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MIB ADSORPTION IN DRINKING WATER TREATMENT

BY
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B.S., Carnegie-Mellon University, 1993
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THESIS
Submitted in partial fulfillment of the requirements
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in Environmental Engineering in Civil Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 1999

Urbana, Illinois
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN
THE GRADUATE COLLEGE

November 13, 1998
(date)

WE HEREBY RECOMMEND THAT THE THESIS BY

THOMAS EDWARD TOKUO GILLOGLY

ENTITLED

MIB ADSORPTION IN DRINKING WATER TREATMENT

BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF

Director of Thesis Research
Head of Department

Committee on Final Examination†

Chairperson

† Required for doctor's degree but not for master's.
"We are healed of a suffering only by experiencing it in full." (Marcel Proust)

Abstract

MIB ADSORPTION IN DRINKING WATER TREATMENT

Thomas Edward Tokuo Gillogly, Ph.D.
Department of Civil and Environmental Engineering
University of Illinois at Urbana-Champaign. 1998
Vernon L. Snoeyink, Advisor

The objective of this research was to provide the tools necessary to determine the effectiveness of activated carbon, in the presence or absence of free chlorine, for the removal of 2-methylisoborneol (MIB) in a drinking water treatment plant.

An alternative approach to analyzing concentrations of MIB was developed for use in laboratory-scale experiments. MIB synthesized with radiolabeled-\(^{14}\)C (\(^{14}\)C-MIB), could be analyzed by liquid scintillation counting, a technique suitable for the rapid collection and analysis of radiolabeled compounds. Using this technique, a 2.5 mL sample aliquot containing \(^{14}\)C-MIB could be analyzed with a 3.0 ng/L limit of detection with greater than 89% confidence, without any sample concentration. This analysis could be used in the presence or absence of free chlorine.

The percent MIB removed by activated carbon, either powdered (PAC) or granular (GAC), was independent of the influent MIB concentration in natural water. It was determined that the adsorption of MIB was controlled by the quantity of natural organic matter adsorbed. Based on these experimental findings and supported by competitive adsorption theory, one protocol was developed to determine the minimum PAC dose required to reduce a known concentration of MIB to a desired level. A second protocol was also developed to determine the remaining GAC bed life for the mitigation of an MIB taste and odor episode. The results from these protocols indicated that adsorption
by activated carbon alone might not provide sufficient protection against taste and odor caused by MIB. It was suggested that an alternative or combination of technologies (ozone, advanced oxidation, biological reduction, adsorption) be investigated to determine which is the most effective.

It was observed that chlorine had a deleterious effect on the ability of both PAC and GAC to adsorb MIB. From this, it was encouraged to avoid contacting activated carbon with chlorine.
“It is better to deserve honors and not have them than to have them and not deserve them.” (Mark Twain)

Dedication

To my grandfather:

May I one day be half the man you saw in me.

“Be anything you want to be; just be the best that you can be.”

-Tokuo Yamamoto
Acknowledgments

Looking back to see how I have gotten to where I am today, I am reminded of the countless people who have influenced my life. While it is impossible to address every one of them here, there are a select few who have played a pivotal role during the past few years. First and foremost is my advisor, Dr. Vernon L. Snoeyink. His sage insight and timeless patience has guided me through my development here at the University of Illinois. Without him, I might actually think that I understand something about adsorption.

My gratitude also goes out to the members of my committee, Dr. Richard Larson, Dr. Benito Mariñas and Dr. Roger Minear. Their endurance, support and insight have been mostly appreciated.

The “Snoeyink Research Group”, both past and present, has been a source of inspiration, insight, and insanity. I have been fortunate enough to be a part of this fine collection of minds...and people. Those who have shared my office, and thus my life, deserve an additional thank you, and more than likely a couple of apologies. In particular, Carlos “Maestro” Campos has been a true friend, helping me though both my personal and professional careers. A special thank you goes to Joseph Elarde, who worked with me countless days, and nights, on this project and constantly provided a unique perspective on research and life.

The City of Chicago, Department of Water, has been kind enough to serve as the primary funding source for this project, without which, this thesis would not have been possible.

Last, but not least, my wife, Mai, and my family has been there every step of the way. Their encouragement, consolation, and patience have been without bounds; their understanding and forbearance, infinite.
"A place for everything, everything in its place." (Benjamin Franklin)

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EFFECT OF INITIAL CONCENTRATION IN MYPONGA RESEVOIR WATER

GREELEY AND HANSEN PILOT STUDY MIB DATA

## Appendix C (Input/Output Files)

EBC OUTPUT FILES
- Watercarb PAC
- Hydrodarco-B PAC
- Calgon F-300 (virgin)
- Calgon F-300 (1 year preload)
- Calgon F-300 (2 year preload)

IAST OUTPUT FILES
- Watercarb PAC
- Hydrodarco-B PAC
- Calgon F-300 (virgin)
- Calgon F-300 (1 year preload)
- Calgon F-300 (2 year preload)

HSDM INPUT/OUTPUT FILES
- Watercarb PAC
- Hydrodarco-B PAC
- Nuchar SA-20 PAC
- WPH PAC
- Cecarbon PAC

FS MODEL INPUT
- Calgon F-300 (virgin)
- Calgon F-300 (1 year preload)
- Calgon F-300 (2 year preload)

## Appendix D (Computer Models)

- EBC: EQUILIBRIUM PARAMETER SEARCH COMPUTER PROGRAM
- IAST: EQUILIBRIUM EQUATION SOLVING COMPUTER PROGRAM
- SEARCH: BATCH KINETIC PARAMETER SEARCH COMPUTER PROGRAM
- HSDM: BATCH KINETIC EQUATION SOLVING COMPUTER PROGRAM
- CSTR: EQUATION SOLVING COMPUTER PROGRAM
- FS-SI: FIXED-BED ADSORPTION KINETIC PARAMETER SEARCH COMPUTER PROGRAM
- FS: FIXED-BED ADSORPTION EQUATION SOLVING COMPUTER PROGRAM

Vita
Introduction

Most utilities considering employing an activated carbon system, as well as some utilities which have one installed, are perplexed. These utilities are not sure how effective their adsorptive systems will be. While many factors contribute to a particular system's effectiveness, answering two questions would go far to alleviate some of their confusion. These two questions are, “how much powdered activated carbon (PAC) will be necessary,” and, “how long will granular activated carbon (GAC) adsorbers last?” For the treatment of organoleptic problems, determining how much PAC is necessary to mitigate predicted levels of earthy-musty contamination, generally indicates if powdered or granular activated carbon should be used. Should GAC be selected, due to large required doses of PAC, ascertaining how long a GAC adsorber would be effective typically indicates if the technology is economically feasible.

The occurrence of earthy-musty tastes and odors caused by compounds such as 2-methylisoborneol (MIB) and geosmin, commonly encountered in surface waters, is a problem water utilities around the world must face. Activated carbon, both powdered and granular, has been widely used for the mitigation of these unacceptable organoleptic occurrences, but this technology has yielded mixed results. The wide variability in the effectiveness of activated carbon appears related to the magnitude and periodic nature of the influent concentration, the concentration and characteristics of the natural organic matter, and the presence or absence of free chlorine.

It is the purpose of this study to obtain the fundamental data necessary to determine the key factors that influence activated carbon performance and dosage requirements for earthy-musty taste and odor control in a water treatment plant using free chlorine as a disinfectant. This will be accomplished by investigating the influences of the influent MIB concentration, natural organic matter, and free chlorine on PAC and GAC.
“If you steal from one author, it’s plagiarism. 
If you steal from two, it’s research.” (Wilson Mizner)

A Musty Review

Of the odors in water supplies, the earthy or musty descriptors are most frequently observed, though they are often masked by stronger odors (Mallevialle et al., 1987; McGuire et al., 1981). 2-Methylisoborneol (MIB) alias 1,2,7,7-tetramethyl-exo-bicyclo(2.2.1.)heptan-2-ol alias 2-exo-hydroxy-2-methylbornane is frequently associated with the earthy-musty tastes and odors. While this compound is the focus of the paper, other causative agents of earthy-musty complaints exist.

The presence of MIB has been detected the world over. However, it has not been until relatively recently that this compound has been readily identifiable at the concentrations typically encountered in the environment. While the sensory analysis of water was initially more sensitive than chemical analysis, the variability inherent to sensory perception often cast doubts on the results.

People’s perception of the odor in the water varies greatly between individuals. This range of sensitivities varies up to a factor of 10,000 or more (Cees et al., 1974). With this wide range of perception, questions of degree of treatment arose. Should the water be treated so that some of the people are satisfied? Most of the people? All of the people?

In 1925 the US Public Health Service’s drinking water standards stated that the taste of drinking water be “generally acceptable”. This was amended in 1946 to state that drinking water should be “not objectionable”, and again in 1962 to “not offensive”. In the early 1970s, the World Health Organization (WHO) wrote that the “absence of color and of any disagreeable taste or smell are of the utmost importance in public supplies of water.” 1984 brought the draft of the WHO guidelines for drinking water quality stated that the drinking water “not be offensive for most of the consumers served.” (Bartels et
al., 1989; Sano, 1988; Mallevalle et al., 1987). These descriptors, however publicly comforting, were still vague in determining to what absolute concentrations a water should be treated. Zoeteman et al. (1980) suggested that the water be treated to a level such that only five percent of the population could detect the compounds. The 1984 draft guidelines for drinking water by the WHO did suggest that the musty odor compounds be decreased to less than ten percent of the odor threshold concentration (OTC) (Sano, 1988). The OTC corresponds to a fifty percent detection by the population; ten percent of the OTC corresponds to approximately fifteen percent of the consumers still being able to detect the odor (Cees et al., 1974). This was later generalized by the final guidelines, stipulating that only the most sensitive (five percent) of the population are permitted to detect an offensive taste. To attain these goals, an extensive amount of information must be collected.

2-METHYLISOBORNEOL

The mid-1960s brought great developments in the arena of chemical analysis of tastes and odors. It was not until this time that the specific compounds that were possibly causing the offensive organoleptic qualities were isolated and analyzed. Gerber and Lechevalier (1965) were the first to isolate a “new” compound, which they named geosmin; “ge” from Greek, meaning earth, and “osmin” meaning odor. Later, Gerber (1968) was able to publish the structure of geosmin, but there was a musty compound that was showing up in their research that had yet to be identified. In 1969, Medsker et al. (1969) isolated and identified this other compound produced by actinomycetes as MIB (Figure 1). MIB was not a new compound, as it had been earlier synthesized by Zelinsky (1901). Collins et al. (1970) confirmed that Streptomyces odorifer, an actinomycete, produced both geosmin and MIB. At the same time of these developments, acrid odors (Henley et al., 1969; Gaines and Collins, 1963) and musty odors besides MIB were also being isolated and identified (Dougherty et al., 1967; Dougherty et al., 1966; Morris et al., 1963).
Physical Properties

This research was important in identifying the problem. The structural properties of this compound and others account for their sensory activity (Veijanen, 1992; Mallevialle, 1987; Gerber, 1983; Gerber, 1968). While the structure is important, other physical and chemical properties are also critical to determine possible analytical and treatment methods, as well as understand how they persist in the environment.

<table>
<thead>
<tr>
<th>Boiling Point (°C)</th>
<th>Source</th>
</tr>
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<tbody>
<tr>
<td>207</td>
<td>Wako (1994)</td>
</tr>
<tr>
<td>196.7</td>
<td>Pirbazari et al. (1992)</td>
</tr>
<tr>
<td>208-209</td>
<td>Zelinsky (1901)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Melting Point (°C)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>162-163</td>
<td>Wako (1994)</td>
</tr>
<tr>
<td>162.1-163.3</td>
<td>Pirbazari et al. (1992)</td>
</tr>
<tr>
<td>158-160</td>
<td>Medsker et al. (1969)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical Properties of MIB</th>
</tr>
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<tbody>
<tr>
<td>Solubility (mg/L)</td>
</tr>
<tr>
<td>Vapor Pressure (atm)</td>
</tr>
<tr>
<td>Henry’s Law Constant (atm m$^3$/mol)</td>
</tr>
<tr>
<td>Log $K_{ow}$</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
</tr>
<tr>
<td>Refractive Index</td>
</tr>
</tbody>
</table>
Odor Threshold

Table 4 shows some of the MIB OTCs reported in the literature. It should be noted that this concentration has systematically decreased over time. It is believed that this correlation is generally related to the analytical detection limits and not to population sensitization. While the results of sensory evaluation techniques typically vary from population to population, and between replicate analyses within a given population, an appropriate MIB OTC, based on the more recent studies would be 5 ng/L.

<table>
<thead>
<tr>
<th>Odor Threshold Concentration (ng/L)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>Young <em>et al.</em>, 1996</td>
</tr>
<tr>
<td>5</td>
<td><em>Ito et al.</em>, 1988</td>
</tr>
<tr>
<td>4 (trained), 12 (untrained)*</td>
<td><em>Sano</em>, 1988</td>
</tr>
<tr>
<td>29</td>
<td><em>Amoore</em>, 1986</td>
</tr>
<tr>
<td>20</td>
<td><em>Zoeteman et al.</em>, 1980</td>
</tr>
<tr>
<td>30-40</td>
<td><em>Persson</em>, 1980</td>
</tr>
<tr>
<td>100</td>
<td><em>Wood and Snoeyink</em>, 1977</td>
</tr>
<tr>
<td>100</td>
<td><em>Rosen et al.</em>, 1970</td>
</tr>
<tr>
<td>100</td>
<td><em>Medsker et al.</em>, 1969</td>
</tr>
</tbody>
</table>

While several technologies have been applied to remove MIB from drinking water, activated carbon has been the treatment most frequently utilized. In comparison to granular activated carbon (GAC), powdered activated carbon (PAC) has been more frequently applied (*Gillogly et al.*, 1998; *Huang et al.*, 1996; *Wittmeyer et al.*, 1995; *Simpson and MacLeod*, 1991; *Lalezary et al.*, 1986). However, GAC has also been regularly employed (*Pirbazari et al.*, 1993; *Lalezary et al.*, 1986; *Chudyk et al.*, 1979; *Herzing et al.*, 1977).

*1 Trained personnel consisted of 25 to 36 water examination laboratory staff members; 46 untrained panelists were randomly selected from the water treatment plant’s distribution area (*Sano*, 1988). Trained personnel tend to be more aware of various attributes of the water, and as a result the perceived OTC of a trained panel is typically lower than an untrained panel (*Meilgaard et al.*, 1991).
Synthesis

Zelinski (1901) first reported the synthesis of 2-methylisoborneol. Since then, several researchers have performed similar syntheses by reacting methylmagnesium halides or methyllithium with camphor to produce MIB (Wood and Snoeyink, 1977).

![Figure 2 - Synthesis of $^{14}$C-MIB from d-Camphor](image)

Radiolabeled $^{14}$C-MIB was used extensively through the research presented in this thesis. This particular material, prepared by American Radiolabeled Chemical, Inc. (St. Louis, MO), was formed by reacting $^{14}$C-labeled methylmagnesium iodide with the d-camphor enantiomer. The d-camphor was selected after Wood and Snoeyink’s (1977) determination that naturally occurring MIB exists in the R form. A radiochemical purity of 100 percent was determined by the manufacturer using high performance liquid chromatography (HPLC). The chemical purity was determined to be greater than 99% by gas chromatography at the University of Illinois. Gas chromatography-mass spectroscopy was used to verify that the compound received from American Radiolabeled Chemicals, Inc. was 2-$^{14}$methylisoborneol.

Adsorption by Activated Carbon

For a given water and target organic micropollutant, activated carbons have displayed a wide range of capacities for the target compound; MIB is no exception (Gillogly et al.,...
Currently the adsorption mechanism controlling the uptake of MIB by activated carbons has not been verified. However, it is believed that in addition to the physical size and chemical nature of MIB, the pore size distribution and the surface chemistry of the activated carbon plays a critical role in determining how MIB adsorbs.

Several researchers (Newcombe and Drikas, 1995; Chudyk et al., 1979; and Pendleton et al., 1997) have been able to show a strong correlation between the surface area/micropore volume of PAC (coal-, coconut-, lignite-, and peat-based) and MIB adsorption capacity. While the data collected from wood-based PACs did not fit this same trend, an increase in the surface area/micropore volume of the wood-based PACs still yielded higher adsorption capacities. It was concluded from additional analyses that the porosity of the carbon could not account for the differences observed with the wood-based carbon, indicating the differences were probably due to surface chemistry (Pendleton et al., 1997).

It has been proposed that surface oxides play a critical role in the adsorption of organic compounds by activated carbon. Boehm (Eley et al., 1966) developed a set of titrations to categorize the surface oxides into four groups: strongly acidic carboxyl, weakly acidic carboxyl, phenolic and carbonyl. Based upon these titrations, Snoeyink et al. (1974) and McGuire and Suffet (1984, 1980) correlated increases in concentrations of these functional groups to increasing reaction between free chlorine and activated carbon. The increasingly oxidized carbons were then correlated to decreasing adsorption quantities of phenol, para-nitrophenol, $n$-butanol, 1,4-dioxane, nitromethane, and methyl ethyl ketone.

Lalezary et al. (1988), and Lalezary-Craig et al. (1986) showed that PAC was less effective for MIB if it was applied together with chlorine. Gillogly et al. (1998b, submitted 1998) reacted varying amounts of free chlorine with activated carbon and found decreasing removals of MIB for increased amounts of free chlorine reacted. These findings are consistent with a study that reported a decrease in MIB adsorption capacity.
with increasing hydrophilic sites, as determined by water adsorption isotherms (Pendleton et al. 1997).

Together these studies suggest that MIB adsorption by activated carbon probably occurs by hydrophobic interaction (sorption to non-polar hydrocarbon-like sites) with the carbon surface. As a result, free chlorine reacting with the surface of the carbon (forming >C=O, -OH and -COOH groups) increases the hydrophilicity of the carbon surface. For more hydrophilic surfaces, less MIB would be expected to adsorb, as it would be more difficult for the MIB to displace the adsorbed water molecules to reach the non-polar adsorption sites.
"The only limit to our realization of tomorrow will be our doubts of today. Let us move forward with strong and active faith."
(Franklin Delano Roosevelt)

Objectives

It was the hypothesis of the author that the methods currently used to determine how effective powdered and granular activated carbon are for the removal of naturally occurring episodes of MIB are too complex and often do not take into consideration how other treatment process affect the effectiveness of the carbon. Therefore, it was the objective of this research to develop simple tools to determine the effectiveness of activated carbon, in the presence or absence of free chlorine, for the removal of 2-methylisoborneol in a drinking water treatment plant. Discussed in the next five chapters, this objective was met by collecting the fundamental data to realize the following goals:

- Demonstrate liquid scintillation counting of $^{14}$C-MIB is a technique suitable for rapid collection and analysis of low spiked concentrations of MIB in natural water environments that do not oxidize the MIB;
- Develop a method to determine the minimum powdered activated carbon dose required to reduce a given MIB concentration to a specific level in natural water;
- Confirm that the method to determine the minimum PAC dose required to mitigate an earthy-musty taste and odor episode is independent of the PAC's starting material, natural water source, or naturally occurring MIB concentration;
- Determine the effect of free chlorine on 2-methylisoborneol adsorption by powdered activated carbon;
- Verify that the removal efficiency of MIB by a GAC adsorber is unrelated to the concentration of MIB in natural water;
• Show that the GAC adsorber removal efficiency of MIB is dependent on the mass of chlorine reacted per mass of activated carbon and/or the amount of previously adsorbed background organic matter;

• Demonstrate that the immediate performance potential of GAC, as determined in laboratory scale columns, is independent of bed dimensions for a given EBCT.

• Postulate a protocol to assess the immediate performance potential of a GAC filter/adsorber based upon the elements of research that proved significant.
"I look on that man as happy, who, when there is a question of success, looks into his work for a reply." (Ralph Waldo Emerson)

A Simplified Method to Determine the PAC Dose Required to Remove MIB

by


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, $C/C_o \times 100\%$, 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.

KEYWORDS

$^{14}$C-MIB; 2-Methylisoborneol; Activated Carbon; Closed-Loop Stripping Analysis (CLSA); Scintillation Counting

* University of Illinois, 205 N. Mathews Avenue, Urbana, Illinois 61801 (V.L. Snoeyink served as an advisor to the project; J.R. Elarde, a masters student, assisted in collecting data from the domestic waters)
** Australian Water Quality Centre, Private Mail Bag, Salisbury South Australia 5108, Australia (G. Newcombe collected the data obtained from the Australian waters)
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., 1997) 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. 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 (1996). 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 compounds 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 14C labeled MIB (14C-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 "Kinetic and Equilibrium Studies of 14C-MIB Adsorption on PAC in Natural Water" (Gillogly et al., 1997).

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 U.S. Standard mesh (44 μm diameter).

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 that 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.

Following a recent development of Knappe (1996), it has been shown that if the natural water equilibrium data are plotted as percent remaining, \( C_e/C_0 \times 100\% \), 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, 1996). 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.

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**Figure 2 - PAC adsorption isotherms in Kankakee River water**

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**Figure 3 - PAC adsorption isotherms in Lake Michigan 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 $C_0$ is 100 ng/L and it must be reduced to 5 ng/L, a removal of 95% is required ($C_0/C_x \times 100\% = 5\%$). 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.

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

<table>
<thead>
<tr>
<th>Water Source</th>
<th>WPH</th>
<th>Hydrodarco-B</th>
<th>Watercarb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kankakee River</td>
<td>20.3</td>
<td>61</td>
<td>-</td>
</tr>
<tr>
<td>Lake Michigan</td>
<td>12.5</td>
<td>22</td>
<td>38</td>
</tr>
</tbody>
</table>

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.

![Graph 1](image1.png)

**Figure 5 -** MIB removed by 13.2 mg/L P1300 from Myponga Reservoir water

![Graph 2](image2.png)

**Figure 6 -** MIB removed by 13.2 mg/L P1100 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.

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 a 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 natural water and type of PAC. 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.
"Nothing can have value without being an object of utility" (Karl Marx)

Kinetic and Equilibrium Studies of $^{14}$C-MIB
Adsorption on PAC in Natural Water

by


INTRODUCTION

Anthropogenic and biogenic taste and odor problems have plagued water sources over the ages. In prehistoric times, people relied upon their senses to warn them of dangerously contaminated water. Even today we are influenced by our senses to determine if a particular food or drink has spoiled or become contaminated. Additionally, the awareness of pollutants in our environment has brought us to a state of hypersensitivity to off-flavors and odors. These objectionable tastes and odors are often presumed to be due to toxic substances (Jensen et al., 1994). A study in The Netherlands showed a 45 percent decrease in water consumption due to people disliking the taste (Cees et al., 1974). Another survey of US consumers, showed that greater than 15 percent of the respondents used either bottled water or a home-treatment device. The majority of these people indicated that their action was due to bad smelling or tasting tap water (Manwaring et al., 1986). Earlier, the Gallup Poll showed the most common complaint with drinking water to be taste (Gallup, 1973).

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* University of Illinois, 205 N. Mathews Avenue, Urbana, Illinois 61801 (V.L. Snoeyink served as an advisor to the project; J.R. Elarde, a masters student, assisted in collecting data)
** City of Chicago, Department of Water, 1000 East Ohio Street, Chicago, Illinois 60611 (C.M. Wilson and E.P. Royal provided information about the problem in Lake Michigan)
Of the odors in water supplies, the earthy or musty descriptors are most frequently observed, though they are often masked by stronger odors (Mallevialle and Suffet, 1987; McGuire et al., 1981). The two compounds most frequently associated with earthy-musty odors are MIB and geosmin. These compounds are problematic due to their odor threshold concentrations in the low nanogram/L levels and resistance to chemical oxidation. Chlorine and potassium permanganate by themselves are generally considered ineffective. As a result, many utilities have used granular activated carbon (GAC) and powdered activated carbon (PAC). Recently, Suffet et al. (1996) reported that utilities responding to a survey considered activated carbon to be the most effective taste and odor control process. Of those utilities, PAC was used more than six times as often as GAC.

Because MIB is frequently present, and more weakly adsorbed than other common earthy or musty compounds, including geosmin, it is reasonable to use it as the target compound in laboratory studies (Lalezary et al., 1986). The analysis of MIB has often handicapped the development of solutions to the taste and odor problem. Although it has been successfully used by many, the Closed Loop Stripping Analysis (CLSA) procedure is inefficient, laborious and time consuming due to requirements of large sample sizes, the need for prolonged stripping of the sample, and extended time for chromatographic analysis (Standard, 1992). This method often yields low reproducibility at low MIB concentrations, creating special problems in adsorption studies.

OBJECTIVES AND APPROACH

The objective of this study was to develop a method which could be easily employed to determine the necessary amount of PAC required to mitigate earthy-musty taste and odor episodes. This study shows that radiolabeled MIB can be used to circumvent most analytical problems discussed above. It has also been shown that both kinetics of MIB adsorption and capacity in the presence of natural organics are important factors in determining the performance of a PAC in a water treatment plant. In order to achieve the
objective, five commercially available PACs were studied in Lake Michigan water. Laboratory kinetic data were analyzed using the pseudo single-solute homogeneous surface diffusion model (HSDM) (Traegner and Suidan, 1989; Qi et al., 1994). The equilibrium results were analyzed using a new approach that involves a percent adsorbate remaining at equilibrium versus carbon dose plot. The results from this research were compared to those obtained by Huang et al. (1996) using the traditional CLSA analysis.

The HSDM model assumes instantaneous equilibrium between the adsorbent and adsorbate at the outer surface of the particle, and that the intraparticle migration of the adsorbate is controlled by surface diffusion. Determination of the kinetic parameters (liquid film mass transfer coefficient - $k_f$, surface diffusion coefficient - $D_s$) for the batch system is accomplished by minimizing the difference between the concentration versus time data collected in a batch test, and that predicted by the HSDM. This comparison between the model prediction and data requires inputs of parameters which can be determined directly (initial MIB concentration - $C_o$, carbon concentration - $C_c$, particle diameter - $d_p$, particle density - $\rho_p$) and experimentally (Freundlich coefficients - $K$, $1/n$). Once the model is calibrated it can be used to predict adsorption as a function of time in different types of reactors, such as plug flow and continuous stirred tank reactors.

The experimentally determined parameters are calculated using the Freundlich isotherm equation (Freundlich, 1906):

$$q_e = K C_e^{1/n}$$

\[1\]

where $q_e$ = Solid phase concentration of MIB in equilibrium with $C_e$;

$K$ = Freundlich isotherm constant;

$C_e$ = Equilibrium liquid phase concentration of MIB;

$1/n$ = Freundlich isotherm constant.
A new method for interpreting both kinetic and equilibrium data for trace compounds in natural waters follows the recent development of Knappe (1996). 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 in the case of atrazine, the trace compound percent removal at equilibrium for a given carbon dose in natural water is independent of its initial concentration (Knappe et al., 1996). Thus, for a given carbon dose, the amount of trace compound adsorbed is directly proportional to its initial concentration. Additionally, the data in this study have demonstrated that the percent removal at any given time for a given carbon dose in natural water, is independent of the MIB initial concentration. Therefore, by plotting the percent of trace compound remaining versus carbon dose for a given contact time, the minimum amount of carbon required to reduce the trace compound to a desired concentration, may be quickly obtained without the need for mathematical models. In order to use this plot, it is important to establish that the range of initial concentrations of interest is less than the value above which this relationship is no longer valid.

MATERIALS AND METHODS

2-Methylisoborneol
The ¹⁴C-labeled 2-methylisoborneol (¹⁴C-MIB) (American Radiolabeled Chemicals, St. Louis, MO) was selected due to ease of analysis and small sample size requirements. Analysis of ¹⁴C-MIB samples was accomplished by mixing 2.5 mL 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). The specific activity (55 mCi/mmol) of the ¹⁴C-MIB yielded a detection limit, with a confidence level greater than or equal to 89%, of 4.5 ng/L without the use of a concentration step (Skoog and Leary, 1992).
The compound was received predissolved in purge and trap grade methanol at a concentration approximately 18.3 μg/μL (chemical purity ≥ 99% confirmed by GC-MS analysis, 100% radiochemical purity confirmed by HPLC). Stock solutions of 100 ng/μL were subsequently prepared by spiking 5.4 μL of the received solution into 1 mL of purge and trap grade methanol. The compound and all solutions were stored at 4°C.

**Water**

*Natural Water.* Lake Michigan water (see Table 1 for composition) was used as the natural water source to study competitive effects between background organic material and MIB. Water was collected from a line running from the South Water Production Plant (Chicago, IL) crib to the shore plant. The water was shipped to the University of Illinois in 208 L (55 gal) stainless steel drums, where it was stored at 4°C in the dark to limit biological activity. (The crib is located two miles off shore in water 32 to 35 feet deep; the water is drawn near the bottom.)

<table>
<thead>
<tr>
<th>Table 1. Characteristics of Lake Michigan Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Alkalinity</td>
</tr>
<tr>
<td>Conductivity</td>
</tr>
<tr>
<td>Turbidity</td>
</tr>
<tr>
<td>Nitrogen, Total Kjeldahl</td>
</tr>
<tr>
<td>Phosphate, Total</td>
</tr>
<tr>
<td>Dissolved Organic Carbon</td>
</tr>
</tbody>
</table>

*Organic-free Water.* Organic-free water for the single-solute isotherms was obtained by passing deionized Urbana, IL, tap water through a Milli-Q water system (Millipore Corp., Bedford, MA) which has three cartridges (activated carbon, ion exchange, ion exchange) and a 0.45μm filter. The water had a resistivity ≥ 18 megohm-cm and a dissolved organic carbon (DOC) content of 0.1-0.3 mg/L.
Activated Carbons

The PACs evaluated in this study were Cecarbon (Elf Atochem North America, Philadelphia, PA), WPH (Calgon Carbon Corp., Pittsburgh, PA), Hydrodarco-B (Norit Americas Inc., Atlanta, GA), Watercarb (Acticarb, Dunnellon, FL), and Nuchar SA-20 (Westvaco Chemicals, Covington, VA). (See Table 2.) Samples of these carbons were obtained from the inventory of the City of Chicago Department of Water, but were not collected in a fashion to assure that they were fully representative of the inventory. The PAC samples were stored in polyethylene bottles until used.

<table>
<thead>
<tr>
<th>PAC</th>
<th>Starting Material</th>
<th>Iodine No. (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cecarbon</td>
<td>Bituminous Coal</td>
<td>1020</td>
</tr>
<tr>
<td>WPH</td>
<td>Bituminous Coal</td>
<td>800</td>
</tr>
<tr>
<td>Hydrodarco-B</td>
<td>Lignite</td>
<td>550</td>
</tr>
<tr>
<td>Watercarb</td>
<td>Wood</td>
<td>550</td>
</tr>
<tr>
<td>Nuchar SA-20</td>
<td>Wood</td>
<td>1000</td>
</tr>
</tbody>
</table>

Prior to use, samples were dried overnight in a 110°C oven, to remove excess water, and subsequently were cooled in a desiccator. Once cooled, the desired amount of carbon, not less than 2 mg, was weighed out on a 4-point scale (LIBROR AEU-210, Shimazdu Corp., Kyoto, Japan).

For experiments which required carbon slurries, a slurry of 10 mg/mL was used. These slurries were prepared by mixing 10 g of the particular carbon, prepared as above, in 1 L of organic-free water. The slurry was mixed with a magnetic stirring bar only when an aliquot was to be drawn. For the remaining time the slurry bottle was quiescent. This was to prevent grinding of the carbon between the storage vessel bottom and magnetic stirring bar, as the kinetics of adsorption is sensitive to particle diameter.17, 18

Equilibrium Isotherm Tests

Adsorption isotherms of 14C-MIB on PAC were obtained in the laboratory using the bottle-point technique (Randtke and Snoeyink, 1983). Into 1 L, 500 mL, 250 mL, or 120
mL acid washed/baked 300°C bottles, a known mass of the oven dried carbon was added, along with a known volume of glass beads. Three of the bottles had no carbon, and were used to determine the initial concentration of 14C-MIB. These bottles were then filled headspace free with the sample water using a 100 mL dispensing pipette (Brinkmann, Westbury, NY). The 120 mL bottles were then covered with a teflon faced silicone septum (Wheaton, Millville, NJ) and an aluminum crimp cap while the 1L, 500 mL and 250 mL bottles were covered with teflon tape (Fisher, Pittsburgh, PA) and a screw cap. These bottles were then agitated on a shaker table in the dark for 4 days. After the four days, samples were collected using a stainless steel needle (Aldrich Chemical Co., Milwaukee, WI) connected to a gas-tight, luer lock syringe (Hamilton Co., Reno, NV). The aliquot was then passed through a 0.22 μm conditioned nylon membrane syringe (Magna, Westboro, MA) supported in a syringe filter holder (Swinney Holder, Gelman Sciences, Ann Arbor, MI). To condition the filter, 5 mL of the sample was filtered and wasted prior to the collection of 2.5 mL into the scintillation vial. The glass beads were used to ensure adequate mixing in the headspace free bottles.

Isotherm solutions were prepared in a floating head delivery vessel (custom manufacture, University of Illinois, IL). For isotherms in natural water, the floating head delivery vessel was filled with Lake Michigan water. The water was chlorinated to 2.5 mg/L as Cl₂ and stirred for 6 to 8 hours. This killed most of the microorganisms, and allowed the water to come to room temperature. After stirring, the free chlorine was measured and subsequently dechlorinated with a stoichiometric amount of sulfurous acid (Fisher Scientific Co., Pittsburgh, PA). The pH of the solution was adjusted as needed back to 8.2 ± 0.1, with 1 M HCl or NaOH. The dechlorinated water was then spiked with a predetermined amount of 14C-MIB and allowed to mix for 1 hour prior to filling the isotherm bottles.

**Batch Kinetic Tests**

The device used for the batch kinetic experiments was a jar test apparatus (Six Paddle Stirrer Model 7790-400, Phipps & Bird, Richmond, VA) and modified square jars (B-
Clear acrylic lids were manufactured for each individual jar to prevent loss of MIB through volatilization. These lids allowed for the experiments to be visually monitored and run with only a small fraction of the solution surface exposed to the atmosphere. In the jars, 2.6 L of Lake Michigan water (pH = 8.2) was brought to room temperature and spiked with \(^{14}\text{C-MIB}\) to the desired initial concentration. The solutions were then stirred at 125 rpm for 5 minutes before the addition of carbon. Carbon was either added by aliquots of a carbon slurry, or by a weighed mass of oven dried, prewetted carbon. (To properly wet the carbon prior to the test, weighed carbon was soaked overnight in a small aliquot of organic-free water.) Samples were then withdrawn at predetermined time intervals up to 240 minutes. The samples were collected in the same fashion as described above in the equilibrium tests. To maintain the jars headspace free, unspiked Lake Michigan water was added to make up volume used in sampling. The resulting measurements were then adjusted for the amount of water added to the system.

Full-scale Treatment
During 1995, the City of Chicago, Department of Water, proactively started the application of approximately 2.4 mg/L of PAC in May, prior to the expected beginning of the taste and odor season. It was not until mid-July that analyses of the influent showed MIB. With the initial detection of MIB, carbon doses were continually increased to a maximum of 11 mg/L at the height of the taste and odor season. The PAC doses decreased along with the MIB, until a residual level of 1.2 mg/L PAC had been applied for approximately one month beyond the last detection of MIB. The effluent concentrations of MIB corresponding to a known dosage of PAC were not collected, therefore, direct comparison between the field data and laboratory predictions was not possible.
RESULTS AND DISCUSSION

Adsorption Equilibria

*Watercarb PAC.* The results from the four day isotherms are shown in the familiar equilibrium solid-phase concentration of MIB, $q_e$, versus the MIB equilibrium solution concentration, $C_e$, plot in Figure 1. This figure shows the effect of the background organics competing with the MIB. The adsorption capacity is much less in natural water than organic-free water, and decreases as the initial concentration of MIB used in the isotherm test decreases. Note that the isotherms in organic-free water ($C_o$ 149 ng/L and 0.374 mg/L) yielded the same Freundlich parameters, indicating that they are not a function of initial MIB concentration. The background organic matter reduces the amount of MIB that can be adsorbed by occupying adsorption sites on the PAC. The capacity of PAC for MIB can be predicted through the use of competitive adsorption models, one of which is the Equivalent Background Compound (EBC) model (Najm *et al.*, 1991; Knappe *et al.*, 1993; Qi, 1992).

\[
K = 9.562 \left(\frac{\text{ng/mg}}{\text{L/ng}}\right)^{1/n} \\
1/n = 0.492
\]

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Within the EBC model the complex mixture of the background organic matter is represented as a single “equivalent background compound”. This allows the competition between the background organics and the target compound to be calculated by the ideal adsorbed solution theory (IAST). The parameters for the EBC (Freundlich - $K_{EBC}$, $1/n_{EBC}$, $C_{o,EBC}$) are determined by calculating the parameters for a single compound which would produce the same amount of competition observed between a single-solute and natural-water isotherms, for the target compound. The EBC model then uses these Freundlich EBC and the single-solute MIB Freundlich parameters, along with the IAST program to calculate isotherms for different initial concentrations of MIB in that particular natural water.

![Figure 2. Percent MIB Remaining as a Function of Watercarb PAC Dose](image)

It has been previously shown that if the natural water equilibrium data are plotted as percent remaining, $C_e/C_o \times 100\%$, versus carbon dose, $C_e$, instead of $q_e$ versus $C_o$, the data converge to a single line if the initial concentrations of the trace compound are sufficiently low (Knappe, 1996). This 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 MIB data for initial concentrations of 150 and 1245 ng/L, almost an order of magnitude in difference, fall on the same line. A best fit line is also displayed on this figure. Calculations with the EBC model for this PAC-natural water system show that if MIB initial concentration, \( C_0 \), equals 4,000 ng/L, the PAC dose to remove 95% of the MIB is only 10% larger than the minimum dose calculated from the line of convergence, and it becomes progressively less as \( C_0 \) decreases. Based on these data, we have assumed that equilibrium data for initial concentrations less than 150 ng/L will similarly produce a single line on a \( C/C_0 \times 100\% \) versus \( C_c \) plot.

![Figure 3. Percent MIB Remaining as a Function of Hydrodarco-B PAC Dose](image)

Extracting critical information from these plots can be done quickly and easily. For example, if the MIB \( C_0 \) is 40 ng/L and it must be reduced to 4 ng/L, a removal of 90% is
required \((C_j/C_o \times 100\% = 10\%)\). The figure shows that a carbon dose, of 31 mg/L of Watercarb PAC would be required. Similarly, 21.5 mg/L PAC would be required for 80% removal.

**Hydrodarco-B PAC.** The percent remaining versus carbon dose plot for Hydrodarco-B PAC is shown in Figure 3. The data in this plot show the minimum carbon dose for a given percent remaining, at equilibrium, of the initial MIB concentration. EBC model calculations for the PAC-natural water system show that if the MIB \(C_o = 200,000\) ng/L, the PAC dose to remove 95% of the MIB is only 10% more than the minimum dose. Thus, the \(C_j/C_o \times 100\%\) versus \(C_c\) plots are independent of the initial MIB concentrations used in this study, as well as any concentration expected in natural water. These findings are consistent with the theoretical development of Knappe (1996) and his observation that the PAC dose required to remove a given percentage of atrazine converged to a minimum for \(C_o < 50\) µg/L (Knappe et al., 1996).

