ACTIVATION AND USE OF POWDERED ACTIVATED CARBON FOR REMOVING 2-METHYLISOBORNEOL IN WATER UTILITIES

By

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This document is dedicated to my family

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By

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Earthy-musty taste and odor episodes caused by 2-methylisoborneol (MIB) and geosmin are concerns for water utilities around the world. These compounds pose no health risks, but consumers of public water supplies question the safety of water with foreign odors and therefore prefer not to drink water with these compounds present. The objective of this work was to improve PAC performance and increase understanding of the phenomena surrounding PAC adsorption of MIB. First, an activation protocol was tailored to produce a PAC with superior performance for tastes and odors in water-treatment plant conditions. Using a paper mill waste product as the carbonaceous precursor, the activation parameters of temperature, time, and steam-to-carbon ratio were investigated in order to create the optimum PAC. All tailored PACs were evaluated for MIB using a bench-scale performance-based testing procedure that mimicked actual conditions found at water utilities. Activation temperature proved to be the dominant parameter, with an optimum operating value of 1173 K. Analysis of the MIB

performance data and the physical and chemical characteristics of the PAC indicated that increasing the carbon's mesoporosity was most important in improving MIB adsorption by the PACs in batch tests. Using this experience, a more detailed study commenced into what PAC parameters most influence MIB adsorption in the presence of varying concentrations of NOM. Two sets of laboratory-produced PACs with specific physical and chemical characteristics were used in batch tests with varying adsorption conditions. The physical characteristics of the PAC (specifically mesoporosity) strongly affected the adsorption of MIB in all conditions. However, surface chemistry had less of an impact as the amount of NOM present in the water increased. Indeed, results from the batch tests performed at the highest total organic carbon concentration indicated that the surface chemistry of the carbon had no effect on MIB adsorption. Lastly, the impact of coagulation (alum) on PAC adsorption of MIB was studied. The effect alum had on PAC performance was contingent on pH, contact time, and the source water. Results indicated that alum was most deleterious to MIB removal when the coagulation pH was approximately 5.

CHAPTER 1
INTRODUCTION

Tastes and Odors

The compounds 2-methylisoborneol (MIB) and geosmin, by-products of certain actinomycetes and cyanobacteria, impart earthy, musty tastes and odors in surface waters throughout the world. Since utilities' customers will not trust unpalatable water, removing these tastes and odors is an important, but difficult task for water treatment plant operators. Although these compounds do not affect human health at any level, they are easily detected at extremely low concentrations, better known as the odor threshold concentration (~ 10 ng/L). Therefore, removing these compounds and providing aesthetically pleasing water is a top priority for water providers.

Geosmin was first identified as a by-product from actinomycetes in 1965 (Gerber and Lechavalier 1965). Three years later, Medsker et al. (1968) found geosmin and another odor-causing compound (MIB) in strains of other actinomycetes and certain cyanobacteria (blue-green algae). Since then 3 decades of research followed, studying these taste- and odor-causing compounds and the microorganisms that produce them. Research will continue though, as there are a number of water bodies around the world, including the United States of America, that are eutrophic and therefore likely to have the microorganisms present that produce MIB and geosmin (EPA 1994). In addition, many water utilities still struggle to effectively remove these odorants and provide palatable drinking water to consumers (Simpson and MacLeod 1993, Suffett 1996, Nerenburg et al. 2000).

Activated carbon, in both powdered (PAC) and granular (GAC) form, has been extensively used for decades to remove pollutants such as synthetic organic chemicals (SOCs), volatile organic compounds (VOCs), and taste-and odor-causing compounds (Snoeyink 1990). Indeed, the longest established use of activated carbon in water treatment is for taste and odor control (Rodriguez-Reinoso 1997). Since taste and odor episodes are often seasonal and unpredictable, PAC is used more often than GAC, as PAC can be added in varying amounts depending on water conditions and the degree of the odor episode. PAC remains a popular option for removing taste and odors by water utilities, as it is more effective than other treatment processes such as chlorination, aeration, biodegradation, and filtration (Lalezary and coworkers 1984, 1986a, Vik et al. 1988, Kim et al. 1997). Despite PAC's popularity and effectiveness in removing MIB, taste and odors continue to be a problem for water utilities (Suffett 1996). MIB is more difficult to remove via adsorption than other common taste and odor causing compounds (Herzing et al. 1977, Kim et al. 1997), and therefore water treatment plant operators often must spend millions on PAC in order to purvey aesthetically pleasing water (MacLeod 2000). Therefore, research continues in order to better understand MIB adsorption so as to improve the effectiveness of removal via activated carbon.

Tailoring Activated Carbon

In a rudimentary form, activated carbon adsorption began several centuries ago, as Egyptians used burnt wood to filter water (Dabrowski 2001). The modern activated carbon industry began roughly 100 years ago, when the Russian Ostrejko (1901) patented techniques for producing activated carbon using elevated temperatures in the presence of a flowing gaseous oxidant. Today, activated carbon is a multi billion-dollar industry with manufacturers and researchers on every inhabited continent. Activated carbon is

produced from numerous carbonaceous precursors, including bituminous coal, lignite coal, peat, coconut shells, and wood. Many different techniques exist for producing or activating these precursors as well. These techniques are typically grouped into two main categories: physical or chemical activation (Wigmans 1989). The combination of the carbonaceous precursor and the activating technique employed determines the physical and chemical characteristics of the finished activated carbon. Industries that utilize activated carbon are likewise extremely diverse; it is not just used in water and wastewater treatment. Manufacturing and energy companies use carbon to remove pollutants from air emissions. Textile plants and the food and beverage industry use activated carbons to remove excess dyes, and to lower organic content in their effluents, respectively.

Despite the myriad of different techniques for producing activated carbons and the multitude of uses for the adsorbent, carbons are often sold and applied as a one-use-fits-all treatment. In the water treatment industry, activated carbon manufacturers often sell the same PACs to utilities around the world. Individual water utilities, however, have unique operating conditions, contaminant problems, and source waters. For example, some treatment plants may use activated carbon to remove color, while others are attempting to abate taste and odor episodes. Other utilities may have several hours of contact time while some have only a few minutes. One carbon cannot possibly handle all of these situations adequately. Therefore, production of specific carbons with characteristics designed for individual water utilities could greatly aid carbon performance.

Tailoring activated carbons began in research attempting to solve calcium catalysis in reactivation of GAC. When Mazyck and Cannon (2000) created reactivation protocols that overcame calcium catalysis, they also created carbons with specific qualities. They found that if the optimum reactivation protocol was applied, the reactivated GACs had properties similar to, or better than, the virgin counterpart (Mazyck and Cannon 2000, 2002). Further work (into tailoring GACs) indicated that the performance for tastes and odors or NOM could in fact be enhanced by the correct activation or reactivation technique (Moore et al. 2001, MacKenzie et al. 2004, Nowack et al. 2004). These researchers proved that the potential exists for production of activated carbons with specific properties to perform specific tasks. The goal in my work was to tailor activation protocols to create a virgin PAC with superior performance for MIB. Application of these techniques in full-scale could revolutionize activated carbon production, and greatly improve water utilities ability to purvey clean and palatable water.

MIB Adsorption onto Activated Carbon

PAC is a common treatment option for water utilities battling earthy-musty taste and odors caused by MIB, but many plant operators still struggle in selecting the proper activated carbon. This is because the exact properties of activated carbon that control adsorption of MIB are not well understood, as is how changes in the operating conditions at different utilities affect adsorption. Therefore many utilities choose their PAC simply on price and/or iodine number (surrogate for surface area), but this likely results in the selection of the wrong PAC.

Early research indicated that activated carbons were able to sorb MIB because of their high internal surface area, thus the reliance on iodine number in the water treatment industry (Herzing et al 1977, Lalazary et al. 1986a). These early tests however, were

performed at equilibrium and how the results translated to the shorter contact times experienced in full-scale water treatment was not known. Later research did test PAC adsorption of MIB at shorter contact times and found that surface area and microporosity did not correlate well to MIB removal (MacLeod and Simpson 1993, Gillogly et al. 1998a). However, micropores were still thought to be important in the adsorption of MIB onto PAC in more recent publications (Newcombe and Drikas 1997, Pendleton et al. 1997). Other results from batch and column tests performed in natural water indicated that mesoporosity was as (or more) important in removing MIB than microporosity (MacLeod and Simpson 1993, Nowack et al. 2001). Clearly, MIB adsorption is controversial. Exactly where MIB sorbs in PACs' pore structure is not well understood today, and the number of different adsorption conditions that exist around the world further complicates the phenomena.

In addition to carbon's physical attributes, some have investigated the importance of its chemical properties on MIB adsorption. Pendleton and coworkers (1997, 2001) found that the surface chemistry of PACs strongly impacted MIB removal in batch tests. Higher concentrations of acidic functional groups on the surface of the carbon were deleterious to MIB adsorption. The authors concluded that the functional groups encouraged water adsorption, and that water could displace MIB already sorbed in carbon pores. Despite strong correlations, these studies were all performed at equilibrium and in the absence of NOM. Therefore, it is unknown how surface chemistry affects PAC performance in actual water treatment plant conditions.

Adsorption of Odorants at Water Utilities

The task of effectively removing MIB and geosmin at water utilities is a daunting one, as PAC is typically added at the head of treatment plants. Here the competition from

natural organic matter (NOM) is greatest and other treatment chemicals (e.g., chlorine, alum) are commonly introduced; both of which can be deleterious to adsorption (Herzing et al. 1977, Najm et al. 1990, Newcombe et al. 1997, Gillogly et al. 1998b, MacLeod 2000). Selecting a PAC that performs in these extreme conditions is of utmost importance to water utilities as yearly PAC expenditures for large plants can be exorbitant. The presence of background organics or NOM in the water impacts adsorption of MIB onto PAC immensely (Herzing et al. 1977, Najm et al. 1990, Newcombe et al.: 1997, 2002a, 2002b, 2002c). NOM commonly exists in raw waters at concentrations in the parts per millions (mg/L), several magnitudes higher than MIB, which causes odor episodes at parts per trillion (ng/L). NOM is deleterious to MIB removal because it too adsorbs onto PAC, and can outcompete MIB for pore sites (Newcombe et al.: 1997, 2002a, 2002c). It is difficult to predict the exact effect that NOM will have on MIB performance as NOM is a wide range of molecules with a variety of diameters and chemistries. Moreover, particular size fractions of NOM impact MIB removal differently (Newcombe et al. 1997). Therefore, it is not just the amount of organics in the water that determine the PAC's ability, but the size fractionation and chemistry of the molecules as well.

Treatment chemicals commonly introduced near PAC at water utilities include coagulants (e.g., alum) and oxidants (e.g., chlorine). Unfortunately, these chemicals have been shown to adversely affect PAC's ability to remove MIB (Lalezary et al. 1986b, Lalezary-Craig et al. 1988, Gillogly et al. 1988b, MacLeod 2000, Cummings et al. 2000). A study into the interactions of chlorine and activated carbon indicated that chlorine oxidizes the carbon surface (McGuire and Suffet 1984). Later work testing

PAC's ability to remove MIB in the presence of chlorine showed a deleterious impact in a variety of contact times (Lalezary et al. 1986b, Lalezary-Craig et al. 1988, Gillogly et al. 1998b). Coagulants, specifically alum, also deter MIB adsorption onto PAC (MacLeod 2000, Cummings et al. 2000). PAC and alum are often added together in rapid mix basins, and removal is thought to be much lower when the coagulant is present.

Despite all of the obstacles PAC faces in removing MIB, it is still the best technology available to water utilities. Other processes (e.g., conventional treatment, aeration, oxidation, and biodegradation) are ineffective in lowering MIB levels to below the odor threshold concentration (Lalezary et al. 1984, Lalezary et al. 1986a, Vik et al. 1988, Kim et al. 1997). Therefore, research into the adsorption of MIB onto PAC in treatment plants should continue in order to maximize removal. A better understanding of how activated carbon adsorbs MIB as well as the impacts other chemicals and treatment processes can help utilities purvey aesthetically pleasing water to consumers in the most effective manner possible.

Hypotheses and Objectives

Hypotheses

- PAC's mesopore volume is most important in adsorption of MIB in actual water utility conditions due to short contact times and competition from NOM. Increased mesopore volume improves the kinetics of adsorption and permits for better internal diffusion of MIB in the presence of NOM.

- Temperature is the dominant parameter in a tailored activation protocol. Increases in temperature during activation increases the rate of burn-off, thus widening micropores into small mesopores.

- In water utility conditions, the adsorption of MIB onto PAC is heavily impacted on the physical characteristics of PAC, and less influenced by the carbon's surface chemistry.

- The deleterious effects of alum on PAC performance for MIB is due to the coagulant coating the carbon surface, thereby not allowing MIB diffusion into the carbon pores.

Objectives

- Perform and utilize a thorough literature review on tastes and odors, carbon activation, and adsorption principles to effectively progress the research in this area

- Build a laboratory-scale activation facility utilizing a fluidized bed and clam-shell furnace and develop a procedure to produce tailored activated carbons

- Create a protocol and produce a tailored PAC from bark char with superior performance for MIB removal

- Develop a bench-scale performance-based testing protocol that simulates full-scale water treatment conditions to assess MIB performance of tailored and commercial PACs

- Create two sets of PACs with specific physical and chemical characteristics to elucidate how these parameters impact MIB adsorption

- Investigate the affects of alum addition on PAC performance by adjusting experimental conditions such as contact time, solution pH, and alum dose

CHAPTER 2
LITERATURE REVIEW

MIB and Geosmin

Gerber and Lechavalier (1965) first identified geosmin as a metabolite from actinomycetes. They isolated six strains of *Streptomyces sp.* and grew them in a culture of soybean. Geosmin, produced in μg/L quantities in laboratory cultures, was identified using gas chromotrography. Field identification was still not possible at this time because of the extremely low concentrations present in nature (ng/L). Medsker et al. (1968) a few years later discovered geosmin and an unnamed compound (later MIB) were also produced by cyanobacteria (blue-green algae). Medsker et al. used laboratory produced strains of *Strepnuscorum sp*. and *Oscillatoria sp*. Following Medsker and colleague's work, Tabachek and Yurkowski (1976) identified MIB as a metabolite of both cyanobacteria and actinomycetes.

Researchers continued to investigate the cyanobacteria and actinomycetes responsible for taste and odor episodes throughout the world in the early 1980s. Izaguirre et al. (1982, 1983) found four species responsible for MIB and geosmin in three southern California reservoirs. They used Grob closed-loop stripping followed by gas chromatography and mass spectrometry. Izaguirre et al. (1983) went further to state that one species (*O. curviceps*), was the principal cause of the 2 previous years' MIB problems. The *O. curviceps* was cultivated in the laboratory both with and without actinomycetes that coexist with the cyanobacteria in the environment, to ensure that the cyanobacterium was the MIB producer. During the same period, Yagi et al. (1983)

isolated two cyanobacteria from Lake Biwa in Japan. Lake Biwa, a large reservoir used for drinking water supply, commonly experienced severe taste and odor episodes. Improvements in analytical equipment allowed Yagi et al. to measure MIB and geosmin at concentrations below the odor threshold. They used purge and trap methods to concentrate the samples before using gas chromatography to identify the pollutants. Similar research continued around the world. In Saskatchewan, Canada, Slater and Blok (1983) found three species of geosmin producing microorganisms in Buffalo Pound Lake. Liquid-liquid extractions isolated the geosmin for analysis. Slater and Blok used the findings from the two previous decades and the improved analytical capabilities to further science by identifying specific cyanobacteria and actinomycetes responsible for the taste and odor episodes. Research after Slater and Blok focused on identifying additional taste- and odor-compound producing organisms, and the factors that influence their proliferation in water supplies.

Identification of MIB and Geosmin-Producing Organisms

The first step in the research of taste and odor producing microorganisms is to identify responsible species. Actinomycetes were first discovered to produce geosmin in 1965 (Gerber and Lechevalier). Other odor-producing actinomycetes are shown in Table 2-1.

Table 2-1: Summary of actinomycetes identified as odor-compound producers.

Actinomycetes			
Dinobryon			
	D. cylindricum		Rashash et al. 1995
Streptomyces			Sugiura et al. 1994*
	S. griseus		Gerber and Lechevalier 1965
Synura			
	S. petersenii		Rashash et al. 1995

* Only genus identified

Following the lead of Gerber and Lechevalier, Medsker et al (1968) discovered geosmin and another unnamed compound (later MIB) produced from cyanobacteria. Like actinomycetes researchers throughout the world have discovered many species of cyanobacteria that produce MIB and geosmin (Table 2-2).

Table 2-2. Cyanobacteria identified as odor-producing microorganisms.

Cyanobacteria			
Anabaena			Slater et al. 1983, van der Ploeg et al. 1992, Saadoun et al 2001*
	A. scheremetievi		Izaguirre et al. 1982
	A. macro		Yagi et al. 1983
	A. circinalis		Rosen et al. 1992, Bowmer et al. 1992
	A. laxa		Rashash et al.1995
Aphanizomenon			Slater et al. 1983, Durrer et al. 1999*
Lyngbya			
	L. allorgei		Sugiura et al. 1998
Nostocaceae			Hu et al. 1996*
Oscillatoria			Slater et al. 1983, Durrer et al. 1999*
	O. tenuis		Medsker et al. 1968, Izaguirre et al. 1982, Hoson et al. 1992
	O. curviceps		Izaguirre et al. 1983
	O. simplicissima		Izaguirre et al. 1983
	O. brevis		Naes et al. 1985, Utkilen and Froshaug 1992
	O. chalybea		van der Ploeg et al. 1992**,van der Ploeg et al. 1995
	O. amphibia		van Breemen et al. 1992
	O. limosa		van Breemen et al. 1992
	O. splendida		van Breemen et al. 1992, Suguira et al. 1998, Hu et al. 2000
	O. bornetii		Utkilen and Froshaug 1992
	O. f. granulata		Tsuchiya and Matasumoto 1999
	O. limnetica		Oikawa and Ishibashi 1999
Phormidium			Izaguirre 1992, Zimmerman et al. 1995*
	P. tenue		Yagi 1998, Sugiura et al. 1998, Sugiura et al. 2000
	P. calcicola		Rashash et al. 1995
	P. uncinatum		Sugiura et al. 1998
Phormidium			Durrer et al. 1999*
Pseudananbaena			Izaguirre and Taylor 1998*
Symploca			
	S. muscorum		Medsker et al. 1968

* Only genus identified

**Identified in sample, but did not produce odors in laboratory

Environmental Effects on MIB and Geosmin Production

Effect of light intensity

Bitton (1999) defined cyanobacteria (formally known as blue-green algae) as prokaryotes that carry out oxygenic photosynthesis. In other words, these species need light for photosynthesis in order to survive and multiply. It is known that increasing light intensity will encourage cyanobacterial blooms, which is why areas such as the southern United States are particularly susceptible to taste and odor episodes. Several researchers have attempted to find a correlation between light intensity and the production of the metabolites MIB and geosmin. Utkilen and Froshaug (1992) studied *O. brevis* and *O. bornetii* and their geosmin production at various light intensities. They found an increase in intercellular geosmin throughout their light intensity range (Figure 2-1).

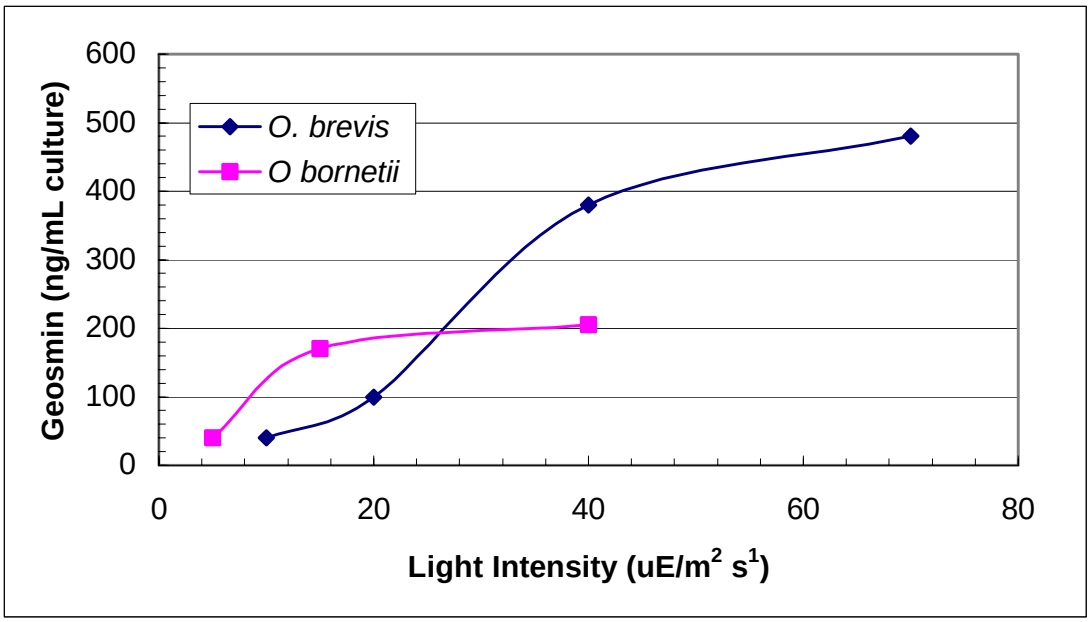

Figure 2-1. The effect of light intensity on geosmin content in two cultures. (Utkilen and Froshaug 1992)

Figure 2-1 shows that as light intensity increased, the concentration of geosmin present in the cultures likewise increased. This phenomenom also correlated with an

increase in chlorophyll a production, which could be an indicator as to the origin of geosmin.

Bowmer et al. (1992) found the same correlations in cultures of *A. circinalis* , as did Hu et al. (1999) for *O. splendida*. Saadoun et al. (2001) found slightly different results for a species of *Anabaena*. In Saadoun and colleagues' work, light intensity increased geosmin production, but favored less chlorophyll a. In a study published by van der Ploeg et al. (1995), an MIB-producing cyanobacteria (*O. cf. chalybea*) was cultured in various light cycles. They found that MIB production was highest in the culture grown under continuous light. In more recent work, Tsuchiya and Matsumoto (1999) cultured *O. f. granulata* at three different light intensities (500, 1000, and 2000 lux) for two durations (20 and 40 days). They found that the cultures under 1000 lux had the highest MIB, geosmin and chlorophyll a production. These samples also had the highest cell count, which shows that optimal growth conditions correlate to the highest MIB and geosmin production. In summation, light intensity is an important environmental factor in the production of MIB and geosmin by cyanobacteria.

Effect of temperature

The influence of temperature on the growth of cyanobacteria and odorant production has been studied. Hoson (1992) studied the *O. tenuis* population in Lake Biwa in Japan and in laboratory cultures. An algal bloom created a taste and odor episode in Lake Biwa in the summer of 1986. Lake temperatures ranged from approximately 10 to 30ºC, but the *O. tenuis* population reached a maximum when the water temperature was between 25 and 30°C, and the pH increase was due to another non-odor-producing algal

bloom. Temperature and pH were not variables in the laboratory cultures, and therefore no further conclusions were made.

Hu et al. (2000) and Saadoun et al. (2001) both varied temperature in their cultures of *O. splendida* and *Anabaena sp*., respectively. Hu et al. (2000) found that cell growth rate, chlorophyll a, and cell-associated geosmin all increased with increasing temperatures (12 to 26°C). They did state, however, that on a pre-chlorophyll basis more geosmin was released (media-associated geosmin) at the lower temperatures. In the experiments performed by Saadoun et al. (2001), the cultures produced the most geosmin at 20°C (Figure 2-2). Interestingly, as temperatures increased past 20ºC the amount of algal blooms rebounded, but the production and release of geosmin continued to decrease.

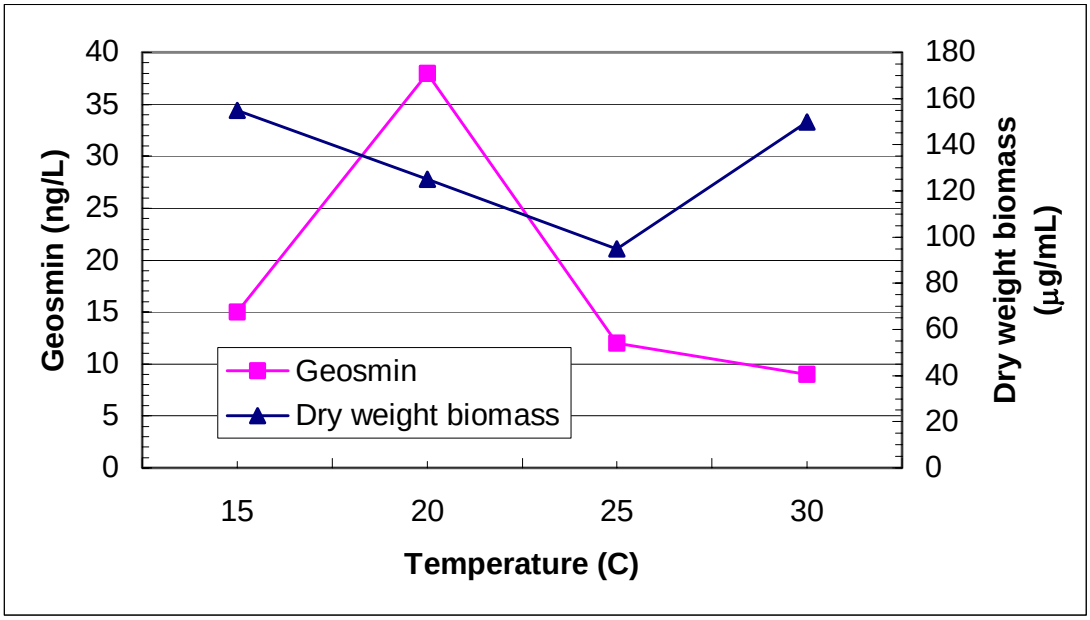

Figure 2-2. Geosmin and cell biomass at various temperatures (Saadoun et al. 2001).

Effect of algal bloom water depth

The depth of the algal bloom in the water body also impacts the production of taste- and odor-causing compounds. The concentrations of MIB and geosmin typically are

greatest at the water surface. In a study of a eutrophic river, van Breemen et al. (1992) found that storage of the water in a deep reservoir helped reduce the concentration of MIB and geosmin. They believed the reduction was due to the lower amount of water surface area, thus less area for algal blooms to produce the odorants. Utkilen and Froshaug (1992) surmised that the production of MIB and geosmin does not differ greatly at various depths, but that the depth affects the likelihood that the microorganism will release the compound. They propose that the greatest amount of MIB and geosmin is released upon cell death. Surface blooms are more often exposed to harm and die off more quickly than do deeper blooms. Thus, the water at the surface has a higher concentration of MIB and geosmin (due to an increase in cell death and odorant release). A later study by Durrer et al. (1999) supports this hypothesis. In a mesotrophic lake, they found that the percentage of geosmin in the media (water) was consistently higher near the surface, even though geosmin was found as deep as 100 meters.

Effect of other species present

In eutrophic and mesotrophic waters, multitudes of species exists along with the microorganisms that produce MIB and geosmin. This has led some researchers to investigate the effects of some other species on the taste and odor producers. For example, Sugiura et al. (1994) isolated the actinomycete *Streptomyces spp.* from the hypertrophic Lake Kasumigaura. Cultures were then grown in the laboratory both with and without non taste- and odor-producing cyanobacteria also found in the lake. They found that the *Streptomyces spp*. grown with the cyanobacteria had a higher overall growth rate and produced more MIB. The actinomycete used the two cyanobacteria as a carbon source thus explaining the increase in MIB. Durrer et al. (1999) found that grazers

also had a major impact on geosmin released in a mesotrophic lake. They identified and cultured three cyanobacteria that produce geosmin from this lake.

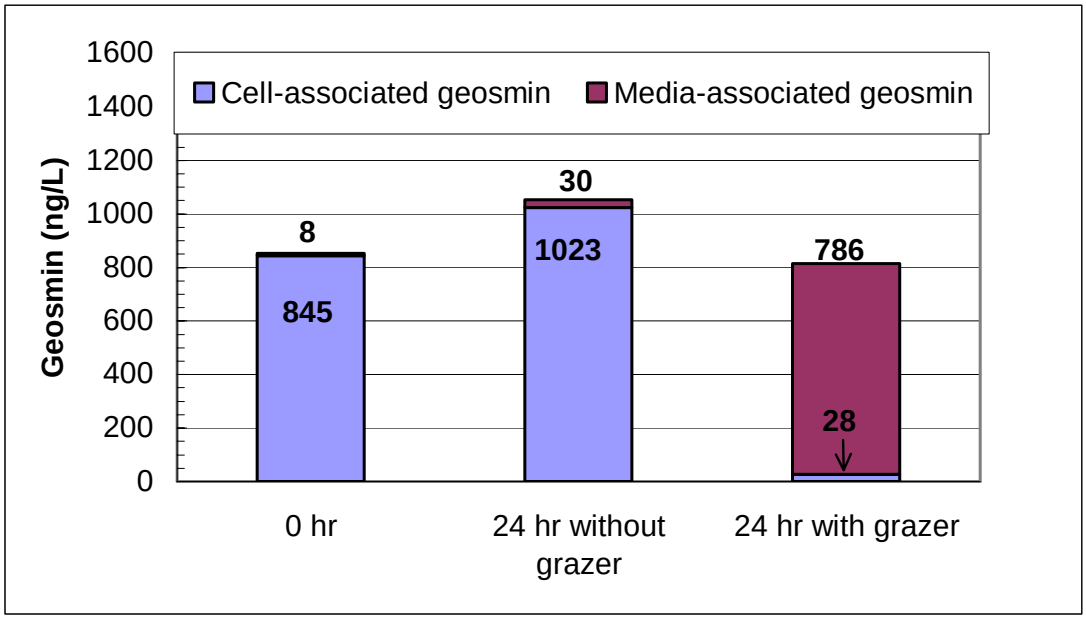

Figure 2-3. A 24-h culture of *A. gracile* grown with and without a grazer (Durrer et al. 1999).

One species, *A. gracile*, was then cultured for 24 h both with and without *Simocephalas*, a known grazer of cyanobacteria. The first column in Figure 2-3 shows the amount of geosmin present in the cell and in the media (water) when the culture began. A vast majority of the geosmin was present in the cells when then study began. The second column shows geosmin levels after 24 h in the culture. The overall amount of geosmin increased, but the ratio of geosmin present in the cell versus in the media remained the same. In this case, the odor episode due to the geosmin would be very low, since most of the odorant is present within the microorganism. The third column shows the effect on geosmin concentrations by adding a grazer to the culture. Adding the grazer lowered the overall geosmin in the culture, but dramatically increased the media-associated portion. In the environment, these grazers would reduce the odor-producing cyanobacteria

present, but hasten any intense taste and odor episode by releasing the geosmin from the cells.

Effect of nutrients and toxins

Cyanobacteria require nutrients such as nitrogen (N), phosphorus (P), and iron (Fe) to survive. These organisms thrive in mesotrophic and eutrophic water bodies (partly because of an increase in these nutrients, often from agricultural runoff and industrial effluents). Hoson (1992) isolated *O. tenuis* from Lake Biwa and created several cultures by differing the nutrient loads. Their initial tests showed that changes in the levels of N and P in filtered lake water did not discourage growth of the cyanobacteria. Thus N and P were not limiting factors of growth in Lake Biwa. The cultures were then subjected to varying concentrations of the chelating agent EDTA. The lowest concentration of EDTA added caused the highest growth rate, but increasing amounts decreased this growth. Hoson believed that the EDTA chelated the soluble iron in the lake water. The higher concentrations of EDTA therefore caused over-chelation, and starved the cyanobacteria of iron necessary for survival. These results led Hoson to the belief that soluble iron was the limiting factor for growth of *O. tenuis* in Lake Biwa. Thus increasing iron in Lake Biwa would cause an increase in these algal blooms and therefore an increase in MIB.

In a later study, Hu et al. (2000) examined *O. splendida* isolated from a Phoenix, AZ water source. They found that dissolved nitrogen was the limiting factor in this water as growth and geosmin production increased after nitrate was added to cultures. Saadoun et al. (2001) showed a different result with *Anabaena sp*. They separated N into ammonium-N and nitrate-N. Both forms were found to increase the overall growth, but nitrate-N increased chlorophyll a production more than ammonium-N. Ammonium-N

however, was found to increase geosmin production while nitrate-N lowered geosmin at higher values (Figure 2-4).

