

Use of Granular Activated Carbon and Carbon Block Filters at  
Municipal and Point of Use Drinking Water Treatment

for Removal of Organics

by

Harsh Satishbhai Ashani

A Thesis Presented in Partial Fulfillment  
of the Requirements for the Degree  
Master of Science

Approved July 2017 by the  
Graduate Supervisory Committee:

Paul Westerhoff, Chair  
Kiril Hristovski  
Otakuye Conroy-Ben

ARIZONA STATE UNIVERSITY

August 2017

## ABSTRACT

Activated Carbon has been used for decades to remove organics from water at large scale in municipal water treatment as well as at small scale in Point of Use (POU) and Point of Entry (POE) water treatment. This study focused on Granular Activated Carbon (GAC) and also activated Carbon Block (CB) were studied.

This thesis has three related elements for organics control in drinking water. First, coagulation chemistry for Alum and Aluminum Chlorohydrate (ACH) was optimized for significant organics removal to address membrane fouling issue at a local municipal water treatment plant in Arizona. Second, Rapid Small Scale Column Tests were conducted for removal of Perfluorinated compounds (PFC), PFC were present in groundwater at a local site in Arizona at trace levels with combined concentration of Perfluorooctanoic Acid (PFOA) and Perfluorooctanesulfonic Acid (PFOS) up to 245 ng/L. Groundwater from the concerned site is used as drinking water source by a private utility. PFC Removal was evaluated for different GAC, influent concentrations and particle sizes. Third, a new testing protocol (Mini Carbon Block (MCB)) for bench scale study of POU water treatment device, specifically carbon block filter was developed and evaluated. The new bench scale decreased the hydraulic requirements by 60 times approximately, which increases the feasibility to test POU at a lab scale. It was evaluated for a common POU organic contaminant: Chloroform, and other model contaminants.

10 mg/L of ACH and 30 mg/L of Alum with pH adjustment were determined as optimal coagulant doses. Bituminous coal based GAC was almost three times better than coconut shell based GAC for removing PFC. Multiple tests with MCB suggested no short circuiting and consistent performance for methylene blue though chloroform removal

tests underestimated full scale carbon block performance but all these tests creates a good theoretical and practical fundament for this new approach and provides directions for future researchers.

## ACKNOWLEDGMENTS

I would first like to thank my advisor Dr. Paul Westerhoff for having faith in me and trusting my academic integrity and capability to handle all these projects. When he first hired me, I couldn't understand completely why he hired me but today when my future employer hired me, I definitely knew why they hired me and I would again like to graciously thank Dr. Westerhoff for being one of the best possible mentor for a new comer in the field of Water Treatment. I would also like to thank my other committee members, Dr. Kiril Hristovski for sharing his insights on my work during the Friday meetings, and Dr. Otakuye Conroy-Ben for sharing her insights about data analysis and Emerging Contaminants. A special thanks to Dr. Shahnawaz Sinha for training me and guiding me with City of Scottsdale project. I would like to thank my colleagues Heuidae Lee, Dr. Ariel Atkinson, Stan Klonowski, Sean Zimmerman, Natalia H, Emmy Pruitt and Marisa Masles. They have me helped me from brainstorming to solving my stupidest doubts. Also, I would like to thank all my family members—Satish Ashani, Jayshri Ashani, Rajvi Ashani and especially my brother as well as my real life mentor Tejas Ashani for his constant support and guidance throughout my life and especially through this adventurous segment of my life

I would especially like to thank Evoqua Water Technologies and City of Scottsdale for giving me an opportunity to work at a full scale water treatment plant and funding the project. I would like to. This project was partially funded by a NSF Engineering Research Center Nanotechnology Enabled Water Treatment (NEWT) and other industry partners like Amway and Carollo Engineers.

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## CHAPTER ONE

### INTRODUCTION

Potable water treatment is divided into three major areas: Municipal Water Treatment, Groundwater Treatment also known as Point of Entry (POE) Water Treatment and Point of Use (POU) Water Treatment (Radovic, 2008). Municipal water treatment is a large scale water treatment for urban communities with influent source water mainly from rivers, lakes and reservoirs, NOM are the most popular contaminant (Radovic, 2008). Groundwater Treatment or Point of Entry treatment is practiced at a medium scale process for individual households or small communities, VOCs and other trace organics are major contaminants (Radovic, 2008). Point of Use water treatment is a small scale treatment for individual houses, commercial buildings and remote areas, Disinfection by-Products (DBP), taste and odor are the major contaminants (Radovic, 2008). POU is the fastest growing field in potable water treatment (Radovic, 2008; Point-of-Use Water Treatment, Forecast to 2020, 2017).

This study focuses on bench scale study in all the major areas of Potable Water Treatment. It focuses on bench scale study for evaluating or predicting the performance of activated carbon based point of use (POU) and point of entry (POE) water treatment systems. It also focuses on bench scale study for predicting the Dissolved Air Flotation (DAF) performance in municipal water treatment. POU systems are used for treating individual sources of water like for drinking, laundry, cooking, bathe etc (EPA POU/POE, 2006 ). Two types of contaminants were considered in this study. Actual contaminants which were present in the groundwater of a contaminated site in Arizona

and in the surface waters of Arizona, and model contaminants which were spiked in the laboratory water sources to create the model test water.

The specific pollutants studied were perfluorinated chemicals (PFC), specifically perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) and High Molecular Weight (HMW) organic compounds, HMW organics are not specific contaminants but they are a class of organic compounds that grow naturally in surface waters and cause problems with the water treatment chain. PFCs were detected at a local groundwater site in Arizona. The utility owning this site uses this groundwater as a drinking water source and they have a granular activated carbon (GAC) system available as a POE water treatment technology for treating basic organic contaminants. The concentration level of PFOA + PFOS was approximately 240 ng/L, which is higher than the 70 ng/L EPA health advisory level (EPA-Health Advisory Level, reference). The utility decided to act on it and planned an investigative pilot scale study, a rapid small-scale column test (RSSCT) was carried out for different kinds of GAC media to simulate the pilot scale study.

The POU water treatment study focused on developing a bench-scale study test for evaluating the performance of a full-scale carbon block filter. The model contaminants used were mainly those popular in drinking water sources like tap water and groundwater like chloroform and arsenic respectively. Also methylene blue was used as a model contaminant in order to set up an initial verification test of the newly developed bench scale apparatus.

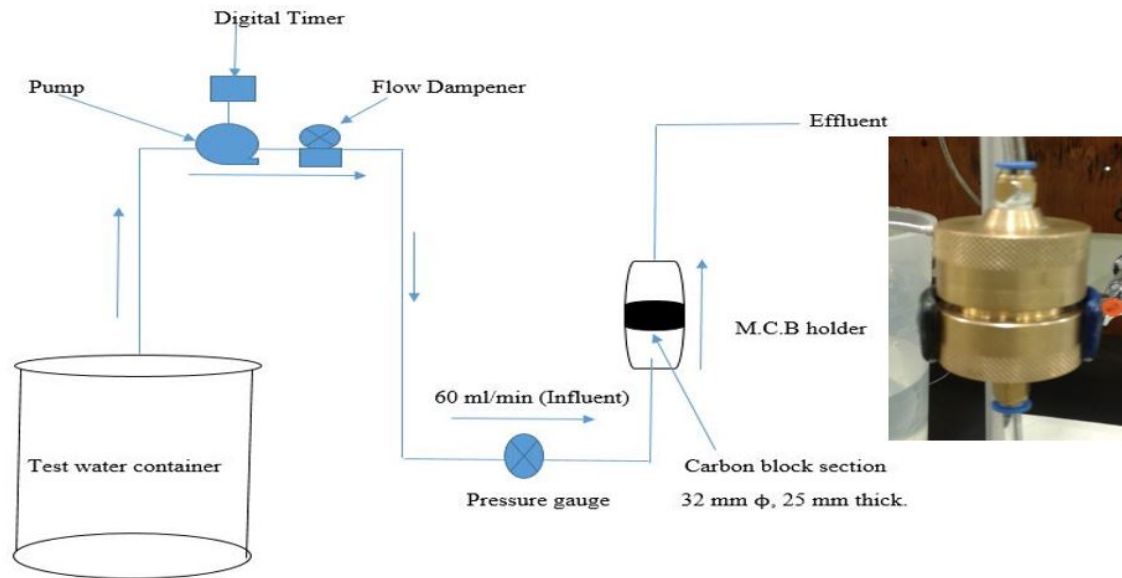


Figure 1.1 Newly Developed Mini Carbon Block Apparatus

The Municipal water treatment study focuses on coagulation enhancement for Central Arizona Project (CAP) water for DAF unit at City of Scottsdale water treatment plant. Increase in irreversible fouling in the membrane filtration unit created a need to optimize Total Organic Carbon (TOC) removal. Specific chapters cover the following topics:

- Chapter Two: Removal of Perfluorinated Compounds from Groundwater
  - RSSCT studies were operated for PFC contaminated groundwater from a local site in Phoenix area of Arizona.
  - Influence of different parameters like type of GAC, size of GAC, influent water concentration and different brands of GAC was analyzed.
  - An optimal option was determined to the utility owning the contaminated groundwater site.



- Chapter Three: Development and Validation of a Bench Scale Carbon Block Filter Performance Test for Organic and Inorganic Point of Use Model Contaminants
  - A method was developed to core out a mini carbon block (MCB) from the full-scale carbon block filter.
  - Design parameters for full scale carbon block were calculated and used to scale down the design parameters for the MCB.
  - Carbon block holder was designed to contain the MCB using PVC materials, a second brass holder was designed considering all the problems faced with PVC holder.
  - A new channeling or short circuiting verification test was developed using methylene blue as a model contaminant.
  - Performance test were carried for chloroform and arsenic and the results were compared with available data of the full-scale performance.
  - Current problems with the test and future recommendations were addressed.
- Chapter Four: Removal of High Molecular Weight Organic Compounds from Surface Water by Coagulation Enhancement
  - Bench scale jar tests were conducted to assess coagulation chemistry for various coagulants at different pH conditions.
  - Characterization of organic matter in the CAP water and the treated effluents was performed using Size Exclusion Chromatography.
  - Key findings were evaluated on pilot and main DAF plants.

- Future steps are discussed.
- Chapter Five: Conclusion
  - A brief summary of the thesis was discussed with major conclusions and future recommendations were suggested.
  - A theoretical fundament was set for the new MCB holder study by addressing the current problems and potential causes.

Organic pollutants occur and create problems at all three parts of drinking water treatment: Municipal Water Treatment, Groundwater Treatment and Point of Use Water Treatment. Figure 1.2 gives an overview of the entire thesis.

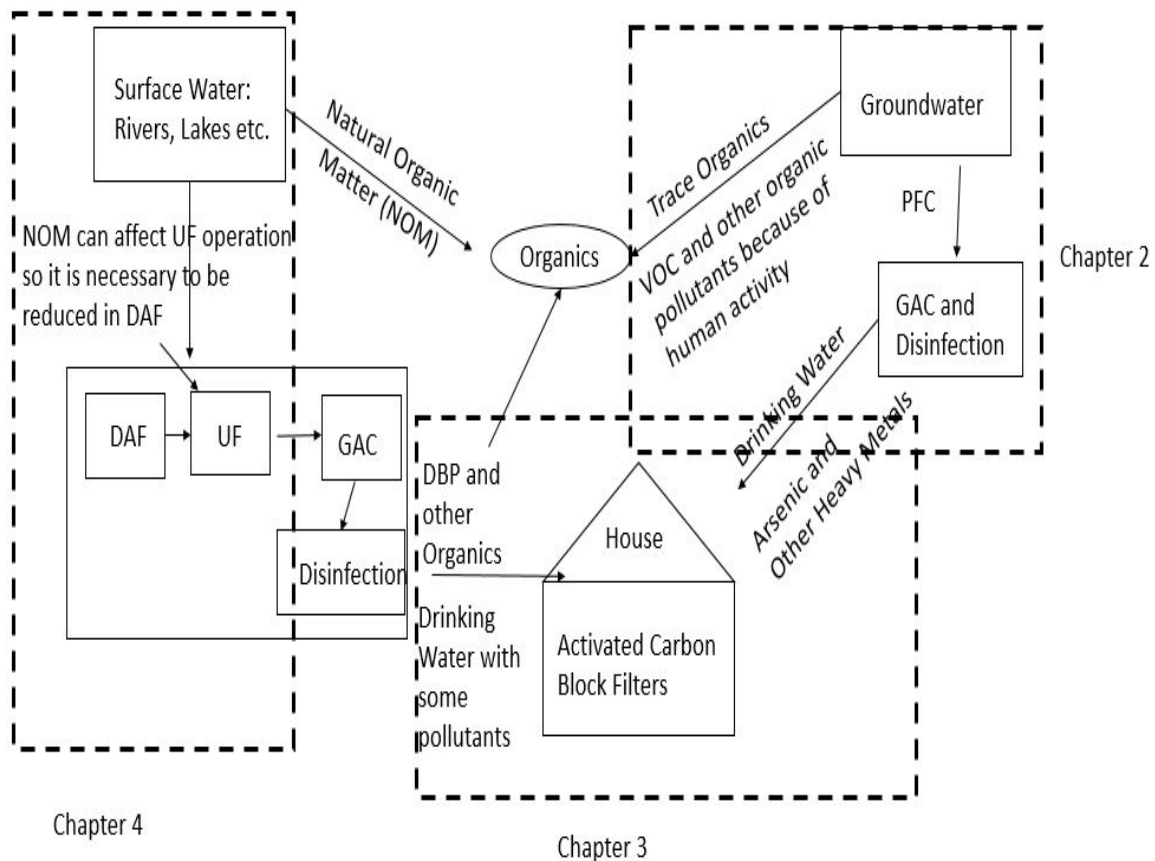


Figure 1.2 Overview of Thesis

## 1.1 Background

### 1.1.1 Point of Use and Point of Entry Water Treatment Systems

The difference between point of use and point of entry lies literally in their name. All the water used for different purposes like drinking, cooking, laundry, bathing, etc. comes from a single source like municipality, private utility, groundwater etc. The point of entry for this source is indeed the POE and the water treatment systems used for that are known as POE water treatment systems (EPA POU/POE, 2006). Now the individual points like drinking, cleaning and others where the water is accessed for that particular use is called POU and the water treatment systems used at that points are called POU water treatment devices. The POU treatment technologies varies from GAC filters, reverse osmosis (RO), ion exchange resins, ultraviolet (UV) etc, the POE treatment technologies cover GAC, aeration and others (EPA POU/POE, 2006). Figure 1.1 (a) describes a typical POU usage and Figure 1.1 (b) describes a typical POE usage.

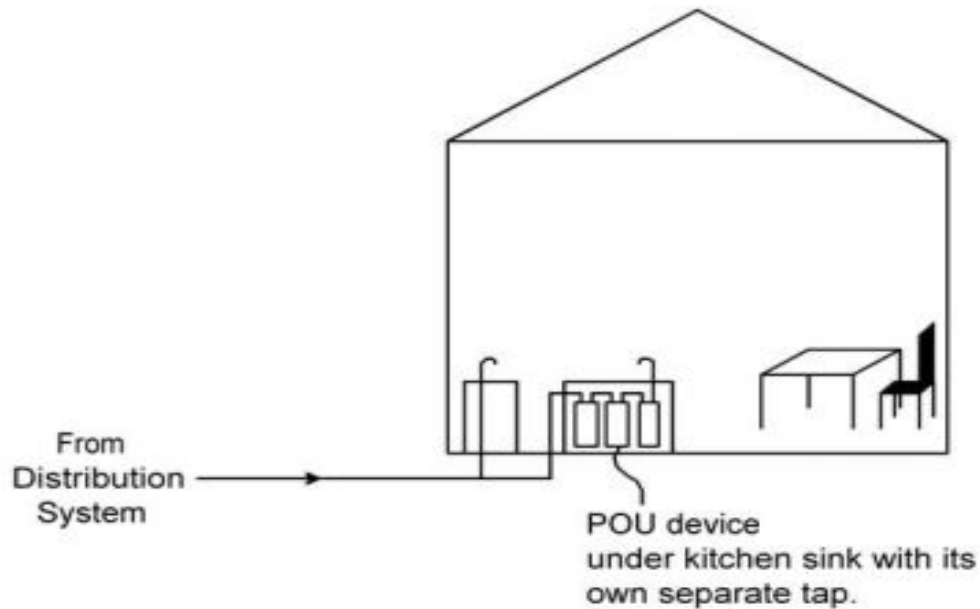


Figure 1.3 (a) Typical POU water treatment usage

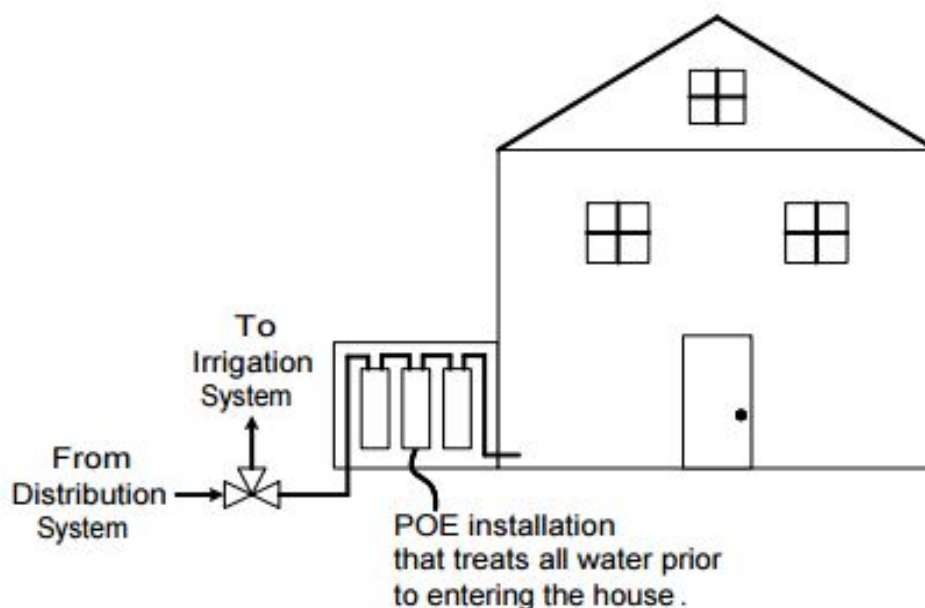


Figure 1.3 (b) Typical POE water treatment usage

### 1.1.2 Perfluorinated Compounds in Environment

Perfluorinated Compounds (PFC) are a massive group of manufactured compounds used in various products, they are used from everyday products to some specific products (Perfluorinated Chemicals, 2016). The uses vary from non-stick cookware, stain repellants, firefighting foam, food packaging, to electronics and aerospace industries. (Perfluorinated Chemicals, 2016; Yu, 2009). They are heavily fluorinated polymers and telomers (Saez, 2007). Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are the major PFC contaminants for water, especially in groundwater (Yao, 2014). Figure 1.2 shows chemical structures of PFOA and PFOS. They are extremely chemically inert hence they are used in firefighting foams but they are also difficult to destroy at the same time, they are hydrophobic as well as lipophobic and hence they are used in stain repellants but it is found that they accumulate in protein

tissues and blood, their surface active properties makes them a good coating material (Darling, 2016).

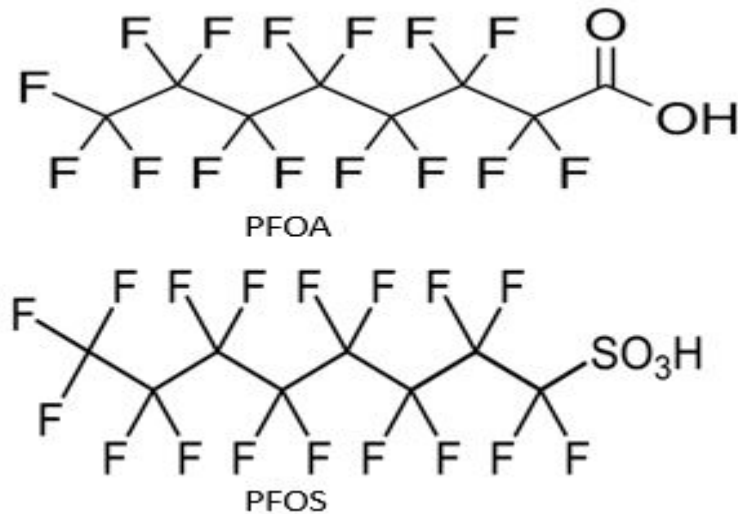


Figure 1.4 PFOA and PFOS structure

### 1.1.3 Engineered Treatment Technologies for PFC

Common water treatment technologies like GAC systems, Reverse Osmosis (RO), Nano Filtration (NF) and Anion Ion Exchange (AIX) resins can be used for treating PFOA and PFOS. GAC is good for removing long-chained Perfluoroalkyl Substances (PFAS), for AIX it varies from resin to resin, RO can treat all PFAS and NF can remove most of them too (Darling, 2016). Figure 1.3 shows an overall idea of the PFOA and PFOS removal across various full scale treatment processes.

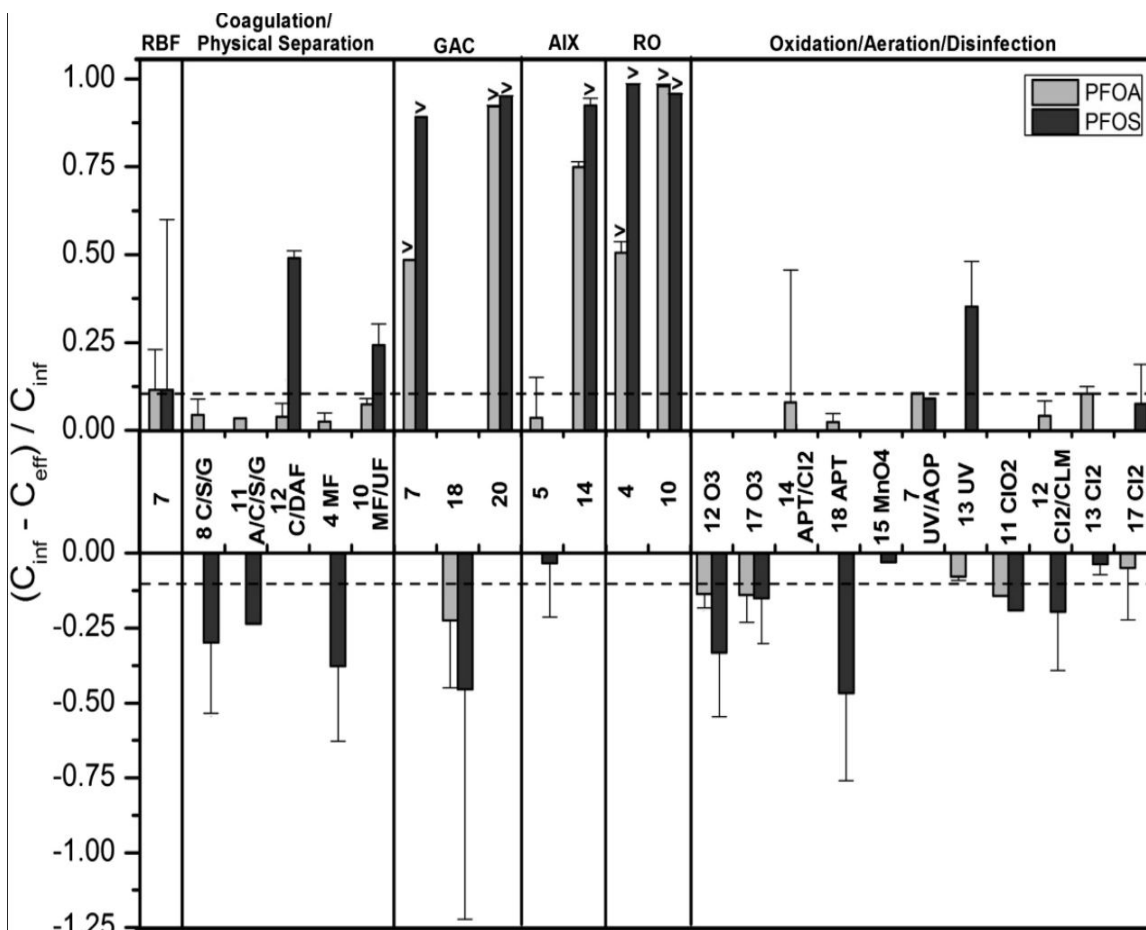


Figure 1.5 Treatment Summary for PFOA and PFOS removal across various Full Scale Treatment Processes (Appleman et al, 2014)

#### 1.1.4 Activated Carbon: History and Application

Activated Carbon is an absorption media which is manufactured from various carbonaceous materials. The most common materials used for making activated carbon for drinking water applications are bituminous coal, lignite coal, coconut shells and wood (Chowdhury et al, 2013). It has been used in drinking water treatment for hundreds of years. It is mainly used for drinking water it is mainly used in two ways: fixed bed reactors with granular activated carbon (GAC) and slurry applications with powdered activated carbon (PAC) (Chowdhury et al, 2013). Since last few decades GAC applications have increased heavily in Point of Use water treatment. Most units are fitted

to a faucet with GAC as the adsorbent. GAC has been replaced with monolithic carbon blocks containing powders or granules held together by a binder (Radovic, 2008). The main advantage of this carbon blocks is the higher surface area that allows rapid adsorption and minimizes the mass transfer limitations (Radovic, 2008). This efficient adsorption has increased the functionality of carbon blocks for various contaminants including some microorganisms.

Activated carbon block filter is one of the most used technology in this industry. Carbon blocks were initially used to target the removal of aesthetics like taste and odor, chlorine residual (Custom Water Filters, 2017). But in the recent years companies have successfully managed to improve the functionality of these carbon block filters for removal of emerging contaminants like disinfection-by-products (DBPs), heavy metals and etc (Custom Water Filters, 2017). There are still few microbial, organic and inorganic contaminants that are not removed by carbon block filters. Reverse Osmosis (RO) membrane technology is a great competitor of carbon block technology (Custom Water Filters, 2017) and it can remove almost everything from the contaminated water. But some primary disadvantages of RO membrane like removal of necessary nutrients and minerals, less percentage of recovery (which means that not all the water passing through RO membrane comes out to be potable, a high percentage of influent is wasted) is encouraging consumers to buy POU devices with carbon block technology only and hence this inspires industry people to research more on improving functionality and efficiency of carbon block filters.

Carbon block filters are made by combining dry ingredients like activated carbon, a binder (mostly a polymer used to bind the activated carbon together in a cylindrical

shape) and sometimes they use a special adsorptive media for heavy metals and other selective contaminants depending on the water quality of a certain region (Custom Water Filters, 2017). There are mainly two techniques used in manufacturing carbon blocks: Extrusion and Compression molding. In Extrusion the ingredients mixture (activated carbon, binder and other media) is forced through a die to form a long continuous block which are trimmed to the desired size (Custom Water Filters, 2017). Compression carbon blocks are made individually in a mold under tremendous pressure and high heat and then trimmed to the desired size (Custom Water Filters, 2017). Considering all those variables, an industry creates a bunch of prototypes for various composition of media, different types of media, special types of media, etc. Carbon block filters should at least meet parameters set by environmental agencies like Environmental Protection Agency (EPA), World Health Organization (WHO) in order to provide safe waters, but these parameters don't specify much about emerging contaminants, heavy metals and etc. To provide the safest water and best performance a POU device should be able to gain certifications like NSF-42 and NSF-53 (NSF), NSF-42 and 53 are created to set the benchmark for evaluating safety and integrity of residential water filters. NSF-42 is for aesthetic or non-health related contaminants like chlorine, taste, odor and particulates, NSF-53 is for health related contaminants like cryptosporidium, lead, volatile organic contaminants (VOCs) and asbestos (Residential Drinking Water Treatment Standards, 2017).

To achieve these certifications, tests with benchmark operating conditions are to be performed, for a single test it requires at least 6000 to 12000 liters of test water depending from companies to companies. It would produce the same volume of waste in most of the cases. So basically a huge amount of water is treated to use it for a water



treatment performance test which again produces waste which has to be treated again. Not only water but factors like energy and cost of chemicals required for making the test water and handling of those hazardous test waters are extreme. Unfortunately there is no bench scale test for the carbon block filter performance unlike Rapid Small Scale Column Test (RSSCT) for GAC bed contactors, or at least it is not published or openly known to the researchers.

### **1.1.5 Central Arizona Project**

The Central Arizona Project (CAP) is a 336 mi diversion canal in Arizona which diverts water from the Colorado river into central and southern Arizona (Central Arizona Project, 2017). About two-thirds of Scottsdale's water supply comes from CAP (Water Supply, 2017). Figure 1.4 and 1.5 shows the map of CAP network and aerial photo of CAP.



Figure 1.6 CAP network (Central Arizona Project, 2017)



Figure 1.7 Aerial phot of CAP (Central Arizona Project, 2017)

### **1.1.6 Dissolved Air Flotation**

Dissolved Air Flotation (DAF) has been used in drinking water industry for many years as an alternative for sedimentation (Edzwald, 2010). In DAF the coagulation and flocculation takes place first and then the coagulated water is saturated and flown into the DAF basin at atmospheric pressure where the pressurized air turns into bubbles and rises to the surface. These bubbles carry the flocs with them which are removed by scrapers from the surface. Whereas in sedimentation the flocs settle down. Figure 1.6 shows process flow chart for conventional DAF plant and the DAF tank showing the contact and separation zones.

## DISSOLVED AIR FLOTATION PLANT

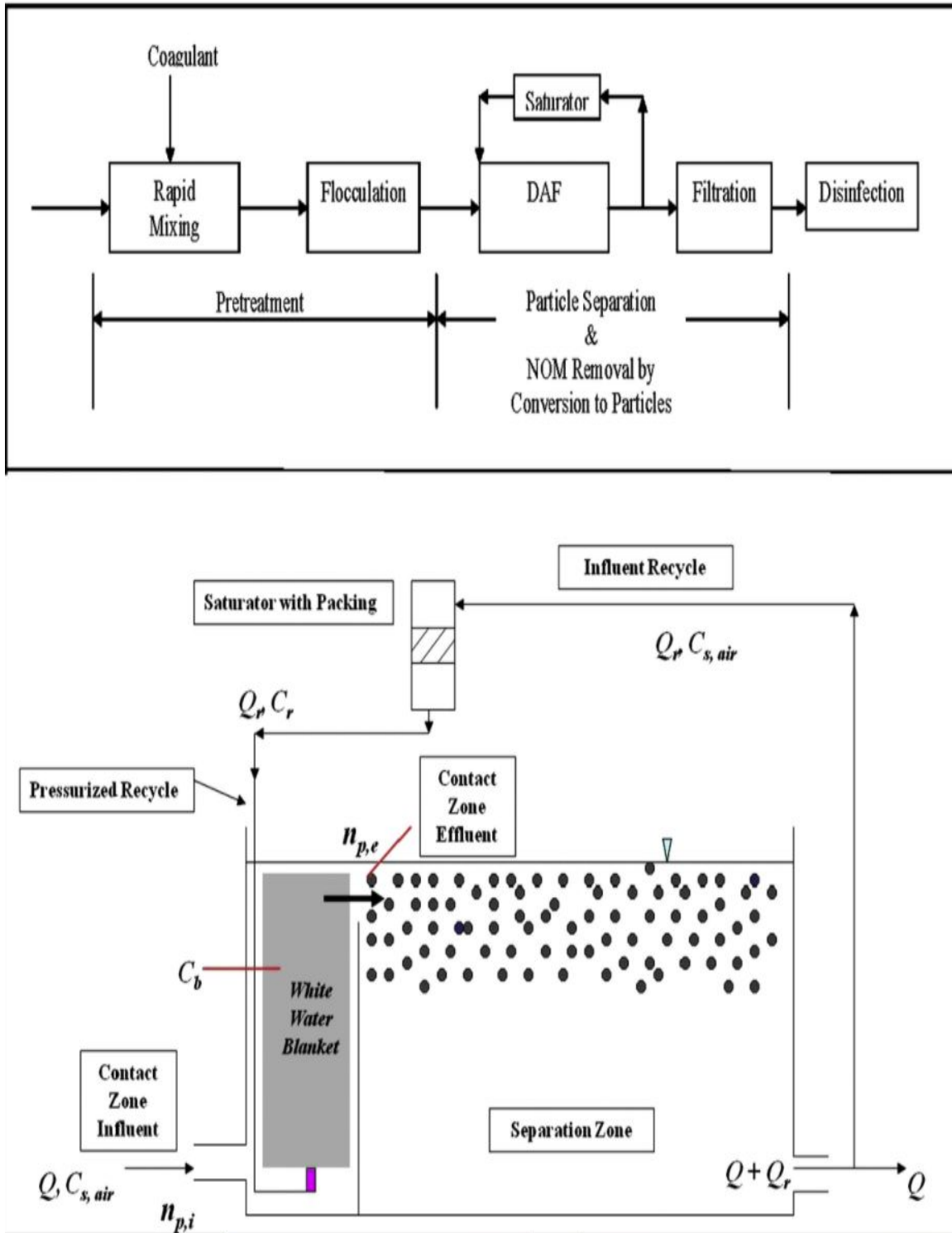


Figure 1.8 Process flow chart for conventional DAF plant and bottom: DAF tank showing the contact and separation zones (Edzwald, 2010).

## 1.2 Thesis Objectives

The goal of this thesis is to develop a new testing protocol for a bench scale approach for POU water treatment and gain bench scale experience in all stages of drinking water treatment. Specific objectives of each chapter are as follows:

- Chapter 2: Perform Rapid Small Scale Column Tests for PFC removal from an impacted groundwater site in Arizona to evaluate the performance of different GAC media under different conditions like different adsorbent particle size, varying influent concentrations.
- Chapter 3: Develop a new bench scale testing protocol to evaluate the performance of full-scale activated carbon block filters and validate it for point of use model contaminants like Chloroform and Arsenic.
- Chapter 4: Conduct bench-scale jar tests to find the optimum coagulation chemistry for CAP water and characterize organic matter to monitor the removal of HMW organics from CAP water. Imply those findings on DAF pilot and main plant and compare the results with jar tests findings.
- Chapter 5: Summarizes key findings, draws conclusions, provides recommendations for utilities and provides directions for future research.

## CHAPTER TWO

# REMOVAL OF PERFLUORINATED CHEMICALS FROM GROUNDWATER USING GRANULAR ACTIVATED CARBON

### 2.1 Introduction

Perfluorinated chemicals (PFC) are present in some groundwaters within Arizona. Work at a private utility site with Carollo Engineers was evaluated for the effectiveness of different types of GAC to remove these PFCs. The combined concentration of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) were detected ( $n=3$ ) to  $235 \pm 10$  ng/L in well site A,  $114 \pm 8$  ng/L in well site B and  $38 \pm 1$  ng/L on well site C. Well site A, B and C are three different well locations at multiple sites (approximately 10-15 miles apart). Water from this site is further treated and consumed as drinking water. Well site A and B exceed the health advisory level set for PFOA and PFOS by EPA (70 ng/L) whereas well site C had PFOA and PFOS concentrations under the health advisory level.

The utility handling the contaminated site decided to conduct a pilot scale investigative study using granular activated carbon (GAC) bed contactor. There were different types and brands of GAC available with the utility and to assess the performance of all those media at a pilot scale was not feasible. So a bench scale study was required to assess the performance of all types of GAC media. Rapid small-scale column tests (RSSCT) were performed on the contaminated groundwater to simulate the performance of the 1.58 MGD pilot scale GAC bed contactor.

RSSCTs were performed to evaluate PFC removal under different conditions like GAC source, influent concentrations, adsorbent particle size, different operating conditions. The results are presented in the form of breakthrough curves.

