Title: Dissolved Organic Matter Removal from Drinking Water with Poly-aluminum Chloride, Clay, and Powdered Activated Carbon
Team: Dissolved Organic Matter, Spring 2023
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Abstract

The Spring 2023 Dissolved Organic Matter subteam aims to compare the effectiveness of implementing poly-aluminum chloride (PACl) with clay and/or powdered activated carbon (PAC) to remove humic acid from drinking water. To ascertain the optimal amounts of clay and/or activated carbon, ProCoDA will be utilized to introduce incremental flow rates of both solutions into the system, which allows for more efficient testing and more control over the amounts of solutions in the system during a run.

Both clay and activated carbon are predicted to increase the density of flocs, so this subteam plans to determine which is more effective and efficient at producing high-density flocs to get the maximum floc removal in the sedimentation tank. Through performing research regarding the optimal concentration of clay and/or activated carbon, the DOM subteam strives to improve the capability of AguaClara water treatment plants.

Introduction

Dissolved organic matter (DOM), a natural transparent water contaminant created from the decomposition of feces and decaying leaves, is present in high amounts at the AguaClara plant in Gracias, Honduras. When DOM reacts with coagulants like PACl, the contaminants clump together into flocs, which are more easily removed in the filtration process. However, to remove DOM by means of flocculation, it is essential that flocs form with a relatively high density, preferably higher than that of water. If the reverse is the case, flocs float to the surface of the water, leading to difficulty in floc blanket formation and filtration in subsequent steps.

One method to achieve high-density flocs is through pre-combining kaolin clay with a coagulant solution prior to the flocculation step (Wu et al., 2020). Clay can be used to simulate the turbidity of influent water and promote coagulation by adhering to the surface of the coagulant and attracting DOM by means of collision aggregation.

An alternative to kaolin clay in the flocculation process is powdered activated carbon, which can be combined with humic acid and water prior to the introduction of coagulant for denser floc formation (Tafvizi et al., 2021). Due to its porous surface, activated carbon particles, having been bound onto coagulant particles, have the capability to adsorb a large amount of dissolved organic matter onto its surface. This ability helps to increase the effectiveness of the coagulant, reduce coagulant dosage, and create heavier flocs.

This semester, the Dissolved Organic Matter subteam is investigating the effectiveness of implementing coagulant with kaolin clay in removing humic acid from influent water. Future steps in this experiment include examining the optimal dosage of clay using automated trials controlled via ProCoDA and floc size analysis using ImageJ.

Literature Review

Clay is useful in the removal of DOM in water due to its ability to produce turbidity. In a 2021 article by Saxena et al., researchers modified a model for hydraulic flocculators and tested for a sludge blanket clarifier by running experiments using synthetic water samples consisting of humic acid and kaolin clay, and PACl as coagulant. In the removal of DOM, clay plays a pivotal role of contributing to inorganic turbidity in surface waters due to the fact that it is larger than PACl nanoparticles. Since turbidity is measured by the amount of light scattered or blocked by suspended particles in a water sample, large particles such as clay will be able to produce turbidity readings since they will most likely be able to block light through the sample in the turbidimeter. The researchers also found that the coverage of PACl on clay increases for the same dose of PACl as the input turbidity decreases meaning that there will be greater coverage of the clay particles by coagulant when there is less clay. Thus, the DOM subteam will monitor how much clay is added in order to maintain high coagulant coverage while providing turbidity readings for analysis.

Like clay, activated carbon has been researched in its potential role for removing dissolved organic matter from drinking water. In a 2021 study by Biswas et al., researchers collected waters from a non-wastewater-impacted reservoir at Big Elk Meadows, CO to test how activated carbon adsorbed the different types of DOM (e.g., humic, aromatic, polyphenol, etc.) within the waters. The results were measured through fluorescence spectroscopy, UV-absorption, and size exclusion chromatography. According to the paper, peaks associated with humic acid were shown to adsorb with activated carbon through fluorescence spectroscopy, indicating that activated carbon should flocculate with humic acid to create dense flocs which will be easily removed from drinking water.

Another variable to take into account when exploring activated carbon's effectiveness in the flocculation process is the effect of varying activated carbon flow rate on its adsorption efficiency. According to Campos et. al. in a 2000 study, for a fixed dosage of activated carbon, decreasing the carbon retention time resulted in a reduction of activated carbon absorption efficiency (Campos et. al. 2000). Thus, careful considerations must be made when deciding on process flow rates during experimental trials since varying the residence time in the upflow blanket reactor may result in a less desirable activated carbon absorption efficiency.

