Fluoride, Fall 2016

Michelle Cheng, August Longo, Briana Vidal

December 10, 2016

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 last semester's fluoride removal reactor, the current subteam hopes to develop a better method of fluoride purification by partnering with the CSFBR subteam and researching the effectiveness of reactors in series versus a single reactor system. At the beginning of this semester, the subteam identified potential issues with floc buildup at the bottom of the apparatus. Thus, a smoothly sloping bottom insert was incorporated into the single system reactor for all comparison experiments. The subteam then analyzed the effectiveness of fluoride removal in a significantly shorter reactor. It was determined that although a shorter reactor would reduce fabrication cost, the lack of sufficient space for floc blanket formation yielded impotable water. After performing a series of side-by-side experiments, some data has been collected to compare functionality between the single reactor system and the CSFBR subteam's reactors in series, the results are not yet conclusive. In future semesters, more comparable data needs to be collected to draw concrete final conclusion as to which system is more effective.

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 - making villagers who rely on these well sources for water at a high risk of overexposure to fluoride (EPA, 2016a). The prevalence of dental fluorosis, an indicator of excessive fluoride concentrations, differs across India, but has been shown to range from 13-91% depending on the age group in question and the water source supplying the state or municipality (Arlappa et al., 2013).

In order to develop a treatment for groundwater saturated with fluoride, teams from previous semesters analyzed the efficiency of fluoride removal by passing a coagulant, polyaluminum chloride (PACl), and a 10 $\frac{\text{mg}}{\text{L}}$ solution of fluoride through a sand filter. However, the sand filter was an inefficient method of removal because of the buildup of headloss. Thus, instead of using a traditional sand filter, the team researched a similar relationship between PACl and fluoride via a floc blanket reactor last semester. In the floc blanket reactor,

flocs of PACl and clay adsorbed the fluoride from water. The flocs then overflowed into a floc weir as the floc blanket grew while the purified water flowed out of the top of the reactor. This reactor was modeled after the floc blanket, floc weir, and plate settlers in the sedimentation tank of a typical AguaClara water treatment plant. 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 head loss. If head loss were to occur, the system would require backwash to counteract the flocs that continuously exit the reactor through the weir.

The subteam developed a purification system last semester and received an EPA Phase II grant for further research. This semester, the team hopes to further test and optimize last year's design. The reactor size was reduced to only five centimeters in order to test the hypothesis that the system works regardless of floc blanket height. This smaller reactor used significantly less PVC, ultimately decreasing the cost of materials and reducing the space needed for each system. However, the shorter reactor proved to be less efficient at removing red dye. The subteam will be working in conjunction with the Countercurrent Stacked Floc Blanket Reactor (CSFBR) subteam for the remainder of the semester. CSFBR is studying the removal of dissolved species, particularly arsenic and fluoride, from groundwater using two reactors in series. The purpose of coordinating the experiments with that of CSFBR is to establish whether multiple reactors in series or a single reactor is more effective in the removal of dissolved species. Theoretically, two reactors in series will allow the flocs to interact with and remove more red dye than a single reactor could, therefore using the flocs to their full potential and resulting in overall cleaner water.

Literature Review

Fluoride Limitations and Hazards

Over-consumption of fluoride can lead to arthritis, dental fluorosis, crippling fluorosis, bone deformation and ligament calcification (Roholm, 1937). Fluoride can cause irritation through inhalation, digestion, and touch and can cause damage to both eyes and exposed skin (of Health, 2010). Though there isn't an established "average" level of fluoride in India, the 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 5-23 $\frac{\text{mg}}{\text{L}}$ 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, with 0.8-1.2 $\frac{\text{mg}}{\text{L}}$ providing a beneficial balance of fluoride and water by preventing tooth decay and strengthening the skeleton. The team will be striving towards the WHO guideline of 1.5 $\frac{\text{mg}}{\text{L}}$ of fluoride this semester.

Polyaluminum Chloride 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 very 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 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 overall higher 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 was necessary for the equivalent treatment (Gebbie, 2001). 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 $Al_2(SO_4)_3$ (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.

Several techniques are currently in existence that use PACl to specifically 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, although actual fluoride removal is done through co-precipitation (Bailey and Fawell, 2004). The technique 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 $\frac{g}{L}$ alum (1.2 g/L as Al) is needed for the Nalgonda method to effectively treat fluoride levels between 9 and 13 $\frac{mg}{L}$. Despite the high concentrations of coagulant, the fluoride residual in the test was still unable to meet the WHO safety guidelines of 1.5 $\frac{mg}{L}$ 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 prefilter and a sand rapid filter to capture granules of fluoride, PACl, NaClO and SO4H2 (Ingallinella and Pacini, 2001).

Floc Blankets

Floc blankets develop when vertical flow sedimentation tanks form a fluidized bed of particles that then facilitates particle removal by "increasing particle-particle interactions that lead to flocculation and filtration occurring in the floc blanket" (Hurst, 2010). The process of forming flocs requires both the precipitation of aluminum hydroxide from the coagulant and contact with raw water colloidal particles (Hurst, 2010). Once the combination of precipitation and mixing forms small particles, those 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. This mass flux can then be used to establish proper combinations of velocities and concentrations to produce clear water, as within an appropriate range of mass fluxes, a distinct interface is established between clear water and a suspension of floc particles. 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 will allow for effective fluoride removal.

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. Through those various experiments, the sand filter provided adequate removal of the fluoride and cheaper removal of fluoride per milligram of PACl used. However, 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 hours, the floc blanket was completely saturated to the point where it was no longer efficient or providing adequate removal of fluoride. Due to this, the system had to be backwashed too frequently to be an effective process. On a much larger scale in a plant for example, this time scale to fail would provide a lot of extra maintenance more frequently than possible or feasible. In order to address this, the team fabricated a new reactor and set up a new apparatus fit with stock tanks, a reactor, a turbidimeter, a flocculator, and stock and waste pumps and referenced research previously conducted on the relationship between the amount of coagulant added and head loss accumulation (Dao et al., 2015). 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 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 then tested the system with fluoride. In short term tests lasting about 10 hours, the team was able to remove around 85% 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.

In an effort to improve reactor efficiency, the team fabricated an entirely transparent version of the flocculator, 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 dye in place of fluoride and found that this 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. This hypothesis should be further tested in future. If it were experimentally verified, then the elimination of clay from the system design could reduce the operating cost needed for fluoride removal.

Methods

Bottom Geometry Effects

The team hoped to create a floc blanket without accumulation of flocs that could clog the bottom of the reactor. In the past, the horizontal steps of the bottom geometry caused some flocs to settle, resulting in a buildup of flocs at

the bottom until the system clogged. The team ran three new experiments with PACl and red dye concentrations of 25, 50, and 100 mg/L using the original bottom insert to test if accumulation and clogging of flocs would occur. In these short term tests, the system did not clog but there was some floc settling on the flat portions of the bottom insert. As a result, the team fabricated a new bottom insert for future tests that would allow flocs to slide down and recirculate instead of settling and clogging. It was expected that the modified bottom geometry would resolve this issue by utilizing a smooth sloped exit for gradual expansion of flow and minimization of the horizontal surface area on which flocs can settle (see Figure 3).

