Title: Automation of Chemical Dosing for Removing Dissolved Organic Matter From Drinking Water

Team: Dissolved Organic Matter, Fall 2023
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Date: 1 December 2023

Abstract

The Fall 2023 Dissolved Organic Matter subteam aims to compare the effectiveness of implementing polyaluminum chloride with clay and/or powdered activated carbon to remove humic acid from drinking water. To ascertain the optimal amounts of activated carbon and clay concentrations, ProCoDA will be utilized to introduce various flow rates of the different solutions into the system, which allows for higher efficiency testing and more control over what amounts of solutions are in the system at a given 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 hopes to improve the capability of AguaClara water treatment plants.

Introduction

Dissolved organic matter, a natural transparent water contaminant, is present in unusually high amounts in AguaClara's plant in Gracias, Honduras. DOM is created from the decomposition of organic matter, such as feces and decaying leaves. 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 a coagulant for denser floc formation (Tafvizi et al., 2021). Due to its porous surface, activated carbon particles, bounded 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 clay and/or powdered activated carbon in removing humic acid from influent water. Future steps in this experiment include examining the optimal dosage of coagulant with clay and/or activated carbon and investigating financial trade-offs between the two.

Literature Review

Clay is important in modeling the removal of dissolved organic matter 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 a coagulant. The reasoning behind the use of clay in the procedure of removing dissolved organic matter is that it is a major contributor 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 Fall 2023 team 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 for its potential role in removing dissolved organic matter from drinking water. In a 2021 study by Biswas et al., researchers collected water 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 that 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 rates 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. 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.

Previous Work

<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. By 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 in future experiments.

<u>Automated Testing with ProCoDA</u>

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 (Kwon et al., 2023). This process involved working through Dr. Monroe Weber-Shirk's ProCoDA tutorial and adjusting his values to reflect those 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 by 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 this 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. The results from the experiment are shown in Figures 1 and 2.

