

# Arsenic Team Final Report

Tanapong Jiarathanakul, Imtiaz Karim, Michelle Wagner

December 14, 2013

## Part I Introduction

The AguaClara Arsenic team for the Fall 2013 semester is the first to begin testing different methods of removing arsenic from drinking water. The initial goal was to develop a reliable method for testing water treatment alternatives and be able to detect small concentrations of arsenic. The work this semester follows the literature review performed in Spring 2013 which evaluated alternative arsenic testing methods and water treatment options for arsenic removal. A key issue is the need to measure low levels of arsenic (below ten parts per billion). Over the summer a graphite furnace atomic absorption spectrophotometer (GFAAS) was repaired for use in arsenic analysis. The lamp and power source of GFAAS have been replaced to improve the arsenic detection limit and the team is learning to operate the instrument. We will be using different coagulants to see which provides the best adsorption of arsenic to remove it from water, and different sample processing methods to simulate larger scale treatment processes. The team has a designated area for handling the solutions and samples as arsenic is toxic and we would like to minimize the contact it has with any person or object in the lab. The issue of arsenic waste is also a concern and this is why we are performing experiments using small sample volumes in order to reduce the amount of toxic waste produced.

## Part II Methods and Materials

Our current method of sample processing and analysis was proposed by Professors Lion and Weber-Shirk. To keep the testing system at a small scale, we will be using plastic vials of approximately one milliliter as our reaction chambers. The AguaClara treatment process train uses flocculation, sedimentation, and filtration in the current full scale system and we will be simulating these processes in the lab. We will add a microliter quantity of coagulant to vial containing a simulated groundwater containing arsenic. The mixing achieved in a flocculator will be accomplished in the lab by placing the vials into a tumbler which will ensure even mixing of the arsenic and coagulant. To mimic sedimentation we

will be using a micro-centrifuge to spin the flocculated particles to the bottom of the vials. If we wish to mimic filtration, the vials that we use will have a filter basket in them. The baskets have micropores to allow the flow of water, but not the arsenic-coagulant flocs. The centrifuge will provide the force necessary to pass the water through the filter as the pore sizes are on the order of micrometers. Some papers which we have looked into have considered using a coated sand filter to adsorb arsenic, and so our team is considering pre-treating our microfilters by centrifuging a precipitated coagulant suspension through the filter before the sample containing arsenic is processed.

## Part III Preparation

Prior to any experimentation, we had a few preparation tasks to complete. Safety is a priority. Since arsenic is a known carcinogen that is odorless and colorless, we had to create a secure lab space so that individuals will not be accidentally exposed to arsenic. We discussed lab space options with Casey Garland and selected a section of first floor laboratory (HLS 150). Next, we collaborated with Bill Leonard from Cornell University Environmental Health and Safety Department to establish proper signage and toxic waste disposal area. We also taped off the lab space area to visually and physically warn individuals about toxic chemicals in the area. A sign has been placed on a string which will further deter people from entering the testing area when we aren't working there.

Once the lab space was secured, we began working to obtain the needed equipment for the experiments. We located a tumbler, which will act as a flocculator for the samples. The device was not functional initially and was repaired by the CEE shop. We also found an operable centrifuge, which will be used for sedimentation of floc. Next, we worked to identify a suitable small vessel that can be used to carry out experiments. This vial has to fit in both the centrifuge and the carousel tray in the GFAAS. Professor Richardson gave us a variety of centrifuge tubes to test. These tubes come in two sizes both with sloped bottoms: 1,000 uL and 500 uL. Unfortunately, neither size fits the carousel slot. The large one was too wide, and the small one was too tall. The GFAAS also has its own 1000 uL tube, which fits the carousel perfectly. However, it does not fit the centrifuge that is available. Therefore, we came up with a hybrid solution, which is to place the small 500 uL centrifuge tube inside the GFAAS tube. By using this method, the sample vessel will be stable when placed in the carousel in GFAAS. However, when placing the centrifuge tube inside a GFAAS tube, the opening on the tube will be elevated higher than normal height of a GFAAS tube. Therefore, we need to ensure that this change in height will not impede the operation of the machine in any way. We also acquired two pipets to use in our experiment. One has a range of 100 uL to 1000 uL and the other has a range of 10 uL to 100 uL.

