# UNIVERSITY OF CINCINNATI

Date: February 16, 2007

I, ZHANGLI CAI,

hereby submit this work as part of the requirements for the degree of:

Doctorate of Philosophy

in:

Environmental Engineering

It is entitled:

Integrated Cyclic Adsorption/Desorption Beds and Biofiltration System
for Treatment of Waste Gas Streams

This work and its defense approved by:

Chair: Dr. George A. Sorial
Dr. Paul. L. Bishop
Dr. Neville G. Pinto
Dr. Margaret J. Kupferle

# Integrated Cyclic Adsorption/Desorption Beds and Biofiltration System for Treatment of Waste Gas Streams

A dissertation submitted to the

Division of Research and Advanced Studies
of the University of Cincinnati

in partial fulfillment of the requirements for the degree of

**DOCTOR OF PHILOSOPHY**

in the Department of Civil and Environmental Engineering
of the College of Engineering

2007

By

**Zhangli Cai**

M.S. Environmental Engineering, East China University of Sci. & Tech., Shanghai, China, 2000

B.S. Materials Protection, East China University of Sci. & Tech., Shanghai, China, 1997

Committee Chair: Dr. George A. Sorial

# ABSTRACT

Fluctuations in influent concentrations and variations in waste air composition challenge the application of biofiltration technology in the chemical industry. As a potential solution to handle the limitation of the biofiltration technology, an integrated system of a cyclic 2-bed adsorption/desorption unit and a trickle bed air biofilter (TBAB) is proposed and applied in this study. The primary goal of the study was to maintain long-term, stable consistent high performance of volatile organic compounds (VOCs) degradation in the TBAB. Five specific studies were conducted to accomplish the primary objective. These studies were: characterization of TBAB for VOC interchange under step-change in loadings; characterization of TBAB for mixture of VOCs; evaluation of a cyclic 2-bed adsorption unit for attenuating fluctuation in the influent concentrations; application of the integrated technology for effective removal of a mixture of VOCs; and microbial diversity investigation for interchanging VOCs and their mixture in TBAB.

Investigations were conducted on independent TBABs under single VOC interchange with periodic backwashing as biomass control. The VOCs considered were common solvents used in paint booth industries.  Two aromatic compounds (styrene and toluene) and two aliphatic compounds (Methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK)) were studied. This study simulated VOC emission rotation as the process of production rotated in certain chemical industries. Experimental findings indicated that the biofilter required apparent re-acclimation period when the VOC was interchanged to aromatic ones.

The second phase investigated two mixtures of these VOCs in two independent parallel trains of TBAB under step change in influent concentration. Critical loadings were determined under backwashing and starvation operating strategies.

In the third phase, the buffering capacity of a cyclic 2-bed adsorption unit under a square wave of fluctuating condition was evaluated for a feeding composition based on EPA industrial emission report. The cyclic 2-bed adsorption unit succeeded in attenuating load fluctuations as compared to non-cyclic operations. Furthermore, the time to breakthrough of contaminants encountered in non-cyclic operations could lead to a starvation period to the followed biofilter and eventually long period of acclimation after breakthrough of VOCs from the adsorber.

In the fourth phase, the integrated system of 2 cyclic adsorption/desorption beds and TBAB was applied to the VOC mixture. Four square wave feeding conditions were applied on the system. A parallel control system with an independent TBAB only was run to compare its performance to the integrated system. Experimental findings revealed that the integrated system was able to achieve high stable performance as compared to the control unit.

Finally, microbial communities were investigated for the biofilters utilized in VOC interchange and VOCs mixture experiments. Microbial diversity showed consistent transition for the interchange of VOCs. Community structure for VOC mixtures showed high independency to the component content in the mixture.

# ACKNOWLEDGEMENTS

My deepest gratitude goes to Dr. George A. Sorial, my advisor for his patient guidance and consistent support throughout my PhD studies. He helped me find the way to approach scientific excellence and perfection. I would also like to take this opportunity to thank my dissertation committee, Dr. Paul L. Bishop, Dr. Neville G. Pinto, and Dr. Margaret J. Kupferle for their time and effort in the critical review of my research work. I gratefully acknowledge the financial support through my PhD study journey from University of Cincinnati and the National Science Foundation under award # BES 0229135.

Also a special thank goes to Dr. Daekeun Kim, my research partner for his active cooperation throughout this study. I would also like to thank Rachael Rhodes for her help during her work here as co-op student in the project. I'd like to thank our research group, in particular Ashraf Aly Hassan, Hao Zhang, Niranjan Deshpnde, Qiuli Lu, Rangesh Srinivasan, and Yi Zhou for their support and sharing fun with me in the lab. Special thanks also go to Kai Zhang, Dr. Lei Wang, Li Yang, Dr. Maher Zein, and Dr. Pascal Saikaly, who significantly helped me with the microbial experiment.

Also my deepest gratitude goes to my wife, Haifang Huang for her full support. Finally, I would like to thank my parents, my sister, my brothers, and all my relatives in China, who have supported me throughout my education. This dissertation is dedicated especially to them.

## TABLE OF CONTENTS

CHAPTER 1. INTRODUCTION

# LIST OF TABLES

# LIST OF FIGURES

# CHAPTER 1

# INTRODUCTION

## 1.1. Background

Volatile organic compounds (VOCs) are an important class of air pollutants, commonly found in the atmosphere at ground level in all urban and industrial centers. There are hundreds of compounds which come within the category of VOCs and the situation is yet further complicated by different definitions and nomenclature. VOCs are present in the atmosphere as a result of human activities, arising mainly from motor exhausts, solvent usage, industrial processes, oil refining, petrol storage and distribution, landfill wastes, food manufacture, and agriculture (Piccot et al. 1992). The VOCs play important roles in a wide range of environmental problems of concern. They can cause the stratospheric ozone depletion (Programme 1992), and can also arise to the ground level photochemical smog formation (Huess and Glasson 1968). Some VOCs have toxic or carcinogenic human health effects (USEPA 1990), for example, benzene and 1,3-butadiene are potential leukemia inducing agents; others can accumulate and persist in the environment (Oehme 1991), such as the Polychlorinated Biphenyls (PCBs), Polychlorinated terphenyls (PCTs), and phathalic acid and its derivatives, and some VOCs like methane enhance the global greenhouse effects (Derwent 1994).

The USA emitted about 141 Mt of pollutants (fires and dust excluded) in 2005, containing 11.3% of VOCs (16 Mt of VOCs), mostly produced and released by the industries (USEPA 2006). The Clean Air Act Amendments of 1990 require maximum achievable control technology standards for 189 hazardous air pollutants (Lee 1991). The intent of the law is to reduce health risks to the population from chronic exposure to toxic VOCs. Ambient air quality standards set by the US Environmental Protection Agency (EPA) states that the maximum 3-hour concentration of hydrocarbon content is $1.6 \times 10^{-4}$ kg/m$^3$ (0.25 ppmv). In view of gasoline emission regulation, the US EPA Standard 40 CFR Part 63 has established an emission limit of 10 g total organic compounds (TOC)/m$^3$. The German TA-Luft Standard has set the emission limit to 0.15 g TOC/m$^3$ (Khan and Ghoshal 2000).

Many processes and technologies have been developed to control VOCs emission. There are six main processes by which a gaseous pollutant may be removed from an air stream. These processes are absorption, adsorption, thermal incineration, catalytic incineration, condensation, and flares (Schnelle and Brown 2002). Absorption and adsorption are both diffusional separation processes that can be used to collect the hazardous air pollutants. In the case of absorption, the target pollutant is transferred to the solvent. Recovery of the solvent might be undertaken by distillation or by stripping the absorbed materials from the solvent. The problem of treating the waste materials in the stream separated from the solvent remains. Adsorption can provide the means for the materials to be more readily recovered. Many organic materials may be removed by condensation. If a suitable coolant is available and the pollutant concentration is high enough, condensation can be more effective in recovering material for reuse. For organic pollutants when the concentration is high or recovering the material is not desired, incineration can be used to convert the pollutant to carbon dioxide and water. For large emissions such as those found in petroleum refineries the pollutant may be flared.

### 1.1.1. Biofiltration Technology

Biotreatment of VOCs offers an inexpensive alternative to other conventional technologies (Don and Feenstra 1984; Ottengraf 1986b) mentioned previously. Biofiltration has emerged as a reliable and cost-effective technology for the control of VOCs emissions. The biofiltration process utilizes a biological microbial film fixed on a support medium where the contaminants are absorbed from the waste gas and biologically converted to benign end products such as water and carbon dioxide.

Biofiltration is a relatively new technology used for effectively controlling VOC emissions, organic and inorganic air tonics, and odor from gaseous streams. This technology has been used in Europe for many years and is considered to be a Best Available Control Technology (BACT) for treating contaminated gaseous streams.. Biofiltration offers many potential advantages over existing control technologies, such as low installation and operation costs, low maintenance requirements, biofilter long life, and environmental safe operation.

Biofilters performance for VOCs control is strongly affected by the packing materials applied. Biofilter media are mainly of two types: natural organic media such as peat, compost, leaves, wood bark, and/or soil (Leson and Winer 1991) and inert synthetic media. Solid nutrients and buffers are incorporated directly in natural organic media, and the bed moisture level is maintained at a constant level by humidification of the influent air. Once the buffering capacity or nutrient source is exhausted, the packing materials can be restored by adding base or nutrient salts in the irrigation water, or it can be replaced. Conversely, synthetic media require the delivery of liquid nutrients and buffers to the microbial population through a nozzle system on the top of the bed. The delivery of the nutrient and buffer liquid flow is usually sufficient to provide the necessary moisture levels for microbial activity. This type of biofilter is usually referred to as a trickle-bed air biofilter (TBAB). TBABs facilitate more consistent operation than do natural media biofilters via better control of overall pressure drop, nutrient concentration, and pH. Furthermore, they do not suffer from the effects of aging as do natural media. The ideal attachment medium is characterized by a high specific surface area, minimal back pressure, and a suitable surface for the attachment of microorganisms.

The number of studies concerning the treatment of contaminated gas stream by TBABs has increased in the past decade (Sorial et al. 1993a; Sorial et al. 1993b; Sorial et al. 1994; Sorial et al. 1995; Zhu et al. 1996; Alonso et al. 1997; Chou and Huang 1997; Pedersen and Arvin 1997; Alonso et al. 1998; Alonso et al. 1999; Alonso et al. 2000; Alonso et al. 2001; Kong et al. 2001; Seignez et al. 2002; Smith et al. 2002; Arulneyam and Swaminathan 2003). Target contaminants included hydrocarbons (e.g., benzene, styrene, hexane, toluene, and naphthalene), oxygenated hydrocarbon (e.g., methanol, ethanol, diethyl ether, acetone and methyl ethyl ketone), chlorinated hydrocarbons (e.g. chlorobenzene and *o*-dichlorobenzene), and sulfur compounds (e.g., hydrogen sulfide). Factors affecting the decontamination efficiency include: nature of the contaminants, packing materials and configurations, empty bed retention time, volumetric loading rates, nutrient feed flow rates, nutrient solution pH, and flow patterns of air. Most studies were performed in bench, pilot, or pilot-field scale reactors. Studies were conducted for studying the impact of influent concentrations, empty bed retention time, nutrient concentrations, etc.

However, fluctuations in concentration and variation in the waste air composition is most commonly encountered in industry. In practice a biofilter will also be exposed to periods of non-use such as shutdown for factory retooling or equipment repair, or during weekends and holidays. Furthermore, biofilter performance is strongly dependent on source characteristics (VOCs concentration, employed loading rates, VOCs composition, and emission modes), which limits the handling efficiency and application of the biofiltration systems.

### 1.1.2. Innovative Biofiltration Technology

One approach to reduce the loading fluctuation to the biofilters is to install activated carbon (AC) bed as buffer unit before a biofilter. When the system is at periods of high VOC loading, the AC bed will act as an adsorption unit to accumulate VOCs. When the system is at periods of low VOC loading, the AC bed will release accumulated VOCs. In this manner, the AC bed could dampen fluctuations in loading to the biofilter and help maintain long-term consistent performance for the biofilter. Although this strategy was first proposed by Ottengraf (1986a) in 1986, experimental testing on this system is very limited (Weber and Hartmans 1995; Li and Moe 2005; Moe and Li 2005). Moe and Li (2005) tested toluene load equalization effect of adsorption columns packed with granular activated carbon (GAC) under intermittent loading scenario. The intermittent loading conditions consisted of 8 hours contaminant loading followed by 16 hours non-loading each day. They found that the GAC columns could successfully achieve load equalization of toluene contaminated air streams. Degree of load attenuation became more pronounced at lower contaminant concentrations and higher GAC empty bed contact times (EBCTs). Li and Moe (2005) investigated performance of an integrated system on removal of acetone and toluene mixture under intermittent loading scenario. The system integrated a granular activated carbon (GAC) bed with a biofilter packed with polyurethane foam cubes. The intermittent loading conditions consisted of 8 hours contaminant loading followed by 16 hours non-loading each day. They found that the GAC bed could lead to more uniform loading as a function of time and improve biofilter treatment performance. Furthermore, the GAC bed showed less equalization effect on acetone than on toluene due to competitive sorption. Weber and Hartmans (1995) tested the buffer capacity of a number of activated carbons to a followed biofilter packed with compost and polystyrene with fluctuating concentrations of toluene. They found that toluene fluctuations could be decreased to around 300 mg.m$^{-3}$ when toluene fluctuations ranged between 0 and 1000 mg.m$^{-3}$.

It is worthwhile to mention that all the above mentioned studies were using a single bed buffer system. A single bed buffer unit will lose buffer capacity to large fluctuations or high loading and in addition could induce an starvation period during the initial start-up period of a biofilter due to adsorption. Meanwhile, it will breakthrough in a relative short period under continuous operation. To overcome the difficulty of single bed buffer unit, a 2-bed adsorption unit with cyclic adsorption and desorption was proposed and applied as a buffer unit for the dampening fluctuating feed condition to the biofilter in Kim's research (Kim 2006).

Kim studied trickle bed air biofilter behavior for the single solute VOC (Kim 2006). He selected toluene, styrene, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) as the target VOCs. A trickle bed air biofilter integrated with a cyclic adsorption/desorption 2-fixed bed unit was investigated on the removal of toluene. The experimental results showed that the integrated system was successful in dampening the fluctuating feed conditions.

Many industrial air emissions contain mixtures of VOCs that possess various physical and chemical properties affecting their biological treatment. Therefore, this study expands the application of the integrated technology to VOC mixtures.

## 1.2. Research Objectives

The primary objective of this proposed study is to apply a novel technology for VOCs removal from contaminated gas stream that will provide stable, consistent high removal efficiency (>99%). A combined system of a 2-bed cyclic adsorption/desorption unit and TBAB was applied for this purpose. Based on previous studies on single solute (Cai et al. 2004; Cai et al. 2005; Kim et al. 2005b; Kim et al. 2005a), VOCs interchange and mixture were studied in order to mimic operations in chemical industries. The 2-bed adsorption unit would serve as a buffer for fluctuating contaminant concentration to the TBAB system and obtain stable, consistent overall efficiency of the biofiltration system. Typical contaminants in paint booth operation are selected as target VOCs. The specific objectives of this study were presented in four major phases:

**Phase I:** Characterization of TBAB for VOC interchange under step-change loadings up to critical loadings previously determined by Kim (2006): Determine the influence of interchanged VOC on the TBAB performance under step-change contaminant concentration conditions.

**Phase II:** Characterization of TBAB for VOCs mixture under two operating conditions: backwashing and starvation. The influence of step-change contaminant concentration and starvation periods on TBAB performance were studied.

**Phase III:** Evaluation of a 2-bed adsorption unit for attenuating fluctuation in the influent concentrations into the TBAB system to be within its effective removal capacity. The adsorption and desorption cycles of the 2-bed adsorption unit was simulated.

**Phase IV:** Application of a novel combined technology for removal of VOCs of concern. Long term performance was studied by employing the combined scheme of a 2-bed adsorption unit with a TBAB unit.

**Phase V:** Microbial diversity investigation for interchanging and mixture of VOCs in TBAB.

## 1.3. Structure of Dissertation

Chapter 1 introduces the research background and the objectives. Phase I for this study on VOC interchange is presented in Chapter 2. The TBAB performance under VOC interchange conditions was investigated. Re-acclimation to the interchanged VOC was studied.

For Phase II, the study on VOC mixtures is presented in Chapter 3. Two typical VOC mixtures were studied under backwashing and non-use strategies. The results from one typical VOC mixture were used to determine the operating conditions for the following integrated system experiments.

For Phase III, the study on adsorption to characterize the 2-bed unit is presented in Chapter 4. A square wave feeding condition was used to simulate the fluctuation in inlet concentrations.

For Phase IV, the study on application of VOC mixture on the integrated system is presented in Chapter 5.

For Phase V, the study on microbial diversity from samples in Phase II and III is presented in Chapter 6.

The final chapter, Chapter 7 presents a summary of this research and the conclusions, and provides recommendations for further research.

## 1.4. References

Alonso, C., Suidan, M. T., Kim, B. R., and Kim, B. J. (1998). "Dynamic mathematical model for the biodegradation of VOCs in a biofilter: Biomass accumulation study." *Environmental Science & Technology*, 32(20), 3118-3123.

Alonso, C., Suidan, M. T., Sorial, G. A., Smith, F. L., Biswas, P., Smith, P. J., and Brenner, R. C. (1997). "Gas treatment in trickle-bed biofilters: Biomass, how much is enough?" *Biotechnology and Bioengineering*, 54(6), 583-594.

Alonso, C., Zhu, X. Q., Suidan, M. T., Kim, B. R., and Kim, B. J. (2000). "Parameter estimation in biofilter systems." *Environmental Science & Technology*, 34(11), 2318-2323.

Alonso, C., Zhu, X. Q., Suidan, M. T., Kim, B. R., and Kim, B. J. (2001). "Mathematical model of biofiltration of VOCs: Effect of nitrate concentration and backwashing." *Journal of Environmental Engineering-Asce*, 127(7), 655-664.

Alonso, C., Zhu, Y., Suidan, M. T., Kim, B. R., and Kim, B. J. (1999). "Mathematical model for the biodegradation of VOCs in trickle bed biofilters." *Water Science and Technology*, 39(7), 139-146.

Arulneyam, D., and Swaminathan, T. (2003). "Biodegradation of methanol vapor in a biofilter." *Journal of Environmental Sciences*, 15(5), 691-696.

Cai, Z., Kim, D., and Sorial, G. A. (2004). "Evaluation of trickle-bed air biofilter performance for MEK removal." *Journal of Hazardous Materials*, 114(1-3), 153-158.

Cai, Z., Kim, D., and Sorial, G. A. (2005). "Removal of methyl isobutyl ketone from contaminated air by trickle-bed ai biofilter." *Journal of Environmental Engineering,* 131(9), 1322-1329.

Chou, M. S., and Huang, J. J. (1997). "Treatment of methylethylketone in air stream by biotrickling filters." *Journal of Environmental Engineering*, 123(6), 569-576.

Derwent, R. G. (1994). "Non-$CO_2$ greenhouse gases. Why and how to control?" Kluwer Academic Publisher, Dordrecht, The Netherlands, 289.

Don, J. A., and Feenstra, L. "Odor abatement through biofiltration." *Pro., Symp. on Characterization and Control of Odoriferous Pollutants in Process Industries*, Louvain-la-Neuve, Belgium, 337-349.

Huess, J. M., and Glasson, W. A. (1968). "Hydrocarbon reactivity and eye irritation." *Environmental Science & Technology*, 2, 1109-1116.

Khan, F. I., and Ghoshal, A. K. (2000). "Removal of volatile organic compounds from polluted air." *Journal of Loss Prevention in the Process Industries*, 13(6), 527-545.

Kim, D. (2006). "Development of integrated treatment scheme of adsorption and biofiltration for VOCs removal," In *Civil and Environmental Engineering*, Ph.D. dissertation, University of Cincinnati, Cincinnati, Ohio, USA.

Kim, D., Cai, Z., and Sorial, G. A. (2005a). "Behavior of trickle bed air biofilter for toluene removal: effect of non-use periods." *Environmental Progress*, 24(2), 155-161.

Kim, D., Cai, Z., and Sorial, G. A. (2005b). "Evaluation of trickle-bed air biofilter performance under periodic stressed operating conditions as a function of styrene loading." *Journal of the Air & Waste Management Association*, 55(2), 200-209.

Kong, Z., Farhana, L., Fulthorpe, R. R., and Allen, D. G. (2001). "Treatment of volatile organic compounds in a biotrickling filter under thermophilic conditions." *Environmental Science & Technology*, 35(21), 4347-4352.

Lee, B. (1991). "Highlights of the Clean Air Act Amendments of 1990." *Journal of the Air & Waste Management Association*, 41(1), 16-19.

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

Li, C., and Moe, W. M. (2005). "Activated carbon load equalization of discontinuously generated acetone and toluene mixtures treated by biofiltration." *Environmental Science & Technology*, 39(7), 2349-2356.

Moe, W. M., and Li, C. (2005). "A design methodology for activated carbon load equalization systems applied to biofilters treating intermittent toluene loading." *Chemical Engineering Journal*, 113(2-3), 175-185.

Oehme, M. (1991). "Dispersion and transport paths of toxic persistent organochlorines to the Arctic:levels and consequences." *The Science of The Total Environment*, 106(1-2), 43-53.

Ottengraf, S. P. P. (1986a). *Biotechnology*, VCH Verlagsgesellschaft, Weinheim.

Ottengraf, S. P. P. (1986b). "Exhaust Gas Purification." Biotechnology, H. J. a. R. Rehn, G., ed., VCH Verlagsgesellsch, Weinheim, Germany, 425-452.

Pedersen, A. R., and Arvin, E. (1997). "Toluene removal in a biofilm reactor for waste gas treatment." *Water Science and Technology*, 36(1), 69-76.

Piccot, S. D., Watson, J. J., and Jones, J. W. (1992). "A global inventory of volatile organic

compound. emissions from anthropogenic sources." *Journal of Geophysical Research-Atmosphere*, 97, 9897-9912.

Programme, U. N. E. (1992). "Montreal Protocol on the Protection of the Ozone Layer." Nairobi, Kenya.

Schnelle, K. B., and Brown, C. A. (2002). *Air pollution control technology handbook*, CRC press, Boca Raton, FL.

Seignez, C., Atti, A., Adler, N., and Peringer, P. (2002). "Effect of biotrickling filter operating parameters on chlorobenzenes degradation." *Journal of Environmental Engineering*, 128(4), 360-366.

Smith, F. L., Sorial, G. A., Suidan, M. T., Biswas, P., and Brenner, R. C. (2002). "Development and demonstration of an explicit lumped-parameter biofilter model and design equation incorporating Monod kinetics." *Journal of the Air & Waste Management Association*, 52(2), 208-219.

Sorial, G. A., Smith, F. L., Suidan, M. T., Biswas, P., and Brenner, R. C. (1995). "Evaluation of trickle-bed biofiltermedia for toluene removal." *Journal of the Air & Waste Management Association*, 45(10), 801-810.

Sorial, G. A., Smith, F. L., Suidan, M. T., Smith, P. J., Biswas, P., and Brenner, R. C. "Development of aerobic biofilter design criteria for treating VOCs." *86th Annual Meeting and exhibition of the Air & Waste management Association*, Denver, CO.

Sorial, G. A., Smith, F. L., Suidan, M. T., Smith, P. J., Biswas, P., and Brenner, R. C. "Evaluation of biofilter media for treatment of air streams containing VOCs." *Proceedings of Water Environment Federation 66th Annual Conference and Exposition*, Anaheim, CA, 429-439.

Sorial, G. A., Smith, F. L., Suidan, M. T., Smith, P. J., Biswas, P., and Brenner, R. C. "Evaluation of performance of trickle bed biofilter-impact of periodic removal of accumulated biomass." *87th Annual Meeting and Exhibition of the Air & Waste Management Association*, Cincinnati, OH.

USEPA. (1990). "Cancer risk from outdoor exposure to air toxics." USEPA OAQPS, Research Triangle Park, North Carolina.

USEPA. (2006). *Toxic release inventory program*. available on the World Wide Web at http://www.epa.gov/tri/index.htm (accessed on June 2005)

Weber, F. J., and Hartmans, S. (1995). "Use of activated carbon as a buffer in biofiltration of waste gases with fluctuating concentrations of toluene." *Applied Microbiology and Biotechnology*, 43(2), 365-369.

Zhu, X., Rihn, M. J., Suidan, M. T., Kim, B. J., and Kim, B. R. (1996). "The effect of nitrate on VOC removal in trickle bed biofilters." *Water Science and Technology*, 34(3-4), 573-581.

# CHAPTER 2

# TBAB STUDY UNDER INTERCHANGING VOCs

## 2.1. Abstract

Trickle bed air biofilters (TBABs) were evaluated under conditions of an interchange of the feed volatile organic compounds (VOCs). Two aromatic compounds (toluene and styrene) and two oxygenated compounds (methyl ethyl ketone and methyl isobutyl ketone) were interchanged as single solutes. The obtained results revealed that the biofilter provided high removal efficiency within the critical loading, which was previously defined in the non-interchanging VOC-fed biofilters. The biofilter easily acclimated to the oxygenated compounds (MEK and MIBK), but re-acclimation was delayed for the aromatic compounds (toluene and styrene). Ratios of the molar mass of $CO_2$ produced per molar mass of VOC removed were investigated. It has been found that the ratios for the aromatic compounds closely resembled the theoretical complete chemical oxidation based ratios while larger differences were encountered with the oxygenated compounds. Oxygenated compounds had higher removal rates along the biofilter media depth than the aromatic. The nitrogen utilization difference between oxygenated compounds and aromatic compounds was reduced significantly under the interchanging conditions as compared to the difference under long term operation of single solute system.

## 2.2. Introduction

Biological treatments are operated best on steady loads of the contaminant. However, variations in contaminant load are common in real applications. The biological solids in a plug-flow reactor can not effectively withstand shock loads as compared to a completely mixed reactor because the incoming contaminant is dispersed uniformly in the latter reactor. Biofilters for VOC control in gaseous waste stream are hydraulically very similar to plug-flow reactors.

During the past decade, numerous studies were performed at the bench, pilot, or pilot-field scale reactors to evaluate the effect of inlet concentration on biofiltration performance (Sorial et al. 1993; Sorial et al. 1994; Sorial et al. 1995; Deshusses et al. 1996; Chou and Huang 1997; Pedersen and Arvin 1997; Krailas et al. 2000; Kong et al. 2001; Atoche and Moe 2004; Cai et al. 2004; Cai et al. 2005; Kim et al. 2005b; Kim et al. 2005a). Target contaminants included hydrocarbons (e.g., benzene, styrene, hexane, toluene, and naphthalene), oxygenated hydrocarbon (e.g., methanol, ethanol, diethyl ether, acetone and methyl ethyl ketone), chlorinated hydrocarbons (e.g. chlorobenzene and *o*-dichlorobenzene), and sulfur compounds (e.g., hydrogen sulfide). Factors affecting decontamination efficiency include: nature of the contaminants, packing materials and biofilter configurations, empty bed retention time, volumetric loading rates, nutrient feed flow rates, nutrient solution pH, and flow patterns of air.

Jorio et al. (2000a) and Sorial et al. (1998) studied the effect of variation of styrene inlet concentration and gas flow rate on the overall biofilter performance. They found that excess biomass accumulated within the biofilter decreased the over-all biofilter performance when the employed inlet concentration exceeded the removal capacity of the biofilter. Deshusses et al. (1996) studied the transient behavior of a biofilter under step change of MEK and MIBK concentrations. They found that the biofilter adapted rapidly (2-5 hours) to the new operating conditions. Cai et al. ( 2004; 2005) studied the biofilter behavior in removing oxygenated compounds, they found that the biofilter could maintain high removal efficiency when the employed loading rate did not exceed its elimination capacity. They also found that oxygenated compounds favored biomass growth which would cause channeling in the biofilter and lead to decrease the biofilter performance. Periodic backwashing operation with media fluidization was necessary for removing the excess biomass in order to maintain a stable high performance.

Biofilter re-acclimation after backwashing or non-use due to shutdown for factory retooling or equipment repair, or during weekends and holidays is an important factor in biofilter operation. To obtain consistent performance and to control the biofilter more effectively, some researchers have focused on biofilter re-acclimation. Torronen et al. (1992) found that 2-4 hours were required following a two-day period of non-use and that five hours were required following a five day period of non-use, for removal efficiency to return to previous levels for hexane and phenolic compounds. Togna and Frisch (1993) reported styrene reacclimation periods after two or more days without chemical contact. Standefer and Van Lith (1993) reported that biofilter removal efficiency returned to previous levels after one hour following a two day period of non-use and after 5-8 hours following a seven day period of non-use. Martin and Loehr (1996) reported biofilter reacclimation after restart-up from two intermittent periods. Moe and Qi (2004) found that weekend shut-down periods caused varying effects on removal efficiency for different compounds. Cai et al. (2004; 2005) and Kim et al. (2005b; 2005a) found that non-use periods did not have noticeable adverse effect on removal efficiency when the employed loading rates did not exceed the elimination capacity of the biofilters and non-use operation could be employed as a means of biomass control for these loading rates.

It is worthwhile to note that biofilters operating in industry are exposed to a spectrum of changing conditions, particularly when are assigned to the treatment of waste air for discontinuous processes. In chemical industries, the most common variation in the waste air composition is weekly rotation in the production. In general, microbial ecosystems are able to respond in a very dynamic manner to changes in their environment, particularly to changes that stress the community (Madigan et al. 2002). However, the greater the variability of substances to be controlled, the greater is the constraints placed on the ability of the biofilter to control VOCs. To our best knowledge, the effects of the interchange of the feed VOCs on biofilter performance have not been fully understood yet. Martin and Loehr (1996) investigated the re-acclimation following changes of contaminant in a biofilter packed with municipal compost. They found that re-acclimation from benzene to toluene was 5.5 hours, 8.1 hours from toluene to benzene, 13 days from benzene to p-xylene, and 14 days from p-xylene to benzene. Still, knowledge about the biofilter performance in adjusting to the new compound needs to be known before hand in a real application.

When VOCs with different physiochemical properties are treated by rotation in a biofilter, the empty bed retention time (EBRT) can be the most important factor in controlling the biofilter performance. In previous studies (Cai et al. 2004; Cai et al. 2005; Kim et al. 2005b; Kim et al. 2005a), biofilter performance for single VOC removal was optimized. It was found that aromatic compounds required longer EBRTs to be utilized than the oxygenated compounds. In general, biofilter performance depends on EBRT. Numerous studies (Kiared et al. 1997; Sorial et al. 1997; Jorio et al. 2000b; Namkoong et al. 2004) reported that an increase of the gas flow rate provides an inverse effect on the elimination capacity and removal efficiency in the biofilter. This can be due to the decrease in the contact time between the pollutant and the microbial population and also a result from the physicochemical properties of the VOCs.

In this study, the impact of interchanging VOCs on the biofilter performance was explored by using three independent parallel lab-scale trickle-bed air biofilters (TBABs). As the empty bed residence time (EBRT) was expected to be the most critical parameter in the condition of interchanging feed VOCs, two biofilters were operated at different EBRTs for different VOCs. The third biofilter was operated under a constant EBRT for all VOCs. The objective of this research was, therefore, to investigate a TBAB behavior under the interchange of feeding VOCs. The evaluations are focused on the following issues: (1) VOC loading rates and elimination capacity, (2) re-acclimation of biofilter after interchanging VOCs, (3) $CO_2$ production.

## 2.3. Materials and Methods

### 2.3.1. Selection of VOCs

The experimental work was performed on three independent parallel trains lab-scale TBABs, named “A”, “B”, and “C” under the interchange of the feed VOCs. Two aromatic compounds (toluene and styrene - Henry’s law constant 0.00674 and 0.00261 atm·$m^3$/mole at 25 °C, respectively) (Watts 1998; Verschueren 2001) and two oxygenated compounds (methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) -Henry’s law constant $1.49 \times 10^{-5}$ and $4.66 \times 10^{-5}$ atm·$m^3$/mole at 25 °C, respectively) (Watts 1998; Verschueren 2001) were employed in this study. The VOCs of concern are common solvents employed in the industry and are major components of paints and varnishes.

### 2.3.2. Experimental Biofilter System

The experimental work was performed on three independent and parallel lab-scale biofilters. The schematic diagram of the experimental system is presented in Figure 2-1. The biofilter is constructed of seven cylindrical glass sections (Ace Glass Inc., Vineland, NJ) with an internal diameter of 76 mm and a total length of 130 cm. The biofilter is equipped with sampling ports to allow sampling of the stream entering and leaving the biofilter, as well as axially along the medium bed. The biofilter is packed with pelletized diatomaceous earth biological support media (Celite® 6 mm R-635 Bio-Catalyst Carrier; Celite Corp., Lompoc, CA) to a depth of about 60 cm. The properties of the pellets are provided elsewhere (Sorial et al. 1995). The biofilters were placed at constant operating temperature of 20 $^oC$ in a constant temperature chamber. Operations of the biofilters were conducted in a co-current gas and liquid downward flow mode.

The air supplied to the biofilter is purified by complete removal of water, oil, carbon dioxide, VOCs, and particulates by Balston FTIR purge gas generator (Paker Hannifin Corporation, Tewksbury, MA). The air pressure is reduced to 20 psig (140 kPa) by a pressure control valve. The air flow to the biofilters was regulated by mass flow controllers (MKS Model 247C four-channel read-out mass flow controller, Andover, Mass). The air flow to the biofilter was set up at the rate of 3.6 L/min for both MIBK and MEK with corresponding empty bed retention time (EBRT) of 0.76 min, while 2.22 L/min, EBRT 1.23 min for toluene, 1.35 L/min, EBRT 2.20 min for styrene. Liquid VOC was injected via a syringe pump (Harvard Apparatus, model NP 70-2208, Holliston, MA) into the air stream where it vaporized, and entered the biofilter through the topmost side port of the column. Each VOC inlet concentration was stepwise increased from 50 ppmv to the maximum allowable inlet concentration, for attaining over 99% removal, which was determined previously by the authors (Cai et al. 2004; Cai et al. 2005; Kim et al. 2005b; Kim et al. 2005a).

The biofilter was equipped with an independent system for feeding buffered nutrient solution, 1.5 L/day for both MIBK and MEK, 2.4 L/day for both toluene and styrene. The feed was sprayed as a fine mist onto the top of the medium bed through a spray nozzle (Corrigan Corporation, Northbrook, IL). The buffered nutrient solution was made from deionized and activated carbon filtered water, according to a formulation that contains all necessary macronutrients, micronutrients, and buffers, as described in a previous study (Sorial et al. 1998). The nutrient formulation for the biofilters contained the same amount of nutrient-nitrogen and phosphorus ratio of a given VOC loading (a COD-to nitrogen ratio of 50:1 and a nitrogen-to-phosphorous ratio of 4:1). Since a coordinated biomass control strategy is unavoidable to attain consistent high removal efficiency of the biofilter, the biomass control strategy for this study involved a periodic *in-situ* upflow washing with the nutrient solution, i.e. backwashing, at a rate of 1 hour a week during the experimental period.

### 2.3.3 Biofilter Operation

The three biofilters continued to be run without reconditioning the media used in pervious runs where MEK (namely, biofilter “A”), MIBK (namely, biofilter “B”), and styrene (namely, biofilter “C”) had been the sole VOC contaminants (Cai et al. 2004; Cai et al. 2005; Kim et al. 2005b). The feed VOCs were stepwise interchanged in the sequence of aromatic compounds and oxygenated compounds or the reverse order. The inlet VOC concentrations were varied from 50 ppmv to the maximum allowable concentration, which was determined to be the corresponding critical loading obtained in a previous study (Cai et al. 2004; Cai et al. 2005; Kim et al. 2005b; Kim et al. 2005a). The critical loadings were 3.52, 1.90, 5.63, 3.26 kg COD/m$^3$·day for toluene, styrene, MEK, and MIBK, respectively. In order to evaluate the biofilter performance under different EBRTs, the operation of biofilter “A” and “B” was conducted at different EBRTs for each feed VOC. These EBRTs corresponded to the stable biofilter performance for 99% removal of each VOC (Cai et al. 2004; Cai et al. 2005; Kim et al. 2005b; Kim et al. 2005a). Biofilter “C” was run at a constant EBRT of 2.02 min. This EBRT corresponded to a stable biofilter performance for 99% removal of styrene (Kim et al. 2005b). The conditions for this study are summarized in Table 2-1.

Since a coordinated biomass control strategy is unavoidable to attain consistent high removal efficiency of the biofilter, the biomass control strategy for this study involved a periodic *in-situ* upflow washing with the nutrient solution, i.e. backwashing, at a rate of 1 hour a week during the experimental period. The backwashing was conducted while the biofilter was shut off by recycling 18 L of the buffered nutrient solution to fluidize the media for a defined time period. Finally, the recycle was shut off and another 18 L of the buffered nutrient solution was passed through the column as a rinse. The backwashing duration and frequency were initially set at 1 hour duration per week for a period of three weeks for each loading rate (if necessary, the backwash duration was extended to 2 hours). Compressed air was introduced if necessary to help break up and scour the media. A schematic diagram of the backwashing system is presented in Figure 2-2.

