

Fluoride, Fall 2017

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Abstract

The Fluoride subteam seeks to develop a sustainable, inexpensive fluoride removal system for implementation in upcoming AguaClara plants located in India. After earning an EPA Phase II grant for the Spring 2016 fluoride removal reactor, the subteam continued to improve fluoride purification by testing lab-scale systems consisting of either a single reactor or two reactors in series. During the experimentation process, clay was incorporated into the influent stream to abate PACl buildup at the bottom of the reactors. As the subteam seeks to transplant their setup to India, it is currently working to optimize fluoride removal by minimizing use of resources. Thus, the team is currently trying to eliminate the use of clay and lower PACl dosages by increasing upflow velocity and further redesigning its reactor. Initial tests suggested insufficient fluoride removal for potable effluent, but the team is looking to repeat its previous experiments using the summer 2017 High Rate Sedimentation subteam's reactor design.

Introduction

With 85% of its drinking water sourced from groundwater, India is the largest user of groundwater in the world. In stark contrast to tap water sources in the United States that are supplemented with fluoride, India's groundwater sources often display excess levels of fluoride due to rocks in aquifers that leak large amounts of fluoride into the water. Consequently, villagers who rely on these well sources for water are at a high risk of overexposure to fluoride. The prevalence of dental fluorosis, an indicator of excessive fluoride concentrations, differs across India, but has been shown to range from 13-91 percent depending on the age group in question and the water source supplying the state or municipality (Arlappa et al., 2013)

In accordance with AguaClara's mission to create affordable, reliable, and sustainable water treatment solutions, the goal of the subteam is to treat groundwater with excessive fluoride concentrations. Teams from previous semesters analyzed the efficiency of fluoride removal by passing a coagulant, polyaluminum chloride (PACl), and a solution of fluoride through a sand filter. However, the sand filter was an inefficient method of removal because of the buildup of headloss from particles deposited in the sand filter that eventually prevented water from flowing through (Dao et al., 2015). Thus, instead of using a traditional sand filter, the team researched a similar relationship between PACl and fluoride via a floc blanket reactor. In the floc blanket reactor, flocs of PACl and clay adsorbed the fluoride from the influent water. The flocs then overflowed into a floc weir as the floc blanket grew and the purified water flowed out the top of the reactor. This reactor was modeled after the floc blanket, floc weir, and plate settlers setup in the sedimentation tank of a typical AguaClara water treatment plant as shown in figure below.



Figure 1: Picture of the Full System Apparatus

The team expected that the floc blanket reactor would be able to remove fluoride with a significantly higher efficiency than the sand filter from previous semesters and could run for extended periods of time due to the absence of headloss buildup in the reactor. The flocs in the floc blanket could exit the floc weir while the fluoride in the sand filter would build up and saturate the sand in a short amount of time (Longo et al., 2016) (Cheng et al., 2016). This semester, the subteam continued the research performed from the summer of 2017, hoping to achieve high fluoride removal with the addition of clay. After switching to a new reactor designed by the High Rate Sedimentation team, the Fluoride subteam is testing different concentrations of PACl and different upflow velocities with the goal of lowering the fluoride concentration to 1.5 mg/L .

Literature Review

Fluoride Limitations and Hazards

Over-consumption of fluoride can lead to arthritis, dental fluorosis, crippling fluorosis, bone deformation and ligament calcification (Rohholm, 1937). Fluoride can cause irritation through inhalation, digestion, and touch, and can cause damage to both eyes and exposed skin (NJ Department of Health, 2010). Though there isn't an established "average" level of fluoride in India, as literature suggests that fluoride levels are seldom above $5 \frac{\text{mg}}{\text{L}}$ in groundwater. However, in the remote Karbi Anglong district of India, fluoride levels range from $5\text{-}23 \frac{\text{mg}}{\text{L}}$ causing severe anemia, stiff joints, painful and restricted movement, mottled teeth and kidney failure (LeChevallier and Au, 2004).

According to the National Research Council (NRC), the maximum contaminant level (MCL) of fluoride in drinking water is $4 \frac{\text{mg}}{\text{L}}$. However, a secondary limit of $2 \frac{\text{mg}}{\text{L}}$ has been established by the EPA to avoid potential cosmetic effects such as tooth and skin discoloration. The World Health Organization (WHO) established a safe upper limit of $1.5 \frac{\text{mg}}{\text{L}}$ to avoid all potential risks of fluoride consumption. The team will be striving towards the WHO guideline of $1.5 \frac{\text{mg}}{\text{L}}$ of fluoride this semester by designing and experimenting with the floc blanket reactor and manipulating the ratios and concentrations of PACl and

clay in the system.

Polyaluminum Chloride (PACl) and Fluoride Removal

One common type of water treatment consists of a series of coagulation, flocculation, and clarification. During coagulation, raw water is mixed with a positively charged coagulant (typically an aluminum salt or iron salt), altering or destabilizing any negatively charged particles or dissolved and colloidal contaminants (EPA, 2016). Depending on the dose of coagulant, there are two methods of particle destabilization. The first, charge neutralization, occurs with a lower coagulant dose and happens as the negative colloids are attracted to the positively charged coagulant particles. The second method, sweep flocculation, requires a high coagulant dose and transpires when the contaminants are caught by precipitates as they settle in the suspension (EPA, 2016). The destabilized particles then proceed through flocculation, where additional mixing increases the rate of particle collision, forming larger precipitates. Following the formation of flocs, clarification removes the agglomerated particles through sedimentation or other removal processes (EPA, 2016).

In recent years, polymerized forms of aluminum salts have been used increasingly to replace standard aluminum salt coagulants (Ingallinella and Pacini, 2001). Polyaluminum chloride, a partially hydrolyzed aluminum salt, is one of the most widely used, as it delivers results similar to aluminum sulfate (alum) coupled with a polyelectrolyte (Ingallinella and Pacini, 2001). The main advantages of using polyaluminum chloride instead of alum include a reduction in sulfates added to treated water, lower sludge production, reduced odor problems, and higher overall removal efficiency (Gebbie, 2001). In the Daylesford Water Filtration Plant, a dose of $45 \frac{\text{mg}}{\text{L}}$ of alum was required to produce potable water, while only $12 \frac{\text{mg}}{\text{L}}$ of PACl were required. Additionally, PACl is advantageous in particulate removal because its hydrolyzed state allows for it to be less affected than typical aluminum salts when temperature conditions are inconsistent (EPA, 2016). Furthermore, PACl has a broader range of raw water pH in which it is an effective coagulant. It shows stable turbidity removal from 5.0-8.0 pH, compared to a range of 6.0-7.0 pH for both AlCl_3 and $\text{Al}_2(\text{SO}_4)_3$ (Yang et al., 2010). For the removal of fluoride, PACl has been found to be the most effective with pH values between 5.2 and 6.2 (EPA, 2016).

Several techniques currently use PACl to reduce high fluoride levels. The Nalgonda technique is a popular fluoride removal method that involves a combination of rapid mixing, flocculation, sedimentation, filtration and disinfection. However, fluoride removal is usually done through co-precipitation (Bailey and Fawell, 2004), which has traditionally been done using aluminum sulfate, but more recent experiments have proven that PACl can be an effective substitute (Kumbhar and Salkar, 2014). The Nalgonda technique typically utilizes a "batch filtration" method, where large quantities of water are treated in buckets. This technique does not utilize continuous flow, and requires a series of treatments to obtain decontaminated water for extended periods of time. For this reason, the Nalgonda technique has been largely introduced as a household treatment method, and has been introduced to various Indian villages, including those in Nalgonda and in the state of Telangana. It is also currently being studied at the pilot scale in Kenya, Senegal and Tanzania (Dahi et al., 1996). In addition to the restrictions implied by batch treatment, the Nalgonda method requires a high dosage of aluminum sulfate to aggregate with fluoride and precipitate. A study conducted by (Dahi et al., 1996) suggests that $13 \frac{\text{g}}{\text{L}}$ alum ($1.2 \frac{\text{g}}{\text{L}}$ as Al) is needed for the Nalgonda method to effectively treat fluoride levels between 9 and $13 \frac{\text{mg}}{\text{L}}$. Despite the high concentrations of coagulant, the fluoride residual in the test was still unable to meet the WHO safety guidelines of $1.5 \frac{\text{mg}}{\text{L}}$ of fluoride. The high dose of aluminum sulfate also leaves high sulfate residuals in the water, which causes taste and odor issues (Bailey and Fawell, 2004).