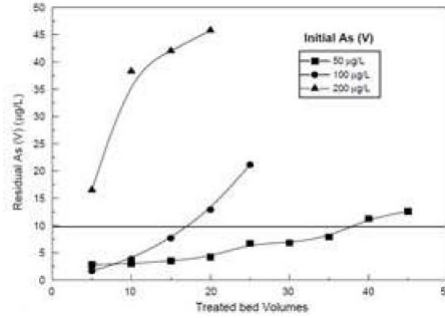
Finally, we have to prepare the GFAAS for use. The GFAAS plays a critical role in our experiment for it is our only means to determine the concentration of arsenic in our samples. Therefore, we need to learn and understand both the hardware and software of the machine. Another important aspect of GFAAS is its calibration. Since the calibration determines the accuracy of the arsenic concentration, we must be able to precisely and carefully calibrate the machine.

## Part IV Prior Research

Zouboulis and Katsoyiannis [3] conducted research showing that a combination of coagulation and filtration was an effective method of removing arsenic. From their work we can see removal percentages of at least ninety percent. The concentration levels which they were working with were less than one part per million and they recorded levels (after treatment) of tens of parts per billion. This is the range of concentrations which we hope to be working in. Their arsenic solution was created using disodium acid arsenate heptahydrate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ), and was diluted with tap water. They took note of the conductivity, hardness, and turbidity of the water before diluting the arsenic solution. In our experiments, we plan to use a “groundwater recipe” from the United States Environmental Protection Agency. This recipe mimics a general groundwater by containing ions which are commonly found in most groundwaters, and so this is what we would use to dilute our arsenic compound with for testing. They used both iron and aluminum based coagulants and found that the polymeric form of both types of coagulants produced better removal percentages. We are planning on using polyaluminum chloride (PACl) in our experiments to begin with, but certainly plan on trying a few other coagulants as well to see if we can produce better results. In order to measure their arsenic concentrations, Zouboulis and Katsoyiannis [7] used a Molybdenum Blue Photometric method as well as a Hydride Generation method. The molybdenum blue method was used for concentrations on the order of a part per million; the molybdenum complexes the arsenate and a photometer and a calibration curve can be used to determine the concentration of arsenic. The hydride generation method was coupled with atomic absorption spectrometry to measure the concentration of low levels of arsenic. In this method arsenic reacts with sodium borohydride to produce arsine which is measured by the AAS. The hydride generation method was used for part per billion levels of arsenic and could be a possible option for our testing if we could get this process to work on small sample volumes.

Katsoyiannis and Zouboulis [3] also conducted experiments on removal of arsenic using adsorptive filtration, which is an emerging technology in water treatment. The method involved coating the surface of polymeric materials (polystyrene and polyHIPE) with appropriate adsorbing agents (iron hydroxides). Arsenic in both III and V oxidation state was diluted with tap water to achieve concentrations ranging from 200 ug/L to 50 ug/L, which is a typical range of arsenic

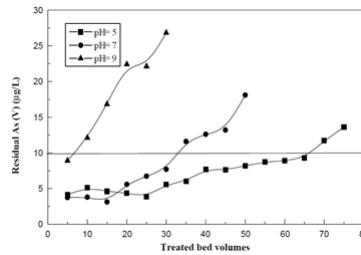
concentrations in Greece. The experimental results show that this method effectively reduced arsenic concentration from 100 and 50 ug/L down to about 2 ug/L, however it was not as effective for removing high levels of arsenic concen-



tration as shown in Figure 1.

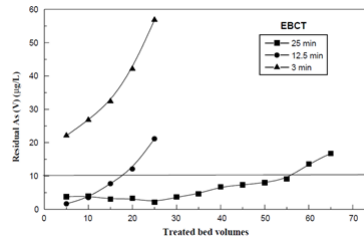
Figure 1. Effect of initial As(V) concentration on residual As at pH = 5, linear velocity = 2.7 m/h and [Fe]coat = 0.025 M

Katsoyiannis and Zouboulis also discovered that arsenic removal capability varies greatly with pH level (Figure 2) and empty bed contact time (EBCT)(Figure 3), and found the optimum level to be pH = 7.0 and EBCT = 12.5 minutes for



both As(V) and As(III).

