Adsorption of Denatonium Benzoate Using Activated Carbon

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ABSTRACT

Adsorption of Denatonium Benzoate Using Activated Carbon

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The "Antifreeze Bittering Act of 2009" (H.R. 615) was introduced to the U.S. House of Representatives on January 21, 2009, and it mandates the addition of 30-50 mg/L denatonium benzoate (DB), a bittering agent, to antifreeze and engine coolant. At 1-10 mg/L, denatonium benzoate's bitter taste can be detected; and water with 30-100 mg/L denatonium benzoate is unpalatable. This project addressed concerns related to the potential release of DB to water supplies by determining if activated carbon treatment, a common method employed to remove taste and odor contaminants from water, is suitable for DB removal. After conducting several contact time tests, powdered activated carbons NORIT® GAC 1240 and HYDRODARCO® 4000 had the most success at
removing denatonium benzoate at the 24-hour time period. Both activated carbons are good treatment methods for removing 5 mg/L concentrations of denatonium benzoate from water. Batch tests conducted using higher concentrations of DB; (70 mg/L) concluded that activated carbon would not be sufficient for the removal of DB from water supplies. The NORIT® GAC 1240, a bituminous based activated carbon, performed slightly better than HYDRODARCO® 4000, a lignite based carbon under all conditions.

Batch tests were also conducted with the use of the organic acid potassium hydrogen phthalate (KHP) to determine the effects of organic material on adsorption. KHP increased the adsorption capacity of the NORIT® GAC 1240 activated carbon. A 3 mg/L concentration of KHP mixed with 5 mg/L concentration of DB and a 5 mg/L concentration of NORIT® GAC 1240 had an 86% removal rate in 24 hours. Ionic strength experiments indicated that no ion exchange was taking place in the presence of KHP. It was surmised that complexation or bonding mechanisms may have contributed to the satisfactory removal of denatonium benzoate in the presence of KHP.
Rapid small-scale column tests (RSSCTs) examined the performance of granular activated carbon (GAC) for removing denatonium benzoate from water. For GAC treatment, using the empty bed contact time (EBCT) of three minutes was found to be sufficient with longer EBCTs yielding inconclusive results. In conclusion, it was determined that activated carbon was sufficient for the removal of low DB concentrations. For higher concentrations of DB, other treatment methods should be considered.
ACKNOWLEDGEMENTS

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I thank my father, Keith Smith, who taught me the values of education from my childhood; and for his love, support and faith in me. I would also like to deeply thank and express my love to my Central State University family.
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<th>Description</th>
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<tr>
<td>AC</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>CUR</td>
<td>Carbon Utilization Rate</td>
</tr>
<tr>
<td>DB</td>
<td>Denatonium Benzoate</td>
</tr>
<tr>
<td>EBCT</td>
<td>Empty-Bed Contact Time</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular Activated Carbon</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural Organic Matter</td>
</tr>
<tr>
<td>KHP</td>
<td>Potassium Hydrogen Phthalate</td>
</tr>
<tr>
<td>MIB</td>
<td>2-Methylisborneol</td>
</tr>
<tr>
<td>PAC</td>
<td>Powdered Activated Carbon</td>
</tr>
<tr>
<td>PPB</td>
<td>Parts Per Billion</td>
</tr>
<tr>
<td>RSSCT</td>
<td>Rapid Small-Scale Column Test</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

1.1 Statement of Problem

The “Antifreeze Bittering Act of 2009” (H.R. 615) was introduced to the U.S. House of Representatives on January 21, 2009, and it mandates the addition of 30-50 mg/L denatonium benzoate, a bittering agent, to antifreeze and engine coolant. At 1-10 mg/L, denatonium benzoate’s bitter taste can be detected; and water with 30-100 mg/L denatonium benzoate (DB) is unpalatable. Although denatonium benzoate’s environmental fate in soil and water systems has been modeled, it has not been empirically studied. Concern exists that the unintentional or intentional release of DB-spiked antifreeze or engine coolant could adversely impact drinking water supplies by rendering water unpalatable. This project addressed concerns related to the potential release of DB to water supplies by determining if activated carbon treatment, a common method employed to remove taste and odor contaminants from water, is suitable for DB removal.
1.2 Significance of Problem

Every year an estimated 10,000 dogs, cats, and children fall victim to accidental poisoning by antifreeze. In 2003 an estimated 1,400 children were hospitalized due to antifreeze poisoning according to the Consumer Product Safety Commission (Tutuni 2010). Three to four teaspoons of antifreeze can be deadly if consumed by a child. A few licks of the sweet tasting substance can be deadly for a dog or cat.

Denatonium benzoate is a harmless bitter tasting substance that in small quantities makes digestion impossible (Tutuni 2010). Denatonium benzoate is a preferred bittering agent because it is inexpensive. One teaspoon of denatonium benzoate is needed for every 50 gallons of antifreeze, which amounts to about 3 to 4 cents per gallon (Tutuni 2010).

Manufacturers claim that denatonium benzoate is biodegradable and is not known to bioaccumulate. Researchers have found that the denatonium ion does not biodegrade during the typical wastewater treatment process and the denatonium ion is responsible for the bitter taste of the compound (Bonacquisti 2006).
Antifreeze should never be dumped on the ground or discharged into a sewer system. Antifreeze will cause bacteria in a sewer or septic tank to stop working. When there are no bacteria present in the tank to break down the contaminants, toxins will pass through the system and pollute the ground water. Improper disposal of antifreeze may result in soil, surface water, and groundwater contamination. Used antifreeze contains heavy metals and other contaminants which may lead to expensive regulatory fines and clean up costs (Schuals 2008 ).

1.3 Objectives of the Research

The objective of this research is to investigate the effectiveness of powdered activated carbon (PAC) and granular activated carbon (GAC) treatments in the removal of denatonium benzoate from water. The effect of contact time, influence of carbon type, optimal carbon dose, optimal empty bed contact time, influence of the background organic content of water, and effect of pH conditions on adsorption were determined. The optimal operating conditions that would provide the most efficient use of activated carbon while removing denatonium benzoate were determined.
2.1 Introduction

Denatonium Benzaote is a bittering agent commonly used in antifreeze to prevent poisonings. The “Antifreeze Bittering Agent Act of 2009” (H.R.615) was written to enforce the addition of DB into the production of antifreeze (Rep Ackerman 2009). Studies on the poisoning of children due to antifreeze have shown DB to be effective in decreasing the amount of ethylene glycol ingestions (White et al. 2009).

Activated carbon (AC) is the compound commonly used in the water treatment process to adsorb taste and odor compounds (United States Environmental Protection Agency 2007). The adsorption capacity of AC is dependent both on chemical and physical characteristics. Adsorption isotherms are used to discern the ability of a particular AC to
remove a specific contaminant. The rapid small-scale column test (RSSCT) is used to predict the adsorption of organic compounds onto granular activated carbon used in filter bed adsorbers or GAC contactors. Adsorption by way of AC has been effective in the removal of taste and odor compounds including 2-methylisoborneol (MIB) and geosmin.

