

**THE EFFECT OF PERIODIC OPERATION ON BIOFILTERS FOR REMOVAL
OF METHYL ETHYL KETONE FROM CONTAMINATED AIR**

A Thesis

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

in

The Interdepartmental Program in Engineering Science

**By
Charles William Norman
B.S., Louisiana State University, 1997
May, 2002**

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ABSTRACT

In recent years, biofiltration technology has been used at numerous locations worldwide as an air pollution control technology for treating gases contaminated with low concentrations of biodegradable volatile organic compounds (VOCs). At the same time, there have been many reports in the literature of contaminant emissions from biofilters during transient loading conditions. There is currently a need to develop methods for controlling such emissions. Periodically operated bioreactors have been used successfully in treatment of wastewater and soils for several decades to mitigate the effects of uncontrolled unsteady-state loading on waste treatment systems. Such operating strategies have only recently been applied to biofilters treating gas-phase contaminants.

Research described herein compared contaminant removal efficiency in biofilters subjected to periodic operating strategies to that of a conventional continuously loaded biofilter. Methyl ethyl ketone (MEK), a compound that is regulated as a hazardous air pollutant (HAP) under the 1990 Clean Air Act amendments, was used as a model compound. Experiments were conducted to assess the ability of biofilters to remove MEK during quasi-steady state conditions (i.e., “normal” operation) as well as during transient periods of elevated contaminant loading (i.e., “shock loading” conditions). An influent MEK concentration of 106 ppm_v was used for normal loading experiments while a concentration of five times that (530 ppm_v) was applied during one-hour shock loading experiments. Shock loading experiments were conducted to evaluate both active and passive control techniques.

Results reported herein demonstrate that controlled periodic operating strategies can enhance contaminant removal of MEK during transient periods of elevated contaminant load. Shock loading experiments testing active control strategies resulted in MEK removal efficiencies greater than 95% for the periodic systems, while ranging from 55 to 70% for the continuously loaded biofilter. Removal efficiencies for the periodically operated systems dropped to less than 30% during experiments conducted to assess biofilter response to uncontrolled contaminant loading in the absence of an active control strategy. Thus, while periodic operation coupled with an active control strategy can improve biofilter performance during at least some transient loading conditions, there is a clear need for adequate control systems if such an operating strategy is adopted.

CHAPTER 1 INTRODUCTION

In recent years, biofiltration has been applied to treat gases contaminated by low concentrations of biodegradable volatile organic compounds (VOCs). Conventional biofilters are designed and operated in a manner that limits implementation of engineering decisions that could result in improved performance during relatively steady state conditions (i.e. normal loading) or during transient periods of elevated contaminant loading (i.e., shock loads). These shock loads produce the relatively uncontrolled, unsteady-state conditions commonly encountered in industrial systems.

In general, methods which could improve overall biofilter performance by increasing an operator's ability to control the spatial distribution or robustness of the biofilter's microbial consortium have received only limited attention in the literature. Periodically operated bioreactors have been used successfully in treatment of wastewater and soils for several decades to mitigate the effects of uncontrolled unsteady-state loading. Such operating strategies have only recently been applied to biofilters.

Research reported herein evaluated periodic operating strategies for biofiltration of a methyl ethyl ketone (MEK) contaminated air stream. A biofilter operated under a continuous VOC load and two biofilters operated with periodic strategies were evaluated. Experiments were first conducted to evaluate the removal efficiencies under normal loading conditions, defined as an influent MEK concentration of 106 ppm_v. The second objective was to evaluate the biofilters response to a shock or transient load. A shock load was defined as five times that of the normal load MEK concentration (i.e. approximately 530 ppm_v). The efficiency with which the continuously and periodically

loaded biofilters treated the transient elevated contaminant load was compared and reported.

To achieve the objectives listed above, the research was divided into several tasks, which are summarized below.

1.1 Selection and Enrichment of Initial Microbial Population

A laboratory-scale sparged gas bioreactor was operated to select and enrich for a microbial population for use as a seed culture in subsequent biofilter experiments. The enrichment reactor consisted of a 4.0 L glass reactor inoculated with 100 mL of activated sludge from a recently completed MEK biodegradation experiment and 2.9 L of a high-strength nutrient solution. MEK was continuously added to the reactor by bubbling MEK contaminated air through the reactor. Oxygen uptake rate (OUR), total suspended solids (TSS), and volatile suspended solids (VSS) were monitored over time until a culture of MEK degrading organisms was enriched.

1.2 Normal Loading Experiments

An initial phase of biofilter experiments was performed to assess the ability of biofilters to remove MEK during “normal” steady loading conditions consisting of an influent MEK concentration of 106 parts per million by volume (ppm_v). Three biofilters were operated under different strategies, and arbitrarily designated as BF1, BF2, and BF3. BF1 served as a control and was operated under continuous loading with an empty bed residence time (EBRT) of 120 seconds. The two periodically operated biofilters were operated on 12 hour cycles. One biofilter (BF2) was operated with a 40 second EBRT and received contaminant addition during only one third of the twelve hour operating cycle. Another biofilter (BF3) was operated with a 20 second EBRT received

contaminant addition during only one sixth of the twelve hour operating cycle. Each biofilter received the same influent MEK concentration (106 ppm_v) and mass of MEK during each 12 hour period, but the biofilters differed in the time period during which contaminants were added (all of the time, one-third of the time, or one-sixth of the time in BF1, BF2, and BF3, respectively). Influent and effluent MEK concentrations were measured to assess the ability of the biofilters to remove contaminants during steady loading conditions.

1.3 Shock Loading Experiments

A second phase of experiments was conducted to assess the ability of the three different biofilters to remove MEK during transient periods of elevated contaminant concentration (i.e., “shock loading” conditions). Three transient loading experiments (arbitrarily named Shock Load I, II, and III) were conducted to assess the ability of the biofilters to remove contaminants during various stages of the operating cycle. During shock loading, the MEK concentration was increased to 530 ppm_v (approximately five times the concentration during normal loading) for a period lasting one hour. Two transient loading experiments (Shock Load I and II) were conducted to test the biofilters’ responses 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 during the transient period of elevated loading. A third shock loading experiment (Shock Load III) was conducted to assess biofilter performance under conditions in which an operator does not modify the operating strategy during the transient period of elevated loading.

1.4 Fixed-Bed Adsorption and Desorption Experiments

Dynamic, fixed-bed sorption experiments were conducted to determine the adsorption and desorption characteristics of the polyurethane foam packing material under various loading conditions. Experiments were conducted at EBRTs of 120, 40, and 20 seconds using MEK concentrations of 106 ppm_v and 530 ppm_v. Each combination of EBRT and MEK concentration was tested in duplicate.

Chapter 2 of this thesis contains a literature review summarizing previous research in the field of biological treatment of gas-phase pollutants with an emphasis on treatment of MEK. Chapter 3 contains a description of the materials and methods used in the experiments. Chapter 4 contains results and discussion. Chapter 5 presents an overall discussion and conclusions as well as recommendations for future research.

CHAPTER 2 LITERATURE REVIEW

2.1 Overview of Processes for the Control of Waste Gas Streams

Passage of stringent air pollution laws and regulations has increased the need for cost effective treatment for many gaseous waste streams contaminated by VOC's. Biofiltration is an emerging technology for control of VOCs emissions from a variety of contaminated air streams (Ottengraff *et al.*, 1986; Leson and Winer, 1991; Deshusses and Johnson, 2000). Biofiltration is well suited for treatment of waste gas streams characterized by high flow rates with low concentrations of biodegradable pollutants (Deshusses and Johnson, 2000).

As early as the 1920's, biological techniques were applied for removal of H₂S emissions in air streams emitted from wastewater treatment facilities (Leson and Winer, 1991). As early as the late 1970's, in both Germany and the Netherlands, biofiltration was viewed as the best available control technology for off-gas treatment for odor control (Leson and Winer, 1991). Until the early 1980's biological treatment focused mainly on control of noxious odors (Van Groenestijn and Hasselink, 1993). In recent years, biological treatment has expanded to applications in control of volatile organic compounds (VOC) in gas streams originating from a variety of industrial facilities and environmental remediation activities.

Various non-biological methods exist for treatment of air contaminated by low concentrations of VOCs, and these are usually described as secondary treatment technologies. Economic and regulatory constraints usually dictate the choice of technology used, and process selection is normally based on the nature, flow, and mode of emission. While several methods of contaminant removal are technically feasible for

dilute VOC concentrations, most of the currently used methods have disadvantages. For example, thermal incineration is one of the most widely used secondary treatment technologies (Deshusses, 1994). During thermal incineration, pollutants are combusted at temperatures between 700 and 1400 °C. While the process is capable of high removal efficiencies, supplemental fuel is required, thus adding to the process cost, and secondary pollutants are generated (e.g., CO, CO₂, and NO_x). Adsorption using activated carbon allows for high VOC removal efficiencies particularly when low pollutant concentrations are involved. However, pollutants are transferred to the adsorbent rather than being destroyed, and the adsorbent must be regenerated or disposed of. Adsorbent regeneration or disposal can lead to high investment costs, while at the same time producing secondary pollutants. Biological treatment of VOC contaminated gases may meet treatment goals for many waste gas streams while at the same time minimize the disadvantages encountered with other treatment technologies.

2.1.1 Biological Processes

Although all biological gas treatment technologies involve biodegradation of contaminants by a microbial population, several different process configurations may be employed. These include biofilters, biotrickling filters, bioscrubbers, and sparged gas reactors. Although the research described herein deals only with biofiltration, each process configuration is described in the following sections to provide a background for the reader.

2.1.2 Biofilters

Biofiltration is the oldest biological method for removing undesired off-gas components (Van Groenestijn and Hasselink, 1993). In this process, contaminated gas is passed through a reactor containing an active microbial biofilm attached to a solid packing medium. Contaminants are transferred from the gas phase to the biofilm where they are oxidized to carbon dioxide, water, and biomass. Contaminant transfer from the gas phase directly into the biofilm minimizes the mass transfer from the gas phase to a large moving aqueous phase and then to the biofilm (Ottengraph, 1987).

The basic components of a biofilter include a packed bed reactor, a system for maintaining moisture content, and a blower to push or pull contaminated air through the porous medium. Several process configurations may be used. For example, air flow may be either up-flow or down-flow and water may be added to maintain moisture content by humidifying influent air or to the filter bed via a sprinkler or soaker hose. Packing media may consist of natural materials (e.g., compost) or synthetic media such as porous ceramic pellets or polyurethane foam cubes (Moe and Irvine, 2000b).

2.1.3 Biotrickling Filters

Biotrickling filters are similar to biofilters except the packing medium is rigid or semi-rigid and a nutrient containing liquid phase is continuously recirculated through the system. Microorganisms grow attached to the packing medium, and they may also be suspended in the recirculating liquid phase. Like biofilters, contaminate mass transfer and biodegradation takes place in a single reactor. Continuous or periodic addition/recirculation of liquid allows for control of nutrient concentrations and reaction

conditions (Van Groenestijn and Hasselink, 1993). One disadvantage of biotrickling filters (in comparison to biofilters) is a lower specific surface area of the packing media. This makes poorly water-soluble compounds difficult to treat (Ottengraph, 1987). Clogging is another potential problem due to a readily available nutrient supply (Webster *et al.*, 1998). Management of the liquid stream and possible treatment of any wastewater generated are other potential problems (Ottengraph, 1987).

2.1.4 Bioscrubbers

Bioscrubbers employ two separate reactors for treatment of undesired VOC components in off-gasses. In the first reactor, a scrubber, contaminated gas is contacted with an aqueous solution, with or without suspended microbes, by means of a fine spray usually onto an inert packing material. This results in contaminant absorption from the gas phase to the aqueous phase. The aqueous phase is then transferred to an activated sludge or fixed film bioreactor where contaminants are biologically degraded. The water may be recycled back to the sprayer (Van Groenestijn and Hasselink, 1993). Advantages of bioscrubbers include an ability to control nutrients, pH, and separate operational strategies for the two-reactor system. However, of the three previously described technologies, bioscrubbers have the lowest gas/liquid surface area for mass transfer (Van Groenestijn and Hasselink, 1993).

2.1.5 Sparged Gas Reactors

Sparged gas reactors involve passing VOC contaminated air through an aerator submerged in an aqueous-phase bioreactor. This results in mass transfer from the gas phase to the aqueous phase where a suspended microbial population degrades the

contaminant. Nutrient concentrations, biomass wasting, and hydraulic retention times in the reactor are controlled in the same manner as activated sludge processes used for wastewater treatment (Bielefeldt and Stensel, 1999). A disadvantage of this process is that contaminated gases must be compressed, and the head loss is comparatively high.

2.1.6 Terminology

Researchers in the field of biofiltration frequently report reactor operating conditions and contaminant removal using terms not often seen in other biological waste treatment applications. The nomenclature commonly used in the field of biological treatment of contaminated gas is summarized in the following paragraphs.

Empty bed residence time (EBRT), a relative measure of gas residence time within the biofilter medium, is commonly used in comparisons of gas residence times in different biofilters. The actual gas residence time in a biofilter may be calculated by multiplying the EBRT by the air-filled porosity available to gas flow. The porosity value is difficult to measure in practice. The gas surface loading rate, the volumetric gas flow rate applied to a biofilter divided by the biofilter's cross-sectional area, may also be used to describe the volumetric loading to the system. Higher surface loading is characteristic of a higher flow and a shorter EBRT.

Contaminant loading rates to biofilters are commonly reported as either surface loading rates or mass loading rates. The contaminant surface loading rate, similar to the gas surface loading rate, is defined as the mass of contaminant supplied per unit time per unit cross-sectional area. The contaminant mass loading rate is defined as the mass of contaminant applied to the biofilter per unit volume of packing material per unit time.

The contaminant mass loading rate is most often reported as an average over the entire bed.

Due to the effects of both flow and contaminant concentration, a particular biofilter can perform differently under identical contaminant mass loading rates. Higher contaminant concentrations allow for higher contaminant diffusion into the biofilm and faster biodegradation kinetics, while high EBRT's permit longer time for diffusion and degradation to occur.

Elimination capacity (EC) is a normalized measure of contaminant removal rate at a given mass loading. EC is defined as the mass of contaminant removed per unit volume per unit time, and is usually averaged over the entire bed. EC is a function of mass loading rate, EBRT, and experimental or environmental conditions. EC data can be misleading if the loading rate is not taken into account (i.e., the EC may be high but the overall contaminant removal in terms of percent removal may be low).

2.2 Problems In Conventional Biofilter Operation

There are a number of common problems encountered in conventional biofilter operation. Start-up is often problematic, where a slow start-up period equates to an excessive period of contaminant breakthrough. Maintaining proper moisture and nutrient content in the packing material is difficult and can lead to system failure. Clogging is one of the most common problems faced in full-scale implementation of biofilters. Clogging occurs when excess biomass accumulates in the void space of the packing material. Clogging usually occurs at the biofilter's inlet due to biomass concentrations being greatest in the area of greatest contaminant loading (Ergas *et al.*, 1994). This

interferes with the passage of the waste gas stream through the biofilter. Clogging can cause channeling within the packing material, limiting the amount of contaminated air being treated (Devinny *et al.*, 1999). Pressure drops, increasing wear and energy demand on the system, are associated with clogging.

Conventional biofilters are continuous flow processes designed and operated to receive a relatively constant stream of contaminated air (Irvine and Moe, 2001). Such systems, normally designed for minimal operator control (often times only allowing adjustment of the system's moisture content), provide little opportunity for implementing engineering decisions which could enhance biofilter performance during relatively steady-state conditions or transient periods of elevated contaminant loading (i.e., shock loads). These transient conditions reflect the uncontrolled, unsteady-state conditions commonly encountered in most industrial processes.

2.3 Periodic and Other Operating Strategies

Other than the research conducted by Moe and Irvine (1998, 2000) and Irvine and Moe (2001) on controlled, unsteady-state periodically operated biofilters, research on unsteady-state operating strategies has focused on continuous flow biofilters and the control of biosolids accumulation and clogging near the inlets (Irvine and Moe, 2001).

Periodic processes allow for the selection, enrichment, and manipulation of the physiological state of the microbial consortium, which minimizes uncertainties that often accompany the design and operation of biological systems. Periodic processes have long been used in wastewater treatment and soil remediation (Moe and Irvine, 2000).

Periodic processes have received limited attention in the literature, and most of this work has focused on control of biomass accumulation near the biofilter inlet to prevent excess biomass accumulation and subsequent clogging. Farmer (1994), experimented with switching the first biofilter in a series of three. Results demonstrated that after a period of operation the first biofilter could be switched to the end and allowed to undergo endogenous respiration to decrease the accumulated biomass therefore decreasing clogging. However, this did nothing to address distribution or robustness of the microbial consortium. Song and Kinney (1999) showed that switching the contaminant inlet from top to bottom allowed for better performance due to a more even distribution of biomass and higher toluene-degrading activity across the biofilter. The frequency with which the directional switching took place had an impact on biofilter performance. A frequency less than three days did not allow the consortium time to restore their degradation capacity. Indicating that a frequency of three days or more allowed for microbial re-generation, along with a small fraction of the inlet concentration (i.e., slip feed) re-directed to the outlet end to maintain microbial activity.

Weber and Hartmans (1995) described another method for mitigating contaminant emissions from biofilters during transient periods of elevated contaminant load. In their system, an activated carbon column was placed before a biofilter packed with compost and polystyrene. Experiments were first conducted to determine desorption profiles for several types of activated carbon adsorbents. Buffering capacities for 100 to 1000 mg toluene/m³ air were determined from the adsorption isotherms. The adsorbent that had the most advantageous buffering capacity was then used to study the removal of fluctuating concentrations of toluene from waste gases with a biofilter. Three

configurations were tested: a biofilter with no activated carbon (as a control), a biofilter with carbon mixed with the compost, and a separate activated carbon trap operated in series before the biofilter. A gas stream containing 900 mg/m^3 of toluene was applied to each system for 8 hours per day. More than 50% toluene breakthrough was reported with the first two configurations, however 100% removal was achieved in the biofilter with an activated carbon column in series. Weber and Hartmans concluded that using a maximum transient load of 1000 mg/m^3 , the activated carbon bed reduced the transient load to a maximum concentration of 300 mg/m^3 which was then completely degraded in the biofilter.

A matter of great concern in the development of a periodically operated biofilter system is how to establish “feast” conditions without contaminant breakthrough. Moe and Irvine (1998) demonstrated that accumulation was possible without breakthrough, but did not determine the ability of the selected and enriched for microbial consortium to sorb the contaminants without degrading them, which would allow for a true feast period to be established. Such a case would result in the microbes degrading the contaminants during a period of famine conditions or a period with no inlet contaminant concentration.

Using the system parameters common to periodic processes applied to wastewater systems, the cycle periods defined by Moe and Irvine (1998) are as follows:

- FEED – period during which contaminated gas flows to one or a grouping of biofilters in a multiple biofilter system. There is contaminant removal during feed due to some combination of sorption and biological

degradation. At the end of REACT, the gas flow is directed to another biofilter and the first biofilter enters REACT.

- REACT – period where contaminants are degraded. Clean air may or may not be circulated through the biofilter at this time, however drying out or oxygen depletion could result without recalculation during this period.
- IDLE – period between REACT and FEED where the biofilter or grouping of biofilters awaits the beginning of a new cycle. Uncontaminated air can be passed through during this time if oxygen is needed as a terminal electron acceptor.

A periodic operating strategy may be implemented using a variety of biofilter configurations and loading strategies. One method is to use multiple biofilters constructed in parallel and operated in sequence. Such a system has a tremendous amount of operational flexibility. For example, a six biofilter system (as shown in Figure 2.1) can be operated in parallel and sequence according to the solid arrows that connect the time periods I – VI. The empty bed resident time (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 in stages REACT or IDLE. Biofilter A is undergoing REACT and/or IDLE during time periods II – VI. Time period VII demonstrates 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 six times longer than when the biofilters are loaded one at a time. Irvine and Moe (2001) demonstrated that such an

operating strategy was successful for minimizing toluene emissions from a laboratory-scale biofilter subjected to a transient condition during which the influent toluene concentration increased from a concentration of 50 ppm_v toluene during normal loading to 500 ppm_v during a transient period.

The same system could be operated such that each biofilter receives contaminated air for only one third of the time as is represented in Figure 2.2. In this case, the EBRT is twice that of the biofilters undergoing FEED for 1/6 of their cycle (See Figure 2.1). Both of these periodic loading scenarios are in contrast to conventional continuous operation which is depicted in Figure 2.3.

Irvine and Moe (2001) reported that a periodically operated biofilter treating a toluene contaminated gas stream was superior to a conventional (i.e., continuous flow) biofilter during transient conditions of high loading. They hypothesized that the superior performance was likely due to two factors. First, that the selected and enriched for microbes in the periodic systems were able to sorb the contaminants during FEED and degrade them during REACT. Second, the higher mass flow rate of contaminants associated with lower EBRT's caused microbial growth to extend farther up the height of the column, thereby providing a biomass spatial distribution better suited to handle transient periods of elevated contaminant concentrations.

