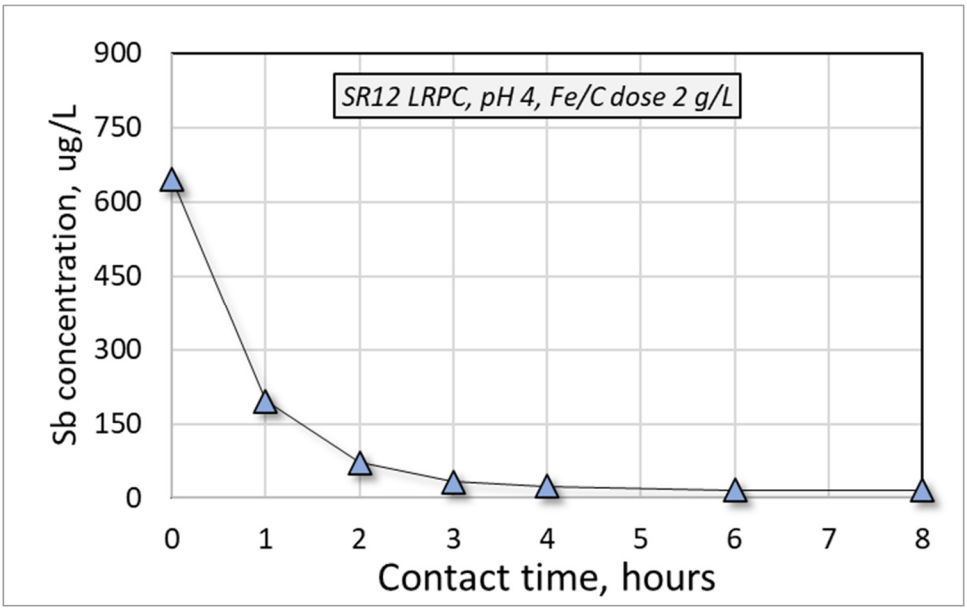

Figure 62 - Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2, adsorbent timing variations (equal Fe/C amounts added at zero and 2-hour treatment time)

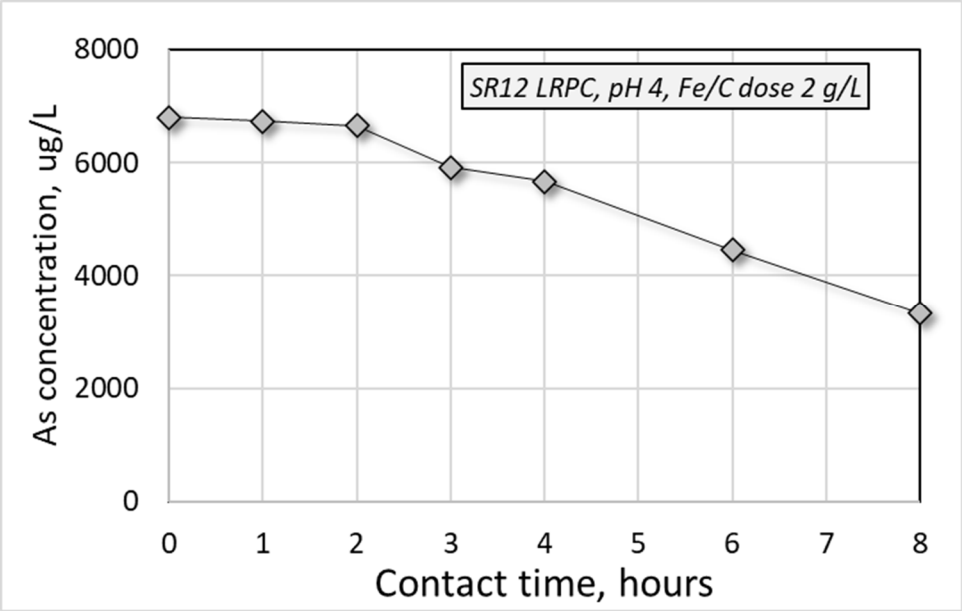

Figure 63 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2, adsorbent timing variations (equal Fe/C amounts added at zero, 1, 2 and 3-hour treatment time)

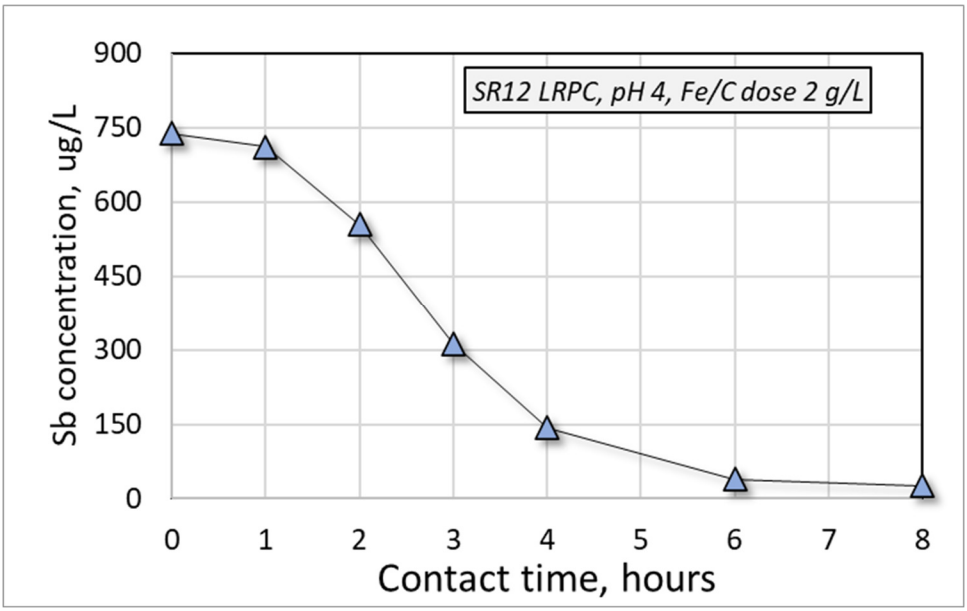

Figure 64 - Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2, adsorbent timing variations (equal Fe/C amounts added at zero, 1, 2 and 3-hour treatment time)

The results from the three adsorbent dose timing experiments indicate that adding the adsorbent in these sequential patterns has little to no positive effect on the removal efficiency of arsenic or antimony from the SR12 LFG condensate. Accordingly, the adsorbent dose timing for further ME column experiments was only Adsorbent Timing 1 (addition the entire Fe/C dose at the initiation of ME treatment).

ICP-MS data – effects of variations of active media addition method

With plans for a full-scale operation in the future, it is important to test different methods for adding the PAC/ZVI mixture. For a small-scale operation, it is relatively simple to add the solid mixture into the liquid through the open top of the reactor column. The flow of CO_2 from the bottom of the column allows for even mixing as the solid is added. However, as the size of the reactor column increases, so does the mass of solids used for an experiment, and it may no longer become viable to add solids through the open top of the column.

For these experiments, four adsorbent addition methods were tested. Their features are outlined below:

- Top addition (Addition Method 1),
- Funnel addition (Addition Method 2),
- DI slurry addition (Addition Method 3),
- Premixed with LFG condensate addition (Addition Method 4).

For all addition methods, the GAC was added to the reactor column and the ZVI had been activated with 0.1M HCl then added to reactor column. Top addition is when both solid materials are added through the open top of the reactor column separately. Funnel addition is when both solid materials are added through the top of the reactor column with the assistance of a 3D

printed funnel. DI slurry addition is when the GAC was premixed with DI water then added through the open top of the reactor column. Addition method 4 (Premixed with LFG condensate) was when the GAC was premixed with the SR of the LFG condensate being used for the experiment then added through the open top of the reactor column. For Addition Methods 3 and 4, the ZVI was activated with 0.1M HCl and added through the open top of the reactor. These experiments were run using filtered LFG condensate from SR12 in batch reactor CR1. The experiments were done using pH 4, 2 g/L adsorbent mixture concentration, and 0.6 LPM constant flow CO_2.