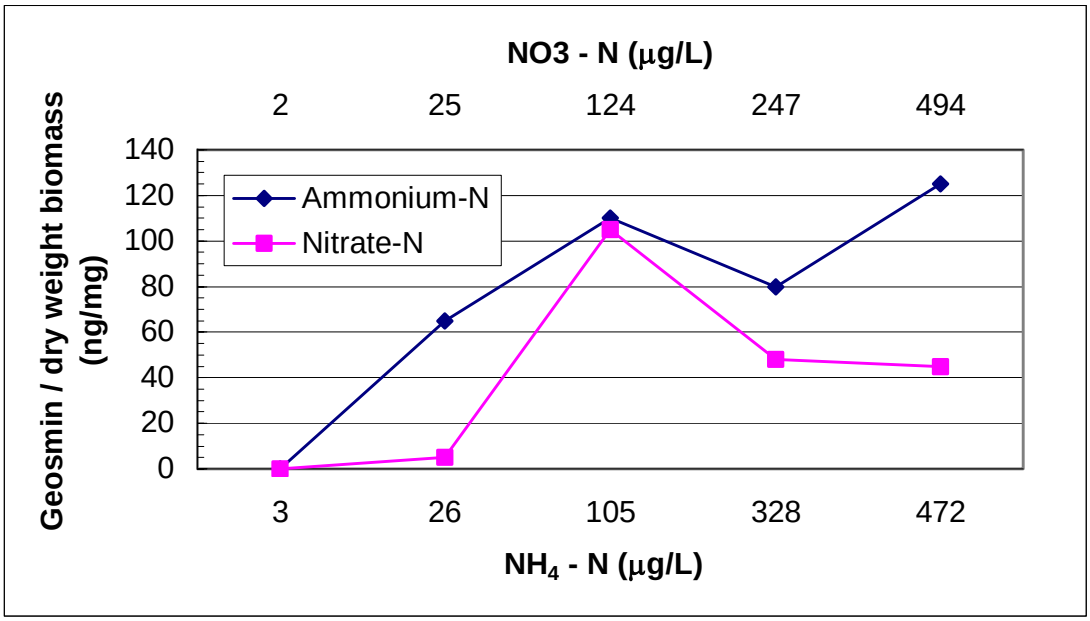

Figure 2-4. Geosmin per biomass versus various concentrations of ammonium-N and nitrate-N (Saadoun et al. 2001).

Saadoun et al. believed that at moderate nitrate-N levels, the cells have a lower phytol demand, and this shifts the isoprenoid precursors to geosmin synthesis. This would account for the lower geosmin production at the highest nitrate-N values. These results are important in discussing of the origin of geosmin and MIB.

Copper (Cu) has long been used as a retardant for cyanobacterial growth. Commonly added as copper sulfate, it is applied to suppress the algal blooms. Saadoun et al. (2001) proved this true in cultures of *Anabaena sp*. Addition of copper sulfate decreased geosmin, cell biomass, and chlorophyll a (Figure 2-5).

Izaguirre (1992) isolated a *Phormidium* species that was found to be tolerant of copper from Lake Matthews, California. Figure 2-5 shows that Cu had a major impact on the cyanobacteria studied by Saadoun et al. (2001) in microgram per liter dosages. The

species from Lake Matthews was copper-tolerant well into the milligram per liter range. This is an important find since copper sulfate is so widely used to curtail algal blooms. Previous data was not available from Lake Matthews as to conclude whether the species adapted to the copper addition or simply survived the treatments through the years and began to proliferate in the time of Izaguirre's study.

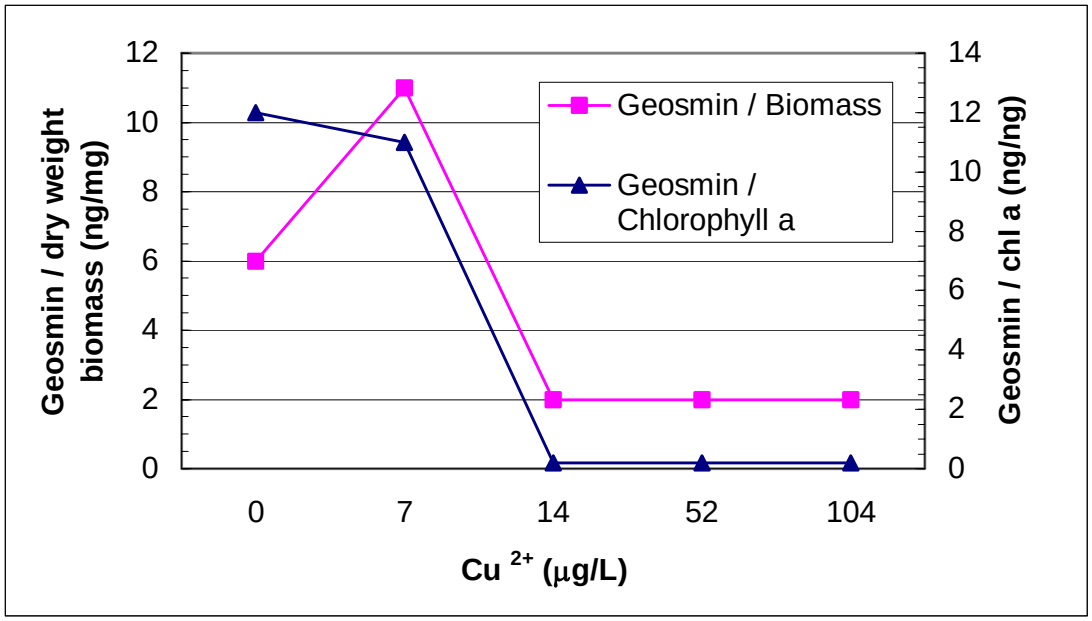

Figure 2-5. Effect of copper sulfate addition of cell of geosmin (Saadoun et al. 2001).

Effect of the growth stage

Occurrences of taste and odor episodes coinciding with the appearance of algal blooms have been noted for many years. It was not known however during which stage of growth was geosmin and MIB produced or released. Three studies were found that investigated this in laboratory cultures (Rosen et al. 1992, Utkilen and Froshaug 1992, Rashash et al. 1995). All three studies found that cell-associated (intercellular) MIB and geosmin increase during the exponential growth phase of the population. They differ on when the odorants are released into the media though. Rashash et al. (1995) found that as the cells age the amount of media-associated geosmin increased to a nearly equal

distribution with cell-associated geosmin. They declined to hypothesize on the mechanisms for this transfer of the geosmin. Rashash et al. did conclude though that the correlation between exponential growth and the production of cell-associated geosmin was more important than any other growth factors they investigated (e.g., light intensity, population density, nutrients). Rosen et al. (1992) found that the media-associated geosmin increased when the *Anabaena circinalis* culture reached the stationary phase of growth. Like Rashash et al. they found that young cells had the greatest amount of geosmin.

In Figure 2-6 the geosmin per cell decreases as the whole population increases. Therefore, the geosmin must be released into the water as the cell population ages. Rosen et al. (1992) believed that the greatest amount of media-associated geosmin was created when the cells lysed. Utkilen and Froshaug (1992) also found that geosmin increased with the death of *O. brevis* and *O. bornetii* cells.

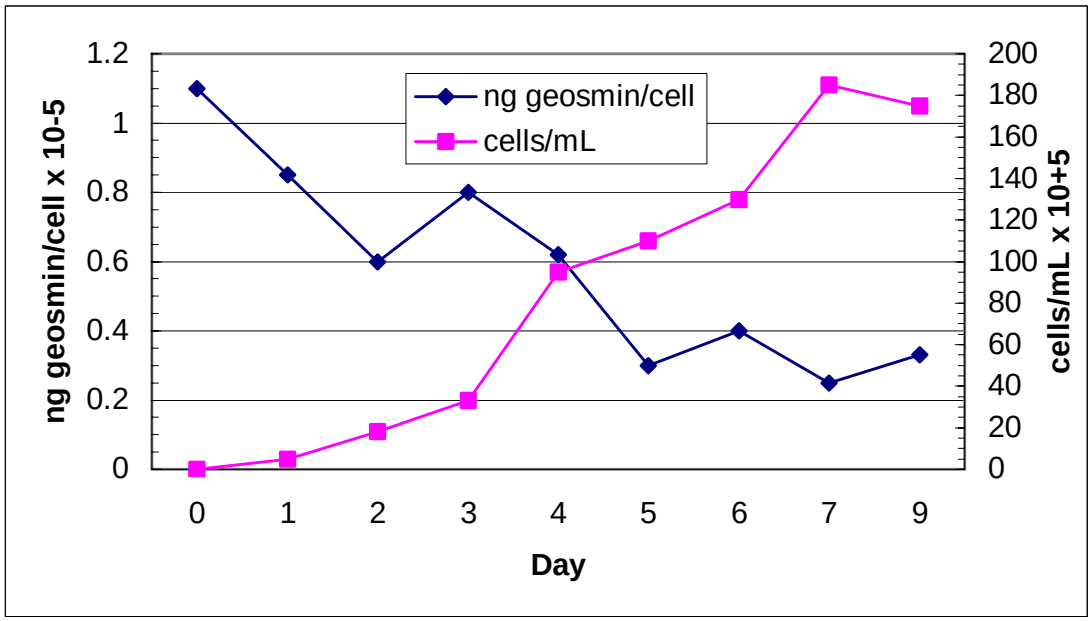

Figure 2-6. Cell-associated geosmin as a function of growth stage in *Anabaena circialis* (Utkilen and Froshaug 1992).

This would agree with the two previously discussed studies. Bowmer et al. (1992) investigated the geosmin production of *A. circinalis*. The *A. circinalis* was also found to contain much of the geosmin internally early in the study. The geosmin was converted to the media after treatment with sonication or copper. Bowmer et al. concluded that the geosmin was released when the cells died, and that treatment options that lyse the cells should be avoided.

Mechanisms of MIB and Geosmin Production in Cyanobacteria

Thus far this review has concentrated on the environmental factors that influence the growth of actinomycetes and cyanobacteria and their production of MIB and geosmin. Knowledge of the impact of these factors, gives researchers the ability to hypothesize as to the origin of the odorants within the cell. Growth of cyanobacteria can only occur when enough light is available; therefore the chlorophyll a concentrations within the cells will also increase with cell growth. Yagi (1988) investigated the relationship between intercellular chlorophyll a and geosmin from cyanobacteria from Lake Biwa, but was unable to produce a strong correlation. Later research by Rosen et al. (1992) showed an excellent correlation in *A. circinalis*. The average r^2 value for three trials between chlorophyll a and cell-associated geosmin was 0.95. The same was not true though for media-associated geosmin. Therefore, Rosen et al. (1992) concluded that there was a strong connection between chlorophyll a and geosmin content, but that it could not predict the amount of geosmin released by the cell. Thus the amount of chlorophyll a in a cell population is not a good indicator of the strength of the taste and odor episode.

Naes and coworkers (1985, 1988) were the first to hypothesize that geosmin was an overflow metabolite from the isoprenoid pathway of cyanobacteria. This idea was formed after geosmin and pigment production responded similarly in cultures of *O. brevis*.

Naes et al. (1988) used inhibitors along the isoprenoid pathway and strengthened this claim. Later work has contradicted this idea. Utkilen and Froshaug (1992) believed that if Naes and coworkers' claim were correct then there would exist an inverse relationship between carotenoid and geosmin concentrations. Working with the same cyanobacteria (*O. brevis*) and also *O. bornetii* they did not find this phenomenon. The results led Utkilen and Froshaug to suggest that geosmin is a by-product of pigment synthesis. They explain Naes and colleagues' earlier results by stating that chlorophyll a and caronentoid production both rely on the isoprenoid pathway, so the environmental factors affecting one would also affect the other. Zimmerman et al. (1995) followed these works with a study on cultures of *Phormidium LM689*. They created cultures with varying amounts of pyruvate or mevalonic lactone to affect the isoprenoid pathway, in an attempt to prove one of the previous hypothesizes. These amendments created a stable growth within the cultures, but enhanced MIB production. Therefore Zimmerman and colleagues' results and conclusions support Utkilen and Froshaug's claim that MIB is a by-product, and not an overflow metabolite.

Research into the microorganisms that produce MIB and geosmin indicate that many factors, such as light, nutrients, and water depth, influence the growth and proliferation of the species producing the odorants. However, the information most relevant to water utilities' taste and odor episodes appears to be the release of MIB and geosmin upon cell death and lysis. At this point, the compounds create problems for the water providers as they enter the source water. Although, techniques such as copper sulfate addition and the existence of predators reduce the population of odorant producers, they did increase the odor episodes by increasing cell lysis. Research

surrounding the microorganisms thus far did little to aid in the removal of the source of MIB and geosmin, but has increased the understanding of species and future work may lead to better alternatives for in-situ treatments of taste and odor problems.

MIB and Geosmin Parameters

Pendleton et al. (1997) found that MIB is a semi-spherical compound with an approximate diameter of 6 Å. Pendleton et al. considers MIB to be hydrophobic, despite it's one hydroxyl group. Pirbazari et al. (1992) reported that MIB has a solubility of 195 mg/L, a relatively low value as compared to phenol's value of 93,000 mg/L (Schwarzenbach et al. 1993). Solubility can be used as an indictor of adsorption as compounds with low solubility values prefer to remain in solution. Experimentation has shown solubility is not a good indicator for MIB as phenol uptake by activated carbon is higher than that of MIB (Mazyck 2000). The Henry's Law constant for MIB was found to be 5.76×10^{-5} (Pirbazari et al.1992). This low value indicates that MIB will remain in the aqueous phase rather than volatilize (Sawyer et al. 1994).

Activated Carbon

History

Activated carbon is a powerful adsorbent utilized by many industries and has been for many years. Water and wastewater treatment, industry effluents, brewery wastes, and textile discharges are some of the applications for activated carbon today. Early examples of rudimentary activated carbon use was found as early as the Egyptians and the Phoenicians (Dabrowski 2001), but the activated carbon industry began when the Russian Ostrejko patented techniques for producing activated carbon using elevated temperatures and oxidant flows (Ostrejko 1901).

Activated Carbon Production

Carbonaceous precursor

Activated carbons can be produced from many different carbonaceous precursors. Ideal precursors have a high percentage of carbon content, are abundant and easy to recover. A high percentage of carbon content (i.e. low ash content) translates to more surface area available for adsorption. Common carbonaceous precursors utilized in the modern activated carbon industry include: peat, bituminous and lignite coal, wood, and coconut shell (Wigmans 1989).

One area of activated carbon research involves the discovery of new, more efficient precursors for use in full-scale production. Precursors such as bituminous and lignite coal are non-renewable, and therefore should not be relied on for long-term usage. In addition, many parts of the world do not have these materials readily available. Alternative sources of carbonaceous precursors allow these regions to produce activated carbon in an economic fashion, without the high cost of long distance shipping. Warhurst et al. (1997) studied the potential for activating seed husks from the *Moringa oleifera* tree. *Moringa oleifera* is common in developing parts of the world and has many uses, therefore finding a use for the seed husks (a waste product) could further aid these communities. Numerous other researchers have studied potential waste products for use as carbonaceous precursors for activated carbon with varying degrees of success. Examples of precursors include: almond shells, olive stones, apricot stones, paper mill sludge, apple pulp, rice husks, cedar nutshells, and corncobs (Linares-Solano et al. 1980, Gonzalez et al. 1994, Gergova and Eser 1996, Khalili et al. 2000, Suarez-Garcia et al. 2001, Baklanova et al. 2003, Guo et al. 2003, El-Hendawy 2003).

Physical activation

Traditionally physical activation of a carbonaceous material is composed of two steps: first pyrolysis in an inert environment at elevated temperatures (650-850°C), followed by oxidation with steam and/or carbon dioxide at similar temperatures (Wigmans 1989, Mazyck and Cannon 2000). The purpose of activation is to create a porous structure that will readily adsorb pollutants whether in a gas or aqueous phase. This is achieved when the oxidant converts carbon from the precursor into CO and CO_2, thus opening pores in the carbonaceous material. The reactions that define this conversion using H_2O are defined below:

$$R\text{-}C_f + H_2O = H_2 + R - C(O) \quad (1)$$

$$R - C(O) = CO + nR' - C_f \quad (2)$$

$$CO + R - C(O) = CO_2 + R' - C_f \quad (3)$$

Where $R - C_f$ = solid phase free active carbon sites, $R - C(O)$ = solid phase active carbon sites occupied by surface oxides, and n = an integer indicating the number of active sites formed as a result of gasification (Ergun and Menster 1965, adapted from Mazyck and Cannon 2000). Ergun and Menster state oxidation with CO_2 undergoes a similar progression.

Wigmans (1989) states that the oxidants most commonly used by commercial carbon producers are carbon dioxide and steam. Wigmans also claims that carbon dioxide increases mesopores (20-500 Å), while steam creates a more microporous (<20 Å) structure. Several carbon researchers concluded otherwise. Towkow et al. (1977) activated brown-coal chars with carbon dioxide and steam. They found that the carbons activated with CO_2 had 63% micropores, while the steam activated samples had only

33% micropores. Later work activating olive stones with carbon dioxide and steam indicated similar results to Towkow et al. (Rodriguez-Reinoso et al. 1995). They found that steam widened micropores into mesopores as a result of its greater diffusivity than carbon dioxide. Other researchers activating olive stones and almond shells have also found results similar to that of Towkow et al. and Rodriguez-Reinoso et al., thus contradicting Wigman's claim (Rodriguez-Reinoso 1982, Gonzalez et al. 1994, Molina-Sabio et al. 1996, Walker Jr. 1996).

Chemical activation

Chemical activation methods require less intensive heat and energy treatment, but include the addition of a chemical agent (Wigmans 1989). Examples of chemical activation agents used in research or in practice include zinc chloride, phosphoric acid, or potassium hydroxide. The chemical is mixed with the precursor prior to a carbonization step. This carbonization is often milder in time and temperature than physical activation techniques. The chemical agent acts to restrict the formation of tar during the heat treatment within the carbon matrix. The chemical is then washed from the carbon, and a porous structure remains. Chemical activation often creates impressive pore structures with large surface areas, however the chemical addition and washing steps leave the resulting carbon with an acidic surface. This higher surface acidity can be deleterious to performance in some adsorption conditions (Coughlin and Ezra 1968, Pendleton et al. 1997, Karanfil et al. 1999).

Tailoring

Knowledge of the carbon oxidant reactions, the effects of different oxidants on the pore structure, and the influence of catalysts allows activated carbon producers to tailor the activation in order to create a desired adsorbent. Addition of a catalyst can have

a major impact on the carbon-oxidant reactions (Matsumoto and Walker Jr. 1986). Calcium is an important catalyst because of its effects on the carbon-oxidant reactions and its ubiquity in water (Matsumoto and Walker Jr. 1986, Knappe et al. 1992, Cannon et al. 1993, Mazyck and Cannon 2000). GAC in service at water treatment plants accumulates calcium within the pores (Knappe et al. 1992, Cannon et al. 1993). This calcium had a detrimental effect when the GAC underwent reactivation, as the calcium encouraged pore widening. Over-reactivation, as called by Cannon et al. (1993), creates a GAC with fewer micropores and a lower apparent density. Since it is difficult to prevent calcium accumulating in GAC (Nowack and Cannon 1997), Mazyck and Cannon (2000) developed a reactivation procedure that discourages the deleterious effects of calcium catalysis. They determined that use of steam at 375 °C, followed by a ramped-temperature nitrogen treatment creates a reactivated GAC with properties similar to that of its virgin counterpart. similar to that of the virgin GAC. Figure 2-7 compares the cumulative pore volume (CPV) for pore widths up to 1000 Å. Conventional reactivation resulted in a GAC with much less microporosity than the virgin counterpart. However, using Mazyck and Cannon's tailored reactivation (steam-curing protocol), the same spent material has physical characteristics. Moreover, the tailored GAC has more porosity in the larger micropores, which are important for removing a number of organic compounds (Kasaoka et al. 1989, Krupa and Cannon 1996, Newcombe et al. 2002). Indeed, these tailored carbons even outperformed the virgin counterparts for MIB removal in column testing as shown in Figure 2-8 (MacKenzie et al. 2004). Further research can explore additional techniques that alter the activation or reactivation parameters to create carbons

with specified properties and uses.

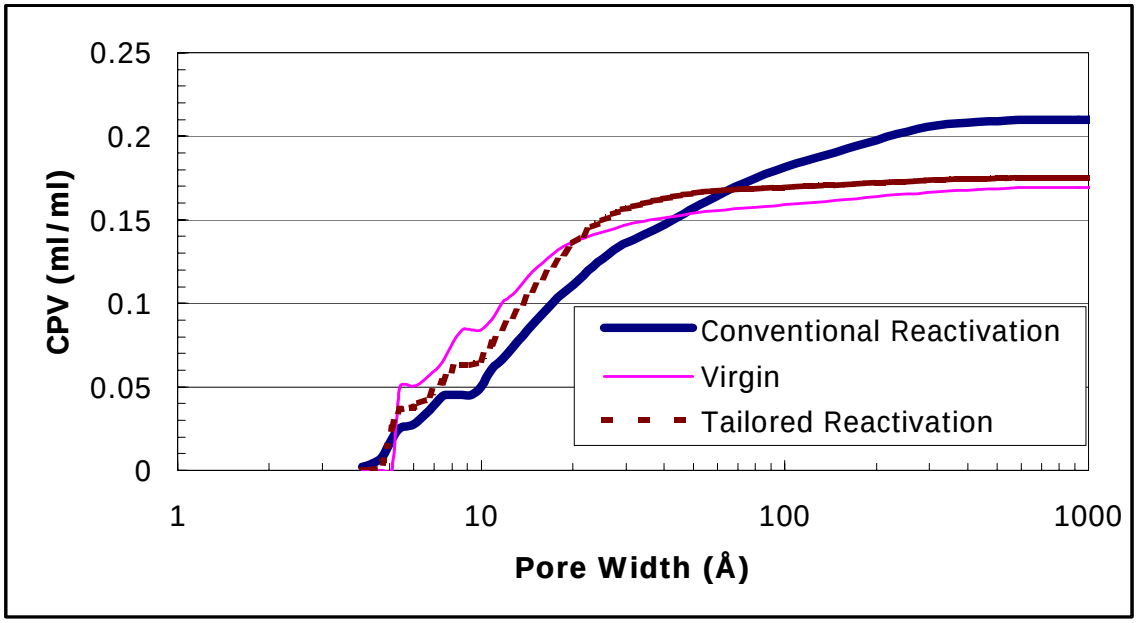

Figure 2-7. Comparison of pore size distribution between three GACs: virgin, conventional reactivation, and tailored activation (Mazyck and Cannon 2000).

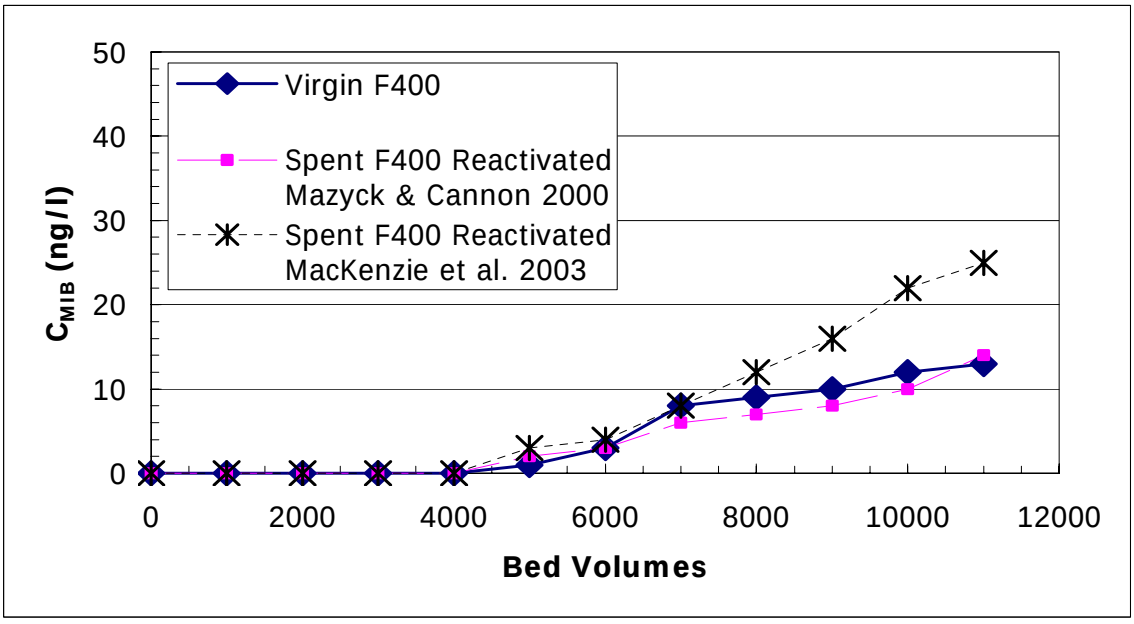

Figure 2-8. MIB breakthrough curves from columns tests comparing virgin and reactivated carbons (MacKenzie et al. 2004).

Current Industry and Recent Trends

The activated carbon industry continues to grow in production capacity throughout the world. Today, activated carbon producers utilize carbonaceous precursors such as peat, bituminous-coal, lignite-coal, wood, and coconut shells. Physical activation procedures with steam and chemical activation are both used in the industry full-scale. In addition several companies make specialty carbons to solve specific problems. These products may be impregnated, or otherwise treated to allow the maximum removal of a particular contaminant.

Water treatment remains the most common use of activated carbon with 35% of all carbon worldwide being used in water treatment (50% in the United States). These numbers should not fall in the future with developing countries using more activated carbon for their increasing industrial needs, and developed countries continuing to improve their potable water treatment. Activated carbon remains a best available technology for water treatment as it removes many organic compounds effectively. Specifically, activated carbon is commonly used for removal of organic taste and odor-causing compounds.

Activated Carbon Adsorption

For many decades a myriad of different industries used activated carbon to remove or separate compounds in the aqueous phase. Specifically water treatment utilities use activated carbon to remove many contaminants, such as synthetic organic chemicals, volatile organic compounds, and taste- and odor-causing compounds (Snoeyink 1990). This ability to remove unwanted compounds from water led the EPA to name activated carbon as a best available technology for water purveyors needing to meet federal regulations. Activated carbon is known as an excellent adsorbent; this is primarily

because of its large surface area, but also because of activated carbon's amphoteric surface. Determining the removal performance for specific compounds as well as the mechanisms involved in the adsorption onto activated carbon is extremely difficult, because of the nano-scale of the interaction and the large number of controls for the experiments. These difficulties have led researchers to many different conclusions throughout the past five decades.

Adsorption Principles

In order for a compound to adsorb to a surface, a driving force must exist so that the compound will leave the aqueous phase. Examples of these include hydrophobic forces, electrostatic forces, chemical attractions or van der Waals forces (Weber Jr. 1972).

Electrostatic forces drive adsorption when an ionic compound encounters oppositely charged ionic adsorbent. Although these forces are a result of the charge of the compounds and their chemical make-up, adsorption due to electrostatic forces is classified as physical adsorption. This is likely because of the low energy level that exists when compounds adsorb in this manner. Despite the lower energy, electrostatic interactions are important to adsorption, since they have longer reaching effects then other major driving forces.

Physical adsorption is commonly associated with van der Waals forces, which also drive adsorption in the aqueous phase. The mechanisms for van der Waals forces to drive adsorption are the result of various dipole interactions, and therefore the two surfaces must be extremely close in order for adsorption to occur. van der Waals forces are very important though in adsorption in the aqueous phase, particularly in activated carbon. A majority of the internal surface area in activated carbon is similar to a graphitic plane

(i.e., without free electrons or other active sites for reactions). On this type of surface, adsorption will primary be a result of van der Waals forces.

Compounds can also adsorb via chemical means as well as the physical methods described above. Chemical adsorption occurs when the adsorption energy between the two surfaces is high. An example of chemical adsorption is when a compound chemically bonds to the surface to which it is adsorbing. Activated carbons often have chemical functional groups at the edges of the graphitic planes, therefore compounds can adsorb strongly via chemical adsorption to these active sites.

Adsorbates and adsorbents affinity to water also affect adsorption. Hydrophobic compounds often adsorb readily to solid surfaces due to their desire to leave the aqueous phase. The tendency of a compound to leave the aqueous phase is often quantified using the octanol-water partition coefficient. Compounds with high octanol-water coefficients are classified as hydrophobic since they prefer to partition into the octanol over water. The hydrophobic/hydrophilic nature of the adsorbent also affects adsorption in the aqueous phase. For example, an absorbent with a hydrophilic surface will wet easily. An adsorbent with a wetted surface may not perform well because of interference of water molecules on the surface or edges of pores.

Diffusion, another important adsorption principle, defines the ability of the adsorbate to get to and find a permanent adsorption site. There are three phases of diffusion according to Weber Jr. (1972): bulk diffusion, intra-particle diffusion, and final adsorption. Understanding each phase of diffusion is important in order to determine which is the limiting step (i.e., longest time) in the particular adsorption conditions. The first, bulk diffusion, is the path the compound takes to get from the aqueous phase into

the solid adsorbent. Bulk diffusion is often the limiting step in systems where there is no mixing and contact between the compound and the adsorbent is not forced. The second phase of diffusion occurs inside the adsorbent, as the compound travels to a spot for permanent adsorption (Weber Jr. 1972). Termed intra-particle diffusion, this phase can be the limiting step when the adsorbent does not have adequate macro- or mesoporosity. Reducing the particle size of the adsorbent can reduce the time of intra-particle diffusion, making permanent adsorption sites closer. The final phase of diffusion is the compound finding a permanent site for adsorption. This last step is impacted greatly by the driving forces discussed above. Adsorbents with numerous adsorption sites that are attractive to the adsorbate promote a rapid final diffusion step.

Activated Carbon Pore Structure

Activated carbons' internal structure is based upon that of pure graphite; the former being much less organized than the latter. Ideal graphite is a limitless system of fused hexagons of carbon atoms. Three of the carbon's atoms' four outer valence electrons engage in covalent bonds with neighboring atoms, while the fourth resonates between different bond structures (Snoeyink and Weber 1967). The parallel layers of carbon hexagons (graphitic planes) are held together via van der Waals forces, at a distance approximately 3.35 Å apart (Snoeyink and Weber 1967). This structure creates a very homogenous physical surface with little internal area. As stated above, activated carbon's structure is much less organized than graphite. During activation, the graphitic planes are disrupted, thereby creating the internal surface area and porous network activated carbon is known for. The increase in the number of pores and surface area also creates many more edges (edge sites) than that of graphite. The higher number of edge sites increases the number of unbonded carbons available, leading to more chemical reactions and

surface functional groups at these edge sites. Therefore, an activated carbon would have more surface functional groups than graphite exposed to the same conditions. Moreover, the increased number of functional groups will contribute heavily to the adsorptive ability of the activated carbon.

The pore structure of activated carbon is commonly divided into micropores (< 20 Å), mesopores (20-500 Å), and macropores (>500 Å). Micropores generally constitute the majority of the surface area and pore volume in activated carbons, over 90% in some cases (Tomkow et al. 1977). Micropores are very important for aqueous and air phase applications as they are closest in size to many of the target pollutants. Meso- and macropores also have important roles as they provide diffusion pathways to the internal pores and serve as adsorption sites for larger compounds (e.g., NOM).

Pore structure affecting the adsorption of organics

The extent to which an organic compound adsorbs is often determined by the surface area and pore volume that exists within the activated carbon. Kasaoka et al. (1989) performed adsorption experiments involving organics and activated carbon in hopes of finding a relationship between the molecular size of the adsorbate and the pore widths in the adsorbent. Here organic compounds preferred to adsorb in pores 1.5 to 2 times their size, and therefore micropores are very important since many target compounds fit into this size range. Other experiments with organic dyes produced similar results, as carbons with more surface area and volume in pores similar in size to that of the target dye performed better in adsorption experiments (Krupa and Cannon 1996). Based on these findings, one could predict that many organic pollutants would adsorb primarily in the micropores of activated carbons. However, these studies were performed

at equilibrium and therefore diffusion did not impact the results. Diffusion will affect the degree of adsorption of all compounds when shorter contact times are used.

Pore structure affecting MIB adsorption

MIB has an effective molecular diameter of approximately 6 Å; therefore the results above suggest that MIB would most likely find permanent adsorption sites in micropores. Pendleton et al. (1997) and Newcombe et al. (1997) studied MIB adsorption onto activated carbon and agreed with this theory. Newcombe et al. (1997) believed micropores were the best sites for MIB because the similar size of the pores and the compound creates more contact points for permanent adsorption. Pendleton et al. (1997) performed MIB adsorption experiments in deionized water with coconut-based and wood-based carbons. The authors listed not only total micropore volume, but also the volume in pores < 7 Å and between 7-20 Å. Results from 3 coconut-based carbons indicated that micropore volume was important, particularly the <7 Å pores. Experiments with wood-based carbons however, did not show the same trend. The 2 wood-based PACs had different micropore volumes, but adsorbed the same amount of MIB. Despite Pendleton and colleagues' claim, their results implied that other factors besides micropore volume influence the adsorption of MIB onto activated carbon.

