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Chemical Engineering Journal 113 (2005) 175–185
Chemical Engineering Journal
www.elsevier.com/locate/cej

A design methodology for activated carbon load equalization systems applied to biofilters treating intermittent toluene loading

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Received 12 November 2004; received in revised form 15 February 2005; accepted 3 April 2005

Abstract

Biofiltration has been used successfully as an air pollution control technology in many applications during the past several decades, however, several design and operational challenges remain. Among these is the fact that contaminant concentrations in most waste gas streams vary with time, and an appropriate basis of design for treatment of dynamically-varying waste gas streams has not yet been well established. Use of an integrated system consisting of a column packed with granular activated carbon (GAC) as a passively controlled load equalization mechanism in series before a biofilter has the potential to mitigate many of the adverse effects of unsteady loading. This paper describes results from a series of experiments conducted to characterize the capacity of Calgon BPL 4 × 6 mesh GAC for load equalization of toluene contaminated air under intermittent loading conditions consisting of contaminant supply during only 8 h/day. Experimental testing was conducted for a variety of loading conditions with GAC column empty bed contact times (EBCTs) as low as 1.5 s and influent toluene concentrations as high as 1000 ppm_v. Results demonstrate that appreciable load equalization can be accomplished at low EBCTs (on the order of a few seconds) for the range of contaminant concentrations typically treated by biofiltration. A pore and surface diffusion model (PSDM), calibrated and validated using experimental data, was successful in predicting dynamic adsorption and desorption behavior. The calibrated PSDM was used to develop a series of design curves that can provide guidance in reactor sizing and operating parameter estimation. Examples are presented to demonstrate how implementation of this load equalization approach may facilitate use of smaller, less expensive biofilters, and how it can minimize much of the uncertainty that accompanies biofilter design and operation.

Keywords: Activated carbon; Attenuation; Biofilter; Biofiltration; Dampening; Diurnal; Load equalization

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1. Introduction

During the past decade, biofilters have attracted increasing popularity for removal of volatile organic compounds (VOCs) from contaminated air streams because of their low cost, operational simplicity, and lack of secondary pollutant generation [1]. In biofiltration, VOC contaminated air is passed through a packed bed, fixed-film bioreactor. As air moves though the bioreactor, contaminants are transferred from the air into a biofilm growing immobilized on a solid support medium. Microorganisms growing in the biofilm metabolize the contaminants, producing environmentally acceptable end products including carbon dioxide, water, and additional biomass.

Although biofiltration has proven successful for removing a wide variety of biodegradable VOCs under conditions of relatively steady loading, dynamically varying loading conditions pose challenges in biofilter design and operation [2]. Due to the unsteady state nature of industrial processes, contaminant concentrations in most waste gas streams vary with time [3]. For example, VOCs are often present in industrial off-gases on a discontinuous basis (e.g., facilities where contaminants are generated in a process utilizing 8-h work days). In a conventional biofilter, contaminants must be treated at the same rate they are generated. A biofilter sized to treat peak contaminant loading for a waste gas generated during only a portion of the day can sit idle with available (but unutilized) capacity during portions of the day when no contaminants are

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doi:10.1016/j.cej.2005.04.002

loaded. From this perspective, the system is over-designed because it has unutilized excess capacity. Conversely, if a biofilter is designed to meet average loading conditions (rather than peak loading) for a waste stream with dynamically varying contaminant concentrations, then dynamic mass loadings may exceed biological reaction capacities and result in unacceptably high contaminant emissions [2,4,5]. Intervals of low or no contaminant loading in biofilter systems are also problematic because of starvation conditions imposed on the microbial populations [6–9].

In the field of industrial wastewater treatment, equalization basins are widely employed as a pre-treatment process. This can serve several purposes including: (1) dampening fluctuations in organic loading to prevent shock loading of biological systems, (2) providing continuous feed to biological systems over periods when wastes are not being generated, (3) preventing high concentrations of toxic materials from entering the biological treatment plant, and (4) providing capacity for controlled discharge of wastes in a more even manner [10]. Load equalization processes could provide similar benefits in the field of biological treatment of contaminated gases; however, they have not been widely studied or implemented.

One approach for achieving the benefits of load equalization in systems treating gas phase contaminants is to install a column packed with granular activated carbon (GAC) as a passively-controlled load equalization mechanism in series before a biofilter (see Fig. 1). The rationale for such a system is that during periods of high contaminant loading, the adsorbent could temporarily accumulate contaminants and then subsequently desorb contaminants during periods when concentration in the waste gas is low. In this manner, it could dampen fluctuations in organic loading to prevent shock loading of the biofilter and provide continuous feed to the biological system over periods when wastes are not generated. Although this strategy, first proposed by Ottengraff [11], has been widely discussed in the literature [1,7,12,13] experimental testing of the approach has been quite limited [9,12]. Furthermore, very little attention has been directed toward development of design or analysis methodologies appropriate for such GAC-biofilter systems [9]. If successfully implemented, such an approach 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.

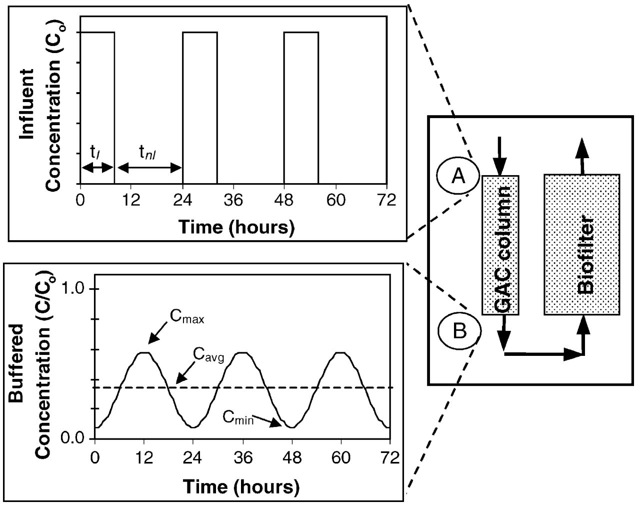

Fig. 1. Conceptual approach for using activated carbon load equalization as a pre-treatment step prior to biofiltration.