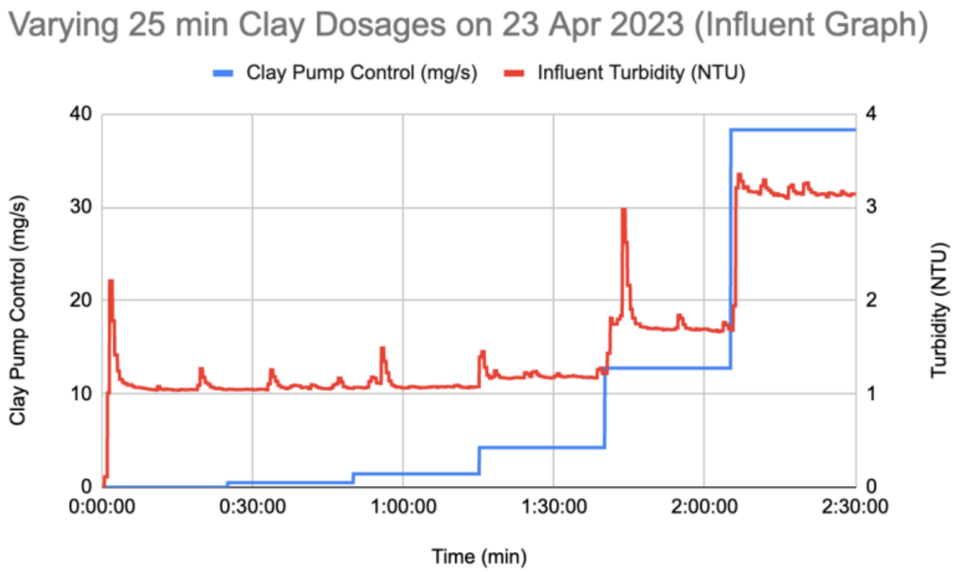

Figure 1. Graph of Influent Turbidity vs Time after Varying Clay Dosages

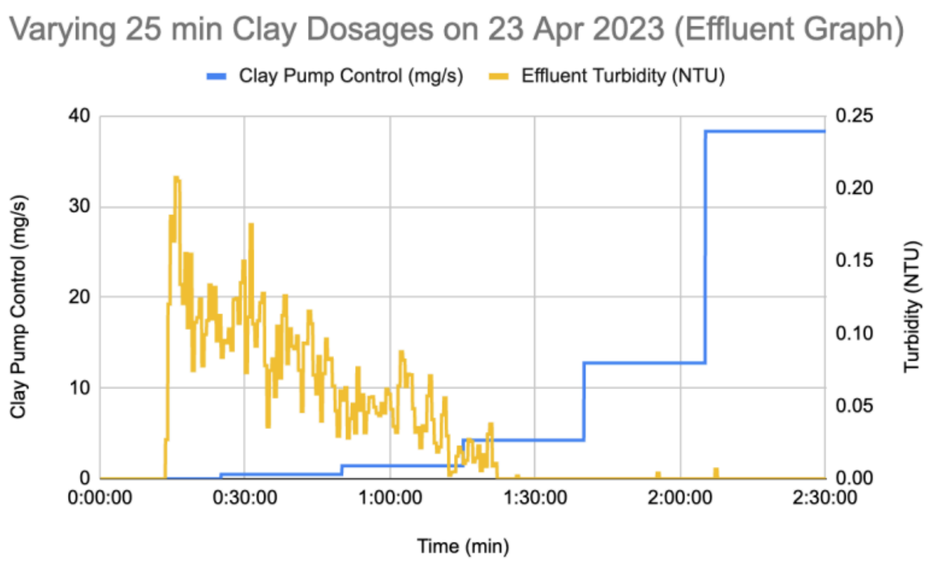

Figure 2. Graph of Effluent Turbidity vs Time after Varying Clay Dosages

Methods

Preparation of New Sedimentation Tank

When testing the upflow velocity, several additional adjustments were made to the system as well to accommodate for the discrepancy of the testing. One of the main adjustments was the preparation of a new sedimentation tank. The new sedimentation tank was cut to reduce the time for the system to travel through the sedimentation tank and prevent the formation of a floc blanket. The tank was cut using an electric reciprocating saw at roughly ~9 cm below the bent portion of the tank. The new shorter sedimentation tank was installed to the right of the original tank and secured at a 60° angle from horizontal for effective separation of flocs. The 60° angle adjustment was made to ensure that there is a large enough planar area for the flocs to settle on and eventually enter the lower arm, thus leaving the system.

Calculating Upflow Velocity and Flow Rates

To mimic the condition in our plant in Gracias, Honduras, the upflow velocity in the clarifier needed to be increased so that the conditions for flocs to settle down are harsher. Experiments were performed by running trials with only humic acid, coagulant, and water. By increasing the upflow velocity in the sedimentation tank, the system would reach failure, which serves as a control group to verify the effectiveness of adding clay and/or activated carbon into the system later on. The purpose of this experimentation process is to provide a contrast between a system with and without clay/activation carbon by creating an environment where flocs are unable to form when only humic acid and coagulant are supplied. Calculations for the flow rates necessary to determine the optimal upflow velocity were made with Deepnote, a collaborative coding program, as shown in Figure 3.

```
#Calculations for upward velocity tests
Conc_PACl_System = 10 * u.milligram/u.L
Conc_HA_System = 10 * u.milligram/u.L

Conc_PACl_Stock = 131.34 * u.milligram/u.L
Conc_HA_Stock = 655.17 * u.milligram/u.L

Up_Velocity = 1 * u.millimeter/u.s #CHANGE THIS

Actual_Inner_Diameter_Sed_Tank = 26.6446 * u.millimeter
Actual_Area_Sed_Tank = ac.area_circle(Actual_Inner_Diameter_Sed_Tank)

Flow_Rate_Total = Up_Velocity * Actual_Area_Sed_Tank

Flow_Rate_PACl = Conc_PACl_System * Flow_Rate_Total / Conc_PACl_Stock * 0.001 * u.milliliter/u.millimeter ** 3
print("Flow Rate of PACl is", Flow_Rate_PACl)
Flow_Rate_HA = Conc_HA_System * Flow_Rate_Total / Conc_HA_Stock * 0.001 * u.milliliter/u.millimeter ** 3
print("Flow Rate of HA is", Flow_Rate_HA)
Flow_Rate_Water = Flow_Rate_Total - Flow_Rate_PACl - Flow_Rate_HA
print("Flow Rate of Water is", Flow_Rate_Water * 0.001 * u.milliliter/u.millimeter ** 3)
```

```
Flow Rate of PACl is 0.04245 milliliter / second
Flow Rate of HA is 0.00851 milliliter / second
Flow Rate of Water is 0.5066 milliliter / second
```

