Comparison of Physicochemical Methods to Remove Arsenic from Landfill Leachate and Gas Condensate

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Abstract

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Arsenic is an important contaminant widely found in municipal solid waste (MSW). It has been accumulating in landfills and its concentrations in the landfill leachate have been observed to increase in several sites, notably at the Cedar Hills Regional Landfill Facility (CHRLF) located in the State of Washington. The chemistry and mobility of arsenic are unusual since it involves an array of solutes, gaseous arsines, and solids whose formation is greatly affected by landfill conditions that are dependent on MSW composition, hydrology, and other site-specific factors. The reducing conditions in a landfill result in intense microbial activity that generates landfill gas (LFG), LFG condensates, and leachate all of which can contain arsenic. The biological activity also results in the formation of methylated and sulfur-containing arsenic complexes that tend to be resistant to the conventional methods of removal.

This thesis evaluated the effectiveness of conventional and emerging technology particularly micro-electrolysis (ME) in the removal of arsenic from landfill leachate and LFG condensate. ME uses a combination of adsorption and zero-valent iron (ZVI) driven reduction that results in the immobilization of arsenic. While this treatment has been researched in the context of COD removal, its usage in the removal of arsenic from landfill systems has not been investigated.

In this study, landfill leachate and LFG condensate were collected over multiple sampling rounds from various locations in CHRLF. Conventional methods including ferric chloride coagulation, coagulation with dispersed gas flotation, and permanganate oxidation resulted in inadequate removal of arsenic. Pre-treatment by ozonation and electrochemical oxidation also did not improve treatment efficiency. In contrast, ME resulted in >90% removal of arsenic from both leachate and LFG condensate at high doses (>20 g/L) of activated carbon and ZVI. This process was enhanced by nitrogen or carbon dioxide purging. Adsorption on activated carbon removed 70-75% of arsenic from landfill leachate at a dose of 20 g/L, but it did not remove arsenic from LFG condensate. Simultaneous removal of organic matter and co-occurring contaminants such as chromium and nickel were also observed.

While ME and activated carbon were successful in arsenic removal from leachate and LFG condensate samples from certain sampling rounds, they were relatively ineffective for others. This highlighted two major concerns: (i) the speciation of arsenic in leachate and LFG condensate appears to vary within the site and, (ii) the chemistry of arsenic in the leachate and its response to treatment may fluctuate seasonally. Therefore, it is essential to elucidate further the speciation of arsenic and other characteristics of the landfill leachate and LFG condensate to establish an efficient and reliable treatment train.

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Go dawgs!

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

A567	Area 5, 6, 7
As(III)	Arsenite
As(V)	Arsenate
AsB	Arsenobetaine
AsC	Arsenocholine
BEW	Bioenergy Washington
CEE	Civil and Environmental Engineering Department
CHRLF	Cedar Hills Regional Landfill Facility
COD	Chemical Oxygen Demand
DIC	Dissolved Inorganic Carbon
DI water	Deionized water
DMA	Dimethylarsinic Acid
DOM	Dissolved Organic Matter
EC	Electrochemical
EEM	Excitation Emission Matrix
EPS	Extracellular Polymeric Substances
FA	Fulvic acid
GAC	Granular Activated Carbon
g/L	gram per liter
HA	Humic acid
HPLC	High-performance Liquid Chromatography
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
KCEL	King County Environmental Laboratory
KCIW	King County Industrial Waste Division
KC SWD	King County Solid Waste Division
LCPF	LCPlus Fine

LD_{50}	Lethal Dose, 50%
LEPS	Leachate Effluent from Pumping Station
LFG	Landfill Gas
LPM	Liters per minute
MCL	Maximum Contaminant Level
ME	Micro-electrolysis
µg/L	microgram per liter
mg/kg	milligram per kilogram
mg/L	milligram per liter
mM	millimoles
M	moles
MMA	Monomethylarsonic Acid
MSW	Municipal Solid Waste
NFS	North Flaring Station
NOM	Natural Organic Matter
PAC	Powdered Activated Carbon
POTW	Publicly Owned Treatment Works
ppb	parts per billion
ppm	parts per million
lb/day	pounds per day
PSI	Pound-force per square inch
QL	Quantitation Limit
RPM	Revolutions per minute
SMP	Soluble Microbial Products
SR	Sampling Round
TDS	Total Dissolved Solids
TIC	Total Inorganic Carbon
TMAO	Trimethylarsine oxide
TOC	Total Organic Carbon
TSS	Total Suspended Solids

US EPA	United States Environmental Protection Agency
UV	Ultraviolet
UW	University of Washington
V1A	Vault 1A
WHO	World Health Organization
ZVI	Zero Valent Iron

1. INTRODUCTION

1.1. BACKGROUND

Arsenic is a metalloid and a non-essential trace element with an atomic weight of 74.92 g/mol, and is the 20th most abundant element found in the earth's crust (Humans 2012). Arsenic commonly exhibits four oxidation states +5, +3, 0, and -3 (PubChem Database n.d., Bencko and Yan Li Foong 2017). It is ubiquitous and geologically associated with igneous and sedimentary rocks. It is also found in sulfide mineral complexes with other naturally occurring metals like arsenopyrite (FeAsS) (Chung, Yu and Hong 2014). Arsenic enters the environment through the natural cycle of weathering and volcanic activity (Hindmarsh and McCurdy 1986). Industrial activities like smelting and mining operations, glass production, manufacturing of agricultural pesticides, and production of wood preservatives have known to be major arsenic contamination sources in the past (Pinel-Raffaitin, et al. 2007). Arsenic was ranked number 1 in the 2001 Priority List of Hazardous substances at Superfund sites by the Agency for Toxic Substances and Disease Registry (ATSDR) (Sarkar and Datta 2007).

Arsenic contamination of water resources is rampant worldwide and has been noted in at least 50 countries, including Bangladesh, India, Taiwan, the USA, Mexico, and Argentina (Figure 1) (Argos, Kalra and Rathouz 2010). Routes of human exposure to arsenic can include contaminated drinking water, ingestion of tainted crops grown on arsenic-contaminated soil or irrigated with arsenic-contaminated water (Chung, Yu and Hong 2014). The absorption of arsenic depends on its metabolic form, where inorganic forms have proven to be more toxic than their organic forms (Arsenic 2018). Arsenic can have extremely detrimental effects on the human organ system that commonly include hyperpigmentation, keratosis, vascular diseases, and over time can also result in cancers of the bladder, kidney, skin, and lung (Argos, Kalra and Rathouz 2010). This elevated health hazard of prolonged human exposure to arsenic has resulted in its classification as a 'Group-A' carcinogen (Sarkar and Datta 2007). According to WHO guidelines, an arsenic concentration above 10 µg/L in drinking water is considered hazardous (Arsenic 2018). This guideline has also been implemented by the United States Environmental Protection Agency (US EPA 2001).

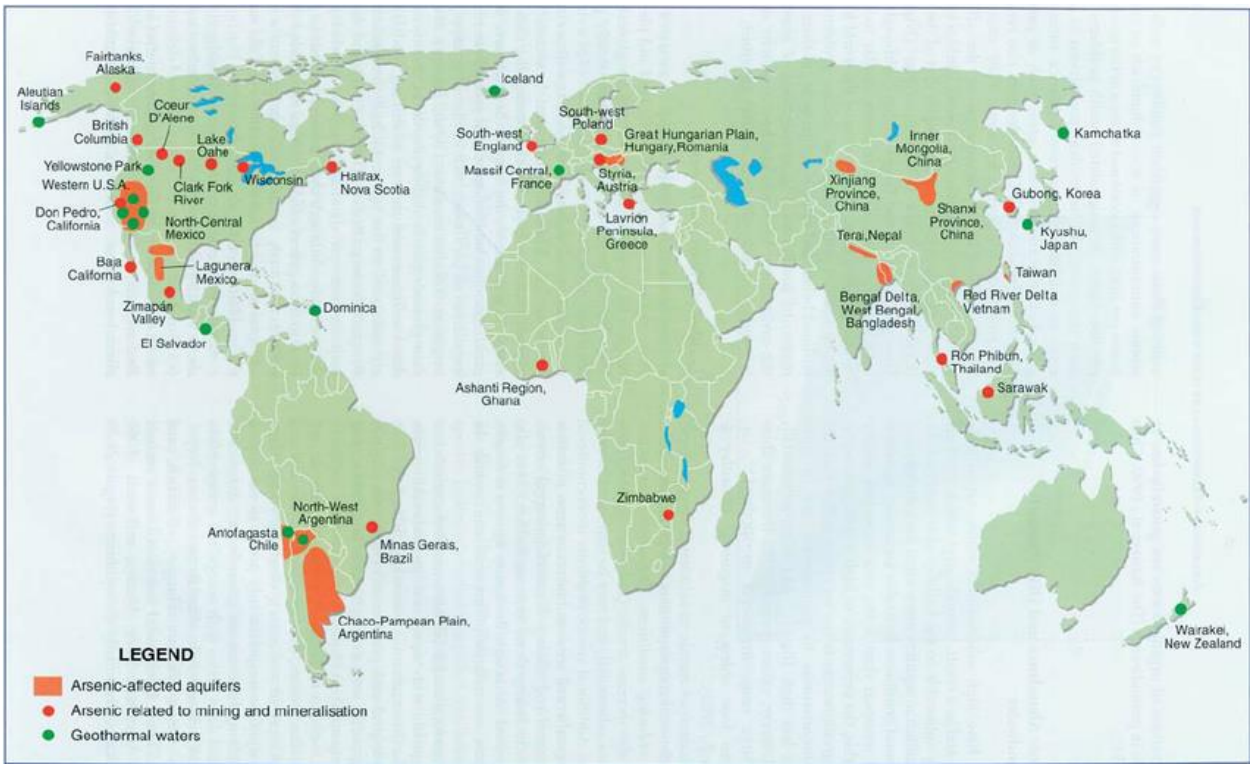


Figure 1. World map of regions with reported groundwater arsenic contamination (Centeno, et al. 2007, Smedley and Kinniburgh 2005)

Accumulation of heavy metals has also been exponentially growing in municipal solid waste (MSW) landfills over the last few decades. Arsenic has been identified as a major MSW contaminant amongst other heavy metals. However, it is often overlooked in the routine analysis (Carbonell-Barrachina, et al. 1999). In the mid-1990s, the recorded global emission of arsenic in the atmosphere from the incineration of MSW was 87 tons per year, with an emission factor of 1.1 to 2.8 g of arsenic per ton of incinerated MSW (Pinel-Raffaitin, et al. 2007).

The complex nature of a landfill system makes it challenging to approach treatment through a single, standard technique. Every landfill system is characterized differently in terms of arsenic speciation and dissolved organic matter content. Arsenic specation is controlled by the composition of the MSW, redox potential, pH, microbiological make-up, internal landfill processes, and hydrological conditions of the landfill. In a typical landfill setup, anaerobic conditions and a reducing environment promote the dominance of arsenite (As(III)) over arsenate (As(V)) in the system (Carbonell-Barrachina, et al. 1999, Li, et al. 2010, Pinel-Raffaitin, et al. 2007). The high microbial activity in a landfill system also creates an ideal atmosphere for the

biomethylation of available arsenic via a pathway described in Section 2.2.4. These methylated forms of arsenic are more resistant to degradation compared to simpler organic and inorganic arsenic species (Challenger 1945).

Conventional methods of arsenic treatment in drinking water treatment plants commonly involves the pre-oxidation of arsenite (As(III)) to arsenate (As(V)) that can be achieved through the application of chlorine, permanganate, and ozone (Johnston, Heijnen and Wurzel 2001). This is followed by either coagulation using ferric chloride or activated alumina, electrochemical coagulation, ion-exchange, or filtration through membrane-based techniques (EPA 2003, Clifford 1999). Adsorption using activated carbon and removal via zero-valent iron are also commonly applied treatment methods for in-situ remediation of arsenic present in groundwater (Ansari and Sadegh 2007, Lein and Wilkin 2005).

1.2. PROBLEM STATEMENT

The Cedar Hills Regional Landfill (CHRLF) facility has been witnessing a rise in total arsenic loading in their effluent discharged to the King County POTW, South Treatment Plant, since 2015. It has been estimated that the landfill facility has been discharging a total arsenic mass load of 0.4-0.5 lb/day, which exceeds the loading permit of 0.27 lb/day. The chromium loading limit of 1.2 lb/day has also been noted to exceed on occasion. Although total arsenic concentrations have not surpassed the permissible daily average concentration of 4.0 mg/L, the continuous increase in annual production of total arsenic despite the seasonal fluctuations is of a significant and growing concern for KC SWD and other agencies.

Conventional methods of arsenic treatment have proven successful after pre-oxidation of process water in drinking water treatment plants. However, in a landfill system, the formation of arsenic complexes under anaerobic and reducing conditions may prove difficult to remove using oxidative methods. Hence, both oxidative, reductive, and physical treatment methods will have to be studied to determine the degree of efficiency of the treatment in removing arsenic from the landfill leachate and LFG condensate. Arsenic treatment methods examined will be deemed successful if at least 80-90% of arsenic removal is achieved.

1.3. OBJECTIVES

Therefore, the main objectives of this research are as follows –

i. Develop an understanding of the physicochemical characteristics of arsenic found in the CHRLF landfill leachates and gas LFG condensates.
ii. Assess the efficiency of conventional methods in arsenic removal.
iii. Evaluate the applicability and efficiency of newly researched reductive techniques on arsenic removal.
iv. Compare the removal of arsenic and the secondary analytes present in the landfill leachate and LFG condensate.
v. Correlate the removal of arsenic to that of dissolved organic matter through spectrofluorometric methods.

2. LITERATURE REVIEW

Arsenic is the 20th most abundant element found in the earth's crust. It is a metalloid and can be found in both organic and inorganic forms (Aitio and Gomez-Caminero 2001, Gong, et al. 2002, Humans 2012, Akter, Owens and David 2005). The oxidation state of arsenic is highly variable. The most common forms exhibit oxidation states of +5 (arsenate), +3 (arsenite), 0 (elemental arsenic), and -3 (arsine) (Bencko and Yan Li Foong 2017, Kumaresan and Riyazuddin 2001, Akter, Owens and David 2005). From a biological and toxicological perspective, arsenic compounds can be categorized into three forms – inorganic arsenic compounds, organic arsenic compounds, and volatile arsines (Humans 2012). The distribution and speciation of arsenic are controlled by the presence of natural organic matter, microorganisms, and oxygen in the environment (Shrivastava, et al. 2015).

2.1. ENVIRONMENT AND ANTHROPOGENIC SOURCES OF ARSENIC

A ubiquitous element, arsenic, can be found in every domain of the earth, from sediment and rocks to water and even organisms. In the geological environment, arsenic is typically associated with its sulfidic mineral form present in igneous, sedimentary, and other rocks. The most dominant forms are 'Realgar or ruby sulfur' (α-As_4S_4) and its arsenic sulfide minerals (MAsS, where M = metals) containing silver, lead, copper, nickel, antimony, cobalt, and iron (Bencko and Yan Li Foong 2017, Humans 2012, Matschullat 2000). Arsenic is introduced into the environmental systems through natural processes of weathering, volcanic, or biological activity. Arsenopyrite (FeAsS) is the most common arsenic mineral form found in the environment. This compound is extremely stable and virtually water-insoluble. However, exposure to the atmosphere through natural weathering or mining activities can result in immediate oxidation to compounds that dissolve in water (Hindmarsh and McCurdy 1986).

$$FeAsS + 13Fe^{3+} + 8H_2O \rightarrow 14Fe^{2+} + SO_4^{2-} + 13H^+ + H_3AsO_{4_{(aq)}} \quad (1)$$

The phenomenon, also known as 'Acid Mine Drainage' or 'Yellow-Boy,' results in an iron and arsenic-rich water with a very low pH due to discharge of [H^+] ions which can harm aquatic life (Corkhill and Vaughan 2009). Other commonly found natural arsenic bearing minerals are 'Scorodite' ($FeAsO_4.2H_2O$) and 'Orpiment' (As_2S_3) (EPA 2006).

Arsenic is emitted into the atmosphere through two major industrial operations involving the smelting of non-ferrous metals and the production of energy through the combustion of fossil fuels. The arsenic mobilized in these processes is eventually deposited onto land surface and water (Bencko and Yan Li Foong 2007, Humans 2012). Commercial production of elemental arsenic was achieved through the reduction of As_2O_3 with charcoal. As_2O_3 was obtained as a by-product of the smelting operations. The As-containing residues from metal-mining operations have been a significant source of environmental contamination. Besides, the presence of sulfur in these tailings has caused the acidification of the contaminated water that leaches into the soil (Aitio and Gomez-Caminero 2001). Approximately 18% of arsenic produced was used in glass production, its inorganic forms in alloys, and at least 70% of it was applied in agricultural pesticides (Kumaresan and Riyazuddin 2001, Pinel-Raffatitin, Le Hecho and Amouroux 2007).

In the 1960s, the agriculture industry saw a shift in herbicide use to inorganic and organic compounds like arsenic acid, sodium arsenate, MMA, and DMA (Aitio and Gomez-Caminero 2001). In the 1970s, the manufacture and use of arsenical pesticides and the production of wood preservatives began to expand. Chromated copper arsenate (CCA or Tanalith), a wood preservative comprised of both arsenic and chromium, as well as copper, was widely used in commercial wood production for protection against termites, fungi, and other pests. Although manufacturers discontinued the production for CCA-treated wood products for homeowner uses, EPA has not banned its use (EPA n.d.). In 2004, the US EPA also deregulated an arsenical herbicide called 'Agent Blue' that contained cacodylic acid (DMA) that was widely used in golf courses, cotton fields, and also to dry plants before harvest. Another widely used compound called 'Roxarsone' ($C_6AsNH_6O_6$) was applied as a feed additive in poultry production to enhance weight gain, promote rapid growth, and also as an antiprotozoal agent (NCBI n.d.). 'Roxarsone' was found to be persistent through the digestive cycle of poultry animals and was excreted unchanged in their litter. Owing to its high nutrient content, this litter was further applied as a routine fertilizer on cropland. On coming in contact with water and composting at a high temperature (~ 40°C), the

speciation of arsenic was observed to shift from 'Roxarsone' to arsenate (As(V)) in under 30 days. In the US, manufacturers voluntarily stopped the use of the compound in 2011, which was followed by a ban on the product altogether in 2013 (FDA 2019, Gabarino and Bednar 2003). Currently, the only allowed use of arsenic is as monosodium methanearsonate (MSMA), a broad-spectrum weed herbicide for cotton and sod farms (Bencko and Yan Li Foong 2017).

2.2. CHEMISTRY OF ARSENIC

Commonly occurring inorganic arsenic species are arsenite (As(III), arsenate (As(V)) and organic species are dimethylarsinic acid (DMA(V)), monomethylarsonic acid (MMA(V)), arsenobetaine (AsB) and trimethylarsine oxide (TMAO) (see Table 1 for the complete list of typically occurring arsenic species). Recent research has reported the wide occurrence of thiol-organoarsenic species - DMDTA(V) and DMMTA(V) in vegetation, animals, and human beings (Li, et al. 2010).

Table 1. List of various arsenic species present in the environment (includes methylated and thiolated -groups compounds and volatile species found in landfill biogas *(Gong, et al. 2002)*.

Species Name	**Abbreviation**	**Chemical Formula**
Arsenite (Arsenous acid)	As (III)	$As(OH)_3$
Arsenate (Arsenic acid)	As (V)	$AsO(OH)_3$
Monomethylarsonous acid	MMA (III)	$CH_3AsO(OH)_2$
Monomethylarsonic acid	MMA (V)	$CH_3AsO(OH)_2$
Dimethylarsinous acid	DMA (III)	$(CH_3)_2AsOH$
Dimethylarsinic acid	DMA (V)	$(CH_3)_2AsO(OH)$
Dimethylmonothioarsinic acid	DMMTA (V)	$(CH_3)_2SAsO(OH)$
Dimethyldithioarsinic acid	DMDTA (V)	$(CH_3)_2S_2AsO(OH)$
Arsenobetaine	AsB	$(CH_3)_3As^+CH_2COO^-$
Arsenobetaine-2	AsB-2	$(CH_3)_3As^+CH_2CH_2COO^-$
Arsenocholine	AsC	$(CH_3)_3As^+CH_2CH_2OH$

Trimethylarsine oxide	TMAO	$(CH_3)_3AsO$
Arsine	-	AsH_3
Methylarsine	-	$As(CH_3)H_2$
Dimethylarsine	-	$As(CH_3)_2H$
Trimethylarsine	TMA (III)	$As(CH_3)_3$
Dimethylethylarsine	-	$As(CH_3)_2(C_2H_5)$
Diethylmethylarsine	-	$As(CH_3)(C_2H5)_2$
Triethylarsine	-	$As(C_2H_5)_3$
Arsenic trioxide	-	As_2O_3
Monosodiummethylarsonate	MSMA	$HAsO_3CH_3Na$
Disodiummethylarsonate	DSMA	$Na_2AsO_3CH_3$
Phenylarsonic acid	PAA	$C_6H_5AsO(OH)_2$
p-Arsanilic acid	*p*-ASA	$NH_2C_6H_4AsO(OH)_2$
4-nitrophenylarsonic acid	4-NPAA	$NO_2C_6H_4AsO(OH)_2$
4-hydroxy-3-nitrophenylarsonic acid	3-NHPAA	$NO_2(OH)C_6H_4AsO(OH)_2$
p-ureidophenylarsonic acid	*p*-UPAA	$NH_2CONHC_6H_4AsO(OH)_2$

2.2.1. Chemistry of Arsenic in Water

The speciation of arsenic in water is dependent on the degree of oxygenation of the water, biological activity (biotransformation), pH, type of water source, and the proximity to an arsenic-rich geological matrix or anthropogenic source (Aitio and Gomez-Caminero 2001, Humans 2012). The arsenic species with lower oxidation states (As(0) and As(-III)) occur under strongly reducing conditions, and higher oxidation states (As(III) and As(V)) occur under oxygenated, or even mildly reducing conditions (Akter, Owens and David 2005).

pH is the most important controlling factor for the speciation of arsenic in marine and freshwater systems. In aerobic aqueous systems, arsenic acid (As(V)) species - H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-} - are stable. The protonated form of arsenic acid (H_3AsO_4) predominates at pH < 2. The dominance of $H_2AsO_4^-$ and $HAsO_4^{2-}$ species is observed within a pH range of 2 to 11. AsO_4^{3-} only appears at a pH greater than 11 (Figure 2) (Bencko and Yan Li Foong 2017, Kumaresan and Riyazuddin 2001).

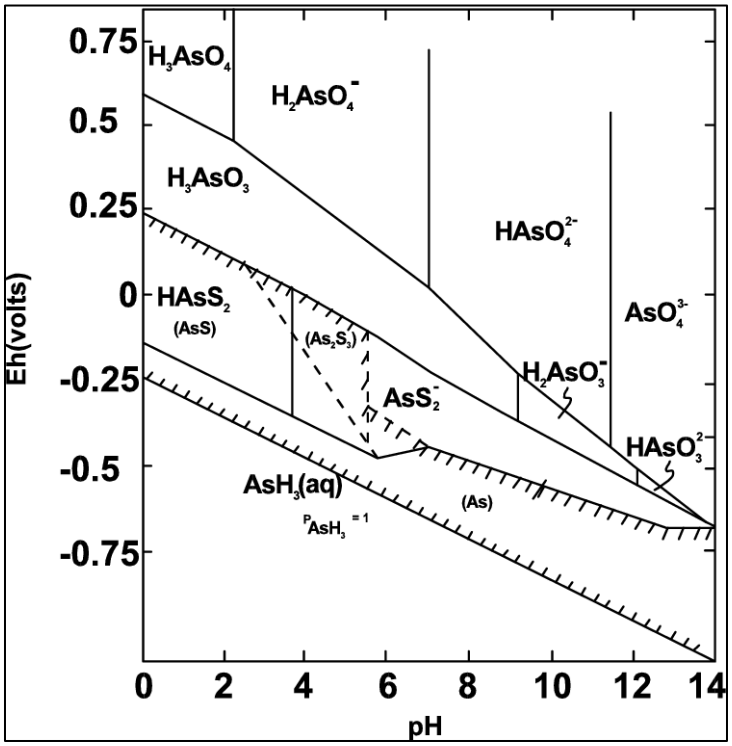


Figure 2. Eh-pH diagram of arsenic speciation at 25°C and 1atm (Nicomel, et al. 2015, Wang and Mulligan 2006).

Under slightly reducing condition, As(III) species, notably arsenous acid become stable. Within the pH range of natural environmental water samples, arsenous acid mainly exists in its neutral or non-dissociated form as H_3AsO_3 and deprotonates to $H_2AsO_3^-$ at pH greater than 10. In anoxic aqueous systems, the biological activity will result in low pE values. The prevalence of dissolved sulfide ions under strongly reducing conditions may also result in the formation of arsenic sulfide complexes (Bencko and Yan Li Foong 2017). The resulting sulfide compounds will be insoluble in water and thus, precipitate out of the water (Figure 3).

Organoarsenicals are widely distributed in the environment and have been detected in the atmosphere, aquatic systems, soils and sediments, and biological organisms. The synthesis of these compounds is linked to metabolic pathways of certain microorganisms in the aquatic environment (Bencko and Yan Li Foong 2017). In aqueous environments, under reducing environments, biological activity can induce the methylation of inorganic arsenic compounds to form dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA) (Bhattacharya , et al. 2002).

According to Carbonell-Barrachina et al. (1999), organic arsenic species are highly soluble in their aqueous form at near-neutral pH (Carbonell-Barrachina, et al. 1999). MMA(V) and DMA(V) have a pk_{a1} of 4.19 and 6.14, respectively, which explains their predominance in an aqueous solution at near-neutral and slightly acidic pH. The pK_a values of the commonly occurring arsenic species is given in Table A-1 (Appendix A).

Biotransformation of arsenic compounds by microorganisms to methylarsines is suspected to be a detoxification mechanism for the bacteria and fungi. This mechanism can also produce volatile methylarsines – arsine (AsH_3), dimethyl-arsine ($HAs(CH_3)_2$), and trimethylarsine ($As(CH_3)_3$) (Kumaresan and Riyazuddin 2001).

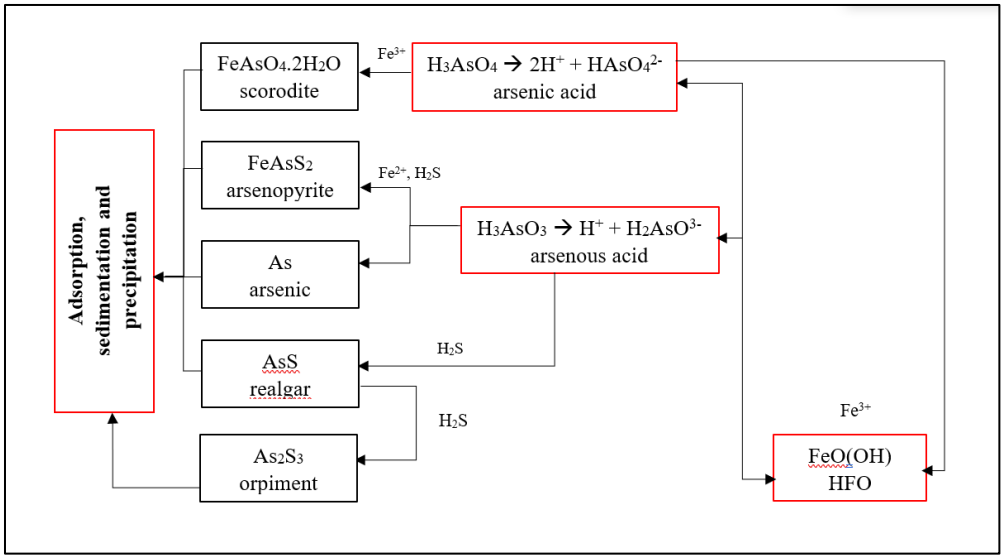


Figure 3. Formation of insoluble arsenic sulfides at low pH and reducing conditions (Korshin 2019).

In the early 19th century, multiple cases of arsenic poisoning occurred that were correlated to the presence and use of arsenic-containing pigments in wallpaper. These pigments were mainly Scheele's green or copper arsenite, and Schweinfurt green, a combination of copper arsenite and copper acetate (Bencko and Yan Li Foong 2017). The poisoning was observed even in cases where arsenic-containing wallpaper was covered with a fresh paper that did not contain any arsenic. A common thread in the environment of symptomatic patients was damp and moldy wallpapers exuding a garlic-like odor. This highlighted that the exposure was most likely a consequence of

the molds growing on the wallpaper that metabolized arsenic to produce volatile, toxic arsines, rather than the mechanical disintegration of the wallpaper.

In 1892, Gosio demonstrated that the molds, which he termed as "arsenic fungi," showed the ability to undergo a biological mechanism and release volatile gases into the atmosphere. He isolated the gas produced from *S. brevicaulis* cultured on potato mash containing arsenious oxide and analyzed it for CO_2 and H_2O after passing it through a red-hot tube. He believed that the gas contained alkyl arsine, diethylarsine ($(C_2H_5)_2AsH$) (Thom and Raper 1932, Challenger 1945). The concept of biomethylation of arsenic was then proposed by Frederick Challenger in 1945, wherein he described the production of methylated arsenic species via the reduction of inorganic species and biological oxidative methylation of trivalent arsenic (Figure 4). He discovered that the volatile arsines termed as 'Gosio gas' were trimethylarsines and not diethylarsines as Gosio had believed (Bencko and Yan Li Foong 2017). He explained that the trimethylarsine arose from cacodylic acid by reduction and dismutation and that aliphatic arsonic acids did not undergo dismutation in mold cultures (Challenger 1945).

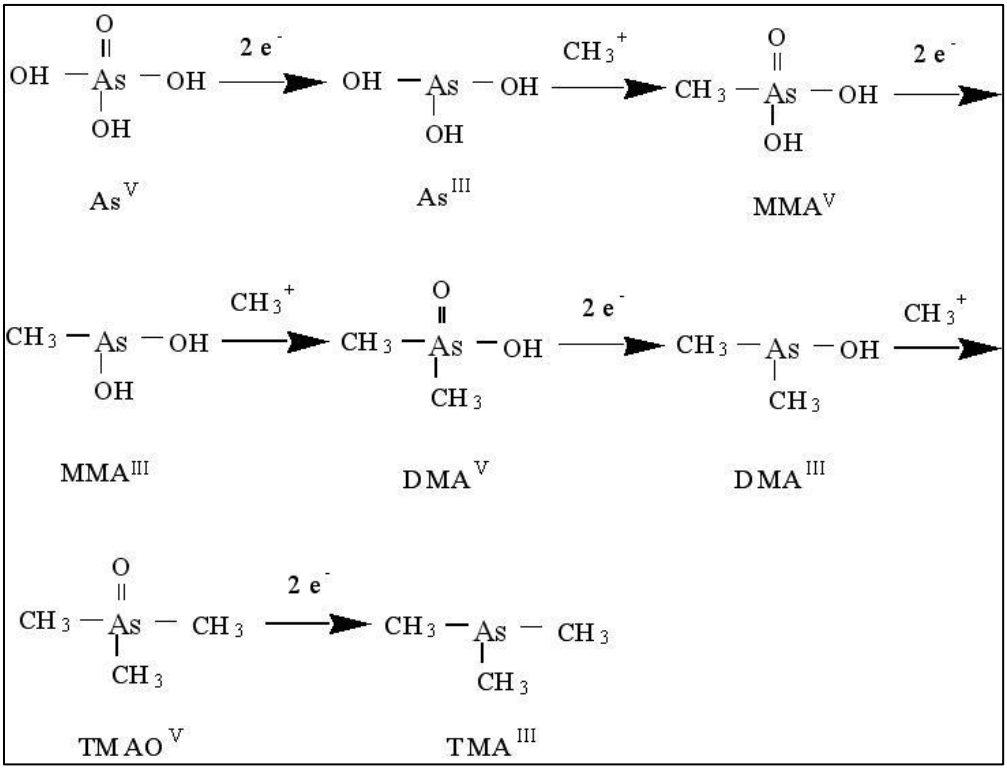


Figure 4. Challenger pathway for arsenic biomethylation (Le 2001-2004).

Theoretically, the process of methylation is only biologically-driven. It is not expected to occur abiotically even in the presence of a carbon source, proteins, and other organic compounds, as the C-As bonds are weaker than that of C-C, C-N, or C-O bonds (Carbonell-Barrachina, et al. 1999).

Organic arsenic compounds have also been detected in marine animals, Arsenobetaine (AsB) being a commonly found example in the aquatic system (Kumaresan and Riyazuddin 2001). Methylarsenicals are more stable than inorganic arsenic in water. The concentrations of DMA(V), MMA(V), and AsB in water are relatively constant. While thermodynamically unstable, organic arsenic compounds can be kinetically stable (Gong, et al. 2002).

In aqueous systems, arsenic speciation tends to be dominated by the anionic forms of arsenic acid. The complexation of reduced forms of arsenic with other compounds also varies across different arsenic species. As(III) reacts with sulfur and sulfhydryl groups (enzymes, proteins, cystine), whereas As(V) forms complexes with reduced nitrogen species like amines. This characteristic of inorganic arsenic species aids in their mobility through the system and prevents sorption and coprecipitation with solid-phase organics (Kumaresan and Riyazuddin 2001). The formation of carbonate complexes of As(III) (($As(CO_3)^{2-}$, $As(CO_3)(OH)^{2-}$, $AsCO_3^{+}$)) has also been hypothesized for cases where an increase in arsenic release was observed at high carbonate concentrations (Kim, Nriagu and Haack 2000, Korshin, Kim, et al. 2006). It is believed that the carbonate system, CO_3^{2-} and HCO_3^{-} in particular, may play a key role in the leaching of arsenic into natural waters over geological time (Anawar, Akai and Sakugawa 2004).

2.2.2. Chemistry of Arsenic in Groundwater

Arsenic contamination of groundwater has been documented in Argentina, Chile, Mexico, Vietnam, Taiwan, the US, and especially in the Ganges delta that comprises West Bengal, India, and Bangladesh (Nordstorm 2002, Berg, et al. 2001, Rahman, et al. 2001). In Bangladesh, most of the regular water supply for drinking and agricultural purposes switched from surface water to groundwater resources in the mid-20^{th} century. The first recorded case of arsenic toxicity in Bangladesh was documented in the 1980s, followed by the first discovery of arsenic contamination

in the groundwater almost a decade later. Groundwater arsenic concentrations much higher than 50 µg/L have been recorded, while the permissible limit established by the WHO for human consumption is 10 µg/L (Chowdhury, et al. 1999).

Arsenic concentrations ranging from 1 to 3050 µg/L, with an average of 159 µg/L, have also been found in private tube wells in the Red River Delta of northern Vietnam. A study noted that a highly affected rural area where the groundwater was sourced as drinking water had an average concentration of 430 µg/L (Berg, et al. 2001). In the US, arsenic contamination of groundwater is commonly found at sites requiring long-term cleanup of hazardous contamination, also known as Superfund sites (U.S. EPA 1997). One such example is the Vineland Chemical Co. Inc. Superfund site in Vineland, New Jersey where the groundwater, soil, and sediment are contaminated with arsenic (WQP 2016).

Many groundwater sources with elevated arsenic concentrations are characterized by low dissolved oxygen (<0.5 mg/L). Such anoxic conditions result in high dissolved iron and manganese concentrations and low redox potential (Kim, Nriagu and Haack 2000). In a reducing environment, arsenic in the form of arsenite As(III) is prevalent and it exists in the mobile or soluble phase (Korte and Fernando 1991, Berg, et al. 2001). Arsenic in sediments is known to be associated with iron oxyhydroxides or arsenic-containing sulfide minerals. The dissolution of iron oxyhydroxides in reducing environments can release arsenic into the groundwater. In oxidizing environments, the introduction of oxygen at the surface can oxidize arsenic-containing sulfide minerals and liberate arsenic into the water (Kim, Nriagu and Haack 2000). Studies performed in the Ganges delta are indicative of the reductive release of arsenic. However, the possibility of natural weathering of granitic and metamorphic rocks in the Himalayas, causing the release of arsenic into the waters has not been ruled out (Harvey and Ahmed 2005).

The leaching of arsenic from sulfide minerals and iron oxyhydroxides has been correlated with high concentrations of bicarbonate in the environment. Studies performed by Anawar et al. (2004) show the mobilization of arsenic from arsenic adsorbed on FeO(OH) by 0.1M $NaHCO_3$, which points to the substitution of arsenic by bicarbonate ion on the available surface sites on iron oxyhydroxide (Anawar, Akai and Sakugawa 2004). Alternatively, the carbonation of arsenic sulfide minerals resulting in stable arseno-carbonate complexes has also been proven to occur

under anaerobic conditions. According to Kim et al., leaching of arsenic into groundwater has been observed for carbonate concentrations above 200 mg/L (Kim, Nriagu and Haack 2000).

2.2.3. Chemistry of Arsenic in Soil

Inorganic forms of arsenic are predominant in soils. Under anoxic conditions, they are most commonly associated with sulfide minerals like arsenopyrite, realgar, and scorodite. The soil chemistry of arsenic is distinct from that of other heavy metals. While most heavy metals, for instance – copper, lead, and cadmium, are mobile under acidic conditions, arsenic is only moderately soluble at relatively low pH due to the increased sorption of As(V) species on abundant soil interfaces. The solubility and speciation of arsenic in soil depend on soil type, amount of clay, presence, and concentration of metal oxides and hydroxides, pH and redox potential, and sorbing capacity (Carbonell-Barrachina, et al. 1999, Shrivastava, et al. 2015). As(V) is prevalent and thermodynamically stable under oxic soil (Eh > 200mV; pH 5.0-8.0) conditions. On the other hand, As(III) is dominant under reducing soil conditions. The inorganic arsenic species can undergo redox reactions and biomethylation in the soils and sediments, and can naturally sorb onto hydrous oxides of iron, aluminum, and manganese (Figure 5) (Akter, Owens and David 2005, Shrivastava, et al. 2015).

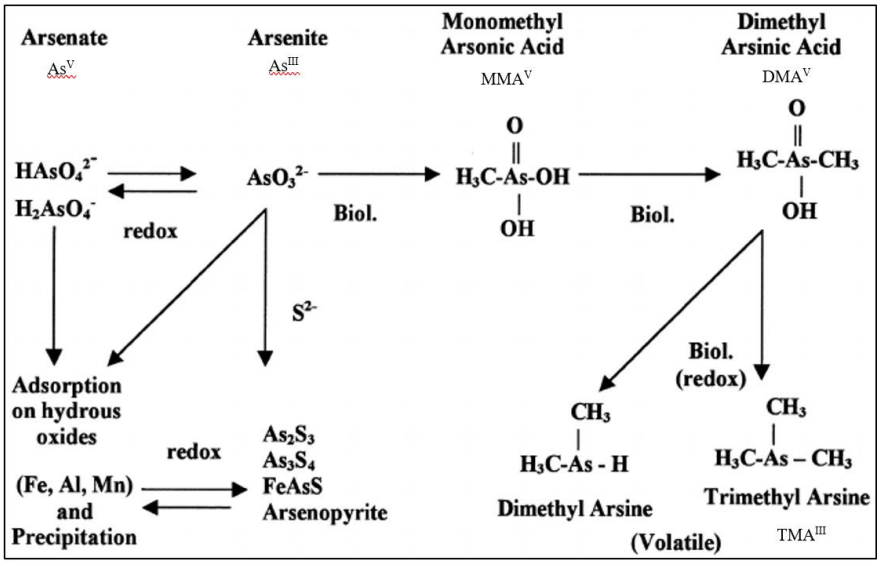


Figure 5. Transformations of arsenic in soil (Akter, Owens and David 2005).

The solubility of arsenic tends to be higher in the neutral to alkaline pH range (6.6 – 7.8) The presence of minerals surfaces, and organic matter in fine-grained soils can affect arsenic speciation as compared to coarse-grained soils. Clayey soils tend to have more arsenic than sandy soils due to the higher presence of ferric oxyhydroxide (FeOOH). Inorganic arsenic species have shown a high affinity for hydrous oxides of Fe, Mn, and Al in acidic soils (Akter, Owens and David 2005). However, it is the presence of FeOOH in addition to higher surface areas of clayey soils that make the arsenic less mobile and, in turn, reduced the toxicity of the soil. According to Shrivastava et al., the bioavailability of arsenic in soils is also influenced by aging and sequestration of contaminated soil (Shrivastava, et al. 2015).

Arsenic concentrations in groundwater and soil tend to be correlated; however, the consequences of groundwater contamination are better known. Arsenic contamination of the soil can have a direct and instantaneous impact on crop growth and yield. Arsenate (As(V)) is chemically analogous to phosphate (PO_4^{3-}) and thus, may interfere with the process of oxidative phosphorylation, which results in the formation of ATP. This will inhibit plant growth and may cause a decrease in yield, a hindrance to photosynthetic activity, inhibition of seed germination, necrosis and possibly, death (Marin, Masscheleyn and Patrick Jr 1992, Shrivastava, et al. 2015). Arsenite (As(III) may also bind to the active sites of thiol-containing (R-SH) enzymes and, ultimately, inhibit enzyme activity (Carbonell-Barrachina, et al. 1999).

2.2.4. Chemistry of Arsenic in Landfills

Arsenic species have been identified in both landfill leachate and biogas. As has been observed in the case of water and soils, arsenic speciation in landfill leachates is controlled by redox potential, microbiological activity, and other complex biological, chemical, and/or physical processes occurring in the landfill and leachate itself (Pinel-Raffaitin, et al. 2007)..

The composition of the effluent generated at a landfill is influenced by the composition of waste accumulated at the landfill. Municipal solid wastes (MSW) typically contain an array of biodegradable and non-biodegradable components, including food residues, construction materials, surfactants, and typical environmentally relevant species such as DOM, iron,

phosphates, ammonia, and others. This complex substrate affects the behavior of arsenic in the landfill leachate (Li, et al. 2010, Kamaruddin, et al. 2015). Typically, the sources of arsenic in MSW through anthropogenic activities are glasses, metallic components, and agricultural products. "According to the French Agency for the Environment and Energy Management, the total arsenic concentration in municipal solid wastes reaches 5 mg/kg dry waste" (Pinel-Raffaitin, et al. 2007). In the US, common sources of arsenic in landfills are - CCA (chromated copper arsenic) treated wood, coal combustion products (CCPs), industrial solid waste, mining and mining processing waste, arsenic bearing solid residuals (ABSRs) from drinking water treatment plants (EPA 2006). Cover soil that is used in daily landfill operations can also be a source of arsenic. Inadequate lining and/or coverage of the landfill site and improper treatment of waste can have an adverse impact on the surrounding area. Leachate percolating through the landfill can deposit the pollutants into the base soil, which can further contaminate the groundwater lying beneath (Kamaruddin, et al. 2015).

During MSW degradation, the landfill system is a reducing environment created by the decomposition of organic matter under anaerobic conditions. As(V) can be readily reduced to As(III). Arsenite dominates under moderately reducing conditions (0±100 mV redox potential). Under these conditions, the dissolution of iron oxyhydroxides is promoted, which results in a significant increase in the mobilization and leaching of arsenic through the landfill (Pinel-Raffaitin, et al. 2007). At more pronounced reducing conditions (redox potentials at or below -250mV), the dissolved arsenic concentration drops, indicating the occurrence of precipitation of arsenic in the solution. This is a consequence of an increase in the total sulfide concentration and its subsequent reaction with divalent transition metal ions (Fe^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Hg^{2+}). Due to the strong affinity of sulfides to arsenic under reducing conditions, the reaction results in the formation of insoluble arsenic sulfide minerals. Under aerobic conditions, the sulfide-containing species can be easily oxidized to sulfate ions and release arsenic back into the sludge (Carbonell-Barrachina, et al. 1999).

The solubility of arsenic is maximum at the neutral pH of the leachate and decreases under both acidic and alkaline conditions. The speciation drastically changes with minute changes in pH. At pH 5.0, inorganic forms of arsenic are dominant; however, at pH 6.5, organic arsenic species are highly soluble in the solution. (Carbonell-Barrachina, et al. 1999).

The nature of the landfill and the presence of extremely active microbial populations creates an ideal atmosphere that promotes the biomethylation of available arsenic by microorganisms via Challenger's pathway (Challenger 1945). The mechanism of degradation of arsenic through different landfill systems (waste, leachate, and biogas) is schematically represented in Figure 6. It outlines the pathway of serial methylation followed by reduction occurring in each landfill compartment. Intermediates formed during the process, like MMA(III) and DMA(III), tend to remain undetected due to their high instability. Methylated arsenic species have been found in landfill leachate and biogas (Pinel-Raffaitin, et al. 2007).

Landfill gas (LFG) is formed as a by-product of microbial degradation of organic matter in the landfill and is majorly composed of CH_4 and CO_2 gases. LFG can be extracted using a series of pipes and wells and physically processed to purify methane gas. LFG condensate is also produced via the artificial or natural cooling of the gas (Speight 2019). Volatile methylated arsenic species can be transported with the LFG and transferred into the LFG condensate.

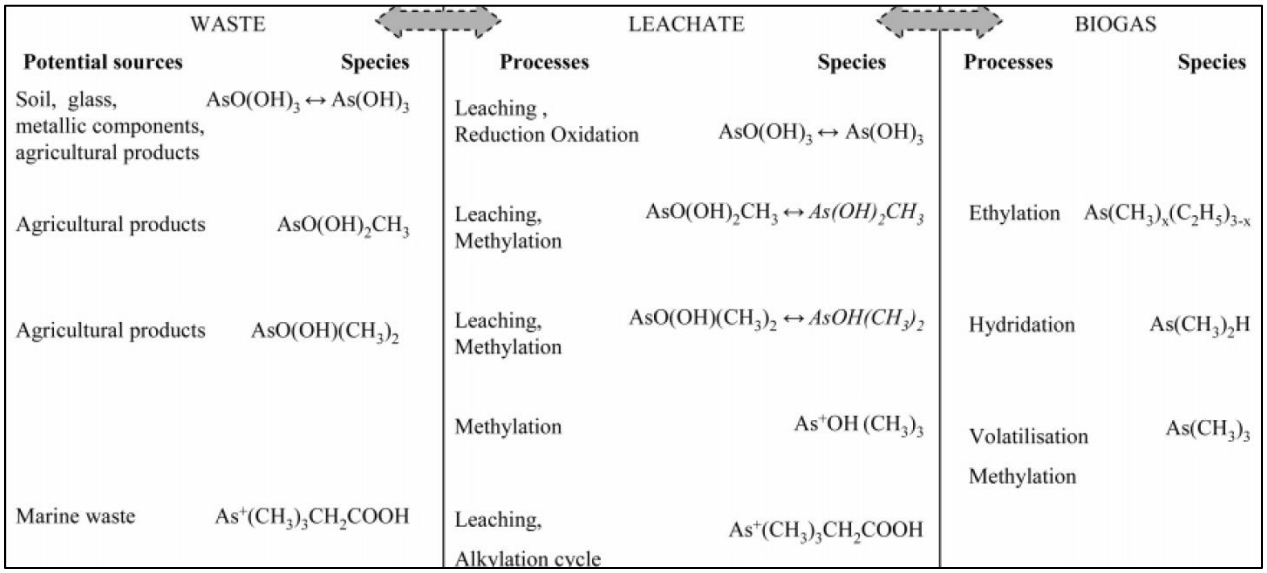


Figure 6. Sources and processes of arsenic occurrence in waste, leachate, and biogas *(Pinel-Raffaitin, et al. 2007).*

High concentrations of volatile, methylated, and to some extent, ethylated arsines have been identified in landfill biogas (Li, et al. 2010). The predominance of trimethylarsines over dimethylarsines in biogas points to the occurrence of peralkylation in the gaseous phase (Ng and

Seawright 1999). The concentration of trimethylarsine ($As(CH_3)_3$) is almost 100 to 1000 times higher than other volatile arsenic species which include dimethylarsine ($As(CH_3)_2H$), dimethylethylarsine ($As(CH_3)_2(C_2H_5)$), diethylmethylarsine ($As(CH_3)(C_2H_5)_2$), and triethylarsine ($As(C_2H_5)_3$) (Pinel-Raffaitin, et al. 2007).

Hydrological conditions, especially rainfall, introduce seasonal variations in the composition of the leachate – metal speciation, COD, TSS, pH, salts, and DIC in the landfill system (Ahmed, Joshi and Kumar 2019). Open landfills without any top cover produce higher leachate and, high COD concentration and load during high rainfalls. Top covers are essential in preventing surface water contamination as baseliners are used to prevent contamination of groundwater by leachate percolation (Rafizul and Alamgir 2012). In tropical regions, excessive and long periods of rainfall is a common phenomenon. Leachate collection during rainfall and recirculation during the dry season is recommended. This improves the rate of biodegradation of MSW during the dry season (Trankler, et al. 2005, Rafizul and Alamgir 2012).

2.2.5. Arsenic in Drinking Water

Arsenic contamination of drinking water supply has been widely reported in Bangladesh, Hanoi (Vietnam), and West Bengal (India) (Hindmarsh and McCurdy 1986, Berg, et al. 2001, Korshin, Kim, et al. 2006). The ingestion of high levels of arsenic in water over a long period (5-20 years) has been associated with a chronic illness known as arsenicosis or arsenic poisoning. The symptoms range from skin problems, cancer, detrimental effects on the blood vessels, and possibly death (Arsenic 2018).

Conventional methods used in drinking water treatment plants can be extremely successful for the removal of arsenate. Primarily, there are four types of commercial treatment processes - coagulation, adsorption, ion-exchange, and membrane-based. However, most of the available arsenic predominantly exists as arsenite, which is more toxic and difficult to remove (EPA 2003, Korshin, Kim, et al. 2006, Mondal, et al. 2013, Singh, et al. 2015). This arises since arsenite is non-charged below a pH of 9.2 (Nicomel, et al. 2015). Therefore, the input stream firstly needs to be pre-oxidized to convert arsenite into arsenate (As(V)) to facilitate removal.

2.3. Treatment of arsenic

2.3.1. Conventional treatment of arsenic

2.3.1.1. Pre-treatment of arsenic by oxidation

Highly effective oxidizers that are used for pre-treatment of arsenic-containing waters include chlorine, permanganate, and ozone. UV and chloramine alone are usually ineffective in oxidizing As(III). Sulfite, ferric ion, or citrate are typically applied to catalyze direct UV application (Johnston, Heijnen and Wurzel 2001). Atmospheric oxygen, as well as bacteria, have also been used in the oxidation process.

The applications of permanganate and active chlorine have been known to achieve >95% conversion of As(III) to As(V). They are critical oxidants used in removing arsenic in drinking water operations developing countries. The significant drawbacks observed in the usage of chlorine are the storage and handling, and formation of toxic disinfection byproducts like trihalomethanes (Johnston, Heijnen and Wurzel 2001). The co-occurrence of NH_3 with arsenic-containing reduced groundwater systems, can also negatively affect the oxidation of As(III) due to the rapid consumption of free available chlorine by NH_3 (Dodd, et al. 2006). The use of permanganate requires additional steps, including post-treatment filtration, to remove the MnO_2 (Equation 2) precipitate formed during the treatment and a subsequent disinfection step.

$$3H_3AsO_3 + 2MnO_4^- \rightarrow 3H_2AsO_4^- + H^+ + 2MnO_2 + H_2O \quad (2)$$

Ozone (O_3) is also another powerful oxidant used in drinking water treatment plants. It is very unstable and highly reactive and, thus, needs to be produced on-site. Ozonation by-products mainly include the formation of bromates, particularly organo-brominated compounds in the presence of high concentrations of NOM, and carbonyls like formaldehyde and acetaldehyde (Wypych 2017, Gunten and Hoigne 1994).

$$H_3AsO_3 + O_3 \rightarrow H_2AsO_4^- + H^+ + O_2 \quad (3)$$

Using atmospheric oxygen as an oxidant is a prolonged process and may take up to hours or even many weeks to completely oxidize the arsenite (Ahmed 2001). Hence, arsenic treatment commonly includes application of more effective chemical oxidants. Limitations in the application of chemical oxidants may arise due to the presence and interference of dissolved iron, manganese, TOC, ammonia, bromide, and sulfide ions (EPA 2003, Nicomel, et al. 2015).

2.3.1.2. Removal of arsenic by coagulation/flocculation

Conventional coagulation methods use iron-based coagulants or alum ($Al_2(SO_4)_3.18H_2O$) for drinking water systems. On application, these reagents rapidly form metal hydroxide flocs (Equation 4 and 6) then bind and coprecipitate with arsenate (Equation 5 and 7). These equations exemplify typical processes in the case of coagulation with ferric chloride.

Ferric hydroxide formation: $$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 \downarrow + HCl \quad (4)$$

Co-precipitation of arsenic: $$Fe(OH)_3 + H_3AsO_4 \rightarrow FeAsO_4.2H_2O + H_2O \quad (5)$$

Aluminum precipitation: $$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 \downarrow + HCl \quad (6)$$

Co-precipitation of arsenic (non-stoichiometric, non-defined product):

$$Fe(OH)_3 + H_3AsO_4 \rightarrow FeAsO_4.2H_2O + H_2O \quad (7)$$

Other critical mechanism of arsenic removal by coagulation is via the adsorption of arsenic species onto the surfaces of the aluminium or iron hydroxides formed. Most coagulative treatments require a series of pre-oxidation, filtration, and pH adjustment before or after the treatment (Saha, Bandyopadhyay and Dikshit 2001). Approximately 90% and >95% arsenate removal has been achieved using alum and iron-based coagulants, respectively (EPA 2003). Arsenic removal through sorption is pH-dependent (Singh, et al. 2015). At an optimal pH, the sorbent's surface is protonated. The microparticles and negatively charged ions present in the solution attach to the flocs and settle out (Ahmed 2001, Johnston, Heijnen and Wurzel 2001). Iron-based coagulants like ferric sulfate ($Fe_2(SO_4)_3.7H_2O$) or ferric chloride ($FeCl_3$) are more effective in the removal of

arsenate than alum (EPA 2003). They are more stable and efficient over a wider pH range (5.0 to 8.0) (Saha, Bandyopadhyay and Dikshit 2001, Singh, et al. 2015).

The technology of dispersed gas flotation in combination with coagulation is also used in BOD/COD removal. On gas purging, the solid particles aggregate with the gas bubbles formed and that reduces the overall density of the particle. The floating particles can then be separated out by the addition of a coagulant. This method has been actively researched as a method to remove oil-based substances from wastewater sources (Saththasivam, Loganathan and Sarp 2016).