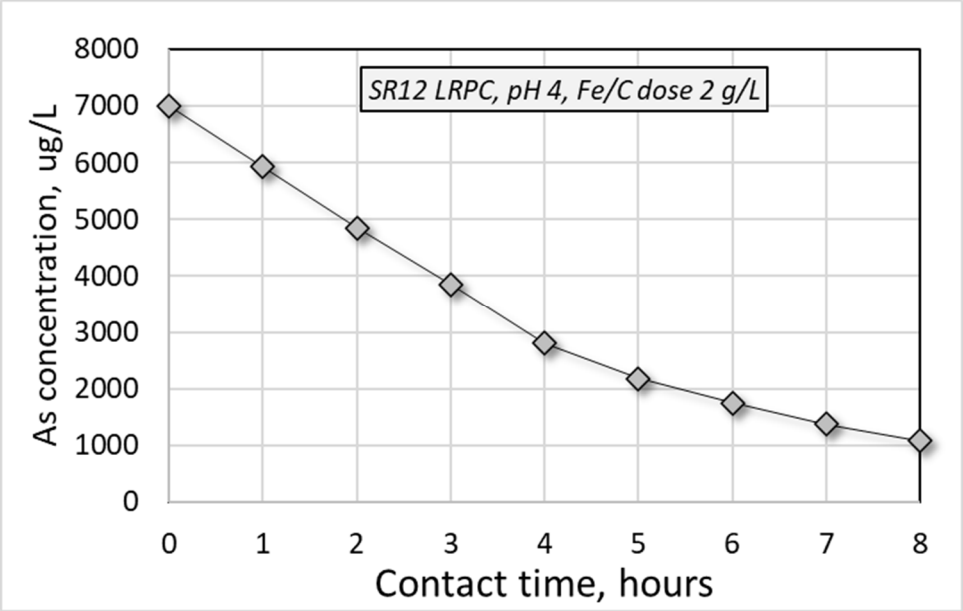

Figure 65 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Active media addition variations, Method 1 (Top addition)

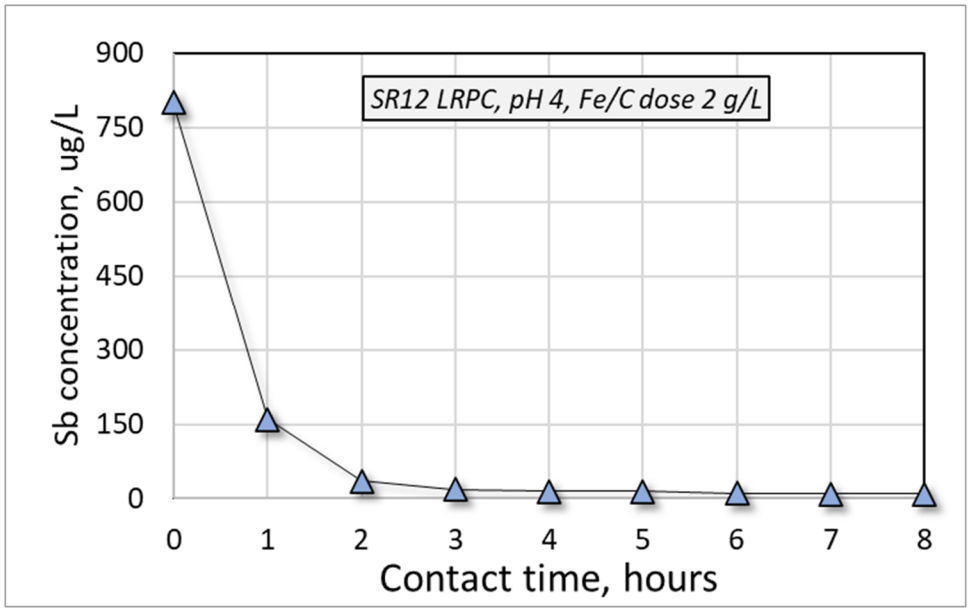

Figure 66 - Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Active media addition variations, Method 1 (Top addition)

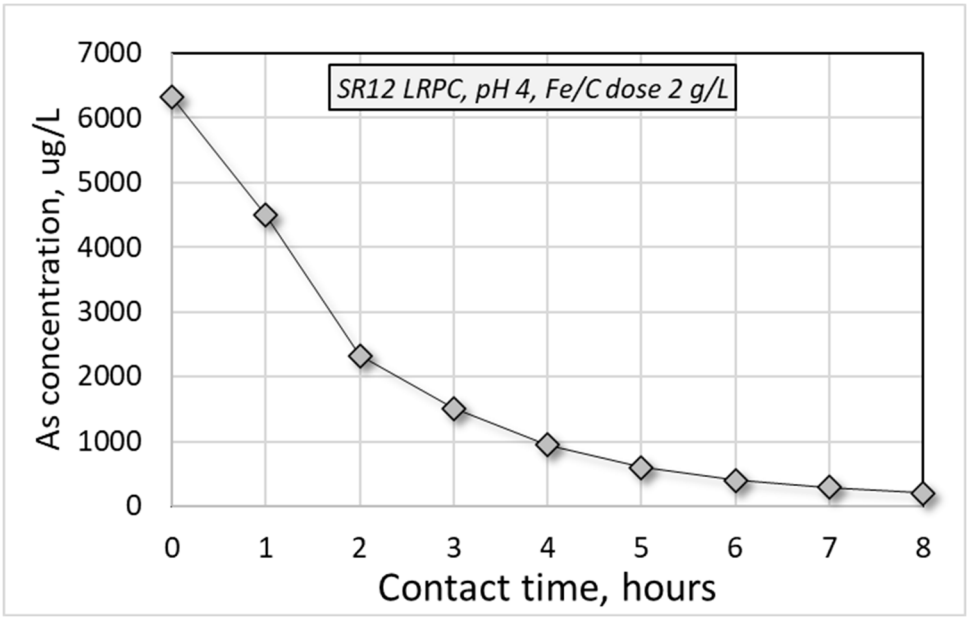

Figure 67 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Active media addition variations, Method 2 (Funnel addition)

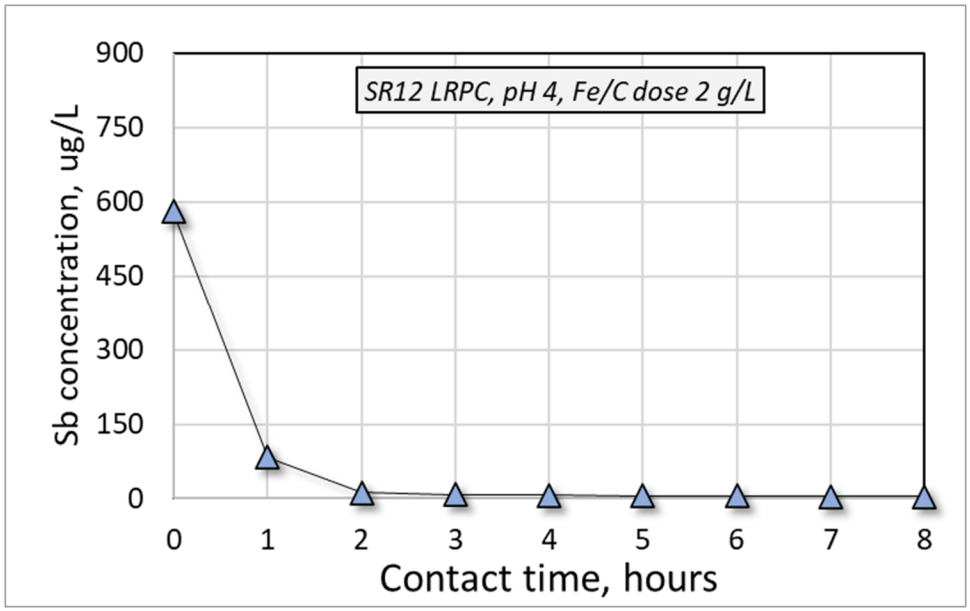

Figure 68 – Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Active media addition variations, Method 2 (Funnel addition)