## **2.2 Material and methods**

### **2.2.1 Rapid Small Scale Column Tests (RSSCT)**

The rapid small-scale column test was developed as an approach to design a pilot scale GAC bed contactor (Crittenden et al., 1987). RSSCT requires less amount of time and small volume of water to predict the performance of a full-scale test, also there is no requirement of isotherm studies when using RSSCT (Crittenden et al., 1987). There was no modeling involved in this study, existing models from previous studies were used. In this study a dispersed-flow, pore-surface-diffusion model (DFPSDM) model was used as it has been proved in the previous studies that this model gives the best relation between full-scale and small-scale column test (Crittenden et al., 1987; Westerhoff et al., 2005). DFPSDM includes mechanisms like advective flow; axial dispersion and diffusion; liquid phase mass transfer resistance; surface and pore diffusion (J. Crittenden et al., 1987). Three assumptions are made while developing scaling equations to obtain similarity between full-scale and small-scale tests (Crittenden et al., 1986, 1987, 1991; Westerhoff et al., 2005). Boundary conditions for both the scales should occur at the same dimensionless conditions in the dimensionless differential equations and dimensionless parameters for the both the scales should be equal in the dimensionless differential equations, also no change in mechanism should occur while reducing the size of the test (Westerhoff et al., 2005). The dimensionless scaling equations obtained from previous

study were used to scale down the full-scale column to RSSCT column (Westerhoff et al., 2005; Lesan, 2015).

$$\frac{D_{SC}}{D_{LC}} = \frac{d_{p,SC}}{d_{p,LC}} \quad (2.1)$$

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[ \frac{d_{p,SC}}{d_{p,LC}} \right]^2 \quad (2.2)$$

Equations (2.1) and (2.2) are used for constant diffusivity (CD) scaling approach which means that diffusivity coefficient  $D_L$  are independent of particle radius (Westerhoff et al., 2005). There is also another scaling approach which is proportional diffusivity (PD), in past research it has been proved that PD gives a more valid performance prediction for full-scale rather than CD, especially for bulk organics (Westerhoff et al., 2005), but PD requires a larger volume than CD and more number of days than CD, also CD can be used for trace organics in groundwater without significant competing adsorbates (Crittenden et al., 1986; Westerhoff et al., 2005). Previous studies recommend CD approach for trace organics (Anumol et al., 2015), mainly because of low molecular weight of PFCs and weak polarity (Redding et al., 2009). Hence equation (2.2) can be used to calculate the empty bed contact time (EBCT) using the particle diameter (d).

$$\frac{V_{F,SC}}{V_{F,LC}} = \frac{R_{P,LC}}{R_{P,SC}} \quad (2.3)$$

$$Re = \frac{V \times \rho_L \times d_p}{\mu} \quad (2.4)$$

$$Sc = \frac{\mu}{D_L \times \rho_L} \quad (2.5)$$

$$Re \cdot Sc = \frac{V \times \rho_L}{D_L} \quad (2.6)$$

Equations (3) – (6) are used to design RSSCT column. Here  $V_{F,SC}$  and  $V_{F,LC}$  are the hydraulic loading rates for small-scale and large-scale column respectively. R is the radius of the particle. Reynolds number (Re) and Schmidt number (Sc) can be calculated from the liquid diffusivity ( $D_L$ ), dynamic viscosity ( $\mu$ ) and density ( $\rho$ ). The product of Re and Sc gives a significant insight on the dispersion effects, if the product value lies between the range of 200-200,000, then dispersion effects are negligible. The design parameters calculated for RSSCT and the pilot scale are tabulated in Table 2.1 Equations 2.3-2.6 were used to obtain some parameters in Table 2.1.

Table 2.1 Design Parameters for RSSCT and Pilot-Scale Column

| <b>Design Parameter</b>      | <b>Pilot-Scale Column</b> | <b>RSSCT (CD)</b> |
|------------------------------|---------------------------|-------------------|
| Column Diameter (cm)         | 365.76                    | 0.4               |
| Particle Diameter (mm)       | 1                         | 0.10              |
| Empty Bed Contact Time (min) | 4.60                      | 0.04              |
| Reynolds-Schmidt Number      | 11736                     | 6023              |
| Hydraulic Loading Rate (m/h) | 23.8                      | 127               |
| Bed Length (cm)              | 150                       | 9                 |
| Bed Volume (mL)              | 17052405                  | 1.13              |
| Flow Rate (mL/min)           | 4163953                   | 26.6              |
| Bed Volumes passed through   | ----                      | 120000            |

### 2.2.2 Groundwater Sampling and Storage

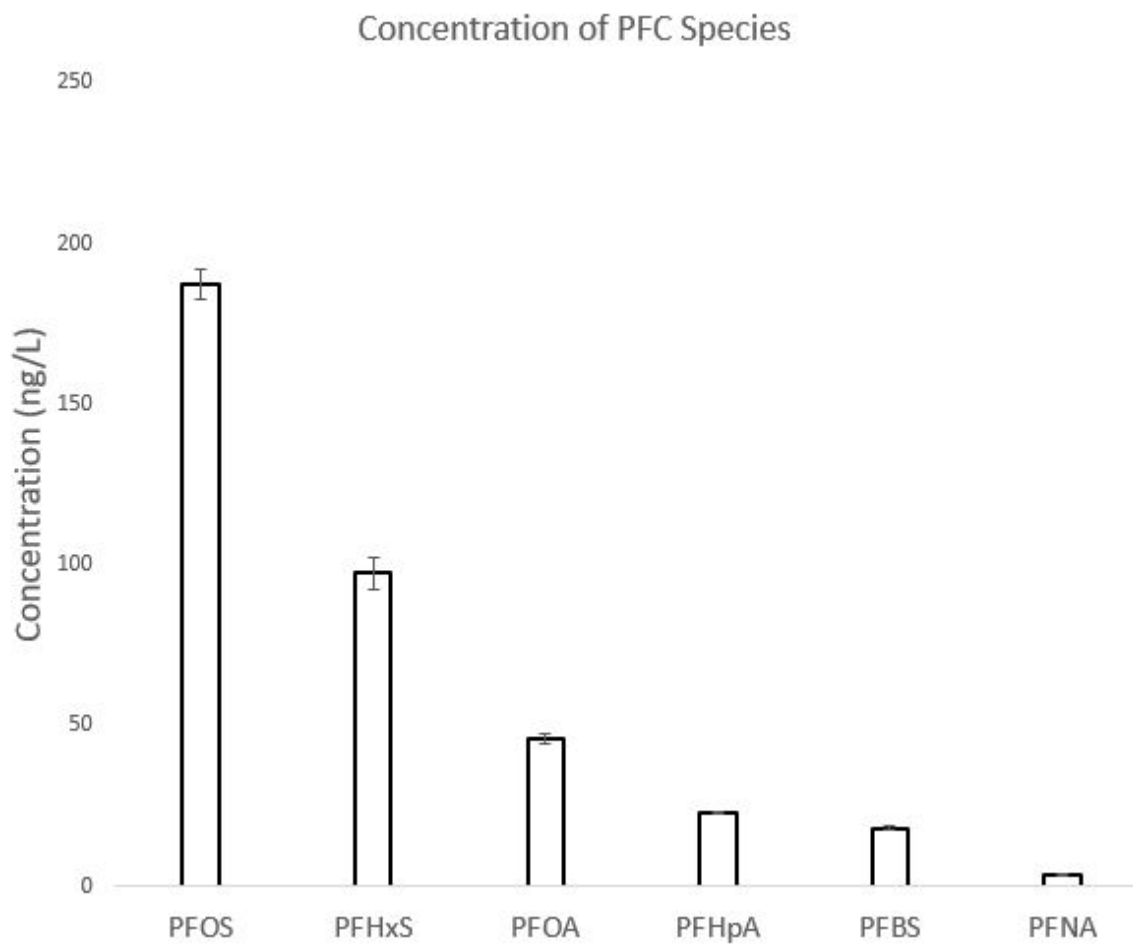
Groundwater was collected from well site by the industry partner using a submersible pump. Water was flushed for two hours to bring down the turbidity and then collected and transported to ASU using a 55 gallon drum. Table 2.2 shows the water quality of the groundwater. Drums were unloaded at ASU and were stored in the same drums at ambient temperature while the columns operated. There were no adjustments made to the water. Concentration of PFC species is shown in Figure 2.1.



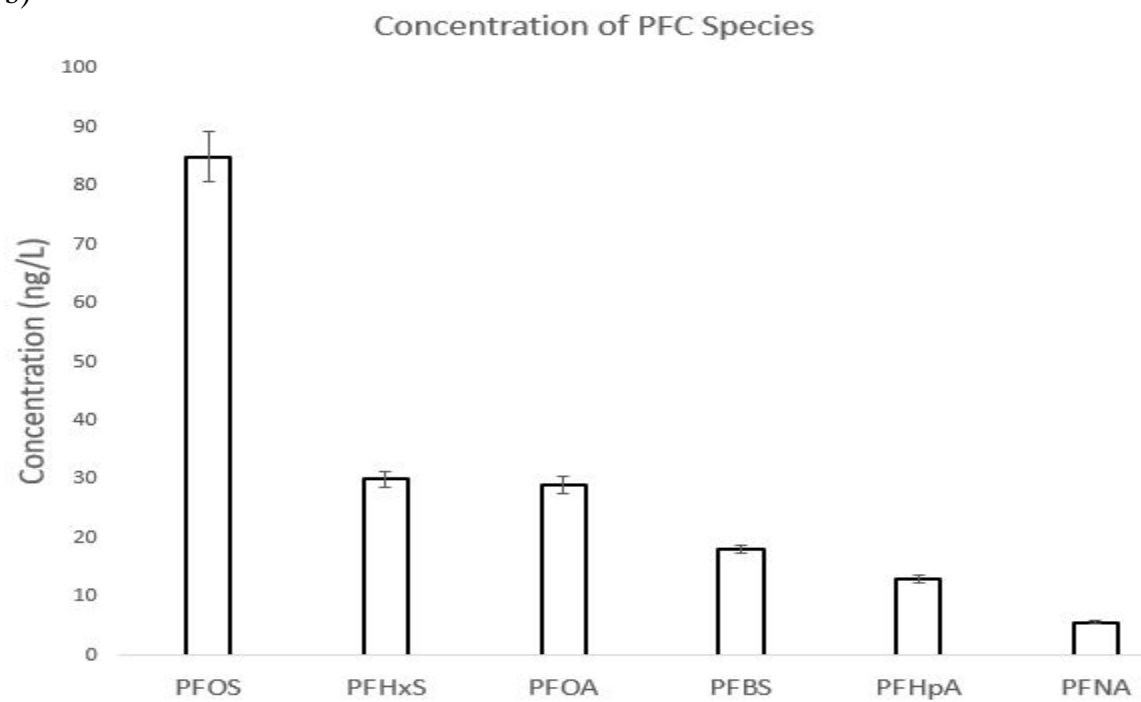
Table 2.2 Groundwater Quality

| Parameter                                | Well site A  | Well site B | Well site C |
|--|--------------|-------------|-------------|
| pH                                       | 7.45         | 7.56        | 7.68        |
| Conductivity ( $\mu\text{S}/\text{cm}$ ) | 884          | 964         | 1162        |
| Temp ( $^{\circ}\text{C}$ )              | 24.6         | 24.6        | 23.8        |
| TOC (mg/L)                               | 0.880        | 0.95        | 0.7         |
| UV-254                                   | 0.008        | 0.01        | 0.01        |
| Turbidity                                | 0.26         | 0.4         | 0.2         |
| PFOA+PFOS concentration (ng/L)           | $235 \pm 10$ | $114 \pm 8$ | $38 \pm 1$  |

a)



b)



c)

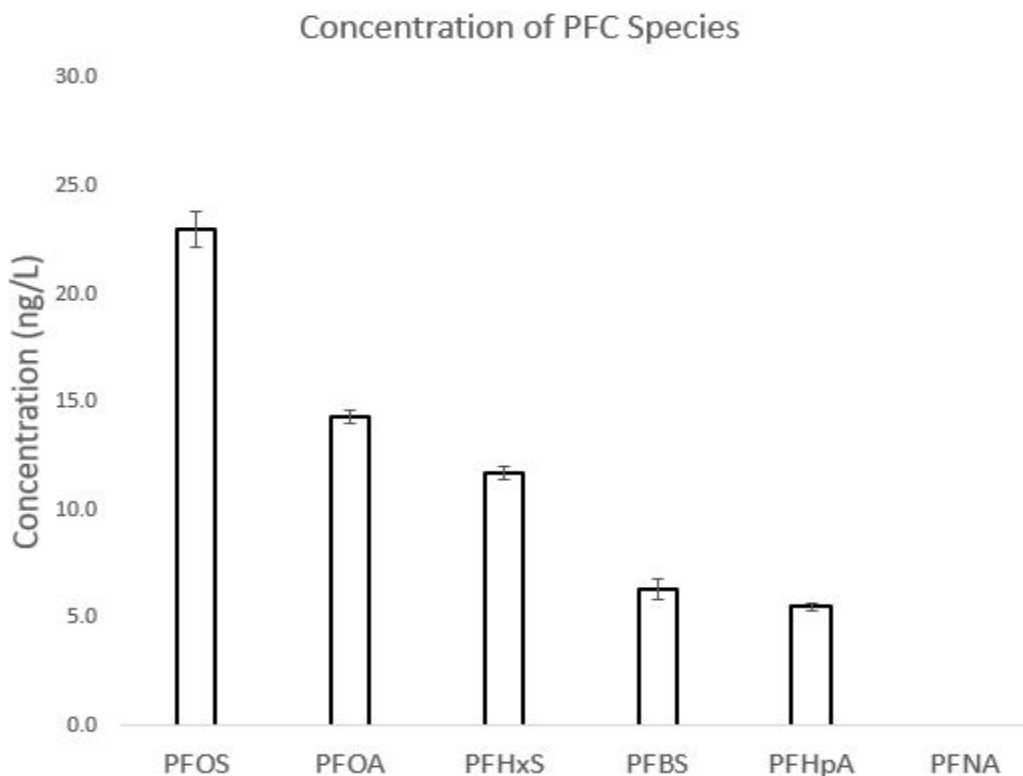


Figure 2.1 Concentration of PFC Species: a) Well Site A, b) Well Site B, c) Well Site C

### 2.2.3 GAC media preparation

There were total three types of GAC used which were GAC-A (AquaCarb 1230 AWC from Evoqua), GAC-B (Calgoncarbon Filtrasorb 400) and GAC-C (Norit GAC 400 M-2194). GAC-A is a coconut shell based activated carbon and GAC-B and GAC-C are bituminous coal based activated carbons. All these media were provided in the company container as dry with particle sizes ranging from particle sizes ranging from 1.68 mm to 0.595 mm (mesh No. 12×30). GAC-B was also provided in a smaller particle size (U.S mesh No. 100×140). All the media (mesh No. 12×30) were crushed to U.S mesh 140×170, for which the particle size ranges from 0.105 mm to 0.088 mm. The media was initially crushed using a coffee grinder for few seconds and then it was crushed using a mortar and pestle and wet sieved with deionized water through the mesh

140×170. The media retained on U.S mesh 140 were collected in 50ml HDPE vials.

Figure 2.2 shows the apparatus used for crushing the media and storing it.



Figure 2.2 GAC media preparation apparatus

#### 2.2.4 RSSCT Column Packing and Operating

All the RSSCT columns were constructed of Polyethylene tubing (ACE hardware). The columns were set on a column stand with the help of scotch tape. The columns (0.5 cm) were then connected with Teflon quick connects on the top and the bottom. The unconnected ends of the quick connectors were then connected with influent and effluent tubing (Polyethylene tubing). The columns were then filled with deionized water and packed with glass wool for a height of 5cm. The columned were filled with deionized water in order to avoid any bubbled in the column. Glass wool prevents the media from flushing down with the effluent. The glass wool was soaked in the deionized water and then packed in the column using a smaller size tubing. The glass wool had to be packed very compactly to avoid any loss of GAC media. Then the crushed and sieved

GAC media was packed in the column above the glass wool using a Pasteur pipette (VWR). The depth of the GAC media bed was adjusted as per the design of that particular RSSCT column test. After the media is settled, the columns are operated with deionized water to check for any operating problems. The deionized water is pumped into the columns using FMI piston pumps (FMI QG-150) for top to bottom flow and the flow pattern is consistent for all RSSCT columns, also the deionized water is used to adjust the piston pump flowrate as required by the RSSCT design. Then the influent tubing are attached with heavy stainless steel weights and inserted into the 55 gallon drum containing the groundwater. Effluent tubing were inserted into a waste container to collect all the discharge. Figure 2.3 (a) shows the sketch of the RSSCT design and Figure 2.3 (b) shows the actual RSSCT design for one of the columns.

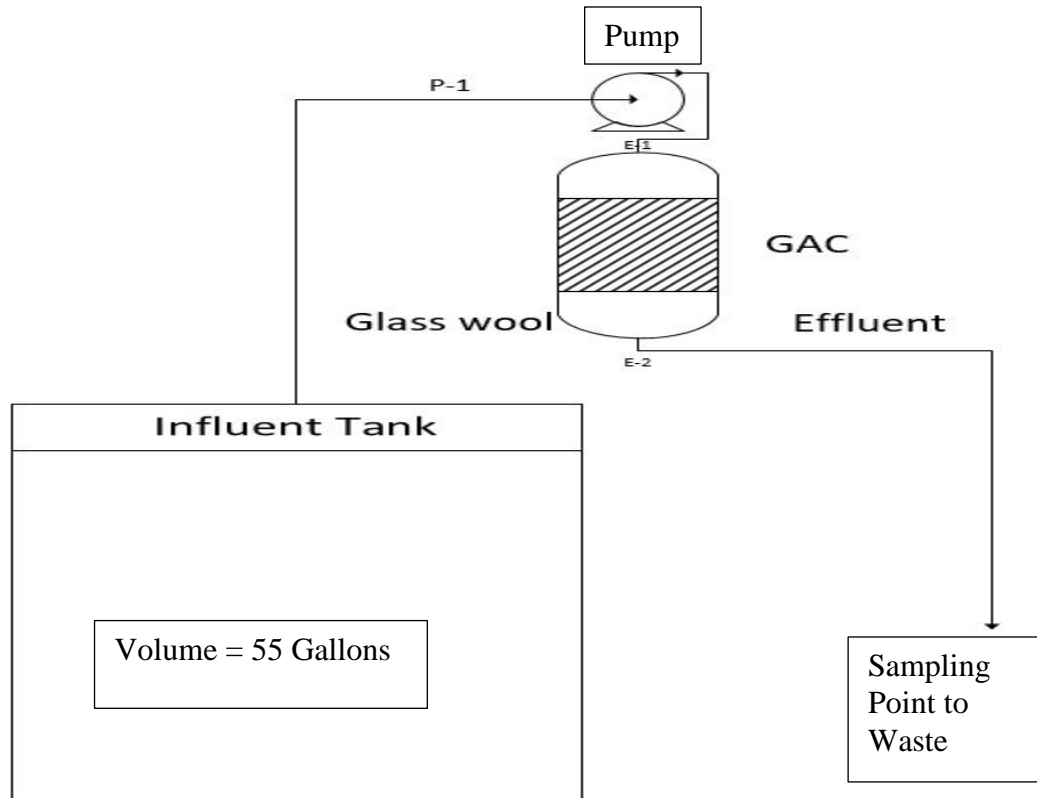


Figure 2.3 (a) General RSSCT sketch



Figure 2.3 (b) RSSCT column used for GAC-A

### 2.2.5 Operational Parameters for different RSSCT

RSSCT-1 was operated for GAC-A (U.S mesh No. 140×170) and well site A, RSSCT-2 was operated for GAC-B (U.S mesh No. 100×140) for well site A and B. RSSCT-3 was operated for GAC-B (U.S mesh No. 140×170) and GAC-C (U.S mesh No. 140×170) for well site A. Here there was lead and lag column design introduced, which basically means that the influent passes through lead column first, then the lag column and then to the effluent waste container, so the lag column has twice the EBCT of lead column. This is a concept used in industry to have a longer period of operation than just a single column. Also as these two columns run in series, so one of them can be taken offline for maintenance. Another advantage of using this concept is that when the lead column has reached a certain level of saturation, the lag column still has much higher

absorbance capacity remaining and then they can switch the lead to lag and vice versa to get the contaminant removal for a longer period. Figure 2.4 shows the visual for lead and lag column setup. RSSCT-4 was operated for GAC-B and for well site C. Table 2.1 shows the design parameters for RSSCT-1 and Table 2.3 shows the design parameters for RSSCT-2,3 and 4.

Table 2.3 Design parameters for RSSCT-2,3 and 4.

| Design Parameter             | Pilot-Scale Column | RSSCT-2 | RSSCT-3 (lead) | RSSCT-4 (lead) |
|------------------------------|--------------------|---------|----------------|----------------|
| Column Diameter (cm)         | 365.76             | 0.4     | 0.4            | 0.4            |
| Particle Diameter (mm)       | 0.84               | 0.11    | 0.1            | 0.1            |
| Empty Bed Contact Time (min) | 4.60               | 0.07    | 0.06           | 0.06           |
| Reynolds-Schmidt Number      | 9860               | 4324    | 3779           | 4724           |
| Hydraulic Loading Rate (m/h) | 23.8               | 83.5    | 79.7           | 99.6           |
| Bed Length (cm)              | 150                | 10      | 8              | 10             |
| Bed Volume (mL)              | 17052405           | 1.26    | 1              | 1.26           |
| Flow Rate (mL/min)           | 4163953            | 17.5    | 16.7           | 20.9           |
| Bed Volumes passed through   | ----               | 142000  | 211000         | 230000         |

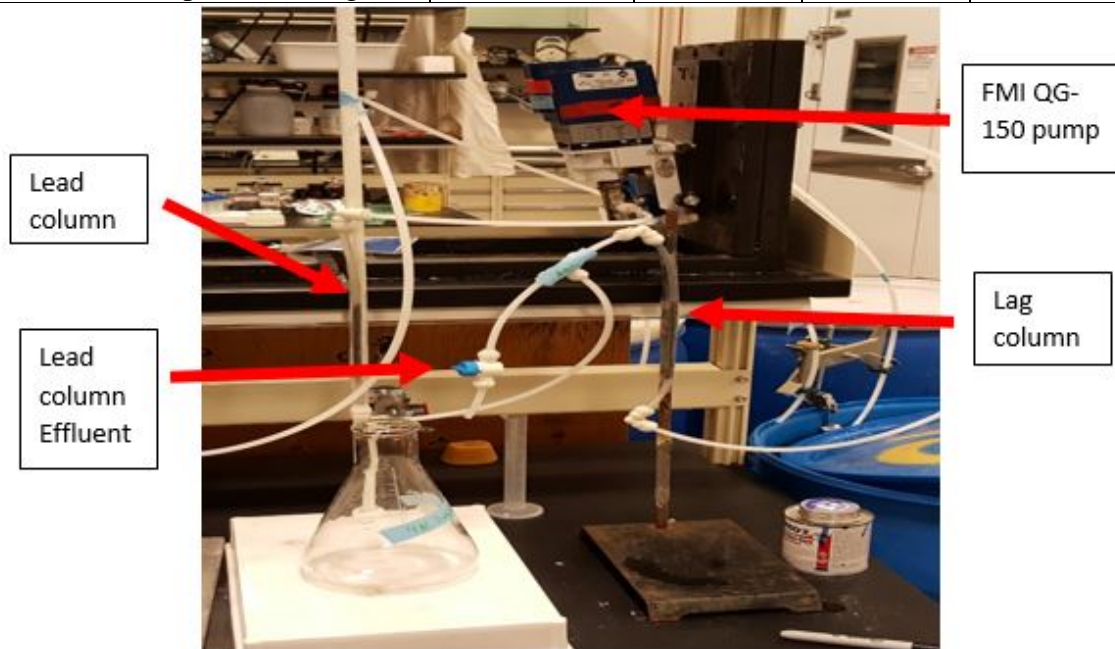


Figure 2.4 Lead and Lag RSSCT column setup

## 2.2.6 Sampling and Analysis

Effluent and influent water samples were collected for Perfluorinated Chemicals (PFC) analysis, Turbidity analysis, UV-254 analysis and Total Organic Carbon (TOC) analysis. Water samples for PFC analysis were collected in 400mL polypropylene sample bottles with Prizma tri set as preservative (provided by the commercial laboratory), water samples were collected in 50mL Falcon Conical Centrifuge Tubes (Fischer Scientific) for Turbidity, UV-254 and TOC. Samples were sent to a commercial drinking water quality Legend Technical Services laboratory in Arizona for PFC analysis. It followed the EPA method 537 for determination of selected Perfluorinated Alkyl Acids in drinking water by solid phase extraction and liquid chromatography/tandem mass spectrometry (LC/MS/MS), (EPA research methods, 2017). It gave characterization for six different compounds of PFC, which are Perfluorobutanesulfonic acid (PFBS); Perfluoroheptanoic acid (PFHpA); Perfluorohexanesulfonic acid (PFHxS); Perfluorononanoic acid (PFNA); PFOS and PFOA, but only PFOA and PFOS were the contaminants of concern in this study. Turbidity was analyzed using a portable HACH 2100P Turbidimeter. UV-254 was analyzed using HACH DR-5000 spectrophotometer (DR 5000 UV-Vis Spectrophotometer, 2017) and TOC was analyzed using Shimadzu TOC-VCSH analyzer (Total Organic Carbon Analysis, 2017).

## **2.3 Results and Discussion**

### **2.3.1 Breakthrough Curves**

Breakthrough curves shows concentration profile of the effluent throughout the duration of a column test. It gives the qualitative as well as quantitative idea about the performance of the GAC media in terms of PFOA and PFOS removal. Breakthrough curves are also plotted for UV-254, TOC and turbidity but they are not that reliable for



qualitative data related to GAC media performance as the PFC concentration/organic concentration was in trace levels and UV-254 and TOC are not a great representation for PFOA and PFOS at such trace levels. Turbidity gives an overall idea about the dissolved solids and dirt particles removal during the test, it would also go high during the test if there is any kind of problem with the column operation.

The independent parameters for breakthrough curve are concentration (PFOA and PFOS concentration, UV-254 and TOC) on one axis and the volume of water passed through the column on the horizontal axis. The volume of water passed through the column is usually presented as bed volumes (BV). One bed volume gives the volume of water passed through the packed media bed. Bed volumes can be converted to the volume of water passed through the column simply by multiplying the BV to the volume of single bed volume, it can also show the amount of time the columns were operated by simply multiplying the EBCT with the BV.

### **2.3.2 RSSCT-1 Breakthrough curves**

RSSCT-1 was run for GAC-A media and for the well site A. It was run for approximately 70,000 BVs. Figure 2.5 gives breakthrough curves for PFOA + PFOS concentration and UV-254 and TOC.

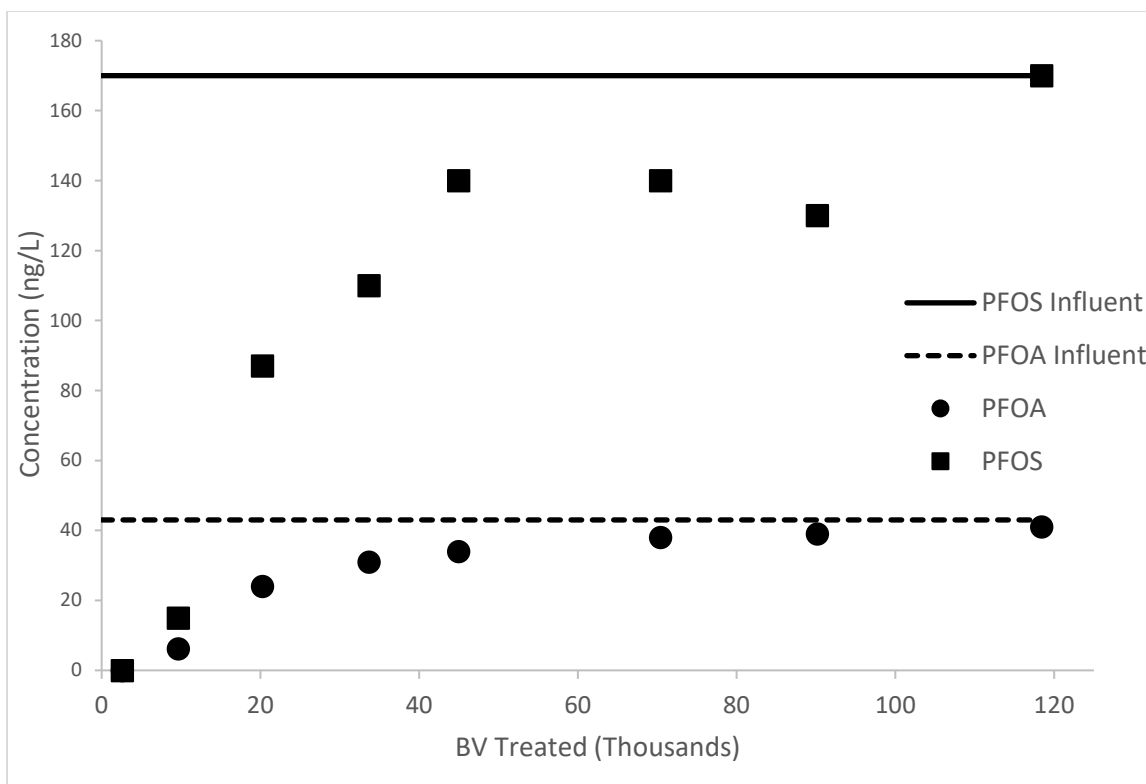


Figure 2.5 (a) Total PFOA and PFOS Breakthrough Curve for GAC-A for well site A

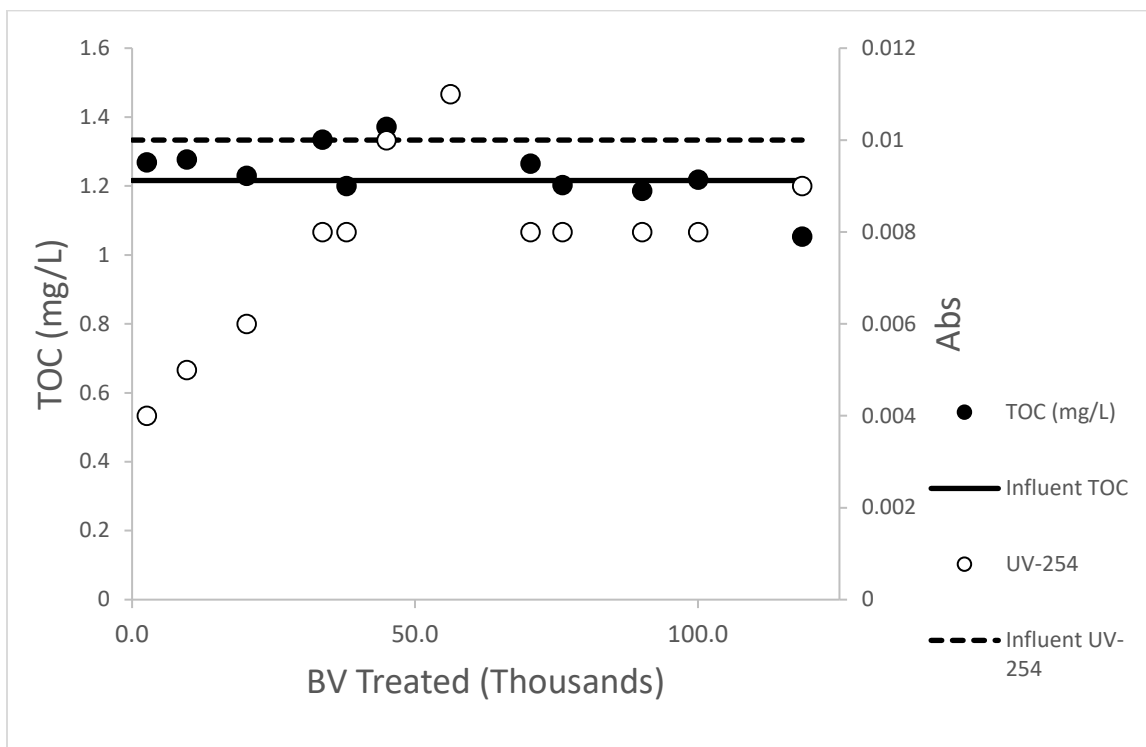


Figure 2.5 (b) TOC and UV-254 Total Breakthrough Curve for GAC-A for well site A

Complete breakthrough (> 95% of Influent) was achieved near 120,000 BVs and the health advisory level breakthrough was achieved near 15000 BVs. TOC is not removed and all other tests also show similar TOC concentration profile. UV-254 breakthrough occurs within 30000 BVs suggesting a minor component of TOC was adsorbate.

### **2.3.3 RSSCT-2 Breakthrough Curves for GAC-B and Well Site A and B**

RSSCT-2 was run for GAC-B and for well site A and B. RSSCT-2 run for well site A is a direct comparison for the performance of coconut shell based (GAC-A) and bituminous coal based (GAC-B). In Figure 2.6 (a) we can see that there was almost 100 % removal of PFOA and PFOS throughout the complete run. Figure 2.6 (b) shows the direct comparison of GAC-A and GAC-B for well site A. Figure 2.6 (c) shows the TOC and UV-254 breakthrough for RSSCT-2 Well site A.