### 2.3.4. Analytical Methods

Gas phase samples for VOC analysis were taken with gas-tight syringe. These VOC concentrations were measured by chromatographic separation on a 30-m length, 0.25 mm inner diameter, 0.25 μm film narrowbore column (DB 624, J and W Scientific, Folsom, CA) using a gas chromatograph (GC) (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with a flame ionization detector (FID). The GC oven temperature was programmed from 40 °C to 120 °C at rate of 10 °C/min with a 2-min hold at 40 °C and a 2-min hold at 120 °C. The carrier gas ($N_2$) flow rate was set at 2.3 mL/min. The FID detector was used with $N_2$ make-up gas at a flow rate of 20 mL/min, a fuel gas flow ($H_2$) of 30 mL/min, and an oxidizing gas flow (air) of 300 mL/min. The detector temperature was 250 °C.

Effluent gas phase sample for $CO_2$ analysis were also taken by using gas-tight syringes through sampling ports in the biofilter. A GC equipped with a thermal conductivity detector (TCD) was used for determining the $CO_2$ concentrations in the effluent gas phase. The GC oven temperature was programmed from 50 °C to 80 °C at 10 °C/min with a 3.2 min hold at 50 °C and a 1.5 min hold at 80 °C. The carrier gas (He) flow rate was set at 30 ml/min, and the TCD detector was used with He make-up gas at flow-rate of 35 ml/min.

Liquid phase samples were analyzed for $NO_3^-$-N, total carbon (TC), inorganic carbon (IC), and volatile suspended solid (VSS) concentration. $NO_3^-$-N was determined according to Standard Methods 4500-$NO_3^-$ B (Standard Methods, 1998) by using a Shimadzu UVmini 1240 UV-VIS spectrophotometer (Shimadzu Corp., Tokyo, Japan) at a wavelength of 220 nm. Samples were filtered through 0.45μm nylon filters (Micron Separation, Westboro, MA) prior to analysis. TC and IC were determined by using a Shimadzu TOC 5050 analyzer (Shimadzu Corp., Tokyo, Japan) according to Standard Methods 5310 (Standard Methods, 1998). The VSS concentrations in the effluent and backwashing water were determined according to Standard Methods 2540 G (Standard Methods, 1998). pH was determined using a Fisher Accumet pH meter, Model 50 (Fisher Scientific Co., Inc., Fair Lawn, NJ). Pressure drop along the biofilters was monitored by a digital manometer (Modus Instruments, Inc., Clinton, MA).

Table 2-1. Experimental conditions for this study

| | Stage I | Stage II | Stage III | Stage IV | Stage V |
|---|---|---|---|---|---|
| **Biofilter A** | | | | | |
| Feed VOC | MEK | Toluene | MIBK | Styrene | MEK |
| Inlet concentration, ppmv | 400 | 50-250 | 50-150 | 50-200 | 400 |
| Loading rate, kg COD/$m^3$·day | 5.63 | 1.14-5.72 | 1.09-3.26 | 0.47-1.90 | 5.63 |
| EBRT, min | 0.76 | 0.76, 1.23 | 0.76 | 2.02 | 0.76 |
| **Biofilter B** | | | | | |
| Feed VOC | MIBK | Toluene | MEK | Styrene | MIBK |
| Inlet concentration, ppmv | 150 | 50-250 | 200-400 | 50-200 | 150 |
| Loading rate, kg COD/$m^3$·day | 3.26 | 0.7-3.52 | 2.8-5.63 | 0.47-1.90 | 3.26 |
| EBRT, min | 0.76 | 1.23 | 0.76 | 2.02 | 0.76 |
| **Biofiler C** | | | | | |
| Feed VOC | Styrene | MEK | Toluene | MIBK | Styrene |
| Inlet concentration, ppmv | 200 | 50-1075 | 50-400 | 50-400 | 200 |
| Loading rate, kg COD/$m^3$·day | 1.90 | 0.26-5.63 | 0.43-3.52 | 0.40-3.26 | 1.90 |
| EBRT, min | 2.02 | 2.02 | 2.02 | 2.02 | 2.02 |

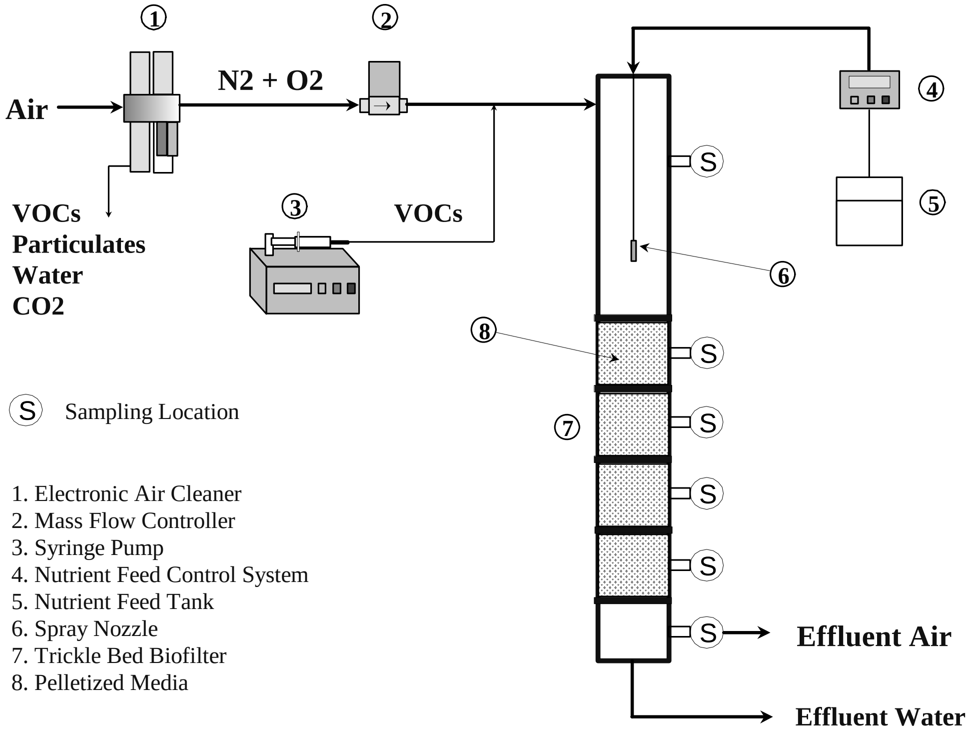


Figure 2-1 Schematic diagram for TBAB system

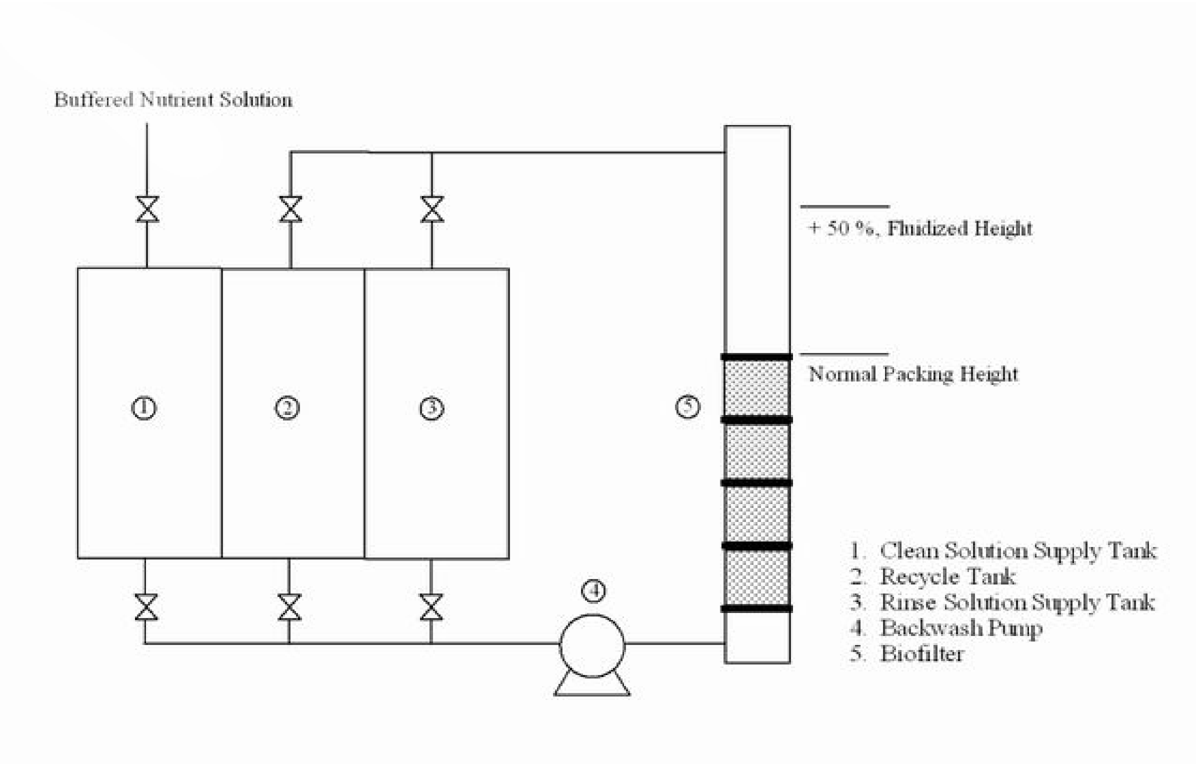


Figure 2-2 Schematic diagram for backwashing system

## 2.4. Results and Discussion

### 2.4.1. TBAB Performance Overview

The performance of biofilter "A", "B" and "C" with respect to VOCs removal is shown in Figure 2-3, Figure 2-4 and Figure 2-5, respectively. Since the VOCs were fed within the critical loading capacity, apparently high removal performances have been achieved for both biofilters during the experimental period.

#### 2.4.1.1. Biofilter "A"

The biofilter "A" performance with respect to VOC removal is shown in Figure 2-3. The feed VOCs were interchanged in the sequence MEK (stage I) → toluene (stage II) →

MIBK (stage III) → styrene (stage IV) → MEK (stage (V).

Stage I was the last 20 days of a previous MEK biofilter study (Cai et al. 2004) at an inlet concentration of 400 ppmv with a corresponding loading rate of 5.63 kg COD/m$^3$-day and 0.76 min EBRT. In stage II, the contaminant was switched to toluene and the EBRT was initially maintained at 0.76 min EBRT. The biofilter got re-acclimated to the 99% removal for 50 ppmv and 100 ppmv inlet concentration, but failed to get re-acclimated for the 250 ppmv even after 31 days of operation. Furthermore, the removal efficiency decreased to 80.4% just prior to the next backwashing. An inlet concentration of 250 ppmv with a corresponding loading rate of 5.72 kg COD/m$^3$-day loading rate exceeded the elimination capacity limit 3.52 kg COD/m$^3$-day (see Table 1) and the 0.76 min EBRT was thought to be not long enough for obtaining a consistent high performance (>99%). Thus on day 62 after backwashing, the EBRT for toluene was increased to 1.23 min while maintaining the inlet concentration at 250 ppmv, which provided a critical loading rate of 3.52 kg COD/m$^3$-day. The overall removal efficiency increased to 92 % just prior to the next backwashing. On day 69, after backwashing was conducted, the removal efficiency increased to 95.7% on the next day, but decreased to 74.5% on day 72. On day 76, after backwashing was conducted, the removal efficiency recovered to 88.9% in 300 min. The removal level was maintained at 92-93% during this cycle. On day 84, after backwashing was conducted, the removal efficiency recovered to 99.3% in 300 min, but decreased to 84.3% just prior to the next backwashing. Twelve backwashing cycles were conducted at this loading rate. Although the overall removal efficiency increased gradually to 99% after backwashing, this removal level could not be maintained for the whole cycle. The removal efficiency was ranging from 92% to 99% during the last two backwashing cycles. The performance in the twelve backwashing cycles for a loading rate of 3.52 kg COD/m$^3$-day showed that the biofilter reached its maximum removal capacity under the current operation conditions.

On day 132, stage III was started. After backwashing was conducted, the target VOC was changed to MIBK with an initial concentration of 50 ppmv at 0.76 min EBRT. The biofilter obtained consistent 99% removal efficiency up to 150 ppmv inlet concentration corresponding to the critical loading rate of 3.26 kg COD/m$^3$-day. On day 159, after backwashing, the VOC was switched to styrene (stage IV) at 50 ppmv initial inlet concentration and 2.02 min EBRT. The biofilter re-acclimated to the 99% removal level after one day and maintained this consistent removal level up to the critical loading rate of 1.90 kg COD/m$^3$-day. However, it is worth mentioning that the re-acclimation was delayed with the increase of the employed loading rates. In stage V, the target VOC was switched back to MEK with 400 ppmv inlet concentration (5.63 kg COD/m$^3$-day) at 0.76 min EBRT. The biofilter obtained consistent over 99% removal efficiency at this loading rate. Figure 2-3 illustrates the time course of the experiment for biofilter “A”.

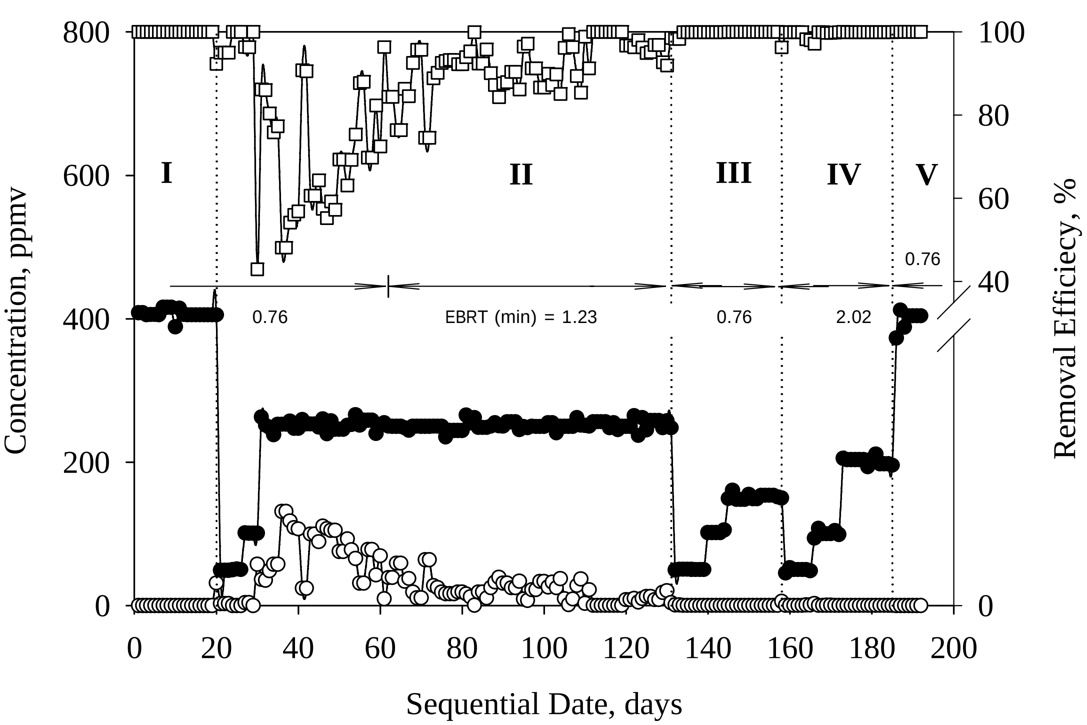


Figure 2-3 Performance of biofilter A as a function of feed VOCs: (I) MEK, (II) Toluene, (III) MIBK, (IV) Styrene, (V) MEK. (□ Removal efficiency, %; ● Inlet concentration, ppmv; ○ Outlet concentration, ppmv)

### 2.4.1.2. Biofilter "B"

The feed VOCs were interchanged in the sequence of MIBK, followed by toluene, MEK, styrene, and finally MIBK. It was started up at 150 ppmv MIBK and a 0.76 EBRT with the corresponding loading rate of 3.26 kg COD/m$^3$·day (stage I represents the last 15 days in a previous study (Cai et al. 2005)). At an EBRT of 0.76 min, toluene was fed up to and within the critical loading rate of 3.52 kg COD/m$^3$·day. At low inlet concentrations of 50 ppmv and 100 ppmv, 99 % removal efficiency was attained after slightly greater than one day of re-acclimation. However, at higher inlet concentration of 150 and 250 ppmv, the removal efficiency initially dropped below 85 %. On day 27, the inlet molar flow of the nitrate-nitrogen in the liquid nutrient was increased to 44 mmol/day in order to be equivalent to that of biofilter “C”. But, the removal efficiency still remained below 85 %. It has been noted by other researchers that large gas flow rate can have an adverse effect on the removal efficiency of a biofilter (Jorio et al. 2000b). Thus, on day 37, the EBRT was increased to 1.23 min. By day 44, the removal efficiency gradually increased to about 94 %. On day 50 when backwashing was conducted, 2243 g VSS/m$^3$ was washed out. Consequently, the removal efficiency dropped to as low as 75 % before regaining the 99 % level on day 55. In a previous study (Kim et al. 2005a), about 1305 g VSS/m$^3$ of biomass was removed through backwashing at the present study, but a constant removal efficiency was attained. From the results of the two studies taken together, it appears that much longer re-acclimation after backwashing was involved in the current study due to removal of a greater amount of accumulated biomass. By day 96, the removal efficiency was over 99%, but it decreased to about 85 % prior to backwashing, which could be a result of mass transfer limitation as the available surface was reduced by biomass accumulation. On day 97, stage III was started up with MEK. The removal efficiency remained stable at the 99% level up to 5.63 kg COD/m$^3$·day. After interchanging the feed VOC to styrene (stage IV), the removal efficiency initially dropped to 70 %, but rose to 99% in 20 hours, and remained at that level. Finally, MIBK was fed into the biofilter at the critical loading rate of 3.26 kg COD/m$^3$·day and the removal efficiency was measured at over 99 %. Figure 2-4 illustrates the time course of the experiment for biofilter “B”.

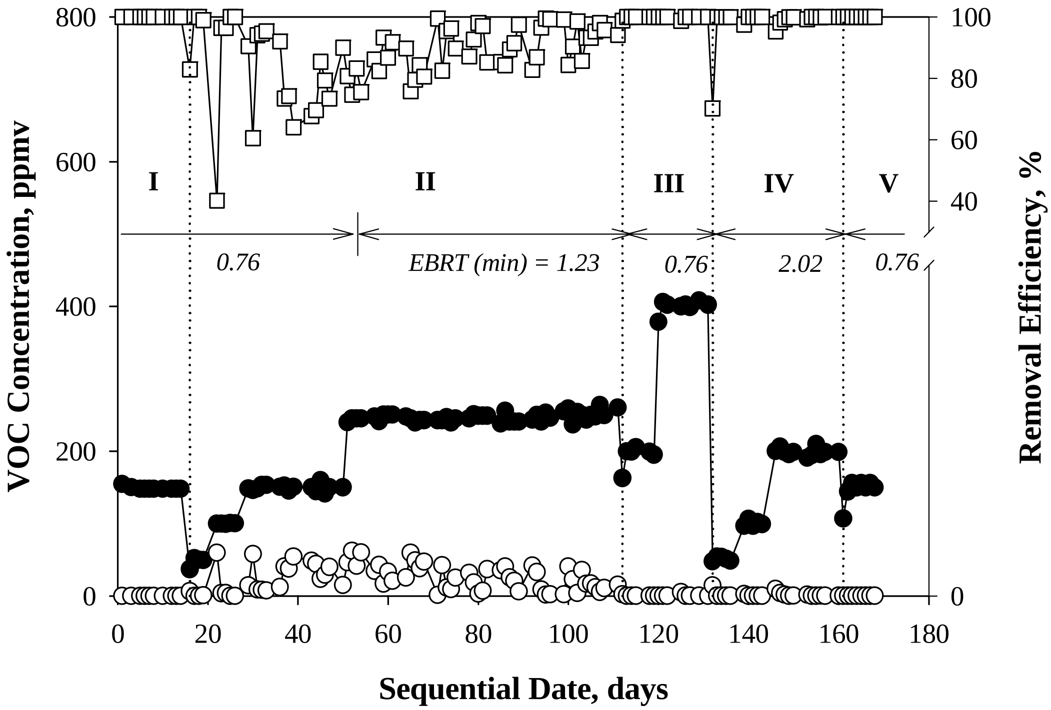


Figure 2-4 Performance of biofilter B as a function of feed VOCs: (I) MIBK, (II) Toluene, (III) MEK, (IV) Styrene, (V) MIBK. (□ Removal efficiency, %; ● Inlet concentration, ppmv; ○ Outlet concentration, ppmv)

### 2.4.1.3. Biofilter "C"

This biofilter was run at a constant EBRT of 2.02 min. The feed VOCs were interchanged in the sequence of styrene, followed by MEK, toluene, MIBK, and finally styrene. Operation stage I was the last 15 days in a previous study (Kim et al. 2005b), in which the styrene was fed at the loading rate of 1.90 kg COD/m$^3$·day with a corresponding inlet styrene concentration of 200 ppmv. Stage II was conducted with MEK, which was fed within the critical loading rate of 5.63 kg COD/m$^3$·day. However, at inlet MEK concentration of 1075 ppmv the removal efficiency dropped to as low as 80 % prior to backwashing. In the biofiltration of MEK as sole contaminant, over 99% removal performance was observed at this loading rate (Cai et al. 2004), but the corresponding inlet concentration was 400 ppmv at 0.76 EBRT. It is speculated that the high inlet concentration in the current study caused the biofilter performance to deteriorate due to oxygen limitations within the biofilm. Yang et al. (Yang et al. 2002) also demonstrated that at high VOC inlet concentration, limitation of nutrients or oxygen in the biofilm can cause deterioration in the biofilter performance.

During stage III, MEK was interchanged with toluene. At 250 ppmv inlet toluene concentration, the removal efficiency decreased to 85 % on day 77 and day 83 prior to the backwashing. In order to improve the desired high removal efficiency by increasing the nitrogen diffusion driving force (Zhu et al. 2001), the inlet molar flow of the nitrate-nitrogen in the liquid nutrient was increased to 44 mmol/day on day 83. On the third day, the overall removal efficiency was over 99 % and remained at this level. When MIBK was fed (Stage IV), the biofilter provided a consistent high removal performance within the critical load. Finally, styrene was introduced into the biofilter at the critical loading rate and the 99 % removal performance was attained. Figure 2-5 illustrates the time course of the experiment for biofilter “C”.

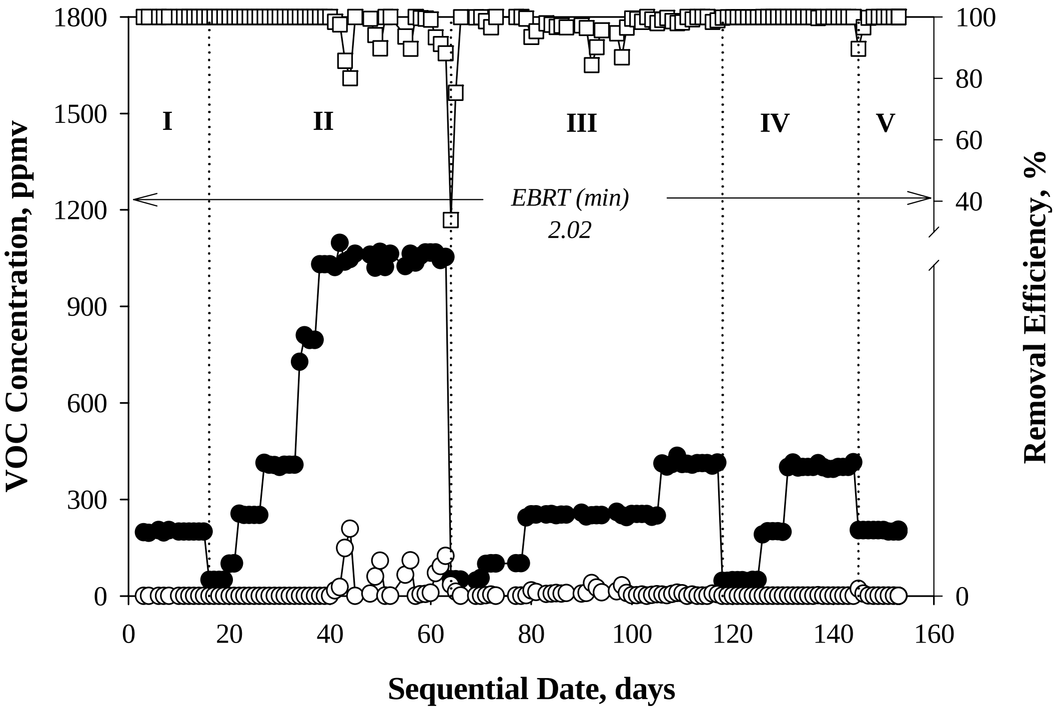


Figure 2-5 Performance of biofilter C as a function of feed VOCs: (I) Styrene, (II) MEK, (III) Toluene, (IV) MIBK, (V) Styrene. (□ Removal efficiency, %; ● Inlet concentration, ppmv; ○ Outlet concentration, ppmv)

### 2.4.2. Biofilter Response after an Interchange of Feed VOCs

In order to investigate the initial response of each biofilter after an interchange of feed VOCs, effluent samples were collected at prescheduled time intervals to evaluate the biofilter response. Re-acclimation period was considered to have been achieved when 99 % of the original biofilter performance was attained. The results obtained are presented in Figure 2-6.

It is observed that MEK and MIBK have much better biofilter recovery immediately after VOC interchange as compared to the other two VOCs (styrene and toluene). In general, it was seen that the biofilter recovered to the 99 % removal within 30 and 300 min after interchanging to MEK and MIBK, respectively, regardless of the previous VOC. However, re-acclimation period for toluene and styrene removal was delayed to 4 and 2 days, respectively. It is common that microorganisms exposed to a new substrate may require a period of acclimation before they begin vital degradation. Furthermore, the acclimation of a microbial community to a new substrate is dependent on its chemical structure (Alexander 1999). It is worthwhile to note that the toxicity of the substrate to a microbial community is dependent on its concentration. Materials that are toxic to one species may enhance the metabolism in another or may have no effect (Gaudy and Gaudy 1980). In this study, it was found that oxygenated compounds such as MEK and MIBK were utilized as a new substrate without any retardation in removal efficiency, while aromatic compounds such as toluene and styrene needed relatively long reacclimation period.

In general, metabolism of aromatic compounds is much complicated as compared to that of oxygenated compounds (Gaudy and Gaudy 1980). Aerobic biodegradation of an aromatic compound involves two steps: activation of the ring involving the incorporation of molecular oxygen into the ring, and ring cleavage involving the cleavage of the bond between carbon atoms of the two hydroxyl groups (Eweis et al. 1998). Furthermore, it is speculated that the mass transfer difference between the oxygenated compounds and aromatic compounds plays an important role in the re-acclimation behavior. For aromatic compounds, the dimensionless Henry’s law constants for styrene and toluene are 0.109 and 0.280, respectively (Watts 1998). In case of the oxygenated compounds, MEK and MIBK, the dimensionless Henry’s constants are 0.00194 and 0.00062, respectively

(Watts 1998). Hence, it is speculated that the microorganisms in the biofilter will have more available carbon in case of oxygenated compounds because of their low Henry's law constants and will favor their growth and eventually will allow re-acclimation response of the biofilter to be quicker as compared to the aromatic compounds.

It is also apparent from Figure 2-6 that with respect to toluene and styrene, biofilter "B" was more effective than biofilter "A" and "C" in recovering to a 99 % removal efficiency. The different behaviors of biofilter "A" and biofilter "B" are further discussed in the following section.

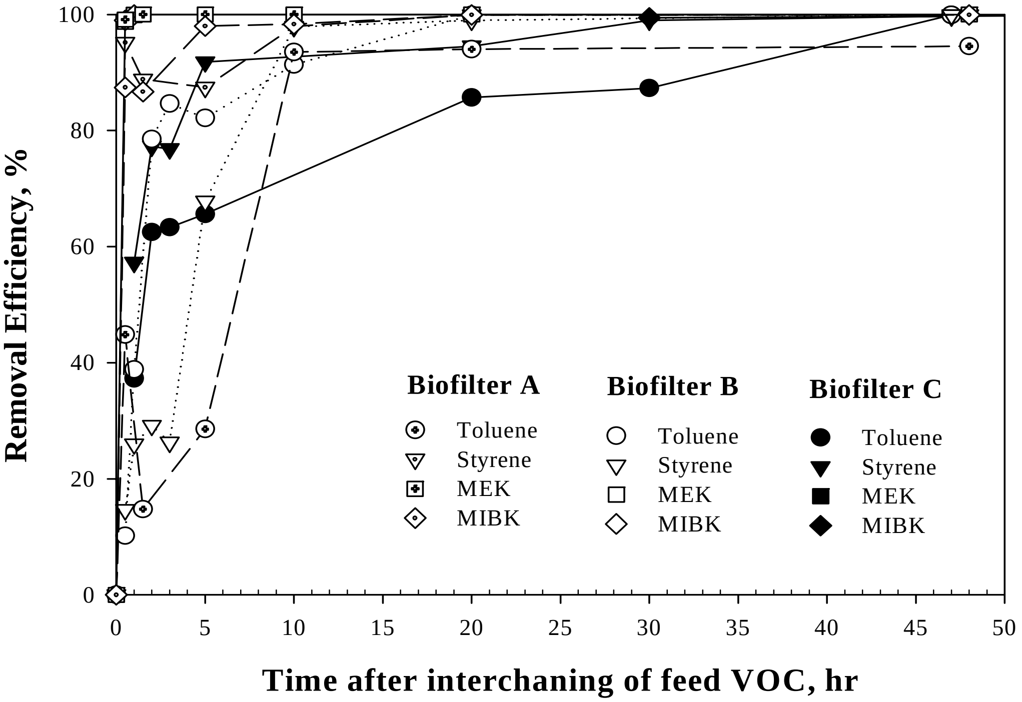


Figure 2-6 Effluent response corresponding to interchange of feed VOCs

### 2.4.3. Concentration Profiles in the Biofilters

To evaluate the biofilter performance and to determine the removal rate constant at the critical loading capacity for each feed VOC, gas samples were taken along the media depth of the biofilter one day following backwashing. The data are expressed as the cumulative EBRT (within the media bed) and plotted using a semi-logarithmic scale for the residual concentration in order to observe if the first-order removal rates are satisfactory approximations to the biokinetics, and to determine the value of the related rate constants (see Figure 2-7). Linear regression analysis was used for obtaining the first order removal rate constants. Table 2-2 provides the first order removal rate constants together with sum of the square of the residuals ($R^2$). The removal rate constant for MEK in biofilter “C” is unexpectedly much lower than that for biofilter “A” and “B” and has low R square values. It should be noted that in order to obtain a critical loading of 5.63 kg COD/$m^3$ day at 2.02 min EBRT for biofilter “C”, an inlet concentration of 1075 ppmv MEK was used. It is hypothesized that at high concentration of a substrate, zero order kinetics might better describe the substrate degradation than first order kinetics. In fact, if one develops the zero order rate constant for MEK in biofilter “C”, it is found that a rate constant of 0.027 g/$m^3$·sec was obtained with 0.96 $R^2$. This strongly suggests that a decrease in the removal rate was caused by the high inlet concentration. Furthermore, if one considers a Monod kinetics formulation, a first-order relation is obtained at low substrate concentration and then changes to a zero-order relation at high substrate concentration (Alexander 1999).

It can be seen in Table 2-2 that the removal rate constants in biofilter “A” and “B” are higher than those in biofilter “C” for all VOCs studied except for styrene. Contrary to this observation, low EBRT generally results in an inverse effect on the biofilter performance (Kiared et al. 1997; Sorial et al. 1997; Jorio et al. 2000b; Namkoong et al. 2004) due to insufficient contact time between the substrate and the biofilm. In this study, it should be noted that in order to maintain the same loading rate for each biofilter, the influent concentration of the VOC of concern was adjusted, according to the EBRT employed. Hence, at the critical loading for each VOC studied, the influent concentration in biofilter “C” was higher than that in biofilter “A” and “B” except for styrene. On the other hand, the depth of the biofilter media that was utilized was similar for both biofilters (see Figure 2-7) regardless of the EBRT. These results suggest that if the loading rate is to be maintained constant and within the critical loading rate for each VOC, the overall biofilter performance is dependent on the influent concentration of the feed VOC, or correspondingly by the oxygen-demand.

Table 2-2 Reaction rate at critical load for feed VOCs

| **Biofilter A** | | | | |
|---|---|---|---|---|
| VOC | Toluene | Styrene | MEK | MIBK |
| EBRT (min) | 1.23 | 2.02 | 0.76 | 0.76 |
| Rate constant (Sec$^{-1}$) | 0.024 | 0.048 | 0.112 | 0.213 |
| $R^2$ | 0.97 | 0.95 | 0.92 | 0.92 |
| **Biofilter B** | | | | |
| VOC | Toluene | Styrene | MEK | MIBK |
| EBRT (min) | 1.23 | 2.202 | 0.76 | 0.76 |
| Rate constant (Sec$^{-1}$) | 0.035 | 0.043 | 0.107 | 0.134 |
| $R^2$ | 0.93 | 0.95 | 0.94 | 0.94 |
| **Biofilter C** | | | | |
| VOC | Toluene | Styrene | MEK | MIBK |
| EBRT (min) | 2.02 | 2.02 | 2.02 | 2.02 |
| Rate constant (Sec$^{-1}$) | 0.022 | 0.044 | 0.039 | 0.063 |
| $R^2$ | 0.97 | 0.97 | 0.84 | 0.99 |

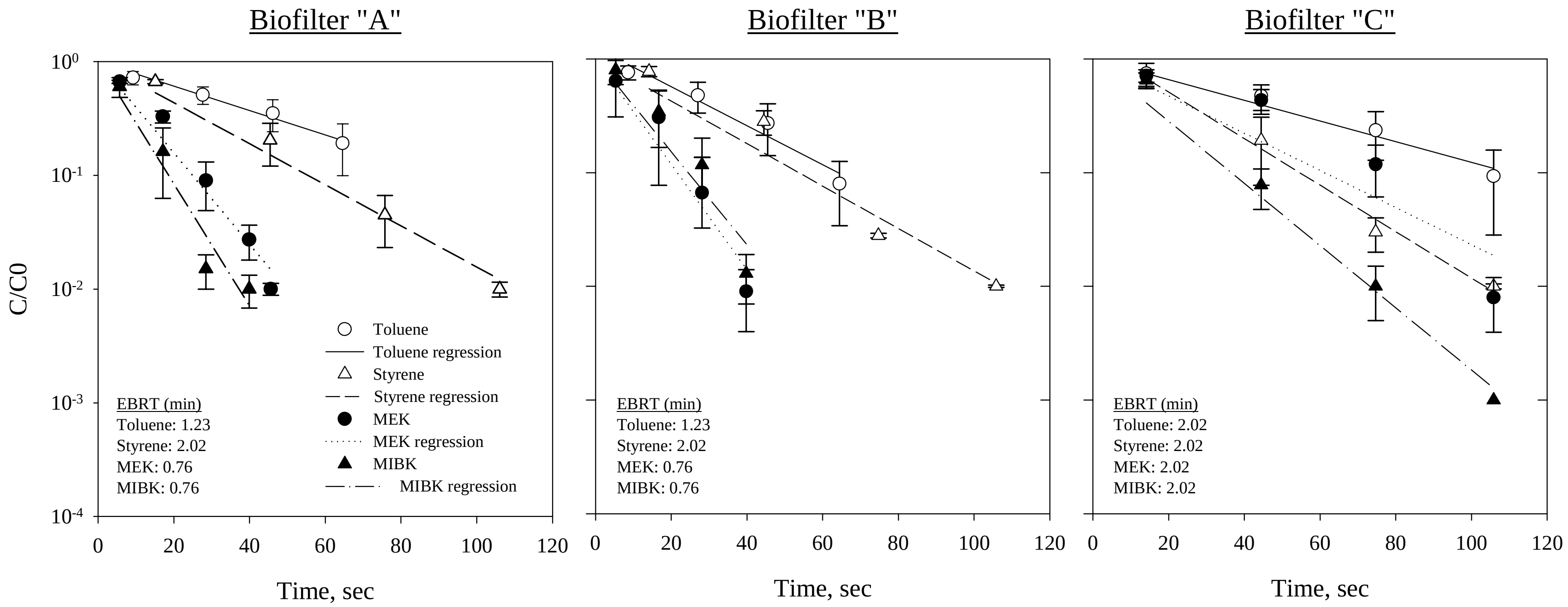


Figure 2-7 Reaction rate as a function of feed VOCs and EBRT. Kinetic constants were determined at critical load for each feed VOC assuming first-order kinetics

### 2.4.4. Production of $CO_2$ in the Biofilters with Change of Contaminants

The change of VOC removal is accompanied with change in the production of $CO_2$ because of VOC degradation by microorganisms. For a more quantitative analysis of these results, the $CO_2$ production rate is plotted against the biofilter VOC removal rate in Figure 2-8, Figure 2-9, and Figure 2-10 for biofilter “A”, “B”, and “C”, respectively. For biofilter “A”, the experimental average ratio of $CO_2$ production to VOC removal was shown in Table 2-3. The stoichiometric ratios in the case of complete chemical oxidation of the corresponding VOCs are 7, 8, 4, and 6 for toluene, styrene, MEK, and MIBK, respectively. The discrepancy between these experimental values and theoretical values is typical during the process of biodegradation of the VOCs, since some of the removed carbon is converted into biomass for microbial growth. Nonetheless, the relatively small difference between the complete chemical oxidation based ratio and the experimental ratio for toluene and styrene for the three biofilters indicates that these aromatic compounds were eliminated by aerobic biodegradation rather than by any other physical or chemical process. On the other hand, the relatively big discrepancy between these two ratios for MEK and MIBK indicates that the oxygenated compounds favored biomass growth and accumulation in the biofilter and a possibility of denitrification may have occurred (Zhu et al. 2004). Meanwhile, the small discrepancies between these experimental values and theoretical values for toluene and styrene could also be caused by a low net energy yield from the degradation of aromatic toluene and styrene (Woo and Rittmann 2000). In contrast, the degradation of oxygenated MEK and MIBK could result in higher net energy yields which allows for the higher production of biomass.

