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**ENHANCING GRAVEL ROUGHING FILTER PERFORMANCE WITH ZERO VALENT
IRON AND ANION EXCHANGE RESIN**

By

Anthony J. Guidice
B.S. Environmental Science, University of New Hampshire, 2014

THESIS

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Master of Science
in
Civil and Environmental Engineering

September 2020

This thesis/dissertation has been examined and approved in partial fulfillment of the requirements for the degree of Master of Science in Civil and Environmental Engineering.

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On June 8, 2020

Original approval signatures are on file with the University of New Hampshire Graduate School.

DEDICATION

This thesis is dedicated to all my loved ones who supported and encouraged me through my years of study.

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Firstly, I would like to acknowledge the United States EPA for providing the funding that enabled this research through the DeRISK Center at the University of Colorado, Boulder.

I would like to thank my advisor, Dr. Robin Collins, for his guidance and encouragement through the years of my research.

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ENHANCING GRAVEL ROUGHING FILTER PERFORMANCE WITH ZERO VALENT IRON AND ANION EXCHANGE RESIN

Anthony Guidice and M. R. Collins
University of New Hampshire

Gravel roughing filters (GRFs) are used as a way to buffer small systems that are sensitive to contaminant spikes within influent waters, however they tend to fall short in the removal of contaminants such as arsenic or organic precursors. A possible solution to this shortcoming is the addition of granular Zero Valent Iron (ZVI) or Ion Exchange Resin to the GRFs. ZVI is non-proprietary and non-deleterious to biofiltration systems. Ion exchange resins are proprietary however they are non-deleterious to biofiltration systems. ZVI or resin can be added as a portion of the media in a vertical upflow filter and as a final filtration step in a horizontal filter. Our research shows the buffering capabilities that GRFs offer as well as some possible enhancements that can be added for additional treatment if desired.

When ZVI is used as a portion of media compared to its typical gravel media without a ZVI portion has many benefits. The iron media is inexpensive making it practical for small communities, enhances removal potential of arsenic and dissolved organic compounds, easily generated and regenerated suggesting a long lifespan, can be found in any geographic location, and in aerobic conditions with pH's greater than 7 iron solubility is rendered to almost undetectable levels making treatment for dissolved iron unnecessary.

Prior research under Dr. M. Robin Collins has demonstrated how ZVI granular media surfaces' removal potential for arsenic while this dissertation focused on the removal potential of organics along with its regeneration capacity. Bench-scale column challenges have shown that ZVI has the capacity to remove more than 50% of organic precursors from raw waters. Regeneration was successful at pH's ranging from 10 to 12 and possibly getting better results as pH goes even higher.

Purolite A502p resin has shown incredible removal potential over an extended period of time. Three different empty bed contact times(2, 5 and 10 minutes) were run to for a total of 47 days testing the affect that the varying empty bed contact time would have on the DOC removals as well as how long the resin would last before becoming exhausted. The 2-minute column treated about 33,900 bed volumes and was determined to be exhausted once it no longer achieved greater than 10% DOC removals.

Two pilot sized surface-loaded horizontal gravel roughing filters (HGRFs) and two vertical gravel roughing filters (VGRFs) were constructed and installed in the pipe gallery of the UNH/Durham Water Treatment Plant. The two HGRFs are were used to evaluate Purolite A502p resin additions to the gravel media and their increased removals of dissolved organic carbon (DOC). Anion exchange resin was added to one of the HGRFs initially by means of a resin box which was easily constructed at the University of New Hampshire. GRF 1 acted as a control with no resin box or resin additions. This resin box was added to the final 7 inch portion of GRF 2 as a final treatment stage. Resin was added to the VGRFs in a similar manner. The resin was added to the final 3-4 inches of media.

Once the single HGRF and two VGRFs received the resin enhancements differences between the orientations became apparent. The HGRF was consistently outperforming both VGRFs regarding DOC and turbidity removals by more than 15%. The results of our experimentation lean to HGRFs being a more successful system for its intended purposes.

CHAPTER 1: INTRODUCTION/LITERATURE REVIEW

1.1 Gravel Roughing Filters

Gravel Roughing Filters (GRFs) are an important pre-treatment process for small water treatment systems. Small systems tend to be inherently vulnerable to excessive fouling from highly turbid waters and GRFs act as a sediment buffer and remove particulate matter from these influent waters more efficiently than many other basic sedimentation processes (Wegelin, 1996) while also being a relatively simple and low maintenance option (Dastanaie, et al. 2007). When compared to other common sediment removal processes, such as the addition of chemical coagulants, one would be hard pressed to find a more simplistic and lower maintenance treatment method than GRFs. The inherent simplicity of the systems is due to the fact that it is mostly a physical treatment process rather than a chemical process which removes the need for dosing equipment or complicated calculations. The absence of chemicals does not mean a sacrifice in performance however. The quality of treatment that can be expected from a properly designed GRF has been shown through many previous studies (Clarke et al., 1996; Collins, 1994) while the most optimum design is still a topic of debate that continues to evolve. Another removal mechanism of GRFs and slow sand filters is that due to their low loading rates they develop an organic “film” or ecosystem on their surface known as the *schmutzdecke* (Hendricks *et al.*, 1991). The *schmutzdecke* and following first few inches of biologically active media has been found to be responsible for most of the contaminant removals for influent waters (Hay *et al.* 2016). This fact is demonstrated within this research and will be discussed later.

The most common designs for GRFs are in one of two orientations, horizontal flow or vertical flow with various sizes of gravel media. Both orientations have their respective benefits and drawbacks. Horizontal Gravel Roughing Filters (HGRFs) tend to be much larger and have longer Empty Bed Contact Times (EBCT) due to the nature of their orientation. This increased time the water is

given to pass through the filter media allows for more opportunity to immobilize the suspended sediments. They also do not tend to run into as many issues with fouling due to the nature of how fouling builds up within HGRFs. “Solids settle on top of the filter medium surface and grow to small heaps of loose aggregates with progressive filtration time. Part of the small heaps will drift towards the filter bottom as soon as they become unstable. This drift regenerates filter efficiency at the top and slowly silts the filter from bottom to top” (Nkwonta and Ochieng, 2009).

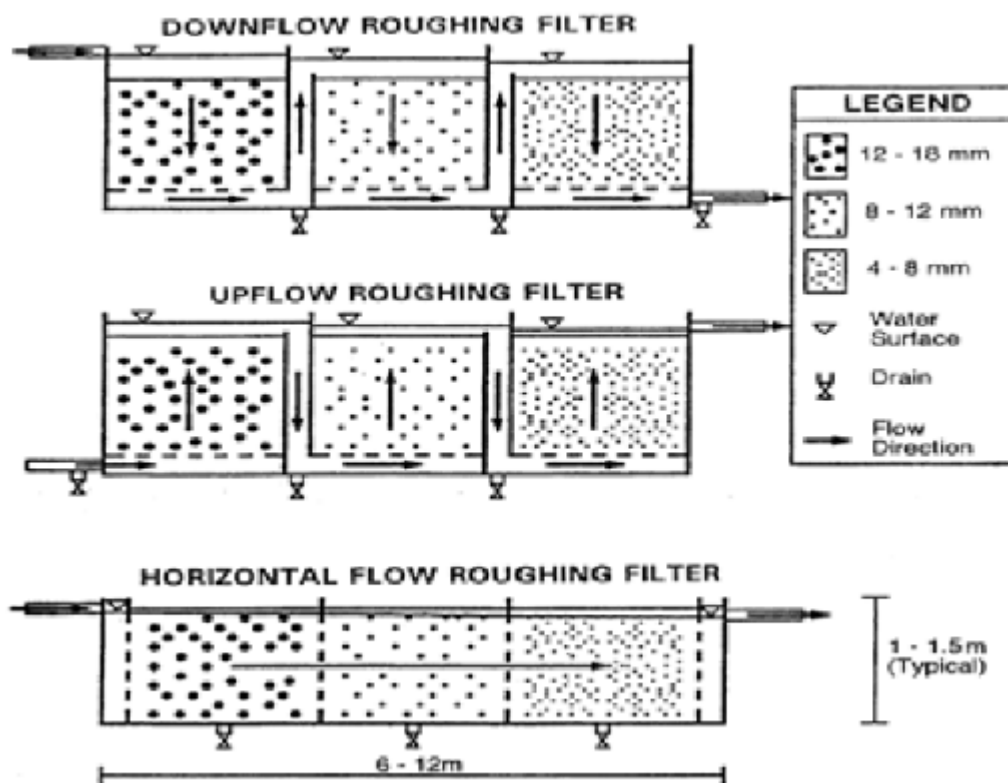


Figure 1.1: Examples of various GRF orientations, flows, and media sizes (Wegelin, 1996).

Vertical Gravel Roughing Filters (VGRFs) operate by passing the influent in a vertical direction requiring much less space than their respective horizontal sibling. VGRFs also have the benefit of changing the direction of flow. They can be designed as either upflow or downflow depending on the specific needs the filter is being designed for. For instance, a downflow VGRF has the benefit of being able to apply a supplemental media, i.e. carbon, Zero Valent Iron, or anion

exchange resin, directly to its gravel surface for added treatment since the influent water is flowing directly downward through the filter. The downsides to the VGRF is that they tend to be sensitive to flow rate changes and are harder to construct to obtain similar contact time as the HGRFs. See Figure 1.1 for a clear representation of typical GRF orientation and media size. While GRFs are a great option for inexpensive pretreatment of sediment contaminated waters they do fall short in the removal of dissolved chemical contaminants such as dissolved organic carbons. Additive medias are a possible way to remedy this shortcoming.

1.2 Zero Valent Iron and Anion Exchange Resin

GRFs act well as a sediment buffer however they fall short in the removal of dissolved chemicals such as organic carbons or metals. Zero valent iron (ZVI) and anion exchange resins are potential options for remedying these short comings of GRFs. “ZVI is was originally developed to mitigate chlorinated hydrocarbon industrial solvents disposed in soil and many other toxic species including arsenic in the environment” (Ahamed, et al. 2009), however its applications have been expanded beyond this. When ZVI granules are placed in oxidizing environments their surfaces begin to oxidize producing positively charged bonding sites. When these positively charged bonding sites come in contact with the negatively charged organic substances or negatively charged dissolved metals within untreated waters, they have a strong affinity to bond with them, immobilizing them from the water (Crompton, 2015). Another benefit to ZVI is that it is a non-proprietary media making it generally easy to obtain. For example, drinking water operations can easily source ZVI from a scientific lab supplier such as Fisher Scientific for ground iron filings.

Anion exchange resins are a manufactured media that is typically in the form of porous microbeads which are composed of organic polymer substrates. The most common application of anion exchange resins is for water purification or water softening purposes. They are particularly

useful in acidic waters because the positively charged microbeads are heavily basic in pH which gives them a strong affinity to bonding with negatively charged organic substances. Studies have also shown that the more strongly basic the anion exchange resins are the better removal of organic acids they tend to achieve (Croue et al, 1999). While they typically achieve better immobilization of organic substances than ZVI they are a proprietary media and can be hard to acquire making their application to GRFs generally prohibitive.

1.3 Research Goals

Three major goals for this research were outlined and are as follows:

- 1.) The first major goal of this research was to evaluate Horizontal GRFs' capabilities in buffering sediment loading spikes. GRFs are known for their ability to trap sediment so this portion of the experiment was designed to quantify and demonstrate these characteristics as clearly as possible. This research goal was significant because the findings can help to reinforce future research's findings in expected GRF treatment. These findings can contribute to the creation of expected treatment curves in comparison to design parameters.
- 2.) The second major goal of this research, which was the primary focus of the research, was to evaluate and compare possible enhancements to GRF's ability to reduce organic precursor materials at bench- and pilot-scale. Two medias were chosen to evaluate as possible additives to establish their potential for application to GRFs. These medias were non-proprietary ZVI and anion exchange resin. This research goal was significant because many regions that rely on GRFs have issues with organic substance contaminants. Evaluating a non-proprietary and proprietary solution for removal of these contaminants can better prepare these regions to treat their waters effectively.

3.) The final goal of this research was to compare different orientations of GRFs to establish if any significant benefits arise from either orientation. This research goal compared the differences between Vertical Upflow GRFs and Horizontal Flow GRFs. This research goal was significant because when GRFs are being designed many constraints need to be considered, such as available space and volume of media. More information that can help to quantify the expected performance and potential problems that come from these various orientations can help designers optimize for their specific situation.

CHAPTER 2: EXPERIMENT DESCRIPTION

2.1 Gravel Roughing Filters

2.1.1 Purpose

The purpose of this experiment was to test and demonstrate the mass loading buffering capabilities various orientations of Gravel Roughing Filters (GRFs) can achieve, along with possible enhancements. Storm events can cause mass loadings of sediment in large slugs that often clog subsequent slow sand filtration (SSF) treatment processes. GRFs act as a buffer to the loadings and as this research shows can remove up to 90% of influent solids allowing for consistent treatment. One of the major benefits to GRFs is that they require minimal maintenance and are easily assembled to the point where any water treatment plant technician can set up and maintain a GRF.

2.1.2 Orientation

Different orientations of gravel roughing filter may be chosen due to unavoidable external factors, namely cases of spatial constraint. In this study, vertical, upflow filters were chosen as the alternative to the more typical horizontal orientation due to their requiring substantially less square footage. These two orientations of GRFs were tested; Vertical Upflow (VGRF) and Horizontal (HGRF). Four pilot-scale GRFs were designed and built, consisting of two VGRFs and two HGRFs. The two HGRFs used a unimix media while one of the VGRFs is a stratified media and the other is a unimix media. The unimix media was evenly mixed gravel ranging from 1mm to 5mm in diameter while the stratified media was gravel between 1mm to 5mm that was placed within the filters as sections. Please see chapter 3 for a more detailed description of the GRFs designs.

2.1.3 Enhancements

The possible enhancements to GRFs that were tested were Zero Valent Iron (ZVI) and anion exchange resin (AER). Both of these enhancements were tested at bench-scale in vertical upflow columns and the AER was then tested at the pilot-scale. The ZVI enhancement was determined to be successful in higher pH conditions inconsistent with the sources available to us and therefore excluded from pilot-scale testing. The AER enhancement was meant to be the last bit of treatment through the GRFs that any influent water would see and was done by passing the water through the resin container upflow. For this reason the resin was chosen to be placed at the end of the treatment process for both VGRFs and HGRFs. These two orientations of GRFs were chosen to be evaluated because they are relatively standard orientations of GRFs (Wegelin, 1996) combined with the constraints of the test site. Please see section 3.4 for a more detailed description of the resin containers design.

2.1.4 Location

The four GRFs were built and placed in the basement at the Durham Water Treatment Plant in Durham, New Hampshire, 03824. The water sources being used were the Lamprey and Oyster Rivers (surface water) with occasional additions of the Spruce Hole aquifer (ground water).

CHAPTER 3: METHODOLOGY

3.1: Pilot-Scale Gravel Roughing Filter Turbidity Spike Challenges

Two pilot-scale gravel roughing filters were set up and operating at the Durham Water Treatment Plant. Figure 3.1 shows the orientation and design of the two filters. The filters were constructed from 173 x 56 x 23 cm (68 x 22 x 9 inch) stainless steel food serving troughs. A 20cm high weir was constructed from PVC sheet, affixed, and sealed 13cm from the end of the trough. The drain system was made from $\frac{3}{4}$ inch PVC pipe with 110 holes of 0.12cm (3/64 inches) in diameter drilled along the length of the pipe.

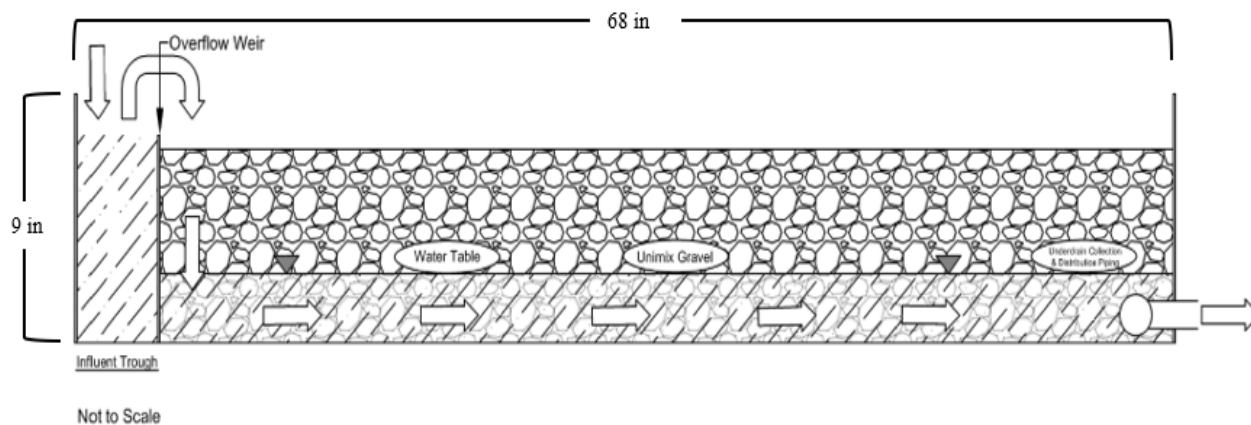


Figure 3.1: Pilot-Scale Horizontal Gravel Roughing Filter Design

Turbidity spike challenges were performed on these two filters to evaluate their buffering capacities. Before the spike challenges were performed both filters were given seven weeks to ripen and develop a schmutzdecke.

The turbidity spikes were made of a kaolinite clay solution which was a simple mixture of water and kaolinite clay particles. Filter 1 acted as the control receiving a lower dose target of 10 NTU which was the chosen dosage because it was the maximum natural spike seen through ripening. Filter 2 received a higher dose target of 20 NTU which was double the maximum natural spike that was seen during ripening to test capabilities during excessive loading. The dosing was added through bed volumes 0 to 1, 1 to 2, 2 to 3, and 3 to 4, which totaled 216 minutes or four bed

volumes. Bed volume times were calculated by taking the bed volume of the filters and dividing it by the influent flow rate of the filters. The EBCT of the filters is as follows:

$$EBCT = \frac{Bed\ Volume}{Influent\ Flow\ Rate}$$

The major variables of focus were UV and turbidity. Samples were collected of the influents and effluents of both filters at bed volumes 0, 1, 2, 3, 4, and 6. Each bed volume lasted 54 minutes with a flow rate of 700 ml/minute which is equivalent to 0.8 meters/hour.

3.2: Bench -Scale Tests for ZVI

3.2.1 ZVI Oxidation Procedure

Degreased iron, diameter 1-2mm was obtained from Acros Organics (a part of Thermo Fisher Scientific, part number: I/0855/60) and oxidized to Zero Valent Iron (ZVI). The first method



Figure 3.2: Gator Jar Oxidation

chosen, as shown in Figure 3.2, to test oxidation was to use 2 liter gator jars and rapidly stir the mixture. Two different quantities of 50 and 200mg of iron filings were chosen to be oxidized for this test.

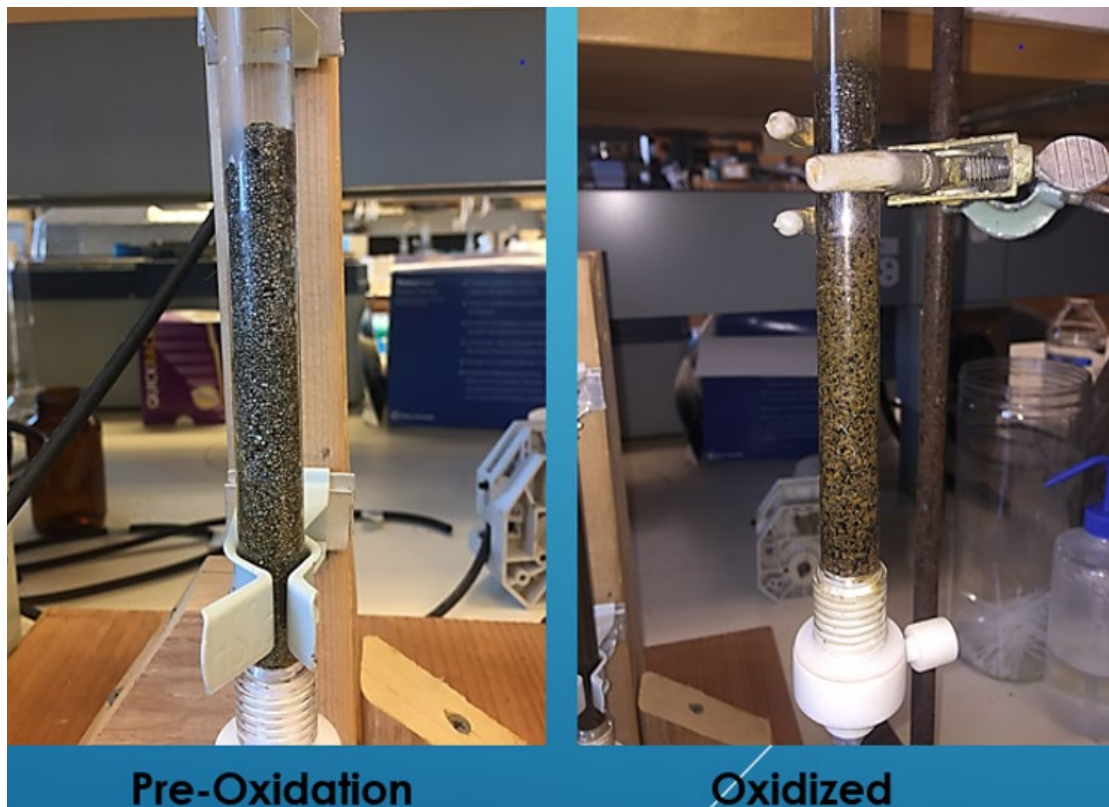


Figure 3.3: Pre-Oxidized vs Oxidized

Following oxidation, the ZVI was mixed with raw water and fed through glass columns containing gravel media.

The second method, as shown in Figure 3.3, was in-situ oxidation. This method included the use of two glass columns that were placed side-by-side. This oxidation used 50mg of iron filings and a basic solution that was constantly recycled and flowing upflow through the columns for a minimum of 15 hours. Two different diameter columns were tested for efficiency and success of oxidation. The first columns of choice were $\frac{1}{4}$ inch diameter by 12 inch height. The second glass columns were $\frac{1}{2}$ inch diameter and a 12 inch height. The loading rate through both of the

different diameter columns was targeted at 0.9 meters/hour to mimic the loading rate through a typical roughing filter. In order to obtain the proper loading rate through the columns the flowrate needed to be adjusted accordingly. The optimal pH for the oxidation solution would minimize dissolved iron leaching while sufficiently oxidizing the ZVI. This pH was found to be 7.2 ± 0.1 with a constant bubbling of air into the stock solution to keep oxygen levels high. The pH was monitored over the 15 hour duration and adjusted as necessary. Figure 3.3 shows the visible results of a successful oxidation.

3.2.2 DOC Loading Challenges

For the DOC loading challenges raw water from the Durham Water Treatment Plant was used. The raw water was pre-filtered before entering the columns using GF/C filters from Whatman Laboratory Products (p/n) to remove excess turbidity. For this research's purposes "raw water" will be defined as water from the Durham Water Treatment Plant that has been filtered using GF/C filters. Raw water characteristics were determined to establish a baseline of the water chemistry and are as follows:

| Raw Water Characteristics | | | |
|--|---------|--------------------|-------------------|
| Constituent | Average | Standard Deviation | Post-Modification |
| Dissolved Organic Carbon (mg/L) | 7.8 | ± 1.3 | Unchanged |
| pH | 6.3 | ± 0.5 | 7.3 ± 0.15 |
| Alkalinity (mg/L as CaCO_3) | 6 | ± 6 | 56 ± 6 |
| Hardness (mg/L as CaCO_3) | 48 | ± 1.2 | Unchanged |
| Temperature ($^{\circ}\text{Celcius}$) | 20 | ± 1 | Unchanged |

Table 3.1: Raw Water Characteristics

For the challenges alkalinity was raised to 50 ± 12 mg/L as CaCO_3 to assist in maintaining a more constant pH. Alkalinity in water as CaCO_3 helps to buffer the OH^- and H^+ ions which stabilizes pH making it more resistant to changes. Following the addition of alkalinity as CaCO_3 the pH was raised and maintained at 7.3 ± 0.15 for the duration of the challenges.

For the DOC loading challenges 50gdw (50 grams dry weight) of ZVI was oxidized *in-situ* in two columns side by side and challenged as duplicates. Each bed volume of raw water was passed through the column one time, upflow at 4 mL/min for a loading rate of 0.9 m/hr. Each empty bed contact time (EBCT) lasted for 6.5 minutes and every bed volume was 24 cm^3 . The duration of the challenges were a total of 530 bed volumes per column, or 12.72 liters of raw water per column.

