

Arsenic Team Research Report

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Abstract

The modification of AguaClara sand filtration unit by coating the media surface with PACl was investigated in this research in order to remove arsenic from contaminated influent. This process is called adsorptive media filtration, which is one of the emerging technologies in water treatment processes. In order to ensure accurate arsenic analysis, the graphite furnace atomic absorption spectrometer (GFAAS) was aligned and calibrated extensively. Since the pre-programmed sampling procedure by the GFAAS had been proven ineffective in measuring low arsenic concentration, two specialized analytical methods called multiple injection method and large injection method were created to detect arsenic at low concentrations. These methods lowered the detection limit of arsenic concentration by the GFAAS down to $2 \mu\text{g/L}$. In the experimental preparation, an upflow sand filter column was fabricated using a 1.20 m transparent PVC pipe with 0.622-inch inner diameter. The sand bed depth was 87 cm. Two peristaltic pumps were connected to stock solutions: coagulant (PACl) and groundwater with diluted arsenic concentration at $100 \mu\text{g/L}$. In this experiment, both pre-treatment and co-treatment methods were employed. Using an approach velocity of 1 mm/s , the results showed the arsenic removal efficiency during the first 80 minutes of the experiment was at least 97%, which validated the removal efficacy of adsorptive media filtration technique.

Introduction

Arsenic is a naturally occurring element that is harmful to human health at very low concentrations. The United States Environmental Protection Agency has set maximum contaminant level in drinking water at $10 \mu\text{g/L}$, however, groundwater may contain arsenic concentration multiple times higher than that standard. The objective of this project is to evaluate the effectiveness and feasibility of adsorptive media filtration and to eventually integrate this design to AguaClara plants. This specialized filtration technique is relatively low cost and high removal efficiency compared with flocculation and sedimentation. Flocculation and sedimentation require a very large dose of coagulant to capture arsenic.

However, a fixed bed coated with coagulant precipitate provides the benefits of a plug flow reactor and superior mass transport from liquid to solid phase.

Prior to any experimentation, an extensive literature review was conducted in order to set a baseline of current research and a standard for expectations. Next, the graphite furnace atomic absorption spectrometer (GFAAS) was aligned and calibrated extensively to ensure accuracy. Furthermore, the experimental apparatus, experimental procedures and results are discussed.

Literature Reviews

Arsenic contamination in water sources has been a serious health concern for many decades especially in regions of the world where exposure is exceeding the reference dosages set by the EPA. Several arsenic removal technologies have been developed including simple filtration units using a number of adsorbents such as iron-coated polymeric material, iron oxide coated sand, iron oxide impregnated activated alumina and many more. Here is a list of arsenic removal technologies in five broad categories[4].

1. Precipitation Processes
 - (a) Coagulation/Filtration
 - (b) Iron/Manganese Oxidation
 - (c) Coagulation Assisted Microfiltration
 - (d) Enhanced Coagulation
 - (e) Lime Softening
2. Adsorptive Processes
 - (a) Activated Alumina
3. Ion Exchange
4. Membrane Processes
 - (a) Micro/Ultra/Nanofiltration
 - (b) Reverse Osmosis
 - (c) Electrodialysis Reversal
5. Alternative Technologies
 - (a) Iron Oxide Coated Sand
 - (b) Sulfur-Modified Iron
 - (c) Granular Ferric Hydroxide

- (d) Iron Filing
- (e) Photo-Oxidation

Since AguaClara has developed advanced understanding of the flocculation process as well as a new filtration technology this research aims to explore arsenic removal using direct filtration or flocculation and filtration. The goal is to develop an arsenic removal process that adheres to AguaClara principles of low cost, low electricity consumption and ease in fabrication, operation and maintenance as well as the environmental conditions at prospective sites. One of the most promising arsenic removal technologies is the adsorptive filtration process using coagulant coated sand. This method is low cost and requires no electricity. Existing literature on this method shows potential for high removal efficiency of arsenic.

Adsorption of Arsenic by Iron Oxide-Coated Sand

Adsorption by iron oxide-coated sand is an emerging technique for arsenic removal. Gupta, Saini and Jain used manganese green sand and iron oxide-coated sand in a ratio 20:1 in experiments to test the effect of various factors and environmental conditions on arsenic removal efficiency[1]. The experiments can be separated into two categories: batch and column studies. Batch experiment was performed in a 500 mL Erlenmeyer flask with a magnetic stirrer. The flask contained an arsenic solution and either coated or uncoated sand. Column experiments were conducted using PVC pipes with a length of 160 cm and a diameter of 2.54 cm. The columns were filled with sand decreasing in size from the bottom to the top, and upflow filtration was evaluated with samples taken from different height of the filter.

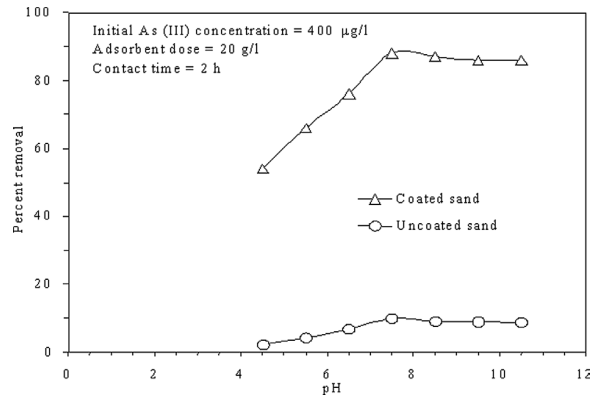


Figure 1: Effect of pH on As(III) adsorption.

In batch studies, Gupta tested the effects of pH, contact time, initial arsenic concentration and adsorbent dose. For pH, the optimal pH level is at 7.5 for both coated and uncoated sand with percent removal of 88% and 9.8% respectively (Figure 1). At pH below 7.5, the percent removal increased with increasing pH. At pH above 7.5, the percent removal decreased slightly but remained largely constant. The effect of contact time on arsenic removal efficient was very prominent. The percent removal of arsenic increased significantly with contact time especially at low contact time. The percent removal plateaued at 93% at approximately 150 minutes of contact time (Figure 2).

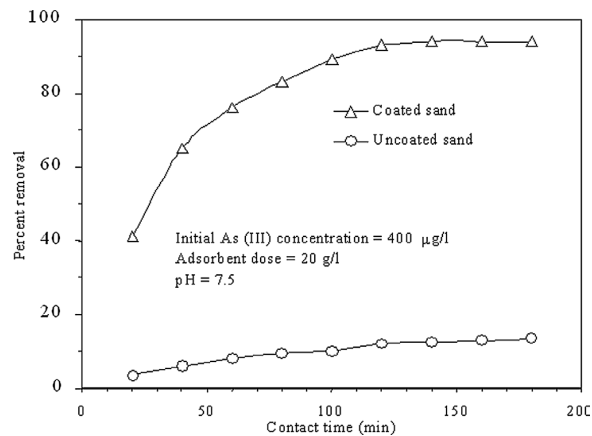


Figure 2: Effect of contact time on As(III) adsorption.

The initial arsenic concentration also played an important role in removal efficiency. At low initial arsenic concentration ($100 \mu\text{g/L}$), the percent removal is very high ($\sim 99\%$). However, as the initial concentration of arsenic increased, the percent removal decreased steadily down to about 75% at initial concentration of $800 \mu\text{g/L}$ (Figure 3).

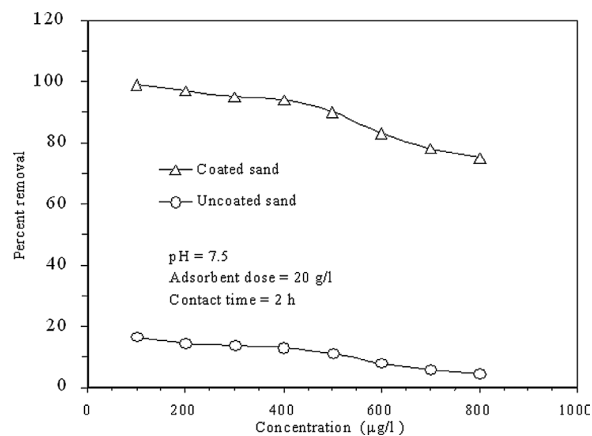


Figure 3: Effect of initial concentration on As(III) adsorption.