The major drawback of coagulative treatment is the production of high levels of arsenic-concentrated sludge. The treatment must be followed by a sedimentation or filtration step to remove the sludge produced and safe disposal of the coprecipitated arsenic (Nicomel, et al. 2015). The removal is efficient at lower concentrations of suspended solids, DOM, sulfates, phosphates, and silicates (Hering, et al. 1997). The presence of phosphates (PO_4^{3-}) is detrimental for arsenic removal since phosphate can aggressively compete with arsenate for adsorption sites due to the similarity in their chemical structures (EPA 2003, Johnston, Heijnen and Wurzel 2001). When applying iron-based sorbents, the treatment plant operators also need to pay close attention to the MCL of iron in the discharge water (Nicomel, et al. 2015).

2.3.1.3. Removal of arsenic by adsorption

Adsorption has been widely used due to its cost-effectiveness, high arsenic removal efficiencies, and straightforward handling (Mohan and Pittman 2007, Nicomel, et al. 2015). Ion-exchange resins and activated alumina are two of the most common adsorption treatments adopted by the water treatment industry.

The efficiency of ion-exchange resins strongly depends on the concentration of other anions present in the water matrix. The anions can compete for the exchange resin sites and hinder the removal of arsenate (Mondal, et al. 2013). The selectivity sequence of anions for the resin is: $SO_4^{2-} > HAsO_4^{2-} > NO_3^-$, $CO_3^{2-} > NO_2^- > Cl^-$ (Clifford 1999)**.** Resin fouling due to mineral scale or ions bound to active sites is a major limitation of this process. If the total dissolved solids (TDS)

and sulfate concentrations in the feed water exceed 500 mg/L and 120 mg/L, respectively, this treatment is not recommended (Wang, Chen and Fields 2000).

Activated alumina (Al_2O_3), another commonly used adsorbent, has a high internal surface area, and behaves like a less-effective ion-exchange resin. The efficiency of activated alumina is pH-dependent. It works best at an optimum pH range of 5.5 to 6.0 (Johnston, Heijnen and Wurzel 2001). The selectivity sequence of anions competing for the sorption sites of activated alumina is: $OH^- > H_2AsO4^- > Si(OH)_3O^- > F^- > HSeO_3- > TOC > SO_4^{2-} > H_3AsO_3$ (Clifford 1999).

Activated carbon (AC) is typically used to remove contaminants like aromatic compounds and heavy metal ions from aqueous solutions. Its hydrophobic nature and high porosity improve the adsorbent's removal capacity (Ansari and Sadegh 2007). The removal efficiency of arsenic and the sorptive capacity of activated carbon depend on the pH of the solution and the arsenic species' oxidation state. The pH regulates the distribution of arsenic species in the solution and the surface charge of the activated carbon, which is positive under acidic conditions and is balanced out with arsenic anions present in the aqueous system (Huang and Fu 1984, Ansari and Sadegh 2007). Arsenite (As(III)) and arsenate (As(V)) are well adsorbed by activated carbon at basic and acidic conditions, respectively. The removal of As(III) increases with pH, and that of As(V) increases with a decrease in pH. According to a study performed by Ansari and Sadegh (2007), the optimum pH value for the removal of As(III) and As(V) using activated carbon was found to be 12 and 3, respectively (Ansari and Sadegh 2007).

On the other hand, Huang and Fu (1984) observed peak As(V) removal at pH near 4.5. However, the regeneration of spent activated carbon is difficult to attain, and thus the use of carbon-based adsorbents for long-term applications in arsenic removal is questionable. Treatment of AC with NaOH can result in the desorption of arsenic species from the surface freeing the surface sites. However, the reuse of the treated AC in further removal has been proven ineffective (Huang and Fu 1984).

2.3.1.4. Removal of arsenic by membrane processes

Membranes are synthetic materials that act as selective barriers (Singh, et al. 2015, Nicomel, et al. 2015). There are two types of pressure-driven membranes: (a) low-pressure (10-30 psi) with larger pore size such as microfiltration (MF) and ultrafiltration (UF), and (b) tighter, high-pressure (75-250 psi) membranes such as nanofiltration (NF) and reverse osmosis (RO) (EPA 2003, Johnston, Heijnen and Wurzel 2001, Nicomel, et al. 2015, Mondal, et al. 2013, Shih 2005). Usually, high-pressure membranes are used for water desalination as they can achieve a high rejection rate of over 99% of low molecular mass compounds (Mondal, et al. 2013, Johnston, Heijnen and Wurzel 2001). Pre-treatment via precipitation or flocculation followed by filtration is necessary when applying membrane treatment to facilitate physical removal of particulate matter in addition to subsequent pre-treatment steps (EPA 2003). This is done for two reasons: (i) membrane longevity is sensitive to suspended solids and DOM present in the feed water, and (ii) to increase the size of the arsenic-bearing solids to improve retention (EPA 2003, Johnston, Heijnen and Wurzel 2001)

The separation of arsenic using membranes is controlled not only by the pore size but also by the electrostatic repulsion between the anionic arsenic species and the charge of the membrane (Yoon, et al. 2009, Mondal, et al. 2013). Thus, the feedwater pH and conductivity are critical factors for efficient retention of ions (Yoon, et al. 2009, Shih 2005, Mondal, et al. 2013). Charged membranes are capable of a higher rejection of charged molecules than of uncharged molecules. Studies performed using RO membranes have also demonstrated >90% removal of charged As(V) as compared to <70% of neutral As(III) (Singh, et al. 2015).

The limitations in the application of membranes are capital and operating costs, rigorous pre-treatment of feed water, and membrane fouling due to DOM and other inorganic ions (Ca^{2+}, Mg^{2+}, Si^{2+}, sulfates, chlorides, carbonates) (EPA 2003).

2.3.2. Zero-valent iron

Zero-valent iron (ZVI) is actively applied in the in-situ groundwater remediation of arsenic (Lein and Wilkin 2005, Biterna, et al. 2010). It is also widely used in the industry to treat halogenated organic compounds and inorganic contaminants such as nitrate, chromate, uranyl,

copper, cadmium, aluminum, zinc, nickel, and metalloids (Bang, Korfiatis and Meng 2005). The treatment mechanism of ZVI is initiated electrochemical reduction of arsenic species at higher oxidation states to As(0). Subsequently, adsorption and coprecipitation of the contaminant via in-situ oxidation or corrosion of iron takes place (Equation 8-9). This results in in the formation of iron corrosion products - iron oxides and hydroxides in the solution (Bang, Korfiatis and Meng 2005, Lein and Wilkin 2005, Sun, et al. 2006, Kanel, et al. 2005). Simultaneously, iron-oxide particles are also produced during the oxidation of Fe(0). The arsenic-iron complexes formed demonstrate low leaching rates of arsenic back into the solution.

The consumption of H^+ ions by Fe^0 and the consequent release of OH^- ions during adsorption increases the pH of the solution.

$$Anaerobic\ corrosion: \quad Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{8A}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{8B}$$

$$Aerobic\ corrosion: \quad 2Fe^0 + 2H_2O + O_2 \rightarrow Fe^{2+} + 4OH^- \tag{9}$$

The Fe^{2+} ions produced further react with hydroxyl ions and produce magnetite (Fe_3O_4) (Equation 11), ferrous hydroxide ($Fe(OH)_2$) (Equation 10), and ferric hydroxide ($Fe(OH)_3$) (Equation 12) in the presence of O_2 (Su and Puls 2001, Kanel, et al. 2005).

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_{2\,(s)} \tag{10}$$

$$6Fe(OH)_{2\,(s)} + O_2 \rightarrow 2Fe_3O_4\,(s) + 6H_2O \tag{11}$$

$$Fe_3O_{4\,(s)} + O_{2\,(aq)} + 18H_2O \rightarrow 12Fe(OH)_{3\,(s)} \tag{12}$$

Under aerobic conditions, adsorption is a predominant mechanism due to the oxidation of iron and the consequent formation of iron corrosion products that aid in arsenic removal. A lower pH in the presence of oxygen promotes the removal of As(V) as the formation of iron corrosion products actively occurs at a lower pH. Meanwhile, under anaerobic conditions, arsenic is reduced, and it undergoes surface precipitation at the ZVI surface. This is evidently observed due to the lack of oxygen intrusion into the water and the lack of oxidation taking place(Sun, et al. 2006).

The removal of arsenic initially occurs at a rapid pace, followed by a decrease in removal rate (Biterna, et al. 2010, Lein and Wilkin 2005).

Physicochemical characteristics of the water, including pH, dissolved oxygen, concentrations of ions (Cl^-, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, BO_3^{3-}), and presence of DOM control the efficiency of arsenic removal using ZVI (Biterna, et al. 2010, Sun, et al. 2006). The presence of NO_3^- and borate ions in the solution negatively affect the removal of arsenic. Additionally, PO_4^{3-} ions can have an inhibitory effect on arsenic removal. Due to the similarity in their chemical composition, arsenate and phosphate ions compete for the same adsorption sites on the iron surface. A high concentration of DOM, particularly humic acids, can impede arsenic removal due to the formation of iron-humate complexes that in turn, curb the formation of iron corrosion products that are essential in the removal of arsenic (Biterna, et al. 2010, Sun, et al. 2006).

The pH of the solution determines the distribution of arsenic species in the water. Adsorption of As(V) via iron oxides increases with a decrease in pH, and that of As(III) increases with an increase in water's pH as described above. The removal of both As(III) and As(V) is relatively consistent at near-neutral pH. However, the increase in pH during the process aids in the removal of As(III). (Su and Puls 2001).

The surface area available for adsorption and the extent of the reaction depends on the type of iron used. Thus, the application of nanoscale iron is sought after in environmental remediation. In addition to its large surface area and high reactivity, nanoscale iron tends to remain in suspension. This characteristic reduces the requirement for stimulation of the experimental system and allows the iron to flow against the current of the water in the case of groundwater remediation (Biterna, et al. 2010, Kanel, et al. 2005, Su and Puls 2001).

2.3.3. Micro-electrolysis

Recent studies have examined the use of a combination of adsorption-coprecipitation using iron and activated carbon, to successfully remove DOM and other analytes present in untreated water. This process referred to in the literature as micro-electrolysis (ME) has been particularly useful for removing organic pollutants with high chemical stability and low biodegradability that

are resistant to conventional methods (Ju and Hu 2011). A successful application of this approach can be in the treatment of landfill leachate with low COD and biodegradability, and high organic matter content. Mature leachate is extremely stable and resistant to conventional oxidative pre-treatment (Ying, et al. 2012).

During ME, the in-situ formation of a large number of microscopic galvanic cells occurs, unlike conventional electrolysis where an external source is used to supply the power. (Ying, et al. 2012). Zero-valent iron at the anode loses two electrons to the activated carbon at the cathode. The electron flow from the anode results in the rapid corrosion of the iron particles with the continuous release of ferrous (Fe^{2+}) ions (Equation 13) into the solution (Ying, et al. 2012). A simultaneous redox reaction occurs between Fe^0 and activated carbon occurs in the solution (Ju and Hu 2011). The cathode accepts the electron accelerating the process of reduction (Yang, et al. 2017). The degradation of organic matter ultimately occurs through a multitude of processes, including electron transfer, electrochemical reduction, adsorption, and co-precipitation (Yang, et al. 2017).

$$Anode: \quad Fe - 2e^- \rightarrow Fe^{2+} \quad (E_\theta(Fe^{2+}/Fe) = -0.44V) \tag{13}$$

$$Cathode: \quad 2H^+ + 2e^- \rightarrow 2[H] \rightarrow H_2 \quad (E_\theta(H^+/H_2) = 0V) \tag{14}$$

Parameters, including the solution's pH, Fe/C mass ratio, the gas type, and flow used for purging, essentially control the efficiency of the process (Yang, et al. 2017, Ying, et al. 2012). Acidic conditions may promote the formation of atomic or molecular hydrogen [H] ions if a sufficiently large concentration of [H^+] ions is present (Equation 14). The low pH accelerates the cathodic reduction that consumes the acidity of the solution (Zhang, et al. 2018, Yang, et al. 2017). This rise in pH supports the formation of iron hydroxides, and consequently, coprecipitation of DOM and other analytes occurs. The ratio of iron to carbon and their respective particle size determine the number of galvanic cells formed between the iron in contact with the activated carbon and, thus, determines the intensity of the reaction efficiency (Yang, et al. 2017).

Purging of gas through the solution during ME is known to improve COD removal efficiency (Yang, et al. 2017). Aeration of the solution produces hydrogen peroxide (H_2O_2) by the reduction of oxygen. H_2O_2, combined with Fe^{2+} ions, forms Fenton's reagent known as a strong oxidant commonly used in wastewater treatment (Ju and Hu 2011). In the Fenton process, H_2O_2 decomposition catalyzed by Fe^{2+} ions rapidly generate hydroxyl radicals (•OH) that oxidizes of

targeted organic contaminants (Li, et al. 2012). The formation of Fenton's reagent in some ME processes has been shown to remove COD from the wastewater (Yang, et al. 2017). However, other studies have shown that the treatment of landfill leachate by ME with aeration results in low COD removal (Wang, Yang, et al. 2016, Ying, et al. 2012).

A ME process is believed to be at its best efficiency under reducing, DO-deficient, and acidic conditions. According to a study done by Ju et al. (2011), elimination of dissolved oxygen by purging N_2 gas into a micro-electrolysis matrix removed 100% chelated-Cu(II) ions within 5 minutes of treatment. On exposure to oxygen, the color changed from dark green to reddish-brown, indicating the oxidation of ferrous hydroxide ($Fe(OH)_2$) to ferric hydroxide ($Fe(OH)_3$). Also, the removal of chelated-Cu(II) ions was noted to have decreased to 43.24%, pointing to the possibility of desorption taking place in the solution (Ju, Hu and Cheng 2011).

$$Fe^{2+} + OH^- \rightarrow Fe(OH)_2 \quad (dark - green) \tag{13}$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \quad (reddish - brown) \tag{14}$$

Despite some attractive aspects of micro-electrolysis, this treatment method also has certain limitations. These include the need to clean and dispose of spent solids, routine replacement of the reagents, and low efficiency of regeneration of activated carbon (Zhang, et al. 2018). Although specific applications of this method in treating arsenic have not been pursued, its efficiency in treating organic contaminants and landfill leachate makes it a promising treatment option.

2.4. TOXICITY OF ARSENIC SPECIES

Speciation of arsenic greatly affects its toxicity and mobility in the environment (Bencko and Yan Li Foong 2017, Kumaresan and Riyazuddin 2001). Speciation also affects the bioavailability of the species to an exposed organism. In the studies of arsenic toxicity, there has been a rising debate on the toxicological studies of arsenic since the discovery of MMA(III) and DMA(III) in human urine (Gong, et al. 2002). Speciation can also help determine the bioavailability of the species to an organism.

Generally, the order of toxicity of arsenic compounds can be stated as – inorganic arsenicals (trivalent > pentavalent) > organoarsenicals > elemental arsenic (Hindmarsh and McCurdy 1986, Akter, Owens and David 2005, Arsenic 2018). The toxicity of organoarsenicals decreases with an increase in substitution of functional groups, with arsenobetaine (AsB) and arsenocholine (AsC) being virtually non-toxic (Goyer, Aposhian and Brown 2001). The methylated species are relatively non-toxic, in accord with the view that methylation is primarily a detoxification mechanism. However, it is suspected that it may not entirely be a detoxification mechanism for some mammalian species as they are deficient in the methyltransferase enzyme required to carry out methylation. As per the mobility of the arsenic species, As(III) is more mobile than As(V). Organoarsenicals like MMA(V) and DMA(V) are also mobile (Arsenic 2018).

Literature reports that arsenic toxicity has affected at least 140 million people in over 50 countries. Many drinking water sources have arsenic levels exceeding the WHO guideline of 10 µg/L in water. Symptoms for chronic arsenic toxicity (arsenicosis) include weakness, loss of appetite and energy, anemia. Hyperpigmentation, hypopigmentation, and wart-like keratoses on the palms and soles of the feet can develop over time and may progress to skin cancer (Arsenic 2018, Hindmarsh and McCurdy 1986). Acute toxicity in humans can cause gastrointestinal discomfort, vomiting, diarrhea, bloody urine, burning and dryness of mouth and throat, coma, and even death. Other adverse effects of prolonged arsenic exposure may include cancers of the bladder, kidney and lung, diabetes, high blood pressure, and reproductive disorders (Arsenic 2018). Arsenic is classified as a 'Group-A' carcinogen (Sarkar and Datta 2007). Highly bioavailable arsenic species present a lower LD_{50} value and pose a higher risk. In a human adult, the lethal range of inorganic arsenic is estimated to be 1-3mg/kg (Akter, Owens and David 2005). According to the Occupational Safety and Health Administration (OSHA), the permissible exposure limit of inorganic arsenic is less than 10 $\mu g/m^3$ of air, averaged over 8 hours.

2.5. CEDAR HILLS LANDFILL SITE

The Solid Waste Division (SWD) of King County manages the Cedar Hills Regional Landfill Facility (CHRLF) in Maple Valley, Washington. SWD is responsible for complying with the King

County Industrial Waste (KCIW) discharge permits (King County - Solid Waste Division 2019, Wood PLC 2020). The effluent discharge is pretreated in aeration lagoons prior to release to the King County POTW, South Treatment Plant (King County - Solid Waste Division 2019). The effluent generated at the CHRLF comprises landfill leachate, contaminated stormwater (including runoff from open refuse and paved work areas), sewage from the buildings on-site, LFG condensate, and process water from BioEenergy Washington (King County - Solid Waste Division 2019, Wood PLC 2020).

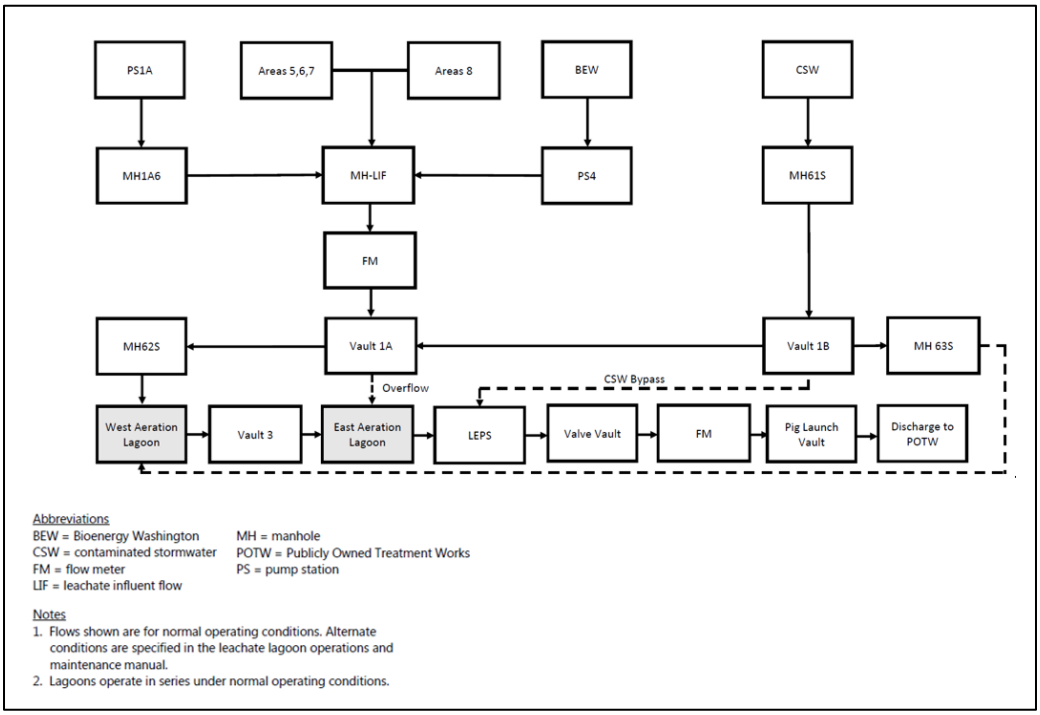


Figure 7. Simplified block diagram of flows at the CHRLF site (Wood Inc. 2020).

Areas 5, 6, and 7 (A567) are currently inactive areas of the landfill site and area 8 is active. Figure 7 provides a simplified description of flow from key locations at the CHRLF site. Leachate from these areas, manholes, and pump stations, along with contaminated stormwater is collected at Vault 1A (V1A). The leachate from V1A is transported to the aeration lagoons for preliminary COD removal. Aerated leachate is collected at the leachate effluent pumping station (LEPS) which is the point from where the effluent is discharged to the wastewater treatment plant. Effluent from BioEnergy Washington (BEW) has two potential sources of arsenic which include the discharged

process water from the conveyance system and the spent gas treatment media (*Norit Cabot Darco BG1*). The effluent is flows into Pump Station (PS) – 4 before being discharged into V1A prior aeration.

KCIW and KC-SWD have noted exceedances in arsenic concentration since 2015 (King County - Solid Waste Division 2019). The maximum discharge limit (MDL) limit for arsenic is 0.27 lb/day. However, the facility has observed an estimated 0.4 to 0.5 lb/day mass load of arsenic discharged from the site (Korshin 2019). Figure 8 shows the increase in arsenic loading (lb/day) as a function of time for LEPS from 2016 to 2018. There has been a consistent pattern of increase in arsenic loading during summer and fall months and decrease in the arsenic loading during winter months synonymous to the hydrological cycle of the area. The constant rise in arsenic concentrations in BEW process water (Figure 9) over the past decade is concerning, and thus it has been identified as an important source in the rise of arsenic in the landfill effluent.

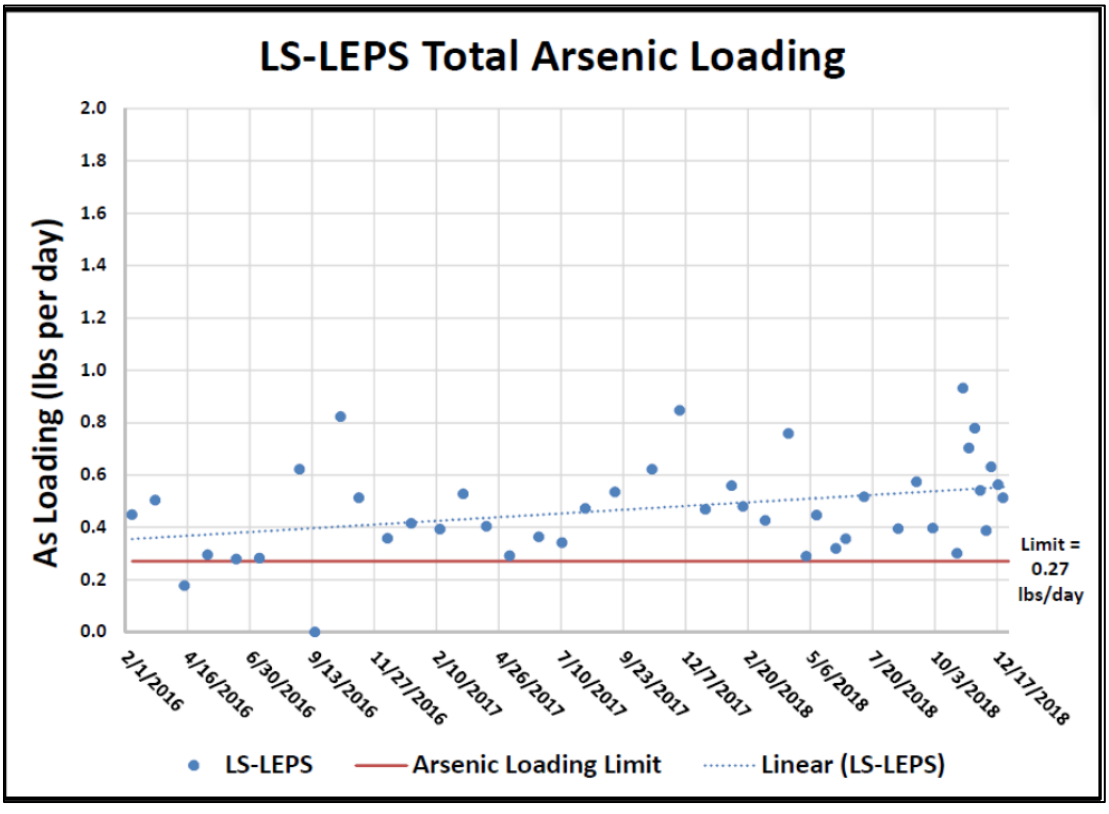


Figure 8. Total arsenic loading time profile for the LEPS stream (King County - Solid Waste Division 2019).

On further analysis, KC-SWD observed a seasonal variation in metals concentration shown in Table A-2 (Appendix A) for arsenic. A decrease in metal concentrations during the wet season implied that the spike during the dry season was possibly due to lower levels of dilution of the metals (Table A-3, Appendix A) (King County - Solid Waste Division 2019). These data indicate a need for an arsenic-specific treatment scheme that would result in the decrease in arsenic concentrations by greater than 50% (Korshin 2019). Accordingly, this study examined the performance of several methods, both conventional and novel, in removing As from CHRLF leachate and associated contaminated streams, notably gas condensates and BEW process water. Results of these experiments as well as a description of the materials and methods used in this study is presented in the sections that follow.

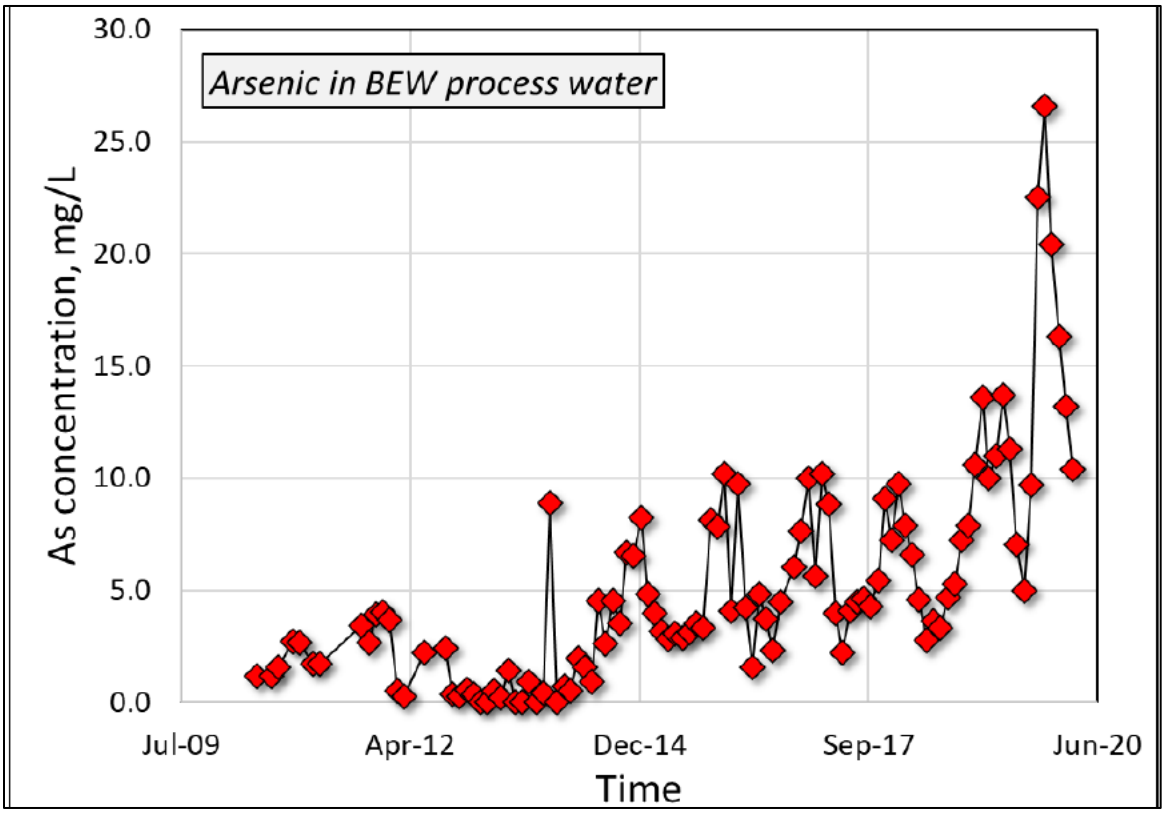


Figure 9. Arsenic concentrations in BEW process water from June 2010 to present. (Data courtesy Kevin Singer, PE) (G. V. Korshin 2020).

3. METHODS

3.1. SAMPLING AND PRESERVATION OF LANDFILL SAMPLES

The experiments reported in this thesis were conducted using leachate and LFG condensate samples from the Cedar Hills Regional Landfill (CHRLF) site. The samples were obtained in multiple sampling rounds, and various treatment methods were applied on each sample type. The sampling rounds (SR) took place in May, June, July, November of 2019, and January, March, and May 2020, and were referred to as SR1, SR2, SR3, SR4, SR5, and SR6, respectively. The leachate sampled was transported in 5-gallon carboys with no headspace. The leachate was then stored in a 4°C refrigerator to preserve its authenticity and avoid any biological activity and chemical transformations.

Analysis of the leachate from the multiple sampling rounds using ICP-MS indicated variability in the leachates and gas LFG condensates from different areas of the landfill with leachate arsenic concentration from 200 to 500 µg/L and LFG condensates arsenic concentrations as high as 50,000 µg/L. In some cases, arsenic concentrations in the leachate and LFG condensate samples from the same area varied across different sampling rounds. The arsenic concentration in the LFG condensate stream from Bioenergy Washington (BEW) ranged from 1,700 µg/L (SR2) to 50,000 µg/L (SR4), and in the leachate stream of LEPS ranged from 35 µg/L (SR5) to 300 µg/L (SR3). The difference in leachate concentrations might have been, for instance, a consequence of excessive rainfall that took place in December 2020. However, the exact cause for LFG condensate concentrations to have increased by almost two orders of magnitude is yet to be determined. While it has been associated with the formation of volatile arsines in the landfill, it is also suspected that the change of gas treatment media used in BEW could have led to the leachate's ongoing increase in arsenic concentrations. Refer Table 2 for the concentrations of arsenic and other secondary analytes, and Table 3 for TOC and TIC data for SR2, SR3, SR4, and SR5 leachate and LFG condensate samples.

3.1.1. Sampling Round 1 (SR1)

One leachate sample from the LEPS and one LFG condensate sample was provided in the first sampling round in May of 2019. The LFG condensate sample was likely to have been tainted with leachate as it had a deep-brown color like the leachate. The arsenic concentrations in these samples were estimated to be 400 µg/L. These samples were used in the initial analysis of conventional oxidative treatment methods like coagulation using ferric chloride, permanganate oxidation, and electrochemical oxidation using lead-based electrodes.

3.1.2. Sampling Round 2 (SR2)

This sampling round took place on July 19th, 2019. One LFG condensate sample from the BEW stream and two leachate samples were provided from Area 6 and Area 7 designated as the old and new leachate, respectively. The samples from SR2 were primarily subjected to coagulation, oxidative treatments and ozonation. They were also used for the initial trials for arsenic treatment using reductive methods of Zero-Valent Iron (ZVI) and micro-electrolysis (ME).

Table 2. Concentrations of total arsenic and selected co-occurring elements in CHRLF. (Analytical data provided by KCEL)

Sampling round	Time period	Sample Type	As conc (µg/L)	Ni conc (µg/L)	Cr conc (µg/L)
SR2	Jul '19	Area 6 (Old)	398	359	526
		Area 7 (New)	139	315	321
		BEW condensate	1700	< QL	< QL
		PS-4	78	40.2	40
		PS-1	273	72	72
		PS-2	32	108	37
		A7-lower	429	368	560
		A7-upper	125	1550	182
		A6-cond	151	86	226
SR3	Aug '19	MH46N	106	298	131
		MHL2	333	209	289
		A6IS	30	182	129
		LEPS	328	301	214

		Area 5,6,7	353	5	308
		BEW condensate	5510	< QL	6
		NFS	14600	10	2
SR4	Nov '19	BEW condensate	49600	< QL	< QL
		Area 5,6,7	336	103	144
		Vault 1A	302	303	279
SR5	Jan '20 and Feb '20	LEPS	35	29	28
		Vault 1A	16	18	19
		NFS	17600	16	< QL
		Area 5,6,7	275	208	180
		Area 8	5	27	16
SR6	Mar '20 and May '20	BPW 03/22	11000	-	-
		BPW 03/23	10300	-	-
		BPW 03/24	10600	-	-
		BPW 03/25	10700	-	-
		BPW 03/26	10100	-	-
		BPW 05/03	15890	< QL	< QL
		BPW 05/04	13237	< QL	79
		BPW 05/05	8690	13.6	< QL
		BPW 05/06	19102	< QL	383
		BPW 05/07	9245	< QL	270

*BPW = BEW Process Water

1. All sample types are leachate unless specified.

2. Refer to Figure 8 for site-specific location of leachate and condensate samples

3.1.3. Sampling Round 3 (SR3)

SR3 that took place on August 19th, 2019, produced a set of 13 samples in total. The samples were collected from different locations in the landfill. Specific sampling locations are labeled in Figure 10. All 13 samples were analyzed for the total concentrations of arsenic and secondary analytes to determine their respective characteristic nature.

The experiments accommodated only three SR3 samples. These included North Flaring Station (NFS) condensate, Bioenergy Washington (BEW) condensate, and Leachate Effluent from Pumping Station (LEPS). Primarily, reductive treatment and adsorption experiments were conducted with these SR3 samples. At this stage in the research, it was established that conventional oxidative methods were not sufficiently successful in achieving required arsenic

removal. Nonetheless, certain experiments were carried out with SR3 leachates using permanganate oxidation and ferric chloride coagulation to reassess their efficiencies.

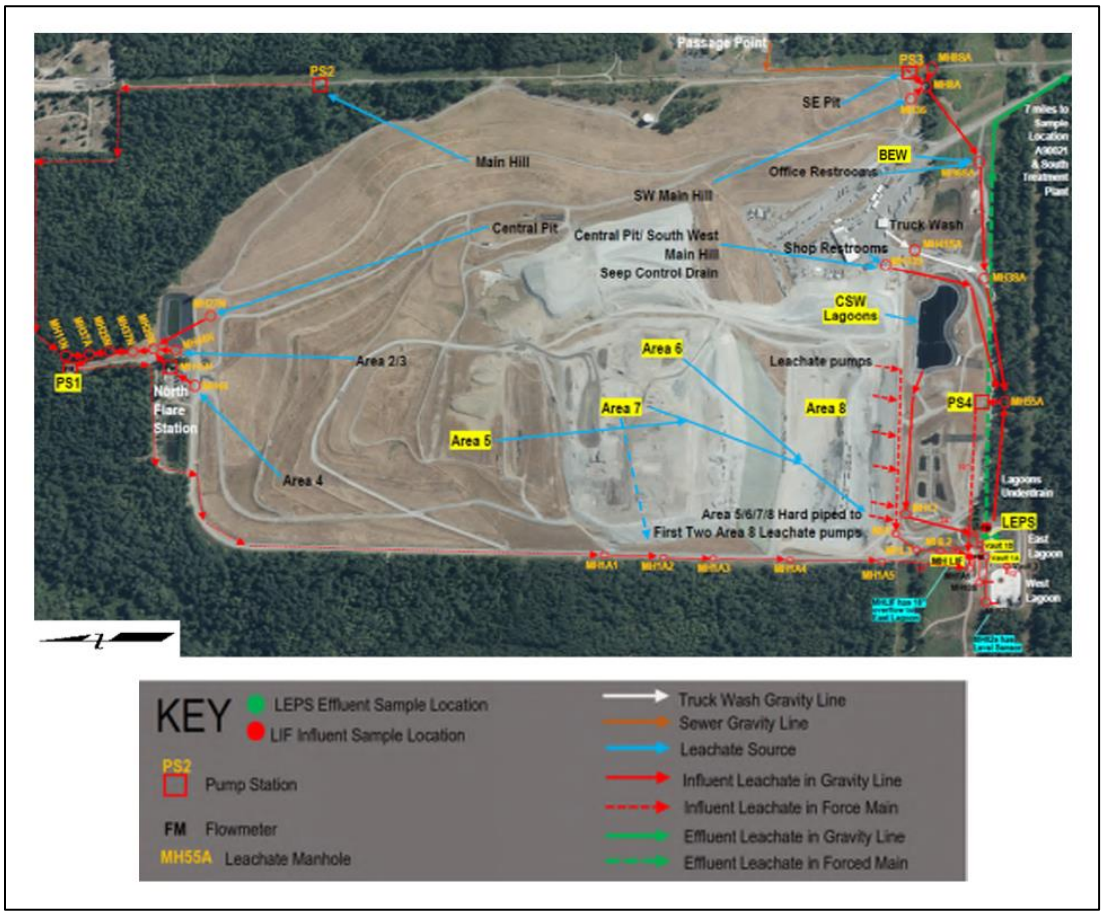


Figure 10. Schematic of leachate influent and effluent locations at the Cedar Hill Regional Landfill site (Data provided by Toraj Ghofrani, PE on 08/04/2019) *(Korshin 2020)*.

3.1.4. Sampling Round 4 (SR4)

In SR4, BEW condensate, Area - 5,6,7 (A567), and Vault 1A (V1A) leachates sampled on November 19th, 2019, were analyzed for arsenic and secondary analytes in the King County Environmental Lab (KCEL). The samples were used exclusively to test the performance of reductive and adsorptive removal methods. The speciation data for the leachates from SR4 is

presented in Figure 11. A stark difference in species concentrations between the two leachates should be noted. The known species of arsenic (As(III), As(V), DMA, MMA) are at a higher concentration in A567 leachate than V1A leachate. The 'unknown' arsenic species are prominent in both leachates, with V1A having a significantly higher concentration.

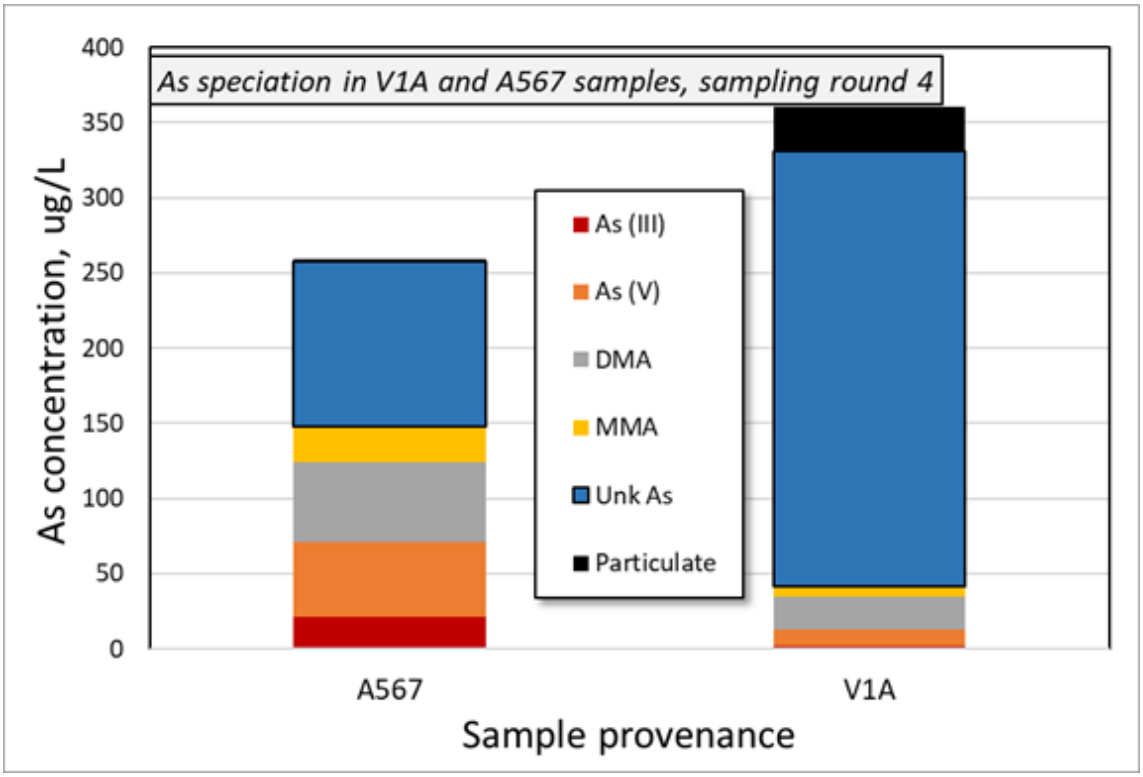


Figure 11. Comparison of the speciation of arsenic in SR4 samples - A567 and V1A leachate (Data provided by Wood PLC analytical laboratory) (Korshin 2020).

Table 3. TOC (mg/L) and TIC (mg/L) of original CHRLF leachate and condensate samples. (Measured at Dept. of Civil and Environmental Engineering)

Sampling round	Time period	Sample Type	TOC (mg/L)	TIC (mg/L)
SR2	19-Jul	Area 6 (Old)	2428	2923
		Area 7 (New)	4715	2224
		BEW condensate	307	4232
SR4	19-Nov	BEW condensate	1323	243
		Area 5,6,7	2263	2024

		Vault 1A	1107	869
SR6*	23-Mar to 27-Mar and 03-May to 07-May	BPW 03/22	1291	55
		BPW 03/23	1243	48
		BPW 03/24	1319	74
		BPW 03/25	1219	80
		BPW 03/26	1106	57
		BPW 05/03	1251	203
		BPW 05/04	1307	200
		BPW 05/05	1226	177
		BPW 05/06	1234	202
		BPW 05/07	1246	181

1. TOC and TIC for SR3 and SR5 samples were not measured.
2. All sample types are leachate unless specified.
*BPW = BEW Process Water

1.1.1. Sampling Round 5 (SR5)

In SR5, leachate effluent from pump station (LEPS), Vault 1A (V1A), Area – 5,6,7 (A567), and NFS condensate were sampled on January 31st, 2020 and February 19th, 2020 (samples were collected over three weeks). The samples were analyzed for arsenic and secondary analyte concentrations via KCEL. These samples were used to evaluate the reductive, adsorptive, and coagulative removal methods through batch and packed column experiments. The arsenic concentrations evaluated by KCEL for LEPS and V1A were approximately 89% and 95% lower than those of the previously sampled LEPS (SR3) and V1A (SR4), respectively. Excessive rainfall from December 2019 to January 2020 in King County was suspected to be the reason for this decrease in arsenic concentrations. Similarly, a decrease in other secondary analyte concentrations, including Cr and Ni, was observed. Arsenic and secondary analyte concentrations found in A567 and NFS SR5 samples were consistent with the data observed in the previous sampling rounds.

1.1.2. Sampling Round 6 (SR6)

In SR6, multiple samples of BEW process water were collected in two series. In SR6A, samples were procured over a week from March 22nd, 2020, to March 26th, 2020. The samples were observed to have colloidal solids' evident presence with a strong, yellow-orange color

(Figure 12). The samples were centrifuged to separate the solids from the process water. The separated solids were resuspended in 15ml of the BEW process water and were stored at 4°C.

(a) (b)

Figure 12. Colloidal solids in BEW process water (sampled on 03/26/20) (a) settled out after storage, and (b) resuspended on agitation.

According to the speciation analysis performed by Wood PLC, the four most common arsenic species – As(III), As(V), DMA(V), and MMA(V) were below detection limits. The unknown arsenic species made up >95% of the dissolved arsenic concentration (Wood PLC 2020). It can be hypothesized that the unknown arsenic species may comprise other methylated complexes like TMAO ($(CH_3)_3AsO$) but the identity of arsenic species in BEW process water remains to be ascertained. The high concentrations of sulfur (25-30 mg/L) observed in the BEW process water samples were also indicative of the presence of thiolated arsenic species.

1.1.3. Sample stability

Even with the necessary precautions taken during sampling, storage, and treatment, species instability is a paramount concern. Prolonged exposure to the atmosphere may result in the oxidation of As(III) to As(V) and disrupt the original species distribution.

1.2. ARSENIC REMOVAL

The experimental approaches for Arsenic removal from landfill leachate and LFG condensate involve an array of physical-chemical treatment methods. –

(i) Electrochemical pre-oxidation followed by coagulation with ferric chloride;
(ii) Electrochemical pre-oxidation followed by permanganate oxidation;
(iii) Permanganate oxidation of arsenic and adsorption via manganese dioxide formed in-situ;
(iv) Pre-treatment via ozonation followed by oxidation with permanganate oxidation
(v) Oxygenation in combination with coagulation with ferric chloride;
(vi) Adsorption on commercially available manganese dioxide;
(vii) Adsorption on activated carbon (AC);
(viii) Reduction and adsorption using zero valent iron (ZVI);
(ix) Reduction and adsorption via micro-electrolysis.

1.2.1. Pre-treatment via filtration

The samples obtained from the CHRLF site were pre-filtered on arrival to remove large particulate matter. A 5-micron membrane filter *(Harmsco Industrial Filters, PT # 801-5)* was used for sample filtration followed by a second filtration step using 1-micron membrane filter *(Harmsco Industrial Filters, PT # 801-1)*. Filtration was done as a two-step process to avoid fouling the small pores of the membrane filter. The leachate or LFG condensate sample was pumped through a 5-micron membrane filter to remove bigger particulate matter before subjecting it to a final filtration

step using the 1-micron membrane filter (Figure 13). The membrane filters were rinsed thoroughly with tap water, followed by deionized water after filtration. The filtered leachates were stored in a refrigerator at 4°C.

Figure 13. Filtration setup in the CEE lab.

Referring to Figure 11, it can be noted that particulate arsenic concentration was less than 30µg/L for V1A leachate and for A567 leachate it is almost negligible. As for BEW process water, it was analyzed that almost 1.5-2.5 g/L of particulate arsenic was present in the solution. The leachates and condensates were predominated by a greater dissolved fraction of arsenic and thus, particulate arsenic, if any, was not taken into consideration for the experiments conducted below.

1.2.2. Electrochemical (EC) oxidation

SR1 and SR2 leachates were used to conduct electrochemical oxidation of arsenic. The EC treatment was a pre-oxidation step followed by either permanganate oxidation or $FeCl_3$

coagulation. A fellow lab member prepared a lead dioxide (PbO_2) anode via the EC deposition of the PbO_2 active phase on titanium substrate. 500ml of the filtered matrix was collected in a beaker and continuously stirred using a magnetic stirrer. An electric current of 0.6A was passed through the batch reactor via an external DC power supply. The duration of EC oxidation was up to 60 minutes, and samples were aliquoted every 15 minutes.

Experiments were conducted to examine the effects of EC oxidation on the removal of different arsenic species. The SR1 leachate was spiked with 200 µg/L of arsenite (As(III)) and DMA *(ARCOS Organics, LOT # A0405090)*, separately. Two batches of leachate - spiked and untreated, and, spiked and EC oxidized (0.6A, 15-minute treatment time), were both subjected to permanganate oxidation and $FeCl_3$ coagulation to ascertain the improvement of arsenic removal by EC oxidation. The individual experimental protocols is described in the sections below.

1.2.3. Coagulation using Ferric Chloride

10,000 mg/L stock solution of ferric chloride ($FeCl_3$) was prepared by adding 20 g of ferric chloride to 200 ml of DI water. Four SR1 leachate samples were used for the experiments. These included – (i) 10x diluted, untreated leachate spiked with 200 µg/L arsenite (As (III)), (ii) electrochemically oxidized 10x diluted leachate @ 0.6A for 15 minutes spiked with 200 µg/L arsenite (As (III)), (iii) 10x diluted, untreated leachate spiked with 200 µg/L DMA, (iv) electrochemically oxidized 10x diluted leachate @ 0.6A for 15 minutes spiked with 200 µg/L DMA. The pH of the systems was adjusted to 6.0 using hydrochloric acid. Each solution was treated using $FeCl_3$ doses ranging from 25 mg/L to 100 mg/L (as $FeCl_3$). No external agitation through mechanical mixing was applied during the experiment.

Aliquots were taken from the solutions after 30 minutes of contact time in 50 ml *Falcon* tubes. The aliquots were centrifuged for 15 minutes at 4000 rpm. This was followed by the filtration of samples using a 0.45-micron filter (VWR). Total arsenic concentration was measured using ICP-MS at the Dept. of Civil and Environmental Engineering.

Experiments conducted with SR6 BEW processes water samples used a $FeCl_3$ stock solution of 100,000 mg/L. 25 ml of BEW process water (sampled on 03/22/2020) was collected in three

beakers, and the pH of each solution was altered to 6.0 using concentrated hydrochloric acid. The BEW samples were dosed with 2 g/L, 4 g/L, and 6 g/L of $FeCl_3$. The pH fluctuations noted during the experiment were regulated using concentration sodium hydroxide. After a contact time of 30 minutes, aliquots were taken from the beakers and filtered using a 0.45-micron filter (VWR). The filtered samples were stored at 4°C and analyzed for arsenic using the ICP-OES instrument at the Dept. of Chemistry.

1.2.4. Permanganate oxidation

50,000 mg/L stock solution of potassium permanganate ($KMnO_4$) was prepared by adding 10 g of crystalline $KMnO_4$ (Fisher Chemical, LOT # 1810124) to 200 ml of DI water. Four solutions were prepared in conical flasks using leachate from SR1 – (i) 10x diluted, untreated leachate spiked with 200 µg/L arsenite (As(III)), (ii) electrochemically oxidized 10x diluted leachate @ 0.6A for 15 minutes spiked with 200 µg/L arsenite (As (III)), (iii) 10x diluted, untreated leachate spiked with 200 µg/L DMA, (iv) electrochemically oxidized 10x diluted leachate @ 0.6A for 15 minutes spiked with 200 µg/L DMA. The pH of the systems was adjusted to 6 using hydrochloric acid. Each system was dosed with a varying concentration of $KMnO_4$, ranging from 25 mg/L to 100 mg/L. No external agitation through mechanical mixing was applied during the experiment. The aliquots taken at the end of 24 hours were centrifuged for 15 minutes at 4000 rpm, followed by filtration of samples using a 0.45-micron filter (VWR).

Using SR2 LFG condensate and leachate, a second set of experiments were conducted. Undiluted condensate and leachate were treated with $KMnO_4$ concentrations, ranging from 500 mg/L to 1000 mg/L at pH 5 and 6, for a contact time of 24 hours. No external agitation through mechanical mixing was applied during the experiment. Samples generated were sent to KCEL for total arsenic measurements.

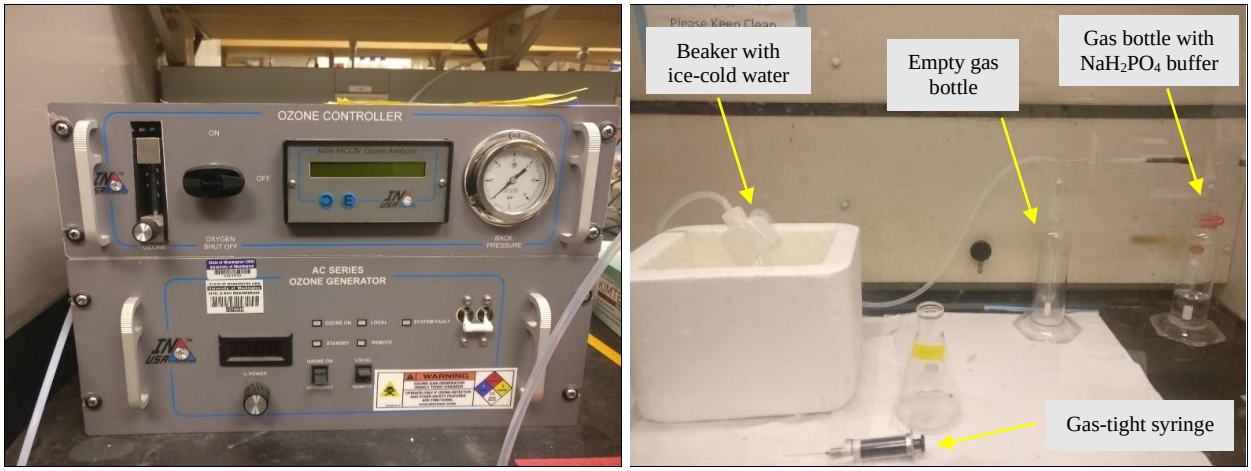
10,000 mg/L stock solution of $KMnO_4$ used in permanganate oxidation of SR6 samples. 25 ml of BEW process water (sampled on 03/22/2020) was collected in nine 50 ml *Falcon* tubes. The pH of each solution was altered to 5.0 using concentrated hydrochloric acid. The BEW solutions were dosed with 1000, 2000, and 4000 mg/L of $KMnO_4$. No external agitation through mechanical

mixing was applied during the experiment. After a contact time of 24 hours, aliquots taken from the tubes were filtered using a 0.45-micron filter (VWR). No aliquots were taken from the sample dosed with 4000 mg/L $KMnO_4$ due to incomplete oxidation of permanganate. The filtered samples were stored at 4°C and were analyzed for arsenic via KCEL and using the ICP-OES (Dept. of Chemistry).

1.2.5. Ozonation

Ozone stock solution was produced using IN USA Corp. ozone generator. A flask with DI water was placed on an ice bath and was connected to the ozone generator via a gas line. Ozone stock solution was produced by passing oxygen through the ozone generator that streamed ozone through a series of two glass gas bottles. The first glass bottle contained monosodium phosphate (NaH_2PO_4) buffer that scrubbed out any source of contamination, followed by an empty gas bottle to avoid liquid carry-over (Figure 14(b)). A heat catalyst was also positioned to destroy any gaseous ozone escaping from the aqueous stock solution into the hood. The ozone controller was set to a flow rate of 500 ml/min, a back pressure of 25 psi, and the power supply to 50% (Figure 14(a)). The objective was to obtain a 1 mM ozone stock solution after a duration 0f 60-90 minutes once the stock's temperature stabilized. The stability of the stock was ensured using measurements of the absorbance of ozone stock solution, with the molar extinction coefficient of ozone at 260 nm being 2950 $cm^{-1}M^{-1}$, as per the data of prior research and those generated in Dr. Korshin's laboratory (G. Korshin 2003).

SR2 LFG condensate was diluted 10 times for the experiment. It was dosed with varying concentrations of ozone from 0.025 mM to 0.25 mM (1.2 to 12 mg/L) in a vial using a gas-tight syringe. The vials were pre-covered with aluminum foil to avoid photochemical decomposition of ozone. Following ozone injection, aliquots were taken after 4-5 hours to allow complete ozone consumption. The samples were filtered using a 0.45-micron filter (VWR) and stored at 4°C. Arsenic concentration was measured using the ICP-OES at the Dept. of Chemistry. The condensate dosed with 0.25 mM of O_3, was dosed with 75 mg/L of $KMnO_4$. The sample was filtered after 24 hours using a 0.45-micron filter and was measured for arsenic concentration using the ICP-OES at the Dept. of Chemistry.



(a) (b)

Figure 14. (a) IN USA Corp. Ozone controller and generator, (b) Experimental setup in the CEE lab.

1.2.6. Oxygenation in combination with coagulation with ferric chloride

Later in the project, a limited set of oxygenation and coagulation experiments were performed with SR5 leachate to assess DOM and arsenic removal from landfill leachate. As part of a preliminary analysis of SR5 samples, oxygenation combined with coagulation was conducted. Oxygen is a much slower oxidant compared with ozone, permanganate and the electrochemical method used in the preceding experiments. However, the increased partial pressure of oxygen along with a long exposure period were deemed sufficient to induce some level of oxidation of the leachate and arsenic present, to make it more susceptible to removal.