There are a number of parameters that must be determined, however, before such a system can be reliably implemented in full-scale applications. For example, a relationship between the size of an activated carbon load equalization system and the degree of buffering that it will achieve must be known. The overall goal of research described herein was to determine such a relationship and to develop an appropriate basis of design for passively operated activated carbon load equalization systems for biofilters treating gas-phase contaminants. In the first stage of research, fixed-bed adsorption/desorption experiments were conducted under steady loading conditions to quantify the reversible adsorption capacity of an activated carbon medium. Second, fixed-bed adsorption/desorption experiments were conducted under intermittent loading conditions (contaminant supply during only 8 h/day) to assess the ability of an activated carbon column to attenuate various inlet concentrations of toluene as an intermittently loaded single-component contaminant under a wide range of empty bed contact times (EBCTs). Third, a pore and surface diffusion model, calibrated and validated using experimental data, was used to predict dynamic contaminant breakthrough from GAC columns under a variety of different loading conditions. Based on the combined experimentally determined and modeled data, a design methodology was developed to provide guidance in reactor sizing and operating parameter estimation. Toluene, a compound frequently encountered in industrial operations and regulated as hazardous air pollutant (HAP) in the US, was selected as a model compound.

2. Materials and methods

2.1. Activated carbon and experimental apparatus

The activated carbon employed in this research was BPL 4 × 6 mesh GAC (Calgon Carbon Corp., Pittsburgh, PA). The GAC was rinsed with distilled water to remove fines and dried at 105 °C prior to use. The general configuration of the apparatus used to test the GAC in fixed-bed toluene adsorption/desorption experiments is depicted in Fig. 2. Contaminant-free compressed air (average relative humidity 20%) flowed through a pressure regulator and a rotameter to measure and regulate airflow. Liquid toluene (ACS reagent grade, Sigma, St. Louis, MO) was delivered by a syringe pump (KD Scientific, Boston, MA) and evaporated into the air stream. Packed-columns, operated in downflow

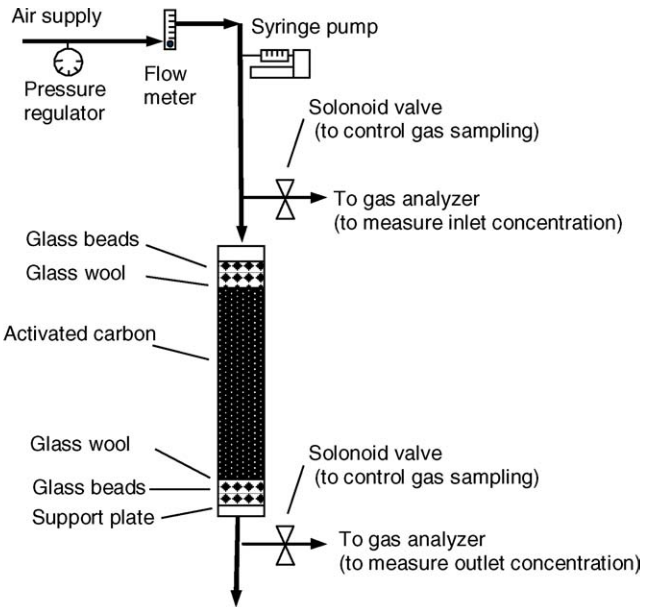

Fig. 2. Schematic diagram of apparatus used for fixed-bed adsorption/desorption experiments.

mode, were constructed of PVC (i.d. 7.62 cm). Within the packed columns, a perforated stainless-steel plate installed at the bottom of each section supported 6 cm depth of glass beads (5 mm diameter) to evenly distribute air flow, a thin layer of glass wool to retain GAC particles, 5–25 cm depth of GAC (with a mass ranging from 100 to 500 g), another thin layer of glass wool, and another 6 cm depth of glass beads. As further described below, some experiments utilized columns comprised of a single section while others used columns constructed with multiple sections to facilitate sampling at multiple spatial locations corresponding to different empty bed contact times. For studies conducted with intermittent loading conditions, a microprocessor-based controller (ChronTrol, San Diego, CA) turned syringe pumps on and off as necessary.

Solenoid valves with stainless steel flow tubes (Asco Valve Inc., NJ) installed prior to the GAC column inlet and after the GAC column allowed automated sampling of inlet and outlet toluene concentrations. In cases where multi-section columns were employed, solenoid valves were also installed at intermediate locations to allow automated sampling of toluene concentrations at various packed bed depths. When a solenoid valve was turned on, a portion of the gas flow was diverted to the analytical instrument used to measure contaminant concentrations. Volumetric flow of gas diverted to the analytical instrument comprised less than 2% of the total gas flow to the GAC column. Gas sampling lines were constructed using Teflon tubing. Initial tests conducted prior to placement of activated carbon demonstrated that column components other than GAC had little or no adsorption capacity for toluene. All experiments were conducted at ambient laboratory temperature of $23 \pm 2\,^{\circ}\mathrm{C}$.

2.2. *Isotherms for reversible adsorption*

Fixed-bed adsorption experiments were conducted under steady loading conditions to quantify the “working capacity” of the activated carbon (i.e., the sorption capacity available for repeated sorption/desorption). In an initial experiment, a column packed with 5.0 cm depth of virgin carbon was subjected to a steady influent toluene concentration of 1000 $\mathrm{ppm_v}$ at an EBCT of 0.90 s and superficial gas velocity of 200 m/h (gas flow rate of 15.2 L/min). Effluent toluene concentration was measured as a function of time until the effluent equaled the influent concentration for a period exceeding 4 h, at which time it was concluded that equilibrium had been reached. Toluene was then removed from the inlet and uncontaminated gas flowed through the column until the effluent toluene concentration was below detection. The column was then subjected to two additional adsorption/desorption cycles following the same procedure as in the first cycle (i.e., alternately loading toluene until complete breakthrough and then immediately desorbing the loaded carbon using flow of uncontaminated air at ambient temperature). The total mass of toluene adsorbed and desorbed during each of the three adsorption/desorption cycles was then calculated by integration.