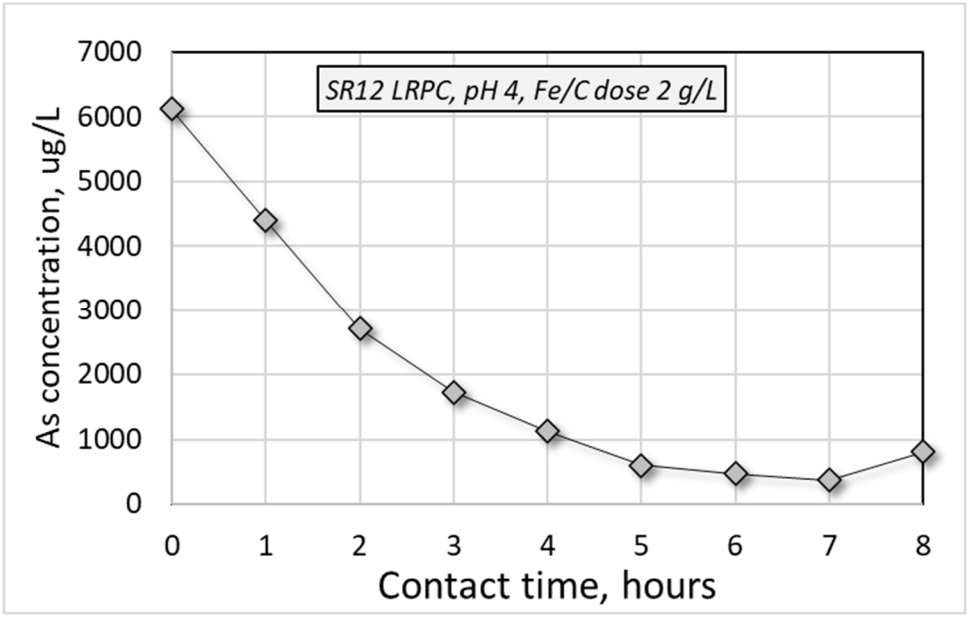

Figure 69 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Active media addition variations, Method 3 (Slurry with DI water addition)

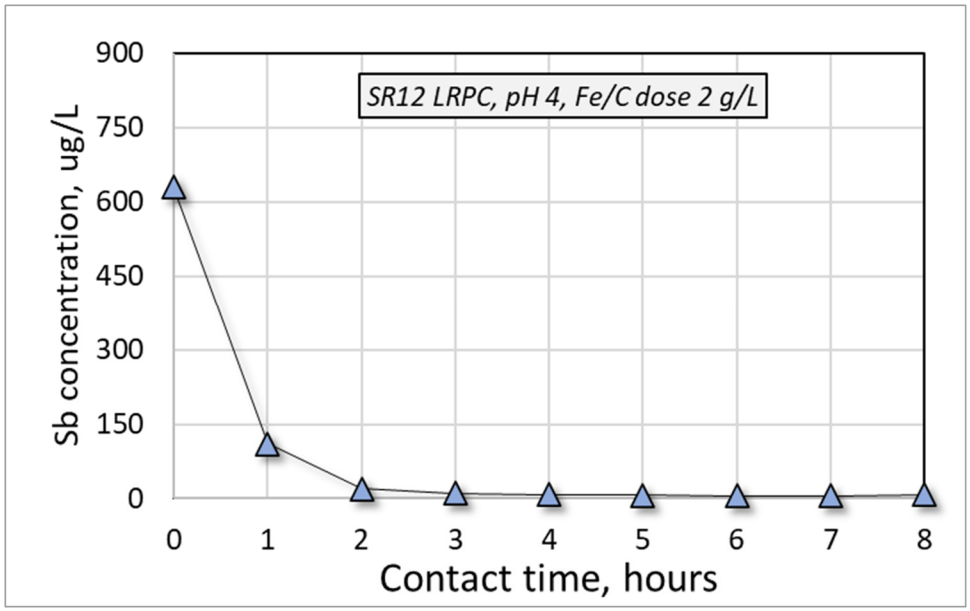

Figure 70 – Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Active media addition variations, Method 3 (Slurry with DI water addition)

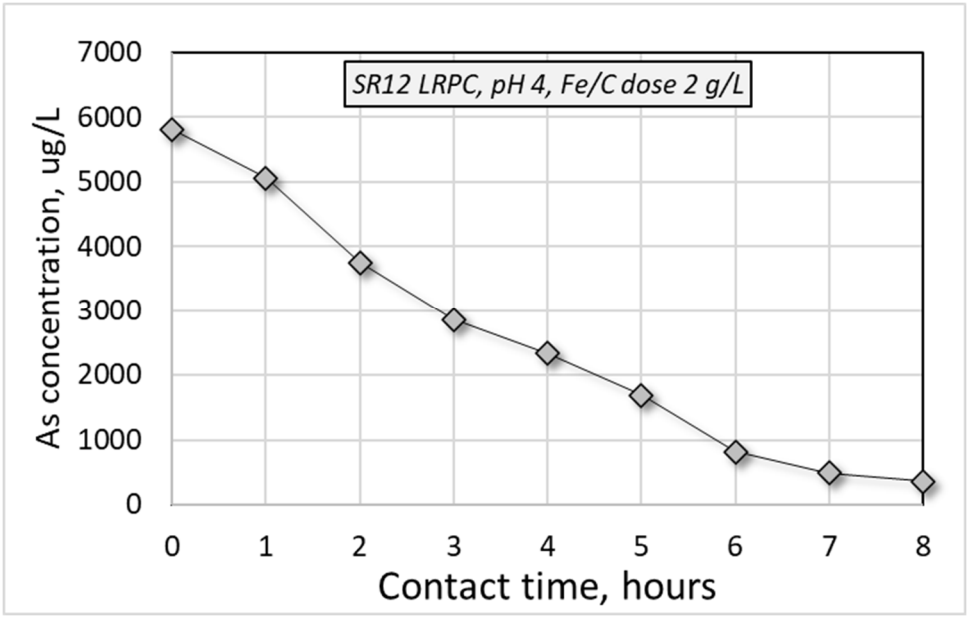

Figure 71 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Active media addition variations, Method 4 (Premixed with LFG condensate addition)

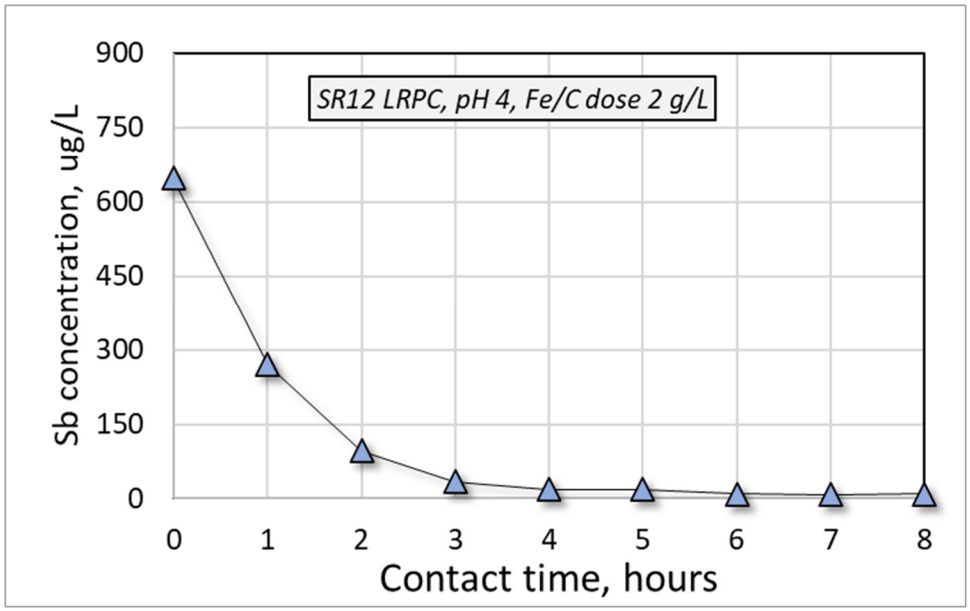

Figure 72 - Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Active media addition variations, Method 4 (Premixed with LFG condensate addition)

By the end of each of the eight-hour experiments, all four methods showed very similar removal profiles for arsenic and antimony. However, the arsenic concentration profiles showed some differences in removal efficiency, but no major differences. In the case of antimony, there were even fewer differences in removal efficiency between the four addition methods. Since there are not any major differences recognized from this set of experiments, ME experiments conducted in the current 1 L reactor column will continue to use the Addition Method 1. As experiments evolve, further experiments testing different addition methods may be conducted.