2.2 Legislation

There are 14 states that have already enacted antifreeze bittering legislation. Antifreeze bittering legislation is pending in three states. Table 2.1 indicates the states that have adopted or are considering the adoption of antifreeze bittering legislation. A few of the states including New Mexico have named their bills after animals who passed due to the ingestion of antifreeze. The bill in New Mexico is known as “Scooby’s law”. “Freddy’s Law” was named after a dog that passed away due to the ingestion of antifreeze in Utah. In Tennessee an 11-year old girl proposed the enactment of the “Haley Ham Act” after her golden retriever passed due to antifreeze poisoning. The act became effective January 1, 2010.
Table 2.1: States that have adopted or are considering adoption of antifreeze bittering legislation

<table>
<thead>
<tr>
<th>State</th>
<th>Name of Bill</th>
<th>Effective Dates</th>
<th>Amount of DB</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>California</td>
<td>Simitian Antifreeze Law</td>
<td>January 1, 2003</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Savage, 2008)</td>
</tr>
<tr>
<td>Georgia</td>
<td>House Bill 40 or Chief's Law</td>
<td>Pending</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Montorfano, 2011)</td>
</tr>
<tr>
<td>Illinois</td>
<td>House Bill 4722</td>
<td>January 1, 2011</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Holmes, 2010)</td>
</tr>
<tr>
<td>Maine</td>
<td>House Bill 400</td>
<td>January 1, 2011</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Coughlin, 2009)</td>
</tr>
<tr>
<td>Maryland</td>
<td>House Bill 897</td>
<td>October 1, 2011</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Murphy, 2011)</td>
</tr>
<tr>
<td>Massachusetts</td>
<td>House Bill 4285</td>
<td>January 1, 2011</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Speliotis, 2008)</td>
</tr>
<tr>
<td>New Hampshire</td>
<td>House Bill 431</td>
<td>Pending</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(The Daily Hampshire Gazette, 2010)</td>
</tr>
<tr>
<td>State</td>
<td>Name of Bill</td>
<td>Effective Dates</td>
<td>Amount of DB</td>
<td>References</td>
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<td>-------------</td>
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<td>-----------------------------------------</td>
</tr>
<tr>
<td>New Jersey</td>
<td>Senate Bill 979</td>
<td>January 1, 2011</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Anonymous, 2008)</td>
</tr>
<tr>
<td>New Mexico</td>
<td>Senate Bill 497 or Scooby Law</td>
<td>July 1, 2005</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Todd, 2010)</td>
</tr>
<tr>
<td>Ohio</td>
<td>House Bill 96</td>
<td>Pending</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Moore, 2009)</td>
</tr>
<tr>
<td>Oregon</td>
<td>Senate Bill 317</td>
<td>January 1, 1991</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(The Seattle Times Company, 1995)</td>
</tr>
<tr>
<td>Tennessee</td>
<td>House Bill 2808 or Haley Ham Act</td>
<td>January 1, 2010</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(The Humane Society Legislative Fund, 2008)</td>
</tr>
<tr>
<td>Utah</td>
<td>Senate Bill 218 or Freddy's Law</td>
<td>January 1, 2011</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Humane Society of Utah, 2007)</td>
</tr>
<tr>
<td>Vermont</td>
<td>House Bill 6</td>
<td>January 1, 2011</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Moore, 2009)</td>
</tr>
<tr>
<td>Virginia</td>
<td>House Bill 2629</td>
<td>January 1, 2011</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Anonymous, 2011)</td>
</tr>
<tr>
<td>State</td>
<td>Name of Bill</td>
<td>Effective Dates</td>
<td>Amount of DB</td>
<td>References</td>
</tr>
<tr>
<td>--------------</td>
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<td>------------------------------------------------------------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td><strong>West Virginia</strong></td>
<td>Senate bill No. 349 Article No. 43</td>
<td>January 1, 2012</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Laird, 2002)</td>
</tr>
<tr>
<td><strong>Wisconsin</strong></td>
<td>2009 Wisconsin Act 381</td>
<td>May 18, 2010</td>
<td>not less than thirty parts per million and not more than fifty parts per million</td>
<td>(Anonymous, 2010b)</td>
</tr>
</tbody>
</table>
2.3 Denatonium Benzoate

The use of bittering agents as “aversives” has been advocated as a possible method to prevent toxic ingestions in children (Rodgers and Tenenbein 1994). Ethylene glycol is the common ingredient in the automobile product antifreeze. Ethylene glycol is a highly toxic, colorless, odorless liquid with a sweet taste. These characteristics have been attributed to the frequency of poisonings due to antifreeze. It has been implicated in 756 poisonings in children younger than 6 years of age reported to the United States Centers of Poison Control in 2004 (White et al. 2009).

Decreasing the palatability of toxic products by adding bittering agents has been used to reduce the death rate due to unintentional poisonings. Denatonium benzoate is the most commonly used bittering agent and listed in the Merck Index “among the bitterest substances known to man” (White et al. 2009). DB (Figure 2.1) was discovered in 1968 by Macfarlan Smith Limited in Edinburgh, Scotland (Henderson et al. 1998). DB was developed initially as a possible local anesthetic. It was found to have a bitter taste at as low as 50 parts per billion (ppb) in liquid products (Rodgers and Tenenbein 1994).
Figure 2.1 Structure of DB (Henderson et al. 1998)

DB is a white solid substance that has a melting point of 168°C. It is found to be stable and partially soluble in cold water. Routes of entry in humans are eye contact, inhalation, and ingestion. DB is toxic to lungs and mucous membranes. It has an acute oral toxicity (LD50) of 584 mg/kg in rats (Anonymous 2010a).

An investigation was conducted on children to determine the impact of adding bittering agents to antifreeze. Data on the pediatric ingestions of antifreeze or ethylene glycol reported to US poison centers from April 30, 1995 through July 31, 2005 were reported by the American Association of Poison Control Centers for the states of California and Oregon. Frequency data from both states were analyzed for 18 months
before the implementation of DB legislation and 18 months after the implementation of DB legislation. To determine the impact of a bittering agent on the amount of poison ingested, the volume of ethylene glycol ingested in bittered versus nonbittered groups was compared. Of the 6,450 children younger than 5 years old reported, there was no significant difference in the proportion of the bittered groups and nonbittered groups (67.1% of the nonbittered group and 64.7% of the bittered group) (White et al. 2009). The monthly nationwide frequency of ethylene glycol ingestions as a percentage of total poison ingestion cases in children younger than 5 years showed a steady decline, dropping by about 40% over the 10.25 year time frame (White et al. 2009).

2.4 Activated Carbon

Activated carbon (AC) is commonly used to adsorb natural organic compounds, taste and odor compounds, and synthetic organic chemicals in drinking water treatment (United States Environmental Protection Agency 2007). AC has been extensively used in water treatment plants for the removal of total organic carbon (TOC) and natural organic matter (NOM) from drinking water and wastewater (Patni et al. 2008). Coal is the most common starting material for AC (Stone et
al. 1999). The starting material chosen greatly impacts the quality of adsorption and filtration.

The manufacturing process of activated carbon can be either a re-agglomeration process or a direct activation process. The first step in the re-agglomeration process is to crush a high grade metallurgical coal to a size of approximately 50 microns. A coal tar or petroleum-based binder is then added. Next, several tons of pressure is added to the compound and it is re-agglomerated into briquettes, which are crushed to a preferred size. The carbon is then baked for volatile organic compound (VOC) removal at temperatures up to 800 degrees F. The carbon is then thermally activated by exposure to temperatures approaching 1900 degrees F in a temperature controlled atmosphere.

Direct activation is the alternative to re-agglomeration. The direct activation skips the initial steps and proceeds straight to crushing, sizing, baking, and activation. Direct activation produces a granule with high surface activity on the outer shell and little surface area in the core of the granule. Both activation processes generate activated carbon with different performance characteristics. The re-agglomerated carbon has increased adsorption capacity due to the addition of the man-made
pores and the well distributed activity of the re-agglomerated granule. It produces an activated carbon that is more dense and more resistant to abrasion (Stone et al. 1999).