Three treatment options were compared –

(i) only purging of O_2 gas through the leachate for 24h at native pH,

(ii) dispersed gas flotation with oxygenation at native pH followed by coagulation using $FeCl_3$ at pH5 for 30 minutes, and

(iii) simultaneous purging and coagulation of leachate at pH5 for 4h.

In the first experimental configuration, 500ml of LEPS leachate was collected in a beaker and purged with O_2 at native pH. O_2 purged through the solution at 0.1LPM and 2.5psi pressure. The matrix was replenished with DI water for any loss in volume due to evaporation.

In the second configuration, 2 solutions of 100ml of LEPS leachate were purged with O_2 for 15 minutes, and 4h, respectively, at native pH. Solution pH was maintained using concentrated NaOH. Samples were collected at the end of the purging. 75ml of each purged sample was dosed with 6g/L of $FeCl_3$ (or 2g/L $FeCl_3$ as Fe) for 30 minutes at pH5. pH was maintained at approximately 5.0 throughout the treatment time, and an aliquot was taken at the end of 30 minutes of treatment time.

In the final configuration, 100ml of LEPS leachate was simultaneously dosed with 6g/L $FeCl_3$ coagulant and purged with O_2 (0.1 LPM and 2.5 psi pressure), at pH5. Solution pH was maintained using concentrated NaOH. No external agitation through mechanical mixing was applied during the experiment. Aliquots collected at 15 minutes, 1h, and 4h, were filtered using a 0.45-micron filter (VWR) before being placed in the refrigerator. The samples were sent to KCEL for total arsenic analysis.

1.2.7. Adsorption using manganese dioxide (MnO_2)

The efficiency of commercially available MnO_2 *(Merck Millipore, S7647958923)* as an adsorptive media was tested using SR2 LFG condensate. 1000 mg/L of solid MnO_2 was added to the matrix for a contact time of 24 hours with no alterations in its initial pH.

After a contact time of 24 hours, aliquots taken from the tubes were filtered using a 0.45-micron filter (VWR). The filtered samples were stored at 4°C and the arsenic concentration was analyzed using the ICP-OES at the Dept. of Chemistry.

1.2.8. Adsorption using activated carbon

Adsorption via activated carbon was evaluated using SR3, SR4 and SR5 leachates and LFG condensates. Doses of activated carbon ranging from 1g/L to 50g/L were used in these experiments. The desired amount of powdered or granular form of activated carbon (PAC or GAC) was weighed and added to the matrix. (Refer Table 4 for the types of activated carbon used for the experiments). 50ml of 0.1µm filtered sample was collected in a beaker and initial pH was measured. The batch experiments were carried out at both the original pH of the matrix and at a pH of 5.0. The contact time of the treatment lasted for 15 minutes to a few hours, depending on the experiment setup. The beakers were placed on an orbital shaker during the experiment. The samples were filtered using a 0.45-micron filter (VWR) before being placed in the refrigerator. Arsenic analysis was carried out using the ICP-MS instrument at the Dept. of Nanoscience for total arsenic concentration.

Table 4. Adsorption experimental setup factors.

Reagent Used	**Landfill Systems**	**Concentration of Activated Carbon**	**pH**
Powdered Activated Carbon *(Fisher Chemical (C272-500))*	LEPS (SR3, SR5) Vault 1A (SR4, SR5) Area - 5,6,7 (SR4, SR5) BEW (SR3, SR4, SR6)	1 - 50 g/L	original pH, 5
4-14 mesh, Granular Activated Carbon *(Sigma-Aldrich, Lot # MKCH4895)*			
8-20 mesh, Granular Activated Carbon *(Sigma-Aldrich, LOT # SHBL3670)*			
12-40 mesh, Granular Activated Carbon *(ARCOS Organics, LOT # A0409724*			

Experiments to determine the effect of regeneration on powdered activated carbon's performance were carried with SR5 leachate. These experiments assessed the efficiency of activated carbon after one treatment cycle. 20g/L of PAC was added to leachate at pH5 for 15 minutes. The beaker was placed on a shaker, and an aliquot of approximately 2-3ml was taken at 2 minutes, 5 minutes, and 15 minutes. After sampling, the experimental matrix was centrifuged at 4000 rpm for 5 minutes. The supernatant was discarded, and the precipitate was resuspended in

50ml of 0.1M NaOH for 5 minutes. The matrix was centrifuged again at the same conditions. The supernatant was discarded, and the precipitate was resuspended in 50ml of fresh leachate. The second cycle also lasted for 15 minutes and was repeated two more times. The beakers were placed on an orbital shaker during the experiment. All samples were filtered using a 0.45-micron filter (VWR) and stored at 4°C. The samples were analyzed using ICP-OES (Dept. of Chemistry) and ICP-MS (Dept. of Nanoscience) for experiments conducted with SR3 samples and via KCEL for SR4 and SR5 samples, for total arsenic and secondary analyte concentrations.

1.2.9. Zero-valent iron

The initiative to implement reductive processes was based on three reasons –

(i) conventional oxidative processes did not result in desired arsenic removal,
(ii) reductive processes maybe successful as the landfill leachate by its nature is a reducing matrix and,
(iii) leachate organic matter may not interfere with the removal process.

The initial approach to evaluate the applicability of reductive methods was through zero-valent iron. Three types of ZVI were used for the experiments. The initial experiments with SR3 were carried out with Iron Accelerator chips (LECO, Lot # 501-077) and Hoganas Cleanit® LCPlus. Most of the experiments carried out with SR4, SR5, and SR6 samples used Hoganas Cleanit® LCPlus Fine. The desired dosage of iron was activated using 0.1 M hydrochloric acid (HCl). The 0.1 M HCl stock solution was prepared using commercially available 1N HCl. The process of activation removes any oxidized films from the iron surface, availing a more significant proportion of the iron to react with the ambient water. Once the desired pH of the experiment was adjusted using concentrated HCl, the iron was added to the system for the set contact time. The beakers were placed on an orbital shaker during the experiment. The samples collected during the experiment were filtered using a 0.45-micron filter (VWR) and stored at 4°C. They were analyzed for total arsenic via ICP-OES (Dept of Chemistry), ICP-MS (Dept of Nanoscience) for SR3 samples and, KCEL for SR4 and SR5 samples. SR6 samples were analyzed via both ICP-OES (Dept. of Chemistry) and KCEL.

1.2.10. Micro-electrolysis (ME)

The next step in reductive treatment was the implementation of micro-electrolysis. The process of micro-electrolysis is a combination of reductive and adsorptive processes using zero-valent iron (ZVI) and activated carbon, respectively. Table 5 summarized the various types of experimental iron and activated carbon used in the micro-electrolysis experiments. This process was performed using the SR3, SR4, SR5, and SR6 leachate and LFG condensate samples. Initial experiments were carried out without the application of gas purging through the solution. After further experimentation, it was observed that the use of gas improved the removal of arsenic species. It was suspected that the purging of gas enhanced the arsenic volatilization. Although, purging of gas alone did not initiate the removal of volatile arsines from the solution.

Table 5. Micro-electrolysis experimental setup factors

Reagent Used	Gas used	Landfill Systems	Concentration of Fe:C (2:1)	pH
Iron Chip Accelerator *(LECO (501-077)*	Carbon dioxide, Nitrogen, Methane, Hydrogen *(Praxair)*	NFS (SR3) LEPS (SR3, SR5) Vault 1A (SR4, SR5) Area - 5,6,7 (SR4, SR5) BEW (SR3, SR4, SR6)	10 -200 g/L	4, 5, 6, 7
Hoganas Cleanit ® LCPlus Fine Powdered Activated Carbon *(Fisher Chemical (C272-500))*				
4-14 mesh, Granular Activated Carbon *(Sigma-Aldrich, Lot # MKCH4895)*				
8-20 mesh, Granular Activated Carbon *(Sigma-Aldrich, LOT # SHBL3670)*				
12-40 mesh, Granular Activated Carbon *(ARCOS Organics, LOT # A0409724*				

In these experiments, a 50ml sample aliquot was placed into a beaker. The sample's pH was measured and decreased to the desired experimental pH using concentrated HCl. An initial 0-minute sample was taken at this point. The solution was dosed with 10g/L to 200g/L of iron and carbon at a ratio of 2:1, depending on the experimental setup. The iron was pre-activated using 0.1M HCl for approximately 2-3 minutes and then rinsed with DI water. Activated iron and carbon

were added to the system, followed by purging by gas through the solution. An added advantage of gas purging was the maintenance of the reagents in suspension mode, allowing continuous contact with the system. No external agitation through mechanical mixing was provided during the experiment.

Periodic additions of concentrated HCl were made to counteract the increase in pH during the experiment. It was noted that the volume of acid required to maintain the pH decreased after 5 minutes of contact time. The treatment time lasted for 15 minutes, and samples were filtered using a 0.45-micron filter (VWR) before being placed in the refrigerator. The samples were analyzed using ICP-OES (Dept. of Chemistry) and ICP-MS (Dept. of Nanoscience) for experiments conducted with SR3 samples and via KCEL for SR4 and SR5 samples, for total arsenic and secondary analyte concentrations. SR6 samples were analyzed via both ICP-OES (Dept. of Chemistry) and KCEL.

A preliminary experiment to evaluate the volatilization and retention of arsenic during micro-electrolysis was conducted. An electrochemical cell was used as a pseudo-reactor to conduct this experiment. The experiment was carried out with 20 ppm of DMA as As treated with 100g/L of LCPlus Fine and PAC at a ratio of 2:1 with CO_2 purging at pH 5. The volatilized gases were intercepted in a gas bottle that contained 100 mg/L of $KMnO_4$. Periodic additions of concentrated HCl were made to counteract the increase in pH during the experiment. The treatment time lasted for 15 minutes, and samples were filtered using a 0.45-micron filter (VWR). The solid samples were collected and rinsed with 1% HNO_3. After 15 minutes of nitric acid exposure, the solids were centrifuged, and the supernatant was filtered for arsenic analysis. The samples were analyzed at KCEL for total arsenic concentrations.

1.3. ANALYSIS OF CONCENTRATIONS OF ARSENIC AND CO-OCCURING ELEMENTS

Total arsenic and secondary analytes (Fe, Cr, Ni, Mn) concentrations were examined using Inductively Coupled Plasma (ICP) combined with mass spectroscopy (MS) or optical emission

spectroscopy (OES). The instruments used on the university campus were – *Perkin Elmer Elan DRC-e* ICP-MS (Dept. of Civil and Environmental Engineering), *Perkin Elmer Optima 8300* ICP-OES (Dept. of Chemistry), and *NexION 2000B* ICP-MS (Dept. of Nanoscience). The standard method of ICP analysis was followed that included – calibration using elemental standards, acidification of sample using trace-metal grade nitric acid, and dilution of samples. The samples and standards were spiked with an internal standard and normalized for any error due to minor fluctuations in the plasma intensity. Selected samples collected from experiments conducted using SR3 to SR6 leachates and LFG condensates were sent to King County Environmental Laboratory (KCEL) for analysis of arsenic and co-occurring contaminants. KCEL is a certified lab that follows appropriate quality control and quality assurance protocols. Dissolved organic carbon (DOC) concentrations were measured using the Shimadzu TOC-L analyzer at the Dept. of Civil and Environmental Engineering.

1.4. MEASUREMENTS OF FLUORESCENCE EXCITATION EMISSION MATRIXES AND ABSORBANCE

Fluorescence Excitation-Emission matrixes (EEM) were measured using the Horiba Aqualog® spectrofluorometer. The EEM approach was employed to determine the presence of several compound classes of DOM present in the landfill leachate. Figure 15 shows the EEM of Area – 5, 6, 7 leachate (SR5), presenting four main features located at the excitation/emission wavelength or ca 225/300 nm, 280/300 nm, 250/450 nm, and 325/425 nm. These features denote the presence of several groups of fluorophores nominally assigned to (‘A’) fulvic and (‘B’) humic acids, (‘C’) soluble microbial polymers (SMP), and (‘D’) extracellular polymer species (EPS). Given the responses of these compound classes, EEM provides “fingerprints” of organic compounds found in environmental samples.

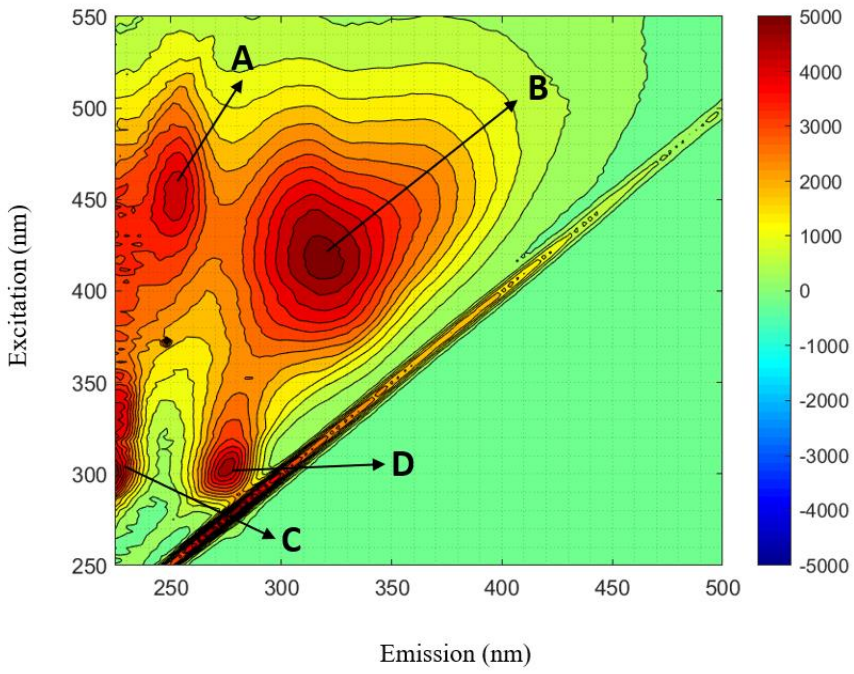


Figure 15. Excitation-emission matrix of A567 leachate (SR5 sample).

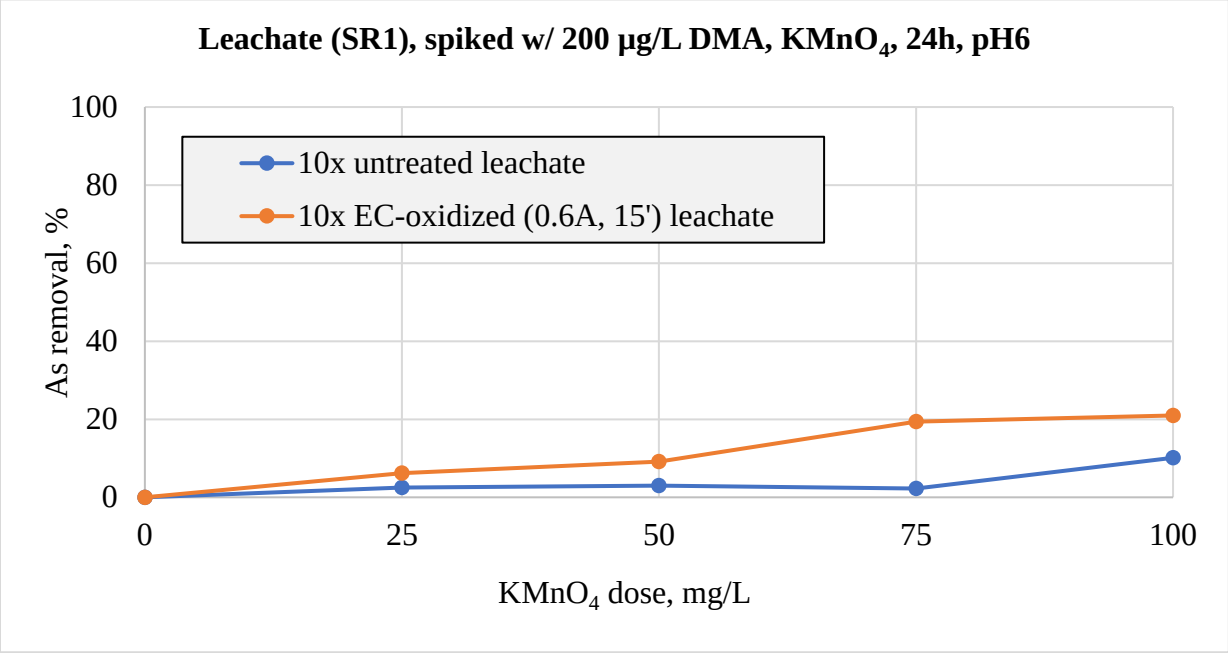
These measurements were conducted as a proxy to track changes in the contribution of different organic matter sources in environmental samples. Possible correlations of the changes in EEM intensity with arsenic concentrations can be used to predict treatment efficiency. The samples used for EEM analysis were diluted 100-200 times with DI water due to the high presence of DOM and distinct, brown coloration of the leachate. The above-mentioned correlations and raw data for the EEM matrixes are presented in Appendix B and C, respectively.

2. RESULTS & DISCUSSIONS

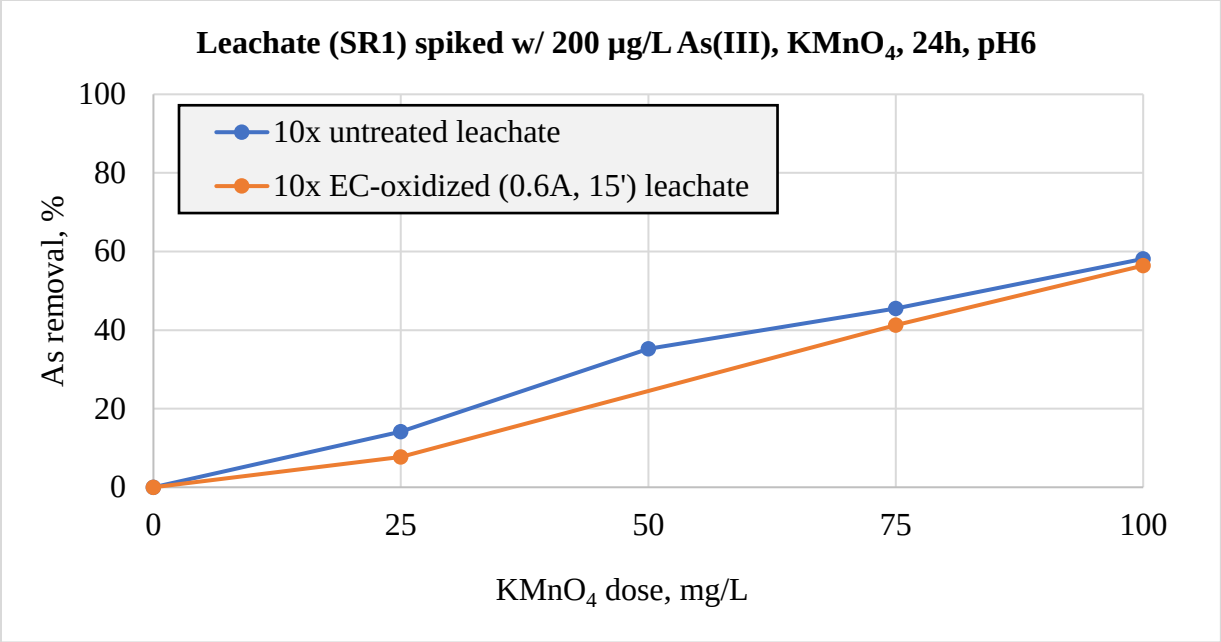
2.1. Oxidative and coagulative treatment of arsenic

2.1.1. Arsenic removal via permanganate oxidation of leachate (SR1 sample)

The 10x diluted leachate (SR1) spiked with 200 µg/L of DMA and 200 µg/L of As(III) (Figure 16(a) and (b)) showed 40% and 60% removal of total arsenic, respectively when dosed with up to 150 mg/L $KMnO_4$. Both untreated and electrochemically treated leachates showed similar removal patterns indicating that electrochemical oxidation failed to improve arsenic removal by permanganate. It was still notable that a more significant removal was obtained for leachate dosed with As(III), which indicated the arsenic removal in this case was the spiked arsenic removed from the leachate. This confirmed the relative ease in oxidizing inorganic forms of arsenic (As(III)) versus its organic, methylated forms (DMA).



(a)



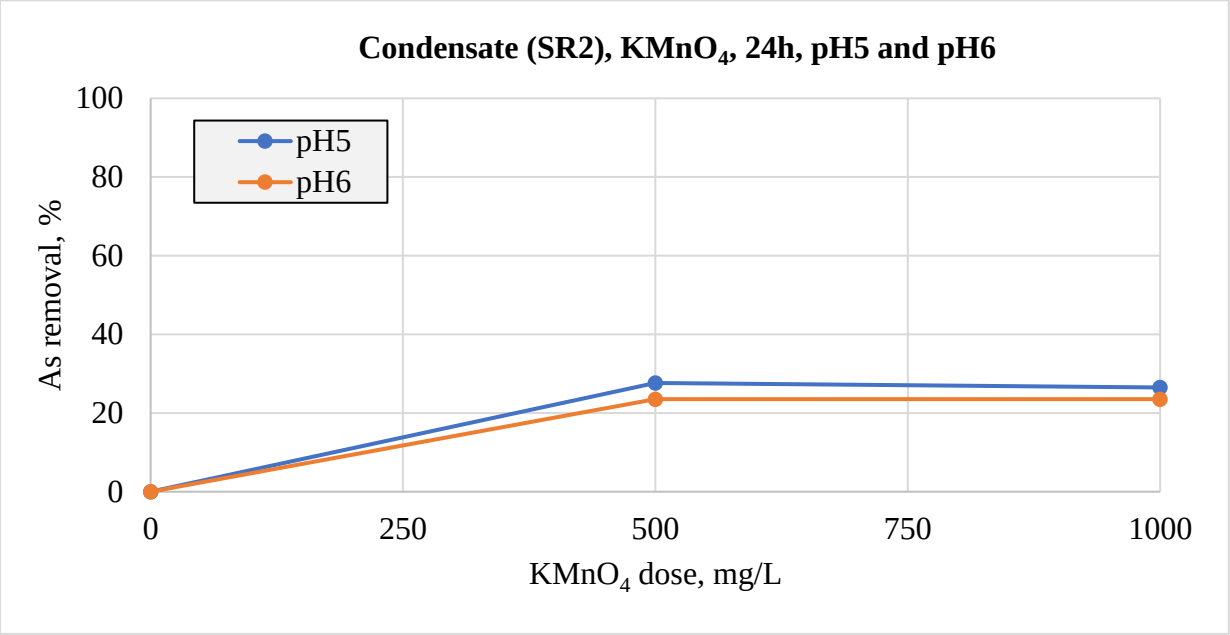
(b)

Figure 16. Comparison of arsenic removal by permanganate oxidation of original versus electrochemically pre-treated (0.6A, 15 minutes) 10x diluted leachate (SR1) spiked with (a) 200 µg/L of DMA, and (b) 200 µg/L of As(III) at pH6 for 24h. *(Samples were tested on 06/24/2019).*

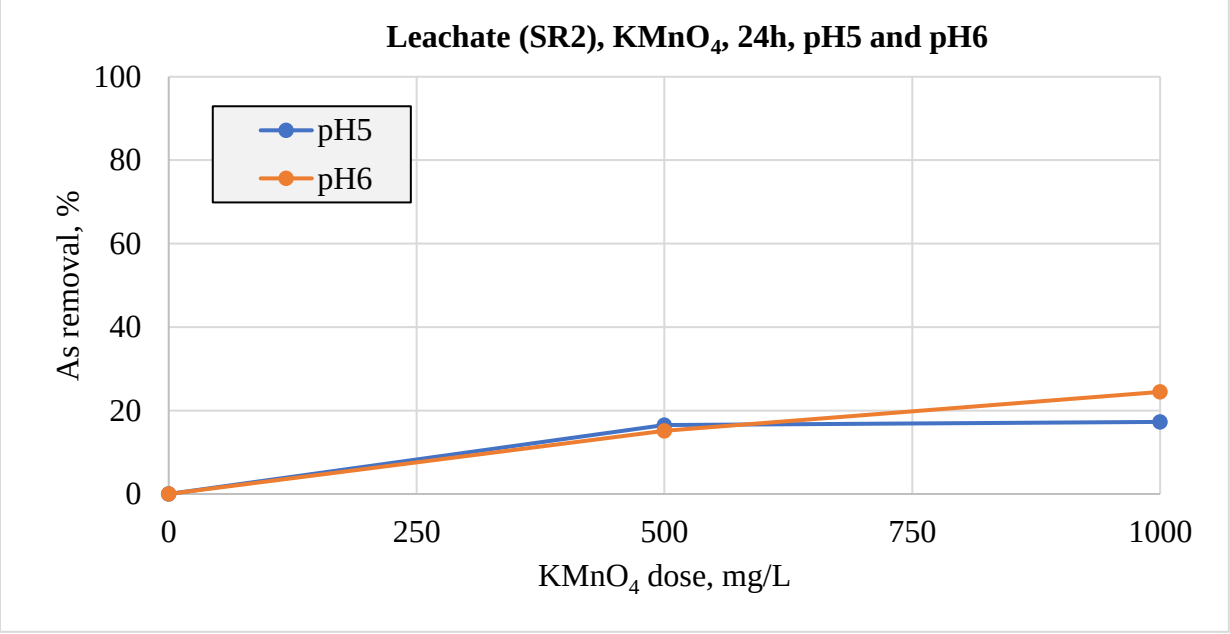
2.1.2. Arsenic removal via permanganate oxidation of LFG condensate and leachate (SR2 sample)

SR2 LFG condensate and leachate were treated with potassium permanganate ($KMnO_4$). The experiments were carried out at pH 5 and pH 6. On the addition of $KMnO_4$, the formation of MnO_2 particles and their precipitation was observed almost immediately. The quantity of precipitate was visually proportional to the dose of $KMnO_4$, that is, more precipitation was observed at higher doses. The treated condensate (Figure 17(a)) showed 25% removal of total arsenic when dosed with up to 1000 mg/L $KMnO_4$ at both pH 5 and pH 6. Approximately 20% of removal was observed in the case of treated leachate at a dose of 1000 mg/L of $KMnO_4$ too (Figure 17(b)).

The critical inference gathered was that the lower arsenic removal from the LFG condensate as compared to the leachate was indicative of the presence of a higher concentration of DOM in the leachate (4715 mg/L) that competed with the arsenic for oxidation despite having a relatively low arsenic concentration than condensate. The resistance to $KMnO_4$ oxidation indicated the presence of complext methylated arsenic species in the LFG condensate and leachate.



(a)



(b)

Figure 17. Effect of permanganate oxidation on the removal of arsenic from (a) LFG Condensate (SR2) and (b) Leachate (SR2) at pH 5 and pH 6 for a contact time of 24h.

As seen in Figure B-1 (Appendix B), a complete reduction in EEM peak intensity occurred in these experiments indicating the removal of HA and FA fluorophores from the condensate. 100% removal was achieved regardless of pH, implying removal of the fluorescing organic matter (fluorophores) from the SR2 condensate. In contrast, there was no indication of fluorescence response for the EPS or SMP peaks for condensate samples. Figure B-2 (Appendix B) shows that 80-90% reduction in EEM peak intensity was observed for HA, FA, and SMP intensities in the case of leachate. A more significant reduction in the fluorescence response was recorded compared to the removal of arsenic at that dose. Removal patterns deviated at higher doses as arsenic removal slightly improved at pH 6.

2.1.3. Arsenic removal via permanganate oxidation of BEW process water (SR6 sample)

SR6 BEW process water sampled on 03/22/2020 was treated with potassium permanganate ($KMnO_4$) at pH 5. The treated process water (Figure 18) showed 10% and 17% removal of total arsenic when dosed with 1g/L and 2 g/L of $KMnO_4$, respectively. BEW process water sample dosed with 4 g/L of $KMnO_4$ remained pink in color after 24 hours of treatment, indicating incomplete consumption and presence of residual permanganate in the solution. Hence, it was not measured. Therefore, inadequate removal of total arsenic was achieved for SR6 samples, which confirmed the observations made in the case of SR2 samples (Section 4.1.2.).

Although the removal of arsenic from the BPW was limited on treatment with $KMnO_4$, Figure B-4 (Appendix B) demonstrated that a 100% reduction in EEM peak intensity was observed for HA and FA. No indication of changes in the intensity of the SMP or EPS peaks were noted in the system.

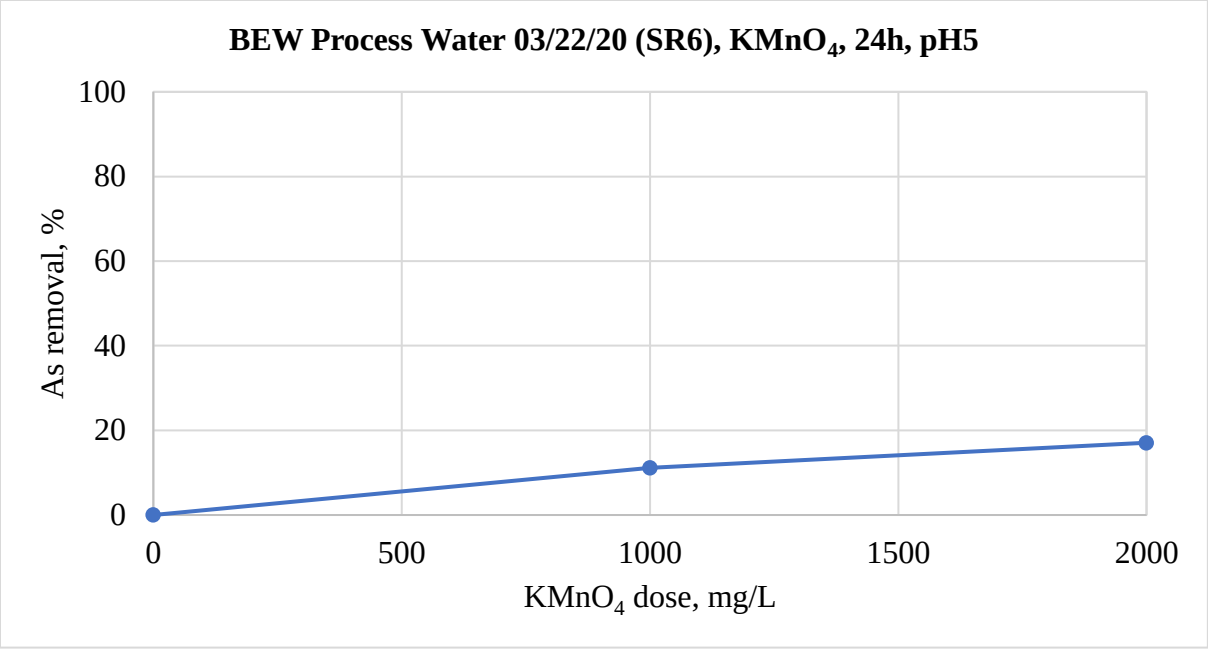


Figure 18. Arsenic removal by permanganate oxidation of SR6 BEW process water (sampled on 03/22/2020) at pH5 for 24h. (Samples were tested on 06/28/2020).

2.1.4. Effects of ozonation pre-treatment on arsenic removal from LFG condensate (SR2 sample)

The treatment of 10x diluted SR2 LFG condensate with varying ozone doses using a contact time of 4 hours did not alter the arsenic concentration. Since ozone is only useful in oxidizing arsenic species and not their removal, the 0.25 mM O_3-treated, 10x diluted LFG condensate was dosed with 75 mg/L of $KMnO_4$. The treatment saw almost 41% removal (Figure 19) of total arsenic from the solution. The removal efficiency compared to that of untreated and undiluted LFG condensate dosed with 750 mg/L of $KMnO_4$ (see section 4.1.2. for details) had improved by a mere 10%. These results supported the assumption that ozone had only oxidized the fraction of the inorganic arsenic, and thus, this treatment promoted arsenic removal via permanganate oxidation by a modest 10% increment.

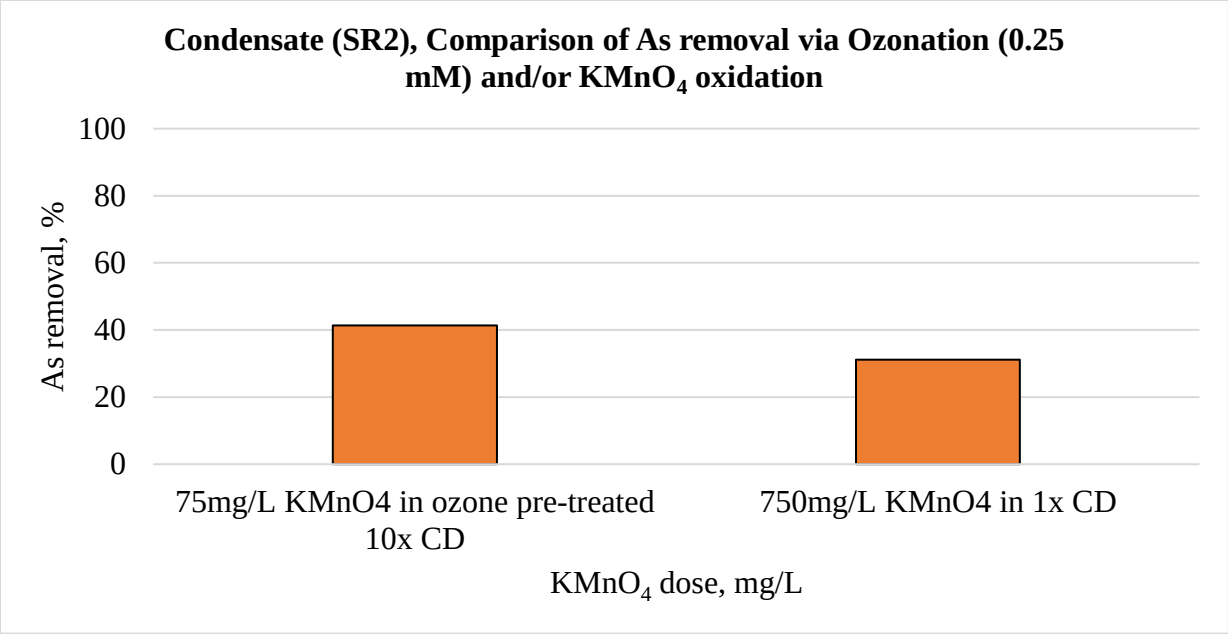
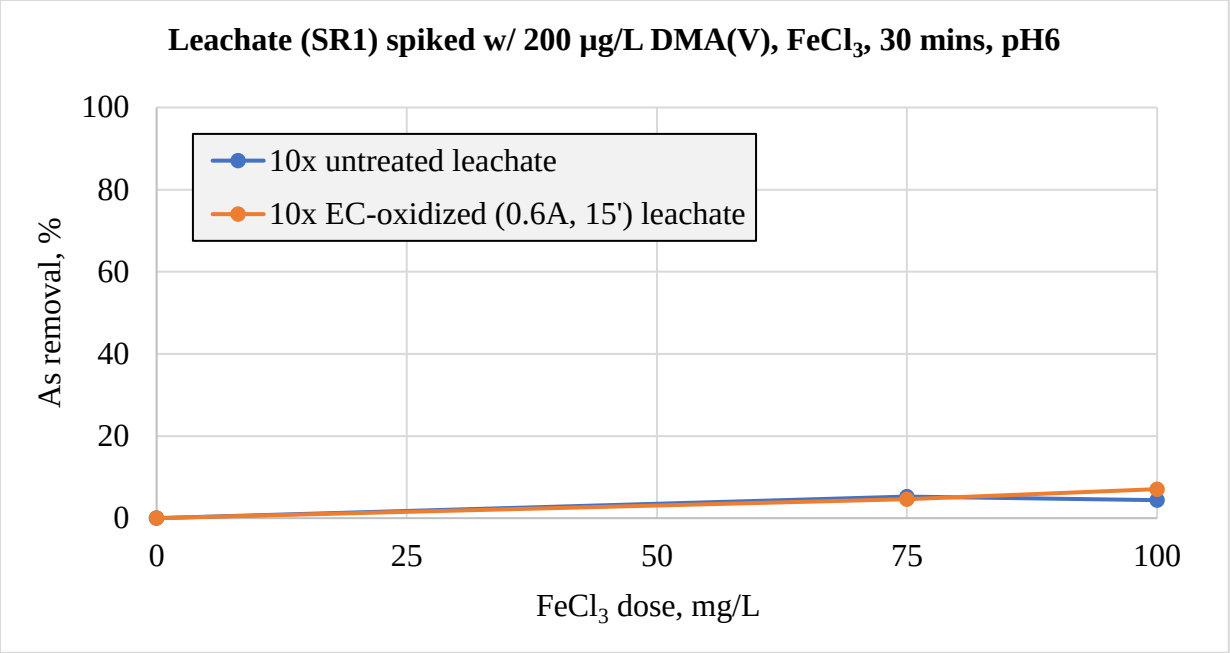


Figure 19. Effects of ozonation (0.25 mM) followed by permanganate oxidation on arsenic removal in LFG condensate (SR2) for a contact time of 24h. (Samples were tested on 08/08/2019).

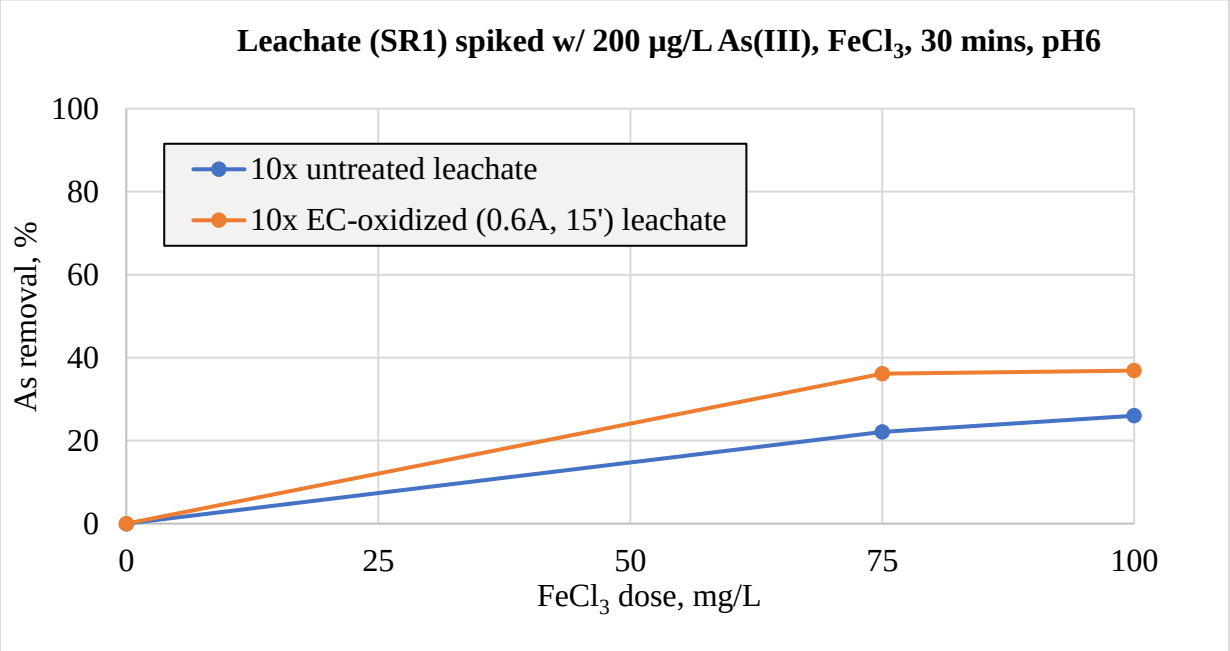
2.1.5. Arsenic removal via coagulation of leachate (SR1 sample) using ferric chloride ($FeCl_3$)

On the addition of $FeCl_3$, precipitation of solids was observed in the solution. The 10x diluted leachate (SR1) spiked with 200 µg/L of DMA and 200 µg/L of As(III) (Figure 20(a) and (b)) showed almost 7% and 25-35% removal of total arsenic, respectively, from the system when dosed with up to 100 mg/L $FeCl_3$. A greater removal was obtained for leachate dosed with As(III), which was indicative of the reduced efficiency of iron-based coagulation in the removal of organic and methylated arsenic species from CHRLF leachates.

Both untreated and electrochemically treated leachates showed similar removal patterns in the case of DMA-spiked leachate (Figure 20(a)). Whereas a relatively small difference of 10% arsenic removed was noted between electrochemically treated and untreated leachate spiked with As(III) (Figure 20(b)). This reinforced the conclusion that electrochemical oxidation had not aided in the significant improvement of arsenic removal and that the complex arsenic species present in the leachate are resistant to treatment via $FeCl_3$ coagulation.



(a)



(b)

Figure 20. Effects of $FeCl_3$ coagulation on arsenic removal from untreated and electrochemically pre-treated (0.6A, 15 minutes) 10x diluted leachate (SR1) spiked with (a) 200 µg/L of DMA, and (b) 200 µg/L of As(III) at pH6 for 30 minutes. *(Samples were tested on 06/14/2019).*

2.1.6. Arsenic removal via oxygenation of LEPS leachate (SR5 sample)

The oxygenation of LEPS (SR5) (0.25 psi pressure and flow rate of 0.1 LPM) did not show any substantial removal of arsenic from the solution (Figure 21). This confirmed that O_2 is a poor oxidant, and oxygenation alone was insufficient in the removal of arsenic from the system. The small fluctuations in the observed arsenic concentrations were due to analytical error.

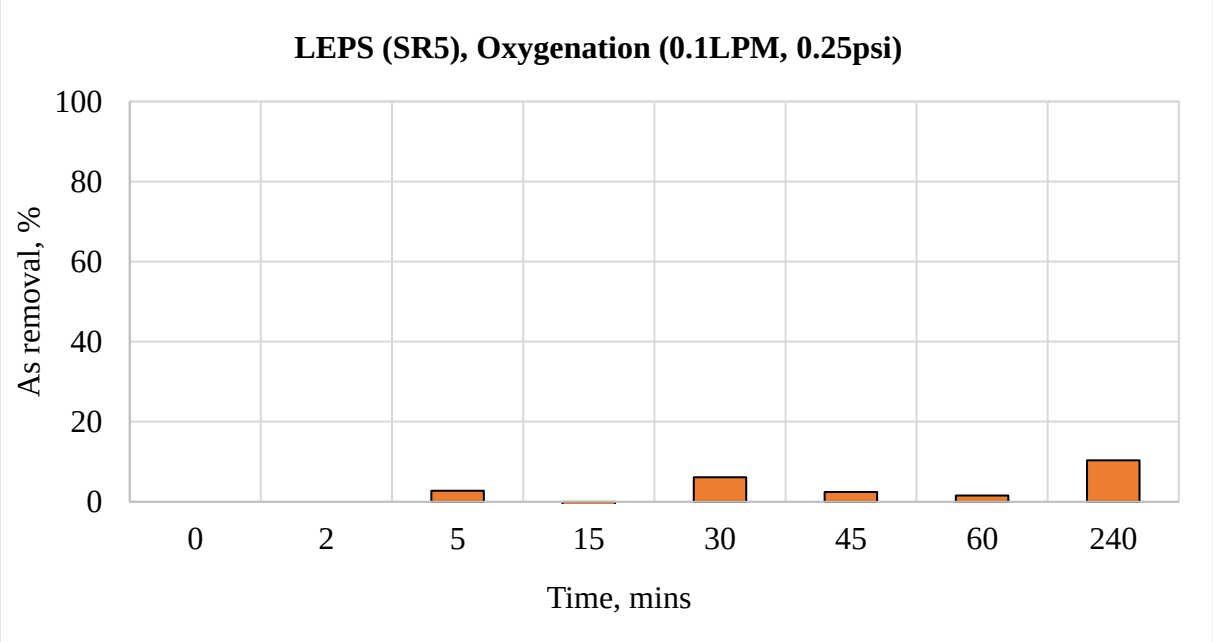


Figure 21. Arsenic removal from LEPS (SR5) purged with 0.1 LPM and 0.25 psi of O_2 for 24 hours. *(Samples were tested on 03/27/2019).*

2.1.7. Arsenic removal via simultaneous oxygenation and coagulation of LEPS leachate (SR5 sample)

SR5 LEPS leachate was treated with simultaneous oxygenation and coagulation using 6 g/L of $FeCl_3$ at pH5. This experiment was conducted to examine the effects of oxygenation on arsenic removal in more detail. On dosing with $FeCl_3$, a drop in pH to 2.0 was observed, and the pH was adjusted back to 5.0 using concentrated sodium hydroxide (NaOH). The treatment

achieved approximately 60% removal within the first 15 minutes of treatment and remained largely the same for the oxygenation time of up to 4 hours (Figure 22). This suggested that oxygenation aided by coagulation was a more substantial treatment for the removal of total arsenic from the system.

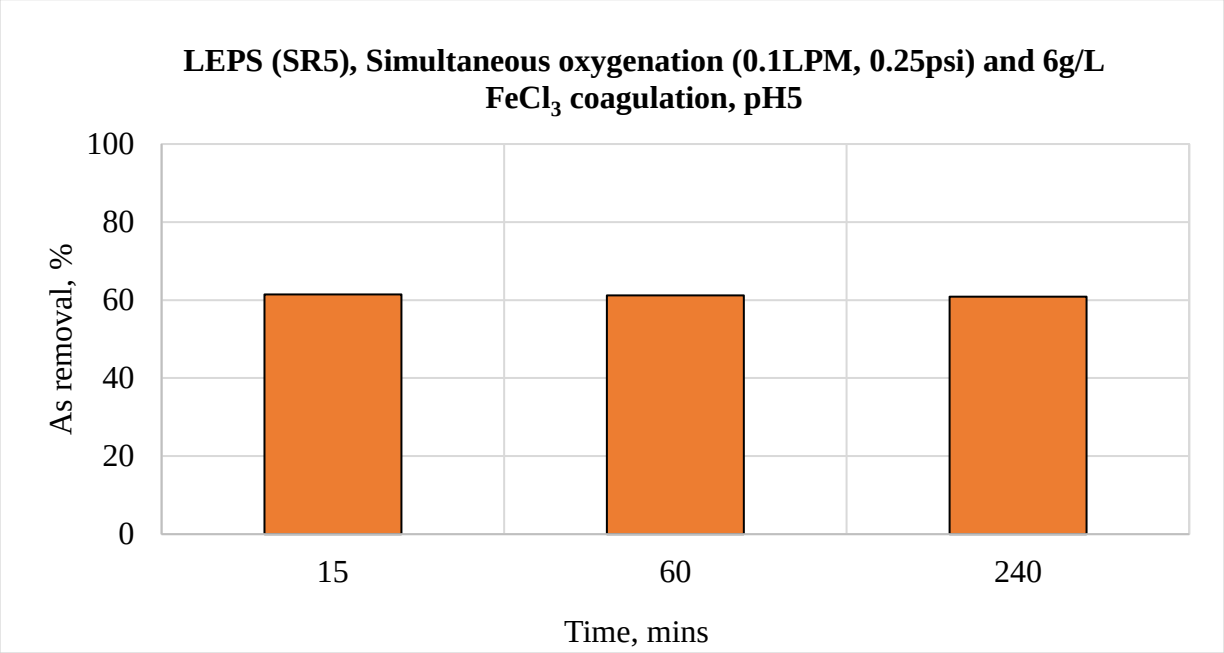


Figure 22. Arsenic removal from LEPS (SR5) treated simultaneously with 0.1 LPM and 0.25 psi of O_2 and 6 g/L of $FeCl_3$ for 4 hours at pH 5. *(Samples were tested on 03/27/2019).*

2.1.8. Arsenic removal via sequential oxygenation and coagulation of LEPS (SR5 sample)

To ascertain the contribution of $FeCl_3$ as a coagulant to the removal process, an experiment involving the sequential addition of oxygen and coagulant was carried out. SR5 LEPS leachate was treated with the sequential addition of oxygen at different treatment times, followed by 6 g/L of $FeCl_3$ at pH 5 for 30 minutes. A similar change in pH, as described in the previous section, was observed during this experiment. The pH was increased back to 5.0 by the addition of concentrated NaOH.

As observed in section 4.1.5., the negligible removal of arsenic occurred when the leachate was solely oxygenated. The addition of coagulant resulted in approximately 55-60% of total arsenic removal regardless of pre-oxidation treatment time (Figure 23). This reinforced that oxygen alone was not useful in removing arsenic from the leachate. In addition, these data showed that gas dispersion methods that successfully use combinations of gas flow and adsorption or coagulation to remove COD/BOD in the treatment of produced water are unlikely to be useful as a technology to remove As from landfill leachate.

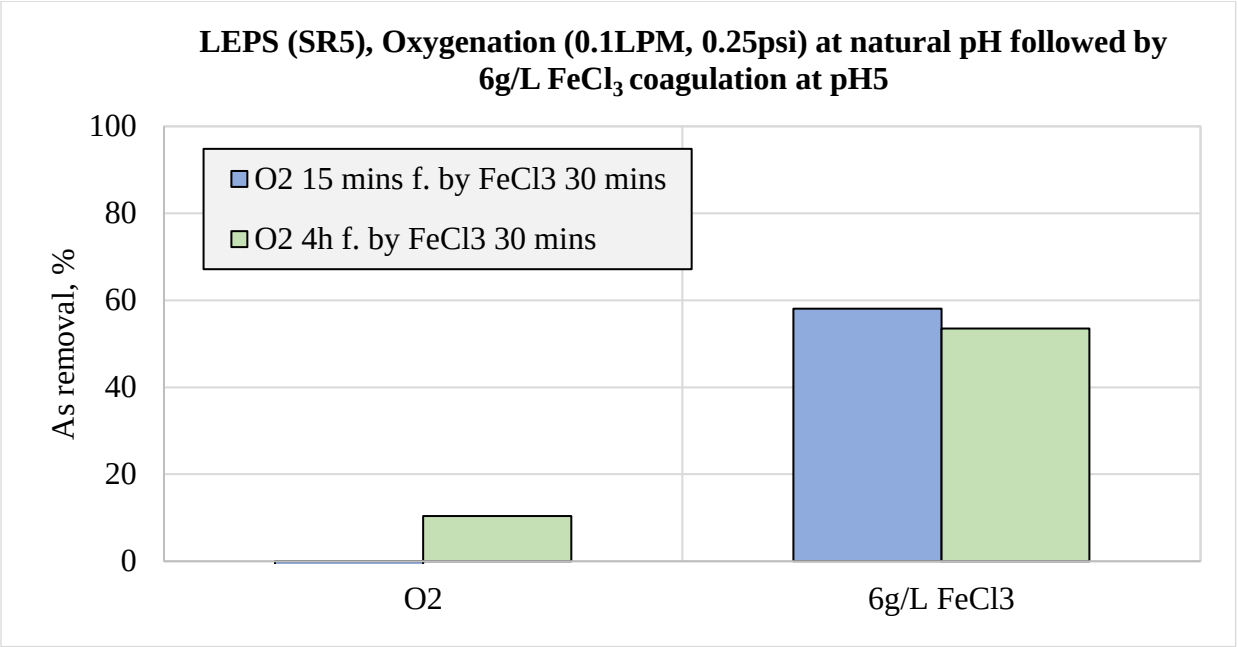


Figure 23. Arsenic removal from LEPS (SR5) treated with 0.1 LPM and 0.25 psi of O_2 for up to 4 hours followed by 6 g/L of $FeCl_3$ for 30 minutes at pH 5. *(Samples were tested on 03/27/2019).*

Even though arsenic removal was constant between both oxygenation periods, the indicative removal of DOM depended on O_2 exposure (Figure B-4 (Appendix B)). HA and EPS intensity removal improved with more extended oxygenation periods, and the opposite was noted for the SMP peak intensity. The FA peak intensity seemed reasonably similar.

2.2. Adsorptive treatment of arsenic

2.2.1. Arsenic removal via adsorption of LFG condensate (SR2 sample) using manganese dioxide

The LFG condensate (SR2) was dosed with 1000 mg/L of solid manganese dioxide (MnO_2) at its original pH (approximately 8). The sample was tested on 08/16/2019, and no appreciable removal of total arsenic was observed after the treatment time of 24 hours.

2.2.2. Effects of contact time on arsenic removal by PAC adsorption. Data for Vault 1A leachate (SR5 sample)

As described in Section 4.3.10., arsenic concentration was observed to behave non-monotonically in samples treated ZVI/carbon micro-electrolysis. Specifically, we observed an increase of arsenic concentration in the supernatant in Vault 1A leachate (SR5) treated with a PAC and ZVI sequentially. The increase of arsenic concentration (or release of arsenic into the leachate) was observed after the initial 5-10 minutes of the treatment. An experiment using only PAC was conducted with Vault 1A leachate (SR5) at pH 5 to examine this unusual trend of arsenic removal.

Figure 24 shows that arsenic removal steadily increased initially, and 75% of the arsenic was removed from the leachate after 5 minutes of treatment time. A consistent decrease followed this in arsenic removal until the end of treatment at 60 minutes. The final arsenic removal at a 60-minute contact time was at 29%. This nonmonotonic trend of arsenic removal can be assumed to be a consequence of competitive adsorption of NOM in the leachate versus arsenic. This observation may be necessary for the optimization of arsenic removal from CHRLF leachate and condensates using carbon-based materials and other adsorbents.