ICP-MS data – Effects of carrier gas flow gas conditions

During the experiments covered in this thesis, counterflow gas was always present. This is because previous experiments in the research group proved a presence of counterflow gas was necessary for successful arsenic removal. With larger reactor columns, however, this gas can become quite costly. In order to test the flow conditions needed for successful arsenic removal,

ME experiments using three different gas timing conditions were tested in 1 L reactor columns. The three conditions were as follows:

- Constant flow of carrier gas (Gas Timing 1),
- 10 minutes on/10 minutes off alternating carrier gas (Gas Timing 2),
- 20 minutes on/20 minutes off alternating carrier gas (Gas Timing 3).

All three experiments were conducted using filtered LFG condensate from SR12, pH 4, 2 g/L adsorbent mixture, and 0.6 LPM CO_2.

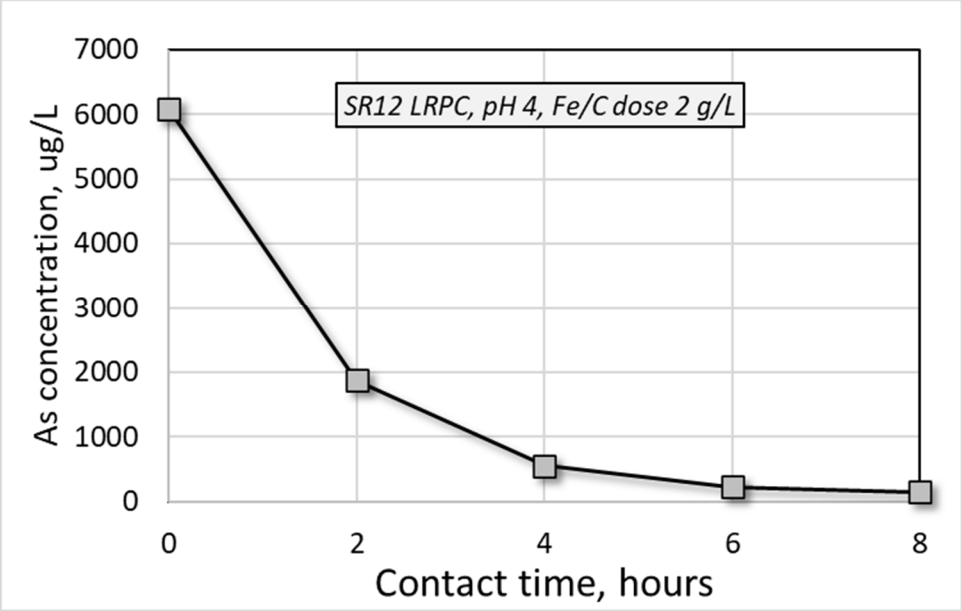

Figure 73 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Gas flow timing variations, Timing 1 (Constant Flow)

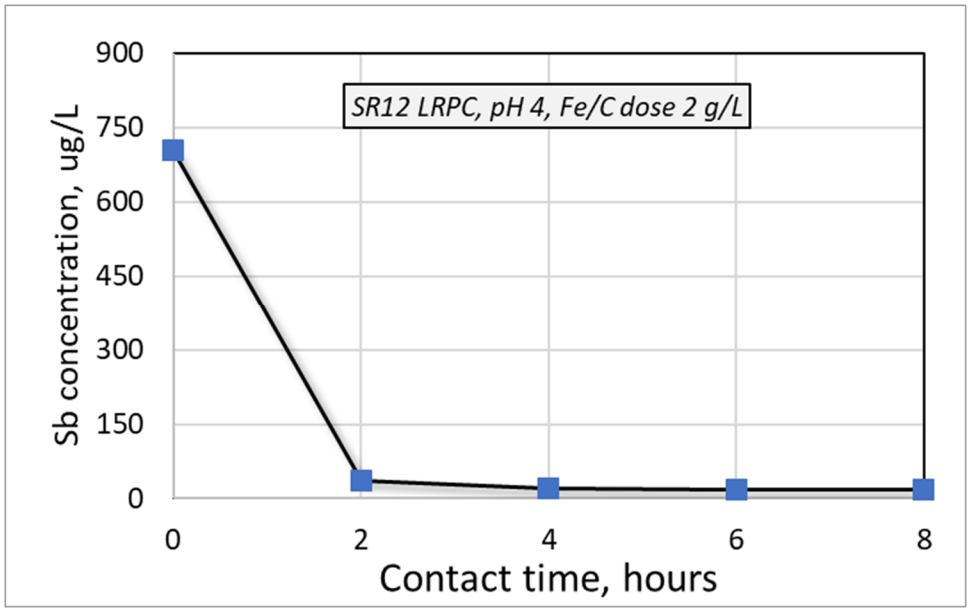

Figure 74 - Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Gas flow timing variations, Timing 1 (Constant Flow)

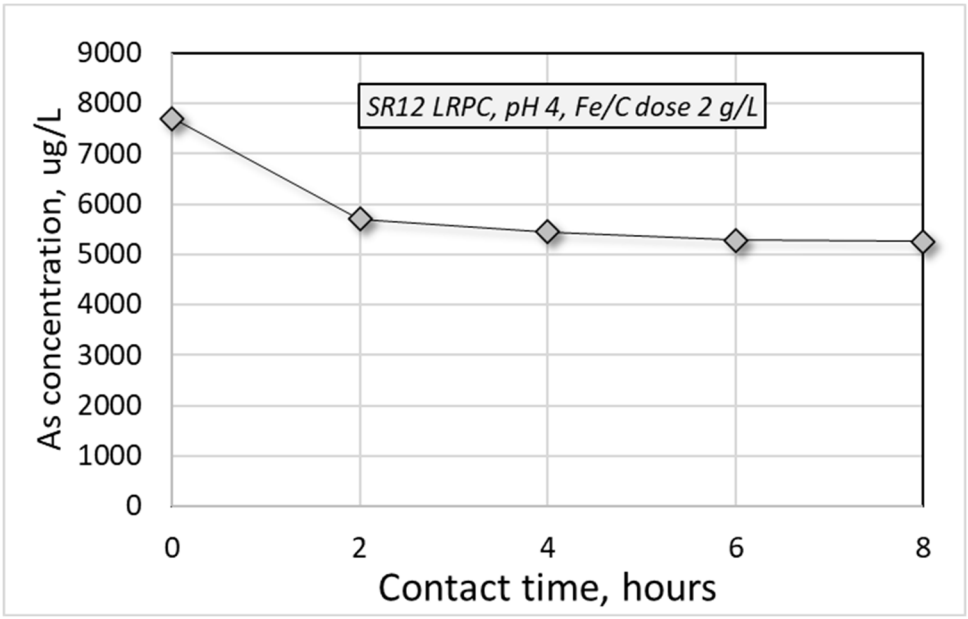

Figure 75 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Gas flow timing variations, Timing 2 (10 minutes on, 10 minutes off)

