A SIMPLIFIED METHOD TO DETERMINE THE POWDERED ACTIVATED CARBON DOSE REQUIRED TO REMOVE METHYLISOBORNEOL

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ABSTRACT

Equilibrium data obtained from a natural water with several different initial concentrations of 2-methylisoborneol (MIB) plot as a single line on a percent remaining, $C_e/C_o \times 100\%$, versus carbon dose, C_c, plot. This indicates that the percent removal of MIB is independent of its initial concentration in natural water for a given PAC dose. The relationship is specific for each type of PAC, and it is not valid at very high MIB concentrations, however. These data show that, predicting the minimum amount of carbon necessary to effectively mitigate any MIB episode, may be accomplished by analyzing a single bottle-point isotherm. The robustness of this approach was shown through the use of four water sources, fourteen different carbons, and MIB concentrations ranging from 45 ng/l to 178 µg/l. © 1999 Published by Elsevier Science Ltd on behalf of the IAWQ. All rights reserved

KEYWORDS

INTRODUCTION

The effective application of activated carbon up to this point has required either complex predictive mathematical modeling with its corresponding calibration experimentation, or extensive trial-and-error testing. Researchers have long been developing and modifying these theories and models to predict adsorbent material capacities for a variety of contaminants. Earthy-musty tastes and odors produced by geosmin and 2-methylisoborneol (MIB) have recently gained considerable attention as two compounds responsible for consumer complaints the world over.

Accurately describing the competitive adsorption between the background organic matter and the compound of interest has made predictions difficult. One approach utilizes the Equivalent Background Compound (EBC) model, (Najm *et al.*, 1991a; Najm *et al.*, 1991b; Knappe *et al.*, 1993; Qi, 1994; Gillogly *et al.*, 1998) while another employs Fictive Components (FCs) (Frick and Sontheimer, 1983; Crittenden *et al.*, 1985;

Smith and Weber, 1990). Both have been applied successfully; however, they require several experiments for calibration, and confirmation, as well as an understanding of how to manipulate the models. This requires specially trained personnel and time, when time may be a critical factor. Other researchers have attempted to determine if a physical characteristic of the carbon could determine *a priori*, how effectively MIB could be removed (Chudyk *et al.*, 1979). Unfortunately, it was determined that characteristics such as surface area and micropore volume could not be consistently used (Newcombe *et al.*, 1994).

The carbon dose required to mitigate a particular organic contamination problem in a water supply generally depends on the adsorptive capacity of the carbon and characteristics of the raw water natural organic matter. Unfortunately, the adsorptive capacity is dependent upon the initial contaminant concentration, which can vary widely. Large data sets are required to fully characterize such systems, and collection of these data for compounds that cause earthy-musty odor is complicated by an analysis procedure that is difficult and time consuming.

Fortunately, recent studies have shown that a single isotherm may be sufficient to yield the necessary information to determine a particular carbon's feasibility. The research contained herein follows a recent development of Knappe (1998). He showed that a unique relationship existed for adsorption of a trace compound such as atrazine in the presence of natural organic matter. If the initial concentration of the trace compound was less than a certain level, approximately 50 µg/l for atrazine, its percent removal at equilibrium for a given carbon dose in a particular natural water is independent of the compound's initial concentration. Thus, for a given carbon dose, the amount of trace compound adsorbed is directly proportional to its initial concentration. The following study has investigated how this trend may be applied to MIB adsorption for a variety of activated carbons and waters.

MATERIALS AND METHODS

2-Methylisoborneol. The concentration of 2-methylisoborneol (MIB) was determined by one of two methods. Those experiments using the Kankakee River or Lake Michigan as its water source relied upon ^{14}C labeled MIB (^{14}C-MIB). These tests were analyzed by mixing 2.5 ml filtered sample aliquots with 18 ml of scintillation cocktail (Ecoscint, National Diagnostics, Manville, NJ) in scintillation vials. The resulting fluorescence was then measured in a liquid scintillation counter (Tri-Carb Model 1600CA, Packard Instrument Co., Downers Grove, IL). This method is described in greater detail in "^{14}C-MIB Adsorption on PAC in Natural Water" (Gillogly *et al.*, 1998).

Experiments utilizing Hope Valley Reservoir and Myponga Reservoir water analyzed MIB as per Method 6040B "Closed-Loop Stripping, Gas Chromatographic/Mass Spectrometric Analysis" (Standard Methods, 1995), with an additional modification to incorporate deuterated standards.