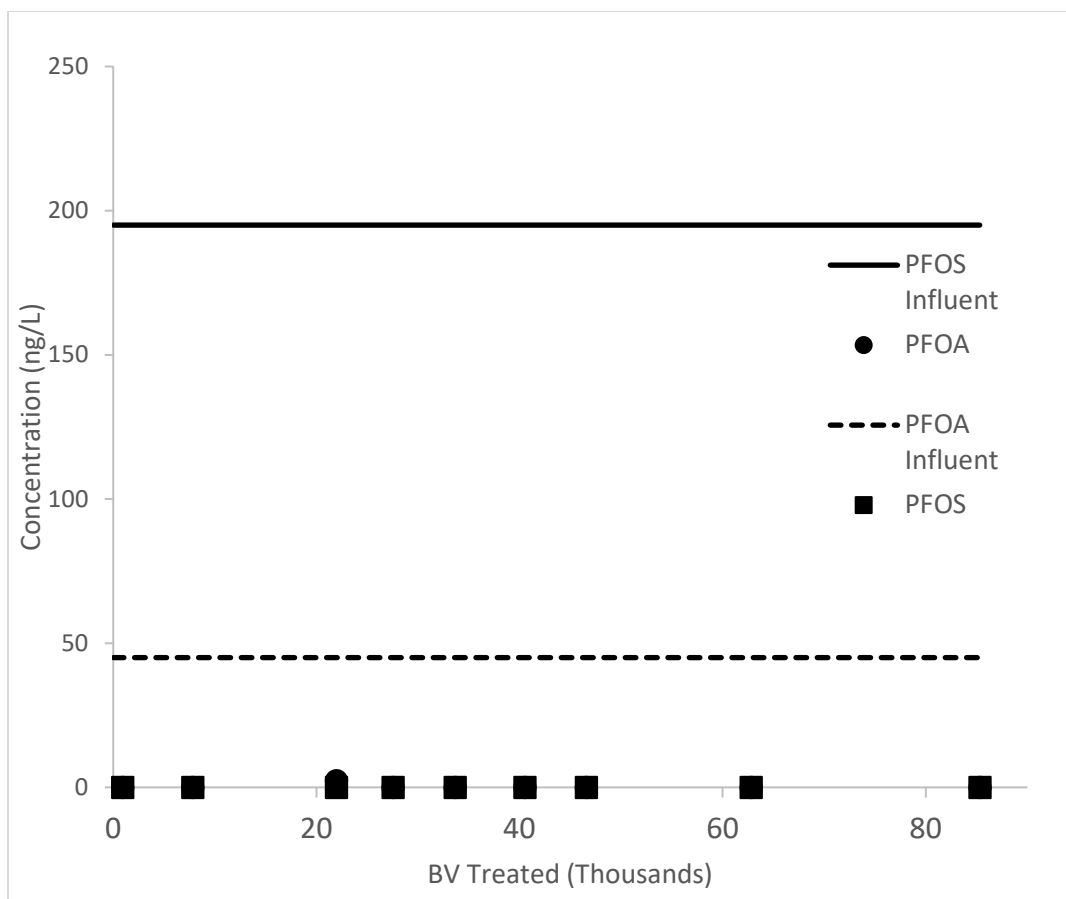


Figure 2.6 (a) PFOA and PFOS Breakthrough curve for GAC-B for Well Site A

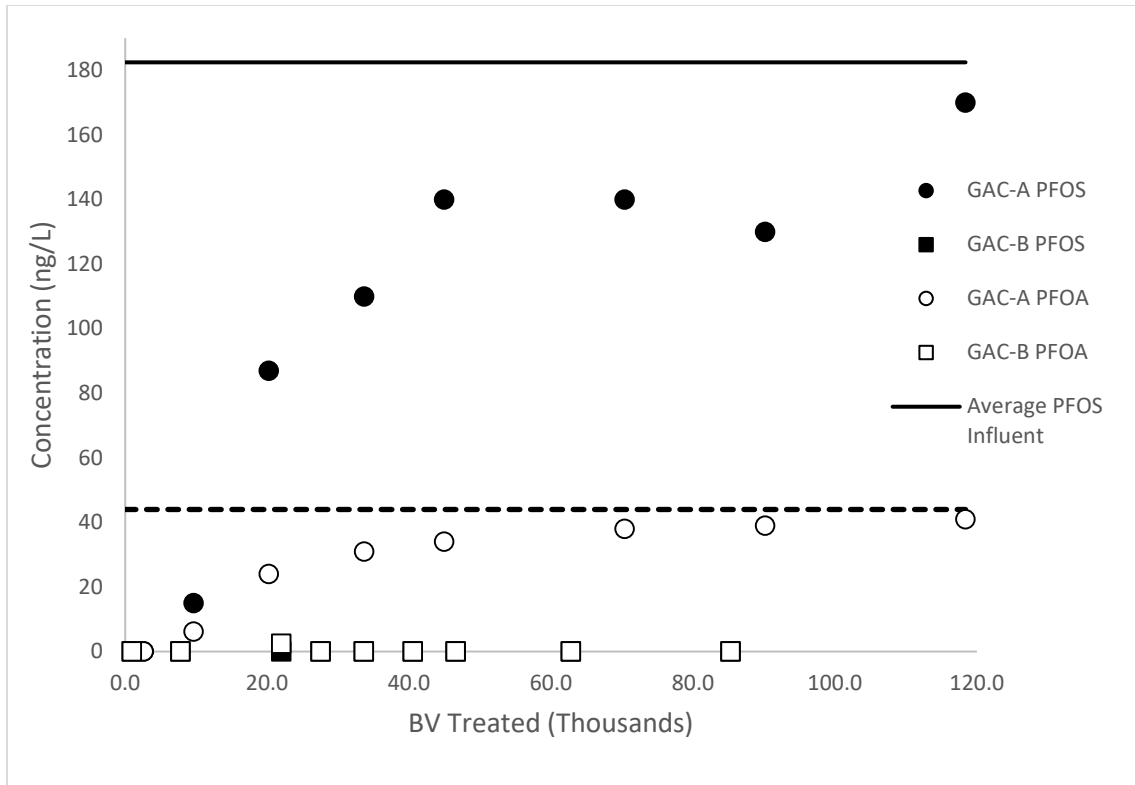


Figure 2.6 (b) Comparison of GAC-A and GAC-B for Well Site A

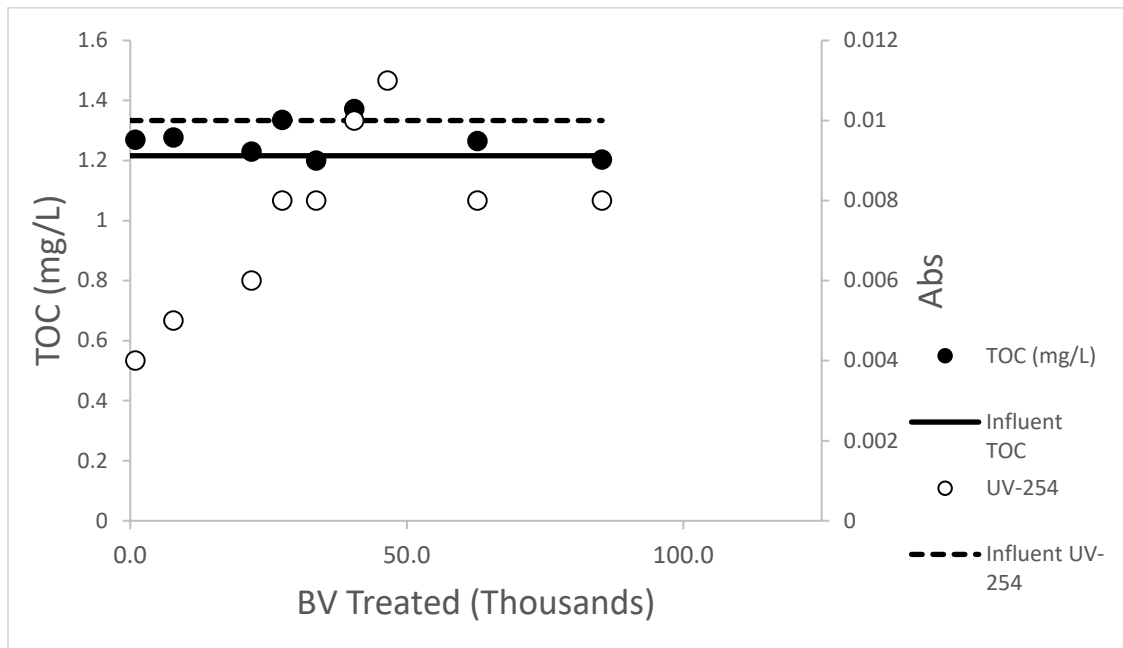


Figure 2.6 (c) RSSCT-2 TOC and UV-254 BT for Well Site A

We can clearly see that GAC-B or bituminous coal based GAC gives better performance than GAC-A or coconut shell based GAC. But one factor to be considered

over here is that GAC-A was crushed and sieved to U.S mesh No. 140×170 where as GAC-B was used for a range of U.S mesh No. 100×140 (as provided by the industry), further in this chapter a more specific comparison would be don for all the three GACs. RSSCT-2 design was also operated for well site B, which has lower concentration. Figure 2.7 (a) shows the breakthrough curve for GAC-B for well site B, this test also gives a direct comparison between well site A and well site B for GAC-B. A lot of times influent concentration can affect the performance of the adsorptive media. In this case the influent concentration of well site B for PFOA and PFOS is almost half the concentration of well site A. Figure 2.7 (b) gives a direct comparison of GAC-B performance for well site A and B.

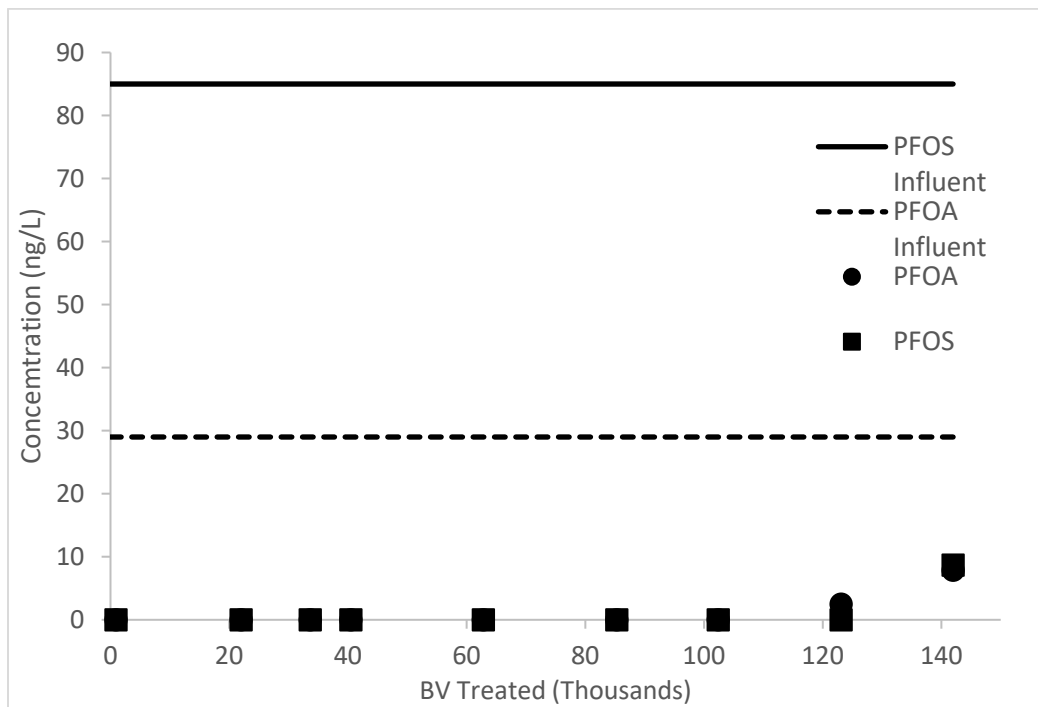


Figure 2.7 (a) PFOA + PFOS Breakthrough Curve for GAC-B for Well Site B

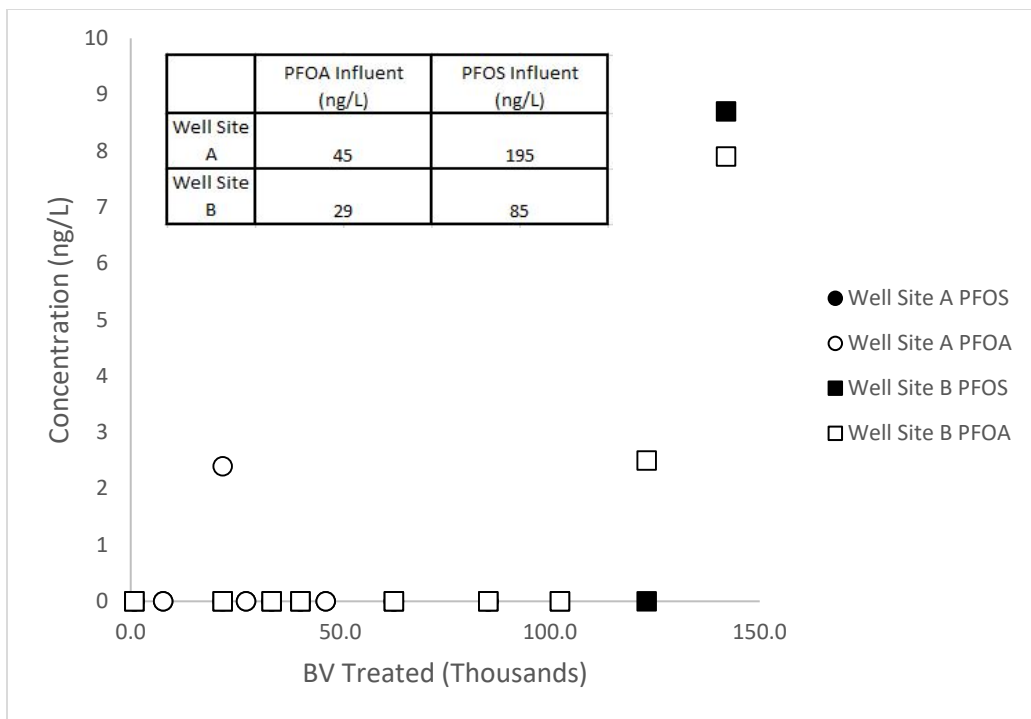


Figure 2.7 (b) Performance Comparison of GAC-B for Well Site A vs Well Site B

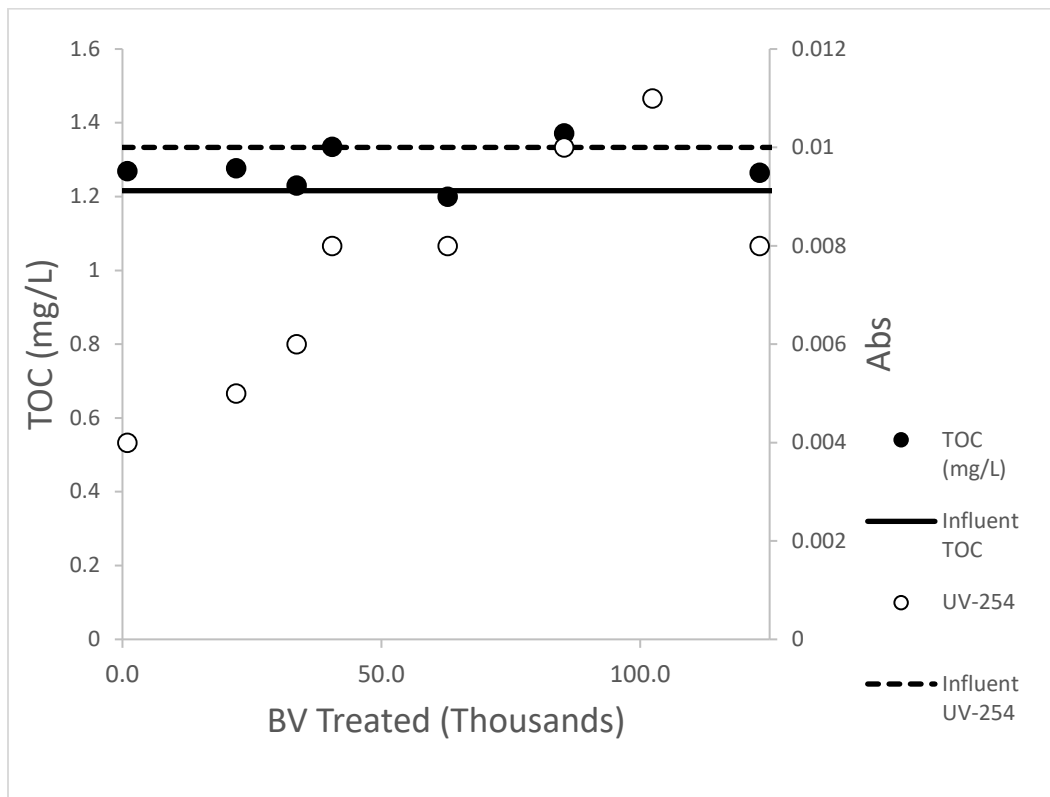


Figure 2.7 (c) RSSCT-2 TOC and UV-254 BT for Well Site B

In Figure 2.7 (b) effluent is the total PFOA + PFOS concentration. Figure 2.7 (c) gives the TOC and UV-254 breakthrough for well site B for RSSCT-2 and both the breakthrough curves looking slightly similar to the BT curves for RSSCT-1 suggesting that the speculation of TOC being a minor constituent of adsorbate could be true. From Figure 2.7 (b) it can be said that there is a similar breakthrough for both the well site or both the concentrations. The well site B RSSCT was run for a higher number of Bed Volumes as per the calculation of the absorbance capacity. The absorbance capacity (q) was suggested by the industrial partner with a range of 30-50  $\mu\text{g}$  of PFOA + PFOS/g of activated carbon. Finally 30  $\mu\text{g/g}$  was asked to use to predict the performance for all the RSSCT design.

#### **2.3.4 RSSCT-3 Breakthrough Curves for GAC-B and C for well site A**

RSSCT-3 was operated for GAC-B as well as GAC-C for well site A. Here the GAC media particle size was in the range of U.S mesh No. 140×170 for both the media. GAC-B and GAC-C are both bituminous coal based media so this experiment's main objective was to see the difference between the adsorptive media from two different companies. Secondary objective of this test was to compare the impact of particle size in these RSSCT tests as GAC-B was common in both these test and influent water from well site A was also common, but one major difference was the particle size. Also these columns were operated as lead and lag design which means two columns with same design parameters run in series with the lag column having twice the EBCT of lead column and mainly the influent for lag is the effluent for lead. There are various benefits for this setup like taking one column offline for maintenance, changing lead to lag and vice versa as per the carbon saturation and the influent water quality. Figure 2.8 (a) and



(b) gives the breakthrough curves for GAC-B and GAC-C for well site A. Considering the breakthrough results for RSSCT-2, this time the columns were operated for much higher BVs. We got high PFOA+PFOS removal for both the GACs.

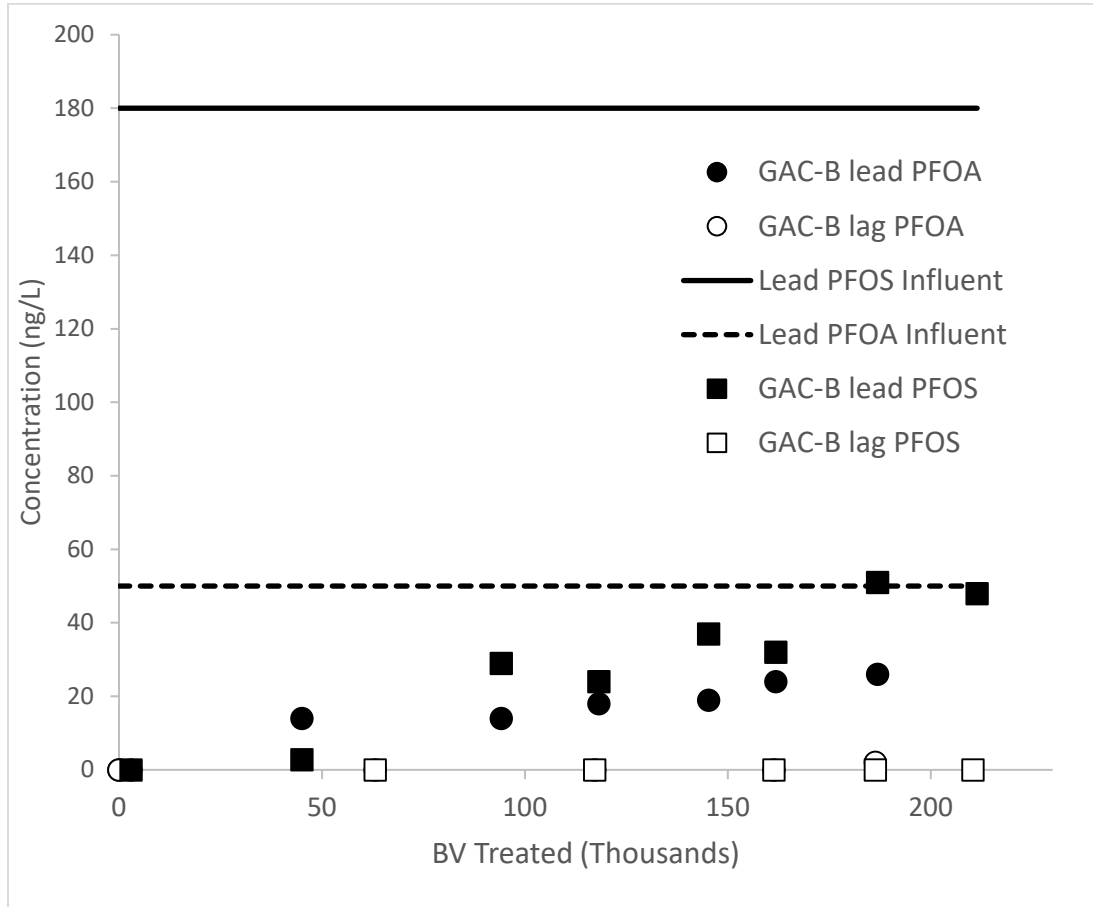


Figure 2.8 (a) Breakthrough Curve for GAC-B lead and lag column for well site A

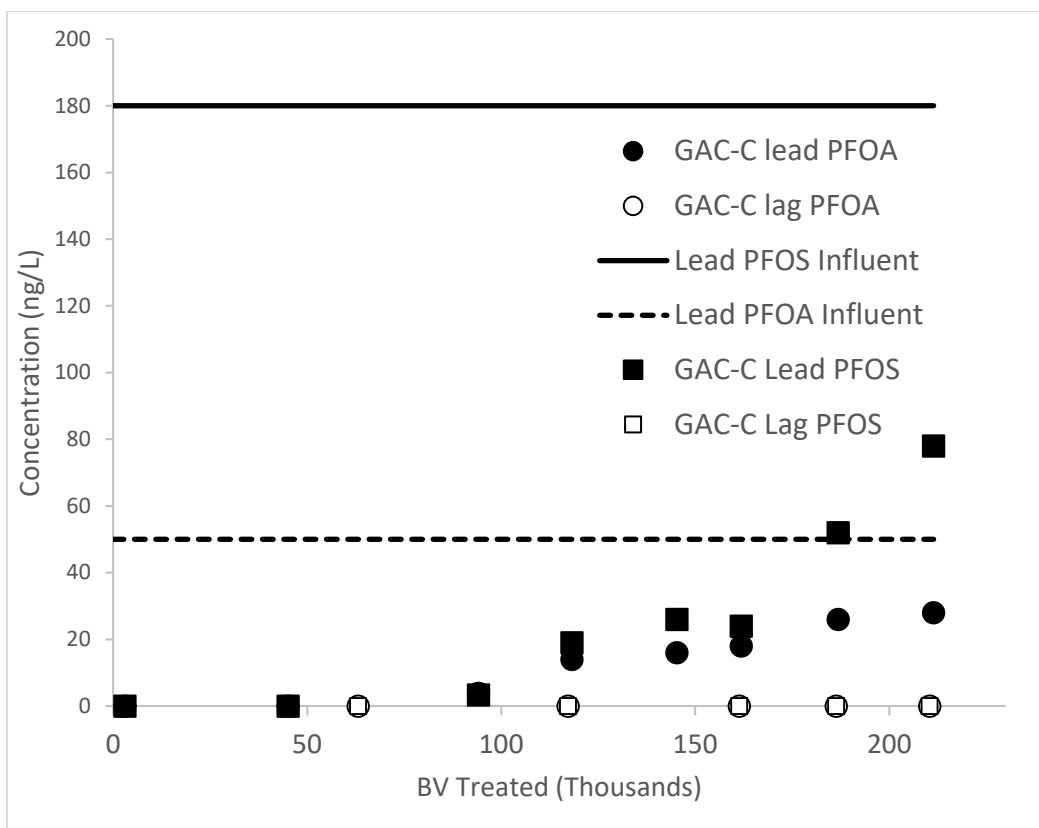


Figure 2.8 (b) Breakthrough Curve for GAC-C lead and lag column for well site B

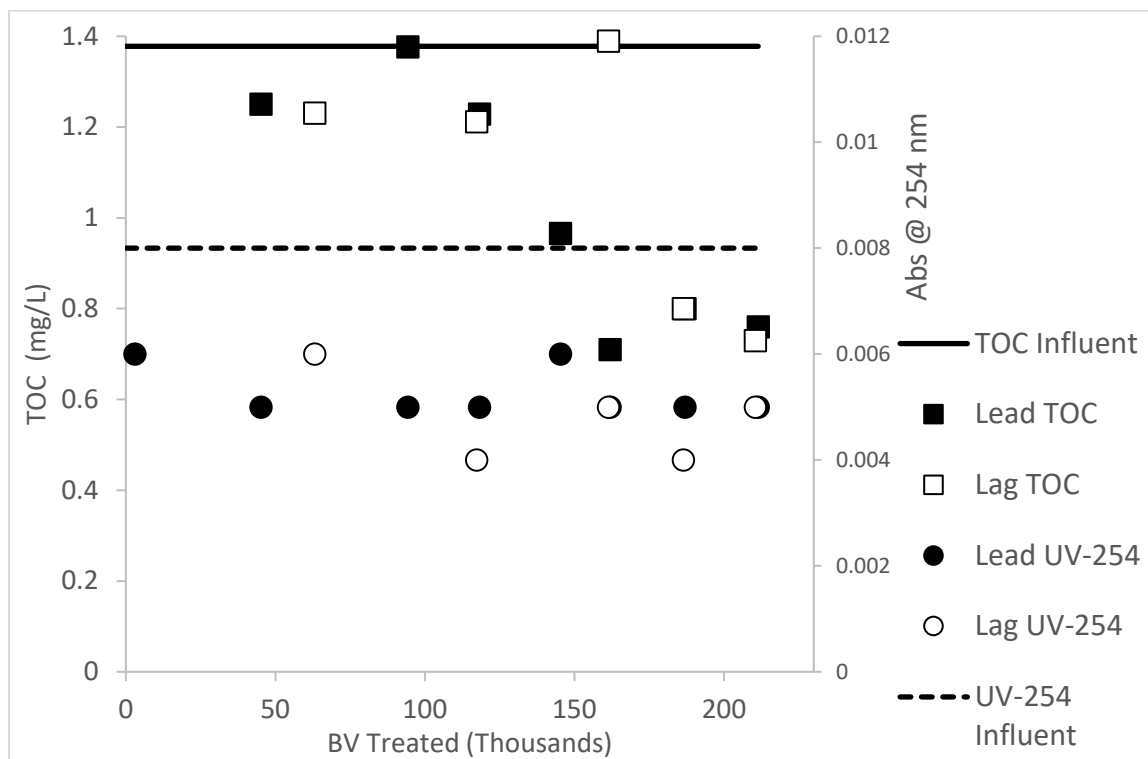


Figure 2.8 (c) TOC and UV-254 BT for GAC-B for Well Site A

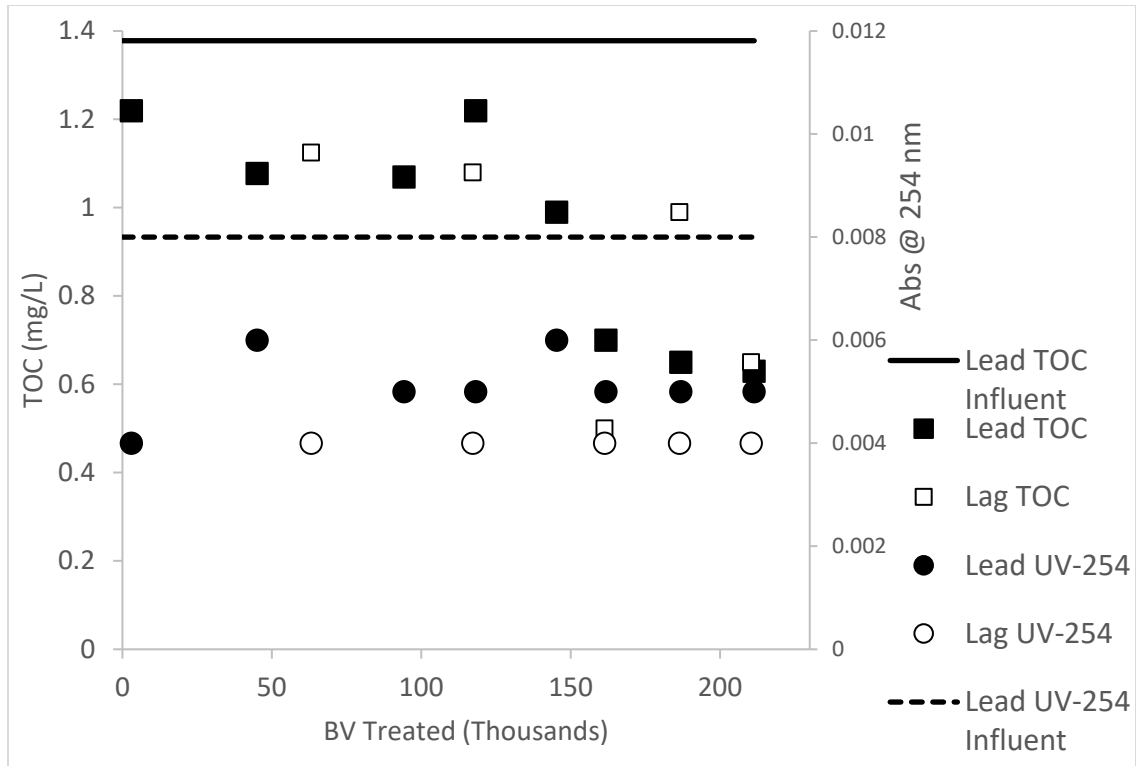


Figure 2.8 (d) TOC and UV-254 BT for GAC-C for Well Site A

Figure 2.8 (c) and (d) plots the TOC and UV-254 BT curve for RSSCT-3 for GAC-B and C respectively. Figure 2.9 (a) presents a direct comparison between these two GAC media and Figure 2.9 (b) gives a good comparison between two different sizes of absorptive media.

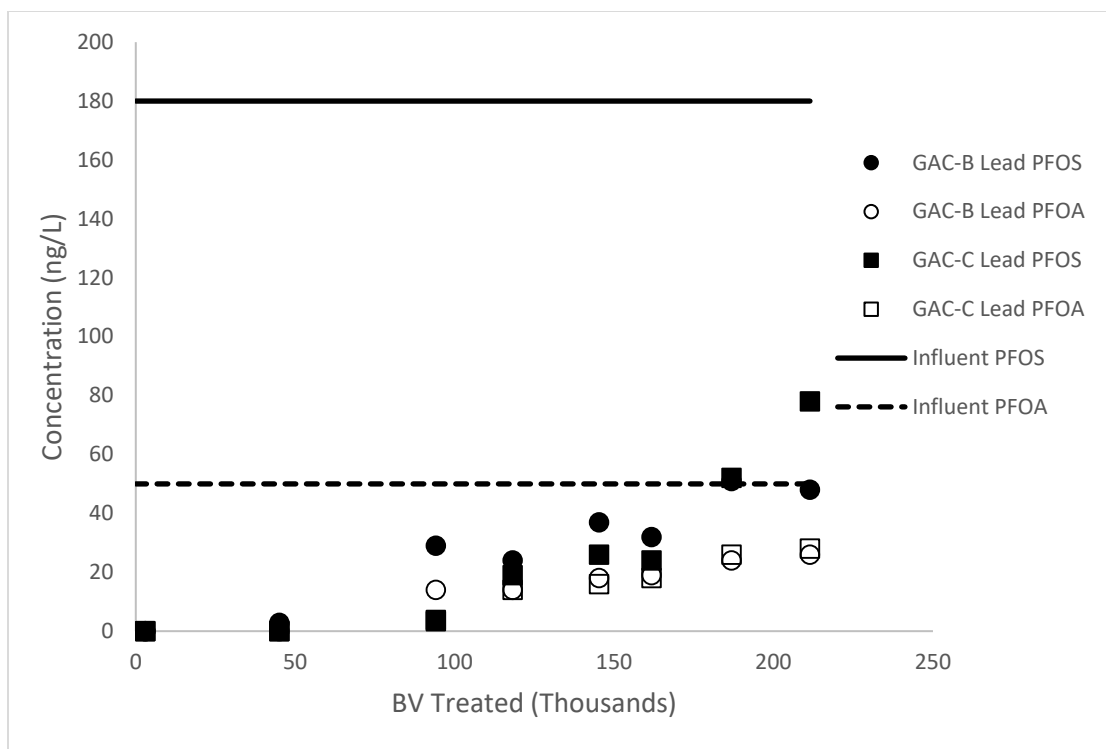


Figure 2.9 (a) GAC-B vs GAC-C lead and lag Breakthrough Curve Comparison for well site A

The performance of GAC-B and GAC-C is almost similar, which is illustrated from Figure 2.9 (a). Also there was complete removal in the lag column. It is also quite evident that bituminous coal based activated carbon are preferable over coconut shell based activated carbon for perfluorocarbons. Figure 2.9 (b) shows a comparison for the performance of GAC-B at two different particle size. From the figure it is determined that the larger size particles are better than the smaller but there is insufficient data to support that statement. Figure 2.10 shows the comparison for all the GACs.

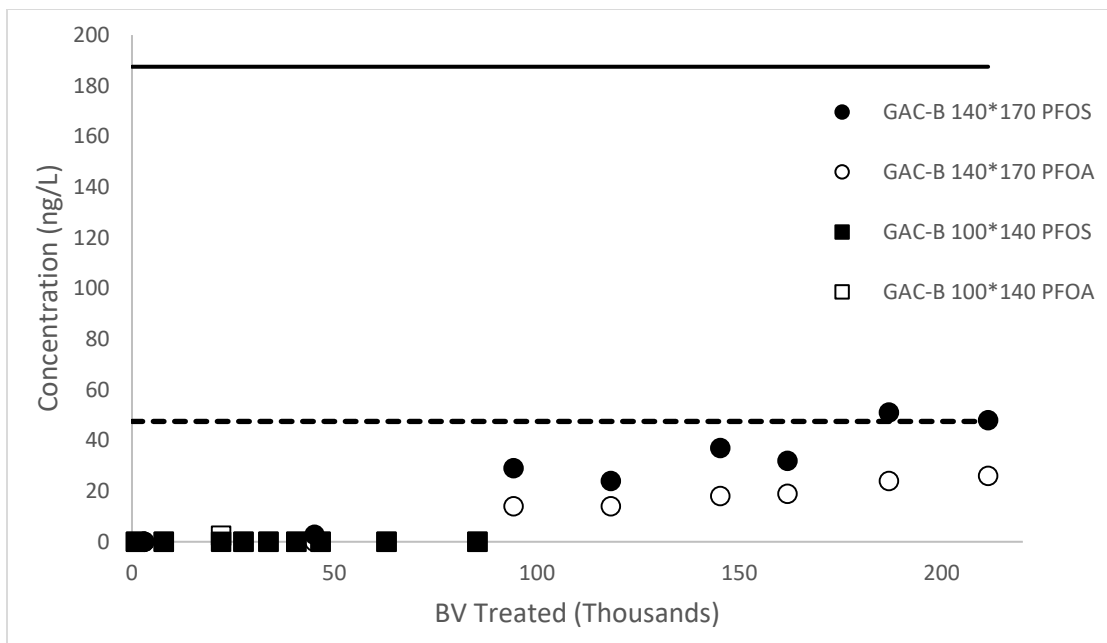


Figure 2.9 (b) Breakthrough Curve comparison for different sizes of absorptive media

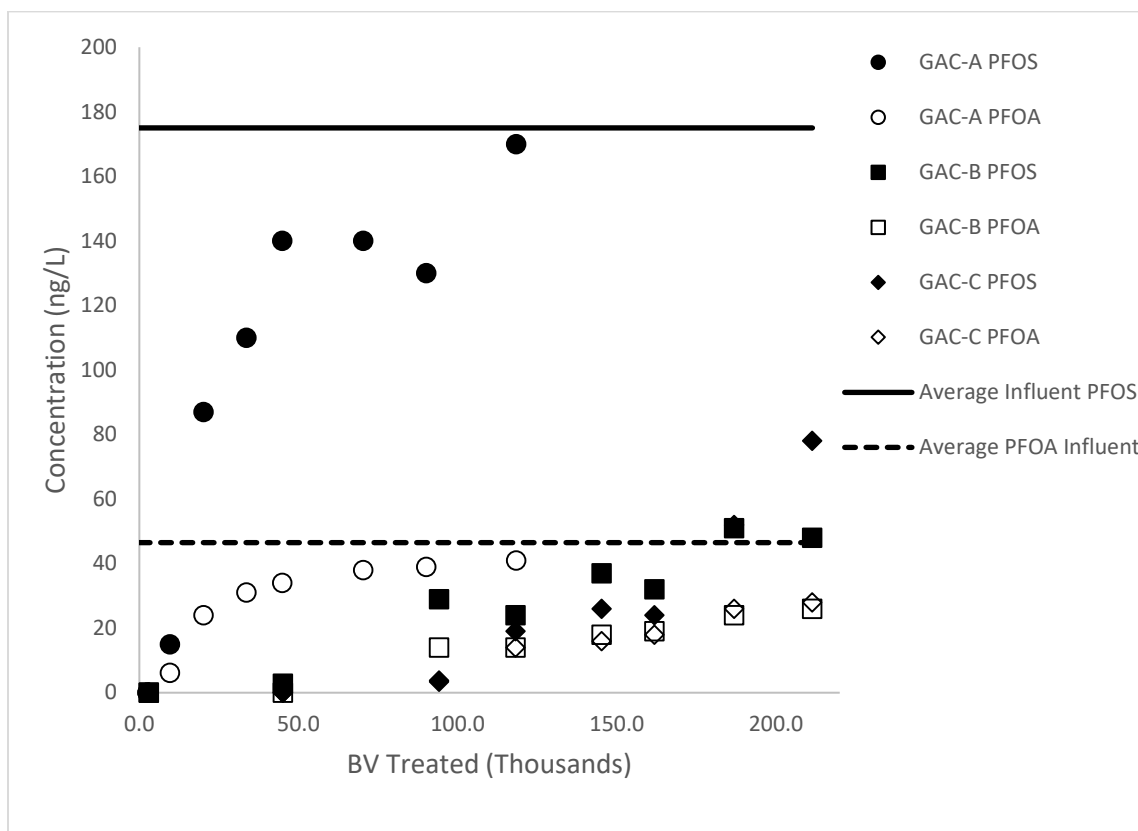


Figure 2.10 Breakthrough Curve comparison for GAC-A, GAC-B and GAC-C for Well Site A

From Figure 2.10 it is quite clear that bituminous coal based have a much higher efficacy for trace perfluorinated chemicals. For further test, the industry partner insisted on using GAC-B as it is cheaper than GAC-C for them. Further details was not shared. Table 2.4 gives the absorbance capacities for all the GACs at different conditions. They are calculated at 100L of volume passed through the column as all the RSSCTS were conducted for at least 100L of contaminated groundwater.

Table 2.4 Absorbance Capacities (at 100 L of water passed through) for GAC under different conditions

| <b>RSSC<br/>T</b> | <b>GAC<br/>Source</b> | <b>GAC<br/>particle size<br/>range (µm)</b> | <b>Well<br/>Site</b> | <b>qPFOA<br/>(µgPFOA<br/>/gGAC)</b> | <b>qPFOS<br/>(µgPFOS<br/>/gGAC)</b> | <b>qPFOA+PFOS<br/>(µgPFOA+PF<br/>OS/gGAC)</b> |
|-------------------|-----------------------|---|----------------------|-------------------------------------|-------------------------------------|---|
| 1                 | A                     | 88-105                                      | A                    | 0.8                                 | 5.8                                 | 8.3   |
| 2                 | B                     | 105-149                                     | A                    | 6.7                                 | 29.1                                | 35.8  |
| 2                 | B                     | 105-149                                     | B                    | 4.3                                 | 12.7                                | 17  |
| 3                 | B                     | 88-105                                      | A                    | 6.8                                 | 28.5                                | 35.3  |
| 3                 | C                     | 88-105                                      | A                    | 7.5                                 | 32.1                                | 39.6  |
| 4                 | B                     | 88-105                                      | C                    | 2                                   | 1.8                                 | 3.7   |

### 2.3.5 RSSCT-4 Breakthrough Curves for GAC-B for Well Site C

Well site C had the lowest PFOA + PFOS concentration, it was actually lower than the EPA health advisory level. This test was operated more from a curiosity perspective rather than an industry requirement. The nature of the breakthrough curves were surprisingly different than all the other breakthrough curves. Figure 2.11 (a) shows the breakthrough curve for RSSCT-4.