Another technique for measuring or quantifying the pore structure of activated carbon is iodine number. Iodine adsorbs in pores in a monolayer coverage, and therefore the amount of iodine adsorbed is a strong indicator of total surface area. Indeed, the iodine number test (ASTM D4607) is reliable and easy compared to gas adsorption and is used extensively by carbon manufacturers and others to evaluate surface area. Gillogly et al. (1998a) performed adsorption experiments with MIB using the five commercial carbons (Table 2-3).

Results from the adsorption tests indicated that the PAC with the highest iodine number (A) did remove the most MIB. However, other results did not correlate as well with iodine number. For example, the two PACs with the same iodine number (C and D), performed quite differently, with the lignite-based carbon adsorbing much more MIB than the wood-based carbon. Moreover, the other wood-based carbon (PAC E) had similar MIB adsorption ability to PAC C despite nearly double the iodine number. Kim et al. (1997) studied the removal of MIB in pilot scale columns using GACs with different iodine numbers. Again iodine number did not have a significant impact on removal efficiency in these tests.

Table 2-3. Characteristics of five commercial PACs (Gillogly et al. 1998)

Name	**PAC Symbol**	**Precursor**	**Iodine Number**
PICA Cepacarbon	A	Bituminous coal	1020
Calgon WPH	B	Bituminous coal	800
NORIT Hydrodarco B	C	Lignite coal	550
Acticarb Watercarb	D	Wood	550
Westvaco Nuchar	E	Wood	1000

Iodine number and its relationship to MIB adsorption were also studied in actual water treatment plant conditions (MacLeod and Simpson 1993). Ten commercial PACs were tested for MIB removal in a bench scale test that simulates the treatment processes at Manatee County Water Treatment Plant. No correlation was found between iodine number and MIB removal in these conditions. Moreover, the researchers compared the MIB performance for the ten carbons against twelve other physical and chemical indices of the PACs in addition to iodine number. The tannin value was the only index to have a good linear relationship with MIB removal, indicating that mesoporosity is important in this system. The lack of quality correlations demonstrates that MIB adsorption onto activated carbon in actual plant conditions is not a trivial matter.

Nowack et al. (2001, 2004) performed GAC column tests using raw waters spiked with MIB, and also found a poor correlation between MIB removal and micropore volume. Instead, in this scenario the small mesopores appeared to control adsorption. The competitive adsorption between NOM and MIB could make the larger micropores and smaller mesopores have a greater impact on MIB adsorption.

Surface Chemistry

The process of activating a carbonaceous precursor into an activated carbon creates a porous matrix with an increased internal surface area. In addition to the textural development, activation also changes the materials' chemical structure. As discussed above, the structure of activated carbon is based upon graphite; that being horizontal planes of connected carbon atoms. The carbon atoms in the graphitic planes are bonded to each other, and therefore the only active sites available are located at the edges of the planes (Snoeyink and Weber Jr. 1967). Activated carbon has a similar bonding arrangement, but activation not only increases porosity but also the number of edge sites. Thus the higher number of edges in activated carbon allows for more active sites, which can bond to other compounds or chemical groups.

Activated carbons' propensity for attracting surface compounds or functional groups often leads to an accumulation on the surface that can affect the carbon's adsorption ability. The impact on performance surface groups have made it necessary to uncover details surrounding them, and therefore several methods exist for identifying functional groups on carbon surfaces. Some common functional groups found on activated carbon are shown in Figure 2-9.

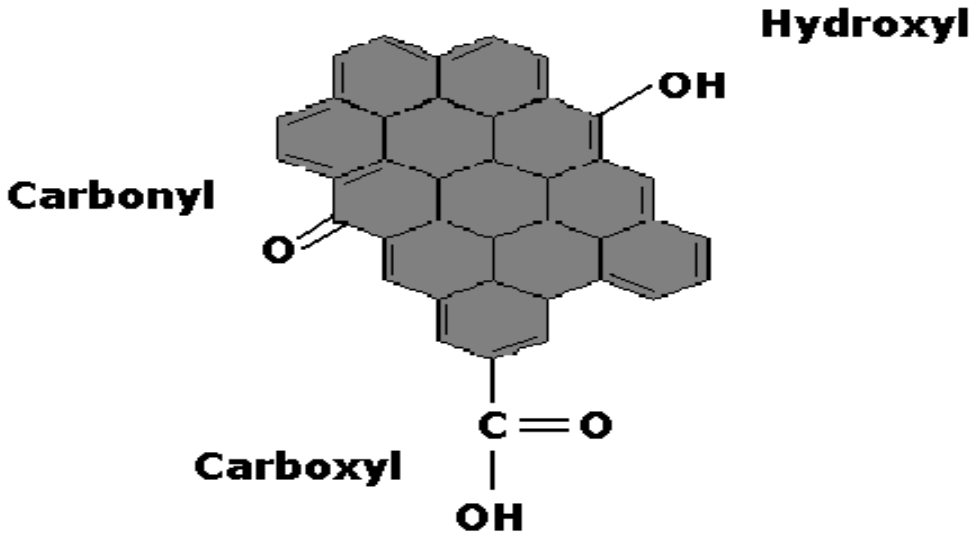

Figure 2-9. Examples of surface functional groups.

Quantification

Titration methods to quantify acidic and basic functional groups were first proposed several decades ago (Boehm 1966). This technique utilizes acids and bases that neutralize specific surface functional groups (e.g., $NaHCO_3$ for carboxyl groups). Often referred to as a Boehm titration, this relatively simple technique remains a standard for surface chemistry analysis despite the emergence of new technologies, as evidenced by the number of researchers using it in the past decade (Tessmer et al. 1997, Bandosz 1999, Karafil et al. 1999, Salame and Bandosz 2001).

Titrations can also determine electrokinetic properties of activated carbon (Boehm 2002). The point of zero charge (PZC) refers to the pH at which the carbon surface is neutral; a point often ascertained via a reverse mass titration. The PZC is often used to predict electrokinetic tendencies of particles, but for activated carbon it also gives insight into the surface functionality that exists on the inner surface. The principal

features on an activated carbon surface that would affect the PZC are acidic functional groups, which are more numerous than basic groups (Boehm 2002). Therefore a carbon with an acidic PZC likely has a number of surface acidic groups, and conversely a carbon with a basic PZC has very few functional groups.

Infrared spectroscopy (IR) has also been used for the identification of functional groups on activated carbon for several decades (Mattson et al. 1969b, Mattson et al. 1970). Quantification using IR is difficult however. New technology has led to improved techniques such as FTIR, DRIFTS, and total reflective spectroscopy. These methods are not without problems though as researchers have disagreed in assignment of peaks from the IR to actual functional groups (Boehm 2002).

A more recent technique for characterizing surface functionality is x-ray photoelectron spectroscopy (XPS). XPS uses x-ray irradiation to excite outer electrons until they leave their atom, and then measures the energy required for this to occur (Boehm 2002). The amount of energy measured relates to the binding energies that exist for surface functional groups. Therefore the concentrations of the groups can be estimated from the peaks on the energy curve. One limitation of XPS though is that it can only affect atoms on the surface and therefore cannot measure internal functionality.

The common surface functional groups on activated carbon are known to desorb at varying temperatures and some as CO, others as CO_2 (Puri and Bansal 1964). This phenomenon is the basis for temperature programmed desorption (TPD). In TPD, carbon samples are subjected to increasing temperatures in an inert environment and the gases evolving are measured by a mass spectrometer. The amount of CO or CO_2 in the effluent gas determines the amount of specific functional groups on the carbon surface.

The above techniques represent the most common methods available to measure surface functionality on activated carbon. Since each technique is not without fault, some researchers utilize a combination of measurements (Salame and Bandosz, 2001). This enables the researcher and reader a more thorough look into the surface chemistry of the carbons.

Effect on phenol adsorption

A discussion on the adsorption of phenol is included in this review for two reasons: first, hundreds of publications are dedicated to the adsorption of phenol onto activated carbon, so much can be learned regarding the impact of surface chemistry on adsorption ability (Radovic et al. 2001). Secondly, MIB and phenol are very similar in size; therefore, determining why they adsorb differently may lead to the effect surface chemistry has on MIB adsorption onto activated carbon (Mazyck 2000).

Garten and coworkers (1957a,b) performed some of the earliest research with activated carbon and aromatics. They created activated carbons with different surface chemistries by exposing them to various oxidizing environments, as well as heat treatments over a range of temperatures. Garten and coworkers found that increasing amounts of oxygen functionality on the carbon surface were deleterious to adsorption of aromatics. Moreover, they determined that different types of functionality had different effects on the uptake of aromatics, an important finding for later research. However, their studies failed to include physical data on the carbon (e.g., surface area), which could partially explain the differences. Nonetheless, the findings were encouraging as more research in the area followed.

Coughlin and coworkers (1968a,b) published what would be an important theory as to the role of acidic functional groups stemming from research detailing the adsorption of

phenol and nitrobenzene onto activated carbon. Two types of adsorbents, activated carbon and a carbon black, were treated in different oxidizing and reducing environments; creating a range of surface functionality. These three activated carbon and five carbon black species were then titrated to determine the quantity of the four types of surface groups, described above. In addition, the authors included the BET surface area of all of the adsorbents; an important parameter so the reader can better ascertain the role of surface chemistry. Phenol and nitrobenzene isotherms agreed with previous research, showing that increasing acidity on the surface resulted in lower adsorption. Comparing the activated carbons' surface areas highlighted an important point; despite having 150 m^2/g less surface area, the reduced carbon adsorbed twice as much phenol as did the oxidized activated carbon in dilute concentration equilibrium tests (Figure 2-10).

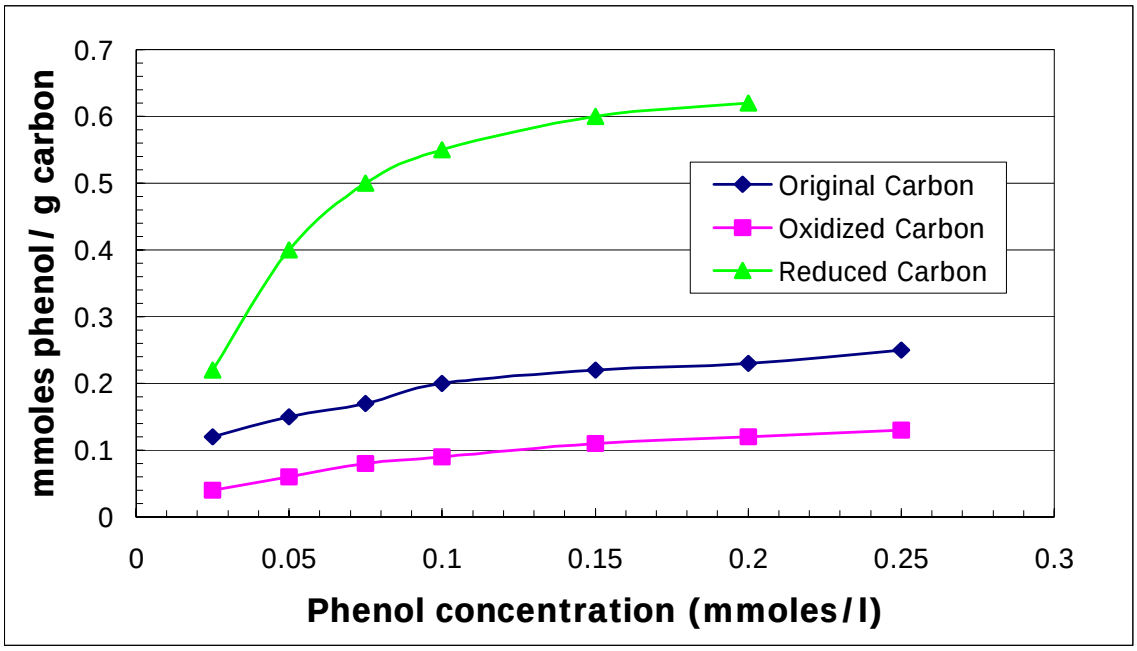

Figure 2-10. Adsorption of phenol on Black Pearls 607 Carbon Black from aqueous solutions, 30 ºC, low concentrations (Coughlin et al. 1968).

Interestingly, isotherms performed at much higher phenol concentrations (Figure 2-11) found that the original and oxidized activated carbons performed the same.

The authors concluded that the carbons performed the same at the second (higher) plateau, because of the geometry of the phenol adsorbing on the carbon surface. They believed that at the lower concentrations the phenol aligned itself in a prone position with the carbon surface, but at the higher concentrations the position becomes vertical.

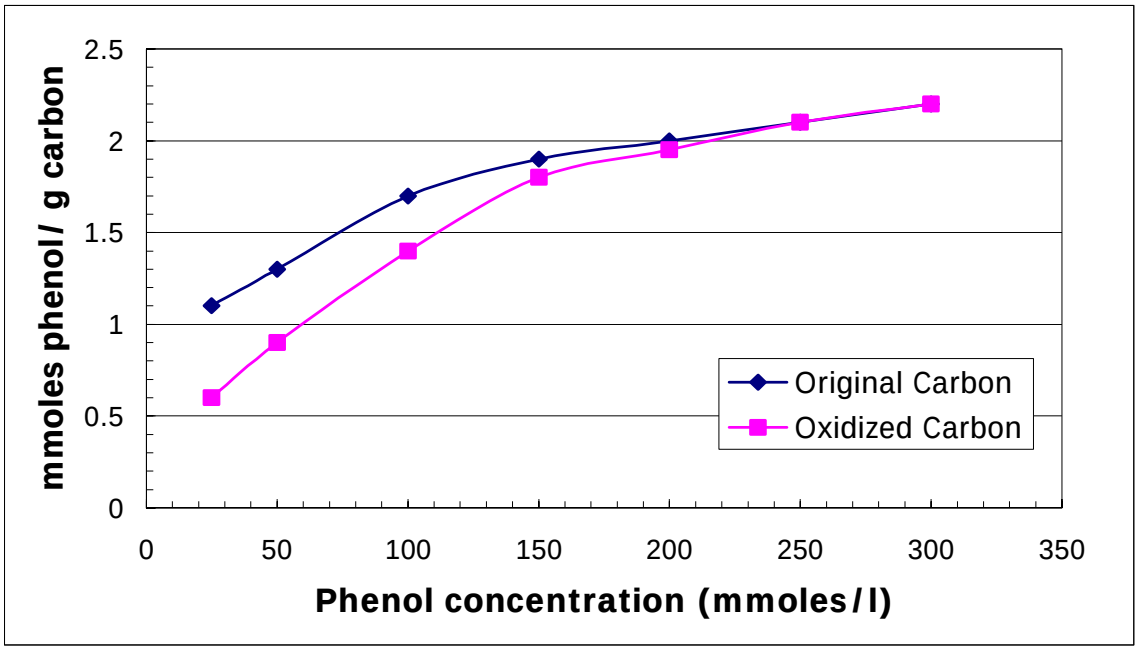

Figure 2-11. Adsorption of phenol on Black Pearls 607 Carbon Black from aqueous solutions, 30 ºC, high concentrations (Coughlin et al. 1968).

This leads to their theory that the adsorption is due to the π-electrons on the carbon surface interacting with the π-electrons of the aromatic compound. The depressed performance of the oxidized carbon in the dilute phenol concentrations, is a result of surface functional groups removing surface electrons from the π-interactions. Moreover, Coughlin and coworkers believe that at the higher concentrations when the phenol adsorbs vertically, the π-π interactions are actually taking place between the aromatic compounds and not with the carbon surface. Indeed, in this case the removal of π-electrons from the carbon surface by functional groups would not hinder adsorption,

and therefore explain the similar phenol removal by the different carbons at the increased solution concentrations.

One year after Coughlin and coworkers (1968a,b) published their π-π interactions theory another important publication by Mattson et al. (1969a) proposed an alternative theory. In this work a single activated carbon was tested for removal of four aromatic compounds, including phenol. One important experimental variable monitored here was the solution pH, which was never mentioned by Coughlin and coworkers. Mattson et al. pointed out that the pH will affect not only the speciation of the adsorbates, but also the charge on the carbon surface. Both of these can impact carbon performance, so pH was monitored and recorded for all equilibrium isotherms. Since previous research had already shown the deleterious effects of increased surface acidity, Mattson et al. instead investigated one carbon and attempted to quantify the reactions occurring when aromatics sorb to the surface. Therefore, they obtained infrared spectra of the aromatic compounds, before and after adsorption onto the carbon. The spectra showed that the OH group on p-nitrophenol disappeared after adsorption; thus indicating that some hydrogen bonding was taking place on the surface. However, nitrobenzene which does not have a polar OH group was removed as well as the phenolic compounds. Therefore, another mechanism must be involved, and Mattson et al. proposed that the aromatic compounds are engaging in an electron donor-acceptor complex. The authors reached this conclusion because the nitrogen containing aromatics adsorbed more strongly than phenol. Nitro groups will act as strong electron acceptors, and thus create strong complexes with surface groups on the carbon. Phenol, however, is not as strong an acceptor and needs strong electron donating groups to adsorb in the same manner. At first this theory seems to contradict previous

studies showing deleterious effects from surface acidity. Indeed, according to Mattson et al. phenol needs oxygen functional groups to adsorb. The authors believed that the adverse effects of oxygen functional groups shown by Coughlin and coworkers among others are due primarily to strongly acidic groups (carboxyl). Moreover, Mattson et al. concluded that higher concentrations of the less acidic carbonyl group, which is a stronger electron donor, actually aids in the uptake of phenol.

Three decades of research that followed these two landmark papers has done little to elucidate this mechanism for phenol adsorption (Radovic et al. 2001). The lack of progress in the topic suggests that accurately measuring the concentration and impacts of surface functional groups on activated carbon are not tasks to be taking likely.

Effect on water adsorption

Unlike phenol, water molecules do not adsorb well to activated carbon surfaces (Barton et al. 1984). Organic compounds often adsorb to carbon via strong dispersion forces on the graphitic planes. This type of adsorption occurs easily at low pressures (Barton et. al 1984) However, water prefers to sorb to functional groups on the carbon surface, via hydrophobic/hydrophilic means (Pierre and Smith 1950). Interestingly, the type of functional group present on the surface does not influence water adsorption (Barton et al. 1994). Instead, the primary factor influencing water adsorption is the location and density of the functional groups according to molecular simulations (Muller et al. 1996, Muller and Gubbins 1998, Muller and Hung 2000). Functional groups prefer to form at the edge sites of activated carbon, therefore when concentration of surface groups increase, the density of the groups also increases significantly (Henning 1966). Moreover, the denser grouping of active sites further intensifies water adsorption (Muller et al. 1996, Muller and Gubbins 1998, Muller and Hung 2000). In this

case, water molecules that sorb to the functional groups are in close proximity so that more water can sorb by hydrogen bonding. Indeed, this arrangement creates water clusters at the edge sites of activated carbon pores, and can thus impact adsorption by blocking the entrance into the pores.

Effect on MIB adsorption

Electrostatic forces affect adsorption in many systems by either attracting an absorbate to the absorbent or by hindering adsorption via repulsive forces. The strength of electrostatic forces is dependent on system variables such as pH, solution ionic strength, and charge of the particles involved. However, these forces do not appear to impact MIB adsorption on activated carbon. Researchers have studied MIB adsorption at several different pH values using many commercial carbons with different charges, but electrostatic forces do not impact adsorption values (Herzing et al. 1977). Surface chemistry can affect adsorption of compounds in other ways, besides electrostatic forces.

The surface chemistry of activated carbon impacts adsorption of many different compounds including: SOCs, NOM, phenol, and other organic compounds (Tessmer et al. 1997, Karanfil and Kilduff 1999, Karanfil et al. 1999, Al-Degs et al. 2000). These studies all showed an increase in the oxygen functional groups on the carbon surface led to a decrease in adsorption. Pendleton et al. (1997) found similar results with MIB. Using five carbons they found an excellent correlation (r^2 = 0.99) between percent oxygen content and hydrophilic sites on the carbon surface. Next, they plotted MIB removal versus hydrophilic sites for the five carbons (Figure 2-12). Figure 2-12 shows a strong relationship between the hydrophilic sites, and therefore percent oxygen, and amount MIB adsorbed. Pendleton et al. believe that the oxygen on the surface encourages water adsorption. Moreover, they believed that water

not only outcompetes MIB for pore sites, but that water could displace MIB already sorbed.

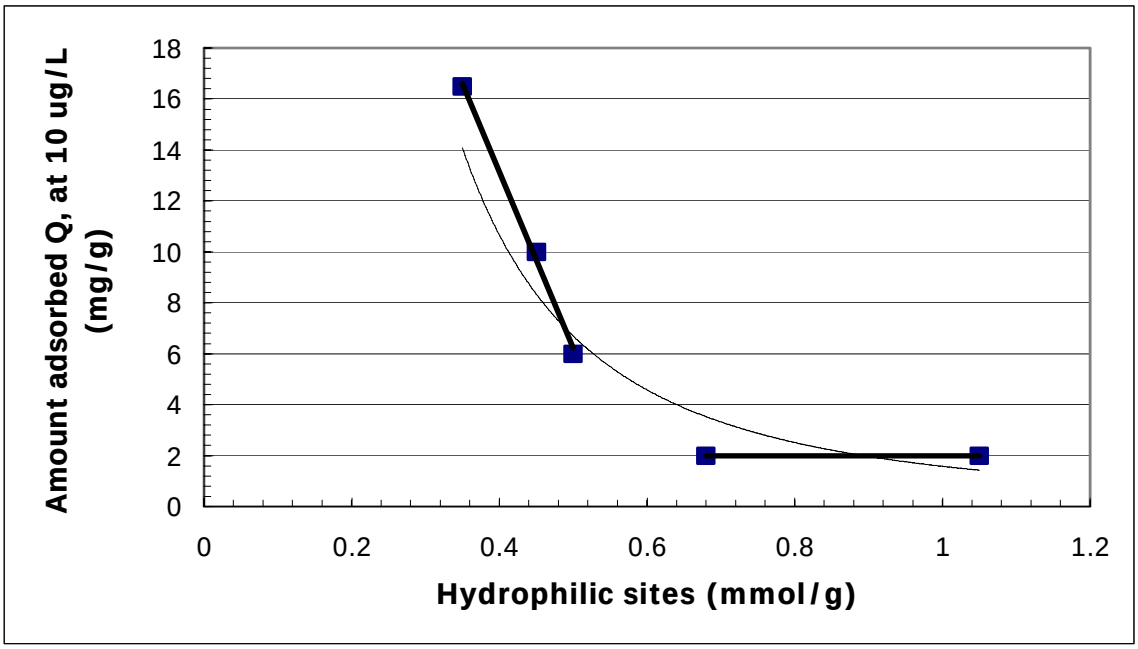

Figure 2-12. Amount adsorbed versus hydrophilic sites (Pendleton et al. 1997).

Further research by this team (Considine et al. 2001) strengthened their claim that water adsorption adversely effects MIB adsorption. In these experiments, carbons were reduced or oxidized to alter the oxygen content without significantly changing the pore size distribution, thus surface chemistry parameters would account for any differences in performance. These carbons showed another strong correlation with an inverse relationship between MIB adsorbed and oxygen content (Figure 2-13). Considine et al. then tested the water adsorption theory by running the same experiments for four carbons in dichloromethane (DCM), a low polarity solvent. Figure 2-14 shows that in DCM no correlation was found between MIB adsorption and oxygen content, thus strengthening the claim that water adsorption adversely affects MIB removal.

One concern was that the carbons used in Figures 2-13 and 2-14 were not the same, so the data are not as powerful as first appeared. Considine et al. (2001) would

have been wise to publish the results of the same carbons tested in water and DCM side by side. Another limitation of this work is that these experiments were not performed in the presence of any competitive compounds.

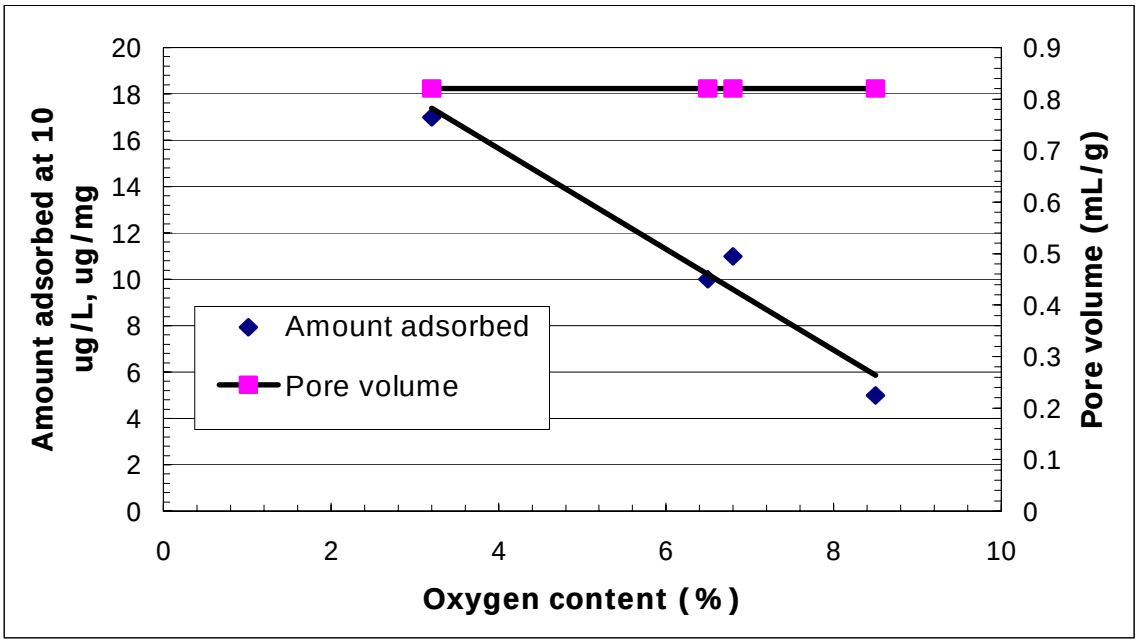

Figure 2-13. Amount MIB adsorbed by oxidized carbons (Considine et al. 2001)

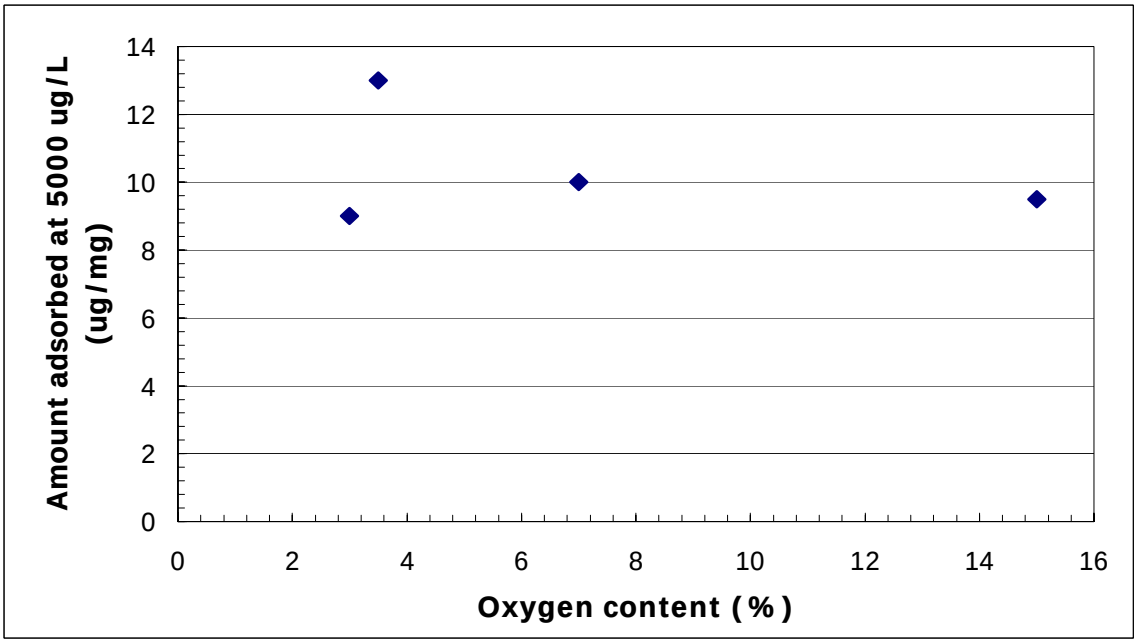

Figure 2-14. Amount MIB adsorbed from DCM as a function of oxygen content (Condisine et al. 2001).

MIB Removal in Water Utilities

MIB Removal via Other Treatment Processes

Removing earthy-musty tastes and odors caused by MIB and geosmin is a priority for water purveyors around the world. Water utilities and researchers tested many treatment processes in hopes of finding the most efficient means for clearing the water of these unpleasant odorants. The conventional treatment train of coagulation, flocculation, and sedimentation is an ideal process to start, as MIB and geosmin occur in surface waters and these treatments exist at a majority of surface water plants. Unfortunately conventional treatment has shown little to no ability to lower MIB to concentrations below the odor threshold level (Kim et al. 1997, MacLeod 2000, Nerenburg et al. 2000). Pilot scale conventional treatment processes were unable to effectively remove MIB and geosmin in two studies in the 1980s and 90s (Vik et al. 1988, Kim et al. 1997). MacLeod (2000) examined the removal of MIB and geosmin by various processes in bench-scale tests, as well as the full-scale plant. Minimal removal of the odorants occurred during conventional treatment and that PAC was required to supply palatable water. Moreover, plants utilizing conventional treatment processes along Lake Michigan were unable to adequately remove MIB and geosmin (Nerenburg et al. 2000). Indeed, in this study investigating the growing number of taste and odor episodes in the Chicago metro area, water utilities needed additional treatment processes (e.g., PAC) to control MIB and geosmin concentrations.

Chemical oxidation, via chlorine or ozone, is another treatment process common to surface water utilities since federal regulations require disinfection to ensure biologically safe water. Treatment plants have this capability already on-site, therefore using additional oxidant to remove taste and odors would be an easy solution for water

purveyors. However, Lalazary et al. (1986a) attempted to oxidize MIB with chlorine and other oxidants, and found limited removal. Other researchers have shown ozone to have a similar null effect (Vik et al. 1988, Kim et al. 1997). Air stripping is another common process found at water treatment plants that was evaluated for taste and odor removal. In order to lower MIB and other common odorants to below their odor threshold, extreme levels of air flow were needed (Lalezary et al. 1984). Therefore, air stripping was deemed infeasible for taste and odor control at water utilities.

One treatment process used extensively at waste water treatment plants that is gaining wider acceptance in water treatment is biodegradation. Controlling tastes and odors with microorganisms is difficult, however, since many odorants (e.g., MIB) cause problems at such small concentrations (part per trillion or ng/L). These concentrations are several magnitudes lower than the NOM that exists in surface waters. Therefore, it could be difficult for the microorganisms to effectively lower MIB concentrations that are already quite low compared to other compounds present in the water. Moreover, MIB problems are often seasonal and sporadic. Thus, microbes must be able to effectively degrade MIB when it is present, continue to survive when it ceases to be a problem, and repeat this cycle. This is quite a grueling task, and laboratory research in this technology has shown mixed results. In 1992, oligotrophic bacterium isolated from a surface water grew on a medium with MIB as its sole carbon source (Ishida and Miyaji 1992). These cells were then seeded onto a biofilm reactor in which natural water spiked with MIB was added. The biofilm with the isolated strain lowered MIB concentrations considerably (Figure 2-15). Figure 2-15 illustrates the potential of biological treatment for taste and odor control, however, some questions were not answered. Indeed, the MIB levels used

in these tests were much higher than would be found at water utilities and the work did not account for seasonal conditions. Three years later, published work regarding biodegradation of odorants was unable to further research in the area (Huck et al. 1995). Despite many experimental problems, results from bench-scale tests led the authors to conclude that biological treatment was not a viable option for MIB removal. However, since the work did have many experimental issues this should not be an end to research in this area.