The last factor that was tested using batch experiment was the effect of adsorbent dose, which was the concentration of coagulant that was coated on to the sand media. As shown in Figure 4, the percent remove rose sharply as the adsorbent dose increased from 5 g/L to 20 g/L . At the adsorbent dose of $20 \mu\text{g/L}$, the percent remove was 94% . As the adsorbent increased above 20 g/L , the percent remove only increased very slightly.

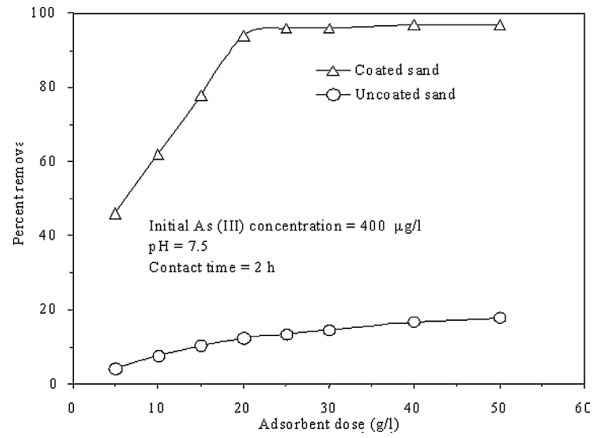


Figure 4: Effect of adsorbent concentration on As(III) adsorption.

In column studies, Gupta focused on testing the effects of filtration rate and bed depth. For filtration rate experiment, three rates were used: $0.13 \text{ mm}^3/\text{s}$, $0.23 \text{ mm}^3/\text{s}$ and $0.33 \text{ mm}^3/\text{s}$. The experiment with the highest filtration rate performed the most poorly. The maximum percent remove was only about 78%. The other two experiment reached the maximum percent remove of about 95%. However, the lower rate ($0.13 \text{ mm}^3/\text{s}$) achieved the maximum percent remove faster by about an hour (Figure 5).

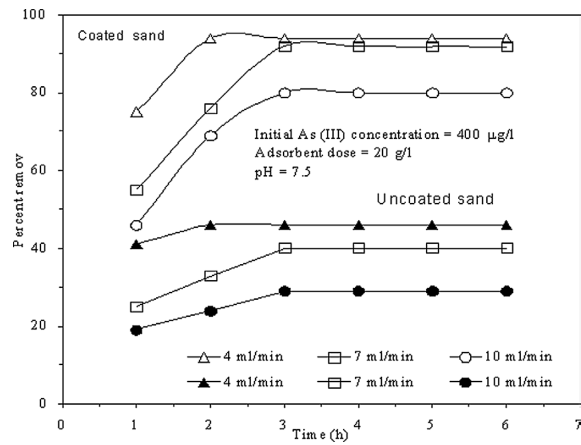


Figure 5: Effect of filtration rate on As(III) with coated and uncoated sand in column.

Finally, the effects of bed depth were studied. Three levels of depth were chosen to be 52 cm, 31 cm and 10 cm. The result showed that as the depth increased the percent removal increased as expected (Figure 6). However, with an increase in bed depth, the head loss in the sand column also increased.

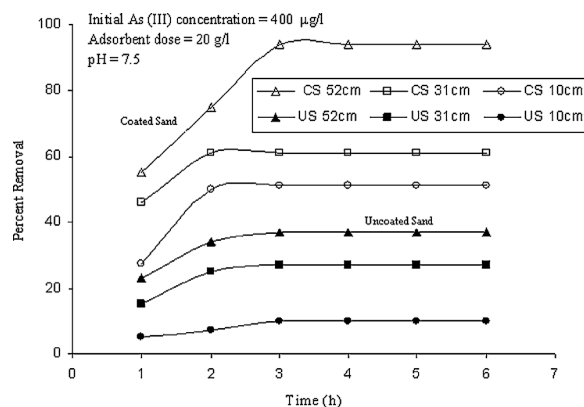


Figure 6: Effect of bed depth on As(III) adsorption in column.

Adsorptive Filtration on Polymeric Materials

Katsoyiannis and Zouboulis 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 hydroxide)[2]. Polystyrene is a cheap material that has been implemented by other researchers on filtration process showing good performance. On the other hand, polyHIPE is a novel microporous media that has never been applied in a drinking water treatment process at the time this research was conducted. Arsenic in both III and V oxidation state was diluted with tap water to achieve concentrations ranging from 100 µg/L to 50 µg/L, which is a typical range of arsenic concentrations in Greece. The experimental results show that this method effectively reduced arsenic concentration from 100 µg/L and 50 µg/L down to about 2 µg/L; however, it was not as effective for removing high levels of initial arsenic concentration as shown in Figure 7.

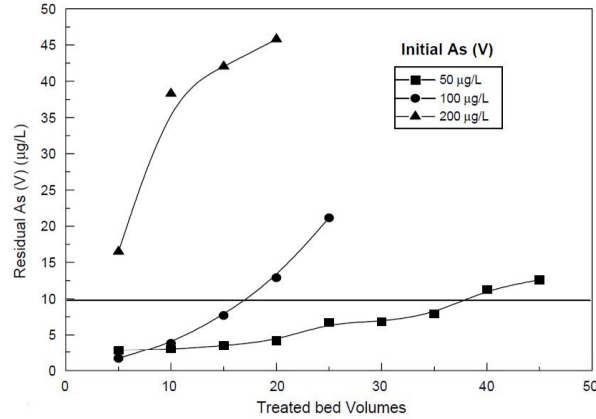


Figure 7: Effect of initial As(V) concentrations on residual As at pH = 5. filtration velocity = 7.5 mm/s and [Fe] coat = 0.025 M.

Katsoyiannis and Zouboulis also discovered that arsenic removal capability varies greatly with pH (Figure 8). Three levels of pH were used in the experiment: 5, 7 and 9. The best pH for arsenic removal was found to be at pH of 7.0. Another crucial factor in the removal effectiveness was the empty bed contact time (EBCT) by adjusting the filtration velocity. Three EBCT were tested: 3, 12.5 and 25 minutes. From Figure 9, the trend shows that the level of residual As decreases as EBCT increases. The highest EBCT was found the most optimal with the corresponding filtration velocity of 1.94 mm/s.

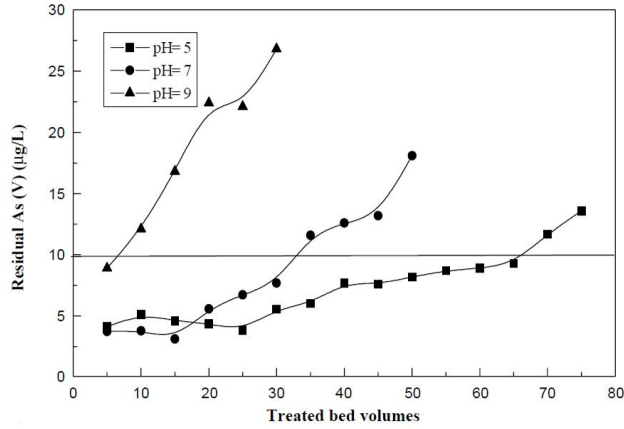


Figure 8: Effect of pH on As(V) removal at As = 50 µg/L, linear velocity - 0.2 mm/s and Fe coat = 0.025 M.

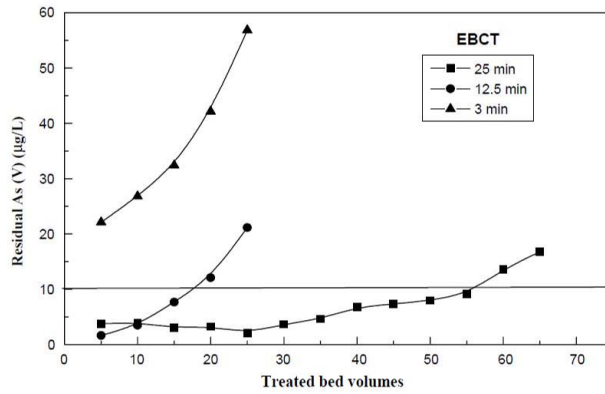


Figure 9: Effect of EBCT on As(V) removal at As = 100 µg/L, pH = 5.0 and Fe coat = 0.025 M.