It reached almost a total breakthrough, which means the effluent concentration was almost equal to the influent concentration. This definitely hints that bituminous coal based activated carbon performance drops down at lower influent concentrations. The

influent water concentration on all the breakthrough curves are the average of the initial influent water sample and the final influent water sample.

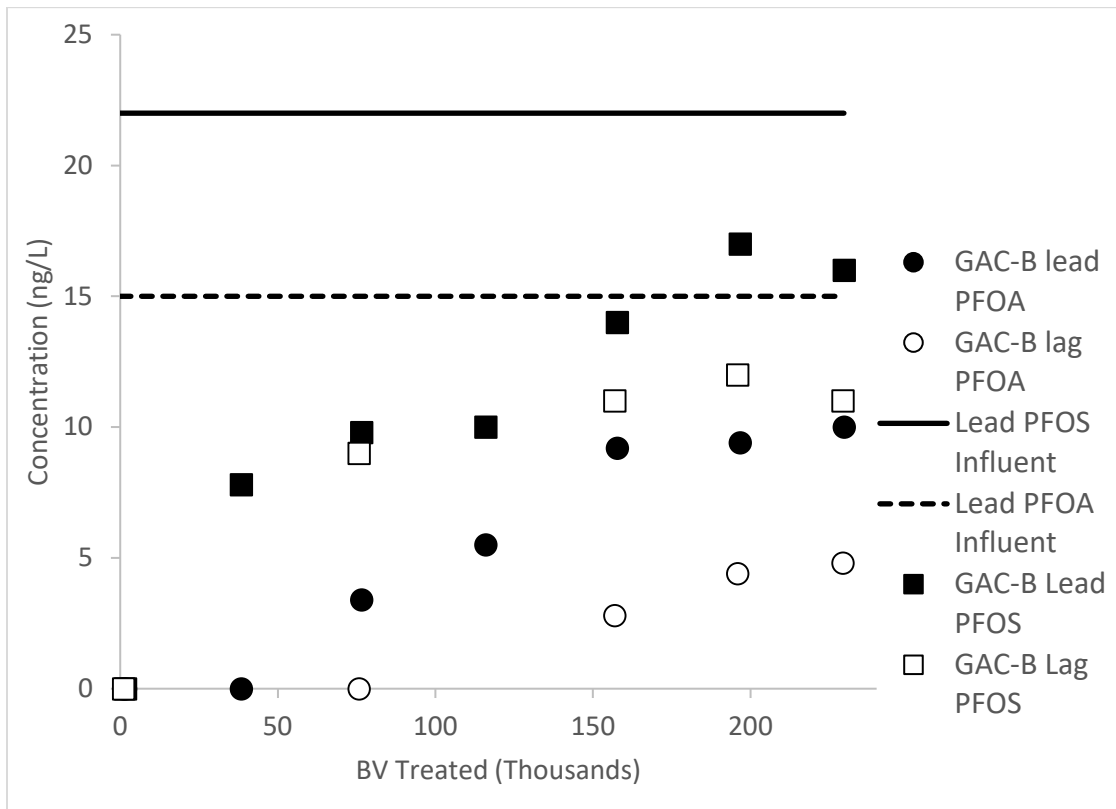


Figure 2.11 (a) GAC-B Breakthrough Curve for Well Site C

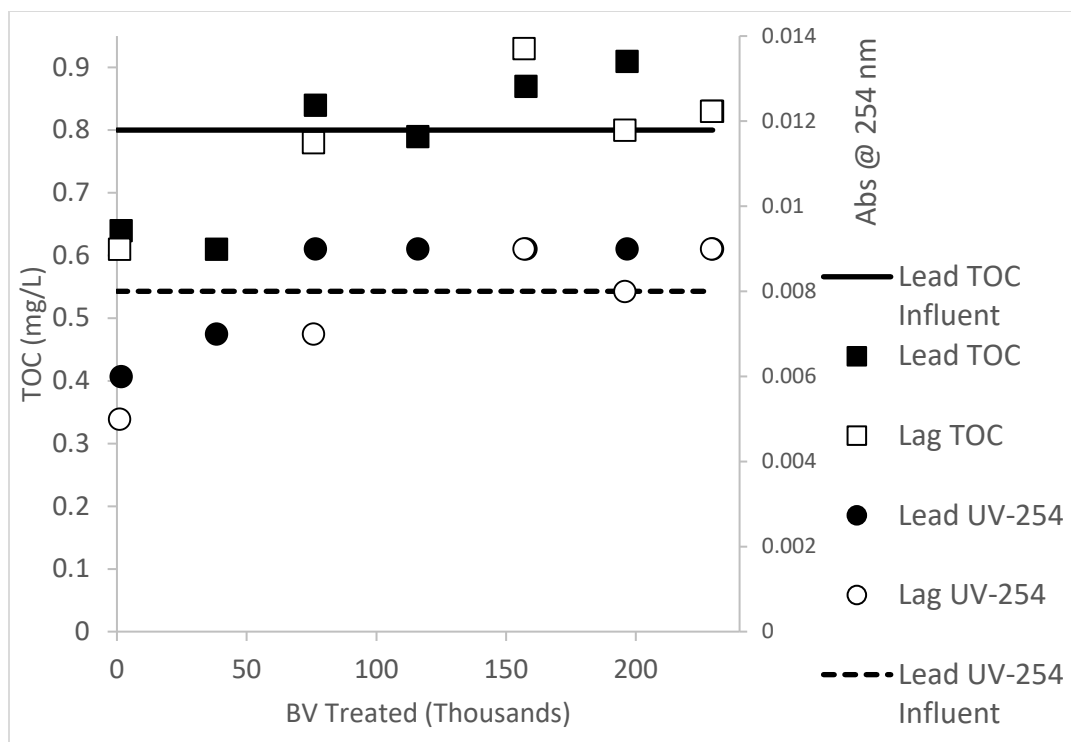


Figure 2.11 (b) TOC and UV-254 BT for GAC-B for Well Site C

## 2.4 Summary and Conclusion

A total of 4 RSSCTs were conducted to evaluate the PFC removal under different conditions like different source of GAC media, different particle size for same GAC media, varying influent concentration. A Summary of key observations are as follows:

- Bituminous coal based GAC (GAC-B and GAC-C) have higher efficacy for PFOA and PFOS than coconut shell based GAC (GAC-A).
- Influent concentrations affect the absorbance capacity of GAC-B.
- Particle Size didn't affect the absorbance capacities for GAC-B
- GAC-B and GAC-C have almost a similar absorbance capacity with GAC-C having slightly higher efficacy for PFC.
- Lag columns removed PFOA and PFOS completely.



Table 2.5 Properties of the three activated carbons evaluated.

| <b>Name</b>            | <b>Calgon F400</b> | <b>Norit F400 M-2194</b> | <b>Evoqua 1230 AWC</b> |
|------------------------|--------------------|--------------------------|------------------------|
| Carbon Type            | Bituminous Coal    | Bituminous Coal          | Coconut Shell          |
| Mesh Size, U.S Sieve   | 12 × 40            | 12 × 40                  | 12 × 30                |
| Iodine no. mg/g        | 1000 (min)         | 1000 (min)               | 1100                   |
| Abrasion no., wt. %    | 75(min)            | 75(min)                  | 85                     |
| Apparent Density g/cc  | 0.54               | 0.49                     | 0.45-0.52              |
| Uniformity Coefficient | 1.9 (max)          | 1.6                      | 2.0                    |

As given in Table 2.4 it can be concluded that bituminous coal based GAC (GAC-B and C) are better than coconut shell based GAC (GAC-A). One explanation for this is that the coconut-based carbons have a more microporous (tighter) structure and it could be possible that this structure can cause kinetic limitation (Appleman et al., 2013). GAC-B and GAC-C were almost equal in terms of performance and also their properties are very similar as shown in Table 2.5. As per the industry GAC-B is cheaper than GAC-C and hence it was recommended to use GAC-B for pilot-scale studies. GAC particle size didn't affect the absorbance capacity that much as shown in the Table 2.4 where GAC-B was used for both the sizes for Well Site A and the q values are 29.1 and 28.5 µg PFOA+PFOS/g of carbon for larger and smaller particle size respectively. But lower influent concentrations had a significant impact on the absorbance capacity. Also it was observed that the absorbance capacity decreased with influent concentrations dropping down. Finally, GAC-B was recommended for well site A and B studies, for well site C it was suggested to blend it with well site B or A. Also ion exchange resin should be studied for this well site as it has been proved more efficient in removing PFCs in previous work.

CHAPTER THREE

DEVELOPMENT AND VALIDATION OF A BENCH SCALE CARBON BLOCK  
FILTER PERFORMANCE TEST FOR ORGANIC AND INORGANIC POINT OF USE  
MODEL CONTAMINANTS

### **3.1 Introduction**

Activated carbon filters have been used for several decades and are considered as one of the oldest and most effective means for water purification (Cheremisinoff, 1980). Over the last few decades carbon filters have been used in various forms and different areas of water treatment chain with Powdered Activated Carbon (PAC) or Granular Activated Carbon (GAC) carbon block filters in the field of Point of Use (POU) water treatment being the latest (Activated Carbon for Water and Wastewater Treatment, 2011).

Point of Use means the water treatment right before direct usage of water. It is majorly applied for drinking and cooking purposes in residential as well as commercial buildings (EPA-POU/POE, 2006). Decades ago activated carbon were used in the POU devices as gravity filters and packed bed filters (Activated Carbon and Carbon Block Water Filters, 2017). After the invention of carbon block technology and carbon block filters it was found that carbon block technology gives much higher surface area and hence higher removal of contaminants or for a longer period (Custom Water Filters, 2017).

The drinking water provided by the municipality is safe to drink, at least in developed countries like USA (EPA, 2017). Developing countries and some rural societies of developed countries still face an issue of potable water either because of

unsafe water quality from municipality, isolated location or poor groundwater quality (Wright, J et al., 2004). They all heavily rely on POU water treatment devices.

Activated carbon block filter is one of the most used technology in this industry. Carbon blocks were initially used to target the removal of aesthetics like taste and odor, chlorine residual (Custom Water Filters, 2017). But in the recent years companies have successfully managed to improve the functionality of these carbon block filters for removal of emerging contaminants like disinfection-by-products (DBPs), heavy metals and etc (Custom Water Filters, 2017). There are still few microbial, organic and inorganic contaminants that are not removed by carbon block filters. Reverse Osmosis (RO) membrane technology is a great competitor of carbon block technology (Custom Water Filters, 2017) and it can remove almost everything from the contaminated water. But some primary disadvantages of RO membrane like removal of necessary nutrients and minerals, less percentage of recovery (which means that not all the water passing through RO membrane comes out to be potable, a high percentage of influent is wasted) is encouraging consumers to buy POU devices with carbon block technology only and hence this inspires industry people to research more on improving functionality and efficiency of carbon block filters.

Carbon block filters are made by combining dry ingredients like activated carbon, a binder (mostly a polymer used to bind the activated carbon together in a cylindrical shape) and sometimes they use a special adsorptive media for heavy metals and other selective contaminants depending on the water quality of a certain region (Custom Water Filters, 2017). There are mainly two techniques used in manufacturing carbon blocks: Extrusion and Compression molding. In Extrusion the ingredients mixture (activated

carbon, binder and other media) is forced through a die to form a long continuous block which are trimmed to the desired size (Custom Water Filters, 2017). Compression carbon blocks are made individually in a mold under tremendous pressure and high heat and then trimmed to the desired size (Custom Water Filters, 2017). Considering all those variables, an industry creates a bunch of prototypes for various composition of media, different types of media, special types of media, etc. Carbon block filters should at least meet parameters set by environmental agencies like Environmental Protection Agency (EPA), World Health Organization (WHO) in order to provide safe waters, but these parameters don't specify much about emerging contaminants, heavy metals and etc. To provide the safest water and best performance a POU device should be able to gain certifications like NSF-42 and NSF-53 (NSF), NSF-42 and 53 are created to set the benchmark for evaluating safety and integrity of residential water filters. NSF-42 is for aesthetic or non-health related contaminants like chlorine, taste, odor and particulates, NSF-53 is for health related contaminants like cryptosporidium, lead, volatile organic contaminants (VOCs) and asbestos (Residential Drinking Water Treatment Standards, 2017).

To achieve these certifications, tests with benchmark operating conditions are to be performed, for a single test it requires at least 6000 to 12000 liters of test water depending from companies to companies. It would produce the same volume of waste in most of the cases. So basically a huge amount of water is treated to use it for a water treatment performance test which again produces waste which has to be treated again. Not only water but factors like energy and cost of chemicals required for making the test water and handling of those hazardous test waters are extreme. Unfortunately there is no bench scale test for the carbon block filter performance unlike Rapid Small Scale Column

Test (RSSCT) for GAC bed contactors, or at least it is not published or openly known to the researchers.

Therefore, this study focuses on developing a bench scale study for evaluating the performance of full-scale carbon blocks. A method to obtain a mini carbon block i.e basically a disc from the full scale carbon block was developed. An optimized holder was designed to contain this mini carbon block disc, which was also used to evaluate the performance of the mini carbon blocks (MCB) derived from commercial carbon blocks. The MCB were evaluated for organic and inorganic model contaminants like chloroform and arsenic. Design parameters for bench scale were normalized to volume of full-scale parameters of the commercial carbon blocks. The Q (flow-rate) for full scale carbon block is 3400 mL/min which was normalized to 59 ml/min (approximately 57 times lower). Performance of bench scale was compared with the available full-scale performance results (provided by the industry).

### **3.2 Material and Methods**

#### **3.2.1 Preparation of Mini Carbon Block**

Several carbon block tubes were purchased from Home Depot and prototypes of carbon block disc were cored out. Initially a hollow cylinder carbon block was separated from the middle forming into two hollow semi cylinders. Then using a drill press and drill bit a carbon block disc was cored out from the semi cylinder, one of the key difficulties faced was the roughness of the carbon block disc obtained. The pressure and the mechanical abrasion of the drill press was breaking down the carbon block or at least wear it down to a rough carbon block disc. A smooth carbon block disc was required to successfully create and fit it inside a holder. A 1 3/8 inch diamond hole saw from Home

Depot was used to get the smooth carbon block disc. A JET bandsaw and a JET drill press was used for the cutting and drilling out of the carbon block disc (JET Tools, 2017). The edge of the cored out carbon block disc was trimmed using a sand paper (ACE Hardware Store, 2017). Figure 3.1 shows the sketch of mini carbon block preparation method and Figure 3.2 shows the actual apparatus.

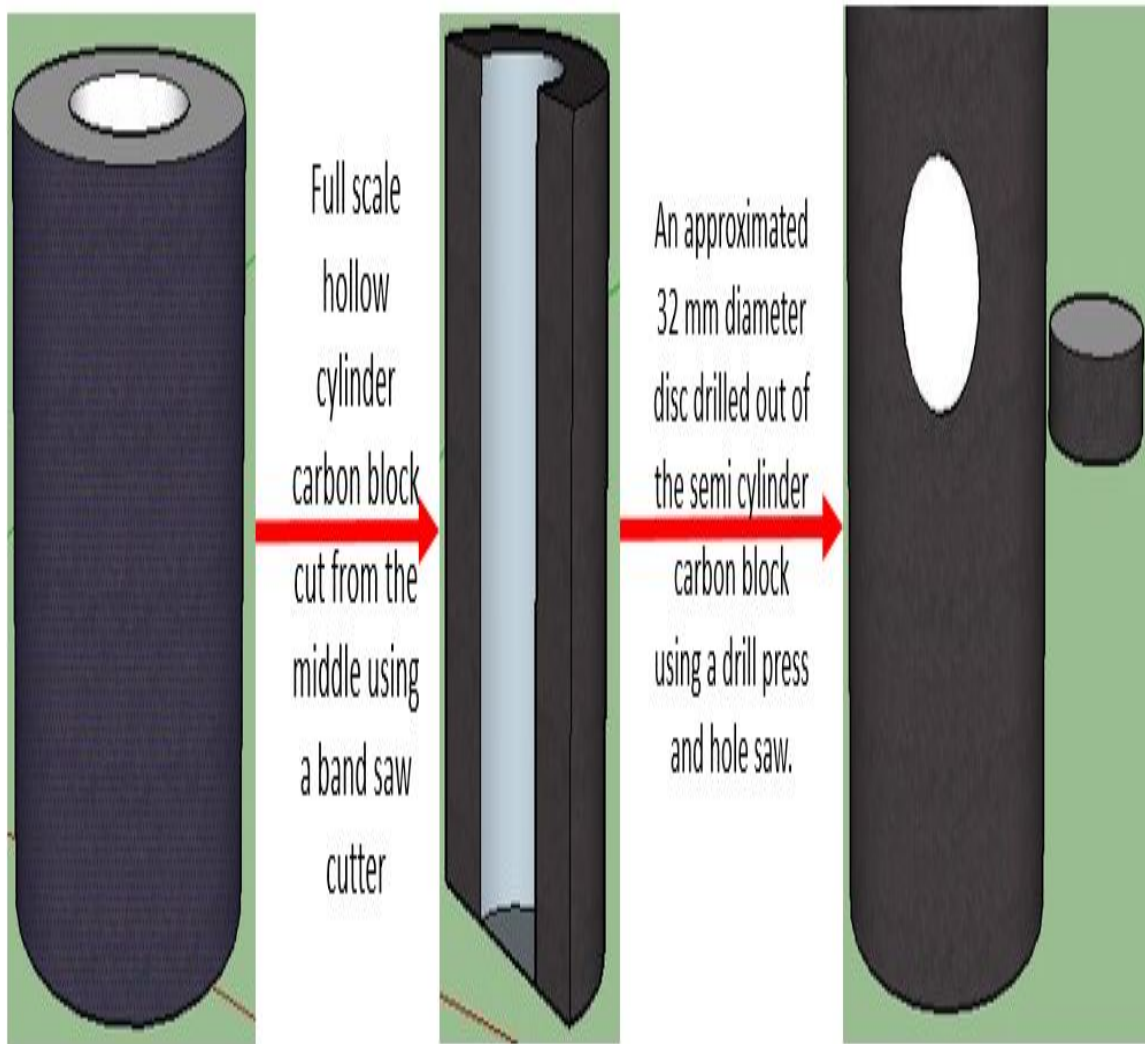


Figure 3.1 A visual sketch of mini carbon block disc preparation

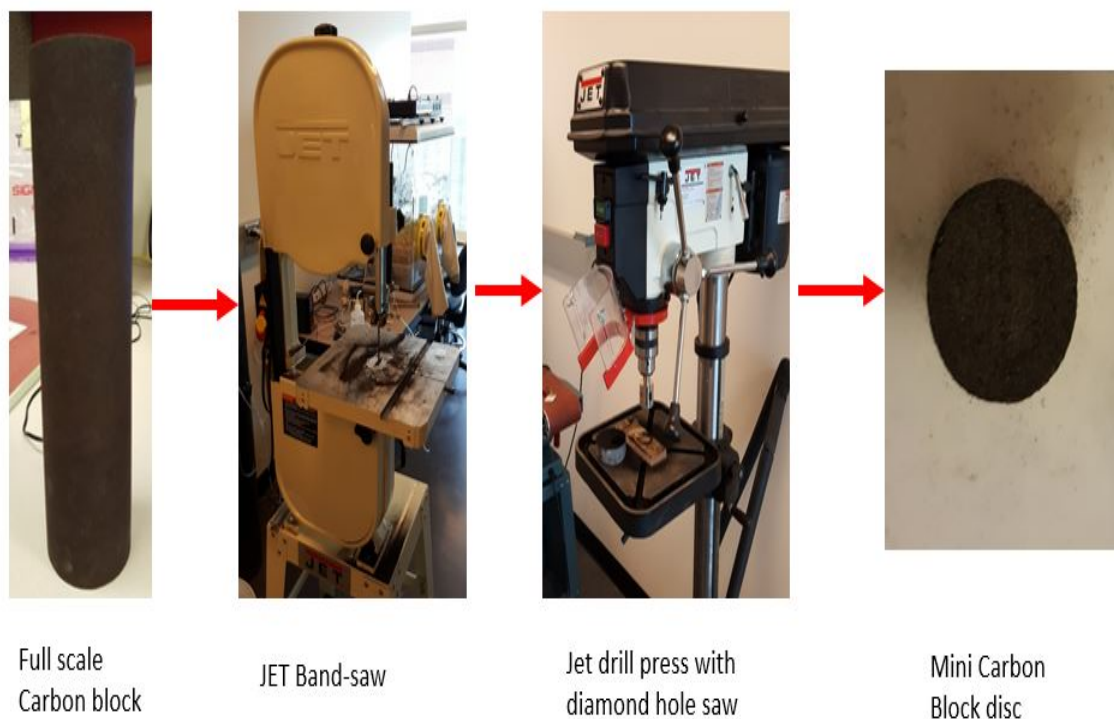


Figure 3.2 Actual visual of the mini carbon block preparation apparatus

### 3.2.2 Mini Carbon Block Apparatus Flow Parameters

There were two approaches used for scaling down the operational parameters like normalizing the surface area of full scale carbon block (dimensions of the full scale carbon block were provided by the industry) to the bench scale or mini carbon block (dimensions measured using the Vernier calipers). But in this approach the Empty Bed Contact Time (EBCT) were not matching as the total volume of carbon media is not accounted when we use surface area to calibrate the bench scale parameters to full scale parameters, hence the second approach normalizing the volume of full scale to bench scale was used. Here the total volume of the carbon media is accounted so this approach gave an equal EBCT for both the scales. So instead of using surface loading rate the contaminant loading rates per volume of carbon was used. Full-scale carbon blocks were procured from two different industry, those will be further addressed as chloroform

carbon block A (CB-A) and arsenic carbon block B (CB-B). Table 3.1 shows the design parameters for both full scale and both the mini carbon blocks. Full-scale CB-B claims to have a life of 10000L of water and hence the bed volumes for CB-B are much higher than CB-A. The bed volumes, EBCT and operating time remains the same for both full scale and bench scale. The main parameters that decrease are operating flow rate and volume of influent water. It reduces by almost 50-60 times. This saves a lot of water, energy and chemicals.

Table 3.1 Design Parameters for Full Scale and Bench Scale Carbon Blocks

| <b>Design Parameters</b>    | <b>CB-A</b> | <b>MCB-A</b> | <b>CB-B</b> | <b>MCB-B</b> |
|-----------------------------|-------------|--------------|-------------|--------------|
| Thickness (mm)              | 25          | 24.6         | 16          | 13.7         |
| Height (mm)                 | 150         | 24.6         | 250         | 13.7         |
| O.D Diameter (mm)           | 110         | 15.9         | 62.5        | 32           |
| I.D Diameter (mm)           | 50          | ----         | 31.5        | ----         |
| Volume of carbon block (mL) | 1130        | 19.52        | 572         | 11           |
| Flow Rate (mL/min)          | 3400        | 59           | 1000        | 19.25        |
| Loading Rate (mm/h)         | 4           | 0.07         | 1.2         | 0.02         |
| Volume Treated (Liters)     | 5000        | 87           | 10000       | 193          |
| Bed Volumes (L/L)           | 4423        | 4423         | 17486       | 17486        |
| EBCT (s)                    | 19.95       | 19.95        | 34.3        | 34.3         |

### 3.2.3 Carbon Block Holder

Two types of carbon block holders were designed and developed. The first was a basic PVC holder made up using PVC pipes and adaptors. First the disc was attached to the inner side of a 1 3/8 inch PVC pipe using an epoxy resin glue and then that PVC pipe was attached to 2 inch male adaptors on both the ends. Then the male adaptors were screwed to female adaptors on both ends using Teflon tape. The female adaptors were taped for ¼ inch Teflon quick connects. All these hardware parts were bought from Home Depot. Figure 3.3 shows the visual of the PVC holder. After some initial tests it



was discovered that there can be a huge potential of channeling or short circuiting in the PVC holder. A methylene blue (MB) test was used to verify for channeling in the holder. Sometimes there was complete removal of MB but sometimes there was not that much of MB removal. From those experiments it was discovered that the epoxy resin gluing part was the most crucial part in the PVC design. There was a high potential of human error with that part and once there is an error then that piece of mini carbon block and pipe became futile. Hence a better design for the carbon block holder was required. An engineer friend in Korea was contacted and consulted about this issue and a new brass carbon block holder was manufactured and provided by him. Figure 3.4 shows the visual of the brass carbon block holder and Figure 3.5 shows the engineering drawing of the brass carbon block holder.



Figure 3.3 PVC Mini Carbon Block Holder



Figure 3.4 Brass Mini Carbon Block Holder

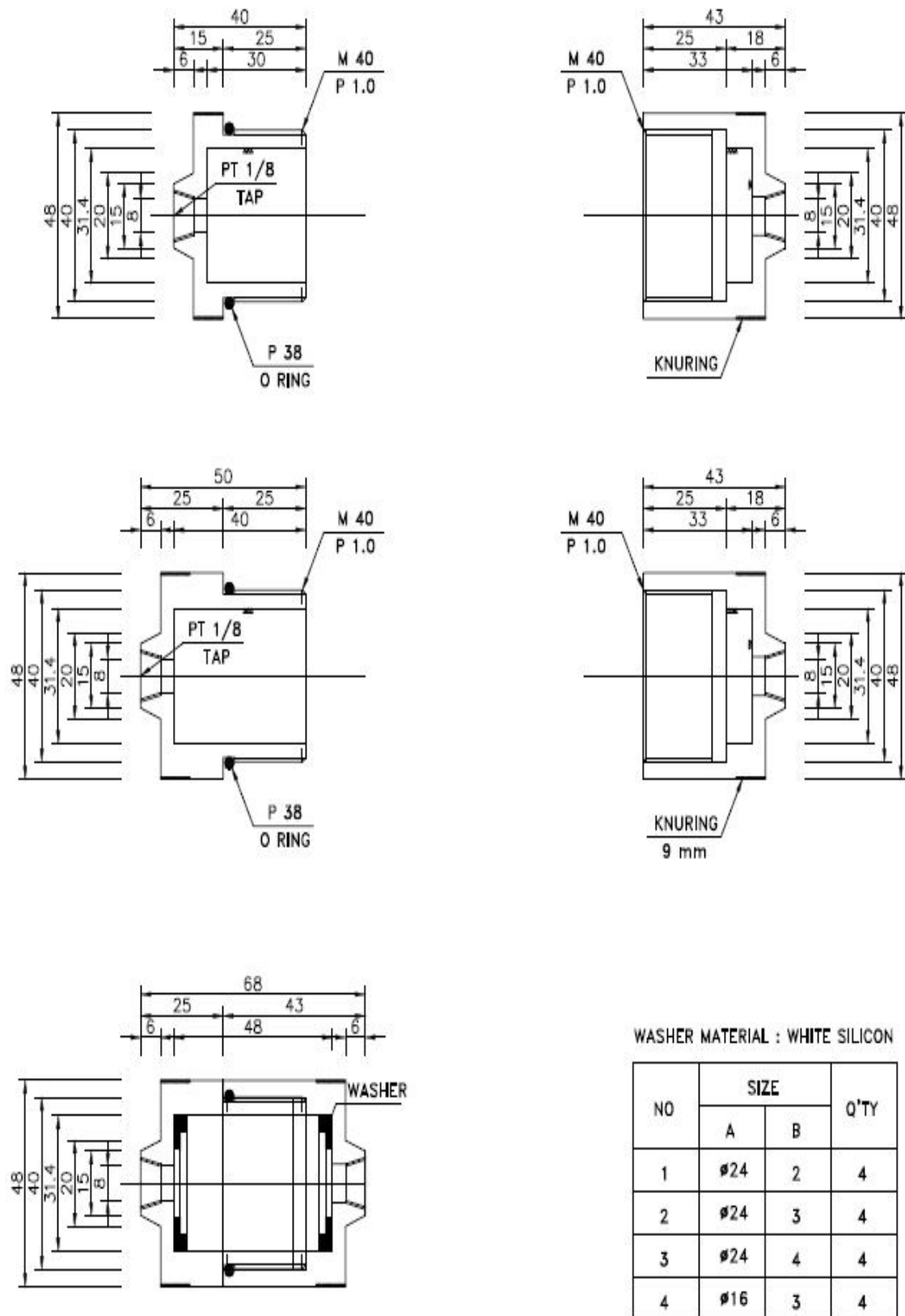


Figure 3.5 Engineering Drawing of Brass Mini Carbon Block Holder

### 3.2.4 Mini Carbon Block Apparatus

The mini carbon block apparatus consists of a brass mini carbon block holder, test water container, waste/effluent container, FMI piston pump, flow dampener, pressure gauge, digital electric timer for on/off operating conditions. Figure 3.6 shows the flow diagram for the mini carbon block apparatus and figure 3.7 shows the actual setup of the mini carbon block apparatus. The holder is connected with  $\frac{1}{4}$  inch tubing to FMI pumps.  $\frac{1}{4}$  inch tubings are inserted in the influent test water tank and then the effluent tubing first passes through flow dampener and then to the pressure gauge and then to the holder. The effluent line for the holder goes into the waste container. Flow dampener is used to smoothen the flow and reducing the pulsation. Pressure gauge is used to monitor the backpressure from the holder. The water flows from bottom to top in the mini carbon block holder. 55 gallon barrel was used for storing test water.

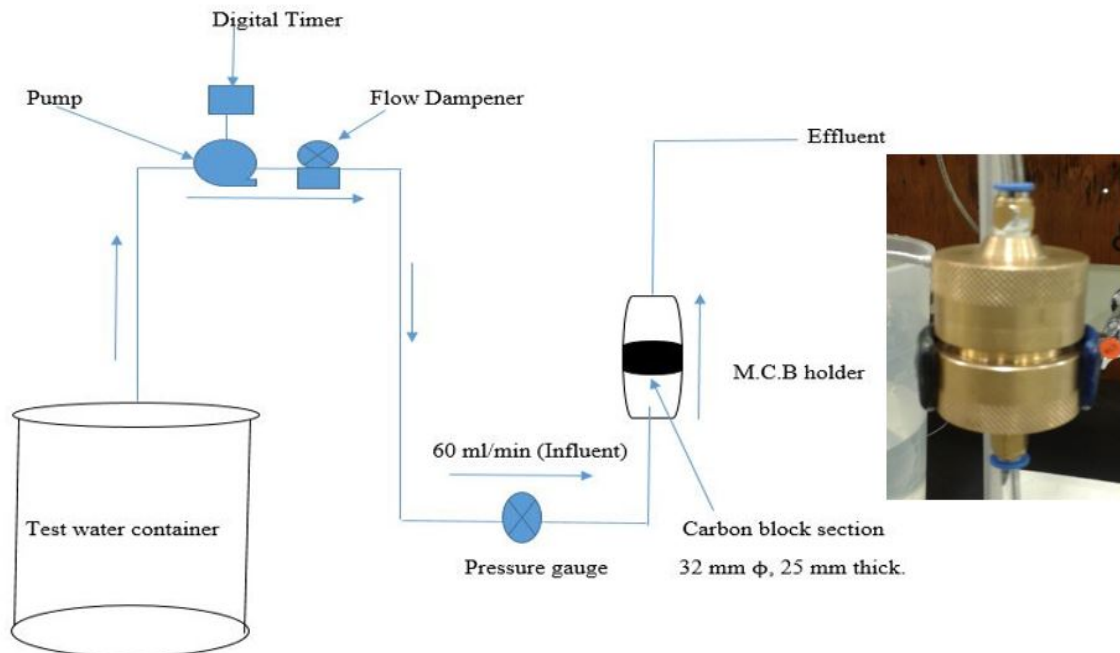


Figure 3.6 Flow Diagram of Mini Carbon Block Apparatus

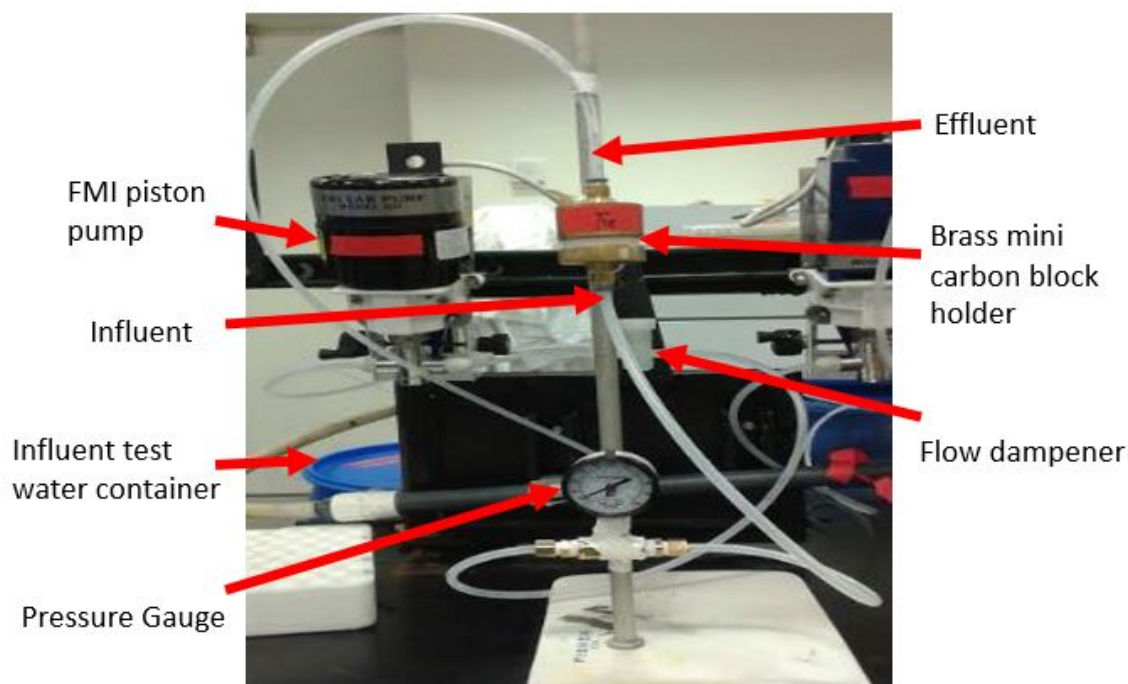


Figure 3.7 Actual Setup of Mini Carbon Block Apparatus

### 3.2.5 Methylene Blue Channeling Test

A methylene blue channeling test protocol was developed in order to look for any channeling issues in the holder. A methylene blue calibration curve at 664 nm absorbance was created and extinction coefficient was determined to be 77000 L/mol·cm. Figure 3.8 shows the calibration curve for methylene blue. A methylene blue solution of approximately 1 mg/L concentration (0.2 Abs at 664 nm) was passed for at least 5 minutes through the mini carbon block and the absorbance of the effluent was measured for 664 nm wavelength. After a few set of repetitive experiments it was established that the absorbance at 664 nm for the effluents for first five minutes should be almost zero.