Figure 3. Example Deepnote code for calculating flow rates to run in the system based on system concentrations, stock concentrations, and upflow velocity.

This code provides the capability to easily adjust system and stock concentrations, as well as upward velocities. To determine the humic acid and coagulant dosages with Deepnote, it was necessary to determine their respective concentrations in the system. Based on the data from Du et al. (2019) in Figure 4, a value of 25 mg/L for system humic acid concentration and values between 2-3 mg/L for system coagulant concentration was chosen for this experimental running.

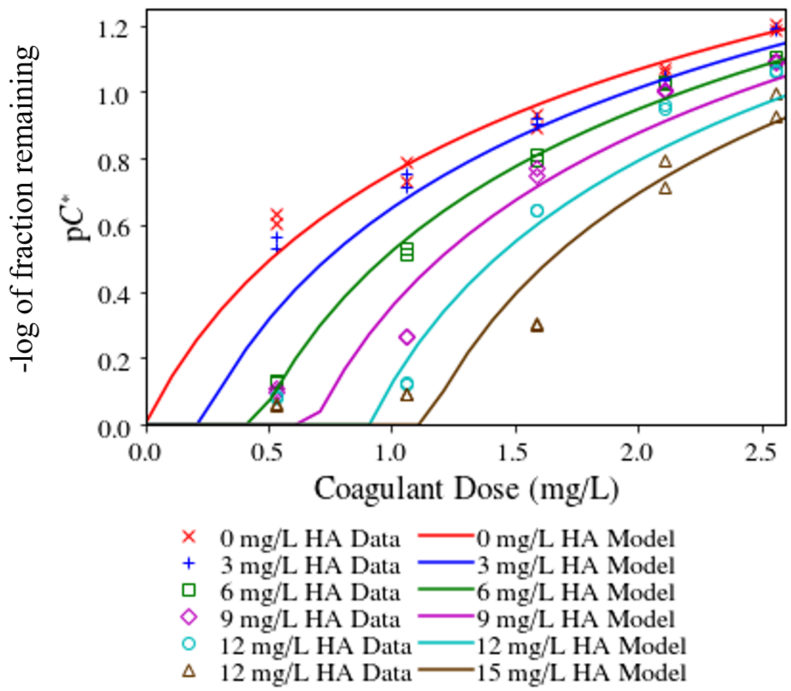

Figure 4. Flocculation performance as a function of coagulant dose and humic acid concentration

<u>Iterating Clay Dosages with Alternating Wash Steps on ProCoDA</u>

In order to remove the floc blanket formed during each trial of clay dosages, the team aimed to implement the addition of wash steps between each incrementation of clay. This was achieved by having 3 states: OFF, Iterate Clay, and Run Water. The specifications of each state are detailed in Table 1. The workflow for these states was automated using conditional loops set in ProCoDA with Iterate Clay's next state being Run Water and vice versa until the maximum number of cycles is reached. An image of ProCoDA's interface where this was done is included in Figure 5.