It is also important to factor in the environmental and health effects of a coagulant when determining which is the best flocculant. Activated carbon is classified as an inorganic chemical flocculant, while kaolin clay is classified as a natural coagulant. The use of chemical coagulants, both inorganic and organic, can cause adverse environmental and health problems. Activated carbon specifically is known to have residual aluminum which is neurotoxic and carcinogenic to humans (Aljuboori et al., 2015). This detail should be kept in mind when discussing the trade-offs between the clay and activated carbon in the drinking water flocculation process.

With the recent switch to automating the flow rate of clay into the system, a more digital and technological approach was introduced to analyze the different stages of floc formation with the gradual increase of clay in the system: floc identification and classification through ImageJ. According to a 2022 study by González-Galvis et al., this simple yet effective process has been proven to be useful in identifying and measuring floc size between 33 µm and 1,200 µm across various surface waters. Since this method requires only a phone camera and a free computer program, the proposed methodology is tested in hopes to optimize and control the coagulation and flocculation process to treat low turbidity waters. Indeed, Image J allows for non-invasive estimation of floc size distributions inside the sedimentation tube corresponding to different clay flow rates and concentrations in the flocculator (Sun et al., 2016). The data obtained from this could be utilized to quantitatively compare floc size between trials and optimize clay dosage.

Previous Work

Schematics:

Fall 2022 Dissolved Organic Matter subteam aimed to vary coagulant dosage and observed flocculation in the sedimentation tank alongside influent and effluent turbidity. The schematic of the subteam's past setup is shown below:

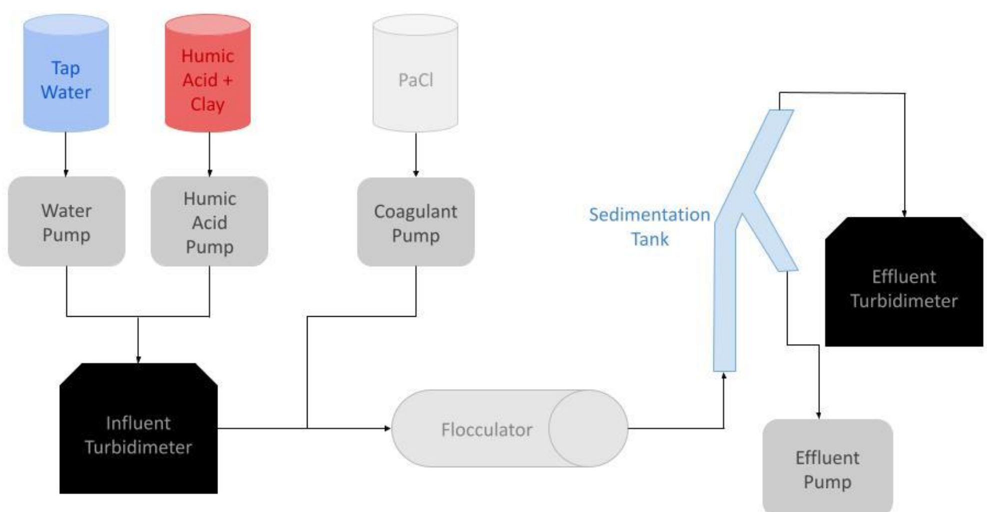

Figure 1. Schematic drawing of the 2022FA experimental setup

As shown in Figure 1, in previous semesters, kaolin clay was mixed with humic acid in the same stock solution with a view to reduce agglomeration between clay particles since humic acid can induce a negative charge and cause the particles to repel. However, the experimental setup for the Spring 2023 Dissolved Organic Matter subteam requires the concentration of humic acid into the flocculator to be kept constant while the concentration of kaolin clay to be varied with ProCoDA. Therefore, separate stock solutions for humic acid and clay, each connected to its own pump, needed to be prepared and Figure 2 shows this semester's schematic.