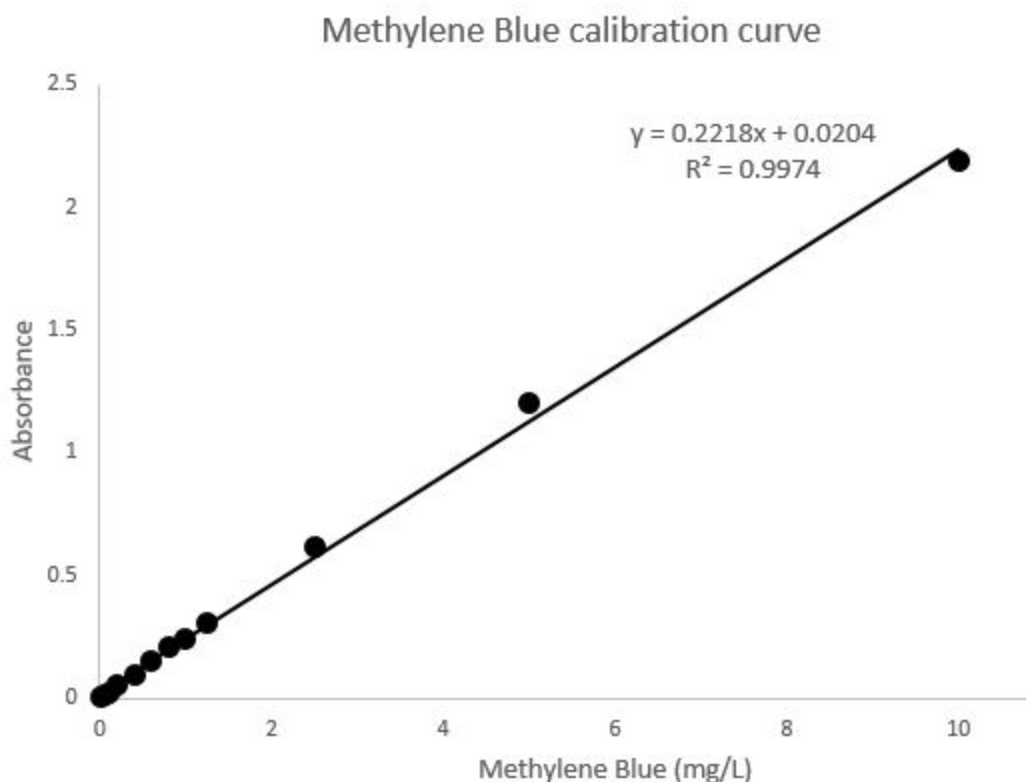


Figure 3.8 Methylene Blue Calibration Curve

### 3.2.6 Test Water Preparation

Three different tests were performed using this carbon block apparatus. Test 1 and Test 2 were performed on CB-A for methylene blue and chloroform. Test 3 was performed on CB-B for Arsenic. CB-A claimed to remove chloroform as per NSF-53 challenge levels and CB-B claimed to remove arsenic as per NSF-53 challenge levels. Also some data about the breakthrough curves for chloroform and arsenic were provided by the industry. Methylene blue test was performed on CB-A to get used to the apparatus and to use it as a first screening test to look for any contaminant removal. Methylene blue test water was prepared by adding methylene blue dye (Sigma-Aldrich, 2017) into the deionized water and then mixing the test water using a heavy duty mechanical mixer. Chloroform test water was prepared by adding 100% pure chloroform into methanol and

then into deionized water. Finally the stock solution was added to the 55 gallon barrel test water container containing dechlorinated tap water and a very light mixing was used. Polyethylene drum liners were supported between test water and the barrel inner surface to avoid any cross contamination. Soon the drum liners were tightly tied with the influent tubes dipped inside the container to avoid any volatilization of chloroform. There was no pH adjustment in any of the above test waters, as the pH of the tap water was 7.6 which was in the same range of pH ( $7.5 \pm 0.5$ ) used by the industry. Arsenic test water was prepared by adding a stock solution prepared by adding the mass of Sodium Arsenate heptahydrate (Sigma-Aldrich, 2017) salt as per the mass balance calculations into the deionized water and then into the desired volume of dechlorinated tap water and then mixed by using the heavy duty mechanical mixer. pH was adjusted to 6.5 (as recommended by the industry) from 7.6 using 1 N nitric acid.

### **3.2.7 Water Quality Analysis and sampling**

A calibration curve was prepared for methylene blue to calculate concentration in mg/L using the UV-664 absorbance. UV-664 absorbance was analyzed using a Hach DR-5000 spectrophotometer (Hach DR-5000 UV-Vis Spectrophotometer, 2017). Chloroform was analyzed by using an online THM analyzer (Parker on-line THM Analyzer) as well as by Gas Chromatography Electron Capture Detector or Gas Chromatography Mass Spectroscopy (GC/ECD or GC/MS) (EPA method 551 (EPA, 2017)). Arsenic was analyzed using Inductively Couple Plasma Mass Spectroscopy ICP-MS. Water samples for methylene blue test were collected in 50 mL Falcon Centrifuge tube (Fischer Scientific, 2017), for chloroform THM analyzer the samples were collected in 50 mL Polyethylene Falcon Centrifuge tube (Fischer Scientific) and straight away transferred to

the sample collector in the analyzer. For GC/MS the samples were collected in 40 mL glass vials with no headspace. For arsenic the samples were collected in 15 mL Polyethylene Falcon Centrifuge tube (Fischer Scientific) and acidified using 3% Nitric Acid. All the samples were stored in cold temperature ( $< 4^{\circ}\text{C}$ ) and dark room.

### **3.3 Results and Discussion**

#### **3.3.1 Methylene Blue Test**

The methylene blue test was performed mainly to verify if the mini carbon block holder actually works and analysis of methylene blue is very quick, easy and cheap. Also methylene blue water solution is blue in color and hence this test provides visual confirmation of pollutant removal. Methylene blue test was performed for CB-A and for continuous and on/off operation mode. The on/off operation mode was for 10 minutes on/off cycle. The industry using CB-A uses 10 min on/off cycle and also NSF-53 recommends of using on/off cycle operation, hence it was repeated in the mini carbon block experiments related to CB-A. The main objective behind using on/off cycle is to simulate real life POU water treatment device (POU-WTD) usage as hardly anyone would use POU-WTD or any tap continuously. Even 10 minutes cycle is a worst case scenario like hospitals or other crowded commercial buildings. The test was run for 104 liters of 4 mg/L ( $0.92\text{ cm}^{-1}$  at 664 nm) to simulate the performance of a full scale carbon block for 120% of the claimed volume of water (5000 liters). Figure 3.9 (a) shows the breakthrough curve for continuous flow MB test and Figure 3.9 (b) shows the breakthrough curve for on/off MB test.

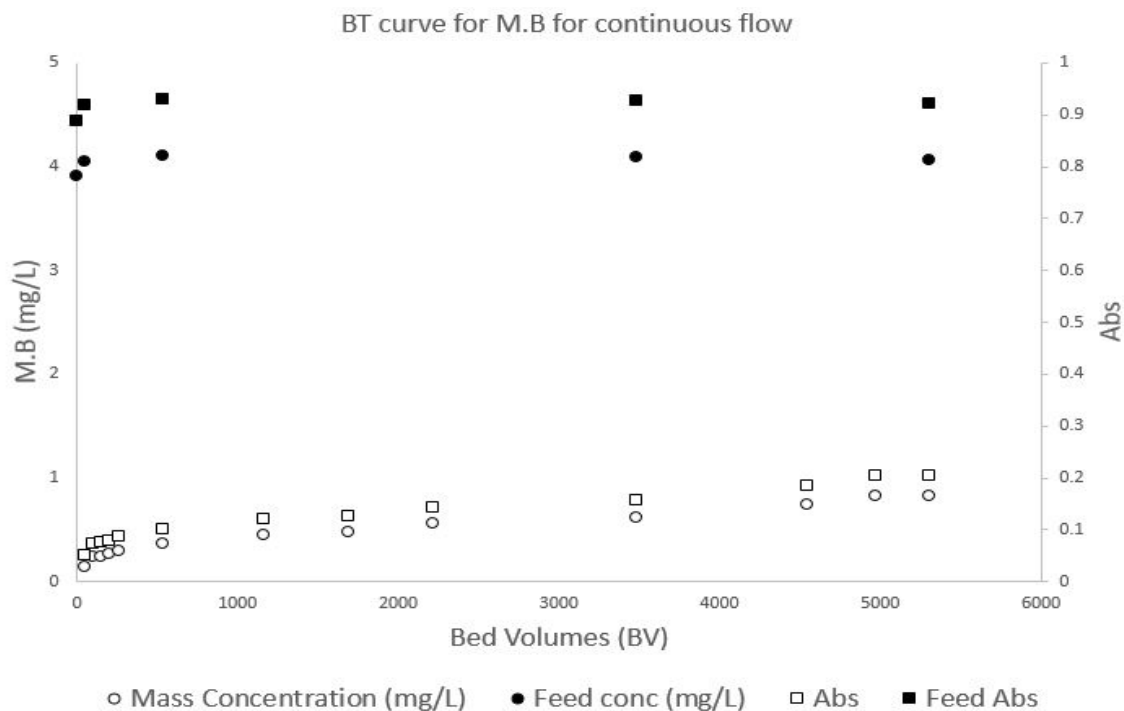


Figure 3.9 (a) 25% Breakthrough Curve for continuous flow CB-A mini carbon block holder test.

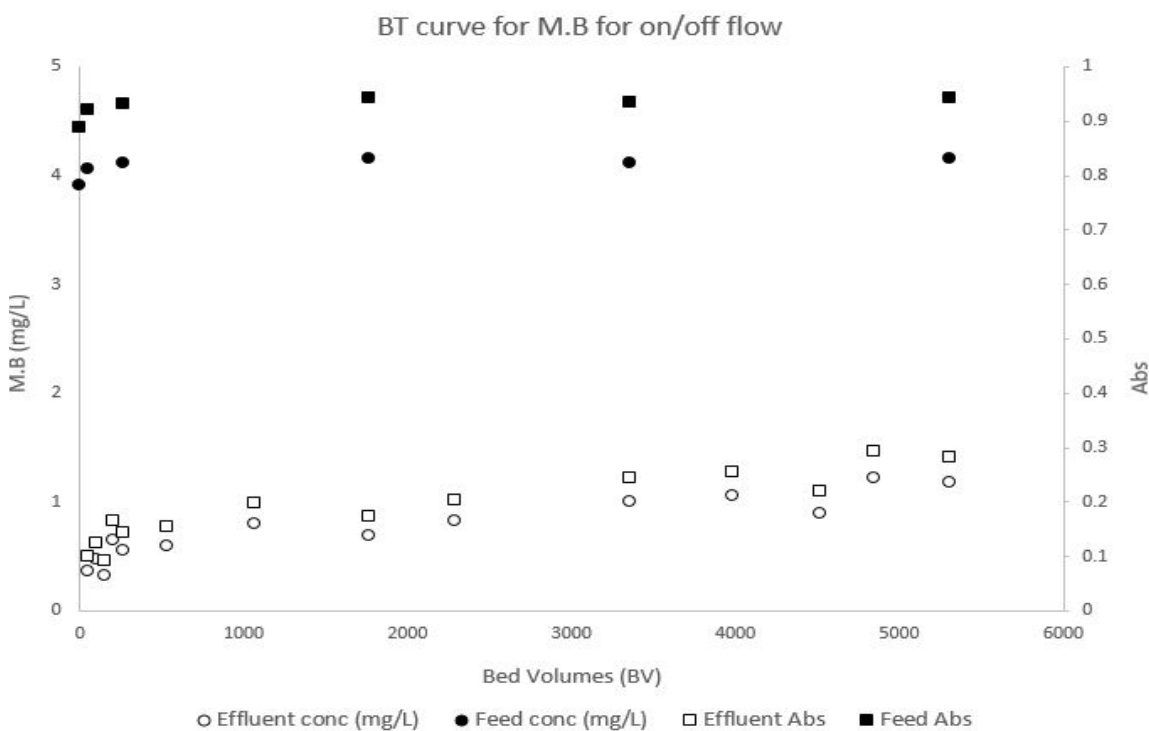


Figure 3.9 (b) 30% Breakthrough Curve for on/off flow CB-A mini carbon block holder test



Few things that can be observed from Figure 3.9. Firstly, that the mini carbon block holder works, removes >90 % for 2000 bed volumes. There is a performance difference between the continuous and on/off operation method. Second, on/off test can provide an interaction while it is off and it can offer more mass transfer at that time (Westerhoff et al.,2005). With the success of these two experiments it creates a need for further verification using the actual emerging contaminants. Figure 3.10 shows a visual of an ongoing MB test. Color change from light blue to colorless is clearly evident from this figure. This picture was taken at the beginning of the test (100 BVs).

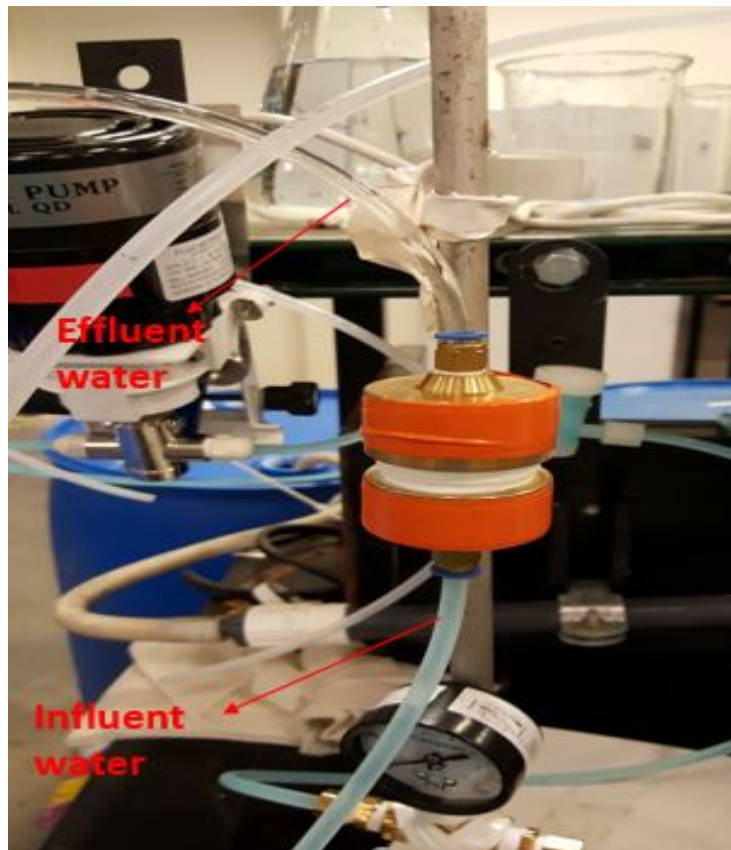


Figure 3.10 Visual of an ongoing MB mini carbon block holder test

There was clear removal of methylene blue confirmed by UV-Vis and visually. But whether the holder performs efficiently was not completely answered and hence

triplicate tests for MB was conducted to evaluate the reproducibility of the holder. A triplicate test for MB was conducted out with higher concentration of 10 mg/L ( $2.4 \text{ cm}^{-1}$  at 664 nm) to evaluate the consistence of this mini carbon block holder. Again, the purpose of using MB was its feasibility, quick results, etc.

Figure 3.11 and 3.12 shows the performance of the triplicate MCB tests for MB removal.

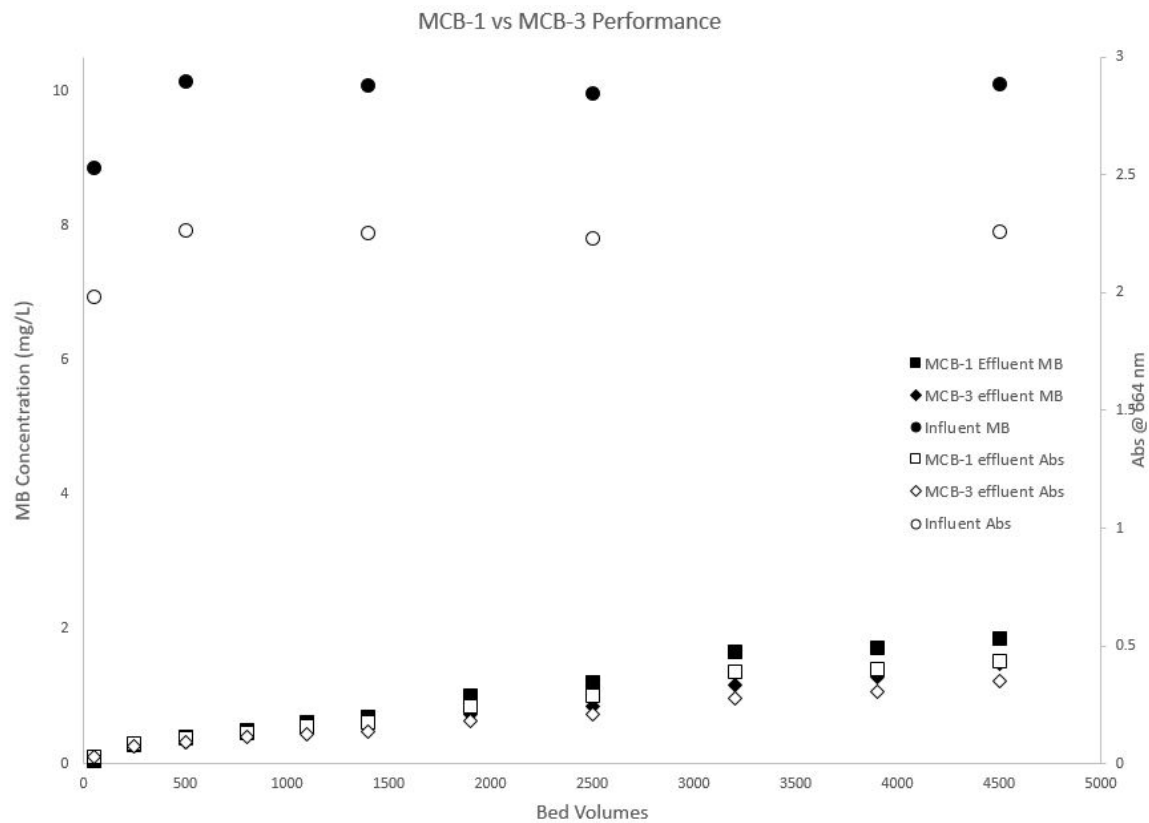


Figure 3.11 Methylene Blue removal for MCB-1 and MCB-3

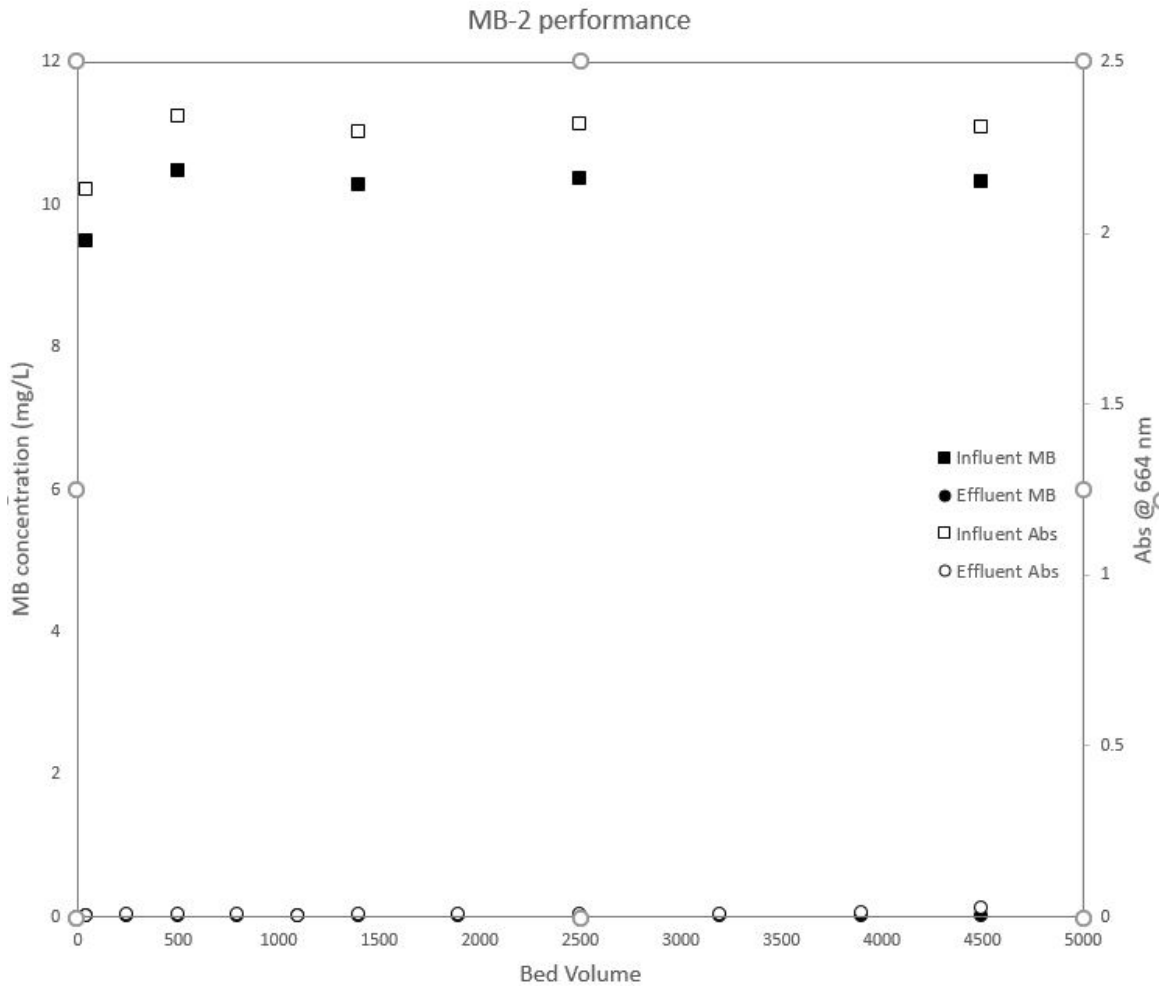


Figure 3.12 Methylene Blue Removal for MCB-2

MCB-1,2 and 3 were all from single full scale carbon block (CB-A) and were operated continuously. The similar performance of MCB-1 and MCB-3 and complete removal for MCB-2 suggested two things, either there were some errors with the MCB-2 test or the holders cannot reproduce the results in a consistent manner. Comparing the previous results of MB removal at 4 mg/L influent and the MCB-1 and MCB-3 for 10 mg/L of MB it seems more likely to have an operational error with MCB-2 but there is definitely a possibility of inconsistent overall carbon block holder performance. Further tests with chloroform and Arsenic would give more idea about it.

### 3.3.2 Chloroform Test

Chloroform is present in all chlorinated tap waters and commonly used by industry to evaluate CB performance. Also chloroform can be used a surrogate for a number of organics testing for NSF-53 validation. Above all of these it was mainly selected as a model contaminant as we had some data about the full scale performance of CB-A for chloroform. Again chloroform test was performed for continuous and on/off flow mode. The industry just tests it for 10 minutes on/off cycle. Figure 3.13 (a) shows breakthrough curve for continuous chloroform CB-A mini carbon block holder test and Figure 3.13 (b) shows breakthrough curve for on/off chloroform CB-A mini carbon block holder test.

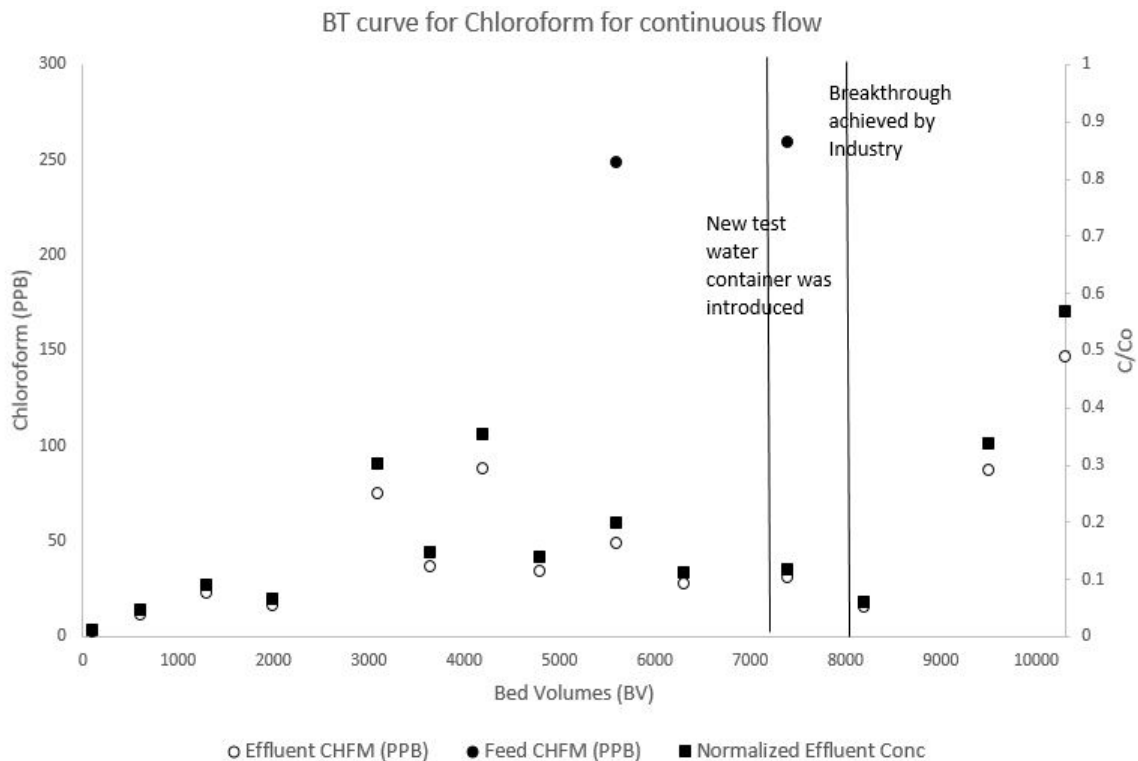


Figure 3.13 (a) Continuous Chloroform test for CB-A holder

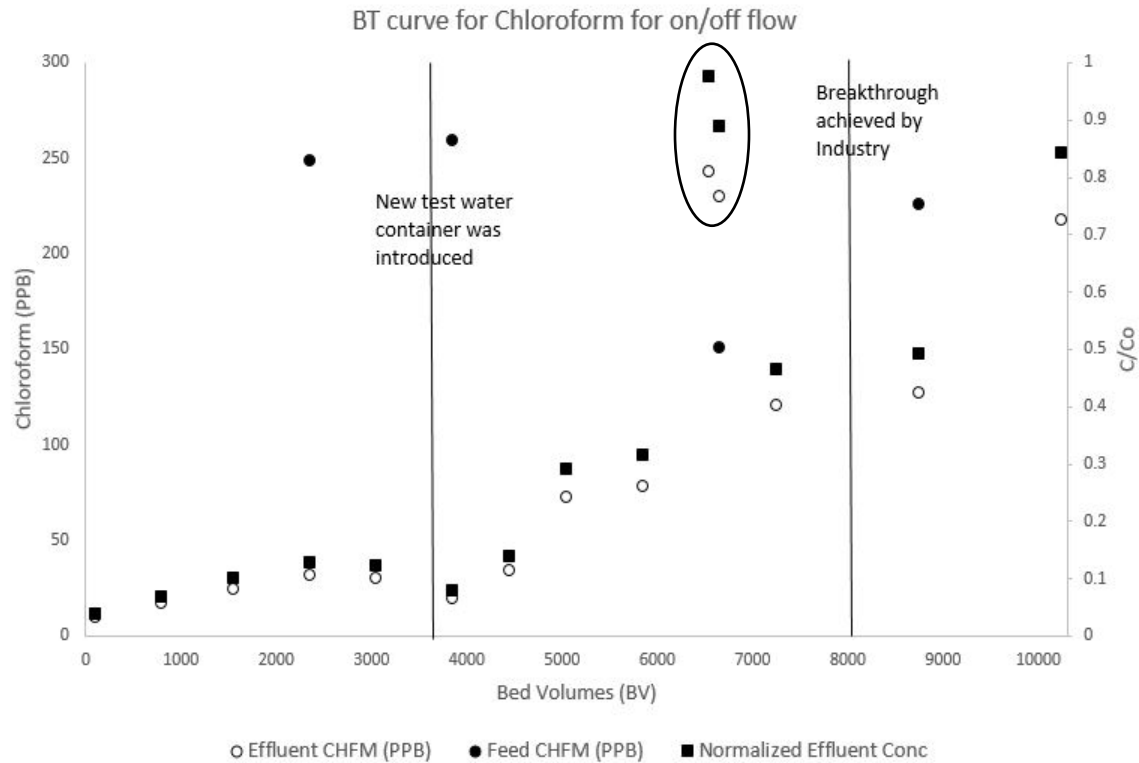


Figure 3.13 (b) On/Off Chloroform test for CB-A holder

Figure 3.13 (a) provides a rough breakthrough curve. It is not as smooth as it was expected, possibly because of different influent water matrix, new holder design flaws, etc. The influent concentration targeted was around 300 ppb, but I was hard to maintain the same throughout the complete test. The target effluent concentration was 15 ppb (as recommended by industry and NSF-53). So the continuous and on/off holders reached target breakthrough almost near to 1200 and 800 BV respectively. One operational problem encountered only during the chloroform testing was the constant dropping influent concentration because chloroform is highly volatile, also there was constant increase in backpressure for both the tests. Figure 3.13 (b) shows a very smooth breakthrough curve except the two weird data points but that actually makes sense because during that time period the MCB holder was being backwashed, on/off column

started producing a high back pressure around 6500 BV (60 psi) and the holder started leaking from the center (female and male connection) and hence backwashing was used in order to troubleshoot the problem of leaking. There was huge rise in backpressure for both the holders after a certain period of time (almost 48 hours) or 7500 BV and 5500 BV for continuous and on/off holder respectively. Continuous column still kept on running without any leakage but the on/off column started leaking heavily from the central joining part. Also the results of GC/MS and the THM analyzer were compared and the data from the THM analyzer looks quite reliable. Figure 3.14 (a) shows analytical methods comparison for continuous MCB holder and Figure 3.14 (b) shows analytical methods comparison for on/off MCB holder. Figure 3.14 (c) shows the backpressure profile for both MCB tests.

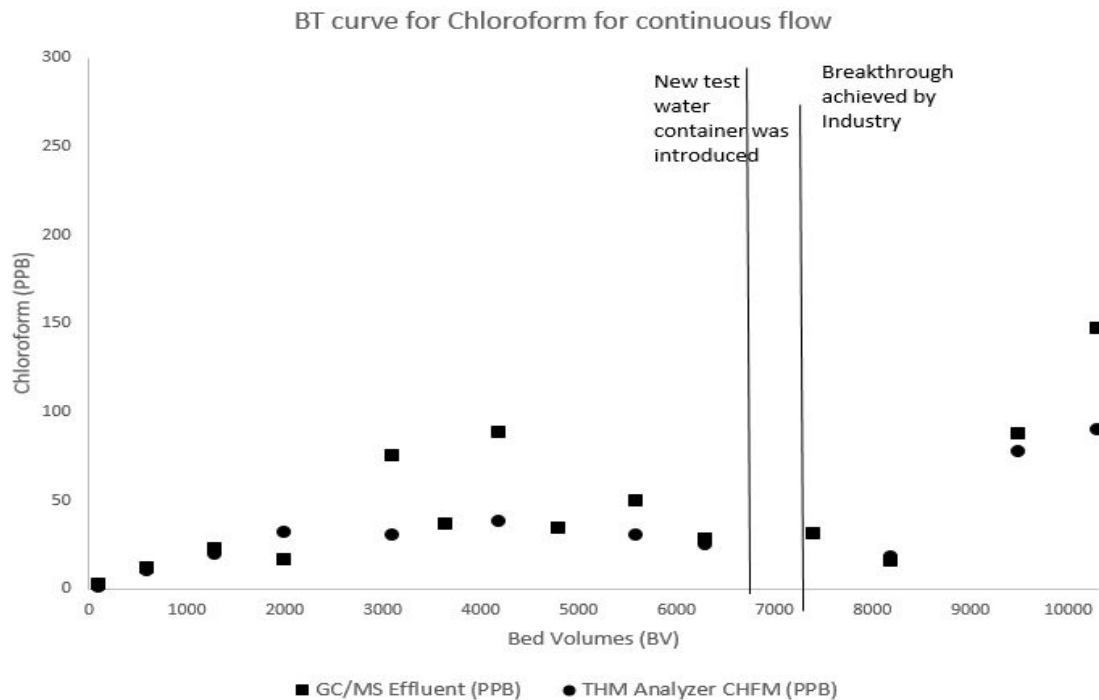


Figure 3.14 (a) Breakthrough Curve comparison for different analytical methods for continuous chloroform MCB holder test

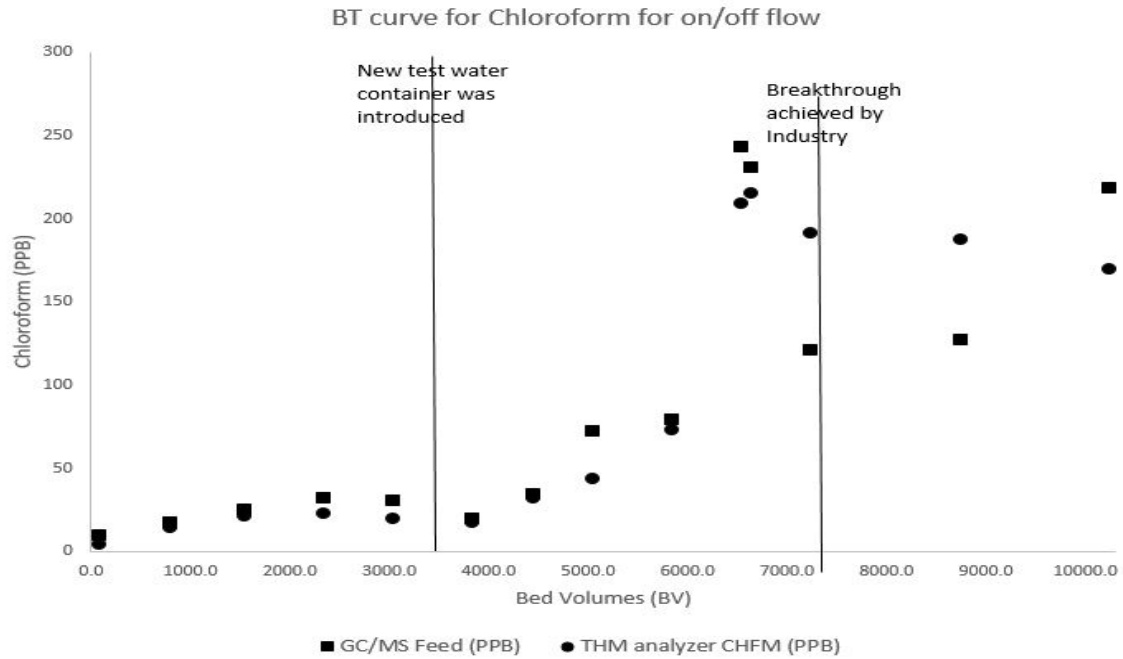


Figure 3.14 (b) Breakthrough Curve comparison for different analytical methods for on/off chloroform MCB holder test

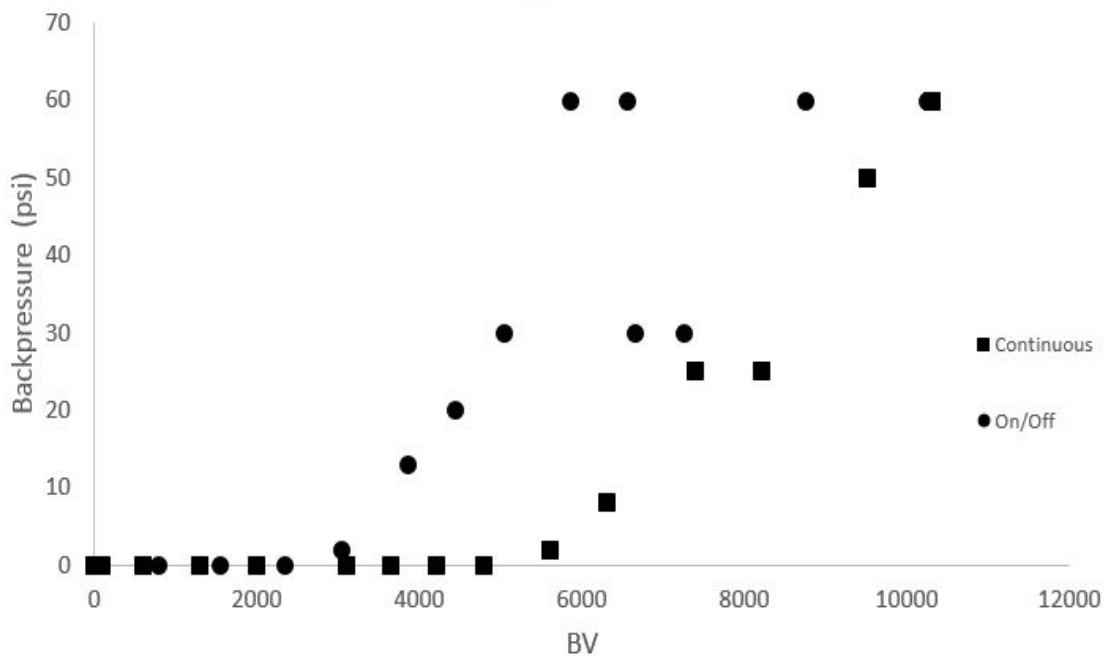


Figure 3.14 (c) Backpressure Profile for Continuous and On/Off Chloroform test

### 3.3.3 Arsenic Test

Arsenic test was performed for a carbon block provided by a CB manufacturer (Altwell) in South Korea. This carbon block claimed to remove the Arsenic up to 10000 L (Altwell Arsenic Carbon Block, 2017). The operational parameters were scaled down using the similar concept used for all other tests (by normalizing the volume of the full scale carbon block to mini scale carbon block) and they are given in Table 3.3. The industry uses tap water in Korea and maintains a pH of 6.5 and the influent concentration was 100 ppb of Arsenic for only continuous operation and no on/off operation. No further information was shared by the industry. There were no operational difficulties encountered throughout the Arsenic test, the back-pressure rise was minimal (10 psi) over the period of the test. The initial channeling test using MB was successful too. Figure 3.16 (a) plots a breakthrough curve for As removal. Figure 3.16 (b) shows the breakthrough curve for the full scale carbon block performance obtained from the industry brochure, the water chemistry of Korea and Arizona tap water would be very different and it could vary the performance between full scale and bench scale carbon block.. Figure 3.16 (c) shows the BT for the MCB test in relation to the volume treated (as per the full scale carbon block). The BT curves show complete removal of Arsenic initially hinting that there shouldn't be any short-circuiting. It also gives a good curve for Arsenic removal but still it under predicts the performance of full scale, there are several explanations to these:

- The complete volume or mass of carbon is not being utilized and the water simply flows through the limited portion of the mini carbon block. Figure 3.15 describes the sketch of the above explanation.