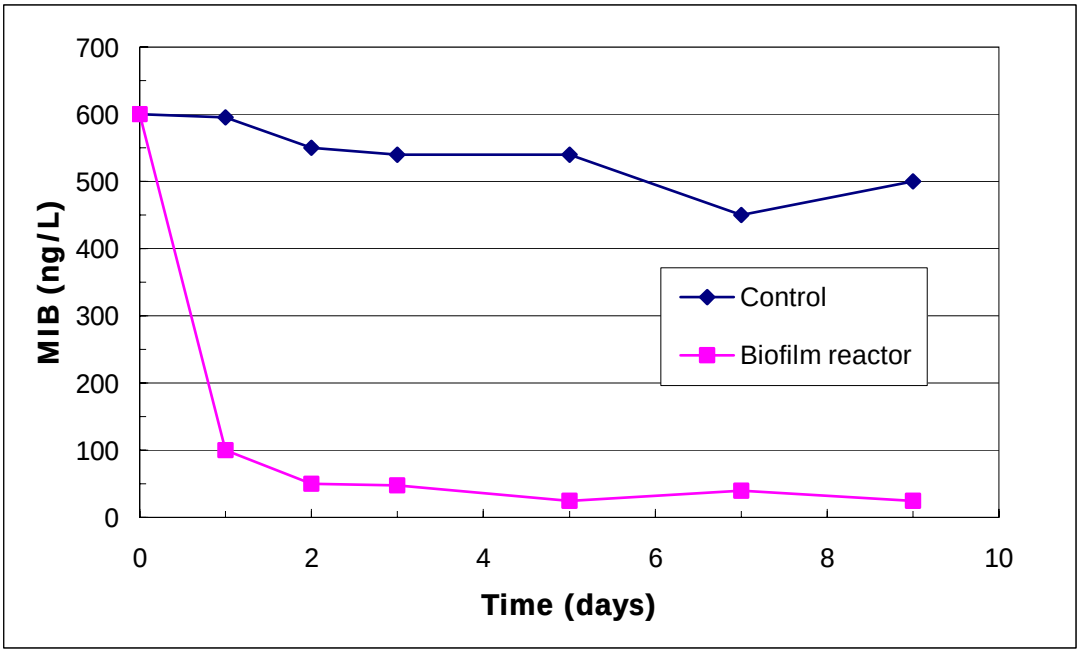

Figure 2-15. Biodegradation of MIB by a bioflim reactor (Ishida and Miyaji 1992).

Transferring the bench scale biodegradation tests to full-scale application resulted in more mixed conclusions in the effectiveness of biological active activated carbon (BAAC) filters for MIB control (Vik et al. 1988, Kim et al. 1997, Nerenburg et al. 2000). In pilot-scale, Vik et al. (1988) evaluated two parallel systems for MIB removal; one used GAC alone and the other GAC preceded by ozone to encourage biological growth in the column. Lake water spiked with synthetic MIB was treated through the two treatment lines and the effluents were measured for TOC and MIB levels. The treatment line with

the BAAC column (ozone and GAC) was not able to remove as much TOC or MIB as the GAC only column. The authors concluded this was because of increased competitive adsorption in the BAAC filter. Moreover, they believed that the smaller organics in the BAAC line caused by the ozone, increased the level of competitive adsorption for MIB. Indeed, this is a feasible theory, as the size of the NOM does greatly affect the amount of competition for adsorption sites on activated carbon (Newcombe et al. 2002b). However, the pilot study by Vik et al. is not a conclusive study on this technology. The authors had many problems in data collection during the several month long study, and much of their MIB data fell below the concentration at which they could reproduce. Vik et al. (1988) presented a model on which to begin research on this topic, but could not conclude whether BAAC is a viable treatment option for MIB episodes.

Approximately a decade later, a similar study followed that corrected many of the procedural and analytical problems that occurred in the Vik et al. pilot study (Kim et al. 1997). Kim et al. treated raw water spiked with five taste and odor causing compounds, including MIB, with conventional treatment (coagulation, flocculation, sedimentation, and sand filtration), and then through two separate pilot plants. The first, Pilot Plant I (PP I), utilized ozone and GAC adsorption to assess the ability of BAAC for removal of these odorants. Pilot Plant II (PP II), followed the same conventional treatment train with only GAC adsorption. In addition, Kim et al. used four different GAC contactors in each pilot plant, adjusting parameters such as empty bed contact time (EBCT) to evaluate the impact of these on taste and odor abatement. Upon examining the results the authors concluded that BAAC was beneficial in removing these taste and odor causing compounds, including MIB, a reverse of findings of Vik and colleagues. However, upon

closer inspection of the results of PP I and II for MIB removal, the conclusion is not particularly strong.

Table 2-4. Percent removal efficiencies of MIB for PP I and II (Kim et al. 1997).

Pilot Plant	**Conven. Treat[1] (+ Ozone PP I)**	**GAC Column A[2]**	**GAC Column D[2]**	**Total Column A**	**Total Column D**
I	28.1	60.8	64.5	71.9	74.4
II	20.7	60.0	64.6	68.3	71.9

1. Conventional treatment as defined above.
2. GAC Columns A and D used two different carbons each with15 min EBCT. GAC Columns B and C had only 10 minutes EBCT. An EBCT of 15 min was found to work much better than the 10 min so only GAC columns A and D are shown for breviety.

Table 2-4 compares the removal efficiency of MIB utilizing two of the GAC columns with and without ozone. The second column in Table 2-4 shows that ozone has a small impact on MIB, as PP I had over 7% more removal after conventional treatment than PP II. The next two columns list the MIB removal in the GAC columns, and one can see very little difference in performance between the biological system and the plant with only adsorption. Finally, the last two columns in Table 2-4 show the total amount of removal between the two pilot scale plants. PP I does have approximately 3% more removal, but closer inspection shows that the difference does not come from degradation due to the BAAC. In fact, the GAC columns in PP II actually removed more MIB than did PP I, when one considers the higher levels of MIB coming from the conventional treatment processes. Indeed, a majority of the MIB removal in both of these systems appears to have come from GAC adsorption, with the differences in total removal resulting from a small amount of ozone oxidation. Therefore, it is still unclear whether BAAC is a plausible technology for the removal of taste and odors.

Following the works by Vik et al. and Kim et al., Nerenburg et al. (2000) published a study on taste and odor episodes in the Chicago metro area. Millions of Chicago area

residents receive their drinking water from Lake Michigan which had many severe taste and odor episodes in the 1990s resulting from high concentrations of MIB and geosmin. Water utilities in this area use conventional treatment and rapid-rate filtration to clean the raw water, and therefore must add PAC in order to lower MIB to levels undetectable to consumers. Only one treatment facility in the area uses ozonation and BAAC in addition to conventional treatment. Moreover, this is the only utility that did not receive consumer complaints about earthy/musty odors during the time of the study. However, ozone and BAAC were not proven to be responsible for the lack of odors in this utility's treated water. Indeed, there were many differences in the numerous treatment plants in the study so the authors could not conclude that the additional technology present at this facility effectively lowered MIB to below its odor threshold concentration. This study however, did again illustrate the potential for ozone and BAAC for taste and odor control and more research in this area is ongoing.

PAC versus GAC

PAC, defined as those particles that pass through a 325 mesh (45 um), is added to the process water in pipe flow or mixing basins. PAC is more commonly used than GAC for the removal of MIB and other taste and odor causing compounds.

Lalezary et al. (1986b, 1988) and Snoeyink (1990) suggest PAC's popularity is because of its low capital and maintenance costs, as well its adaptability of treatment. This adaptability is very important, as MIB episodes are often seasonal and sometimes sporadic. PAC dosages can be easily adjusted to combat the MIB concentrations at that moment. The amount of GAC needed to treat the peaks of a MIB episode would be unnecessary for most of the year, thus the capital costs of the GAC adsorber would not be worth the benefit. Another advantage of PAC is that the smaller particle size helps

diffusion. Najm et al (1990) and. Snoeyink (1990) state that the smaller grains of the PAC adsorb organic compounds more rapidly than GAC, and this time can be important in full-scale operations. A smaller grain size can help the rate of adsorption and thus the amount adsorbed in times commonly found at water treatments plants (Figure 2-16).

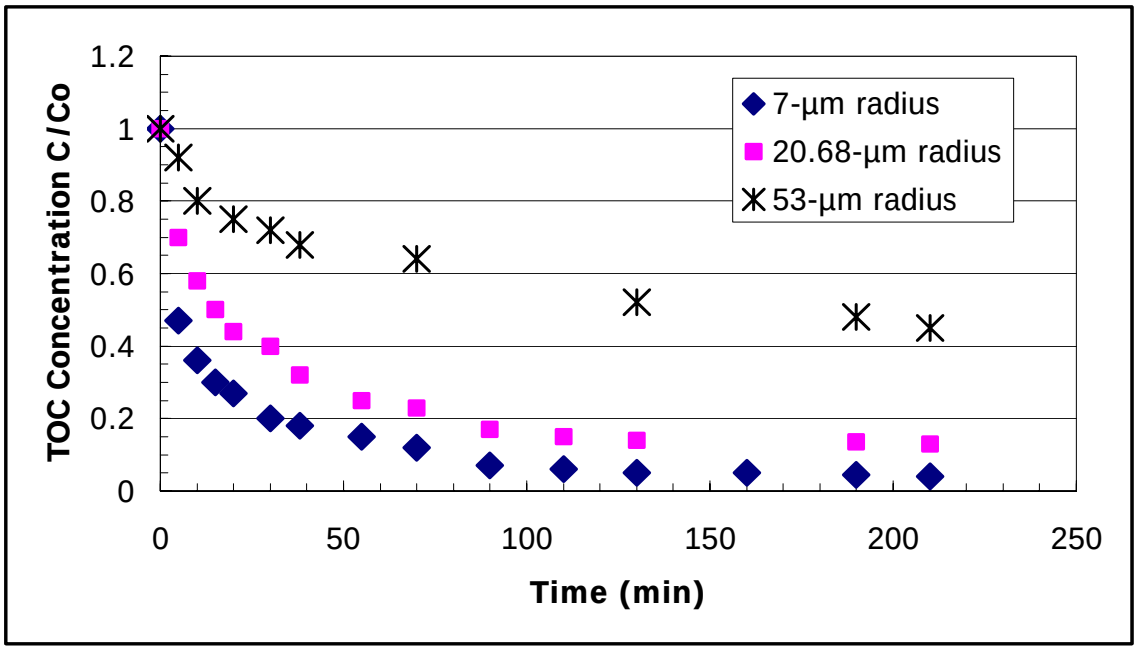

Figure 2-16. Effect of particle size on the rate of adsorption of TCP on a PAC in batch tests (Najm et al. 1990).

PAC does have some disadvantages though. The inlets of surface water treatment plants often have high levels of NOM, which creates a highly competitive atmosphere for adsorption of MIB. Other treatment chemicals, such as oxidants and coagulants, are also commonly added with PAC, and can adversely effect MIB removal. GAC contactors or filter adsorbers are used after conventional treatment so the competition for removal is not as great. GAC also does not come into contact with oxidants as often as PAC could. Although it is more expensive than PAC, GAC is more efficient as its entire capacity can be utilized in a properly designed system. When the capacity of the GAC is spent, it can be reactivated and placed back into service, also meaning improved efficiency over PAC.

In some cases the reactivated GACs actually outperform the virgin counterparts, as is shown in Figure 2-17 (Moore et al. 2001, MacKenzie et al. 2004).

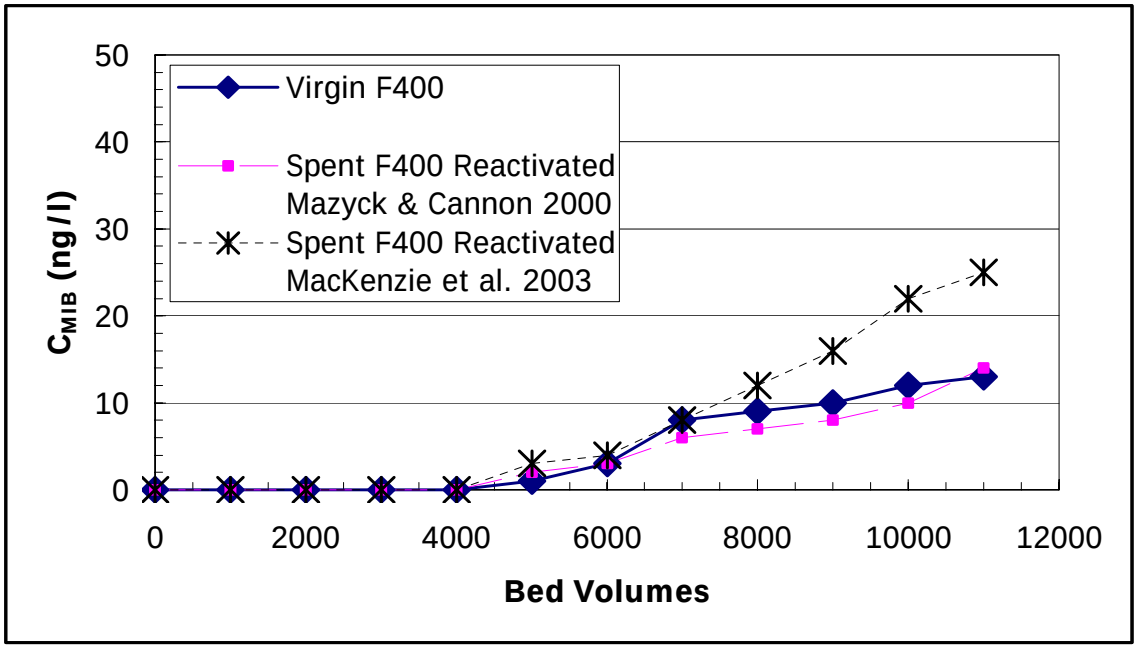

Figure 2-17. MIB breakthrough curves for F400 and two tailored reactivations of spent F400 in raw water (Mazyck and Cannon 2000, Mackenzie et al. 2004).

PAC Design

The design of a PAC dosage system can be very important in the PAC's ability to remove tastes and odors. PAC is most often applied wet, as a slurry (MacLeod et al. 1995). Water treatment plants use a variety of equipment to introduce the PAC slurry, so the length of time that a PAC has been wetted varies from a few minutes to a few days. MacLeod et al. (1995) showed in bench-scale testing that wetting time does not have a significant impact on MIB performance (Figure 2-18). The data in Figure 2-18 would suggest that if the hypothesis concerning water adsorption put forth by Pendleton et al. (1997) were true, then the diffusion of water in the PAC pores occurs extremely quickly.

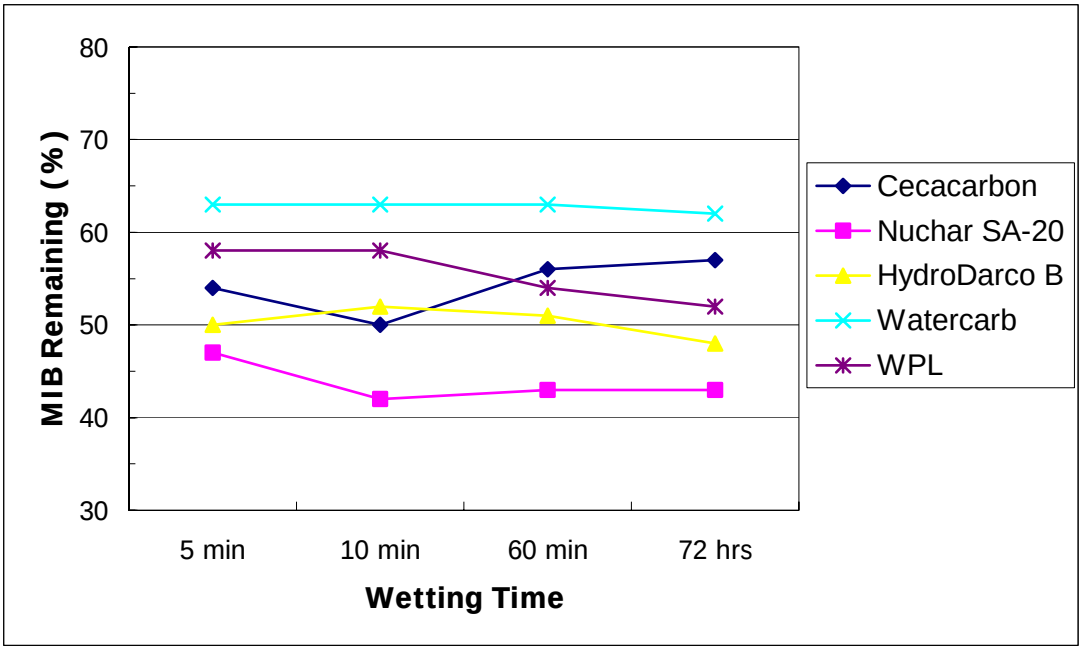

Figure 2-18. MIB remaining in solution versus the wetting time of the PAC (MacLeod et al. 1995)

Other concerns for water treatment plants exist in designing the PAC dosage. One problem for water utilities lies in the fact that much of the MIB testing that has been described was performed under unrealistic conditions. Experiments testing MIB removal by PAC performed at equilibrium or in deionized water do little to predict the performance in actual treatment plants. Some researchers have performed meaningful studies however, in attempts to optimize the PAC dosage required (Lalezary-Craig et al. 1988, Gillogly et al. 1999, Cook et al. 2001). Lalezary-Craig et al. (1988) began this work by showing the impacts of carbon dosage and contact time on MIB removal. Moreover, these authors altered the conditions by adding background organics, treatment chemicals, in addition to adjusting the contact time. Later work found that the initial concentration of MIB present in the source water did not affect the percent removal for a given PAC dose (Gillogly et al. 1999). This discovery simplified the procedure for predicting the necessary PAC dose required to abate odor episodes.

Moreover, this technique showed additional promise when single point isotherm tests predicted the dosages required in four different raw waters. Continuation on this work used the homogenous surface diffusion model to predict the PAC dose required (Cook et al. 2001). Jar test data performed in similar conditions to those found at existing treatment plants confirmed the model's predictions. Therefore, the potential exists for water utilities to effectively counter odor episodes with PAC with limited laboratory testing.

Despite improvements in models, the most effective means to predict and respond to MIB problems at a water utility is to use performance-based testing (MacLeod 2000). Laboratory tests can effectively predict full-scale performance if properly designed and utilized. As Water Quality Supervisor at Manatee County Water Treatment Plant (MCWTP), Bruce MacLeod has spent several years studying MIB and geosmin. MacLeod created a bench-scale protocol that yielded excellent correlations for MIB ($r^2 = 0.92$) and geosmin ($r^2 = 0.96$) to the full-scale removal. These excellent correlations allow MCWTP to test all PACs from companies bidding for their contract prior to making any purchasing decisions. The bench-scale tests results produce a performance factor for each PAC that will be multiplied by the price of each PAC. Knowledge of how the PAC will perform in the full-scale plant allows MCWTP to get the best PAC for their plant. Use of performance based testing is an important step towards proper use of activated carbon in water treatment plants.

Competition from NOM

The presence of NOM is central to the adsorption of MIB onto activated carbon for two primary reasons: NOM is ubiquitous in surface waters and has the ability to outcompete MIB for adsorption sites on the carbon. As described above, MIB is a

metabolic by-product of cyanobacteria and actinomycetes that are present in surface waters throughout the world. These same surface waters will invariably have NOM present at concentrations magnitudes higher than MIB. Moreover, conditions that worsen taste and odor episodes such as drought, increased nutrients, and warm temperatures can also increase NOM levels in the surface water. Indeed, it is impossible to research the adsorption of MIB onto activated carbon without considering the impact of NOM on performance.

The first demonstration of the impact of NOM on carbon's ability to sorb MIB occurred in 1977 by Herzing et al. The authors performed bench-scale adsorption tests with PAC and small column tests with GAC to evaluate adsorption of MIB and geosmin. All tests showed more adsorption of geosmin than MIB, which was later confirmed by other researchers (Lalezary et al. 1986a, Vik et al. 1988, Kim et al. 1997).

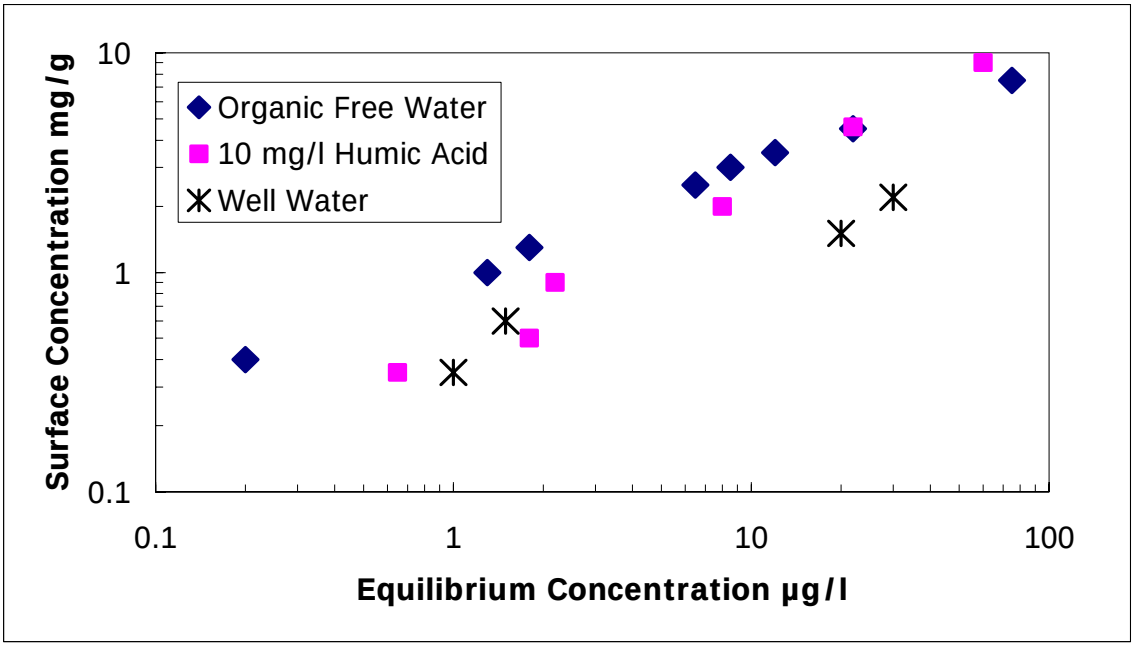

Figure 2-19. Adsorption of MIB (Herzing et al. 1977).

Tests that had humic acid, or other natural organics present in solution resulted in less MIB adsorption compared to tests in which no other organics were present

(Figure 2-19). Similar tests after this work showed that NOM had the same deleterious effects on MIB adsorption (Chudyk et al. 1979, Lalezary et al. 1986b, Lalezary-Craig et al. 1988).

Newcombe and coworkers performed many studies concerning the adsorption of NOM and the effects on MIB adsorption (Newcombe et al. 1997, Newcombe and Drikas 1997, Newcombe et al. 2002, Newcombe et al. 2003a,b). In order to understand how NOM competes with MIB for carbon sites, NOM adsorption should be examined. However, the adsorption of NOM onto activated carbon is difficult to characterize, much like NOM itself. NOM is a group of compounds with a wide range of sizes and different surface characteristics, therefore it is difficult if not impossible to pinpoint carbon's physical or chemical characteristics responsible for adsorption (Swcharzenbach 1993). Research has proven though, that both pore size distribution and surface chemistry impact NOM adsorption (Lee et al. 1988, Summers and Roberts 1988, Newcombe et al. 1997, Newcombe and Drikas 1997, Newcombe et al. 2002a). Size fractionation on NOM illustrated that the pore size distribution heavily impacts adsorption because of physical limitations (Newcombe et al. 1997, 2002a). Expectedly, the smaller weight fractions of NOM adsorbed in the micropores, while larger weight fractions adsorbed in mesopores (Newcombe et al. 1997, 2002a). Therefore the amount of NOM adsorbed on a specific carbon was related to the amount of volume and surface area in pores available to the size of the NOM (Summers and Roberts 1988, Newcombe et al. 1997, 2002a). An example of this in Figure 2-20 is the adsorption of a mid-weight fraction of NOM using different activated carbons. The amount of this NOM

weight fraction adsorbed had a direct relationship with mesopore volume; HP had the most mesopore volume, F400 next highest, and PCO the least.

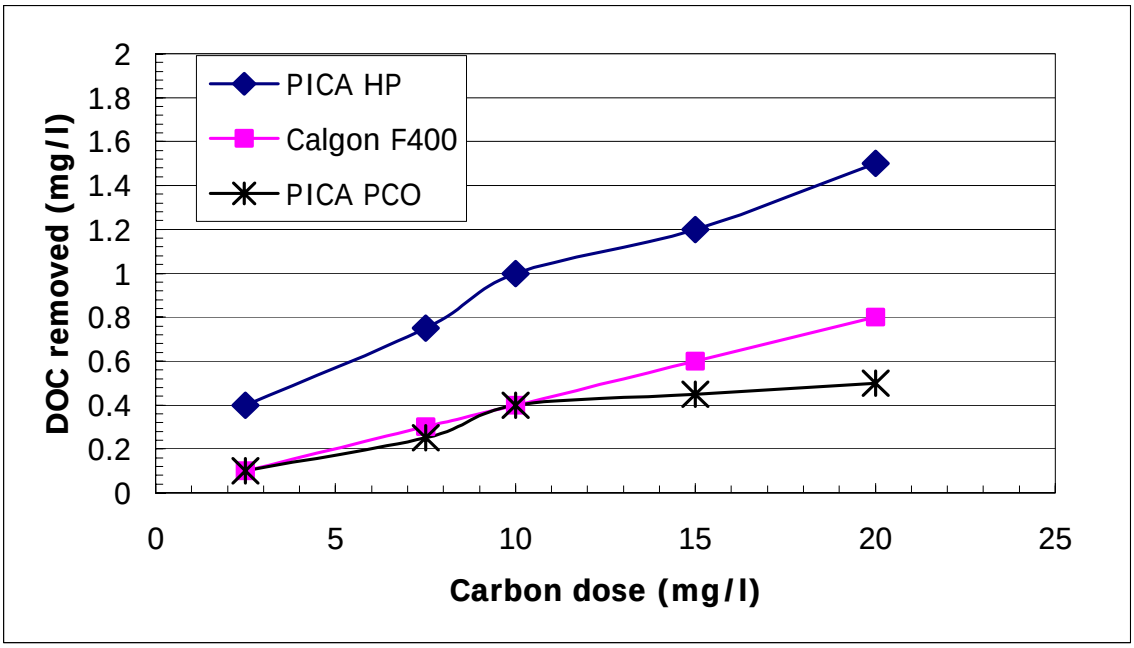

Figure 2-20. DOC removed as a function of carbon dose (Newcombe et al. 2002b).

Electrostatic forces also affect adsorption of NOM onto activated carbon (Summers and Roberts 1988, Newcombe and Drikas 1997, Newcombe et al. 2002a). NOM and activated carbon have functional groups on their surface giving them a charge at certain pH values, with NOM typically having a negative charge (Schwarzenbach 2003). Different activated carbons have a range of charges, which are affected by their carbonaceous precursor and activation technique (Wigmans 1989, MacLeod and Simpson 1993). Summers and Roberts (1988) performed adsorption tests with NOM and activated carbons with and without ionic salts present to assess the role of electrostatic forces on adsorption. Interestingly, increasing the ionic strength of the solution affected two different carbon adsorbents differently. Moreover, a positively charged carbon was negatively impacted by the increased ionic strength, while a negatively charged carbon had greater adsorption in these conditions. Indeed, this

suggests that electrostatic forces do impact adsorption, as the predominantly negatively charged NOM was drawn to the positively charged carbon in the low ionic strength solution. Increases in the solution ionic strength suppressed the electrostatic forces and therefore hindered NOM adsorption onto the positively charged carbon.

Newcombe and Drikas (1997) found similar results testing NOM adsorption onto two activated carbons. In addition to supporting the findings described above, these authors also investigated the effect of pH and the charge of the carbon surface. Electrostatic forces can exist between individual NOM in addition to between the NOM and activated carbon. Therefore, at high surface concentration and high pH values, adsorption can be hindered by repulsive forces between NOM. Moreover, increases in ionic strength at these conditions actually increased adsorption by negating the repulsive forces. These works show the importance of considering electrostatic forces when examining NOM adsorption onto activated carbon. Recent work by Newcombe et al. (2002a) however lessens the role of surface charge in the adsorption of NOM. Here, the authors thoroughly characterized the physical and chemical attributes of six activated carbons and then tested their ability to adsorb different forms of NOM. The performance of the carbons' adsorption of different fractions of NOM related well to the physical characteristics of the adsorbents. Indeed, these tests led the authors to conclude that the major influence on NOM adsorption onto activated carbon was the pore size distribution.

Once the deleterious effects of NOM on MIB removal by activated carbon were discovered, attempts to uncover the reasons for this phenomenon began. It follows that as different size fractions of NOM adsorb in different size pores, then different size fractions

will impact MIB more so than others. The presence of the smallest of four size fractions separated by Newcombe et al. (1997) was the most detrimental to MIB adsorption.

Figure 2-21 compares MIB isotherms in three different competitive scenarios: with the smallest fraction of NOM (MW < 500), the largest size fraction of NOM (MW > 3000), and NOM-free water. MIB adsorption was influenced radically by the different compounds that are present in the water.

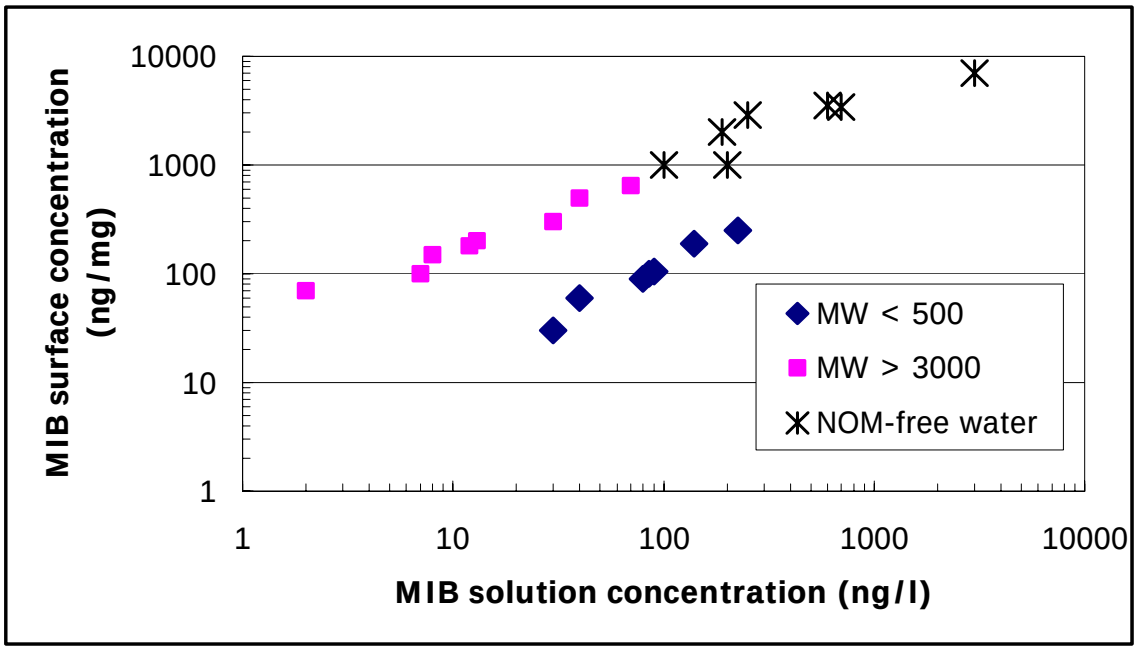

Figure 2-21. Log-log plots of MIB adsorption isotherms in the presence and absence of NOM (Newcombe et al. 1997).

Interestingly, the largest weight fraction of NOM (MW > 3000) had little to no impact on MIB adsorption when compared to the NOM-free water. These large molecules do not compete for the small adsorption sites as MIB prefers. However, the presence of the smallest fraction NOM is quite deleterious to MIB adsorption. Moreover, Newcombe and coworkers believed that the smaller NOM outcompete MIB for adsorption sites because of the increased concentration, and pore blockage and pore restriction (Newcombe et al. 1997, Newcombe et al. 2002b). Indeed, adsorption

experiments with different size NOM fractions and different activated carbons show that the low-molecular weight NOM impact performance of microporous carbons and larger molecular weight NOM hindered MIB adsorption of mesoporous carbons (Newcombe et al. 2002b). NOM restricts MIB adsorption onto activated carbons by utilizing active sites for adsorption and restricting diffusion by blocking pores.

