BIOFILTRATION OF MTBE CONTAMINATED AIR STREAMS – A STUDY OF REACTOR START-UP, STEADY STATE AND TRANSIENT STATE BEHAVIOR

By

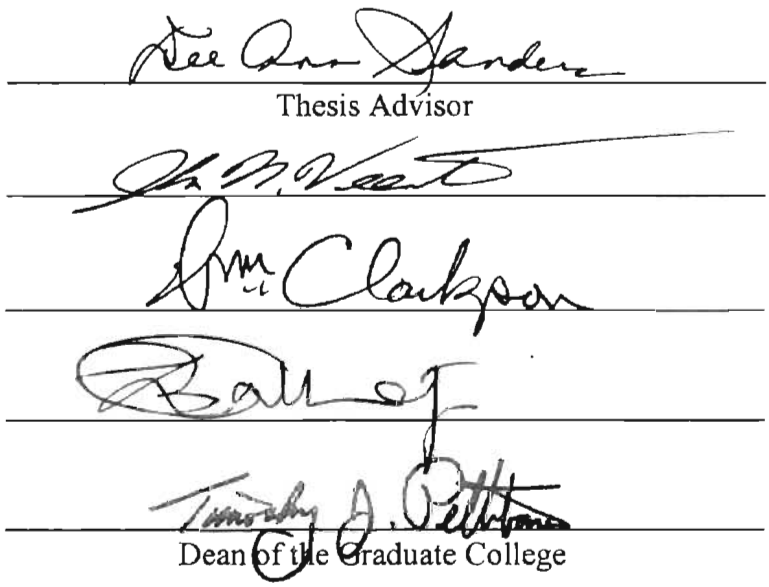
HARVINDER SINGH

Bachelor of Engineering
Thapar Institute of Engineering and Technology
Punjab, India
1999

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
May, 2002

BIOFILTRATION OF MTBE CONTAMINATED AIR STREAMS – A STUDY OF REACTOR START-UP, STEADY STATE AND TRANSIENT STATE BEHAVIOR

Thesis Approved:



Thesis Advisor

Dean of the Graduate College

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Dr. John N. Veenstra, member of my advisory committee. No appraisal can be made for guidance, constant encouragement, deep interest and concern he conferred throughout my research work. I am deeply indebted for the pains he took throughout the project to clear my doubts and solve problems promptly. I would also like to extend my appreciation to Dr. Dee Ann Sanders, my principal advisor for her guidance and assistance during this project. My thanks are due, to Dr. Babu Fathepure for his willingness to let me use his laboratory equipment and for his constructive suggestions from time to time. I am also grateful to Dr. William W. Clarkson for his invaluable support and guidance during my research.

Thanks to Dr. Gregory G. Wilber for his guidance and advice, concerning operation and maintenance of gas chromatographs. I also appreciate the support of Mr. David Porter in setting up the bench scale biofiltration apparatus.

Special thanks are due to Dr. Robert Cowan and Mr. Gunaseelan Alagappan (Department of Environmental Sciences, Cook College, Rutgers University, New Brunswick, NJ) for providing me with MTBE degrading culture and for their help and suggestions from time to time.

Many thanks to my friends, Sripriya Subramanian, Sivasankar, Kanchan Joshi, Vijay, and Sunderraja Mani for their invaluable help at different stages of my research.

This thesis is dedicated to my parents, Swaran Singh Luthra and Promila Luthra, and my Spiritual teacher, Guruji who provided constant encouragement and blessings during difficult times. Finally thanks to the Almighty GOD without whose help this work would not have been possible.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

APHA	American Public Health Association
ASTM	American Society For Testing Materials
BACT	best available control technology
CAA	Clean Air Act
EBCT	empty bed contact time
EBRT	empty bed residence time
GAC	granular activated carbon
GC/MS	gas chromatograph/mass spectrometer
HIBA	2-hydroxyisobutyric acid
LUFT	leaking underground fuel tanks
MHP	2-methyl-2-hydroxy-1-propanol
MTBE	methyl tertiary butyl ether
ORC®	oxygen release compound
PHS	peat humic substances
ppm	parts per million
RH	relative humidity
TBA	tertiary butyl alcohol
USEPA	United States Environmental Protection Agency
VOC's	volatile organic compounds

CHAPTER I

INTRODUCTION

Background

The 1990 Clean Air Act Amendments (CAA) established two fuel programs – the Reformulated Gasoline Program and Wintertime Oxyfuel Program. The Wintertime Oxyfuel Program requires the use of fuel with no less than 2.7% oxygen by weight during winters in carbon monoxide (CO) non-attainment areas (Squillace et al., 1997). The Reformulated Gasoline Program requires the use of year round use of reformulated gasoline that contains at least 2% by weight of oxygen in the areas of most severe ozone pollution (Squillace et al., 1997). No specific oxygenate was prescribed by the 1990 Clean Air Act Amendments, but MTBE became oxygenate of choice because of its low cost, ease of production, and favorable blending characteristics with conventional gasoline (Report to Governor and Legislature of the State of California, 1999; Gullick and LeChevallier, 2000). Reformulated gasoline accounts for 30% of gasoline sold nationwide and MTBE is used in about 84% of reformulated gas (USEPA, 1997). The Oxyfuel Program involves the use of MTBE in 3% of all oxyfuels in 13 states across the United States. This widespread use has led to contamination of groundwater and drinking water supplies through leaking underground fuel tanks, spills at industrial and refueling terminals, transport accidents, atmospheric deposition and storm runoff (USEPA, 1999; Hartley et al., 1999). The seriousness of the problem can be judged from the fact that in

the survey of eight urban areas conducted by the United States Geological Survey (USGS) in 1993-94, MTBE was the second most frequently detected volatile organic compound (Squillace et al., 1996). Several other studies have established the widespread nature of MTBE contamination at low concentrations in various drinking water sources in the states like California and Maine (California Department of Health Services, 2001; Maine Geological Survey, 2001)

MTBE is problematic because of its high solubility, weak sorption to subsurface solids, ability to move at velocities that are similar to the velocities of local groundwater, low taste and odor thresholds and potential health risks (Squillace et al., 1997; Report to Governor and Legislature of the State of California, 1999). The USEPA has classified MTBE as a possible human carcinogen and has issued a health advisory of 20 - 40 μg/l to prevent unpleasant taste and odor and to provide a large margin of safety from possible health effects (USEPA, 1997). Several physical-chemical and bioremediation strategies have been tried for MTBE clean-up in groundwater including air stripping, granular activated carbon (GAC) adsorption, air sparging, soil vapor extraction, biostimulation and bioaugmentation. In many remediation cases, such as air stripping, soil vapor extraction, air sparging, or wastewater treatment operations, large air streams contaminated with MTBE are generated that require further treatment (Fortin and Deshusses, 1999a). Physical-chemical treatment strategies for these vapors such as GAC adsorption, catalytic oxidation, advanced oxidation process and membrane processes involve many technical and economic constraints. Alternatively, biofiltration has emerged as a promising method in treatment of dilute, high-flow waste gas streams containing odors or VOC's because of low capital and operating costs, low energy

requirements and an absence of residual products requiring further treatment or disposal (Devinny et al., 1999; Fortin and Deshusses, 1999a).

In biofiltration, a humid air stream is passed through a porous support material on which pollutant degrading cultures are immobilized. The aim of this research was to study the treatment of MTBE vapors by compost biofilters and to address questions and problems raised by previous research.

Need of the Study

A few studies have been conducted on biofiltration of MTBE. In these studies compost based biofilters (Eweis et al., 1997), biofilter containing Celite™ R-635 (an extruded diatomaceous earth averaging 1 cm in size) (Eweis et al., 1998), and biotrickling filters containing pall rings and lava rocks (Fortin and Deshusses, 1999a) have been successfully used for the treatment of MTBE vapors. Recently a study was reported in which MTBE vapors were treated in a biofilter using cometabolism with pentane (Dupasqier et al., 2002). However in this study the MTBE degradation rates were much lower than the earlier reports. In spite of these relatively successful studies, there are still some problems and questions that need to be answered. The first and foremost problem is the start-up time of the biofilter treating MTBE. It took one year for Eweis et al. (1997) to see a little degradation in the biofilter operating at a wastewater treatment plant. It took three weeks of acclimation in another study on biofiltration of MTBE even after inoculation of the biofilter with MTBE degrading culture (Eweis et al., 1998). Fortin and Deshusses (1999a) also observed the same unusually long acclimation phase in the biotrickling filters treating MTBE despite vigorous inoculation with competent

microorganisms. According to these researchers, the causes for the slow start-up were the difficulty to establish a thriving consortium, the slow growth rate, and the low biomass yield of the process culture. Not only in the case of MTBE, this lag has also been observed by Ergas et al. (1994) even after inoculation with actively degrading liquid culture, in their study concerning biofiltration of another relatively recalcitrant compound, dichloromethane. They also give similar reason for this, that redistribution and growth of microbial populations or attachment of the organisms to the media may be required before significant removal is observed after inoculation. Thus this issue of start-up time is not just confined to MTBE biofiltration but to other relatively recalcitrant compounds also and needs to be addressed. In this context, Fortin and Deshusses (1999a) suggested that peat humic substances (PHS) appeared to have a positive effect on the performance of the biotrickling filters in their study and may have a role in decreasing the start-up times of the biotrickling filters treating MTBE. However, no further study was conducted to ascertain this role. So the role of PHS in improving the start-up of the biofilter needs further research.

Almost all the studies conducted so far on MTBE biofiltration were conducted at relatively high concentrations of MTBE and relatively high loading rates. In many operations like air stripping, low concentrations of MTBE are expected in the off-gas. This study attempts to address this issue by investigating the performance of biofilters at low concentrations and low loading rates of MTBE.

Another issue that needs to be addressed is the transient behavior of the biofilter treating MTBE. In the field transient behavior is the rule rather than the exception. Moreover, in the case of MTBE, the long start-up time required for biofiltration of MTBE

raises questions about the ability of the bioreactors to treat effluents with changing conditions (Fortin and Deshusses, 1999b). Transient behavior has been studied for the biotrickling filters by Fortin and Deshusses (1999b) but no good study has been conducted in the case of biofilters. Thus this gap needs to be filled for successful application of biofilters in the field.

In addition to above issues, this study also addresses the issue of comparison of performance of the biofilters treating MTBE vapors, containing adsorbing vs. non adsorbing materials in the biofilter media.

Objectives of the Study

Some of the objectives of the present study are:

1. To investigate the role of PHS in biodegradation of MTBE.
2. To study the response of the biofilters treating MTBE vapors at various steady state loading conditions obtained by different combinations of flow rates and inlet MTBE concentrations. Particular emphasis was placed on low concentrations of MTBE, which are usually encountered in MTBE air-stripping operations (Fortin and Deshusses, 1999a).
3. To study the transient response of the biofilters to step change in concentrations and flow rates.
4. To compare the performance of biofilters containing adsorbing (granular activated carbon) and non adsorbing materials (perlite) in relation to start-up times, steady state, transient state conditions.

CHAPTER II

LITERATURE REVIEW

Biofiltration – an Introduction

Biofiltration is an air pollution control (APC) technology that uses microorganisms immobilized over a porous medium to break down the pollutants present in the air stream (Devinny et al., 1999). Initially biofilters were used for the control of odors from wastewater, composting, food processing and livestock breeding operations (Leson, 1998; Pomeroy, 1957; Carlson and Leiser, 1966). In the early odor treatment systems, contaminated gases were passed through soil beds and the units were termed as soil filters (Kinney et al., 1998). However, in the 1970's, more advanced biofilters using a mixture of compost or peat and structural support (branches, wood chips, bark or mineral granulates) were developed (Leson, 1998). With the emergence of these systems, biofiltration became increasingly popular in Germany and the Netherlands. Presently in these countries, biofiltration is a widely used APC technology and is considered the best available control technology (BACT) for a variety of volatile organic compounds (VOC) and odor control applications. Since 1990, research and application of biological gas treatment have greatly increased in the United States as well (Kinney et al. 1998). Biofilters have treated off-gases from a wide range of source categories. They have been used for deodorization of off-gases from wastewater treatment plants, composting, food processing etc. Their applications in VOC and air toxic control involve treatment of gases

from coating and printing operations, production of adhesives, polymers, pharmaceuticals, plastics, solvents, and furniture etc. Biofilters have also been used in operations such as chemical and petroleum storage, and treatment of gases produced during soil remediation by methods of such as soil vapor extraction (Leson, 1998).

Principle of Operation

A biofilter for the control of air pollutants consists of one or more beds of porous solid state filter material whose surface is covered with a biofilm in which microorganisms are immobilized. Contaminated gas is vented through the reactor, and as a result contaminants diffuse into the biofilm where they are aerobically biodegraded by the resident microorganisms. Products of this biooxidation may include water and carbon dioxide, microbial biomass, inorganic acids if the VOC's contain chlorine (Cl), sulfur (S) or nitrogen (N), intermediates from incomplete biooxidation of VOC's, and heat (Leson, 1998).

Design and Operational Considerations

Media selection

Biofilters use a porous solid medium to support microorganisms and give them access to the contaminants in the air flow. The nature of the medium is a fundamental factor for successful application of biofilters. It will affect the frequency at which the medium is replaced and will have a major impact on key factors such as bacterial activity and pressure drop across the reactor (Devinny et al., 1999). Thus, selection of the proper biofilter media is an important step towards developing a successful biofiltration

operation. Desirable media properties include optimal microbial environment, large specific surface area, structural integrity, high moisture retention, high porosity and low bulk density. (Swanson and Loehr, 1997).

Common components of biofilter media include biological residues such as compost, peat, soil and inert substances like wood chips, perlite, activated carbon and vermiculite. Table 1 summarizes the important properties of common biofilter media components.

Table 1. Important Properties of Common Biofilter Media Components

Property	Compost	Peat	Soil	Activated carbon, perlite, and other inert materials	Synthetic materials
Indigenous microorganisms population density	High	Medium-Low	High	None	None
Surface area	Medium	High	Low	High	High
Air permeability	Medium	High	Low	Medium-high	Very high
Assimilable nutrient content	High	Medium-high	High	None	None
Pollutant sorption capacity	Medium	Medium	Medium	Low-high	None to high, very high
Lifetime	2-4 years	2-4 years	>30 years	>5 years	>15 years
Cost	Low	Low	Very low	Medium-high	Very high
General applicability	Easy, cost effective	Medium, water control problems	Easy, low activity biofilters	Needs nutrients, may be expensive	Prototype only or biotrickling filters

Source: Devinny et al., 1999

Moisture content

Maintaining optimum moisture content in the filter is the major operational requirement of a biofilter (Leson and Winer, 1991). There are many reasons why maintaining an optimum moisture level is critical. Some of these are addressed below:

An overwet biofilter medium causes:

- High backpressures and low gas retention times, due to filling of the pore space with water.
- Oxygen transfer problems due to reduced air/water interface per unit biofilm volume.
- Creation of anaerobic zones that promote odor formation and slow degradation rates.
- Nutrient washing from the biofilter medium.
- Production of high strength, low pH, leachate requiring disposal (Swanson and Loehr, 1997).

A dry biofilter medium causes:

- Deactivation of VOC-degrading microorganisms.
- Contraction and consequent medium cracking, resulting in reduced retention times.
- Frustrated attempts to rewet dry, hydrophobic medium materials (Swanson and Loehr, 1997).

Optimal biofilter medium moisture content ranges from 40-60% (wet weight) (Leson and Winer, 1991). This can be maintained by influent gas humidification, direct water addition to the surface of biofilter media or a combination of both.

Microorganisms

Bacteria and fungi are the two dominant groups of microorganisms in biofilters. These microorganisms may be indigenous to the selected medium as in the case of compost or may be inoculated (Devinny et al., 1999). Inoculation of the biofilter with pre-grown cultures is generally carried out in the following three cases:

- When the selected medium does not have sufficient population and diversity of microorganisms, such as in the case of GAC and perlite.
- When the compound to be treated is difficult to biodegrade
- When there is a need to reduce acclimation time and improve startup time for a biofilter.

There is a disagreement among researchers about the inoculation of a biofilter with laboratory grown cultures. Many investigators have suggested inoculation using a single ideal species, known to vigorously degrade the compound of interest, as inoculum for a biofilter (Devinny et al. 1999). While others, like Bohn (1992), have suggested that inoculation with laboratory grown cultures may increase the degradation rates for only a short time due to the high probability that these organisms will be outcompeted by the microorganisms native to the medium (Bohn, 1992). Swanson and Loehr (1997) have noted that seeding compost based biofilters has not been demonstrated to improve the performance in removing easily degradable chemicals. In spite of the above mentioned disagreement, it has become a common practice to inoculate the biofilters with a single ideal species of microorganisms, bacterial consortium, or activated sludge, to degrade more complex contaminants or to reduce adaptation time of the biofilter (Devinny et al., 1999; Wani et al., 1997).

Temperature

Temperature is a key concern in all biological treatment systems, and thus it is also a vital factor for efficient biofilter operation (Wani et al., 1997). There are three general temperature classes of aerobic microorganisms: psychrophilic microorganisms that grow best below a temperature of 20^0C; mesophilic microorganisms that achieve highest growth rates between 20 - 40^0C; and thermophilic organisms that grow best at temperature above 45^0C (Wani et al., 1997). Biofiltration relies predominantly on the activity of mesophillic and to some extent, thermophilic microorganisms (Leson and Winer, 1991). Leson and Winer (1991) recommended that off gas temperature be maintained between 20 – 40^0C for optimum results.

pH

For maximum pollutant removal, near neutral pH conditions (6 to 8) are optimal in most microbial bioreactor systems treating volatile organic compounds (Kinney et al., 1999). In some cases biodegradation of pollutants can generate acidic by-products. Examples are oxidation of sulfur or nitrogen- containing compounds and chlorinated organics (Leson and Winer, 1991). Thus, measures must be taken to prevent pH drop. Three measures were recommended by Ergas et al. (1994), who encountered a pH drop in the filter medium in biofiltration of dichloromethane. These three measures are:

- Formulate the medium with an increased buffer concentration using additives such as limestone, crushed oyster shells and marl.
- Periodically wash the medium with a buffer solution.

- Operate the system in a downflow mode and periodically replace upper media layers.

Nutrients

In addition to carbon and energy derived from the degradation of the contaminant, nutrients such as nitrogen, phosphorous, sulfur and trace elements are required for microbial growth (Wani et al., 1997). Typically, compost-based filter materials will provide sufficient inorganic nutrients. However some researchers have found that nutrient limitation may be responsible for reduced biofilter performance even in compost-based biofilters. Corsi and Seed (1995) have suggested available nitrogen levels of greater than 200 mg/kg of dry packing material or more for effective biofilter performance. In another study, Gribbins and Loehr (1998) observed that for a toluene elimination capacity of 30 $g/m^3/hr$, an available nitrogen concentration of greater than 1000 mg/kg of dry packing material was required for optimal biofilter performance. Presently there are no guidelines developed that identify the amount of available nutrients needed in biofilters. However some possible solutions to overcome nutrient limitation problem in compost based systems are:

- Addition of excess nutrients (e.g. NH_4NO_3) to the packing media prior to start up of the system
- Addition of slow release fertilizers (Kinney et al., 1999)

Waste gas pretreatment

Biofilters being biological systems, can be poisoned by the presence of toxic contaminants, the excessive concentrations of contaminants in the raw gas stream, and

excursions in environmental conditions such as temperature and moisture content (Wani et al., 1997). Therefore, waste gas pretreatment is essential for optimal biofilter operation. Pretreatment may include:

1. Particulate removal,
2. Load equalization by the use of GAC etc., if VOC concentrations in the influent stream are highly variable,
3. Temperature regulation, and
4. Humidification.

Maintenance and Monitoring

Routine maintenance of biofilters includes monitoring waste gas temperature and relative humidity; and filter bed moisture content, temperature, pH and back pressure (Wani et al., 1997).

Biofiltration Studies

Numerous bench and pilot scale studies have been conducted on biofiltration. For the purpose of this review, studies are classified based upon their objective as follows:

- Studies conducted to investigate the influence of design and operational parameters, such as moisture content, nutrient supply, or media type, on the biofilters. A few such studies are summarized in Table 2.
- Studies conducted to demonstrate the performance of biofilters in treating one or more pollutants during steady state and/or transient operation. These studies are summarized in Table 3.

- Studies conducted to model physical and chemical processes occurring in the biofilters.

Table 2. Biofilter Studies Investigating the Effect of Design and Operational Parameters

Parameter investigated	Reference	Contaminant	Biofilter medium	Results
Nutrient supply (specifically nitrogen supply)	Gribbins and Loehr (1998)	Toluene	Compost and Perlite	• A "threshold amount" of soluble nitrogen is required for optimum performance. This requirement is more critical at high VOC loadings or after long periods of operation • At toluene loading of 30 $g/m^3/hr$ the non-limiting soluble nitrogen concentration in the media is greater than 1000 mg/kg as N (dry wt.)
	Corsi and Seed (1995)	Benzene, Toluene, o-Xylene	Composted municipal solid waste, composted bark fines, composted food and yard waste or composted sewage sludge and Perlite	• Available nitrogen levels of 200 mg/kg or more appear to be necessary for effective biofilter performance
Moisture content	Govind and Bishop (1998)	Isopentane	Compost and foam fluff or Peat and foam fluff	• Optimum water content for the peat biofilter was 56% (dry weight basis) • Optimum water content for compost biofilter was 65% (dry weight basis)
	Auria et al. (1998)	Ethanol	Peat with $Ca(OH)_2$ as a pH buffer	• Elimination capacity dropped from 27 $g/m^3/hr$ to 4 $g/m^3/hr$ when the water content was dropped from 49% to 35%

Table 2. Contd.

Temperature	Govind and Bishop (1998)	Isopentane	Compost or Peat	• Maximum removal efficiencies of isopentane were observed above the bed temperatures of 35°C. Below 25°C, the removal efficiencies decreased almost linearly with temperature.
pH	Devinny and Hodge (1995)	Ethanol	GAC	• Rapid ethanol consumption at high loading was associated with the production of acetaldehyde, acetic acid and ethyl acetate. The resulting pH reduction inhibited treatment.
	Smet et al. (1996)	Dimethyl sulfide and Dimethyl disulfide	Compost or wood bark	• Gradual decrease in elimination capacity was observed as a result of acidification.
Effect of inoculation	Devinny and Hodge (1995)	Ethanol	GAC	• Inoculation with ethanol degrading microorganisms eliminated the initial perdiod of poor performance generally associated with GAC biofilters. Most rapid treatment was observed in the biofilter with the highest amount of seed culture.
	Smet et al. (1996)	Dimethyl sulfide and Dimethyl disulfide	Compost or wood bark	• Inoculation increased the dimethyl sulfide elimination capacity from less than 10 $g/m^3/hr$ to 680 $g/m^3/hr$ for compost biofilter and from 5 $g/m^3/hr$ to 35 $g/m^3/hr$ for wood bark biofilter

Table 3. Biofilter Studies Demonstrating the Performance of the Biofilters to Treat One or More Pollutants

Contaminant(s)	Biofilter Medium	Empty Bed Contact Time	Critical Load* (g/m^3/hour)	Maximum Elimination Capacity (g/m^3/hour)	Maximum Removal Efficiency (%)	Reference
Toluene	Peat Compost	20 – 357 seconds	< 10	20	N.R.	Ottengraf et al. (1983)
Methanol	Peat and Perlite (40:60 v/v)	2.82 – 5.6 minutes	68	112.8	100	Shareefdeen et al. (1993)
Dichloromethane	Compost and Perlite (50:50 v/v)	0.7 – 1 minutes	N.R.	N.R.	>98%	Ergas et al. (1994)
Ethanol	GAC	3.1 minutes	N.R.	156	N.R.	Devinny and Hodge (1995)
Dimethyl Sulfide	Wood Bark	14 – 113 seconds	4.8	1.46	100	Smet et al. (1996)
Dimethyl Sulfide	Compost	31 seconds	20.83	28.3	100%	Smet et al. (1996)
Styrene	Perlite	30 seconds	80-83	79	96-98%	Cox et al. (1996)
Toluene	Peat	54 seconds	190	70	65%	Bibeau et al. (1997)
MTBE	Compost	1 minute		6-8	100	Eweis et al. (1997)
Isopentane	Peat and Foam fluff	<2 - > 12 minutes	N.R.	N.R.	95%	Govind and Bishop (1998)

N. R. = Not reported

* At low loadings, elimination capacity essentially equals the load, but if the loading is increased, a point will be reached where the overall mass loading will exceed the overall elimination capacity. This point is typically called the critical load.

Table 3. – Contd.

Contaminant(s)	Biofilter Medium	Empty Bed Contact Time	Critical Load (g/m3/hour)	Maximum Elimination Capacity (g/m3/hour)	Maximum Removal Efficiency (%)	Reference
Isopentane	Compost and Foam fluff	<2 - > 12 minutes	N.R.	N.R.	100%	Govind and Bishop (1998)
Toluene	Pelletized activated carbon	2 minutes	N.R.	N.R.	>99%	Govind and Bishop (1998)
TCE	Pelletized activated carbon	2 minutes	N.R.	N.R.	>99%	Govind and Bishop (1998)
Methylene Chloride	Pelletized activated carbon	2 minutes	N.R.	N.R.	>99	Govind and Bishop (1998)
MTBE and Toluene	Celite™ R-635	1 minute	N.A.	N.A.	100	Eweis et al. (1998)
1-Nitropropane	Peat	2.19 – 3.65 minutes	12-13	6	N.R.	Wu et al. (1998)
MTBE	Pall rings and Lava Rocks	54 - 90 seconds	40 – 50	50	97	Fortin and Deshusses (1999a)
Styrene	Pellets composed of preconditioned biomass	0.52-3.12 minutes	164	141	97	Jorio et al. (2000b)
Carbon disulfide and hydrogen sulfide	Peat	17-69 seconds	N.R.	187.5 (expressed in terms of Sulfur)	99%	Hartikainen et al. (2001)
MTBE and Pentane	Vermiculite	0.06-2.85 hours	N.R.	12 (Pentane) 1.8 (MTBE)	N.R.	Dupasquier et al. (2002)

N. R. = Not reported

Biofilter Modeling

Biofilter models were developed to achieve the following objectives:

1. To organize experimental data and to understand relationships between parameters such as media surface area, biological activity, biofilm thickness, and pollutant removal (Devinny et al. 1999).
2. To predict elimination capacity and efficiency as a function of reactor design, properties of pollutants and microbiological parameters, and for designing and sizing filters (Bibeau et al. 1997).
3. To optimize the process.

Numerous models have been developed to describe biological and physical processes in biofilters (Ottengraf and van den Oever (1983), Hodge and Devinny (1995), Shareefdeen et al. (1993), Shareefdeen and Baltzis (1994), van Lith et al. (1990), Deshusses et al. (1995) a, b). Of these, Ottengraf's model is still the most commonly referenced model (Devinny et al. 1999) and is described in detail in the following section.

Ottengraf's model

Ottengraf's model was first published in 1983 (Ottengraf and van den Oever, 1983, Ottengraf, 1986) and is based on the following simplifying assumptions:

1. Interfacial resistance in the gas phase is neglected and equilibrium is assumed between concentrations in the gas-phase and interfacial concentration of the contaminant.
2. The flow of the gas phase through the filter bed is of the plug flow type.

3. In the biolayer, pollutant transfer takes place by diffusion which can be described by the effective diffusion coefficient, D_{eff}.
4. The biofilm thickness is small compared to the support medium, so flat geometry is assumed for the biofilm.
5. The microkinetics for substrate elimination in the biofilm can be described by a Michaelis-Menton equation or relationship of Monod:

$$r = \frac{\mu}{y} \frac{C}{C+K} X \quad \text{.....1}$$

where:

r = Substrate utilization rate (mass/unit volume . time)

μ = Maximum growth rate ($time^{-1}$)

y = Cell yield coefficient (mg/mg)

K = Monod or Michaelis-Menton constant (mass/unit volume)

X = Active microorganism concentration (mass/unit volume)

C = Concentration in the liquid phase (mass/unit volume)

To allow for the analytical solution of differential equations, the Ottengraf's model differentiates among three operating situations, i.e. First-order kinetics, zero order kinetics with reaction rate limitation, and zero order kinetics with diffusion rate limitation.

First Order Kinetics

If the Michaelis-Menton constant (K) is very large compared to the concentration in the liquid phase (C), the rate expression approaches first order kinetics. The results for

the gas-phase pollutant concentration with respect to filter height for first order kinetics is given by:

$$\frac{Co}{Ci} = \exp\left(\frac{-hR}{mU}\right) \quad \text{.....2}$$

$$R = \frac{a\,D}{\delta}\,\phi \tan h\,\phi$$

ϕ is Thiele number. For the first order kinetics the Thiele number is given by:

$$\phi = \delta \sqrt{\frac{k}{D}}$$

Co = Outlet concentration of pollutant in gas-phase (g/m^3)

Ci = Inlet concentration of pollutant in gas-phase (g/m^3)

h = Height in the biofilter (m)

k = First-order reaction rate consant ($hour^{-1}$)

m = Gas liquid partition coefficient (dimensionless)

U = Superficial velocity of gas (m/hour)

Φ = Thiele number

δ = Biolayer thickness (m)

D = Diffusion coefficient (m^2/s)

a = interfacial area per unit volume (m^2/m^3)

Zero Order kinetics

If the Michaelis-Menton constant (K) is very small compared to concentration in the liquid phase (C), the rate expression approaches zero order kinetics. In this case two situations are possible; zero order rate with diffusion limitation, and zero order rate with

reaction rate limitation. The Thiele number (Φ), which reflects the ratio of the maximum rate degradation and the maximum rate of diffusion in the biofilm, is used to differentiate between reaction and diffusion limitations. For a zero order reaction the Thiele number is defined by:

$$\Phi = \delta \sqrt{\frac{Ko\,m}{D\,Ci}} \quad \text{.....3}$$

where

Ko = Zero order reaction rate constant (mol m^{-3} $hour^{-1}$)

If the Thiele number is greater than $\sqrt{2}$, the overall reaction rate is determined by the diffusion rate, and if the Thiele number is less than $\sqrt{2}$, the overall reaction rate is determined by the biological reaction rate.

Diffusion limitation: In case of diffusion limitation, the biolayer is not fully active and depth of penetration in it is smaller than the layer thickness. In this case, removal of the pollutant is controlled by the rate of diffusion. The results for the gas-phase pollutant concentration with respect to filter height for zero order kinetics with diffusion limitation is given by:

$$\frac{Co}{Ci} = \left(1 - \frac{h \bullet a}{U}\sqrt{\frac{Ko\,D}{2\,m\,Ci}}\right)^2 \quad \text{.....4}$$

Reaction limitation: There is no diffusion limitation in this case. This means that the biolayer is fully active and conversion is controlled by the reaction rate. The results for the gas-phase pollutant concentration with respect to filter height for zero order kinetics with reaction limitation is given by:

$$\frac{Co}{Ci} = 1 - \left(\frac{h\,Ko}{Ci\,U} \right) \quad \text{.....5}$$

From equations 2, 4 and 5, it can be concluded that the concentration profile along the height of the biofilter is exponential, linear or quadratic for first-order, zero-order with reaction rate limitation, and zero-order with diffusion limitation, respectively.

MTBE – an Introduction

Methyl tertiary butyl ether (MTBE) was first introduced in U.S. gasoline in 1979, primarily in premium grades of gasoline at levels of 2-3% by volume, as an octane booster (Report to Governor and Legislature of the State of California, 1999). However, since November 1, 1992, the 1990 Clean Air Act Amendments require areas that exceed the national ambient air-quality standard for carbon monoxide to use oxygenated gasoline during the winters, when the concentration of carbon monoxide is highest (Squillace et al., 1997). According to the Oxygenated Fuel Program, gasoline must contain no less than 2.7% oxygen by weight, which is equal to 15 % MTBE by volume, to meet this oxygen requirement (Squillace et al., 1996). Furthermore, since February 1995, the Clean Air Act Amendments also require nine metropolitan areas that have the most severe

ozone pollution to use year-round reformulated gasoline that contains fuel oxygenates (Squillace et al., 1997). Reformulated gasoline must contain at least 2% oxygen by weight, which is equal to 11% MTBE by volume, to meet this oxygen requirement (Squillace et al., 1996). While other oxygenates such as methanol, ethanol, or aliphatic ethers are sporadically used in reformulated gasoline, MTBE has become the oxygenate of choice among refiners, because of its low cost, ease of production and favorable blending characteristics with conventional gasoline (Report to Governor and Legislature of the State of California, 1999; Gullick and LeChevallier, 2000)

Currently, 32 areas in 18 states sell reformulated gasoline. Reformulated gasoline accounts for about 30% of the gasoline sold nationwide, and MTBE is used in about 84% of the reformulated gas (USEPA, 1997). The oxyfuel program involves 19 areas in 13 states, with MTBE used in 3% of all oxyfuel at levels of 10 - 15% by volume (Johnson et al., 2000). This widespread use of MTBE has led to contamination of groundwater and drinking water supplies. There are both point as well as non point sources of MTBE contamination. Typical point sources include releases from gasoline storage and distribution systems, spills at industrial and refueling terminals, and transport accidents (USEPA, 1999; Hartley et al. 1999). Non-point discharges include atmospheric deposition and storm runoff (USEPA, 1999).

