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ARSENIC BIOREMEDIATION: IMPORTANCE OF SAMPLE PREPARATION FOR ENVIRONMENTAL ARSENIC SPECIES IDENTIFICATION

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Abstract: Industrial development and increasing anthropogenic activities such as mining continue to be of concern as they lead to pollution of waters. Mine wastes contain heavy metals, such as arsenic, that can contaminate surface waters and groundwater. Arsenic is found in four oxidation states in species including inorganic and organic compounds that are dependent on the existence of sorbent materials, pH, redox potential, and microbial metabolic activity. The As(III)/As(V) states dominate in water given their solubility's with As(III) being 10 times more toxic than As(V). Thus, knowing the specific arsenic species in wastes is important for understanding both their toxicity potential and for development of specific treatment technologies. The problem with determining arsenic speciation is the need for advanced analytical instruments for the analysis that are not readily available. Thus, suitable sample processing and storage procedures are vital to preserve the species from the time of sampling to analysis. Currently, we used three methods for preservation including: (1) no acid; (2) ethylene diaminete tetra acetic acid (EDTA); and (3) 2% nitric acid (HNO_3). The overall objective of our research program is to investigate and mitigate arsenic from mine waste rock that will be stored in water in Saskatchewan, Canada, with focus on bioremediation of arsenic at relevant in situ temperatures. Thus, the samples preserved we taken from these experimental reactors for the current study. Overall, the no acid treatment resulted in the most consistent speciation preservation for experimental samples. Interestingly, both standard method acid treatments resulted in unexpected oxidation of arsenic.

1 INTRODUCTION

Water is an irreplaceable natural resource and fundamental for human and environmental health and sustainability. Industrial development and increasing anthropogenic activities such as mining continue to be of concern as they can result in the pollution of water resources. Mine wastes often contain heavy metals, such as arsenic, that can contaminate surface waters and groundwater. Thus, investigating the vulnerability of water resources due to mine activities is essential to ensure healthy aquatic ecosystems. The occurrence of arsenic in ground water worldwide has had numerous documented negative impacts on both environment and human health (Jain and Ali 2000). The primary routes of arsenic exposure are ingestion and inhalation with ingestion through drinking water being the primary concern for human exposure, especially in developing countries lacking sophisticated drinking water treatment technologies. The World Health Organization (WHO) reported that over 200 million people worldwide are exposed to drinking water containing arsenic concentrations exceeding its guideline value of 10 µg/L (WHO 2017). Arsenic is a naturally occurring metalloid and ubiquitous element that ranks 20th in abundance in the earth's crust, 14th in the sea water, and 12th in human body (Mandal, and Suzuki 2002). The United State Environmental Protection Agency (EPA) has listed arsenic as a primary contaminant for some superfund sites and it is considered as the "king" of poison (Nriagu et al. 2007; Sundaram et al. 2008).

Popular treatment technologies that are being used or considered for the remediation or arsenic include coagulation and flocculation, oxidation, various membrane processes, electrochemical methods, adsorption, and biological options such as phytoremediation and bioremediation (Kumar et al. 2004; Shih 2005; Mohan and Pittman 2007; Hu et al. 2012; Liu et al. 2014; Pous et al. 2015; Ungureanu et al. 2015; Nicomel et al. 2016.). Our current research program focusses on bioremediation of arsenic found in mine water and waste rock at the relevant in-situ temperatures (about 8 °C) found in northern Saskatchewan mining site waste pits. Arsenic is found in four oxidation states (As^{-3}, As^{0}, As(III) and As(V)) in a variety of species including inorganic and organic compounds that are dependent on the existence of sorbent materials, pH, redox potential (Eh), and microbial metabolic activity (Yong and Mulligan 2004). The As(III) and As(V) states are dominant in water given their higher solubility's versus As^{-3} and As^{0} with As(III) being shown to be potentially 10 times more toxic than As(V) (Jain and Ali 2000). Being more soluble than As(V), As(III) generally needs to be oxidized to As(V) in order to be efficiently removed from various waters (Issen and Frimmel 2003). The determination of the redox state of dissolved arsenic in water samples is important to understand and estimate its toxicity, migration, and geochemical transformation in the environment. Therefore, proper sample preservation technique is essential to stabilize the arsenic states prior to analysis in order to obtain truly representative data in arsenic speciation studies. Knowledge of the oxidation states is also needed for the implementation of appropriate treatment technologies whose efficiencies are typically dependent on the arsenic speciation.