Conclusion

Previous research showed that adsorptive filtration by coagulant-coated media is a viable method of arsenic removal. The efficiency and effectiveness of arsenic removal by this technique vary significantly based on the following factors.

- pH

- Contact time
- Initial influent arsenic concentration
- Type of coating coagulant
- Adsorbent concentration
- Bed depth
- Filtration rate

Previous researchers pre-treated the filter media with the coagulant. Our research will also evaluate adding the coagulant at a low continuous dose. We are planning to first evaluate removal at much lower contact times and faster filtration velocities.

Materials and Method Analysis

Reagents and stock solutions

Since arsenic is most commonly found in groundwater, the solvent in this experiment will be a combination of dissolved ions that mimic the properties of groundwater. Many other studies conducted on arsenic removal used a standard groundwater composition created by the National Sanitation Foundation International called NSF1-53 challenge water[3]. The composition of the groundwater is as followed.

1. Sodium nitrate (5.289 mg/L)
2. Sodium bicarbonate (252 mg/L)
3. Sodium phosphate monohydrate (0.00699 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)

The arsenic stock solution has a concentration of 1000 mg/L with 2% nitric acid.

Analytical Determination using GFAAS

The determination of arsenic concentration is performed by a graphite furnace atomic absorption spectrometer (GFAAS). This method is based on atomizing arsenic in the sample by heating it up to 2,500 Celsius in the furnace unit. The heated arsenic will emit wavelengths, which will be compared to those emitted from an arsenic lamp. The absorbance is then converted to concentration using a calibration curve. A matrix modifier, which consists of magnesium and palladium, is also incorporated in the analytical process to prevent arsenic in the sample from atomizing too early, which can lead to inaccuracy in the results.

Hardware Issues

Issue with Autosampler Arm

The autosampler arm, as the name implies, serves to transport a small volume of sample from the sample tray to the furnace. This arm is fully automated and can be programmed to take liquid from multiple samples in the tray. It also often rinse itself with nitric acid to avoid contamination. However, the arm malfunctioned. There was either a mechanical issue with the arm, which prevented the arm from rinsing itself with nitric acid, or communication problem amongst each component of the machine that caused the arm to not respond to commands from the software. We sought expert help from Mr. Andrew Rodman, who is a GFAAS sales representative from Perkin Elmer, to troubleshoot this problem.

A solution for this issue was provided by Mr. Rodman, who suggested that GFAAS has a fail-safe system that stops the auto-sampler from function in case that the argon gas is not flowing. This prevents any damages from occurring to the furnace chamber since, without argon gas, the chamber can potentially react with air and cause unprecedented damages. This problem arisen during hardware calibration, which argon gas was turn off since no samples were analyzed. Now, with argon gas flowing, the auto-sampler behaves normally and is functioning properly.

New Arsenic Lamp Malfunction

The current arsenic lamp employed in the GFAAS is on loan from Perkin Elmer. A new arsenic lamp of the same model was recently purchase. However, when trying to install the new lamp, it was not responding to the electricity input from the power supply unit and emitted no detectable wavelengths. We were unsure whether the new lamp has a defect and needs to be replace, but we tried to install it a few more times to ensure that the lamp was actually not operational. Unfortunately, after multiple tests, we concluded that the lamp was not capable of producing sufficient energy to be implemented in the GFAAS. We will contact Perkin Elmer for a replacement. In the mean time, we will continue to use the old lamp, which is on loan from Perkin Elmer as our main arsenic lamp.

Analysis of Calibration Curves

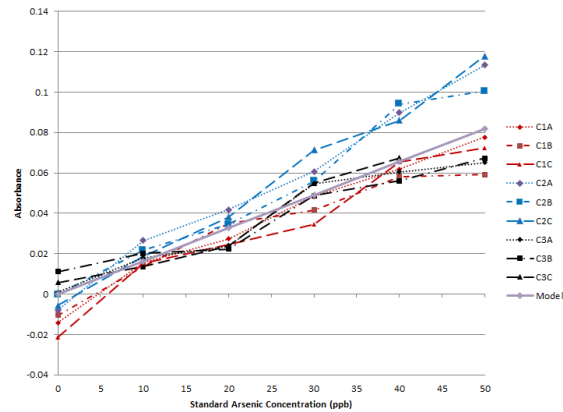


Figure 10: Arsenic calibration curve using standard ranging from $0 \mu\text{g/L}$ to $50 \mu\text{g/L}$ using a standard concentration of $50 \mu\text{g/L}$ at an interval of $10 \mu\text{g/L}$ with automated dilution by GFAAS.

There are a total of five calibration curves created. Three with standard concentrations ranging from $0 \mu\text{g/L}$ to $50 \mu\text{g/L}$ and two from $0 \mu\text{g/L}$ to $10 \mu\text{g/L}$ as shown on Figure 10 and Figure 11 respectively. Note that the numbers in the legend indicate number of calibration performed and the letters represent each duplicate. The calibration curves with standard concentrations ranging from $0 \mu\text{g/L}$ to $50 \mu\text{g/L}$ seemed to have different slopes and the calibration curves with standard concentrations ranging from $0 \mu\text{g/L}$ to $10 \mu\text{g/L}$ have a significant variation on absorbance at each standard concentration.

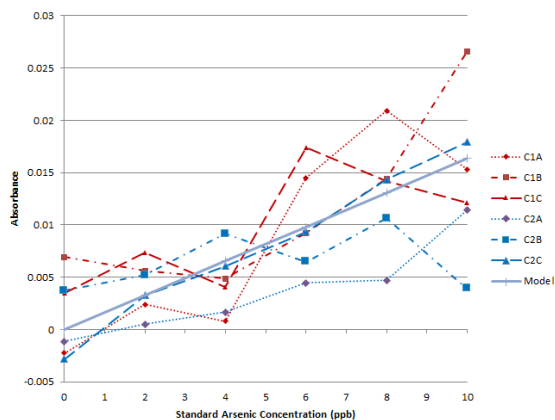


Figure 11: Arsenic calibration curve using standard ranging from 0 to 10 $\mu\text{g/L}$ using a standard concentration of 10 $\mu\text{g/L}$ at an interval of 2 $\mu\text{g/L}$ with automated dilution by GFAAS.

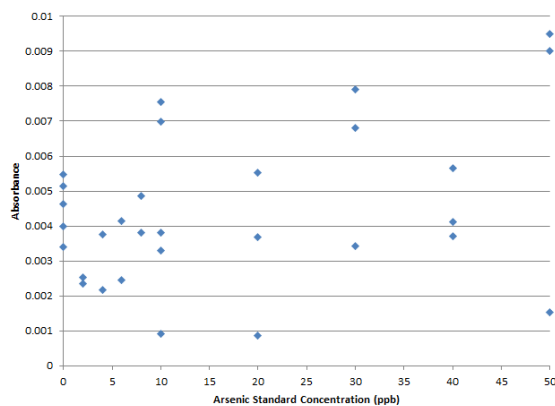


Figure 12: Standard deviation of triplicate's absorbance at each standard concentration for each of three standard curves.

Further analysis was conducted in order to determine the standard deviation of these measurements. First, since GFAAS re-samples three times at every concentration, we examined the consistency of the GFAAS in measuring one standard by analyzing the standard deviation of the duplicates at each sample to

study for any patterns. This graph is display in Figure 12 below. By examining the graph, there appears to be no obvious pattern to the standard deviation of the duplicates at each standard. The mean for the standard deviation seems to stay constant over the entire range of concentrations. Thus it implies that the GFAAS is functioning properly throughout the standard range. In order to determine the accuracy of the GFAAS, we calculated the average standard deviation of the absorbance at each standard concentration, which was found to be 0.0044 absorbance units. We can convert this into a concentration unit by using the slope of the data. The slope of the model was calculated using the relationship between absorbance and standard concentration to be 0.00164 with a unit of absorbance per $\mu\text{g/L}$, which is represented in the graphs above. Using this slope, we found the standard deviation of the standards to be $2.71 \mu\text{g/L}$. This is very important to keep in mind especially when sampling at low arsenic concentrations. This standard deviation of $2.7 \mu\text{g/L}$ can be used to calculate the method detection limit. One definition of the detection limit is 3 standard deviations or $8.1 \mu\text{g/L}$, which is 0.162 pg .