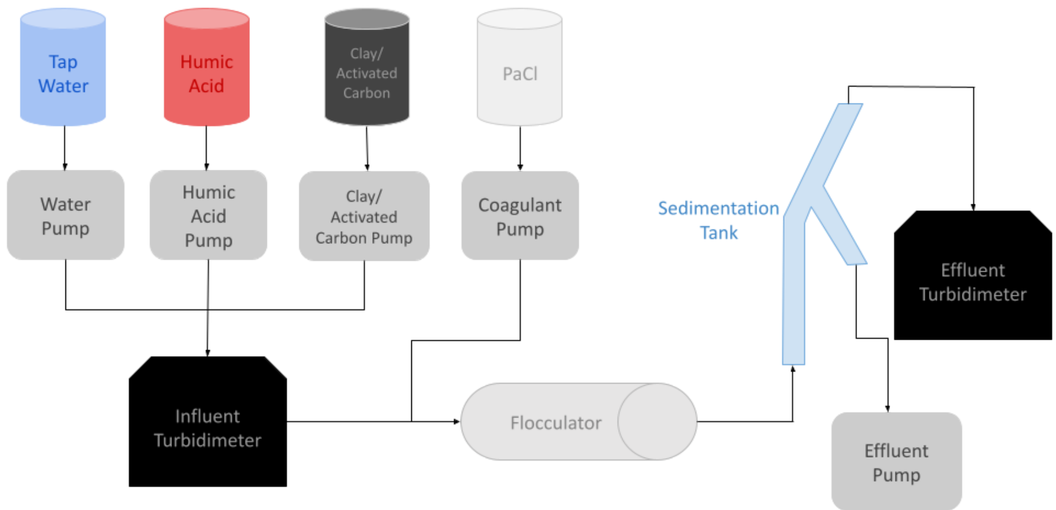

Figure 2. Schematic drawing of the 2023SP experimental setup

Floc Formation:

In order to display the difference in flocculation that was found last semester, below are two photographs of floc formation which vary in effectiveness.

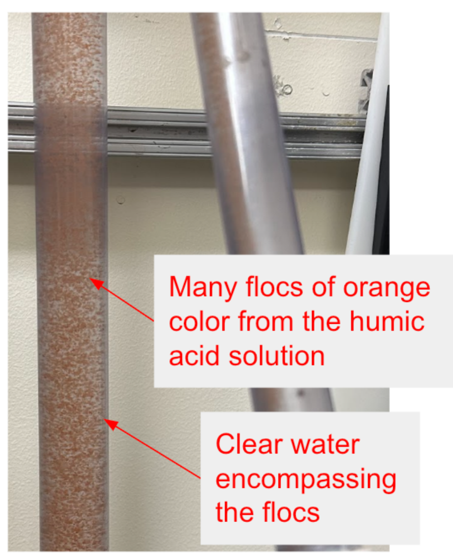

Figure 3. Image of sedimentation tank from experiments from Spring 2022

Figure 3 above is representative of what the separation of flocs and water should look like; flocs should be clearly distinguishable from the surrounding water. To increase visibility for making qualitative observations, red dye was added to the humic acid solution. This dye adhered to the humic acid resulting in a multitude of red-colored flocs.

Figure 4. Run with 100 mg/L of PACl stock solution and 5 g/L of clay stock solution with 5 mg/L of humic acid stock solution from Fall 2022

Figure 4 starkly contrasts the previous figure, Figure 3, which had clear water and distinct, colored flocs in the sedimentation tank. Figure 4 shows murky reddish water, and it is difficult to clearly discern any flocs. This remained a continuing problem throughout the Fall semester–it was hard to tell whether humic acid was even forming flocs. It was speculated that the dye might not have been adhering to the flocs. To test this, the DOM subteam switched to a lab-grade dye, but still, the issue persisted. To test whether the white particles were flocs, the DOM team added more coagulants. Theoretically, if more coagulant was used, there should have been more flocs. The result of this experiment was the formation of more particles, which supported the theory that the white particles could be flocs. However, the water still remained murky and muddy in the sedimentation tank. It is important to note that the concentrations mentioned in Figure 4 are referring to the stock solution concentrations, not the concentrations in the sedimentation tank. Traditionally, concentrations listed are of the sedimentation tank, so adjustments were made this semester to abide by that convention.

Methods

<u>Flow Rate Tests for Each Pump's Volume/Revolution:</u>

In order to properly implement ProCoDA in the experimental procedure, the volume per revolution values for each pump setup needed to be experimentally determined. Through tracking the number of revolutions and volume pumped (with an electronic balance) for each pump within a certain time limit, the values for each pump's volume per revolution could be calculated. Once this test was performed for all of the pumps in the system, the calculated values were inputted into the ProCoDA method file for more accurate results on future experiments.