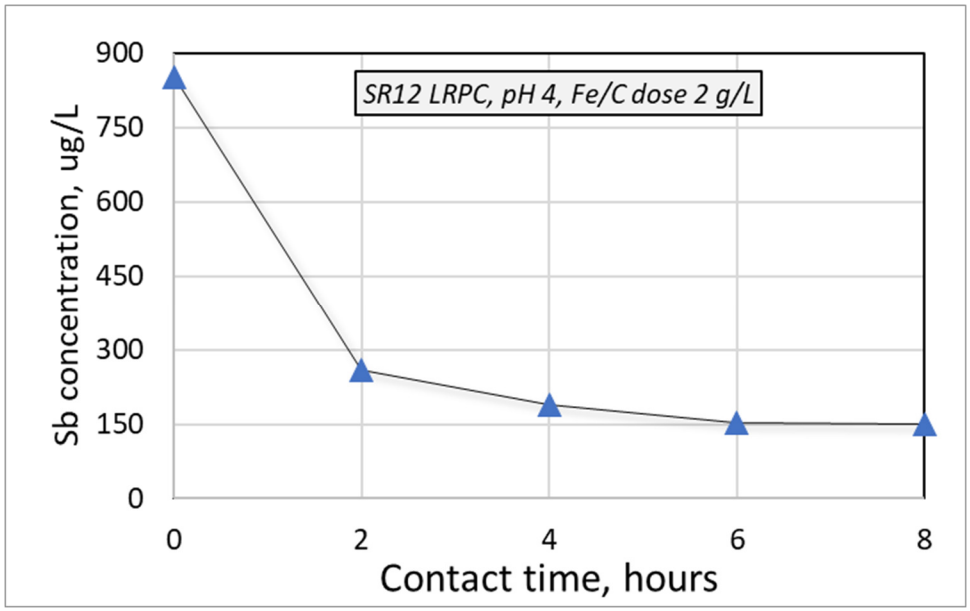

Figure 76 - Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Gas flow timing variations, Timing 2 (10 minutes on, 10 minutes off)

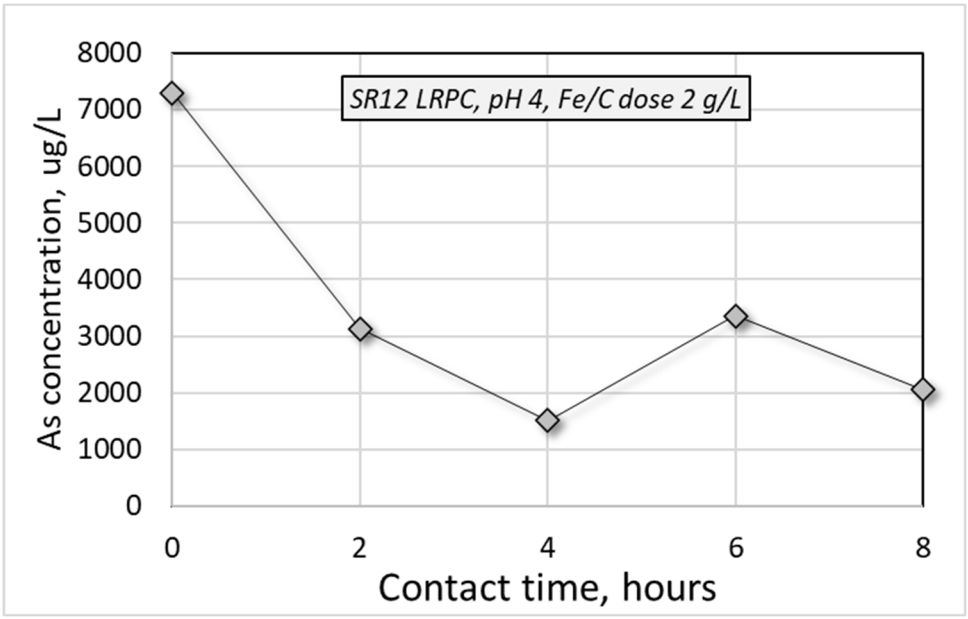

Figure 77 - Changes of arsenic concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Gas flow timing variations, Timing 3 (20 minutes on, 20 minutes off)

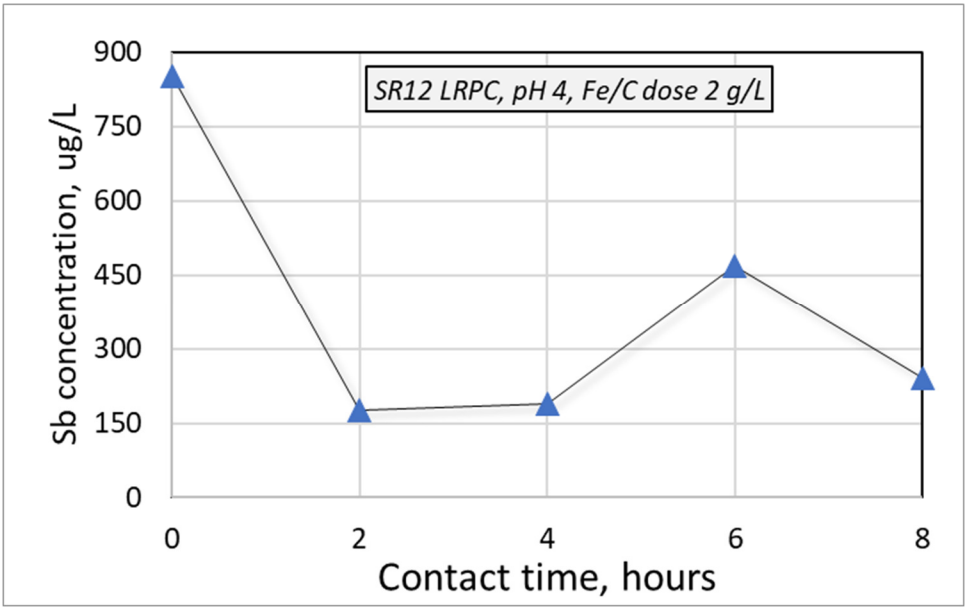

Figure 78 - Changes of antimony concentrations in ME batch reactor CR1, SR12 (filtered), 2 g/L FeC, pH4, 0.6 LPM CO_2. Gas flow timing variations, Gas Timing 3 (20 minutes on, 20 minutes off)

This round of experiments shows a clear connection between a constant flow of carrier gas and removal of arsenic. By the end of the experiment, Figure 74 shows that Gas Timing 1 allows for almost complete removal of arsenic from the LFG condensate, while Figures 76 and 78 show that the other gas timings do not have effective removal. While these data show that a constant flow of carrier gas is necessary for arsenic removal, these experiments were limited and there are plans for additional testing of gas timings in future experiments.

ICP-MS data – Effects of filtration method

In order to avoid contamination when running samples on the ICP-MS, samples must be filtered before analyzing them on the instrument. To test whether the method of filtering has an effect on the efficacy of arsenic removal within ME reactor column experiments, three experiments were run testing three filtration methods, as outlined below:

- Filtration Method 1 uses no filtration step before or after sample collection during the experiment.
- Filtration Method 2 involves filtering collected samples using a 0.45 µm filter before preparing the samples for analysis on the ICP-MS.
- Filtration Method 3 involves filtering the samples as they are being collected on-line.

All three experiments used filtered LFG condensate from SR12 which was treated in batch column reactor CR2 using pH 4, 4 g/L adsorbent, and 0.6 LPM CO_2. To clarify, the LFG condensate had been filtered once through a 1 µm filter before used for an experiment, and the variation in the filtration methods refers to the sample collected during the experiment.