Experimental Apparatus

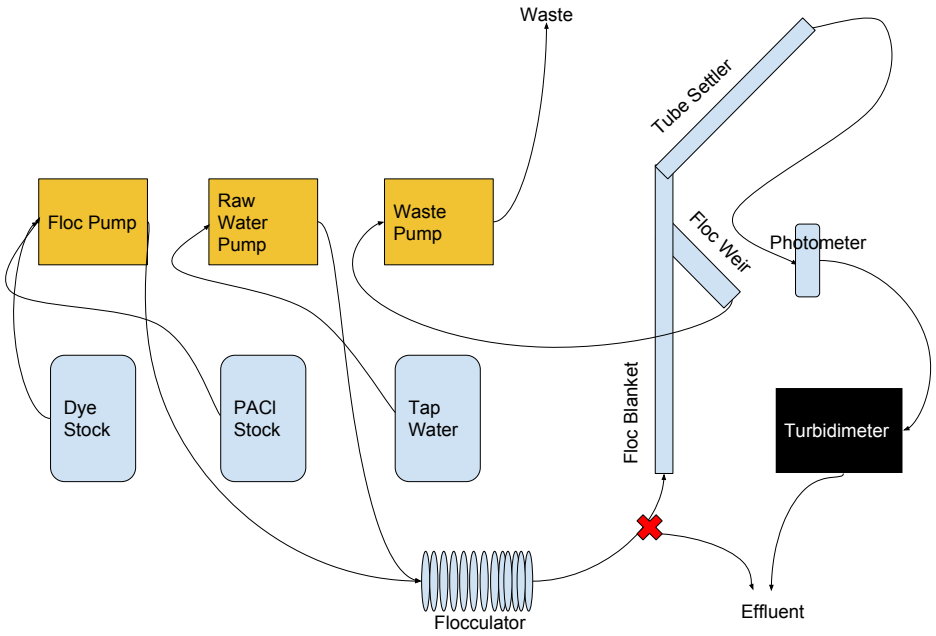

Figure 1: Dye Reactor Schematic

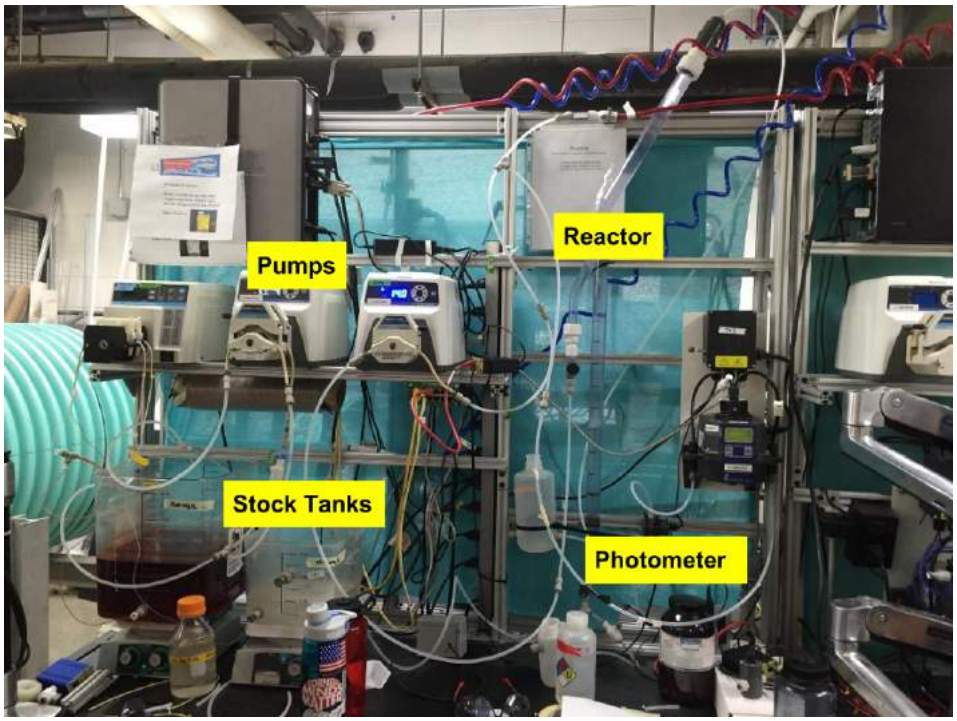

Figure 2: Shown above is an image of the complete apparatus as it appears on the lab bench

Materials:

- Two 600 RPM pumps and one 100 RPM pump
- Transparent 2.54 cm (1") PVC piping
- Various white PVC attachment pieces and push-to-connects
- Flexible and hard 0.635 cm (1/4") tubing
- Turbidimeter
- Polyaluminum Chloride (PACl), Red Dye #40
- Various connectors and buckets for stocks
- Two stir plates with stir bars
- Photometer

The construction of this apparatus and the fabrication of the reactor was completed last semester. The above list references materials used in the making of the entire apparatus and the following is a table of 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 last semester's paper (Dao et al., 2016).

The first piece of new equipment fabricated this semester was the improved bottom insert. This bottom insert was made using 1" solid, clear PVC. A hole was drilled through the center using a $\frac{1}{4}$" drill bit, and one side of the bottom insert was cut using a 1" diameter countersink drill bit so that no flat parts on the insert could potentially lead to floc buildup. The $\frac{1}{4}$" hole was then threaded so a push-to-connect fitting could be used. The new bottom insert is shown in Figure 3. In order to incorporate this new bottom geometry into the reactor, the original bottom insert was cut off of the reactor and the new bottom insert was inserted into the bottom of the reactor and secured using PVC cement.

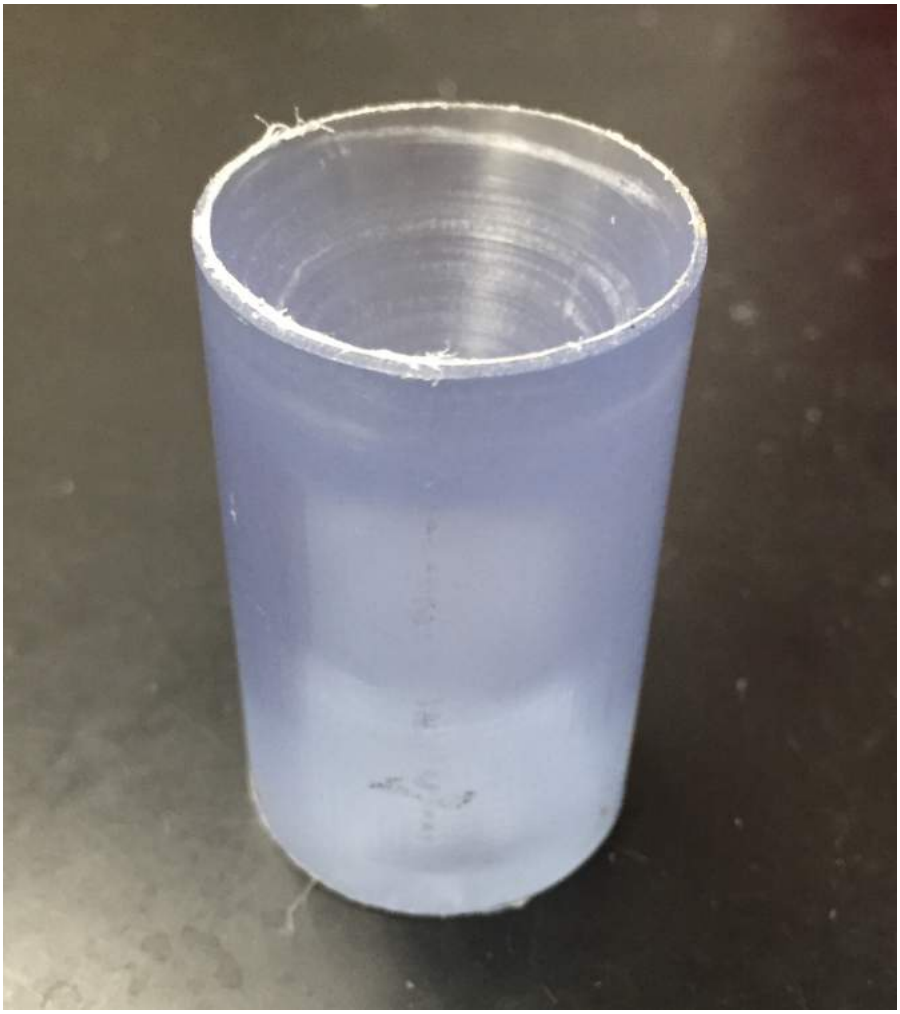

Figure 3: Modified bottom geometry

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

ProCoDA Methods

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, two states were made: ON and OFF. 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. 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.

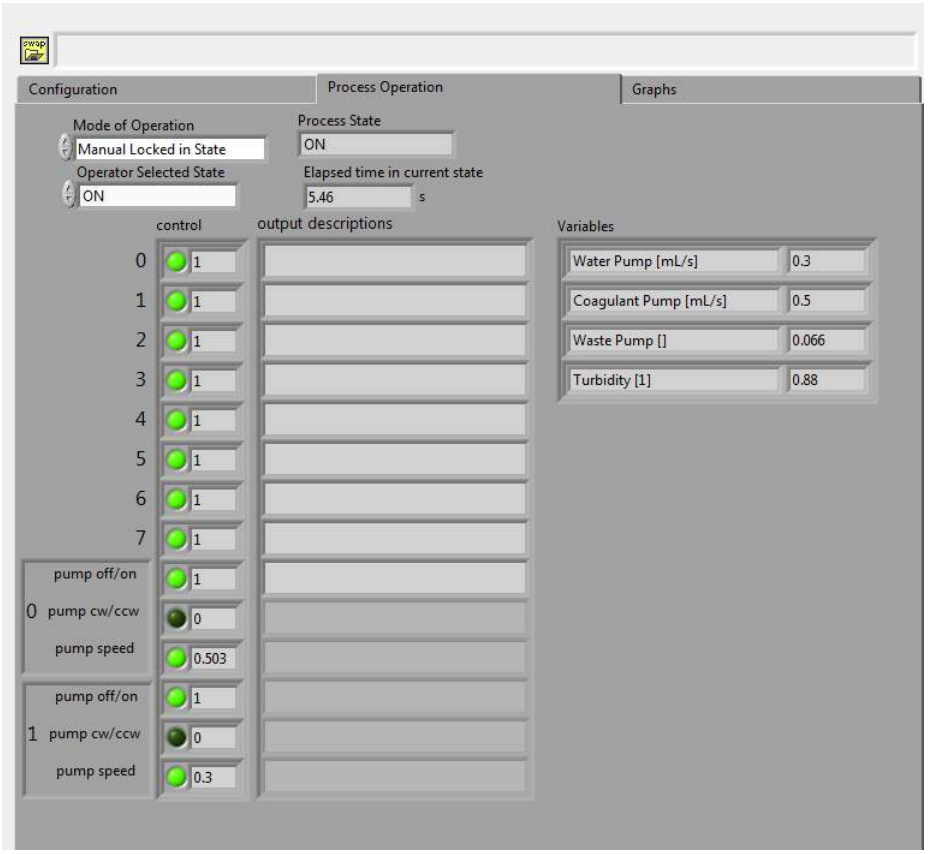

Figure 4: ScreenShot of ProCoDA Panel

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 AguaClara server, and 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 2: 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