Automated Testing with ProCoDA:

To implement timed trials using ProCoDA, the Spring 2023 DOM team updated the old method file to include the automated testing necessary for experimenting with different clay/activated carbon dosages. As referenced in Figure 9 and 10 in the Appendix, this process involved working through Dr. Monroe Weber-Shirk's ProCoDA tutorial and adjusting his values to reflect that of this experiment. Specifically, this involved changing set points in the "Rules and Outputs" tab to reflect Run, Warmup, and OFF states for that cycle after a set time interval. All the set points that control flow rates were modified to be variables, whose values could be incrementally adjusted using the ProCoDA mathematical functions. Desired clay flow rates were set through adjusting constant set points such that a new geometric series was generated with different base and coefficient values. The waste flow was also changed from a constant to a variable where it was set equal to a certain percentage (e.g., 30%) of the total incoming flow of the system.

For our experiment, clay flow rate increments were based on the geometric series:

$$\mathbf{0.5*3^x \text{ for } x = 0, 1, 2, 3, 4 \text{ (in rpm)}}$$

with base (3) and coefficient (0.5) values chosen and set as constant on ProCoDA. Geometric series were chosen instead of arithmetic, on the basis that the increase in clay dosage is more significant between intervals for geometric series. This allows for a wider range of clay dosages for analysis. In addition, the ProCoDA built-in math function for geometric series–"Increment by factor rep"–was more easily accessible and faster to implement than other series. The total run time for each run was set to be 25 minutes to allow for clay/activated carbon dosages to fully take effect in the flocculator and sedimentation tank.

Analyzing Floc Sizes for Incremental Clay Dosages:

Thus far, the Dissolved Organic Matter subteam has been using qualitative observations to collect data on the size of the flocs formed during experiments. This semester, the subteam planned to quantitatively measure the flocs using digital image analysis. The process involved taking an image of the flocs on a cell phone with a ruler in the background to scale it. The photos were then processed and analyzed using the computer software ImageJ.

In order to input the image into ImageJ, it must be turned into a JPEG. Then, on ImageJ, the JPEG should be changed to Imagen-Type-8bit by going to Image, Type, and then selecting 8-bit. To improve the ability to differentiate between the flocs and the surrounding water, the colors are inverted by going to Image, Lookup Tables, and then selecting the Invert LUT command. ImageJ can then analyze using set measurements and scale. The polygon tool was then used to trace around flocs, whose area and perimeter (in mm^2 and mm) were measured and tabulated using the Result function.

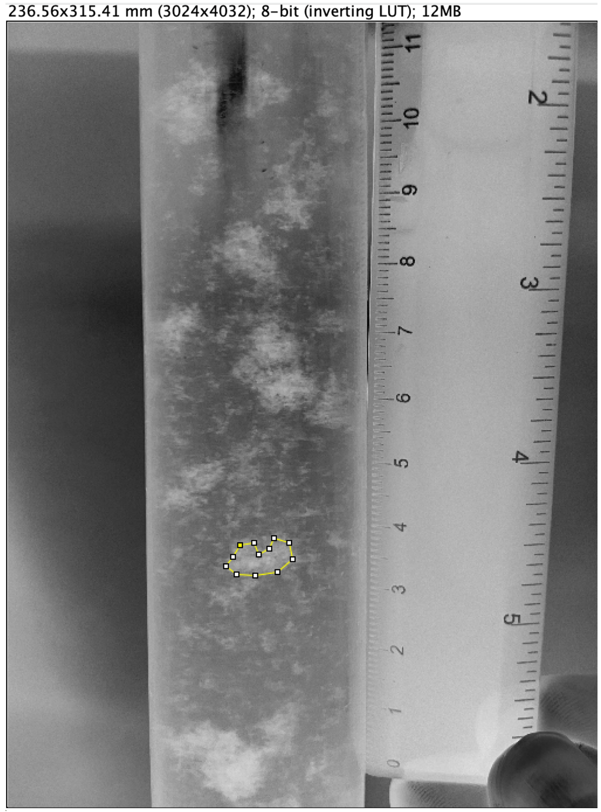

Figure 5. Example of outlined floc for ImageJ analysis

Results, Analysis, and Discussion

Flow Rate Tests for Each Pump's Volume/Revolution:

Table 1. Average Volume per Revolution (mL/rev) for each Pump

Pump type	Overhead type	Average volume per rev (mL/rev)
Clay/Activated carbon	Ismatic	0.113
Coagulant	Ismatic	0.118
Humic acid	Ismatic	0.109
Water	Masterflex	2.66
Waste	Masterflex	0.850

In Table 1, the average volume per revolution values were found for each pump used in the experimental setup. These values for the clay/activated carbon (0.113 mL/rev), coagulant (0.118 mL/rev), humic acid (0.109 mL/rev), water (2.66 mL/rev), and waste (0.850 mL/rev) pumps were inputted into the ProCoDA method file to ensure that the expected flow rates for each pump were being used. Variance between the clay/activated carbon, coagulant, and humic acid pumps was unexpected since all three had the same setup (Ismatic overhead and yellow-blue tubing). However, it was reasoned that there may still be minute clogs in the tubing which may have affected the volume per rev values for each pump. Through implementing these values in the ProCoDA method file, these errors should be nullified.