**Adsorption Kinetics**

**Watercarb PAC.** Headspace free batch kinetic tests at a pH of 8.2 were used to evaluate the MIB adsorption rate. Watercarb PAC was the first of the five PACs to be analyzed. Figure 4 shows the experimental data collected for a four hour batch kinetic test, with an MIB initial concentration of 175 ng/L and a 11.5 mg/L PAC dose. In order to analyze the data using the HSDM, the Freundlich parameters, \(K\) and \(1/n\), corresponding to the \(C_i\) and carbon dose of the kinetic test need to be known. A \(K\) value of 2.37 \((\text{ng/mg})(\text{L/ng})^{1/n}\) and a \(1/n\) of 0.303 were calculated for this initial concentration from the \(C_j/C_o \times 100\%\) versus \(C_c\) plot. This was accomplished by generating a \(q_e\) versus \(C_c\) isotherm for this initial concentration by determining the \(C_j/C_o \times 100\%\) values corresponding to several carbon doses. The \(C_j/C_o\) value for each carbon dose was then used to calculate \(q_e\), the surface concentration, as a function of \(C_c\), using: \(q_e = (C_o - C_j)/C_c\). The \(q_e\) versus \(C_c\) data were plotted on a log-log plot; the slope of the linear portion of the isotherm was used as the \(1/n\) value. The \(q_e\) (mg/g) for the carbon dose of interest (11.5 mg/L) and the \(1/n\) value were used in the Freundlich equation (see equation 1) to calculate \(K\). The input of these
Freundlich values along with the batch kinetic data into the HSDM model yielded a surface diffusion coefficient, $D_s$, equal to $0.110 \times 10^9$ cm$^2$/min, as determined by the Levenberg-Marquardt algorithm, a nonlinear least squares optimization routine (International, 1991).

The HSDM fit to the data is also shown in Figure 4. Once the surface diffusion coefficient was determined, the HSDM was used to predict the percent removal of MIB as a function of time for a PAC dose of 34.6 mg/L. (See Figure 5.) The prediction is in acceptable agreement with the experimental data. Therefore, this approach to calibrating the HSDM can be used to give reasonable results.

![Graph showing percent MIB remaining against time with experimental data and HSDM fit.]

Figure 4. Batch Kinetic Test Data for MIB Adsorption with Watercarb PAC

The HSDM was able to give a better fit and prediction of the data in the Figures 4 and 5 if it was assumed that equilibrium was reached in 4 hours rather than 4 days. Using the 4-hour plateau values from the kinetic data for 3 to 4 different carbon doses, a $C_{\text{eq}}/C_0 \times 100\%$ versus $C_c$ plot was generated. (Refer to Figure 13.) From this plot and the procedure described above with the $C_c/C_0 \times 100\%$ versus $C_c$ plot, $K$ and $1/n$ values were
generated. (See Table 3 for values.) By using these new values, a much better fit of the first 4 hours of data was obtained. (See Figure 6) A similar approach was employed by Huang et al. (1996). Its application was able to successfully simulate field data for the adsorption of MIB from Niagara River water.

The difference in the agreement between measured and predicted values is a result of the difference between the pseudo-equilibrium reached within 4 hours and true equilibrium at 4 days. The slow increase in capacity after 4 hours is not consistent with a mechanism of uptake that can be characterized by a single surface diffusion coefficient for the entire kinetic curve. This "second step" may be another surface or pore diffusion controlled step in which MIB must pass through pores partially blocked by background organic matter. Using the approach that emphasizes the first 4 hours of data is most important if only short contact times are used for PAC in the full scale plant, but the true equilibrium data should be used if the PAC is to be used with very long contact times.
HSDM Fit and Prediction of Batch Kinetic Test Data for MIB Adsorption with Watercarb PAC, Based Upon 4-Hour Kinetic Test Plateau Values ($D_s = 3.69 \times 10^{-10}$ cm$^2$/min)

Table 3. 4 Hour Freundlich Isotherm Constants

<table>
<thead>
<tr>
<th>PAC</th>
<th>K (ng/mg)(L/ng)$^{1/n}$</th>
<th>$1/n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mg/L)</td>
<td>(based upon kinetic test plateau values)</td>
<td></td>
</tr>
<tr>
<td>Cecarbon</td>
<td>4.13</td>
<td>0.396</td>
</tr>
<tr>
<td>WPH</td>
<td>3.52</td>
<td>0.359</td>
</tr>
<tr>
<td>Nuchar SA-20</td>
<td>2.20</td>
<td>0.418</td>
</tr>
<tr>
<td>Hydrodarco-B</td>
<td>2.49</td>
<td>0.341</td>
</tr>
<tr>
<td>Watercarb</td>
<td>2.50</td>
<td>0.216</td>
</tr>
</tbody>
</table>

*Hydrodarco-B* PAC. The kinetic experiments were repeated using Hydrodarco-B. The fit and prediction of the first 4 hours of data, using true equilibrium data to calibrate the HSDM, was similar to that obtained with Watercarb PAC and are not shown here. However, a better fit and prediction of the first 4 hours of kinetic data was again obtained using 4-hour plateau values to obtain the Freundlich parameters for the HSDM. (See Figure 7.)
Additional batch kinetic tests were performed with 11.5 mg/L Hydrodarco-B to determine what effect changes in the initial concentration of MIB would have on the observed percent removal over time. Figure 8 shows the percent removal at any given time for a particular carbon dose, is not a function of the initial concentration of MIB. This is an important finding because it shows that the diffusion coefficient is not a function of initial concentration. Therefore, percent removal versus time predictions is valid for any MIB concentration typically encountered in natural water. Based upon this information, the percent remaining at equilibrium, \( C/C_0 \times 100\% \), versus \( C_c \) plot described above may be expanded to a percent remaining at a fixed time, \( C/C_0 \times 100\% \), versus \( C_c \) plot, which will not change as \( C_0 \) changes. (See Figure 9) This family of curves was developed using the HSDM that was calibrated with the data in Figure 7. From this new plot, the amount of Hydrodarco-B required to reduce various episodes to the threshold odor concentration, given different amounts of contact time in an ideal reactor, may be quickly determined. (See Table 4.)

![Figure 7](image-url)
Other Powdered Carbons. Kinetic tests were run with the remaining three carbons in order to observe trends between carbons, without doing the extensive equilibrium tests previously done with Watercarb and Hydrodarco-B. Initial MIB concentrations varied from 170 to 175 ng/L, and a pH of 8.2 ± 0.1 was used in these evaluations.

For each carbon, batch kinetic tests with two different carbon doses were performed. A 4-hour response to an additional two carbons doses was also obtained, though the full kinetic response for these doses was not developed. Figures 10 through 12 show the first 4 hours of kinetic data for Nuchar SA-20, WPH, and Cecarbon, respectively. These figures also show the HSDM fit and prediction of the kinetic data based upon the available 4-hour data shown in Figure 13. The Freundlich parameters that were obtained from the data in Figure 13 are given in Table 4.
Figure 9 Percent MIB Remaining as a Function of Contact Time versus Hydrodarco-B Dose

Figure 10. HSDM Fit and Prediction of Batch Kinetic Test Data for MIB Adsorption with Nuchar SA-20 PAC, Based Upon Kinetic Test Plateau Values ($D_s = 3.55 \times 10^{-10}$ cm²/min)

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Figure 11. HSDM Fit and Prediction of Batch Kinetic Test Data for MIB Adsorption with WPH PAC, Based Upon Kinetic Test Plateau Values ($D_s = 2.08 \times 10^{-10} \text{ cm}^2/\text{min}$)

Figure 12. HSDM Fit and Prediction of Batch Kinetic Test Data for MIB Adsorption with Cecarbon PAC, Based Upon Kinetic Test Plateau Values ($D_s = 1.73 \times 10^{-10} \text{ cm}^2/\text{min}$)
Figure 13. Percent MIB Remaining After 4 Hours of Contact for All Five PACs

Table 4. Required Hydrodarco-B Dose (mg/L) to Reduce the MIB Concentration to 5 ng/L for Different MIB Episodes and Contact Times*

<table>
<thead>
<tr>
<th>Contact Time</th>
<th>Initial Concentration</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 ng/L</td>
<td>50 ng/L</td>
<td>25 ng/L</td>
<td></td>
</tr>
<tr>
<td>7.5 min</td>
<td>77</td>
<td>61</td>
<td>44</td>
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<tr>
<td>15 min</td>
<td>58</td>
<td>44</td>
<td>32</td>
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<tr>
<td>30 min</td>
<td>44</td>
<td>34</td>
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<td></td>
</tr>
<tr>
<td>1 hour</td>
<td>36</td>
<td>28</td>
<td>21</td>
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<tr>
<td>4 hours</td>
<td>32</td>
<td>23</td>
<td>17</td>
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</tbody>
</table>

* These doses have been calculated assuming contact takes place in an ideal reactor.

From Figure 13, the minimum required dose for each PAC, with 4 hours of contact, can quickly be determined for any initial concentration. Table 5, gives an example of reducing initial concentrations of 100, 50 and 20 ng/L down to 5 ng/L (95%, 90%, 80% removal, respectively) in 4 hours.
Table 5. Required PAC Dose to Reduce the MIB Concentration to 5 ng/L for Different MIB Episodes and 4 Hours of Contact Time*

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Initial Concentration</th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 ng/L</td>
<td>50 ng/L</td>
<td>25 ng/L</td>
<td></td>
</tr>
<tr>
<td>Cecarbon</td>
<td>18</td>
<td>13</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>WPH</td>
<td>24</td>
<td>18</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Nuchar SA-20</td>
<td>30</td>
<td>22</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Hydrodarco-B</td>
<td>32</td>
<td>23</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Watercarb</td>
<td>38</td>
<td>33</td>
<td>27</td>
<td></td>
</tr>
</tbody>
</table>

* These doses have been calculated assuming contact takes place in an ideal reactor.

The data for the higher carbon doses of each PAC were compared to the results obtained in Niagara River water, another Great Lakes water, by Huang et al. (1996). For a PAC dose of 30 mg/L in Niagara River water (pH = 8.3; TOC ≈ 2.5 mg/L), the percent MIB remaining after 1.5 hours depended on the brand of carbon used. Watercarb and Nuchar SA-20 were found to remove 83 and 95% of the MIB, respectively. For the same dose and amount of time in Lake Michigan water (pH = 8.2; TOC ≈ 1.8 mg/L), Watercarb and Nuchar SA-20 were predicted to remove 81 and 94%, respectively.

Using the maximum possible PAC dosage for the Chicago water treatment plants (12 mg/L PAC), a comparison of all five powdered activated carbons is shown in Figure 14. Each curve represents the HSDM model prediction for that PAC under plug flow conditions. At 4 hours, the predicted percent MIB remaining for the carbons ranges from 10 to more than 40 percent. Modeling the system as a completely mixed reactor to account for an exponential residence time distribution of PAC, decreases the percent remaining to 6 to more than 35 percent. An actual water treatment plant would probably have conditions somewhere between plug flow and completely mixed. More importantly, these wide range of percent removals imply that the selection of a particular PAC should not be based solely upon cost per weight, but should instead be founded upon a cost per unit MIB removal.
A comparison of Figure 13 to Figures 2 and 3 shows, that there can be significant differences between the amount of PAC required for 4 hours versus 4 days of contact. For a 90% removal, increasing the dose of Watercarb PAC by 7%, or 2 mg/L, would be required if the contact time was decreased from 4 days to 4 hours. This difference is larger with Hydrodarco-B PAC, which would require increasing the dose 45%, or 7.5 mg/L, for this same decrease in contact time. This emphasizes the importance of having an extended contact time to minimize the carbon dose. Increased contact time may be available if PAC is applied directly to a filter, or in a solids contact clarifier.

The methodologies presented here can be utilized to choose the most cost effective PAC. It must be remembered that conditions in the full-scale plant may lead to results that vary somewhat from laboratory experiments. Specifically, if the PAC is very dense, more of it may settle out early in a sedimentation basin, thus shortening the effective contact time for that carbon and reducing the amount adsorbed. Further, a difference in the particle size distribution of the PAC relative to the sample of PAC used in the laboratory tests...
may affect kinetics. Some interaction with treatment chemicals used at the plant, although probably unavoidable, may also affect performance, as may hydraulic short circuiting. These issues make it necessary to obtain full-scale plant data on MIB removal to compare to the predicted performance in order to assess the importance of these factors. The data presented here are also specific to Lake Michigan water. Different results would be expected if another water source were to be used.

CONCLUSIONS

The use of $^{14}$C-MIB allows for reproducible, accurate, and timely data collection. The protocol for data collection and analysis developed above is a viable tool to investigate the effects of alternative waters, carbons and types of natural organic matter, on the kinetics of MIB adsorption and the equilibrium capacity. Using this material, and a scintillation counter to determine concentration, it was found that:

- For a given PAC dose in natural water, the percent MIB adsorbed at equilibrium is independent of the initial MIB concentration. This is supported in theory by a competitive adsorption model (EBC) and confirmed by both kinetic and equilibrium batch experiments.
- For any given PAC dose in natural water, and any fixed time of contact, the percent MIB adsorbed in an ideal reactor is independent of the initial MIB concentration. Thus for any contact time of interest, the PAC dose required to mitigate any MIB episode for any contact time of interest, may be quickly determined from a $C_r/C_o \times 100\%$ versus $C_e$ plot.
ACKNOWLEDGMENTS

The studies described in this paper were funded primarily by the City of Chicago, Department of Water. The authors would also like to thank Karen A. Marley and Thomas S. Gittelmann for their helpful advice.
"Men love to wonder and that is the seed of our science." (Ralph Waldo Emerson)

Effect of Chlorine on 2-Methylisoborneol Adsorption by Activated Carbon

by


INTRODUCTION

Musty or earthy odors, generally attributed to 2-methylisoborneol (MIB) and geosmin, are the most frequently observed odors in water supplies (Mallevialle and Suffet, 1981). Surveys of utilities have found that the use of activated carbon seems to be one of the most effective methods for the control of tastes and odors (Suffet et al., 1996; Sigworth, 1957). However, the activated carbon is often applied without a full understanding as to how other treatment chemicals may affect adsorption.

The application of chlorine as a part of the water treatment process is still a common practice for disinfection, taste and odor control and ammonia removal. As a result, chlorine is one of the chemicals that often comes into contact with activated carbon. When free chlorine, monochloramine and dichloramine contact activated carbon, they oxidize its surface and in the process are converted primarily to Cl⁻ and other products (Snoeyink and Suidan, 1975). Oxidation of the surface of activated carbon results in a

* University of Illinois, 205 N. Mathews Avenue, Urbana, Illinois 61801 (V.L. Snoeyink served as an advisor to the project; A. Holthouse, an undergraduate student, assisted in collecting data)
** City of Chicago, Department of Water, 1000 East Ohio Street, Chicago, Illinois 60611 (C.M. Wilson and E.P. Royal provided information about the problem in Lake Michigan)
decrease in adsorptive capacity for a variety of organic compounds (Snoeyink and Suidan, 1975; McGuire and Suffet, 1984; McGuire and Suffet, 1980; Snoeyink et al., 1974; Coughlin, 1970; Coughlin and Ezra, 1968). Also, activated carbon catalyzes many types of reactions with aqueous chlorine (McGuire and Suffet, 1984; Hwang et al., 1990; Jackson et al., 1987; Voudrais et al., 1985; McCreary et al., 1982; Snoeyink et al., 1981; McCreary and Snoeyink, 1981). MIB, however, is very difficult to oxidize and is not directly affected by chlorine (Glaze et al., 1990; Lalezary et al., 1986). The purpose of this article is to show the effect of reacting a range of amounts of free chlorine with a unit mass of PAC on the ability of the PAC to adsorb MIB. Previous research of Lalezary et al. (1988), and Lalezary-Craig et al. (1986), showed that PAC is less effective for MIB if it is applied together with chlorine, and the findings reported herein expand on this research to show the effect on kinetics and equilibria, and the impact of allowing a short time of PAC contact before chlorine is added.

MATERIALS AND METHODS

2-Methylisoborneol

Concentration Determination. The $^{14}$C-labeled 2-methylisoborneol ($^{14}$C-MIB) (American Radiolabeled Chemicals, St. Louis, MO) was selected due to ease of analysis and small sample size requirements. Analysis of $^{14}$C-MIB samples was accomplished by mixing 2.5 mL 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). The specific activity (55 mCi/mmol) of the $^{14}$C-MIB yielded a detection limit of 4.5 ng/L, with a confidence level greater than or equal to 89%, without the use of a concentration step (Skoog and Leary, 1992).

Degradation Analysis. While the use of scintillation counting to determine the concentration of $^{14}$C-MIB has been previously documented, its use is only valid if the
MIB is not oxidized to other compounds. To validate that MIB was not oxidized, selected samples were analyzed by gas chromatography-mass spectroscopy (5890 Series II Gas Chromatograph with a 5971 Series Mass Selective Detector, Hewlett-Packard Co., Palo Alto, CA) to determine if there were any breakdown products. Prior to GC-MS analysis, the organic compounds in the selected samples were concentrated using solid phase extraction (3M Empore C₁₈ Extraction Disks for Environmental Analysis, St. Paul, MN) using the procedure recommended by the manufacturer.

**Stock Solution.** The compound was received predissolved in purge and trap grade methanol at a concentration of approximately 18.3 μg/μL (chemical purity ≥ 99% confirmed by GC-MS analysis, 100% radiochemical purity confirmed by high performance liquid chromatography (HPLC)). Stock solutions of 100 ng/μL were subsequently prepared by spiking 5.4 μL of the received solution into 1 mL of purge and trap grade methanol. The compound and all solutions were stored at 4°C.

**Water**  
*Natural Water.* Lake Michigan water (see Table 1 for composition) was used as the natural water source to study competitive effects between background organic material and MIB. Water was collected from a line running from the South Water Production Plant (Chicago, IL) crib to the shore plant. The water was shipped to the University of Illinois in 208 L (55 gal) stainless steel drums, where it was stored at 4°C in the dark to limit biological activity. (The crib is located two miles off shore in water 32 to 35 feet deep; the water is drawn near the bottom.)

<table>
<thead>
<tr>
<th>Table 1. Characteristics of Lake Michigan Water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH</strong></td>
</tr>
<tr>
<td><strong>Alkalinity</strong></td>
</tr>
<tr>
<td><strong>Conductivity</strong></td>
</tr>
<tr>
<td><strong>Turbidity</strong></td>
</tr>
<tr>
<td><strong>Nitrogen, Total Kjeldahl</strong></td>
</tr>
<tr>
<td><strong>Phosphate, Total</strong></td>
</tr>
<tr>
<td><strong>Dissolved Organic Carbon</strong></td>
</tr>
</tbody>
</table>

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Organic-free Water. Organic-free water for the single-solute isotherms was obtained by passing deionized Urbana, IL, tap water through a Milli-Q water system (Millipore Corp., Bedford, MA) which has three cartridges (activated carbon, ion exchange, ion exchange) and a 0.45μm filter. The water had a resistivity ≥ 18 megohm-cm and a dissolved organic carbon (DOC) content of 0.1-0.3 mg/L.

Activated Carbon
The PAC evaluated in this study was Hydrodarco-B (Norit Americas Inc., Atlanta, GA). A grab sample of this carbon was obtained from the inventory of the City of Chicago Department of Water. The PAC was stored in polyethylene bottles until used. Prior to use, samples were dried overnight in a 110°C oven to remove excess water, and subsequently were cooled in a desiccator. Once cooled, the desired amount of carbon, not less than 2 mg, was weighed out on a 4-point scale (LIBOR AEU-210, Shimazdu Corp., Kyoto, Japan).

For experiments that required carbon slurries, a slurry of 10 mg/mL was used. These slurries were prepared by mixing 10 g of the carbon, prepared as above, in 1 L of organic-free water. The slurry was mixed with a magnetic stirring bar only when an aliquot was to be drawn. For the remaining time the slurry bottle was quiescent. This was to prevent grinding of the carbon between the storage vessel bottom and magnetic stirring bar, as the kinetics of adsorption is sensitive to particle diameter (Najm et al. 1990; Mathews and Zayas, 1989).

The PAC was prepared in large batches for experiments that utilized carbon that had been oxidized prior to the experiment. Ca(OCl)₂ was added to 20 L of Milli-Q water to make up a 10 mg/L as Cl₂ solution. To the chlorine solution, dried PAC was added to give the desired mass ratio of chlorine to PAC. The mixture was allowed to mix for 2 days in the dark, or until all the chlorine had reacted, whichever was longer. The carbon was then filtered out of the mixture and dried overnight in a 110°C oven to remove excess water,
and then cooled in a desiccator. For an experiment using the preoxidized carbon, a portion of the desired carbon was weighed out and wetted in 10 mL of Milli-Q water for 24 hours prior to its use.

**Batch Kinetic Tests**

The apparatus used for the batch kinetic experiments was a jar test apparatus with modified B-KER\(^2\) square jars (Six Paddle Stirrer Model 7790-400, Phipps & Bird, Richmond, VA). Clear acrylic lids were manufactured for each individual jar to prevent loss of MIB through volatilization. These lids allowed for the experiments to be visually monitored and run headspace free. In the jars, 2.6 L of Lake Michigan water (pH = 8.2) was brought to room temperature and spiked with \(^{14}\)C-MIB to the desired initial concentration. The solutions were then stirred at 125 rpm for 5 minutes before the addition of carbon. Carbon was either added as an aliquot of a carbon slurry, or as a weighed mass of oven dried, prewetted carbon. (To properly wet the carbon prior to the test, weighed carbon was soaked overnight in a small aliquot of organic-free water.) Samples were then withdrawn at predetermined time intervals up to 240 minutes. The samples were collected using a stainless steel needle (Aldrich Chemical Co., Milwaukee, WI) connected to a gas-tight, luer lock syringe (Hamilton Co., Reno, NV). The aliquot was then passed through a 0.22 \(\mu\)m conditioned nylon membrane syringe (Magna, Westboro, MA) supported in a syringe filter holder (Swinney Holder, Gelman Sciences, Ann Arbor, MI). To condition the filter, 5 mL of the sample was filtered and wasted prior to the collection of 2.5 mL into the scintillation vial. To maintain the jars headspace free, unspiked distilled deionized water was added to make up volume used in sampling. The resulting measurements were then adjusted for the amount of water added to the system.
RESULTS AND DISCUSSION

Effect of Chlorine on MIB Adsorption and the Time of Addition of Chlorine Relative to PAC

A series of experiments was carried out to show the effect of the presence of aqueous chlorine on the ability of PAC to adsorb MIB from Lake Michigan water, the effect of the initial chlorine concentration, and the effect of delaying the chlorine addition until after PAC had been added to simulate the effect of using an alternative point of chlorine addition. Application of chlorine at the same time that PAC was added dramatically reduced the amount of MIB adsorbed by activated carbon. The data shown in Figure 1 were obtained from two batch tests. The control, represented by the open circles, was performed by adding 11.5 mg/L Hydrodarco-B PAC to pH 7.4 Lake Michigan water spiked with $^{14}$C-MIB. The other batch test was spiked with chlorine (3 mg/L as Cl$_2$) at the time of the addition of 11.5 mg/L Hydrodarco-B. The chlorine caused the percent MIB removed in 4 hours to be reduced from 68% to 26%, a 60% loss of capacity. A similar trend has been reported for Calgon WPH, by Lalezary-Craig et al. (1988). In

Figure 1 - Effect of Free Chlorine on MIB Adsorption

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Weymouth plant influent water, 10 mg/L WPH PAC adsorbed 73% of the MIB in 4 hours. However, if 2 mg/L of chlorine was simultaneously dosed with the WPH, only 56% of the MIB was removed.

The simultaneous addition of 3 mg/L chlorine and 11.5 mg/L PAC to Lake Michigan water was repeated in another batch test. This time, however, the concentration of chlorine was monitored. Within 9 minutes more than 90% of the free chlorine had reacted, and by 90 minutes none was detectable. An additional 0.11 mg/L of combined chlorine as Cl₂ was measured at 9 minutes. This concentration slowly decreased to 0.03 mg/L as Cl₂, measured at 4 hours.

Experiments were then conducted to show the effect of adding chlorine a short time after the addition of PAC. Figure 2 compares the results obtained from adding 3 mg/L chlorine 12 minutes after the application of 11.5 mg/L PAC, to those collected from the first experiment with (3 mg/L of chlorine simultaneously with PAC) and without chlorine. From this figure it can be seen that delaying the time of addition of chlorine by 12 minutes was beneficial (46 percent removal versus 26 percent removal) even though
there was a release of the previously adsorbed MIB as a result of the application of chlorine. While delaying the addition of chlorine improved MIB removal to 46 percent after 4 hours, removal was still far short of the 68 percent achieved when no chlorine was present. Two significant conclusions can be made from this experiment: 1) chlorine can oxidize adsorption sites containing MIB, thereby releasing the MIB back into the aqueous phase; 2) the later that chlorine is applied with respect to the addition of PAC, the greater the expected MIB removals.

Several additional experiments were conducted to show the effect of chlorine doses of 0, 3 and 5 mg/L as Cl₂ on the MIB removal that could be achieved by several PAC doses. To this end, headspace free reactors containing pH 7.4 Lake Michigan water and MIB were dosed simultaneously with chlorine and PAC. The resulting MIB concentrations were monitored over time. The percent of MIB remaining at 4 hours as a function of PAC dose is shown in Figure 3. It has been previously shown that for a given PAC dose in natural water, and any fixed time of contact, the percent MIB adsorbed in an ideal reactor is independent of the initial MIB concentration (Mathews and Zayas, 1989). From this graph, the necessary amount of PAC necessary to remove any initial concentration of MIB down to threshold odor levels may be quickly determined when reasonable levels of chlorine and PAC are added simultaneously. Table 3 gives the amount of Hydrodarco-B required to reduce MIB to threshold odor levels (5 ng/L) for several different initial concentrations, given 4 hours of contact in an ideal reactor and initial chlorine concentrations of 0, 3 and 5 mg/L as Cl₂.

It can be observed that as the concentration of PAC increased, the lines in Figure 3 converged for the different initial concentrations of chlorine. This can be explained by looking at the mass of chlorine reacted per mass of PAC. (See Table 4) For a fixed initial concentration of chlorine, the amount of chlorine reacted per mass of PAC decreases as the carbon concentration increases. It would appear that below a given ratio of chlorine to carbon, the effect is negligible. Further research is necessary to determine if this ratio is specific to a given water or carbon.
Figure 3 - Effect of a Fixed Initial Concentration of Chlorine on the 4-Hour MIB Adsorption Capacity: Percent Remaining Versus PAC Dose

Table 3 - Required PAC Dose (mg/L) to Reduce MIB Concentration To 5 ng/L with 4 Hours of Contact Time

<table>
<thead>
<tr>
<th>Initial Chlorine Concentration</th>
<th>Initial MIB Concentration</th>
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<tbody>
<tr>
<td></td>
<td>20 ng/L</td>
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<tr>
<td>0 mg/L</td>
<td>15</td>
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<tr>
<td>3 mg/L</td>
<td>22</td>
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<tr>
<td>5 mg/L</td>
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Table 4 - Milligrams of Chlorine Reacted within 4 Hours per Milligram of PAC²

<table>
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<th>PAC (mg/L)</th>
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<td>3 mg/L</td>
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<td>46.2</td>
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</tbody>
</table>

² For the lower PAC concentrations, not all of the chlorine initially present was reacted within 4 hours. These numbers indicate the actual amount reacted.
Cause of the Decrease in MIB Adsorption

There were several possible reasons for the observed decrease in MIB capacity caused by chlorine. Because it has been shown through many studies that activated carbon may catalyze many types of reactions with chlorine, it was important to establish that the radiolabeled MIB was not being catalytically degraded on the PAC (Hwang et al., 1990, Jackson et al., 1987; Voudrais et al., 1985; McCreary et al., 1982; Snoeyink et al., 1981, McCreary and Snoeyink, 1981, Glaze et al. 1990). The experiment with addition of 3 mg/L of chlorine 12 minutes after the PAC was repeated and a solution sample was collected at 22 minutes, the time of maximum MIB release. Analysis of the sample by GC-MS showed no additional compounds that might have come from a chlorine-MIB reaction on the PAC surface indicating activated carbon does not catalyze a reaction between MIB and chlorine.

![Graph showing the effect of disinfection by products on the adsorption of MIB.](image)

Figure 4 - Effect of Disinfection By Products on the Adsorption of MIB

An additional experiment was performed to verify that the observed chlorine effect was not attributable to increased competition for adsorption sites by disinfection-by-products (DBPs). Lake Michigan water was chlorinated with 5 mg/L as Cl₂ and allowed to react in
the dark for 24 hours. The remaining free chlorine was dechlorinated by adding sulfite, after which the water was spiked with MIB and 11.5 mg/L PAC. The kinetic curves for MIB adsorption in the presence of DBPs (shown in Figure 4) indicated that they did not influence adsorption.

The most probable reason for the observed decrease in MIB capacity was the buildup of surface oxides. Previous studies have shown that increasing the amount of chlorine reacted per mass of activated carbon increased the concentration of surface oxides on the carbon, and correspondingly decreased the capacity of F-400 activated carbon to adsorb phenol and \( p \)-nitrophenol (PNP) (Snoeyink et al. 1974). However, the impact observed on the ability of Hydrodarco-B PAC to adsorb MIB was much greater than for phenol and \( p \)-nitrophenol, as shown in Table 5.

Table 5 - Single Solute Percent Capacity Reduction as a Function of Chlorine Reacted

<table>
<thead>
<tr>
<th>Compound / Carbon</th>
<th>Free Chlorine Reacted (mg Cl(_2)/mg carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>PNP / F-400(^7)</td>
<td>29%</td>
</tr>
<tr>
<td>Phenol / F-400(^8)</td>
<td>54%</td>
</tr>
<tr>
<td>MIB / Hydrodarco-B(^*)</td>
<td>(~75%)</td>
</tr>
<tr>
<td></td>
<td>(~92%)</td>
</tr>
</tbody>
</table>

Factors Affecting the Decrease in MIB Adsorption

Experiments were conducted to determine the importance of the initial chlorine concentration versus the mass of chlorine reacted per gram of PAC for the decrease in MIB adsorption. (See Figure 5) In deionized-distilled water, chlorine was reacted with Hydrodarco-B in the absence of MIB. In one group of tests 5 mg of chlorine as Cl\(_2\) was reacted with 11.5 mg PAC, with the chlorine applied in three different ways. First, 5 mg/L chlorine was reacted with 11.5 mg/L PAC; second, the chlorine was reacted with 11.5 mg/L PAC in two consecutive steps of 2.5 mg/L chlorine in each step; and third, the chlorine was applied to 11.5 mg/L PAC in 5 dosings of 1 mg/L chlorine each. For each test, subsequent additions of chlorine were not added until all of the previously dosed

---

\(^3\) This study, assuming plateau values in Figure 5 approximate equilibrium.
chlorine had reacted. After all the chlorine had reacted, each of the three reactors were spiked with $^{14}$C-MIB and monitored over time. Each means of application resulted in a 4-hour MIB removal about 23 percent, or a reduction in capacity of 75%, showing that initial chlorine concentration was not an important factor. Another group of tests looked at a total of 10 mg/L of chlorine reacted with 11.5 mg/L Hydrodarco-B. For this group 10 mg/L of chlorine added all at once, and 10 mg/L added in 5 additions of 2 mg/L was investigated. Both application methods resulted in an MIB removal of 8 percent, or a 92% reduction in MIB capacity, further substantiating that it is the amount of chlorine reacted, not its initial concentration, which determines the magnitude of the chlorine effect.

![Figure 5 - Effect of Total Chlorine Dosed and Initial Concentration](image)

Once it was determined that the mass of chlorine reacted per mass of activated carbon governed the decrease in capacity, additional experiments were run to determine how great of an effect could be expected for different ratios of chlorine reacted to PAC. Hydrodarco-B was preoxidized in DDI water with chlorine to PAC mass ratios of 0.5:1, 1:1 and 2:1, and subsequently dried. The adsorption of MIB in Lake Michigan water by

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these oxidized carbons was then monitored over time. With 11.5 mg/L Hydrodarco-B 68% of the MIB initially present was adsorbed in 4 hours. As the chlorine reacted to PAC ratio increased from 0.5, to 1.0 to 2.0, MIB removals of 49 percent, 31 percent, and 15 percent were observed, as shown in Figure 6. The trend observed in this figure further supports the hypothesis that the formation of surface oxides is reducing the capacity of the PAC for MIB.

![Figure 6 - Dependence of MIB Removal on Mass Chlorine Reacted Per Mass PAC](image)

It was noticed that the percent removal for the PAC which had been preoxidized to a 1:1 chlorine to PAC mass ratio gave similar percent removals to the experiment with a simultaneous addition of 3 mg/L of chlorine with 11.5 mg/L of unoxidized PAC (0.26:1 chlorine to PAC mass ratio). It was determined that the drying step of the preoxidation process recovered some of the capacity that was lost during the oxidation process. Figure 7 shows the results from an experiment carried out in DDI water. In the first reactor, 5.8 mg/L PAC and 5.8 mg/L chlorine were allowed to react until all the chlorine had been reduced, prior to the addition of the MIB. This gave a 1:1 chlorine to PAC mass ratio carbon which had not been dried. The second reactor contained 5.8 mg/L of 1:1 chlorine to PAC mass ratio preoxidized carbon, which had been dried. The third reactor contained
5.8 mg/L of unoxidized PAC. The response of these three reactors to MIB was markedly different. The oxidized carbon which had not been dried removed only 11% of the MIB initially present, as compared to an 86% removal by the unoxidized PAC. This reduction in the 4-hour capacity due to oxidation, constitutes a 87% reduction in capacity. However, if the oxidized carbon is dried some of the capacity is recovered. In 4 hours the dried oxidized carbon is able to remove 38% of the MIB, a 56% loss of capacity.

![Figure 7 - Stability of Oxidized Adsorption Sites](image)

It is believed that the drying process volatilized some of the weakly bound surface oxides. These easily volatilizable oxides may be surface carboxyl groups. It has been previously reported that the dechlorination capacity of activated carbon may be restored by heating to 500-700°C in an inert environment. During this heating primarily CO₂ was evolved, which can be derived from carboxyl groups.
CONCLUSIONS

The conclusions are as follows:

- **Activated carbon's adsorptive capacity for MIB is significantly reduced by free chlorine.** While certain levels of chlorine must be added to satisfy federal disinfection regulations, the best efficiency will be achieved if contact between PAC and chlorine is minimized or eliminated. For reasonable concentrations of chlorine, the amount of chlorine reacted per unit mass of activated carbon determines the extent of reduction in MIB adsorption capacity.

- **Chlorine can oxidize adsorption sites containing MIB.** A release of MIB back into the aqueous phase was observed immediately after an addition of chlorine to a system in which activated carbon had previously adsorbed MIB.

- **The later that chlorine is applied with respect to the addition of PAC, the greater the expected MIB removals.** In Lake Michigan water, 11.5 mg/L of Hydrodarco-B was able to remove 68% of the MIB in 4 hours. If chlorine (3 mg/L as Cl₂) was simultaneously added with the PAC, only 26% of the MIB was removed in 4 hours. However, if the chlorine addition was delayed by 12 minutes 54% of the MIB was adsorbed in the same amount of time.

- **Drying an oxidized carbon recovers a large portion of the lost MIB capacity.** In deionized-distilled water 5.8 mg/L of unoxidized Hydrodarco-B removed 86% of the MIB initially present in 4 hours. If the carbon had been oxidized to a 1:1 chlorine to PAC mass ratio removed only 11% of the MIB in 4 hours. However, when this carbon had been reacted to the same chlorine to PAC mass ratio and was dried prior to MIB adsorption 38% of the MIB was adsorbed.
"Few enterprises of great labor or hazard would be undertaken if we had not the power of magnifying the advantages we expect from them." (Samuel Johnson)

Determining the Remaining GAC Bed Life for Taste and Odor Control

by

Thomas E.T. Gillogly*, Vernon L. Snoeyink*,
John C. Vogel**, Claude M. Wilson***, Earl P. Royal***

ABSTRACT

This study has developed an alternative approach to rapidly and effectively evaluate the remaining life of a GAC bed for the mitigation of taste and odor episodes. Using laboratory-scale columns packed with GAC taken from full-scale operating adsorbers, the approach was shown to simulate the performance of pilot-scale columns very well. It was concluded from this study that the maximum attenuation of a transient MIB load by GAC, reported as percent removal, was independent of the influent MIB concentration but dependent on the amount of natural organic matter adsorbed on its surface. It was also discovered that adsorption alone might be insufficient to provide full protection against typical MIB episodes.

* University of Illinois, 205 N. Mathews Avenue, Urbana, Illinois 61801 (V.L. Snoeyink served as an advisor to the project)
** Greeley and Hansen, 100 South Wacker Drive, Chicago, Illinois 60606 (J.C. Vogel provided pilot-plant data)
*** City of Chicago, Department of Water, 1000 E. Ohio Street, Chicago, Illinois 60611 (C.M. Wilson and E.P. Royal provided information about the problem in Lake Michigan)
INTRODUCTION

One of the questions most frequently asked while using granular activated carbon (GAC) adsorbers is, "how much longer will it last?" Heilker (1979) indicated that taste and odor substances from algal blooms exhausted a biologically active bed after a four month run. Newcombe et al. (1994) concluded that even for a GAC filter exposed to periodic low nanogram per liter concentrations of 2-methylisoborneol (MIB) with an empty bed contact time (EBCT) of 20 minutes, 18 months was the longest that the filter could be expected to reduce MIB concentrations to below the odor threshold concentration. Additionally, GAC filter beds treating the same water with EBCTs of 6.5 and 13 minutes were expected to be exhausted within 10 months. After only seven weeks, geosmin, at periodic influent concentrations of hundreds of nanograms per liter, was observed in the effluent of a GAC system that had chlorine in the influent water (CH2M, 1987). In contrast, others have reported bed lives on the order of years for the removal of MIB and geosmin (Yagi et al. 1988; Suffet, 1980; Schulhof, 1979).

Predicting Bed Life

While not a simple task, many researchers have attempted the challenge of predicting the effective service life of GAC adsorbers. The most obvious first step was to determine the GAC capacity for the particular adsorbate of interest in batch systems. It was determined that GAC particle size had no noticeable effect on the equilibrium adsorption capacity (Najm et al. 1990; Weber and Wang, 1987; Thacker et al. 1983; Randtke and Snoeyink, 1983; Lee et al. 1981). While it was expected that carbons with higher adsorption capacities would have longer bed lives, it was found that adsorption kinetics had a dramatic impact on bed life and would often shift the expected order of breakthrough (Weber and Wang, 1987; Lee et al. 1981).
While equilibrium theory alone has been used to predict pilot- and full-scale column performance, the use of fixed bed mass transfer models that incorporate both kinetics and equilibrium is much more common. Mass transfer models have been used to develop equations that relate the operation of large-scale adsorbers and small-scale predictive columns (Crittenden et al. 1987; Crittenden et al. 1991). The test procedure, including the application of the scaling equations, is commonly referred to as the rapid small-scale column test (RSSCT). The RSSCT takes particle size, hydraulic loading, and empty bed contact time (EBCT) into account.

