THESIS

PRE-OXIDATION AND ADSORPTION WITH POWDERED ACTIVATED CARBON FOR TASTE AND ODOR CONTROL AND OPTIMIZING COAGULATION FOR DISSOLVED ORGANIC CARBON REMOVAL

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ABSTRACT

PRE-OXIDATION AND ADSORPTION WITH POWDERED ACTIVATED CARBON FOR TASTE AND ODOR CONTROL AND OPTIMIZING COAGULATION FOR DISSOLVED ORGANIC CARBON REMOVAL

Geosmin and MIB (2-Methylisoborneol) are the two natural organic compounds produced by certain types of blue-green algae which cause taste and odor (T&O) issues in the sources of drinking water. Geosmin and MIB are not regulated by United States Environmental Protection Agency (USEPA) as they do not pose a health risk, but these two organic compounds seriously hinder the aesthetic appeal of finished drinking water due to the earthy or musty odor produced by them even at very lower concentrations (below 10 ng/L). Geosmin and MIB cannot be eliminated by conventional drinking water treatment processes, hence more advanced treatment techniques involving an adsorption agent like Powdered Activated Carbon (PAC) is necessary to remove these odorants and achieve concentration below the odor threshold.

Boyd Lake Water Treatment Plant in Greeley region, gets it intake of raw water from two main drinking waters sources namely Boyd Lake and Lake Loveland. The plant has been experiencing T&O related issues mostly during the mid-summer to late autumn. This study was conducted for BLWTP in three phases to determine the optimal conditions to address the seasonal T&O issue and also help reduce the Dissolved Organic Carbon (DOC) content of the source waters efficiently with PAC. Preliminary testing was conducted on Lake Loveland and Boyd Lake water with an incremental alum dosage from 30 to 70 mg/L followed by three five minute stages of flocculation and 45 minutes settling time. Turbidity, TOC and DOC were

measured before and after coagulant testing. The results indicated that Boyd Lake water was the hardest to treat, hence it was selected for further testing.

In the initial phase of the study, about ten different PACs were tested in five batches, with Boyd Lake and plant mix water collected at different time periods. The results from the five batches were averaged and ranked based on the DOC reduction values. The results indicated that PAC Hydrodarco M was the cost and performance wise effective of the ten PACs tested. The second phase of the study involved testing four different PACs at four different contact times (15, 30, 45 and 60 minutes) with one constant dosage of 30mg/L for the kinetic study part. The results showed that maximum DOC removal was achieved at 45 minutes contact time. Similarly, the same four different PACs were tested with four PAC doses (10, 20, 30 and 40 mg/L) with one preset contact time of 45 minutes for the dosage study part. The results from these tests indicated that 30 mg/L was the optimal PAC dosage for maximum DOC removal. In the final phase, the raw water was initially treated with the various pre-oxidants with dosages of 1mg/L ClO_2, 5 and 10 mg/L of $NaMnO_4$ with a contact time of 60 seconds followed by PAC treatment with a dosage of 30 mg/L and a 45 minutes contact time. Test results revealed that pre-oxidants did not have a significant impact in DOC removal at any dosage levels. Additionally, two dosages 20 and 70 mg/L of coagulant alum were tested with pre-oxidant and PAC treated water. Detailed analysis was performed with coagulant alum in combination with pre-oxidant and PAC treated water. The results of the alum testing illustrated that a higher dosage of coagulant alum at 70 mg/L had a substantial effect on the DOC removal when compared to a lower dosage of 20 mg/L. Further, the results showed a two-fold increase in the DOC reduction at an alum dosage of 70 mg/L without the presence of any pre-oxidants.

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INTRODUCTION

Drinking water sources like rivers and lakes are subject to contamination from various microbial agents including bacteria, viruses, protozoan, and parasites (Pandey et al., 2014). The water from natural sources require appropriate treatment to remove the disease and odor causing metabolites produced by these microscopic organisms. Public drinking water systems use a variety of water treatment methods to provide safe drinking water for their communities. However, consumers nowadays require not only safe water, but also water that is aesthetically pleasant (e.g., odorless, colorless, tasteless). Musty and earthy odors in the sources of drinking water like rivers, lakes and reservoirs are often associated with the metabolites produced due to the degradation of cyanobacteria, actinomyces, fungi and blue green algae (Izaguirre and Taylor, 2004; Gerber, 1967; Gerber et al., 1965). Cyanobacterial species produce non-toxic secondary metabolites such as geosmin and 2-methylisoborneol (MIB) (Butakova, 2013). The consumers of the drinking water can detect geosmin and MIB at very low levels in the water, because of their low odor threshold concentrations (OTC) which is below 10 ng/L (Mallevialle and Suffet, 1987; Pirbazari et al., 1993). Hence, even small spikes in the concentration of these T&O compounds can cause a significant impact to the taste and odor of the water. The secondary metabolites of cyanobacteria namely geosmin and MIB, generally do not pose a threat to human health (Dionigi et al., 1993) and are not regulated by United States Environmental Protection Agency (US EPA). However, presence of such metabolites might substantially reduce the consumer's faith in the safety of the drinking water and can instigate consumers to shift to sources that provide quality tasteless and odorless water. Water Treatment Plants (WTPs) all over the U.S allocate funds in their budgets exclusively to take care of the drinking water off-flavor issues that disrupt consumer trust. The taste and odor causing metabolites geosmin and MIB cannot be easily removed by conventional water treatment operations like coagulation, sedimentation or chlorination. The most effective and simplest method to remove these T&O compounds is by adsorption using Powdered Activated Carbon (PAC) (Srinivasan and Sorial, 2011).

This study was conducted to provide the Greeley Water and Sewer Department's Boyd Lake Water Treatment Plant (BLWTP) with appropriate design parameters and an economical PAC to achieve effective geosmin and MIB removal from their source waters. BLWTP obtains its main raw water supply from two sources namely, Boyd Lake and Lake Loveland. BLWTP has been experiencing an increase in Total Organic Carbon (TOC) concentration, which has corresponded with an increase in taste and odor (T&O) complaints, particularly in the southern section of their distribution system that is seasonally supplied with mostly BLWTP water. This study was focused mainly on determining three key facts for the BLWTP which is set to undergo physical upgrades, planned for completion in the year 2018. The first one was to determine the PAC that is cost and performance wise effective in the removal of odorants (geosmin, MIB) and Dissolved Organic Carbon (DOC). The second part of the analysis was to determine an optimal PAC dosage and contact time required for maximum odorants and DOC reduction. The third part was to determine the effectiveness of PAC in combination with oxidants ($NaMnO_4$, ClO_2) on T&O compounds and DOC reduction. A total of 10 different PACs from three different Manufactures namely Cabot, Standard purification and Calgon were used throughout the whole study, in order to determine the PAC that is economical and effective in addressing the T&O issue and DOC content reduction of the source water. The kinetic study of PACs was conducted with 4 different contact times (15, 30, 45 and 60 minutes) and one PAC dosage of 30 mg/L with the best PACs from each of the three Manufacturers namely Hydrodarco M from the manufacturer Cabot, Pulsorb WP 260-90 from manufacturer Calgon and Watercarb 1000 from manufacturer Standard Purification with Watercarb 800 as baseline. The dosage study of PACs was conducted with 4 different dosages (10, 20, 30 and 40 mg/L) and one PAC contact time of 45 minutes with the same PACs used in kinetic study. The pre-oxidant study used ClO_2 and $NaMnO_4$ as pre-oxidants with different water blends under different pre-oxidant dosages, in combination with PAC and coagulant alum to determine the impact of oxidants on off-flavor compounds (geosmin, MIB) and DOC removal.

This thesis consists of two main chapters. The first chapter gives an insight about the research through a literature review on algae, problems with algal metabolites, and treatment options to remove such metabolites from source waters. The second chapter is written in a manuscript format for submission to an academic journal. In the second chapter materials, experimental methods, results, discussions and conclusions obtained from this research are presented. The data, results and graphs of the complete study are also provided in appendices attached at the end of this thesis.

CHAPTER 1. LITERATURE REVIEW

1.1. Sources of T&O compounds in Aquatic Ecosystems

1.1.1. Organic Sources

The predominant taste and odor outbreaks in drinking water sources all over the world are caused by microbial production of geosmin and MIB. Studies have shown that majority of the taste and odor compounds like geosmin and MIB are produced by certain groups of benthic and pelagic aquatic microorganisms found in water sources such as lakes, reservoirs, and running waters (Juttner et al., 2007). A vast diversity of autotrophs, heterotrophs, prokaryotes and eukaryotes also produce geosmin and MIB (Watson, 2003). Zaitlin and Watson (2006) have demonstrated that certain types of filamentous bacteria or actinomycetes can also produce off-flavor compounds. Cyanobacteria among algae produce geosmin and MIB exclusively (Juttner, 1995). These cyanobacteria produce odorants geosmin and MIB during the growth phase and release or store these odorants depending on the environmental factors. Most of the odorants are released during the death and biodegradation of these algal cells (Srinivasan and Sorial, 2011). Many types of actinomycetes and other non-cyanobacterial microorganism like *Penicillium, Aspergillus, Streptomyces violaceusniger, Streptomyces griseofuscus* also produce geosmin and MIB in significant quantities that can cause off-flavor outbreaks in water sources (Saadoun et al., 1997; Aoyama et al., 1993). The biological synthesis of geosmin and MIB happens in various pathways (shown in Fig 1.1).

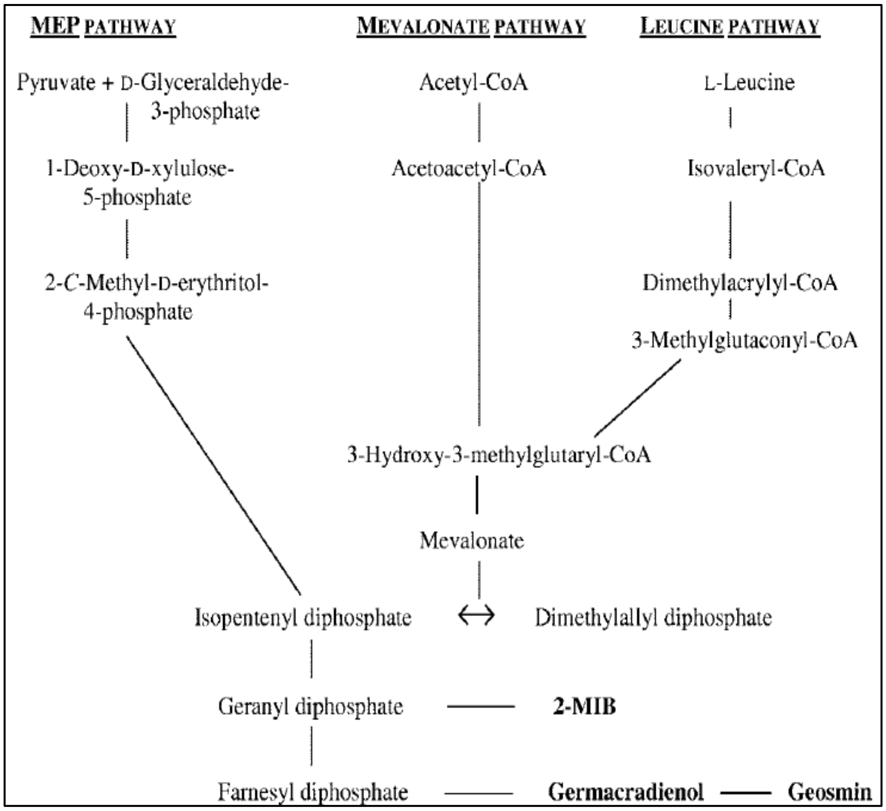

Figure 1.1: Biosynthetic process chain for production of MIB and geosmin in streptomycetes and myxobacteria (Jüttner and Watson, 2007).

1.2. Essential Conditions for algae development

1.2.1. Nutrients

Blue-Green Algae (Cyanobacteria) will grow in response to various environmental conditions, among them the most vital factor is the nutrient content of the water sources. Nitrogen and phosphorus are two most important nutrients which are known to have a significant influence on the growth of cyanobacteria (Dolman et al., 2012). Some cyanobacteria have a special ability to fix atmospheric nitrogen (N_2) which helps them survive even when the ratio of nitrogen to phosphorus is low and nitrogen availability causes a limitation to phytoplankton growth rates (Tilman et al., 1982). Rueter et al. (1987) showed that trace metals like iron, molybdenum play a crucial role in the growth and metabolic processes of cyanobacterial populations. In addition, Rueter et al. (1987) also determined that copper limits the nitrogen fixation and hence affects the growth of cyanobacteria.

1.2.2. Light Intensity

Cyanobacteria are aerobic photoautotrophic microorganisms which depend on light for photosynthesis, which is the primary mode of energy production (Chorus and Bartman, 1999). Numerous studies have reported variations in geosmin and MIB production under different intensities of light. Studies conducted by Naes et al., 1985, Bowmer et al., 1992, Utkilen and Frøshaug, 1992 determined that geosmin-producing cyanobacterium Oscillatoria (Fig 1.2) had strong correlation between varying intensities of light and geosmin production. Similarly, another study conducted by Zimba et al. (1999) showed that there was strong connection between MIB production and varying light intensity.

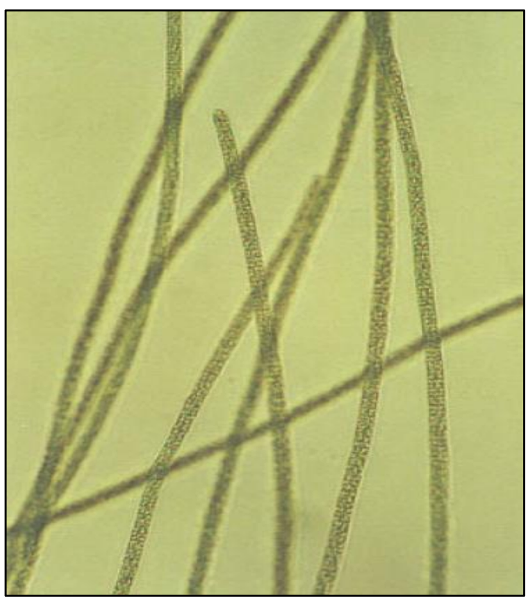

Figure 1.2: Microscopic pic of Planktothrix (Oscillatoria) agardhii

1.2.3. Temperature

Temperature is one of the crucial factors that is studied at various levels in order to determine its influence on off-flavor compounds synthesis by cyanobacteria. Cyanobacteria thrive mostly during late summer and autumn (Chorus and Bartman, 1999), which indicates that water temperature plays a vital role in the growth of cyanobacteria in surface drinking water sources like lakes and rivers. Optimum temperatures are required by cyanobacteria for energy production and cell growth through photosynthesis. This important factor is considered as the main reason for the seasonal drinking water T&O issues, which arise mostly during late summer and autumn, due to the production and release of metabolites like geosmin and MIB by cyanobacteria during this period (Bruce et al., 2002). Maximum growth rates have been observed in most cyanobacterial species at temperatures above 25^0C (Robarts and Zohary, 1987). The study by Robarts and Zohary (1987) also determined that subcritical temperatures of 10 to 15^0C stopped growth before photosynthesis and respiration in most of the cyanobacterial species.

1.2.4. Organic Carbon Source

Studies conducted by Valiente et al. (1992), Lewitus and Kana (1994), Vonshak et al. (2000) have showed that cyanobacterial cultures supplied with dissolved organic carbon achieved greater biomass and grew faster than the ones with no DOC addition. DOC uptake depends on light intensity, but some cyanobacterial species have shown uptake of DOC at any level of irradiance (Kirkwood et al., 2003)

1.2.5. pH

pH is one of the abiotic factor that determines the growth of cyanobacterial species. In a study conducted by Chandra and Rajashekhar (2016) it was determined that cyanobacteria prefer neutral to alkaline pH (7.0 to 8.5) for their optimal growth. In addition, the study also found that there was an increase in the phycobilin pigments necessary for the photosynthesis in freshwater cyanobacteria with increase in pH. Elevated pH reduces nitrogen loss and also increases the nitrogen supply, which in turn helps in the growth of cyanobacteria (Gao et al., 2014).

1.3. Types of Algal Metabolites

1.3.1. Off-flavor Compounds

Cyanobacteria produces different types of metabolites, but the ones that causes off-flavors in the drinking water sources are geosmin and MIB. The cyanobacterial secondary metabolites, geosmin and MIB are not regulated by United States Environmental Protection Agency (US EPA) as they are not related to any health issues (Dionigi et al., 1993). The primary concern with geosmin and MIB is that they cannot be eliminated by conventional drinking water treatments like coagulation, sedimentation, filtration and chlorination (Bruce et al., 2002). Geosmin and MIB have very low OTC, which is below 10 ng/L (Mallevialle and Suffet, 1987; Pirbazari et al., 1993), hence removal of these organics compounds is a major hurdle for the drinking water treatment plants. In presence of necessary nutrients and warmer temperatures cyanobacteria synthesizes T&O compounds like geosmin and MIB during growth phase and releases them during the biodegradation phase (shown in Fig 1.3)

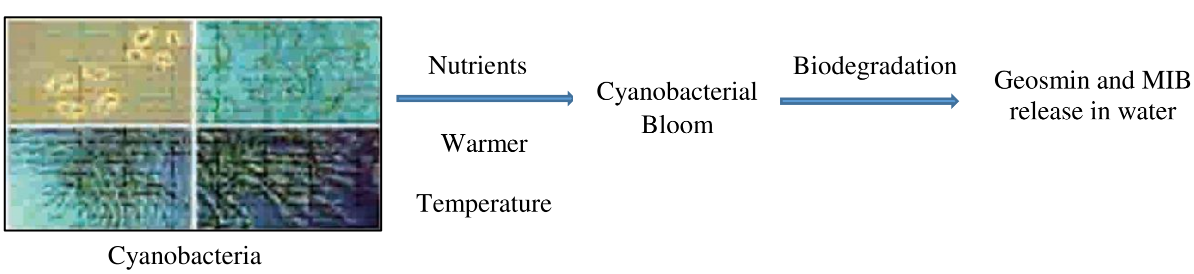

Figure 1.3: Process of geosmin and MIB release (Srinivasan and Sorial, 2011)

Geosmin has a molecular weight of 182.3 g/mol, water solubility of 5.5 x 10^{-5} mg/L , density of 0.95 g/mL at 20^0C and Henry's Law constant of 0.0023 at 25^0C (Lalezary et al., 1984; Pirbazari et al., 1992). MIB has a molecular weight of 154.3 g/mol, water solubility of 7.3 x 10^{-5} mg/L, density of 0.93 g/mL at 20^0C, and Henry's Law constant of 0.0027 at 25^0C (Lalezary et al., 1984; Pirbazari et al., 1992). Geosmin and MIB occur in water sources due to metabolism and biodegradation of different types of cyanobacterial species that show a rapid growth during the warmer temperatures in the presence of essential nutrients (Watson et al., 2008)

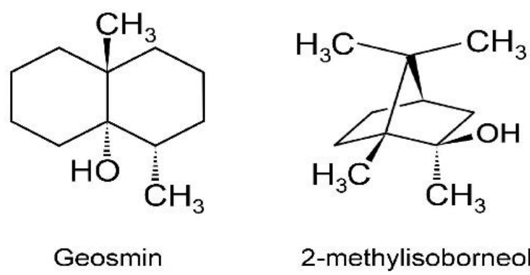

Figure 1.4: Molecular Structure of geosmin and MIB

1.3.2. Toxins

Cyanobacteria also produces toxic secondary metabolites called cyanotoxins. These cyanotoxins can be classified into five important groups based on their biological effects such as hepatotoxins, neurotoxins, cytotoxins, dermatotoxins and irritant toxins also called lipopolysaccharides (Chorus and Bartman, 1999). These cyanotoxins cause acute health effects in humans and animals. In most parts of the world, fresh water cyanobacterial blooms which contain liver-toxic (hepatotoxic, microcystin) are common than neurotoxic cyanobacterial blooms (Chorus and Bartman, 1999). Toxins like microcystin-LR can cause liver tumor in humans (Nishiwaki-Matsushima et al., 1992).