Furthermore, the higher $CO_2$ production to VOC removal ratio for toluene in biofilter C indicates that prolonged EBRT improves removal of toluene, and similar ratios to biofilter “A” and “B” for MEK and MIBK in biofilter “C” indicates that prolonged EBRT has no effect on performance on oxygenated compounds removal, which is consistent with the performance described in section 2.4.1.

Table 2-3 Statistic ratio of $CO_2$ production to VOC removal

| VOC | Toluene | Styrene | MEK | MIBK |
|---|---|---|---|---|
| **Biofilter A** | | | | |
| $CO_2$ mmol/d per VOC removal mmol/d | 5.23 | 7.85 | 2.77 | 3.98 |
| **Biofilter B** | | | | |
| $CO_2$ mmol/d per VOC removal mmol/d | 5.65 | 7.91 | 2.43 | 3.24 |
| **Biofilter C** | | | | |
| $CO_2$ mmol/d per VOC removal mmol/d | 6.29 | 7.79 | 2.66 | 3.18 |

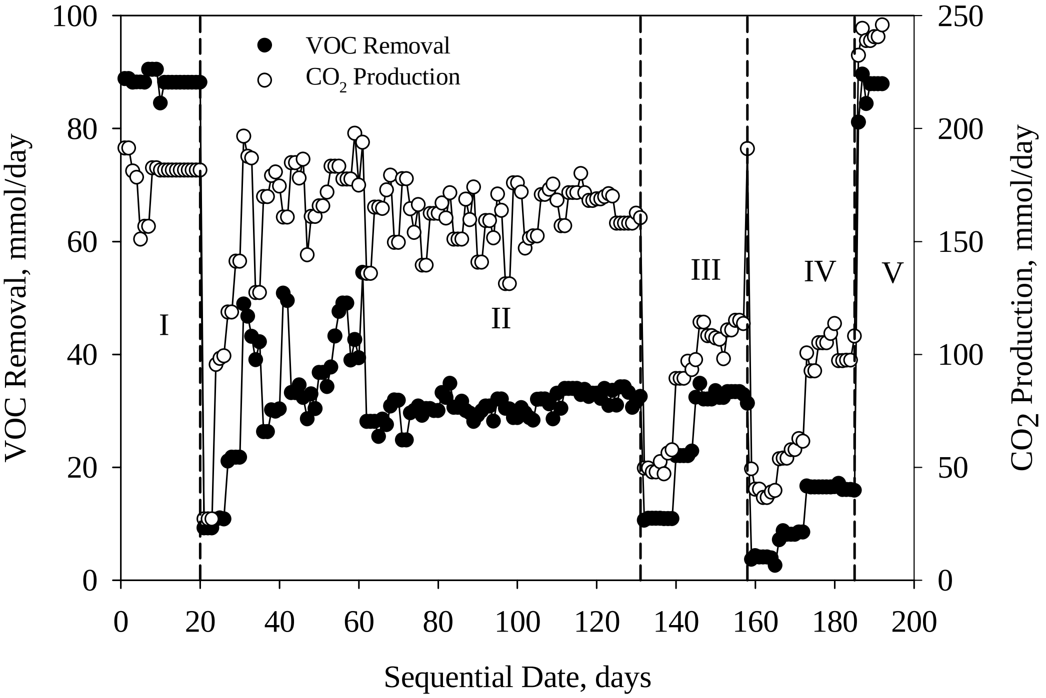


Figure 2-8 Biofilter "A" VOC removal and $CO_2$ production with time (I- MEK, II- Toluene, III- MIBK, IV- Styrene, and V- MEK)

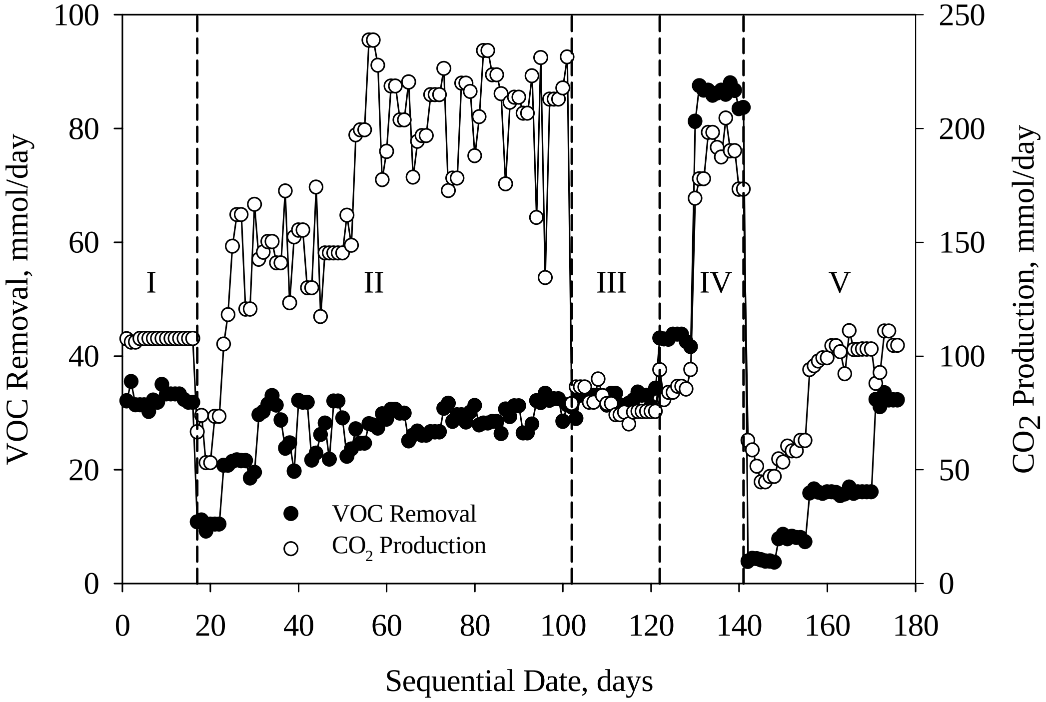


Figure 2-9 Biofilter "B" VOC removal and $CO_2$ production with time (I- MIBK, II- Toluene, III- MEK, IV- Styrene, and V- MIBK)

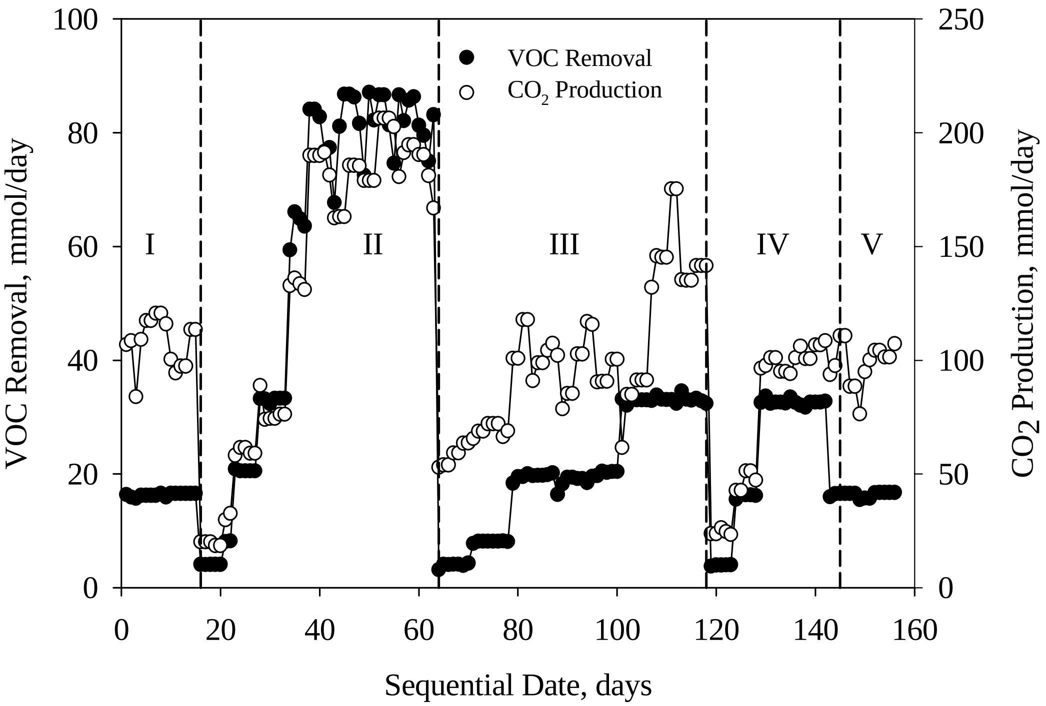


Figure 2-10 Biofilter "C" VOC removal and $CO_2$ production with time (I- Styrene, II-MEK, III- Toluene, IV- MIBK, and V- Styrene)

### 2.4.5. Nitrogen Utilization and VOC Removal

Daily analyses for the influent and effluent concentrations of $NO_3^-$-N were conducted. The net nitrogen utilization was calculated by subtracting the amount of the $NO_3^-$-N species in the effluent water from the $NO_3^-$-N species present in the nutrient feed. COD removal was calculated as the difference between the COD of the feed and the COD of the effluent gas and liquid stream.

Figure 2-11, Figure 2-12, and Figure 2-13 show COD/N ratios plotted against the sequential date. The ratios don't show dependency on the employed loading rate. However, lower COD/N ratios occurred just after interchanging VOCs, which indicates that more $NO_3^-$-N was utilized during the initial periods just after interchanging VOCs.

Since backwashing was conducted before the VOCs were interchanged, most of the biomass in the biofilters has been washed out. Hence, more $NO_3^-$ as the only nitrogen source was consumed to synthesize biomass to biodegrade the contaminants. Aerobic heterotrophs degrade most VOCs by using VOC carbon source for growing during the re-acclimation periods. With the increasing of biomass, microbial viability reaches stability after initial re-acclimation and then stable nitrogen utilization occurred. The heterotrophs degrade most VOCs by using VOC carbon source as energy source for maintaining microbial viability.

Furthermore, the nitrogen utilization difference between aromatic compounds (toluene and styrene) and oxygenated compounds (MEK and MIBK) was reduced significantly under interchanging VOC conditions compared with that under long term single solute conditions (Cai et al. 2004; Cai et al. 2005; Kim et al. 2005b; Kim et al. 2005a). It is speculated that microbial diversity increased and more microorganisms species were sustained for each interchanged VOC compared with the microbial diversity and microorganisms species in the single solute, which could result in the close nitrogen utilization among the interchanged VOCs. Meanwhile, it is interesting to notice that the initial VOC (long term single solute running) and prolonged EBRT (biofilter “C”) did not have apparent effect on the nitrogen utilization under VOC interchanging conditions.

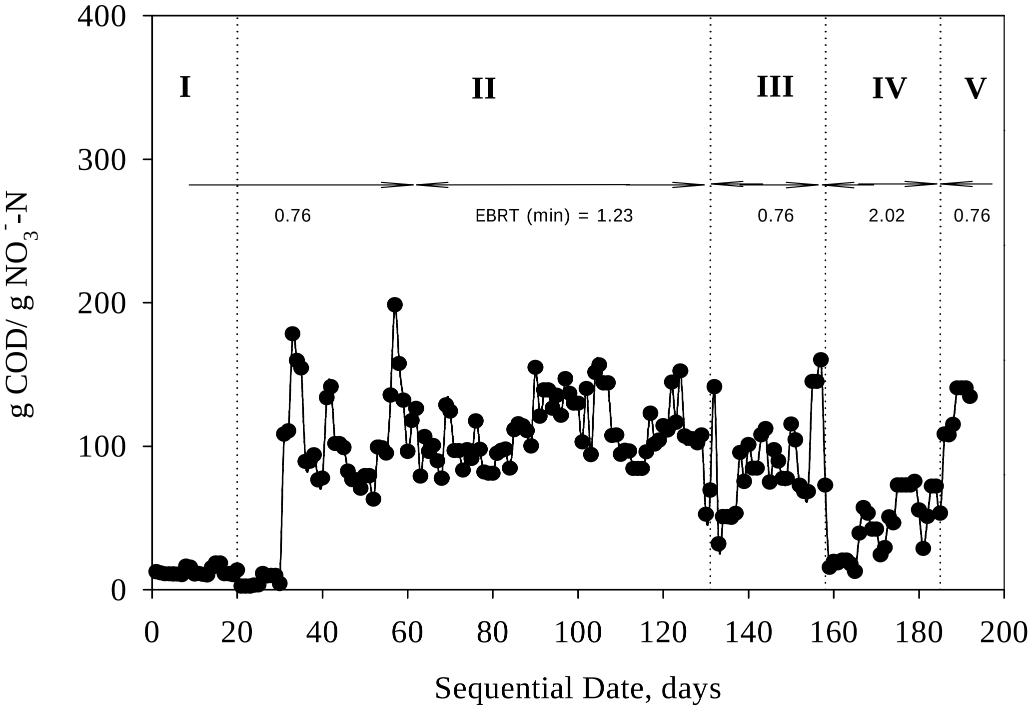


Figure 2-11 Biofilter “A” g COD/ g $NO_3^-$-N with respect to time (I- MEK, II- Toluene, III- MIBK, IV- Styrene, and V- MEK)

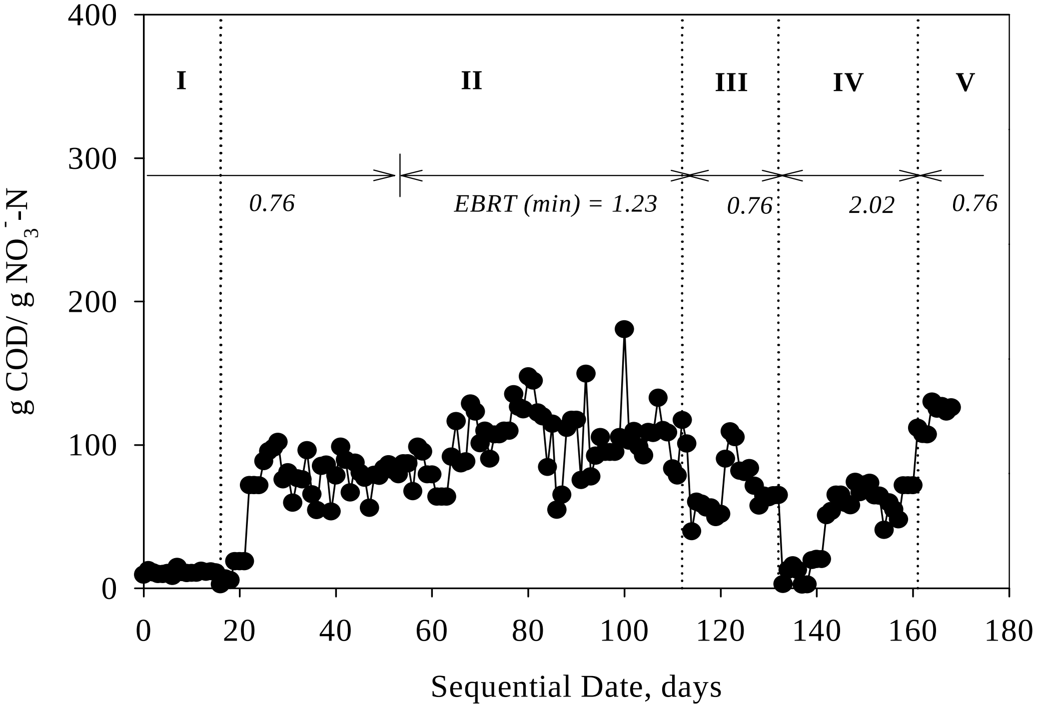


Figure 2-12 Biofilter “B” g COD/ g $NO_3^-$-N with respect to time (I- MIBK, II- Toluene, III- MEK, IV- Styrene, and V- MIBK)

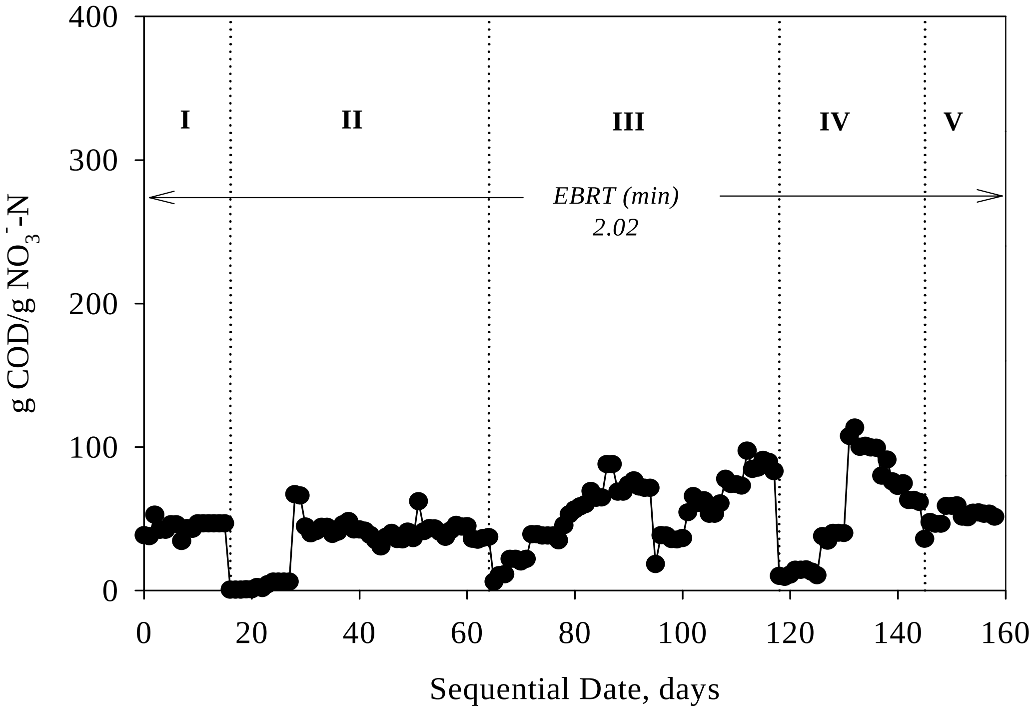


Figure 2-13 Biofilter “C” g COD/ g $NO_3^-$-N with respect to time (I- Styrene, II- MEK, III- Toluene, IV- MIBK, and V- Styrene)

### 2.4.6. Carbon Balance

The cumulative $CO_2$ equivalent of VOC consumed during all experimental runs was compared to the cumulative $CO_2$ produced within the biofilter in Figure 2-14, Figure 2-15, and Figure 2-16. The cumulative $CO_2$ produced was estimated as the difference between the total cumulative $CO_2$ in the effluent and the cumulative $CO_2$ present in the influent aqueous and gaseous streams plus the cumulative $CO_2$ equivalent of the VSS lost from the system. It is seen from Figures 2-14, 15, 16 that there is a good closure between the two cumulative values. The overall carbon recovery of the consumed VOCs was 91.0 % 88.6%, and 90.6% for biofilter “A”, “B”, and “C”, respectively. However, the divided VOC carbon recovery in the three figures shows that there is a good closure between the two cumulative values for hydrophobic VOCs (toluene and styrene), while it is not good for hydrophilic VOCs (MIBK and MEK). This may be due to accumulation of extra biomass in the biofilter bed without being washed out during backwashing and attached firmly on the media surface for hydrophilic VOCs.

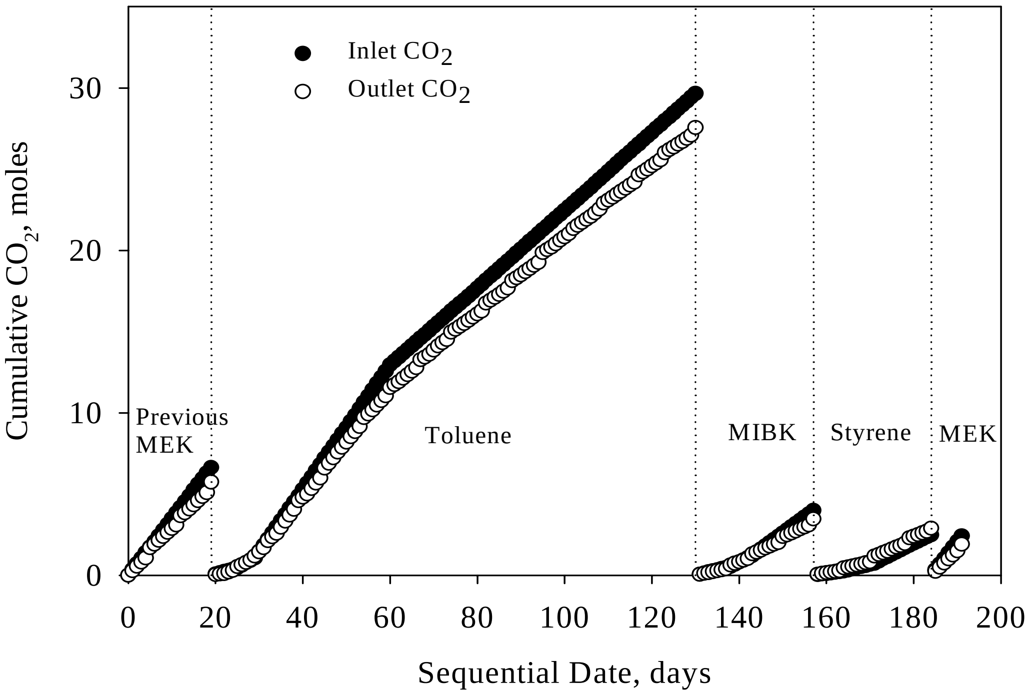


Figure 2-14. Development of $CO_2$ closure for biofilter "A" with time (The carbon closure for divided VOC is: Toluene-94.2%, MIBK-86.5%, Styrene-96.0%, and MEK-78.9%)

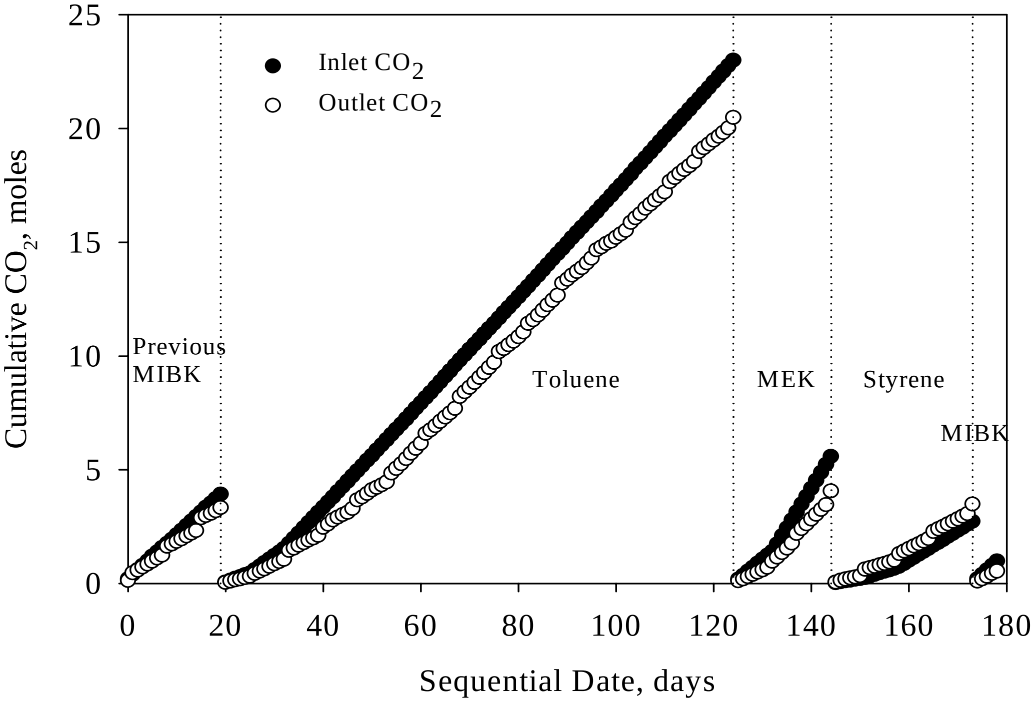


Figure 2-15. Development of $CO_2$ closure for biofilter “B” with time (The carbon closure for divided VOC is: Toluene-93.4%, MEK-72.8%, Styrene-92.1%, and MIBK-55.1%)

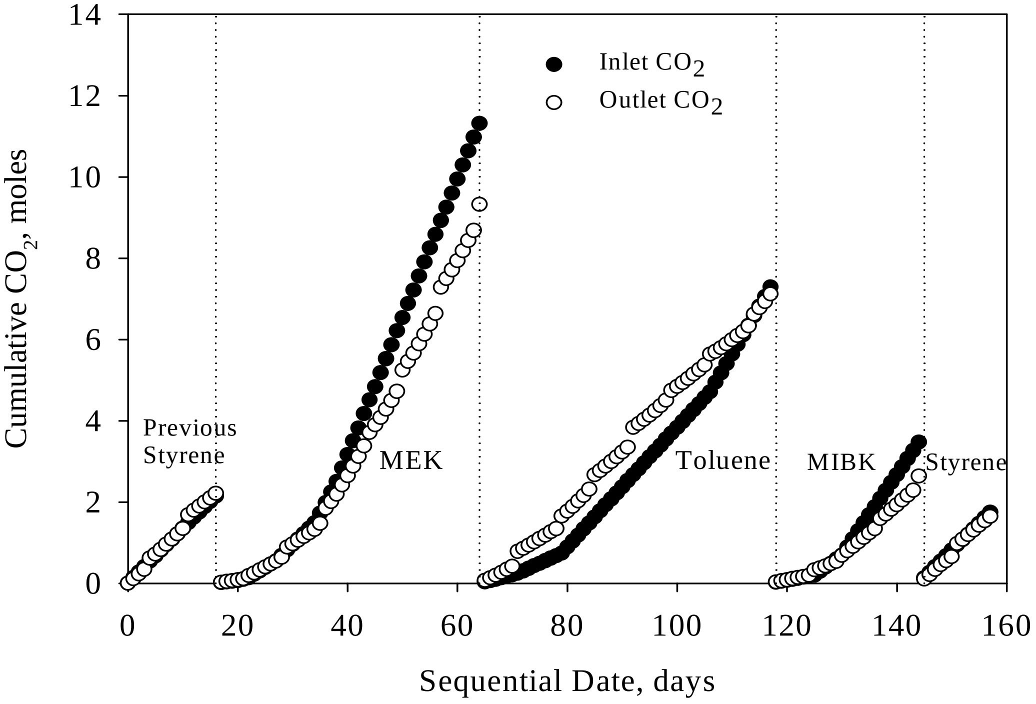


Figure 2-16. Development of $CO_2$ closure for biofilter “C” with time (The carbon closure for divided VOC is: MEK-82.4%, Toluene-98.3%, MIBK-75.6%, and Styrene-94.0%)

## 2.5. Conclusions

This study demonstrated the effect of interchanging the feed VOCs on the behavior of the biofilter. The specific conclusions that can be drawn from this study include the following:

(1) High removal performances could be maintained in the interchanging VOCs-fed biofilters, once the biofilters got re-acclimated to the new contaminant.

(2) Prolonged EBRT could improve the biofilter performance on aromatic compounds significantly, but it did not have apparent effect in improving biofilter performance on oxygenated compounds.

(3) The biofilter easily acclimated to oxygenated compounds (MEK and MIBK), regardless of the previous compound. While the biofilter re-acclimation was delayed for period over 2 days for the aromatic compounds (styrene and toluene).

(4) Oxygenated compounds had higher removal rate along the biofilter media than the aromatic compounds.

(5) The destructed aromatic compounds (toluene and styrene) were eliminated exclusively by aerobic biodegradation; however, the destructed oxygenated compounds (MEK and MIBK) were eliminated by aerobic biodegradation.

(6) After interchanging the feed VOCs, low ratios of COD/N were observed initially due to biomass synthesis. Nitrogen utilization difference between oxygenated compounds and aromatic compounds was reduced significantly under the interchanging conditions compared with the difference under the long term single solute conditions.

(7) There is a good $CO_2$ closure between the two cumulative values for hydrophobic VOCs (toluene and styrene), while it is not good for hydrophilic VOCs (MIBK and MEK).

## 2.6. References

Alexander, M. (1999). *Biodegradation and Bioremediation*, Academic Press, San Diego, CA.

Atoche, J. C., and Moe, W. M. (2004). "Treatment of MEK and toluene mixtures in biofilter: effect of operating strategy on performance during transient loading." *Biotechnology and Bioengineering*, 86(4), 468-481.

Cai, Z., Kim, D., and Sorial, G. A. (2004). "Evaluation of trickle-bed air biofilter performance for MEK removal." *Journal of Hazardous Materials*, 114(1-3), 153-158.

Cai, Z., Kim, D., and Sorial, G. A. (2005). "Removal of methyl isobutyl ketone from contaminated air by trickle-bed ai biofilter." *Journal of Environmental Engineering*, 131(9), 1322-1329.

Chou, M. S., and Huang, J. J. (1997). "Treatment of methylethylketone in air stream by biotrickling filters." *Journal of Environmental Engineering*, 123(6), 569-576.

Deshusses, M. A., Hamer, G., and Dunn, I. J. (1996). "Transient-state behavior of a biofilter removing mixtures of vapors of MEK and MIBK from air." *Biotechnology and Bioengineering*, 49(5), 587-598.

Eweis, J. B., Ergas, S. J., Chang, D. P. Y., and Schroeder, E. D. (1998). *Bioremediation*

*Principles*, WCB/McGraw-Hill, Boston.

Gaudy, A. F., and Gaudy, E. T. (1980). *Microbiology for environmental scientists and engineers*, McGraw-Hill, New York.

Jorio, H., Bibeau, L., and Heitz, M. (2000a). "Biofiltration of air contaminated by styrene: Effect of nitrogen supply, gas flow rate, and inlet concentration." *Environmental Science & Technology*, 34(9), 1764-1771.

Jorio, H., Bibeau, L., Viel, G., and Heitz, M. (2000b). "Effects of gas flow rate and inlet concentration on xylene vapors biofiltration performance." *Chemical Engineering Journal*, 76(3), 209-221.

Kiared, K., Fundenberger, B., Brzezinski, R., Viel, G., and Heitz, M. (1997). "Biofiltration of air polluted with toluene under steady-state conditions: Experimental observations." *Industrial & Engineering Chemistry Research*, 36(11), 4719-4725.

Kim, D., Cai, Z., and Sorial, G. A. (2005a). "Behavior of trickle bed air biofilter for toluene removal: effect of non-use periods." *Environmental Progress*, 24(2), 155-161.

Kim, D., Cai, Z., and Sorial, G. A. (2005b). "Evaluation of trickle-bed air biofilter performance under periodic stressed operating conditions as a function of styrene loading." *Journal of the Air & Waste Management Association*, 55(2), 200-209.

Kong, Z., Farhana, L., Fulthorpe, R. R., and Allen, D. G. (2001). "Treatment of volatile organic compounds in a biotrickling filter under thermophilic conditions." *Environmental Science & Technology*, 35(21), 4347-4352.

Krailas, S., Pham, Q. T., Amal, R., Jiang, J. K., and Heitz, M. (2000). "Effect of inlet mass loading, water and total bacteria count on methanol elimination using upward flow and downward flow biofilters." *Journal of Chemical Technology and Biotechnology*, 75(4), 299-305.

Madigan, M. T., Martinko, J. M., and Parker, J. (2002). *Brock Biology of Microorganisms*, Prentice Hall/Pearson Education, Upper Saddle River, NJ.

Martin, F. J., and Loehr, R. C. (1996). "Effect of periods of non-use on biofilter performance." *Journal of the Air & Waste Management Association*, 46(6), 539-546.

Moe, W. M., and Qi, B. (2004). "Performance of a fungal biofilter treating gas-phase solvent mixtures during intermittent loading." *Water Research*, 38(9), 2259-2268.

Namkoong, W., Park, J. S., and VanderGheynst, J. S. (2004). "Effect of gas velocity and influent concentration on biofiltration of gasoline off-gas from soil vapor extraction." *Chemosphere*, 57(7), 721-730.

Pedersen, A. R., and Arvin, E. (1997). "Toluene removal in a biofilm reactor for waste gas treatment." *Water Science and Technology*, 36(1), 69-76.

Sorial, G. A., Smith, F. L., Suidan, M. T., Biswas, P., and Brenner, R. C. (1995). "Evaluation of trickle-bed biofiltermedia for toluene removal." *Journal of the Air & Waste Management Association*, 45(10), 801-810.

Sorial, G. A., Smith, F. L., Suidan, M. T., Biswas, P., and Brenner, R. C. (1997). "Performance of peat biofilter: Impact of the empty bed residence time, temperature and toluene loading." *Journal of Hazardous Materials*, 53(1-3), 19-33.

Sorial, G. A., Smith, F. L., Suidan, M. T., Pandit, A., Biswas, P., and Brenner, R. C. (1998). "Evaluation of trickle-bed air biofilter performance for styrene removal." *Water Research*, 32(5), 1593-1603.

Sorial, G. A., Smith, F. L., Suidan, M. T., Smith, P. J., Biswas, P., and Brenner, R. C. "Development of aerobic biofilter design criteria for treating VOCs." *86th Annual Meeting and exhibition of the Air & Waste management Asociation*, Denver, CO.

Sorial, G. A., Smith, F. L., Suidan, M. T., Smith, P. J., Biswas, P., and Brenner, R. C. "Evaluation of performance of trickle bed biofilter-impact of periodic removal of accumulated biomass." *87th Annual Meeting and Exhibition of the Air & Waste Management Association*, Cincinnati, OH.

Standefer, S., and Van Lith, C. (1993). "Biofilters minimize VOC emissions." *Environmental Protection*, 4(3), 48-58.

Standard Methods for the Examination of Water and Wastewater. 20th ed., APHA, AWWA, and WEF, 1998

Togna, A. P., and Frisch, S. "Field-pilot study of styrene biodegradation using biofiltration." *86th Annual Meeting and Exhibition of the Air & Waste Management Association,* Dever, CO.

Torronen, M. E., Lehtomaki, J. T., and Laukkarinen, A. J. "A feasibility study of biological waste air purification in cold climates." *Proceedings of the 9th World Clean Air Congress*, Montreal, Canada.

Verschueren, K. (2001). *Handbook of Environmental Data on Organic Chemicals*, John Wiley, New York.

Watts, R. J. (1998). *Hazardous wastes: sources, pathways, receptors*, John Wiley, New York.

Woo, S. H., and Rittmann, B. E. (2000). "Microbial energetics and stoichiometry for degradation of aromatic compounds involving oxygenated reactions." *Biodegradation*, 11(4), 213-227.

Yang, H., Minuth, B., and Allen, D. G. (2002). "Effects of nitrogen and oxygen on biofilter performance." *Journal of the Air & Waste Management Association*, 52(3), 279-286.

Zhu, X., Suidan, M., Pruden, A., Yang, C., Alonso, C., Kim, B. J., and Kim, B. R. (2004). "Effect of substrate Henry's constant on biofilter performance." *Journal of the Air & Waste Management Association*, 54(4), 409-418.

Zhu, X., Suidan, M. T., Alonso, C., Yu, T., Kim, B. J., and Kim, B. R. (2001). "Biofilm structure and mass transfer in a gas phase trickle-bed biofilter." *Water Science and Technology*, 43(1), 285-293.

# CHAPTER 3

# TBAB STUDY ON VOC MIXTURES

## 3.1. Abstract

Two independent parallel trickling bed air biofilters (TBABs) (“A” and “B”) with two different VOCs mixtures were investigated. Toluene, styrene, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) were the target VOCs in the mixtures. Biofilter “A” was fed equal molar ratio of the VOCs and biofilter “B” was fed a mixture based on EPA 2003 emission report. Backwashing and substrate starvation operation were conducted as a means of biomass control. Biofilter “A” and “B” maintained 99% overall removal efficiency for influent concentration up to 500 ppmv and 300 ppmv under backwashing operating condition, respectively. The starvation study indicated that it can be an effective biomass control for influent concentrations up to 250 ppmv for biofilter “A” and 300 ppmv for “B”. Re-acclimation of biofilter performance was delayed with increase of influent concentration for both biofilters. Starvation operation helped the biofilter to recover at low concentrations and delayed re-acclimation at high concentrations. Furthermore, re-acclamation for biofilter “B” was delayed due to its high toluene content as compared to biofilter “A”. The pseudo first-order removal rate constant decreased with increase of volumetric loading rate for both biofilters. MEK and MIBK were completely removed in the upper 3/8 media depth. While biofilter depth utilization for the removal of styrene and toluene increased with increase of influent concentrations

for both biofilters. However, toluene removal utilized more biofilter depth for biofilter “B” as compared to biofilter “A”.