Procedure

The floc blanket was created with varying dosages of PACl and dye in order to determine the maximum concentration (if any) allowed in the reactor before the system began to clog. Using the apparatus and design flow rates from last semester, various dosages of dye from 25 $\frac{mg}{L}$ to 100 $\frac{mg}{L}$ were tested to see if the floc blanket clogged the reactor. The team used a 1:1 ratio of PACl concentration to dye concentration and eighty percent of the influent stream flow rate to the reactor was water and twenty percent was flocs consisting of PACl and dye. The 1:1 ratio of PACl to dye and 80:20 water to floc composition of the flow into the reactor was determined last semester through various tests. In varying the PACl to dye ratio and the concentrations of water and flocs in the influent stream, the ratios above were found to create a stable floc blanket while providing a high dye removal efficiency. For more information on these experiments, refer to last semester's report (Dao, 2016). The stock tanks consisted of 500 $\frac{mg}{L}$ of dye and 500 $\frac{mg}{L}$ of PACl. By adjusting the flow rates of the dye, PACl, and water streams, different concentrations of dye were produced in the reactor. The run time of the experiments was around 2 hours. This provided enough time to create and then sustain the floc blanket to make appropriate conclusions about the bottom geometry effect.

Table 3: Flow Rates and Concentrations for Flocs and Water

Concentration in Reactor (mg/L)	PACl and Dye Flow Rate (mL/s)	Water Flow Rate (mL/s)	Run Time (Hours)
25	0.025	0.456	2
50	0.051	0.405	2
100	0.101	0.304	2

Results

As the concentration of dye and PACl in the reactor increased, the density of the floc blanket in the reactor increased significantly. Despite the increase in density, there was not enough buildup of flocs on the bottom of the reactor to clog the system and the flocs continued to circulate. This suggested that the original bottom insert was sufficient. However, there was a slight amount of floc settling on the steps of the bottom insert produced by the step drill.

Table 4: Results of Varying Concentrations of Floc Blanket

Concentration in Reactor	Observations of Clogging
25 mg/L	No Clog and Good Circulation
50 mg/L	No Clog and Good Circulation
100 mg/L	No Clog and Good Circulation

Analysis

As seen in Figures 5 to 10, the reactor did not clog and there was a high density floc blanket that removed a significant amount of dye, regardless of the concentration of dye in the reactor. This held true even at very high dye concentrations of 100 $\frac{mg}{L}$. Using last year's bottom reactor geometry, there was no floc clogging and most of the flocs recirculated near the bottom of the system. The small amount of settling observed in these short tests could lead

to clogging after longer periods of time, such as the 24 hour tests that needed to be performed, therefore a potential area for improvement was fabricating the bottom insert with a smooth drill instead of a step drill to eliminate this settling.

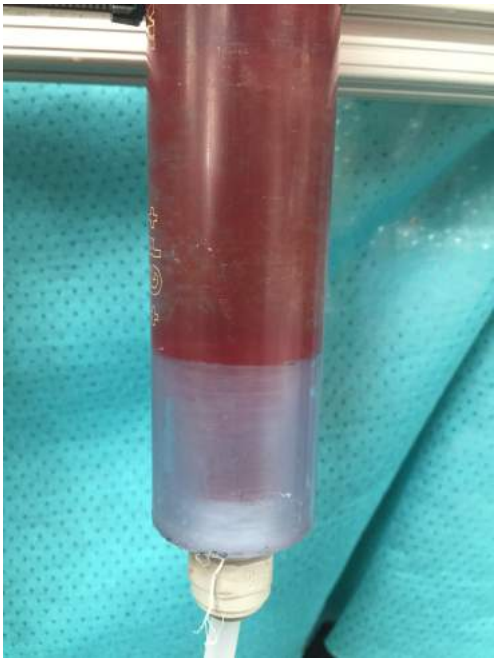

Figure 5: Base of reactor at red dye and PACl concentration of 25 $\frac{\text{mg}}{\text{L}}$.

Figure 6: Floc weir and top of floc blanket at red dye and PACl concentration of 25 $\frac{\text{mg}}{\text{L}}$.

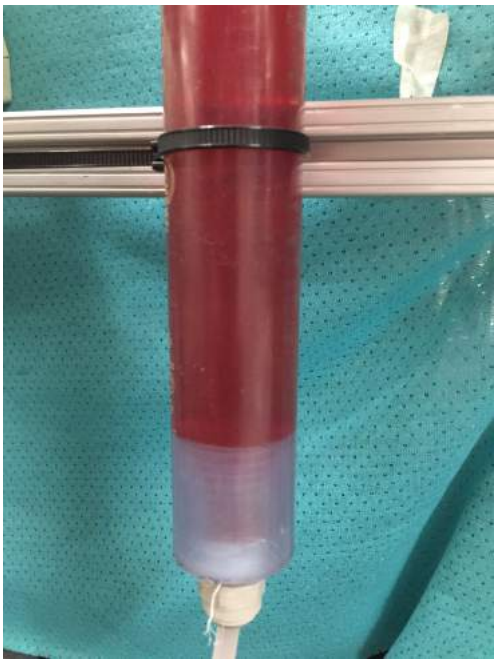

Figure 7: Base of reactor at red dye and PACl concentration of 50 $\frac{\text{mg}}{\text{L}}$.

Figure 8: Floc weir and top of floc blanket at red dye and PACl concentration of 50 $\frac{\text{mg}}{\text{L}}$.

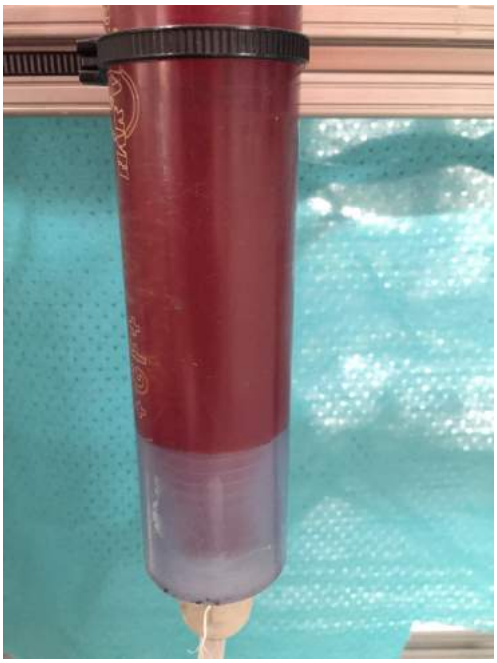

Figure 9: Base of reactor at red dye and PACl concentration of 100 $\frac{\text{mg}}{\text{L}}$.

Figure 10: Floc weir and top of floc blanket at red dye and PACl concentration of 100 $\frac{\text{mg}}{\text{L}}$.

Short Floc Blanket Reactor

The team sought to determine the minimum length of the reactor needed in order to provide the highest removal efficiency for the reactor. If an equally efficient, shorter reactor could be designed, fewer materials would be needed for the fabrication of the reactor, saving space, money, and resources.

Experimental Apparatus

The experimental apparatus was nearly identical to that of the previous iteration except a new reactor was fabricated with a shorter floc blanket length (see Figure 11). The total floc blanket length for the reactor was five centimeters instead of 61 cm. Five centimeters was chosen as the length of the floc blanket with the assumption that this is the minimum size that could reasonably be fabricated. There needed to be enough pipe that the weir hole could be drilled and the new bottom geometry could be inserted into the bottom of the reactor without breaking the pipe. Also, it needed to have enough length to allow the flocs to accumulate and the floc blanket to develop before entering the weir. The ProCoDA methods were also kept the same; all ProCoDa settings and details can be found in the discussion of the first iteration.

The short reactor was fabricated by heating the PVC and bending the tube settler to a 30°angle. The weir was attached at an angle of 30°relative to the floc blanket portion of the reactor (see Figure 12). The weir was welded onto the reactor using a plastic welder in order to make the system water tight (see Figure 13).

The photometer was added inline after the reactor in order to determine effluent concentration. The photometer consisted of a blue LED that passed light through the red dye solution. The absorbance of the dye solution was then calculated by ProCoDA and converted into a concentration in $\frac{\text{mg}}{\text{L}}$ using a calibration curve that was created by the team. In order to create the calibration curve, the team ran a range of concentrations of dye from 0.625 $\frac{\text{mg}}{\text{L}}$ to 40 $\frac{\text{mg}}{\text{L}}$ through the photometer to determine the voltage reading at each concentration. The voltage readings were then converted to absorbance, and then absorbance was graphed with respect to dye concentration. Bubbles trapped in the photometer also caused the concentration to change continuously. In order to prevent bubbles from getting trapped, the inlet tubing was put into the bottom of the photometer so that the bubbles could be pushed out through the outlet by the water at the top and not interfere with the readings of photometer concentrations.