Figure 2. Effect of pH on As(V) removal at [As] = 50 ug/L, linear velocity =



0.7 m/h, [Fe]coat = 0.025 M

Figure 3. Effect of empty bed contact time (EBCT) on As(V) removal at [As] = 100 ug/L, pH = 5.0, [Fe]coat = 0.025 M

We can apply some of the results of this study to our research including the following:

1. We need to estimate the range As(V) concentration in groundwater in India and Honduras in order to establish our experimental solutions, yet we will keep concentrations below 50 ppb for safety reasons.
2. We need to consider the effect of pH on arsenic removal efficiency and determine the best chemical to lower the pH. Professor Lion suggested nitric acid to lower the pH of samples since the resulting nitrate anions in the solution are relatively inert with respect to forming complexes.
3. We need to study the performance of other filter coating agents.
4. We need to study the benefits and costs of adsorptive filtration method as compare to other arsenic removal techniques.

In the paper “Comparisons of Polymeric and Conventional Coagulants in Arsenic (V) Removal”, written by Maohong Fan, et. al (2002) [5] the authors evaluated the effectiveness of coagulants such as polymeric ferric chloride, polymeric ferric sulfate, polymeric aluminum chloride, polymeric aluminum sulfate, ferric chloride, ferric sulfate, aluminum chloride and aluminum sulfate in the arsenic removal. They analyzed some coagulation conditions including temperature, pH, type of coagulant, the addition of a coagulant aid, and the initial arsenic concentration. The results of this study showed that the polymeric and iron-based coagulants were more efficient than conventional and aluminum-based coagulants. The investigators concluded that the effects of filtration on arsenic removal were more significant at lower coagulant dosages. The authors evaluated whether activated silica, used as a coagulant aid to facilitate coagulation, would have different effects on the arsenic removal abilities of polymeric and conventional coagulants, and the results demonstrated that the silica did improve As removal; moreover, the polymeric coagulant ferric sulfate was the least affected by the addition of activated silica and the conventional coagulant aluminum sulfate was the most affected. The experimental results also indicated that pH has a significant influence on the arsenic removal process. Arsenic removal by polymeric and iron-based coagulants was less influenced by pH than conventional and aluminum-based coagulants and at lower pH (for example pH =5.5) the removal of arsenic is more effective. Finally, initial concentrations of arsenic in the range of 6 to 160 ug/L seemed to have no effect on arsenic removal efficiencies (as a percentage) by both the polymeric and conventional coagulants studied. These previous results are very important for our research of arsenic removal, since they show how the coagulation conditions affect removal, and it is essential to comprehend and analyze the differences that each variable can make. To optimize the removal of arsenic, a range of conditions may need to be tested.

# Part V Completed Tasks

## Dilution Series

We have completed a dilution series with methylene blue, and William Penock prepared arsenic standards. The methylene blue was used as a way of practicing our dilution techniques and to see if we could create good standard curve before we began to involve ourselves with any arsenic compounds. This dilution series included concentrations of 1-5 mg/l of methylene blue and the solutions we made were then analyzed for concentration in a UV/visible diode array spectrophotometer. We got very good results from this exercise and our data produced a correlation value of 0.9978 (Figure 4 below shows these results).

In order to calibrate the GFAAS calibration curves for arsenic dilution series were made both manually and automatically. The diluent used was 0.2% nitric acid ( $\text{HNO}_3$ ) and the solution sample was the arsenic stock solution in the following concentrations: 0 g.L-1, 20 g.L-1, 30 g.L-1, 40 g.L-1 and 50 g.L-1. An electroless discharge lamp (EDL) was used, in tandem with graphite furnace tubes that contain a sample platform. The As lamp current was 300 mA.

One series of As standards was created automatically by the GFAAS. The instrument initially withdrew the necessary volume of diluent ( $\text{HNO}_3$  0.2%) from one sample location, and then it went to the As stock solution, with a concentration of 50 g.L-1, and it withdrew the necessary volume of solution. Then, it deposited the mixture in the graphite tube for analysis and recorded the resulting absorption peak areas and peak heights.

A series of manually diluted As standards ranging from 10 to 50 g.L-1 in 0.2%  $\text{HNO}_3$  was also prepared and analyzed.