<u>Automated Testing with ProCoDA:</u>

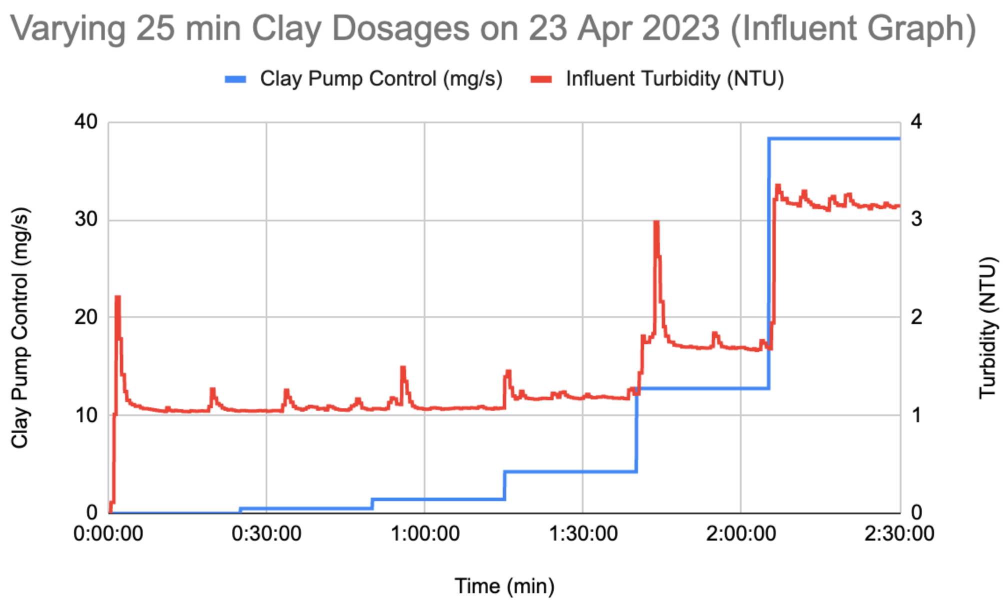

Figure 6. Graph of Influent Turbidity vs Time after Varying Clay Dosages

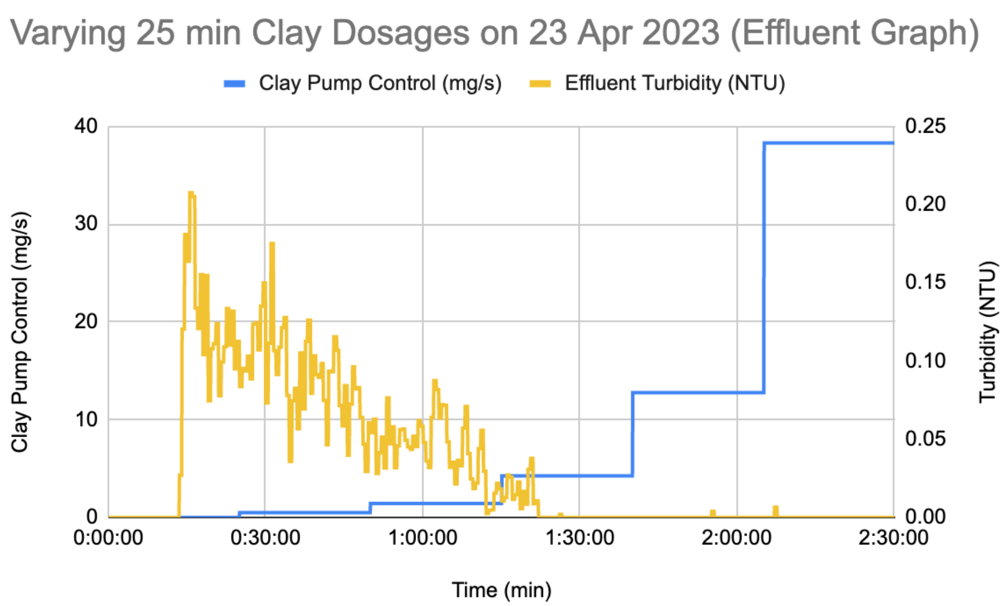

Figure 7. Graph of Effluent Turbidity vs Time after Varying Clay Dosages

Table 2. Clay dosage increments at Constant Coagulant and Humic Acid dosages

Dosage #	Clay Dosage (mg/s)	Coagulant Dosage (mg/s)	Humic Acid Dosage (mg/s)
1	0	23.64	23.64
2	0.473	23.64	23.64
3	1.42	23.64	23.64
4	4.26	23.64	23.64
5	12.8	23.64	23.64
6	38.3	23.64	23.64