The turbidimeter was added inline after the photometer. The purpose of the turbidimeter was to determine when spikes in NTU occurred during an experiment. Spikes in NTU usually indicated that flocs were exiting through the reactor and into the effluent water, which determined the failure of the reactor.

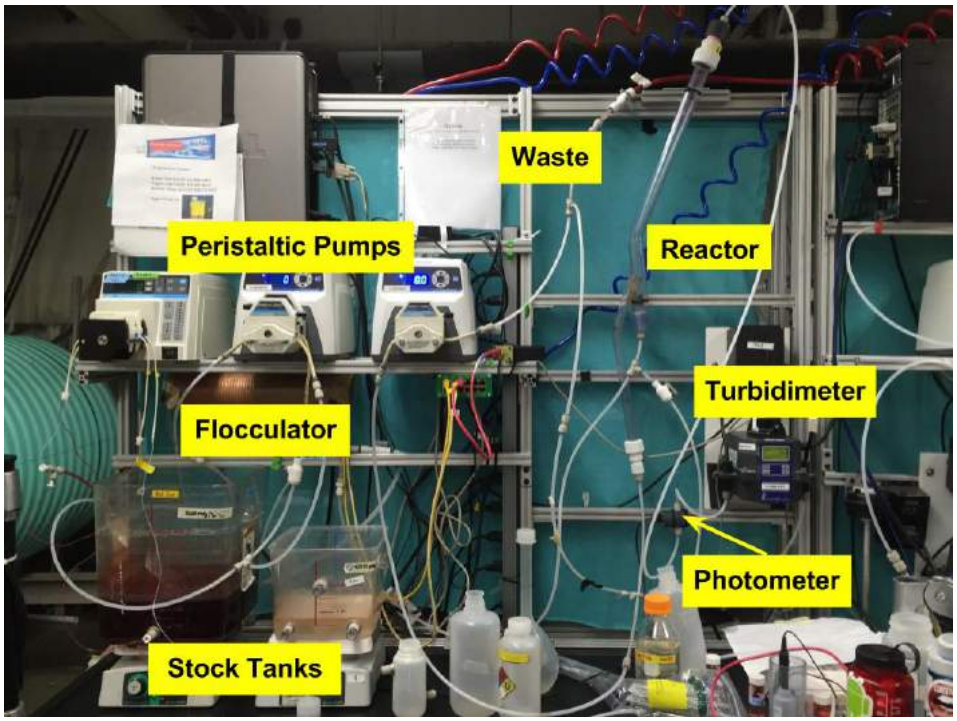

Figure 11: The new experimental apparatus with the fabricated short reactor, photometer, and rearranged waste tubing.

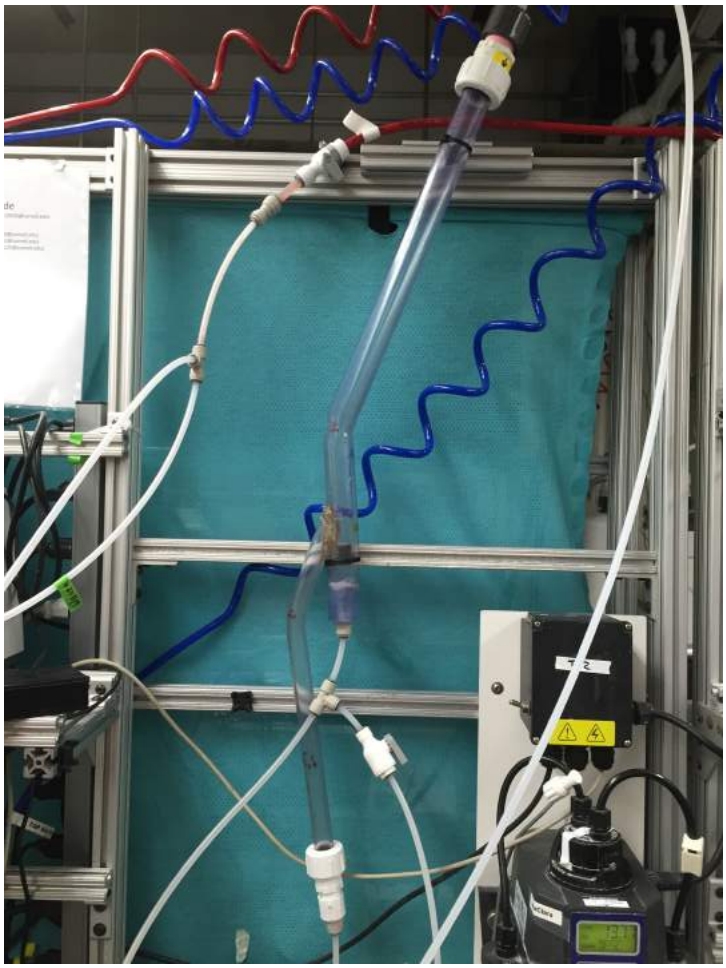

Figure 12: The fabricated reactor with a floc blanket length of 5 cm attached to the apparatus.

Figure 13: A picture of the welding done to attach the weir to the rest of the apparatus.

Procedure

The procedure for this iteration was identical to that of the previous iteration. The concentrations of PACl and Dye tested in the reactors were 25 $\frac{\text{mg}}{\text{L}}$, 50 $\frac{\text{mg}}{\text{L}}$ and 100 $\frac{\text{mg}}{\text{L}}$. For details regarding flow rates, please refer to Table 3. First, the short reactor was tested in short term experiments to gather qualitative data for the characteristics of the floc blanket with a short reactor. One three hour test was run for each dye concentration. The longer term experiments were tested with both the short reactor and long reactor to gather effluent concentration and turbidity data to compare the efficiency of the reactors at each of the three concentrations. One 24 hour test was run for each dye concentration in both the long and short reactor, with the exception of a 100 $\frac{\text{mg}}{\text{L}}$ test in the short reactor.

Results

For the short term, short reactor tests, although some flocs flowing into the reactor went over the weir and down the floc hopper, the majority of flocs continued to rise and flow up past the weir into the tube settler, forming a floc blanket there. The floc blanket reached stability with heights that varied for each concentration (see Table 5, Figure 14, Figure 15, and Figure 16).

Table 5: Results of Varying Concentrations of the Short Floc Blanket

Concentration in Reactor	Floc Blanket Height	Observations of Floc Blanket
25 mg/L	21 cm	Low density floc blanket without a distinct maximum
50 mg/L	33 cm	Flat line of floc blanket at maximum
100 mg/L	21 cm	Deep orange tint to water

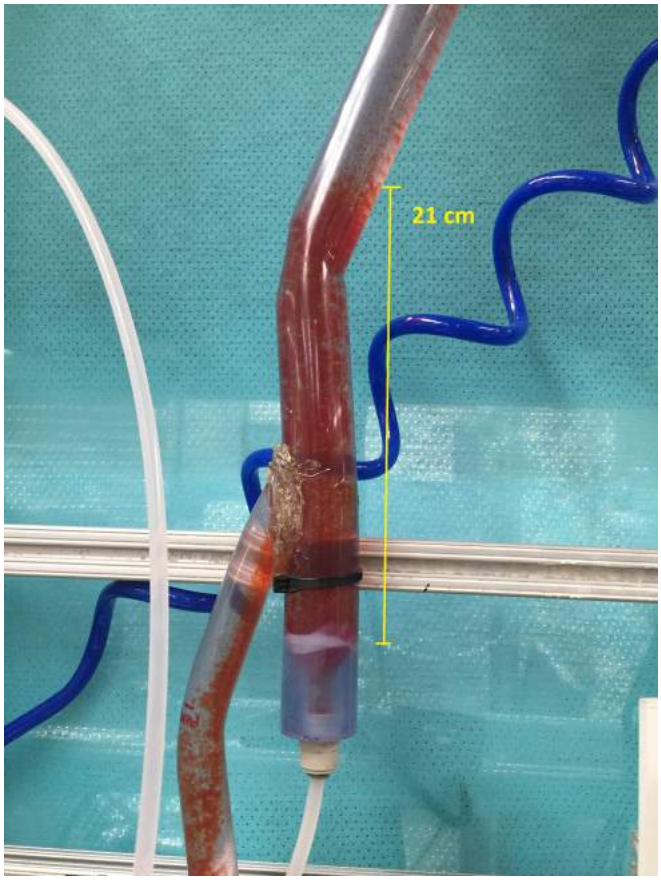

Figure 14: Floc blanket development with a concentration of 25 $\frac{\text{mg}}{\text{L}}$.

