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Treatment of mixtures of methyl ethyl ketone (MEK) and toluene using continuous and sequencing batch operated biofilters

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TREATMENT OF MIXTURES OF METHYL ETHYL KETONE (MEK) AND TOLUENE USING CONTINUOUS AND SEQUENCING BATCH OPERATED BIOFILTERS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University
Agricultural and Mechanical College
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requirements for the degree of
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in

The Department of Civil and Environmental Engineering

by

Jorge C. Atoche
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ABSTRACT

During the past decade, biofiltration has increasingly been applied as an air pollution control technology to minimize or eliminate emissions of volatile organic compounds from industrial sources. Although of the ability of this technology to maintain high removal efficiency during relatively steady conditions has been well established for many waste streams, a limitation of this technology has been its inability to maintain high removal efficiency during transient loading conditions typical of industrial operations.

In the research described herein, a conventional continuous-flow biofilter (CFB) and a sequencing batch biofilter (SBB) were operated for more than 295 days to treat a model waste gas stream containing a two-component mixture of toluene and methyl ethyl ketone (MEK). During “normal” loading conditions, the model waste stream contained toluene concentrations ranging from 28 to 30 ppmv and MEK concentrations ranging from 80 to 89 ppmv. On a regular basis, the influent toluene and MEK concentrations were temporarily increased to five times the normal influent concentration for duration of one hour to test performance during shock loading. Profile studies were conducted in both biofilters during the loading conditions tested. Biomass distribution within the biofilters and head loss was also measured.

Data presented herein establish that sequencing batch operation of biofilters treating air contaminated with mixtures of toluene and MEK is not only a feasible technology, it also offers advantages over conventional CFBs in several important measures of performance, namely, minimum instantaneous removal efficiency, overall contaminant removal efficiency, and head loss. During normal loading conditions both biofilters exhibited stable long-term performance with greater than 99% contaminant removal. During shock loading experiments, the SBB was able to remove more than 99% and 87% of the influent contaminants when subjected to loading
rates of 209 and 449.5 g m$^{-3}$ h$^{-1}$, respectively. In comparison, the CFB exhibited lower overall removal efficiency. The SBB exhibited lower head loss than the CFB, likely because of a more homogeneous spatial distribution of biomass within the system. Accumulation of undegraded contaminants during the loading period and the subsequent biodegradation during the recirculation period in the SBB was demonstrated, even after long-term operation.
CHAPTER 1 INTRODUCTION

Biofiltration is an air pollution control technology that holds great promise for effectively and economically removing biodegradable organic and inorganic compounds from gas-phase waste streams. Important applications include control of odors generated by wastewater treatment plants and control of volatile organic compound (VOC) emissions from industrial sources. Although of the ability of this technology to maintain high removal efficiency during steady-state loading conditions has been widely demonstrated, a critical limitation of the technology has been its inability to maintain high removal efficiency during transient periods of elevated contaminant loading which are typical of industrial operations.

The use of biofilter packing media containing substantial contaminant sorption capacity combined with implementation of sequencing batch operation is one potential strategy for enhancing treatment performance and reducing many of the disadvantages encountered with conventional biofilter operation. Recently reported research using methyl ethyl ketone (MEK) as a model contaminant demonstrated that this approach can be used to achieve higher overall removal efficiency and higher minimum instantaneous removal efficiency than can be achieved by a continuous flow system (Li and Moe, 2003; Moe and Li, 2003). Although this new operating strategy has been demonstrated to have advantages over conventional continuous flow biofilters for systems treating a single-component waste gas (i.e., gases containing MEK), performance in treating VOC mixtures has not yet been evaluated.

The research described in this thesis was conducted to accomplish the following four primary objectives:
• To compare contaminant removal efficiency in a continuous flow biofilter (CFB) with that of a biofilter subjected to sequencing batch biofilter (SBB) operation during steady loading conditions for a VOC mixture.

• To compare contaminant removal efficiency in a CFB with that from a SBB during transient periods of elevated loading (i.e., shock loading conditions) for a VOC mixture.

• To determine the spatial distribution of contaminant removal, CO\textsubscript{2} production, and biomass production within each of the systems.

• To determine the role of packing media, water, and biomass in temporarily sorbing contaminants in a SBB used to treat gases containing a two-component VOC mixture.

To achieve the objectives listed above, the research was divided into several tasks, each of which is briefly summarized below.

1.1. Selection and Enrichment of Initial Microbial Populations

Laboratory studies employed a sparged-gas reactor to enrich for toluene-degrading microorganisms. A second, identical reactor was used to enrich for MEK-degrading microorganisms. Oxygen uptake rate (OUR) and total suspended solids (TSS) were monitored over time until the cultures were enriched with microbes able to degrade toluene and MEK, respectively. The two enrichment cultures were then used as a seed culture in subsequent biofilter experiments.

1.2. Normal Loading Experiments

Following inoculation, one of the biofilters was operated as an SBB and the other was operated as a CFB (i.e., conventional biofilter). There were three distinct periods of operation (arbitrarily named Phases 1, 2, and 3). Phase 1 encompassed the initial period of operation, and Phases 2 and 3 involved progressively higher gas flow rates and contaminant loading rates.
During all three phases of testing, the influent contaminant concentration and mass of contaminants loaded per day were identical for the two biofilters; however, the biofilters differed with respect to the fraction of time during which contaminants were added and the overall operating strategy employed. Influent and effluent toluene and MEK concentrations were measured to assess the ability of both biofilters to remove MEK and toluene during “normal” steady loading conditions consisting of target influent toluene concentration of 28 to 30 ppm, and MEK concentration of 80 to 89 ppm.

1.3. Shock-loading Experiments

To assess biofilter response to uncontrolled variation in influent contaminant concentration (i.e., shock-loading), each biofilter was periodically subjected to a loading condition during which the influent toluene and MEK concentrations were increased to five times that of the normal loading for a period of one hour.

During all three phases of testing, the sequencing batch biofilter’s response to the transient loading was tested under conditions in which an operator does not modify the operating strategy during the transient period of elevated loading (i.e., a passive control strategy was employed). During the Phase 3 portion of the study, experiments were also conducted to test the sequencing batch biofilter’s response to shock loading conditions using an active control strategy. Such a strategy could be implemented in cases in which an operator has on-line monitoring and/or process knowledge of the transient loading condition so that the biofilter operating strategy could be modified to maximize contaminant removal. During all three phases of testing, the continuous flow biofilter’s response to the transient loading condition was evaluated using a passive control strategy because active control strategies are not possible in conventionally designed biofilters.
1.4. Profile Studies, Track Studies, Biomass Distribution Studies, and Head Loss

At various time intervals, studies were conducted to determine the spatial distribution of contaminant removal and CO$_2$ production in each of the biofilters. In order to do that, the concentration of VOCs and CO$_2$ were measured along the height of each column. Also, the spatial distribution of biomass within the two systems was estimated using a water displacement method to measure the volume of pore space in each section of the biofilter columns.

For the SBB, track studies were conducted during the REACT period to determine the VOC and CO$_2$ concentrations in the recirculating gas at different time intervals. Samples collected at the sampling port located at the bottom of the column were analyzed using gas chromatography.

Occasionally, a water manometer was used to measure pressure drop across the packing medium in each of the biofilters.

1.5. Sorption Experiments

At the conclusion of biofilter operation, the SBB was disassembled, the packing medium was removed, and batch isotherm experiments were conducted to quantify the sorption characteristics of MEK and toluene to the packing medium and its associated biomass. Sorption studies included separate tests to evaluate contaminant sorption to virgin packing medium which had not been used in biofilter experiments, packing medium which was covered with biomass after long-term use in the biofilter, packing medium that had been subjected to long-term use in the biofilter but had subsequently been treated to remove accumulated biomass, and biomass which had been removed from the packing medium (with no foam packing material). The sorption characteristics of the various media were modeled using Freundlich isotherms.
1.6. **Thesis Organization**

The organization of this thesis is as follows. Chapter 2 of this thesis contains a literature review summarizing previous research and providing the rational for the research described herein. Chapter 3 contains a description of the materials and methods used in the experiments. Chapter 4 contains results and discussion. Chapter 5 contains overall conclusions as well as recommendations for future research.
CHAPTER 2 LITERATURE REVIEW

2.1. Overview of Air Pollution Control

The removal of volatile organic compounds (VOCs) from contaminated air streams has been a major air pollution concern since passage of the 1990 Clean Air Act Amendments (CAAA) (Leson and Winer, 1991). In fact, many VOCs are subject to increasingly severe environmental constraints because of their potential impact on human health. These VOCs include olefins, paraffins, esters, ketones, and aromatics, which are all commonly found in emissions from manufacturing operations as well as industrial facilities such as chemical plants, refineries, and color, paint, and ink manufacturers and users (Geoghegan et al., 1997; Aizpuru et al., 2001). In particular, off-gases from painting operations represent a significant source of VOCs because of the frequency of use and vast amount of surface area painted each year (Geoghegan et al., 1997; Fortmann et al., 1998; Kim et al., 2000). Two particular solvents of interest normally encountered in paint spray booth off-gases are methyl ethyl ketone (MEK) and toluene (Geoghegan et al., 1997; Kazenski and Kinney, 2000; US EPA 2001, 2002a). These are two of the 188 compounds regulated as Hazardous Air Pollutants (HAPs) under the 1990 Clean Air Act Amendments (US EPA, 2002a, b).

To meet VOC emission standards, various techniques for off-gas treatment have been applied. Among these are physico-chemical methods including particle separation with gas cyclones, adsorption on activated carbon, scrubbing, thermal incineration, catalytic oxidation, (electro) filtration, dry-chemical treatment, and biological methods such as biofiltration, bioscrubbing and biotrickling filtration (van Groenestijn and Hesselink, 1993; Lee et al., 2001). While technologies such as thermal incineration, scrubbing and activated carbon adsorption are suitable for many applications, they are often cost intensive when the off-gas contains relatively
low VOC concentrations (Mohseni and Allen, 1999; Quinlan et al., 1999; Deshusses et al., 1999; Lee et al., 2001). In the last decade, biological abatement technologies have attracted an increasing popularity because of low costs, operational simplicity, and because they are intrinsically clean technologies (van Groenestijn and Hesselink, 1993; Devinny et al., 1999).

2.2. Biological Methods of Air Pollution Control

Air pollution control processes based on the ability of microorganisms to degrade a variety of inorganic and organic compounds currently constitute an emerging environmental control option. Biological off-gas treatment can occur through the absorption of volatile contaminants in an aqueous phase or biofilm followed by oxidation through the action of microorganisms (Brauer, 1986). Under the appropriate aerobic conditions, microorganisms are able to oxidize numerous compounds (substrates) into mineral end products and new cell material (Bailey and Ollis, 1986; Brauer, 1986; Aizpuru et al., 2001). This treatment technology is particularly effective for treating large volumes of moist airstreams with low concentrations of biodegradable pollutants (Mohseni and Allen, 1999).

The three process configurations most commonly used for biological air treatment are the biofilter, the biotrickling filter, and the bioscrubber (van Groenestijn and Hesselink, 1993). Each of these is further described below.

In a biofilter, the waste gas is forced through a layer of biologically active packing material containing a relatively high specific surface area. Several different packing materials may be used, including but not limited to peat, compost, soil, and polyurethane foam (Moe and Irvine, 2000a). All of these packing materials can be seeded with microorganisms capable of degrading particular contaminants, or, in the case of “natural” packing media such as compost, the appropriate microorganisms may be indigenous. Regardless of the packing media selected,
the air pollutants are transferred from the gas phase and into a biofilm where they are subsequently biodegraded to water, CO$_2$ and microbial biomass. Biofilters usually incorporate some form of water addition to control moisture content and add nutrients. In general, the gas stream is humidified before entering the biofilter reactor (Hwang and Tang, 1997; Swanson et al., 1997; Gostomski et al., 1997). Supplemental moisture may be provided by sprinkler irrigation or use of soaker hoses embedded in the packing medium (Devinny et al., 1999).

A biotrickling filter system (BTF) is very similar to a biofilter system; however, BTFs generally use different packing materials and operation strategies. A BTF system contains relatively inert packing material such as wood chips, ceramics, or plastics, and is operated to recirculate liquid flow over and through the packing on a continuous or discontinuous basis. Hence, a biofilm develops on the surface of the packings shortly after the start-up of the system. Microorganisms fixed to the packings and suspended in the liquid phase degrade contaminants transferred from the gas phase to the liquid phase as gas passes through the reactor (Brauer, 1986; Chou and Huang, 1997).

In a bioscrubber, contaminated gas is contacted with liquid; generally water, in a spraying tower with inert packing, resulting in contaminant absorption in an aqueous phase. Water containing the dissolved target compounds is subsequently treated in a separate reactor before it is either reused or discharged.

Compared to biofilters, bioscrubbers and biotrickling filters are generally more complex in construction and operation because of the additional components involved (Devinny and Arnold, 1997; Devinny et al., 1999). Chou and Cheng (1997) mentioned that over the past decade, biofiltration has been shown to be a more economical and effective technology for controlling odors and VOCs in chemical and process industries.
2.3. **Conventional Biofilter Design and Operation**

Conventional biofilters are continuous flow processes designed and operated to receive a relatively constant stream of contaminated air. Biofilter design usually assumes little or no appreciable variation in organic load (Irvine and Moe, 2001). These conventional systems, normally designed for minimal operator control, (often restricted to adjustment of the medium’s moisture content or nutrient supply) limit implementation of engineering decisions, which could improve performance during steady and unsteady-state loading conditions (Moe and Li, 2003).

2.4. **Common Problems in Conventional Biofilter Operation**

There are a number of common problems encountered in conventional biofilter systems. Clogging is one of the most common problems faced in full-scale implementation. Clogging normally occurs in the biofilter’s inlet due to biomass accumulation in the area of greatest contaminant loading. This can lead to severe bioreactor operating problems including high-pressure drops and low contaminant removal efficiencies. The rate at which clogging can occur depends on the nature of the packing material, the organic loading rate, the supply of nutrients, and other factors that influence the net yield of biomass (Song and Kinney, 2001; Moe and Irvine, 2000b).

Maintaining proper moisture and nutrient content in the packing material is also an issue (Gostomski *et al.*, 1997). The start-up is often problematic, leading to an excessive period of contaminant emission from the biofilter (Deshusses, 1997).

Conventional biofilter operation has been successfully applied to remove biodegradable VOCs from a wide variety of industrial processes and waste treatment operations; however, a critical limitation of this technology has been its inability to maintain high removal efficiency during transient periods of elevated contaminant loading which are typical from industrial
operations. Excessive contaminant emissions during transient loading conditions is particularly problematic in cases where air pollution control regulations require a specified removal efficiency (e.g., 95%) on a continuous basis. Contaminant emissions during short-term unsteady-state loading conditions have been reported for a number of biofilter applications treating a wide variety of different compounds (Chang and Yoon, 1995; Martin and Loehr, 1996; Mohseni et al., 1998; Deshusses et al., 1999; Irvine and Moe, 2001; Moe and Li, 2003).

2.5. Polyurethane Foam Support Materials

Selecting or engineering the proper biofilter medium is an important step toward developing a successful biofiltration operation. Desirable media properties include: surface properties conducive to microbial attachment and growth, large specific surface area, structural integrity, sufficient moisture retention, high porosity, and low bulk density (Swanson et al., 1997; Cardenas et al., 1999; Moe and Irvine 2000a).

Moe and Irvine (2000a) reported that polyurethane foam packing media can offer low head loss, high porosity, high surface area, and an ability to readily sorb water and nutrient solutions. This type of medium also permits use of novel nutrient addition and biosolids wasting strategies (Moe and Irvine, 2000b). Other studies also suggest that polyurethane foam can provide the necessary requirements for good overall biofilter performance (Norman, 2002; Qi et al., 2003). Furthermore, the capacity of polyurethane foam medium for sorption of VOCs can be controlled and increased by adding powdered activated carbon (PAC) during foam manufacture (Lupton and Zupancic, 1991; Moe and Irvine 2000a; Martinez, 2001; Cardenas et al., 1999).

2.6. Biomass Removal and Nutrient Addition

The issue of nutrient availability and nutrient addition is important in biofilter design and operation. When an inorganic support medium is used, nutrients are usually added with the
packing material before biofilter assembly or in a nutrient solution sprayed on or mixed with the packing material after construction (Swanson et al., 1997; Kinney et al., 1998; Devinny et al., 1999; Moe and Irvine 2000a). Because nutrients are often added in aqueous solution, simultaneous control of moisture and nutrient levels is difficult to achieve when using natural organic packing materials (e.g., compost, peat). Research by Moe and Irvine (2001b) demonstrated that nutrient limitations could adversely affect biofilter performance during transient periods of elevated load even when biofilter performance is seemingly unaffected during continuous loading. Research reported by Song et al. (2003) demonstrated that nutrient limitations could adversely affect removal of one or more compounds present in a complex mixture.

When excess biomass, a natural product of the biodegradation process, accumulates in the packing material’s pore spaces, channeling, short-circuiting, and excessive head loss occurs, and treatment efficiency decreases (Smith et al., 1998; Song and Kinney, 2001). Different biomass removal techniques have been proposed for controlling biomass accumulation in biofilters. For example, Sorial et al. (1995) tested two different biomass wasting techniques: (1) utilization of a hose to flush the excess of biomass from a channelized medium and (2) implementation of a backwashing strategy in a palletized medium by using full medium fluidization. Kim et al. (2002) increased the rotational speed of a rotating drum biofilter when needed to remove excessive biomass on the surface of the media and to prevent bed clogging. Also, the medium could be squeezed, if necessary, using two rollers installed on opposite sides of the medium. Moe and Irvine (2000b) reported an increase in biofilter performance when using a regular nutrient addition and biomass removal strategy. The biomass removal technique
made possible by use of polyurethane foam medium conveniently prevented the clogging and channeling problems associated with conventional biofilter operations.

2.7. Periodically Operated Biofilters

Most research on unsteady-state operating strategies in biofilters treating gas-phase contaminants has focused on continuous flow biofilters and the control of biosolids accumulation and clogging near the inlets. For example, Farmer et al. (1994) reported results for a system of three biofilters connected in series that was operated in a way such that the order of the biofilters was periodically changed (e.g., the last biofilter in the series was relocated to be the first in the series). Results demonstrated that alternating the order of the biofilters decreased the clogging as a result of endogenous respiration. Song and Kinney (2001) improved biomass distribution, stability and performance in a vapor-phase bioreactor treating toluene by switching, periodically, the contaminant inlet from the top to the bottom of a system (i.e., directional switching).

Periodic processes have long been used in wastewater treatment and soil remediation. Periodically operated bioreactors designed to treat hazardous and non-hazardous contaminants presents in wastewaters and soils are used to select and enrich for microbial consortia that readily handle appreciable variations in organic load (Irvine et al., 1997). Periodic processes allow for the selection, enrichment, and manipulation of the physiological state of the microbial population, which can minimize the uncertainty that often accompanies the design and operation of a biological system (Irvine et al., 1997; Moe and Irvine, 2001a).

The most widely used controlled, unsteady-state periodic process is the Sequencing Batch Reactor (SBR). Several researchers have successfully treated industrial wastewaters containing volatile and/or inhibitory components, including toluene and mixtures of phenolic compounds, using a variation of the SBR known as Granular Activated Carbon – Sequencing Batch Biofilm
Reactor (GAC-SBBR). In this system, granular activated carbon (GAC), placed inside the reactor, adsorbs a fraction of the influent contaminants during the FILL period. During the REACT period, microorganisms growing attached to the GAC or other support surfaces biologically regenerate the activated carbon to allow reuse in the process. For toxic and inhibitory constituents, the activated carbon can provide an important role as a buffer that reduces the aqueous-phase concentration of contaminants (Chozick and Irvine, 1991; Kolb and Wilderer, 1997; Ha et al., 2000; Buitron et al., 2001).

The operating modes used in SBRs can be applied to biological treatment of gas-phase contaminants (Moe and Irving, 2000c). Terminology proposed for this operating strategy is Sequencing Batch Biofilter (SBB) operation. A SBB system would normally include two or more reactors. Terminology established for each cycle of a periodically operated biofilter system is as follows (Irvine and Moe, 2001):

- **FEED**: period during which contaminated gas flows to one of the reactors or to a grouping of the reactors in a multiple biofilter system. Contaminant removal during FEED results from some combination of sorption and biological transformation. At the end of FEED, REACT begins as the inflow of contaminated gas is diverted to the next reactor or grouping of reactors in the system.

- **REACT**: period during which contaminants are biotransformed to acceptable products. Air may or may not be recirculated within the reactor or grouping of reactors. Addition and/or recirculation with uncontaminated air or pure oxygen may be necessary if oxygen is the desired electron acceptor.

- **IDLE**: period between FEED and REACT during which the reactor or grouping of reactors awaits the beginning of a new cycle. Oxygen may or may not be added
during IDLE. If added, uncontaminated air may be recirculated or passed continuously through the biofilter.

In practice, periodicity can be achieved using a variety of biofilter configuration and loading strategies for both normal and uncontrolled transient loading conditions. In applications where there is an intermittent discharge of contaminated gases (e.g., during an eight hour work day), it may be possible to use a single biofilter, while in cases where a continuous contaminated gas flow is generated, multiple units installed in parallel and operated in sequence will be necessary (Irvine and Moe, 2001).

Li and Moe (2003) employed a SBB packed with polyurethane foam containing powdered activated carbon (PAC) to treat air streams contaminated by low concentrations (106 to 530 ppm) of methyl ethyl ketone (MEK). The biofilter was operated with three distinct periods that comprised one complete cycle: FEED, REACT, and IDLE. During the FEED period, contaminated air entered the biofilter, and treated air exited. The mechanism for contaminant removal was expected to be a combination of biodegradation, bioaccumulation, and contaminant sorption to the PAC-containing medium. The sorption capacity of the PAC was “filled” during this portion of the cycle and microbes degraded a portion of the incoming organics. The SBB operation sequence is graphically depicted in Figure 2.1. The black filter bed shown in the FEED period represents a biofilter with contaminants entering the system and accumulating within the packing medium. The gray biofilter bed shown in the REACT period represents a biofilter with some stored substrate but in a quantity less than the peak amount accumulated during FEED. The white biofilter bed shown in the IDLE period represents a biofilter with no stored substrate. During transient loading periods, the systems’ sorption capacity can provide the important role of temporarily storing contaminants when their loading rate exceeds the biological reaction
capacity. In order to impose high growth rate conditions on the microbial population and at the same time produce a system comparable in size or smaller than a conventional continuous-flow biofilter system, biodegradable contaminants must be forced to accumulate in the biofilter without contaminant breakthrough and that there be an appreciable reduction in the empty bed residence time (EBRT). Li and Moe (2003) concluded that sequencing batch biofilter (SBB) operation is a feasible technology for treating air streams contaminated with low concentrations of MEK during both normal loading periods and transient periods of elevated contaminant loading.