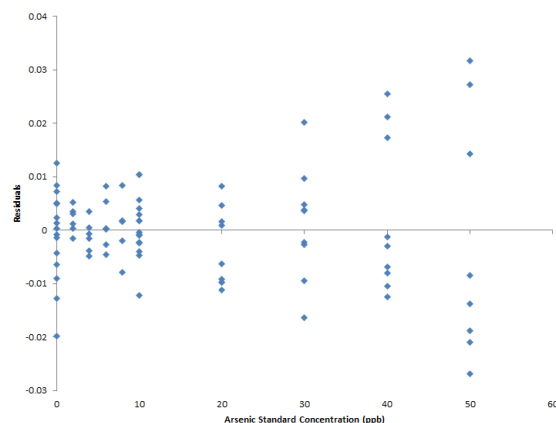


Figure 13: Residual plot of the calibration data using regression analysis in Excel.

A full regression analysis of the calibration data was also performed using the Regression function in Excel Analytical Toolpack to determine the potency of the model. The summary output showed that the adjusted R-squared value was 0.89, which is high but not ideal. However, the most disconcerting discovery was from the residual plot in Figure 13 below. For any linear fit, there is an underlying assumption that the variation of the residuals must remain constant and must have no pattern. However, from looking at Figure 13, there is a significant variation in the residual as the standard concentration increases. The

increasing variance with absorbance may be a characteristic of the fluctuations in the heated cloud of gas in the graphite furnace.

In conclusion, all analysis showed that the calibration regression model using calibration data from 5 total attempts ranging from 0 - 10 $\mu\text{g/L}$ and 0 to 50 $\mu\text{g/L}$ is invalid and can not be used for future reference. Therefore a new calibration curve will be required prior to every sampling session. The GFAAS detection limit is 0.162 pg of arsenic. This translates to 8.1 $\mu\text{g/L}$ assuming a total injection volume of 20 μL or 1.62 $\mu\text{g/L}$ assuming a 100 μL injection volume. Assuming that GFAAS results follow a Gaussian curve, we may still be able to obtain a true sample concentration by utilizing multiple duplicates and find the mean.

Analytical Determination at Low Concentrations

Multiple Injection Method

From the previous section, it is concluded that the current analytical method of GFAAS is not capable of measuring arsenic concentration at less than 10 $\mu\text{g/L}$. However, there is a promising solution to this problem. The GFAAS WinLAB software is flexible in that the sampling and analysis method can be modified. In the furnace section of the method, there is a “sequence” tab where the sampling sequence can be adjusted. By modifying the sequence, the GFAAS can pipet a regular amount of sample to the furnace and burn off non-arsenic solution then resample as many times as required. An example of this sequencing is shown in Figure 15. In this sequence, the furnace only runs step 1 except for the last step. In these steps, the furnace runs at 120 Celsius in order to remove excess water. The matrix modifier is also only added during the first repetition. The furnace steps and their respective run time and temperature are shown in Figure 14.

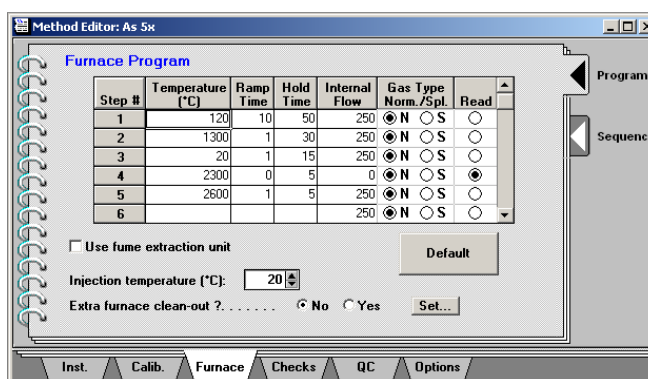


Figure 14: Furnace program steps window in GFAAS WinLAB.

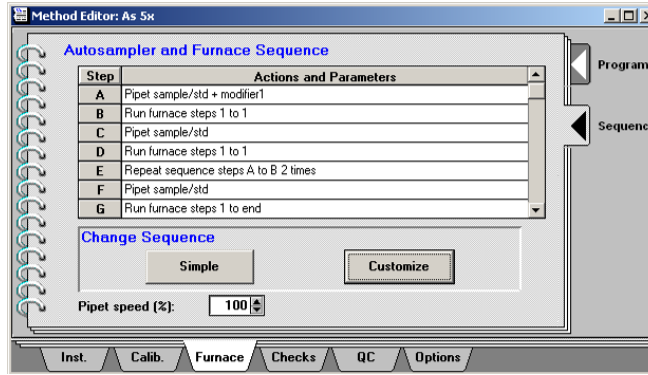


Figure 15: Autosampler and furnace sequence window in GFAAS WinLAB.

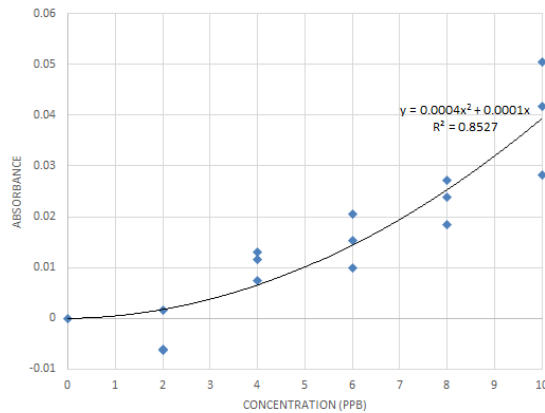


Figure 16: Arsenic calibration curving using multiple injection method from 0 to 10 $\mu\text{g}/\text{L}$ using a standard concentration of 10 $\mu\text{g}/\text{L}$ at an interval of 2 $\mu\text{g}/\text{L}$ with automated dilution by GFAAS.

Since the GFAAS detection limit is 0.162 pg of arsenic, the mass of arsenic injected will be increased by repeating the injection sequence five or ten times, the overall mass of arsenic analyzed will also increase by five or ten times, which will place the mass of arsenic above the detection limit. The resulting calibration curve using this method is shown in Figure 16 below. From this

plot, it is apparent that there is a distinct pattern, which validates the accuracy of this method. However, it is important to note that the absorbance of each standard is significant lower than the absorbance in calibration curve from 0 to 50 $\mu\text{g}/\text{L}$ in Figure 10. Therefore, during the furnace sequence, some arsenic is dissipated before atomization or the arsenic solution does not completely evaporate between injections and some of the arsenic solution is overflowing the platform and being lost.

Large Injection Method

The multiple injection method detects arsenic at lower concentrations since it increases the mass of arsenic in the sample. However, a problem with this method is that it takes a long time to analyze. One sample with triplicates can take up to half an hour. Another method to increase the mass of arsenic for GFAAS to analyze is to simply apply a single injection with larger volume of sample into the furnace chamber. In a regular sample, 20 μL of sample is injected into the furnace chamber. The auto-sampler can be program to inject up to 99 μL of sample. However, at large volume, there is a risk of sample overflowing out of the platform inside the furnace chamber. In a preliminary test of this method, a volume of 50 μL was selected to create a calibration curve ranging from 0 $\mu\text{g}/\text{L}$ to 10 $\mu\text{g}/\text{L}$ using a standard concentration of 10 $\mu\text{g}/\text{L}$ with automated dilution by GFAAS. The matrix modifying remained at 5 μL . During the injection step, it was observed that the sample remained on the platform after injection. As shown in the calibration curve in Figure 17 below, this method is very promising. While multiple injection method has a non-linear trend, the large injection method has a distinctive linear trend with a very high R^2 value of 0.988. From observing the data, the variation among the triplicate values are very small as well. Furthermore, one sample using this method only takes approximately 8 minutes.

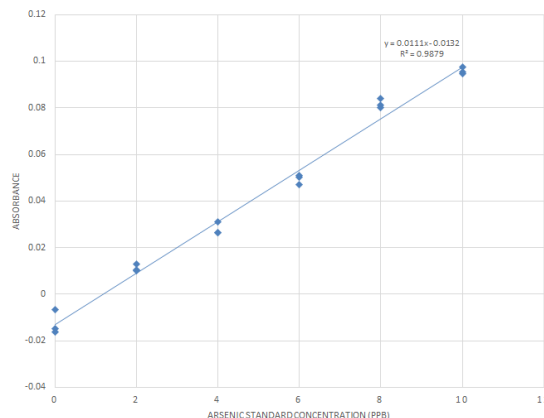


Figure 17: Arsenic calibration curve using large injection method ranging from $0 \mu\text{g/L}$ to $10 \mu\text{g/L}$ using a standard concentration of $10 \mu\text{g/L}$ with automated dilution by GFAAS.