There is uncertainty about chronic toxicity and carcinogenic effects of MTBE on humans (Hartley et al., 1999; USEPA, 1998). The USEPA has classified MTBE as possible human carcinogen and has issued a health advisory of 20 - 40 μg/l to prevent unpleasant taste and odor and to provide a large margin of safety from possible health effects (USEPA, 1997). On March 20, 2000, the USEPA announced the beginning of

regulatory action under the Toxic Substance Control Act (TSCA) to significantly reduce or eliminate the use of MTBE in gasoline (USEPA, 2001).

Physiochemical Properties and Environmental Fate of MTBE

MTBE is an ether with the structural formula $CH_3OC(CH_3)_3$. It is a volatile, flammable, colorless liquid at room temperature and has a terpene - like odor (Squillace et al., 1996). Table 4 lists some important physical and chemical properties of MTBE. Of particular significance are its high aqueous solubility, and low Henry's constant and octanol - water partitioning coefficient (K_{ow}) (Gullick and LeChavallier, 2000). High solubility in water, combined with its high concentrations in oxygenated gasoline, can result in high amount of MTBE being dissolved when gasoline containing MTBE comes in contact with surface water and ground water (Squillace et al., 1997). Once MTBE is in groundwater, its high solubility, weak sorption to subsurface solids, and resistance to biodegradation by indigenous bacteria make it a fairly mobile and persistent contaminant in groundwater (Squillace et al., 1997; Gullick and LeChavallier, 2000). In surface water, volatilization of MTBE can play an important role in decreasing its concentrations. However for very deep and slow moving rivers or lakes, the half-lives can be of the order of months, especially at low temperatures (Squillace et al., 1997). In the atmosphere, reactions with $OH^{\cdot}$ radicals may degrade MTBE, giving it a half life as short as 3 days in a regional airshed, or it may partition into atmospheric water including precipitation (Squillace et al., 1997; Gullick and LeChavallier, 2000).

Table 4: Physical-Chemical Properties of MTBE

Molecular weight (g/mole)	88.15
Molecular formula	$C_5H_{12}O$
Boiling point (at 760 mm Hg at 20^0C)	55.2^0C
Vapor pressure (mm Hg at 20^0C)	240
Solubility (mg/100 g water)	4.8
Henry's law constant (dimensionless)	0.022-0.12
Log K_{oc}	0.94-1.3
Log K_{ow}	0.55-0.91

Source: US Environmental Protection Agency, 1998

MTBE Contamination

Widespread MTBE use has led to its contamination of shallow groundwater and drinking water supplies across the United States (Squillace et al., 1996; Gullick and LeChavallier, 2000). The great majority of these detections to date have been well below levels of public health concern, however the detections at lower levels have raised consumer taste and odor concerns that have caused water suppliers to stop using some water supplies and to incur costs of treatment and remediation (USEPA, 1999). One of the earliest and most comprehensive national occurrences survey of MTBE in groundwater resources was performed by the USGS as a part of its National Water Quality Assessment (NAWQA) program (Squillace et al., 1996). Of the 60 VOC's analyzed in samples of shallow urban ground water collected from eight urban areas during 1993-1994, MTBE was the second most frequently detected chemical (27% of the

sites) ranking just behind chloroform. The frequency of detection of MTBE was much higher in the urban land-use wells. While only 3% of the urban land-use wells had concentration exceeding 20 µg/l (lower limit of the drinking water health advisory level set by USEPA), the maximum concentration detected was over 100 µg/l.

One of the most recent studies on MTBE contamination has been carried out in the form of a survey of the surface and subsurface drinking water supplies in the American Water System (AWS) of the American Water Works Company from 1997-1998 (Gullick and LeChavallier, 2000). MTBE was detected at least once in 8.8% of the wells during the course of the study with maximum concentration detected as 14.1 µg/l. A summary released by the California Department of Health Services (California Department of Health Services, 2001) reveals that MTBE was detected in 4% of the 1,920 public water systems sampled and 1.8% of the 7,818 drinking water sources sampled. In public water systems, 1.9% of the detections were greater than the secondary MCL of 5 µg/l, and 0.8% were greater than the California primary MCL of 13 µg/l. In case of drinking water sources 0.6% were greater than the secondary MCL (5 µg/l for the state of California) and 0.3% were greater than the primary MCL (13 µg/l for the state of California). A comprehensive survey of the MTBE contamination in its drinking water supplies conducted by the state of Maine (Maine Geological Survey, 2001) revealed that MTBE was the most frequently detected gasoline constituent in private residential water supplies as well as in public water supplies. The study also predicted that approximately 1400-5200 private wells may have concentrations of MTBE greater than Maine's drinking water standard of 35 µg/l.

Apart from the above mentioned surveys, there have also been many reports on point source MTBE contamination, such as from leaking underground storage tanks. Lawrence Livermore National Laboratory in California examined groundwater data from 236 leaking underground fuel tank sites located in 24 counties within California (Hapel et al., 1998). In 1995/96 MTBE detections were reported at 78% of these sites. Seventy percent of the sites had MTBE concentrations greater than 20 µg/l, and 10% had concentrations greater than 10,000 µg/l. In Maine, a gasoline leak from an overturned car was likely to be responsible for contamination of 24 domestic wells within 2,200 feet, ten of which attained MTBE levels greater than 100 ppb (Maine Geological Survey, 2001). Leaking underground storage facilities led to the contamination of groundwater used as a drinking water source in the Santa Monica area with an MTBE concentration of more than 600 µg/l (USGS, 2001). According to Johnson et al. (2000) there are perhaps some 250,000 leaking underground fuel tanks (LUFT) releases involving MTBE, and a significant number of MTBE releases may continue to reveal themselves as problematic sources of contamination for the nation until at least 2010.

Remediation and Water Treatment Technologies for MTBE Clean-up

As stated earlier MTBE has high solubility, a low octanol - water partition coefficient, a low Henry's constant and is a relatively recalcitrant compound. These properties make MTBE highly mobile contaminant and present significant challenges for its treatment and remediation by conventional technologies. Some of the remediation strategies and treatment technologies used and proposed for MTBE clean up are discussed below.

Ground water extraction

Ground water extraction is an effective method to remove dissolved-phase MTBE (Creek and Davidson, 2000). Creek and Davidson (1998) describe six case studies in which ground water extraction has been used with treatment techniques like air stripping or advanced oxidation processes to remediate MTBE contaminated sites. Based upon the data review, the authors conclude that ground water extraction led to preferential removal of MTBE in comparison to more highly retarded compounds such as benzene.

Air stripping

Air stripping is one of the most commonly considered strategies for removal of MTBE from water (Gullick and LeChevallier, 2000). It has been used in conjunction with ground water extraction at some MTBE contaminated sites. However, because of MTBE's relatively low Henry's constant, air stripping is less effective for MTBE removal than for other VOC's usually encountered in contaminated ground water (Davis and Powers, 2000). Gullick and LeChevallier (2000) describe two case studies in which air stripping systems designed for VOC's such as benzene and tetrachloroethylene were not able to remove MTBE effectively from water. Creek and Davidson (1998) present some case studies in which air stripping was used effectively as an MTBE treatment technology, but the air-to-water ratios used in all these were relatively high (>180:1).

Adsorption

Granular activated carbon (GAC) use for MTBE treatment has not been generally successful. Of the eight case studies presented by Creek and Davidson (1998) where

GAC was used for the treatment of MTBE, only one case study was considered a successful application of GAC for treating MTBE - impacted water. Most of the remaining sites had to shift to some other treatment technology such as air stripping because of the poor performance of the GAC. The reason for this is, MTBE is poorly adsorbed on GAC and often breaks through relatively quickly which may lead to frequent carbon change out requirements (Creek and Davidson, 2000, Brown et al., 1997). Although GAC does not seem to be effective for the treatment of high concentrations of MTBE, some researchers have recommended its use as a polishing step for low levels of MTBE removal (Creek and Davidson, 2000, Brown et al., 1997). In spite of all this, GAC technology for MTBE remediation needs further investigation, as it has been claimed in some reports that coconut shell GAC and new products like Filtrasorb 600® are much more effective for MTBE removal than coal based GAC (Creek and Davidson, 2000, http://www.calgoncarbon.com/news/pr000410.html). There are a few reports in which other adsorbents like carbonaceous resins, porous graphitic carbon and high silica zeolites have been investigated for MTBE removal (Anderson, 2000; Davis and Powers, 2000). Based upon these studies, it has been established that adsorbents like Ambersorb® 563 and 572, and high silica zeolites like high mordenite are much more effective for MTBE removal than activated carbon.

Advanced Oxidation Processes

Several relatively successful laboratory scale studies have been conducted in which advanced oxidation processes have been used for destroying MTBE in water. Barreto et al (1995) demonstrated photocatalytic degradation of MTBE using TiO_2 as catalyst; Yeh and Novak (1995) used H_2O_2 in the presence of ferrous iron (Fenton's

reagent) to chemically oxidize MTBE; Chang and Young (2000) demonstrated removal of MTBE by using UV/H_2O_2. Creek and Davidson (1998) regard advanced oxidation a promising technology, provided currently available methods are refined to make it more cost effective. It can also be used as a part of a treatment train e.g. in combination of GAC or biological degradation for groundwater remediation (Creek and Davidson, 2000; Yeh and Novak, 1995).

Air sparging/Biosparging

Air sparging/biosparging appears to be applicable for MTBE remediation, because MTBE is volatile (although less so than BTEX), and somewhat biodegradable (less so than BTEX) (Creek and Davidson, 2000). Creek and Davidson (1998) report a case study of the site at which there was evidence that air sparging was physically removing MTBE and adding oxygen to groundwater. At another site where biosparging was being used, it appeared that it did somewhat accelerate the natural degradation and attenuation processes that were apparently already decreasing MTBE and BTEX levels at the site (Creek and Davidson, 2000).

Soil vapor extraction

For the site where MTBE still resides in the soil-entrapped gasoline, soil vapor extraction is expected to work better for MTBE than BTEX compounds due to MTBE's relatively high vapor pressure (Creek and Davidson, 2000). Creek and Davidson (1998) report several case studies in which soil vapor extraction was not only successful in removing large amount of MTBE from soil, but in some cases also led to the

improvement in groundwater conditions, probably by preventing contaminant recharge to the groundwater system (Creek and Davidson, 2000).

Bioremediation of MTBE

Several mixed and pure cultures have been isolated that can metabolize (Cowan et al., 1996; Eweis et al., 1997; Fortin and Deshusses, 1999a; Hanson et al., 1999; Salanitro et al., 1994) and cometabolize (Garnier et al., 1999; Steffan et al., 1997; Hardison et al., 1997, Hyman et al., 1998) MTBE in laboratory microcosms under aerobic conditions. There are few studies that have demonstrated MTBE biodegradation under methanogenic (Wilson and Cho, 2000), denitrifying (Bradley et al., 2001), and iron reducing conditions (Finneran and Lovley, 2001). There are now several reports where it has been shown that MTBE can also be biodegraded in the field. Three strategies have been tested for MTBE bioremediation – intrinsic bioremediation, biostimulation and bioaugmentation. A study conducted on intrinsic biodegradation of MTBE in the Coastal Plain aquifer, Sampson County, North Carolina, by Borden et al. (1997) showed that MTBE can be biologically degraded under aerobic and denitrifying conditions. The decay rate observed in this study was very low (0 - 0.001 d^{-1}), however in another study conducted in the Borden aquifer, Ontario, Canada (Schirmer and Baker, 1998), significant reductions in MTBE mass were observed after the period of 8 years, which was attributed to biodegradation. Recently, researchers from U. S. G. S. demonstrated tremendous potential for intrinsic biodegradation of MTBE in surface water sediments and shallow ground waters, with the help of laboratory and field studies (Bradley et al., 2001; Bradley et al., 1999; Landmeyer et al., 2001). Their studies show that oxygen supply appears to be the most important

constraint in bioremediation of MTBE by indigenous bacteria. In surface - water sediments, additional constraints appear to be parameters such as percentage content of silt, clay, and organic matter. The most important observation was that the prior redox conditions, or previous MTBE exposure did not seem to affect the MTBE biodegradation in laboratory microcosm studies (Bradley et al., 2001) conducted with surface - water sediments. In a study conducted at U.S. Coast Guard Support Center, Elizabeth City (NC), Wilson and Cho (2000) suggested that the anaerobic biodegradation of MTBE was capable of bringing its concentration below regulatory standards before the plume had traveled 800 ft.

Because of the apparent oxygen limitation in the subsurface, several studies have been conducted in which attempts have been made to stimulate the biodegradation of MTBE by injection of oxygen to the subsurface. Hicks (1999) presents two case studies in Wisconsin where biostimulation by use of oxygen release compound (ORC®) appeared to decrease the MTBE concentrations substantially in the subsurface. In a recent study conducted by Landmeyer et al. (2001), rapid biodegradation of MTBE was observed after dissolved oxygen levels in the shallow ground water were increased by adding an ORC® slurry. Within 60 days, MTBE removals up to 87% and 79% took place in the wells located close to and further downgradient respectively. Salanitro et al. (2000) observed the similar rapid removal of MTBE after the lag period of 173-230 days upon injection of oxygen to the subsurface. A recent study by Wilson et al. (2002) showed decrease in MTBE concentration from several hundred to less than 10 μg/l by introduction of an aerobic zone using diffusive oxygen release. The lag time for degradation was less than 2 months and apparent pseudo first order degradation rate was 5.3day^{-1}. These studies show

that intrinsic bioremediation and biostimulation can be promising strategies for MTBE clean ups, however still there are some constraints associated with these technologies. The first constraint is that the intrinsic biodegradation of MTBE may be too slow and may not be effective at some distance from the source of contamination as happened in case of the Coastal plain aquifer study in North Carolina (Borden et al., 1997). The resulting delay in clean up can lead to further spreading of the contamination as MTBE can move in groundwater at velocities that are similar to the velocities of the local ground water (Squillace et al., 1996). Also, intrinsic bioremediation may fail if large amount of organic matter and readily degradable substrates are present along with MTBE, as this can lead to competitive inhibition of MTBE biodegradation by other carbon sources, or competitive consumption of oxygen to support MTBE biodegradation (Bradley et al., 2001). Bradley et al. (2001) observed an inverse relationship between MTBE mineralization and percentage content of silt and clay (grain diameter < 0.125mm) in surface-water sediments, which can be of concern when dealing with clayey soils. Biostimulation also has its potential disadvantages, e.g. in the study conducted at Port Hueneme, California (Salanitro et al., 2000), there was a long lag time before significant biodegradation of MTBE was observed. Moreover it was not effective in removing tertiary butyl alcohol (TBA), which is also a contaminant of concern in MTBE remediation. In contrast to this, biostimulation worked exceptionally well at Vandenberg Air Force base, California where the lag time for MTBE degradation was low, and degradation rates were relatively high (Wilson et al., 2002).

Some of these constraints may be eliminated by bioaugmentation. Although very few studies have been been reported so far, where bioaugmentation has been used for MTBE

clean up (Salanitro et al., 2000; Spinnler et al., 2001), it appears to be a promising strategy. Salanitro et al. (2000) injected oxygen and MTBE degrading culture (MC-100) to the aquifer and observed decrease in MTBE concentrations after only 30 days and throughout the 261-day experiment eventually to ≤ 0.001-0.01 mg/l. TBA concentrations also declined to < 0.01 mg/l. However there are certain disadvantages associated with bioaugmentation. These disadvantages also apply to biostimulation by oxygen injection and ORC. Bioaugmentation and oxygen injection may reduce the permeability of the aquifer within the intended treatment zone. This might lead to reduced groundwater flow through the treatment zone and result in partial bypass of contaminated groundwater around it (Wilson et al. 2002). In short it can be said that intrinsic biodegradation, biostimulation and bioaugmentation appear to be promising strategies for MTBE remediation but following factors should be investigated to assess their feasibility with respect to other strategies and also with respect to each other:

1. Presence or absence of indigenous microorganisms capable of degrading MTBE.
2. Extent and the rate of degradation of MTBE by indigenous bacteria.
3. Dissolved oxygen levels at the site.
4. Type of soil.
5. Existence of other contaminants or organic matter that can serve as alternative carbon sources.
6. Financial constraints and time available.

Air-phase Treatment of MTBE by Biofiltration

In many remediation cases, such as air stripping, soil vapor extraction, air sparging, or wastewater treatment operations, large air streams contaminated with MTBE are generated that require further treatment (Fortin and Deshusses, 1999a). Many treatment technologies such as carbon adsorption, catalytic oxidation, membrane processes, and biofiltration are available for the treatment of MTBE contaminated air. Of all these, biofiltration offers an attractive option mainly because it has low operating costs and produces minimal secondary pollutant waste streams (Devinny et al. 1999). Few reports have been published showing effective MTBE removal from air streams using biofilters and biotrickling filters (Fortin and Deshusses, 1999a, b; Eweis et al., 1998; Schroeder et al., 2000). Recently a study was reported in which MTBE vapors were treated in a biofilter using cometabolism with pentane (Dupasquier et al. 2002). All the studies using metabolic degradation of MTBE in general have one thing in common, that it took a large amount of time (6 months-1 year) to get at least some biodegradation of MTBE in the biofilters that were not inoculated with competent MTBE degrading organisms. It took more than one year before MTBE biodegradation began in the biofiltration work conducted at a wastewater treatment plant (Eweis et al., 1997). In another study conducted by Fortin and Deshusses (1999a), it took six months to enrich MTBE degraders in the biotrickling filters. It is also interesting to note that after the biofilters were inoculated with competent and highly active MTBE degrading microorganisms, the start-up times were reduced to a few weeks, but still they are longer than usually observed in other biofilter applications (Fortin and Deshusses, 1999a; Eweis et al. 1998; Schroeder et al, 2000). According to Fortin and Deshusses (1999a), the main

causes of this appear to be the difficulty in establishing a thriving consortium due to shear stresses experienced by the organisms in the biotrickling filters, slow growth rate and low biomass yield of the process culture. However in spite of slow start-up, the studies have shown that once the biofilters start, they can be very effective in removing MTBE from air. In a study conducted by Eweis et al. (1997), a compost biofilter at the Joint Water Pollution Control Plant of the Los Angeles County Sanitation District that was creating air streams containing other hydrocarbons removed MTBE effectively after the lag period of 1 year. The elimination capacity was 6-8 g/m^3/hour. Concentrations up to 200 ppb MTBE in the gas phase were removed at an average removal efficiency of 90%. In another study, Eweis et al. (1998) observed removal efficiencies of greater than 95% at an inlet concentration of 35 ppm MTBE, using a pilot scale biofilter filled with the media composed of extruded diatomaceous earth and inoculated with MTBE degrading organisms. In this study, the impact of toluene on removal of MTBE was also studied by introducing different concentrations of toluene into the inlet air during the course of the experiments. Toluene concentrations of 8 and 25 ppm reduced the MTBE removal efficiencies for a short interval of time but the biofilters quickly recovered to achieve removal efficiencies close of 98% for MTBE and 100% for toluene. In another study, addition of 70 ppm toluene led to significant breakthrough of MTBE (due to nitrogen limitation) but the biofilter did recover after some time to achieve near 100% removal of both toluene and MTBE (Schroeder et al. 2000). Fortin and Deshusses (1999a) observed greater than 97% removal efficiencies of MTBE at the inlet concentrations of 0.65 - 0.85 g/m^3 using biotrickling filters filled with lava rocks and pall rings. In the study conducted by Dupasquier et al. (2002), pentane oxidizing bacteria were to used degrade MTBE in a

biofilter filled with Vermiculite. MTBE degradation rates obtained in this study were much lower than those using consortia or pure strains that can mineralize MTBE. At the residence time of 1.1 hours and inlet pentane concentration of 18 g/m^3, the elimination capacity of MTBE was between 0.3 and 1.8 g/m^3/hour with inlet MTBE concentration ranging from 1.1 to 12.3 g/m^3.

Thus these studies demonstrate that biofiltration can be considered as a strategy for off-gas treatment containing MTBE but some issues need further research. The problem areas include long start-up time of the biofilters treating MTBE, behavior of MTBE degrading biofilters under transient conditions, and removal of MTBE in biofilters in the presence of BTEX and other contaminants.

CHAPTER III

MATERIALS AND METHODS

Experimental System

An illustration of the experimental biofiltration system is provided in Figure 1. The system consisted of two Plexiglass columns (Biofilter P and C) of 40 cm height with an internal diameter of 9.8 cm. Each column contained four sampling ports that enabled determination of concentration of the contaminant prior to, at the exit of and at two levels along the length of the columns. Distances of the two intermediate sampling ports were 13 cm and 27 cm from the inlet of the column. Filter bed materials filling the entire height of biofiltration columns were supported by a stainless steel sieve plate. Compressed air, after being passed through activated carbon to remove any particulates or organics, was humidified and contaminated with MTBE before being fed tangentially at the base of the column. Humidification was carried out by bubbling the air through two liquid reservoirs of capacity 1 L and 0.5 L. MTBE was introduced to the air flow stream using a programmable syringe pump (kdScientific model 2000 series) equipped with 5 mL gas tight glass syringe (Hamilton Company, Reno, NV). Pure liquid MTBE was pumped into a heated tee junction in the supply line where it was allowed to volatilize into the air stream. Air flow rates at the inlet and exhaust ends were metered by means of previously calibrated gas flow meters.

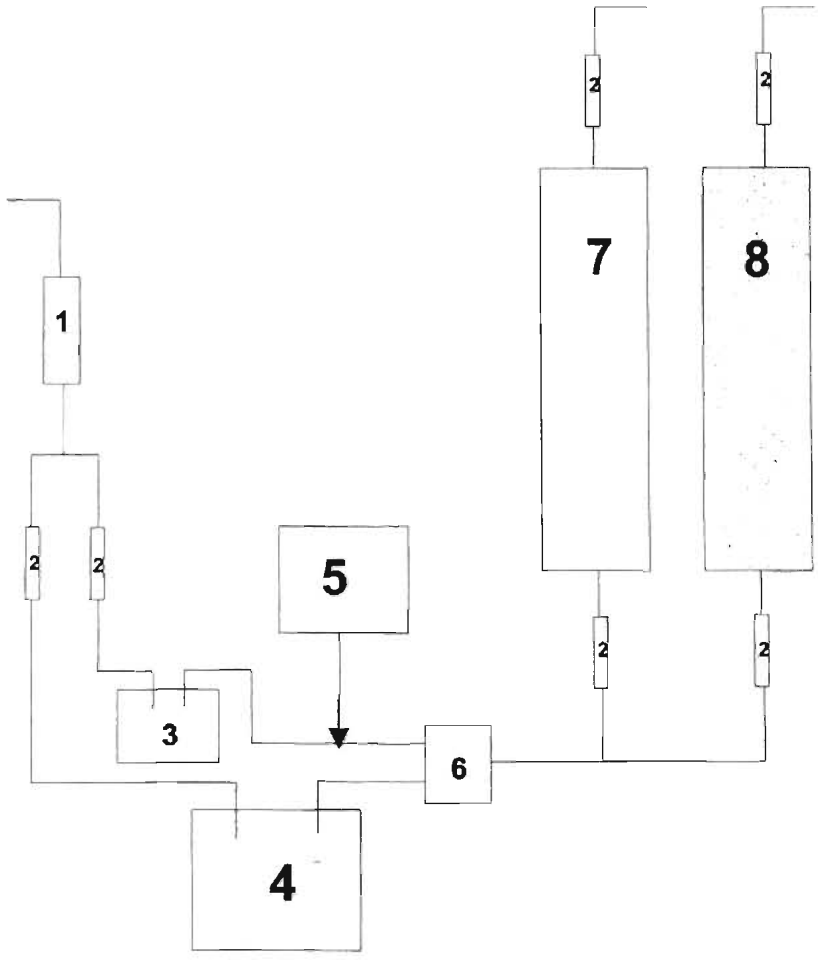


Figure 1. Biofiltration system: 1, activated carbon filter; 2, flow meter; 3, small water reservoir (0.5 L); 4, big water reservoir (1 L); 5, syringe pump; 6, mixing chamber; 7, biofilter P; 8, biofilter C.

Filter Media

Most of the biofilter media include a mixture of biological residues and inert bulking agents as this combination provides low pressure drop, reduced compaction, improved porosity, homogeneous gas flow, and reduced channeling (Devinny et al., 1999; Swanson and Loehr, 1997). In the present study compost/bulking agent was selected as a filter media because of the following specific advantages in addition to the general one provided above:

1. High surface area, high air permeability, high water retention capacity and low cost (Devinny et al., 1999; Swanson and Loehr, 1997).
2. Easy moisture control as compared to peat beds (Devinny et al., 1999).
3. Low pressure drop and space requirements as compared to soil biofilters (Devinny et al., 1999).

The compost used in this study was obtained from the city of Norman, Oklahoma, yard waste composting facility. The bulking agents used in this research were perlite (Pursell Industries Inc., Sylacauga, AL) and granular activated carbon (F600 12x40, Calgon Carbon Corporation, Pittsburgh, PA). The mean particle diameter of GAC was 1 mm. The perlite was sieved through # 10 mesh U.S. sieve (2.00 mm). Residue containing the fines was discarded and that which was retained on the sieve was used in the media. The compost was sieved through # 4 mesh U.S. sieve (4.75 mm) to discard big pieces of wood chips before it was used. Biofilter P was packed with compost and perlite in the ratio of 60:40 by volume. Biofilter C was packed with compost, perlite and carbon in the ratio of 60:20:20 by volume.

Geometric Mean Diameter (D_{50}) Determination

Geometric mean diameter for the media used in biofilter P and biofilter C was determined by sieve analysis. Specifications of sieves used in sieve analysis are given in Table 5. Sieves were weighed to the nearest 0.1 grams and a known weight of medium was sieved through them. The weight of individual sieve along with the medium retained on it was then determined, from which the weight of the media retained on each sieve was calculated. This data allowed the calculation of the mass fraction of each particle size range. The plot of cumulative percentage less than top sieve size vs. sieve size on log-probability paper, gave the required geometric mean diameter (D_{50}).

Partition Coefficient Studies

Partitioning coefficient was estimated using the procedure described by Hodge and Devinny (1995). Serum bottles (160 ml) (Wheaton) sealed with Teflon® lined rubber septa (diameter 20 mm, Supelco, Bellefonte, PA) and containing 25 ml (Biofilter P) or 10 ml (Biofilter C) of media were used in this experiment. Three replicates were taken for each case. The bottles and media were autoclaved for 1 hour (121^0C, 15 psi) before addition of a known amount of MTBE. The bottles were kept in constant-temperature incubator to eliminate the effect of temperature on partitioning and were mixed occasionally with a vortex machine. Headspace samples were taken for several days; the lack of further change indicated equilibrium had been reached between the air and solid/water phases. The partitioning coefficient (k_h) was determined by the following relationship:

Table 5: Specifications of Sieves Used in Sieve Analysis

Sieve #	Opening (mm)
4	4.76
10	2
20	0.85
30	0.6
40	0.42
50	0.297
60	0.25

$$k_h = \frac{C_{ads}}{C_{air}}$$

$$= \frac{(M_a - M_{air})}{(V_{sw})(C_{air})}$$

From the above value of partition coefficient, the value of mass partition coefficient (k_m) was determined using the following formula:

$$k_m = \frac{M_{ads}}{M_{air}}$$

$$= \frac{k_h (1 - \theta)}{\theta}$$

The value of retardation coefficient (R) was then determined by the following relationship:

$$R = \frac{M_{ads} + M_{air}}{M_{air}}$$

$$= 1 + k_m$$

where:

M_a = Mass of the contaminant added, mg

M_{air} = Mass of the contaminant in air phase, mg

V_{sw} = Volume of solid/water phase

C_{air} = Concentration in air phase, mg/l

C_{ads} = Concentration in adsorbed phase, mg/l

M_{ads} = Mass of contaminant in the solid/water phase, mg

θ = Filter material porosity

Nutrient Media

Daigger mineral salts media (Daigger, 1979) was used for maintaining the MTBE degrading culture, soaking compost and GAC, and for irrigation of the biofilters. The media was prepared by mixing 100 ml of phosphate stock, and 10 ml each of nitrogen, sulfate and chloride stock, and diluting to 1 L volume by adding distilled/deionized water. The components of phosphate, nitrogen, sulfate and chloride stock are given in Table 6.

Inoculum Preparation

At start-up, both the biofilters were inoculated with a MTBE degrading bacterial consortium. This consortium was supplied by the Department of Environmental Sciences, Cook College, Rutgers University, New Brunswick, NJ. The enriched consortium was diluted (2 times dilution) with sterile Daigger mineral salts media in 0.5 L or 1 L culture bottles. The headspace of 250 mL (in case of 0.5 L bottle) and 500 mL (in case of 1 L bottles) was provided to ensure availability of sufficient amount of oxygen. These bottles were fitted with Hungate tubes, sealed with Teflon® lined rubber septa (diameter 20 mm, Supelco, Bellefonte, PA), and were kept on the shaker at room temperature (approx. 25^{0}C). The culture was maintained for approximately 20 days during which it was fed MTBE many times before inoculation of the biofilters.

Reactor Start-up and Operation

Before packing the reactors, the compost and GAC were soaked in the nutrient

Table 6. Composition of Daigger Mineral Salts Media

Stock	Chemical	Concentration (g/l)
Nitrogen stock	NH_4Cl	101.2
Phosphate stock	K_2HPO_4	43.5
	KH_2PO_4	34.0
Sulfate stock	$MgSO_4.7H_2O$	15.0
	$MnSO_4.H_2O$	0.45
	$Na_2MoO_4.2H_2O$	0.05
Chloride stock	$CaCl_2$	2.0
	$FeCl_3.6H_2O$	1.5
	$CoCl_2.6H_2O$	0.15
	$ZnCl_2$	0.15
	$CuCl_2.2H_2O$	0.05
	H_3BO_3	0.015
	Conc. HCl	3 mL/L

Source: Daigger, 1979

solution (Daigger mineral salts media) several times to bring their initial pH of 9, down to neutral. Media for biofilter P was prepared by mixing 3 L of compost with 2 L of perlite (60:40 v/v) and 400 ml (VSS = 58 mg) of the MTBE degrading culture. Similarly, media for Biofilter C was prepared by mixing 3 L of compost with 1 L of perlite, 1 L of GAC and 400 ml (VSS = 146 mg/L) of the MTBE degrading culture. In both cases the moisture content of the mixture was brought to field capacity by addition of Daigger mineral salts media, before packing the reactors with the media. Contaminated air flow was then started and samples were taken after 30 minutes.

The reactors were maintained at room temperature (approx. 25^0C) and apart from packing material, the operation of the two parallel biofilters was identical. During the three months of operation of the reactors, they were subjected to different loading rates obtained through the combination of different air flow rates and MTBE concentrations. Experimental schedule and operating conditions are shown in Table 7.

Peat Humic Substances (PHS) Effect Evaluation Experiments

A previous study (Fortin and Deshusses, 1999) had indicated that PHS may have a role in shortening the startup time of the biofilters treating MTBE. Therefore experiments were conducted to determine the effect of PHS on biodegradation of MTBE. These experiments were conducted in two stages. In the first stage, the effect of low concentrations of PHS (0.2, 2 and 20 mg/l) on MTBE biodegradation was investigated (low concentration experiment). In the second stage, the effect of high concentrations of PHS (50, 100, 150 ad 200 mg/l) on MTBE biodegradation was investigated (high concentration experiment).

Table 7: Experimental Schedule and Operating conditions

DAY	Empty Bed Residence Time (minutes)	Biofilter P		Biofilter C	
		Average Concentration (g/m^3)	Loading rate (g/m^3/hour)	Average Concentration (g/m^3)	Loading rate (g/m^3/hour)
1-38	1.4	0.2	8.27	0.19	7.94
39-55	1.4	0.34	14.14	0.33	13.81
56-65	2.3	0.3	7.9	0.33	8.66
66-77	2.3	0.1	2.76	0.09	2.46
78-87	2.3	0.05	1.44	0.05	1.36
88-100	3.5	0.06	1.02	0.06	1.01

Experiments were performed with 160 ml serum bottles containing 50 ml of sterile Daigger mineral salts media, and sealed with Teflon® lined rubber septa and aluminum crimp caps. Autoclaved controls (121^0C, 15 psi for 30 minutes) were used to evaluate abiotic losses. Corresponding to each concentration of PHS, six bottles were used. Two of these six bottles were used as controls and remaining four were inoculated with 1 ml of MTBE degrading culture. A known amount of PHS was then added to the two of four inoculated bottles and incubation was carried out at 25^0C. Consumption of MTBE was monitored by headspace analysis with the help of GC/MS until all of it was degraded.