The hydraulic loading of the RSSCT is selected by assuming that intraparticle diffusion is either independent (constant diffusivity; CD-RSSCT) or proportional (proportional diffusivity; PD-RSSCT) to particle size. Unfortunately, it cannot be determined a priori whether proportional or constant diffusivity should be used. While both CD-RSSCT (Crittenden et al. 1987; Vidić et al. 1992; McGuire et al. 1991; Crittenden et al. 1986) and PD-RSSCT (Crittenden et al. 1991; Summers; et al. 1989) have been able to successfully predict breakthrough in known and unknown mixtures, there are many times when predictions have not been accurate (Crittenden et al. 1986; Summers et al. 1989; Speth and Miltner, 1981).

An alternative approach has recently been taken in applying the RSSCT. Using virgin GAC, Matsui et al. (1994) observed that the removal efficiency of intermittently applied pesticides (simazine, napropamid, bentazon, asulam, hymexazol) in natural water was not related to the concentration of the pesticide itself. Similarly, Namuduri and Summers (1991) found that the percent breakthrough of chloroform, 1,2-dichloroethene and 1,2-dichloropropane was generally insensitive to the input pulse concentration. These findings support and expand upon the results of other researchers who showed that the percent removal of a micropollutant from natural water by powdered activated carbon was independent of the micropollutant's initial concentration (Knappe et al. 1998, Gillogly et al. 1998, Gillogly et al. 1997; Graham et al. 1997).
Matsui et al. (1994) also found that the breakthrough curves for both intermittently and continuously applied pesticides were nearly identical. The effluent pesticide concentration was determined by the amount of background organic matter adsorbed on the GAC and not by the amount of pesticide adsorbed. Comparing columns exposed to intermittently and continuously applied pesticides, a difference in the percent pesticide removal was only found when the mass loading of pesticide was greater than about 50 percent of the loading at complete saturation of the GAC.

The RSSCT has proven useful for defining the behavior of fresh GAC but has not been used to determine the remaining life of an existing GAC adsorber due to particle size restrictions. RSSCTs typically use particles with geometric mean diameters less than 250 μm. While grinding fresh GAC to obtain the appropriate particle size does not alter its capacity, grinding partially saturated GAC will change its adsorptive properties because adsorption sites that were blocked by previously adsorbed compounds are now accessible.

Considering the inapplicability of the RSSCT, it was the objective of the authors to develop an alternative tool to rapidly and effectively evaluate the remaining life of GAC for mitigation of a taste and odor episode. The test should determine how effluent concentrations of taste and odor causing compounds change as influent concentrations change, without grinding the carbon. This test should also provide the information necessary to determine if the GAC is currently effective and if it will last through an impending taste and odor season, or if it is sufficiently spent to require regeneration or replacement.

MATERIALS AND METHODS

Pilot-Scale MIB Analysis. MIB and geosmin concentrations for the pilot-plant study were determined by Montgomery Watson Laboratories using Standard Method 6040B “Closed-Loop Stripping, Gas Chromatographic/Mass Spectrometric Analysis” (Standard, 1995). The detection limits were 3.0 and 5.0 ng/L for geosmin and MIB, respectively.
Laboratory-Scale MIB Analysis. Due to ease of analysis and small sample size requirements, \(^{14}\)C-labeled 2-methylisoborneol (\(^{14}\)C-MIB) (American Radiolabeled Chemicals, St. Louis, MO) was utilized. Analysis of \(^{14}\)C-MIB samples was accomplished by mixing sample aliquots with 18 mL of scintillation cocktail (Ecoscint, National Diagnostics, Manville, NJ) in scintillation vials. The resulting fluorescence was measured in a liquid scintillation counter (Tri-Carb Model 1600CA, Packard Instrument Co., Downers Grove, IL). It was not necessary to concentrate the sample for analysis. The compound was received predissolved in purge and trap grade methanol at an approximate concentration of 18.3 \(\mu\)g/\(\mu\)L (chemical purity \(\geq 99\%\) confirmed by GC-MS analysis, 100\% radiochemical purity confirmed by high performance liquid chromatography - HPLC). Stock solutions of 100 ng/\(\mu\)L were subsequently prepared by spiking 5.4 \(\mu\)L of the received solution into 1 mL of purge and trap grade methanol. The compound and all solutions were stored at 4°C. The limit of detection for this analysis is 3.0 ng/L with greater than 89\% confidence.

Virgin GAC. The virgin granular activated carbon used in this study was F-300 (Calgon Carbon Corp., Pittsburgh, PA).

<table>
<thead>
<tr>
<th>Table 1 – Physical Characteristics of the Granular Activated Carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Effective size, mm</strong></td>
</tr>
<tr>
<td>--------------------------</td>
</tr>
<tr>
<td>Uniformity coefficient</td>
</tr>
</tbody>
</table>

Preloaded GAC. When the pilot testing begun, the Hammond, Indiana and Michigan City, Indiana water treatment plants had been using F-300 GAC over sand in dual media filter-adsorbers for approximately 1 and 2 years, respectively. Both of these plants use Lake Michigan as their raw water source and are relatively near the Chicago, Illinois water treatment plants. Therefore, the concentration of the soluble organics in their raw waters should be similar (see Table 2). From each water treatment plant, representative
samples of the entire GAC bed depth were collected for use in the studies. The samples were used immediately in the pilot study, and stored in 5 gallon sealed polyethylene containers until their use in the laboratory-scale experiments.

Additional preloaded GAC samples were collected from the Hammond, Indiana, Michigan City, Indiana, and Lake County, Illinois water treatment plants for laboratory experimentation. After collection, these samples were immediately used in the laboratory-scale experiments. GAC that had been in service for 0.2 and 3 years was collected from the Hammond, Indiana water treatment plant. Carbon from the Michigan City, Indiana water treatment plant was withdrawn after 4 years in service. The Lake County, Illinois water treatment plant also uses Lake Michigan water and was the source of GAC that had been in service for approximately 6 years.

Table 2 - Total Organic Carbon (TOC) in Water Treatment Plant Influent

<table>
<thead>
<tr>
<th>Location</th>
<th>TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chicago, Illinois</td>
<td>1.8-2.0</td>
</tr>
<tr>
<td>Hammond, Indiana</td>
<td>1.5-2.0</td>
</tr>
<tr>
<td>Michigan City, Indiana</td>
<td>1.5-2.5</td>
</tr>
</tbody>
</table>

Table 3 - Characteristics of Lake Michigan Water

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.2</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>117 mg/L as CaCO₃</td>
</tr>
<tr>
<td>Turbidity</td>
<td>2 NTU</td>
</tr>
<tr>
<td>Conductivity</td>
<td>281 μmhos</td>
</tr>
</tbody>
</table>

Water. The water used in both the pilot- and laboratory-scale experiments was drawn from a line running from the South Water Production Plant (Chicago, Illinois) crib to the shore plant. For the laboratory experiments, this untreated water was shipped to the University of Illinois in 208 L (55 gal) stainless steel drums, where it was stored at 4°C in the dark to limit biological activity. It was verified that the water collected for laboratory experiments did not contain a detectable concentration of MIB. (The crib is located 3.2
km [2 mi] offshore in water 9.6-10.5 m [32-35 ft] deep; the water is drawn near the bottom of the crib.)

_Pilot-Scale GAC Columns._ The pilot-scale columns consisted of 15.2 cm (6 inch) diameter columns, 53.3 cm (21 inches) of the selected GAC and 30.5 cm (12 inches) of sand (effective size - 0.5 mm; uniformity coefficient - 1.3). Each column was equipped with a slotted underdrain nozzle and a surface wash spray nozzle. The influent flow to the facility was equally distributed to the pilot filters through the use of a constant head box and flow splitting boxes.

A short distance downstream of the raw water pump, sodium hypochlorite was added to the raw water via a peristaltic pump. The chlorinated raw water then flowed through approximately 274 m of pipe to the test facility. A chlorine analyzer was used to monitor the chlorine residual of the raw water as it entered the test facility. The output of the peristaltic pump was adjusted to keep residuals in the desired range.

_Laboratory-Scale GAC Columns._ For the laboratory-scale experiments, GAC was packed into glass columns (Kontes, Vineland, New Jersey) with an inside diameter of 1.0 cm and a length of 30 cm. Each end was sealed with a threaded PTFE fitting equipped with 20 μm filters. The GAC was contained within a bed of glass beads by two 316 stainless steel, number 20 U.S. Standard mesh size (0.841 mm) screens. The glass beads were used to insure uniform flow through the GAC. The GAC beds were approximately 1 cm deep. A 12x14 U.S. Standard mesh (1.41 to 1.68 mm) size fraction of GAC particles was selected for use in the laboratory columns, because it was determined that these particles accounted for the largest fraction of the external surface area in the filters of the three water treatment plants. By using a representative size fraction rather than the same particle size distribution as the distribution in the full-scale plants, it was possible to more easily and rapidly obtain a laboratory column representative of the full-scale plant. The equivalency of performance was established using both approaches. Uniform packing of both glass beads and GAC particles was obtained through the use of a vibratory
engraving tool (Vibro-Graver; Burgess, Chadwicks, New York) to vibrate the column as the column was being filled. A double plunger HPLC pump (Model 6000A; Waters Corporation, Milford, MA) was used to maintain constant low flow rates through the columns.

Feed solutions were prepared by filtering raw Lake Michigan water through a 0.45 μm membrane filter. Filtration of the water served to remove particulate and colloidal material that could otherwise plug or foul the laboratory columns. A taste and odor episode at the laboratory-scale was simulated by changing from this filtered Lake Michigan water to an influent solution of filtered Lake Michigan water spiked with 14C-MIB to the desired influent MIB concentration. Feeding this spiked filtrate continued until the end of the episode, whereupon the influent was changed back to the unspiked filtrate.

**Reaction of Chlorine with GAC.** The reaction between chlorine and GAC was carried out prior to packing the carbon in the laboratory-scale columns. To react the chlorine with the GAC, a known mass of 12x14 U.S. Standard mesh size fraction GAC was placed in a steel mesh basket made from number 20 U.S. Standard mesh, 316 stainless steel (custom manufacture; University of Illinois, Urbana, Illinois). The basket, positioned towards the side of a 13-L glass carboy covered with aluminum foil, revolved at 20 rotations per minute. An overhead 3-blade teflon turbine rotating at 1550 rotations per minute ensured that a constant flow of the well mixed chlorine solution passed through the stainless steel basket. The rotation of the basket kept the GAC particles mixed, so that the reaction between the chlorine and the carbon particles was evenly distributed. A 13 L chlorine solution was prepared using calcium hypochlorite and 1.0 mM phosphate (buffered to pH 8.2). The pH was adjusted as needed with 0.5 N NaOH or HCl.

An initial concentration of approximately 10 mg/L free chlorine as Cl₂ was used to react with the carbon. Another setup identical to the first was operated in the absence of carbon to serve as a control. The chlorine residual of both vessels was monitored using Standard Method 4500-Cl F, “DPD Ferrous Titrimetric Method” (Standard, 1995).
amount of chlorine reacted with the carbon was adjusted according to the rate of chlorine decay in the control. If the residual reached 2 mg/L as Cl₂, and the desired chlorine reacted to carbon mass ratio had not yet been reached, the chlorine concentration was increased to approximately 7 mg/L as Cl₂. Once the desired amount of reaction had occurred, the basket was removed from the solution and rinsed with deionized-distilled water. The reacted GAC was then transferred to a column and packed as previously described.

RESULTS AND DISCUSSION

Pilot-scale MIB Removal

During the summer of 1996, Greeley and Hansen operated pilot-scale filters at the City of Chicago South Water Purification Plant to evaluate the effectiveness of GAC for the removal of MIB and geosmin. The naturally occurring MIB and geosmin concentrations in Lake Michigan were used to compare virgin and preloaded (1 year, 2 year) GAC. The one-year preloaded GAC was collected from Hammond, Indiana, and the two-year preloaded GAC was obtained from Michigan City, Indiana. Over the course of the three-month evaluation, influent geosmin concentrations were typically below the 3 ng/L detection limit. Thus, only MIB removal could be evaluated.

The influent MIB concentrations varied widely from day to day (see Figure 1). This natural variability increased the difficulty of using conventional predictive methods to determine the effectiveness of GAC. The data were analyzed by determining the percent MIB removed across each filter every time a sample was taken. These removals were then averaged for each filtration rate investigated. Filtration rates of 3, 4, and 5 gallons per square foot per minute (gpm) were used, corresponding to an EBCT (i.e. the volume of GAC bed/flow rate of applied water) of 4.4, 3.3 and 2.6 minutes, respectively. These
rates were selected to span the projected range of filtration rates expected during the high water demand of the summer months.

![Graph](image)

**Figure 1 - MIB Removal by GAC: South Water Purification Plant Pilot Study**

For the purpose of data analysis, the effluent samples in which MIB was not detected were assigned an MIB concentration of 2.5 ng/L (0.5 times the limit of detection). Table 4 shows the average percent removals obtained from the pilot study. The initial concentration range was 8 to 64 ng/L for the 4.4 minute EBCT, 12 to 38 ng/L for the 3.3 minute EBCT, and non-detectable to 28 ng/L for the 2.6 minute EBCT.

**Table 4 - Summary of South Water Production Plant Pilot Study, Percent MIB Removal**

<table>
<thead>
<tr>
<th>Filtration Rate (gfm)</th>
<th>EBCT (min)</th>
<th>Average Percent Removals*</th>
<th>Virgin</th>
<th>1 yr preload</th>
<th>2 yr preload</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4.4</td>
<td>83%</td>
<td>38%</td>
<td>39%</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.3</td>
<td>72%</td>
<td>37%</td>
<td>32%</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.6</td>
<td>34%</td>
<td>-24%</td>
<td>-45%</td>
<td></td>
</tr>
</tbody>
</table>

* Average of daily percent removals (less than detection limit effluents set to 0.5 times the limit of detection)
† EBCT: empty bed contact time (volume of GAC/flow rate)
‡ gfm: gallons per square foot per minute
It can be observed in Figure 1 that the changes in filtration rates seemed to coincidentally correspond to the natural fluctuation in the influent MIB concentration. As discussed later, it is believed that decreased removal efficiencies will be observed with decreasing influent concentrations. This is attributed to the desorption of a portion of the MIB adsorbed during periods of high influent concentration. For this reason, the dramatically reduced and negative removals observed with the 2.6 minute EBCT were not unexpected.

**Laboratory-Scale Column MIB Removal**

Pilot-plant studies give excellent data on GAC performance for a given history of MIB influent concentrations, but it is difficult to use these tests to accurately determine the effect of influent concentration because of it is highly variable in the influent water. Additionally, due to the cost and time for analysis of these earthy-musty compounds, samples were only collected twice per week. The goal of the laboratory-scale experiments was to develop a tool that would simulate the performance of the pilot-scale filters, yet not be encumbered by the difficulties often faced with larger scale experiments. The results discussed below indicate that pilot-scale performance may be reproduced using small-scale laboratory tests.

**Effect of Service Time.** The results of the pilot study were compared to the performance of the small-scale laboratory columns for a range of GAC preloading times. This was to determine if the laboratory columns could simulate the performance of the larger scale system, while simultaneously studying how the length of time that the GAC had been in use affects GAC performance. Each of these laboratory-scale (1.0 cm diameter) columns were prepared with a 12x14 US Standard mesh (1.41 to 1.68 mm) size fraction of GAC that had been in service from 0 to 6 years. A sieve analysis of the representative GAC samples from each of the three water treatment plants showed that the largest fraction of external surface area was in the 12x14 mesh size range; thus, the performance of this size range was likely to be the same as the full-scale adsorber. Each bed of GAC was approximately 1 cm deep.
Fresh GAC was first tested in these laboratory-scale columns at a 3.3 minute EBCT. Lake Michigan water spiked to 50 ng/L MIB was applied to the column for more than two days (> 873 bed volumes). After this period the influent was switched to unspiked Lake Michigan water. The effluent MIB concentration was monitored during the entire experiment. From these data (Figure 2) it can be seen that once the spiked influent was applied, the effluent concentration reached a pseudo-steady state within 6 hours (110 bed volumes). After this pseudo-steady state, or plateau, was reached, the effluent MIB concentration was essentially constant for the remainder of the two-day MIB application. While the effluent MIB concentration would be expected to slowly increase with a continued input of MIB and natural organic matter (NOM), it was felt that this initial plateau was representative of the ability of this GAC to remove the suddenly-appearing MIB during a taste and odor episode. After the influent was switched to Lake Michigan water without MIB, the effluent MIB concentration quickly dropped below the limit of detection. Less than three percent of the adsorbed MIB desorbed back into the aqueous phase, consistent with the fact that the surface coverage of the GAC with MIB was very low. Based upon these data, the remainder of the laboratory-scale GAC columns were evaluated at a two-day effluent plateau value.

Figure 2 — Laboratory Column Two-Day Response to MIB (virgin GAC; 3.3 min EBCT)
Following this test with the virgin GAC, columns prepared with the carbons that had been collected from the different full-scale filters were evaluated at a 3.3 minute EBCT. The data show an increase in the percent MIB passing through the column with increasing service time (Figure 3). This figure also shows that the laboratory column data were in excellent agreement with the pilot study results.

![Figure 3 - Effect of Service Time on Percent MIB Breakthrough (3.3 Minute EBCT)](image)

The observed increase in the effluent MIB concentration could have been attributed to several possible factors: 1) MIB adsorption, 2) NOM adsorption, 3) impact of treatment chemicals. The earthy-musty taste and odor problems in Lake Michigan are generally limited to the summer and early fall months. Even during this problematic time the MIB concentration rarely exceeds 50 ng/L. As a result, the amount of MIB adsorbed during the course of one year is a small fraction of the virgin capacity and is not expected to be the primary reason for the decreased effectiveness of the GAC. Based upon work presented later and the findings of other researchers, adsorption of NOM plays a major role in controlling the adsorption of MIB (Matsui et al. 1994; Knappe et al. 1998). In addition to NOM adsorption, the Hammond and Michigan City, Indiana water treatment plants allowed free chlorine onto their GAC beds. The deleterious effect of chlorine on the adsorptive capacity of activated carbon is well documented. Additional work
specifically for MIB adsorption by GAC, presented later in this paper, confirms that the free chlorine should be considered a factor in the decrease of the GAC’s effectiveness with increasing service time.

Using the same approach, the GAC was evaluated at a 4.4 minute EBCT. The two-day effluent concentration plateau values were used to calculate the percent MIB breakthrough for each of the carbons, and the results are shown in Figure 4. Comparing the data collected in the pilot study to the laboratory data, good agreement was again observed, except for the one-year service time. There is no apparent explanation for this difference.

![Figure 4 - Effect of Service Time on Percent MIB Breakthrough (4.4 Minute EBCT)](image)

The 2.3 minute EBCT was the final contact time tested in this series of experiments, and the laboratory- and pilot-scale data are compared in Figure 5. There is poor agreement between the two sets of data. Evaluation of the pilot data shows that due to the natural fluctuations in the concentration of MIB in Lake Michigan, the majority of the data for this EBCT was obtained when the influent concentration was decreasing. As a result, it was very likely that desorption of previously adsorbed MIB was contributing to the MIB measured in the effluent. This effect should be considered when using these laboratory
columns to evaluate the effectiveness of a given GAC. If a carbon sample is collected during or soon after the GAC is exposed to MIB the results could be biased by desorption, especially if the influent concentration is much lower than that of the previous exposure.

![Figure 5: Effect of Service Time on Percent MIB Breakthrough (2.3 Minute EBCT)](image)

The EBCTs evaluated here (2.6, 3.3, 4.3) are typical of the contact times encountered with GAC filter caps in filter-adsorbers. These data suggest, however, that 28 ng/L was the maximum influent MIB concentration that fresh GAC with a 4.3 minute EBCT could reduce to threshold odor concentrations. This maximum concentration was lowered to less than 13 ng/L if a 2.6 minute EBCT was used. This indicates that adsorption alone may be insufficient to control MIB, and additional treatment technologies, such as ozone, advanced oxidation processes and biological oxidation, may be necessary to protect the consumer from unacceptable levels of tastes and odors. (Note: An additional laboratory-scale column, prepared with GAC that had been in service for 1 year, was operated at 4°C with a 3.3 minute EBCT. The percent MIB breakthrough was identical to the column operated at 25°C indicating biodegradation was not contributing to the observed removals.)

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Laboratory Column Design

The excellent agreement between the pilot-plant results and the laboratory column data showed that short term lab tests can be used to effectively predict the results of large-scale systems. However, several questions about the design and methods of operation needed to be answered so that the laboratory column test could be used with confidence. Therefore, specific questions concerning the effect of the GAC column design (bed depth, column diameter and GAC particle size) on column performance were addressed. Also, the role of biological activity, influent MIB concentration and the concentration of chlorine were carefully examined.

**Bed Depth.** To determine if the bed depth affected GAC performance, four 1.0 cm diameter columns were packed with 12x14 GAC to depths between 0.8 and 3.3 cm, and each was operated with a different flow rate but the same EBCT. A solution containing approximately 50 ng/L MIB was applied to each column. The resulting MIB removal efficiency was calculated for each column using the two-day effluent concentration plateau. From the data presented in Figure 6, it can be seen that even the shortest GAC bed (0.8 cm) removed the same fraction of MIB as a bed approximately four times deeper (3.3 cm) when the columns were operated at the same EBCT. This means that this approach was not dependent on the bed depth or flow rate.

**Column Diameter.** The column diameter to particle diameter ratio can also affect column performance; short circuiting, and thus higher effluent concentrations, can result if this ratio is too small. In order to examine this effect, four 1.0 cm diameter columns and one 2.5 cm diameter column were packed with the same 12x14 GAC (1.41 to 1.68 mm particle diameter) that had been in service for one year. As seen in Figure 6, even though the 1.0 cm diameter columns had an average particle to column diameter ratio of only 6.5, they yielded the same removal as the larger column with a ratio of approximately 16.2. These data indicate that through proper packing of the GAC and the use of glass beads, low particle to column diameter ratios may be used.
Figure 6 – Effect of GAC Bed Dimensions on Percent MIB Breakthrough (1 year service time)

Figure 7 – Comparison of Sieved and Unsieved GAC (2 year service time)

It is interesting to note that even at contact times more typical of adsorbers, 10 to 15 minutes, approximately 85% of the MIB was removed for this carbon. This means that if threshold odor levels of approximately 5 ng/L MIB or less were desired, the GAC that had been in service for just one year could only be expected to control episodes less than approximately 30 ng/L MIB with ten minutes of contact.
**GAC Particle Size.** Ideally, a particle size distribution identical to the pilot- or full-scale adsorber would be used in these laboratory columns. However, by using a representative size fraction in the laboratory columns rather than the same particle size distribution as the full-scale plants, it was possible to more easily and rapidly obtain a laboratory column that could simulate a larger scale system. To test if the 12x14 mesh size fraction would yield results representative of the entire particle size distribution, two columns were prepared with GAC that had been in service for two years. The first column held an unsieved sample with the same particle size distribution as the full-scale filter. The second column was prepared with a 12x14 mesh size fraction of the same carbon. Both columns were fed an influent of Lake Michigan water spiked to approximately 50 ng/L MIB and monitored over time. The two-day effluent concentration plateau was used to calculate the percent MIB breakthrough at each EBCT evaluated. The close agreement between the results of the two columns indicated that the use of the 12x14 mesh size fraction was appropriate (see Figure 7).

**Influent MIB Concentration**

The issue of which influent MIB concentration to use is closely related to the question of the dependence of percent MIB breakthrough on influent concentration. If the percent breakthrough is independent of the concentration used, the influent concentration can be selected to provide easy-to-analyze sample concentrations. To test the dependence on influent concentration, the GAC that had been in service for one year was exposed to increasing influent concentrations of MIB. For approximately 2 days each, 25 ng/L, 51 ng/L and 100 ng/L MIB in Lake Michigan water were applied to the column with an EBCT of 3.1 minutes. The percent MIB passing through the GAC bed at each of the influent concentrations approached the same plateau value, approximately 55%.

The results of Figure 8 were encouraging because they demonstrated the independence of percent MIB breakthrough on the influent MIB concentration. However, the experiment only simulated step increases in taste and odor intensity. Figure 1 clearly shows through
a taste and odor season, there may be several periods of alternating high and low concentrations of taste and odor causing compounds. As previously discussed, the data from the pilot study seemed to indicate that desorption might influence the effluent concentration.

An additional experiment tested a variable influent MIB concentration on the GAC that had been in service for one year. The column was sequentially fed an influent of 52 ng/L, 25 ng/L and 100 ng/L MIB in Lake Michigan water, each for approximately two days. The resulting percent breakthroughs for the 2.3 minute EBCT were 66 percent, 77 percent and 68 percent, respectively (Figure 9). These data indicated that when the carbon experienced a decrease in the influent MIB concentration, desorbing MIB elevated the effluent concentration above that which would normally occur had the carbon not been pre-exposed to a higher influent concentration. This suggests that if a GAC sample is collected during or soon after it has been exposed to MIB, the minimum percent breakthrough could be biased by desorption if the laboratory column influent concentration is lower than that of the previous exposure.
Natural Organic Matter Loading

As previously stated, several researchers have reported that the loading of organic matter on activated carbon controls the adsorption of micropollutants. To support this hypothesis, specifically for the adsorption of MIB by GAC, an additional experiment was performed. A laboratory column was packed with 12x14 mesh virgin GAC. Deionized-distilled (DDI) water was continuously applied to the column with a 3.3 minute EBCT, periodically switching the influent to a batch of DDI water containing 50 ng/L MIB, for two days. The effluent MIB concentration was continuously monitored to determine what percentage of MIB in each simulated episode passed through the GAC. The percent MIB breakthrough for each application was approximately 9 percent.

![Figure 9 - Effect of Variable Influent MIB Concentrations on Percent MIB Breakthrough](image_url)

Figure 9 - Effect of Variable Influent MIB Concentrations on Percent MIB Breakthrough
(1 year service time; 2.3 min EBCT)

Figure 10 compares the data collected during this experiment to the results previously obtained while evaluating the effect of service time on the percent MIB breakthrough. Starting with fresh carbon, twice as much MIB passed through the GAC in natural water than in DDI water. As the length of service time increased and additional NOM was adsorbed in the natural water system, the percent MIB passing through the column

78
increased. No such increase was observed in the DDI system. The initial increase in the percent MIB breakthrough in the natural water system could not be attributed to the loading of MIB. Assuming the complete adsorption of a constant 50 ng/L MIB influent for 0.25 years with a 3.3 minute EBCT, a conservative estimate based on the data displayed in Figure 1, only 2.3 percent of the maximum MIB surface loading would have been utilized. As a result, a portion of the decrease in the MIB removal efficiency was attributed to the adsorption of NOM. It is likely that the reaction of chlorine with the GAC contributed to this decrease in MIB removal efficiency. The effect of chlorine on the ability of GAC to remove MIB is discussed below. [Note: The maximum MIB surface loading was determined from DDI water isotherms prepared with an unground 30x40 U.S. Standard mesh (0.420 to 0.595 mm diameter) size fraction of virgin GAC. The resulting Freundlich parameters for these single-solute isotherms were 8.738 (ng/mg)(ng/L)^1/n and 0.746 for K and 1/n, respectively.]

![Figure 10 - Effect of Natural Organic Matter on MIB Breakthrough (3.3 min EBCT)](image)

**Effect of Chlorine**

Many treatment plants with GAC beds that use free chlorine as a disinfectant have chlorine entering the activated carbon bed. When running the laboratory experiments, an
important decision to be made is whether to include chlorine in the influent water to simulate field conditions. Several researchers have shown that chlorine reduces the adsorption capacity of activated carbon for numerous organic compounds (McGuire and Suffet, 1984; Snoeyink and Suidan, 1975; Snoeyink et al. 1974; Coughlin, 1970; Coughlin and Ezra, 1968). Lalezary et al. (1988) and Gillogly et al. (1998) have shown this specifically for powdered activated carbon and MIB. Based upon these results, a similar reduction in removal efficiency was expected between GAC and MIB once chlorine was allowed to react with the carbon.

To test this hypothesis, virgin GAC was reacted with chlorine [chlorine (as Cl₂) mass reacted to carbon mass ratio of 0.15 and 0.30] in a batch system before being transferred to a column. This allowed for uniform reaction of the chlorine with all carbon particles. As a result, these laboratory-scale columns are not representative of the entire depth of a GAC bed. However, these columns may simulate the performance of the top fraction of GAC in a full-scale system because most of the free chlorine entering such an adsorption system reacts with the GAC in the upper layer. Filtered Lake Michigan water was fed to these laboratory GAC beds, periodically switching to a 50 ng/L MIB Lake Michigan water solution for two-day intervals. The resulting breakthrough of each MIB episode is shown in Figure 11. [Note: A chlorine (as Cl₂) mass reacted to carbon mass ratio of 0.15 or 0.30 is equivalent to a water treatment plant with a 3.3 min GAC EBCT and 1.0 mg/L of chlorine as Cl₂ completely reacting with the carbon for 0.5 or 1.0 years, respectively.]

In a full-scale system, the chlorine would have reacted with aqueous and adsorbed NOM in addition to the GAC, so the approach used in this experiment does not exactly simulate a full-scale system reacting with chlorine. However, the laboratory results indicated the reaction of chlorine with GAC can significantly reduce the MIB adsorption efficiency, and thus the exposure of GAC to chlorine should be avoided if possible.
Biological Activity

It needed to be verified that the MIB removal observed in the laboratory-scale columns was not influenced by biological activity (i.e. no biodegradation of MIB). Several steps were taken to minimize the potential of a biological influence. All of the natural water used in the experiments was filtered through a 0.45 μm membrane filter. In addition to removing particulate and colloidal material that could otherwise plug or foul the laboratory columns, this filtration had the added benefit of removing potentially MIB degrading microorganisms present in the water. While this was probably sufficient for the limited time that the virgin GAC columns were operated, the preloaded GACs could themselves introduce attached microorganisms. However, the preloaded GAC samples were all collected before to the taste and odor season began. By collecting the samples at this time, the GAC and potentially attached microorganisms had not been exposed to MIB for 6 to 8 months. This meant that if an acclimation time were necessary for the MIB degrading microorganisms, the organisms would not already be acclimated when they were introduced into the experiment.
To verify that biological activity was not influencing the observed percent MIB breakthroughs, two columns were prepared with GAC that had been in service for 1 year. These laboratory-scale columns were operated at 4 and 25°C. If biological MIB degradation was present, it was expected that the column run in the 4°C temperature controlled cold room would have different results from the column operated at room temperature (25°C). Based on this assumption, Figure 12 indicates that biological activity was not influencing the observed percent MIB breakthroughs. Additional work, presented in the following chapter, shows that all of the trends observed in these laboratory-scale columns were predicted using competitive adsorption models, further indicating the percent MIB breakthroughs were not influenced by biological activity.

SUMMARY AND CONCLUSIONS

A test was developed to rapidly and effectively evaluate the remaining life of a GAC bed for the mitigation of a taste and odor episode. The results showed that adsorption alone may be insufficient to control MIB episodes. The need for additional treatments, such as
ozone, advanced oxidation processes, or biological oxidation is evident, and additional research is necessary to determine which combination of these technologies can most effectively be used. Specific conclusions of this study are:

- **Laboratory-scale columns simulated the performance of a pilot-plant very well.** The test used a representative GAC size fraction (12x14 U.S. Standard mesh – 1.41 to 1.68 mm diameter) packed in a small laboratory column (1.0 cm diameter). The percent removal of MIB pulse-loadings was essentially the same in the laboratory columns as it was in the pilot-plant. These laboratory columns were also able to show the impact of variable influent MIB concentrations, the accumulation of natural organic matter and the reaction of GAC with free chlorine.

- **Adsorption by GAC alone, will often provide insufficient protection against MIB taste and odor episodes.** The laboratory- and pilot-scale experiments often showed that GAC would not reduce MIB to threshold odor concentrations. For short contact times (~ 4 minute EBCT), virgin GAC could only be expected to control episodes less than approximately 30 ng/L MIB. Even with longer contact times (~ 10 minute EBCT), a 30 ng/L MIB episode was the most MIB a GAC that had been in service for one year could reduce to acceptable levels.

- **The maximum attenuation of a transient MIB load by granular activated carbon, reported as percent removal, was independent of the influent concentration but dependent on the surface loading of natural organic matter.** The percent MIB removed by a bed of granular activated carbon was independent of the influent MIB concentration, for increasing influent concentrations. However, when the GAC had been exposed to higher influent concentrations, a subsequent and lower concentration episode was not removed at the same efficiency due to desorption and redistribution of MIB from the previous loading. Based upon these results, if a GAC sample was collected during or soon after it has been exposed to MIB, the minimum percent
breakthrough observed in these laboratory-scale columns could be biased if the influent concentration selected for the test was too low.

- **In natural water, MIB removal was controlled by the adsorption of the other adsorbable organic matter.** In deionized-distilled water, a constant percent removal was observed for a series of simulated MIB episodes. However, for a natural water system, a significant decrease in MIB removal efficiency was observed and attributed to the adsorption of natural organic matter from Lake Michigan water. This indicated that for limited amounts of MIB accumulation, the breakthrough of continuous and intermittent MIB loadings would be similar, since the background organic matter was primarily controlling the removal efficiency.

- **Chlorine has a deleterious effect on the ability of granular activated carbon to remove MIB.** The greater the amount of chlorine allowed to react with the GAC, the lower the percent removals. Thus, the application of chlorine to GAC should be avoided if possible.

**ACKNOWLEDGMENT**

The authors would like to thank Gary Williams, Randy Russell and William Soucie for providing samples of GAC, and Kathryn Force for her assistance with the pilot-study.
"Doing [research] without [publishing] is like winking at a girl in the dark. You know what you are doing, but nobody else does." (Steuart H. Britt)

Predicting GAC Performance

The water industry has long been attracted to predicting the performance of granular activated carbon. If the performance of GAC can be predicted, the technical and economic feasibility of activated carbon for a particular application can be decided. To obtain a prediction two general approaches have been utilized. The first approach uses laboratory-scale columns to simulate the performance of large-scale systems, as discussed in the previous chapter. The second approach utilizes the physical and adsorptive characteristics of an activated carbon, obtained from laboratory experiments, to initialize a predictive mathematical model. The use of one such model, "FS", will be discussed here.

PSEUDO SINGLE-SOLUTE HOMOGENEOUS SURFACE DIFFUSION MODEL

The program "FS", written by Yuasa (1982), has been used with some success (Knappe, 1996). By assuming axial dispersion through a GAC filter/adsorber was negligible (Weber and Liu, 1980), the program solves a system of equations for plug flow pseudo-single solute homogeneous surface diffusion (PFHSDM) through a fixed bed adsorber to model the adsorption rate of the target compound from natural water onto GAC. Pseudo single-solute homogeneous surface diffusion assumes that the rate at which the target compound is adsorbed from natural water by activated carbon can be modeled as if the target compound was the only compound present. To solve the PFHSDM, equilibrium \([K(C_{inf}), 1/n]\) and kinetic \((D_s, k_f)\) parameters are needed. The pseudo single-solute \(K(C_{inf})\) and \(1/n\) can be determined using the equivalent background compound (EBC) method (Qi et al., 1992). Once these parameters have been calculated the \(D_s\) and \(k_f\) can be determined from a short bed adsorber test.
PFHSDM Calibration and Use

**Pseudo Single-Solute Capacity.** The pseudo single-solute equilibrium capacity is determined by the EBC method. Initially it is assumed that a single hypothetical compound, the equivalent background compound, can represent the natural organic matter (NOM) in the water, besides the target compound. This allows competitive adsorption to be described by a bi-solute version of the ideal adsorbed solution theory (IAST). The bi-solute IAST may then be used to predict the equilibrium surface capacity of the target compound that a specific mass of activated carbon will adsorb for any given initial concentration of the target compound. This competitive capacity is equivalent to the pseudo single-solute equilibrium capacity for the particular system predicted. This approach is outlined in greater detail in the chapter discussing “Kinetic and Equilibrium Studies of $^{14}$C-MIB Adsorption on PAC in Natural Water”.

Critical to predicting a pseudo single-solute capacity, is precisely determining the single-solute and competitive adsorption equilibrium capacity of activated carbon for the target compound. Several researchers have reported that particle size had no noticeable affect on the equilibrium adsorption capacity of either ground or unground virgin GAC, for both single-solute and competitive systems (Najm *et al.*, 1990; Weber and Wang, 1987; Thacker *et al.*, 1983; Randtke and Snoeyink, 1983; Lee *et al.*, 1981). The time required to reach equilibrium, however, depends on particle size (Najm *et al.*, 1990). Therefore, the smallest attainable particle size should be used in the isotherms to minimize the time required for experimentation.

Other researchers studying atrazine (Knappe, 1996) and trichloroethene adsorption (Carter *et al.*, 1992) have found that grinding preloaded GAC can significantly alter its capacity. They agreed that this process increases the Freundlich K value by opening up adsorption sites previously blocked by preloaded natural organic matter. The researchers also observed a decrease in the slopes of the isotherms ($1/n$) with grinding, indicating an
increase in site energy heterogeneity. For these reasons it was felt that grinding preloaded carbon would not yield adsorptive capacity parameters descriptive of the unground GAC.

Unfortunately, the role of particle size in preloading has not been completely characterized. Summers et al. (1990) determined that after 1 week of preloading, the capacity for cis-1,2-dichloroethene was independent of particle size. Carter et al. (1992) observed a convergence of trichloroethene capacity within 4 weeks of preloading for 30/40 and 80/100 size fractions of activated carbon. These studies seem to indicate that the influence of GAC particle size on the degree of preloading diminishes over time, but further study is needed.

Rate of Adsorption. Once the pseudo single-solute equilibrium capacity parameters had been calculated, the kinetic parameters could be determined from a short bed adsorber (SBA) test. The SBA test was designed such that immediate but not complete breakthrough was observed (i.e., the mass transfer zone of the target compound was longer than the depth of the GAC bed). Using the data collected from the SBA and the program “FS-SI”, the $D_s$ and $k_r$ are calculated by performing a nonlinear least-squares optimization technique that minimizes the error between the experimental data and the model prediction from the pseudo single-solute PFHSDM (see Appendix D: FS-SI).

Model Prediction. Once the parameters describing the adsorption of the target compound by activated carbon have been determined, the program “FS” can then be used to predict the performance of a GAC bed. The model uses a moving-grid finite difference method to numerically solve the PFHSDM (see Appendix D: FS).

GAC Preparation. Prior to use, the virgin GAC was washed with deionized-distilled water to remove the fines. The carbon was then dried to remove the water and sieved to collect the desired size fractions (20x25 U.S. Standard mesh - 0.707 to 0.841 mm diameter, and 30x40 U.S. Standard mesh - 0.420 to 0.595 mm diameter). The sized
virgin GAC was then rinsed again with deionized-distilled water to remove any fines generated during sieving, dried at 105 °C to remove the water, and stored in a desiccator until use.

The preloaded carbons collected from the water treatment plants were initially washed with deionized-distilled water to remove the fines. The washed carbon was then wet-sieved to obtain the size fractions of interest (12x14 U.S. Standard mesh – 1.14 to 1.68 mm diameter, 16x18 U.S. Standard mesh – 1.00 to 1.19 mm diameter, and 20x25 U.S. Standard mesh - 0.707 to 0.841 mm diameter). The 20x25 mesh fraction was the smallest size fraction of the preloaded GACs that could be collected that did not have a significant amount of sand. The wet-sieved GAC particles were then blotted to remove the excess water and immediately weighed out for use. Additional portions of the preloaded sized GAC were weighted out and dried to determine their moisture content. The weighed mass(es) of preloaded GAC were then adjusted by the corresponding moisture content to determine the dry mass of activated carbon used in the experiment.