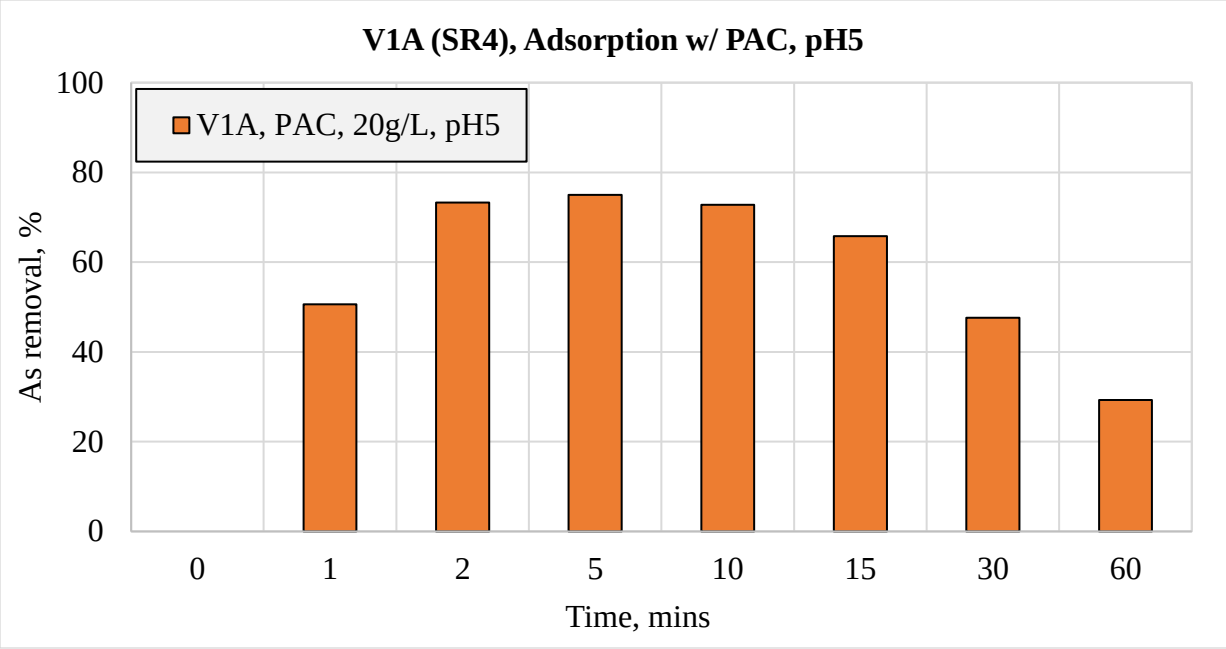


Figure 24. Arsenic removal from V1A (SR5) dosed with 20 g/L of PAC for 60 minutes at pH 5. *(Samples were tested on 02/24/2019).*

2.2.3. Arsenic removal via adsorption of LEPS leachate (SR5 sample) at pH5

A similar experiment, as described in the previous section, was conducted with SR5 LEPS leachate for a longer treatment time of 6 hours. 68% of arsenic was removed from the leachate after 5 minutes of contact time (Figure 25). The trend of arsenic removal was consistent with the results of PAC-treated Vault 1A leachate (SR4). These results reiterated the strong likelihood of arsenic leaching during long treatment times of adsorption of CHRLF leachate using activated carbon. The assumption of competitive adsorption occurring in this case was still valid, however, further experimentation and analysis are required to confirm this.

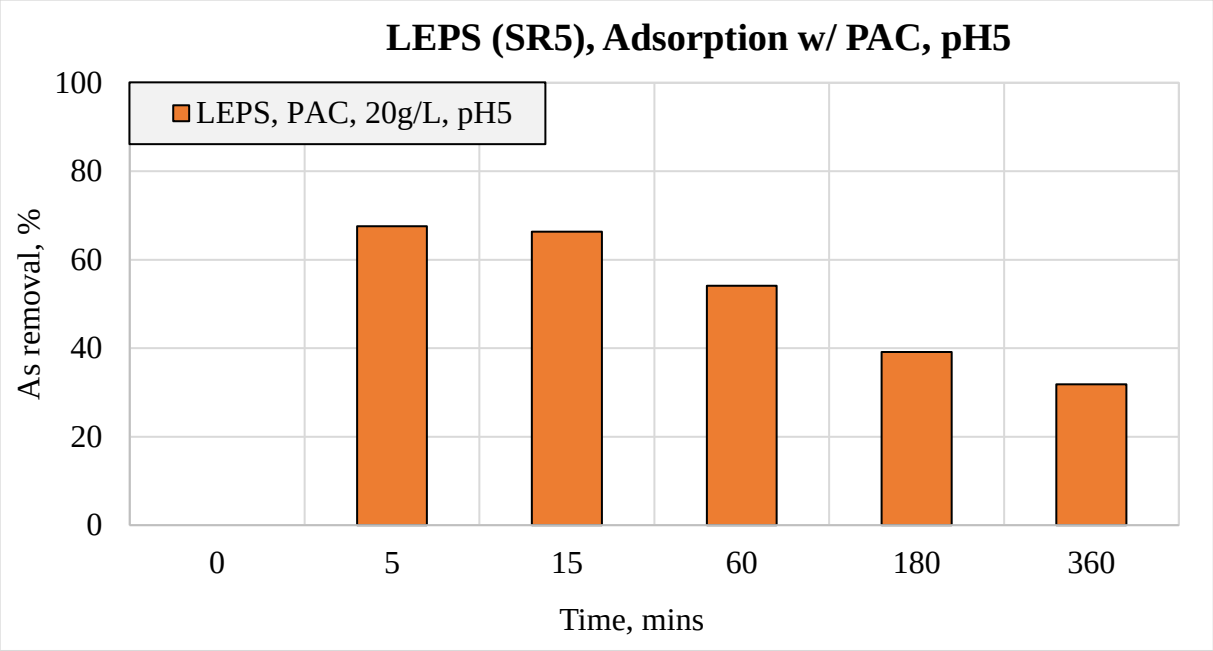


Figure 25. Arsenic removal from LEPS (SR5) dosed with 20 g/L of PAC for 6 hours at pH 5. *(Samples were tested on 02/24/2019).*

Another test was carried out to evaluate the efficiency of adsorption via granular activated carbon (GAC). On dosing LEPS (SR5) leachate with 20 g/L of 8-20 mesh GAC, it was observed that only 14% of arsenic was removed within 15 minutes of treatment time (Figure 26). This was only a quarter of the arsenic removed from the leachate via PAC. This reinforced the theory that size of the activated carbon was vital in determining the removal efficiency of arsenic. Hence, a smaller particle-sized AC with greater specific surface area available would remove higher concentrations of arsenic from the matrix. The visualAlso, no leaching of arsenic back into the solution was observed in this case.

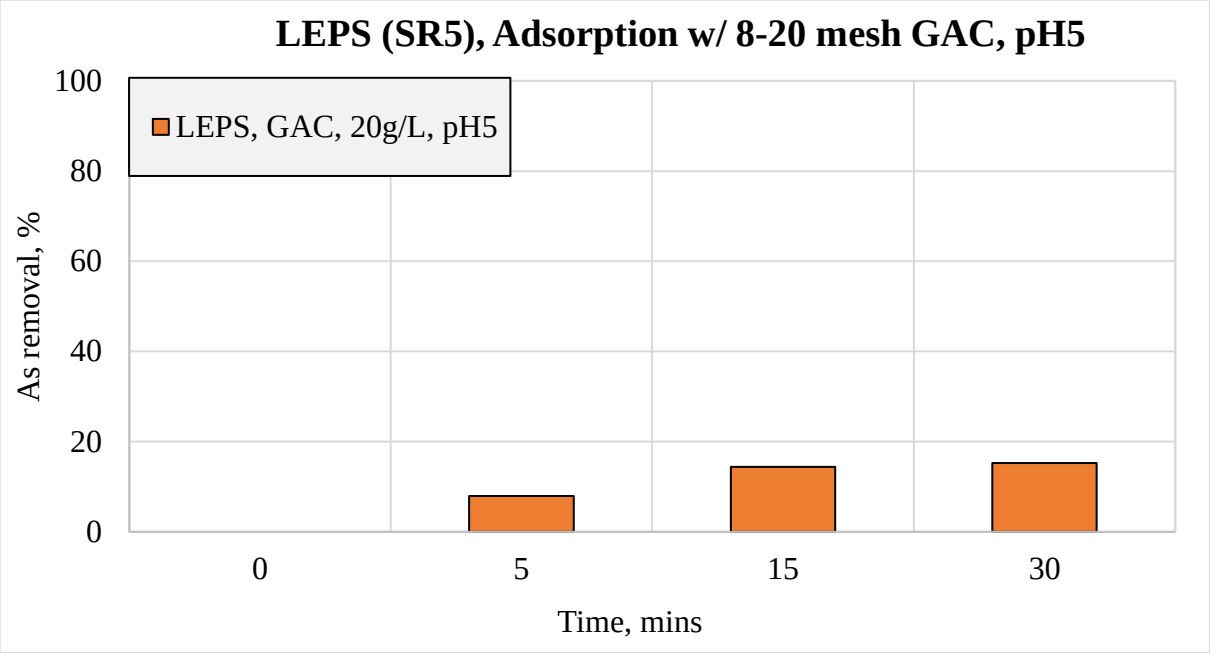


Figure 26. Arsenic removal from LEPS (SR5) dosed with 20 g/L of 8-20 mesh GAC for 30 minutes at pH 5. *(Samples were tested on 02/24/2019).*

2.2.4. Arsenic removal from A567 leachate via PAC adsorption at pH 5 (SR5 sample)

A567 leachate (SR5) was treated with smaller doses of PAC to understand arsenic removal concerning the adsorbent dosage. Unlike in the cases of Vault 1A leachate (SR4) and LEPS leachate (SR5), PAC was unsuccessful in adsorbing a significant amount of arsenic from the A567 leachate (SR5). Only 32% of arsenic removal was achieved at a dose of 20 g/L of PAC (Figure 27). Rates of arsenic removal decreased even further at lower doses of 5 g/L and 10 g/L with 13% and 20% arsenic removed. These differences in the treatment response of both leachates pointed to the variability in the nature and composition of leachate from different landfill locations.

Figure B-5 (Appendix B) shows the correlation between changes in EEM peak intensities and the removal of arsenic from the leachate. It can be noted that the fluorescence response reduced with an increase in PAC dose and the consequent decrease in arsenic concentrations in the leachate.

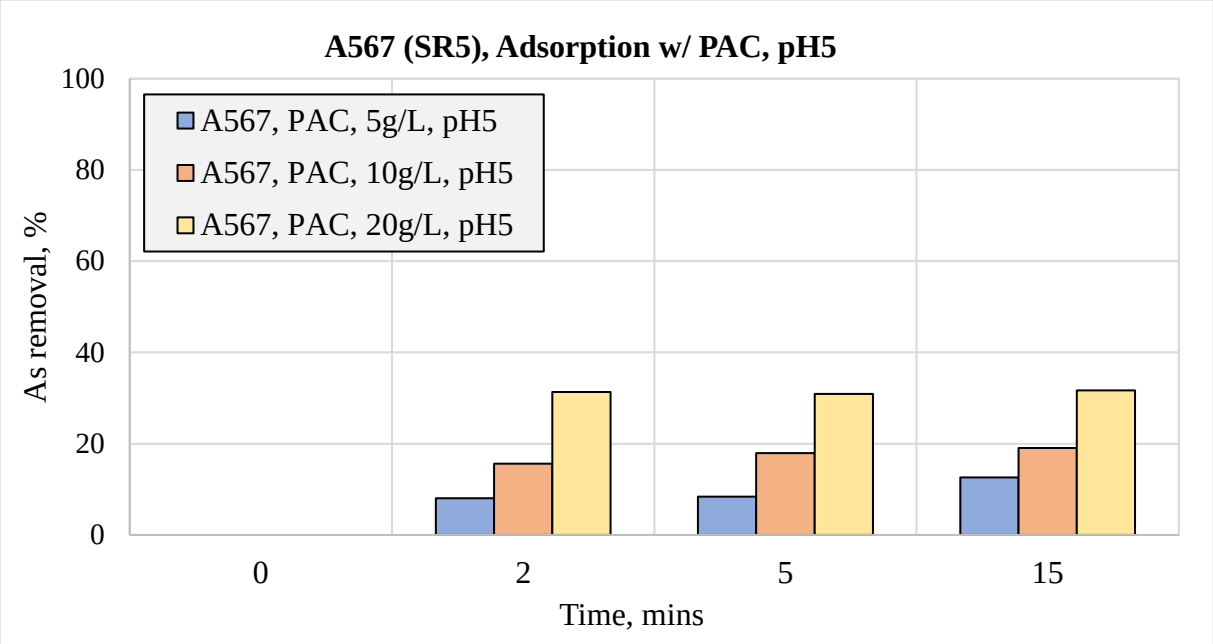


Figure 27. Arsenic removal from A567 (SR5) dosed with 5-20 g/L of PAC for 15 minutes at pH 5. *(Samples were tested on 03/10/2019).*

2.2.5. Arsenic removal from LEPS leachate via PAC adsorption at native pH (SR5 sample)

Experiments to determine the effects of adsorption using varying doses of PAC was carried out with SR5 LEPS leachate at the native pH (= 7.80) of the landfill leachate. This was done to establish if the efficiency of the adsorbent was pH-dependent. Approximately 73% of arsenic was removed from the leachate at a 20 g/L dose. Compared to 68% of arsenic removed at the same dose at pH 5 (see Section 4.2.3.), it was concluded that pH was not a controlling factor in removing arsenic using PAC from LEPS leachate (SR5). 61% and 41% of arsenic removal were achieved for PAC doses of 10 g/L and 5 g/L, respectively. As shown in Figure 28, arsenic removal by adsorption at the native pH of the leachate decreases with increase in contact time. This trend of arsenic removal is consistent with that observed in the previous sections.

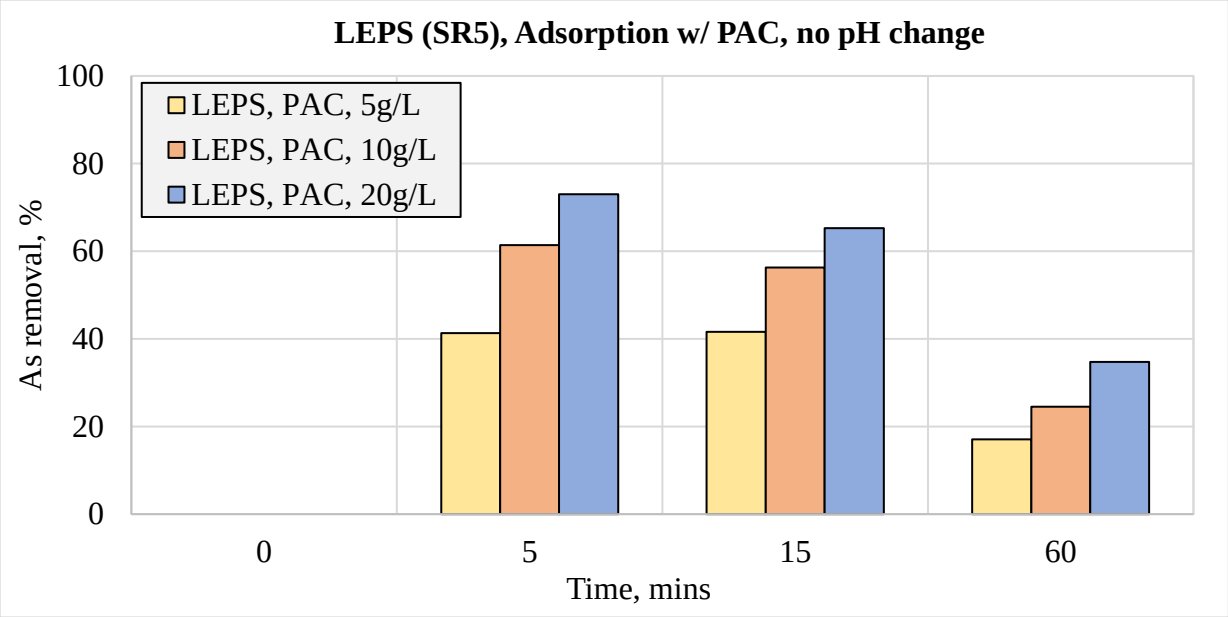


Figure 28. Arsenic removal from LEPS (SR5) dosed with 5-20 g/L of PAC for 15 minutes at the original pH. (Samples were tested on 03/11/2019).

Figure B-6 (Appendix B) shows that a 100% reduction of fluorescence response was recorded regardless of PAC dose, unlike arsenic removal, which increased with higher dosage. This demonstrates that the removal of the fluorophores of leachate organic matter precedes that of the arsenic found in the leachate, which is indicative of a strong preference for PAC adsorbent to interact with the organic matter rather than with the arsenic solutes.

2.2.6. Arsenic removal from A567 leachate via PAC adsorption at native pH (SR5 sample)

Similar experiments were carried out for SR5 A567 leachate, as in the previous section. Figure 29 shows that 27%, 15%, and 7% of arsenic was removed from the leachate at PAC doses of 20 g/L, 10 g/L, and 5 g/L, respectively. This trend was consistent with that observed in the adsorptive treatment of SR5 A567 leachate using PAC at pH 5 (Section 4.2.4.). Thus, the process of arsenic removal via PAC adsorption is pH-independent. The nonmonotonic trend in arsenic removal was also observed in this case.

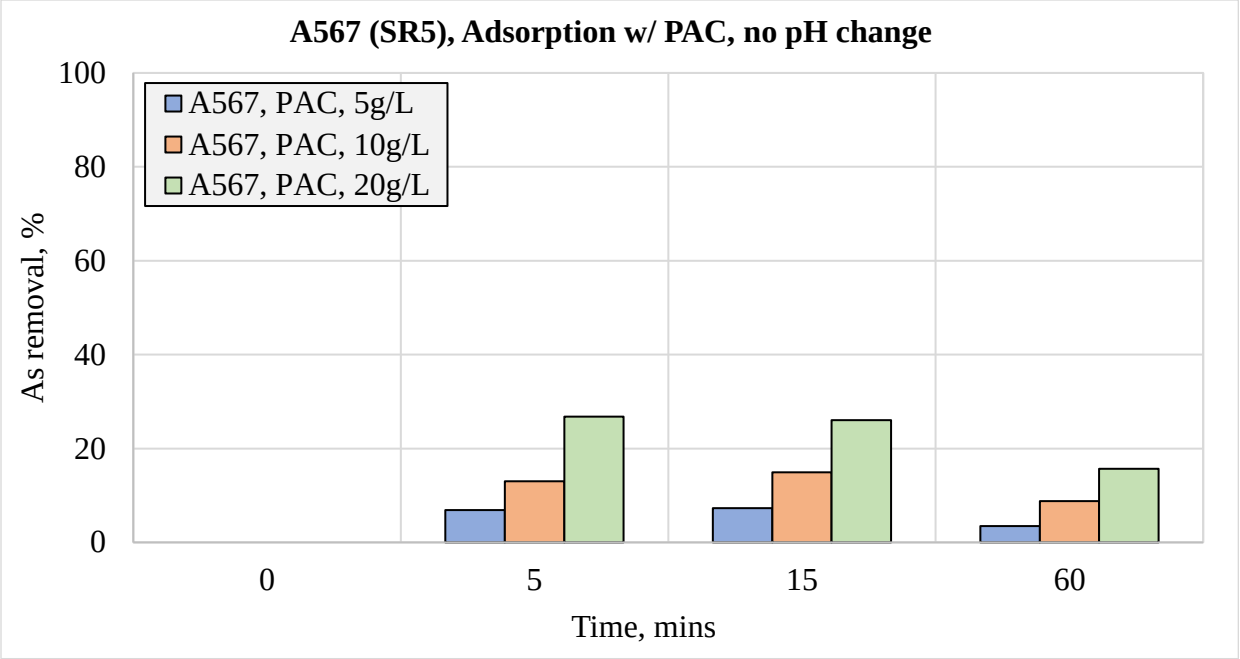


Figure 29. Arsenic removal from A567 (SR5) dosed with 5-20 g/L of PAC for 15 minutes at the original pH. (Samples were tested on 03/11/2019).

Figure B-7 (Appendix B) shows that the reduction of fluorescence response was recorded in proportion with an increase in PAC dose and arsenic removal from the leachate. This response was different from that observed in the previous section for LEPS leachate (SR5). This was probably due to the dilution of LEPS leachate during excessive rainfall, which decreased the arsenic and DOM composition of the leachate. Also, only a modest 5% decrease in EEM peak intensity was observed at the original pH compared to pH 5 (see Section 4.2.4.).

2.2.7. Evaluation of the feasibility of PAC regeneration using A567 leachate (SR5 sample)

Several experiments were carried out to evaluate whether PAC used to remove arsenic can be regenerated. While prior research has shown that PAC or GAC regeneration tends to have low practical utility, the leachate's chemical matrix is different from that used in prior studies. As a result, regeneration experiments were deemed to be important in the context of this study.

These experiments were performed for SR5 A567 leachate. Section 3.2.8. provides further details on the experimental procedure. Approximately 38% of arsenic removal was achieved in the first cycle of adsorptive treatment (Figure 30). The adsorptive capacity of PAC decreased consistently with each regeneration cycle. The regeneration cycles 1, 2, 3, and 4 resulted in 38%, 19%, 12%, and 9%, respectively. These results demonstrate that the regeneration of PAC using 0.1M NaOH was of limited value.

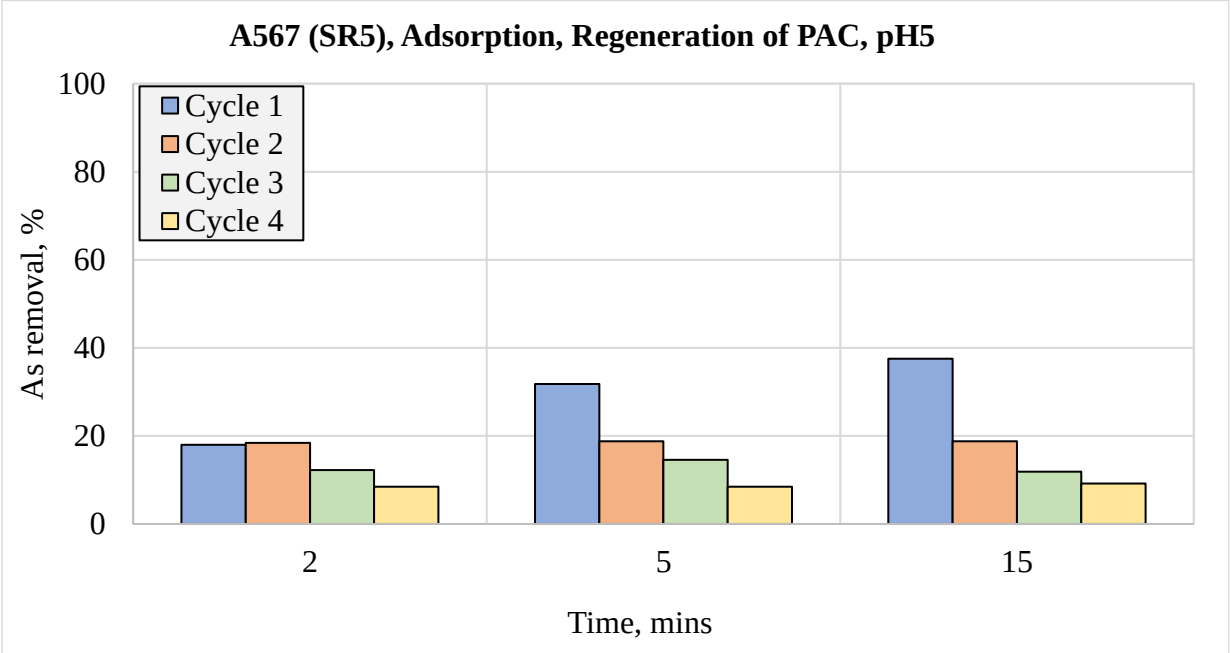


Figure 30. Analysis of regeneration and recycling of PAC. *(Samples were tested on 03/27/2019).*

Figure B-8 (Appendix B) showed the decrease in efficiency or degree of regeneration of PAC was also similarly observed in the EEM fingerprints. The removal of the fluorophores reduced proportionally with an increase in arsenic removal. Also, the extent of fluorophores removed also decreased with every cycle.

2.3. Reductive treatment of arsenic

2.3.1. Comparison of arsenic removal from landfill gas condensate (SR2 sample) and DMA model compound via ZVI treatment

LFG condensate (SR2 sample) and DMA model solution (stock concentration 2000 mg/L) were subjected to reductive treatment using zero-valent iron (ZVI). For this experiment, *LECO* Fe accelerator chips were used as ZVI. The experiment was carried out at pH 4 and near-neutral pH 6. The overall arsenic removal efficiency observed in these experiments was independent of pH (Figure 31). Approximately 80% of total arsenic removal was observed in the case of DMA model solution, proving that methylated organoarsenicals can be removed. The mechanisms of arsenic removal by ZVI may have involved the reduction of DMA to less soluble forms of arsenic (e.g., As(0)), and formation of DMA-containing precipitates with Fe^{2+} and Fe^{3+} ions formed in the solution. However, only 7-8% removal was obtained in the case of LFG condensate. This raised a concern about the composition of possible unknown species of arsenic in the condensate.

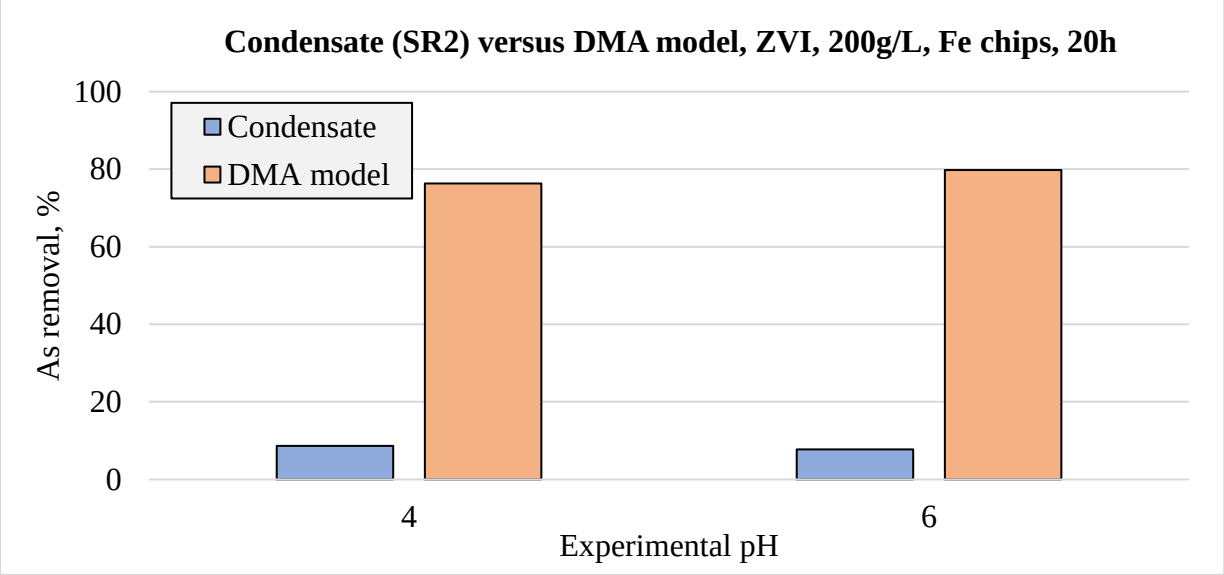


Figure 31. Comparison of arsenic removal from a) LFG condensate (SR2), and (b) 2000 mg/L stock DMA model system dosed with 200 g/L of Fe chips at pH 4 and 6, for 20 hours. *(Samples were tested on 08/16/2019).*

2.3.2. Arsenic removal via ZVI treatment of BEW process water (SR6 sample)

ZVI treatment of BEW process water (SR6) sampled on 03/26/20 was conducted as a preliminary experiment to understand the response of the new sample set to reduction using Fe^0 in the form of *Hoganas* Cleanit® LCPlus Fine. The process water was treated with 50 g/L of LCPF at pH 5 for a contact time of 24 hours.

73% of total arsenic removal was observed over 24 hours compared to a mere 35% in the first 30 minutes of treatment (Figure 32). These results implied that half of the arsenic removal from the process water was achieved within the initial moments of exposure to ZVI, after which removal gradually increased. Nanoscale iron, as compared to granular iron (see the previous section), proved to be more efficient in arsenic removal owing to its greater surface area available for reaction.

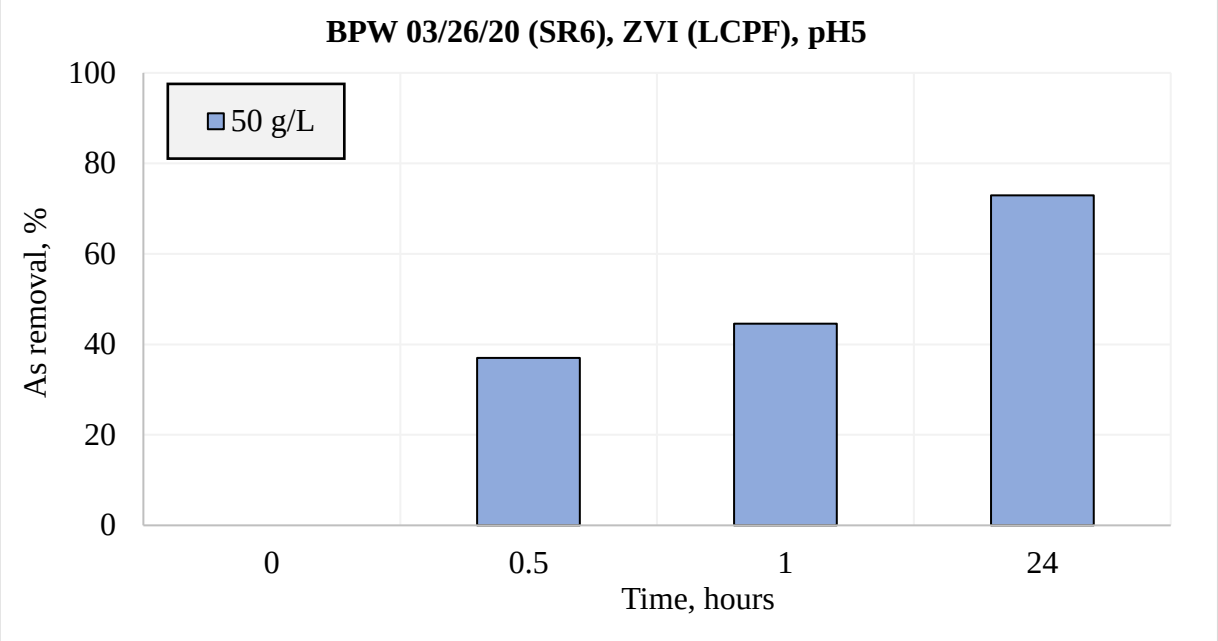


Figure 32. Arsenic removal from SR6 BEW process water (sampled on 03/26/2020) dosed with 50 g/L of LCPF at pH 5 for 24 hours. *(Samples were tested on 06/29/2020).*

2.3.3. Arsenic removal via micro-electrolysis of LEPS leachate (SR3 sample)

Initial micro-electrolysis experiments were carried out with LEPS SR3 leachate. Fe accelerator chips (*LECO*) and 4-14 mesh GAC (*Sigma-Aldrich*) were added to the leachate at different ratios to determine the best Fe/C ratio for optimal removal of total arsenic. Overall, the treatment did not result in a satisfactory removal of total arsenic or significant difference in removal efficiency from the leachate (Figure 33).

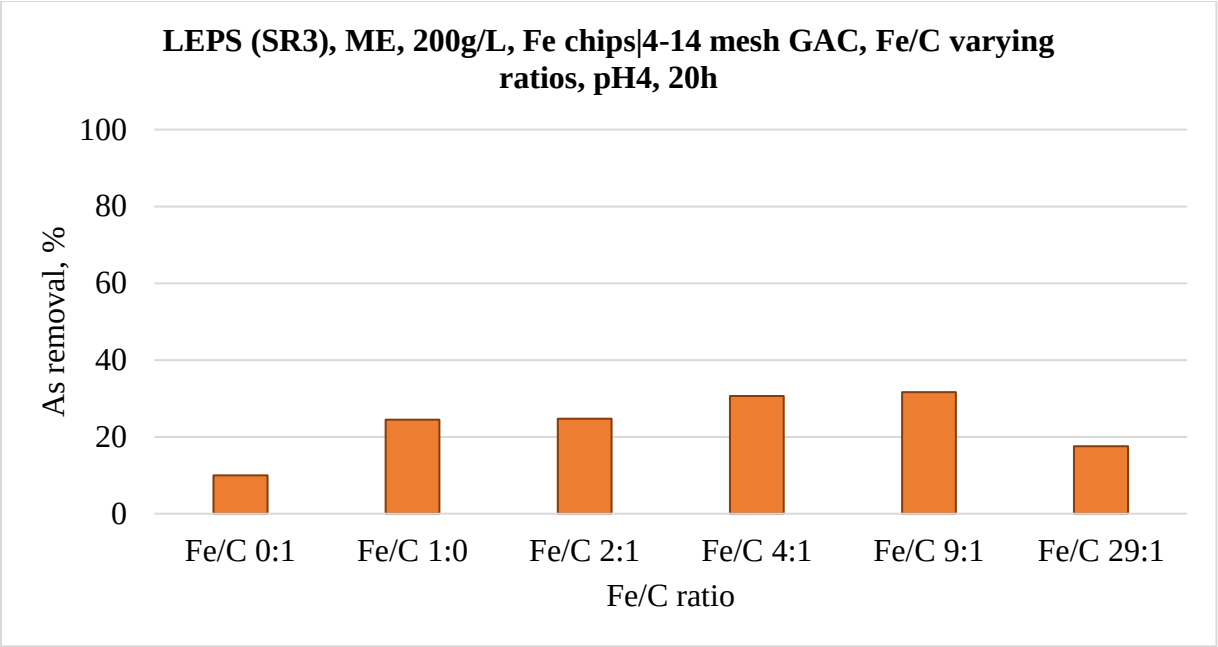


Figure 33. Comparison of arsenic removal from BEW (SR3) dosed with 200 g/L of Fe chips and 4-14 mesh GAC at varying ratios, pH 4 for 20 hours. *(Samples were tested on 08/28/2019).*

2.3.4. Comparison of arsenic removal via micro-electrolysis of LEPS leachate using different reagents (SR3 sample)

Following the initial ME experiment, SR3 LEPS leachate was treated with a variety of ZVI reagents obtained from *Hoganas* company. The Fe/C ratio of 2:1 was chosen in these experiments

for consistency. 4 ZVI types were used along with the Fe accelerator chips (*LECO*). The description of the physical and chemical natures of the iron materials obtained from *Hoganas* is given in Table A-4 in Appendix A.

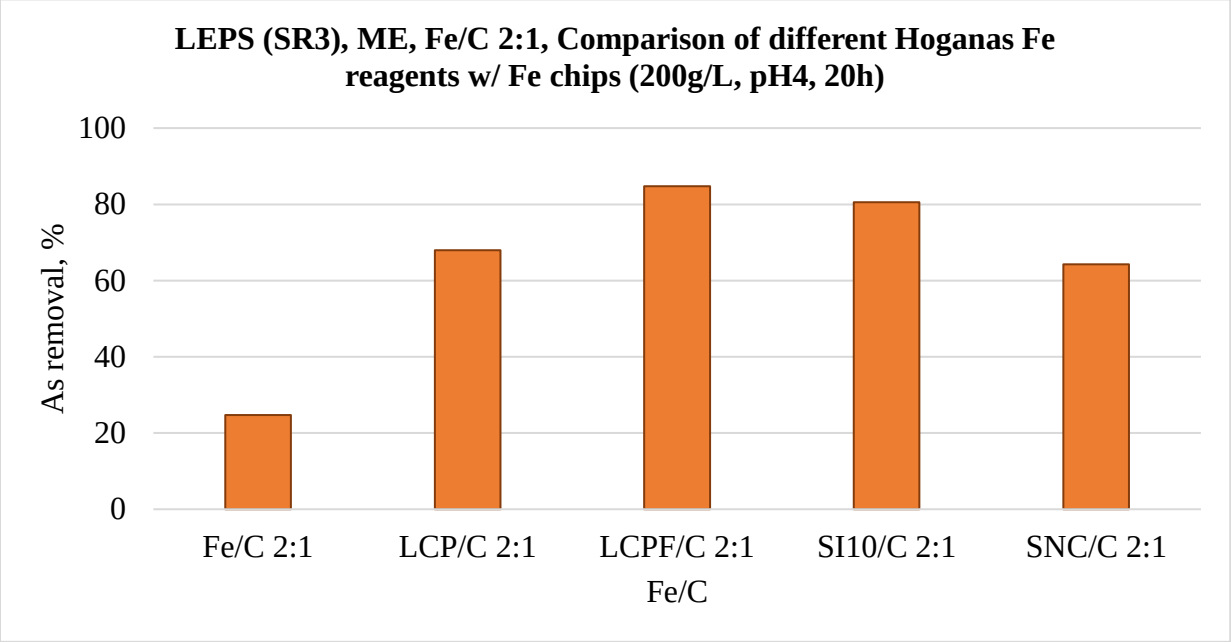
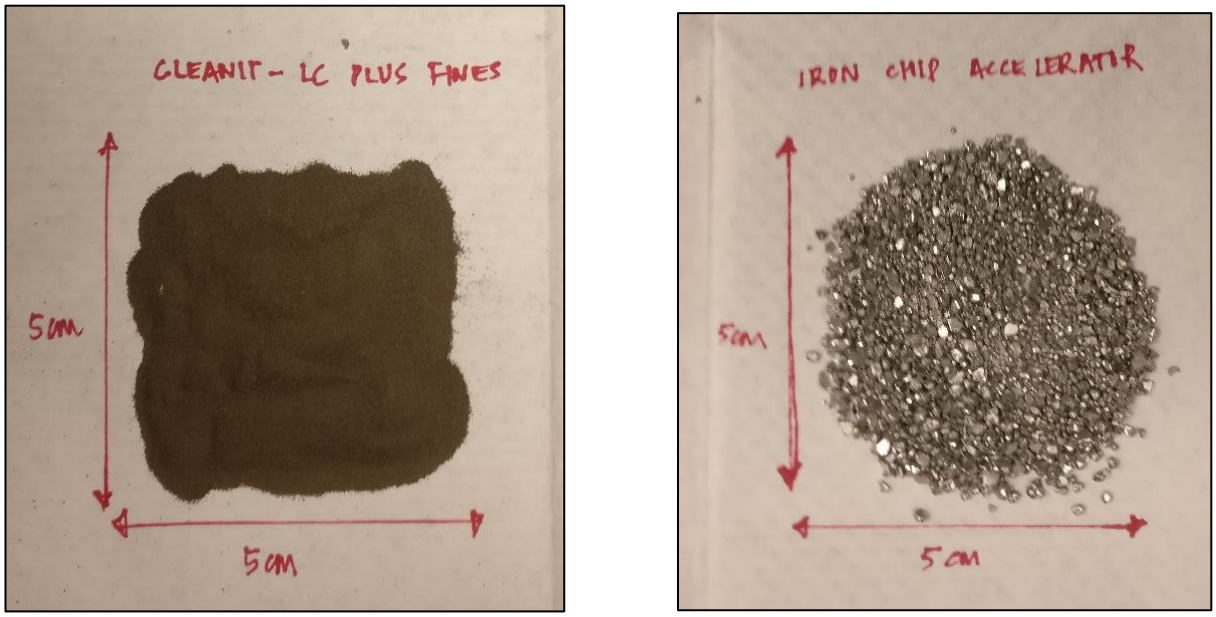


Figure 34. Comparison of arsenic removal from LEPS (SR3) dosed with 200 g/L of different types of iron and 4-14 mesh GAC at a ratio of Fe/C - 2:1, pH 4 for 20 hours. *(Samples were tested on 08/28/2019).*

As presented in Figure 34, the highest total arsenic removal rate of 85% from the leachate was achieved using *Hoganas* Cleanit® LCPlus Fine (LCPF), and the lowest removal of 25% was achieved using 4-14 mesh GAC (*Sigma-Aldrich*) (see Table 6 for complete results). Based on the physical appearance, the LCPF iron is in a fine, powdered form as compared to the granular, iron accelerator chips (Figure 35). This indicated that a smaller particle with a greater specific surface area available for adsorption and interfacial reactions aided in the removal of arsenic via the reduction and subsequent coprecipitation of arsenic from the solution.

Table 6. Total arsenic removal from LEPS (SR3) dosed with 200 g/L of different types of iron and 4-14 mesh GAC at a ratio of Fe/C - 2:1, pH 4 for 20 hours.

Type of iron used	Manufacturer	% Total As removal
Iron accelerator chips	LECO	25%
Cleanit® LCPlus	Hoganas	68%
Cleanit® LCPlus Fine		85%
Cleanit® SI10		81%
Cleanit® SNC		64%



(a) (b)

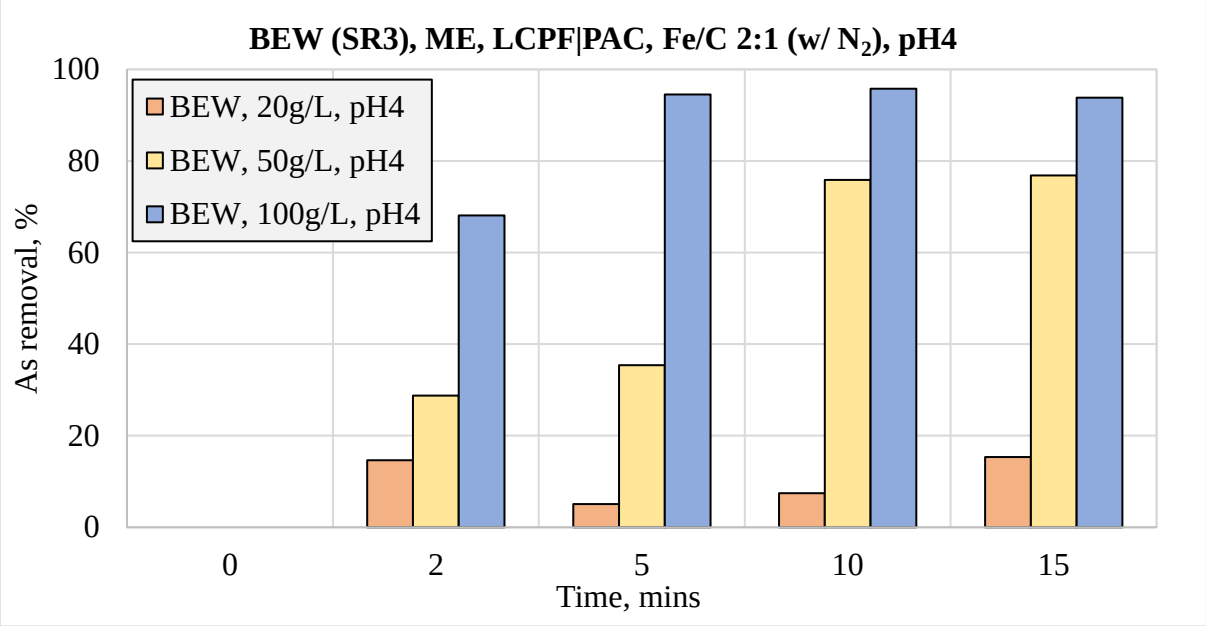
Figure 35. Visual appearance of the two types of iron used for experiments: (a) Hoganas Cleanit® LC Plus Fines and (b) LECO Iron chip accelerator.

2.3.5. Comparison of arsenic removal via micro-electrolysis aided by N_2 gas of BEW condensate at varying pH (SR3 sample)

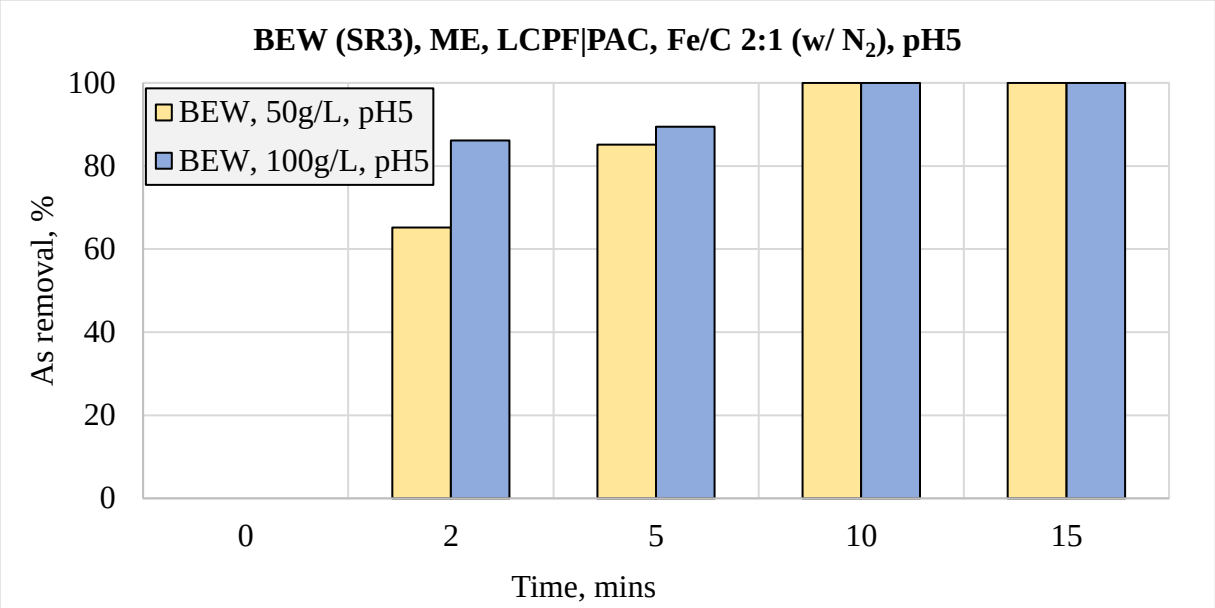
Further experiments that utilized the micro-electrolysis approach showed that reductive and adsorptive processes appeared to have higher efficiency in the absence of ingress of oxygen to the solution. Accordingly, to drive the oxygen out of the solution, the ME experiments were carried out with continuous purging of N_2 gas (0.25 psi). The BEW condensate (SR3) was dosed

with varying LCPF and PAC concentrations at 2:1 Fe/C ratio and varying pH. This was done to understand further dose optimization and the effect of pH on the process.

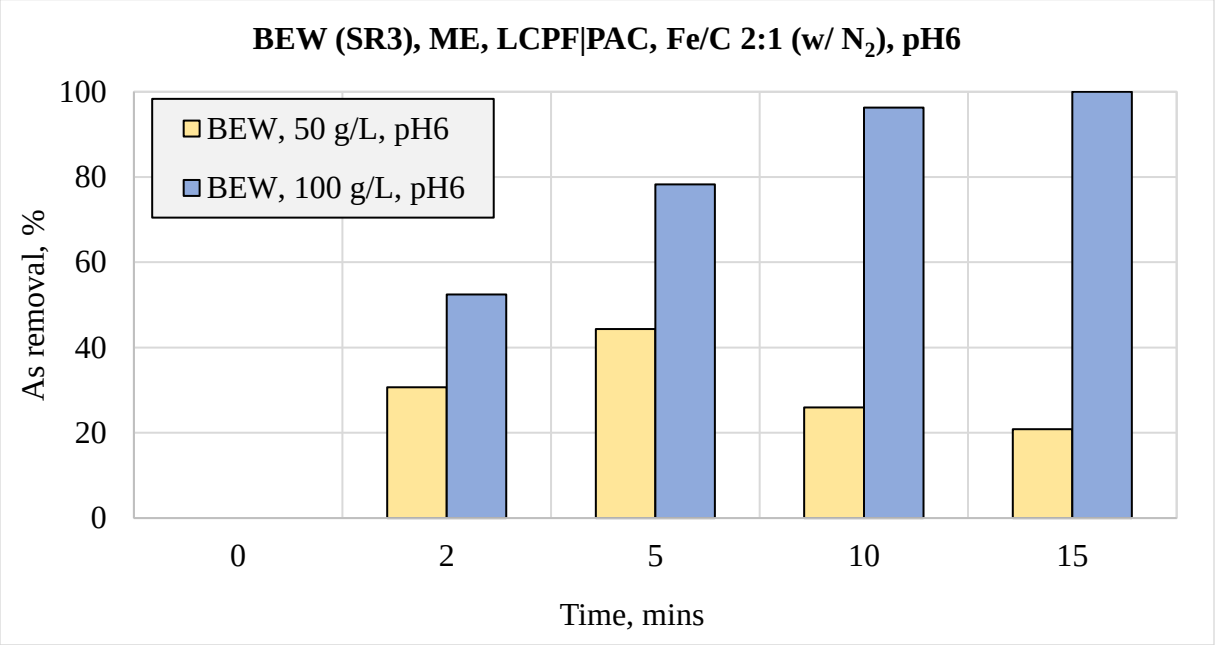
The data showed that almost >90% of total arsenic removal from SR3 BEW condensate was achieved for a total Fe/C dose of 100 g/L at a ratio of 2:1 at pH 4-6 (Figure 36(a)-(c)). >80% removal was achieved within the first 5 minutes of the treatment. In some cases, a smaller dose of 50 g/L achieved >80% removal at pH 4 and 100% removal at pH 5. Thus, effective removal of arsenic by micro-electrolysis can be carried out at slightly acidic pH values. However, the micro-electrolysis treatment was relatively ineffective at pH 7, with only 60% of the total arsenic removed from the system (Figure 36(d)). The replacement of GAC with PAC also enhanced removal at lower doses compared to previous experiments carried out at a dose of 200 g/L (see the previous section). Hence, it was concluded that the availability of a sufficiently high surface area for adsorption was essential in achieving adequate adsorption and consequent removal of arsenic in ME processes.



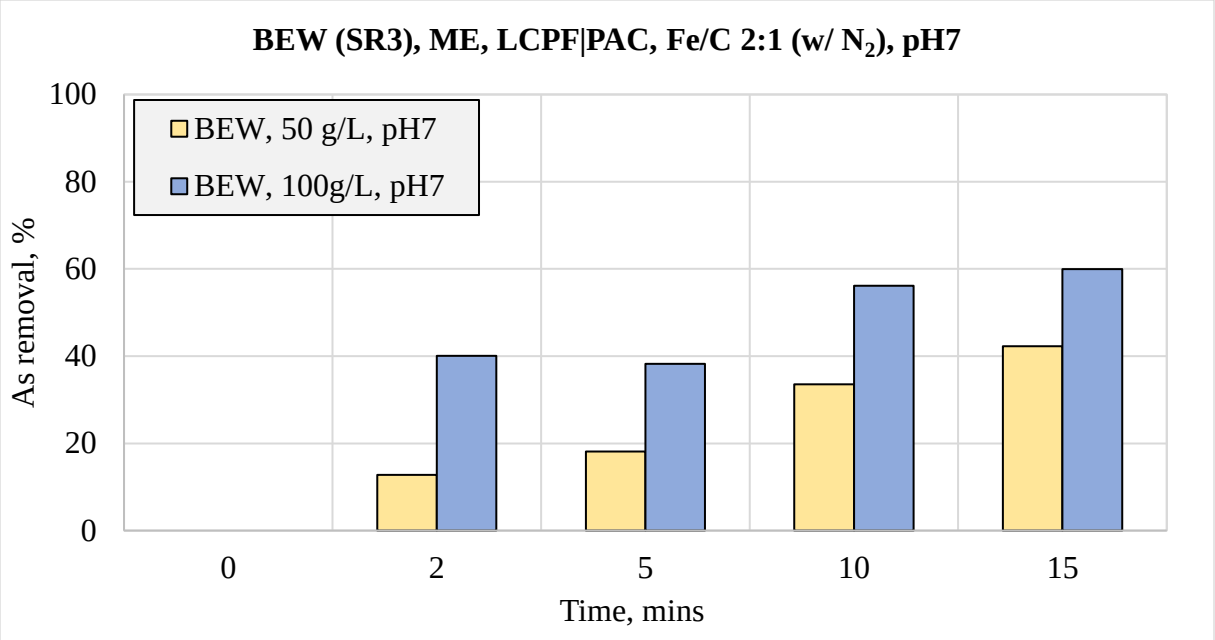
(a)


BEW (SR3), ME, LCPF|PAC, Fe/C 2:1 (w/ N_2), pH5
BEW, 50g/L, pH5
BEW, 100g/L, pH5
As removal, %
100
80
60
40
20
0
0
2
5
10
15
Time, mins

(b)


BEW (SR3), ME, LCPF|PAC, Fe/C 2:1 (w/ N_2), pH6
BEW, 50 g/L, pH6
BEW, 100 g/L, pH6
As removal, %
100
80
60
40
20
0
0
2
5
10
15
Time, mins

(c)

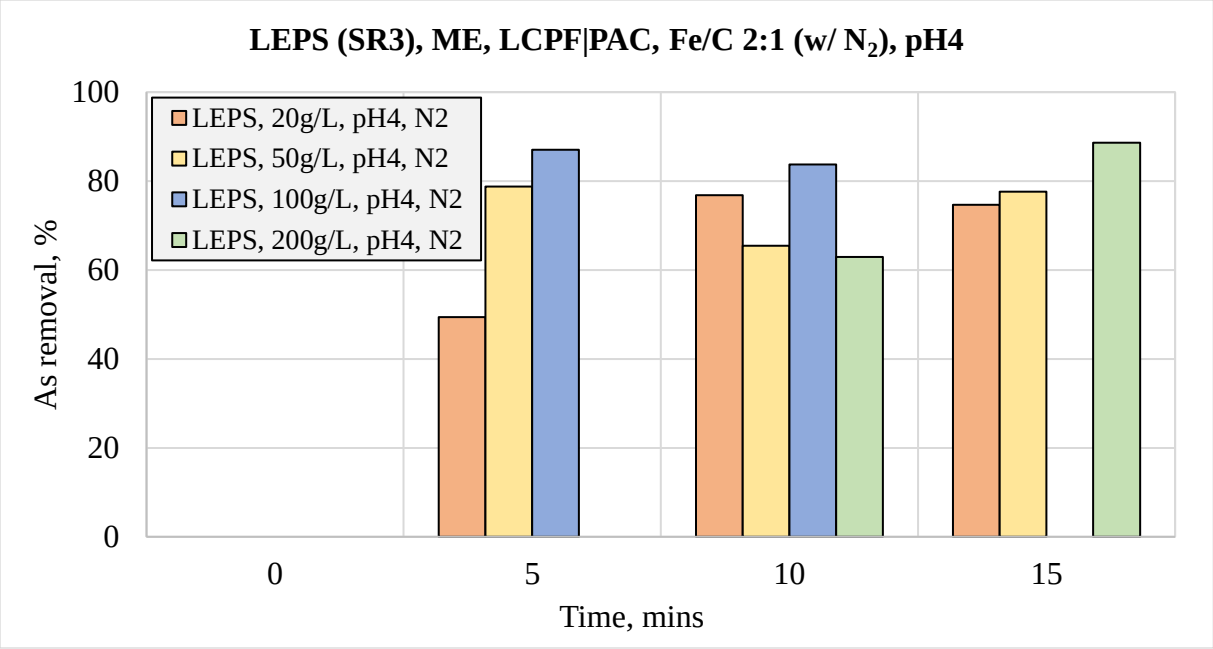


(d)

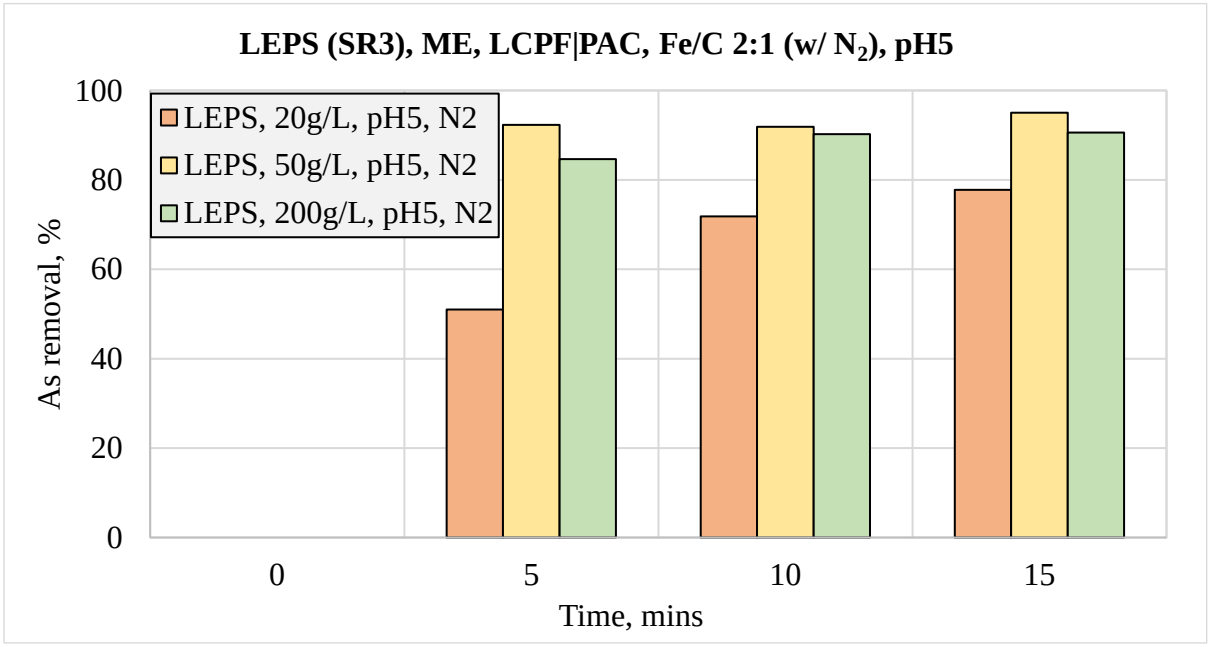
Figure 36. Arsenic removal from BEW (SR3 sample) dosed with varying doses of LCPF iron and PAC at a ratio of Fe/C - 2:1 and purged with N_2 gas for 15 minutes at (a) pH 4, (b) pH 5, (c) pH 6, and, (d) pH 7. *(Samples were tested on 10/11/2019 and 11/01/2019).*

2.3.6. Comparison of arsenic removal from LEPS leachate via micro-electrolysis aided by N_2 gas at varying pH (SR3 sample)

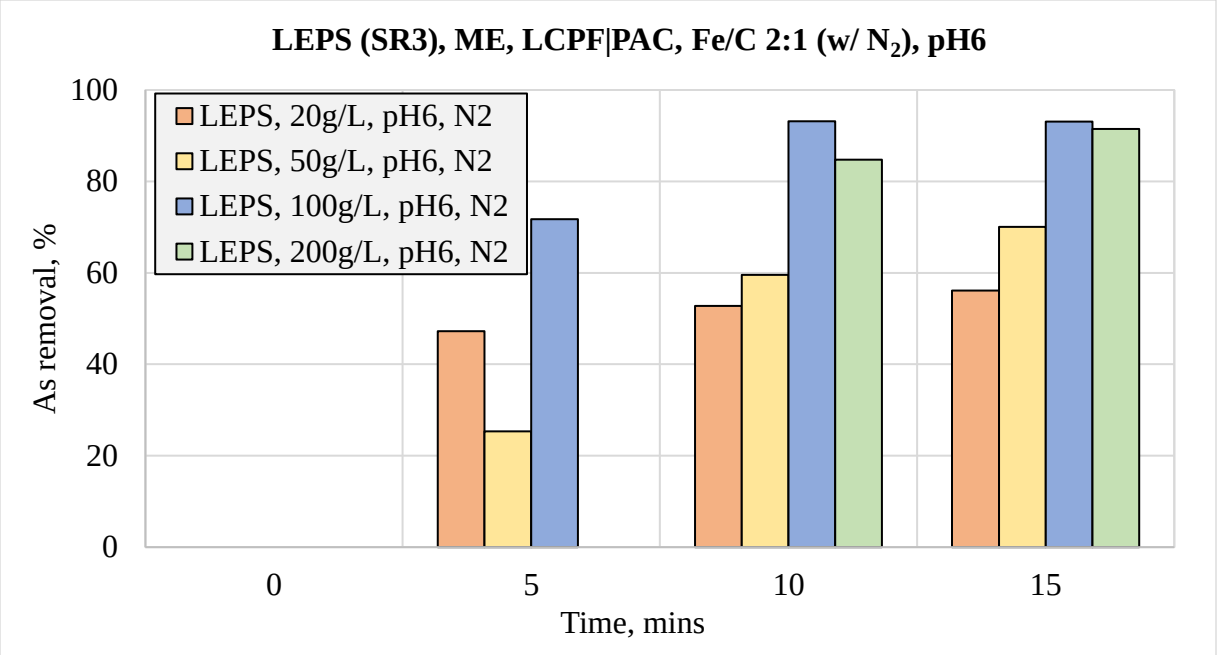
The experimental protocol implemented here is identical to that described in Section 4.3.4. The pattern of total arsenic removal from the leachate was similar to that observed in the case of SR3 BEW condensate. Approximately 70-80% of total arsenic removal was achieved within the first 5 minutes of treatment for experiments carried out at a dose of 100 g/L at pH 4 to 6 (Figure 37(a)-(c)). ≥80% removal was obtained for leachate dosed with 50 g/L of Fe:C at pH 4 to 5. The removal efficiency decreased for treatment performed at pH 7, as previously observed with SR3 BEW condensate treatment (Figure 37(d)). However, the overall removal efficiency was relatively higher for BEW condensate (SR3) than for LEPS (SR3) leachate. The higher concentrations of DOM in leachate than that in the condensate can be assumed to result in a more prominent competition of DOM for the adsorption sites, and thus, in the hindering of arsenic removal.