In chemical activation the raw material is impregnated with a strong dehydrating agent. The agent used is typically phosphoric acid ($P_2O_5$) or zinc chloride ($ZnCl_2$). The agent is mixed into a paste and then heated to temperatures of 500 - 800°C to activate the carbon. Activated carbons produced by chemical activation generally exhibit a very open pore structure. This aids in the adsorption of large molecules (Stone et al. 1999).

There are three primary types of AC: bituminous, sub-bituminous, and lignite (Stone et al. 1999). Activated carbon is used in the forms of granules or powder. Bituminous-based activated carbons are known to have a broad range of pore diameters. This helps in the removal of a wide range of organic pollutants. Pore size determines the size of the organic compounds the carbon can remove. Bituminous-based activated carbon is known to have excellent adsorption properties for the removal of impurities from chemical, pharmaceutical, and water applications. Lignite activated carbons contain pores large enough for
common organic molecules, but this results in a reduced total surface area. To remove the same amount of organics as bituminous-based carbon, more lignite carbon must be used (Stone et al. 1999).

2.5 Adsorption

Adsorption is both the chemical and physical process of accumulating a substance at the interface between the liquid and solid phases. The compound that adsorbs at the interface is the adsorbate and the solid on which adsorption occurs is the adsorbent. If a reaction is reversible, particles continue to accumulate on the activated carbon until equilibrium is reached; at this time accumulation no longer occurs (United States Environmental Protection Agency 2007). The adsorptive nature of activated carbon is dependent on both the physical and the chemical characteristics of the activated carbon surfaces (Patni et al. 2008). As pore sizes increase, there is a reduction in surface area. As surface area decreases, adsorption decreases also.

2.6 Isotherms

Adsorption isotherms are commonly used by carbon manufacturers to differentiate the ability of a particular AC to remove a specific contaminant at a constant temperature. An important trait of AC is the
quantity of adsorbate that it can accumulate. The adsorption isotherm describes the equilibrium correlation between the adsorbate concentration, mass loading, adsorbent dose, and the equilibrium concentration of the adsorbate concentration at a selected temperature. AC isotherms are shown on log-log plots. Adsorbable compounds have higher and flatter lines than less adsorbable compounds (United States Environmental Protection Agency 2007).

The two most familiar mathematical expressions used to relate the adsorption isotherms are the Freundlich and the Langmuir equations (United States Environmental Protection Agency 2007). The Freundlich isotherm has been widely used in the analysis of activated carbon adsorption and also heterogeneous adsorbents. The isotherm is considered simple to use and can be applied to an assortment of organic compounds and adsorbents (Furuya et al. 1997). The Freundlich equation is an empirical equation that precisely describes adsorption data. The main drawback of this isotherm is that it requires experiments to determine its coefficients because it is an empirical formula (Furuya et al. 1997).

The Freundlich equation consists of the following:

\[ q_e = K C_e^{1/n} \]  
(Equation 2.1)
It can be linearized as follows:

\[
\log q_e = \log K + \frac{1}{n} \log C_e \quad (\text{Equation 2.2})
\]

\(q_e\) = equilibrium loading on the GAC (mg chemical/g GAC)

\(C_e\) = equilibrium concentration in the water (mg chemical/L)

\(K\) = adsorption capacity at unit concentration (mg/g) \((L/mg)^{1/n}\)

\(1/n\) = strength of adsorption (dimensionless)

The Langmuir equation has the following structure:

\[
q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (\text{Equation 2.3})
\]

It can be linearized as follows:

\[
\frac{1}{q_e} = \frac{1}{q_{max} b C_e + 1/q_{max}} \quad (\text{Equation 2.4})
\]

\(q_{max}\) = ultimate adsorption capacity (mg chemical/g GAC)

\(b\) = relative energy of adsorption (L/mg). The Langmuir equation is used for fixed monolayer and adsorption sites (United States Environmental Protection Agency 2007).

An isotherm is normally determined by running several batch reactors, typically in parallel. The bottles should contain the same chemical concentration and water volume when doing constant adsorbate testing. Each bottle is dosed with a different quantity of
carbon or other adsorbent and gently mixed until equilibrium between phases is reached. The equilibrium concentration is measured and the AC loading \((q_e)\) in each bottle is calculated assuming conservation of mass all the way through the complete experiment by preparing controls to check. A plot of the equilibrium loading and the equilibrium concentration is made and isotherm parameters are determined by linear regression analysis (United States Environmental Protection Agency 2007).

There are fairly few factors that must be considered and controlled during AC isotherm development. If the adsorbing material is volatile, the bottles are filled completely headspace free. Control of pH is imperative for compounds whose isotherms are a function of pH since pH changes can leave the compound in ionized form, which will have a higher similarity to water and reduce AC capacity. Biodegradation must be minimized if the adsorbing compound is biodegradable. The AC isotherm should be determined within the concentration range of each particular application, since isotherm applications sometimes change with assorted concentrations. Adsorption capacity increases with temperature. These tests are performed isothermally, which means at a constant temperature. Adsorption capacity is also affected by the type of carbon used. Coal-
based materials have higher adsorption capacities than wood-based or other materials (United States Environmental Protection Agency 2007).

The size of the compound considerably impacts the rate of adsorption. It takes longer to eliminate large molecular weight compounds than those of a lesser molecular weight. The AC particle mesh size also affects the adsorption rate because it determines the time necessary to move the compound within the pore to available adsorption sites. AC is generally pulverized to a sieve size of less than 365 for the isotherm measurement to shorten the equilibrium time to a range of a range of days to weeks versus weeks to months. Grinding the AC does not impact the total surface available for adsorption (United States Environmental Protection Agency 2007).

AC isotherms are capable of contrasting different AC manufacturers, as a quality control measure of purchased AC, and to predict performance of an AC system. Isotherms can be used to attain a rough estimate of the carbon usage rate (CUR) and bed life, which can be helpful in determining the applicability of GAC. The CUR is calculated by dividing the amount of impurity removed by the carbon loading rate \( q_e \) (Norit Americas Inc. 2007b). Isotherm parameters can be used as
input parameters for mathematical models to forecast performance of a
GAC adsorption process (United States Environmental Protection Agency
2007).

2.7 Rapid Small-Scale Column Test

The rapid small-scale test (RSSCT) was developed to predict the
adsorption of organic compounds in activated carbon adsorbers. The
RSSCT is a scaled-down version of a pilot or full-scale GAC column. An
RSSCT may be conducted in a fraction of the time necessary to conduct
pilot studies. A small volume of water is required to perform the test.
Replacing a pilot study with an RSSCT can reduce the cost and the time
of a full-scale design (Crittenden et al. 1986).

Mathematical models are used to scale-down the full-scale
absorber to an RSSCT and conserve similitude between the performances
of the adsorbers. If perfect similarity is maintained, the RSSCT which uses a
smaller adsorbent particle size and the full-scale adsorber will have
identical breakthrough profiles. RSSCTs can be used to evaluate design
variables such as empty-bed contact (EBCT) or bed operations in parallel
(Crittenden et al. 1991). The EBCT is calculated by dividing the volume of
the bed by the flow rate (Vissman et al. 2009). As the EBCT increases, the
time available for particles to adsorb solutes from the water also increases. The amount of solute removed from the water during its transport through the bed also increases. The selection of hydraulic loading and EBCT of the RSSCT is determined by mechanisms that cause spreading in the mass transfer zone and breakthrough curve: (1) external mass transfer resistance, (2) axial mixing, and (3) the internal mass transfer resistances of pore and surface diffusion. Dispersion is usually insignificant if the hydraulic loading is sufficient enough (Crittenden et al. 1986).