### 3.2. Introduction

Emission control of volatile organic compounds (VOCs) has become one major concern in air pollution prevention since the 1990 Clean Air Act Amendments (CAAA) went into effect. Biotreatment of VOCs offers an inexpensive alternative to conventional technologies such as catalytic and thermal oxidations, wet scrubbing, ozonation, and activated carbon adsorption (Don and Feenstra 1984; Ottengraf 1986). Biofiltration has emerged as a reliable and cost-effective technology for the control of VOCs emissions. Trickling-bed air biofilters (TBABs) facilitate more consistent operation than traditional biofilters do via better control of overall pressure drop, nutrient concentration, and pH. During the past decade, many studies concerning the treatment of contaminated gas stream by biofiltration had been conducted (Sorial et al. 1994; Sorial et al. 1995; Zhu et al. 1996; Arnold et al. 1997; Chou and Huang 1997; Cox and Deshusses 1998; Wu et al. 1999; Bibeau et al. 2000; Delhomenie et al. 2002; Cai et al. 2004; Cai et al. 2005). Most of the studies were involved in treating single VOC, and factors found to affect the decontamination efficiency include: nature of the contaminants, packing materials and configurations, empty bed retention time (EBRT), volumetric loading rates, nutrient feed flow rates, nutrient solution pH, and flow patterns of air. However, many industrial air emissions contain mixtures of VOCs that possess various physical and chemical properties affecting their biological treatment.

Studies on removal of VOCs mixture by biofiltration are reported by a number of researchers (Deshusses and Hamer 1993; Deshusses et al. 1995a; Deshusses et al. 1995b; Deshusses et al. 1996; Deshusses 1997; Mohseni and Allen 1999; Mohseni and Allen 2000; Aizpuru et al. 2001; Chitwood and Devinny 2001; Cox and Deshusses 2002a; Yoon and Park 2002; Aizpuru et al. 2003a; Aizpuru et al. 2003b; Chang and Lu 2003; Pruden et al. 2003; Sologar et al. 2003; Atoche and Moe 2004; Moe and Qi 2004). Deshusses et al. (1993) investigated the removal of methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) mixtures from the air biofilters. The packing materials were equivolume mixture of compost and polystyrene spheres. They found that MEK required much lower residence time (16 seconds) than MIBK did (50 seconds). And they also found that MEK degradation utilized less biofilter depth than MIBK degradation did. Deshusses et al.(1995a; 1995b) studied the transient mass balances and developed a diffusion reaction model by employing MIBK and MEK as the target contaminants in an equivolume mixture of compost and polystyrene spheres biofilter unit. In a later study, Deshusses et al.(1996) investigated the transient-state behavior of a biofilter removing mixtures of MEK and MIBK from air. Deshusses (1997) further studied the transient behavior of biofilters during startup and the interaction between pollutants in a horse manure, yard waste compost, and redwood chips mixture biofilter unit. Mohseni et al. (1999; 2000) studied transient and long-term performance of methanol and α-pinene mixture. They found that the biofilters had much higher removal capacity to methanol (170-180 $g/m^3/h$) than those to α-pinene (45 $g/m^3/h$) with empty bed retention time (EBRT) as low as 20 seconds.

Most of the methanol was removed in the top section of the biofilter, and α-pinene degradation utilized the whole biofilter depth. Furthermore, the α-pinene removal decreased in the top section with the increasing of methanol inlet concentration. However, they found that methanol removal was not affected by the α-pinene step increase. Aizpuru et al. (2001; 2003a; 2003b) investigated and compared 11 VOCs mixture performance in a peat biofilter and a biofilter packed with granular activated carbon. They found that the packing materials played an important role in the the removal stratification of VOCs concerned. For the peat biofilter, elimination of oxygenated compounds occurred in the first 50 cm of the column. In contrast, for packing materials of GAC, the removal of oxygenated and aromatic compounds took place along the whole column. Meanwhile, the two biofilters did not provide successful removal for chlorinated compounds although the peat biofilter had higher removal of the chlorinated compounds (60%) than the GAC biofilter did (20%). Cox et al. (2002a), Chitwood et al. (2001), and Sologar et al. (2003) tried to co-treat odors and VOCs from publicly owned treatment works (POTWs) employing biofiltration. Cox et al. (2002a) investigated the treatment of $H_2S$ and toluene in a biotrickling biofilter. The authors focused on studying the pH effect on $H_2S$ and toluene removal. They found that the biofilter operated at low pH (around 4) had a faster and more stable response to a change of the pH. Chitwood et al. (2001) treated a mixed $H_2S$ and organic vapors stream with a biofilter with rock medium. They found that a rock biofilter at a low pH (around 4) could effectively remove $H_2S$ with EBRT as low as 12 seconds. The co-treatment of VOCs with $H_2S$ was found to depend on the VOCs concentrations. Sologar et al. (2003) investigated the treatment of mixtures of $H_2S$ and methanol in a porous inflated glass packed biofilter. They found that the interaction effects between $H_2S$ and methanol were negligible. Yoon and Park (2002) studied the operation parameters effect on VOC mixtures removal performance in a peat-packed biofilter. They found there was an optimum operation temperature for VOC removal at 32 °C and lengthened EBRT could improve removal efficiency. Chang and Lu (2003) investigated the performance of toluene and acetone mixture in a trickle-bed air biofilter. They found that the removal efficiency of toluene was higher than that of acetone.

Non-use operation occurs periodically in industry due to shut-off during weekends and holidays. In experiments where the influent contaminant loading was suspended for longer periods (2 days to 2 weeks), diminished contaminant removal for a period lasting several hours or even few days following resumption of contaminant loading had been reported (Torronen et al. 1992; Standefer and Van Lith 1993; Togna and Frisch 1993; Martin and Loehr 1996; Mohseni et al. 1998; Webster et al. 1999; Wani et al. 2000; Metris et al. 2001; Park and Kinney 2001; Cox and Deshusses 2002b; Cai et al. 2004; Moe and Qi 2004; Cai et al. 2005; Kim et al. 2005b; Kim et al. 2005a). Torronen et al. (1992) found that 2-4 hours were required following a two-day period of non-use and that five hours were required following a five day period of non-use, for removal efficiency to return to previous levels in biofilter experiments with hexane and phenolic compounds. Togna and Frisch (1993) reported styrene reacclimation periods after two or more days without chemical contact.

Standefer and Van Lith (1993) reported that biofilter removal efficiency returned to previous levels after one hour following a two day period of non-use and after 5-8 hours following a seven day period of non-use. Martin and Loehr (1996) reported biofilter reacclimation after restart-up from two intermittent periods. Cai et al. (2004; 2005) and Kim et al. (2005b; 2005a) found that non-use periods did not have noticeable adverse effect on removal efficiency when the employed loading rates did not exceed the elimination capacity of the biofilters. Furthermore, non-use operation could be employed as a means of biomass control for these loading rates. While fewer investigation of non-use operation for VOC mixtures was conducted. Moe and Qi (2004) studied the performance of a fungal biofilter treating n-butyl acetone, methyl ethyl ketone (MEK), methyl propyl ketone (MPK), and toluene mixtures during intermittent loading. They found that shutdown of loading had varying effects on removal efficiency for different compounds. Shutdown had no noticeable adverse affect on removal of n-butyl acetone while removal of MEK and MPK was impacted for a few hours, and toluene removal was adversely impacted for a few days. Furthermore, the fungal biofilter required a longer time to recover for long term loading shutdown than shorter term shutdown.

The objective of this research was to evaluate the performance of TBAB for VOC mixtures (ketones and aromatic compounds) under different loading conditions. The goal was to maintain consistently high removal efficiencies for long-term operation and determine the critical loading capacity. The evaluations are focused on the following parameters: (1) mixture loading, (2) recovery of biofilter performance after backwashing and starvation operation, (3) nitrogen utilization, (4) development of preliminary kinetic data, and (5) $CO_2$ (carbon mass balance) closures.

## 3.3. Materials and Methods

### 3.3.1. Mixtures of Volatile Organic Compounds

The VOCs used were two oxygenated compounds, namely, methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) and two aromatic compounds styrene and toluene (Fisher Scientific, Fair Lawn, N.J, pure 99%). These VOCs are common solvents employed in industry and are major components of paints and varnishes. The dimensionless Henry's law constants for toluene, styrene, MEK and MIBK are 0.280. 0.109, 0.00194, and 0.00062 (Verschueren 2001), respectively. Two different VOC mixtures were employed in this study. The first one, fed to biofilter "A", was an equal molar ratio of the four VOCs. The second one, fed to biofilter "B", was a mixture based on EPA 2003 emission report from chemical industry. The molar ratio of the four VOCs on biofilter "B" was 0.448: 0.260: 0.234: 0.058 for toluene: styrene: MEK: MIBK, respectively.

### 3.3.2. Trickling Biofilter

The biofilter continued to be run without reconditioning the media used in pervious runs where the four VOCs were interchanged as the sole VOC contaminant (Cai et al. 2006) described in Chapter 2. An illustration of the biofilter system is provided in Figure 2-1 in Chapter 2. Details about the biofilter system are found in the section 2.3.2.

Air flow was set up at the rate of 1.35 L/min with corresponding empty bed retention time (EBRT) of 2.02 min. These conditions were chosen based on our previous study for styrene biodegradation, which required the highest EBRT among the four VOCs (Cai et al. 2004; Cai et al. 2005; Kim et al. 2005b; Kim et al. 2005a). Liquid VOC was injected via a syringe pump and vaporized into the air stream. Each VOC inlet mixture concentration was stepwise increased from 50 ppmv to the maximum allowable inlet mixture concentration, for attaining over 99% removal. Buffered nutrient solution was supplied at a rate of 2.4 L/day, the composition of the nutrient solution was provided in a previous study (Sorial et al. 1995). *In-situ* upflow backwashing with media fluidization was employed at a rate of 1 hour a week as a strategy for biomass control during the backwashing experimental periods. An illustration of the backwashing system is provided in Chapter 2 (Figure 2-2). However, no backwashing was employed during starvation experimental periods. During starvation (2 days/week) only pure air and nutrients solution were allowed to pass through the biofilter. The conditions employed during the experimental runs are summarized in Table 3-1.

### 3.3.3. Analytical Methods

The concentrations of VOCs in the gas phase were measured by using a gas chromatograph (GC) (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with a flame ionization detector (FID). A GC (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with a thermal conductivity detector (TCD) was used for

Table 3-1. Biofilter operating conditions

**Biofilter “A”**

| Experimental Stage | I | II | III | IV | V |
|---|---|---|---|---|---|
| Concentration, ppmv | 50 | 100 | 250 | 500 | 1000 |
| Toluene loading rate kg COD/$m^3$.day | 0.11 | 0.22 | 0.54 | 1.07 | 2.14 |
| Styrene loading rate kg COD/$m^3$.day | 0.12 | 0.24 | 0.60 | 1.19 | 2.39 |
| MEK loading rate kg COD/$m^3$.day | 0.07 | 0.13 | 0.33 | 0.66 | 1.32 |
| MIBK loading rate kg COD/$m^3$.day | 0.10 | 0.20 | 0.51 | 1.02 | 2.03 |
| Total Loading rate<br>kg COD/$m^3$·day<br>(g/$m^3$.hr) | <br>0.40<br>(5.73) | <br>0.79<br>(11.47) | <br>1.98<br>(28.67) | <br>3.94<br>(57.34) | <br>7.88<br>(114.67) |

**Biofilter “B”**

| Experimental Stage | I | II | III | IV | V* | VI |
|---|---|---|---|---|---|---|
| Concentration, ppmv | 50 | 100 | 250 | 500 | 350 | 300 |
| Toluene loading rate kg COD/$m^3$.day | 0.19 | 0.38 | 0.96 | 1.92 | 1.34 | 1.15 |
| Styrene loading rate kg COD/$m^3$.day | 0.12 | 0.25 | 0.62 | 1.24 | 0.87 | 0.74 |
| MEK loading rate kg COD/$m^3$.day | 0.06 | 0.12 | 0.31 | 0.62 | 0.43 | 0.37 |
| MIBK loading rate kg COD/$m^3$.day | 0.02 | 0.05 | 0.12 | 0.24 | 0.17 | 0.14 |
| Total Loading rate<br>kg COD/$m^3$·day<br>(g/$m^3$.hr) | <br>0.39<br>(5.66) | <br>0.80<br>(11.32) | <br>2.01<br>(28.29) | <br>4.02<br>(56.59) | <br>2.81<br>(39.61) | <br>2.40<br>(33.95) |

* stage V: biofilter B was conducted with backwashing operation only.

determining the $CO_2$ concentrations in the effluent gas phase. A detailed method for GC-FID and GC-TCD is provided in Chapter 2. Liquid phase samples were analyzed for $NO_3^-$-N, total carbon (TC), inorganic carbon (IC), and volatile suspended solid

(VSS) concentration. $NO_3^-$-N was determined according to Standard Methods 4500-$NO_3^-$ B (Standard methods, 1998) by using a Shimadzu UVmini 1240 UV-VIS spectrophotometer (Shimadzu Corp., Tokyo, Japan). TC and IC were determined by using a Shimadzu TOC 5050 analyzer (Shimadzu Corp., Tokyo, Japan) according to Standard Methods 5310 (Standard methods, 1998). The VSS concentrations in the effluent and backwashing water were determined according to Standard Methods 2540 G (Standard methods, 1998).

## 3.4. Results and Discussion

### 3.4.1. Biofilter Performance

Biofilter “A” and “B” were both started up at 50 ppmv inlet mixture concentration with 2.02 min EBRT, and 17.1 mmol $NO_3^-$-N/day. The operating conditions are summarized in Table 3-1.

Biofilter “A” performance with respect to VOC removal at different loading rates is given in Figure 3-1 and Figure 3-2 for backwashing and starvation operation, respectively.

Biofilter “A” got re-acclimated and maintained 99% overall removal efficiency for inlet mixture concentrations up to 500 ppmv with a total corresponding loading rate of 3.94 kg COD.$m^{-3}$.$day^{-1}$ (57.34 g.$m^{-3}$.$hr^{-1}$) under backwashing operation with toluene removal efficiency round 95%. When the total concentration was increased further to 1000 ppmv with a corresponding loading rate of 7.88 kg COD.$m^{-3}$.$day^{-1}$ (114.67 g.$m^{-3}$.$hr^{-1}$), the biofilter performance did not get re-acclimated to the original performance and the overall removal efficiency could just be maintained at around 80%. With regards to the mixture components, toluene removal efficiency decreased sharply to round 50% and styrene removal efficiency decreased to around 82%. However, the removal efficiencies for MEK and MIBK were maintained over 99% for all employed influent concentrations. Biofilter “A” performance under starvation operation decreased to 95% and 70% when the inlet mixture concentration was increased to 500 ppmv and 1000ppmv, respectively. The performance under starvation operation indicated that it had adverse effect on the biofilter performance when the employed loading exceeded 3.94 kg COD.m$^{-3}$.day$^{-1}$ (57.34 g.m$^{-3}$.hr$^{-1}$).

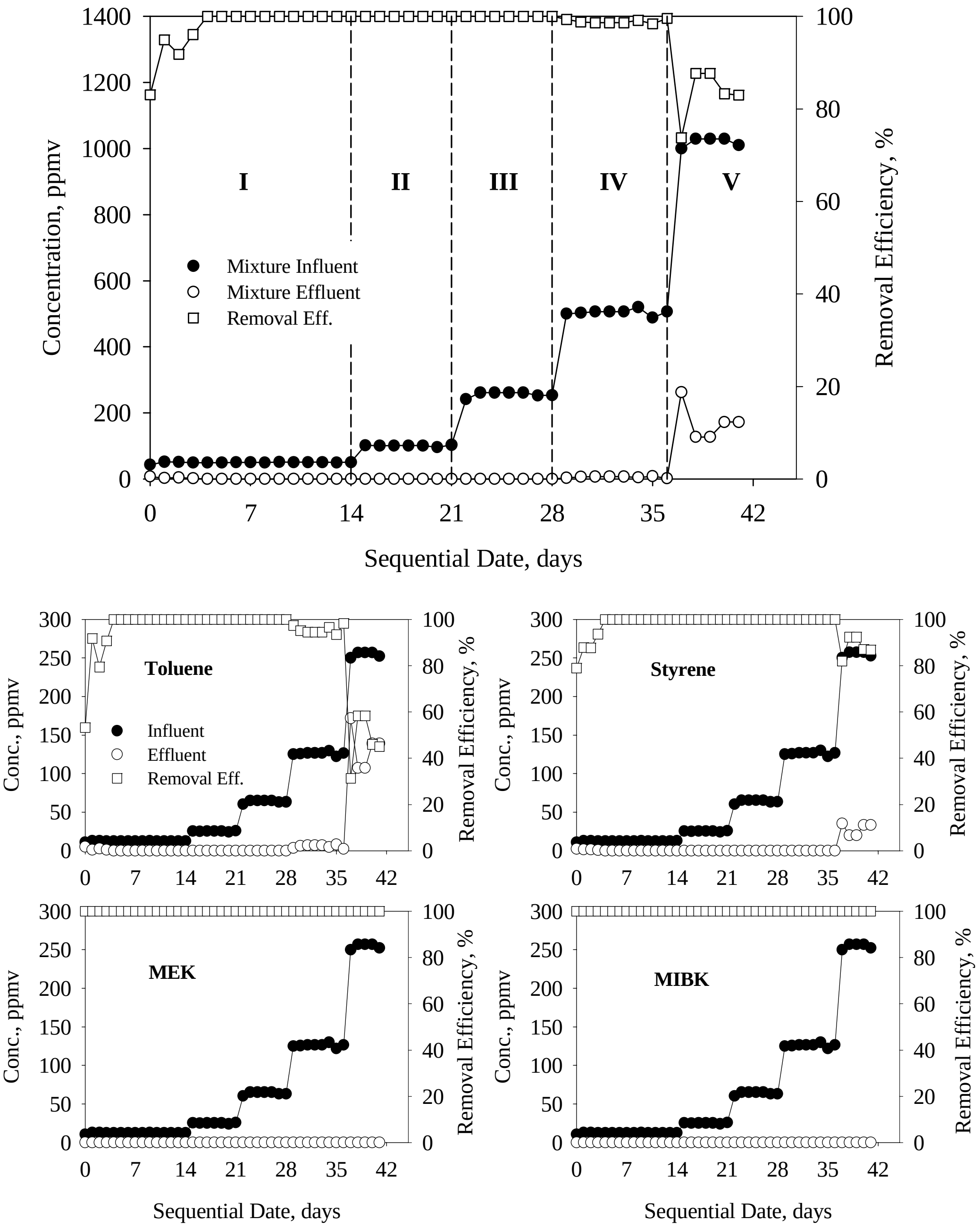


Figure 3-1 Biofilter "A" performance with respect to VOC removal under backwashing operation (I) 50 ppmv, (II) 100 ppmv, (III) 250 ppmv, (IV) 500 ppmv, (V) 1000 ppmv

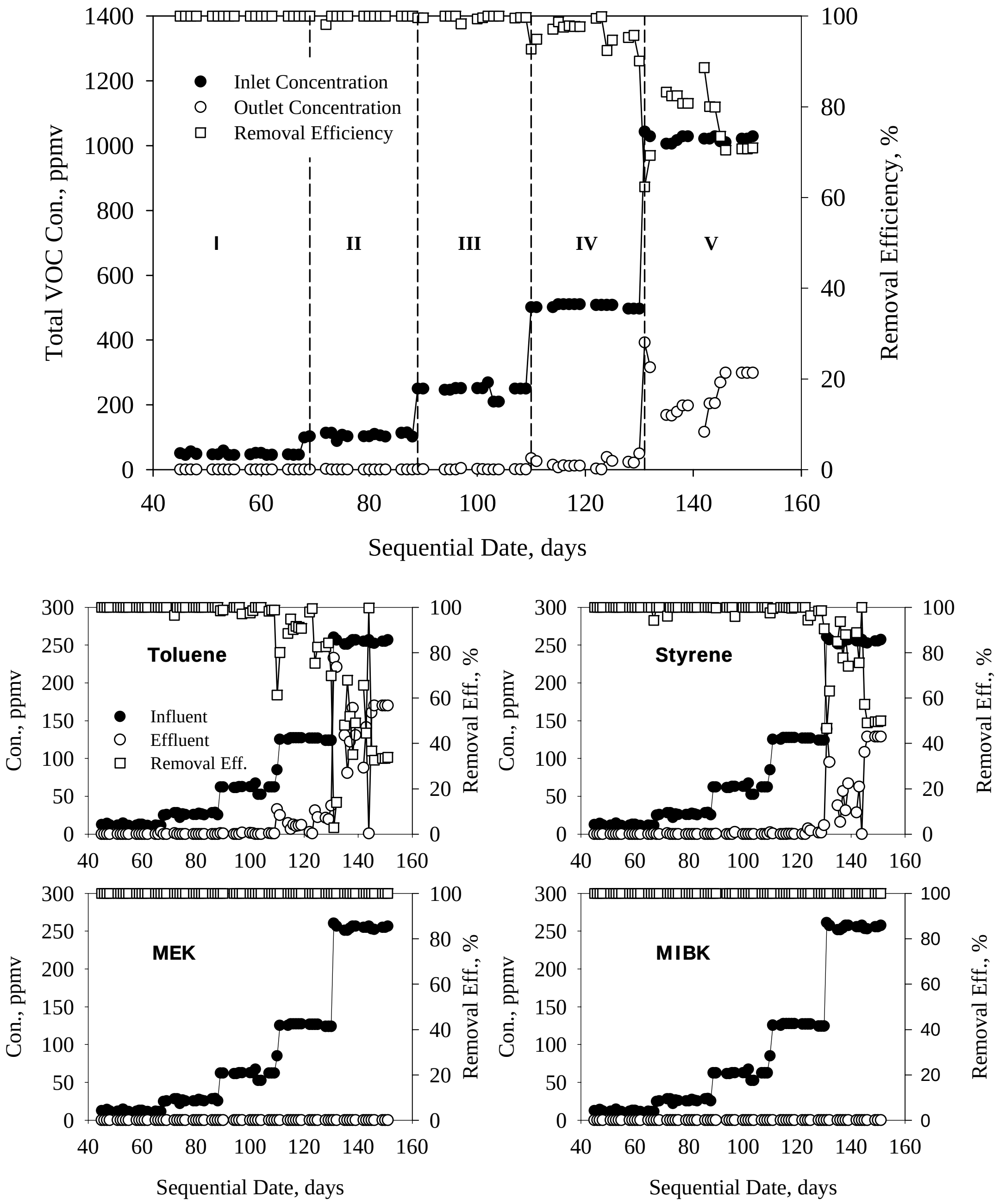


Figure 3-2 Biofilter “A” performance with respect to VOC removal under starvation operation (I) 50 ppmv, (II) 100 ppmv, (III) 250 ppmv, (IV) 500 ppmv, (V) 1000 ppmv

Biofilter “B” performance with respect to VOC removal at different loading rates was shown in Figure 3-3 and Figure3-4 under backwashing and starvation operation, respectively.

Biofilter “B” showed significant different performance as compared to biofilter “A”. The biofilter maintained 99% removal efficiency for loading rates up to 2.41 kg COD.m$^{-3}$.day$^{-1}$ (33.95 g.m$^{-3}$.hr$^{-1}$) (300 ppmv inlet mixture concentration) for both operations (backwashing and starvation). However, the overall removal efficiency decreased to 95% and further to 90% when the inlet mixture concentration increased to 350 ppmv and 500 ppmv, respectively, for backwashing strategy. The performance under starvation operation decreased to 80% for inlet mixture concentration 500 ppmv. The removal efficiencies of styrene, MEK, and MIBK in biofilter “B” were maintained at 99% for all employed loading rates for the backwashing strategy. For starvation strategy, styrene took longer time to get re-acclimated to attain the 99% removal level for an inlet mixture concentration of 500 ppmv. However, the removal efficiency for toluene decreased to 85% and 60-80% for backwashing and starvation strategies, respectively, when the inlet mixture concentration increased to 500 ppmv.

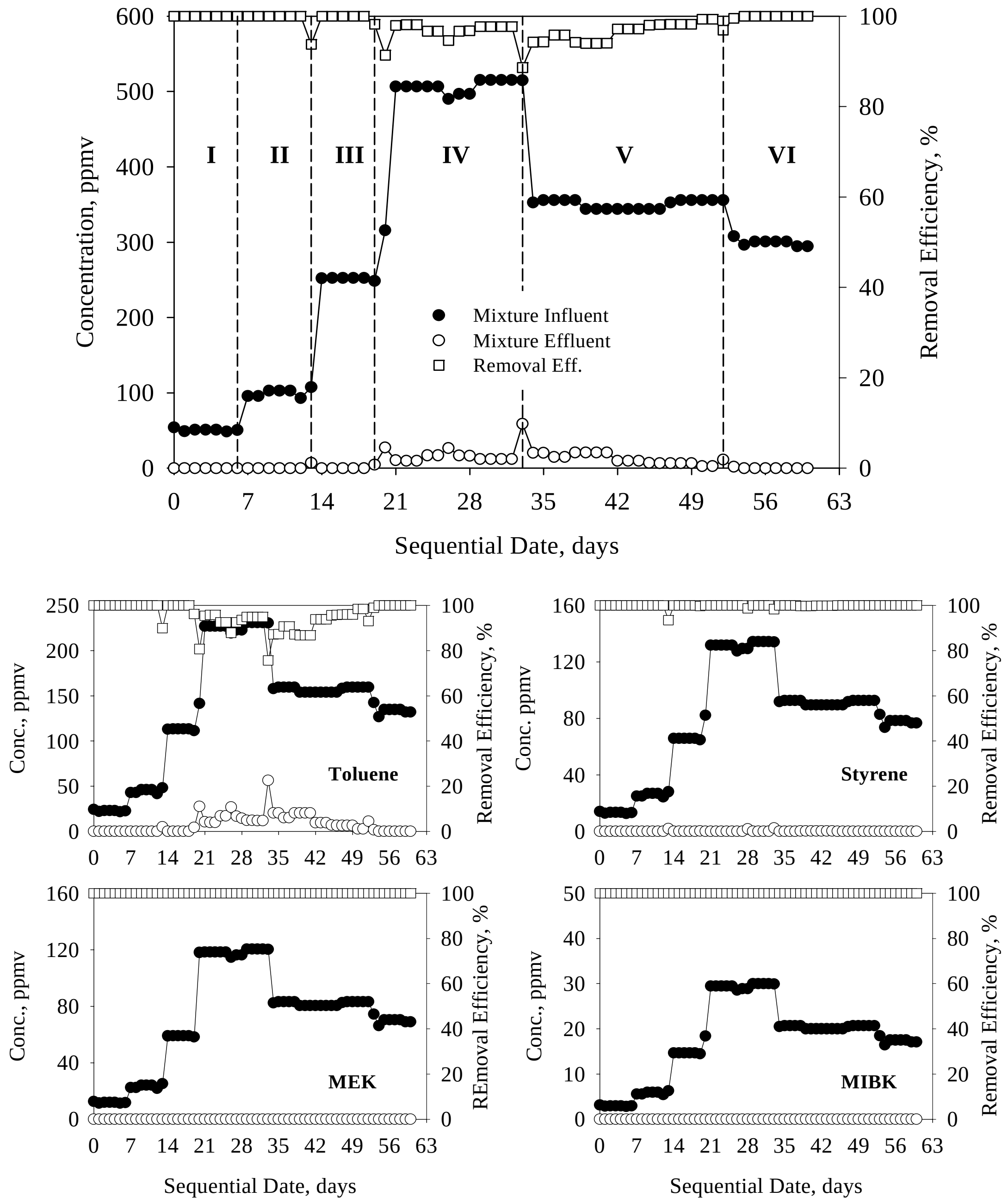


Figure 3-3 Biofilter “B” performance with respect to VOC removal under backwashing operation (I) 50 ppmv, (II) 100 ppmv, (III) 250 ppmv, (IV) 500 ppmv, (V) 350 ppmv, (VI) 300 ppmv

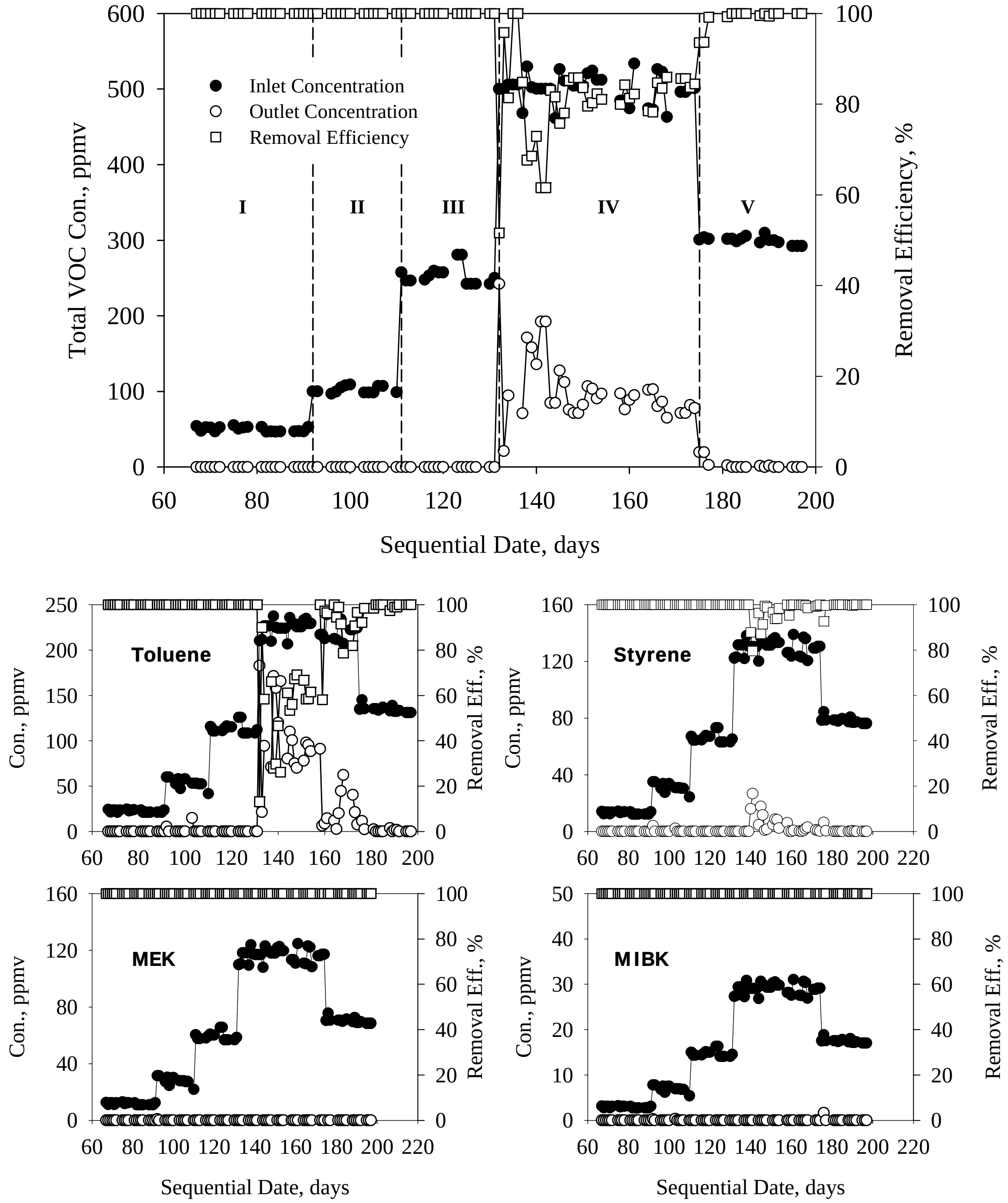


Figure 3-4 Biofilter "B" performance with respect to VOC removal under starvation operation (I) 50 ppmv, (II) 100 ppmv, (III) 250 ppmv, (IV) 500 ppmv, (V) 300 ppmv

The elimination capacity for biofilter "A" with respect to loading rate is presented in Figure 3-5. Figure 3-5(a) indicates that under the backwashing strategy, the biofilter elimination capacity for the mixture is similar to toluene elimination capacity in a single solute study (Kim et al. 2005a). The critical loading for the mixture at which over 99% overall efficiency is attained was 3.94 COD.m$^{-3}$.day$^{-1}$(57.34 g. m$^{-3}$.hr$^{-1}$). However, the toluene critical loading in biofilter "A" was 1.03 kg COD.m$^{-3}$.day$^{-1}$ (13.73 g. m$^{-3}$.hr$^{-1}$), which was much lower than that in the single solute study (3.52 kg COD.m$^{-3}$.day$^{-1}$(46.92 g. m$^{-3}$.hr$^{-1}$)). Meanwhile, styrene critical loading in biofilter "A" under the backwashing strategy was 1.87 kg COD.m$^{-3}$.day$^{-1}$(25.36 g. m$^{-3}$.hr$^{-1}$), which was similar to the single solute study (1.90 kg COD.m$^{-3}$.day$^{-1}$ (25.77 g. m$^{-3}$.hr$^{-1}$)) (Kim et al. 2005b). Therefore, it can be deduced that the elimination capacity of styrene under backwashing strategy in biofilter "A" was not significantly affected by the presence of the other VOCs. However, the removal of toluene was significantly affected. On the other hand, the biofilter elimination capacity decreased under starvation strategy when the loading rate exceeded 3.94 kg COD.m$^{-3}$.day$^{-1}$ (57.34 g. m$^{-3}$.hr$^{-1}$) as shown in Figure 3-5(b). The critical loadings for toluene and styrene in biofilter "A" under starvation strategy were at 0.94 and 1.20 kg COD.m$^{-3}$.day$^{-1}$ (12.53 and 16.27 g. m$^{-3}$.hr$^{-1}$), respectively.

No critical loading for MEK and MIBK in the biofilter could be determined for both backwashing and starvation strategies because at all concentration levels studied because the removal for both components were above 99%.

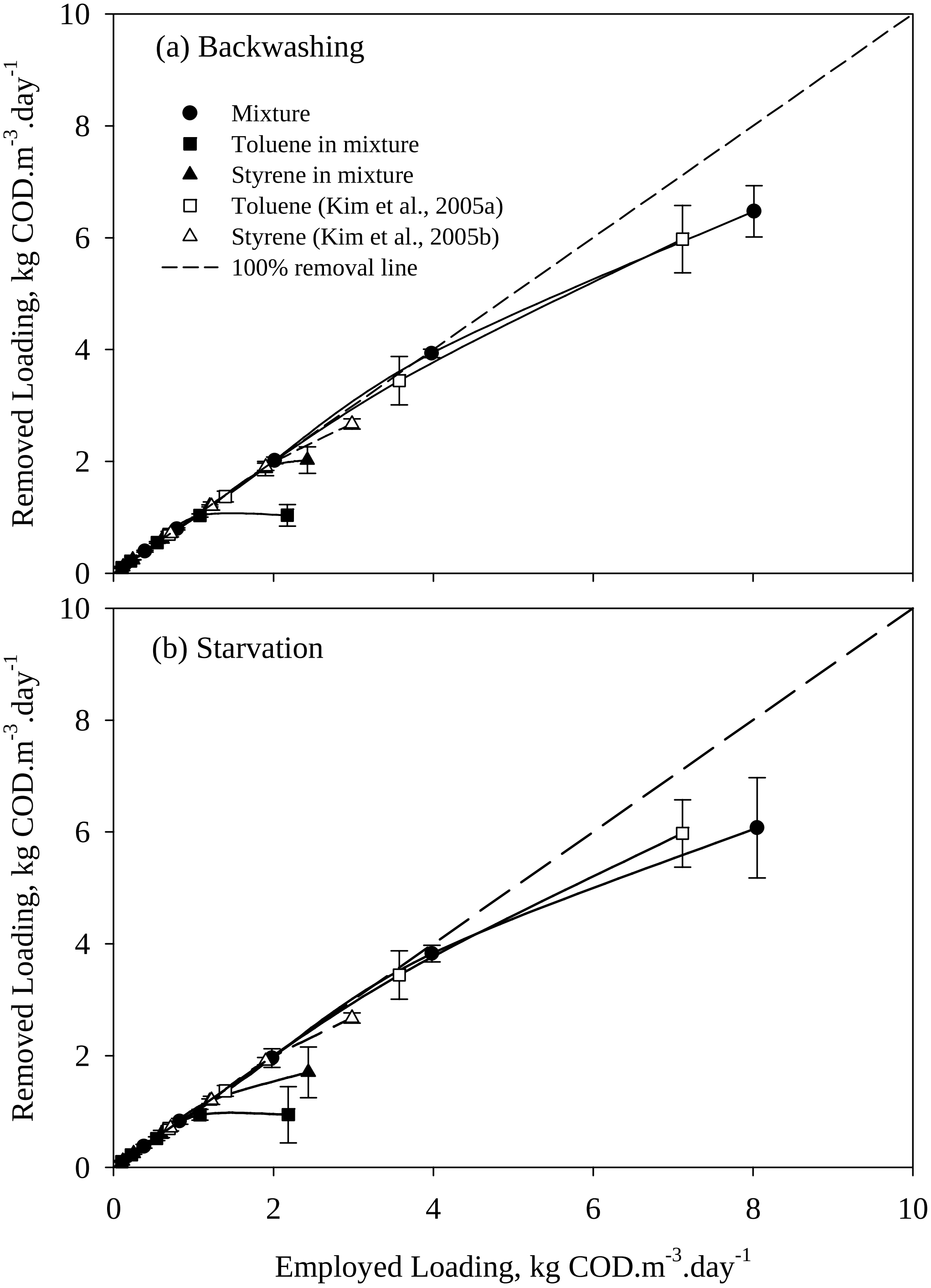


Figure 3-5. Biofilter “A” elimination capacity with respect to loading rate

The elimination capacity for biofilter “B” was much lower than that for biofilter “A” (shown in Figure 3-6). The critical mixture loading for biofilter “B” was 2.40 kg COD.$m^{-3}$.$day^{-1}$. The toluene critical loading under backwashing strategy was 1.30 kg COD.$m^{-3}$.$day^{-1}$ (17.33 g. $m^{-3}$.$hr^{-1}$). No critical loading for styrene, MEK and MIBK could be determined because at all mixture concentration levels studied the removal was above 99%. Under starvation strategy, the toluene critical loading was 1.13 kg COD.$m^{-3}$.$day^{-1}$ (15.06 g. $m^{-3}$.$hr^{-1}$) and the styrene critical loading was 1.20 kg COD.$m^{-3}$.$day^{-1}$ (16.27 g. $m^{-3}$.$hr^{-1}$).