![Figure 2.1: Cycle for one biofilter in a periodically operated multiple-reactor biofilter system (redrawn from Li and Moe, 2003).](image)

In multiple biofilter systems, the length of time for one biofilter to complete REACT and IDLE will be set equal to the total FEED time of all other biofilters in the system. For example, if a biofilter can be loaded for one hour before an unacceptably large contaminant breakthrough is reached during FEED, but two hours are needed for REACT and IDLE, then the system will require three biofilters (i.e., as the other two biofilters are in FEED [1 hours each, 2 hours total],...
the third biofilter would be in REACT and IDLE [2 hours]). This can also be expressed as shown in Equation 2.1 below (Moe and Li, 2003).

\[(n - 1) t_{feed} = t_{react} + t_{idle}\]  

(2.1)

where: \(n\) = number of biofilters in the system, and  
\(t\) = time devoted to a specific period of operation

The described system, which has a tremendous amount of operational flexibility, is depicted in Figure 2.2. As shown in the Figure, a three-biofilter system can be operated in parallel and sequence according to the solid arrows that connect the time periods I - III. The EBRT for this system is equal to that of one “properly” designed conventional biofilter. In this case, biofilter A is undergoing FEED in time period I, while the other biofilters are undergoing REACT. Biofilter A is undergoing REACT during time periods II and III. Figure 2.3 depicts a loading condition where gas flow is simultaneously directed to all of the biofilters. Such a loading strategy could be implemented by an operator during a transient or “shock load,” resulting in an EBRT that is three times longer than when the biofilters are loaded one at a time.

Figure 2.2: Schematic of three biofilters loaded periodically with FEED for one-third of the operating cycle during normal loading conditions.
Irvine and Moe (2001) conducted experiments using one continuous biofilter and two periodically operated biofilters to treat air contaminated with toluene. The two periodically operated biofilters received contaminated air during one third and one sixth, respectively, of its operating cycle. Results demonstrated that the removal efficiency of contaminants for both periodically operated biofilters during shock-loading conditions was superior to that of the continuously operated biofilter. Periodic operating strategies can provide operators with an effective alternative for controlling biofilters during transient conditions of high loading and enhancing contaminant removal (Moe and Irvine, 2000c).

Norman (2002) conducted experiments using continuous biofilters and periodically operated biofilters to treat air contaminated with MEK during transient conditions of high loading. The results also indicated superior performance for the periodically operated biofilters in comparison to the continuously operated biofilter, with removal efficiencies greater than 98%. There were several possible explanations for the better performance of the periodically operated biofilters during the transient conditions of high loading. First, the higher gas flow rates likely produced a more favorable spatial distribution of the microbial population. Visual inspection of the biofilters revealed that biomass (easily observed as a brown biofilm growing on the white packing medium) was more evenly distributed along the height of the periodically operated
biofilter columns. Second, the microbes selected and enriched for in the periodically operated systems may have been different. Third, the physiological state of the microbes present in the periodically operated systems may have been different.

In further studies, Moe and Li (2003) conducted experiments to compare performance of a continuous biofilter and a SBB to treat a model waste gas stream containing MEK. The packing medium for both biofilters consisted of activated carbon coated polyurethane foam cubes with much higher sorption capacity than previous SBB experiments. During normal loading conditions, both biofilters exhibited stable long-term performance with greater than 99 % contaminant removal. Once an appropriate operating strategy was selected, the SBB was able to remove more than 99 % of the influent MEK at a transient loading rate of 380 g m⁻³ h⁻¹ and 83 % of the influent MEK at a transient loading rate of 760 g m⁻³ h⁻¹. The operational flexibility of the SBB system facilitated selection of operational conditions that led to higher overall removal efficiency and higher minimum instantaneous removal efficiency than were achieved in the continuous biofilter. Moreover, it was demonstrated that application of an active control strategy (e.g., simultaneously loading more than one biofilter in a multiple-biofilter system), made possible by SBB operation, can result in more complete contaminant removal during a transient period of elevated contaminant loading than would have otherwise occurred.

Weber and Hartmans (1995) demonstrated that application of an activated-carbon filter before treatment of waste gases with fluctuating contaminant content can result in a better overall performance of a biofilter.

2.8. Degradation of Mixtures of VOCs

The gaseous effluents emitted into the atmosphere by industries are often a complex mixture of different VOCs. Although many constituents have been successfully treated using
biological methods when they are present as individual compounds or simple mixtures, complex mixtures can be problematic when biological treatment systems are applied (Ottengraff, 1987).

Interactions between multiple pollutants undergoing treatment have demonstrated a tremendous influence on the removal process (Deshusses, 1997). Usually, one or more compounds is not degraded until after other compounds have been degraded to very low concentrations, often resulting in spatial separation of zones for biodegradation of different compounds as a function of height in a biofilter bed (Aizpuru et al., 2001). For example, when Aizpuru et al. (2001) treated a mixture of VOCs containing oxygenated, aromatic and halogenated compounds in a laboratory-scale biofilter, the oxygenated compounds were eliminated in the first 50 cm of the column. The aromatic and halogenated compounds were, respectively, eliminated on the last 80 and 70 cm of the column.

Ergas and McGrath (1997) observed that in a biofilter treating a mixture of toluene and dichloromethane, toluene elimination occurred in the first few centimeters of the column, and dichloromethane elimination occurred in the second half of the column. Therefore, the authors showed, at steady state, stratification in terms of biodegradation and hypothesized that two different microbial communities colonized the reactor.

For the treatment of a mixture of ethyl acetate and toluene, Deshusses et al. (1999) also observed stratification in terms of degradation. Ethyl acetate was degraded in the first portion of the column, and toluene elimination occurred on the second portion of the column.

Liu et al. (2002) tested two identical biofilters to treat a mixture of ethyl acetate and toluene. One of the biofilters was acclimated with ethyl acetate and the other with toluene. It was observed that the presence of ethyl acetate in the system significantly reduced the removal capacity of toluene. However, the removal efficiency of ethyl acetate was not affected by the
presence of toluene in air streams. The biofilter acclimated with ethyl acetate had a higher elimination capacity for ethyl acetate than the biofilter acclimated with toluene.

Mohseni and Allen (1999) reported that in treating a mixture of \( \alpha \)-pinene and methanol, \( \alpha \)-pinene removal was inhibited by presence of methanol. Deshusses and Hamer (1993) reported and inhibitory effect on the degradation rate of MEK when a biofilter received a mixture of MEK and methyl isobutyl ketone (MIBK).

Kazenski and Kinney (2000) studied the interactions of common VOCs found in paint spray booth off-gases. In their study they used methyl \( \pi \)-propyl ketone (a compound which is molecularly similar to MEK). Results showed a common order of degradation: \( \pi \)-butyl acetate, ethyl 3-ethoxypropionate, methyl \( \pi \)-propyl ketone, toluene, and p-xylene. Biofiltration of VOC mixtures introduces new complexities as the pollutants can be involved in both kinetic interactions and physical interactions regarding their adsorption on the biofilter packing material (Baltzis et al., 1997).

Although problems associated with inhibition or other complex kinetics can be overcome by designing biofilters with sufficiently deep beds or sufficiently long residence times to allow for complete degradation of different compounds at different locations in the bed, such solutions may not be satisfactory when dealing with the unsteady-state conditions frequently encountered in industrial operations. As presented in Section 2.7, Li and Moe (2003) concluded that sequencing batch biofilter (SBB) operation is a feasible technology for treating air streams contaminated with low concentrations of MEK during both normal loading periods and transient periods of elevated contaminant loading. Therefore, the use of periodically operated biofilter systems could be also the alternative to overcome limitations related to the interactions between multiple pollutants undergoing treatment, even during transient periods of elevated contaminant
loading. This postulation is based in the fact that in a SBB the mechanism for contaminant removal is expected to be a combination of biodegradation, bioaccumulation by the microorganisms selected and enriched in the system as a result of a change in their physiological state, and contaminant sorption to the PAC-containing medium. During transient loading periods, the systems’ sorption capacity can provide the important role of temporarily storing contaminants when their loading rate exceeds the biological reaction capacity. Moreover, the recirculating air through the filter medium during REACT will allow the electron donors and electron acceptors to be more uniformly distributed throughout the filter medium and thus allow for more spatially homogenous growth of microorganisms within the biofilter resulting in more complete degradation of the different compounds.

2.9. Toluene and Methyl Ethyl Ketone Biodegradation

Bulk organic chemicals are produced either as process feedstock or as utility products, particularly solvents. The former group of products may become pollutants during their manufacture or their utilization, but the fraction of the total production released in waste streams is relatively small. However, in the case of the latter products, production essentially matches losses in waste streams (Geoghegan et al., 1997). Two particular compounds belonging to the latter category are toluene and Methyl Ethyl Ketone (MEK). Some physical/chemical properties of these compounds are presented in Table 2.1. In 2000, the total on-site and off-site releases of MEK were estimated in 35,547,685 pounds. In the same year, the total on-site and off-site releases of toluene were estimated in 83,590,224 pounds (U.S. EPA, 2002b). Both toluene and MEK are regulated as Hazardous Air Pollutants (HAPs) under the 1990 Clear Air Act Amendments (US EPA, 2002b). Long-existing air emission control technologies such as incineration, absorption and adsorption have become a major preoccupation of environmental
organizations and those industries dealing with such emissions. In contrast, biological processes are found to be more economical and environmentally viable and particularly biofilters are suitable for the treatment of emissions of VOCs and HAPs (Aizpuru et al., 2001; Kazenski and Kinney, 2000).

Table 2.1: Physical/chemical properties of toluene and MEK.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Formula</th>
<th>CAS #</th>
<th>Molecular Weight (g/mole)</th>
<th>Density at 20 °C (g/mL)</th>
<th>Solubility in water (mg/L)</th>
<th>Henry’s Law Constant (atm*m^3/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>C₇H₈</td>
<td>108-88-3</td>
<td>92.14</td>
<td>0.870</td>
<td>515</td>
<td>6.74E-03</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone (2-butanone)</td>
<td>C₄H₈O</td>
<td>78-93-3</td>
<td>72.11</td>
<td>0.805</td>
<td>22300</td>
<td>5.69E-05</td>
</tr>
</tbody>
</table>
CHAPTER 3 MATERIALS AND METHODS
3.1. Experimental Apparatus

Laboratory studies employed two glass biofilter columns, one operated as a sequencing batch biofilter (SBB) and the other operated as a continuous flow biofilter (CFB). Schematic diagrams of each biofilter and its associated equipment are depicted in Figures 3.1 and 3.2. Each of the biofilters consisted of a bottom, a top, and six 25 cm sections. The columns had an inner diameter of 9.9 cm. The two 25-cm sections in the extremes of each column (i.e., those nearest the inlet and outlet) were filled with 18.5 cm of packing medium to provide space for sampling operations, and the other four 25-cm sections were each filled with 24 cm of packing medium. This provided a total packed bed depth of 1.33 meters and a total packed bed volume of 10.2 L in each biofilter. A perforated stainless steel plate supported the packing medium located in each section. The columns were assembled by placing Viton™ O-rings between the sections and then clamping the assembly together using horseshoe type clamps. Gas sampling ports, located at heights of 3 and 13 cm in each column section, were filled with Thermogreen™ LB-1 half-hole type septa (Supelco, Bellefonte, PA). All surfaces that contact the contaminated air were made of glass, stainless-steel, Teflon™, or Viton™.

For each biofilter, compressed air was split into two streams with 95% of the air humidified by passing through an aeration stone submerged in deionized water in a 20 L glass carboy heated by electrical heating tape. The remaining 5% of air flow was used to volatilize the test contaminants. One syringe pump (KD Scientific model 1000, Boston, MA) delivered toluene (ACS grade, Fisher Scientific, Fair Lawn, NJ) from a glass gas-tight syringe (Hamilton Co., Reno, NV) through a needle into a glass injection port and into the air stream.
Figure 3.1: Schematic diagram of laboratory-scale Sequencing Batch Biofilter (SBB).

Figure 3.2: Schematic diagram of laboratory-scale Continuous Flow Biofilter (CFB).
A second, identical, syringe pump was used to introduce MEK (ACS grade, Sigma Chemical Co., St. Louis, MO) into the air stream. Glass marbles were placed in the bottom of each column to evenly distribute air flow. Flow meters (Cole-Parmer Instrument Co., Vernon Hills, IL) measured and regulated air flow rates.

In the SBB, a diaphragm pump with stainless steel heads and Teflon diaphragm (Air Dimensions Inc., FL) was used to recirculate air through the biofilter during the REACT periods. Solenoid valves with stainless steel bodies and flow tubes (Automatic Switch Company, New Jersey) were used to turn air flows on and off. A microprocessor controller (Model XT, Chron-Trol Corp., San Diego, CA) was used to control operation of the syringe pumps, diaphragm pump, and solenoid valves. During FEED periods, only the syringe pump and air flow valves 1, 2, and 5 (see Figure 3.1) were switched on. During REACT/IDLE periods, only the diaphragm pump and valves 3 and 4 were switched on to recirculate air in the closed system. Flexible Teflon tubing (Cole-Parmer Instrument Co., Vernon Hills, IL) was used to connect various components. A 500 mL gas-washing bottle (Fisher Scientific, Fair Lawn, NJ) connected to the bottom of the biofilter was used to prevent water from entering the gas recirculation system. The total volume of air recirculated in the SBB prior to inoculation with the microorganisms was 13.0 L. This volume of air included the space occupied in the glass column filled with the packing medium, the gas-washing bottle and the recirculation line.

The second biofilter, which was operated as a conventional CFB (see Figure 3.2), was identical to the SBB except that the valves and other equipment associated with gas recirculation were omitted.
3.2. Packing Media

Packing material used in the SBB consisted of polyurethane foam cubes coated with powered activated carbon (type M-2CC, Honeywell-PAI, Lakewood, CO). The medium, supplied by the vendor in the form of cubes approximately 5.0 cm per side, was cut into cubes approximately 1.25 cm per side prior to use. Packing material used in the CFB consisted of polyurethane cubes (Honeywell-PAI, Lakewood, CO) identical to those used in the SBB except that the cubes did not contain an activated carbon coating.

3.3. Culture of Enrichment Cultures

Laboratory studies employed a 4.0 L glass kettle reactor (Pyrex, Acton, MA) with a working liquid volume of 3.0 L as depicted in Figure 3.3 to enrich for toluene-degrading microorganisms in a manner similar to that employed by Lee et al. (2002). Initially, the sparged-gas reactor was filled with 100 mL of activated sludge from an oil refinery wastewater treatment facility (Exxon-Mobil, Baton Rouge, LA) and 2.9 L of nutrient solution containing the following constituents added to tap water (mg/L): NaNO$_3$ (29,300), KH$_2$PO$_4$ (2,380), Na$_2$HPO$_4$ (1,000), MgSO$_4$ (1,290), CaCl$_2$.2H$_2$O (630), FeSO$_4$.7H$_2$O (480), ZnSO$_4$.H$_2$O (2.0), EDTA (1.0), MnSO$_4$.H$_2$O (0.4), CuSO$_4$.5H$_2$O (0.04), Na$_2$B$_4$O$_7$.10H$_2$O (0.04), (NH$_4$)$_6$Mo$_7$O$_24$.4H$_2$O (0.04), and CoCl$_2$.6H$_2$O (0.033).

Compressed air from a laboratory air tap flowed through an activated carbon filter (Calgon) and was regulated and measured with a pressure regulator and a flow meter (Manostat, New York, NY) before to pass through a glass tube equipped with a septum-filled injection port. A KD Scientific model 1000 syringe pump (Boston, MA) delivered toluene (HPLC grade, Aldrich Chemical Co., Milwaukee, WI) from a glass gas-tight syringe (Hamilton Co., Reno, NV) through a needle that pierced the septum into the injection port and into the air stream.
Figure 3.3: Schematic diagram of sparged gas reactor used to culture inoculum.

The toluene-contaminated air then was passed through an aeration stone submerged in the glass kettle reactor. A Teflon-coated magnetic stir bar was used to provide mixing. The reactor was operated with an influent toluene concentration of approximately 106 ppm, and a gas flow rate of 2.5 L/min for a period of 32 days prior to inoculation of the biofilters. The hydraulic and solids residence times were maintained at 6 days. At the time of inoculation, the TSS concentration was 1900 mg/L.

A second sparged-gas reactor, identical to that described above, was used to enrich for MEK-degrading microorganisms. The reactor was filled with 3000 mL of the nutrient solution described above inoculated with liquid drained from an on-going biofilter experiment in which MEK was supplied as the sole contaminant. The sparged-gas reactor was operated for a period of 53 days with an influent MEK concentration of approximately 106 ppm, a gas flow rate of 2.5 L/min, and solids and hydraulic residence times of 6 days. At the time of inoculation, the TSS concentration was 1866 mg/L.
3.4. **Biofilter Inoculation and Start-up**

For inoculation of each biofilter, 1.5 L of MLSS from each of the two sparged-gas reactors was mixed with 3.0 L of freshly prepared nutrient medium (6.0 L total per biofilter). The packing medium for each biofilter section was submerged separately in 1.0 L of the resulting culture. The medium was then placed in the biofilter column and allowed to drain by gravity. No special attempt was made to retain biomass on the foam packing media. Time was measured in days from the time of inoculation.

3.5. **Biofilter Operation**

Following inoculation, one of the biofilters was operated as an SBB and the other was operated as a CFB (i.e., conventional biofilter). There were three distinct periods of operation (arbitrarily named Phases 1, 2, and 3) as summarized in Table 3.1. During all three phases of testing, the influent contaminant concentration and mass of contaminants loaded per day were identical for the two biofilters. As further described below, the two biofilters differed, however, in terms of the fraction of time in which contaminants were loaded to the systems and the overall operating strategy as described in the following section.

3.5.1. **Normal Loading Experiments**

As summarized in Table 3.1, during the initial stage of biofilter operation (Phase 1, days 0 to 137), the operating strategy in the SBB consisted of 1.0 hour FEED and 2.0 hours REACT. There was no IDLE period. Thus, the cycle length was 3.0 hours (eight cycles per day). The EBRT was set at 30 seconds and the target influent concentrations for toluene and MEK were 28 and 80 ppm, respectively, during “normal” (steady loading) operation. This corresponds to a loading rate of approximately 12.7 g·m⁻³·h⁻¹ and 28.2 g·m⁻³·h⁻¹ for toluene and MEK, respectively, and simulates the loading condition experienced by one biofilter in a set of three
biofilters constructed in parallel and operated in sequence to treat a continuous gas flow. Because the SBB received contaminated air during only one third of the cycle length, the average toluene and MEK loading rates considering the entire cycle length were 4.2 g·m⁻³·h⁻¹ and 9.4 g·m⁻³·h⁻¹, respectively. Influent and effluent MEK and toluene concentrations were measured on a regular basis to assess the ability of the biofilters to remove contaminants.

During Phase 1, the EBRT was set at 90 seconds in the CFB. The target influent concentrations for toluene and MEK were 28 and 80 ppm, respectively, during “normal” operation. This corresponds to a loading rate of approximately 4.2 g·m⁻³·h⁻¹ and 9.4 g·m⁻³·h⁻¹ for toluene and MEK, respectively, and simulates the loading condition experienced by a conventionally operated (continuous-flow) biofilter identical in size to the three-reactor system simulated by the SBB.

**Table 3.1: Summary of biofilter operating conditions during “normal” loading.**

<table>
<thead>
<tr>
<th>Continuous Flow Biofilter (CFB)</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Days of operation</td>
<td>0-137</td>
<td>138-172</td>
<td>173-295</td>
</tr>
<tr>
<td>EBRT (seconds)</td>
<td>90</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>Influent MEK concentration (ppm)</td>
<td>80</td>
<td>80</td>
<td>89</td>
</tr>
<tr>
<td>MEK loading rate (g·m⁻³·h⁻¹)</td>
<td>9.4</td>
<td>14.1</td>
<td>31.4</td>
</tr>
<tr>
<td>Influent Toluene concentration (ppm)</td>
<td>28</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Toluene loading rate (g·m⁻³·h⁻¹)</td>
<td>4.2</td>
<td>6.8</td>
<td>13.6</td>
</tr>
<tr>
<td>Total VOC loading rate (g·m⁻³·h⁻¹)</td>
<td>13.6</td>
<td>20.9</td>
<td>45</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sequencing Batch Biofilter (SBB)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Days of operation</td>
<td>0-137</td>
<td>138-172</td>
<td>173-295</td>
</tr>
<tr>
<td>EBRT (seconds)</td>
<td>30</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>Influent MEK concentration (ppm)</td>
<td>80</td>
<td>80</td>
<td>89</td>
</tr>
<tr>
<td>MEK loading rate during FEED (g·m⁻³·h⁻¹)</td>
<td>28.2</td>
<td>28.2</td>
<td>62.7</td>
</tr>
<tr>
<td>Influent Toluene concentration (ppm)</td>
<td>28</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Toluene loading rate during FEED (g·m⁻³·h⁻¹)</td>
<td>12.7</td>
<td>13.6</td>
<td>27.2</td>
</tr>
<tr>
<td>Total VOC loading rate during FEED (g·m⁻³·h⁻¹)</td>
<td>40.9</td>
<td>41.8</td>
<td>89.9</td>
</tr>
<tr>
<td>Length of FEED Period (hr)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Length of REACT Period (hr)</td>
<td>2.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Number of cycles per day</td>
<td>8</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>
During Phase 2 (days 138 to 172), the FEED period in the SBB remained one hour and the REACT period was also one hour. The EBRT remained 30 seconds and the influent MEK concentration remained 80 ppm, but the influent toluene concentration was adjusted slightly to 30 ppm. This corresponds to a loading rate during the FEED period of approximately 13.6 g·m⁻³·h⁻¹ and 28.2 g·m⁻³·h⁻¹ for toluene and MEK, respectively (total VOC loading rate of 41.8 g·m⁻³·h⁻¹), and simulates the loading condition experienced by one biofilter in a set of two biofilters constructed in parallel and operated in sequence to treat a continuous gas flow. Because the SBB received contaminated air during only one half of the cycle length, the average toluene and MEK loading rates considering the entire cycle length were 6.8 g·m⁻³·h⁻¹ and 14.1 g·m⁻³·h⁻¹, respectively (total VOC loading rate of 20.9 g·m⁻³·h⁻¹). During Phase 2, the CFB had an EBRT of 60 seconds, and target influent concentrations of 30 ppm and 80 ppm, for toluene and MEK, respectively. This corresponds to a loading rate of approximately 6.8 g·m⁻³·h⁻¹ and 14.1 g·m⁻³·h⁻¹ for toluene and MEK, respectively.