The EBCT of the RSSCT is determined by intraparticle mass transfer resistances. If the dependence of the pore and surface diffusion coefficients on particle size is known, similitude can be achieved by equating the dimensionless groups that consider the intraparticle dispersion resistances in small and large columns. If the bulk densities void fractions, and capacities are identical for the carbons used in the RSSCT and full-scale process, the proper scaling can be determined by the use of the following equation (Crittenden et al. 1991):

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]^{2-X} = \frac{t_{SC}}{t_{LC}} \quad (Equation \ 2.5)$$

in which $EBCT_{SC}$ and $EBCT_{LC}$ are the EBCTs of the small and large columns; $d_{p,SC}$= adsorbent particle sizes for small scale GAC columns.
The bed life, bed volumes, carbon usage rate, and volume of water that may be treated per mass of carbon for the full-scale adsorber can be determined by RSSCT bed life. The bed volumes that can be treated in the full-scale column are equal to the bed life of the RSSCT divided by the EBCT\textsubscript{SC}. The specific throughput of the full-scale process is equivalent to the volume of water fed to the RSSCT divided by the mass of GAC in the RSSCT. The volume of water treated is equal to the bed life of the RSSCT times the flow rate to the RSSCT. The carbon usage rate is the reciprocal of the specific throughput. When evaluating GAC performance, it is vital to use bed volumes fed, carbon usage rate, or specific throughput, and not bed life. The other parameters standardize the results with respect to bed size.

The value of X does not have an impact on normalized parameters; it only relates EBCT\textsubscript{SC} and EBCT\textsubscript{LC} and determines the run time of the RSSCT.
(Crittenden et al. 1991). If the inference is made that the intraparticle
diffusivities do not vary with particle size (X=0), then the similarities
between RSSCT and pilot-plant effluent profiles can be kept the same.

Equation (2.6) ensures the the amount of spreading caused by
intraparticle mass transfer resistance in the RSSCT and the pilot plant are
indistinguishable in respect to the adsorber length.

\[
\frac{EBCT_{SC}}{EBCT_{LC}} = \left(\frac{dp_{SC}}{dp_{LC}}\right)^2 = \frac{t_{SC}}{t_{LC}} \quad (\text{Equation 2.6})
\]

When the Reynolds numbers for the small and large carbon particles are
set equivalent, an equal amount of dispersion in the mass transfer zone is
assumed. This is given by the following equation:

\[
\frac{V_{SC}}{V_{LC}} = \left(\frac{dp_{IC}}{dp_{LC}}\right) \quad (\text{Equation 2.7})
\]

In the equation, \(V_{SC}\) and \(V_{LC}\) are hydraulic loadings in the RSSCT and pilot
columns (Crittenden et al. 1991).

When spreading is mostly caused by intraparticle diffusion in the
mass transfer zone and the intraparticle diffusivity is proportional to a
particle size (X=1), proportional diffusivity equations are used. Equation 2.8
is used to determine the empty-bed contact time of the small scale
adsorber.
Intraparticle diffusion usually causes most of the spreading in the mass transfer zone. The amount of spreading caused by dispersion and external mass transfer can be reduced in the selection of the RSSCT hydraulic loading without affecting the RSSCT results. In order to reduce the pressure drop and RSSCT column length, Crittenden proposed the following:

\[
\frac{EBCT_{SC}}{EBCT_{LC}} = \left( \frac{d_{p,SC}}{d_{p,LC}} \right) = \frac{t_{SC}}{t_{LC}} \quad \text{(Equation 2.8)}
\]

2.8 Taste and Odor Compounds

The presence of taste and odor compounds in potable water supplies worldwide has been increasing in intensity and frequency in recent years (Yu et al. 2007). The most commonly identified compounds are geosmin and 2-methylisobornel (MIB). These compounds are responsible for the earthy-musty odor in finished water. These compounds cause off-tastes in drinking water and resist oxidation. They are difficult to remove by the conventional water treatment process. Algae blooms have been known as a pest to many drinking water facilities due to the foul taste and odors that have been associated with their presence. Blue-green algae produce an earthy-musty odor which is caused by the
compounds 2-methylisoborneol and geosmin. These compounds are volatile saturated tertiary alcohols that can be detected at extremely low concentrations between 10 and 20 mg/L. Due to the detection at low concentrations, many drinking water customers complain about the taste and odor of their water. This is the case though the numbers of algal cells detected in the water are deemed acceptable (Drikas et al. 2009).

A study conducted by Drikas et al. (2009) on the removal of MIB and geosmin found that MIB and geosmin spiked at concentrations between 50 and 200 mg/L were removed by GAC filters. After the first ten months of the study, it was determined that the available adsorption capacity at an EBCT of 20 minutes was sufficient in removal to compensate for any dissolved organic compounds also entering the GAC filters. At the EBCT of 5 minutes breakthrough occurred.

It has been found that the adsorption of MIB is very dependent on the type of activated carbon used. Wood-based, chemically activated carbons display inferior adsorption for MIB compared with coconut and coal-based carbons. Evidence has been found that surface chemistry and pore size plays an important role in the adsorption of activated carbon. The presence of natural organic matter reduces the equilibrium
capacity of activated carbon for MIB, and also influences the kinetics of adsorption (Newcombe et al. 2002). Some researchers have found that the lignite and wood-based chemically activated carbons displayed inferior adsorption for MIB compared with bituminous-based carbons.
CHAPTER III
MATERIALS AND METHODS

3.1 Introduction

Constant adsorbate isotherm tests were performed to determine the type of carbon best suited for the removal of DB. Isotherm tests also determined the dosage of carbon needed for DB removal. Batch tests were performed of various durations to determine the optimal contact time to remove DB from water. They were also conducted under various pH conditions to determine the effect of pH on adsorption. Batch tests were also conducted using potassium hydrogen phthalate to see the outcome of adsorption when organic material is present. To determine if ionic strength had any affects on adsorption when organic material is present, batch tests were carried out using sodium chloride. Rapid small-scale column tests (RSSCTs) were performed to establish the empty-bed contact time necessary for treatment. RSSCTs also determined the adsorption capacity of the granular activated carbon.
3.2 Materials

3.2.1 Activated Carbon

Norit® GAC 1240 is an acid washed, bituminous-based activated carbon produced by steam activation (Norit Americas Inc. 2007a). It offers excellent adsorption properties for the removal of impurities from chemical, food, pharmaceutical, and water applications (Norit Americas Inc. 2007b).

HYDRODARCO 4000® is an acid washed activated carbon produced by high temperature steam activation of lignite coal (Norit Americas Inc. 2007b). HYDRODARCO® 4000 has a wide pore size distribution and large pore volume. It has a rapid adsorption rate and high capacity for dissolved organics. HYDRODARCO® 4000 has been known to adsorb taste, odor, color, and toxic organics from drinking water. It provides a high tolerance for natural organic matter, which is known to interfere with the adsorption of other organic compounds (Norit Americas Inc. 2007b). Both activated carbons were used as received.
3.2.2 Chemical Reagents

Table 3.1 Chemical Reagents

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Manufacturer</th>
<th>Location</th>
<th>Process Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Denatonium Benzoate (DB)</td>
<td>MP Biomedicals</td>
<td>Solon, Ohio</td>
<td>Batch Tests and RSSCTs</td>
</tr>
<tr>
<td>Potassium Hydrogen Phthalate (KHP)</td>
<td>Hach</td>
<td>Loveland, Colorado</td>
<td>Batch Tests</td>
</tr>
<tr>
<td>Sodium Chloride (NaCl)</td>
<td>FisherScientific</td>
<td>Fairlawn, New Jersey</td>
<td>Batch Tests</td>
</tr>
</tbody>
</table>

**Denatonium Benzoate** - Concentrations of 5 mg/L and 70 mg/L were used to conduct high and low dose batch test experiments. The denatonium benzoate used in the experiment was obtained from MB Biomedicals in Solon, Ohio.