Figure 1.5: Cyanobacterial bloom at Lake Erie. Source: (NASA's Earth Observatory)

Neurotoxins like anatoxins and saxitoxins have caused animal poisoning in North America, Europe and Australia (Chorus and Bartman, 1999). Human exposure to cyanobacterial toxins can happen through different routes like skin contact, inhalation, haemodialysis, ingestion, drinking and recreational water, diet and dietary supplements (Codd et al., 1999). As drinking water is one of the primary ways to get exposed to cyanobacterial toxins, the World Health Organization (WHO) has set 1 μg/L as the threshold limit for cyanotoxin microcystin-LR which is one of the major toxic metabolites produced by cyanobacteria, known to cause health issues in humans (Chorus and Bartman, 1999).

1.3.3. Allelopathic and other organic compounds

Cyanobacteria produces allelopathic compounds that have a negative or positive impact on the other organisms. The allelopathic compounds can have negative effects on other organisms through different modes of action like inhibition of photosynthesis, enzyme inhibition, cellular paralysis and inhibition of nucleic acid synthesis (Leflaive et al., 2007). Allelopathic compounds like Calothrixine A, Cyanobacterin can cause growth inhibition in bacteria, aquatic and terrestrial plants (Doan et al., 2000; Gleason et al., 1986). Algal cells when chlorinated can produce trihalomethanes (THMs) and haloacetic acids (HAAs) (Plummer and Edzwald, 2001). THM and HAAs are disinfection by-products (DBPs) which are considered as a potential health risk to humans due to their carcinogenic nature and hence are regulated by both United States Environmental Protection Agency (US EPA) and the World Health Organization (WHO) (U.S.EPA, 2006; WHO, 2006). In addition, Algal cells can also produce haloacetonitriles (HANs) when chlorinated (Oliver, 1983), most of these HANs are regulated by WHO's drinking water guidelines (WHO, 2006). Fang et al. (2010) determined that increasing the reaction time, chlorine dosage and temperature in the chlorinated water that contained algal cells, increased the formation of DBPs like THM, HAA. The study also determined that different pH values affected DBPs formation. Nitrogenous DBPs like trichloronitromethane (TCNM) were also formed by chlorination of algal cells that are rich in organic nitrogen (Fang et al., 2010).

1.4. Problems related to algal metabolites

1.4.1. Taste and Odor Compounds (Geosmin and MIB)

Taste and odor related complications are a big concern throughout the world due to eutrophication. Geosmin and MIB are two predominant organic compounds responsible for most of the T&O outbreaks in drinking water sources. These T& O compounds are comparatively stable to biological and chemical degradation in surface waters in their dissolved form for a particular time span (Peter and Von Gunten, 2007; Westerhoff et al., 2006). Geosmin and MIB have low OTC, which is below 10 ng/L (Mallevialle and Suffet, 1987; Pirbazari et al., 1993), the extremely low OTC make it difficult for the water treatment plants to eliminate these compounds during drinking water treatment. The two algal secondary metabolites geosmin and MIB are not regulated by United States Environmental Protection Agency (US EPA) as they are not known to cause any health issues (Dionigi et al., 1993). Taste and odor in drinking water can lower the consumer trust and reduce water consumption. The off-flavor issue can trigger consumers to switch to a different source of drinking water or use an in-house drinking water treatment and filtration system or use bottled water (Srinivasan and Sorial, 2011). The off-flavor issue has become a major economic burden to the water treatment facilities because they cannot be treated by conventional water treatment techniques.

1.4.2. Water Disinfection & Chlorination by-products

Algal metabolites are known to produce trihalomethanes (THMs) and haloacetic acids (HAAs) (Plummer and Edzwald, 2001) on chlorination. Occurrence of the chlorination by-products (CBPs) in chlorinated waters, varies in proportion to the availability of the precursors like natural organic matter (NOM) in the treated waters before the disinfection process (Croue et al., 1999). Unlike geosmin and MIB, CBPs like THMs and HAAs are regulated by United States Environmental Protection Agency (US EPA). The maximum contaminant levels (MCLs) set by US EPA (1998) for THMs is at 0.08 mg/L and 0.06 mg/L for HAAs. These chlorination by-products are some of the most regulated compounds in the drinking water industry because of their carcinogenic properties (Cantor et al., 1987; McGeehin et al., 1993)

1.4.3. Human Health Risks

Cyanobacteria produce a wide variety of toxins apart from the T&O compounds like geosmin and MIB. According to Chorus and Bartman (1999) cyanobacterial toxin microcystin had caused severe health issues in 50 dialysis patients in Brazil. In addition, Chorus and Bartman (1999) also determined that 140 children who consumed water contaminated with *Cylindrospermopsis raciborskii* supplied from a dam in Australia had adverse health issues

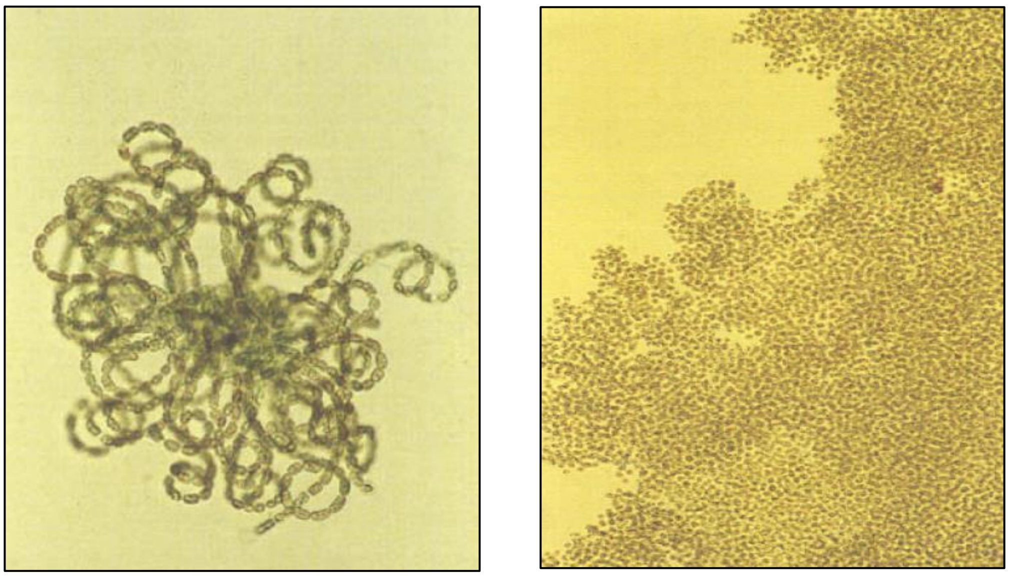

Figure 1.6: Microscopic image of *Anabaena lemmermannii* (*left*) and *Microcystis aeruginosa* (*right*) (Chorus and Bartman, 1999)

due to cyanobacterial poisoning. Several studies of WHO have shown that many cases of the skin irritation, allergies and gastroenteritis were reported in different parts of the world like North and South America, Africa Asia and Europe due to cyanobacterial toxins produced by algal blooms in drinking water sources. One of the most fatal cyanobacterial poisoning occurred in Brazil, when an enormous *Anabaena* and *Microcystis* bloom in Itaparica Dam caused gastroenteritis in 2000 people of which 88 deaths, mostly of children was reported (Teixera et al., 1993). Cyanobacterial toxins like cyclic peptides are the most dangerous toxins to human health, due to the risk of long term exposure to low concentration of these toxins in the drinking water supplies. Cyclic peptides like microcystins and nodularins can cause severe liver poisoning, liver haemorrhage or liver failure, they may also promote the growth of tumors in liver on chronic exposure to low doses (Chorus and Bartman, 1999). Numerous other cyanobacterial toxins like anatoxins, saxitoxins and lipopolysaccharides are known to cause allergy, gastrointestinal and respiratory health issues in humans (Chorus and Bartman, 1999).

1.5. Treatment techniques for Algal Metabolites

1.5.1. Activated Carbon

1.5.1.1. Methods to Activate Carbon

Activated carbon is a highly porous form of carbon that has superior adsorptive characteristics. The high surface area per unit volume and microscopic pores makes it ideal for adsorption of particles on its surface. Activated carbon is manufactured from various materials like hard and soft wood, coconut shells, walnut shells, peat, lignite coal, bituminous coal, olive pits and other carbon rich sources. Activated carbon is used for many purposes like drinking water treatment, air purification, industrial pollution control, medical treatment, food and beverage processing. The superior adsorptive power of activated carbon makes it ideal for drinking water treatment purposes too. Activated carbon is produced by carbonizing and activating the original carbon-rich material (Martinez et al., 2006). The carbon can be activated by physical or chemical treatment (Rodriguez-Reinoso and Molina-Sabio, 1992). The physical activation process consists of thermal treatment carried out in two different stages, In the first stage the precursor carbonization takes place followed by controlled gasification (steam flow, temperature, heating rate, etc.) of the crude char in the second stage (Gonzalez et al., 1994). The chemical activation technique starts with the infusion of the material with a chemical agent, like an acid or base, and the mix is heated to a temperature of 450–900^{o}C. Chemical activation process increases the carbon yield by reducing the formation of tar and other byproducts (Gonzalez-Serrano et al., 1997; Evans et al., 1999)

1.5.1.2. Off-flavor compounds removal with activated carbon

Off-flavor compounds like geosmin and MIB cannot be removed by conventional water treatment methods due to their low detection levels. The two important forms of activated carbon widely used in the drinking water treatment for T&O compounds removal and DOC reduction are granular activated carbon (GAC) and powdered activated carbon (PAC) (Fig 1.7).

Figure 1.7: GAC (*left*) and PAC (*right*) (Calgon Carbon)

GAC can be used as a filtration bed on the top of gravel or sand filter media for removal of off-flavor and organic compounds. Effectiveness of GAC in removal of off-flavor and organic compounds in drinking water treatment depends on several factors, like the type of material GAC is made of (mainly wood, coconut or lignite), contact time with water, dissolved organic carbon (DOC) content of the water. GAC can be fined tuned with thermal treatment to improve geosmin and MIB removal (Rangel-Mendez and Cannon, 2005). Ridal et al. (2001) studied the removal of geosmin and MIB using GAC filter beds in water treatment facility in Canada. The study determined that an increase in contact time from 3.1 to 14.2 minutes increased the filter efficiency from 43% to 78% for geosmin and 43% to 66% for MIB, confirming that contact time with GAC filter beds played vital role in the removal of T&O compounds. Ridal et al. (2001) also determined that chlorine residual and filter age also affect the GAC filter efficiency in removing geosmin and MIB from water. Kim et al. (1997) studied the removal of geosmin and MIB in pilot plants with conventional treatments like coagulation, flocculation, sedimentation, filtration followed by ozone and determined that only 33.3% geosmin and 28.1% MIB were removed without GAC. They tested the conventional treatments with ozone followed by GAC filter towers with different empty bed contact times (EBCT), and determined that EBCT of 10 minutes in two different GAC filter towers had 50.9% and 59.6% geosmin and 52.5% and 47.5% of MIB removal rates. Additionally, the testing was done with EBCT of 15 minutes in two different GAC filter towers which resulted in 62.5% and 74.2% geosmin and 60.8% and 64.5% of MIB removal. The studies show that increased contact times are an essential factor in determining the GAC filter efficiency, hence filters should be designed to increase contact time in order to maximize removal efficiency.

The most effective and simplest method to remove these T&O compounds is by adsorption using powdered activated carbon (PAC) (Srinivasan and Sorial, 2011). The PAC is relatively inexpensive and can be applied only when the off-flavor issue arises due to the dosage flexibility. In a study conducted by Cook et al. (2001) it was determined that PAC dosages required for off-flavor compounds removal varies, depending on various factors like type of activated carbon used, natural organic matter present in the source water and PAC contact time which varies for each water treatment plant depending on their operating conditions. The study by Lalezary et al. (1988) determined that PAC dosages in the range of 10 mg/L were able to reduce the water with an initial geosmin and MIB concentrations of 66 ng/L each to 2 ng/L of geosmin and 7 ng/L of MIB, similarly the metropolitan's water which generally has a geosmin and MIB concentration of upto 20 ng/L for each was estimated to be reduced to less than 1 ng/L of each geosmin and of MIB with a PAC dosage of 5 mg/L. The same study by Lalezary et al. (1988) also determined that PAC contact time does not have a significant effect on removal efficieny and addition of chlorine reduces the PAC adsorption efficiency of geosmin and MIB. Bituminous coal based PACs showed better performance than wood or coal based PACs. (Bruce et al., 2002). Optimization of PAC dosages based on the DOC and natural organic matter present in the source water is necessary for water treatment plants in order to prevent PAC overdosing, which can in turn result in increased operating cost and sludge production.

1.5.2. Advanced Oxidation Processes

1.5.2.1. UV/Hydrogen Peroxide

Oxidation techniques like ultraviolet irradiation are gaining attention in odorant treatment field recently, this is due to the fact that disinfection and odorant removal can be done with same UV treatment. In a study by Rosenfeldt et al. (2005) it was determined that medium pressure UV lamps were more effective than low pressure UV lamps for direct photolysis of geosmin and MIB. The same study also found that geosmin and MIB show a greater absorbance at a wavelength below 250nm. Rosenfeldt et al. (2005) studied the effects of hydrogen peroxide addition to the UV process, it was identified that addition of 2.3 and 7.2 mg/L of hydrogen peroxide increased the geosmin and MIB destruction to a great extent, instead of using the UV process without any hydrogen peroxide. It was also determined that hydrogen peroxide addition to the UV process produced highly reactive hydroxyl radical based advanced oxidation, which improved the geosmin and MIB removal. It is worth noting that this study also found that UV irradiation greater than the normal range required for disinfection was needed to remove the persistent odorants like geosmin and MIB. Kutschera et al. (2009) determined that UV irradition at wavelength of 254nm showed poor absorption of geosmin and MIB. The study also found that UV in combination with Vacuum UV (VUV) with wavelengths of 254 and 185 nm respectively showed effective absorption of geosmin and MIB. Kutschera et al. (2009) also indicated that a low-pressure UV/VUV lamp can lower energy and life cycle costs. The authors specified that UV/VUV irradiation was disadvantageous due to the formation of nitrite which is regulated and may require further treatment to remove it.

1.5.2.2. Ozone

Ozone is one of the most effective oxidant that is used in the drinking water treatment processes. Ozone can be used for disinfection and also odorant treatment. Bruce et al. (2002) determined that ozone application oxidized both geosmin and MIB. Bruce et al. (2002) conducted experiments to determine the mechanism behind the oxidation of geosmin and MIB, by using t-butanol to scavenge hydroxyl (HO) radicals produced during ozonation. The experimental analysis confirmed that addition of t-butanol resulted in lesser oxidation of geosmin and MIB. Hence Bruce et al. (2002) confirmed that HO radicals were behind the oxidation mechanism of geosmin and MIB. Westerhoff et al. (2006) also conducted similar experiments to reinforce the fact that HO radicals were responsible for the oxidation of both geosmin and MIB, by using t-butanol to scavenge hydroxyl (HO) radicals. Ozone rapidly oxidized over 90% of geosmin and MIB without t-butanol addition (Westerhoff et al., 2006). Ozonation can form halogenated DBPs like dibromoacetonitrile in waters that contain bromide and non-halogenated DBPs like carboxylic acids and aldehydes (Richardson et al., 2000). Ozone in combination with other water treatment technologies like UV or biofiltration can be very effective in removing the geosmin and MIB from drinking water.

1.5.3. Biological Treatment

1.5.3.1. Biofiltration/Biodegradation

Biological processes are used commonly to treat wastewater. Unlike wastewater, drinking water treatment had been confined to biodegradation or biofiltration. In a study by Elhadi et al. (2006) biological filtration with two types of filtration media GAC (Granular Activated Carbon)/sand and anthracite/sand were tested for geosmin and MIB removal at different temperatures and Biodegradable Organic Matter (BOM) levels. The study used ozonation by-products as BOM to replicate filtration following the ozonation process, the results indicated that geosmin and MIB removal was higher at 20^0C than at 8^0C. In addition, the study determined that odorant removal was more effective with GAC/sand than anthracite/sand media. A superior removal rate of the odorants was also observed in the study at a higher BOM concentration due to greater biomass density. Ho et al. (2007) studied biodegradation of geosmin and MIB in the presence of sand filter biofilm in a bioreactor. The study determined that biodegradation of geosmin and MIB was a pseudo-first-order reaction where rates are affected by the initial concentration of the biofilm and not by initial concentration of the off-flavor compounds. In addition Ho et al. (2007) observed that the rate of biodegradation increased with the re-exposure of the biofilm to geosmin and MIB, demonstrating that biofilm acts as a catalyst for increasing the rate of biodegradation process. This study also made a crucial discovery of four bacterial species namely *Pseudomonas* sp., *Alphaproteobacterium*, *Sphingomonas* sp. and *Acidobacteriaceae* member, which are capable of degrading geosmin within the sand filters and bioreactors.

1.5.4. Algaecides and other chemicals

Algaecides are used to control algal blooms in lakes and reservoirs. Algaecides can be either natural, copper-based or synthetic organic. Barley straw can be a used as natural algaecide in small ponds, lakes or reservoirs. A study by Wagner (2004) indicated that barley straw can be used as a low-cost alternative to control algal blooms, however usage of barley straw can result in reduction of oxygen levels and was generally not reliable due to changing water conditions. Copper is one of the essential micronutrients needed for growth and development of algae and cyanobacteria. An increased concentration of copper can be toxic to the microbial cells (Florence, 1982). Copper sulfate is one the most widely used algaecide in the U.S (Kellerman and Moore, 1905). Moreover, Copper sulfate is safe to use in drinking water (McGuire et al., 1984). In a study by McGuire et al. (1984) chunks of copper sulfate were used to regulate the growth of earthy and musty odorants producing blue-green algae in Lake Mathews in California. Studies have shown that other copper based algaecides like chelated copper have been effective in controlling the algal blooms.

1.5.5. Advanced Integrated Technologies

Due to the low OTC of geosmin and MIB, using one treatment method may not be sufficient in order to achieve of below OTC concentration removal of the T&O compounds. Integration of various treatment techniques have proved to be effective in various studies conducted to eliminate off-flavor compounds and achieve satisfactory drinking water quality. Matsui et al. (2007) studied normal PAC and micro-ground PAC with particle size of less than 1μm called super-PAC (S-PAC) in a pilot plant experiment, where S-PAC was applied before ceramic membrane filtration for enhanced removal of geosmin from water. The study found that a dosage of 20mg/L of normal PAC was required to reduce geosmin concentration from 241 to

5ng/L and a dosage of just 2mg/L of S-PAC reduced the geosmin concentration to less than 2ng/L. This study showed that with less than 10% of dosage required by normal PAC, S-PAC can achieve superior results and can reduce the PAC dosages by nearly 90%. Moreover, the water treated with S-PAC when used as microfiltration feed water had negligible particle clogging in the microfiltration membrane. A study by Young Wan Ham et al. (2012) demonstrated that a combined process of ozone and GAC was able to remove geosmin and MIB above 95% of their initial concentrations. Jung et al. (2004) conducted several experiments to evaluate the combination of PAC adsorption and oxidation with oxidants like ozone, chlorine and chlorine dioxide. The study determined that adsorption efficiency of geosmin was better than that of MIB and odorant removal effectiveness of chlorine and chlorine dioxide was poor when compared to ozone. Also, the study found that maximum removal of geosmin and MIB occurred at the PAC containing adsorptive section of the treatment process. Nerenberg et al. (2000) documented that ozonation followed by biofiltration was effective in removal of geosmin and MIB in a water treatment facility in Lake Bluff, Illinois. The study mentioned that ozonation alone can cause partial destruction of off-flavor compounds like geosmin, MIB and other odor causing compounds and create a biological instability by converting non-biodegradable NOM into smaller and more oxidized compounds that act as substrates for the bacteria. The biofiltration followed by ozonation helps bring down the concentration of biodegradable organic matter in water and make it devoid of off-flavor compounds like MIB. The ozonation step before biofiltration can act as a disruptor of NOM which in turn can create substrates for the bacteria in the biofilter to effectively degrade the T&O compounds like MIB. The study suggests that ozonation-biofiltration can be an effective combination in eliminating the off-flavor compounds from water. Park et al. (2007) did a comparative study on ozone and ferrate (Fe(VI)) to determine most effective method for the oxidation of geosmin and MIB. The study determined that Fe(VI) was not effective in oxidizing geosmin and MIB when compared to ozone, this was due to the high oxidation selectivity of ferrate and the structure of odorants, geosmin and MIB.