Analytical Techniques

Gas-Concentration Determination

MTBE in the inlet and the outlet air was measured using a Gas Chromatograph/Mass Spectrometer (Model: GCMS-QP5050, Shimadzu Corporation, Kyoto, Japan). Integration of peak areas was carried out using Class 5000 software (Shimadzu Corporation, Kyoto, Japan). The GC was equipped with a 60 m DB-624 column (J&W Scientific, Folsom, CA), with an internal diameter 0.32 mm and film thickness 1.8 μm. Oven temperature was held at 100^0C for 2 minutes and then increased to 130^0C at 20^0C/min. The injector was kept at 150^0C and column pressure was 25 psi. The carrier gas used was helium. 200 μl samples were injected into the GC from a 500 μl gas tight syringe (Hamilton Company, Reno, NV) into the split injector (split ratio = 5). The mass spectrometer was tuned to optimize the signal in the 35-125 m/z range. Under these conditions the retention times of MTBE and tertiary butyl alcohol (TBA) were

approximately 3.1 and 2.97 minutes respectively. It should be noted that TBA could be reliably quantified up to the concentration as low as 0.002 mg/l, but it could be detected at lower concentrations by matching of the mass spectra corresponding to its peak with library mass spectra. At standard operating conditions, influent and effluent streams were analyzed in triplicate once per day. Gas standards for MTBE and TBA were prepared as follows:

1. Stock solutions of MTBE were prepared in methanol with concentrations 14.88 g/l and 74.4 g/l and stored at 4^0C.
2. In case of MTBE different volumes of these stock solutions, or in some cases known amount of pure MTBE were added to the 120 mL serum bottles containing deionized water. The bottles were sealed with Teflon® lined rubber septa and aluminium crimp caps. In case of TBA, known volumes of pure TBA were injected into the sealed serum bottles containing deionized water.
3. These bottles were kept in the constant temperature incubator at 25^0C for at least 1 hour to equilibrate.
4. Henry's constants (25^0C) of 0.000587 atm m^3/mol for MTBE and 0.0000144 atm m^3/mol for TBA were used to calculate headspace concentrations of MTBE and TBA.
5. Calibration of the instrument was performed regularly by injecting at least three known concentrations.

Humidity

Humidity of the influent and effluent air was measured using a Digital Themometer/Hygrometer (Model DTH1, Davis Instruments, Baltimore, MD) that had effective range of 20 – 90% Relative Humidity (RH).

Pressure Drop

Pressure drop across each column was determined with an Air Velocity Meter (Model 400, Dwyer Instruments, Inc. Michigan City, IN). This meter can also function as a manometer with a range of 0-10 inches of water.

Moisture and Ash Content

Moisture and ash content of the media was measured before packing the columns. This was done according to ASTM method D 2974 – 00 (2001).

Volatile Solids

The procedure used in section 209F of Standard Methods (APHA et al., 1985) was used to determine the volatile solids.

Density Measurements

Biofilter material density was measured by weighing a sample of known volume (50 ml) using analytical balance (Fisher Scientific).

Porosity Measurements

The porosity of media samples was estimated by measuring the volume of the sample with a graduated cylinder (50 ml). The sample was weighed with an analytical balance and water (22^0C) was then added to fill the void-space volume. Air bubbles were dislodged by periodically tapping the cylinder. The saturated sample weight was then determined and percent porosity was calculated from the following relationship:

$$\% \text{ porosity} = \frac{\text{(void space volume)}}{\text{(volume of the sample)}}$$

$$\% \text{ porosity} = \frac{\text{(weight of sample + cylinder + water) - (weight of sample + cylinder)}}{\text{(density of water) * (volume of sample)}}$$

pH determinations

The pH values of the samples were measured using a pH meter (Accumet, pH meter 900, Fisher Scientific). Samples were saturated with distilled water, covered with parafilm and allowed to stand for approximately 1 hour before pH measurement was taken using pH meter. The pH meter was calibrated using buffer solutions of pH 4, 7 or 10.

CHAPTER IV

RESULTS AND DISCUSSION

The results of this study are divided into the following categories:

1. Culture maintenance
2. Biofilter media characterization
3. Peat Humic Substances (PHS) effect evaluation experiment
4. Start-up response of the biofilters
5. Behavior of the biofilters under different steady state loading conditions
6. Behavior of the biofilters under transient conditions
7. Validation of Ottengraf's model

Culture Maintenance

MTBE degrading culture was a gift from Dr. Robert Cowan of the Department of Environmental Sciences, Cook College, Rutgers University, New Brunswick, NJ. The culture was transported from New Jersey by the next day air delivery. It was diluted (2 times dilution) and maintained in three glass bottles (Active 1, 2 and 3) of 0.5 L or 1 L capacity. During this period MTBE was repeatedly fed to the culture and degradation was monitored by analysis on GC/MS. The results of culture maintenance are shown in Figure 2, 3 and 4. The culture showed a lag period of about 11 days before it started to degrade MTBE rapidly. One probable reason for this lag was the temperature

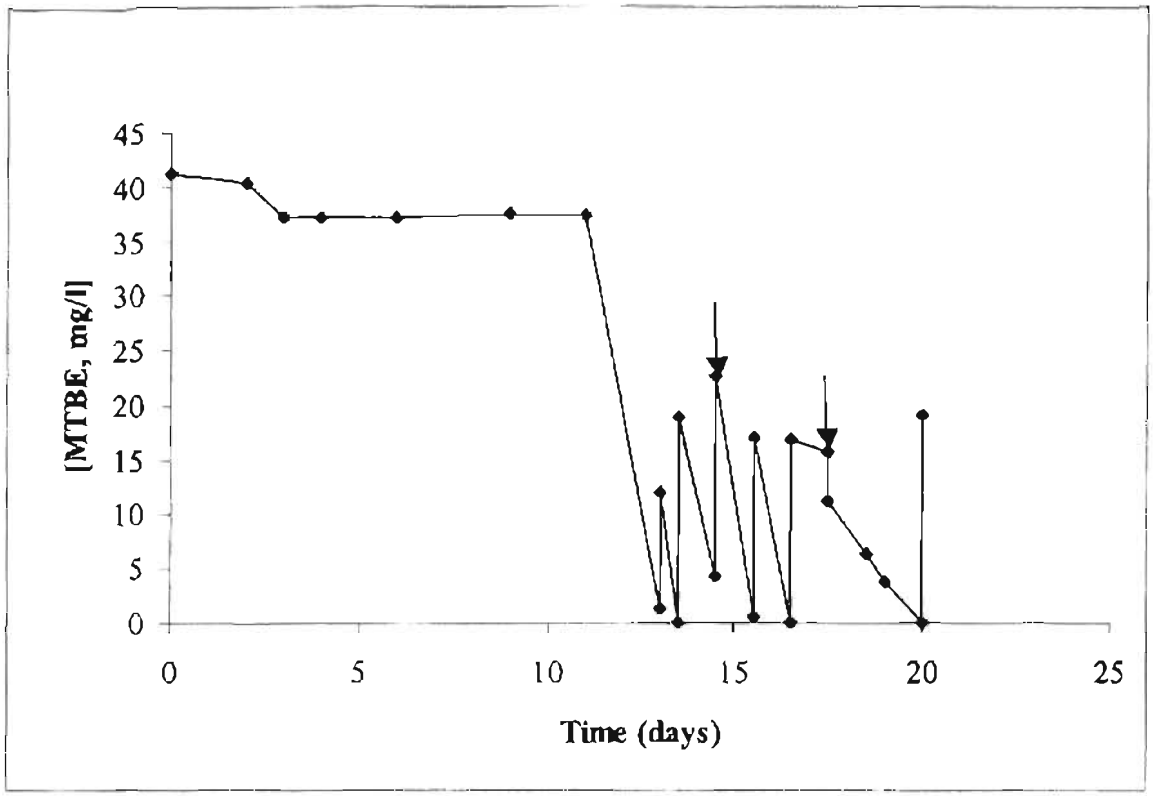


Figure 2. Biodegradation of MTBE by Rutgers culture (Active 1).
(Note: The peaks correspond to the time when the culture was spiked with MTBE. The arrows indicate the time when the bottles were flushed with air and also spiked with MTBE)

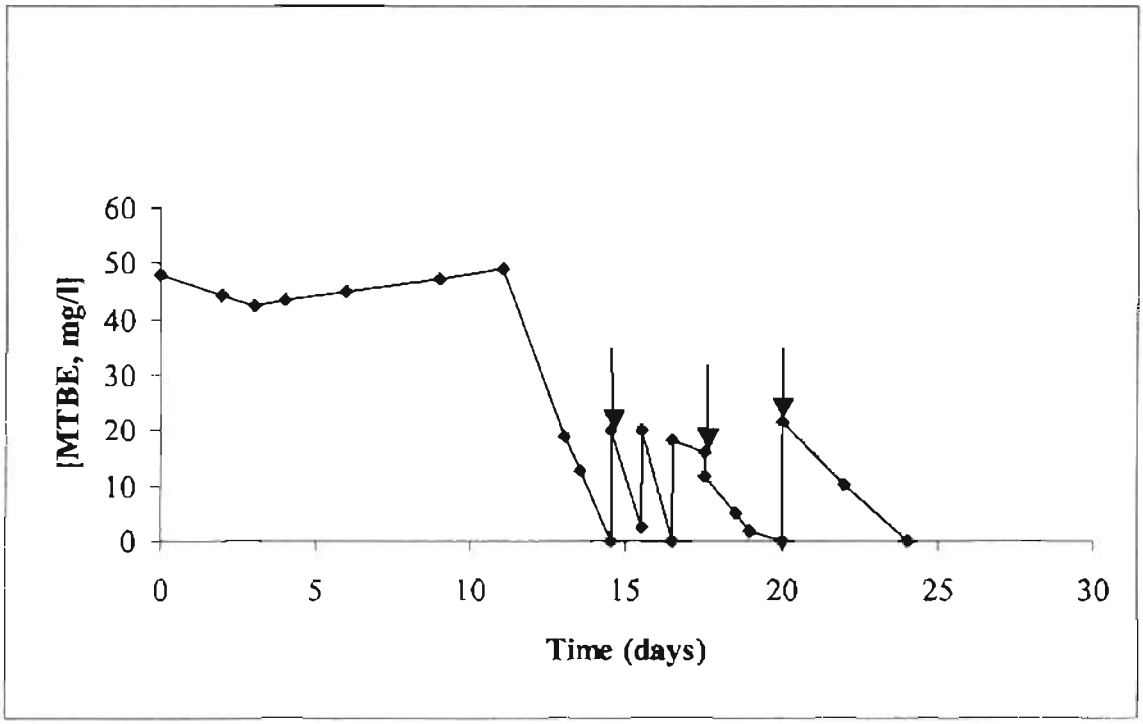


Figure 3. Biodegradation of MTBE by Rutgers culture (Active 2)
(Note: The peaks correspond to the time when the culture was spiked with MTBE. The arrows indicate the time when the bottles were flushed with air and also spiked with MTBE)

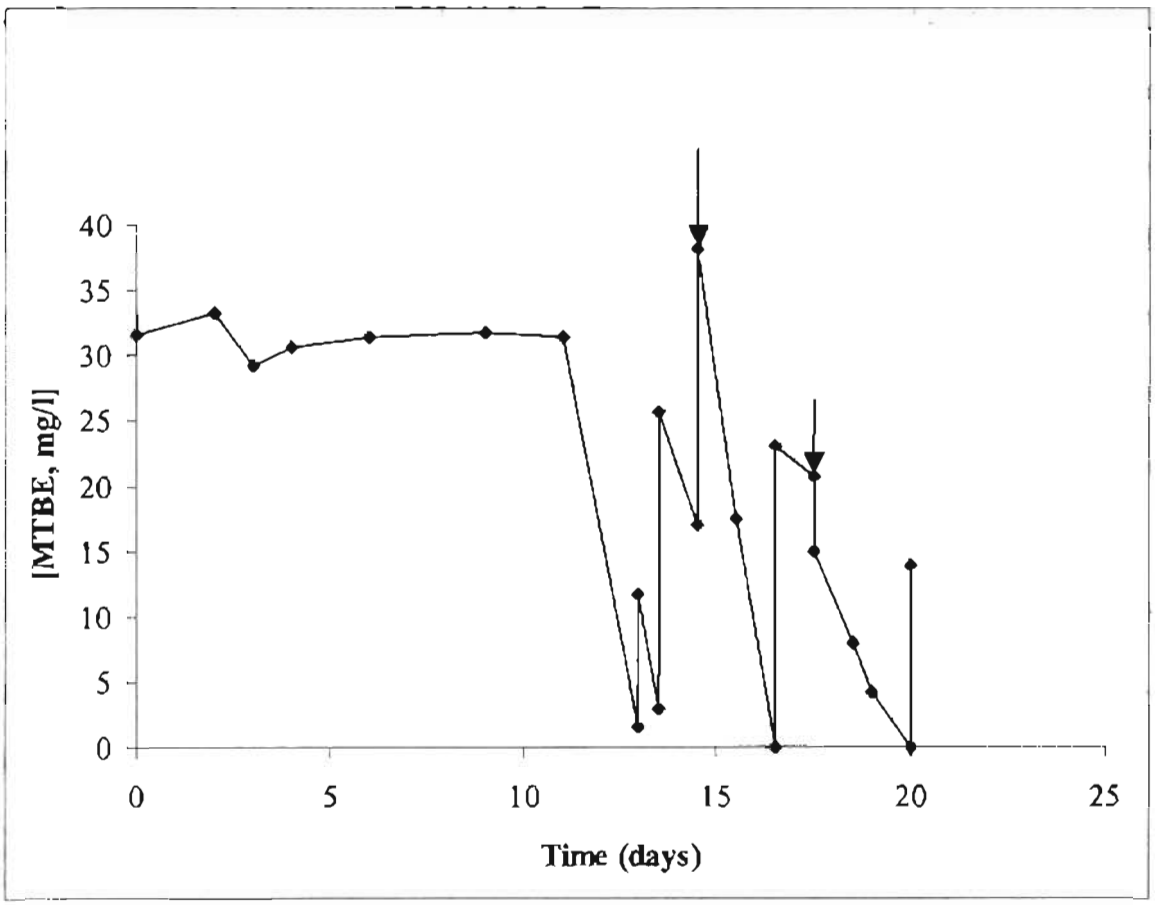


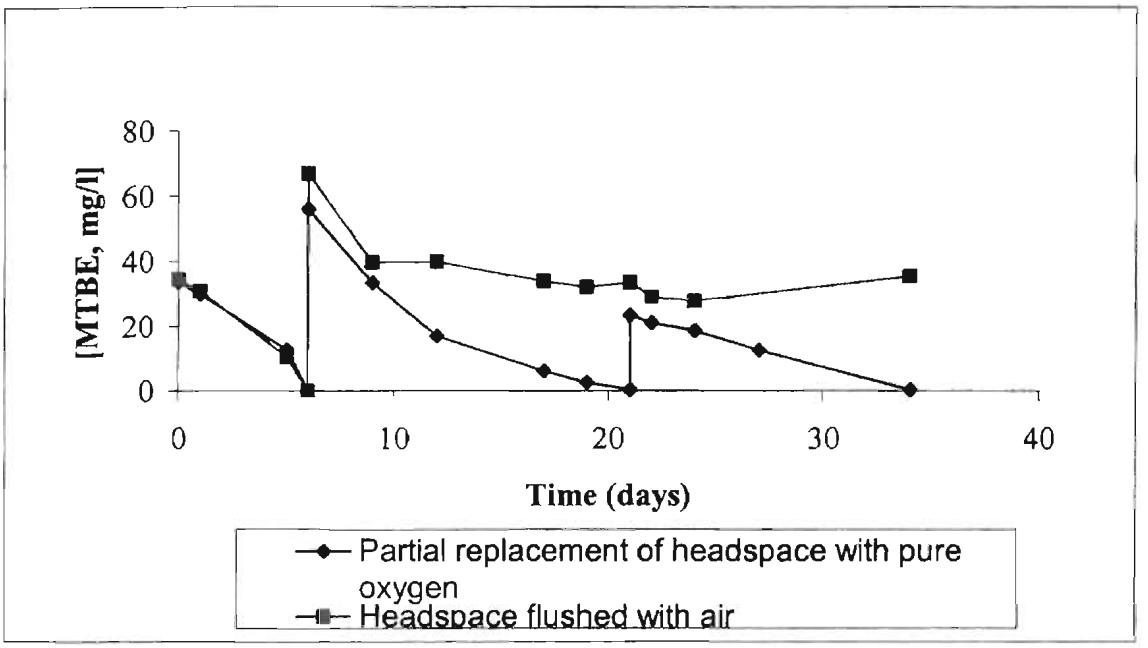
Figure 4. Biodegradation of MTBE by Rutgers culture (Active 3)
(Note: The peaks correspond to the time when the culture was spiked with MTBE. The arrows indicate the time when the bottles were flushed with air and also spiked with MTBE)

variations to which culture might have been subjected during transportation.

To ensure availability of sufficient amount of oxygen, the bottles were flushed with air for approximately 15 minutes on day 14. However on day 17 all the bottles showed a decrease in the rate of MTBE biodegradation. So on the same day, all the bottles were opened, pH was checked and after flushing the headspace with air, they were again incubated at 25^{0}C. The pH was found to be near neutral and depletion of nutrients and oxygen was not expected, but inspite of this, rates of MTBE biodegradation did not reach the previous values.

An exact reason for this slow down is not known. However a possible explanation is the formation and accumulation of toxic metabolites. Some of the metabolites of MTBE degradation shown by previous studies are TBA, 2-methyl-2-hydroxy-1-propanol (MHP) and 2-hydroxyisobutyric acid (HIBA) (Steffan et al. 1997). It is speculated that further breakdown produces intermediates such as 2-propanol, acetone and hydroxyacetone (Steffan et al. 1997; Salanitro et al. 1998) (see Appendix B for degradation pathway). Of all these metabolites, the analysis system used in this work was able to detect only the most commonly encountered metabolite of MTBE, i.e. TBA. No TBA accumulation was observed at any stage of the experiment in any of the bottles. This is in accordance with the observations of Alagappan and Cowan (2001) with this culture. They did not find any accumulation of TBA even at MTBE concentrations greater than 1000 mg/l.

While Active 1 and Active 3 bottles were used to inoculate the biofilters on day 20, some experiments were conducted with the Active 2 bottle to investigate the reason for the slow down of the culture activity. After day 24, the culture in Active 2 bottle was



Figures 5. Effect of oxygen on biodegradation of MTBE by Rutgers culture

split into two bottles. Both the bottles were flushed with air and in one bottle 20 ml of headspace was replaced with pure oxygen. The bottles were then kept on the shaker and incubated at 25^0C (See Figure 5). The rate of consumption of the first spike of MTBE was nearly the same in the two bottles. But for the second spike, the culture in the bottle that was flushed with air (Active 2a) stopped degrading MTBE while the culture in the bottle with partial replacement of headspace with pure oxygen (Active 2b) continued to degrade MTBE at relatively slower rate. On day 21, when MTBE concentration was nearly zero in Active 2b, the headspace in both the bottles was replaced with 40 ml oxygen. This was done to see whether the degradation activity could be restored in active 2a after being supplied with excess oxygen, but this did not happen. Even after 16 days of incubation (after the partial replacement of the headspace with pure oxygen) no degradation of MTBE was observed in Active 2a while the culture in Active 2b was still able to degrade MTBE. It should be noted that the culture in Active 2b also stopped degrading MTBE after few days (data not shown).

As no duplicates were used in this experiment, no definite conclusion regarding the effect of oxygen concentration can be derived from it, however limited data does suggest that excess oxygen might be helpful in maintaining this particular culture for longer times. Also the slow down in the rate of MTBE degradation after each successive spike of MTBE and the subsequent cessation of MTBE biodegradation do support the hypothesis of the accumulation of toxic metabolites.

Another interesting point to note is while in the batch mode the culture lost its activity after some time, no loss of activity with time was observed after inoculation into the biofilters. This may be because the toxic compounds were not able to accumulate in

the biofilters due to continuous air flow through the system. Also it has been suggested that for cultures with slow growth rates such as this (μ_{max} = 0.033 hour^{-1} at 25^{0}C (Alagappan and Cowan, 2001), attached growth might provide a more favorable environment (Fortin and Deshusses, 1999a).

Biofilter Medium Characterization

Characteristics of biofilter materials such as particle size, density, moisture and ash content, pH, porosity, partition coefficient, mass partition coefficient and retardation factor (see Chapter II for definitions) are shown in Table 8. Moisture content of both the media was close to 55% which is within the recommended operating range (40-60%) of the biofilters (Leson and Winer, 1991). Throughout the study the influent air humidity was kept greater than 90% to ensure minimum loss of moisture from the biofilter media. pH of the biofilter P media was neutral, however, biofilter C media was slightly alkaline due to the presence of activated carbon. The activated carbon used in this study had a pH of 9, and although it was soaked in the nutrient/buffer solution several times, the pH did not come exactly down to neutral.

Values of k_h, k_m and R were considerably higher for biofilter C medium than biofitler P medium. This was due to the presence of activated carbon and the relatively high amount of adsorption taking place in biofilter C medium. According to Hodge and Devinny (1994), values of R typically vary from 2 or 3 to tens of thousands, so the values obtained in the present study are within the acceptable range. It should be noted that theoretically the detention time of the contaminant in the biofilter is the air detention time

Table 8. Biofilter Medium Characterization

Parameter	Biofilter P	Biofilter C
Particle size, d50 (mm)	2.4	2.7
Density (g/l)	736	724
Moisture content (%)	55	56
Ash content (%)	24	25
pH	7	7.5
Porosity	0.34	0.37
Partition coefficient (k_h)	62	6145
Mass partition coefficient (k_m)	120	10462
Retardation factor (R)	121	10463

multiplied by the retardation coefficient, therefore it is expected that MTBE had much higher detention times in biofilter C than biofilter P.

PHS Effect Evaluation Experiment

A previous study (Fortin and Deshusses, 1999a) has indicated that PHS may have a beneficial effect on the performance of biofilters treating MTBE, and may shorten their start-up times also. Therefore experiments were conducted to determine the effect of PHS on biodegradation of MTBE. These experiments were conducted in two stages. In the first stage, the effect of low concentrations of PHS (0.2, 2 and 20 mg/l) on MTBE biodegradation was investigated (low concentration experiment). In the second stage, the effect of high concentrations of PHS (50, 100, 150 and 200 mg/l) on MTBE biodegradation was investigated (high concentration experiment). The results of 'low concentration experiment' are shown in Figures 6a, 6b and 6c, and the results of 'high concentration experiment' are shown in Figures 7a, 7b, 7c and 7d. It can be clearly seen from the above mentioned figures that PHS did not have any favorable or adverse effect on the biodegradation of MTBE for the range of concentrations investigated. It should also be noted that these experiments were conducted in suspended growth reactors for the sake of simplicity. The response in attached growth systems might be different, but in our case no further studies on the effect of PHS were carried out.