**Ultrapure Millipore™ Water** - The ultrapure Millipore™ water used in each experiment was kept at room temperature. The water that was used to run each experiment was the same water that was used as a blank in the UV-VIS spectrophotometer.
**Potassium Hydrogen Phthalate (KHP)** - The Hach KHP used in each experiment was stored inside of a desiccator at room temperature. It was used at concentrations of 1, 3, and 5 mg/L.

**Sodium Chloride (NaCl)** - The Hach sodium chloride was used to test the effects of ionic strength on DB adsorption in the presence of KHP. It was used in concentrations of 5, 10, and 20 mg/L.

### 3.2.3 Equipment

#### Table 3.2 Equipment

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Manufacturer</th>
<th>Location</th>
<th>Process Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber Glass</td>
<td>Pyrex</td>
<td>Corning, NY</td>
<td>RSSCTs</td>
</tr>
<tr>
<td>Gas Tight Syringes</td>
<td>Hamilton</td>
<td>Reno, Nevada</td>
<td>RSSCTs</td>
</tr>
<tr>
<td>Fittings and Female Tee</td>
<td>(Swagelock) Cincinnati Valve and Fitting Co.</td>
<td>Cincinnati, Ohio</td>
<td>RSSCTs</td>
</tr>
<tr>
<td>HPLC Pump</td>
<td>Waters (Analytical Instrument Service)</td>
<td>Milford, MA</td>
<td>RSSCTs</td>
</tr>
<tr>
<td>Millipore Reverse Osmosis water System</td>
<td>Millipore</td>
<td>Bedford, MA</td>
<td>Batch Tests and RSSCTs</td>
</tr>
</tbody>
</table>
Reverse Osmosis Water System (Millipore Bedford, MA) - The Millipore Reverse Osmosis Water System (Millipore Bedford, MA) was checked to ensure proper operating conditions before each use. Every two weeks the system’s automatic cleaning system was run and flushed before a new experiment took place.
**UV-VIS Spectrophotometer (Columbia, MD)** - At least one hour before every experiment, the UV-VIS spectrophotometer (Columbia, MD) was turned on (Figure 3.1). A full spectrum was run on standards to determine the location of the peak of DB. The peak was found at or near 270 nm which is a characteristic peak location for DB.

![Shimadzu UV-VIS 1201 Spectrophotometer (Columbia, MD)](image)

**Boekel Hybridization Oven Rotary Shaker (Boekel Scientific Feasterville, PA)** - The Boekel Hybridization Oven (Boekel Scientific Feasterville, PA) contains a carousel that can rotate to speeds of 60 rpm (Figure 3.2). For each batch test experiment, the carousel was set at a speed of 60 rpm. The rotary shaker contained clips that each amber vial fit tightly into. It
also contained a drip pan at the bottom in case of any spills or accidents occurred.

Figure 3.2 Rotating Shaker (Boekel Scientific Feasterville, PA)

**pH Meter Electrode (Fisher Scientific, Denver, CO)** - The Mettler-Toledo pH electrode meter (Fisher Scientific, Denver, CO) was used to measure the pH of the water used in the batch test experiments. The meter was kept in buffer solution and rinsed with ultrapure Millipore™ water before and after each reading took place.

**Disposable Syringe** - BD Luer Lock disposable syringes (5 mL) were used to extract samples from the amber vials after the batch tests were run. The
syringes were stored in their individual sleeves at room temperature. The syringes were properly disposed of after each use.

**Syringe Filter** - The 0.22 µm mixed esters and acetate acrylic membrane filters were used to filter any remaining powder activated carbon from the batch test samples collected in syringes. The membranes used in each experiment were stored at room temperature in their individual sleeves. After each use the membrane filter was properly disposed of in a covered waste container.

**Sieves** - Steel sieve #170 (0.0035 inches) and steel sieve #200 (0.0029 inches) were used to sieve both carbons Norit GAC 1240 and Hydrodarco 4000 after they were ground in a coffee grinder. The carbon was sieved and any carbon that was too large was ground again in the coffee grinder. Carbon that was too small to be used was disposed of in a covered waste container.

**HPLC Pump** – The 510 Water HPLC pump was used specifically to pump water for the RSSCT experiments. It distributed water through the column at a rate of 3 mL/min.
**Fittings and Female Tee** - Stainless steel fittings were used to construct the RSSCT. A stainless steel female tee was used as the port to take samples from the RSSCT.

**Gas Tight Syringe** – A 10 mL gas tight syringe was used to extract samples of DB contaminated water from the RSSCT. The syringe was rinsed with ultrapure Millipore™ water after each use.

**Amber Vials** - The glass amber vials used in the batch test were stored in a cardboard box at room temperature. After each experiment each vial was cleaned with FisherBrand Versa-Clean liquid concentrated soap. The amber vials were then placed in a 10% HCL acid bath for sterilization and to remove metals. The vials were rinsed with Millipore water and drained in an oven at 100°C.

**Quartz Cuvette** - The same quartz cuvette was used throughout the study to ensure there would be no variance in each absorbance reading. The cuvette was rinsed with ultrapure water before and after each reading. The cuvette was stored inside of a plastic cuvette case at room temperature.
Glass Wool - Glass wool made from fiberglass was used to hold the carbon inside the column in place. Small pieces were torn and distributed evenly on each side of the carbon to ensure its security. The glass wool was disposed of after each RSSCT run.

Coffee Grinder (Mr. Coffee, Rye, NY) - A Mr. Coffee coffee grinder (Rye, New York) was used to grind Norit GAC 1240 and Hydrodarco 4000. The coffee was ground under a fume hood to prevent any release of carbon dust into the room.
3.3 Methods

3.3.1 Denatonium Benzoate Analysis

Batch Tests Analysis

Absorbance readings of the batch test samples were analyzed using the Shimadzu UV-VIS spectrophotometer (Columbia, MD) (Figure 3.1) to determine the concentration of denatonium benzoate. The Shimadzu UV-VIS spectrophotometer (Columbia, MD) was turned on one hour prior to sample analysis. This allowed the lamp inside to warm up for the same amount of time. The sample was placed into the quartz cuvette using a BD Luer lock disposable syringe (5 mL) with a 0.22-mm Millipore Millex sterile syringe filter attached to the end to remove the remaining PAC. The same quartz cuvette was rinsed with ultrapure Millipore™ water before and after each absorbance reading. A different disposable filter and sterile syringe was used for each amber vial used in the batch tests.

A calibration curve was developed each time a batch test was run. The calibration curve was made using DB standards. Adsorption readings were taken where the DB peak appeared when the full spectrum was run.
on every standard. A characteristic peak for DB can be found at approximately 270 nm (Bucci, 2006).

**RSSCT Analysis**

Effluent samples of water containing DB that were run through the activated carbon bed were collected from the RSSCT at various times. A gastight Hamilton syringe was used to extract the water sample from the effluent tee. The sample was placed into a quartz cuvette and into the Shimadzu UV-VIS 1201 spectrophotometer (Columbia, MD) for quantification. A UV-VIS spectrum was collected each time a sample was analyzed. Adsorption readings were taken at 270 nm where the characteristic peak for DB was found.

**Standards**

Standards were used to develop a standard curve to determine the amount of DB remaining in the solution. The standard curve established a linear relationship between DB concentration and absorbance (AU). Standards with the DB concentration of 5, 10, and 30 mg/L (Figure 3.3) were used in conjunction with low dose experiments. Standards with the concentration of 50, 75, and 100 mg/L were used in conjunction with
higher concentrated DB experiments (Figure 3.4). Standards were prepared for each experiment.

