Pre-treatment of dynamically varying waste gas concentrations using activated carbon prior to biofiltration: effect of cycle length on degree of load equalization

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PRE-TREATMENT OF DYNAMICALLY VARYING WASTE GAS CONCENTRATIONS USING ACTIVATED CARBON PRIOR TO BIOFILTRATION: EFFECT OF CYCLE LENGTH ON DEGREE OF LOAD EQUALIZATION

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering in

The Department of Civil and Environmental Engineering

by

Kodi L. Collins
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ABSTRACT

Dynamically varying waste gas concentrations pose challenges to the operation and design of air pollution control techniques such as biofilters. Although design approaches are becoming well established for biofilters treating gases containing VOC concentrations that are constant as a function of time, many industrial processes emit gas streams contaminated with volatile organic compounds at concentrations that fluctuate with time. Application of an effective load equalization technique could eliminate some challenges associated with fluctuating pollutant concentrations. Recent research has demonstrated that granular activated carbon (GAC) can serve as a passively controlled system to provide load-equalization as a pre-treatment prior to biofiltration.

Research described in this thesis was conducted to evaluate the effect of cycle length and fraction of time of contaminant loading on the degree of load equalization achieved by GAC columns subjected to intermittent pollutant loading. Columns filled with Calgon BPL 4 x 6 mesh GAC were experimentally tested with influent toluene concentrations of 250 ppmv and 1000 ppmv at cycle lengths as short as 6 hours and as long as 48 hours. The fraction of time that toluene was loaded to the columns ranged from 1/2 to 1/6 of the total cycle length. During non-loading intervals, contaminated-free air flowed through the columns at the same rate as contaminated air was supplied during loading intervals. Results revealed that passively operated GAC columns could provide effective load equalization by temporarily accumulating toluene during periods of high loading and subsequently desorb toluene during periods of no loading. Results also showed that the degree of load equalization increased as cycle length decreased, the fraction of time toluene was loaded decreased, and the influent contaminant concentration decreased. A pore and surface diffusion model (PSDM) was used to simulate the degree of load
dampening achieved by GAC columns under various discontinuous loading conditions. The PSDM was able to predict the degree of load equalization achieved by each experimentally tested cyclic loading scenario within a reasonable degree of accuracy.
CHAPTER 1 INTRODUCTION

1.1 Rationale

Biofiltration is an emerging technology that is applied to remove volatile organic compounds (VOCs) from contaminant airstreams. Reasons for the increasing application of this treatment technology include low operational cost, operational simplicity, and lack of secondary pollutant generation (Devinny et al., 1999). Design and operation of biofilters is becoming well defined for treating VOC concentrations that do not vary with time. Many industrial processes, however emit gas streams contaminated with volatile organic compounds at concentrations that fluctuate with time (Dirk-Faitakis et al., 1996). Because of the inherent nature of these processes, many of these industrial processes emit contaminants at regular intervals on a repeating basis. For example, an industrial process with a fixed workday and overnight shutdown will result in cyclic waste gas generation over a 24 hour cycle length (i.e. 8 hours of contaminants present followed by 16 hours of no contaminants present). Regular transient loading can also occur over shorter time intervals and longer time intervals.

Several studies have demonstrated that fluctuations in concentrations of organic vapors present in gas streams can hinder biofilter performance and removal efficiency. Temporary periods of high contaminant loading can produce dynamic mass loading rates that exceed the biological reaction capacity and result in unacceptably high contaminant emissions that do not comply with regulations and standards set by federal or state regulations. On the other hand, periods of very low or no loading for an extended period of time (that can occur during periods of shutdown) can impose starvation conditions on the microbial community in the biofilter, resulting in diminished performance when “normal” contaminant loading resumes (Martin and Loehr, 1996; Moe and Irvine, 2001; Martin et al., 2002; Atoche and Moe, 2004; Li and Moe, 2005; Wright et al., 2005).
Recent studies have demonstrated that columns packed with granular activated carbon (GAC) can serve as a passively controlled system to provide load-equalization prior to biofiltration. The rationale for such system is that during periods of high loading, the GAC can adsorb contaminants temporarily and subsequently desorb the contaminants during periods of low or no loading. The GAC could dampen fluctuations in organic loading to prevent shock loading of the biofilter and provide continuous feeding to the biofilter during periods of no waste generation. Ultimately, effective application of GAC as a pre-treatment technique has the potential to minimize or eliminate periods of high contaminant emissions and starvation in biofilters. This strategy was first proposed by Ottengraff (1986), and has since been recommended by various other authors (Weber and Hartmans, 1995; Li and Moe, 2005; Moe and Li, 2005).

The majority of studies investigating such applications of GAC as a load equalization mechanism for VOC-contaminated gas streams have been conducted using a fixed cycle length and fraction of time for contaminant supply (i.e., 8 hours of contaminant loading followed by 16 hours of no contaminant loading) (Weber and Hartmans, 1995; Li and Moe, 2005; Moe and Li, 2005). It is also important, however to evaluate performance of GAC load equalization systems under conditions where contaminants fluctuate over various other time scales because industrial processes often emit contaminants over time intervals that are longer or shorter than 8 hour/day (Dirk-Faitakis et al., 2003). In the research proposed herein, laboratory scale experiments and modeling were conducted to systematically assess the effects of cycle length and fraction of time of contaminant supply on the degree of load equalization achieved by GAC columns. Toluene was used as the model contaminant.
1.2 Objective

The overall objective of this research was to better understand the effects of cycle length and fraction of time in loading on load equalization of granular activated carbon. This objective involved a two part approach: 1) experimental testing 2) model simulations. The following objectives were identified:

1) To assess the degree of load equalization achieved by GAC columns subjected to intermittent loading at specific cycle lengths.

2) To assess the buffering capacity of GAC columns subjected to intermittent loading at various fractions of times of loading and no loading.

3) To further evaluate the affects of contaminant concentration on the degree of load equalization achieved by GAC.

4) To predict the degree of load equalization achieved by each experimentally tested loading condition using modeling software.

1.3 Thesis Organization

The organization of the remainder of this thesis is as follows: Chapter 2 provides a brief literature review pertinent to this research. Chapter 3 explains the materials and methods employed in experimental testing. Chapter 4 contains the results from experimental testing. Chapter 5 describes the methods employed for modeling simulations. Chapter 6 shows results of modeling simulations, and a comparison between model predictions and experimental measurements. Chapter 7 provides a summary of overall conclusions along with recommendations for future research.
CHAPTER 2  BACKGROUND AND LITERATURE REVIEW

2.1 Air Pollution Control

In recent years, the effects of air pollution on the environment and those that habitat it have become better understood. The growth in this awareness has resulted in various federal and state regulations governing industrial air emissions that reflect potential health risks and environmental degradation that contaminant emissions create (Devinny et al., 1999). For example, in the U.S., enactment of the Clean Air Act (CAA) has resulted in stricter regulations for air emissions. Many industries that produce emissions apply treatment technologies to reduce the contaminant emission level to meet regulatory standards, or corporate environmental stewardship goals. Biological treatment is an emerging treatment option that many industries are adopting.

2.4 Biological Treatment of Waste Gas Streams

Biological treatment is a pollutant control technique that utilizes microbial reactions to treat gas phase contaminants. Biological treatment is effective and cost efficient for many industrial process that produce gas phase contaminants. Biological treatment relies on different types of microorganisms such as fungi, bacteria, protozoa, and algae to interact with the contaminants. Oxidation and occasional reductive reactions are carried out, and the contaminants are converted to carbon dioxide, water vapor, and organic biomass. The pollutants may be organic or inorganic, and can be acted upon by naturally occurring microorganisms that are present in the system. These naturally occurring microorganisms exist in a population that usually contains a dominant microbial species that interacts with other species to attack the contaminant. In return, the contaminant is used as an energy and carbon source by the microbial community to help maintain growth in the microbial population (Devinny et al., 1999).
For biological treatment to be successful, the contaminant must be able to be biodegraded by the microbial species present. Microorganisms biodegrade substances that are most readily biodegradable. In general, low molecular weight and highly soluble organic compounds with simple bond structures are more easily degraded than high molecular weight or sparingly soluble compounds that are complex in structure. The chemicals treated by biofilters are usually volatile organics, reduced sulfur, and nitrogen compounds (Swanson et al., 1997). Compounds that are biodegradable can come from a broad range of sources, such as chemical manufacturers, petroleum industries, adhesive production, and furniture manufacturing (Devinny et al., 1999).

Biofilters, biotrickling filters, and bioscrubbers are the three main types of biological treatment technologies. The main differences in the techniques are the phase of the microbes, which can be suspended or fixed, and the state of the liquid, which may be flowing or stationary (LaGrega et al., 2001). Biofiltration utilizes microorganisms that are fixed to the support medium with a stationary water phase. Biotrickling filters have fixed microorganisms with a flowing stationary phase, and bioscrubbers have suspended microorganisms with a flowing water phase. Additional information about biofilters in particular is presented below in Section 2.5.

2.5 Biofilters

Biofiltration is a biological air pollution control technology that originated in Europe for odor abatement. Over the past decades, biofiltration has developed into a more sophisticated technique used to treat contaminant emissions associated with industrial processes (Swanson et al., 1997). Biofiltration utilizes microorganisms that are fixed to an inert support medium to degrade contaminants. The solid support medium may be made of moss, peat, compost, polyurethane foam, or essentially any other medium able to support biofilm attachment. Microorganisms grow in the form of biofilm or biomass that is attached to the surface of the
packing materials, or they may be present in the water phase surrounding the medium particle (See Figure 2.1).

![Figure 2.1 Internal mechanisms of a biofilter. Contaminated air passes through the filter medium with O\textsubscript{2} and sorbs into the biofilm. Microbes convert the contaminant to CO\textsubscript{2} and water (Devinny et al., 1999).](image)

Before gases enter a biofilter they may be preconditioned to adjust moisture level and gas temperature, and particulates are removed (See Figure 2.2). Preconditioning may involve adding water to control the moisture content (Devinny et al., 1999). According to Swanson et al. (1997) five pretreatment processes usually occur before the air stream enters a biofilter, namely, particulate removal, load equalization, temperature regulation, humidification, and gas distribution.