The calibration curves were created using Excel, and they interrelate the peak areas, and peak heights with the As concentrations of 0 g.L-1, 20 g.L-1, 30 g.L-1, 40 g.L-1 e 50 g.L-1 in order to obtain the equations and the regression coefficient  $R^2$ , which should be close to 1. Unfortunately, the calibration curves were not what we expected, since the  $R^2$  coefficients were low. We have thought of some strategies to fix this. One option is to add a matrix modifier, which would hold the analyte on the graphite surface to a higher temperature for better atomization, by decreasing the volatility of the analyte. Also, we can increase the 20 L sample volume or try to make multiple sample volume additions, with a dry cycle between them.

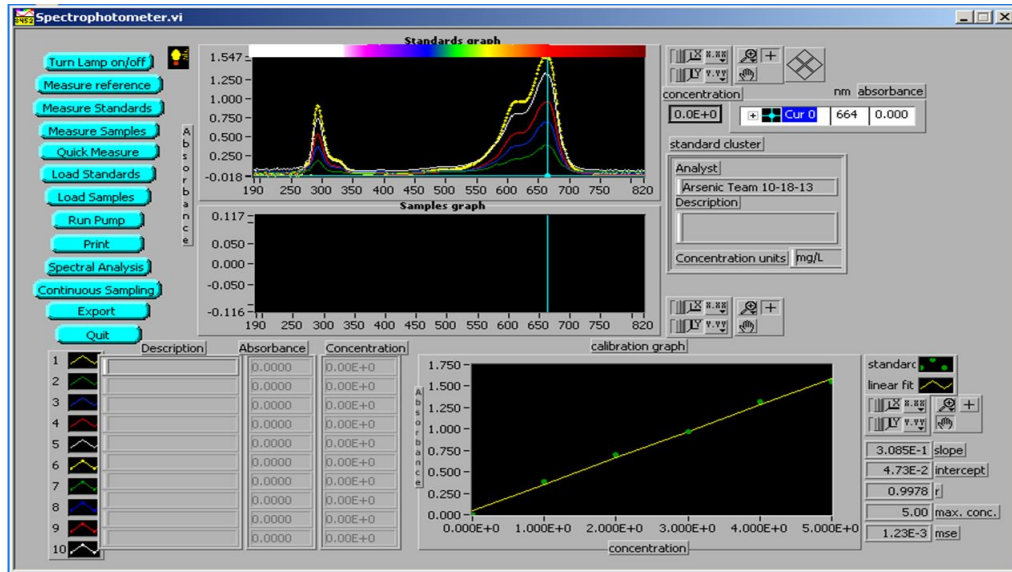


Figure 4. Spectrophotometer results from Methylene Blue calibration exercise.

## Preliminary Exploration of Testing Procedure

Before testing with arsenic, we have to set a standard experimental procedure in order to create consistency. There are several testing attributes that we have to determine. In this preliminary exploration, we aimed to test the capacity of the centrifuge to deposit flocs of precipitated coagulant. The first round of testing included four standard 1-mL centrifuge tubes. These tubes contained PACL at concentrations of 0.2, 2, 20, 200 mg/L in groundwater solution. The total volume of the sample was 1 mL. Since tumbler was not available at that time, these tubes were shaken by hand to simulate rapid mix and flocculation for 1 minute. They were then placed in a centrifuge for 5 minutes spinning at power of 5. After the tubes were removed from the centrifuge, there was no observable deposition or sedimentation on the side or bottom of the tubes (see the top row in the image below).

Since the result was not what we expected, we questioned whether the centrifuge was able to separate suspended solid. Therefore, we decided to conduct another experiment to test if there will be any sedimentation if we add high concentration of kaolin clay to the sample. Four tubes were prepared using the same concentrations of PACl as the first round, however, this time we added 100 mg/L of kaolin clay to each tube. These tubes were manually shaken and placed in the centrifuge using the same duration and power as previous test. Visual observation showed that floc firmly deposited on the side

and bottom of the tubes, which are shown on the bottom row in Figure 5.



Figure 5. Preliminary sedimentation testing. First row contains PACl at .2, 2, 20, and 200 mg/L concentrations in groundwater solution. Second row contained 100 mg/L of kaolin clay with PACl at 2, 2, 20, and 200 mg/L concentrations in groundwater solution.

Since the result of the second preliminary test showed that centrifugation is an effective method to mimic sedimentation, we revisited the result of the first test and analyzed why no deposition occurred. After consulting with Professor Weber-Shirk and Professor Lion, we came up with two hypotheses. First, concentrations of ions in the groundwater and PACl are very low, thus no observable deposition should occur. Second, the pH of the solution influences precipitation of coagulant. Since PACl is most effective in the pH range around 7, if the synthetic groundwater was slightly acidic or basic, the PACl will not behave properly. We tested the pH of the groundwater stock using a hand-held pH meter and found that it is slightly basic with a pH of 7.98, which should not be a problem.