Although the studies described by Irvine and Moe (2001) suggest that periodic loading strategies offered advantages for treatment of toluene contaminated gas streams, tests with other compounds have not yet been reported. The experiments described in the

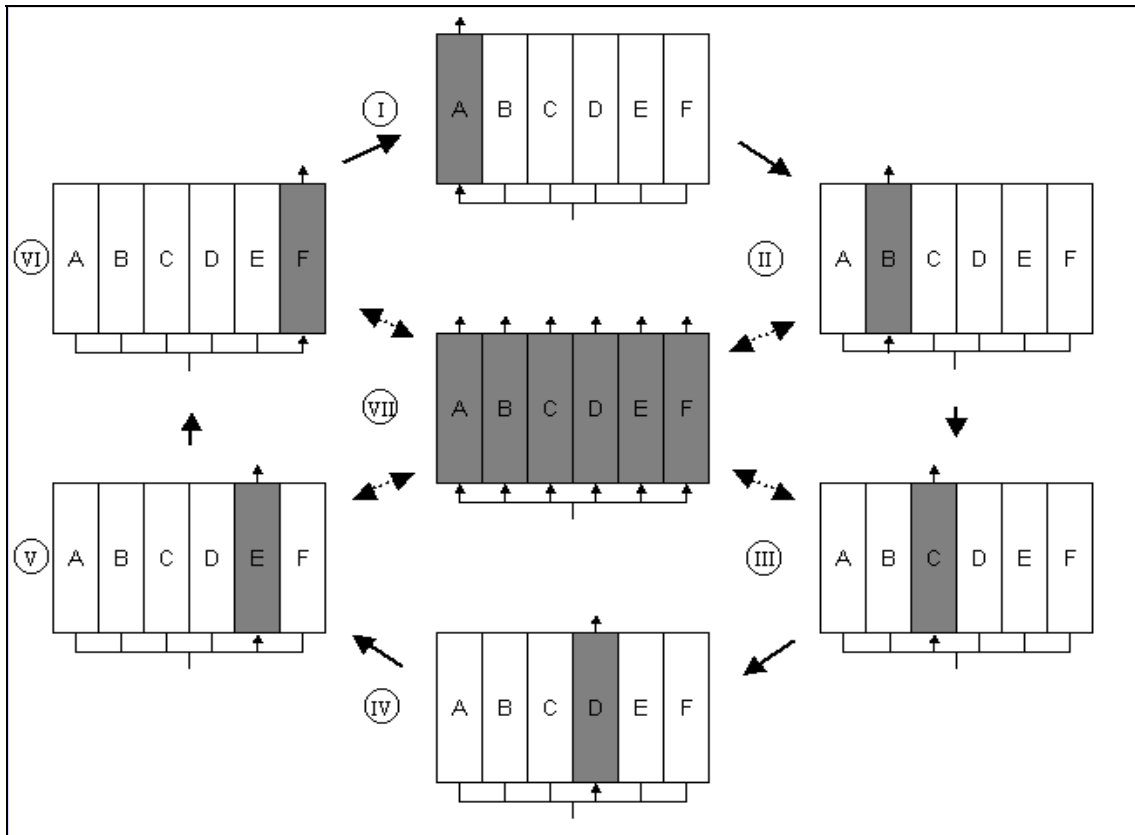


Figure 2.1: Schematic of six biofilters loaded periodically with FEED for one-sixth of the operating cycle during normal (I to VI) and transient (VII) time periods (redrawn from Irvine and Moe (2001)).

following chapter were conducted to determine if periodic loading strategies offer similar advantages for biological treatment of MEK contaminated gases.

2.4 Methyl Ethyl Ketone Biodegradation

MEK is one of the 188 compounds regulated as a Hazardous Air Pollutant (HAP) under the 1990 Clean Air Act Amendments (Brownell *et al.* 1998). The U.S. EPA lists MEK as one of the top 20 chemicals in terms of largest total on-site and off-site releases in 1999, with 40,720,712 pounds in total releases (US EPA, 2001). VOC emissions from

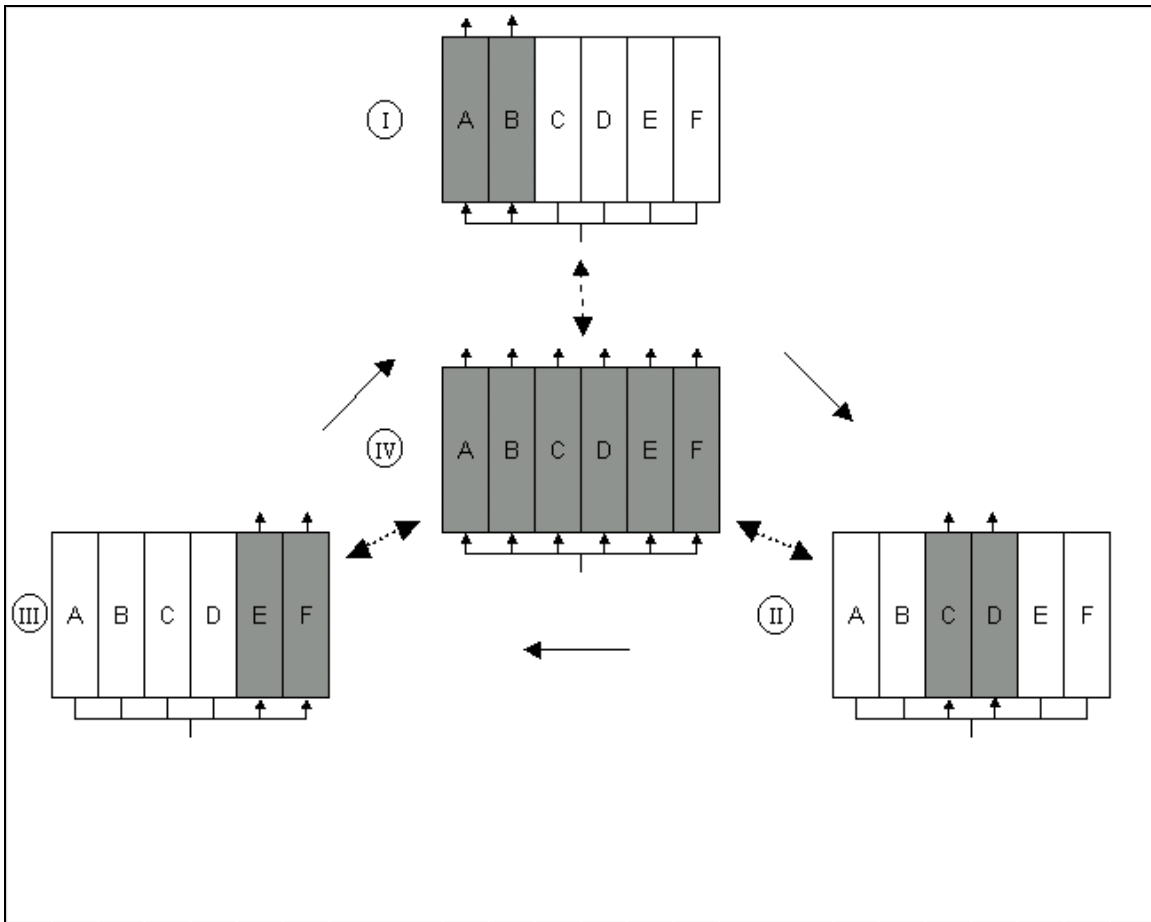


Figure 2.2: Schematic of a six biofilter system loaded periodically during normal (I to III) and transient (IV) time periods (Redrawn from Moe and Irvine (2000)).

painting operations are the largest source of manufacturing emissions for the automotive industry (Kim *et al.*, 2000a, 2000b). MEK is one of the solvents commonly found in paint spray booth off-gases (Kazenski and Kinney, 2000; Kim *et al.*, 2000a, 2000b). Aircraft and automotive paint spray operations produce high-flow, low-concentration waste gas streams that are expensive to treat using conventional methods. Due to its low operating costs and potentially high removal efficiencies, biofiltration is an attractive control technology for this purpose.

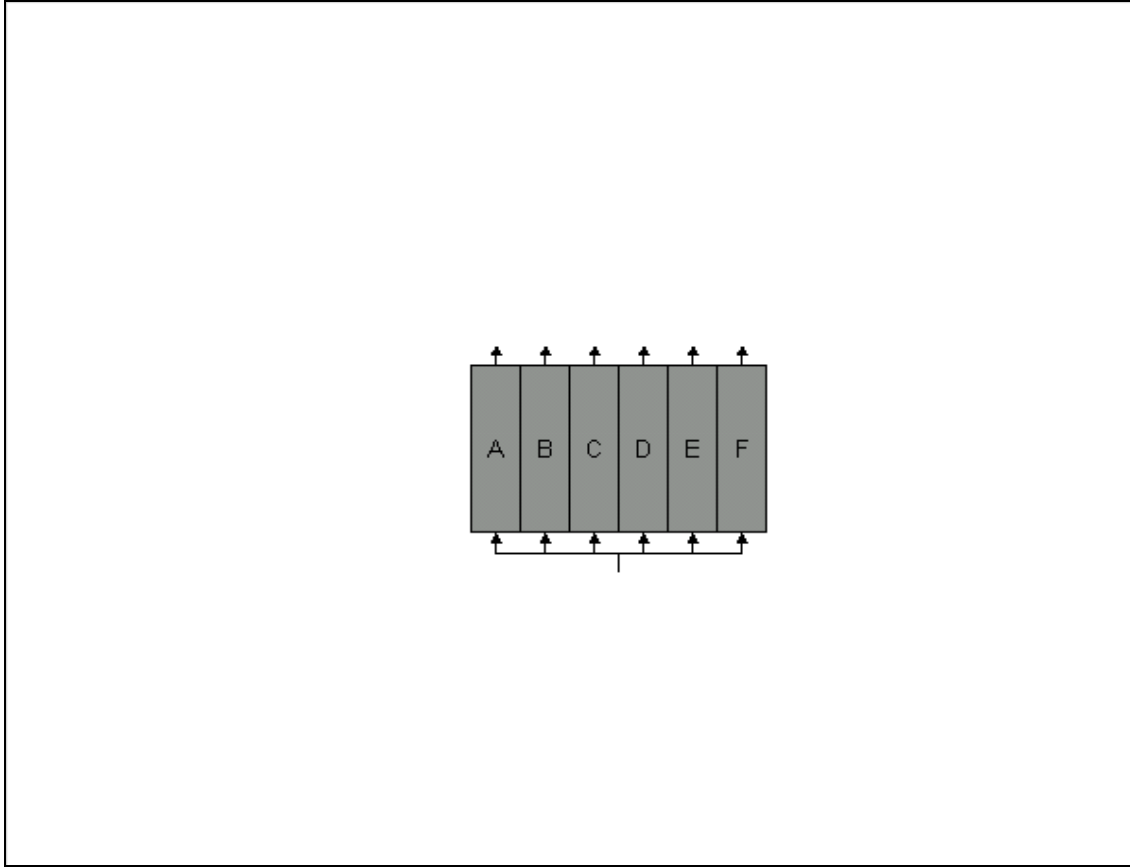


Figure 2.3: Schematic of a six biofilter system loaded continuously

2.4.1 MEK Biodegradation Pathway

Although specific degradation pathways of ketones have not been well documented, it has been speculated that their metabolism is similar to that of n-alkanes (Lukins and Foster, 1962; Britton, 1984; Deshusses 1994). The main degradation pathway of n-alkanes is thought to involve an initial oxidative attack on the terminal methyl group, possibly by a monooxygenase. This leads to the formation of an alcohol intermediate, and then to an homologous fatty acid (Lukins and Foster, 1962; Britton 1984). The subsequent metabolism through beta-oxidation is thought to cleave the

acetate groups furnishing the cell with the carbon and energy required for cell formation (Deshusses, 1994).

2.4.2 Biological Treatment of MEK Contaminated Waste Gas Streams

Previous research reported in the literature on biological treatment of gas contaminated with MEK is summarized in Table 2.1. Treatment processes described in the table include biofilters, biotrickling filters, and a tubular biofilm reactor. A variety of filter bed packing materials were used, including compost, polypropylene spheres, and polyurethane foam tested in laboratory-scale reactors. Reactor volumes (i.e., packing volume) ranged from 0.007 to 0.141 m³. The reactors were operated under a number of EBRTs ranging from 20 to 186 seconds (0.33 to 3.1 minutes). Volumetric loading rates tested ranged from 4.07 to 230 g/m³*hr. Treatment efficiency or percent removal, in most cases, was directly proportional to volumetric loading rate; with treatment efficiency diminishing as the loading rate exceeds the treatment capacity of a particular system. More detailed information about each of the particular studies is presented below.

Deshusses *et al.* (1995) studied the behavior of biofilters in the treatment of an air stream contaminated with MEK. Experiments were conducted using a biofilter packed with 0.005 m³ of Bioton (ClairTech, Utrecht, The Netherlands). Bioton is a commercially available packing media composed of an equ-ivolume mixture of compost and polystyrene spheres. Two EBRT's, 90 and 45 seconds, were tested over a loading rate range of 0 – 350 g/m³*hr. Deshusses, *et al.* reported elimination capacities ranging from 0 – 120 g/m³*hr.

Amanullah *et al* (2000) performed equilibrium and kinetic studies on MEK adsorption in compost and granular activated carbon. Reaction rates and selectivity of microorganisms for MEK biodegradation, and the role of adsorption capacity of the support medium on biofilter dynamics were also investigated. Experiments were conducted using a stainless steel column with a treatment volume of 0.008 m³. Two types of support media, compost and granular activated carbon (GAC), were evaluated. The compost consisted of soil particles and bark chips ranging from 2 – 20 mm in size. Commercially available GAC was used. The experimental procedure used EBRT's ranging from 25 to 50 seconds and an MEK influent concentration 1.1869 g/m³. Reported removal efficiencies ranged from 25 to 30% under the conditions tested.

Chou and Huang (1997) reported use of biotrickling filters to study treatment of MEK contaminated air streams. Two types of packing materials, polypropylene spheres and wood bars, were tested in reactors with a treatment volume of 0.141 m³. Influent MEK concentrations ranging from 0.9 to 5 g/m³ were tested. Removal efficiencies ranging from 40 to greater than 97% were reported.

Farmer (1994) studied treatment of a MEK contaminated gas stream using three separate reactor columns connected in series. The columns were packed with 13 mm ceramic Berl saddles as an inert support for the biofilm, and the system had a total treatment volume of 0.003 m³. Data and results reported here and in Table 2.1 used only the data Farmer reported to identify steady-state conditions. Influent MEK concentrations ranged between approximately 60 and 70 g/m³, and removal efficiencies ranged between 56 and 96%.

Agathos *et al.* (1997) reported a novel type of bioreactor design to treat VOC contaminated air stream. The reactor design consisted of mixing contaminated gas and a mist of nutrient solution and microorganisms in order to maximize contact and transfer between gas, liquid and microorganisms. The bioreactor was void of packing material; however, a biofilm developed attached to the glass reactor wall. A reactor volume of 0.017 m³ and influent concentrations ranging from 1.17 to 10 g/m³ were used. They reported removal efficiencies ranging from 0 to 70%.

2.4.3 Degradation of Mixtures Including MEK

Inhibition, induction, and repression are processes that can cause a decrease in biodegradation rates of specific compounds. Real life conditions dictate that biofilters will usually receive a complex mixture of VOCs. Ottengraph *et al.* (1991) reported that the greater the complexity of a waste stream in terms of number of constituents present, the lower the biodegradation of compounds achieved. Deshusses (1994) reported an inhibitory effect on the degradation rate of MEK when a biofilter received a mixture of MEK and methyl isobutyl ketone (MIBK). Removal efficiencies for MEK and MIBK when introduced as the sole substrate were 120 g/m³*h and 30 g/m³*h, respectively. When mixed at equal (mass) influent concentrations, both MEK and MIBK elimination capacities were reduced to a maximum of 40 and 18 g/m³*h, respectively (Deshusses and Hamer, 1993).

Table 2.1: Previous research reported in the literature on biological treatment of gas contaminated with MEK

Reference	EBRT (sec)	Vol (m ³)	Ci (g/m ³)	Mass Flow (g/hr)	Cross Sectional area (m ²)	Loading Rate (vol) g/m ³ *hr	Loading Rate (cross-area) g/m ² *hr	Percent Removal (%)	Elimination Capacity (g/m ³ *hr)	Packing	Operation
Deshusses <i>et al.</i> (1995)	90	0.005	0 – 8.75	0 – 1.75	0.005	0 - 350	0 - 350	0 34.3	0 - 120	Compost and polystyrene spheres	Biofilter
	45		0 – 4.38								
Amanullah, Md <i>et al</i> (2000)	50	0.008	1.1869	1.73	0.008	216	216	30	64.8	Compost and GAC	Biofilter
	25			3.47		432	432	25	108		
Chou and Huang (1997)	88.4	0.141	0.9	5.17	0.071	36.7	72.8	> 97	35.6	Polypropylene spheres and Wood Bars	Biotrickling Filter
	88.4		0.1 - 5	0.574 - 28.7		4.07 - 203.5	8.08 - 404.2	> 97	4 – 197		
	88.4		0.7, 1.8, 3.7	4.02, 10.33, 21.24		28.51, 73.26, 151	56.6, 145.5, 299.1	>95	27 – 143		
	186.7		0.1 - 4.5	0.574 - 25.83		4.07 - 183.2	8.08 - 363.8	40 - 50	1.6 – 91.6		
Farmer (1994)	60	0.003	70.6	0.212	0.002	70.6	106	56	39.5	Ceramic Berl Saddles	Biofilter
	180		63.9	0.064		21.3	32	96	20.5		
Agathos <i>et al.</i> (1997)	68.4	0.017	10.0000	8.5	0.017	500	558.8	0	0	none	Tubular Biofilm reactor
			2.0000	2.13		125	140	20 and 50	25, 62.5		
			1.1780	1.06		62.5	70	67	41.9		
			2.7685	2.48		145.8	162.9	43	62.7		
			4.3294	3.9		229.2	255.9	35	80.2		

Biofilter performance and process efficiency is a product of both the component characteristics and operation of the biofilter, as well as the chemical properties of the compounds being treated. Differences in biodegradation rates and inhibition rates can mainly be attributed to differences in packing affinities, Henry coefficients, intrinsic biodegradation rates, and affinity with the degradation key enzymes (Deshusses, 1997). This was experimentally shown by the step input of hexane, acetone, MIBK and 1-propanol, or mixtures of these solvents to a biofilter degrading MEK. Hexane was neither sorbed nor degraded, due to its high Henry's coefficient and low water solubility. Acetone was sorbed and well degraded, as was 1-propanol. Carbon dioxide values peaked 2-5 hours after the step injection of a transient VOC load, suggesting that pollutants were first sorbed to the packing material, and subsequently degraded. MIBK showed the greatest inhibitory affect on MEK.

Kazenski and Kinney (2000) studied the interactions of common VOC's found in paint spray booth off-gasses. MEK is a common constituent of this waste stream, but in their study they used methyl n-propyl ketone, which is molecularly similar to MEK. Results showed a common order of degradation: n-butyl acetate, ethyl 3-ethoxypropionate, methyl n-propyl ketone, toluene, and p-xylene. Bottle studies confirmed this order.

2.5 Salinity Effects on MEK removal

In many biofilter applications, a nutrient solution is periodically added to the packing medium to provide nutrients (e.g., nitrogen and phosphorous) necessary for

microbial growth. Some of the nutrient solutions used in this manner contain relatively high salt concentrations. Previously reported experimental evidence suggests that high salinity can greatly effect biodegradation of ketones. For example, Mahmoud and Davis (1970) reported significant changes in substrate utilization due to salt concentrations. Batch studies, where cultures were acclimated at certain salt concentrations and then shocked with markedly greater or lower media solutions containing ketones, were conducted to test this. They concluded that salinity shocks on the order of +/- 10,000 mg/L had very little effect on the metabolic response of the mixed cultures. However, a mixed culture acclimated to fresh water and shocked with seawater showed a 50% reduction in substrate removal efficiency. Likewise, a mixed culture acclimated to seawater and shocked with fresh water showed an 86% reduction in removal efficiency. In general, it was shown that negative shock magnitudes resulted in greater reduction in substrate removal compared to positive shock magnitudes. They also reported higher oxygen uptake per unit substrate removed, for mixed cultures acclimated to higher salinity levels.

CHAPTER 3 MATERIALS AND METHODS

3.1 Packing Medium

3.1.1 Polyurethane Foam Manufacture

The procedure used to make the polyurethane foam packing medium was similar to that employed by Moe and Irvine (2000) and Martinez *et al.* (2000). A surfactant solution was made by dissolving 30 g PluronicTM P-65 surfactant (BASF Corporation, Mount Olive, NY) per 1.0 L of deionized water, and then cooling overnight at 8 °C in a laboratory refrigerator. HypolTM 3000 prepolymer (Hampshire Chemical Company, Lexington, MA) was heated to 55 °C in a constant temperature water bath and then maintained at that temperature for at least 2 hours before use. Molds for the foam cylinders were constructed of poster board. The inside diameter for the foam molds was calculated by measuring the inside diameter of a section of the biofilter column and adding 0.5 cm to this measurement. The extra 0.5 cm was to allow the foam cylinders to be self supporting in the biofilter by exerting pressure on the glass walls of the column. A finished mold had a circumference of 32.7 cm, an average height of 22 cm, and a cellophane bottom secured by a rubber band.

Working under a fume hood, 110 g of surfactant solution and 110 g of prepolymer were measured separately (using an analytical balance) in disposable 470 mL plastic cups (Solo Cup Co., Highland Park, IL). The surfactant solution was then poured into the prepolymer, and mixed with a high torque mechanical mixer (Lightnin, Rochester, NY) at 1000 RPM for approximately 20 seconds. When the

foaming mixture began to rise, the mixture was poured into the mold. The foam was allowed to cure in the fume hood.

3.1.2 Packing Medium Rinsing Procedure

After the foam was allowed to cure for two hours, the cardboard molds were removed, and the top and the bottom 1.0 cm of each cylinder were sliced off using a disposable microtome blade. Resulting foam cylinders were dried in a laboratory oven at 65°C for 24 hours before being weighed and then rinsed to remove excess surfactant using the following procedure. The foam cylinders were initially rinsed five times with deionized water to remove excess surfactant. After the initial rinse, the cylinders were placed in a five gallon plastic bucket filled with 9.0 L of deionized water and allowed to soak for approximately two hours. Next, the cylinders were removed, compressed to remove excess water, and then rinsed three times with deionized water before being placed back into the container with 9.0 L of fresh deionized water. This process was repeated until there was less than 0.5 mg/L (as soluble TOC) of surfactant remaining in the foam rinse water. After the rinse was completed, cylinders were dried at 65 °C over night, and then the dry mass of each cylinder was recorded. The TOC analysis method is described in section 3.7.1.

3.2 Experimental Apparatus

Laboratory experiments described herein employed three identical glass biofilter columns: (arbitrarily named BF1, BF2, and BF3) as shown in Figure 3.1. Each biofilter consisted of five sections plus a top and a bottom. Each section had an inner diameter of 9.9 cm and a height of 22 cm. Each column section was filled with

20 cm of polyurethane foam medium providing a total bed depth of one meter and a total packed bed volume of 7.7 L. Columns were assembled by placing Viton™ O-rings between each section and securing with a horse-shoe clamp.

Compressed air from a laboratory air tap flowed through tubing to an activated carbon filter (Calgon type F-300) to remove any unwanted contaminants from that air supply. A manifold system split the air stream into 3 separate flows that each made up 95% of the total flow to one biofilter. A pressure regulator (series R35, Arrow Pneumatics, Inc., Broadview, IL) was used to control the air-pressure to each biofilter. The flow rates were measured and regulated with Cole-Palmer Rotometers (Gilmont Instruments, 150 mm scale Accucal flow meter Cole-Palmer Instrument Co., Vernon Hills, IL). Each rotometer was calibrated using an Aalborg® GFM37 digital mass flow meter (Orangeburg, NY).