Biofilters are most effective in treating air streams that contain a total organic load of 1500 ppmv or less (LaGrega et al., 2001). Swanson et al. (1997) identified load equalization as a positive pre-treatment application, especially if the waste gas VOC concentration is “highly variable with time”. The idea is that a load equalization technique would dampen peak loading to a biofilter. Activated carbon was the suggested load equalization technique identified in their
study. However, they did not report any data or modeling results or identify appropriate design criteria.

Figure 2.2 Schematic of an above ground closed biofilter (Devinny et al., 1999).

According to Devinny et al. (1999), characteristics that determine the overall effectiveness of the biofilter removal capacity include: support medium porosity, degree of compaction, water retention capabilities, and ability to host microbial community. Swanson et al. (1997) explored numerous factors that affect the design, operation, and performance of biofilters, including: media selection, moisture content, acclimation, microorganisms present, pH level, and nutrient availability.

2.6 Activated Carbon and Adsorption

Previous studies have demonstrated that activated carbon can be applied as a passively operated pre-treatment technique to provide load equalization to a biofilter (Weber and Hartmans, 1995; Moe and Li, 2005; Li and Moe, 2005). Activated carbon is prepared by making a char from products such as almond, coconut, walnut hulls, woods, or coal. These materials are first heated to a red heat in a retort to eliminate hydrocarbons that are present and produce a char.
The char is activated by introducing an oxidizing gas at a high temperature. A porous structure is formed in the char causing a large internal surface area to form. The surface properties are characteristic of the preparation procedure and the initial product composition. The initial product may also affect the pore-size that forms. Many variations of activated carbon are applied in the industry; however, there are two size classifications that characterize activated carbon. The two size classifications are powdered, which has a diameter of less than 200 mesh; and granular, which has a diameter greater than 0.1 mm (Pontius, 1999).

Pontius (1999) describes adsorption in three steps: macrotransport, microtransport, and sorption. Macrotransport is the movement of the organic material to the liquid-solid interface by advection or diffusion. Microtransport involves the movement of the organic material through the macropores to the micropores and submicropores (adsorption sites) of the granule. The microspores and submicropores have a surface area substantially larger than the macropores and mesopores; therefore, absorption at the macropores and mesopores is usually negligible. Lastly, adsorption is a process by which a component or organic material attaches to granular activated carbon. When the rate of sorption equals the rate of desorption, equilibrium has been reached, thus the adsorption capacity has been reached. LaGrega et al. (2001) illustrates adsorption as a four step phenomena: bulk fluid transport, film transport, intraparticle (pores and/or surface diffusion), and physical attachment (See Figure 2.3).

The film and intraparticle transport is slow compared to the bulk transport and adsorption processes. The slow nature of the film transport and intraparticle transport govern these transport mechanisms as the rate-limiting steps that control design. The driving forces that control and affect adsorption include: electrical attraction, a chemical affinity of the particle organic molecule for the adsorbent, Van der Waal’s forces, and hydrophobic nature of the organic. Table 2.1 list factors that affect carbon adsorption (LaGrega et al., 2001).
Figure 2.3. Transport process (LaGrega et al., 2001).

Table 2.1. Factors affecting carbon adsorption (LaGrega et al., 2001).

<table>
<thead>
<tr>
<th>Factor</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility</td>
<td>Less soluble compounds are adsorbed to a greater extent than more soluble compounds.</td>
</tr>
<tr>
<td>Molecular structure</td>
<td>Branch-chain organics are more easily adsorbed than straight-chain organics.</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Larger molecules are generally more easily adsorbed than smaller molecules. However, when pore diffusion governs the adsorption process, the adsorption rate decreases with molecular weights above values specific to each type of carbon and with in a given class of organics.</td>
</tr>
<tr>
<td>Polarity</td>
<td>Less polar (or weakly ionized) organics are more easily adsorbed than polar (or strongly ionized) organics.</td>
</tr>
<tr>
<td>Hydrocarbon saturation</td>
<td>Double- or triple-carbon bond (unsaturated) organics are adsorbed more easily than single-carbon bond (saturated) organics.</td>
</tr>
</tbody>
</table>
There are two widely used equations for describing adsorption characteristics of activated carbon under equilibrium conditions. The first, the Freundlich isotherm, is defined in equation 2.1 (Pontius, 1999):

\[
\frac{x}{m} = K_f C_e^{1/n}
\]  
\hspace{1cm} (2.1)

where \(x/m\) = amount adsorbate adsorbed per unit weight of adsorbent (carbon); \(C_e\) = equilibrium concentration of adsorbate in solution after adsorption; \(K_f\) and \(n\) are empirical constants.

The second, the Langmuir isotherm, is defined in equation 2.2 (Pontius, 1999):

\[
\frac{x}{m} = \frac{a b C_e}{1 + b C_e}
\]  
\hspace{1cm} (2.2)

where \(x/m\) is the amount adsorbed per unit weight of adsorbent; \(a\) and \(b\) are empirical constants; and \(C_e\) is the equilibrium concentration of adsorbate in solution after adsorption. One approach of selecting an appropriate isotherm equation involves selecting the isotherm equation that best describes the experimental data (Tchobanoglous and Burton, 1991).

2.7 The Effect of Unsteady State Loading Conditions on Biofiltration and Application of GAC

Conventional biofilters are generally designed to treat VOC contaminant concentrations that are relatively constant with time. Many industrial processes, however, emit gas streams contaminated with volatile organic compounds at concentrations that fluctuate with time (Dirk-Faitakis et al., 2003). Dirk-Faitakis et al. (2003) noted various industrial processes that have periodic emission patterns including brownstock washers in Kraft pulp mills, and tank vents and press vents in the production of wood products. In many of these operations, fluctuations in the contaminant concentrations occur at regular intervals over a time period. For example, an industrial process with an 8-hour workday and overnight process shutdown will result in a cyclic
waste gas generation over a 24 hour cycle length, with 8 hours of contaminants present followed by 16 hours of no contaminants present. This type of transient loading can also occur over time intervals as short as minutes or as long as days.

Several previous studies indicate that unsteady-state loading conditions can hinder biofiltration performance. For example, temporary periods of high contaminant loading can result in dynamic mass loading rates that exceed the biological reaction capacity and result in unacceptably high contaminant emissions. On the other hand, periods of very low to no loading for an extended period of time can impose starvation conditions on the microbial community in the biofilter, resulting in diminished performance when “normal” contaminant loading resumes (Martin and Loehr, 1996; Al-Rayes et al., 2001; Moe and Irvine, 2001; Martin et al., 2002; Atoche and Moe, 2004; Li and Moe, 2005; Wright et al., 2005). Martin and Loehr (1996) observed the effects of periods of non-use on biofilter performance. They characterized periods of non-use in two ways: 1) “no chemical loading”: where no contaminants were present in the gas stream and 2) “stagnant”: no flow was being passed through the biofilter. They found that both periods of non-use required microorganisms in the biofilter to re-acclimate to differences in loading when the waste stream was re-applied to the biofilter. They found that re-acclimation times ranged from several hours to longer than a day, with the longer periods being observed when there were longer periods of non-use. Comparing the two types of non-use scenarios, stagnant times required longer re-acclimation time than periods where no chemicals were in the gas stream. Biofilter media acclimation is a very important factor in the performance of a biofilter. Insufficient acclimation of the microorganisms present in the biofilter media cause the performance of the biofilter to diminish (Martin and Loehr, 1996).

According to Weber and Hartmans (1995), for reliable operation, the design of a biofilter should be based on peak contaminant concentration. However, this is not an economically
favorable situation. On the other hand, if biofilters were designed based on average waste concentrations in an air stream that had transient elevated concentrations, then the dynamic mass loading may exceed the biological reaction capacities resulting in unacceptably high effluent contaminant concentrations.

Incorporation of an adsorptive substance into a biofilter packing medium has been suggested by various authors to address the unsteady state nature of many industrial processes. This strategy was first proposed by Ottengraff (1986), and has since been recommended by various other authors (Devinny et al., 1999; and Swanson et al., 1997). Ottengraff (1986) discussed the use of an adsorbing particle (such as activated carbon particles) in combination with the natural packing media to treat industrial processes that have varying waste gas streams or discontinuous processes. He suggested that the adsorbent would adsorb contaminants during periods of peak loading and desorb contaminants during periods of reduced loading to sustain the microbial decomposition; however, no experimental or modeling results were present to support this notion. Experimental testing of a system where GAC was mixed with the biofilter media was reported by Mohseni et al. (1999). Mohseni et al. (1999) compared removal of α-pinene in two biofilters. One biofilter was composed of a mixture of wood chips, mushroom compost, and perlite (an inert medium with little or no adsorption capacity); and the second biofilter was composed of wood chips, mushroom compost, and activated carbon. Research found that the biofilter amended with activated carbon performed very similarly to the biofilter amended with perlite. Very little or no benefit was seen by the biofilter amended with activated carbon after long-term operation. Mohseni et al., (1999) attributed that this phenomenon could have occurred from humidification, water occupying the active sites, or the active sites being covered in biofilm.
Recent studies have demonstrated that columns packed with granular activated carbon (GAC) can serve as a passively controlled system to provide load-equalization when applied in series prior to biofiltration (Weber and Hartmans, 1995; Li and Moe, 2005; Moe and Li 2005). The rationale for such system is that during phases of high loading, the GAC can temporarily adsorb contaminants and desorb the contaminants during phases of low or no loading, with this process occurring before the air stream enters a downstream air pollution treatment system such as a biofilter. If successfully implemented, the GAC could reduce fluctuations in organic loading to prevent shock loading of the biofilter (thereby minimizing or eliminating high contaminant emissions), and provide constant feeding to the biofilter during periods of no waste generation (thereby minimizing or eliminating starvation conditions). Weber and Hartmans (1995) also studied the use of activated carbon as a buffer for waste gases with fluctuating concentrations of toluene. In their study, effluent toluene concentrations were analyzed in three different configurations of a biofilter system. The first system was designed without any activated carbon (a conventional biofilter). The second system incorporated activated carbon into the compost of the biofilter. The third system placed activated carbon in series with the biofilter. The removal efficiency of the system that incorporated activated carbon into the compost of the biofilter was about the same as the removal efficiency of the biofilter that had no activated carbon, both averaging around 50%. The system that used activated carbon in series with the biofilter buffered the concentration to about 300 mg, which was completely degraded by the biofilter. Moe and Li (2005) tested the adsorption capacity of Calgon BPL 4 x 6 mesh GAC for load equalization of toluene contaminated air when the GAC column received toluene for 8 hours a day followed by 16 hours of no toluene present. Experiments tested a variety of influent contaminant concentrations (ranging from 210 ppmv to 1000 ppmv), and empty bed contact times (EBCT) (ranging from 1.5 seconds to 10 seconds). Results showed that efficient load
equalization could be achieved by low EBCT for the range of concentrations that biofilters typically treat (Moe and Li, 2005). Moe and Li (2005) also described how the application of a GAC pre-treatment system can allow for the incorporation of a safety factor in the design of biofilters. Passively operated GAC load equalization systems, have only been tested for systems receiving contaminants at a fixed cycle length and fixed fraction of time of contaminant supply (i.e., 8 hr. contaminant loading followed by 16 hr. no contaminant lading).