1.5.6. Other unconventional Methods

Many studies have been conducted with unconventional methods to remove off-flavor compounds like geosmin and MIB with great success, but these techniques may require further research in order to make them potentially viable for large scale applications. In a study by Bu et al. (2017) degradation of geosmin and MIB by electrochemical oxidation (EO) using boron-doped diamond (BDD) electrode was analyzed. The study was conducted with different types of electrolytes like sulfate, nitrate, perchlorate and different types of anodes like boron-doped diamond (BDD), mixed metal oxides (MMO), Pt. Bu et al. (2017) determined that BDD was effective in degrading geosmin and MIB when compared to other anodes and sulfate electrolyte performed better than the nitrate and perchlorate electrolytes in degradation of T&O compounds. The study also found that in-situ formed persulfate during the EO process was responsible for the degradation of geosmin and MIB. Park et al. (2017) discovered that photo-Fenton process was an effective technique to degrade geosmin and MIB in drinking water sources. But the study also mentions the limitations of photo-Fenton process like lower pH requirement, with maximum degradation occurring at pH 3, lower concentration of organic matter and lower initial concentration of geosmin and MIB that were required for the process to be effective. However, photo-Fenton process also degraded trihalomethanes (THMs) and microcystin-LR (MC-LR), obtained from cyanobacterial blooms without any toxic by-product production. Lawton et al. (2003) studied photocatalysis with titanium dioxide (TiO_2) to remove geosmin and MIB from water. The studied demonstrated rapid degradation of both geosmin and MIB with over 99%

decomposition happening within 60 minutes of TiO_2 photocatalysis. The authors point out that experiments were not performed on natural waters and the process need more refining in order to be implemented on a commercial scale. Song and O'Shea (2007) studied the use of ultrasonic irradiation to eliminate T&O compounds like geosmin and MIB in water. The study used ultrasonic irradiation at 640 kHz, to degrade geosmin and MIB in water, after 40 minutes of ultrasonic irradiation over 90% degradation on both the compounds was accomplished. It was determined that the main process responsible for the degradation of T&O compounds was the pyrolysis induced by ultrasonic irradiation. The authors also suggested that ultrasonic-induced degradation method can be used for removal of geosmin and MIB from drinking water or aquaculture sources.

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CHAPTER 2. PRE-OXIDATION AND ADSORPTION WITH POWDERED ACTIVATED CARBON FOR TASTE AND ODOR CONTROL AND OPTIMIZING COAGULATION FOR DISSOLVED ORGANIC CARBON REMOVAL

2.1. Overview

Geosmin and MIB (2-Methylisoborneol) are the two natural organic compounds produced by certain types of blue-green algae which cause taste and odor (T&O) issues in the sources of drinking water. Geosmin and MIB are not regulated by United States Environmental Protection Agency (USEPA) as they do not pose a health risk, but these two organic compounds seriously hinder the aesthetic appeal of finished drinking water due to the earthy or musty odor produced by them even at very lower concentrations (below 10 ng/L). Geosmin and MIB cannot be eliminated by conventional drinking water treatment processes, hence more advanced treatment techniques involving an adsorption agent like Powdered Activated Carbon (PAC) is necessary to remove these odorants and achieve concentration below the odor threshold.

Boyd Lake Water Treatment Plant in Greeley region, gets it intake of raw water from two main drinking waters sources namely Boyd Lake and Lake Loveland. The plant has been experiencing T&O related issues mostly during the mid-summer to late autumn. This study was conducted for BLWTP in three phases to determine the optimal conditions to address the seasonal T&O issue and also help reduce the Dissolved Organic Carbon (DOC) content of the source waters efficiently with PAC. Preliminary testing was conducted on Lake Loveland and Boyd Lake water with an incremental alum dosage from 30 to 70 mg/L followed by three five minute stages of flocculation and 45 minutes settling time. Turbidity, TOC and DOC were measured before and after coagulant testing. The results indicated that Boyd Lake water was the hardest to treat, hence it was selected for further testing.

In the initial phase of the study, about ten different PACs were tested in five batches, with Boyd Lake and plant mix water collected at different time periods. The results from the five batches were averaged and ranked based on the DOC reduction values. The results indicated that PAC Hydrodarco M was the cost and performance wise effective of the ten PACs tested. The second phase of the study involved testing four different PACs at four different contact times (15, 30, 45 and 60 minutes) with one constant dosage of 30mg/L for the kinetic study part. The results showed that maximum DOC removal was achieved at 45 minutes contact time. Similarly, the same four different PACs were tested with four PAC doses (10, 20, 30 and 40 mg/L) with one preset contact time of 45 minutes for the dosage study part. The results from these tests indicated that 30 mg/L was the optimal PAC dosage for maximum DOC removal. In the final phase, the raw water was initially treated with the various pre-oxidants with dosages of 1mg/L ClO_2, 5 and 10 mg/L of $NaMnO_4$ with a contact time of 60 seconds followed by PAC treatment with a dosage of 30 mg/L and a 45 minutes contact time. Test results revealed that pre-oxidants did not have a significant impact in DOC removal at any dosage levels. Additionally, two dosages 20 and 70 mg/L of coagulant alum were tested with pre-oxidant and PAC treated water. Detailed analysis was performed with coagulant alum in combination with pre-oxidant and PAC treated water. The results of the alum testing illustrated that a higher dosage of coagulant alum at 70 mg/L had a substantial effect on the DOC removal when compared to a lower dosage of 20 mg/L. Further, the results showed a two-fold increase in the DOC reduction at an alum dosage of 70 mg/L without the presence of any pre-oxidants.

Keywords: MIB, Geosmin, Powdered Activated Carbon, Dissolved Organic Carbon, alum, Hydrodarco M, pre-oxidants

2.2. Introduction

Clean and safe drinking water is one of the essential resources required for human survival. Pure water is colorless, odorless and tasteless, however natural water sources like rivers, lakes and reservoirs can be imparted with musty and earthy odors by certain metabolites produced due to degradation of cyanobacteria, blue green algae, fungi and actinomyces (Izaguirre and Taylor, 2004; Gerber, 1967; Gerber et al., 1965). The primary source of musty and earthy odors are non-toxic secondary metabolites produced by cyanobacteria namely geosmin and MIB (Butakova, 2013). Various environmental factors contribute to the formation of algal blooms in natural water sources like rivers and lakes. Light intensity is the predominant factor that regulates the growth of cyanobacteria. Aerobic photoautotrophic microorganisms like cyanobacteria rely on light for photosynthesis, which is their main mode of energy production (Chorus and Bartman, 1999). Nutrients like nitrogen and phosphorus are necessary for the growth of cyanobacteria (Dolman et al., 2012), along with trace metals like iron, molybdenum which also play a vital role in metabolism and growth of cyanobacterial populations (Rueter et al., 1987). The off-flavor issues with drinking water are seasonal. Geosmin and MIB occur in water sources due to the biodegradation of different types of cyanobacterial species, that show a rapid growth in presence of essential nutrients during the warmer temperatures months of the year (Watson et al., 2008). Other factors like pH and turbidity also contribute to the wide spread growth of algal blooms.

Geosmin has a molecular weight of 182.3 g/mol, water solubility of 5.5 x 10^{-5} mg/L, density of 0.95 g/mL at 20^{0}C and Henry's Law constant of 0.0023 at 25 ^{0}C (Lalezary et al., 1984;

Pirbazari et al., 1992). MIB has a molecular weight of 154.3 g/mol, water solubility of 7.3 x 10^{-5} mg/L, density of 0.93 g/mL at 20^{0}C, and Henry's Law constant of 0.0027 at 25^{0}C (Lalezary et al., 1984; Pirbazari et al., 1992).

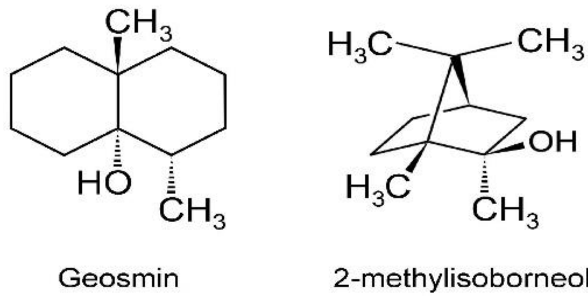

Figure 2.1: Molecular Structure of geosmin and MIB

The cyanobacterial secondary metabolites like geosmin and MIB are not regulated by regulated by United States Environmental Protection Agency (US EPA). Although presence of T&O compounds in water do not pose a threat to human health (Dionigi et al., 1993), they may considerably reduce the consumer trust and in some cases, can lead to the reduction in the consumption of water or can encourage the consumers to switch to an alternative source that can provide aesthetically pleasant water. One of the main concerns with T&O compounds like geosmin and MIB is that they have very low OTC, which is below 10 ng/L (Mallevialle and Suffet, 1987; Pirbazari et al., 1993), so even minute changes in the concentrations of these compounds in the drinking water sources, can cause significant T&O issues in water.

The Greeley region gets its water from different sources like Cache la Poudre River, Laramie River, Colorado River and Big Thompson River. The city of Greeley gets its drinking water supplied from two water treatment plants namely, the Bellvue Water Treatment Plant which is located at the mouth of Poudre Canyon and operates throughout the year and the Boyd Lake Water Treatment Plant (BLWTP) which is located in Loveland, and operates seasonally during peak water supply periods to support Bellvue Water Treatment Plant meet the high demand. BLWTP also serves as a back-up for the Bellvue Plant in the event of an emergency. BLWTP was built in 1964 and it produces 38 million gallons of water per day. BLWTP get its raw water from Boyd Lake and Lake Loveland as shown in Fig 1.3 and Fig 1.4. Greeley Water and Sewer Department's BLWTP has been experiencing an increase in total organic carbon

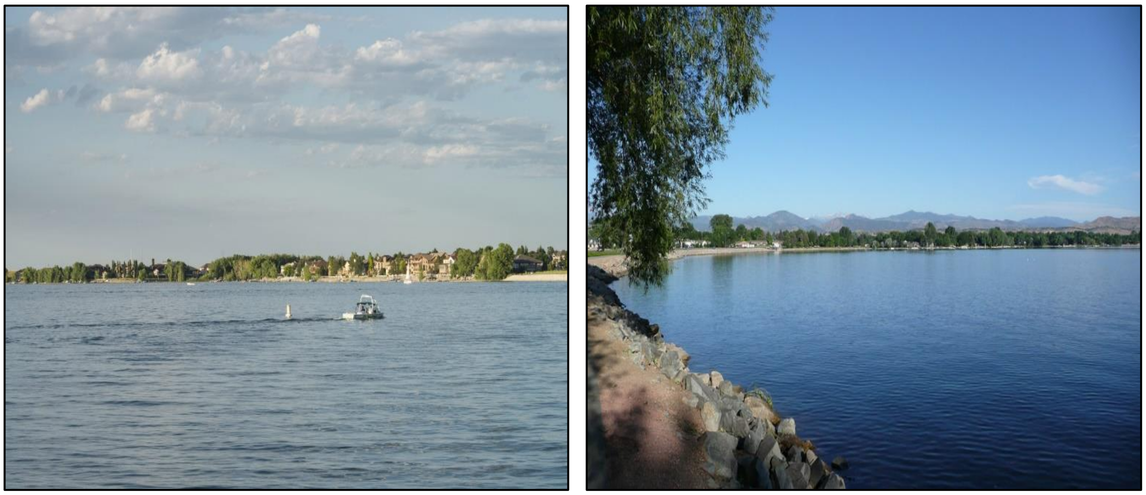

Figure 2.2: Boyd Lake (*left*) and Lake Loveland (*right*)

concentration (TOC) and this has corresponded with an increase in taste and odor (T&O) complaints, particularly in the southern section of their distribution system that is seasonally supplied with mostly BLWTP water. The BLWTP will undergo physical upgrades to the facility beginning late 2016 with completion set for mid-2018.These plant upgrades include providing headworks for chlorine dioxide (ClO_2) and/or powdered activated carbon (PAC) 500 feet from the plant that will bring in water from Boyd Lake and Lake Loveland (Fig 2.2). More importantly, the plant will convert existing floc basins into PAC contact basins with a contact time of 26.6 minutes at the design flow of 20 MGD per basin using an efficiency factor of 0.7. Typical current summertime flows have been around 24 to 26 MGD total, or 12 to 13 MGD per basin, indicating approximately 40 to 43 minutes of contact time in the PAC zone. T&O issue had been on the rise, especially during the warmer temperature periods of the year, numerous consumer complaints were raised due to earthy or musty smell and taste of the finished drinking water supplied by BLWTP. The earthy or musty taste and odor is imparted to the surface water by the off-flavor compounds, geosmin and MIB which are relatively stable to biological and chemical degradation in surface waters in their dissolved form for a particular time span (Peter and Von Gunten, 2007; Westerhoff et al., 2006). These cyanobacterial secondary metabolites are difficult to be removed by conventional water treatment methods like coagulation, flocculation, sedimentation and filtration. Advanced treatments techniques like GAC, PAC, ozone, UV/Hydrogen peroxide, biological treatment methods or a combination of one or more advanced treatment techniques are needed in order to eliminate these off-flavor compounds from water. Oxidation techniques have been successful in the removal of geosmin and MIB to a considerable extent, Rosenfeldt et al. (2005) determined that medium pressure UV lamps were more effective than low pressure UV lamps for direct photolysis of geosmin and MIB. Kutschera et al. (2009) determined that UV in combination with Vacuum UV (VUV) with wavelengths of 254 and 185 nm respectively showed effective absorption of geosmin and MIB. Also, the study by Westerhoff et al. (2006) showed that ozone rapidly oxidized over 90% of the geosmin and MIB without t-butanol (HO radical scavenger) addition. Oxidation methods like ozone and UV require substantial capital and operating costs from WTPs to use these methods exclusively for taste and odor control, which may not be economical for the WTPs in the long run. Biological methods on the other hand, can be economical and effective in controlling the off-flavor compounds, Ho et al. (2007) discovered four bacterial species namely *Pseudomonas sp*., *Alphaproteobacterium*, *Sphingomonas sp*. and *Acidobacteriaceae* member, which are capable of degrading geosmin within the sand filters and bioreactors. Algaecides like Copper sulfate have been used to control algal blooms in lakes and reservoirs (Kellerman and Moore, 1905; McGuire et al., 1984). Integrated technologies have also shown to be effective in taste and odor control, Young Wan

Ham et al. (2012) demonstrated that a combined process of ozone and GAC was able to remove geosmin and MIB above 95% of their initial concentrations. Similarly, Nerenberg et al. (2000) documented that ozonation followed by biofiltration was effective in removal of geosmin and MIB in a water treatment facility in Lake Bluff, Illinois.

One of the simplest and economical method to remove these T&O compounds is by adsorption, using powdered activated carbon (PAC) (Srinivasan and Sorial, 2011). Dosage flexibility make PAC easier for the WTPs to use and alter dosages according to the initial concentration levels of the odorants in raw water. Unlike GAC which is used in WTPs which need a constant removal of odorants from the water, PAC can be used only when taste and odor control is needed. The versatility of PAC makes it an attractive option for T&O control. Bruce et al. (2002) reported that geosmin and MIB adsorption on to the PAC depends on water chemistry of the source water. Hence, the PAC dosages vary according to the chemical composition of the source waters. Bruce et al. (2002) also mentioned that, DOC of the source water will compete with geosmin and MIB for the sorption sites on the surface of PAC which can affect the odorant removal efficiency of PAC. Hence, the removal of DOC from the source water can play a vital role in the enhancing the T&O compounds removal efficiency of PAC.

The main purpose of the study was to determine an efficient and cost-effective PAC for T&O control and DOC removal. Additionally, the study also examines activated carbon dosages, contact times and the effectiveness of pre-oxidants with PAC and alum in DOC reduction. Several batches of testing were performed with a uniform PAC dosage on different brands of PACs, to screen out the better performing ones from the rest. This was followed by kinetic and dosage studies, conducted with the high-performance PACs from each manufacturer along with the PAC used at BLWTP as a baseline. Finally, one best performing, economical PAC was selected and tested to determine if pre-oxidants had any effect on the DOC removal, with only PAC or PAC in combination with a coagulant like alum.

2.3. Materials and Methods

2.3.1. Materials and Apparatuses

2-Methylisoborneol and geosmin solutions were purchased from Sigma Aldrich. Thermo Scientific RT Basic Series Magnetic Stirrers, Fisherbrand Octagon Spinbar, Fisherbrand PTFE Stirring Bar Retriever, KIMAX 100 ml Graduated Cylinder, 500 ml PYREX Flasks with standard taper Stoppers, 2000 mL PYREX, 50 ml PYREX, 100 ml PYREX Glass beakers and Thermo Scientific Finnpipette F1 (0.5-5ml) were purchased from Fisher Scientific. TraceClean TOC-Free Vials and 125ml clear wide mouth glass bottles, were obtained from VWR. Powdered activated carbons Hydrodarco B, Hydrodarco M, Hydrodarco S and Norit PAC 20BF were purchased from by Norit Americas Inc. Powdered activated carbons Watercarb 800 and Watercarb 1000 were acquired from Standard Purification Inc. Powdered activated carbons Pulsorb WP220-90, Pulsorb WP260-90, WPH and WPH 1000 were obtained from Calgon Carbon Corporation. Whatman 934-AH RTU Glass Microfiber Filters with particle retention of 1.5µm were purchased from Fisher Scientific. Aluminum potassium sulfate dodecahydrate and Sodium permanganate solution 40 wt. % in H_2O were purchased from Sigma Aldrich. Chlorine Dioxide Solution with concentration of 3000 ppm was obtained from KV laboratory solutions Inc. Phipps & Bird PB-900 Series Programmable Jar Testers were used for coagulation testing. Turbidity was measured with Hach 2100N Turbidimeter. Water quality parameter pH was measured with Hach HQ40D Portable Multi Meter and Intellical PHC101 pH Electrode, Alkalinity was measured with Hach Alkalinity Test Kit, Model AL-AP, mg/L. Chlorine dioxide content was measured with TK1181-Z, Chlorine Dioxide Test Kit obtained from AquaPhoenix

Scientific Inc. TOC and DOC were measured with Shimadzu TOC-V CSH Total Organic Carbon Analyzer.