During Phase 3 of the study (days 173 to 295), the MEK and toluene loading rates were adjusted to be twice that of Phase 2. To accomplish this, the EBRT was adjusted to 15 seconds and 30 seconds for the SBB and CFB, respectively. Both, the FEED and REACT periods in the SBB remained one hour each. The influent MEK concentration was adjusted to 89 ppm, but the influent toluene concentration remained 30 ppm. This corresponds to a loading rate of approximately 27.2 g·m⁻³·h⁻¹ and 62.7 g·m⁻³·h⁻¹ for toluene and MEK, respectively, during the FEED period (total VOC loading rate of 89.9 g·m⁻³·h⁻¹). The average toluene and MEK loading rates averaged over the entire cycle length were 13.6 g·m⁻³·h⁻¹ and 31.4 g·m⁻³·h⁻¹, respectively (total of 45.0 g·m⁻³·h⁻¹). During Phase 3, the CFB had influent concentrations of 30 ppm, and 89 ppm, for toluene and MEK, respectively. This corresponds to a loading rate of approximately
13.6 g·m⁻³·h⁻¹ and 31.4 g·m⁻³·h⁻¹ for toluene and MEK, respectively (total VOC loading rate of 45.0 g·m⁻³·h⁻¹). Effluent toluene and MEK concentrations were measured to determine contaminant removal rate in each biofilter. Carbon dioxide concentrations were also monitored to evaluate contaminant degradation rates.

3.5.2. Shock-loading Experiments

To assess biofilter response to uncontrolled variation in influent contaminant concentration (i.e., shock-loading), each biofilter was periodically subjected to a loading condition during which the influent toluene and MEK concentrations were both increased to five times that of the normal loading for a period of one hour. The loading conditions during these experiments are summarized in Table 3.2 below. During all three phases of operation, the sequencing batch biofilter’s response was tested under conditions in which an operator does not modify the operating strategy during the transient period of elevated loading (e.g., passive control). Finally, during Phase 3, experiments were conducted to test the sequencing batch biofilter’s response under conditions in which an operator has on-line monitoring and/or process knowledge of the transient loading condition so that the biofilter operating strategy could be modified to maximize contaminant removal (e.g., active control). The shock-loading conditions were conducted at least three times during each of the phases of operation. A minimum of three cycles of “normal” loading occurred between each shock-loading experiment. Effluent toluene and MEK concentrations were monitored to evaluate contaminant removal. Carbon dioxide concentrations were also monitored.

Occasionally, to quantify endogenous respiration, each biofilter was periodically subjected to a no-load condition (0 ppm, toluene and MEK influent) by removing the syringes for a period of 6 hours.
Table 3.2: Summary of biofilter operating conditions during “shock loading.”

<table>
<thead>
<tr>
<th>Continuous Flow Biofilter (CFB)</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>EBRT (seconds)</td>
<td>90</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>MEK concentration (ppm&lt;sub&gt;v&lt;/sub&gt;)</td>
<td>400</td>
<td>400</td>
<td>445</td>
</tr>
<tr>
<td>MEK loading rate (g·m&lt;sup&gt;-3&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>47</td>
<td>71</td>
<td>157</td>
</tr>
<tr>
<td>Toluene concentration (ppm&lt;sub&gt;v&lt;/sub&gt;)</td>
<td>140</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Toluene loading rate (g·m&lt;sup&gt;-3&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>21</td>
<td>34</td>
<td>68</td>
</tr>
<tr>
<td>Total VOC loading rate (g·m&lt;sup&gt;-3&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>68</td>
<td>105</td>
<td>225</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sequencing Batch Biofilter (SBB)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>EBRT (seconds)</td>
<td>30</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>MEK concentration (ppm&lt;sub&gt;v&lt;/sub&gt;)</td>
<td>400</td>
<td>400</td>
<td>445</td>
</tr>
<tr>
<td>MEK loading rate during FEED (g·m&lt;sup&gt;-3&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>141</td>
<td>141</td>
<td>314</td>
</tr>
<tr>
<td>Toluene concentration (ppm&lt;sub&gt;v&lt;/sub&gt;)</td>
<td>140</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Toluene loading rate during FEED (g·m&lt;sup&gt;-3&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>64</td>
<td>68</td>
<td>136</td>
</tr>
<tr>
<td>Total VOC loading rate during FEED (g·m&lt;sup&gt;-3&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>205</td>
<td>209</td>
<td>450</td>
</tr>
</tbody>
</table>

3.5.3. Nutrient Addition and Biomass Wasting

To supply nutrients, on days 15 and 30, each of the columns was filled with 10.0 L of nutrient solution identical in composition to that used to grow the initial inoculum. Then, the columns were drained by gravity and restored to normal operation. From day 30 to the end of the experiment, the nutrient addition procedure was repeated at approximately one-week intervals. Although nutrient addition to full-scale biofilters containing inert packing medium is normally accomplished by spraying nutrient solutions over the medium and allowing it to trickle through the packed bed, a fill-and-drain method similar that described here has proven convenient for adding nutrients in laboratory-scale systems (Moe and Li, 2003). On days 164, 233, and 284 of operation, to provide biomass wasting, both biofilters columns were disassembled and the mass of foam covered with biomass located in each section of each column was removed and submerged in a separate container along with 1.5 L of freshly-prepared nutrient solution identical to that described previously. The packing medium was manually compressed several times to
physically shear off biomass. Then, the packing material was drained and replaced in its original biofilter section. Then, the biofilters were reassembled and restored to normal operation.

3.5.4. Profile Studies, Track Studies, Biomass Distribution Studies, and Head Loss Measurements

To determine the spatial distribution of contaminant removal and CO$_2$ production, concentrations of VOCs and CO$_2$ were measured along the height of each biofilter by taking gas-phase samples from the sampling ports available in each of the biofilters. Profile studies were conducted during “normal” loading conditions, shock-loading conditions and endogenous loading conditions in each of the biofilters. For the CFB, concentration profiles for the shock loading condition were measured in the last 20 min of the shock-loading event. For the SBB, concentration profiles for the normal loading, shock loading, and endogenous loading conditions were also measured in the last 20 min of the FEED period. In these studies, gas samples were analyzed using a California Analytical Instruments model 1312 photoacoustic multigas monitor (as further described in Section 3.7.1.). Because concentrations could not be measured simultaneously at all sampling ports using the equipment available, VOC and CO$_2$ concentrations along the heights of the biofilters were measured during the course of several cycles.

Track studies were conducted during the REACT period in the SBB to determine the VOCs and CO$_2$ concentrations in the recirculating gas at different time intervals. Gas-phase samples were collected at the sampling port located at the bottom of the column and were analyzed using gas chromatography to determine the concentrations of MEK, toluene, and CO$_2$. Track studies were conducted during normal loading conditions, shock-loading conditions and endogenous loading conditions.
Occasionally, oxygen consumption and CO$_2$ production during the REACT period in the SBB was measured at the start of the FEED period following the REACT period of interest. For these measurements, samples were continuously withdrawn and analyzed during the first 5 minutes of the FEED period to determine the oxygen and CO$_2$ concentrations in the air leaving the SBB using an Oxygen and Carbon Dioxide Meter (Servomex, UK). These studies were conducted during both normal loading conditions and shock-loading conditions.

During part of Phase 2 and during Phase 3 of operation, the spatial distribution of biomass within each of the biofilters was estimated using a water displacement procedure. In this procedure, each of the biofilter columns was filled from bottom to the top (by means of a peristaltic pump) with freshly prepared nutrient solution. The volume of nutrient solution required to fill the void space of each section was recorded. Using the total volume of each empty section, the measured void volume of each section, and the volume of packing material originally placed in each section, the volume of wet biomass and water was calculated by difference as shown in Equation 3.1 below.

\[
V_{wb} = V_s - V_f - V_v
\]  

(3.1)

where:

- \(V_{wb}\) = volume of wet biomass and water,
- \(V_s\) = total volume of each empty section,
- \(V_f\) = volume of packing material originally placed in each section, and
- \(V_v\) = measured void volume of each section

Prior to most water displacement tests and also after biomass wasting, to determine spatial distribution of biomass within each biofilter system, a water manometer was used to
measure pressure drop across the packing medium. During Phase 2 of operation, the pressure drop was measured at air flow rates of 10.2 and 20.4 L/min for the CFB and the SBB, respectively; during Phase 3, the air flow rates were 20.4 and 40.8 L/min for the CFB and the SBB, respectively. These gas flow rates are the same as those used for normal loading studies. Head loss was recorded to the nearest 1 mm.

3.5.5. Analysis of Biofilter Performance

The contaminant loading rate to each of the columns was calculated in two different ways based on the parameter measurements available. In most cases, the contaminant loading rate was calculated using Equation 3.2. The total contaminant loading rate, in terms of mass of contaminant supplied per unit volume of packed bed per unit time, was calculated by adding the loading rate for toluene with the loading rate for MEK.

\[
\text{Mass loading rate} = \frac{Q_{\text{syringe}}}{V_{\text{bed}}} \times \rho_{\text{VOC}}
\]  (3.2)

Where:

\[Q_{\text{syringe}}\] = VOC volumetric flow rate entering the system via the syringe pump (mL/hr)

\[V_{\text{bed}}\] = Biofilter packed bed volume (m³)

\[\rho_{\text{VOC}}\] = Density VOC as a liquid solvent (g/mL)

Direct measurement of the influent MEK and toluene concentrations using an on-line instrument during various time periods confirmed that the measured concentrations were approximately the same as the target values (within 5.0 %, average of 10 measurements) of the calculated concentrations. Thus, the loading rate calculated using Equation 3.3, was approximately the same as that calculated using Equation 3.2.
\[ Mass\ loading\ rate = \frac{Q_{\text{gas}} \times C_{\text{in}}}{V_{\text{bed}}} \]  

(3.3)

Where:

\[ Q_{\text{gas}} = \text{Volumetric flow rate of gas entering the system (m}^3/\text{hr)} \]

\[ C_{\text{in}} = \text{Measured VOC concentration in the influent gas stream (g/m}^3) \]

\[ V_{\text{bed}} = \text{Biofilter packed bed volume (m}^3) \]

On an instantaneous basis, the removal efficiency for each of the test compounds (MEK and toluene) was calculated using Equation 3.4. The removal efficiency was calculated separately for MEK and toluene, and the total removal efficiency (on a mass basis) was also calculated based on the total inlet and outlet concentration of both constituents.

\[ Instantaneous\ Removal\ Efficiency = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% \]  

(3.4)

Where:

\[ C_{\text{in}} = \text{Calculated or measured VOC inlet concentration at time, } t \text{ (ppm}, \text{v}) \], and

\[ C_{\text{out}} = \text{Measured VOC outlet concentration at time } t \text{ (ppm}, \text{v}) \]

As further discussed in Chapter 4, because the biofilters were clearly at unsteady state during the transient loading conditions, the instantaneous removal efficiency calculated using Equation 3.4 above yielded negative values for cases in which the effluent contaminant concentration temporarily exceeded the inlet concentration. To provide a more general basis of comparison, the removal efficiency for shock loading conditions was also calculated using Equation 3.5 as shown below. As further described in Chapter 4, the removal efficiency associated with each shock loading event was calculated using the mass of each contaminant...
entering the system during the shock loading period and the total mass of contaminants exiting
the system during and after the shock loading event.

\[
\text{Overall Removal Efficiency} = \frac{M_{in} - M_{out}}{M_{in}} \times 100 \%
\]  

(3.5)

Where:

\(M_{in}\) = Mass of VOC entering the system during the period under consideration (mg)

\(M_{out}\) = Mass of VOC emitted from the system during the period under consideration (mg)

3.6. Batch Sorption Experiments

At the conclusion of biofilter performance experiments (i.e., at the end of the 295 days of
operation), experiments were conducted to assess the sorption characteristics of the packing
medium in the SBB. Prior to the sorption studies, the SBB was operated for 48 hours without
any VOC loading. During this 48-hour period, contaminant flow was terminated (by removing
syringes from the syringe pumps); however, uncontaminated air continued to flow through the
biofilter column at the same rate as it did during the preceding time period (i.e., with an EBRT of
15 seconds). Then, the column was disassembled and the biofilm-covered packing medium from
the entire column was removed and manually mixed together in a large plastic container to
homogenize packing medium originally present at various locations in the column. The material
was then divided in two equal parts with one portion used to quantify sorption characteristics for
MEK and the other to quantify sorption characteristics for toluene. Samples not analyzed
immediately after collection were preserved by refrigeration at 4 °C until further analysis.

Batch isotherm experiments were then conducted to quantify the sorption characteristics
of MEK and toluene to the packing medium and its associated biomass. The sorption tests
included separate tests to evaluate contaminant sorption to virgin packing medium which had not
been used in biofilter experiments, packing medium which was covered with biomass after long-
term use in a biofilter, packing medium that had been subjected to long-term use in a biofilter but which was subsequently treated to remove accumulated biomass, and biomass removed from the packing medium (with no foam packing material). In order to remove the accumulated biomass from the packing medium that had been subjected to long-term use in a biofilter, the material was submerged in a beaker with deionized water, then it was repeatedly compressed until most of the attached biomass was removed (assessed by visual inspection). Then, the material was continuously squeezed and rinsed with deionized water until there was not any visually observable amount of biomass remaining attached. The biomass removed from the packing medium and accumulated in the beaker during the washing process was recovered by filtration and collected to be used in the sorption experiments. Prior to the start of sorption experiments, the moisture content associated with the packing medium covered with biomass, packing medium that was removed from the biofilter and then treated to remove accumulated biomass, and biomass removed from the packing medium were each determined by drying triplicate samples at 105°C.

Separate experiments were conducted for each of the different materials tested (foam, foam plus biomass, etc.). Different masses of the various materials tested (i.e., foam combined with biomass, virgin foam, foam after removal of biomass, or biomass) were placed in separate 260 mL amber glass bottles (I-Chem, New Castle, DE), which were then filled with a solution containing only MEK or only toluene, amended with 1000 mg/L of NaN₃. The bottles were covered with Teflon caps and placed in a rotary tumbler for 48 hours. The mass of dry material placed in each bottle ranged from 0 to 6 g. The bottles were filled with MEK solutions that ranged from 170 to 4250 mg/L or with toluene solutions that ranged from 90 to 360 mg/L. In order to avoid any MEK and toluene volatilization during the course of the experiments, care
was taken to ensure that no head-space was left in the isotherm bottles. One blank of each of the solution concentrations was included in each batch of samples to determine the initial concentration in the isotherm bottles and to test if there were significant losses of test contaminants, in the absence of sorbents, during the course of the experiment.

After the 48–hour equilibration period, aqueous samples were removed, filtered using a 0.45 \( \mu \)m PTFE syringe filter (Millex, Bedford, MA), and analyzed using gas chromatography to determine the equilibrium concentrations of MEK or toluene. The dry mass of each of the materials, calculated based on the percentage of moisture determined from wet samples analyzed prior to the sorption study, was then used as the amount of adsorbent in subsequent calculations.

The sorption characteristics of the various media were modeled using Freundlich isotherms. The empirically derived Freundlich isotherm equation is defined as follows (Metcalf and Eddy, 1991).

\[
\frac{x}{m} = K_f \cdot C_e^{1/n}
\]  

(3.6)

Where:

\[
\frac{x}{m} = \text{mass of adsorbate adsorbed per unit mass of adsorbent (mg/mg)}
\]

\[C_e = \text{equilibrium concentration of adsorbate in solution after adsorption (mg/L)}\]

\[K_f \text{ and } n = \text{empirical constants}\]

Prior to the sorption experiments described above, a preliminary set of batch isotherm experiments was conducted using various concentrations of sodium azide (NaN\(_3\)) as a biocide in order to determine what concentration of sodium azide would be adequate to inhibit microbial biodegradation inside the bottles. In this case, various concentrations of sodium azide were added to serum bottles containing test contaminants (toluene or MEK) as well as biomass-coated
foam packing media. Dissolved oxygen concentrations were measured immediately prior to sealing the serum bottles and then again after 48-hours of incubation. Results (data not shown) indicated that a sodium azide concentration of 1000 mg/L was adequate to prevent biodegradation under the conditions tested (i.e., there was negligible consumption of dissolved oxygen during the 48-hour period).

3.7. **Analytical Techniques**

3.7.1. **Online Analysis of VOCs and CO$_2$**

During the FEED period of the periodically operated biofilter and during all periods of the continuously operated biofilter, toluene, MEK and CO$_2$ were measured using a California Analytical Instruments model 1312 photoacoustic multigas monitor (Orange, CA) equipped with four optical filters (UA# 971, 974, 983, and SB0527) to allow simultaneous measurement of MEK, toluene, CO$_2$, and H$_2$O. The instrument was factory calibrated using concentrations of 142.8, 52.14, and 5.7 ppm$_v$ MEK; 100, 46.6, and 11 ppm$_v$ toluene; and 1010, 505, and 101 ppm$_v$ CO$_2$. An additional external calibration consisting of 34, 198, 520 and 1090 ppm$_v$ MEK, 23 and 507 ppm$_v$ toluene and 953 and 5,080 ppm$_v$ CO$_2$ was also performed. During all measurements performed with the instrument, the “cross-compensation” setting was turned on. Using this instrument, each constituent (MEK, toluene, and CO$_2$) was measured and recorded at approximately 54-second intervals. For concentration profile studies, measurements collected over a period of at least five minutes were averaged together.

3.7.2. **Gas Chromatography**

Gas-phase toluene and MEK concentrations were also measured using a gas chromatograph (6890 Series, Agilent Technologies, Palo Alto, CA) equipped with a 60 m capillary column (Model DB-624, Hewlett Packard, Palo Alto, CA) and flame ionization
detector (FID). 100 µL samples collected from the biofilters using glass gas-tight syringes (Hamilton Co., Reno, NV) were introduced to the GC by direct, splitless injection. Calibration curves were prepared using various dilutions of certified calibration standards (BOC, Port Allen, LA).

Gas-phase CO$_2$ concentrations were measured using a gas chromatograph (6890 Series, Agilent Technologies, Palo Alto, CA) equipped with a 6' packed column (80/100 Chromosorb 102, Supelco, Bellefonte, PA) and a thermal conductivity detector (TCD). 100 µL samples were injected using a glass gas-tight syringe (Hamilton Co., Reno, NV). Based on three standard gases (BOC Gases, Port Allen, LA) including 953 ppm, CO$_2$, 5080 ppm, CO$_2$, and 50,000 ppm, CO$_2$ a calibration curve for CO$_2$ was developed.

Aqueous-phase MEK and toluene concentrations were measured using an Agilent Gas Chromatograph 6890 Series (Agilent Technologies, Palo Alto, CA) equipped with a purge and trap auto sampler and concentrator (series 2016 and 3000, respectively, from Tekmar, Mason, Ohio). Aqueous samples of 3 mL were placed in the purge and trap auto sampler and concentrator. Helium was used to purge solutions for 10 minutes, desorption time was 2 minutes, and the bake time was 10 min. A 60 m capillary column Model: DB-624 (Hewlett Packard, Palo Alto, CA) was used for the separation of the components. A flame ionization detector (FID) was used to measure the MEK and toluene. A split injection was used, with a 1:30 split ratio. UHP helium was used as carrier gas. Calibration curves were prepared using different dilutions of certified standards (Supelco, Bellefonte, PA).

### 3.7.3. Online Analysis of CO$_2$ and O$_2$

During the FEED period of the periodically operated biofilter and during all periods of the continuously operated biofilter, gas-phase oxygen concentrations were measured using an
Oxygen and Carbon Dioxide Meter (Servomex, UK). The inlet sample flow rate was approximately 200 mL/minute. Calibration was performed using nitrogen gas and 5,080 or 50,000 ppm CO₂ and 20% O₂ standard (BOC, Port Allen, LA). Each constituent (O₂ and CO₂) was measured and recorded at approximately one-second intervals.

3.7.4. Total Suspended Solids

Total Suspended Solids (TSS) were measured following Standard Methods (APHA, 1998).

3.7.5. Flow Meter Calibration

Flow meters were calibrated using an AALBORG electronic flow meter model GFM-37 (AALBORG Co., Orangeburg, NY).
CHAPTER 4 RESULTS

4.1. Phase 1 of Operation

4.1.1. Phase 1 Normal Loading

Immediately after the biofilters were inoculated, normal loading experiments (described in Section 3.5.1) were initiated. Figure 4.1 depicts average loading rates and overall contaminant removal efficiency for both the CFB and SBB during normal steady-loading conditions along Phase 1. For comparison purposes, the average loading rates and removal efficiencies depicted in Figure 4.1 (bottom) for the SBB are the loading rates averaged over a complete cycle. The loading rate during the FEED period in the SBB (1/3 of the cycle length during Phase 1) was three times as high as the average over the cycle length. The VOC loading rates depicted in Figure 4.1 were calculated based on the measured syringe pump flow rates and the measured gas flow rates using Equation 3.2, and removal efficiencies were calculated based on measured effluent VOC concentrations and gas flow rates using Equation 3.5.

As shown in Figure 4.1, on day 3, the SBB removed greater than 99% of the MEK and 92% of the toluene. On day 9 (the next time data were collected) and thereafter, the SBB removed greater than 99% of both the MEK and toluene. In contrast, on day 3, the CFB removed only 67% of the influent MEK and 27% of the toluene. On day 9 (the next day data were collected) the CFB removed greater than 99% of the influent MEK but only 20% of the toluene. Throughout the next 21 days of operation, the CFB removed essentially all of the MEK, but toluene removal efficiency was lower and much more variable. On day 15, the nutrient addition procedure (described in Section 3.5.3) was conducted in each biofilter. Higher toluene removal efficiency was observed in the period immediately after nutrient addition, and subsequently decreased until the next nutrient addition. This suggests that a nutrient limitation
was likely at least partially responsible for the diminished toluene removal. After day 30, nutrients were added on a weekly basis, and the CFB exhibited stable long-term performance with essentially complete toluene and MEK removal (greater than 99% removal efficiency) throughout the remainder of the Phase 1 normal loading periods.

Figure 4.1: Average loading rate and removal efficiency for toluene and MEK in the CFB (top) and SBB (bottom) during normal operation of Phase 1. For comparison purposes, data for the SBB depicted in the figure is the average daily loading rate rather than the loading rate during the FEED period.

As clearly shown in the figure above, the two biofilters exhibited different treatment performance during the first 30 days of operation following the start of contaminant loading at
time zero, with the SBB exhibiting a much more rapid increase in performance during startup. The rapid increase in performance of the SBB provides a clear demonstration that an inoculation procedure using enrichment cultures acclimated to the contaminants and nutrient medium can provide rapid start-up of polyurethane foam-based sequencing batch operated biofilters treating contaminant mixtures as was previously reported for a similar system treating a single component (MEK) contaminated gas stream (Moe and Li, 2003). Furthermore, the SBB operating strategy may facilitate a more rapid startup that CFB operating strategy for multi-component waste gas mixtures.

As shown in Figure 4.1, on the basis of overall performance during normal loading, both the SBB and the CFB were essentially identical after day 30, and throughout the remainder of the Phase 1 normal loading periods. On a daily basis, both biofilters received the same influent toluene and MEK mass and concentration, and both removed essentially all of the influent contaminants. For all practical purposes, they exhibited identical treatment performance.