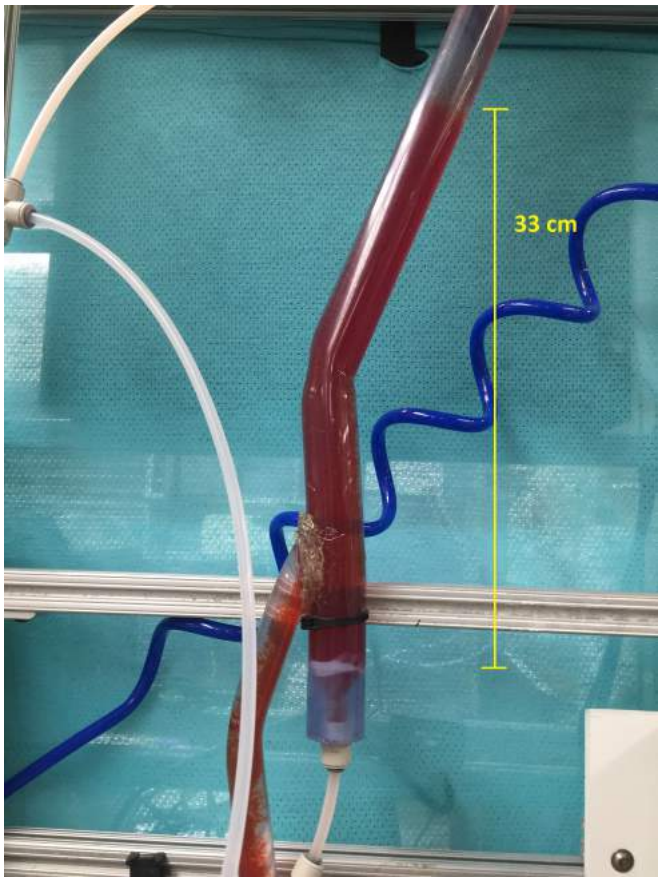

Figure 15: Floc blanket development with a concentration of 50 $\frac{\text{mg}}{\text{L}}$.

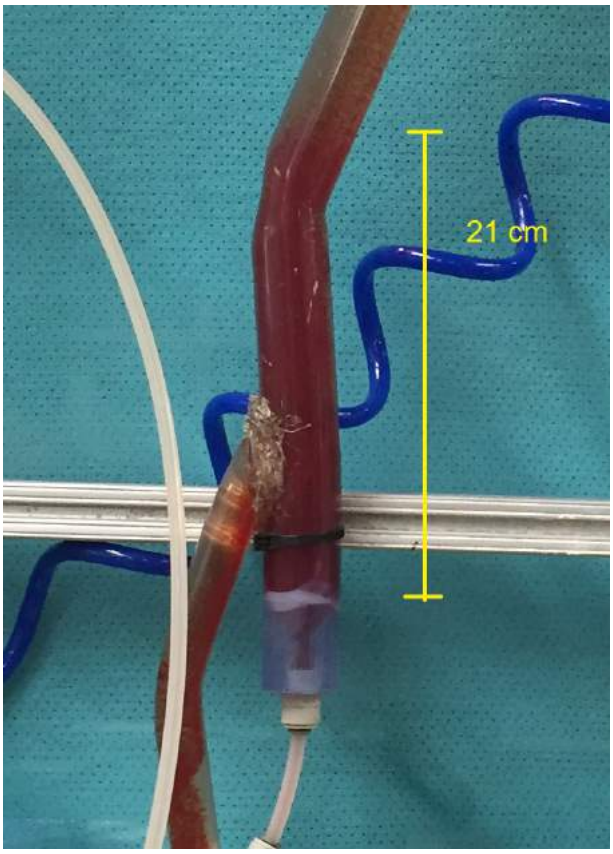

Figure 16: Floc blanket development with a concentration of 100 $\frac{\text{mg}}{\text{L}}$.

The long term experiments for the short and long reactor showed very different results. The short reactor failed for the 50 $\frac{\text{mg}}{\text{L}}$ test early on, so the 100 $\frac{\text{mg}}{\text{L}}$ test was not run. The long reactor failed for the 100 $\frac{\text{mg}}{\text{L}}$ test early on but showed very promising results for the 25 $\frac{\text{mg}}{\text{L}}$ and 50 $\frac{\text{mg}}{\text{L}}$ tests as seen in Table 6. The term failed is defined as when the floc blanket built up so much that flocs went through the tube settler and then reached the turbidimeter so that the turbidity spikes up to around 100-500 NTU.

Figure 17: General Appearance of successful floc blanket at weir for concentrations of 100, 50 and 25 $\frac{\text{mg}}{\text{L}}$.

Figure 18: Failed floc blanket test of 100 $\frac{\text{mg}}{\text{L}}$.

Table 6: Comparison of Results of Varying Concentrations in the Short and Long Floc Blanket Reactors

Initial Concentration in Reactor	Short Reactor Final Concentration	Long Reactor Final Concentration	Time to Fail SR	Time to Fail LR
25 mg/L	10 mg/L	2.7 mg/L	7 Hours	Did not Fail
50 mg/L	3.1 mg/L	1.2 mg/L	4.2 Hours	Did not Fail
100 mg/L	Did Not Test	1.1 mg/L	Did Not Test	3 Hours

Analysis

The source of failure for the shorter reactor is most likely the decreased length of active tube settler, since the floc blanket itself occupied some of the tube settler. Additionally, the floc blanket may have grown taller if a larger vertical portion of tubing was available. As seen in the pictures above, the experiments suggest that there is a minimum height a floc blanket will reach when it is fully developed. The relationship between concentration of dye and PACl in the reaction and floc blanket height is not yet known but the height of the floc blanket is significant and a very small reactor is not feasible for this system. When comparing the results to the longer reactor, the short reactor not only performed worse than the longer reactor, but it failed a lot quicker as well.

Therefore, the long reactor was more feasible and provided a better removal efficiency than the short reactor, so the short reactor is not a viable reactor and the results suggested that the floc blanket required a certain amount of length for good removal efficiencies. In light of this conclusion, only the long reactor was used until the relationship between floc blanket height and reactor concentrations were determined.

CSFBR Collaboration

Before moving forward with fluoride removal, the team must work together with the CSFBR subteam to determine whether a single reactor or two reactors in series will work more effectively to remove red dye. With two reactors in series, flocs are recycled from reactor 2 and used as the preliminary coagulant for dissolved species removal in reactor 1, and the water treated in reactor 1 comes into contact with new coagulant and flows through reactor 2 before leaving the system (see Figure 19). The goal in using such a system is to push the flocs to their highest capacity of red dye removal and produce even lower concentration effluent while using the same amount of coagulant as a single reactor. The role of the fluoride subteam at this stage is to run tests at varying concentrations in the single reactor that are otherwise identical to the tests being run by CSFBR. For easier analysis, both systems are being run at lower efficiency and therefore will produce higher effluent concentrations than would normally be produced.

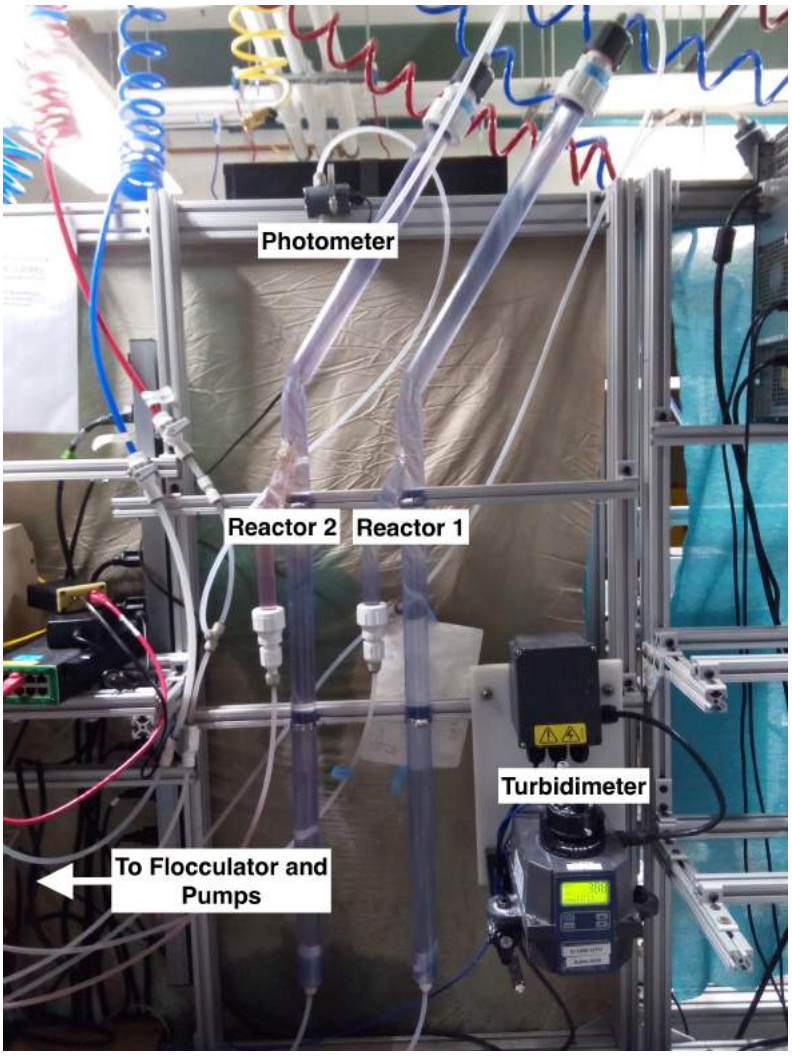

Figure 19: Two reactors in series as used by the CSFBR subteam.