Each of the airstreams making up 95% of the flow was passed through an aeration stone submerged in a 20 L glass carboy heated with electrical heating tape. To insure at least 95% relative humidity in the air entering the bottom of the biofilters, the relative humidity was measured with an NIST traceable digital hygrometer (Fisher Scientific, Sewanee, GA) The remaining 5% of the airflow to each biofilter was directed through a separate rotometer to control the flow rate to an injection port for MEK volatilization. MEK volatilization into the influent air stream was accomplished using a KD Scientific model 100 syringe pump (KD Scientific Inc., New Hope, PA)

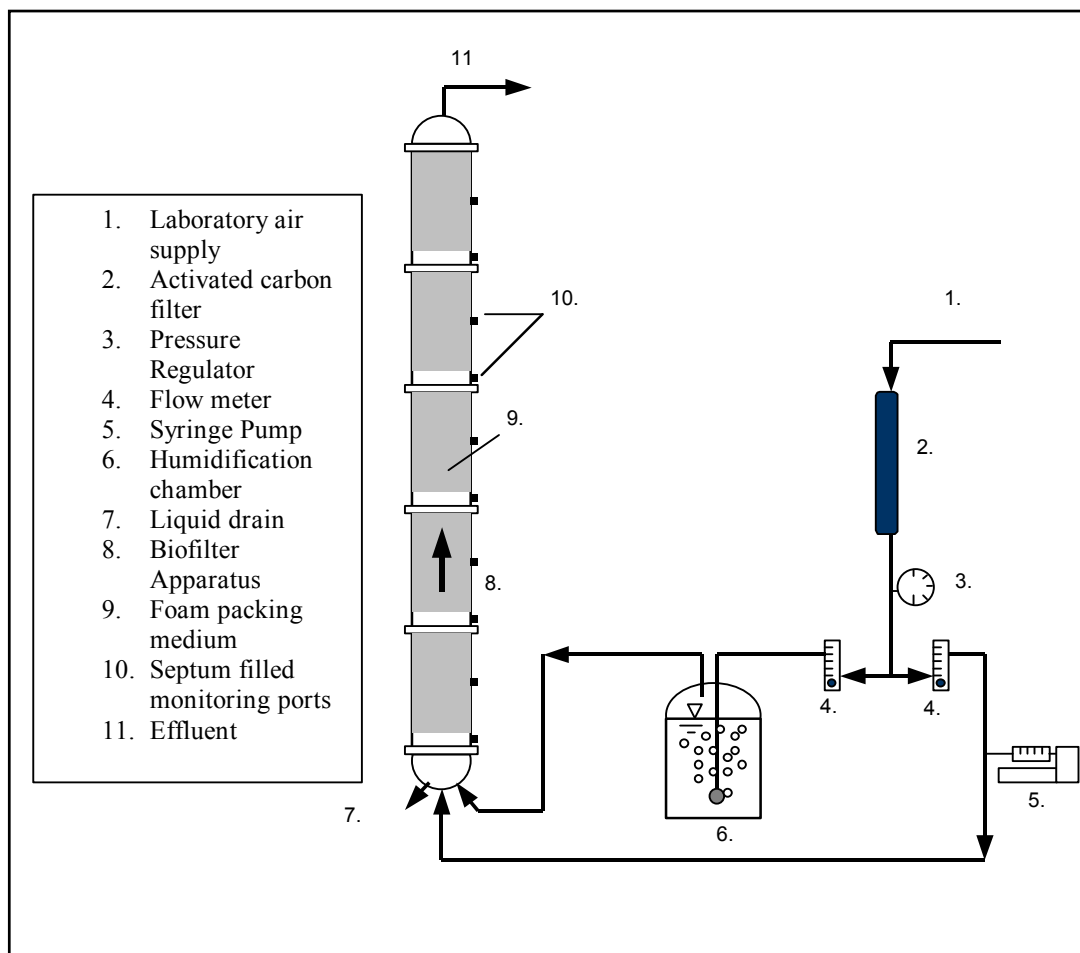


Figure 3.1: Schematic Diagram of Laboratory biofilter apparatus.

with a gas tight syringe (Hamilton Scientific, model 1005TLL, Reno, NV). The injection port consisted of a glass tube with airtight compression fittings, and a port where a Thermogreen LB-1 half-hole septum (Supelco, Bellefonte, PA) was inserted for the point of needle insertion. To minimize contaminant sorption to the experimental apparatus, all surfaces contacting the gas stream after the point of MEK injection were made of glass, Teflon, or Viton™ tubing.

3.3 Culture of Enrichment Culture and Biofilter Inoculation Process

A laboratory-scale sparged-gas bioreactor was operated (beginning on December 14th, 2000) to select and enrich for a microbial population for use as a seed culture in subsequent biofilter experiments. As depicted in Figure 3.2, the enrichment reactor consisted of a 4.0 L glass reactor (Pyrex®, Corning, NY). Reactor start-up consisted of adding 100 mL of activated sludge from a recently completed MEK biodegradation experiment and 2.9 L of nutrient solution to bring the total volume to 3.0 L. The nutrient solution consisted of the following compounds added to tap water: NaNO_3 (29.3 g/L), KH_2PO_4 (2.38 g/L), Na_2HPO_4 (1.00 g/L), MgSO_4 (1.29 g/L), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.632 g/L), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.482 g/L), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ((0.002 g/L), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.0004 g/L), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.00004 g/L), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.000033 g/L), EDTA (0.001 g/L).

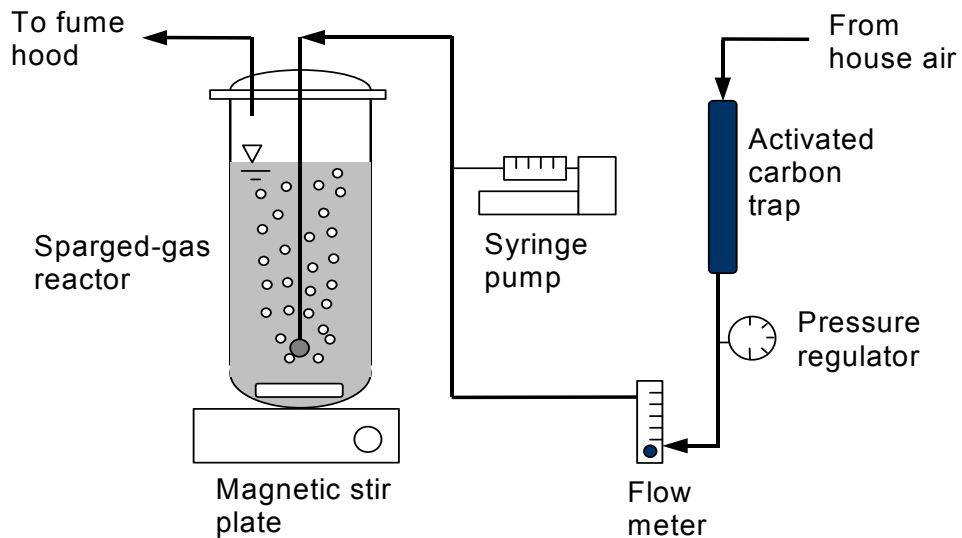


Figure 3.2: Schematic diagram of the sparged-gas bioreactor use to culture MEK degrading organisms used to inoculate biofilters.

House air was used for the air stream, and a carbon trap (type F-300, Calgon Carbon Corporation, Pittsburgh, PA) was employed to eliminate any oil or other contaminants from the house air compressor. An Arrow Pneumatics, series R35, pressure regulator (Arrow Pneumatics, Inc., Broadview, IL) was used to control the air pressure. A flow rate of 5.0 L/min was achieved with a Cole Palmer Rotometer (Gilmont Instruments, 150 mm scale Accucal flow meter Cole-Palmer Instrument Co., Vernon Hills, IL). MEK volatilization into the influent air stream was accomplished using a KDScientific, model 100 syringe pump (KD Scientific Inc., New Hope, PA) with a gas tight syringe (Dynatech Precision Sampling Corp., series A-2, 5.0 mL Pressure-Lok syringe, Baton Rouge, LA).

The injection port consisted of a glass tube with airtight seals, and an injection port where a septum (Thermagreen LB-1 septum, Supelco, Bellefonte, PA) was inserted for the point of needle insertion. All surfaces after the MEK was injected into the air stream were made of glass, Teflon, or VitonTM tubing. These relatively inert materials were used to minimize contaminant sorption to the reactor apparatus. Contaminated air stream was introduced into the reactor using a fine bubble air diffuser stone (Fisher Scientific, Sewanee, GA) connected to the influent airline by VitonTM tubing and a 1 mL glass pipette. The reactor was placed on a magnetic stir plate to allow mixing using a Teflon-coated stir bar.

The sparged-gas reactor was operated with a gas flow rate of 5.0 L/min (0.30 m³/hr) and a syringe pump setting of 0.07 mL/hr for MEK delivery. This corresponds to an influent gas-phase MEK concentration of 106 ppm_v and a MEK mass flow rate

of 0.0531 g/hr. On a daily basis, 10% of the reactor volume was removed and replaced with fresh nutrient solution to produce a sludge age of 10 days. The reactor was cleaned every two days to minimize biomass accumulation on reactor surfaces.

Oxygen uptake rate (OUR) was measured using a YSI Biological Oxygen Monitor (Model 100). Total suspended solids (TSS) and volatile suspended solids (VSS) were measured using *Standard Methods for the Examination of Water and Waste Water* (APHA, 1998). For the OUR measurements, conducted in triplicate using a 4 mL sample volume, dissolved oxygen concentrations were recorded over a five-minute period. The OUR was determined from a linear regression, and the average of the three measurements for each day was used in conjunction with the average TSS to calculate the SOUR.

The sparged gas reactor was operated for a 75 day period (beginning on December 14th, 2000) prior to inoculation of the biofilters (on February 27th, 2001). OUR, TSS, and VSS measurements (in triplicate) were taken before and after the inoculating culture was allowed to settle. On the day of biofilter inoculation, the OUR of the initial reactor, before settling, was 12.6 mg/L*hr. The endogenous OUR, measured by aerating a sample for thirty minutes prior to analysis, was 4.8 mg/L*hr. A spike of 1.5 μ L MEK was injected into the oxygraph chamber following completion of the endogenous experiment to determine the microbes' ability to degrade MEK (i.e., use MEK as a source of carbon). The spiked OUR was 181 mg/L*hr. The average TSS and VSS of the microbial consortium were 2680 mg/L and 1400 mg/L, respectively.

The biomass was allowed to settle for one hour and then 3.5 L was decanted, 0.5 L was re-suspended with 3.5 L of nutrient solution; resulting in 4.0 L of inoculum consortium. After re-suspension, the OUR was 3.46 mg/L*hr, TSS and VSS were 2560 and 1160 mg/L, respectively. The decrease in OUR of the resuspended consortium with respect to the initial was probably due to insufficient settling. An interface did not form during reactor settling, therefore biomass was lost when the supernatant was drained. With less biomass, a lower OUR would be expected. The spike experiment described above was repeated for the re-suspension inoculum, and the OUR was 245 mg/L*hr. These results clearly indicate the microbes' ability to degrade MEK.

Once these measurements had been conducted, four liters of inoculum were pumped from the glass kettle reactor into a five-gallon bucket. The foam cylinders were then brought to 65% moisture content by evenly squeezing the cylinders while they were immersed in the inoculum. After the biofilters were packed, 0.49 L of inoculum consortium remained. The TSS and VSS of the remainder was 3360 and 1480 mg/L respectively. Therefore, the total biomass inoculated was approximately 1300 mg VSS per biofilter.

3.4 Normal Loading Experiments

Following the inoculation procedure, each of the three biofilters (arbitrarily designated as BF1, BF2, and BF3) was operated using a different loading strategy. BF1 served as a control and was operated under continuous loading with an EBRT of 120 seconds and an influent MEK concentration of 106 ppm_v. This operating strategy

is the same as that depicted in Figure 2.3 and corresponds to a biofilter that continuously receives an influent waste stream.

The periodically operated biofilters (BF2 and BF3) were operated with a loading strategy that consisted of contaminant addition during only a fraction of a 12 hour cycle. BF2, operated with a 40 second EBRT, received contaminant addition during a four hour FEED period and then underwent an eight hour REACT period during which uncontaminated air continuously flowed through the biofilter. BF3, operated with a 20 second EBRT, received contaminant addition during a two hour FEED period and then underwent a ten hour REACT period during which uncontaminated air continuously flowed through the biofilter. BF2 simulated the loading condition experienced by one biofilter in a three biofilter system as depicted in Figure 2.2. BF3 simulated the loading condition experienced by one biofilter in a six biofilter system as depicted in Figure 2.1.

Influent MEK concentrations for the normal loading period are depicted in Figure 3.3. For the periodically loaded biofilters, uncontaminated air was supplied throughout the REACT period at the same flow rate as during the FEED period. Operational parameters are summarized in Table 3.1 below. For each of the biofilters, the influent MEK concentration was identical and the mass MEK entering the biofilter during a 12 hour cycle was identical. The biofilter loading differed only in the EBRT and the time period during which the contaminants were applied. “Normal loading” refers to all three biofilters receiving an influent MEK concentration of 106 ppm_v or 113.28 g/m³ over one cycle of contaminant load.

MEK concentration in the influent and effluent was measured to determine contaminant removal rate in each reactor. Carbon dioxide concentrations were also monitored to evaluate contaminant degradation rates.

3.5 Shock Loading Experiments

Experiments were conducted to assess the ability of the three different biofilters to remove MEK during a transient period of elevated contaminant concentration (i.e., “shock loading” conditions). These experiments were arbitrarily named Shock Load I, II, and III. During shock loading experiments, the influent MEK concentration was increased to 530 ppm_v (five times the concentration during normal loading) for a period lasting one hour.

Shock loading experiments took into account that in practice, an uncontrolled transient load to a biofilter could occur at any time during an operating cycle and an operator could take various actions in response to the transient loading condition. For example, with a set of three biofilters constructed in parallel and operated in sequence (see Figure 2.1, section 2.3), a shock load encountered during period III may have a different effect than one encountered during period I. As the system switches to period VII for the shock load, biofilters A and C are the only biofilters in the six biofilter system that were being operated similarly. Biofilter B in period III had just entered REACT, however biofilter B in period I had been undergoing REACT for a substantial fraction of the cycle length. Experiments were designed and conducted to represent the range of loading conditions that might arise.

Table 3.1: Comparison of biofilters during “normal” operation

Parameter	BF1	BF2	BF3
Operating policy for biofilter	continuous	periodic	periodic
Number of cycles/day	---	2	2
Time for cycle (hr)	---	12	12
Time for FEED (hr)	---	4	2
Time for REACT + IDLE (hr)	---	8	10
FEED Time / Total cycle time (ratio)	1/1	1/3	1/6
EBRT (seconds)	120	40	20
Daily mass flow rate of MEK (g)	1.73	1.73	1.73
MEK mass flow rate during FEED (g/hr)	0.072	0.217	0.434
Equivalent # of biofilters operated in parallel	1	3	6

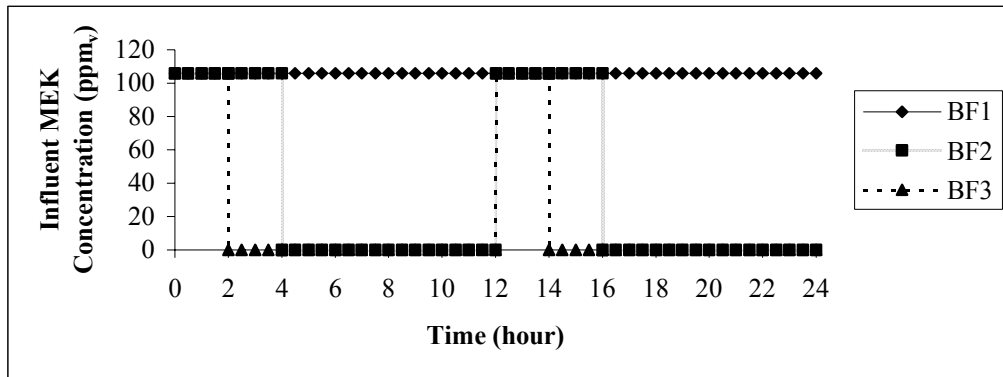


Figure 3.3: Step input of MEK over two cycles of normal loading.

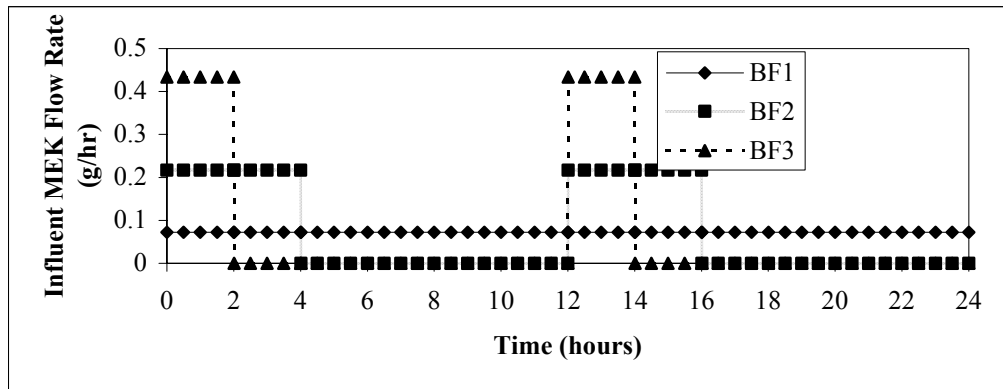


Figure 3.4: Influent MEK flow rate over two cycles of normal loading.

Shock Loading experiments I and II were conducted with the assumption that an operator would have online monitoring and process knowledge so that the EBRTs of BF2 and BF3 could be adjusted to the 120 second EBRT of BF1 when a transient period of elevated loading occurred. This corresponds to loading condition VII depicted in Figure 2.1 and simulates the loading condition where all biofilters installed in parallel are loaded simultaneously. In such a case, the EBRTs in BF2 and BF3 increase to three and six times as long as during “normal” loading, respectively, while that of BF1 remains unchanged. Shock Load III tested the systems’ ability to treat a shock load without operator control (i.e., the EBRTs were not changed in any of the biofilters).

Effluent MEK concentrations were monitored to evaluate the mass of MEK breakthrough. Each shock loading experiment was performed in triplicate (with replicates arbitrarily named A, B, and C) for each of the biofilters. Effluent CO₂ concentrations were measured during one Shock Load I experiment, and during all Shock Load II and III experiments. Influent CO₂ concentrations were measured prior to each experiment so that the CO₂ production in each biofilter could be calculated.

For Shock Load I, the shock load was applied one hour into the REACT period in BF2 and BF3. After the shock load, periodically operated biofilters (BF2 and BF3) were put into REACT (while the EBRT remained at 120 seconds for a period of 2 hours) before returning to the normal operating cycle. BF1 received a continuous loading before and after the shock. Table 3.2 summarizes the operational parameters for shock load experiments IA, IB, and IC.

During Shock Load II, the one-hour shock load was applied during the last hour of FEED for BF2 and BF3. After the shock load, the periodically operated biofilters were switched to a normal REACT period but with the EBRT remaining at 120 seconds for a two-hour period. Table 3.3 summarizes the operational parameters for shock load experiments IIA, IIB, and IIC.

During Shock Load III, the one-hour shock load period was applied during the last hour of FEED in BF2 and BF3. In contrast to Shock Load I and II experiments, the EBRTs remained at 40 and 20 seconds in BF2 and BF3, respectively, during and after the shock load period. Table 3.4 summarizes the operational parameters for Shock Load IIIA, IIIB, and IIIC.

3.6 Fixed-Bed Adsorption and Desorption Experiments

Dynamic, fixed-bed sorption experiments were conducted to determine the adsorption and desorption characteristics of the polyurethane foam packing material under various loading conditions. Experiments were conducted at EBRTs of 120, 40, and 20 seconds using MEK concentrations of 106 ppm_v and 530 ppm_v. Each combination of EBRT and MEK concentration was tested in duplicate.

In the adsorption studies, packing media prepared exactly as that used in subsequent biofilter experiments (see section 3.1) was adjusted to 65% moisture content using deionized water and then placed into a glass column identical to that used in biofilter experiments (see section 3.2). The total depth of the packing medium was 1.0 m and the total packed bed volume was approximately 7.7 L. Adsorption

Table 3.2: Comparison of biofilters during Shock Load I.

Parameter	BF1	BF2	BF3
EBRT (seconds)	120	120	120
Time for transient (hr)	1	1	1
MEK concentration during transient (ppm _v)	530	530	530
Mass flow rate of MEK during transient in g/hr or g/m ³ *hr [in brackets]	0.363 [51.9]	0.363 [51.9]	0.363 [51.9]
Normal mass flow rate of MEK during FEED (g/hr) [g/m ³ *hr]	0.072 [10.3]	0.217 [31]	0.434 [62]
Ratio of FEED mass flow rates (transient:normal)	5.01 : 1	1.67 : 1	0.84 : 1
Period prior to transient	Normal	IDLE	IDLE
EBRT prior to transient (seconds)	120	40	20
Period after transient	Normal	REACT	REACT
EBRT after transient (seconds)	120	120	120

Table 3.3: Comparison of biofilters during Shock Load II

Parameter	BF1	BF2	BF3
EBRT (seconds)	120	120	120
Time for transient (hr)	1	1	1
MEK concentration during transient (ppm _v)	530	530	530
Mass flow rate of MEK during transient in g/hr or g/m ³ *hr [in brackets]	0.363 [51.9]	0.363 [51.9]	0.363 [51.9]
Normal mass flow rate of MEK during FEED (g/hr) [g/m ³ *hr]	0.072 [10.3]	0.217 [31]	0.434 [62]
Ratio of FEED mass flow rates (transient:normal)	5.01 : 1	1.67 : 1	0.84 : 1
Period prior to transient	Normal	FEED	FEED
EBRT prior to transient (seconds)	120	40	20
Period after transient	Normal	REACT	REACT
EBRT after transient (seconds)	120	120	120

experiments were conducted by setting the syringe pump and influent air flow rates to the desired levels and then measuring the effluent MEK concentration over time until complete breakthrough was reached. Breakthrough was defined as the point where the effluent concentration was equal to the influent concentration within analytical error.