Sample preservation is of a great importance for arsenic, and other heavy metals, speciation research in order to stabilize arsenic species during inevitable time gaps (at least days but sometimes weeks to months) between the sampling and analysis stages. The distribution of arsenic species must be preserved to avoid changes in speciation by processes such as redox reactions, metal oxyhydroxide precipitation, and photochemical oxidation (Bednar et al. 2002). Despite the importance of the issue, limited research has been conducted to develop and/or validate appropriate sample preservation techniques for arsenic prior to speciation analysis. In addition, a detailed standardized method could not be found in the limited previous reported studies (Feldman 1979; Hall et al. 1999; Bednar et al. 2002). Further, there are agreements and disagreements among reported results on sample preservation for arsenic speciation. For example, there is agreement among various research studies that using filtration (Feldman, 1979; US EPA 1982; McCleskey et al., 2004; USGS 2005) is a necessary step prior to sample preservation since it removes microorganisms that can affect arsenic redox species (Wilkie and Hering 1996; McCleskey et al. 2004). As well, the maintenance of samples at 4 °C as a needed step for arsenic speciation sample preservation is commonly agreed upon among previous studies (Quevauviller et al. 1995; Rassler et al. 1998; Daus et al. 2002). However, there are inconsistencies among the previous research studies on the need for acidifying arsenic samples as a necessary step for arsenic preservation. The inconsistency includes whether samples should be acidified or not, in addition to the selection of an appropriate acid for use in the preservation of samples. For example, a more recent study suggested storage without any acidification or addition of other preservatives as necessary to preserve speciation of arsenic (Wolf et al. 2011). In contrast, other researchers have suggested that acidification is needed as one of the steps in arsenic speciation sample preservation (Bednar et al. 2002; McCleskey et al. 2004). The need for the addition of acid to samples for preservation of arsenic oxidation species has been explained by the theory that acidification could reduce oxidation and precipitation of Fe and Mn hydroxides that could potentially precipitate and adsorb arsenic in samples containing arsenic species (Wilkie and Hering, 1996; McCleskey et al. 2004). Clearly, there is a need to investigate the need and impact of various sample preservation techniques to produce accurate analytical results and, subsequently, implement appropriate treatment technologies informed by the determined arsenic speciation.

Given the gap in understanding of sample preservation needs, the developing of a detailed standard method of sample preservation for arsenic speciation has not been well-investigated. Hence, the objective of this paper is to develop an appropriate sample preservation method for maintaining of arsenic speciation in samples through comparison of three different recommended methods based on our literature review including: 1) acidifying using nitric acid (HNO_3); 2) acidifying using ethylenediaminetetraacetic acid (EDTA); and 3) without acidification. All samples were filtered prior to preservation for each method and stored at 4 °C prior to analysis.

The arsenic-containing samples considered currently were taken from ongoing experiments on arsenic bioremediation being conducted by our research team. These experiments have included the addition of a carbon source, molasses, to experimental reactors with a goal of releasing arsenic from mine waste rock and then precipitating the arsenic via microbial activity. The use of real-world samples in the preservation investigation is essential as using standard arsenic solutions would not provide for the potential impacts of matrix effects on the preservation technique. However, we will also include standard arsenic As(III) and As(V) solutions, and mixtures, in future research work as standards for analytical comparisons. Standard solutions of As(III) and As(V) (as well as mixtures) were analyzed without preservation using the hard X-ray microanalysis (HXMA) beamline at the Canadian Light Source (CLS) synchrotron prior to commencing the current project. The HXMA beamline methodology is used as a comparison to the preserved samples in the current study given its ability to show real-time As(III) and As(V) speciation without preservation. It should be noted here that the HXMA results are qualitative, not quantitative, thus indicating only the existence of the species and not the actual concentrations. In addition, the use of the CLS is prohibitively expensive for consideration as an arsenic speciation methodology for general samples.