In regards to other filtration methods, a study by Inganiella achieved 33.3% removal of fluoride using a combination of a gravel pre-filter and a sand rapid filter to capture granules of fluoride, PACl, NaClO and SO_4H_2 (Ingallinella and Pacini, 2001).

Floc Blankets

Floc blankets develop when vertical flow sedimentation tanks form a fluidized bed of particles like the one in the figure below that then facilitates particle removal by "increasing particle-particle interactions that lead to flocculation and filtration occurring in the floc blanket" (Hurst, 2010).



Figure 2: Flocs in the floc blanket of the reactor

The process of forming flocs requires both the precipitation of aluminum hydroxide from the coagulant and the contact with raw water colloidal particles (Hurst, 2010). Once the combination of precipitation and mixing forms small particles, these new flocs collide to form larger, more porous flocs that can then be used for clarification (Hurst, 2010).

This floc blanket clarification is considered hindered settling, which is a form of sedimentation (Gregory et al., 1996). Sedimentation processes are characterized by the removal of suspended particles, e.g. flocs, sand, and clay, from water. Removal is possible due to the differences in density between water and the suspended particles, but is also dependent on the size of the suspended particles, water temperature, turbulence, stability of flow, bottom scour, and flocculation (Sun, 2004). Floc blanket clarification, however, is primarily governed by upflow velocity of the water and by floc concentration (Gregory et al., 1996). The relationship between upflow velocity, concentration and water quality can be combined into the mass rate of settling, which is equal to the product of upflow velocity and concentration. Within a range of mass fluxes, a distinct interface is established between clear water and the floc blanket and thus one can deduce appropriate values of velocity and floc concentration. At concentrations above that ideal mass flux range, the aggregation of flocs becomes thick enough that compression settling occurs. At concentrations below that appropriate range, flocs are not inhibited by other particles and a suspension with different settling velocities is formed (Gregory et al., 1996).

Floc blanket clarification is used to purify water in many ways around the world. In Taiwan, a process of pre-sedimentation, floc blanket clarification, and sand filtration is used to reduce 100 NTU water down to potable levels (Lin et al., 2004). Floc blankets have also been used extensively to purify water of algae, protozoa and specific virus strains (LeChevallier and Au, 2004). Therefore, it is believed that the adaptability of this method in conjunction with the use of PACl would allow for effective fluoride removal.

Coagulation

Many sources have shown that PACl seems to be the optimal coagulant for the purposes of removing arsenic and fluoride from influent water. (Zonoozi et al., 2009). PACl has been and continues to be used as the most common form of dye removal at the industrial scale. Despite its cost, a main reason as to why PACl is so popular as opposed to other coagulants is that PACl does not cause any leaching of hazardous chemicals into the water from dye decomposition (Golob et al., 2005). A drawback of PACl is that once its coagulation capabilities are saturated, the dye coagulation drops drastically while other coagulants are able to reach a maximum capacity and plateau. The team has been using PACl as the coagulant since the start of the project. Thus, for the sake of consistency in results, PACl will be used until the reactor design can be optimized. Only once the reactor is optimized can coagulant experimentation be considered.

Countercurrent Flow Theory

The use of countercurrent flow for separation of clean and dirty water is a major component of the Countercurrent Stacked Floc Blanket Reactor (CSFBR) system. Countercurrent flow is a common concept that can be observed in biological systems such as the kidneys. Countercurrent parallel vessels exchange NaCl through passive diffusion to remove excess NaCl from fluid that would be circulated throughout the body (Kokko and Rector, 1972). The CSFBR utilized the concept of countercurrent flow to decrease the concentration of dissolved species in reactor 1 by moving flocs from an area of low concentration of dissolved species (reactor 2) to a high concentration of dissolved species (reactor 1). This is accomplished by removing the flocs from reactor 2 using the floc hopper and directing them to the influent stream of reactor 1. Consequently, the effluent flocs from reactor 1 will be more concentrated with the dissolved species and the system will produce less waste per mass of contaminant removed (see Figure 7).

Previous Work

In the spring of 2016, the team analyzed data that suggested that the sand filter system was inefficient and decided to move towards the idea of a single floc blanket reactor (to see details about this system, refer to Longo et al. (2016)). Although the sand filter provided cheaper, more adequate removal of fluoride per milligram of PACl used, a key issue that arose with the sand filter was the system run time. The sand filter became saturated with PACl and fluoride too quickly and the head loss built up rapidly. In a matter of a couple of hours, the floc blanket was completely saturated to the point where it was no longer efficient or providing adequate removal of fluoride. Consequently, the system had to be backwashed too frequently to be an effective process (about every couple hours). On a much larger scale, such as a full size plant, a reduction in time to failure would require more maintenance than is feasible. In order to address this, the team fabricated a new reactor as seen in the figure below mirroring that of the floc blanket and plate settlers in the current Aguacleara plants. The team set up a new apparatus fit with stock tanks, a reactor, a turbidimeter, a flocculator, and stock and waste pumps, referencing research previously conducted on the relationship between the amount of coagulant added and head loss accumulation (Dao et al., 2015).

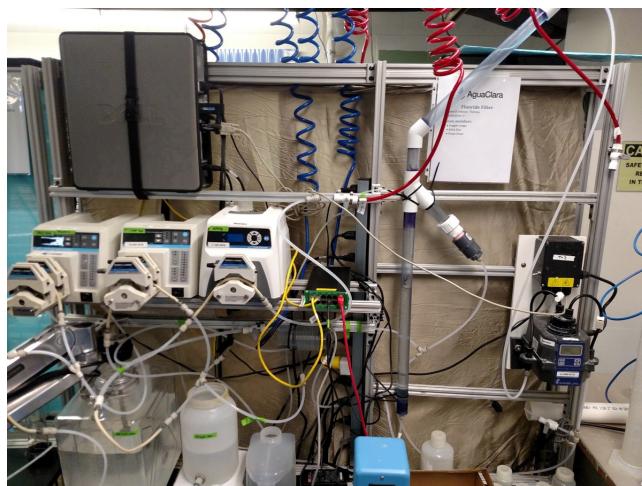


Figure 3: Picture of the System Apparatus

The team then developed a MathCad file to calculate flow rates of pumps from a given set of parameters including upflow velocity, tubing diameters, and reactor concentrations. The team also created a ProCoDA method file to turn the flow rates into RPMs for the pumps so that the process of changing PACl and fluoride concentrations within the reactor was more user-friendly.

After the calculations and fabrication were completed, the team was able to successfully create a floc blanket composed of clay and PACl. When the floc blanket had stabilized, the team tested the system with fluoride. By performing short term, 10 hours tests, the team was able to remove around 85% of the initial concentration of fluoride. The final concentration of fluoride in the effluent was lower than the WHO regulation, indicating that the floc blanket reactor was a viable method to remove fluoride (Longo et al., 2016).

In an effort to improve reactor efficiency, the team fabricated an entirely transparent version of the reactor, where the important contact points (the floc weir and the bend to the tube settler) were visible so that interactions occurring in those areas could be analyzed. The team then used this reactor at an EPA competition to analyze red dye in place of fluoride and found that it was a successful dye removal apparatus. Finally, the team performed some initial jar tests which suggested that the use of clay may not be necessary for the removal of fluoride (Longo et al., 2016). These tests included putting PACl and fluoride into a beaker to mix for 5 minutes then settle for 15 minutes. Then, the surface water was tested for fluoride to reveal low levels of fluoride. If this was experimentally verified, then the elimination of clay from the system design could reduce the operating cost needed for fluoride removal.

In the fall of 2016, the team fabricated a new bottom insert to prevent the accumulation of flocs that clogged the bottom of the reactor. The newly fabricated geometry with a smooth sloped bottom allowed for gradual flow expansion and the recirculation of the flocs that would have settled to the bottom of the reactor with the old bottom geometry as shown in the figure below.

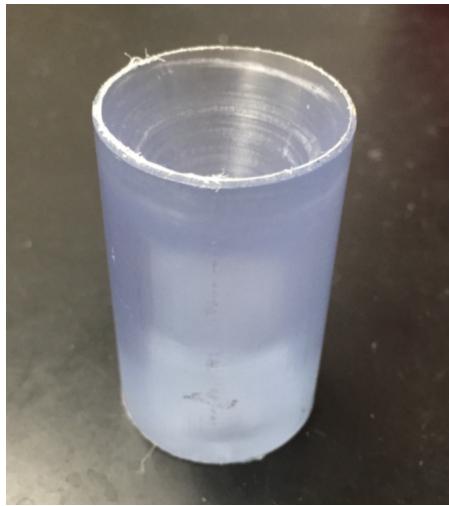


Figure 4: Picture of the Full System Apparatus

Various concentrations of dye were tested (from $25 \frac{\text{mg}}{\text{L}}$ to $100 \frac{\text{mg}}{\text{L}}$) using a 1:1 PACl to dye ratio to see whether higher concentrations of dye would clog the reactor. However, even though increasing the concentration of dye increased the density of the floc blanket, the reactor did not clog and the bottom insert proved to be successful for these tests (Cheng et al., 2016).