Activated carbons. The activated carbons employed in this study were Cecarbon (Elf Atochem North America, Philadelphia, PA), F-400 (Calgon Carbon Corp., Pittsburgh, PA), WPL (Calgon Carbon Corp., Pittsburgh, PA), WPH (Calgon Carbon Corp., Pittsburgh, PA), prototype carbon (not commercially available), ASTM M325 (Haycarb Holdings, Victoria, Australia), Picatif PCO (PICA, Levallois, France), Picazine (PICA, Levallois, France), P1100 (PICA, Levallois, France), P1300 (PICA, Levallois, France), W20 (Norit Americas Inc., Atlanta, GA), Hydrodarco-B (Norit Americas Inc., Atlanta, GA), Watercarb (Acticarb, Dunnellon, FL), and Nuchar SA-20 (Westvaco Chemicals, Covington, VA). Granular activated carbon samples were ground so that ≥95% passed a #325 US standard sieve mesh (44 µm sieve size).

Waters. Several natural water sources were drawn upon in this study, including: Hope Valley Reservoir (South Australia, Australia; 5.0 mg/l DOC), Kankakee River (Illinois, USA; 4.0 mg/l DOC), Lake Michigan (Illinois, USA; 1.8 mg/l DOC), Myponga Reservoir (South Australia, Australia; 5.8 mg/l DOC). Prior to use, these waters were passed through a 1 µm filter for particulate removal. Any water not immediately used was stored in the dark at 4°C to limit biological activity.

RESULTS AND DISCUSSION

The difficulty in predicting the amount of an organic contaminant which can be removed for a particular carbon dose has been in describing the reduction of adsorptive capacity due to competing background organics. The familiar equilibrium solid-phase concentration of MIB, q_e, versus the MIB equilibrium solution concentration, C_e, plot, shows how the amount of MIB adsorbed per unit mass of activated carbon changes with the initial concentration (see Figure 1). Typically several experiments are necessary to calibrate and verify a competitive adsorption model, so that the model can be used to predict the capacity of a particular carbon dose for an initial concentration of interest. This process can have many steps, take a considerable amount of time, and requires personnel knowledgeable of the model and its operation.
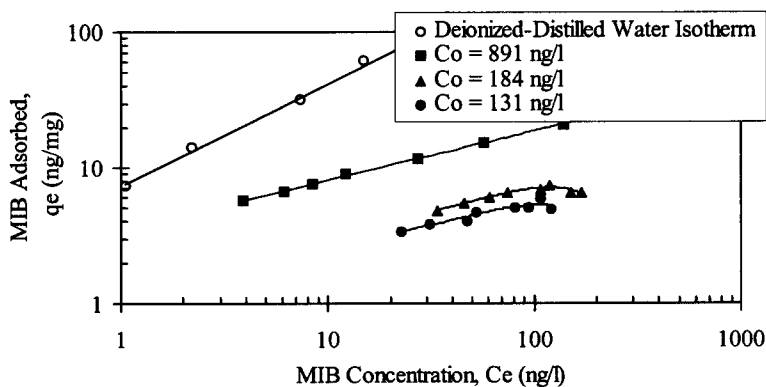

Figure 1. Hydrodarco-B adsorption isotherms in Kankakee River water.

Following a recent development of Knappe (1998), it has been shown that if the natural water equilibrium data are plotted as percent remaining, C_e/C_o x 100%, versus carbon dose ,C_c, instead of q_e versus C_e, the data plot as a single line if the initial concentrations of the trace compound are sufficiently low. This behavior of the data is predicted from the Ideal Adsorbed Solutions Theory if the solid phase concentration of the competing background organic matter at a given carbon dose is not affected by trace levels of the target compound (Knappe, 1998). This behavior of the data indicates that the percent removal of a trace organic is independent of its initial concentration in natural water for a given PAC dose. From this type of plot, the minimum carbon dose required to achieve a desired removal can be quickly obtained for any reasonable initial concentration without the need for mathematical models. As shown in Figure 2, the Hydrodarco-B MIB adsorption data in Kankakee River water for the initial concentrations of 131, 184 and 891 ng/l, now fall on the same line. A similar trend is also seen with WPH PAC.
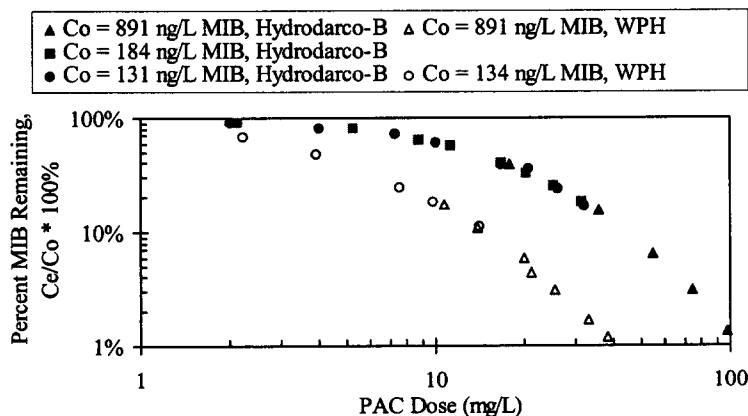