LEPS (SR3), ME, LCPF|PAC, Fe/C 2:1 (w/ N2), pH4
LEPS, 20g/L, pH4, N2
LEPS, 50g/L, pH4, N2
LEPS, 100g/L, pH4, N2
LEPS, 200g/L, pH4, N2
As removal, %
100
80
60
40
20
0
0
5
10
15
Time, mins

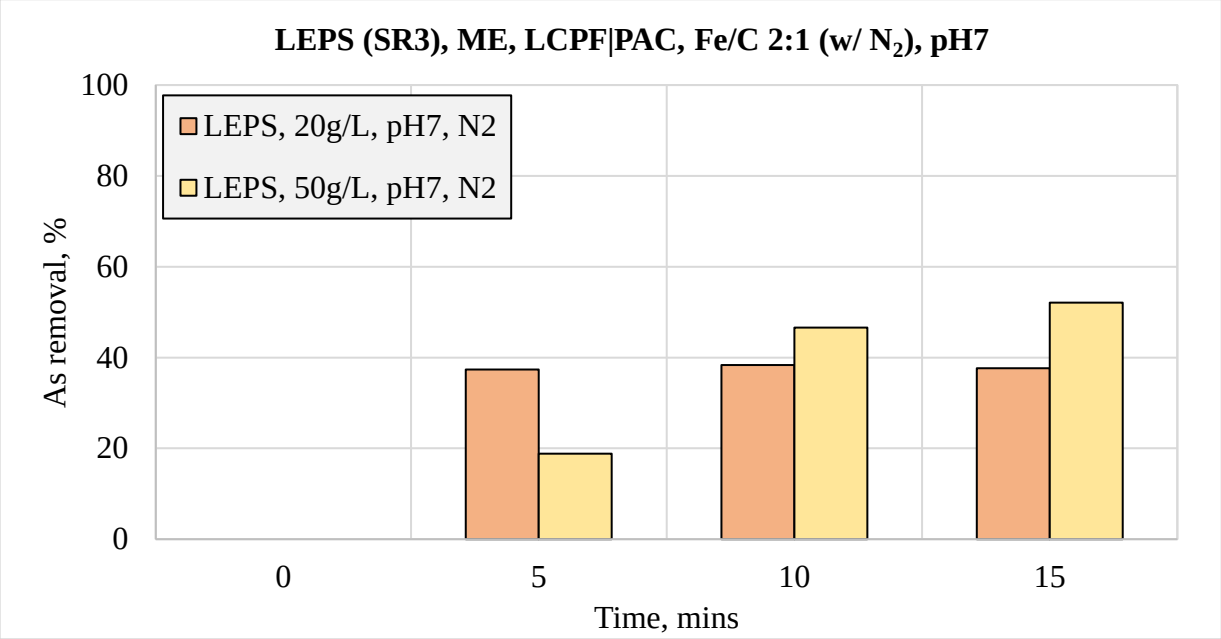
(a)


LEPS (SR3), ME, LCPF|PAC, Fe/C 2:1 (w/ N2), pH5
LEPS, 20g/L, pH5, N2
LEPS, 50g/L, pH5, N2
LEPS, 200g/L, pH5, N2
As removal, %
100
80
60
40
20
0
0
5
10
15
Time, mins

(b)



(c)



(d)

Figure 37. Arsenic removal from LEPS (SR3) dosed with varying doses of LCPF iron and PAC at a ratio of Fe/C - 2:1 and purged with N_2 gas for 15 minutes at (a) pH 4, (b) pH 5, (c) pH 6, and, (d) pH 7. *(Samples were tested on 11/01/2019 and 11/14/2019).*

An increase in pH was observed from the onset of treatment due to the consumption of H^+ ions during cathodic reduction. The rate of variability in the pH was also proportional to the dosage of Fe:C. Concentrated HCl was added in increments to maintain the pH. This rate of change of pH of the solution also decreased as the treatment time increased. On purging the solution with N_2, foaming was observed, which was not noted in the case of BEW condensate.

2.3.7. Arsenic removal from LEPS leachate via micro-electrolysis aided by CO_2 gas (SR3 sample)

The next experimental work stage involved ME experiments carried out with continuous purging of CO_2 gas (0.25 psi). SR3 LEPS leachate was dosed with varying concentrations of LCPF and PAC at a 2:1 Fe/C ratio and pH 6. In the case of CO_2 gas application, a natural decrement in the leachate's or condensate's pH was observed. Introduction of CO_2 results in the formation and dissociation of carbonic acid in the solution that released protons [H^+], thus, decreasing the pH. So, in this case, acid was added to the leachate or condensate to obtain the desired pH, after the it stabilized under the influence of CO_2 gas. Changes in pH during the treatment, as described in the previous section, were stabilized using concentrated HCl.

The data clearly showed that almost 90% and 96% of total arsenic removal was achieved for a dose of 100 g/L and 200 g/L, respectively (Figure 38) within the first 5 minutes of treatment time. Approximately 78% removal was achieved with a dose of 50 g/L after 15 minutes of the treatment. On the other hand, lower doses of 10 g/L and 20g/L could only achieve 20-25% of arsenic removal from the leachate.

These data were compared to those pertinent to the removal observed using N_2 gas (Figure 37). Based on the assessment of the data, it was concluded that adequate arsenic removal could be achieved at pH 5 using either gas.

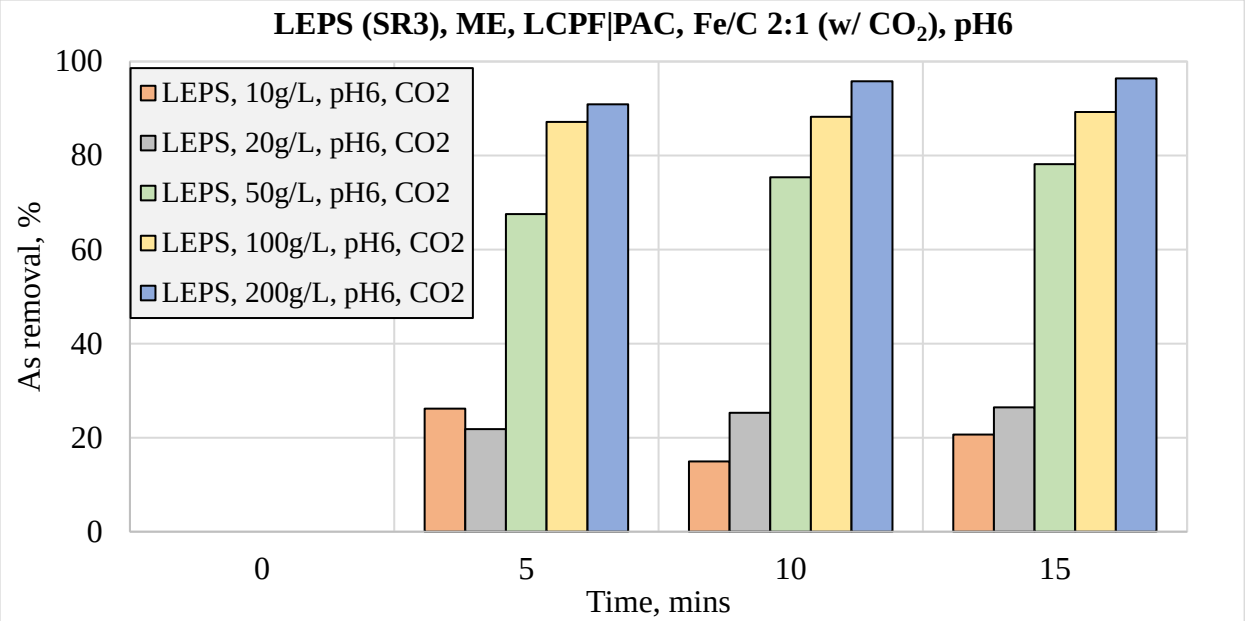


Figure 38. Arsenic removal from LEPS (SR3) dosed with 10-200 g/L of LCPF iron and PAC at a ratio of Fe/C - 2:1 and purged with CO_2 gas for 15 minutes at pH 6. *(Samples were tested on 11/22/2019).*

As seen in Figure B-9, complete reduction of fluorescence response was noted for higher doses of Fe/C > 50 g/L indicating removal of DOM from the leachate at higher doses.

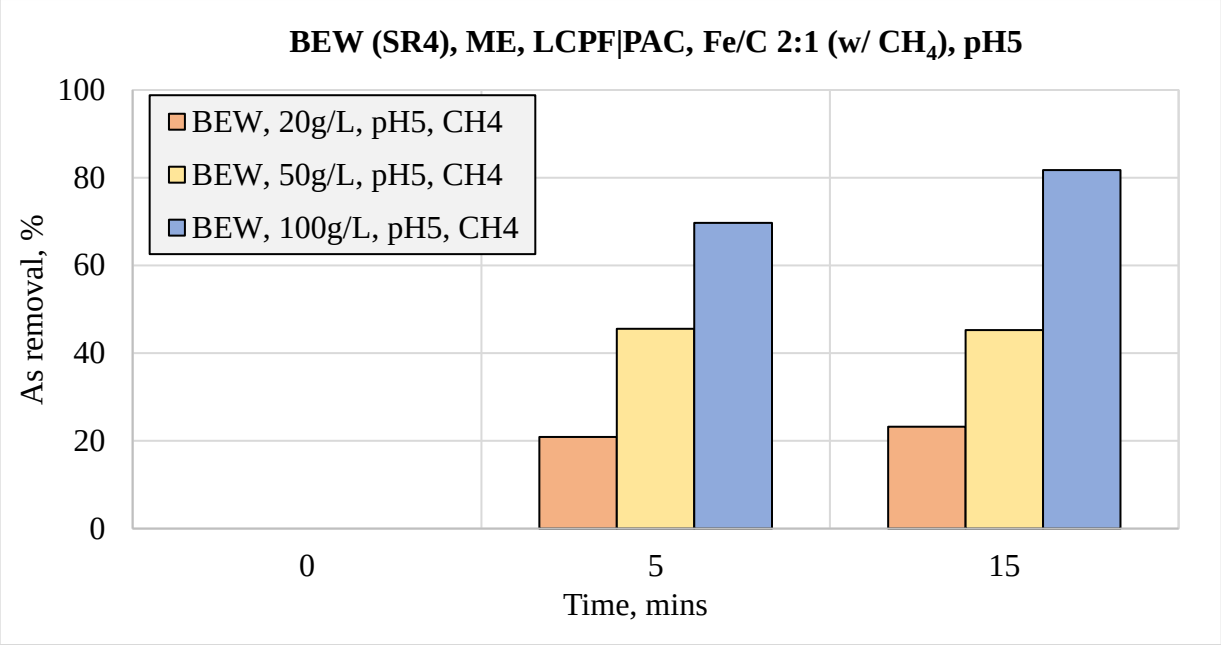
2.3.8. Comparison of arsenic removal from BEW condensate using micro-electrolysis aided by different gases (SR4 sample)

Further micro-electrolysis experiments were carried out with different gases to compare the effect of the type of gas used on arsenic removal. SR4 BEW condensate was dosed with varying concentrations of LCPF and PAC at 2:1 Fe/C ratio and pH 5. The suspensions were purged with (i) methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), and hydrogen (H_2) gases.

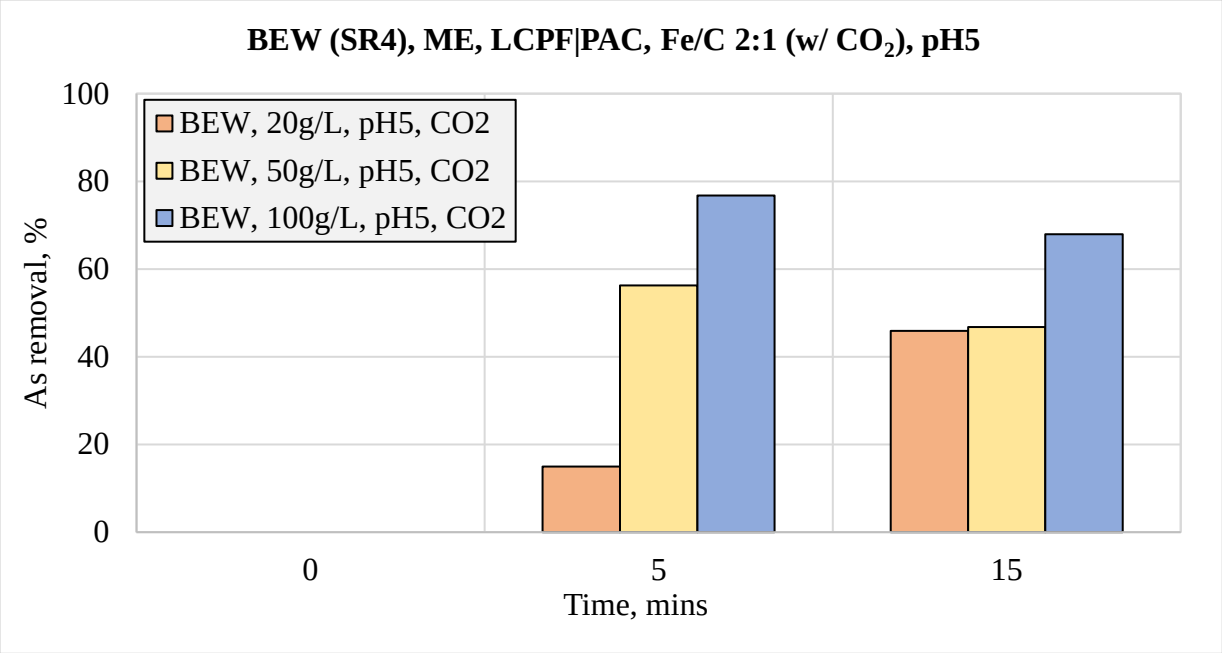
The results presented in Figure 39(d) indicate that almost >90% of total arsenic removal was achieved for a dose of 100 g/L using N_2 gas within the first 5 minutes of treatment. 80% and 70% of removal were achieved at the same dose using CH_4 and CO_2 gases, respectively (Figure 39(a) and (b)). On the other hand, only 50% of arsenic was removed from the system using H_2 gas

(Figure 39(c)). Smaller Fe/C doses of 20 g/L and 50 g/L failed to achieve adequate arsenic removal from SR4 BEW condensate.

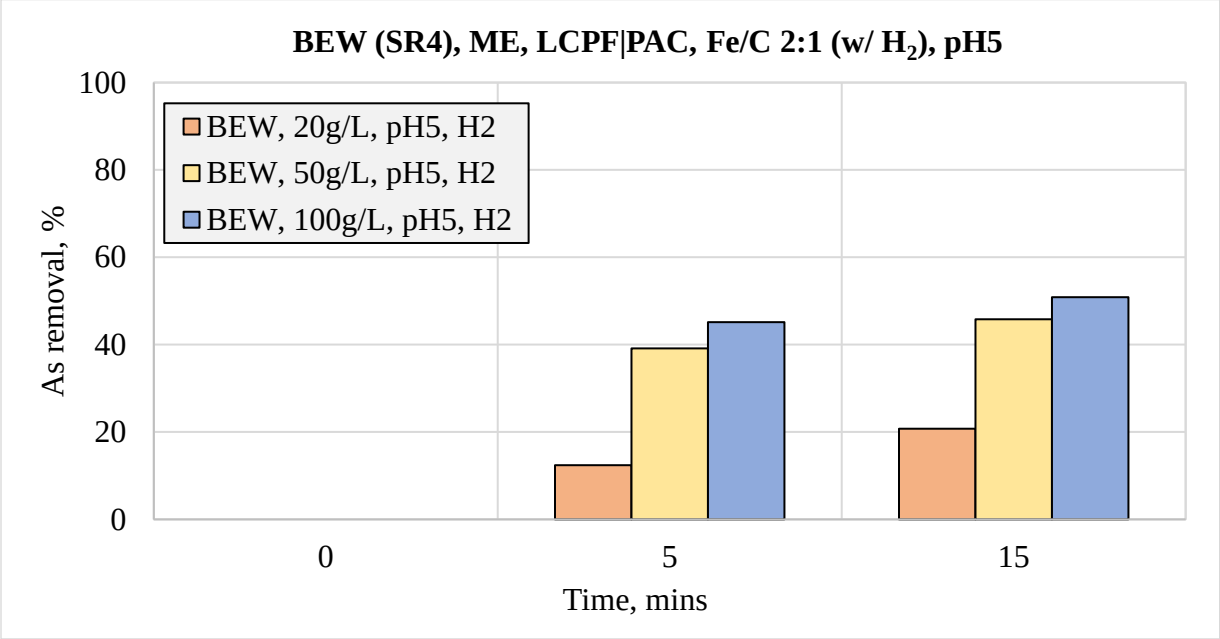
These results were compared with those reported in Section 4.3.5. for SR3 BEW condensate. For SR3 BEW, 100% total arsenic removal was achieved at a dose of 50 g/L at pH 5 compared to 55% of removal achieved for SR4 BEW at the same conditions. It is important to note that the arsenic concentration of BEW (SR4 sample) was far higher than that of BEW (SR3 sample) (see Table 2 for reference). The differences between the removal of arsenic raised a question of the leachate's seasonal variability and resulting differences in their responses to the examined treatment options.



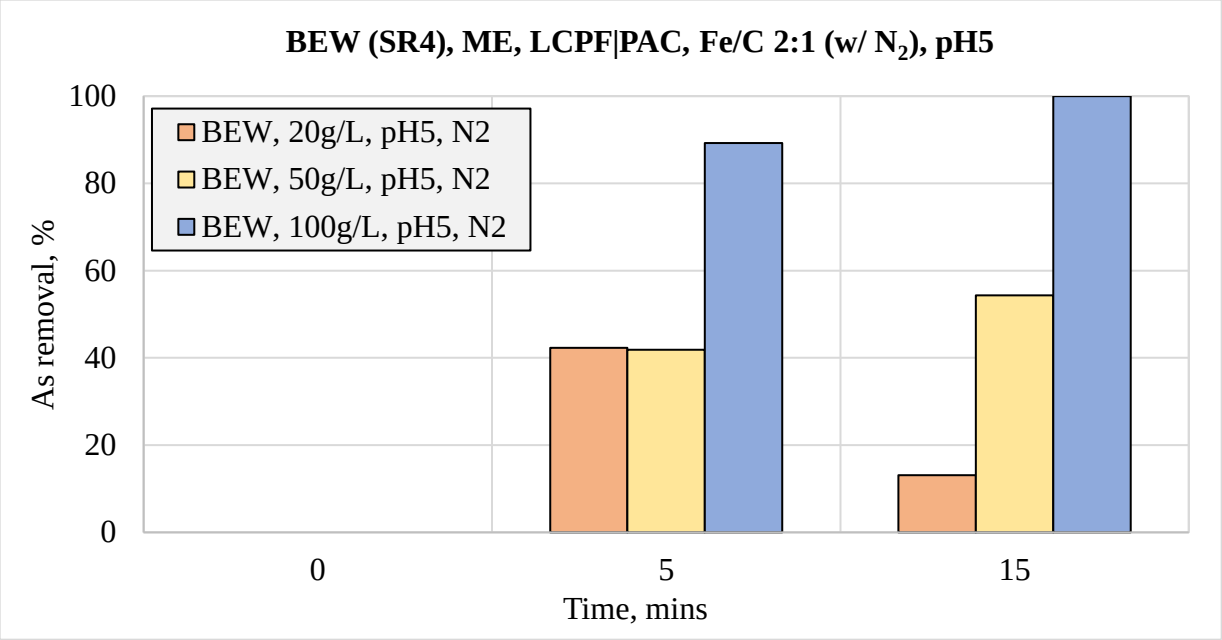
(a)


BEW (SR4), ME, LCPF|PAC, Fe/C 2:1 (w/ CO_2), pH5
BEW, 20g/L, pH5, CO2
BEW, 50g/L, pH5, CO2
BEW, 100g/L, pH5, CO2
As removal, %
100
80
60
40
20
0
0
5
15
Time, mins

(b)


BEW (SR4), ME, LCPF|PAC, Fe/C 2:1 (w/ H_2), pH5
BEW, 20g/L, pH5, H2
BEW, 50g/L, pH5, H2
BEW, 100g/L, pH5, H2
As removal, %
100
80
60
40
20
0
0
5
15
Time, mins

(c)

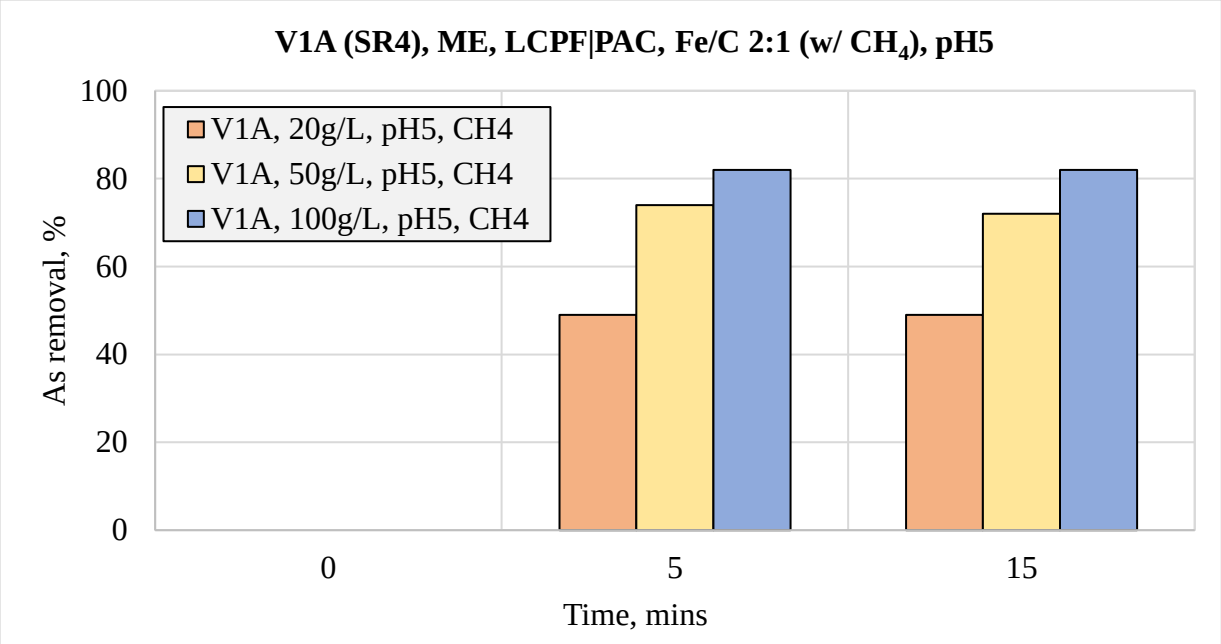


(d)

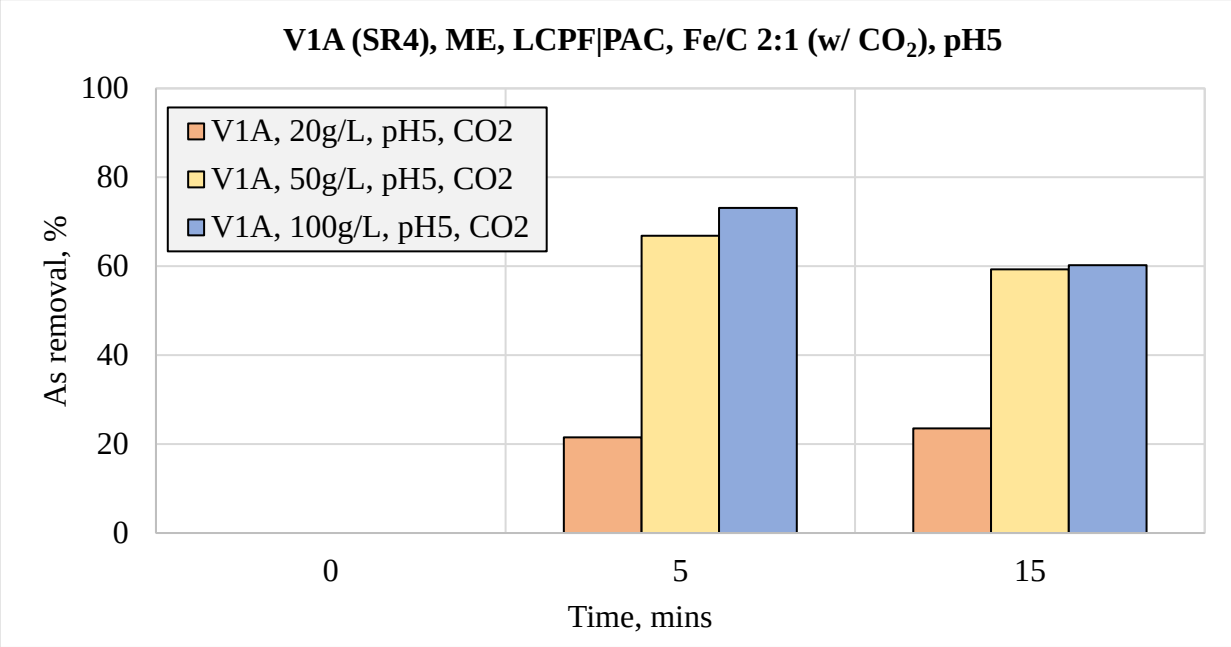
Figure 39. Arsenic removal from BEW (SR4) dosed with varying doses of LCPF iron and PAC at a ratio of Fe/C - 2:1 for 15 minutes at pH 5, with (a) CH_4, (b) CO_2, (c) H_2, and, (d) N_2 gas. *(Samples were tested on 11/27/2019, 12/18/2019, and 01/27/2020).*

2.3.9. Comparison of arsenic removal via micro-electrolysis of Vault 1A leachate aided by different gas types (SR4 sample)

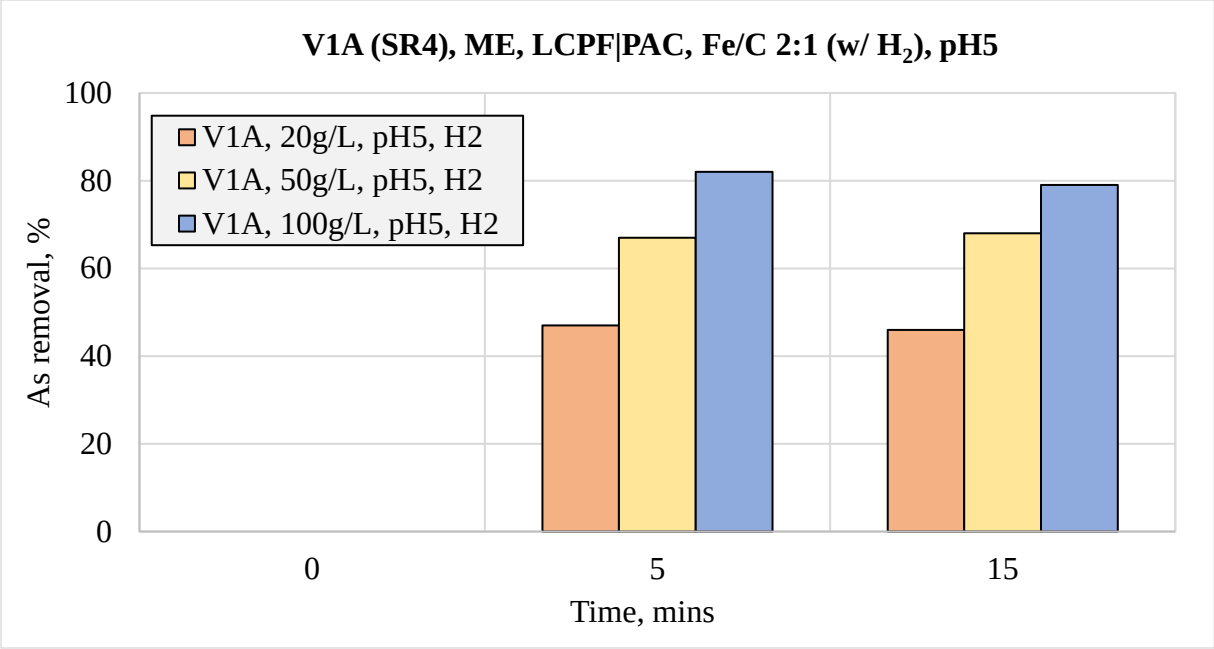
Experiments with SR4 Vault 1A leachate were carried out using the experimental protocol described in Section 4.3.8. These experiments showed that 70-80% of total arsenic removal was achieved for SR4 Vault 1A leachate dosed with 100 g/L of Fe:C for gas types used in the experiment (Figure 40). However, smaller doses of 20 g/L and 50 g/L of the Fe/C media failed to achieve adequate arsenic removal from the leachate. The inference obtained from similar experiments performed with condensate in the previous section were deemed applicable to this set of experiments performed with leachate. Excessive foaming was observed when the leachate was purged with N_2 gas. This issue of foaming was suppressed on the application of other gases to this process.


V1A (SR4), ME, LCPF|PAC, Fe/C 2:1 (w/ CH4), pH5
V1A, 20g/L, pH5, CH4
V1A, 50g/L, pH5, CH4
V1A, 100g/L, pH5, CH4
As removal, %
100
80
60
40
20
0
0
5
15
Time, mins

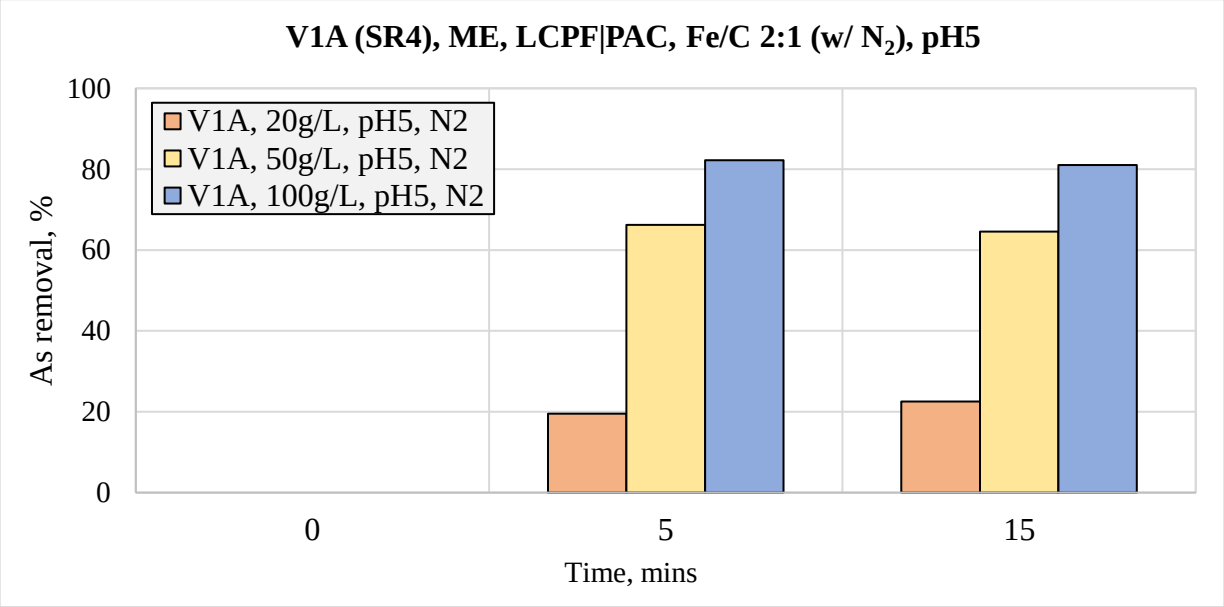
(a)


V1A (SR4), ME, LCPF|PAC, Fe/C 2:1 (w/ CO2), pH5
V1A, 20g/L, pH5, CO2
V1A, 50g/L, pH5, CO2
V1A, 100g/L, pH5, CO2
As removal, %
100
80
60
40
20
0
0
5
15
Time, mins

(b)



(c)



(d)

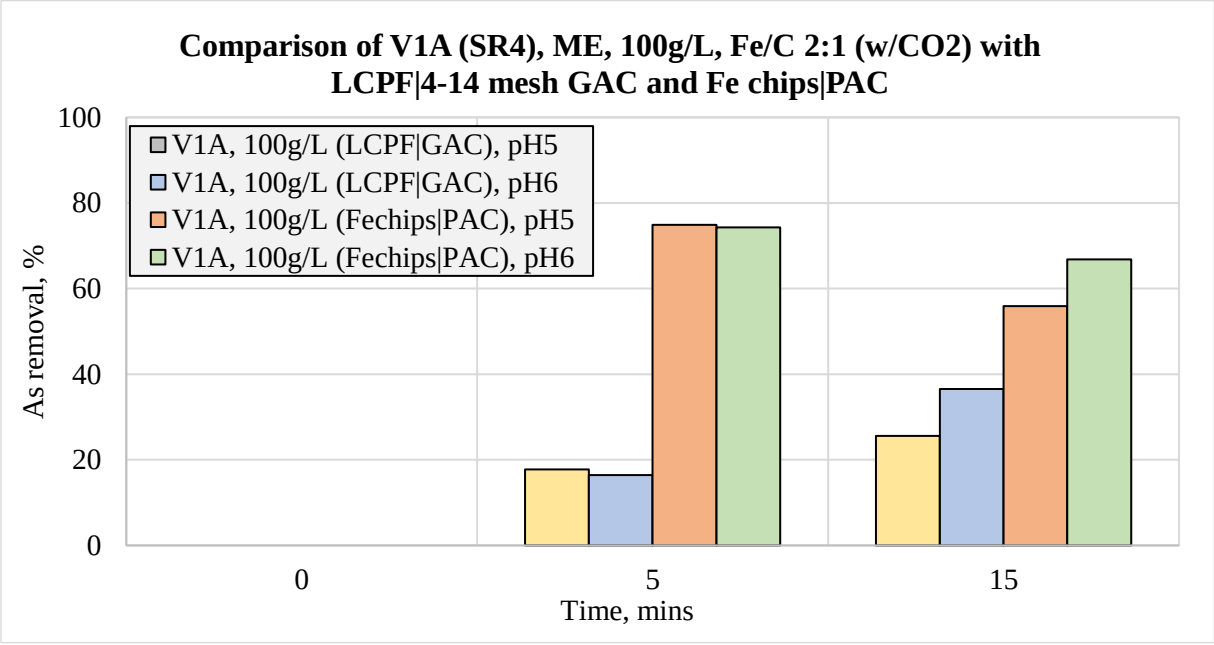
Figure 40. Arsenic removal from V1A (SR4) dosed with varying doses of LCPF iron and PAC at a ratio of Fe/C - 2:1 for 15 minutes at pH 5, with (a) CH_4, (b) CO_2, (c) H_2, and, (d) N_2 gas. (Samples were tested on 12/06/2019, 12/18/2019, and 01/27/2020).

While more research is needed to interpret the data in more detail, methane and hydrogen gases were chosen to not be used in arsenic removal from landfill leachate and condensate. CO_2

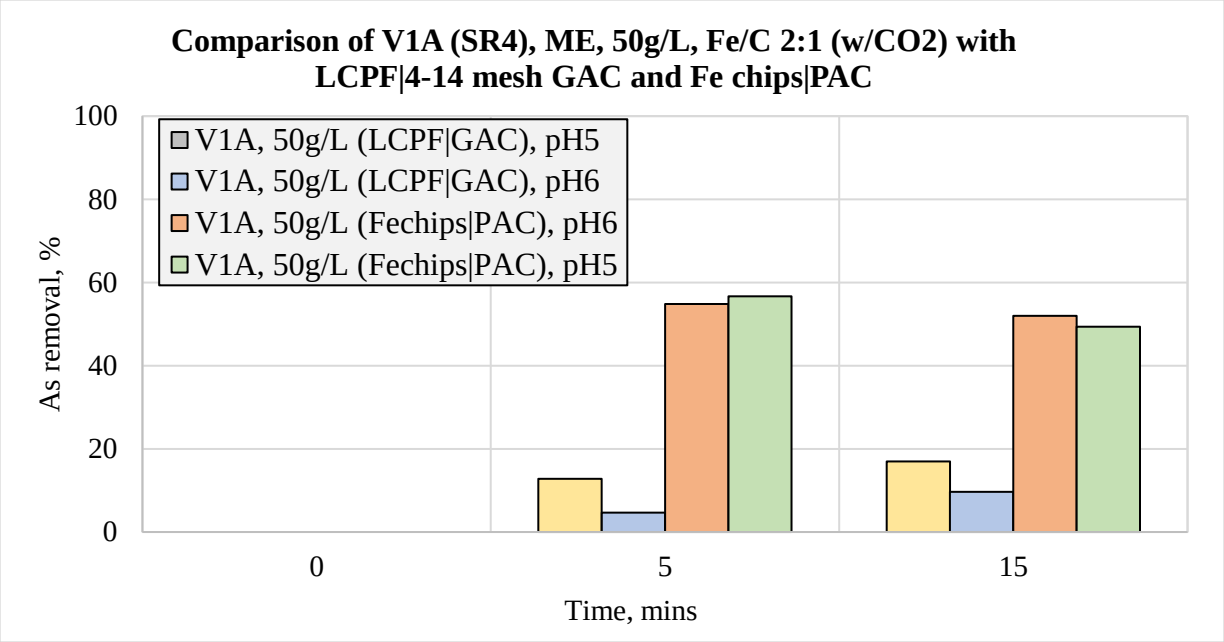
gas was chosen as the gas for the optimal efficiency of removal. Apart from surpressing foaming in the case of leachate, CO_2 gas naturally reduced pH due to the dissociation of carbonic acid which favors the treatment efficiency. Also, CO_2 is an important by-product of the LFG and thus, can be produced on-site.

2.3.10. Evaluation of arsenic removal via micro-electrolysis of Vault 1A leachate using varying combinations of iron and activated carbon reagents (SR4 sample)

The micro-electrolysis experiments described in this section were performed using several combinations of iron and carbon with varying particle sizes. SR4 Vault 1A leachate was dosed in with 50 g/L and 100g/L of LCPF and 4-14 mesh GAC, and Fe accelerator chips and PAC at a ratio of Fe/C 2:1. These experiments were performed at pH 5 and 6 using CO_2 gas.



(a)



(b)

Figure 41. Comparison of cross-combination of iron and carbon reagents based on particle size; Arsenic removal from V1A (SR4) dosed with 50-100 g/L of (a) LCPF iron and GAC, and (b) Fe chips and PAC at a ratio of Fe/C 2:1, and purged with CO_2 gas for 15 minutes at pH 5 and pH 6. *(Samples were tested on 12/17/2019).*

As shown in Figure 41, the combination of Fe accelerator chips and PAC achieved higher arsenic removal than LCPF and 4-14 mesh GAC. The Fe chips and PAC setup achieved approximately 65-75% and 50-60% of arsenic removal at a dose of 100 g/L and 50 g/L, respectively compared to the LCPF and 4-14 mesh GAC that achieved only 15-35% and 10-15% of total arsenic removal at the same conditions. These results indicate that adsorption on PAC may have a higher role in arsenic removal from this leachate matrix than that of reduction by LCPF in previous micro-electrolysis experiments.

Figure B-10 (Appendix B) shows that a 100% reduction of fluorescence response was recorded regardless of Fe chips and PAC dose. No substantial removal was recorded in the case of LCPF and GAC. This highlighted the contribution of the nanoscale PAC in the adsorption of DOM compared to larger sized GAC.

2.3.11. Arsenic removal via micro-electrolysis of Vault 1A leachate by sequential addition of activated carbon and iron (SR4 sample)

To further understand the difference in the contributions of activated carbon and iron in the removal of arsenic from leachate via micro-electrolysis, these reagents were sequentially added to the leachate at a dose of 100 g/L at pH 5 using CO_2 gas with activated carbon added first, followed by ZVI.

It was observed that 80% of arsenic found in SR4 Vault 1A leachate was adsorbed using PAC within the first 5 minutes of treatment time (Figure 42). However, the arsenic concentration in the supernatant was found to increase for contact times exceeding 15 minutes as observed in Section 4.2.2. Arsenic concentrations in the leachate remained unchanged after the addition of LCPF to the leachate. This result indicated that the role of PAC in arsenic removal was higher than that of LCPF. Additionally, the LCPF was not efficient enough to treat the Vault 1A leachate (SR4) alone.

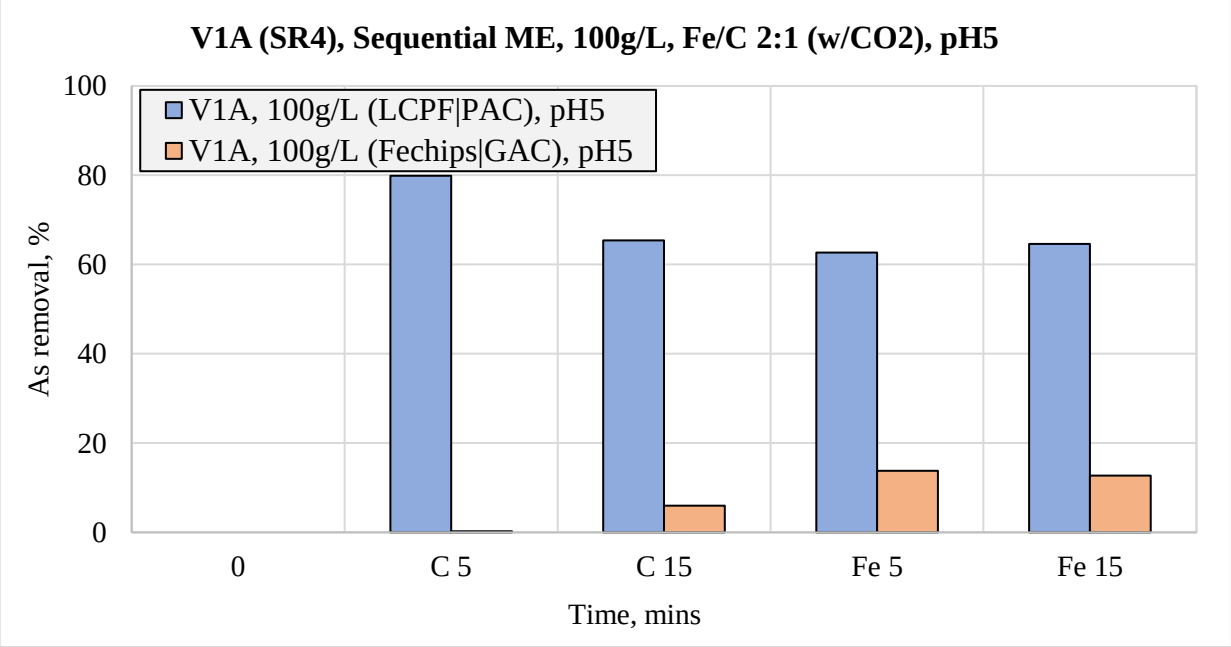


Figure 42. Comparison of sequential addition of carbon followed by iron-based on particle size; Arsenic removal from V1A (SR4) dosed with 100 g/L of (a) LCPF iron and PAC, and (b) Fe chips

and GAC at a ratio of Fe/C - 2:1, and purged with CO_2 gas for 15 minutes each at pH 5. *(Samples were tested on 12/17/2019).*

Only 5% of arsenic was removed using GAC, followed by 15% of arsenic removal using Fe chips. The insufficient removal of arsenic, in this case, confirmed that the use of reagents with higher surface area is needed for the successful removal of arsenic from the landfill leachate.

Figure B-11 (Appendix B) demonstrated that a 100% reduction in EEM peak intensity was observed for leachate treated with the sequential addition of LCPF and PAC regardless of pH. On the other hand, no substantial changes in fluorescence response were noted for leachate treated with Fe chips and GAC. This reinforced the significance of the role of PAC in the removal of DOM from the leachate.

2.3.12. Arsenic removal from BEW process water via micro-electrolysis aided by CO_2 gas (SR6 sample)

The preliminary analysis of the treatability of BEW process water (SR6) included the micro-electrolysis treatment of BPW sampled on 03/26/20. The sample was treated with 20 g/L, 50 g/L, and 100 g/L of LCPF and PAC at a ratio of 2:1 at pH 5. The experiment was aided by CO_2 purging. The data showed a ca. 85% removal of total arsenic from the process water dosed with 50 g/L and 100 g/L of iron and carbon (Figure 43). The majority of arsenic was removed in the first 5 minutes of treatment. The minimal difference between the removal efficiencies of both doses indicated that a lower dose of 50 g/L was sufficient to achieve the required arsenic removal.

Figure B-12 (Appendix B) represents the correlation between total arsenic removed after the ME treatment described in this section and the removal of fluorophores after treatment. As seen in the figure, the decrease in the EEM intensity for each fluorophore was synonymous with the decrease in total arsenic concentration from the BPW. 100% removal of the fluorescing organic matter from the SR6 BPW was achieved regardless of dosage.

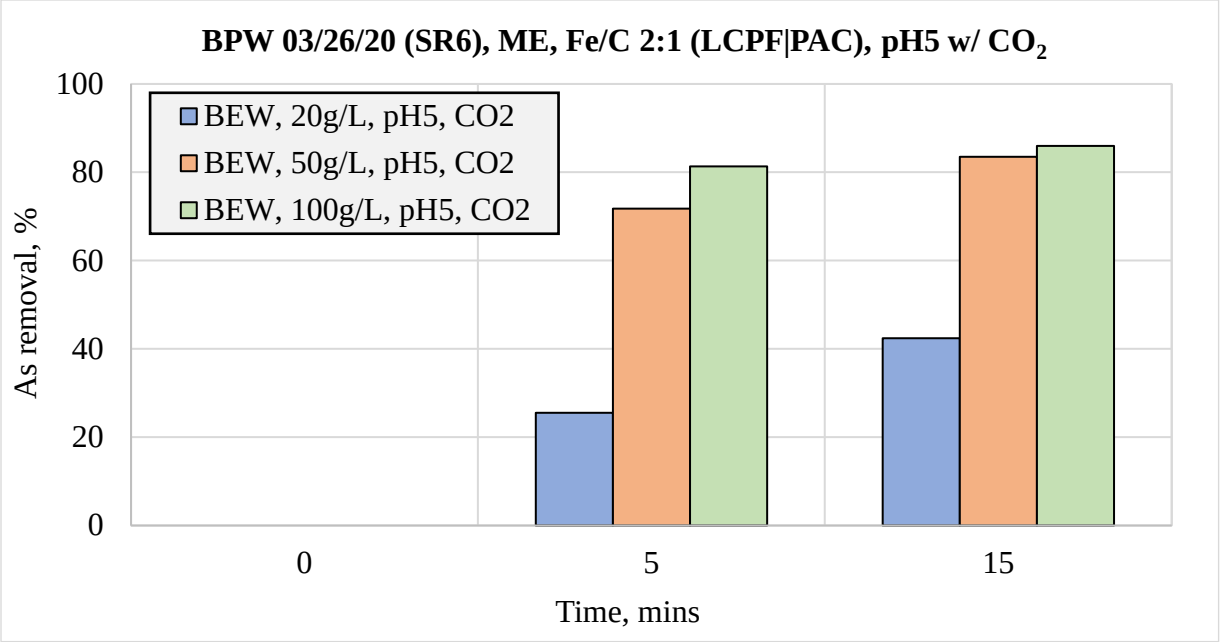


Figure 43. Arsenic removal from SR6 BEW process water (sampled on 03/26/2020) dosed with varying doses of LCPF iron and PAC at a ratio of Fe/C - 2:1 and purged with CO_2 gas for 15 minutes at pH 5. *(Samples were tested on 06/29/2020).*

2.3.13. Evaluation of volatilization and retention of arsenic via micro-electrolysis aided by gas purging

A preliminary analysis was conducted to evaluate the volatilization and retention of arsenic during micro-electrolysis. The first experiment conducted with CO_2 gas noted almost no volatilization of arsenic from the system. 23% of the arsenic was accounted for in the solids generated through adsorption on PAC and co-precipitation with iron. However, this still did not account for the remaining 30% of the arsenic removed from the solution (Figure 44).

At this point in the analysis, the protocol for intercepting volatilized gases and extracting arsenic from retained solids was very preliminary and was not established. Further experimentation is required to refine the procedure and that might bridge the gap in measuring the arsenic removed and arsenic volatilized or retained.