While the CFB was a quasi steady-state system, the SBB was clearly operated as an unsteady-state process during the entire period of experiments conducted in Phase 1. Throughout the three phases of experiments, during the REACT period in the SBB, oxygen was consumed and CO$_2$ was produced in the closed biofilter system. Subsequently, during each normal loading cycle, at the start of the FEED period, the effluent CO$_2$ concentration increased rapidly to a maximum value within the first 10 seconds after the FEED period began and air flow through the biofilter resumed. Likewise, the O$_2$ concentration reached a minimum value within the first 10 seconds after the FEED period began. Typical effluent CO$_2$ and O$_2$ concentrations for the first 5 minutes of the FEED period during Phase 1 (average data from three measurements conducted on day 106 [two measurements] and day 121 [one measurement]) are depicted in
Figure 4.2. As shown in the figure, the CO\textsubscript{2} concentration reached a maximum value of 6,750 ppm\textsubscript{v} (0.675\%) and the O\textsubscript{2} concentration reached a minimum value of 17.9\% within the first 10 seconds after the FEED period began.

Assuming that the gas flow through the biofilter occurred with minimal back-mixing, the maximum effluent CO\textsubscript{2} concentration and the minimum effluent O\textsubscript{2} concentration measured in the biofilter outlet at the start of FEED are equal to the concentration of the recirculating gas at the end of REACT. As depicted in Figure 4.3, average data of direct GC measurements of the CO\textsubscript{2} concentration during the REACT period on days 121 and 128 confirmed than the average maximum CO\textsubscript{2} concentration measured at the end of REACT was essentially equivalent to the average concentration measured during the start of FEED in experiments conducted during Phase 1. As shown in the figure, the CO\textsubscript{2} concentration increased to a concentration of 4,744 ppm\textsubscript{v} (0.47\%) after 30 minutes and reached a maximum value of 6,650 ppm\textsubscript{v} (0.66\%) at the end of the REACT period.
Direct GC measurements of the toluene and MEK concentrations were also performed during the REACT period. Average results from two of these track studies (both conducted on day 106) conducted during Phase 1 are depicted in Figure 4.3. As shown in the figure, the maximum toluene and MEK concentrations measured in the sampling port located at the bottom of the biofilter (see Figure 3.1) were 1.9 and 3.5 ppm, respectively, at a time of 3 minutes after the start of the REACT period (when the first samples were collected during the REACT period). The toluene concentration in the recirculation gas decreased to a concentration below the detection limit after 15 minutes in the REACT period. The MEK concentration in the recirculation gas decreased to a concentration of 0.7 ppm after 15 minutes in the REACT period, and it was below detection after 30 minutes.

![Figure 4.3: CO2, toluene and MEK concentrations in the SBB during the REACT period during Phase 1 normal loading experiments (bars denote the range of concentrations measured).](image)

The pattern of elevated CO2 concentration and depleted O2 concentration during the first few minutes of the FEED period is consistent with that expected from degradation during the REACT period of toluene and MEK sorbed into the column during previous cycle’s FEED and
endogenous respiration. These track studies of toluene and MEK also indicated that the contaminants sorbed and/or accumulated by organisms during the FEED portion of each normal loading cycle were biotransformed during the REACT portion of each cycle.

During Phase 1, contaminant concentration profiles were measured (as described in Section 3.5.4) along the height of the CFB three different times during “normal” loading conditions to determine the spatial distribution of contaminant removal and CO₂ production. The toluene, MEK, and CO₂ concentrations along the height of the column during Phase 1 normal loading conditions in the CFB (average data of three measurements conducted on days 11, 18 and 24) are shown in Figure 4.4.

![Figure 4.4: CO₂, toluene, and MEK concentrations in the CFB along the height of the packing material during a profile study conducted in Phase 1 normal loading experiments (bars denote the range of concentrations measured).](image)

As shown in the figure, MEK was rapidly removed in the first section of the column and was then more slowly eliminated up to a height of 106 cm after which it could not be detected. Toluene was slowly eliminated throughout the column height; however, a slight increase in toluene removal rate was observed after a considerable decrease in the MEK concentration starting at 69 cm of height. CO₂ production increased sharply in the first 20 cm of packing
material (where MEK removal was most rapid) and continued to increase at a lower rate in the remaining portion of the packing material.

During the first 30 days of operation, when the profiles studies were conducted, there were nutrient limitations that affected the performance of the CFB. However, after day 30, when nutrients were added on a weekly basis, the CFB exhibited stable long-term performance with essentially complete toluene and MEK removal throughout the remainder of the Phase 1 normal loading experiments.

4.1.2. Phase 1 Shock Loading

Beginning on day 32, sixteen separate shock-loading experiments were conducted in each of the biofilters during Phase 1. As described in Section 3.5.2, during the model shock loading condition, the influent toluene and MEK concentrations were increased to five times that of the normal loading for a period of one hour. This corresponded to approximately 140 and 400 ppm, for toluene and MEK, respectively.

For the CFB, typical effluent toluene, MEK, and CO₂ concentrations as a function of time during and after the shock loading events are shown in Figure 4.5 (average data from days 33, 39, 79, 82, 86, 90, 93, 95, 97, 102, 104, 112, 114, 119, 127, and 130). As shown in the figure, the effluent MEK concentration in the CFB during the first 50 minutes of the shock loading period remained below the instrument detection limit indicating essentially 100% contaminant removal. Ten minutes before the return to “normal loading” (80 ppm, MEK influent); however, MEK was detected in the effluent. The MEK concentration increased to a maximum concentration of 48.5 ppm, after an additional 40 minutes and then subsequently decreased to zero after approximately 45 additional minutes. The effluent toluene concentration increased to a maximum value of 11 ppm, approximately 40 minutes after the beginning of the shock loading.
period and remained relatively constant for 25 additional minutes. Five minutes after the end of the shock loading period, the effluent toluene concentration began to rapidly decrease, reaching zero after approximately 25 more minutes.

![Figure 4.5: Contaminant influent concentrations during shock loading (top) and typical results of shock loading experiments conducted during Phase 1 in the CFB (bottom).](image)

The average overall MEK removal efficiency (calculated using Equation 3.5 using the mass of MEK input to the system during the transient loading period and the total mass of MEK
escaping the system during and after the shock loading event) for the CFB during the shock loading events conducted in phase 1 was 91.9%. The average overall toluene removal efficiency for the CFB (calculated using the same procedure) was 92.1%. Accounting for both MEK and toluene, the average overall percentage of contaminant mass removed in the CFB was 92.0%.

The average MEK minimum instantaneous removal efficiency (calculated using Eqn. 3.4) for the CFB during the shock loading events conducted in Phase 1 was 37.2%. The average toluene minimum instantaneous removal efficiency was 47.2%. The average combined minimum instantaneous removal efficiency (on a mass basis) was 52.8%.

Sixteen shock-loading tests were also conducted in the SBB during Phase 1. As shown in Figure 4.6 (average data from days 32, 39, 79, 82, 86, 90, 93, 95, 97, 102, 104, 112, 114, 119, 127 and 130), for the shock loading tests conducted during Phase 1 in the SBB, the average effluent MEK concentration during the 60 minutes of the shock loading period remained below the instrument detection limit indicating essentially 100% contaminant removal. However, the toluene effluent concentration increased to a maximum value of 20 ppm in the first 35 minutes and then remained at that value during the following 25 minutes of the shock loading FEED period, at which time the REACT period began. No MEK or toluene was detected in the effluent of the SBB during the FEED period following REACT.

The average toluene minimum instantaneous removal efficiency for the SBB during the shock loading events conducted in Phase 1 was 81.0%. The average overall MEK removal efficiency for the SBB during the shock loading events conducted in Phase 1 was greater than 99.9%. The average overall toluene removal efficiency was approximately 87.8%. The average combined overall removal efficiency for the shock loading events conducted in Phase 1 was 96.2%. The average combined minimum instantaneous removal efficiency was 95.0%.
At the end of the FEED period, the REACT period started, and gas was recirculated within the closed SBB system. Direct GC measurements of the toluene, MEK, and CO\textsubscript{2} concentrations were performed during the REACT period. The average result from toluene and MEK track studies conducted on days 82, 86, 102, 104 and 130 are depicted in Figure 4.7. The average result from the CO\textsubscript{2} track studies conducted on days 95, 97, 112, 114, 119, and 127 are also depicted in Figure 4.7. Error bars denote the range of concentrations measured. As shown in the figure, the average maximum toluene and MEK concentrations measured in the sampling
port located at the bottom of the biofilter (see Figure 3.1) were 10.7 and 129.0 ppm, respectively, at a time of 3 minutes after the start of the REACT period. The toluene concentration in the recirculation gas decreased to a concentration below 1.0 ppm after 30 minutes in the REACT period, and it was below detection after 45 minutes. The MEK concentration in the recirculation gas decreased to a concentration of 2.5 ppm after 30 minutes in the REACT period, and it was below detection after 60 minutes. The CO₂ concentration increased to an average concentration of 20,400 ppm (2.04%) after 30 minutes and reached a maximum value of 25,900 ppm (2.59%) at the end of the REACT period.

![Figure 4.7: CO₂, toluene, and MEK concentrations in the SBB during the REACT period during Phase 1 shock loading experiments (bars denote the range of concentrations measured).](image)

Effluent CO₂ and O₂ concentrations for the first 5 minutes of the FEED period following the shock loading event were also measured using on-line instruments. As shown in Figure 4.8 (average of four measurements conducted on days 93, 95, 97, and 104), the CO₂ concentration reached a maximum value of 25,900 ppm (2.59%) and the O₂ concentration reached a minimum value of 14.1% within the first 10 seconds after the FEED period began.
The higher CO\textsubscript{2} concentration and lower O\textsubscript{2} concentration measured at the end of the REACT period (in comparison to normal loading), indicate that the contaminants sorbed and/or accumulated by organisms during the shock loading cycle were degraded during the REACT period immediately following the shock-loading event. Therefore, there were not contaminants detected in the biofilter effluent at the beginning of the subsequent FEED period (i.e., that immediately following the REACT period of the shock loading event).

![Figure 4.8: Effluent CO\textsubscript{2} and O\textsubscript{2} concentration during the first 5 minutes of FEED period immediately following the shock loading REACT period during Phase 1.](image)

Table 4.1 summarizes results from shock loadings experiments conducted during Phase 1. As shown in the table, the SBB was slightly better than the CFB in terms of overall mass of contaminants removed (96.2% for the SBB vs. 92% for the CFB). However, in terms of minimum instantaneous removal efficiency, the SBB presented a markedly superior performance in spite of the fact that the SBB received a contaminant mass loading rate three times higher than the CFB during the shock-loading period (63 g m\textsuperscript{-3} h\textsuperscript{-1} vs. 21 g m\textsuperscript{-3} h\textsuperscript{-1} for toluene and 141 g m\textsuperscript{-3} h\textsuperscript{-1} vs. 47 g m\textsuperscript{-3} h\textsuperscript{-1} for MEK).
Table 4.1: Summary of biofilter performance during shock loading experiments in Phase 1.

<table>
<thead>
<tr>
<th>VOC</th>
<th>Continuous Flow Biofilter (CFB)</th>
<th>Sequencing Batch Biofilter (SBB)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shock-loading</td>
<td>Shock-loading</td>
</tr>
<tr>
<td></td>
<td>Range of Removal Efficiency (%)</td>
<td>Average Removal Efficiency (%)</td>
</tr>
<tr>
<td></td>
<td>Range of Minimum Instantaneous Removal (%)</td>
<td>Average Minimum Instantaneous Removal (%)</td>
</tr>
<tr>
<td>Toluene</td>
<td>79.6 – 99.0</td>
<td>92.1 -81.0 –  95.0</td>
</tr>
<tr>
<td>MEK</td>
<td>83.5 – 99.9</td>
<td>91.9 -23.5 –  97.0</td>
</tr>
<tr>
<td>Combined</td>
<td>82.3 – 99.3</td>
<td>92.0 - 5.0 – 97.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>73.0 - 100</td>
<td>87.8 52.0 - 100</td>
</tr>
<tr>
<td>MEK</td>
<td>100 - 100</td>
<td>100 100 - 100</td>
</tr>
<tr>
<td>Combined</td>
<td>91.6 - 100</td>
<td>96.2 87.5 - 100</td>
</tr>
</tbody>
</table>

Several previous researchers have reported that for mixtures of VOCs, ketones are preferentially removed in comparison to aromatic compounds (Deshusses et al., 1999; Mohseni and Allen, 1999; Kazenski and Kinney, 2000; Aizpuru et al., 2001; Qi et al., 2003; Song et al., 2003). Therefore, it was expected a higher removal efficiency of MEK when compared to toluene. This could be explained by the aqueous solubility of the compounds and the biodegradability of the pollutants.

The fact that toluene and MEK concentrations were not detected in the gas phase after 45 and 60 minutes, respectively, during the REACT period of the shock loading events in the SBB (see Figure 4.7), suggests that an operation strategy with a maximum REACT period length of 60 minutes would be sufficient to minimize toluene and MEK discharges in the effluent. Therefore, the operation strategy used in the Phase 2 included a 1 hr FEED and 1 hr REACT period.
Plots of the individual shock loading studies conducted in the CFB and the SBB during Phase 1, track studies performed during the REACT period in the SBB, typical effluent CO₂ and O₂ concentrations for the first 5 minutes of the FEED period during Phase 1, plots of the individual profiles studies conducted during Phase 1 in the CFB, and plots of the influent VOC concentrations in the CFB during the 15 minutes prior and during the 15 minutes after the end of the shock loading are presented in Appendix A. Mass balances (calculated on the basis of carbon) for each of the systems for Phases 1, 2, and 3 are presented in Section 4.5.

4.2. Phase 2 of Operation

4.2.1. Phase 2 Normal Loading

At the start of Phase 2 experiments on day 138, the length of the REACT period in the SBB was decreased from 2 hours to 1 hour. Thus, the cycle length decreased to 2 hours. Because the length of FEED and REACT were both 1 hour, the system simulated one biofilter in a set of two biofilters constructed in parallel and operated sequentially to treat a continuous flow of gas. The EBRT of the SBB remained 30 seconds. To keep the daily mass loading of contaminants identical, the EBRT of the CFB was decreased from 90 seconds to 60 seconds. For both biofilters, the target influent MEK concentration remained 80 ppmv, while the toluene concentration was increased from 28 to 30 ppmv. Figure 4.9 depicts average loading rates and overall contaminant removal efficiency for both the CFB and SBB during normal steady-loading conditions along Phase 2. For comparison purposes, the average loading rates and removal efficiencies depicted in Figure 4.9 (bottom) for the SBB are the loading rates averaged over a complete cycle. The loading rate during the FEED period in the SBB (1/2 of the cycle length during Phase 2) was two times as high as the average over the cycle length. The VOC loading rates depicted in Figure 4.9 were calculated based on the measured syringe pump flow rates and
the measured gas flow rates using Equation 3.2, and removal efficiencies were calculated based on measured effluent VOC concentrations and gas flow rates using Equation 3.5.

Figure 4.9: Average loading rate and removal efficiency for toluene and MEK in the CFB (top) and SBB (bottom) for normal operation during Phase 2. For comparison purposes, data for the SBB depicted in the figure is the average daily loading rate rather than the loading rate during the FEED period.

As shown in Figure 4.9, on day 139 (the first time data were collected during Phase 2) and thereafter, both the SBB and CFB continued to exhibit greater than 99% removal efficiency for both MEK and toluene, even immediately following the increase in loading on day 138.
As shown in Figure 4.9, on the basis of overall performance during normal loading, both the SBB and the CFB were essentially identical during the entire duration of the Phase 2 normal loading experiments. On a daily basis, both biofilters received the same influent toluene and MEK mass and concentration, and both removed essentially all of the influent contaminants. For all practical purposes, they exhibited identical treatment performance.

4.2.2. Phase 2 Shock Loading

During Phase 2, each biofilter was subjected to five separate shock-loading events. During the shock loading events, for a period of one hour, the influent toluene and MEK concentrations were increased to 150 and 400 ppm, for toluene and MEK, respectively, approximately five times that of the normal loading. The overall performance during Phase 2 shock loading conditions is described below for each of the systems.

For the CFB, typical effluent toluene, MEK, and CO$_2$ concentrations as a function of time during and after the shock loading events during Phase 2 are shown in Figure 4.10 (average data from days 149, 152, 156, 158 and 160). As shown in the figure, MEK was detected in the effluent starting 24 minutes after the beginning of the shock loading. It increased to an average maximum concentration of 99.5 ppm after an additional 54 minutes (78 minutes after shock loading began) and then subsequently decreased to below the detection limit after 72 additional minutes (150 minutes after the shock loading began). The effluent toluene concentration increased to a maximum value of 18.0 ppm after 15 minutes of the shock loading period and remained relatively constant for the next 48 minutes. Ten minutes after the end of the shock loading period, the effluent toluene concentration began to rapidly decrease to zero.
During the shock loading period, the effluent \( \text{CO}_2 \) concentration increased rapidly from an initial concentration of approximately 985 ppm, to a concentration of 1500 ppm after 25 minutes. The effluent \( \text{CO}_2 \) concentration continued to increase at a slower rate to a maximum of 1600 ppm during the next 35 minutes, at which time the shock loading period ended and the loading rate returned to its “normal” level. The effluent \( \text{CO}_2 \) concentration then decreased, reaching a concentration of 1112 ppm after an additional 90 minutes, at which point monitoring

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**Figure 4.10**: Contaminant influent concentrations during shock loading (top) and typical results of shock loading experiments conducted during Phase 2 in the CFB (bottom).
was discontinued. The CO₂ concentration data suggests that the microorganisms in the system were able to rapidly increase their degradation rate following the start of the shock loading event, but as MEK and toluene data show, the increase in degradation rate was insufficient to remove all of the influent contaminant loading.

For MEK, the packing medium attenuated the peak loading somewhat, leading to the maximum effluent concentration of 99.5 ppm, being observed at a time 78 minutes after shock loading began (18 minutes after the shock loading ended), and after the influent MEK concentration was reduced to 80 ppm, the “normal” loading rate. The average MEK minimum instantaneous removal efficiency for the CFB during the shock loading events conducted in Phase 2 was -27.2%. The negative instantaneous removal efficiency reflects the fact that the effluent concentration was higher than the influent concentration. For toluene, the attenuation effect was much less pronounced and breakthrough was much more rapid. The average toluene minimum instantaneous removal efficiency for the CFB during the shock loading events was 42.4%. The average combined minimum instantaneous removal efficiency was 4.5%. In terms of the mass of contaminant removed by the CFB during the shock loading events, the average MEK removal was 79.6% and the average toluene removal was 88.6% (i.e., 20.4% of the mass of MEK and 11.4% of the mass of toluene entering the system during the shock loading events was emitted from the system.) Therefore, the average combined overall removal efficiency for the CFB during the shock loading events conducted in Phase 2 was 82.5%.

Average results of the shock loading events conducted in the SBB during Phase 2 are shown in Figure 4.11. (average data from days 149, 152, 156, 158 and 160). As shown in the figure (bottom), the effluent MEK concentration remained below the instrument detection limit during the entire 60 minutes of the shock-loading period indicating essentially 100%
contaminant removal. The effluent toluene concentration remained below 3 ppm, during the entire 60 minutes of the shock loading.

Figure 4.11: Contaminant influent concentrations during shock loading (top) and typical results of shock loading experiments conducted during Phase 2 in the SBB (bottom).

Following the 60 minute FEED period of shock loading, the system entered REACT and no air entered or exited the system. After 1 hour of REACT, the biofilter entered a “normal” FEED period. No MEK or toluene was detected in the effluent of the SBB during the subsequent FEED period. In terms of the mass of contaminant removed by the SBB during the shock loading events, the average MEK removal was 100% and the average toluene removal was
98.0%. This corresponds to an average combined overall removal efficiency for the SBB during the shock loading events conducted in Phase 2 of 99.3%.

Within 18 minutes after shock loading was applied, the effluent CO$_2$ concentration increased rapidly from roughly 900 to 1350 ppm$_v$. The effluent CO$_2$ concentration continued to increase at a slower rate to a maximum of 1476 ppm$_v$ at the end of the FEED period. This implies that there was an increase in the contaminants biodegradation rate following the increase in influent contaminant concentration during the shock loading.

At the end of the FEED period of the shock loading event, the REACT period started, and gas was recirculated within the closed SBB system. Direct GC measurements of the toluene, MEK and CO$_2$ concentrations were performed during the REACT period. The average results from the toluene and MEK track studies conducted on days 149, 152 and 156 are depicted in Figure 4.12. Average result from CO$_2$ track studies conducted on days 158 and 160 are also depicted in Figure 4.12. Error bars denote the range of concentrations measured.

As shown in the figure, the maximum toluene and MEK concentrations measured in the sampling port located at the bottom of the biofilter (see Figure 3.1) were 0.3 and 106 ppm$_v$, respectively, at a time of 3 minutes after the start of the REACT period. The toluene concentration in the recirculation gas decreased to a concentration below the detection limit after 15 minutes in the REACT period, and remained below detection during the following 45 minutes. The MEK concentration in the recirculation gas decreased to a concentration of 1.2 ppm$_v$ after 30 minutes in the REACT period, and it was below detection after 45 minutes. The CO$_2$ concentration increased to a concentration of 16,140 ppm$_v$ (1.61%) after 30 minutes and reached a maximum value of 16,500 ppm$_v$ (1.65%) at the end of the REACT period.
Figure 4.12: CO\textsubscript{2}, toluene, and MEK concentrations in the SBB during the REACT period during Phase 2 shock loading experiments (bars denote the range of concentrations measured).

Effluent CO\textsubscript{2} and O\textsubscript{2} concentrations for the first 5 minutes of the FEED period following shock-loading events were also measured using on-line instruments. As shown in Figure 4.13 (average of three measurements conducted on days 152, 158, and 160), the CO\textsubscript{2} concentration reached a maximum value of 14,500 ppm\textsubscript{v} (1.45\%) and the O\textsubscript{2} concentration reached a minimum value of 17.5\% within the first 10 seconds after the FEED period began.

Figure 4.13: Effluent CO\textsubscript{2} and O\textsubscript{2} concentrations during the first 5 minutes of the FEED period immediately following the shock loading REACT period during Phase 2 (average data for measurements collected on days 152, 158, and 160).
Table 4.2 summarizes results from shock loadings experiments conducted during Phase 2. As shown in the table, the SBB exhibited higher overall contaminant removal (ranging from 98.6 to 100.0% with a mean of 99.3% for all replicate experiments), and higher minimum instantaneous removal efficiency (ranging from 97.0 to 100.0% with a mean of 98.9% for all replicates). These removal efficiencies are appreciably higher than those observed in the CFB even though the contaminant mass loading rate to the SBB during the shock loading event was two times higher (68 g·m⁻³·h⁻¹ vs. 34 g·m⁻³·h⁻¹ and 141 g·m⁻³·h⁻¹ vs. 70.5 g·m⁻³·h⁻¹ for toluene and MEK, respectively).