Figures 6 and 7 represent the turbidity change vs time that occurred after varying 25 minute clay dosages. In Figure 6, it can be seen that increasing the clay concentration (blue) in the system increased the influent turbidity (red), which is expected since clay was said to increase turbidity readings. In Figure 7, it can be seen that increasing the clay concentration (blue) in the system decreased the effluent turbidity (orange). It should be noted that the effluent turbidity did lag behind each clay dosage and influent turbidity reading since it took time for the effects of the dosage to be shown in the effluent turbidimeter. A key threshold to note in this graph is that the effluent turbidity values reached 0 after implementing 4.26 mg/s of clay (from Table 2), which meant that this was the lowest clay dosage tested that provided a turbidity of 0. However, since turbidites of 0 are quite difficult to achieve, this experiment will likely need to be tested again next semester after recalibrating the turbidimeters to ensure that the most accurate values were obtained.

This experimental procedure may not fully test the effectiveness of clay in removing humic acid from drinking water since the conditions may have allowed humic acid to form flocs with just coagulant and no clay after a long period of time (>25 min). Therefore, to ensure that this experimental procedure tests the effectiveness of clay dosages, just humic acid and coagulant should be tested to ensure that little to no flocculation occurs after a long period of time.

Analyzing Floc Sizes for Incremental Clay Dosages:

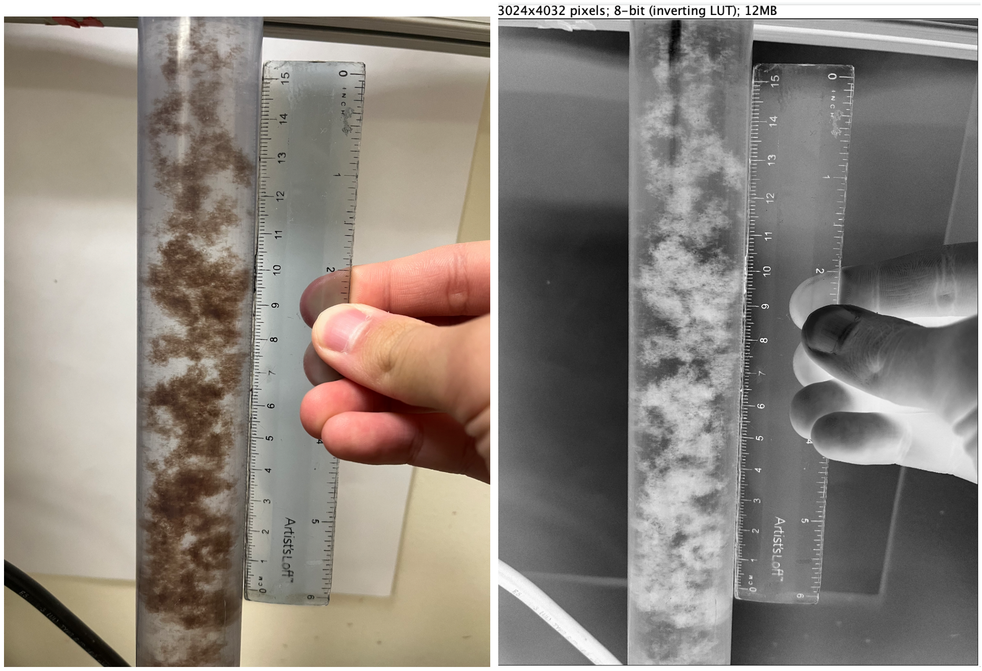

Figure 8. Original photo vs B/W-contrasted photo of flocs in the sedimentation tank

Figure 8 displays a sample of the before and after photos of the flocs in the digital analytics with ImageJ. With that being said, one issue that occurred with the implementation of ImageJ was that it was difficult to distinguish individual flocs for specific trials within the gradual clay flow rate increments from ProCoDA. As shown above for the 1.6 rpm iteration of clay, once more flocs begin to form and accumulate, floc blanket forms and the out-of-focus flocs make it much harder to isolate individual flocs for digital evaluation and scaling.