The team also determined the minimum length of the reactor needed to save resources and space. A shorter reactor, with a height of 5 cm below the weir, was tested with concentrations of $25 \frac{\text{mg}}{\text{L}}$, $50 \frac{\text{mg}}{\text{L}}$, and $100 \frac{\text{mg}}{\text{L}}$ of dye. Although the floc blankets reached a short term steady state height of around 20-30 cm, the reactor failed in the long term as flocs built up and went through the tube settler to the turbidimeter in the long term. This suggested that there was a minimum height that a floc blanket would reach; thus the shorter reactor system was not feasible. (Cheng et al., 2016).

During the final portion of the semester, the subteam performed 24-hour experiments with the longer reactor in order to compare its results with those of the CSFBR subteam. The CSFBR subteam had hypothesized that a species removal system composed of two reactors in series could lead to cleaner water than the Fluoride team's single reactor system. During each iteration, the two teams ran each system for approximately twenty four hours with the same red dye and PACl concentrations. However, the results of these experiments were inconclusive because the CSFBR team found that PACl would clog their system midway through each experiment; rendering the reactors incapable of further purification (Dokko and Espada Fraile, 2016). Thus, the current subteam seeks to reexamine the benefits of reactors in series versus a single reactor and conclude which system yields the lowest effluent concentrations of red dye and fluoride.

Over the summer of 2017, tests performed during the previous semester were repeated in order to finally determine whether the second reactor in series made enough significant improvements to be implemented on a larger scale. A new fluoride probe was purchased, and experiments conducted on this probe showed that a plant using last semester's parameters could produce effluent water with as low as 0.05 mg/L , significantly below the WHO's standards. However, clay that remained in the effluent

caused turbidity to often rise above 5 NTU. In consideration of this turbidity and as an effort to lower the number of resources needed to implement the reactor, it was determined that clay needed to be eliminated from the system. Additionally, the unusually high PACl dosage of 25 g/L needed to be lowered. While no data was collected that definitively pointed to using one or two reactors, the team tentatively hypothesized that the second reactor would not justify the added expenses when built on a larger scale. However, once the reagent parameters were optimized, further tests and a cost analysis could be conducted to verify this.

Methods

Experimental Apparatus

The construction of this apparatus and the fabrication of the reactor was completed last semester. The list below references materials used to make the apparatus and Table 1 lists the necessary constraints on the reactor for it to perform as designed. To view complete instructions for apparatus construction and a more in-depth discussion of design and calculations, please refer to the spring 2016 AguaClara report (Longo et al., 2016). For information on how to run an experiment, refer to the manual at the end of this report.

The reactor system was setup in such a way that it had the ability to be used as either a one reactor system or a two reactor system by turning several valves. The effective setup of the one-reactor system can be seen in Figure 5 and the effective setup of the two-reactor system can be seen in Figure 6. When running a one-reactor test, Reactor 2 (on the right in the two-reactor system) is used. The entire apparatus at the lab bench is shown in Figure 7.

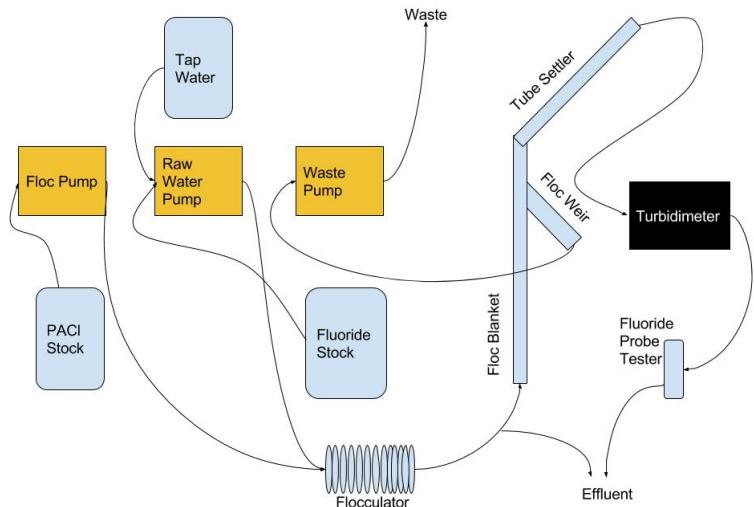


Figure 5: One reactor schematic

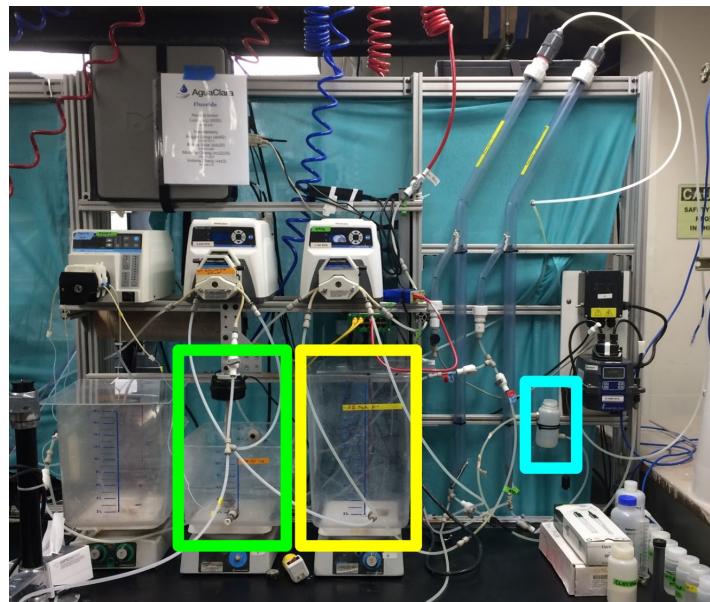


Figure 6: Two reactor schematic

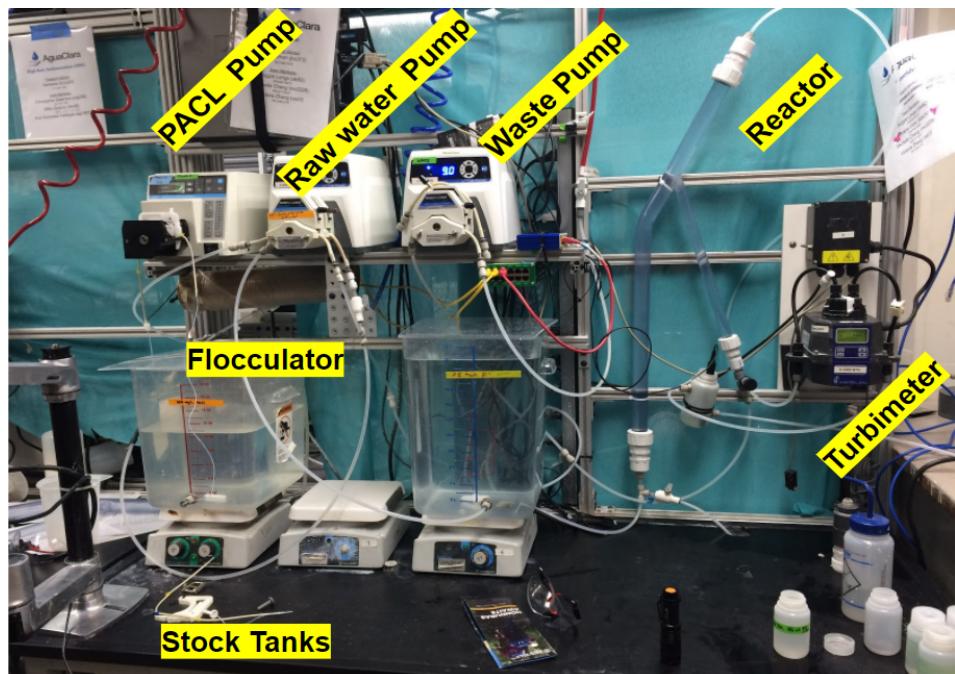


Figure 7: Picture of the Full System Apparatus

Water Flow Through Reactor

1. Fluoride and tap water were mixed by pumping them with the Raw Water Pump
2. PACl was pumped through the Floc Pump and mixed with the diluted fluoride stream , which proceeded into the flocculator to make flocs
3. The PACl-fluoride floc mixture flowed through the floc blanket and tube settler with flocs settling out through the floc weir
4. The effluent of the tube settler went through the turbidimeter and fluoride probe tester to waste.