Since we had performed preliminary solids separation tests with observable results, we expanded on these tests to identify the best testing procedure to mimic real flocculation, sedimentation and filtration processes. In order to compare solids separation results, we must be able to measure the turbidity in NTU. Therefore, we created three calibration curves using a UV/visible spectrometer with known concentrations of turbid solution as the samples. We analyzed the solutions at a wavelength of 600 nm as this is where the clay spectra tends to peak. All samples came from a stock of 100 NTU clay suspension.



First, we used the following concentrations: 1, 2, 3, 4, 5 and 6 NTU. However, these concentrations proved to be low, and the resulting calibration curve was not precise, with a correlation coefficient = 0.6297 (Figure 6).

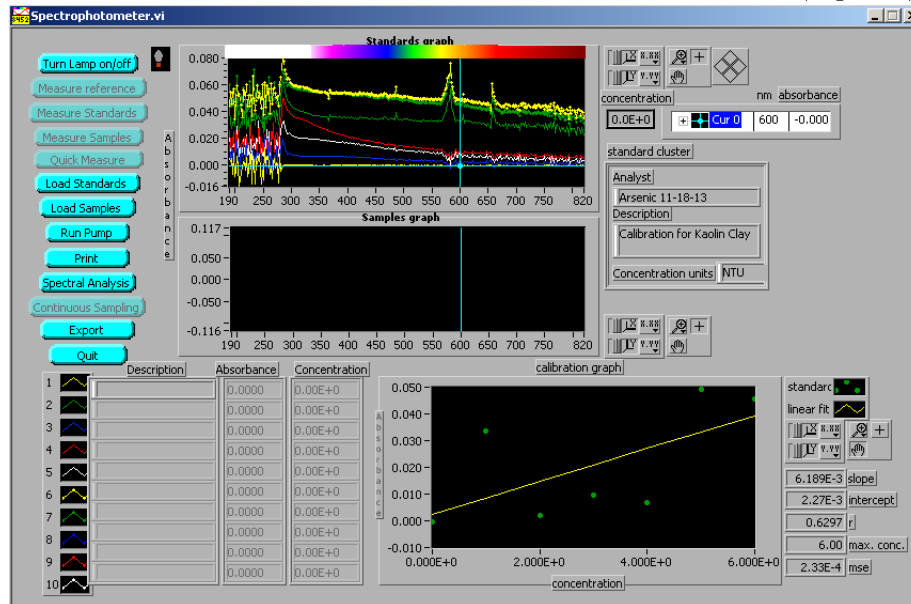


Figure 6. First Clay Calibration Curve

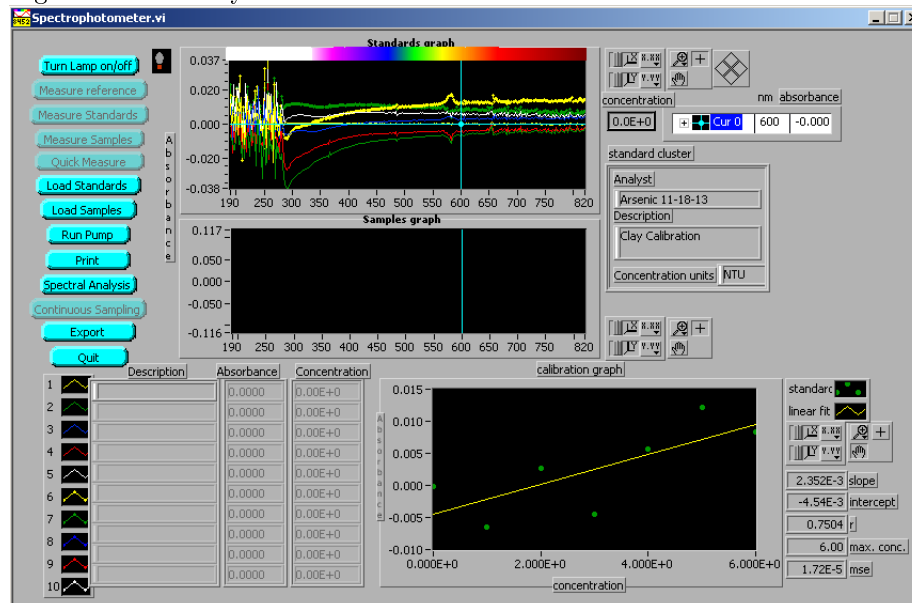


Figure 7. Second Clay Calibration Curve

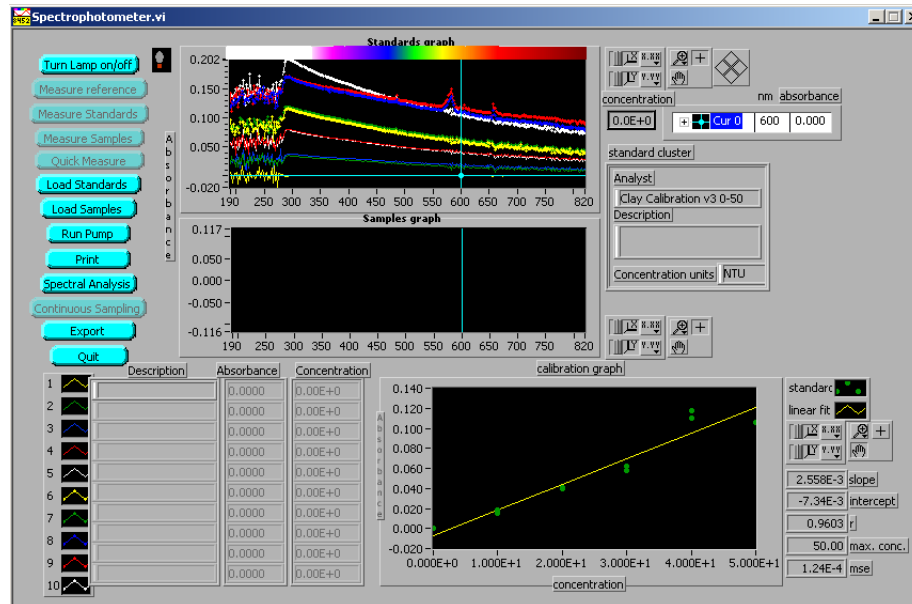


Figure 8. Third Clay Calibration Curve

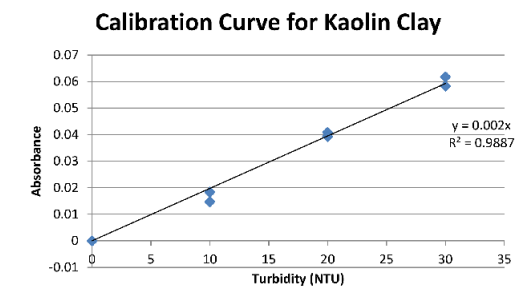


Figure 9. Calibration curve for kaolin clay using samples of known turbidity (0, 10, 20 and 30 NTU)

In order to determine the best solids removal technique, we set up an experiment to test two factors. First, we wanted to test the removal efficiency among four types of testing vessels: a centrifuge tube with coagulant dose (flocculation and sedimentation), a tube with coagulant dose and a filter basket (flocculation and filtration), a tube with a coated filter basket (pre-treated filtration) and tube with coagulant dose with a coated filter basket (flocculation and pre-treated filtration). Second, we wanted to observe the removal efficiency with different concentrations of coagulant. We tested PACl concentrations of 2, 20 and 200 mg/L. Therefore, we had three tests for each type of vessel, each with 5 NTU of kaolin clay and groundwater solution. To summarize:

Case A: Centrifuge tube with 5 NTU clay, groundwater and three different concentrations of PACl with a total volume of 1.5 mL.

Case B: Filter basket tube with clay, groundwater and three different concentrations of PACl with a total volume of 0.9 mL.

Case C: PACl-coated filter basket tube with clay and groundwater only with a total volume of 0.9 mL.

Case D: PACl-coated filter basket tube with clay, groundwater and three different concentrations of PACl with a total volume of 0.9 mL.

The pre-treated filter was created by centrifuging a concentrated solution of PACl (2 g/L) through the filter basket in a centrifuge using power of 1 for 10 minutes.