Prior to equilibrium adsorption tests at other influent toluene concentrations, sufficient virgin activated carbon was subjected to one conditioning cycle by continuously loading toluene until complete breakthrough and then desorbing the activated carbon using the flow of uncontaminated air until effluent toluene was below detection. This “conditioned” carbon was subsequently used in separate fixed-bed adsorption tests conducted with GAC packed bed depths of 7.5 cm at target influent toluene concentrations of 750, 500, 250, 100, and 50 $\mathrm{ppm_v}$ and a superficial gas velocity of 300 m/h (gas flow rate of 22.8 L/min). The mass of toluene reversibly adsorbed to the conditioned carbon was then used to calculate Freundlich isotherm parameters used in subsequent modeling.

2.3. *Experimental testing of load attenuation with toluene supplied 8 h/day*

The packed column used in toluene adsorption/desorption experiments to characterize load-dampening effects during intermittent loading conditions had a total GAC packed bed depth of 83.3 cm (total GAC packed bed volume of 3.8 L). The column was divided into four sections (arbitrarily designated Sections A, B, C, and D, respectively, beginning from the top of the column) with GAC packed bed depths of 12.5, 20.8, 25, and 25 cm, respectively. The perforated stainless steel support plates in Sections A, B, C, and D supported 250, 417, 500, and 500 g of activated carbon, respectively (total GAC mass of 1667 g). Monitoring ports located in the plenum between adjacent column sections were used to sample gas flow for measurement of toluene concentrations.

The intermittent loading scenario investigated in this research consisted of 8 h contaminant loading followed by 16 h non-loading each day (intended to simulate off-gases generated during an 8 h/day work schedule). During non-loading intervals, uncontaminated air flowed through the columns at the same rate as during contaminant loading intervals. The gas flow rate was 22.8 L/min, corresponding to GAC column EBCTs of 1.5, 4.0, 7.0, and 10 s at the end of Sections A, B, C, and D, respectively (i.e., at cumulative packed bed depths of 12.5, 33.3, 58.3, and 83.3 cm, respectively) and a superficial gas velocity of 300 m/h. During initial experiments, target influent toluene concentration during the daily 8-h loading cycle was 1000 ppm_v. After quasi steady state conditions were achieved, additional experiments were conducted with 8 h/day loading at influent toluene concentrations of 700, 420, and 210 ppm_v. Loading at each toluene concentration lasted until quasi-steady state was reached and in all cases was at least 16 days.

Table 1
Parameter values used in model simulations

Parameter	Value
Fixed-bed properties	
Bed length (cm)	12.5–83.3[a]
Bed diameter (cm)	7.62[a]
Bed mass (kg)	0.25–1.67[a]
Bed porosity	0.483[a]
Adsorbent properties	
Particle apparent density (p_a) (g/cm^3)	0.85[b]
Average particle diameter (d_p) (cm)	0.372[b]
Particle void fraction (ε_p)	0.595[b]
Particle shape factor	0.72[b]
Freundlich isotherm parameters	
K (mg/g) (L/mg)$^{1/n}$	152[c]
$1/n$	0.249[c]
Air properties	
Temperature (°C)	23[a]
Density (g/cm^3)	1.18×10^{-3}[d]
Viscosity (g/(cm s))	1.80×10^{-4}[d]
Kinetic parameters	
K_f (film mass-transfer coefficient) (cm/s)	1.01[e]
D_s (surface diffusion coefficient) (cm^2/s)	5.12×10^{-6} to 1.65×10^{-5}[f]
D_p (pore diffusion coefficient) (cm^2/s)	8.24×10^{-2}[g]
Surface to pore diffusion flux ratio	16[h]
Tortuosity	1[h]

[a] Experimentally measured.

[b] Data provided by Calgon Carbon Corp. (Pittsburgh, PA).

[c] Calculated by regression using data measured in experiments to determine reversible isotherm.

[d] Calculated by correlation using the StEPP$^{\text{TM}}$ database [16].

[e] Model fit parameter.

[f] Calculated by AdDesign using the Sontheimer correlation as described by Mertz et al. [16].

[g] Calculated by AdDesign using the Wilke-Lee modification of the Hirschfelder–Bird–Spotz method [16].

[h] Assumed parameter based on experimental fit determined by Crittenden et al. [29].

2.4. Analytical techniques

Toluene concentration was measured using a model 1312 photoacoustic multigas monitor (California Analytical, Orange, CA) equipped with four optical filters (UA# 0971, 0974, 0983, and SB0527) as described previously [9]. Relative humidity was measured using a traceable digital hygrometer/thermometer (Fisher Scientific, Pittsburgh, PA). Rotameters used to measure and regulate airflows were calibrated using an NIST traceable Aalborg Instruments model GFM37 digital mass flow meter (Orangeburg, NY).

2.5. Modeling attenuation under discontinuous loading conditions

The pore and surface diffusion model (PSDM) described by Crittenden et al. [14] and Hand et al. [15] was used to predict the degree of load-dampening achieved by GAC columns under discontinuous loading conditions. The PSDM is a dynamic fixed-bed model that incorporates assumptions and governing equations described elsewhere [14,16]. Simulations using the PSDM were performed using AdDesignS$^{\text{TM}}$ software (Michigan Technological University). In AdDesignS$^{\text{TM}}$, an orthogonal collocation method is used to convert partial differential equations of the PSDM into a set of ordinary differential equations that are solved using a backward differential method [14,16,17].

Dynamic adsorption calculations using this model require equilibrium parameters, kinetic parameters, physical properties of adsorbing compound and adsorbent, fluid properties, influent concentrations, flow characteristics, and column dimensions. A summary of parameter values and sources of data input to the model is presented in Table 1. Influent gas flow rates input to the model were identical to those experimentally tested. Measurements in the experimental system revealed that influent toluene concentration increased to near the target level within 3 min after the start of loading and decreased to below detection within 3 min after syringe pumps turned off (data not shown). Accordingly, in model simulations, contaminant concentrations entering the GAC column as a function of time were assumed to linearly increase from zero to the target level over a period of 3 min at the start of each 8-h loading period and linearly decrease to zero 3 min after the end of the 8-h loading interval.

The model was calibrated by optimizing the value of the film transfer coefficient (K_f) to achieve a best fit with experimentally determined contaminant breakthrough curves obtained at quasi-steady state for intermittent (8 h/day) loading of toluene at an influent concentration of 1000 ppm_v and EBCTs of 1.5, 4, 7, and 10 s. In calibrating the model, primary consideration was given to matching the model prediction for C_{max} (maximum outlet VOC concentration at any time during the loading cycle) with the measured data. Secondary consideration was given to matching model prediction for C_{min} (minimum outlet VOC concentration at any time during the loading cycle) and shape of the quasi-steady state breakthrough curves. Experimental data from intermittent loading with influent toluene concentrations of

700, 420, and 210 $\mathrm{ppm_v}$ at EBCTs of 1.5, 4, 7, and 10 s were used for model validation.