2.3.2. Methods

For the experimental analysis, plant mix water was collected from the BLWTP's main raw water inlet, whereas Boyd Lake and Lake Loveland water was collected from different pumping stations and other BLWTP water inlets in five gallon buckets and stored at 4-6^{o} in walk-in cold storage rooms. The water was stored for at least a day in the cold storage before the testing was performed. The holding period was to ensure that all the different test runs had water at uniform temperature. The water was collected at various time periods ranging from early June to mid-September as T&O issues occur mostly during late summer till the beginning of autumn. The water was collected at different time intervals to know how TOC of the natural water changes with time. Stock solutions of both geosmin and MIB were prepared with methanol in clear wide mouth glass bottles, with concentration of 0.04 mg/L each. The PAC stock solutions for all the 10 PACs were prepared individually, with deionized water to a concentration of 12g/L each. All the prepared stock solutions were stored at 4-6^{o}C in walk-in cold storage. Phipps & Bird PB-900 Series Programmable Jar Tester was used to do preliminary alum testing with the collected water. A set of 5 jar tests were performed (Fig 2.3), with 5 different doses of alum ranging from 30 to 70 mg/L in increments of 10 mg/L, with each type of water collected. The alum addition was followed by three five minute stages of flocculation with paddle speed of the Jar Testers set at 45, 30 and 15 rpm for each stage. The initial paddle speed was set at 45 rpm to give a rapid mix and then the paddle speed was reduced to 30 rpm for a gradual mix and then finally to 15 rpm for a slow mix. The flocculation step was followed by 45 minutes of settling time. The same testing cycle was conducted again with each type of water collected, to

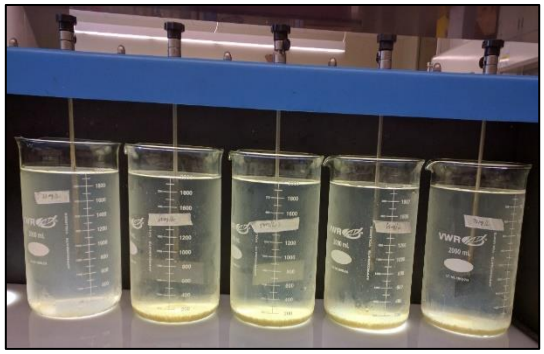

Figure 2.3: Preliminary alum testing

determine the water with lowest TOC removal rate in the presence of coagulant alum. Turbidity, TOC, DOC, pH and alkalinity were measured in each jar before and after alum addition. The percent TOC removal was then calculated with raw water TOC as reference point. A total of 11 PYREX 2L beakers, each filled with 2L of sample water were placed on a separate magnetic stirrer set at medium speed. For each jar, a PTFE coated magnetic stir bar was placed in it. After the identification of the source water in the preliminary phase of testing, a total of 11 jar tests were conducted as a part of the initial phase of testing. The first jar served as the control and the remaining ten jars were dosed with 10 PACs from three different manufactures (Table 2.1). For the spiked testing part, the control jar and the rest of the 10 jars were spiked with 20 ng/L of MIB (1 mL of 0.04 mg/L stock solution) and 40 ng/L geosmin (2 mL of 0.04 mg/L stock solution)

Table 2.1: PAC Specifications

PAC Name	PAC Manufacturer	PAC Cost ($/lb)	Iodine Number (minimum) (mg/g)	Moisture (maximum) (%)	Bulk Density (g/mL)	Less than 100 Mesh (150 µm) (%)	Less than 200 Mesh (75 µm) (%)	Less than 325 Mesh (45µm) (%)
Hydrodarco B	Cabot	0.6	500	8	0.51	99	95	90
Hydrodarco M	Cabot	0.65	550	8	0.56	99	95	90
Hydrodarco S	Cabot	0.56	500	8	0.51	99	95	90
Norit PAC 20BF	Cabot	0.71	800	8	0.51	99	95	90
Watercarb 800	Standard Purification	0.87	800	8	0.4-0.5	-	-	90
Watercarb 1000	Standard Purification	1.05	1000	8	0.3-0.5	-	-	>70
Pulsorb WP220-90	Calgon	0.96	800	10	NA	-	-	90
Pulsorb WP260-90	Calgon	1.07	1000	10	NA	-	-	90
WPH	Calgon	1.03	500	8	NA	99	95	90
WPH 1000	Calgon	0.95	500	8	NA	99	95	90

The 10 jars of water were then treated with 10 different PACs (Fig 2.4) with dosage set at a constant 30 mg/L per PAC (5ml from 12g/L stock solution) except the control jar where no PAC

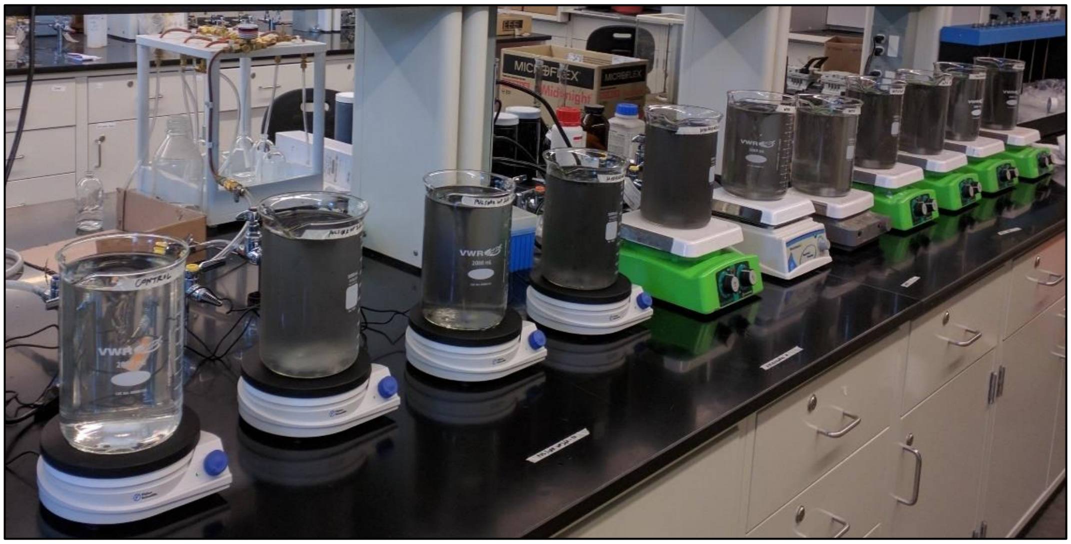

Figure 2.4: PAC-DOC testing with 10 PACs

was added. The control jar served as a baseline to determine the DOC, geosmin and MIB removal efficiency of each PAC. The contact time was maintained at 45 minutes for all the 11 jars. No coagulation treatment was performed on any jar after the PAC testing. After PAC treatment, the water from each jar was filtered with a 1.5µm filter. The filtration of the samples was carried out with the help of a vacuum filtration apparatus (Fig 2.5)

Figure 2.5: Glass fiber filter paper (*Left*) and Vacuum Filtration apparatus (*Right*)

The filtered samples were then transferred to a 40 ml TOC vial for DOC, geosmin and MIB analysis. The samples were tested for geosmin and MIB concentration by Dr Pinar Omur-Ozbek team with the help of GC/MS. DOC was measured for all the 11 jars with Shimadzu TOC-V CSH Total Organic Carbon analyzer. The primary purpose of this test run was to determine the percent DOC reduction of all the 10 PACs when compared to the spiked control. Due to spiked geosmin and MIB interfering with the DOC measurements, all further test runs were performed with just PAC and the natural water, without any spiking of geosmin and MIB.

Similar experimental set up as mentioned above was used for unspiked PAC testing. All the 11 PYREX glass beakers were filled with the 2L of sample water, but this time there was no spiking of geosmin and MIB. The natural DOC and odorant content present in the raw water was considered as the control for each run. The first jar has no PAC added and was set as control for the test run. The remaining 10 jars were treated with 10 different PACs with dosage set at 30 mg/L and contact time set at 45 minutes. A total of 5 unspiked tests were conducted with 2 types of Boyd Lake and 3 types of plant mix water collected at different time periods. The plant mix water was collected directly from the BLWTP raw water inlet, the plant operators mix the water from Boyd Lake and Lake Loveland depending on the availability of water in the two lakes. Different blends of plant mix water that were tested are namely plant mix water (70% Boyd Lake and 30% Loveland Lake), plant mix water (60% Loveland Lake and 40% Boyd Lake) and plant mix water (50% Loveland Lake and 50% Boyd Lake).

After the phase one testing, kinetic and dosage studies were conducted in the second phase of the experimental analysis. The kinetic study part of testing was conducted with Boyd Lake water to determine the optimal PAC contact time for maximum odorants (geosmin, MIB) and DOC removal. For the kinetic study one best PAC was selected from each of the 3 PAC manufacturers, in addition to PAC Watercarb 800 used at the BLWTP as a baseline. The four different PACs were tested at four different contact times (15, 30, 45 and 60 minutes) with a constant PAC dosage of 30mg/L for each contact time. For this set of tests, all PAC dosing was done to the raw water and no coagulation was run. Additionally, one more separate test run was also conducted to determine any major changes in the DOC removal. No geosmin or MIB was spiked in the raw water for the kinetic study. The samples from the two test runs were filtered, collected in TOC vials and tested for remaining DOC, geosmin and MIB content after PAC treatment. For the dosage study part, the testing was conducted with Boyd Lake water and the same four PACs used in the kinetic study were tested at four different PAC dosages (10, 20, 30 and 40 mg/L) with contact time set at a constant 45 minutes. Similar to kinetic study, an additional test run was conducted to determine any major changes in the DOC removal. No geosmin or MIB was spiked in the raw water and all PAC dosing was done to the raw water with no coagulation treatment. Additional dosage studies were also performed with plant discharge 1, plant discharge 2 and plant mix (50% Boyd Lake& 50% Lake Loveland) water samples collected from the BWLTP discharge outlets and inlets, to study the PAC performance with different types of water. The final part of the dosage study was conducted with the cost-effective PAC. The pre-selected PAC was tested with different blends of water namely, plant mix 1 (50% Boyd Lake and 50% Lake Loveland) and plant mix 2 (90% plant mix 1 water, 5% plant discharge 1 and 5% plant discharge 2). For this particular PAC of interest, PAC efficiency was also calculated.

The formula is as below:

PAC efficiency* = (mg C removed/ mg PAC)

where:

mg C removed = milligrams of organic carbon removed by the PAC (mg/ L) mg PAC = milligrams of PAC required for the organic carbon removal (mg/L)

PAC efficiency = operating efficiency of the PAC

(*) efficiency is unit less

The mg C removed is the difference between initial DOC concentration before any PAC addition and DOC concentration after the treatment of the sample water with the specified PAC. The mg PAC is the dosage of PAC (10, 20, 30 and 40 mg/L) used in that particular run. PAC efficiency is the value obtained from the division of mg C removed by mg PAC. PAC efficiency is a measure of PAC effectiveness in DOC removal with different PAC dosages. The PAC efficiency is a vital number needed to determine the peak efficiency of the PAC. Dosing the water with PAC beyond the peak efficiency may result in wastage of PAC and increased cost dealing with the waste generated. PAC efficiency also helps in the reduction operating cost of the drinking water treatment plant as it helps to determine the ideal dosage for the maximum DOC removal. PAC wastage can also be reduced to a minimal amount with the use of PAC efficiency.

The final segment of the study includes pre-oxidant testing with pre-selected PAC to determine the impact of pre-oxidant on DOC reduction. Two types of pre-oxidant (ClO_2 and $NaMnO_4$) were used along with the previously selected PAC Hydrodarco M. For the pre-oxidant testing 4 jar tests were conducted (shown in Fig 2.6), and the first jar served as control. The control jar was treated with a dosage of 30mg/L of PAC and 45 minutes contact time with no pre-oxidant added to it. The rest of the 3 jars were treated initially with 1 mg/L of ClO_2, 5 mg/L of $NaMnO_4$ and 10 mg/L of $NaMnO_4$ respectively with a 60 seconds contact time. The three jars after pre-oxidant treatment were treated with a dosage of 30mg/L of PAC allowing a 45 minutes contact time. PAC and pre-oxidant dosing was done in separate stages to the raw plant mix water and no coagulation treatment was performed. The pre-oxidant and PAC treated water was filtered with 1.5µm filters using vacuum filtration apparatus and then tested for DOC content.

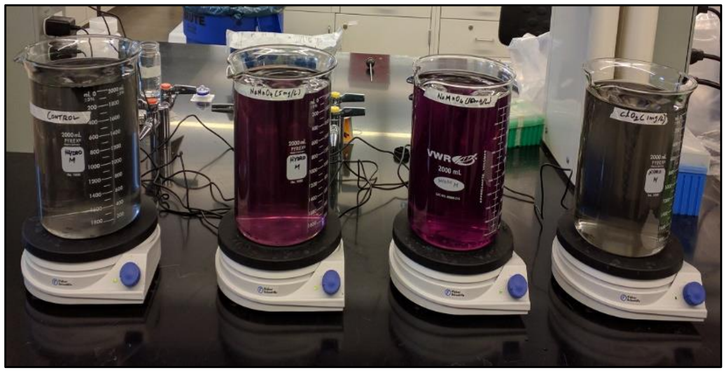

Figure 2.6: Pre-Oxidant testing with PAC

Additionally, two separate test runs were also conducted with similar setup, but with 1 mg/L ClO_2 and 5 mg/L $NaMnO_4$ pre-oxidant dosages.

The next part of the pre-oxidant study was to determine the effects of coagulant in combination with pre-oxidants and PAC on DOC removal. The same plant mix water used for the pre-oxidant study without coagulant was used in this part of the testing too. Initially, the raw water jar was not dosed with PAC, pre-oxidant or alum. The treatment process was staged for rest of the four jars. For the control jar, the raw water was dosed with 30 mg/L of the selected PAC with a 45 minutes contact time. For the PAC and alum jar, the PAC was added initially to the water, after 45 minutes of PAC contact time, the jar was dosed with the 20 mg/L of coagulant alum followed by three five minute stages of flocculation and 60 minutes settling time. For the pre-oxidant ClO_2 part, the raw water was dosed with 1 mg/L of ClO_2 with a contact time of 60 seconds, then the water was dosed with 30 mg/L of selected PAC with a 45 minutes contact time. After 45 minutes of PAC contact time the pre-oxidant ClO_2 treated water was dosed with the 20 mg/L of coagulant alum, followed by three five minute stages of flocculation and 60 minutes settling time. For the pre-oxidant $NaMnO_4$ part, the same procedure as the pre-oxidant ClO_2 was followed, except for the initial step where the raw water was dosed with 10 mg/L of $NaMnO_4$ with a contact time of 60 seconds. The DOC before and after PAC treatment and filtration through 1.5µm filter was measured for all the jars. Turbidity was also measured with HACH Turbidimeter (shown in Fig 2.7).

Figure 2.7: Turbidimeter

Further, two separate batches of tests were conducted with similar testing procedure with same plant mix water with 1 mg/L of ClO_2, 5 mg/L of $NaMnO_4$ and a higher alum dosage of 70 mg/L to determine if higher coagulant dosage may result in maximum DOC reduction of the water when compared to a lower coagulant dosage of 20 mg/L. Additionally, two more test runs were conducted with a new blend of water (90% plant mix & 5% plant discharge 1 & 5% plant discharge 2) to be treated with 1 mg/L of ClO_2, 5 mg/L of $NaMnO_4$ and 70 mg/L alum dosage. Pre-selected PAC Hydrodarco M was used throughout the pre-oxidant study with and without coagulant.

All the TOC and DOC measurements for the entire study were performed by Shimadzu TOC-V CSH Total Organic Carbon Analyzer. The Total Organic Carbon Analyzer uses the Total Carbon (TC) - Inorganic Carbon (IC) method to determine Total organic carbon(TOC). The operation of the Total Organic Carbon Analyzer starts with a small amount of the sample being pulled from the TOC vial placed in the auto sampler.

Figure 2.8: Total Organic Carbon Analyzer

The sample extracted is then injected into a TC combustion tube that is filled with oxidation catalyst (Pt/Al_2O_3), the carrier gas (purified air) is passed at a set rate of 150mL/min to the TC combustion tube heated to around 680^oC. The high heat turns the sample to vapor, and the organic and inorganic carbon content present in the sample get converted to carbon dioxide and water vapor. The mixture of carbon dioxide and water vapor get cooled and dehumidified by a dehumidifier unit. Then the dehumidified gas mixture is sent to halogen scrubber for the removal of any trace halogens like fluorine, chlorine, bromine, iodine. Finally, the cooled and dehumidified carbon dioxide is then carried by the carrier gas to the non-dispersive infrared detector (NDIR) chamber. The NDIR unit detects the carbon dioxide and calculates the TC of the sample. In order to determine the TOC, we need the IC part of the sample too. The source of inorganic carbon in the water is different forms of carbonate dissolved in it. So, in order to determine the IC of the sample, the sample is first acidified with a strong acid, in this case HCl. The acidification of the sample helps in the conversion of carbonates to carbon dioxide. The sample acidified earlier is then sparged with carrier gas, to produce carbon dioxide from the inorganic carbon present in the sample, which is then transported to the non-dispersive infrared detector (NDIR) unit to detect the carbon dioxide.

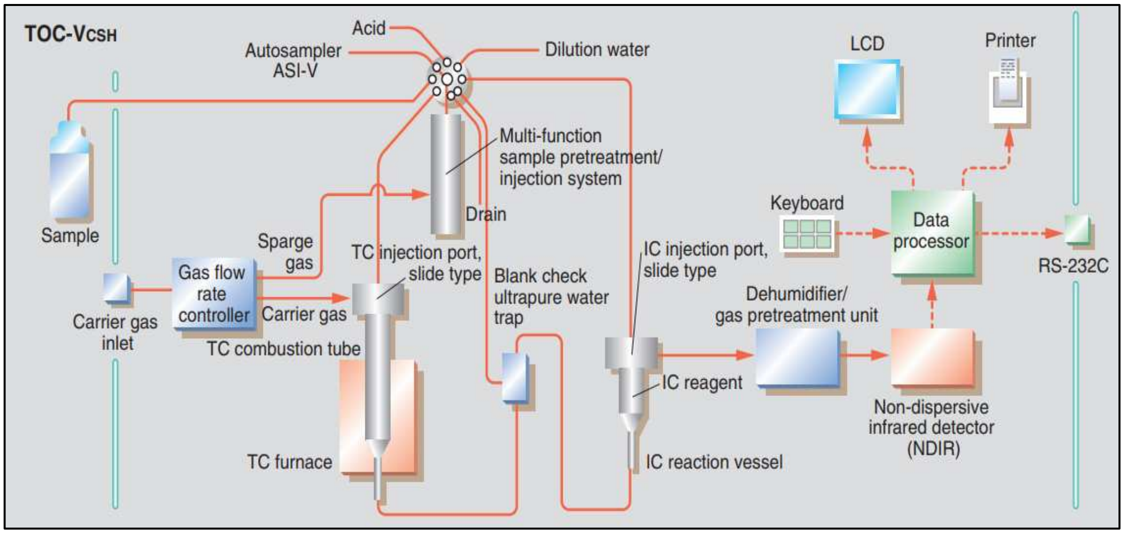

Figure 2.9: Measurement Flow Line Diagram (Shimadzu Corporation)

The Analyzer prints out the TOC results using the formula, Total Carbon (TC) - Inorganic Carbon (IC) = Total organic carbon(TOC).

2.4. Results and Discussion

2.4.1. Results

2.4.1.1. Preliminary Coagulant Trial

The results obtained from the six individual test runs showed that plant mix and Boyd Lake water had least TOC removal rates. Since plant mix was essentially a mixture of Boyd Lake and Lake Loveland, the least effective Boyd Lake water was selected as the source water for further studies. Figure 2.10 shows that plant mix and Boyd Lake had lowest TOC removal rates when compared Lake Loveland at a 70 mg/L alum dosage. The alkalinity of the Boyd Lake and plant mix water due to higher pH levels than Lake Loveland (Appendix A), was attributed to the low TOC removal.

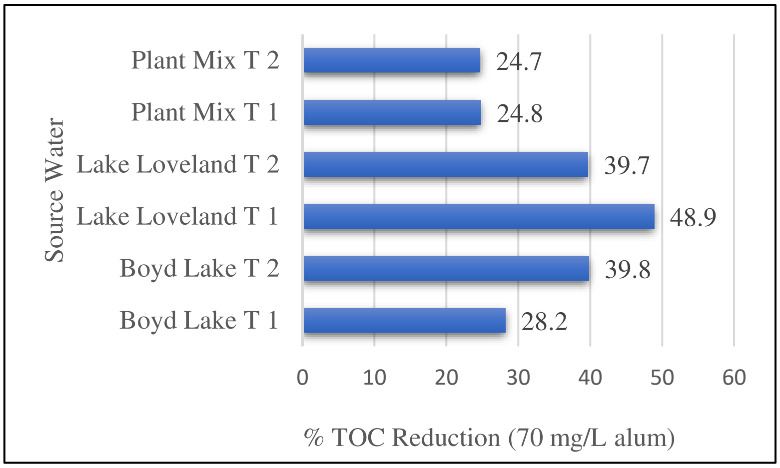

Figure 2.10: Source Water Screening Test

2.4.1.2. PAC Performance Test

DOC results from the geosmin and MIB spiked PAC testing with 10 different PACs are shown below (Table 2.2). The results indicate that, most of the PACs did not show a significant reduction in DOC when compared to the control.