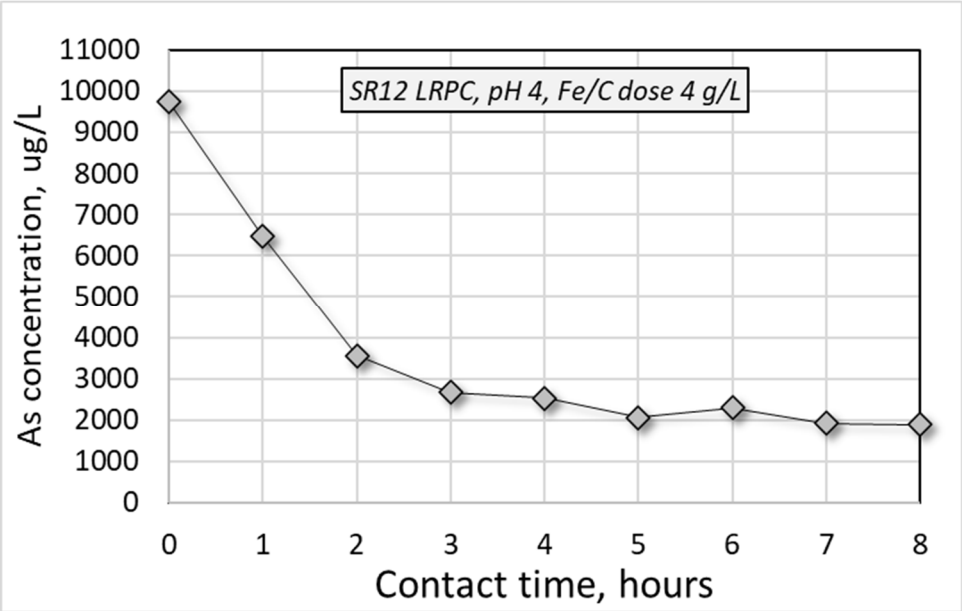

Figure 79 - Changes of arsenic concentrations in ME batch reactor CR2, SR12 (filtered), 4 g/L FeC, pH4, 0.6 LPM CO_2, Filtration Method 1 (no filtration)

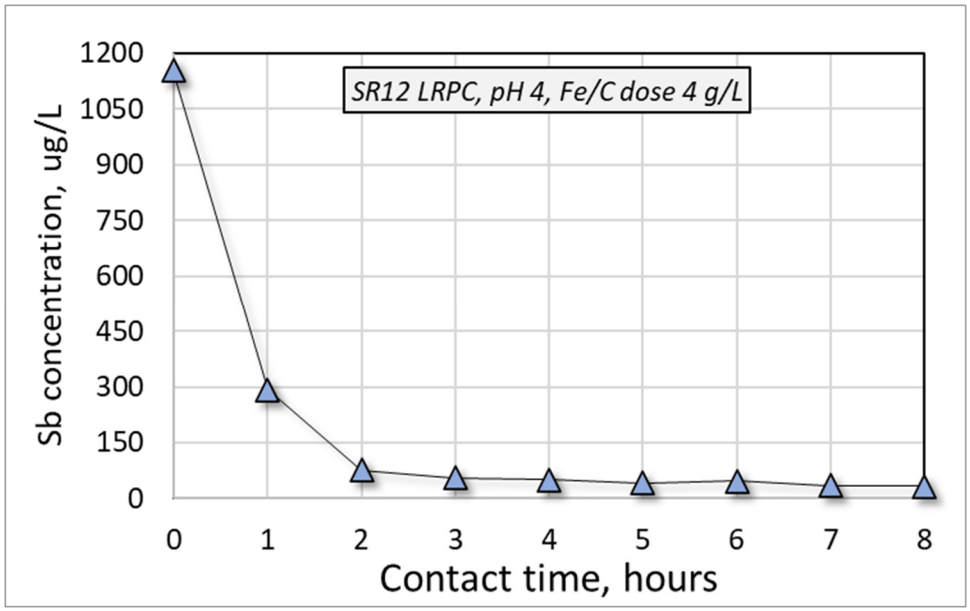

Figure 80 - Changes of antimony concentrations in ME batch reactor CR2, SR12 (filtered), 4 g/L FeC, pH4, 0.6 LPM CO_2, Filtration Method 1 (no filtration)

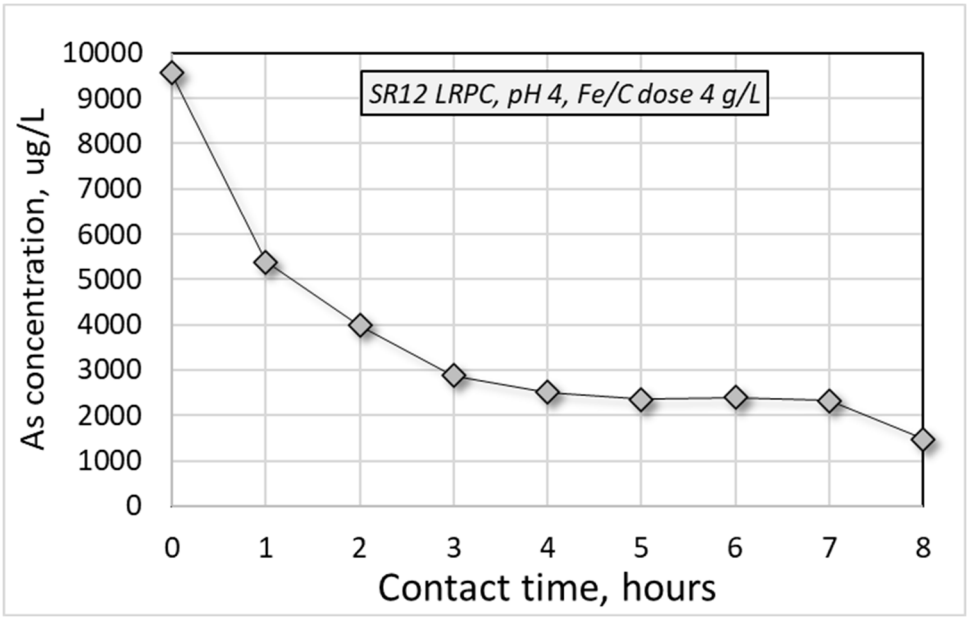

Figure 81 - Changes of arsenic concentrations in ME batch reactor CR2, SR12 (filtered), 4 g/L FeC, pH4, 0.6 LPM CO_2, Filtration Method 2 (filtered after sampling)

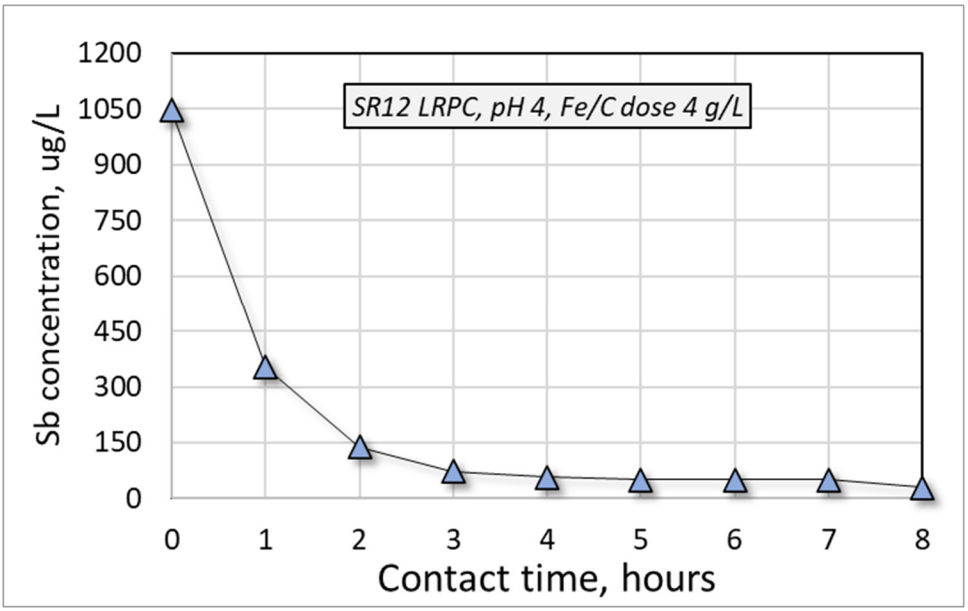

Figure 82 - Changes of antimony concentrations in ME batch reactor CR2, SR12 (filtered), 4 g/L FeC, pH4, 0.6 LPM CO_2, Filtration Method 2 (filtered after sampling)