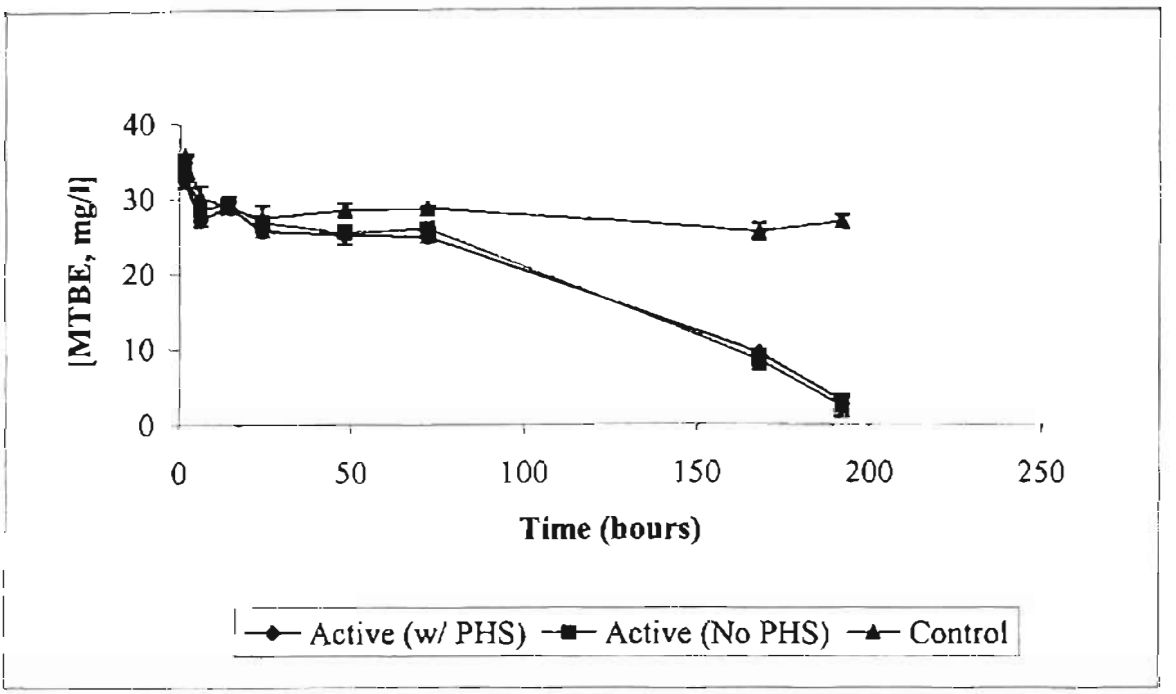


Fig. 6a: Effect of PHS (0.2 mg/l) on biodegradation of MTBE

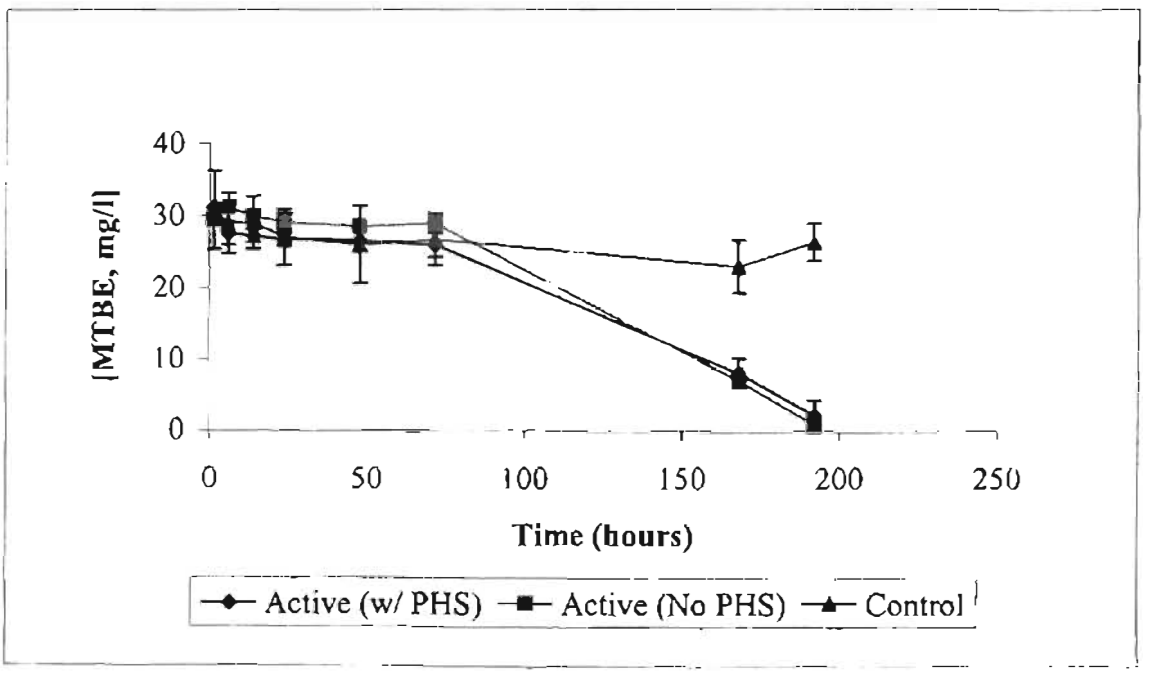


Fig. 6b: Effect of PHS (2 mg/l) on biodegradation of MTBE

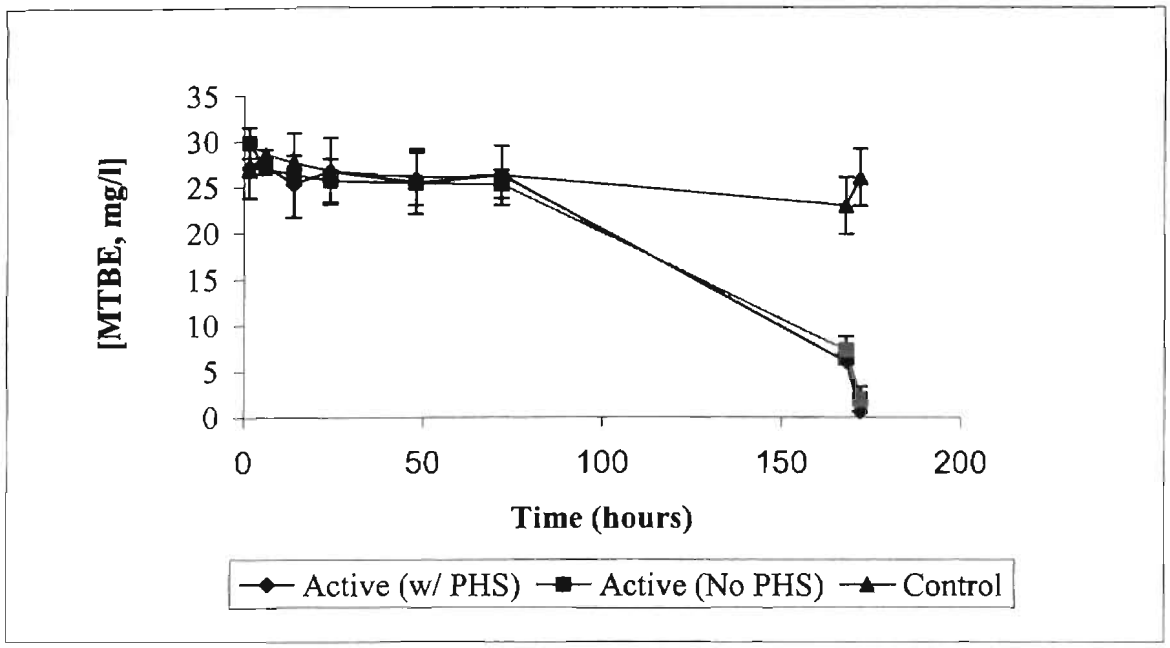


Fig 6c: Effect of PHS (20 mg/l) on biodegradation of MTBE

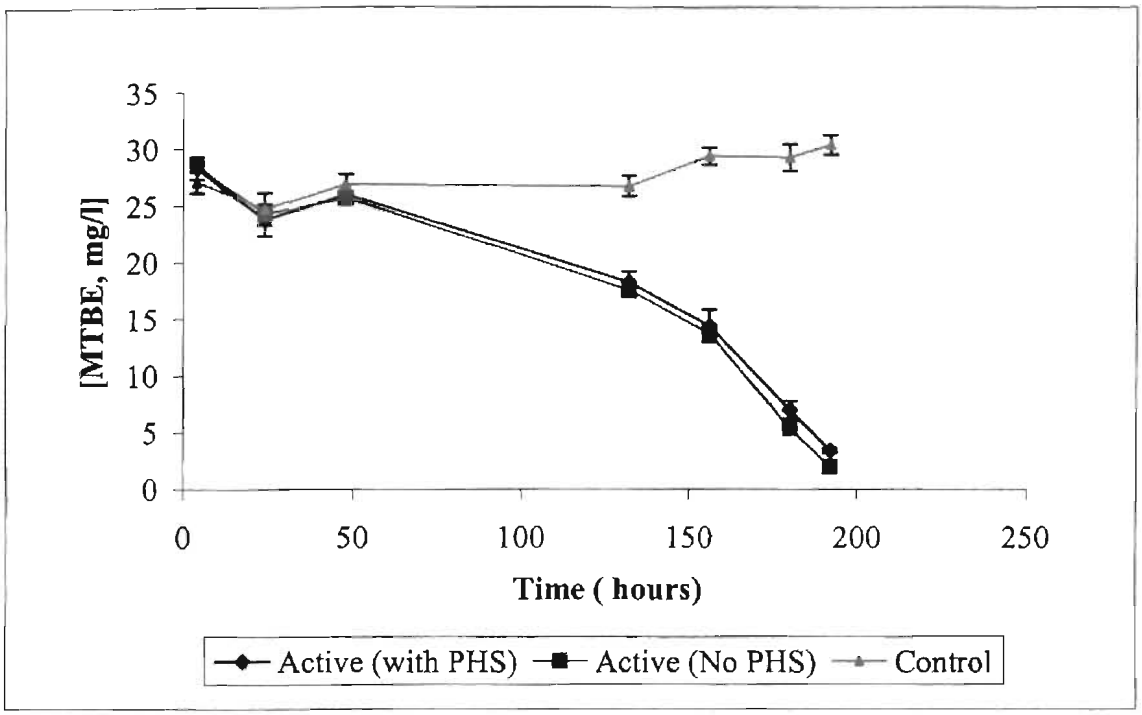


Fig 7a: Effect of PHS (50 mg/l) on biodegradation of MTBE

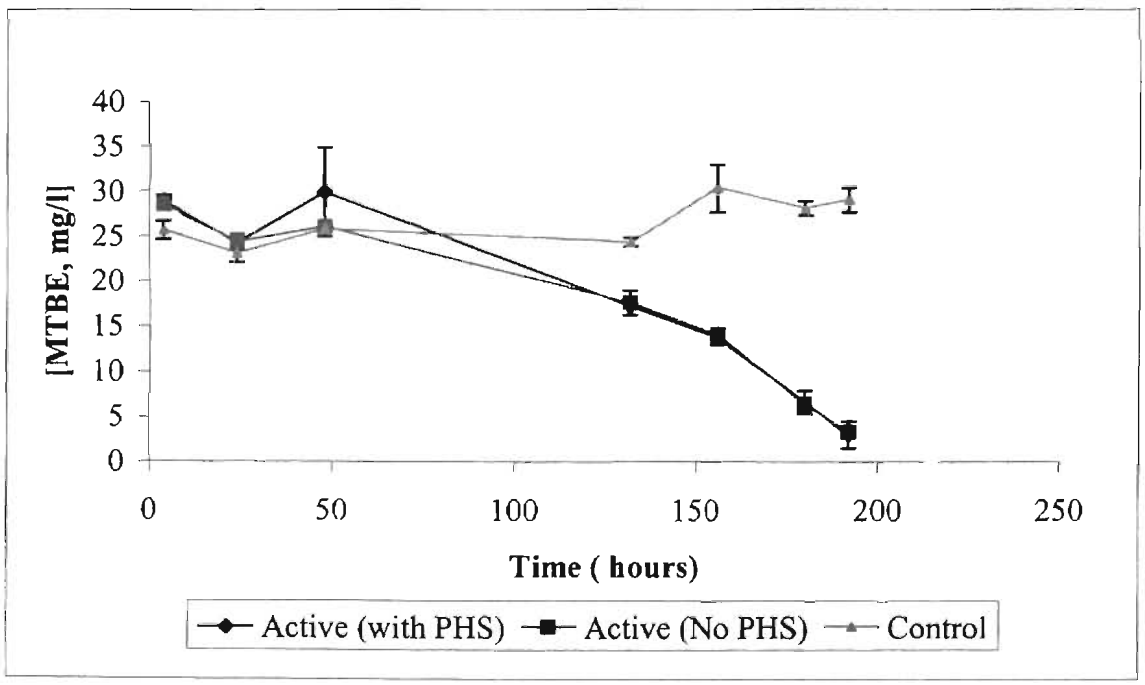


Fig 7b: Effect of PHS (100 mg/l) on biodegradation of MTBE

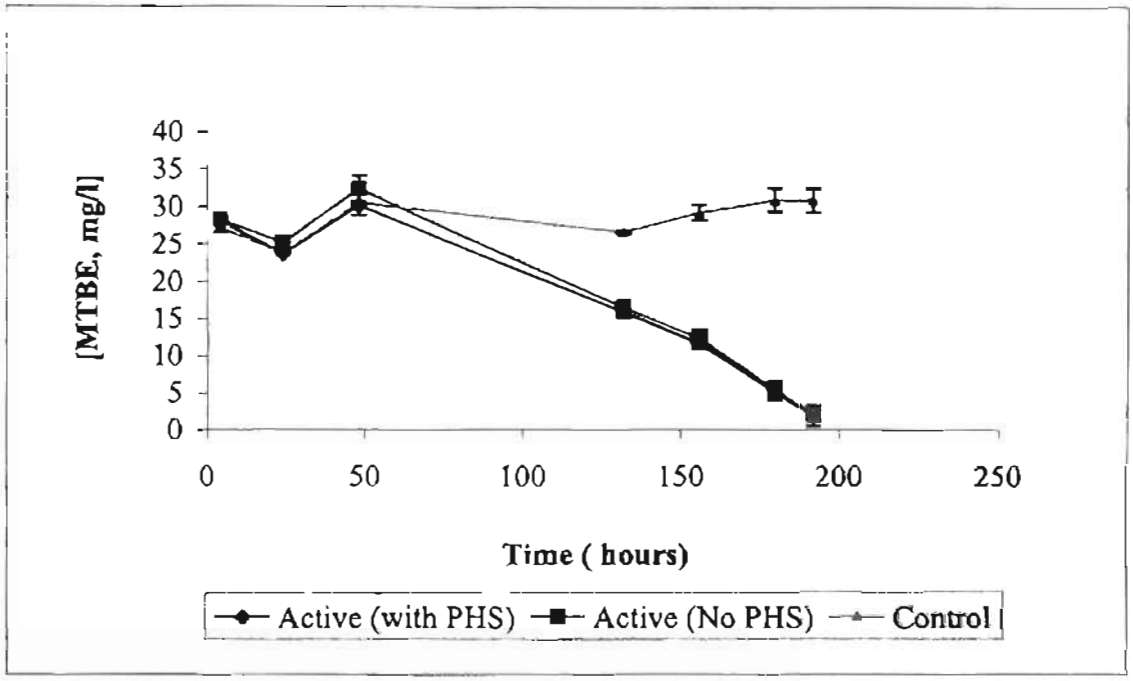


Fig 7c: Effect of PHS (150 mg/l) on biodegradation of MTBE

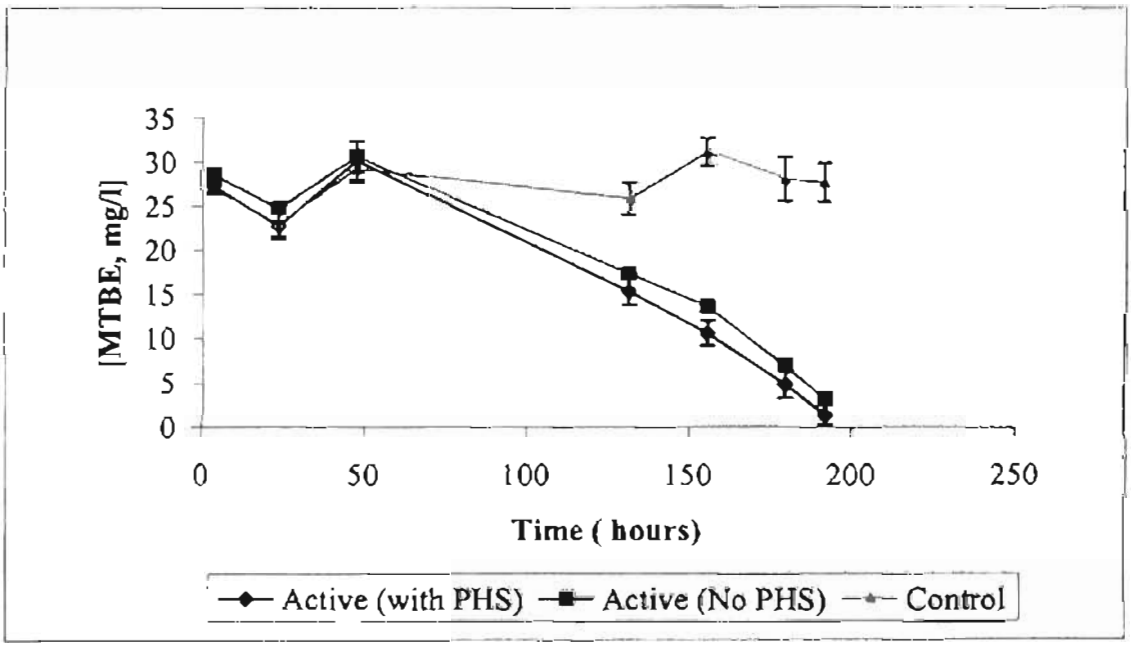


Fig 7d: Effect of PHS (200 mg/l) on biodegradation of MTBE

Start-up Response of the Biofilters

Very few studies have reported the details of the start-up period of biofilters. Start-up response is very important in the case of MTBE biofiltration, as previous studies have shown that relatively long start-up times are required by biofilters treating MTBE compared to other biofilter applications (Devinny et al., 1999).

In the present study, after packing the columns with the media inoculated with 400ml MTBE degrading culture (VSS = 58 mg), the contaminated air flow was started to both the biofilters. Figures 8 and 9 show the start-up response of the two biofilters. It should be noted that there was some syringe pump malfunctioning for the first 9 days of the operation of the biofilters. Due to malfunction there was some inconsistency in the data, especially in case of biofilter P. Due to this problem with the syringe pump, MTBE was not fed to the reactors for about 38 hours after 8^{th} day, although the flow of air was not stopped to the two reactors.

In the case of biofilter C, for the first 7 days of its operation, nearly constant removal of about 30% was seen. This is assumed to be due to adsorption on activated carbon. The breakthrough of the carbon led to the considerable decrease in removal efficiencies on 8^{th} and 9^{th} days. On the 12^{th} and 13^{th} day, due to the possible regeneration of activated carbon by the passage of clean air through the biofilter (due to above mentioned syringe pump malfunctioning), removal efficiency of 28-29% was observed. After this the removal efficiency of the biofilter was unstable, however the general trend indicates a steady increase from day 20 up to day 26, when a relatively steady removal of about 50% was observed. In contrast to biofilter C, removal in biofilter P was nearly zero for the first 9 days, suggesting poor adsorption of MTBE on perlite and compost.

Removal efficiencies were fluctuating after that but from day 21st to day 33 there was a steady increase in removal efficiency from 0 to about 40%.

Visual observation revealed the growth of white, filamentous, fungus like material throughout the biofilter beds on 16th day. The growth of this fungus like material continued to increase until day 22, when 2-3 strands of this material, about 2-3 cm long were observed in both the biofilters. Usually fungus growth in the biofilters is associated with low pH and low moisture conditions (Devinny et al., 1999). However in this case the chances of both these problems developing in our biofilters were very remote. That is because the biofilters were started at near neutral pH and high moisture content, and moreover the inlet air was humidified to greater than 90% relative humidity before entering the filters. The fact that the growth of this fungus like material was negligible in the later stages of the biofilter operation also refutes the occurrence of low pH and low moisture conditions in the biofilters. In spite of no visible signs of bed drying, 150 ml water was poured to both the biofilters on day 22 and visual observation suggested that fungus started to decay after that. This problem was not encountered again during the entire operation of the biofilters.

TBA was detected in the outlet air of both the biofilters on day 23 suggesting that biodegradation had started in both the reactors. The detection of TBA was confirmed by matching the mass spectra corresponding to TBA peak with the NIST62 library, mass spectra of TBA from Shimadzu Class5000 software. This unusually long acclimation time even after inoculation of the biofilters with active MTBE degrading culture has been observed in the previous biofiltration studies also. In the study by Eweis et al. (1998) the acclimation phase was about three weeks. Fortin and Deshusses (1999a) also mentioned

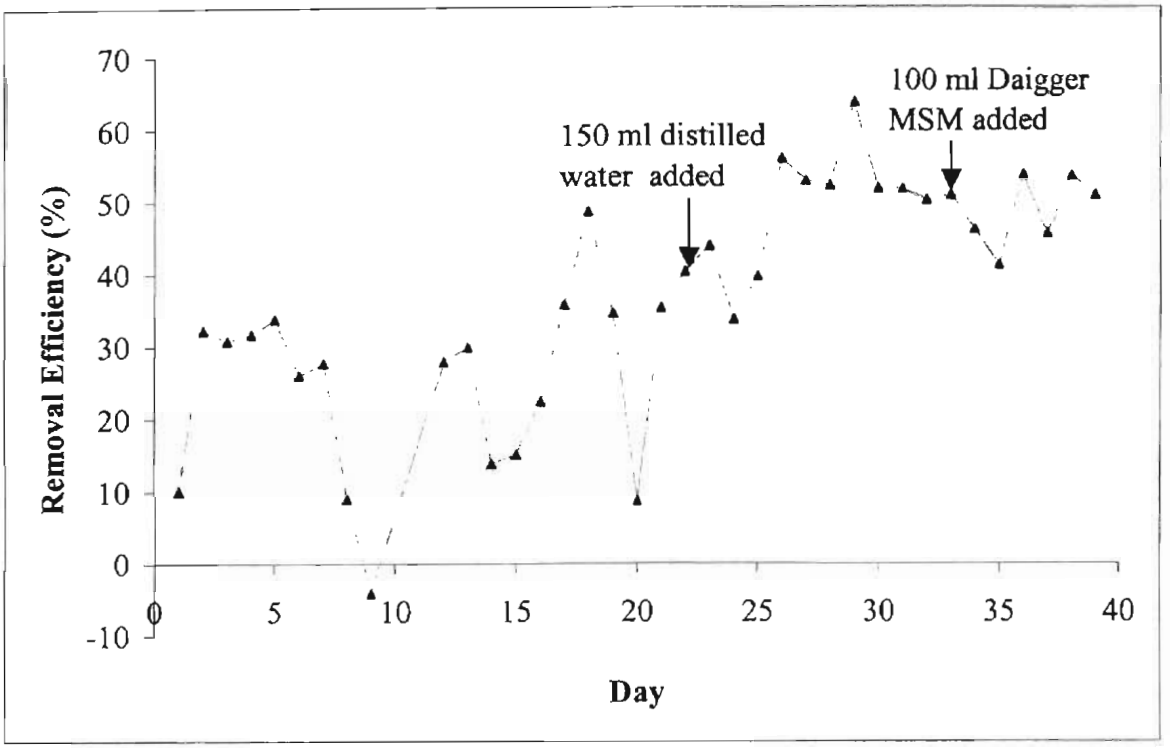


Figure 8: Start-up response of Biofilter C

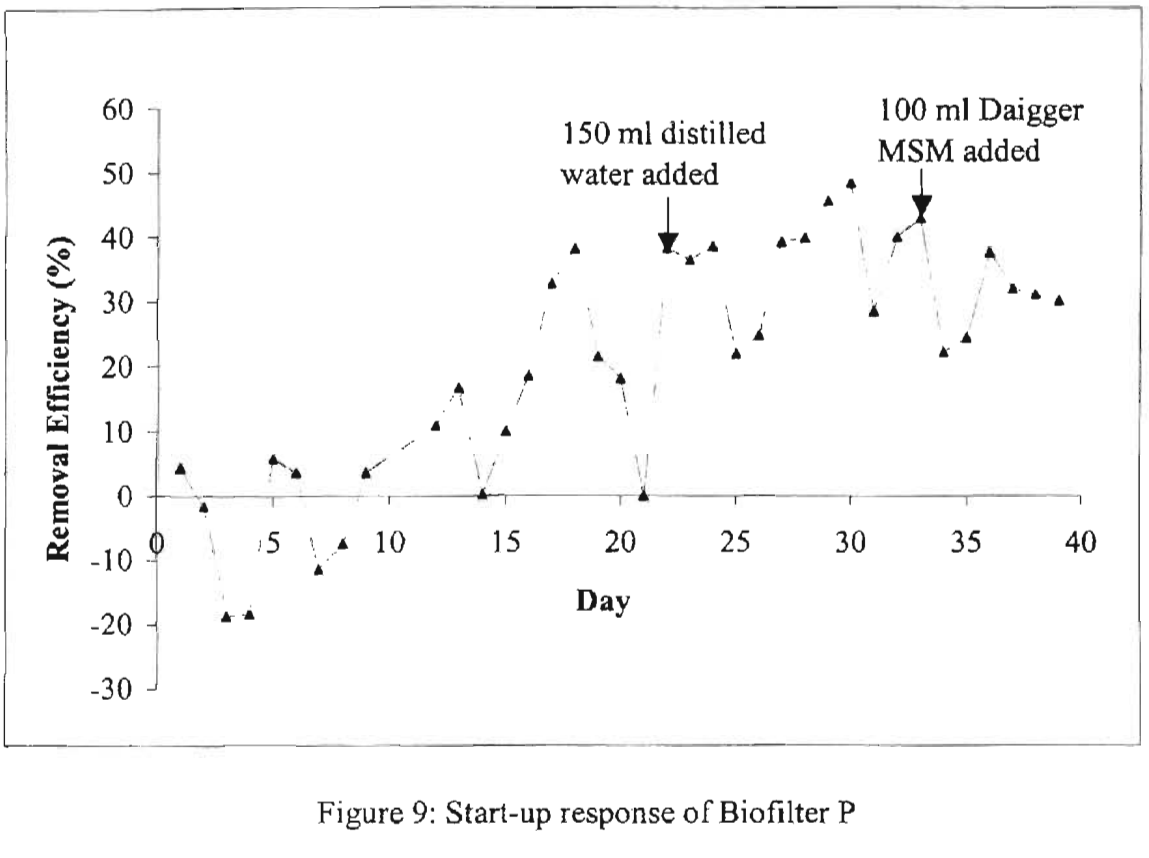


Figure 9: Start-up response of Biofilter P

the long acclimation times required by the biotrickling filters used in their study. They observed a lag time of about 25-35 days before removal efficiencies started to increase in their biotrickling filters. Long start-up times have also been observed in the case of some other relatively recalcitrant compounds such as dichloromethane. Ergas et al. (1994) observed a lag time of about a week before little degradation of dichloromethane started to occur in their biofilter even after inoculation with active dichloromethane degraders. They explained that the redistribution and growth of microbial populations or attachment of the organisms to the media may be required before significant removal is observed after inoculation (Ergas et al., 1994). In the present case, low specific growth rate of the culture (0.033 $hour^{-1}$ at 25^0C) and moderate cellular yields (0.35 mg cells COD/mg substrate COD at 25^0C) might be the reason for slow start-up (Alagappan, 2001).

One hundred ml of Daigger mineral salts media was poured from the top to each biofilter on day 33 to overcome any possible nutrient limitation. Interestingly both the biofilters showed a decrease in removal efficiencies for the next two days following the addition of nutrient media. This might be due to the drainage of some active biomass with the leachate produced after nutrient addition or oxygen and contaminant mass transfer problems due to reduced air/water interface per unit biofilter volume as a result of high water content.

Behavior of the Biofilters Under Steady State Loading Conditions

Long Term Performance of Biofilters

Biofilter P and Biofilter C were operated at various steady state loading rates obtained by the combination of different gas flow rates and inlet concentrations. In total

the biofilters were subjected to 6 different loading rates designated by run numbers 1, 2, 3, 4, 5 and 6. Operating conditions for each run are shown in Figures 10 and 11. Variation of removal efficiencies and elimination capacities over time for both the biofilters are shown in Figures 12 and 13 respectively.

In run 1, the biofilters were subjected to average MTBE concentration of about 0.2 mg/L and gas flow rate of 2.12 L/min, giving the empty bed residence time of 1.4 minutes. Under these conditions Biofilter C exhibited higher removal efficiencies than Biofilter P. A fraction of MTBE removed in both the biofilters was converted to TBA (see Figure 14 and Table 9). TBA was detected in the outlet stream of both the biofilters on day 23 by matching of its mass spectrum with the NIST62 library mass spectrum from Class5000 software, however quantification of TBA was carried out starting from day 27. The appearance of TBA in the outlet air of both the biofilters was slightly surprising because no accumulation of TBA was ever observed in the liquid batch cultures. Concentration of TBA started to decrease in the outlet air stream of Biofilter C starting from day 33 and in the Biofilter P starting from day 34. It is possible that initially the degradation rate of TBA lagged behind the MTBE degradation but as the culture matured TBA degradation rate increased and its accumulation in the biofilters decreased.

After day 39 the inlet concentration of MTBE was increased to both the biofilters, keeping the flow rate constant (see Figure 12). This led to a decrease in removal efficiencies for both the biofilters. The elimination capacity of biofilter C increased for some days presumably due to adsorption on activated carbon, but decreased in the later days of run 2 (see Figure 13). Immediately after the increase in concentration, there was an increase in TBA in the outlet stream of biofilter C. This increase was not seen in case

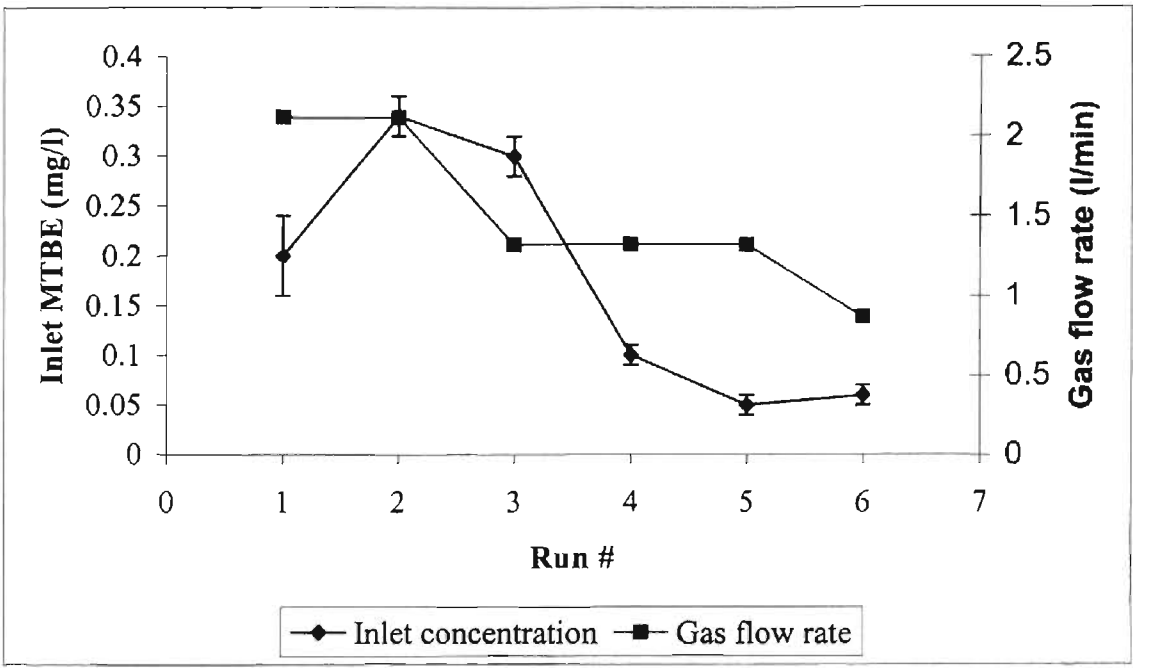


Figure 10: Operating conditions for various runs (Biofilter P)

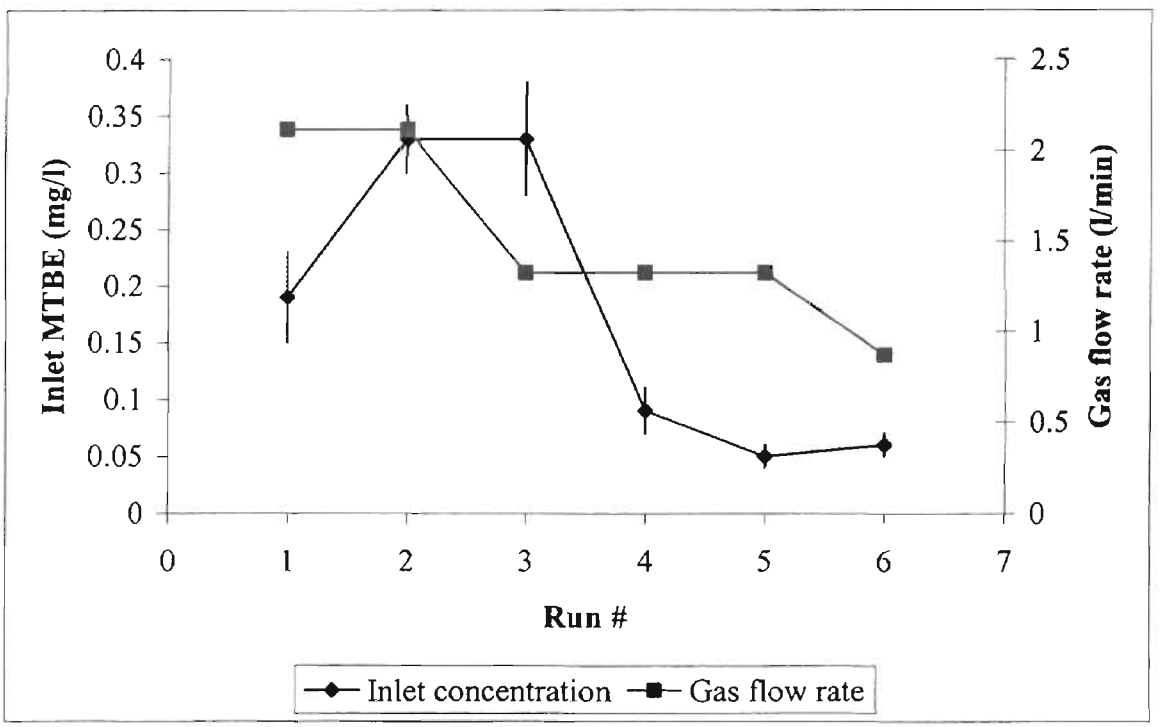


Figure 11: Operating conditions for various runs (Biofilter C)

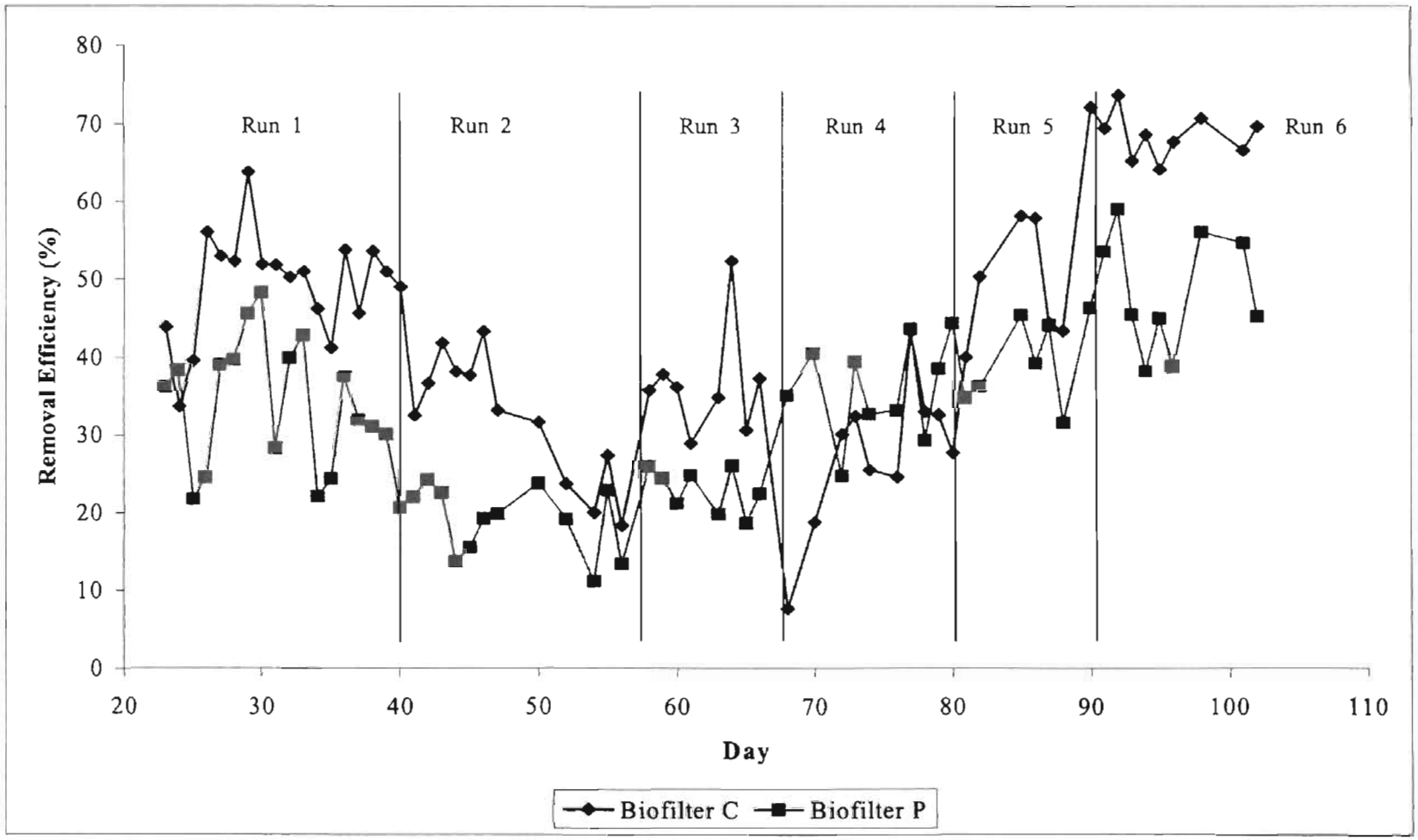


Figure 12: MTBE removal efficiency over time for Biofilter P and C

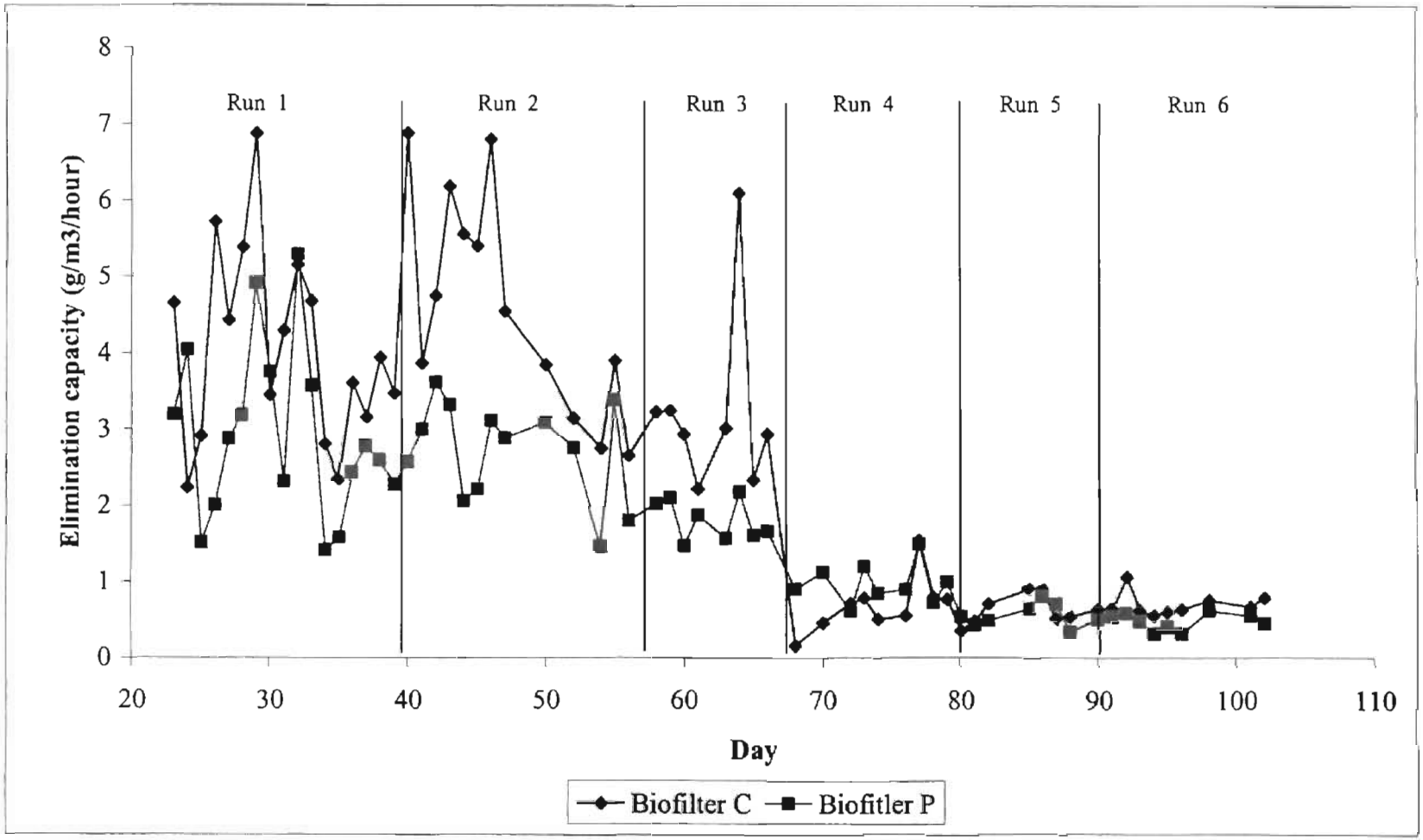


Figure 13. MTBE elimination capacity over time for Biofilter P and C

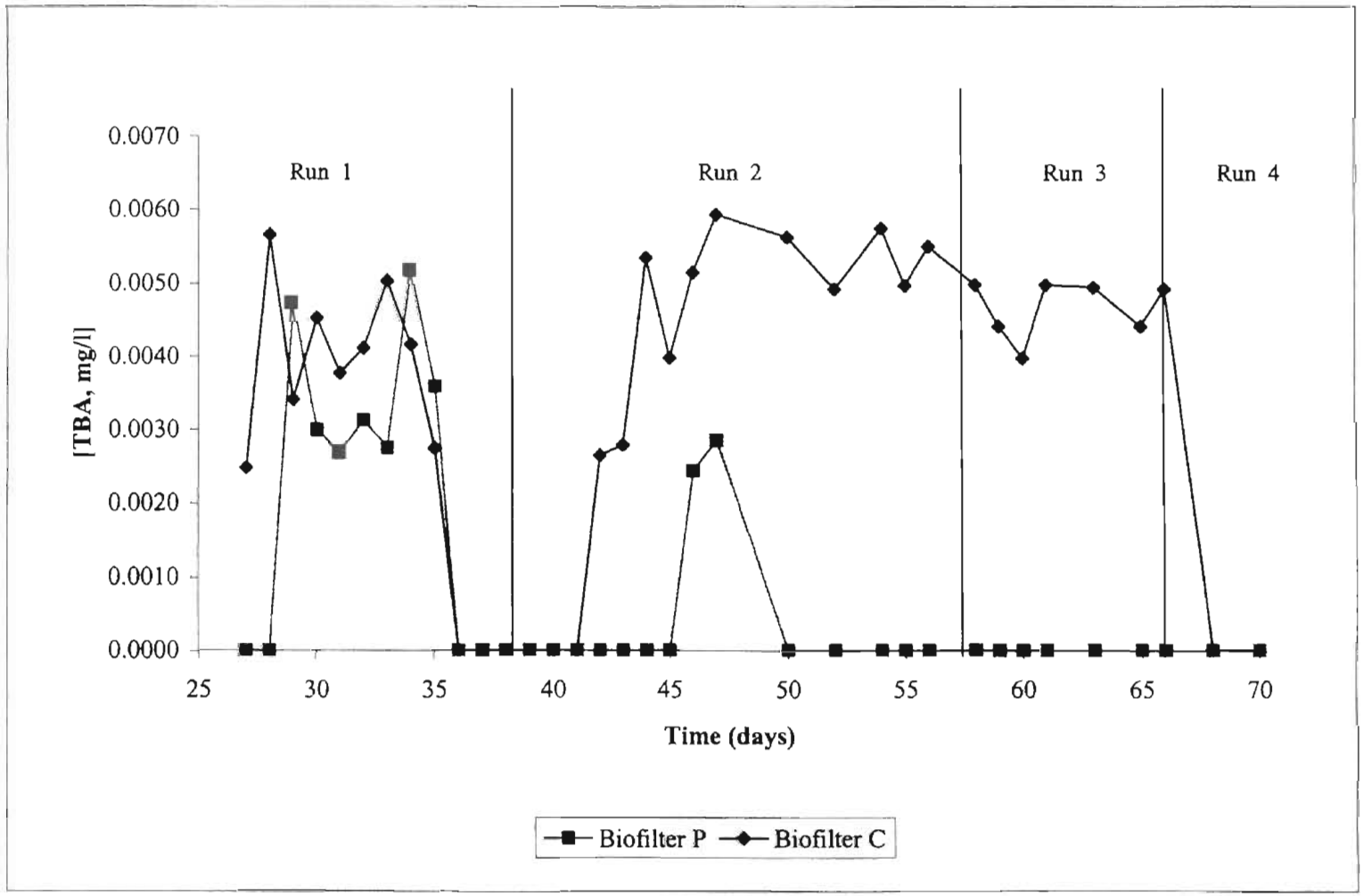


Figure 14: TBA production in Biofilter P and C over time

Table 9: Stochiometric Amount of TBA From Biofilter P and C

Run #	Air Flow (l/min)	Average inlet concentration of MTBE (mg/l)	Mass of MTBE into the column (moles/min)	Mass of TBA produced* (moles/min)	Removal Efficiency of Biofilter C (%)	Removal Efficiency of Biofilter P (%)	Concentration of TBA ** (Biofilter C) (mg/l)	Concentration of TBA ** (Biofilter P) (mg/l)
1	2.12	0.2	4.8×10^{-6}	4.8×10^{-6}	48.54	31.0	0.086	0.054
2	2.12	0.33	7.9×10^{-6}	7.9×10^{-6}	23.74	16.75	0.069	0.049
3	1.32	0.33	4.95×10^{-6}	4.95×10^{-6}	36.84	23.34	0.107	0.066
4	1.32	0.1	1.5×10^{-6}	1.5×10^{-6}	29.19	33.91	0.0254	0.0297
5	1.32	0.05	7.5×10^{-7}	7.5×10^{-7}	53.60	39.54	0.0230	0.0175
6	0.87	0.05	4.92×10^{-7}	4.92×10^{-7}	68.54	46.34	0.0297	0.0201

* Assuming 1 mole of MTBE gives 1 mole of TBA

** Assuming all the MTBE is converted to TBA

of biofilter P until day 45. It may be possible that following the increase in concentration, a significant portion of the MTBE was adsorbed onto the surface of the activated carbon, and when this MTBE was metabolized, TBA was produced. TBA continued to show up in the outlet stream of biofilter C for the entire duration of run 2, but its concentration was almost negligible in the case of biofilter P after the 50^{th} day.