Table 2.2: DOC Results – Spiked PAC Testing

PAC	DOC (mg/L)
Control	12.8
Hydrodarco B	11.6
Hydrodarco M	10.6
Hydrodarco S	11.8
Norit PAC 20BF	11.2
Watercarb 800	11.4
Watercarb 1000	12.0
Pulsorb WP220-90	10.6
Pulsorb WP260-90	10.7
WPH	11.7
WPH 1000	11.0

The percent DOC reduction was calculated with control as initial DOC reference. On the basis of percent DOC reduction (Fig 2.11), it clearly indicates that Hydrodarco M from the manufacturer Cabot and Pulsorb WP 220-90, Pulsorb WP 260-90 from manufacturer Calgon are the PACs with best overall percent DOC reduction. The figure below shows that the PAC used at the BLWTP, Watercarb 800 performed moderately when compared to the best PACs in this test run.

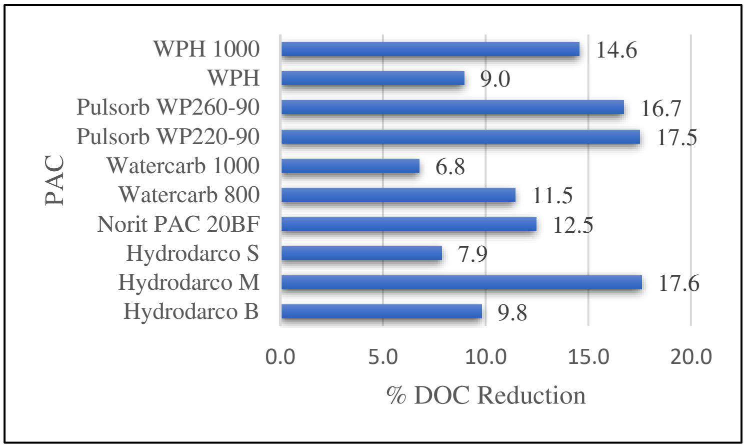

Figure 2.11: Spiked PAC testing PAC Vs DOC Reduction

The geosmin and MIB content of the PAC tested water was determined with GC-MS analytical method. The results shown in Table 2.3, indicate that almost all the 10 PACs performed reasonably well in geosmin and MIB removal of the Boyd Lake water.

Table 2.3: Geosmin and MIB results post PAC testing

PAC	Geosmin (ng/L)	MIB (ng/L)
Control	40	20
Hydrodarco B	4.4	3.4
Hydrodarco M	0.5	2.7
Hydrodarco S	6.4	6.6
Norit PAC 20BF	2.9	1.9
Watercarb 800	5.4	7.1
Watercarb 1000	3.3	3.6
Pulsorb WP220-90	3.5	0.5
Pulsorb WP260-90	3.1	2.3
WPH	3.7	0.5
WPH 1000	2.7	3.1

The Figure 2.12 shows that, the best PACs with highest percent geosmin removal are Hydrodarco M, WPH 1000, Pulsorb WP 260-90. Similarly, the PACs with highest percent MIB removal are Hydrodarco M, Norit PAC 20BF, WPH, Pulsorb WP 220-90 and Pulsorb WP 260-90. The PAC Watercarb 800 used at BLWTP showed poor MIB removed rates as shown in Figure 2.12. As most PACs are effective in the removal of geosmin and MIB above 60%, further testing was focused on determining the PAC which was also cost-effective. The economical PAC can reduce the BLWTP operating cost to a considerable extent, if the PAC discovered in this study was cheaper than the PAC Watercarb 800 used currently at the plant.

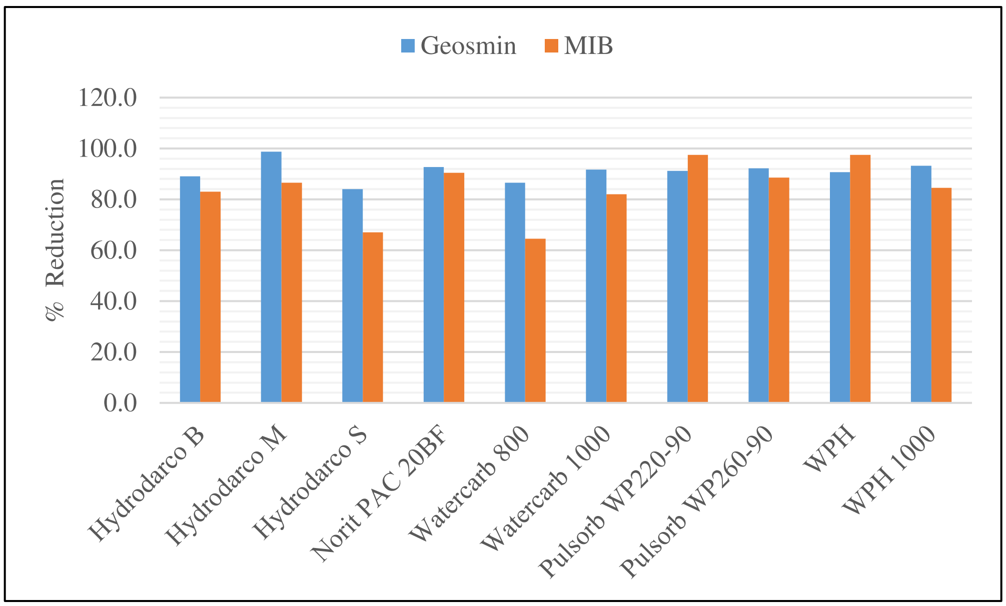

Figure 2.12: Comparison of Geosmin and MIB reduction for PACs

The phase one testing was continued without any geosmin and MIB spiking, due to the interference caused by the spiked odorants in the DOC measurements. A total of 5 separate batches of tests were conducted with different types water collected from mid-July to mid-September. Each batch includes a control and 10 jars dosed with 10 different PACs. In addition to the DOC measurements, percent DOC reduction values were also calculated for each batch with the collected raw water DOC as a baseline. For all the 5 batches, no geosmin or MIB was spiked in the water and no coagulation treatment was performed. DOC and percent DOC reduction results for the five batches are as shown in Table 2.4. Average DOC and average percent DOC reduction values from the five different batch experiments conducted from July to September were calculated. For every batch, individual ranks were assigned for each PAC, based on the calculated percent DOC reduction values. The data (shown in Table 2.4) clearly indicates that Pulsorb WP 260-90 from manufacturer Calgon and Hydrodarco M from the manufacturer Cabot are the PACs ranked one and two, based on average percent DOC reduction values of five batch tests conducted over a span of three months. The Figure 2.13 also shows that PACs Watercarb 800, WPH, Norit PAC 20 BF underperformed in all the five batch tests. The maximum DOC removal of 50.2 % was achieved by PAC Pulsorb WP 260-90 in the first batch test conducted with Boyd Lake water (Fig 2.13).

Table 2.4: PAC ranking based on DOC reduction

Date	7/15/2016			7/19/2016			7/21/2016			8/2/2016			9/15/2016						
PAC	Boyd 1			Boyd 2			Plant Influent (30% LL 70% BL)			Plant Influent (60% LL 40% BL)			Plant Influent (50% LL 50% BL)			Average of 5 Tests			Cost
	DOC (mg/L)	% DOC Reduction	Rank	DOC (mg/L)	% DOC Reduction	Rank	DOC (mg/L)	% DOC Reduction	Rank	DOC (mg/L)	% DOC Reduction	Rank	DOC (mg/L)	% DOC Reduction	Rank	DOC (mg/L)	% DOC Reduction	Rank	$/lb
Control	9.7			9.3			8.8			9.2			8			9			
Hydrodarco B	6.3	35.2	5	8.6	7.8	9	6.1	30.5	2	5.7	37.4	2	5.9	26	3	6.5	27.4	3	0.6
Hydrodarco M	5.5	43.9	4	6.8	26.9	1	7.1	18.7	5	6.8	25.9	4	5.8	27.4	2	6.4	28.6	2	0.65
Hydrodarco S	6.4	34.7	6	7.8	15.9	4	7.5	14.6	9	7.1	22.8	6	6.1	24.2	5	7	22.4	7	0.56
Norit PAC 20BF	8.9	8.7	10	8.6	7.2	10	7.2	18.5	6	7.5	18.5	9	6.6	17.8	9	7.7	14.1	9	0.71
Watercarb 800	8.9	9.1	9	8.3	10.1	8	7.4	15.4	8	7.4	19.4	8	6.3	21.7	8	7.7	15.1	8	0.87
Watercarb 1000	5.2	46.9	3	8	14.3	5	7.4	16.4	7	7.1	22.3	7	6.2	22.5	6	6.8	24.5	5	1.05
Pulsorb WP220-90	5.2	47.1	2	8.2	11.2	6	6.6	25.4	3	6.8	25.4	5	7.1	11.1	10	6.8	24	6	0.96
Pulsorb WP260-90	4.9	50.2	1	6.9	25.6	2	4.9	43.9	1	6.5	29.1	3	5.8	27.4	1	5.8	35.2	1	1.07
WPH	8.7	10.8	8	8.3	10.2	7	7.8	11.3	10	8.1	11.2	10	6.2	22.1	7	7.8	13.1	10	1.03
WPH 1000	6.7	31.5	7	7.7	17.1	3	7	20.4	4	5.4	40.8	1	5.9	26	4	6.5	27.1	4	0.95

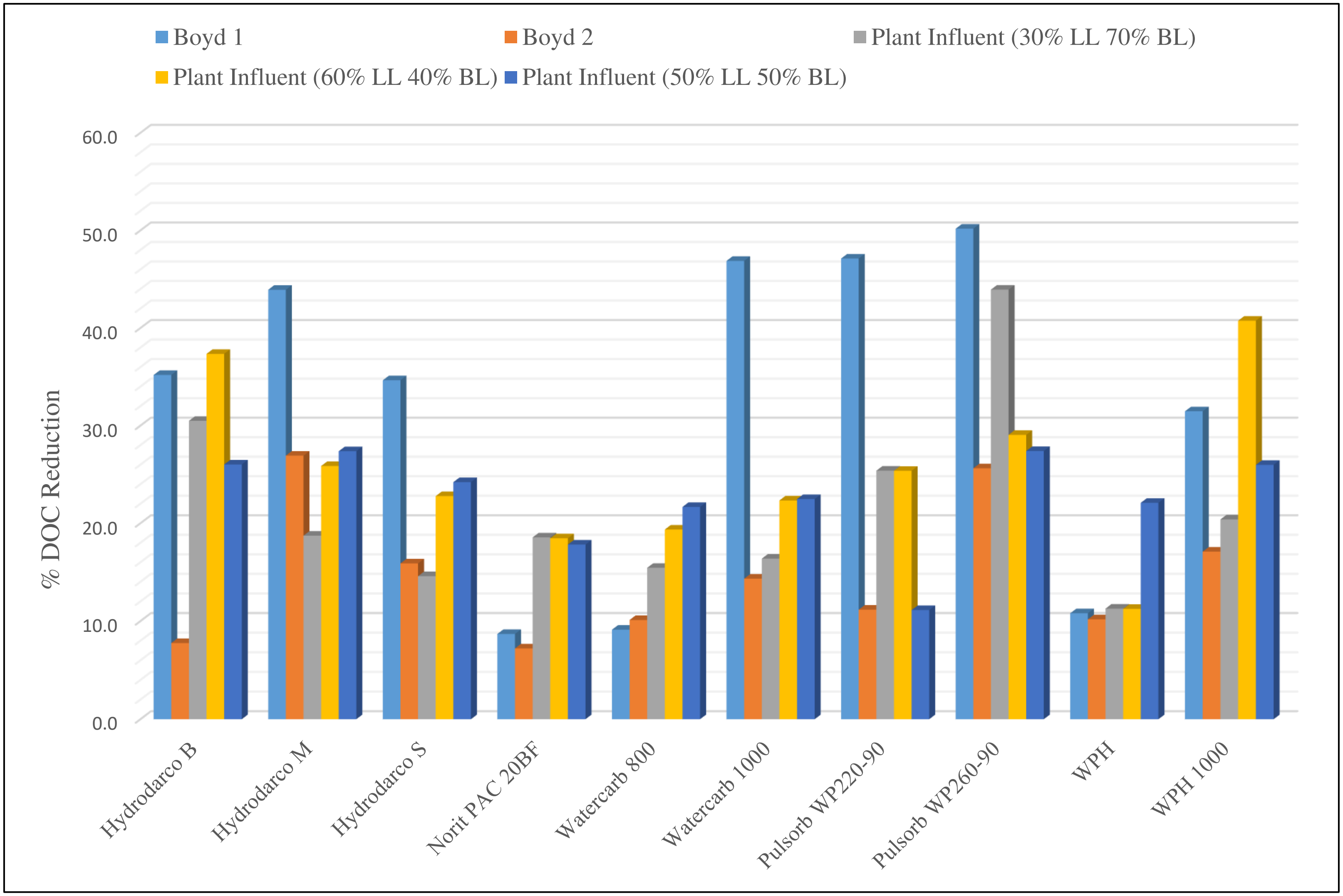

Figure 2.13: Comparison of DOC Reduction for 5 different waters with PAC

The $/mg DOC removed was calculated by dividing the $/lb of each PAC with the difference of average DOC of control and individual PAC. The $/mg DOC removed of each PAC was calculated to determine the PACs that are the most cost-effective of the group. Based on the calculated $/mg DOC removed values of each PAC shown in Figure 2.13, it clearly indicates that Hydrodarco B, Hydrodarco M, Hydrodarco S from the manufacturer Cabot followed by Pulsorb WP 260-90 from manufacturer Calgon are the most cost-effective PACs among the 10 PACs tested.

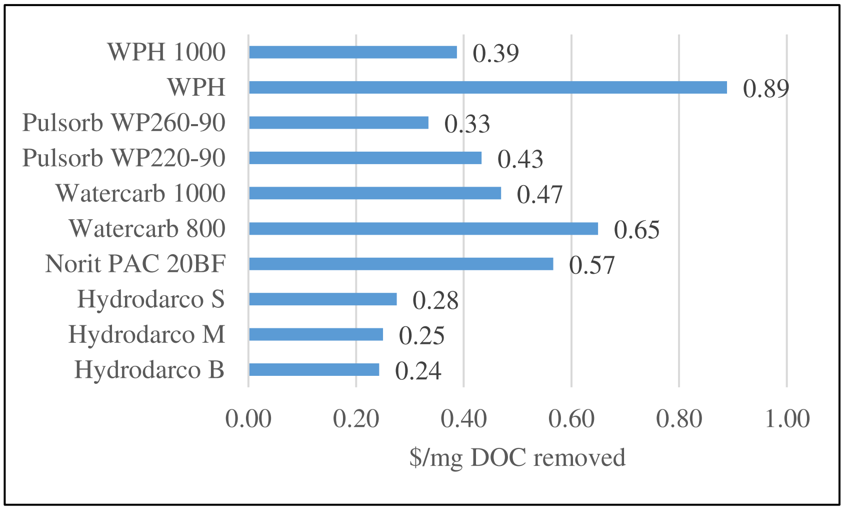

Figure 2.14: PAC-DOC price-based effectiveness

For further studies, a PAC both cost effective and efficient in DOC removal was required. Based on the data shown in Figure 2.15, PAC Hydrodarco M from the manufacturer Cabot was selected as the best PAC that fulfills the dual conditions required for further PAC study. As indicated in the Figure 2.15, even though the PAC Pulsorb WP 260-90 had a higher average percent DOC reduction, the costs of 1.07 $ per lb makes it the most expensive PAC compared to the rest of them tested.

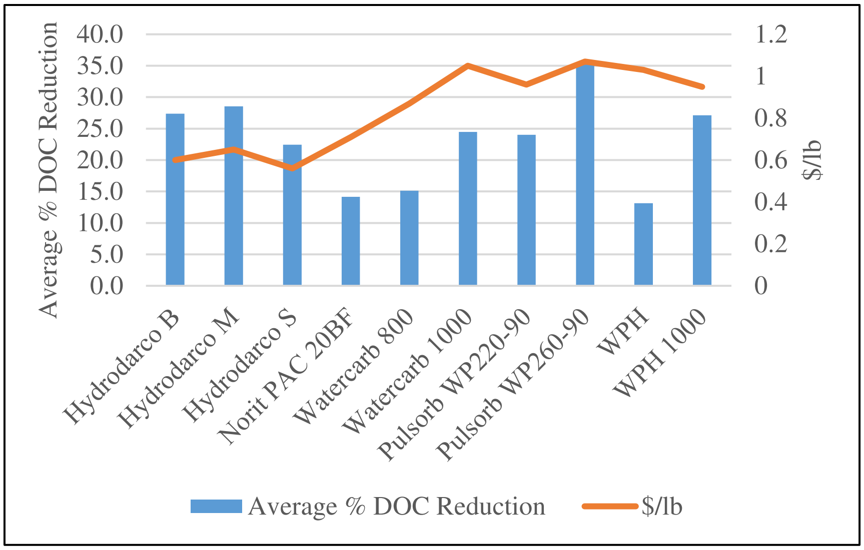

Figure 2.15: PAC Cost-Analysis

2.4.1.3. Kinetic Study

The kinetic study part of PAC testing was conducted with Boyd Lake water with four different PACs and four different contact times namely 15, 30, 45 and 60 minutes. The testing was done with constant dosage 30mg/L throughout the kinetic study. Table 2.5 and 2.6 show the DOC results of the two test runs that were conducted with Boyd Lake water. The raw water DOC was considered as control, due to non-addition of PAC. As per the results shown (Table 2.5 and 2.6), moderate DOC removal occurred at 15 and 30 minutes contact time, when compared to the control DOC. In the first run except for the PAC Hydrodarco M, rest of the three PACs showed significant DOC reduction at contact time of 45 minutes. However, in the second test run except for the PAC Watercarb 800, predominant DOC removal was shown by rest of the three PACs at 45 minutes contact time. A further increase in the contact time to 60 minutes level had minimal effect on the DOC reduction.

Table 2.5: Kinetic Study DOC Results - Set 1 Boyd Lake

Time	Hydrodarco M DOC (mg/L)	Pulsorb WP260-90 DOC (mg/L)	Watercarb 800 DOC (mg/L)	Watercarb 1000 DOC (mg/L)
0	9.2	9.2	9.2	9.2
15	7.9	6.4	8.3	8.4
30	7.8	6.1	8.1	8.1
45	7.6	5.7	7.4	7.1
60	7.1	5.6	7.2	7.0

Table 2.6: Kinetic Study DOC Results - Set 2 Boyd Lake

Time	Hydrodarco M DOC (mg/L)	Pulsorb WP260-90 DOC (mg/L)	Watercarb 800 DOC (mg/L)	Watercarb 1000 DOC (mg/L)
0	10.6	10.6	10.6	10.6
15	9.1	9.2	8.8	8.8
30	8.6	8.2	8.1	8.2
45	6.5	6.3	7.8	7.1
60	6.1	6.0	7.3	7.1

The percent DOC reduction values of the two runs shown in Figure 2.16, illustrate that most of the DOC reduction curves of PACs, start with a steep rise until the 45 minutes contact time and then start to flatten out. The flattening of the curves show that a further increase in the contact time, beyond the point of 45 minutes may not have a significant impact on the DOC reduction by PAC and may increase the operating cost of the water treatment facility. As portrayed in the Figure 2.16, the point of curve flattening starts at 45 minutes contact time, confirming that the optimal contact time threshold was reached at that particular time. Based on two test runs, the study estimated that 45 minutes will be the optimal PAC contact time needed for maximum DOC reduction for a water treatment plant like BLWTP.