**Figure 3.3** Standard Concentrations of 5, 10, and 30 mg/L

**Figure 3.4** Standard Concentrations of 50, 100, and 150 mg/L
3.3.2 Performing Batch Tests

Batch Tests

Constant adsorbate isotherm tests were conducted to evaluate the adsorption of DB onto two powdered activated carbons (PACs). Both NORIT® GAC 1240 and HYDRODARCO® 4000 were ground using a coffee grinder. They were then sieved to a mesh size of less than 365. PAC slurries were made by adding the ground carbon to ultrapure Millipore™ water mixed inside of an amber vial. The amber vial was then placed in a desiccator under constant vacuum seal at room temperature. A DB stock solution was prepared by mixing 0.52 grams of solid crushed DB into an Erlenmeyer flask filled with 250 mL of ultrapure Millipore™ water. The stock solution was kept in the refrigerator at 5°C.

Low and high DB contamination scenarios were examined by spiking ultrapure Millipore™ water with DB to achieve 5 mg/L or 70 mg/L concentrations. PAC doses of 5, 10, 20, 50, 100 and 150 mg/L were tested. All batch tests were conducted in triplicate and a blank was run for each test to ensure DB losses were from adsorption. Amber vials containing the appropriate DB and PAC slurry concentrations were placed onto a Boekel
rotary shaker (Boekel Scientific, Feasterville, PA) for continuous mixing at 25°C at a speed of 60 rpm for 3, 12, and 24 hours (Figure 3.1).

To measure the effect of pH on the adsorption of DB, pH readings were taken using the pH meter when carbon and DB was added before mixing took place. Solutions with pH values of 7, 8, and 10 were added to amber vials containing a concentration of 5 mg/L DB and a 10 mg/L concentration of NORIT® 1240. The vials were placed onto a rotating shaker at a speed of 60 rpm for continuous mixing at 25°C for 24 hours. Readings of pH were taken after adsorption and mixing ended at the 24 hour equilibrium time. After use, the pH meter probe was rinsed with ultrapure Millipore™ water and placed inside of buffer solution.

Contamination scenarios were also conducted using an organic compound surrogate. The organic compound used was potassium hydrogen phthalate (KHP). Batch tests were conducted by spiking ultrapure Millipore™ water with DB to achieve 5 mg/L concentrations. Each amber vial also contained 5 mg/L of PAC and either 1, 3, or 5 mg/L of KHP. The vials were placed onto a rotating shaker at a speed of 60 rpm for continuous mixing at 25°C for 24 hours. To determine the effects of ionic strength, experiments were conducted using the same procedure as
the organic compound simulation but only using a 3 mg/L concentration of KHP and adding 5, 10, and 20 mg/L concentrations of sodium chloride with the ionic strengths of 0.000085, 0.000171, and 0.000342, respectively.

All batch tests were conducted in triplicate and a blank for each test was run to ensure DB loss was only from adsorption. All glassware, including amber vials used in each batch test experiment were washed thoroughly with Versa-Clean liquid concentrated soap and placed in a bath of 10% HCl for sterilization after each use.

3.3.3 Rapid Small Scale Column Tests (RSSCTs)

Constructing the RSSCT

Rapid small-scale column tests were conducted by building a scaled-down version of a full-scale (GAC) column (Figure 3.5). Two 10 gallon plastic buckets served as the influent and effluent tanks for the RSSCTs. The influent tank was connected directly to the RSSCT by way of teflon tubing. The pump had an additional teflon of plastic tubing extending from a port serving as means to get the DB spiked ultrapure Millipore™ water to the polycarbonate plastic column carbon bed. The RSSCT was performed by placing the bituminous-based powder activated
carbon bed inside of the polycarbonate plastic 2 cm column with an area of 0.317 cm$^2$. Glass wool was then placed at the top and bottom of the bed to ensure stability. The polycarbonate plastic column had swagelock-stainless steel fittings connected at both ends to ensure a tight fit between the column and the plastic tubing. Teflon tubing was also placed at the top of the column to connect the stainless steel female tee and column together. At the opposite end of the female tee was additional teflon tubing that connected the female tee to the effluent tank.

Figure 3.5 Diagram of the Rapid Small-Scale Column Test
Operating the RSSCT

During the test ultrapure Millipore™ water spiked with denatonium benzoate with concentrations of 10 (mg/L) was placed in the influent tank and run through the PAC column by way of the HPLC pump at a rate of 3 mL/min. The column tests were repeated using various carbon bed lengths of 3, 7.5, and 10 mm. The bed length of 3 mm had a carbon mass of 0.05 grams. The 7.5 and 10 mm bed lengths had masses of 0.084 and 0.127 grams. After each RSSCT the column was rinsed with ultrapure Millipore™ water.
CHAPTER IV

RESULTS & DISCUSSION

4.1 Introduction

The contact time, influence of carbon type, optimal carbon dose, optimal empty bed contact time, effect of organic content of water, and effect of pH conditions on activated carbon adsorption of DB was assessed. The optimal operating conditions that will provide the most efficient use of activated carbon while removing denatonium benzoate were also determined. This was done through batch adsorption tests and rapid small-scale column tests.

4.2 Contact Time

Batch tests were conducted to determine the absolute amount of adsorption and minimal contact time for DB onto AC. These batch tests were conducted with a DB concentration of 5 mg/L and a PAC concentration of 5 mg/L. There was a new calibration curve used for each carbon at each experiment conducted for each contact time.
HYDRODARCO® 4000 had an 8% DB removal at the 12 hour time interval (Figure 4.1). NORIT® GAC 1240 had a removal rate of -3%. This was due to the use of a poor calibration curve that produced an $R^2$ value of 0.94. The experiment was repeated with fresh standards, PAC slurry, and DB stock solution. A new calibration curve gave an $R^2$ value of 0.99 (Figure 4.2). The new 12 hour batch test with NORIT® GAC 1240 had a DB removal of 19% (Figure 4.2). The batch tests confirmed that after 12 hours the carbon had not reached its optimal adsorption. At 24 hours, the optimal contact time for DB adsorption onto both NORIT® GAC 1240 and HYDRODARCO® 4000 carbon was reached. At the 24 hour contact time NORIT® GAC 1240 had a DB removal rate of 42%. HYDRODARCO® 4000 had a removal of 38% after 24 hours. At the 30 hour contact time DB adsorption was lower. The 48 hour batch test had comparable results to the 24 hours. After concluding that 24 hours was the optimal adsorption contact time, subsequent batch tests were conducted at this time.
Figure 4.1 Optimal Adsorption Contact Time

Figure 4.2 Comparisons of Calibration Curves
4.3 Optimal Carbon Type and Dosage for DB Removal

These experiments used ultrapure water spiked with DB to achieve a concentration of 5 mg/L, which is within the 1-10 mg/L concentration range at which water consumers could detect the bitter DB flavor. The batch tests were performed at a contact time of 24 hours. There was a DB concentration of 5 mg/L and carbon dosages of 5, 10, and 20 mg/L were tested for PACs, NORIT® GAC 1240 and HYDRODARCO® 4000. All of the tests were performed in triplicate. NORIT® GAC 1240 had the highest DB adsorption at 20 mg/L (Figure 4.3). NORIT® GAC 1240 removed 95% of the DB at this dose, whereas HYDRODARCO® 4000 only removed 60% of the DB. As the carbon dosage increased for NORIT® GAC 1240 the amount of DB removed was increased. The same trend was observed for HYDRODARCO® 4000.
Subsequent batch tests yielded the same results with different numerical values. As the dosage of carbon increases so does the removal of DB. Figure 4.4 shows 27% DB removal with a 5 mg/L dose of NORIT® GAC 1240. At the 10 and 20 mg/L it displays a removal of 41 and 56%. Figure 4.5 compares HYDRODARCO® 4000 at 10 and 20 mg/L carbon dosages. At 10 mg/L there is a 26% DB removal and at 20 mg/L there is a 55% removal.
Low dose batch tests were repeated comparing a 20 mg/L dose of NORIT® 1240 and a 20 mg/L dose of HYDRODARCO® 4000 (Figure 4.6). The removal of DB is lower for the same tested conditions due to problems with the ultrapure water system. A new stock solution and standards was
used for these experiments. NORIT® 1240 gave a 93% removal and HYDRODARCO® 4000 had a 48% removal. NORIT® GAC 1240 continued to outperform HYDRODARCO® 4000. The increase in removal with the increase in carbon dosage can still be observed.