Filter Design

The filter is designed with the goal to minimize the total volume of water required to run experiments in order to reduce the production of hazardous waste. The filter column is assembled using a half-inch PVC column of 1.20 m total length and 1.6 cm inner diameter. The column is filled up to 0.87 m with sand. A tube coupling connection is installed at a height of 0.92 m that allows access to the sand in case there need to be changes in sand height. The influent groundwater and coagulant are pumped in from the bottom of the filter, which simplifies the tubing connection for backwash water and the effluent stream. Sieving has shown that 95 of the sand is between 0.850 mm and 0.425 mm with only 5% smaller than that. As there is no intermediate stratum, we estimate, based on appearance of homogeneity, a D_{60} of 0.5 mm and an $\epsilon = 0.4$ for calculations. A filter column of this diameter has an area of $1.96 * 10^{-4} m^2$ therefore superficial velocities up to 2.3 mm/s can be achieved prior to fluidization at the cost of tiny flowrates. The total influent flow rate is the sum of two flows, groundwater and coagulant. Two separate peristaltic pumps, one for groundwater with arsenic and another for a concentrated PACl solution are used to dilutes the two flows at appropriate PACl concentrations for given head velocities. The pumps have a maximum speed of 100 rpm. Head loss as calculated using equation 1 Minimum fluidization velocity is measured to be 2.4 mm/s at porosity $\epsilon = 0.4$. For filtration velocity of 1.0 mm/s used in our standard experimental procedure, headloss is 0.36 mm

$$h = 36H_{fs}K_c \frac{(1 - \epsilon)^2}{\epsilon^3} \frac{\nu v_a}{g d_c^2} \quad (1)$$

where,

h is headloss

$K_c = 5$ Carmen-Kozeny constant

$H_{fs} = 87$ cm Height of sand

$\epsilon = 0.4$ porosity

$\nu = 1 * 10^{-6}$ m²/s Kinematic viscosity at 20C

v_a approach velocity

$d_c = 1.6$ cm Filter's diameter



Figure 18: Experimental set up of the upflow sand filter.

The filter and surrounding apparatus is shown in Figure 18 below. For safety measures, the filter, pumps and all tubing connections must be contained within a tray that can contain any hazardous liquid in case of leaks or other accidents. However, the current tray is quite small and the drain is not yet connected appropriately. On the right side of the tray is a large container containing 3 L of effluent waste that has been created during the first experiment.

Head Loss Analysis

A continuous assessment of head loss is done using the manometer seen crawling on the wall with the scorpion-like tail. The manometer is a tube connected right before the influent of the filter and extends towards the ceiling where it is open to atmospheric pressure. The equivalent point of atmospheric pressure at the filter stream occurs at the effluent end 20 cm above ground level. A quarter inch diameter effluent tube is used to ensure that air can not penetrate higher into the tube. The range of head loss shown on the manometer is from 20 cm at low flow rates to the maximum ~ 120 cm that occurs at fluidization.

Continuous Flow Experiment with Arsenic

Experimental Procedure

Preparation

Arsenic Solution in Groundwater

In this experiment, the arsenic influent concentration used was $100 \mu\text{g/L}$. Since the stock arsenic solution is 1000 mg/L , $100 \mu\text{L}$ from stock was pipeted into $1,000 \text{ mL}$ of groundwater to achieve 10^5 time dilution. Two liters of groundwater-arsenic solution were prepared for the two hours run of this experiment.

PACl stock solution

A liter of 100 mg/L PACl stock concentration was prepared with distilled water. A magnetic stirrer was used to keep the solution well-mixed. Equation 2 is used to determine the flow rate of each pump for a specific PACl influent concentration and flow rate.

$$Q_{total}C_{in} = Q_{PACl}C_{stock} \quad (2)$$

Calibration of pumps

There are two pumps for this experiment supplying PACl and groundwater with arsenic solution. PACl pump has a size 13 tube and groundwater pump has a size 16 tube (to be changed to 17). The relationship between pump rate, rpm, and flow rate, mL/min , is evaluated by measuring the effluent volume at different flow rates. The calibration equations for PACl and groundwater pumps are equation 3 and equation 4 respectively.

$$RPM = 0.0717Q - 0.0417 \quad (3)$$

$$RPM = 1.2Q \quad (4)$$

Procedure

Initial Backwash

Before every experiment, the filter is backwashed using tap water at maximum flow rate. It is recommended that backwash velocity is 11 mm/s . However, at maximum flow rate with 16 tube, the approach velocity is only 7.1 mm/s , which corresponds to an estimated 122% fluidization assuming a porosity $\epsilon = 0.4$. Therefore it is possible that the filter could contain traces of coagulant from previous trials due to ineffective backwash.

Filter Pre-treatment with PACL

For this experiment, the filter is pre-treated at 30 mg/L PACL concentration at an approach velocity of 2.015 mm/s , which is a little lower than the 2.4 mm/s minimum fluidization velocity. The pre-treatment lasted until the head loss increased to about half the total length of the sand column. In the initial trial, tap water was used for this process. However, the influent pH seemed too low for PACL to precipitate and headloss wasn't building for over 15 minutes. The pH at the effluent end was measured to be around 6. Therefore, after backwashing again, groundwater was used for pre-treatment to ensure that the pH was close to neutral to allow aluminum hydroxide to form and precipitate. The pH was measured using paper strips at the effluent end and found to be 7. The 'clean' head loss at this flow rate begun at 80 cm and pre-treatment was stopped when it reached 120 cm, after ten minutes. This headloss is, according to memory, the maximum headloss we observed when the sand bed was lifted. The total mass of coagulant added during pre-treatment was 2 mg.

Sampling

Samples were collected every ten minutes into the plastic vials, which were placed directly into the GFAAS sampling tray. Although the peristaltic pumps have some flow pulsations and the effluent solution may not be uniform over time, it was assumed that the solution was mixed throughout the length of the filtration column. Thus, the effluent was expected to have low variability over short periods of time. Each vial took approximately 1 mL.

Final Backwash

After the experimental run, the filtration column was backwashed using the same procedure as the initial backwash for 10 minutes. Backwash samples were collected every 1 minute for the first 5 minutes and once more at 10 minute. A sample was also collected from total discharge.

Sample Analysis

The GFAAS was used to analyze samples in this experiment. A calibration curve from 0 to 100 $\mu\text{g/L}$ at an interval of 10 $\mu\text{g/L}$ was prepared prior to starting the experiment using normal single injection method. The calibration curve was ready before the experiment begins so that samples could be analyzed as soon as they were collected. This allowed almost real time evaluation of the results and allowed for alterations of the experimental procedure.

Summary of co-treatment experimental parameters

- Arsenic concentration in groundwater = 100 $\mu\text{g/L}$
- PACl influent concentration = 1 mg/L
- Upflow velocity = 1 mm/s
- Total inflow = 0.196 mL/s
- Groundwater flow = 14 rpm = 0.194 mL/s
- PACl flow = 2.2 rpm = 0.00197 mL/s

Results

Before results are discussed, it is important to note that during the sampling process with the GFAAS, there was an incident where the integrity of the graphic tube inside the furnace chamber was compromised due to extensive use, which caused the sampling process to halt. The graphite tube was then replaced and samples were re-analyzed. Therefore, these results are divided into two sections: before and after replacement of the graphic tube. The implications of this incident is discussed further on.