Table 4.2: Summary of biofilter performance during shock loading experiments in Phase 2.

<table>
<thead>
<tr>
<th>VOC</th>
<th>Continuous Flow Biofilter (CFB)</th>
<th>Shock-loading</th>
<th>Continuous Flow Biofilter (CFB)</th>
<th>Shock-loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range of Removal Efficiency (%)</td>
<td>Average</td>
<td>Range of Minimum Instantaneous Removal (%)</td>
<td>Average</td>
</tr>
<tr>
<td>Toluene</td>
<td>73.1 – 96.3</td>
<td>88.6</td>
<td>-32.0 – 85.0</td>
<td>42.4</td>
</tr>
<tr>
<td>MEK</td>
<td>74.0 – 87.0</td>
<td>79.6</td>
<td>-136 – -3.0</td>
<td>-27.2</td>
</tr>
<tr>
<td>Combined</td>
<td>74.0 – 89.5</td>
<td>82.5</td>
<td>-18.5 – 25.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VOC</th>
<th>Sequencing Batch Biofilter (SBB)</th>
<th>Shock-loading</th>
<th>Sequencing Batch Biofilter (SBB)</th>
<th>Shock-loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range of Removal Efficiency (%)</td>
<td>Average</td>
<td>Range of Minimum Instantaneous Removal (%)</td>
<td>Average</td>
</tr>
<tr>
<td>Toluene</td>
<td>94.6 - 100</td>
<td>98.0</td>
<td>89.0 – 99.0</td>
<td>95.7</td>
</tr>
<tr>
<td>MEK</td>
<td>100 - 100</td>
<td>100</td>
<td>100 – 100</td>
<td>100</td>
</tr>
<tr>
<td>Combined</td>
<td>98.6 - 100</td>
<td>99.3</td>
<td>97.0 – 100</td>
<td>98.9</td>
</tr>
</tbody>
</table>

When compared to the results achieved during Phase 1, the SBB presented better overall removal efficiencies for both toluene and MEK during Phase 2. In contrast, the CFB experienced a decline in the overall removal efficiencies of the two contaminants tested. The better results achieved by the SBB are probably due to a combination of the higher sorption
capacity associated with the packing media coated with activated carbon and the increase in biomass accumulation within the biofilter (more biodegradation and bioaccumulation).

The SBB was clearly able to accumulate undegraded contaminants during the shock loading FEED period and then complete contaminant transformation during the subsequent REACT period. Thus, it was able to separate in time the period during which contaminants entered the system and when they were fully transformed. These data clearly demonstrate that such an operating strategy can increase an operator’s capacity for minimizing contaminant emissions when treating waste gas streams with dynamically varying influent contaminant concentrations.

Plots of the individual shock loading studies conducted in the CFB and the SBB during Phase 2, track studies performed during the REACT period in the SBB, effluent CO$_2$ and O$_2$ concentrations for the first 5 minutes of the FEED period during Phase 2 and plots of the influent VOC concentrations in the CFB during the 15 minutes prior and during the 15 minutes after the end of the shock loading are presented in the Appendix B.

4.3. Phase 3 of Operation

4.3.1. Phase 3 Normal Loading

At the start of Phase 3 experiments on day 173, the EBRT of both biofilters was decreased by a factor of two (i.e., the gas flow rate was doubled). The target influent concentration of MEK was increased slightly, to 89 ppm, the target influent toluene concentration remained 30 ppm. The average mass loading rate to the systems (averaging over the entire cycle length for the SBB) was 31.4 g·m$^{-3}$·h$^{-1}$ MEK and 13.6 g·m$^{-3}$·h$^{-1}$ toluene (45 g·m$^{-3}$·h$^{-1}$ total VOC loading). Figure 4.14 depicts average loading rates and overall contaminant removal efficiency for both the CFB and SBB during normal steady-loading conditions along
Phase 3. The VOC loading rates depicted in Figure 4.14 were calculated based on the measured syringe pump flow rates and the measured gas flow rates using Equation 3.2, and removal efficiencies were calculated based on measured effluent VOC concentrations and gas flow rates using Equation 3.5.

Figure 4.14: Average loading rate and removal efficiency for toluene and MEK in the CFB (top) and SBB (bottom) during normal operation along Phase 3. For comparison purposes, data for the SBB depicted in the figure is the average daily loading rate rather than the loading rate during the FEED period.

For comparison purposes, the average loading rates and removal efficiencies depicted in Figure 4.14 (bottom) for the SBB are the loading rates averaged over a complete cycle. Because
the SBB received contaminant loading only during the FEED period of its operating cycle (one half of the cycle length), the loading rate during the FEED period was twice that of the CFB.

As shown in Figure 4.14, on day 175 (the first time data were collected during Phase 3 in both the CFB and the SBB) and thereafter, both the SBB and CFB continued to exhibit greater than 99% removal efficiency for both MEK and toluene, even though that the loading rate of both contaminants was increased by factor of two on day 173. On the basis of overall performance during normal loading, both the SBB and the CFB were essentially identical during the entire duration of the Phase 3 normal loading experiments. On a daily basis, both biofilters received the same influent toluene and MEK mass and concentration, and both removed essentially all of the influent contaminants. For all practical purposes, they exhibited identical treatment performance.

During Phase 3, direct GC measurements of the toluene, MEK and CO₂ concentrations were also performed during the REACT period in the SBB. Average results from three of these track studies (data from days 228 [one replicate] and 229 [two replicates]) are depicted in Figure 4.15. As shown in the figure, the toluene and MEK concentrations in the recirculation gas measured in the sampling port located at the bottom of the biofilter (see Figure 3.1) were below the detection limit, at a time of 3 minutes after the start of the REACT period (when the first samples were collected during the REACT period) and remained below the detection limit for the remaining time of the REACT period. As also shown in the figure, the CO₂ concentration increased to a concentration of 4,630 ppm, (0.46%) after 15 minutes and reached a maximum value of 6,780 ppm, (0.67%) at the end of the REACT period.
As was observed in Phases 1 and 2, track studies of toluene, MEK and CO$_2$ indicated that the contaminants sorbed and/or accumulated by organisms during the FEED portion of each normal loading cycle were biotransformed during the REACT portion of each cycle.

To determine the spatial distribution of contaminant removal and CO$_2$ production during Phase 3 of the experiment, profile studies were conducted in both the CFB and the SBB three different times during “normal” loading conditions, and two different times during endogenous loading conditions as described in Section 3.5.4. Toluene, MEK, and CO$_2$ concentrations along the height of the CFB (average data of three measurements conducted on days 229, 254, and 255) during normal loading conditions are shown in Figure 4.16. Error bars denote the range of concentrations measured. As shown in the figure, MEK was eliminated within the first 60 cm of the packing material. Toluene was eliminated between 0 cm and 90 cm of the packing material, with a higher removal rate observed after MEK was no longer present. CO$_2$ production increased sharply in the first 32 cm of packing material and then continued to increase at a lower rate in the remainder of the column. These contaminant removal and CO$_2$ production profile is
consistent with the results from Phase 1 as well as previous reports that degradation of aromatic compounds can be adversely affected by the presence of ketones.

![Figure 4.16: CO₂, toluene, and MEK concentrations in the CFB along the height of the packing material during a profile study conducted in Phase 3 normal loading experiments (bars denote the range of concentrations measured).](image)

Profile studies were also conducted in the SBB during Phase 3. In order to conduct these profiles studies, measurements were taken from 2 sampling ports, starting from the top to the bottom of the column, in the last 20 minutes of the FEED period during several cycles of operation in order to collect samples along the height of the column. Toluene, MEK, and CO₂ concentrations along the height of the packing material during normal loading conditions in the SBB (average data of three measurements conducted on days 256, 263 and 272) are shown in Figure 4.17. As shown in the figure, MEK was eliminated in the first 70 cm of the packing material. Toluene was removed slowly near the inlet where MEK concentrations were high, and then more rapidly after MEK concentrations became low. CO₂ production increased sharply in the first 55 cm of packing material and continued to increase at a lower rate in the following 65
cm of packing material. These results also showed stratification in terms of biodegradation as observed in the CFB during Phase 3.

![Graph showing CO₂, toluene, and MEK concentrations in the SBB along the height of the packing material during a profile study conducted in Phase 3 normal loading experiments (bars denote the range of concentrations measured).](image)

**Figure 4.17:** CO₂, toluene, and MEK concentrations in the SBB along the height of the packing material during a profile study conducted in Phase 3 normal loading experiments (bars denote the range of concentrations measured).

In both the CFB and the SBB, MEK was metabolized before toluene during normal loading conditions and the length of the packing material was adequate to allow complete elimination of both toluene and MEK at the loading conditions experimented during Phase 3 normal loading experiments. In general, during the normal loading conditions tested, the general pattern of the spatial locations of contaminant removal and CO₂ production was similar for both biofilters.

As mentioned before, two profile studies were also conducted during endogenous loading in both the SBB and the CFB during Phase 3. Figure 4.18 depicts CO₂ produced during endogenous respiration along the height of the packing material for both the CFB and SBB (average data of two measurements for each biofilter conducted on days 254, 255 and 256).
As shown in the figure, the CO₂ concentration in the CFB increased sharply in the first 25 cm of the packing material and continued increasing to a lower rate in the remaining part of the column. This clearly indicates high accumulation of biomass in the lower section of the packing material, which is usually observed in CFB systems. In contrast, the SBB presented a more homogeneous CO₂ production along the height of the packing material, which is a clear indication of more homogeneous distribution of active biomass. Although the CFB exhibited a
higher outlet CO$_2$ concentration than the SBB, this does not indicate that the CFB had a higher overall biomass accumulation. Because the gas flow rate of the SBB was twice that of the CFB, the CO$_2$ concentration exiting the SBB would be only half that of the CFB if the CO$_2$ production rate was identical in both systems. The fact that the effluent CO$_2$ concentration for the SBB was more than half that of the CFB indicates that the endogenous CO$_2$ production rate (mass CO$_2$ produced per unit time) was higher in the SBB than the CFB.

During Phase 3, direct GC measurements of the CO$_2$ concentration were also performed during the REACT period in the SBB during endogenous loading conditions. Average results from three of these track studies (data from days 251, 252 and 254) are depicted in Figure 4.19. As shown in the figure, the CO$_2$ concentration increased to a concentration of 4,080 ppm, (0.40%) after 15 minutes and reached a maximum value of 4,560 ppm, (0.45%) at the end of the REACT period.

![Figure 4.19: CO$_2$ concentrations in the SBB during the REACT period during Phase 3 endogenous loading experiments (bars denote the range of concentrations measured).](image)
4.3.2. Phase 3 Shock Loading

During Phase 3, each biofilter was subjected to the model shock loading condition on five separate occasions. Effluent toluene, MEK, and CO$_2$ concentrations during the shock loading events in the CFB (average data from days 177, 183, 185, 194 and 196) are shown in Figure 4.20. As shown in the figure, MEK was detected in the effluent 7 minutes after the beginning of the shock loading and increased to a maximum concentration of 245 ppm$_v$ after an additional 58 minutes (65 minutes after the shock loading began) and then subsequently decreased to below the detection limit after 45 additional minutes (110 minutes after the shock loading began). Toluene was detected in the effluent starting one minute after the beginning of the shock loading. The toluene concentration increased rapidly to a maximum concentration of 38 ppm$_v$ and remained at that value until the end of the shock loading (60 minutes after the shock loading began). Nine minutes after the end of the shock-loading period, the toluene effluent concentration decreased to zero. During the shock loading period, the effluent CO$_2$ concentration increased rapidly from an initial concentration of approximately 936 ppm$_v$ to a concentration of 1230 ppm$_v$ after 10 minutes. The effluent CO$_2$ concentration continued to increase at a slower rate to a maximum of 1302 ppm$_v$ during the next 50 minutes, at which time the shock loading period ended and the loading rate returned to its “normal” level. The effluent CO$_2$ concentration then decreased, reaching a concentration of 1033 ppm$_v$ after an additional 60 minutes, at which point monitoring was discontinued.

The CO$_2$ concentration data suggests that the microorganisms in the system were able to rapidly increase their degradation rate following the start of the shock loading event, but as MEK and toluene data show, the increase in degradation rate was insufficient to remove all of the influent contaminant loading.
Figure 4.20: Contaminant influent concentrations during shock loading (top) and typical results of shock loading experiments conducted during Phase 3 in the CFB (bottom).

For MEK, the packing medium attenuated the peak loading somewhat. For toluene, the attenuation effect was almost negligible. The average MEK minimum instantaneous removal efficiency (calculated using Equation. 3.4) for the CFB during the shock loading events conducted in Phase 3 was -175%. The average toluene minimum instantaneous removal efficiency was –38.9%. The average combined minimum instantaneous removal efficiency (on a mass basis) was -138%. The average overall MEK removal efficiency (calculated using...
Equation 3.5) for the CFB during the shock loading events conducted in Phase 3 was 49.5%. The average overall toluene removal efficiency for the CFB (calculated using the same procedure) was 73.0%. Accounting for both MEK and toluene, the average overall percentage of contaminant mass removed by the CFB was 56.6%.

Five shock-loading tests were also conducted in the SBB during Phase 3. Effluent toluene, MEK, and CO$_2$ concentrations during the FEED period of these shock-loading events (average data from days 177, 183, 185, 194 and 196) are depicted in Figure 4.21. As shown in the figure, MEK was detected in the effluent 9 minutes after the beginning of the shock loading and then steadily increased, reaching a maximum concentration of 126 ppm, at the end of the shock loading period (60 minutes after the shock loading began). Toluene was detected in the effluent starting two minutes after the beginning of the shock loading and increased rapidly to a concentration of 31 ppm, after 5 minutes. It then slowly increased to an average concentration of 39 ppm, until the end of the shock loading (60 minutes after the shock loading began). No toluene was detected in the effluent of the SBB during the FEED period following REACT; however, MEK was detected at a concentration of approximately 2 ppm, during the first few minutes. Clearly, the loading rate exceeded the degradation capacity of the system.

Within 5 minutes after shock loading was applied, the effluent CO$_2$ concentration increased rapidly from roughly 944 to 1130 ppm. The effluent CO$_2$ concentration continued to increase at a slower rate to a maximum of 1208 ppm, at the end of the FEED period. This implies that there was an increase in contaminant biodegradation rates following the increase in influent contaminant concentration during the shock loading. The overall pattern of CO$_2$ production in the biofilter during the FEED period was similar to that observed in earlier phases.
Figure 4.21: Contaminant influent concentrations during shock loading (top) and typical results of shock loading experiments conducted during Phase 3 in the SBB (bottom).

The average MEK minimum instantaneous removal efficiency (calculated using Equation 3.4) for the SBB during the shock loading events conducted in Phase 3 was 71.7%. The average toluene minimum instantaneous removal efficiency was 72.3%. The average combined minimum instantaneous removal efficiency (on a mass basis) was 72.3%. The average overall MEK removal efficiency (calculated using Equation 3.5) for the SBB during the shock loading events conducted in Phase 3 was 88.0%. The average overall toluene removal efficiency
for the SBB (calculated using the same procedure) was 75.6%. Accounting for both MEK and toluene, the average overall percentage of contaminant mass removed in the SBB was 84.3%.

At the end of the FEED period of the shock loading events, the REACT period started, and gas was recirculated within the closed SBB system. Direct GC measurements of the toluene, MEK and CO$_2$ concentrations were performed during the REACT period. Results from the toluene and MEK track studies conducted during the shock loading events are depicted in Figure 4.22 (average data from days 177 and 183). Results from the CO$_2$ track studies conducted during the shock loading events are also depicted in Figure 4.22 (average data from days 185, 194, and 196). As shown in the figure, no appreciable concentration of toluene was detected during REACT. As also shown in the figure, however, unlike previous phases in which all of the accumulated MEK was transformed by the end of the REACT period, during this event, the MEK concentration at the end of REACT was 3.5 ppm$_v$. This is consistent with the fact that MEK was detected in the effluent for the first few minutes the subsequent FEED period.

![Figure 4.22: CO$_2$, toluene and MEK concentrations in the SBB during the REACT period during Phase 3 shock loading experiments (bars denote the range of concentrations measured).](image-url)
The CO₂ concentration at the end of REACT period following the shock loading condition was approximately 17,000 ppm (1.70%) and the O₂ concentration was 16.2%. Effluent CO₂ and O₂ concentrations measured using on-line analyzers for the first 5 minutes of the FEED period following the shock loading event confirmed the results obtained from the track studies. The results of these measurements are presented in Figure 4.23. (average of three measurements conducted on days 183, 185, and 194).

![Figure 4.23: Effluent CO₂ and O₂ concentrations during the first 5 minutes of the FEED period immediately following the shock loading REACT period during Phase 3.](image)

Table 4.3 summarizes results from shock loadings experiments conducted during Phase 3. The combined overall removal efficiency for the SBB ranged from 80.9 to 86.9% with a mean of 84.3%. Clearly, the SBB outperformed the CFB even though the loading to the SBB was two times higher (136 g·m⁻³·h⁻¹ vs. 68 g·m⁻³·h⁻¹ for toluene and 313.5 g·m⁻³·h⁻¹ vs. 157 g·m⁻³·h⁻¹ for MEK, respectively) during the shock loadings experiments conducted in this phase.

The lower overall removal efficiencies observed during Phase 3 shock loadings (in comparison to those of Phase 2) likely resulted from the fact that the loading rate to each of the
biofilters was twice as high, and there was limited sorption capacity available to dampen the transient elevated loading at the higher rate experienced during Phase 3.

Table 4.3: Summary of biofilter performance during shock loading experiments in Phase 3.

<table>
<thead>
<tr>
<th>VOC</th>
<th>Continuous Flow Biofilter (CFB)</th>
<th>Shock-loading</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range of Removal Efficiency (%)</td>
<td>Average Removal Efficiency (%)</td>
<td>Range of Minimum Instantaneous Removal (%)</td>
</tr>
<tr>
<td>Toluene</td>
<td>58.7 – 80.8</td>
<td>73.0</td>
<td>-113 – 10.0</td>
</tr>
<tr>
<td>MEK</td>
<td>46.1 – 52.9</td>
<td>49.5</td>
<td>-196 – -165</td>
</tr>
<tr>
<td>Combined</td>
<td>50.0 – 59.0</td>
<td>56.6</td>
<td>-170 – -124</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VOC</th>
<th>Sequencing Batch Biofilter (SBB)</th>
<th>Shock-loading</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range of Removal Efficiency (%)</td>
<td>Average Removal Efficiency (%)</td>
<td>Range of Minimum Instantaneous Removal (%)</td>
</tr>
<tr>
<td>Toluene</td>
<td>67.2 – 80.0</td>
<td>75.6</td>
<td>64.0 – 77.0</td>
</tr>
<tr>
<td>MEK</td>
<td>86.4 – 89.8</td>
<td>88.0</td>
<td>68.0 – 75.0</td>
</tr>
<tr>
<td>Combined</td>
<td>80.9 – 86.9</td>
<td>84.3</td>
<td>69.0 – 76.0</td>
</tr>
</tbody>
</table>

Profile studies were also conducted during shock loading conditions in both the CFB and the SBB. As described for the profiles conducted during normal loading conditions, at the time to conduct the profiles studies during shock loading conditions, measurements were taken from 2 sampling ports, starting from the top to the bottom of the column, in the last 20 minutes of the shock loading FEED period during several cycles of shock loading in order to collect samples along the height of the column. There was at least one cycle of normal loading between each of the shock loadings cycles conducted during the profile studies in Phase 3. Toluene, MEK, and CO₂ concentrations along the height of the packing material for shock loading conditions in the CFB (average data of three measurements conducted on days 282, 333 and 336) are shown in Figure 4.24. Error bars denote the range of concentrations measured.
As shown in the figure, MEK was degraded over the complete height of the packing material. Noticeably faster removal was observed in the first 56 cm than was removed in the later portions of the column. Toluene, on the other hand, was removed more rapidly in the last 60 cm of the column than it was closer to the inlet. The CO$_2$ concentration increased at a relatively constant rate in the first 56 cm of packing material and then continued to increase but at a lower rate in the remainder of the column. These results also reveal some stratification in terms of zones of biodegradation for each of the compounds as was observed during normal loading conditions. However, in this case, clearly the loading rate exceeded the loading capacity of the system, which resulted in breakthrough. Toluene, MEK, and CO$_2$ concentrations along the height of the packing material during Phase 3 shock loading conditions in the SBB (average data of three measurements conducted on days 282, 333 and 336) are shown in Figure 4.25.

As shown in the figure, the MEK concentration decreased at a relatively constant rate throughout the height of the biofilter column. The toluene concentration decreased throughout
the column but was removed more rapidly in the last 65 cm of the packing material. CO₂ production was almost constant along the height of the packing material. As was observed in the CFB, during Phase 3 shock loading in the SBB, the loading rate exceeded the combined biodegradation and sorption capacity of the system resulting in contaminant breakthrough.

During shock loading conditions, both biofilters experienced contaminant breakthrough, and the general pattern of the spatial locations of contaminant removal and CO₂ production was similar. In both cases, the profile results revealed stratification in terms of zones of biodegradation for each of the compounds with MEK being more readily degraded than toluene. One plausible explanation for the observed shock-loading profile data is that an MEK degrading microbial population predominated near the inlet sections of the biofilters where MEK was primarily degraded during the normal loading conditions, and a toluene degrading microbial population predominated at sections further from the inlet of the biofilters where toluene was primarily degraded during the normal loading conditions. Another plausible explanation is that

Figure 4.25: CO₂, toluene, and MEK concentrations in the SBB along the height of the packing material during a profile study conducted in Phase 3 shock loading experiments (bars denote the range of concentrations measured).
the microbial populations were the same throughout the height of the biofilters, but the VOC mixture caused inhibition and/or catabolic repression when both MEK and toluene were present in the gaseous stream. The fact that toluene removal rates appear to increase in later sections of the biofilters even when MEK was still present favors the former explanation; however, it is impossible from the data collected to conclusively determine which (if either) of these effects dominated the system.

Two additional experiments would have allowed one to further discern which of these effects may play a role. One way would be to assess the microbial populations at various spatial locations along the height of the column using denaturing gradient gel electrophoresis (DGGE) or to use a technique to identify the predominant microorganisms colonizing the packing material at various spatial locations along the height of the column. This would allow a direct assessment of whether the populations were different as a function of location in the biofilters. A second method would be to conduct the transient loading studies with just one contaminant at a time (i.e., loading only MEK or only toluene) while monitoring the contaminant concentrations as a function of height in the biofilters. This would provide a direct indication of whether the mixture of contaminants caused interactions that resulted in decreased degradation rates by the microbial populations (i.e., it would allow one to determine if toluene would have been degraded more rapidly if MEK was not present). Unfortunately, however, these experiments were not conducted and thus the data are not available to allow further analysis of this issue in the systems studied.