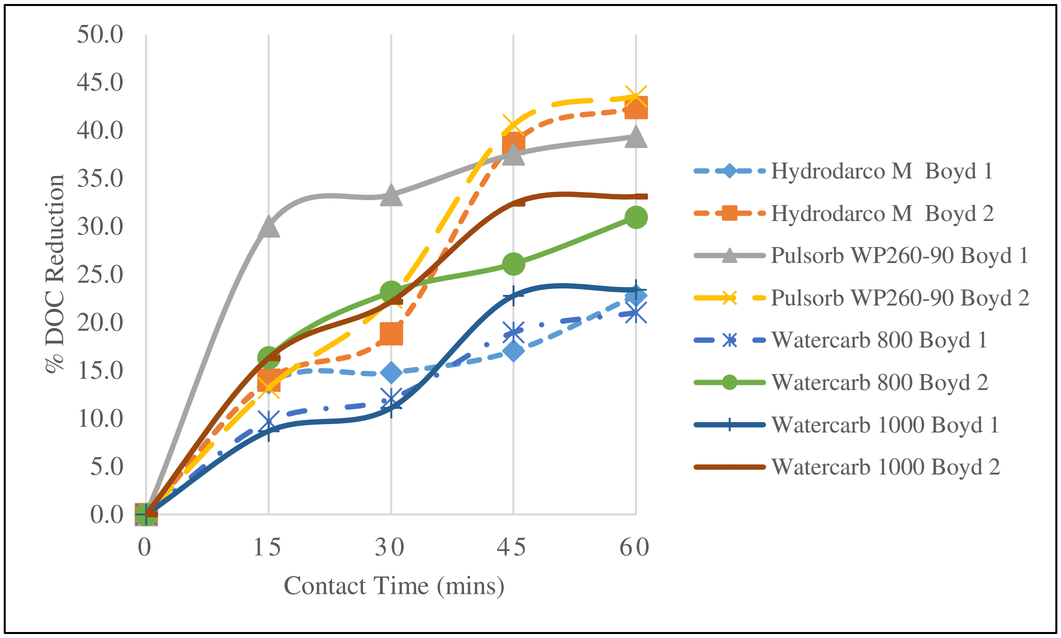

Figure 2.16: Kinetic Study - DOC Reduction Vs PAC Contact time for Boyd Lake water

Geosmin and MIB content of the water treated with the 4 PACs was also tested. The results are shown in Table 2.7, the MIB content in the water treated with all the four PACs was below detection level. As per the data shown in Table 2.7, PACs Pulsorb WP 260-90 and Watercarb 800 reached below detection range at 45 and 60 minutes respectively. However, PACs Hydrodarco M and Watercarb 1000 had below detection level geosmin content at 15 minutes contact time. The results show that optimal contact time ranges from 45 to 60 minutes for the geosmin to reach below detection levels for all the 4 PACs tested.

Table 2.7: Kinetic Study Geosmin Results - Boyd Lake

Time	Hydrodarco M (ng/L)	Pulsorb WP260-90 (ng/L)	Watercarb 800 (ng/L)	Watercarb 1000 (ng/L)
0	15.4	15.4	15.4	15.4
15	0	2.8	2.9	0
30	0	1.2	1.6	0
45	0	0	1.25	0
60	0	0	0	0

2.4.1.4. Dosage Study

As a part of the dosage study, four different PACs were tested at four different PAC dosages (10, 20, 30 and 40 mg/L) with PAC contact time set at a constant 45 minutes. The DOC results shown in Table 2.8 and 2.9, indicate that PACs Hydrodarco M and Pulsorb WP 260-90 had decent DOC removal at 30 mg/L PAC dosage in both the test runs,

Table 2.8: Dosage Study DOC Results – Set 1 Boyd Lake

PAC Dosage (mg/L)	Hydrodarco M DOC (mg/L)	Pulsorb WP260-90 DOC (mg/L)	Watercarb 800 DOC (mg/L)	Watercarb 1000 DOC (mg/L)
0	10.3	10.3	10.3	10.3
10	9.1	9.3	9.9	8.8
20	8.5	8.3	8.7	8.0
30	7.7	5.9	8.4	7.6
40	7.1	5.2	7.1	7.3

Table 2.9: Dosage Study DOC Results – Set 2 Boyd Lake

PAC Dosage (mg/L)	Hydrodarco M DOC (mg/L)	Pulsorb WP260-90 DOC (mg/L)	Watercarb 800 DOC (mg/L)	Watercarb 1000 DOC (mg/L)
0	10.6	10.6	10.6	10.6
10	8.3	9.0	8.7	9.5
20	7.8	8.2	8.5	8.6
30	6.9	6.1	8.2	8.0
40	6.5	5.8	8.1	7.6

whereas PACs Watercarb 800 and Watercarb 1000 showed only minor changes in DOC from dosages 20 to 40 mg/L. Since substantial changes in the DOC happened for the two highest ranked PACs Hydrodarco M and Pulsorb WP 260-90 at 30 mg/L PAC dosage as shown above in Table 2.8 and 2.9., the optimal PAC dosage was estimated to be 30 mg/L.

The percent DOC reduction values of the two dosage study trials are shown in Figure 2.17, the DOC reduction curves steadily rise till the 30 mg/L mark and then start to flatten out from that point onwards indicating that the DOC reduction had reached a threshold level. Any further increase in dosage may not provide a significant reduction in DOC, due to the reduced efficiency from 30 mg/L dosage point.

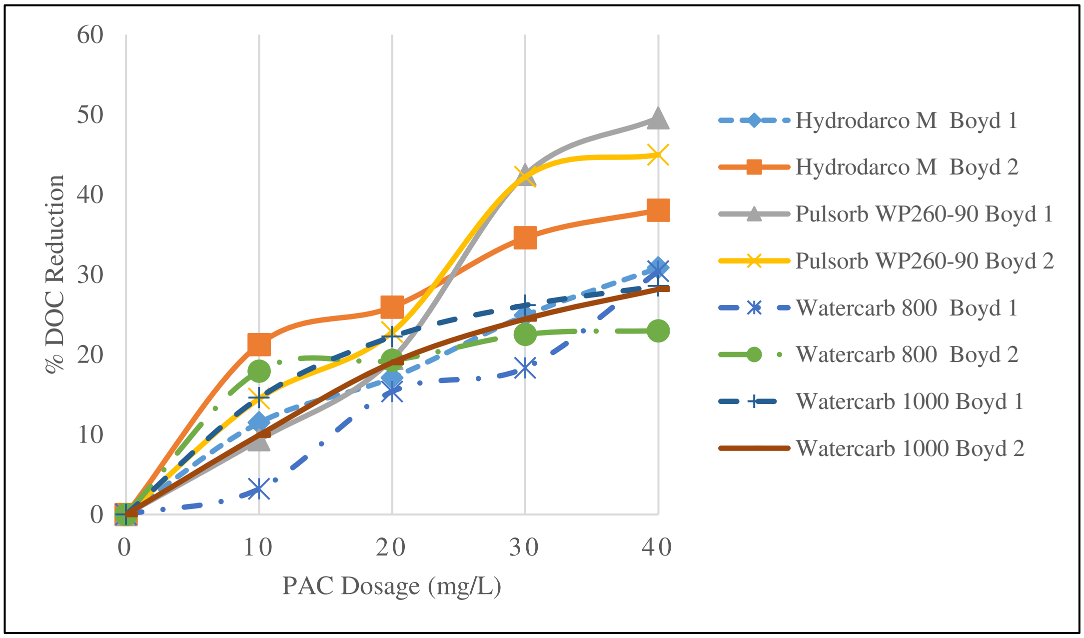

Figure 2.17: Dosage Study - DOC Reduction Vs PAC Dosage for Boyd Lake water

Dosage of PAC being a vital parameter that governs how efficiently odorants and DOC can be removed from water, further trails were needed to confirm the above results. Hence, the dosage study was also conducted on three different types of water to reinforce the previous finding of the optimal PAC dosage. The different types of waters used in this part of the dosage study are plant discharge 1, plant discharge 2 and plant mix (50%LL & 50%BL) collected from various discharge outlets and plant inlets. The results in Table 2.10-2.13 show that, for the plant discharge 1 water test run, the DOC of the raw water was very low and moderate DOC removal happened at the PAC dosage range of 30 to 40 mg/L for all the four PACs. Since the DOC of the raw water was very low and major changes in the DOC were not clearly observed, the dosage study was conducted on the plant discharge 2 water which had a much higher initial raw water DOC.

Table 2.10: Dosage Study DOC Results – Plant Discharge 1

PAC Dosage (mg/L)	Hydrodarco M DOC (mg/L)	Pulsorb WP260-90 DOC (mg/L)	Watercarb 800 DOC (mg/L)	Watercarb 1000 DOC (mg/L)
0	4.5	4.5	4.5	4.5
10	3.6	3.5	3.5	3.9
20	3.3	3.1	3.3	3.0
30	2.9	2.8	3.3	2.8
40	2.5	2.5	3.2	2.3

Table 2.11: Dosage Study DOC Results – Plant Discharge 2

PAC Dosage (mg/L)	Hydrodarco M DOC (mg/L)	Pulsorb WP260-90 DOC (mg/L)	Watercarb 800 DOC (mg/L)	Watercarb 1000 DOC (mg/L)
0	22.5	22.5	22.5	22.5
10	20.6	19.5	20.1	20.2
20	19.1	18.7	19.3	19.0
30	17.3	16.3	18.9	18.7
40	16.2	15.0	17.9	17.4

Table 2.12: Dosage Study DOC Results – Plant Mix

PAC Dosage (mg/L)	Hydrodarco M DOC (mg/L)	Pulsorb WP260-90 DOC (mg/L)	Watercarb 800 DOC (mg/L)	Watercarb 1000 DOC (mg/L)
0	8.0	8.0	8.0	8.0
10	7.7	7.2	7.9	7.7
20	6.7	6.6	7.1	6.7
30	6.0	5.4	6.2	6.1
40	5.5	5.0	5.4	5.4

The plant discharge 2 test run showed a noticeable increase in DOC reduction at PAC dosage of 30 mg/L for PACs Hydrodarco M and Pulsorb WP 260-90. However, PACs Watercarb 800 and Watercarb 1000 performed poorly at the same dosage. Additionally, the dosage study was also conducted on the plant mix water which had an equal proportion of Boyd Lake and Lake Loveland water. The study conducted on the plant mix water showed that PAC dosage of 30 mg/L had greater DOC removal than the dosage 40 mg/L for all the four PACs tested. The above dosage testing demonstrated that the best performing PACs Hydrodarco M and Pulsorb WP 260-90 had maximum DOC removal at PAC dosage of 30 mg/L than a higher PAC dosage. The flattening of the percent DOC reduction curves by majority of the PACs after the 30 mg/L dosage point shown in Figure 2.18 confirms the results of the previous findings that, 30 mg/L was the optimal dosage level.

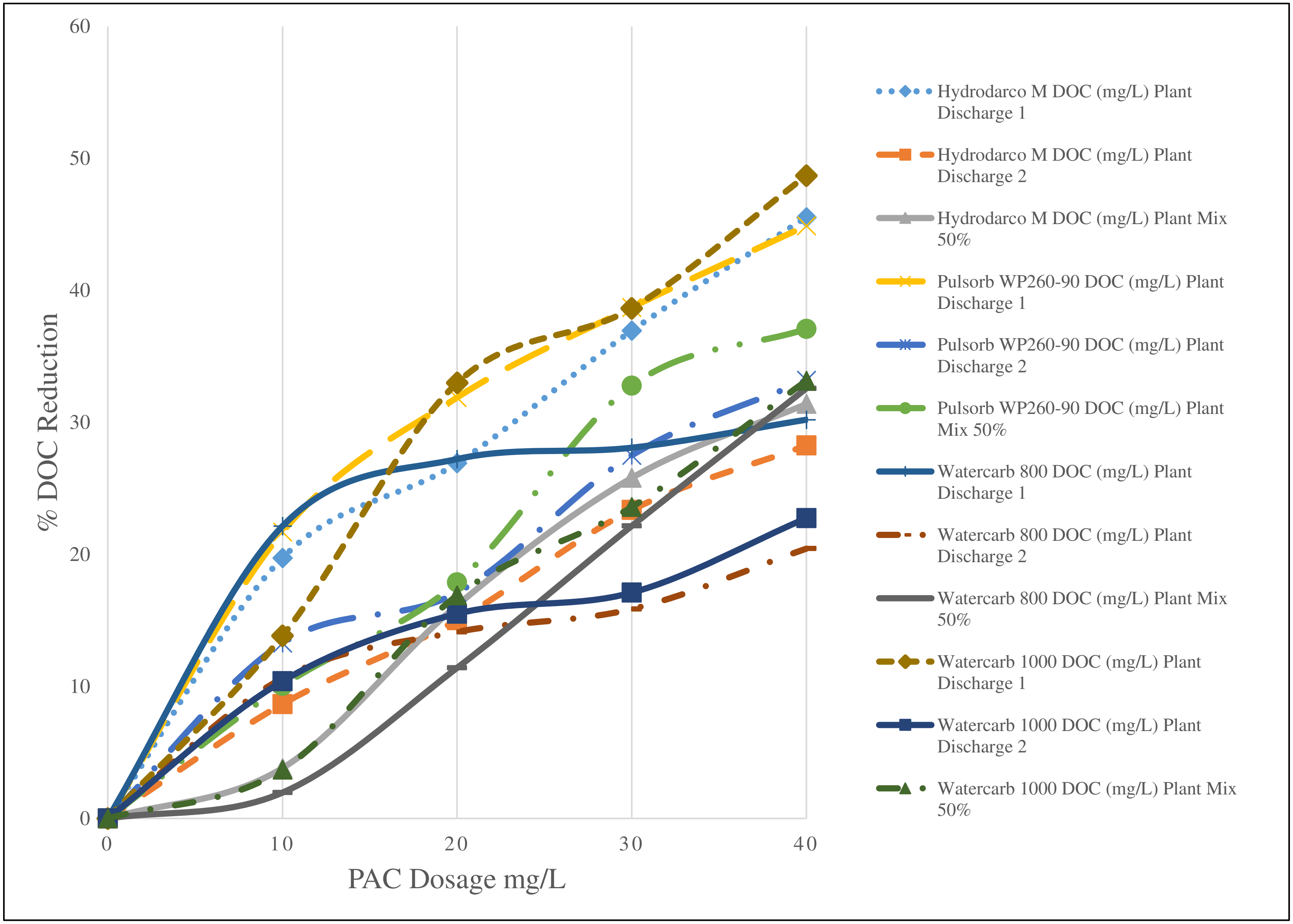

Figure 2.18: Dosage Study – DOC Reduction Vs PAC Dosage for Plant Mix & Discharge Water

As per the PAC-DOC ranking analysis conducted earlier, Hydrodarco M was selected as the most economical PAC for further study. The dosage study was conducted with the single PAC Hydrodarco M to determine the PAC efficiency at different PAC dosages. The testing was performed initially with the water blend (90% Plant Mix, 5% Discharge 1 and 5% Discharge 2). The results in Table 2.13 show two spikes in the PAC efficiency, measured by mg of carbon removed per mg PAC at two different dosages 10 and 30 mg/L. Additionally, a greater percentage of DOC removal also occurred at the same two dosages. As this test run did not yield a unique optimal dosage. Further testing was needed to confirm the PAC efficiency threshold.

Table 2.13: PAC Hydrodarco M - Dosage Study Results with Plant Mix and Discharge water

PAC Dosage (mg/L)	Contact Time (Mins)	DOC (mg/L)	% DOC Reduction	mg C removal / mg PAC
0	0	8.8	0	0
10	45	7.2	18.1	0.1603
20	45	7.1	19.3	0.0855
30	45	5.9	32.8	0.0966
40	45	5.5	37.7	0.0834

Since the initial test results with the PAC Hydrodarco M were unclear, additional two test runs were conducted with plant mix water blend having an equal composition of 50% Boyd Lake and Lake Loveland water. The results shown in Table 2.14 and 2.15, indicate that maximum percent DOC reduction occurred at 20 to 30 mg/L dosage range. Figure 2.19 shows that, for the two test runs PAC efficiency gradually increases as the PAC dosage increases, and then sharply declines after reaching the 30 mg/L dosage point, even after an increase in PAC dosage to 40 mg/L. The change in the trend of PAC efficiency shows that a threshold is attained at 30mg/L dosage point. The decrease in efficiency after 30 mg/L dosage point strongly confirms that, it is the optimal PAC dosage for maximum DOC removal.

Table 2.14: PAC Hydrodarco M - Dosage Study Results with Plant Mix Water, Set 1

PAC Dosage (mg/L)	Contact Time (Mins)	DOC (mg/L)	% DOC Reduction
0	0	8.0	0
10	45	7.9	1.2
20	45	6.5	18.8
30	45	4.9	39.0
40	45	4.4	44.7

Table 2.15: PAC Hydrodarco M - Dosage Study Results with Plant Mix Water, Set 2

PAC Dosage (mg/L)	Contact Time (Mins)	DOC (mg/L)	% DOC Reduction
0	0	8.0	0
10	45	7.7	3.8
20	45	6.7	16.1
30	45	6.0	25.8
40	45	5.5	31.4

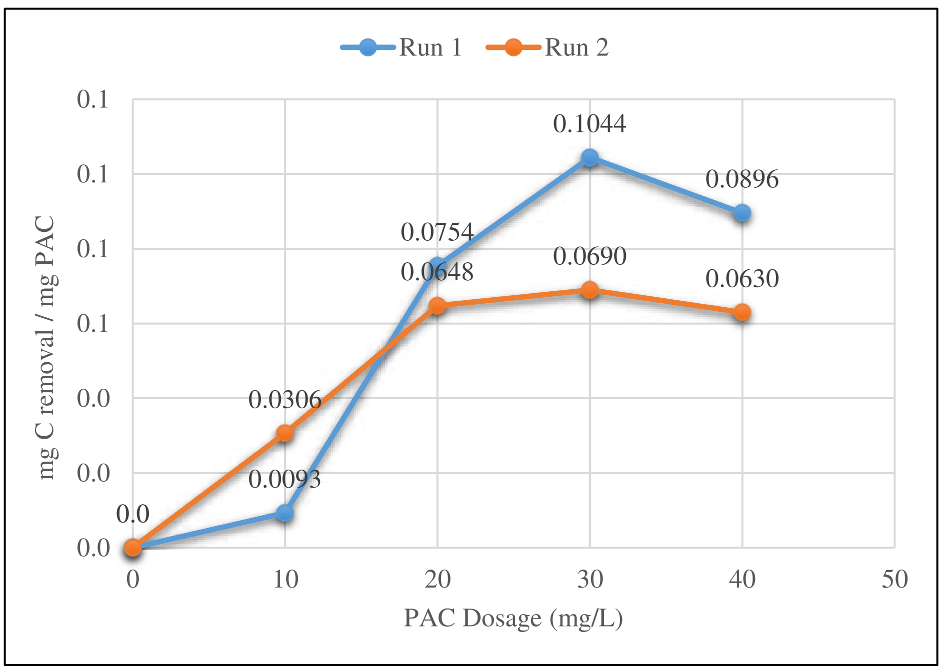

Figure 2.19: PAC Removal Efficiency for Different Dosages

2.4.1.5. Pre-oxidant and Coagulant Study

The final phase of this study was to determine the impact of various pre-oxidants with and without coagulant treatment on DOC reduction. Initially the pre-oxidant testing was performed without any coagulant addition, with plant mix (50% Lake Loveland & 50% Boyd Lake) water at 1mg/L ClO_2, 5 and 10 mg/L $NaMnO_4$ dosages. The preliminary test results in the Table 2.16 show that the pre-oxidant ClO_2 did not have any significant impact on the DOC reduction at 1 mg/L concentration, similarly pre-oxidant $NaMnO_4$ also did not have a substantial impact on the DOC reduction at both 5 and 10 mg/L dosage levels. The pre-oxidants in combination with the PAC Hydrodarco M did not assist in the DOC reduction of the water. The PAC dosage for Hydrodarco M was kept constant at 30 mg/L throughout the study for uniformity and to determine the effectiveness of the pre-oxidant at that particular optimal PAC dosage.