Table 3.4: Comparison of biofilters during Shock Load III

Parameter	BF1	BF2	BF3
EBRT (seconds)	120	40	20
Time for transient (hr)	1	1	1
MEK concentration during transient (ppm _v)	530	530	530
Mass flow rate of MEK during transient in g/hr or g/m ³ *hr [in brackets]	0.363 [51.9]	1.089 [155.7]	2.179 [311.4]
Normal mass flow rate of MEK during FEED (g/hr) [g/m ³ *hr]	0.072 [10.3]	0.217 [31]	0.434 [62]
Ratio of FEED mass flow rates (transient:normal)	5.01 : 1	5.01 : 1	5.01 : 1
Period prior to transient	Normal	FEED	FEED
EBRT prior to transient (seconds)	120	40	20
Period after transient	Normal	REACT	REACT
EBRT after transient (seconds)	120	40	20

The mass of contaminant adsorbed to the foam packing medium was calculated giving consideration to the fact that a portion of the contaminant was absorbed in water associated with the wet packing media. The mass of water present (65% moisture content) was assumed to be in equilibrium with the influent gas-phase concentration at the end of each adsorption experiment when the influent and effluent contaminant concentrations were equal and unchanging over time. The dimensionless Henry's Law constant (2.35×10^{-3} , Deshusses 1994) was used to calculate the concentration of contaminant in the aqueous phase. The mass of contaminant in the aqueous phase was calculated by multiplying the concentration by the mass of water present in the wet foam. The mass of MEK adsorbed to the foam was calculated as the total mass of contaminant sorbed minus the mass absorbed by water. The same procedure was applied to obtain the mass of contaminant desorbed from the foam.

3.7 Analytical Techniques

3.7.1 TOC Measurement

The foam cylinders were wetted with deionized water to bring the moisture content to 65%. The wet cylinders were submerged into a plastic bucket containing 9 L of deionized water. After submersion for at least three hours, each cylinder was squeezed to remove excess water. Using glass microfiber filters GF/F 47mm Ø (Whatman, England), the 9.0 L of water was filtered with a vacuum pressure station from Cole-Palmer Instrument Co. (Vernon, IL). One filter was used for every 3.0 L of water. After the initial filtration, the 9.0 L was mixed and 10.0 mL of filtered water was filtered into sample vials using a 0.45 µm syringe filter (Millex, Bedford, MA). The total organic carbon content of each sample was analyzed using a TOC-5050A from Shimadzu (Kyoto, Japan). This procedure was repeated until the TOC content was found to be less than 0.5 mg/L.

3.7.2 CO₂ Analysis

A Servomex Ir1520 infrared CO₂ analyzer (Servomex Company, Inc., Norwood, MA) was used to measure effluent CO₂ concentrations during shock loading experiments. Windaq software (Datataq Instruments, Akron, OH) was used for online data acquisition. Concentrations were measured and recorded at one second intervals. Average influent CO₂ concentrations measured immediately prior to shock loading experiments were subtracted from effluent concentrations measured during the shock loading experiments to calculate the CO₂ increase across the biofilter height.

To avoid damage to the instrument from the humidified air stream, a separate sample port off of the condensation loop was used for CO₂ measurements.

3.7.3 Gas-phase MEK Analysis

Gas-phase MEK concentrations were measured using a MiniRAE 2000 portable photoionization detector (PID) (RAE Systems Inc., Sunnyvale, CA). This was calibrated using a two point calibration. The zero point was set using N₂ (BOC Gases, Port Allen, LA). The second calibration point was measured using either a 198 ppm_v or a 1090 ppm_v MEK balance nitrogen certified calibration gas standard (BOC, Port Allen, LA). The higher calibration gas was used to verify calibration during the shock loading experiments (where the concentration was higher than the 198 ppm_v calibration point).

The effluent gas stream was passed through a condensation loop to remove moisture from the gas stream. This was necessary due to the PID's sensitivity to condensing moisture present in the gas stream being analyzed. A constant temperature re-circulating water bath was set at 0°C, and the water was re-circulated through a glass water jacket.

3.8 Nutrient Addition

Nutrients were added to each biofilter approximately every 40 days. At this time, 9.0 L of nutrient solution described in section 3.3 was made. Each biofilter was disassembled and washed with hot tap water. All the packing material for a particular biofilter was placed in a five gallon bucket containing 3.0 L of the nutrient solution, and each foam cylinder was brought to approximately 65% moisture content.

3.9 Nitrate Analysis

During the nutrient addition procedure described above, a pre-cut and pre-weighed foam wedge was removed to determine the $\text{NO}_3\text{-N}$ concentration in each system. The foam wedge was placed in an Erlenmeyer flask containing 250 mL of deionized water and mixed vigorously. The solution was then diluted as necessary for the $\text{NO}_3\text{-N}$ concentration to fall into the range of a standard curve. A HACH Nitrate Test Kit (HACH Company, Loveland CO) was used to prepare the samples for spectrophotometric analysis at 500 nm. The samples were run against a blank containing all the reagents in DI water with no sample.

CHAPTER 4 RESULTS

4.1 Fixed-Bed Adsorption and Desorption Experiments

Figure 4.1 depicts abiotic adsorption data at all three EBRTs (120, 40, and 20 seconds) for both 106 ppm_v and 530 ppm_v influent MEK concentrations. Effluent MEK concentrations were normalized (by dividing by the influent MEK concentration) so that both 106 and 530 ppm_v could be depicted on the same graph. For the 120 second EBRT (top) 10% of the influent MEK concentration was observed in the effluent after approximately 100 minutes for both the 106 and 530 ppm_v concentrations. For the 40 second EBRT (middle), 10% of the influent concentration was observed in the effluent after approximately 40 and 38 minutes for the 106 and 530 ppm_v concentrations, respectively. For an EBRT of 20 seconds (bottom), 10% of the influent MEK was observed in the effluent after 7 and 15 minutes for the 106 and 530 ppm_v concentrations, respectively. As expected, the time needed to reach 10% breakthrough decreased as the EBRT decreased (flow rate increased).

For an influent gas-phase MEK concentration of 106 ppm_v, the mass of MEK sorbed to the packing medium (total absorbed in the water plus adsorbed to the foam) was calculated to be 138, 325, and 394 mg for EBRTs of 120, 40, and 20 seconds, respectively, (average of replicate data). Likewise, for an influent gas-phase MEK concentration of 530 ppm_v, the mass of MEK sorbed to the packing medium (total absorbed in the water plus adsorbed to the foam) was calculated to be 730, 936, and 993 mg for EBRTs of 120, 40, and 20 seconds, respectively, (average of replicate data). For an influent MEK concentration of 106 ppm_v, the mean mass of MEK

sorbed to the packing medium (average of all data) was calculated to be 286 mg (37.1 g MEK/m³ wet packing medium). For an influent MEK concentration of 530 ppm_v, the mean mass of MEK sorbed to the packing medium (average of all data) was calculated to be 886 mg (115.1 g MEK/m³ wet packing medium).

Figure 4.2 presents dimensionless MEK effluent concentrations during desorption experiments conducted immediately after the adsorption experiments presented in Figure 4.1. For desorption following equilibration with an influent gas-phase MEK concentration of 106 ppm_v, it took approximately 169, 69, and 86 minutes for the effluent MEK concentrations to decrease to 10% of the initial influent concentration for EBRTs of 120, 40, and 20 seconds, respectively. Likewise, for desorption following equilibration with an influent gas-phase MEK concentration of 530 ppm_v, it took approximately 169, 69, and 37 minutes for the effluent MEK concentrations to decrease to 10% of the initial influent concentration for EBRTs of 120, 40, and 20 seconds, respectively. The time required for the effluent MEK concentration to decrease to 10% of the initial concentration was proportional to the EBRT.

For desorption following equilibration with an influent gas-phase MEK concentration of 106 ppm_v, the mass of MEK desorbed from the packing medium (total absorbed in the water plus adsorbed to the foam) was calculated to be 132, 221, and 243 mg for EBRTs of 120, 40, and 20 seconds, respectively, (average of replicate data). Likewise, desorption following equilibration with an influent gas-phase MEK concentration of 530 ppm_v, the mass of MEK desorbed from the packing medium

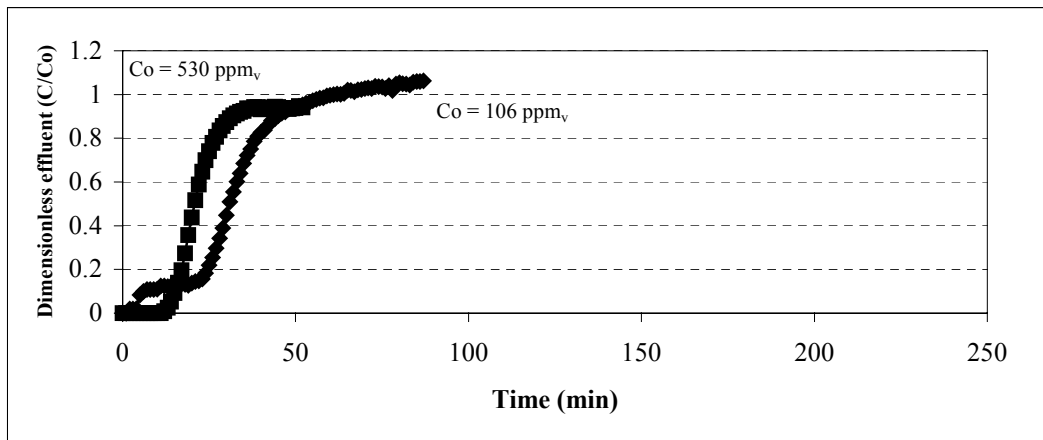
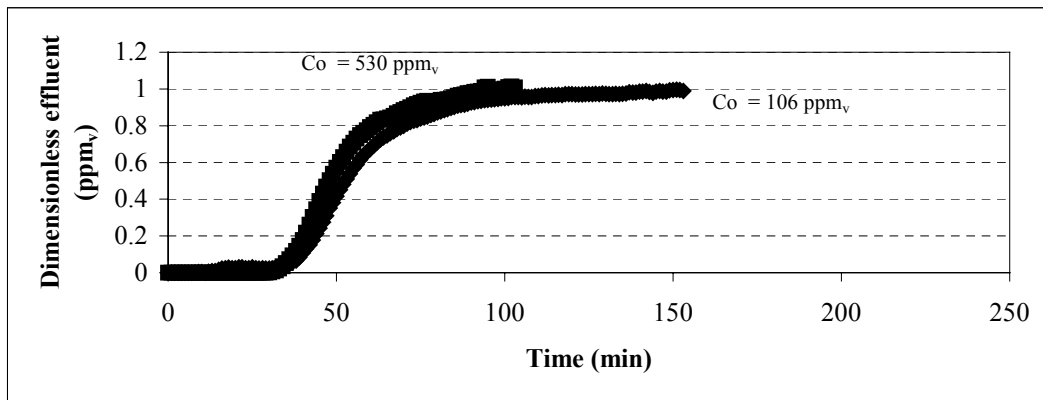
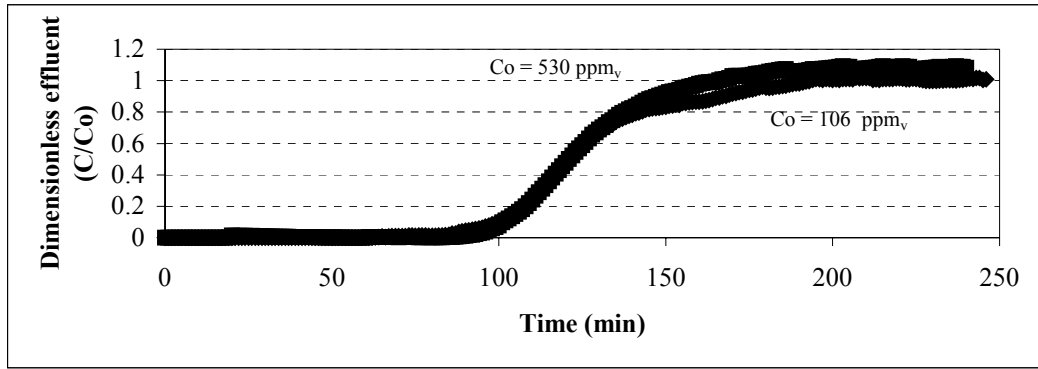


Figure 4.1: Sorption of MEK to foam packing medium with influent concentrations of 106 and 530 ppm_v for EBRTs of 120 seconds (top), 40 seconds (middle), and 20 seconds (bottom).

(total absorbed in the water plus adsorbed to the foam) was calculated to be 856, 904, and 909 mg for EBRTs of 120, 40, and 20 seconds, respectively, (average of replicate

data). For an initial MEK concentration of 106 ppm_v, the mean mass of MEK desorbed from the wet packing medium (average of all data) was calculated to be 199 mg (25.8 g MEK/m³ wet packing medium). For an initial MEK concentration of 530 ppm_v, the mean mass of MEK desorbed from the wet packing medium (average of all data) was calculated to be 890 mg (115.6 g MEK/m³ wet packing medium).

For an MEK concentration of 106 ppm_v, the mean mass of MEK sorbed (37.1 g MEK / m³ wet packing medium) and desorbed (25.8 g MEK / m³ wet packing medium) are within 30% of one another. For an MEK concentration of 530 ppm_v, the mean mass of MEK sorbed (115.1 g MEK / m³ wet packing medium) and desorbed (115.6 g MEK / m³ wet packing medium) are within 0.5% of one another.

Concluding that flow (i.e. stripping) is a key factor in the sorption properties of this medium, or the sorptive properties of this medium are relatively low.

4.2 Normal Loading

Immediately after the biofilters were inoculated, normal loading experiments (described in Section 3.4) were initiated. Effluent MEK concentrations were monitored over a period lasting more than 228 days to assess treatment efficiency for the different biofilters. Results from these experiments are depicted in Figure 4.3. For the continuously operated biofilter (BF1) removal efficiency was calculated as the average over a period lasting at least 30 minutes. For the periodically operated

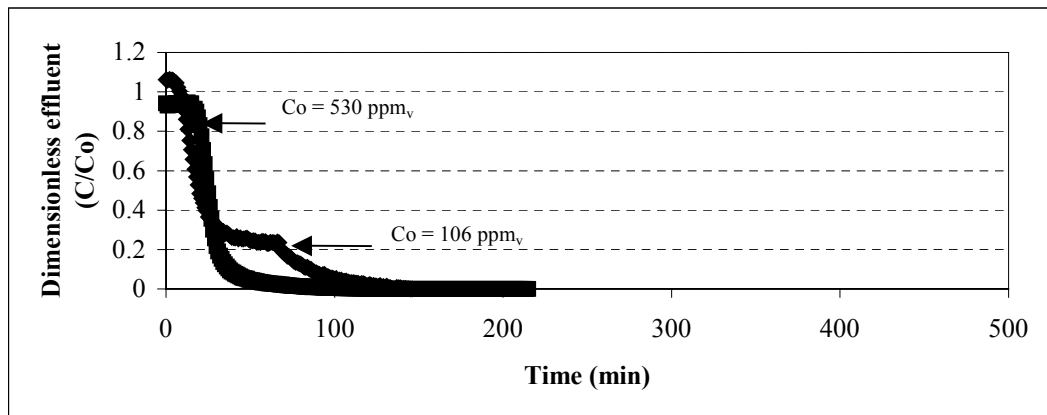
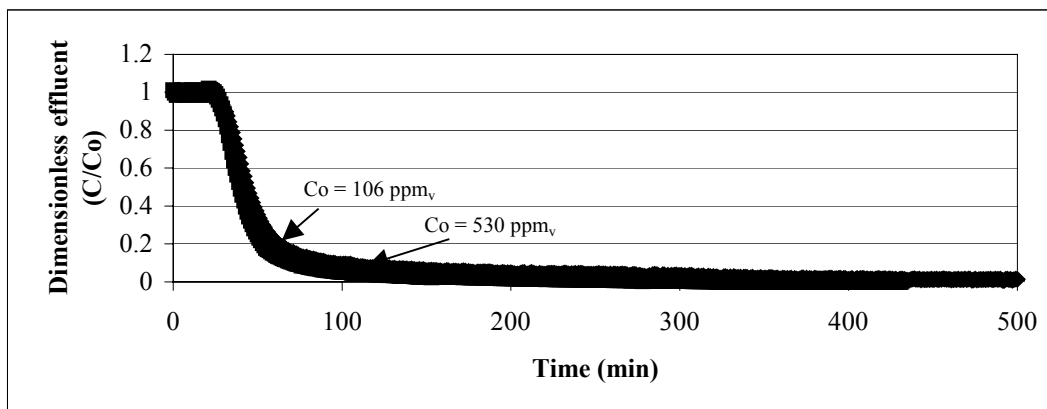
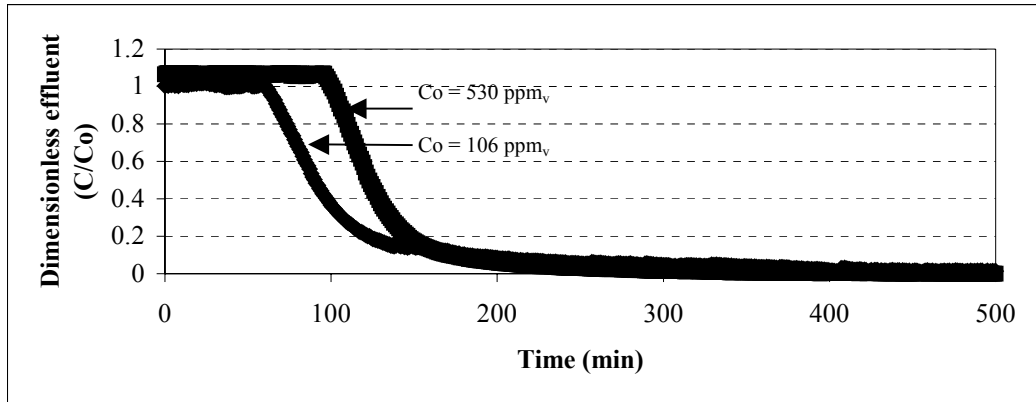


Figure 4.2: Desorption of MEK from foam packing medium following loading with influent concentrations of 106 and 530 ppm_v for EBRTs of 120 seconds (top), 40 seconds (middle), and 20 seconds (bottom).

biofilters (BF2 and BF3), removal efficiency was calculated as one minus the mass of effluent MEK during the experiment (effluent was monitored until less than 1 ppm_v was detected) divided by the mass of MEK entering the system during the experiment. As shown in the figure, BF1 removed approximately 96% of the MEK on Day 1 while removal in BF2 and BF3 was approximately 32% and 40%, respectively. Removal efficiency in BF1 increased to approximately 99% by Day 2, and remained at that level throughout the experiment.

Removal efficiency in BF2 increased to approximately 80% by Day 2 and fluctuated between 77 and 94% during the first 56 days of operation. BF3 removal efficiency increased from approximately 40% on Day 0 to approximately 84% on Day 18 where it remained relatively stable until Day 26. Removal efficiency in BF3 subsequently declined, reaching a value of approximately 25% on Day 54.

On Day 55, the biofilters' nutrient content was re-normalized by immersing all foam cylinders from all biofilters into 9.0 L of freshly prepared nutrient solution. Following the nutrient addition procedure on Day 56, removal efficiency in BF1 remained at greater than 99%. Removal efficiency in BF2 ranged from 92% to greater than 99%. Removal efficiency in BF3 increased to 68% on Day 58, the first time removal efficiency was measured following nutrient addition. BF3 performance continued to improve, reaching a maximum of approximately 93% on Day 67. Performance subsequently decreased, reaching a removal efficiency of approximately 42% from Day 71 to Day 81.

On Day 84, nutrient addition was conducted with each biofilter's foam packing immersed in a 3.0 L volume of the nutrient solution. For this nutrient addition and subsequent nutrient additions, the contents of each biofilter were kept separate from the other biofilters during nutrient. BF1 and BF2 performance had stabilized at greater than 99% removal by Day 68, while BF3 performance stabilized at approximately 80% removal.

Figure 4.4 depicts the data presented in Figure 4.3 in terms of elimination capacity for each biofilter averaged over the cycle. Figure 4.5 presents the elimination capacity data over each biofilters feed cycle. BF3's greater EC during the FEED period results from its much higher loading rate during FEED.

4.2.1 Discussion

During the normal loading experiments, BF2 and BF3 showed somewhat sporadic treatment efficiency. MEK removal efficiency in BF2 remained greater than 90% after the nutrient normalization, and remained close to 100% for the remainder of the experiment. MEK removal efficiency in BF3 was unstable for the duration of the normal loading, and only after 100 days did it remain above 75% removal efficiency. Based on these results it was concluded that BF2 and BF1 showed far superior treatment over BF3 during the normal loading experiments.

There a number of different phenomena that could have had resulted in BF3's unstable treatment. If the biofilters had been operated at the 120 second EBRT for the first couple of weeks, we might have seen a far better comparison over the first 50

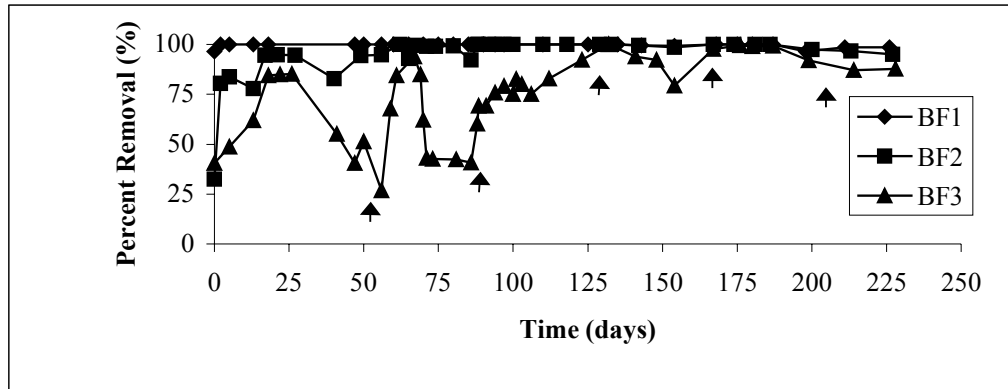


Figure 4.3: MEK removal efficiency for the biofilters during normal loading periods. Arrows indicate dates of nutrient addition.