Figure 2. PAC adsorption isotherms in Kankakee River water.

Additional isotherms run in Lake Michigan water using Watercarb, Hydrodarco-B and WPH PAC also show that the adsorption data for each carbon plot as a single line (refer to Figure 3). Critical information can be extracted from these plots quickly and easily. For example, if the MIB C_o is 100 ng/l and it must be reduced to 5 ng/l, a removal of 95% is required (C_e/C_o x 100% = 5%). Drawing upon the data in Figure 3, a carbon dose of 12.5 mg/l WPH would be required for a 95% removal. The data in Figure 2 and 3 can now be used to compare the minimum carbon doses required to remove 95% of the MIB from Kankakee River water and Lake Michigan water, as shown in Table 1. Substantially more competition between natural organic matter and MIB occurs in Kankakee River water than in Lake Michigan water.
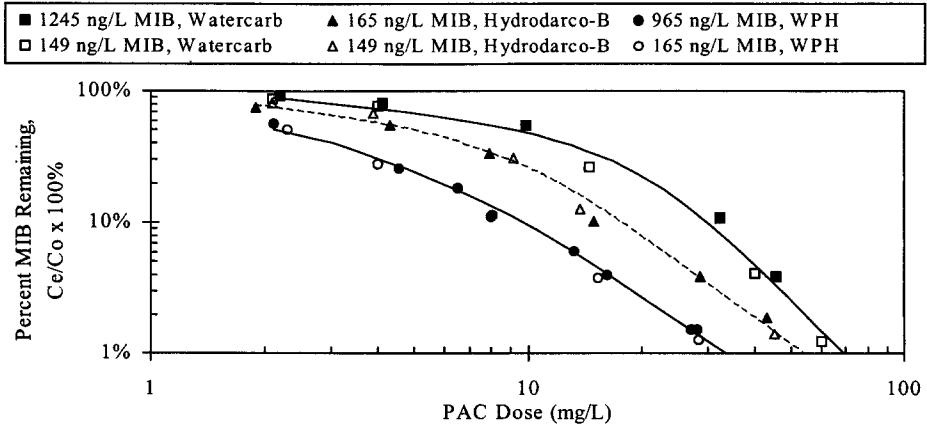
| ■ 1245 ng/L MIB, Watercarb | ▲ 165 ng/L MIB, Hydrodarco-B | ● 965 ng/L MIB, WPH |
| □ 149 ng/L MIB, Watercarb | △ 149 ng/L MIB, Hydrodarco-B | ○ 165 ng/L MIB, WPH |

Figure 3. PAC adsorption isotherms in Lake Michigan water.

Table 1. PAC dose required to remove 95% of the MIB initially present

Water Source	WPH	Hydrodarco-B	Watercarb
Kankakee River	20.3	61	-
Lake Michigan	12.5	22	38

| ■ Co = 98 ng/L |
| ■ Co = 39 ng/L |

1 - Cecarbon, Atochem   2 - WPL, Calgon
3 - prototype, not available   4 - ASTM M325, Haycarb
5 - PicatifPCO, PICA   6 - Picazine, PICA
7 - Nuchar SA-20, Westvaco   8 - W20, Norit
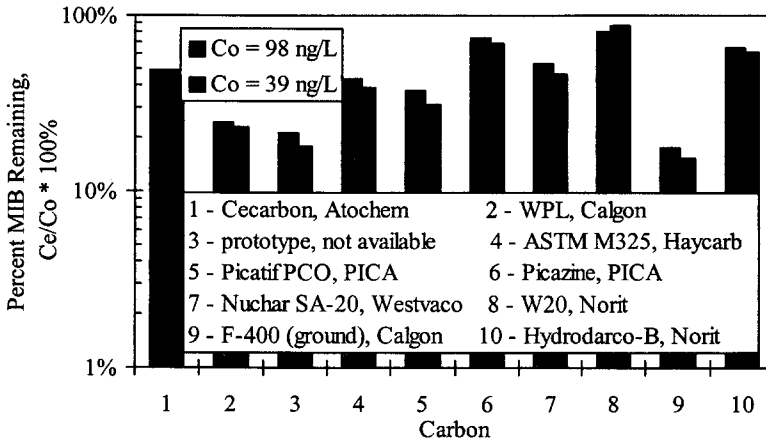9 - F-400 (ground), Calgon   10 - Hydrodarco-B, Norit

Figure 4. Comparison of 10 carbons; 13.2 mg/l PAC in Hope Valley water.