Effect of Treatment Chemicals on MIB Adsorption

Coagulants

Despite the propensity for surface water utilities to use PAC and coagulants together, little in known about how these treatment processes work together. MacLeod (2000) has investigated the impacts of PAC and alum together in bench and full-scale. At Manatee County Water Treatment Plant, PAC is dosed at the plant intake, while alum is added approximately three minutes later in the rapid mix basin. MacLeod believes little MIB removal occurs once the PAC comes into contact with the coagulant. Bench-scale performance-based tests (which correlate well to the full-scale plant), show that PAC alone for three minutes removes approximately the same amount of MIB as it does in tests with PAC and the full assortment of conventional treatment. Thus, the PAC is removing little to no MIB once the alum is added. Additional tests illustrated the detrimental effects of alum, when PAC was added before and after alum addition. The causes of this phenomenon are not known, but additional publications highlight this problem in order to make utilities aware that PAC may not be used in the most efficient manner if the impacts of other treatment processes are not considered (Snoeyink 1990, Cummings et al. 2000).

Chlorine

Chlorine is another treatment chemical added to source water while also in contact with PAC. McGuire and Suffet (1984) found that chlorine oxidized the carbon surface. The performance of the oxidized carbons was then compared with their virgin counterparts for the uptake of four SOCs. McGuire and Suffet found that the oxidized carbons removed less SOCs than did the virgin carbons. They concluded that the amount of chlorine that was reduced on the carbon surface was responsible for the PACs diminished capacity for the SOCs. Lalezary and coworkers (1986b, 1988) showed similar effects of chlorine on PAC removal of MIB. Gillogly et al. (1998b) continued this work and their results agreed with those of Lalezary and coworkers, as chlorine was detrimental on PAC's ability to remove MIB over a variety of contact times (Figure 2-22).

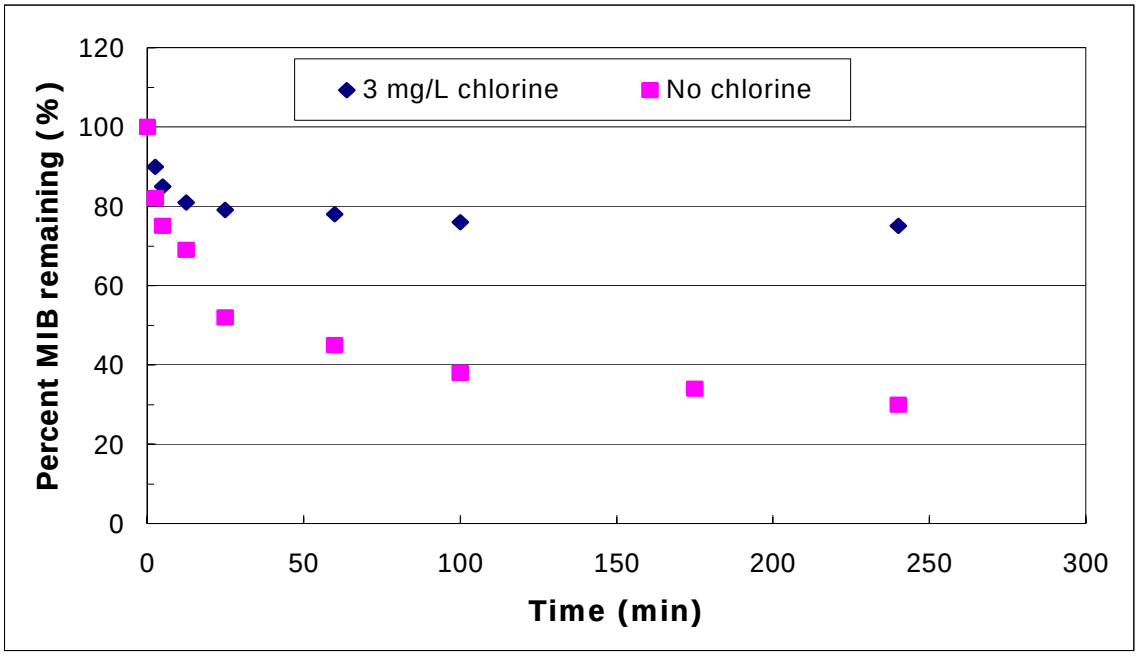

Figure 2-22: Effect of free chlorine on MIB adsorption (Gillogly et al. 1998b).

Figure 2-22 shows that free chlorine severely limits the PACs performance. Gillogly et al. (1998b) believed that chlorine oxidized the carbon, thus adding acidic

functional groups to the surface. The increase in functional groups was shown to decrease MIB removal in batch tests (Pendleton et al. 1997, Considine et al. 2001). Therefore, Gillogly et al. proposed that chlorine was deleterious to MIB removal by PAC because of increased acidity on the surface.

CHAPTER 3
EXPERIMENTAL METHODS

PAC Activation

The wood-based precursor was pre-charred in a paper mill boiler at approximately 923 K before shipment in sealed containers to the laboratory. The particle size of this precursor was roughly a few centimeters in length and less than one centimeter in width. Prior to activation the precursor was dried in a gravity oven at 110 ºC to drive off moisture. After drying the precursor was subsequently stored in a desiccator until use.

Activations were conducted in a quartz-fluidized bed placed in an Applied Test Systems, Inc. clamshell furnace similar to that used by Mazyck and Cannon (2000, 2002). Three grams of the precursor were added to the fluidized bed where it rested upon a porous plate, whereby when gases flowed through, the precursor became fluidized. All activation protocols had two phases: first, high temperature exposure to steam at various flow rates to develop mesoporosity, followed by an inert atmosphere (N_2 at 1.2 L/min) at the same temperature to rid the surface of oxygen functionality. The temperature ranges investigated were between 650 and 900 ºC. Steam to carbon ratios between 0.02 and 0.68 lb H_2O/ lb PAC were utilized in the furnace. The amount of steam was controlled with a flowmeter using volumetric flowrates of water between 0.015 and 0.4 mL/min. The water was piped through a tube furnace set at 300 ºC, which served as a pre-heater for the clamshell furnace. This arrangement assured that the water would enter the fluidized bed as steam. Lastly, the activation time was investigated. The time the precursor was in contact with steam was varied between 5 and 15 min; short times to

maximize the potential for full-scale implementation. In every activation protocol steam was followed by 15 min in an inert environment at the same temperature as the steam step. At the end of every activation, the furnace was turned off and the sample was allowed to cool in an inert environment. After cooling, the sample was removed from the fluidized bed, weighed and placed in a desiccator. Mass losses for duplicates were typically within 3%.

After activation, all samples were mechanically powdered for 10 min to less than 325 mesh. A homogenous 10,000 mg/L slurry was made using 0.2 g of the powdered sample added to 20 mL of nanopure water. All powders and slurries were stored in desiccators between experiments.

Commercial Activated Carbons

Common commercial activated carbons received from the manufacturer were dryed before use in an oven at 110 ºC. Three commercial PACs and one commercial GAC were used in various experiments throughout this work. Commercial PACs, Calgon WPH, NORIT Hydrodarco B, and Mead Westvaco Aquanuchar were used in performance based testing for MIB removal. These three PACs were used as a comparison for the tailored bark char carbons produced in the laboratory. The GAC, Calgon F400, was used as the starting material in creating chemically treated activated carbons discussed in Chapter 5 of this work. Additionally, Calgon's WPH was the PAC used for all studies investigating the effects of alum on PAC performance for MIB. These results are discussed in Chapter 6.

Raw Water

The water used in all of the MIB batch tests was raw source water from one of four Florida utilities: Manatee County Water Treatment Plant (MAN), West Palm Beach

Water Treatment Plant (WPB), Lake Washington (Melbourne) Water Treatment Plant (MEL), and Hillsborough River (Tampa) Water Treatment Plant (HIL). All samples were collected on site and stored in 20-gallon jerricans. The raw water was then stored at 4 ºC until use in laboratory tests. All waters contained high levels of natural organic matter (NOM), with TOC concentrations ranging from 10-20 mg/L.

Performance Testing

MIB

^{14}C radiolabeled MIB, purchased from American Radiolabeled Chemical (St. Louis, Mo), was used for all laboratory MIB testing. The ^{14}C MIB arrived as 1.53×10^5 ng MIB/mL in purge and trap grade methanol, and after receipt was used to make a 20 mL stock solution of 306,000 ng ^{14}C MIB/L-methanol. Five aqueous standards (30.6, 61.2, 122.4, 183.6, 244.8 ng MIB/L) were subsequently made from this stock solution. The standards were measured regularly to develop a standard curve for calculating ^{14}C-MIB concentrations.

TOC Analysis

All TOC samples were measured using a Tekmar Apollo 9000 Combustion TOC analyzer. Each sample was measured three times and the mean of these used for the final value. Standard deviations for the samples were typically less than 5 %. Standard curves were updated regularly, and standards were also run as samples during runs to ensure accuracy between calibrations.

Batch Tests

All batch experiments were carried out in 50 mL gas tight syringes at room temperature. 50 mL of raw water was measured in a graduated cylinder, then added to the syringe, followed by 25 μL of the ^{14}C-MIB stock solution; creating a MIB concentration

of 153 ng/L in the syringe. This concentration is higher than what is typically found in source waters, but the influent concentration does not significantly affect the percent removal (Gillogly et al. 1999). Immediately after the ^{14}C-MIB addition, alum, acid (HNO_3) or base (NaOH) for pH adjustment, and PAC in slurry form were added via automatic pipetter as needed. The syringe was then sealed with a small amount of headspace and allowed to mix on a rotisserie style mixer for the desired contact time. Upon completion of the mixing period, a 0.45 μm luer-lock nylon filter was attached to the syringe and the PAC was separated from solution. 3 mL of this filtrate was promptly added to 18 mL of scintillation cocktail and the vial was placed in a Packard scintillation counter in a manner similar to previous studies using radiolabeled MIB (Gillogly et al. 1998a, Nowack et al. 2004). All samples were counted twice in the scintillation counter for ten minutes each time.

Batch tests performed for TOC analysis used the same steps as above until after mixing. Following the mixing the syringe plunger was carefully removed so as not to disrupt any floc formation. The syringe was placed in the upright with the open end exposed. Twenty milliliters was promptly pipetted from the top of the syringe and then filtered through a 0.45 μm membrane filter using vacuum filtration. The filtrate was stored at 4º C until analyzed for TOC levels.

Pore size distribution analysis

A Quantachrome Autosorb I was used to measure all pore size distributions. Each powdered sample was outgassed at 383 K for 24 hours. The sample, between 0.01 and 0.024 g, was then analyzed at –196 ºC (77 K) with N_2 as the adsorbate. The density functional theory (DFT) was used to develop the pore size distribution data in the micropores (< 20 Å) from the nitrogen isotherm, while the BJH model was used for all

pores greater than 20 Å. Duplicate samples were analyzed by the Autosorb for all PACs created, and their averages are shown in the figures. The average error was found to be less than 5%.

Chemical Characterization

Point of Zero Charge

The point of zero charge (PZC) determined the amount of surface acidity on the PACs. The PZC is the pH value at which the external and internal surface of the carbon is at equilibrium. These values were measured from a one-point reverse mass titration (10% PAC/water), after mixing for 24 hours. Before mixing DI water was purged with N_2 for 20 minutes to drive off CO_2. The purged water was then added to the carbon mass via an automatic pipetter, and the sample was then mixed on a shaker table. After mixing the sample was removed, and the pH promptly recorded.

Boehm Titration

Surface acidity concentrations were also determined from titration techniques based upon previous experiments (Boehm 1966, Salame and Bandosz 2001). Individual 0.5 g samples of carbon were mixed for 24 hours in 25 mL of 0.05 N NaOH. After passing the solution through a 0.45 μm filter, 20 mL of the filtrate was titrated with 0.1 N H_2SO_4. The amount of base (NaOH) consumed by the carbon sample was determined by comparing this titration to that of a blank. Since any base consumed by the carbon sample occurred via neutralization of surface functional groups, the concentration of the surface acidity is known.

CHAPTER 4
TAILORING THE ACTIVATION OF BARK CHAR TO PRODUCE A PAC WITH SUPERIOR ODORANT REMOVAL CAPABILITY

Analysis of the Carbonaceous Precursor

Creating an activation protocol, tailored for MIB removal, began with the selection of the carbonaceous precursor. A wood-based material, previously charred, was chosen for its availability and because it is typically landfilled. Therefore, I wanted to demonstrate that this waste material could be used for a beneficial purpose. Once the precursor was selected, a pore analysis was performed in order to determine the most applicable activation technique(s).

There are numerous models that have been used to characterize the physical structure of adsorbents; with each model designed based on factors, such as the method of pore filling and pore geometry. Moreover, knowing that one method cannot accurately portray every pore type within the PACs created (Thommes 2002), the authors decided to combine two generally accepted models: DFT for the micropores (< 20 Å) and BJH for the meso- and macropores (> 20 Å). DFT has often been used to characterize microporous carbons using nitrogen adsorption (Ryu et al. 1999, Mazyck and Cannon 2000, Khalili et al. 2000, Do et al. 2001). Reviewers of gas adsorption models have stated that the DFT method is the latest and most accurate model for quantitative micropore analysis (Blacher et al. 1999, Dabrowski 2001). Moreover, DFT has been shown experimentally to accurately portray micropore structures in various adsorbents when compared with other established models (e.g., Dubinin-Stoeckli, Horvath-Kawazoe)

(El-Merraoui et al. 2000, Korili and Gil 2001), so it was chosen as the model for micropore characterization. Since the authors felt that the entire pore structure should be analyzed, an alternative method was found for analyzing the PACs' meso- and macropores.

The meso- and macropores were modeled using the well-established BJH method, first developed in 1951 (Barrett et al. 1951). The Kelvin equation, theoretical basis for the BJH method, lends itself well to mesopore characterization, but not for pores less than 15 Å (Dubinin 1966). That being known, the BJH method has been used to characterize carbonaceous materials that are primarily mesoporous (Yoshizawa et al. 1997), or used in conjunction with other techniques for materials that have micro- and mesopore development (Khalili et al. 2000, Do et al. 2001). Therefore, combining the DFT and the BJH models can provide a reasonably accurate picture to compare the physical structures of the PACs created in the laboratory.

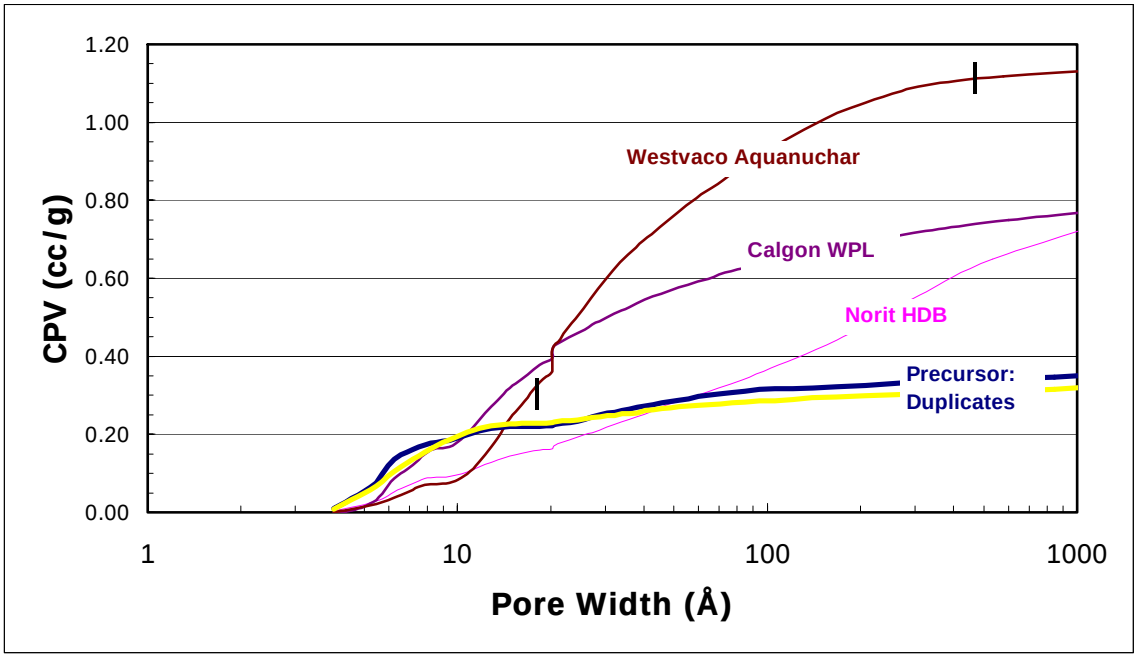

Figure 4-1. PSD of carbonaceous precursor and three commercially available PACs using DFT and BJH. (CPV = Cumulative Pore Volume)

Figure 4-1 shows the pore size distribution (PSD) of the carbonaceous precursor along with three commercially available PACs. Duplicates are shown for the precursor to illustrate the typical error found in the analysis. As seen in the figure the duplicate PSD curves are nearly identical at 20 Å and differ by less than 6% at 1000 Å.

Table 4-1 lists the surface areas and pore volumes of the precursor along with the above commercially available PACs. The data indicated that most of the precursor's surface area and pore volume existed in the micropores. This pore range would seem important since micropores would likely serve as the sites for permanent adsorption of MIB since its largest diameter is only 6 Å. Thus, since adequate microporosity existed within the precursor, the principal goal was to increase mesoporosity during activation.

Table 4-1. Surface areas, pore volumes and MIB performance data for the precursor and three commercially available PACs.

Absorbent	**BET Surface Area (m^2/g)**	**DFT Micropore Volume (cc/g)**	**BJH Mesopore Volume (cc/g)**	**MIB Removal (%)**
Precursor	494	0.2250	0.1055	30
Calgon WPL	1064	0.3953	0.3547	75
Norit HDB	452	0.1623	0.4877	60
Westvaco Aquanuchar	1263	0.3622	0.7578	75

The performance data from the three commercial PACs from Table 1 further supports the theory that mesoporosity should be increased. Calgon's WPL and Westvaco's Aquanuchar both have a strong combination of micro- and mesopores, while Norit's HDB is more of a mesoporous PAC. Since WPL and Aquanuchar outperformed

the mesoporous HDB (Table 4-1), it was assumed that pore volume throughout the micro- and mesopore range was important.

Optimization of Activation Parameters

Activation temperature, activation time, and steam-to-carbon ratio were the three parameters investigated. These activation variables have been investigated for various materials in the past, but the success was often based on the resulting carbon's physical properties, such as mass loss, surface area, or pore volume (Tomkow et al. 1977, Rodriguez-Reinoso 1982, Gonzalez et al. 1994, Molina-Sabio et al. 1996). The success of the tailored PACs in this study were judged strictly on performance in laboratory batch studies designed to simulate water treatment plant conditions, while the PSD data were collected and analyzed in hopes of learning which pore sizes were important for MIB removal.

Activation Temperature

Temperature, being the dominant activation parameter because it impacts the rate of gas diffusion, reaction rate, and thermodynamic stability of the carbon, was the first parameter investigated. Arbitrarily, 0.085 lb H_2O/lb PAC for 5 min followed by pyrolysis for 15 min were chosen as the initial conditions while temperature was varied between 923 and 1173 K in 50 K increments. After each activation, the resulting PAC was tested for MIB removal from the three raw waters, and these results are presented in Figure 4-2 (all data from tailored PACs in Appendix A). As activation temperature increased up to 1123 K, MIB removal likewise increased. Interestingly, the PAC produced at 1173 K did not continue this trend. This decrease in performance could be attributed to a mild collapse of graphene layers, which resulted in a loss of pore volume. Therefore, 1123 K was determined as the recommended operating temperature for subsequent activations.

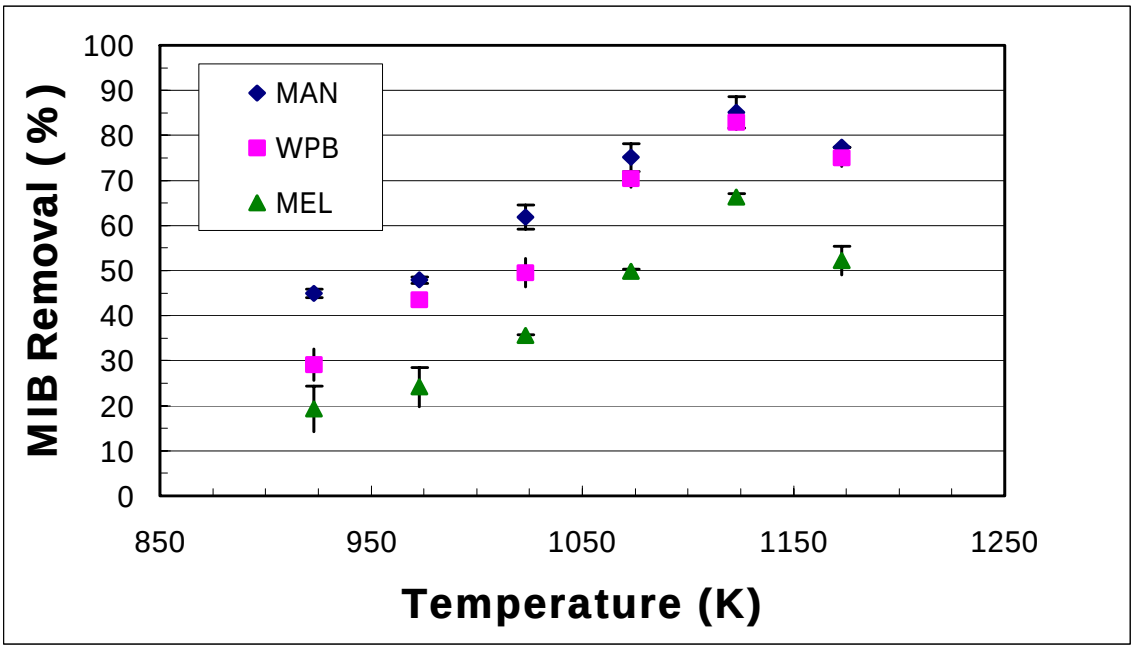

Figure 4-2. MIB removal in three Florida utilities' raw waters versus activation temperature (MAN = Manatee County Water Treatment Plant, WPB = West Palm Beach Water Treatment Plant, MEL = Lake Washington (Melbourne) Water Treatment Plant)

The surface areas and pore volumes for the four carbons activated at 923, 1023, 1123, and 1173 K are listed in Table 4-2. Interestingly, the PAC activated at 923 K had an almost identical pore structure to the precursor (Figure 4-1). Therefore, because the precursor was charred at a temperature close to 923 K, further activation at this temperature did not have much effect. In contrast, activating at 1023 K increased the micropore pore volume by 14 %, and also resulted in a modest 30 % increase in mesopores (i.e., 20 – 500 Å). The PAC activated at 1123 K showed the largest improvement in both of these pore ranges with pore volume increases of 29 % in the micropores and over 120 % in the mesopores. Further increasing the activation temperature to 1173 K was deleterious. The micropore volume of the 1173 K activated PAC was only 19 % greater than that of the precursor, while the mesopore volume

increased by 80 %. Considering the MIB performance data from Figure 4-2, it appears that the larger pore widths (i.e., > 20 Å) are necessary for superior removal.

Table 4-2. Surface areas and pore volumes for four PACs activated at increasing temperature.

Activation Temperature (K)*	BET Surface Area (m^2/g)	DFT Micropore Volume (cc/g)	BJH Mesopore Volume (cc/g)
923	518	0.2255	0.1116
1023	533	0.2630	0.1370
1123	696	0.2914	0.2603
1173	641	0.2691	0.2150

* All PACs activated for 5 min in steam and 15 min in N_2 @ 0.085 lb H_20/lb PAC.

Since one objective of this work was to assist water utilities solve their taste and odor problems without increasing their PAC expenditures, the mass loss of the precursor during activation must not be excessive. An unreasonably high mass loss, or conversely low yield, would negate any improvements in performance, since the cost of PAC production would be high. The mass loss that occurred during activation in the fluidized bed is shown versus activation temperature in Figure 4-3. As expected, the highest temperatures resulted in the highest mass losses, so operating at elevated temperatures without changing activation time would decrease the overall yield. However, the mass losses found here are not unreasonable for activated carbon production, as activation of other precursors have had similar or higher mass losses (Wigmans 1989). Therefore, considering the yield of PAC and MIB performance, the optimum activation temperature remained at 1123 K. Figure 4-3 also demonstrates that mass loss should not be used as a tool for predicting performance because the 1173 K activated carbon had the highest mass loss, but did not perform as well as the 1123 K activated carbon.

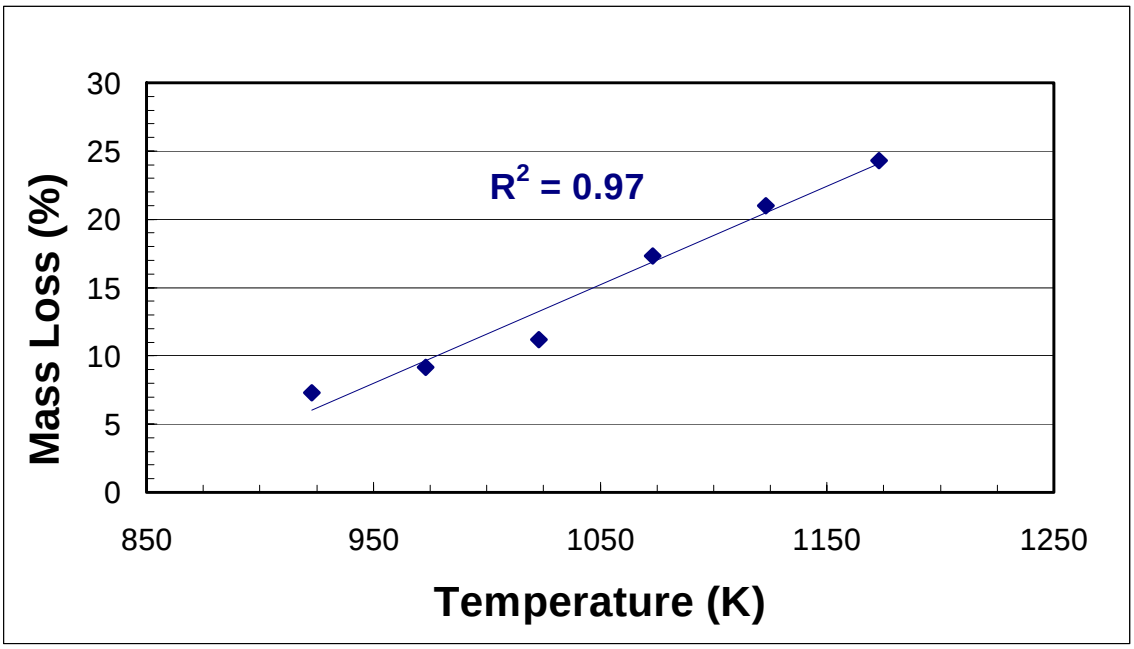

Figure 4-3. Mass loss versus temperature resulting from activation (All PACs activated for 5-min in steam at 0.085 lb. steam/lb. carbon, followed by 15-min in an inert environment).

Steam-to-carbon ratio

After the influence of temperature on MIB removal was explored, the steam-to-carbon ratio was investigated to discern how steam would influence MIB removal and PSDs. At the three temperatures investigated (923, 1023, and 1123 K), MIB removals had little improvement above a steam-to-carbon ratio of ca. 0.17 lb. steam/lb. carbon (Figure 4-4). This ratio was considered to be the best operating point for optimizing MIB removal. Increasing the steam rate past 0.17 lb./lb. showed only minor improvements with respect to MIB removal, and steam rates less than this produced carbons that performed 7-15 % worse. For example, when no steam was applied at 1123 K the resulting PAC removed ca. 75 % of the MIB, while the carbon activated at 1123 K in 0.17 lb./lb. removed almost 90 % of the MIB.

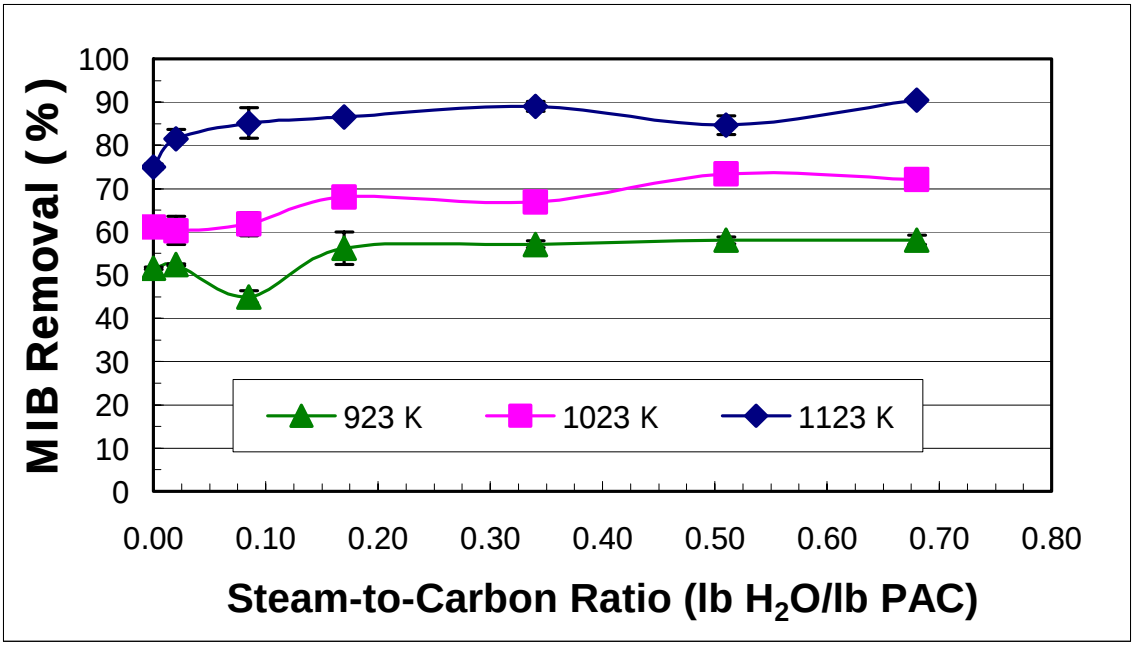

Figure 4-4. MIB removal in MAN versus steam-to-carbon ratio for 5 min in steam.

The effect of steam-to-carbon ratios on the pore volumes is shown in Table 4-3. These four PACs were activated at 1123 K for 5 min in steam followed by 15 min in an inert environment with four different steam-to-carbon ratios (0, 0.02, 0.085, 0.17 lb./lb.). None of the four steam-to-carbon ratios manifested any appreciable difference in microporosity, but the PACs produced at 0.085 and 0.17 lb./lb. had a significant increase in pore volume past 20 Å, compared to the PAC activated with 0.02 lb./lb. As with the activation temperature comparisons, the PSD data for these PACs also agrees with the MIB performance data. The MIB removal plateaued quickly with respect to increasing steam-to-carbon ratio (Figure 4-4); the pore volume in the mesopores likewise plateaued, as there was very little difference in the PAC produced with 0.085 and 0.17 lb./lb. Indeed, the hypothesis that steam would increase mesoporosity was correct, as a significant increase in mesoporosity occurred between 0 and 0.085 lb/lb (ca. 40%). However, activation temperature had the greatest overall effect on mesoporosity. When comparing the pore volumes of the precursor in Table 4-1 with the PAC activated at 1123 K with no

steam (0 lb/lb), the increase in mesoporosity is approximately 80 %. Therefore the combination of steam at 0.17 lb/lb and the optimum temperature of 1123 K produced the most mesoporous PAC.

Table 4-3. Surface areas and pore volumes for four PACs activated at 1123 K for 5 min in steam with an increasing steam-to-carbon ratio.

Steam-to-Carbon Ratio (lb./lb.)	BET Surface Area (m^2/g)	DFT Micropore Volume (cc/g)	BJH Mesopore Volume (cc/g)
0	605	0.2573	0.1560
0.020	660	0.2702	0.1903
0.085	696	0.2914	0.2323
0.170	672	0.2840	0.2210

Activation time

The last activation parameter investigated was the time the precursor contacted the steam, called here the activation time. Only short activation times were investigated (5 –15 min) in order to mimic conditions commonly found in the activated carbon industry (the 15 min pyrolysis step followed every activation). Figure 4-5 shows the insignificance of changing activation time on MIB performance, over this limited time range. Indeed, at the optimal temperature (1123 K), the difference in MIB removal was less than 3% for all three times investigated.

The surface areas and pore volumes of three carbons produced at the different times (all at 1123 K, 0.17 lb/lb) are shown in Table 4-4. Interestingly, the PAC with only 5 min of contact time with the steam had the most pore volume throughout the pore widths shown. Closer inspection of the pore volumes for these PACs indicated that the difference in the cumulative pore volume comes primarily from the micropores; as beyond 20 Å the PSDs have very similar slopes. In fact, the difference between the pore volumes past 20 Å for these three PACs was only 3%. Therefore, the small changes in

MIB performance found between the PACs created at the three different times is likely due to the similar pore structure seen in the PSD beyond 20 Å.