Materials

- Two 600 RPM pumps and one 100 RPM pump
- Transparent 2.54 cm (1") PVC piping
- Flexible and hard 0.635 cm (1/4") tubing and Microtubing
- Turbidimeter
- Polyaluminum Chloride (PACl), 10,000 ppm Fluoride Solution
- Various connectors and buckets for stocks
- Two stir plates with stir bars
- Push-to-Connects and Valves

Table 1: List of important parameters for reactor

Parameter	Symbol	Value
Residence Time	θ	4513 s
Hydraulic Gradient	G	75.2 s ⁻¹
Velocity Gradient	$G\theta$	13000
Upflow Velocity	v	1 mm/s
Capture Velocity	v_{cap}	0.12 mm/s
Total Flow Rate	Q	30 mL/min
Floc Flow Rate Percentage	Q_{Floc}	20%
Water Flow Rate Percentage	Q_{Water}	80%
Reactor Floc Blanket Length	L	24 inches
Flocculator Tubing Length	l	46 feet
Tube Settler Length	L_{TS}	14.75 inches

[Refer to the manual for detailed information about how each test was run].

Results and Analysis

The initial tests that were run in the beginning of the semester attempted to achieve high removal rates without the addition of clay since research in summer 2017 reported that clay remained in effluent water, which created complications with settling in stocks. The team tested concentrations of 12.5, 25, and 50 mg/L of PACl with an upflow velocity of 1 mm/s. The team's goal was to produce effluent water with a concentration of 1.5 mg/L to meet WHO standards from an initial fluoride concentration of 10 mg/L.

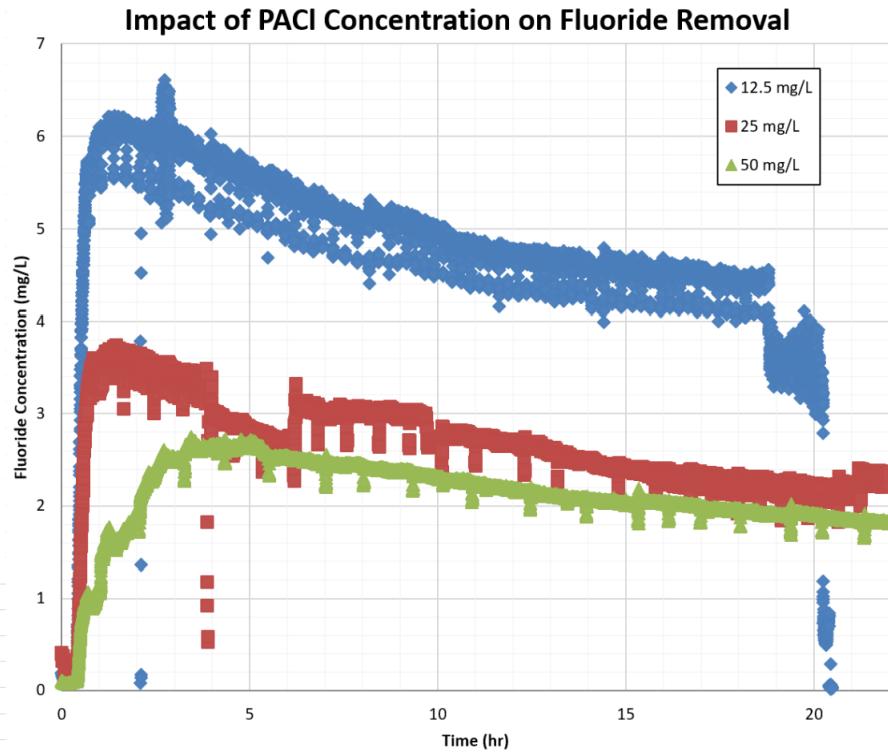


Figure 8: Fluoride Removal for Different Concentrations of PACl

As shown in Figure 8 and Table 2, the increase in PACl concentration from 12.5 mg/L to 25 mg/L dramatically improved fluoride removal as the effluent fluoride concentration dropped from 4.4 mg/L to 2.2 mg/L (all tests began with influent fluoride concentrations of 10 mg/L). However, the increase in PACl concentration from 25 mg/L to 50 mg/L only reduced effluent concentrations from 2.2 mg/L to 1.8 mg/L, which is not as significant of an improvement. In the field, this would equate to adding a significant amount of reagent and operating cost without achieving the same fluoride removal that the reagent provided in the first two-fold concentration increase. As the concentration of PACl increased, the removal efficiency of fluoride began to level off. Moreover, all three tests did not produce concentrations below the WHO standard. During these tests, the flocs in the floc blanket looked similar to Figures 2 and 9. These flocs were generally larger than those from the Spring 2017 system that utilized clay. Additionally, since clay was no longer added, the flocs were also transparent so a flashlight was needed to see them. A summary of the results of this test are shown in Table 2.

Table 2: Summary of Fluoride Removal for Various Concentration of PACl

PACl Concentration (mg/L)	Ending Fluoride Concentration (mg/L)	Time to failure (hr)
12.5	4.4	18.6
25	2.22	9.5
50	1.84	4.5



Figure 9: Flocs in the weir area of the reactor

In addition, the reactors continuously failed regardless of different concentrations of PACl as flocs were seen in the tube settler exiting with the effluent water. Failure is defined either as a spike in effluent turbidity due to entrainment of flocs by fast flow or a buildup of flocs that do not exit the weir and eventually reach the turbidimeter. In these experiments, there was no recirculating floc blanket present and the current floc weir proved to be inept at removing the necessary flocs from the effluent water. As seen in Figure 10, the failure of this test occurred around only 10 hours when the turbidity shot up. As seen in Table 2, the time to failure decreases when the PACl dosage increases. This means that a higher PACl concentration in the influent causes larger and more adsorbent flocs. These flocs cause the system to clog and prevent recirculation. Ideally, the reactor should not fail over the course of its lifetime, so a new reactor and higher upflow velocity were chosen to prevent the reactor from failing.

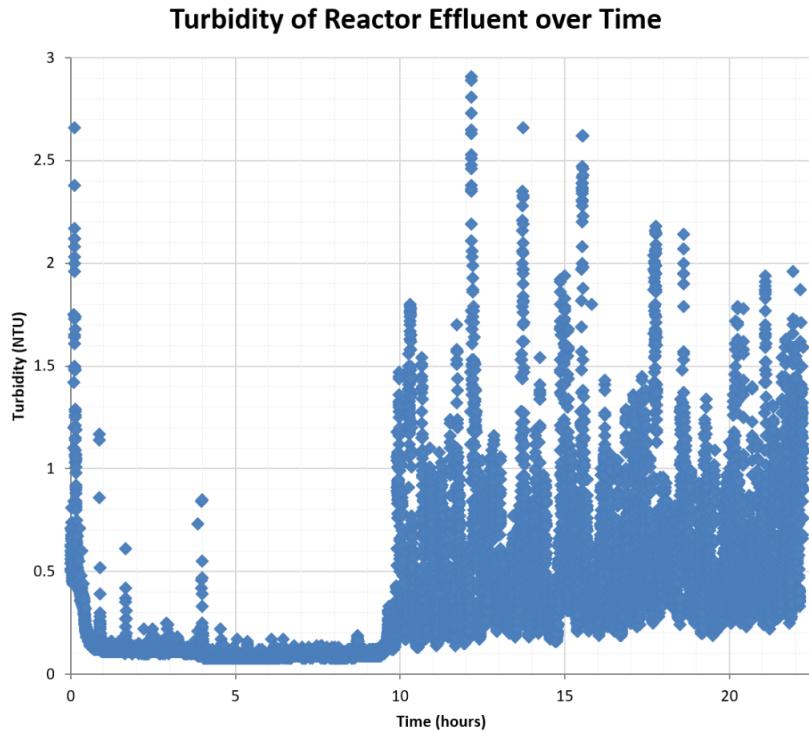


Figure 10: Failure of the reactor due to a spike in NTU around 10 hours into the test. This test was for a PAcL dosage of 25 mg/L and influent fluoride concentration of 10 mg/L.