3. Results and discussion

3.1. Experimental testing of equilibrium isotherms

Initial fixed-bed adsorption/desorption experiments were conducted using steady (as opposed to intermittent) toluene loading to assess the reversible sorption capacity of the GAC medium. Breakthrough curves for toluene adsorption in a GAC column with an EBCT of 0.90 s and stable influent concentration of 1000 $\mathrm{ppm_v}$ are depicted in Fig. 3. During the first loading cycle (using virgin GAC), complete breakthrough was reached after approximately 16.5 h. The mass of toluene adsorbed by the virgin carbon after equilibrium with an influent toluene concentration of 1000 $\mathrm{ppm_v}$, 0.333 g toluene per gram GAC, was close to that (within 7%) predicted using toluene isotherms from Calgon's proprietary model for this type of virgin GAC [18]. The mass of toluene desorbed from the carbon following this initial adsorption step, however, was only about two-thirds of that initially adsorbed. The fact that a portion of the toluene adsorption was irreversible (desorption did not occur when the inlet concentration was decreased to zero) is consistent with previously reported results and can be attributed to the fact that low-temperature desorption does not provide sufficient energy to reverse the adsorptive force for contaminants occupying some high energy adsorption sites and the fact that covalent bonds can form between adsorbate molecules and the adsorbent surface, resulting in chemisorption that is irreversible [19].

The pattern of contaminant breakthrough during the second and third loading cycles was essentially indistinguishable from one another. The mass of toluene adsorbed during the second and third cycles (see Fig. 3) and the mass desorbed during each cycle was essentially identical (0.218 ± 0.004 g toluene per gram GAC), averaging 65% of the mass adsorbed during the first loading cycle. This suggests that although a portion of contaminants remains adsorbed within the carbon particles after initial loading, after undergoing one conditioning cycle, the GAC exhibited a stable fully reversible adsorption and desorption capacity.

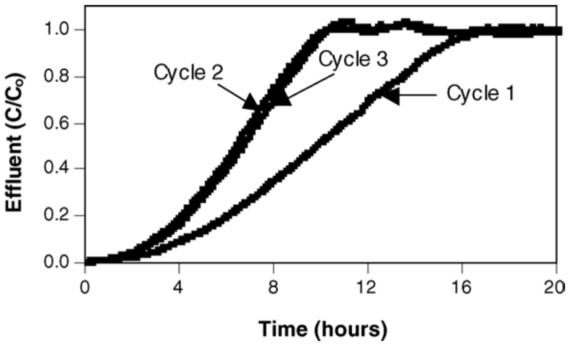

Fig. 3. Breakthrough curves for toluene adsorption at influent concentration of 1000 $\mathrm{ppm_v}$ during the first three conditioning cycles. Conditions: packed bed depth 5 cm, superficial gas velocity of 200 m/h, EBCT = 0.90 s.

Subsequent breakthrough curves at influent toluene concentrations ranging from 50 to 1000 $\mathrm{ppm_v}$ were determined using "conditioned" GAC (i.e., GAC that that was pre-loaded and then desorbed prior to use). Mass of toluene adsorbed per unit mass activated carbon at equilibrium was calculated for each gas-phase concentration tested. Based on these data, a regression analysis was used to calculate Freundlich isotherm parameters K and $1/n$, which have values of 152 and 0.249, respectively, when gas-phase equilibrium concentration has units of (mg/L) and mass toluene adsorbed per unit mass GAC has units of (mg/g). The high correlation coefficient (0.991) indicates that the Freundlich equation adequately describes adsorption data over the toluene concentration range tested. These Freundlich parameter values, which reflect only the reversible adsorption capacity of the carbon, are appreciably different from isotherm parameters for the virgin carbon (where $K = 305$ and $1/n = 0.107$) [18], and reflect the fact that a portion of the sorption capacity of virgin GAC is irreversible under the desorption conditions employed here.

3.2. Load attenuation by GAC columns receiving contaminant supply 8 h/day

Experimentally measured quasi-steady state GAC breakthrough curves for intermittent loading of toluene (8 h/day), conducted under various influent concentrations and GAC column EBCTs are depicted in Fig. 4. Each graph in the figure shows data from two continuous loading cycles (48 h total) with contaminant concentrations measured at 10-min intervals. Time zero in each graph corresponds to the point at which minimum daily effluent concentration was reached in the experimentally measured data. The y-axis of each graph is the dimensionless effluent concentration (effluent concentration divided by corresponding target influent concentration entering during the 8 h loading interval). Measured inlet concentrations were found to closely match target concentrations (within 3%, data not shown).

As illustrated in Fig. 4, at each quasi-steady state loading condition tested, a consistent pattern of attenuated effluent concentration was exhibited on a daily basis. Daily minimum and maximum effluent concentrations were consistently reproducible (differing less than 5% on a day to day comparison), and mass balance calculations verified that contaminant mass entering and exiting the GAC columns on a daily basis were essentially the same (within 3%) after quasi-steady state was reached at each loading condition. These data clearly demonstrate that the contaminant mass temporarily accumulated in a GAC column during intervals when influent contaminant concentrations are high can desorb within a sufficiently short time interval (i.e., during each loading cycle when influent contaminant concentrations are low) to be of practical benefit as a passively-operated load dampening equalization mechanism. The only driving force necessary