Another method for pre-treating unsteady state contaminant loading is described by Hashisho et al., 2007. Hashisho et al. (2007) used an activated carbon fiber cloth in conjunction with microwave swing adsorption to buffer methyl ethyl ketone (MEK) in an air stream. The system was controlled by a microwave generator that provided power to periodically regenerate the adsorbent. Experimental testing of this system demonstrated that it could successfully control the MEK concentration. Furthermore, by controlling the power delivered by the microwave generator, the system could ultimately allow the user to achieve a user-selected MEK concentration during desorption. Such capabilities could allow a biofilter to be optimized for a selected constant concentration. Although this technique is promising, it requires a sophisticated control system that has not yet been tested at pilot-scale.

2.8 Background to Model Configuration

The model used in this research to simulate performance of GAC columns during intermittent loading conditions was a pore and surface diffusion model described by Crittenden et al. (1986) and Hand et al. (1997). The PSDM incorporates the following assumptions: 1) Constant flow rate, 2) Plug-flow conditions exist in the bed, 3) Linear driving force describes the local bulk phase mass flux at the exterior surface of the adsorbent particle, 4) Local adsorption equilibrium exists between the solute adsorbed onto the GAC particle and the solute in the intra-aggregate stagnant fluid. 5) Intraparticle mass flux is described by surface and pore diffusion.
Adsorption equilibrium of individual compounds can be represented by the Freundlich isotherm equation and IAST describes the competition between the compounds. 7) There are no interactions between adsorbing compounds during the diffusion process (Mertz et al., 1999).

Two partial differential equations are obtained for the bulk phase and adsorbent phase from mass balances on each adsorbing component. Assuming local equilibrium at the exterior of the adsorbent particle, a coupling equation between the bulk phase and the adsorbent phase is obtained. In cases where pore and surface diffusion are present, local equilibrium is assumed along the pore walls. These equations are solved by numerical methods. The orthogonal collocation method is used to convert the partial differential equations into a set of ordinary differential equations (Finlayson, 1972 and 1980; Villadsen, 1978). The set of ordinary differential equations is solved using the Gear’s Stiff method, a backward differentiation method formula. Crittenden et al. (1986) and Friedman (1984) have presented the derivation of the equations and the computer algorithms that were used to solve the model equations. The detailed derivation of these equations is given by Friedman (1984). The PSDM model equations are summarized below:

The fluid phase mass balance for component \( i \) is given by:

\[
\frac{\partial C_i(z,t)}{\partial t} + V \frac{\partial C_i(z,t)}{\partial z} + \frac{3k_{fi}(1 - \varepsilon)}{\varepsilon R} [C_i(z,t) - C_{pi}(r = R,z,t)] = 0 \tag{2-1}
\]

Where \( C_i \) is the gas-phase concentration (mmol/L) of absorbent \( i \) at time \( t \) (sec) and axial position along the bed \( z \) (cm). \( k_{fi} \) is the film mass transfer coefficient (L/T). \( R \) is the average absorbent particle radius (L). \( \varepsilon \) is the particle void fraction (porosity). \( V \) is the loading rate (L/T).

The initial condition for equation 2-1 is:
\[ C_i(z,t) = 0 \quad \text{at} \quad 0 \leq z \leq L, t = 0 \quad (2-2) \]

The boundary condition for equation 2-1 is:

\[ C_i(z,t) = C_{o,i} \quad \text{at} \quad z = 0, t > 0 \quad (2-3) \]

The intraparticle phase mass balance for component i is given by:

\[
\frac{I}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_{s,i} \frac{\partial q_i(r,z,t)}{\partial r} + \frac{r^2 D_{p,i}}{\rho_a} \frac{\varepsilon_p}{\partial r} C_{p,i}(r,z,t) \right] = \frac{\partial}{\partial t} \left[ q_i(r,z,t) + \frac{\varepsilon_p}{\rho_a} C_{p,i}(r,z,t) \right] \quad (2-4)
\]

\(D_{s,i}\) is the surface diffusivity (L^2/T). \(D_{p,i}\) (L^2/T) is the pore diffusivity. \(C_{p,i}(r,z,t)\) (M/L^3) is the adsorbate concentration in the absorbent pores and \(q_i(r,z,t)\) is the adsorbent phase concentration (M/M). \(\rho_a\) (M/L^3) is the apparent adsorbent density.

The initial condition for equation 2-4 is:

\[ q_i(r,z,t) + \frac{\varepsilon_p}{\rho_a} C_{p,i}(r,z,t) = 0 \quad \text{at} \quad 0 \leq r \leq R, \quad t = 0 \quad (2-5) \]

The first boundary condition for equation 2-4 is:

\[
\frac{\partial}{\partial r} \left[ q_i(r,z,t) + \frac{\varepsilon_p}{\rho_a} C_{p,i}(r,z,t) \right] = 0 \quad \text{at} \quad r = 0, t \geq 0 \quad (2-6)
\]

The second boundary condition for equation 2-4 is:

\[ D_{s,i} \rho_a \frac{\partial q_i}{\partial r}(r = R,z,t) + D_{p,i} \varepsilon_p \frac{\partial C_{p,i}}{\partial r}(r = R,z,t) = k_{f,i} \left[ C_i(t) - C_{p,i}(r = R,z,t) \right] \quad (2-7) \]

The equation coupling the aqueous phase concentration of component i within the adsorbent pores to the adsorbent phase concentration of component i is given by:

\[
C_{p,i}(r,z,t) = \frac{q_i(r,z,t)}{\sum_{k=1}^{m} q_k(r,z,t)} \left[ \frac{\sum_{k=1}^{m} n_k q_k(r,z,t)}{n_i K_i} \right]^{n_i} \quad (2-8)
\]
The above equation is derived assuming that the adsorption reaction rate is much faster than the mass transfer rate (assumption of local equilibrium). Where m is the number of component adsorption calculations. Using this model requires equilibrium and kinetic parameters combined with several physical properties of the adsorbing compound(s) and the adsorbent. These parameters and physical properties are easily obtained using the AdDesignS™ databases, which are integrated with parameter estimation techniques (Crittenden et al., 1980; Crittenden et al., 1986; Mertz et al., 1999; Ramakrishnan et al., 2004).
CHAPTER 3 MATERIALS AND METHODS FOR EXPERIMENTAL APPROACH

3.1 Introduction

As described in Chapter 2, the majority of studies investigating applications of GAC as a load equalization device have been conducted using a fixed cycle length and fraction of time for contaminant supply (i.e., 8 hours of contaminant loading followed by 16 hours of no contaminant loading) (Weber et al., 1995; Moe et al., 2005). It is also important to evaluate the performance of GAC load equalization systems under conditions where contaminants fluctuate over various other time scales because industrial processes often emit contaminants over time intervals that are longer or shorter than 8 hour/day (Dirk-Faitakis et al., 2003). As described in this chapter, laboratory-scale packed-bed experiments were conducted to evaluate GAC load equalization systems under conditions where contaminants fluctuate over various other time scales. Specifically, the effects of cycle length (6 to 48 hours) and fraction of time for contaminant supply (1/2, 1/3, or 1/6 of the cycle length) on the degree of load equalization were systematically assessed. Toluene was used as the model contaminant in all experiments.

3.2 Granular Activated Carbon and Experimental Apparatus

The granular activated carbon utilized in this research was BPL 4x6 mesh GAC (Calgon Carbon Corp, Pittsburg, PA). The GAC was prepared by first washing with distilled water to remove fine particles present, and then dried in an oven at 105 °C. After drying, the activated carbon was placed in a desiccator until use in construction of the activated carbon columns. Each column was constructed with 50 cm long PVC (7.62 cm i.d.). 6 cm depth of glass beads (5mm in diameter) were supported by a mesh screen. A layer of glass wool separated the glass beads from 33.3 cm depth of GAC, and a second layer of glass wool separated the GAC from another layer of 6 cm of glass beads (5mm in diameter). The general configuration of the GAC column and schematic operation of the system can be found in Figure 3.1.
Figure 3.1 Schematic diagram of apparatus used for fixed bed adsorption/desorption experiments.

Non-contaminated air flowed through a pressure regulator and then a filter to regulate and cleanse the air entering the system. A mass flow controller (Model GFMC37, Aalborg Instruments, Orangeborg, NY) set at 22.8 l/min was incorporated in the system to ensure correct deliverance of uncontaminated air. Syringe pumps (KD Scientific, Boston, MA) delivered a specified rate of liquid toluene (ACS reagent grade, Sigma, St.Louis, MO) to the system to be evaporated in the air stream. To control the times of loading, a micro-processor based controller (Chron-Trol, San Diego, CA) was programmed to turn the syringe pumps on and off at specific time intervals. Teflon tubing connected the inlet ports (where toluene was loaded) to the inlet of the activated carbon columns, and teflon tubing connected the effluent of the carbon column to an on-line gas analyzer (Model 1312 Photoacoustic Multigas Analyzer; California Analytical, Orange, CA). The columns were operated in a down flow mode. The inlet and outlet
concentrations were measured by the gas analyzer at 5 minute intervals. All experiments were conducted at an ambient temperature of 23±2 ºC.