- Different water chemistry can also significantly affect the performance of full scale and mini scale.
- The difference in operating water pressure might contribute to different performance of full scale and mini scale.

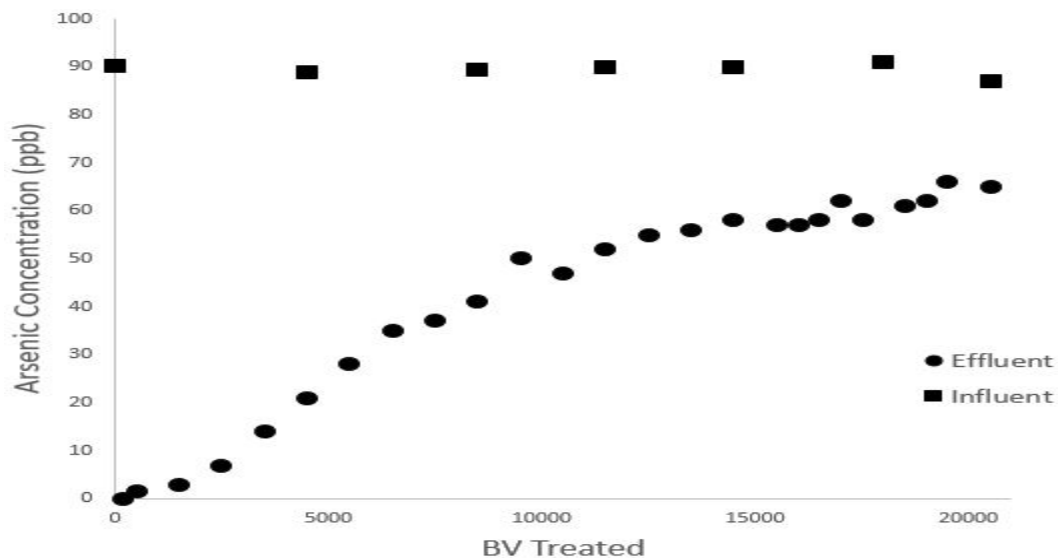
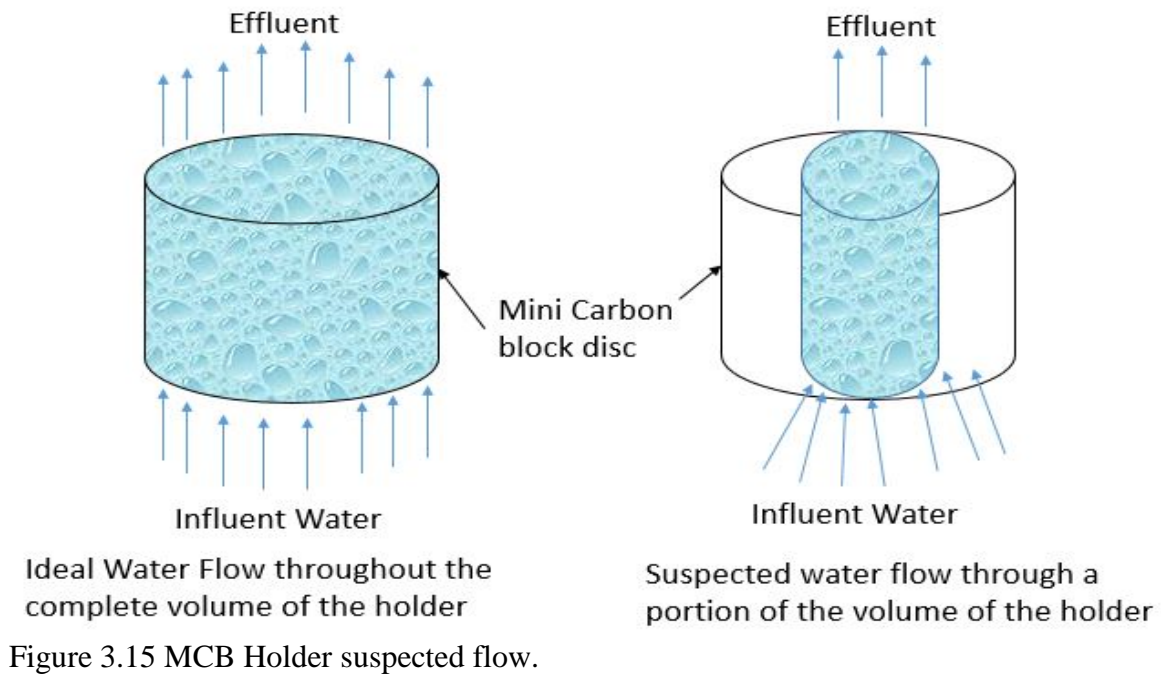


Figure 3.16 (a) BT curve for Arsenic Removal

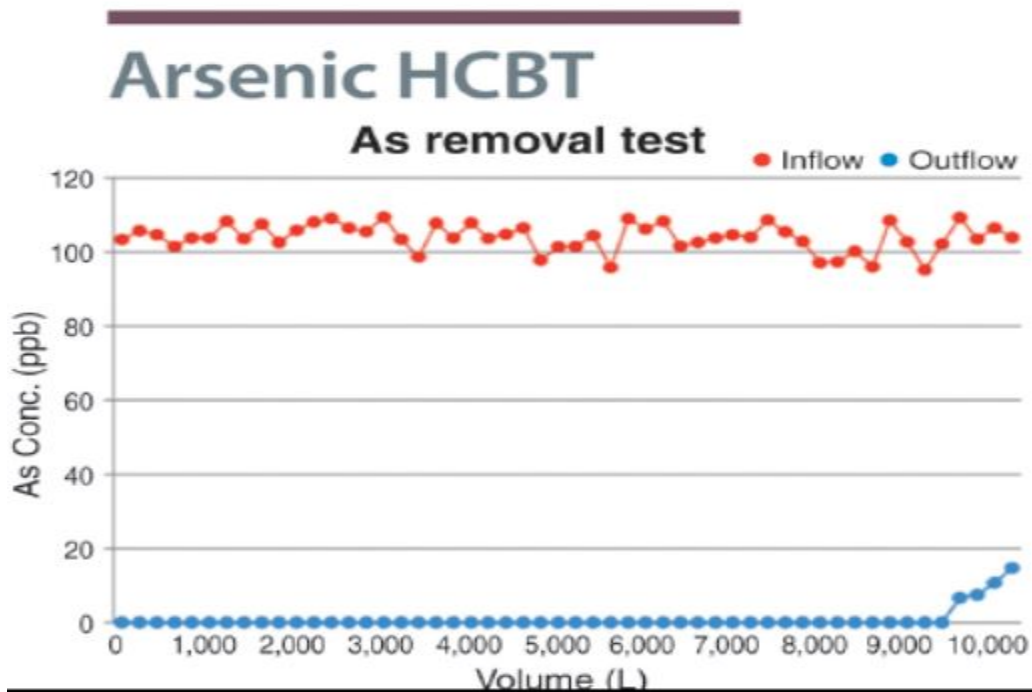


Figure 3.16 (b) BT for Full-Scale Carbon Block Performance

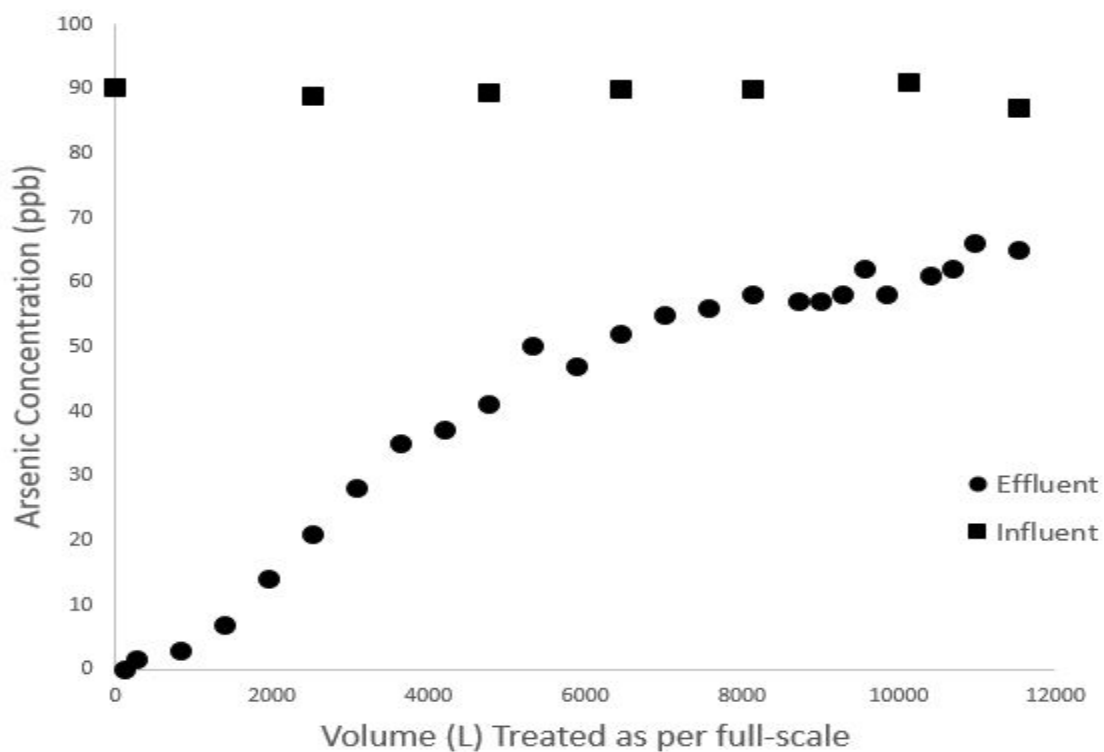


Figure 3.16 (c) BT curve for Arsenic Removal in relation to Volume Treated as per Full-Scale Carbon Block

### 3.4 Summary and Conclusion

There were lot of key observations made in this study, some of them were expected and some were not as expected. But every observation contributed towards the understanding required to develop this new testing protocol. As this concept was something new to the research field, there was not much literature to help with the operational problems and different results. The key summary is listed below:

- A successful protocol was developed to evaluate the MCB for channeling within the holder using methylene blue.
- There was no short-circuiting observed in any of the MCB holder tests.
- 60% or more MB was removed throughout the continuous and on/off MCB tests.
- 60% and 85% breakthrough was achieved for continuous and on/off chloroform tests respectively.
- Several operational problems were encountered during the chloroform tests.
- 75% BT was achieved for Arsenic test unlike 20% BT for full-scale carbon block performance.

The methylene blue test is a good indicator for the initial check and validation of mini carbon block holder. It would be more significant if a full scale test is performed for same operating conditions as the MCB holder test. Also a relation between methylene blue number ( $MB_N$ ) and the known weight/volume of mini carbon block disc should be further studied, if those two can be connected than we can predict the removal of methylene blue using the  $MB_N$  and the known mass of activated carbon in the MCB, that

can cross verify for short-circuiting. MB reproducibility test had two MCB showing similar performance whereas the third showing complete removal.

The chloroform test gives a lot of valuable information for follow up tests. On a brief conclusive note the chloroform test can be suggested as a failure or maybe a good initial success, but in both the cases it creates a great theoretical and practical fundament for further researchers. It shows that chloroform is removed by the mini carbon block, it also suggests to take extra measures for securing the influent water concentration. After the heavy back-pressure rise during the chloroform tests, two follow up tests were conducted using the same mini carbon block and the same source of dechlorinated tap water (without any chloroform,) and back pressure was monitored throughout the test. The back-pressure reached a maximum of 10 psi for both the tests which confirmed the involvement of chloroform for creating operational problems during the chloroform test. It was speculated that there might be some biological growth due to the presence of chloroform or the chloroform would be affecting the binder and its capability of holding the carbon block together. Also one explanation to this sudden increase in the backpressure can be because of the degradation of plastic tubing, O-rings by chloroform. The backpressure increase can also be because of other reasons like activated carbon saturation, dissolved solids layer formation, silica, zinc or other elements layer formed, but as the backpressure started rising in both continuous as well as on/off holders at almost the same time. It indicates that it is independent of bed volumes and dependent of time. But further research needs to be done on that matter also, and lastly the complete dissimilarity in the breakthrough curves of the bench scale and full scale columns can be because of the different water matrix used by industry (Michigan tap water) and ASU

(Arizona tap water). More information from the industry is required to understand this dissimilarity. The almost 0 psi operating water pressure for bench scale MCB instead of 30-60 psi operating pressure for full scale CB can also affect the performance. If more information cannot be procured then it is recommended to operate a full scale carbon block test for chloroform simultaneously with a mini carbon block for the same water matrix.

The Arsenic test did not encounter any operational problems but the breakthrough curve was significantly different than the full-scale carbon block. Again, the water matrix can have a major impact on this difference in the performance. The BT curves shows complete removal of Arsenic initially hinting that there shouldn't be any short-circuiting. It also gives a good curve for Arsenic removal but still it under predicts the performance of full scale. There are three major speculation for this dissimilar performance of bench-scale and full-scale carbon block:

- Different water matrix can affect the performance of mini carbon block performance.
- Full-Scale carbon blocks perform under operating pressure of 30-60 psi (general tap water pressure) whereas the mini carbon block runs under almost 0 psi operating pressure.
- There could be some flaw in the design of the mini carbon block holder which needs to be reassessed like water not passing through the entire volume of the carbon block disc and hence not reacting with entire mass of the carbon block.

Figure 3.15 explains this speculation visually.

## CHAPTER FOUR

### REMOVAL OF HIGH MOLECULAR WEIGHT ORGANIC COMPOUNDS FROM SURFACE WATER BY COAGULATION ENHANCEMENT

#### **4.1 Introduction**

City of Scottsdale water treatment plant (COSWTP) uses Central Arizona Project (CAP) water as the influent source (Water Supply, June 2017). CAP water delivers Colorado River water to central and southern Arizona (Central Arizona Project, June 2017). COSWTP is divided into three treatment chains, the first two are conventional WTP with sedimentation and sand filtration before GAC bed contactors while the third (concerned treatment chain) has a Dissolved Air Flotation (DAF) unit followed by Ultra Filtration (UF) Membrane Filtration (MF) before GAC bed contactors. COSWTP-3 has a Dissolved Air Flotation (DAF) unit in pretreatment followed by Ultra Filtration (UF) Membrane Filtration (MF) with filtrate passing through GAC bed contactors before going into disinfection and distribution as shown in Figure 4.1. GAC bed contactors is good for removing organic compounds, taste and odor, etc. But sometimes there is a need of organics removal at the pretreatment (DAF) for more efficient performance of the MF unit. This study focuses on solving that need of organics removal at pretreatment.

UF membrane filtration plant has been facing irreversible membrane fouling issues over the past few years. City of Scottsdale (utility) and Evoqua Water Technologies (product and service provider for membrane filtration plant) decided to conduct a pilot scale investigative study to enhance the coagulation for higher Total Organic Carbon (TOC) removal. From the previous experience of Evoqua it was speculated that organic fouling is the primary reason for the ongoing irreversible fouling

issues. This speculation was backed by some Chromatic Elemental Imaging (CEI) images of the fouled and cleaned membranes. Figure 4.2 shows the CEI images of the solids loaded and cleaned fiber.

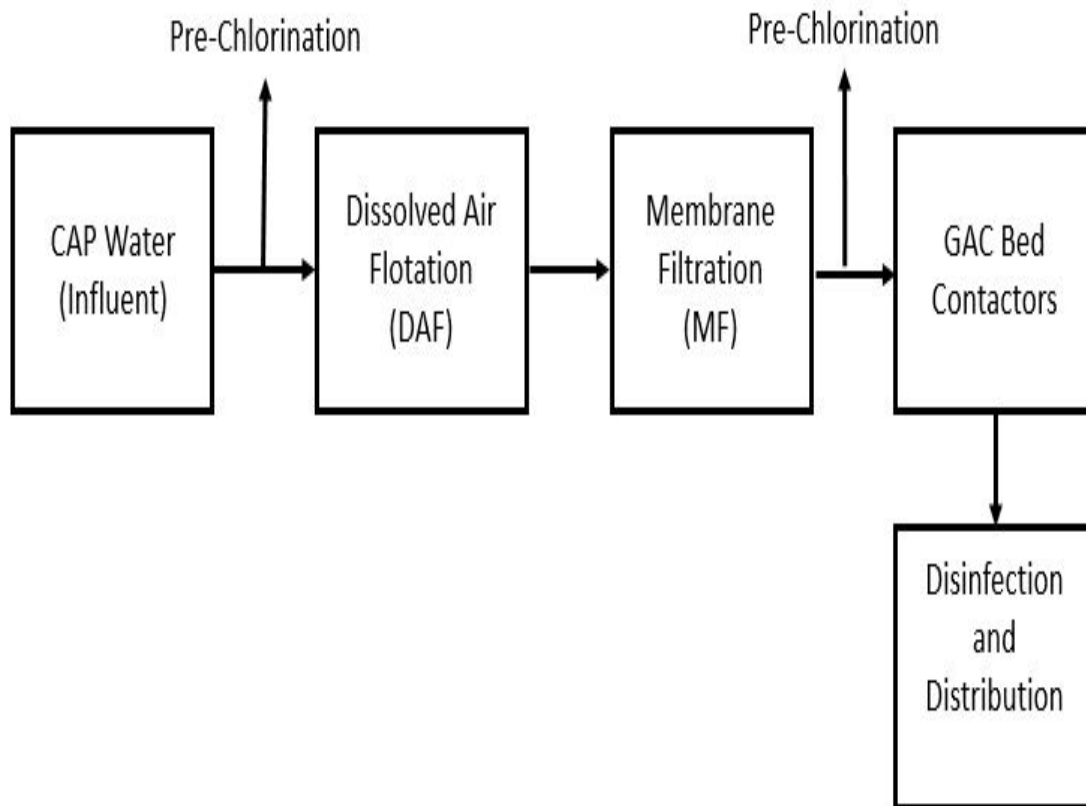
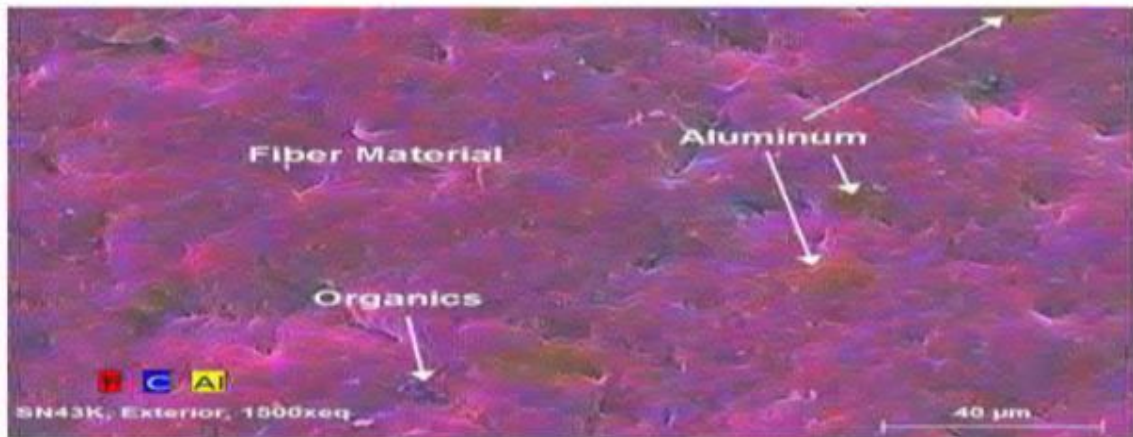


Figure 4.1 City of Scottsdale Water Treatment Chain



CEI image of solids loaded fiber



CEI image of cleaned fiber surface

Figure 4.2 CEI images of membrane fiber

From the CEI images, it looks like the primary contributors to the irreversible fouling are traces of organics and aluminum. Membrane fibers were sent to Avista technologies for CEI imaging. Again from the previous findings and experience of Evoqua it was speculated that the high molecular weight (HMW) organics like biopolymers (Huber et al., 2002; 2011), present in the natural organic matter (NOM) of the CAP water are sensitive to their membranes and they cause the organic irreversible



fouling with all other membrane foulants being washed in backwash, maintenance wash and clean in place (CIP).

The objective of this study was to conduct a bench-scale jar test study for different coagulants and different doses. The organics were characterized for molecular weight distribution using size exclusion chromatography. Then the optimized coagulant and dose was used in the pilot-scale DAF system to compare the results on the qualitative basis. Finally, the optimized coagulant and dose had to be tested on the full-scale DAF plant.

## **4.2 Material and Methods**

### **4.2.1 Water Sampling and Storage**

Influent water was collected using the influent CAP water tap before and after pre-chlorination, DAF effluent samples for main and pilot plants were collected using DAF effluent taps on main and pilot plants respectively. A TOC profile was done on all these above samples to monitor the TOC removal of the main plant and the pilot plant. All these samples were collected using 50 mL Falcon centrifuge tubes (Fischer Scientific, June 2017). The influent water for Jar tests was collected using the same influent CAP water after pre-chlorination. The supernatant from Jar test was collected from supernatant tap on the jar test beaker using 50 mL Falcon tubes. All these samples were straight away analyzed for TOC. Samples for SEC were stored in a refrigerator (4 °C) in a dark room.

### **4.2.2 Chemical Preparation**

Two coagulants were used in this study which are Alum ( $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) and Aluminum Chlorohydrate (ACH) ( $\text{Al}_2(\text{OH})_5\text{Cl}$ ). A 0.5 % w/w solution of Alum and ACH were prepared from 47% w/w and 40% w/w solutions respectively. Calibration

curves for Alum and ACH were prepared to calculate the effect on pH because of the coagulant addition. 1 % solutions of HCl and NaOH were used for pH adjustment. pH calibration curves were prepared for HCl and NaOH. Figure 4.3, 4.4, 4.5 and 4.6 shows the calibration curve for Alum, ACH, HCl and NaOH respectively.

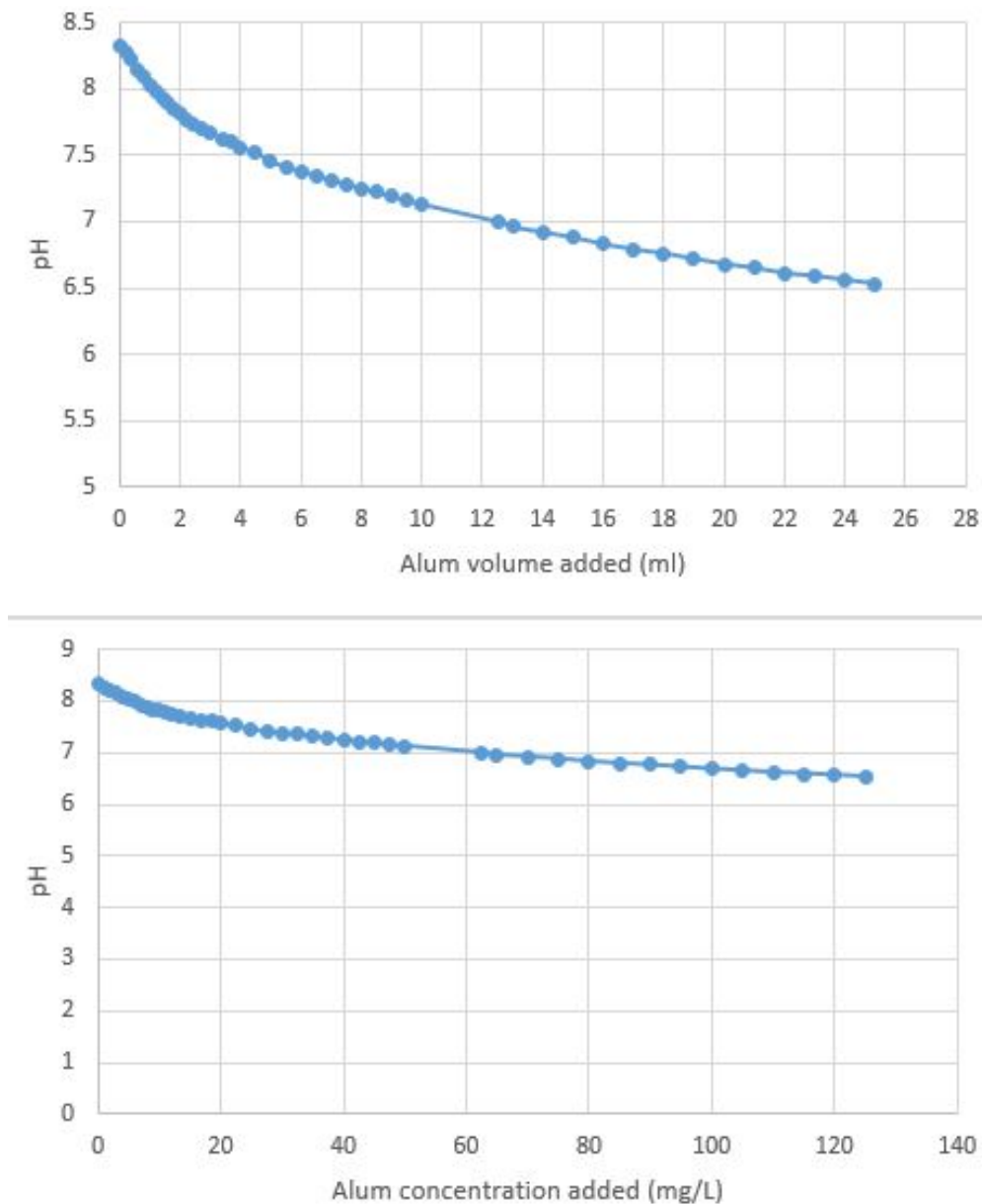


Figure 4.3 pH Calibration for Alum

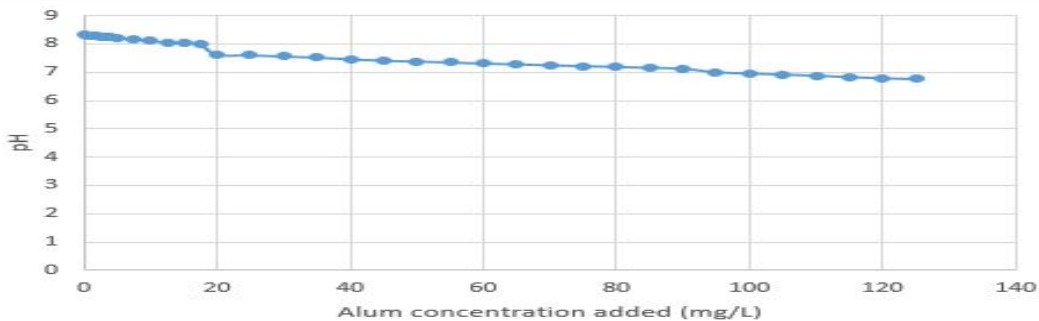
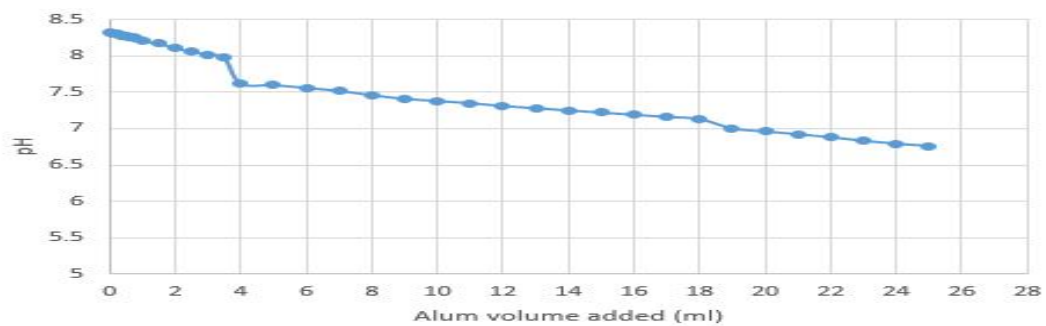


Figure 4.4 pH calibration for ACH

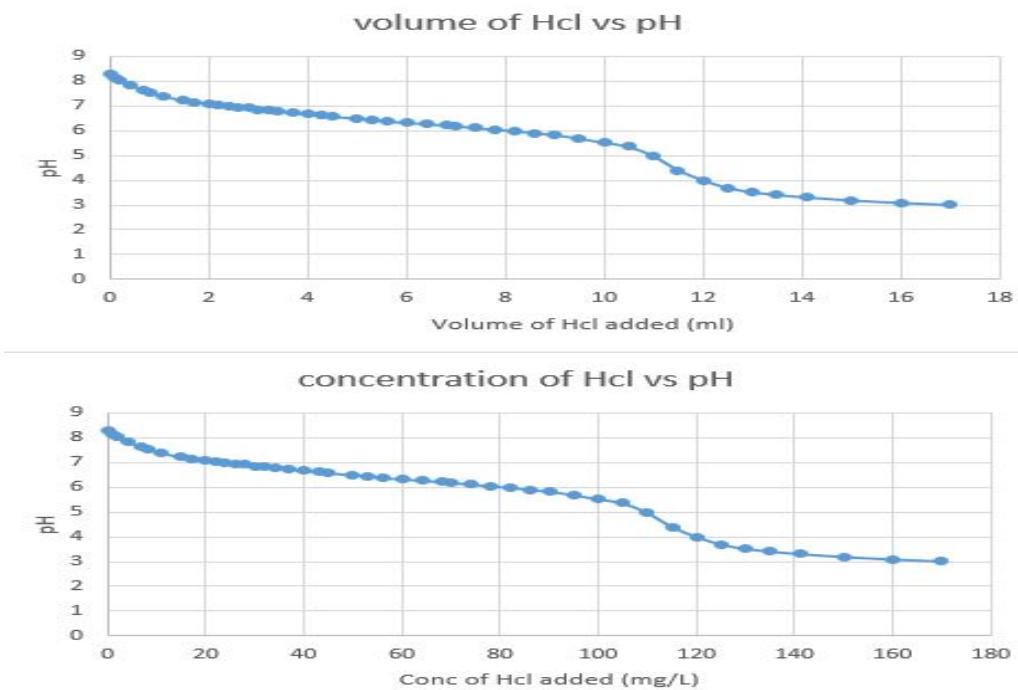


Figure 4.5 pH calibration for HCl

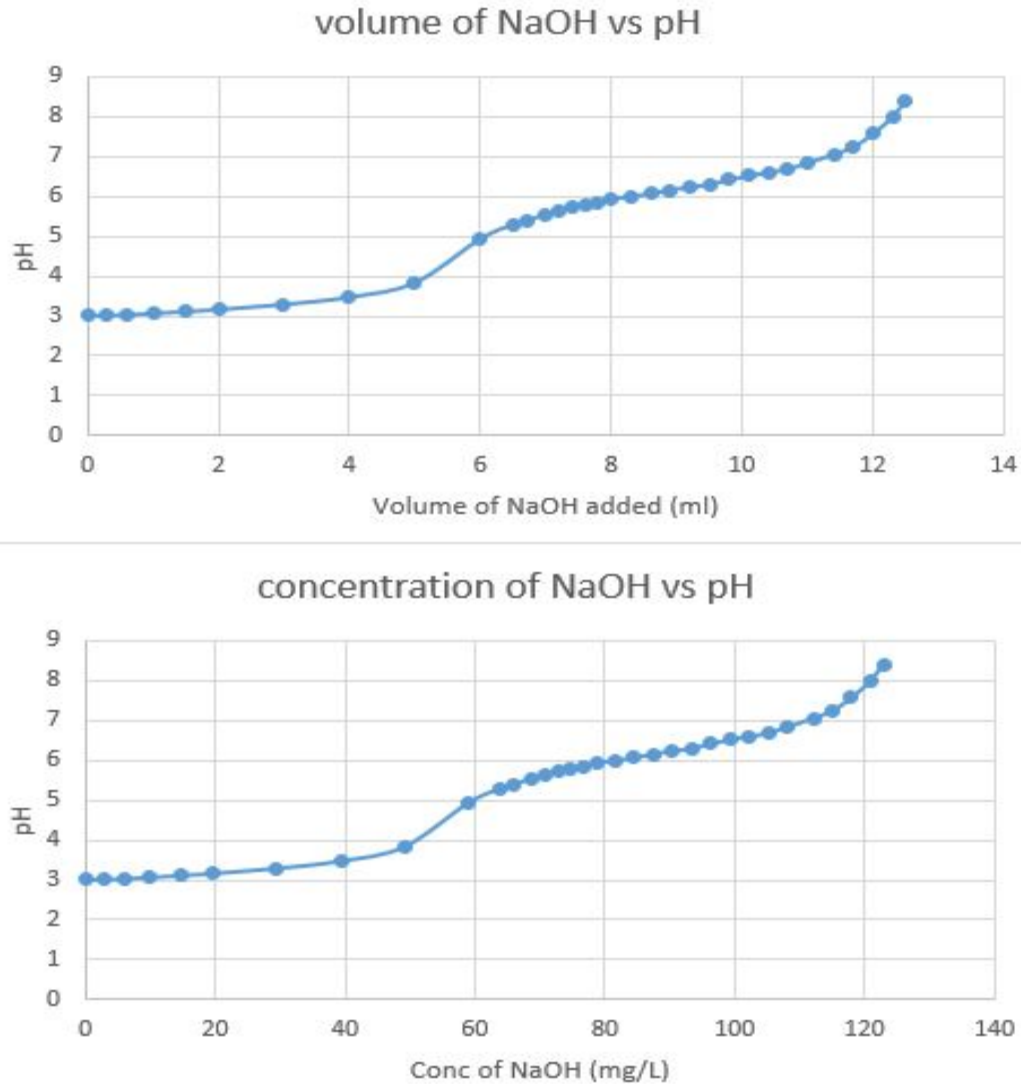


Figure 4.6 pH Calibration for NaOH

#### 4.2.3 Jar Test Apparatus

Jar tester from Phipps and Bird was used with six 2L B-Ker Floc jars. Figure 4.7 shows the visual of the Jar test apparatus. Table 4.1 presents the fixed operating parameters for the Jar test, these parameters were provided by the industry as these parameters were previously proved to be the most optimal parameters. The only varying parameters were pH and coagulant dose.