Prior to Replacement of Graphite Tube

Before beginning the experiment, a calibration curve was created ranging from 0 to 100 $\mu\text{g/L}$ with an interval of 10 $\mu\text{g/L}$ using the GFAAS automatic dilutions from standard concentrations of 50 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$ as shown in Figure 19. The plotted data has a distinct pattern. A polynomial trend line was traced in Excel giving the regression equation 5 and a corresponding R^2 value of 0.9275, which shows that the trend line represents the data well. It is theoretically expected that concentration and absorption do not follow a linear pattern.

$$\text{Absorbance} = -3 * 10^{-6} C^2 + 0.0008C \quad (5)$$

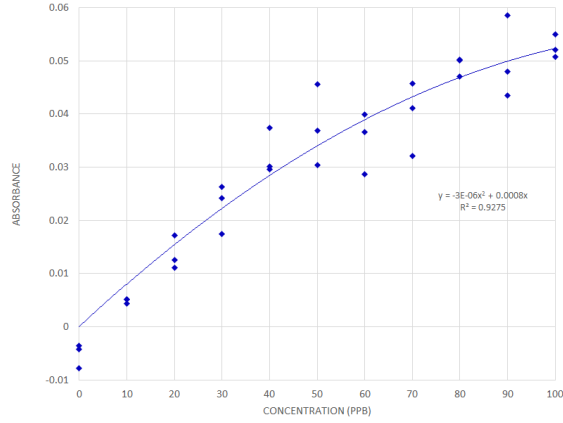


Figure 19: Arsenic calibration curve from 0 to 100 $\mu\text{g}/\text{L}$ using single injection method with standard concentrations of 50 $\mu\text{g}/\text{L}$ and 100 $\mu\text{g}/\text{L}$ using GFAAS automated dilution at an interval of 10 $\mu\text{g}/\text{L}$ prior to running the experiment.

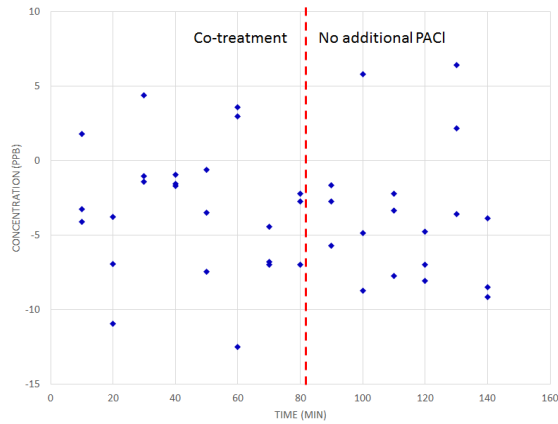


Figure 20: Arsenic concentration in effluent over time.

Equation 5 was used after the samples were analyzed to quantify the concentration of the samples. The resulting plot of sample concentrations with time is shown in Figure 20. After 80 minutes and 8 samples, the effluent arsenic concentrations were consistently low with no upward trend along with negative values, which indicated the concentrations were in no-detection range, therefore we decided to change one of the experimental conditions. The co-treatment process

was discontinued, turning off PACl pump and slightly increasing groundwater flow in order to maintain the same approach velocity of 1 mm/s. After running this new procedure for 55 minutes, the same trend continued and the experiment was terminated.

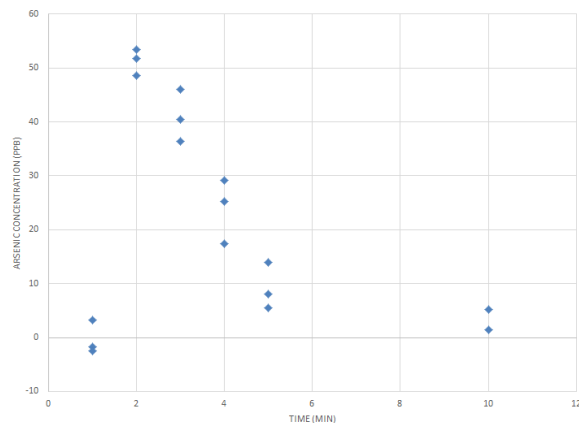


Figure 21: Arsenic concentration in backwash effluent over time.

Moreover, the backwash samples were analyzed using the calibration curve in Figure 19. The resulting plot is shown in Figure 21 below. The arsenic concentration in backwash effluent was very high directly after the process began and decreased down to around $10 \mu\text{g/L}$ after 5 minutes and below $10 \mu\text{g/L}$ after 10 minutes, which implies that most of the arsenic inside the sand filter column was removed after 10 minutes of backwash. However, it is crucial to note that the graphic tube was compromised during the GFAAS analysis of the sample at 10-minute mark. As shown, there are only two replicates for that sample.

After the Replacement of Graphite Tube

As discussed in the Method Analysis Section, the multiple injection method has been used to measure sample concentrations at concentrations below $10 \mu\text{g/L}$. After the graphite tube was replaced, a new calibration curve using this method was created from $0 \mu\text{g/L}$ to $10 \mu\text{g/L}$ at intervals of $2 \mu\text{g/L}$ using GFAAS automatic dilution from a standard concentration of $10 \mu\text{g/L}$ as shown in Figure 22. The pattern in this plot was not clear but a polynomial trend line was plotted using Excel to give equation 6, which has a corresponding R^2 value of 0.906. Using this new relationship between concentration and absorbance, 9 of the previous 13 samples were reprocessed at five injections. The results are plotted in Figure

23 and Arsenic effluent concentrations are measured to be below $10 \mu\text{g/L}$.

$$\text{Absorbance} = 0.0017C^2 - 0.0021C \quad (6)$$

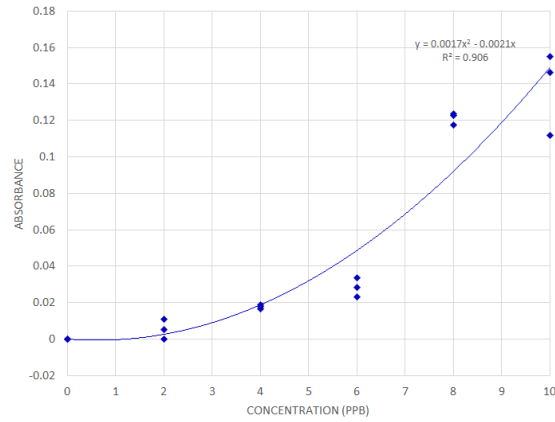


Figure 22: Arsenic calibration curve from 0 to $10 \mu\text{g/L}$ using multiple injection method using a standard of $10 \mu\text{g/L}$ with GFAAS automated dilution at an interval of $2 \mu\text{g/L}$.

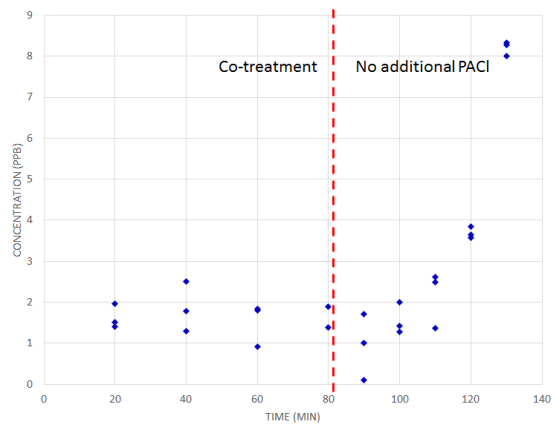


Figure 23: Arsenic concentration in effluent time analyzed using multiple injection method.

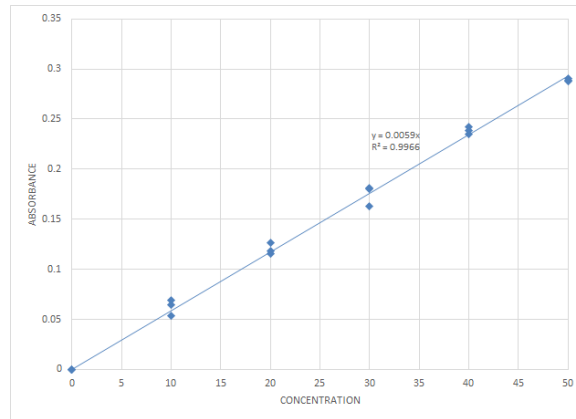


Figure 24: Arsenic calibration curve from 0 to 50 $\mu\text{g/L}$ using a single injection method with a standard concentration of 50 $\mu\text{g/L}$ with GFAAS automatic dilution at an interval of 10 $\mu\text{g/L}$.