Experimental Apparatus

The experimental apparatus for this iteration is the same as the previous two, with the exception that the long reactor with the smooth bottom insert was used for all tests in this iteration.

Procedure

The procedure for this iteration was the same as the previous two iterations. Also, the procedures for the Fluoride and CSFBR teams were the same so that the results from each team can be comparable. The teams used identical flow rates, reactors, and calibrations. Since stocks had to be replenished often, shared drums of 250 $\frac{\text{mg}}{\text{L}}$ PACl and 500 $\frac{\text{mg}}{\text{L}}$ red dye were used. This helped to remove another possible source of discrepancy between CSFBR and Fluoride tests. The

1:2 PACl to red dye ratio was used so that at a non-ideal efficiency (since the ratio of dye to PACl in a reactor affects its efficiency in removing dye), the final reactor concentrations can be compared between the CSFBR and Fluoride teams. The concentrations that were run in the reactor were $25\frac{\text{mg}}{\text{L}}$ and 50 $\frac{\text{mg}}{\text{L}}$ of dye. In addition, various upflow velocities were run in order to prevent the possibility of sludge buildup in the reactor that CSFBR was experiencing. The upflow velocities that were run included 1.2 $\frac{\text{mm}}{\text{s}}$, 1.4 $\frac{\text{mm}}{\text{s}}$, and 1.5 $\frac{\text{mm}}{\text{s}}$.

Results

In the experiments where 25 $\frac{\text{mg}}{\text{L}}$ of dye and 12.5 $\frac{\text{mg}}{\text{L}}$ of PACl were tested in the reactor, there were distinct differences between tests with various upflow velocities. As seen in Figure 21, the experiment with higher upflow velocity began to fail around 10 hours and the effluent concentration slowly increased over the following 15 hours. The experiment with lower upflow velocity showed relatively constant effluent concentration for the entire duration after reaching steady state (see Figure 20).

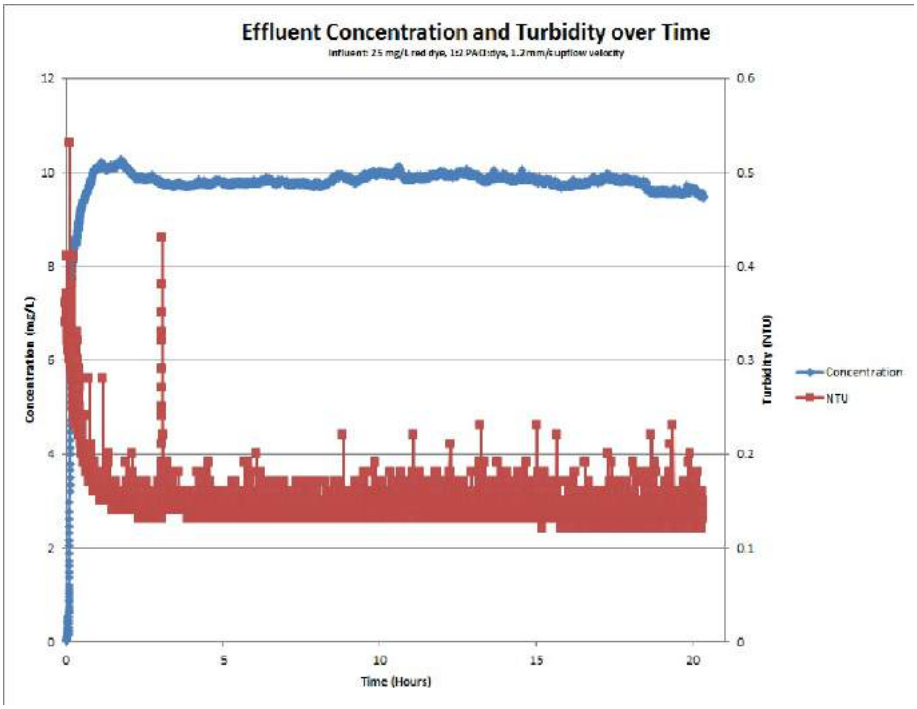

Figure 20: Concentration and turbidity over time for 25 mg/L concentration of dye and 1.2 mm/s upflow velocity.

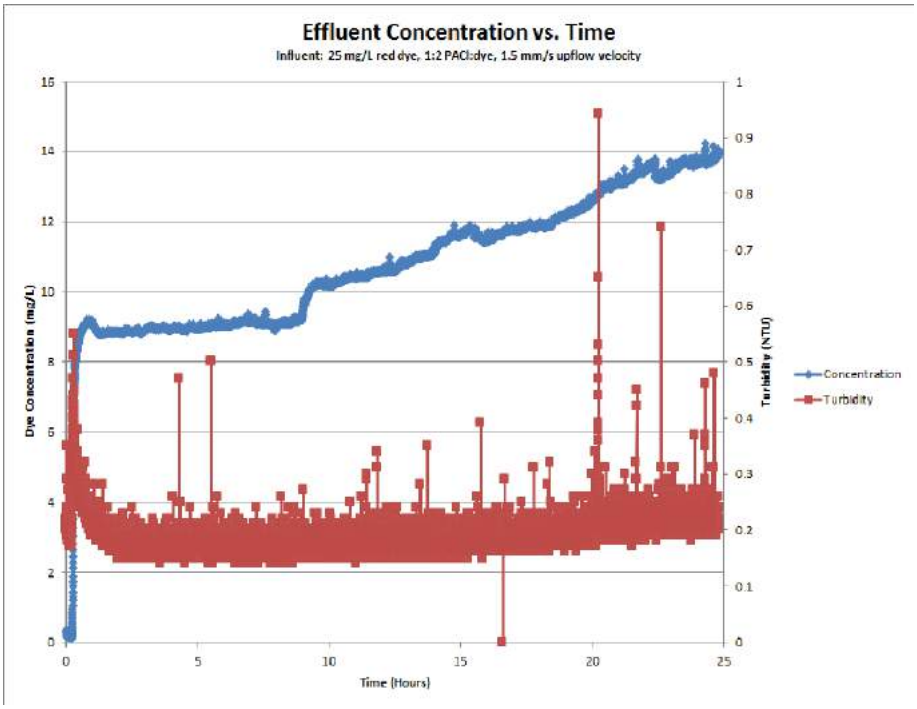

Figure 21: Concentration and turbidity over time for 25 mg/L concentration of dye and 1.5 mm/s upflow velocity.

As seen in Figures 23 and 24, both of the 50 $\frac{\text{mg}}{\text{L}}$ tests failed. However, these failures were not due to the reactor itself failing but due to failure in the apparatus because of clogging in the stock tanks. In Figure 23, the dye stock tank got clogged around 10 hours through as the concentration dropped rapidly to close to zero. In Figure 24, the PACl stock tank clogged as the dye concentration spiked up close to 50 $\frac{\text{mg}}{\text{L}}$ after around 5 hours.

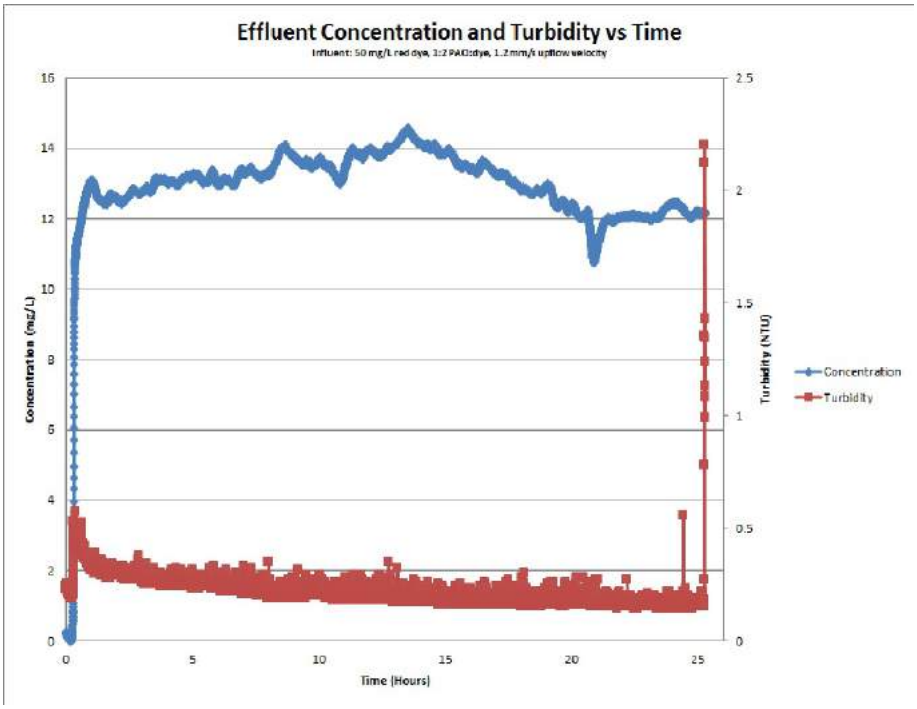

Figure 22: Concentration and turbidity over time for 50 mg/L concentration of dye and 1.2 mm/s upflow velocity.