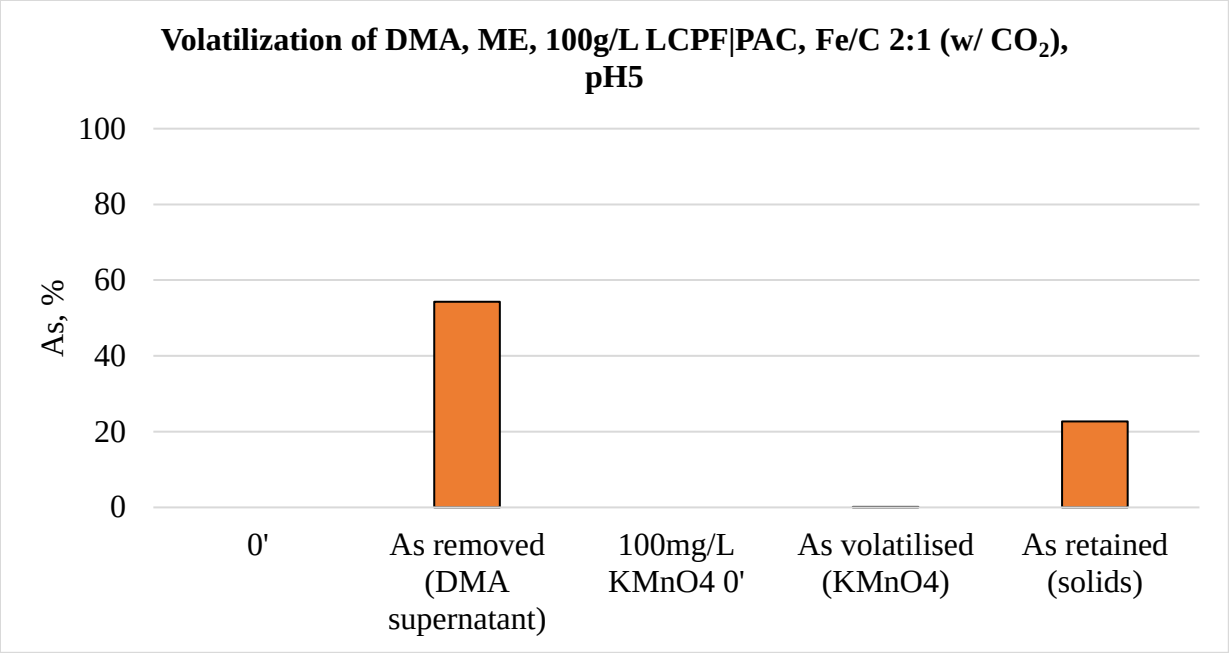


Figure 44. Arsenic removal from DMA model solution (20 ppm DMA as As) dosed with 100 g/L of LCPF iron and PAC at a ratio of Fe/C - 2:1 and purged with CO_2 gas for 15 minutes at pH 5. *(Samples were tested on 12/16/2019).*

3. CONCLUSIONS

This study demonstrates that the removal of arsenic from landfill leachate and LFG condensate is a complex and challenging process. There exists a high variability in the composition and speciation of each landfill stream based on their respective locations and even hydrological conditions. Therefore, location, composition, and season play a contributing factor in removing arsenic from the landfill leachate and condensate.

Drastic changes in arsenic concentrations in the leachate and LFG condensate were noted for different sampling rounds. For example, BEW condensate had an arsenic concentration of 5510 µg/L in SR3 and 49,600 µg/L in SR4, and LEPS leachate had an arsenic concentration of 328 µg/L in SR3 and 35 µg/L in SR5. The LEPS leachate sampled in SR5 was after a period of extreme precipitation in the CHRLF area. However, the cause behind change in arsenic concentration for BEW condensate is still unknown. Overall, it was observed that LFG condensates had a higher arsenic concentration than landfill leachates. This indicates that arsenic volatilization might be taking place in the landfill, with the resultant introduction of the mobilized arsenic into the gas stream.

Conventional oxidative treatments of landfill leachate and LFG condensates resulted in modest, generally insufficient arsenic removal levels. Electrochemical oxidation using PbO_2 electrodes as a pre-treatment showed no improvement in arsenic removal. Permanganate oxidation resulted in approximately 40% and 20% removal of total arsenic for SR2 leachate and SR6 BEW process water, respectively. The efficiency of $KMnO_4$ as an oxidant for landfill leachate and LFG condensate samples was independent of pH. Leachate samples spiked with inorganic arsenic (As(III)) showed considerably higher arsenic removal than those spiked with organic arsenic (DMA) species. This observation reinforced the notion that inorganic arsenic species are more easily oxidized to pentavalent arsenic (As(V)) than the corresponding methylated arsenic species. Coagulation with ferric chloride resulted in inadequate removal of arsenic from leachates, albeit it exhibited a marginally better removal from BEW process water. This might be due to the presence of a high concentration of organic matter in landfill leachate. The organic matter would compete with the arsenic present in the solution to co-precipitate with iron-based coagulants.

Oxygen as a carrier gas did not support arsenic removal with or without the addition of a coagulant. Ozonation as a pre-treatment method resulted in only <10% improvement in arsenic removal from LFG condensate. The inefficiency of a strong oxidant like ozone highlighted the strong resistance of landfill condensates to oxidative treatment. Overall total arsenic removal was lower from high arsenic, low organic matter containing condensates compared to low arsenic, high organic matter containing leachate. These results indicated the presence of complex, methylated arsenic species that are resilient against oxidative treatments.

Adsorption treatment using manganese dioxide barely removed any arsenic from the LFG condensate. Activated carbon as an adsorbent showed high removal of arsenic for some landfill solutions within 5 minutes of treatment. This method's performance was difficult to optimize because arsenic concentrations in the liquid phase decreased initially and then increased with an increase in contact time. This indicated that arsenic was being released back from the adsorbent into the solution. This nonmonotonic trend of arsenic removal was assumed to occur due the competitive adsorption of organic matter present in the leachate against arsenic. It was suspected that relatively small molecules of arsenic solutes are adsorbed initially and then replaced by macromolecules of leachate dissolved organic matter. Further research is required to determine the exact nature of the reaction taking place within the matrix during the adsorption process using activated carbon.

Additionally, leachates sampled from different locations in the same sampling round showed different responses to PAC adsorption. Area – 5, 6, 7 leachate (higher arsenic concentration) was resistant to adsorption compared to LEPS leachate (10-fold lower arsenic concentration) that demonstrated significant arsenic removal levels. These results reinforced the observation that landfill leachates can vary considerably in terms of arsenic species and composition, and thus, response to treatment. A drawback of PAC as a treatment option was is its lack of regenerative potential. Our attempt to regenerate PAC using sodium hydroxide resulted in a only limited return of its efficiency, which decreased with every regeneration cycle.

The reductive treatment of CHRLF leachates and condensates was carried out using either ZVI or a combination of ZVI and activated carbon. The overall removal rate of arsenic via reductive treatment was higher than that of oxidative treatment. The application of granular ZVI at a high dose achieved 80% removal of DMA, confirming the view that methylated and organic arsenic

species can be eliminated using reductive methods. However, >70% removal of arsenic was only achievable for a more extended contact period. Large particle size ZVI materials like iron accelerator chips demonstrated a weaker ability to remove arsenic than more dispersed materials exemplified by LCPF. This was likely due to the greater availability of surface area available for a reaction for a small-sized particle. The same was observed in the case of GAC and PAC.

Micro-electrolysis conducted with the application of CO_2 and N_2 as carrier gases showed similar rates of removal. For certain leachate samples, N_2 purging resulted in foaming, which was considered a drawback for this process's large-scale application. CO_2 gas suppressed the foaming and decreased the pH, which favored the slightly acidic conditions required for higher treatment efficiency. This was an advantage since CO_2 gas can be generated on-site and can also be easily replaced by landfill gas for the same application. Besides, the initial decrease in pH of the solution also negates the requirement of acid to reduce the pH for the required treatment conditions. It was recorded that the removal rate of arsenic decreased considerably for $pH \geq 7$. When compared to ZVI as a treatment option, ME achieved higher arsenic removal at shorter reaction times. In some instances, 100% removal was achieved within 15 minutes of treatment for doses higher than 50 g/L. Moreover, the pH of the solution was observed to increase with treatment time. This, too, refuted the need for base addition at the end of treatment to neutralize the leachate's and condensate's pH.

The contribution of PAC to the process of ME seemed to be larger than that of LCPF iron. This was noticed when PAC combined with iron accelerator chips, demonstrated a far better removal efficiency than LCPF and GAC combined. However, it was also noted that LCPF and PAC's removal rate was improved than that of PAC alone. So, the redox reaction's impact occurring between the carbon and iron particles was deemed essential to the treatment efficiency.

The variability in the treatment response was also noted for reductive processes. Arsenic removal via ME from LEPS leachate sampled in SR3 and SR4 was considerably higher (>85%) than recorded in the case of SR5 LEPS leachate. Also, the treatment of LFG condensates resulted in somewhat higher arsenic removal than that observed for the leachates, possibly due to the strong presence of organic matter in leachates. A significant drawback for ME treatment is the high demand for treatment media. This is highly relevant to process's applicability at a larger scale and the disposal of the solids. Regeneration of the iron and carbon media is also a concerning aspect

of this process. As mentioned earlier, the regenerative capacity of PAC is limited and LCPF iron is still under review. This attribute of the media will be essential in determining the economic impact of the treatment.

Measurements of fluorescence excitation-emission matrices (EEM) can be used to determine the effects of DOM in the removal of arsenic from landfill leachates and LFG condensates. However, the analysis of EEM fluorescence data in this thesis is preliminary. The entire scope and significance of the correlations between changes of the characteristic EEM features and arsenic removal are yet to be explored in more detail. Further examination of these trends, especially in conjunction with DOC measurements and more detailed interpretation of the nature of DOM in landfill leachates and LFG condensates, can be beneficial for a deeper understanding of processes controlling arsenic removal in adsorptive/reductive processes. These aspects of the exploration of intrinsic mechanisms of arsenic reactivity and removal must be considered as a part of future experiments.

The variability in the landfill composition reflects the presence of several difficulties. For instance, the unpredictability in the properties and concentration of leachate dissolved organic matter and differences in the speciation of arsenic in these streams. These will, in turn, affect the treatment response of the leachate or condensate. As outlined above, these variations appear to occur both seasonally and at different locations within the landfill itself, possibly during the leachate's transit through the collection system. It is essential to be aware of the aspects and patterns of these changes in designing the appropriate treatment for arsenic removal.

Micro-electrolysis stands out between the numerous treatment methods researched in this thesis. Future investigations must include –

(i) Determination of arsenic speciation in the original leachate and condensate for targeted treatment;

(ii) Development of disposal methods of solids generated and evaluation of the composition of those solids;

(iii) Arsenic source identification at the landfill;

Dose optimization via evaluation of different methods to regenerate reagents, or application of catalysts to improve reaction rate, or assessing low-impact and low-cost alternatives that may economically benefit large-scale applicability.

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APPENDIX – A

Table A - 1. pK_a values for commonly occurring arsenic species

As species	pK_{a1}	pK_{a2}	pK_{a3}
Arsenous acid (H_3AsO_3)	9.22	12.13	13.4
Arsenic acid (H_3AsO_4)	2.2	6.97	11.53
MMA(V) ($H_2AsO(CH_3)$)	4.19	8.77	-
DMA(V) ($HAsO_2(CH_3)_2$)	6.14	-	-

Table A - 2. Summary of analytical data for arsenic at various locations at the CHLRF facility for February to June 2018 and July 2016 and June 2018 (King County - Solid Waste Division 2019)

Parameter	Units	Permit Limit	July 2016 to July 2018		February to June 2018					
			LEPS	API	LEPS	API	PS1	PS4	CSW	MH5
		Total Arsenic concentration								
Average	mg/L	1.0	0.147	0.197	0	0	0	0	0	0
99th percentile	mg/L	4.0	0.335	2.030	0.282	0.358	0.170	0.135	0.093	0.351
% dissolved	%	NA	NA	NA	90	96	98	94	68	94
		Total Arsenic Loading								
Average	lb/day	NA	0.526	0.769	0.516	0.813	0.043	0.093	0.029	0.67
Average % of API	%	NA	NA	NA	NA	NA	5	11	4	82
99th percentile	lb/day	0.270	2.509	2.425	2.237	2.191	0.107	0.390	0.079	2.423

Abbreviation(s):

API = aeration pond influent

LEPS = leachate effluent pump station

CSW = contamined stormwater

MH5 = manhole 5 (receiving water from Area 5, 6, 7)

PS1 = pump station 1

PS4 = pump station 4

Table A - 3. Flow Summary for July 2016 to July 2018 (Adapted (King County - Solid Waste Division 2019))

Parameter	Units	LEPS	API	PS1	PS4	CSW	MH5
Annual Flow							
Average	MGD	0.641	0.659	0.110	0.165	0.148	0.289
Average % Flow at API	%	NA	NA	17	25	23	44
99th percentile	MGD	2.403	2.030	0.350	0.516	0.457	0.974
Summer Months (June to Sept)							
Average	MGD	0.225	0.239	0.020	0.051	0	0.171
Average % Flow at API	%	NA	NA	8	21	0	72
Winter Months (Oct to May)							
Average	MGD	0.831	0.867	0.153	0.224	0.148	0.346
Average % Flow at API	%	NA	NA	18	26	17	40

Abbreviation(s):

API = aeration pond influent

LEPS = leachate effluent pump station

CSW = contamined stormwater

MH5 = manhole 5 (receiving water from Area 5, 6, 7)

PS1 = pump station 1

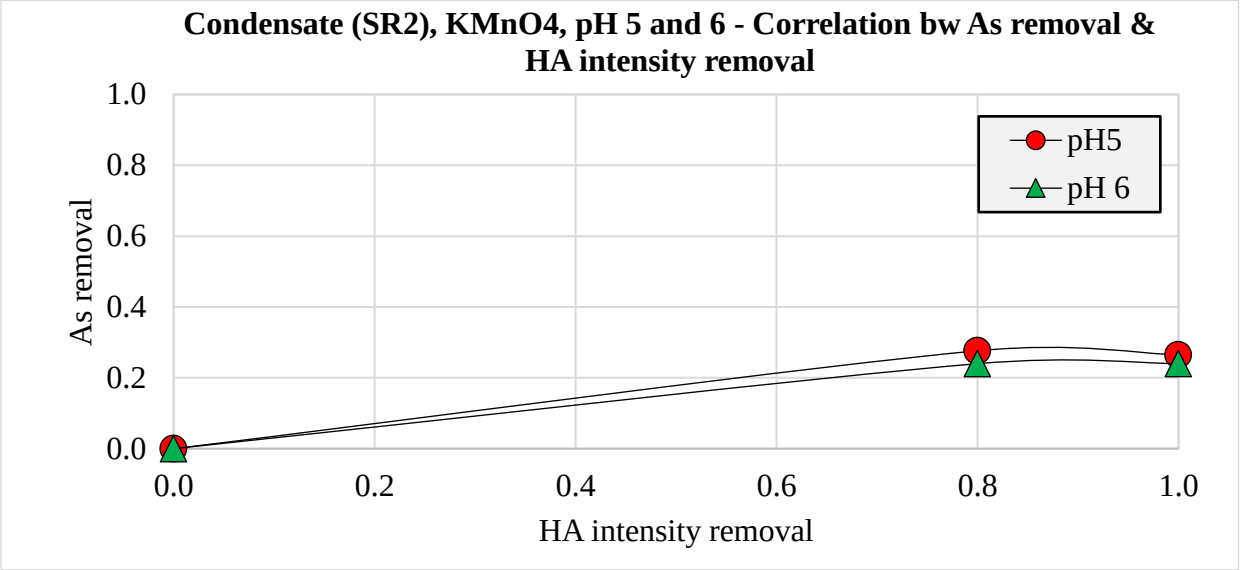
PS4 = pump station 4

Table A - 4. Properties of Hoganas iron-based material

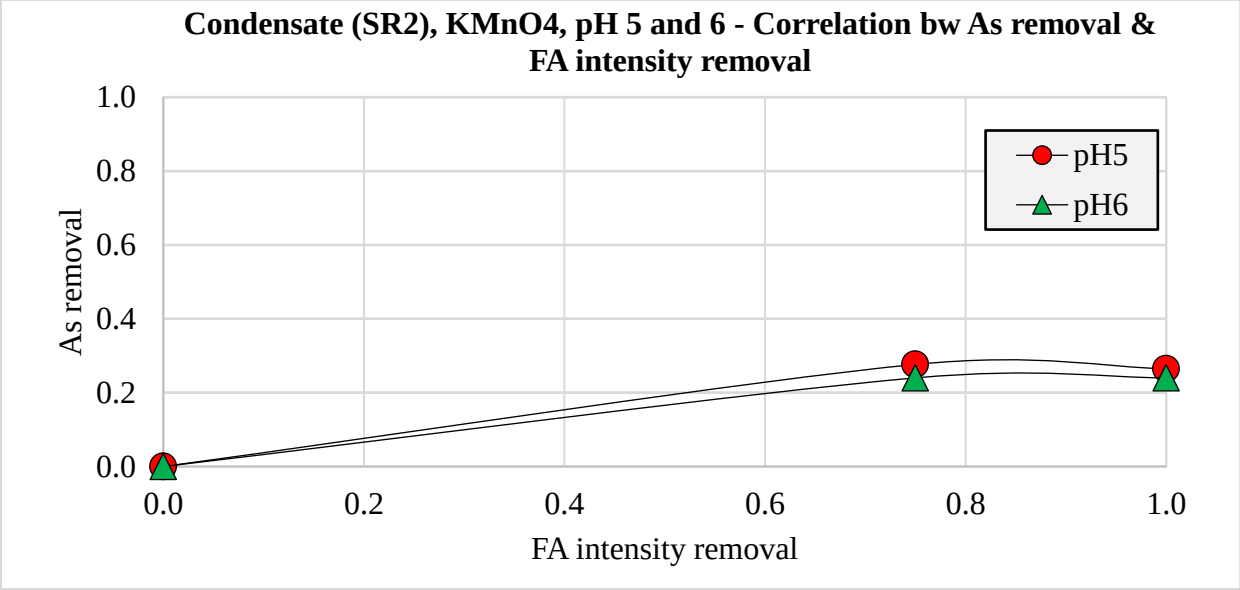
Hoganas Iron-based reagent	Chemical Properties (%)		Apparent Density (g/cc)
Cleanit® SI.10	Fe	93%	1.3
Cleanit® LC Plus Fine	Fe	97%	1.25 - 3.0
SNC100.24	Fe	99.08 - 98.83%	2.55 - 2.70
	C	0.02%	
	S	0.90 - 1.15%	
Cleanit® LC Plus	Fe	97.84%	1.42
	O	2.02%	
	Mn	0.14%	

APPENDIX – B

Correlations of arsenic removal with change in EEM spectra upon treatment

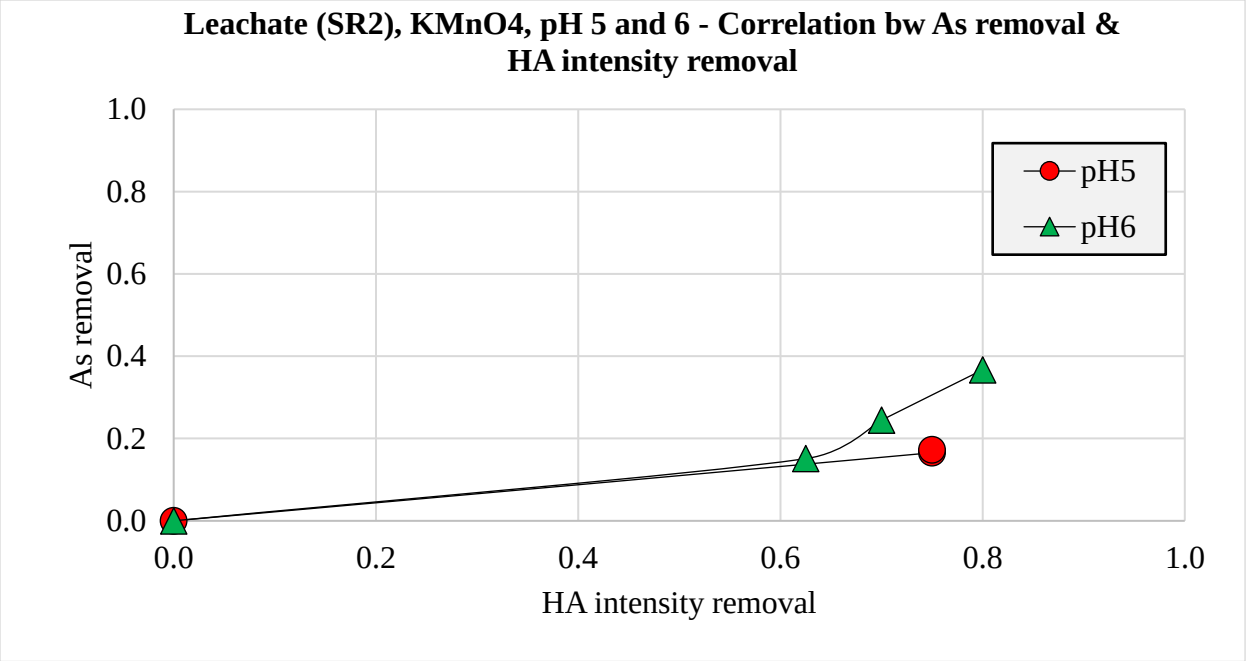


(a)

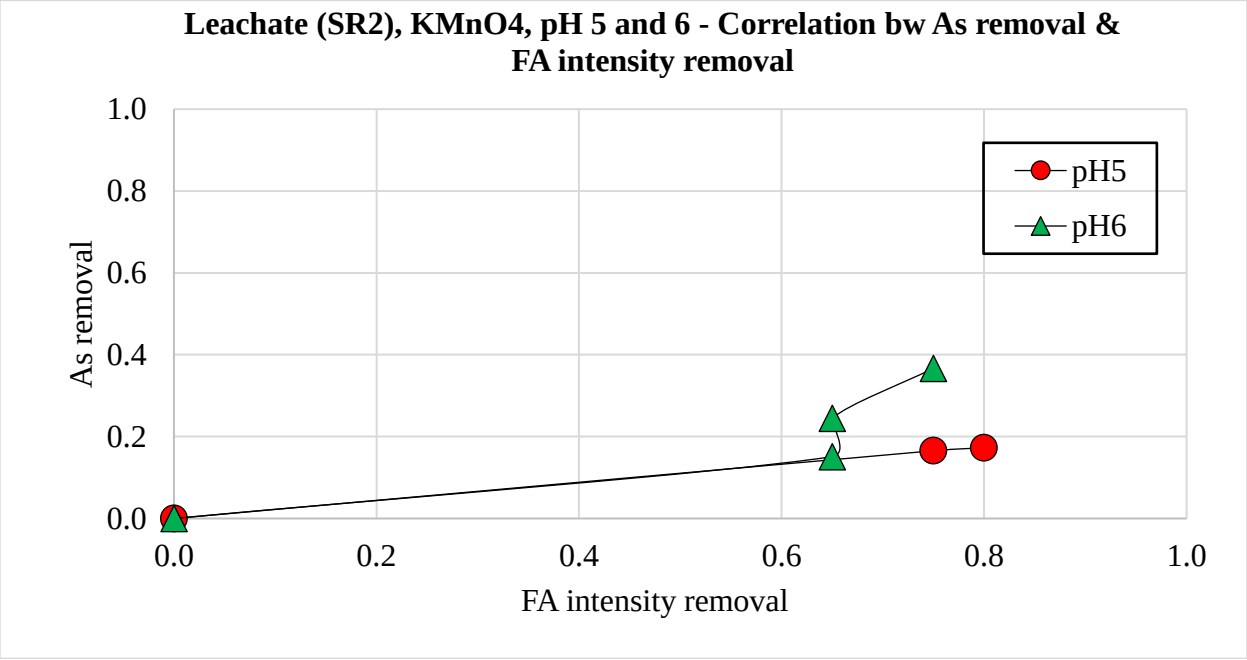


(b)

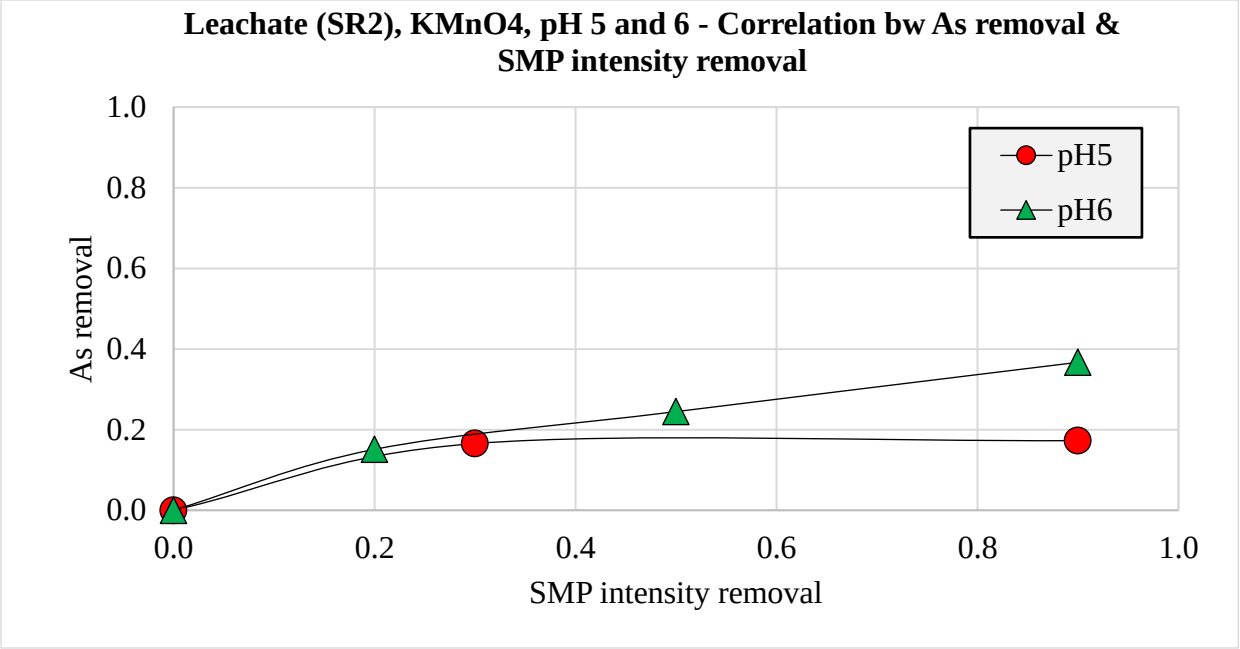
Figure B - 1. Correlation between arsenic removal from LFG condensate (SR2 sample) changes in the EEM spectra: (a) HA intensity removal, and (b) FA intensity removal. SR2 condensate was treated with a varying dose of $KMnO_4$ at pH 5 and 6 for 24 hours.


Leachate (SR2), KMnO4, pH 5 and 6 - Correlation bw As removal & HA intensity removal
As removal
HA intensity removal
pH5
pH6
0.0
0.2
0.4
0.6
0.8
1.0

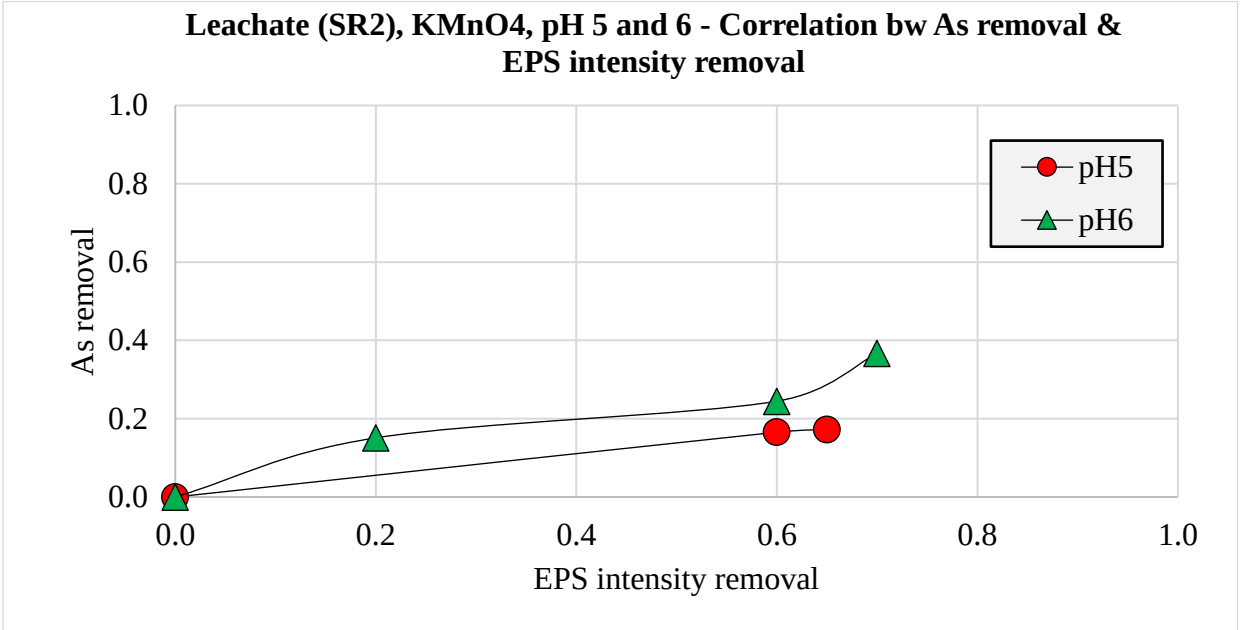
(a)


Leachate (SR2), KMnO4, pH 5 and 6 - Correlation bw As removal & FA intensity removal
As removal
FA intensity removal
pH5
pH6
0.0
0.2
0.4
0.6
0.8
1.0

(b)

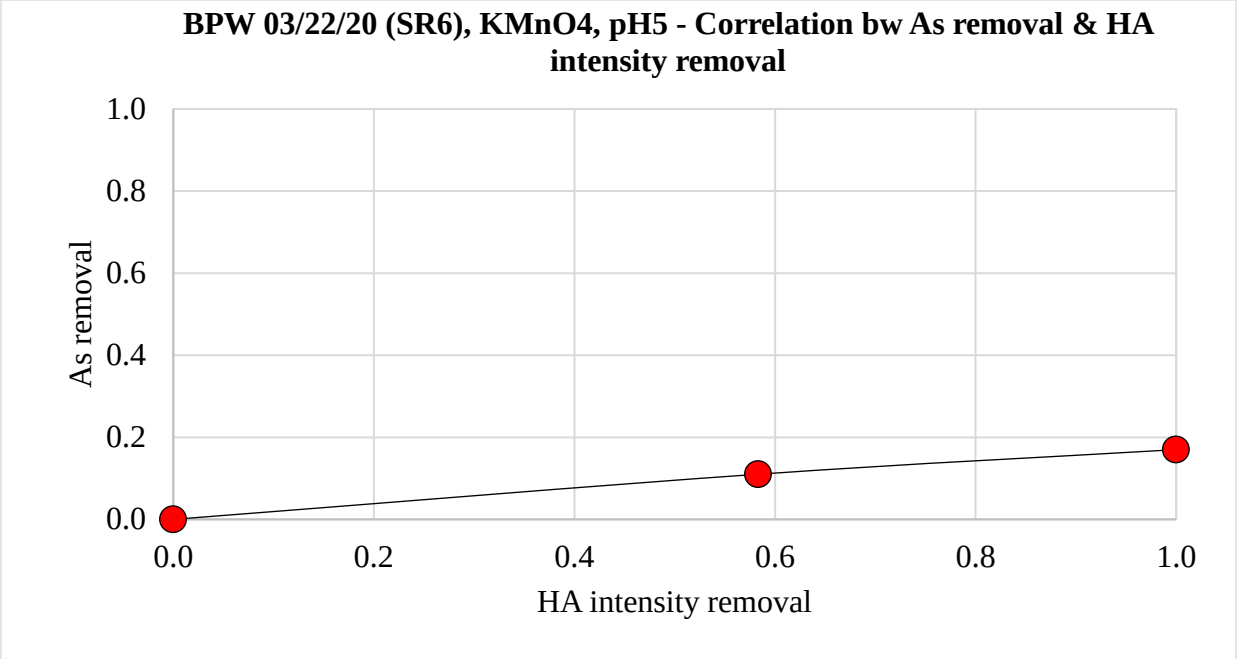


(c)

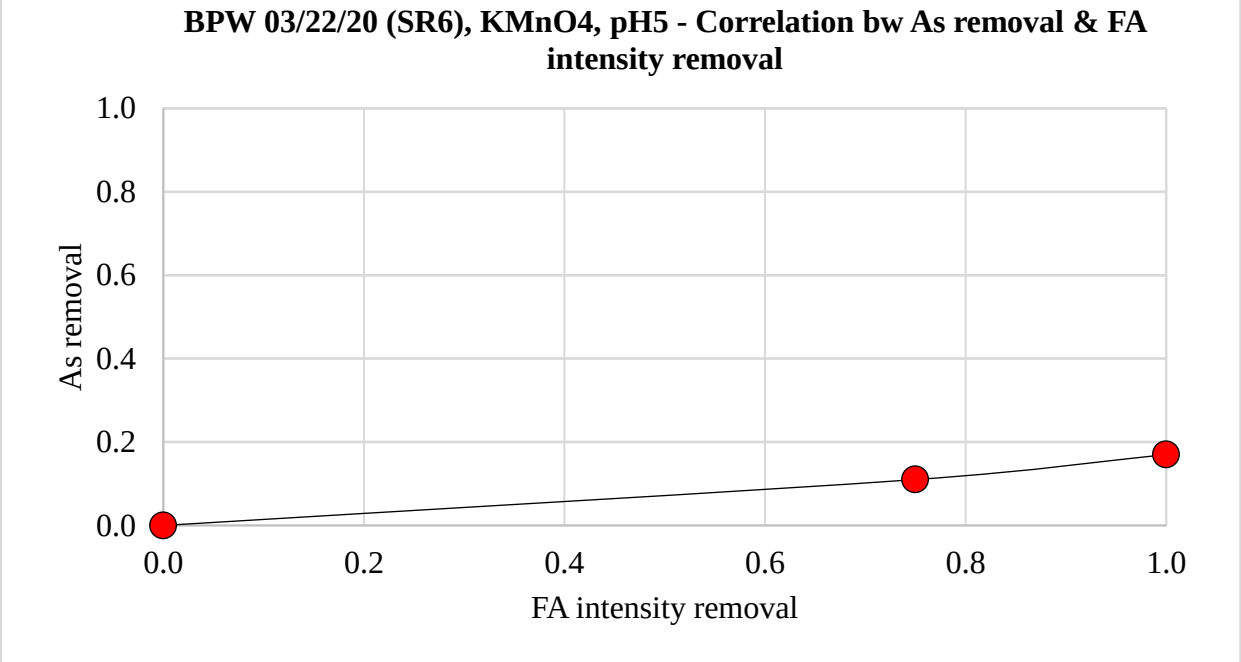


(d)

Figure B - 2. Correlations between arsenic removal from leachate (SR2 sample) and changes in the EEM spectra: (a) HA intensity removal, (b) FA intensity removal, (c) SMP intensity removal, and (d) EPS intensity removal. Leachate was treated with a varying dose of $KMnO_4$ at pH 5 and 6 for 24 hours.

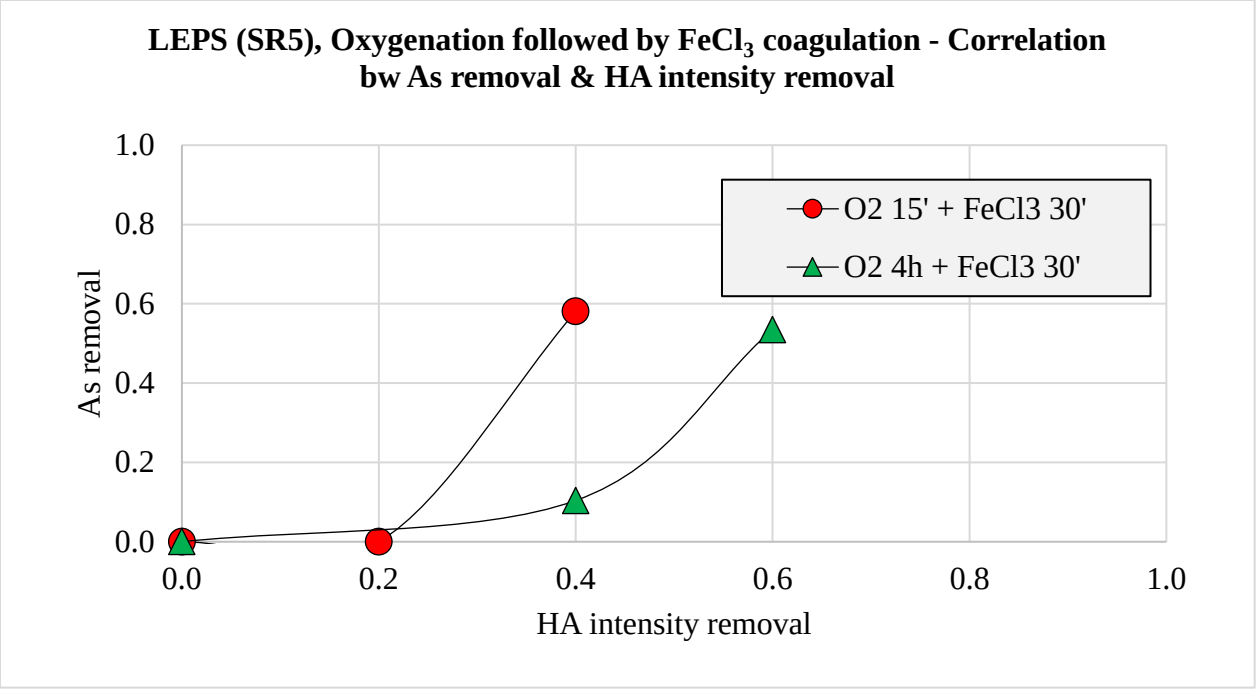


(a)

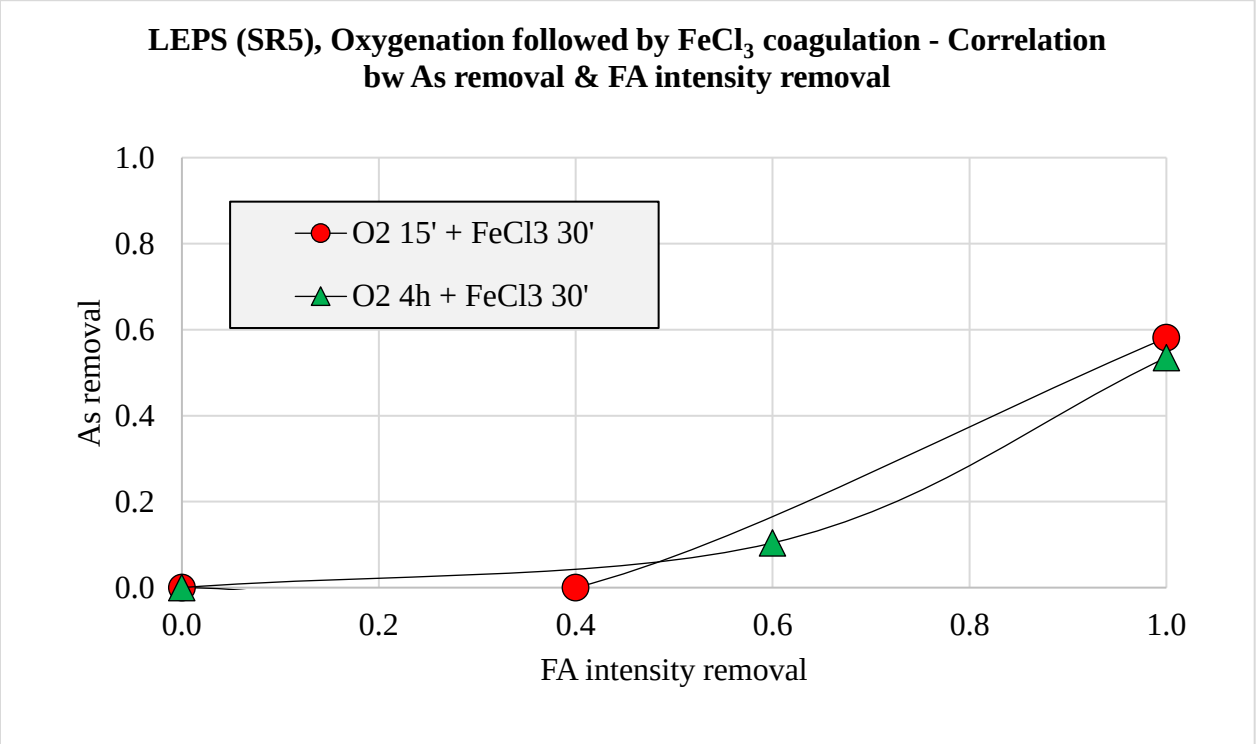


(b)

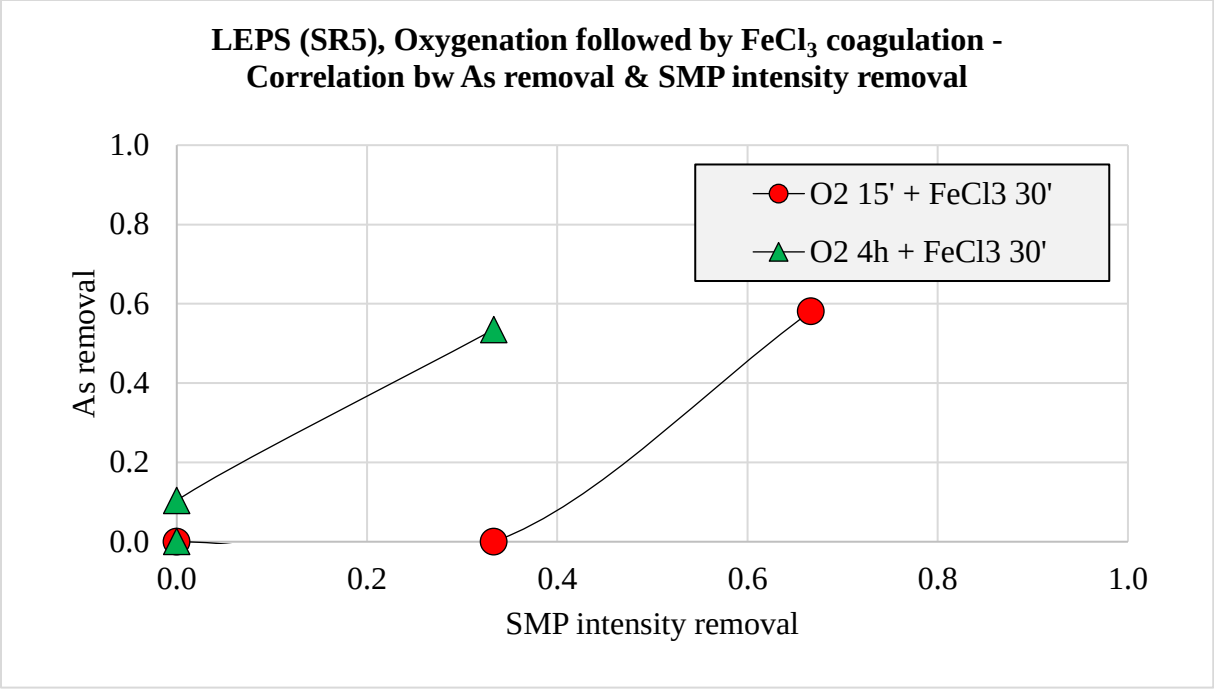
Figure B - 3. Correlation between arsenic removal from BEW process water (SR6 sample collected on 03/22/20) and changes in the EEM spectra: (a) HA intensity removal and (b) FA intensity removal. BPW was treated with a varying dose of $KMnO_4$ at pH 5 for 24 hours.


LEPS (SR5), Oxygenation followed by FeCl3 coagulation - Correlation bw As removal & HA intensity removal
As removal
HA intensity removal
O2 15' + FeCl3 30'
O2 4h + FeCl3 30'
0.0
0.2
0.4
0.6
0.8
1.0

(a)


LEPS (SR5), Oxygenation followed by FeCl3 coagulation - Correlation bw As removal & FA intensity removal
As removal
FA intensity removal
O2 15' + FeCl3 30'
O2 4h + FeCl3 30'
0.0
0.2
0.4
0.6
0.8
1.0

(b)



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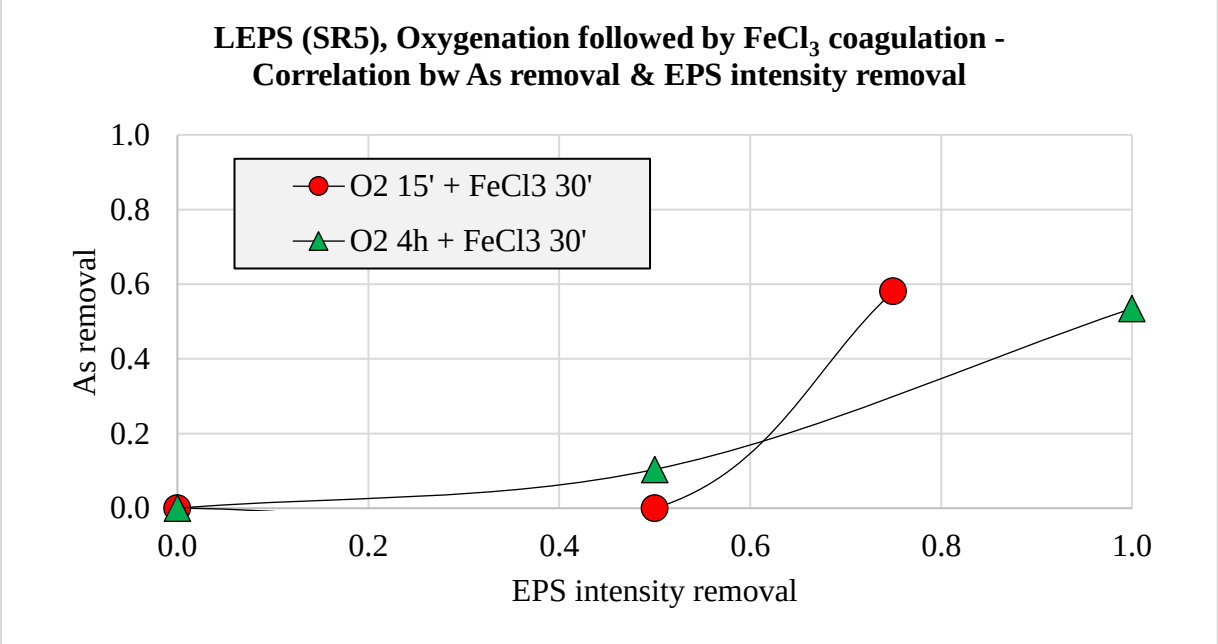
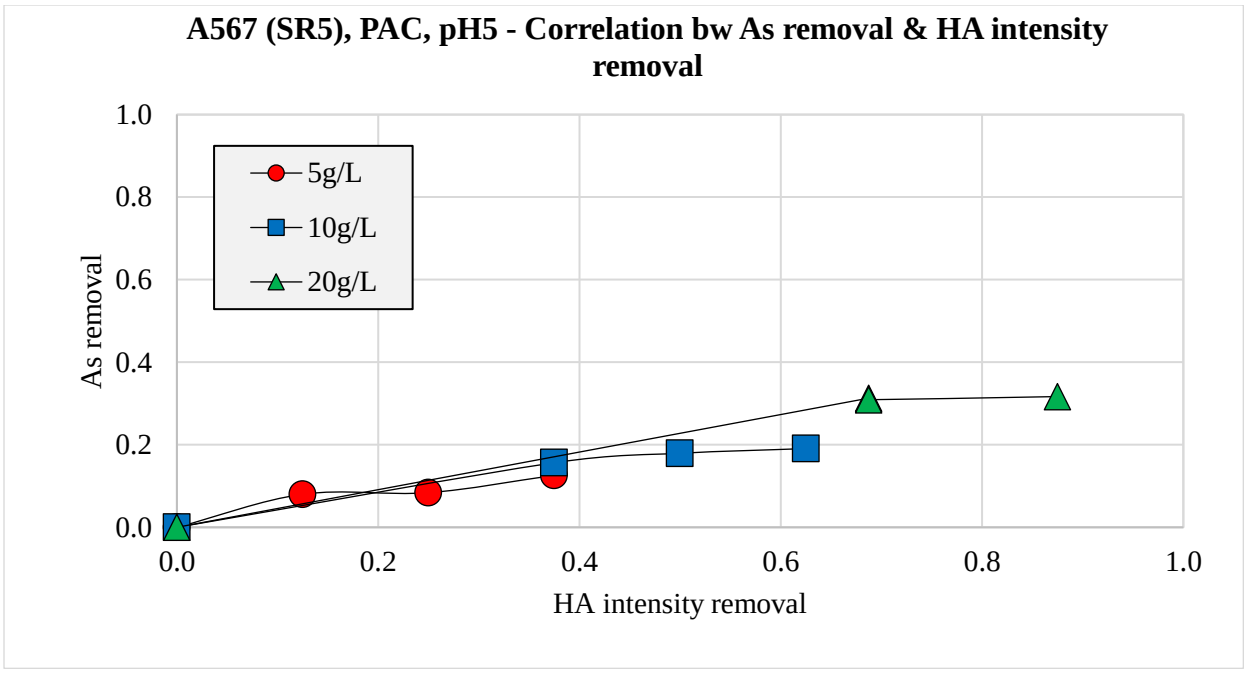
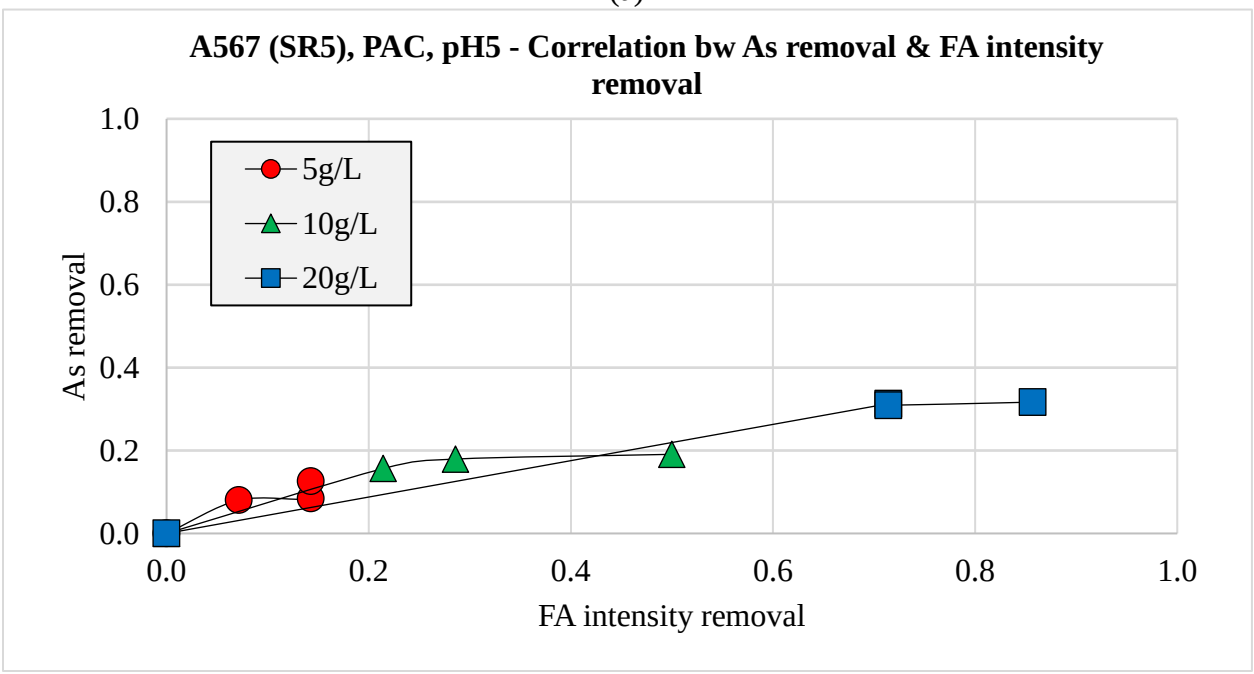


(d)

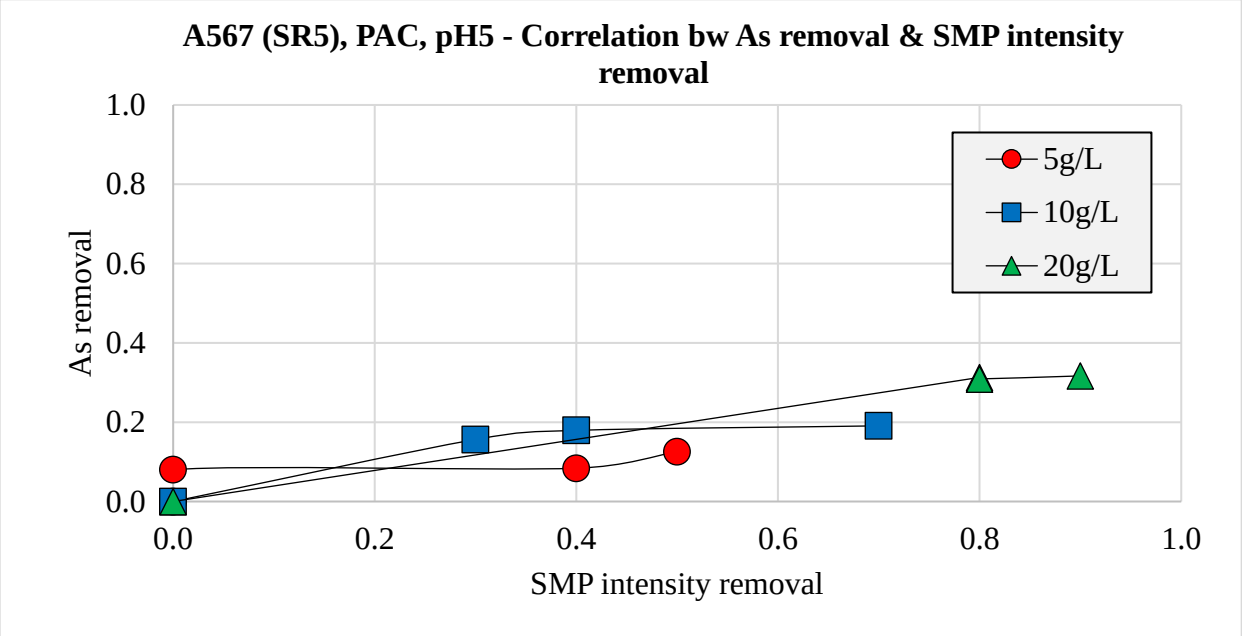
Figure B - 4. Correlations between arsenic removal from LEPS leachate (SR5 sample) and changes in the EEM spectra: (a) HA intensity removal, (b) FA intensity removal, (c) SMP intensity removal, and (d) EPS intensity removal. Leachate was treated with sequential oxygenation followed by 6 g/L $FeCl_3$ coagulation at pH 6 for 30 minutes.