3.3 Experimental Test of Intermittent Loading

The dynamic loading scenarios consisted of periods of contaminant loading followed by periods of no contaminant loading. During periods of no loading, air flowed through the system at the same rate as contaminated air during periods of loading. The gas flow rate of 22.8 l/min corresponds to a superficial velocity of 300 m/hr that exists in the GAC column and an empty bed contact time (EBCT) of 4 seconds. The cyclic loading conditions were conducted with influent toluene concentrations of 1000ppmv and 250ppmv. The time when toluene was present was designated as $t_{\text{loading}}$ and the time where no toluene was present in the synthetic gas stream was designated as $t_{\text{no loading}}$. The ratio of $t_{\text{loading}}$:$t_{\text{no loading}}$ was varied, and 1:1, 1:2, and 1:5 ratios were experimentally tested at cyclic lengths of 6, 12, 24, and 48 hours. For example, the cycle length of 6 hours and a $t_{\text{loading}}$:t_{\text{no loading}}$ ratio of 1:1 is a dynamic loading condition where toluene is in the gas stream for 3 hours followed by 3 hours where no toluene is present. The fraction of time when the contaminant is present in the influent gas stream can then be described as $[t_{\text{loading}}/(t_{\text{loading}}+t_{\text{no loading}})]$. The fraction of times of loading tested were 0.5, 0.333, and 0.167 or 1/2, 1/3, and 1/6 respectively (See Table 3.1).

As further described in Section 4.2, after the start of toluene loading in each of the dynamic loading conditions tested, there was an initial period of accumulation in the column until breakthrough was observed. All columns were monitored at quasi-steady state for at least 3 days or five cycles (whichever condition produced the most cycles). The influent concentration was measured with the gas analyzer to measure the concentrations being delivered to the system. Also, a daily mass balance was also conducted for each dynamic loading condition.
Table 3.1 Cyclic Loading Scenarios Experimentally Tested.

<table>
<thead>
<tr>
<th>Cycle length</th>
<th>$t_{\text{loading}}:t_{\text{no loading}}$</th>
<th>Fraction of time loading $\frac{t_{\text{loading}}}{(t_{\text{loading}}+t_{\text{no loading}})}$</th>
<th>hours on:hours off</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 hrs</td>
<td>1:1</td>
<td>1/2</td>
<td>3:3</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>13</td>
<td>2:4</td>
</tr>
<tr>
<td></td>
<td>1:5</td>
<td>1/6</td>
<td>1:5</td>
</tr>
<tr>
<td>12 hrs</td>
<td>1:1</td>
<td>1/2</td>
<td>6:6</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>1/3</td>
<td>4:8</td>
</tr>
<tr>
<td></td>
<td>1:5</td>
<td>1/6</td>
<td>2:10</td>
</tr>
<tr>
<td>24 hrs</td>
<td>1:1</td>
<td>1/2</td>
<td>12:12</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>1/3</td>
<td>8:16</td>
</tr>
<tr>
<td></td>
<td>1:5</td>
<td>1/6</td>
<td>4:20</td>
</tr>
<tr>
<td>48 hrs</td>
<td>1:1</td>
<td>1/2</td>
<td>24:24</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>1/3</td>
<td>16:32</td>
</tr>
<tr>
<td></td>
<td>1:5</td>
<td>1/6</td>
<td>8:40</td>
</tr>
</tbody>
</table>
CHAPTER 4 RESULTS AND DISCUSSION OF EXPERIMENTAL DATA

4.1 Introduction

As summarized in Chapter 2, previous research had demonstrated that load equalization can be beneficial in design and operation of biofilters when applied to various industrial processes. Load equalization can serve several important purposes, including: 1) dampening fluctuations in organic loading to prevent shock loading to biofilters, 2) providing continuous feed to biological systems over periods when waste streams are not being generated (could ultimately prevent starvation to microbial species in the biofilter), and 3) providing capacity for controlled discharge of waste in a more even manner. If successfully implemented, the use of a load equalization device, such as a GAC column, could allow smaller and therefore less expensive biofilters for treating discontinuously generated waste gases because the biofilter bed could be used more efficiently as a function of time (Moe and Li, 2005). Chapter 4 presents results from experiments conducted to test the degree of load equalization achieved by three loading scenarios \( \frac{t_{\text{loading}}}{t_{\text{loading}} + t_{\text{no loading}}} \) of 0.5, 0.333, and 0.167 at cycle lengths \( t_{\text{loading}} + t_{\text{no loading}} \) of 6 hrs., 12 hrs., 24 hrs., and 48 hrs.

4.2 Load Equalization Potential of GAC with Influent Contaminant Loading of 1000 ppmv Toluene

Following the start of intermittent loading to each GAC column, an initial period of accumulation was observed. Thereafter, breakthrough occurred, and a consistent pattern of attenuated effluent concentration was exhibited on a cyclic basis with a frequency corresponding to the total cycle length. An example of this phenomenon is shown in Figure 4.1 which illustrates results from cyclic loading condition of 2 hours on 4 hours off with an influent toluene concentration of 1000 ppmv. Figure 4.2 shows the target inlet concentration along with the effluent concentration measured when toluene was loaded for 2 hours followed by 4 hours of no
loading. The experimentally loaded influent was very close to the target influent loading concentration. See Appendix A for a graph showing this phenomenon.

Figure 4.1. Accumulation, breakthrough, and quasi-steady state observed in cyclic loading condition of 2 hours on 4 hours off (influent loading of 1000 ppmv).

Figure 4.2. Experimental measurement showing target influent and experimentally measured effluent. (experimentally measured effluent, blue; target influent, pink)
The experimentally measured quasi-steady state breakthrough curves for GAC columns that received an influent toluene concentration of 1000 ppmv for one half of the time \[\frac{t_{\text{loading}}}{t_{\text{loading}} + t_{\text{no loading}}} = 0.5\] are shown in Figure 4.3. As shown in Figure 4.3, the maximum dimensionless toluene concentration exiting the GAC column \((C_{\text{max}}/C_o)\) is substantially lower than the influent concentration \((C/C_o = 1)\) for the cases of 1000 ppmv in the 6, 12, and 24 hour cycle lengths. Likewise, the minimum concentration exiting the system \((C_{\text{min}}/C_o)\) is substantially higher than the minimum concentration entering the system during periods of no loading \((C/C_o = 0)\). Table 4.1 shows the average \(C_{\text{max}}/C_o\) and \(C_{\text{min}}/C_o\) values experimentally measured at each cycle length when a GAC column was loaded for one half of the total cycle length. The degree of load equalization, which can be defined by lower \(C_{\text{max}}/C_o\) and higher
$C_{\text{min}}/C_o \ n$, increased as cycle length decreased. For example, the condition where toluene was loaded for 3 hours followed by 3 hours of no loading has a higher degree of load equalization than a GAC column loaded for 6 hours followed by 6 hours of no loading. It is important to recognize that the effluent in both cases was substantially lower than the influent toluene concentration of 1000 ppmv. 3 hours of loading followed by 3 hours of no loading exhibited an effluent $C_{\text{max}}/C_o$ of 0.504, and 6 hours of loading followed by 6 hours of no loading had an effluent $C_{\text{max}}/C_o$ of 0.652.

The condition where toluene was loaded to the system one third of the time \( t_{\text{loading}}/(t_{\text{loading}} + t_{\text{no loading}}) = 0.333 \) exhibited the same overall trends observed for GAC columns loaded for one half of the time. Table 4.2 summarizes $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ values measured at each cycle length when a GAC column as loaded with 1000 ppmv of toluene for one third of the total cycle length.

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average $C_{\text{max}}/C_o$</th>
<th>$C_{\text{max}}/C_o$ Range</th>
<th>$C_{\text{max}}/C_o$ Standard Deviation</th>
<th>Average $C_{\text{min}}/C_o$</th>
<th>$C_{\text{min}}/C_o$ Range</th>
<th>$C_{\text{min}}/C_o$ Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.504</td>
<td>0.494-0.516</td>
<td>0.00668</td>
<td>0.460</td>
<td>0.452-0.470</td>
<td>0.00663</td>
</tr>
<tr>
<td>12</td>
<td>0.652</td>
<td>0.598-0.659</td>
<td>0.00781</td>
<td>0.342</td>
<td>0.337-0.348</td>
<td>0.00416</td>
</tr>
<tr>
<td>24</td>
<td>0.826</td>
<td>0.813-0.827</td>
<td>0.00518</td>
<td>0.274</td>
<td>0.274-0.278</td>
<td>0.00367</td>
</tr>
<tr>
<td>48</td>
<td>0.955</td>
<td>0.947-0.963</td>
<td>0.00551</td>
<td>0.170</td>
<td>0.163-0.171</td>
<td>0.00294</td>
</tr>
</tbody>
</table>

The degree of load equalization increased as cycle length decreased (See Figure 4.4). The effluent $C_{\text{max}}/C_o$ value of 0.347 measured at a cycle length of 6 hours when 1000 ppmv of toluene was supplied to the GAC column for one third of the total cycle length is lower than the effluent $C_{\text{max}}/C_o$ value of 0.823 observed at a cycle length of 48 hours.
Table 4.2. Average $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ values measured at each cycle length when 1000 ppmv of toluene was loaded to the GAC column for one third of the total cycle length

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average $C_{\text{max}}/C_o$</th>
<th>$C_{\text{max}}/C_o$ Range</th>
<th>$C_{\text{max}}/C_o$ Standard Deviation</th>
<th>Average $C_{\text{min}}/C_o$</th>
<th>$C_{\text{min}}/C_o$ Range</th>
<th>$C_{\text{min}}/C_o$ Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.347</td>
<td>0.342-0.353</td>
<td>0.00442</td>
<td>0.319</td>
<td>0.314-0.325</td>
<td>0.00353</td>
</tr>
<tr>
<td>12</td>
<td>0.344</td>
<td>0.331-0.353</td>
<td>0.00676</td>
<td>0.296</td>
<td>0.293-0.301</td>
<td>0.00246</td>
</tr>
<tr>
<td>24</td>
<td>0.506</td>
<td>0.501-0.513</td>
<td>0.00444</td>
<td>0.198</td>
<td>0.195-0.202</td>
<td>0.00274</td>
</tr>
<tr>
<td>48</td>
<td>0.823</td>
<td>0.812-0.829</td>
<td>0.00629</td>
<td>0.141</td>
<td>0.136-0.145</td>
<td>0.00432</td>
</tr>
</tbody>
</table>