In run 3, a loading rate similar to that of run 1 was obtained by decreasing the gas flow rate and keeping the concentration the same as in run 2. The increase in residence time improved the removal efficiencies of both the biofilters, either due to improved gas liquid mass transfer of MTBE or due to the fact that microorganisms had more time to act on the contaminant. During this run, no TBA was observed in the outlet stream of biofilter P but TBA continued to show in the outlet stream of biofilter C until the 66^{th} day. As discussed earlier, the metabolism of adsorbed MTBE and relatively high elimination capacities of biofilter C compared to biofilter P might be responsible for this difference.

Run 4 was started at the end of the 66^{th} day. In this run, the concentration of MTBE was decreased to 0.1 mg/l, keeping the residence time same as in run 3. Removal efficiencies of biofilter P increased, while that of biofilter C decreased considerably in the first few days of its operation (see Figure 12). This may be due to desorption of MTBE from the activated carbon. Elimination capacities of both the biofilters decreased, indicating that the reactors were operating in the regime where diffusion limitation occurs and elimination capacity varies directly with inlet concentration (for constant gas flow rate) (Ottengraf and van den Oever, 1983). This aspect will be discussed in more detail in the 'steady state performance' section.

It should be noted that just after two days of reduction of MTBE inlet concentration, TBA concentration in the outlet stream of the biofilter C decreased to zero (see Figure 14). After that, TBA was never detected in the outlet stream of any of the biofilters for the remaining period of their operation.

At the end of the 78th day, run 5 was started by decreasing the inlet MTBE concentration to 0.05 mg/l, keeping the flow rate same as in run 4. After a small period of poor removal, presumably due to desorption, removal efficiencies of biofilter C started to increase and remained greater than biofilter P for the entire period of the run. Biofilter P also showed improvement in removal efficiencies.

Run 6 was started on day 88 by decreasing the gas flow (residence time = 3.5 minutes) and keeping the inlet MTBE concentration same as in run # 5. Removal efficiencies of both the biofilters showed an increase and performance of biofilter C was better than biofilter P for the entire duration of the run.

Steady State Performance of Biofilters

This section discusses the steady state performance of the biofilters. The results presented here were obtained in the pseudo-steady state, which was identified by nearly constant exit gas concentration of MTBE. Figures 15 and 16 show the plots of elimination capacity vs. load for biofilters P and C respectively. It can be easily seen from Figures 15 and 16 that elimination capacity is an increasing function of inlet load up to the loading rate of about 8 g/m^3/hour. Beyond the loading rate of 8 g/m^3/hour elimination capacity in both the biofilters reached a maximum value that was independent of the inlet loading rate. This value was about 2.5 g/m^3/hour for biofilter P and about 3.2 g/m^3/hour for biofilter C (see Figures 15 and 16).

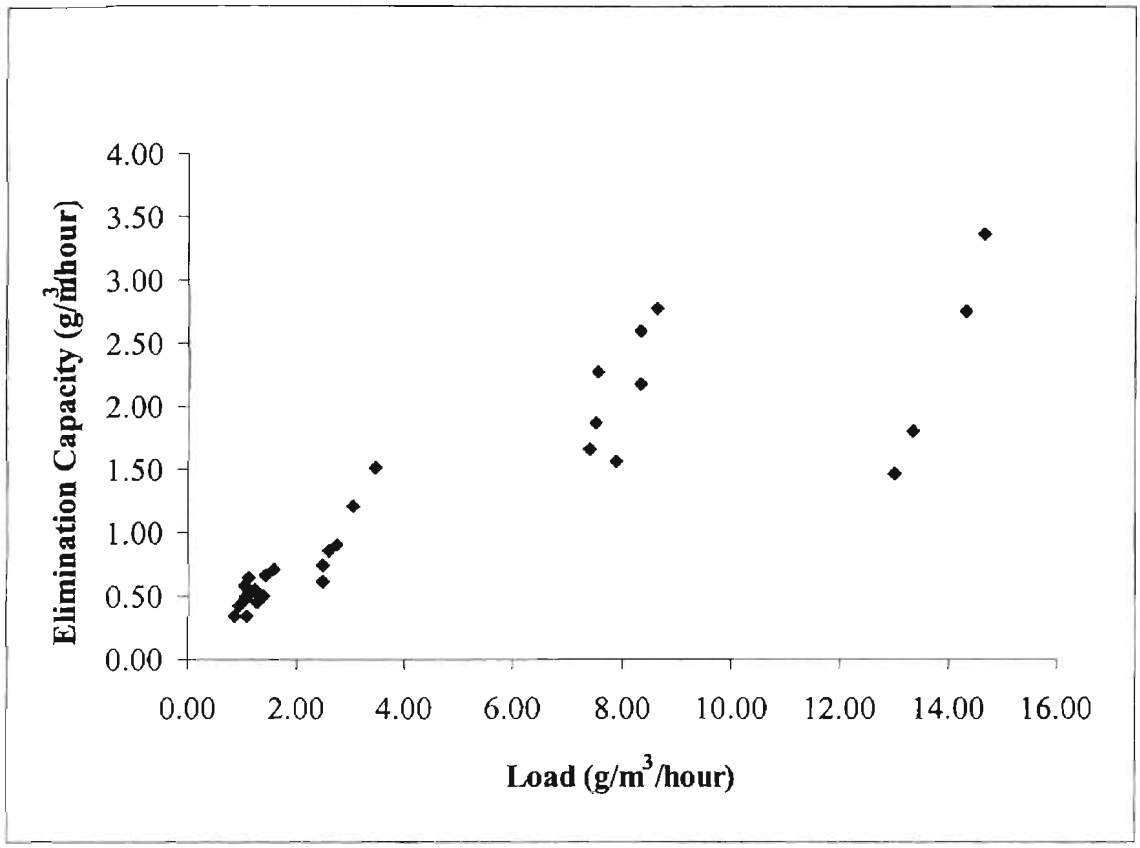


Figure 15: Elimination capacity vs. inlet load (Biofilter P)

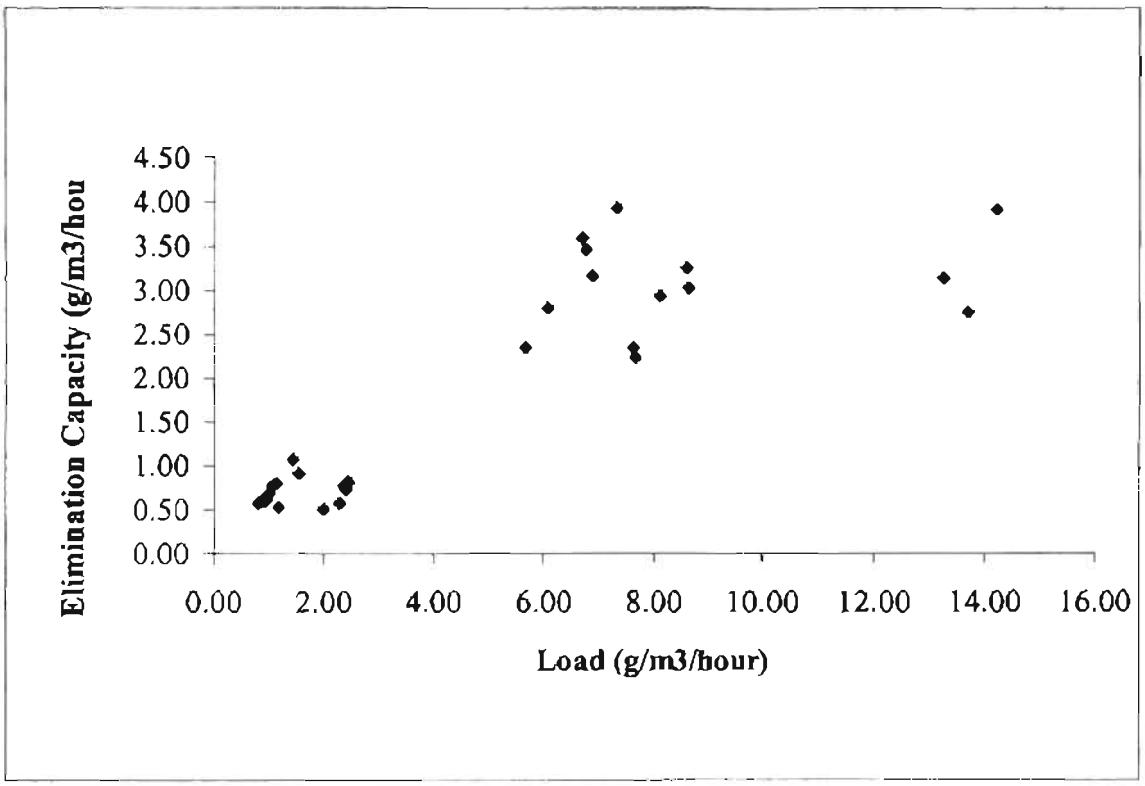


Figure 16: Elimination capacity vs. inlet load (Biofilter C)

In run 1, the biofilters were subjected to a loading rate of about 8 g/m^3/hour and steady state elimination capacities of 2.54 g/m^3/hour and 3.2 g/m^3/hour were obtained for biofilters P and C, respectively (see Tables 10 and 11). Increasing MTBE concentration from 0.2 mg/l to 0.33 mg/l did not increase the elimination capacities of both the biofilters. They were still operating at approximately same elimination capacity as during run 1. This suggests that both the biofilters were limited by the degradation reaction rate because if they had been limited by diffusion limitation, the increase in concentration would have enhanced the transfer rate of the pollutant from gas phase to biofilm enabling more microorganisms to act on the pollutant and thereby increasing the elimination capacity.

In run 3, loading rates similar to run 1 were obtained with a different combination of gas flow rate and inlet concentration. Ideally the biofilters should have shown the same elimination rate as in run 1 and 2 (because of the degradation reaction limitation), but both of them had slightly lower elimination capacities compared to earlier values. This may be due to the inhibition effect of high concentration of MTBE (0.33 mg/l) applied in run 2 and 3. Such inhibition effect has also been observed in other biofiltration studies (Jorio et al., 2000a; Jorio et al., 2000b). This inhibition effect might have damaged to the culture so the biofilters were not able to reach the previously obtained value of maximum elimination capacity.

Lowering of MTBE concentration in run # 4 reduced the elimination capacities of both the biofilters suggesting the diffusion limitation regime (Ottengraf and van den Oever, 1983). At this low concentration biolayer was not fully active and elimination capacity was limited by the diffusion rate from gas phase into the biofilm rather than the

Table 10: Experimental Results at Various Flow Rates and Concentrations for Biofilter P

Run #	EBRT (minutes)	Inlet Concentration (g/m^3)	Inlet Load (g/m^3/hour)	Removal Efficiency (%)	Elimination Capacity (g/m^3/hour)
1	1.4	0.2 ± 0.04	8.27 ± 1.88	31.0 ± 0.96	2.54 ± 0.25
2	1.4	0.34 ± 0.02	14.14 ± 1.02	16.75 ± 5.37	2.35 ± 0.88
3	2.3	0.3 ± 0.02	7.9 ± 0.6	23.34 ± 2.77	1.82 ± 0.27
4	2.3	0.1 ± 0.01	2.76 ± 0.32	33.91 ± 6.8	0.97 ± 0.33
5	2.3	0.05 ± 0.01	1.44 ± 0.31	39.54 ± 5.92	0.53 ± 0.13
6	3.5	0.06 ± 0.01	1.02 ± 0.1	46.34 ± 7.01	0.47 ± 0.12

Table 11: Experimental Results at Various Flow Rates and Concentrations for Biofilter C

Run #	EBRT (minutes)	Inlet Concentration (g/m^3)	Inlet Load (g/m^3/hour)	Removal Efficiency (%)	Elimination Capacity (g/m^3/hour)
1	1.4	0.19 ± 0.04	7.94 ± 1.71	48.54 ± 5.01	3.22 ± 0.58
2	1.4	0.33 ± 0.03	13.81 ± 1.06	23.74 ± 3.66	3.26 ± 0.58
3	2.3	0.33 ± 0.05	8.66 ± 1.32	33.73 ± 3.76	2.76 ± 0.45
4	2.3	0.09 ± 0.02	2.46 ± 0.45	29.76 ± 3.75	0.7 ± 0.13
5	2.3	0.05 ± 0.01	1.36 ± 0.16	53.60 ± 7.88	0.78 ± 0.22
6	3.5	0.06 ± 0.01	1.01 ± 0.18	68.54 ± 2.89	0.71 ± 0.15

reaction rate. Typical of diffusion limitation regime, further lowering of inlet MTBE concentration led to still lower values of elimination capacities in the biofilters.

However a look at the steady state removal efficiency values for runs 2 through 6 reveals that their values increase with the decrease in loading rates (see Tables 10 and 11). Increase in residence time possibly led to improved gas liquid mass transfer or more time for the microorganisms to act on the contaminant, and decrease in inlet concentration led to increased fraction of MTBE being converted. Maximum removal efficiency for both the biofilters was achieved at lowest loading of about 1 g/m^3/hour. Thus biofilters were most efficient in removal of MTBE at low loadings.

Concentration profiles of MTBE along the height of the biofilters

Figures 17 and 18 show the steady state concentration profiles of MTBE along the height of biofilter C and P respectively. As stated earlier, if zero order kinetics are assumed in the biofilter then according to Ottengraf's model, the shape of concentration profile is linear in case of reaction limitation and quadratic in case of diffusion limitation (see 'biofilter modeling section of chapter II). A look at the concentration profiles for runs 4, 5 and 6 for both biofilters, reveals that they show dependence on the column height according to equation 4 (Chapter II). This gives further evidence that the loading rates during these runs corresponded to diffusion limited regime. However for runs 2 and 3 the profiles are fairly linear for both the biofilters, suggesting reaction limitation. As far as run 1 in concerned, the profiles for both the biofilters do not clearly show the nature of limitation but as the loading rate in this was similar to run 3, this should correspond to reaction limitation.

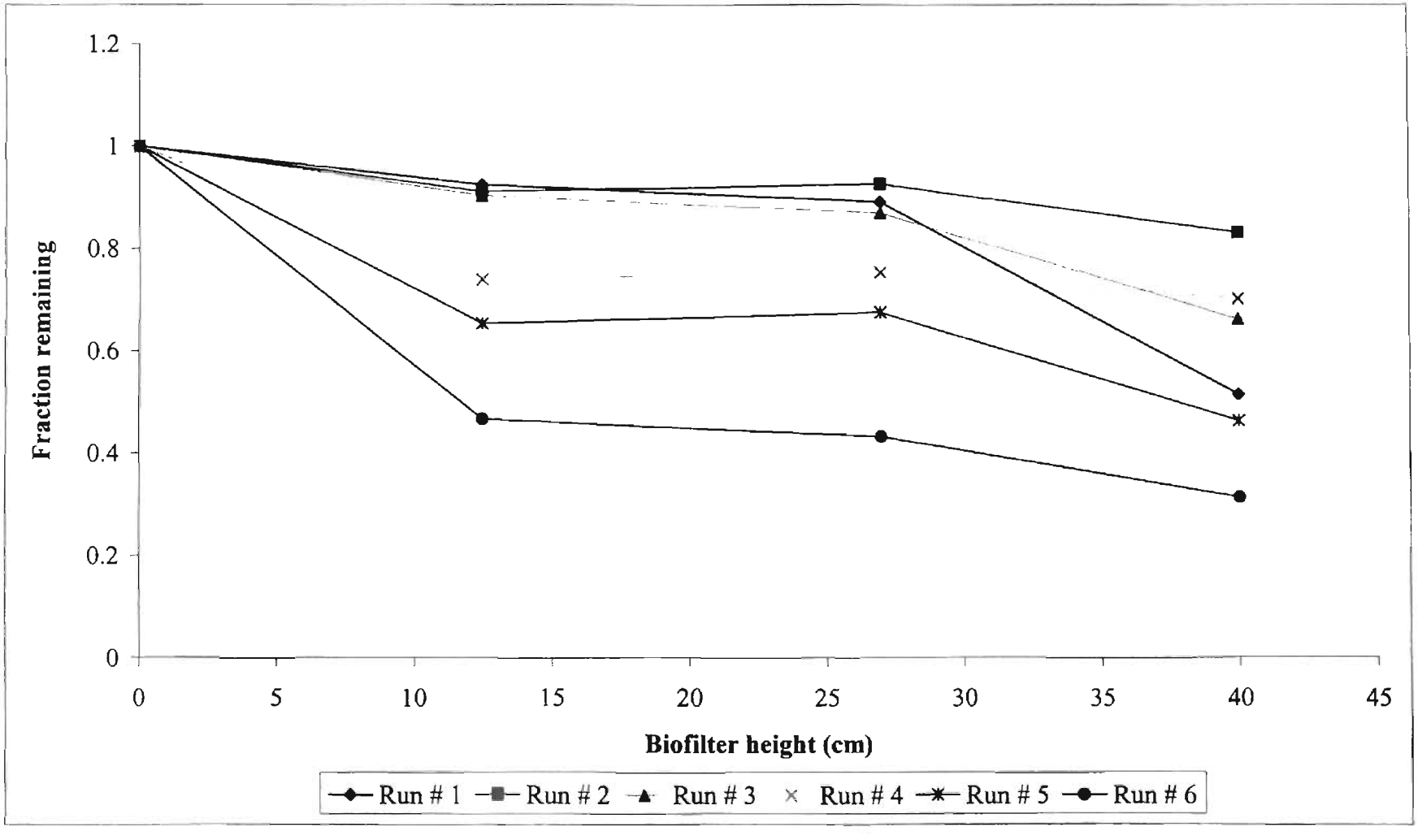


Figure 17. Steady state concentration profiles of MTBE along the height of biofilter C

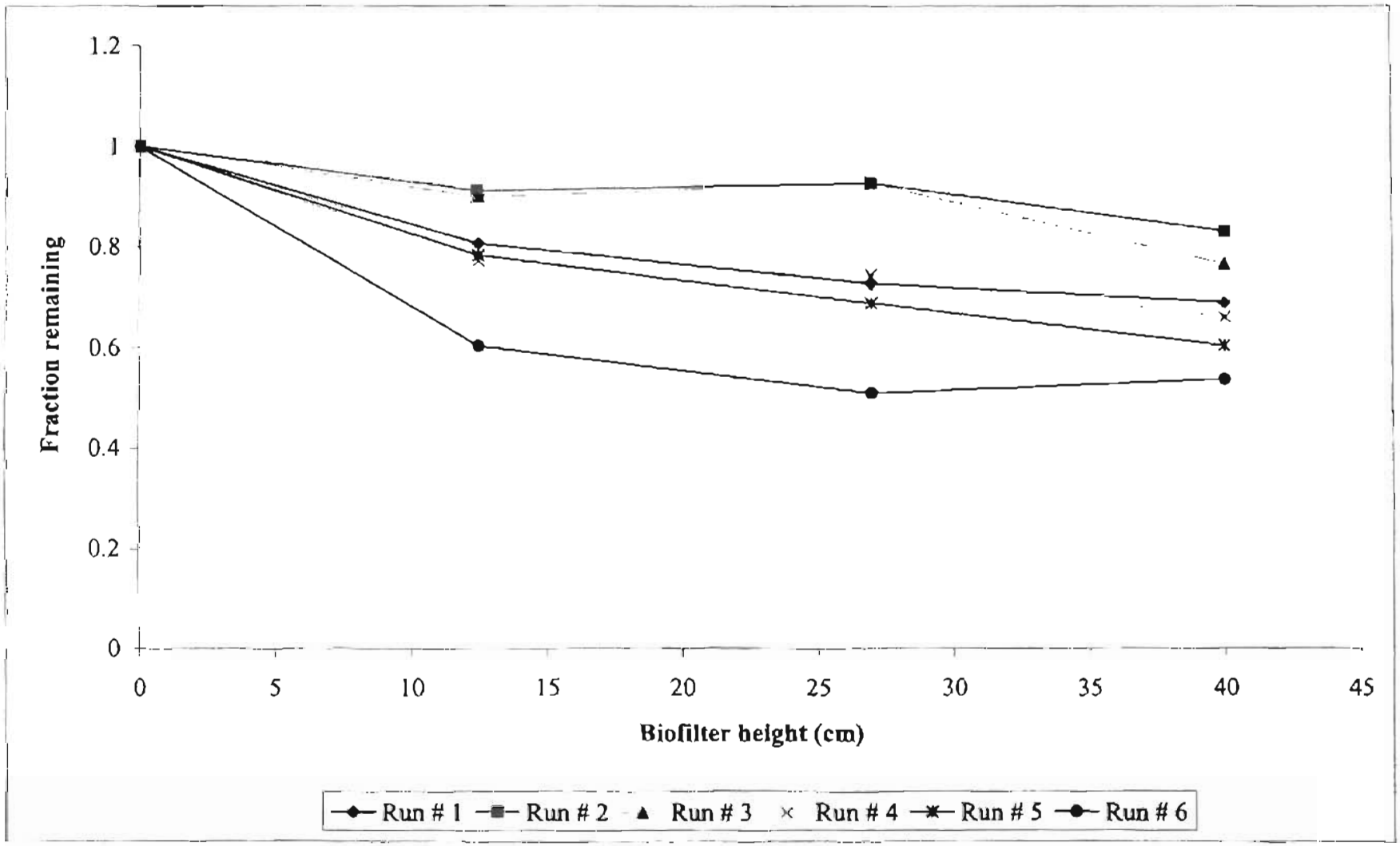


Figure 18. Steady state concentration profiles of MTBE along the height of biofilter P

Another interesting thing that should be noticed is the flattening of the concentration profiles at low loading conditions (run 4, 5 and 6) for both the biofilters. This effect is undesirable because in this case lengthening of the column may have a little or no effect on removal efficiency.

Some inconsistency in data was observed in case of runs 2 and 3 for biofilter P and runs 2, 4, and 5 for biofilter C where the observed MTBE concentration for sampling port 3 was more than sampling port 2. This may be due to channeling in the bed.

Concentration profiles of TBA along the height of the biofilters

Concentration profiles of TBA along the height of biofilter C for 35th day (run 1), 52nd day (run 2) and 61st day (run 3) are presented in Figure 19. For all the profiles, TBA concentration increases with the height of the biofilters up to sampling port 3 (height = 27 cm), suggesting that more and more MTBE was being converted as it moved through the bed. However for 32nd day and 61st day profiles, the concentration of TBA in the outlet of the biofilter was observed to be lesser than sampling port 3. This provides indication that degradation of TBA was taking place inside the bed.

Comparison of steady state performance of two biofilters

It should be noted that the except for the run 4, the steady state removal efficiency and elimination capacity of biofilter C was always higher than biofilter P (see Tables 10 and 11). This can be explained by the presence of activated carbon in biofilter C medium. The research carried out in the field of drinking water treatment by the use of activated carbon has suggested that carbon, with its unique properties, performs better than other

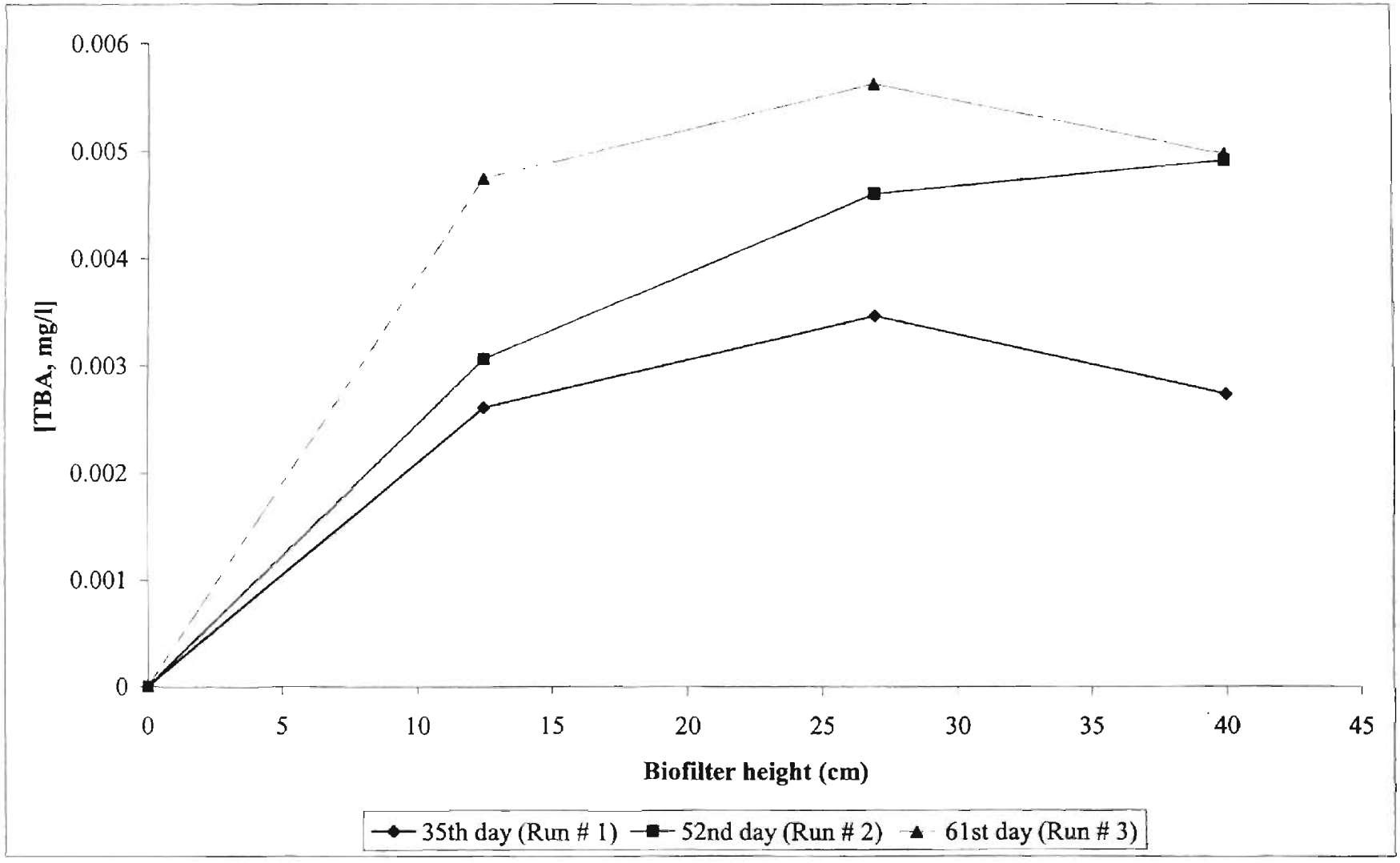


Figure 19. Concentration profiles of TBA along the height of biofilter C

conventional media. Dussert and Vanstone (1994) noted that the adsorption capacity of activated carbon serves to concentrate substrates, nutrients and oxygen, extends the contact time between the biomass and adsorbed organic substances and reduces the concentration of toxic substances in local microbial environment. These factors lead to better performance of activated carbon in drinking water treatment. In the present case the same factors are likely to be responsible for better performance of biofilter C as compared to biofilter P. Abumaizer et al. (1998) got similar results when they compared the performance of compost biofilters with and without activated carbon in the case of BTEX biofiltration. As far as run 4 is concerned, slightly inferior performance of activated carbon may be due to desorption of MTBE from the activated carbon because of decrease in inlet concentration of MTBE as compared to run 3.

Comparison of present study with previous studies on MTBE biofiltration

Few studies have been conducted on MTBE biofiltration so far. Comparison of the present study with past studies on MTBE biofiltration is presented in Table 12. It can be noticed that removal efficiency and elimination capacity attained in the present study are lower than all the other studies except for the study by Dupasquier et al. (2002). One of the reason for this may be that the culture used in the present study was not able to metabolize MTBE at the fast rate. The initial toxicity problem referred to in the culture maintenance section, might be responsible for this in the sense that it may have never been able to revert back to its original activity even after being inoculated into the biofilter.