A567 (SR5), PAC, pH5 - Correlation bw As removal & HA intensity removal
1.0
0.8
0.6
0.4
0.2
0.0
As removal
5g/L
10g/L
20g/L
0.0
0.2
0.4
0.6
0.8
1.0
HA intensity removal

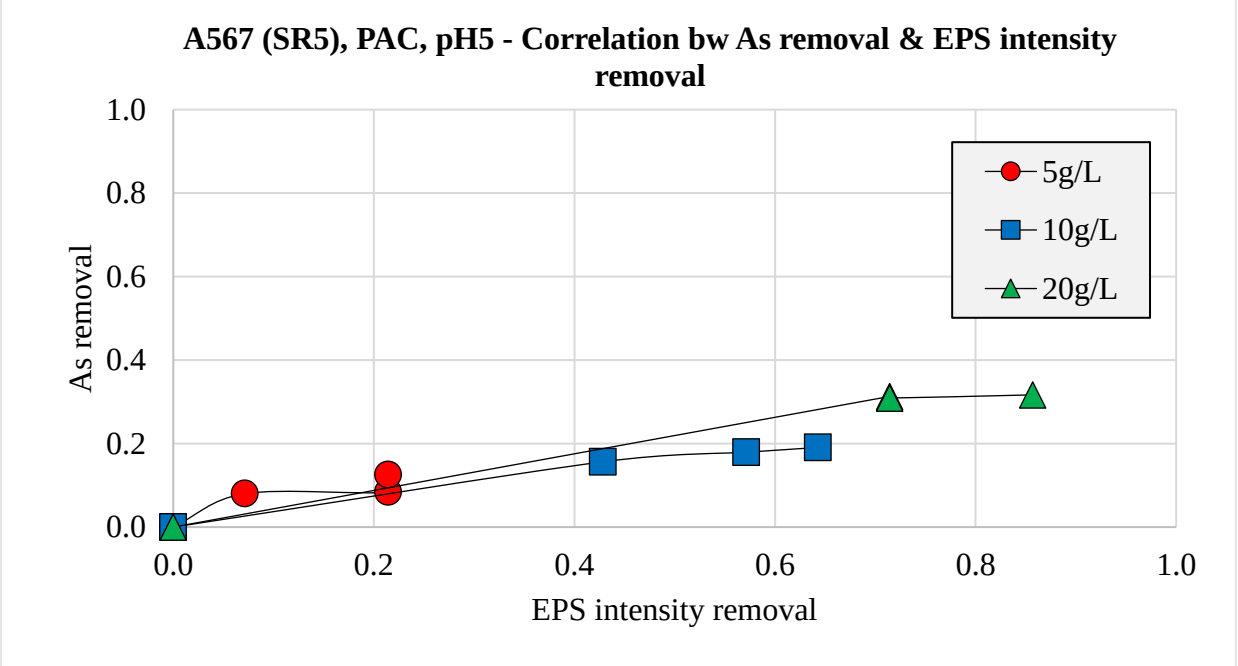
(a)


A567 (SR5), PAC, pH5 - Correlation bw As removal & FA intensity removal
1.0
0.8
0.6
0.4
0.2
0.0
As removal
5g/L
10g/L
20g/L
0.0
0.2
0.4
0.6
0.8
1.0
FA intensity removal

(b)

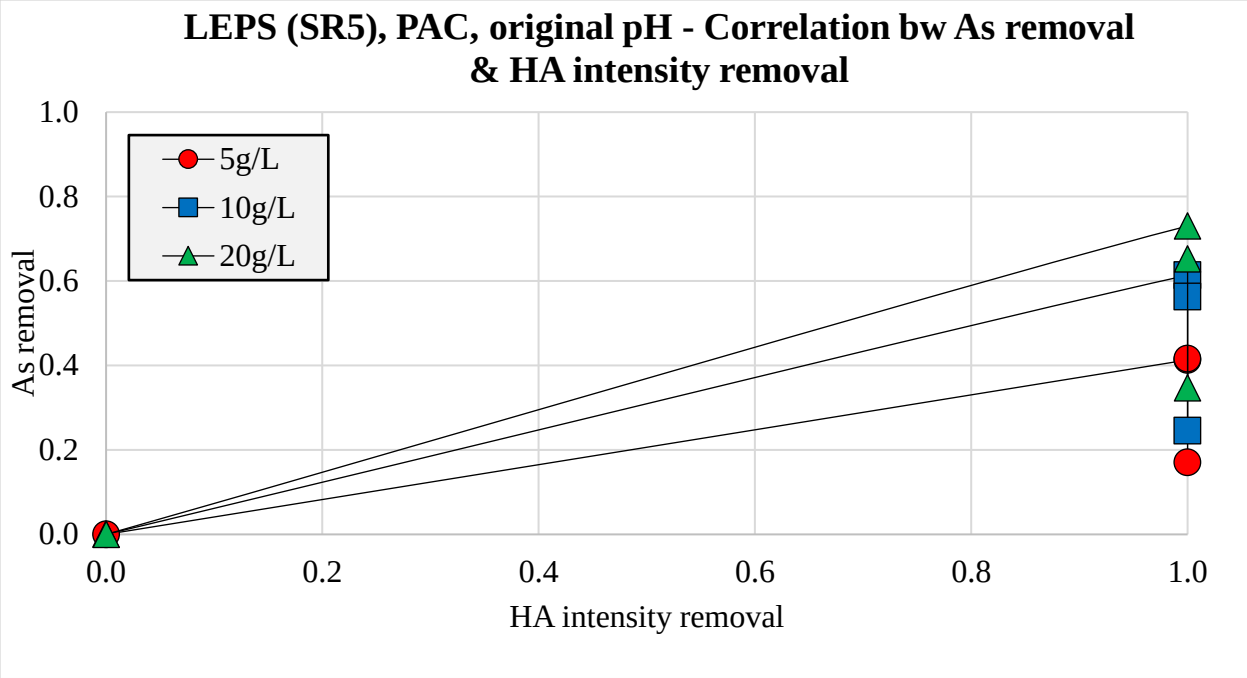


(c)

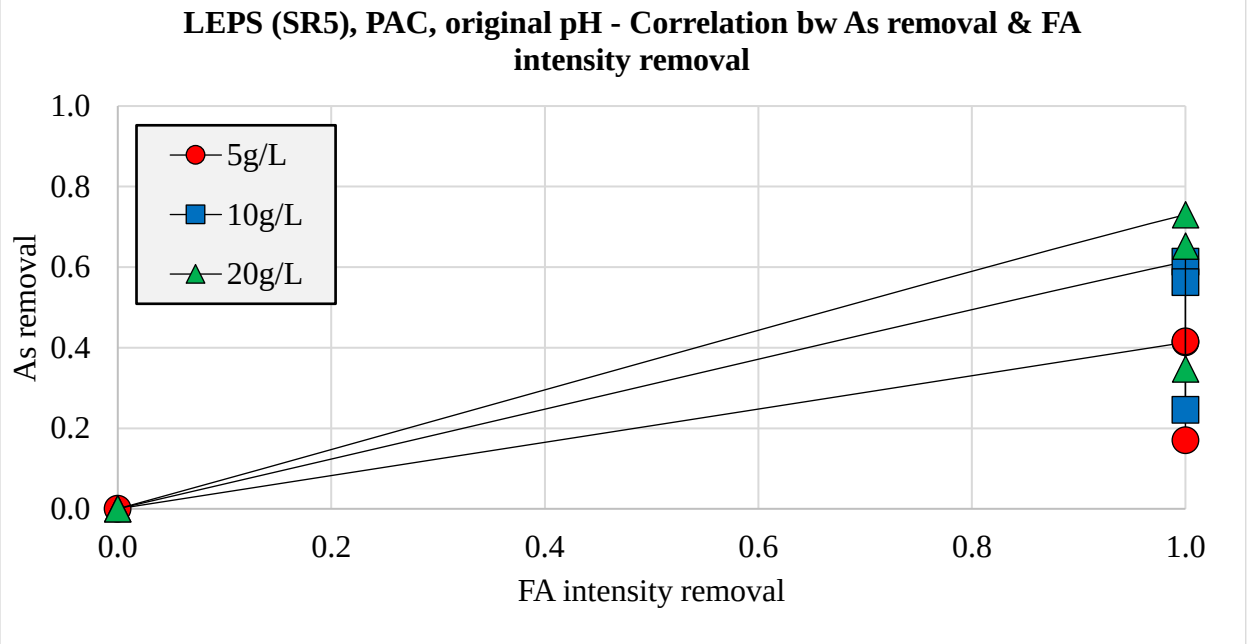


(d)

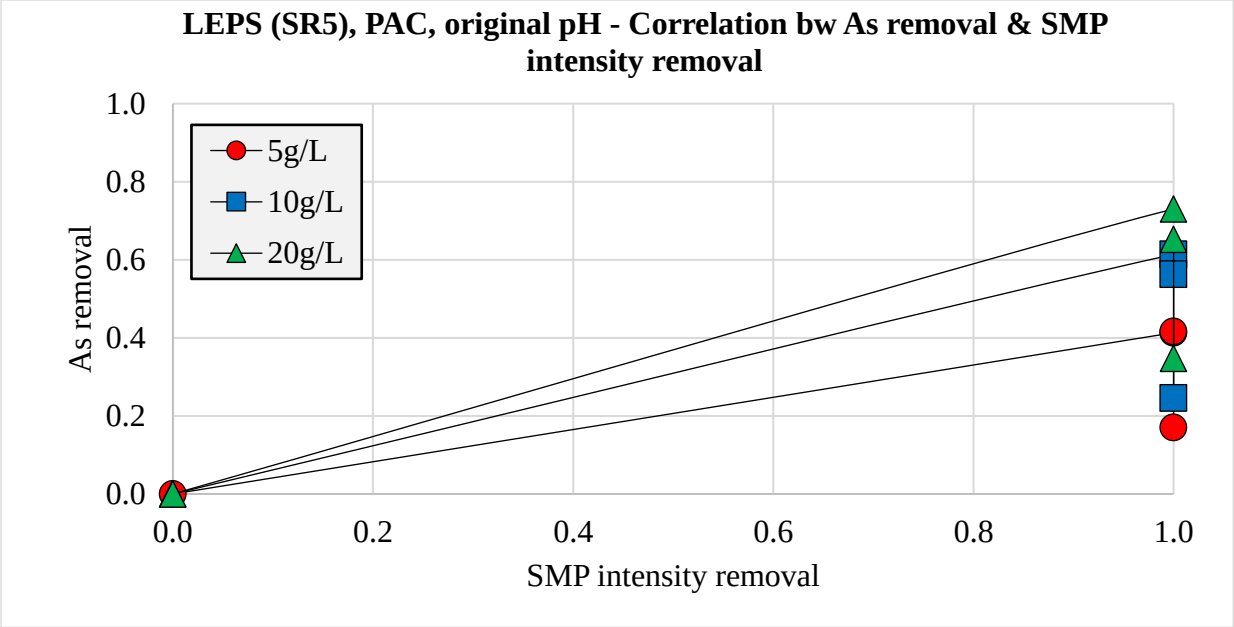
Figure B - 5. Correlations between arsenic removal from A567 leachate (SR5 sample) and changes in the EEK spectra: (a) HA intensity removal, (c) FA intensity removal, (c) SMP intensity removal, and (d) EPS intensity removal. Leachate was treated with varying dose of PAC at pH 5 for 15 minutes.


LEPS (SR5), PAC, original pH - Correlation bw As removal & HA intensity removal
1.0
0.8
0.6
0.4
0.2
0.0
As removal
5g/L
10g/L
20g/L
0.0
0.2
0.4
0.6
0.8
1.0
HA intensity removal

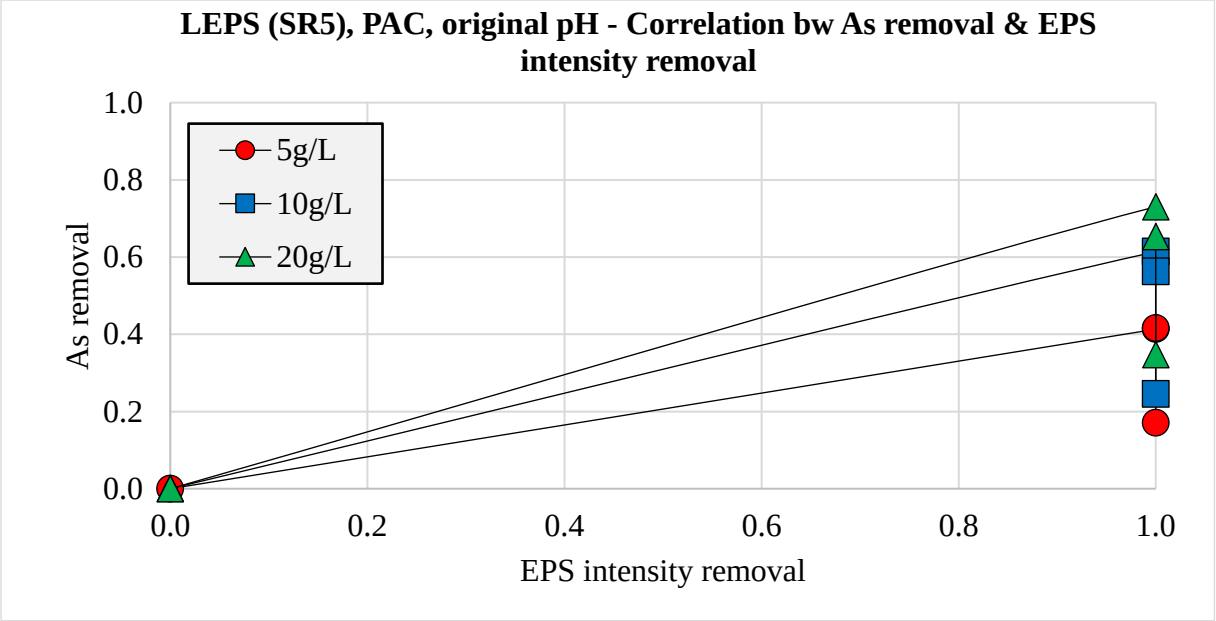
(a)


LEPS (SR5), PAC, original pH - Correlation bw As removal & FA intensity removal
1.0
0.8
0.6
0.4
0.2
0.0
As removal
5g/L
10g/L
20g/L
0.0
0.2
0.4
0.6
0.8
1.0
FA intensity removal

(b)

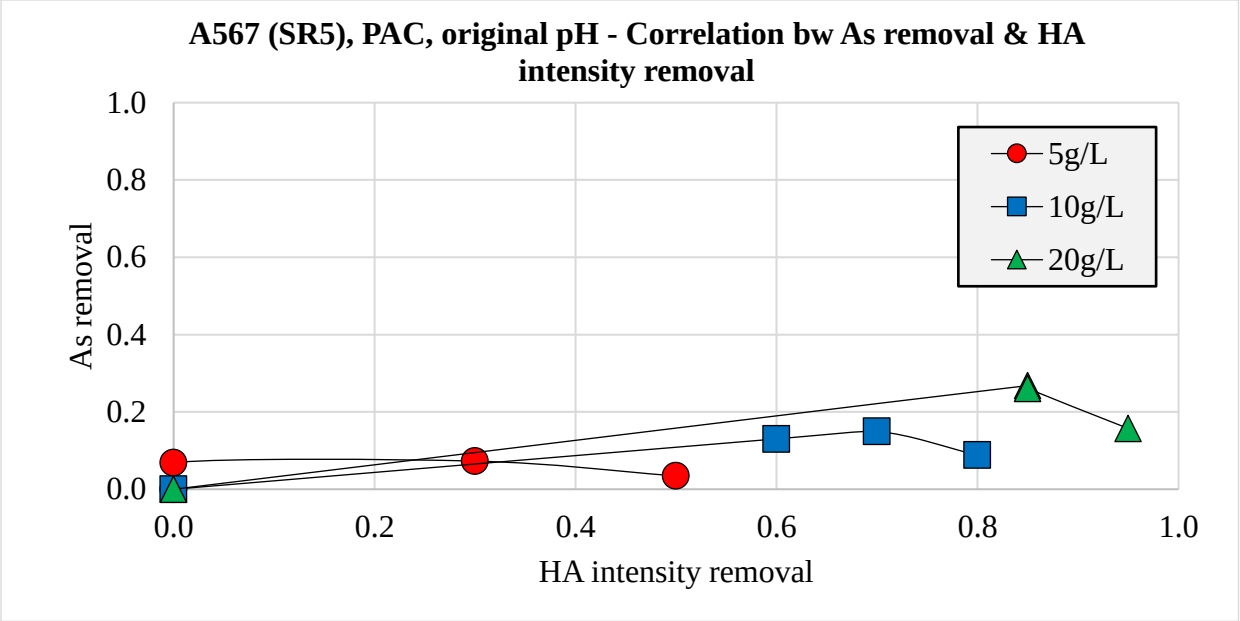


(c)

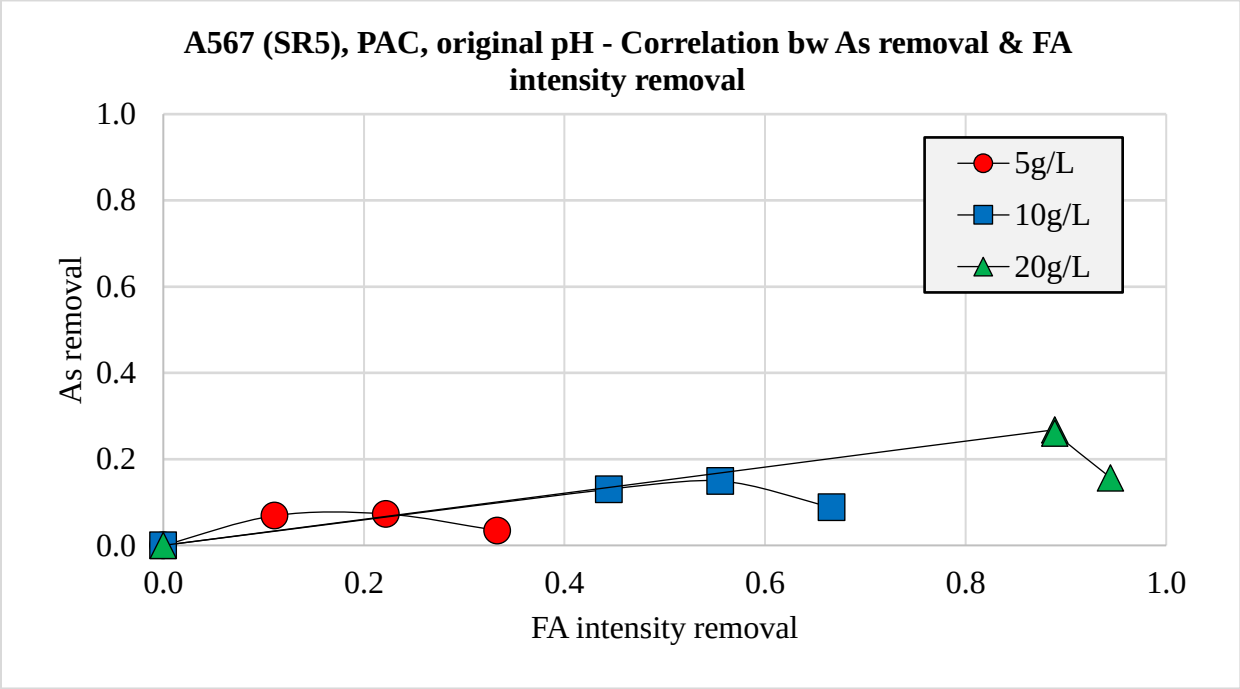


(d)

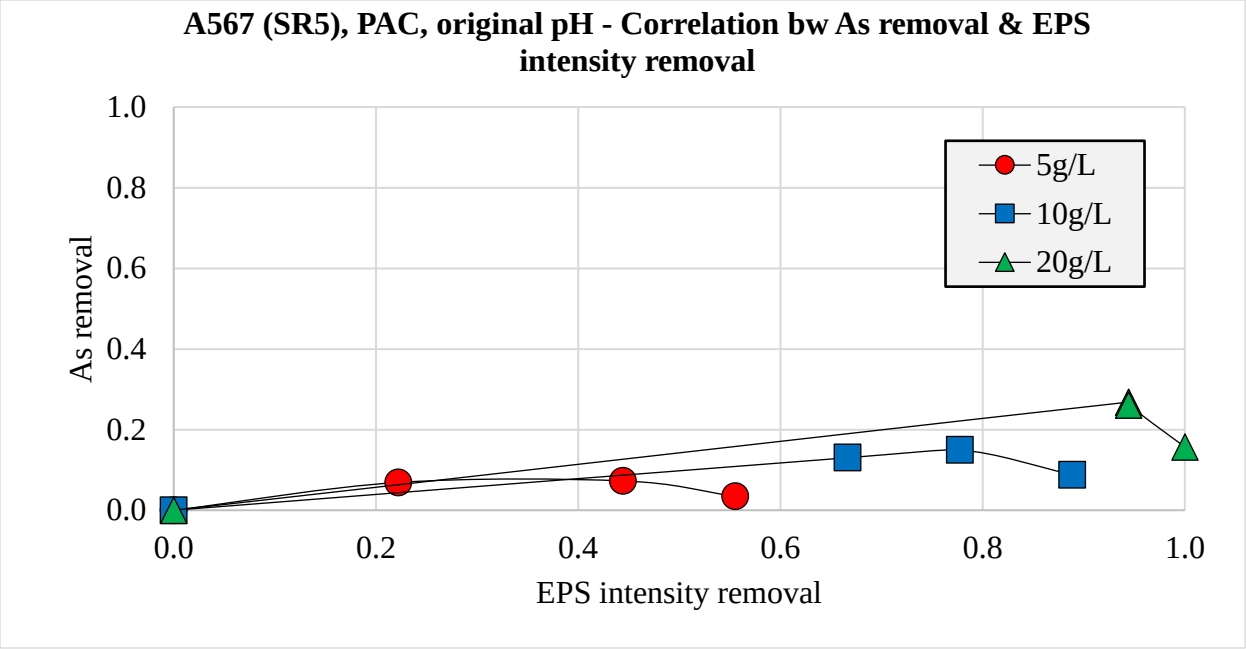
Figure B - 6. Correlations between arsenic removal from LEPS leachate (SR5 sample) and changes in the EEK spectra: (a) HA intensity removal, (b) FA intensity removal, and (c) EPS intensity removal. Leachate was treated with varying dose of PAC at the original pH for 15 minutes.


A567 (SR5), PAC, original pH - Correlation bw As removal & HA intensity removal
As removal
HA intensity removal
5g/L
10g/L
20g/L
0.0
0.2
0.4
0.6
0.8
1.0

(a)

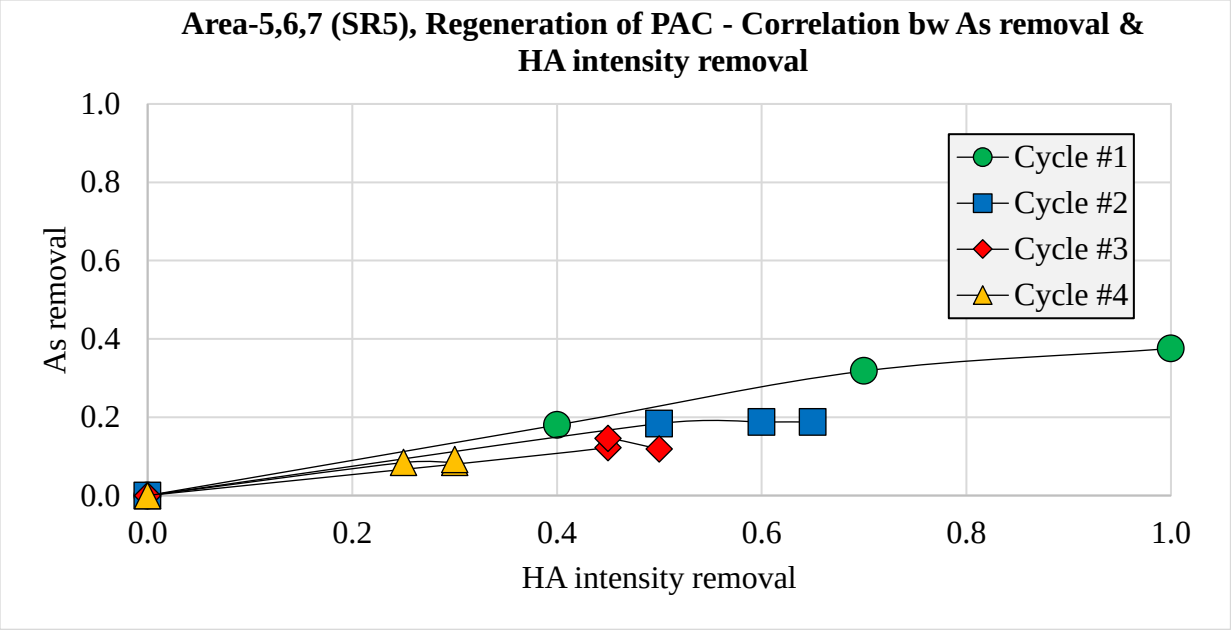

A567 (SR5), PAC, original pH - Correlation bw As removal & FA intensity removal
As removal
FA intensity removal
5g/L
10g/L
20g/L
0.0
0.2
0.4
0.6
0.8
1.0

(b)

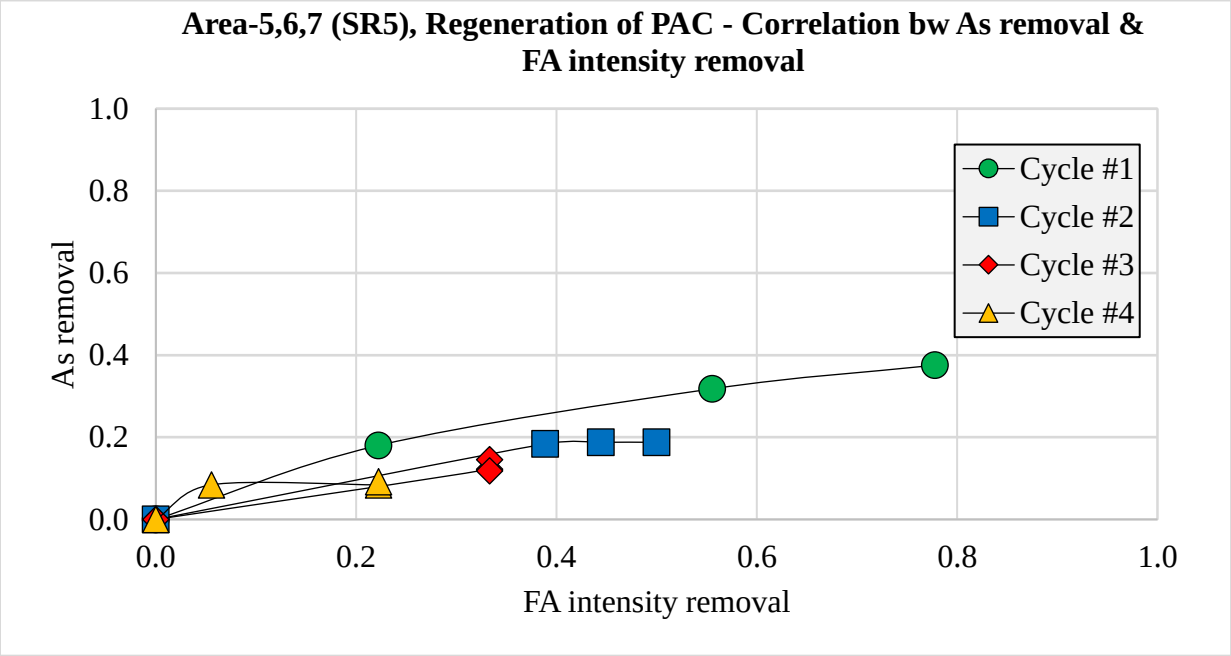


(c)

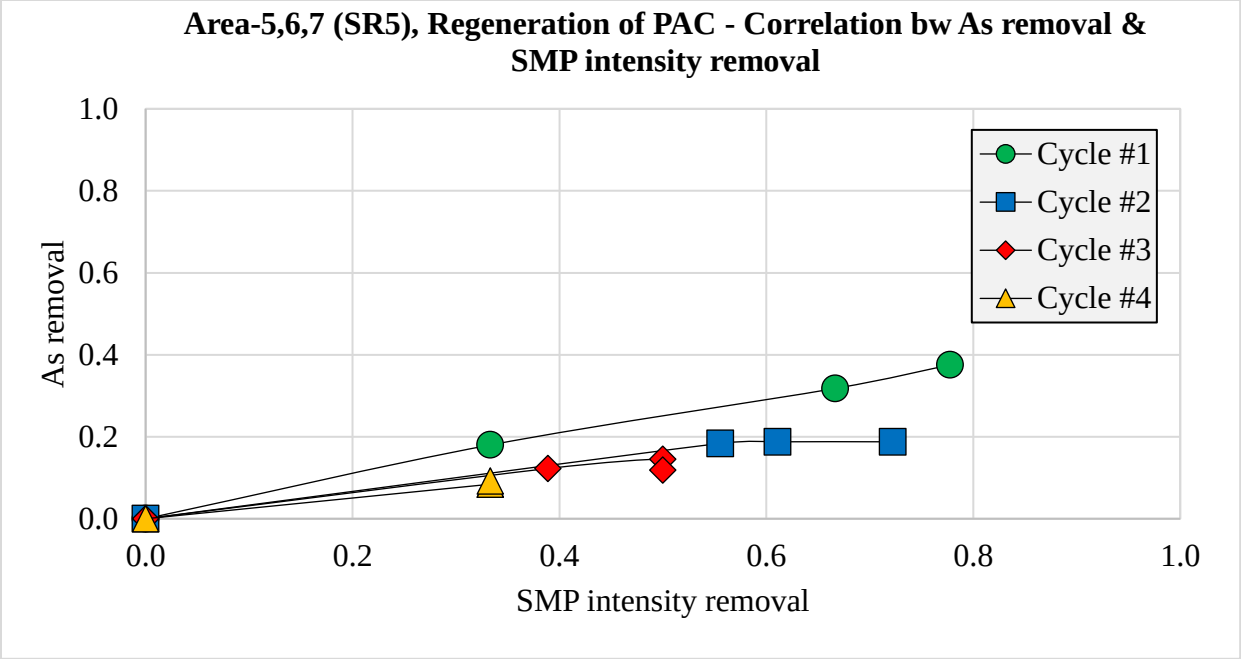
Figure B - 7. Correlations between arsenic removal from A567 leachate (SR5 sample) and changes in the EEK spectra: (a) HA intensity removal, (b) FA intensity removal, and (c) EPS intensity removal. Leachate was treated with varying dose of PAC at the original pH for 15 minutes. (*Immediate removal of SMP intensity was observed)


Area-5,6,7 (SR5), Regeneration of PAC - Correlation bw As removal & HA intensity removal
As removal
HA intensity removal
0.0
0.2
0.4
0.6
0.8
1.0
Cycle #1
Cycle #2
Cycle #3
Cycle #4

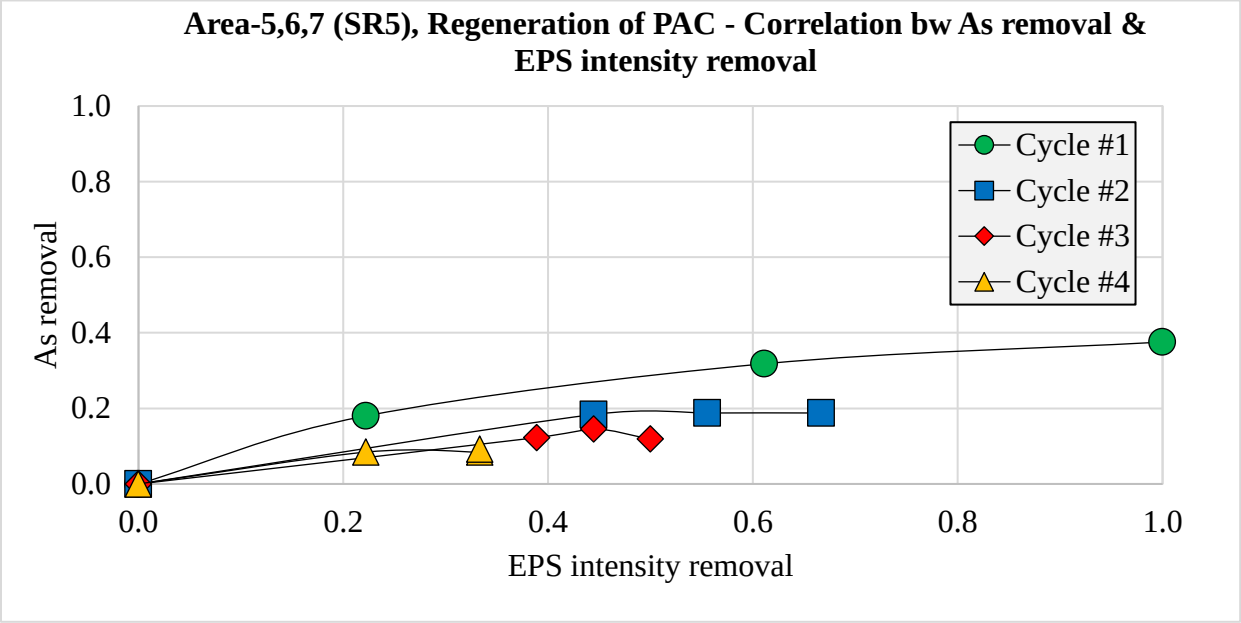
(a)


Area-5,6,7 (SR5), Regeneration of PAC - Correlation bw As removal & FA intensity removal
As removal
FA intensity removal
0.0
0.2
0.4
0.6
0.8
1.0
Cycle #1
Cycle #2
Cycle #3
Cycle #4

(b)

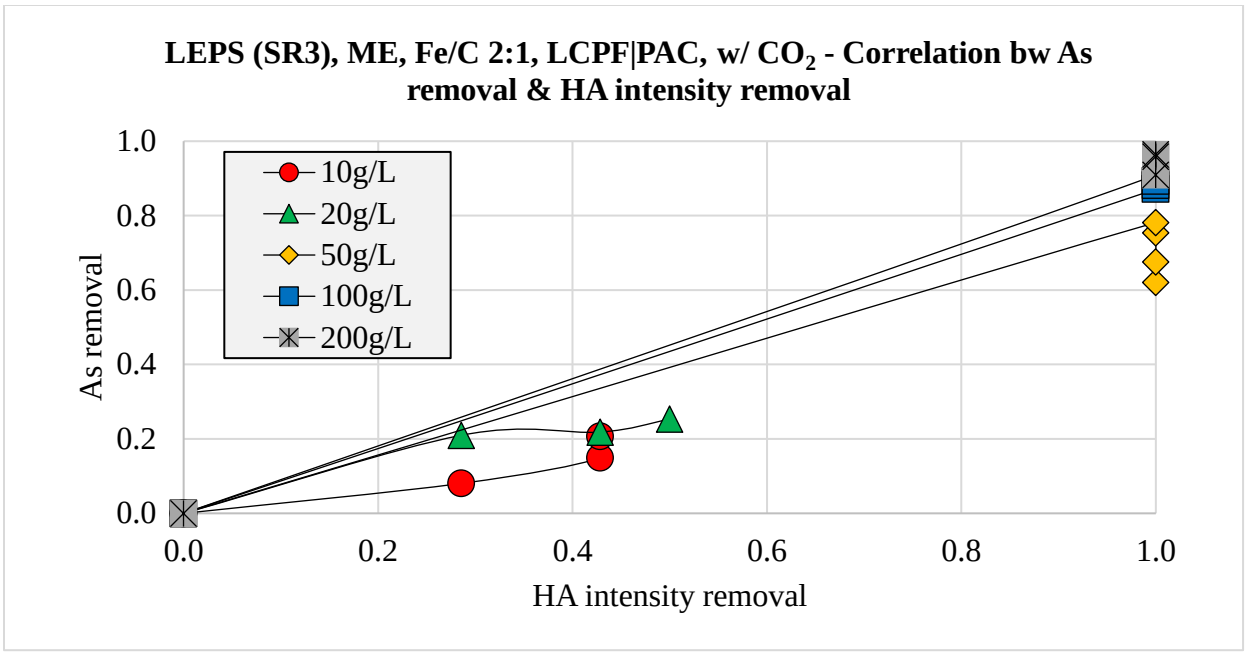


(c)

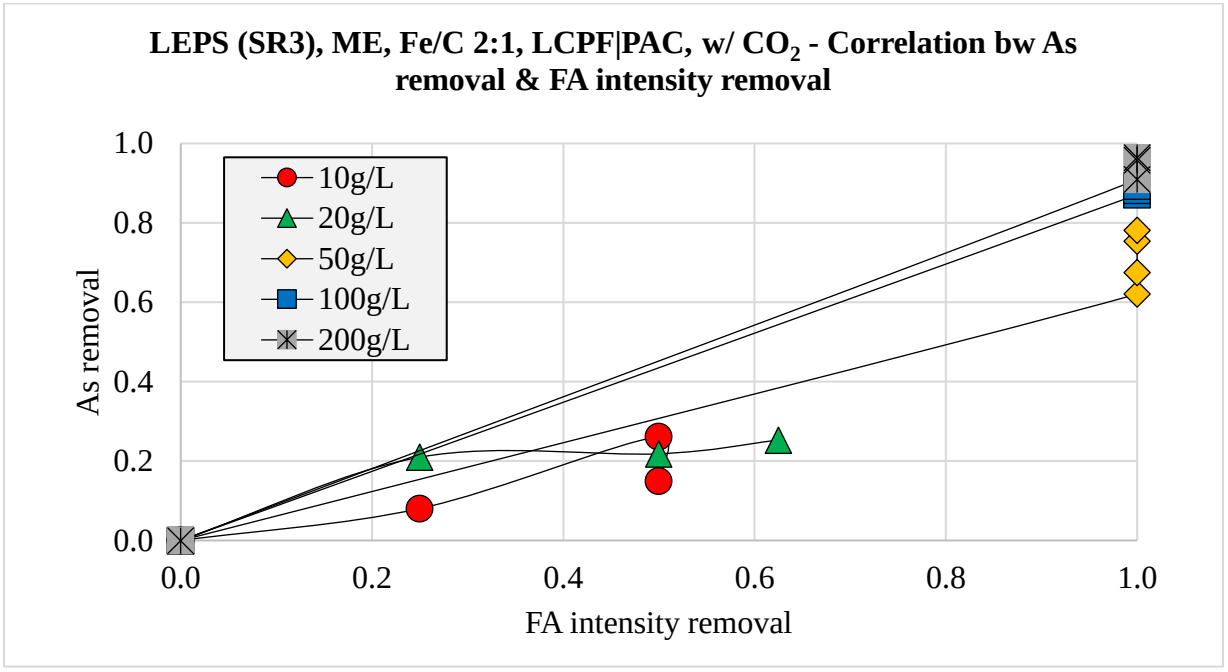


(d)

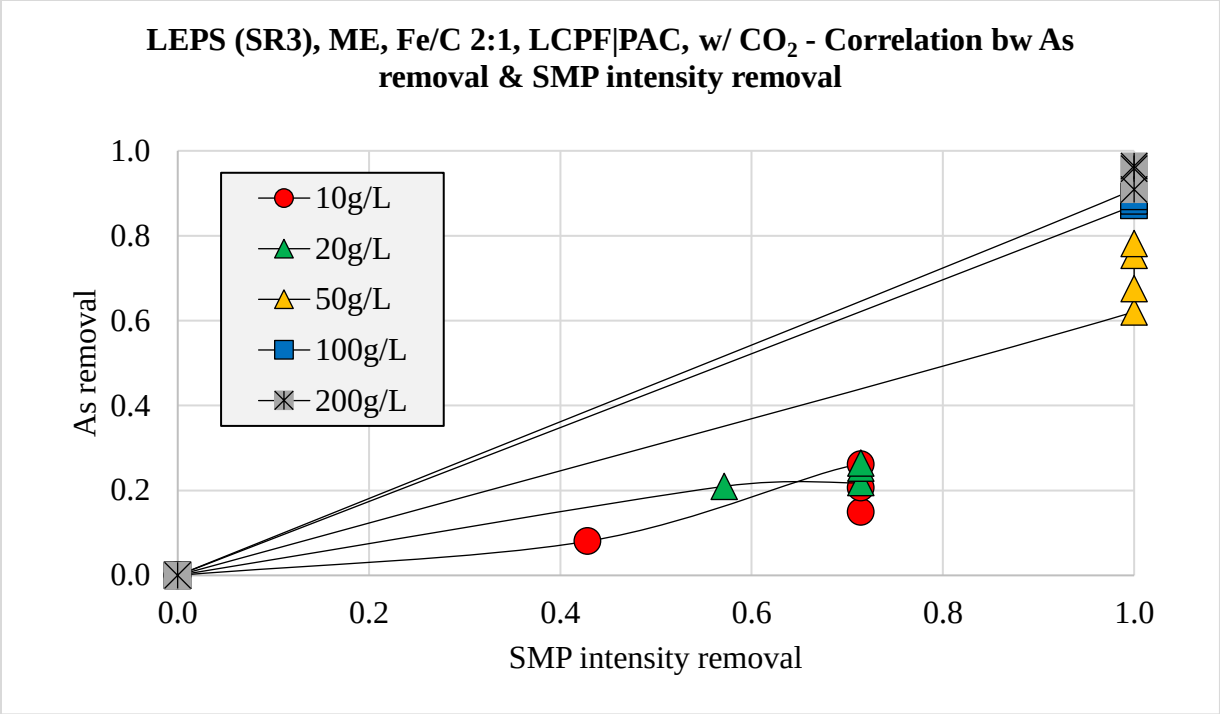
Figure B - 8. Correlations between arsenic removal from A567 leachate (SR5 sample) and changes in the EEK spectra: (a) HA intensity removal, (b) FA intensity removal, (c) SMP intensity removal, and (d) EPS intensity removal. Leachate was treated with 20 g/L of PAC at the pH 5 for 15 minutes that was regenerated and reused for three additional cycles.


LEPS (SR3), ME, Fe/C 2:1, LCPF|PAC, w/ CO2 - Correlation bw As removal & HA intensity removal
As removal
HA intensity removal
10g/L
20g/L
50g/L
100g/L
200g/L
0.0
0.2
0.4
0.6
0.8
1.0

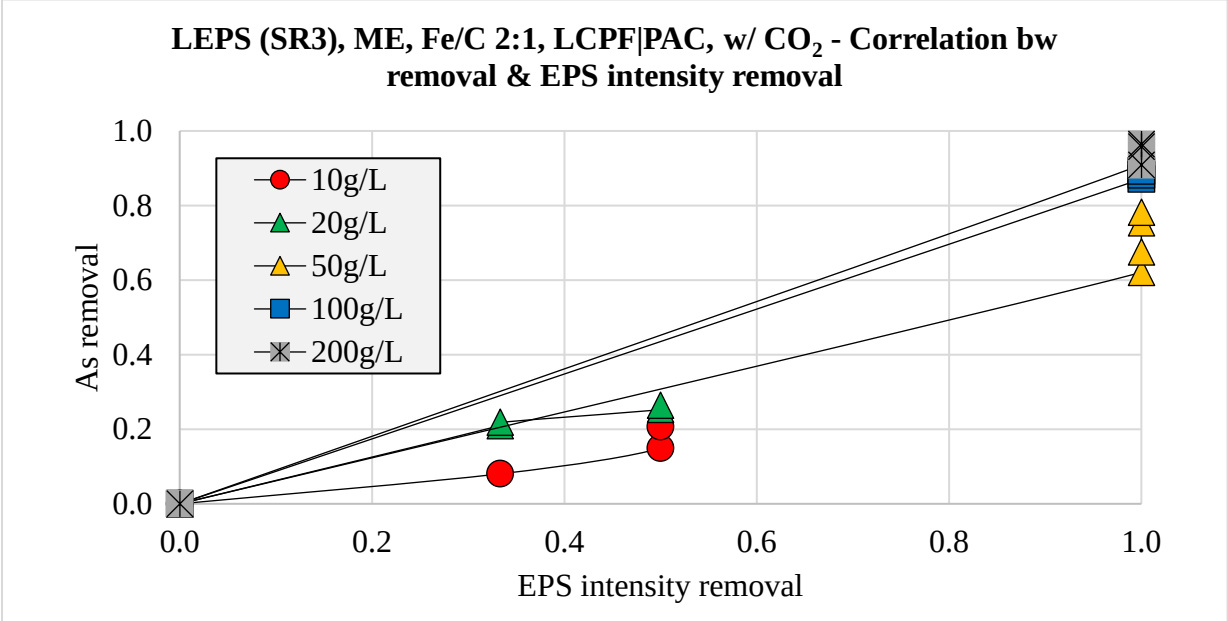
(a)


LEPS (SR3), ME, Fe/C 2:1, LCPF|PAC, w/ CO2 - Correlation bw As removal & FA intensity removal
As removal
FA intensity removal
10g/L
20g/L
50g/L
100g/L
200g/L
0.0
0.2
0.4
0.6
0.8
1.0

(b)

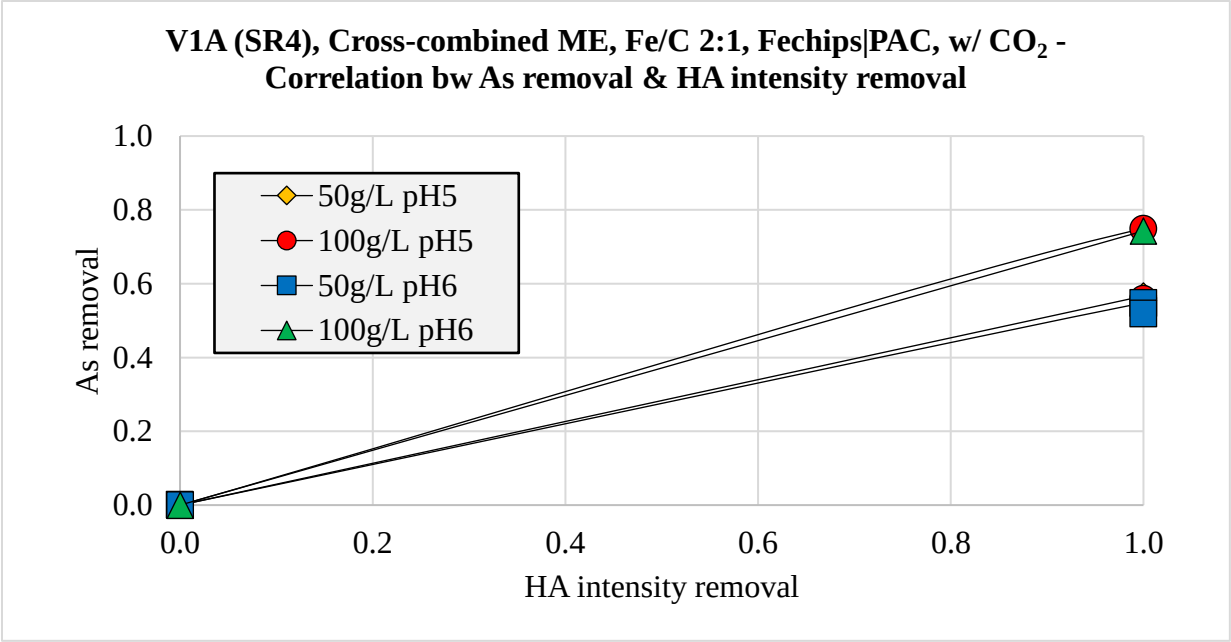


(c)

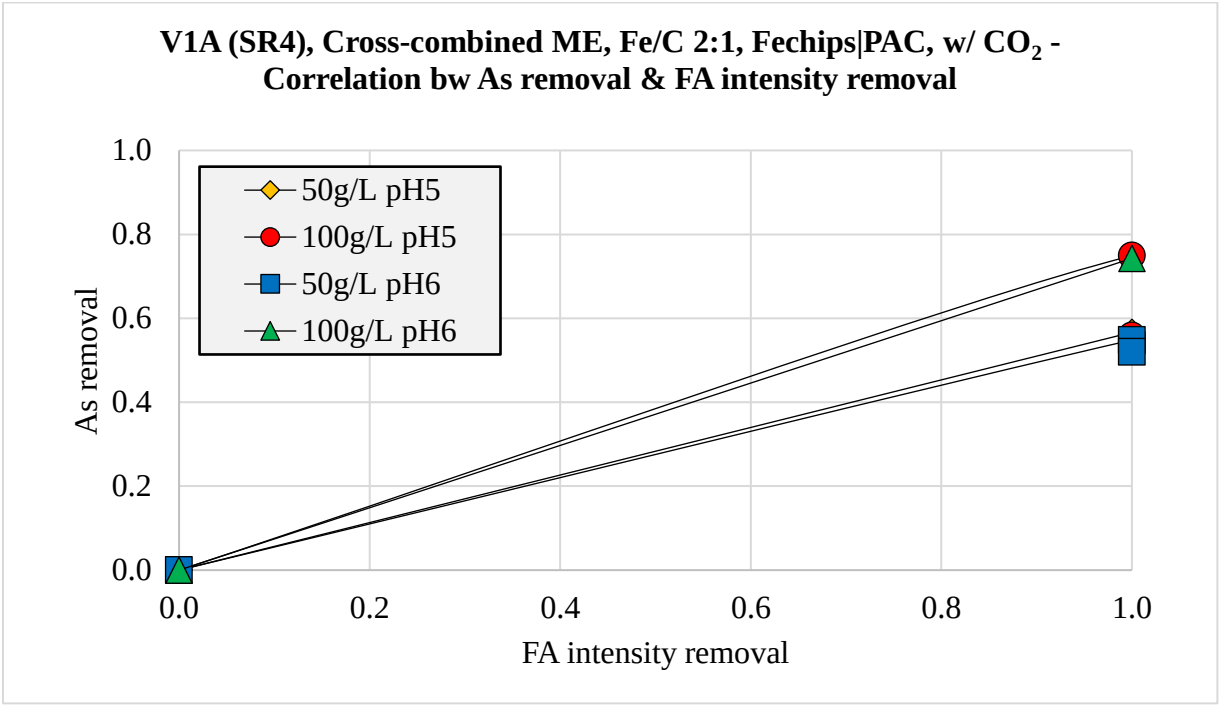


(d)

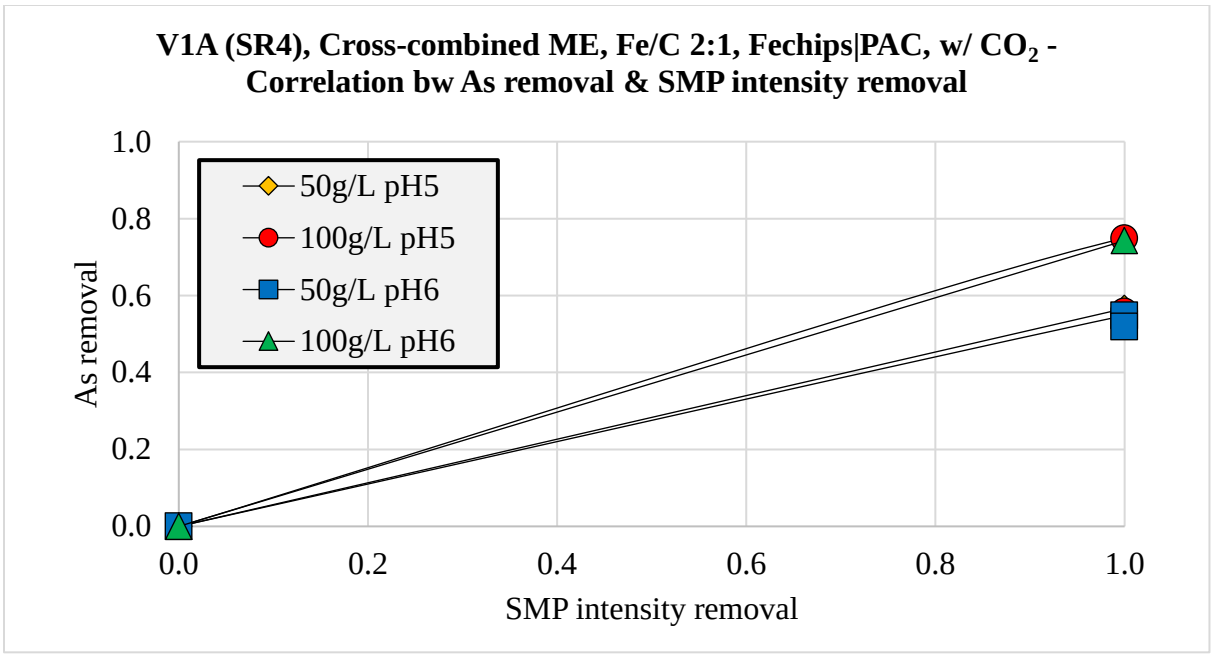
Figure B - 9. Correlations between arsenic removal from LEPS leachate (SR3 sample) and changes in the EEK spectra: (a) HA intensity removal, (b) FA intensity removal, (c) SMP intensity removal, and (d) EPS intensity removal. Leachate was treated with micro-electrolysis and dosed with LCPF and PAC at a ratio of Fe/C 2:1 AC at pH 6 with CO_2.