When all preparations of solutions were completed, all the tubes were rotated in the tumbler to mimic mixing and flocculation for 5 minutes. Then, the tubes were moved to a centrifuge, which ran at power of 1 for 10 minutes. Once completed, we removed samples using a pipette and used a spectrometer to determine the residual turbidity. Note that for Case A, we had to avoid resuspension of settled particles when pipeting solution to the spectrometer cuvette. Therefore, we wanted to remove as little volume of the sample as possible while getting accurate results from the spectrometer. In order to determine the minimum volume needed to perform spectrometry, we ran tests on the spectrometer using an incremental volume of de-ionized water of 0.3 mL from 0 to 1.5 mL. We found that the spectrometer started to detect the solution at 0.6 mL.

The result of this experiment is shown in Figure 10 below. From this result, the best removal techniques are coated filtration with and without PACl dose in the solution. The both were analyzed to give predominately negative values for turbidity, which imply zero NTU. On the other hand, the results from sedimentation and filtration are puzzling. The turbidity for sedimentation technique varies quite dramatically with each concentration of PACl. We suspected that this could be caused by resuspension of clay during the transfer of solution from the centrifuge to the spectrometer. However, we do not have an explanation as to why the turbidity increases with PACl concentration for filtration technique. Since there were discrepancies in the results, we decided to rerun the experiment with duplicates to obtain more reliable results.

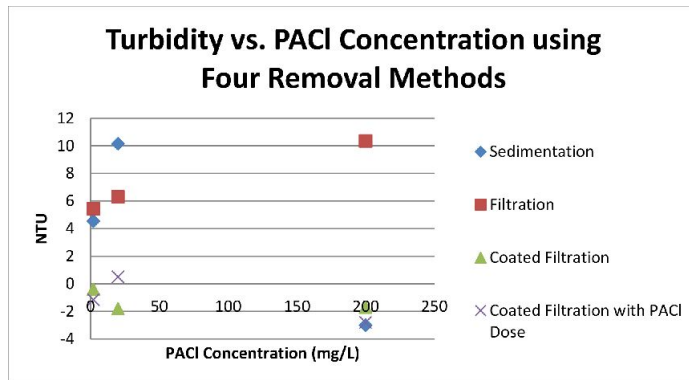


Figure 10. Turbidity remained in each sample for each type of treatment at PACI concentration of 2, 20 and 200 mg/L.

## Materials and Equipment

We have successfully acquired all materials and equipment necessary to our future research. These items are listed below.

- Safety equipment and features:
  1. Syringes
  2. Chemical labels
  3. Tinted lab goggles
  4. Lab coats
  5. Secondary containers
  6. Gloves
  7. Hazardous waste containers
- Research equipment and supplies:
  1. GFAAS
  2. Centrifuge
  3. Tumbler
  4. Sampling tubes
  5. Micro pipets and micropipet tips
  6. Various flasks and bottles
- Chemicals
  1. Liquid arsenic standard (1 g/L)
  2. Nitric acid solution (2%)
  3. Synthetic groundwater components (see list below)

## Synthetic Groundwater

Since arsenic contamination often associates with groundwater, we wanted to create an aqueous condition that mimics groundwater as closely as possible. Based on the previous year's research, we decided to implement the National Sanitation Foundation International standard (NSFI-53). This is the standard challenge water for testing arsenic adsorbents since it has a composition similar to groundwater, containing appropriate amounts of silica, sulfate, phosphate, fluoride, and hardness. All of these elements are known to affect arsenic adsorption capacity. This water is prepared using the following chemicals (final concentration shown in parentheses).

1. Sodium nitrate (5.289 mg/L)
2. Sodium bicarbonate(252 mg/L)
3. Sodium phosphate monohydrate (0.0699 mg/L)
4. Sodium fluoride (2.22 mg/L)
5. Disodium metasilicate nona-hydrate (35.32 mg/L)
6. Magnesium sulfate heptahydrate (62.6 mg/L)
7. Calcium chloride dehydrate (111.1 mg/L)

We initially attempted to prepare a stock synthetic groundwater with 10X the desired concentration. However, some of the medium components were not soluble at the higher concentration. Thus, the synthetic groundwater should be directly prepared with all components at the final desired concentrations. In the future we will also try to make a stronger solution of the compounds which dissolve easily, and then also make a concentrated solution of the smaller mass compounds (as these are difficult to add into a 1x solution). We can take the appropriate volumes from both of the respective stock solutions to create our test water.