Plots of the individual shock loading studies conducted in the CFB and the SBB during Phase 3, track studies performed during the REACT period in the SBB, typical effluent CO₂ and O₂ concentrations for the first 5 minutes of the FEED period during Phase 3, plots of the
individual profiles studies conducted during Phase 3 in both the CFB and the CFB, and plots of
the influent VOC concentrations in the CFB during the 15 minutes prior and during the 15
minutes after the end of the shock loading are presented in Appendix C.

4.3.3. Phase 3 Shock Loading (Active Control Strategy)

In addition to the studies described in the previous section, during Phase 3 shock loading
conditions, experiments were also conducted during which the SBB was operated using an active
control strategy as described in Section 3.5.2. In this case, the EBRT of the SBB was adjusted
to 30 sec from an initial value of 15 sec (i.e., the flow rate decreased to one-half of the original
value) to simulate conditions where an operator simultaneously diverts contaminated air to all
biofilters in a SBB system containing two biofilters constructed in parallel and operated in
sequence. It is anticipated that an operator could make such adjustments to the SBB loading
strategy when on-line instrumentation or process knowledge indicates that higher than normal
VOC concentrations are present in the influent to the gas treatment system. Because the influent
toluene and MEK concentrations in the SBB increased by a factor of five and the gas flow rate
decreased by a factor of two, the toluene and MEK loading rates increased by a factor of 2.5 (to
68 g m$^{-3}$ h$^{-1}$ and 157 g m$^{-3}$ h$^{-1}$, respectively) when compared to normal loading conditions.
Because active control strategies are not possible in a continuous-flow biofilter, the CFB was
operated exactly as it was operated in prior shock loading experiments conducted during Phase 3.

During Phase 3, the SBB was exposed to the active-control shock-loading conditions on	hree separate occasions (days 272, 274, and 280). For comparison purposes, the CFB was also
subjected to shock loading conditions on days 272 and 275.

Effluent toluene, MEK and CO$_2$ concentrations during the shock loading events in the
CFB (average data from days 272 and 275) are show in Figure 4.26. As shown in the figure,
MEK was detected in the effluent 7 minutes after the beginning of the shock loading and increased to a maximum concentration of 213 ppm, after an additional 58 minutes (65 minutes after the shock loading began) and then subsequently decreased to below the detection limit after 55 additional minutes (120 minutes after the shock loading began).

Figure 4.26: Contaminant influent concentrations during shock loading (top) and typical results of shock loading experiments conducted during Phase 3 in the CFB (bottom).

Toluene was detected in the effluent starting one minute after the beginning of the shock loading. The toluene concentration increased to a maximum concentration of 33 ppm, and
remained in that value until the end of the shock loading (60 minutes after the shock loading began). Immediately after the end of the shock loading period, the toluene concentration decreased to below the detection limit in less than two minutes. The overall pattern of contaminant breakthrough and CO$_2$ production in the CFB was similar to that observed in earlier shock loadings conducted in Phase 3. As was the case in prior shock loading events, the loading rate clearly exceeded the degradation capacity of the system.

The average MEK minimum instantaneous removal efficiency (calculated using Equation. 3.4) for the CFB during the shock loading events was –139.5%. The average toluene minimum instantaneous removal efficiency was –23.0%. The average combined minimum instantaneous removal efficiency (on a mass basis) was –105.5%. The average overall MEK removal efficiency (calculated using Equation 3.5) was 54.5%. The average overall toluene removal efficiency (calculated using the same procedure) was 77.7%. Accounting for both MEK and toluene, the average overall percentage of contaminant mass removed in the CFB was 61.5%.

As mentioned before, three active-control shock-loading tests were conducted in the SBB. Effluent toluene, MEK, and CO$_2$ concentrations during the FEED period of these shock-loading events (average data from days 272, 274 and 280) are depicted in Figure 4.27. As shown in the Figure, the effluent MEK concentration during the first 45 minutes of the shock loading period remained below the instrument detection limit, but in the last 15 minutes it increased to a maximum value of 5.0 ppm$_v$. The effluent toluene concentration increased to a maximum value of 4.5 ppm$_v$ after the first three minutes and remained at that value during the following 57 minutes of the shock-loading period. No MEK or toluene was detected in the effluent of the
SBB during the subsequent FEED period (after the REACT period that followed the shock-loading FEED period).

The average MEK minimum instantaneous removal efficiency (calculated using Equation. 3.4) for the SBB during the active-control shock loading events conducted in Phase 3 was 98.7%. The average toluene minimum instantaneous removal efficiency was 95.3%. The average combined minimum instantaneous removal efficiency on a mass basis was 97.7%. The
average overall MEK removal efficiency (calculated using Equation 3.5) for the SBB during the active-control shock loading events was 99.8%. The average overall toluene removal (calculated using the same procedure) was 96.7%. Accounting for both MEK and toluene, the average overall percentage of contaminant mass removed was 98.9%.

The overall pattern of CO$_2$ production in the biofilter during the FEED period was similar to that observed in earlier phases. Direct GC measurements of the toluene and MEK concentrations (data not shown) performed during the REACT period confirmed that both toluene and MEK were below the detection limit after 15 minutes and remained below the detection limit for the following 45 minutes. This clearly indicates that the contaminants sorbed and/or accumulated by organisms during the shock loading cycle were biotransformed during the REACT period following the shock-loading event.

Table 4.4 summarizes results from shock loadings experiments conducted during Phase 3 in which the SBB was operated using an active control strategy. For comparison purposes, the results of the shock loadings studies conducted in the CFB at the same period of time are summarized in the same table.

According to the results presented in the Table, the application of the active control strategy during Phase 3 shock loading clearly resulted in more complete contaminant removal during the transient period of elevated contaminant loading than would have otherwise occurred. Moreover, the SBB demonstrated a superior performance than the CFB, while operated using an active control strategy, even though that both the SBB and the CFB received the same loading of contaminants during this particular experiment.

In the particular case of a SBB system containing two biofilters constructed in parallel and operated in sequence, the conditions prevailing during the shock loading period would be the
same for both biofilters (i.e., both biofilters would simultaneously undergo a FEED period); however, the sequence of operation in one of the two biofilters would need to be altered in the next period of operation (i.e., FEED or REACT) in order to satisfy conditions of continuous flow in the whole system. Therefore, the performance of each of the biofilters may be different during the shock loading and subsequent periods of operation.

Table 4.4: Summary of biofilter performance during shock loading experiments conducted in Phase 3 (Active control strategy)

<table>
<thead>
<tr>
<th>VOC</th>
<th>Continuous Flow Biofilter (CFB)</th>
<th>Regular Shock-loading</th>
<th>Sequencing Batch Biofilter (SBB)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range of Removal Efficiency (%)</td>
<td>Average Removal Efficiency (%)</td>
<td>Range of Minimum Instantaneous Removal (%)</td>
</tr>
<tr>
<td>Toluene</td>
<td>77.4 – 78.0</td>
<td>77.7</td>
<td>-24 – -22.0</td>
</tr>
<tr>
<td>MEK</td>
<td>53.6 – 55.4</td>
<td>54.5</td>
<td>-141 – -138</td>
</tr>
<tr>
<td>Combined</td>
<td>60.8 – 62.2</td>
<td>61.5</td>
<td>-106 – -105</td>
</tr>
<tr>
<td>Toluene</td>
<td>94.2 – 98.8</td>
<td>96.7</td>
<td>93.0 – 97.0</td>
</tr>
<tr>
<td>MEK</td>
<td>99.6 – 99.9</td>
<td>99.8</td>
<td>98.0 – 99.0</td>
</tr>
<tr>
<td>Combined</td>
<td>98.0 – 99.6</td>
<td>98.9</td>
<td>97.0 – 98.0</td>
</tr>
</tbody>
</table>

During the active control strategy tested in Phase 3 active-control shock loading conditions, the monitored SBB experienced a REACT period before and after the shock-loading event. Therefore, the second SBB in the system of two biofilters would have experienced a FEED period prior and after the shock loading event. The fact that the monitored SBB in the system experienced REACT periods before and after the shock loading event could have lead to a better removal efficiency when compared to the other hypothetical SBB in the system. The results achieved during the active control strategy tested in the SBB were also compared with the results
obtained during Phase 2 shock loading conditions in the SBB and the CFB because the loading rates were equivalent. Clearly, the average results achieved during the active control strategy tested in Phase 3 were very similar when compared to the average results achieved during the shock loading condition tested during Phase 2 in the SBB. When compared to the behavior of the CFB during Phase 2 shock loading experiments, accounting for both MEK and toluene, the average overall percentage of contaminant mass removed was approximately 17% higher in the SBB.

Plots of the individual shock loading studies conducted in the CFB, and the SBB while operated using an active control strategy during Phase 3 and track studies performed during the REACT period in the SBB are presented in the Appendix D.

4.4. Biomass Distribution Tests

As described in Section 3.5.4, the spatial distribution of biomass within the two biofilters was measured at various time intervals during the last 9 days of Phase 2 and during Phase 3 operation. Figure 4.28 depicts the spatial distribution of biomass within the system for both the CFB and SBB. Figure 4.29 depicts the total volume of biomass accumulated within the systems over time. As shown in Figure 4.28, the volume of biomass accumulated in the first two sections of the CFB (those closest to the inlet) was clearly higher than that in the upper sections (those closest to the outlet). This is consistent with the contaminant removal and CO₂ concentrations measured as a function of height in the CFB (see Figure 4.16) which indicate that the majority of contaminant mass was removed in the sections closest to the inlet. This is also consistent with previous reports of continuous-flow systems where excess microbial growth near the biofilter inlet can cause clogging (Chou and Cheng, 1997; Smith et al., 1998; Song and Kinney, 2001).
In somewhat of a contrast, the SBB presented more spatially homogenous biomass (see Figure 4.28). This is expected from a system that utilizes batch operating strategies because the recirculating air through the filter medium during REACT allows a portion of the electron donors and electron acceptors to be more uniformly distributed throughout the filter medium.

Figure 4.28: Spatial distribution of biomass within the biofilter systems: CFB (top) and SBB (bottom).
As shown in Figure 4.29, both the CFB and the SBB presented almost the same rate of overall biomass accumulation in the whole column between each of the times that biomass was wasted from the systems. Moreover, the effect of the biomass wasting technique in terms of volume of wet biomass removed is clearly appreciated in both of the figures.

![Figure 4.29: Overall volume of biomass accumulated within the biofilter systems.](image)

**Figure 4.29:** Overall volume of biomass accumulated within the biofilter systems.

To facilitate a mass balance on carbon in the SBB, the data presented in Figure 4.29 for the SBB was used to calculate the volume of air recirculated within the SBB at various time intervals. This involved measuring the volume of the empty reactor column and the gas washing bottle (see Figure 3.1) using a water displacement protocol. The volume of the tubing associated with the recirculation line in the apparatus was calculated using the tubing length and diameter. The volume of air recirculated in the system was calculated by subtracting the mass of wet biomass volume, the volume of dry packing medium, and the volume of the glass marbles placed
in the inlet from the total volume of the empty system. The volume of air recirculated in the SBB at various time intervals is depicted in Figure 4.30.

![Sequencing Batch Biofilter](image)

**Figure 4.30: Volume of air recirculated in the SBB at various time intervals.**

### 4.4.1. Head Loss Tests

Each time that the spatial distribution of biomass within the system was determined during Phase 3 of operation, head loss across the packed bed was measured. During the first three measurements, the air flow rates were 10.2 and 20.4 L/min for the CFB and the SBB, respectively. During the remaining days of monitoring, the air flow rates were 20.4 and 40.8 L/min for the CFB and the SBB, respectively.

Figure 4.31 depicts the head loss (expressed as cm of H\textsubscript{2}O) across the packed bed depth for both the CFB and SBB. As shown in the figure, the SBB had considerably less head loss than the CFB, even though that the SBB received twice the air flow rate of the CFB. Also, the rate of increment of head loss in the CFB between the days of biomass wasting was considerably
higher when compared to the SBB reaching values greater than 45 cm of H$_2$O. This was likely the result of excessive biomass accumulation in the lower section of the column. In contrast, the increase of head loss in the SBB between the biomass wasting events was considerably lower reaching a maximum value of 6.5 cm of H$_2$O. This was likely due to a more spatially homogenous growth of microorganisms. As shown in Figure 4.31, the biomass wasting technique was effective to decrease the head loss in both the CFB and the SBB.

![Figure 4.31: Head loss across the packing material in both the CFB and the SBB.](image)

Although the use of batch operating strategies offered no significant advantage with respect to overall biomass accumulation, it promoted a more even distribution of biomass within the biofilter system. Clearly, the SBB exhibited better performance in terms of head loss. In contrast, the CFB exhibited greater pressure drops as a result of the accumulation of excess biomass on the packing media in the inlet section (bottom section of the columns) where the greatest contaminant removal took place. The excess biomass also reduced the specific surface
area, potentially resulting in mass transfer limitations. This may have limited contaminant removal capacity.

4.5. Carbon Balance in the Biofilter Systems

Because several parameters involving carbon input to and removed from the biofilters were not measured, a complete carbon balance on the biofilters is not possible. Specifically, the quantity of biomass present in the biofilters at the start of operation is unknown (i.e., the concentration of suspended solids in the inoculation culture before and after the inoculation procedure was not measured), and the quantity of incidental biomass removed from the system during the weekly nutrient addition procedures is unknown, and the carbon content of biomass intentionally wasted from the systems on days 164, 233 and 284 was not measured. Nevertheless, after making several assumptions regarding the parameters that were not measured, carbon balances on the two biofilters were conducted and comparisons were made to verify whether the measurements appear reasonable. The procedures used to calculate the various parameters involved in the carbon balance are described in the following sections.

4.5.1. Carbon Entering the Systems

For each of the three phases of operation, the mass of carbon entering each biofilter as MEK (hereafter referred to as MEK-C) during normal operation was calculated as the mass flow rate of MEK entering the system during normal loading (g/day) multiplied by the total duration of normal loading (d) and multiplied by the grams of carbon per gram of MEK (48 g MEK-C per 72 g MEK). Likewise, the mass of carbon entering each system as toluene (hereafter referred to as toluene-C) during normal operation was calculated as the mass flow rate of toluene entering the system during normal loading (g/day) multiplied by the total duration of normal loading and multiplied by the grams of carbon per gram of toluene (84 g toluene-C per 92 g toluene). For
each of the three phases of operation, the mass of carbon entering each biofilter as MEK during
shock loading was calculated as the mass flow rate of MEK entering the system during shock
loading (g/day) multiplied by the total duration of shock loading (d) and then multiplied by the
grams of carbon per gram of MEK. Likewise, the mass of carbon entering each system as
toluene during shock loading was calculated as the mass flow rate of toluene entering the system
during shock loading (g/day) multiplied by the total duration of shock loading and then
multiplied by the grams of carbon per gram of toluene. Tables 4.5 and 4.6 summarize the mass
of MEK-C and toluene-C entering the CFB and SBB during normal and shock loading operation.

For both normal loading and shock loading calculations, the mass flow rates of MEK and
toluene entering the system used in the calculations described above were the target loading
rates. As described previously in this Chapter, the measured loading rates closely matched the
target loading rates.

As shown in the tables, the mass of MEK and toluene entering the SBB during shock
loading was higher than that entering the CFB. This results from the fact that although the
duration of each shock loading event, the contaminant concentrations during the shock loading,
and the number of shock loadings to each biofilter were identical, the gas flow rate to the SBB
was three times higher than that of the CFB during Phase 1 and two times higher than that of the
CFB during Phases 2 and 3. This resulted in the total mass of MEK and toluene entering the
SBB during shock loading to be more than twice as high for the CFB. Because the shock
loading periods comprised a relatively minor fraction of the total period of biofilter operation,
the total mass of MEK-C and toluene-C entering the two biofilters were quite similar.
Table 4.5: Mass of constituents entering the CFB.

<table>
<thead>
<tr>
<th>Period of Operation</th>
<th>Normal Loading</th>
<th>Shock Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass MEK (g)</td>
<td>Mass MEK-C (g)</td>
</tr>
<tr>
<td>Phase 1 (days 0-137)</td>
<td>315</td>
<td>210</td>
</tr>
<tr>
<td>Phase 2 (days 138-172)</td>
<td>117</td>
<td>78.2</td>
</tr>
<tr>
<td>Phase 3 (days 173-284)</td>
<td>851</td>
<td>567</td>
</tr>
<tr>
<td>TOTAL</td>
<td>1283</td>
<td>855.2</td>
</tr>
</tbody>
</table>

Table 4.6: Mass of constituents entering the SBB.

<table>
<thead>
<tr>
<th>Period of Operation</th>
<th>Normal Loading</th>
<th>Shock Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass MEK (g)</td>
<td>Mass MEK-C (g)</td>
</tr>
<tr>
<td>Phase 1 (days 0-137)</td>
<td>315</td>
<td>210</td>
</tr>
<tr>
<td>Phase 2 (days 138-172)</td>
<td>117</td>
<td>78.2</td>
</tr>
<tr>
<td>Phase 3 (days 173-284)</td>
<td>851</td>
<td>567</td>
</tr>
<tr>
<td>TOTAL</td>
<td>1283</td>
<td>855.2</td>
</tr>
</tbody>
</table>

4.5.2. CO₂ Production in the Continuous Flow Biofilter (CFB)

The CO₂ concentration entering the two biofilters was measured on 10 separate days. On each of these days, the CO₂ concentration (measured in terms of ppm, using the Innova Instrument – see Section 3.7.1) was measured over a 30-minute interval and then the average influent concentration over that interval was calculated. The average influent CO₂ concentration was 449 ppm, (average for the 10 separate days).

For each of the days when effluent CO₂ concentrations were measured during normal loading conditions in the CFB, the average effluent CO₂ concentration was measured over a 20-minute period, and the average effluent concentration during that period was calculated. The increase in CO₂ concentration across the height of the biofilter was then calculated by subtracting the average influent CO₂ concentration from the effluent concentration. Data for the CO₂
production in the CFB during normal loading conditions are depicted below in Figure 4.32 along with lines indicating the CO$_2$ production expected from mineralization of the influent MEK and toluene during each of the three phases of operation. Arrows in the figure indicate days when biomass wasting was conducted.

![Graph showing CO$_2$ production and CO$_2$ expected from mineralization during normal loading conditions in the CFB](image)

**Figure 4.32:** CO$_2$ production and CO$_2$ expected from mineralization during normal loading conditions in the CFB (arrows indicate days when biomass wasting was conducted).

The rate of CO$_2$ production in the biofilter was then calculated by multiplying the increase in CO$_2$ concentration across the biofilter (expressed as ppm$_v$) by a conversion factor to obtain units of g/L, and then multiplying by the air flow rate (in L/day). Then, the average mass of CO$_2$ produced per day was calculated for each of the three phases of operation. Finally, the mass of CO$_2$ produced during normal loading during each of the three phases was calculated using the average daily CO$_2$ production rate after accounting for time intervals when the biofilter was not subjected to normal loading (i.e., when it was subjected to shock loading or endogenous loading conditions). The mass of CO$_2$ produced during normal loading in the CFB during each
of the three phases of operation is summarized in Table 4.7 along with the total mass of CO$_2$ produced during normal loading during the 284 days considered for this study (total of all three phases of operation). Along with the mass of CO$_2$ produced, the table also summarizes the data in terms of CO$_2$-C (mass of carbon present in the form of CO$_2$).

For each of the days when a shock loading experiment was conducted in the CFB and the effluent CO$_2$ concentration was measured over time, the mass of CO$_2$ produced during the shock loading event was calculated averaging the data collected in a time window of 90 minutes starting at the beginning of the shock loading. The average influent CO$_2$ concentration was subtracted from the average effluent CO$_2$ concentration (ppm$_v$) calculated for the 90-min period. The average CO$_2$ concentration produced in the system (expressed as ppm$_v$) was converted to g/L, multiplied by the corresponding air flow rate in L/min to obtain g/min, then multiplied by 90 min to obtain the mass (in g) of CO$_2$ produced during the shock loading. Then, the average mass of CO$_2$ produced per shock loading event was calculated for each of the three phases. The total mass of CO$_2$ produced during the shock loading events for each phase of operation was then calculated by multiplying the average CO$_2$ produced per shock loading event by the number of shock loading events during the phase. The mass of CO$_2$ produced in the CFB during shock loading is summarized in Table 4.7. The mass of CO$_2$ produced during shock loading was calculated following this procedure because the effluent CO$_2$ concentration was not measured during all of the shock loading events (e.g., those associated with profile measurements). This calculation procedure assumed that the effluent CO$_2$ concentration returned to the “normal” level within 30 minutes after the shock loading ended.
Table 4.7: Mass of CO₂ produced in the CFB.

<table>
<thead>
<tr>
<th>Period of Operation</th>
<th>Mass CO₂ (g)</th>
<th>Mass CO₂-C (g)</th>
<th>Mass CO₂ (g)</th>
<th>Mass CO₂-C (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase 1 (days 0-137)</td>
<td>1009</td>
<td>275</td>
<td>18.1</td>
<td>4.93</td>
</tr>
<tr>
<td>Phase 2 (days 138-172)</td>
<td>488</td>
<td>133</td>
<td>8.26</td>
<td>2.25</td>
</tr>
<tr>
<td>Phase 3 (days 173-284)</td>
<td>3101</td>
<td>846</td>
<td>25.9</td>
<td>7.06</td>
</tr>
<tr>
<td>TOTAL</td>
<td>4598</td>
<td>1254</td>
<td>52.3</td>
<td>14.2</td>
</tr>
</tbody>
</table>

4.5.3. CO₂ Production in the Sequencing Batch Biofilter (SBB)

The mass of CO₂ produced in the SBB during normal loading conditions was calculated using a slightly different procedure than was used for the CFB because of the unsteady-state nature of the system and data available. For Phase 1, the average effluent CO₂ concentrations during the first 5 minutes of the FEED period was calculated using CO₂ concentrations measured at 1-second intervals using the Servomex analyzer (see section 3.7.3). The average effluent CO₂ concentrations during the first 5 minutes of the FEED period calculated during Phase 1 were also used for the calculations conducted during Phase 2 and Phase 3 due to the fact that these types of measurements during the first 5 minutes of the FEED period were not conducted during Phase 2 and Phase 3 during normal loading conditions. For each of the three phases, the average CO₂ concentration during the remainder of the FEED period was calculated using data from the Innova Instrument – see Section 3.7.1). The average influent CO₂ concentration was then subtracted from the time-weighted average effluent CO₂ concentration to calculate the increase in CO₂ concentration across the system during the FEED period. Data for the CO₂ production in the SBB during normal loading conditions are depicted below in Figure 4.33 along with lines indicating the CO₂ production expected from mineralization of the influent MEK and toluene during each of the three phases of operation. Arrows in the figure indicate days when biomass wasting was conducted.
Figure 4.33: CO₂ production and CO₂ expected from mineralization during normal loading conditions in the SBB (arrows indicate days when biomass wasting was conducted).