Table 12: Comparison of Various Studies on MTBE Biofiltration

Reference	Biofilter medium	Empty bed contact time	Start-up time	Inlet MTBE concentration	Maximum removal efficiency (%)	Maximum elimination capacity (g/m^3/hour)	Comments
Eweis et al. (1997)	Compost	1 minute	1 year	200 ppb#	100%	8	Biofilter was not inoculated with any MTBE degrading culture and the inlet air stream contained other hydrocarbons besides MTBE
Eweis et al. (1998)	Extruded diatomaceous earth	1 minute	3 weeks	35 ppm	100%	N. R.	Biofilter was inoculated with MTBE degrading microbial culture
Fortin and Deshusses (1999)	Pall rings and lava rocks	54-90 seconds	25-35 days	0.65-0.85 g/m3	97%	50	Biotrickling filters were inoculated with MTBE degrading microbial consortium
Dupasquier et al. (2002)	Vermiculite	0.06-2.85 hours	N.R.	1.1-12.3 g/m3	30%*	12 (Pentane) 1.8 (MTBE)	Cometabolism of MTBE with pentane was used in this study. The biofilter was inoculated with P. aeruginosa capable of cometabolizing MTBE in the presence of pentane.
Present study	Compost and perlite/activated carbon	1.42-3.47 minutes	23 days	0.05-0.34 mg/l	69%	3.26	Biofilter was inoculated with MTBE degrading microbial consortium

* Calculated from their steady state elimination capacity and loading data.
# Maximum concentration of MTBE in the study

Headloss in the biofilters

Headloss in the bed or resistance to the gas flow is an important parameter since it determines the energy required to force the contaminated gas through the filter bed. Headloss was monitored occasionally during the course of the experiment and the data are presented in Table 13. It should be noted that the headloss values for both biofilter P and C were negligible during the entire period of their operation. They never exceeded 0.3 cm of water in case of biofilter P and 0.18 cm of water in case of biofilter C. This suggests that the porosity of the beds was adequate throughout the experiment. Another thing to notice is the dependence of headloss values on air flow rate. Headloss values decreased with the decrease in air flow rate for both the biofilters.

Table 13: Headloss in Biofilters

Day	Air Flow (l/min)	Headloss			
		Biofilter P (inches H2O)	Biofilter P (cm H2O)	Biofilter C (inches H2O)	Biofilter C (cm H2O)
17	2.117	0.1	0.254	0.05	0.127
29	2.117	0.12	0.3048	0.07	0.1778
38	2.117	0.12	0.3048	0.07	0.1778
55	2.117	0.12	0.3048	0.07	0.1778
62	1.3225	0.04	0.1016	0.02	0.0508
78	1.3225	0.04	0.1016	0.02	0.0508
90	0.868	0.01	0.0254	0.005	0.0127

Transient Behavior of the Biofilters

The transient response to step changes in inlet concentration or gas flow rate was investigated for both the biofilters. A total of five changes were made in the loading rate during the entire period of operation of the biofilters, and transient response was observed by sampling influent and effluent ends.

Inlet MTBE concentration increase from 0.2 mg/L to 0.33 mg/L

Transient response of the biofilters to step change in inlet MTBE concentration from 0.2 mg/l to about 0.33 mg/l is shown in Figures 20 and 21. Immediately after the concentration increase, elimination capacity of biofilter P dropped considerably presumably due to stress experienced by bacteria as a result of shock loading. Following this, elimination capacity suddenly increased, and this period of relatively high performance was maintained for a few hours, after which the elimination capacity dropped again. Fortin and Deshusses (1999b) observed same kind of transient response for their biotrickling filters treating MTBE. According to them, one explanation of this phenomenon can be that the culture was under significant stress after the increase in loading which made it highly active for some time to release that stress.

In the case of biofilter C, no drop in elimination capacity was seen after the increase in concentration. Rather than dropping the elimination capacity increased considerably, which can be attributed to adsorption on activated carbon. This relatively high performance continued to drop in the subsequent days due to decrease in adsorption capacity of carbon. Following the change, biofilter C took approximately 13 days to achieve relatively steady elimination capacities, while biofilter P achieved it within a day.

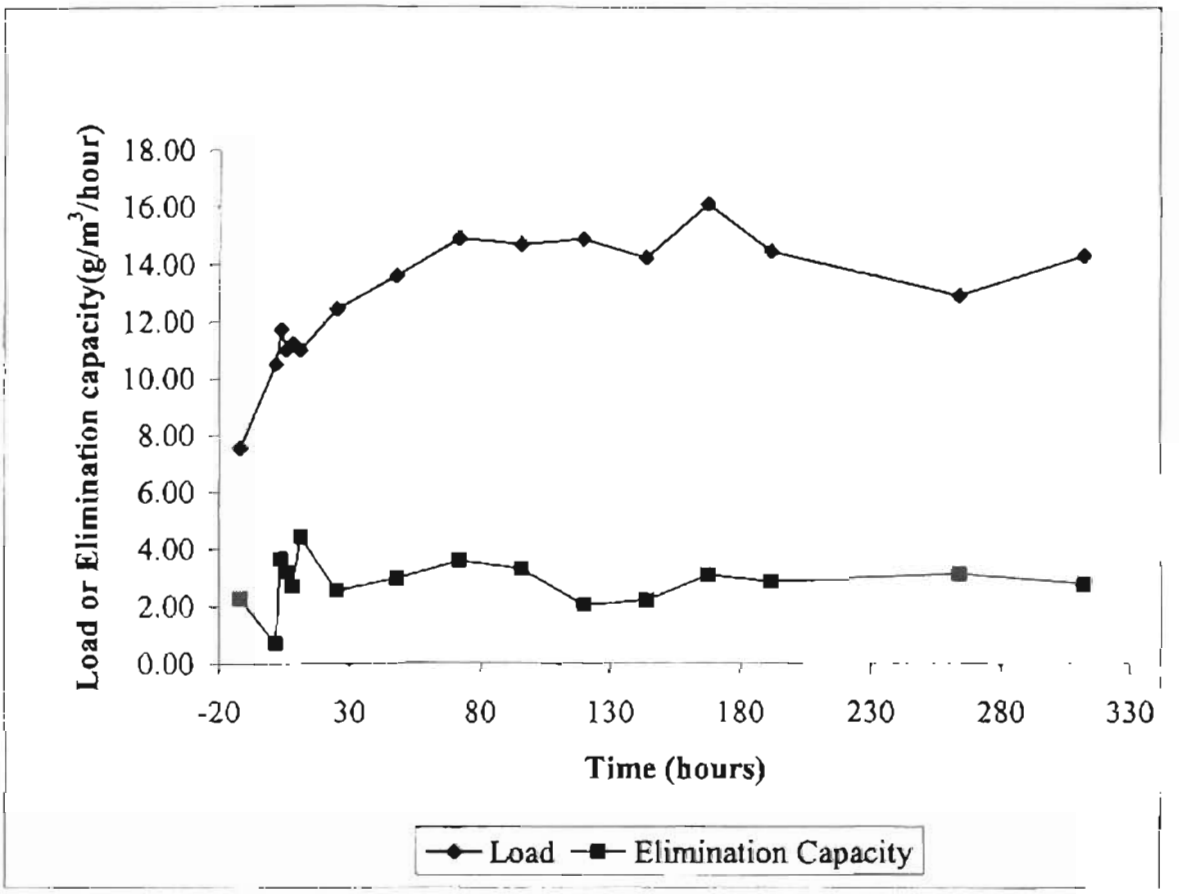


Figure 20: Transient response of biofilter P to step increase in inlet MTBE concentration from 0.2 mg/l to 0.33 mg/l

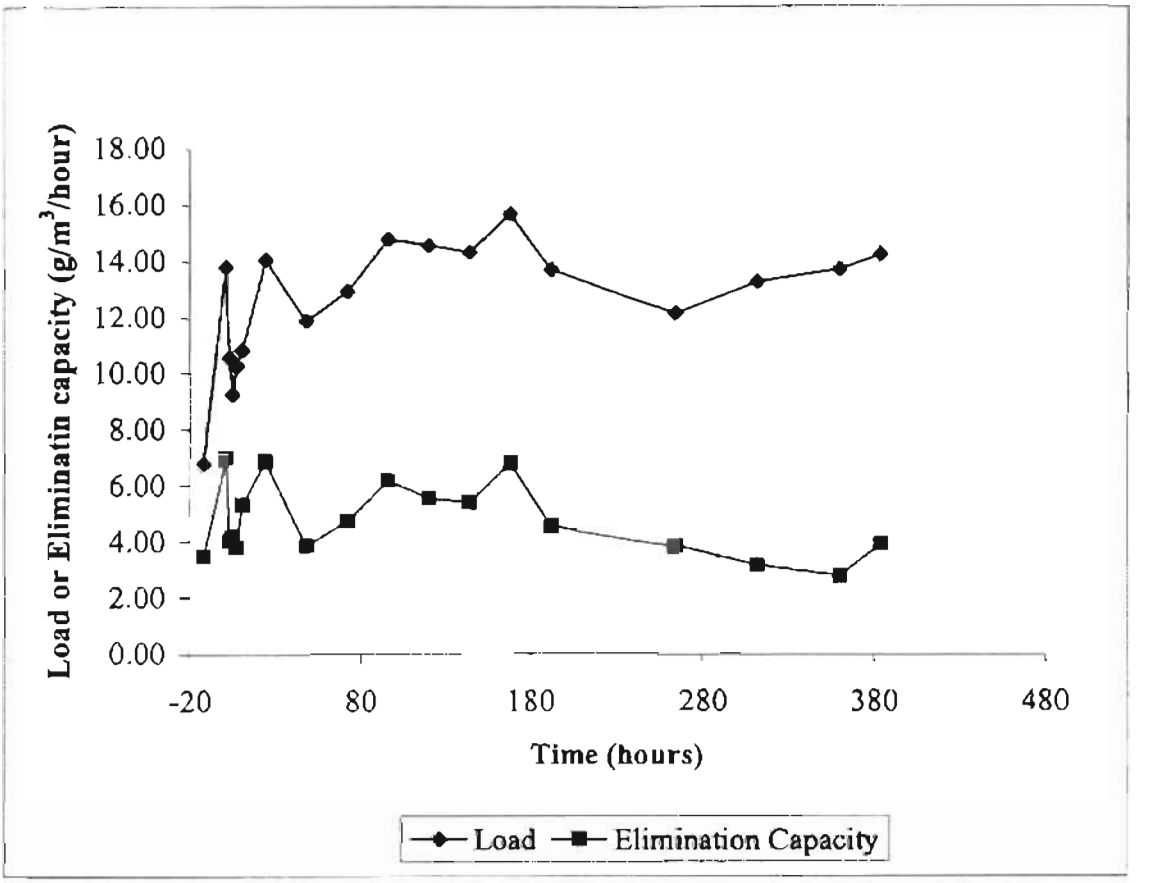


Figure 21: Transient response of biofilter C to step increase in inlet MTBE concentration from 0.2 mg/l to 0.33 mg/l

Flow rate decrease from 2.12 L/min to 1.32 L/min

On the 57th day, EBRT was increased by decreasing the flow rate from 2.12 L/min to 1.32 L/min. The transient response of the biofilters to this change in loading is shown in Figures 22 and 23. Both the biofilters were very fast in achieving new steady elimination rates following this change. Acclimation to the new conditions was achieved in less than two hours. As discussed earlier, loadings before and after this change probably corresponded to the reaction limited regime, so there was no significant change in elimination rates before and after the change in loading.

Inlet MTBE concentration decrease from 0.33 mg/L to 0.1 mg/L

Inlet concentration of MTBE was decreased from 0.33mg/L to about 0.1 mg/L to both the biofilters on 67th day. Transient response of the biofilters to this change is shown in Figures 24 and 25. Following the decrease, the elimination capacities of both biofilter P and C dropped, suggesting that they were entering the regime where diffusion limitation governs elimination of the pollutant. In fact, biofilter C exhibited negative elimination capacities for some hours following the change, which was most likely due to desorption of MTBE from activated carbon. However, elimination rates continued to increase after that, suggesting biological removal. Steady elimination capacities were reached after about 4 to 5 days. Contrary to this, biofilter P achieved relatively steady elimination capacities within hours.

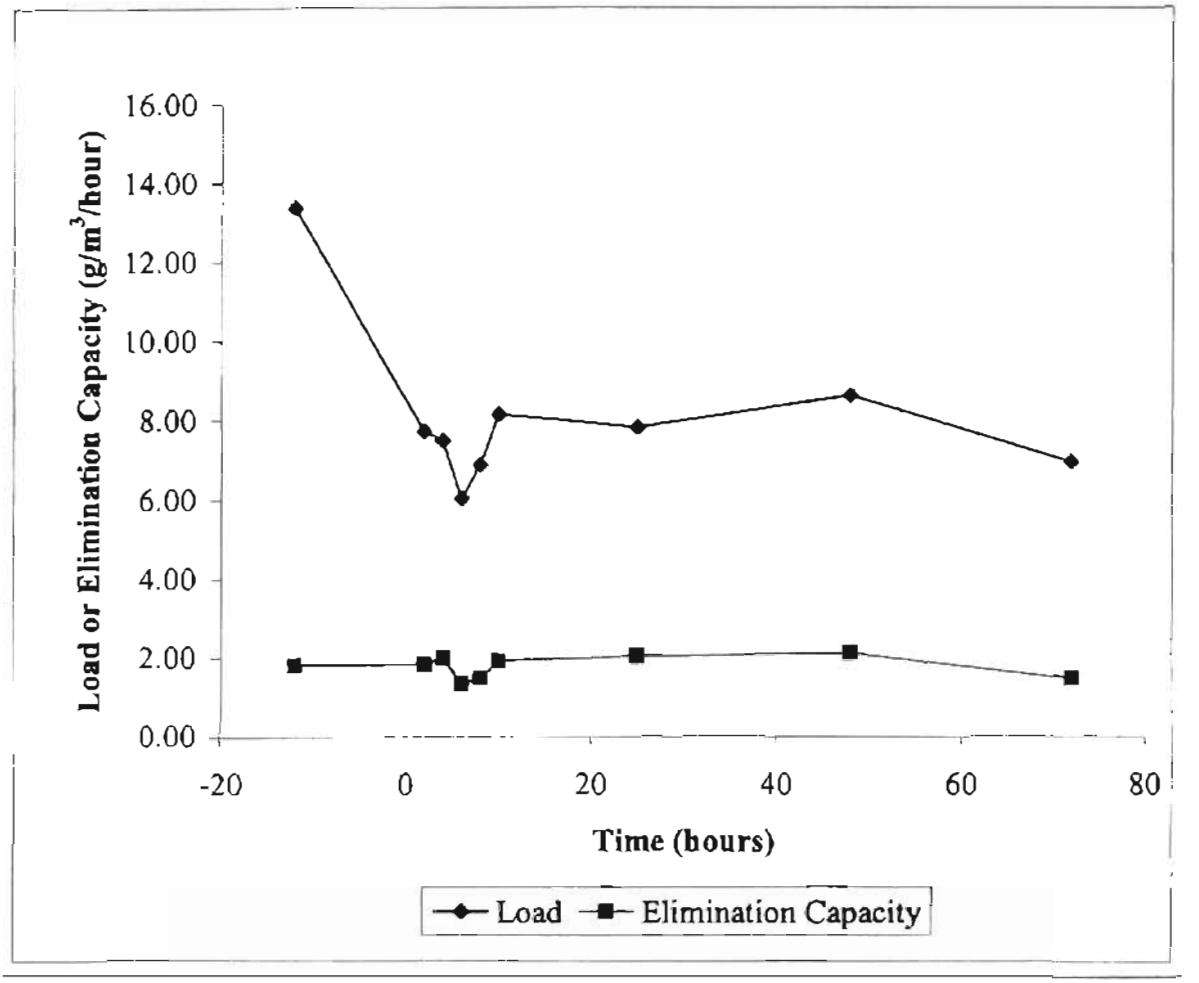


Figure 22: Transient response of biofilter P to decrease in gas flow rate from 2.12 L/min to 1.32 L/min

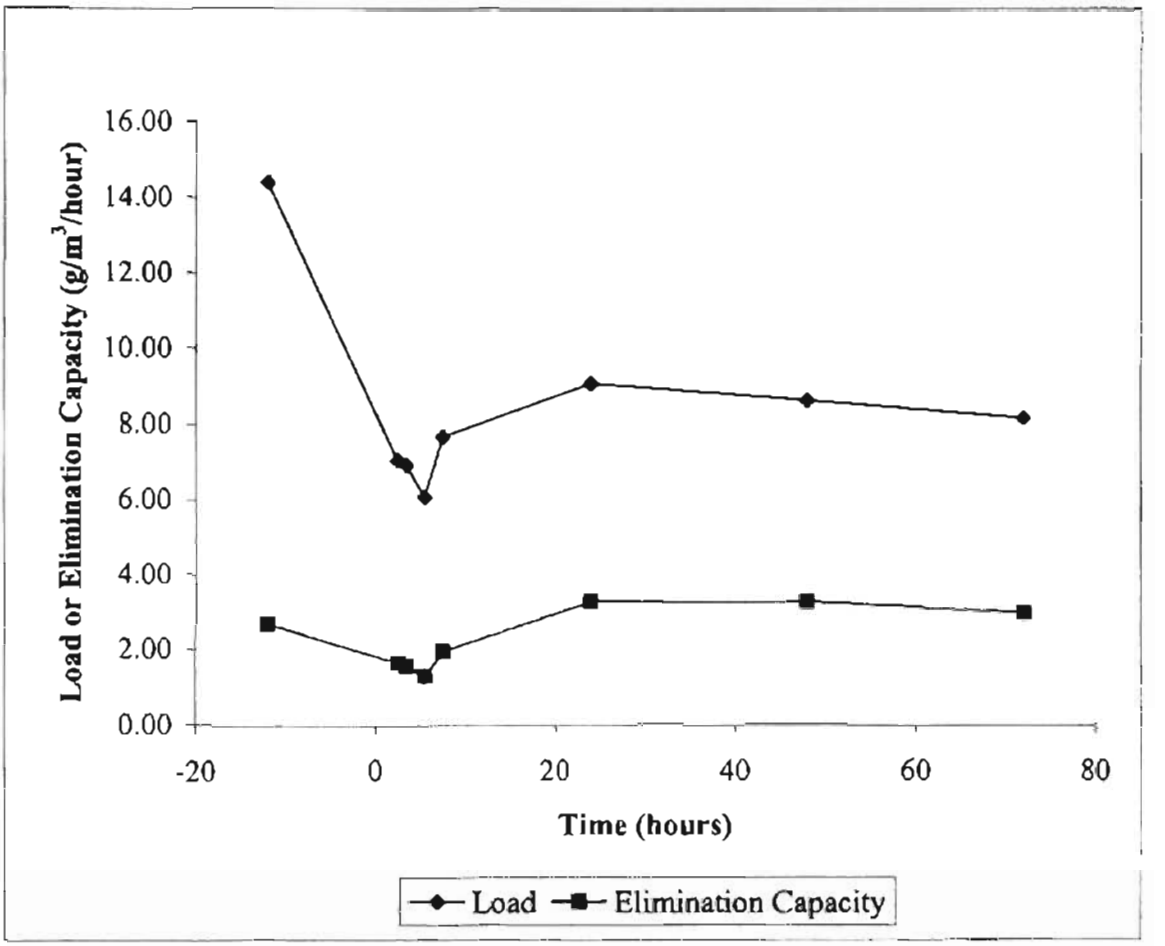


Figure 23: Transient response of biofilter C to decrease in gas flow rate from 2.12 L/min to 1.32 L/min

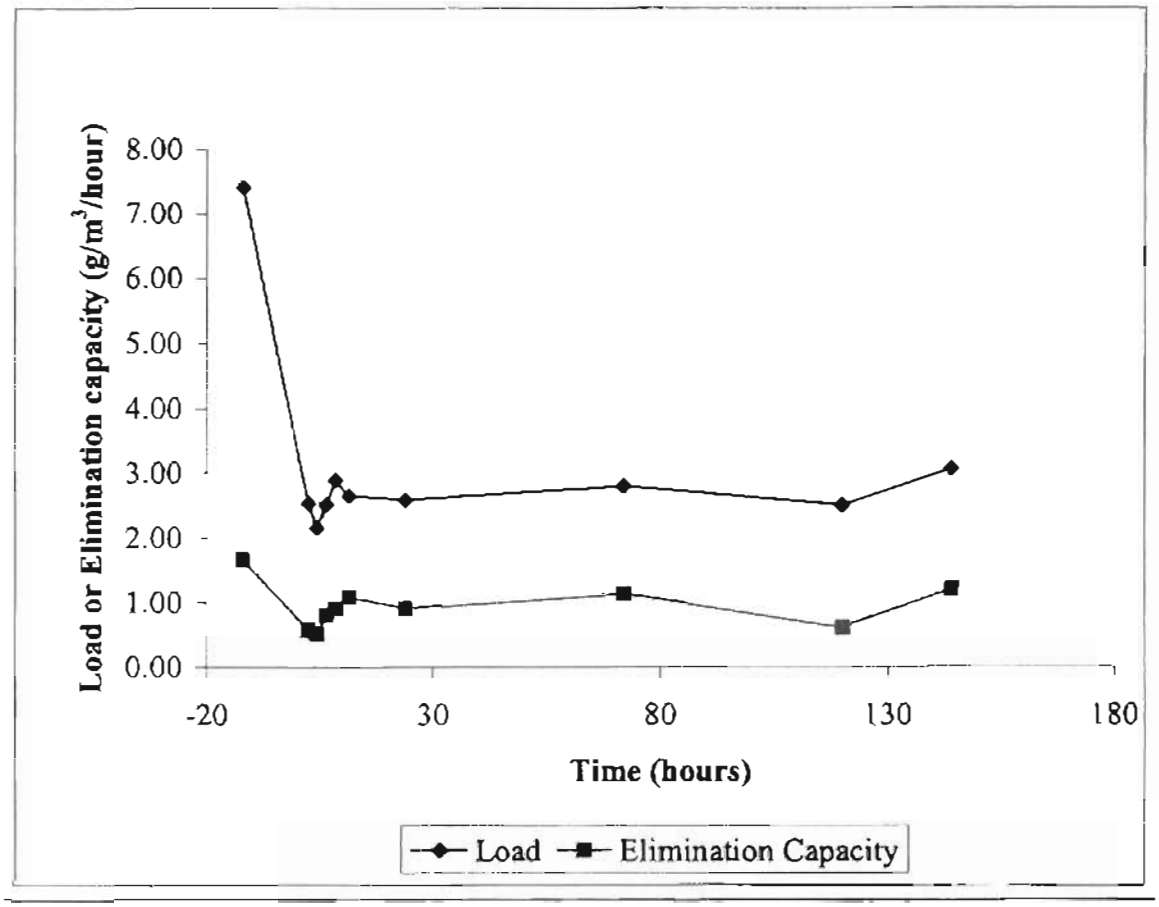


Figure 24: Transient response of biofilter P to decrease in inlet MTBE concentration from 0.33 mg/L to 0.1 mg/L

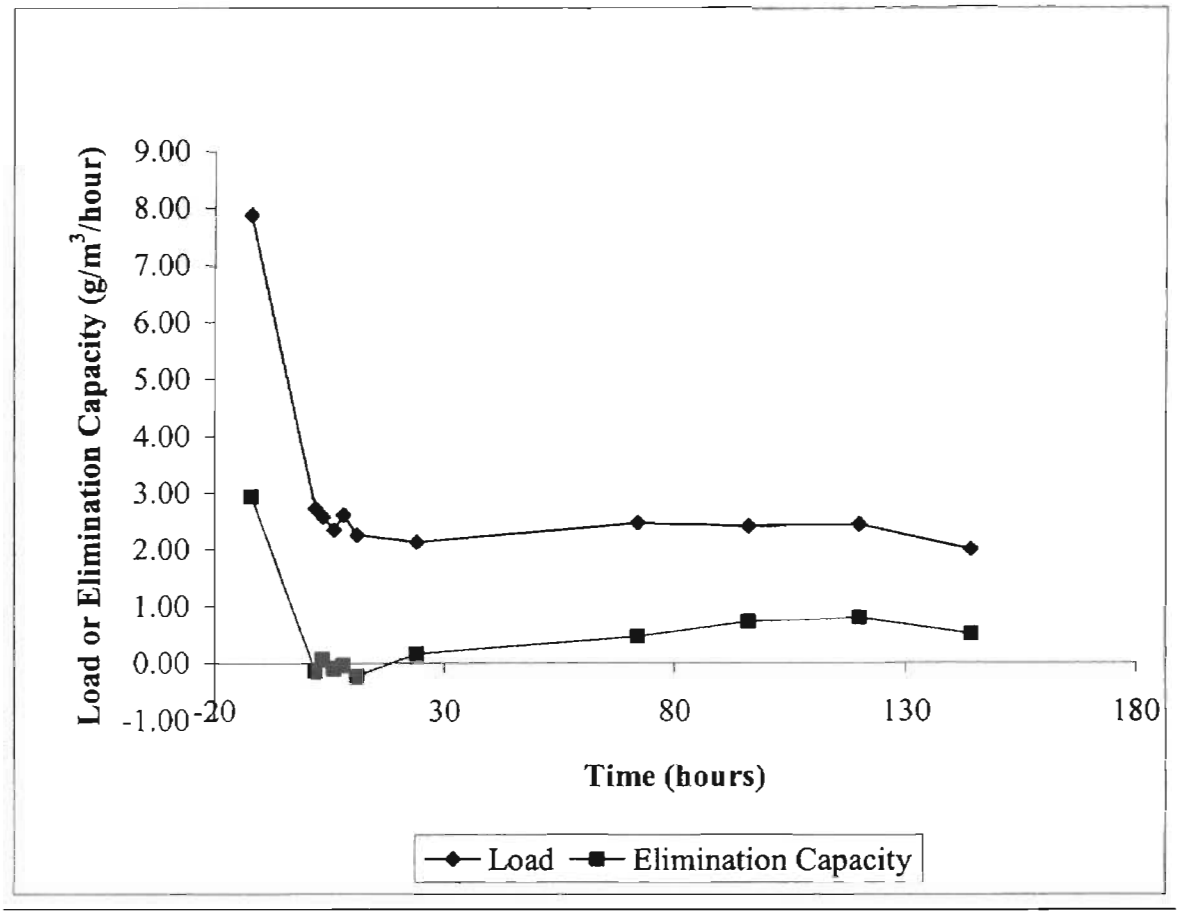


Figure 25: Transient response of biofilter C to decrease in inlet MTBE concentration from 0.33 mg/L to 0.1 mg/L

Inlet MTBE concentration decrease from 0.1 mg/L to 0.05 mg/L

The inlet concentration of MTBE was further dropped from 0.1 to 0.05 mg/L on 79^{th} day. Figures 26 and 27 show transient response of biofilters to this change. The behavior of the biofilters to this decrease in concentration was very similar to the previous one. Elimination capacities of both the biofilters decreased due to possible diffusion limitation. Nearly zero elimination capacities were observed for biofilter C for few hours, that increased steadily for many days before reaching relatively steady values. In this case also, biofilter C took more time to reach steady elimination rates than biofilter P.

Flow rate decrease from 1.32 L/min to 0.868 L/min

The flow rate to both the biofilters was decreased further from 1.32 L/min to 0.868 L/min. Unfortunately following the change in flow rate there were some operational problems with the syringe pump which prevented us to observe the transient behavior of the biofilters to this change. However it is expected that transient response to this change should be similar to previous flow rate decrease.

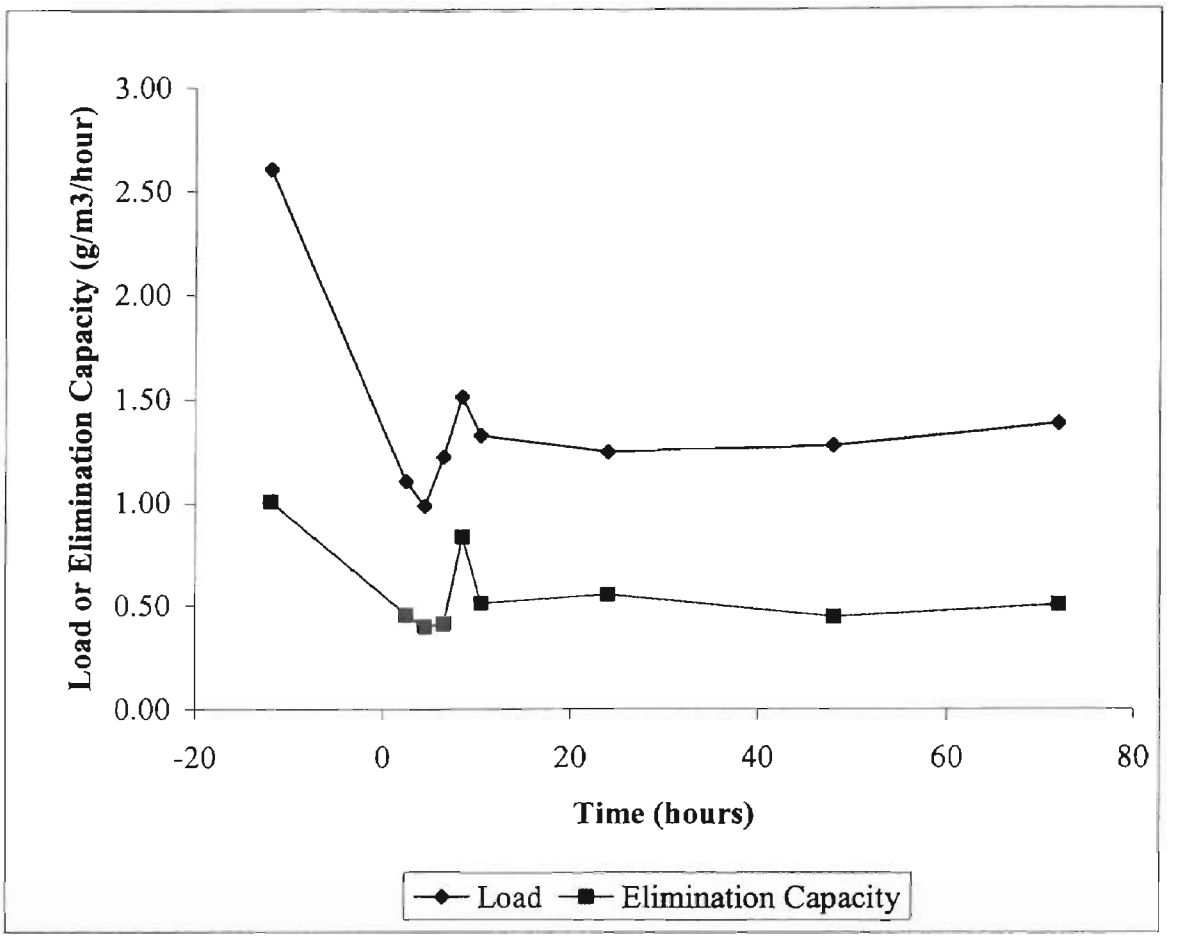


Figure 26: Transient response of biofilter P to decrease in inlet MTBE concentration from 0.1mg/L to 0.05 mg/L

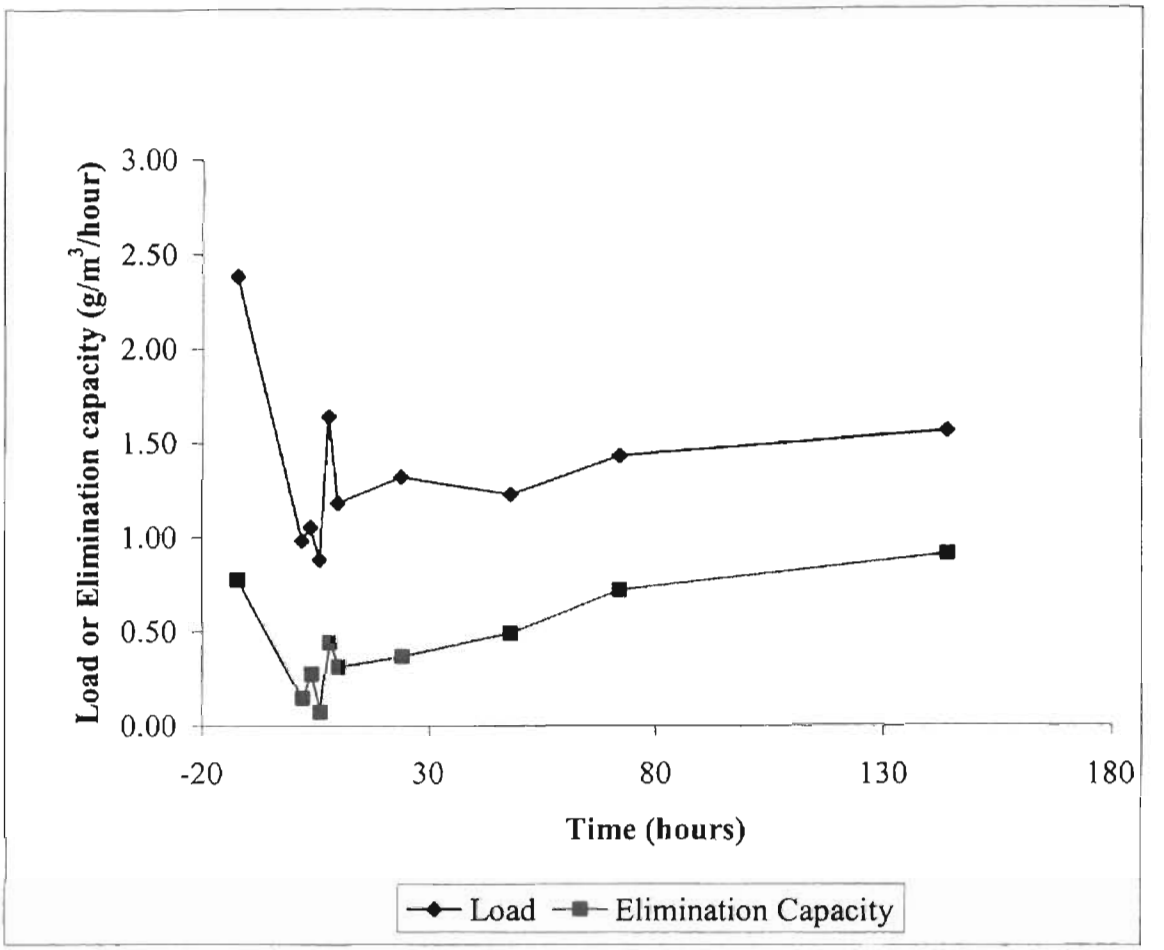


Figure 27: Transient response of biofilter C to decrease in inlet MTBE concentration from 0.1mg/L to 0.05 mg/L

CHAPTER V

CONCLUSIONS

Present study demonstrated biofiltration of MTBE contaminated air streams and gives the comparison of performance of biofilter media containing adsorbing (Biofilter C) and non-adsorbing material (Biofilter P), at various loading rates. Some of the important findings of this study are:

1. For both the biofilters, decrease in loading rates led to more efficient removal of MTBE. Maximum steady state removal efficiency for biofilter P was about 46% and for boifilter C was 69%, obtained at the lowest loading rate of approximately 1 g/m^3/hour.
2. Maximum elimination capacities for both the biofilters were obtained at relatively high loading rates of 8 to 14 g/m^3/hour. For biofilter P maximum elimination capacity was approximately 2.5 g/m^3/hour and for biofilter C it was about 3.2 g/m^3/hour.
3. The removal efficiencies and elimination capacities obtained in the present study were considerably lower than that obtained in the most previous studies. The reason for this may be the slow rate of degradation of MTBE by the culture due to possible toxicity during maintenance of culture in the batch mode.