Table 1. Different States in ProCoDA with the Corresponding Flow Rates of Each Substance

	State Name		
Pump Control	Off	Iterate Clay	Run Water
Clay/PAC	Off	Iterate <50 rpm	Off

Water	Off	Iterate <50 rpm	50 rpm
PACl	Off	Constant <50 rpm	Off
Humic Acid	Off	Constant <50 rpm	Off
Waste	Off	50 rpm	50 rpm

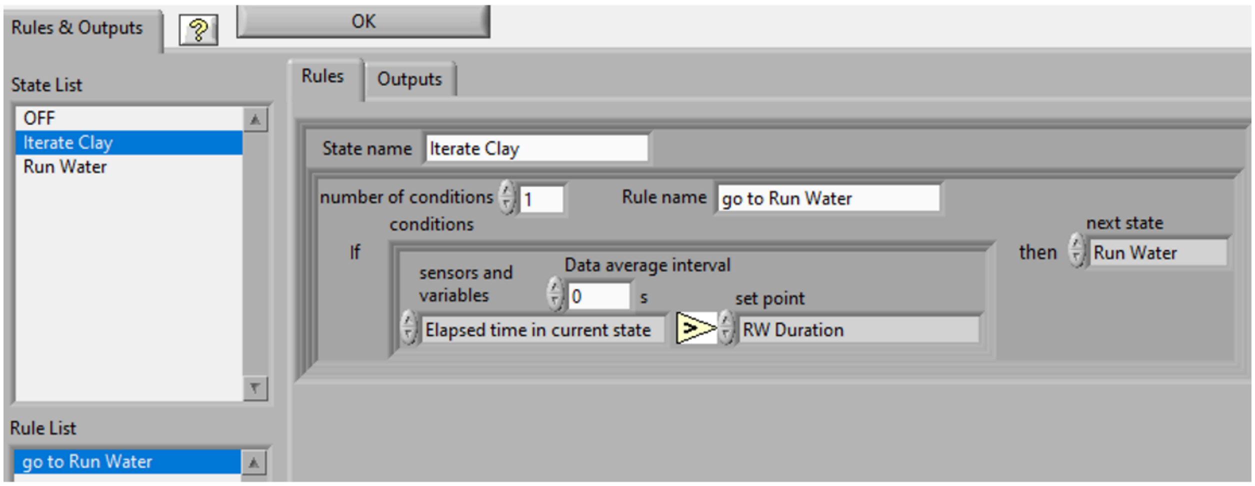

Figure 5. The Iterate Clay state with its conditions and rules on ProCoDA.

Results and Analysis

Many trials were conducted to determine the optimal upflow velocity to model the conditions in our plant in Gracias, Honduras. We started with an upflow velocity of 1.5 mm/s and incrementally increased to 3.5 mm/s. The findings are summarized in Table 2.

Table 2: Summary of the Upflow velocities and Turbidites

Upflow Velocity (mm/s)	Influent (NTU)	Effluent (NTU)
1.5	6.33	0.83
2	5.99	3.92
2.5	5.69	4.75
3	5.75	5.68
3.15	5.57	5.65
3.25	5.64	5.58
3.5	5.53	5.8

To determine the optimal upflow velocity, the differences between the influent and effluent turbidities were graphed with the upward velocities in Figure 6. The variations in turbidities were minimal when the upflow velocity exceeded 3 mm/s.