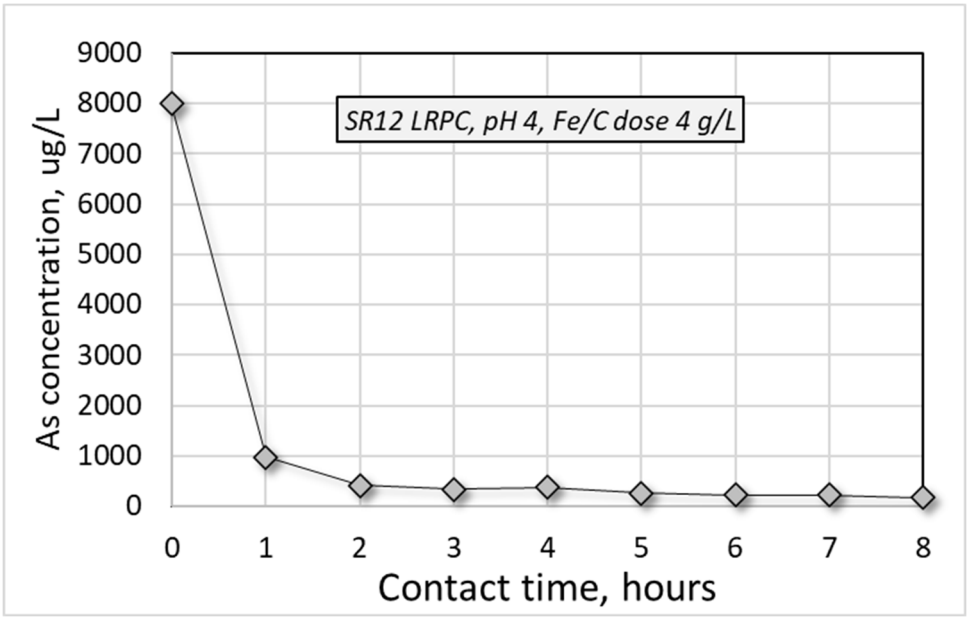

Figure 83 - Changes of arsenic concentrations in ME batch reactor CR2, SR12 (filtered), 4 g/L FeC, pH4, 0.6 LPM CO_2, Filtration Method 3 (filtered in-line before sampling)

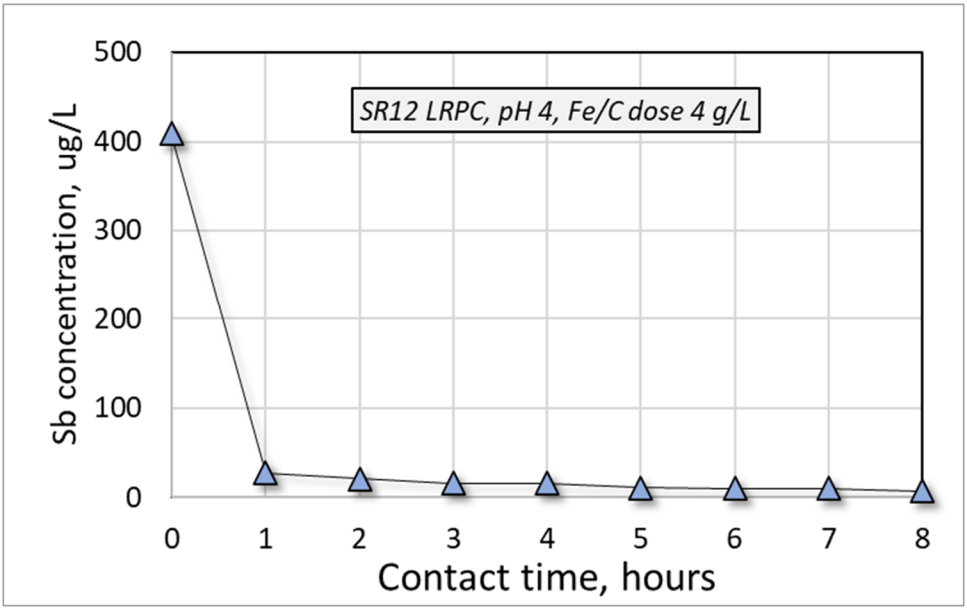

Figure 84 - Changes of arsenic concentrations in ME batch reactor CR2, SR12 (filtered), 4 g/L FeC, pH4, 0.6 LPM CO_2, antimony Filtration Method 3 (filtered in-line before sampling)

Figure 84 shows the advantage of using Filtering Method 3 in terms of arsenic and antimony removal. In addition to the efficient removal of almost all arsenic and antimony from the samples, this method also saves time and materials since an extra step of filtration is not needed after the experiment was finished. This set of experiments was completed in February 2022 and since then, ME experiments conducted in the 1 L reactor column have used Filtration Method 3. A negative aspect of this method is that the type of filter selected does not have a very long life and if it is not regularly changed, can lead to blockages in the sample line. Should this method be used in larger scale operations of ME experiments, alternative filter option with a longer life will be considered.

ICP-MS data – Test of ME treatment repeatability using different batch reactors

In order to move onto larger sized columns, repeatability experiments were conducted in four different column reactors that have the same dimensions and were operated under the same

conditions. These experiments were conducted using LFG condensate from SR12, pH 4, 4 g/L adsorbent, and 0.6 LPM CO_2. Unlike previous figures from this section, there will be two figures, one for arsenic removal and one for antimony removal. This is because the goal of these experiments was to determine repeatability of the system, rather than to identify contaminant removal rate under different conditions, and that is much easier to visualize with one figure containing data from all four columns.

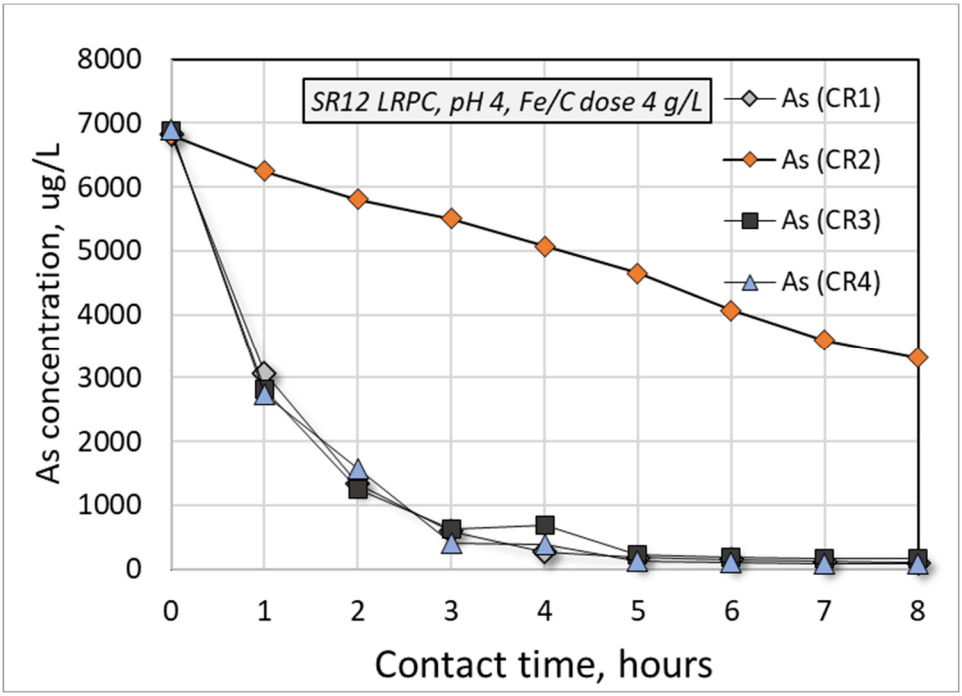

Figure 85 – Comparison of changes of arsenic concentrations in four ME identical batch reactors. SR12 (filtered), 4 g/L FeC, pH4, 0.6 LPM CO_2. Repeatability experiment