4. Steady state performance of biofilter C was almost always better than biofilter P, which can be attributed to more favorable environment provided by activated carbon for the microorganisms in biofilter C medium.
5. Adsorption on activated carbon was likely responsible for the removal of MTBE during the first 8 days of the operation of biofilter C when nearly zero removal took place in biofilter P. This suggests that use of higher volume of activated carbon or better adsorbents such Ambersorb 563® may reduce or eliminate the period of poor performance during the start-up phase.
6. There was no difference in start-up time of the biofilters (23 days), as indicated by the presence of TBA in their outlet stream. Presence of activated carbon had no effect in decreasing the lag time of the microorganisms.
7. Transient behavior of the biofilters revealed that the presence of activated carbon in biofilter medium may prevent decrease in MTBE elimination in case of step increase in concentration due to shock experienced by microorganisms. However it may also lead to poor performance for few days following the decrease in MTBE concentration due to desorption.
8. Biofilter C was always slow to attain relatively steady elimination capacities compared to biofilter P, after the step change in inlet concentrations, which can be attributed to the presence of activated carbon in biofilter C medium. While it usually took less than a day for biofilter P to achieve relative steady elimination rates, it took 4-12 days for biofilter C to achieve the same.

9. Flattening of concentration profiles along the biofilter bed at low loading rates or diffusion limited regime was observed. This effect is undesirable because in this case lengthening of the column may have little or no effect on removal efficiency.
10. Retardation factor of biofilter C medium was much higher than biofilter P medium because of the presence of activated carbon in the former. As retardation factor is directly proportional to the contaminant detention time, for the same flow rate MTBE detention time in biofilter C is expected to be more than biofilter P.
11. Slowdown and subsequent loss of activity of MTBE degrading microorganisms observed in case of batch cultures was not observed after their inoculation into biofilters. This may be due to reduced toxicity in the biofilters due to continuous air flow through the system or better environment provided by attached growth to slow growing microorganisms like these.
12. Peat humic substances had no favorable or adverse effect on MTBE biodegradation in the range of concentrations studied (0.2 - 200 mg/l).
13. While no accumulation of TBA was observed in the batch cultures, it was seen in the outlet stream of both the biofilters on 23rd day. TBA concentration continued to increase in both the biofilters until 33rd day after which it started to drop. This suggests that initially TBA degradation lagged behind MTBE degradation but as the culture matured the degradation rates of TBA increased and consequently its accumulation decreased in both the biofilters.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE STUDY

There are a lot of questions that still need to be answered in case of MTBE biofiltration. Some of the suggestions for the future study are:

1. The response of the biofilters to low residence times (< 1minute) and low concentrations should be investigated as this would most probably be the case for air stripping operations and emissions from wastewater treatment plants involving MTBE.
2. The start-up times of the biofilters for MTBE are still high. To improve them following strategies could be investigated:
    a) The volume of activated carbon in the biofilter media could be increased allowing better removal in the initial days of its operation.
    b) Better adosbents like Ambersorb 563® for MTBE could be used in the biofilter media (Davis and Powers, 2000). However care should be taken while doing this, as there may be problems with maintaining near neutral pH with the use of resins in biofilter beds.
3. Biofiltration of MTBE using cometabolism in the presence of some other compounds such as straight chain alkanes or benzene should be investigated. This may eliminate some problems relating to the slow growth rate of MTBE metabolizing bacteria, such as start-up times.

4. Biofiltration of MTBE using cometabolism in the presence of some other compounds such as straight chain alkanes or benzene, should be investigated. This may eliminate some problems relating to the slow growth rate of MTBE metabolizing bacteria, such as start-up times.
5. Biofiltration of MTBE in the presence of compounds such as BTEX, which are likely to be present with it at the contaminated sites, should be studied.
6. Studies should be conducted with different biofiltration media to investigate which media performs best in relation to start-up, steady state and transient state performance.
7. Studies should be conducted to determine the fate of MTBE in the biofilters, whether it is mineralized or converted to some other metabolite.
8. Some pilot scale studies should be conducted for successful implementation of biofiltration for MTBE vapor treatment in the field.

CHAPTER VII

ENGINEERING SIGNIFICANCE OF THE STUDY

This study investigated the biofiltration of MTBE at various steady state loading rates ranging from 1 g/m^3/hour to 14 g/m^3/hour. In addition to this, the start-up response and transient response of the biofilters were studied, and performance of the biofilters containing adsorbing (granular activated carbon) and non adsorbing materials (perlite) was compared. Some of the significant conclusions relevant to the field application of biofiltration for the treatment of MTBE vapors are:

1. Relatively low values of removal efficiencies and elimination capacities obtained in the present study indicate that the present system (i.e. present design of the reactor, medium and culture) should only be used if low performance is sufficient to meet the off gas standards in soil vapor extraction, air sparging, or air stripping operations.
2. Target loading should be considered before using the present system in the field. If the desired removal efficiencies are relatively high, low loading rates have to be applied.
3. Flattening of the concentration profiles along the depth of the biofilters at low loading rates suggests that the performance of the biofilters cannot be increased by increasing the height.

4. The use of adsorbing material in the biofilter medium may lead to better steady state performance. Depending on its quantity in the medium, the adsorbing material may eliminate the period of poor performance during start-up and immediately after the step increase in inlet concentration.
5. More research is needed, especially on the important issues delineated in Chapter VI, before effective full-scale biofilters can be designed and operated in the field.

REFERENCES

1. Alagappan, G., Cowan, R. M. Biodegradation kinetics of MTBE degrading enrichment cultures obtained from a gasoline contaminated groundwater: Inhibition and toxicity at high MTBE contaminations. Proceedings of the NGWA conference, MTBE in Groundwater: Assessment, Remediation Technologies, and Public Policy, June 2001, Baltimore, MD.

2. Alagappan, G. Effect of environmental parameters on the growth kinetics of benzene, toluene and MTBE degrading microorganisms. PhD. Dissertation submitted to the graduate program in Environmental Sciences, Rutgers University, New Brunswick, NJ, 2001.

3. Anderson, M. A. Removal of MTBE and other organic contaminants from water by sorption to high silica zeolites. Environmental Science & Technology (2000); 34 (4): 725-727.

4. APHA, AWWA, WPCF. "Standard Methods for the Examination of Water and Wastewater." Greenberg, A. P.; Trussell, R. R.; and Clesceri, L. S. (Eds.). American Public Health Association (1985), Washington, DC.

5. ASTM. Standard test methods for moisture, ash and organic matter of peat and other organic soils (Standard method D2974-00). ASTM (2001).

6. Auria, R., Aycaguer, A., Influence of water content on degradation rates for ethanol in biofiltration. Journal of Air and Waste Management Association (1998); 48: 65-70

7. Barreto, R. D., Gray, K. A., Anders, K. Photocatalytic degradation of methyl-tert-butyl ether in TiO_2 slurries: A proposed reaction scheme. Water Research (1995); 29(5): 1243-1248.

8. Bibeau, L., Kiared, K., Leroux, A., Brzezinski, R., Viel, G., Heitz, M. Biological purification of exhaust air containing toluene vapor in a filter-bed reactor. The Canadian Journal Of Chemical Engineering (1997); 75: 921-929.

9. Bohn, H. Consider biofiltration for decontaminating gases. Chemical Engineering Progress (1992); April: 34-40.

10. Borden, R. C., Daniel, R. A., LeBrun IV, L. E., Davis, C. W. Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer. Water Resources Research (1997); 33 (5): 1105-1115.

11. Bradley, P. M., Landmeyer, J. E., Chapelle, F. H. Widespread potential for microbial MTBE degradation in surface-water sediments. Environmental Science and Technology (2001); 35 (4): 658-662.

12. Bradley, P. M., Landmeyer, J. E., Chapelle, F. H. Aerobic meineralization of MTBE and tert-butyl alcohol by stream-bed sediment microorganisms. Environmental Science and Technology (1999); 33 (11): 1877-1879.

13. Brown, A., Devinny, J. S., Davis, M. K., Browne, T. E., Rodriguez, R. A. A review of potential technologies for the treatment of methyl tertiary butyl ether (MtBE) in drinking water. Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Remediation Conference (1997): 126-141.

14. Calgon Carbon. Calgon carbon installs solution for removal of MTBE from drinking water. http://www.calgoncarbon.com/news/pr000410.html (Accessed on March 01, 2001).

15. California Department of Health Services. MTBE in California drinking water. http://www.dhs.cahwnet.gov/org/ps/ddwem/chemicals/MTBE/mtbeindex.htm (Accessed on March 01, 2001).

16. Carlson, D. A., Leiser, C. P. Soil beds for the control of sewage odors. Journal of the Water Pollution Control Federation (1966); 38(5): 429-440.

17. Chang, P. B. L., Young, T. M. Kinetics of methyl tert-butyl ether degradation and by-product formation during UV/Hydrogen peroxide water treatment. Water research (2000); 34(8): 2233-2240.

18. Christensen, B. E., Characklis, W. G. Physical and chemical properties of biofilms, pp. 93-130. In: Characklis, W. G., Marshall, K. C. (eds.), Biofilms. Wiley, New York, 1990.

19. Corsi, R. L., Seed, L. Biofiltration of BTEX: Media, Substrate, and Loading Effects. Environmental Progress (1995); 14(3): 151-158.

20. Cowan, R. M., Keeyong, P. Biodegradation of the gasoline oxygenates MTBE, ETBE, TBA, and TAA by aerobic mixed cultures. Proceedings of the Mid-Atlantic Industrial Waste Conference, 28 (1996). 523-530.

21. Cox, H. H. J., Moerman, R. E., van Baalen, S., van Heiningen, W. N. M., Doddema, H. J., Harder, W. Performance of a styrene-degrading biofilter

containing the yeat exophiala jeanselmei. Biotechnology and Bioengineering (1997); 53(3): 259-266.

22. Creek, D. N., Davidson, J. M. Granular activated carbon for MTBE removal. The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, 22-25 May, 2000, Monterey, CA. Battele Press, Columbus, OH.

23. Creek, D. N., Davidson, J. M. The performance and cost of MTBE remediation technologies. Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Remediation Conference (1998). 560-568.

24. Daigger, G. T. The interation of physiological adaptation and transient response for Pseudomonas putida and its implications for dynamic modeling of microbial growth. PhD. Dissertation, Purdue University, W. Lafayette, IN, 1979.

25. Davis, S. W., Powers, S. E. Alternative sorbents for removing MTBE from gasoline-contaminated ground water. Journal of Environmental Engineering (2000); 126 (4): 354-360.

26. Deshusses, M. A. Hamer, G., Dunn, I. J. Behavior of biofilters for waste air biotreatment. 1. Dynamic model development, Environmental Science and Technology (1995a); 29 (4): 1048-1058.

27. Deshusses, M. A. Hamer, G., Dunn, I. J. Behavior of biofilters for waste air biotreatment. 2. Enxperimental evalulation of a dynamic model. Environmental Science and Technology (1995b); 29 (4): 1059-1068.

28. Devinny, J.S., Deshusses, M.A., Webster, T.S. Biofiltration for Air Pollution Control, CRC-Lewis Publishers, Boca Raton, FL, 1999.

29. Devinny, J. S., Hodge, D. S. Formation of acidic and toxic intermediates in overloaded ethanol biofilters. Journal of Air and Waste Management Association (1995); 45: 125-131.

30. Dupasquier, D., Sergio, R., Auria, R. Biofiltration of methyl tert-butyl ether vapors by cometabolism with pentane: Modeling and experimental approach. Environmental Science and Technology (2002); 36(2): 247-253.

31. Ergas, S. J. Kinney, K., Fuller, M. E. Scow, K. M. Characterization of a compost biofiltration system degrading dichloromethane. Biotechnology and Bioengineering (1994); 44: 1048-1054.

32. Eweis, J. B., Schroeder, E. D., Chang, D. P. Y., Scow, K. M. Bioderadation of MTBE in a pilot-scale biofilter. In: Natural Attenuation: Chlorinated and

Recalcitrant Compounds. Wickramanayake, G. B., Hinchee, R. E. (eds.) Battelle Press (1998) Columbus, Ohio, 341-346.

33. Eweis, J. B., Schroeder, E. D., Chang, D. P. Y., Scow, K. M., Morton, R., Caballero, R. Meeting the challenge of MTBE biodegradation. Proceedings of the 90th Annual Meeting & Exhibition, Air & Waste Management Association, Pittsburgh, PA, 1997.

34. Finneran, K. T., Loveley, D. R. Anaerobic degradation of methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA). Environmental Science & Technology (2001); 35(9): 1785-1790.

35. Fortin, N.Y., Deshusses, M.A. Treatment of methyl tert-butyl ether vapors in biotrickling filters. 1. Reactor startup, steady state performance and culture characteristics. Environmental Science and Technology (1999a); 33(17): 2980-2986.

36. Fortin, N.Y., Deshusses, M.A. Treatment of methyl tert-butyl ether vapors in biotrickling filters. 2. Analysis of rate limiting step and behavior under transient conditions. Environmental Science and Technology (1999b); 33(17): 2987-2991.

37. Garnier, P. M. Auria, R., Revah, S. Cometabolic biodegradation of methyl t-butyl ether by Pseudomonas aeruginosa grown on pentane. Applied Microbiology and Biotechnology (1999); 51: 498-503.

38. Govind, R., Bishop, D. F. Biofiltration for treatment of volatile organic compounds (VOC's) in air. In: Sikdar, S. K., Irvine, R. L. (Eds.). Bioremediation: Principles and Practice (Vol. III) Bioremediation technologies. Technomic Publishing Company, Inc., 1998

39. Gribbins, M. J., Loehr, R. C. Effect of media nitrogen concentration on biofilter performance. Journal of Air and Waste Management Association (1998); 48: 216-226.

40. Gullick, R.W., LeChevallier, M.W. Occurrence of MTBE in drinking water sources. Journal of the American Water Works Association (2000); 92(1): 100-112.

41. Hanson, J.R., Ackerman, C.E., Scow, K.M. Biodegradation of methyl tert-butyl ether by bacterial pure culture. Applied and Environmental Microbiology (1999); 65(11): 4788-4792.

42. Happel, A. M., Beckenbach, E. H., Halden, R. U. An evaluation of MTBE impacts to California groundwater resources. Lawrence Livermore National Laboratory Report, UCLR-AR-130897, June 1998.

43. Hardison, L. K., Curry, S. S., Cinffetti, L. M., Hyman, M. R. Metabolism of diethyl ether and cometabolism of methyl tert-butyl ether by a filamentous fungus, a graphium sp. Applied and Environmental Microbiology (1997); 63: 3059-3067.

44. Hartikainen, T., Ruuskanen, J., Martikainen, P. J. Carbon disulfide and Hydrogen sulfide removal with a peat biofilter. Journal of Air and Waste Management Association (2001); 51: 387-392.

45. Hartley, W. R., Englade, A. J., Harrington, D. J. Health risk assessment of groundwater contaminated with methyl tertiary butyl ether (MTBE). Water Science and Technology (1999); 39 (10-11): 305-310.

46. Hicks, P. Aerobic bioremediation of methyl tertiary butyl ether. In: Environmental Remediation Science and Technology. Battelle Press (1999), Columbus, Ohio. 53-61.

47. Hodge, D. S. Devinny, J. S. Modeling removal of air contaminants by biofiltration. Journal of Environmental Engineering (1995), 121(1): 21-32.

48. Howard, H. P., Meylan, W. M. (ed.). Handbook of Physical Properties of Organic Chemicals. Lewis Publishers, Boca Raton, FL, 2000.

49. Hyman, M., Kwan, P., Williamson, K., O'Reilly, K. Cometabolism of MTBE by alkane-utilizing microorganisms. In: Wickramanayake, G. B., Hinchee, R. E. *(Eds.)*. Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds. May 1998, Monterey, CA, Vol. 3: 321-326. Battelle Press, Columbus, OH.

50. Johnson, R., Pankow, J., Bender, D., Price, C., Zogorski, J. MTBE To what extent will past releases contaminate community water supply wells. Environmental Science & Technology (2000); 34(9): 210A-217A.

51. Jorio, H., Bibeau, L., Viel, G., Heitz, M. Effects of gas flow rate and inlet concentration on xylene vapors biofiltration experience. Chemical Engineering Journal (2000a); 76: 209-221.

52. Jorio, H., Bibeau, L., Heitz, M. Biofiltration of air contaminated by styrene: effect of nitrogen supply, gas flow rate, and inlet concentration. Environmental Science and Technology (2000b); 34(9): 1764-1771.

53. Kinney, K. A., Loehr, R. C., Corsi, R. L. Vapor-phase bioreactors: Avoiding problems through better design and operation. Environmental Progress (1999); 18(3): 222-230.

54. Kinney, K. A., Wright, W., Chang, D. P. Y. Schroeder, E. D. Biodegration of Vapor-phase contaminants. In: Sikdar, S. K., Irvine, R. L. Bioremediation: Principles and Practice (Vol. III) – Bioremediation technologies. Tehnomic Publishing Company, Inc., 1998

55. Landmeyer, J. E., Chapelle, F. H., Herlong, H. H., Bradley, P. M. Methyl tert-butyl ether biodegradation by indigenous aquifer microorganisms under natural and artificial oxic conditions. Environmental Science and Technology (2001); 35 (6): 1118-1126.

56. Leson, G. Biofilters in Practice. In: Sikdar, S. K., Irvine, R. L. (Eds.). Bioremediation: Principles and Practice (Vol. III) – Bioremediation technologies. Tehnomic Publishing Company, Inc., 1998

57. Leson, G., Winer, A. M. Biofiltration: An innovative air pollution control technology for VOC emissions. Journal of Air and Waste Management Association (1991); 41 (8): 1045-1054

58. Maine Geological Survey, Bureau of Health, Bureau of Waste Management and Remediation. The Presence of MTBE and other gasoline compounds in Maines drinking water. A preliminary report, October 13, 1998. http://www.state.me.us/dhs/boh/mtbe/mtbe.pdf. (Accessed on March 01, 2001)

59. Ottengraf, S. P. P. Exhaust gas purification. In: Biotechnology (Vol. 8). Rehm, H. J., Reed, G. (eds.). VCH Verlagsgesellschaft, Weinheim, 1986.

60. Ottengraf, S. P. P., van den Oever, A. H. C. Kinetics of organic compound removal from waste gases with a biological filter. Biotechnology and Bioengineering (1983); 25(12): 3089-3102.

61. Pineda, J., Auria, R., Perez-Guevara, F., Revah, S. Biofiltration of toluene vapors using a model support. Bioprocess Engineering (2000); 23: 479-486.

62. Pomeroy, R. D. (1957). Deodorizing gas streams by the use of microbiological growths. U.S. Patent # 2,793,096.

63. Report to Governor and Legislature of the State of California as sponsored by SB 521. Health and environmental assessment of MTBE. Volume 1, summary and recommendations. http://tsrtp.ucdavis.edu/mtberpt/vol1.pdf (Accessed on April 03, 1999).

64. Salanitro, J. P., Johnson, P. C., Spinnler, G. E., Maner, P. M., Wisniewski, H. L., Bruce, C. Field-scale demonstration of enhanced MTBE bioremediation through aquifer bioaugmentation and oxygenation. Environmental Science & Technology (2000); 34(19): 4152-4162.

65. Salanitro, J. P., Chou, C. S., Wisniewski, H. L., Vipond, T. E. Perspectives on MTBE biodegradation and the potential for in situ aquifer bioremediation. Proceedings of the Southwwestern Regional Conference of the National Groundwater Association, MTBE and Perchlorate in Groundwater, 3-4 June, 1998, Anaheim, California.

66. Salanitro, J.P., Diaz, L.A., Williams, M.P., Wisniewski, H.W. Isolation of a bacterial culture that degrades methyl t-butyl ether: Applied and Environmental Microbiology (1994); 60(7): 2593-2596.

67. Schirmer, M., Barker, J. F. A study of long-term MTBE attenuation in the Borden Aquifer, Ontario, Canada. Ground Water Monitoring and Remediation (Spring 1998): 113-122.

68. Shareefdeen, Z., Baltzis, B., Oh, Y-S, Bartha, R. Biofiltration of methanol vapor. Biotechnology and Bioengineering (1993); 41: 512-524.

69. Shareefdeen, Z., Baltzis, B. Biofiltration of toluene vapor under steady-state and transient conditions: theory and experimental results. Chemical Engineering Science (1994); 24A: 4347-4360.

70. Schroeder, E. D., Eweis, J. B., Chang, D. P. Y., Veir, J. K. Biodegradation of recalcitrant components of organic mixtures. Water, Air and Soil Pollution (2000); 123: 133-146.

71. Smet, E., Chasaya, G., Van Langenhove, H., Verstraete, W. The effect of inoculation and the type of carrier material used on the biofiltration of methyl sulphides. Applied Microbiology and Biotechnology (1996); 45: 293-298.

72. Spinnler, G. E., Salanitro, J. P., Maner, P. H., Lyons, K. A. Enhanced bioremediation of MTBE (Bioremedy) at retail gas stations. Contaminated Soil Sediment and Water (Spring 2001), Speciaal issue; 47-49.

73. Squillace, P.J., Pankow, J.F., Korte, N.E., Zogorski, J.S. Review of environmental behavior and fate of methyl tert-butyl ether. Environmental Toxicology and Chemistry. (1997); 16(9): 1836-1844.

74. Squillace, P.J., Zogorski, J.S., Wilber, W.G., and Price, C.V. Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-1994: Environmental Science & Technology (1996), 30(5): 1721-1730.

75. Steffan, R.J., McClay, K., Vanberg, S., Condee, C.W., Zhang, D. Biodegradation of gasoline oxygenates methyl tert-butyl ether, ethyl tert-butyl ether and tert-amyl methyl ether by propane oxidizing bacteria. Applied and Environmental Microbiology (1997); 63(11): 4216-4222.

76. Swanson, W. J., Loehr, R. C. Biofiltration: Fundamentals, design and operational principles and applications. Journal of Environmental Engineering (1997); 123(6): 538-546.

77. USEPA. Methyl tertiary butyl ether, Recommendations and Actions. http://www.epa.gov/mtbe/action.htm (Accessed on April 19, 2001).

78. USEPA. Blue Ribbon Panel on oxygenates in gasline. Achieving clean air and clean water: The report of the Blue Ribbon Panel on oxygenates in gasoline. EPA-A20-R-99-021 (Sept. 15, 1999).

79. USEPA. Oxygenates in Water: Critical Information and Research Needs. Office of Research and Development. EPA/600/R-98/048 (1998).

80. USEPA. Drinking Water Advisory: Consumer acceptability advice and health effects analysis on methyl tertiary butyl ether (MTBE). Office of Water. EPA-822-F-97-009 (1997).

81. USGS Water Resources of California. Methyl tertiary-butyl ether. http://water.wr.usgs.gov/mtbe/ (Accessed on March 3, 2001).

82. Van Lith, C., David, S. L., Marsh, R. Design criteria for biofilters. Trans I ChemE, (May 1990); 68B: 127-132.

83. Wani, A. H., Branion, R. M. R., Lau, A. K. Biofiltration: A promising and cost effective technology for odors, VOC's and air toxics. Journal of Environmental Science and Health (1997); A 32(7): 2027-2025.

84. Wilson, J. T., Cho, J. S. Rate of biotransformation of MTBE in methanogenic groundwater. In: Wickramanayake, G. B., Gavaskar, A. R., Gibbs, J. T., Means, J. L. (eds.). Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds. May 2000, Monterey, CA. Battele Press, Columbus, OH.

85. Wilson, R. D., Mackay, D. M., Scow, K. M. In situ MTBE biodegradation supported by diffusive oxygen release. Environmental Science & Technology (2002); 36(2): 190-199.

86. Wu, G., Chabot, J. C., Caron, J. J., Heitz, M. Biological elimination of volatile organic compounds from waste gases in a biofilter. Water, Air and Soil Pollution (1998); 101: 69-78.

87. Yeh, C. K., Novak, J. T. The effect of hydrogen peroxide on the degradation of methyl and ethyl tert-butyl ether in soils. Water Environment Research (1995); 67(5): 828-834.

APPENDIXES

APPENDIX A

SAMPLE CALCULATIONS FOR DETERMINATION OF HEADSPACE AND LIQUID PHASE CONCENTRATIONS OF MTBE AND TBA

Dimensionless Henry's constant for MTBE (25^0C) = 0.0216

Dimensionless Henry's constant for TBA (25^0C) = 0.00059

Specific gravity of MTBE = 0.744 g/ml

Specific gravity of TBA = 0.786 g/ml

According to Henry's law, following relations are valid for MTBE or TBA when equilibrium is reached between the headspace and aqueous phase:

$M = (C_g V_g) + (C_l V_l)$ A1

By definition Henry's constant (H) is,

$H = (C_g/C_l)$ A2

where:

M = Mass of MTBE or TBA added to the bottle

C_g = Concentration in the gas phase

C_l = Concentration in the liquid phase

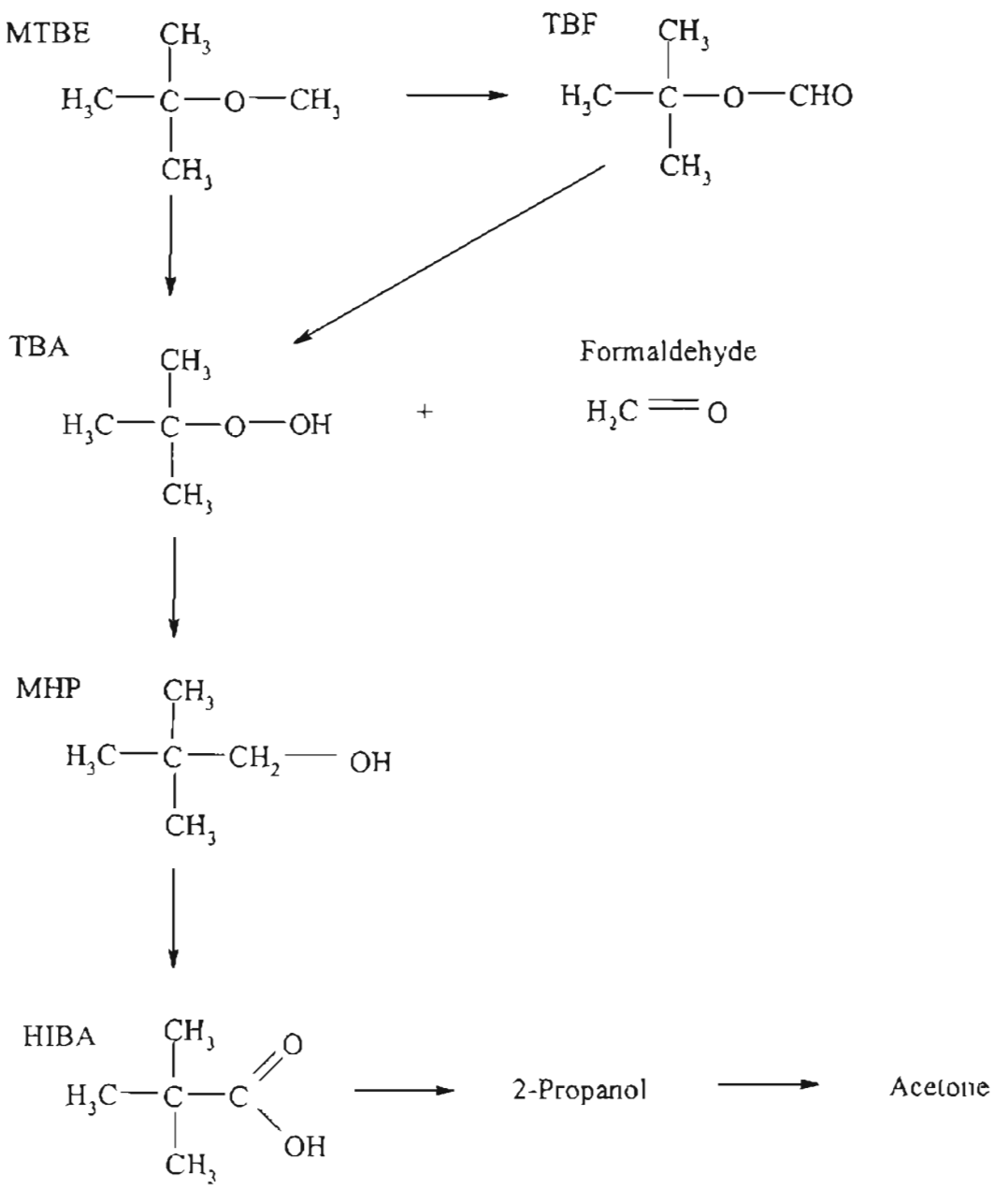
V_g = Volume of the gas phase

V_l = Volume of the liquid phase

If M is known as in the case of MTBE or TBA calibration standards, C_g or C_l can be calculated using equation A1 and A2. If C_g is known as in the case of culture maintenance experiments and PHS effect evaluation experiment, C_l can be calculated using equation A2.

APPENDIX B

BIODEGRADATION PATHWAY OF MTBE *



*Adapted from Hardison et al. (1997), Salanitro et al. (1998) and Steffan et al. (1997)

APPENDIX C

RAW DATA FOR CULTURE MAINTENANCE

Active 1		Active 2		Active 3	
Day	[MTBE, mg/l] Aqueous phase	Day	[MTBE, mg/l] Aqueous phase	Day	[MTBE, mg/l] Aqueous phase
0	41.17692685	0	47.86490833	0	31.65596759
2	40.27309444	2	44.42211481	2	33.36922222
3	37.16128889	3	42.28923426	3	29.25241204
4	37.1087537	4	43.39618333	4	30.73775833
6	37.17249074	6	44.91853333	6	31.3881537
9	37.52128796	9	47.03503889	9	31.76842037
11	37.25968426	11	48.88883056	11	31.49801204
13	1.351574074	13	18.93417659	13	1.628667989
13	11.94335714	13.5	12.74479938	13	11.710625
13.5	0	14.5	0	13.5	2.925780864
13.5	18.89848688	14.5	20.03198225	13.5	25.67816667
14.5	4.368115741	15.5	2.497714506	14.5	16.89132562
14.5	22.6316659	15.5	20.14826157	14.5	38.08920756
15.5	0.550618056	16.5	0	15.5	17.49279244
15.5	16.98681096	16.5	18.37060957	16.5	0
16.5	0	17.5	16.1241088	16.5	23.09847068
16.5	16.80402778	17.5	11.70658102	17.5	20.76210725
17.5	15.71658642	18.5	5.237587191	17.5	14.98902623
17.5	11.19379784	19	1.944997685	18.5	7.907838735
18.5	6.392294753	20	0	19	4.264030864
19	3.642982253	20	21.46234877	20	0
20	0	22	10.20491049	20	13.87680401

APPENDIX D

RAW DATA FOR OXYGEN EFFECT EXPERIMENT

Day	Active 1*	Active 2*
0	33.57766	34.40427
1	30.00921	31.00361
5	12.72243	10.47329
6	0	0
6	56.13872	66.99433
9	33.6118	39.78513
12	17.03858	40.07527
17	6.311539	34.00131
19	2.62135	32.12342
21	0.420475	33.59801
21	23.5259	33.59801
22	21.01929	29.0496
24	18.75291	27.87918
27	12.69903	N.A.**
34	0.411917	35.48194

*Active 1 – Partial replacement of headspace with pure oxygen

*Active2 – Headspace flushed with air

**N.A. = Not analyzed

APPENDIX E

RAW DATA FOR BIOFILTER MEDIUM CHARACTERIZATION

Moisture Content and Ash Content

Biofilter C

Description	Sample 1	Sample 2
Weight of empty dish	158.57 g	159.84 g
Weight of dish and wet media	248.28 g	222.08 g
Weight of dish and dry media (after 24 hours at 105^0C)	197.47 g	187.77 g
Weight of dish and dry media (after 30 minutes at 550^0C)	187.88 g	N.A.