For each of the three phases of operation, the average CO₂ concentration produced in the system during the FEED periods (in ppm) was converted to g/L, multiplied by the corresponding air flow rate in L/min to obtain g/min, then multiplied by the length of the FEED period (in min) to result in the average mass of CO₂ produced per cycle in the SBB. The mass of CO₂ produced during normal operation was then calculated by multiplying the average mass of CO₂ produced per FEED period by the number of normal loading FEED periods in the phase of operation.

As discussed in previous sections of this chapter, throughout all three phases of experiments, oxygen was consumed and CO₂ was produced in the closed biofilter system during the SBB’s REACT periods. Subsequently, at the start of the FEED periods, the effluent CO₂ concentration increased rapidly to a maximum value within the first 10 seconds after the FEED period began and air flow through the biofilter resumed. Consequently, CO₂ produced in the
SBB as a result of contaminants accumulated in the system during shock loading conditions were actually emitted from the biofilter during the FEED period following the shock loading FEED period. To account for this in calculating the mass of CO₂ produced during shock loading, the average effluent CO₂ concentrations during the first 5 minutes of the FEED period following the shock loading FEED period was calculated using CO₂ concentrations measured at 1-second intervals using the Servomex analyzer (see section 3.7.3). The average CO₂ concentration during all but the first 5-minutes of the shock loading FEED period was calculated using data from the Innova Instrument – see Section 3.7.1). For the purposes of this carbon balance, the mass of CO₂ produced during the shock loading events was calculated using the time-weighted average effluent CO₂ concentration during the first five minutes of the FEED period following shock loading and all except for the first five minutes of the shock loading FEED period itself. The average influent CO₂ concentration was then subtracted from the time-weighted average effluent shock loading CO₂ concentration to calculate the increase in CO₂ concentration across the system during the shock loading FEED period. For each of the three phases of operation, the average CO₂ concentration produced in the system during the shock loading FEED periods (in ppmₐ) was converted to g/L, multiplied by the corresponding air flow rate in L/min to obtain g/min, then multiplied by the length of the FEED period (in min) to result in the average mass of CO₂ produced per cycle of shock loading in the SBB. The total mass of CO₂ produced during the shock loading events for each phase of operation was then calculated by multiplying the average CO₂ produced per shock loading event by the number of shock loading events during the phase.

The mass of CO₂ produced in the SBB during both normal and shock loading during each of the phases is summarized below in Table 4.8. The data are also presented in terms of CO₂-C.
Table 4.8: Mass of CO\textsubscript{2} produced in the SBB.

<table>
<thead>
<tr>
<th>Period of Operation</th>
<th>Normal Loading</th>
<th>Shock Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass CO\textsubscript{2} (g)</td>
<td>Mass CO\textsubscript{2}-C (g)</td>
</tr>
<tr>
<td>Phase 1 (days 0-137)</td>
<td>1188</td>
<td>324</td>
</tr>
<tr>
<td>Phase 2 (days 138-172)</td>
<td>539</td>
<td>147</td>
</tr>
<tr>
<td>Phase 3 (days 173-284)</td>
<td>3405</td>
<td>929</td>
</tr>
<tr>
<td>TOTAL</td>
<td>5132</td>
<td>1400</td>
</tr>
</tbody>
</table>

4.5.4. Mass of Contaminants Escaping the Biofilters

The overall average removal efficiency for each of the contaminants during normal loading in Phase 1 was calculated using a time weighted average of the data available for the removal efficiencies (calculated as described in section 3.5.5) for two separate time intervals of Phase 1: when 100% removal was observed, and when it was not (i.e., the first 30 days) in both the CFB and the SBB. Then, the overall fraction of each contaminant escaping the system was multiplied by the total mass of each contaminant loaded to the system during normal loading in Phase 1 to calculate the corresponding mass of contaminants escaping the systems. During Phase 2 and Phase 3 there was no measured breakthrough observed during normal loading.

In order to calculate the mass of contaminants escaping the systems during shock loading in each of the three phases of operation, the average removal efficiency of each of the contaminants in each of the phases (calculated as described in section 3.5.5) was used to calculate the corresponding fraction emitted, by difference, and the calculated fraction was multiplied by the total mass of each of the contaminants loaded to the systems during the shock loadings to obtain the mass of each contaminant emitted during shock loading in each phase of operation. The same procedure was used for both the CFB and the SBB.
The results are summarized in Table 4.9 as masses of MEK and toluene emitted during normal loading and shock loading for the CFB during each of the three phases of operation. Also, the total mass of contaminants emitted during the 284 days considered for this study (total of all three phases of operation) is presented. Along with the masses of contaminants emitted, the table also summarizes the data in terms of MEK-C and toluene-C (mass of carbon present in the form of MEK and toluene). Table 4.10 summarizes the results for the SBB.

Table 4.9: Mass of constituents exiting the CFB.

<table>
<thead>
<tr>
<th>Period of Operation</th>
<th>Normal Loading</th>
<th>Shock Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MEK (g)</td>
<td>MEK-C (g)</td>
</tr>
<tr>
<td>Phase 1 (days 0-137)</td>
<td>3.2</td>
<td>2.1</td>
</tr>
<tr>
<td>Phase 2 (days 138-172)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Phase 3 (days 173-284)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>3.2</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 4.10: Mass of constituents exiting the SBB.

<table>
<thead>
<tr>
<th>Period of Operation</th>
<th>Normal Loading</th>
<th>Shock Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MEK (g)</td>
<td>MEK-C (g)</td>
</tr>
<tr>
<td>Phase 1 (days 0-137)</td>
<td>5.4</td>
<td>3.6</td>
</tr>
<tr>
<td>Phase 2 (days 138-172)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Phase 3 (days 173-284)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>5.4</td>
<td>3.6</td>
</tr>
</tbody>
</table>

4.5.5. Biomass Carbon

The mass of carbon present in biomass (hereafter referred to as biomass-C) wasted from the system or remaining in the system at the end of the experiment was estimated using data
from the water displacement studies (see Section 4.4.). Based on water displacement measurements, the volume of wet biomass removed from the CFB was 0.55 L on day 164, 1.55 L on day 233 and 2.15 L on day 284, while approximately 1.6 L remained in the system on day 284 (total of 5.85 L wet biomass removed from the CFB during the biomass wasting process or present at the end of the time period considered for the carbon balance). Likewise, for the SBB, the volume of wet biomass removed from the system was 0.93 L on day 164, 1.3 L on day 233 and 1.4 L on day 284, while approximately 2.1 L remained in the system on day 284 (total of 5.73 L wet biomass removed from the SBB during the biomass wasting process or present at the end of the time period considered for the carbon balance).

For purposes of the carbon balance, it was assumed that: 1) the wet biomass had a density of 1100 g/L; 2) the wet biomass was 92% water on a mass basis (see section 4.8); and 3) dry biomass is 50% carbon by mass. Using these three assumptions and the volume of wet biomass removed from the biofilters during the biomass wasting process and that present at the end of the experiment, the mass of biomass-C produced in the CFB and SBB were calculated to be 257.4 and 252.2 g biomass-C, respectively.

For purposes of the carbon balance, the mass of biomass-C present at the start of the experiment (from the inoculum) was assumed to be negligible. The mass of biomass-C removed from the systems during cleaning of biofilter components at various time intervals was also assumed to be negligible as was the quantity of biomass-C removed from the biofilters during the nutrient addition procedures.

4.6. Carbon Balance Comparison and Discussion

Figure 4.34 depicts the total mass of MEK-C and toluene-C entering the CFB (total of 284 days of operation) during both normal and shock loading conditions. The figure also depicts
the mass of CO₂ produced in the system (during both normal and shock-loading operation), the masses of MEK-C and toluene-C escaping the system untreated (during both normal and shock-loading operation) and the mass of biomass-C removed from the CFB during the biomass wasting process or present at the end of the experiment. Figure 4.35 depicts corresponding data for the SBB.

![CFB - Carbon Balance](image)

**Figure 4.34:** Total mass of MEK-C and toluene-C entering the CFB during both normal and shock loading conditions. Mass of CO₂-C produced in the system and masses of MEK-C and toluene-C escaping the system untreated during both normal and shock loading operation. Mass of biomass-C removed from the CFB during the biomass wasting process or present at the end of the experiment.

For the CFB, the total mass of carbon entering the system as MEK or toluene was 1404 g, and the total mass of carbon exiting the system as CO₂, MEK, or toluene plus the carbon associated with biomass removed from the system or remaining at the end of the experiment on day 284 was 1550 g. For the SBB, the total mass of carbon entering the system as MEK or toluene was 1443 g, and the total mass of carbon exiting the system as CO₂, MEK, or toluene
plus the carbon associated with biomass removed from the system or remaining at the end of the experiment on day 284 was 1693 g.

The difference between the mass of carbon entering the system and that accounted for by the mass of carbon exiting the system or being present as biomass at the end of the experiment was 10.4 and 17.3 % of the influent carbon mass for the CFB and SBB, respectively. The calculated percentage of difference between the mass of carbon entering and exiting the biofilter systems is in the expected range. Taking into account all the assumptions those were made in order to make all the required calculations, a deviation from the actual values is not surprising.

The total mass of MEK degraded by the CFB and SBB (calculated as the total mass MEK influent minus the total mass effluent) was 1298.5 and 1339 g, respectively. The mass of toluene

Figure 4.35: Total mass of MEK-C and toluene-C entering the SBB during both normal and shock loading conditions. Mass of CO₂-C produced in the system and masses of MEK-C and toluene-C escaping the system untreated during both normal and shock loading operation. Mass of biomass-C removed from the SBB during the biomass wasting process or present at the end of the experiment.

The difference between the mass of carbon entering the system and that accounted for by the mass of carbon exiting the system or being present as biomass at the end of the experiment was 10.4 and 17.3 % of the influent carbon mass for the CFB and SBB, respectively. The calculated percentage of difference between the mass of carbon entering and exiting the biofilter systems is in the expected range. Taking into account all the assumptions those were made in order to make all the required calculations, a deviation from the actual values is not surprising. The total mass of MEK degraded by the CFB and SBB (calculated as the total mass MEK influent minus the total mass effluent) was 1298.5 and 1339 g, respectively. The mass of toluene
degraded by the CFB and SBB was 562 and 590 g, respectively. Using balanced stoichiometric equations for mineralization of MEK and toluene (see equations 4.1 and 4.2), the COD equivalent of the degraded contaminants was calculated. For the CFB, the total mass of COD degraded by the system was 4927.5 g COD. For the SBB, the total mass of COD degraded by the system was 5114 g COD.

\[
\begin{align*}
(-1 \text{ g}) \text{C}_7\text{H}_8 + (-3.13 \text{ g}) \text{O}_2 & \rightarrow (3.347 \text{ g}) \text{CO}_2 + (0.782 \text{ g}) \text{H}_2\text{O} & \text{(4.1)} \\
(-1 \text{ g}) \text{C}_4\text{H}_8\text{O} + (-2.44 \text{ g}) \text{O}_2 & \rightarrow (2.44 \text{ g}) \text{CO}_2 + (1 \text{ g}) \text{H}_2\text{O} & \text{(4.2)}
\end{align*}
\]

The estimated yield of biomass in the two systems was then calculated dividing the total mass of dry biomass removed from the biofilters during the biomass wasting process and that present at the end of the experiment (calculated in Section 4.5.5) by the total mass of COD degraded by each biofilter system. Therefore, the calculated yield of biomass for the CFB was approximately 0.104 g biomass (dry basis) produced per 1.0 g COD consumed. For the SBB, the calculated yield of biomass was approximately 0.098 g biomass (dry basis) produced per 1.0 g COD consumed. Thus, although a completely rigorous carbon balance on the system was not possible because some parameters were not measured, the data appear to be reasonable. The low yield could be explained because of the use of nitrate versus ammonia as a nitrogen source and also an enhanced endogenous decay resulting from a long solids residence time in the moist environment. The relatively low yield and corresponding rate of biomass accumulation likely benefited both CFB and SBB systems due to a low rate of loss of specific surface area.

4.7. Carbon Accumulated during the REACT Period in the SBB

Accumulation of undegraded contaminants during the FEED period and the subsequent biodegradation during the REACT period is a fundamental characteristic of the operation of Sequencing Batch Biofilters. CO₂ data collected during Phases 1 and 3 were used to estimate the
amount of carbon produced in the SBB during REACT periods associated with endogenous, normal, and shock loading conditions.

To calculate the mass of CO$_2$ produced during normal operation conditions in the SBB during Phase 1, the CO$_2$ concentration (expressed as ppm$_v$) measured at the end of the REACT period of two separate normal loading track studies (data from days 121 and 128) were averaged, multiplied by a conversion factor to obtain units of g/L, and multiplied by the average total gas volume (in L) recirculated in the closed system during the REACT period. The total volume of gas recirculated in the system during the REACT period was calculated using the average of data from water displacement tests on days 124 and 132 and accounted for the volume of gas contained in the recirculation tubing, packed bed sections, inlet and outlet sections, and other components. The mass of CO$_2$-C accumulated in the system at the end of the REACT period was then calculated from the mass of CO$_2$.

For comparison purposes, the mass of CO$_2$ produced during endogenous loading conditions in the SBB during Phase 1 was calculated in a similar manner to that described above. In this case, CO$_2$ concentrations measured at the end of REACT during two track studies conducted during endogenous loading on days 123 and 128 were averaged in order to calculate the mass of CO$_2$ produced in the REACT period during endogenous loading conditions.

The mass of CO$_2$ produced during shock loading conditions in the SBB during Phase 1 was calculated in a similar manner to the mass calculated during normal and endogenous loading, as described above. In this case, CO$_2$ concentrations measured at the end of REACT during four track studies conducted during shock loading on days 112, 114, 119 and 127 were averaged in order to calculate the mass of CO$_2$ produced in the REACT period during shock loading conditions.
Additionally, the same calculation procedures performed for Phase 1 were also performed for Phase 3. The mass of CO₂ produced normal loading conditions in the SBB during Phase 3 was calculated using the average of CO₂ concentrations measured at the end of REACT during three track studies conducted during normal loading on days 228, 229 and 230. The total volume of gas recirculated in the system during the REACT period was calculated using the average of data from water displacement tests on days 189, 197, 205, 216, 224, 233, and 241 and as before accounted for the volume of gas contained in the recirculation tubing, packed bed sections, inlet and outlet sections, and other components. The mass of CO₂-C accumulated in the system at the end of the REACT period was then calculated from the mass of CO₂.

The mass of CO₂ produced during endogenous loading conditions in the SBB during Phase 3 was calculated using the average of CO₂ concentrations measured at the end of REACT during three track studies conducted during endogenous loading on days 251, 252 and 254.

Finally, the mass of CO₂ produced during shock loading conditions in the SBB during Phase 3 was calculated. In this case, CO₂ concentrations measured at the end of REACT during three track studies conducted during shock loading on days 185, 194 and 196 were averaged in order to calculate the mass of CO₂ produced in the REACT period during shock loading conditions. Calculations of CO₂ concentrations, gas volumes, and mass of CO₂ accumulated under the various conditions during Phases 1 and 3 are summarized in Table 4.11. Footnotes listed below the table provide details about which data were used in calculating the various parameters.

It is expected that not all of the carbon-containing constituents accumulated during the FEED period would be transformed to CO₂ during REACT. A portion would also go to cell yield.
Table 4.11: Summarized results of the CO$_2$-C production during REACT in both Phase 1 and Phase 3 of operation during normal and shock loading conditions.

<table>
<thead>
<tr>
<th>Estimation of carbon accumulation in the system during REACT</th>
<th>Phase 1</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average maximum CO$_2$ concentration during endogenous loading (ppm.)</td>
<td>5,335$^a$</td>
<td>4,584$^a$</td>
</tr>
<tr>
<td>Average maximum CO$_2$ concentration during normal loading (ppm.)</td>
<td>6,650$^b$</td>
<td>6,777$^b$</td>
</tr>
<tr>
<td>Average maximum CO$_2$ concentration during shock loading (ppm.)</td>
<td>26,373$^c$</td>
<td>17,400$^d$</td>
</tr>
<tr>
<td>Average volume of gas recirculated in the closed system during REACT (L)</td>
<td>10.9$^d$</td>
<td>10.0$^d$</td>
</tr>
<tr>
<td>Mass of CO$_2$ produced during endogenous loading REACT (mg)</td>
<td>105</td>
<td>83.6</td>
</tr>
<tr>
<td>Mass of CO$_2$ produced during normal loading REACT (mg)</td>
<td>131</td>
<td>123</td>
</tr>
<tr>
<td>Mass of CO$_2$ produced during shock loading REACT (mg)</td>
<td>520</td>
<td>317</td>
</tr>
<tr>
<td>Mass of CO$_2$-C produced during endogenous loading REACT (mg)</td>
<td>28.7</td>
<td>22.7</td>
</tr>
<tr>
<td>Mass of CO$_2$-C produced during normal loading REACT (mg)</td>
<td>35.7</td>
<td>33.7</td>
</tr>
<tr>
<td>Mass of CO$_2$-C produced during shock loading REACT (mg)</td>
<td>141</td>
<td>86.5</td>
</tr>
</tbody>
</table>

$^a$ Calculated using average CO$_2$ concentrations measured on days 123 and 128.
$^b$ Calculated using average CO$_2$ concentrations measured on days 121 and 128.
$^c$ Calculated using average CO$_2$ concentrations measured on days 112, 114, 119, and 127.
$^d$ Calculated using data from water displacement tests conducted on days 124 and 132.
$^e$ Calculated using average CO$_2$ concentrations measured on days 251, 252, and 254.
$^f$ Calculated using average CO$_2$ concentrations measured on days 228, 229, and 230.
$^g$ Calculated using average CO$_2$ concentrations measured on days 185, 194, 196.
$^h$ Calculated using data from water displacement tests conducted on days 189, 197, 205, 216, 224, 233, and 241.

To account for this in estimating the total mass of carbon accumulated in the SBB, the mass of accumulated carbon converted to biomass during REACT was estimated using the following procedure. The ratio of the total mass of biomass-C produced in the SBB (calculated during the carbon balance in Section 4.5.5.) to the total mass of CO$_2$-C exiting the system (also calculated during the carbon balance in Section 4.5.3.) was calculated and assumed to be the same during FEED and REACT. The calculated ratio of mass of biomass-C to mass of CO$_2$-C exiting the system was 0.176. This ratio was then multiplied by the difference of the mass of CO$_2$-C produced during normal loading and the mass of CO$_2$-C produced during endogenous loading to estimate the total mass of biomass-C produced in the REACT period during normal loading conditions. Likewise, the same calculated ratio was also multiplied by the difference of the mass of CO$_2$-C produced during shock loading and the mass of CO$_2$-C produced during endogenous loading to estimate the total mass of biomass-C produced in the REACT period.
during shock loading conditions. This procedure was conducted for both Phase 1 and Phase 3 data.

The calculated masses of CO$_2$-C accumulated during normal and shock loading were added to the corresponding calculated masses of biomass-C produced to obtain the total estimated masses of carbon accumulated during the FEED period during normal and shock loading conditions in Phases 1 and 3. Calculations of the masses of CO$_2$-C accumulated, the masses of biomass-C produced and the total masses of carbon accumulated during the REACT period during normal and shock loading conditions in Phases 1 and 3 are summarized in Table 4.12.

Table 4.12: Summarized results of the total carbon accumulation during FEED in both Phase 1 and Phase 3 of operation during normal and shock loading conditions.

<table>
<thead>
<tr>
<th></th>
<th>Phase 1</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of CO$_2$-C</td>
<td>7.07</td>
<td>10.9</td>
</tr>
<tr>
<td>accumulated during normal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>loading REACT (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass of CO$_2$-C</td>
<td>113.2</td>
<td>63.7</td>
</tr>
<tr>
<td>accumulated during shock</td>
<td></td>
<td></td>
</tr>
<tr>
<td>loading REACT (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass of biomass-C produced during normal</td>
<td>1.24</td>
<td>1.9</td>
</tr>
<tr>
<td>loading REACT (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass of biomass-C produced during shock</td>
<td>19.9</td>
<td>11.2</td>
</tr>
<tr>
<td>loading REACT (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total mass of carbon accumulated during normal</td>
<td>8.31</td>
<td>12.8</td>
</tr>
<tr>
<td>loading REACT (mg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total mass of carbon accumulated during shock</td>
<td>133.1</td>
<td>74.9</td>
</tr>
<tr>
<td>loading REACT (mg)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From the data collected, it is impossible to discern whether the carbon accumulated in the SBB was in the form of MEK, toluene, intermediate metabolites, intracellular storage compounds, or some combination of these. To provide a general indication of the mass of contaminants accumulated, further calculations were performed assuming that all of the accumulated carbon was in the form of only MEK or only toluene.

Based on the total estimated mass of carbon accumulated during REACT, the equivalent masses of MEK or toluene were calculated assuming that the total mass of carbon was associated with only one of the contaminants. The calculations of the estimated masses of each individual contaminant accumulated during the REACT period during normal and shock loading conditions
in Phases 1 and 3 are summarized in Table 4.13. Although the data demonstrate that contaminant accumulation did occur during normal loading FEED periods, as shown in the table, the estimated mass of contaminants accumulated during normal loading FEED periods was small in comparison to the mass of contaminants entering the system during the period. The mass of contaminants entering the system during each normal loading FEED period was 287.5 mg MEK and 130 mg toluene during Phase 1 and 639 mg MEK and 276.7 mg toluene during Phase 3. On a carbon basis, the estimated carbon accumulated during normal loading FEED periods was 2.7% and 1.9% of the entering contaminant-carbon during Phase 1 and 3, respectively.

Table 4.13: Summarized estimate of the total mass of each individual contaminant accumulated during FEED in both Phase 1 and Phase 3 of operation during normal and shock loading conditions.

<table>
<thead>
<tr>
<th>Description</th>
<th>Phase 1</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of MEK accumulated during normal loading REACT (mg)</td>
<td>12.5</td>
<td>19.2</td>
</tr>
<tr>
<td>Mass of toluene accumulated during normal loading REACT (mg)</td>
<td>9.1</td>
<td>14.0</td>
</tr>
<tr>
<td>Mass of MEK accumulated during shock loading REACT (mg)</td>
<td>199.7</td>
<td>112.4</td>
</tr>
<tr>
<td>Mass of toluene accumulated during shock loading REACT (mg)</td>
<td>145.8</td>
<td>82.0</td>
</tr>
</tbody>
</table>

As also shown in the table, the estimated mass of contaminants accumulated during shock loading FEED periods was also quite small in comparison to the mass of contaminants entering the system during the period. The mass of contaminants entering the system during each shock loading FEED period was 1440 mg MEK and 650 mg toluene during Phase 1 and 3200 mg MEK and 1400 mg toluene during Phase 3. On a carbon basis, the estimated carbon accumulated during shock loading FEED periods was 8.6% and 2.2% of the entering contaminant-carbon during Phase 1 and 3, respectively.