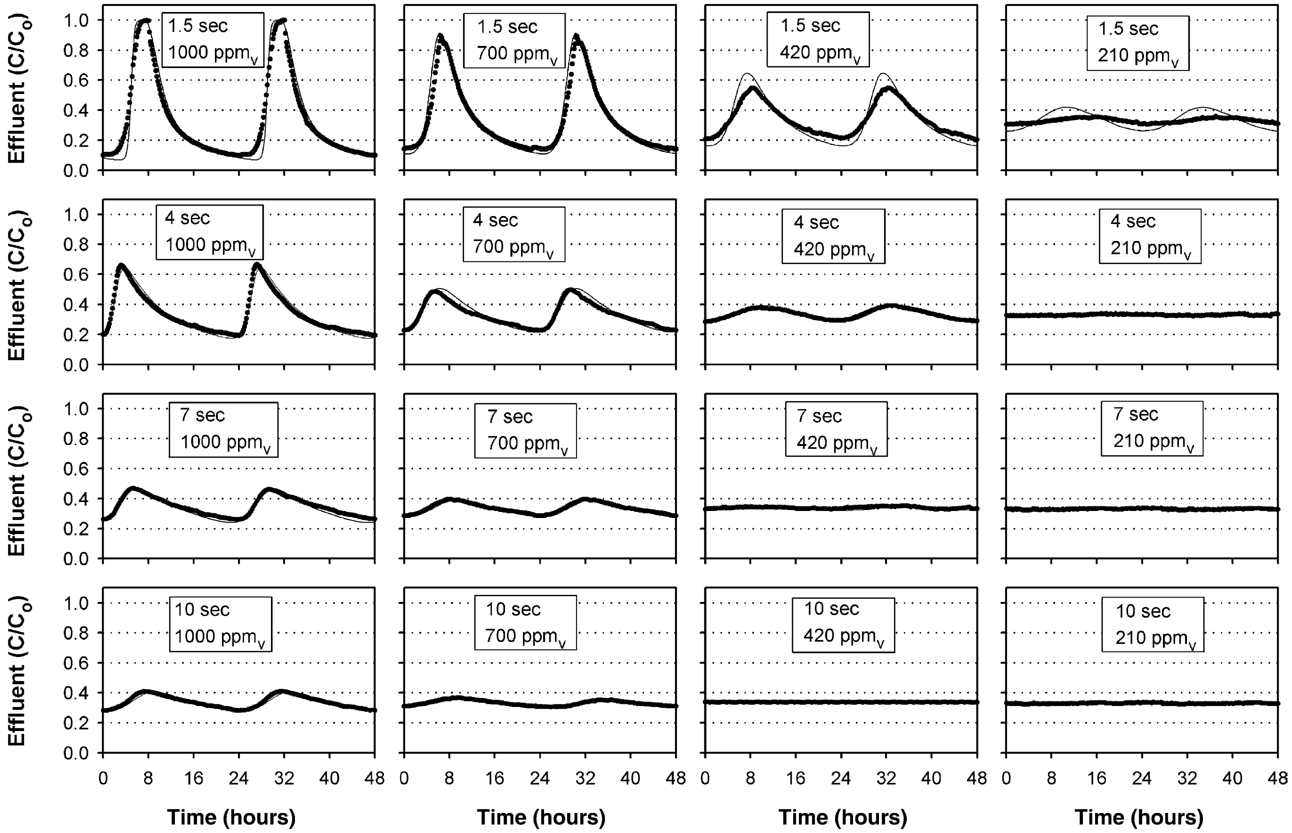

Fig. 4. Experimentally measured (data points) and model simulation (thin lines) quasi-steady state breakthrough curves for various EBCTs (ranging from 1.5 to 10 s) and influent toluene concentrations (ranging from 210 to 1000 ppm_v). The time scale (x-axis) for graphs shown in the bottom row apply to all graphs in each column. The scale for dimensionless effluent concentration (y-axis) shown in the first column applies to all graphs in each row. Loading conditions: Calgon BPL 4 × 6 mesh GAC, toluene contaminated air-supplied 8 h/day and uncontaminated air supplied 16 h/day, superficial gas velocity of 300 m/h.

for contaminant desorption was the naturally occurring decrease in influent contaminant concentration imposed on the waste stream. Regeneration of the GAC column through other means (e.g., heating) was not necessary. The fact that essentially identical quasi-steady state breakthrough curves were observed after more than 60 consecutive daily loading cycles (data not shown) further demonstrates that the reversible sorption capacity was not diminished over time.

As further discussed in the following section, the degree of load attenuation observed in these experiments is clearly a function of both influent contaminant concentration as well as the EBCT. The degree of attenuation (i.e., characterized by lower C_{max}/C_o and higher C_{min}/C_o) increased as the influent contaminant concentration decreased. For example, at all EBCTs tested, the effluent concentration was much more attenuated for an influent concentration of 210 ppm_v than it was for an influent concentration of 1000 ppm_v. Toluene was also more attenuated as EBCT increased. For example, at the highest influent toluene concentration tested (i.e., 1000 ppm_v), at an EBCT of 1.5 s the maximum effluent concentration was equal to the influent for a portion of each cycle (i.e., C_{max}/C_o was equal to 1.0), while at EBCT of 10 s, C_{max}/C_o was 0.41.

For all four toluene concentrations tested, an EBCT of 7 s was sufficient to decrease C_{max}/C_o to less than 0.5. Such load equalization could provide an obvious practical benefit in design and operation of biofilters. Peak loading to the biofilter could be greatly reduced and starvation during periods of low or no contaminant loading could be minimized or entirely avoided. If a biofilter's design is to be based on peak loading as advocated by some authors [5,20], then the biofilter could be markedly reduced in size compared to a system without buffering.

3.3. Model prediction of load attenuation by GAC columns

The PSDM model was calibrated using experimental data for intermittent loading (8 h/day) of 1000 ppm_v toluene (i.e., data points depicted in the first column of Fig. 4). The x-axis scales of modeled data depicted in Fig. 4 are shown aligned to produce the best fit with experimental data. Best agreement between experimental and modeled data was achieved with a film mass-transfer coefficient (K_f) value of 1.01 cm/s. Under the four tested EBCT levels for an influent concentration of 1000 ppm_v loaded 8 h/day, difference between modeled and measured C_{max} were within 2%, while differences between modeled and measured C_{min} ranged from 3.3 to 15.4% (see Fig. 4, first column). The somewhat larger difference between

$C_{\min}$ was due in part to the fact that higher priority was given to matching $C_{\max}$ during model calibration.

The model was validated by comparing model predictions with experimental data from the other loading conditions tested (i.e., influent concentration levels of 700, 420, and 210 ppm_v at four different EBCTs each). Visual comparison of dynamic model predictions shown in Fig. 4 in comparison to experimental measurements reveals that there is good fit in terms of overall breakthrough curve shape. In fact, in most cases the thin lines denoting model simulations are obscured by the experimentally measured data points because of the close fit and the size of symbols denoting experimental measurement.