Conclusion

Once the experimentally determined flow rate of the pumps has been calculated, it was found to differ slightly from ProCoDA's setting. DOM used these flow rates to calibrate the set points and determine concentrations of clay, coagulant, and humic acid in the flocculator. Additionally, DOM has automated the experiment process using ProCoDA, which dispenses different dosages after a set time interval. Using ProCoDA to run trials instead of constantly making new dilutions of solutions by hand is much more time efficient, allowing DOM to collect more data on different clay dosages within the same time period as previous runs. Additionally, the time interval that ProCoDA used is spaced out enough, so that it was easy to distinguish between one trial's dosage and the next. DOM has recently begun quantifying floc size using ImageJ, on the basis that, ideally, flocs should be denser and smaller in size as clay dosage increases. However, ImageJ was found to be not very efficient as it required all flocs to be outlined by hand, and the observer still had to decide where one floc ends and the next floc begins (which is made complicated by the out-of-focus flocs). In the future, DOM aims to find a different and more accurate method that will yield better analyses of the relative floc size.

Future Work:

Another accuracy-related issue arose as a result of the interactions of flocs with the pre-established floc filters. In recent experiments, the same floc filter has been reused for trials, even though there were different coagulant dosages in each trial. While this had shortened the experiment duration (a new trial can be run without waiting for the floc filter to leave the sedimentation tank), reusing the floc filter didn't come without concerns. Recycling the floc filter could be skewing the data collected, as it could make the system appear to be working better or worse than it is in reality. To address this problem, the DOM subteam plans to eliminate the floc filter altogether by reducing the length of our sedimentation tank by sawing. This will prevent the formation of floc filters and shorten flocs' residence time, thus allowing for shorter experimental cycles.

The optimal coagulant dosage remains unknown and more data needs to be collected. DOM is currently in the process of running automated trials using PACl. Future experiments will be conducted with extremely low dosages of PACl (2 and 5 mL) to find the minimum PACl dosage that would still allow flocs to form. Once this data has been obtained, DOM plans to switch to using activated carbon in the experimental procedure to see if it can provide turbidity while having an enhanced effect in forming flocs. The experiments will involve using the same concentrations of humic acid that were tested with its corresponding optimal coagulant concentrations and varying the concentrations of activated carbon. The experiments will be run in exactly the same way as the clay experiments, but the clay will be substituted with activated carbon.

The most immediate future work of the DOM subteam is to run trials with only humic acid and coagulant. This will serve as a control group to verify clay's effectiveness in the flocculation process and enable the subteam to find a repeatable upward velocity. If flocs are still forming in our setup without the help of clay, it is an indication that our experimental condition is not disturbing enough. Increasing upward velocity in the system and lowering coagulant dosage would be sufficient to create unfavorable conditions for flocs to form. The purpose of this experiment is to provide a contrast between a system with and without clay, by creating an environment where flocs are unable to form when only humic acid and coagulant are supplied.

Manual

Lab Procedure for Iterative Testing:

1. Open the water (blue) and waste (red) lines to the left of the system
2. Turn on pumps, turbidimeters, and computer
3. Open ProCoDA → Open relevant method file
4. Check to see that solutions do not need to be refilled
    a. Usually want more than half left in each bottle
5. Click Edit Rules → Change Setpoints and Rules & Outputs based on what should be tested
6. Click Mode of Operation → Change from Manual Locked in State to Automatic Operation
7. Click Operator Selected State → Change from Off to Warmup
8. Click on Graphs Tab → Ctrl+Click on relevant Data to Plot
    a. Right click upward facing arrows to change y-axis