4.8. **Batch Sorption Experiments**

To quantify the sorption characteristics of MEK and toluene to the packing medium and its associated biomass, batch isotherm experiments were conducted as described in Section 3.6.
The sorption tests included separate tests to evaluate contaminant sorption to virgin packing medium which had not been used in biofilter experiments, packing medium which was covered with biomass (Foam + Biomass) after long-term use in a biofilter, packing medium that had been subjected to long-term use in a biofilter but had subsequently been treated to remove accumulated biomass (Foam – Biomass), and biomass which had been removed from the packing medium (with no foam packing material). The sorption characteristics of the various mediums were modeled using Freundlich isotherms.

Figures 4.36 and 4.37 depict Freundlich adsorption isotherms for toluene and MEK, respectively. The Freundlich constants ($K_f$ and $1/n$) for each medium tested and contaminant type were calculated along with the correlation coefficients ($R^2$ values). Tables 4.14 and 4.15 summarize the Freundlich parameters for the different media tested.

For toluene sorption to the different media, the $K_f$ value was higher for the virgin foam, than for the packing medium that had been subjected to long-term use in a biofilter and then had been treated to remove accumulated biomass. This was likely because active sites of the activated carbon could be occupied by other components (e.g., extracellular polysaccharides, EPS) after long-term use. Although much lower than for the foam packing media, biomass exhibited some sorption capacity for toluene.

The slopes of the Freundlich adsorption equations for the various mediums tested are not parallel, so a general comparison of parameters is difficult. For MEK sorption to the different media, the higher $K_f$ value was for the virgin foam and the lower value for the packing medium that had been subjected to long-term use in a biofilter and then had been treated to remove accumulated biomass. However, from Figure 4.37 it can be observed that for equilibrium concentrations over 100 mg/L, the sorption of MEK to the biomass, the packing medium that had
been subjected to long-term use in a biofilter and then had been treated to remove accumulated biomass, and the packing medium, which was covered with biomass after long-term use in a biofilter, is higher than the sorption to the virgin foam.

Figure 4.36: Freundlich isotherms adsorption for toluene sorption to various media.

Figure 4.37: Freundlich isotherms adsorption for MEK sorption to various media.
When comparing the sorption characteristics of both toluene and MEK to the same medium, toluene had a higher affinity than did MEK in all cases in the conditions tested. It should be noted; however, that the Henry’s Law constant for MEK is roughly two orders of magnitude smaller than that of toluene (see Table 2.1). During biofiltration, compounds have to be transferred from a gas stream to an aqueous biofilm layer, and the equilibrium MEK concentration would be expected to be much higher than toluene. Thus, although toluene had a higher affinity for the packing media, because MEK was present at a higher concentration in the gas phase and the Henry’s Law constant is much lower, appreciable MEK accumulation would be possible.

Table 4.14: Summary of Freundlich parameters for toluene sorption to various media.

<table>
<thead>
<tr>
<th>Media Tested</th>
<th>Moisture Content (% by weight)</th>
<th>K_f</th>
<th>1/n</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin Foam</td>
<td>5.0</td>
<td>0.00316</td>
<td>1.1536</td>
<td>0.70</td>
</tr>
<tr>
<td>Foam - Biomass</td>
<td>60.5</td>
<td>0.00180</td>
<td>1.294</td>
<td>0.82</td>
</tr>
<tr>
<td>Foam + Biomass</td>
<td>81.5</td>
<td>0.00143</td>
<td>0.8716</td>
<td>0.92</td>
</tr>
<tr>
<td>Biomass</td>
<td>92.0</td>
<td>0.00025</td>
<td>0.7105</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Table 4.15: Summary of Freundlich parameters for MEK sorption to various media.

<table>
<thead>
<tr>
<th>Media Tested</th>
<th>Moisture Content (% by weight)</th>
<th>K_f</th>
<th>1/n</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin Foam</td>
<td>5.0</td>
<td>0.00132</td>
<td>0.2131</td>
<td>0.60</td>
</tr>
<tr>
<td>Foam - Biomass</td>
<td>60.5</td>
<td>0.00026</td>
<td>0.5646</td>
<td>0.90</td>
</tr>
<tr>
<td>Foam + Biomass</td>
<td>81.5</td>
<td>0.00038</td>
<td>0.5128</td>
<td>0.85</td>
</tr>
<tr>
<td>Biomass</td>
<td>92.0</td>
<td>0.00028</td>
<td>0.6377</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Finally, the batch sorption experiments conducted with the packing material of the SBB suggest that contaminants can be accumulated in the biofilter system, and that the overall
accumulation was a combination of sorption to the activated carbon-polyurethane foam packing medium, the biomass and the aqueous phase that is present in the biofilm, and the packing medium. Because the slopes of the Freundlich adsorption equations for the various mediums tested are not parallel, an expected decline in the sorption properties of the packing medium as a result of biofilm growth was not strictly confirmed.
CHAPTER 5 OVERALL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

5.1. Conclusions

Data presented herein established that sequencing batch operation of biofilters treating air contaminated with mixtures of toluene and MEK is not only a feasible technology, it also offers advantages over conventional continuous flow biofilters (CFBs) in several important measures of performance; namely, minimum instantaneous removal efficiency, overall contaminant removal efficiency and head loss.

Both the CFB and the SBB exhibited stable long-term performance with greater than 99% contaminant removal when subjected to “normal” loading conditions consisting of influent toluene concentrations ranging from 28 to 30 ppm and MEK concentrations ranging from 80 to 89 ppm, at average daily loading rates ranging from 4.2 to 13.6 g·m$^{-3}$·h$^{-1}$ toluene and 9.4 to 31.4 g·m$^{-3}$·h$^{-1}$ MEK, when nutrients were added approximately on a weekly basis.

During transient periods of elevated contaminant loading, the SBB system was able to accumulate a portion of the contaminants during the FEED period and subsequently degrade the accumulated pollutants during the following REACT period. The ability of the system to accumulate contaminants during the FEED period was demonstrated even after long-term operation. Once an appropriate operating strategy was selected, the SBB was able to remove more than 99% of the influent contaminant at a transient loading rate of 204.5 g·m$^{-3}$·h$^{-1}$ (toluene plus MEK), more than 99% of the influent contaminant at a transient loading rate of 209 g·m$^{-3}$·h$^{-1}$ (toluene plus MEK) and 87% of the influent contaminant at a transient loading rate of 449.5 g·m$^{-3}$·h$^{-1}$ (toluene plus MEK). The operational flexibility of the SBB system facilitated selection of operational conditions that led to higher overall removal efficiency and higher minimum
instantaneous removal efficiency than was achieved in the CFB, even though that the SBB received twice the contaminant loading of the CFB during the FEED period.

It was demonstrated that application of an active control strategy (e.g., simultaneously loading more than one biofilter in a multiple-biofilter system), made possible by SBB operation, can result in more complete contaminant removal during the transient period of elevated contaminant loading than would have otherwise occurred. This provides an effective alternative for removing contaminants during transient periods of elevated contaminant loading in cases where on-line instrumentation or sufficient process knowledge allow implementation of process control decisions.

Profile studies were conducted in both the CFB and the SBB. During the normal loading conditions, the general pattern of the spatial locations of contaminant removal and CO₂ production was similar for both biofilters. Profile studies conducted during shock-loading conditions revealed stratification in terms of zones of biodegradation for each of the compounds with MEK being more readily degraded than toluene. Toluene removal was adversely affected by the presence of MEK.

Although that the use of batch operating strategies offered no significant advantage with respect to overall quantity of biomass accumulation, it promoted a more even distribution of biomass within the biofilter system. The more homogeneous spatial distribution of biomass throughout the height of the SBB was likely responsible for the better performance observed in the system with respect to head loss. In contrast, the CFB exhibited greater pressure drops and channeling as a result of the accumulation of excess biomass on the packing medium in the inlet section where the greatest contaminant removal took place.
The carbon balance conducted in both the CFB and the SBB did not demonstrated appreciable differences between the systems in terms of biomass accumulation and CO₂ production; however, the yield clearly suggested that the production of biomass within the systems was low enough that provided good operational conditions. Additionally, the calculation of the total mass of carbon accumulated during the REACT period, clearly demonstrated that the SBB is able to sorb contaminants during the FEED period and biodegrade them during REACT.

From the batch sorption experiments, results suggest that contaminants can be accumulated in the biofilter system by some combination of sorption to the activated carbon-polyurethane foam packing medium, the biomass, and the aqueous phase that is present in the biofilm and the packing medium. Results also suggested that the sorption properties of the packing medium, could change after long-term use in a biofilter.

5.2. **Recommendations for Future Research**

Some additional experiments could be conducted to obtain information to answer other important questions in biofiltration research. For example, additional operation strategies could be tested in order to obtain more information of the operational capabilities of the systems. This could be done during, normal and shock loading conditions. Also, different types of packing materials could be tested under sequencing batch operation to see if the overall sorption capacity of the system can be improved. Moreover, the use of an activated carbon buffer in conjunction with the biofilter unit could be evaluated. The active control strategy tested could be repeated simulating all the possible conditions that can take place during the operation of a biofilters system of two or more units. Additional profiles studies could be conducted loading the contaminants at different times to have a better understanding of the way that the contaminants are being biodegraded at different locations in the columns, and also to have a better
understanding of the interactions between microbial populations and substrates. Monitoring of the pH conditions along the height of the columns could be important in future experiments. A more strict control during biomass wasting and nutrient additions could lead to more accurate information for future carbon balances. Fixed bed sorption and desorption studies after a period of biofiltration operation could be also helpful to understand how contaminants are being accumulated in the system. Finally, it is important to consider testing sequencing batch operation in a pilot-scale system to discern whether there are likely to be scale-up issues in full-scale implementation.
REFERENCES


APPENDIX A

INDIVIDUAL PLOTS OF STUDIES CONDUCTED DURING PHASE 1

The appendix A include the plots of the individual shock loading studies conducted in the CFB and the SBB during Phase1, the track studies performed during the REACT period in the SBB, typical effluent CO$_2$ and O$_2$ concentrations for the first 5 minutes of the FEED period during Phase 1, and plots of the individual profiles studies conducted during Phase 1 in the CFB.

Figure A.1: Effluent CO$_2$ and O$_2$ concentration during the first 5 minutes of FEED for normal loading (data from day 106).

Figure A.2: Effluent CO$_2$ and O$_2$ concentration during the first 5 minutes of FEED for normal loading (data from day 106).
Figure A.3: Effluent CO$_2$ and O$_2$ concentration during the first 5 minutes of FEED for normal loading (data from day 121).

Figure A.4: Toluene and MEK concentrations in the SBB during the REACT period during Phase 1 normal loading experiments (data from day 106).

Figure A.5: Toluene and MEK concentrations in the SBB during the REACT period during Phase 1 normal loading experiments (data from day 106).
Figure A.6: CO$_2$ concentrations in the SBB during the REACT period during Phase 1 normal loading experiments (data from day 121).

Figure A.7: CO$_2$ concentrations in the SBB during the REACT period during Phase 1 normal loading experiments (data from day 128).

Figure A.8: CO$_2$, toluene, and MEK concentrations in the CFB along the height of the packing material during a profile study conducted in Phase 1 normal loading experiments (data from day 11).
Figure A.9: CO₂, toluene, and MEK concentrations in the CFB along the height of the packing material during a profile study conducted in Phase 1 normal loading experiments (data from day 18).

Figure A.10: CO₂, toluene, and MEK concentrations in the CFB along the height of the packing material during a profile study conducted in Phase 1 normal loading experiments (data from day 24).
Figure A.11: Typical results of shock loading experiments conducted during Phase 1 in the CFB (data from day 90).

Figure A.12: Typical results of shock loading experiments conducted during Phase 1 in the CFB (data from day 95).
Figure A.13: Typical results of shock loading experiments conducted during Phase 1 in the CFB (data from day 104).

Figure A.14: Typical results of shock loading experiments conducted during Phase 1 in the SBB (data from day 90).
Figure A.15: Typical results of shock loading experiments conducted during Phase 1 in the SBB (data from day 102).

Figure A.16: Typical results of shock loading experiments conducted during Phase 1 in the SBB (data from day 122).
Figure A.17: Toluene, and MEK concentrations in the SBB during the REACT period during Phase 1 shock loading experiments (data from day 82).

Figure A.18: Toluene, and MEK concentrations in the SBB during the REACT period during Phase 1 shock loading experiments (data from day 102).

Figure A.19: Toluene, and MEK concentrations in the SBB during the REACT period during Phase 1 shock loading experiments (data from day 104).
Figure A.20: CO$_2$ concentrations in the SBB during the REACT period during Phase 1 shock loading experiments (data from day 97).

Figure A.21: CO$_2$ concentrations in the SBB during the REACT period during Phase 1 shock loading experiments (data from day 114).
Figure A.22: CO$_2$ concentrations in the SBB during the REACT period during Phase 1 shock loading experiments (data from day 119).

Figure A.23: Effluent CO$_2$ and O$_2$ concentration during the first 5 minutes of FEED period immediately following the shock loading REACT period during Phase 1 (data from day 93).
Figure A.24: Effluent CO$_2$ and O$_2$ concentration during the first 5 minutes of FEED period immediately following the shock loading REACT period during Phase 1 (data from day 95).

Figure A.25: Effluent CO$_2$ and O$_2$ concentration during the first 5 minutes of FEED period immediately following the shock loading REACT period during Phase 1 (data from day 97).
Figure A.26: Transition of the VOC influent concentrations between shock loading and normal loading in the CFB during Phase 1 shock loading experiments.
APPENDIX B

INDIVIDUAL PLOTS OF STUDIES CONDUCTED DURING PHASE 2

Appendix B include plots of the individual shock loading studies conducted in the CFB and the SBB during Phase 2, track studies performed during the REACT period in the SBB, and effluent CO$_2$ and O$_2$ concentrations for the first 5 minutes of the FEED period during Phase 2.

Figure B.1: Typical results of shock loading experiments conducted during Phase 2 in the CFB (data from day 152).

Figure B.2: Typical results of shock loading experiments conducted during Phase 2 in the CFB (data from day 156).
Figure B.3: Typical results of shock loading experiments conducted during Phase 2 in the SBB (data from day 149).

Figure B.4: Typical results of shock loading experiments conducted during Phase 2 in the SBB (data from day 152).
Figure B.5: Toluene, and MEK concentrations in the SBB during the REACT period during Phase 2 shock loading experiments (data from day 149).

Figure B.6: Toluene, and MEK concentrations in the SBB during the REACT period during Phase 2 shock loading experiments (data from day 152).

Figure B.7: Toluene, and MEK concentrations in the SBB during the REACT period during Phase 2 shock loading experiments (data from day 156).
Figure B.8: CO$_2$ concentrations in the SBB during the REACT period during Phase 2 shock loading experiments (data from day 158).

Figure B.9: CO$_2$ concentrations in the SBB during the REACT period during Phase 2 shock loading experiments (data from day 160).
Figure B.10: Effluent CO₂ and O₂ concentration during the first 5 minutes of FEED period immediately following the shock loading REACT period during Phase 2 (data from day 152).

Figure B.11: Effluent CO₂ and O₂ concentration during the first 5 minutes of FEED period immediately following the shock loading REACT period during Phase 2 (data from day 158).
Figure B.12: Effluent CO$_2$ and O$_2$ concentration during the first 5 minutes of FEED period immediately following the shock loading REACT period during Phase 2 (data from day 160).

Figure B.13: Transition of the VOC influent concentrations between shock loading and normal loading in the CFB during Phase 2 shock loading experiments.
APPENDIX C

INDIVIDUAL PLOTS OF STUDIES CONDUCTED DURING PHASE 3

Appendix C include the plots of the individual shock loading studies conducted in the CFB and the SBB during Phase 3, the track studies performed during the REACT period in the SBB, typical effluent CO₂ and O₂ concentrations for the first 5 minutes of the FEED period during Phase 3, and plots of the individual profiles studies conducted during Phase 3 in both the CFB and the CFB.

![Figure C.1: Toluene and MEK concentrations in the SBB during the REACT period during Phase 3 normal loading experiments (data from day 229).](image1)

![Figure C.2: Toluene and MEK concentrations in the SBB during the REACT period during Phase 3 normal loading experiments (data from day 229).](image2)
Figure C.3: Toluene and MEK concentrations in the SBB during the REACT period during Phase 3 normal loading experiments (data from day 229).

Figure C.4: CO$_2$ concentrations in the SBB during the REACT period during Phase 3 normal loading experiments (data from day 228).

Figure C.5: CO$_2$ concentrations in the SBB during the REACT period during Phase 3 normal loading experiments (data from day 229).
Figure C.6: CO₂ concentrations in the SBB during the REACT period during Phase 3 normal loading experiments (data from day 229).

Figure C.7: CO₂, toluene, and MEK concentrations in the CFB along the height of the packing material during a profile study conducted in Phase 3 normal loading experiments (data from day 229).
Figure C.8: CO₂, toluene, and MEK concentrations in the CFB along the height of the packing material during a profile study conducted in Phase 3 normal loading experiments (data from day 254).

Figure C.9: CO₂, toluene, and MEK concentrations in the CFB along the height of the packing material during a profile study conducted in Phase 3 normal loading experiments (data from day 254).
Figure C.10: CO₂, toluene, and MEK concentrations in the SBB along the height of the packing material during a profile study conducted in Phase 3 normal loading experiments (data from day 256).

Figure C.11: CO₂, toluene, and MEK concentrations in the SBB along the height of the packing material during a profile study conducted in Phase 3 normal loading experiments (data from day 263).
Figure C.12: CO$_2$, toluene, and MEK concentrations in the SBB along the height of the packing material during a profile study conducted in Phase 3 normal loading experiments (data from day 272).

Figure C.13: CO$_2$ produced during a profile study conducted in the CFB during Phase 3 endogenous loading experiments (data from day 256).
Figure C.14: CO$_2$ produced during a profile study conducted in the CFB during Phase 3 endogenous loading experiments (data from day 256).

Figure C.15: CO$_2$ produced during a profile study conducted in the SBB during Phase 3 endogenous loading experiments (data from day 254).
Figure C.16: CO$_2$ produced during a profile study conducted in the SBB during Phase 3 endogenous loading experiments (data from day 255).

Figure C.17: CO$_2$ concentrations in the SBB during the REACT period during Phase 3 endogenous loading experiments (data from day 251).
Figure C.18: CO₂ concentrations in the SBB during the REACT period during Phase 3 endogenous loading experiments (data from day 251).

Figure C.19: CO₂ concentrations in the SBB during the REACT period during Phase 3 endogenous loading experiments (data from day 254).
Figure C.20: Typical results of shock loading experiments conducted during Phase 3 in the CFB (data from day 183).

Figure C.21: Typical results of shock loading experiments conducted during Phase 3 in the CFB (data from day 194).
Figure C.22: Typical results of shock loading experiments conducted during Phase 3 in the SBB (data from day 183).

Figure C.23: Typical results of shock loading experiments conducted during Phase 3 in the SBB (data from day 194).
Figure C.24: Toluene, and MEK concentrations in the SBB during the REACT period during Phase 3 shock loading experiments (data from day 177).

Figure C.25: Toluene, and MEK concentrations in the SBB during the REACT period during Phase 3 shock loading experiments (data from day 183).
Figure C.26: CO$_2$ concentrations in the SBB during the REACT period during Phase 3 shock loading experiments (data from day 185).

Figure C.27: CO$_2$ concentrations in the SBB during the REACT period during Phase 3 shock loading experiments (data from day 194).

Figure C.28: CO$_2$ concentrations in the SBB during the REACT period during Phase 3 shock loading experiments (data from day 196).
Figure C.29: Effluent CO₂ and O₂ concentration during the first 5 minutes of FEED period immediately following the shock loading REACT period during Phase 3 (data from day 183).

Figure C.30: Effluent CO₂ and O₂ concentration during the first 5 minutes of FEED period immediately following the shock loading REACT period during Phase 3 (data from day 185).
Figure C.31: Effluent CO\textsubscript{2} and O\textsubscript{2} concentration during the first 5 minutes of FEED period immediately following the shock loading REACT period during Phase 3 (data from day 194).

Figure C.32: CO\textsubscript{2}, toluene and MEK concentrations in the CFB along the height of the packing material during a profile study conducted in Phase 3 shock loading experiments (data from day 282).
Figure C.33: CO₂, toluene and MEK concentrations in the CFB along the height of the packing material during a profile study conducted in Phase 3 shock loading experiments (data from day 333).

Figure C.34: CO₂, toluene and MEK concentrations in the CFB along the height of the packing material during a profile study conducted in Phase 3 shock loading experiments (data from day 336).
Figure C.35: CO₂, toluene and MEK concentrations in the SBB along the height of the packing material during a profile study conducted in Phase 3 shock loading experiments (data from day 282).

Figure C.36: CO₂, toluene and MEK concentrations in the SBB along the height of the packing material during a profile study conducted in Phase 3 shock loading experiments (data from day 333).
Figure C.37: CO₂, toluene and MEK concentrations in the SBB along the height of the packing material during a profile study conducted in Phase 3 shock loading experiments (data from day 336).

Figure C.38: Transition of the VOC influent concentrations between shock loading and normal loading in the CFB during Phase 3 shock loading experiments.
APPENDIX D

INDIVIDUAL PLOTS OF STUDIES CONDUCTED DURING PHASE 3 (ACTIVE CONTROL STRATEGY)

Appendix D includes the plots of the individual shock loading studies conducted in the CFB and the SBB while operated using an active control strategy during Phase 3. Also, the individual track studies performed during the REACT period in the SBB are shown.

Figure D.1: Typical results of shock loading experiments conducted during Phase 3 in the CFB (data from day 272).

Figure D.2: Typical results of shock loading experiments conducted during Phase 3 in the CFB (data from day 275).
Figure D.3: Typical results of shock loading experiments conducted during Phase 3 in the SBB while operated using an active control strategy (data from day 272).

Figure D.4: Typical results of shock loading experiments conducted during Phase 3 in the SBB while operated using an active control strategy (data from day 274).
Figure D.5: Toluene, and MEK concentrations in the SBB during the REACT period during Phase 3 shock loading experiments while operated using an active control strategy (data from day 272).

Figure D.6: Toluene, and MEK concentrations in the SBB during the REACT period during Phase 3 shock loading experiments while operated using an active control strategy (data from day 274).
VITA

Jorge C. Atoche was born in Merida, Mexico. Jorge received his Bachelor of Science in Chemical Engineering from the Autonomous University of Yucatan, Mexico, in 1999. Jorge conducted the project “Evaluation of Three Compost Bins for the Treatment of the Organic Fraction of Household Solid Wastes in Yucatan” as his undergraduate research thesis. Before completing his studies, he worked for Rotoplas Sureste S.A. as engineer assistant. In 2000, he decided to continue with his education and moved to Louisiana to study English in the English Language and Orientation Program at LSU. During the spring of 2001, Jorge entered the graduate school of Louisiana State University to obtain a Master of Science in Civil Engineering. He worked under the guidance of Dr. William M. Moe, developing and testing operating strategies for bioreactors treating mixtures of volatile organic compounds (VOCs).