3.2.3 Bench-Scale Tests for ZVI Regeneration

When looking at possible regeneration the first steps were to isolate some pH's that were believed to possibly facilitate the desorption of DOC from the ZVI. To determine these pH's that would facilitate the most desorption the first ZVI regeneration trial was run following the first ZVI loading trial detailed above. The quantity of DOC immobilized on the ZVI would be known, therefore various pH solutions could be run through the same columns that the ZVI was contained in and quantify by batch sample collection and analysis of each varying pH which contained the most DOC. Since the pH solutions were created using reverse osmosis (RO) treated water and hydroxide solution there was no native DOC within it allowing for the clear conclusion that whichever pH sample contained the most DOC then that pH facilitates the most desorption of DOC. Another analysis of interest was the amount of dissolved iron that would potentially be

released as pH reached the extreme end of the basic spectrum so that was measured for as well as DOC.

To test the regeneration potential for ZVI two challenges were performed using two columns as duplicates. Each challenge was performed immediately following a DOC Loading when a known amount of DOC was sorbed to the ZVI. Both challenges were upflow at a rate of 4mL/min and a loading rate of 0.9m/hr. The first challenge was used to determine the pH's that promote DOC desorption from the ZVI the most successfully while dissolving minimal iron into solution. The second challenge targeted the most successful of the pH's to better analyze their potential for desorption and further analyze iron dissolving.

For the first challenge the pH's that were being observed were pH's 8-12. Each pH was given 7 bed volumes to pass through the columns and was collected as a 170 mL batch. These batches were tested for DOC content. Following sample collection the pumping was turned off briefly and the pH was raised to the next target pH using sodium hydroxide (NaOH). This process was repeated until pH 12 was reached.

The second regeneration challenge targeted pH 11. A batch stock solution was prepared of pH 11 using NaOH. The batch was recycled for 300 bed volumes per column and sampled for dissolved iron every 50 bed volumes. The final samples were then tested for a total concentration of DOC.

3.3: Bench-Scale Tests for Anion Exchange Resin

3.3.1 DOC Loading Challenge

One long term column challenge was performed on two different anion exchange resins. The challenge's goal was to analyze how contact time affects DOC removals as well as how much

DOC the resin could remove before exhaustion. For this research's purposes "Resin Exhaustion" was defined as when effluent DOC of treated waters is within 10% of the influent. This level of removal was determined to be the point of exhaustion because 10% DOC reductions can be seen in the HGRF Control filter which has no additive media to it (See Figure 4.7). This would suggest the resin is no longer doing anything beyond what the control filter could achieve.

The two anion exchange resins being tested were Purolite A502P and A860, while A502P was the resin of focus. See Appendix I for both A502P and A860 product specifications.

A502P was the focus because it had a larger diameter than the A860 resin. The A860 resin had a smaller diameter which means there would be less void space between the resin particles. The smaller void space compounded with fouling over time would generate more headloss requiring

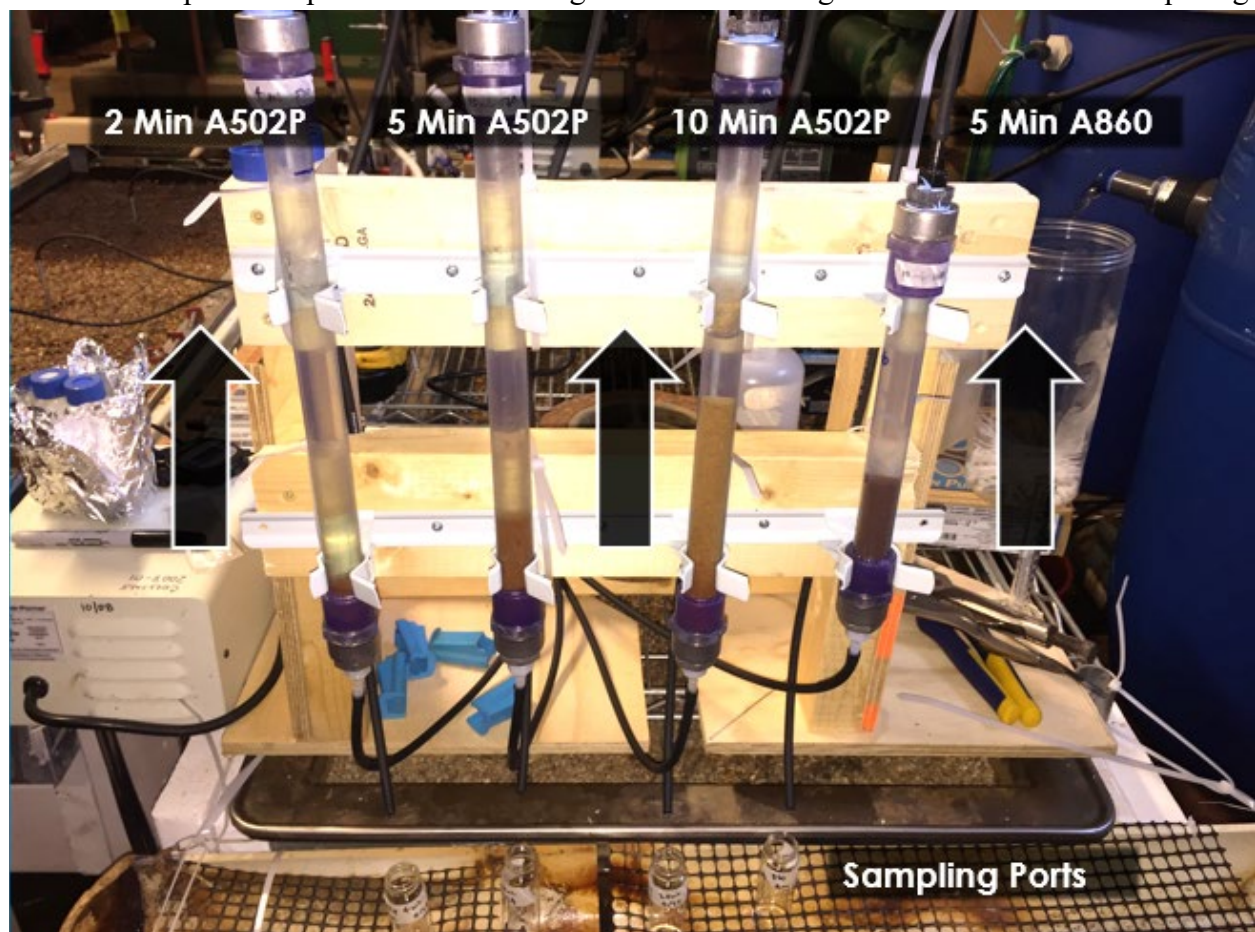


Figure 3.4: Anion Exchange Resin Column Challenge

frequent cleanings. This is not ideal for a filter mechanism that is seeking to be low maintenance, therefore the larger diameter A502P is the better choice. Four, ¼ inch columns were set up at the Durham Water Treatment Plant. Three columns of A502P were with varying bed volumes of 4mL or a 2 minute Empty Bed Contact Time (EBCT), 10mL(5 minute EBCT), and 20mL(10 minute EBCT) while the fourth column was A860 with a bed volume of 10mL(5 minute EBCT). The flow rate was set at 2mL/min at a loading rate of 0.9m/hr. The influent water to the columns was the effluent of the control Horizontal Gravel Rousing Filter (HGRF). Influent and effluent samples being analyzed for DOC content were taken each day for a duration of 47 days before exhaustion was reached.

3.4: Pilot-Scale Gravel Rousing Filter Enhancements and Challenges

3.4.1 HGRF Resin Container

Figure 3.5 below shows a schematic of the before and after of the modifications that were made to one of the existing HGRFs. The final 10% of the gravel was removed and replaced with a resin box that was made of PVC. This resin box was designed to flow the water upwards through 2 liters of resin at a hydraulic loading rate of 0.8 meters/hour. The resin box had dimension of width of 19.5”x length of 2” x height of 4.5” and held a total of 2.1 liters of resin. For this study the VGRFs were designed to have the same EBCT through the resin box enhancement as the HGRFs rather than through the rest of the gravel media. This gave the passing water an empty bed contact time of 3.65 minutes within the resin. The resin box was to be isolated from the gravel by a PVC dividing wall. The open sides of the box as well as the open bottom were sealed by the edges of the existing HGRF. To install the box it was glued into the base and walls of the HGRF and sealed it from short circuiting using waterproof caulking. In order to convey water from the

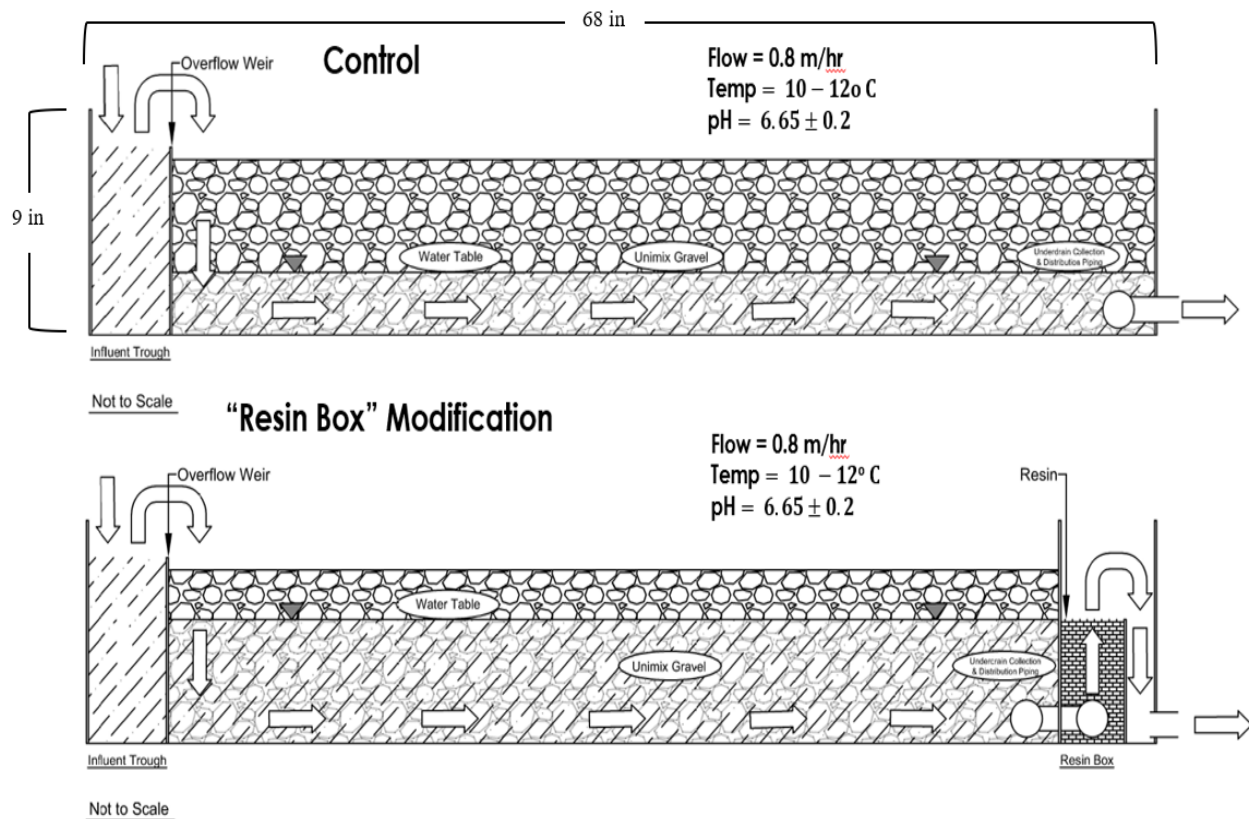


Figure 3.5: HGRF Resin Box Enhancement

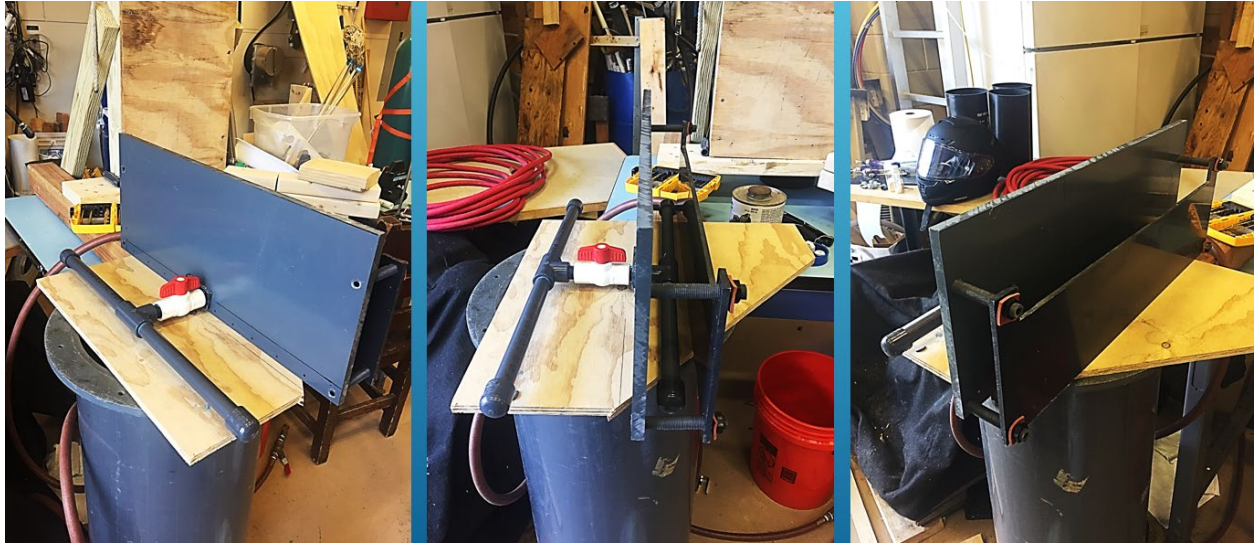


Figure 3.6: Resin Box

gravel treatment stage through to the resin treatment stage and minimize short-circuits/bypasses the flow needed to be distributed evenly within the resin box. An underdrain collection system was built to achieve this. The underdrain collection system was crafted using two PVC pipes of ½” diameter and place them horizontally across the width of the HGRF. The next step was to drill small 1/16” holes in them to allow an inflow of water. These small holes proved to allow enough water into the system but controlled the flow enough to prevent causing any preferential pathing of water flow. These two pipes were then connected to a PVC Tee fitting and attached to a shut off valve. The shut off valve was installed to completely cut off the flow of influent water for when maintenance was needed to be done. After the shut-off valve the collection pipe on the HGRF side was similar to the distribution pipe on the resin box. Figures 3.7 and 3.8 below show the resin box post-installation.

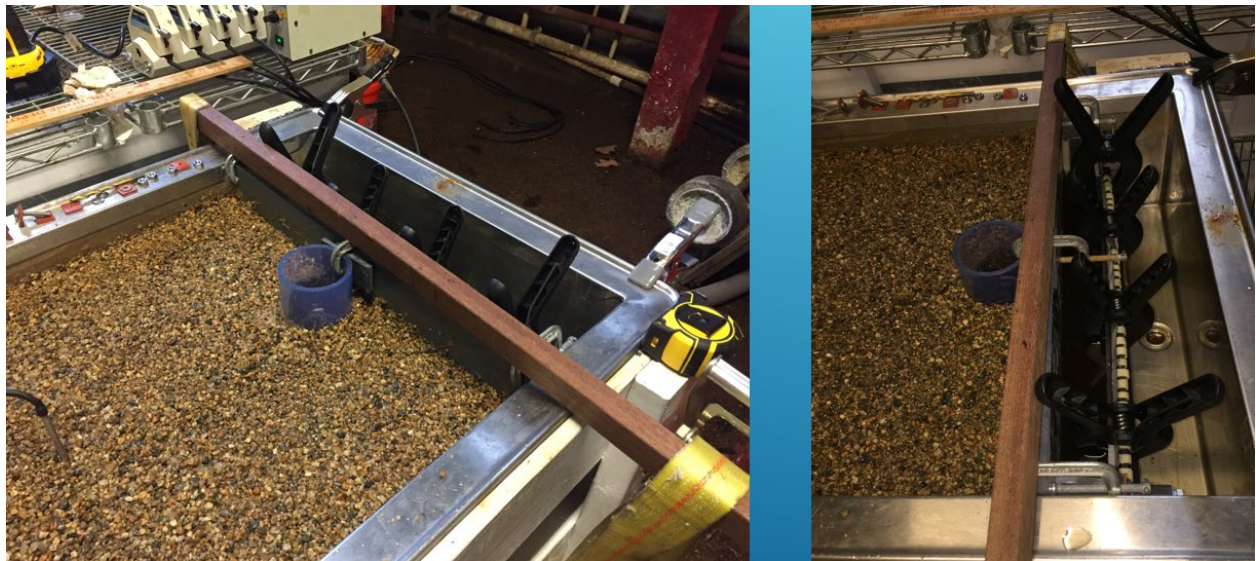


Figure 3.7: Resin Box Installed 2

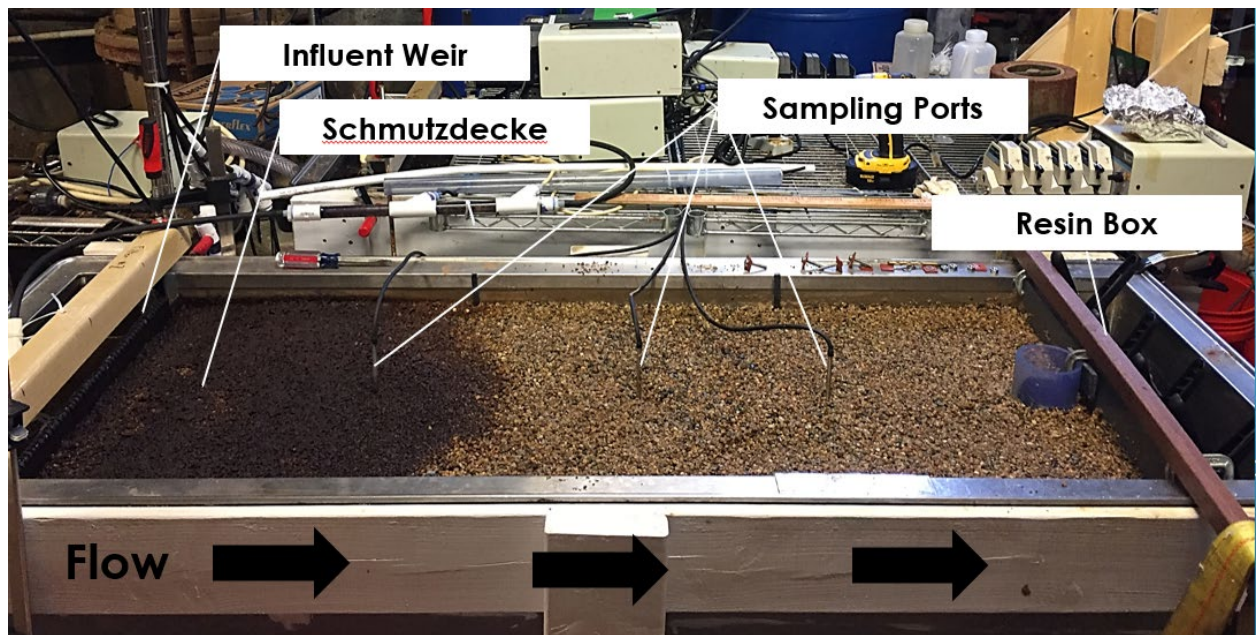


Figure 3.8: Resin Box Installed 1

3.4.2 Vertical Gravel Roughing Filter Design

Two upflow vertical gravel roughing filters were designed using PVC piping, see Figure 3.9, section 3.4.3 for a schematic. The PVC piping was 10 inches in diameter, 36 inches tall, and contained 16 inches of gravel media. One of the filters was chosen to contain a unimix gravel media with an average diameter of 1.6mm and a uniformity coefficient of 2.375 while the second VGRF contained a stratified gravel media of sizes of one, three, and five millimeters. See the sieve analysis for the gravel used in Table 3.2 below. Data was acquired from Kyle Hay's "Methods in Culturing Algae and the Addition of Algae to Enhance the Performance of Gravel Roughing Filtration Pretreatment", page 43.

| Gravel Sieve Analysis | | |
|------------------------------|----------------------|-----------|
| Sieve Opening (mm) | % Retained per Sieve | % Passing |
| 4.76 | 26.4 | 73.6 |
| 2.36 | 43.1 | 30.5 |
| 2.00 | 14.4 | 16.1 |
| 1.41 | 14.4 | 1.8 |
| 1.18 | 1.4 | 0.4 |
| 1.00 | 0.4 | 0 |
| Pan | 0 | - |

Table 3.2: Unimix Gravel Sieve Analysis

A grate was installed to elevate the media off the filter column bottom and an to ensure uniform distribution of the influent water. The grate lifted the entire media a total of three inches from the base where the influent piping was installed two inches from the base. The stratified media VGRF was designed in three layers with the five-millimeter gravel starting at the base of the filter, the three-millimeter gravel in the middle and the one-millimeter diameter gravel towards the top.

The depth of the five-millimeter layer was a total of four inches, the three-millimeter layer was eight inches, and the final layer of one-millimeter gravel was a depth of four inches, which totals 16 inches of gravel media.

At 25 inches from the base of the VGRF an effluent sample port was installed which was a simple overflow type of notch in the sidewall of the VGRF. This was installed roughly six inches from the top of the media giving enough headspace between the effluent and the media for the future addition of a resin container.

After the filters were given time to equilibrate and reach steady state sample ports were installed to sample at multiple depths/lengths and corresponding EBCTs.

3.4.3 VGRF Resin Container

The VGRF resin container contained Purolite A502P anion exchange resin and was designed for the same amount of contact time of 3.65 minutes through the resin and contained 1.6L of resin. Figure 3.9 shows the design of the VGRFs with the resin addition. The VGRFs were run upflow at a rate of 400mL/min which corresponds to 0.48 meters/hour. The resin container was a generic nylon mesh laundry bag that was of tight enough mesh to contain the anion exchange resin.

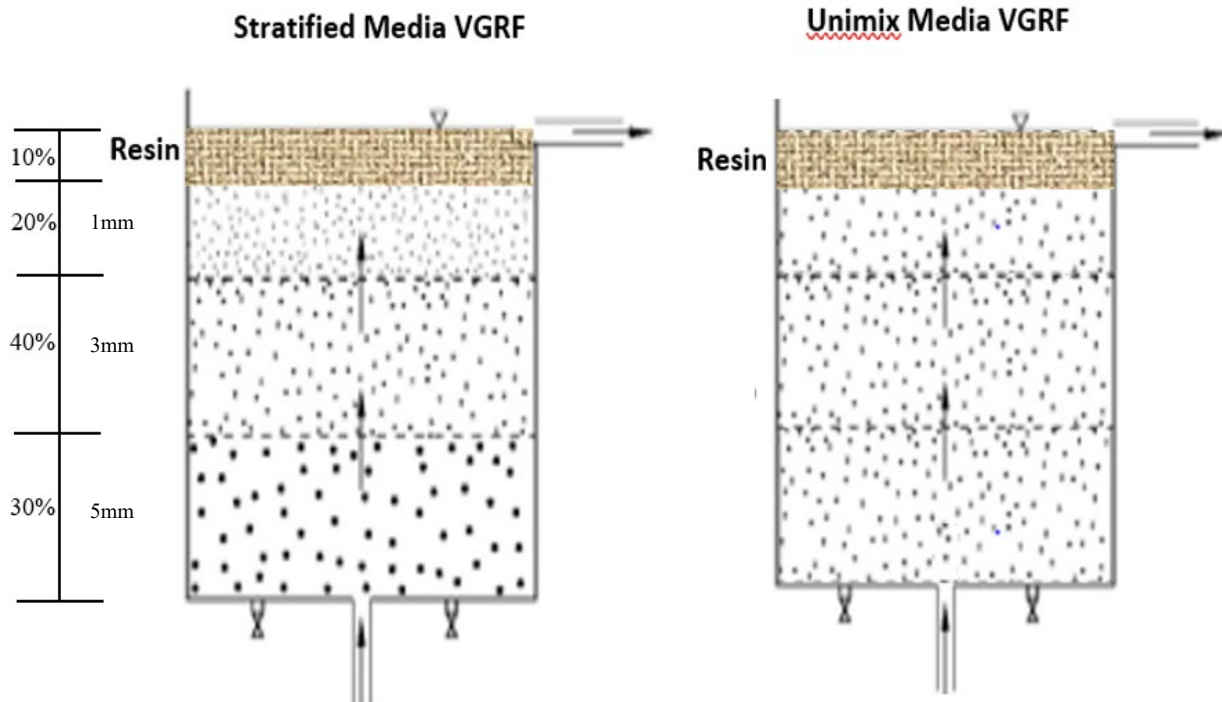


Figure 3.9: Stratified VGRF and Unimix VGRF (NOT TO SCALE)

3.4.4 *E. coli* Loading Challenge

An *E. coli* loading challenge was run in order to determine the removals of an organic containment across the horizontal length of the horizontal roughing filters. Three samples were taken across the filter's horizontal distances; influent, sample port at 30% of filter length, and effluent values. These samples were collected in DOC vials and then cultured using the IDEXX\ Quanti Tray/2000 method.

3.5: Analytical Methods

3.5.1 Turbidity

Turbidity samples were analyzed using a Hach 2100Q Turbidimeter within a 20mL glass vial. The glass vial was rinsed with RO water before being filled with the sample. The outside of glass vial was then wiped using a lint-free tissue to ensure there were no obstructions during analysis. Samples were analyzed in duplicates.