2 MATERIALS AND METHOD

2.1 Overview of Arsenic Bioremediation Experiment

For clarity of understanding of the samples used in preservation experiments and results, the bioremediation experimental setup is described briefly herein. The arsenic bioremediation experimental set up included treatment (molasses), positive control, and negative control reactors (Figure 1). The positive control included waste rock and mine water without supplementation with a carbon source. The negative control included sterile (achieved by autoclaving) waste rock and water amended with sodium azide to inhibit microbial growth.

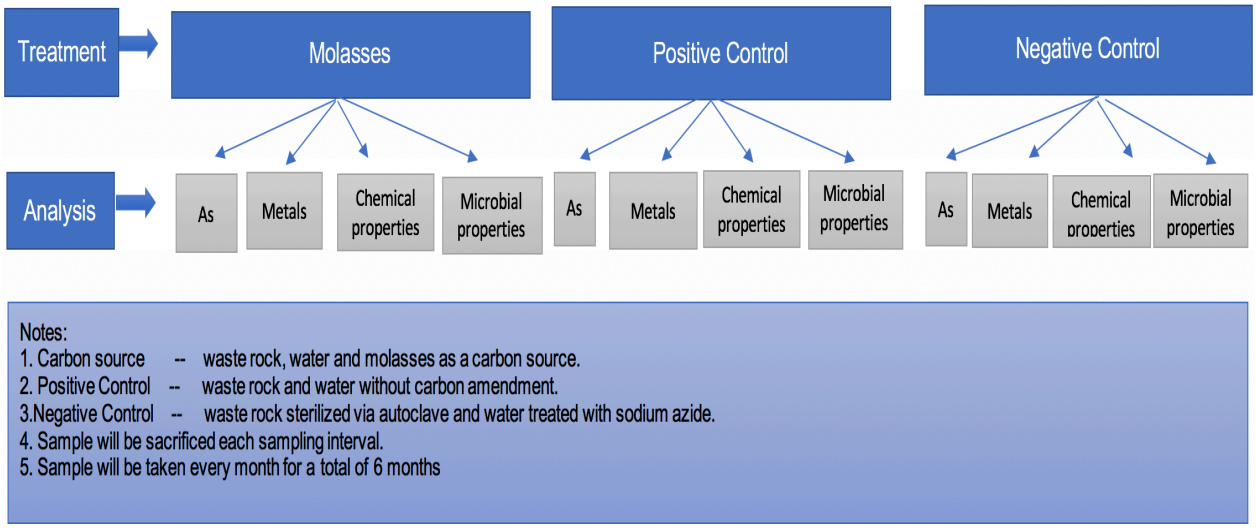

Figure 1: Schematic of experimental setup to assess bioremediation potential for arsenic removal from waste rock water. Notes indicate experimental details with analysis including arsenic (As) speciation, metals, physicochemical and microbial properties

Treatment reactors included molasses added as a carbon source to help promote microbial growth and metabolism, mine water, and mine waste rock. The waste rock and water were collected from a uranium mining site in northern Saskatchewan, Canada. The reactors were prepared in 2 L glass vessels containing 500 g of mine waste rock and filled to a total volume of 1.7 L with mine water. The reactors were prepared in several anaerobic bag chambers that were continuously flushed with nitrogen and air was continuously vacuumed to prevent oxidation of arsenic in air (Figure 2). Each of the reactors were saturated with nitrogen

up to the point that the dissolved oxygen of the water in the reactors was less than 0.1 mg/L, thus creating an anaerobic condition for the duration of the experiments. Each anaerobic chamber included three reactors: a positive control, a negative control and a molasses amended reactor. Six sets of anaerobic bag chambers containing 18 reactors in total were prepared and stored in the dark in an 8°C controlled temperature chamber at the Phytotron facility at the University of Saskatchewan. Starting after one month, a set of three reactors was sacrificed for sample preparation for completing a suite of analyses once a month for a total duration of 6 months.

Water samples were collected from each reactor for arsenic speciation As(III) and As(V) that was conducted using an ion exchange speciation technique at the environmental laboratory of Saskatchewan Research Council (SRC). Prior to the arsenic speciation by ion exchange, 50 mL from each sample were filtered using 0.45 μm glass fiber membrane filters. The samples were then acidified with 0.5 mL of concentrated HCl acid before being stored at 4 °C before sending to the SRC. The final set of sampled reactors (after 6 months of storage) were used for the experiments at the Canadian Light Source Synchrotron HXMA beamline (CLS).