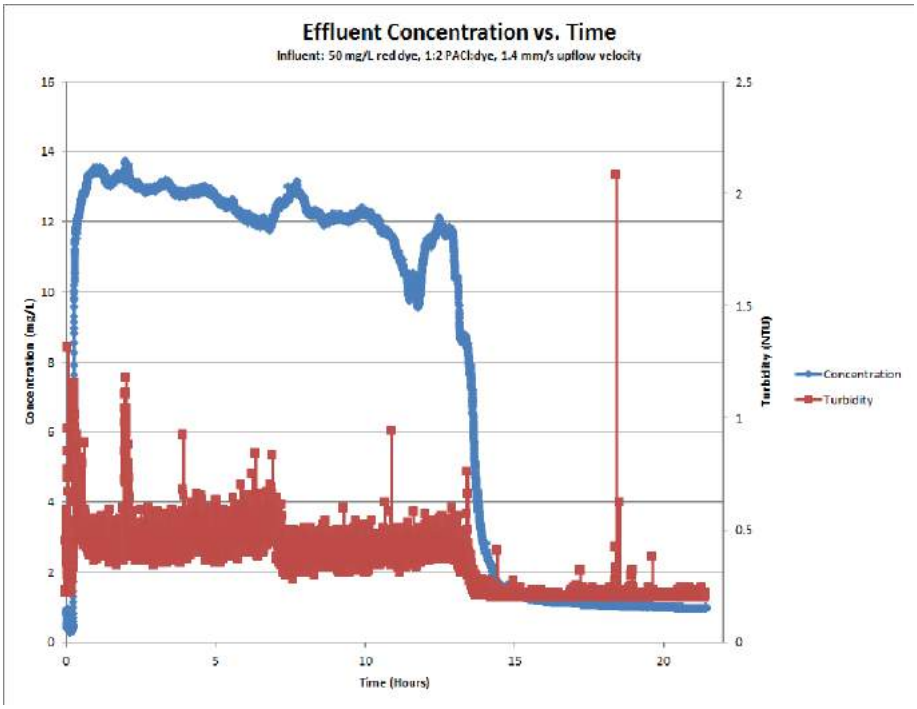

Figure 23: Concentration and turbidity over time for 50 mg/L concentration of dye and 1.4 mm/s upflow velocity.

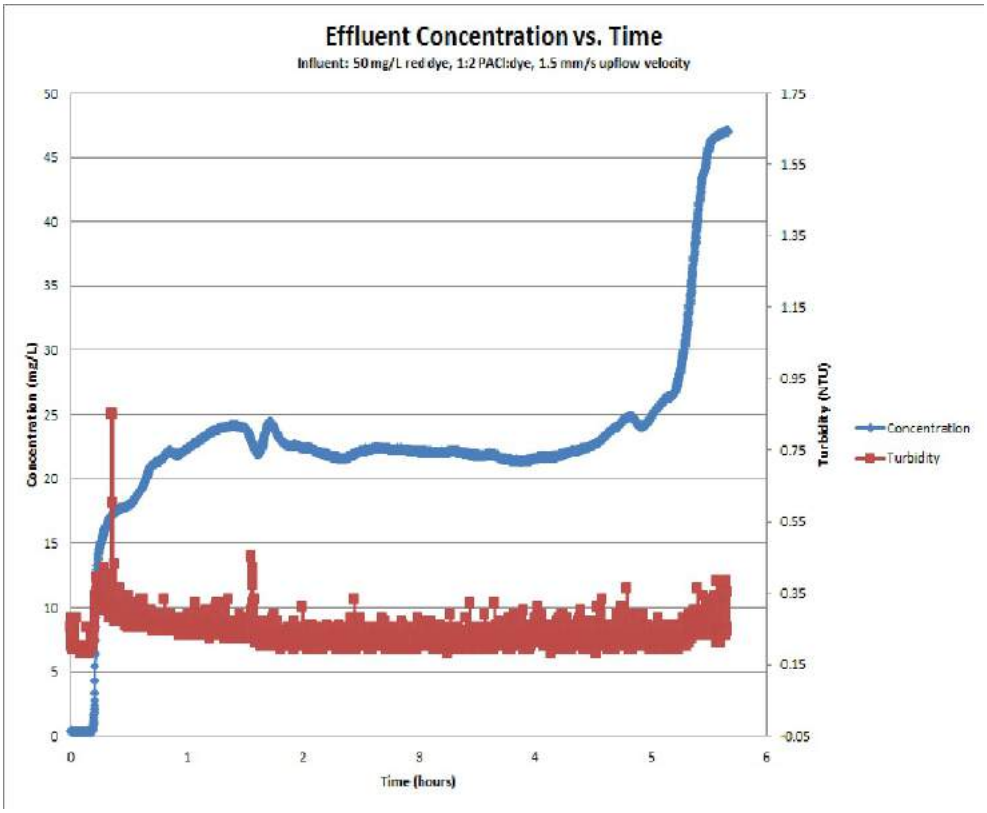

Figure 24: Concentration and turbidity over time for 50 mg/L concentration of dye and 1.5 mm/s upflow velocity.

Table 7: Summary of tests of 25 mg/L of dye and 12.5 mg/L of PACl in the reactor at different upflow velocities

Upflow Velocity	Final Concentration	Percent Removal	Time Run (Or time to fail)
1.2 mm/s	9.82 mg/L	60.7%	20 Hours Run
1.5 mm/s	11.4 mg/L	54.3%	8.5 Hours Until Fail

Table 8: Summary of tests of 50 mg/L of dye and 25 mg/L of PACl in the reactor at different upflow velocities

Upflow Velocity	Final Concentration	Percent Removal	Time Run (Or time to fail)
1.2 mm/s	13.0 mg/L	74.0%	25 Hours Run
1.4 mm/s	12.6 mg/L	74.7%	10 Hours Until Fail*
1.5 mm/s	22.4 mg/L	55.1%	5 Hours Until Fail*

*These two tests did not fail due to the reactor itself but due to clogging in the stock tanks

Analysis

As seen in the results above, higher upflow velocities caused lower removal efficiency. This was due to the fact that flocs could not settle as quickly with faster flow, and thus the floc blanket was less dense than floc blankets created with lower upflow velocities. Also, the tests with higher upflow velocities had a tendency to fail after a certain period of time while the tests with lower upflow velocities maintained a steady effluent concentration throughout the duration of the test.

Comparing the results from the CSFBR subteam to the single reactor results, it is not clear which system is most efficient at removing red dye. In Figure 25, it appears that with an upflow velocity of 1.5 $\frac{mm}{s}$, 50 $\frac{mg}{L}$ concentration of dye, and 25 $\frac{mg}{L}$ concentration of PACl, both systems reached steady state after about an hour, and CSFBR produced an effluent concentration of about 10 $\frac{mg}{L}$ versus the single reactor which produced effluent concentration of 22.4 $\frac{mg}{L}$. However, Figure 26 shows that with 1.5 $\frac{mm}{s}$ upflow velocity, 25 $\frac{mg}{L}$ of dye, and 12.5 $\frac{mg}{L}$ of PACl, a single reactor and two reactors in series produce similar results. In fact, the final effluent concentration of two reactors in series was higher than that of the single reactor. The final comparison, shown in Figure 27, showed that for 50 $\frac{mg}{L}$ of red dye, 25 $\frac{mg}{L}$ of PACl, and an upflow velocity of 1.4 $\frac{mm}{s}$, the effluent concentration obtained from two reactors in series started at about 5 $\frac{mg}{L}$ and slowly increased to about 12 $\frac{mg}{L}$, whereas the single reactor showed a somewhat decreasing trend before the test failed. Since these test results are contradictory and two of the three tests did not produce a constant effluent concentration, more tests are needed to come to a conclusion about whether a single reactor or two reactors in series is the most effective and efficient for red dye removal.

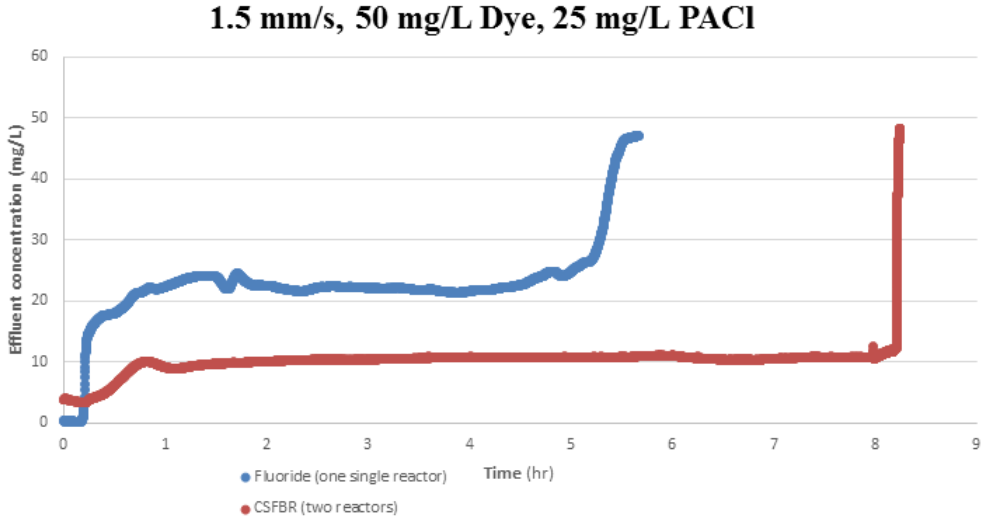

Figure 25: Effluent concentration of two-single reactor vs one single reactor system at 1.5 mm/s upflow velocity, 25mg/L PACl, 50mg/L dye.