Figure 4.4. Experimentally measured quasi-steady state toluene breakthrough curves for GAC columns loaded with 1000 ppmv of toluene for one third of the total cycle length.
Experimentally measured quasi-steady state breakthrough curves for GAC columns loaded for one sixth of the time \[ \frac{t_{\text{loading}}}{t_{\text{loading}} + t_{\text{no loading}}} = 0.167 \] with 1000 ppmv toluene are shown in Figure 4.5. Table 4.3 summarizes the experimentally measured \( \frac{C_{\text{max}}}{C_o} \) and \( \frac{C_{\text{min}}}{C_o} \)

![Figure 4.5. Experimentally measured quasi-steady state toluene breakthrough curves for GAC columns loaded with 1000ppmv of toluene for one sixth of the total cycle length.](image)

Table 4.3. \( \frac{C_{\text{max}}}{C_o} \) and \( \frac{C_{\text{min}}}{C_o} \) values measured at each cycle length when 1000 ppmv of toluene was loaded to the GAC column for one sixth of the total cycle length

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average ( \frac{C_{\text{max}}}{C_o} )</th>
<th>( \frac{C_{\text{max}}}{C_o} ) Range</th>
<th>( \frac{C_{\text{max}}}{C_o} ) Standard Deviation</th>
<th>Average ( \frac{C_{\text{min}}}{C_o} )</th>
<th>( \frac{C_{\text{min}}}{C_o} ) Range</th>
<th>( \frac{C_{\text{min}}}{C_o} ) Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.172</td>
<td>0.158-0.215</td>
<td>0.0139</td>
<td>0.156</td>
<td>0.148-0.161</td>
<td>0.00424</td>
</tr>
<tr>
<td>12</td>
<td>0.171</td>
<td>0.166-0.174</td>
<td>0.00270</td>
<td>0.157</td>
<td>0.156-0.159</td>
<td>0.00117</td>
</tr>
<tr>
<td>24</td>
<td>0.209</td>
<td>0.206-0.213</td>
<td>0.00267</td>
<td>0.140</td>
<td>0.139-0.145</td>
<td>0.00248</td>
</tr>
<tr>
<td>48</td>
<td>0.281</td>
<td>0.274-0.284</td>
<td>0.00409</td>
<td>0.096</td>
<td>0.0950-0.0962</td>
<td>0.000557</td>
</tr>
</tbody>
</table>
values observed at each cycle length when a GAC column was loaded with 1000 ppmv of toluene for one sixth of the total cycle length. Comparison of Figures 4.3, 4.4, and 4.5 reveals that the degree of load equalization increased as the fraction of time that toluene was loaded decreases. For example, for a cycle length of 6 hours, the highest average $C_{\text{max}}/C_o = 0.504$, and was observed when toluene was loaded one half of the time (See Figure 4.3, bottom right graph).

At a cycle length of 6 hours, the $C_{\text{max}}/C_o$ averaged 0.347 when toluene was loaded one third of the time (See Figure 4.4, bottom right graph). The lowest $C_{\text{max}}/C_o$ was 0.172 at a cycle length of 6 hours, and was observed when toluene was loaded one sixth of the time (See Figure 4.5, bottom right graph). Cycle lengths of 12, 24, and 48 all exhibited the same trend. At a given cycle length, the highest effluent $C_{\text{max}}/C_o$ at a particular cycle length was measured when toluene was delivered to the column one half of the time, and the lowest $C_{\text{max}}/C_o$ was observed when toluene was loaded to the column one sixth of the time.

4.3 Load Equalization Potential of GAC with Influent Contaminant Loading of 250 ppmv Toluene

Loading scenarios tested with an influent toluene concentration of 1000 ppmv were also tested with an influent toluene concentration of 250 ppmv. Experimentally measured quasi-steady state curves for a condition where the influent concentration was 250 ppmv being loaded one half \( t_{\text{loading}}/(t_{\text{loading}} + t_{\text{no loading}}) = 0.50 \) of the time is presented in Figure 4.6. As in the case where this same cyclic loading scenario was tested with an influent containing 1000 ppmv toluene, the maximum toluene concentration exiting the GAC column, $C_{\text{max}}$, was lower than the influent concentration (250 ppmv). Likewise, the minimum toluene concentration exiting the GAC columns was higher than the influent concentration (0 ppmv) during periods of no loading. Table 4.4 shows the corresponding $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ values for a GAC columns that were loaded for one half of the total cycle length with 250 ppmv toluene. A higher degree of load
equalization was achieved when the GAC column received a gas flow containing 250 ppmv toluene than was observed from 1000 ppmv toluene. The ideal buffering level 

\[ C_{\text{ideal}} = \frac{t_{\text{loading}}}{(t_{\text{loading}} + t_{\text{no loading}})} \]

of 0.5 was closely approximated in the 6, 12, and 24 hour cycle lengths (See Chapter 6 for further discussion of \( C_{\text{ideal}} \)).

![Figure 4.6. Experimentally measured quasi-steady state toluene breakthrough curves for GAC columns loaded with 250ppmv of toluene for one half of the cycle length.](image)

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average ( C_{\text{max}}/C_o )</th>
<th>( C_{\text{max}}/C_o ) Range</th>
<th>( C_{\text{max}}/C_o ) Standard Deviation</th>
<th>Average ( C_{\text{min}}/C_o )</th>
<th>( C_{\text{min}}/C_o ) Range</th>
<th>( C_{\text{min}}/C_o ) Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.500</td>
<td>0.486-0.518</td>
<td>0.0103</td>
<td>0.481</td>
<td>0.468-0.494</td>
<td>0.00911</td>
</tr>
<tr>
<td>12</td>
<td>0.491</td>
<td>0.479-0.505</td>
<td>0.00893</td>
<td>0.471</td>
<td>0.460-0.484</td>
<td>0.00858</td>
</tr>
<tr>
<td>24</td>
<td>0.513</td>
<td>0.507-0.518</td>
<td>0.00432</td>
<td>0.462</td>
<td>0.451-0.476</td>
<td>0.00929</td>
</tr>
<tr>
<td>48</td>
<td>0.713</td>
<td>0.695-0.729</td>
<td>0.0147</td>
<td>0.348</td>
<td>0.340-0.352</td>
<td>0.00765</td>
</tr>
</tbody>
</table>
Figure 4.7 shows the experimentally measured quasi-steady state curves for a cyclic loading condition where 250 ppmv of toluene was delivered to the GAC column for one third of the time \(\frac{t_{\text{loading}}}{t_{\text{loading}} + t_{\text{no loading}}} = 0.333\).

![Graphs showing quasi-steady state toluene breakthrough curves](image)

**Figure 4.7.** Experimentally measured quasi-steady state toluene breakthrough curves for GAC columns loaded with 250ppmv of toluene for one third of the cycle length.

In this loading scenario, the ideal buffering level \(C_{\text{ideal}} = \frac{t_{\text{loading}}}{t_{\text{loading}} + t_{\text{no loading}}}\) is 0.333. The \(C_{\text{max}}/C_o\) values observed at cycle lengths of 6, 12, and 24 hours closely approximated the ideal buffering level. Table 4.5 shows \(C_{\text{max}}/C_o\) values when 250 ppmv of toluene was loaded to the GAC column for one third of the total cycle length. When the GAC column is loaded for one third of the total cycle length with 250 ppmv toluene, the maximum concentration exiting the column at a cycle length of 12 hours was 79.25 ppmv or \(C_{\text{max}}/C_o\) of 0.317 (See Figure 4.7,
This is lower than the $C_{\text{max}}/C_o$ of 0.491 at a cycle length of 12 hours for the loading condition where toluene is supplied to the system for one half of the time (see Figure 4.6, bottom left graph).

**Table 4.5. Average $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ values measured at each cycle length when 250ppmv of toluene was loaded to the GAC column for one third of the total cycle length**

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average $C_{\text{max}}/C_o$</th>
<th>$C_{\text{max}}/C_o$ Range</th>
<th>$C_{\text{max}}/C_o$ Standard Deviation</th>
<th>Average $C_{\text{min}}/C_o$</th>
<th>$C_{\text{min}}/C_o$ Range</th>
<th>$C_{\text{min}}/C_o$ Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.317</td>
<td>0.315-0.319</td>
<td>0.00134</td>
<td>0.305</td>
<td>0.300-0.307</td>
<td>0.00183</td>
</tr>
<tr>
<td>12</td>
<td>0.317</td>
<td>0.311-0.321</td>
<td>0.00404</td>
<td>0.304</td>
<td>0.299-0.337</td>
<td>0.003435</td>
</tr>
<tr>
<td>24</td>
<td>0.331</td>
<td>0.329-0.335</td>
<td>0.002828</td>
<td>0.313</td>
<td>0.311-0.315</td>
<td>0.00179</td>
</tr>
<tr>
<td>48</td>
<td>0.386</td>
<td>0.375-0.388</td>
<td>0.00936</td>
<td>0.280</td>
<td>0.274-0.287</td>
<td>0.00471</td>
</tr>
</tbody>
</table>

Experimentally measured quasi-steady state breakthrough curves for GAC columns receiving 250 ppmv toluene intermittently loaded for one sixth of the cycle length [$t_{\text{loading}}/(t_{\text{loading}} + t_{\text{no loading}}) = 0.1667$] is shown in Figure 4.8. In this loading scenario the ideal buffering level [$C_{\text{ideal}} = t_{\text{loading}}/(t_{\text{loading}} + t_{\text{no loading}})$] is 0.167. Table 4.6 shows the average $C_{\text{max}}/C_o$ values for a GAC column loaded with 250 ppmv for one sixth of the total cycle length. Figure 4.8 shows that the ideal buffering level was achieved at all four cycle lengths. The $C_{\text{max}}/C_o$ at a cycle length of 48 hours was 0.171 when toluene was loaded for one sixth of the cycle. This is substantially lower than the $C_{\text{max}}/C_o$ of 0.713 observed when toluene was loaded for one half of the time, and lower than the $C_{\text{max}}/C_o$ of 0.386 observed when toluene was loaded one third of the time at a cycle length of 48 hours. This is consistent with the trend of as the fraction of time that toluene was loaded decreased, the degree of load equalization increased.