The overall employed loading rates were similar for both biofilters under the same overall influent concentrations (see Table 3-1). The major difference between the two biofilters was toluene and MIBK content. It is worthwhile to note that there is no significant difference in performance between the two biofilters with respect to styrene, MEK, and MIBK. However, the overall performance of biofilter “B” was poor as compared to biofilter “A” which could be attributed to the higher toluene content in biofilter “B”.

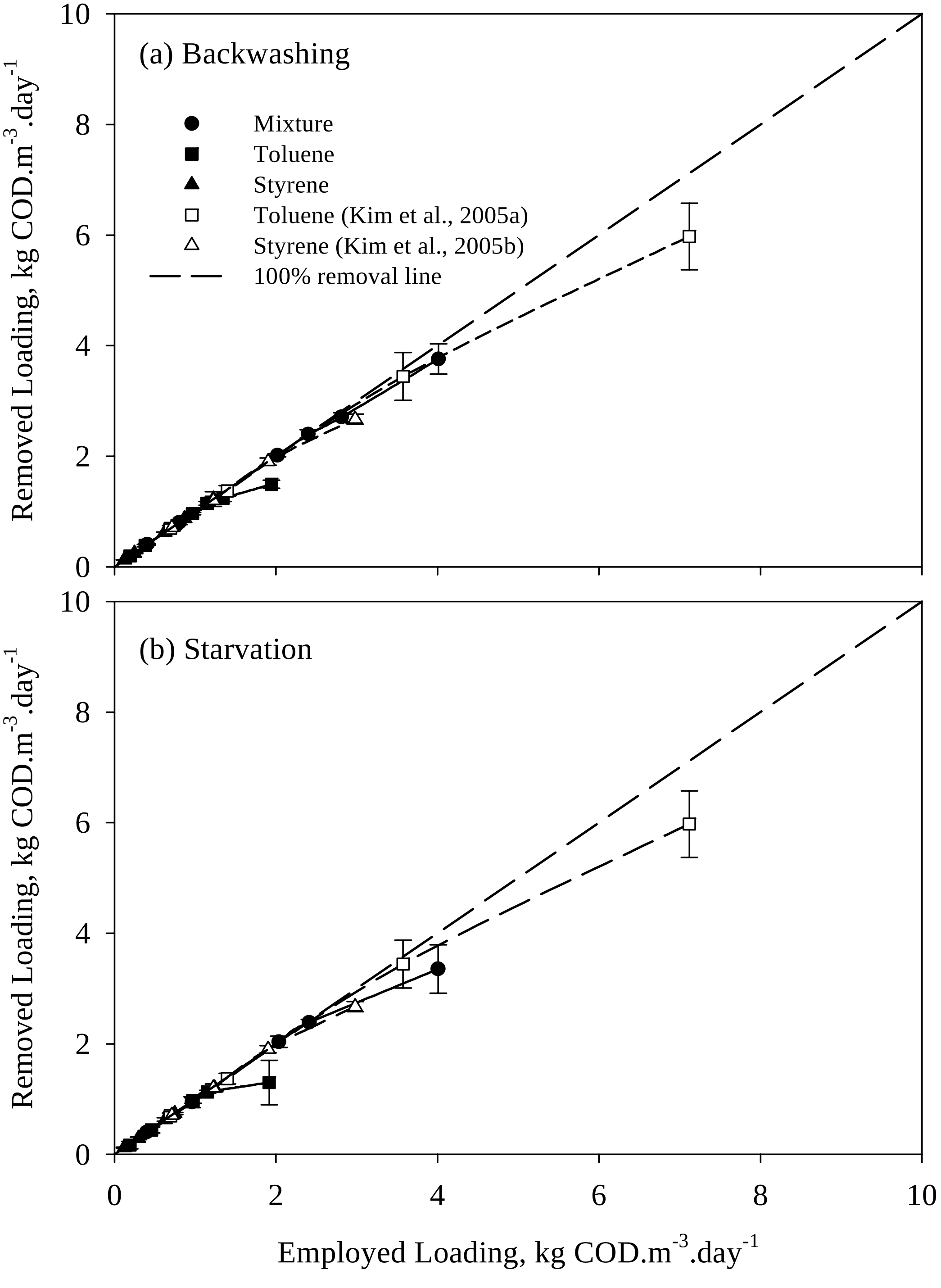


Figure 3-6. Biofilter “B” elimination capacity with respect to loading rate

### 3.4.2. Biofilter Response after Backwashing and Starvation Operation

Effluent samples were collected at prescheduled time intervals to evaluate biofilter response after backwashing and starvation. Re-acclimation was considered to have been achieved when 99% of the original performance was attained. Table 3-2 and 3-3 indicate that the recovery of biofilter performance was delayed with increase of loading rate for both mixtures. Under backwashing strategy, both biofilters recovered to 99% removal efficiency for an overall influent concentration up to 500 ppmv (biofilter “A”) and 300 ppmv (biofilter “B”). However, under starvation strategy, the biofilters could just recover to 99% level at an overall influent concentration up to 250 ppmv and 300 ppmv for biofilter “A” and biofilter “B”, respectively.

The starvation strategy helped the biofilter recover its original performance at lower inlet mixture concentration due to more available biomass without causing adverse effect. However, at high inlet mixture concentration, starvation operation decreased the overall performance of the biofilters due to excess biomass retained in the biofilters. Furthermore, it is noticed that each biofilter obtained a higher removal level just after re-starting from starvation operation. The initial higher removal level could be attributed to the adsorption of VOCs by the accumulated biomass in the biofilter and not due to biodegradation because of the decreased performance after the initial high removal level and then recovering gradually to a high level performance. Meanwhile, re-acclimation required longer time for biofilter “B” due to the higher toluene content in the mixture as compared to biofilter “A”. The re-acclimation of each component in the mixtures (see appendix) indicated that the required re-acclimation period was controlled by the re-acclimation of toluene and styrene in the mixtures. Re-acclimation of MEK and MIBK for both mixtures was within 30 minutes for all loading rates studied.

Table 3-2 Biofilter “A” response after backwashing and starvation

Removal Efficiency, %

**Backwashing**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 86.8 | 95.3 | 97.7 | 98.8 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 84.5 | 89.2 | 89.2 | 92.6 | 96.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 88.8 | 86.6 | 82.8 | 87.5 | 96.1 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 80.6 | 84.0 | 79.0 | 81.7 | 93.3 | 98.6 | 99.9 | 99.9 | 99.9 |
| 1000 ppmv | 79.0 | 80.3 | 73.0 | 72.5 | 79.4 | 80.6 | 81.3 | 81.7 | 80.5 |

**Starvation**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 98.7 | 92.5 | 96.4 | 99.3 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 96.0 | 92.8 | 98.5 | 96.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 98.8 | 95.9 | 93.7 | 88.0 | 90.0 | 92.5 | 92.4 | 94.7 | 95.2 |
| 1000 ppmv | 92.9 | 94.2 | 94.7 | 78.6 | 65.3 | 83.3 | 73.5 | 70.4 | 70.9 |

Table 3-3 Biofilter “B” response after backwashing and starvation

| Removal Efficiency, % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Backwashing** | | | | | | | | | |
| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
| 50 ppmv | 82.7 | 93.6 | 94.3 | 95.6 | 96.4 | 97.5 | 99.8 | 99.9 | 99.9 |
| 100 ppmv | 77.7 | 88.4 | 87.9 | 90.4 | 92.7 | 95.2 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 75.9 | 82.2 | 84.6 | 87.2 | 87.7 | 93.1 | 98.5 | 99.9 | 99.9 |
| 300 ppmv | 74.9 | 80.2 | 82.2 | 85.7 | 88.1 | 91.9 | 95.0 | 99.8 | 99.9 |
| 350 ppmv | 72.1 | 68.8 | 81.4 | 83.7 | 86.1 | 89.2 | 94.2 | 95.4 | 96.1 |
| 500 ppmv | 71.4 | 74.9 | 79.4 | 81.0 | 83.4 | 86.7 | 90.0 | 87.8 | 91.3 |
| **Starvation** | | | | | | | | | |
| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
| 50 ppmv | 82.8 | 62.1 | 75.7 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 86.5 | 83.2 | 70.0 | 82.1 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 98.0 | 89.2 | 72.9 | 64.3 | 85.2 | 91.4 | 99.9 | 99..9 | 99.9 |
| 300 ppmv | 97.7 | 86.9 | 77.4 | 68.4 | 83.4 | 99.1 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 94.4 | 90.7 | 83.2 | 63.3 | 77.4 | 79.8 | 83.2 | 80.3 | 81.6 |

### 3.4.3. Nitrogen Utilization and VOCs Removal

Daily analyses for the influent and effluent concentrations of $NO_3^-$-N were conducted. The net nitrogen utilization was calculated by subtracting the amount of the $NO_3^-$-N species in the effluent water from the $NO_3^-$-N species present in the nutrient feed. COD removal was calculated as the difference between the COD of the feed and the COD of the effluent gas and liquid streams. Figure 3-7 and Figure 3-8 show COD/N ratios plotted against the sequential date for biofilter “A” and “B”, respectively.

The ratios in Figure 3-7(a) under backwashing strategy show apparent dependency on the employed loading rate and time. As the employed loading rate was increased up to 1.98 kg COD.$m^{-3}$.$day^{-1}$ (28.67 g. $m^{-3}$.$hr^{-1}$) (stage III), the ratio of COD/N increased. When the loading rate exceeded 1.98 kg COD.m$^{-3}$.day$^{-1}$, the ratios of COD/N remained constant at around 55 g COD/g N after the initial acclimation of the biofilter. The decrease of nitrogen utilization with increase of loading rate up to 1.98 kg COD.m$^{-3}$.day$^{-1}$ (28.67 g. m$^{-3}$.hr$^{-1}$) could be due to a decrease in microbial viability. When the loading rate was further increased, stability in microbial viability is reached after initial acclimation of the biofilter to the new loading rate. Furthermore, it is noticed that as the loading rate was increased, longer time was required to attain stable COD/N ratio which is consistent with the VOC removal described previously.

However, the ratios of COD/N in Figure 3-7(b) for starvation strategy did not show apparent dependency on loading, which could mean that the microbial viability reached stability under starvation operation due to retained biomass in the biofilter. Meanwhile it showed dependency on time in each starvation cycle. The ratios of COD/N were high just after re-start from starvation period and then decreased quickly to a relative stable value (around 45 g COD/g N). The transition period in ratios of COD/N from high to stable values for each starvation cycle could be attributed to the process regaining stable microbial viability after re-start from starvation period.

The nitrogen utilization for biofilter “B” (shown in Figure 3-8) was similar to biofilter “A” and the ratios of COD/N after stabilization were 40 and 45 g COD/g N for backwashing and starvation operation, respectively.

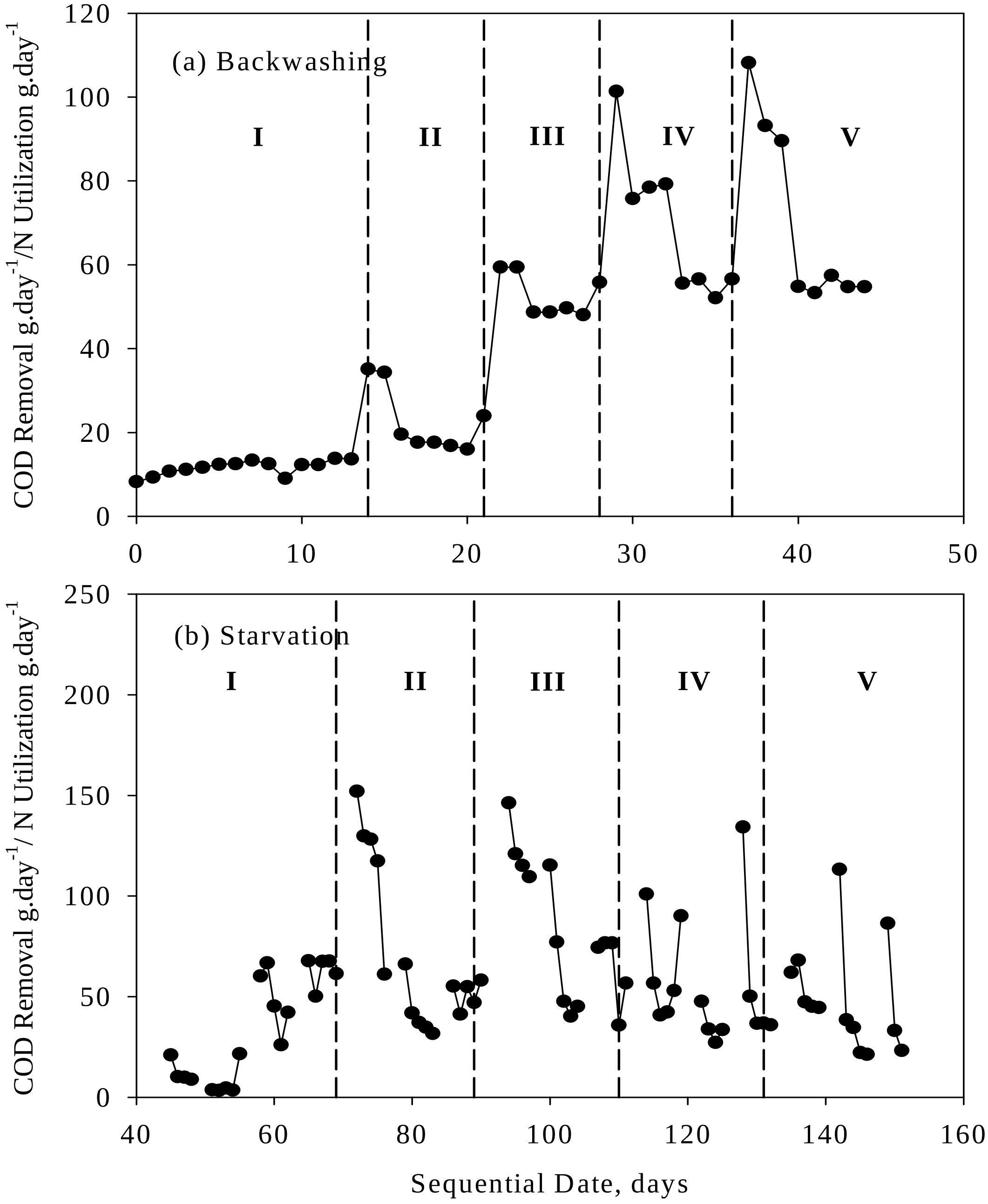


Figure 3-7 COD removal per nitrogen utilization under backwashing and starvation for biofilter “A”

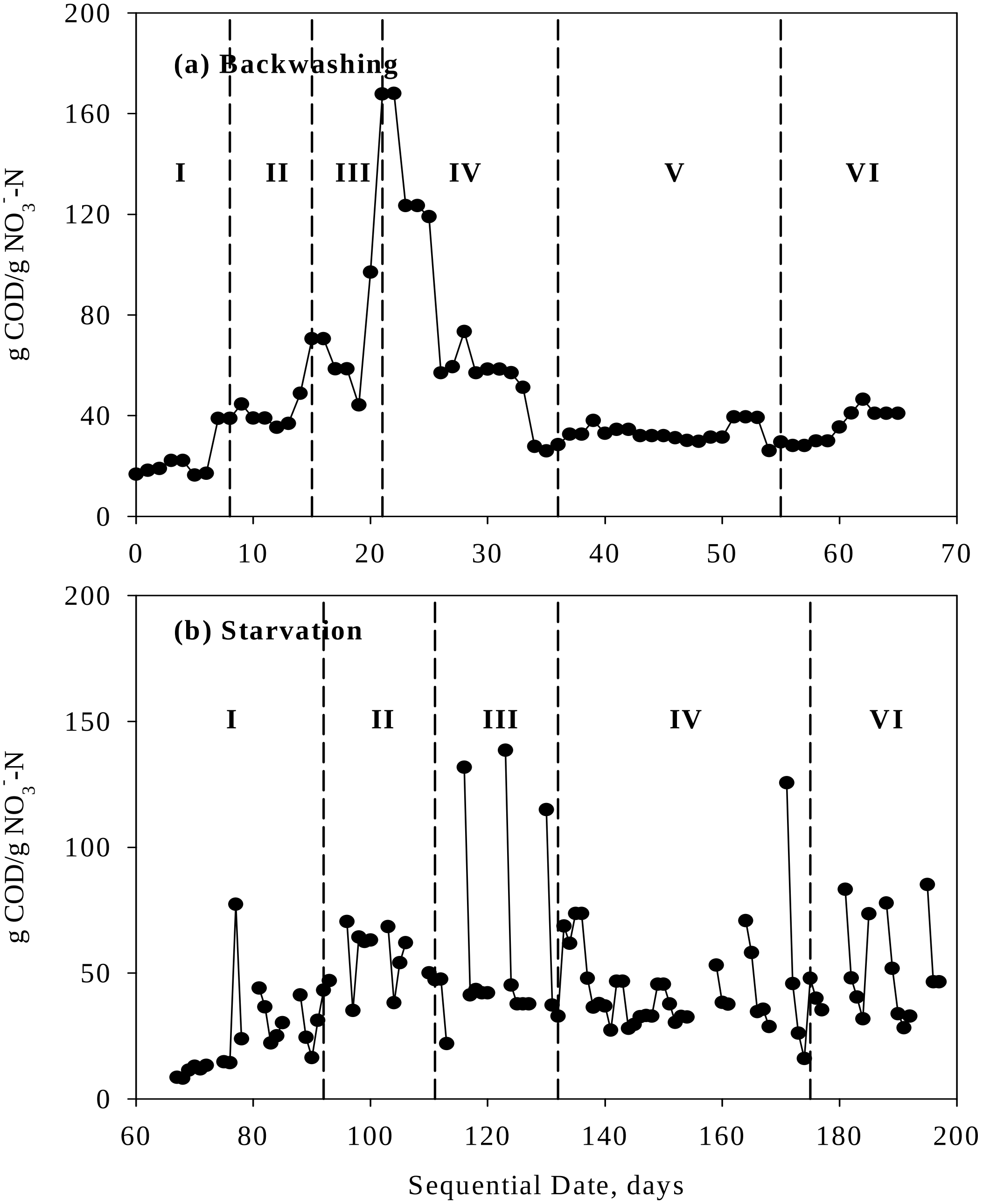


Figure 3-8 COD removal per nitrogen utilization under backwashing and starvation for biofilter "B"

### 3.4.4. Kinetics Analysis of Biofilter Performance

One day following backwashing, gaseous samples were taken along the media depth of the biofilter to assess the removal kinetics for both mixtures. The kinetic analyses were based on pseudo first-order removal rate as a function of biofilter depth. By plotting the natural logarithmic scale of the ratio of residual concentration of each component in the mixture to its inlet concentration as a function of depth into the biofilter (expressed as the cumulative EBRT), i.e., ($\ln(C/C_o)$ vs. time), the pseudo first order removal rate constants were obtained from the slopes of the regression lines.

Figure 3-9 represents plots of the first order removal rate constants of toluene and styrene in the two biofilters under the different loading rates for the two operating conditions considered in this study. No rate constants could be obtained for MEK and MIBK because they were removed completely in the upper 3/8 biofilter media bed at all employed concentrations in this study.

The result in Figure 3-9 indicates that the removal rate constants decreased as the employed loading rates increased for toluene and styrene in both biofilters. The effect of starvation operation showed apparent transition from positive to negative for both biofilters, which is consistent with the biofilter performance. The corresponding rate constants for biofilter “A” are apparently greater than those for biofilter “B” for toluene and styrene under similar loading rates. Lower rate constant values for toluene in biofilter “B” could be contributed to the much higher toluene content in the mixture than that in biofilter “A” (see Table 3-1). The different rate constants for styrene in the two biofilters could indicate that styrene is affected by the relative concentration of the other components in the mixtures. Since the overall performances of the two biofilters with respect to styrene were similar, hence the difference in removal rates indicates more utilization of biofilter depth for biofilter “A” as compared to “B”.

On comparing the rate constants from our previous single solute study (Kim et al. 2005b; Kim et al. 2005a) to the current mixture study, it can be seen that toluene was significantly impacted by the presence of other components (see Figure3-9(a)). However, styrene removal rate constants in Figure 3-9(b) showed slight difference between the single solute and the two mixtures studied. This behavior could indicate that toluene biodegradation along the biofilter depth was affected significantly by the other VOCs in the mixtures and styrene biodegradation was not affected.

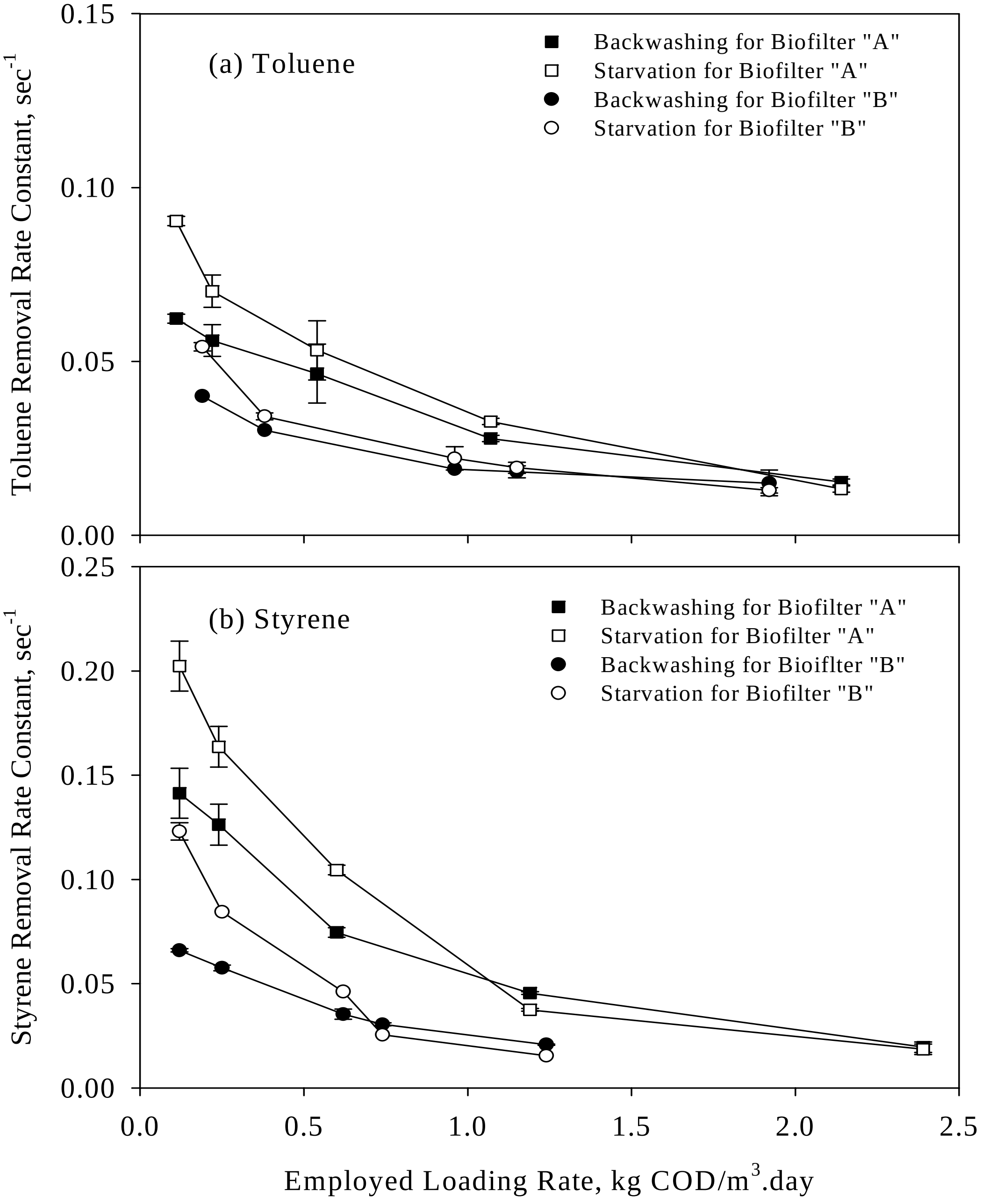


Figure 3-9 Toluene and styrene removal rate for the two operating conditions

### 3.4.5. $CO_2$ Closure (Carbon Mass Balance)

The cumulative $CO_2$ equivalent of VOCs consumed in the mixtures during all experimental runs was compared to the cumulative $CO_2$ produced within the biofilter (Figure 3-10). The inlet (or outlet) cumulative $CO_2$ was estimated as the total cumulative $CO_2$ in the influent (or effluent) aqueous and gaseous stream. For biofilter “A”, the outlet cumulative $CO_2$ was about 98.4% and 84.7 % of the inlet cumulative $CO_2$ for backwashing and starvation operation, respectively. For biofilter “B”, the outlet cumulative $CO_2$ was about 96.5% and 83.2 % of the inlet cumulative $CO_2$ for backwashing and starvation operation, respectively. The results indicate that the cumulative $CO_2$ provided a very good closure for backwashing operation for both mixtures. The big deviations between the input cumulative $CO_2$ and the output cumulative $CO_2$ for starvation operation could be due to unwashed biomass within the biofilter which is not accounted for and might also be due to indigenous respiration during starvation periods which were not also accounted.

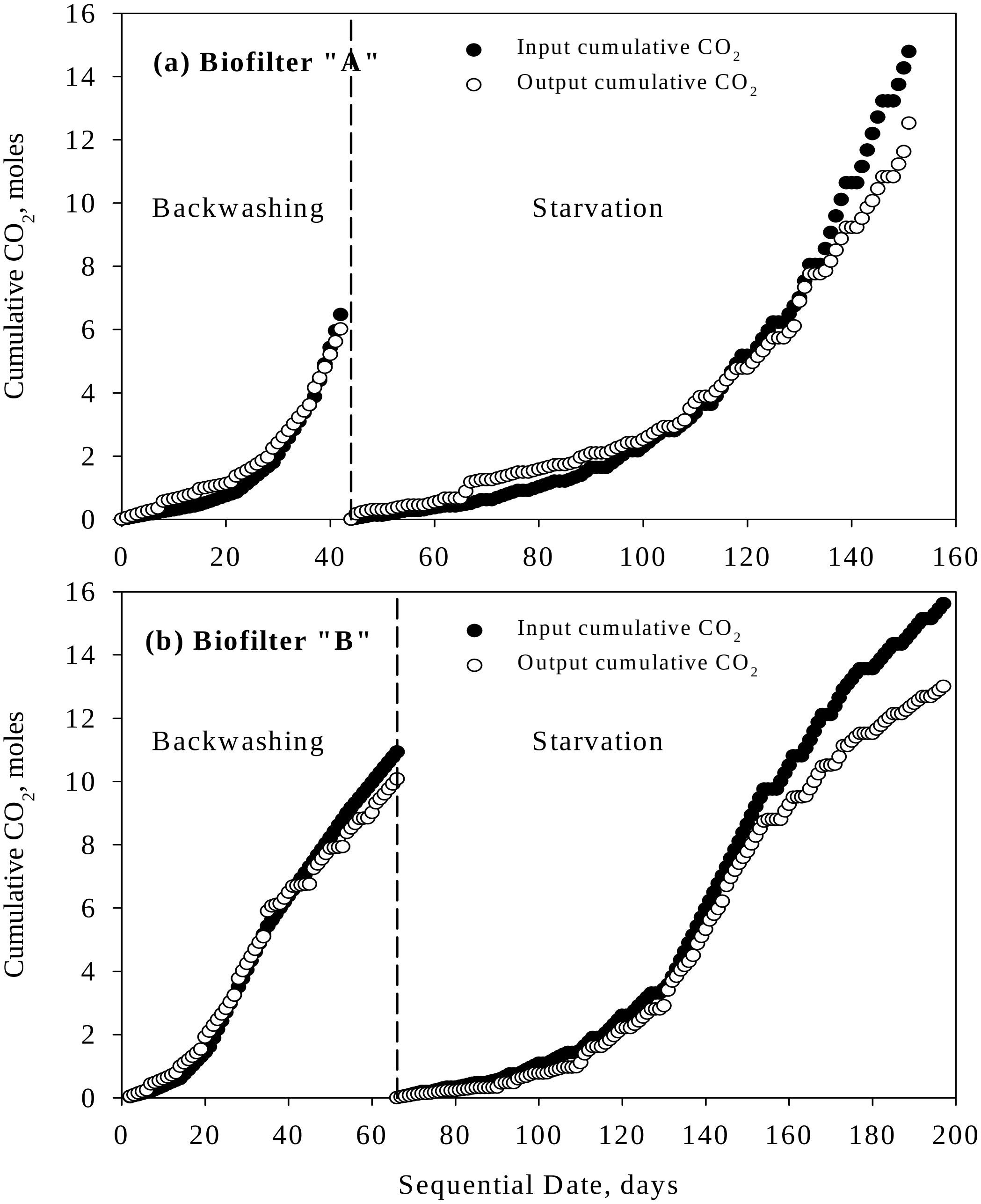


Figure 3-10 Development of carbon balance with time ($CO_2$ closure)

## 3.5. Conclusions

This study investigated biofilter performance on two parallel trickling biofilters for two VOC mixtures. Step change in VOC concentrations revealed that over 99% removal efficiency could be maintained at an inlet mixture concentrations up to 500 ppmv (loading rate 3.94 kg COD.m$^{-3}$.day$^{-1}$) and 300 ppmv (loading rate 2.40 kg COD.m$^{-3}$.day$^{-1}$) for biofilter “A” and biofilter “B”, respectively. Toluene content in the mixtures played a major role in the biofilter overall performance. Furthermore, starvation operation helped in maintaining high level performance and could be used as another means of biomass control provided the inlet mixture concentration did not exceed 250 ppmv (2.01 kg COD.m$^{-3}$.day$^{-1}$) and 300 ppmv (2.40 kg COD.m$^{-3}$.day$^{-1}$) for biofilter “A” and biofilter “B”, respectively.

Biofilter re-acclimation study showed that re-acclimation was delayed for both biofilters with increase of inlet mixture concentrations. The performance of biofilter “B” required longer time to recover than that of biofilter “A” due to the higher toluene content in biofilter “B”.

Nitrogen utilization investigation indicated that biofilters required a transition period to get re-acclimated to new operating conditions and nitrogen utilization showed corresponding changing. There is no apparent difference in nitrogen utilization for the two biofilters.

VOCs removal kinetic analysis indicated that biofilter depth utilization increased with increase of inlet mixture concentrations for both biofilters. MEK and MIBK in the mixtures were removed in the upper biofilter depth, and removal of styrene and toluene utilized more biofilter depth. Meanwhile, biofilter “B” had higher removal rates for toluene and styrene than biofilter “A”. The removal rate constant for toluene in the two mixtures studied were significantly different from the single solute.

## 3.6. References

Aizpuru, A., Khammar, N., Malhautier, L., and Fanlo, J. L. (2003a). "Biofiltration for the treatment of complex mixtures of VOC - Influence of the packing material." *Acta Biotechnologica*, 23(2-3), 211-226.

Aizpuru, A., Malhautier, L., Roux, J. C., and Fanlo, J. L. (2001). "Biofiltration of a mixture of volatile organic emissions." *Journal of the Air & Waste Management Association*, 51(12), 1662-1670.

Aizpuru, A., Malhautier, L., Roux, J. C., and Fanlo, J. L. (2003b). "Biofiltration of a mixture of volatile organic compounds on granular activated carbon." *Biotechnology and Bioengineering*, 83(4), 479-488.

Arnold, M., Reittu, A., von Wright, A., Martikainen, P. J., and Suihko, M. L. (1997). "Bacterial degradation of styrene in waste gases using a peat filter." *Applied Microbiology and Biotechnology*, 48(6), 738-744.

Atoche, J. C., and Moe, W. M. (2004). "Treatment of MEK and toluene mixtures in biofilter: effect of operating strategy on performance during transient loading." *Biotechnology and Bioengineering*, 86(4), 468-481.

Bibeau, L., Viel, G., and Heitz, M. (2000). "Biofiltration of xylene polluted air with a new filtering bed composed of cellulose." *Canadian Journal of Civil Engineering*, 27(4), 814-828.

Cai, Z., Kim, D., and Sorial, G. A. (2004). "Evaluation of trickle-bed air biofilter performance for MEK removal." *Journal of Hazardous Materials*, 114(1-3), 153-158.

Cai, Z., Kim, D., and Sorial, G. A. (2005). "Removal of methyl isobutyl ketone from contaminated air by trickle-bed ai biofilter." *Journal of Environmental Engineering*, 131(9), 1322-1329.

Cai, Z., Kim, D., and Sorial, G. A. (2006). "Performance and microbial diversity of trickle-bed Air biofilter under interchanging contaminants." *Engineering in Life Science*, 6(1), 37-42.

Chang, K., and Lu, C. Y. (2003). "Biofiltration of toluene and acetone mixtures by a trickle-bed air biofilter." *World Journal of Microbiology & Biotechnology*, 19(8), 791-798.

Chitwood, D. E., and Devinny, J. S. (2001). "Teatment of mixed hydrogen sulfide and organic vapors in a rock medium biofilter." *Water Environment Research*, 73(4), 426-435.

Chou, M. S., and Huang, J. J. (1997). "Treatment of methylethylketone in air stream by biotrickling filters." *Journal of Environmental Engineering*, 123(6), 569-576.

Cox, H. H. J., and Deshusses, M. A. (1998). "Biological waste air treatment in biotrickling filters." *Current Opinion in Biotechnology*, 9(3), 256-262.

Cox, H. H. J., and Deshusses, M. A. (2002a). "Co-treatment of H2S and toluene in a biotrickling filter." *Chemical Engineering Journal*, 87(1), 101-110.

Cox, H. H. J., and Deshusses, M. A. (2002b). "Effect of starvation on the performance and re-acclimation of biotrickling filters for air pollution control." *Environmental Science & Technology*, 36(14), 3069-3073.

Delhomenie, M. C., Bibeau, L., Bredin, N., Roy, S., Broussau, S., Brzezinski, R., Kugelmass, J. L., and Heitz, M. (2002). "Biofiltration of air contaminated with toluene on a compost- based bed." *Advances in Environmental Research*, 6(3), 239-254.

Deshusses, M. A. (1997). "Transient behavior of biofilters: Start-up, carbon balances, and interactions between pollutants." *Journal of Environmental Engineering-Asce*, 123(6), 563-568.

Deshusses, M. A., and Hamer, G. (1993). "The removal of volatile ketone mixtures from air in biofilters." *Bioprocess Engineering*, 9(4), 141-146.

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

Deshusses, M. A., Hamer, G., and Dunn, I. J. (1995b). "Behavior of biofilters for waste air biotreatment.2. Experimental evaluation of a dynamic-model." *Environmental Science & Technology*, 29(4), 1059-1068.

Deshusses, M. A., Hamer, G., and Dunn, I. J. (1996). "Transient-state behavior of a biofilter removing mixtures of vapors of MEK and MIBK from air." *Biotechnology and Bioengineering*, 49(5), 587-598.

Don, J. A., and Feenstra, L. "Odor abatement through biofiltration." *Pro., Symp. on Characterization and Control of Odoriferous Pollutants in Process Industries,* Louvain-la-Neuve, Belgium, 337-349.

Kim, D., Cai, Z., and Sorial, G. A. (2005a). "Behavior of trickle bed air biofilter for toluene removal: effect of non-use periods." *Environmental Progress*, 24(2), 155-161.