## Part VI Upcoming Work

This semester we were not able to get the AA machine up and running to measure arsenic, but this will hopefully be completed for next semester. Once the AA is up and running we can then verify whether or not our treatment methods are effective, by creating an appropriate calibration curve for arsenic. We may narrow our processes down to one or two methods which produces the best removal. We may also check to see if there are any other coagulants that would work better than PACl (but still be readily available in locations such as Honduras and India), such as  $\text{Fe}(\text{Cl})_3$  and alum. Adding an oxidant may also prove useful and therefore we would also test out this hypothesis. Another

hypothesis that needs to be tested is to analyze the effect of pH on arsenic removal efficiency and determine the best chemical to lower the pH, such as nitric acid, since the resulting nitrate anions in the solution are relatively inert with respect to forming complexes. In regard of the testing procedures, it is important to try to see how much coagulant stayed in solution or suspension by measuring aluminum with the GFAAS, which estimates how many nanoglobs of aluminum hydroxide precipitate would be in the tube, in order to analyze whether there will be a reduction in arsenic concentration. Also, since adding a small amount of clay as a coagulant aid is not yet proved to be effective, more tests are necessary.

If the coagulant based-system does not prove to be effective there are several other alternative treatment methods that can be evaluated:

1. Adsorption processes are considered a highly efficient method in water treatment for arsenic removal. The most common adsorbents are activated carbon, hydrous metal oxides like activated alumina, and ion exchange resins. There are also new adsorbents that are being evaluated and considered such as activated red mud. Adsorption by activated carbon is one of the most commonly used methods for As removal [6]. The capacity of an adsorbent depends on the activated carbon properties, adsorbate chemical properties, temperature, pH, ionic strength, etc. Many activated carbons are available commercially, however they are considered expensive and carbon only removes few milligrams of metal ions per gram of activated carbon. Dissociation of acidic arsenic compounds leads to anionic species which can be adsorbed onto solid surfaces with a positive charge. Such solids may be synthetic polymeric ion exchangers or inorganic materials. [1], [4].

2. Precipitation. The basic principle of precipitation is the insolubility of certain inorganic arsenic compounds. The most commonly used precipitation methods to remove arsenic from process streams are by precipitation of As(III)-sulphide, calcium arsenate and ferric arsenate.

3. Membrane Processes. One of the major advantages of membrane processes over adsorption is that removal efficiency is relatively less affected by the chemical composition and pH of the raw water. To ensure better total arsenic removal, oxidation of As(III) to As(V) is also required with this type of treatment. However, oxidizing agents, like chlorine, could damage the membrane material (Kartinen and Martin 1995) [2], and special attention should be paid to the choice of the membrane used for this application. [4]

## References

- key-1 [1] Deschamps, E.; Matschullat, J. "Arsenic:Natural and Anthropogenic". Taylor & Francis Group, London, UK (2011)
- key-2 [2] Kartinen, E.O.; Martin, C.J. "An Overview of Arsenic Removal Processes". Desalination, Volume 103, 1. November 1995, pp. 79-88.
- key-3 [3] Katsoyiannis, Ioannis A., and Anastasios I. Zouboulis. "Removal of Arsenic from Contaminated Water Sources by Sorption onto Iron-oxide-coated Polymeric Materials." Water Research 36 (2002): 5141-155.
- key-4 [4] Ng, K.S.; Ujang, Z.; Le-Clech, P. "Arsenic removal technologies for drinking water." Environmental Science and Bio/Technology 3: 43-53, 2004.
- key-5 [5] Maohong Fan, Robert C. Brown, Shin Wu Sung, Chin-Pao Huang, Say K. Ong and J. (Hans) van Leeuwen. "Comparisons of Polymeric and Conventional Coagulants in Arsenic (V) Removal." Water Environment Research , Vol. 75, No. 4 (Jul. - Aug., 2003), pp. 308-313
- key-6 [6] Mohan, D.; Pittman Jr., C. "Arsenic removal from waste/wastewater using adsorbents- A critical review." Journal of Hazardous Materials, Vol.142, 1-53
- key-7 [7] Zouboulis, A., & Katsoyiannis, I. (2002). Removal of Arsenates from Contaminated Water by Coagulation-Direct Filtration. Separation Science and Technology. Water Research Vol. 37, Issue 12. 2859 - 2873.