**ADSORPTION EQUILIBRIA RESULTS**

**Virgin GAC**

The adsorption capacity of GAC for MIB was first evaluated for the virgin GAC. While these Freundlich K and 1/n were being determined using the bottle-point isotherm technique described in previous chapters, it was felt that the independence of capacity on GAC particle size should be verified for MIB. While additional information about the relationship between particle size and preloading was also necessary, this could only be evaluated with the preloaded GAC. Without considering the influence of these factors, there would be insufficient confidence in the results obtained.

Headspace-free deionized-distilled water bottle-point isotherms were prepared with 30x40 (0.420 to 0.595 mm diameter) and 20x25 (0.707 to 0.841 mm diameter) U.S.
Standard mesh GAC particles. After 25 days of agitation, a select number of the bottles were sampled and topped-off with deionized-distilled water. Once a total of 125 days had passed, the MIB concentration in all of the bottles was analyzed. The concentration of MIB from the bottles that had been previously sampled at 25 days was adjusted to account for the addition of the small volume of deionized-distilled water to keep the bottles headspace-free.

The data (Figure 1) show a difference in the MIB surface loading between the two GAC particle sizes after 25 days of agitation. An additional agitation of 100 days showed a significant increase in the MIB surface loading, indicating, 25 days was not long enough to reach equilibrium. The data after 125 days of agitation show the capacities of the two GAC size fractions converging. This convergence suggests that the virgin GAC’s capacity for MIB was independent of particle size and the particles were in equilibrium with the aqueous MIB concentration. The corresponding Freundlich parameters for the virgin GAC single-solute isotherms at 125 days were $8.738 \text{(ng/mg)}(\text{ng/L})^{-1/n}$ and 0.746 for $K$ and $1/n$, respectively.

![Figure 1 - Effect of Time and Particle Size on MIB Surface Loading (virgin GAC)](image-url)
These isotherms draw attention to a potential problem with the use of mathematical models. Even when using a 30x40 mesh fraction of particles, 25 days was an insufficient amount of time to reach equilibrium. Should the Freundlich K and 1/n be determined prior to equilibrium, the parameters assumed for equilibrium could be significantly different than the true values. This low value would affect all subsequent parameter determinations, ultimately affecting the final GAC performance prediction.

Using the 20x25 mesh size fraction of virgin GAC an additional isotherm was prepared with Lake Michigan water. Again a difference was noted between the 25 and 125 day MIB surface loading (Figure 2). The data collected at 125 days were used for the EBC method.

Table 1 lists the Freundlich parameters and initial concentration of the EBC as determined by the EBC method. Applying these EBC and single-solute parameters to the bi-solute version of the IAST, an isotherm was predicted for an initial MIB concentration of 53.3 ng/L (Figure 3). At complete saturation, the carbon in a fixed bed of GAC should come to equilibrium with the influent MIB concentration. To determine the competitive adsorption parameters for this condition, the MIB surface loading ($q_e$) at the initial MIB
concentration of the isotherm ($C_e \approx C_0$) predicted by the IAST was obtained by extrapolating from the MIB surface loadings corresponding to low carbon doses (100, 50 and 5 μg/L). Applying these values to the Freundlich equation, with $1/n$ equivalent to the slope of the single-solute isotherms, the competitive capacity Freundlich $K$ was determined for this initial concentration. Table 2 lists these predicted competitive capacity Freundlich parameters.

### Table 1 - Equivalent Background Compound Freundlich Parameters

<table>
<thead>
<tr>
<th>GAC</th>
<th>Virgin</th>
<th>1 Year Preload</th>
<th>2 Year Preload</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_e$ (mmol/g)(μmol/L)$^{1/n}$</td>
<td>2.64x10^{-2}</td>
<td>2.74x10^{-2}</td>
<td>1.78x10^{-3}</td>
</tr>
<tr>
<td>$1/n$</td>
<td>0.0171</td>
<td>0.796</td>
<td>0.841</td>
</tr>
<tr>
<td>$C_{eq}$, μmol/L</td>
<td>4.53x10^{-4}</td>
<td>6.90x10^{-3}</td>
<td>7.89x10^{-3}</td>
</tr>
</tbody>
</table>

![Figure 3 - IAST Fit and Prediction (virgin GAC)](image-url)

### Table 2 - Natural Water Freundlich Parameters

<table>
<thead>
<tr>
<th>GAC (ng/L $\approx C_{inf}$)</th>
<th>Virgin</th>
<th>1 Year Preload</th>
<th>2 Year Preload</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_e$ (ng/L)</td>
<td>53.3</td>
<td>51.7</td>
<td>51.7</td>
</tr>
<tr>
<td>$K_e$ (ng/mg)(ng/L)$^{1/n}$</td>
<td>0.0191</td>
<td>0.1215</td>
<td>0.1945</td>
</tr>
<tr>
<td>$1/n$</td>
<td>0.7459</td>
<td>0.6471</td>
<td>0.5882</td>
</tr>
</tbody>
</table>
Preloaded GAC

While the same general approach was used to determine the competitive adsorption Freundlich parameters for the preloaded GACs, additional tests were necessary to obtain information about the relationship between particle size and degree of preloading. If the degree of preloading were dependent on size of the particles, the equilibrium MIB capacity would be dependent on particle size. Should a particle size/MIB capacity dependence exist, further experimentation would be necessary to determine which size fraction of particles would yield an MIB capacity representative of the entire distribution of particle sizes.

![Graph showing MIB adsorption vs MIB concentration](image)

Figure 4 - Effect of Time and Particle Size on Surface MIB Loading (1 year service time)

For both the 1 and 2 year preloaded GACs, 25 and 125 day single-solute and natural water isotherms were analyzed (Figure 4 and 5, respectively). As expected for both activated carbons, the initial 25 days of agitation was insufficient to reach equilibrium. There was no significant difference between the MIB surface loadings of the 12x14, 16x18 or 20x25 mesh GAC size fractions after 125 days of agitation. This suggests that for these carbons the degree of preloading is independent of particle size. Based upon the
available data, this conclusion cannot be substantiated for preloading times less than one year.

The single-solute Freundlich parameters were obtained from the 125-day isotherms. A $K$ and $1/n$ of 0.4126 (ng/mg)(ng/L)$^{1/n}$ and 0.6471, respectively, were recorded for the 1 year preloaded GAC. Slight differences were observed for the 2 year preloaded GAC ($K = 0.4602$ (ng/mg)(ng/L)$^{1/n}$ and $1/n = 0.5882$). The EBC method was then applied to the 125-day natural water isotherms. The resulting Freundlich EBC parameters and predicted competitive MIB equilibrium capacities are listed in Tables 1 and 2, respectively.

![Graph](image)

Figure 5 - Effect of Time and Particle Size on MIB Surface Loading (2 year service time)

It is interesting to note that after 25 days of agitation there was no observable competition. Focusing on the 1 year preload GAC (see Figure 6), the single-solute and natural water MIB isotherms could be characterized by a single set of Freundlich parameters. Knappe (1996) saw similar results with atrazine. The natural water and single-solute atrazine isotherms were compared after 28 days of agitation, from which it was concluded that there was no competition with the preloaded GACs tested. Isotherms of longer duration were not tested to verify that equilibrium had been reached.
It is understandable that for preloaded GAC isotherms of "short" contact times, competition might not be readily apparent. In both the single-solute and natural water isotherms the NOM already adsorbed, or preloaded, onto the GAC would be present. The additional adsorbable organic matter contributed by a short contact time in the natural water isotherm is likely to be small in comparison to the quantity of previously adsorbed NOM. Finally, based upon the results obtained in previous chapters, concluding that the quantity of NOM adsorbed controls the adsorption of MIB, the amount of MIB adsorbed and its corresponding competition would be characterized by comparing a small or undetectable difference in two large quantities of adsorbed NOM.

![Figure 6 - Adsorptive Competition at 25 days (1 year preload, 20x25 mesh GAC)](image)

**Figure 6** - Adsorptive Competition at 25 days (1 year preload, 20x25 mesh GAC)

**GAC PHYSICAL CHARACTERISTICS**

Some of the physical properties of the GAC and GAC beds needed to be determined before the adsorption kinetics could be characterized. The skeletal density and particle porosity of the carbons were determined through mercury intrusion porosimetry (Autopore #9220; Micrometrics, Norcross, Georgia). A comparative skeletal density was determined by helium pycnometry (Accupyc 1330; Micrometrics, Norcross, Georgia). The skeletal density and particle porosity were used to calculate the GAC particle density.
used in the FS model. Table 3 lists the values obtained for the characterization of the GAC particles.

Some researchers have combined helium pycnometry with mercury intrusion porosimetry to determine the particle density. Table 3 indicates that this may lead to results different than if mercury intrusion porosimetry was used alone. It is expected that helium would be able to access pores smaller than mercury, leading to larger skeletal densities and particle porosities. While the "functional" porosity and skeletal density should be based only on the pores accessible to NOM and MIB would produce kinetic parameters most descriptive of the system, a technique to determine this was not readily available. For the work presented here only the data obtained by mercury intrusion porosimetry was considered.

### Table 3 – GAC Particle Characteristics

<table>
<thead>
<tr>
<th>GAC</th>
<th>Hg Intrusion Porosimetry</th>
<th>He Pycnometry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Skeletal Density (g/mL)</td>
<td>Particle Porosity</td>
</tr>
<tr>
<td>Virgin</td>
<td>1.30</td>
<td>0.392</td>
</tr>
<tr>
<td>1 Year Preload</td>
<td>1.59</td>
<td>0.381</td>
</tr>
<tr>
<td>2 Year Preload</td>
<td>1.55</td>
<td>0.395</td>
</tr>
</tbody>
</table>

Additional information (GAC bed depth, bulk density) was required about the GAC beds used to determine the kinetic parameters, as well as the GAC beds to be predicted. The GAC bed depth was measured directly through the glass column; if variations in the depth were noted, an average was used. The bulk density of the GAC was calculated by the dividing the mass of GAC used to prepare the bed, by the volume of the bed.

### ADSORPTION KINETICS RESULTS

To obtain the kinetic parameters $D_s$ and $k_0$, a short bed adsorber was prepared for the virgin GAC. The preparation of the SBA was identical to the laboratory test columns
discussed at length in the previous chapter. Since the PFHSDM assumes that the rate at which MIB was adsorbed from natural water by the GAC could be modeled as if the MIB was the only compound present, the competitive adsorptive capacity predicted for the influent MIB concentrations of the laboratory-scale columns was used as a pseudo single-solute adsorption capacity. Figure 7 shows the breakthrough curve obtained from this SBA test. While the film mass transfer coefficient \( k_f = 2.40 \times 10^{-3} \text{ cm/s} \) calculated from this SBA was in the general range expected, the surface diffusion coefficient \( D_s = 1.63 \times 10^{-6} \text{ cm}^2/\text{s} \) was several orders of magnitude larger than expected, based on the kinetics for MIB adsorption onto PAC (see the chapter discussing "Kinetic and Equilibrium Studies of "C-MIB Adsorption on PAC in Natural Water"). The reason for this higher than expected surface diffusion coefficient was explored and is discussed later. These kinetic parameters were subsequently used to predict the performance of the laboratory scale results obtained in the previous chapter.

![Figure 7 - Kinetic Parameters Determined with Laboratory Column (virgin GAC)](image)

Similar fits were obtained for the preloaded GACs. The film mass transfer and surface diffusion coefficients obtained for the virgin and preloaded GAC are listed in Table 4.
(Note: the “SBA test” is actually one of the two-day spikes applied to the laboratory-scale columns. It was felt that the kinetic parameters obtained directly from these systems would be the most appropriate.)

Table 4 – MIB Adsorption Kinetic Coefficients

<table>
<thead>
<tr>
<th>GAC</th>
<th>Virgin</th>
<th>1 Year Preload</th>
<th>2 Year Preload</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(D_c) cm(^2)/s</td>
<td>(k_f) cm/s</td>
<td>(D_c) cm(^2)/s</td>
</tr>
<tr>
<td>Virgin</td>
<td>1.63x10(^{-6})</td>
<td>3.90x10(^{-4})</td>
<td>9.21x10(^{-12})</td>
</tr>
<tr>
<td>1 Year</td>
<td>7.86x10(^{-12})</td>
<td>2.23x10(^{-4})</td>
<td></td>
</tr>
</tbody>
</table>

It can be seen from this table that the film mass transfer coefficient is generally independent of the preloading time. This is consistent with \(k_f\) being dependent only on the flow rate of the system and the diameter of the GAC particles. The surface diffusion coefficient, however, dramatically changed after preloading. These data may indicate that the previously adsorbed NOM hinders the transport of MIB into the GAC particle. However, this will be discussed further later in the chapter.

GAC PERFORMANCE PREDICTIONS

Using the equilibrium and kinetic MIB adsorption parameters along with the GAC bed characteristics and experimental flow conditions, the performance of the laboratory-scale columns described in the previous chapter were predicted. Figure 8 shows the predicted percent MIB breakthrough for a virgin GAC bed exposed to a 2.6 or 4.5 min EBCT. The PFHSDM closely simulated the percent MIB breakthrough at two days (2880 minutes). The two-day percent MIB breakthrough value was used to characterize the GAC performance in the laboratory-scale columns used in the previous chapter, “Determining the Remaining GAC Bed Life for Taste and Odor Control”.

Similar PFHSDM predictions were performed for the preloaded GAC. Figure 9 shows the PFHSDM fit and prediction of the GAC preloaded for 2 years. Similar fit and predictions of the 1 year preloaded GAC were also obtained. Additional predictions of
the performance of the 1 year preloaded carbon were made for a range of EBCTs, between 2.3 and 13.5 minutes, and for two different column diameters (1.0 and 2.5 cm). Figure 10 shows that the PFHSDM was able to predict well the two-day percent MIB breakthrough of a wide variety of EBCTs and two different column diameters. Even at EBCTs over four times longer than what the model was calibrated at, there was only a 10 percent difference between the percent MIB breakthrough of the laboratory-scale column and the PFHSDM prediction.

![Figure 8 - PFHSDM Predictions of Virgin GAC Performance](image)

A final set of predictions were made for the 1 year preloaded carbon to determine if the PFHSDM would predict that the percent MIB breakthrough was independent of the influent MIB concentration. Figure 11 clearly shows that the PFHSDM predicted the same percent MIB breakthrough for MIB influent concentrations of 25, 52 and 100 ng/L. It should be noted that this was based upon the 125-day isotherms. When the 25-day isotherm data were used, and no competition was evident, the PFHSDM did not predict the same percent MIB breakthrough, as expected.
Figure 9 – PFHSDM Prediction of Preloaded GAC (2 year preload)

Figure 10 – The Influence of Bed Dimensions and EBCT on PFHSDM Predictions (1 year service time)
DIFFUSION LIMITATIONS

While the model was able to closely fit and predict the laboratory-scale column conditions presented in the preceding chapter, the modeling approach yielded some coefficients that did not seem to be physically realistic. The first question arose with the surface diffusion coefficient \( D_s = 1.63 \times 10^{-6} \text{ cm}^2/\text{s} \) obtained for the virgin GAC. As this value was considerably higher than expected, a sensitivity analysis was performed. Figure 12 indicated that if all of the other parameters were held constant, the fit obtained was generally insensitive to the surface diffusion coefficient. It was not until \( D_s \) had been decreased several orders of magnitude did the shape of the breakthrough curve change significantly. This implied that the model presented the film diffusion coefficient \( k_f = 3.90 \times 10^{-4} \text{ cm/s} \) as the rate limiting step of adsorption. This was verified by increasing \( k_f \) to \( 1 \times 10^{-1} \text{ cm/s} \) and varying the surface diffusion coefficient (Figure 13).

Figure 13 shows that the breakthrough of MIB for a virgin GAC system with less film resistance \( k_f = 1 \times 10^{-1} \text{ cm/s} \) than originally proposed by the model \( k_f = 3.90 \times 10^{-4} \text{ cm/s} \) was sensitive to surface diffusion when \( D_s \geq 1 \times 10^{-12} \text{ cm}^2/\text{s} \). This was supported by using
a $D_s$ of $1 \times 10^{-12}$ cm$^2$/s and varying the film diffusion coefficient (Figure 14). For this $D_s$, $1 \times 10^{-12}$ cm$^2$/s, the convergence of the MIB breakthroughs indicated that at these film diffusion coefficients, $k_f \geq 1 \times 10^{-3}$ cm/s, the surface diffusion was the rate limiting step. Based upon the range of surface diffusions tested and assuming the mass transfer zone is longer than the bed depth a film resistance coefficient between $10^{-4}$ and $10^{-3}$ cm/s would be required to match the laboratory-scale columns. This correlates well with the $3.9 \times 10^{-4}$ cm/s determined by the optimization routine for this model.

Figure 12 – Sensitivity of Percent MIB Breakthrough to the Surface Diffusion Coefficient

Figure 13 – MIB Breakthrough Sensitivity to Internal Diffusion with Less External Resistance

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At such low approach velocities (0.361 cm/min) it is not unreasonable to expect film diffusion to have a significant effect on the breakthrough of MIB. The larger systems, however, operate at much higher velocities. This significant difference in flows was concerning. Assuming that the laboratory-scale columns do simulate the performance of larger-scale systems the model was initialized so that the model was trying to characterize a 1 m deep bed with the same contact time (approach velocity = 301 cm/min). With $k_r$
and $D_s$ equal to $4.03\times10^{-4}$ cm/s and $1.55\times10^{-7}$ cm$^2$/s, respectively, the model again assumes that film resistance is a limiting factor (Figure 15). All of these modeling results consistently indicate that MIB adsorption in GAC is a film diffusion controlled process.

CAPACITY LIMITATION

The data in Figures 3-5 indicate that the GAC capacity decreases with preloading time. The laboratory-scale column capacities predicted by the IAST, however, did not show the same trend (Table 5). The reason for this is due to the predicted effects of competition at equilibrium capacities close to the initial or influent MIB concentration. Assuming reversible adsorption, it is shown in Figure 3 that the MIB capacity dramatically decreases as the influent concentration is approached.

| Table 5 — GAC Pseudo Single-Solute MIB Capacity |
|------------------|------------------|
| Co = Ce (ng/L) | K (mg/g)(L/ug)$^n$ |
| Virgin | 53.29 | 0.003 |
| 1 yr preload | 51.67 | 0.011 |
| 2 yr preload | 51.67 | 0.011 |

It is believed that this dramatic decrease of capacity is due to the presence of a strongly adsorbing competing fraction of NOM that could displace previously adsorbed MIB. Figure 16 shows that the IAST prediction for the 1 year preloaded GAC did not show the same decrease of capacity at equilibrium concentrations close to the initial concentration. A similar IAST fit and prediction were obtained for the 2 year preloaded carbon. The IAST results of the preloaded carbons indicated that adsorbing an incremental amount of additional NOM to the preloaded carbons did not affect MIB adsorption as dramatically as with the virgin GAC. This resulted in the unexpected trend in the IAST predictions shown in Table 5. For the purpose of consistency, the IAST predictions presented in Table 5 were the capacity values used in the PFHSDM.
Instead of using the IAST predicted capacity determined at the influent concentration, and a capacity was determined from the portion of the isotherm parallel to the single solute for the virgin GAC a Freundlich K of 0.26 (mg/g)^(L/µg)^(1/n) could be obtained. If the film diffusion remained at 3.90x10^-4 cm/s, a lower surface diffusion coefficient was selected (D_s = 1x10^-12 cm^2/s), and the Freundlich K was increased to 0.26, it can be seen that a reasonable fit can be obtained (Figure 17). It can be proposed that while the system...
is still primarily controlled by film diffusion, a more realistic surface diffusion can be obtained with a Freundlich K that is more physically reasonable.

SUMMARY AND CONCLUSIONS

Based on carefully collected equilibrium and kinetic MIB adsorption data, the plug flow pseudo single-solute homogeneous surface diffusion model was used to predict the two-day percent MIB breakthrough of laboratory-scale fixed bed GAC adsorbers. The model used the isotherm parameters from a batch test and determined the mass transfer parameters $D_s$ and $k_r$ by fitting the data from a laboratory-scale column test. Performance predictions were then made of the effect of changing EBCT and initial concentration. These model predictions closely matched the performance of the laboratory-scale columns at EBCTs close to the EBCT at which the model was calibrated. Even at EBCTs more than four times longer than the calibration EBCT, only a 10 percent difference was observed between the predicted and actual percent MIB breakthrough values. Additionally, the model was able to predict the performance of a larger diameter (2.5 cm) laboratory-scale column.

During the evaluation of the PFHSDM it was determined that poor predictions may be reached if sufficient time is not given for determining the equilibrium MIB adsorption parameters. It was also discovered that while satisfactory predictions were obtained the adsorptive parameters describing the system were not necessarily physically realistic. The model did indicate, however, that the adsorption of MIB in a fixed bed of GAC is controlled by film diffusion. Finally, the PFHSDM supported the findings reported in the previous chapter, which concluded, the percent MIB breakthrough was independent of the influent MIB concentration.
"I like work; it fascinates me. I can sit and look at it for hours." (Jerome K. Jerome)

Activated Carbon Testing Protocols

Developed from the work discussed in the previous chapters, protocols evaluating the use of powdered and granular activated carbon for MIB removal are described below.

POWDERED ACTIVATED CARBON

The protocol outlined here should provide the user with a method to assist in the selection of different PACs. The approach should also indicate the minimum PAC dose required to remove a desired fraction of MIB.

1. Obtain a representative sample of the natural water and powdered activated carbon(s) of interest;
2. Based upon the user’s limit of MIB detection, select an initial concentration of MIB so that two to three logs of removal may be observed (the lower the concentration the better, however, make sure that at least 2 logs of removal can be analyzed);
3. Prepare a natural water isotherm with a range of carbon doses wide enough to remove the MIB to the analytical detection limit (PAC doses between 2.0 and 150 mg/L are often used; isotherms should be prepared headspace free to minimize losses due to volatilization; glass beads should be used in headspace free isotherms to insure proper mixing);
4. Analyze the isotherm at a time representative of the PAC contact time expected in the water treatment facility;
5. Plot the results of the isotherm as percent MIB remaining (C/C_o*100%) versus PAC dose on a log-log scale, and draw a line of best fit through the data;
6. Determine the influent and desired effluent MIB concentration to calculate the corresponding percent MIB remaining;
7. On the plot of the isotherm data, read horizontally across at the calculated percent MIB remaining until the line of best fit is intersected. At this point move vertically down to determine which PAC dose this corresponds.

8. The corresponding PAC dose read from the plot should indicate the minimum PAC dose required to reduce the concentration of MIB to the level selected in step #6.

(Note: the PAC dose determined from the graph is a minimum. Higher doses may be required due to interactions with other treatment chemicals, poor mixing conditions or shorter than expected contact times.)

GRANULAR ACTIVATED CARBON

This procedure can assist in determining the minimum amount of MIB expected to pass through a GAC filter/adsorber. This should indicate to the operator whether or not the activated carbon needs to be regenerated/replaced to serve as an effective barrier against tastes and odors.

1. Dewater the filter/adsorber of interest;
2. Collect a representative core sample;
3. Perform a sieve analysis to determine the GAC fraction which accounts for the largest fraction of the filter's external surface area (the carbon should be rinsed free of particulates if the filter was not backwashed prior to sampling);
4. Calculate the empty bed contact time (EBCT = bed volume/flow rate) of the large scale filter;
5. Select the flow rate to be used in the laboratory scale column (selection is often based on the pump used or the analytical sample volume requirements);
6. Using the information in #4 & 5, calculate the bed volume of the laboratory scale column to have the same EBCT as the large scale system;
7. Assuming an apparent bed density, and moisture content of the wet GAC, calculate the mass of wet GAC that should be weighed for the laboratory scale column (apparent bed density ~ 0.5 to 0.6; wet GAC moisture content ~ 30%);
8. Weigh the appropriate amount of the size fraction determined in step #3;
9. Prepare the laboratory column with the GAC centered in a bed of glass beads (make sure that the beads and GAC are well packed and do not have any air bubbles trapped between particles) and measure the actual bed dimensions;
10. Spike the influent natural water to the desired MIB concentration (note: the carbon’s history may influence MIB removals; the influent concentration should be high enough so that desorption from previous exposure does not occur, however, it should not be so high that it significantly increases the carbons surface MIB concentration);
11. Set the flow rate for the actual bed dimensions determined in step #9 to obtain the EBCT determined for the larger scale system, and pass the spiked influent through the column at this flow rate for approximately two days to determine the effluent plateau concentration;
12. Normalizing this plateau value to the influent concentration will yield the minimum percent of MIB expected to pass through the larger scale column for any influent concentration (note: higher percentages of MIB may appear to pass through the larger scale column due to short circuiting, other treatment chemicals or previous loadings of MIB).
"In everything we ought to look to the end." (Jean de La Fontaine)

Summary and Conclusions

The work presented here has addressed the goals outlined for this study. To determine the effectiveness of activated carbon, in the presence or absence of free chlorine, for the removal of MIB in a drinking water treatment plant, two protocols were developed. One protocol was developed to determine the minimum FAC dose required to reduce a given MIB influent concentration to a specific level in natural water. The second protocol was used to determine the remaining life of an existing GAC bed for taste and odor control.

Through the development of these protocols it was found that:

- Liquid scintillation counting of $^{14}$C-MIB was a technique suitable for the rapid collection and analysis of low concentrations of MIB in the presence and absence of free chlorine;
- The percent MIB removed by activated carbon, either powdered or granular, is independent of the influent MIB concentration, but dependent on the natural organic matter adsorbed;
- Chlorine has a deleterious effect on the ability of activated carbon, both powdered and granular, to adsorb MIB, and thus the contact of chlorine with activated carbon should be avoided;
- Adsorption by activated carbon alone does not appear to provide sufficient protection against taste and odor caused by MIB.
Future Research Needs

The results presented in this study have shown that adsorption by activated carbon alone does not appear to provide a sufficient barrier against taste and odor problems caused by MIB. Additional work is necessary to determine the best, or combination of, technologies that will mitigate the earthy-musty organoleptic problems caused by this compound. Circumstantial evidence from water treatment plants, such as the Lake County, Illinois WTP, indicates that MIB is "controlled" in advanced water treatment processes such as ozone followed by biologically active GAC filtration. In this particular case the GAC has been in place for over six years. Through this example, and others, it appears that determining where is the "removal" actually occurring, and what are the respective roles of, 1) adsorption, 2) biodegradation, 3) oxidation/advanced oxidation, is very important.

Assuming biodegradation is important, the following questions arise:

- While many organisms have been shown to degrade MIB, which organisms are responsible for its degradation to the low concentrations necessary to produce palatable water?
- What conditions are necessary to stimulate the growth of these desirable organisms? (e.g. water quality parameters, post ox/AOP DOC characteristics)
- Do these organisms require time to acclimate before they start degrading the seasonal occurrences of MIB? If so, how long do these organisms require to acclimate, and can this amount of time be reduced or eliminated so that the organisms have been "triggered" to degrade MIB as soon as it appears in the influent?
• Is the adsorbent capacity of the GAC required, beneficial or even necessary? (i.e. can an alternative/cheaper support media be used with an equal or superior effectiveness?)

Providing answers to these questions would help to determine the most effective approach to controlling MIB related taste and odor problems. Since the consumers’ confidence in the quality and safety of their drinking water is directly connected to its aesthetics, these answers would also give the water treatment plants information critical to the production of water acceptable to the population they service.
"Only those things are beautiful which are inspired by madness and written by reason"

(André Gide)

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Wittmeyer, S., R. Cap, C. Lange, S. Carder, D.W. Fredricksen. 1995. Investigations Into the Sources and Removal of Taste and Odor Causing Compounds at Two Water


"It is surprising what a man can do when he has to,
and how little most men will do when he don’t have to.” (Walter Linn)

Appendix A  (Mathematical Modeling)

A number of theories and formulations have been applied to the mathematical modeling of adsorption processes. This research has only relied upon the use of the Freundlich and Ideal Adsorbed Solution Theory (IAST) equilibrium models and two-resistance, homogeneous surface diffusion kinetic models. As a result, only these will be focused upon here.

** ADSORPTION EQUILIBRIA MODELING **

The use of the Langmuir (1918) isotherm has been used extensively in the representation of single-solute adsorption equilibria. The expression was later extended to a multi-component system by Butler and Ockrent (1930). Jain and Snoeyink (1973) also modified the Langmuir isotherm for a bi-solute system. However, an underlying assumption of the Langmuir expression is a constant adsorption site energy, which does not typically correlate well with adsorption into activated carbon. For highly heterogeneous surfaces, the Freundlich (1906) expression is generally more applicable, though the equation does not reduce to Henry’s Law as the concentration approach zero.

\[ q = K C^{1/n} \]  \hspace{1cm} (A.1)

where \( q \) = equilibrium solid phase concentration, ng adsorbate/mg adsorbent;
\( C \) = equilibrium liquid phase concentration, ng/L;
\( K \) = Freundlich constant, (ng/mg)(L/ng)\(^{1/n}\);
\( 1/n \) = Freundlich constant, dimensionless.

While the Freundlich equation (see equation A.1) was originally empirically obtained, theory was later developed to explain it based on a heterogeneous adsorbent (Halsey and
Taylor, 1947). This equation has been typically used to describe single-solute systems and has been used in this fashion for all single-solute systems in this research. However, Crittenden et al. (1985) has incorporated the Freundlich equation into the ideal adsorbed solution theory (IAST) to model multisolute systems. The application of the IAST to a system with N components could then characterize that multisolute system by:

\[
C_i = \frac{q_i}{\sum_{k=1}^{N} q_k} \left[ \frac{\sum_{k=1}^{N} n_k q_k}{n_i K_i} \right]^{n_i}
\]

(A.2)

where \( C_i \) = equilibrium liquid phase concentration of component i; 
\( q_i \) = equilibrium solid phase concentration of component i; 
\( n_i \) and \( K_i \) = single solute Freundlich isotherm constants of component i.

The IAST was originally developed for the adsorption of gaseous mixtures (Myers and Prausnitz, 1965). Radke and Prausnitz (1972) later adapted it to dilute aqueous systems. Since the application of the Freundlich expression to the IAST, it has been extensively and successfully employed (Knappe, 1996; Crittenden et al., 1985; Najm et al., 1991; Schmidt, 1994; Qi et al., 1994).

The application of the IAST to natural water systems has been limited by the unknown composition of the background organic matter. Two main approaches have been employed to deal with this problem. One approach as been to describe the background organics as a mixture of fictive components.

Another approach has been to characterize the background organic matter as a single compound - the equivalent background compound (EBC). Using this method, natural water isotherms are performed for the target compound of interest. These are compared to the single-solute isotherm for that compound. The characteristics of the EBC are then assigned such that they yield the same amount of competition.
Reduction of equation A.2 into a bi-solute system yields:

\[ C_1 = \frac{q_1}{q_1 + q_2} \left( \frac{n_1 q_1 + n_2 q_2}{n_1 K_1} \right)^{n_1} \]  \hspace{1cm} (A.3)

\[ C_2 = \frac{q_2}{q_1 + q_2} \left( \frac{n_1 q_1 + n_2 q_2}{n_2 K_2} \right)^{n_2} \]  \hspace{1cm} (A.4)

An isotherm bottle, a batch adsorption system, can be described by a mass balance equation:

\[ q_i = \frac{C_{i,0} - C_i}{C_c} \]  \hspace{1cm} (A.5)

solving for \( C_i \):

\[ C_i = C_{i,0} - q_i C_c \]  \hspace{1cm} (A.6)

where \( C_{i,0} \) = initial concentration of compound \( i \);

\( C_c \) = carbon concentration in the isotherm bottle.

Using equation A.6 equations A.3 and A.4 can be rewritten for a bi-solute batch adsorption system as:

\[ C_{1,0} - q_1 C_c - \frac{q_1}{q_1 + q_2} \left( \frac{n_1 q_1 + n_2 q_2}{n_1 K_1} \right)^{n_1} = 0 \]  \hspace{1cm} (A.7)

\[ C_{2,0} - q_2 C_c - \frac{q_2}{q_1 + q_2} \left( \frac{n_1 q_1 + n_2 q_2}{n_2 K_2} \right)^{n_2} = 0 \]  \hspace{1cm} (A.8)
A method by Najam et al. (1991) groups all of the background organic matter (BOM) into a hypothetical compound called the equivalent background compound (EBC) so that a complex organic system can now be modeled as the bi-solute system described above. While the initial concentration and Freundlich parameters for the EBC are unknown they may be determined by the following procedure:

1. Determine Freundlich parameters, $K_1$ and $1/n_1$, for the target compound by performing a single-solute isotherm (i.e., a MIB isotherm in organic-free water);
2. Collect isotherm data, $q_1$ versus $C_c$, for the target compound in natural water at two different initial concentrations that are low enough to observe competition;
3. Utilize the EBC program (Knappe et al., 1993; Matsui, 1994) to solve for the EBC Freundlich parameters ($K_2$, $1/n_2$, $C_{2,0}$) (see Appendix D).

With the EBC Freundlich parameters determined, adsorbent capacity predictions for the target compound with any given initial concentration is possible. For these predictions we used a computer program of the IAST equations written by Qi (1992) and modified by Matsui (1994) (see Appendix D).

HOMOGENEOUS SURFACE DIFFUSION FOR A BATCH SYSTEM

The batch reactor adsorption of a target compound from natural water onto PAC may be described by a pseudo single-solute homogeneous surface diffusion model (HSDM). The basic assumptions made when applying the pseudo single-solute HSDM to this system are:

1. Intraparticle surface diffusion is the only rate limiting mechanism;
2. The surface diffusion coefficient is not a function of $C_c$ or $C_{1,0}$ (i.e., BOM's effect on the adsorption rate of the target compound is constant).
3. Competitive effects are assumed to be fully accounted for by multi-solute equilibrium expressions (i.e., there are no multi-component diffusion interactions).
Figure 15. Adsorbate Transport Mechanisms Through an Activated Carbon Particle

This system of equations may be summarized as below:

\[ \frac{\partial q}{\partial t} = D_s \left( \frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \]  \hspace{1cm} (A.9)

at \( t = 0, \ 0 \leq r \leq R \): \( q = 0 \) \hspace{1cm} (A.10)

at \( r = 0, \ t \geq 0 \): \( \frac{\partial q}{\partial r} = 0 \) \hspace{1cm} (A.11)

at \( t \geq 0 \):
\[ \frac{dC_1}{dt} = \frac{3C_e}{R^3} \frac{\partial}{\partial t} \int_0^\infty qr^2 \text{d}r \] \hspace{1cm} (A.12)

at \( t \geq 0, \ r = R \): \( C_s = C_1 \) \hspace{1cm} (A.13)

at \( t = 0 \):
\[ C_1 = C_{1,0} \] \hspace{1cm} (A.14)
where, \( D_s \) = surface diffusion coefficient;
\( r \) = radial distance;
\( t \) = time;
\( R \) = particle radius;
\( C_i \) = bulk liquid phase concentration of the target compound;
\( C_s \) = liquid phase concentration at the external surface of the particle.

\( D_s \) was determined by a fit to the batch kinetic data, by a computer search program, “SEARCH” (see Appendix D). The search program consisted of the Levenberg-Marquardt unconstrained optimization algorithm and the numerical solution of the HSDM (International, 1991; Matsui, 1994).

In order to solve this system of equations, a relationship between the liquid phase concentration, \( C_s \), and the solid phase concentration at the external surface, \( q_s \), was needed. Equation A.15 was used for this purpose:

\[
q_s = K(C_{1,0}, C_c)C_s^{1/n}
\]

(A.15)

where, \( K(C_{1,0}, C_c) \) = the capacity parameter which is a function of initial concentration, \( C_{1,0} \), and carbon dose, \( C_c \);

\( 1/n \) = assumed to be the single-solute Freundlich constant.

\( K(C_{1,0}, C_c) \) was determined by:

1. Determining the Freundlich parameters for the EBC with respect to the target compound, as outlined in the previous section;
2. Finding the solid and liquid phase concentrations of the target compound at equilibrium by the IAST. This is dependent on the carbon dose, initial concentration, and Freundlich parameters of both the target compound and EBC;
3. Calculating \( K(C_{1,0}, C_c) \) using equation A.15 and the solid and liquid phase concentrations determined in Step 2.
Once $K(C_{1,0}, C_0)$, $1/n$, $D_s$ and $k_f$ have been determined, the “HSDM” program can be used to solve for the liquid phase concentration for plug flow systems (Traegner and Suidan, 1988) (see Appendix D).

For applications where it is desired to model the system as a CSTR (e.g., rapid mix, flocculation basin), the single-solute HSDM assumptions previously used, can be incorporated into the mass balance of a CSTR. Additional assumptions including a non-rate limiting film mass transfer and an exponential age distribution of PAC in the reactor allow for the resulting equation:

$$C_{\text{in}} - C_{\text{eff}} - C_t K(C_{\text{in}}, C_c) C_{\text{eff}}^{1/n} \left[ 1 - \frac{6}{\pi^2} \sum_{i=1}^{n} \frac{1}{i^2} \frac{1}{1 + i^2 \pi^2 \frac{D_s}{R^2} \tau} \right] = 0 \quad (A.16)$$

where, 
- $C_{\text{in}}$ = influent concentration; 
- $C_{\text{eff}}$ = effluent concentration; 
- $K(C_{\text{in}}, C_c)$ = capacity parameter as a function of the influent concentration, $C_{\text{in}}$, and the carbon concentration, $C_c$. This is equivalent to $K(C_{1,0}, C_0)$ as previously described; 
- $t$ = average PAC residence time. 
- $\tau$ = hydraulic retention time of CSTR.

This non-linear equation is solved in the computer program “CSTR” written by Traegner and Suidan (1991) (see Appendix D).

**ADSORPTION THROUGH A GRANULAR ACTIVATED CARBON BED**

Adsorption through a bed of GAC has also been modeled using the pseudo single-solute HSDM. The fundamental nondimensional equations for a fixed bed, assuming negligible longitudinal dispersion, are (Knappe, 1996; Smith 1991; Crittenden *et al.*, 1986):
Liquid-Phase (Smith 1991)

\[
\frac{\partial \bar{c}(z, \tilde{t})}{\partial \tilde{t}} = -\frac{D_g}{\varepsilon} \frac{\partial \bar{c}(z, \tilde{t})}{\partial z} - D_g \frac{\partial \bar{q}_{\text{avg}}(z, \tilde{t})}{\partial \tilde{t}}
\]

(A.17)

where, \( \bar{c}(z, \tilde{t}) \) = nondimensional liquid-phase MIB concentration: \( c(z, t)/c_0 \);

\( z \) = dimensionless axial distance;

\( \tilde{t} \) = dimensionless time: \( t/(\tau D_g) \);

\( c_0(t) \) = influent concentration;

\( D_g \) = MIB distribution parameter: \( M q_e / V \varepsilon C_0 \); \( M = (1 - \varepsilon) V_p \)

\( \bar{q}_{\text{avg}}(z, \tilde{t}) \) = average MIB concentration within the GAC particles evaluated at the bed step:

\[
\bar{q}_{\text{avg}}(z, \tilde{t}) = 3 \int q(\tilde{r}, z, \tilde{t}) \tilde{r}^2 d\tilde{r}
\]

(A.20)

where, \( q(\tilde{r}, z, \tilde{t}) \) = solid-phase concentration of solute as a function of dimensionless radial distance from the center of GAC particle, \( \tilde{r} \), length and time.