Kim, D., Cai, Z., and Sorial, G. A. (2005b). "Evaluation of trickle-bed air biofilter performance under periodic stressed operating conditions as a function of styrene loading." *Journal of the Air & Waste Management Association*, 55(2), 200-209.

Martin, F. J., and Loehr, R. C. (1996). "Effect of periods of non-use on biofilter performance." *Journal of the Air & Waste Management Association*, 46(6), 539-546.

Metris, A., Gerrard, A. M., H., C. R., Weigner, P., and Paca, J. (2001). "Modelling shock loadings and starvation in the biofiltration of toluene and xylene." *Journal of Chemical Technology and Biotechnology*, 76(6), 565-572.

Moe, W. M., and Qi, B. (2004). "Performance of a fungal biofilter treating gas-phase solvent mixtures during intermittent loading." *Water Research*, 38(9), 2259-2268.

Mohseni, M., and Allen, D. G. (1999). "Transient performance of biofilters treating mixtures of hydrophilic and hydrophobic volatile organic compounds." *Journal of the Air & Waste Management Association*, 49(12), 1434-1441.

Mohseni, M., and Allen, D. G. (2000). "Biofiltration of mixtures of hydrophilic and hydrophobic volatile organic compounds." *Chemical Engineering Science*, 55(9), 1545-1558.

Mohseni, M., Allen, D. G., and Nichols, K. M. (1998). "Biofiltration of alpha-pinene and its application to the treatment of pulp and paper air emissions." *Tappi Journal*, 81(8), 205-211.

Ottengraf, S. P. P. (1986). "Exhaust Gas Purification." Biotechnology, H. J. a. R. Rehn, G., ed., VCH Verlagsgesellsch, Weinheim, Germany, 425-452.

Park, J., and Kinney, K. A. (2001). "Evaluation of slip feed system for vapor-phase bioreactors." *Journal of Environmental Engineering*, 127(11), 979-985.

Pruden, A., Sedran, M. A., Suidan, M. T., and Venosa, A. D. (2003). "Biodegradation of MTBE and BTEX in an aerobic fluidized bed reactor." *Water Science and Technology*, 47(9), 123-128.

Sologar, V. S., Lu, Z. J., and Allen, D. G. (2003). "Biofiltration of concentrated mixtures of hydrogen sulfide and methanol." *Environmental Progress*, 22(2), 129-136.

Sorial, G. A., Smith, F. L., Suidan, M. T., Biswas, P., and Brenner, R. C. (1995). "Evaluation of trickle-bed biofiltermedia for toluene removal." *Journal of the Air & Waste Management Association*, 45(10), 801-810.

Sorial, G. A., Smith, F. L., Suidan, M. T., Smith, P. J., Biswas, P., and Brenner, R. C. "Evaluation of performance of trickle bed biofilter-impact of periodic removal of accumulated biomass." *87th Annual Meeting and Exhibition of the Air & Waste Management Association*, Cincinnati, OH.

Standard Methods for the Examination of Water and Wastewater. 20th ed., APHA, AWWA, and WEF, 1998

Standefer, S., and Van Lith, C. (1993). "Biofilters minimize VOC emissions." *Environmental Protection*, 4(3), 48-58.

Togna, A. P., and Frisch, S. "Field-pilot study of styrene biodegradation using biofiltration." *86th Annual Meeting and Exhibition of the Air & Waste Management Association*, Dever, CO.

Torronen, M. E., Lehtomaki, J. T., and Laukkarinen, A. J. "A feasibility study of biological waste air purification in cold climates." *Proceedings of the 9th World Clean Air Congress*, Montreal, Canada.

Verschueren, K. (2001). *Handbook of Environmental Data on Organic Chemicals*, John Wiley, New York.

Wani, A. H., Lau, A. K., and Branion, R. M. R. (2000). "Performance of compost and hog-fuel biofilters: Impact of periods of non-use and varying methyl mercaptan loading." *Environmental Technology*, 21(3), 271-283.

Webster, T. S., Cox, H. H. J., and Deshusses, M. A. (1999). "Resolving operational and performance problems encountered in the use of a pilot/full-scale biotrickling fiber reactor." *Environmental Progress*, 18(3), 162-172.

Wu, G., Dupuy, A., Leroux, A., Brzezinski, R., and Heitz, M. (1999). "Peat-based toluene biofiltration: A new approach to the control, of nutrients and pH." *Environmental Technology*, 20(4), 367-376.

Yoon, I.-K., and Park, C.-H. (2002). "Effects of gas flow rate, inlet concentration and temperature on biofiltration of volatile organic compounds in a peat-packed biofilter." *Journal of Bioscience and Bioengineering*, 93(2), 165-169.

Zhu, X., Rihn, M. J., Suidan, M. T., Kim, B. J., and Kim, B. R. (1996). "The effect of nitrate on VOC removal in trickle bed biofilters." *Water Science and Technology*, 34(3-4), 573-581.

# CHAPTER 4

# CYCLIC 2-BED ADSORPTION UNIT

## 4.1. Abstract

A cyclic 2-bed adsorption/desorption unit was evaluated for dampening load fluctuation of a mixture of volatile organic compounds (VOCs). The behavior of the 2-bed system under cyclic operation was compared to that without cyclic operation. The prediction of the plug flow surface diffusion model (PSDM) of the experimental adsorption data showed that cyclic 2-bed unit was superior to the non cyclic 2-bed unit in attenuating contaminants load fluctuation.

## 4.2. Introduction

Removal of VOCs is a very important issue for the chemical industry because of their toxicity to human health and the environment. Biofiltration systems have recently emerged as an efficient and cost-effective technology for control of VOCs emission.

Fluctuations in concentration and variation in the waste air composition is most commonly encountered in industry, which challenges the application of biofiltration technology. One approach for reducing the load fluctuation to the biofilters is to install an activated carbon (AC) bed as a buffer unit before a biofilter. When the system is under periods of high VOC loading, the AC bed will act as an adsorption unit to accumulate VOCs. When the system is under periods of low VOC loading, the AC bed will release accumulated VOCs. In this manner, the AC bed could dampen load fluctuations to the biofilter and help maintain a long-term consistent performance. Although this strategy was first proposed by Ottengraf (1986), experimental testing on this system is very limited (Weber and Hartmans 1995; Li and Moe 2005; Moe and Li 2005). Weber and Hartmans (1995) tested the buffer capacity of a number of activated carbons to a followed biofilter packed with compost and polystyrene with fluctuating concentrations of toluene. They found that the toluene fluctuations could be decreased to around 300 mg. $m^{-3}$ when its fluctuations were between 0 and 1000 mg.$m^{-3}$. Moe and Li (2005) tested toluene load equalization effect of adsorption columns packed with granular activated carbon (GAC) under intermittent loading scenario. The intermittent loading conditions consisted of 8 hours contaminant loading followed by 16 hours non-loading each day. They found that the GAC columns could successfully achieve load equalization of toluene contaminated air streams. The degree of load attenuation became more pronounced at lower contaminant concentrations and higher GAC empty bed contact times (EBCTs). Li and Moe (2005) investigated the performance of an integrated system on removal acetone and toluene mixture under intermittent loading scenario. The system integrated a granular activated carbon (GAC) bed with a biofilter packed with polyurethane foam cubes. The intermittent loading conditions consisted of 8 hours contaminant loading followed by 16 hours non-loading each day. They found that the GAC bed could lead to more uniform loading as a function of time and improve the biofilter treatment performance. Furthermore, the GAC bed showed less equalization effect on acetone than on toluene due to competitive adsorption.

However, all the above mentioned studies on the buffer unit followed by a biofilter unit employed a single adsorption bed. The single bed buffer unit will lose its buffer capacity for large fluctuations or high loading and could cause starvation period during the initial start-up period due to adsorption until breakthrough. To overcome the difficulty of a single bed buffer unit, a 2-bed adsorption unit with cyclic adsorption and desorption was proposed and applied as a buffer unit for the dampening fluctuating feed condition to the followed biofilter in this study.

The idea of the cyclic 2-bed adsorption was inspired by the basic concept of pressure swing adsorption (PSA). PSA is a cyclic process used to selectively adsorb and separate components of a feed gas mixture, thereby producing partially purified gas products(Yang 1987; Ruthven et al. 1994). A typical PSA cycle includes four steps: pressurization, adsorption, depressurization, and regeneration (Knaebel et al. 2005). The cyclic operation in adsorption and regeneration (desorption) has the potential to attenuate the fluctuation in feeding loads. Figure 4-1 shows the cyclic 2-bed concept in this study.

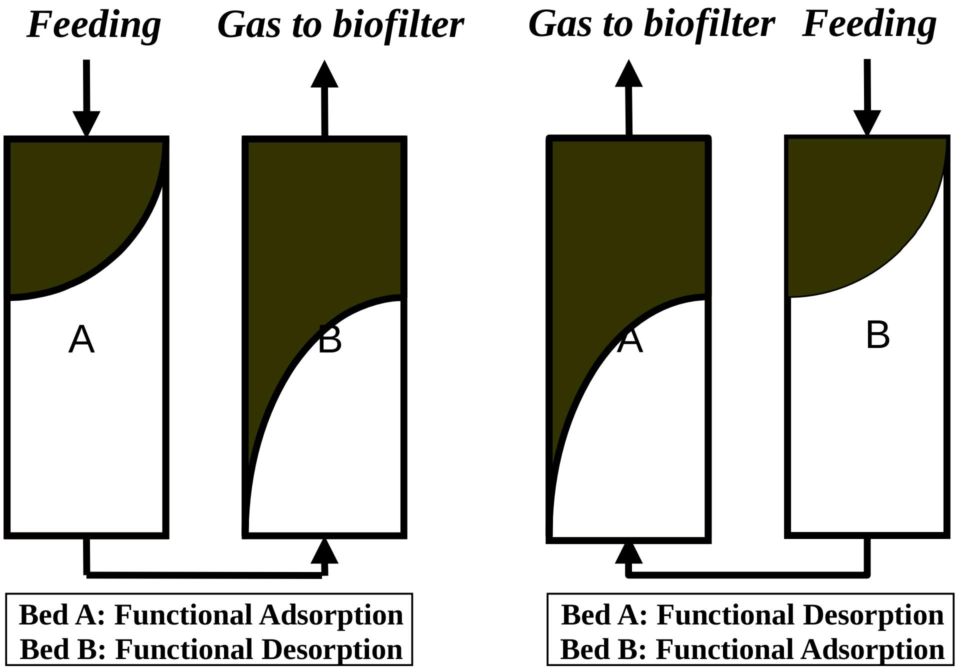


Figure 4-1 Concept about the cyclic 2-bed adsorption unit

When the gas is in counterclockwise direction, bed A is expected to function adsorption, bed B is expected to function desorption. When the gas direction is reversed, bed A is expected to function desorption, bed B is expected to function desorption. By this way, the contaminants loadings to the followed biofilters can be buffered. During the initial start-up periods of the biofilters, the 2-bed system is expected to act as a polishing unit. Furthermore, the cyclic 2-bed unit can act as contaminants source to the biofilter during starvation periods such as weekends or holidays.

### 4.3. Materials and Methods

The two adsorption beds are cylindrical and constructed of stainless steel with an external diameter of 2.54 cm and a length of 20.3 cm. The total volume of the two cylindrical adsorption beds was $2.06\times10^{-4}$. $m^3$. The schematic diagram of the 2-bed system is shown in Figure 4-2. The beds were packed with 165g of bituminous based BPL activated carbon (Calgon Carbon Co, apparent density = 0.85 g/mL). The air supplied to the system was purified with complete removal of water, oil, carbon dioxide, VOCs, and particles by Balston FTIR purge gas generator (Paker Hannifin Corporation, Tewksbury, MA). Liquid VOC was injected via syringe pumps (Harvard Apparatus, model NP-70-2208, Holliston, MA) into the air stream where it vaporized, and entered the equalizing vessel before the system. An additional air valve was installed to introduce the supplemental fresh air within the two adsorption beds for reducing gas pressure in the other fixed bed where desorption occurs, if necessary. Cyclic operation is generated through an electrically operated 4-way solenoid valve (ASCO 8342G 701, Florham Park, NJ), which is controlled by an electronic timer (Digi 42A-120; GRASSLIN Controls Corp., Mahwah, NJ). The cycle duration for the 2-bed unit is based on investigation conducted for the single solute, toluene (Kim 2006). The frequency of the cyclic duration was set at 8h which provided each bed to have 4h feeding and 4h purging. Sampling ports were installed for both the feed and exhaust gases. The concentrations of VOCs in the gas phase were measured by using a gas chromatograph (GC) (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with a flame ionization detector (FID).

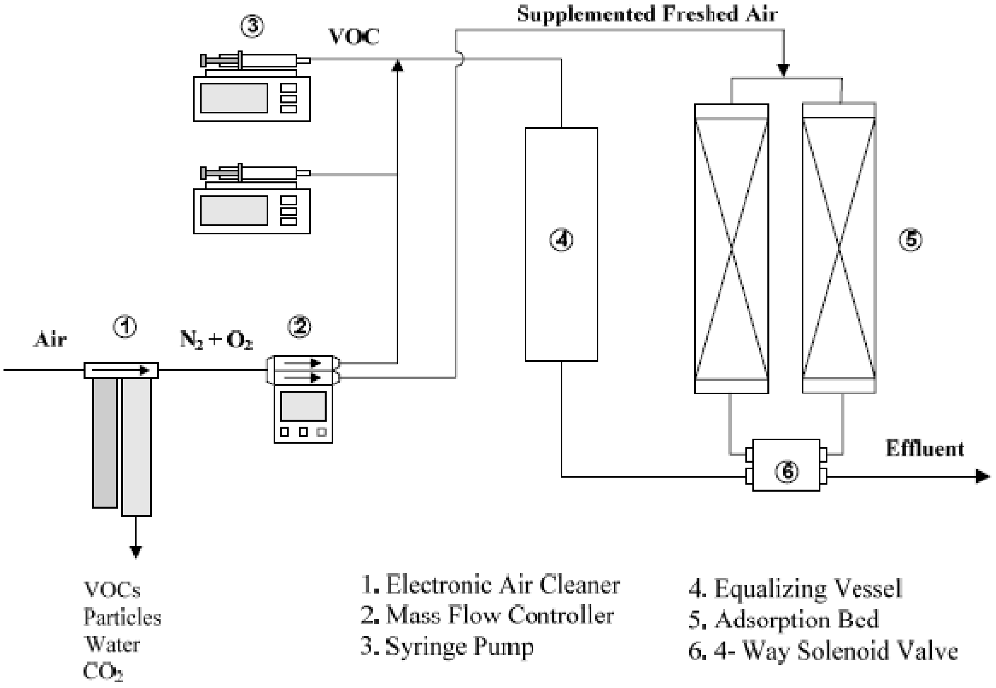


Figure 4-2 Schematic diagram of the cyclic 2-bed system

The target VOC mixture fed to the 2-bed adsorption unit was a mixture of toluene, styrene methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) based on EPA 2003 emission report from chemical industry described in Chapter 3. The molar ratio of the four VOCs was 0.448: 0.260: 0.234: 0.058 for toluene: styrene: MEK: MIBK.

The employed EBRT for the 2-bed adsorption unit was designed to be 9.1 sec (at an air flow rate of 1.35 L/min). To simulate transient loading conditions in the industry, a square wave change of inlet concentrations was considered as shown in Figure 4-3. Pore and surface diffusion model (PSDM) embedded in AdDesignS$^{TM}$ software (Mertz et al. 1999) was used to predict the adsorption behavior in the system. Parameters for the fixed bed and adsorbent employed in this study are summarized in Table 4-1. Adsorption equilibrium was described by the Freundlich equation. The Freundlich parameters were obtained through an isotherm study of the single solute system (Kim et al. 2006). The Freundlich parameters for the single solute, together with the ideal adsorbed solution theory (IAST), which is embedded in the software were then used for predicting equilibrium on the surface of the adsorbent for the mixture solute system. The kinetic parameters, surface diffusion coefficient, pore diffusion coefficient, and film transfer coefficient, were calculated by using empirical equations embedded in the software. The impact of the kinetic parameters on the breakthrough behavior was evaluated by making step changes in their obtained empirical correlations values. It has been found that the film transfer coefficient is the rate controlling mechanism. No significant changes were encountered by changing the surface and the pore diffusion coefficients. A detailed methodology of the model is described in the manual of AdDesignS$^{TM}$ software (Mertz et al. 1999). Adsorbates parameters used in the model are summarized in Table 4-2.

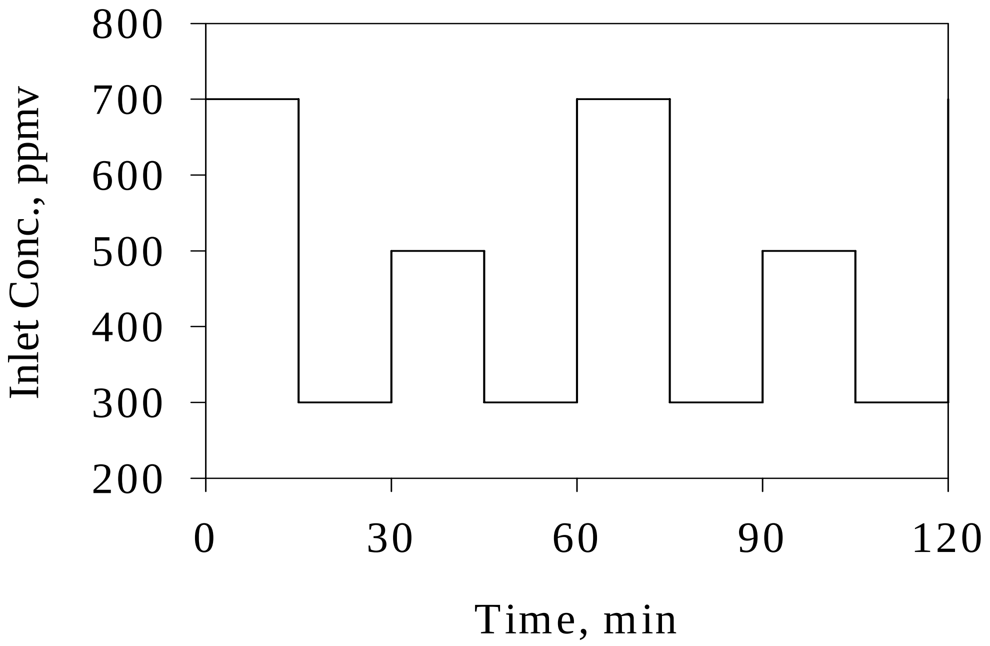


Figure 4-3 Theoretical feeding condition for a square wave change of inlet concentration

Table 4-1 Properties of adsorption bed, adsorbent and air flow

| Parameter | Value | Unit |
|---|---|---|
| Fixed Bed Properties | | |
| Bed Length | 40.6 | cm |
| Bed Diameter | 2.54 | cm |
| Carbon Mass | 165 | g |
| Flow rate | 1.35 | L/min |
| Adsorbent Properties* | | |
| Name | Calgon BPL 6×16 | |
| Apparent Density | 0.85 | g/mL |
| Particle Radius | 0.186 | cm |
| Porosity | 0.595 | |
| Particle Shape Factor | 0.72 | |
| Air Properties | | |
| Pressure | 1 | atm |
| Temperature | 20 | ℃ |

* Data provided by Calgon carbon

Table 4-2 Modeling simulation parameters for the adsorbates

| Parameter | Toluene | Styrene | MEK | MIBK |
|---|---|---|---|---|
| Freundlich Isotherm Parameters [a] | | | | |
| K ((mg/g)(L/mg)$^{1/n}$) | 339 | 368 | 119 | 288 |
| 1/n | 0.314 | 0.144 | 0.298 | 0.103 |
| Kinetic Parameters [b] | | | | |
| Film Diffusion (cm/s) | 0.32 | 3.20 | 0.52 | 4.67 |
| Surface Diffusion (cm$^2$/s) | $0.58\times10^{-6}$ | $2.45\times10^{-6}$ | $1.64\times10^{-6}$ | $1.85\times10^{-7}$ |
| Pore Diffusion (cm$^2$/s) | $8.08\times10^{-2}$ | $8.34\times10^{-2}$ | $9.16\times10^{-2}$ | $7.47\times10^{-2}$ |

a Experimental measurement by Kim et al. (2006)

b Calculated by AdDesignS™

## 4.4. Results and Discussion

### 4.4.1. 2-Bed adsorption unit without cyclic operation

In order to compare the behavior of the buffering capacity with non cyclic operation, the solenoid valve that operates the cyclic operation was shut off and the two beds will act in behavior as one bed. The experimentally measured and the model simulation of the VOC mixture effluent profiles are presented in Figure 4-4. The effluent profiles for the four components in the VOCs mixture are shown in Figure 4-5. Within the two figures, there are two insert plots: One represents a short period of the initial performance, and the other represents a short period of the breakthrough.

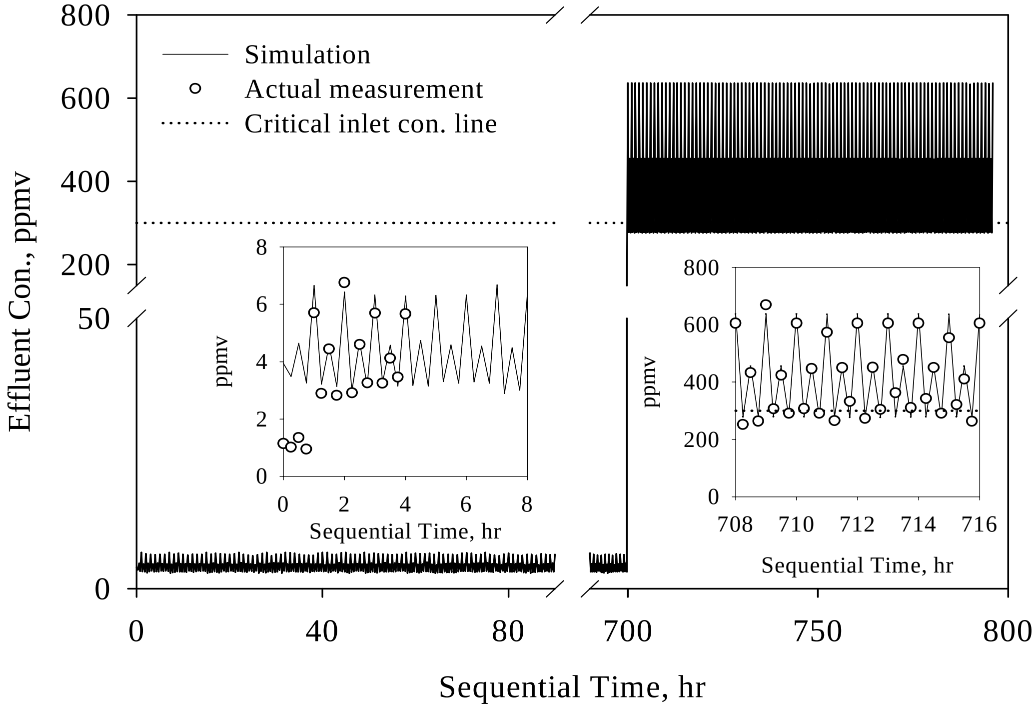
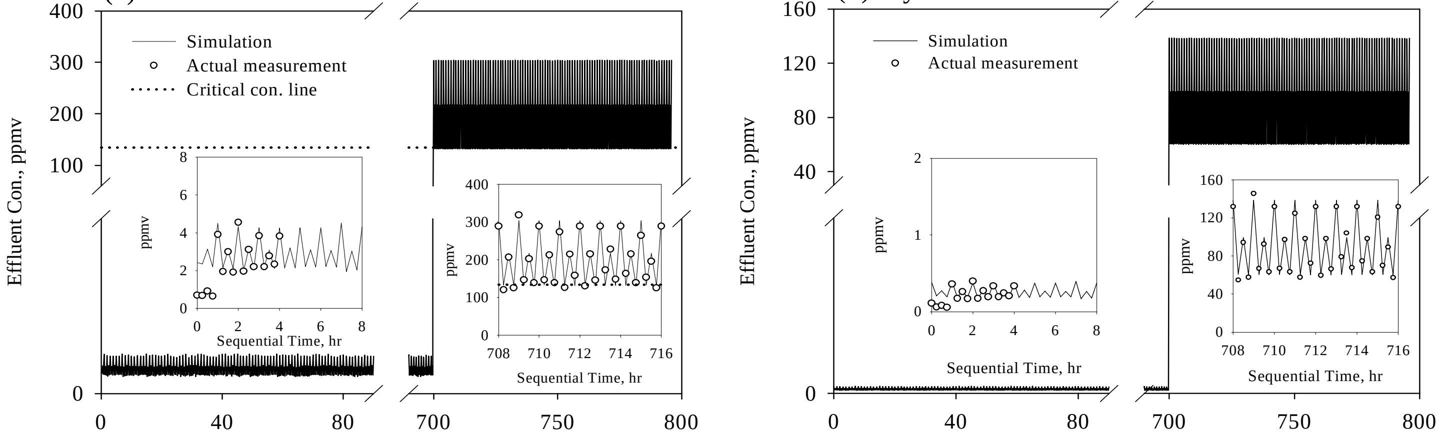
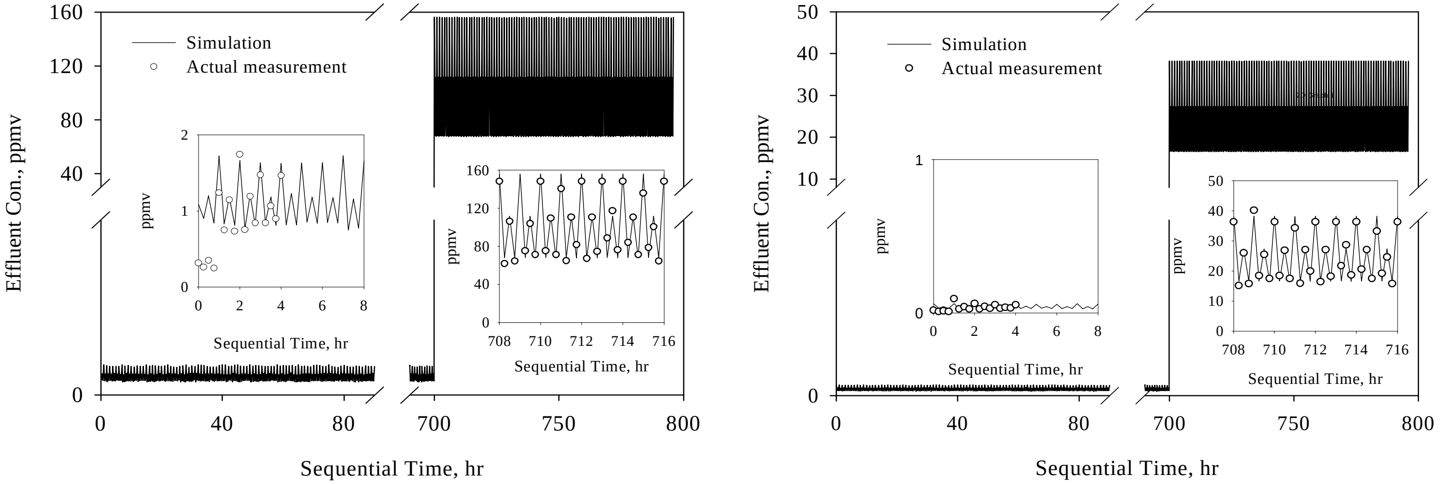


Figure 4-4 Experimental measurement and model simulation of the VOC mixture without cyclic operation



(a) Toluene

(b) Styrene



(c) MEK

(d) MIBK

Figure 4-5 Experimental measurement (open symbols) and model simulation (solid line) of the four components in the mixture

Figure 4-4 and Figure 4-5 show that the PSDM can predict the adsorption behavior of the non-cyclic 2-bed adsorption unit.

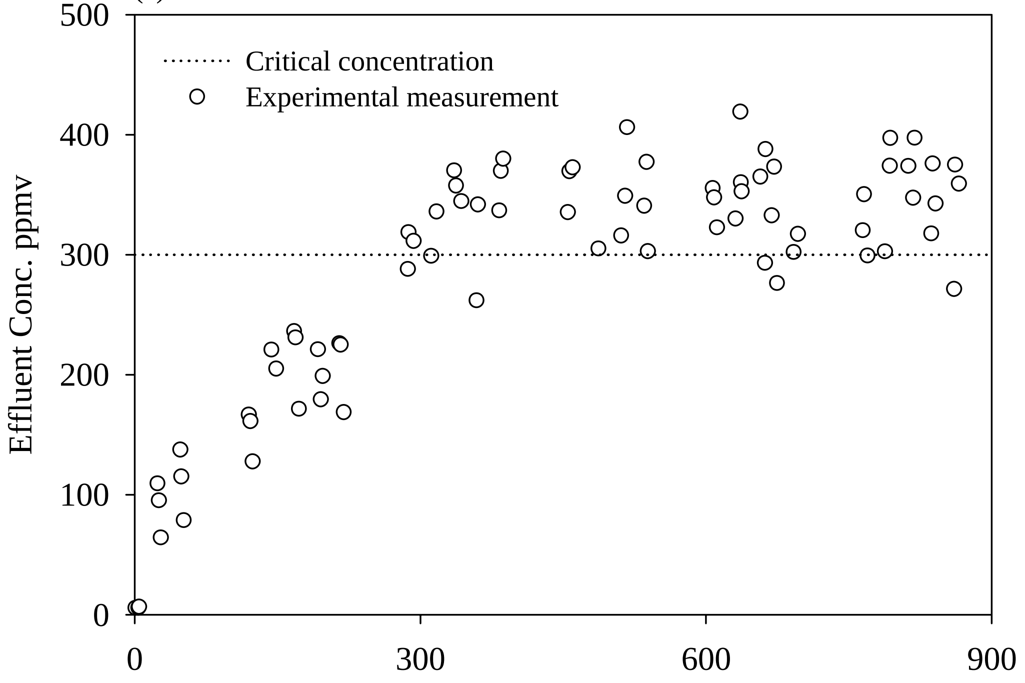
It is seen from Figure 4-4 that the total concentrations of the effluent VOCs from the non-cyclic 2-bed adsorption unit were below 10 ppmv before breakthrough till around 700 hours. Once it brokethrough, the total concentrations of the effluent VOCs fluctuated between 250 to 650 ppmv, which was over the critical concentration for a followed biofilter, i.e. above the critical concentration of 300 ppmv ( see Chapter 3). Such a low VOCs concentration from the adsorption unit prior to breakthrough will cause the followed biofilter to be operated under starvation condition, which will delay the acclimation of the biofilter to the employed contaminants. The sudden breakthrough after 700 hrs will introduce a shock loading to the followed biofilter. Furthermore, the wide fluctuation (250-650 ppmv) in the effluent from the adsorption unit after breakthrough will lead to unstable performance of the biofilter which could lead to failure in effective removal of VOCs. The influent fluctuation shown in Figure 4-3 was between 300 and 700 ppmv. Based on the effluent profile, it can be concluded that the single bed adsorption unit failed to act as a buffering unit to the followed biofilter for such square wave condition.

Effluent profiles for components in the mixture shown in Figure 4-5 were consistent with the overall effluent profile in Figure 4-4. The effluent concentrations of toluene in the mixture fluctuated between 130 and 310 ppmv and exceeded the critical inlet concentration of 134.4 ppmv (see Chapter 3). It has been revealed in Chapter3 that the overall performance of the biofilter for this mixture was controlled by the removal of toluene. Therefore, it is expected that using a single adsorption bed will lead to failure in performance of a followed biofilter due to the wide fluctuations in the toluene concentration (130-310 ppmv). The effluent concentrations of styrene from the adsorption bed fluctuated between 60 and 140 ppmv with most of the experimental period under 120 ppmv. Based on the study conducted in Chapter 3, it is expected that such fluctuations in styrene concentration would not have significant impact on the followed biofilter. It has been determined in Chapter 3 for styrene inlet concentration of 135 ppmv in such a mixture, the removal efficiency was over 99% (see Figure 3-3). The effect of effluent fluctuation of MEK and MIBK in the mixture to the followed biofilter would not be significant (see Figure 3-3). It is expected that their effect on the overall biofilter performance can be neglected due to their superior performance in the mixture (see Chapter 3) and the single solute system (Cai et al. 2004; Cai et al. 2005).

### 4.4.2. 2-Bed adsorption unit with cyclic operation

The behavior of the 2-bed adsorption unit with cyclic operation under the square wave feeding condition described in Figure 4-3 was investigated for evaluating its buffering capacity. The effluent profiles from the 2-bed adsorption unit are shown in Figure 4-6.

(a) Mixture



(b) Components

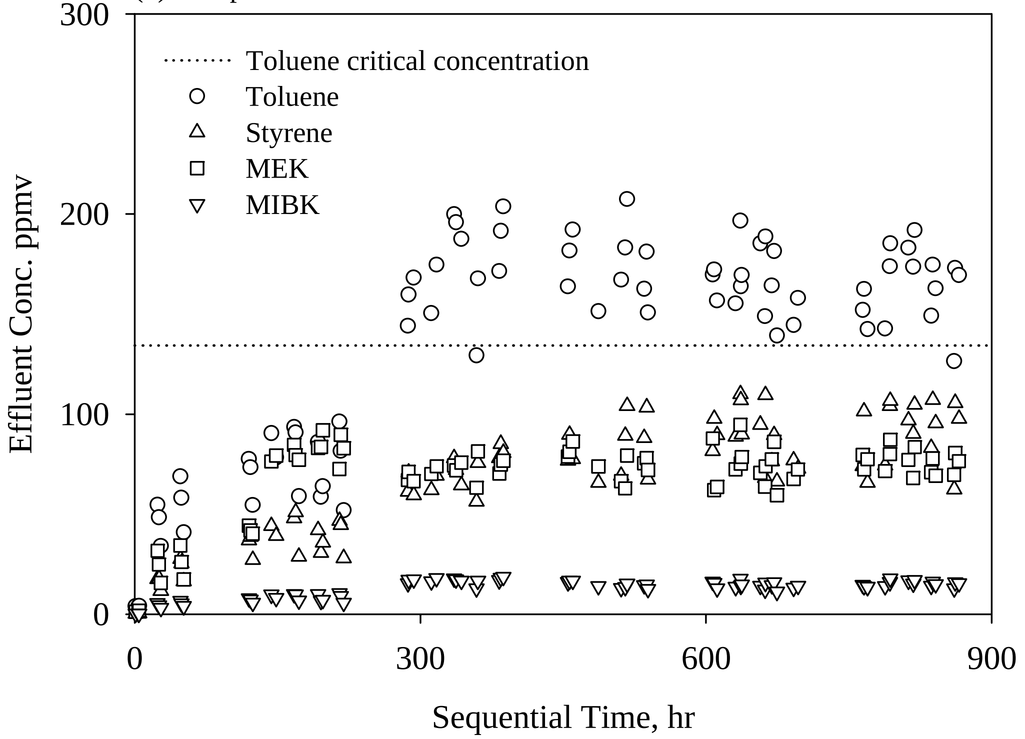


Figure 4-6 (a) Experimental measurement of the VOC mixture and (b) experimental measurement of the components in the mixture with cyclic operation

It is seen from Figure 4-6(a) that the effluent from the 2-bed adsorption unit increased gradually with time and stabilized after 300 hours. The total effluent from the 2-bed adsorption unit then fluctuated between 260 and 370 ppmv with an average concentration of 338 ppmv (see Figure 4-6(a)). Such an effluent profile could be of significant impact during initial acclimation of the followed biofilter. Although the effluent exceeded the critical inlet concentration at 300 ppmv in most of the period after stabilization, the magnitude of fluctuation was attenuated significantly as compared with the fluctuation in feeding condition. A more stable removal performance can be expected from the followed biofilter as compared to a biofilter performance with the feeding condition after breakthrough in Figure 4-4.

Effluent profiles for the components in the mixture from the adsorption unit are shown in Figure 4-6(b). After stabilization, the effluent of toluene fluctuated between 150 and 200 ppmv with an average concentration of 167 ppmv, styrene fluctuated between 60 and 110 ppmv with an average concentration of 82 ppmv, MEK fluctuated between 60 and 100 ppmv with an average concentration of 74 ppmv, and MIBK fluctuated between 5 and 20 ppmv with an average concentration of 15 ppmv.

The effluent mole fraction with sequential time for the four components of the mixture is shown in Figure 4-7. It can be seen from Figure 4-7 that initial effluent of toluene and styrene had a low percentage in the effluent mixture and then increased and stabilized at 0.49 and 0.24, respectively. Furthermore, styrene stabilized sooner than toluene. MEK had high mole fraction initially and then decreased and stabilized at around 0.22. MIBK maintained a stable mole fraction in the effluent mixture at around 0.04. Compared to the mole fraction in the feeding condition (0.448, 0.260, 0.234, and 0.058 for toluene, styrene, MEK, and MIBK, respectively), it can be deduced that competitive adsorption occurred in the 2-bed adsorption unit. The competitive adsorption effects can be contributed to adsorbates differences in physicochemical properties (Ruthven 1984; Yang 1987). This finding is consistent with the findings by Li and Moe (2005).