Figure 2: An example experimental anaerobic bag chamber shown in the controlled temperature chamber in the Phytotron facility of the University of Saskatchewan

2.2 Overview of Sample Processing and Preservation

The experimental schematic used to investigate the different sample preservation methods of the bioremediation experiment samples is depicted in Figure 2. Sample preservation for arsenic speciation was investigated using three well-known methods including: (1) acidifying with 1% EDTA; (2) acidifying with 2% HNO_3; (3) and without acidification. Both the EDTA and HNO_3 were analytical grade acids. Each of these methods was used for each of the treatments including molasses, positive control, and negative control using the 3 month sample of the bioremediation experiments. Samples were prepared directly in the prepared anaerobic bag chambers under anaerobic condition in which the chamber was flushed with nitrogen and inside air was vacuumed continuously to maintain the anaerobic conditions. All samples were filtered using a 0.45 μL filter and placed into Nalgene plastic bottles. Acidification with EDTA and HNO_3 were conducted in compliance with the procedures recommended by United States Geological Surveys (USGS) and US EPA Method 600, respectively (US EPA 1982; USGS 2005). The prepared samples were

maintained in an anaerobic chamber filled with nitrogen at 4 °C and a dark negative pressure room until removal for analyses.

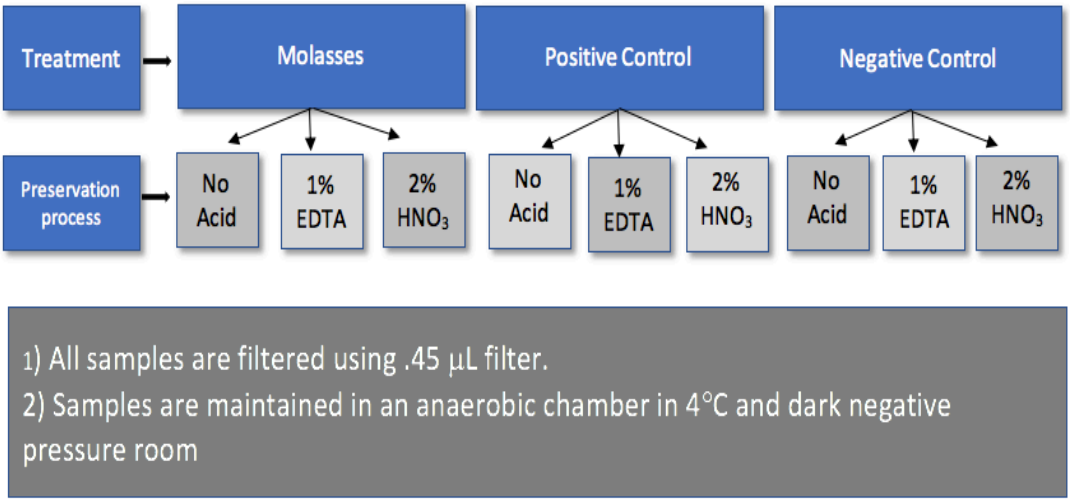

Figure 3: Schematic of the sample preservation techniques including no acid, 1% EDTA, and 2% HNO_3. Positive and negative controls follow Figure 1 notes

2.3 Sample Preservation Details and Timeline

Table 1 summarizes the sample preparation details and timeline. To investigate the different proposed preservation methods, sampling from the reactors were conducted first on November 2018. In total, 12 samples were prepared from three different reactor treatments (molasses, positive and negative controls) of which three samples were analyzed immediately to determine arsenic species concentrations of the fresh samples. The remaining nine samples (three for each treatment) were preserved for the later analyses for comparison to the fresh sample speciation. Each of the samples collected from the reactors were preserved via the three different preservation methods as discussed in section 2.3. Analysis of the preserved samples were conducted in SRC lab on January 2019 after maintaining the samples for 106 days (approximately 3 months). Further samples will be analyzed after approximately 6 months and 12 months; these samples are not included in the current study scope.