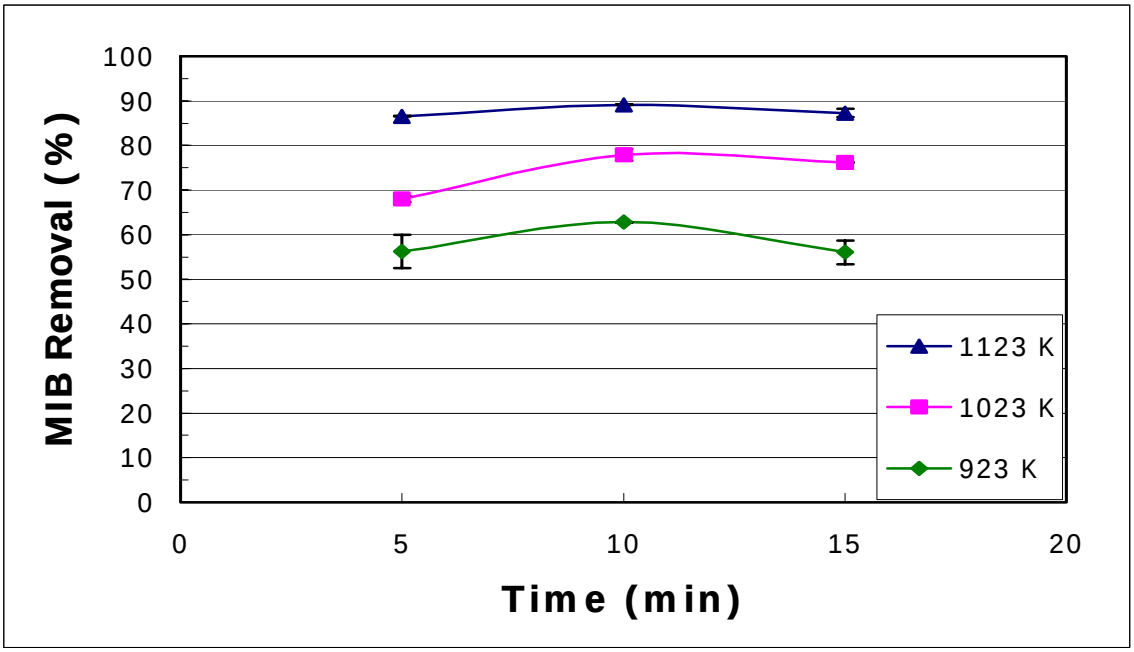

Figure 4-5. Effect of activation time on MIB removal in MAN.

Table 4-4. Surface areas and pore volume for three PACs activated at 1123 K with 0.17 lb/lb for three different times in steam followed by 15 min in an inert environment.

Activation Time (min)	BET Surface Area (m^2/g)	DFT Micropore Volume (cc/g)	BJH Mesopore Volume (cc/g)
5	672	0.2840	0.2210
10	584	0.2373	0.2205
15	621	0.2564	0.2160

Diffusion and MIB Removal in Raw Water

Analyzing the previously discussed pore volume values indicated that there exists a relationship between the physical structure of the tailored PACs and their performance in removing tastes and odors from raw water. The pore volume data in specific pore width ranges was determined in hopes of finding specific regions of importance for MIB adsorption.

Improvements in the microporosity (< 20 Å) of the tailored PACs did not contribute to improved performance in the batch tests (Figure 4-6). However, increasing the pore volume in the mesopores showed a strong correlation ($R^2 = 0.92$) to MIB removal in the raw water. It is not likely that these pores serve as the final adsorption sites for MIB because of its small size, but instead these pores aid in diffusion. Due to the small particle size of PAC, intra-particle diffusion is often the limiting factor for adsorption unlike bulk diffusion in GAC (Weber Jr. 1972). Thus, with adequate microporosity, increased pore volume in the larger pores allows MIB to diffuse more rapidly into the micropores for permanent adsorption. Indeed, the mesopores likely further increase in importance in extreme conditions such as even shorter contact times and even higher NOM levels. These results also indicate the importance of site specific testing, as every water utility has unique PAC operating parameters. Experimentation mimicking the plant's conditions in their source water is necessary to discern which PAC has the ability to best remove MIB.

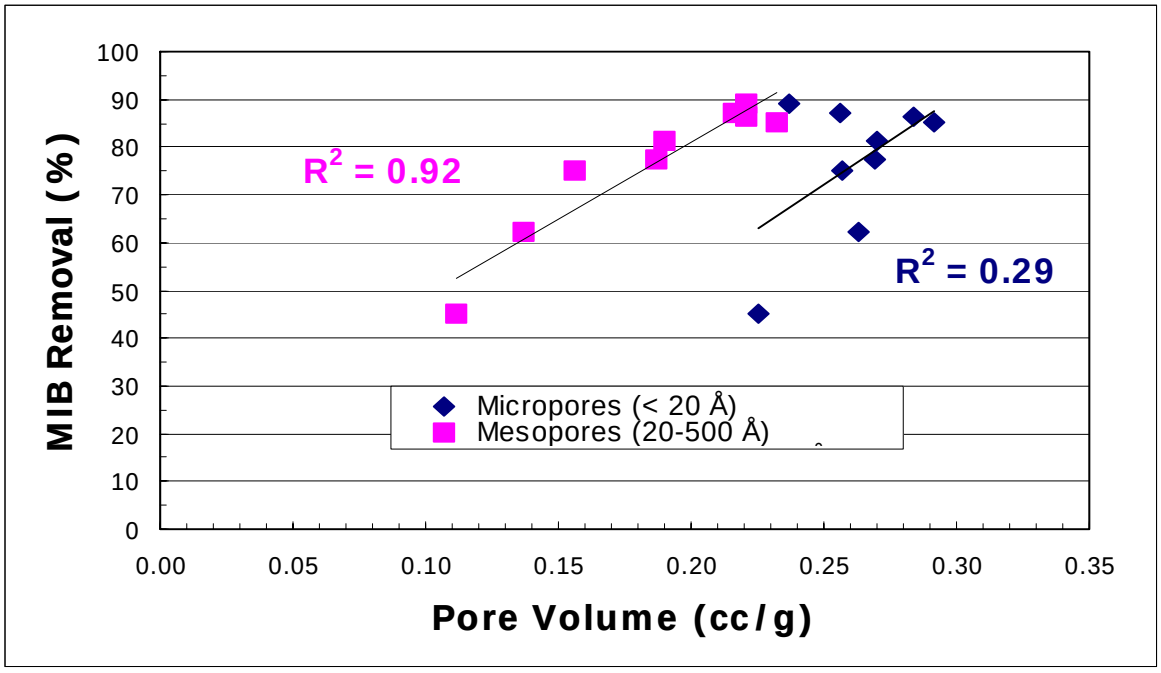

Figure 4-6. MIB Removal in MAN for a 20 min contact time versus pore volume.

Surface Chemistry of the Tailored PACs

Much was written above concerning the effects of surface oxygen functional groups on activated carbon's ability to adsorb MIB. Previous research showed in equilibrium tests using organic free water that increased functionality (e.g., oxygen groups) decreased carbon performance for MIB (Pendleton et al. 1997). Knowledge about the impact that surface groups have on PACs in non-equilibrium tests in competitive solutions is not known. Despite this lack of data, the authors hypothesized that creating PACs with limited oxygen functionality could only assist in optimizing performance, regardless of the role of surface chemistry in the batch experiments. In addition to improved pore structures, steam-pyrolysis activation protocols successfully created PACs with the desired surface chemistry. The PZC measurements for all of the tailored PACs revealed high values (> 10), indicating very basic surfaces (i.e., low oxygen functionality). The tailored PACs, however, were unable to give insight on the impact of surface chemistry on MIB adsorption, as all of the PZC values were similar. Chapter 5 investigates the role of PACs' surface chemistry on MIB performance in short contact time, high competition aqueous solutions to discern the importance of oxygen functional groups on MIB removal from natural waters.

Comparison to Commercially Available PACs

The success of the optimized tailored PAC (1123 K, 0.17 lb/lb, 5 min steam – 15 min pyrolysis) cannot be limited to comparisons between the different PACs created in the laboratory, but also in the ability to compete with existing products. Therefore, three commercially available PACs, all with 98% passing the 325 mesh, were tested in

the same raw water using identical conditions (Appendix B). Figure 4-7 shows that the tailored PAC not only competes with established PACs, but indeed outperforms them.

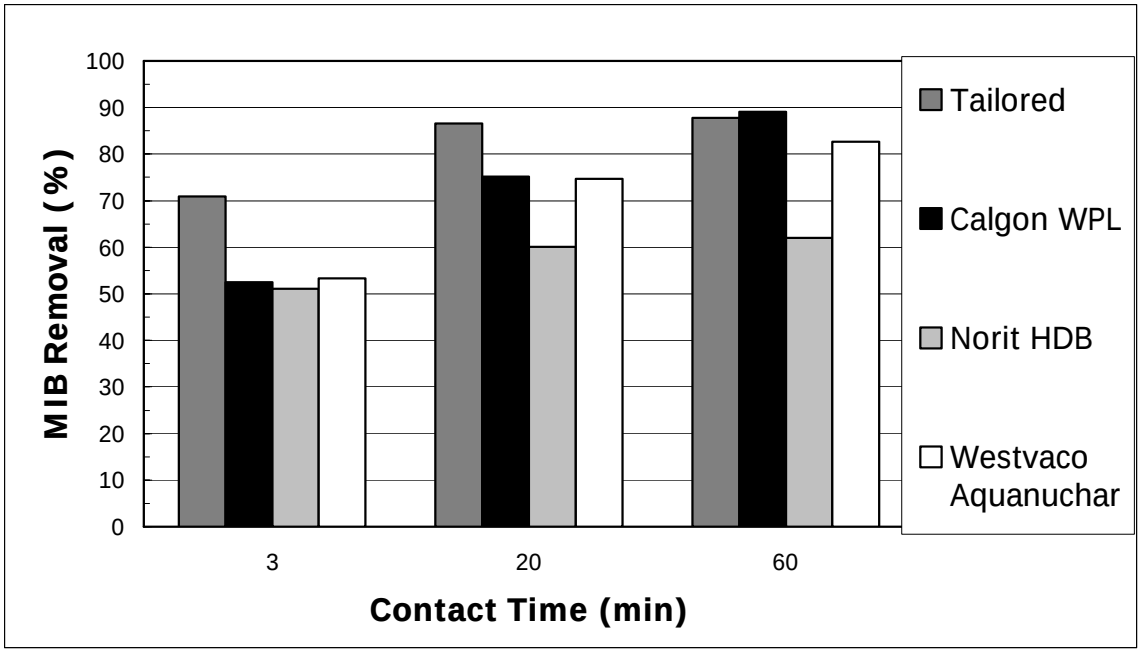

Figure 4-7. Comparison of various commercially available PACs to the tailored PAC.

However, since the PAC shown was tailored to perform well in the batch tests used here, its success is not surprising. Therefore, additional batch tests were completed at two additional contact times (3 min and 60 min), to simulate other operating conditions. Again the tailored PAC performed well and was only slightly surpassed by Calgon WPL at the longest contact time. These results are very encouraging and indicate that an activation protocol can be optimized to produce a high quality PAC for MIB removal in raw water experiments.

CHAPTER 5
PHYSICAL AND CHEMICAL CHARACTERISTICS OF ACTIVATED CARBON AFFECTING THE ADSORPTION OF MIB

The first objective of this research was to create two classes of PACs (as defined as 95% passing a 325-mesh, but retained by the 400-mesh) with specific physical and chemical characteristics: first, a set of PACs with similar surface chemistries and differing pore structures; and a second set with different surface chemistries, but with similar pore structures. In order to create the former, three grams of one of two sources of pine bark char was thermally treated in a fluidized bed furnace. The specifics of this activation method are found in Chapters 3 and 4. These PACs are herein called physically activated (PA), and the individual protocols for each are listed in Table 5-1.

Table 5-1. Activation protocols for physically activated PACs.

PAC	Precursor	Activation Protocol
PA-1	Wood Source 1	Steam @ 850 °C for 90 min, N_2 @ 850 °C for 15 min
PA-2	Wood Source 1	Steam @ 850 °C for 30 min, N_2 @ 850 °C for 15 min
PA-3	Wood Source 2	Steam @ 850 °C for 60 min, N_2 @ 850 °C for 15 min
PA-4	Wood Source 1	Steam @ 850 °C for 15 min, N_2 @ 850 °C for 15 min
PA-5	Wood Source 2	Steam @ 850 °C for 15 min, N_2 @ 850 °C for 15 min

The creation of the latter group of PACs described above utilized a combination of chemical and thermal treatments. The process began by mixing a large sample of Calgon F400 (ca. 50g) with a 50% nitric acid solution for 24 hours, followed by 24 hours of rinsing in DI water in a flow-through column. Upon drying, three equal masses of the treated carbon were exposed to an inert environment at different temperatures in a fluidized bed furnace, while another sample was untreated. The four PACs resulting from this procedure are called chemically treated (CT), and are described further in Table 5-2.

Table 5-2. Treatment protocols for chemically treated PACs.

PAC	Precusor	Chemical Treatment
CT-1	Calgon F400	50% Nitric Acid for 24 hrs, DI Rinse 24 hrs
CT-2	Calgon F400	50% Nitric Acid for 24 hrs, DI Rinse 24 hrs, N_2 @ 250 °C for 1 hr
CT-3	Calgon F400	50% Nitric Acid for 24 hrs, DI Rinse 24 hrs, N_2 @ 550 °C for 1 hr
CT-4	Calgon F400	50% Nitric Acid for 24 hrs, DI Rinse 24 hrs, N_2 @ 850 °C for 1 hr

In order to determine how pore structure impacts MIB adsorption, the surface chemistry for the carbons in the comparison should be equal. The precursor for the PA carbons was a wood char. In addition, they were all activated at the same temperature using the same oxidant; therefore the surface chemistries of these carbons should be very similar. The point of zero charge (PZC), or the pH at which the carbon surface is neutral, was used as a surrogate for total surface acidity to verify that each carbon was similar with respect to surface chemistry (Table 5-3).

Table 5-3. Characteristics of physically activated PACs.

PAC	Micropore Vol. (cc/g)	Mesopore Vol. (cc/g)	Macropore Vol. (cc/g)	PZC
PA-1	0.3675	0.4305	0.0810	11.6
PA-2	0.3090	0.3170	0.0590	11.5
PA-3	0.3275	0.2380	0.0580	11.1
PA-4	0.2840	0.2077	0.0467	11.2
PA-5	0.2352	0.1277	0.0470	11.3

All five PA carbons had extremely basic surfaces which were different by a negligible 0.5 pH, indicating all had low amounts of acidic oxygen functional groups. The difference in the activating time led to the different pore developments, as steam is known to widen micropores (Gonzalez et al. 1994, Walker Jr. 1996, Molina-Sabio et al. 1996, Mazyck and Cannon 2000). The wide range of pore development is illustrated in Table 5-3 and Figure 5-1. Since the set of PA PACs has differences in micro- and mesoporosity comparisons can be made as to which most influences MIB adsorption, as was the goal in this work. Comparing PACs PA-2 and PA-3 could particularly advantageous because PA-3 has slightly more microporosity,

while PA-2 has considerably more mesoporosity. The performance-based test results for these two PACs will be helpful to elucidate which pores are most important for MIB removal.

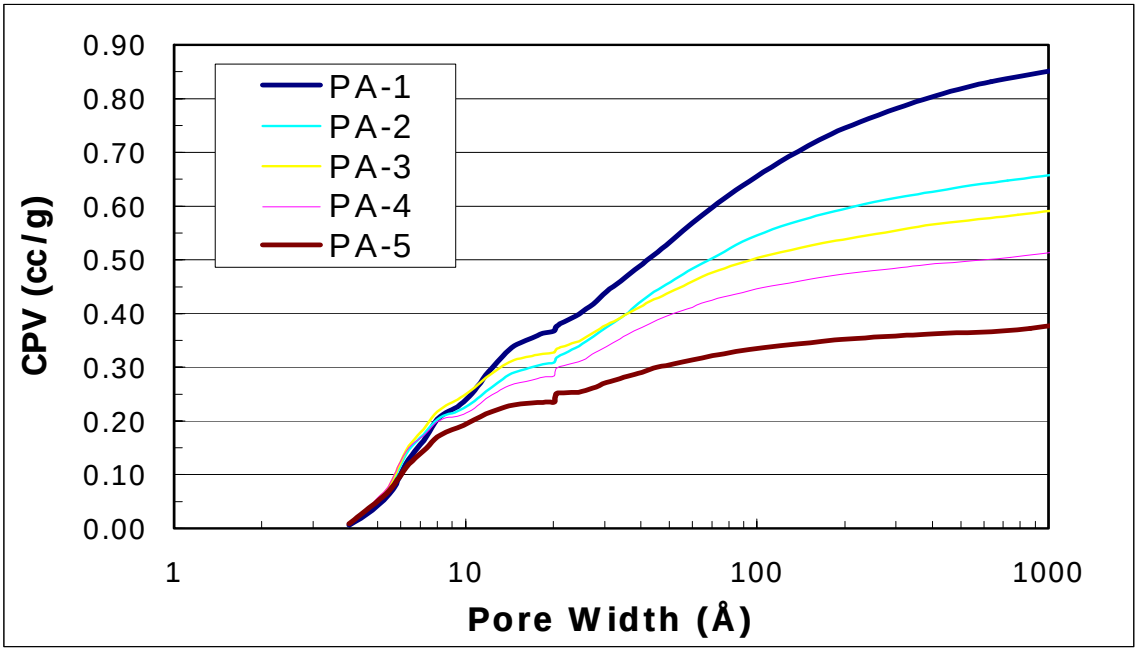

Figure 5-1. Pore size distribution of physically activated PACs (CPV = cumulative pore volume).

Traditional comparisons of activated carbon performance typically involve creating isotherms, which use results typically expressed in mass of adsorbate per mass of adsorbent from equilibrium batch experiments. However, in this work MIB data are presented in percent removal, from the results of batch tests that use contact times and carbon doses that better simulate actual PAC applications. Nevertheless, since many ideas concerning carbon properties and adsorption ability are rooted in isotherm data, it was advantageous to perform some experiments at these conditions (i.e., DI water, near-equilibrium contact time). The percent removals by the PA carbons in these conditions are shown in Figure 5-2A. A wide range of performance is exhibited despite the 24-hour contact time.

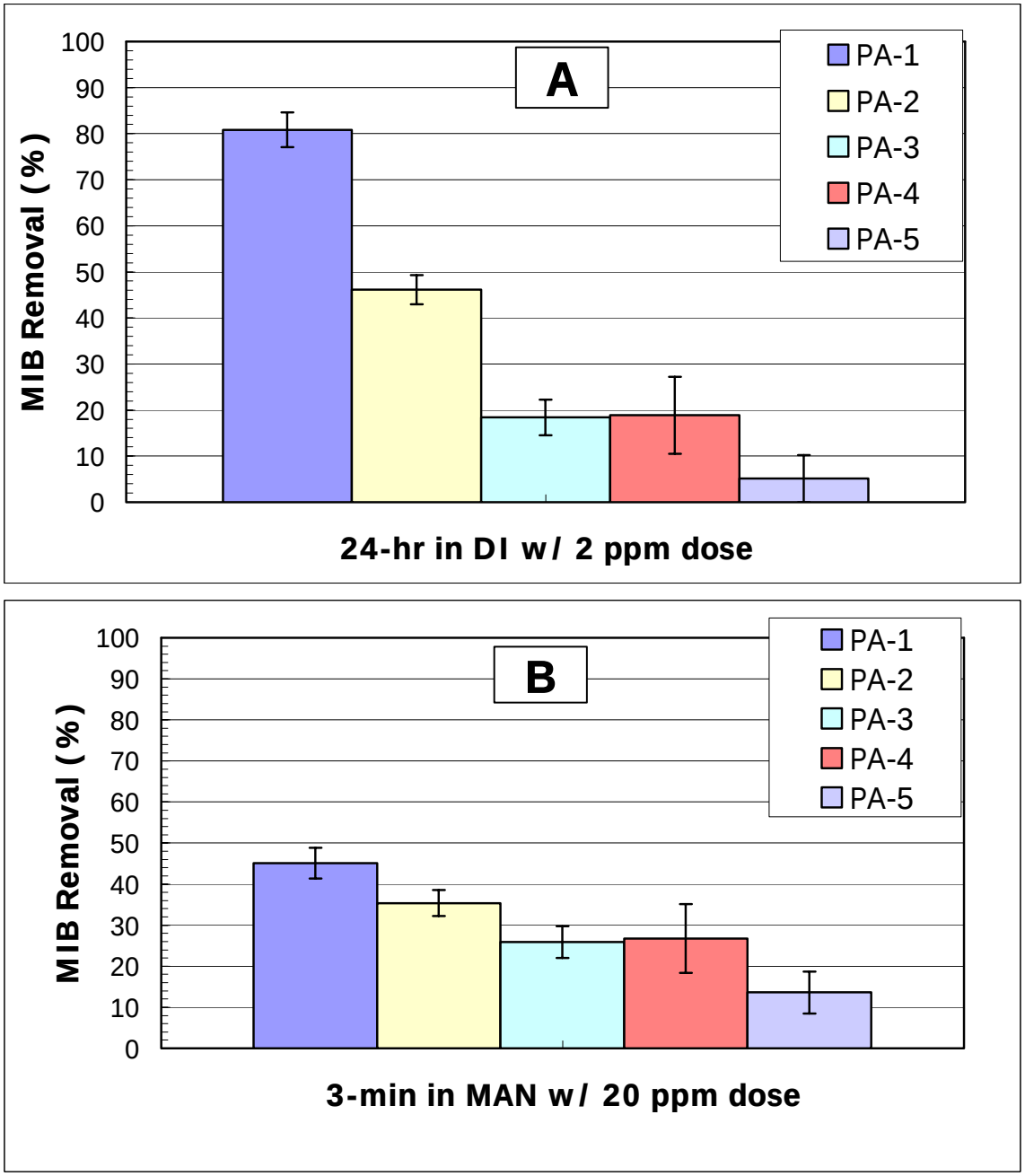

Figure 5-2. Physically activated PACs removal of MIB in DI water (A); Removal of MIB in natural water (B).

Additionally, and perhaps more pertinently, batch tests employing conditions that mimicked those found at water utilities were also conducted. These tests used shorter contact times and raw water from a Florida utility. Expectedly, the more competitive conditions (i.e., the presence of NOM and a shorter contact time) required higher PAC

doses in order to better compare the effects of pore size distribution among the PA carbons. Results from batch tests using 20 ppm of carbon with three minutes of contact time are shown in Figure 5-2B. (Three minutes of contact time mimics conditions found at many utilities that dose PAC prior to coagulation, as the coagulant can adversely impact adsorption by the carbon after it is added). The differences in percent removal between the PA carbons were not as large as in DI water, but the trends remained the same.

To further investigate the role of PSD on MIB removal, the correlations and slopes that exist between pore volume in two pore size ranges and MIB removal were found (Table 5-4). Pore volume in small micropores (6-12 Å) showed a poor relationship with MIB removal in both DI and raw water experiments. This could be surprising as these pores are similar in size to MIB (diameter ca. 6 Å), and previous work indicated that these pores are preferential for MIB removal (Pendleton et al. 1997, Newcombe et al. 2002b). The pore volume found in the larger micropores and small mesopores (12-100 Å) had the strongest relationship to MIB removal in both waters, indicating that a wide range of pores are necessary for MIB removal by PAC regardless of the competing compounds present. The slopes of the data set plots also points to the importance of mesoporosity. The slopes indicate the effect pore volume has on MIB removal throughout the range of values tested. A slope and R^2-value close to 1 for the 12-100 Å pore volume shows that MIB removal is affected by a wider range of values than the small micropores and fits the data more closely. Comparing two of the PACs individually leads to the same conclusion. PA-2 has more volume in the mesopores than PA-3, while PA-3 has greater micropore

volume. PA-2 outperforms PA-3 in both waters, highlighting the importance of mesopores even when adequate microporosity exists.

Table 5-4. Correlation coefficients and slopes for relationships between various pore volumes and adsorption ability for physically activated PACs.

	MIB Removal in DI		MIB Removal in MAN	
Pore Width Range	R^2-Value	Slope	R^2-Value	Slope
6-12 Å	0.65	8.20	0.62	2.92
12-100 Å	**0.93**	**3.22**	**0.99**	**1.21**

The set of CT carbons allow the comparison of the effects of different surface chemistries without the influence of pore structure on MIB adsorption. Altering the surface chemistry of a PAC whether via physical or chemical means inherently changes its textural formation. The goal therefore is to get the maximum variation in chemical treatment with minimal physical change, which was achieved in the four PACs listed in Table 5-5. In addition to the properties listed for the PA PACs, the amount of total surface acidity is quantified for the CT carbons. Since the differences in surface acidity would determine the performance for these PACs, performing titrations to better understand the surface was necessary. These values are listed along with the PZC values for the CT carbons. As expected, the total number of acidic groups and the point of zero charge values correlated extremely well (R^2-value = 0.98), thereby giving support to each value and technique.

Table 5-5. Characteristics of chemically treated PACs.

PAC	Micropore Vol. (cc/g)	Mesopore Vol. (cc/g)	Macropore Vol. (cc/g)	PZC	Acidic Functional Groups (µeq/g)
CT-1	0.2968	0.2086	0.1120	4.4	240
CT-2	0.3011	0.2155	0.0940	5.3	210
CT-3	0.3274	0.2390	0.0870	6.2	155
CT-4	0.3432	0.2310	0.1180	8.1	100

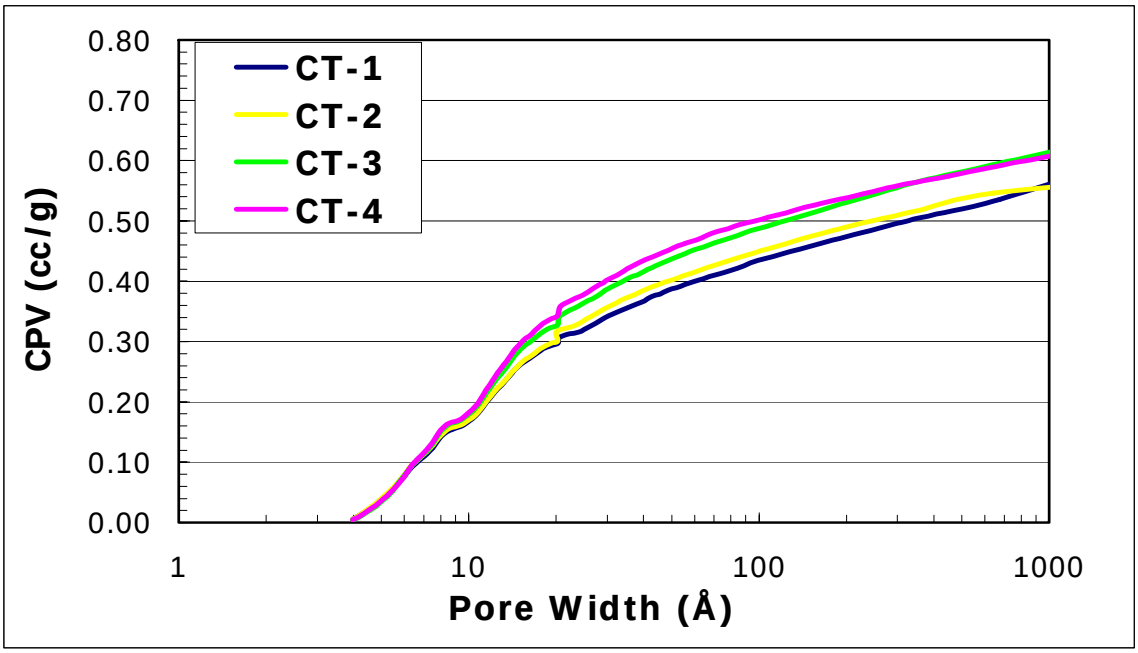

Figure 5-3. Pore size distribution of chemically treated PACs.

The pore structures of the CT PACs are similar as evidenced by the data in Table 5-5 and the pore size distributions shown in Figure 5-3. Therefore, the differences in surface chemistry should be the major factor for any variations in MIB performance. Batch tests using the same conditions as above highlighted differences in MIB performance between the PA and CT carbons.

Figure 5-4 plots MIB removal versus the concentration of acidic functional groups on the surface of the CT carbons to assess any differences in adsorption. The difference between the results of two test scenarios is illustrated by the widely different trendlines. All four CT PACs performed approximately the same in the raw water, as shown with a nearly flat slope. Moreover, this indicates that the similar pore structures of the carbons were primarily responsible for the amount of MIB adsorbed in these conditions, while the different surface chemistries had no effect. In contrast, the results of the batch tests in DI water showed a wide degree of variation in performance. In these tests, an increase in surface acidity led to a linear decrease in MIB removed. In fact, when comparing the two

data sets the slopes differ by over 30 times. Indeed, these tests illustrate that surface chemistry does impact MIB adsorption onto activated carbon, but its influence can vary greatly depending on the application. However, using two batch tests with different parameters makes it difficult to ascertain when surface chemistry has the greatest impact on MIB removal.

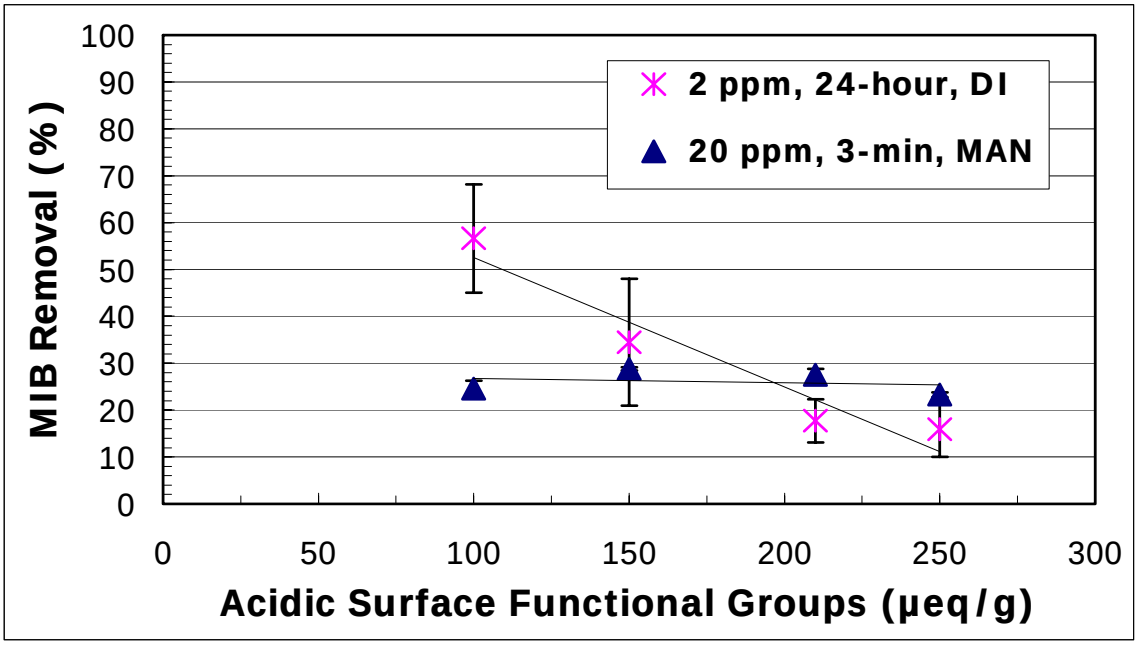

Figure 5-4. MIB removal versus acidic surface functional groups for the CT PACs in two adsorption scenarios.

There were two major differences in the performance tests discussed above: contact time and presence of competing organics (NOM concentration). Therefore, the next step taken was to equalize the dose and contact time of the batch tests to assess the affects of competition on surface chemistry. Shortening the time of the test in DI water to three minutes did not significantly change the effect of surface chemistry on the results; the carbons with more surface acidity again removed less MIB. Moreover, this indicates that changing the contact time between the PAC and MIB is not impacting the influence

of surface chemistry (Figure 5-5). Further tests were necessary to determine how the amount of NOM in the system affected the adsorption of MIB.