V1A (SR4), Cross-combined ME, Fe/C 2:1, Fechips|PAC, w/ CO2 - Correlation bw As removal & HA intensity removal
As removal
HA intensity removal
50g/L pH5
100g/L pH5
50g/L pH6
100g/L pH6
0.0
0.2
0.4
0.6
0.8
1.0

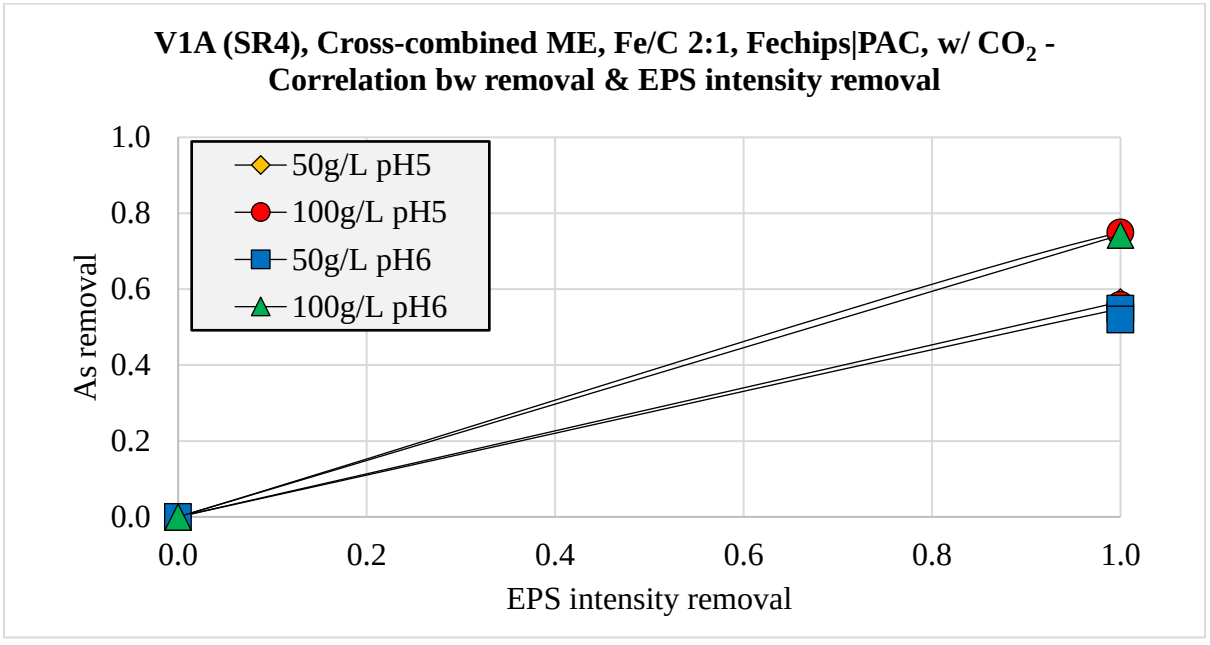
(a)


V1A (SR4), Cross-combined ME, Fe/C 2:1, Fechips|PAC, w/ CO2 - Correlation bw As removal & FA intensity removal
As removal
FA intensity removal
50g/L pH5
100g/L pH5
50g/L pH6
100g/L pH6
0.0
0.2
0.4
0.6
0.8
1.0

(b)

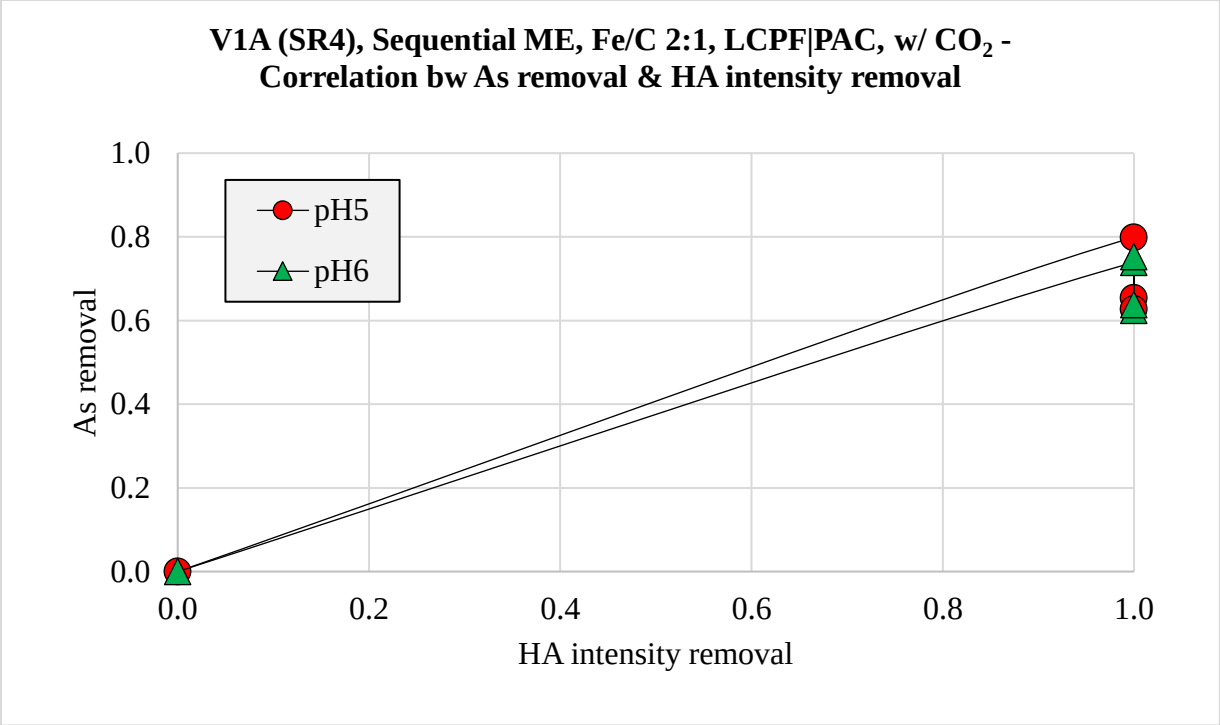


(c)

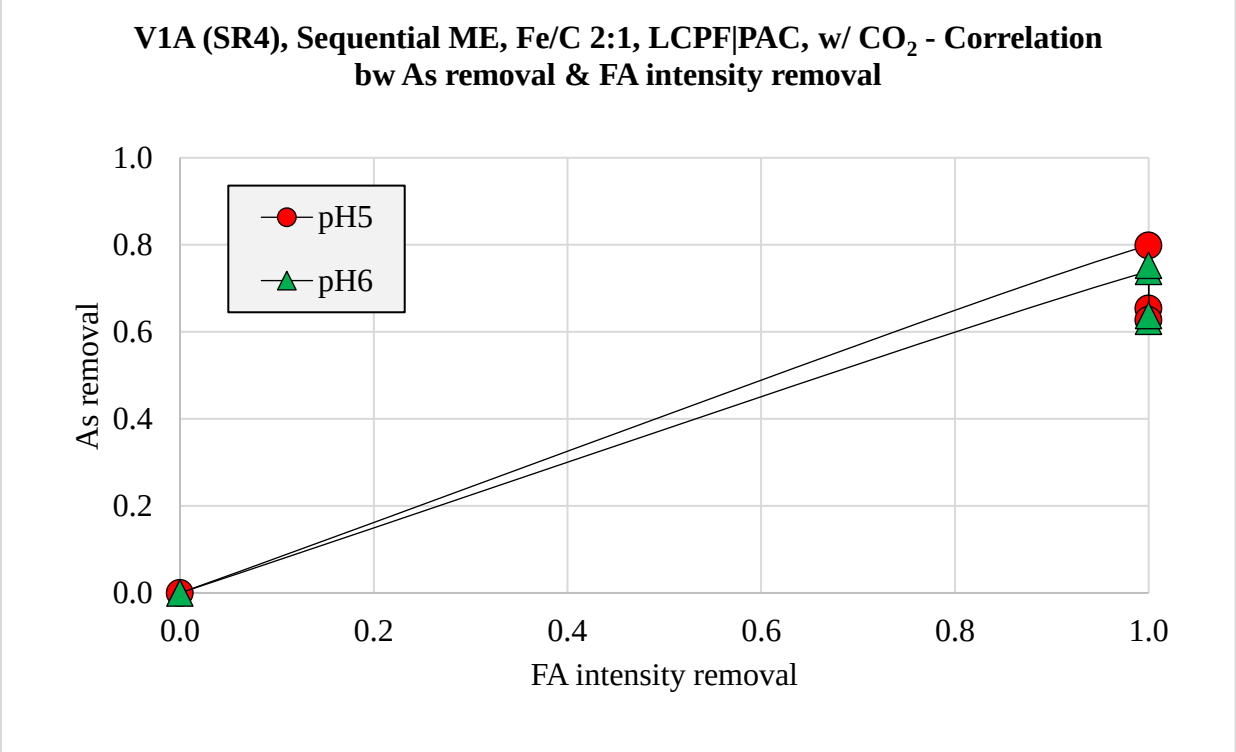


(d)

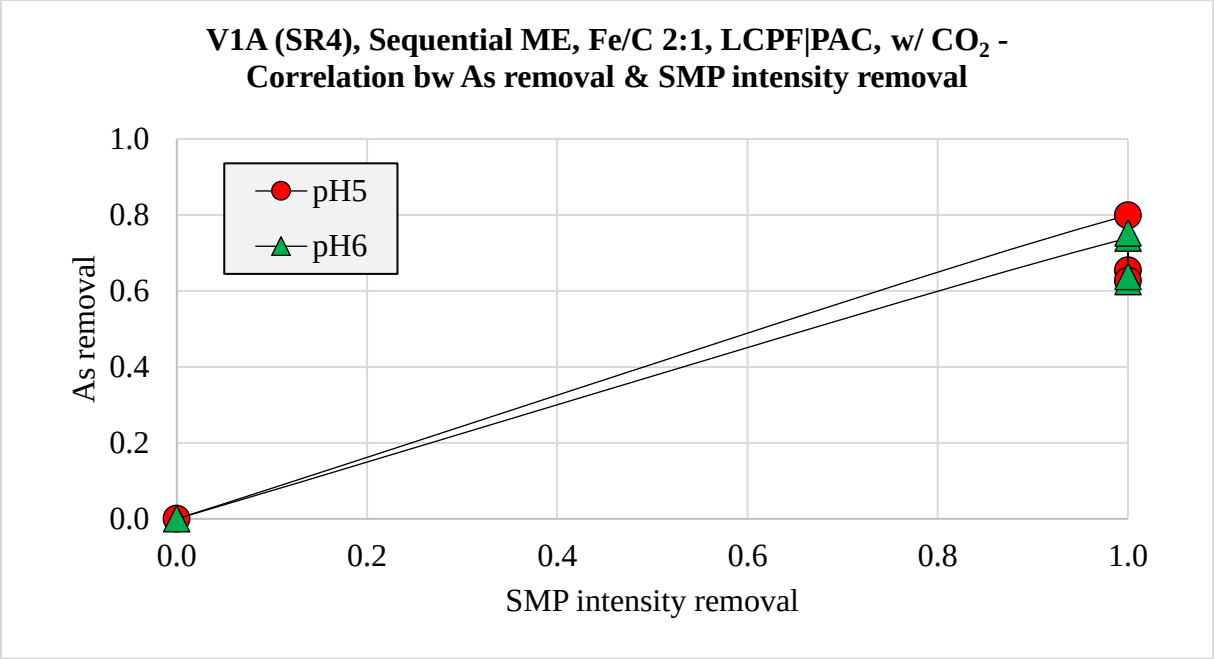
Figure B - 10. Correlations between arsenic removal from Vault 1A leachate (SR4 sample) and changes in the EEK spectra: (a) HA intensity removal, (b) FA intensity removal, (c) SMP intensity removal, and (d) EPS intensity removal. Leachate was treated with a cross-combination of Fe chips and PAC at pH 5 and 6.


V1A (SR4), Sequential ME, Fe/C 2:1, LCPF|PAC, w/ CO2 - Correlation bw As removal & HA intensity removal
pH5
pH6
As removal
HA intensity removal
0.0
0.2
0.4
0.6
0.8
1.0

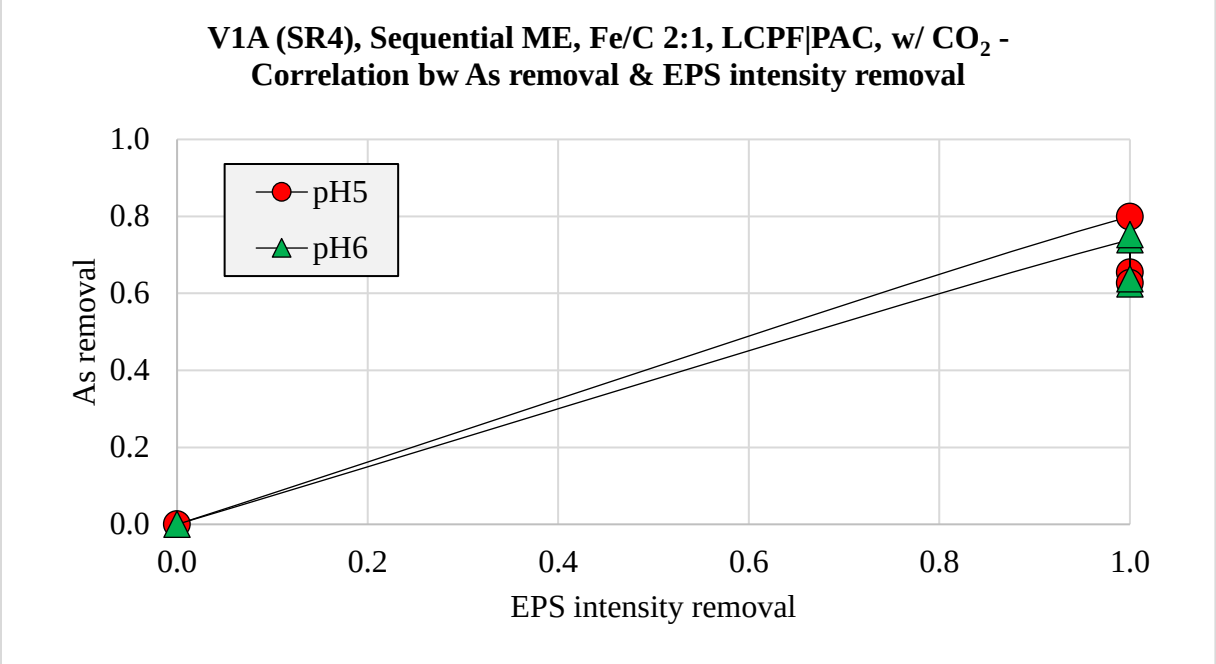
(a)


V1A (SR4), Sequential ME, Fe/C 2:1, LCPF|PAC, w/ CO2 - Correlation bw As removal & FA intensity removal
pH5
pH6
As removal
FA intensity removal
0.0
0.2
0.4
0.6
0.8
1.0

(b)

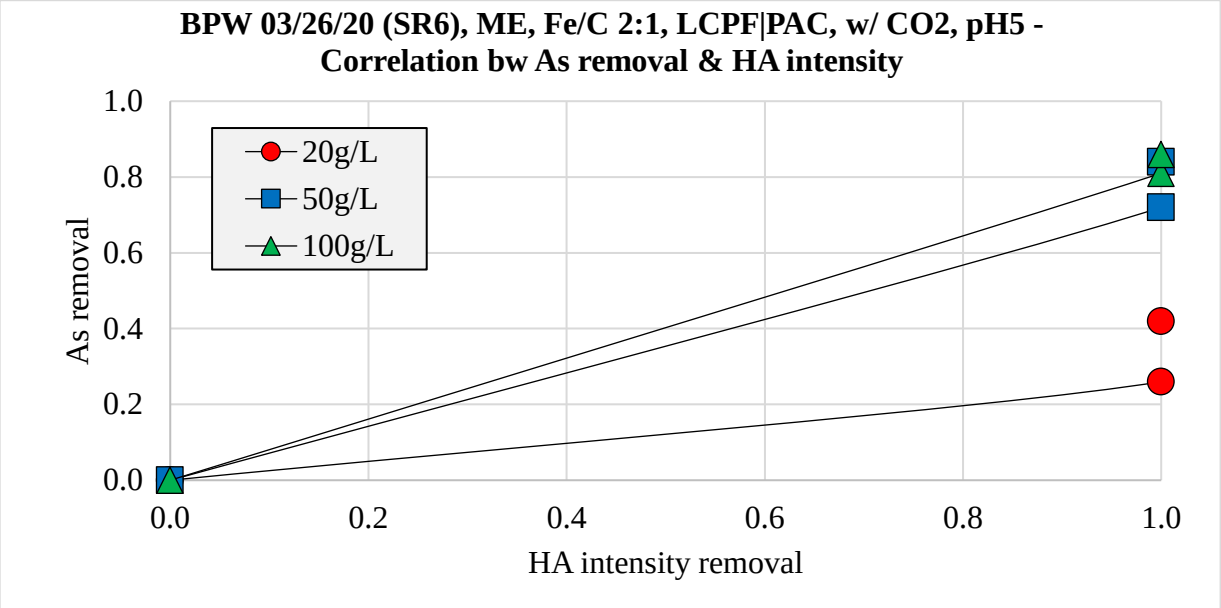


(c)

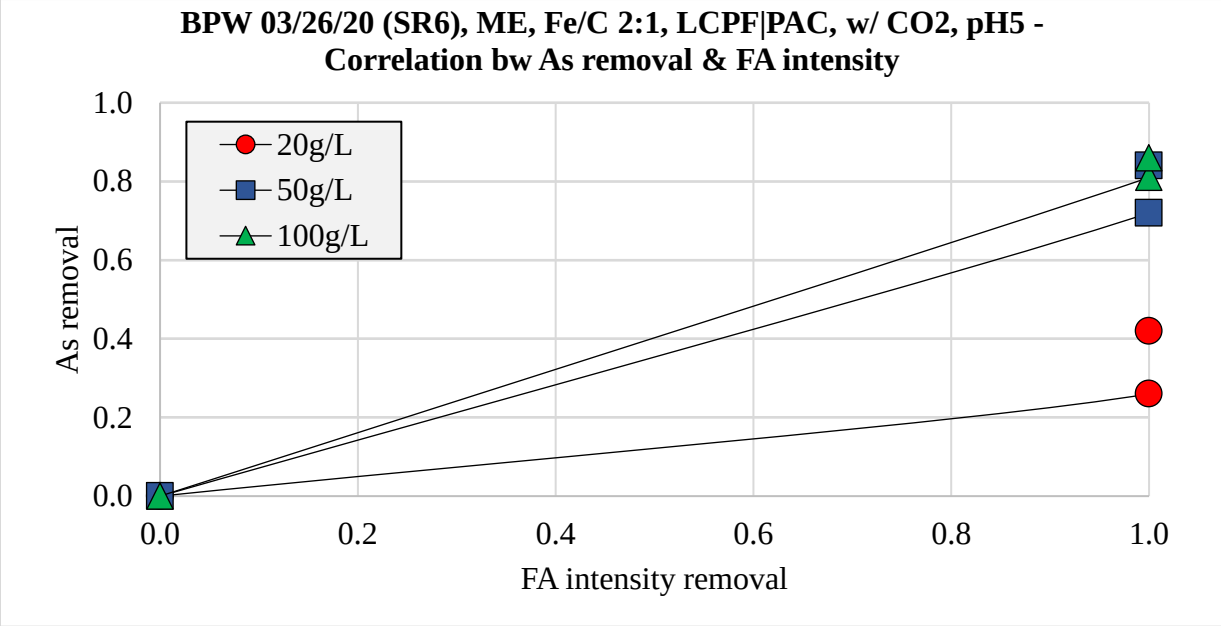


(d)

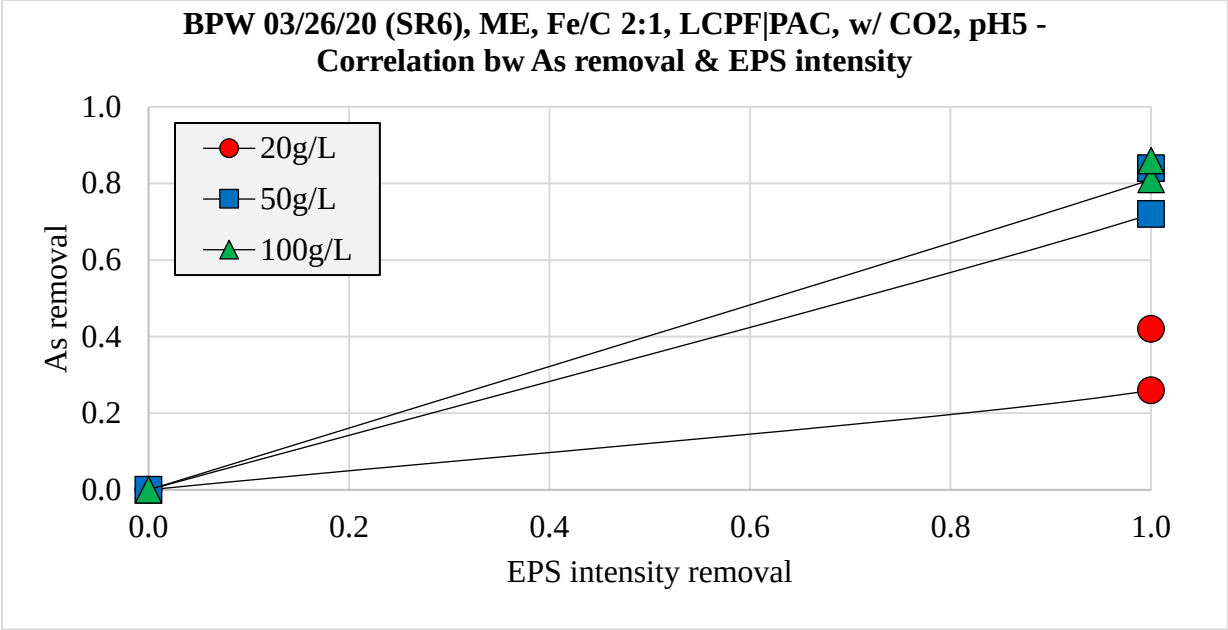
Figure B - 11. Correlations between arsenic removal from Vault 1A leachate (SR4 sample) and changes in the EEK spectra: (a) HA intensity removal, (b) FA intensity removal, (c) SMP intensity removal, and (d) EPS intensity removal. Leachate was treated with sequential addition of PAC and LCPF for 15 minutes each at pH 5 and 6.


BPW 03/26/20 (SR6), ME, Fe/C 2:1, LCPF|PAC, w/ CO2, pH5 -
Correlation bw As removal & HA intensity
As removal
HA intensity removal
20g/L
50g/L
100g/L
0.0
0.2
0.4
0.6
0.8
1.0

(a)


BPW 03/26/20 (SR6), ME, Fe/C 2:1, LCPF|PAC, w/ CO2, pH5 -
Correlation bw As removal & FA intensity
As removal
FA intensity removal
20g/L
50g/L
100g/L
0.0
0.2
0.4
0.6
0.8
1.0

(b)



(c)

Figure B - 12.. Correlations between arsenic removal from BPW (SR6 sample collected on 03/26/20) and changes in the EEK spectra: (a) HA intensity removal, (b) FA intensity removal, and (c) EPS intensity removal. BPW was treated with a varying dose of LCPF and PAC at a ratio of Fe/C 2:1 at pH 5 for 15 minutes.

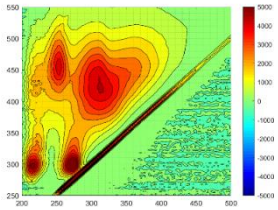
APPENDIX – C

Raw data for EEM matrices

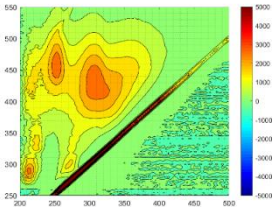
*(*Y-axis = Excitation (nm) and X-axis = Emission (nm) for EEM spectra)*

Leachate (SR2), $KMnO_4$ oxidation, pH5, 24h

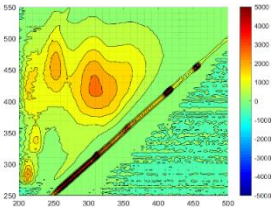
0 mg/L



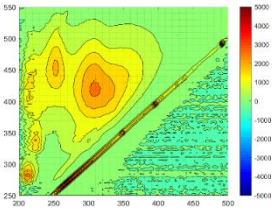
500 mg/L



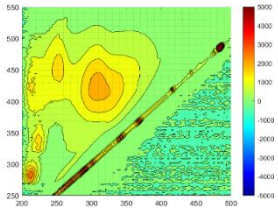
1000 mg/L



1500 mg/L

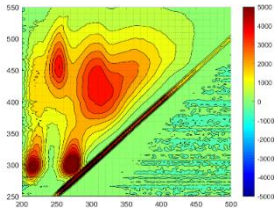


2000 mg/L

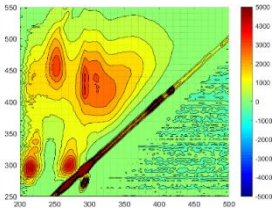


Leachate (SR2), $KMnO_4$ oxidation, pH6, 24h

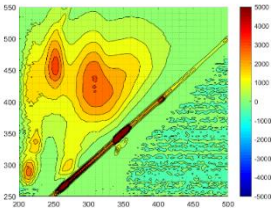
0 mg/L



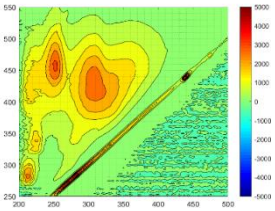
500 mg/L



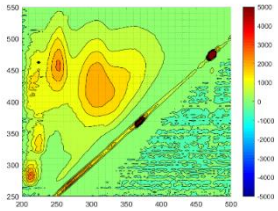
1000 mg/L



1500 mg/L

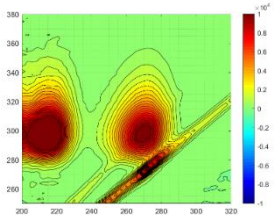


2000 mg/L

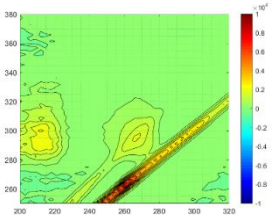


Condensate (SR2), $KMnO_4$ oxidation, pH5, 24h

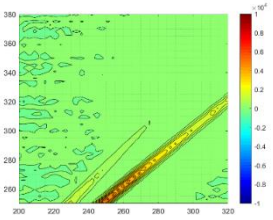
0 mg/L



500 mg/L

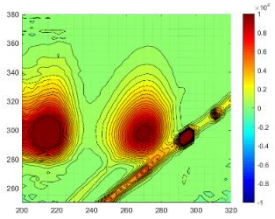


1000 mg/L

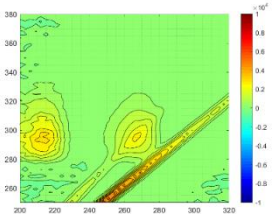


Condensate (SR2), $KMnO_4$ oxidation, pH6, 24h

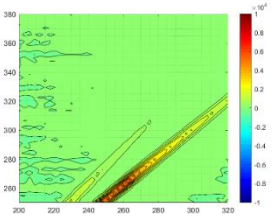
0 mg/L



500 mg/L

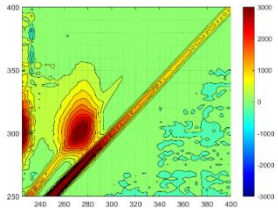


1000 mg/L

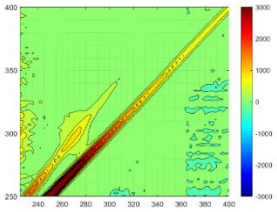


BPW 03/22/20 (SR6), $KMnO_4$ oxidation, pH5, 24h

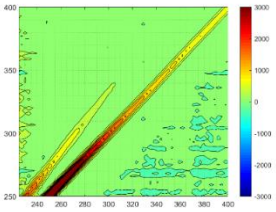
0 mg/L



1000 mg/L

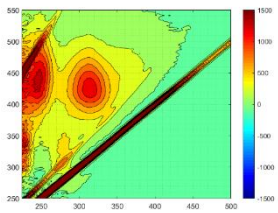


2000 mg/L

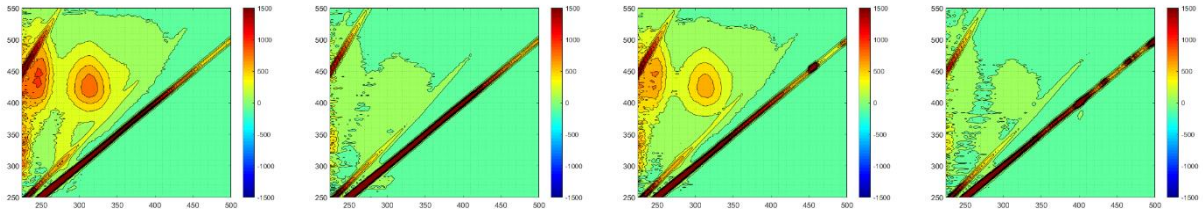


LEPS leachate (SR5), Oxygenation at original pH followed by 6 g/L of $FeCl_3$ for 30 mins at pH 6

0 minutes

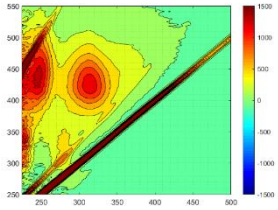


O_2 15 mins | O_2 15 mins + $FeCl_3$ 30 mins | O_2 4h | O_2 4h + $FeCl_3$ 30 mins

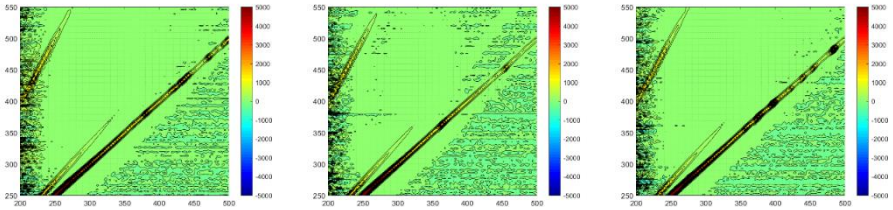


LEPS leachate (SR5), PAC adsorption, pH5

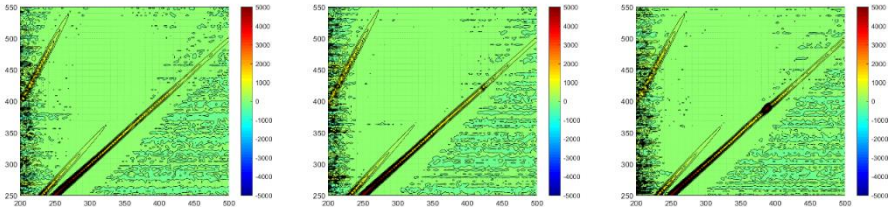
0 mins



5 g/L - 2 mins | 5 mins | 15 mins

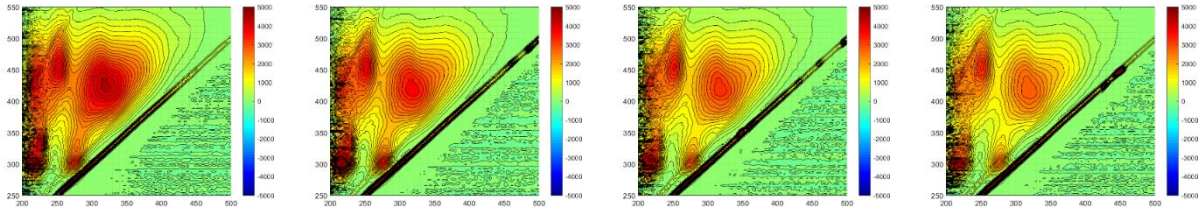


10 g/L - 2 mins | 5 mins | 15 mins

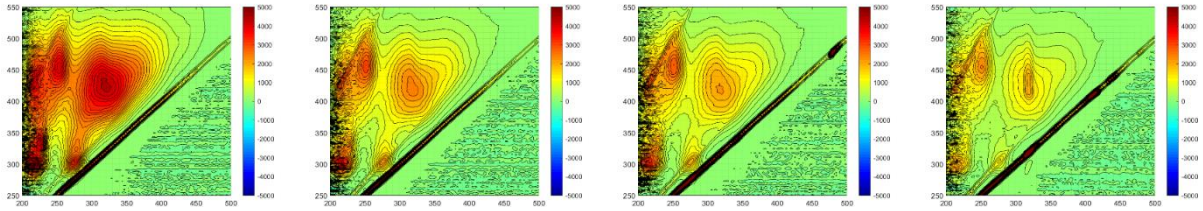


A567 leachate (SR5), PAC adsorption, pH5

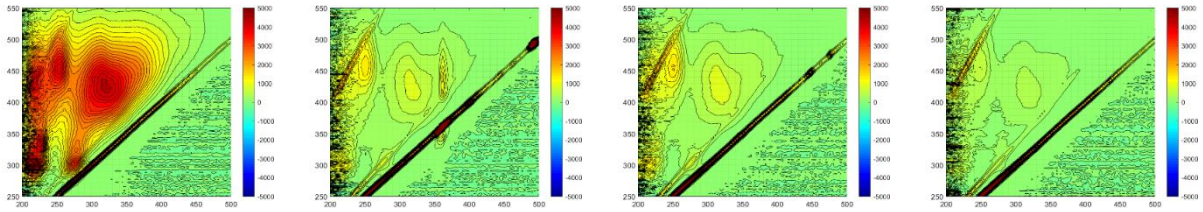
5 g/L - 0 mins 2 mins 5 mins 15 mins



10 g/L - 0 mins 2 mins 5 mins 15 mins

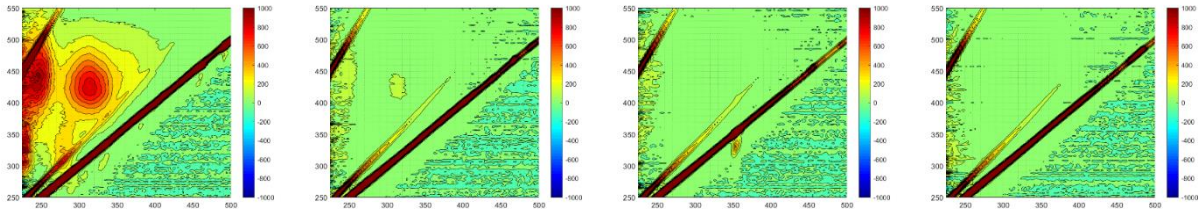


20 g/L - 0 mins 2 mins 5 mins 15 mins

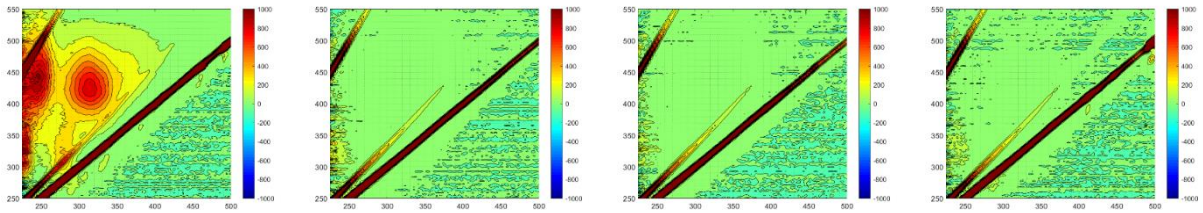


LEPS leachate (SR5), PAC adsorption, original pH

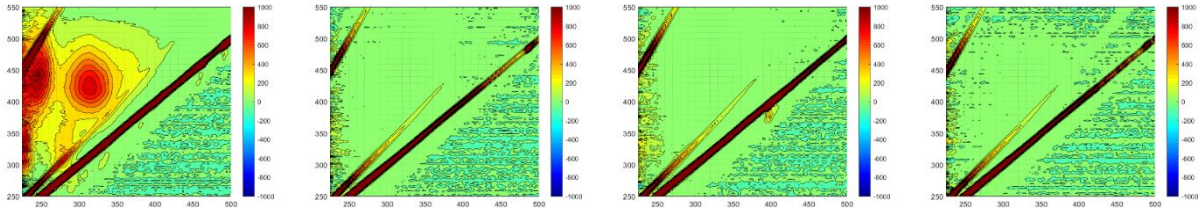
5 g/L - 0 mins 5 mins 15 mins 60 mins



10 g/L - 0 mins 5 mins 15 mins 60 mins

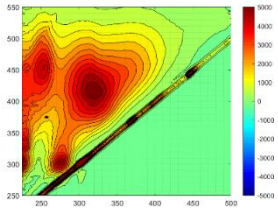


20 g/L - 0 mins | 5 mins | 15 mins | 60 mins

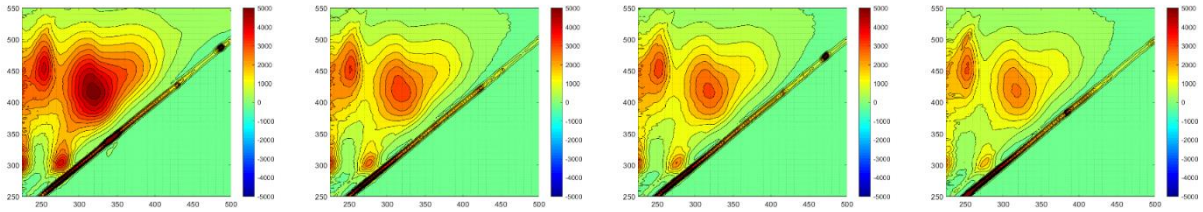


A567 leachate (SR5), PAC adsorption, original pH

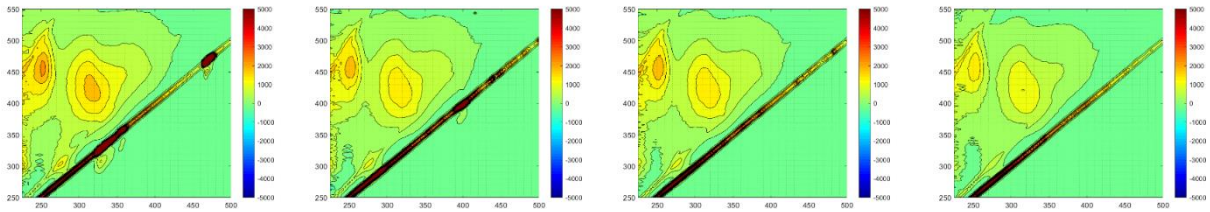
0 mins



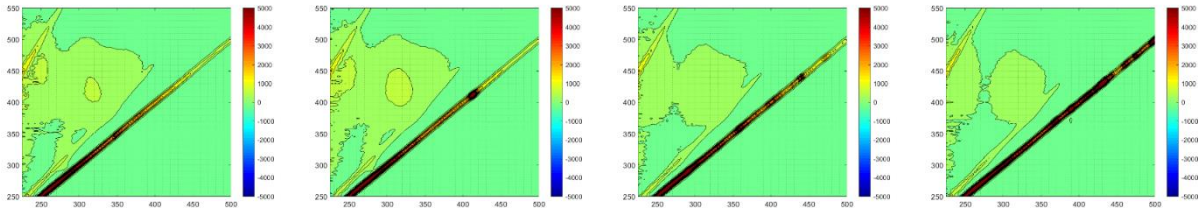
5 g/L - 5 mins | 15 mins | 30 mins | 60 mins



10 g/L - 5 mins | 15 mins | 30 mins | 60 mins

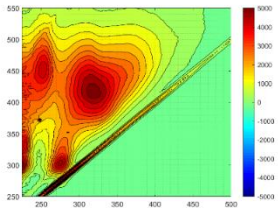


10 g/L - 5 mins | 15 mins | 30 mins | 60 mins

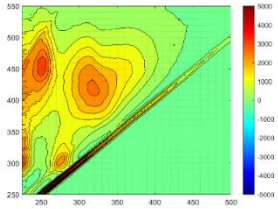


A567 leachate (SR5), Regeneration of PAC, 20 g/L PAC, pH5

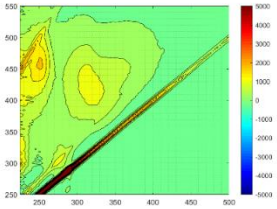
0 mins



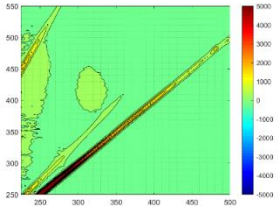
Cycle #1 - 2 mins



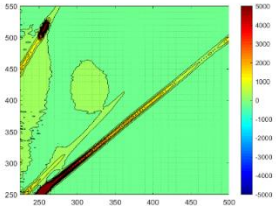
5 mins



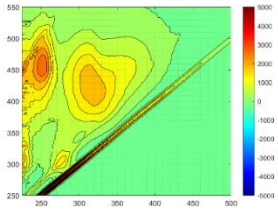
10 mins



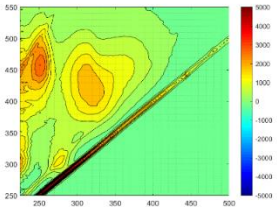
15 mins



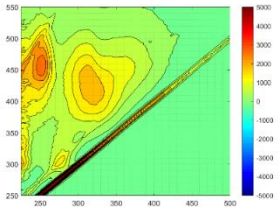
Cycle #2 - 2 mins



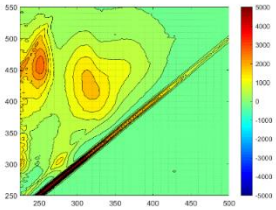
5 mins



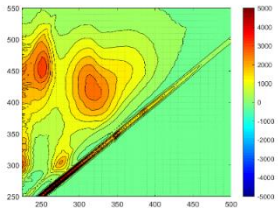
10 mins



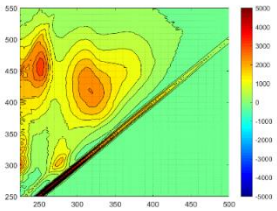
15 mins



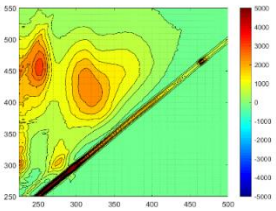
Cycle #3 - 2 mins



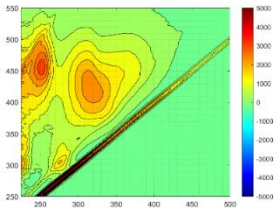
5 mins



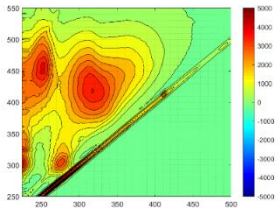
10 mins



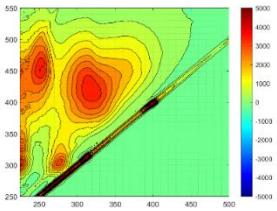
15 mins



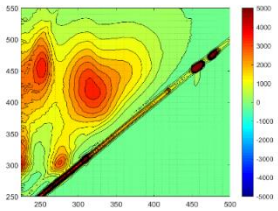
Cycle #4 - 2 mins



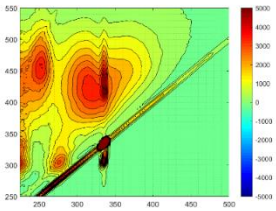
5 mins



10 mins

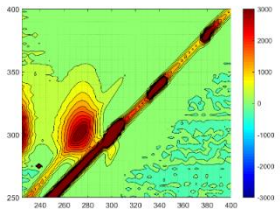


15 mins

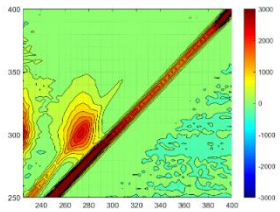


BPW 03/26/20 (SR6), ZVI reduction, LCPF, 24h

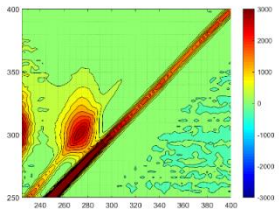
50 g/L - 0 mins



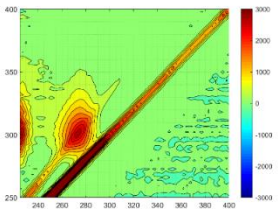
0.5h



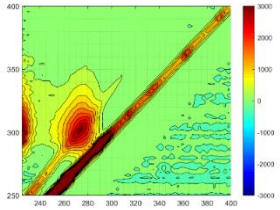
1h



4h

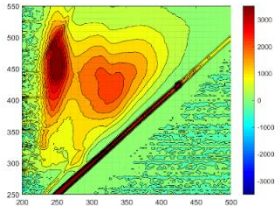


24h

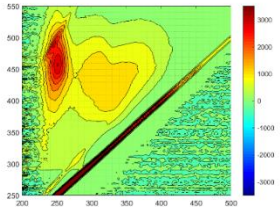


LEPS leachate (SR3), ME, Fe/C 2:1, LCPF|PAC, w/ CO_2, pH6

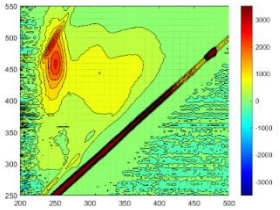
0 mins



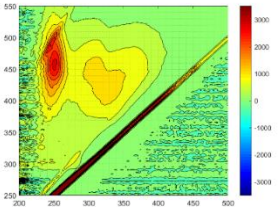
10 g/L - 2 mins



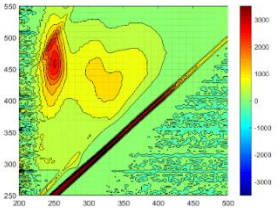
5 mins



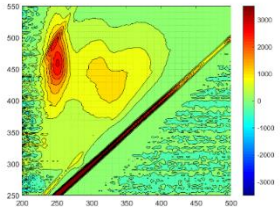
10 mins



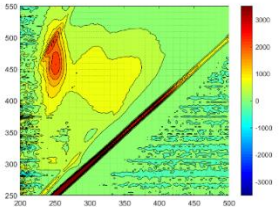
15 mins



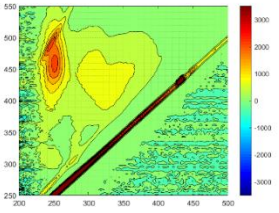
20 g/L - 2 mins



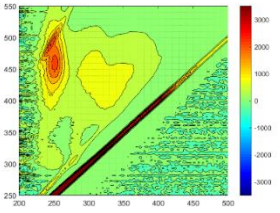
5 mins



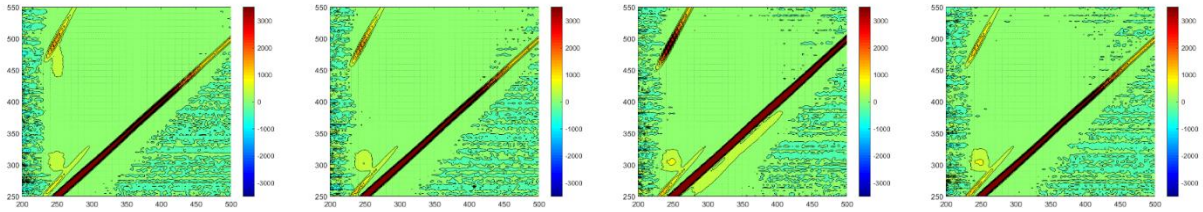
10 mins



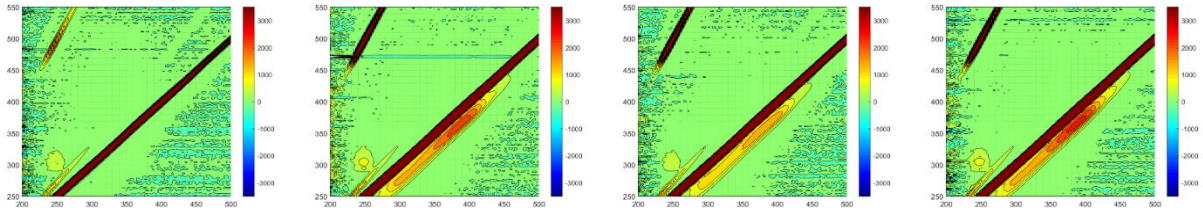
15 mins



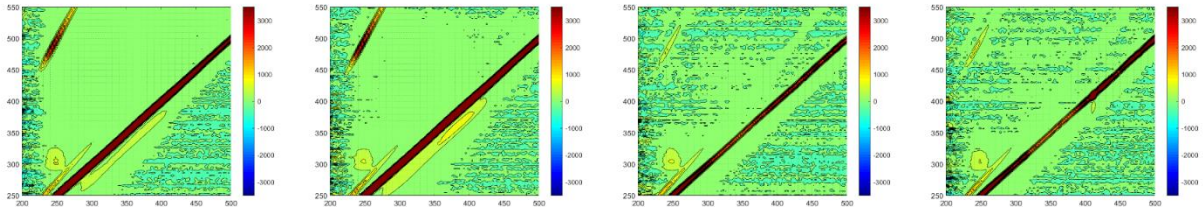
50 g/L - 2 mins 5 mins 10 mins 15 mins



100 g/L - 2 mins 5 mins 10 mins 15 mins

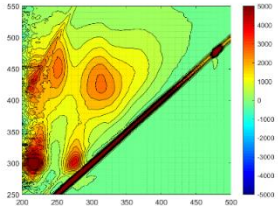


200 g/L - 2 mins 5 mins 10 mins 15 mins



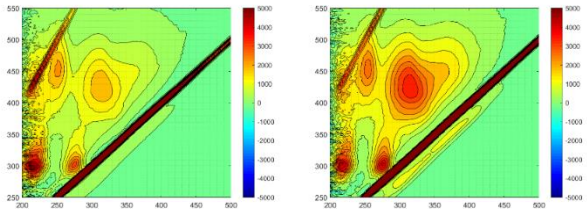
<u>V1A leachate (SR4), Cross combination ME, Fe/C 2:1, w/ CO_2</u>

0 mins

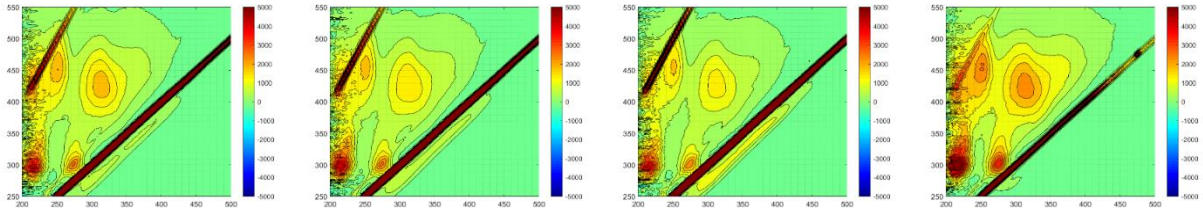


LCPF|GAC –

pH6 - 50g/L - 5 mins 15 mins

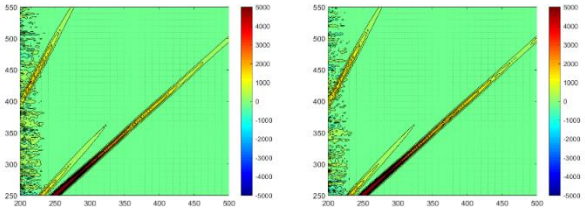


pH5 - 50g/L - 5 mins 15 mins 100 g/L - 5 mins 15 mins

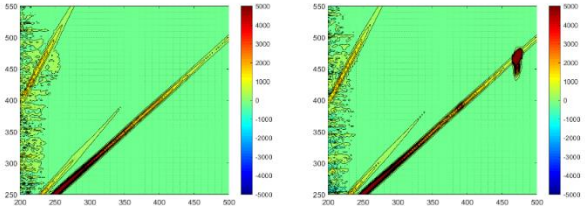


Fe chips|PAC –

pH5 - 50g/L - 5 mins 15 mins

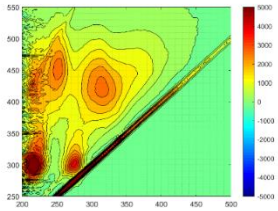


pH6 - 50g/L - 5 mins 15 mins



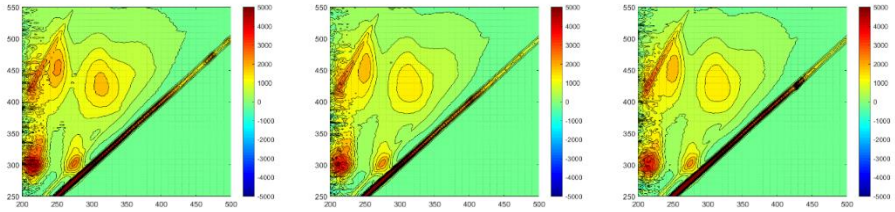
<u>V1A leachate (SR4), Sequential ME, Fe/C 2:1, w/ CO_2</u>

0 mins

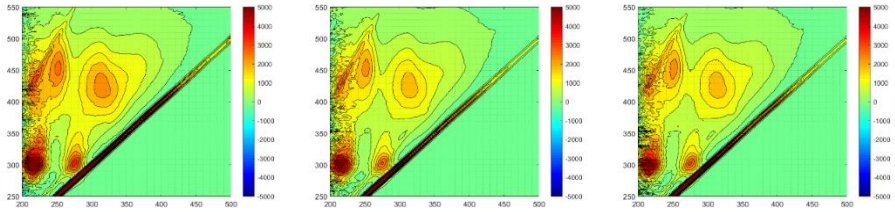


Fe chips|GAC –

pH5 – C – 15 mins Fe – 5 mins Fe – 15 mins

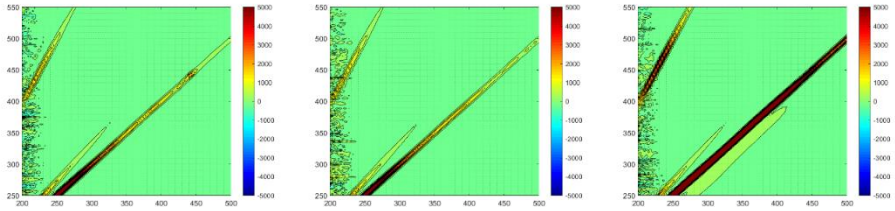


pH6 – C – 5 mins Fe – 5 mins Fe – 15 mins

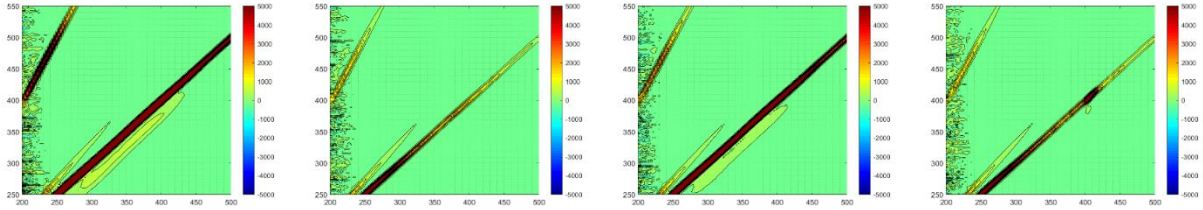


LCPF PAC –

pH5 – C – 15 mins Fe – 5 mins Fe – 15 mins

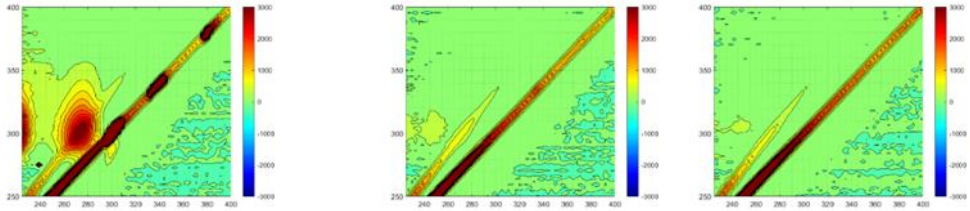


pH6 – C – 5 mins C – 15 mins Fe – 5 mins Fe – 15 mins

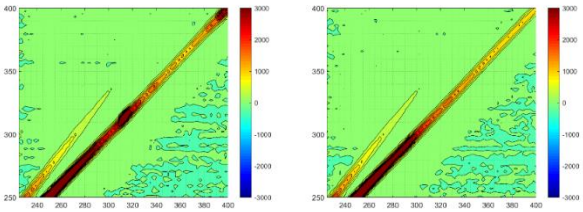


<u>BPW 03/26/20 (SR6), ME, Fe/C 2:1, LCPF|PAC, w/ CO_2, pH5</u>

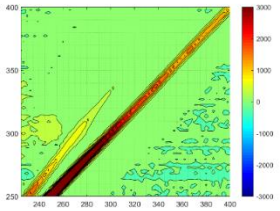
0 mins 20 g/L - 5 mins 15 mins



50 g/L - 5 mins 15 mins



100 g/L - 5 mins



15 mins