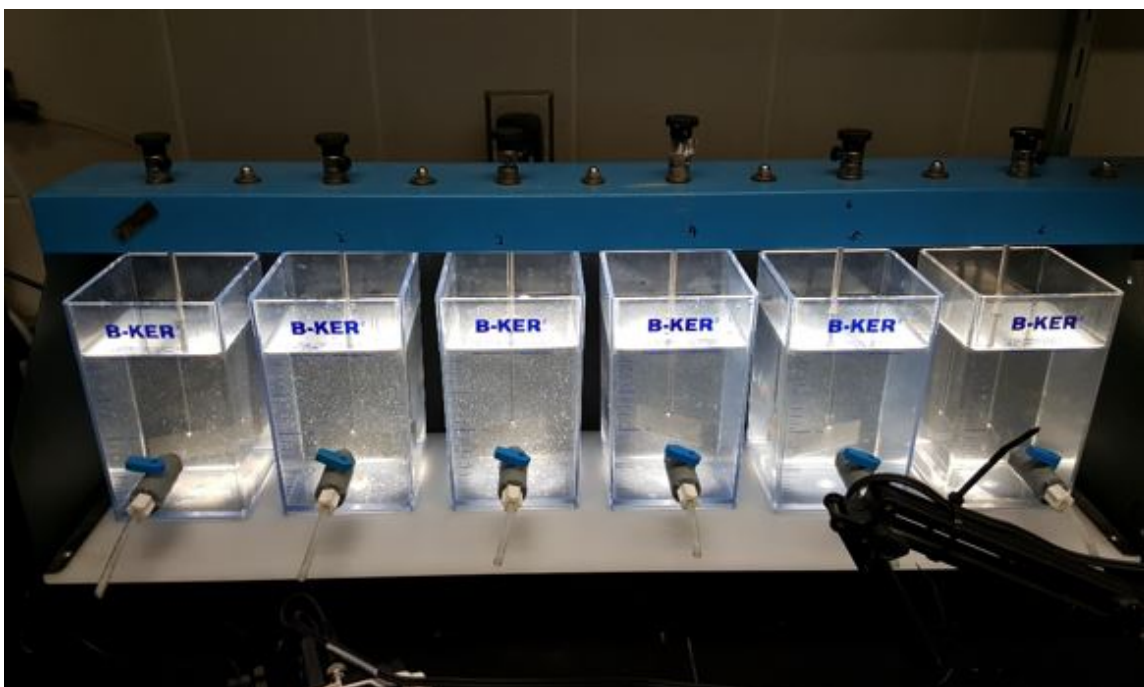


Figure 4.7 Jar Test Apparatus

Table 4.1 Jar Test Operational Parameters

| Jar                  | 1      | 2      | 3      | 4      | 5      | 6      |
|----------------------|--------|--------|--------|--------|--------|--------|
| Rapid Mix @ 100 rpm  | 1 min  | 1 min  | 1 min  | 1 min  | 1 min  | 1 min  |
| Slow Mix @ 30 rpm    | 15 min | 15 min | 15 min | 15 min | 15 min | 15 min |
| Settling Time        | 45 min | 45 min | 45 min | 45 min | 45 min | 45 min |
| Coagulant Dose (ppm) | ----   | ----   | ----   | ----   | ----   | ----   |
| pH                   | ----   | ----   | ----   | ----   | ----   | ----   |

#### 4.2.4 Size Exclusion Chromatography-Dissolve Organic Carbon (SEC-DOC)

The SEC-DOC system is an assembly of a High-Performance Liquid Chromatography System (Waters 2695 Separation Module) followed by an online TOC detector (Sievers Total Organic Carbon Analyzer 800 Turbo) connected to an inorganic carbon remover (900 ICR, GE). More details about the column setup and operation can be found in the earlier work (Wang et al., 2013). The MW range 10KDa-30KDa gives the peak for the biopolymers like polysaccharides, Extracellular Polymeric Substances (EPS) (Huber et al., 2002; 2011).

#### **4.2.5 Water Quality Analysis**

TOC was analyzed using Sievers 900 On-Line TOC Analyzer, pH was measured using ThermoScientific pH meter, turbidity was measured using HF Scientific Micro 100 Turbidimeter and dissolved Al was measured using Hach DR-890 Colorimeter.

### **4.3 Results and Discussions**

#### **4.3.1 Alum Jar Tests**

Four Jar Tests were conducted to find an optimal pH and dose for Alum. Jar test 1 was performed for pH scan, the dose used for pH scan was 6 ppm of Alum which was also the main plant dose at that time, the pH range was recommended by the Industry and also it is common range for optimum pH for Alum. Table 4.2 describes the jar test 1 result in a tabular form. The main objective of these jar tests was to enhance the coagulation by finding the right coagulation chemistry for the CAP water and hence TOC removal was the most important deciding factor. Figure 4.8 shows the TOC removal for jar test 1. The optimized pH concluded from the pH scan was from 6.2-6.3 and hence 6.2 was preferred because of a slightly higher TOC removal. Jar tests 2 and 3 were conducted for dose scan ranging from 0-50 ppm of Alum. Tables 4.3, 4.4 and Figure 4.9 and 4.10 gives and overall analysis of the results of those two jar tests. Jar test 4 was conducted for finding an optimized dose for the optimum pH. Table 4.5 and Figure 4.11 presents the findings of jar test 4. In all these results the pH, Turbidity and TOC were measured for the supernatants after the settling. All these results and the SEC-DOC results were

Table 4.2 Jar Test Parameters and Results for Jar Test 1

| Jar #       | Raw  | 1    | 2    | 3    | 4    | 5    | 6    |
|-------------|------|------|------|------|------|------|------|
| Alum (ppm)  | 0    | 6    | 6    | 6    | 6    | 6    | 6    |
| Targeted pH | 8.27 | 7.2  | 7    | 6.8  | 6.6  | 6.4  | 6.2  |
| pH          | 8.27 | 7.23 | 7.01 | 6.79 | 6.56 | 6.28 | 6.19 |
| TOC         | 3.3  | 3.22 | 3.19 | 3.19 | 3.96 | 3.11 | 3.1  |
| Turbidity   | 3.5  | 0.75 | 1.1  | 0.9  | 0.85 | 0.8  | 1.5  |

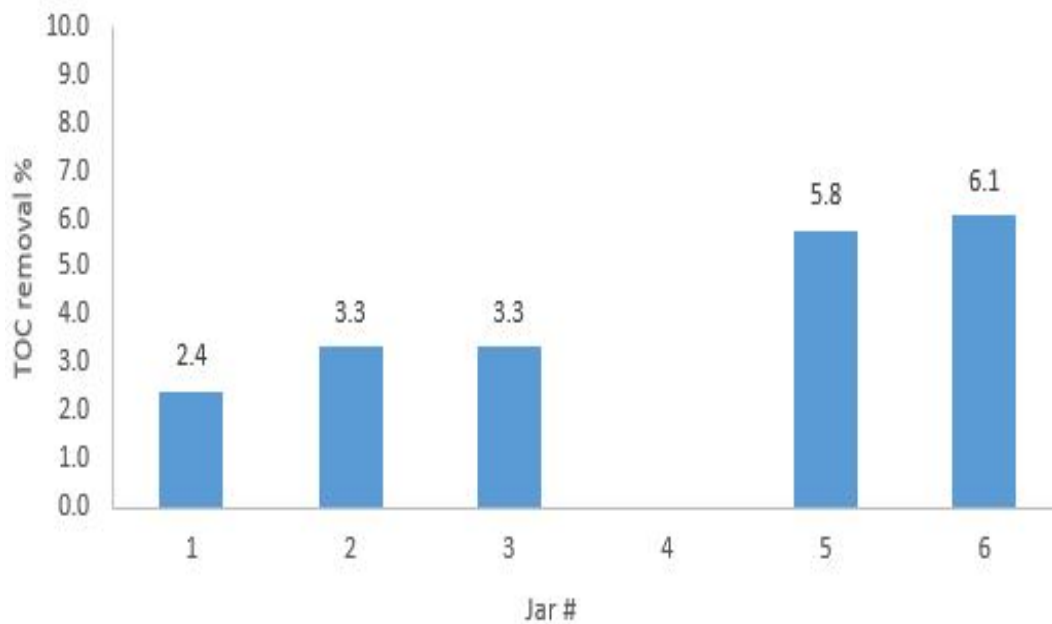


Figure 4.8 TOC Removal for Jar Test 1

Table 4.3 Jar Test Parameters and Results for Jar Test 2

| Jar #      | Raw  | 1    | 2    | 3    | 4    | 5    | 6   |
|------------|------|------|------|------|------|------|-----|
| Alum (ppm) | 0    | 0    | 3    | 6    | 9    | 12   | 20  |
| pH         | 8.33 | 8.36 | 8.19 | 8.04 | 7.93 | 7.8  | 7.6 |
| TOC        | 3.43 | 3.45 | 3.44 | 3.45 | 3.35 | 3.21 | 3   |
| Turbidity  | 4.6  | 2.5  | 1.9  | 2    | 1.5  | 0.9  | 0.4 |

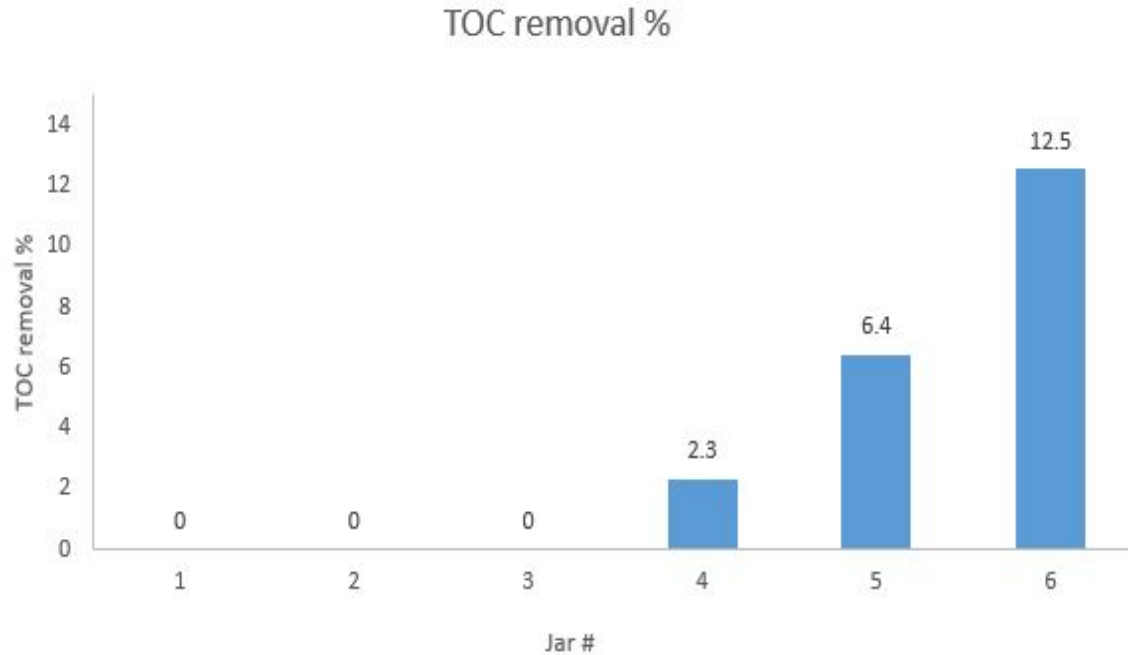


Figure 4.9 TOC Removal for Jar Test 2

Table 4.4 Jar Test Parameters and Results for Jar Test 3

| Jar #      | Raw  | 1    | 2    | 3    | 4    | 5    | 6    |
|------------|------|------|------|------|------|------|------|
| Alum (ppm) | 0    | 0    | 10   | 20   | 30   | 40   | 50   |
| pH         | 8.3  | 8.27 | 7.9  | 7.66 | 7.48 | 7.3  | 7.19 |
| TOC        | 3.99 | 3.59 | 3.43 | 3.1  | 2.9  | 2.68 | 2.91 |
| Turbidity  | 2.6  | 1.4  | 0.75 | 0.47 | 0.26 | 0.36 | 0.35 |

Table 4.5 Jar Test Parameters and Results for Jar Test 4

| Jar #       | Raw  | 1    | 2    | 3    | 4    | 5    | 6    |
|-------------|------|------|------|------|------|------|------|
| Alum (ppm)  | 0    | 0    | 6    | 12   | 20   | 30   | 40   |
| Targeted pH | 8.32 | 6.2  | 6.2  | 6.2  | 6.2  | 6.2  | 6.2  |
| pH          | 8.32 | 6.17 | 6.18 | 6.18 | 6.18 | 6.16 | 6.17 |
| TOC         | 3.56 | 3.26 | 3    | 2.7  | 2.47 | 2.25 | 2.16 |
| Turbidity   | 2.2  | 0.9  | 0.75 | 0.36 | 0.48 | 0.18 | 0.13 |



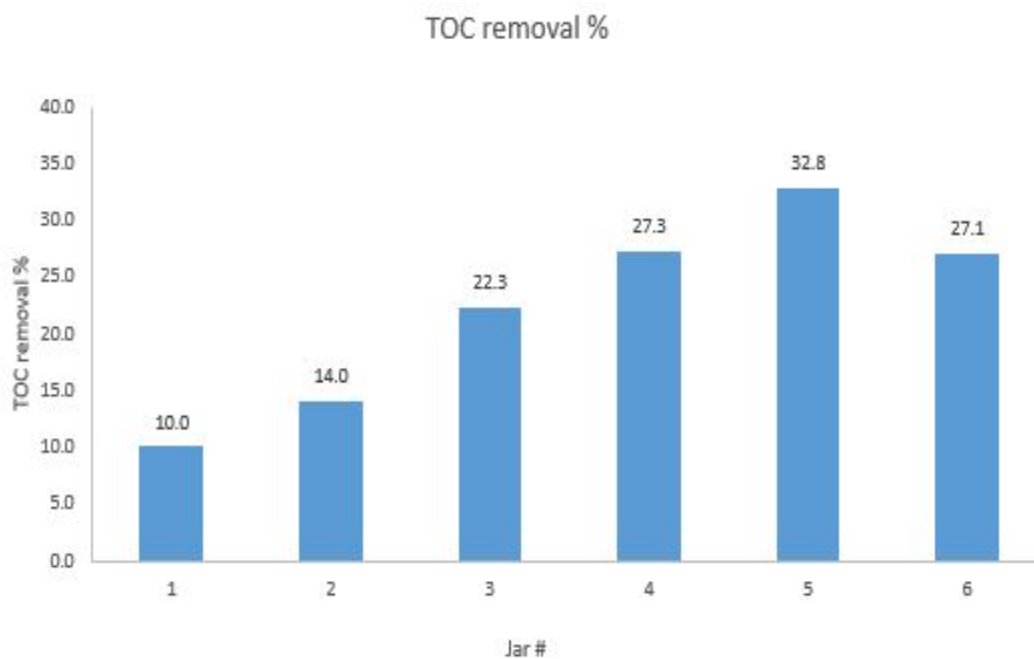


Figure 4.10 TOC Removal for Jar Test 3

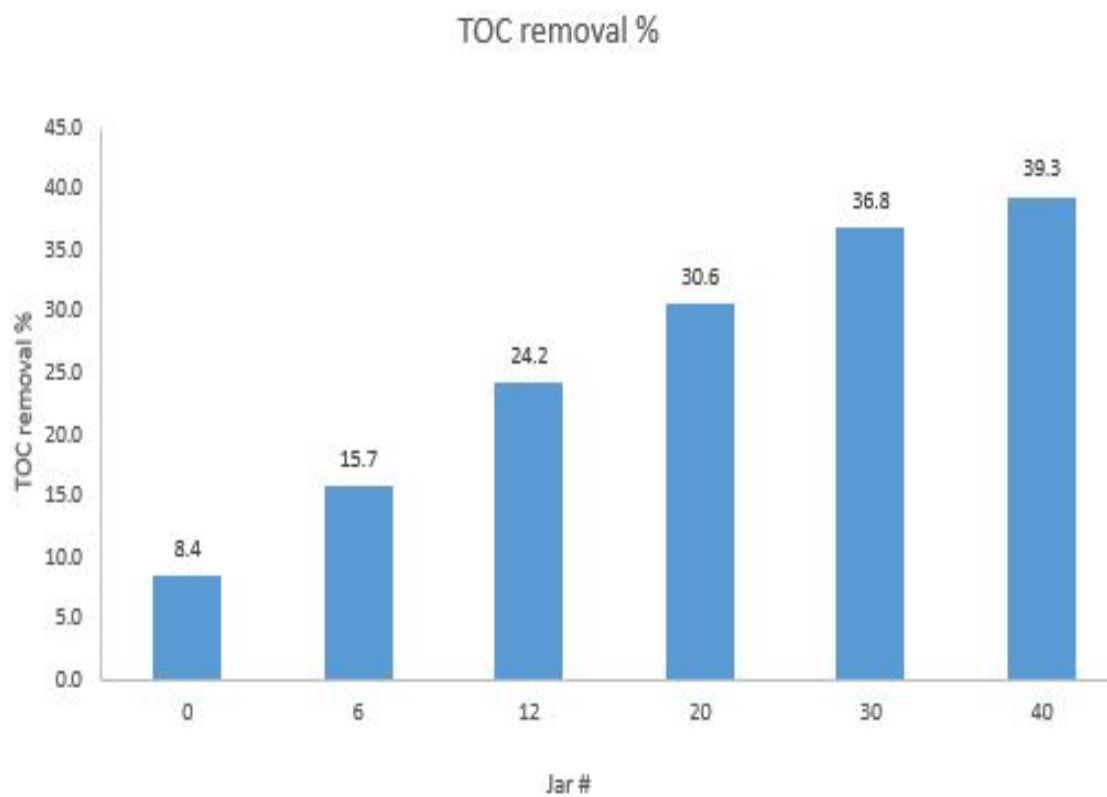


Figure 4.11 TOC Removal for Jar Test 4

From all the above results it was concluded that pH adjustment is required for Alum for better TOC removal at all the coagulant doses. Just considering the TOC removal 30 ppm of alum can be considered an optimum dose for Alum. SEC-DOC results for Jar Test 4 added to the 30 ppm of alum as optimum dosage conclusion. The intensity of chromatograms for DOC are measured in millivolts every 3 seconds which forms the DOC peaks. As shown in Figure 4.12 the peaks in terms of removal of HMW organics the 30 ppm and 40 ppm of Alum gives the same result.

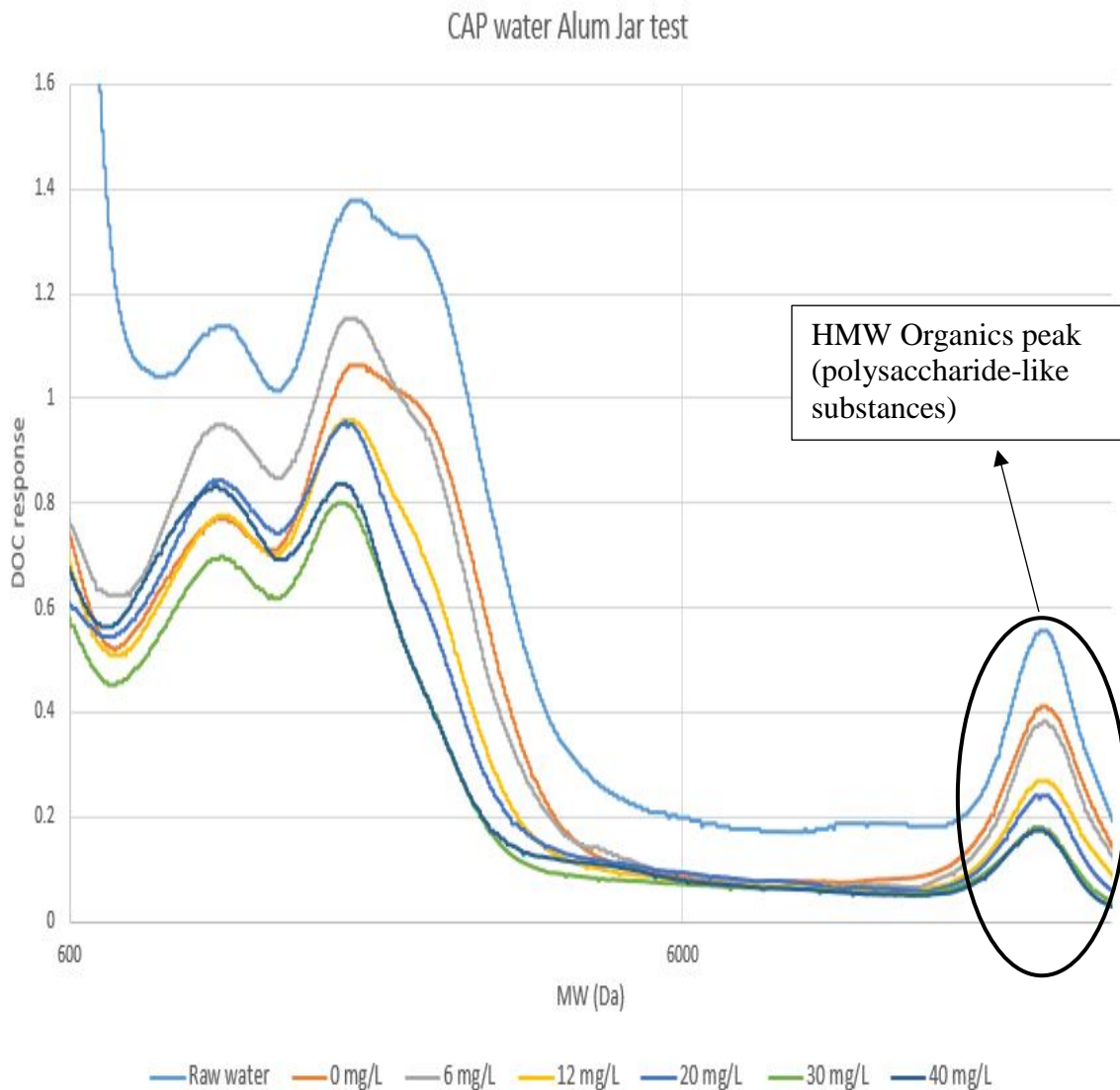


Figure 4.12 SEC-DOC results for Jar Test 4

### 4.3.2 ACH Jar Tests

There were total of five jar tests run for ACH with jar test 5 and 6 focusing on dose scan and jar test 7 and 8 focusing on pH scan for a lower and higher ACH dose respectively. The Al concentration of ACH is approximately 3 times higher than the Al concentration of alum which means 1 ppm of ACH would have the same Al concentration as of 3 ppm Alum. Using that fact the dose scan range for ACH was approximately derived from the dose scan range of Alum. From the previous experience of the industry it was suggested that ACH is not that sensitive of pH and it gives almost equal results from 6 to 8 pH. Still pH scan was conducted for a lower ACH concentration (4 ppm) and a higher ACH concentration (10 ppm). Tables 4.6-4.9 describes the Jar tests results in a tabular form and Figures 4.13-4.16 gives the information of TOC removal for all the Jar tests.

Table 4.6 Jar Test Parameters and Results for Jar Test 5

| <b>Jar #</b> | <b>Raw</b> | <b>1</b> | <b>2</b> | <b>3</b> | <b>4</b> | <b>5</b> | <b>6</b> |
|--------------|------------|----------|----------|----------|----------|----------|----------|
| ACH (ppm)    | 0          | 0        | 1        | 2        | 3        | 5        | 7        |
| pH           | 8.33       | 8.34     | 8.34     | 8.26     | 8.29     | 8.26     | 8.23     |
| TOC          | 3.47       | 3.37     | 3.31     | 3.12     | 3.11     | 2.92     | 2.82     |
| Turbidity    | 2.2        | 1.1      | 1.2      | 0.6      | 0.9      | 0.69     | 0.35     |

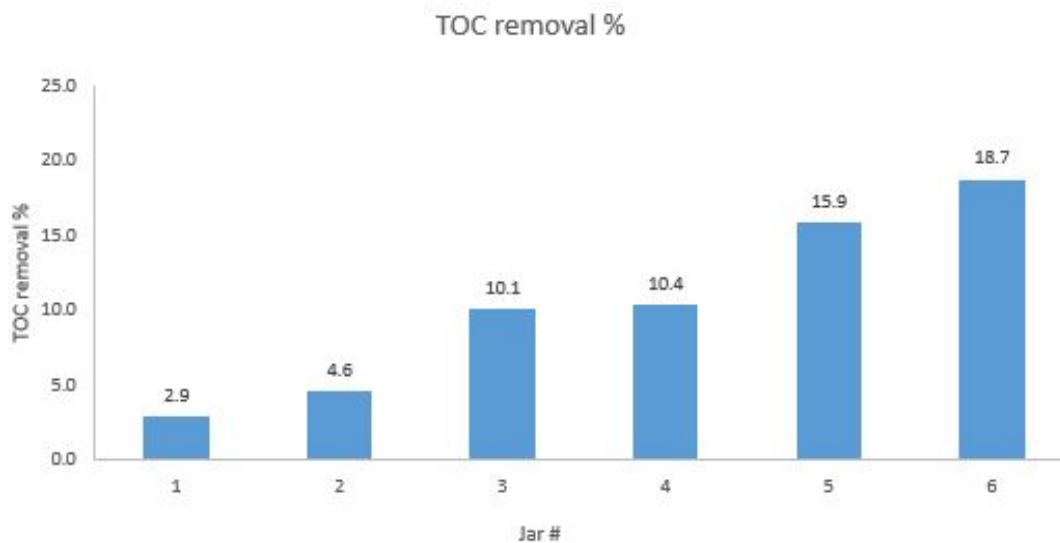


Figure 4.13 TOC Removal for Jar Test 5

Table 4.7 Jar Test Parameters and Results for Jar Test 6

| Jar #       | Raw  | 1    | 2    | 3    | 4    | 5    | 6    |
|-------------|------|------|------|------|------|------|------|
| ACH (ppm)   | 0    | 0    | 2    | 2    | 4    | 10   | 14   |
| Targeted pH | 8.27 | 7.4  | 7.4  | ---- | ---- | ---- | ---- |
| pH          | 8.27 | 7.36 | 7.39 | 8.19 | 8.19 | 8.14 | 8.07 |
| TOC         | 3.34 | 3.35 | 3.26 | 3.22 | 3.06 | 2.73 | 2.56 |
| Turbidity   | 2.45 | 1.1  | 1.25 | 0.95 | 0.76 | 0.58 | 0.39 |

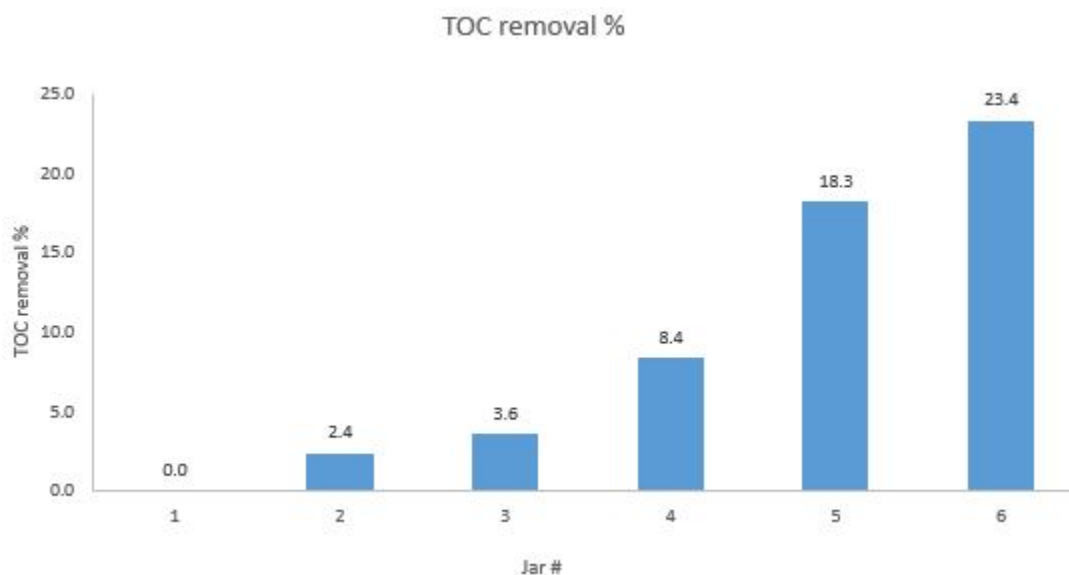


Figure 4.14 TOC Removal for Jar Test 6

Table 4.8 Jar Test Parameters and Results for Jar Test 7

| Jar #       | Raw  | 1    | 2    | 3    | 4    | 5    | 6    |
|-------------|------|------|------|------|------|------|------|
| ACH (ppm)   | 0    | 4    | 4    | 4    | 4    | 4    | 4    |
| Targeted pH | 8.27 | 6.5  | 6.7  | 6.9  | 7.1  | 7.3  | 7.5  |
| pH          | 8.27 | 6.54 | 6.72 | 6.91 | 7.19 | 7.3  | 7.6  |
| TOC         | 3.21 | 3.22 | 2.95 | 3.02 | 3.03 | 3.08 | 3.04 |
| Turbidity   | 0.95 | 0.67 | 0.74 | 0.81 | 0.64 | 0.59 | 0.8  |

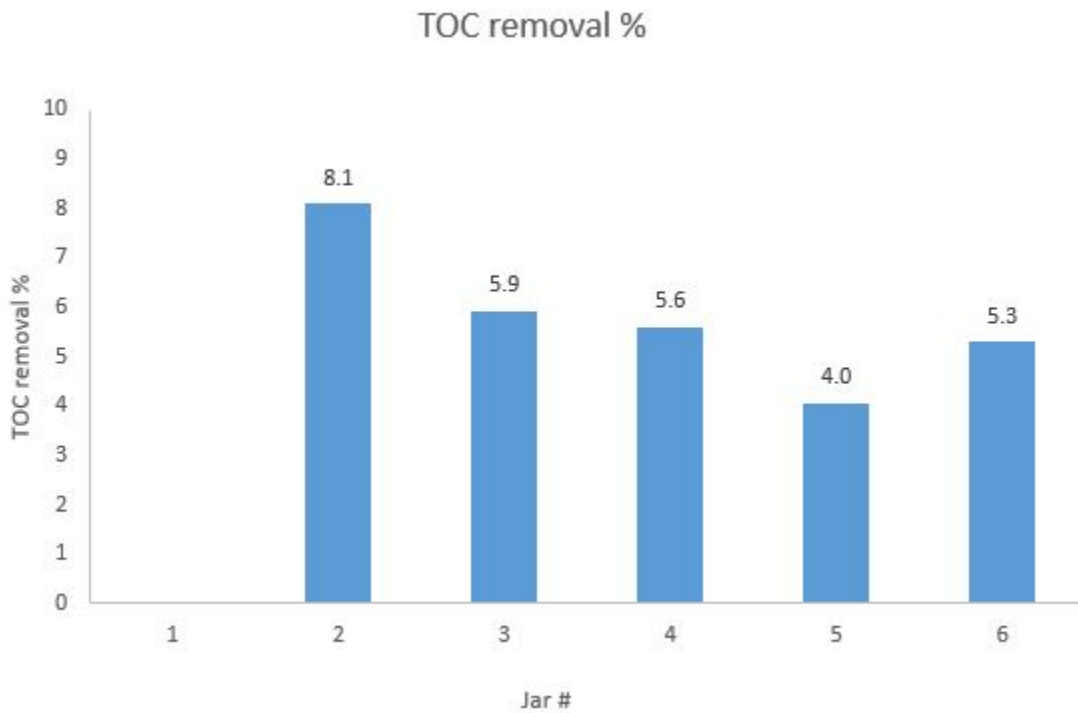


Figure 4.15 TOC Removal for Jar Test 7

Table 4.9 Jar Test Parameters and Results for Jar Test 8

| Jar #       | Raw  | 1    | 2    | 3    | 4    | 5    | 6    |
|-------------|------|------|------|------|------|------|------|
| ACH (ppm)   | 0    | 10   | 10   | 10   | 10   | 10   | 10   |
| Targeted pH | 8.35 | 6.4  | 6.7  | 7    | 7.3  | 7.6  | None |
| pH          | 8.35 | 6.43 | 6.7  | 6.96 | 7.27 | 7.67 | 8.03 |
| TOC         | 3.22 | 2.67 | 2.48 | 2.58 | 2.61 | 2.69 | 2.69 |
| Turbidity   | 1.2  | 0.96 | 0.34 | 0.36 | 0.63 | 0.42 | 0.48 |

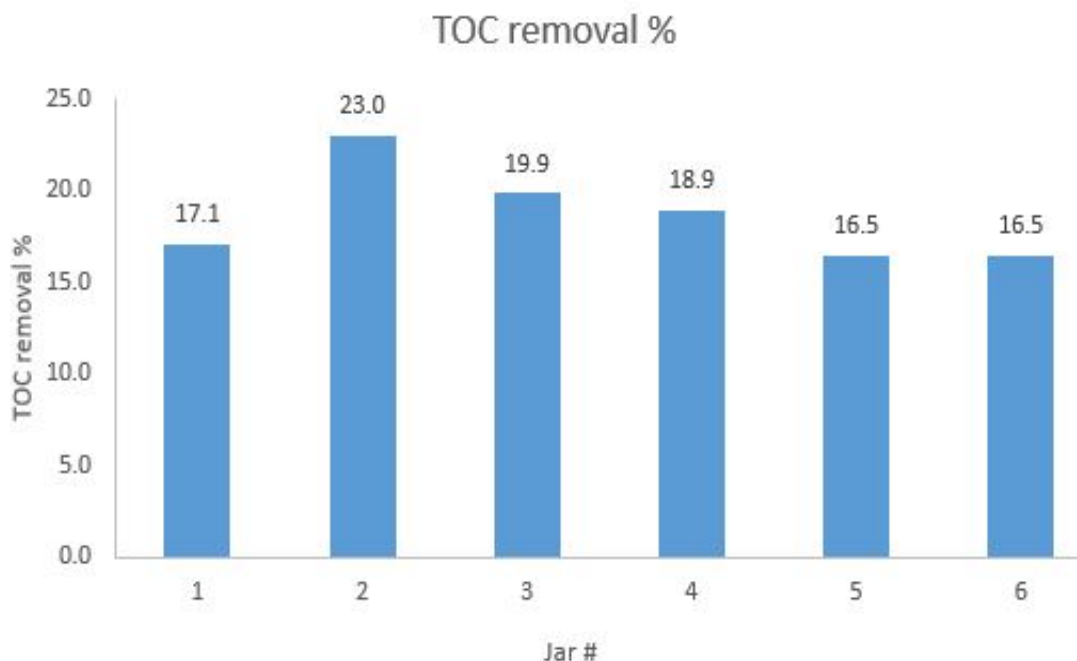


Figure 4.16 TOC Removal for Jar Test 8

From Jar tests 5-8 the optimum dose for ACH was still not fixed but the optimum pH was definitely 6.7 as higher TOC removal was achieved for pH 6.7 for 4 and 10 ppm of ACH. Jar test 9 was conducted in order to finalize an optimum dose and pH for ACH.

Table 4.10 Jar Test Parameters and Results for Jar Test 9

| Jar #       | Raw  | 1    | 2    | 3    | 4    | 5    | 6    |
|-------------|------|------|------|------|------|------|------|
| ACH (ppm)   | 0    | 0    | 2    | 4    | 7    | 10   | 20   |
| Targeted pH | 8.35 | 6.7  | 6.7  | 6.7  | 6.7  | 6.7  | 6.7  |
| pH          | 8.35 | 6.76 | 6.75 | 6.73 | 6.81 | 6.75 | 6.88 |
| TOC         | 3.65 | 3.27 | 3.2  | 2.94 | 2.74 | 2.56 | 2.32 |
| Turbidity   | 0.95 | 0.69 | 0.85 | 0.59 | 0.53 | 0.46 | 0.37 |

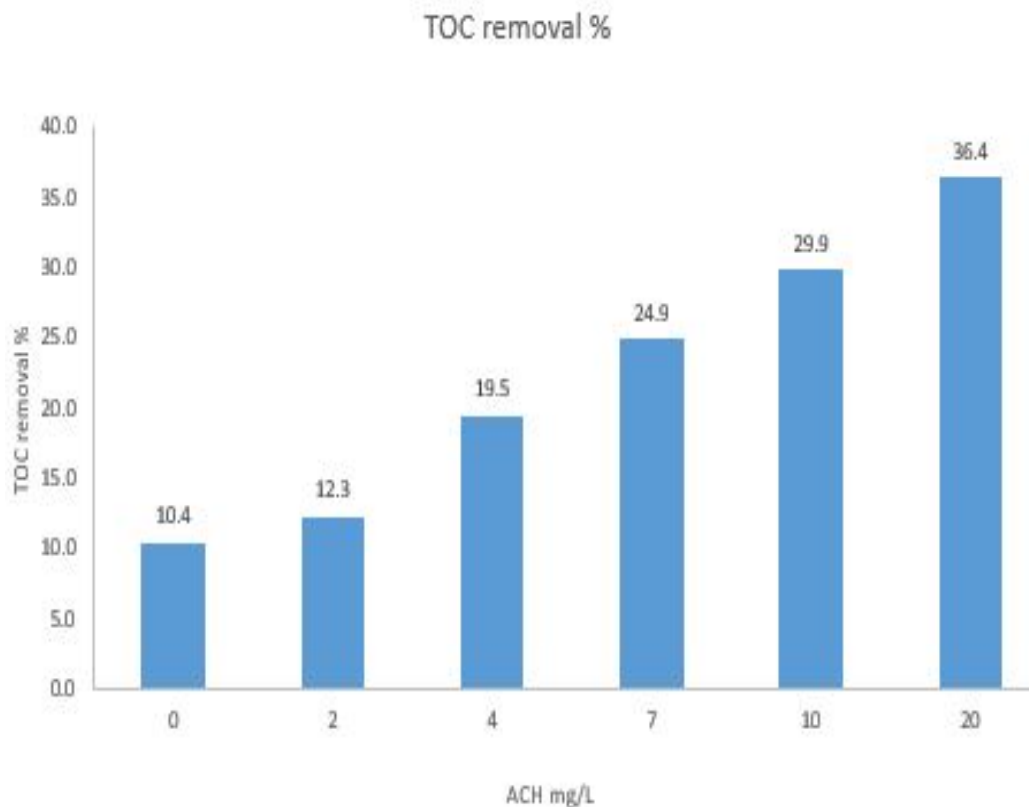


Figure 4.17 TOC Removal for Jar Test 9

The TOC removal for 10 ppm of ACH and 20 ppm of ACH was very close and when compared the price of using 10 ppm and 20 ppm of ACH, 10 ppm can easily be considered as an optimum dose. But, again the conclusion were verified by SEC-DOC. Figure 4.18 gives SEC-DOC for the Jar Test 9. From the figure it can be assumed that the HMW organics removal for 10 and 20 ppm ACH is almost same. Hence 10 ppm was preferred as the optimum dose.