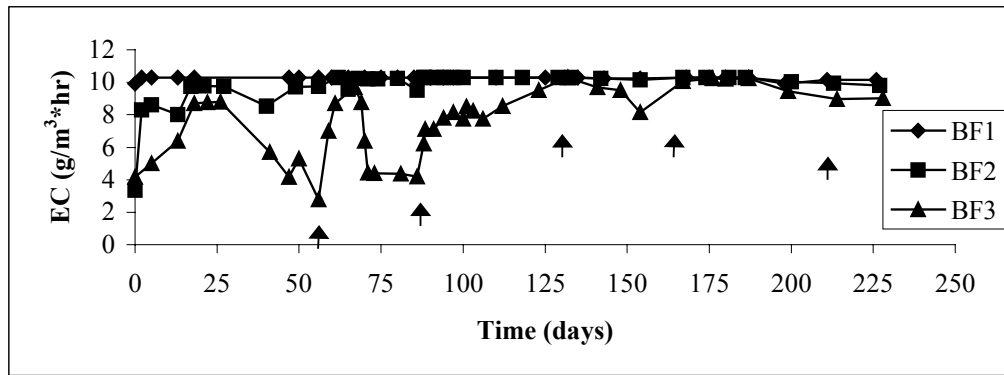


Figure 4.4: MEK elimination capacity for each biofilter averaged over the entire cycle. Arrows indicate dates of nutrient addition.

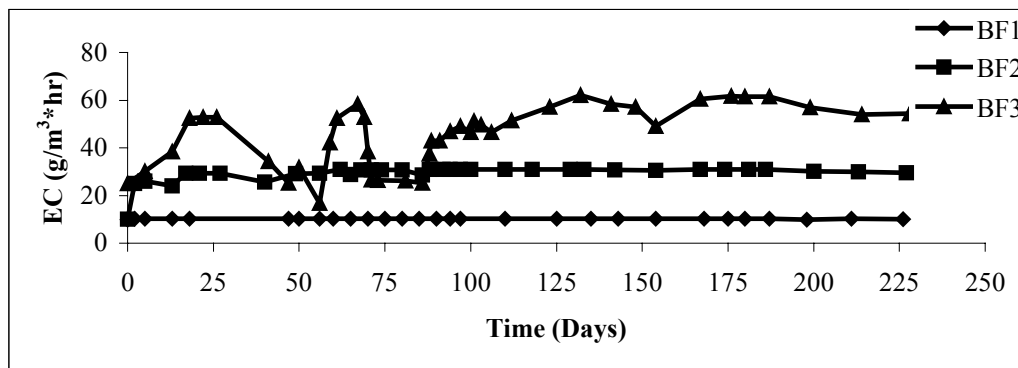


Figure 4.5: MEK elimination capacity for each biofilter during the FEED period.

days. Figure 4.5, shows the far greater EC BF3 had over the FEED period, which correlates with more contaminant degraded during this period and could result in a higher percent of breakthrough after FEED.

4.3 Shock Loading I

Shock Loading I experiments (described in section 3.5) were performed in triplicate beginning on Day 114. Gas flow rate calibration and influent MEK concentrations were periodically measured to insure that the target influent concentrations were achieved. Figure 4.6 depicts the target influent MEK concentrations as a function of time for BF1, BF2, and BF3 during Shock Load I. For the continuously operated biofilter (BF1), the increased MEK concentration during the shock loading experiment is arbitrarily depicted as starting at time equal to 1 hour.

Shock Load I experiments were conducted on BF1 on Days 114, 133, and 153. Time zero in Figure 4.7, along with the subsequent graphs for Shock Load I, designates the beginning of the shock load. On Day 114 (27 days since nutrient addition), the top graph of Figure 4.7, MEK was detected in the effluent at approximately 1.3 hrs after the influent concentration was increased to five times that of the normal loading (500 ppm_v). In BF1 MEK was detected in the effluent for approximately 1.7 hours, and reached a maximum concentration during this time period of approximately 270 ppm_v. A total of 157 mg of MEK was detected in the effluent of BF1. The second experiment was performed on Day 133 (4 days since nutrient addition) and is represented by the middle graph of Figure 4.7. No clear

breakthrough time could be determined for this run. The maximum MEK effluent concentration detected in BF1 was 110 ppm_v, detected 1.5 hours after the shock load. The third experiment conducted on Day 153 (24 days since nutrient addition), represented by the bottom graph of Figure 4.7, had a maximum MEK effluent concentration detected in BF1 was 215 ppm_v, detected 2 hours after the shock load. CO₂ production was monitored over this last run. The CO₂ production data reached a maximum value at approximately the end of the shock load (i.e., the first hour). The drop in CO₂ production and the increase in MEK breakthrough were proportional. Suggesting the system had reached its treatment capacity (i.e. breakthrough).

Shock Load I was conducted on BF2 on Days 115, 132, and 143. Results are presented in Figure 4.8. Time zero in Figure 4.8 designates the beginning of the shock load (i.e., one hour into REACT). The effluent MEK concentration during the initial shock load test on BF2 on Day 115 (28 days since nutrient addition) is presented in the top graph. No obvious pattern for MEK breakthrough could be determined. The effluent MEK concentration reached a maximum of approximately 13 ppm_v, and a total of 25 mg of MEK was detected in the effluent. The second shock load, conducted on Day 132 (3 days since nutrient addition), showed a maximum MEK effluent concentration of 5.5 ppm_v detected at 1.3 hours after the shock load ended (see middle graph of Figure 4.8). MEK was detected in BF2's effluent 1.07 hours after the shock load ended and lasted for 1.2 hours, with a total of 2.38 mg of MEK detected in the effluent. The bottom graph of Figure 4.8 shows the shock load conducted on Day 143 (14 days since last nutrient addition). A maximum MEK

effluent concentration of 4.4 ppm_v was detected at 1.5 hours after the shock load ended. A distinct breakthrough time could not be determined from the data.

Shock Load I was conducted on BF3 on Days 124, 132, and 140. The first shock load, Day 124 (37 days since nutrient addition), is represented by the top graph of Figure 4.9. MEK was detected in the effluent approximately 1.8 hours after the shock load was initiated. MEK was detected for approximately 0.6 hours, and reached a maximum of 13 ppm_v. A total of 5 mg of MEK was detected in the effluent. The shock load conducted on Day 132 (3 days since nutrient addition), represented by the middle graph, shows an effluent concentration that remained below 1.0 ppm_v throughout the experiment. A mass of 0.06 mg MEK was detected in the effluent. Data from the final replicate of Shock Load I for BF3 on Day 140 (11 days since nutrient addition), is presented in the bottom graph of Figure 4.9. Once again, the MEK effluent concentration remained below 1.0 ppm_v throughout the experiment, and a total of 0.007 mg of MEK detected in the effluent. CO₂ concentrations were measured during this final replicate for BF3. Greater CO₂ production for BF3, depicted in this bottom graph, compared to BF1 would be a very good indicator of the superior performance of the periodically operated biofilter to the continuously operated biofilter for these conditions.

It is interesting to note, that MEK was not detected in the effluent until after the one-hour shock load was over and the influent concentration had been decreased to 106 ppm_v for all three biofilters. This suggests that switching back to the lower EBRT would likely have caused stripping of the contaminant from the packing medium.

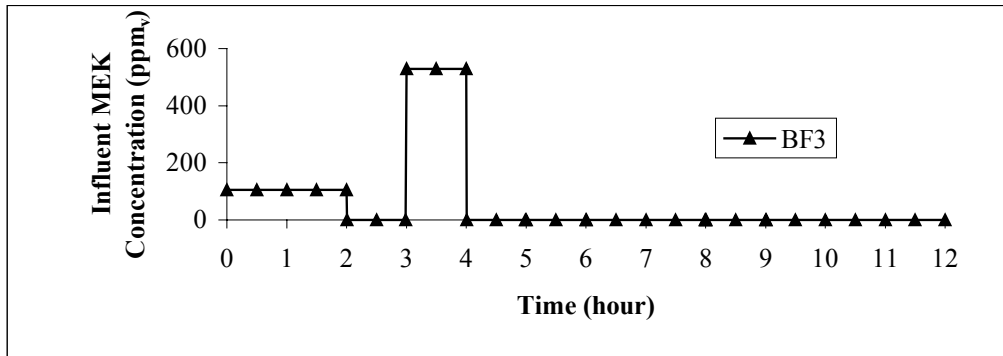
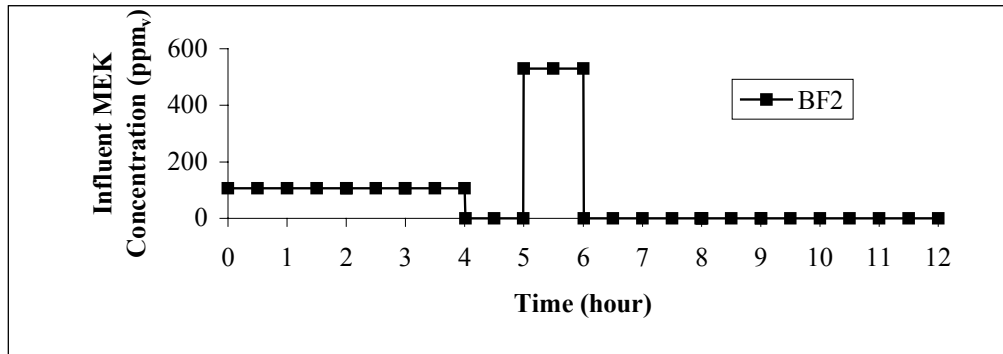
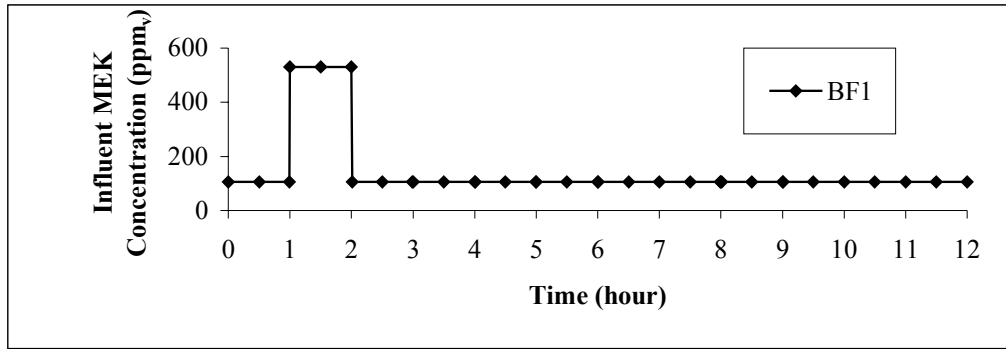


Figure 4.6: Influent MEK concentration for BF1 (top), BF2 (middle), and BF3 (bottom) during Shock Load I.

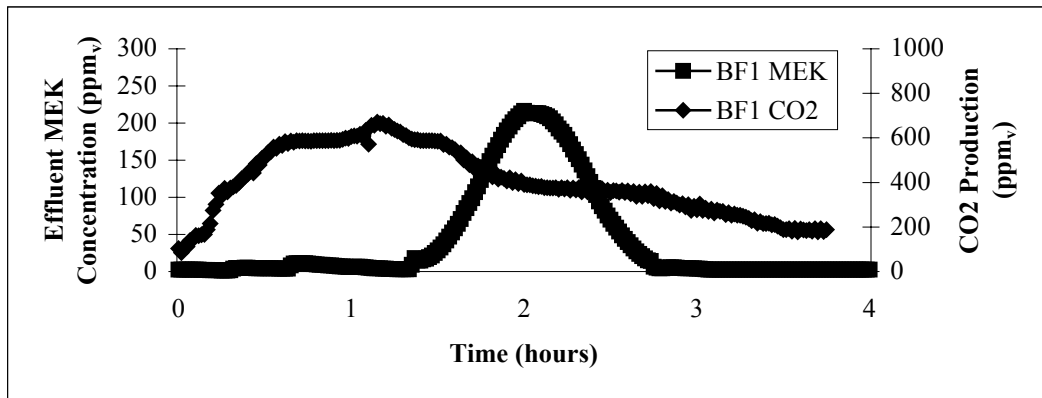
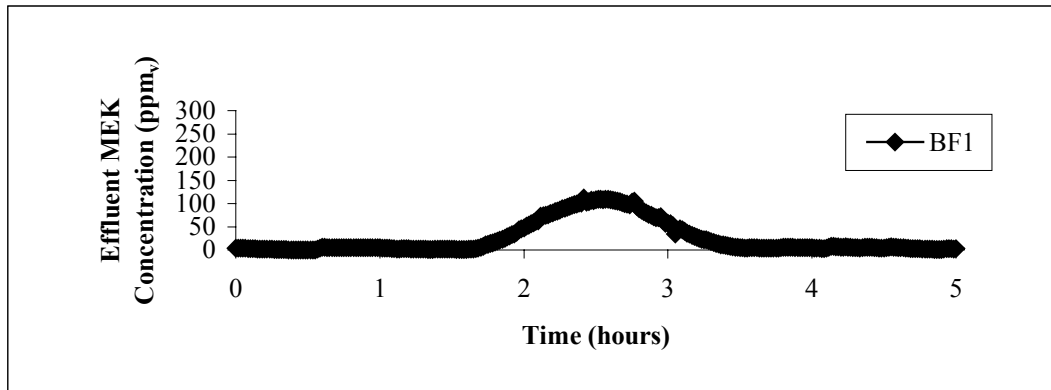
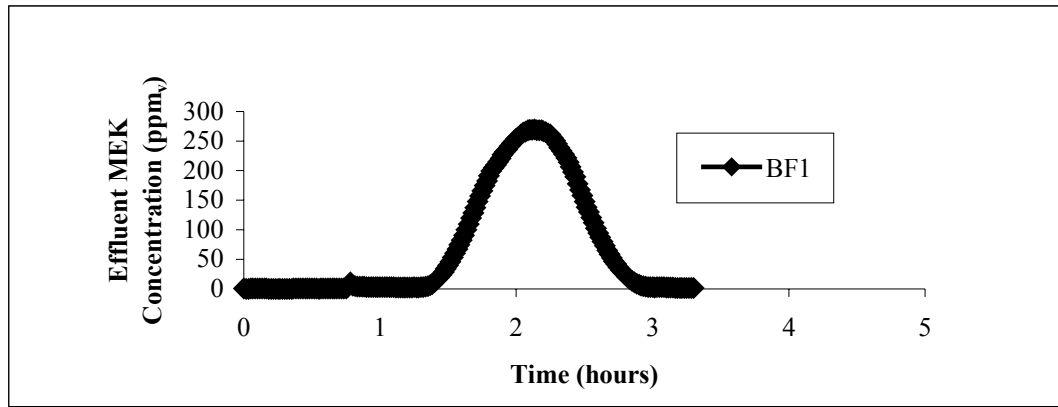


Figure 4.7: Effluent MEK and CO₂ concentrations for BF1 during Shock Load I performed on Days 114 (top), 133 (middle), and 153 (bottom).

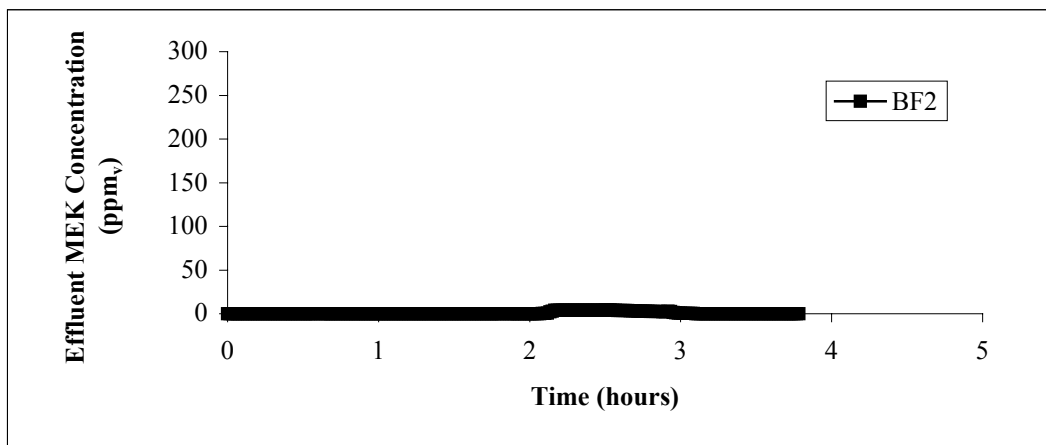
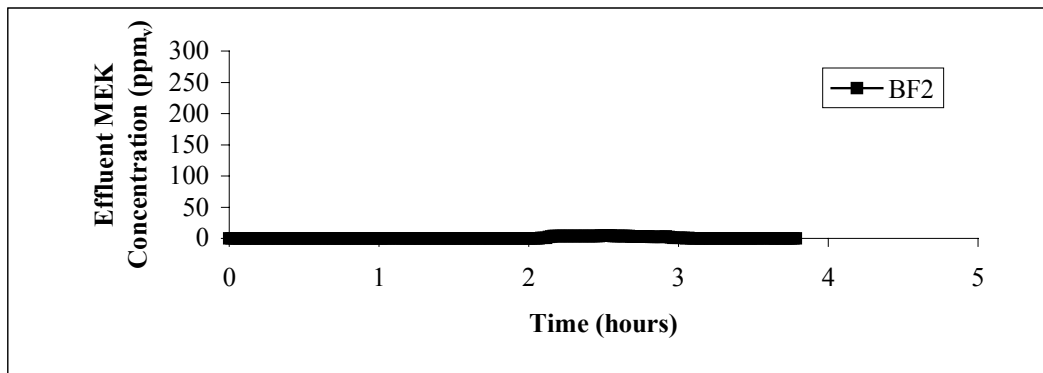
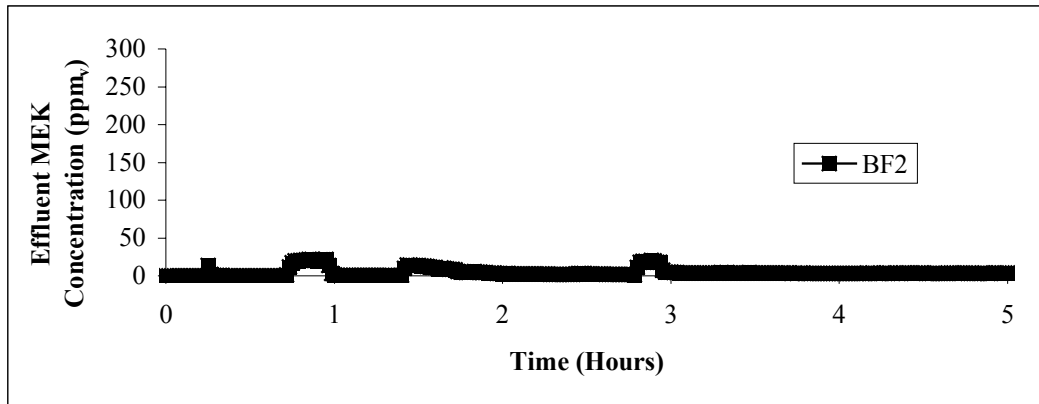


Figure 4.8: Effluent MEK concentrations for BF2 during Shock Load I performed on Days 115 (top), 132 (middle), and 143 (bottom).

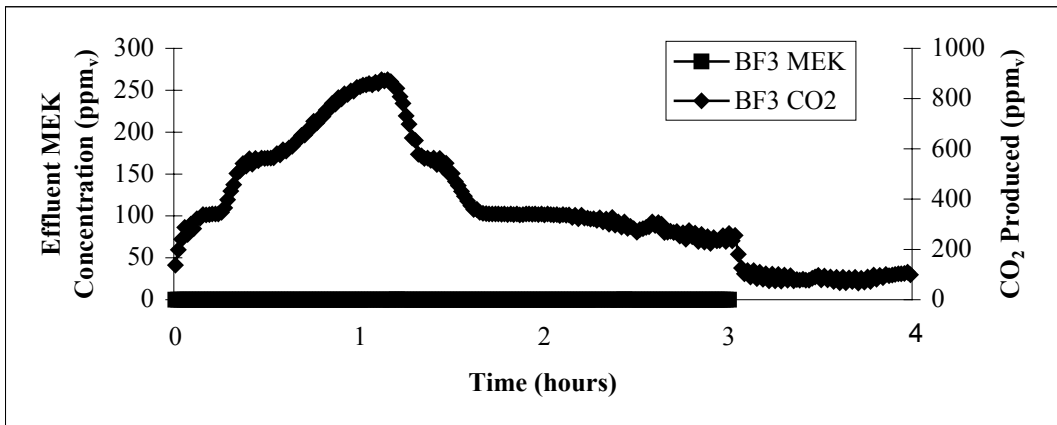
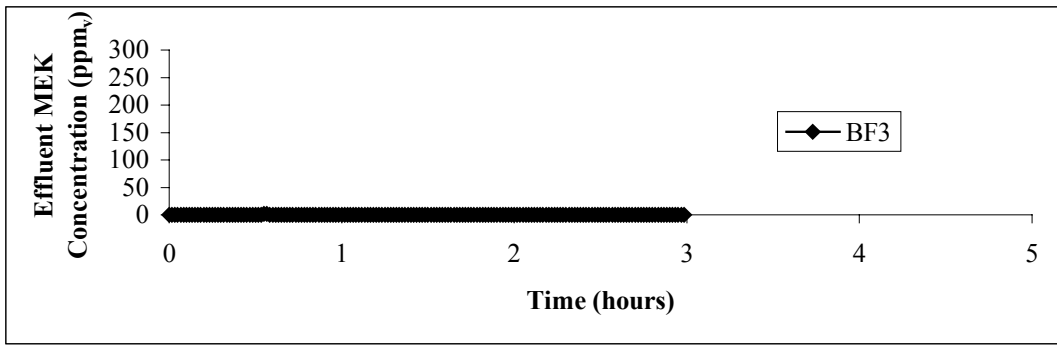
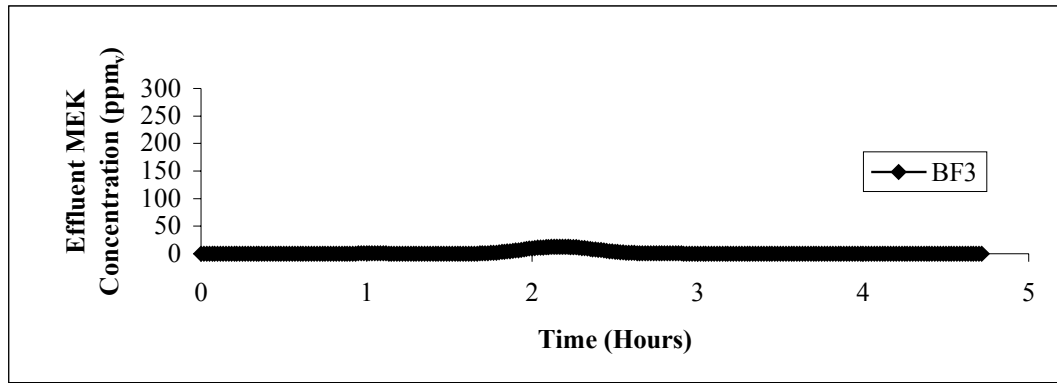


Figure 4.9: Effluent MEK and CO₂ concentrations for BF3 during Shock Load I performed on Days 124 (top), 132 (middle), and 140 (bottom).