3.5.2 DOC

A GE Sievers5310C Laboratory TOC analyzer was used to measure Dissolved Organic Carbon. Samples were collected within a glass vial and then filtered using a Whatman® GF/C filter before DOC analysis. Samples were analyzed in duplicates.

3.5.3 pH

Sample pH was checked with a Fisher Scientific accumet™ Excel XL50 pH meter with a Fisher Scientific pH probe (cat. #13-620-299A). The meter was calibrated with Fisher Scientific buffer standards with pH of 4, 7, and 10.

3.5.4 UV₂₅₄

Samples were collected within a glass vial and then filtered with a Whatman® GF/C filter. After filtration samples were analyzed in a Hach DR500 spectrophotometer which was set to a single wavelength of 254 nm. Samples were left to reach room temperature before analysis. Samples were analyzed through the Hach DR500 glass vial which was wiped down with a lint-free tissue before analysis to ensure there were no obstructions. Samples were analyzed in duplicates.

3.5.5 Temperature

Temperature measurements were made using a NIST calibrated thermometer. During analysis the tip of the thermometer was verified to be submersed properly in the fluid while recording the results.

3.5.6 Dissolved Oxygen

Dissolved Oxygen measurements were made using a YSI Model 5000 DO meter and YSI 5739 probe. During data collection the probe was continuously swirled in the sample ensuring optimal dissolved oxygen exposure.

3.5.7 Hardness and Alkalinity

The HACH Traditional Method was used in order to test hardness and alkalinity. Samples were diluted based on the estimated hardness levels. Buffer solutions and a ManVer® 2 Hardness Indicator color packet were used. A 0.8M EDTA Tetrasodium salt cartridge was used and a Hach digital titrator fed the chemicals into the samples until they turned from pink to purple in color. To calculate hardness a multiplying factor based on the sample dilution was added.

The Hach digital titration method was used for analysis of the alkalinity. Sample dilution was applied based on the estimated alkalinity levels. A Phenolphthalein Indicator Powder coloring packet was added to the sample. A 1.6N sulfuric acid cartridge was used and a digital titrator fed the chemical into the continuously mixed sample until the sample turned from pink to clear. A Bromcresol Green-Methyl Red Indicator Powder coloring packet was then added to the sample. Additional sulfuric acid was added until a light green/blue gray, light violet/gray, or light pink color was achieved, based on the final pH of the sample. The dilution multiplying factor was applied to calculate both phenolphthalein and total alkalinity of the sample. (Hay *et al.*, 2016)

3.5.8 *E. coli* MPN

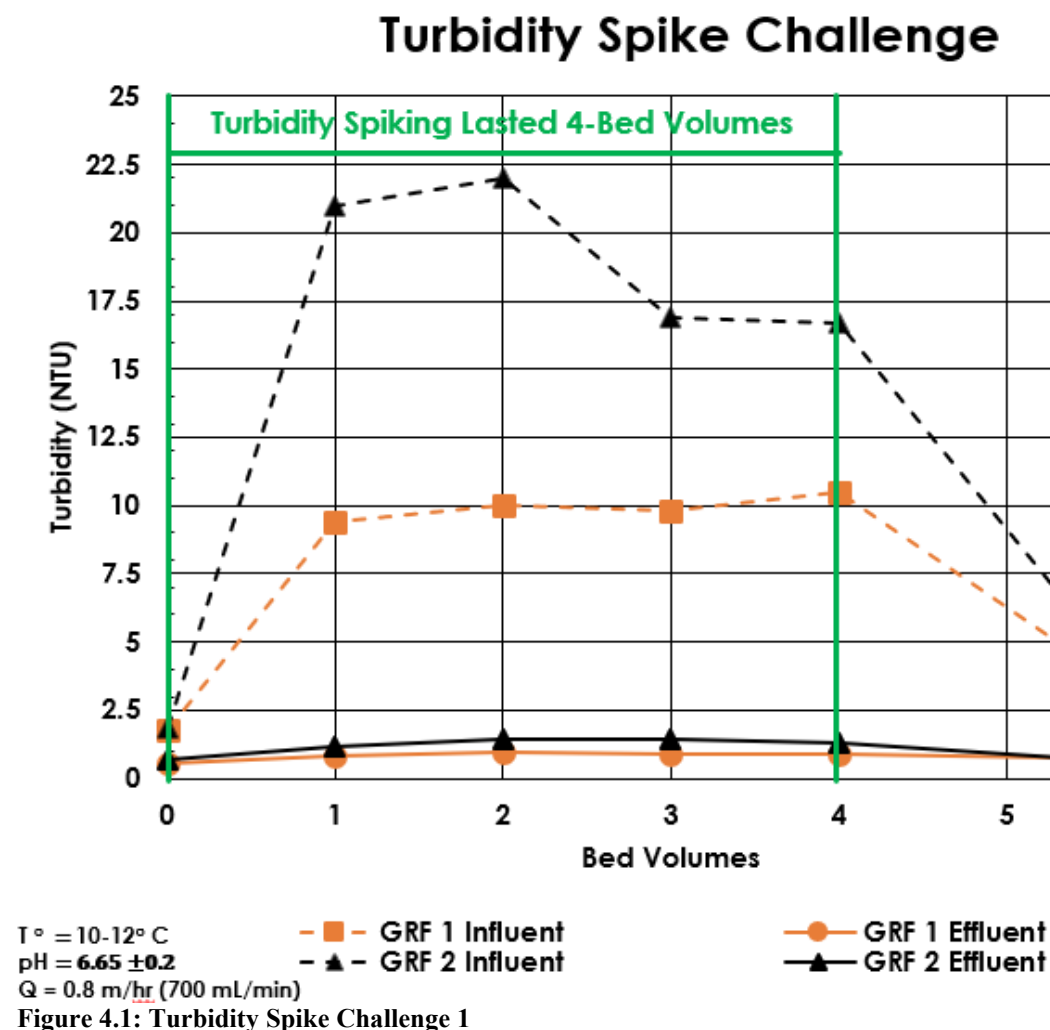
The IDEXX\ Quanti Tray/2000 method was used which provides an easy, rapid, and accurate count of coliforms and *E. coli*. The IDEXX Quanti-Tray/2000 is a semi-automated quantification method based on the Standard Methods Most Probable Number (MPN) model. The Quanti-Tray ® Sealer automatically distributes the sample/reagent mixture into separate

wells. After incubation, the number of positive wells is converted to an MPN using a table provided. Quanti-Tray/2000 counts from one to 2,419/100 mL.

CHAPTER 4: RESULTS AND DISCUSSION

4.1: Pilot-Scale Gravel Roughing Filter Turbidity Spike Challenges

For the first turbidity spike challenge GRF 1 acted as the control receiving a target spike of 10 NTUs and GRF 2 was given a larger spike at 20 NTUs. In Figure 4.1 the dotted lines represent the influent while the solid lines represent the effluent. The K-Clay spike was added until the end of the third bed volume (stopped before the fourth bed volume began). Regardless of the size of the influent mass load both filters performed exceptionally well during the spike with removals of 89% for GRF 1 and 91% for GRF 2. This is an average removal of 90% at the peak of the spike



between the two GRFs.

After the K-Clay additions are halted it took no more than two additional bed volumes for the influent turbidity levels of both filters to return to steady state of just under 2.5 Nephelometric Turbidity Units (NTUs). This shows that most of the influent turbidity has been trapped within the GRFs and was not being released over time. One common concern for media filters is the possibility that after significant fouling contaminants will begin to be rereleased by the filters but this trial did not yield those results.

4.2: Bench -Scale Tests for ZVI

4.2.1. ZVI Generation

During the ZVI generation process it was determined that the micro particles of ZVI that were produced from the rapid mixing oxidation process were too small to be trapped within the filter without using some sort of small mesh net, which was undesirable for the chosen applications, and could not accomplish the goals of organic precursor removal that were hoped for.

As oxidation was occurring, much like in the gator jars, the small particles were still continuing to break off. Using smaller ¼ inch columns about 50% of the iron volume broke off into smaller particles and would form a pile on top of the larger media. This was significantly less breaking than the gator jars however still not as much as preferred. In order to avoid this phenomenon, there would need to be a reduction in the upward pressure on the particles while maintaining the same loading rate. To achieve this a larger diameter glass column of ½ inch was used. Using the ½ inch diameter and a loading rate of 0.9m/hr about 80% of the total volume of ZVI was maintained as large granules which proved to be the most successful method. Determination for the level of success of ZVI generation was based on coloration and retention of

the mass of the iron granules. Figure 3.3, seen in chapter 3.2.1, shows that the granules would start the process shiny and silver in color while after a period of 15 hours of oxidation (Little, et al. 2011) the iron would become the brown dull color.

4.2.2. DOC Loading Challenges

Once the ideal ZVI generation process was determined the next step was identifying removal capacities of organic precursor materials for the ZVI. A total of three upflow column challenges were performed using raw colored water from the Durham Water Treatment Plant which was collected in the early March, April, and September of 2017. The raw water's characteristics were as follows on average:

| Raw Water Characteristics | | |
|---|------------------|--------------------|
| Constituent | Average Quantity | Standard Deviation |
| Dissolved Organic Carbon (mg/L) | 8.5 | ± 0.86 |
| pH | 6.3 | ± 0.5 |
| Alkalinity (mg/L as CaCO ₃) | 6 | ± 6 |
| Hardness (mg/L as CaCO ₃) | 48 | ± 1.2 |
| Turbidity (NTU) | 2.17 | ± 0.88 |
| Temperature (°Celcius) | 12 | ± 5 |

Table 4.1: Raw Water Characteristics

Following the raw water characterization the temperature was adjusted to 20 °C and the pH to 7.2 to stop dissolution of the iron into the water (Little, et al. 2011). For these column challenges a target was set for total DOC that the columns would be exposed to and decided that a minimum ratio of 1mg DOC/1 gdw of Iron for each column was desired.

With this total DOC in mind the flowrate was set to 4 mL/min per column and the trial lasted for a total of 3,450 minutes or 57.5 hours. Each bed volume was a total of 26 mL with an EBCT of 6.5 minutes. A total of roughly 530 bed volumes over the total duration of the challenges. The raw water for this first challenge had a DOC concentration of 9.2 ± 0.3 mg/L which at this

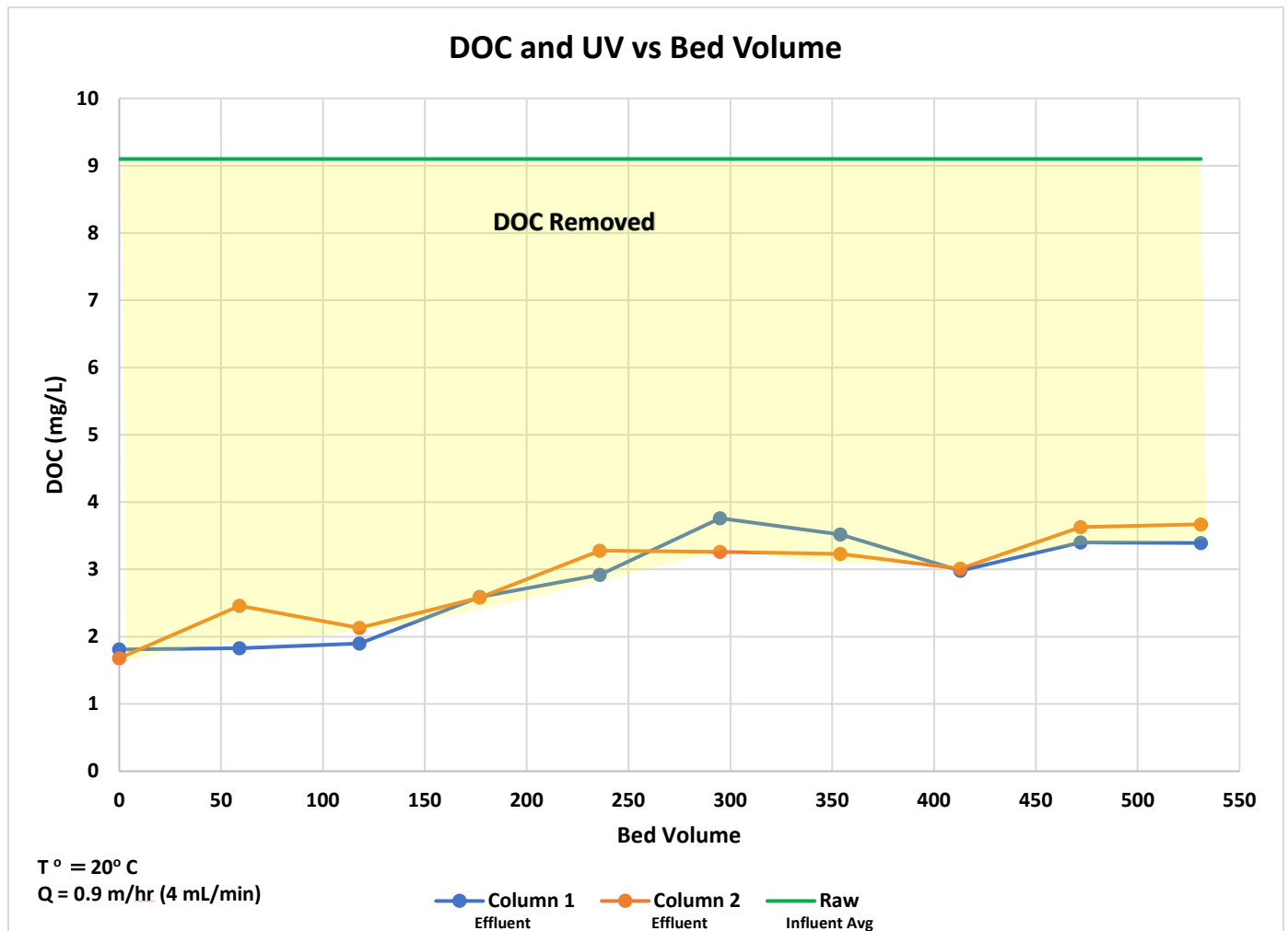


Figure 4.2: DOC vs Bed Volume

duration and flowrate totals to an estimated 127 mg of DOC/column. Each sample during this trial was of each column's effluent using a batch collection method to analyze the DOC, UV and dissolved iron concentration. Two columns were set up identically for replication of the results. Figure 4.2 below shows that over the duration of this entire DOC loading challenge Column 1 performed at an average removal of 69% while Column 2 performed at an average removal of 68%. Impressively, for the early bed volumes the ZVI had removals of up to almost 82% of DOCs. Using these instantaneous DOC concentrations for each sample point gives an average removal over the duration of the trial. With this average and having the calculated total DOC that passed

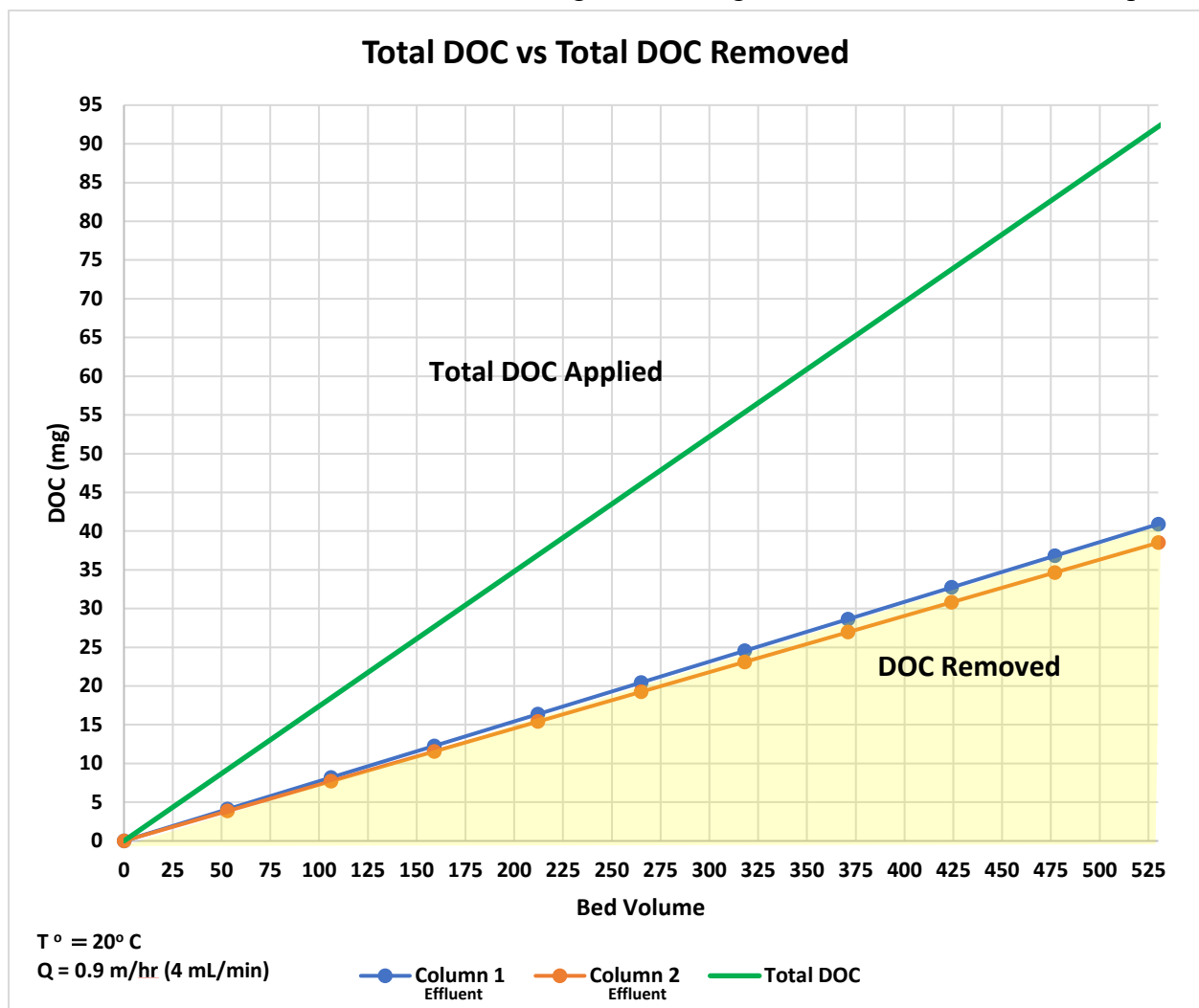


Figure 4.3: Total DOC vs Total DOC Removed

through each column the conclusion that about 68.5% of total DOC which passed through the columns was immobilized by the ZVI was reached. This comes to a total immobilized DOC of 87 mg of DOC/column.

The second trial was a duplicate method of the first trial however the raw water DOC concentration was lower at 6.67 mg/L. This trial yielded lower removals than the first having an average removal rate between Columns 1 and 2 of 43.2%. Figure 4.3 below shows a cumulative graph for the entire duration of trial two which applied a total of about 92 mg of DOC through each column. Both columns performed similarly to one another in respect to removals achieving roughly 43% immobilization of total DOC totaling about 40mg of DOC immobilized per column.

When looking at a comparison of the two trials there is variability in the removals of DOC by 25.3%. In order to fairly compare them the removal capacities were normalized by mg of DOC immobilized/grams dry weight of Iron (Fe). Trial one yielded a normalized removal capacity of $87 \text{ mg DOC}/50 \text{ gdw Fe} = 1.75$ while trial two yielded a normalized removal capacity of $40 \text{ mg DOC}/50 \text{ gdw Fe} = 0.8$.

While in trial one the ZVI demonstrated clearly that it has a large capacity for removal of organics, i.e. DOC, an analysis for what the cause for variation could have been in the second trial was needed.

After analyzing the two trials the only significant difference between them must have laid in the oxidation procedure of the ZVI before the DOC loading began. After the first trial the small micro-ZVI granules that break free from the larger ZVI granules were visibly clogging the influent and effluents of the columns. These ports were cleaned to what was considered suitable. Cleaning may not have been as successful as hoped however due to the nature of the small porous pieces

and the ports may have generated a head loss that was not noticed for this trial. Another issue with the oxidation procedure is that occasionally air bubbles would be seen passing through the media due to potentially imperfect sealing of the column's tubing connections. This would cause inherent variability within the oxidation procedure since these air bubbles are not evenly distributed, or more ideally, evenly prevented throughout the media. One hypothesis for the clogging of these ports as well as the movement of air bubbles caused for a less ideal oxidation of ZVI for trial two was due to the constriction of flow. Due to imperfect oxidation of the ZVI this would mean less oxidized surface area of the iron granules, less oxidized surface area means less positively charged bonding sites for the negatively charged humic substances and therefore less immobilization causing lesser DOC removals.

Regardless of the variability between the trials within these lab-controlled experiments with ZVI has shown a potential for long-term capacity of organic precursor removals of up to 69% and an impressive short-term removal capacity of up to 81%. It should be noted that care needs to be taken to ensure proper oxidation for maximization of removals. The next question lies within its ability or inability to regenerate its sorption sites and extend its useful life.

After analyzing the data of these trials it can be seen that the oxidation procedure plays a significant role in the removal capacity of ZVI. ZVI needs to be maintained in an oxidizing atmosphere in order generate enough bonding sites to remove organic substances effectively. This means that for any waters under pH of 7.2 ZVI is most likely not a suitable treatment application unless one plans to adjust pH prior to treatment. For specific applications however, ZVI being a non-proprietary and relatively inexpensive product could serve as a great alternative to something such as anion exchange resins which tend to be on the other end of the expense spectrum.

4.2.3. Regeneration Challenges

For this regeneration trial the chosen pH's were ranging from 8 to 12 in ascending order. Using a single large batch solution of hydroxide and RO water each pH was given five full bed volumes to run through the columns. At the end of the fifth bed volume a batch collection was started. Once the batch collection began the flow of solution was paused while its pH was raised to the next corresponding pH of interest. Once the pH had been reached and stabilized then the flow would commence. This occurred all the way from pH 8 to pH 12. Figure 4.4 below shows

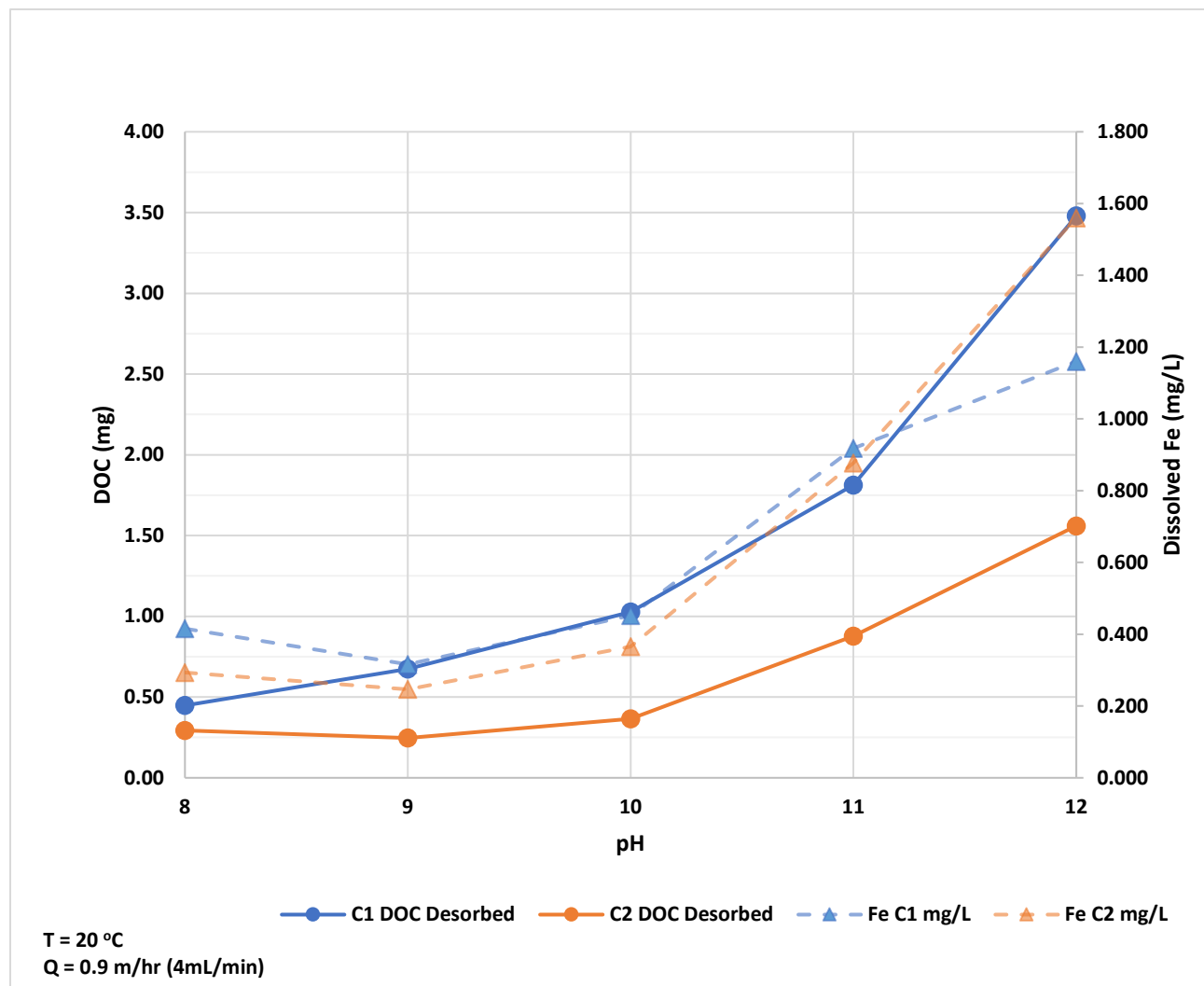


Figure 4.4: DOC Desorption and Iron Dissolution vs pH

the cumulative response curve of DOC per pH. The biggest jump of cumulative DOC occurs between pH's 10, 11, and 12 suggesting that these three pH's facilitate the most desorption of DOC from the ZVI. As for dissolved iron Figure 4.4 shows that along with the most desorption of DOC at pH's 10, 11, and 12 there was also the largest quantity of iron in those samples.