Table 2.16: PAC Hydrodarco M - Pre-Oxidant Study Results with Plant Mix Water

Sample	PAC Dosage (mg/L)	DOC (mg/L)	% DOC Reduction
Raw Water	0	8.0	0.0
Control (PAC Only)	30	5.6	30.1
ClO_2 (1 mg/L)	30	5.2	35.1
$NaMnO_4$ (5 mg/L)	30	5.6	29.8
$NaMnO_4$ (10 mg/L)	30	5.2	35.5

Additionally, two separate runs were conducted with the same plant mix (50%Lake Loveland & 50% Boyd Lake) water in order to reinforce the previous test results. The same dosages of the pre-oxidants ClO_2 and $NaMnO_4$ as used in the preliminary test were used in the current two test runs, with the exception of 10mg/L $NaMnO_4$ dosage. The results shown in Table 2.17 and 2.18, indicate that in both the test runs neither ClO_2 nor $NaMnO_4$ in combination with the PAC Hydrodarco M did not aid in the DOC content reduction of the water to a considerable level. This strongly implies that the pre-oxidants did not play any major role in the DOC reduction of the water when compared to control, which had been treated with only PAC and no pre-oxidants.

Table 2.17: PAC Hydrodarco M - Pre-Oxidant Study Results with Plant Mix Water Set 1

Sample	PAC Dosage (mg/L)	DOC (mg/L)	% DOC Reduction
Raw Water	0	8.0	0.0
Control (PAC Only)	30	4.8	39.8
ClO_2 (1 mg/L)	30	4.6	43.1
$NaMnO_4$ (5 mg/L)	30	4.7	41.0

Table 2.18: PAC Hydrodarco M - Pre-Oxidant Study Results with Plant Mix Water Set 2

Sample	PAC Dosage (mg/L)	DOC (mg/L)	% DOC Reduction
Raw Water	0	8.0	0.0
Control (PAC Only)	30	4.9	39.2
ClO_2 (1 mg/L)	30	5.1	37.0
$NaMnO_4$ (5 mg/L)	30	5.3	33.5

The pre-oxidant study was further extended to determine whether, the inclusion of a coagulant treatment process along with existing PAC and pre-oxidant testing combination, will help in the intensification of the DOC removal from the water. The preliminary coagulant impact testing was done with a lower dosage of 20mg/L of coagulant alum. Pre-oxidants ClO_2 and $NaMnO_4$ as used in previous tests were used in this part of the experimental study too. The PAC dosage and contact time were maintained at 30 mg/L and 45 minutes respectively. This preliminary testing was performed with plant mix (50%Lake Loveland & 50% Boyd Lake) water. The results in Table 2.19 show that the pre-oxidants ClO_2 and $NaMnO_4$ at dosages of 1 and 10 mg/L respectively, in combination with coagulant alum and PAC underperformed, when compared to control, that was treated with just PAC. However, the water treated with PAC followed by 20 mg/L alum showed a significant DOC removal when compared to control. In addition, the turbidity measurements of the water did not show a substantial change when compared to the control, even after filtration with 1.5μm filter. These results evidently indicate that the pre-oxidants and PAC treatment when used in combination with a low dosage of coagulant did not have a substantial impact on the DOC reduction of the water.

Table 2.19: PAC Hydrodarco M - Plant Mix Water with 20 mg/L Alum

Sample	PAC Dosage (mg/L)	Alum Dosage (mg/L)	Raw Turbidity (NTU)	After 1.5μm Turbidity (NTU)	DOC (mg/L)	% DOC Reduction
Raw	0	0	10.22	0.41	8.0	0
Control (PAC Only)	30	0	8.64	0.39	5.8	27.5
PAC and Alum	30	20	6.04	0.28	4.6	42.5
ClO_2 (1 mg/L)	30	20	6.35	0.24	5.9	26.5
$NaMnO_4$ (10 mg/L)	30	20	7.07	0.25	5.7	29.2

Following the initial coagulant impact testing with a lower coagulant dose, two individual test runs were performed with the same plant mix water but with a higher dosage of the coagulant alum. In this part of experimental analysis, the dosage of coagulant alum was set at 70 mg/L. The results of the two test runs shown in Table 2.20 and 2.21, illustrate that when compared to the control, PAC treatment in combination with alum at 70 mg/L dosage showed a substantial increase in the DOC reduction. However, the pre-oxidants ClO_2 and $NaMnO_4$ did not have any considerable effect on the DOC reduction even after the inclusion of PAC and alum in their treatment process. The raw turbidity and turbidity after filtration with 1.5μm filter did not provide much insight on the effectiveness of each type of experiment.

Table 2.20: PAC Hydrodarco M - Plant Mix Water with 70 mg/L Alum, Set 1

Sample	PAC Dosage (mg/L)	Alum Dosage (mg/L)	Raw Turbidity (NTU)	After 1.5µm Turbidity (NTU)	DOC (mg/L)	% DOC Reduction
Raw Water	0	0	10.22	0.41	8.0	0
Control (PAC Only)	30	0	8.11	0.35	5.5	31.3
PAC and Alum	30	70	6.94	0.39	2.5	69
ClO_2 (1 mg/L)	30	70	6.22	0.32	2.7	66.7
$NaMnO_4$ (5 mg/L)	30	70	7.16	0.37	2.6	67.3

Table 2.21: PAC Hydrodarco M - Plant Mix Water with 70 mg/L Alum, Set 2

Sample	PAC Dosage (mg/L)	Alum Dosage (mg/L)	Raw Turbidity (NTU)	After 1.5µm Turbidity (NTU)	DOC (mg/L)	% DOC Reduction
Raw Water	0	0	10.22	0.41	8.0	0
Control (PAC Only)	30	0	8.84	0.4	5.2	35.0
PAC and Alum	30	70	7.24	0.34	2.6	67.2
ClO_2 (1 mg/L)	30	70	6.1	0.3	2.9	63.4
$NaMnO_4$ (5 mg/L)	30	70	7.55	0.31	3.0	62.8

The coagulant testing was also conducted with a different blend of water in order to determine, whether higher alum dosage and PAC combination will perform with the same effectiveness under diverse conditions. Two individual test runs were conducted with plant mix and discharge (90% plant mix, 5% discharge 1 and 5% discharge 2) water blend with alum dosage set at 70 mg/L. The results of the two test runs shown in Table 2.22 and 2.23 are on par with the findings from the previous experiments, proving that pre-oxidants did not have a noteworthy effect on the DOC reduction even if treated in combination with PAC and higher alum dosage. Additionally, the results of these two test runs showed a two-fold increase in DOC reduction for the alum addition at a higher dosage of 70 mg/L after PAC treatment, even without the presence of pre-oxidants.

Table 2.22: PAC Hydrodarco M - Plant Mix & Discharge Water with 70 mg/L Alum, Set 1

Sample	PAC Dosage (mg/L)	Alum Dosage (mg/L)	Raw Turbidity (NTU)	After 1.5μm Turbidity (NTU)	DOC (mg/L)	% DOC Reduction
Raw Water	0	0	13.55	0.62	8.8	0
Control (PAC Only)	30	0	10.62	0.59	6.3	28.4
PAC and Alum	30	70	8.21	0.58	3.1	64.8
ClO_2 (1 mg/L)	30	70	7.54	0.51	2.6	70.4
$NaMnO_4$ (5 mg/L)	30	70	7.96	0.56	3.2	63.7

Table 2.23: PAC Hydrodarco M - Plant Mix & Discharge Water with 70 mg/L Alum, Set 2

Sample	PAC Dosage (mg/L)	Alum Dosage (mg/L)	Raw Turbidity (NTU)	After 1.5μm Turbidity (NTU)	DOC (mg/L)	% DOC Reduction
Raw Water	0	0	13.55	0.62	8.8	0
Control (PAC Only)	30	0	9.81	0.60	6.1	30.7
PAC and Alum	30	70	8.84	0.55	3.5	60.5
ClO_2 (1 mg/L)	30	70	7.91	0.49	2.7	69.5
$NaMnO_4$ (5 mg/L)	30	70	8.19	0.51	3.5	59.9

2.4.2. Discussion

The GC/MS results depict that among the 10 different PACs tested, majority of them had greater than 80 percent removal for both geosmin and MIB. As mentioned in numerous analyses (Srinivasan and Sorial, 2011; Chorus and Bartman, 1999), the results from this study indicate that PAC treatment was a far superior and effective process for the removal T&O compounds and DOC, which might not be possible through conventional treatment techniques used in water treatment plants like coagulation, flocculation, sedimentation and filtration. For large scale usage, the selection of a PAC from a wide variety of PAC brands available in the market, depend on two main conditions, namely the cost and efficiency of the PAC in removing the odorants.

The ranking of PACs from different brands based on the average values of percent DOC reduction obtained from 5 separate batch tests, smoothed out the wide variations arising from the different test results obtained from each batch of testing. Pulsorb WP 260-90, even though being the best ranked PAC as per the percent DOC reduction criteria, was not selected as the PAC for further study due to the cost of the PAC per pound being the highest among set of PACs tested. The PAC Hydrodarco M which was ranked next to Pulsorb WP 260-90 and had the second best $/mg DOC removed was selected as the best cost and performance wise effective PAC based on various conditions like, the percent DOC reduction, $/lb and $/mg DOC removed. The averaging method helped to improve the accuracy and narrow down the effective PAC to one from a group of ten PACs.

Lalezary-Craig et al. (1988) studied the removal effectiveness of geosmin and MIB at 1-hour and 4-hour contact times and determined that there was no significant difference between the removal efficiencies of the two contact times. However, the study also reported that longer contact times had a minor effect on the removal efficiency of geosmin and MIB at lower carbon dosages than at higher dosages. Similarly, Bruce et al. (2002) indicated that 4-hour contact time with PAC dosage of 10 mg/L helped to eliminate 82% geosmin and 42% MIB with maximum removal happening within the first hour of contact time. The kinetic study results from the current analysis are comparable to results of the studies conducted in the past, the data from GC/MS shows that for the highest ranked PAC Pulsorb WP 260-90, a 45 minutes contact time was required to reach below detect levels for geosmin from an initial concentration of 15.4 ng/L. Also, the two main PACs of interest Hydrodarco M and Pulsorb WP 260-90 achieved 10 to 20% higher removal of DOC, in the second kinetic study test run at 45 minutes, when compared to 30 minutes contact time.

Lalezary-Craig et al. (1988) also demonstrated that initial concentrations up to 66 ng/L of each geosmin and MIB can be reduced to low levels of 2 and 7 ng/L respectively with PAC dosages of 10 mg/L. However, Bruce et al. (2002) mentioned that geosmin and MIB can be removed by adsorption on to the PAC, but the adsorption depends on water chemistry of the water being tested. Hence, different types of water need different PAC dosages. Bruce et al. (2002) also mentioned that DOC of the water can play a vital role in the removal efficiency of PACs, as DOC will compete with geosmin and MIB for the sorption sites on the surface of PAC. The test results from this study show that the PAC efficiency starts to plummet after the PAC dosage of 30 mg/L, which shows that removal of the DOC will be less effective even after an increase in PAC dosage beyond the PAC efficiency threshold dosage of 30 mg/L. Since maximum DOC removal is required for effective geosmin and MIB removal as indicated by Bruce et al. (2002), PAC dosage of 30 mg/L was identified as the optimal dosage for these water blends.

The research conducted to investigate the effects of oxidants on T&O compounds by Lalezary et al. (1986), indicate that pre-oxidants are least effective in dissolved organics removal which is in line with the current pre-oxidants study results. Lalezary et al. (1986) experimental results from ClO_2 studies showed that T&O compounds like geosmin and MIB exhibited a 30 percent or less removal rates for a commonly used dosage, however this study used 1 mg/L ClO_2 dosage to reduce the Disinfection By-Products(DBPs) formation due to excessive chlorine usage in the drinking water. This is mainly due to the fact that BLWTP conforms to Safe Drinking Water Act,1974, which restricts the level of DBPS in the drinking water. The ClO_2 dosage was not effective in reduction of DOC in this study as explained by Lalezary et al. (1986). Research findings of Lalezary et al. (1986) and Ho et al. (2009) explained that pre-oxidation with potassium permanganate was ineffective in removal of the off-flavor compounds like geosmin and MIB from water. Paralleling the findings of the Lalezary et al. (1986) and Ho et al. (2009), this study employed sodium permanganate as a pre-oxidant which had a negligible effect on DOC removal from the water at dosages of 5 and 10 mg/L.

In addition, the pre-oxidants were tested with coagulant alum and PAC, the results again indicated that pre-oxidants with or without coagulant had minimal effect on the DOC removal. However, Szlachta and Adamski (2009) performed detailed analysis on effects of the combination of coagulation treatment with PAC and showed that for NOM with medium range molecular weight, had removal efficiencies of 25.9% for coagulant alone and 38.8 % and 57.1% for coagulant-PAC combination at a PAC dosage of 30 and 75 mg/L respectively. They also observed increase in organic compounds removal with an increase in coagulant dosage, which is similar to the results of this study where 20 mg/L alum with PAC had only 42.5% DOC removal compared to 70 mg/L alum dosage which had greater than 60% DOC removal rates in different test runs. The results also show that PAC enhanced coagulation treatment was twice as effective, when compared to PAC treatment alone in DOC removal at a higher coagulant dosage.

2.5. Cost Analysis

The PAC currently in use at the Boyd Lake Water Treatment Plant (BLWTP) is Watercarb 800 from the Manufacturer Standard Purification. The current study revealed that PAC Watercarb 800 was one of the least effective and expensive PACs when to compared to others tested for their effectiveness in the removal of off-flavor compounds and DOC. Additionally, the study helped BLWTP identify PAC Hydrodarco M which serves a dual purpose of being cost and performance wise effective in the removal of organics of interest.

Table 2.24: PAC Hydrodarco M Vs PAC Watercarb 800 Cost Savings

PAC	PAC Manufacturer	Cost ($/lb)	Cost ($/1000 lb)	Cost Savings ($/1000 lb)
Hydrodarco M	Cabot	0.65	650	220
Watercarb 800	Standard Purification	0.87	870	N/A

The estimated cost savings from using 1000 lbs. of PAC Hydrodarco M instead of Watercarb 800 is $220 (shown in Table 2.24). In the long run, Boyd Lake Water Treatment Plant (BLWTP) will be able to save a significant amount of time, money and reduce carbon wastage by switching over to PAC Hydrodarco M which works efficiently at the optimal dosage and contact time when compared to PAC Watercarb 800 currently in use at the plant.

2.6. Conclusion

Off-flavor compounds like geosmin and MIB cannot be removed by conventional water treatment methods, water treatments plants need specialized treatment techniques to mitigate consumer complaints related to water quality issues. The study conducted for BLWTP determined that PAC treatment was economical and effective in addressing the seasonal taste and odor issue with the lake water, which arises mainly during the warmer temperature periods of the year. The ranking based on averaging the results from various tests determined that Hydrodarco M from the Manufacturer Cabot and Pulsorb WP 260-90 from the Manufacturer Calgon as the two best performing PACs for Taste and Odor compound (geosmin, MIB) and DOC removal when compared to the other PACs tested. However, when the cost was taken into account, of the two best ranked PACs Hydrodarco M was more economical. Kinetic and dosage studies helped to optimize PAC usage to reduce wastage and increase efficiency. The kinetic study showed up to 20% increase in DOC removal rates at a contact time of 45 minutes and a further increase in contact to 60 minutes had minimal effect on the removal of DOC by PAC.

Additionally, GC/MS results indicated that, a 45 minute contact time was needed by highest ranked PAC Pulsorb WP 260-90 to go below detection level for geosmin. Moreover, the flattening of the percent DOC reduction curves after 30 mg/L dosage point, confirmed that the DOC removal efficiency reached a saturation level at 30 mg/L PAC dosage. In the dosage study, the drop in PAC efficiency (mg C removal/ mg PAC) after 30 mg/L PAC dosage indicated that the threshold for maximum efficiency was reached at 30 mg/L dosage and dosing above this level will not have a significant impact on the DOC removal rates of the water due to reduced PAC efficiency. However, it should be noted that DOC removal rates depend on the water chemistry of the source water, which varies for each type of water. The results from different test runs showed that the pre-oxidants (ClO_2 and $NaMnO_4$) were not effective in the removal of DOC when used with PAC alone or PAC and alum combination. This shows that commonly used pre-oxidation chemicals were not effective in the removal of dissolved organics. Further, the testing illustrated that a higher dosage of coagulant alum at 70 mg/L had substantial effect on the DOC removal when compared to a lower dosage of 20 mg/L. The results of the coagulant testing showed that the addition of coagulant alum at a dosage of 70 mg/L after the PAC treatment had caused two-fold increase in the DOC reduction even without the presence of pre-oxidants. This shows that PAC enhanced-coagulation can help improve the water quality to a great extent with minimal processing. However, it is unclear that to what extent the point of PAC application will play a crucial role in the DOC removal efficiency. More studies are needed to evaluate the effect of PAC addition points and spilt PAC dosages, when used in combination with alum, so that the treatment process can be further fine-tuned to improve effectiveness. WTPs must conduct periodic comparative analysis on the type of PAC currently in use at the plant with new and upgraded brands of PACs available in the market, in order to identify new types PACs that reduce cost and increase odorant removal efficiency of the drinking water treatment process. There is lot of potential in this field of study for optimization, which can help save lot of chemical fee and ultimately bring down the operating costs of the WTPs. Future studies can focus on determining effective alternative treatments methods like biofiltration or use of integrated technologies to reduce DOC, eliminate the troublesome odorants and improve the taste and quality of water. Biological degradation of odorants is another promising area where future research can be performed.