Consequently, the team decided to switch to another reactor built by the High Rate Sedimentation team in the summer of 2017, shown in Figure 11. After performing several tests, the team concluded that the new reactor not only created denser, recirculating floc blankets, but also dramatically increased time to failure. The old reactor failed after 5 hours whereas the new reactor failed after 15 hours (Figure 13). However, the fluoride removal was about the same between both reactors, as shown in Figure 12. The new reactor could also run at higher upflow velocities while maintaining the floc blanket. Thus, the team sought to optimize reagent concentrations and upflow velocities with the new reactor in hopes of achieving a sustainable system that never fails as explained later on in the report. A summary of the results is listed in Table 3

Table 3: Difference in Fluoride Removal between Old and New Reactor

Reactor	Ending Fluoride Concentration (mg/L)	Time to failure (hr)
Old Reactor	1.84	4.5
New Reactor	1.78	15

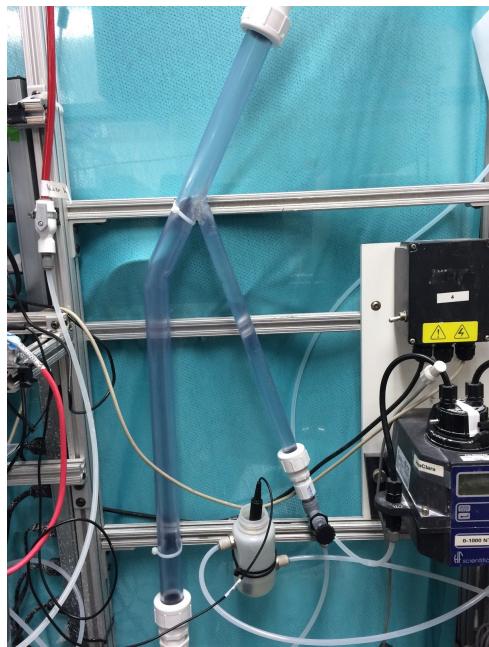


Figure 11: The new reactor used for testing higher upflow velocities where the weir is on the sloped part instead of the vertical part.

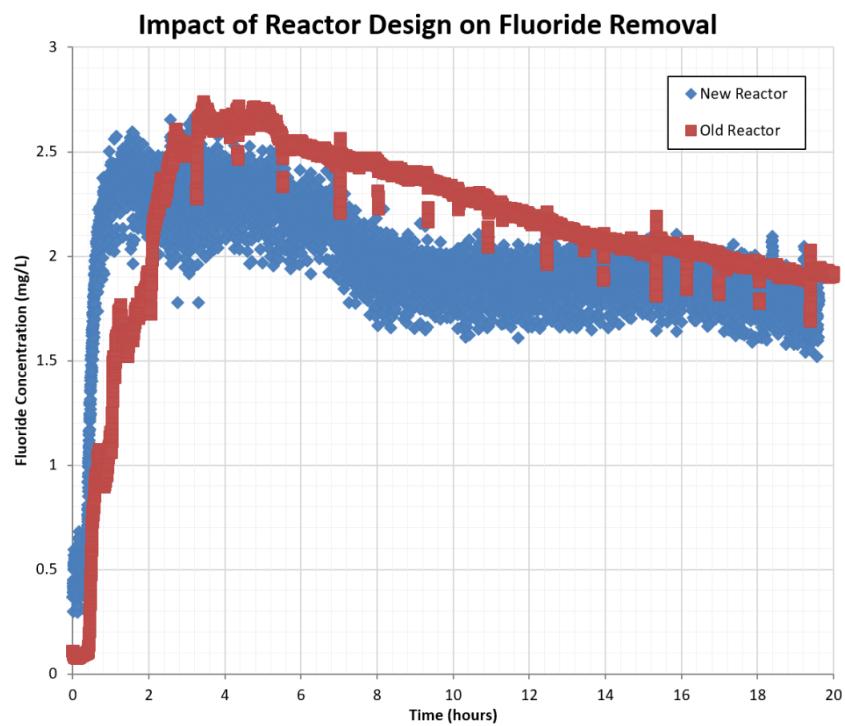


Figure 12: The performance of the new and old reactors are similar and reach the same final fluoride concentration after 20 hours

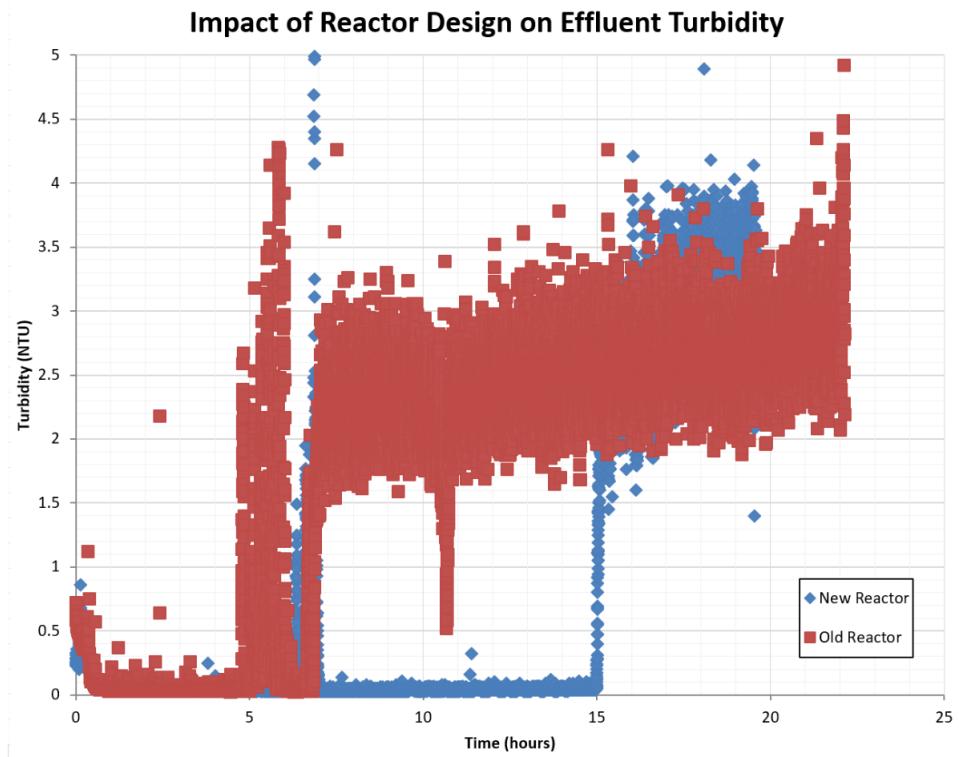


Figure 13: The difference in failure times between the new and old reactor as NTU spikes in the new reactor occur 10 hours after those in the old reactor

Testing new reactors focused on finding the optimal upflow velocity; therefore, the upflow velocity had to be high enough to prevent the buildup of PAcI sludge but low enough to prevent flocs from being entrained by the flow of water. The team ran tests at upflow velocities of 1, 1.5, 2, and 3 mm/s with 1.5 mm/s proving to be the optimal upflow velocity. However, similar to earlier tests, each of these 4 tests yielded effluent fluoride concentrations higher than the desired concentration of 1.5 mg/L. The team first tested a PAcI dosage of 25 mg/L with an upflow velocity of 1 mm/s, which failed after 15 hours due to sludge buildup. The upflow velocity was not high enough to allow for a recirculating floc blanket. Instead, clumps of sludge built up in the reactor until they exited out the effluent stream and reached the turbidimeter, yielding a sudden increase in turbidity that sustained itself for the remainder of the test. When the upflow velocity was increased to 3 mm/s for the same PAcI concentration, flocs were observed in the tube settler since the high upflow velocity pumped flocs out of the reactor. Thus, the effluent fluoride concentration was much higher than desired since it was contaminated by flocs. This was also observed for the 2 mm/s test. At an upflow velocity of 1.5 mm/s, the team observed no turbidity spike and thus no failure. A summary of these tests are shown in Table 4 and Figure 17

Table 4: Summary of Fluoride Removal for Various Upflow Velocities

Upflow Velocity (mm/s)	Ending Fluoride Concentration (mg/L)	Time to failure (hr)
1	1.78	15
1.5	2.47	No Failure
2	3.5	Instant
3	3.9	Instant