Solid-Phase (Smith 1991)

\[
\frac{\partial q(\tilde{r}, z, \tilde{t})}{\partial \tilde{t}} = 2E_d \frac{\partial q(\tilde{r}, z, \tilde{t})}{\partial \tilde{r}} + E_d \frac{\partial^2 q(\tilde{r}, z, \tilde{t})}{\partial \tilde{r}^2}
\]

(A.21)

at \( \tilde{r} = 0 \), \( \frac{\partial q(\tilde{r}, z, \tilde{t})}{\partial \tilde{t}} = 0 \)

(A.22)

at \( \tilde{r} = 1 \), \( \frac{\partial q(\tilde{r}, z, \tilde{t})}{\partial \tilde{r}} = Sh[\bar{c}(z, \tilde{t}) - \bar{c}_s(z, \tilde{t})] \)

(A.23)

or

\[
St[\bar{c}(z, \tilde{t}) - \bar{c}_s(z, \tilde{t})] = \frac{\partial}{\partial \tilde{t}} \int q(\tilde{r}, z, \tilde{t}) \tilde{r}^2 d\tilde{r}
\]

(A.24)
at $\bar{t} = 0$, $q(\bar{r}, \bar{z}, \bar{t}) = 0$ \hspace{1cm} (A.25)

where, $E_d$ = surface diffusion modulus: $\frac{D_s D_e \tau}{R^2}$;

$Sh$ = Sherwood number (ratio of film to surface diffusion): $\frac{k_f R}{D_s}$;

$St$ = modified Stanton number (ratio of mass transport through the film to advection): $\frac{k_f}{\alpha R} \left( \frac{1 - \varepsilon}{\varepsilon} \right)$;

$\tau$ = hydraulic retention time;

$\bar{c}(\bar{z}, \bar{t})$ = bulk liquid-phase MIB concentration for a given bed step;

$\bar{c}_s(\bar{z}, \bar{t})$ = liquid-phase MIB concentration at the surface of the GAC particle for a given bed step;

$\alpha$ = mole fraction ratio of solid- to liquid-phase MIB

A similar system of equations are solved in the computer program “FS” written by Yuasa (1982) (see Appendix D).
## Appendix B  (Raw Data)

### SINGLE-SOLUTE PAC ISOTHERM DATA IN MILLI-Q WATER

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### SINGLE-SOLUTE GAC ISOTHERM DATA IN MILLI-Q WATER

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COMPETITIVE GAC ISOTHERM DATA IN CHICAGO CRIB WATER

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**COMPETITIVE PAC ISOTHERM DATA IN CHICAGO CRIB WATER**

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BATCH KINETIC PAC DATA WITH CHLORINE IN CHICAGO CRIB WATER

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<thead>
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<th>Hydrodarco-B (11.5 mg/L)</th>
<th>Hydrodarco-B (11.5 mg/L)</th>
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<tbody>
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<td>MIB (ng/L)</td>
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Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
<table>
<thead>
<tr>
<th>Time (min)</th>
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</thead>
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4-hour MIB concentration (ng/L) with varied initial Cl\(_2\) concentrations

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<th>Cl(_2) (5 mg/L)</th>
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## BATCH KINETIC PAC DATA WITH CHLORINE IN DEIONIZED-DISTILLED WATER

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<th>Time (min)</th>
<th>MIB (ng/L)</th>
<th>Time (min)</th>
<th>MIB (ng/L)</th>
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<td>0.0</td>
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2-DAY PERCENT MIB BREAKTHROUGH IN CHICAGO CRIB WATER FOR LABORATORY- AND PILOT-SCALE GAC COLUMNS

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<tr>
<td>G&amp;H</td>
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<td>1.8904</td>
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2-DAY PERCENT MIB BREAKTHROUGH FOR A CONTINUOUSLY OPERATED DEIONIZED-DISTILLED WATER LABORATORY-SCALE GAC COLUMN (50 NG/L 2-DAY PULSES; 3.3 MIN EBCT)

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<th>Bed Vol</th>
<th>Ceff/Cinf</th>
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<td>4962</td>
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<td>8174</td>
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2-DAY PERCENT MIB BREAKTHROUGH IN CHICAGO CRIB WATER FOR DIFFERENT GAC BED DIMENSIONS (1 YEAR PRELOAD)

<table>
<thead>
<tr>
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2-DAY PERCENT MIB BREAKTHROUGH IN CHICAGO CRIB WATER FOR DIFFERENT GAC PARTICLE SIZE FRACTIONS (2 YEAR PRELOAD)

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2-DAY PERCENT MIB BREAKTHROUGH IN CHICAGO CRIB WATER FOR GAC PREREACTED WITH FREE CHLORINE

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<td>Cinf (ng/L)</td>
<td>Time</td>
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Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
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<th>ime (min)</th>
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### MIB SINGLE-SOLUTE FREUNDLICH PARAMETERS FROM GAC ISOTHERMS

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<th>GAC</th>
<th>K (ng/mg)(L/ng)^1/n</th>
<th>1/n</th>
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</thead>
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<tr>
<td>Virgin</td>
<td>2.8072</td>
<td>0.8228</td>
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<tr>
<td>Hammond - 1 yr</td>
<td>0.23118</td>
<td>0.5365</td>
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<tr>
<td>Michigan City - 2 yr</td>
<td>0.0099</td>
<td>1.0352</td>
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<th>K (ng/mg)(L/ng)^1/n</th>
<th>1/n</th>
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</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>8.7383</td>
<td>0.7459</td>
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<tr>
<td>Hammond - 1 yr</td>
<td>0.4126</td>
<td>0.6471</td>
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<tr>
<td>Michigan City - 2 yr</td>
<td>0.4602</td>
<td>0.5882</td>
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### EBC SINGLE-SOLUTE FREUNDLICH PARAMETERS FROM GAC ISOTHERMS

**Based on 125 day**

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<th>EBC</th>
<th>Virgin</th>
<th>1 yr</th>
<th>2 yr</th>
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</thead>
<tbody>
<tr>
<td>K (mg/g)(L/ug)^1/n</td>
<td>23.48857</td>
<td>0.11181225</td>
<td>0.005322366</td>
</tr>
<tr>
<td>1/n</td>
<td>0.01710</td>
<td>0.7963007</td>
<td>0.84143995</td>
</tr>
<tr>
<td>Co (ug/L)</td>
<td>0.45270</td>
<td>6.9036</td>
<td>78.920173</td>
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<tr>
<td>K (mmol/g)(L/umol)^1/n</td>
<td>0.026433217</td>
<td>0.027377355</td>
<td>0.001780019</td>
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<tr>
<td>1/n</td>
<td>0.01710</td>
<td>0.79630</td>
<td>0.84144</td>
</tr>
<tr>
<td>Co (umol/L)</td>
<td>0.000452697</td>
<td>0.0069036</td>
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**Based on 25 day**

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<th>Co (ug/L)</th>
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<tbody>
<tr>
<td>K (mg/g)(L/ug)^1/n</td>
<td>0.01495</td>
<td>0.00664</td>
<td>0.10589</td>
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<tr>
<td>Co (ug/L)</td>
<td>0.010589</td>
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<tr>
<td>K (mmol/g)(L/umol)^1/n</td>
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<td>0.00664</td>
<td>0.000105886</td>
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<tr>
<td>Co (umol/L)</td>
<td>0.000105886</td>
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### MIB PSEUDO SINGLE-SOLUTE FREUNDLICH PARAMETERS FOR GAC LABORATORY-SCALE COLUMNS

<table>
<thead>
<tr>
<th>IAST</th>
<th>Cc (mg)</th>
<th>Ce (ng/L)</th>
<th>qe (ng/mg)</th>
<th>(ng/mg)(L/ng)^((1/n))</th>
<th>(mg/g)(L/ug)^((1/n))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin - 125</td>
<td>0</td>
<td>53.29</td>
<td>0.37</td>
<td>0.0191</td>
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<td>501.7</td>
<td>0.29</td>
<td>0.11</td>
<td>0.2769</td>
<td>0.04787</td>
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<td>Virgin - 25</td>
<td>0</td>
<td>53.29</td>
<td>0.53</td>
<td>0.0201</td>
<td>0.00592</td>
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<tr>
<td></td>
<td>501.7</td>
<td>1.32</td>
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<td>0.0796</td>
<td>0.02340</td>
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<td>1 yr - 125</td>
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<td>51.67</td>
<td>1.56</td>
<td>0.1215</td>
<td>0.01061</td>
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<td>356.3</td>
<td>0.80</td>
<td>0.14</td>
<td>0.1617</td>
<td>0.01413</td>
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<tr>
<td>1 yr - 125</td>
<td>0</td>
<td>25.09</td>
<td>0.76</td>
<td>0.0944</td>
<td>0.00825</td>
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<tr>
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<td>356.3</td>
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<td>0.01144</td>
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<tr>
<td>1 yr - 125</td>
<td>0</td>
<td>100.47</td>
<td>3.01</td>
<td>0.1524</td>
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<td>0.2057</td>
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<td>2 yr - 125</td>
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### PHYSICAL CHARACTERISTICS OF GACs USED

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<thead>
<tr>
<th>Hg Porosity</th>
<th>keletal Density (g/mL)</th>
<th>article Porosity</th>
<th>Particle Density</th>
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<tbody>
<tr>
<td>Virgin</td>
<td>1.3004</td>
<td>0.3916</td>
<td>0.79116336</td>
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<td>1 yr</td>
<td>1.5886</td>
<td>0.3814</td>
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<td>2 yr</td>
<td>1.5492</td>
<td>0.3947</td>
<td>0.93773076</td>
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</table>

<table>
<thead>
<tr>
<th>He Pycnometry</th>
<th>keletal Density (g/mL)</th>
</tr>
</thead>
<tbody>
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<td>Virgin</td>
<td>2.012</td>
</tr>
<tr>
<td>1 yr</td>
<td>1.66516</td>
</tr>
<tr>
<td>2 yr</td>
<td>1.7271</td>
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COMPARISON OF CARBON BRANDS IN HOPE VALLEY RESERVOIR WATER
(DATA PROVIDED BY GAYLE NEWCOMBE)

<table>
<thead>
<tr>
<th>Activated Carbon Brand</th>
<th>Ce (ng/L)</th>
<th>Ce (ng/L)</th>
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<tbody>
<tr>
<td>(13.3 mg/L)</td>
<td>[Co = 98 ng/L]</td>
<td>[Co = 39 ng/L]</td>
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<tr>
<td>Cecarbon</td>
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<td>19</td>
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<tr>
<td>Calgon WPL</td>
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<td>9</td>
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<tr>
<td>Australian Prototype</td>
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<td>7</td>
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<td>ASTM M325 from Haycarb</td>
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<td>Picatif PCO</td>
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<td>Picazine</td>
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<td>Nuchar SA, Westvaco</td>
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<td>Norit W20</td>
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<td>Calgon F400</td>
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<td>Hydrodarco</td>
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EFFECT OF INITIAL CONCENTRATION IN MYPONGA RESEVOIR WATER
(DATA PROVIDED BY GAYLE NEWCOMBE)

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<td>Ce (ng/L)</td>
<td>(13.3 mg/L)</td>
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## GREELEY AND HANSEN PILOT STUDY MIB DATA

**MIB Concentration (ng/L)**

<table>
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</tbody>
</table>

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Appendix C  (Input/Output Files)

EBC OUTPUT FILES

Watercarb PAC

PARAMETER # 1 === K ; IG: 100.000000000000000
PARAMETER # 2 === 1/n ; IG: 1.0000000000000000
PARAMETER # 3 === Co ; IG: 10000.000000000000000

3 10

EBC
K = .33178046E+04 (mg/g)(ug/L)^-1/n
1/n = .49304968E+00
Co = .34048691E+02 ug/L
MW = .10000000E+04 g/mol

TARGET COMPOUND
K = .28652000E+00 (mg/g)(ug/L)^-1/n
1/n = .49220000E+00
Co = .15000000E+00 ug/L
Co = .12452000E+01 ug/L
MW = .16800000E+03 g/mol

h2o-lo.dat Co = 149.1 ng/L
h2o-hi.dat Co = 1245.2 ng/L

no, Q-obs Q-cal C-obs C-cal AC-dose
Q( 1) = .2458E-02 .2441E-02 mg/g .1800E-02 .2787E-02 ug/l.6030E+02 mg/l
Q( 2) = .3577E-02 .3577E-02 mg/g .6200E-02 .6200E-02 ug/l.4020E+02 mg/l
Q( 3) = .7582E-02 .7692E-02 mg/g .3930E-01 .3770E-01 ug/l.1460E+02 mg/l
Q( 4) = .9050E-02 .6710E-02 mg/g .1138E-01 .1232E-01 ug/l.4000E+01 mg/l
Q( 5) = .9381E-02 .3983E-02 mg/g .1303E+00 .1416E+00 ug/l.2100E+01 mg/l
Q( 1) = .2617E-01 .2621E-01 mg/g .4910E-01 .4723E-01 ug/l.4570E+02 mg/l
Q( 2) = .3430E-01 .3563E-01 mg/g .1340E+00 .9094E-01 ug/l.3240E+02 mg/l
Q( 3) = .5736E-01 .6932E-01 mg/g .6773E+00 .5589E+00 ug/l.9900E+01 mg/l
Q( 4) = .5544E-01 .5501E-01 mg/g .1018E+01 .1020E+01 ug/l.4100E+01 mg/l
Q( 5) = .4641E-01 .3411E-01 mg/g .1143E+01 .1170E+01 ug/l.2200E+01 mg/l
F( 1) = .74240E+00
F( 2) = .16470E-03
F( 3) = .21359E+00
F( 4) = .33242E+00
F( 5) = .34817E+00
F( 6) = .20891E+00
F( 7) = .67183E+00
F( 8) = .72938E+00

153
\[ F(9) = 0.83444 \times 10^{-1} \]
\[ F(10) = 0.32458 \times 10^{0} \]
\[ \text{Error sum of squares} = 0.19678 \times 10^{0} \]

**Hydrodarco-B PAC**

\[
\text{PARAMETER} \ # \ 1 = K ; \ IG: 100.00000000000000000000000
\]
\[
\text{PARAMETER} \ # \ 2 = l/n ; \ IG: 1.00000000000000000000000
\]
\[
\text{PARAMETER} \ # \ 3 = Co ; \ IG: 10000.00000000000000000000000
\]

\[
\text{EBC} \quad K = 0.14737048 \times 10^{4} (mg/g)(ug/L)^{-1/n}
\]
\[
l/n = 0.61053013 \times 10^{0}
\]
\[
Co = 0.41283323 \times 10^{0} \text{ ug/L}
\]
\[
MW = 0.10000000 \times 10^{4} \text{ g/mol}
\]

**TARGET COMPOUND**

\[
\text{K} = 0.12231800 \times 10^{1} (mg/g)(ug/L)^{-1/n}
\]
\[
l/n = 0.72110000 \times 10^{0}
\]
\[
Co = 0.14920000 \times 10^{0} \text{ ug/L}
\]
\[
co = 0.16500000 \times 10^{0} \text{ ug/L}
\]
\[
MW = 0.16800000 \times 10^{3} \text{ g/mol}
\]

\[
149.2
\]
\[
165.0
\]

\begin{tabular}{cccccc}
\text{ Q-obs} & \text{ Q-cal} & \text{ C-obs} & \text{ C-cal} & \text{ AC-dose} \\
\hline
\text{Q(1)} & 0.3746E-02 & 0.3676E-02 & 0.1600E-02 & 0.4360E-02 & 0.3940E+02 & 0.3940E+02 \\
\text{Q(2)} & 0.9457E-02 & 0.9577E-02 & 0.1870E-01 & 0.1704E-01 & 0.1380E+02 & 0.1380E+02 \\
\text{Q(3)} & 0.1246E-01 & 0.2194E-01 & 0.1006E-01 & 0.6364E-01 & 0.3900E+01 & 0.3900E+01 \\
\text{Q(4)} & 0.1329E-01 & 0.2579E-01 & 0.1213E+00 & 0.9504E-01 & 0.2100E+01 & 0.2100E+01 \\
\text{Q(5)} & 0.3730E-02 & 0.3704E-02 & 0.3100E-02 & 0.4232E-02 & 0.4340E+02 & 0.4340E+02 \\
\text{Q(6)} & 0.5507E-02 & 0.5475E-02 & 0.6400E-02 & 0.7330E-02 & 0.2880E+02 & 0.2880E+02 \\
\text{Q(7)} & 0.9867E-02 & 0.9867E-02 & 0.1700E-01 & 0.1700E-01 & 0.1500E+02 & 0.1500E+02 \\
\text{Q(8)} & 0.1401E-01 & 0.1632E-01 & 0.5430E-01 & 0.3604E-01 & 0.1790E+01 & 0.1790E+01 \\
\text{Q(9)} & 0.1737E-01 & 0.2326E-01 & 0.9030E-01 & 0.6497E-01 & 0.4300E+01 & 0.4300E+01 \\
\text{Q(10)} & 0.2147E-01 & 0.2879E-01 & 0.1242E+00 & 0.1103E+00 & 0.1900E+01 & 0.1900E+01 \\
\hline
\text{F(1)} & 0.1332E+01 & 0.1332E+01 & 0.1332E+01 & 0.1332E+01 & 0.1332E+01 & 0.1332E+01 \\
\text{F(2)} & 0.3458E+00 & 0.3458E+00 & 0.3458E+00 & 0.3458E+00 & 0.3458E+00 & 0.3458E+00 \\
\text{F(3)} & 0.1027E+01 & 0.1027E+01 & 0.1027E+01 & 0.1027E+01 & 0.1027E+01 & 0.1027E+01 \\
\text{F(4)} & 0.8397E+00 & 0.8397E+00 & 0.8397E+00 & 0.8397E+00 & 0.8397E+00 & 0.8397E+00 \\
\text{F(5)} & 0.6214E+00 & 0.6214E+00 & 0.6214E+00 & 0.6214E+00 & 0.6214E+00 & 0.6214E+00 \\
\text{F(6)} & 0.4031E+00 & 0.4031E+00 & 0.4031E+00 & 0.4031E+00 & 0.4031E+00 & 0.4031E+00 \\
\text{F(7)} & 0.1142E-03 & 0.1142E-03 & 0.1142E-03 & 0.1142E-03 & 0.1142E-03 & 0.1142E-03 \\
\text{F(8)} & 0.8221E+00 & 0.8221E+00 & 0.8221E+00 & 0.8221E+00 & 0.8221E+00 & 0.8221E+00 \\
\text{F(9)} & 0.8669E+00 & 0.8669E+00 & 0.8669E+00 & 0.8669E+00 & 0.8669E+00 & 0.8669E+00 \\
\text{F(10)} & 0.6089E+00 & 0.6089E+00 & 0.6089E+00 & 0.6089E+00 & 0.6089E+00 & 0.6089E+00 \\
\hline
\text{Error sum of squares} & 0.6003E+00 & 0.6003E+00 & 0.6003E+00 & 0.6003E+00 & 0.6003E+00 & 0.6003E+00 \\
\end{tabular}
Calgon F-300 (virgin)

PARAMETER # 1 = K ; IG: 1.000000000000000E-001
PARAMETER # 2 = 1/n ; IG: 3.000000000000000E-001
PARAMETER # 3 = C0 ; IG: 100.000000000000000

EBC
K = .23488573E+02 (mg/g)(ug/L)^-1/n
1/n = .17097794E-01
C0 = .45269657E+00 ug/L
MW = .10000000E+04 g/mol

TARGET COMPOUND
K = .15105000E+01 (mg/g)(ug/L)^-1/n
1/n = .74590000E+00
C0 = .33974000E+00 ug/L
C0 = .33974000E+00 ug/L
MW = .16800000E+03 g/mol

virgil25.dat
virgil25.dak

no Q-obs Q-cal C-obs C-cal AC-dose
Q(1) = .3683E-01 .1461E-01 mg/g .2624E+00 .3091E+00 ug/l .2100E+01 mg/l
Q(2) = .2576E-01 .2576E-01 mg/g .1852E+00 .1852E+00 ug/l .6000E+01 mg/l
Q(3) = .2055E-01 .2548E-01 mg/g .1856E+00 .1486E+00 ug/l .7500E+01 mg/l
Q(4) = .1722E-01 .1967E-01 mg/g .1090E+00 .7612E-01 ug/l .1340E+02 mg/l
Q(5) = .1536E-01 .1536E-01 mg/g .4950E-01 .4950E-01 ug/l .1890E+02 mg/l
Q(6) = .1294E-01 .1264E-01 mg/g .2930E-01 .3644E-01 ug/l .2400E+02 mg/l
Q(7) = .9441E-02 .9165E-02 mg/g .1307E-01 .2262E-01 ug/l .3460E+02 mg/l
Q(8) = .75471E+00
F( 1) = .75471E+00
F( 2) = .48823E-05
F( 3) = .71363E+00
F( 4) = .75974E+00
F( 5) = .18172E-03
F( 6) = .55089E+00
F( 7) = .90071E+00
F( 8) = .75471E+00
F( 9) = .48823E-05
F(10) = .71363E+00
F(11) = .75974E+00
F(12) = .18172E-03

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\[ F(13) = \text{.55089E+00} \]
\[ F(14) = \text{.90071E+00} \]
\[ \text{Error sum of squares} = \text{.39583E+00} \]

Calgon F-300 (1 year preload)

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<th>PARAMETER #</th>
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<tr>
<td>PARAMETER #</td>
<td>3 = Co ; IG:</td>
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</table>

EBC
\[ K = \text{.11181225E+00 (mg/g)(ug/L)^-1/n} \]
\[ I/n = \text{.79630070E+00} \]
\[ C0 = \text{.69036052E+01 ug/L} \]
\[ MW = \text{.10000000E+04 g/mol} \]

TARGET COMPOUND
\[ K = \text{.36040000E-01 (mg/g)(ug/L)^-1/n} \]
\[ I/n = \text{.64710000E+00} \]
\[ C0 = \text{.33974000E+00 ug/L} \]
\[ C0 = \text{.33974000E+00 ug/L} \]
\[ MW = \text{.16800000E+03 g/mol} \]

no, Q-obs Q-cal C-obs C-cal AC-dose
\[
\begin{array}{cccc}
Q(1) &=& \text{.4061E-02} & \text{.9535E-02 mg/g} & \text{.3251E+00} & \text{.3054E+00 ug/l} & \text{.3600E+01 mg/l} \\
Q(2) &=& \text{.1050E-01} & \text{.9340E-02 mg/g} & \text{.2767E+00} & \text{.2837E+00 ug/l} & \text{.6000E+01 mg/l} \\
Q(3) &=& \text{.8830E-02} & \text{.8830E-02 mg/g} & \text{.2444E+00} & \text{.2444E+00 ug/l} & \text{.1080E+02 mg/l} \\
Q(4) &=& \text{.8046E-02} & \text{.8231E-02 mg/g} & \text{.2126E+00} & \text{.2097E+00 ug/l} & \text{.1580E+02 mg/l} \\
Q(5) &=& \text{.9204E-02} & \text{.7847E-02 mg/g} & \text{.1649E+00} & \text{.1906E+00 ug/l} & \text{.1900E+02 mg/l} \\
Q(6) &=& \text{.6711E-02} & \text{.6855E-02 mg/g} & \text{.1525E+00} & \text{.1485E+00 ug/l} & \text{.2790E+02 mg/l} \\
Q(7) &=& \text{.5991E-02} & \text{.5991E-02 mg/g} & \text{.1175E+00} & \text{.1175E+00 ug/l} & \text{.3710E+02 mg/l} \\
Q(1) &=& \text{.4061E-02} & \text{.9535E-02 mg/g} & \text{.3251E+00} & \text{.3054E+00 ug/l} & \text{.3600E+01 mg/l} \\
Q(2) &=& \text{.1050E-01} & \text{.9340E-02 mg/g} & \text{.2767E+00} & \text{.2837E+00 ug/l} & \text{.6000E+01 mg/l} \\
Q(3) &=& \text{.8830E-02} & \text{.8830E-02 mg/g} & \text{.2444E+00} & \text{.2444E+00 ug/l} & \text{.1080E+02 mg/l} \\
Q(4) &=& \text{.8046E-02} & \text{.8231E-02 mg/g} & \text{.2126E+00} & \text{.2097E+00 ug/l} & \text{.1580E+02 mg/l} \\
Q(5) &=& \text{.9204E-02} & \text{.7847E-02 mg/g} & \text{.1649E+00} & \text{.1906E+00 ug/l} & \text{.1900E+02 mg/l} \\
Q(6) &=& \text{.6711E-02} & \text{.6855E-02 mg/g} & \text{.1525E+00} & \text{.1485E+00 ug/l} & \text{.2790E+02 mg/l} \\
Q(7) &=& \text{.5991E-02} & \text{.5991E-02 mg/g} & \text{.1175E+00} & \text{.1175E+00 ug/l} & \text{.3710E+02 mg/l} \\
F(1) &=& \text{.39109E+00} \\
F(2) &=& \text{.24055E+00} \\
F(3) &=& \text{.15030E-04} \\
F(4) &=& \text{.16605E+00} \\
\end{array}
\]

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F(5) = .52636E+00
F(6) = .21254E+00
F(7) = .82628E-04
F(8) = .39109E+00
F(9) = .24055E+00
F(10) = .15030E-04
F(11) = .16605E+00
F(12) = .52636E+00
F(13) = .21254E+00
F(14) = .82628E-04
Error sum of squares = .80087E-01

Calgon F-300 (2 year preload)

PARAMETER # 1 == K ; IG: 1.000000000000000
PARAMETER # 2 == l/n ; IG: 3.000000000000000E-001
PARAMETER # 3 == Co ; IG: 100.000000000000000

K = .53223659E-02 (mg/g)(ug/L)^-1/n
l/n = .84143995E+00
Co = .78920173E+02 ug/L
MW = .10000000E+04 g/mol

TARGET COMPOUND
K = .26760000E-01 (mg/g)(ug/L)^-1/n
l/n = .58820000E+00
Co = .33974000E+00 ug/L
MW = .16800000E+03 g/mol

mich125.dat
mich125.dak

no, Q-obs Q-cal C-obs C-cal AC-dose
Q(1) = .2650E-01 .9608E-02 mg/g .2470E+00 .3061E+00 ug/l .3500E+01 mg/l
Q(2) = .6304E-02 .9333E-02 mg/g .3095E+00 .2949E+00 ug/l 1.4800E+01 mg/l
Q(3) = .2676E-01 .9129E-02 mg/g .1845E+00 .2868E+00 ug/l 1.5800E+01 mg/l
Q(4) = .8491E-02 .8491E-02 mg/g .2616E+00 .2616E+00 ug/l .9200E+01 mg/l
Q(5) = .7178E-02 .7300E-02 mg/g .2184E+00 .2164E+00 ug/l .1690E+02 mg/l
Q(6) = .5332E-02 .5332E-02 mg/g .1467E+00 .1467E+00 ug/l .3620E+02 mg/l
Q(1) = .2650E-01 .9608E-02 mg/g .2470E+00 .3061E+00 ug/l .3500E+01 mg/l
Q(2) = .6304E-02 .9333E-02 mg/g .3095E+00 .2949E+00 ug/l 1.4800E+01 mg/l
Q(3) = .2676E-01 .9129E-02 mg/g .1845E+00 .2868E+00 ug/l 1.5800E+01 mg/l
Q(4) = .8491E-02 .8491E-02 mg/g .2616E+00 .2616E+00 ug/l .9200E+01 mg/l
Q(5) = .7178E-02 .7300E-02 mg/g .2184E+00 .2164E+00 ug/l .1690E+02 mg/l
Q(6) = .5332E-02 .5332E-02 mg/g .1467E+00 .1467E+00 ug/l .3620E+02 mg/l

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\[ F(1) = 0.70626 \times 10^0 \]
\[ F(2) = 0.33278 \times 10^0 \]
\[ F(3) = 0.10014 \times 10^1 \]
\[ F(4) = 0.70650 \times 10^{-4} \]
\[ F(5) = 0.13602 \times 10^0 \]
\[ F(6) = 0.30580 \times 10^{-4} \]
\[ F(7) = 0.70626 \times 10^0 \]
\[ F(8) = 0.33278 \times 10^0 \]
\[ F(9) = 0.10014 \times 10^1 \]
\[ F(10) = 0.70650 \times 10^{-4} \]
\[ F(11) = 0.13602 \times 10^0 \]
\[ F(12) = 0.30580 \times 10^{-4} \]
Error sum of squares = 0.27180 \times 10^1
IAST OUTPUT FILES

Watercarb PAC

PROPERTIES of COMPONENTS

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IAST PREDICTION

DOSAGE EBC MIB

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Hydrodarco-B PAC

PROPERTIES of COMPONENTS

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<tr>
<th>COMPONENT</th>
<th>K (mg/g)(µg/L)**-1/n</th>
<th>1/n</th>
<th>CO (µg/l)</th>
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Calgon F-300 (virgin)

PROPERTIES of COMPONENTS

COMPONENT   K (mg/g)(ug/L)**-1/n   1/n   CO (ug/l)   MW(dalton)

EBC         23.489     .17098E-01 .45270     1000.000
MIB         1.5105     .74590       .53290E-01 168.000

IAST PREDICTION

DOSAGE EBC MIB
(mg/l)      C ug/l  q mg/g  C ug/l  q mg/g

.00        .453  23.2   .05329  .00037
.05        .610E-24 9.05  .05326  .00051
.10        .151E-41 4.53  .05323  .00064
.15        .759E-52 3.02  .05318  .00074
.20        .374E-59 2.26  .05313  .00081
.25        .803E-65 1.81  .05307  .00088
.30        .188E-69 1.51  .05301  .00093
.40        .927E-77 1.13  .05288  .00103
.50        .199E-82 .905  .05273  .00111
.60        .466E-87 .754  .05258  .00118
.80        .230E-94 .566  .05225  .00130
1.00       .495-100 .453  .05189  .00140

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Calgon F-300 (1 year preload)

PROPERTIES of COMPONENTS

COMPONENT  K (mg/g)(ug/L)**-1/n  l/n  CO (ug/l)  MW(dalton)

EBC  .11181  .79630  6.9036  1000.000

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596.80  .586E-01  .115E-01  .00036  .00009  
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Calgon F-300 (2 year preload)

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HSDM INPUT/OUTPUT FILES

Watercarb PAC

IN:

0 1 1 /IPRC,IPRL,IPRO (do not change)
1.7512D-04 /C0 (initial concentration in mg/L)
11.5385D-03 /CCONC (carbon concentration in g/L)
0.369030D-09 /DS (surface diffusion coefficient in cm2/min)
1.000000D+13 /XKF (film mass transfer coefficient in cm/min)
1.1146733D-2 /XK (Freundlich K value in (mg/g)(ug/l)^-1/n)
0.2162 /XN (Freundlich 1/n)
5.0D-04 /RADP (particle radius in cm)
0.74D0 /RHOP (particle density in g/cm3) (do not change for PAC)
10 /NCP (do not change)
0.1D-04 2 2 /TOL,METH,MITER (do not change)
1.0D-50 /DTINIT (do not change)
1.5D0 /DTOUT (time increment in min)
240.000D0 /TFINAL (final time in min)
10000 /ITMAX (do not change)

Out:

C0 = .175120E-03 TFINAL = 27.00 .734666
CCONC = .115385E-03 .240000E+03 28.50 .729375
01 NULL 30.00 .724317
CD = .503930E+00 .00 1.000000 31.50 .719472
1.50 .924126 33.00 .714826
DS = .36903E-09 3.00 .895187 34.50 .710364
XKF = .10000E+14 4.50 .873973 36.00 .706075
BIOT = .41923E+15 6.00 .856734 37.50 .701947
RADP = .50000E-03 7.50 .842029 39.00 .697970
RHOP = .74000E00 9.00 .829123 40.50 .694136
XK = .49630E-01 10.50 .817574 42.00 .690437
XN = .21620E+00 12.00 .807098 43.50 .686864
TFAC = .14761E-02 13.50 .797498 45.00 .683411
NTOT = 11 15.00 .788627 46.50 .680071
TOL = .100000E-04 16.50 .780378 48.00 .676840
METH = 2 18.00 .772667 49.50 .673711
MITER = 2 19.50 .765426 51.00 .670680
DTINIT = .100000E-49 21.00 .758600 52.50 .667743
49 22.50 .752146 54.00 .664895
DTOUT = 24.00 .746026 55.50 .662132
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Hydrodarco-B PAC

In:

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1.7445D-04 /C0 (initial concentration in mg/L)
11.5385D-03 /CCONC (carbon concentration in g/l)
0.380000D-09 /DS (surface diffusion coefficient in cm2/min)
1.000000D+13 /XKF (film mass transfer coefficient in cm/min)
2.62498017D-2 /XK (Freundlich K value in (mg/g)(ug/l)^1/n)
0.3409 /XN (Freundlich 1/n)
5.0D-04 /RADP (particle radius in cm)
0.74D0 /RHOP (particle density in g/cm3) (do not change for PAC)
10 /NCP (do not change)
0.1D-04 2 2 /TOL,METH,MITER (do not change)
1.0D-50 /DTINIT (do not change)
1.5D0 /DTOUT (time increment in min)
240.000D0 /TFINAL (final time in min)
10000 /ITMAX (do not change)

Out:

C0 = .174450E-03 NULL
  CCONC = .115385E-00 .00 1.000000 34.50 .510619
  01
  CD = .957393E+00 3.00 .805903 37.50 .498944
  4.50 .768709 39.00 .493491
  DS = .38000E-09 6.00 .739048 40.50 .488274
  XKF = .10000E+14 7.50 .714167 42.00 .483275
  BIOT = .21430E+15 9.00 .692651 43.50 .478484
  RADP = .50000E-03 10.50 .673665 45.00 .473887
  RHOP = .74000E+00 12.00 .656664 46.50 .469473
  XK = .27658E+00 13.50 .641272 48.00 .465231
  XN = .34090E+00 15.00 .627216 49.50 .461154
  TFAC = .15200E-02 16.50 .614291 51.00 .457231
  NTOT = 11
  TOL = .100000E-04 19.50 .591224 54.00 .449818
  METH = 2
  MITER = 2
  DTINIT = .100000E-49
  24.00 .562025 58.50 .439676
  25.50 .553433 60.00 .436532
  DTOUT = 27.00 .545320 61.50 .433496
  .150000E+01
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  TFINAL = .240000E+03
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Nuchar SA-20 PAC

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9.00000D-03 /CCONC (carbon concentration in g/L)
0.35513D-09 /DS (surface diffusion coefficient in cm2/min)
1.00000D+13 /XKF (film mass transfer coefficient in cm/min)
3.9332237D-2 /Xk (Freundlich K value in (mg/g)(ug/l)^1/n)
0.4176 /XN (Freundlich 1/n)
5.0D-04 /RADP (particle radius in cm)
0.74D0 /RHOP (particle density in g/cm3) (do not change for PAC)
10 /NCP (do not change)
0.1D-04 2 2 /TOL,METH,MITER (do not change)
1.0D-50 /DTINIT (do not change)
1.5D0 /DTOUT (time increment in min)
240.000D0 /TFINAL (final time in min)
10000 /ITMAX (do not change)

Out:

C0 = .175090E-03 NULL 33.00 .534285
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BIOT = .17534E+15 7.50 .721974 42.00 .502511
RADP = .50000E-03 9.00 .701356 43.50 .497979
RHOP = .74000E+00 10.50 .683197 45.00 .493630
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In:

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1.7411D-04 /C0 (initial concentration in mg/L)
11.5385D-03 /CCONC (carbon concentration in g/l)
0.20778D-09 /DS (surface diffusion coefficient in cm²/min)
1.000000D+13 /XKF (film mass transfer coefficient in cm/min)
4.2080508D-2 /XK (Freundlich K value in (mg/g)(ug/l)^–1/n)
0.3592 /XN (Freundlich 1/n)
5.0D-04 /RADP (particle radius in cm)
0.74D0 /RHOP (particle density in g/cm³) (do not change for PAC)
10 /NCP (do not change)
0.1D-04 2 2 /TOL,METH,MITER (do not change)
1.0D-50 /DTINIT (do not change)
1.5D0 /DTOUT (time increment in min)
240.000D0 /TFINAL (final time in min)
10000 /ITMAX (do not change)

Out:

C0 = .174110E-03 NULL 33.00 .438869
CCONC = .115385E-01 .00 1.000000 34.50 .417538
01 1.50 .836167 36.00 .424331
CD = .148837E+01 3.00 .776214 37.50 .411032
4.50 .733108 39.00 .404795
DS = .20778E-09 6.00 .698727 40.50 .398809
XKF = .10000E+14 7.50 .669845 42.00 .387531
BIOT = .25210E+15 9.00 .644837 43.50 .377089
RADP = .50000E-03 10.50 .622742 45.00 .367392
RHOP = .74000E+00 12.00 .602937 46.50 .359200
XK = .50313E+00 13.50 .584986 48.00 .354078
XN = .35920E+00 15.00 .568575 49.50 .350078
TFAC = .83112E-03 16.50 .553467 51.00 .349931
NTOT = 11 18.00 .539479 52.50 .349929
TOL = .100000E-04 19.50 .526464 54.00 .348362
METH = 2 21.00 .514303 55.50 .347089
MITER = 2 22.50 .502901 57.00 .349935
DTINIT = .100000E-09 24.00 .492178 58.50 .345929
49 25.50 .482064 60.00 .342052
DTOUT = 27.00 .472503 61.50 .338299
.150000E+01 28.50 .463444 63.00 .334666
TFINAL = 30.00 .454843 64.50 .331141
.240000E+03 31.50 .446662 66.00 .327726

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173
Cecarbon PAC

In:

0 1 1 /IPRC,IPRI,IPRO (do not change)
1.7024D-04 /C0 (initial concentration in mg/L)
11.5385D-03 /CCONC (carbon concentration in g/l)
0.172720D-09 /DS (surface diffusion coefficient in cm2/min)
1.000000D+13 /XKF (film mass transfer coefficient in cm/min)
6.3553424D-2 /XK (Freundlich K value in (mg/g)(ug/l)^A^-1/n)
0.3956 /XN (Freundlich 1/n)
5.0D-04 /RADP (particle radius in cm)
0.74D0 /RHOP (particle density in g/cm3) (do not change for PAC)
10 /NCP (do not change)
0.1D-04 2 2 /TOL,METH,MITER (do not change)
1.0D-50 /DTINIT (do not change)
1.5D0 /DTOUT (time increment in min)
240.000D0 /TFINAL (final time in min)
10000 /ITMAX (do not change)

Out:

C0 = .170240E-03 NULL 33.00 .331793
CCONC = .115385E-00 1.000000 34.50 .324288
01 1.50 .789472 36.00 .317168
CD = .213813E+01 3.00 .715149 37.50 .310402
4.50 .662451 39.00 .303966
DS = .17272E-09 6.00 .621069 40.50 .297836
XKF = .10000E+14 7.50 .586787 42.00 .291990
BIOT = .21111E+15 9.00 .557465 43.50 .286410
RADP = .50000E-03 10.50 .531856 45.00 .281078
RHOP = .74000E+00 12.00 .509146 46.50 .275979
XK = .97710E+00 13.50 .488779 48.00 .271097
XN = .39560E+00 15.00 .470345 49.50 .266420
TFAC = .69088E-03 16.50 .453537 51.00 .261936
NTOT = 11 18.00 .438118 52.50 .257632
TOL = .100000E-04 19.50 .423902 54.00 .253499
METH = 2 21.00 .410737 55.50 .249527
MITER = 2 22.50 .398499 57.00 .245706
DTINIT = .100000E-49 24.00 .387083 58.50 .242030
25.50 .376403 60.00 .238491
DTOUT = 27.00 .366385 61.50 .235080
.150000E+01 28.50 .356966 63.00 .231792
TFINAL = 30.00 .348093 64.50 .228622
.240000E+03 31.50 .339715 66.00 .225563