4.3.1 Discussion

Table 4.1 summarizes results from Shock Load I experiments. As shown in the table, the removal efficiency in BF2 and BF3 (97.3% and 99.5%, respectively) were superior to BF1 (54.8%). It should be noted that BF3 actually receives a smaller mass load during the transient period compared to normal operation (see Table 3.3). The mass loaded to BF3 over a normal FEED cycle is 62 g/m³/hr, where as over the shock load BF3 received 51.9 g/m³/hr. Therefore, BF3 actually receives a lower mass load of MEK during the shock load than during normal loading.

Table 4.1: Summary of Shock Load I.

Biofilter	Shock Load	Mass MEK in During 1 hr shock load (mg)	Mass MEK Escaped (mg)	% MEK Escaping	Maximum MEK Concentration Escaping. (ppm _v)
BF1	IA	363	157	43.3	270
	IB		222	61.2	110
	IC		112	30.9	215
	Average		164	45.1	198
BF2	IA	363	25	6.89	13
	IB		2.38	0.66	5.5
	IC		2.09	0.56	4.4
	Average		9.82	2.71	7.6
BF3	IA	363	5	1.38	13
	IB		0.06	0.02	< 1.0
	IC		0.01	0.01	< 1.0
	Average		1.69	0.47	~ 5.0

4.4 Shock Loading II

Shock Loading II experiments (described in section 3.6) were begun on Day 158. The experiments were performed in triplicate, with each biofilter being tested once before the second run was administered. Gas flow rate calibration and influent MEK concentrations were periodically measured to insure the concentrations were correct. Figure 4.10 shows the influent MEK concentration as a function of time for BF1, BF2, and BF3 during Shock Load II. For the continuously operated biofilter (BF1), the MEK loading imposed on the biofilter was identical to that imposed during Shock Load I experiments. For comparison purposes, the increased MEK concentration for BF1 during Shock Load II experiments is arbitrarily depicted as starting at time equal to 1 hour.

Shock Load II experiments were conducted on BF1 on Days 159, 165, and 167. It should be noted that time zero in Figure 4.11, along with the subsequent graphs for Shock Load II, designates the beginning of the shock load. On day 159 (30 days since nutrient addition) MEK was detected in the effluent approximately 1.4 hrs after the influent concentration was increased to 530 ppm_v (see top graph of Figure 4.11). MEK was detected in the effluent for approximately 1.6 hours, and reached a maximum concentration during this time period of approximately 270 ppm_v. A total of 209 mg of MEK was detected in the effluent of BF1. The second experiment was performed on Day 165 (36 days since nutrient addition) and is represented by the middle graph of Figure 4.11. MEK was detected in the effluent approximately 1.8 hrs after the influent concentration was increased to 530 ppm_v, and reached a maximum

concentration during this time period of approximately 140 ppm_v. A total of 80 mg of MEK was detected in the effluent of BF1. The third experiment conducted on Day 167 (2 days since nutrient addition), represented by the bottom graph of Figure 4.11. MEK was detected in the effluent approximately 1.8 hrs after the influent concentration was increased to 530 ppm_v, and reached a maximum concentration during this time period of approximately 60 ppm_v. A total of 22 mg of MEK was detected in the effluent of BF1.

Shock Load II was performed on BF2 on days 158, 160, and 167. The top graph of Figure 4.12 represents the shock load data collected on Day 158 (29 days since nutrient addition). No clear breakthrough time could be determined from the data. BF2's effluent MEK concentration reached a maximum of approximately 5 ppm_v, with a total of 16 mg of MEK detected in the effluent. Data from the second shock load experiment, conducted on Day 160 (31 days since nutrient addition), is presented in the middle graph in Figure 4.12. Once again, such small readings make it difficult to report and breakthrough times with certainty. The BF2 effluent MEK concentrations were less than 1.0 ppm_v. The readings were so small that an accurate mass of MEK could not be determined. Effluent MEK and CO₂ data from the third Shock Load II replicate, conducted on Day 167 (2 days since nutrient addition), is presented in the bottom graph in Figure 4.12. Once again, BF2 effluent MEK concentrations were less than 1.0 ppm_v. A total of 0.27 mg of MEK was detected in the BF2 effluent.

Shock Load II was performed on BF3 on Days 160, 165, and 169. Data from the Day 160 shock load (31 days since nutrient addition) is presented in the top graph of Figure 4.13. BF3 had a maximum effluent MEK concentration of 3 ppm_v, resulting in 1.5 mg of MEK in the effluent. BF3 received a second shock load on Day 165 (36 days since nutrient addition) with the data being presented in the middle graph of Figure 4.13. MEK effluent concentrations reached a maximum of 5 ppm_v, while a total of 1.5 mg of MEK was detected in the BF3 effluent. Data from the third shock load, conducted on Day 169 (4 days since nutrient addition), is shown in the bottom graph of Figure 4.13. There was less than 1.0 ppm_v breakthrough of MEK, which resulted in small of a mass value to report with certainty.

CO₂ data was not available for BF1's Day 159 Shock Load II, but should be similar to the data from Days 165 and 167 since the experimental parameters were identical. Data from BF1's Day 167 run showed a maximum CO₂ production value of approximately 1000 ppm_v, and was observed 45 minutes after the shock load was completed. BF2's CO₂ data from Day 158 showed a maximum production value of approximately 1210 ppm_v 0.15 hours after the end of the shock load. CO₂ data for BF3 on Day 160 reached a maximum of approximately 1030 ppm_v 0.30 hours after the end of the shock load. However, a much faster reduction of the CO₂ levels of BF2 would indicate a smaller amount of time that would need to be allotted for REACT. CO₂ values were greater in the periodically operated biofilters, which along with the amount of MEK breakthrough for BF1, depict superior performance.

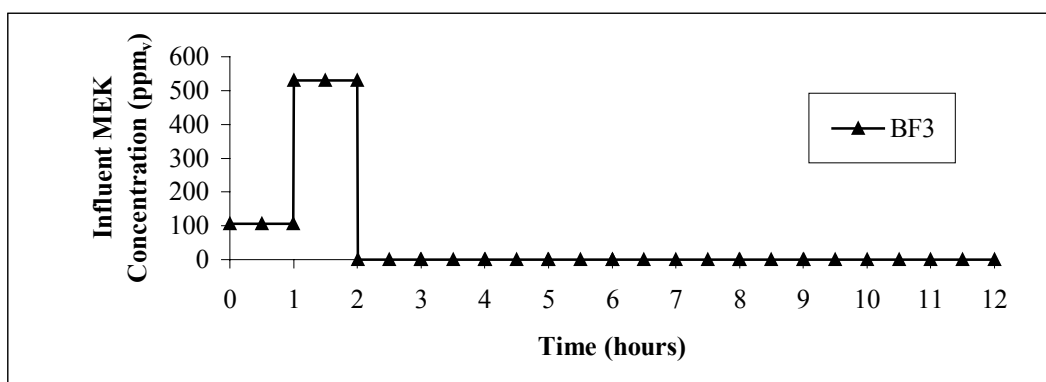
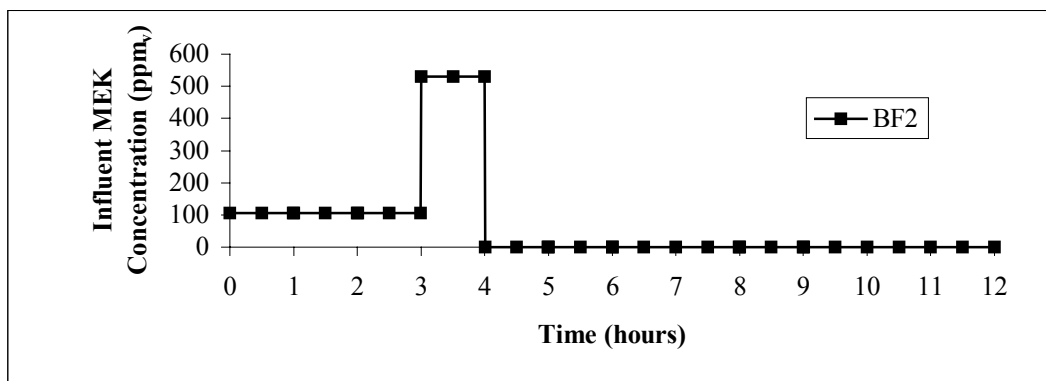
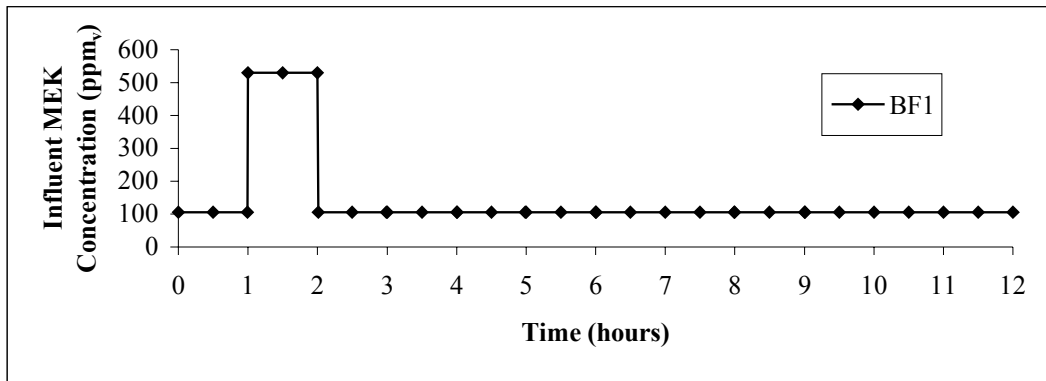


Figure 4.10: Influent MEK concentrations for BF1 (top), BF2 (middle), and BF3 (bottom) during Shock Load II.

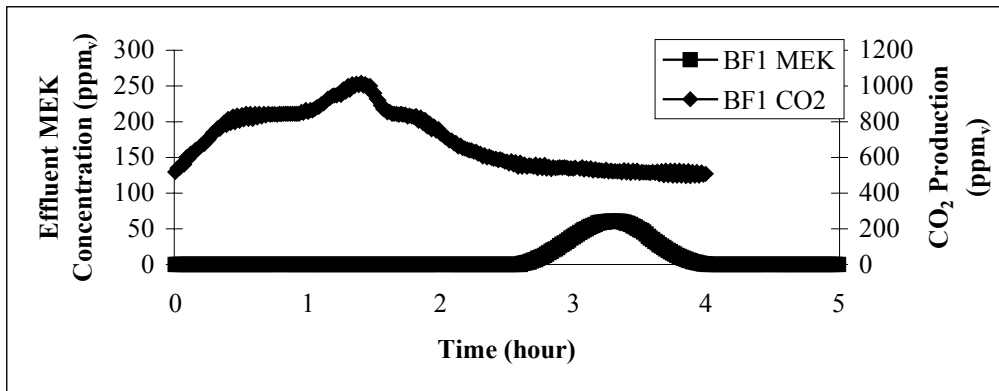
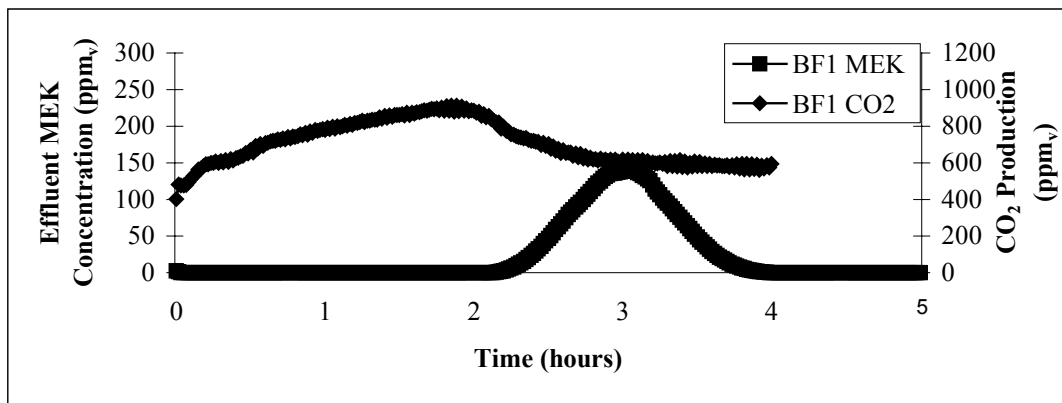
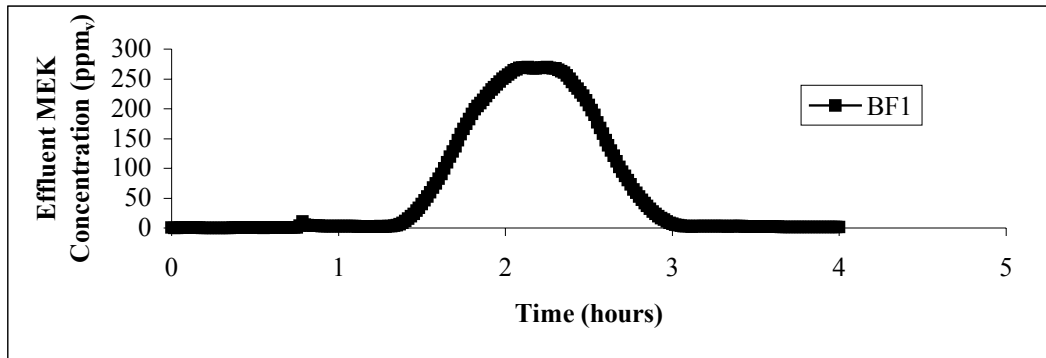


Figure 4.11: Effluent MEK and CO₂ concentrations during Shock Load II on BF1 performed on Days 159 (top), 165 (middle), and 167 (bottom).

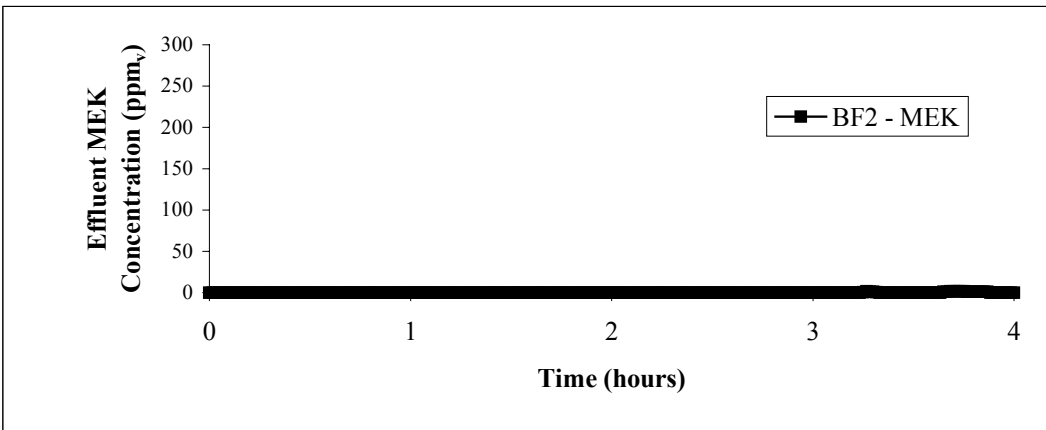
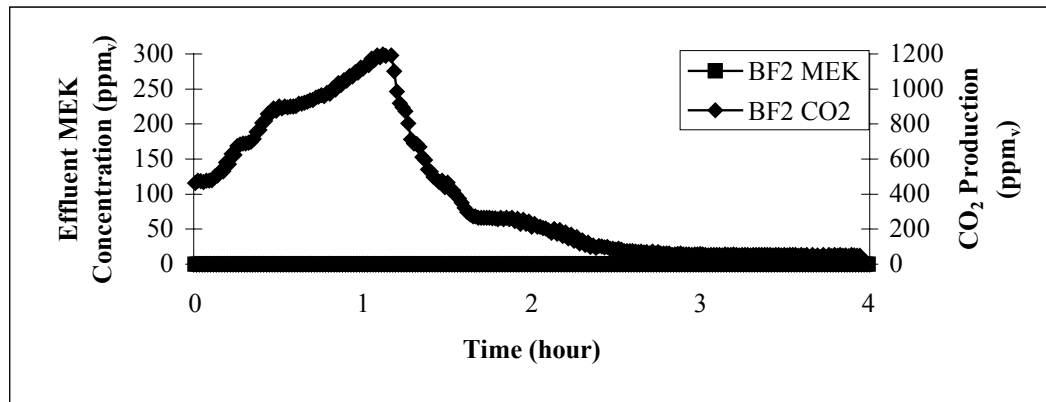
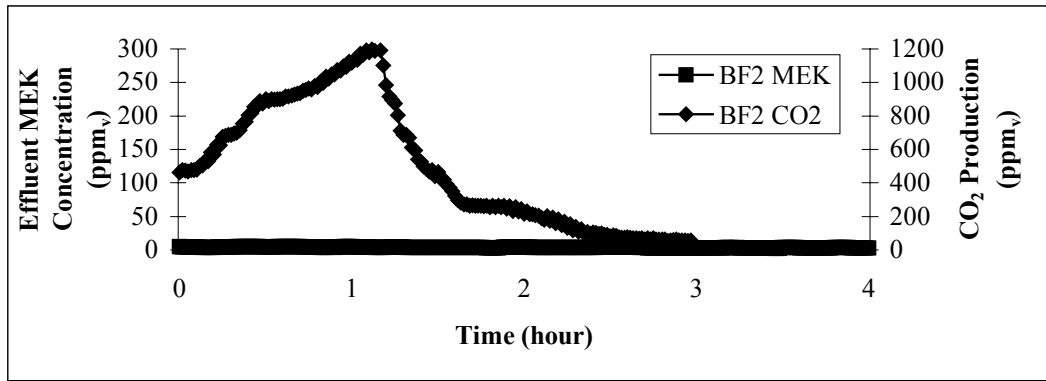


Figure 4.12: Effluent MEK and CO₂ concentrations during Shock Load II on BF2 performed on Days 158 (top), 160 (middle), and 167 (bottom).

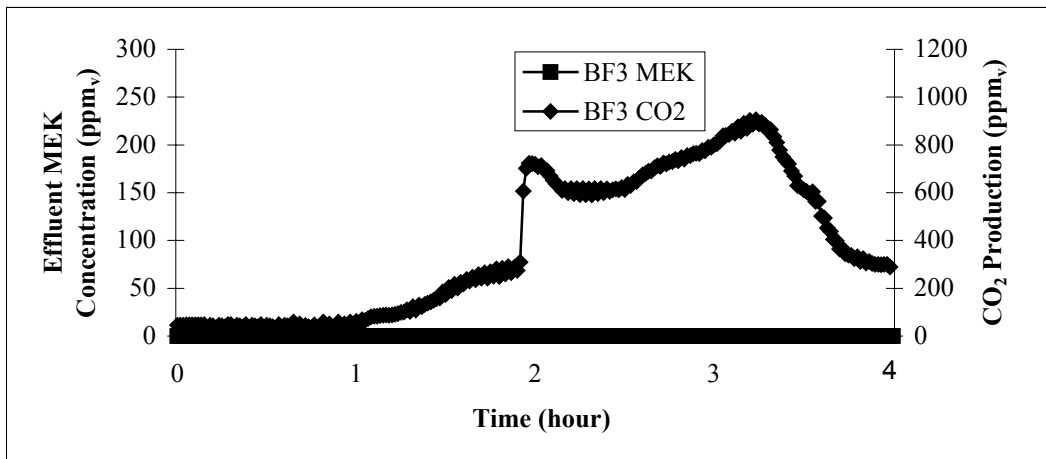
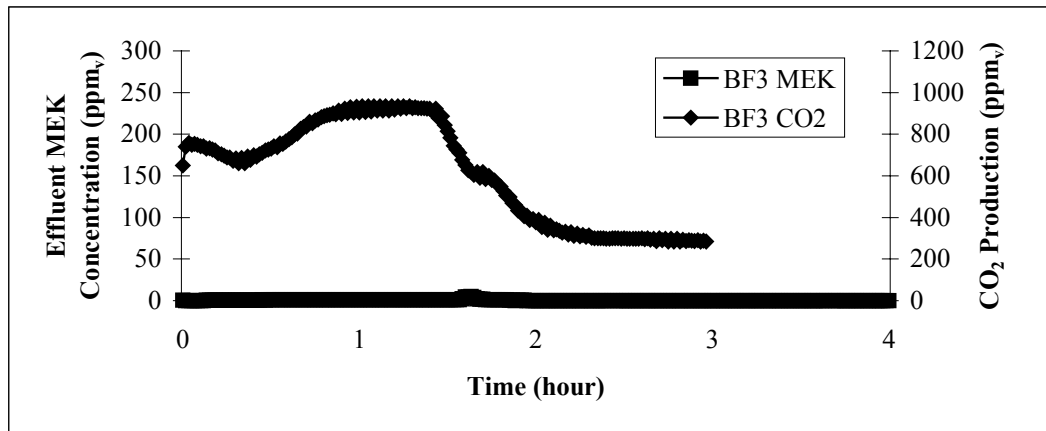
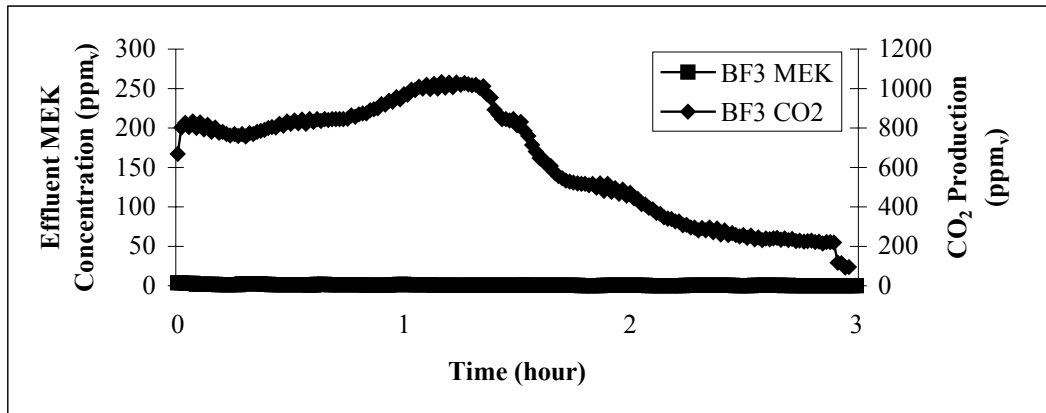


Figure 4.13: Effluent MEK and CO₂ concentrations during Shock Load II on BF3 performed on Days 160 (top), 165 (middle), and 169(bottom).