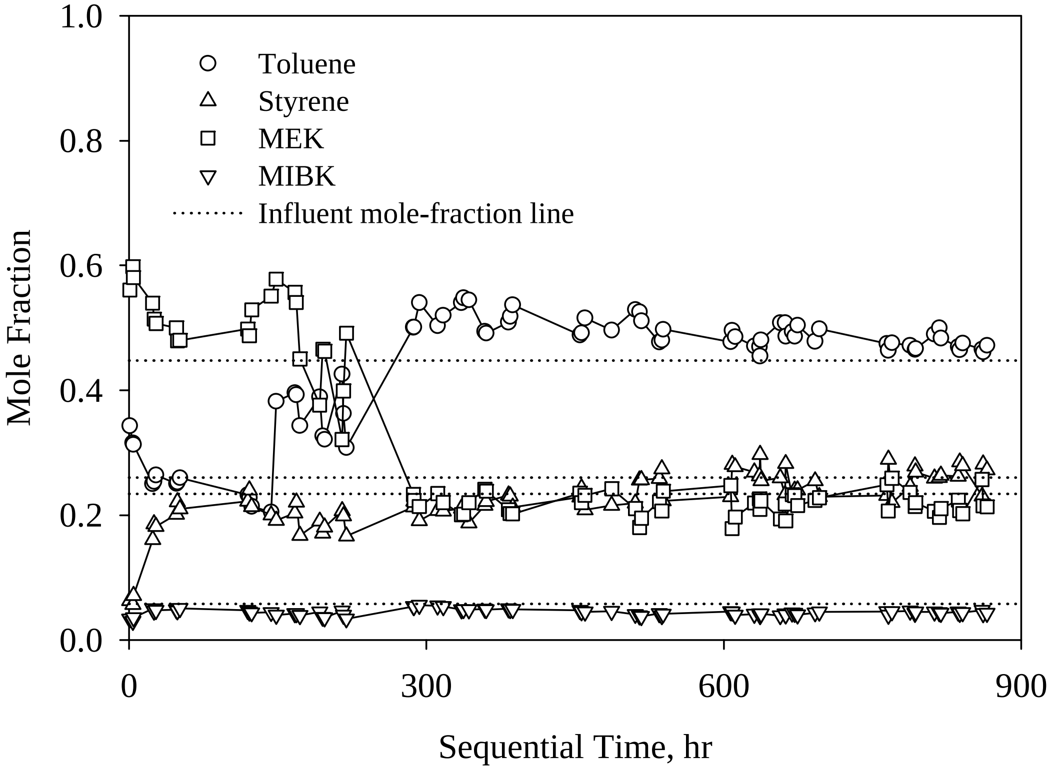


Figure 4-7 Comparison of the components mole-fraction in the effluent of the 2-bed cyclic adsorption unit to the influent mole-fraction

### 4.5. Conclusions

This study evaluated the buffering capacity of a 2-bed cyclic adsorption. A square wave feeding condition was employed to simulate fluctuation in the inlet concentrations. The behavior of the 2-bed adsorption unit under non-cyclic and cyclic operation indicated the following:

(1), A single adsorption bed failed to act as a buffering unit to the followed biofilter during the initial acclimation period and also failed to attenuate fluctuation in inlet concentrations after breakthrough.

(2), The 2-bed adsorption unit with cyclic operation succeeded in providing low effluent that will help the initial acclimation of a followed biofilter and also attenuating significantly the fluctuation in inlet concentration after stabilization.

(3), Competitive adsorption occurred in the adsorption bed for the different components in the mixture due to their differences in physicochemical properties.

## 4.6. References

Cai, Z., Kim, D., and Sorial, G. A. (2004). "Evaluation of trickle-bed air biofilter performance for MEK removal." *Journal of Hazardous Materials*, 114(1-3), 153-158.

Cai, Z., Kim, D., and Sorial, G. A. (2005). "Removal of methyl isobutyl ketone from contaminated air by trickle-bed air biofilter." *Journal of Environmental Engineering*, 131(9), 1322-1329.

Kim, D. (2006). "Development of integrated treatment scheme of adsorption and biofiltration for VOCs removal," PhD dissertation, In *Civil and Environmental Engineering*, University of Cincinnati, Ohio, USA.

Kim, D., Cai, Z., and Sorial, G. A. (2006). "Determination of gas phase adsorption isotherm: A simple constant volume method." *Chemosphere*, 64(8), 1362-1368.

Knaebel, S. P., Ko, D. H., and Biegler, L. T. (2005). "Simulation and optimization of a pressure swing adsorption system: Recovering hydrogen from methane." *Adsorption*, 11(Supplement 1), 615-620.

Li, C., and Moe, W. M. (2005). "Activated carbon load equalization of discontinuously generated acetone and toluene mixtures treated by biofiltration." *Environmental Science & Technology*, 39(7), 2349-2356.

Mertz, K. A., Gobin, D., Hand, D. W., Hokanson, D. R., and Crittenden, J. C. (1999). "Adsorption Design Software for Windows (AdDesignS$^{TM}$)." Michigan Technological University, Houghton, MI.

Moe, W. M., and Li, C. (2005). "A design methodology for activated carbon load equalization systems applied to biofilters treating intermittent toluene loading." *Chemical Engineering Journal*, 113(2-3), 175-185.

Ottengraf, S. P. P. (1986). *Biotechnology*, VCH Verlagsgesellschaft, Weinheim.

Ruthven, D. M. (1984). *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons, New York.

Ruthven, D. M., Farooq, S., and Knaebel, K. S. (1994). *Pressure Swing Adsorption*, VCH Publishers, Weinheim, New York, Cambridge.

Weber, F. J., and Hartmans, S. (1995). "Use of activated carbon as a buffer in biofiltration of waste gases with fluctuating concentrations of toluene." *Applied Microbiology and Biotechnology*, 43(2), 365-369.

Yang, R. T. (1987). *Gas Separation by Adsorption Processes*, Butterworths, Boston, MA.

# CHAPTER 5

# TREATMENT OF VOC MIXTURE IN A TRICKLING-BED AIR BIOFILTER INTEGRATED WITH CYCLIC ADSORPTION/DESORPTION BEDS

## 5.1. Abstract

An integrated technology by coupling cyclic adsorption/desorption beds with a trickling-bed air biofilter (TBAB) was studied for removal of a mixture of volatile organic compounds (VOCs). Toluene, styrene, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) were selected as target VOCs. To compare the performance of the integrated system, the air stream was divided equally into two sub-air streams. One steam passed to the 2-bed cyclic adsorption/desorption unit followed by a biofilter (Biofilter “A”), and the other stream passed directly through the control system - another biotrickling-bed air biofilter - Biofilter “B”. Four square waves of influent concentrations were employed on the integrated and control systems to mimic fluctuating conditions. Backwashing once a week with duration of one hour was employed as the biomass control for both systems.

The cyclic adsorption/desorption beds successfully performed its function as a buffering unit for the fluctuating inlet loadings. The cyclic beds could also act as feeding source during starvation periods of the system which greatly enhanced the re-acclimation for the biofilter. The obtained pseudo first order removal rates for toluene and styrene showed great difference between the low and the high peak inlet concentration for

Biofilter “B”, and the removal rates at low peak inlet concentration were apparently higher than those at high peak inlet concentrations. However, the removal rates between low and high peak inlet concentrations were very close for Biofilter “A”, which could be contributed to the effective dampening of the inlet concentration fluctuations by the cyclic 2-bed adsorption unit.

## 5.2. Introduction

Volatile organic compounds (VOCs) are major contaminants in waste gases. The USA emitted about 141 Mt of pollutants (fires and dust excluded) in 2005, containing 11.3% of VOCs (16 Mt of VOCs), mostly produced and released by industries (USEPA 2006). Removal of VOCs is a very important issue for the chemical industry because of their toxicity on human health and the environment. Biofiltration systems have recently emerged as an efficient and cost-effective technology for the control of VOCs emission. This technology has been used in Europe for many years and is considered to be a Best Available Control Technology (BACT) for treating contaminated gaseous streams. Biofilters function efficiently and economically for removing low concentrations of VOCs and odor. Biofiltration offers many potential advantages over existing control technologies, such as low installation and operation costs, low maintenance requirements, long life for the biofilter, and environmental safe operation as compared with other available control technologies: absorption, adsorption, thermal incineration, catalytic incineration, and condensation (Schnelle and Brown 2002).

Fluctuations in concentration and variation in the waste air composition is most commonly encountered in industry, which challenges the application of biofiltration technology.

To dampen fluctuation in influent loadings and maintain long term high level removal efficiency, a 2-bed adsorption unit with cyclic adsorption and desorption proposed in Chapter 4 was employed as a buffer unit to the biofilter in this study. An integrated system of a 2-bed cyclic adsorption/desorption unit and trickle bed air biofilter (TBAB) is proposed and applied for this purpose. The performance study on single solute toluene by employing this integrated system has been conducted in our previous study (Kim et al. 2005a). The integrated system proved to dampen the toluene fluctuation and help maintain long-term high level performance (Kim 2006). The primary objective of this study is, therefore, to extend the application of the integrated technology to the multicomponent system. The evaluations are focused on the following aspects: (1) comparison in performance between the integrated system and a control biofilter, (2) $CO_2$ (carbon mass balance) closures, (3) development of preliminary kinetic analysis.

## 5.3. Materials and Methods

A mixture of toluene, styrene, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) was chosen as the model VOC mixture. They are common solvents used in chemical industries. The ratio of the four VOCS in the mixture was based on EPA 2003 emission report from chemical industry (USEPA 2003). The molar ratio of the four VOCs was 0.448: 0.260: 0.234: 0.058 for toluene: styrene: MEK: MIBK, respectively.

### 5.3.1. Adsorption Unit

The system was designed for operation in a 2-step cycle, i.e., feeding (adsorption) and purging (desorption) within two adsorption beds. The two-bed system diagram is shown in Figure 5-1. Details about the cyclic 2-bed system can be found in the section 4.3 in Chapter 4. The operating parameters for the 2-bed unit are based on investigations conducted for the single solute toluene (Kim 2006). The frequency of the cyclic duration was set at 8h which provided each bed to have 4h feeding and 4h purging. Sampling ports were installed for both the feed and exhaust gases.

**1. Carbon bed**
**2. Electronic switch**
**3. Electronic timer**
**4. 4-way solenoid valve**
**5. Inlet gas stream**
**6. Outlet gas stream**

Figure 5-1 2-bed cyclic system diagram

### 5.3.2. Biofilter Unit

Two identical lab scale trickling-bed air biofilters were set up. The biofilter followed the 2-bed adsorption unit is named Biofilter “A”. The other one (Biofilter “B”) was connected directly to the contaminated air stream to act as a control for comparing its performance with the integrated system (2-bed adsorption unit + Biofilter “A”). Details about the biofilter system are found in the section 2.3.2 in Chapter 2.

Buffered nutrient solution was supplied at a rate of 2.4 L/day, which provided 17.1 mmol /day $NO_3^-$-N feeding, the composition of the nutrient solution was provided in a previous study (Sorial et al. 1995). *In-situ* upflow backwashing with media fluidization was employed at a rate of 1 hour a week as a strategy for biomass control during the backwashing experimental periods. An illustration of the backwashing system is provided in Figure 2-2 in Chapter 2. During starvation experimental periods, liquid VOC injection syringe pump was shut off for a period of 2 days per week. Only pure air and nutrients solution passed through Biofilter “B” without VOCs feeding. On the other hand, Biofilter “A” received a feed consisting of desorbed VOCs from the cyclic 2-bed adsorption unit. No backwashing was employed during starvation experimental periods except when needed as determined by deterioration in performance.

The main air stream was set up at 2.70 L/min and was spilt evenly into two 1.35 L/min sub-air streams, which would result in a corresponding empty bed retention time (EBRT) of 2.02 min for the biofilters. One stream was introduced to the 2-bed adsorption unit followed by Biofilter “A”. The other stream was introduced directly to Biofilter “B”.

Liquid VOC mixture was injected via a syringe pump and vaporized into the main air stream. The schematic diagram of the treating system is shown in Figure 5-2.

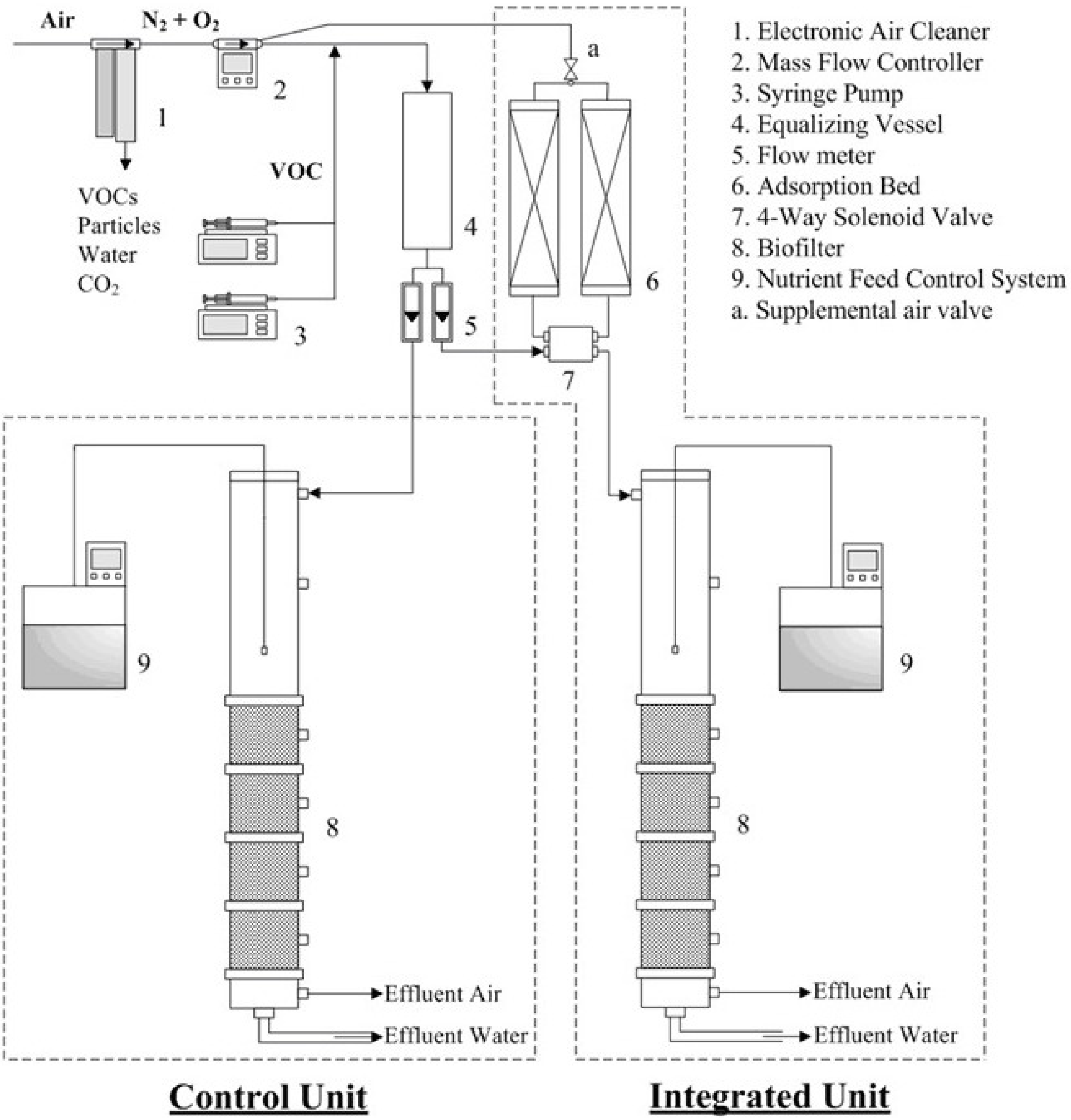


Figure 5-2 Schematic diagram of the experimental set-up

### 5.3.3. VOC Feeding Conditions

Four square wave changes of inlet concentration shown in Figure 5-3 were considered to simulate transient emission in the chemical industry. For this purpose, two or three syringe pumps were used to provide a square wave change in contaminant concentrations. For the first square wave, during the first 7 min of operation, the VOC mixture appeared at a peak concentration of 700 ppmv and then it dropped to a lower concentration of 250 ppmv during the next 53 min. For the second square wave, during the first 12 min of operation, the VOC mixture appeared at a peak concentration of 500 ppmv and then it dropped to a lower concentration of 250 ppmv during the next 48 min. These two feeding operations provided the same average concentration of 300 ppmv. This average concentration was the critical loading of the biofilter obtained previously in our studies under similar operating conditions (see Chapter 3). For the third square wave, more fluctuations in inlet concentrations were employed. During the first 18 min of operation, the VOC mixture appeared at a low concentration of 250 ppmv, and then increased to a peak concentration of 500 ppmv for 12 min, the concentration then dropped to 250 ppmv for a period of 18 min, and finally increased to 500 ppmv for a period of 12 min. This operation provided an average concentration of 350 ppmv. The last square wave employed more fluctuations in the inlet concentration as compared to the third square wave. During the first 15 min of operation, the mixture appeared at the concentration of 700 ppmv, then dropped to 300 ppmv with duration of another 15 min, then increased to 500 ppmv for 15 min, and finally dropped again to 300 ppmv for 15 min. This operation provided an average concentration of 450 ppmv.

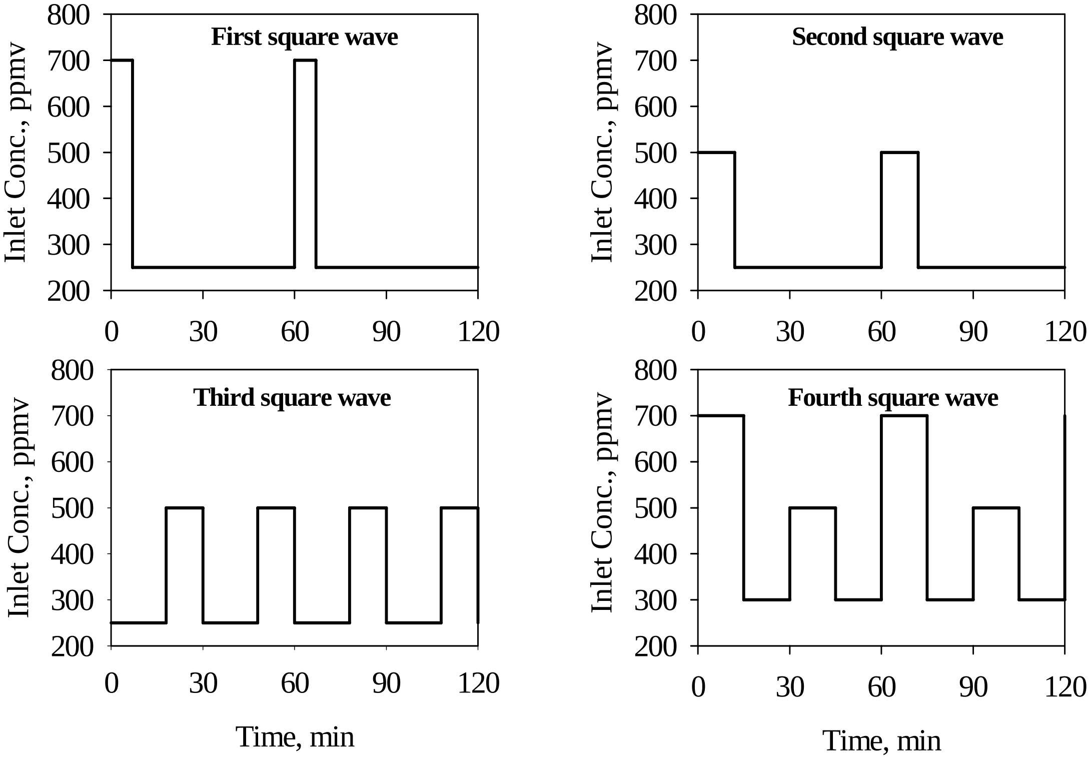


Figure 5-3 Inlet concentration profile for the four square wave studied

### 5.3.4. Analytical Methods

The concentrations of VOCs in the gas phase were measured by using a gas chromatograph (GC) (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with a flame ionization detector (FID). Effluent gas phase sample for $CO_2$ analysis were also taken by using gas-tight syringes through sampling ports in the biofilter. A GC (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with a thermal conductivity detector (TCD) was used for determining the $CO_2$ concentrations in the effluent gas phase. Liquid phase samples were analyzed for $NO_3^-$-N, total carbon (TC), inorganic carbon (IC), and volatile suspended solid (VSS) concentration. $NO_3^-$-N was determined according to Standard Methods 4500-$NO_3^-$ B (Standard method, 1998) by using a Shimadzu UVmini 1240 UV-VIS spectrophotometer (Shimadzu Corp., Tokyo, Japan). TC and IC were determined by using a Shimadzu TOC 5050 analyzer (Shimadzu Corp., Tokyo, Japan) according to Standard Methods 5310 (Standard method, 1998). The VSS concentrations in the effluent and backwashing water were determined according to Standard Methods 2540 G (Standard methods, 1998).

## 5.4. RESULTS AND DISCUSSION

### 5.4.1. Comparison of the Biofilters Performances

The performance of Biofilter "A" and Biofilter "B" for the first square wave of inlet concentration is shown in Figures 5-4 and 5-5. The inlet VOC mixture concentration to Biofilter "A" was the effluent from the 2-bed adsorption unit. After the effluent concentration from the adsorption unit stabilized, the inlet concentration to Biofilter "A" fluctuated from 180 ppmv to 280 ppmv. Since the variations of the inlet concentration to Biofilter "A" were below the critical concentration (300 ppmv), Biofilter "A" consistently maintained a removal level above 99% after a very short initial acclimation period as shown in Figure 5-4(a). Biofilter "A" showed a very short period of initial acclimation to toluene (Figure 5-4(b)) and styrene (Figure 5-4(c)), and then maintained consistent over 99% removal efficiency for both components. For the remaining two components MEK and MIBK acclimation was not needed and the biofilter maintained a consistent removal of 99% for these two components (see Figures 5-4(d) and 5-4(e)). On the other hand, the performance of Biofilter “B” fluctuated from 85% to 99% removal level as shown in Figure 5-5(a). Biofilter “B” required a much longer initial acclimation period to reach stability. It showed periodical fluctuation in performance corresponding to the backwashing cycles. After backwashing, the biofilter removal efficiency increased, then gradually decreased with time and reached sometimes removal efficiency as low as 85% just prior to next backwashing operation. Biofilter “B” required apparent initial acclimation to toluene and styrene in the mixture as shown in Figure 5-5(b) and (c). The over all performance for the mixture was strongly dependent on the performance of toluene in the mixture. The biofilter maintained consistent over 99% removal efficiency for styrene removal after initial acclimation (see Figure 5-5(c)). It did not require an acclimation period for MEK (Figure 5-5(d)) and MIBK (Figure 5-5(e)) and the biofilter maintained consistent over 99% removal efficiency for these two components.

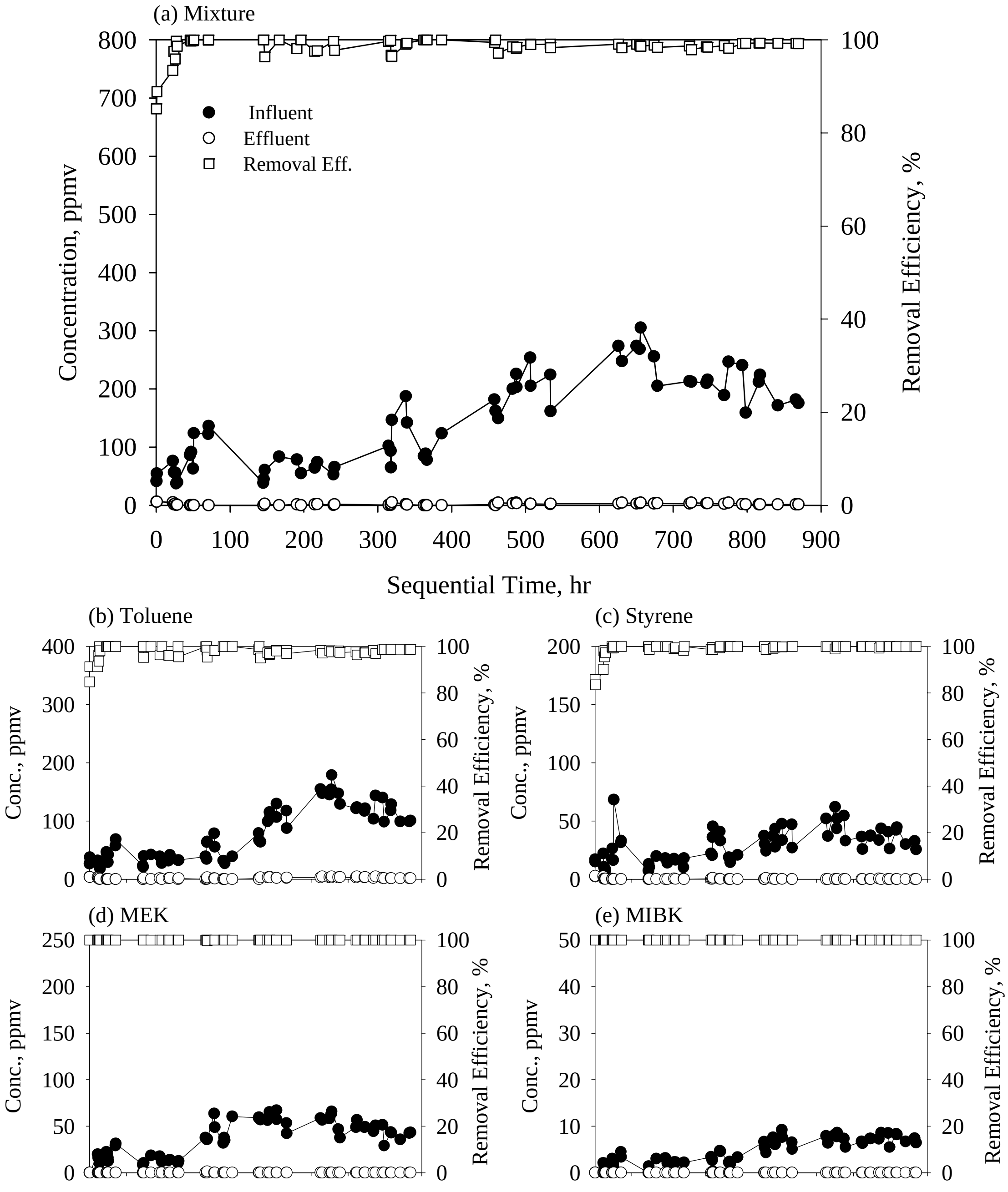


Figure 5-4 Biofilter "A" performance with respect to VOC removal under the first square wave feeding condition

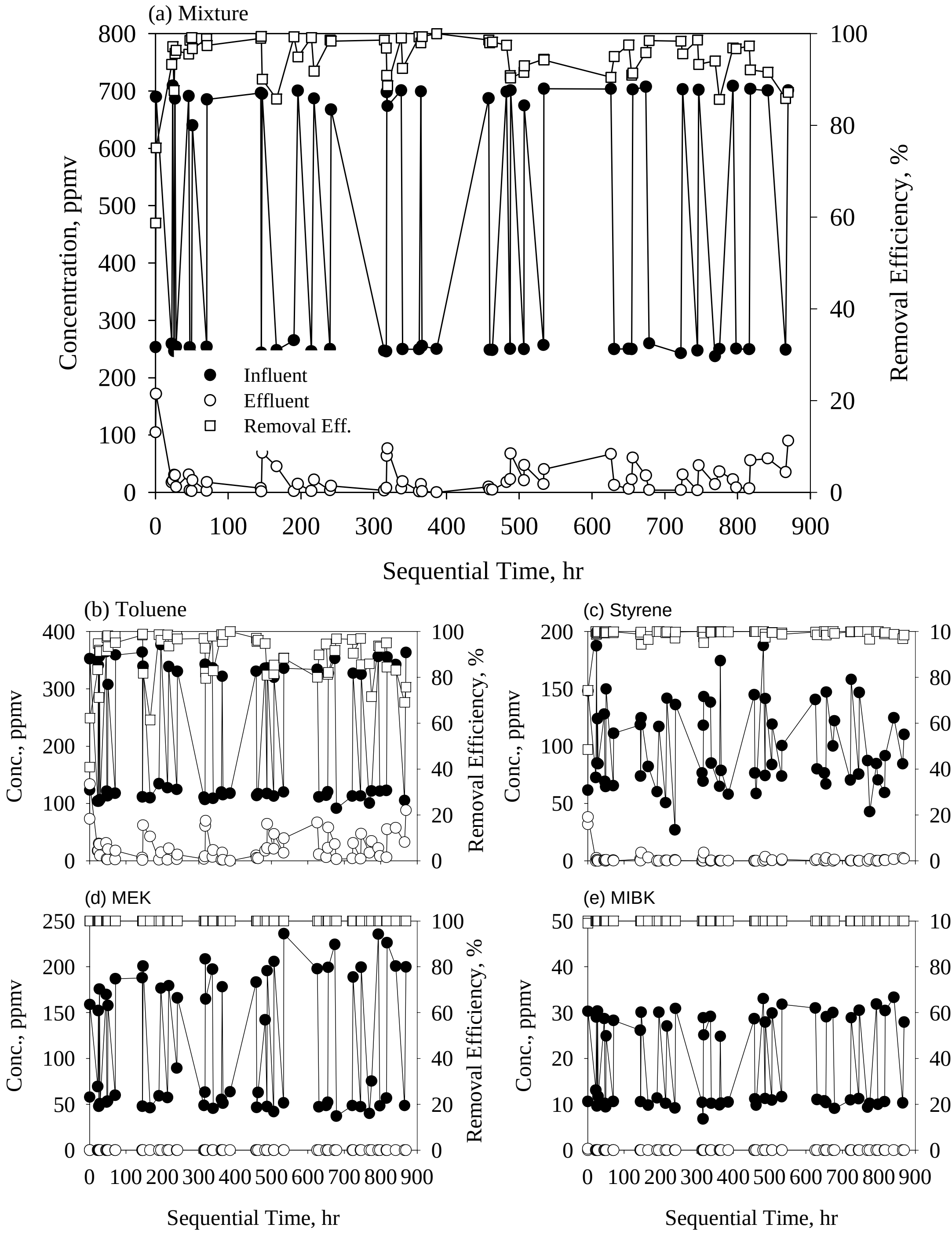


Figure 5-5 Biofilter “B” performance with respect to VOC removal under the first square wave feeding condition

The performance for Biofilter “A” and Biofilter “B” for the second square wave feeding condition was different from that for the first square wave. The performances of these two biofilters are represented in Figures 5-6 and 5-7. After a short period of stabilization period, the inlet concentration for Biofilter “A” was about 200 ± 50 ppmv. At this concentration level, Biofilter “A” maintained consistent 99% removal efficiency without apparent acclimation period because the inlet concentration did not exceed the critical concentration of 300 ppmv (2.40 kg COD/$m^3$-day) (see Figure 5-6(a)). It is seen from Figure 5-6 (b-e) that the four components in the mixture maintained consistent 99% removal efficiency. On the other hand, the control experiment (Biofilter “B”) could not maintain consistent 99% removal efficiency although the average inlet concentration was at the critical concentration of 300 ppmv. The removal efficiency fluctuated from 90% to 99% due to the high inlet concentration fluctuations between 250 ppmv and 500 ppmv. It is further seen from Figure 5-7(b) that the overall performance of the biofilter was controlled by toluene. The removal efficiency for toluene in the mixture fluctuated between 80%-99% after an initial acclimation period. The removals of other components in the mixture were maintained consistently above 99% removal efficiency without apparent acclimation period (see Figure 5-7 (c-e)).

On comparing the performance of Biofilter “B” under the second square wave feeding condition to the first square wave, it is seen that the second square wave provided better performance although the average inlet concentration was the same for the two feeding conditions (300 ppmv). The first square wave had higher peak concentration with shorter duration compared with the second square wave feeding condition. This indicates that the magnitude in inlet concentration fluctuation had more impact on the biofilter performance than its duration under similar overall loading rates.

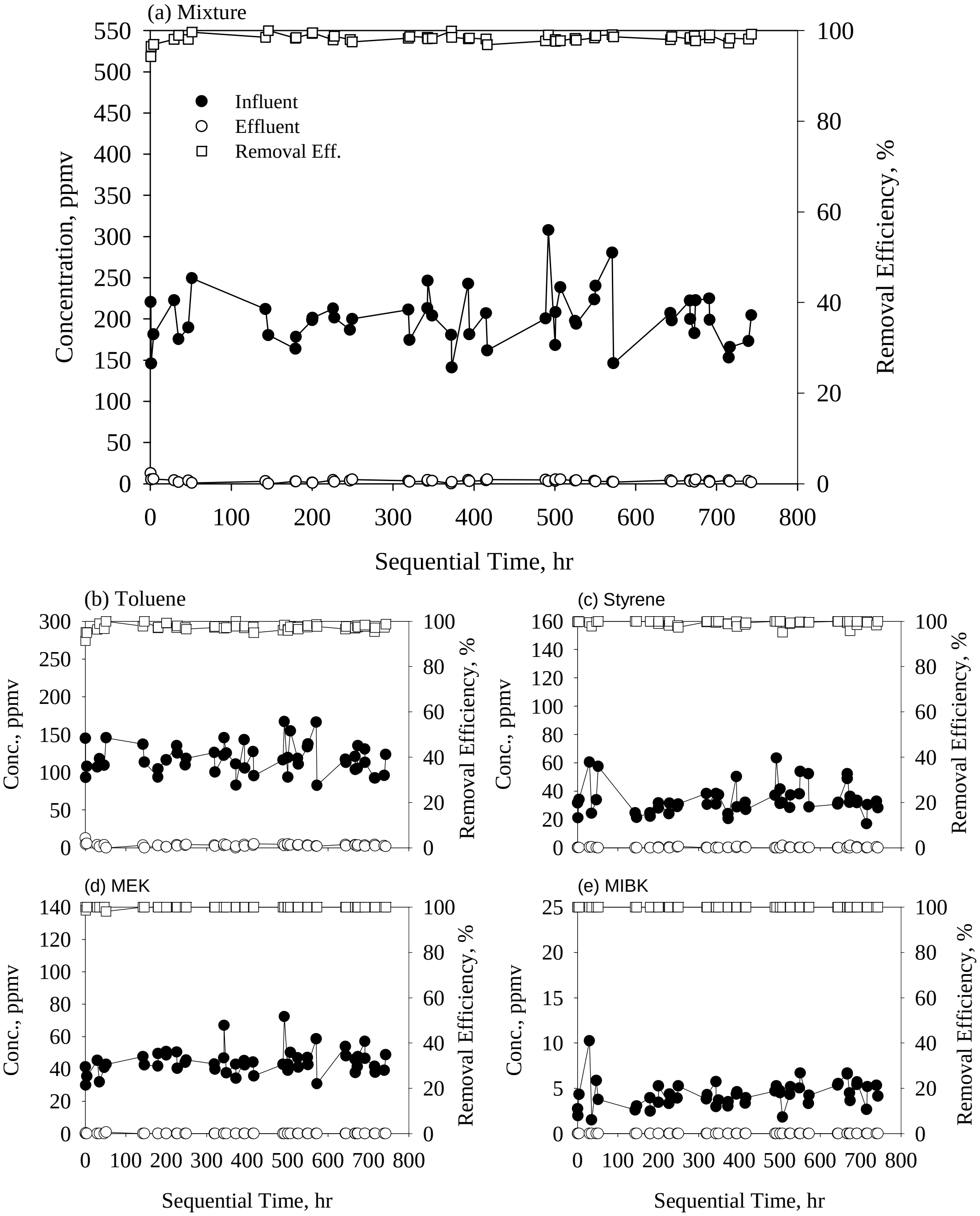


Figure 5-6 Biofilter “A” performance with respect to VOC removal under the second square wave feeding condition

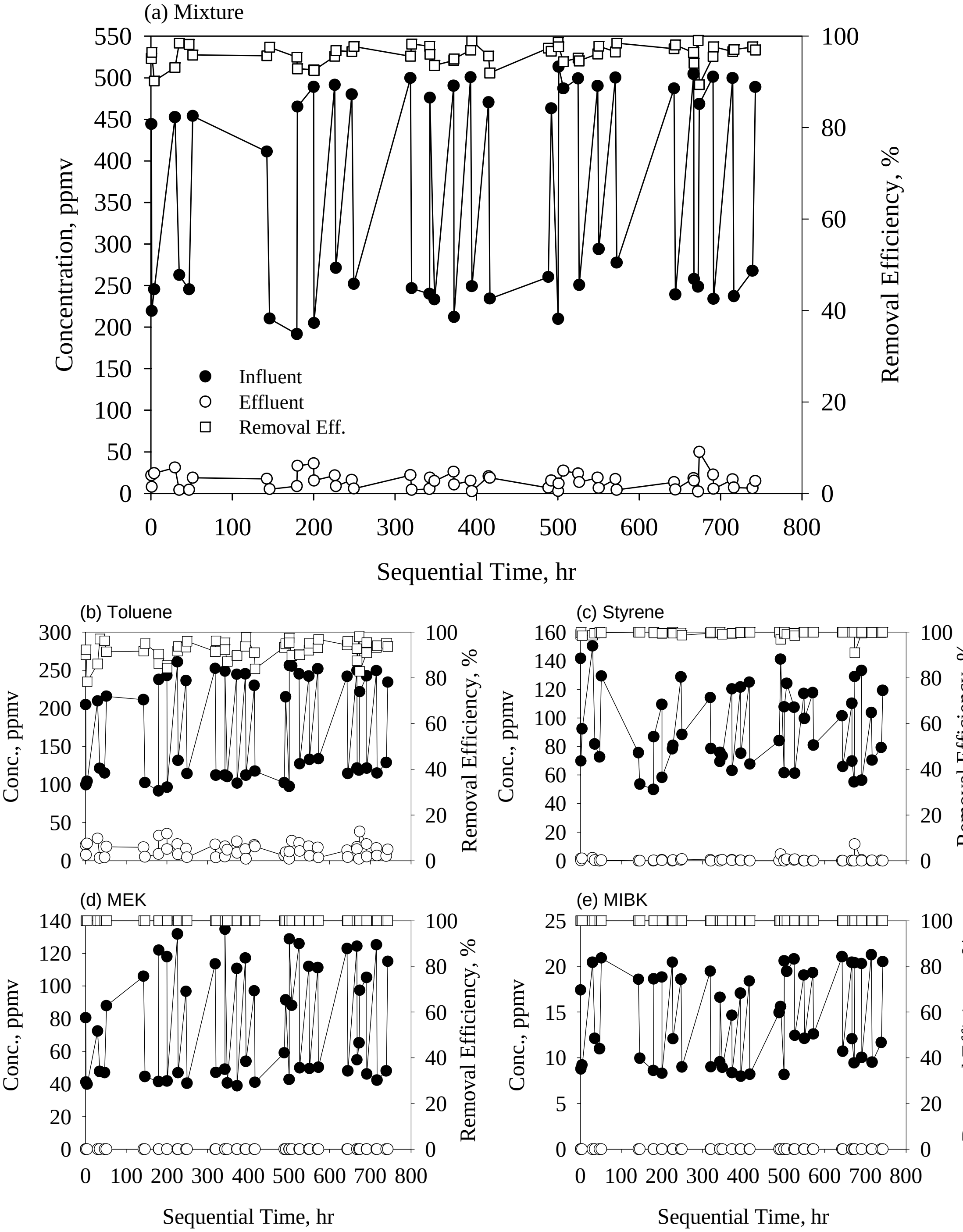


Figure 5-7 Biofilter “B” performance with respect to VOC removal under the second square wave feeding condition

For the third and fourth square wave feeding conditions, more fluctuations were employed. The performance of Biofilter “A” and Biofilter “B” for the third square wave of inlet concentration is shown in Figures 5-8 and 5-9. After initial stabilization period for the effluent from the 2-bed adsorption unit, the inlet concentration for Biofilter “A” fluctuated between 200 ppmv and 330 ppmv (see Figure 5-8). The removal efficiency was maintained over 97%, but the 99% removal level could not be maintained due to peak concentrations over the critical concentration of 300 ppmv to the biofilter from time to time. Toluene removal efficiency fluctuated between 95%-99% (see in Figure 5-8(b)). The removals of the other three components in the mixture were maintained consistently over 99% as shown in Figure 5-8(c-e). It is thus seen that the biofilter overall performance was controlled by toluene performance in the mixture. On the other hand, the removal efficiency for Biofilter “B” fluctuated from 76% to 95% (see Figure 5-9(a)). Toluene removal efficiency in the mixture fluctuated between 50%-93% (see Figure 5-9(b)). Styrene removal efficiency could be maintained at 99% after backwashing, however, it then decreased gradually to around 85% just prior to next backwashing (see Figure 5-9(c)). This biofilter maintained consistent over 99% removal efficiency for MEK and MIBK in the mixture (see Figure 5-9(d and e)). For Biofilter “B” the overall performance was controlled by the performance of toluene and styrene in the mixture.