N.A. = Not applicable

Biofilter P

Description	Sample 1	Sample 2
Weight of empty dish	164.37 g	157.42 g
Weight of dish and wet media	237.00 g	225.61 g
Weight of dish and dry media (after 24 hours at 105^0C)	196.01 g	189.04 g
Weight of dish and dry media (after 30 minutes at 550^0C)	188.34 g	N.A.

N.A. = Not applicable

Media density and porosity

Density and Porosity determinations

Biofilter C

Description	Sample 1
Weight of measuring cylinder	133 g
Volume of media taken	50 ml
Weight of cylinder and media	169.2 g
Weight of cylinder, media and water (at 22^0C)	187.6 g
Density of water at 22^0C	0.997 g/cc

Biofilter P

Description	Sample 1
Weight of measuring cylinder	131.5 g
Volume of media taken	50 ml
Weight of cylinder and media	168.3 g
Weight of cylinder, media and water (at 22^0C)	185 g
Density of water at 22^0C	0.997 g/cc

Partition Coefficient Studies

Biofilter C

Volume of serum bottle used = 160 ml

Volume of media taken = 10 ml

Volume of headspace = 150 ml

Volume of MTBE added to the serum bottle = 20 µl

Specific gravity of MTBE = 0.744 mg/µl

Therefore mass of MTBE added to the serum bottle = 14.88 mg

Porosity of medium = 0.37

Time (days)	Headspace concentration of MTBE (mg/l)
2	0.505918633
5	0.26490805
9	0.269421562
12	0.24416963
16	0.2337988
18	0.247174865

Note: k_h was calculated for the last three observations in the above table and average value rounded of to the nearest whole number was reported

Biofilter P

Volume of serum bottle used = 160 ml

Volume of media taken = 25 ml

Volume of headspace = 135 ml

Volume of MTBE added to the serum bottle = 10 µl

Specific gravity of MTBE = 0.744 mg/µl

Therefore mass of MTBE added to the serum bottle = 7.44 mg

Porosity of medium = 0.34

Time (days)	Headspace concentration of MTBE (mg/l)
0	4.767241243
2	4.456892176
3	4.393054271
4	4.505596843
5	4.412165552

Note: k_h was calculated for the last four observations in the above table and average value rounded of to the nearest whole number was reported

APPENDIX F

RAW DATA FOR PHS EFFECT EVALUATION EXPERIMENT

PHS = 0.2 mg/l

Incubation time (hours)	Aqueous phase MTBE (mg/l) (with PHS)	Aqueous phase MTBE (mg/l) (No PHS)	Aqueous phase MTBE (mg/l) Control
1.5	32.50435532	33.75298814	35.81114323
6	27.05249711	28.51396325	30.28799248
14	28.91611574	29.23217332	28.80095226
24	25.62196094	26.80110301	27.41004369
48	25.11412103	25.40772619	28.39496462
72	24.84925039	25.99008526	28.6998966
168	9.447594907	8.486858796	25.45146019
192	3.09896875	2.437436343	26.83999074

PHS = 2 mg/l

Incubation time (hours)	Aqueous phase MTBE (mg/l) (with PHS)	Aqueous phase MTBE (mg/l) (No PHS)	Aqueous phase MTBE (mg/l) Control
1.5	31.20577546	29.45052025	30.76591348
6	27.54823929	31.1758941	28.89194647
14	27.15081539	29.88153906	29.00992216
24	26.64113889	29.04704832	26.93811834
48	26.5402877	28.50249868	25.90632176
72	25.92405826	28.90166667	26.68473187
168	7.96604213	6.914394444	22.8567588
192	2.120885417	0.817561343	26.26644387

PHS = 20 mg/l

Incubation time (hours)	Aqueous phase MTBE (mg/l) (with PHS)	Aqueous phase MTBE (mg/l) (No PHS)	Aqueous phase MTBE (mg/l) Control
1.5	27.18628646	29.90408883	27.07549971
6	27.43414554	27.11503414	28.63613831
14	25.36314381	26.37839728	27.7472691
24	26.82470457	25.79587818	26.85057841
48	25.53448049	25.49856283	26.15771362
72	26.36416512	25.36599035	26.3050625
168	6.067243519	7.28030787	23.04902778
192	0.643877315	1.968728009	26.10898958

PHS = 50 mg/l

Incubation time (hours)	Aqueous phase MTBE (mg/l) (with PHS)	Aqueous phase MTBE (mg/l) (No PHS)	Aqueous phase MTBE (mg/l) Control
4	28.35412235	28.58735913	27.12864352
24	23.75796065	24.27816104	24.73454431
48	26.03210378	25.71802662	26.89435417
132	18.21402685	17.51610185	26.71190509
156	14.3610787	13.68990451	29.36300637
180	6.980348958	5.370394097	29.25640683
192	3.421152778	1.962089699	30.34020139

PHS = 100 mg/l

Incubation time (hours)	Aqueous phase MTBE (mg/l) (with PHS)	Aqueous phase MTBE (mg/l) (No PHS)	Aqueous phase MTBE (mg/l) Control
4	28.86266005	28.49224239	25.65802183
24	24.18075033	24.33334127	23.1048254
48	29.91129082	26.00676042	25.76118981
132	17.24805972	17.64796574	24.35760324
156	13.76764236	14.12068808	30.31568576
180	6.607968171	6.449956019	28.10369387
192	3.025103588	3.297157407	29.03118866

PHS = 150 mg/l

Incubation time (hours)	Aqueous phase MTBE (mg/l) (with PHS)	Aqueous phase MTBE (mg/l) (No PHS)	Aqueous phase MTBE (mg/l) Control
4	28.20389484	28.37474603	**27.2727662**
24	23.8166789	25.32299901	23.87180787
48	30.27769491	**32.47595972**	30.60528241
132	15.97264213	16.5658963	26.71190509
156	11.73281713	12.41511053	29.31684954
180	5.18510706	5.509889468	30.98301042
192	1.886958912	2.038636574	30.98301042

PHS = 200 mg/l

Incubation time (hours)	Aqueous phase MTBE (mg/l) (with PHS)	Aqueous phase MTBE (mg/l) (No PHS)	Aqueous phase MTBE (mg/l) Control
4	27.33428406	28.67714054	**27.05592526**
24	22.82023446	24.82183267	23.15172222
48	30.25171759	30.73604815	29.32180185
132	15.4148463	17.43468796	25.90890833
156	10.66095949	13.72993403	31.25199421
180	4.931456019	6.975391204	28.16552083
192	1.393051505	3.304799769	27.79441551

APPENDIX G

RAW DATA OF MTBE CONCENTRATIONS AT DIFFERENT SAMPLING PORTS

Day	Biofilter P (MTBE, mg/l)				Biofilter C (MTBE, mg/l)			
	Inlet	SP-2 (12.5 cm)	SP-3 (27 cm)	Outlet	Inlet	SP – 2 (12.5 cm)	SP – 3 (27 cm)	Outlet
1	0.25	N.A.	N.A.	0.24	0.19	N.A.	N.A.	0.17
2	0.23	N.A.	N.A.	0.23	0.25	N.A.	N.A.	0.17
3	0.18	N.A.	N.A.	0.22	0.25	N.A.	N.A.	0.17
4	0.21	N.A.	N.A.	0.24	0.27	N.A.	N.A.	0.19
5	0.22	N.A.	N.A.	0.21	0.26	N.A.	N.A.	0.17
6	0.24	N.A.	N.A.	0.23	0.24	N.A.	N.A.	0.18
7	0.22	N.A.	N.A.	0.25	0.29	N.A.	N.A.	0.21
8	0.24	N.A.	N.A.	0.25	0.24	N.A.	N.A.	0.22
9	0.25	N.A.	N.A.	0.24	0.19	N.A.	N.A.	0.20
12	0.23	N.A.	N.A.	0.21	0.23	N.A.	N.A.	0.17
13	0.18	N.A.	N.A.	0.15	0.17	N.A.	N.A.	0.12
14	0.18	N.A.	N.A.	0.18	0.17	N.A.	N.A.	0.15
15	0.22	N.A.	N.A.	0.19	0.19	N.A.	N.A.	0.16
16	0.18	N.A.	N.A.	0.14	0.16	N.A.	N.A.	0.12
17	0.18	N.A.	N.A.	0.12	0.29	N.A.	N.A.	0.18
18	0.28	N.A.	N.A.	0.17	0.31	N.A.	N.A.	0.16
19	0.15	N.A.	N.A.	0.12	0.23	N.A.	N.A.	0.15
20	0.16	N.A.	N.A.	0.13	0.14	N.A.	N.A.	0.12
21	0.15	N.A.	N.A.	0.15	0.16	N.A.	N.A.	0.10
22	0.20	N.A.	N.A.	0.12	0.18	N.A.	N.A.	0.10
23	0.21	N.A.	N.A.	0.13	0.25	N.A.	N.A.	0.14
24	0.25	N.A.	N.A.	0.15	0.16	N.A.	N.A.	0.1
25	0.16	N.A.	N.A.	0.13	0.17	N.A.	N.A.	0.11
26	0.19	N.A.	N.A.	0.15	0.24	N.A.	N.A.	0.11
27	0.17	0.11	0.11	0.11	0.20	0.09	N.A.	0.09
28	0.19	0.11	0.14	0.11	0.24	0.12	N.A.	0.12
29	0.26	0.14	0.17	0.14	0.26	0.09	N.A.	0.09
30	0.18	0.10	0.11	0.10	0.16	0.08	N.A.	0.08
31	0.19	0.14	0.18	0.14	0.20	0.09	N.A.	0.09
32	0.31	0.19	0.17	0.19	0.24	0.12	0.17	0.12
33	0.20	0.11	0.13	0.11	0.22	0.11	0.13	0.11
34	0.15	0.12	0.10	0.12	0.14	0.08	0.12	0.08
35	0.15	0.12	0.14	0.12	0.13	0.08	0.15	0.08
36	0.15	0.10	0.13	0.10	0.16	0.07	0.13	0.07

SP-2 = Sampling port # 2 at 12.5 cm from the inlet of the column
SP-3 = Sampling port # 3 at 27 cm from the inlet of the column
N. A. = Not analyzed

Day	Biofilter P (MTBE, mg/l)				Biofilter C (MTBE, mg/l)			
	Inlet	SP-2 (12.5 cm)	SP-3 (27 cm)	Outlet	Inlet	SP – 2 (12.5 cm)	SP – 3 (27 cm)	Outlet
37	0.21	0.14	0.17	0.15	0.16	0.09	0.17	0.16
38	0.20	0.14	0.16	0.15	0.17	0.08	0.16	0.15
39	0.18	0.13	0.14	0.13	0.16	0.08	0.14	0.13
40	0.30	0.23	0.25	0.24	0.33	0.17	0.24	0.24
41	0.32	0.25	0.28	0.28	0.28	0.19	0.27	0.26
42	0.35	0.27	0.31	0.31	0.31	0.19	0.32	0.29
43	0.35	0.27	0.30	0.30	0.35	0.20	0.32	0.31
44	0.35	0.30	0.33	0.31	0.35	0.21	0.29	0.31
45	0.34	0.29	0.31	0.29	0.34	0.21	0.29	0.31
46	0.38	0.31	0.36	0.32	0.37	0.21	0.34	0.32
47	0.34	0.28	0.30	0.31	0.32	0.22	0.29	0.29
50	0.31	0.23	0.28	0.28	0.29	0.20	0.29	0.29
52	0.34	0.27	0.27	0.28	0.31	0.24	0.30	0.29
54	0.31	0.27	0.30	0.33	0.33	0.26	0.30	0.29
55	0.35	0.27	0.30	0.31	0.34	0.25	0.33	0.29
56	0.32	0.27	0.32	0.30	0.34	0.28	0.33	0.31
58	0.30	0.22	0.25	0.25	0.34	0.22	0.29	0.27
59	0.33	0.25	0.25	0.28	0.33	0.20	0.29	0.28
60	0.26	0.21	0.25	0.28	0.31	0.20	0.27	0.26
61	0.29	0.22	0.27	0.28	0.29	0.21	0.31	0.25
63	0.30	0.24	0.26	0.26	0.33	0.21	0.27	0.25
64	0.32	0.23	0.27	0.27	0.44	0.21	0.27	0.27
65	0.33	0.27	0.27	0.27	0.29	0.20	0.25	0.29
66	0.28	0.22	0.26	0.28	0.30	0.19	0.27	0.28
68	0.10	0.06	0.07	0.08	0.08	0.07	0.07	0.09
70	0.11	0.06	0.08	0.08	0.09	0.08	0.08	0.09
72	0.10	0.07	0.08	0.08	0.09	0.06	0.08	0.09
73	0.12	0.07	0.08	0.08	0.09	0.06	0.08	0.08
74	0.10	0.07	0.07	0.06	0.08	0.06	0.06	0.07
76	0.10	0.07	0.07	0.08	0.09	0.07	0.08	0.08
77	0.13	0.07	0.09	0.09	0.14	0.08	0.09	0.09
78	0.09	0.07	0.09	0.08	0.09	0.06	0.08	0.08
79	0.10	0.06	N.A.	N.A.	0.09	0.06	N.A.	N.A.
80	0.05	0.03	0.04	0.03	0.05	0.04	0.05	0.04
81	0.05	0.03	0.05	0.04	0.05	0.03	0.03	0.04
82	0.05	0.03	0.03	0.03	0.05	0.03	0.03	0.04
85	0.05	0.03	0.04	0.03	0.06	0.02	0.04	0.04
86	0.08	0.05	0.05	0.05	0.06	0.02	0.03	0.03
87	0.06	0.03	0.04	0.03	0.04	0.02	0.03	0.04

SP-2 = Sampling port # 2 at 12.5 cm from the inlet of the column
SP-3 = Sampling port # 3 at 27 cm from the inlet of the column
N. A. = Not analyzed

Day	Biofilter P (MTBE, mg/l)				Biofilter C (MTBE, mg/l)			
	Inlet	SP-2 (12.5 cm)	SP-3 (27 cm)	Outlet	Inlet	SP – 2 (12.5 cm)	SP – 3 (27 cm)	Outlet
88	0.04	0.03	0.03	0.03	0.05	0.03	0.03	0.03
90	0.06	0.03	0.04	0.03	0.05	0.01	0.03	0.03
91	0.06	0.03	0.04	0.03	0.05	0.02	0.03	0.03
92	0.06	0.02	N.A.	N.A.	0.08	0.02	N.A.	N.A.
93	0.06	0.03	0.04	0.04	0.06	0.02	0.04	0.03
94	0.05	0.03	0.03	0.03	0.05	0.01	0.02	0.02
95	0.05	0.03	0.04	0.03	0.05	0.02	0.04	0.03
96	0.05	0.03	0.03	0.03	0.05	0.02	0.03	0.03
98	0.07	0.03	N.A.	N.A.	0.06	0.02	N.A.	N.A.
101	0.06	0.03	0.04	0.04	0.06	0.02	0.04	0.04
102	0.06	0.03	0.05	0.04	0.07	0.02	0.04	0.03

SP-2 = Sampling port # 2 at 12.5 cm from the inlet of the column
SP-3 = Sampling port # 3 at 27 cm from the inlet of the column
N. A. = Not analyzed

APPENDIX H

RAW DATA OF TBA CONCENTRATIONS IN THE OUTLET STREAM OF THE BIOFILTERS

Day	Biofilter C (TBA, mg/l) Outlet	Biofilter P (TBA, mg/l) Outlet
27*	0.0025	0.0000
28	0.0057	0.0000
29	0.0034	0.0047
30	0.0045	0.0030
31	0.0038	0.0027
32	0.0041	0.0031
33	0.0050	0.0027
34	0.0042	0.0052
35	0.0027	0.0036
36	0.0000	0.0000
36	0.0000	0.0000
37	0.0000	0.0000
38	0.0000	0.0000
39	0.0000	0.0000
40	0.0000	0.0000
41	0.0026	0.0000
42	0.0028	0.0000
43	0.0054	0.0000
44	0.0040	0.0000
45	0.0051	0.0024
46	0.0059	0.0029
47	0.0056	0.0000
50	0.0049	0.0000
52	0.0057	0.0000
54	0.0050	0.0000
55	0.0055	0.0000
56	0.0050	0.0000
58	0.0044	0.0000
59	0.0040	0.0000
60	0.0050	0.0000
61	0.0050	0.0000
63	0.0025	0.0000

Day	Biofilter C (TBA, mg/l) Outlet	Biofilter P (TBA, mg/l) Outlet
65	0.0044	0.0000
66	0.0049	0.0000

*Note: Quantification of TBA was started on 27th day and no TBA was detected in any of the biofilters after 66th day

APPENDIX I

CALCULATION OF BIOFILTER PERFORMANCE AND OTHER PARAMETERS

Some of the biofiltration parameters used in the present study and their calculation is presented below:

1. Mass loading rate (volumetric) = $\frac{Q \times Ci}{V}$

2. Removal Efficiency = $\frac{(Ci - Co)}{Ci} \times 100$

3. Elimination Capacity = $\frac{Q(Ci - Co)}{V}$

where:

Q = Air flow rate (m^3/hour)

V = Volume of the biofilter (m^3) = 3.016 x 10^{-3} m^3

Ci = Inlet MTBE concentration (g/m^3)

Co = Outlet MTBE concentration (g/m^3)

Biofilter C

Day	Air Flow rate (m^3/hour)	Inlet [MTBE] (mg/l)	Outlet [MTBE] (mg/l)	Loading rate (g/m^3/hour)	Removal Efficiency (%)	Elimination Capacity (g/m^3/hour)
1	0.1272	0.19	0.17	7.8157	10.1107	0.7902
2	0.1272	0.25	0.17	10.7298	32.2262	3.4578
3	0.1272	0.25	0.17	10.3405	30.8296	3.1879
4	0.1272	0.27	0.19	11.5697	31.7398	3.6722
5	0.1272	0.26	0.17	10.9826	33.8118	3.7134
6	0.1272	0.24	0.18	10.1293	26.1073	2.6445
7	0.1272	0.29	0.21	12.1748	27.6922	3.3715
8	0.1272	0.24	0.22	10.1352	9.0549	0.9177
9	0.1272	0.19	0.20	7.9821	-4.1253	-0.3293
12	0.1272	0.23	0.17	9.7396	27.8964	2.7170

Day	Air Flow rate (m^3/hour)	Inlet [MTBE] (mg/l)	Outlet [MTBE] (mg/l)	Loading rate (g/m^3/hour)	Removal Efficiency (%)	Elimination Capacity (g/m^3/hour)
13	0.1272	0.17	0.12	7.2092	29.9290	2.1576
14	0.1272	0.17	0.15	7.3185	13.8253	1.0118
15	0.1272	0.19	0.16	7.9495	15.1066	1.2009
16	0.1272	0.16	0.12	6.5628	22.3868	1.4692
17	0.1272	0.29	0.18	12.0266	35.7111	4.2948
18	0.1272	0.31	0.16	12.9614	48.6867	6.3105
19	0.1272	0.23	0.15	9.6890	34.5328	3.3459
20	0.1272	0.14	0.12	5.6967	8.6697	0.4939
21	0.1272	0.16	0.10	6.6751	35.2558	2.3533
22	0.1272	0.18	0.10	7.3879	40.2321	2.9723
23	0.1272	0.25	0.14	10.6103	43.8691	4.6546
24	0.1272	0.16	0.10	6.6415	33.7032	2.2384
25	0.1272	0.17	0.11	7.3591	39.6213	2.9158
26	0.1272	0.24	0.11	10.2019	56.0917	5.7224
27	0.1272	0.20	0.09	8.3645	52.9572	4.4296
28	0.1272	0.24	0.12	10.2980	52.3014	5.3860
29	0.1272	0.26	0.09	10.7843	63.7798	6.8782
30	0.1272	0.16	0.08	6.6482	51.9251	3.4521
31	0.1272	0.20	0.09	8.2834	51.8363	4.2938
32	0.1272	0.24	0.12	10.2560	50.2366	5.1523
33	0.1272	0.22	0.11	9.1780	50.9582	4.6769
34	0.1272	0.14	0.08	6.0808	46.1725	2.8077
35	0.1272	0.13	0.08	5.6885	41.2298	2.3453
36	0.1272	0.16	0.07	6.7094	53.7342	3.6052
37	0.1272	0.16	0.09	6.9205	45.5933	3.1553
38	0.1272	0.17	0.08	7.3545	53.5775	3.9403
39	0.1272	0.16	0.08	6.8141	50.9131	3.4693
40	0.1272	0.33	0.17	14.0624	48.9504	6.8836
41	0.1272	0.28	0.19	11.8914	32.4653	3.8606
42	0.1272	0.31	0.19	12.9524	36.6350	4.7451
43	0.1272	0.35	0.20	14.7932	41.7999	6.1835
44	0.1272	0.35	0.21	14.5729	38.1284	5.5564
45	0.1272	0.34	0.21	14.3326	37.6693	5.3990
46	0.1272	0.37	0.21	15.7060	43.3338	6.8060
47	0.1272	0.32	0.22	13.7026	33.1639	4.5443
50	0.1272	0.29	0.20	12.1326	31.6651	3.8418
52	0.1272	0.31	0.24	13.2555	23.7300	3.1455
54	0.1272	0.33	0.26	13.7093	20.0829	2.7532
55	0.1272	0.34	0.25	14.2394	27.4125	3.9034
56	0.1272	0.34	0.28	14.4077	18.4204	2.6540
58	0.0792	0.34	0.22	9.0107	35.8174	3.2274
59	0.0792	0.33	0.20	8.5758	37.8714	3.2478

Day	Air Flow rate (m^3/hour)	Inlet [MTBE] (mg/l)	Outlet [MTBE] (mg/l)	Loading rate (g/m^3/hour)	Removal Efficiency (%)	Elimination Capacity (g/m^3/hour)
60	0.0792	0.31	0.20	8.1061	36.2251	2.9364
61	0.0792	0.29	0.21	7.6592	28.9680	2.2187
63	0.0792	0.33	0.21	8.6432	34.8746	3.0143
64	0.0792	0.44	0.21	11.6455	52.3717	6.0990
65	0.0792	0.29	0.20	7.6138	30.7019	2.3376
66	0.0792	0.30	0.19	7.8638	37.3421	2.9365
68	0.0792	0.08	0.07	2.1296	7.7283	0.1646
70	0.0792	0.09	0.08	2.4566	18.8726	0.4636
72	0.0792	0.09	0.06	2.3960	30.1760	0.7230
73	0.0792	0.09	0.06	2.4346	32.4836	0.7908
74	0.0792	0.08	0.06	1.9925	25.5588	0.5093
76	0.0792	0.09	0.07	2.2824	24.6605	0.5628
77	0.0792	0.14	0.08	3.5789	43.3820	1.5526
78	0.0792	0.09	0.06	2.4353	33.0731	0.8054
79	0.0792	0.09	0.06	2.3796	32.6367	0.7766
80	0.0792	0.05	0.04	1.3161	27.7879	0.3657
81	0.0792	0.05	0.03	1.2202	40.1288	0.4897
82	0.0792	0.05	0.03	1.4246	50.4556	0.7188
85	0.0792	0.06	0.02	1.5607	58.3029	0.9099
86	0.0792	0.06	0.02	1.5555	57.9950	0.9021
87	0.0792	0.04	0.02	1.1669	44.5077	0.5193
88	0.0792	0.05	0.03	1.2418	43.4792	0.5399
90	0.0521	0.05	0.01	0.8828	72.2171	0.6375
91	0.0521	0.05	0.02	0.9308	69.5610	0.6475
92	0.0521	0.08	0.02	1.4484	73.7462	1.0681
93	0.0521	0.06	0.02	0.9526	65.3710	0.6227
94	0.0521	0.05	0.01	0.8101	68.7279	0.5568
95	0.0521	0.05	0.02	0.9359	64.2837	0.6016
96	0.0521	0.05	0.02	0.9476	67.8152	0.6426
98	0.0521	0.06	0.02	1.0793	70.8029	0.7642
101	0.0521	0.06	0.02	1.0153	66.7551	0.6778
102	0.0521	0.07	0.02	1.1423	69.8088	0.7974

Biofilter P

Day	Air Flow rate (m^3/hour)	Inlet [MTBE] (mg/l)	Outlet [MTBE] (mg/l)	Loading rate (g/m^3/hour)	Removal Efficiency (%)	Elimination Capacity (g/m^3/hour)
1	0.1272	0.25	0.24	10.3606	4.2443	0.4397
2	0.1272	0.23	0.23	9.6596	-1.7215	-0.1663
3	0.1272	0.18	0.22	7.6662	-18.7655	-1.4386
4	0.1272	0.21	0.24	8.6808	-18.4431	-1.6010
5	0.1272	0.22	0.21	9.4823	5.7114	0.5416
6	0.1272	0.24	0.23	9.9823	3.5099	0.3504
7	0.1272	0.22	0.25	9.4434	-11.5185	-1.0877
8	0.1272	0.24	0.25	9.9347	-7.5665	-0.7517
9	0.1272	0.25	0.24	10.6025	3.5122	0.3724
12	0.1272	0.23	0.21	9.7912	10.7652	1.0540
13	0.1272	0.18	0.15	7.4108	16.6005	1.2302
14	0.1272	0.18	0.18	7.6628	0.1633	0.0125
15	0.1272	0.22	0.19	9.1266	9.9382	0.9070
16	0.1272	0.18	0.14	7.4456	18.5149	1.3786
17	0.1272	0.18	0.12	7.6207	32.6893	2.4911
18	0.1272	0.28	0.17	11.8289	38.0033	4.4954
19	0.1272	0.15	0.12	6.3878	21.4308	1.3690
20	0.1272	0.16	0.13	6.6802	17.9942	1.2021
21	0.1272	0.15	0.15	6.3651	-0.1124	-0.0072
22	0.1272	0.20	0.12	8.5071	38.1081	3.2419
23	0.1272	0.21	0.13	8.8083	36.2782	3.1955
24	0.1272	0.25	0.15	10.5334	38.4099	4.0459
25	0.1272	0.16	0.13	6.9524	21.8308	1.5178
26	0.1272	0.19	0.15	8.1345	24.6542	2.0055
27	0.1272	0.17	0.11	7.3544	39.1258	2.8775
28	0.1272	0.19	0.11	8.0142	39.7393	3.1848
29	0.1272	0.26	0.14	10.7947	45.5756	4.9197
30	0.1272	0.18	0.10	7.7952	48.2250	3.7593
31	0.1272	0.19	0.14	8.1673	28.3318	2.3139
32	0.1272	0.31	0.19	13.2350	39.9743	5.2906
33	0.1272	0.20	0.11	8.3440	42.8357	3.5742
34	0.1272	0.15	0.12	6.3923	22.1209	1.4140
35	0.1272	0.15	0.12	6.4817	24.3807	1.5803
36	0.1272	0.15	0.10	6.4968	37.5097	2.4369
37	0.1272	0.21	0.14	8.6769	31.9343	2.7709
38	0.1272	0.20	0.14	8.3523	31.0428	2.5928
39	0.1272	0.18	0.13	7.5628	30.0251	2.2707
40	0.1272	0.30	0.23	12.4600	20.6442	2.5723
41	0.1272	0.32	0.25	13.6336	21.9520	2.9929

Day	Air Flow rate (m^3/hour)	Inlet [MTBE] (mg/l)	Outlet [MTBE] (mg/l)	Loading rate (g/m^3/hour)	Removal Efficiency (%)	Elimination Capacity (g/m^3/hour)
42	0.1272	0.35	**0.27**	14.9388	24.1878	3.6134
43	0.1272	0.35	0.27	14.7407	22.5179	3.3193
44	0.1272	0.35	0.30	14.9134	13.7649	2.0528
45	0.1272	0.34	0.29	14.2603	15.5114	2.2120
46	0.1272	0.38	0.31	16.1459	19.2641	3.1104
47	0.1272	0.34	0.28	14.4970	19.8624	2.8795
50	0.1272	0.31	0.23	12.9568	23.8333	3.0880
52	0.1272	0.34	0.27	14.3466	19.2364	2.7598
54	0.1272	0.31	0.27	13.0226	11.2520	1.4653
55	0.1272	0.35	0.27	14.6844	23.0192	3.3802
56	0.1272	0.32	0.27	13.3849	13.4764	1.8038
58	0.0792	0.30	0.22	7.7806	26.0013	2.0231
59	0.0792	0.33	0.25	8.5914	24.5050	2.1053
60	0.0792	0.26	0.21	6.9333	21.2166	1.4710
61	0.0792	0.29	0.22	7.5189	24.9062	1.8727
63	0.0792	0.30	0.24	7.8921	19.8551	1.5670
64	0.0792	0.32	0.23	8.3381	26.1160	2.1776
65	0.0792	0.33	0.27	8.5767	18.7412	1.6074
66	0.0792	0.28	0.22	7.3954	22.4867	1.6630
68	0.0792	0.10	0.06	2.5805	35.1521	0.9071
70	0.0792	0.11	0.06	2.7841	40.4585	1.1264
72	0.0792	0.10	0.07	2.4964	24.8002	0.6191
73	0.0792	0.12	0.07	3.0545	39.4265	1.2043
74	0.0792	0.10	0.07	2.5999	32.7923	0.8526
76	0.0792	0.10	0.07	2.7263	33.2727	0.9071
77	0.0792	0.13	0.07	3.4550	43.7265	1.5107
78	0.0792	0.09	0.07	2.4886	29.4359	0.7326
79	0.0792	0.10	0.06	2.6005	38.6288	1.0046
80	0.0792	0.05	0.03	1.2404	44.4859	0.5518
81	0.0792	0.05	0.03	1.2717	34.8913	0.4437
82	0.0792	0.05	0.03	1.3764	36.4188	0.5013
85	0.0792	0.05	0.03	1.4341	45.5187	0.6528
86	0.0792	0.08	0.05	2.0438	39.3674	0.8046
87	0.0792	0.06	0.03	1.5962	44.2134	0.7057
88	0.0792	0.04	0.03	1.0814	31.6845	0.3426
90	0.0521	0.06	0.03	1.0933	46.4033	0.5073
91	0.0521	0.06	0.03	1.0128	53.6778	0.5437
92	0.0521	0.06	0.02	0.9873	59.1957	0.5845
93	0.0521	0.06	0.03	1.0674	45.5556	0.4863
94	0.0521	0.05	0.03	0.8412	38.3259	0.3224
95	0.0521	0.05	0.03	0.9145	45.1191	0.4126
96	0.0521	0.05	0.03	0.8367	38.8465	0.3250

Day	Air Flow rate (m^3/hour)	Inlet [MTBE] (mg/l)	Outlet [MTBE] (mg/l)	Loading rate (g/m^3/hour)	Removal Efficiency (%)	Elimination Capacity (g/m^3/hour)
98	0.0521	0.07	0.03	1.1150	56.2543	0.6273
101	0.0521	0.06	0.03	1.0220	54.8858	0.5610
102	0.0521	0.06	0.03	1.0174	45.3712	0.4616

VITA

Harvinder Singh

Candidate for the Degree of

Master of Science

Thesis: BIOFILTRATION OF MTBE CONTAMINATED AIR STREAMS – A STUDY OF REACTOR START-UP, STEADY STATE AND TRANSIENT STATE BEHAVIOR

Major Field: Environmental Engineering

Biographical:

Personal Data: Born in Jalandhar, India on October 17, 1976, the son of Swaran Singh Luthra and Promila Luthra

Education: Graduated from M. G. N. Public School, Jalandhar, Punjab, India in May 1995; received Bachelor of Engineering degree in Civil Engineering from Thapar Institute of Engineering and Technology, Patiala, Punjab, India in May 1999. Completed the requirements of Master of Science degree with a major in Environmental Engineering at Oklahoma State University, Stillwater, Oklahoma in May 2002.

Experience: Research Assistant, Department of Microbiology and Molecular Genetics, Oklahoma State University, August 2000 to January 2002; Teaching Assistant, School of Civil and Environmental Engineering, Oklahoma State University, August 2001 to December 2001; Research Assistant, School of Civil and Environmental Engineering, Oklahoma State University, August 1999 to August 2001; Teaching Assistant, School of Civil and Enviromental Engineering, Oklahoma State University, August 1999 to December 1999; Student Intern, Central Road Research Institute, New Delhi, India, June 1998 to December 1998.

Professional Memberships: Air & Waste Management Association, American Society for Microbiology, Phi Kappa Phi National Honor Society.