Using this data it was determined that most logical pH to pursue for further analysis was pH 11. While pH 12 had the highest desorption of DOC it also significantly increased the dissolution of iron. As for pH 11 however there was a clear potential for removal of DOC while also keeping the dissolution of iron to a minimum giving us the best ratio of minimizing dissolved iron while maximizing DOC desorption.

The second regeneration trial was done immediately following the second DOC loading trial. Once again, the amount of DOC immobilized on the ZVI was known, therefore quantifying how much DOC was desorbed from the media was possible. The major difference in this trial was that pH 11 was isolated and chose to run a batch of hydroxide solution through it a total of 300 bed volumes. Figure 4.5 shows that both columns performed similarly and most of the desorption occurred during the first 125 bed volumes. The first 50 had effluent DOC concentrations of between 8.5 and 10 mg/L. Between bed volumes 50 and 125 however there is a sharp and constant decline in the concentration of DOC for the samples. Between bed volumes 125 and 200 there is still removal however it appears to begin to plateau. After the 200th bed volume it looks as though the DOC concentration has hit a definite plateau and starts to level off to a minimum concentration of about 0.65 mg/L by the 300th bed volume.

When analyzing the trends of both columns it appears most of the desorption occurred between bed volumes 0 to 200. After bed volume 200 the DOC concentrations were below 1 mg/L and this may prove that continuing to backwash is no longer beneficial due to the low rate of

desorption. Using these instantaneous DOC sample results and averaging the DOC concentrations over the entire backwash allows for an interpolation of total mass desorbed from the media. Column one had an average DOC concentration of 4.03 mg/L per sample while Column 2 had an average DOC concentration of 3.94 mg/L.

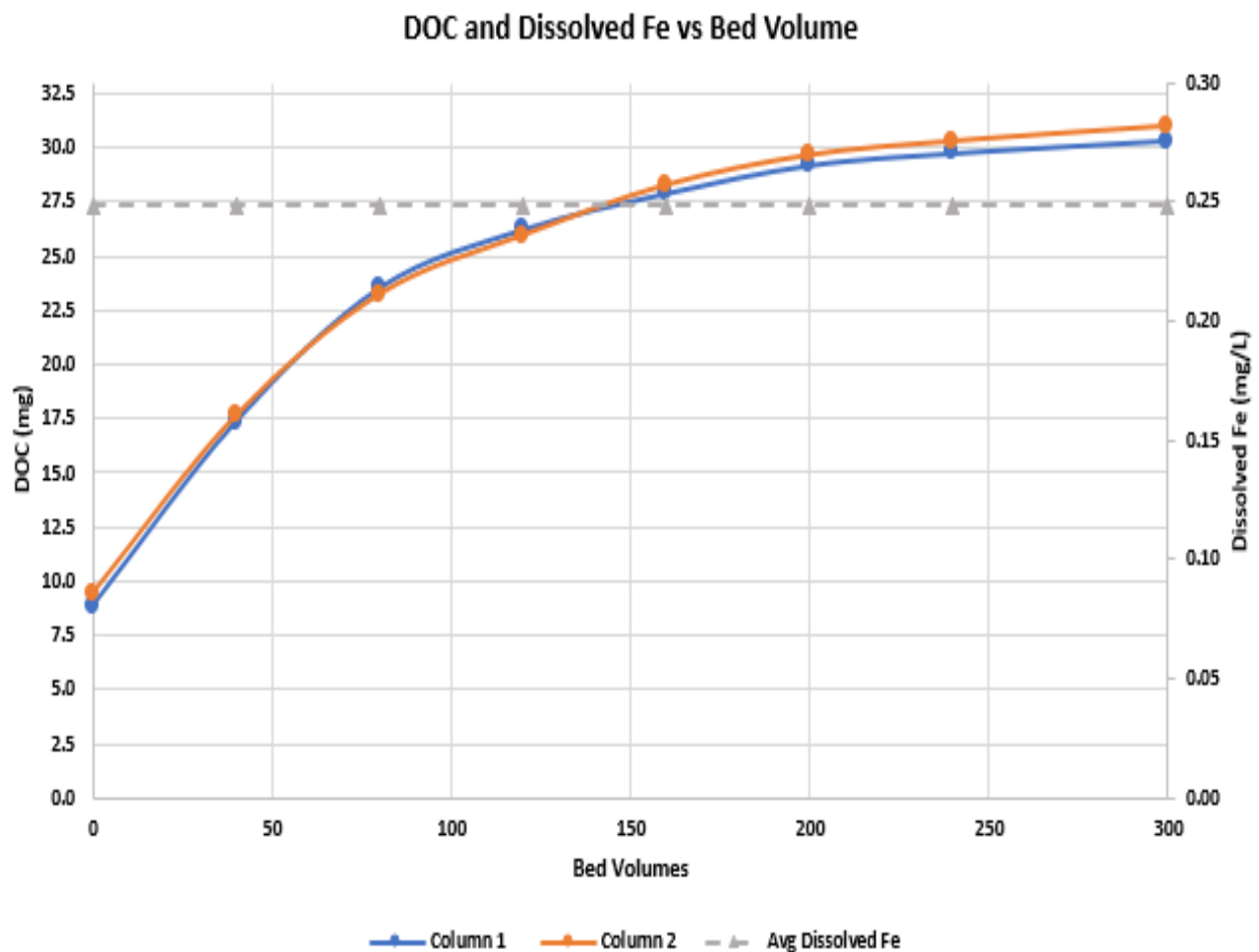


Figure 4.5: Cumulative DOC and Dissolved Fe Desorption vs Bed Volume at pH 11

The following equation was used to interpolate the total quantity of DOC desorbed for each column:

$$\left(C_{Avg} \div \left(\frac{BV_T}{\eta} \right) \right) \times BV_T = Total\ mg\ of\ DOC$$

Where:

C_{Avg} = Average DOC concentration of all samples of the backwash
 BV_T = Total bed volumes
 η = Number of samples

The above equation shows that Column 1 had desorbed a total of 30.98 mg of DOC while Column 2 performed similarly with a desorption of 30.31 mg of DOC. Averaging these quantities together yields an average of 30.64 mg of DOC desorbed. As stated previously it is already known that the average amount of DOC immobilized on the ZVI at the start the backwash was 127 mg, so that means that the ZVI was regenerated about 24% over 300 bed volumes using a hydroxide solution of pH 11. At pH 11 the ZVI showed a clear potential for regeneration as well as quite less iron dissolution than was expected.

Figure 4.5 above shows that the average dissolution of iron between the two columns was about 0.25mg/L. This low quantity of dissolved iron shows that much of the ZVI would be retained during the backwash procedure due to a small amount of dissolution. Any water treatment technology is an investment, and if that technology is only a onetime use then is not practical for real world applications. Treatment technologies need to have some form of reusability so verification that during a backwash too much ZVI would not dissolve was important for establishing the viability of the media.

In order to verify the ZVI did not dissolve at too high of a rate the same calculation was used as previously to interpolate for total DOC desorbed. For these circumstances over the course of a backwash lasting 300 bed volumes and using pH 11 solution an average of 2 mg of iron was

dissolved. In these trials a total quantity of 50gdw of iron per column was used, so losses totaled less than 0.1% of the total media and were negligible.

When analyzing the potential for regeneration of ZVI pH 11 produced replicable results of about 25% regeneration. It was also noticed that the dissolved iron content at pH 11 was not as much of an issue as previously hypothesized. After the first backwash it was decided pH 12 looked to be dissolving too much iron but it had the largest facilitation of DOC desorption. +

Zero Valent Iron showed itself to be a viable option as an additive media to increase DOC removal from influent waters over the course of many bench-scale challenges. ZVI needs to be properly generated and then can be applied. Proper generation of ZVI proved to be a relatively simple yet time consuming process. Bench scale tests, which were performed on locally sourced raw waters, proved that in ideal conditions ZVI has the capacity to remove up to 49% of total DOC over an extended period. When testing the removal capacity of ZVI removals were still being obtained after 550 bed volumes with no signs of slowing down. The longevity of removal capability shows that ZVI is a low maintenance option for DOC removals.

4.3: Bench-Scale Tests for Anion Exchange Resin

4.3.1. DOC Loading Challenge

The bench-scale test performed on the anion exchange resin was a long term upflow challenge. This challenge's goal was to test the duration that the anion exchange resin could remain useful at removing DOC as well as test the effect of varying bed volume sizes on the removal of DOC. This challenge consisted of four vertical half inch diameter columns and passing raw water through them at 2ml/min for a total of 47 days. The two types of anion exchange resin were Purolite A502P (this study's focus) and A860. The first three columns contained the A502P anion exchange resin and had varying contact times of 2 minutes, 5 minutes, and 10 minutes while the fourth contained

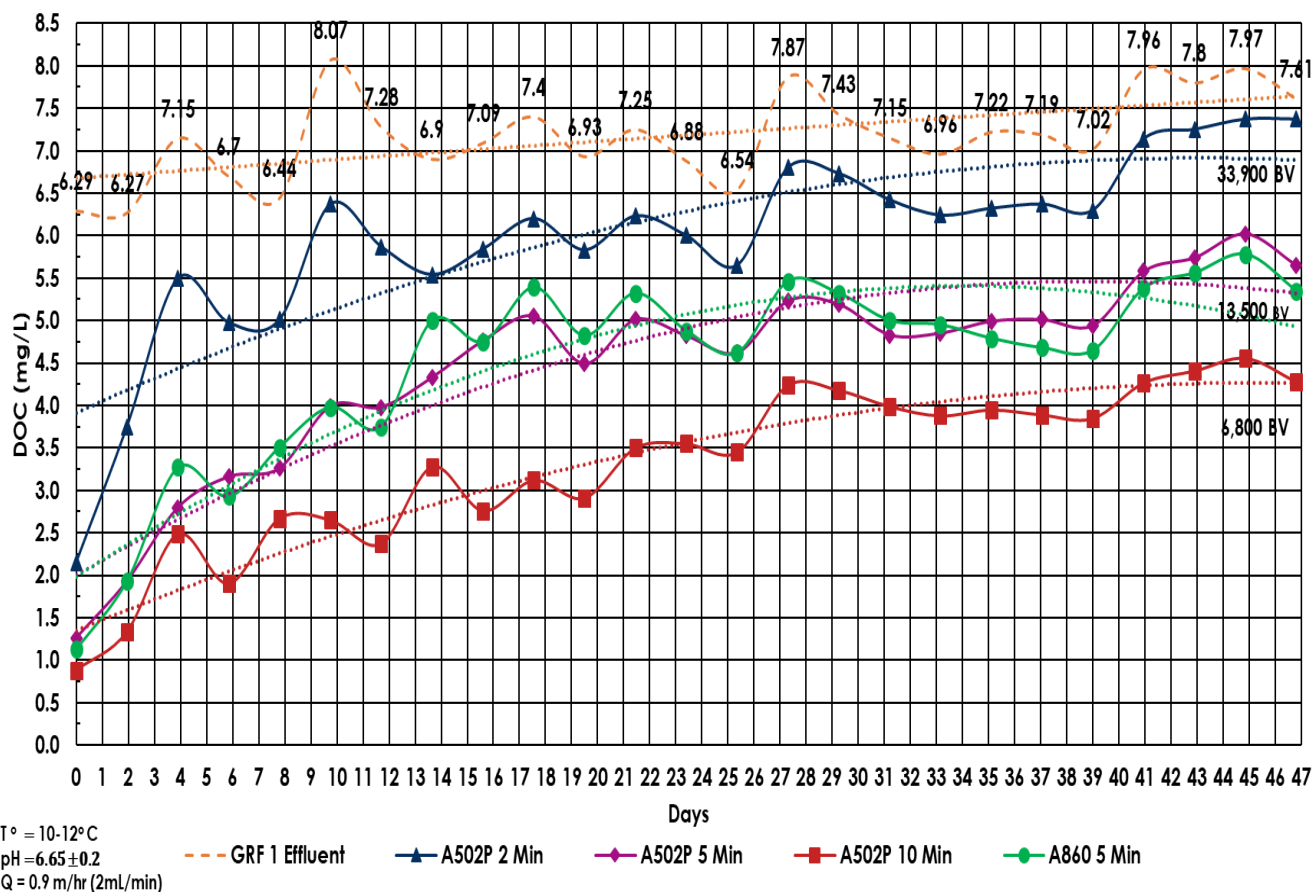


Figure 4.6: Bench-Scale Exhaustion Resin Challenge

the A860 and a contact time of 5 minutes. Figure 4.6 shows a direct time comparison between each column. The 2 minute and 5 minute bed volume columns get less removals consistently while the 10 minute bed volume performs the best for the entire duration of the study. By the 47th day the 2 minute bed volume column has seen roughly 34,000 bed volumes while the 10 minute has seen only roughly 7,000. Figure 4.7 shows the same data as percent removal over time.

This was quite a surprising result in regard to the duration that the anion exchange resin lasted. It took almost 34,000 bed volumes for the anion exchange resin to become almost completely exhausted and for removals to disappear. As for the performance of the columns it was

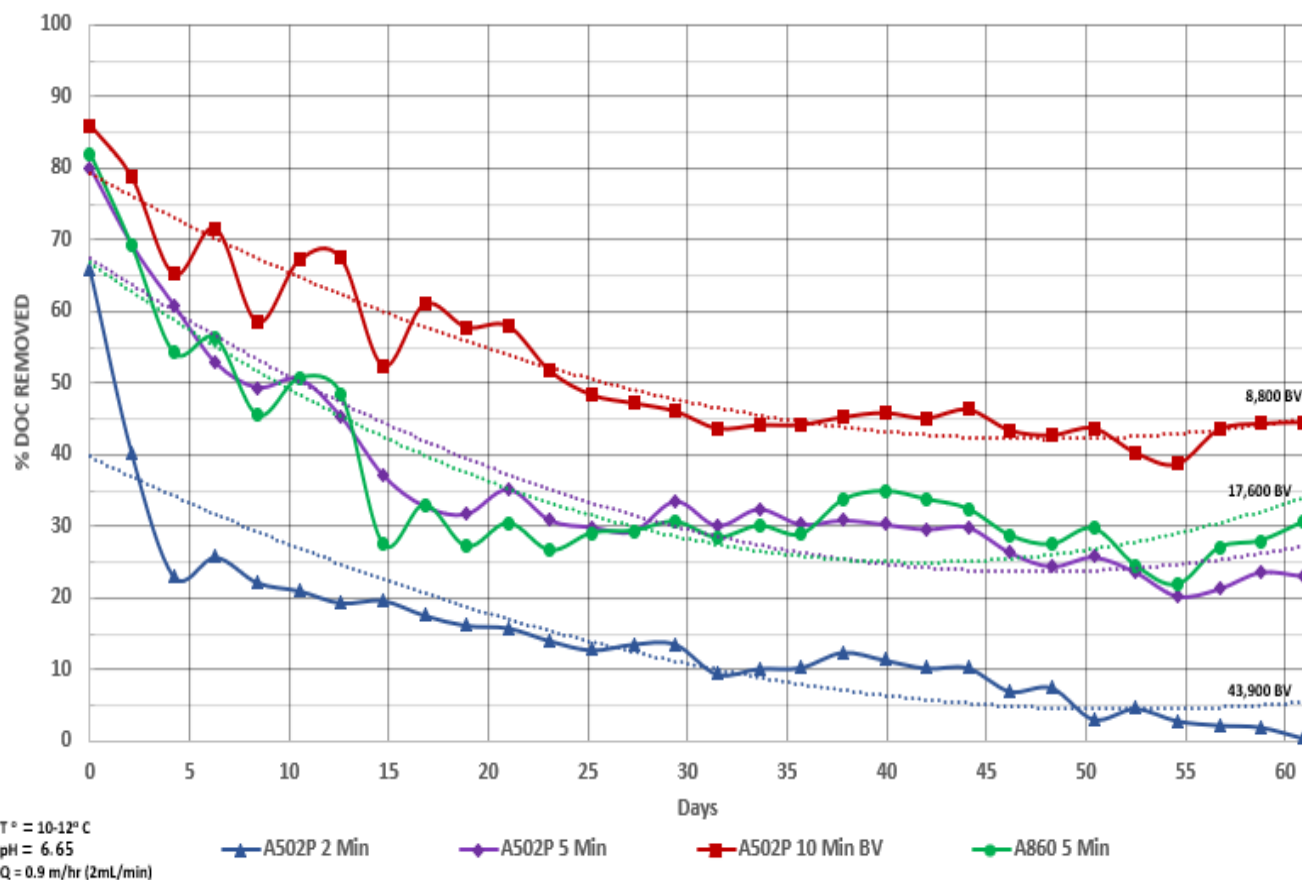


Figure 4.7: Bench-Scale Exhaustion Resin Challenge

expected that the 10 minute column would continue to outperform over the 47 days. This figure does not show a direct comparison for the effect that the bed volume change had on the resin

however. In order to see the effect of the larger bed volume each of the columns were compared at the same respective bed volume as the other.

Figure 4.8 shows the comparison of the columns at the equivalent number of bed volumes. At the same bed volume the 10 minute EBCT column still performed best. This result was somewhat expected due to the increased contact time that the raw water had on the resin. The longer the contact time the more bonding sites that the DOC was forced to pass over and potentially bond to causing immobilization. This translates to better removals at the same number of bed volumes as can be seen above.

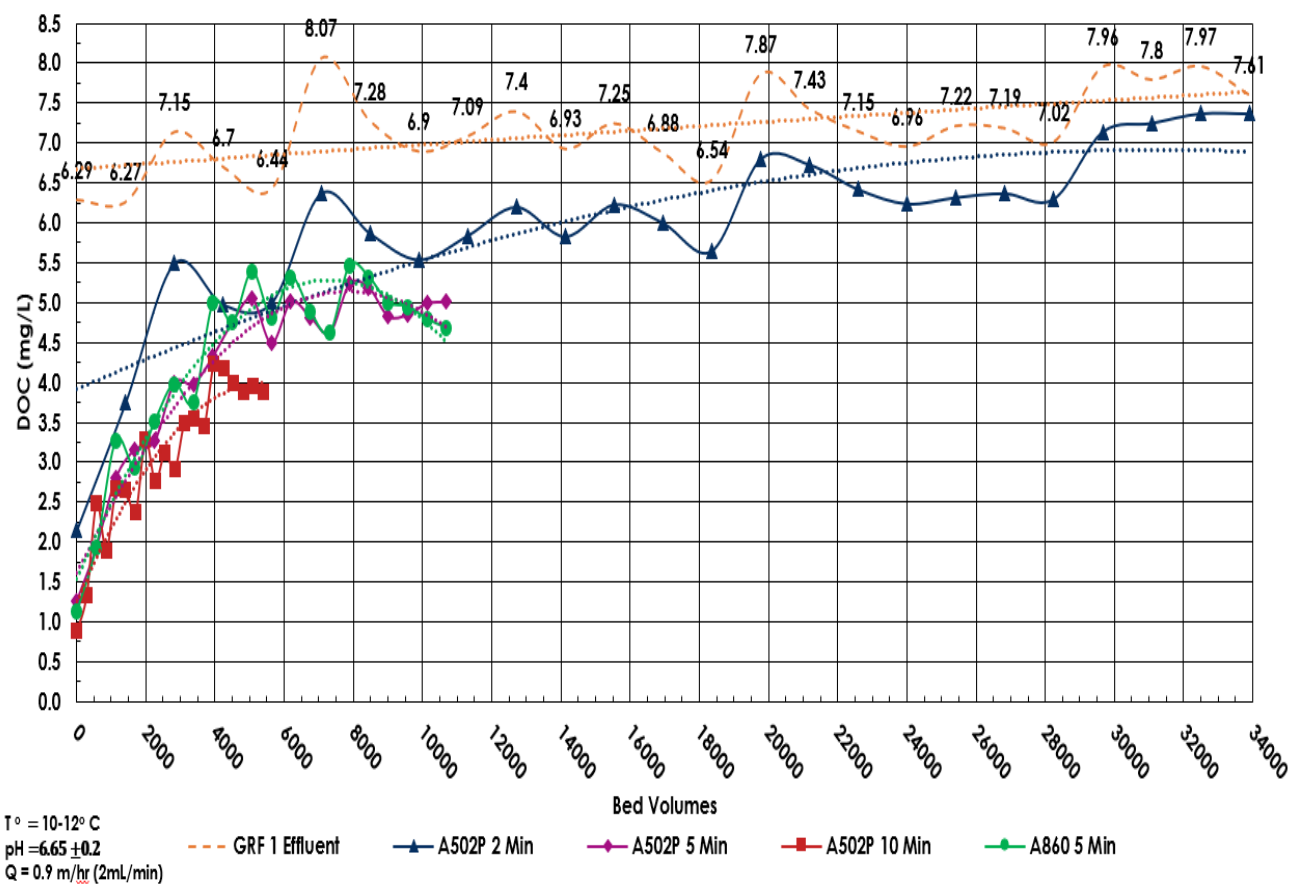


Figure 4.8: Influence of Resin Bed Volume on DOC Removal.

4.4: Pilot-Scale Gravel Roughing Filter Enhancements

4.4.1 Horizontal GRF Resin Container

Once the Resin Container was installed, HGRF 2 was given time to return back to a steady state before the resin was added to the box. This time was also used to verify if there was any obvious short circuiting or leaking occurring. After it was confirmed that the box had been installed correctly without any leaks 2.1 Liters of Purolite A502P anion exchange resin was added. This resin was left for 41 days within the box being sampled for DOC content daily. Figure 4.8 below shows a graph of the compared removals between the control GRF and the resin GRF. On the left Y axis DOC is measured in mg/L while on the right Y axis it is percent removal of DOC. The graph shows that the resin box with an empty bed contact time of just 3.65 minutes was able to achieve removals of up to three times that of the control filter over the course of the entire 41-day trial. The average DOC removal of the control GRF sat at 9% in the while the resin GRF had an average removal of 36%. This increase in DOC removals of 27% could most likely have been increased even further had more resin been used. This system design has proven to be incredibly efficient, achieving an average of 36% removal of DOC. Another important point to take from Figure 4.8 is that as expected at the start of the trial when the resin was first installed it had increased removals from about 5% in the control filter to a surprising 45% for roughly the first 14 days. After the 14 day period removals started to reach a steady state of roughly 30% for the remaining 27 days showing almost no signs of exhaustion at this point.

The signs of little exhaustion, even up to the 41st day, are in line with the bench-scale column challenge of the anion exchange resin. Each EBCT of the resin box is 3.65 minutes. 41 days of constant flow equates to roughly 16,000 complete bed volumes having passed through the resin. The column challenge showed that the 2 minutes bed volume column was achieving about 5% removals at the 34,000th bed volume. Given the prior study, one can assume that the resin box would get removals up to minimally the equivalent number of bed volumes, if not more due to the increased volume of resin.

