

ROLE OF PHYSICAL AND CHEMICAL CHARACTERISTICS OF POWDERED ACTIVATED CARBON IN THE ADSORPTION OF 2-METHYLISOBORNEOL

Matthew F. Tennant¹, David W. Mazyck¹

¹ *Department of Environmental Engineering Sciences, University of Florida*

Corresponding author e-mail address: dmazyck@ufl.edu

Introduction

2-methylisoborneol (MIB) has long been a problem for utilities throughout the world by imparting earthy, musty tastes and odors in water supplies. Although it poses no health threats, MIB can cause water to be unpalatable at part per trillion (ppt) levels. Consumers will not trust and likewise not drink such water, and therefore utilities must remove MIB to below odor threshold concentrations (~10 ng/L). However, many common treatment processes cannot effectively remove MIB, and therefore utilities often turn to powdered activated carbon (PAC) adsorption.

Therefore, the objective of this work was to enhance the understanding of how PAC's characteristics impact MIB adsorption, especially in natural waters. Previous research identifies both pore structure and surface chemistry as factors affecting performance of MIB removal (1-5). In order to make inferences as to the specific roles of the carbon properties, experimental controls must be set. That meant creating two sets of carbons: one set with similar surface chemistry and differing pore structures, and another with similar pore structures and a range of surface chemistry properties. Performance for MIB removal by these PACs will allow a more definitive answer as to the properties of carbon that affect adsorption the greatest.

Experimental

Sorbents. 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. In order to create the first set, three grams of pine bark char was thermally treated in a fluidized bed furnace. The specifics on this activation method can be found elsewhere (3). These PACs are herein called physically activated (PA).

The creation of the second 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. 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).

Characterization. The physical structure for all PACs were quantified using nitrogen gas adsorption with a Quantachrome Autosorb I. All pore volumes shown here are from two widely accepted models: the DFT for the PSD of the micropores ($< 20 \text{ \AA}$), and the BJH theory for meso- and macropore pore volumes (20).

The surface chemistry of the PACs was determined by the point of zero charge (PZC) and Boehm titrations. The PZC experiment used one-point reverse mass titration (10% wt PAC/water), after mixing for 24 hours. The Boehm titration techniques calculated total acidity from NaOH uptake and were based upon previous experiments (10-11).

Adsorption Experiments. ^{14}C radiolabeled MIB, purchased from American Radiolabeled Chemical (St. Louis, Mo), was used for all laboratory MIB testing. 50 mL of organic-free or raw water was measured into a graduated cylinder, then added to the syringe, followed by 10 μL of the ^{14}C MIB stock solution; creating a MIB concentration of 153 ng/L in the syringe. Immediately after the ^{14}C MIB addition, the PAC slurry was added at the desired dose with an automatic pipetter. The syringe was then sealed with headspace and allowed to mix on a rotisserie style mixer for the appropriate contact time. Upon completion of the mixing period, a 0.45 μm luer-lock filter was attached to the syringe and the PAC was separated from solution. All samples were counted twice in the scintillation counter for ten minutes each time, with a typical error of less than three percent.

Solvents. The organic-free water used in the batch experiments was Gainesville, FL tap water distilled and deionized at the University of Florida. It had a resistance of ca. 18 megaohm-cm, a pH between 6-7, and DOC levels < 1 ppm. The raw water used was from the Manatee County Water Treatment Plant source water (MAN). At the time of sampling, it had a pH between 6-7 and DOC level of approximately 11 ppm.

Results and Discussion

In order to determine how pore structure impacts MIB adsorption, the surface chemistry for the carbons in the comparison should be similar. All five PA carbons had extremely basic surfaces (i.e., $> \text{pH } 11$), which were different by a negligible 0.5 pH, indicating all had low amounts of acidic oxygen functional groups. The differences in the activation times gave a set of PACs with a range of micro- and mesoporosity (Table 1). This range of pore volumes was desired to elucidate which pores were most impacting MIB adsorption.

Table 1. 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

The PA carbons were tested for MIB removal, and the correlations and slopes that exist between pore volume in two pore size ranges and MIB were found (Table 2). 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). 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 via PAC regardless of the competing compounds present. The slope of the data sets also points to the importance of mesoporosity, as the slopes closer to unity demonstrate the strong dependence MIB removal has on a wide range of pores.

Table 2. Correlation Coefficients and Slopes for Relationships between Various Pore Volumes and Adsorption Ability for Physically Activated PACs.

<u>Pore Width Range</u>	MIB Removal in DI		MIB Removal in MAN	
	<u>R²-Value</u>	<u>Slope</u>	<u>R²-Value</u>	<u>Slope</u>
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 3. 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 = 0.96), thereby giving support to each value and technique.

Table 3. Characteristics of Chemically Treated PACs.

PAC	Micropore Vol. (cc/g)	Mesopore Vol. (cc/g)	Macropore Vol. (cc/g)	PZC	Acidic Functional Groups ($\mu\text{eq/g}$)
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

The CT carbons were then tested for MIB removal in DI water, a raw water, and three dilutions of the raw water (3 min of contact time using a dose of 20 ppm). Figure 1 shows MIB removal versus concentration of surface acidic functional groups on the carbons for the series of five different batch tests.

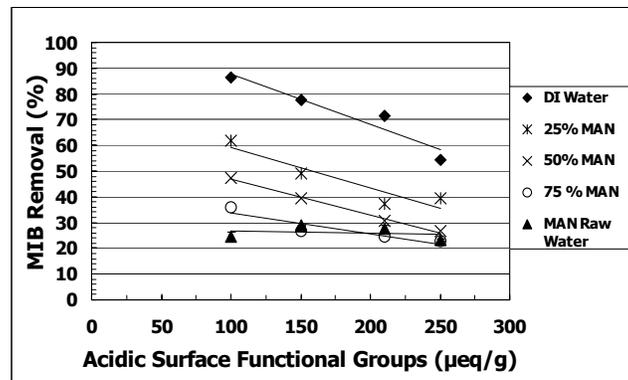


Figure 1. MIB Removal versus Acidic Surface Functional Groups for the CT PACs with Varying Amounts of NOM.

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 due to 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 1; the results from the batch test in the undiluted raw water. This trendline has a near flat slope. Indeed, this series of batch test results asserts 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. Pendleton and coworkers (4-5) 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 batch tests performed here in DI water at two different

contact times showed the same relationship between surface chemistry and MIB removal. It is well established that an increase in acidic functional groups on a carbon surface will cause an increase in water adsorption (8-9). These acidic groups contain oxygen (which creates polarity), which 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. Since acidic functional groups tend to form on the more reactive edges of carbon pores (10), water adsorbed to these sites can block the entrance to the pores, making adsorption sites inaccessible to MIB. Moreover, increasing concentrations of surface acidity further exacerbates the pore blockage effects, by increasing the density of the functional groups at the edge of the carbon pores. When acidic functional groups become density arranged on activated carbon, additional water molecules can bridge via hydrogen bonding between other water molecules already adsorbed (11-13). Therefore, water that adsorbs at the edges of carbon pores due to the presence of a dense arrangement of acidic functional groups on the surface 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 (1) 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 due to their makeup. 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.

Conclusions

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 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 well-developed pore structures 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 could 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 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 certain conditions.

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