To show the differences which can exist between carbons, ten activated carbons made from a wide variety of starting materials (coal, coconut, wood, peat, lignite) were analyzed using two initial MIB concentrations and a PAC dose of 13.2 mg/l in water from the Hope Valley Reservoir. As seen in Figure 4, the difference

in percent remaining for the two initial concentrations was less than 7% for all carbons, with an average difference of 4%. The carbons removed from 13 to 85% of the MIB, however, showing a great variability in adsorptive capacity. This difference emphasizes the importance of evaluating carbons on a cost per unit MIB removed basis rather than on a cost per unit weight basis.
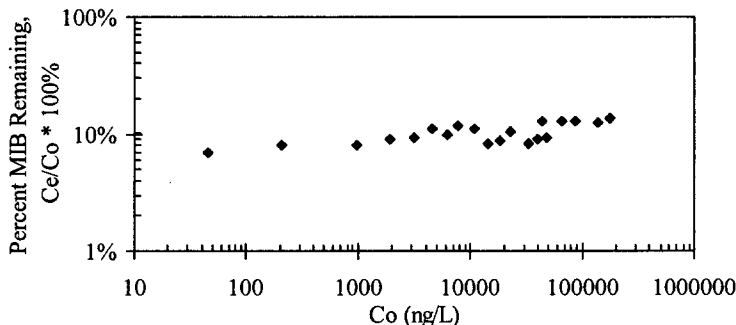

Figure 5. MIB removed by 13.2 mg/l P1300 from Myponga Reservoir water.

Two final series of experiments were performed to show that the percent MIB removed by one carbon dose was constant over a wide range of initial MIB concentrations. Myponga Reservoir water was spiked with MIB between 45 ng/l and 178 µg/l. To the spiked water, 13.2 mg/l of P1300 or P1100 was added and allowed to come to equilibrium. While these MIB concentrations covered three to four orders of magnitude, the percent remaining showed an impressive consistency (see Figures 5 and 6). Over this wide range, the difference in the measured maximum and minimum percent remaining was less than 6.6% for P1300, with an average of 10.2% remaining. While a larger difference, 13.7%, was observed between the maximum and minimum percent remaining with P1100, average 21.6% remaining, the approach yields excellent reproducibility.
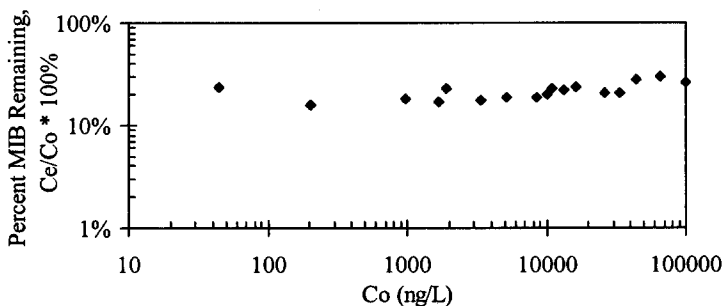

Figure 6. MIB removed by 13.2 mg/l P1100 from Myponga Reservoir water.

CONCLUSIONS

These data support a simplification in the procedure for determining the PAC dose required to remove a desired amount of MIB. It has been shown that for a given water/carbon system, a particular carbon dose will remove a fixed percentage of the MIB initially present. This has been shown to hold true regardless of the activated carbon's starting material, brand of carbon, carbon dose, natural water source, or initial concentration of MIB. However, the relationship is specific for each type of PAC and each natural water. The calculated dosage is a minimum dosage, and will be higher in a specific treatment plant if the method of PAC application does not result in the achievement of equilibrium.

This implies that predicting the minimum amount of carbon necessary to effectively mitigate any MIB episode, may be accomplished by analyzing a single bottle-point isotherm. This test may also serve as a

rapid method for comparing carbons, or for determining at what point another technology should be investigated for the control of earthy-musty taste and odor episodes.

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