Table 1: Sample preservation details and timeline

Sample	Preservation process	Date of analysis (fresh sample)	Date of analysis (preserved samples)	Future sampling (preserved samples)
Molasses, Positive control, Negative control	None	14 Nov/2018		
Molasses	2% HNO_3 1% EDTA No acid		28 Jan/2019	Apr 2019 and Nov 2019
Positive control	2% HNO_3 1% EDTA No acid		28 Jan/2019	Apr 2019 and Nov 2019
Negative control	2% HNO_3 1% EDTA No acid		28 Jan/2019	Apr 2019 and Nov 2019

2.4 Brief Overview of CLS Arsenic Speciation Experiments

For the preparation of standard arsenite (As(III)) solutions (using As_2O_3), sodium hydroxide was added to the solution to increase the pH as As(III) does not readily dissolve in water at neutral pH. The solution was then neutralized using sulfuric acid and subsequent dilutions were used to prepare various standard solution concentrations ranging from 1 to 1000 ppm. No pre-treatment of the water was needed for preparing the stock solution of arsenate (As(V)) and similar dilutions were used to created concentrations ranging from 1 to 1000 ppm. Standard As(III) and As(V) solutions (various ratios) were prepared and pipetted into a CLS beamline sample holder and covered with Kapton tape prior to placement in the HXMA beamline. All the beamline experiments were conducted at room temperature.

For arsenic speciation, a technique was developed to determine arsenic speciation in water samples. It was previously reported that X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were able to measure thioarsenates and thioarsenites in solution (Suess et al. 2009). Thus, a similar experimental design was used for the current arsenic speciation experiments. We found that the EXAFS experiments required the HXMA beamline (BL) to use a Si(111) monochromator crystal and an Rh mirror. During the experiments, the BL monochromator energy was first calibrated by using a gold metal standard foil kindly provided by XAFS Materials Inc. The data collection mode was in the transmission mode for concentrated samples and the fluorescence mode for the low concentration samples. The gold standard foil was placed between the ion chamber detectors I1 and I2 throughout the experiment. A stepwise energy calibration was made for each XAFS scan. The arsenic K edge data acquisition configuration was front edge (-200 to -40 eV), 10 eV / step, 1-2 sec / point; edge area (-30 to 50eV), 0.25 to 0.3eV / step, 1-2 Seconds/point; EXAFS area (50eV to 13k), 0.05k / step, 1-2 to 5-10 seconds / point.

3 RESULTS AND DISCUSSION

3.1 HXMA Beam Analysis

For the arsenic speciation in the HXMA beamline of CLS, standard solutions of each of the individual arsenic species were used to determine the detection limit of the beamline. The detection limit research is out of scope for the current study and will be presented elsewhere. As seen in Figure 4, six variations of the different arsenic species solution mixtures were tested. For the first sample tested in the CLS, 125 ppm As(III) solution and 375 ppm As(V) solution were mixed and pipetted into the sample holder, covered with Kapton tape. The result indicated a low concentration for As(III) and high concentration for As(V) were found in the analysis for this sample. For the second sample, 250 ppm solution for both As(III) and As(V) were equally mixed. For this sample, two peaks were expected: one for As(III) and for As(V). However, only As(V) peaks were observed in the analysis as shown in Figure 4. In all other samples where higher concentration of As(III) solutions were mixed with lower concentration of As(V) solution, peaks for As(V) were observed in HXMA beam analysis as depicted in Figure 4. These results suggested that the use of room temperature experiments and the creation of aerobic conditions were leading to the rapid oxidation of As(III) to As(V). This was an interesting result showing that samples collected for analysis that are anaerobic (likely containing As(III) as the dominate species) could easily be oxidized and incorrectly determined to be As(V). Therefore, this result indicates the need for sample preservation as an essential issue in As speciation studies. Further HXMA beamline studies were later conducted using flash-freezing of samples as a sample preservation technique specific to the CLS beamline. However, this technique is not feasible for standard analytical instruments and for use by those collecting samples for analysis under typical conditions in the field or laboratory environments.