4.4.1 Discussion

Table 4.2 summarizes results from Shock Load II. The data for BF2 and BF3 did not show a significant change from the Shock Load I data, with removal efficiencies for BF's I, II, and II of 71.6, 98.5, and 99.7%, respectively. While the periodically operated biofilters showed far greater ability to handle the shock load than the continuously operated biofilter, the data were not conclusive to when the periodically operated system could best handle a transient or shock load.

Table 4.2: Summary of Shock Load II.

Biofilter	Shock Load	Mass MEK in During 1 hr shock load (mg)	Mass MEK Escaped (mg)	% MEK Escaping	Maximum MEK Concentration Escaping. (ppm _v)
BF1	IIA	363	209	57.6	270
	IIB		80	22	140
	IIC		22	6.1	60
	Average		103	28.7%	157
BF2	IIA	363	16	4.4	5
	IIB		0	0	< 1.0
	IIC		0.28	0.28	< 1.0
	Average		5.43	1.56	2.3
BF3	IIA	363	1.5	0.41	3
	IIB		1.5	0.41	5
	IIC		0	0	< 1.0
	Average		1.00	0.27	3.0

4.5 Shock Load III

Shock Loading III experiments (described in Section 3.5) were begun on Day 229. The experiments were performed in triplicate, with each biofilter being tested once before the second run was administered. Flow calibration and influent concentrations were checked at the beginning of these experiments to insure that the

desired shock load was achievable for each system. Influent concentrations were periodically checked to make sure target influent MEK concentrations were achieved. Influent MEK concentrations as a function of time for BF1, BF2, and BF3 during Shock Load III are identical to Shock Load II (see Figure 4.10); however, with this experiment, the biofilter EBRTs remained at their normal setting (i.e., 120, 40, and 20 seconds for BF1, BF2, and BF3, respectively).

Shock Load III experiments were conducted on BF1 on days 229, 231, and 233. Time zero in Figure 4.14, along with the subsequent graphs for Shock Load III, designates the beginning of the shock load. On day 229 (18 days since nutrient addition) MEK was detected in the effluent approximately 1.8 hrs after the influent concentration was increased to 530 ppm_v (see top graph of Figure 4.14). MEK was detected in the effluent for approximately 1.0 hour, and reached a maximum concentration of approximately 70 ppm_v during this time period. A total of 25.5 mg of MEK was measured in the effluent.

Data from the second shock load, conducted on Day 231 (20 days since nutrient addition), is shown in the middle graph of Figure 4.14. MEK was detected in the effluent approximately 1.6 hrs after the shock load was initiated. MEK was detected in the effluent for approximately 1.0 hours, and reached a maximum concentration during this time period of approximately 69 ppm_v. A total of 30 mg of MEK was measured in the effluent. Data from the third Shock Load III replicate on Day 233 (22 days since nutrient addition) is presented in the bottom graph from Figure 4.14. MEK was detected in the effluent approximately 2.0 hrs after the shock load

was initiated. MEK was detected in the effluent for approximately 1.0 hour, and reached a maximum concentration during this time period of approximately 66 ppm_v. A total of 25.3 mg of MEK was measured in the effluent.

Shock Load III experiments were conducted on BF2 on Days 229, 231, and 233. Effluent MEK data from Day 229 (18 days since nutrient addition) is depicted in the top graph of Figure 4.15. Time zero in Figure 4.15, designates the beginning of the shock load (i.e., last hour of FEED). As shown in the figure, MEK was detected approximately 0.9 hours after the shock load was initiated, with breakthrough lasting for approximately 1.8 hours. A maximum concentration of approximately 439 ppm_v was observed, resulting in a total mass of 755 mg of MEK in the effluent.

The middle graph in Figure 4.15 shows the data from Day 231 (20 days since nutrient addition). MEK was detected approximately 0.85 hours after the shock load was initiated. MEK was detected in the effluent from BF2 for approximately 1.8 hours, reaching a maximum concentration of approximately 475 ppm_v. A total of 798 mg of MEK was detected in the effluent over this experiment. Data from Day 233 (22 days since nutrient addition) is presented in the bottom graph of Figure 4.15. MEK was detected approximately 0.9 hours after the shock load was initiated. MEK was detected in the effluent from BF2 for approximately 1.6 hours, reaching a maximum concentration of approximately 440 ppm_v. A total of 755 mg of MEK was detected in the effluent over this experiment.

BF3 received Shock Load III on Days 230, 232, and 234. Effluent MEK data from Day 230 (19 days since nutrient addition) is presented in the top graph of Figure

4.16. MEK was measured in the biofilter effluent at the start of the shock loading event at a concentration of approximately 30 ppm_v. Starting approximately 0.3 hours, after the shock load was initiated the effluent MEK concentration rapidly increased to a concentration of approximately 460 ppm_v at 0.58 hours. The effluent MEK concentration gradually increased to a concentration of 498 ppm_v over the next 0.6 hours. Subsequently, the MEK concentration rapidly decreased to approximately less than 10 ppm_v during the next 0.5 hours. The maximum effluent MEK concentration during this time period was approximately 490 ppm_v, and a total of 1673 mg of MEK was detected in the effluent during and after the shock loading event.

Data from Day 232 (21 days since nutrient addition) is depicted in the middle graph of Figure 4.16. MEK was measured in the biofilter effluent at a concentration of approximately 10 ppm_v. Starting approximately 0.3 hours after the shock load was initiated the effluent MEK rapidly increased to a concentration of approximately 480 ppm_v. The concentration gradually increased to approximately 495 ppm_v over the next 0.6 hours. Subsequently, the MEK concentration rapidly decreased to less than 10 ppm_v over the 0.3 hours. The maximum MEK effluent concentration during this time period was approximately 495 ppm_v. A total of 1952 mg of MEK was detected in the effluent. Data from the final shock load for BF3 conducted on Day 234 (23 days since nutrient addition) is shown in the bottom graph of Figure 4.16. MEK was measured in the biofilter effluent at a concentration of approximately 10 ppm_v. Starting approximately 0.3 hours after the shock load was initiated the effluent MEK rapidly increased to a concentration of approximately 455 ppm_v. The concentration gradually increased to approximately 480 ppm_v over the next 0.6 hours. Subsequently, the MEK

concentration rapidly decreased over the next 0.35 hours to approximately 20 ppm_v before gradually decreasing to less than 10 ppm_v. The maximum MEK effluent concentration during this time period was approximately 480 ppm_v. A total of 1936 mg of MEK was detected in the effluent during this period.

Normal loading data from Days 214 and 228, (see Figures 4.17 and 4.18) showed removal efficiencies of 86.98 and 87.67%, respectively. Both experiments had breakthrough times of approximately 2.0 hours, and the total MEK masses during these events were 205 and 198 mg, for Days 214 and 228. An analysis of the data shows that over these two experiments the breakthrough masses were proportioned as follows: during the first hour of feed 40 and 38 mg were present in the breakthrough over the first hour, 133 and 121 mg over the second hour, and 32 and 39 mg of MEK was present over the REACT time period monitored. Data from Day 214 showed an MEK concentration of 2.3 ppm_v detected in the effluent at 0.5 hours. The concentration increased to a value of approximately 34 ppm_v at 1.13 hour where it remained until the 2.18 hour mark. The MEK concentration in the effluent then decreased to 0 at 2.4 hours. Data from Day 228 had a MEK breakthrough concentration of 3.1 ppm_v at 0.52 hours. The concentration increased to a value of approximately 30 ppm_v at the 1.0 hour mark. The MEK effluent concentration remained at approximately 20 ppm_v until the 2.0 hour mark. The effluent MEK concentration then dropped to 0 at 2.31 hours. Assuming the Shock Loading III data for BF3 included normal loading MEK, and taking the mean mass from the REACT periods of Days 214 and 228, 35.5 mg; the percent removal would be 16.5% instead of 14.9%, which is negligible.

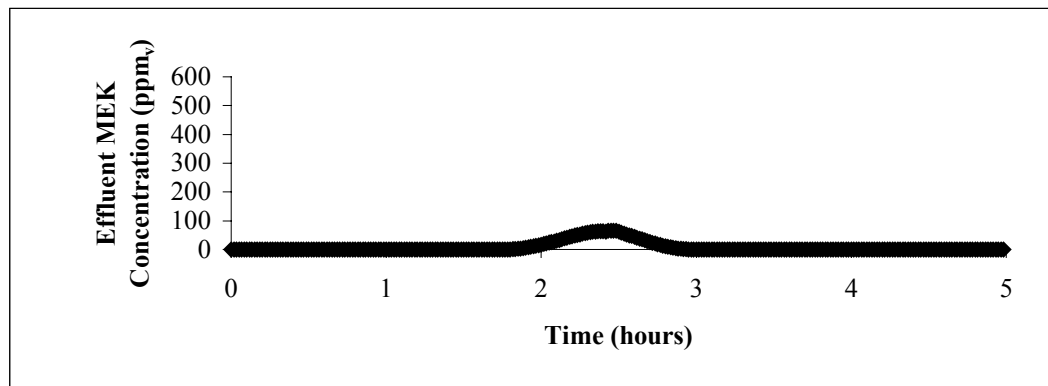
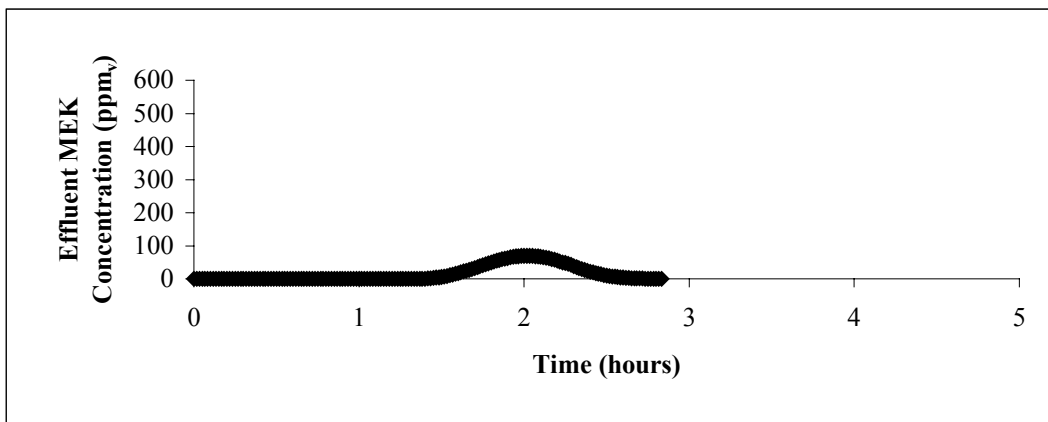
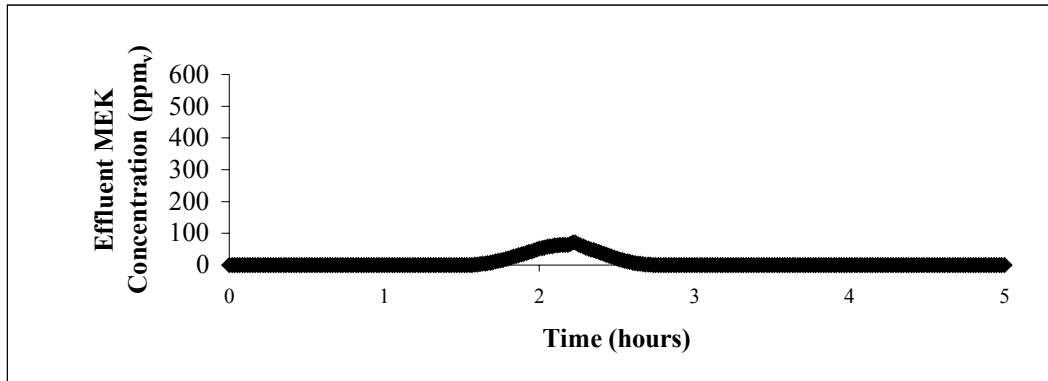


Figure 4.14: Effluent MEK concentrations for BF1 during Shock Load III performed on Days 229 (top), 231 (middle), and 233 (bottom).

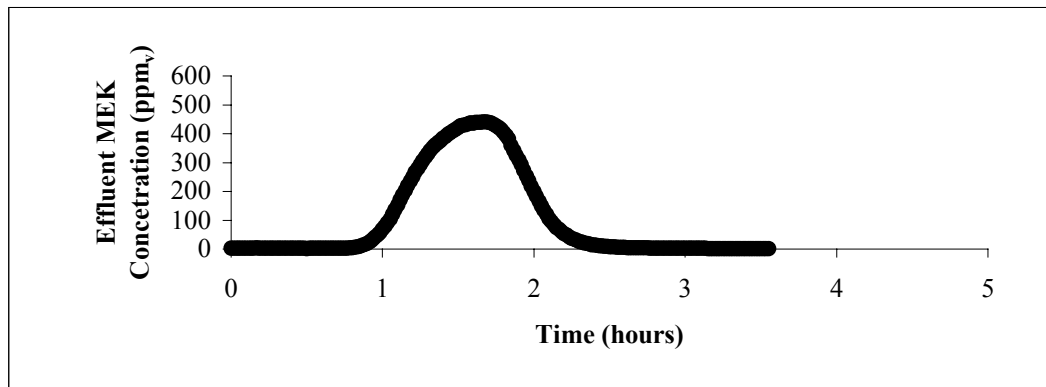
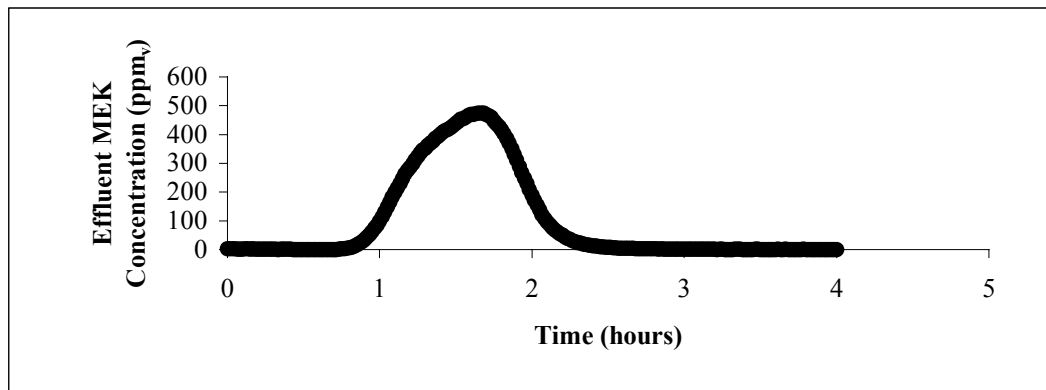
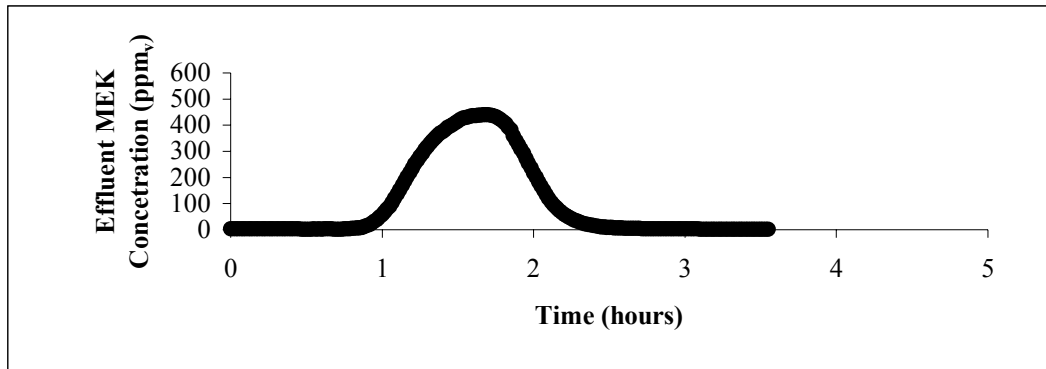


Figure 4.15: Effluent MEK concentrations for BF2 during Shock Load III performed on Days 229 (top), 231 (middle), and 233 (bottom).

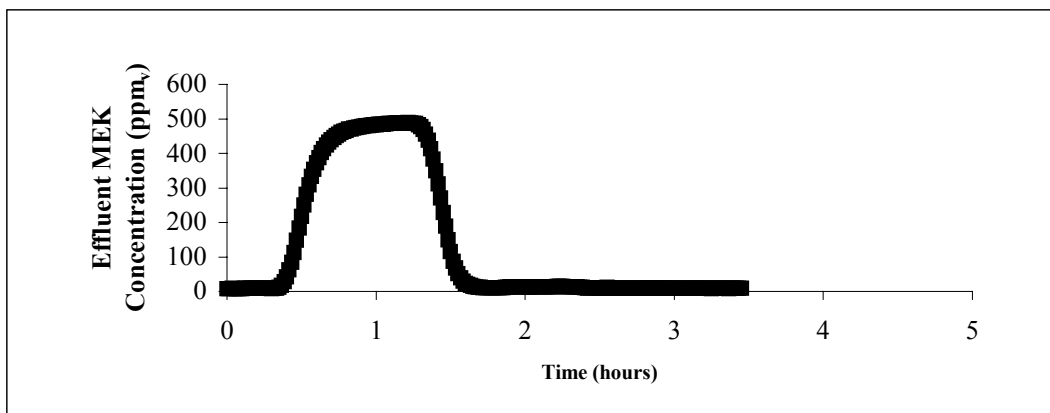
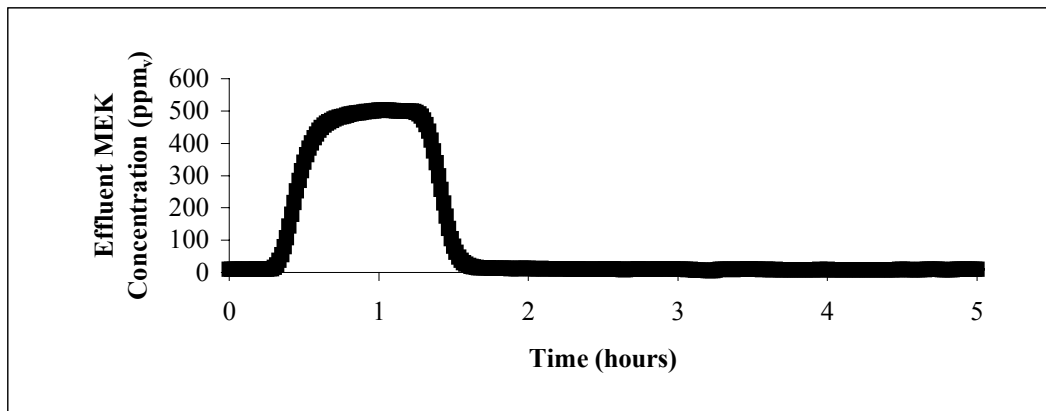
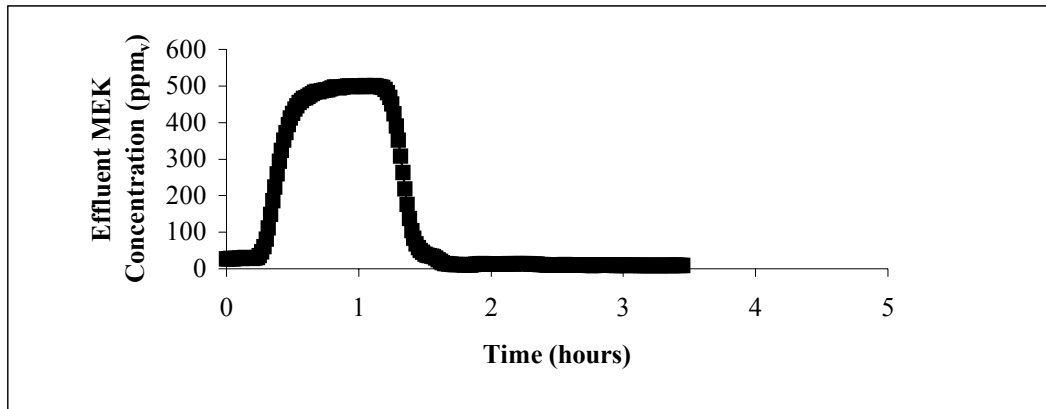


Figure 4.16: Effluent MEK concentrations for BF3 during Shock Load III performed on Days 230 (top), 232 (middle), and 234 (bottom).

4.5.1 Discussion

Table 4.3 summarizes the results from the Shock Load III experiments. As would be expected, the ability to make operational adjustments during a transient event is a necessity. When BF2 and BF3's EBRTs were not adjusted to the 120 second EBRT, representing the transient loading condition where all six biofilters would be loaded (see Figures 2.1 and 2.2, transient loading condition VII and IV, respectively), a very large amount of breakthrough would be expected as was shown with these experiments. BF1 performed much far greater over Shock Load III with respect to Shock Load's I and II (7.44% MEK escaping compared to 28.7 and 45.1%, for Shock Load's III, II, and I, respectively). This could be due to a number of things, but was most likely the result of increased growth over the packed bed during all three experimental periods. As shown in the table, BF1's removal efficiency (92.8%) was far greater than BF2 and BF3's (29.4 and 14.9%, respectively), indicating that without online monitoring or the ability to make operational adjustments, a periodic operational strategy does not work.

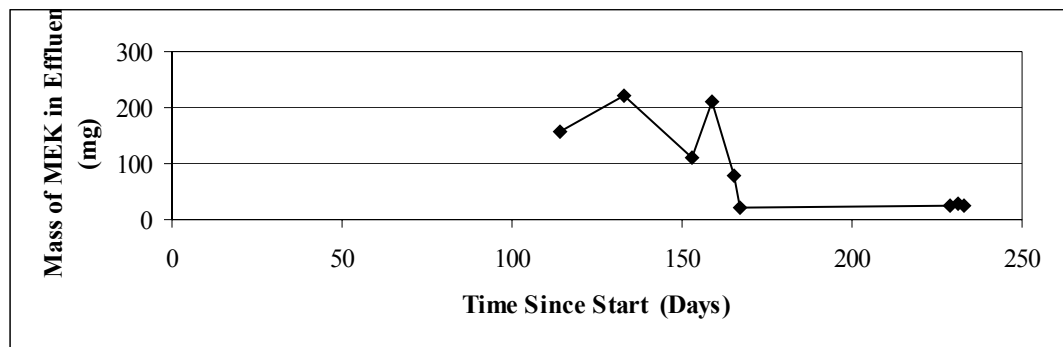


Figure 4.17: Summary of BF1 performance over all three Shock Loads relative to the start-up of the Biofilter.