174
FS MODEL INPUT

Calgon F-300 (virgin)

(F-S)MODEL MIB Virgin 125 day isotherm pseudo single solute data and $C_e = C_{inf}$

Hg skeletal density

\[ 0.0033 \quad / A \quad K \quad (\text{mg/g})(\text{L/ug})^{(1/n)} \]

\[ 0.7459 \quad / B \quad 1/n \]

\[ 0.05329 \quad / C_0 \quad \text{Co influent concentration (ug/L)} \]

12 \quad / IR0 \quad \text{Initial division parameter, more than 10 recommended} \]

\[ 0.3614 \quad / U \quad \text{Approach velocity (cm/min)} \]

\[ 0.1545 \quad / DIA \quad \text{Diameter of adsorbent (cm) - Ave for 12x14 size fraction is 0.1545 cm} \]

\[ 0.7912 \quad / RS \quad \text{Apparent particle density of adsorbent (g/cm**3)} \]

\[ 0.5323 \quad / RB \quad \text{Bulk density of bed (g/cm**3)} \]

\[ 3.9013400E-04 \quad / AKF \quad K_f \quad \text{film transfer coefficient (cm/sec)} \]

\[ 1.6257934E-06 \quad / D_S \quad \text{Surface diffusion coefficient (cm**2/sec)} \]

\[ 0.00 \quad / DB \quad \text{Dispersion coefficient of flow through bed (cm**2/sec)} \]

\[ 1.00E-05 \quad / DELT \quad \text{initial time step (hr) DTMIN} \]

\[ 0.101 \quad / DELTMX \quad \text{Maximum time step (hr)} \]

\[ DTMAX = \text{MIN(DTMAX,DTMIN*10*N)} \]

51.6000 \quad / TEND \quad \text{Total run time (hr)} \]

0.1 \quad / DELZ \quad \text{Initial difference of bed depth (cm)} \]

1.20 \quad / ZEND \quad \text{Total bed depth (cm)} \]

1.0 \quad / DTUBE \quad \text{Diameter of column (cm)} \]

10 \quad / IITM \quad \text{Frequency of output eg. 10 means 1 out of 10 time-steps} \]

32 \quad / NDATA \quad \text{Number of experimental data // less than 10 ignored} \]

\[ 50.00 \quad 0.00699742 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 55.00 \quad 0.00617917 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 60.00 \quad 0.00738303 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 65.00 \quad 0.00657418 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 73.00 \quad 0.00597226 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 80.00 \quad 0.00693158 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 85.00 \quad 0.00616036 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 90.00 \quad 0.00519163 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 270.00 \quad 0.00772161 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 342.00 \quad 0.00878439 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 462.00 \quad 0.00878439 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 707.00 \quad 0.00944275 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

\[ 952.00 \quad 0.00848343 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

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\[ 1062.00 \quad 0.00886904 \quad / \text{TDAITA(I) CDI(I) Time(min) Conc.(ug/L)} \]

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Calgon F-300 (1 year preload)

(F-S)MODEL MIB Hammond 125 day isotherm pseudo single solute data and Ce = to Cinf Hg skeletal density
0.00825 / A  K ((mg/g)(L/ug)**(1/n))
0.6471 / B  1/n
0.02509 / C0  Co influent concentration (ug/L)
12 / IR0 Initial division parameter, more than 10 recommended
0.3671 / U  Approach velocity (cm/min)
0.1545 / DIA Diameter of adsorbent (cm)- Ave for 12x14 size fraction is 0.1545 cm
0.9827 / RS  Apparent particle density of adsorbent (g/cm**3)
0.5653 / RB  Bulk density of bed (g/cm**3)
2.9514371E-04 / AKF Kf film transfer coefficient (cm/sec)
1.3153105E-011 / DS  Surface diffusion coefficient (cm**2/sec)
0.00 / DB  Dispersion coefficient of flow through bed (cm**2/sec)
1.00E-05 / DELT initial time step (hr) DTMIN
0.101 / DELTMX Maximum time step (hr)
DTMAX=MIN(DTMAX,DTMIN*10*N)
45.000 / TEND Total run time (hr)
0.1 / DELZ Initial difference of bed depth (cm)
1.15 / ZEND Total bed depth (cm)
1.0 / DTUBE Diameter of column (cm)
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<td>0.013031999</td>
<td>/</td>
<td></td>
</tr>
</tbody>
</table>

Calgon F-300 (2 year preload)

(F-S)MODEL MIB michigan city 125 day isotherm pseudo single solute data and Ce = to Cinf Hg skeletal density
0.01131 / A  K ((mg/g)(L/ug)**(1/n))
0.5882 / B  1/n
0.05167 / C0  Co influent concentration (ug/L)
12 / IR0 Initial division parameter, more than 10 recommended
0.3686 / U  Approach velocity (cm/min)
0.1545 / DIA Diameter of adsorbent (cm) Ave for 12x14 size fraction is 0.1545 cm
0.9377 / RS Apparent particle density of adsorbent (g/cm**3)
0.5341 / RB Bulk density of bed (g/cm**3)
2.2296223E-04 / AKF Kf film transfer coefficient (cm/sec)
7.8588405E-012 / DS Surface diffusion coefficient (cm**2/sec)
0.00 / DB Dispersion coefficient of flow through bed (cm**2/sec)
1.00E-05 / DELT initial time step (hr) DTMIN
0.101 / DELTMX Maximum time step (hr)
DTMAX=MIN(DTMAX,DTMIN*10*N)
52 / TEND Total run time (hr)
0.1 / DELZ Initial difference of bed depth (cm)
1.00 / ZEND Total bed depth (cm)
1.0 / DTUBE Diameter of column (cm)
10 / IITM Frequency of output eg. 10 means 1 out of 10 time-steps
17 / NDATA Number of experimental data // less than 10 ignored
136 0.02449206 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
286 0.024050761 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
526 0.026674698 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
706 0.028463745 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
1066 0.029656443 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
1126 0.025893274 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
1246 0.028525985 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
1306 0.030100857 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
1546 0.030398003 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
1696 0.031729215 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
1786 0.031348869 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
2446 0.031741101 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
2506 0.031169743 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
2596 0.032694285 / TDATAI(I) CDI(I) Time(min) Conc.(ug/L)
2656 0.032051119
2688 0.03142346
2696 0.032199926

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Appendix D  (Computer Models)

EBC: EQUILIBRIUM PARAMETER SEARCH COMPUTER PROGRAM

PROGRAM EBCM

This program incorporates data from several isotherms to determine the
Freundlich parameters for the EBC.

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

REAL*8 MWS(10),MCS(10,50)
CHARACTER*16 INPUT(10),OUTPUT

COMMON PARS(50),QS(10,3,50),CES(10,3,50),
& XKS(10),XNS(10),C0(10,10),
& MCS,VS(10,50),NDS(10),NCS(10),SSQ,IPS(4),MWS,NDSETS

COMMON /BLOCK2/QD(10,3,50),CD(10,3,50),CMEAN,ERRREL,ITMAX

DIMENSION X(30),XGUESS(30),XSCALE(30),FSCALE(500),
& IPARAM(6),RPARAM(7),FVEC(500),FJAC(500,30),FDD(500)

EXTERNAL FCN,LSJAC,DNEQBJ,DU4LSF
EXTERNAL FS

ERRREL=0.001
ITMAX=100

OPEN(UNIT=I,FILE='EBC.IN',STATUS='OLD')

K=0
CONTINUE

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

READ(1,1000) INPUT(K)
IF (INPUT(K).NE.'NULL') THEN
    NDSETS=K
    GOTO 5
ELSE

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

READ(1,1000) OUTPUT
READ(1,*)(IPS(I),I=1,4)
ENDIF

DO 101 I=1,4
IPS(I)=1

101 CONTINUE
CONTINUE

WRITE(*,*) 'YOUR INPUT DATA FILES ARE:'
WRITE(*,*) (INPUT(JJ),JJ=1,NDSETS)
WRITE(*,*) 'YOUR OUTPUT DATA FILE IS:'
WRITE(*,*) OUTPUT

DO 45 JJ=1,NDSETS

OPEN(JJ,FILE=INPUT(JJ),STATUS='OLD')

READ (JJ,*) NDS(JJ),NCS(JJ)
DO 20 I=1,NDS(JJ)
  READ (JJ,*) MCS(JJ,I),VS(JJ,I),(CES(JJ,J,I),J=1,NCS(JJ))
  MCS(JJ,I)=MCS(JJ,I)/1000.0D0
  VS(JJ,I)=VS(JJ,I)/1000.0D0
20 CONTINUE

DO 40 I=1,NCS(JJ)
  IF(JJ.EQ. I ) THEN
    READ (JJ,*) XKS(D,XNS(I),C0(JJ,I),MWS(I)
    XKS(I)=XKS(I)*(1000.0D0/MWS(I))*
    MWS(I)**XNS(I)
    XNS(I)=1.0D0/XNS(I)
  ELSE
    READ (JJ,*) DUMXKS,DUMXNS,CO(JJ,I),DUMMWS
  END IF
  C0(JJ,I)=C0(JJ,I)/MWS(I)
  DO 30 J=I,NDS(JJ)
    CES(JJ,I,J)=CES(JJ,I,J)/MWS(I)
    QS(JJ,I,J)=(C0(JJ,I)-CES(JJ,I,J))*VS(JJ,J)/MCS(JJ,J)
    CEQ=CES(JJ,I,J)*MWS(I)
    QEQ=QS(JJ,I,J)*MWS(I)/1000
    WRITE(*,*) CEQ,QEQ
30 CONTINUE
40 CONTINUE
45 CONTINUE

I=2
NDAT=0
CMEAN=0
DO 46 JJ=1,NDSETS
  NDAT=NDAT+NDS(JJ)
  DO 31 J=1,NDS(JJ)
    CMEAN=CMEAN+CES(JJ,I,J)
31 CONTINUE
46 CONTINUE
CMEAN=CMEAN/NDAT

OPEN (NDSETS+1,FILE=OUTPUT,STATUS='OLD')
WRITE (NDSETS+1,*) (XKS(I),I=1,NCS(I))
WRITE (NDSETS+1,*) (XKS(I),I=1,NCS(2))
WRITE (NDSETS+1,*) (QS(1,2,I),I=1,NDS(1))

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WRITE (NDSETS+1,*),(QS(2,2,I),I=1,NDS(2))

K=0
PARS(1)=XKS(1)
IF(IPS(1).EQ.1) THEN
  K=K+1
  XGUESS(K)=PARS(1)
  XGUESS1=XGUESS(K)
& ((1000.0/MWS(1))*MWS(1)***(1.0/XNS(1)))
  WRITE(*,*) 'PARAMETER # ',’K,’ == K,’ ; IG: ’XGUESS1
  WRITE(NDSETS+1,*),'PARAMETER # ',’K,’ == K,’ ; IG: ’XGUESS1
END IF

PARS(2)=XNS(1)
IF(IPS(2).EQ.1) THEN
  K=K+1
  XGUESS(K)=PARS(2)
  XGUESS2=1.0/XGUESS(K)
  WRITE(*,*) 'PARAMETER # ',’K,’ == 1/n’,’ ; IG: ’XGUESS2
  WRITE(NDSETS+1,*),'PARAMETER # ',’K,’ == 1/n’,’ ; IG: ’XGUESS2
END IF

PARS(3)=C0(I,1)
IF(IPS(3).EQ.1) THEN
  K=K+1
  XGUESS(K)=PARS(3)
  XGUESS3=XGUESS(K)*MWS(I)
  WRITE(*,*) 'PARAMETER # ',’K,’ == Co,’ ; IG: ’XGUESS3
  WRITE(NDSETS+1,*),'PARAMETER # ',’K,’ == Co,’ ; IG: ’XGUESS3
END IF

N=K
M=0
DO 70 JJ=1,NDSETS
  M=M+NDS(JJ)
70 CONTINUE
WRITE (NDSETS+1,*),(XGUESS(I),I=1,N)
WRITE (NDSETS+1,*),N,M
WRITE (*,*) N,M
C ************************************************************
C Call to the search routine
C ************************************************************
DO 150 I=1,N
  XSCALE(I)=1.0D0
150 CONTINUE
DO 160 J=1,M
  FSCALE(J)=1.0D0
160 CONTINUE
LDFJAC=M
XGUESS(1)=XGUESS(1)
XGUESS(2)=XGUESS(2)**2
XGUESS(3)=XGUESS(3)
CALL DU4LSF(IPARAM,RPARAM)
IPARAM(3)=400
IPARAM(4)=2500

CALL DUNLSF(FCN,M,N,XGUESS,XSCALE,FSCALE,
& IPARAM,RPARAM,X,FVEC,FJAC,LDFJAC)

CALL FCN(M,N,X,FDD)

Q  * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
Send results to output file
**********************************************
X(1)=(ABS(X(1)))
X(2)=(ABS(X(2)))**0.5
X(3)=(ABS(X(3)))

WRITE(NDSETS+1,1000) 'EBC'
K=0
IF (IPS(1).EQ.1) THEN
  K=K+1
  XKOUT=X(K)/
  & ((1000.0/MWS(1))*MWS(1)**(1.0/XNS(1)))
ELSE
  XKOUT=PARS(1)/
  & ((1000.0/MWS(1))*MWS(1)**(1.0/XNS(1)))
ENDIF
WRITE (NDSETS+1,1003) XKOUT

IF (IPS(2).EQ.1) THEN
  K=K+1
  XNOUT=1.0D0/X(K)
ELSE
  XNOUT=1.0D0/PARS(2)
ENDIF
WRITE (NDSETS+1,1004) XNOUT

IF (IPS(3).EQ.1) THEN
  K=K+1
  C0OUT=X(K)*MWS(1)
ELSE
  C0OUT=PARS(3)*MWS(1)
ENDIF
WRITE (NDSETS+1,1005) C0OUT
WRITE (NDSETS+1,1001) MWS(1)

WRITE(NDSETS+1,1000) 'TARGET COMPOUND'
XKOUT2=XKS(2)/
& ((1000.0/MWS(2))*MWS(2)**(1.0/XNS(2)))
XNOUT2=1.0/XNS(2)
WRITE (NDSETS+1,1003) XKOUT2
WRITE (NDSETS+1,1004) XNOUT2
DO 249 JJ=1,NDSETS
  C0OUT2=C0(JJ,2)*MWS(2)
  WRITE (NDSETS+1,1005) C0OUT2
249   CONTINUE

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249 CONTINUE
  WRITE (NDSETS+1,1001) MWS(2)
C
  DO 248 JJ=1,NDSETS
  WRITE (NDSETS+1,1002) INPUT(JJ)
248 CONTINUE
C
  WRITE(NDSETS+1,*), 'no, Q-obs Q-cal', &
   ' C-obs C-cal AC-dose'
  DO 250 JJ=1,NDSETS
    DO 200 J=1,NDS(JJ)
      Q =QS(JJ,2,J)* MWS(2)/1000.0
      QOUT=QD(JJ,2,J)*MWS(2)/1000.0
      CEQ=CES(JJ,2,J)*MWS(2)
      XMCSJ=MCS(JJ, J)* 1000.0
      CEQOUT=CD(JJ,2,J)*MWS(2)
    WRITE (NDSETS+1,1006) J,Q,QOUT,CEQ,CEQOUT,XMCSJ
200 CONTINUE
250 CONTINUE
C
  DO 210 1=1,M
    WRITE (NDSETS+1,1007) I,FVEC(I)
210 CONTINUE
C
  WRITE (NDSETS+1,1008) SSQ
C
1000 FORMAT(A)
1001 FORMAT(1X,'MW = ',E17.8,' g/mol')
1002 FORMAT(1X,A20)
1003 FORMAT(1X,'K = ',E17.8, '(mg/g)(ug/L)^-1/n')
1004 FORMAT(1X,'1/n = ',E17.8)
1005 FORMAT(1X,'C0 = ',E17.8, ' ug/L')
1006 FORMAT(1X,'Q(',I2,') = ',E10.4,E10.4,' mg/g'
   & ,E10.4,E10.4,' ug/l',E10.4,' mg/l')
1007 FORMAT(1X,'F(',I2,') = ',E14.5)
1008 FORMAT(1X,'Error sum of squares = ',E14.5)
C
STOP ' all done'
END
C
********************************************************************
C This subroutine evaluates the function that defines the least
C squares problem
C********************************************************************
SUBROUTINE FCN(M,N,X,F)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
REAL* 8 MW(10),XMC(10,50)
C
COMMON PAR(50),Q(10,3,50),CES(10,3,50),
 & XK(10),XN(10),C0(10,10),
 & XMC,V(10,50),ND(10),NC(10),SSQ,IPS(4),MW,NDSETS
C
COMMON /BLOCK1/JJ,J,K
COMMON /BLOCK2/QD(10,3,50),CD(10,3,50),CMEAN,ERRREL,ITMAX

C DIMENSION F(M),X(N)
& X(10),XIGUESS(10),XIG1(10),XIG2(10)
DIMENSION QQ(10),QQD(2),FF(2)

C DIMENSION XSCALE(2),FSCALE(2)
& IPARAM(6),RPARAM(5),FVEC(2)
EXTERNAL FCNIAS,LSJAC,DNEQBJ,DZBREN
EXTERNAL FS

C DATA ICALL/0/
C
C WRITE(*,*) 'FCN IN DUNLSF
ICALL=ICALL+1
C*************************************************************************
C If trouble, limit the parameters to the smallest value of 10D-30
C*************************************************************************
C
X1=(ABS(X(1)))
X2=(ABS(X(2)))**0.5
X3=(ABS(X(3)))

IF (X1 .LT. 0.000001) X1=0.000001
IF (X2 .LT. 0.01) X2=0.01
IF (X3 .LT. 0.000001) X3=0.000001

IF (IPS(1).EQ. I) XK(1)=X1
IF (IPS(2).EQ. I) XN(1)=X2
IF (IPS(3).EQ. I) THEN
DO 117 JJ=1,NDSETS
CO(JJ,1) =X3
117 CONTINUE
ENDIF
X11=X1/
& (((1000.0/MW(1))*MW(1)**(1.0/X2))
X22=1.0/X2
X33=X3*MW(1)
WRITE(*,*) X11,X22,X33

I=0
DO 115 JJ=1,NDSETS
NN=NC(JJ)
DO 110 J=1,ND(JJ)
I=I+1

DO 100 K=1,NN
QMAX1 = CO(JJ,K)*V(JJ,J)/XMC(JJ,J)
QMAX2 = XK(K)*CO(JJ,K)**(1.0/XN(K))
IF(QMAX1.LE.QMAX2) THEN
QMAX=QMAX1
ELSE
QMAX=QMAX2
ENDIF
QEST = QMAX * 1.00001
QMIN = 0
EABS = 0
EREL = 0.002
MAXFN = 100

C F1 = FS(QMIN)
C F2 = FS(QEST)
C WRITE(*,*) JJ, JJ, K, QEST
C WRITE(*,*) F1, F2
C WRITE(*,*) C0(JJ, K), V(JJ, JJ), XMC(JJ, J)
C WRITE(*,*) XK(K), XN(K)
CALL DZBREN(FS, EABS, EREL, QMIN, QEST, MAXFN)
C WRITE(*,*) JJ, JJ, K, QEST
QQ(K) = QEST
100 CONTINUE
C
C WRITE(*,*) JJ, JJ, (QQ(K), K = 1, NN), ' QQ'
C
KMAX = 1000
PD = 1.1
MR = 1
FMAX = 1.0D99
C
FMIN1 = FMAX
NFLG = 0
DO 202 K2 = 1, KMAX
  QQD(2) = QQ(2) / PD ** (K2 - 1)
  FABS = FMAX
  DO 203 K1 = 1, KMAX
    QQD(1) = QQ(1) / PD ** (K1 - 1)
    CALL FCNIAS(NN, QQD, FF)
    FABS = FABS
    FABS = (FF(1) / C0(JJ, 1)) ** 2
    & + (FF(2) / C0(JJ, 2)) ** 2
    IF(FABS.LT.FMIN1) THEN
      FMIN1 = FABS
      XIG1(1) = QQD(1)
      XIG1(2) = QQD(2)
      K11 = K1
      K22 = K2
      NFLG = 1
    ELSE
      IF(FABS.GT.FABS) GO TO 205
    ENDIF
  203 CONTINUE
  K = K22
  NFLG = 0
  DO 302 K1 = 1, KMAX
QQD(1) = QQ(1)/PD**(K1-1)
FABS = FMAX
DO 303 K2 = 1, KMAX
    QQD(2) = QQ(2)/PD**(K2-1)
    CALL FCNIAS(NN, QQD, FF)
    FABSB = FABS
    FABS = (FF(1)/C0(JJ,1))^**2 &
        + (FF(2)/C0(JJ,2))^**2
    IF(FABS.LT.FMIN) THEN
        FMIN = FABS
        XIG2(1) = QQD(1)
        XIG2(2) = QQD(2)
        K11 = K1
        K22 = K2
        NFLG = 1
    ELSE
        IF(FABS.GT.FABSB) GO TO 305
    ENDIF
303 CONTINUE
305 IF(K1-K11.GE.MR.AND.NFLG.EQ.1) GO TO 304
302 CONTINUE
304 CONTINUE
C IF(FMIN .LT.FMIN2) THEN
    XIGUESS(1) = XIG1(1)
    XIGUESS(2) = XIG1(2)
ELSE
    XIGUESS(1) = XIG2(1)
    XIGUESS(2) = XIG2(2)
ENDIF
C WRITE(*,*) JJ, J, (QQ(K), K = 1, NN), 'QQ'
C WRITE(*,*) K11, K22, 'k1, k2'
C WRITE(*,*) JJ, J, (XIGUESS(K), K = 1, NN), 'XIG'
C CALL DNEQNJ(FCNIAS, LSJAC, ERRREL, NN, ITMAX, XIGUESS, XI, FNORM)
DO 98 K = 1, NN
    XSCALE(K) = 1.0
    FSCALE(K) = 1.0
98 CONTINUE
CALL DN4QBJ(IPARAM, RPARAM)
IPARAM(1) = 0
C WRITE(*,*) IPARAM(3), RPARAM(1), RPARAM(2)
IPARAM(3) = 500
RPARAM(1) = 0.0D0
RPARAM(2) = 0.0D0
CALL DNEQBJ(FCNIAS, LSJAC, NN, XIGUESS &
    , XSCALE, FSCALE, IPARAM, RPARAM, XI, FVEC)
C CALL DNEQBF(FCNIAS, NN, XIGUESS &
    , XSCALE, FSCALE, IPARAM, RPARAM, XI, FVEC)
C WRITE(*,*) JJ, J, (XI(K), K = 1, NN)
DO 103 K=I,NN
QD(JJ,K,J)=XI(K)
CD(JJ,K,J)=LO(JJ,K)-XMC(JJ,J)/V(JJ,J)*XI(K)
103 CONTINUE
C
C QG=Q(JJ,2,J)*MW(2)
C QDG=QD(JJ,2,J)*MW(2)
C
C ebcml
C F(I)=DABS(DLOG(CES(JJ,2,J))-DLOG(CD(JJ,2,J)))
C & +DABS(DLOG( Q(JJ,2,J)-DLOG(QD(JJ,2,J))))
C ebcn3
C F(I)=DLOG(CES(JJ,2,J))-DLOG(CD(JJ,2,J))
C
C ebcn4
C F(I)=(CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J)**0.5*10
C ebcn5
C F(I)=CES(JJ,2,J)-CD(JJ,2,J)
C ebcn6
C F(I)=(CES(JJ,2,J)-CD(JJ,2,J))
C & /(DLOG(C0(JJ,2))/CES(JJ,2,J))**0.5
C ebcn7
C F(I)=(CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J)
C ebcn8
C F(I)=DABS(CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J)
C & *(1.0D0/CES(JJ,2,J)+1.0D0/CMEAN)
C ebcn11
C F(I)=DSQRT( (DLOG(CES(JJ,2,J))-DLOG(CD(JJ,2,J)))**2
C & +DLOG( Q(JJ,2,J)-DLOG(QD(JJ,2,J)))**2 )
C ebcn12
C F(I)=DSQRT( ((CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J))**2
C & + (( Q(JJ,2,J)-QD(JJ,2,J))/Q(JJ,2,J))**2)
C ebcn13
C F(I)=DSQRT( (CES(JJ,2,J)-CD(JJ,2,J))**2
C & *(1.0D0/CES(JJ,2,J)**2+1.0D0/CMEAN**2 )
C ebcn14
F(I)=DSQRT(DABS(CES(JJ,2,J)-CD(JJ,2,J))
C & *(1.0D0/CES(JJ,2,J)+1.0D0/CMEAN )
C ebcn15
C F(I)=DSQRT(DABS(CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J))
C ebcn16
C F(I)=DSQRT(DABS(DLOG(CES(JJ,2,J))-DLOG(CD(JJ,2,J))))
C ebcn17
C F(I)=DSQRT(DABS(DLOG(CES(JJ,2,J))-DLOG(CD(JJ,2,J))))
C & + DABS(DLOG( Q(JJ,2,J)-DLOG(QD(JJ,2,J))))
C ebcn18
C F(I)=DSQRT(DABS(CES(JJ,2,J)-CD(JJ,2,J))/CES(JJ,2,J))
C & + DABS(( Q(JJ,2,J)-QD(JJ,2,J))/Q(JJ,2,J))
C ebcn19
C IF(I)=DSQRT( DABS(CES(JJ,2,J)-CD(JJ,2,J))
C & *(1.0D0/CES(JJ,2,J)+1.0D0/CMEAN)
C & +DABS((Q(JJ,2,J)-QD(JJ,2,J))/Q(JJ,2,J))
C ebcm20
C F(I)=DABS( (Q(JJ,2,J)-QD(JJ,2,J))/Q(JJ,2,J) )
C ebcm21
C F(I)=DABS( Q(JJ,2,J)-QD(JJ,2,J) )
C
WRITE(*,*) JJ,J,QG,QDG
WRITE(*,*) JJ,J,I,F(I)
110 CONTINUE
115 CONTINUE
C
SSQ=0
DO 120 K=1,M
   IF (DABS(F(K)).GT. 1.0D-30) THEN
      IF (DABS(F(K)).LT. 1.0D30) THEN
         SSQ=SSQ+F(K)**2.0D0
      ENDIF
   ENDIF
120 CONTINUE
SSQ=SSQ/M
C
WRITE (*,1009) ICALL, SSQ
1009 FORMAT(1X,'Iteration No.:',15,4X,'Error sum of sq. = ',E14.6)
C
RETURN
END
C
**************************************************************************************
C This set up the equations that will be solved by the
C subroutine DNEQNF
C The equation is derived from IAST plus Freundlich equations
C for a target compound and a background compound
C**************************************************************************************
C SUBROUTINE FCNIAS(X,F,N)
SUBROUTINE FCNIAS(N,X,F)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
REAL*8 MW( 10),XMC( 10,50)
C
COMMON PAR(50),Q(10,3,50),CES(10,3,50),
& XK(10),XN(10),C0(10,10),
& XMC,V(10,50),ND(10),NC(10),SSQ,IPS(4),MW,NDSETS
C
COMMON /BLOCK 1/JJ,J,KK
C
DIMENSION X(N),F(N)
C
QS=X(1)+X(2)
QNS=XN(1)*X(1)+XN(2)*X(2)
C
DO 1000 I=1,N
   F(I)=C0(JJ,1)-X(I)*XMC(JJ,J)/V(JJ,J)
   & -X(I)/QS*(QNS/XN(1)/XK(I))**XN(I)
1000 CONTINUE
C WRITE(*,*) JJ, JJ, XI, F(I), F
1000 CONTINUE
C
RETURN
END

C**********************************************************************
C This set up the equations that will be solved by the
C subroutine DNEQNF
C The equation is derived from IAST plus Freundlich equations
C for a target compound and a background compound
C**********************************************************************

SUBROUTINE LSJAC(N, X, FJAC)
SUBROUTINE LSJAC(N, X, FJAC, LDFJAC)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
REAL*8 MW( 10), XMC(10, 50)
INTEGER N, I, J
C
DIMENSION X(N), FJAC(N, N)
DIMENSION X(N), FJAC(LDFJAC, *)
C
COMMON PAR(50), Q(10, 3, 50), CES(10, 3, 50),
& XK(10), XN(10), C(10, 10),
& XMC, V(10, 50), ND(10), NC(10), SSQ, IPS(4), MW, NDSETS
C
COMMON /BLOCK I/JJ, JJ, KK
C
QS = X(1) + X(2)
QNS = XN(1) * X(1) + XN(2) * X(2)
C
DO 1000 I = 1, N
XNI = XN(I)
XKI = XK(I)
XI = X(I)
DO 1100 K = 1, N
IF(I.NE.K) THEN
FJAC(I,K) = XI/QS**2*(QNS/XNI/XKI)**XNI
& -(XI*XNI*XN(K)/QS)
& *(QNS**(XNI-1.0)/(XNI*XKI)**XNI
ELSE
FJAC(I,K) = XMC(JJ,J)/V(JJ,J)
& -1.0/QS*(QNS/XNI/XKI)**XNI
& +(XI/QS**2)*(QNS/XNI/XKI)**XNI
& -(XI*XNI**2/QS)
& *(QNS**(XNI-1.0)/(XNI*XKI)**XNI
ENDIF
C WRITE(*,*) I, J, FJAC(I,K), 'JAC*
C FJAC(I,K) = FJAC(I,K) * 0.5
1100 CONTINUE
1000 CONTINUE
C
RETURN
END
REAL*8 FUNCTION FS(X)

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGER JJ, KK
REAL*8 MW(10), XMC(10,50)

COMMON PAR(50), Q(10,3,50), CES(10,3,50), 
& XK(10), XN(10), C0(10,10), 
& XMC, V(10,50), ND(10), NC(10), SSQ, IPS(4), MW, NDSETS

COMMON /BLOCK I/JJ, J, KK

FS = C0(JJ, KK) - X* XMC(JJ, J)/V(JJ, J) 
& - (X*KK)**XN(KK)

WRITE(*,*) JJ, FS, ' FSINGLE'

RETURN
END
C IAST PREDICTION
C 'IASTM.FOR'
C
C This program solves the Freundlich-type ideal adsorbed solution
C theory for a closed multi-solute equilibrium system, given the
C single solute isotherm constants, the carbon dosage, the
C solution volume.
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGER ITMAX, N, MAXFN
REAL*8 ERRREL
REAL*8 LSJAC, X(10), XGUESS(10),XG1(10),XG2(10)
C
EXTERNAL FCNIAS,LSJAC,DNEQNJ,F
C
INTEGER NC,ND,I
DIMENSION Q(10,50),C(10,50)
REAL*8 MW(10),M(50),K(10),V(50),CO(10),XN(10)
C
DIMENSION IPARAM(6), RPARAM(5)
& , XSCALE(2), FSCALE(2), FVEC(2)
REAL*8 QQD(2),FF(2)
C
CHARACTER CHAR(10)*80
COMMON PAR(50)
COMMON /B1/I
C
C Open files and read input data
C
OPEN (9, FILE = 'DATA.IN', STATUS = 'OLD')
OPEN (10, FILE = 'DATA.OUT', STATUS = 'OLD')
READ (9,*) NC, ND
DO 15 I = 1, ND
READ (9,*) M(I), V(I)
M(I) = M(I)/1000.0D0
V(I) = V(I)/1000.0D0
15 CONTINUE
C
DO 20 I = 1,NC
READ (9,16) CHAR(I)
16 FORMAT (A10)
READ (9,*) K(I), XN(I), CO(I), MW(I)
WRITE (*,*) K(I),XN(I),CO(I),MW(I)
K(I)=K(I)*(1000.0/MW(I))*MW(I)**XN(I)
CO(I) = CO(I)/MW(I)
XN(I) = 1/XN(I)
20 CONTINUE
C
C Solve each dosage individually
C
DO 100 J = 1, ND  
C Put 'DATA.IN' into a one dimensional array  
C  
IF (J.EQ.1) THEN  
DO 25 I = 1, NC  
PAR(I) = K(I)  
PAR(10+I) = XN(I)  
PAR(20+I) = CO(I)  
25 CONTINUE  
ENDIF  
PAR(30) = M(J)  
PAR(40) = V(J)  
C  
C Calculate initial guesses on surface loadings  
C  
DO 30 I = 1, NC  
QMAX2 = K(I)*CO(I)**(1.0/XN(I))  
IF(M(J).GT.0) THEN  
QMAX1 = CO(I)*V(J)/M(J)  
ELSE  
QMAX1 = QMAX2  
ENDIF  
IF(QMAX1.LE.QMAX2) THEN  
QMAX=QMAX1  
ELSE  
QMAX=QMAX2  
ENDIF  
QEST=QMAX+1.1  
QMIN = 0  
EABS=0  
EREL=0.002  
MAXFN = 100  
F1=F(QMIN)  
F2=F(QEST)  
C WRITE(*,*) J,I,F1,F2  
CALL DZBREN(F,EABS,EREL,QMIN,QEST,MAXFN)  
Q(I,J)=QEST  
30 CONTINUE  
C  
KMAX=1000  
PD=1.1  
MR=1  
C  
FMIN1=1.0D99  
NFLG=0  
DO 202 K2=1,KMAX  
QQD(2)=Q(2,J)/PD**(K2-1)  
FABS=1.0D99  
DO 203 K1=1,KMAX  
QQD(1)=Q(1,J)/PD**(K1-1)  
CALL FCN1AS(NC,QQD,FF)  
FABSB=FABS  
C FABS=DABS(FF(1))/CO(1)+DABS(FF(2))/CO(2)  
FABS=(FF(1)/CO(1)**2+(FF(2)/CO(2))**2
C FABS=DABS(FF(1))+DABS(FF(2))
C FABS=(FF(1))**2+(FF(2))**2
IF(FABS.LT.FMIN1) THEN
  FMIN1=FABS
  XG1(1)=QQD(1)
  XG1(2)=QQD(2)
  K22=K2
  K11=K1
  NFLG=1
ELSE
  IF(FABS.GT.FABSB) GO TO 205
ENDIF
203 CONTINUE
205 IF(K2-K22.GE.MR.AND.NFLG.EQ.1) GO TO 204
202 CONTINUE
204 CONTINUE
C
C GO TO 304
FMIN2=1.0D99
NFLG=0
DO 302 K1=1,KMAX
  QQD(1)=Q(1,J)/PD**(K1-1)
  FABS=1.0D99
DO 303 K2=1,KMAX
  QQD(2)=Q(2,J)/PD**(K2-1)
  CALL FCNIAS(NC,QQD,FF)
  FABSB=FABS
C
  FABS=DABS(FF(1))/CO(1)+DABS(FF(2))/CO(2)
  FABS=(FF(1)/CO(1))**2+(FF(2)/CO(2))**2
C
  FABS=DABS(FF(1))+DABS(FF(2))
C
  FABS=(FF(1))**2+(FF(2))**2
IF(FABS.LT.FMIN2) THEN
  FMIN2=FABS
  XG2(1)=QQD(1)
  XG2(2)=QQD(2)
  K11=K1
  K22=K2
  NFLG=1
ELSE
  IF(FABS.GT.FABSB) GO TO 305
ENDIF
303 CONTINUE
305 IF(K1-K11.GE.MR.AND.NFLG.EQ.1) GO TO 304
302 CONTINUE
304 CONTINUE
C
IF(FMIN1.LT.FMIN2) THEN
  XGUESS(1)=XG1(1)
  XGUESS(2)=XG1(2)
ELSE
  XGUESS(1)=XG2(1)
  XGUESS(2)=XG2(2)
END IF
C

194
C QS=Q(1,J)+Q(2,J)
C QNS=PAR(11)*Q(1,J)+PAR(12)*Q(2,J)
C
DO 40 I=1,NC
C Q(I,J)=CO(I)
C ! M(J)/V(J)+(QNS/PAR(I)/PAR(10+1))**PAR(10+1)/QS
C XGUESS(I)=Q(I,J)
C WRITE(*,*) QMAX,QEST
C40 CONTINUE
C
Enter the rest of parameters for DNEQNF
C
IF (J.EQ.1) THEN
READ (9,*) ITMAX, ERRREL
ENDIF
N = NC
C
Call DNEQNJ to solve the system of equations
C
WRITE(*,*) J,(Q(I,J),I=1,NC)
WRITE(*,*) FMINS1(XG1(I),I=1,NC)
WRITE(*,*) FMINS2(XG2(I),I=1,NC)
WRITE(*,*) J,XGUESS(I),I=1,NC)
C
CALL DNEQNJ (FCNIAS, LSJAC, ERRREL, N, ITMAX, XGUESS, X, FNORM)
IPARAM(1)=0
IPARAM(3)=500
DO 201 I=1,N
XSCALE(I)=1
FSCALE(I)=1
201 CONTINUE
CALL DNEQBJ (FCNIAS, LSJAC, N, XGUESS
& XSCALE, FSCALE, IPARAM, RPARAM, X, FVEC)
C
CALL DNEQNF (FCNIAS, ERRREL, N, ITMAX, XGUESS, X, FNORM)
C
Store the calculated surface loadings back to Q(I,J)
QS=0.0
QNS=0.0
DO 50 I=1,NC
Q(I,J)=X(I)
QS=QS+X(I)
QNS=QNS+PAR(10+I)*X(I)
50 CONTINUE
XMJ=M(J)*1000.0D0
WRITE(*,*) J,XMJ, 'a.c. dose'
WRITE(*,*) J,(X(I),I=1,NC)
C
Calculate the liquid phase concentrations
C
DO 60 I=1,NC
CD = CO(I)-M(J)/V(J)*Q(I,J)
C(I,J) = Q(I,J)/QS*(QNS/PAR(I)/PAR(10+1))**PAR(10+1)
C WRITE(*,*) CD,C(I,J)
60 CONTINUE
CONTINUE

change units for printing

DO 120 J =1, ND
  DO 110 I=1,NC
    Q(I,J) = Q(I,J)*MW(I)/1000.D0
    C(I,J) = C(I,J)*MW(I)
  110 CONTINUE
  120 CONTINUE

Print out results

WRITE (10, 200)
  200 FORMAT ('PROPERTIES of COMPONENTS')
WRITE (10,210)
  210 FORMAT ('COMPONENT,T15,'K (mg/g)(ug/L)**-1/n'.T38,'1/n'.T45,
    &'CO (ug/l),X,MW(dalton)'//)
DO 300 I =1, NC
  XN(I) = 1.0D0/XN(I)
  CO(I) = CO(I)*MW(I)
  K(I)=K(I)/
  & (1000.0/MW(I))*MW(I)**XN(I))
WRITE (10,250) CHAR(I),K(I),XN(I),CO(I),MW(I)
  250 FORMAT ( 1X,AI0,T20,G11.5,T31,G11.5,T43,G11.5,T55,F10.3//)
  300 CONTINUE

WRITE (10,310)
  310 FORMAT ('LAST PREDICTION')
WRITE (10,320) CHAR(1), CHAR(2), CHAR(3)
  320 FORMAT (///, 1X,'DOSAGE',T20,A10,T42,A10,T65,A10)
WRITE (10,330)
  330 FORMAT (/2X,'(mg/l)' ,T14,'C ug/l',T24,'q mg/g',T35,'C ug/l',T45,
    '&q mg/g',T56,' C ug/l' ,T66,'q m g/g'/)
DO 340 J =1, ND
  M(J) = M(J)/V(J)*1000.0D0
  WRITE (10,360) M(J),C(1,J),Q(1,J),C(2,J),Q(2,J)
  340 CONTINUE
IF (NC.GT.2) THEN
  WRITE (10,320) CHAR(4), CHAR(5), CHAR(6)
WRITE (10,330)
  DO 350 J =1, ND
    WRITE (10,360) M(J),C(3,J),Q(3,J),C(4,J),Q(4,J)
  350 CONTINUE
ENDIF
IF (NC.GT.6) THEN
  WRITE (10,320) CHAR(7), CHAR(8), CHAR(9)
WRITE (10,330)
  DO 355 J =1, ND
    WRITE (10,360) M(J),C(7,J),Q(7,J),C(8,J),Q(8,J),C(9,J),
      &Q(9,J)
  355 CONTINUE
ENDIF

END
&T65,F9.4/)

C

C

do 400 I =1,N
write ('*','*) PAR(I), PAR(I+10), PAR(I+20),PAR(30), PAR(40)
400 continue
STOP
END

C
*************
C subroutine FCNIAS
C This subroutine will set up the equations that will be solved
C by the subroutine DNEQNF
C
C SUBROUTINE FCNIAS(X,F,N)
SUBROUTINE FCNIAS(N,X,F)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGER N,I
REAL* 8 X(N),F(N), CC
COMMON PAR(50)
CC = PAR(30)/PAR(40)
QS = 0.0D0
QNS = 0.0D0
DO 1000 1=1,N
 IF(X(I).LT.0) X(I)=0
QS = QS+X(I)
QNS = QNS+PAR(10+I)*X(I)
1000 CONTINUE
DO 1200 1=1,N
C WRITE(*,*) I,X(I),PAR(I),PAR(10+I),PAR(20+I),CC,QS,QNS
F(I) = PAR(20+I)-CC*X(I)-X(I)/QS*(QNS/PAR(10+I))/
& PAR(I)**2*PAR(10+I)
C WRITE(*,*) I,F(I)
1200 CONTINUE
RETURN
END

C
SUBROUTINE LSJAC(N,X,FJAC)
SUBROUTINE LSJAC(N,X,FJAC,LDFJAC)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGER N,I,J
C REAL* 8 X(N),FJAC(N,N),CC
REAL* 8 X(N),FJAC(LDFJAC,*)
COMMON PAR(50)
CC = PAR(30)/PAR(40)
QS = 0.0
QNS = 0.0
DO 1000 I =1,N
 IF(X(I).LT.0) X(I)=0
QS = QS+X(I)
QNS = QNS+PAR(10+I)*X(I)
1000 CONTINUE
DO 1200 I =1,N
DO 1300 J=1,N
C      WRITE(*,*) I,J
IF(I.NE.J) THEN
   FJAC(I,J)=X(I)/QS**2*(QNS/PAR(I))/PAR(I)**PAR(I)
   &   -(X(I)*PAR(I)/PAR(I)/QNS/PAR(I))**PAR(I)
   &   *QNS***(PAR(I))/PAR(I)**PAR(I)**PAR(I)
ELSE
   FJAC(I,J)=CC
   &   -1.0/QS*(QNS/PAR(I)/PAR(I))**PAR(I)
   &   +(X(I)/QS**2)**(QNS/PAR(I)/PAR(I))**PAR(I)
   &   -(X(I)*PAR(I)/PAR(I))**2/QS
   &   *QNS**(PAR(I)/PAR(I)-1)/(PAR(I)**PAR(I)**PAR(I))
END IF
C      WRITE(*,*) I,J,FJAC(I,J)
C      FJAC(I,J)=FJAC(I,J)**10.0
1300  CONTINUE
1200  CONTINUE
      RETURN
END
C
REAL*8 FUNCTION F(X)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGER I
COMMON PAR(50)
COMMON /BI/I
CC = PAR(30)/PAR(40)
F=PAR(20+I)-CC*X-(X/PAR(I))**PAR(I)
C      WRITE(*,*) I,X,F,PAR(20+I)
      RETURN
END
SEARCH: BATCH KINETIC PARAMETER SEARCH COMPUTER PROGRAM

This FORTRAN program is used to simultaneously search for the optimum set of kinetic parameters and/or equilibrium parameters that would best fit the HSDM to the experimental batch adsorption data. The IMSL optimization subroutine DUNLSF coupled with the subroutine HSDM (same as <HSDM.FOR> program) will be used to determine the optimum parameter values.