To further assess differences between the model predictions and measured data, plots of $C_{\max}/C_o$ and $C_{\min}/C_o$ versus EBCT were constructed as shown in Fig. 5. Each measured data point in Fig. 5 represents the average of at least three replicate loading cycles measured after the columns reached quasi-steady state. Overall, the PSDM was quite successful in quantitatively predicting the magnitude of attenuated contaminant concentrations exiting the GAC columns. With respect to $C_{\max}/C_o$, the difference between measured and modeled data averaged 3.9% (average of 12 data points used for validation—influent concentrations of 700, 420, and 210 ppm_v each at EBCTs of 1.5, 4, 7, and 10 s). The largest difference between model prediction and measured data for $C_{\max}/C_o$ was 18.7% (for influent toluene concentration of 420 ppm_v at EBCT 1.5 s). With respect to $C_{\min}/C_o$, the difference between measured and modeled data averaged 5.9% (average of 12 data points used for validation). The largest difference between model prediction and measured data for $C_{\min}/C_o$ was 23.8% (for influent toluene concentration of 700 ppm_v at EBCT 1.5 s). Discrepancies between measured and modeled $C_{\max}/C_o$ and $C_{\min}/C_o$ were largest for the lowest EBCT (i.e., 1.5 s). The model's small over-prediction of $C_{\max}/C_o$ and under-prediction of $C_{\min}/C_o$, particularly at EBCT of 1.5 s may have resulted from the 10 min sampling interval being insufficient to capture the true maximum and minimum effluent concentrations in experimental measurements when less buffering was achieved and thus effluent concentrations changed relatively quickly (see Fig. 4). At EBCTs of 4 s or longer, differences between measured and modeled $C_{\max}$ and $C_{\min}$ were consistently small (average difference of 1.2% and maximum difference of 4.5% for $C_{\max}/C_o$; average difference of 1.1% and maximum difference of 4.3% for $C_{\min}/C_o$).

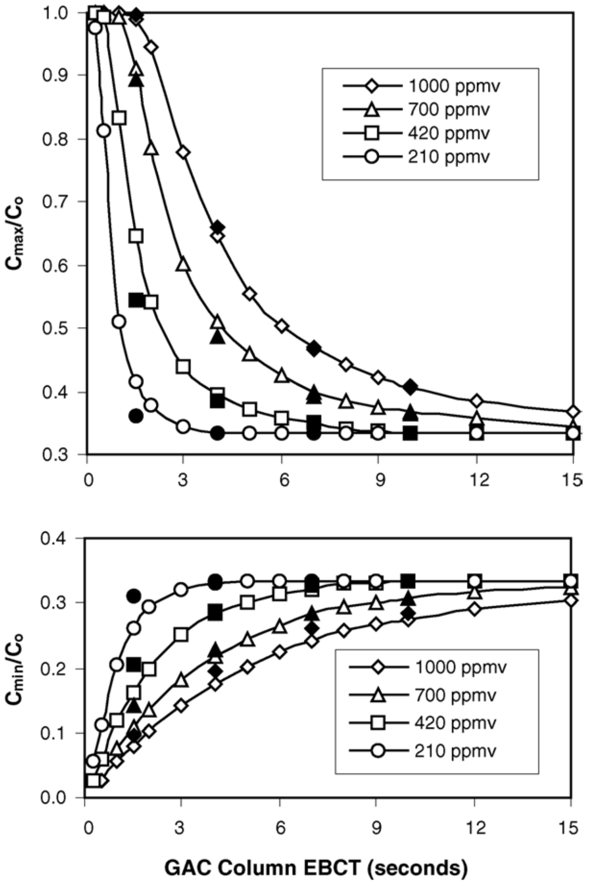

Fig. 5. Maximum (top) and minimum (bottom) dimensionless effluent concentrations observed at quasi-steady state under intermittent (8 h/day) toluene loading of Calgon BPL 4 × 6 mesh GAC at a superficial gas velocity of 300 m/h. Filled symbols denote measured data and opened symbols denote model prediction.

For all influent concentrations, toluene was more attenuated (i.e., characterized by lower $C_{\max}/C_o$ and higher $C_{\min}/C_o$) as EBCT increased, asymptotically approaching "ideal" buffering at high contact time. "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 contaminant concentrations that has a fixed periodicity and amplitude with a constant influent concentration during the loading interval, ideal buffering occurs if the contaminant concentration exiting the GAC column is constant with respect to time. In such cases, as shown in Eq. (1), the dimensionless concentration exiting the buffering system is equal to the fraction of time during which contaminants are loaded to the system,

$$\frac{C_{\min}}{C_o} = \frac{C_{\max}}{C_o} = \frac{C_{\text{average}}}{C_o} = \frac{t_l}{t_l + t_{nl}} \tag{1}$$

where $C_{\min}$ is the minimum outlet VOC concentration at any time during the loading cycle, $C_{\max}$ the maximum outlet VOC concentration at any time during the loading cycle, C_o the inlet VOC concentration during the loading interval, C_{average} the average outlet VOC concentration, t_l the duration of the loading interval per cycle and t_{nl} is the duration of the non-loading interval per cycle (see Fig. 1).

This is in contrast to cases where less than ideal buffering is observed. For less than ideal buffering of a single component contaminant, the concentration exiting a GAC load dampening system will vary with time with minimum and maximum concentrations constrained within the following ranges described by Eq. (2).

$$0 \leq \frac{C_{\min}}{C_o} \leq \frac{t_l}{t_l + t_{nl}} \quad \text{and} \quad \frac{t_l}{t_l + t_{nl}} \leq \frac{C_{\max}}{C_o} \leq 1 \qquad (2)$$

In the contaminant loading scenario investigated in this study, toluene was supplied in the influent for 8 h/day and uncontaminated air was supplied 16 h/day. Thus, in the case of ideal buffering, the dimensionless effluent concentration (both $C_{\min}/C_o$ and $C_{\max}/C_o$) would equal 0.33 (8 h/24 h = 0.33). The experimental data, supported by model predictions, demonstrate that load attenuation very close to ideal buffering can be achieved in GAC columns with relatively low EBCTs (on the order of a few seconds). The EBCT required to achieve ideal buffering (or partial buffering at a level less than “ideal”) decreases as the influent toluene concentration decreases. Thus, to achieve the same magnitude of attenuation (i.e., the same $C_{\max}/C_o$), a shorter EBCT is required for lower influent contaminant concentrations. To further assess this, a series of design curves were constructed as described in the following section.