Comparing the 250 ppmv and 1000 ppmv loading conditions, the 250 ppmv loading scenarios had a higher degree of load equalization (i.e., lower $C_{\text{max}}/C_o$ and higher $C_{\text{min}}/C_o$). For
example, when 1000 ppmv of toluene was loaded for 12 hours followed by 12 hours of no
loading the $C_{\text{max}}/C_o$ value was 0.826. On the other hand, when 250 ppmv of toluene was loaded
for 12 hours followed by 12 hours of no loading, $C_{\text{max}}/C_o$ was 0.513.

![Figure 4.8. Experimentally measured quasi-steady state toluene breakthrough curves for
GAC columns loaded with 250 ppmv of toluene for one sixth of the cycle length.](image)

Table 4.6. $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ values measured at each cycle length when 250 ppmv toluene
was loaded to the GAC column for one sixth of the total cycle length.

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average $C_{\text{max}}/C_o$</th>
<th>$C_{\text{max}}/C_o$ Range</th>
<th>$C_{\text{max}}/C_o$ Standard Deviation</th>
<th>Average $C_{\text{min}}/C_o$</th>
<th>$C_{\text{min}}/C_o$ Range</th>
<th>$C_{\text{min}}/C_o$ Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.167</td>
<td>0.165-0.170</td>
<td>0.00149</td>
<td>0.159</td>
<td>0.157-0.161</td>
<td>0.00130</td>
</tr>
<tr>
<td>12</td>
<td>0.161</td>
<td>0.159-0.164</td>
<td>0.00194</td>
<td>0.151</td>
<td>0.149-0.154</td>
<td>0.00179</td>
</tr>
<tr>
<td>24</td>
<td>0.173</td>
<td>0.171-0.175</td>
<td>0.00160</td>
<td>0.162</td>
<td>0.157-0.161</td>
<td>0.00256</td>
</tr>
<tr>
<td>48</td>
<td>0.171</td>
<td>0.165-0.177</td>
<td>0.00579</td>
<td>0.155</td>
<td>0.151-0.161</td>
<td>0.00483</td>
</tr>
</tbody>
</table>
In summary, experimental results presented in this chapter demonstrated that as the cycle length decreased the degree of load equalization increased. Results also showed that as the fraction of time toluene was loaded to the system decreased, the degree of load equalization increased. Further comparisons and discussion are shown in Chapter 6, sections 6.1 through 6.3, which shows model support for the experimental conditions tested in this chapter.

Mass balances were conducted based on the measured effluent in comparison to the calculated influent. In all loading cases that received 1000 ppmv influent toluene, the mass balance closure ranged from 99.27%-95.59%. In the loading conditions that received 250 ppmv influent toluene, the mass balance closure ranged from 99.94%-92.39%. See Appendix B for tabulated values.
CHAPTER 5 MATERIALS AND METHODS FOR MODELING SIMULATION OF DYNAMIC LOADING CONDITIONS

5.1 Introduction

A pore and surface diffusion model (PSDM) was used to further investigate performance of the GAC columns at various discontinuous dynamic loading scenarios. Chapter 2 provided an overview of the pore and surface diffusion model used in this research. This chapter (Chapter 5) presents the model methodology employed in this research. Conditions identical to those used in experimental testing procedures were used as input parameters in the modeling.

5.2 Pore and Surface Diffusion Model Methodology

The pore and surface diffusion model described by Crittenden et al. (1986) and Hand et al. (1997) was used to simulate the degree of load equalization achieved by the GAC columns under various discontinuous loading conditions. Simulations used AdDesignS™ software package (Michigan Technological University). Input parameters used in the simulation are summarized in Table 5.1. The influent gas flow rate input for model simulations was identical to the experimental flow rate. The breakthrough and $C_{\text{max}}/C_o$ and $C_{\text{min}}/C_o$ values were obtained from the model. Using the parameters listed in Table 5.1, simulations were run using identical conditions that were observed during experimental analysis of the performance of GAC columns under various loading conditions. The input file used in the PSDM was reflective of the loading ratio that each column was subjected to. It was assumed that the contaminant concentration entering the GAC column linearly increased from zero to the target level over a period of 3 minutes, and linearly decreased from the target concentration to zero over a period of 3 minutes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed-bed properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bed Length (cm)</td>
<td>33.3a</td>
<td>cm</td>
</tr>
<tr>
<td>Bed diameter (cm)</td>
<td>7.62a</td>
<td>cm</td>
</tr>
</tbody>
</table>

Table 5.1 Parameter values used in model simulations.

Table 5.1 Continued
Table 5.1 Continued

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed mass (kg)</td>
<td>0.720a</td>
<td>kg</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>0.442d</td>
<td>dimensionless</td>
</tr>
<tr>
<td><strong>Adsorbent properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle apparent density ($p_a$)</td>
<td>0.85b</td>
<td>g/cm$^3$</td>
</tr>
<tr>
<td>Average particle radius ($r_p$)</td>
<td>0.186b</td>
<td>cm</td>
</tr>
<tr>
<td>Particle void fraction ($\varepsilon_p$)</td>
<td>0.595b</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Particle shape factor</td>
<td>0.72b</td>
<td>dimensionless</td>
</tr>
<tr>
<td><strong>Freundlich isotherm parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K$ (mg/g) $\left(1/\text{mg}\right)^{1/n}$</td>
<td>152c</td>
<td>(mg/g)(L/mg)$^{1/n}$</td>
</tr>
<tr>
<td>$1/n$</td>
<td>0.249c</td>
<td>dimensionless</td>
</tr>
<tr>
<td><strong>Air properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>23a</td>
<td>degrees C</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>1.19 x 10$^{-3}$d</td>
<td>g/cm$^3$</td>
</tr>
<tr>
<td>Viscosity (g/(cm s))</td>
<td>1.79 x 10$^{-4}$d</td>
<td>g/(cm sec)</td>
</tr>
<tr>
<td>Flow rate</td>
<td>22.8</td>
<td>L/min</td>
</tr>
<tr>
<td><strong>Kinetic parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_f$ (film mass-transfer coefficient) (cm/s)</td>
<td>1.01e</td>
<td>cm/s</td>
</tr>
<tr>
<td>$D_s$ (surface diffusion coefficient) (cm$^2$/s)</td>
<td>$5.81 \times 10^{-6}$f or $1.65 \times 10^{-5}$f</td>
<td>cm$^2$/s</td>
</tr>
<tr>
<td>$D_p$ (pore diffusion coefficient) (cm$^2$/s)</td>
<td>$8.24 \times 10^{-2}$g</td>
<td>cm$^2$/s</td>
</tr>
<tr>
<td>Surface to pore diffusion flux ratio</td>
<td>16h</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>1h</td>
<td>dimensionless</td>
</tr>
</tbody>
</table>

*a Experimentally measured
*b Data provided by Calgon Carbon Corp. (Pittsburgh, PA).
*c Assumed parameter based on experimental measurements by Moe and Li (2005).
*d Calculated by correlation using StEPP$^\text{TM}$ database (Mertz et al., 1999).
*e Model fit parameter determined by Moe and Li (2005).
*f Calculated by AdDesignS$^\text{TM}$ using the Sontheimer correlation as described by Mertz et al. 1999. Parameter value of 1.64E-5 was used when influent toluene concentration was 1000 ppmv, and parameter value of 5.81E-6 was used when influent toluene concentration was 250 ppmv.
*g Calculated by AdDesignS$^\text{TM}$ using the Wilke0Lee modification of the Hirschfelder-Bird-Spotz method (Mertz et al., 1999).
*h Assumed parameter based on experimental fit determined by Crittenden et al. 1988.
CHAPTER 6 RESULTS AND DISCUSSION OF MODELING DATA

6.1 Introduction

This chapter presents the results of pore and surface diffusion model simulations of the load equalization process. It also presents a comparison of model simulation with experimental data presented in Chapter 4.

6.2 Load Equalization Potential of GAC Columns with Influent Contaminant Loading of 1000 ppmv Toluene: Model Comparison to Experimental Data

The model and experimental breakthrough curves for a loading condition that provided 1000 ppmv toluene to the system for one half of the cycle length are shown in Figure 6.1. As shown in the figures, the model simulations produced quasi-steady state curves that accurately predicted the degree of load equalization observed in the experimental testing. When the GAC column was loaded with 1000 ppmv of toluene for one half of the cycle length, the degree of load equalization increased as cycle length decreased. This trend is shown through experimental testing as well as modeling simulations. For example, the experimentally measured $C_{\text{max}}/C_o$ value at a cycle length of 12 hours was 0.652. The modeled $C_{\text{max}}/C_o$ value at a cycle length of 12 hours was 0.638. Both of these values are larger than the experimentally measured $C_{\text{max}}/C_o$ value of 0.504 at a cycle length of 6 hours and the modeled value of 0.507 at a cycle length of six hours. In this loading scenario the maximum difference between the experimentally measured $C_{\text{max}}/C_o$ and the model predicted $C_{\text{max}}/C_o$ was 0.126. The minimum difference was 0.003.

Table 6.1 shows the average modeled and experimentally measured $C_{\text{max}}/C_o$ values when the GAC column was loaded with 1000 ppmv for one half of the total cycle length.

Figure 6.2 shows the experimentally measured and modeled quasi-steady state curves for a GAC column loaded with 1000 ppmv of toluene for one third of the total cycle length. As was the case with toluene being loaded for one half of the total cycle length, the degree of load equalization increased as cycle length decreased.
Figure 6.1. Experimental (closed symbols) and modeled (open symbols) quasi-steady state toluene breakthrough curves for GAC columns loaded with 1000 ppmv of toluene for one half of the cycle length.