The control input file <SEARCH.IN> will identify the name of the experimental data input file, the name of the output file, and the parameters to be searched.

The experimental data input file <SEARCH.DAT> needs to be filled with the appropriate data, including an initial guess for Ds and kf. Then, the program is run to evaluate the Ds and kf values that result in the best fit for the experimental data. If the error for the obtained result is high, a different initial guess should be used. The output of the search program is contained in the file <SEARCH.OUT>. All other files are intermediate files containing control parameters that do not need to be changed.

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IMPLICIT DOUBLE PRECISION (A-H,O-Z)

COMMON /PARI/ C0V(10),CCONCV(10),RADPV(10),RHOPV(10),
& PARV(4,10),NDPV(10),NDSET,IPS(4),ISCALE(4),
& TM(50,10),YM(50,5,10),IDREP(10),NDPSV(10),
& YF(50,10)

CHARACTER*80 IFNAME(IO)

DIMENSION X(4),F(500),XGUESS(4),XSCALE(4),FSCALE(500),
& IPARAM(6),RPARAM(7),FVEC(500),FJAC(500,4)

EXTERNAL FIND

OPEN(1,FILE='SEARCH.IN',STATUS='OLD')

K=1
123 CONTINUE
READ(1,1000) IFNAME(K)
IF(IFNAME(K),NE.'null') THEN

199
C Read in the name(s) of the data file(s)

NDSET=K
K=K+1
GO TO 123
ELSE

Name of output file

READ(1,1000) IFNAME(K)
ENDIF

READ(1,*),(IPS(I),I=1,4)

WRITE(*,'YOUR INPUT NDSET, DATA FILE(S):')
DO 1 K=1,NDSET
  WRITE(*,*) IFNAME(K)
1 CONTINUE

WRITE(*,'YOUR OUTPUT DATA FILE IS:')
WRITE(*,*) IFNAME(NDSET+1)

IPSSUM=0
DO 2 K=1,4
  IF(IPS(K).EQ.1) THEN
    IPSSUM=IPSSUM+1
  END IF
2 CONTINUE

DO II K=1,NDSET
  OPEN(K,FILE=IFNAME(K),STATUS='OLD')
  REWIND(K)
  READ(K,*) NDPV(K),C0V(K),IDREP(K)
  DO 22 IP=1,NDPV(K)
    READ(K,*) TM(IP,K),(YM(IP,I,K),I=1,IDREP(K))
  22 CONTINUE
  READ(K,*) CCONCV(K)
  READ(K,*) RADPV(K)
  READ(K,*) RHOPV(K)
  READ(K,*) PARV(3,K)
  READ(K,*) PARV(4,K)
  PARV(3,K)=PARV(3,K)*(1000.0D0**PARV(4,K))
  READ(K,*) PARV(1,K)
  READ(K,*) PARV(2,K)
II CONTINUE

Count total number of data points

DO 95 II=1,NDSET
  NDPSV(II)=0
  DO 94 IJ=1,NDPV(II)
    DO 93 JJ=1,IDREP(IJ)
      IF(YM(IJ JJ II).LE.1.1D0) THEN
        NDPSV(II)=NDPSV(II)+1
      END IF
    93 CONTINUE
  94 CONTINUE
95 CONTINUE

200
END IF
93 CONTINUE
94 CONTINUE
95 CONTINUE
C
M1=0
DO 211 KK=1,NDSET
   M1=M1+NDPV(KK)
211 CONTINUE
C
M=0
DO 21 KK=1,NDSET
   M=M+NDPSV(KK)
21 CONTINUE
C
WRITE(*,*)' TOTAL OBSERVATION TIMES : ,M1
WRITE(*,*)' TOTAL DATA POINTS : ,M
WRITE(*,*)' YOU ARE SEARCHING FOR 'IPSSUM ' PARAMETERS'
C
K=1
IF(IPS(1) .EQ. 1) THEN
   SCALE=DLOG10(PARV(1,1))
   IF(SCALE .GT. 0.0D0) THEN
      ISCALE(K)=DINT(SCALE)+1
   ELSE
      ISCALE(K)=DINT(SCALE)
   END IF
   XGUESS(K)=PARV(1,1)/(10.0D0**ISCALE(K))
   XXX=XGUESS(K)*10.0D0**ISCALE(K)
   WRITE(*,*)' PARAMETER # ,K, = kf ; IG : ,XXX
   K=K+1
END IF
C
IF(IPS(2) .EQ. 1) THEN
   SCALE=DLOG10(PARV(2,1))
   IF(SCALE .GT. 0.0D0) THEN
      ISCALE(K)=DINT(SCALE)+1
   ELSE
      ISCALE(K)=DINT(SCALE)
   END IF
   XGUESS(K)=PARV(2,1)/(10.0D0**ISCALE(K))
   XXX=XGUESS(K)*10.0D0**ISCALE(K)
   WRITE(*,*)' PARAMETER # ,K, = Ds ; IG : ,XXX
   K=K+1
END IF
C
IF(IPS(3) .EQ. 1) THEN
   SCALE=DLOG10(PARV(3,1))
   IF(SCALE .GT. 0) THEN
      ISCALE(K)=DINT(SCALE)
   ELSE
      ISCALE(K)=DINT(SCALE)
   END IF
   XGUESS(K)=PARV(3,1)/(10.0D0**ISCALE(K))
XXX=XGUESS(K)*10.0D0**ISCALE(K)
WRITE(*,*),'PARAMETER #',K,'== ',K,' ; IG: ' ,XXX
K=K+1
END IF

C IF(IPS(4) .EQ. 1) THEN
SCALE=DLOG10(PARV(4,1))
IF(SCALE .GT. 0) THEN
ISCALE(K)=DINT(SCALE)+1
ELSE
ISCALE(K)=DINT(SCALE)
END IF
XGUESS(K)=PARV(4,1)/(10.0D0**ISCALE(K))
XXX=XGUESS(K)*10.0D0**ISCALE(K)
WRITE(*,*),'PARAMETER #',K,'== n' ; IG: ' ,XXX
ENDIF

Q ************
C Call to the search routine
Q ************
OPEN(NDSET+1,FILE=IFNAME(NDSET+1),STATUS='OLD')

C N=IPSSUM
DO 150 I=1,N
XSCALE(I)=1.0D0
150 CONTINUE
DO 160 J=1,M
FSCALE(J)=1.0D0
160 CONTINUE
IPARAM(1)=0
LDFJAC=M

C CALL DUNLSF(FIND,M,N,XGUESS,XSCALE,FSCALE,IPARAM,PARAM,
& X,FVEC,FJAC,LDFJAC)
C ************
C Send results to output file
C ************
DO 222 IP=I,NDPV(K)
WRITE(NDSET+1,1001) TM(IP,K),(YM(IP,II,K),II=I,IDREP(K)),YF(IP,K)
222 CONTINUE
111 CONTINUE

C 1000 FORMAT(A)
1001 FORMAT(2X,6E16.6)

C STOP ' all done'
END

C This subroutine evaluates the function that defines the least
C squares problem

C ************
SUBROUTINE FIND(M,N,X,F)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

COMMON /PARI/ COV(10),CCONCV(10),RADPV(10),RHOPV(10),
      & PARV(4,10),NDPV(10),NDSET,IPS(4),ISCALE(4),
      & TM(50,10),YM(50,5,10),IDREP(10),NDPSV(10),
      & YF(50,10)

DIMENSION X(4),F(500)
DIMENSION TT(50),YY(50)
DIMENSION SSQV(10),XXV(4),YYM(50,5)

DATA ICALL /0/

ICALL=ICALL+1

* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

C If trouble, limit the parameters to the smallest value of 10D-30
C
DO 1 KK=1,N
   X(KK)=DMAX1(X(KK),1.0D-30)
1 CONTINUE

C
WRITE(*,1000) ICALL,(X(KK)*10.0D0**ISCALE(KK),KK=1,N)
WRITE(NDSET+1,1000) ICALL,(X(KK)*10.0D0**ISCALE(KK),KK=1,N)

C
LL=1
DO 111 K=1,NDSET
   ************
   DO 2 L=1,NDPV(K)
      TT(L)=TM(L,K)
      DO 229 KI=1,IDREP(K)
         YYM(L,KI) = YM(L,KI,K)
229 CONTINUE
2 CONTINUE

C
LLL=0
DO 9 II=1,4
   IF(IPS(II).EQ.1) THEN
      LLL=LLL+1
      XXV(II)=X(LLL)*10.0D0**ISCALE(LLL)
   ELSE
      XXV(II)=PARV(II,K)
   END IF
9 CONTINUE

C
CALL HSDM(COV(K),CCONCV(K),RADPV(K),RHOPV(K),XXV(1),XXV(2),
      & XXV(3),XXV(4),TT,YY,NDPV(K),YYM,IDREP(K))
C
C Set up the residual vector F
C
SSQV(K)=0.0D0
DO 3 L=1,NDPV(K)
\[ YF(L,K) = YY(L) \]
\[
\text{DO 4 \textbf{ID} = 1, IDREP(K)}
\]
\[
\text{IF (YM(L,ID,K).LE.1.1D0) THEN}
\]
\[
F(LL) = (YM(L,ID,K) - YY(L)) / YM(L,ID,K)
\]
\[
\text{WRITE(*,*) LL, F(LL)}
\]
\[
SSQV(K) = SSQV(K) + F(LL) * F(LL)
\]
\[
LL = LL + 1
\]
\[
\text{END IF}
\]
\[
4 \text{ CONTINUE}
\]
\[
3 \text{ CONTINUE}
\]
\[
111 \text{ CONTINUE}
\]
\[
\text{C}
\]
\[
\text{WRITE(*,1000) ICALL,(SSQV(I),I=1,NDSET)}
\]
\[
\text{WRITE(NDSET+1,1000) ICALL,(SSQV(I),I=1,NDSET)}
\]
\[
1000 \text{ FORMAT (1X,15,6E16.6)}
\]
\[
\text{C}
\]
\[
\text{RETURN}
\]
\[
\text{END}
\]

---

**Subroutine HSDM(C01, CCONC1, RADP1, RHOP1, XKFI, DS1, XK1, XN1, & TT, YY, NDP, YYM, IDREP1)**

- **Purpose:** Numerically solves the HSDM

```
DIMENSION TT(1), YY(1), YYM(1,1)
DATA ICALL /0/
OPEN(31, FILE='PART.C', STATUS='OLD')
OPEN(32, FILE='HSDM.RAW', STATUS='OLD')
IF(ICALL .EQ. 0) THEN
    CALL INPUT
    CALL INCOL
    ICALL=1
    END IF
C0=C01
CCONC=CCONC1
RADP=RADP1
RHOP=RHOP1
```
XK=XK1
XN=XN1
XKF=XKF1
DS=DS1
C
CALL INIT
C
CALL CALCC(TT,YY,NDP,YYM,IDREP1)
C
RETURN
C
END
C-----------------------------------------------------------------
SUBROUTINE INPUT
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XJCN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
OPEN(30,FILE='HSDM.C',STATUS='OLD')
REWIND (30)
READ(30,*) IPRC,IPRI,IPRO
C
Control Parameters
C
READ(30,* ) NCP
READ(30,* ) TOL,METH,MITER
READ(30,* ) DTINIT
C
CLOSE (30)
C
RETURN
END
C-----------------------------------------------------------------
SUBROUTINE INCOL
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XP,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
DIMENSION DUMMY(14)
C
IFL1=0
IFL2=0
10 CONTINUE

READ(31,*) ID
IF(ID.EQ.999) THEN

C
SOMETHING IS WRONG
C
WRITE(*,*) 'REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE'
STOP 'ERROR - all done'
END IF

C
IF(ID.EQ.NCP) THEN
IF(L1=1
END IF

C
READ IN AND DISTRIBUTE
C
IF(IFL1.NE.0) THEN
READ(31,1001) (WP(I),I=1,ID)
DO 2 I=1,ID
READ(31,1001) (BP(I,J),J=1,ID)
2 CONTINUE
C
IF(IFL1.EQ.0) GO TO 10
IF(IFL1.EQ.1) GO TO 11
C
END IF
C
IF(IFL1.EQ.0) THEN
READ(31,1001) (DUMMY(I),I=1,ID)
DO 6 I=1,ID
READ(31,1001) (DUMMY(J),J=1,ID)
6 CONTINUE
GO TO 10
END IF
C
10 CONTINUE
C
WRITE THE MATRICES
C
IF(IPRC.EQ.1) THEN
WRITE(*,*) 'WEIGHTS ' WRITE(*,1001) (WP(I),I=1,NCP)
WRITE(*,*) 'COLLOCATION MATRIX (B)' DO 13 I=1,NCP
WRITE(*,1001) (BP(I,J),J=1,NCP)
13 CONTINUE
END IF
C
1001 FORMAT(4D20.12)
C
RETURN
END

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SUBROUTINE INIT
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
NTOT=NCP+1
C INITIAL CONDITION FOR SOLID PHASE
DO 11 I=1,NTOT-1
  Y(I)=0.0D0
11 CONTINUE
C LIQUID PHASE
Y(NTOT)=1.0D0
C COMPUTE DEPENDENT PARAMETERS
Q0=XK*C0**XN
CD=CCONC*Q0/C0
B1=XKF*RADP*C0
B2=DS*RHOP*Q0*1000.0D0
BIOT=B1/B2
TFAC=DS/(RADP*RADP)
IF(IPRI.EQ.1) THEN
  WRITE(32,1001) C0,CCONC,CD
  WRITE(32,1004) DS
  WRITE(32,1005) XKF
  WRITE(32,1006) BIOT
  WRITE(32,1007) RADP
  WRITE(32,1008) RHOP
  WRITE(32,1009) XK
  WRITE(32,1010) XN
  WRITE(32,1011) TFAC
ENDIF
C CONTROL PARAMETER
WRITE(32,1013) NTOT,TOL,METH,MITER,DTINIT,DTOUT,TFINAL
END IF
C FORMAT STATEMENTS
C
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SUBROUTINE CALCC(TT,YY,NDP,YYM,IDREP1)

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(I4),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XICXN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(I5),NTOT

DIMENSION TT(I),YY(I),YYM(I,1)

DIMENSION A(I,1),PARAM(50)

EXTERNAL FCN,FCNJ

N=NTOT
IDO=1
DO 50 I=1,50
    PARAM(I)=0.0D0
50 CONTINUE
    PARAM(1)=DTINIT
    PARAM(12)=METH
    PARAM(13)=MITER

T=0.0D0
ITRY=0
ITRYT=0
TPHYS=0.0D0
ITER=0

C DO 100 IP=1,NDP
C ITER=ITER+1
TEND=TT(IP)*TFAC
C IF(TT(IP) .LE. 0.01) THEN
   YY(IP)=1.0D0
   GO TO 100
END IF
C ITRY=0
C CALL DIVPAG(IDO,N,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
C ITRYT=ITRYT+ITRY
T=TEND
TPHYS=T/TFAC
C WRITE(*,1000) TPHYS,(YYM(IP,KKI),KKI=1,IDREP1),Y(NTOT)
1000 FORMAT(1X,5E16.6)
C YY(IP)=Y(NTOT)
C 100 CONTINUE
C IDO=3
CALL DIVPAG(IDO,N,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
C RETURN
END

C-------------------------------------------------------------------------
SUBROUTINE FCNJ(N,T,Y,PD)
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C DIMENSION Y(N),PD(N,N)
C RETURN
END
C-------------------------------------------------------------------------
SUBROUTINE FCN(N,T,Y,YPRIME)
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
C

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DIMENSION Y(N), YPRIME(N)
DIMENSION BB(I4)

C
ITRY=ITRY+1
C
NTOT=N
KK=0
II=0
C
NICP=NCP-1
C
DO 30 J=1,NICP
BB(J)=0.0D0
30 CONTINUE
C
WW=0.0D0
C
DO 50 I=1,NICP
II=II+1
LL=0
C
DO 40 J=1,NCP
LL=LL+1
BB(I)=BB(I)+BP(I,J)*Y(LL)
40 CONTINUE
C *****************************************************************
C MASS BALANCE INSIDE PARTICLE (EXCEPT BOUNDARY)
C *****************************************************************
YPRIME(II)=BB(I)
WW=WW+WP(I)*YPRIME(II)
50 CONTINUE
C *****************************************************************
C SOLID-LIQUID INTERFACE (HEAT EQ. AT INTERFACE
C *****************************************************************
II=II+1
BSUM=0.0D0
C
DO 11 KKK=1,NCP
BSUM=BSUM+BP(NCP,KKK)*Y(KKK)
11 CONTINUE
C
IF(Y(II).LT.0.0D0) THEN
YPRIME(II) = (((BIOT*(Y(NTOT)-0.0D0)/WP(NCP))+BSUM)*0.5D0
ELSE
YPRIME(II) = (((BIOT*(Y(NTOT)-(Y(II)**(1.0D0/XN)))-WW)/
& WP(NCP))+BSUM)*0.5D0
ENDIF
C *****************************************************************
C LIQUID PHASE MASS BALANCE
C *****************************************************************
YPRIME(NTOT)=-3.0D0*CD*(WW+(YPRIME(II)*WP(NCP)))
C RETURN
END
PROGRAM HSDM

C This FORTRAN program <HSDM.FOR> solves the HSDM system of partial differential equations for a closed batch reactor or a plug flow reactor using the orthogonal collocation technique. The IML subroutine DIVPAG is used to solve for the bulk concentration profile versus time.

C The input file <HSDM.IN> requires the user to enter the parameters Co, Ds, kf, K, 1/n, apparent density, and final time. The other control terms do not need to be changed. After running the program, the output file <HSDM.OUT> will contain the bulk concentration profile as a function of time.

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IMPLICIT DOUBLE PRECISION (A-H,O-Z)

COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ CO,QO,CCONC,DS,XKF,
               & X*LXN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTTNIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT

OPEN(30,FILE='HSDM.IN',STATUS='OLD')
OPEN(31,FILE='PART.C',STATUS='OLD')
OPEN(32,FILE='HSDM.OUT',STATUS='OLD')

CALL INPUT
CALL INCOL
CALL INIT
CALL CALCC
STOP ' all done'
END

--------------------------------------------------------------------------------

This subroutine reads the data from the input file HSDM.IN

--------------------------------------------------------------------------------
SUBROUTINE INPUT

C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
READ(30,*) IPRC,IPRI,IPRO
C
C Physical parameters
C
READ(30,*) C0
READ(30,*) CCONC
READ(30,*) DS
READ(30,*) XKF
READ(30,*) XK
READ(30,*) XN
XK = XK*1000.0D0**XN
READ(30,*) RADP
READ(30,*) RHOP
C
C Control parameters
C
READ(30,*) NCP
READ(30,*) TOL,METH,MITER
READ(30,*) DTINIT
READ(30,*) DTOUT
READ(30,*) TFINAL
READ(30,*) ITMAX
C
RETURN
END

C This subroutine determines the weights and collocation matrix
C
SUBROUTINE INCOL
C
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
DIMENSION DUMMY(14)
C
IFL1=0

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IFL2=0

10 CONTINUE

C

READ(31,*) ID
IF(ID .EQ. 999) THEN
C SOMETHING IS WRONG
WRITE(*,*) ' REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE'
STOP ' ERROR - all done'
END IF

C

IF(ID .EQ. NCP) THEN
IFLI=1
END IF

C *****************************************************************
C Read weights into array WP and collocation matrix into array BP
C *****************************************************************

IF(IFLI .NE. 0) THEN
READ(31,IOO1) (WP(I),I=1,ID)
DO 2 I=1,ID
READ(31,1001) (BP(I,J),J=1,ID)
2 CONTINUE
IF(IFLI .EQ. 0) GO TO 10
IF(IFLI .EQ. 1) GO TO 11
END IF

C

IF(IFLI .EQ. 0) THEN
READ(31,1001) (DUMMY(I),I=1,ID)
DO 6 I=1,ID
READ(31,1001) (DUMMY(J),J=1,ID)
6 CONTINUE
GO TO 10
END IF

C

11 CONTINUE

C Write the arrays to the screen if desired
C

IF(IPRC .EQ. 1) THEN
WRITE(*,*) ' WEIGHTS '
WRITE(*,IOO1) (WP(I),I=1,NCP)
WRITE(*,*) ' COLLOCATION MATRIX (B)'
DO 13 I=1,NCP
WRITE(*,IOO1) (BP(I,J),J=1,NCP)
13 CONTINUE
END IF

C

1001 FORMAT(4D20.12)
C

RETURN
END

C*****************************************************************
C This subroutine writes initial data to the output file HSDM.OUT
C

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SUBROUTINE INIT

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,W(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
  & XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(I5),NTOT

NTOT=NCP+1

DO 11 I=1,NTOT-1
  Y(I)=0.0D0
11 CONTINUE

DO 11 CONTINUE

Y(NTOT)=1.0D0

Q0=XK*C0**XN

CD=CCONC*Q0/C0

B1=XKF*RADP*C0
B2=DS*RHOP*Q0*1000.0D0
BIOT=B1/B2

TFAC=DS/(RADP*RADP)

IF(IPRI .EQ. 1) THEN
  WRITE(32,1001) C0,CCONC,CD
  WRITE(32,1004) DS
  WRITE(32,1005) XKF
  WRITE(32,1006) BIOT
  WRITE(32,1007) RADP
  WRITE(32,1009) XK
  WRITE(32,1010) XN
  WRITE(32,1011) TFAC
  WRITE(32,1013) NTOT,TOL,METH,MITER,DTINIT,DTOUT,TFINAL
END IF

FORMAT STATEMENTS

1001 FORMAT(2X,'C0 = ',E12.6/,
  & 2X,'CONC = ',E12.6/,
  & 2X,'CD = ',E12.6/)
C
1004 FORMAT(1X,'DS = ',E12.5)
1005 FORMAT(1X,'XKF = ',E12.5)
1006 FORMAT(1X,'BIOT = ',E12.5)
1007 FORMAT(1X,'RADP = ',E12.5)
1008 FORMAT(1X,'RHOP = ',E12.5)
1009 FORMAT(1X,'XK = ',E12.5)
1010 FORMAT(1X,'XN = ',E12.5)
1011 FORMAT(1X,'TFAC = ',E12.5)
C
1013 FORMAT(1X,'NTOT = ',I4,/,&
1X,'TOL = ',E16.6,/,&
1X,'METH = ',I4,/,&
1X,'MITER = ',I4,/,&
1X,'DTINIT = ',E16.6,/,&
1X,'DTOUT = ',E16.6,/,&
1X,'TFINAL = ',E16.6,/&
1X,'NULL')
C
RETURN
END
C
********************************************************************
C Set parameters for IMSL subroutine DIVPAG
********************************************************************
N=NTOT
IDO=1
DO 50 I=1,50
   PARAM(I)=0
50 CONTINUE
   PARAM(1)=DTINIT
   PARAM(12)=METH
   PARAM(13)=MITER
C
T=0.0D0
C
ITRY=0

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ITRYT=0
TPHYS=0.0D0
ITER=0

C
WRITE(*,*) TPHYS,Y(NTOT)
WRITE(32,1500) TPHYS,Y(NTOT)

C
100 CONTINUE
C
ITER=ITER+1
TEND=T+DTOUT*TFAC
C
ITRY=0
CALL DIVPAG(IDO,N,FCN,FCNJ,N,TA,TEND,TOL,PARAM,Y)
C
ITRYT=ITRYT+ITRY
T=TEND
TPHYS=T/TFAC
C
WRITE(*,*) TPHYS,Y(NTOT)
WRITE(32,1500) TPHYS,Y(NTOT)
C
1500 FORMAT(1X,F8.2,T10,F10.6)
C
IF (T/TFAC .LT. TFINAL) GO TO 100
C
WRITE(*,*) 'ITRYT = ,ITRYT
WRITE(32,*) '999 999 999 999 999 999 999' RETURN
END
C-------------------------------------------------------------------------
Q * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C This is a dummy subroutine that is required by DIVPAG
Q * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
SUBROUTINE FCNJ(N,T,Y,PD)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
DIMENSION Y(N),PD(N,N)
C
RETURN
END
C-------------------------------------------------------------------------
Q * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C This subroutine calculates the Jacobian required by DIVPAG
Q * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
SUBROUTINE FCN(N,T,Y,YPRIME)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
&                          XK,XN,RADP,RHOP,BIOT,CD,TFAC

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COMMON /WORK/ DTINIT, DTOUT, TFINAL, ITMAX, ITRY

C
DIMENSION Y(N), YPRIME(N)

DIMENSION BB(I4)

C
ITRY = ITRY + 1

C
NTOT = N

KK = 0

II = 0

C
NICP = NCP - 1

C
DO 30 J = 1, NICP

BB(J) = 0.0D0

30 CONTINUE

C
WW = 0.0D0

C
DO 50 I = 1, NICP

II = II + 1

LL = 0

C
DO 40 J = 1, NCP

BB(I) = BB(I) + BP(I, J) * Y(LL)

40 CONTINUE

C
Mass balance inside particle (except boundary)

C
YPRIME(II) = BB(I)

C
WW = WW + WP(I) * YPRIME(II)

50 CONTINUE

C
Solid-liquid interface (heat eq. at interface)

C
II = II + 1

BSUM = 0.0D0

C
DO 11 LLL = 1, NCP

BSUM = BSUM + BP(NCP, LLL) * Y(LLL)

11 CONTINUE

C
IF(Y(II) .LT. 0.0D0) THEN

YPRIME(II) = (((BIOT * (Y(NTOT) - 0.0D0) - WW) / WP(NCP)) + BSUM) * 0.5D0

C
ELSE

YPRIME(II) = (((BIOT * (Y(NTOT) - (Y(II)**(1.0D0/XN)))) - WW) / WP(NCP) + BSUM) * 0.5D0

END IF

C
Liquid phase mass balance
C  ***********************************************************************
YPRIME(NTOT)=-3.0D0*CD*(WW+(YPRIME(I1)*WP(NCP)))
C
RETURN
END
CSTR: EQUATION SOLVING COMPUTER PROGRAM

PROGRAM CSTR
C
C ***************************************************************
C * This FORTRAN program is used to solve for the steady-state *
C * performance of PAC in a CSTR with or without solids residence *
C * time distribution. The program uses the secant method to solve *
C * the nonlinear equation (i.e the CSTR model). The convergence *
C * criterion for the infinite series is a relative error of <.1%. *
C * *
C * The input file <CSTR.IN> should be used to enter the parameters*
C * R, Ds, K, N, Cin, Ccin, and final time. The other parameters *
C * are the first and second guesses for the value of Ceff in ug/l *
C * which do not need to be changed. Finally the tolerable error is*
C * set to 1.0e-04; it can be increased to 1.0e-03 depending on *
C * the sensitivity of the required data. *
C * *
C * The output file <CSTR.OUT> contains the input parameters as *
C * well as the list of the steady-state effluent concentrations *
C * as a function of solids residence time. *
C * *
C * Department of Civil Engineering *
C * UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN *
C ******************************************************************************
C
C The following are the input variables to the program:
C
C R = radius of carbon particle, cm
C Ds = surface diffusion coefficient, cm2/min
C K = Freundlich coeff, (mg/g)(ug/L)^-1/n
C N = Freundlich constant n, (inverse of 1/n)
C Cin = influent adsorbate concentration, ug/L
C CCin = influent PAC dose, mg/L
C TFINAL = final desired time, min
C A = first guess for the value of Ceff, ug/L
C B = second guess for the value of Ceff, ug/l
C E = tolerable error
C
C IMPLICIT REAL(A-H,N-Z)
C
C
C DATA INP,IOUT/5,6/
C OPEN(INP,FILE='CSTR.IN',STATUS='OLD')
C OPEN(IOUT,FILE='CSTR.OUT',STATUS='OLD')

C
C READ(INP,*) R
C READ(INP,*) DS
C READ(INP,*) FRK
C READ(INP,*) N

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READ(INP,*) CIN
READ(INP,*) CCIN
READ(INP,*) A,B,E
READ(INP,*) TFINAL
WRITE(*,*) 'Is This Completely Mixed Reactor?'
WRITE(*,*) '(1) WITH a Solids Age Distribution, or'
WRITE(*,*) '(2) WITHOUT a Solids Age Distribution ?'
READ(*,*) FLAG

WRITE(IOUT,20) R
WRITE(IOUT,25) DS
WRITE(IOUT,30) FRK
WRITE(IOUT,35) N
WRITE(IOUT,50) CIN
WRITE(IOUT,55) CCIN
WRITE(IOUT,*)

IF(FLAG.EQ.1) THEN
  WRITE(IOUT,*)'** THIS IS A CSTR WITH PAC AGE DISTRIBUTION **'
ELSE
  WRITE(IOUT,*)'** THIS IS A CSTR WITHOUT PAC AGE DISTRIBUTION ***'
END IF
WRITE(IOUT,*)

20 FORMAT(1X,'PARTICLE RADIUS, R =',F10.4,' cm')
25 FORMAT(1X,'DIFFUSION COEFFICIENT, Ds =',E10.2,' cm2/min')
30 FORMAT(1X,'FREUNDLICH CONSTANT, K =',F10.4,' (mg/g-ug/L)')
35 FORMAT(1X,'FREUNDLICH CONSTANT, N =',F10.4)
50 FORMAT(1X,'INFLUENT ADSORBATE CONCENTRATION =',F10.4,' ug/L')
55 FORMAT(1X,'INFLUENT PAC CONCENTRATION =',F10.4,' mg/L')

ZZ=0
WRITE(IOUT,90) ZZ,CIN/CIN
WRITE(*,90) ZZ,CIN/CIN
XII=0.0
13 IF(XII .LT. 4.95) THEN
  XII=XII+1.0
ELSE
  XII=XII+5.0
END IF
THS = XII
PI = 3.141590

IF(FLAG.EQ.2) THEN
  CALL XSUM(R,THS,DS,PI,S)
ELSE
  CALL SUM(R,THS,DS,PI,S)
END IF

COEF = CCIN*FRK*(H6*S/PI**2)

220

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CALL ITER(CIN,CONC,COEF,N,A,B,E)

CONCNON = CONC/CIN
WRITE(OUT,90) THS/60,CONCNON
WRITE(*,90) THS/60,CONCNON
90 FORMAT(1X,F10.4,T20,F10.4)
IF(XII .LT. TFINAL) GOTO 13

STOP
END

SUBROUTINE SUM(R,THS,DS,PI,S)
IMPLICIT REAL(A-H,N-Z)

CKAPPA = R*2/THS/DS/PI**2
S = 0
DO 15 I=1,100
SP = S
S = S + (1/(I**2*(1+I**2/CKAPPA)))
IF(((S-SP)/S) .LT. 0.001) GOTO 77
15 CONTINUE
77 RETURN
END

SUBROUTINE ITER(CIN,X,COEF,N,A,B,E)
IMPLICIT REAL(A-H,N-Z)

40 X = A
CALL FUNCT(Y,CIN,X,COEF,N)
U = Y
X = B
CALL FUNCT(Y,CIN,X,COEF,N)
V = Y
CE = (B*U-A*V)/(U-V)
X = CE
CALL FUNCT(Y,CIN,X,COEF,N)
IF(ABS(Y) .GT. E) THEN
A = B
B = CE
GOTO 40
END IF
RETURN
END
SUBROUTINE FUNCT(Y,CIN,X,COEF,N)
IMPLICIT REAL(A-H,N-Z)

Y = CIN - X - COEF*X**(I/N)
RETURN
END

SUBROUTINE XSUM(R,THS,DS,PI,S)
IMPLICIT REAL(A-H,N-Z)
CKAPPA=R**2/THS/DS/PI**2
S=0
DO 185 I=1,100
   SP=S
   FACT=(EXP(-1.0*I**2/CKAPPA))/I**2
   S=SP+FACT
   IF((FACT/S) .LT. 0.001) GOTO 187
185 CONTINUE
187 CONTINUE
RETURN
END

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FS-SI: FIXED-BED ADSORPTION KINETIC PARAMETER SEARCH
COMPUTER PROGRAM

C       FS-SI.FOR
C
C       FIXED BED ADSORPTION, FS MODEL
C       MAIN PROGRAM
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
DIMENSION X(2),XGUESS(2),XSCALE(2),FSCALE(100)
*    ,IPARAM(6),RPARAM(7),FVEC(100),FJAC(100,2),FDUMY(100)
C
DIMENSION CB(21),CCB(21)
*    ,Q(21,21),QQ(21,21)
*    ,SOLUTE(18)
*    ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
C
DIMENSION CDI(200),TDATAI(200)
COMMON /BLOCKC/ FMIN,TP(4000),CP(4000)
*    ,TD(200),CD(200),CINT(200),RES(200),NDATA
C
COMMON /BL1/CB,Q,QSD,F,FD
*    /BL2/CCB,QQ
*    /BL3/S1,S2,S3,S4
*    /BL4/DATA/SOLUTE,ISO,A,B,C0,Q0,IR0
*    ,U,DIA,RS,RB,AKF,DS,DB
*    ,DELT,DELTMX,TEND,DELZ,ZEND,DTUBE
*    ,IITM
C
EXTERNAL FCN,DU4LSF
C
OPEN(5,FILE='FS.IN')
OPEN(6,FILE='FS-SI.OUT')
C
READ(5,1001) SOLUTE
ISO=2
READ(5,*) A
READ(5,*) B
READ(5,*) C00
READ(5,*) IR0
C
READ(5,*,END=500) U
READ(5,*,END=500) DIA
READ(5,*,END=500) RS
READ(5,*,END=500) RB
READ(5,*,END=500) AKF
READ(5,*,END=500) DS

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READ(5,*,END=500) DB
READ(5,*) DELT
READ(5,*) DELTMX
READ(5,*) TEND
READ(5,*) DELZ
READ(5,*) ZEND
READ(5,*) DTUBE
C
READ(5,*) IITM
C
C0=C00/1000.0
Q0=A*C00**B
C
WRITE(6,1008) SOLUTE,A,B,C00,Q0,IR0
  * ,U,DIA,RS,RA,KF,DS,DR
  * ,DELT,DELMX,TEND,DELZ,ZEND,DTUBE
WRITE(*,1008) SOLUTE,A,B,C00,Q0,IR0
  * ,U,DIA,RS,RA,KF,DS,DR
  * ,DELT,DELMX,TEND,DELZ,ZEND,DTUBE
1001 FORMAT(18A4)
1002 FORMAT(110,3F10.0,110)
C 1003 FORMAT(F10.0)
C 1007 FORMAT(110)
1008 FORMAT(1H,'FIXED BED ADSORPTION, FS MODEL'/
  * ,1H,'SOLUTE = ',5X,A4/
  * ,1H,'A,B,C0,Q0,IR0 = ',1P4E16.5,110/
  * ,1H,'U,DIA,RS,RA,KF,DS,DR ='/1H,1P7E16.5/
  * ,1H,'DELT,DELMX,TEND,DELZ,ZEND,DTUBE ='/1H,1P6E16.5/
C
READ(5,*) NDATA
IF (NDATA.LE.0) STOP
DO 10 I=1,NDATA
  READ(5,*) TDATAI(I),CDI(I)
  CD(I)=CDI(I)/C0/1000.0
  TD(I)=TDATAI(I)/60.0
10 CONTINUE
C
A=A*1000.0**B
C
R=U*60.
RS=RS*1000.
RB=RB*1000.
C
AKF=AKF*3600.
C
DS=DS*3600.
DB=DB*3600.
C
searching for Kf and Ds
N=2
M=NDATA
LDFJAC=M
XGUESS(1)=AKF
XGUESS(2)=DS*1.0E10
DO 50 I=1,N
  XSANE(I)=1.0
50 CONTINUE