As a high removal efficiency is illustrated in these measurements, it is expected that the concentration of backwash effluent should sum up in the mass balance. A new calibration curve was created ranging from 0 $\mu\text{g/L}$ to 50 $\mu\text{g/L}$ in order to analyze backwash samples as the previous calibration curve with the higher concentration range might have been inaccurate due to the damaged graphite tube. As shown in Figure 24 below, this calibration curve shows a strong linear relationship between absorbance and concentration with a slope of 0.0059 and R^2 of 0.9966, which indicates that the trend line almost matches the data perfectly. The fact that the calibration curve in Figure 19 showed an asymptotic tendency while this one is perfectly linear may indicate that the graphite tube was already compromised before the initiation of this experiment.

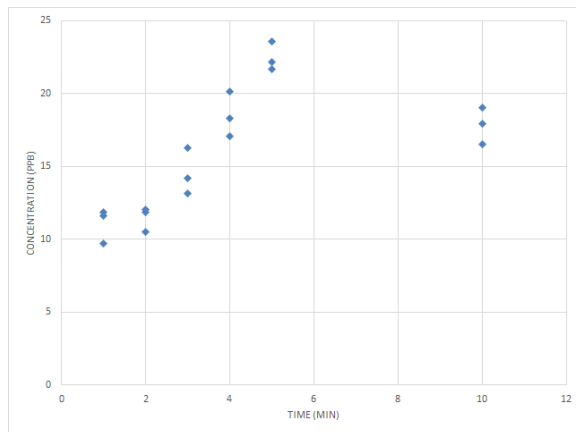


Figure 25: Arsenic effluent concentration during backwash.

Using this calibration curve, the backwash effluent concentrations are plotted in Figure 25. As predicted, the arsenic concentration in backwash effluent was significantly higher than during the experiment. The concentration of arsenic increased as time increased for the first five minutes. At the end of the backwash period, the arsenic concentration was approximately $18 \mu\text{g/L}$. The overall concentration of Arsenic in backwash was only $35 \mu\text{g/L}$ although the expectation was for $200 \mu\text{g/L}$.

Discussion

Arsenic Removal Efficiency

From the data obtained using the multiple injection method after a new graphite tube was installed, as shown in Figure 23, the concentration of Arsenic in the samples does not exceed $3 \mu\text{g/L}$ throughout the first 80 minutes of the experiment during the co-treatment process. However, when the co-treatment process was ended and the additional supply of PACl was terminated, there was a rapid increase of arsenic in the effluent. It is suggested from literature that the initial concentrations of influent arsenic has a significant impact on the arsenic removal capacity of the filter column. Therefore, it is more intuitive to express the result in term of arsenic removal efficiency, which is the amount of arsenic removed as a percentage of the influent concentration. This is calculated by using equation 7. As shown in Figure 26, the arsenic removal efficiency during co-treatment period was consistently above 97%. Once the co-treatment process ended, the removal efficiency dropped by 5% after 50 minutes.

$$RemovalEfficiency = \frac{(C_{in} - C_{out})}{C_{in}} * 100\% \quad (7)$$

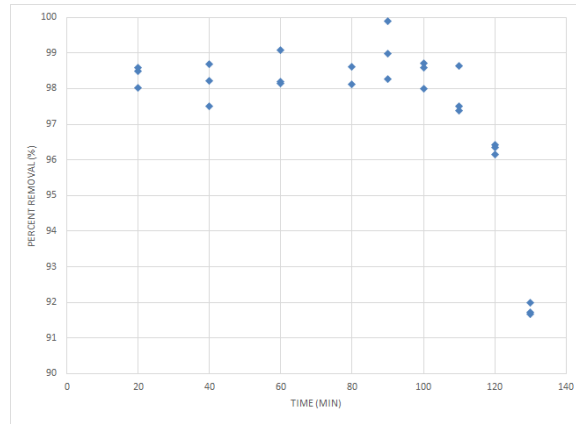


Figure 26: Percent of arsenic removed by filtration over time.

Since plotting the percent removal makes a false plateau that is simply the result of using the wrong dimensionless parameter, a better method to analyze the effectiveness of the filter is to compute pC^* , which is defined by equation 8. This equation describes the removal efficiency in log unit. As shown in Figure 27, pC^* of 1, 2 and 3 indicates a 90%, 99% and 99.9% removal efficiency respectively. Most of the results during co-treatment process have pC^* close to 2 log unit with an outlier 3 log unit at 90-minute mark.

$$pC^* = -\log\left(\frac{C_{out}}{C_{in}}\right) \quad (8)$$

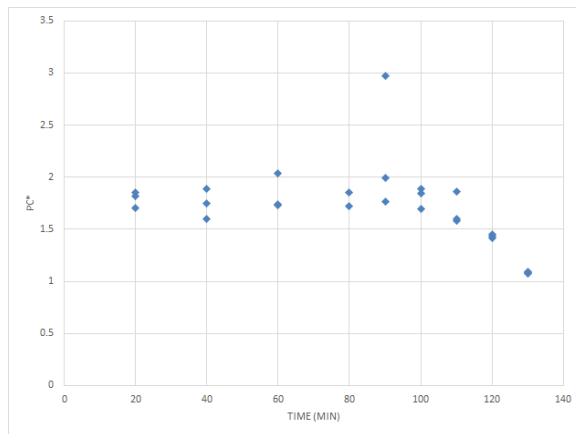


Figure 27: Arsenic removal efficiency during the experiment displayed in log unit as pC^* .

Co-Treatment vs. Pre-Treatment

Perhaps the most valuable discovery from this experiment was the diminishing effectiveness of arsenic removal after the co-treatment process ended. It seemed that co-treatment might be essential for effective arsenic removal. There are a few possible hypotheses that offer explanation to this phenomenon. Even though the total mass of PACl added throughout the 80 minutes of co-treatment only aggregated to a third of the PACl added during pre-treatment, its effect appeared to be significant. Possibly this was due to the mixing between arsenic and PACl prior to entering the sand column. The higher available surface area of coagulant enhanced the likelihood of arsenic to stick to it. Another possibility was that the softer pulses during co-treatment allowed the coagulant to precipitate more quickly and let it stick on the surface of the filter forming a type of *schmutzdecke* that was filtering arsenic more effectively over a small cross section at the bottom of the upflow filter. This was not to suggest that it was actually filtering arsenic but that the contact between arsenic and aluminum was improved. Since the total amount of coagulant was very small and the contact time was very short, an increased likelihood of contact could be the explanation for the improved removal during co-treatment, whilst as the available bonding space of this *schmutzdecke* was being saturated less effective removal was observed. Another explanation was that the coagulant throughout the filter was saturated after adsorbing arsenic for 80 minutes.

In order to evaluate any of these hypotheses, another experiment is necessary. Nevertheless, the hypothesis about the coagulant's surface area is an important factor to consider, regardless of this case. It is intuitive that small dispersed

flocs should be more effective at binding arsenic than agglomerates of coagulant. Therefore, this raises the question about the extent at which flocs can grow in the filter and the effect that the treatment process has in the size and distribution of flocs. It has been observed that the mass of coagulant added is not linearly related to headloss, but depends on the concentration at which the coagulant is being added. On one experiment it took 10 minutes to increase headloss by 40 cm at PACl concentration of 30 mg/L and velocity of 2 mm/s, while it took 250 minutes to get the same headloss buildup at 1 mg/L and 1 mm/s. In other words, at the lower concentration of PACl 50% more coagulant was added for the same headloss, which implies that the coagulant is differently distributed. Furthermore, after the 1 mg/L pre-treatment experiment had increased tap water at 1.8 mm/s for 90 additional minutes to push the coagulant higher up, although no additional coagulant was added was measured to be 10 cm higher after running. This suggests that larger flocs might have been forming. If this could be equivalently tied to a diminishing arsenic removal efficiency the floc size will need to be treated very seriously.