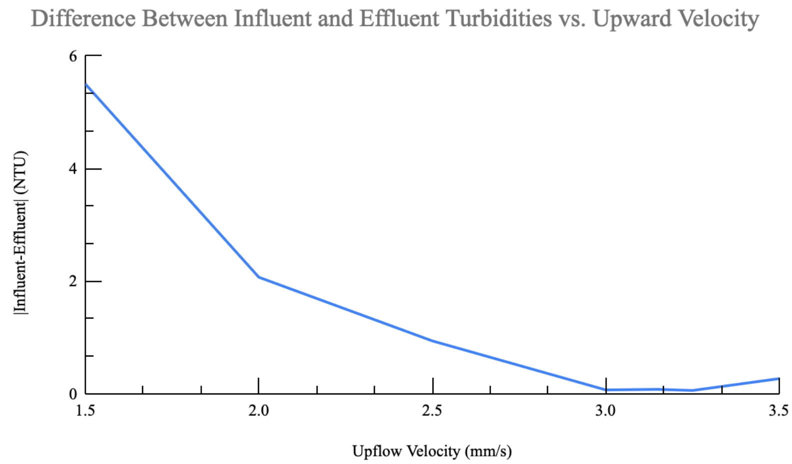

Figure 6. Effect of increasing upflow velocity in clarifier on the difference between influent and effluent turbidites

After comparing the various upflow velocities, additional tests were performed to confirm the test from Figure 6. Based on the additional tests, it was determined that at 3.35 mm/s (Figure 7) the system would indeed reach failure with just humic acid, coagulant, and water present in the system. This would be the system upflow velocity once experimentation with incrementations of clay and/or activated carbon starts.

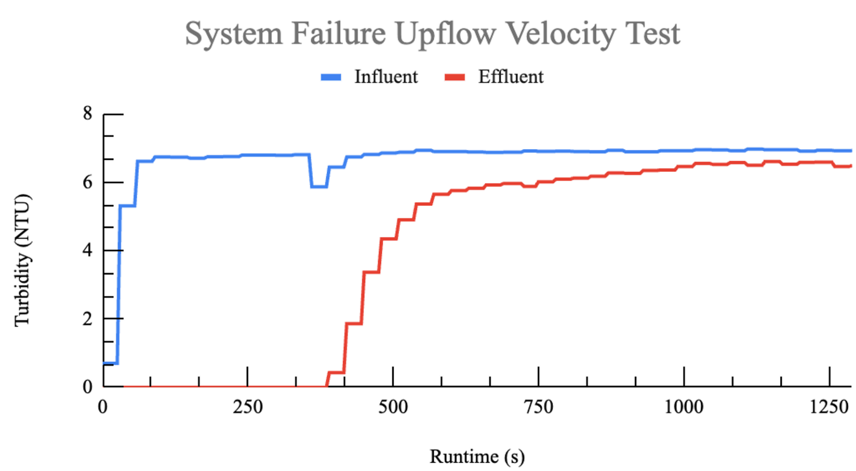

Figure 7. Graph demonstrating the system approaching failure with only coagulant (PACl) and humic acid (DOM) at 3.35 mm/s upflow velocity.

Discussion

As presented in Figure 7, an upflow velocity of 3.35 mm/s generates an upward force within the water, hindering the sedimentation of flocs. This interference in the settling process is crucial, as it leads to the ultimate failure of the system where the effluent turbidity closely approaches the influent turbidity. From a system perspective, when the effluent and influent turbidity are relatively close, it implies that flocs are not settling out and the majority of dissolved organic matter flows through to the end, implying that no clarifications occur to the input flow. The system upflow velocity is much greater than the value present at the Gracias AguaClara plant of 1 mm/s. This discrepancy is likely due to the difference in scale of the clarifier in the lab and the plant.

Some weaknesses in our experimental set-up include the accuracy of our turbidimeters and our closed water lines. The accuracy of our turbidimeters may be in question even after turbidimeter calibration at the beginning of the semester. Our water lines have been closed for an extended period of time, which forces us to pour water from the sink into a bucket to serve as our water source.