3.4. Design curves for load dampening system treating discontinuously-loaded toluene

If an integrated system consisting of a GAC buffering column followed by a biofilter is to be designed or analyzed, there is an obvious need to relate GAC column size to the degree of load equalization that will result from its use. In this regard, the dimensionless term $C_{\max}/C_o$ provides a useful measure of the buffering system’s peak attenuation capacity and can serve as a design parameter. Following model calibration and validation, model simulations of dynamic toluene sorption were conducted for numerous GAC column EBCTs (ranging from 0.25 to 15 s) and influent concentrations (ranging from 100 to 1000 ppm$_v$). To represent the data in a form amenable to direct use as a tool for design or analysis, design curves were then generated by plotting $C_{\max}/C_o$ versus EBCT as shown in Fig. 6. In all cases, the simulated loading condition was for 8 h/day loading and 16 h/day non-loading with model input parameters shown in Table 1. Each line shown in the figure was generated using output from at least 15 separate model simulations.

For a defined influent contaminant concentration, curves such as those shown in Fig. 6 can be used to directly determine the EBCT required for a GAC column in order to achieve a specified level of load equalization. Based on the buffered concentration exiting the GAC column, a biofilter can then be sized using an appropriate method (e.g., a graph of loading rate versus elimination capacity determined from pilot-scale testing as described by Devinny et al. [1]). As demonstrated by the example discussed below, use of an activated carbon load equalization system can allow for much smaller biofilter systems to meet treatment goals. By decreasing the peak contaminant concentration entering the biofilter, such a design methodology could also be used to avoid toxicity [21] or O_2 limitation [22] in cases where they would otherwise occur.

3.5. Examples of design process implementation

The process of how a graph such as that depicted in Fig. 6 may be used in design of a GAC column load equalization system integrated with a biofilter and the potential benefits of doing so can be demonstrated by considering the following example.

3.5.1. Problem statement

An industry emits an air stream with constant flow rate of 150 m^3/min, temperature of 23 °C, and relative humidity of

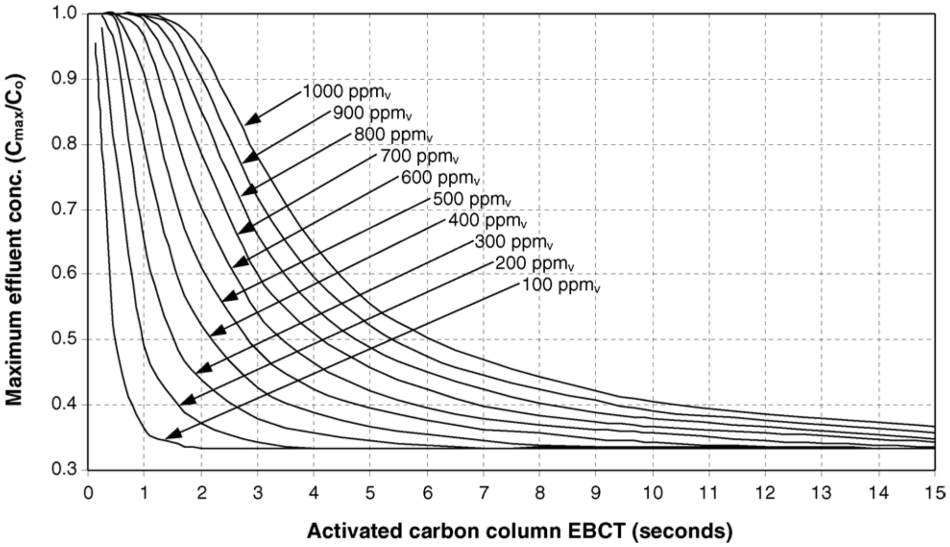

Fig. 6. Design curves for Calgon BPL 4 × 6 mesh GAC used as a load equalization mechanism for treatment of discontinuously loaded (8 h/day) toluene concentrations ranging from 100 to 1000 ppm$_v$ in a 23 °C air stream at a superficial velocity of 300 m/h.

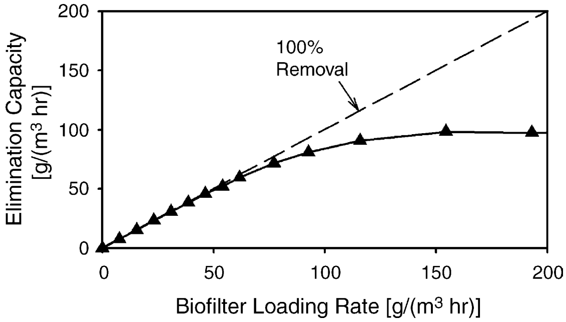

Fig. 7. Example elimination capacity graph determined from pilot-scale testing of a biofilter system treating toluene contaminated air.

20%. Toluene is present as a contaminant in the waste gas for 8 h/day at a concentration of 300 $\mathrm{ppm_v}$ (1.14 $\mathrm{g/m^3}$), and during the remainder of the day, no contaminant is present in the airflow. Using data provided in Fig. 6 and the biofilter elimination capacity curve provided in Fig. 7 (determined during pilot-scale testing), calculate the size of an activated carbon buffering system and biofilter required to remove 90% of the daily contaminant mass loading if the GAC column is to achieve $C_{\max}/C_o = 0.4$. Compare the volume of the integrated system (GAC column + biofilter) to the size of a system comprised of only a biofilter to achieve the same treatment goal.