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APPENDIX A: RESULTS FROM ALUM BASED SCREENING TEST

Table B.1: Boyd Lake 6/10/2016

Alum Dosage	Raw	30 mg/L	40 mg/L	50 mg/L	60 mg/L	70 mg/L
Turbidity (NTU)	2.8	1.0	0.9	1.2	1.1	1.1
TOC (mg/L)	7.9	6.8	6.2	5.0	3.6	5.6
% TOC Removal	0.0	13.2	21.2	37.0	54.1	28.2
pH	8.03	7.05	6.98	6.95	6.86	6.73
DOC (mg/L)	6.0					
Alkalinity (mg/L)	120					

Table B.2: Boyd Lake 6/13/2016

Alum Dosage	Raw	30 mg/L	40 mg/L	50 mg/L	60 mg/L	70 mg/L
Turbidity (NTU)	2.8	3.7	1.3	0.9	1.3	1.4
TOC (mg/L)	7.9	9.5	8.2	8.6	8.3	4.7
% TOC Removal	0.0	-21.1	-4.7	-9.7	-5.1	39.8
pH	8.03	6.85	6.87	6.91	6.84	6.76
DOC (mg/L)	6.0					
Alkalinity (mg/L)	120					

Table B.3: Lake Loveland 6/10/2016

Alum Dosage	Raw	30 mg/L	40 mg/L	50 mg/L	60 mg/L	70 mg/L
Turbidity (NTU)	8.8	10.3	3.8	5.2	5.4	9.5
TOC (mg/L)	7.9	6.1	3.8	3.9	3.8	4.0
% TOC Removal	0.0	22.6	51.7	51.0	51.7	48.9
pH	7.57	6.69	6.56	6.45	6.23	5.65
DOC (mg/L)	6.9					
Alkalinity (mg/L)	45					

Table B.4: Lake Loveland 6/13/2016

Alum Dosage	Raw	30 mg/L	40 mg/L	50 mg/L	60 mg/L	70 mg/L
Turbidity (NTU)	8.8	8.3	5.3	5.1	5.4	10.6
TOC (mg/L)	7.9	6.5	5.4	5.2	4.2	4.8
% TOC Removal	0.0	18.3	32.0	34.9	47.5	39.7
pH	7.57	6.92	6.73	6.39	6.07	5.92
DOC (mg/L)	6.9					
Alkalinity (mg/L)	45					

Table B.5: Plant Mix 6/10/2016

Alum Dosage	Raw	30 mg/L	40 mg/L	50 mg/L	60 mg/L	70 mg/L
Turbidity (NTU)	3.1	4.4	3.4	2.1	1.5	1.3
TOC (mg/L)	7.5	8.1	7.6	6.4	6.0	5.6
% TOC Removal	0.0	-8.5	-1.8	14.6	19.7	24.8
pH	8.22	7.13	7.07	6.99	6.93	6.79
DOC (mg/L)	6.9					
Alkalinity (mg/L)	90					

Table B.6: Plant Mix 6/13/2016

Alum Dosage	Raw	30 mg/L	40 mg/L	50 mg/L	60 mg/L	70 mg/L
Turbidity (NTU)	3.1	3.9	2.1	1.8	1.5	1.0
TOC (mg/L)	7.5	9.6	8.1	8.5	7.2	5.6
% TOC Removal	0.0	-28.2	-7.9	-14.0	3.9	24.7
pH	8.22	6.8	6.86	6.87	6.74	6.7
DOC (mg/L)	6.9					
Alkalinity (mg/L)	90					

APPENDIX B: RESULTS FROM PAC TESTING

Table C.1: Boyd Lake water tested on 7/15/2016

Experiment #	PAC Name	PAC Dosage (mg/L)	MIB Dosage (ng/L)	Geosmin Dosage (ng/L)	Contact Time (min)	DOC (mg/L)
0	Control	0	0	0	0	9.7
1	Hydrodarco B	30	0	0	45	6.3
2	Hydrodarco M	30	0	0	45	5.5
3	Hydrodarco S	30	0	0	45	6.4
4	Norit PAC 20BF	30	0	0	45	8.9
5	Watercarb 800	30	0	0	45	8.9
6	Watercarb 1000	30	0	0	45	5.2
7	Pulsorb WP220-90	30	0	0	45	5.2
8	Pulsorb WP260-90	30	0	0	45	4.9
9	WPH	30	0	0	45	8.7
10	WPH 1000	30	0	0	45	6.7

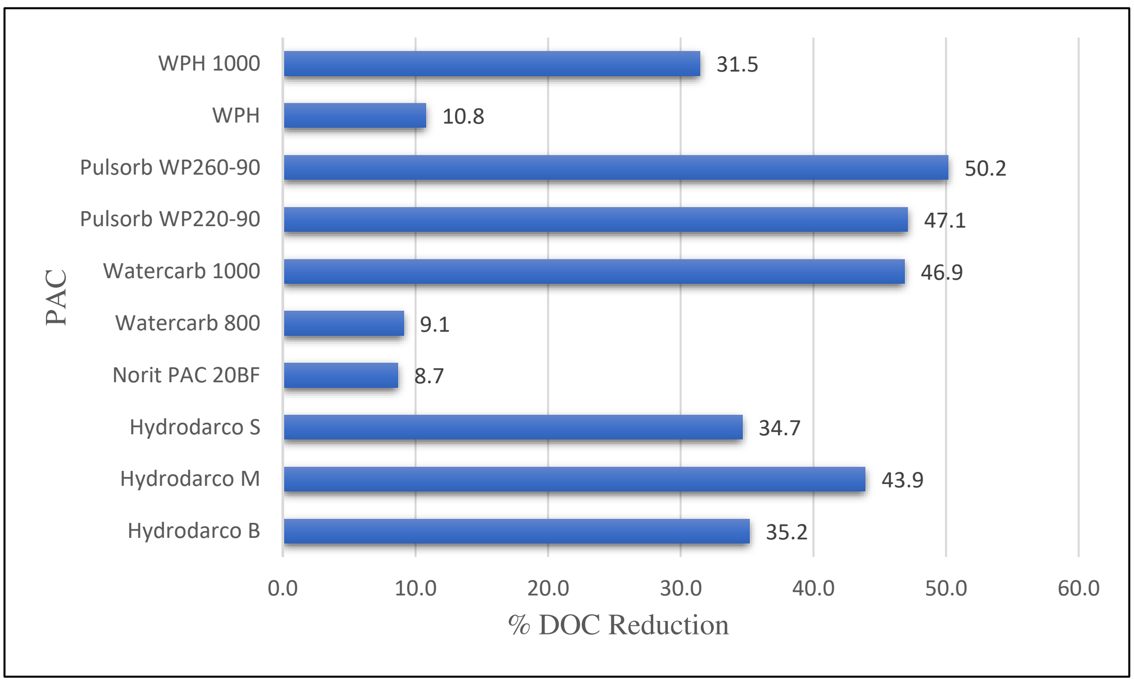

Figure C.1: Boyd Lake DOC reduction by PAC

Table C.2: Boyd Lake water tested on 7/19/2016

Experiment #	PAC Name	PAC Dosage (mg/L)	MIB Dosage (ng/L)	Geosmin Dosage (ng/L)	Contact Time (min)	DOC (mg/L)
0	Control	0	0	0	0	9.3
1	Hydrodarco B	30	0	0	45	8.6
2	Hydrodarco M	30	0	0	45	6.8
3	Hydrodarco S	30	0	0	45	7.8
4	Norit PAC 20BF	30	0	0	45	8.6
5	Watercarb 800	30	0	0	45	8.3
6	Watercarb 1000	30	0	0	45	8.0
7	Pulsorb WP220-90	30	0	0	45	8.2
8	Pulsorb WP260-90	30	0	0	45	6.9
9	WPH	30	0	0	45	8.3
10	WPH 1000	30	0	0	45	7.7

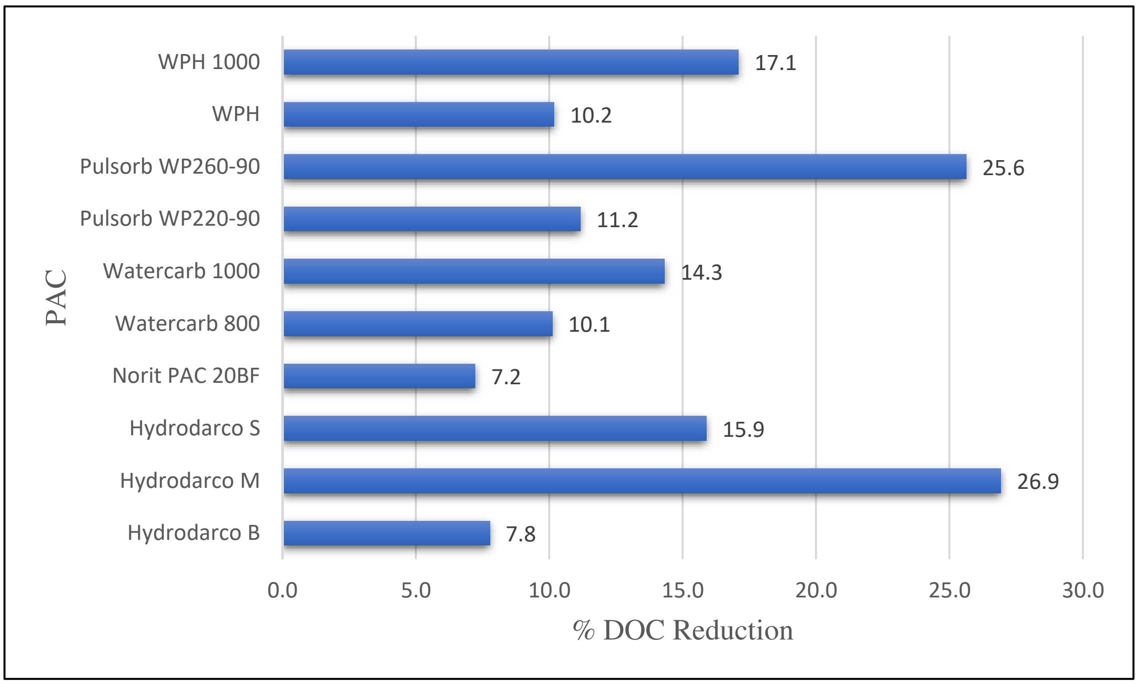

Figure C.2: Boyd Lake water DOC reduction by PAC

Table C.3: Plant mix (70% Boyd Lake and 30% Lake Loveland) water tested on 7/21/2016

Experiment #	PAC Name	PAC Dosage (mg/L)	MIB Dosage (ng/L)	Geosmin Dosage (ng/L)	Contact Time (min)	DOC (mg/L)
0	Control	0	0	0	0	8.8
1	Hydrodarco B	30	0	0	45	6.1
2	Hydrodarco M	30	0	0	45	7.1
3	Hydrodarco S	30	0	0	45	7.5
4	Norit PAC 20BF	30	0	0	45	7.2
5	Watercarb 800	30	0	0	45	7.4
6	Watercarb 1000	30	0	0	45	7.4
7	Pulsorb WP220-90	30	0	0	45	6.6
8	Pulsorb WP260-90	30	0	0	45	4.9
9	WPH	30	0	0	45	7.8
10	WPH 1000	30	0	0	45	7.0

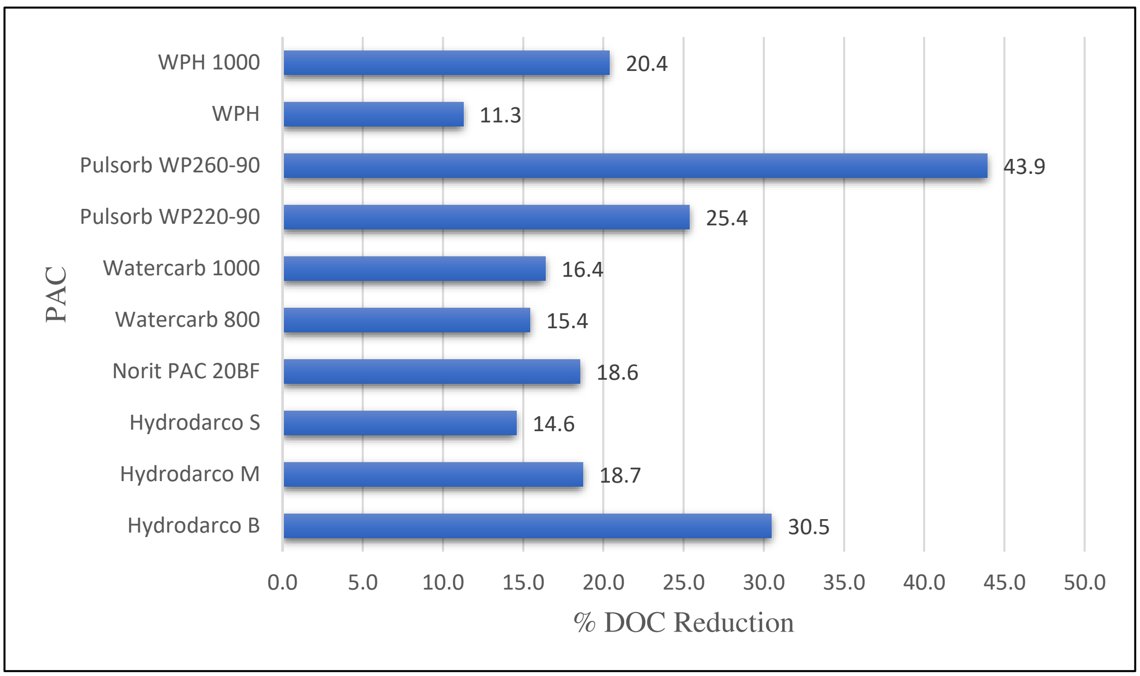

Figure C.3: Plant mix water DOC reduction by PAC

Table C.4: Plant mix (50% Lake Loveland and 50% Boyd Lake) water tested on 9/15/2016

Experiment #	PAC Name	PAC Dosage (mg/L)	MIB Dosage (ng/L)	Geosmin Dosage (ng/L)	Contact Time (min)	DOC (mg/L)
0	Control	0	0	0	0	9.2
1	Hydrodarco B	30	0	0	45	5.7
2	Hydrodarco M	30	0	0	45	6.8
3	Hydrodarco S	30	0	0	45	7.1
4	Norit PAC 20BF	30	0	0	45	7.5
5	Watercarb 800	30	0	0	45	7.4
6	Watercarb 1000	30	0	0	45	7.1
7	Pulsorb WP220-90	30	0	0	45	6.8
8	Pulsorb WP260-90	30	0	0	45	6.5
9	WPH	30	0	0	45	8.1
10	WPH 1000	30	0	0	45	5.4

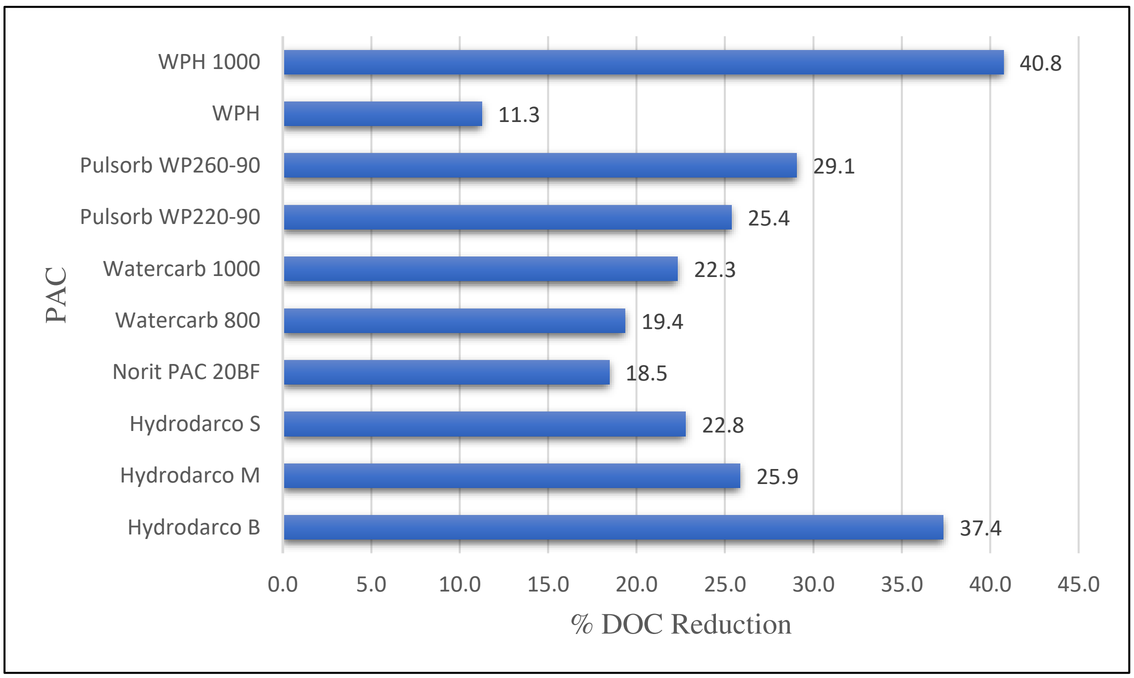

Figure C.4: Plant mix water DOC reduction by PAC

Table C.5: Plant mix (50% Lake Loveland and 50% Boyd Lake) water tested on 9/15/2016

Experiment #	PAC Name	PAC Dosage (mg/L)	MIB Dosage (ng/L)	Geosmin Dosage (ng/L)	Contact Time (min)	DOC (mg/L)
0	Control	0	0	0	0	8.0
1	Hydrodarco B	30	0	0	45	5.9
2	Hydrodarco M	30	0	0	45	5.8
3	Hydrodarco S	30	0	0	45	6.1
4	Norit PAC 20BF	30	0	0	45	6.6
5	Watercarb 800	30	0	0	45	6.3
6	Watercarb 1000	30	0	0	45	6.2
7	Pulsorb WP220-90	30	0	0	45	7.1
8	Pulsorb WP260-90	30	0	0	45	5.8
9	WPH	30	0	0	45	6.2
10	WPH 1000	30	0	0	45	5.9

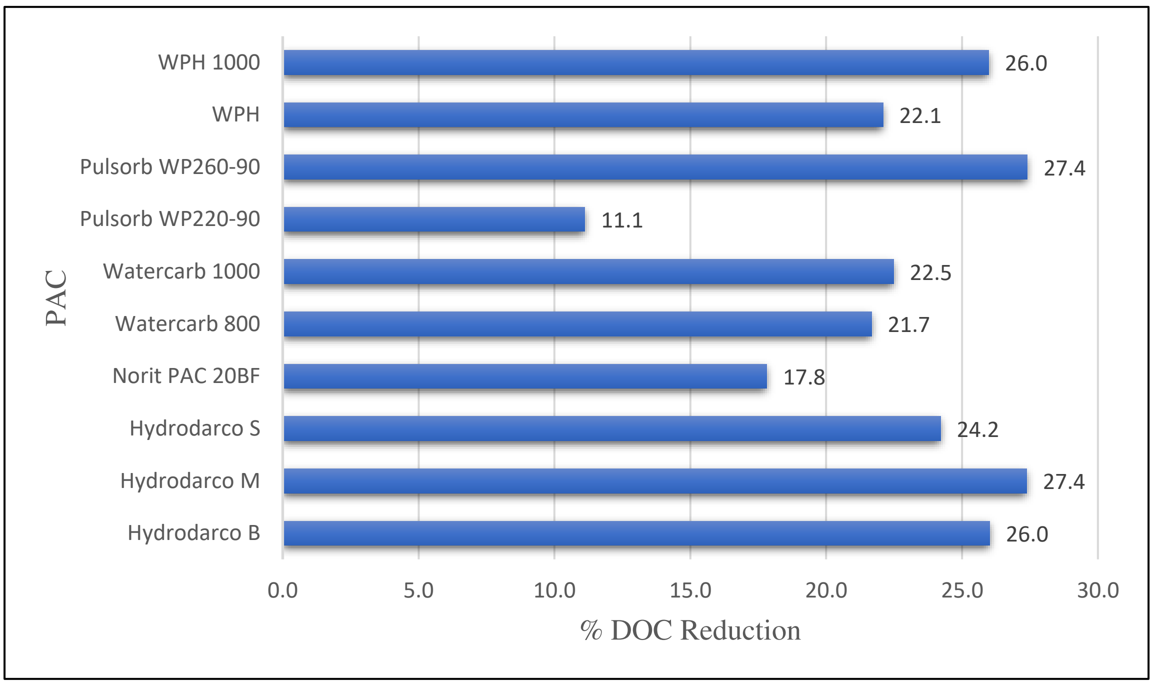

Figure C.5: Plant mix water DOC reduction by PAC

APPENDIX C: RESULTS FROM KINETIC AND DOSAGE STUDY

Table D.1: Boyd Lake Kinetic Study % DOC reduction

Time (mins)	Hydrodarco M		Pulsorb WP260-90		Watercarb 800		Watercarb 1000	
	Boyd 1	Boyd 2	Boyd 1	Boyd 2	Boyd 1	Boyd 2	Boyd 1	Boyd 2
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
15	13.7	14.0	30.0	13.2	9.7	16.3	8.7	16.3
30	14.8	18.8	33.3	22.6	12.1	23.2	11.1	22.1
45	17.0	38.7	37.5	40.6	19.0	26.1	22.8	32.4
60	22.8	42.4	39.4	43.6	21.0	30.9	23.4	33.1

Table D.2: Boyd Lake Dosage Study % DOC reduction

Dosage (mg/L)	Hydrodarco M		Pulsorb WP260-90		Watercarb 800		Watercarb 1000	
	Boyd 1	Boyd 2	Boyd 1	Boyd 2	Boyd 1	Boyd 2	Boyd 1	Boyd 2
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	11.5	21.2	9.3	14.5	3.2	17.9	14.6	9.9
20	17.1	25.9	19.5	22.8	15.4	19.3	22.2	19.0
30	24.9	34.6	42.5	42.2	18.3	22.5	26.2	24.4
40	30.8	38.1	49.6	45.0	30.4	23.0	28.6	28.2

Table D.3: Plant Mix and Discharge Dosage Study % DOC reduction

Dosage (mg/L)	Hydrodarco M			Pulsorb WP260-90			Watercarb 800			Watercarb 1000		
	Plant Discharge 1	Plant Discharge 2	Plant Mix 50%	Plant Discharge 1	Plant Discharge 2	Plant Mix 50%	Plant Discharge 1	Plant Discharge 2	Plant Mix 50%	Plant Discharge 1	Plant Discharge 2	Plant Mix 50%
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	19.7	8.7	3.8	21.7	13.3	10.0	22.1	10.6	2.0	13.8	10.4	3.7
20	26.9	15.0	16.1	31.9	17.1	17.9	27.2	14.1	11.4	33.0	15.5	16.9
30	36.9	23.4	25.8	38.7	27.5	32.8	28.1	15.9	22.2	38.6	17.1	23.6
40	45.5	28.3	31.4	44.9	33.2	37.1	30.2	20.4	32.6	48.7	22.7	33.2