Conclusion

Geometric clay dosage incrementations were successfully automated with ProCoDA, which manages the dispensation of increasing dosages at specified time intervals. Utilizing ProCoDA to conduct trials instead of manually preparing new dilutions of solutions is significantly more time-efficient. This efficiency enables the collection of a greater amount of data on various clay dosages within the same timeframe as previous runs. Furthermore, the conditions for system failure have been identified, notably an upflow velocity of approximately 3.35 mm/s. This velocity provides a foundation for a model of the flocculation issue in the Gracias plant.

Our next steps involve conducting experiments where we incrementally add clay in an arithmetic progression, following the conditions outlined in Figure 1. The ProCoDA code utilized for running these experiments will closely resemble the one employed for incrementing clay dosages in a geometric series while maintaining a consistent upflow velocity of 3.35 mm/s. Following this, we plan to replicate the process, substituting clay with activated carbon. We will perform a comparative analysis to assess performance variations and explore the financial trade-offs associated with each material.

References

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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 Iterate Clay
8. Click on Graphs Tab → Ctrl+Click on relevant Data to Plot
    a. Right click upward facing arrows to change y-axis

Appendix

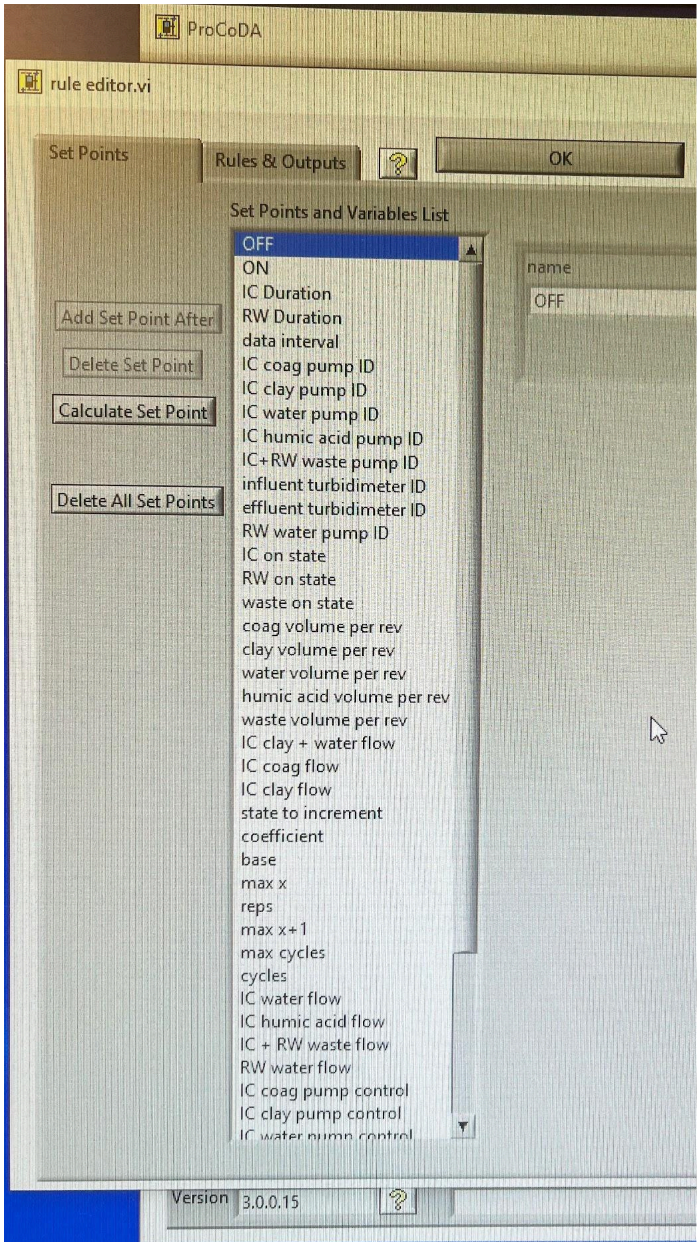

Figure 8. Image of the iterative testing Setpoints of the ProCoDA method file