Appendices

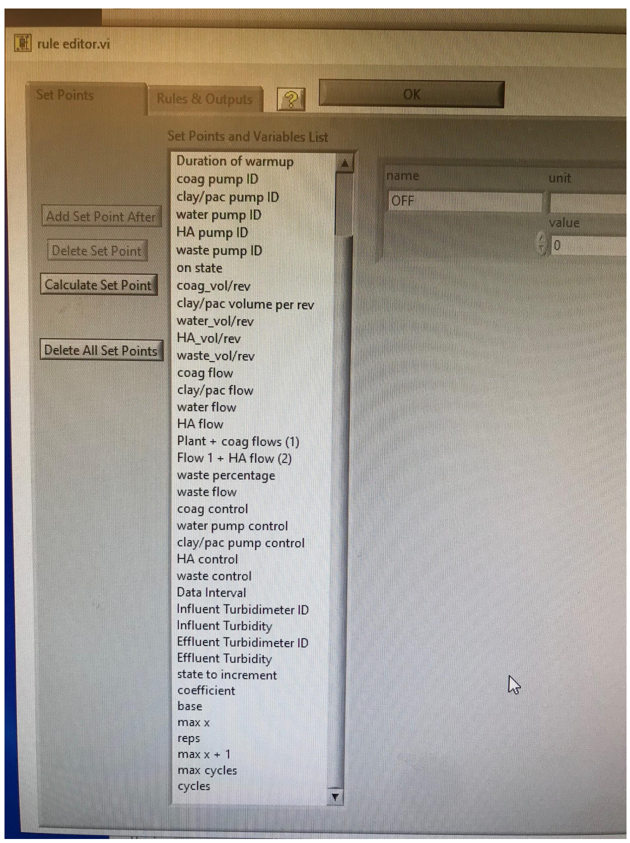

Figure 9. Image of the iterative testing Setpoints of the ProCoDA method file

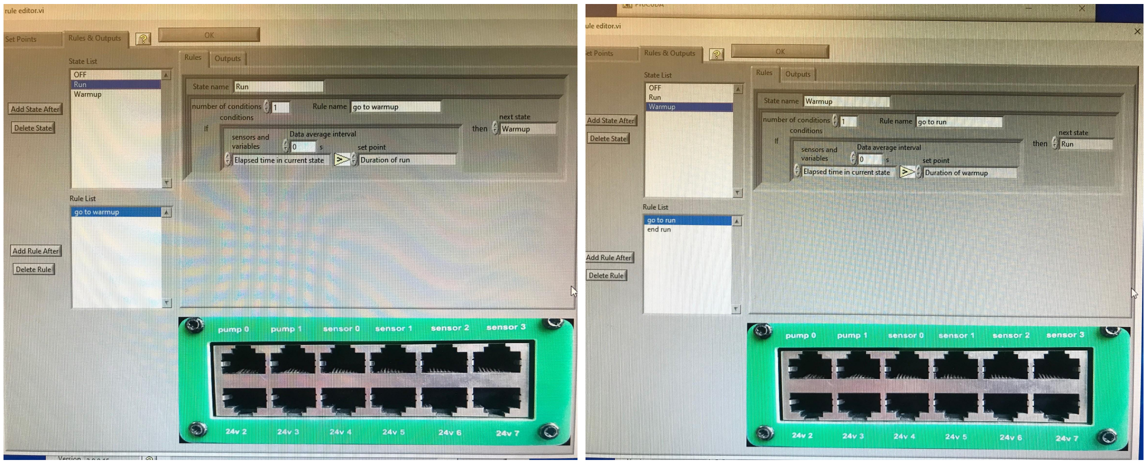

Figure 10. Images of the iterative testing Rules & Outputs in the ProCoDA method file

Table 3. Number of Revolutions, Volume Pumped, and Volume per Revolution for Multiple Flow Rate Tests of Pumps and Average Volume per Revolution for each Pump

Pump type	Overhead type	Number of revolutions (rev)	Volume pumped (mL)	Volume per rev (mL/rev)	Average volume per rev (mL/rev)
Clay/ Activated carbon	Ismatic	32.5	3.66	0.113	0.113
		34.5	3.78	0.110	
		10	1.21	0.121	
		10.5	1.15	0.110	
		10.75	1.2	0.112	
Coagulant	Ismatic	10.25	1.25	0.122	0.118
		13.6	1.64	0.121	
		16.25	1.95	0.120	
		18.5	2.11	0.114	
		22	2.52	0.115	
		22.6	2.59	0.115	
Humic acid	Ismatic	12	1.3	0.108	0.109

		15	1.65	0.110	
		16.5	1.79	0.108	
		19	2.09	0.110	
		21.25	2.33	0.110	
		23	2.52	0.110	
Water	Masterflex	10.5	28.22	2.69	2.66
		12	30.43	2.54	
		5.5	14.85	2.70	
		4.75	12.85	2.71	
		10.5	28.22	2.69	
Waste	Masterflex	6.2	5.26	0.848	0.850
		8.25	7.13	0.864	
		8.5	7.11	0.836	
		10	8.46	0.846	
		9.75	8.3	0.851	
		12	10.23	0.853	

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