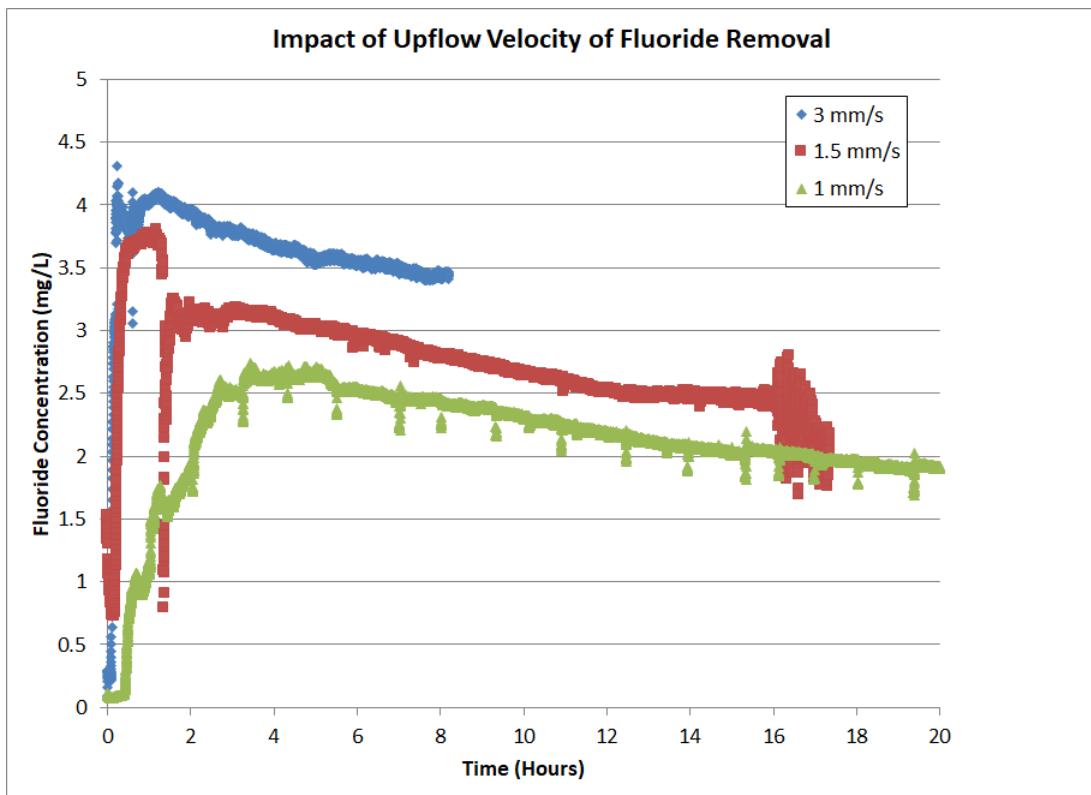


Figure 14: Comparison of effluent fluoride concentrations for various upflow velocities

In order to test a large variety of PACl concentrations, the team performed tests at an upflow velocity of 1.5 mm/s and different values of influent fluoride concentration while varying the concentration of PACl throughout the test. The team checked on the test at two to three hour intervals and increased the PACl flow rate, which would increase the concentration of PACl in the reactor, when the fluoride concentration reached a steady state. For example, the team first performed a test with a 8 mg/L initial fluoride concentration in which the PACl concentration varied from 15 mg/L to 25 mg/L to 50 mg/L. A PACl concentration of 25 mg/L was found to provide adequate fluoride removal in all previous tests and was thus used for the baseline of predicting PACl concentrations in future tests. The values of PACl concentration for each test were chosen by either doubling or halving the baseline 25 mg/L to provide an easy comparison between tests. Therefore 6.25 mg/L and 12.5 mg/L PACl concentrations were used for the lower initial fluoride concentrations to find a minimum PACl dosage necessary to reach the 1.5 mg/L fluoride WHO limit. Additionally, the 50 mg/L PACl dosage was used for higher initial fluoride concentrations to reach the WHO limit. Table 5 details the fluoride removal for different concentrations of fluoride obtained from three tests.

Table 5: Summary of Fluoride Removal for Various Influent Fluoride and PACl Concentrations

PACl Concentration (mg/L)	Initial Fluoride Concentration (mg/L)	Final Fluoride Conc (mg/L)	W
6.25	2	1.46	0.087
12.5	2	1.01	0.080
25	2	0.57	0.057
6.25	4	3.20	0.13
12.5	4	2.18	0.15
25	4	1.52	0.010
50	4	0.54	0.069
15	8	5.61	0.16
25	8	4.93	0.12
50	8	2.72	0.11
50	10	1.05	0.18

The variable w, defined as:

$$W = \frac{\text{mass adsorbate}}{\text{mass adsorbent}} = \frac{\text{mass fluoride, adsorbed}}{\text{mass aluminum}} = \frac{C_{\text{fluoride, initial}} - C_{\text{fluoride, final}}}{C_{\text{PACl}}} \quad (1)$$

was used to create the absorption model shown in the following figure to predict the PACl dosage needed for a desired effluent fluoride concentration, where C is the concentration in mg/L. In this case, fluoride is the adsorbate and aluminum is the adsorbent.

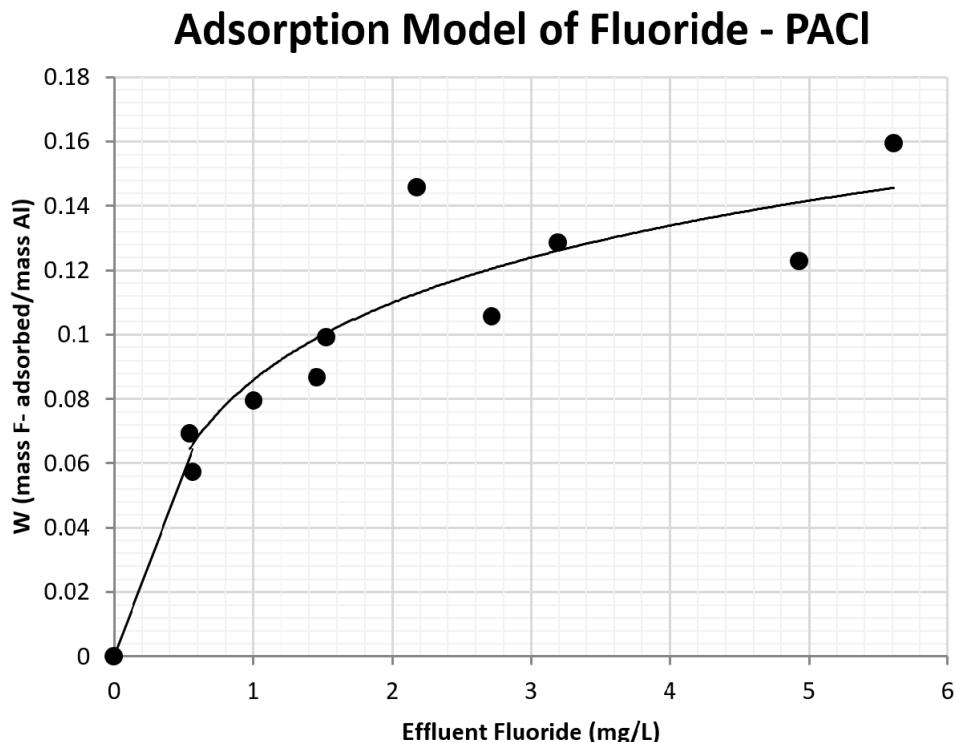


Figure 15: Adsorption Model for PACl - Fluoride Interactions

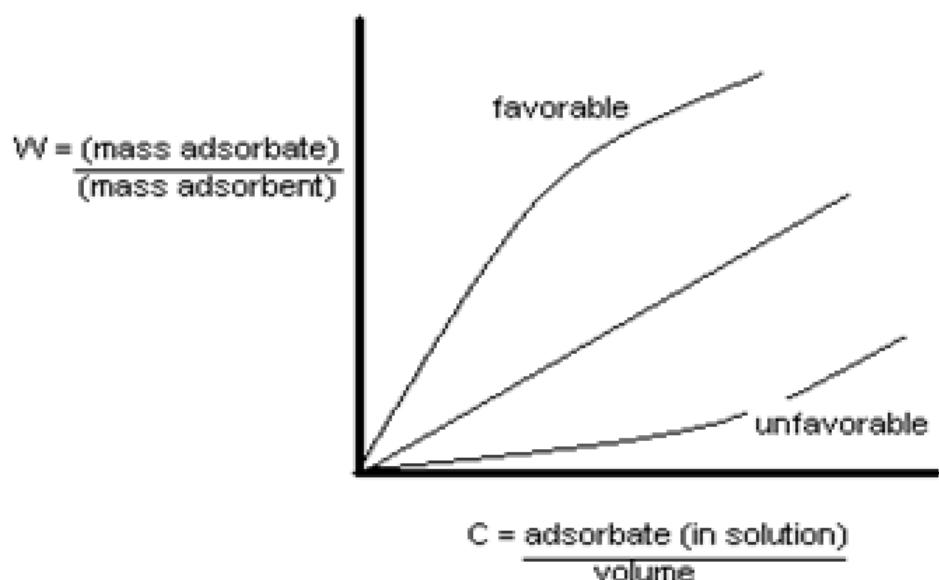


Figure 16: Typical adsorption models for various adsorbates and adsorbents.