Table 6.1. Average \( C_{\text{max}}/C_o \) values experimentally measured and modeled at each cycle length when 1000 ppmv of toluene was loaded to the GAC column for one half of the total cycle length.

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average Experimental ( C_{\text{max}}/C_o )</th>
<th>Average Model ( C_{\text{max}}/C_o )</th>
<th>Difference in ( C_{\text{max}}/C_o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.504</td>
<td>0.507</td>
<td>0.003</td>
</tr>
<tr>
<td>12</td>
<td>0.652</td>
<td>0.638</td>
<td>0.014</td>
</tr>
<tr>
<td>24</td>
<td>0.826</td>
<td>0.952</td>
<td>0.126</td>
</tr>
<tr>
<td>48</td>
<td>0.955</td>
<td>1.00</td>
<td>0.045</td>
</tr>
</tbody>
</table>
Figure 6.2. Experimental (closed symbols) and modeled (open symbols) quasi-steady state toluene breakthrough curves for GAC columns loaded with 1000 ppmv of toluene for one third of the cycle length.

Table 6.2 shows the average $C_{max}/C_o$ values for model simulations along with experimental measurements when GAC received an influent of 1000 ppmv of toluene for one third of the total cycle length. The maximum difference between the modeled predicted $C_{max}/C_o$ and the experimentally measured $C_{max}/C_o$ was 0.159. The minimum difference was 0.008. Comparison of Figures 6.1 and 6.2 reveals that as the fraction of time toluene was loaded decreased, the degree of load equalization increased. For example, the modeling value for $C_{max}/C_o$ is 0.507 for a cycle length of 6 hours where toluene is loaded for one half of the total cycle length. The model predicted $C_{max}/C_o$ value is 0.339 for a cycle length of 6 hours where toluene is loaded for
one third of the total cycle. This supports the trend of as the fraction of time toluene is supplied to the system decreases, the degree of load equalization increases.

Table 6.2. Average $C_{\text{max}}/C_o$ values experimentally measured and modeled at each cycle length when 1000 ppmv of toluene was loaded to the GAC column for one third of the total cycle length.

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average Experimental $C_{\text{max}}/C_o$</th>
<th>Average Model $C_{\text{max}}/C_o$</th>
<th>Difference in $C_{\text{max}}/C_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.347</td>
<td>0.339</td>
<td>0.008</td>
</tr>
<tr>
<td>12</td>
<td>0.344</td>
<td>0.374</td>
<td>0.030</td>
</tr>
<tr>
<td>24</td>
<td>0.506</td>
<td>0.601</td>
<td>0.095</td>
</tr>
<tr>
<td>48</td>
<td>0.823</td>
<td>0.982</td>
<td>0.159</td>
</tr>
</tbody>
</table>

The quasi-steady state curves for a loading condition that supplied 1000 ppmv toluene to the system for one sixth of the total cycle length is shown in Figure 6.3. Figure 6.3 also supports the trends previously observed. Table 6.3 shows the experimental and modeled average $C_{\text{max}}/C_o$ values observed at each cycle length. When 1000 ppmv of toluene was supplied to the system for one sixth of the total cycle length, the maximum difference between the $C_{\text{max}}/C_o$ of the modeled data in comparison to the $C_{\text{max}}/C_o$ of the experimental data was 0.097. The minimum difference was 0.001.

6.3 Load Equalization potential of GAC with influent Contaminant Loading of 250ppmv toluene: Model comparison to experimental data

The model and experimental breakthrough curves for a loading condition that provided 250 ppmv toluene to the GAC system for one half of the time are shown in Figure 6.4. Table 6.4 shows the experimentally measured $C_{\text{max}}/C_o$ and the model predicted $C_{\text{max}}/C_o$ values. Just like the condition that loaded 1000 ppmv to the column for one half of the cycle length, an influent concentration of 250 ppmv resulted in the same trend: as cycle length decreased, the degree of
load equalization increased. This trend is demonstrated by both the experimental curves and modeled curves. Figure 6.4 shows that the model simulations predict the degree of load

![Image of breakthrough curves](image.png)

Figure 6.3. Experimental (closed symbols) and modeled (open symbols) quasi-steady state toluene breakthrough curves for GAC columns loaded with 1000 ppmv of toluene for one sixth of the cycle length.

Table 6.3. Average $C_{\text{max}}/C_o$ values experimentally measured and modeled at each cycle length when 1000 ppmv of toluene was loaded to the GAC column for one sixth of the total cycle length.

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average Experimental $C_{\text{max}}/C_o$</th>
<th>Average Model $C_{\text{max}}/C_o$</th>
<th>Difference in $C_{\text{max}}/C_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.172</td>
<td>0.167</td>
<td>0.005</td>
</tr>
<tr>
<td>12</td>
<td>0.171</td>
<td>0.168</td>
<td>0.003</td>
</tr>
<tr>
<td>24</td>
<td>0.209</td>
<td>0.208</td>
<td>0.001</td>
</tr>
<tr>
<td>48</td>
<td>0.281</td>
<td>0.378</td>
<td>0.097</td>
</tr>
</tbody>
</table>
Figure 6.4. Experimental (closed symbols) and modeled (open symbols) quasi-steady state toluene breakthrough curves for GAC columns loaded with 250 ppmv of toluene for one half of the cycle length.

Table 6.4. Average $C_{\text{max}}/C_o$ values experimentally measured and modeled at each cycle length when 250 ppmv of toluene was loaded to the GAC column for one half of the total cycle length.

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average Experimental $C_{\text{max}}/C_o$</th>
<th>Average Model $C_{\text{max}}/C_o$</th>
<th>Difference in $C_{\text{max}}/C_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.500</td>
<td>0.500</td>
<td>0.0</td>
</tr>
<tr>
<td>12</td>
<td>0.491</td>
<td>0.500</td>
<td>0.009</td>
</tr>
<tr>
<td>24</td>
<td>0.513</td>
<td>0.545</td>
<td>0.032</td>
</tr>
<tr>
<td>48</td>
<td>0.713</td>
<td>0.795</td>
<td>0.082</td>
</tr>
</tbody>
</table>

equalization within a reasonable degree of accuracy. The maximum difference between the model predicted $C_{\text{max}}/C_o$ and the experimentally measured $C_{\text{max}}/C_o$ was 0.082. The minimum difference was 0 ppmv (no difference). The experimental and measured quasi-steady state
curves for a condition where 250 ppmv of toluene was loaded for one third of the cycle length is seen in Figure 6.5. In comparison to Figure 6.4, Figure 6.5 illustrates a greater degree of load equalization at each cycle length. The maximum difference between the experimentally measured $C_{\text{max}}/C_0$ and the model predicted $C_{\text{max}}/C_0$ was 0.071. The minimum difference was 0.010. Table 6.5 shows the experimentally measured $C_{\text{max}}/C_0$ and model simulated $C_{\text{max}}/C_0$.

![Figure 6.5](image)

Figure 6.5. Experimental (closed symbols) and modeled (open symbols) quasi-steady state toluene breakthrough curves for GAC columns loaded with 250 ppmv of toluene for one third of the cycle length.

Figure 6.6 shows the experimentally measured and model predicted quasi-steady state curves for a GAC column that received 250 ppmv of toluene for one sixth of the total cycle length. Just like the two previous scenarios, the model and experimental curves show that as cycle length decreases, the degree of load equalization increase. The maximum difference
between the $C_{\text{max}}/C_o$ value of the experimental measurement and the model prediction was 0.007. The minimum difference was 0 ppmv. Table 6.6 shows both the experimental and model predicted $C_{\text{max}}/C_o$ values.

Table 6.5. Average $C_{\text{max}}/C_o$ values experimentally measured and modeled at each cycle length when 250 ppmv of toluene was loaded to the GAC column for one third of the total cycle length.

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average Experimental $C_{\text{max}}/C_o$</th>
<th>Average Model $C_{\text{max}}/C_o$</th>
<th>Difference in $C_{\text{max}}/C_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.317</td>
<td>0.333</td>
<td>0.016</td>
</tr>
<tr>
<td>12</td>
<td>0.317</td>
<td>0.333</td>
<td>0.016</td>
</tr>
<tr>
<td>24</td>
<td>0.331</td>
<td>0.341</td>
<td>0.010</td>
</tr>
<tr>
<td>48</td>
<td>0.386</td>
<td>0.457</td>
<td>0.071</td>
</tr>
</tbody>
</table>

Figure 6.6. Experimental (closed symbols) and modeled (open symbols) quasi-steady state toluene breakthrough curves for GAC columns loaded with 250 ppmv of toluene for one sixth of the total cycle length.
Table 6.6. Average $C_{\text{max}}/C_o$ values experimentally measured and modeled at each cycle length when 250 ppmv of toluene was loaded to the GAC column for one sixth of the total cycle length.

<table>
<thead>
<tr>
<th>Cycle length (hrs)</th>
<th>Average Experimental $C_{\text{max}}/C_o$</th>
<th>Average Model $C_{\text{max}}/C_o$</th>
<th>Difference in $C_{\text{max}}/C_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.167</td>
<td>0.167</td>
<td>0.0</td>
</tr>
<tr>
<td>12</td>
<td>0.161</td>
<td>0.167</td>
<td>0.006</td>
</tr>
<tr>
<td>24</td>
<td>0.173</td>
<td>0.167</td>
<td>0.006</td>
</tr>
<tr>
<td>48</td>
<td>0.171</td>
<td>0.178</td>
<td>0.007</td>
</tr>
</tbody>
</table>

6.4 Further assessment of Intermittent Loading Scenarios

Figure 6.7 depicts the average $C_{\text{max}}/C_o$ values for each experimentally tested loading scenario supplied with 1000 ppmv toluene along with results from the model simulations. Data points designated by filled points are the experimentally measured data, and open symbols denote the model predictions.