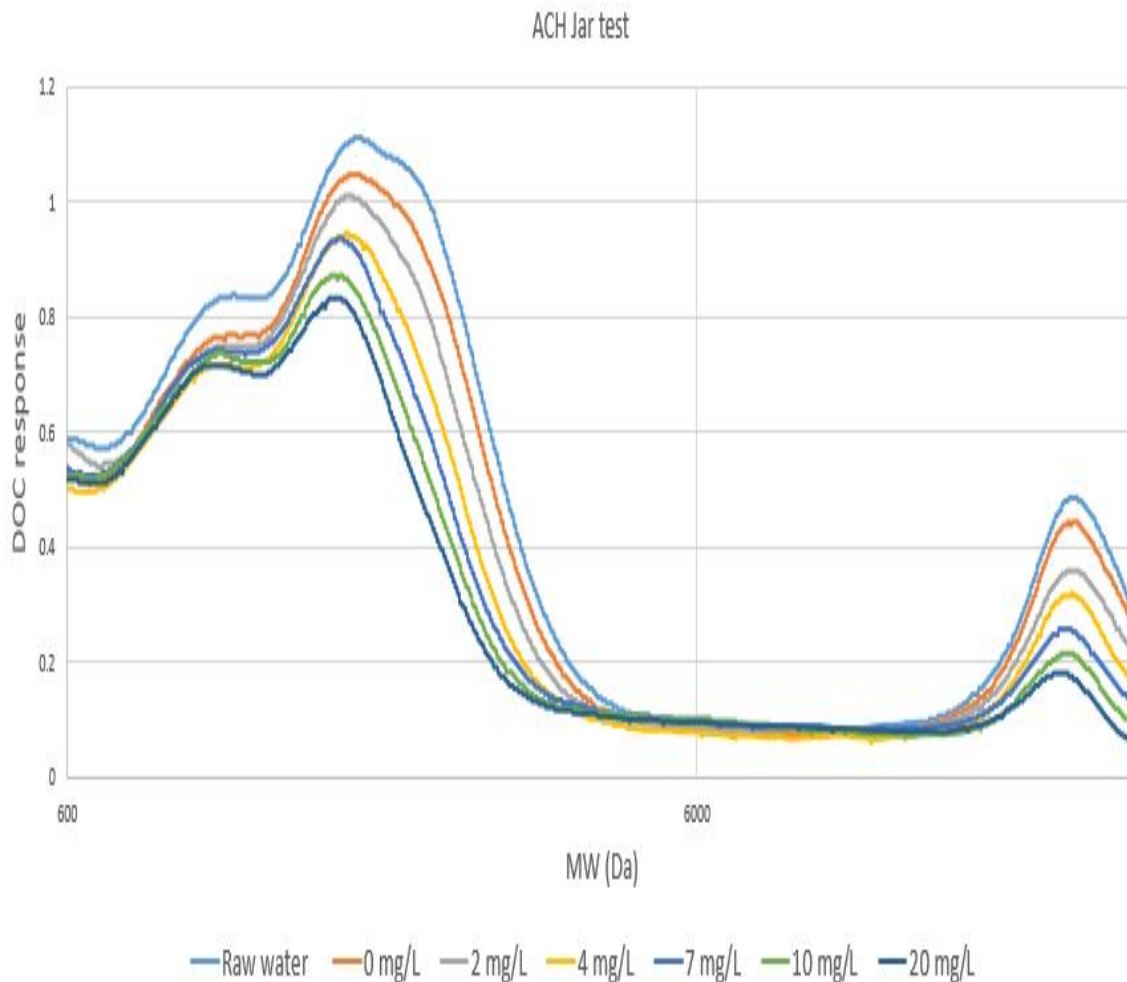


Figure 4.18 SEC-DOC for ACH Jar Test Supernatants

A combined Jar Test for evaluating Alum and ACH performance under optimal operational conditions with and without pH adjustment was performed.

Table 4.11 Jar Test Parameters and Results for Jar Test 10

| Jar #           | Raw  | 1    | 2    | 3            | 4            | 5           | 6           |
|-----------------|------|------|------|--------------|--------------|-------------|-------------|
| Coagulant (ppm) | 0    | 0    | 0    | 30<br>(Alum) | 30<br>(Alum) | 20<br>(ACH) | 20<br>(ACH) |
| Targeted pH     | 8.3  | 6.5  | ---- | 6.2          | ----         | ----        | 6.7         |
| pH              | 8.3  | 6.48 | 8.27 | 6.19         | 7.36         | 7.84        | 6.74        |
| TOC             | 3.84 | 3.89 | 3.65 | 2.62         | 2.96         | 2.51        | 2.47        |
| Turbidity       | 1.25 | 0.71 | 0.82 | 0.31         | 0.42         | 0.28        | 0.38        |
| Dissolved Al    | 0    | 0    | 0    | 0.124        | 0.178        | 0.033       | 0.05        |



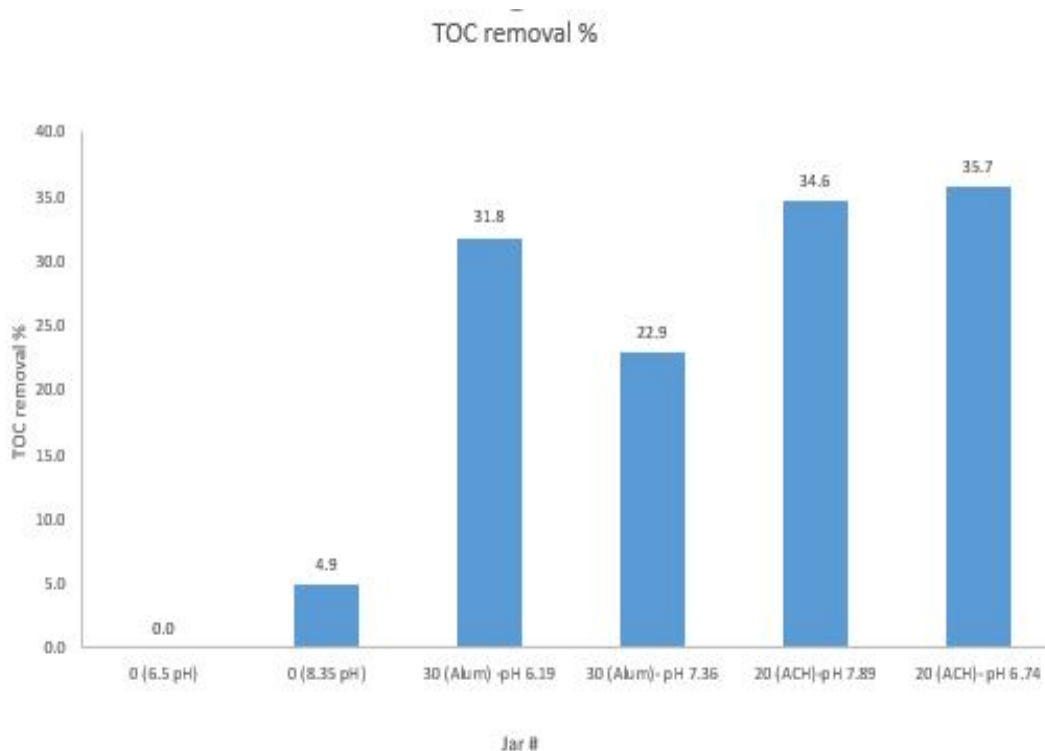


Figure 4.19 TOC Removal for Jar Test 10

The main reason for using 20 ppm for ACH was to get another data-point for the performance of ACH at 20 ppm concentration as there were a lot of 10 ppm ACH data points. But it is clear from the last few experiments that 10 ppm would be a cheaper as well as feasible option rather than 20 ppm. When it comes to Alum, whatever the concentration be, it will perform better at an adjusted pH. So for continuing with Alum, the WTP needs to manage the pH adjustment during the coagulation and at the end to make it basic again. Also dissolved Al was measured in the supernatants to compare the flocculation process. As per the industry suggestion ACH produces less flocs and the carryover of ACH flocs are less harmful to the membrane fibers than the carry overs from Alum. The cost factor was not discussed but that might be one of the deciding factors.

### 4.3.3 TOC Profile and SEC-DOC on Pilot and Main Plant Samples

After the findings from the bench-scale jar tests, the industry decided to imply some of the key findings to the pilot plant. Also over the period of this investigative study of 7 months several samples were collected for influent, DAF effluents and Filtrates for main and pilot plants were grab sampled and analyzed for TOC and sometimes for SEC-DOC and Dissolved Al.

Table 4.12 TOC profile for Main and Pilot DAF Effluent

| Date     | Influent TOC (ppm) | Main DAF effluent TOC (ppm) | Pilot DAF Effluent TOC (ppm) | Main Plant Coagulant Dose (ppm) | Pilot Plant Coagulant Dose (ppm) |
|----------|--------------------|-----------------------------|------------------------------|---------------------------------|----------------------------------|
| 10/3/16  | 3.13               | 3.22                        | 3.32                         | 6                               | 6                                |
| 10/11/16 | 3.11               | 3.19                        | ----                         | 6                               | 6                                |
| 10/13/16 | 3.56               | 3.29                        | 3.3                          | 6                               | 6                                |
| 10/16/16 | 3.34               | 3.56                        | ----                         | 6                               | 6                                |
| 10/28/16 | 3.21               | 3.18                        | ----                         | 6                               | 6                                |
| 11/2/16  | 3.22               | 3.71                        | 3.19                         | 6                               | 6                                |
| 11/9/16  | 3.52               | 3.48                        | 3.4                          | 6                               | 6                                |
| 11/12/16 | 3.74               | 3.02                        | 3.21                         | 6                               | 6                                |
| 11/28/16 | 3.35               | 3.09                        | 3.04                         | 6                               | 6                                |
| 12/3/16  | 3.11               | ----                        | 2.96                         | 6                               | 6                                |
| 12/5/16  | 3.16               | ----                        | 2.98                         | 6                               | 30                               |
| 12/7/16  | 3.1                | ----                        | 2.98                         | 6                               | 10 (ACH)                         |
| 1/9/17   | 2.94               | ----                        | 2.89                         | 8                               | 10 (ACH)                         |
| 1/17/17  | 3.2                | 2.95                        | 2.88                         | 8                               | 10 (ACH)                         |
| 3/9/17   | 2.78               | ----                        | 2.55                         | 8                               | 10 (ACH)                         |
| 3/21/17  | 2.82               | 2.78                        | 2.77                         | 8                               | 10 (ACH)                         |
| 3/29/17  | 2.8                | 2.93                        | 2.68                         | 8                               | 10 (ACH)                         |
| 4/6/17   | 2.95               | 2.95                        | 2.92                         | 8                               | 10 (ACH)                         |
| 4/12/17  | 3.12               | 2.98                        | 2.74                         | 12                              | 10 (ACH)                         |
| 4/16/17  | 3.11               | 2.76                        | 2.95                         | 16                              | 10 (ACH)                         |
| 4/26/17  | 3.12               | 2.87                        | 3.03                         | 20                              | 10 (ACH)                         |

Table 4.12 shows the TOC profile for the main DAF plant and pilot DAF plant. As given in the table there was not significant (> 5%) TOC removal for main plant DAF as well as pilot plant DAF unit throughout this period. There was consistently slight

better TOC removal for pilot plant when coagulant dose was increased and changed from Alum to ACH in December 2016. Coagulant dose was increased on main plant DAF to collect few samples and analyze for SEC-DOC.

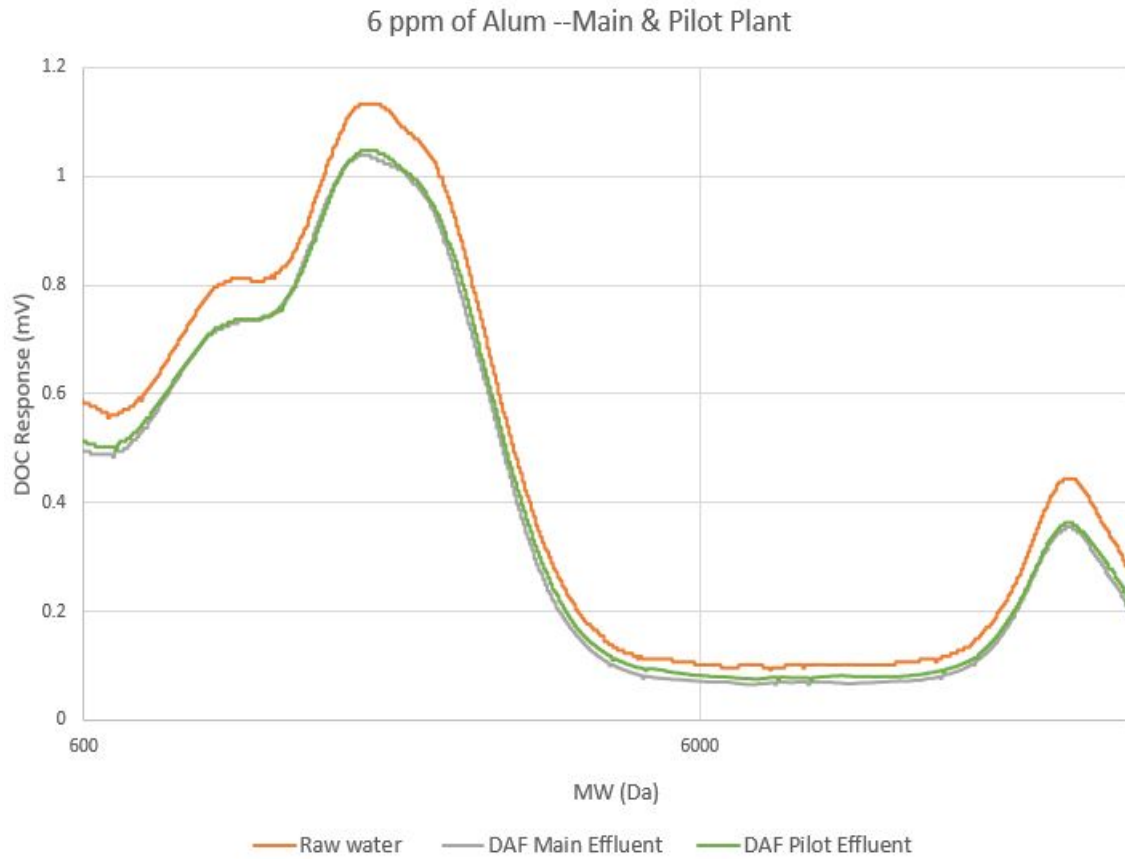


Figure 4.20 SEC-DOC Comparison for Main and Pilot DAF (6 ppm Alum)

From Figure 4.20 it can be assumed that SEC-DOC results can be consistently used to relate main plant and pilot plant performance for qualitative conclusions.

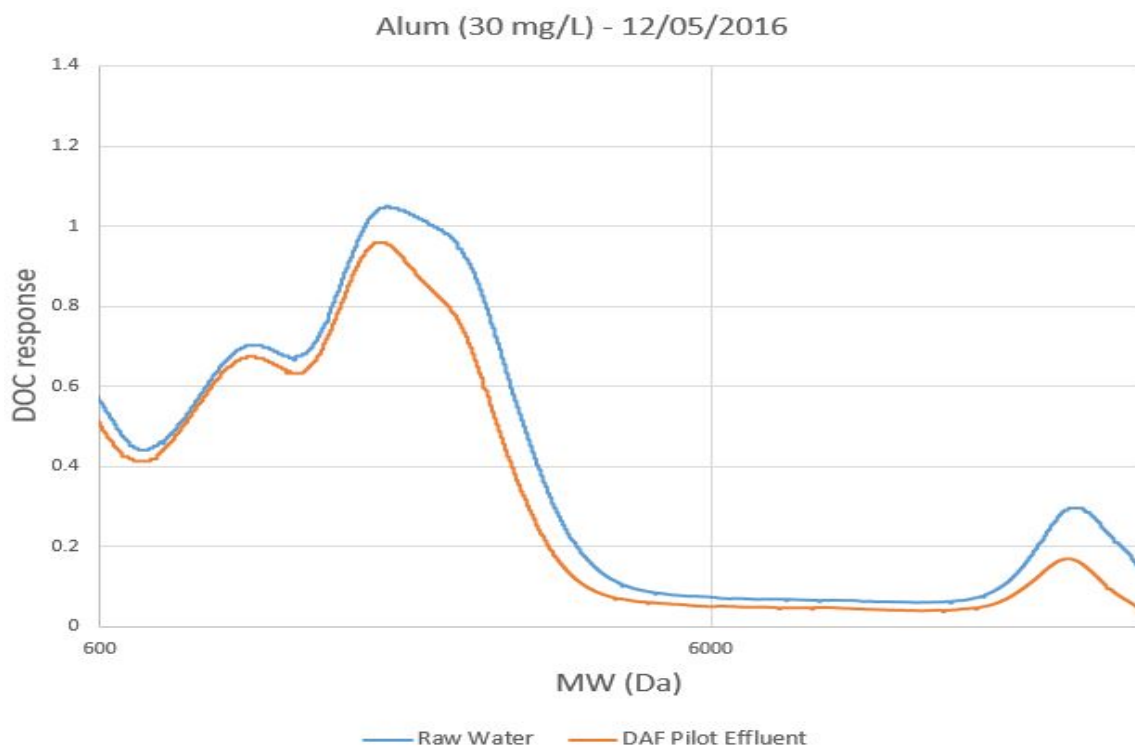
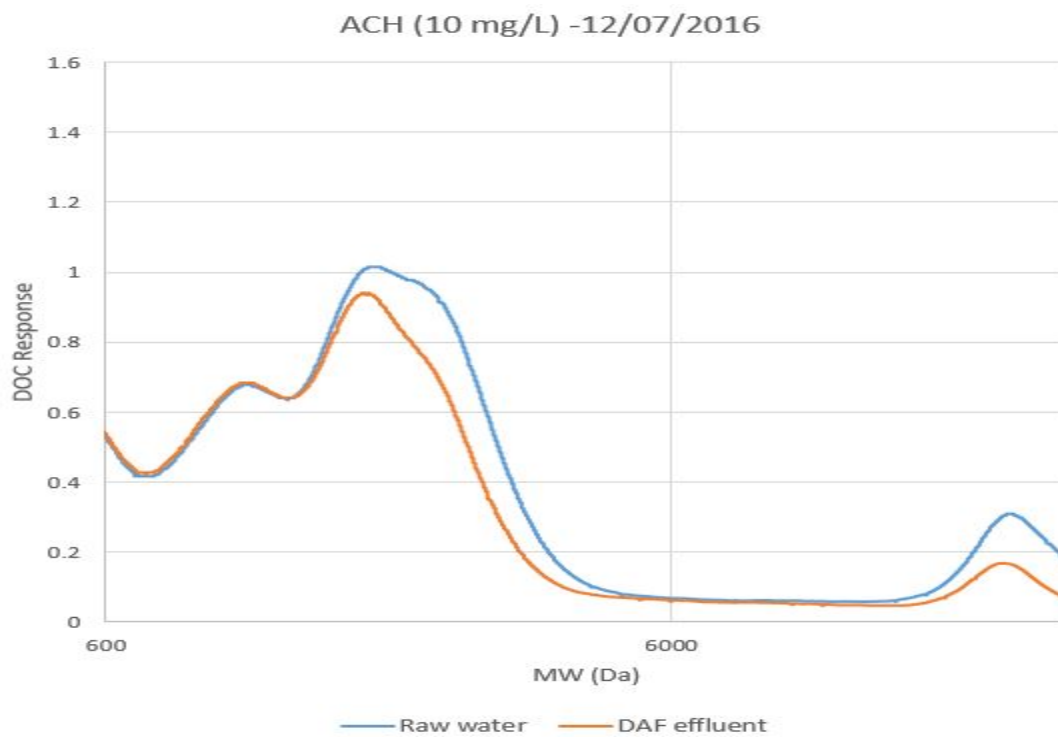


Figure 4.21 SEC-DOC for DAF Pilot Plant (30 ppm Alum)

(a)



(b)

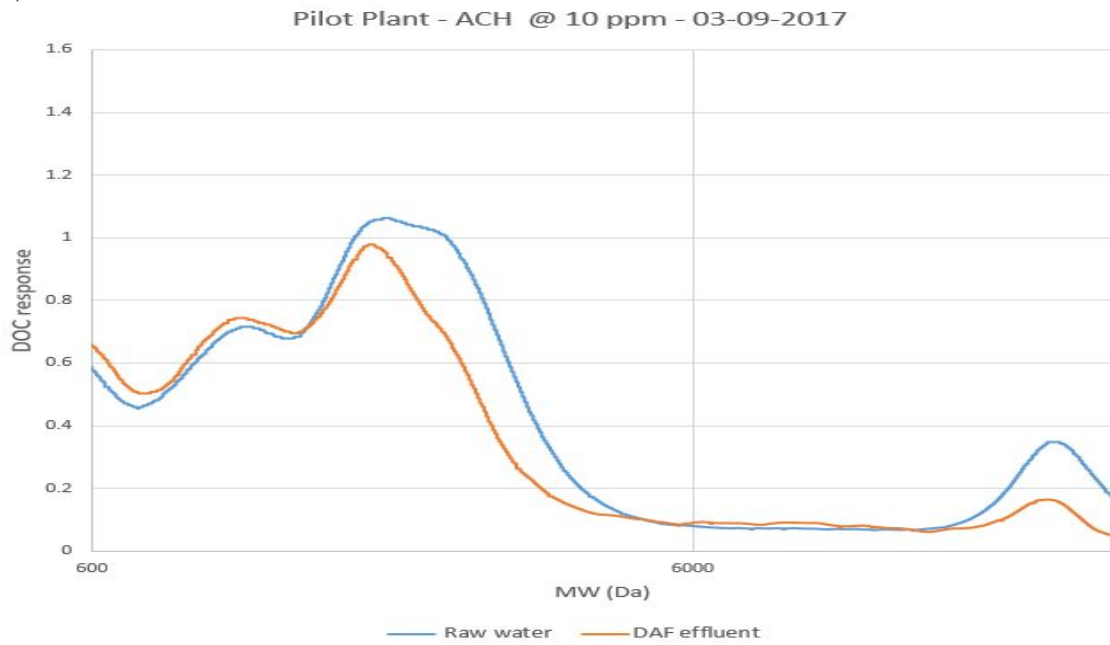


Figure 4.22 SEC-DOC for DAF Pilot Plant: (a) December, 2016 (b) March, 2017

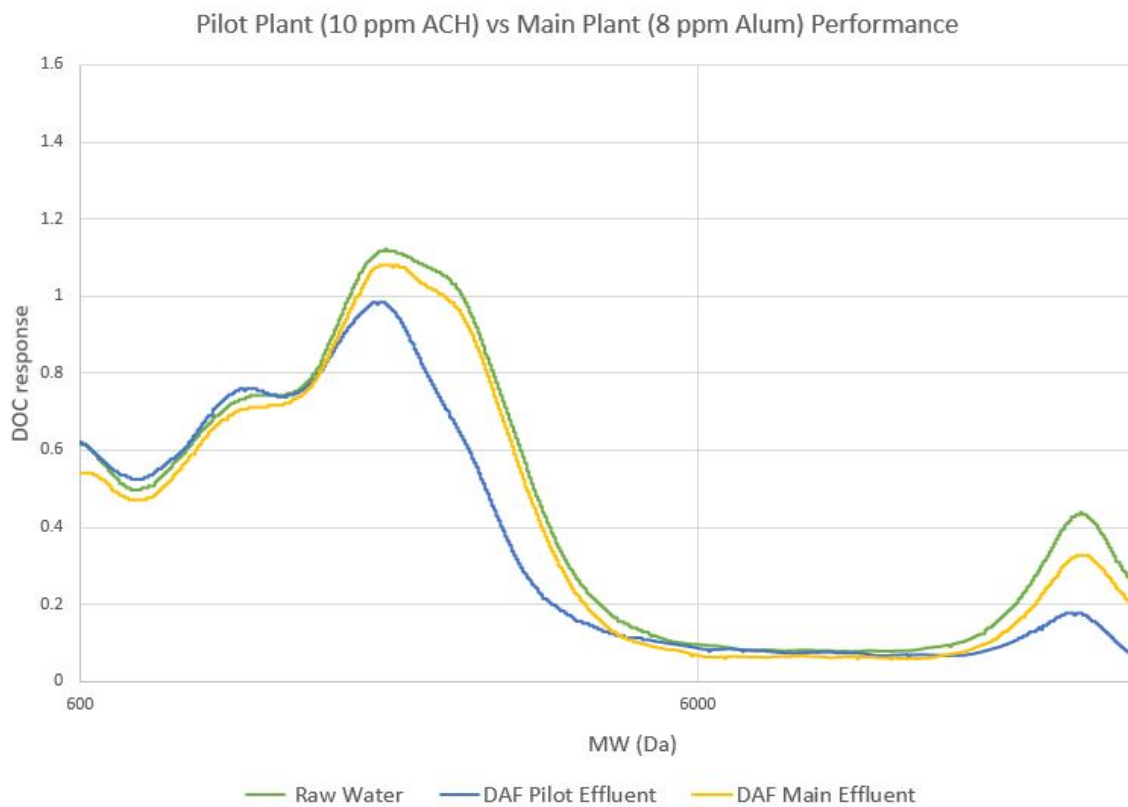


Figure 4.23 SEC-DOC for DAF Pilot (10 ppm ACH) vs Main (8 ppm Alum)

Figure 4.21 and 4.22 gives SEC-DOC for DAF Pilot Plant for 30 ppm Alum and 10 ppm ACH on two different dates which are very similar like they were expected to be considering the Jar test results for 30 ppm Alum and 10 ppm ACH and also the fact of both the concentrations having equal Al concentration. Figure 4.23 suggests that lower doses of Alum does not remove HMW organics significantly from CAP water. Hence, the main plant DAF needs coagulant enhancement.

Considering the fact that in DAF the flocs float on the surface and removed via scraper and in Jar tests the flocs settle down there was always concern about implying Jar test results to the main plant DAF. Also, there were concern over the model of the pilot plant used in this study because of different TOC removal results and the floc formation was much less than the floc formation for main plant. Figure 4.24 shows the visual of floc formation in pilot and main plant.

(a)



**DAF Main Plant**

(b)



### DAF Pilot Plant

Figure 4.24 DAF Floc Formation: (a) Main plant (b) Pilot Plant

Therefore a quick comparison between jar test and main plant was done for higher doses of Alum (mainly for 20 ppm). Table 4.13 shows the Jar test comparison with main plant. Figure 4.25 gives the vital SEC-DOC curve for Jar test vs DAF main plant. The HMW organics peak on SEC-DOC and the dissolved Al suggest that jar test results can be qualitatively used to predict the DAF main plant performance. TOC removal results still shows uncertainty.

Table 4.13 Jar Test Findings Comparison with Main Plant Performance

| Sample             | Raw Water<br>(Jar Test) | Raw Water<br>(Main Plant) | 20 ppm Alum<br>Jar Test<br>Supernatant | 20 ppm Alum<br>DAF Main<br>Effluent |
|--------------------|-------------------------|---------------------------|--|-------------------------------------|
| TOC (ppm)          | 3.21                    | 3.11                      | 2.74                                   | 2.87                                |
| Dissolved Al (ppm) | 0                       | 0                         | 0.34                                   | 0.313                               |
| TOC Removal %      | ----                    | ----                      | 15                                     | 8                                   |

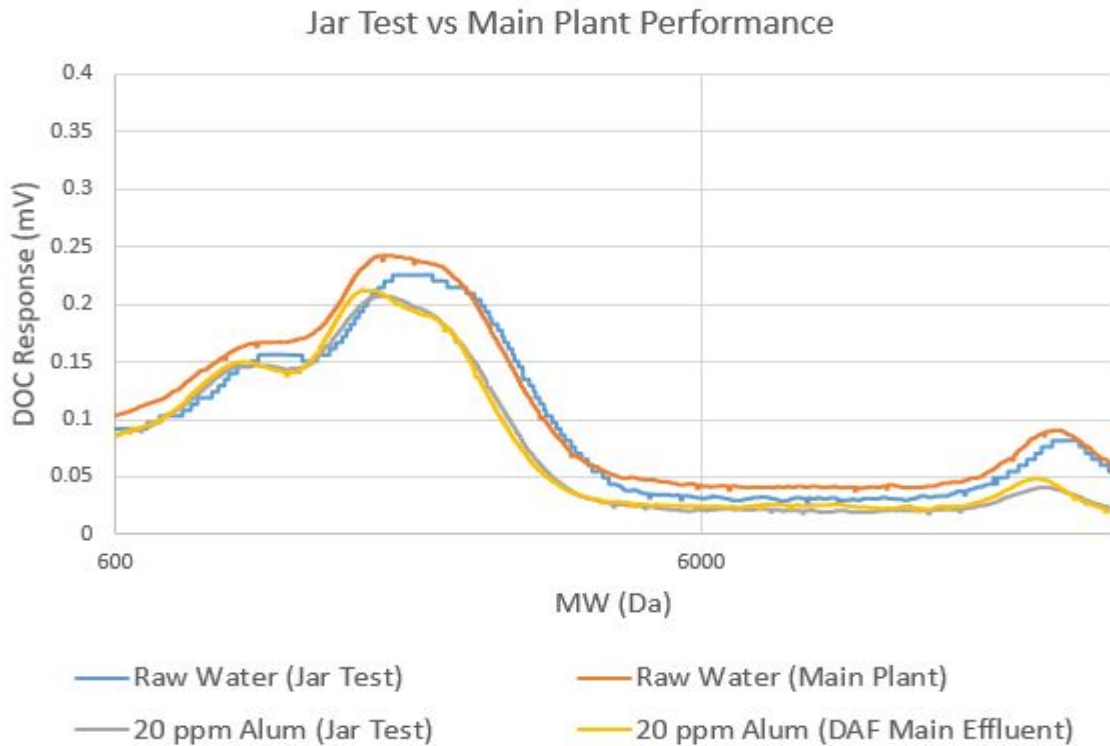


Figure 4.25 SEC-DOC for Jar Test vs DAF Main Plant

#### 4.4 Summary and Conclusions

After several Jar tests and organics characterization of DAF pilot and main plant samples these were the significant observations:

- Low dose of Alum (6-8 ppm) does not contribute significantly in the removal of TOC or HMW organics.
- Higher dose of Alum would require pH adjustment for more efficient performance.
- 30 ppm of Alum with pH adjustment and 10 ppm of ACH without pH adjustment were considered feasible and optimal coagulant doses.
- TOC removal results for jar tests had uncertainties when compared to pilot plant as well as main plant.



- SEC-DOC gave a relatively better resemblance between jar test and DAF pilot and main plant performance.
- 10 ppm of ACH (finding from jar test) showed significant removal of HMW organics in DAF pilot plant effluent.
- 20 ppm of Alum showed similar performance between DAF main plant and jar test in terms of HMW organics removal and dissolved Aluminum.

From all these findings it was concluded that lower doses of Alum were not sufficiently removing TOC which was not a requirement at the pre-treatment as the water treatment plant has GAC bed contactors at the end which removes significant TOC. But as the irreversible fouling kept on increasing in the MF unit, enhancement of coagulation was required. 10 ppm of ACH was preferred over 30 ppm of Alum because of no pH adjustment required for ACH, ACH floc carryovers contain less dissolved Al and are less sensitive to hollow membrane fibers in the MF unit and previous results for similar cases at different locations.

Finally it was concluded in the final meeting to stop the pilot scale study and change the coagulant in the main plant DAF from Alum to 10 ppm of ACH and monitor the TOC removal, SEC-DOC and flux and permeability of the membrane filtration unit for several months.

## CHAPTER FIVE

### SUMMARY AND CONCLUSIONS

This chapter summarizes key findings from each chapter and draws significant conclusions followed by recommendations for utilities and future research.

#### 5.1 Summary

The objective of chapter 2 was to evaluate the absorbance efficiency of different types of GAC for PFC removal under different conditions using bench scale approach by conducting RSSCTs and recommend an optimal GAC media to utility for further pilot scale study. The key findings from this chapter are as follows:

- Bituminous coal based GAC (GAC-B and GAC-C) have higher efficacy for PFOA and PFOS than coconut shell based GAC (GAC-A).
- Influent concentrations affect the absorbance capacity of GAC-B.
- Particle Size didn't affect the absorbance capacities for GAC-B
- GAC-B and GAC-C have almost a similar absorbance capacity with GAC-C having slightly higher efficacy for PFC.
- Lag columns removed PFOA and PFOS completely.

The objective of chapter 3 was to develop a new bench scale testing protocol for simulating full-scale carbon block filter performance and validate the protocol for POU model contaminants like chloroform and arsenic. Key findings of this chapter includes:

- A successful protocol was developed to evaluate the MCB for channeling within the holder using methylene blue.
- There was no short-circuiting observed in any of the MCB holder tests.

- 60% or more MB was removed throughout the continuous and on/off MCB tests.
- 60% and 85% breakthrough was achieved for continuous and on/off chloroform tests respectively.
- Several operational problems were encountered during the chloroform tests.
- 75% BT was achieved for Arsenic test unlike 20% BT for full-scale carbon block performance.

The objective of chapter 4 was to optimize the coagulation chemistry for TOC removal in CAP water using bench-scale jar tests. Also, to characterize the organic matter to analyze the HMW organics removal for main plant and optimal jar tests. Evaluate the pilot plant performance for key findings from jar tests and recommend the utility an optimal coagulant and dose. Key findings from this chapter are as follows:

- Low dose of Alum (6-8 ppm) does not significantly remove TOC or HMW organics.
- Higher dose of Alum would require pH adjustment for optimum performance.
- 30 ppm of Alum with pH adjustment and 10 ppm of ACH without pH adjustment were considered feasible and optimal coagulant doses.
- TOC removal results for jar tests had uncertainties when compared to pilot plant as well as main plant.
- SEC-DOC gave a relatively better resemblance between jar test and DAF pilot and main plant performance.
- 10 ppm of ACH (finding from jar test) showed significant removal of HMW organics in DAF pilot plant effluent.

- 20 ppm of Alum showed similar performance between DAF main plant and jar test in terms of HMW organics removal and dissolved Aluminum.

## 5.2 Conclusions

Major conclusions for this thesis include:

- Bituminous coal based GAC have higher efficacy for PFC removal than coconut shell based GAC, this could be due to the kinetic limitation because of the tighter structure of coconut shell based GAC. The efficiency decreases for lower influent concentrations and there is no major impact of particle size in adsorption capacity.
- There is no short-circuiting in the newly developed mini carbon block holder and it can remove methylene blue consistently. It can also remove chloroform and arsenic but not in a similar pattern to full-scale carbon blocks. There are several speculations for this different removal performance between full scale and mini scale carbon block like different water matrix, influent operating pressure and operational flaw in the design of the holder. Over all this study creates a good theoretical and practical fundament for this new approach. Future research on these speculations are suggested.
- ACH at 10 ppm gives better TOC and HMW organics removal than Alum at 30 ppm without any pH adjustment. SEC-DOC results could be consistently used for comparing pilot plant and main plant performance with the jar test results on a qualitative basis.

### **5.3 Recommendations to Utilities**

Calgon Filtrasorb F-400 should be used for pilot-scale GAC study and water with lower influent PFC concentrations should be blended with higher influent PFC concentrations. Also ion exchange resin should be evaluated for PFC removal using RSSCT.

ACH at dose of 10 ppm should be used in the main plant DAF for several months and TOC and HMW organics removal should be monitored in addition to flux and permeability for MF unit during the course of this several months.

### **5.4 Recommendations for Future Research**

More chloroform and arsenic tests should be performed for MCB holder to evaluate the reproducibility of MCB holder for those contaminants. Full scale carbon blocks should be tested with the MCB holder for similar water matrix and at same time. Influent operating pressure for water should be equal while conducting those tests. Further investigation should be conducted for chloroform interaction with the carbon block like X-Ray Fluorescence on the carbon blocks surface before and after the test. Chloroform interaction with the binder should be studied and discussed with the industry partner. Chloroform compatibility with the MCB holder apparatus should be evaluated. Tap water quality should be analyzed for more parameters that could clog the carbon block surface or could initiate biological growth.

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