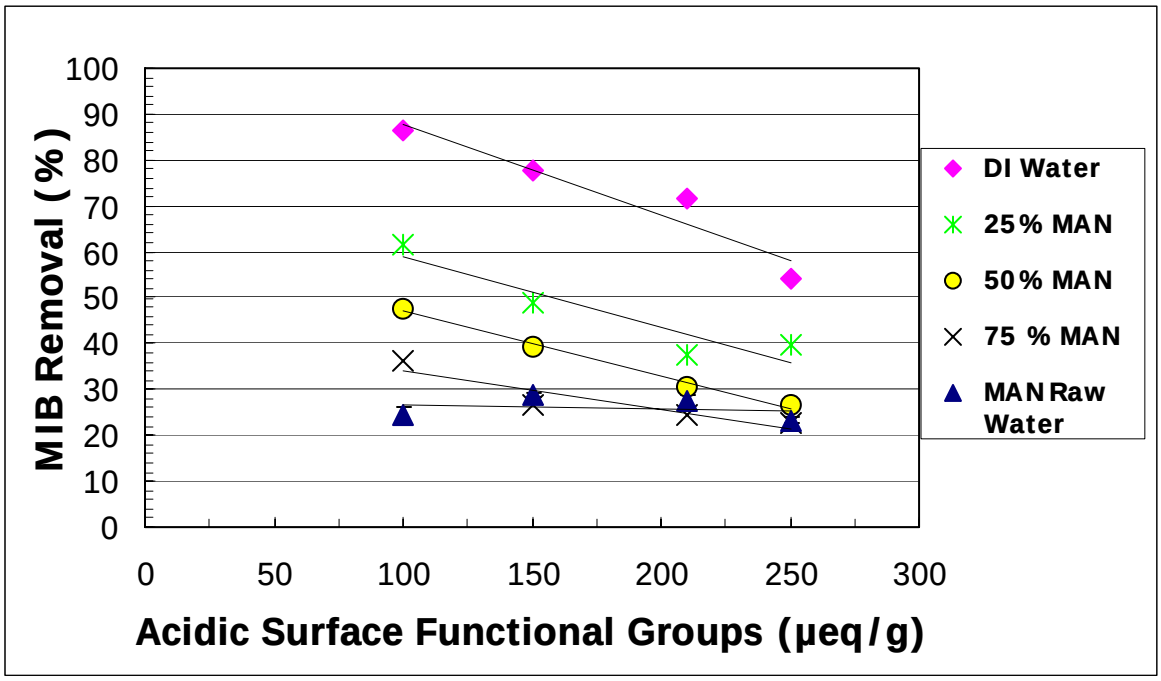

Figure 5-5. MIB removal versus acidic surface functional groups for the CT PACs with varying amounts of NOM.

Much is known about the adsorption of NOM onto activated carbon, and specifically how it competes with MIB for available pores. In this work however, NOM present in the water affects different activated carbons differently. The batch test results from Figure 5-4 show MIB removals from two very different waters representing a wide range of NOM levels. Therefore, additional batch tests were performed using the MAN raw water at three different dilutions to assess intermediate points. Figure 5-5 shows MIB removal versus concentration of surface acidic functional groups on the carbons for the series of five different waters, all using 20 ppm of PAC for 3 minutes of contact time.

Trendlines were added to help illustrate the trends in the different waters. As expected, as the concentration of NOM in the system increased the overall removal of MIB decreased because of competitive adsorption. More interesting though, is the slope

of the trendlines for the data sets. Starting at the top of the figure, the data from the batch test in DI water has a steep negative slope. This indicates that surface acidity has a strong effect on PACs MIB performance. However as the NOM level increases, the batch test results show that the slopes of the trendlines get less negative. Moreover, this trend continues until the bottom data set in Figure 5; the results from the batch test in the undiluted raw water. Again, this trendline has a near flat slope. Indeed, this series of batch test results strengthens the assertion that the surface chemistry of PACs effect on MIB adsorption is reliant on the amount of NOM present in the water. In performance tests designed to mimic actual plant conditions for PAC usage, higher surface acidity did not greatly hamper MIB removal. Instead, all of the PAC's showed decreased performance due to increased NOM competition.

Previous works support the above findings. First, Pendleton and coworkers (Pendleton et al. 1997, Considine et al. 2001) found that increasing surface acidity lowered MIB removal in equilibrium tests in DI water. They believed that the increase in surface acidity lead to increased water adsorption that lowered MIB removal. The results from the batch tests performed here in DI water (at two different contact times) showed the same relationship between surface chemistry and MIB removal as did Pendleton and coworkers.

It is well established that an increase in acidic functional groups on a carbon surface will cause an increase in water adsorption (Barton et al. 1984, Barton et al. 1994). These acidic groups contain oxygen, which creates polarity, and in turn encourages the adsorption of other polar compounds (e.g., water). MIB, however, is an aliphatic compound and is not polar. Therefore, MIB and water should not be competing for the

same adsorption sites on activated carbon. Indeed, polar compounds (e.g., water) prefer to bond with the active functional groups while non-polar compounds (e.g., MIB) adsorb via physical means on the graphitic planes inside the pores. However, acidic functional groups form on the reactive edge sites of carbon pores (Hennig 1966). Water adsorbed to these sites can hinder MIB adsorption by restricting the diffusion into or blocking the entrance to pores, thereby making adsorption sites inaccessible to MIB. Moreover, increasing concentrations of surface acidity further exacerbates the pore blockage effects. When acidic functional groups become density arranged on activated carbon, water molecules adsorbed to them are in close proximity to each other. This arrangement can lead to additional water adsorption via hydrogen bonding to already adsorbed water molecules. These additional water molecules can bridge across adsorbed water creating what researchers have called water clusters on the carbon surface (Muller et al. 1996, Muller and Gubbins 1998, Muller et al. 2000). Therefore, these large water clusters formed at the edges of carbon pores due to the presence of a dense arrangement of acidic functional groups can severely hinder MIB adsorption and can explain how surface chemistry impacts MIB adsorption in DI water experiments.

The above relationship however, did not hold when NOM levels increased. NOM is known to inhibit MIB adsorption by out competing MIB for adsorption sites, blocking smaller pores, or restricting diffusion pathways. Since NOM adsorption is largely dependent on pore size distribution and not heavily influenced by surface chemistry (Newcombe et al. 1997) within the narrow range of pH values typically experienced in potable water treatment, it follows that the CT PACs should adsorb the same amount of NOM because of their makeup. Moreover, separate batch tests revealed that these

carbons all had similar DOC removal values from the undiluted raw water. Indeed, this indicates that the primary influence on MIB adsorption in natural waters is competition from NOM. Therefore, using PACs with a wide pore size distribution is the best choice for water utilities to combat taste and odor episodes, particularly where NOM is present at high levels.

Overall, the creation of two sets of PAC each with specific physical and chemical characteristics proved to be helpful in determining causes for MIB adsorption. Five PACs with similar surface acidity and a range of pore volumes and surface areas indicated that a range of pore sizes is necessary for superior MIB uptake. Large pore volumes in the small micropores, close to the diameter of MIB, did not lead to high removal values. Instead, PACs with a range of micropores and mesopores showed superior performance for MIB, indicating the importance of intra-particle diffusion. Moreover, these trends were evident in batch tests with very different parameters, so PACs with adequate micro- and mesoporosity should perform well in a myriad of applications. A second set of carbons was utilized to determine the impact of surface chemistry on MIB adsorption. Results from batch tests with these PACs indicated that surface chemistry can influence MIB removal depending on the conditions. In DI water, carbons with higher amounts of surface acidity showed lower removal regardless of the contact time. This is likely due to pore blockage caused by increased water adsorption and the formation of water clusters at the edge sites of carbon pores. However, as the amount of NOM present in the water increased, the effects of the surface functional groups became less pronounced. Moreover, in the undiluted raw water from a Florida utility all of the PACs performed the same indicating no impact from surface chemistry. Therefore, the effects on MIB

removal from a PAC's pore structure will likely impact adsorption in all scenarios, while surface chemistry impacts adsorption in certain conditions.

CHAPTER 6
PAC ADSORPTION IN THE PRESENCE OF ALUM

Two raw (source) waters from Florida water treatment plants were utilized in batch tests to assess the impact alum has on PAC's ability to remove MIB. These water samples were collected at Manatee County Water Treatment Plant (MAN) and Hillsborough River Water Treatment Plant (HIL). Both waters have high TOC concentrations (> 15 mg/L) and color, which required alum concentrations of 120 mg/L to achieve effective flocculation. These conditions lead to coagulation during batch experiments that could be visually inspected.

The first set of experiments highlighting the impact of alum on PAC performance for these two utilities are shown in Figure 6-1.

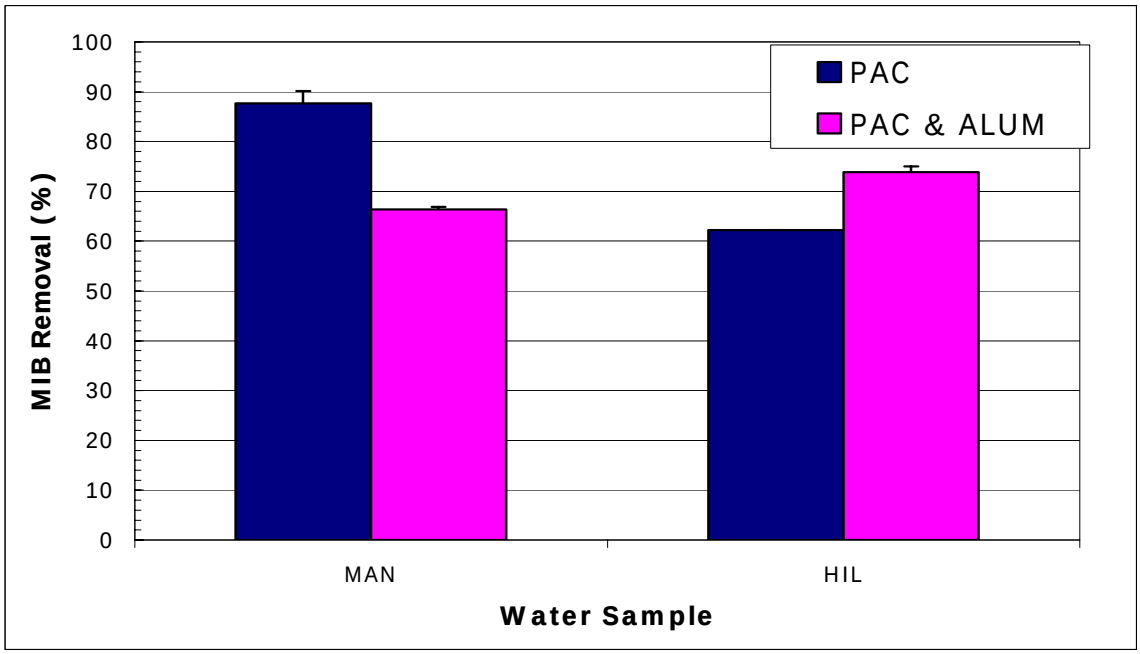

Figure 6-1. MIB removal in MAN and HIL with PAC (Calgon WPH) alone and PAC with alum.

The first column for each water indicates the amount of MIB adsorbed by PAC after a contact time of twenty minutes. Much greater removal occurred in MAN (88%) as compared to HIL (62%). Both sets of tests had the same PAC dosage (60 mg/L), but differences in the source waters, such as the size fractionation of the NOM present likely affected MIB adsorption (Newcombe et al. 1997, 2002a, 2002c). The next column shows the MIB removed when PAC and alum were added simultaneously. In the MAN water, alum addition was quite deleterious to the PAC's performance; as PAC with alum removed only 66% of the MIB, or about 20% less than compared to the PAC alone. However, in HIL water, alum addition appears to actually aid the PAC in removing MIB. The results in HIL water contradict the phenomena observed in MAN, and what researchers have stated in previous publications (Snoeyink 1990, MacLeod 2000). Although all of the batch tests used the same PAC and alum dosages, other conditions such as coagulation pH and floc formation (visually observed) were considerably different.

Upon closer inspection of the conditions surrounding the results shown in Figure 6-1, the different results for the two waters can be partially explained by first focusing on the HIL results. Previous research has indicated that conventional treatment, including coagulation, is not an effective option for eliminating taste and odor problems caused by MIB (Vik et al. 1988, Nerenburg 2000). However, pilot-scale studies have shown that conventional treatment can remove small amounts of MIB and geosmin (Kim et al. 1997). The amount removed in this study was not sufficient to eradicate the odor episode completely, but does highlight the fact that coagulation can remove some MIB in certain waters. Therefore, batch tests employing only alum (i.e., no PAC) were performed to

quantify the percent of MIB that could be removed with alum coagulation. Table 1 lists the removals found in MAN and HIL with only alum present, at the final coagulation pH.

Table 6-1. MIB removal in MAN and HIL with alum in batch tests.

Water	MIB Removal (%) at pH 5	MIB Removal (%) at pH 7
MAN	0	0
HIL	8.5	14.7

Coagulation via alum was unable to remove MIB in MAN, but in HIL the removal was significant. This data supports that the additional MIB removal observed in the HIL water likely resulted from the fact that coagulation was beneficial to MIB removal.

Another difference between the two waters in the batch tests results from Figure 6-1 was the coagulation pH. Both raw waters had a pH of 7, and therefore the tests performed with only PAC operated at this pH value, because WPH has a near neutral pH which did not impact the waters' pH. However, after the addition of alum the pH of the MAN water (low alkalinity) dropped considerably to less than 5, while the pH of the HIL water was affected very little (pH = 6.8). Therefore it became necessary to normalize the coagulation pH in the batch tests to better ascertain alum effects on PAC performance.

Figure 6-2 compares MIB removal percentages in MAN and HIL for PAC only and PAC with alum for two final pH values, 5 and 7, after twenty minutes of contact time. The first four columns are results from MAN water and the last four from HIL water. The first two columns indicate that normalizing the pH between tests in MAN water did impact the MIB removal and somewhat lessen the difference between tests with and without alum as seen before (Figure 6-1). At pH 5, the MIB removal of PAC alone was 81 %, as compared to 87 % at pH 7. However, at the same pH of 5, alum addition still resulted in 15 % less MIB removal. Also in MAN water, at the higher pH of 7, alum had very little affect on MIB removal. Moving over to the results in HIL water, a first

inspection would indicate that opposite trends are occurring from the ones seen in MAN. At coagulation pH of 5, alum addition only slightly lowered MIB removal (5%), and at the higher pH, MIB removal actually increased. These percent removals do not take into account MIB that alum was able to remove in HIL. The areas on top of the columns for PAC and alum in HIL indicate the MIB removal that was found in tests with alum alone. Assuming that alum removes this same amount in tests with PAC present, one could predict the amount of MIB that just the PAC is removing in these conditions.

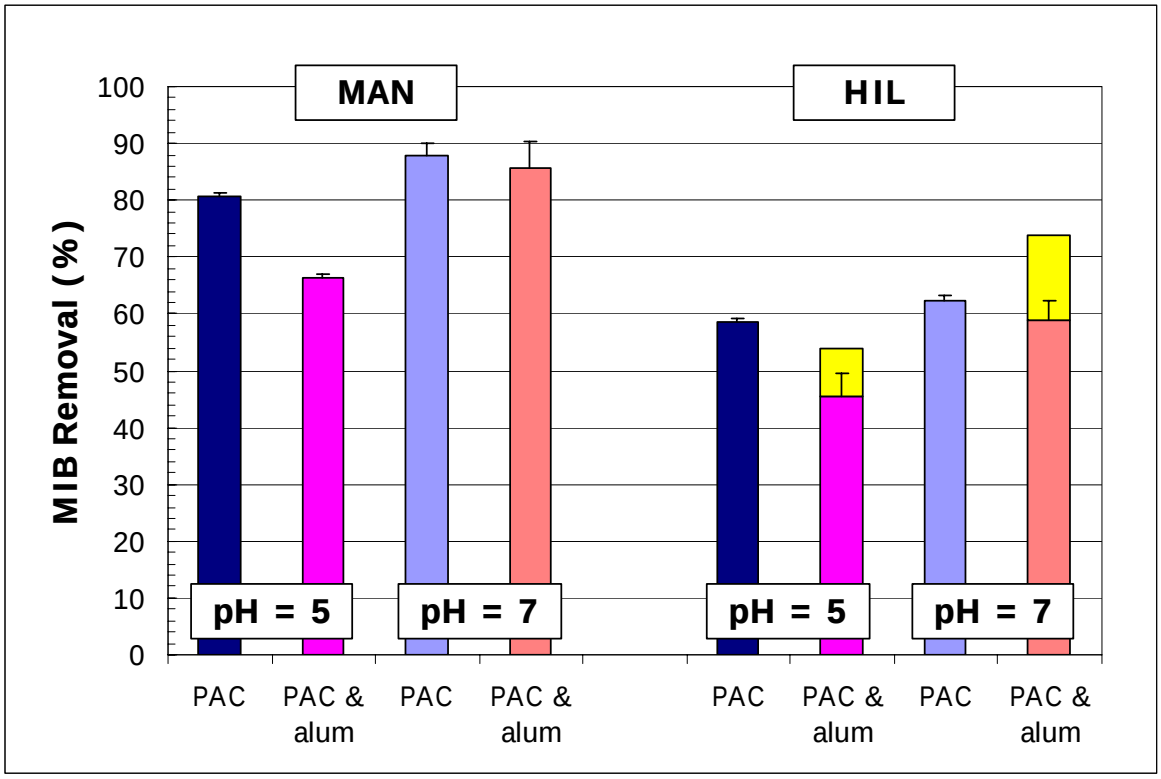

Figure 6-2. MIB removal in MAN and HIL for PAC only and PAC with alum at pH 5 and 7.

Therefore when PAC and alum are both present, the PAC removed 45 % of the MIB at pH 5 and 59 % at pH 7. Comparing these removal percentages to those in the PAC only trials is a better indicator of the impact of alum on MIB adsorption. Thus, at pH 5, PAC was adversely affected by alum, while at pH 7 the PAC was minimally

impacted. Moreover, these trends are the same found in the MAN water where alum was unable to remove any MIB. Indeed, the batch tests performed in these two waters highlight the fact that alum can have a deleterious effect on MIB adsorption by PAC. However, the effects are not clear since alum did not impact MIB removal by PAC at a coagulation pH of 7, but did at pH 5. Therefore, in order to pinpoint when alum hinders PAC performance and examine the mechanisms that cause the effects, additional tests were performed further investigating variables such as pH, alum dose, coagulation, and contact time. All additional tests utilized MAN water, since alum alone did not remove any MIB in batch tests (Table 6-2).

Since pH is an important variable in these tests, as it is in much of water treatment, it was important to separate the effects it had on the adsorption of MIB by PAC. As seen in the previous data (Figure 6-2), lowering the pH from 7 to 5 reduced the MIB removal in the PAC only trials. However, in previous work, pH did not affect the adsorption of MIB (Herzing et al. 1977). Batch tests performed in deionized water over a range of pH values for Calgon WPH support the same results (Figure 6-3).

Therefore, the impact that pH had on MIB adsorption in Figure 6-2 must have been manifested by something other than pH. For example, NOM is known to compete with MIB for pore sites on activated carbon, and performance for tastes and odors suffers as a result (Newcombe et al. 1997, 2002a, 2002b, 2002c). Additionally, NOM is made up of several compounds, with varying charges. Changes in solution pH will affect the charge of the NOM and can make the organics more favorable to carbon adsorption (Summers and Roberts 1988). Knowing this, MIB and TOC removal were measured in batch tests by PAC alone over a range of pH values (Figure 6-4).

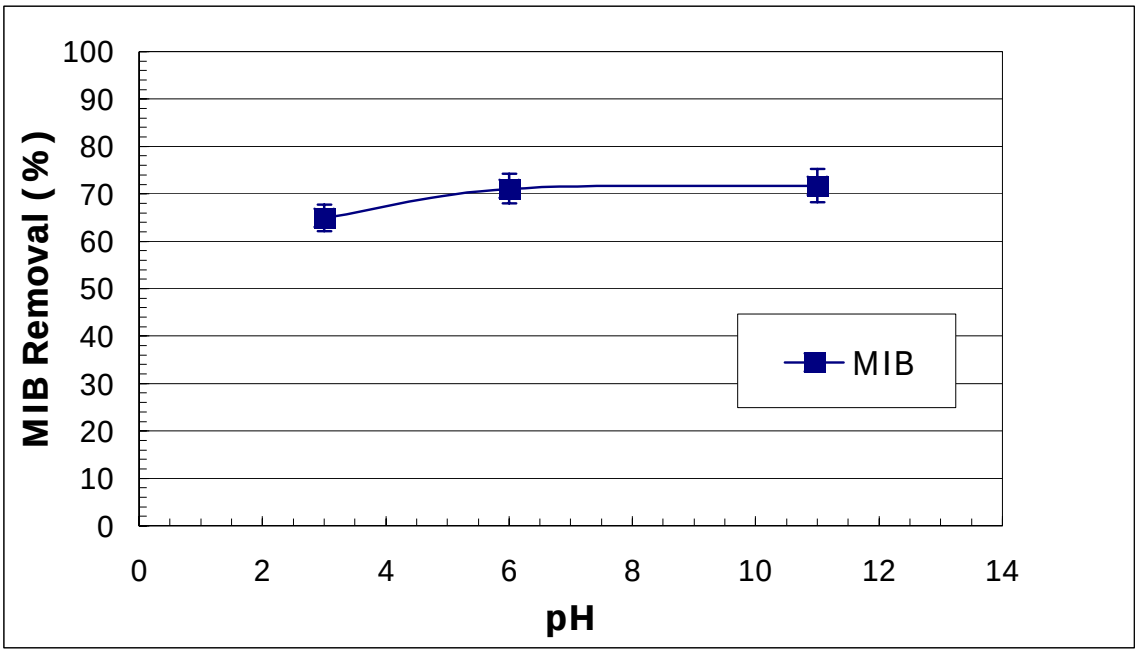

Figure 6-3. Effect of pH on MIB removal by PAC in DI water.

MIB adsorption onto PAC is greatly impacted by pH in MAN water, especially at pH values below 5. The bottom curve indicates the amount of TOC adsorbed by the PAC.

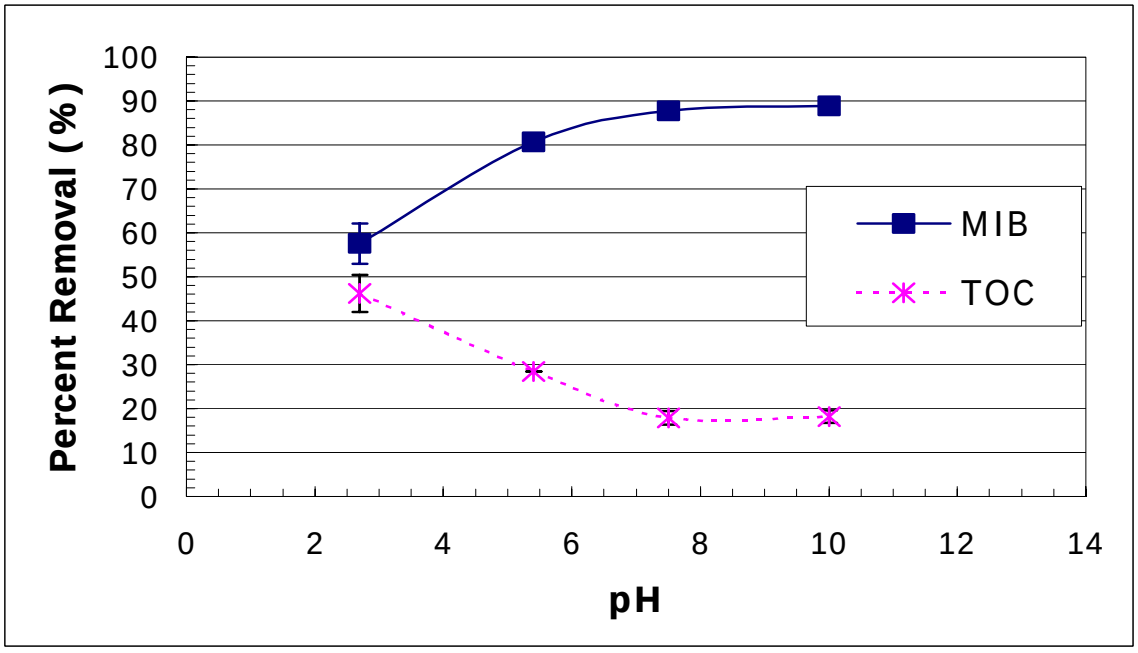

Figure 6-4. MIB and TOC removal by PAC in MAN water over a range of pH values.

The exact opposite trend is seen for TOC removal, for as pH increases less organic matter is adsorbed. Moreover, since pH was shown not to affect the adsorption of MIB

directly in DI water (Figure 6-3), the impact in MAN water must be due to competitive adsorption from NOM. Indeed, the decrease in performance for MIB is a result of greater NOM adsorption at low pH values. Electrostatic forces which attract the oppositely charged NOM and the PAC WPH are heightened as pH decreases. Therefore, more NOM adsorption by PAC occurs at the lower pH values seen in Figure 6-4. So, at these condition greater NOM adsorption means more pore sites within the carbon are occupied that could otherwise sorb MIB.

Further investigation into the effects of pH on PAC adsorption of MIB led to a comparison of MIB removals by PAC and PAC with alum over a wider pH range then those employed in Figure 6-1 and 6-2. Thus, additional tests were performed at pH 3 and pH 10 to go along with the two at pH 5 and 7 (Figure 6-5).

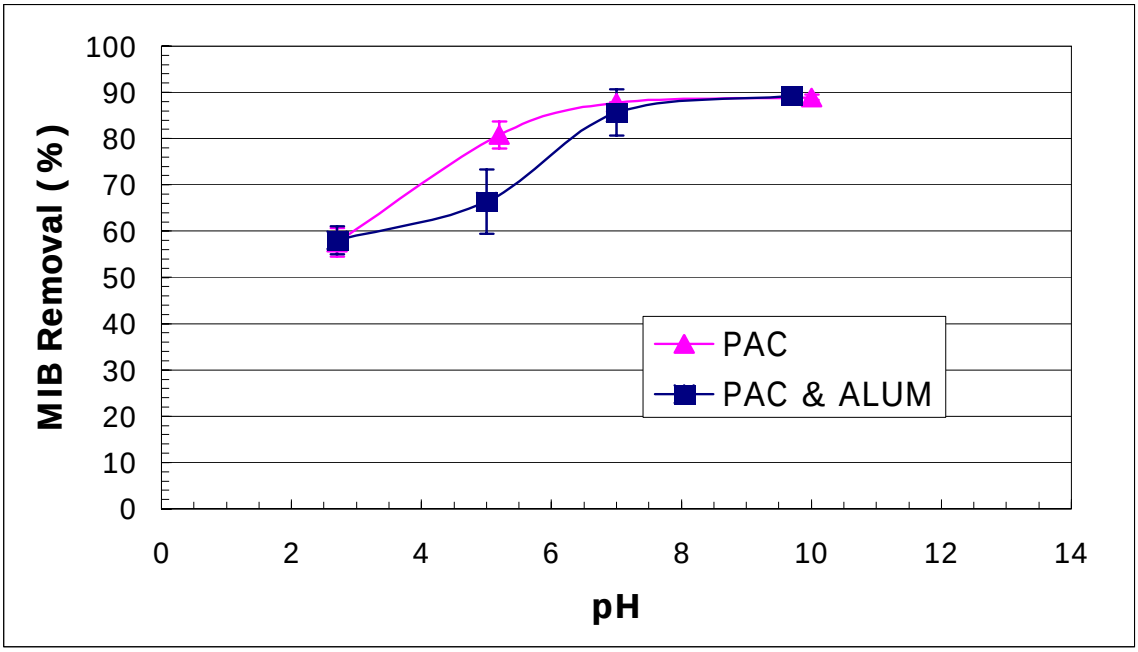

Figure 6-5. Effect of changing pH on MIB removal for PAC only and PAC with alum.

This provides more information into the role of pH in these tests. Interestingly at the four pH values tested in Figure 6-5, only the results from the batch tests performed at pH 5 showed a difference when alum was present versus when no alum was present. At

pH 3, 7, and 10, alum showed no adverse effects on MIB removal. Had a difference in MIB removal between PAC alone and PAC in the presence of alum at pH 3 occurred, then it would be surmised that pH was the primary variable contributing to the adverse effects alum has on MIB adsorption. However, since this was not the case, another explanation is necessary for the phenomenon occurring at pH 5.

One possible explanation for the deleterious effects caused by alum could be in the amount of coagulation occurring in the batch tests that contain alum. At the ideal conditions (i.e., optimum pH, alum dose and contact time) coagulation occurs, followed by floc formation. As coagulation occurs and floc forms, it is likely that many PAC particles become coated with the coagulant, entrapped in the floc, or get alum precipitate within the pores. Any of these phenomena, would explain the hindrance alum has on PAC adsorption of MIB.

The amount of TOC in water samples such as MAN and HIL has a strong correlation to the amount of NOM present as very few other carbon sources are present in these waters. Therefore, measuring the amount of TOC removed during batch tests with PAC and alum will be an excellent indicator as to the amount of coagulation and flocculation occurring. Figure 6-6 shows the amount of TOC removed in batch tests over four pH values.

The MIB removal curve for these same conditions is also shown for comparison. The amount of TOC removed was the worst at the low and high pH values. Visual inspection of these samples agreed with the results as very little floc formation was seen. The best coagulation conditions occurred near pH 5, with near 80 % of the TOC

removed. This is not surprising as pH 5 is similar to the pH value recommended for to achieve enhanced coagulation as prescribed by the EPA's Surface Water Treatment Rule.

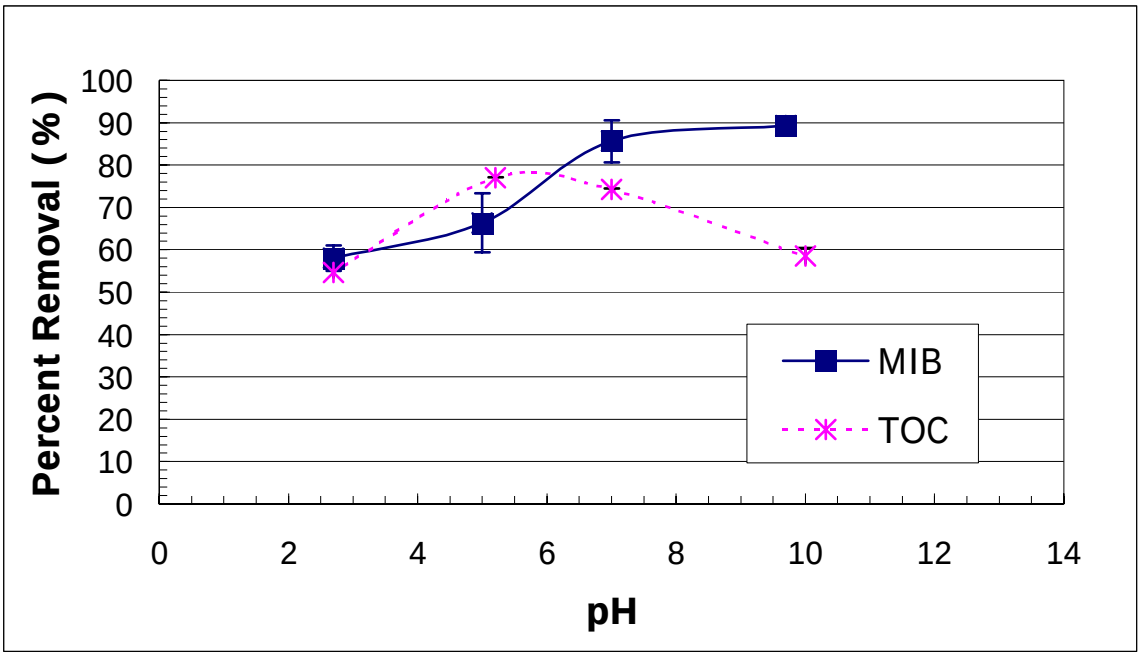

Figure 6-6. MIB and TOC removal by PAC with alum over a range of pH values.

The trials performed at these conditions had excellent floc formation. The PAC was certainly involved as the floc was quite dark, quite different from the previous experiments using only alum (Floc in the only alum trials was white or yellow). Since the PAC is being incorporated within the floc, this could explain why MIB removals were lower. When PAC particles are entrapped in a floc it may have shorter contact time with MIB. Thus, when alum is present and floc is formed, the time PAC is in contact with MIB is greatly reduced. However, the TOC removals found at pH 7 were just 3% lower than that found at pH 5, and as the MIB removal curve in Figure 6-6 illustrates PAC performance for tastes and odors was much greater. Visual inspection of the samples performed at pH 7 support the results as these tests also had strong floc formation after twenty minutes. This floc also had the same dark color as the pH 5 tests floc, again

indicating that PAC was part of it. The tests performed at both pH 5 and 7 had similar amounts of TOC removal and coagulation, but the alum present had quite different effects on PACs ability to remove MIB. Therefore, the amount of coagulation and floc formation alone does not explain the lower MIB removal found at pH 5 in the presence of alum.