Graphite Tube Discrepancy

The main uncertainty in the results from this experiment lies with the integrity of the graphite tube used in the GFAAS analysis. Figure 28 and 29 compare the condition of the compromised graphite tube, which was installed into the GFAAS in September 2013, with a new unused one. Figure 28 shows that the opening where the auto-sampler normally enters and injects sample into the tube was completely destroyed and burst open. This may have direct effect during the heating process since the vapor can easily escape from the tube through the large opening, and thus reducing the concentration of arsenic measured by the GFAAS. This effect is exemplified in Figure 21 where the concentrations at 5 and 10-minute marks were significantly lower than the results in Figure 25 that were analyzed after the tube was replaced. Figure 29 shows the side view of the graphic tubes. In an unused tube, the image shows a clear discernible platform. On the other hand, the platform inside the compromised tube was in a terrible condition and almost indistinguishable from the wall, which could impact how the sample was contained inside the tube and the heating process. There were also noticeable debris inside the tube, which could have partially blocked the light path from the lamp and altered the absorbance. In conclusion, the integrity of the graphite tube decreases after multiple uses, which will lead to significant reduction in the accuracy of GFAAS. Therefore, it is important to check the condition of the graphite tube before each analysis, which includes two main parts. The small circular entrance to the platform is visible when standing in front of the GFAAS. However, the platform inside the tube requires a mirror to observe.

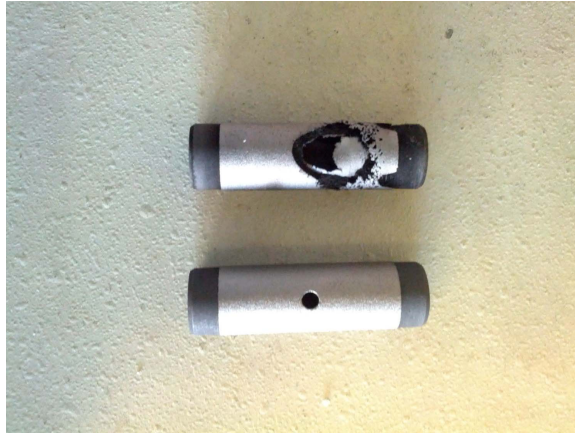


Figure 28: A comparison of the auto-sampler entrance condition between the compromised graphite tube (top) and a new one (bottom).



Figure 29: A comparison of the sample platform condition between the compromised graphite tube (top) and a new one (bottom).

Sources of Uncertainty

There were two dimensions of error about these findings. First, the GFAAS analytical method of arsenic at low concentration is still under evaluation. Therefore, arsenic concentration data obtained in this experiment may contain a certain degree of error. Additionally, the filter may still contain coagulant residue after initial backwash that improved the removal efficiency. Both of these should be verified in future experiments. Another factor of potential error that must be evaluated is whether the arsenic in the solution was arsenite or arsenate. The two oxidation states have distinctly different solubility properties and absorption behavior. In case that the arsenic in the solution was predominantly at the more oxidized As(V) state, then the results from this experiment may be illegitimate since As(V) is already insoluble. In groundwater with lower redox potential, there would be predominantly As(III) oxidation state, which is highly soluble and difficult to treat. Further investigation is required to clear this discrepancy.

Conclusion

The efforts of this semester produced promising results that suggest arsenic removal using adsorptive media filtration with co-treatment method is a potentially high performing option. Little can be said at this moment about the mechanisms of the removal as all the conclusions rely on a single experiment, however, the apparatus is set in place for future researchers to delve deeper into the process. The procedure established is relatively simple to perform and it is safe to assume that all of the coagulant precipitates in the filter due to the slightly alkaline pH of the groundwater solution. However, it is not very likely that a uniform distribution of coagulant was achieved. Distribution is likely to be improved by pre-treating at upflow velocities much closer to minimum fluidization velocity and we expect the effect of better distribution to be critical for high removal efficiency. Additionally, it remains to be seen at what rate does the coagulant saturate. It is important to experimentally establish some threshold of coagulant concentration that is required to achieve high As removal and to obtain some stoichiometric relationship between As and PACl that would allow to estimate how many liters of contaminated water can be filtered at every cycle to remove most As. This estimate is likely to be a wide range that will depend on the distribution of the coagulant in the filter and of the size and available surface area of the flocs.

Additionally, the observation on the concurrent treatment has raised more questions than answers at this point. It is not only that the mass of PACl during co-treatment was a third of that of pretreatment but also that the mixing of groundwater with coagulant in our setup was far from perfect. When running at 1 mm/s and 1 mg/L PACl the rate at which coagulant is added is 2 rpm, and with 3 rollers on the drive this results in six flow pulses per minute. Therefore the

effective concentration of coagulant in the groundwater during the first seconds that it travels through the filter is not 1mg/L but varies periodically from 0 mg/L to about 15 mg/L.

Finally, the contact time of an As atom from the moment of mixing with coagulant to the time it reaches the top of the sand is about 3 minutes, since interstitial velocity is 4-5 times higher than superficial velocity as measured for a clean filter at 1 mm/s superficial velocity. Therefore if we are to assume that a big chunk of the removal occurs at contact in the initial section of the filter during few seconds then a filter saturated with well distributed coagulant at consistently available flocs should have very efficient and long runs.

Future Work

According to the pleasant surprises of these recent results it is expected that more interesting results will arise from future experiments. As discussed in detail above the first factor to be evaluated will be the relative merits of pretreatment vs co-treatment. The next experiment will begin with an effective backwash, followed by a single sample at a clean filter run, followed by co-treatment to evaluate whether this process on its own can achieve good removal. Co-treatment should begin at 1 mg/L and change according to feedback to evaluate whether it is the mixing or the accumulation that is more important. After these results it will be decided how to proceed. The effect of pretreatment on its own would probably come next to evaluate the rate of saturation over long runs.

Additionally, the question of the oxidation state of Arsenic will be addressed and if it is observed that our solution contains the most oxidized Arsenic the feasibility of converting it to As (III) shall be investigated.

Another challenge that will require some research is the fate of the Arsenic in the backwash water which contains concentrations that could get extremely unsafe. Methods to bind the As in non-reactive forms must be evaluated, like binding As to some element like sulfide. This could be a concurrent experiment to treat our waste water on site in the Agua Clara lab. Finally, if the aforementioned procedures fly through with success, the next step should be another prototype at a different scale and in a downflow filtration mode which could find use

Detailed Task List

Literature Reviews*

Finish by 2/12/2014 - Completed

- Review papers on Arsenic removal technique focusing on media filtration

- Summarize important findings from each paper
- Integrate findings to design experiments

Learning How to Use GFAAS*

Finish by 3/14/2014 - Completed

- Read the GFAAS manual
- Understand the mechanism of GFAAS
- Meet with William Pennock to learn how to operate GFAAS
- Prepare a calibration curve

Designing Experimental Apparatus*

Finish by 3/14/2014 - Completed

- Consult with sand column expert on how to create a sand filter
- Find a way to coat the media with coagulant
- Design how to minimize or recycle waste water and materials

Fabrication of Sand Column*

Finish by 3/21/2014 - Completed

- Test the flow rate
- Test backwash mechanism
- Set up recycling/waste system
- Study hazardous waste disposal method and set up all safety measures*
- Pre-treat the filter with coagulant

GFAAS Calibration*

Finish by 3/21/2014 - Completed

- Switch out the Arsenic lamp with William Pennock
- Correct the temperature*
- Create another calibration curve*

Batch Experiment on the Effect of Nitric Acid

Finish by 3/21/2014- Incomplete

- Prepare a neutralized Arsenic sample by adding base
- Test the following cases with varying Arsenic concentration:
 - Control condition: Arsenic with nitric acid
 - Tumbler
 - Stationary

Batch Experiment on Arsenic precipitation mechanism

Finish by 3/28/2014 - Incomplete

- Test hypotheses on arsenic precipitation mechanism of co-precipitation versus surface reaction
- Test with the following cases
 - Control condition: No coagulant
 - Coagulant first
 - Arsenic first
 - Simultaneous

Continuous Flow Experiment

Finish by End of Semester - Completed

- Experiment on various hypotheses:
 - Types of coagulant*
 - Column depths/residence times
 - Amounts of coagulant
 - Levels of pH
 - Concentrations of arsenic
 - Temperatures
 - Reversibility of arsenic precipitation
 - Oxidation states of arsenic

Note

Completed steps are denoted by *

Roles and Responsibilities

Team Coordinator - Tanapong Jiarathanakul

- Coordinated amongst team members, student adviser, faculty, AguaClara leadership team and other subteams
- Facilitated team meetings
- Tracked progress over the course of the semester
- Analyzed results using GFAAS

Material Coordinator - Mingze Niu

- Prepared stock solutions
- Evaluated coagulant mechanism

Data & Material Coordinator - Jason Koutoudis

- Designed experimental apparatus
- Assembled sand filter

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