Figure 16 shows different models for interactions between various adsorbates and adsorbents. The model developed for fluoride and PACl compares to the favorable reaction in Figure 16 as more fluoride tends to adsorb to the PACl instead of remain in the water.

The adsorption model can be used to calculate a PACl concentration needed to achieve a certain fluoride effluent concentration given an initial fluoride concentration. Since the desired fluoride level set by the WHO is 1.5 mg/L, this is the desired effluent fluoride concentration. However, the target effluent fluoride concentration is around 0.75 - 1 mg/L to account for error in the adsorption model. Therefore, the model will calculate a range of W values that will result in the target effluent concentration. Additionally, the model will calculate the PACl dosage necessary to treat an initial fluoride concentration given the range of W values.

At a certain maximum PACl dosage, the reactor will clog due to insufficient shear to break down the PACl flocs, thereby causing the bed to fluidize. The maximum PACl dosage has not yet been determined. However, if the adsorption model calculates an excessive PACl dosage, a second reactor may be necessary to decrease the max concentration of PACl necessary to run the system. Adding a second reactor decreases the PACl dosage for each reactor since less removal is required for each individual reactor to achieve the desired effluent fluoride concentration. A multiple reactor system can use the solver function on excel or a model to vary the intermediate effluent concentration between the reactors and thus calculate the minimum overall amount of PACl necessary given an initial fluoride concentration and desired effluent concentration.

Towards the end of the semester, the team discovered that the voltage read by the fluoride probe in tap water differed significantly from the voltage reading using deionized, (DI), water. The results are shown in table 6 for a test measuring the concentration of a 20 mg/L solution of fluoride prepared using tap water and DI water.

Table 6: Tap Water Interactions with Fluoride Probe

	Voltage Reading	Fluoride Concentration Reading
20 mg/L Standard with Tap Water	0.021	16.4 mg/L
20 mg/L Standard with DI Water	0.0146	22.8 mg/L

The difference in the perceived fluoride concentration is thought to be due to ions in tap water, such as calcium or hydroxide ions, that may react with fluoride ions to form various compounds. Since the probe is selective to fluoride ions, it will not register the fluoride present in other forms; therefore, the fluoride concentration reading in tap water will be lower than the actual concentration of fluoride present. This means that our current adsorption model may be incorrect and needs to be remade. A brief method for remaking the model is described in the future work.

Conclusions

The newer reactor system based on the HRS subteam's summer research allowed for significantly less sludge buildup in the team's long duration tests. The best upflow velocity to combat sludge buildup was 1.5 mm/s. Thus, all future experiments should be conducted with these settings. Additionally, according to the adsorption model utilized in the latter portion of the semester, a maximum coagulant dosage exists such that a single reactor system will always clog, even at 1.5 mm/s upflow. If future experiments deem coagulant dosages beyond the maximum necessary for fluoride removal, a second reactor will likely be necessary. The adsorption model created by the subteam can be an effective predictor of fluoride removal once additional experiments are performed to verify its validity. Finally, the ions present in tap water and stock solutions created using tap water interfere with the functionality of the fluoride probe, giving inaccurate readings. Next semester, the adsorption model should be remade with this in consideration, and corrections should be made to calculations performed on the experiments utilizing tap water solutions.

Future Work

Since the ions in the tap water gave a lower reading of fluoride than there actually existed in the water, a new adsorption model needs to be made. All the experiments completed in Table 5 need to be completed again with a recreated adsorption model. One potential method of correcting for ion presence in tap

water may be using a set of tap water standards throughout the semester of accurate concentrations (i.e. created by pipette and volumetric flask), and comparing the voltages of experimental stock solutions to these standards each time a test is run. For instance, if the experimental stock was supposed to contain 20 mg/L fluoride and was made precisely and accurately, but read 0.04 mV off of the standard created at the start of the semester, all measurements taken during that experiment would be corrected by that 0.04 mV. Once these fluoride probe inaccuracies are taken into account and all the tests are run, the new adsorption model can be confirmed and used to calculate PACl concentrations. At this point, if there are no other research studies or experiments done at other universities or companies that remove fluoride with lower PACl concentrations than the team uses, a paper can be published about the results.

After the adsorption model is made, a benchtop apparatus that is solely gravity powered needs to be developed in the lab and then tested to again confirm the adsorption model. This can then be used to create a larger system to be sent to India in the future for field testing.

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Semester Schedule

Task List

1. Setup a one reactor system without clay addition (9/7/17) - Everyone. Clay causes problems on larger scale. Test apparatus without clay to see if similar removal with clay.
2. Test apparatus for smallest PACl dosage (9/22/17) - Victoria. Test reactor without clay, if there's sludge buildup, then increase/decrease PACl dosage appropriately to have no sludge and adjust (according to gamma value from Spring 2017 semester for 2x PACl coverage).
3. Increase upflow velocity if sludge unavoidable (10/6/17) - Auggie. If sludge present without clay usage, increase upflow velocity and test same dosages
4. Fabricate updated floc blanket reactor (9/29/17) - Auggie. If higher upflow velocity necessary, fabricate the new reactor with updated bends.
5. Test new system with a two reactor countercurrent apparatus - Michelle (11/1/17).
6. If time allows, design and begin fabricating pilot scale reactor that is electricity free (0.1 L/s) for testing next semester (12/5/17) - Victoria.

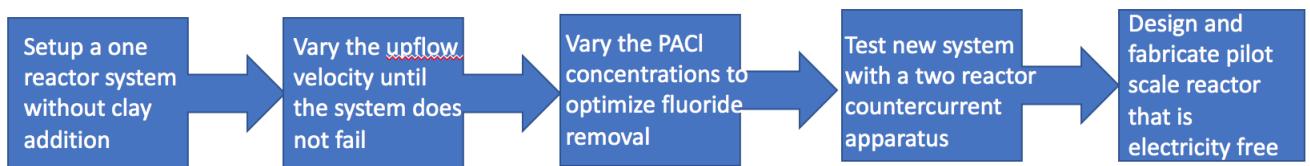


Figure 17: Task Map

Report Proofreader: August Longo

Manual

Experimental Methods

Fluoride Experimentation

0.0.1 Protocol for Running Just Water Through the Reactors

1. Turn on Just Water process in ProCoDA and fill system completely with water.
 - (a) Open fluoride line and close the fluoride valve as to not pump fluoride into the system during backwash
 - (b) Close the waste line
 - (c) Make sure the sample bottle with the fluoride probe does not overflow from the high flow rate of the water
2. Continue to run water until turbidimeter reads less than 0.5 NTU and fluoride concentration is less than 0.5 mg/L.
 - (a) Record the initial voltage reading to make sure the initial concentration of fluoride in the sample bottle is about 0 mg/L

0.0.2 Protocol for Start Up and Running of Reactors

1. Fill stock tanks with appropriate concentration of PACl, fluoride, and clay and make sure to have enough stock to run for 24 hours.
2. Calculate the flow rates of the PACl and fluoride pumps from the MathCAD file and run the pumps at the appropriate RPM using ProCoDA
3. Run the waste pump at the appropriate RPM as calculated from ProCoDA.
4. Calibrate the fluoride probes and record the initial concentration of fluoride in the sample bottle
5. Empty the bucket at the bottom and make sure it doesn't overflow through the length of the test

0.1 Experimental Checklist Before Starting Test

- (a) Waste line is open (System will explode if this is not open)
 - (b) No leaks anywhere in system
 - (c) Pumps are all turned on and running at the correct RPM (Check ProCoDA)
 - (d) Pumps are all pumping water in the correct direction (in the direction of the flocculator and reactor)
 - (e) The fluoride pump line is closed and fluoride valve is open after running just water through the system
 - (f)
6. Write a text file in ProCoDA saying "Start Test" with appropriate descriptors including fluoride concentration, PACl concentration, upflow velocity,etc. and then change the process to the ON state.
 7. During the test: Recheck everything periodically to ensure it is running how it should be and that there are no water leaks and the stocks don't run out.
 8. At the end of the test, change the process to the OFF state.
 9. Clean the reactor using the "Cleaning Procedure" after the experiment is completed.

Cleaning Procedure

1. Put a piece of sponge in the tube between the flocculator and PACl insert.
2. Run a high velocity jet through the tube to purge the flocculator of excess clay buildup.
3. Drain both reactors through the valves at the bottom of the reactors.
4. Flush water through both reactors until no clay remains in the system.
5. If there is not a noticeable amount of buildup, (a) and (b) can be skipped.