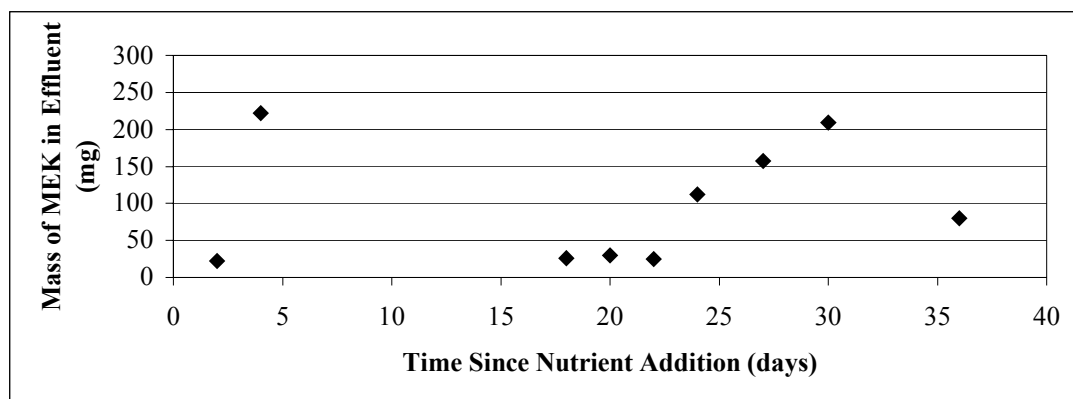


Figure 4.18: Summary of BF1 performance over all three Shock Loads relative to the time since nutrient addition.

Table 4.3: Summary of Shock Load III.

Biofilter	Shock Load	Mass MEK in During 1 hr shock load (mg)	Mass MEK in Effluent (mg)	% MEK Escaping	Maximum MEK Concentration Escaping. (ppm _v)
BF1	IIIA	363	26	7.16	70
	IIIB		30	8.26	69
	IIIC		25	6.89	66
	Average		26	7.44	68
BF2	IIIA	1089	755	69.3	439
	IIIB		798	73.3	475
	IIIC		755	69.3	440
	Average		769	70.63	451
BF3	IIIA	2179	1673	76.8	490
	IIIB		1952	89.6	500
	IIIC		1936	88.8	489
	Average		1853	85.1	493

CHAPTER 5 DISCUSSION AND CONCLUSIONS

5.1 Conclusions

Polyurethane foam manufactured in the laboratory for this study proved to have low sorptive capacity for MEK. When the wet packing medium (65% moisture content) was equilibrated with a humidified gas stream containing MEK at concentrations of 106 or 530 ppm_v, the mean mass of MEK sorbed to the wet medium (absorbed in the liquid phase and adsorbed to the foam) was 37.1 and 115.1 g/m³, respectively. Furthermore, essentially all of the initially sorbed MEK desorbed from the medium when contaminant-free air was purged through it. This indicates that MEK sorption to the foam medium is not expected to be an appreciable sink for MEK in biofilters constructed using this medium. Martinez (2001), determined that incorporation of powdered activated carbon (PAC) into the polyurethane foam greatly increased the sorptive properties of the medium without changing the porosity and other structural characteristics of the foam; however, that medium was not used in the biofilter experiments described herein.

Following inoculation of the biofilters, the continuously operated biofilter (BF1) removed approximately 96% of the MEK after just one day of operation and approximately 99% after two days. This rapid increase in performance following system start-up indicates that the inoculation procedure (using an enrichment culture acclimated to the contaminant and nutrient medium) can provide rapid start-up of polyurethane foam based biofilters. In contrast, start-up periods of considerable length (several weeks) have been reported for biofilters using alternate media and inoculation procedures. Although the periodically operated biofilters took somewhat longer to reach such a high removal efficiency, the elimination capacity (overall biodegradation rate) during the FEED period was comparable to that of the continuously operated biofilter.

During the first 54 days of operation, treatment performance in the continuously loaded biofilter (BF1) was quite stable with essentially 100%

contaminant removal (effluent MEK concentration below detection limit). Treatment performance in the periodically operated biofilter loaded for one-third of its cycle (BF2) exhibited removal efficiency with an average of approximately 88%. On the other hand, treatment performance of the periodically operated biofilter loaded for only one-sixth of its operating cycle (BF3) reached a maximum removal efficiency of approximately 80% from Days 23 to Day 28 and subsequently declined to approximately 25% on Day 54. Such diminished performance was not surprising considering previous research indicating that nutrient limitations (particularly in the case of nitrogen) can become kinetically limiting in a biofilter system at high loading rates long before an overall stoichiometric limitation is observed (Moe and Irvine, 2001).

Once a regular nutrient addition strategy was employed (starting on Day 54), the contaminant removal efficiency in the continuously operated biofilter (BF1) and the periodically operated biofilter loaded for one-third of its cycle (BF2) exhibited nearly identical treatment efficiency during normal loading periods with greater than 99% removal observed in each. Treatment performance in the periodically operated biofilter loaded for only one-sixth of its operating cycle (BF3) exhibited unstable performance for the duration of the normal loading, and only after 100 days did it remain above 75%. The gradual increase in BF3 removal efficiency from Day 100 to Day 180 suggests that the microbial populations may acclimate to the periodic loading over time; however, because no attempt was made to characterize the microbial population or its spatial distribution, such conclusions cannot be drawn from the experimental results reported herein. The loading rate during the FEED period of BF3 was twice that of BF2 and six times that of BF1. The obviously superior treatment in BF2 and BF1 (in comparison to BF3) during the normal loading experiments suggest that the loading rate during the FEED period of BF3, which clearly exceeded the biodegradation rate in the system (as evident from contaminant breakthrough), was too high to ensure consistently high removal efficiency.

Because other loading rates were not examined in this study (e.g., FEED period lasting only one-fourth or one-fifth of the cycle) it is not certain what the maximum loading rate is during the FEED period which could be completely removed. It is clear, however, from the results of BF2 experiments, that periodic operation where the biofilter is loaded for only a portion of the cycle (but at a proportionally higher rate so that the mass loading over a complete cycle is the same as for a comparable continuous-flow system) can effectively remove MEK from a contaminated gas stream in a stable manner over long time periods (more than 200 days).

Shock Loading I results demonstrated that the removal efficiencies in the periodically operated biofilters (97.3% in BF2 and 99.5% in BF3, respectively) were superior to the continuous-flow biofilter (54.8% in BF1). This is consistent with the findings of Irvine and Moe (2001) who reported similar results when comparing the performance of continuous-flow and periodically-operated biofilters treating a toluene-contaminated gas stream. It thus appears that these results may be generalized to other waste gas streams.

It should be noted that the mass loading rate to BF3 during a normal FEED cycle was $62 \text{ g/m}^3/\text{hr}$, whereas during the Shock Load I conditions, BF3 received an MEK loading of $51.9 \text{ g/m}^3/\text{hr}$. Therefore, BF3 actually received a lower mass load of MEK during the shock load than during normal loading. It is not surprising, then, that the system exhibited higher removal efficiency during the shock-loading condition than it did during normal loading conditions.

Results from Shock Load II experiments also indicated superior performance for the periodically operated biofilters in comparison to the continuously operated biofilter, with removal efficiencies for BFI, BFII, and BFIII of 71.6, 98.5, and 99.7%, respectively. While the periodically operated biofilters showed far greater ability to handle the shock load than the continuously operated biofilter, the data was not conclusive to during which portion of the FEED period (i.e., the start of the FEED period in Shock Load I and the end of the FEED period in Shock Load II) the

periodically operated system could most effectively degrade MEK when subjected to a transient period of elevated contaminant load.

Experimental results from the Shock Loading I and II studies described herein demonstrate that controlled periodic operating strategies can enhance contaminant removal of MEK during transient periods of elevated contaminant load. The laboratory-scale biofilters subjected to periodic operation coupled with an active control strategy exhibited substantially higher contaminant removal efficiency than did the continuous flow system. There are several possible explanations for the better performance of the periodically operated biofilters during the Shock Load I and II conditions. 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. A substantial body of previous research on sequencing batch reactors and other periodic processes used for wastewater treatment indicates that periodic loading strategies can markedly affect selection and enrichment and physiological state in a manner that produces microbes with higher specific substrate uptake rates under dynamically loaded conditions (see for example Chiesa and Irvine, 1983; and Wilderer *et al.*, 2001). Additionally, results reported by Moe and Irvine (2001) indicate that microorganisms selected in periodically operated gas-phase biofilters may have higher RNA content than microbes in continuous-flow systems. Microorganisms with higher RNA content are likely able to more quickly respond to transient periods of elevated loading (Daigger and Grady, 1982).

Shock Loading III results indicated a very key factor in the success of the periodic operation strategy. When the EBRTs of BF2 and BF3 were not adjusted to the 120 second EBRT, representing the transient loading condition where all biofilters

constructed in parallel would be loaded simultaneously (see Figures 2.1 and 2.2, transient loading condition VII and IV, respectively), a large amount of MEK breakthrough occurred. As shown in Table 4.3, the removal efficiency in BF1 (92.8%) was far greater than BF2 and BF3's (29.4 and 14.9%, respectively). This indicates that without operational adjustments during transient loading events, periodic operating strategies can result in substantially diminished treatment performance. Thus, there is a clear need for adequate control systems if such an operating strategy is adopted.

Direct comparison of results reported herein to those values found in the literature (see Table 2.1) were difficult to make due to varying treatment systems and experimental parameters. Agathos *et al.* (1997) and Chou and Huang (1997) use of a tubular biofilm reactor and a biotrickling filter, respectively, made any direct comparison of experimental results difficult. Results reported by Amanullah *et al.* (2000) dealt mostly with equilibrium and kinetic studies on MEK adsorption in compost and granular activated carbon. Data reported from Farmer (1994) was only from conditions he used to establish steady state, where the biofilters were operated with a continuous flow strategy, making a comparison of the data of little benefit. Although Deshusses *et al.* (1995) used a similar treatment system, the use of a second compound and constantly changing operational conditions allowed for little confidence in a direct comparison of the reported results.

Experimental results from laboratory studies reported herein demonstrated that periodically operated biofilters are able to treat MEK contaminated gas streams during both normal and shock loading. Particularly, a biofilter operated with a 40 second EBRT (i.e., BF2, see Figure 2.2) had removal efficiencies equal to that of a continuously operated biofilter during normal loading and superior removal efficiencies during shock loading events.

A start-up period allowing the biofilters to be operated using a longer EBRT (e.g., 120 seconds) for a period of time (e.g., two weeks), might eliminate the sporadic treatment performance of BF3 during start-up. A more regulated nutrient addition

would likely have aided in the performance as shown in Figure 4.3, where removal efficiency greatly increased after nutrient addition.

This is not to say that a 40 second EBRT would give the highest removal efficiency. Results presented herein would lead one to conclude that an EBRT of 30 seconds might be the best periodic operation strategy. Cycle lengths could be changed and experimented with which could result in longer or shorter FEED and REACT periods, and ultimately better treatment performance. More sorptive packing would most likely have a large impact on both removal efficiency and operating strategies.

BIBLIOGRAPHY

- Agathos, S.N.; Hellin, E.; Ali-Khodja, H.; Deseveaux, S.; Vandermesse, F.; & Naveau, H. (1997). Gas-Phase Methyl Ethyl Ketone Biodegradation in a Tubular Biofilm Reactor: Microbiological and Bioprocess aspects. *Biodegradation*, 8, 251-264.
- Amanullah, Md., Viswanathan, S., and Farooq, S. (2000). Equilibrium, Kinetics, and Column Dynamics of Methyl Ethyl Ketone Biodegradation. *Industrial and Engineering Chemistry Research*. 39 (3), 3387 – 3396.
- American Public Health Association (1998). Standard Methods for the Examination of Water and Wastewater, 20th ed., APHA Washington DC.
- Bezborodov, A.M.; Rogozhin, I.S.; Ushakova, N.A.; Zhukov, V.G.; Kurlovich, A.E.; and Popov, V.O. (1998) Interaction of Pseudomonas oleovorans and Nocardia rugosa in a Model System for Air Purification from a Toluene-Methyl Ethyl Ketone Mixture. *Applied Biochemistry and Microbiology*, 34(5):466-468.
- Bielefeldt, A.R. and Stensel, H.D. (1999). Treating VOC-Contaminated Gases in Activated Sludge: Mechanistic Model to Evaluate Design and Performance. *Environmental Science and Technology* 33, 3234 – 3240.
- Brauer, H. (1986) Biological Purification of Waste Gases. *International Chemical Engineering*. 26(3). July 1986. 387 – 395.
- Britton, L.N. (1984). Microbial Degradation of Aliphatic Hydrocarbons. Microbial Degradation of Organic Compounds. Volume 13 Microbiology Series. Edited by David T. Gibson. Marcel Dekker, Inc. New York and Basel. 1984.
- Brownell, F.W. (1998). Clean Air Handbook, 3rd Edition. Government Institutes Inc., Rockville, MD.
- Chiesa S.C., Irvine R.L. and Manning J.F. Jr., Feast/famine growth environments and activated sludge population selection. *Biotechnology and Bioengineering*, 27, 562-569 (1985).

- Chou, M. and Huang, J. (1997). Treatment of Methyl Ethyl Ketone in Air Stream by Biotrickling Filters. *Journal of Environmental Engineering*. June 1997.
- Daigger, G.T., and Grady, C.P.L. Jr. (1982) An Assessment of the Role of Physiological Adaptation in the Transient Response of Bacterial Cultures, *Biotechnology and Bioengineering*, 24, 1427-1444
- Deshusses, Marc A. (1994). Biodegradation of Mixtures of Methyl Ethyl Ketone Vapors in Biofilters for the Treatment of Waste Air. Ph.D. Dissertation, Swiss Federal Institute of Technology, Zurich, 1994.
- Deshusses, M.A. (1997). Transient Behavior of Biofilters: Start-Up, Carbon Balances, and Interaction Between Pollutants. *Journal of Environmental Engineering*. June 1997.
- Deshusses, M.A. & Johnson, Camdon T. (2000). Development and Validation of A Simple Protocol to Rapidly Determine the Performance of Biofilters for VOC Treatment. *Environmental Science and Technology*. 34; 461-467.
- Deshusses, M. A.; Hamer, G.; and Dunn, I. J. (1995). Behavior of Biofilters for Waste Air Biotreatment. 1. Dynamic Model Development. *Environmental Science and Technology*. 29(4), 1048-1058.
- Deshusses, M. A.; Hamer, G.; and Dunn, I. J. (1995). Behavior of Biofilters for Waste Air Biotreatment. 2. Experimental Evaluation of a Dynamic Model. *Environmental Science and Technology*. 29(4), 1059-1068.
- Deshusses, M.A. and Hamer, G. (1992). Methyl Isobutyl and Methyl Ethyl Ketone Biodegradation in Biofilters. In: *Biocatalysts in Non-Conventional Media*. Edited by J Tamper et al., Elsevier Science Publishers B. V.
- Deshusses, M.A.; and Hamer, G. (1993). The Removal of Volatile Ketone Mixtures from Air in Biofilters. *Bioprocess Engineering*. 9 141-146.
- Devinny, Joseph S.; Deshusses, Marc A.; Webster, Todd S. (1999). Biofiltration for Air Pollution Control. Lewis Publishers.

- Dharmavaram, S.; Casey, J.; Van Lith, C. (1993). Experimental Evaluation of a Biofiltration Unit for Removal of Acetone. *Air and Waste Management Association. Presentation at the 86th Annual Meeting and Exhibition*. June 13-18, 1993.
- Dolfing, J.; van den Wijngaard, A.J.; Janssen, D.B. (1993). Microbiological Aspects of the Removal of Chlorinated Hydrocarbons from Air. *Biodegradation* 4: 261-282.
- Ergas, S.; Schroeder, E.D.; Chang, D.P.; and Scow, K.M. (1994). Spatial distribution of microbial populations in biofilters, 94-RP115B01, *Proc. of the 87th Annual Meeting of the Air & Waste Management Association*, Cincinnati, OH.
- Farmer, R.W. (1994). Biofiltration: Process Variables and Optimization Studies. M.S. Thesis, University of Minnesota. December 1994.
- Finn, Larry; Spencer, Robert. (1997). Managing Biofilters for Consistent Odor and VOC Treatment. *Biocycle*. January, 01, 1997.
- Groenestijn, Johan W. van; Hesselink, Paul G.M. (1993). Biotechniques for Air Pollution Control. *Biodegradation* 4: 283-301.
- Irvine, R.L. and Moe, W.M. (2001) Periodic Operation for Enhanced Performance During Unsteady-State Loading Conditions. *Water Science and Technology*, 43(3), 231-239.
- Kazenski, S.L. (2000). Biofiltration for Paint Spray Booth Applications. M.S. Thesis, University of Texas at Austin. May 2000.
- Kazenski, S.L. and Kinney, K.A. (2000) Biofiltration of Paint Spray Booth Emissions: Packing Media Considerations and VOC Interactions. *Proc. 2000 Annual Meeting and Exposition of the Air & Waste Management Association*, Salt Lake City, UT.
- Kirchner, K.; Schlachter, U.; Rehm, H.J. (1989). Biological Purification of Exhaust Air Using Fixed Bacterial Monocultures. *Applied Microbiology and Biotechnology*, 31:629-632.

- Kirchner, K.; Wagner, S.; Rehm, H.J.(1992) Exhaust Gas Purification using Biocatalysts (fixed bacteria monocultures)-The Influence of Biofilm Diffusion Rate (O_2) on the Overall Reaction Rate. *Applied Microbiology and Biotechnology* 37:277-279.
- Kirchner, K.; Wagner, S.; Rehm, H.J. (1994). Biological Purification of Waste Gases by Means of Immobilized Bacteria (Monocultures). *Air and Waste Management Association. For presentation at the 87th Annual Meeting and Exhibition.* June 1994 19-24.
- Kopchynski, D M.; Farmer, R W.; Maier, W.J. Factors Affecting the process Performance of Biofiltration. *Paper Submitted for Publication in the Proceedings of the 50th Annual Purdue University Industrial Waste Conference.*
- Leson, G.; Winer, A.M. (1991) Biofiltration: An Innovative Air Pollution Control Technology for VOC Emissions. *J. Air and Waste Management Association.* 41(8), 1045-1054.
- Lukins, H.B. and Foster, J.W. (1963). Methyl Ethyl Ketone Metabolism in Hydrocarbon-Utilizing Mycobacteria. *Journal of Bacteriology*, 85.
- Mahmoud, T.A.; Davis, W.B. (1970). The Effect of Salinity on the Removal of Some Aliphatic Ketones. *Sea Grant Publication.* July 1970.
- Martinez, F. A. (2001). Polyurethane Foam Based Packing Media for Biofilters Removing Volatile Organic Compounds From Contaminated Air. M.S. Thesis. Louisiana State University. 2001.
- Moe, W.M. and Irvine, R.L., (2001). Effect of Nitrogen Limitation on Performance of Toluene Degrading Biofilters, *Water Research*, 35(6), 1407-1414.
- Moe, W.M. and Irvine, R.L. (2000). Polyurethane Foam Medium for Biofiltration. I: Characterization. *ASCE Journal of Environmental Engineering*, 126(9), 815-824.
- Moe, W.M. and Irvine, R.L. (2000). Polyurethane Foam Medium for Biofiltration. II: Operation and Performance. *ASCE Journal of Environmental Engineering*, 126(9) 826-832.

- Moe, W.M. and Irvine, R.L. (2000). Performance of Periodically-Operated Gas-Phase Biofilters During Transient Loading Conditions. *Water Science and Technology*, 41(4-5), 441-444.
- Moe, W.M. and Irvine, R.L. Application of Periodic Processes to the Biofiltration of Toluene Vapor, Air Pollution VI, Eds. Brebbia, C.A., Ratto, C.F., and Power, H., WIT Press, Computational Mechanics Publications, Southampton, UK, 267-276.
- Moe, W.M. and Irvine, R.L. (2001) Intracellular Dynamics of Ribonucleic Acid (RNA) and Protein in Microorganisms from Periodically Operated Biofilters, *Water Science and Technology*, 43(3), 241-248.
- Ottengraph, S.P.P. (1987) Biological Systems for Waste Gas Purification. *Trends in Biotechnology* (vol 5) May 1987.
- Ottengraf, S.P.P.; Konings, J.H.G. (1991) Emission of Microorganisms from Biofilters. *Bioprocess Engineering* 7: 89-86.
- Ottengraph, Simon P.P. (1986). Biological Elimination of Volatile Xenobiotic Compounds in Biofilters. *Bioprocess Engineering*, 1: 61-69.
- Song, JiHyeon and Kinney, Kerry A. (2000). Effect of Vapor-Phase Bioreactor Operation on Biomass Accumulation, Distribution, and Activity: Linking Biofilm Properties to Bioreactor Performance. *Biotechnology and Bioengineering*, 68(5). 2000.
- Strauss, Johannes M.; du Pleiss, Chris A.; Riedel, Karl-Heinz J. (2000). Empirical Model for Biofiltration of Toluene. *Journal of Environmental Engineering*, 7, pp. 644-648.
- Togna, A. Paul; Singh, Manjari. (1994). Biological Vapor-Phase Treatment Using Biofilter and Biotrickling Filter Reactors: Practical Operating Regimes. *Environmental Progress* Vol. 13, no. 2. May 1994.
- US EPA (2001). *1999 Toxic Release Inventory (TRI) Public Data Release Report*, EPA 260-R-01-001, Washington D.C.

Visscher, K and Brinkman, J.(1989). Biological Degradation of Xenobiotics in Waste Management. *Hazardous Waste and Hazardous Materials*. 6(2) 1989.

Weber, F.J. and Hartmans, S. (1995). Use of activated carbon as a buffer in biofiltration of waste gases with fluctuating concentrations of toluene. *Applied Microbiology and Biotechnology*, 43, pp. 365 – 369.

Wilderer P.A., Irvine R.L. and Goronszy M.C., *Sequencing Batch Reactor Technology*. IWA Scientific and Technical Report No. 10, IWA Publishing, London (2001).

VITA

Will Norman is from Vicksburg, Mississippi. He received his Bachelor of Science degree in Microbiology from Louisiana State University in December 1997. After graduation he worked at Waterways Experiment Station in Vicksburg, Mississippi, before enrolling into the Engineering Science graduate program at Louisiana State University in August of 1999.