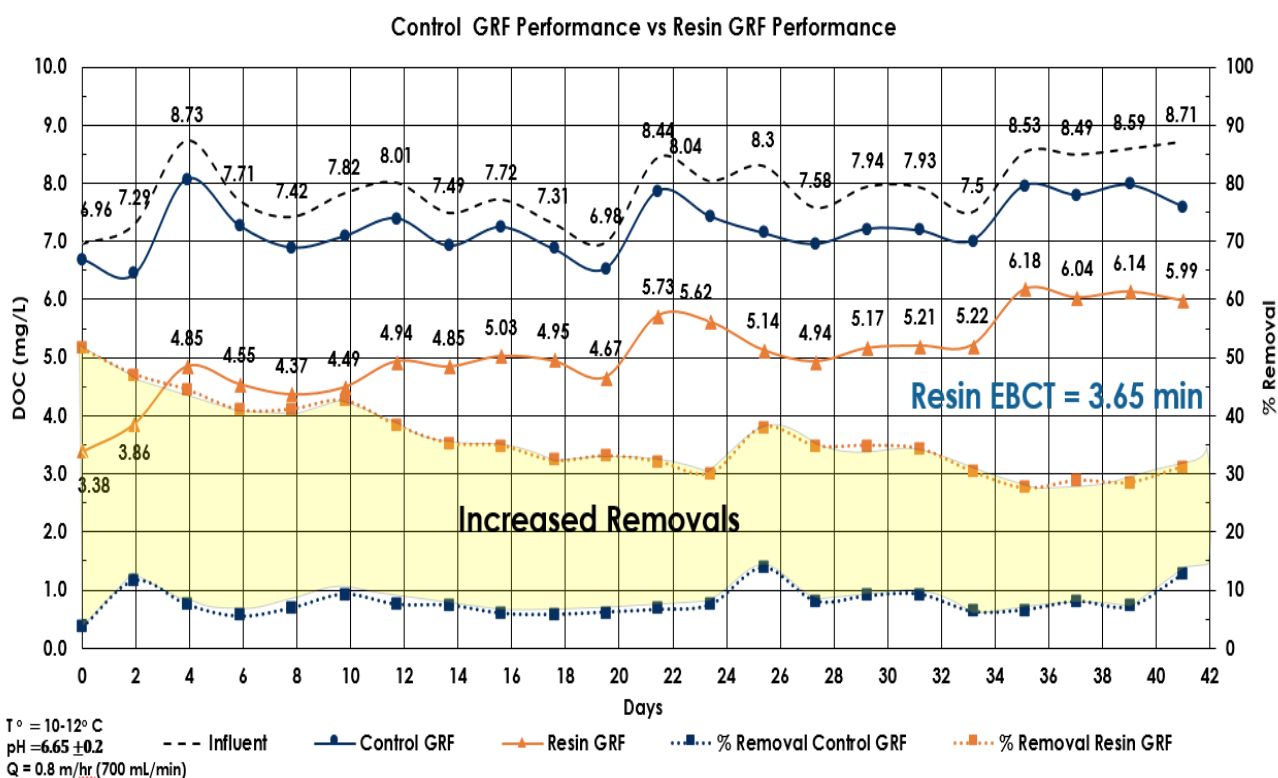


Figure 4.9: Control GRF Performance vs Resin GRF Performance

Over the course of the 41 day trial some issues did start to arise. One issue that was noticed after just 10 days was that there were flow patterns developing within the system. Figure 4.9 below shows that there is a portion of resin that is being bypassed which reduced the efficiency of the system.

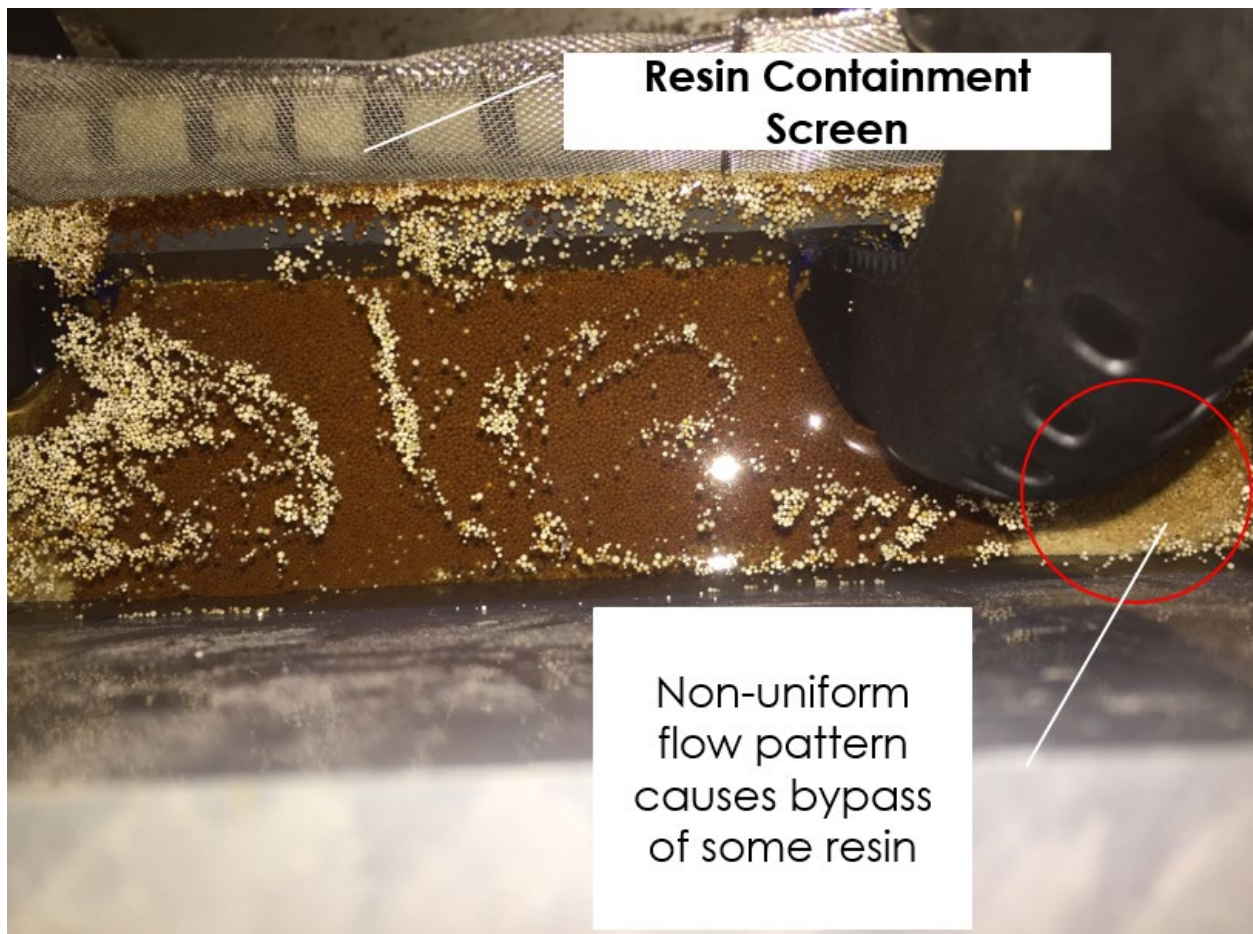


Figure 4.10: Resin Bypassing Example

Another issue that was encountered was maintaining the seal of the resin box to the GRF housing to stop water from bypassing the resin treatment. The sealant that was used to bond the resin box with the GRF housing started to break in some small areas by around the 35th day. Having a portion of the water bypass the resin and pass through untreated inflated the DOC content of the readings but only by roughly 3-4%. Figure 4.9 shows that on the 35th day of the trial there was slight jump in DOC for the resin GRF's effluent. Even with the bypass occurring the resin box was able to achieve 30% removals of DOC for the remainder of the trial.

For future studies looking into a resin box form of treatment some recommendations to remedy the issues that were encountered and improve the potential for organic precursor removal.

The first recommendation is regarding the preferential flow development within the box. An upflow cylindrical design of the box may have been a better option for the containment area of the resin since box shapes with corners tend to develop dead spaces leading to resin bypass. Using a cylindrical design could have avoided these dead spaces and better used the full volume of resin within the box.

Once the resin box has been optimized to the point that none of the resin it contains is being bypassed the next recommendation to improve removals would be to increase the volume of resin within the container. Future studies could draw a strong correlation between the empty bed contact time, volume of resin, and expected DOC removals for waters of similar characteristics. The column study showed that the bed volume of the resin box has a significant role on DOC removal potential as well as exhaustion rate. Increasing the resin bed volume will indeed achieve higher removals and last longer before needing regeneration.

4.4.2 Vertical GRF Resin Container

In designing a VGRF one major hurdle is that they are difficult to get similar EBCTs to HGRFs due to the nature of their orientation. When VGRFs are sized too largely their height becomes a problem due to the inherent difficulty of maintenance. This forces a compromise to be made on sizing of the filters, therefore a reduction in EBCT making a side by side comparison between HGRFs and VGRFs difficult.



Figure 4.11: Vertical Gravel Roughing Filters

The VGRF resin containers were not a disruptive installation due to the design's simplicity in combination with the vertical upflow filter orientation. Since the filter was upflow and vertical the top of the filter media is under about 6 inches of water. This allowed for the resin container to be gently placed on the surface of the gravel media causing minimal disruption (Figure 4.11).

After the resin container was added the VGRFs and HGRFs underwent a 39 day DOC loading trial. All filters were given the same influent waters from the DWTP. Disparities between the two orientations of filters quickly began to arise. Both HGRFs, control and resin enhanced, outperformed the resin enhanced VGRFs.



Figure 4.12: Vertical Gravel Roughing Filter's gravel media and water surface

Over the 39 day loading trial all gravel roughing filters received an average DOC content of 8.42 ± 3.3 mg/L while the VGRFs had an average effluent DOC content of 6.94 mg/L. This equates to just 18% of DOC removals while the resin HGRF achieved an average of 30% removals and the control HGRF achieved just 8% DOC removals.

The resin VGRFs did not only underperform the resin HGRF over the long term duration at a reasonably steady state of influent DOC levels but they also showed to be less capable of buffering a DOC loading spike as well. Figure 4.12 shows that on the 16th day of the DOC loading trial there was a substantial influx of influent DOC to all filters. The average DOC leading up to

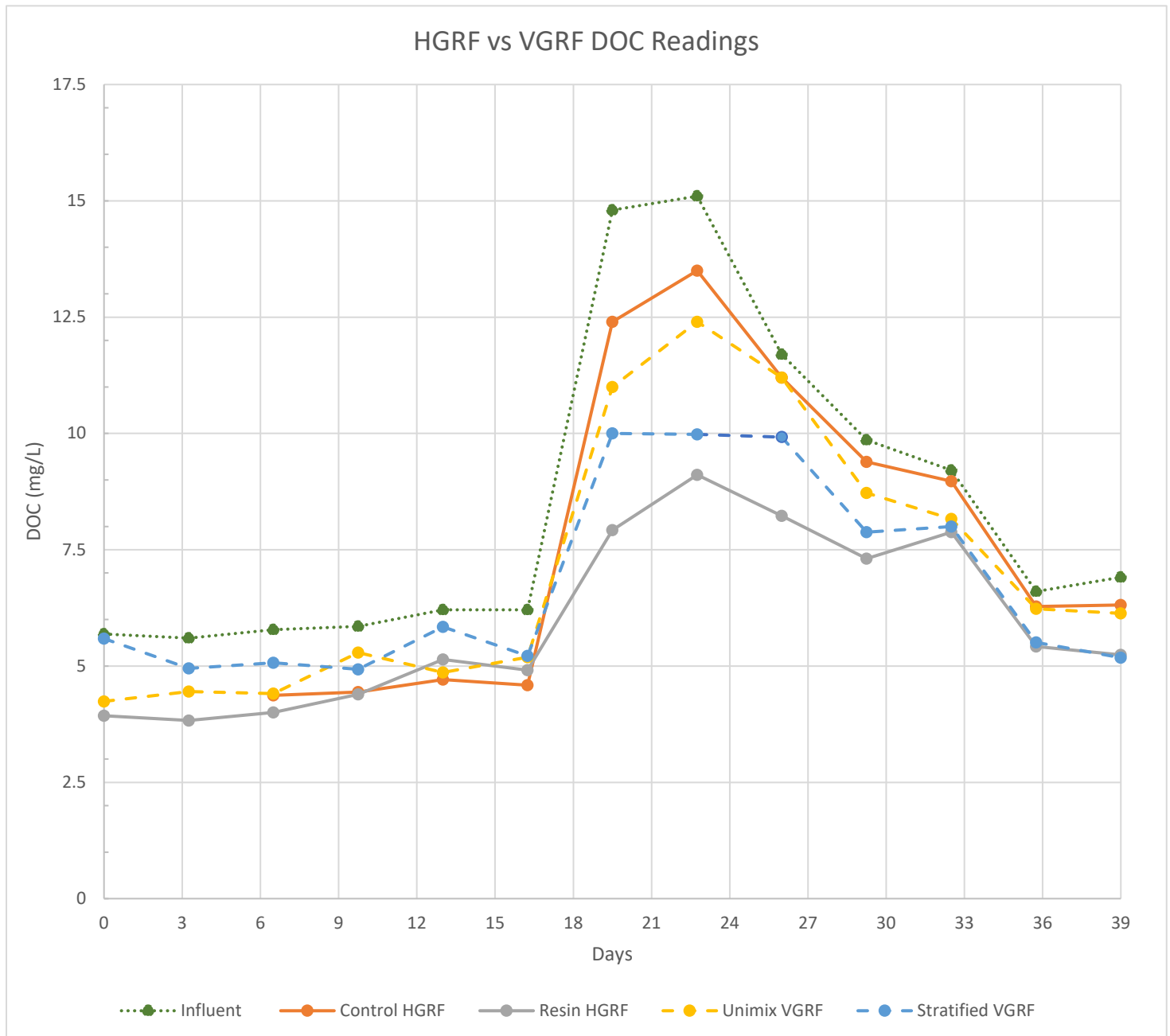


Figure 4.13: Control HGRF, Resin HGRF, and Resin VGRFs DOC Comparison

the 15th day was 5.83 mg/L while on the 16th day the DOC content more than doubled to 14.8 mg/L and maintained a higher level for the remainder of the trial. During this loading event which lasted almost the entire remaining 23 days of the trial the resin VGRFs buffered about 12% of the influent DOC while the resin HGRF buffered about 24% of influent DOC.

Modifications to the resin HGRF were made in order to remedy the bypass issue and allow for continued data collection of the four filters. Total organic carbon (TOC) data was continued to be collected following the modification of the HGRF and the initial DOC loading trial to identify long term differences between the two orientations of filters. Data collection was performed by Shannen Pimental, an undergraduate research assistant for the M.R. Collins research lab, for a total of five months. Figure 4.13 shows how over the long term the two VGRFs had varying results. The stratified media VGRF outperformed the resin HGRF for roughly the first 30

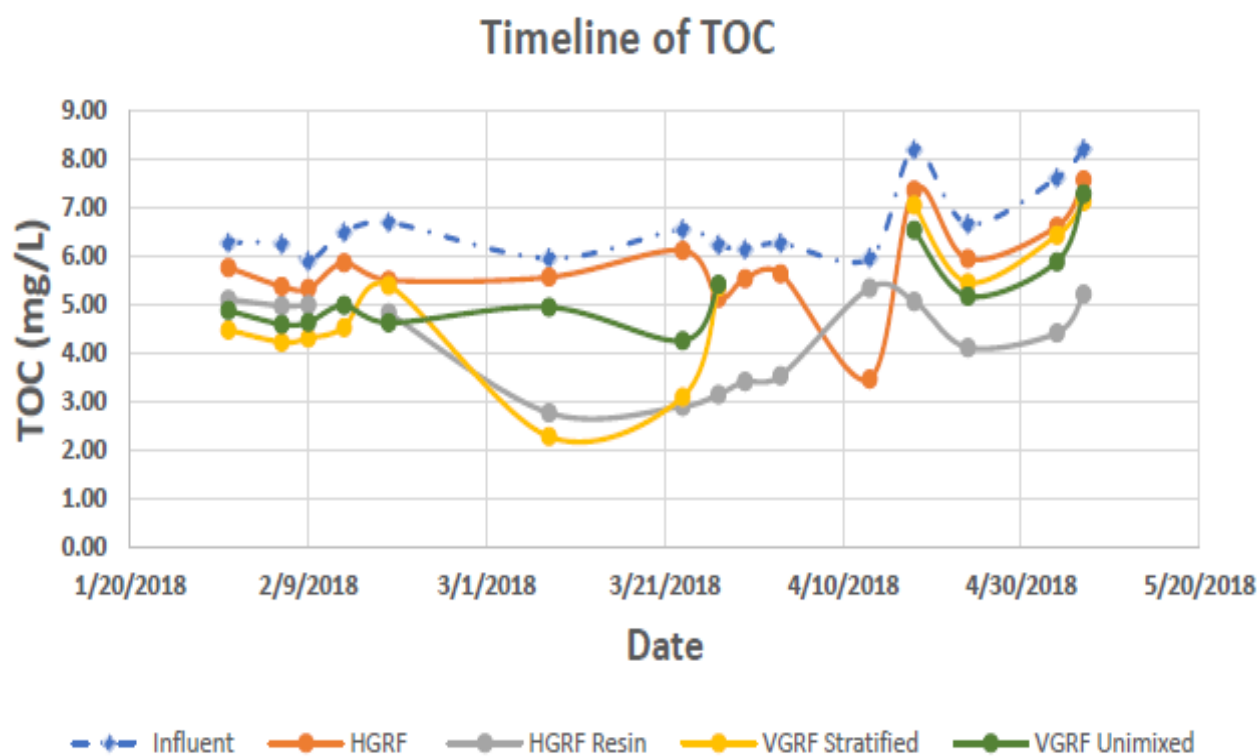


Figure 4.14: Long term TOC data collection between resin VGRFs and HGRFs

days and then an additional 20 days in the month of March while the unimix media VGRF performed at about have the removal rate of the both HGRF and stratified VGRF. Data collections started in January of 2018 and ended in early May 2018. The resin HGRF was clearly the most consistent of the four filters and continued to perform the best over the course of this study.

4.4.3 Horizontal GRF *E. coli* Challenge

Following the final resin loading challenge an *E. coli* loading challenge was run in order to determine the removals of an organic containment across the horizontal length of the horizontal roughing filters. Three samples per filter were taken; influent, a sample port at 30% of filter length immediately following the schmutzdecke, and the effluent. These sample ports can be seen in Figure 3.8. Figure 4.15 shows that the influent *E. coli* counts were at 18,000 CFU/100mL and that

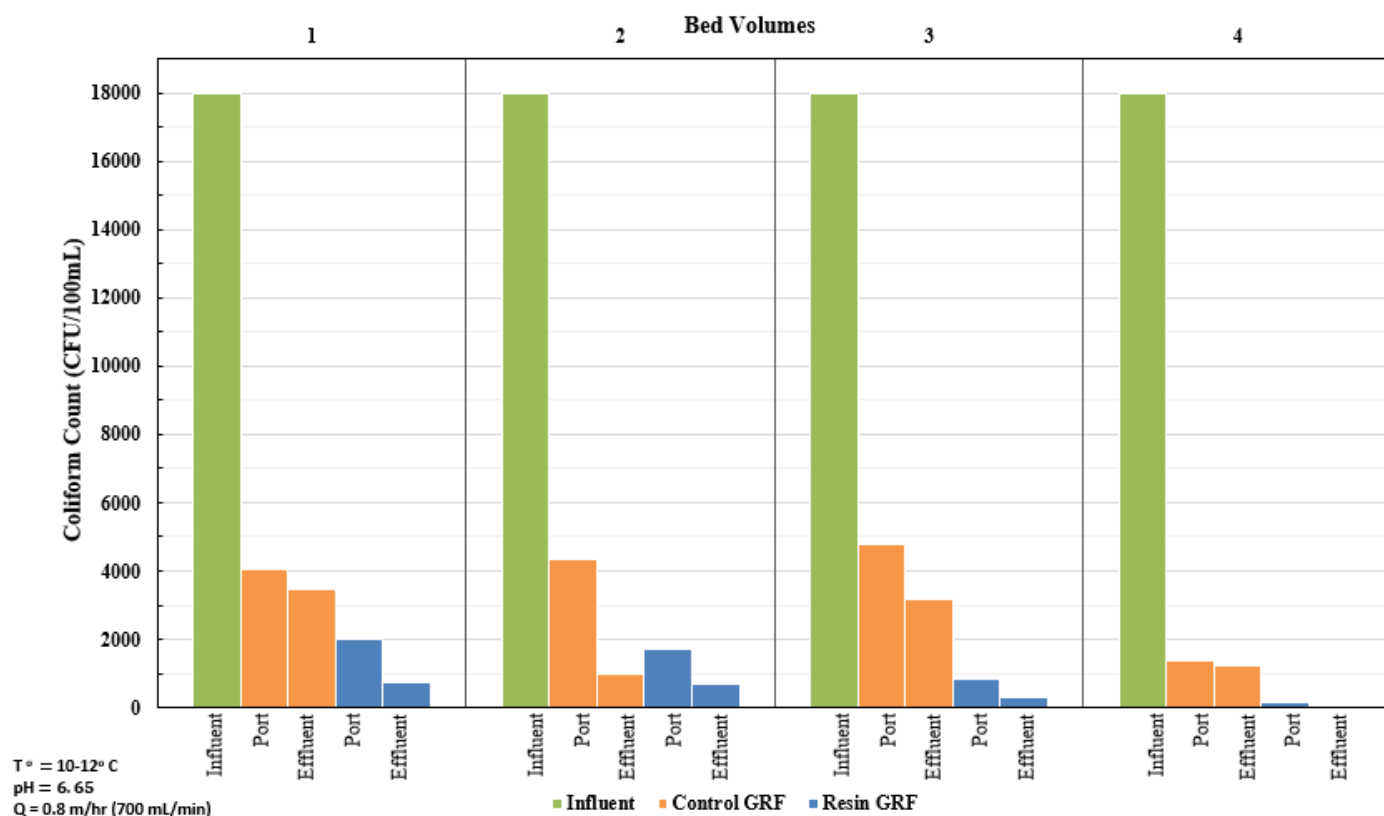


Figure 4.15: *E. coli* loading challenge showing *E. coli* count by distance across Horizontal GRFs

the most significant decrease of *E. coli* count occurs following the passing through the schmutzdecke. The schmutzdecke appeared to have reduced influent values by an average of 80% for the Control GRF and 93% for the Resin GRF. Following the schmutzdecke the next samples taken were from the effluent and passing through the resin. These samples showed a further reduction of the remaining *E. coli* by 34% for the Control GRF and 63% by the Resin GRF. This is a total *E. coli* coliform reduction of the influent values by 88% of influent for the Control GRF and 98% for the Resin GRF.

Both filters showed that they have high ability to buffer influent *E. coli* spikes however the Resin GRF outperformed the Control GRF with an almost 100% removal capacity which is likely due to the added capabilities of the resin. The Control GRF's results were almost identical to that of the turbidity spike challenges which suggest roughing filters to be a viable option for pretreatment of *E. coli* contaminated waters.

A major factor in the removals of *E. coli* for both filters that should be noted was that the schmutzdecke was responsible for more than 80% of *E. coli* removals for both filters. The schmutzdecke is the very first stage of the filter, which can be seen in figure 3.8, acting as a prefiltration to the gravel within the GRFs. The organisms within the schmutzdecke appear to have played in a significant role in the removals of the *E. coli* before the waters had even reached any gravel. This would suggest that the major factor in the *E. coli* removal for these GRFs was the schmutzdecke and not necessarily the gravel or the resin.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1: Major Findings

Gravel roughing filters are ideal for smaller systems that tend to have issues with turbidity fouling. They require minimal maintenance and are generally inexpensive due to the low-cost of construction and materials yet perform well in reducing turbidity loading to subsequent treatment processes. The test performed within this research also showed there are viable alternative options for the orientation of GRFs as well as the addition of supplemental media for targeting DOC removals including ZVI or anion exchange resin.

The turbidity spike challenges performed in this research consistently achieved up to roughly 90% turbidity reduction over the duration of the simulated storm events. Another major benefit to the removals was after the active turbidity spiking had stopped and the raw water turbidity levels returned to a natural steady state the HGRFs were not shown to release the previously trapped sediments. The HGRFs were successfully acting as a sink for the turbidity without delayed releases. Both HGRF filters had been operating for almost two years to this point and had a substantial quantity of sediments within them. This displays that these filters can retain a significant quantity of contaminants before terminal fouling.

After the ZVI proved its potential for DOC removal it was then tested for its regeneration potential. By backwashing the ZVI columns with solutions of varying pH's it was determined that pH's of 11 and 12 were the most successful for desorption of DOCs from the media. After further testing of pH 11, 25% regeneration was achieved while pH 12 needs further analysis. With all the positive benefits of ZVI addition it also proved to be quite narrow about the conditions under which it can successfully remove DOC.

Zero valent iron is best suited in pH waters 7.2 or above. One problem ZVI has is when at pH 7.2 and below iron will dissolve, which means over extended periods of time the filter will lose its treatment media. Another issue ZVI runs into is it tends to be brittle and fragile which limits how it is applied within the treatment process. Due to the fragility of ZVI if the flow rate is too great the small ZVI particles can break off and wash away. These issues leave ZVI with a relatively limited window to be legitimately considered for use, so designers can look to other common alternatives for DOC removals such as anion exchange resins.

The anion exchange resins chosen to test for application to GRFs and their DOC removal potential was Purolite's A502P and A860. The larger diameter anion exchange resin A502P was our focus because the nature of GRFs are to be low maintenance and smaller particles are counter to this process. The smaller resin would cause more headloss through the filter and potentially decrease time to terminal fouling.

The first test was to determine how many bed volumes the anion exchange resin would effectively achieve removals before terminal fouling. Through a long-term bench-scale loading trial, the A502P lasted roughly 33,900 bed volumes at 2 minutes per bed volume over 47 days before removals fell below 10%. At this point it was determined the resin would need to be regenerated however each operator can choose what quantity of removals is sufficient for their purposes. Taking this further, if 34,000 bed volumes at 20 minutes per bed volume is assumed as an estimate for treatment, this would equate to about 472 days before requiring regeneration. This low amount of service A502P resin requires fits the low maintenance criteria for GRFs.

Through the bench-scale trial the A502P not only showed that it has an exceptional useful life before exhaustion, but also showed how the duration of bed volume influences the removals that it achieves. 2-minute, 5-minute, and 10-minute EBCTs were tested to determine what an

effective contact duration would be. The 10-minute bed volume performed best with the highest removals achieving up to 85% DOC removals at the start of the challenge and by the 6,800th bed volume 44% of DOC removed. With this in mind the GRF designer can tailor each filter to their specific needs. For the purposes in this pilot-scale study a resin box was added to one of the HGRFs that allowed for a EBCT of 3.65 minutes which required 2.1 liters of A502P anion exchange resin.