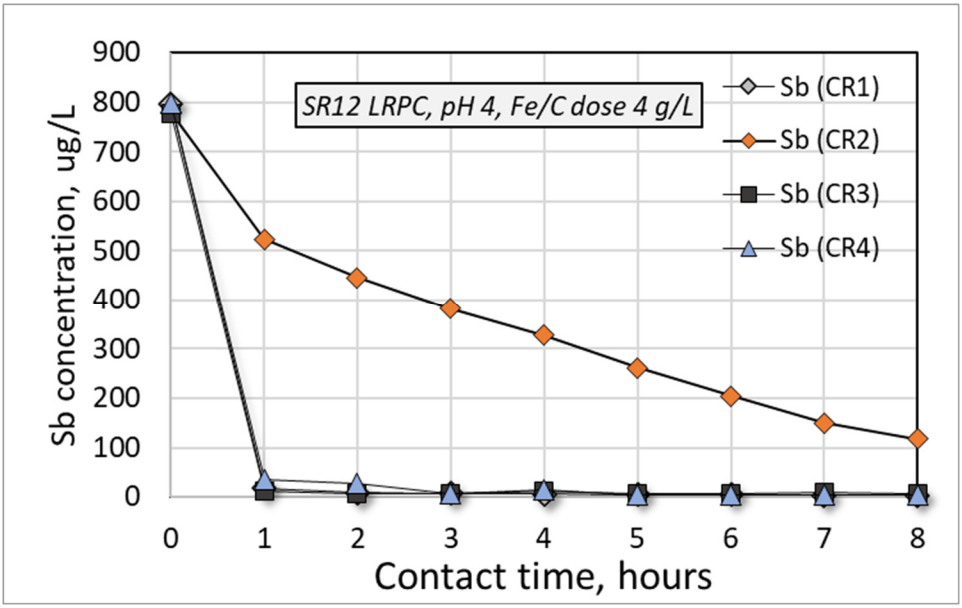

Figure 86 - Comparison of changes of antimony concentrations in four ME identical batch reactors. SR12 (filtered), 4 g/L FeC, pH4, 0.6 LPM CO_2. Repeatability experiment

Both Figures 86 and 87 show nearly identical removal curves for both arsenic and antimony for CR1, CR3, and CR4. It is currently unknown why the performance of reactor CR2 did not match that of the other reactors. Possible reasons for that include a contamination of the sample or a block in the diffuser leading to lower rates of CO_2 flow throughout the experiment, or less even distribution of the carrier gas and the active media.

Conclusions

Arsenic, with its complex speciation, multiple redox and adsorption reactions, provides a uniquely difficult problem in the field of environmental engineering. This thesis helps address the problem of removing arsenic from LFG condensate and quantify the complexities of treating the LRPC collected from a landfill utility in KC. This thesis also covers data generated for two types of treatment, one of which shows promise for future work. These treatments are fixed bed column treatment, which underwent a short experimental time due to hydraulic flow problems within the treatment columns; and a size expanded ME batch column treatment. The tests of the latter type of LRPC treatment are currently ongoing.

The fixed bed column experiments included variations in adsorbent material, height of bed layers, and pH and makeup of LFG condensate. Data from the ICP-MS showed a relatively more effective arsenic and antimony removal using a combination of GAC and ZVI (activated with 0.1M HCl), compared to treatment using GAC or ZVI alone. This is because the reduction that occurs between the uncharged iron and the activated carbon allows for the volatilization of arsenic species to one that is more treatable. Additionally, treatment using LFG condensate at a low controlled pH, such as 3 or 4, was more effective than treatment at 5 or 6. A low pH results in a higher redox potential, which helps for the same reason as listed previously. Height variation results were inconclusive, showing no major changes in arsenic or antimony removal between different adsorbent layer heights. Using a GAC cartridge for pretreatment helped by lowering the initial concentration of the arsenic in the LFG condensate, however there was no overall improvement in the treatment efficiency. The fixed bed columns were halted due to the consistent occurrence of hydraulic blocking within the column, with tentative plans to continue the experiments later in the project.

The ME batch column experiments showed much more effective removal rates and are continuing to be run. This thesis covers experiments varying column designs, operating pH, adsorbent changes, counterflow gas conditions, filtration methods, and variations in gas diffuser materials. Unlike the previous experimental results, certain variations of these experiments led to effective removal of arsenic and antimony. Only ICP-MS data are available for these experiments.

After conducting initial ME batch column experiments using a flat-bottomed PVC column, other designs were considered to better facilitate contact between PAC and ZVI, a necessary component for arsenic and antimony removal. These included a 3D printed dome and 3D printed funnel. The 3D printed funnel bottom part of the column reactors proved to be the most effective design, with 98.6% arsenic removal over a 24-hour experiment. The next set of experiments tested effects of pH variations, showing that pH 4 and pH 5 had the most effective removal, with 98.6% and 99.0% respectively, by the end of an 8-hour experiment. pH was chosen as the standard operating pH, since the data also showed more immediate removal within the pH 4 experiment, compared to the pH 5 results.

Tests that examined effects of the adsorbent dose showed that a concentration of 4 g/L proved to be the most effective. In addition to a removal efficiency of 99.7% over a 24-hour experiment, a higher concentration of adsorbent also results in a more immediate removal of arsenic and antimony, with some experiments showing 90%+ removal by the 4-hour mark of a 24-hour experiment. Several different methods of adding the adsorbent, as well as different timings were also tested. As of now, the preferred method of addition and timing are addition method 1 and timing method 1, where the solids are added all at the beginning of the experiment through the

top of the column. Future experiments, especially those in larger reactors, may test different adsorbent conditions.

After performing the filtration experiments, testing the differences in removal efficiency between filtering inline vs. filtering the samples after collection, it became clear that an inline filtration was a more effective method. In an 8-hour experiment, the experiment using an inline filtration has removed 97.9% of the arsenic, whereas the experiment where samples were filtered post-collection had removed only 84.6% of the arsenic. One of the recent developments to the experiments is testing the differences in arsenic removal between metal and ceramic diffusers for the counterflow of CO_2 gas. These experiments are ongoing, and results will be available later in the project.

Overall, the ME column treatment has proven to be an effective tool at removing both arsenic and antimony within a reasonable experiment time. Future developments to the project will see this treatment expand to a pilot scale and then a full-scale operation with the cooperation and help from the previously mentioned landfill utility.

Future research

The future work for the project will focus on better understanding the chemistry of the LRPC, as well as scaling up the ME batch column reactor from 1 L to a higher volume (e.g., 4 L), and further to pilot plant-scale and full-scale operations.

Over the life of the project so far, much has been learned about the chemistry of the LRPC. However, more knowledge has to be gained on the identities and reactivities of the arsenic species present in LRPC, as this knowledge may greatly facilitate the engineering development of the reactor. This furthermore involves calculating and/or determining experimental Henry

constants for the volatile As species formed during the ME treatment of LRPC. It is also necessary to perform hydraulic modeling of the reactor, including the movement of the gas bubbles and solid PAC and ZVI particles in its, to understand better what controls the overall performance of the reactor and how to optimize it. In the context of scaling operations up, this project has partially addressed the repeatability of ME treatment, as it was quantified using 1 L column reactors designs, so the next step of the project is to construct and test larger columns and possibly to expand this treatment to a continuous flow mode. Results of such experiments will definitely help develop a better understanding of the ME approach in full-scale LRPC treatment operations.

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