Fluoride Probe Calibration Procedure

1. Make the stock calibration concentrations of .1 mg/L, 1 mg/L, 10 mg/L, and 20 mg/L in small bottles. Individually pipette fluoride stocks into all four bottles, do not use serial dilutions.
2. Rinse the fluoride probe with DI water and carefully dab the end of the probe on a Kimwipe. If any sediments from prior experiments remain, rub off with polishing strip provided and rinse with DI water again.
3. Insert the probe into one of the calibration solutions.
4. Swirl the probe around, then let settle. Record the voltage once it reaches a steady state
5. Make sure to record the voltage at the minimum voltage (the voltage will spike first and eventually reach a steady state voltage before increasing again).
6. Repeat with the other fluoride concentrations and record the values in Google Docs (labeled "Fluoride Calibration").
7. The R squared value, slope, and y-intercept will be updated as the voltages are updated (make sure the R squared value is at least .99 to ensure accurate fluoride calibrations).
8. If R squared value is not 0.99, rinse let settle in TSIAB solution for 5 minutes, then rinse thoroughly with DI water. Sand with polishing strip, and repeat procedure, gently shaking probe up and down before first calibration measurement.

ProCoDA Method File

ProCoDA is a process control system that was developed by Monroe Weber-Shirk in order to set process parameters through a computerized system. It can be adjusted to different system states that control the system pumps depending on what flow rates are desired. Additionally, ProCoDA collects the data from probes, allowing for compilation of dye concentration data.

To begin the ProCoDA method file, three states were made: ON and OFF and Just Water. In the OFF state, all the valves were closed and no pumps were on. In the ON state, all the pumps were ON and all valves were opened, in the Just Water state, only the water valve was open. ProCoDA turned this pump on and off via a normal valve control, so long as the pump was already set to a proper flow rate. The system was set to run on Manual setting, as a proper run time had not yet been determined.

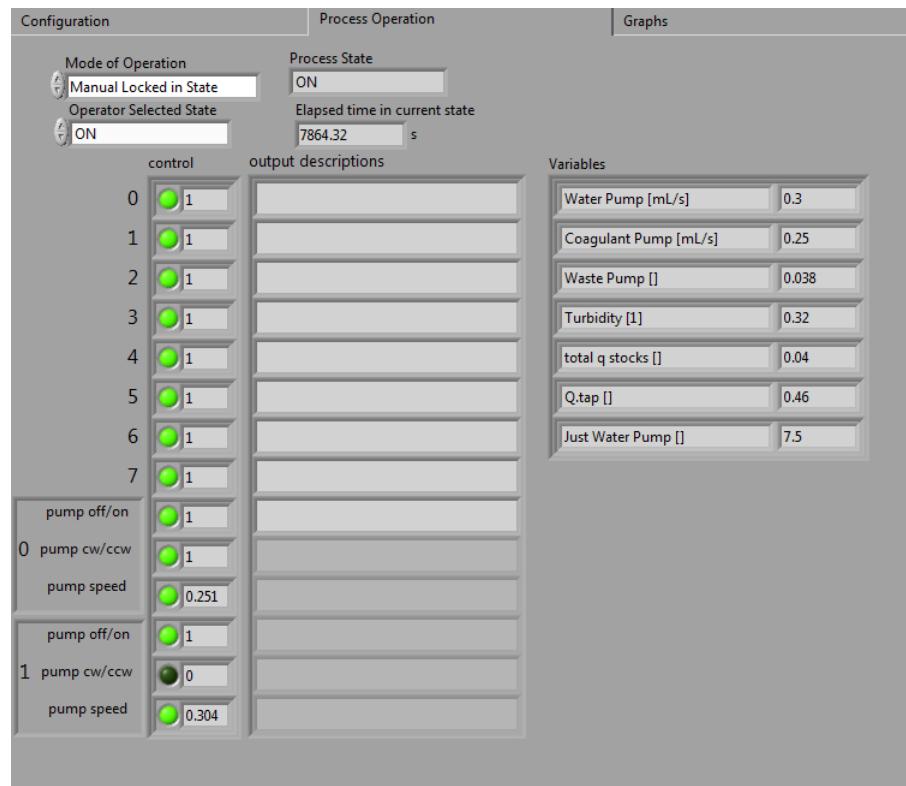


Figure 18: ScreenShot of ProCoDA Panel

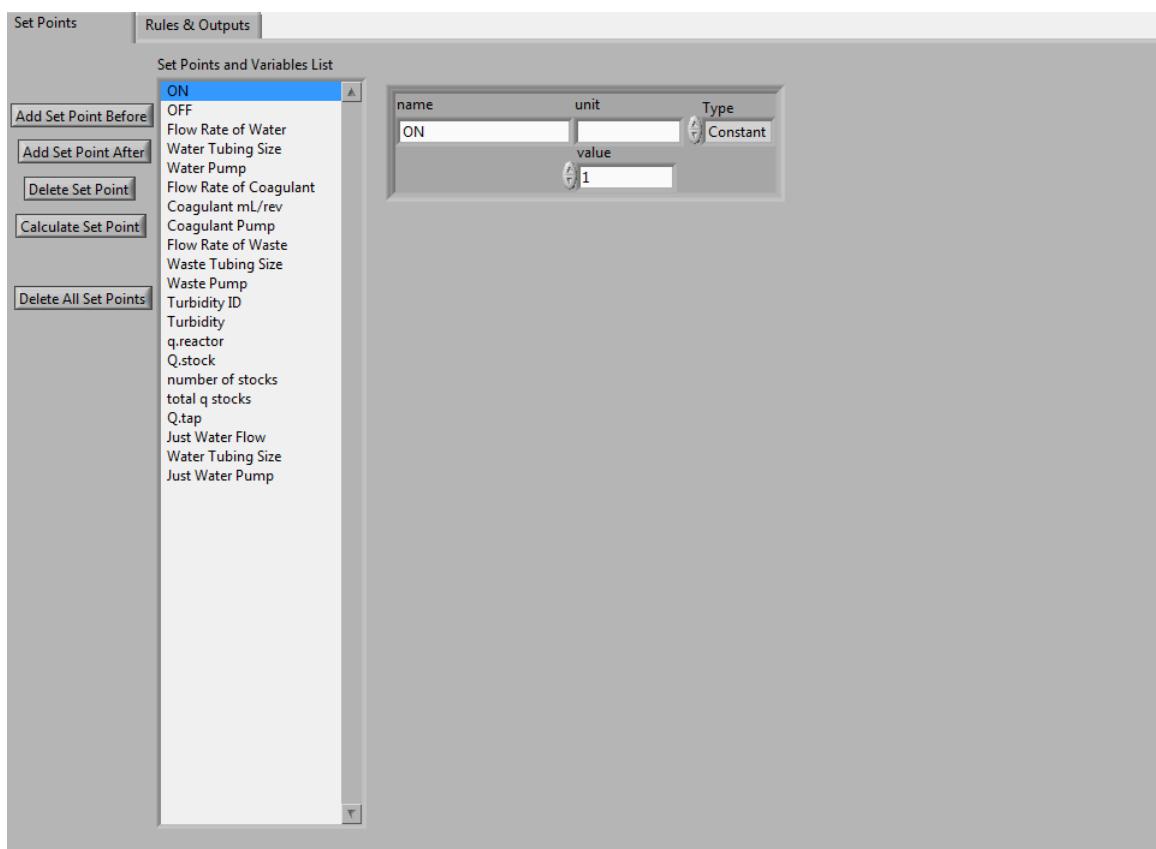


Figure 19: ScreenShot of ProCoDA Set Points

The method file was set to control the revolutions per minute (RPM) of the PACl/dye pump and the tap water pumps. This was done using the peristaltic pump ProCoDA file available in the AguacClara server as well as inputs for desired flow rate and tubing size. For the PACl and dye pump heads, inputs of $\frac{\text{mL}}{\text{rev}}$ and flow rate were needed to calculate RPM since microtubing was used, and for the water pump head, tubing ID and flow rate were needed to calculate RPM. The set points used for the method file included a water pump set point for the water pump RPM and a floc pump set point for the PACl/dye pump RPM.

Table 7: List of variables for ProCoDA

Set Point	Definition	Value
Water Flow Rate	Flow rate of water through the system	Variable
Water Tubing ID	Pump tubing size	16
Water Pump	Water pump RPM	Variable
Floc Flow Rate	Flow rate of PACl and dye through the system	Variable
Floc mL/Rev	Volume of water per revolution of the pump	0.012195
Floc Pump	Dye and PACl pump RPM	Variable