The pilot-scale study of the HGRFs lasted 41 days. Over this period the removals averaged about 45% for the first 14 days and then 30% for the remaining days for a total of roughly 16,000 bed volumes. Using the findings from the bench-scale study it was estimated that the resin was only about 45% exhausted and had plenty of life left in it before needing regeneration. Ideally, the resin would have been run to exhaustion however the study was cut short due to malfunctions with the resin box. The box started to separate from the housing of the HGRF allowing raw water to bypass the resin box all together.

The problems associated with the anion exchange resin addition mostly stemmed from the resin box and not the resin itself. The resin is a relatively small media and the design of the resin box needed to accommodate this to avoid washout. The design performed sufficiently in this regard. The issues that arose came from the bonding of the box to the housing of the GRF. Bonding PVC to the metal housing proved to be difficult and short lived. Another issue that arose were some dead zones within the box, mostly at the corners. This meant a portion of the resin was bypassed during treatment and the full removal potential was not achieved. Perhaps a circular design of the resin box might have reduced the dead zones. Further consideration of these issues should be taken into account for future designs. Regardless of the issues that were encountered, the 41 days of data showed anion exchange resin can be added to GRFs for DOC removals with relative ease and have a long lifespan given no mechanical failures.

The final portion of the GRF experimentation was on a vertically oriented design. These vertical GRFs or VGRFs were designed as upflow columns, one having a unimix gravel media while the other having a stratified gravel media of varying diameters. The goal of this testing was to study the effects of the vertical orientation, the size and distribution of the media contained within, and how anion exchange resin influences the quality of treatment.

The VGRFs were constructed and operated for five months before any further modifications were made so they could ripen and reach steady state. For the five-month ripening period influent and effluent turbidity and UV was tracked to measure both filters' performance. Over the course of the ripening period both the unimix and stratified media filters performed almost the same for turbidity and UV removal. They performed with an average turbidity removal of 63% and an average UV removal of 14%. This removal of turbidity was not quite as good as the HGRFs 90% removal.

Both VGRFs performed similarly for turbidity and UV reductions staying within 10% of one another with no consistent leader in reductions. For turbidity they reached an average effluent NTU of 0.73 with a standard deviation of 0.078, while for UV an average effluent concentration of 0.27 1/cm with a standard deviation of 0.0087 1/cm for each reading. There was not enough variance between the two media orientations at this stage to suggest any significant difference. Loading trials were to be performed to further test the comparison of the filters, which led to adding sampling ports, piezometers, and anion exchange resin containment system for future testing.

After the sampling ports were added the two filters were given one week to reach steady state before started to collecting DOC data. After two weeks of data collection a higher concentration colored water source and the anion exchange resin was added to all filters, at this point the VGRFs' performance flipped. When the new water source was added along with the

anion exchange resin there was a spike of DOC that lasted roughly 17 days. After the 17 days the filters reached a steady state once again.

Previous to the addition of the anion exchange resin and the colored water the unimix VGRF outperformed the stratified VGRF by roughly 7%. After the addition of the colored water and resin the stratified VGRF outperformed the unimix VGRF by 7%. This change in performance between the two filters started to occur only after the addition of the resin and the new water source. It is hypothesized this change may have been caused by a disturbance of the unimix filter causing the retained turbidity(sediment, silt, etc.) to slough off of the gravel and leach over time. The stratified filter may not have been disturbed to the extent of the unimix filter, meaning the turbidity contained within it did not slough off.

Given enough time it can be assumed the unimix filter would return to its previous steady state, however this did not prove to be the case. The stratified filter continued to outperform the unimix filter by about 16% for turbidity removals and 7% for UV removals for the remaining duration of the trial.

5.2: Conclusions

- Gravel roughing filters have a large capacity for buffering turbidity spikes from subsequent water treatment processes however orientation may play a large role. Buffer capacities of up to 91% were shown in the Horizontal GRF configuration with consistency while the vertical GRFs consistently buffer 63%.
- GRFs are simplistic systems and requiring minimal maintenance which will vary with the size of the GRF.
- Neither the horizontal nor the vertical orientation proved significantly better than the other for either UV reduction or DOC removal before the addition of resin. Both VGRFs and HGRFs consistently removed roughly 32% of UV and about 10% of DOC from influent waters. Gravel media is not known for its organic precursor removal capacity.
- Arrangement of the gravel media may have played a role in the success of the VGRFs. Over time the unimix filter started to fall behind in turbidity, UV and DOC removals. This may have been due to increased fouling of the filter as compared to the stratified filter.
- In ideal conditions ZVI showed to readily remove organic precursors at a consistent rate of about 69% while at peak performance up to 81%.
- ZVI is not a good choice for any waters under pH 7.2 due to the dissolution of the iron within the waters. Iron will dissolve leading to the user losing their media as well as having to remove the dissolved iron from the water in subsequent processes.
- ZVI proved to be about 25% regenerable at pH 11 while at pH's higher than 11 regeneration is also successful however the iron begins to dissolve. The rate of dissolution was not able to be determined so these higher pH's may still be a viable option for regeneration.

- A502P and A860 anion exchange resins from Purolite proved to have high removal capacities for organic precursors. For the HGRFs the resin addition increased DOC removals by 27% for a total removal capacity of 36%. It should be kept in mind this 27% increase was achieved with only a 3.65-minute EBCT within the resin. If the EBCT is increased it is likely that an even larger increase in DOC removals would be seen.
- The HGRFs proved to remove more DOC than the VGRFs. EBCT was designed to be equivalent, however the horizontal filters still outperformed the verticals. This may be due to the nature of gravity's affects on the particles in combination with the direction of the water's flow through the filter.
- Anion exchange resin is known to be highly regenerable. However, as resin is also extremely costly, it may not ideal for low cost treatment systems.
- The anion exchange resin was relatively simple to implement within both the HGRFs and VGRFs. A form of bag or box can be designed by the user in order to keep the resin contained while forcing the untreated water through it. Cost should be taken into consideration.

5.3: Recommendations

- Further research should be performed on the orientation of the GRFs. The research seemed to show the HGRFs were more effective at removals of turbidity.
- Further research on the gravel placement and stratification of gravel with the GRFs should be performed. The stratified media VGRF performed better in reference to turbidity removals however the HGRFs performed better than both VGRFs with unimix gravel.
- Further research should be performed on the regeneration capabilities of ZVI, specifically pH's higher than 11. There is evidence that the higher pH's may more effectively regenerate ZVI, but it was unable to be proven.
- Further research should be performed on the effect that EBCT within resin has on DOC removals. If a trend could be identified it would allow for the establishment of a standard procedure of determining the proper quantity of resin needed to achieve target DOC removals. Ultimately this would simplify the design process making it much more user friendly and marketable.

5.4: Limitations

- This study did not include an analysis on the impact of performance when moving from bench-scale to pilot-scale to field scale. An analysis should be performed on the major performance differences or difficulties that arise between the various scales of operation.
- Size constraints due to the operating locations of the pilot-scale GRFs did not allow for analysis of larger systems.

- Water sources were not always highly contaminated with DOCs so this could not push the pilot-scale systems to their extremes. If the water sources were more contaminated for longer durations resin exhaustion may have been able to be achieved within the GRFs.
- Implementation of the resins were not optimized due to material and size constraints. Better DOC removals may have been achieved had the resin boxes been perfected. This study did not push the resin or GRFs to their limits suggesting that there may be more efficiency improvements left to be made.

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APPENDIX I: FIGURES AND TABLES

Figures:

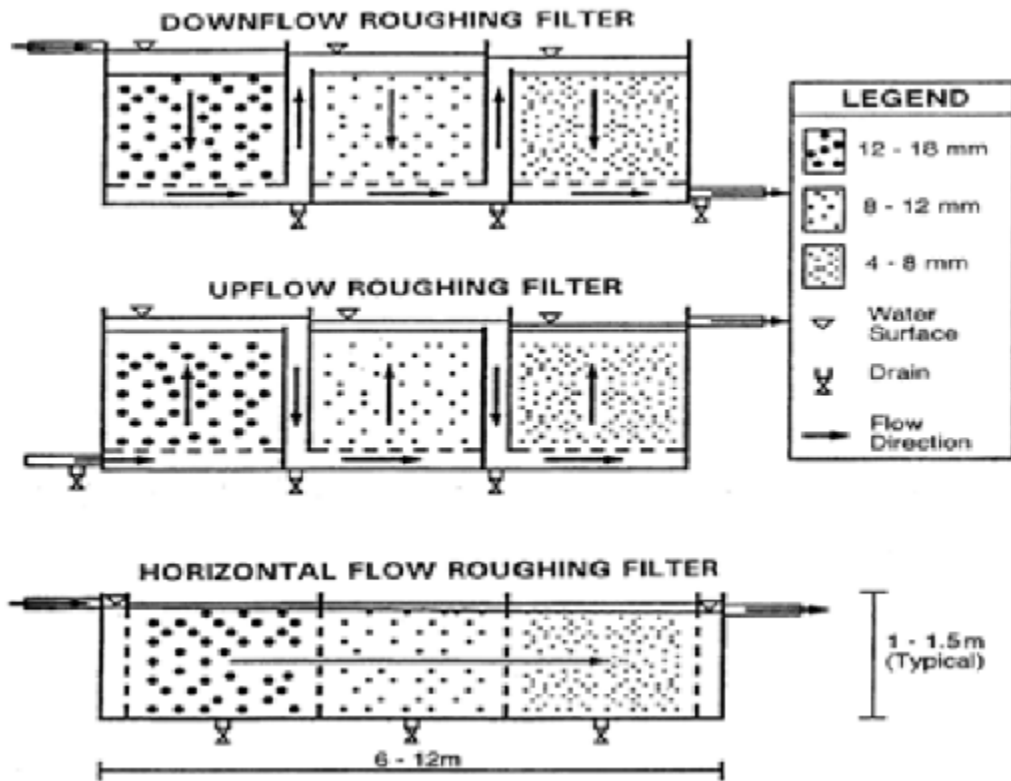


Figure 1.1: Examples of various GRF orientations, flows, and media sizes (Wegelin, 1996).