224
50 CONTINUE
DO 51 I=1,M
FSCALE(I)=1.0
51 CONTINUE
C
CALL DU4LSF(IPARAM,RPARAM)
IPARAM(3)=400
IPARAM(4)=2500
C
WRITE(*,*) 'start searching'
C
CALL DUNLSF(FCN,M,N,XGUESS,XSCALE,FSCALE,
& IPARAM,RPARAM,X,FVEC,FJAC,LDFJAC)
C
CALL FCN(M,N,X,FDUMY)
C
AKF=DABS(X(1))
DS=DABS(X(2)/1.0E10)
WRITE(*,120) AKF,DS,FMIN
WRITE(6,120) AKF,DS,FMIN
120 FORMAT(1X,'OPTIMUM/'
& 'KF=',1PG15.7,4X,'DS=',G15.7/
& 'I9X,'ERROR=',G15.7)
WRITE(6,*)
& ' TIME(hr) C/Co(obs) C/Co(cal) error(%)'
DO 11 I=1,NDATA
WRITE(6,121) TD(I),CD(I),CINT(I),RES(I)
11 CONTINUE
121 FORMAT(1X,4(1PG15.5))
C
500 CONTINUE
STOP 'ALL DONE.'
END
C
C
SUBROUTINE FCN(MS,NS,XX,FF)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
DIMENSION XX(NS),FF(MS)
C
DIMENSION CB(21),CCB(21),QT(21),Z(21)
* ,Q(21,21),QQ(21,21),CS(21),CCS(21)
* ,N(21),NR(21),INDEX(21),IR(21),F1(21),F2(21)
* ,CK(50),QK(50),FK(50),CKK(50),SOLUTE(18)
* ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
* ,CBX(25),QTX(25)
C
COMMON /BLOCKC/ FMIN,TP(4000),CP(4000)
* ,TD(200),CD(200),CINT(200),RES(200),NDATA
C
COMMON /BL1/CB,Q,QSD,F,FD
* /BL2/CCB,QQ
* /BLS/S1,S2,S3,S4

225

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BLDATA/SOLUTE,ISO,A,B,C0,Q0,IR0
,UDIA,RS,RB,AKF,DS,DB
,DELT,DELTM,TEND,DELZ,ZEND,DTUBE
,IITM

DELT=DELTT

AKFF=DABS(XX(1))
DSS=DABS(XX(2)/1.0E10)
WRITE(*,*) 'K f & Ds ',AKFF,DSS
AKF=AKFF*3600.0
DS=DSS*3600.0
WRITE(*, 1008) SOLUTE,ISO,A,B,C0,Q0,IR0
,UDIA,RS,RB,AKF,DS,DB
,DELT,DELTM,TEND,DELZ,ZEND,DTUBE
1008 FORMAT( IH , 'SOLUTE = ', 5X , 18A4/
IH ,1P7E16.5/
IH.1P6E16.5)

NKK=25
CKK(1)=0.0
CKK(2)=0.0001
CKK(3)=0.0002
CKK(4)=0.0005
CKK(5)=0.001
CKK(6)=0.002
CKK(7)=0.005
CKK(8)=0.0075
CKK(9)=0.01
CKK(10)=0.02
CKK(11)=0.05
CKK(12)=0.075
CKK(13)=0.1
CKK(14)=0.15
CKK(15)=0.2
CKK(16)=0.3
CKK(17)=0.4
CKK(18)=0.5
CKK(19)=0.6
CKK(20)=0.7
CKK(21)=0.8
CKK(22)=0.9
CKK(23)=1.0
CKK(24)=1.5
CKK(25)=2.0

NK=NKK
DO 120 K=1,NK
CK(K)=C0*CKK(K)
IF(ISO.EQ.1) QK(K)=A*B*CK(K)/(1.+B*CK(K))
IF(ISO.EQ.2) QK(K)=A*CK(K)**B
IF(ISO.EQ.3) QK(K)=A*CK(K)
IF(K.EQ.1) GO TO 120

226
FDK(K)=CK(K)-CK(K-1)/(QK(K)-QK(K-1))
120 CONTINUE
Q0=QK(23)

C
RADIUS=DIA/2.
NR0=20*2**IR0
C NR0=5*2**IR0
DELR=RADIUS/DFLOAT(NR0)
AV=3.*RB/RS/RADIUS
EB=1.-RB/RS
COEF=DTUBE**2*3.14/4.*U/1000.
F10=DELR**2/DS/DELT
F20=AKF/RS/DS/RADIUS*DELR*(RADIUS+DELR)
IF(DB.EQ.0.) FY=-AKF*AV/U
IF(DB.NE.0.) FY=(U-DSQRT(U**2+4.*AKF*AV*EB*DB))/2./EB/DB
F3=U/AKF/AV/DELT
F4=DEXP(FY*DELT)
F5=AKF*AV*DELT/2./RB
6 DO 130 I=1,121
ZX=DELT*DFLOAT(I-1)
IF(ZX.GE.ZEND) GO TO 7
CX=DEXP(FY*ZX)
IF(CX.LT.0.001) M=I-1
IF(CX.LT.0.001) M1=I
IF(CX.LT.0.001) GO TO 8
130 CONTINUE
DELT=2.*DELT
F3M1=F3
F4M1=F4
F3=M=20
M1=21
DELT=ZEND/20.
F3M1=F3
F4M1=F4
8 DO 150 I=1,M1
Z(I)=DFLOAT(I-1)*DELT
CB(I)=DEXP(FY*Z(I))*C0
CBX(I)=CB(I)/C0
CCB(I)=CB(I)
CS(I)=0.
CCS(I)=0.
QT(I)=0.
IR(I)=IR0
NR(I)=NR0
F1(I)=F10
F2(I)=F20
N(I)=11
INDEX(I)=0
DO 140 J=U,1
Q(J,I)=0.
QQ(J,I)=0.
140 CONTINUE
227
CONTINUE
T=0.

IIT=0
IITT=0

KW=0
KC=0
KXY=0
NPT=0
KWH=10
KCH=100
KXYH=10

WRITE(*,10I0) T
WRITE(*,10I11) (Z(I),I=1,M1)
WRITE(*,10I2) (CBX(I),I=1,M1)

WRITE(6,1010) T
WRITE(*,1010) T

10 T=T+DELT
IIT=IIT+1

KXY=KXY+1
KW=KW+1
KC=KC+1
DO 200 I=1,M1
20 QSD=QQ(I,21)
DO 210 K=2,NK
IF(QSD.LT.QK(K)) GO TO 21
21 FD=FDK(K)
F=FDK(K)*(QSD-QK(K-1))+CK(K-1)
IF(I.NE.1) X=CCS(I-1)
IF(I.NE.1) Y=CCB(I-1)
IF(Z(I).NE.ZEND) F3I=F3
IF(Z(I).NE.ZEND) F4I=F4
IF(Z(I).EQ.ZEND) F3I=F3M1
IF(Z(I).EQ.ZEND) F4I=F4M1
CALL KEISU(I, N(I), NR(I), INDEX(I), IR(I))
* ,F1(I), F2(I), F3I, F4I, X, Y, CS(I))
CALL GAUSS(I, N(I))
IF(ISO.EQ.3) GO TO 22
ERR=(QQ(I,21)-QSD)/QQ(I,21)
IF(ABS(ERR).GT.1.E-4) GO TO 20
22 CCS(I)=F
CUTQ=QQ(I,21)*0.01
IF(QQ(I,N(I)).LT.CUTQ) GO TO 200
IF(N(I).EQ.1) GO TO 23
N(I)=N(I)-1
GO TO 20
23 IF(IR(I).EQ.0) GO TO 200

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\begin{verbatim}
IR(I)=IR(I)-1
NR(I)=NR(I)/2
DELR=RADIUS/DFLOAT(NR(I))
F1(I)=DELR**2/DS/DELT
F2(I)=AKF/RS/DFLOAT(RADIUS+DELR)
N(I)=10
INDEX(I)=0
DO 220 J=21,11,-1
  JJ=2*J-21
  Q(I,J)=Q(I,JJ)
  QQ(I,JJ)=QQ(I,JJ)
220 CONTINUE
DO 230 J=1,10
  Q(I,J)=0.
  QQ(I,J)=0.
230 CONTINUE
GO TO 20
200 CONTINUE
DO 240 I=1,M1
  QT(I)=F5*(CCB(I)+CB(I)-CCS(I)-CS(I))+QT(I)
  CB(I)=CCB(I)
  CS(I)=CCS(I)
  DO 240 J=1,21
    Q(I,J)=QQ(I,J)
240 CONTINUE
IF(Z(M1).LT.ZEND) GO TO 30
  IF(Z(M1).LT.ZEND*.9999) GO TO 30
  IF(KXY.LT.KXYH) GO TO 30
  NPT=NPT+1
  TW(NPT)=T
  CWNPT=CB(M1)/CO
  VOL(NPT)=T*COEF
  KXY=0
30 IF(KW.LT.KWH) GO TO 40
  DO 300 I=1,M1
    CBX(I)=CB(I)/CO
    QTX(I)=QT(I)/Q0
300 CONTINUE
IF(IIT.GE.IITM) IIT=0
  IF(IIT.EQ.0) THEN
    IITT=IITT+1
  ELSE
    END IF
  WRITE(6,*) M1,M
  WRITE(6,1010) T,CWNPT
  WRITE(*,1010) T,CWNPT
  TP(IITT)=T
  CP(IITT)=CWNPT
END IF
WRITE(6,1011) (Z(I),I=1,M1)
WRITE(6,1012) (CBX(I),I=1,M1)
WRITE(6,1013) (QTX(I),I=1,M1)
1010 FORMAT(1H,,T=',1PE10.3,,(HR),,,CB/CO=' ,1PE11.4)
\end{verbatim}
1011 FORMAT(1H,' Z=*1P11E11.4/1H,7X,1P11E11.4)
1012 FORMAT(1H,' C/C0=1P11E11.4/1H,7X,1P11E11.4)
1013 FORMAT(1H,' Q/Q0=1P11E11.4/1H,7X,1P11E11.4)

KW=0
KXY=0
IF(CB(M1)/C0.GE.0.98) GO TO 50
IF(T.GE.TEND) GO TO 50
IF(KC.LT.KCH) GO TO 40
KC=0
KCH=90
IF(10.*DELT.GE.DELTMX) KWH=10
IF(10.*DELT.GE.DELTMX) GO TO 40
DELT=10.*DELT
F10=F10/10.
F5=F5*10.
DO 310 I=1,M1
F1(I)=F1(I)/10.
INDEX(I)=0
310 CONTINUE
40 IF(QT(2)/Q0.LT.0.999) GO TO 45
IF(M.EQ.1) GO TO 50
M=M-1
M1=M1-1
DO 400 I=1,M1
II=I+1
Z(I)=Z(II)
CB(I)=CB(II)
CCB(I)=CCB(II)
CS(I)=CS(II)
CCS(I)=CCS(II)
QT(I)=QT(II)
IR(I)=IR(II)
NR(I)=NR(II)
F1(I)=F1(II)
F2(I)=F2(II)
N(I)=N(II)
INDEX(I)=INDEX(II)
DO 400 J=1,21
Q(I,J)=Q(I,J)
QQ(I,J)=QQ(I,J)
S1(I,J)=S1(I,J)
S2(I,J)=S2(I,J)
S3(I,J)=S3(I,J)
400 CONTINUE
CB(1)=C0
CCB(1)=C0
45 IF(CB(M1)/C0.LT.0.001) GO TO 10
IF(Z(M1).GE.ZEND) GO TO 10
C IF(Z(M1).GE.ZEND*.0.99999) GO TO 10
IF(M1.EQ.21) GO TO 46
M=M+1
M1=M1+1
GO TO 47
46 DELZ=2.*DELT

230
F3 = U/AFK/AV/DELZ
F4 = DEXP(FY*DELZ)
DO 410 I = 2, 11
II = 2*I - 1
Z(I) = Z(II)
CB(I) = CB(II)
CCB(I) = CCB(II)
CS(I) = CS(II)
CCS(I) = CCS(II)
QT(I) = QT(II)
IR(I) = IR(II)
NR(I) = NR(II)
F1(I) = F1(II)
F2(I) = F2(II)
N(I) = N(II)
INDEX(I) = INDEX(II)
DO 410 J = 1, 2I
Q(I, J) = Q(II, J)
QQ(U) = Q(IU)
S1(I, J) = S1(I, J)
S2(I, J) = S2(I, J)
S3(I, J) = S3(I, J)
410 CONTINUE
M = 11
M1 = 12
C M = 10
C M1 = 11
47 Z(M1) = Z(M) + DELZ
CB(M1) = CB(M) + 4 + CS(M) + (F3 - F4 - F3*F4)
IF(Z(M1).LT.ZEND) GO TO 48
DELZM1 = ZEND - Z(M)
F3M1 = U/AFK/AV/DELZM1
F4M1 = DEXP(FY*DELZM1)
Z(M1) = ZEND
CB(M1) = CB(M) + 4M1 + CS(M) + (F3M1 - F4M1 - F3M1*F4M1)
48 CCS(M1) = CB(M1)
CS(M1) = 0.
QT(M1) = 0.
IR(M1) = IR0
NR(M1) = NR0
F1(M1) = F10
F2(M1) = F20
N(M1) = 11
INDEX(M1) = 0
DO 420 J = 1, 2I
Q(M1, J) = 0.
QQ(M1, J) = 0.
420 CONTINUE
GO TO 10
50 CONTINUE
C
C WRITE(*,*) 'END OF NTH SEARCH'
NP = IITT
CALL OBJFUN ( NP )
DO 81 J = 1, NDATA
   RES(J) = ((CINT(J) - CD(J))/CD(J))\times100.0
   FF(J) = DABS(RES(J))
C   WRITE(*,*) CD(J), CINT(J)
81 CONTINUE
WRITE(*,112) NDATA, FMIN
112 FORMAT(5X,'FMIN BASED ON',I4,2X,'DATA POINTS: ',3X,'FMIN = ',G15.8)
C
RETURN
END
C
C SUBROUTINE OBJFUN ( NP )
C
C******************************************************************************
C** This subroutine calculates the standard deviation between                *
C** the predicted concentrations and experimental data, if any             *
C** is given. If no data is given this subroutine is ignored.              *
C******************************************************************************
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON/BLOCKC/ FMIN, TP(4000), CP(4000)
*   TD(200), CD(200), CINT(200), RES(200), NDATA
FMIN = 0.0D0
NP1 = NP - 1
DO 10 J = 1, NDATA
   DO 5 I = 1, NP1
      IF( TD(J) .LT. TP(I) .OR. TD(J) .GT. TP(I+1) ) GO TO 5
      CAP = CP(I) + ((TD(J)-TP(I))/(TP(I+1)-TP(I)))*
            (CP(I+1)-CP(I))
      CINT(J) = CAP
      FMIN = FMIN + ((CAP-CD(J))/CD(J))**2
   GO TO 10
5 CONTINUE
10 CONTINUE
FMIN = SQRT(FMIN/FLOAT(NDATA-1))\times100.0D0
RETURN
END
C
C SUBROUTINE KEISU
SUBROUTINE KEISU (I,N,NR,INDEX, IR, F1, F2, F3, F4, X, Y, CS)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION CB(21), Q(21,21)
*   S1(21,22), S2(21,22), S3(21,22), S4(21,22)
COMMON /BL1/CB, Q, QSD, F, FD
*   /BLS/S1, S2, S3, S4
IF(INDEX.NE.0) GO TO 10
DO 100 J = 1, 20
   EJ = NR - 21 + J
IF(EJ.EQ.0.) GO TO 100
   S1(I,J) = (EJ-1)/EJ
100 CONTINUE
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S2(I,J)=F1+1.
S3(I,J)=-(EJ+1.)/2/EJ
100 CONTINUE
IF(IR.EQ.0) S2(I,1)=F1+3.
IF(IR.EQ.0) S3(I,1)=3.
S1(I,21)=-1.
S3(I,21)=-F2
S2(I,22)=1.
INDEX=1
10 DO 110 J=N,20
IF(J.EQ.1 .AND.IR.EQ.0) S4(I,1)=3*(Q(I,2)-Q(I,1))+F1*Q(I,1)
IF(J.EQ.1 .AND.IR.NE.0) S4(I,1)=(F1-1.)*Q(I,1)-S3(I,1)*Q(I,2)
IF(J.NE.1) S4(I,J)=S1(I,J)*Q(I,J-1)+(F1-1.)*Q(I,J)
*   -S3(I,J)*Q(I,J+1)
110 CONTINUE
S2(I,21)=1.+F1+F2*FD
S4(I,21)=(Q(I,20)-F2*(CS+FD*QSD)+(F1-1.)*Q(I,21)+F2*CB(I)
IF(LNE.1) S1(I,22)=(-1.+F3-F4)*FD
IF(LNE.1) S4(I,22)=(1.-F3+F4)*(F-FD*QSD)+(F3-F4)*X+F4*Y
RETURN
END
C
C SUBROUTINE GAUSS-SEIDEL
SUBROUTINE GAUSS(I,N)
IMPLICIT DOUBLE PRECISION (A-H.O-Z)
DIMENSION CB(21),QQ(21,21),QG(21)
*   ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
COMMON /BL2/CB,QQ
*   /BLS/S1,S2,S3,S4
1 DO 100 J=1,21
QG(J)=QQ(I,J)
100 CONTINUE
CBG=CB(I)
1 IF(L.EQ.1) GO TO 10
CBG(I)=(S4(I,22)-S1(I,22)*QG(21))/S2(I,22)
10 QQ(I,21)=(S4(I,21)-S1(I,21)*QG(20)-S3(I,21)*CB(I))/S2(I,21)
10 DO 110 J=20,N,-1
1 IF(L.EQ.1) QQ(I,1)=(S4(I,1)-S3(I,1)*QQ(I,2))/S2(I,1)
1 IF(L.NE.1) QQ(I,J)=(S4(I,J)-S1(I,J)*QG(J-1)-S3(I,J)*QQ(I,J+1))
*   /S2(I,J)
110 CONTINUE
1 IF(L.EQ.1) GO TO 20
ERR=(CBG(I)-CBG(I))/CBG(I)
1 IF(ABS(ERR).GT.1.E-4) GO TO 1
20 DO 120 J=21,N,-1
1 IF(QQ(I,J,EQ.0.) GO TO 120
ERR=(QQ(I,J)-QG(J))/QQ(I,J)
1 IF(ABS(ERR).GT.1.E-4) GO TO 1
120 CONTINUE
RETURN
END

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FS: FIXED-BED ADSORPTION EQUATION SOLVING COMPUTER PROGRAM

C FS.FOR

C

C FIXED BED ADSORPTION, FS MODEL

C MAIN PROGRAM

C IMPLICIT DOUBLE PRECISION (A-H,O-Z)

C

DIMENSION CB(21),CCB(21),QT(21),Z(21)
* Q(21,21),QQ(21,21),CS(21),CCS(21)
* N(21),NR(21),INDEX(21),IR(21),F1(21),F2(21)
* CK(50),QK(50),FDK(50),CKK(25),SOLUTE(18)
* S1(21,22),S2(21,22),S3(21,22),S4(21,22)
* CBX(25),QTX(25)

C COMMON /BL1/CB,Q,QSD,F,FD
* /BL2/CCB,QQ
* /BLS/S1,S2,S3,S4
C * /BLXY/TW,CW,VOL
C * /BLDATA/SOLUTE,ISO,A,B,CO,QO,IR0
C * ,U,DIAR,RS,AKF,DS,HB
C * ,DELT,DELTMX,TEND,DELZ,ZEND,DCLUBE
C DATA NKK/22/
C * ,CKK/0., 0.001, 0.002, 0.005, 0.0075, 0.01, 0.02
C * ,0.05, 0.075, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5
C * ,0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0/

DATA NKK/25/
* ,CKK/0., 0.0001, 0.0002, 0.0005
* ,0.001, 0.002, 0.005, 0.0075, 0.01, 0.02
* ,0.05, 0.075, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5
* ,0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0/

C

OPEN(5,FILE='FS.IN')
OPEN(6,FILE='FS.OUT')

C READ(5,1001) SOLUTE
ISO=2
READ(5,*) AA
READ(5,*) B
READ(5,*) C00
READ(5,*) IR0

C C0=C00/1000.0
IF(ISO.EQ.2) A=AA*1000.0**B

C 1001 FORMAT(18A4)
C 1002 FORMAT(110,3F10.0,110)
1004 FORMAT(1H1////1H ,SOLUTE = *,18A4///)
1005 FORMAT(1H ,CK (MG/L)/1H ,1P10E12.3))
1006 FORMAT(1H ,QK (MG/G)/1H ,1P10E12.3))
C 1007 FORMAT(7I10)
2 NK=NKK
DO 120 K=1,NK
    CK(K)=CO*CKK(K)
    IF(ISO.EQ.1) QK(K)=A*B*CK(K)/(1.+B*CK(K))
    IF(ISO.EQ.2) QK(K)=A*CK(K)**B
    IF(ISO.EQ.3) QK(K)=A*CK(K)
    IF(K.EQ.1) GO TO 120
    FDK(K)=(CK(K)-CK(K-1))/(QK(K)-QK(K-1))
120 CONTINUE
Q0=QK(23)
3 CONTINUE
C
5 CONTINUE
READ(5,*,END=500) U
READ(5,*,END=500) DIA
READ(5,*,END=500) RS
READ(5,*,END=500) RB
READ(5,*,END=500) AKF
READ(5,*,END=500) DS
READ(5,*,END=500) DB
READ(5,*) DELT
READ(5,*) DELTMX
READ(5,*) TEND
READ(5,*) DELZ
READ(5,*) DTUBE
C
READ(5,*) IITM
C
WRITE(6,1008) SOLUTE,AA,B,C00,Q0,IR0
* ,U,DIA,RS,RB,AKF,DS,DB
* ,DELT,DELTMX,TEND,DELZ,ZEND,DTUBE
WRITE(*,1008) SOLUTE,AA,B,C00,Q0,IR0
* ,U,DIA,RS,RB,AKF,DS,DB
* ,DELT,DELTMX,TEND,DELZ,ZEND,DTUBE
1008 FORMAT(1H ,FIXED BED ADSORPTION, FS MODEL/
* 1H ,'SOLUTE = ',5X,18A4/
* 1H ,'A,B,C0,Q0,IR0 = ',/1H ,1P4E16.5,1I10/
* 1H ,'U,DIA,RS,RB,AKF,DS,DB ='/1H ,1P7E16.5/
* 1H ,'DELT,DELTMX,TEND,DELZ,ZEND,DTUBE ='/1H ,1P6E16.5/)
DELR=RADIUS/DFLOAT(NR0)
AV=3.*RB/RS/RADIUS
EB=1.-RB/RS
COEF=DTUBE**2*3.14/4.*U/1000.
F10=DELR**2/DS/DELT
F20=AKF/RS/DS/RADIUS*DELR*(RADIUS+DELR)
IF(DB.EQ.0.) FY=-AKF*AV/U
IF(DB.NE.0.) FY=(U-DSQRT(U**2+4.*AKF*AV*EB*DB))/2./EB/DB
F3=U/AKF/AV/DELZ
F4=DEXP(FY*DELZ)
F5=AKF*AV*DELT/2./RB
6 DO 130 1=1,21
ZX=DELZ*DFLOAT(I-1)
IF(ZX.GE.ZEND) GO TO 7
CX=DEXP(FY*ZX)
IF(CX.LT.0.001) M=I-1
IF(CX.LT.0.001) M1=I
IF(CX.LT.0.001) GO TO 8
130 CONTINUE
DELZ=2.*DELZ
F3=U/AKF/AV/DELZ
F4=DEXP(FY*DELZ)
GO TO 6
7 M=20
M1=21
DELZ=ZEND/20.
F3=U/AKF/AV/DELZ
F4=DEXP(FY*DELZ)
F3M1=F3
F4M1=F4
8 DO 150 I=1,M1
Z(I)=DFLOAT(I-1)*DELZ
CB(I)=DEXP(FY*Z(I))*C0
CBX(I)=CBG)/C0
CCB(I)=CB(I)
CS(I)=0.
CCS(I)=0.
QT(I)=0.
IR(I)=IR0
NR(I)=NR0
F1(I)=F10
F2(I)=F20
N(I)=I1
INDEX(I)=0
DO 140 J=1,21
Q(I,J)=0.
QQ(I,J)=0.
140 CONTINUE
150 CONTINUE
T=0.
C
IIT=0
C
KW=0
KC=0
KXY=0
NPT=0
KWH=10
KCH=100
KXYH=10
WRITE(*,1010) T
WRITE(*,1011) (Z(I),I=1,M1)
WRITE(*,1012) (CBX(I),I=1,M1)
C
WRITE(6,1010) T
WRITE(*,1010) T
C
10 T=T+DELT
C
IIT=IIT+1
C
KXY=KXY+1
KW=KW+1
KC=KC+1
DO 200 I=1,M1
20 QSD=QQ(I,21)
DO 210 K=2,NK
IF(QSD.LT.QK(K)) GO TO 21
210 CONTINUE
21 FD=FDK(K)
F=FDK(K)*(QSD-QK(K-1))+CK(K-1)
IF(I.NE.1) X=CCS(I-1)
IF(I.NE.1) Y=CCB(I-1)
IF(Z(I).NE.ZEND) F3I=F3
IF(Z(I).NE.ZEND) F4I=F4
IF(Z(I).EQ.ZEND) F3I=F3M1
IF(Z(I).EQ.ZEND) F4I=F4M1
CALL KEISU(I, N(I), NR(I), INDEX(I), IR(I))
*   ,F1(I), F2(I), F3I, F4I, X, Y, CS(I))
CALL GAUSS(I, N(I))
IF(ISO.EQ.3) GO TO 22
ERR=(QQ(I,21)-QSD)/QQ(I,21)
IF(ABS(ERR).GT.1.E-4) GO TO 20
22 CCS(I)=F
CUTQ=QQ(I,21)*0.01
IF(QQ(I,N(I)).LT.CUTQ) GO TO 200
IF(N(I).EQ.1) GO TO 23
N(I)=N(I)-1
GO TO 20
23 IF(IR(I).EQ.0) GO TO 200
IR(I)=IR(I)-1
NR(I)=NR(I)/2
DELR=RADIUS/DFLOAT(NR(I))
F1(I)=DELR**2/DS/DELT
F2(I)=AKF/RS/DS/RADIUS*DELR*(RADIUS+DELR)
N(I)=10
INDEX(I)=0
DO 220 J=21,11,-1

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JJ=2*J-2
Q(I,J)=Q(I,J)
QQ(I,J)=QQ(I,J)
220 CONTINUE
DO 230 J=1,10
Q(J)=0.
QQ(I,J)=0.
230 CONTINUE
GO TO 20
200 CONTINUE
DO 240 I=1,M1
QT(I)=F5*(CCB(I)+CB(I)-CCS(I)-CS(I))+QT(I)
CB(I)=CCB(I)
CS(I)=CCS(I)
DO 240 J=1,21
240 CONTINUE
IF(Z(M1).LT.ZEND) GO TO 30
C IF(Z(M1).LT.ZEND*0.99999999) GO TO 30
IF(KXY.LT.KXYH) GO TO 30
NPT=NPT+1
C TW(NPT)=T
CWNPT=CB(M1)/C0
C VOL(NPT)=T*COEF
KXY=0
30 IF(KW.LT.KWH) GO TO 40
DO 300 I=1,M1
CBX(I)=CB(I)/C0
QTX(I)=QT(I)/Q0
300 CONTINUE
C IF(IIT.GE.IITM) IIT=0
C IF(IIT.EQ.0) WRITE(6,1010) T,CWNPT
C WRITE(6,*). M1,M
C IF(IIT.EQ.0) WRITE(*,1010) T,CWNPT,DELT
C WRITE(6,1011) (Z(I),I=1,M1)
C WRITE(6,1012) (CBX(I),I=1,M1)
C WRITE(6,1013) (QTX(I),I=1,M1)
1010 FORMAT(1H,T=',1PE10.3,(HR),5X,\CB/C0=',1PE11.4,3X,1PE9.2)
1011 FORMAT(1H, Z=,'1P11E11.4/1H,7X,1P11E11.4)
1012 FORMAT(1H, C/C0=',1P11E11.4/1H,7X,1P11E11.4)
1013 FORMAT(1H, Q/Q0=',1P11E11.4/1H,7X,1P11E11.4)
KW=0
KXY=0
IF(CB(M1)/C0.GE.0.98) GO TO 50
IF(T.GE.TEND) GO TO 50
IF(KC.LT.KCH) GO TO 40
KC=0
KCH=90
IF(10.*DELT.GE.DELTMX) KWH=10
IF(10.*DELT.GE.DELTMX) GO TO 40
DELT=10.*DELT
F10=F10/10.
F5 = F5*10.
DO 310 I = 1, M1
   F1(I) = F1(I)/10.
   INDEX(I) = 0
310 CONTINUE
40 IF(QT(2)/Q0.LT.0.999) GO TO 45
   IF(M.EQ.1) GO TO 50
   M = M - 1
   M1 = M1 - 1
   DO 400 I = 1, M1
      I = I + 1
      Z(I) = Z(I)
      CB(I) = CB(I)
      CCB(I) = CCB(I)
      CS(I) = CS(I)
      CCS(I) = CCS(I)
      QT(I) = QT(I)
      IR(I) = IR(I)
      NR(I) = NR(I)
      F1(I) = F1(I)
      F2(I) = F2(I)
      N(I) = N(I)
      INDEX(I) = INDEX(I)
   DO 400 J = 1, 21
      Q(I,J) = Q(I,J)
      QQ(I,J) = QQ(I,J)
      SI(I,J) = SI(I,J)
      S2(I,J) = S2(I,J)
      S3(I,J) = S3(I,J)
400 CONTINUE
   CB(I) = C0
   CCB(I) = C0
45 IF(CB(M1)/C0.LT.0.001) GO TO 10
   IF(Z(M1).GE.ZEND) GO TO 10
   IF(M1.EQ.21) GO TO 46
   M = M + 1
   M1 = M1 + 1
   GO TO 47
46 DELZ = 2.*DELZ
   F3 = U/AKF/AV/DELZ
   F4 = DEXP(FY*DELZ)
   DO 410 I = 2, 11
      I = 2*I - 1
      Z(I) = Z(I)
      CB(I) = CB(I)
      CCB(I) = CCB(I)
      CS(I) = CS(I)
      CCS(I) = CCS(I)
      QT(I) = QT(I)
      IR(I) = IR(I)
      NR(I) = NR(I)
      F1(I) = F1(I)
      F2(I) = F2(I)
      N(I) = N(I)
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\begin{verbatim}
INDEX(I)=INDEX(II)
DO 410 J=1,21
Q(I,J)=Q(I,IJ)
QQ(I,J)=QQ(I,IJ)
S1(I,J)=S1(I,IJ)
S2(I,J)=S2(I,IJ)
S3(I,J)=S3(I,IJ)
410 CONTINUE
M=11
M1=12
C  M=10
C  M1=11
47 Z(M1)=Z(M)+DELZ
        CB(M1)=CB(M)*F4+CS(M)*(F3-F4-F3*F4)
        IF(Z(M1).LT.ZEND) GO TO 48
        DELZM1=ZEND-Z(M)
        F3M1=U/AKF/AV/DELZM1
        F4M1=DEXP(FY*DELZM1)
        Z(M1)=ZEND
        CB(M1)=CB(M)*F4M1+CS(M)*(F3M1-F4M1-F3M1*F4M1)
48 CCB(M1)=CB(M1)
        CS(M1)=0.
        CCS(M1)=0.
        QT(M1)=0.
        IR(M1)=IR0
        NR(M1)=NR0
        F1(M1)=F10
        F2(M1)=F20
        N(M1)=11
        INDEX(M1)=0
        DO 420 J=1,21
        Q(M1,J)=0.
        QQ(M1,J)=0.
        420 CONTINUE
        GO TO 10
50 CONTINUE
C  GO TO 5
500 CONTINUE
STOP
END
C SUBROUTINE KEISU
SUBROUTINE KEISU(I,N,NR,INDEX,IR,F1,F2,F3,F4,X,Y,CS)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION CB(21),Q(21,21)
*     ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
COMMON /BL1/CB,Q,QSD,F,FD
*     /BLS/S1,S2,S3,S4
IF(INDEX.NE.0) GO TO 10
DO 100 J=1,20
EJ=NR-21+J
IF(EJ,EQ.0.) GO TO 100
S1(I,J)=-(EJ-1.)/EJ
S2(I,J)=F1+1.
S3(I,J)=-(EJ+1.)/EJ
100 CONTINUE
STOP
END
\end{verbatim}
100 CONTINUE
   IF(IR.EQ.0) S2(I,1)=F1+3.
   IF(IR.EQ.0) S3(I,1)=-3.
   S1(I,21)=-1.
   S3(I,21)=-F2
   S2(I,22)=1.
   INDEX=1
10 DO 110 J=N,20
   IF(J.EQ.I.AND.IR.EQ.0) S4(I,1)=3.((Q(I,2)-Q(I,1))+F1*Q(I,1)
   IF(J.EQ.I.AND.IR.NE.0) S4(I,1)=(F1-I)*Q(I,1)-S3(I,1)*Q(I,2)
   IF(J.NE.1) S4(I,J)=-S1(I,J)*Q(I,J-1)+(F1-I)*Q(I,J)
          * -S3(I,J)*Q(I,J+1)
110 CONTINUE
   S2(I,21)=1.+F1+F2*FD
   S4(I,21)=Q(I,20)-F2*(CS+FD-QSD)+(F1-I)*Q(I,21)+F2*CB(I)
   IF(I.NE.1) S1(I,22)=(-1.3-F3*FD)
   IF(I.NE.1) S4(I,22)=(1.-F3+F3*FD)*(F-FD-QSD)+(F3-F4-F3*FD)*X+F4*Y
   RETURN
END

C SUBROUTINE GAUSS-SEIDEL
SUBROUTINE GAUSS(I,N)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DIMENSION CCB(21),QQ(21,21),QG(21)
* ,S1(21,22),S2(21,22),S3(21,22),S4(21,22)
COMMON /BL2/CCB,QQ
* /BLS/S1,S2,S3,S4
10 DO 100 J=1,21
   QG(J)=QQ(J,J)
100 CONTINUE
   CBG=CCB(I)
   IF(I.EQ.1) GO TO 10
   CCB(I)=(S4(I,22)-S1(I,22)*QG(21))/S2(I,22)
10 QQ(I,21)=(S4(I,21)-S1(I,21)*QG(20)-S3(I,21)*CB(I))/S2(I,21)
   DO 110 J=20,N,-1
      IF(J.EQ.1) QQ(I,J)=(S4(I,1)-S3(I,1)*QG(I,2))/S2(I,1)
      IF(J.NE.1) QQ(I,J)=(S4(I,J)-S1(I,J)*QG(J-1)-S3(I,J)*QG(I,J+1))
          * /S2(I,J)
110 CONTINUE
   IF(I.EQ.1) GO TO 20
   ERR=(CCB(I)-CBG)/CCB(I)
   IF(ABS(ERR).GT.1.E-4) GO TO 1
20 DO 120 J=21,N,-1
      IF(QQ(I,J).EQ.0.) GO TO 120
      ERR=(QQ(I,J)-QG(J))/QQ(I,J)
      IF(ABS(ERR).GT.1.E-4) GO TO 1
120 CONTINUE
   RETURN
END
"In the ordinary business of life, industry can do anything which genius can do, and very many things which it cannot." (Henry Ward Beecher)

Vita

THOMAS EDWARD TOKUO GILLOGLY

PERSONAL INFORMATION

Date of Birth: June 5, 1971
Place of Birth: San Francisco, CA

EDUCATION

University of Illinois, IL

Doctor of Philosophy in Environmental Engineering in Civil Engineering, January 1999
Dissertation: “Effect of Chlorine on MIB Removal by Activated Carbon”
Advisor: Vernon L. Snoeyink

Master of Science in Civil Engineering, May 1995
Advisor: Vernon L. Snoeyink

Carnegie Mellon University, PA

Bachelor of Science in Chemical Engineering and Engineering & Public Policy (with an Environmental Engineering minor), May 1993

EXPERIENCE

12/93 - present Graduate Research Assistant - Advisor: Vernon L. Snoeyink, Ph.D.
University of Illinois Environmental Engineering Program, Urbana, IL
- Research the theory and basic design of processes used in water treatment
- Correlate physical/chemical measurements to adsorption phenomena

9/93 – 12/93 Teaching Assistant - CE342: Water and Wastewater Treatment Unit Operations
University of Illinois, Environmental Engineering Program, Urbana, IL

6/93 – 9/93 Health Services Officer – Public Health Service (0-1 ensign)
U.S. Environmental Protection Agency (EPA, OSWER, OPM), Washington, D.C.
• Analyzed and compiled regional data for Superfund directoral meetings
• Reviewed external reports concerning the Superfund Program
• Wrote internal document consolidating Superfund program information

9/92 – 5/93 Undergraduate Research Assistant - Advisor: David A. Dzombak, Ph.D., P.E.
Carnegie Mellon University, Department of Civil and Environmental Engineering, Pittsburgh, PA
• Wrote, “Synthesis of MnO2 Coated Granular Activated Carbon for the Removal of Heavy Metals From Aqueous Media”
• Developed methodologies to produce various MnO2 coatings
• Analyzed stability and adsorptive capacity of coatings

6/92 – 9/92 Health Services Officer – Public Health Service (0-1 ensign)
U.S. Environmental Protection Agency (EPA, ORD, SITE Program), Cincinnati, OH
• Analyzed proposed innovative technologies for hazardous waste site remediation
• Orchestrated work on scaling up a dehalogenation process

6/91 – 9/91, Engineering Intern – (GS-4)
• Wrote, “The Development of a Soil Sampling Plan for the RDX Manufacturing Area, Newport Army Ammunition Plant”
• Assisted project managers in data analysis/management

PUBLICATIONS AND PRESENTATIONS

Peer Reviewed

Conference Proceedings
Gillogly, T.E.T., V.L. Snoeyink, G. Newcombe & J.R. Elarde. A Simplified Method to Determine the PAC Dose Required to Remove MIB. In


**Invited Lectures**


**Platform Presentations**


**PROFESSIONAL REGISTRATION AND MEMBERSHIP**

<table>
<thead>
<tr>
<th>Year</th>
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<td>1993-present</td>
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