![Figure 4.6 Percent Removal of 5 mg/L of Denatonium Benzoate for 20 mg/L Doses of NORIT® GAC 1240 and HYDRODARCO® 4000](image)

Shown in the appendix (Figures A2 and A3) are results from low dose batch tests that were deemed inconclusive. The results yielded values over 100%. It was presumed that these tests were conducted with ultrapure water that was high in organics and other constituents because the ultrapure water system needed a filter replacement. To investigate this problem the DB stock solution and carbon slurry were freshly prepared again with properly filtered water from the ultrapure system. After the
system was drained a new filter was installed. New DB stock solution and carbon slurry were prepared and used for the experiments from figures 4.3 to 4.6 which yielded reasonable values.

High carbon dose batch tests were performed at contact time of 24 hours (Figure 4.7). These high dose carbon experiments contained a DB concentration of 5 mg/L and carbon dosages of 50, 100, and 150 mg/L tested for both PACs NORIT® GAC 1240 and HYDRODARCO® 4000. All of the tests were performed in triplicate. NORIT® GAC 1240 had the highest DB removal of 68% at 150 mg/L. HYDRODARCO® 4000 had a comparable removal rate of 68%. The 50 and 100 mg/L concentrations of HYDRODARCO® 4000 had very minimal differences in removal. The 50 mg/L dose had a removal of 33% and the 100 mg/L had a removal of 36%. The NORIT® GAC 1240 PAC continued to show the same trend as in the low dose scenario. As the carbon dose increased so did the removal of DB. Adsorption of DB using HYDRODARCO® 4000 increased with an increasing carbon dosage also. Based on the low and high carbon dose experiments, NORIT® GAC 1240 is the optimal carbon for DB adsorption. NORIT® GAC 1240 works better for a variety of carbon doses. Thus a bituminous-based carbon may achieve better DB removal than a lignite-based carbon.
Figure 4.7 Percent Removal of Denatonium Benzoate for High Doses of HYDRODARCO® 4000 and NORIT® GAC 1240

Isotherms

High and low dose DB and carbon batch tests results were used to generate isotherm plots (Figures 4.3, 4.7). Adsorption isotherms describing DB adsorption onto HYDRODARCO® 4000 and NORIT® GAC 1240 (Figure 4.8, 4.9) indicated that the Freundlich isotherm adequately modeled DB adsorption. The Freundlich isotherm is commonly used to describe sorption to heterogeneous adsorbents such as activated carbon. The isotherms were plotted using a mass-based solid concentration (qlog in mg DB adsorbed/g of PAC) versus a liquid concentration (clog in mg/L).
In the low dose isotherm NORIT® GAC 1240 had a $R^2$ value of 0.9969 (Figure 4.8). It had a high dose isotherm $R^2$ value of 0.9223 (Figure 4.9) HYDRODARCO® 4000 had an $R^2$ value of 0.9898 for the low dose isotherm (Figure 4.8) and 0.8929 (Figure 4.9) for the high dose isotherm. The closer the $R^2$ value is to 1 the better the fit. NORIT® GAC 1240 displayed the best fit between the two PACs for the Freundlich isotherm.

Based on $R^2$ values the carbon usage rate for the NORIT® GAC 1240 low dose (Figure 4.8) isotherm was 0.009 g/L. For the high dose NORIT® GAC 1240 (Figure 4.9) the carbon usage rate was 0.002 g/L. The HYDRODARCO® 4000 had higher carbon utilization rates than that of NORIT® GAC 1240. HYDRODARCO® 4000 at the low dose (Figure 4.8) had a carbon usage rate of 0.01055 g/L, and at the high dose (Figure 4.9) a carbon usage rate of 0.0037 g/L. The lower the carbon usage rates the better because it indicates how much carbon must be used to achieve a target contaminant concentration. Therefore less money would have to be spent when a carbon has a lower carbon usage rate.

The target contamination concentration used for calculating the carbon usage rate was 30 mg/L. The increase in carbon usage rate means that more carbon is needed to achieve a target equilibrium.
concentration level of DB. The increase in carbon amounts to an increase in the cost of activated carbon treatment.

Figure 4.8 Freundlich Isotherm for Denatonium Benzoate Adsorption onto Low Doses of 5-20 mg/L of PACs HYDRODARCO® 4000 and NORIT® GAC 1240

Figure 4.9 Freundlich Isotherm for Denatonium Benzoate Adsorption onto High Doses of 50-150 mg/L of PACs HYDRODARCO® 4000 and NORIT® GAC 1240
4.4 Water Quality Conditions

When water contains a concentration of DB of 70 mg/L or higher water would become unpalatable. Batch tests were performed using a DB concentration of 70 mg/L and carbon dosages of 20, 100 and 150 mg/L (Figure 4.10). Since NORIT® GAC 1240 was determined to be the optimal carbon for DB removal, it was the carbon selected for high DB contamination scenario experiments. The low NORIT® GAC 1240 dosage of 20 mg/L removed 36% of the DB (Figure 4.10). The high NORIT® GAC 1240 PAC dosage of 100 mg/L removed 55%. A carbon dose of 150 mg/L yielded 67% DB removal. DB adsorption increased with the increase of carbon dosage, however at these carbon doses the removal of DB from water does not yield DB concentrations that would make water palatable.
4.5 Effect of pH on DB Adsorption

The pH experiments were conducted using 5 mg/L of DB and 20 mg/L NORIT® GAC 1240. Samples were mixed on the rotary shaker for 24 hours, which was determined to be the optimal contact time. NORIT® GAC 1240 was used because it was determined to be the optimal carbon type for DB removal. The Metter Toledo pH electrode meter (Fisher Scientific, Denver, CO) was used to measure the pH of the samples. The meter was kept in buffer solution and rinsed with ultrapure Millipore™ water before and after each reading took place. The adsorption of DB decreased as the pH condition of the batch test increased (Figure 4.11).
At pH 7 there was 93% removal of DB. At pH 8 DB was removed by 89%. When the pH was adjusted to 10 the removal was 72%. These trends are consistent with published research that indicates most organics are less soluble and more readily adsorbed at a lower pH using PAC. Desilva et al. determined as the pH increases, the removal of organics from water decreases.

Figure 4.11 Percent Removal of DB at pH of 7, 8, and 10
4.6 Effect of Organic Matter on DB Adsorption

Batch tests were conducted with the use of the surrogate organic potassium hydrogen phthalate (KHP) (Figure 4.12). The batch tests were conducted using 5 mg/L of NORIT® GAC 1240 PAC, 5 mg/L of DB, and 1, 3, and 5 mg/L of KHP in triplicate. KHP was used due to the lack of a functioning Total Organic Carbon (TOC) Analyzer. The organic carbon concentration in natural water samples (river water or groundwater) were unable to be measured accurately so a surrogate organic compound, KHP, was used. KHP is a standard used to measure total organic carbon in natural water samples. With 1 mg/L of KHP present, 79% removal of DB was observed. For 3 mg/L of KHP, 96% DB removal was achieved. In the presence of 5 mg/L, 100% DB removal occurred. Typically as background organics (e.g. NOM) concentration increases, adsorption of a target contaminant decreases. However, with the KHP experiments, the opposite trend was observed. Adsorption increased with the addition of KHP.