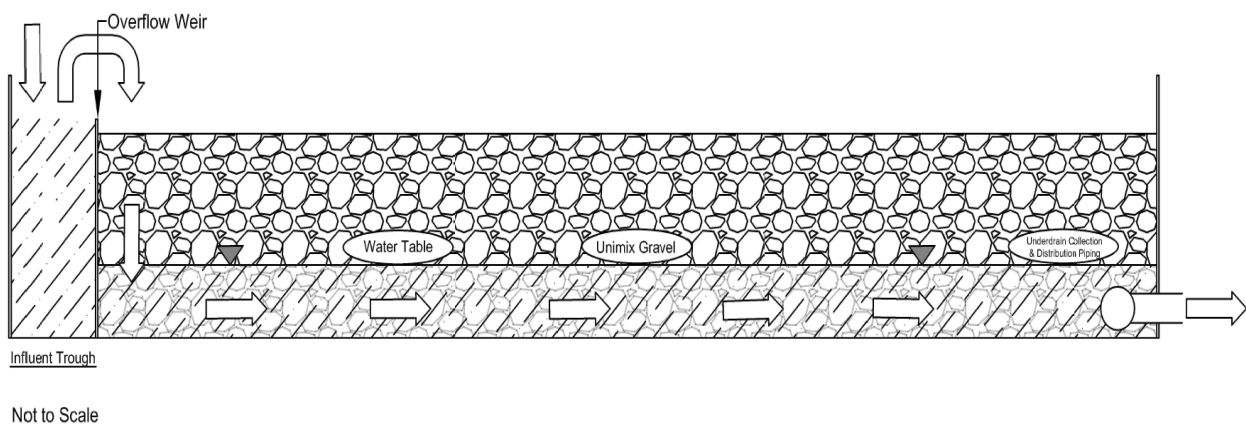


Figure 3.1: Pilot-Scale Horizontal Gravel Roughing Filter Design



Figure 3.2: Gator Jar Oxidation

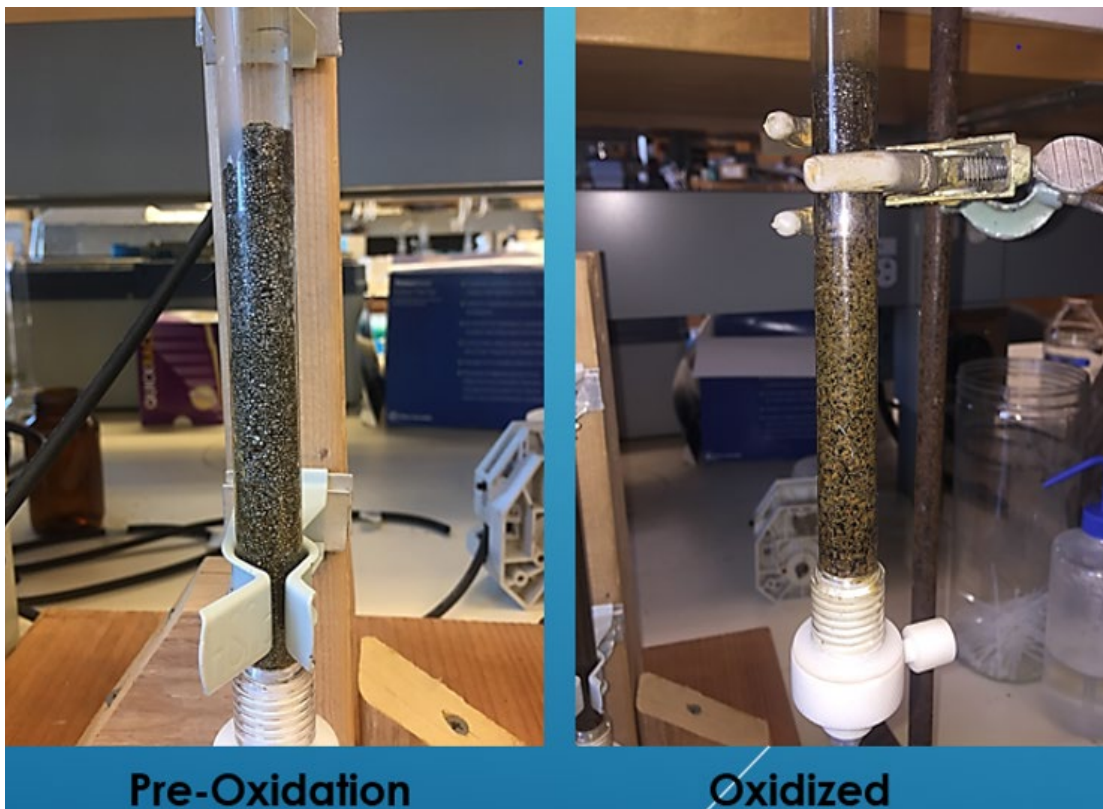


Figure 3.3: Pre-Oxidized vs Oxidized

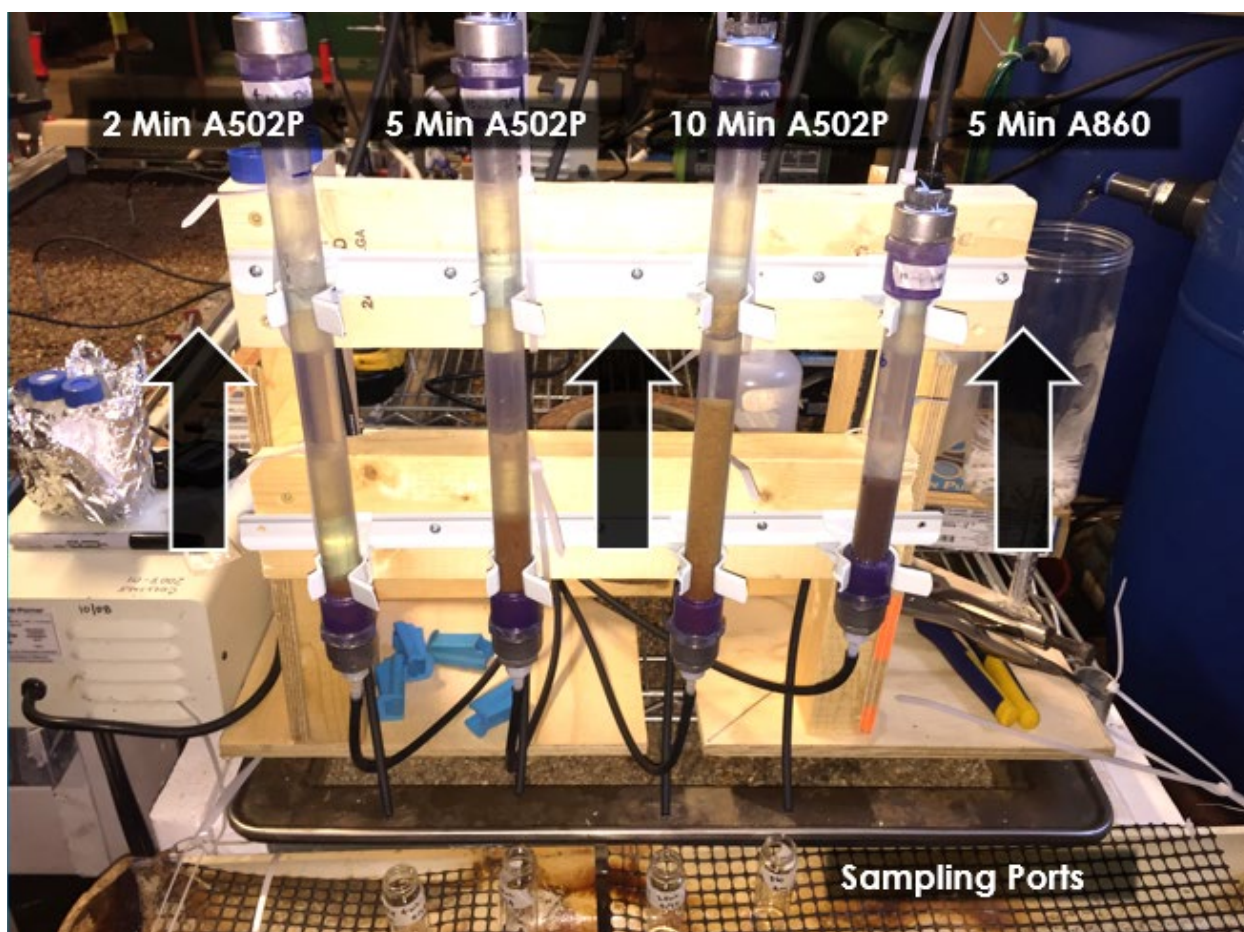


Figure 3.4: Anion Exchange Resin Column Challenge

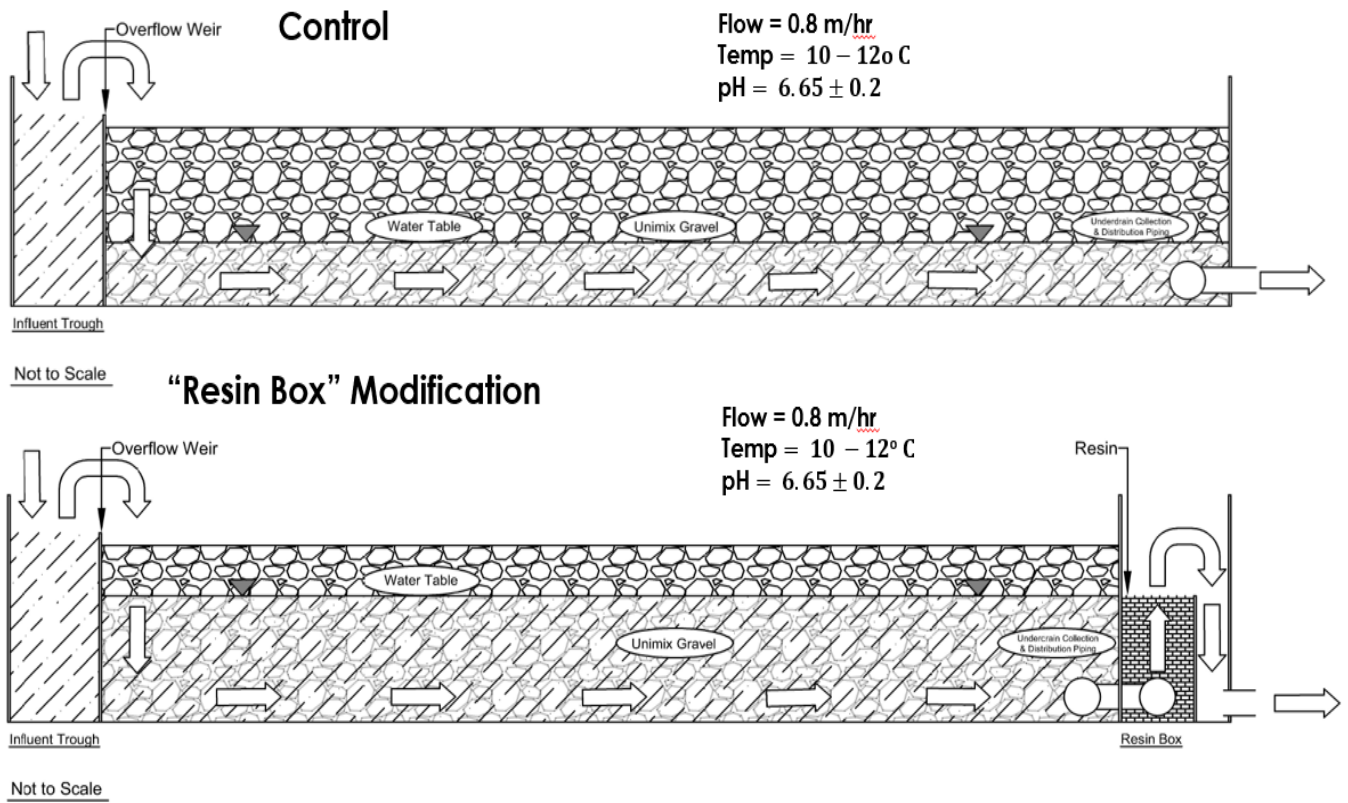


Figure 3.5: HGRF Resin Box Enhancement

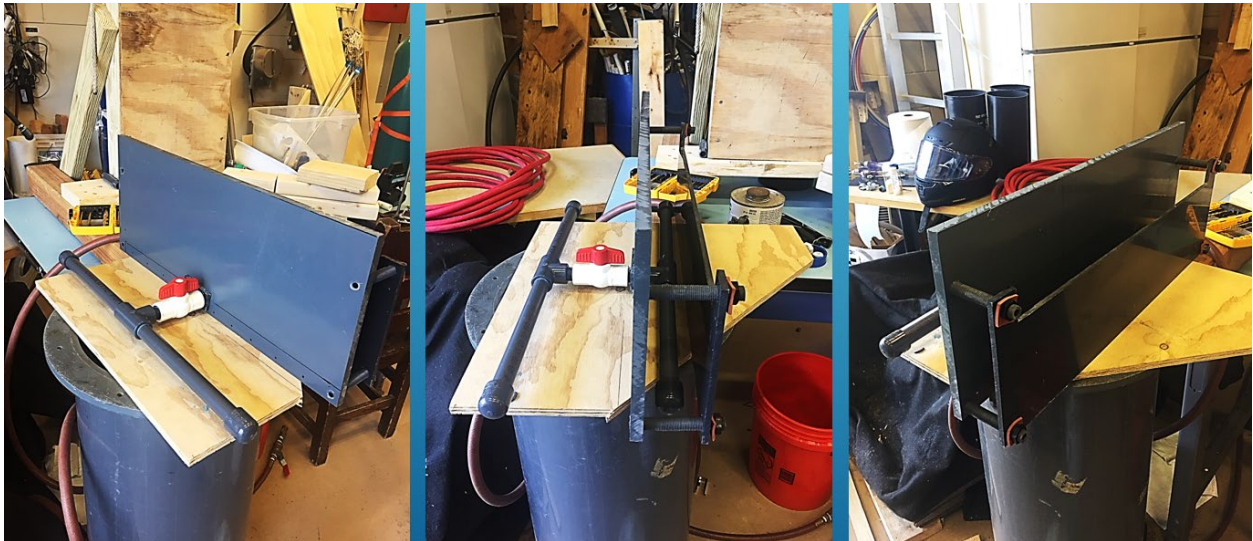


Figure 3.6: Resin Box



Figure 3.7: Resin Box Installed 2

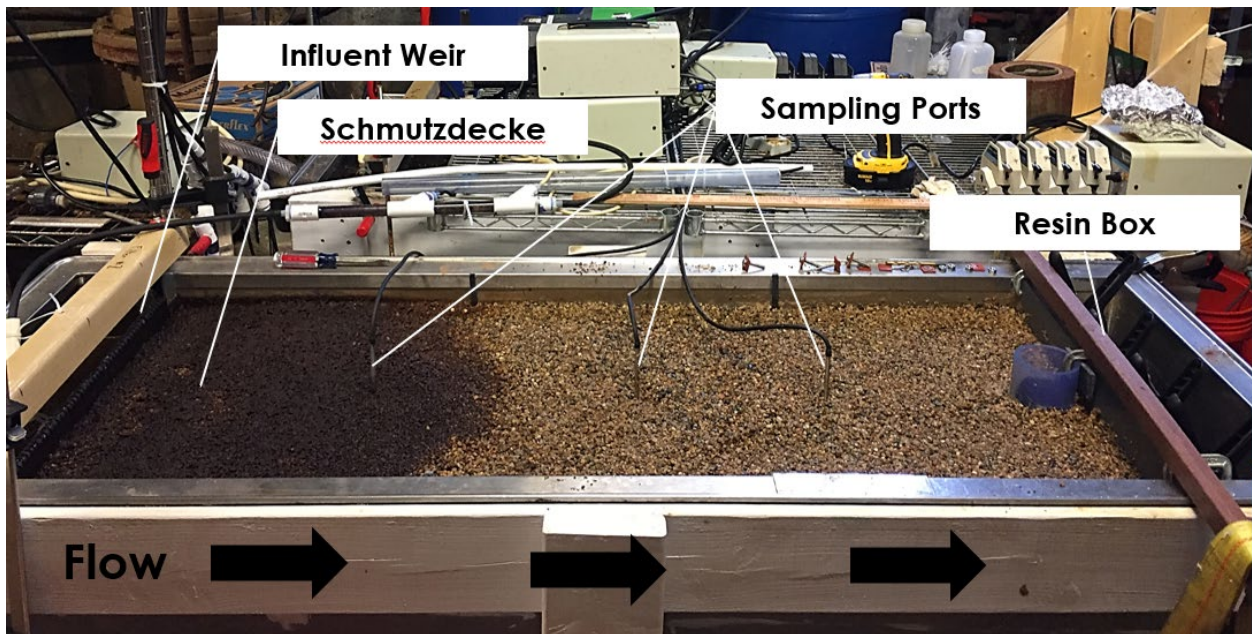


Figure 3.8: Resin Box Installed 1

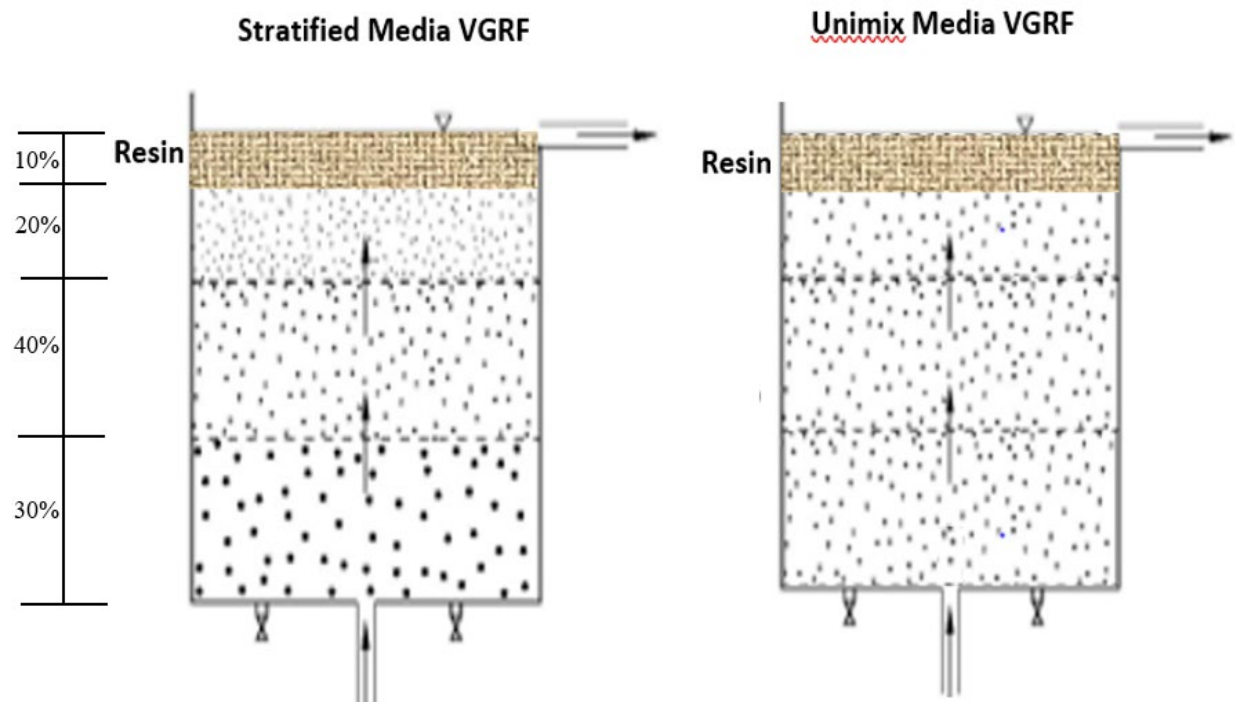
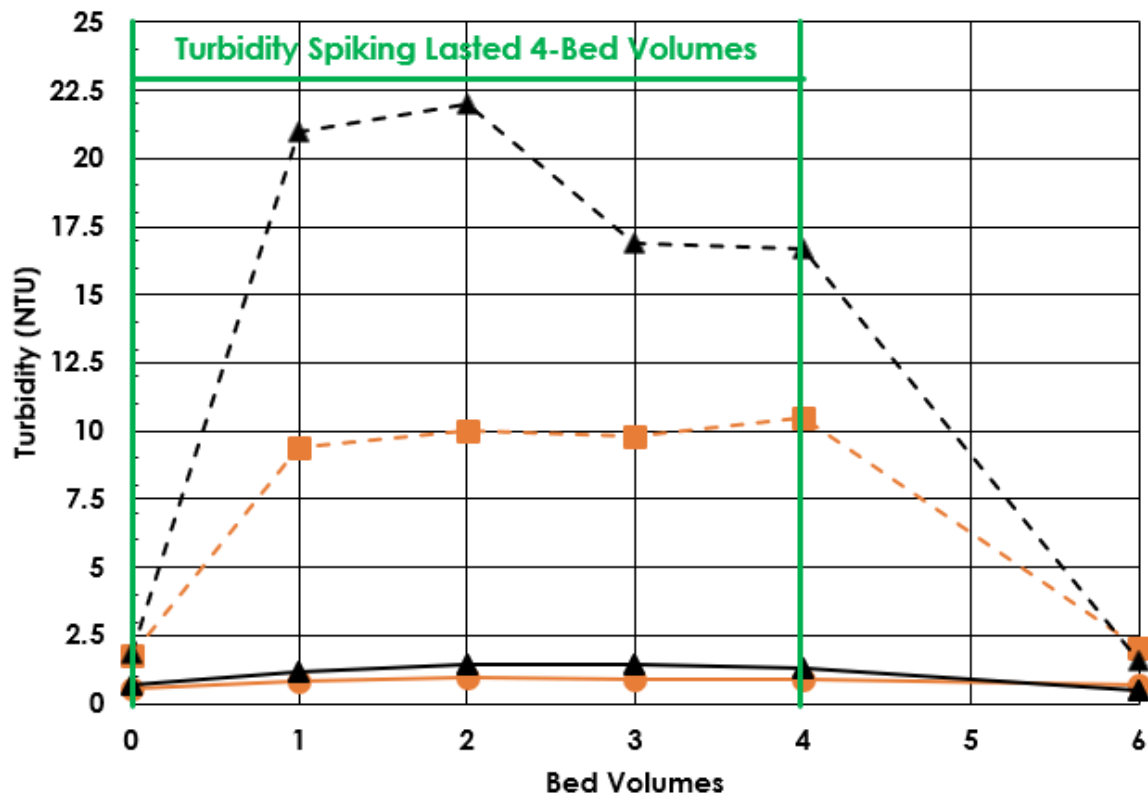


Figure 3.9: Stratified VGRF and Unimix VGRF (NOT TO SCALE)