Determining the exact mechanisms during coagulation occurring in the pH 5 and pH 7 tests is difficult because the interactions cannot be seen visually. Altering other experimental variables such as contact time and alum dose could provide more insight into the phenomena. Lower or higher alum dosages in MAN water gauges the magnitude of the interactions that occur between the alum, NOM, PAC and MIB. Three additional alum dosages (40, 80 and 160 ppm) at both pH 5 and pH 7, along with the 120 ppm data from previous tests are shown in Figures 6-7 and 6-8.

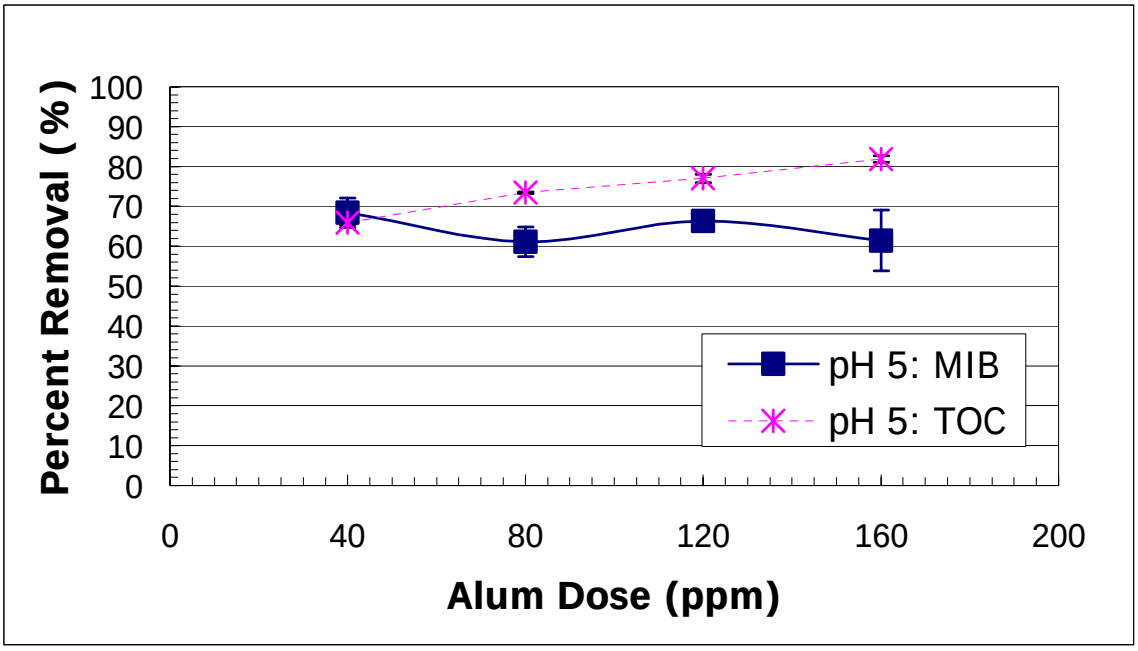

Figure 6-7. Tests at pH 5 for MIB and TOC removal in MAN for PAC with alum.

At pH 5 increasing the alum dose led to a steady increase in TOC removal, as expected (Figure 6-7). PAC performance was not greatly affected by increasing the dose,

as tests responding with similar amounts of MIB removed. At pH 7 the same trend occurred, but with a more pronounced difference in the removal of NOM. The TOC curve in Figure 6-8 shows a dramatic increase in removal from 40 to 120 ppm of alum, followed by a leveling off at 160 ppm. Despite this near doubling of the removal of NOM, the MIB removal curve was relatively flat. PAC removed over 80 % of the MIB at pH 7 at all four alum doses.

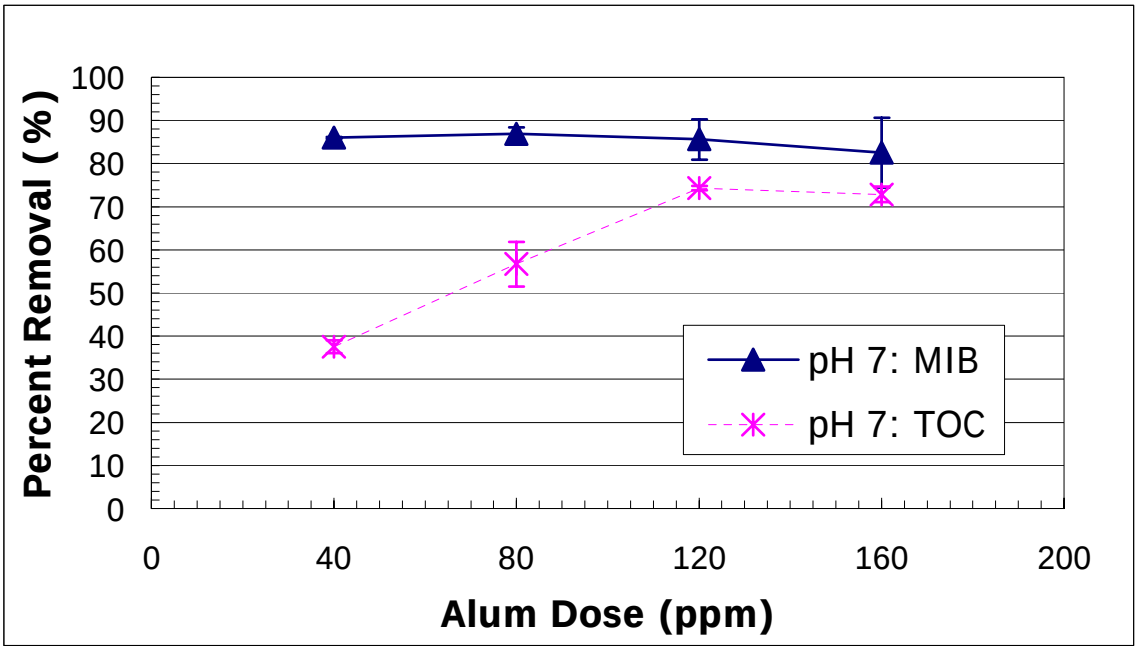

Figure 6-8. Tests at pH 7 for MIB and TOC removal in MAN for PAC with alum.

The MIB removal data in Figures 6-7 and 6-8 echoes that found in Figure 6-6, and supports the hypothesis that the magnitude of coagulation has not directly impacted MIB adsorption onto PAC. Despite large differences in the coagulation and flocculation of NOM (i.e., TOC removal), the amount of MIB removed by the PAC remained constant. Therefore, it appears that the manner in which the alum coagulates the organic matter causes the hindrance to PAC performance. At pH 5, the alum is binding to the NOM differently than that at pH 7.

Shortening the contact time that the PAC and alum has in MAN water gives information as to the rate of removal for MIB and NOM. Figure 6-9 displays the percent TOC removed after 5, 10, 15 and 20 minutes of contact time at both pH 5 and pH 7. Figure 6-10 shows the MIB removal for the same conditions. The TOC removal curve for the tests at pH 5 in Figure 6-9 indicates that after just 5 minutes much of the coagulation between the alum and the TOC has taken place. It seems that any additional time beyond 5 minutes simply allows the flocs to increase in size. The same tests performed at pH 7 present a potentially important difference. According to the TOC data, after 5 minutes at pH 7 a large portion of the NOM is removed but further removal occurs up to twenty minutes. These data suggest that coagulation is occurring more rapidly at pH 5 compared to pH 7. A more rapidly developing floc at pH 5 means that more PAC would also become entrapped in the floc more quickly. The faster the PAC particles are incorporated into the flocs, the less time it has to contact and adsorb MIB.

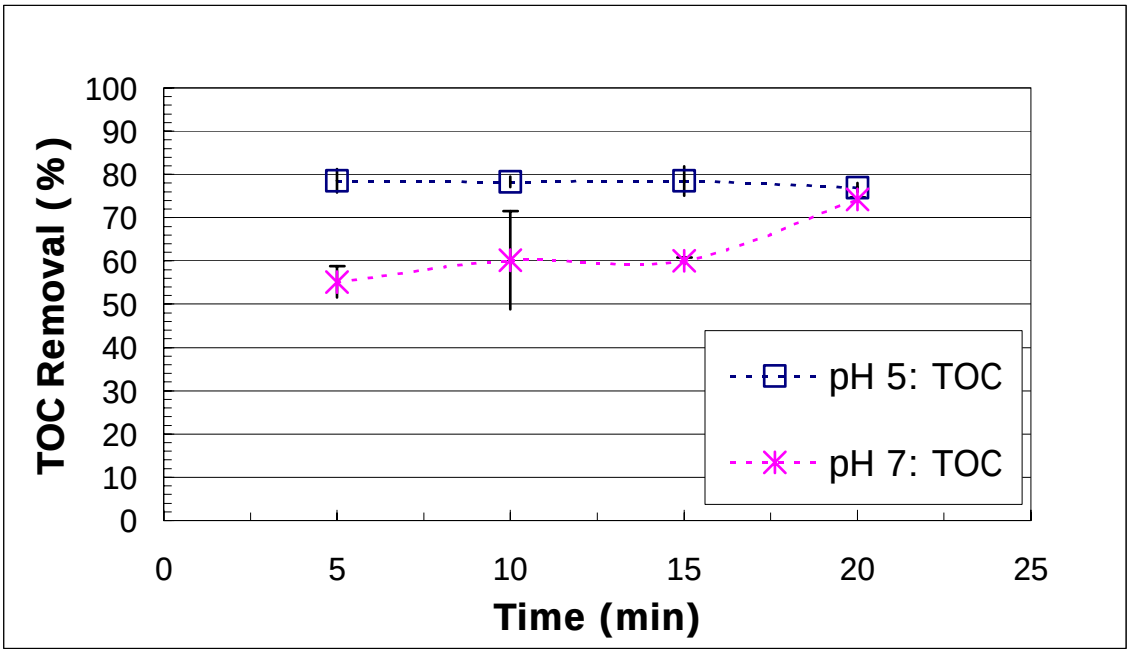

Figure 6-9. TOC removal in MAN by PAC with alum over four contact times.

The MIB removal data by PAC and alum over the four contact times for coagulation pH 5 and pH 7 however, does not paint as clear of a picture (Figure 6-10). The MIB removal curves for both pH values increase by similar amounts over the entire time span. The major difference between the two curves occurs between 15 and 20 minutes. At pH 5 MIB removal increases less than 3%, while at pH 7 MIB removal increases over 10% during the last five minutes. This agrees with the hypothesis formed by examining the TOC data that at coagulation pH of 7 PAC has more time in contact with MIB due to slower floc formation.

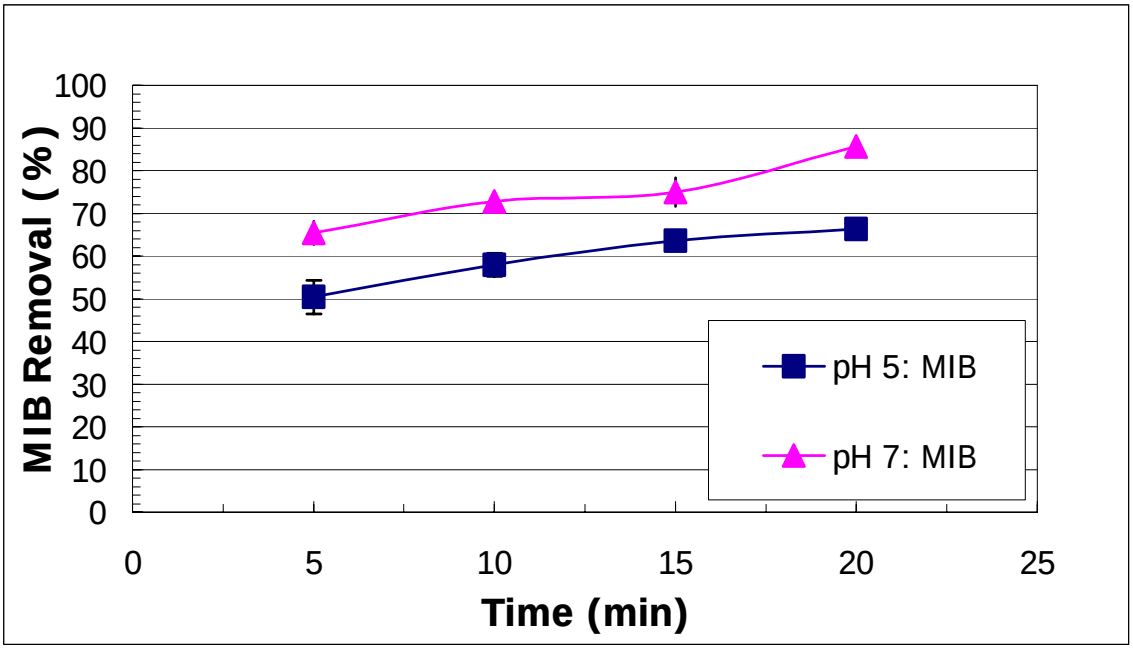

Figure 6-10. MIB removal in MAN by PAC with alum over four contact time

CHAPTER 7
CONCLUSIONS

Adsorption of MIB by PAC at water utilities is impacted by several different conditions. Optimizing the removal of MIB requires using a carbon with the suitable characteristics, understanding the adsorption process, and the proper application of PAC within the water treatment processes. This work investigated PAC removal of MIB in actual water treatment plant conditions. First, by creating tailored PACs with superior MIB performance and then studying why these PACs had increased removal. Next, the characteristics of activated carbon most important to removal were investigated using two sets of laboratory created PACs with specific qualities. Lastly, the impacts of alum on the ability of PAC to adsorb MIB in treatment plants were researched using a commercially available PAC.

An activation protocol of a wood-based precursor was optimized by altering activation temperature, activation time, and steam-to-carbon ratio to create a PAC with superior MIB removal in three Florida raw waters. The activation temperature had the greatest impact on pore development and the variable most responsible in increasing mesopore volume. When the PACs were tested in batch studies for MIB removal, the PAC activated at 1173 K provided the optimal results. The other activation parameters, activation time and steam to carbon ratio, had far less influence on pore development or MIB performance, so optimum values were not found. However, in order to maintain relevance to potential full-scale implementation, operating conditions of 0.17 lb-steam/lb-PAC for 5 minutes followed by 15 minutes in an inert environment were recommended.

Analysis of the PSD data indicated that activation protocols which increased the pore volume in the diffusion pores (mesopores) had the greatest effect on MIB removal. This is likely because of the importance of intra-particle diffusion in PACs under short contact times and high competition from NOM. Consequently, the increased mesopore volume of the tailored PACs allows MIB to diffuse more rapidly to permanent adsorption sites.

Further investigation into the physical and chemical properties was performed using two sets of laboratory produced PACs. The first set had PACs with similar surface chemistries and different pore structures, while the second set had similar pore development and different surface chemistries. Batch tests utilized different adsorption conditions in order to ascertain when different characteristics of activated carbon influenced MIB adsorption and to what extent this occurred. The results indicated that pore size distribution strongly affected PAC performance in all test conditions (i.e., varying contact time and NOM concentrations). PACs with a wide range of pore development in all pore sizes performed the best, with mesopores showing particular importance. The effects of surface chemistry were not as far reaching. In NOM-free water, PACs with lower amounts of surface functional groups performed the best for MIB removal. However, increasing the amount of NOM present in the water severely lessened the impact of surface chemistry. Moreover, the second set of PACs (i.e., similar pore structure, different surface chemistries) all performed the same in the water with the highest TOC level. Indeed, PAC performance in actual water treatment plant conditions is most impacted by PACs physical characteristics and less by the chemistry of the carbon surface. In addition, these results reinforce the importance that the presence of

NOM has on MIB removal by PAC. Moreover, since MIB adsorption is always impacted by NOM, site specific analysis is required to determine PAC performance.

Investigation into the impact coagulants on PAC performance indicated that many experimental factors must be considered. Initially, different trends were found in two separate waters. In one water (MAN), alum severely lowered the pH, which accounted for a portion of the lost performance. In addition, alum alone removed a small percentage of MIB in HIL water, while having no effect in MAN water. Normalizing the batch test results with these phenomena indicated that similar trends did occur and that alum was most deleterious to PAC adsorption of MIB at a pH of 5. Further tests showed that the amount of coagulation (TOC removal) occurring during the contact period did not influence the PAC as the tests at pH 5 and pH 7 both removed similar amounts of TOC. Variations in the alum dose utilized in the tests showed the same trend, as all of the tests at pH 7 had more MIB removal than the ones performed at pH 5, regardless of the amount of TOC removed. However, shortening the contact time the PAC and alum have in the raw water did indicate that different phenomena occurred at the two different pH values. TOC removal levels showed that higher amounts of NOM were removed at the shorter contact times at pH 5 compared to pH 7. Therefore, it appears that alum coagulates the particles (including the PAC) in solution at a faster rate at pH 5, thus the carbon has less time to contact MIB. Alum is deleterious to PAC performance for MIB by reducing the effective contact time of the PAC as it coagulates particles in the solution.

Contributions to Science

- Created a tailored activation protocol for producing a virgin activated carbon with superior performance for MIB in water utilities.

- Further explained the role of physical and chemical characteristics of PAC in adsorbing PAC. Mesopores aid in the adsorption of MIB by enhancing diffusion in short contact times and high competition. Functional groups which attach to the edge sites of carbon pores do adsorb water molecules that can bridge together and hinder MIB adsorption. However, in natural waters this phenomenon does not severely impact MIB adsorption due to the presence of NOM competing for pore sites.

- Provided insight into the impact that alum has on PAC performance for MIB, and showed that pH, contact time, and water make-up all impact performance.

Further Research

- Explore tailoring activated carbons for MIB removal in various water around the world, to evaluate the viability of full-scale application.

- Investigate MIB adsorption onto PACs with known characteristics in additional waters to see if trends continue.

- Continue tests with coagulants and PACs in waters where the NOM is well characterized to determine if the charge of the NOM affects the performance for MIB with and without the coagulant.

APPENDIX A
MIB REMOVAL FOR TAILORED PACS

Table A-1. MIB removal in MAN raw water by tailored PACs.

						Manatee Raw Water # 2					
Sample	Batch	Mass Loss %	Temp (°C)	Time (min)	S/C (lb/lb)	% Removal	Dup	Trip	Avg.		
127B	P	11.20	750	5	0.085	**59.18**	**61.46**		**61.83**	**0.37**	**2.69**
127A	P	10.20	750	5	0.085	**65.58**	**61.11**			**65.58**	
128	P	9.19	700	5	0.085	**47.23**	**48.53**		**47.88**	**0.65**	**0.92**
129	P	7.28	650	5	0.085	**45.96**	**44.03**		**44.99**	**0.97**	**1.37**
130	R	25.24	850	5	0.085	**52.94**			**52.94**	**0.00**	**#DIV/0!**
131	J	20.61	850	5	0.085	**64.93**			**64.93**	**0.00**	**#DIV/0!**
132	B	15.85	850	5	0.085	**47.62**			**47.62**	**0.00**	**#DIV/0!**
133	P	21.00	850	5	0.085	**87.56**	**81.16**	**86.81**	**85.18**	**2.38**	**3.50**
134	4	27.70	800	5	0.680				**#DIV/0!**	**#DIV/0!**	**#DIV/0!**
135	P	9.61	750	5	0.020	**62.26**	**62.08**	**56.62**	**60.32**	**1.94**	**3.20**
136	P	8.78	750	5	0.170	**68.49**	**67.26**	**68.31**	**68.02**	**0.47**	**0.66**
136B	P	14.72	750	5	0.170					**0.00**	**#DIV/0!**
137	P	13.72	750	5	0.340	**66.66**	**67.05**		**66.86**	**0.19**	**0.27**
138	P	18.60	750	5	0.510	**71.74**	**75.21**		**73.48**	**1.73**	**2.45**
139	P	24.30	900	5	0.085	**77.37**			**77.37**	**0.00**	**#DIV/0!**
140	P	17.30	800	5	0.085	**71.87**	**78.01**	**75.47**	**75.12**	**2.89**	**3.08**
141	P	18.10	750	5	0.680	**71.24**	**72.93**		**72.09**	**0.85**	**1.20**
142	P	19.30	850	15	0.255	**76.01**			**76.01**	**0.00**	**#DIV/0!**
143	P	10.92	750	15	0.255	**63.48**	**60.67**		**62.08**	**1.41**	**1.99**
144	P	6.96	650	15	0.255	**45.98**	**47.03**		**46.50**	**0.52**	**0.74**
145	P	18.40	850	5	0.020	**79.88**	**83.08**		**81.48**	**1.60**	**2.26**
146	P	25.10	850	5	0.170	**86.52**	**86.59**		**86.55**	**0.04**	**0.05**
147	P	29.70	850	5	0.340	**88.20**	**89.86**		**89.03**	**0.83**	**1.17**
148	P	23.80	850	5	0.510	**82.29**	**85.14**	**86.50**	**84.64**	**1.86**	**2.15**
149	P	7.00	650	5	0.020	**52.25**	**52.54**		**52.40**	**0.14**	**0.20**
150	P	6.70	650	5	0.170	**51.95**	**59.01**	**57.73**	**56.23**	**2.78**	**3.76**
151	P	6.60	650	5	0.340	**56.56**	**57.71**		**57.13**	**0.57**	**0.81**
152	P	29.30	850	5	0.680	**90.62**	**90.37**		**90.49**	**0.13**	**0.18**
153	P	6.73	650	5	0.000	**51.22**	**51.89**		**51.56**	**0.32**	**0.33**
153B	P	7.54	650	5	0.000	**51.58**				**51.58**	
154	P	10.68	750	5	0.000	**60.82**	**63.24**		**61.16**	**2.08**	**1.93**
154B	P	7.12	750	5	0.000	**59.43**				**59.43**	
155	P	14.70	850	5	0.000	**75.49**	**74.64**		**75.07**	**0.43**	**0.61**
156	P	6.84	650	5	0.510	**58.61**	**57.46**		**58.03**	**0.57**	**0.81**
157	P	6.04	650	5	0.680	**58.87**	**57.41**		**58.14**	**0.73**	**1.03**
158	P	13.00	750	10	0.170	**72.20**	**66.42**		**69.31**	**2.89**	**4.08**
159	P	15.60	750	10	0.340	**78.84**	**77.01**		**77.92**	**0.91**	**1.29**
160	P	16.84	750	15	0.510	**76.25**			**76.25**	**0.00**	**#DIV/0!**
161	P	14.02	750	15	0.165				**#DIV/0!**	**#DIV/0!**	**#DIV/0!**
162	P	28.62	850	10	0.340	**89.08**	**89.17**		**89.12**	**0.04**	**0.06**
163	P	28.11	850	15	0.510	**86.63**	**87.94**		**87.29**	**0.66**	**0.93**
164	P	9.10	650	10	0.340	**62.88**	**62.72**		**62.80**	**0.08**	**0.11**
165	P	6.62	650	15	0.510	**57.89**	**54.20**		**56.05**	**1.85**	**2.61**

Table A-2. MIB removal in MEL raw water by tailored PACs.

						Melbourne Raw Water				
Sample	Batch	Mass Loss %	Temp (°C)	Time (min)	S/C (lb/lb)	% Removal	Dup	Trip	Avg.	
127B	P	11.20	750	5	0.085	**39.20**	**38.81**	**28.56**	**35.52**	**0.27**
127A	P	10.20	750	5	0.085					
128	P	9.19	700	5	0.085	**26.31**	**19.05**	**27.04**	**24.14**	**4.42**
129	P	7.28	650	5	0.085	**20.96**	**13.59**	**23.28**	**19.28**	**5.06**
130	R	25.24	850	5	0.085	**36.33**			**36.33**	**#DIV/0!**
131	J	20.61	850	5	0.085	**52.97**			**52.97**	**#DIV/0!**
132	B	15.85	850	5	0.085	**48.69**			**48.69**	**#DIV/0!**
133	P	21.00	850	5	0.085	**67.22**	**65.73**	**65.99**	**66.31**	**0.80**
134	4	27.70	800	5	0.680				**#DIV/0!**	**#DIV/0!**
135	P	9.61	750	5	0.020				**#DIV/0!**	**#DIV/0!**
136	P	8.78	750	5	0.170				**#DIV/0!**	**#DIV/0!**
136B	P	14.72	750	5	0.170					**#DIV/0!**
137	P	13.72	750	5	0.340				**#DIV/0!**	**#DIV/0!**
138	P	18.60	750	5	0.510				**#DIV/0!**	**#DIV/0!**
139	P	24.30	900	5	0.085	**54.18**	**48.57**	**53.77**	**52.18**	**3.13**
140	P	17.30	800	5	0.085	**50.29**	**49.43**		**49.86**	**0.60**

Table A-3. MIB removal in WPB raw water by tailored PACs.

						WPB Raw Water				
Sample	Batch	Mass Loss %	Temp (°C)	Time (min)	S/C (lb/lb)	% Removal	Dup	Trip	Avg.	
127B	P	11.20	750	5	0.085	**46.29**	**52.69**		**49.49**	**4.52**
127A	P	10.20	750	5	0.085					
128	P	9.19	700	5	0.085	**42.50**	**44.52**		**43.51**	**1.43**
129	P	7.28	650	5	0.085	**25.69**	**32.65**		**29.17**	**4.92**
130	R	25.24	850	5	0.085	**47.50**			**47.50**	**#DIV/0!**
131	J	20.61	850	5	0.085	**63.03**			**63.03**	**#DIV/0!**
132	B	15.85	850	5	0.085	**53.48**			**53.48**	**#DIV/0!**
133	P	21.00	850	5	0.085	**84.57**	**81.32**		**82.94**	**2.30**
134	4	27.70	800	5	0.680	**73.26**			**73.26**	**#DIV/0!**
135	P	9.61	750	5	0.020				**#DIV/0!**	**#DIV/0!**
136	P	8.78	750	5	0.170				**#DIV/0!**	**#DIV/0!**
136B	P	14.72	750	5	0.170					**#DIV/0!**
137	P	13.72	750	5	0.340				**#DIV/0!**	**#DIV/0!**
138	P	18.60	750	5	0.510				**#DIV/0!**	**#DIV/0!**
139	P	24.30	900	5	0.085	**73.06**	**76.94**		**75.00**	**2.75**
140	P	17.30	800	5	0.085	**68.90**	**69.78**	**72.42**	**70.36**	**1.83**

APPENDIX B
MIB PERFORMANCE FOR COMMERCIAL PACS

Table B-1. MIB removal for commercial PACs in Manatee (MAN) raw water.

PAC	Dose (ppm)	Time (min)	Water	1	2	3	AVG.	% Error
	80	3	MAN	26.03	30.01		28.02	1.99
	80	20	MAN	45.61			45.61	0.00
	60	3	MAN	22.36	25.67	18.76	22.26	3.40
Acticarb	60	20	MAN	35.27	33.56	35.52	34.78	0.73
Watercarb	60	60	MAN	46.32	45.12		45.72	0.60
	40	3	MAN	14.80	8.61		11.71	3.10
	40	20	MAN	20.04	16.20	21.93	19.39	2.54
	20	3	MAN	5.81	5.14		5.47	0.34
	20	20	MAN	14.09	12.59		13.34	0.75
	80	3	MAN	61.37	51.25		56.31	5.06
	80	20	MAN	67.99			67.99	0.00
Norit	60	3	MAN	55.23	45.64	52.31	51.06	4.17
Hydrodarco B	60	20	MAN	60.98	61.02	58.28	60.09	0.93
	60	60	MAN	65.61	58.34		61.98	3.63
	40	3	MAN	32.37	30.40		31.38	0.98
	40	20	MAN	46.28	45.89		46.09	0.19
	20	3	MAN	19.88	25.75	16.14	20.59	5.16
	20	20	MAN	22.84	27.82		25.33	2.49
	80	3	MAN	64.72			64.72	0.00
	80	20	MAN	85.31			85.31	0.00
Calgon	60	3	MAN	54.39	47.62	55.56	52.52	3.03
WPL	60	20	MAN	77.33	73.12		75.23	2.10
	60	60	MAN	88.94	89.13		89.03	0.09
	40	3	MAN	43.68	43.60		43.64	0.04
	40	20	MAN	65.35	57.29		61.32	4.03
	20	3	MAN	24.45	26.07		25.26	0.81
	20	20	MAN	43.13	33.97		38.55	4.58
	80	3	MAN	67.72			67.72	0.00
	80	20	MAN	79.97			79.97	0.00
	60	3	MAN	60.83	61.20		61.02	0.18
Central Minerals	60	20	MAN	74.29	70.16		72.22	2.06
	60	60	MAN	77.92	78.99		78.45	0.54
	40	3	MAN	42.85	42.34		42.59	0.25
	40	20	MAN	59.80	51.05		55.43	4.38
	20	3	MAN	23.86	27.31		25.59	1.73
	20	20	MAN	31.62	32.39		32.00	0.39
Westvaco	60	3	MAN	57.18	49.83	53.08	53.37	3.82
Aquanuchar	60	20	MAN	74.28	75.11		74.70	0.42
	60	60	MAN	84.13	81.23		82.68	1.45

Table B-2. MIB removal for commercial PACs in Melbourne (MEL) raw water.

PAC	Dose (ppm)	Time (min)	Water	1	2	3	AVG.	% Error
Acticarb	60	3	MEL	22.02	14.70	19.24	18.66	3.37
Watercarb	60	20	MEL	23.07	24.46		23.77	0.70
	60	60	MEL	36.11	32.10		34.10	2.00
Norit	60	3	MEL	40.38	32.67	37.79	36.95	3.44
Hydrodarco B	60	20	MEL	39.90	39.22		39.56	0.34
	60	60	MEL	60.31	55.70		58.01	2.30
Calgon	60	3	MEL	42.72	36.64		39.68	3.04
WPL	60	20	MEL	55.97	55.31		55.64	0.33
	60	60	MEL	74.99	77.45		76.22	1.23
	60	3	MEL	45.44	46.93		46.18	0.75
Central Minerals	60	20	MEL	53.16	55.88		54.52	1.36
	60	60	MEL	68.33	66.93		67.63	0.70

Table B-3. MIB removal for commercial PACs in West Palm Beach (WPB) raw water.

PAC	Dose (ppm)	Time (min)	Water	1	2	3	AVG.	% Error
Acticarb	60	3	WPB	24.68	10.19		17.44	7.24
Watercarb	60	20	WPB	29.96	32.79		31.37	1.41
	60	60	WPB	44.63	37.63		41.13	3.50
Norit	60	3	WPB	49.89	43.56		46.73	3.17
Hydrodarco B	60	20	WPB	44.22	51.52		47.87	3.65
	60	60	WPB	69.55	71.05		70.30	0.75
Calgon	60	3	WPB	53.16	54.65		53.91	0.74
WPL	60	20	WPB	76.54	75.00		75.77	0.77
	60	60	WPB	85.78	84.37		85.07	0.70
Central Minerals	60	3	WPB	59.97	59.65		59.81	0.16
	60	20	WPB	73.96	71.64		72.80	1.16
	60	60	WPB	78.73	81.57		80.15	1.42

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BIOGRAPHICAL SKETCH

I was born on November 25th, 1975 to Jeffrey Lynn and Sue Hill Tennant. Raised in Gainesville, FL, I graduated from Gainesville High School in June, 1993. In the fall of 1993 I enrolled at the Georgia Institute of Technology in Atlanta, GA. I majored in Civil Engineering, and worked with the Gwinnett County (GA) Department of Transportation for six quarters during my second through fourth years in college, as part of the cooperative plan. I spent my fifth and final year at Georgia Tech taking courses primarily in the environmental arena. I graduated in the spring of 1998 receiving a B.S. in Civil Engineering with Honors and the Cooperative plan distinction. In twelve quarters at Georgia Tech, I was on the Dean's List 9 times, and received Faculty Honors once.

After earning my undergraduate degree, I began working with Schlumberger as a Field Engineer in Elk City, OK. After a training period, I managed a crew and truck and was responsible for performing high-level measurements at newly drilled oil and gas wells. The intense working environment taught me many new lessons, and reinforced several old ones. After nearly 2 years with Schlumberger, I did not foresee a career in the oilfield, and went home to Florida, where I applied to the Department of Environmental Engineering. I began work on my master's degree in the Fall of 2000 under the advisement of Dr. David Mazyck. I completed one year of coursework and research at the University of Florida, and decided to bypass the master's degree and work toward a Ph.D.