It was surmised that the high removal rates of DB in the presence of KHP could have been due to cation exchange with KHP. To test this theory, ion exchange experiments were conducted (Figure 4.13), with the premise that ion exchange might be occurring between K⁺ ions at the
carbon surface and the denatonium ion. If the premise held true, then variations in DB adsorption with changes in the ionic strength might be observed. A KHP dose of 3 mg/L and a 5 mg/L dose of PAC were used to conduct the ionic strength experiments. The adsorption for the different ionic strength conditions ranged from 90-94% (Figure 4.13). This was not a dramatic decrease in comparison to the 3 mg/L KHP dose which had a 95% removal (Figure 4.12). Additionally, the removal percentage was similar to the DB removal observed with the 20 mg/L dose of NORIT® 1240 GAC only (Figure 4.3). The ionic strength did not have an effect on the DB removal in the presence of KHP. Thus, another mechanism such as binding of KHP and DB maybe occurring that leads to enhance DB removal in the presence of KHP, or the pH of the solution could be lowered when KHP is added leading to more DB adsorption. As previously discussed herein, lower pH conditions yielded more DB adsorption.
Initial experiments to determine the effects of organics on adsorption using a 1, 3, and 5 mg/L dose of KHP, 5 mg/L dose of NORIT® GAC 1240, and a 5 mg/L dose of DB were conducted under the same
conditions as above. The 1 mg/L of KHP had a -22% removal. The 3 mg/L had an 87% removal. The 5 mg/L had a 160% removal. These results can be seen in Appendix B (Figure 1). To determine the error in the experiment fresh DB stock solution, standards, and carbon slurry were made. A new calibration curve was produced and the results in Figure 4.12 were obtained. The confusion in the experiment seemed to be due to some kind of contamination either from the standards or ultrapure water used to make stock solutions.

When the ionic strength was tested for the previous experiment a strange array of adsorption values appeared once again. The adsorption for the different ionic strength conditions ranged from 16-23% (Appendix B, Figure 2). The experiments were run using the same stock solution as the initial organic experiments that yielded inconclusive results possibly due to ultrapure water contamination or poor quality standards.

4.7 Rapid Small-Scale Column Tests (RSSCTs) Results

RSSCTs were conducted using for 3-min, 7.5-min, and 10-min EBCTs using a initial DB concentration of 10 mg/L and carbon masses of 0.05, 0.127, 0.169 grams. These EBCTs used activated carbon bed lengths of .3, .75, and 1 cm for the 3-min, 7.5-min, and 10-min EBCTs respectively.
Results from the RSSCTs were inconclusive. The DB concentrations in samples from each RSSCT were negative values, which is not possible (Appendix C, Figure 1). The negative values were possibly due to poor standards producing a poor calibration curve or contamination of ultrapure water. Figure 4.14 displays the original calibration curve with an $R^2$ value of 0.9575. Readings were taken at 268 nm, based on the observed location of the characteristic DB peak.

A fresh DB stock solution and standards were prepared and a new calibration curve was developed. The standards were then measured at 270 nm (where the characteristic DB peak appeared) and the new calibration curve had an $R^2$ value of 0.9991. Two days later the standards were measured again at 268 nm and produced an $R^2$ value of 0.9987. The large variance between the original calibration curve and the two most recent curves is presumed to be due to poor quality standards. This could have been caused by lack of maintenance (regular cleaning and changing of the filter cartridges) of the ultrapure water system. The fact that the new standards yielded calibration curves on two separate dates that were close together and had suitable $R^2$ values indicated that the UV-VIS spectrophotometer instrument was working properly and was not the cause of negative data values and the inconclusive results. Thus,
RSSCTs experiments should be repeated (as future work) ensuring the ultrapure water system is regularly maintained and experiments are conducted with high quality water.

Figure 4.14 Empty-Bed Contact Time Calibration Curve Comparisons

**Standard Curve**

- Original: $y = 0.0074x + 0.1152$, $R^2 = 0.9575$
- Second: $y = 0.006x - 0.0141$, $R^2 = 0.9991$
- Newest: $y = 0.0054x - 0.0137$, $R^2 = 0.9987$

**ABS (AU)** vs. **DB concentration (mg/L)**

Figure 4.14 Empty-Bed Contact Time Calibration Curve Comparisons
PART V
CONCLUSIONS & RECOMMENDATIONS

Activated carbon is effective for the removal of the bittering agent, denatonium benzoate, from water. Activated carbons NORIT® GAC 1240 and HYDRODARCO® 4000 are both good treatment methods for removing lower concentrations of denatonium benzoate (5 mg/L or lower) from water. After conducting several contact time tests both powdered activated carbons had the most success at removing denatonium benzoate at the 24 hour time period. The optimal carbon dose for a 5 mg/L DB contamination scenario was 20 mg/L when using the PAC NORIT® GAC 1240, with the carbon achieving a DB removal of 95%. For higher concentrations of DB (70 mg/L or higher) other treatment methods should be considered including tailoring of carbon surface, investigating other carbon types to improve DB adsorption, or the use of oxidation. The addition of KHP slightly enhances the adsorption of DB on activated carbon, but the effect is minimal. Ionic strength experiments indicted that ionic strength had no affect on the adsorption of DB on to activated carbon in the presence of KHP.
Thus, a bituminous-based carbon at a dose of 20 mg/L is sufficient for the removal of low concentrations of 5 mg/L or less of DB. The pH of the water treated for DB removal should be kept in a range of 6.25 and 8, and organic material may not have a significant impact on DB adsorption.

In comparison, it was determined that powdered activated carbon was effective in the removal of geosmin and MIB, two common taste and odor compounds, when the correct carbon dose was applied. NOM decreases the adsorption capacity of MIB and geosmin onto activated carbon, and higher doses of PAC were required to get MIB and geosmin to acceptable water quality levels (Yu et al. 2007). Thus, treatment facilities using activated carbon for removing MIB or geosmin, could possibly remove DB in the water as well.

Further studies on the adsorption of DB onto AC should include conducting experiments using natural water spiked with DB. Experiments using other types of activated carbon (wood and coconut shell) should also be conducted. Rapid small-scale column tests should be repeated ensuring the ultrapure water system is properly maintained. RSSCTs should also be conducted under constant and proportional diffusivity conditions,
so the constant and proportional RSSCTs results can be compared. Batch
tests should also be performed using tailored carbons that can increase
DB adsorption capacity. Additional experiments should be conducted to
further investigate the effect of ionic strength on DB adsorption in the
presence of organics.
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APPENDIX A

BATCH TESTS WITH EXPERIMENTAL ERROR

Figure A1. Optimal Contact Time Studies

Figure A2. Percent Removal of 5 mg/L of Denatonium Benzoate for Low Doses of HYDRODARCO® 4000
Figure A3. Percent Removal of 5 mg/L of Denatonium Benzoate for Low Doses of NORIT® GAC 1240
APPENDIX B

EFFECTS OF ORGANICS EXPERIMENTAL ERROR

Figure B1. Potassium Hydrogen Phthalate (KHP) Effects on the Adsorption of 5 mg/L of DB Using 3 mg/L of NORIT® GAC 1240

Figure B2. Effects of Ionic Strength on Adsorption
APPENDIX C

RAPID SMALL-SCALE COLUMN TESTS EXPERIMENTAL ERROR

Figure C1. Empty Bed Contact Time