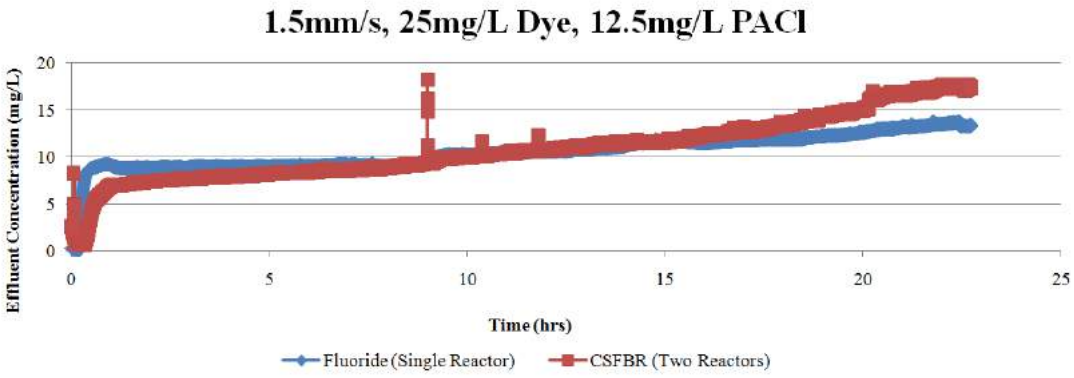

Figure 26: Effluent concentration of two-single reactor and one single reactor system at 1.5 mm/s upflow velocity, 12.5mg/L PACl, 25mg/L dye

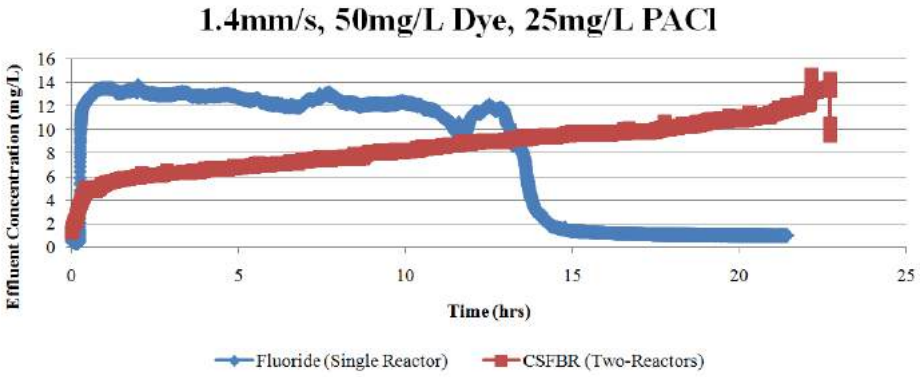

Figure 27: Effluent concentration of two-single reactor vs one single reactor system at 1.4 mm/s upflow velocity, 25mg/L PACl, 50mg/L dye

Conclusions

Through the iterations of experiments performed during the Fall 2016 semester, conclusions may be made about the most effective methods for use with a single reactor system, though conclusions about the effectiveness of a single reactor versus reactors in series cannot yet be made. From the first iteration, it was determined that a smooth-sloped bottom insert is best in order to reduce settling at the base of the reactor. The second iteration established that although the floc blanket may be effective with lengths shorter than the current design, there is a minimum height requirement. The system failed with a floc blanket height of 5 cm, therefore the minimum height is greater than 5 cm. Having a floc blanket longer than the minimum height should not reduce effectiveness, though it requires slightly more material for fabrication. The minimum height has not yet been determined. With the longer reactor, higher upflow velocities should not be used since the data from iteration three suggests that higher upflow

velocities cause the reactor to fail and provide lower removal efficiency because the flocs do not settle from the tube settler. These conclusions may be utilized in Fluoride's single reactor system and in CSFBR's multiple reactors in series.

Future Work

In future semesters, more tests need to be run comparing the effluent concentrations produced by a single reactor versus reactors in series. Once it is determined which system is the most efficient at removing red dye, the teams should test the system with fluoride according to the appropriate conditions determined from this semester. After initial fluoride testing, the apparatus needs to be scaled up to a flow rate of 100 $\frac{\text{mL}}{\text{s}}$ (this past semester was run at around 0.5 $\frac{\text{mL}}{\text{s}}$). If time allows, a relationship between floc blanket height and concentration of PACl and dye in the reactor can be determined, though this could be done by another team or a grad student. Also, the system needs to work without any electricity when it is employed in the field, so a design needs to be created in which hydraulics is the driving force.

References

Bailey, K. and Fawell, J. (2004). Fluoride in Drinking-water.

Dahi, E., Mtalo, F., Njau, B., and Bregnhj, H. (1996). Defluoridation using the Nalgonda Technique in Tanzania. In *Reaching the Unreached: Challenges for the 21st Century*, New Delhi, India.

Dao, K., Desai, P., and Longo, A. (2015). Fluoride, Fall 2015.

EPA (2016). Water Treatability Database.

Gebbie, P. (2001). Using Polyaluminum Coagulants in Water Treatment.

Gregory, R., Head, R. J. M., and Graham, N. J. D. (1996). The Relevance of Blanket Solids Concentration in Understanding the Performance of Floc Blanket Clarifiers in Water Treatment. *Chemical Water and Wastewater Treament*, IV.

Hurst, M. W. (2010). *Evaluation of Parameters Affecting Steady-State Floc Blanket Performance*. Degree of Master of Science, Cornell University, Ithaca, New York.

Ingallinella, A. M. and Pacini, V. A. (2001). Simultaneous removal of arsenic and fluoride from groundwater by coagulation-adsorption with polyaluminum chloride. *Journal of Environmental Science and Health, Part A*.

Kumbhar, V. S. and Salkar, V. D. (2014). Use of PAC as a Substitute for Alum in Nalgonda Technique. *International Journal of Emerging Technology and Advanced Engineering*, 4(10).

LeChevallier, M. W. and Au, K.-K. (2004). Water Treatment and Pathogen Control.

Lin, W., Chen, L. C., Chung, H. Y., Wang, C. C., Wu, R. M., Lee, D. J., Huang, C., Juang, R. S., Peng, X. F., and Chang, H.-L. (2004). Treating High Turbidity Water Using Full-Scale Floc Blanket Clarifiers. *Journal of Environmental Engineering*, 130(12):1481–1487.

of Health, N. D. (2010). Sodium Fluoride.

Roholm, K. (1937). *Fluorine Intoxication: A Clinical-Hygienic Study*. Copenhagen, Denmark.

Sun, S. F. (2004). Sedimentation. In *Physical Chemistry of Macromolecules: Basic Principles and Issues, Second Edition*, pages 243–266. John Wiley & Sons, Inc.

Semester Schedule

Task Map

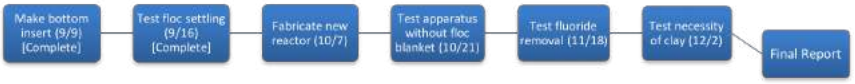

Figure 28: Fall 2016 Task Map

Task List

1. Make bottom insert (09/09) - Briana Vidal. Fabricate new PVC bottom expansion in order to prevent flocs from settling on edges. [Complete; not needed]

2. Test floc settling on old instrument (09/16) - August Longo. Test varying concentrations of PACl and dye in the reactor and observe settling patterns at bottom of device. [Complete]

3. Fabricate new reactor (10/07) – Briana Vidal. Fabricate reactor that will eliminate the floc blanket, but still allow flocs to flow over floc weir to waste. [Complete]

4. Test apparatus without floc blanket (10/21) - Michelle Cheng. Test device using only the flocculator tube and floc hopper. [Complete]

5. Obtain data to compare with CSFBR (11/18) - Briana Vidal. Run tests that have identical parameters to the tests run by CSFBR to determine whether a single reactor or reactors in series are more effective. [In progress]

6. Test Fluoride removal (11/25) – August Longo. Determine which apparatus and removal system most effectively removed red dye and repeat experiments on Fluoride and clay. [To be completed next semester]

7. Test necessity of clay for Fluoride removal (12/02) – Michelle Cheng. Determine whether or not the presence of clay affects the efficiency of Fluoride removal in the apparatus. [To be completed next semester]

Team Roles

Team Coordinator: Briana Vidal
Materials Coordinator: Michelle Cheng
Data Coordinator: August Longo

Report Proofreader: Briana Vidal