Turbidity Spike Challenge



$T^{\circ} = 10-12^{\circ}C$

$pH = 6.65 \pm 0.2$

$Q = 0.8 \text{ m/hr (700 mL/min)}$

Figure 4.1: Turbidity Spike Challenge 1

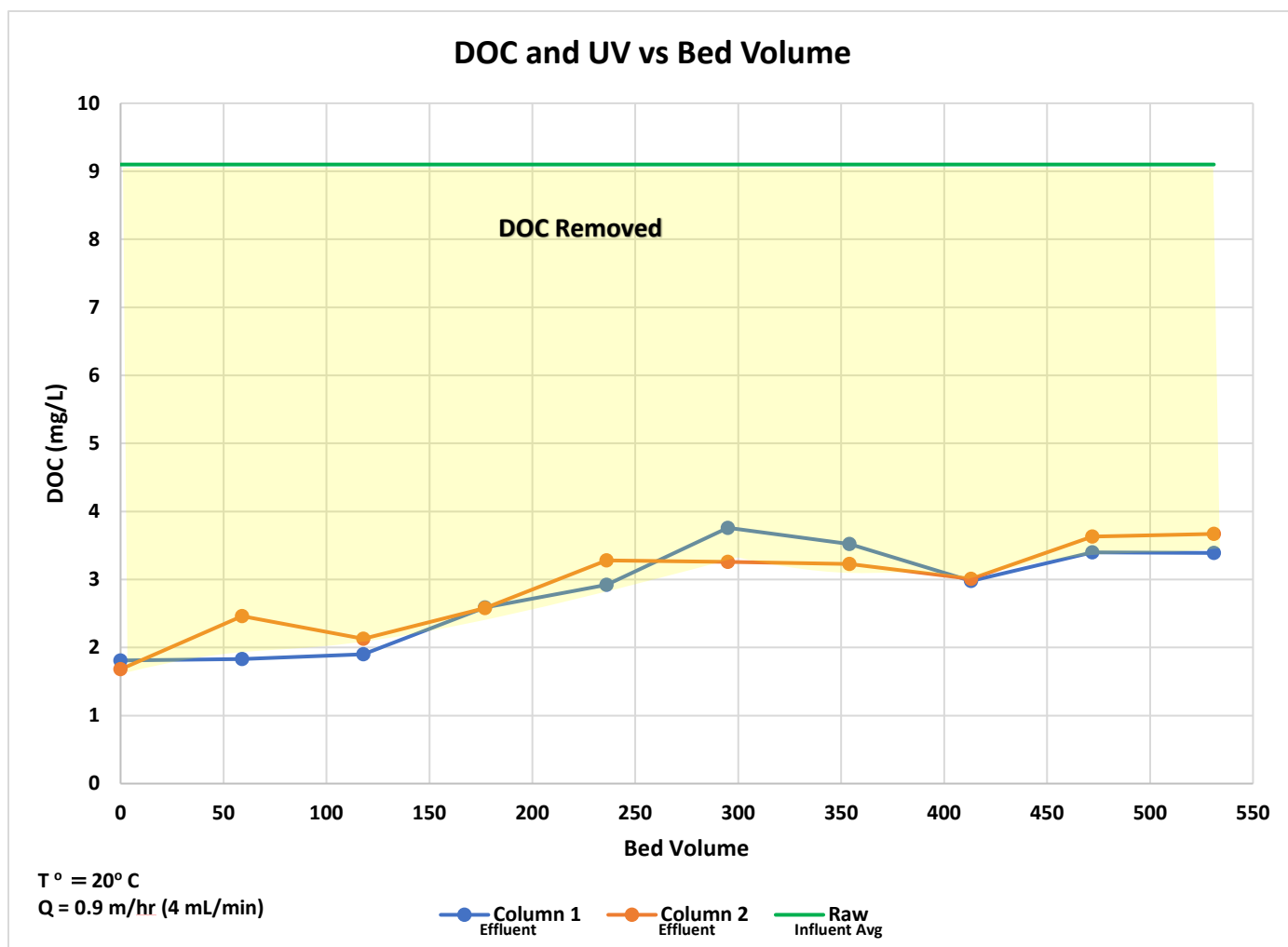


Figure 4.2: DOC vs Bed Volume

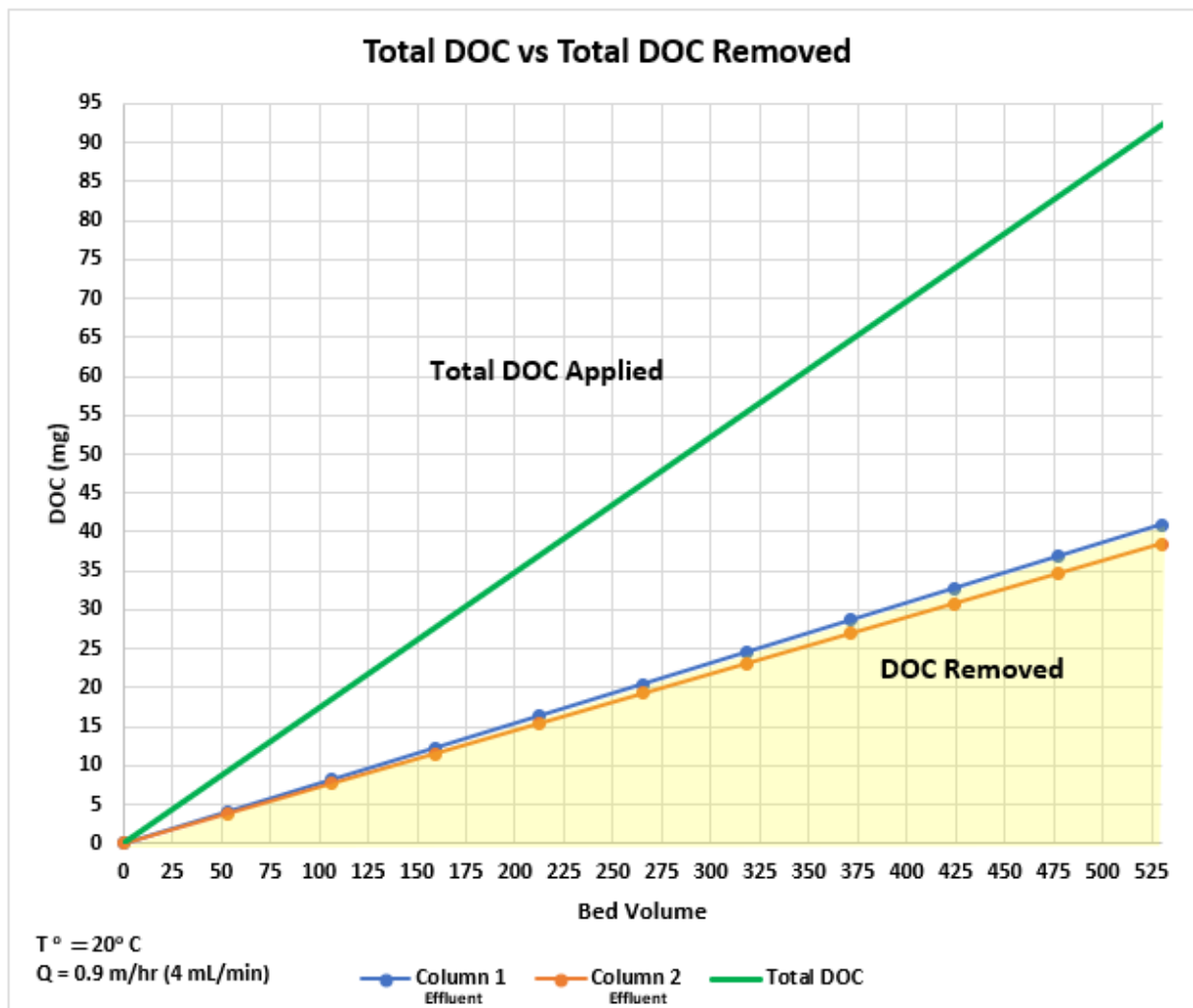


Figure 4.3: Total DOC vs Total DOC Removed

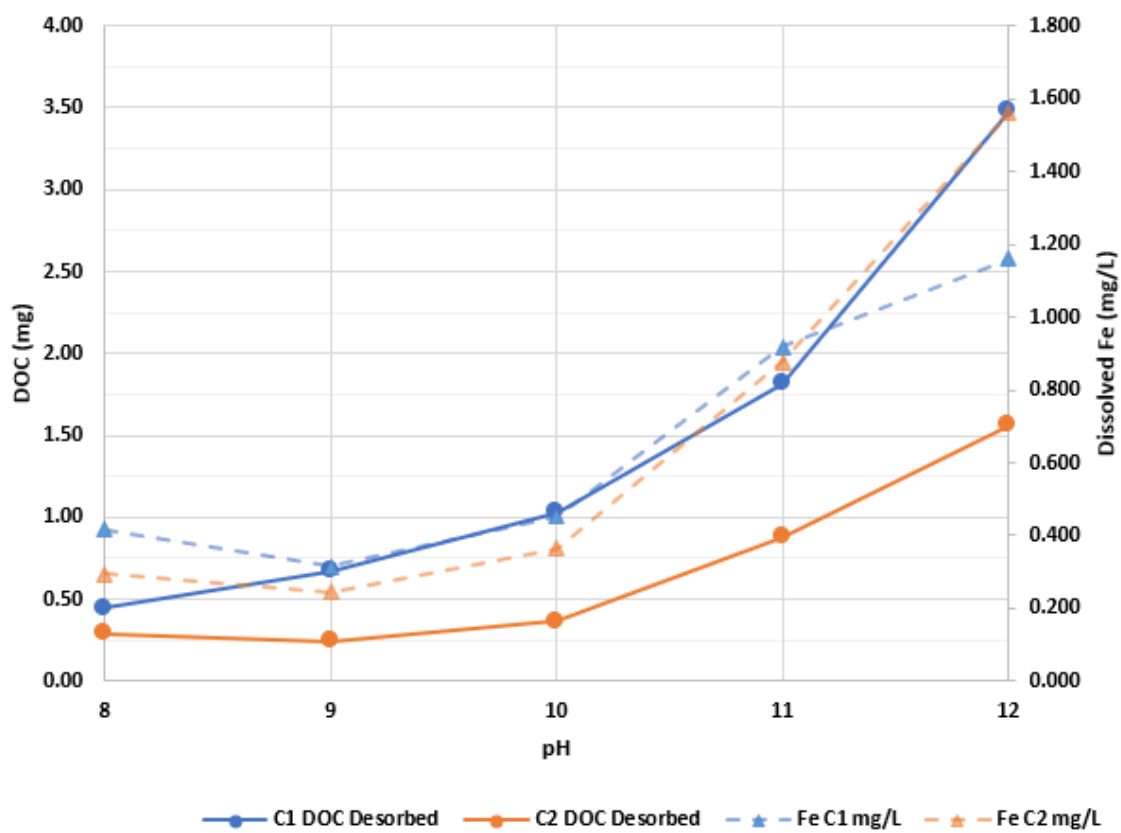


Figure 4.4: DOC Desorption and Iron Dissolution vs pH

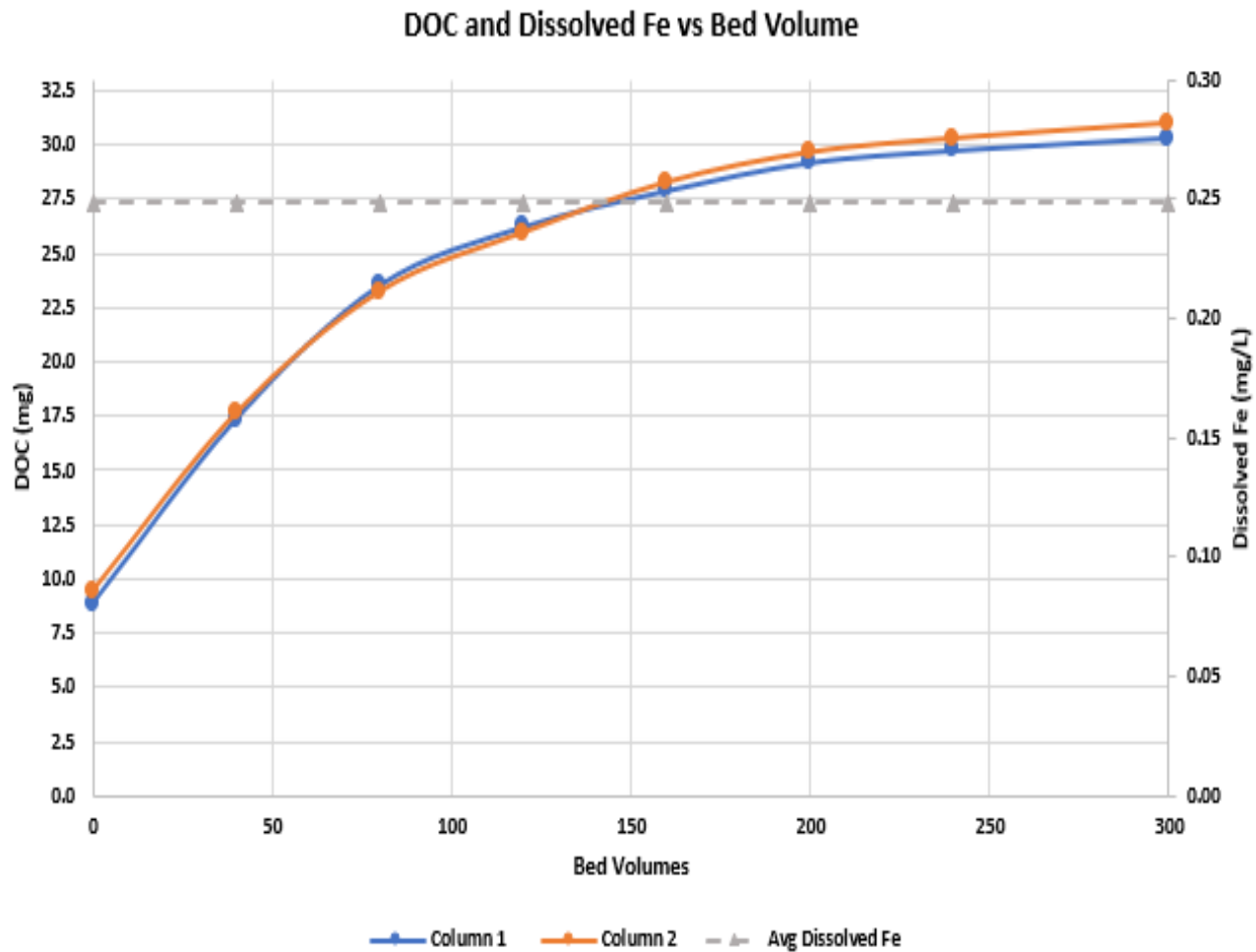


Figure 4.5: Cumulative DOC and Dissolved Fe Desorption vs Bed Volume at pH 11

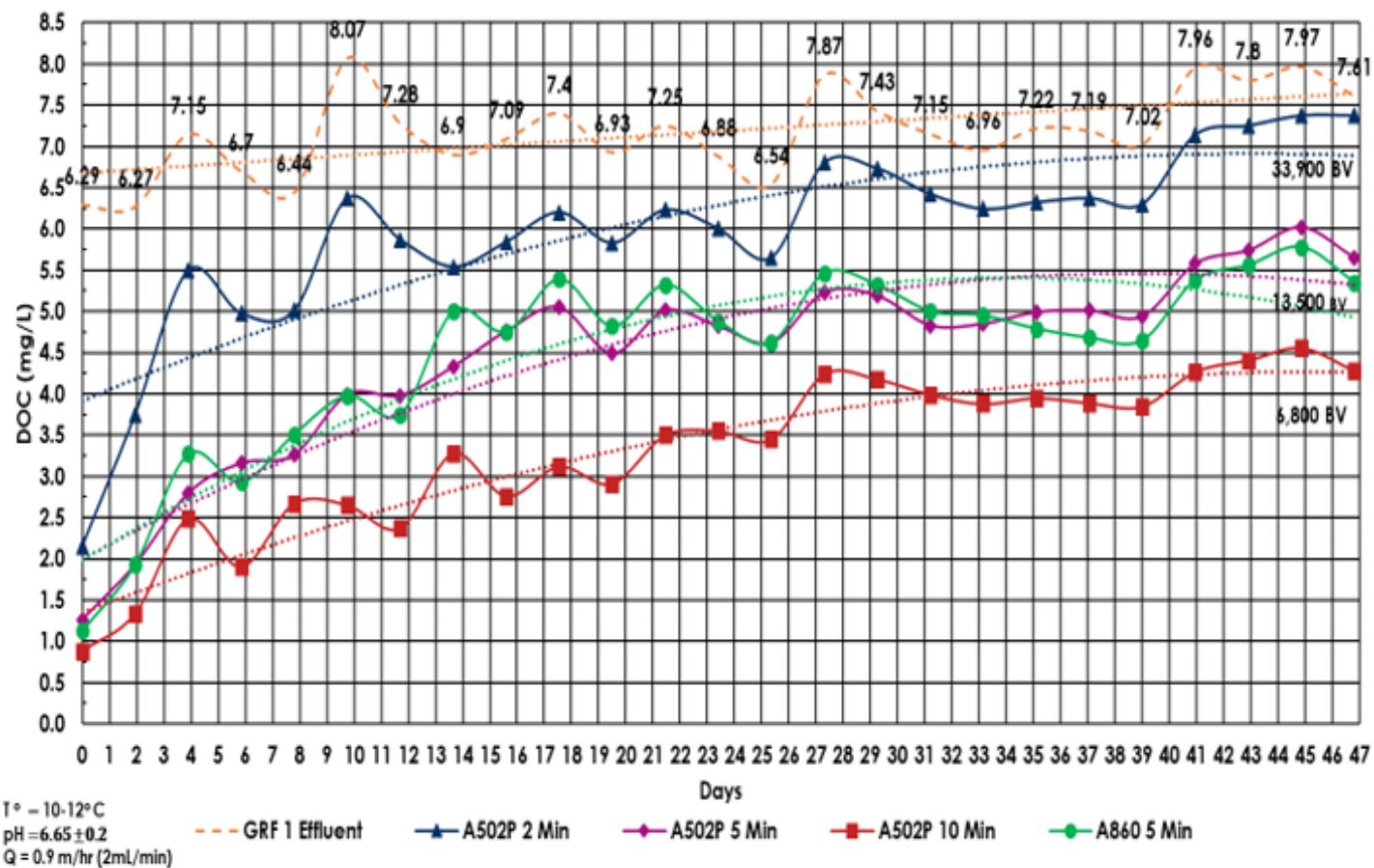


Figure 4.6: Bench-Scale Exhaustion Resin Challenge

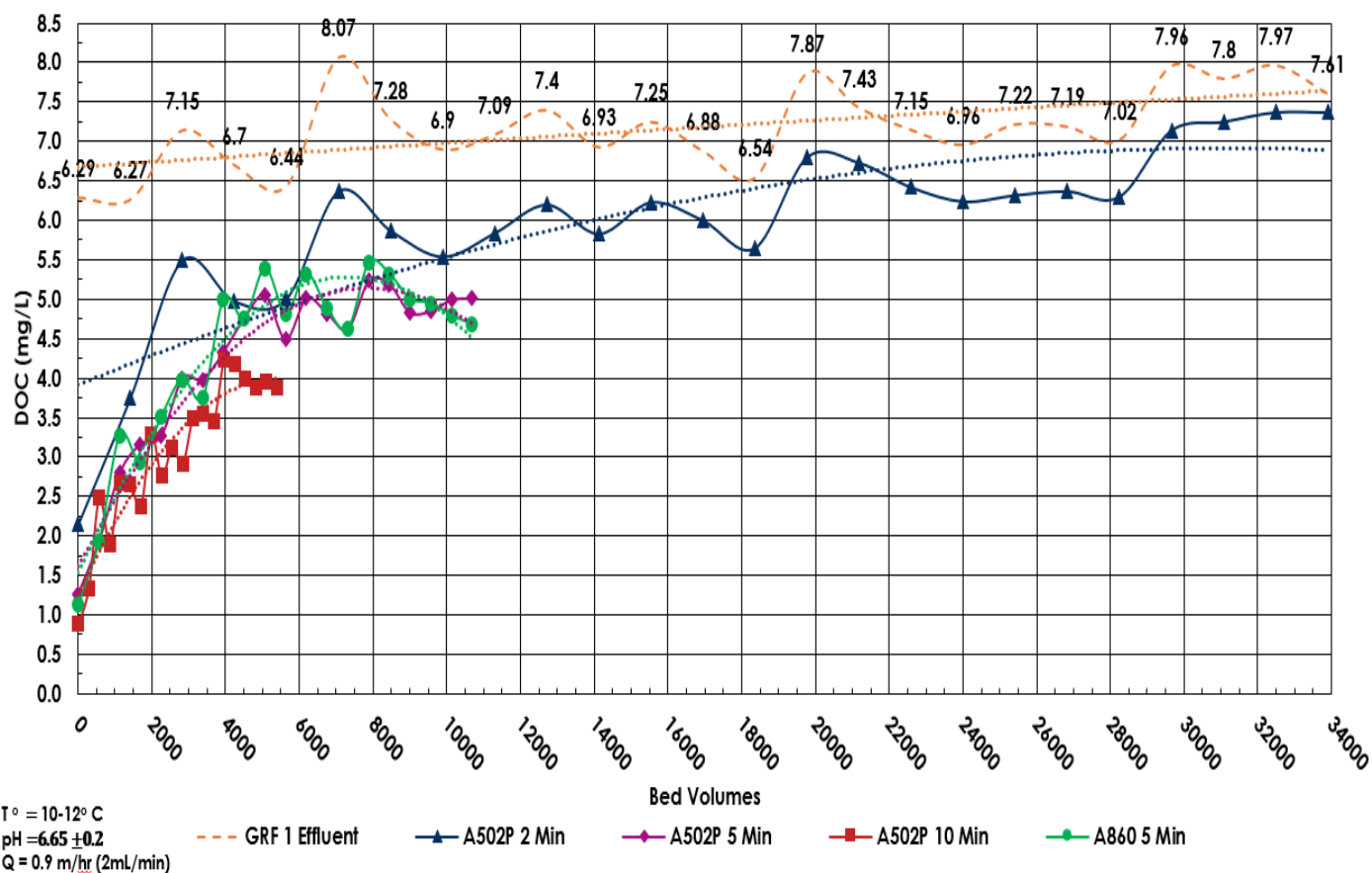


Figure 4.7: Influence of Resin Bed Volume on DOC Removal.

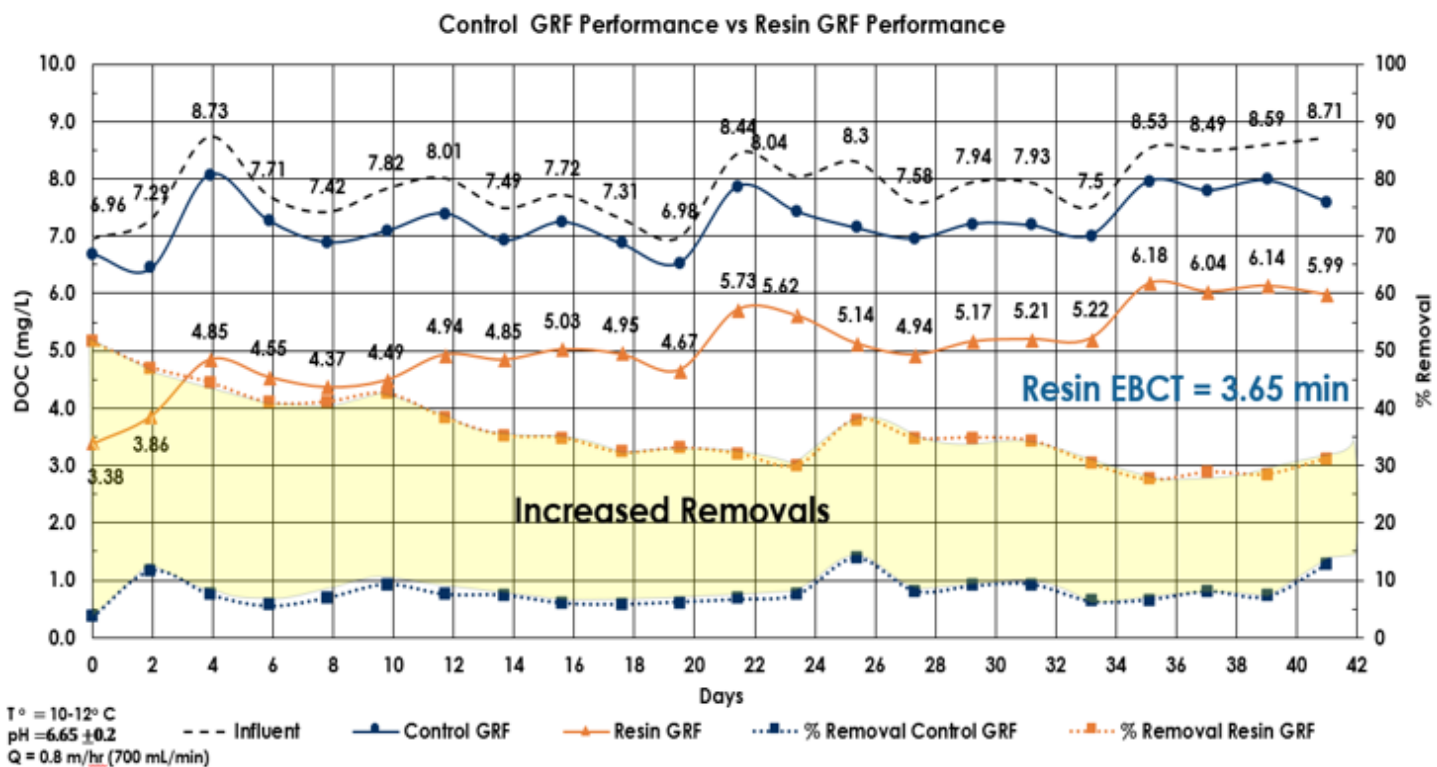


Figure 4.8: Control GRF Performance vs Resin GRF Performance

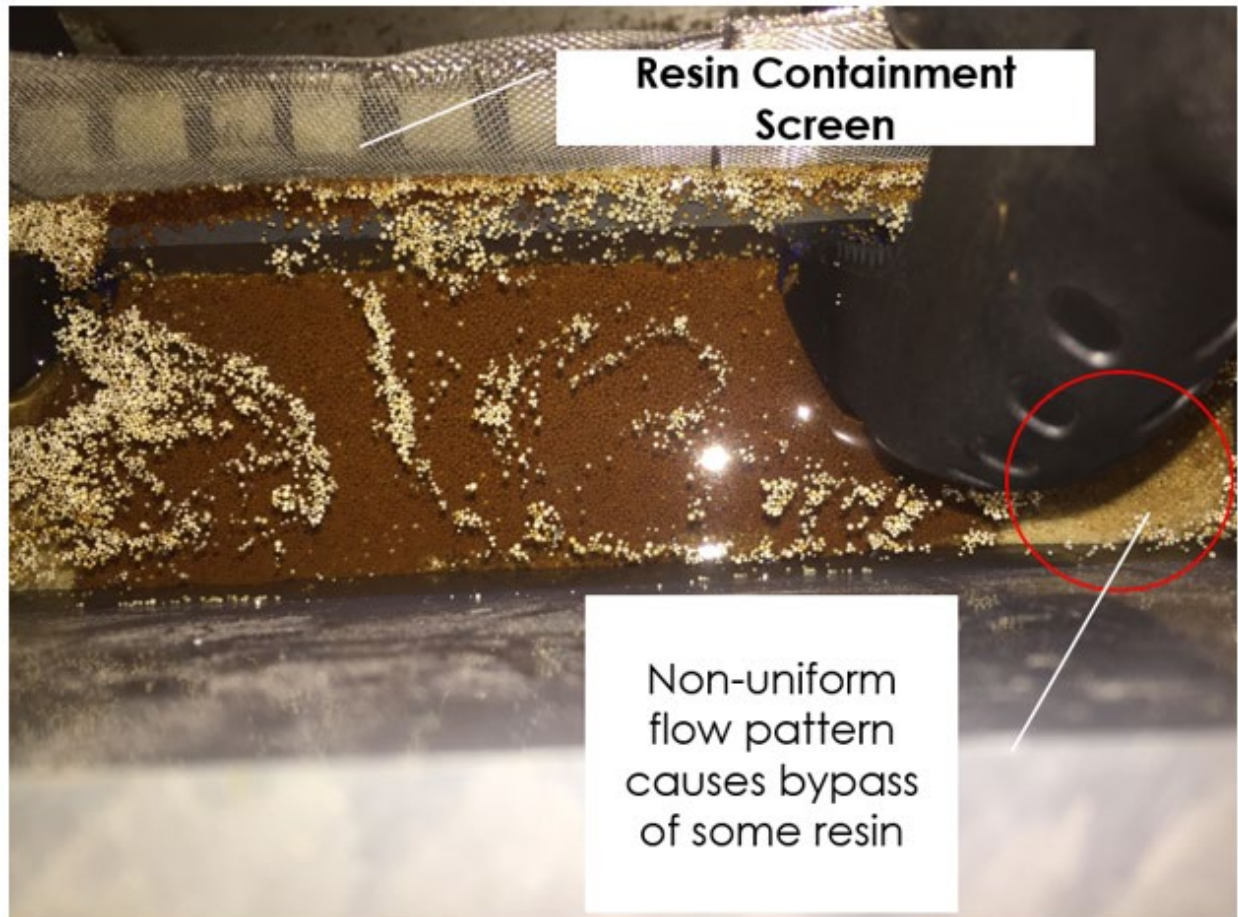


Figure 4.9: Resin Bypassing Example



Figure 4.10: Vertical Gravel Roughing Filters



Figure 4.11: Vertical Gravel Roughing Filter's gravel media and water surface

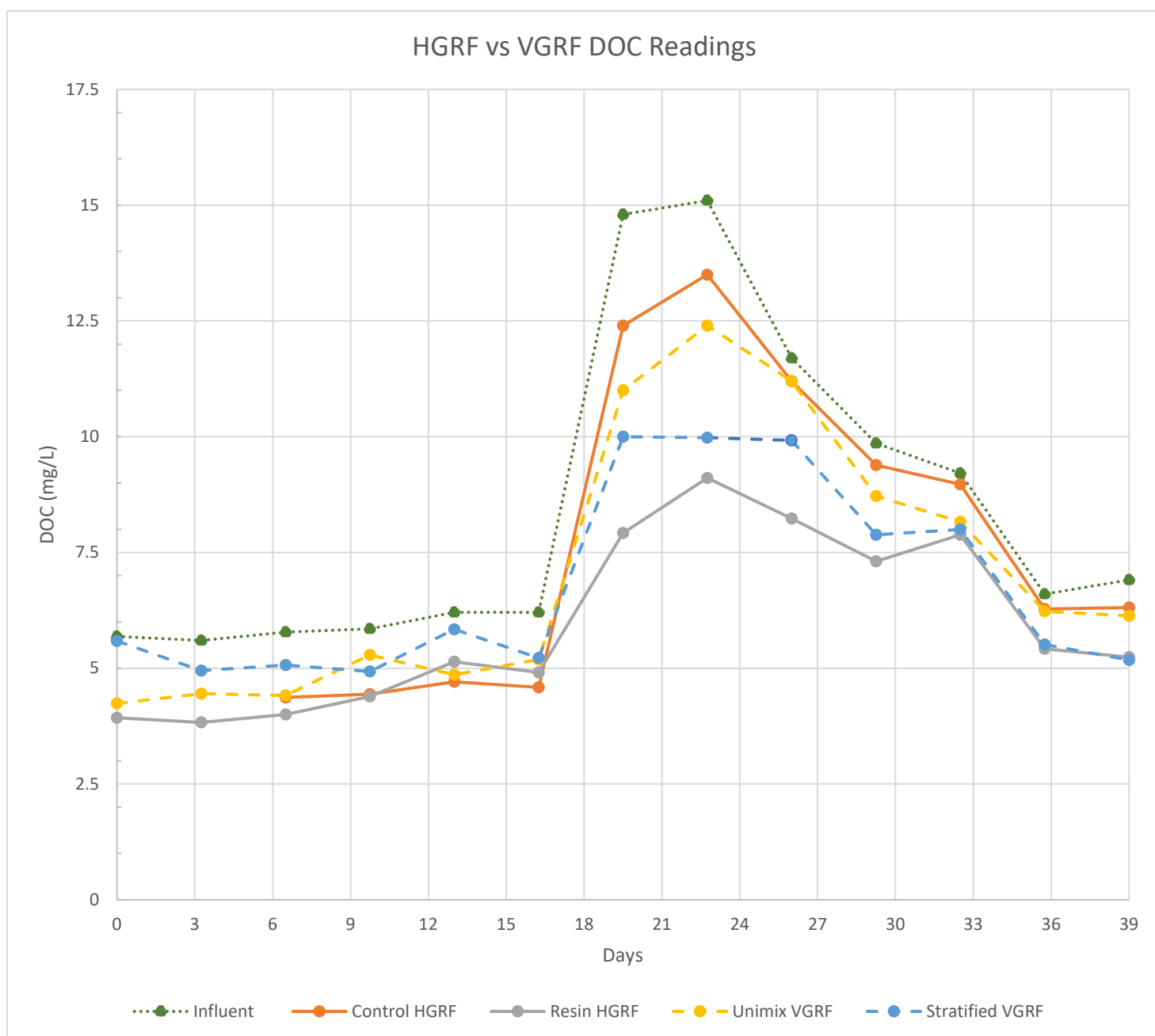


Figure 4.12: Control HGRF, Resin HGRF, and Resin VGRFs DOC Comparison

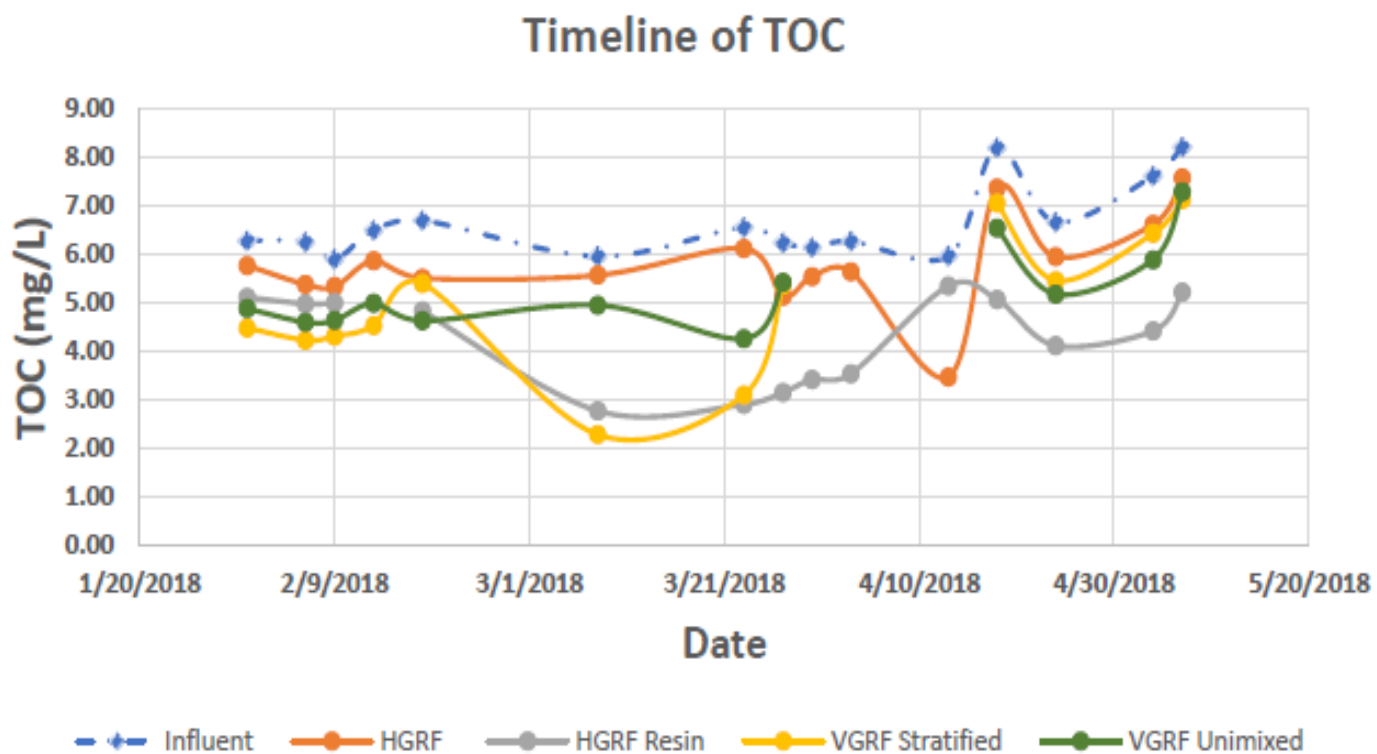


Figure 4.13: Long term TOC data collection between resin VGRFs and HGRFs

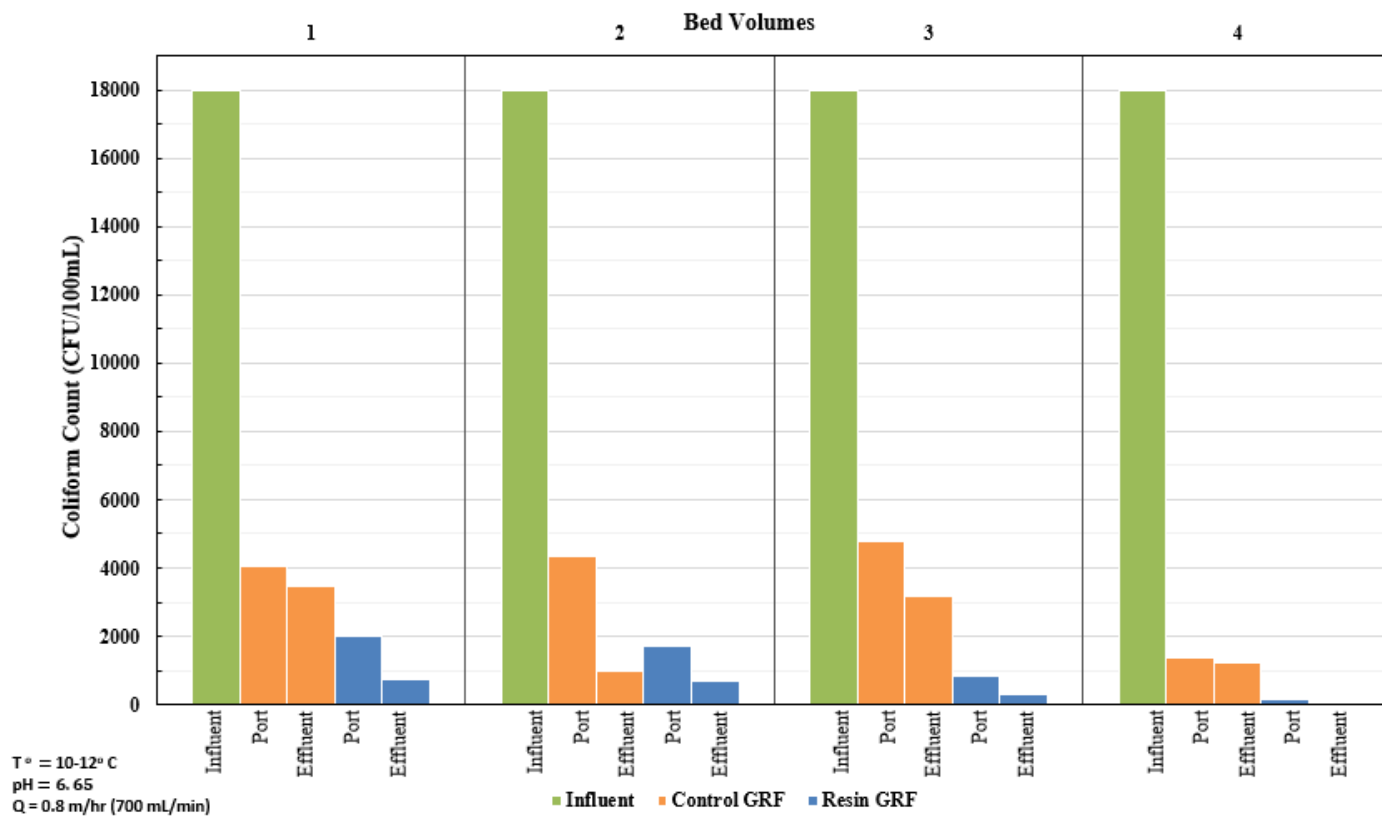


Figure 4.15: *E. coli* loading challenge showing *E. coli* count by distance across Horizontal GRFs

Tables:

| Raw Water Characteristics | | | |
|---|---------|--------------------|-------------------|
| Constituent | Average | Standard Deviation | Post-Modification |
| Dissolved Organic Carbon (mg/L) | 7.8 | ± 1.3 | Unchanged |
| pH | 6.3 | ± 0.5 | 7.3 ± 0.15 |
| Alkalinity (mg/L as CaCO ₃) | 6 | ± 6 | 56 ± 6 |
| Hardness (mg/L as CaCO ₃) | 48 | ± 1.2 | Unchanged |
| Temperature (°Celsius) | 20 | ± 1 | Unchanged |

Table 3.1: Raw Water Characteristics

| Gravel Sieve Analysis | | |
|-----------------------|----------------------|-----------|
| Sieve Opening (mm) | % Retained per Sieve | % Passing |
| 4.76 | 26.4 | 73.6 |
| 2.36 | 43.1 | 30.5 |
| 2.00 | 14.4 | 16.1 |
| 1.41 | 14.4 | 1.8 |
| 1.18 | 1.4 | 0.4 |
| 1.00 | 0.4 | 0 |
| Pan | 0 | - |

Table 3.2: Unimix Gravel Sieve Analysis

| Raw Water Characteristics | | |
|---|------------------|--------------------|
| Constituent | Average Quantity | Standard Deviation |
| Dissolved Organic Carbon (mg/L) | 8.5 | ± 0.86 |
| pH | 6.3 | ± 0.5 |
| Alkalinity (mg/L as CaCO ₃) | 6 | ± 6 |
| Hardness (mg/L as CaCO ₃) | 48 | ± 1.2 |
| Turbidity (NTU) | 2.17 | ± 0.88 |
| Temperature (°Celsius) | 12 | ± 5 |

Table 4.1: Raw Water Characteristics