Figure 6.7. $C_{\text{max}}/C_o$ values for $t_{\text{loading}}/(t_{\text{loading}} + t_{\text{no loading}}) = 0.500, 0.333, \text{ and } 0.167$. Influent concentration of 1000ppmv toluene. Model simulations (open symbols), experimental data (closed symbols), and ideal buffering level (dashed lines).
Also depicted in Figure 6.7 is the ideal buffering level for each loading condition. “Ideal” buffering refers to the situation in which dynamically-varying concentrations of contaminants entering a GAC column are attenuated to such an extent that contaminants exit the GAC system at a concentration evenly distributed as a function of time. For a waste gas stream with intermittent loading, ideal buffering occurs when the contaminants exiting the system are constant with respect to time. As shown by equation 6.1, the contaminant concentration exiting the column is equal to the fraction of time during which contaminants are loaded to the system when ideal buffering is achieved.

\[
C_{\text{ideal}} = \frac{t_{\text{loading}}}{t_{\text{loading}} + t_{\text{no loading}}} \quad (6.1)
\]

For loading conditions where toluene is supplied for one half, one third, and one sixth of the cycle length, ideal buffering occurs when the effluent \( \frac{C_{\text{max}}}{C_o} \) is constant at 0.500, 0.333 and 0.167, respectively.

Figure 6.8 shows the effluent \( \frac{C_{\text{max}}}{C_o} \) values when 250 ppmv was the influent loading conditions. Ideal buffering when toluene is supplied to the system for one half, one third, and one sixth of the cycle still occurs when the effluent \( \frac{C_{\text{max}}}{C_o} \) is constant at 0.500, 0.333 and 0.167, respectively. Figure 6.9 and 6.10 show that as the cycle length gets longer, eventually each loading condition will reach an effluent Cmax/Co value of 1.00. Figure 6.9 shows the effluent \( \frac{C_{\text{max}}}{C_o} \) values when the influent toluene concentration is 1000 ppmv, and Figure 6.10 shows the effluent \( \frac{C_{\text{max}}}{C_o} \) value when the influent toluene concentration was 250 ppmv. The difference between the experimental and modeled \( \frac{C_{\text{max}}}{C_o} \) averaged 0.049 for conditions that were loaded with an influent toluene concentration of 1000 ppmv, and 0.021 for conditions that were loaded with 250 ppmv. These values correspond to 49 ppm for 1000 ppmv and 5.25 ppm for 250 ppmv.
Figure 6.8. $C_{\text{max}}/C_o$ values for $t_{\text{loading}}/(t_{\text{loading}} + t_{\text{no loading}})$ = 0.500, 0.333, and 0.167. Influent concentration of 250 ppmv toluene. Model predictions (open symbols), experimental data (closed symbols), and ideal buffering level (dashed lines).

Figure 6.9. $C_{\text{max}}/C_o$ values for $t_{\text{loading}}/(t_{\text{loading}} + t_{\text{no loading}})$ = 0.500, 0.333, and 0.167. Influent concentration of 1000 ppmv toluene. Modeling simulations (open symbols), experimental data (closed symbols), and ideal buffering level (dashed lines) with an expanded cycle length of 180 hrs.
Cmax/Co Observed at Quasi-Steady State Under Intermittent Loading with Influent Concentration of 250ppmv

Figure 6.10. $C_{\text{max}}/C_0$ values for $t_{\text{loading}}/(t_{\text{loading}} + t_{\text{no loading}}) = 0.500$, 0.333, and 0.167. Influent concentration of 250 ppmv toluene. Modeling simulations (open symbols), experimental data (closed symbols), and ideal buffering level (dashed lines) with an expanded cycle length of 400 hrs.

The largest difference in the $C_{\text{max}}/C_0$ was observed at the longest cycle lengths tested, with the maximum difference of 0.159 occurring for a cycle length of 48 hours with toluene was loaded for one third of the total cycle length. As such it can be concluded that the PSDM was reasonably successful in predicting the degree of load equalization achieved in the experimentally tested loading scenarios. Model predictions also support the experimentally trends that: (1) as the cycle length decreases, the degree of load equalization increased; (2) as the fraction of time toluene is loaded decreased, the degree of load equalization increased; and (3) as the influent toluene concentration decreased, the degree of load equalization increased.
CHAPTER 7  OVERALL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 Overall Conclusions

Packed columns containing Calgon BPL 4x6 mesh GAC were experimentally tested with intermittent loading of toluene-contaminated air at influent toluene concentrations of 250 ppmv and 1000 ppmv. Experiments were conducted for cycle lengths as short as 6 hours and as long as 48 hours. The fraction of time that the toluene was loaded ranged from 1/2 to 1/6 of the total cycle length. As previously reported, a pore and surface diffusion model was used to simulate column performance under conditions identical to the experimental testing.

Both experimental testing (Chapter 4) and model simulations (Chapter 6) showed three obvious trends concerning the load equalization potential of passively-operated GAC columns subjected to intermittent loading of toluene-contaminated air streams after quasi-steady state conditions were achieved: 1) As cycle length increased, the degree of load equalization (defined by lower $C_{\text{max}}/C_o$ and higher $C_{\text{min}}/C_o$) decreased; 2) As the fraction of time that toluene was loaded decreased, the degree of load equalization increased; and 3) As influent contaminant concentration decreased, the degree of load equalization increased. At the influent contaminant concentrations typically treated by biofiltration, load attenuation very close to “ideal buffering” was achieved in GAC columns with low EBCTs (4.0 seconds) when the cycle length or fraction of time in loading was sufficiently short. The concentration gradient imposed by flow of uncontaminated air through the columns during periods of no toluene loading was sufficient to desorb each day the mass of contaminants that were adsorbed during loading intervals each day. As such, the columns were able to achieve load equalization using passive operation (i.e., without external regeneration of the GAC by heating or other means and without any operator intervention).
7.2 Recommendations for Future Research

Experiments conducted in the research described in this thesis were conducted in laboratory-scale columns. It is recommended that future tests be conducted using larger, pilot-scale GAC columns to assess whether there is a problem in process scale-up to gas flow rates markedly higher than those tested up to now. Also, studies conducted on passively-operated GAC load equalization to date have been conducted at ambient temperatures of approximately 23°C. Real-world gas streams are often warmer or colder than this temperature, and the effect of temperature on the load equalization potential of GAC columns remains almost entirely unexplored. Thus, it is recommended that future experiments be conducted to assess the effects of temperature on GAC load equalization performance.

In the research described in this thesis, the gas flow through the GAC systems was kept at a constant rate during periods both when toluene was present and when it was absent. In full scale installations where biofilters are employed as the method for ultimately removing and destroying VOCs, it may be desirable to decrease the air flow rate to the treatment system during periods when contaminant concentrations are low or zero. For example, this operating strategy could be used to reduce electricity costs associated with running a blower during periods of no waste generation. It has not yet been determined what influence changes in air flow rate would have on the GAC load equalization process. Further experimental testing and/or modeling of this would be beneficial.

GAC load equalization systems also have not yet been tested with particulate matter present as contaminants in the waste gas stream. Particulate matter could potentially alter the performance of such GAC systems because of clogging of pore spaces and/or masking of adsorption sites. Also, the GAC load equalization system tested in this research has not yet been
evaluated at high relative humidity or at varying superficial gas velocities. It is recommended that future research be conducted to investigate these phenomena.
Figure A.1. Measured influent toluene concentrations compared to target loading level. Loading conditions: $C_o = 1000$ ppmv toluene at a cycle length of 6 hours and a fraction of time of loading of 0.5 (2 hr ON followed by 4 hr OFF, 6 hr total cycle length).
## APPENDIX B  MASS BALANCE CLOSURES FOR EACH LOADING SCENARIO

Table B.1. Mass balance closures for each loading scenarios when the influent loading condition was 1000 ppmv

<table>
<thead>
<tr>
<th>Loading Condition (hours on:hours off)</th>
<th>Toluene Concentration (ppmv)</th>
<th>Percent Closure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:3</td>
<td>1000</td>
<td>96.50</td>
</tr>
<tr>
<td>2:4</td>
<td>1000</td>
<td>99.27</td>
</tr>
<tr>
<td>1:5</td>
<td>1000</td>
<td>97.57</td>
</tr>
<tr>
<td>6:6</td>
<td>1000</td>
<td>97.93</td>
</tr>
<tr>
<td>4:8</td>
<td>1000</td>
<td>96.50</td>
</tr>
<tr>
<td>2:10</td>
<td>1000</td>
<td>96.94</td>
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<td>8:16</td>
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</tr>
<tr>
<td>4:20</td>
<td>1000</td>
<td>99.18</td>
</tr>
<tr>
<td>24:24</td>
<td>1000</td>
<td>95.59</td>
</tr>
<tr>
<td>16:32</td>
<td>1000</td>
<td>97.26</td>
</tr>
<tr>
<td>8:40</td>
<td>1000</td>
<td>97.06</td>
</tr>
</tbody>
</table>

Table B.2. Mass balance closures for each loading scenarios when the influent loading condition was 250 ppmv

<table>
<thead>
<tr>
<th>Loading Condition (hours on:hours off)</th>
<th>Toluene Concentration (ppmv)</th>
<th>Percent Closure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:3</td>
<td>250</td>
<td>99.81</td>
</tr>
<tr>
<td>2:4</td>
<td>250</td>
<td>92.39</td>
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<tr>
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<td>97.61</td>
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<td>6:6</td>
<td>250</td>
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<tr>
<td>4:8</td>
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<td>93.38</td>
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<td>2:10</td>
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<tr>
<td>12:12</td>
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<td>8:16</td>
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<td>96.58</td>
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<tr>
<td>4:20</td>
<td>250</td>
<td>99.34</td>
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<tr>
<td>24:24</td>
<td>250</td>
<td>99.94</td>
</tr>
<tr>
<td>16:32</td>
<td>250</td>
<td>99.79</td>
</tr>
<tr>
<td>8:40</td>
<td>250</td>
<td>97.35</td>
</tr>
</tbody>
</table>
REFERENCES


VITA

Kodi L. Collins was born March 15, 1983 in Baton Rouge, Louisiana. In December 2005, she obtained a Bachelor of Science in Biological Engineering at Louisiana State University in Baton Rouge, Louisiana. After completing her undergraduate studies, she enrolled in the graduate program at Louisiana State University in the Department of Civil and Environmental Engineering in January 2006. She is currently pursuing a Master of Science in Civil Engineering with a specialization in environmental engineering. She plans to receive her Master of Science in Civil Engineering at the Spring 2007 Commencement.