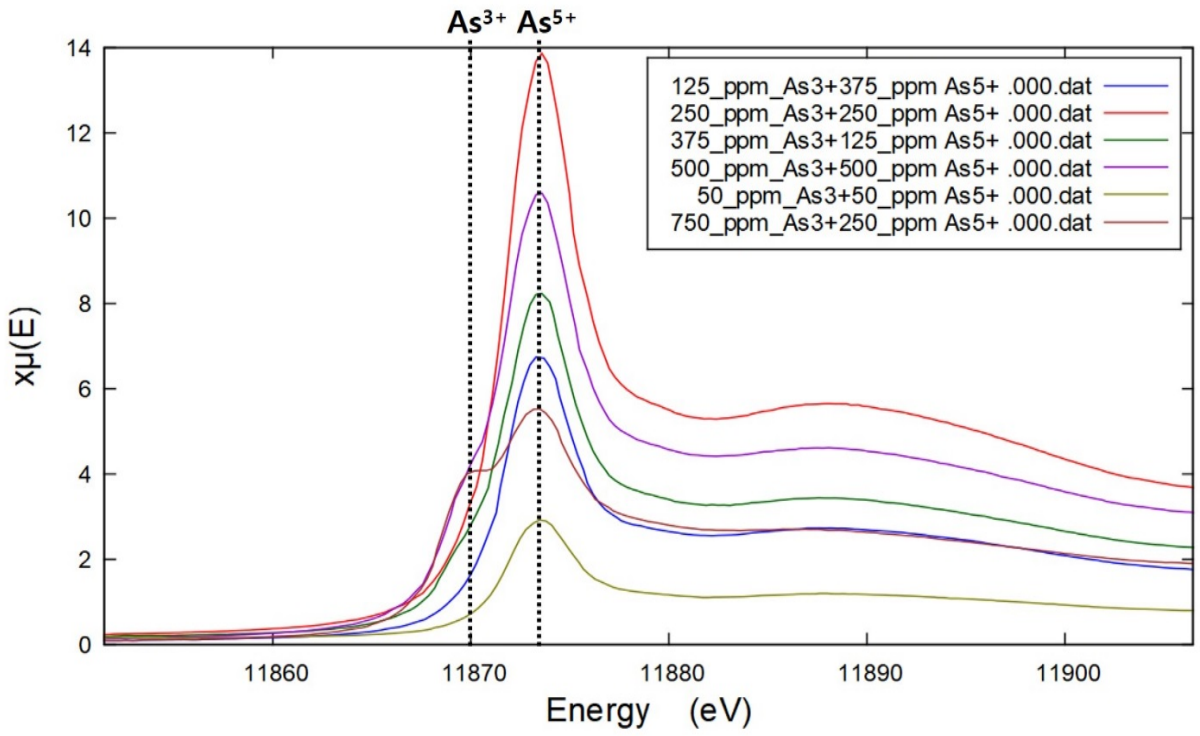

Figure 4: Standards of various arsenic species mixtures measured using the HXMA beamline of the CLS at room temperature

3.2 Evaluation of Preservation Methods

Initial As(III) and As(V) concentrations (Day 0) were measured for samples prepared from a molasses, a positive control and a negative control reactor in November 2018. However, these samples were incorrectly processed by the SRC laboratories due to improper amounts of resins used for the ion exchange speciation method. This resulted in inaccurate concentrations, however, the results could be compared on a qualitative rather than quantitative method (results are not presented herein due to space limitations). Based on this, it was apparent that the As(III) concentrations were significantly higher than As(V) concentrations as would be expected given the anaerobic conditions of the processed samples. Using this information, the expectation was that the preserved samples should also have As(III) dominated concentrations if the preservation technique was successful.

Preserved samples were analyzed for arsenic speciation after 106 days in January 2019 as illustrated in Figure 5. In general, without taking preservation into consideration the overall arsenic concentrations were highest in the molasses treatment and similar for the positive and negative controls. This result has been unexpected for our bioremediation as it was expected that the carbon amended treatment would release arsenic from waste rock and then bacteria would metabolize and precipitate out the arsenic. However, this process was not occurring, or was rate limited, leading to the bacteria aiding the release of arsenic from waste rock and increasing the water concentration. Further research to capture (or prevent the release) the released arsenic is currently underway in our research lab.