3.5.2. Solution

From the curve shown in Fig. 6 corresponding to an influent of 300 $\mathrm{ppm_v}$, the EBCT required for a GAC column to achieve $C_{\max}/C_o = 0.4$ is 2.6 s. The volume of the GAC bed can then be calculated using Eq. (3),

$$V_c = Q_g \times \theta_c \qquad (3)$$

where V_c is the volume of the GAC packed bed ($\mathrm{m^3}$), Q_g the volumetric gas flow rate ($\mathrm{m^3/min}$), and θ_c is the empty bed contact time of the GAC column (min). Solving for the conditions given:

$$V_c = 150\,\mathrm{m^3/min} \times 2.6\,\mathrm{s} \times \frac{1\,\mathrm{min}}{60\,\mathrm{s}} = 6.50\,\mathrm{m^3}$$

From the biofilter elimination capacity graph provided, the maximum loading rate that will result in 90% toluene removal is 85 $\mathrm{g/(m^3\,h)}$ [grams toluene per cubic meter biofilter bed per hour]. The biofilter bed volume can then be calculated using Eq. (4),

$$V_B = \frac{\frac{C_{\max}}{C_o} \times C_o \times Q_g}{L} \qquad (4)$$

where V_B is the volume of the biofilter packed bed ($\mathrm{m^3}$); $C_{\max}/C_o$ the dimensionless maximum concentration exiting the activated carbon column, C_o the influent toluene concentration during the loading interval ($\mathrm{g/m^3}$), and L is the biofilter loading rate, $\mathrm{g/(m^3\,h)}$. In this case, V_B is calculated as:

$$V_B = \frac{0.4 \times 1.14\,\mathrm{g/m^3} \times 150\,\mathrm{m^3/min} \times 60\,\mathrm{min/h}}{85\,\mathrm{g/(m^3\,h)}} = 48.3\,\mathrm{m^3}$$

Total volume (V_{Total}) of the integrated system can then be calculated.

$$V_{\mathrm{Total}} = V_C + V_B = 6.5\,\mathrm{m^3} + 48.3\,\mathrm{m^3} = 54.8\,\mathrm{m^3}$$

If the GAC load equalization system is omitted, then the $C_{\max}/C_o$ term in Eq. (4) equals 1.0. The required biofilter bed volume would be:

$$V_B = \frac{1.0 \times 1.14\,\mathrm{g/m^3} \times 150\,\mathrm{m^3/min} \times 60\,\mathrm{min/h}}{85\,\mathrm{g/(m^3\,h)}} = 121\ \mathrm{m^3}.$$

The treatment system comprised of only a biofilter would need to be 2.2 times as large as an integrated system comprised of a GAC load equalization system and biofilter.

3.6. Incorporation of safety factors in design

Another potential advantage of using an activated carbon load equalization system in design is that such a procedure easily allows incorporation of a safety factor in design. For example, in solving the example described above, the maximum biofilter loading rate that met the treatment goal (90% toluene removal) was selected as the basis of design for the biofilter. If elimination capacity of the full-scale biofilter was any lower than observed in pilot-scale testing, then performance objectives would not be met. There are numerous conditions that can result in lower degradation rates in full-scale systems operated over long time intervals than are observed in relatively short-term pilot-scale or laboratory-scale testing. For example, a biofilter may become nutrient-limited [23], experience excessive drying [1,24,25], or experience higher than anticipated contaminant loading. While some phenomena can be accounted for in conducting appropriate pilot-scale testing, a considerable amount of uncertainty remains unavoidable in the design process, and inclusion of a safety factor in design can help to ensure reliable system performance.

Use of an activated carbon buffering system could provide such a safety factor without the need for a dramatic increase in system size and cost compared to conventionally designed systems. This can be easily demonstrated by considering an alternate solution to the example problem presented above. A safety factor of two could be incorporated into design of both the GAC load equalization system and the biofilter by making each twice as large as that specified in the example. This would result in a total size of the integrated system of 110 $\mathrm{m^3}$ (13 $\mathrm{m^3}$ GAC column + 97 $\mathrm{m^3}$ biofilter), which is still smaller than the size of the unbuffered biofilter (121 $\mathrm{m^3}$) that did not include any safety factor. Incorporating the safety factor would allow the integrated system to meet the required treatment objectives even if the biofilter exhibited only half of the elimination capacity observed in pilot-scale tests or if the influent toluene concentration was twice that assumed during design. If the loading condition and elimination capacity were the same as those assumed during design, then performance goals would be exceeded. Thus, use of a GAC load equalization system has the potential not only to mitigate the adverse effects of unsteady loading, it also has the potential to minimize much of the uncertainty that accompanies design and operation of biofilter systems.

3.7. Further discussion

There are a number of constraints in applying design curves such as those presented in Fig. 6. Such curves will generally be applicable only to the specific contaminant, contaminant concentration, adsorbent, interstitial velocity, relative humidity, and load periodicity for which it was generated. Application to other loading conditions will require generation of other design curves. Further, because of competitive adsorption [14,15,26–28], different contaminants can exhibit different levels of attenuation in systems treating multi-component contaminant mixtures (as opposed to the single contaminant waste gas examined herein). More extensive modeling and/or experimental testing may be necessary for such systems [9]. Nevertheless, the general approach presented here may prove useful for design of passively operated GAC load equalization systems for use in conjunction with biofilter treatment or other air pollution control technologies.

4. Conclusions

Experimental testing demonstrated that passively operated GAC columns can successfully achieve load equalization of toluene-contaminated air streams subjected to intermittent loading conditions. A PSDM model calibrated by optimizing a single parameter (i.e., the film mass-transfer coefficient, K_f) and validated using experimental data was successful in quantitatively predicting the magnitude of load equalization achieved by GAC columns under a wide range of influent loading conditions. Experimental and model results demonstrated that contaminant mass temporarily accumulated in GAC columns during periods of high influent contaminant concentration can desorb within a sufficiently short time interval (i.e., during each loading cycle) to be of practical benefit as a passively operated load dampening mechanism for biofilter pretreatment. The degree of load attenuation becomes more pronounced at lower contaminant concentrations and higher GAC EBCTs. Based on the combined experimentally determined and modeled data, a series of design curves were developed to provide guidance for reactor sizing and operating parameter estimation. Implementation of this design methodology could allow use of smaller biofilters to treat intermittently generated contaminants, and it could also provide a mechanism for incorporating a safety factor that would minimize uncertainty in the design process.

Acknowledgements

The authors gratefully acknowledge the Louisiana Board of Regents, Hazardous Substance Research Center South & Southwest (through the HSRC Environmental Biotechnology Initiative), and BioReaction Industries for financial support and Calgon Carbon Corp. for providing activated carbon medium.

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