As shown in Figure 5, the preservation via acidification with HNO_3 oxidized all three of the treatments with the decrease of As(III) and subsequent increase in As(V). This oxidization was highest for the molasses sample, considerable for negative control sample and low for positive control samples. Oxidization by acidification was also observed for the preservation via EDTA with a similar magnitude to HNO_3 for the molasses treatment samples where arsenic concentration was initially higher than two control treatment samples. However, unlike HNO_3, the oxidization impact of EDTA showed little impact on the preservation of the positive and the negative control samples in which initial arsenic concentrations were considerably

lower than molasses sample. In contrast to the acid treatments, the no acid preservation treatment showed an excellent performance for sample preservation of arsenic speciation for both of the molasses and positive control treatment samples. This better performance of preservation lacking the use of an acid for arsenic samples was suggested previously in a study conducted by Wolf et al. (2011). However, a precipitation issue for the no acid preservation was observed in the negative control treatment sample that was not found in the acidified samples. This phenomenon of adsorption of arsenic to Mn and Fe hydroxides in the absence of an acid, followed by their co-precipitation has also been reported by previous studies (Wilkie and Hering, 1996; McCleskey et al., 2004). It is unknown why this occurred in only the negative control reactors, thus further work is needed to determine if this result was only an outlier for the current research. Overall, we suggest that the elimination of acidification would be the best approach for sample preservation as it simplifies the sample processing and provided the most consistent performance for the preservation of speciation.

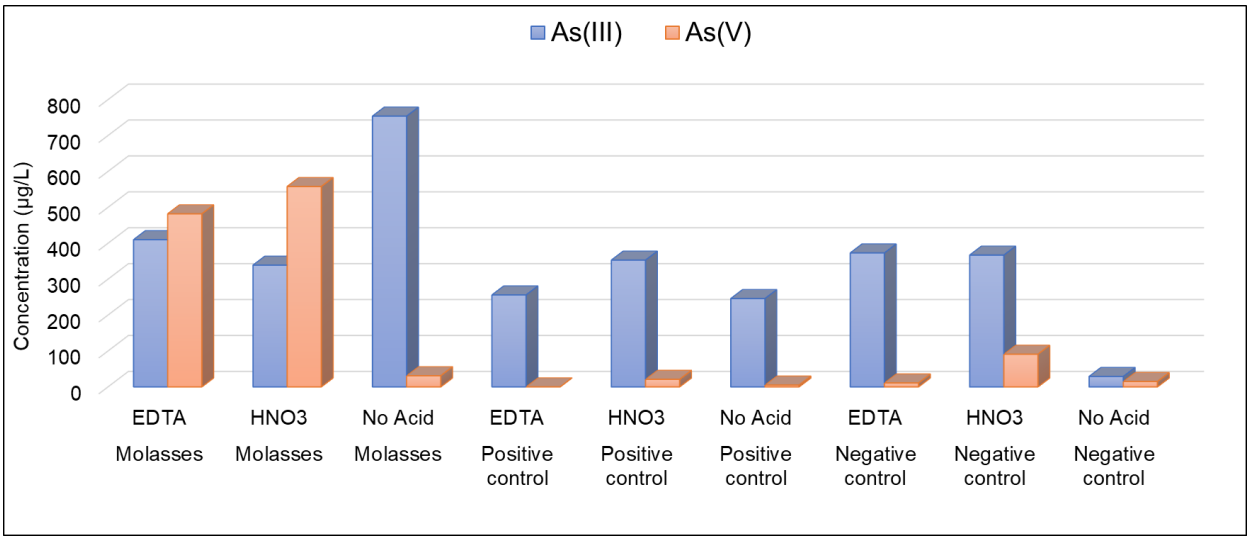

Figure 5: Comparison of three preservation treatments for different samples speciation analysis

4 CONCLUSIONS

Industrial activities like mining lead to the creation of wastewaters that need to be treated prior to release into the receiving environments. The selection and implementation of appropriate treatment technologies relies on the accurate characterization of contaminants found in these waters for their efficient treatment. Currently, our research group is investigating the treatment of arsenic-contaminated mine waters. This research success is highly dependent on the knowledge of arsenic speciation in each treatment. In general, samples used for analysis of arsenic need to be properly preserved prior to their analysis to have accurate speciation results. We found that filtered samples stored at 4 °C without acidification provided the best results for maintaining appropriate arsenic speciation. For the current study, this methodology maintained the appropriate As(III) species composition as compared with acidification which created As(V) not found in the non-preserved samples (or would be expected under anaerobic treatment conditions). This result will simplify the collection of arsenic samples, especially in the field, given the elimination of the need for acids to be used. However, the impact of the elimination of acidification may need to be determined for accurate analyses of other metals and metalloids in preserved samples.

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