For the fourth square wave feeding conditions, after an initial stabilization period, the inlet concentration for Biofilter “A” fluctuated between 300 ppmv and 400 ppmv (see Figure 5-10(a)). The removal efficiency fluctuated from 88% to 97%. Toluene removal in the mixture fluctuated between 75%-99% (see Figure 5-10(b)). Styrene removal reached 99% after backwashing and then decreased gradually to 95% just prior to next backwashing (see Figure 5-10(c)). Biofilter “A” maintained consistent over 99% removal efficiency for MEK and MIBK in the mixture (see Figure 5-10(d and e)). In case of the control biofilter (Biofilter “B”), it is seen in Figure 5-11(a) that the removal efficiency for the mixture fluctuated from 60% to 85%. Toluene removal efficiency fluctuated between 40%-75% (see Figure 5-11(b)). Styrene removal efficiency fluctuated between 78%-99% (see Figure 5-11(c)). Biofilter “B” could maintain consistent over 99% removal efficiency for MEK and MIBK in the mixture as shown in Figure 5-11(d and e).

The performances of Biofilter “A” and “B” under the fourth square wave feeding condition showed lower removal capacity as compared to the previous square waves studied due to the increase of frequency and magnitude of the square wave. However, the inlet concentration profiles for biofilter “A” indicated that the proceeded cyclic 2-bed adsorption/desorption unit succeeded in attenuating the fluctuation as compared with the inlet concentration profiles for Biofilter “B”. This led to significant improvement of the performance of Biofilter “A” as compared to Biofilter “B”.

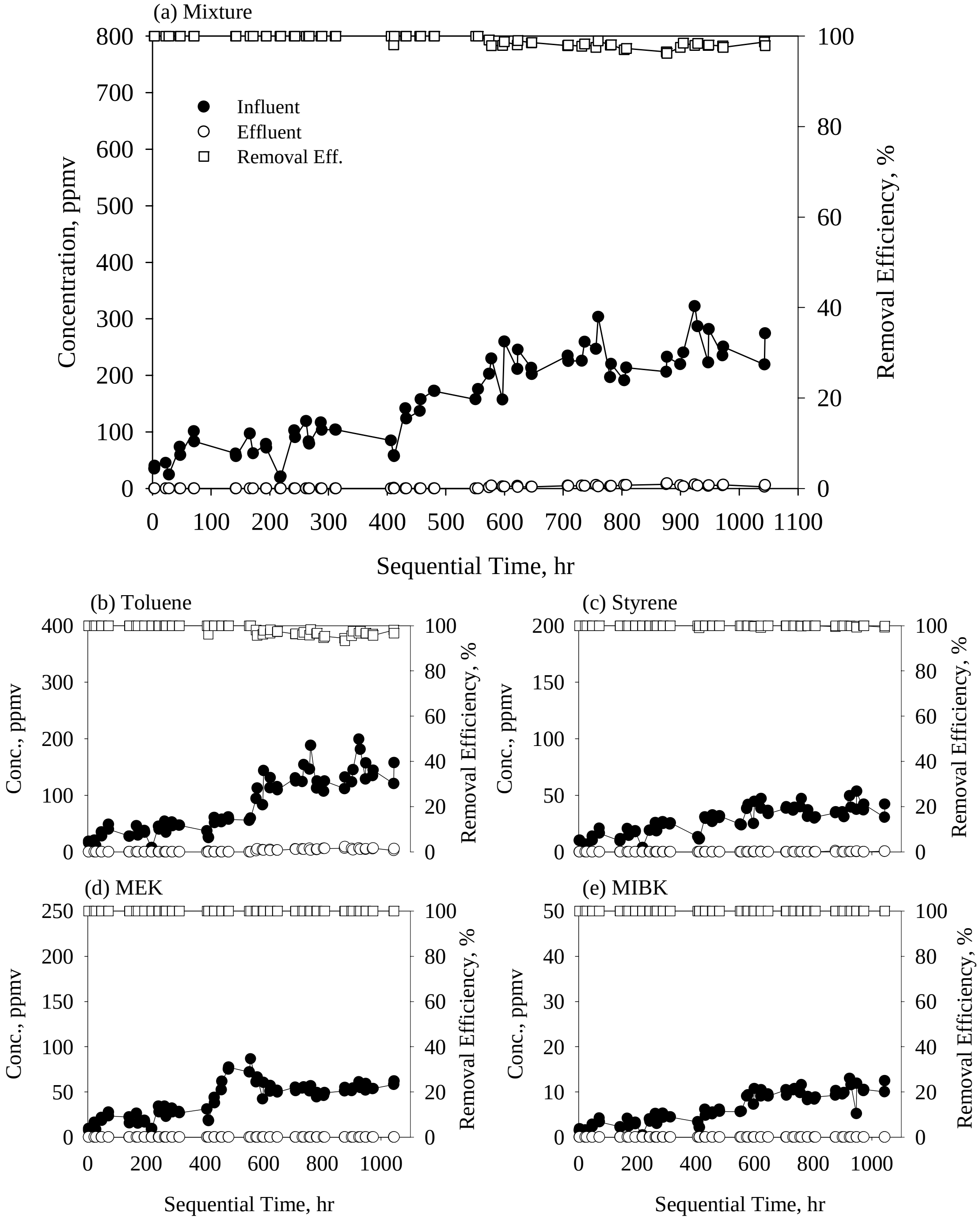


Figure 5-8 Biofilter “A” performance with respect to VOC removal under the third square wave feeding condition

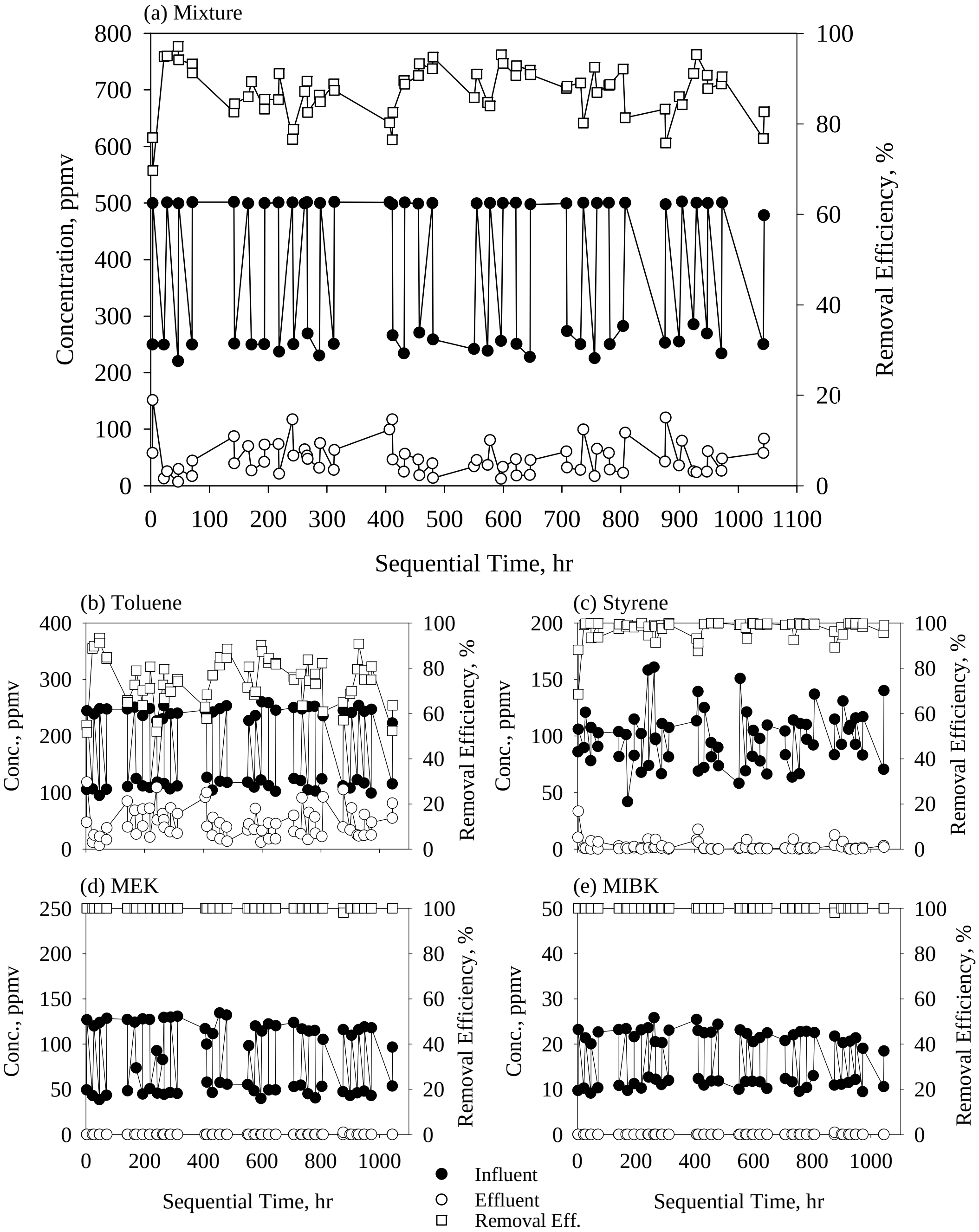


Figure 5-9 Biofilter "B" performance with respect to VOC removal under the third square wave feeding condition

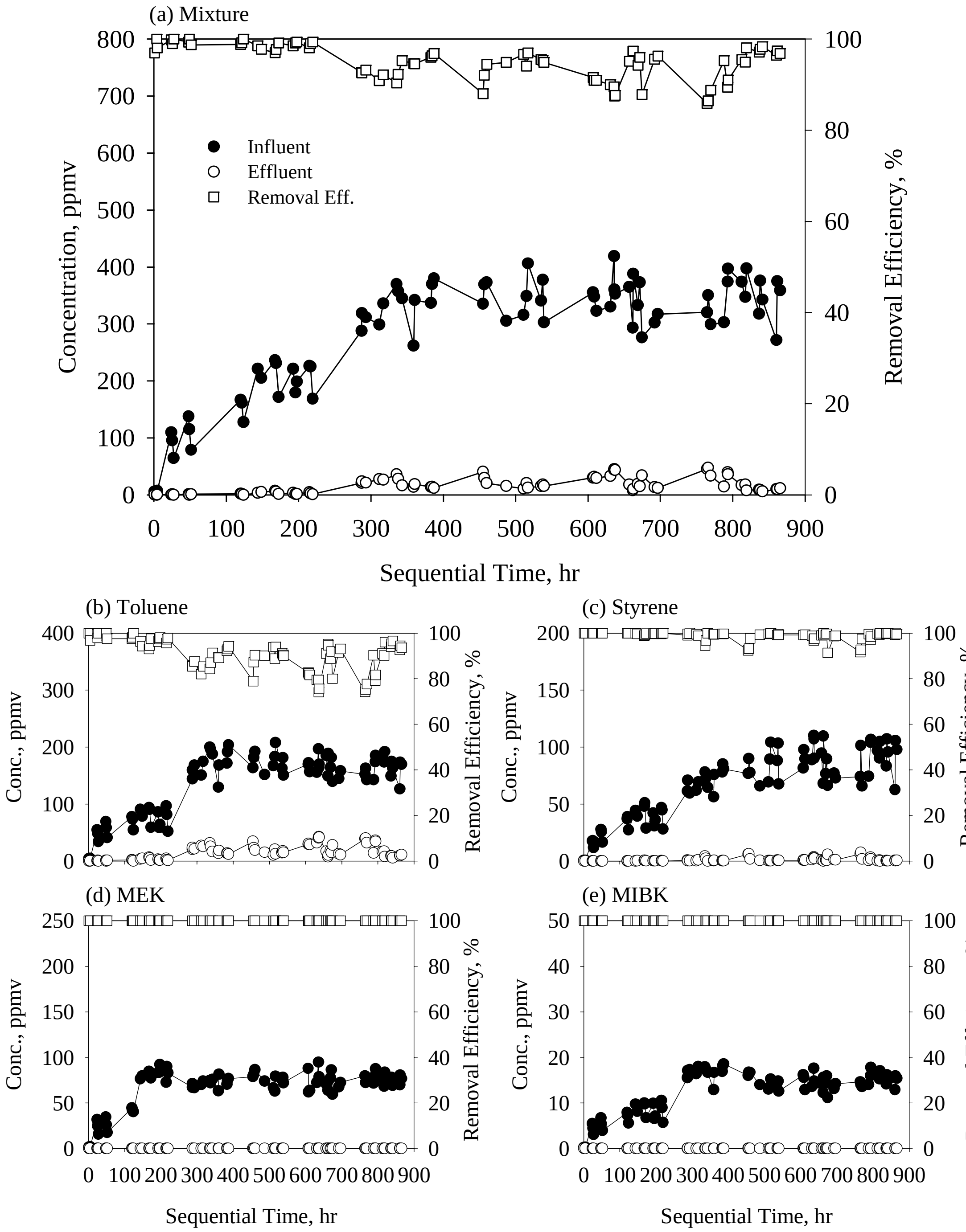


Figure 5-10 Biofilter "A" performance with respect to VOC removal under the fourth square wave feeding condition

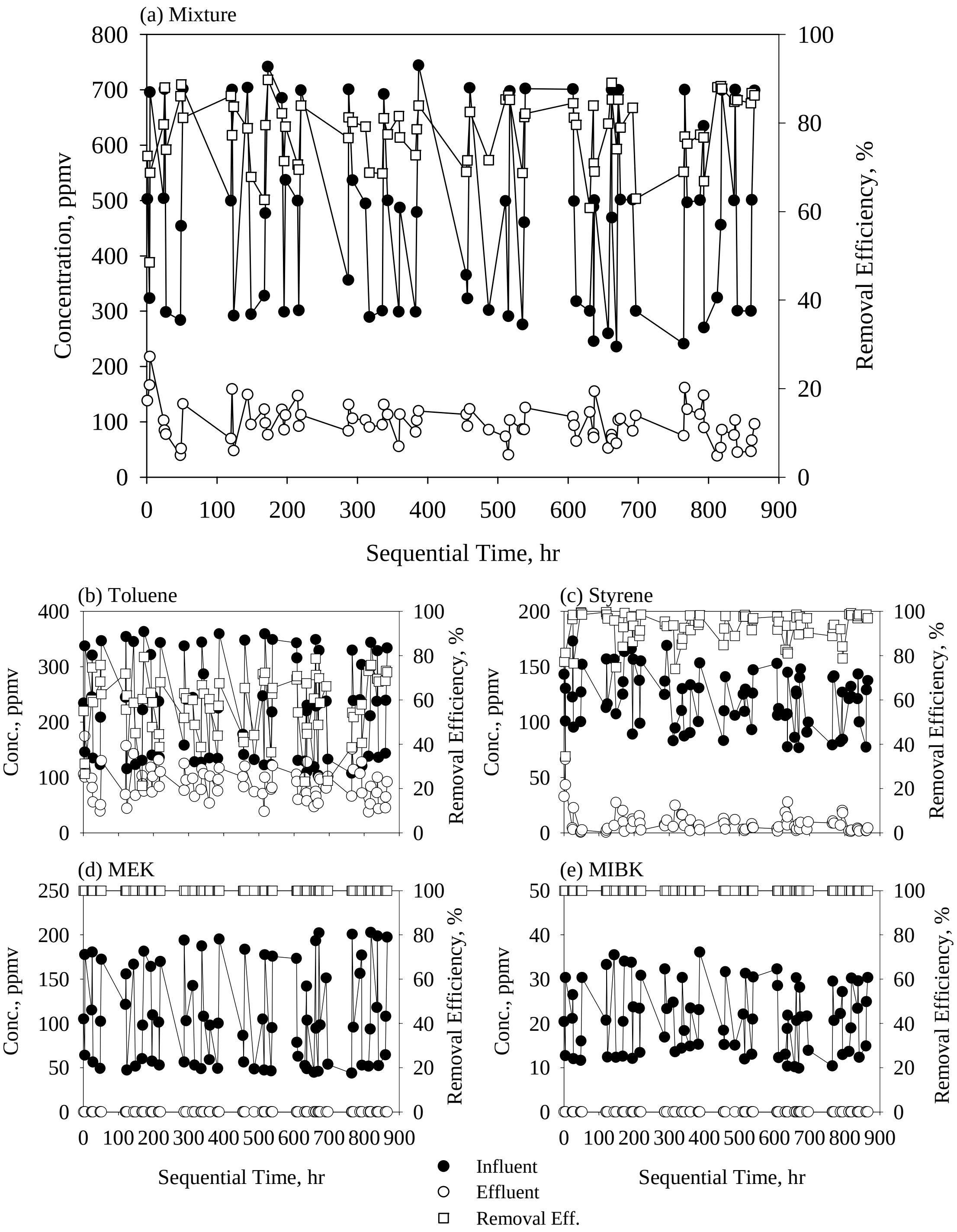


Figure 5-11 Biofilter "B" performance with respect to VOC removal under the fourth square wave feeding condition

Figure 5-12 provides a box plot for the effluent concentrations from biofilters “A” and “B” under the four square wave feeding conditions. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. The error bars above and below the box indicate the 90th and 10th percentiles. For the first two square waves, it is seen from Figure 5-12 that the effluent concentration from the integrated system was varying within a narrow range almost approaching zero while the control system (Biofilter “B”) provided wide variations that sometimes exceeded 50 ppmv for the first square wave. The effluent concentration from the integrated system for the third square wave showed significant improvement over the control system. For the fourth square wave which was more aggressive in fluctuations as compared to the previous three square waves, the effluent from the control system (Biofilter “B”) was exceedingly high with the 75th percentile above 100 ppmv while that for the integrated system was less than 40 ppmv. The results clearly indicate that the integrated system provided superior performance as compared to the control system.

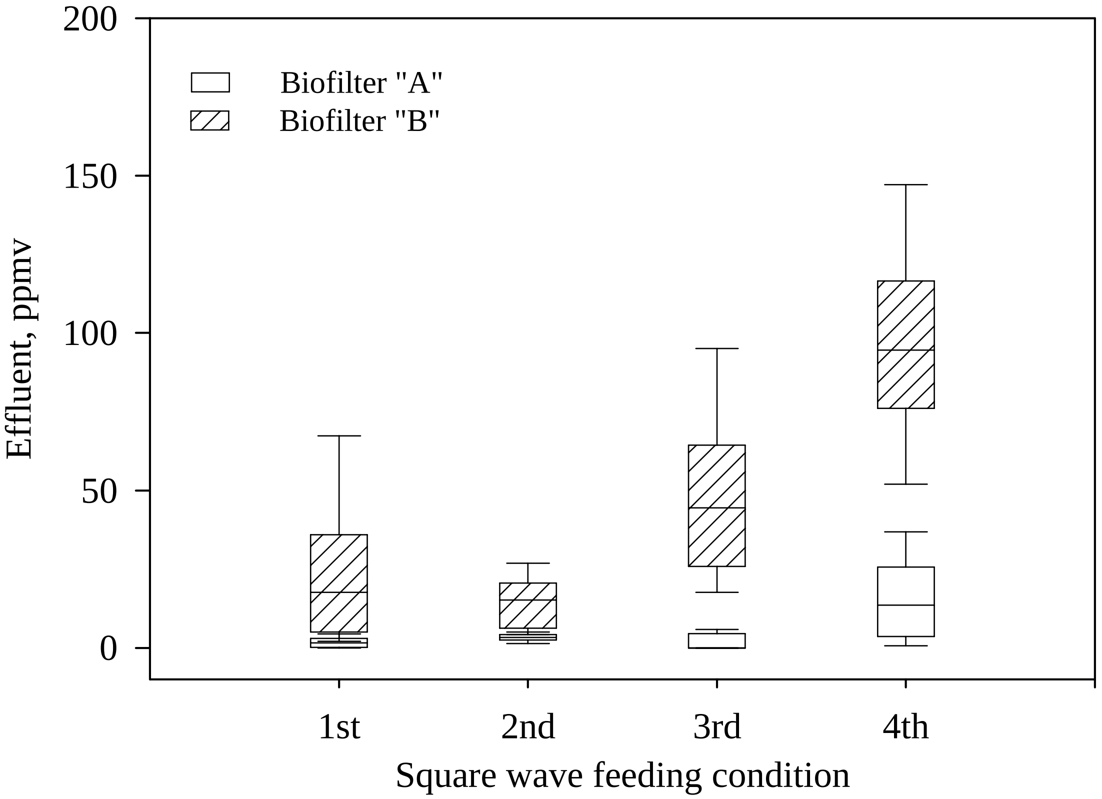


Figure 5-12 Comparison between the integrated system (2-bed adsorption + Biofilter “A”) and the control system (Biofilter “B”)

### 5.4.2. Starvation Effect on the Integrated and Control Systems

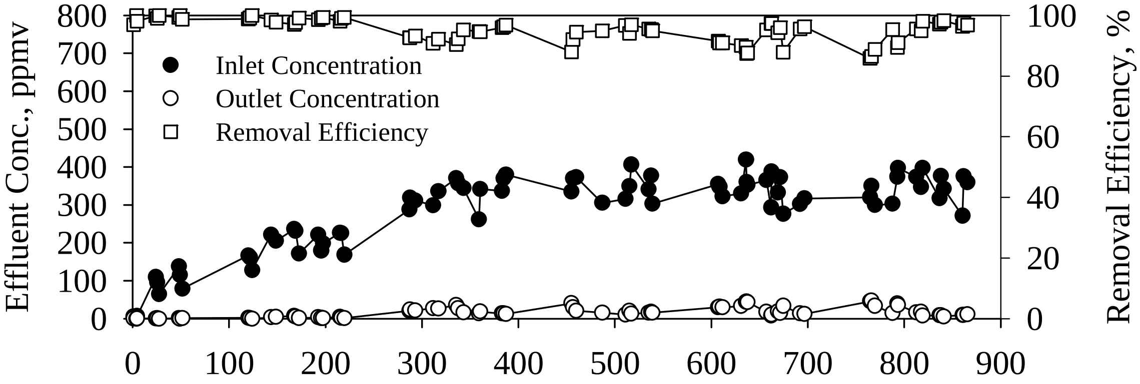
After the fourth cycle of backwashing during the fourth square wave feeding condition, the syringe pumps feeding the VOCs to the system were stopped for a period of 2 days per week in order to study the impact of starvation on both biofilters. In case of Biofilter “A” the 2-bed adsorption system acted as a feeding source to the biofilter by desorbing the adsorbed VOCs during the off periods of the syringe pumps. Figure 5-13 compares the performance of Biofilter “A” under the two operating strategies, i.e., backwashing which was discussed previously and starvation. The results shown in Figure

5-13 (b) indicate that the variations in the influent which sometimes dropped to 100 ppmv were due to desorption of the VOCs from the 2-bed adsorption unit during the starvation period. Meanwhile, the influent concentration to Biofilter “A” during the days of operation of the syringe pumps decreased to around 300 ppmv as compared to around 350 ppmv for backwashing operation. The decreased overall influent to the biofilter resulted in providing consistent over 99% removal efficiency initially. The biofilter later showed drop in removal efficiency due to excess accumulation of biomass which could induce channeling of air within the biofilter. Therefore, after 600 hours, the biofilter was backwashed to remove the excess biomass, and the biofilter regained its consistent 99% removal efficiency.

The results in Figure 5-13 indicate that cyclic 2-bed unit successfully acted as feeding source to the followed biofilter during starvation operating periods and no apparent re-acclimation periods were required for recovering the original performance. The desorption of the VOCs by the 2-bed adsorption system during starvation periods reduced the accumulated VOCs in the adsorption beds and helped in maintaining the buffer capacity of the 2-bed adsorption unit for a longer period. Meanwhile, periodic backwashing was necessary to maintain consistent high level performance for the biofilter under starvation operating conditions because the loading rate was around the critical loading capacity for the biofilter.

Figure 5-14 shows a comparison between the two strategies, i.e., backwashing and starvation for the control biofilter (Biofilter “B”). It is clearly seen that the starvation strategy under the aggressive fourth square wave of inlet concentration provided poor performance. The performance sometimes dropped to below 50% and the over all performance was worse than that under backwashing. This behavior was expected because starvation could not be used as a means of biomass control for high loading rates exceeding the critical loading rate.

(a) Backwashing



(b) Starvation

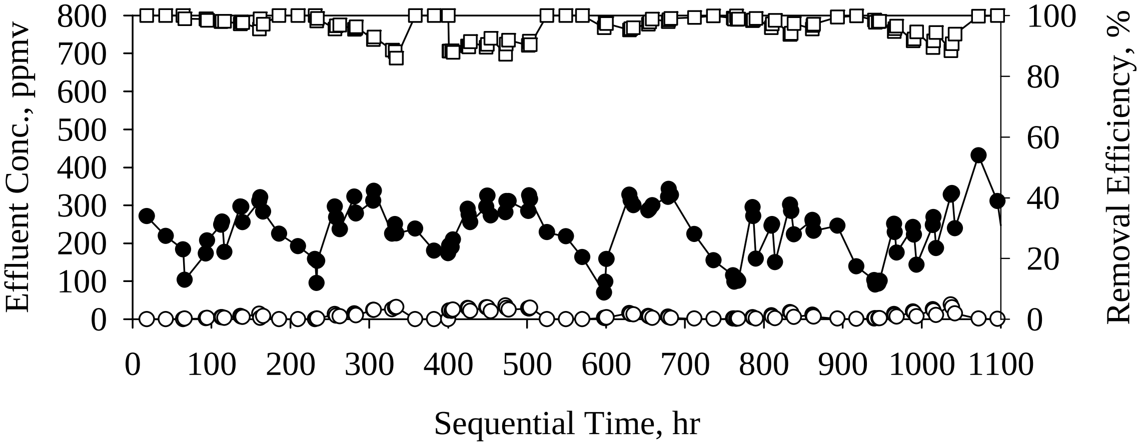
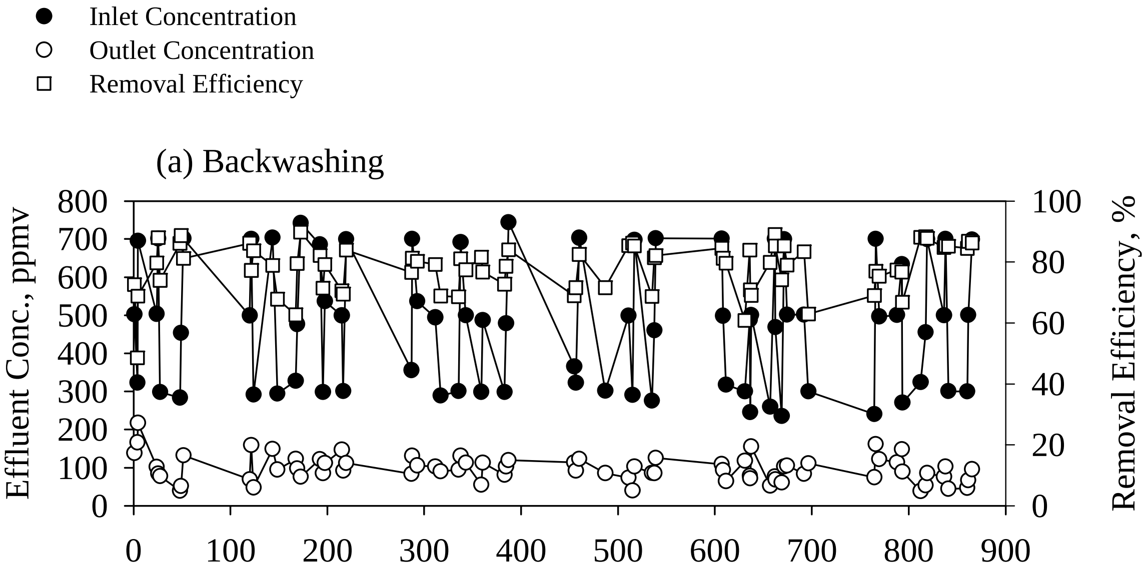
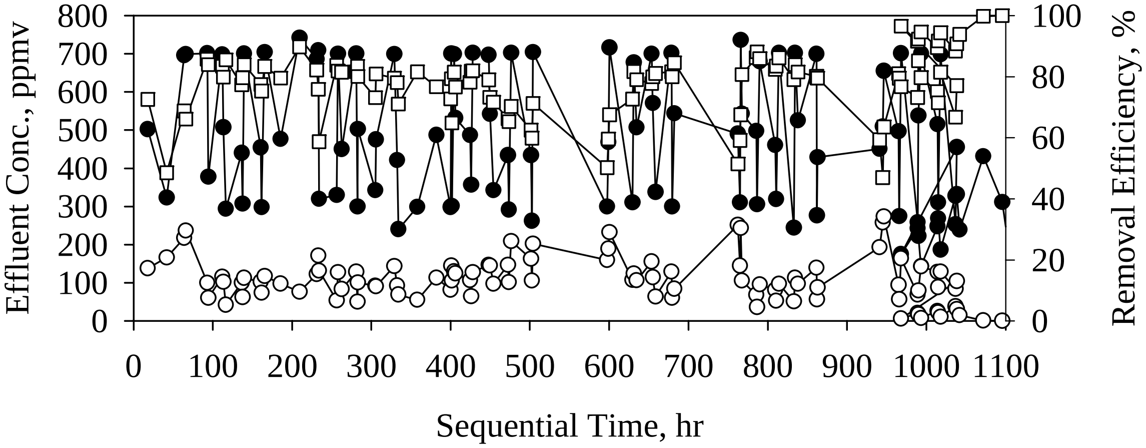


Figure 5-13 Comparison of the performance of biofilter “A” under the two operating strategies, backwashing and starvation, for the fourth square wave feeding condition



(a) Backwashing



(b) Starvation

Figure 5-14 Comparison of the performance of biofilter “B” under the two operating strategies, backwashing and starvation, for the fourth square wave feeding condition

### 5.4.3. CO$_2$ Closure (Carbon Mass Balance)

The cumulative CO$_2$ equivalent of VOCs consumed during all experimental runs was compared to the cumulative CO$_2$ produced within Biofilter “A” and Biofilter “B”. The inlet (or outlet) cumulative CO$_2$ was estimated as the total cumulative CO$_2$ in the influent (or effluent) aqueous and gaseous streams. The $CO_2$ closure for the first three square waves is shown in Figure 5-15. It is seen from Figure 5-15 that there is very good closure between the two cumulative values for both biofilters under the first three square waves inlet concentration conditions.

Under the first square wave feeding condition, for Biofilter “A”, the outlet cumulative $CO_2$ was about 96.6% of the inlet cumulative $CO_2$ at the end of experiment. For Biofilter “B”, the outlet cumulative $CO_2$ was about 96.4% of the inlet cumulative $CO_2$ at the end of experiment. It is worthwhile to note that the inlet cumulative $CO_2$ for Biofilter “A” was 69.9% of the inlet cumulative $CO_2$ for Biofilter “B”. This difference was due to adsorption in the 2-bed adsorption unit. The average inlet concentration for Biofilter “A” was 205 ppmv which was 68.3% of the average inlet concentration for Biofilter “B” indicating around 32% of the VOCs in the mixture were adsorbed by the adsorbent in the 2-bed adsorption unit.

Under the second and third square wave feeding conditions, for Biofilter “A”, the outlet cumulative $CO_2$ was about 96.1% and 99.6% of the inlet cumulative $CO_2$ at the end of experiment, respectively. For Biofilter “B”, the outlet cumulative $CO_2$ was about 95.7% and 97.5% of the inlet cumulative $CO_2$ at the end of experiment, respectively. The inlet cumulative $CO_2$ for Biofilter “A” was 71.7% and 65.2% of the inlet cumulative $CO_2$ for Biofilter “B”, respectively. The average inlet concentration for Biofilter “A” was 198 ppmv which was 66% of the average inlet concentration for Biofilter “B” indicating around 34% of the VOCs in the mixture were adsorbed by the adsorbent in the 2-bed adsorption unit. For the third square wave, the average inlet concentration for Biofilter “A” was 230 ppmv which was 65.7% of the average inlet concentration for Biofilter “B” indicating around 34.3% of the VOCs in the mixture were adsorbed by the adsorbent in the 2-bed adsorption unit.

The $CO_2$ closure for the fourth square wave is shown in Figure 5-16. It is seen from Figure 5-16(a) that there is very good closure between the two cumulative values for the biofilter for the backwashing strategy. For Biofilter “A”, the outlet cumulative $CO_2$ was about 98.1% of the inlet cumulative $CO_2$ at the end of experiment. For Biofilter “B”, the outlet cumulative $CO_2$ was about 97.4% of the inlet cumulative $CO_2$ at the end of experiment. It is worthwhile to note that the inlet cumulative $CO_2$ for Biofilter “A” was 63.9% of the inlet cumulative $CO_2$ for Biofilter “B”, which indicated that 36.1% of the VOCs in the mixture were adsorbed by the adsorbent in the 2-bed adsorption unit. In case of the starvation strategy, it is seen from Figure 5-16(b) that there is excessive deviation between the two cumulative values. These deviations could be due to unwashed biomass within the biofilter which is not accounted for. The inlet cumulative $CO_2$ for Biofilter “A” was 85.2% of the inlet cumulative $CO_2$ for Biofilter “B”, which indicated that 14.8% of the VOCs in the mixture were adsorbed by the adsorbent in the 2-bed adsorption unit. Compared with the operation under backwashing strategy, most of the adsorbed VOCs in the 2-bed adsorption unit were released during starvation operation indicating that the cyclic 2-bed adsorption system successfully functioned as feeding source to biofilter “A” during starvation periods and in turn delayed the saturation time to the 2-bed adsorption unit significantly.

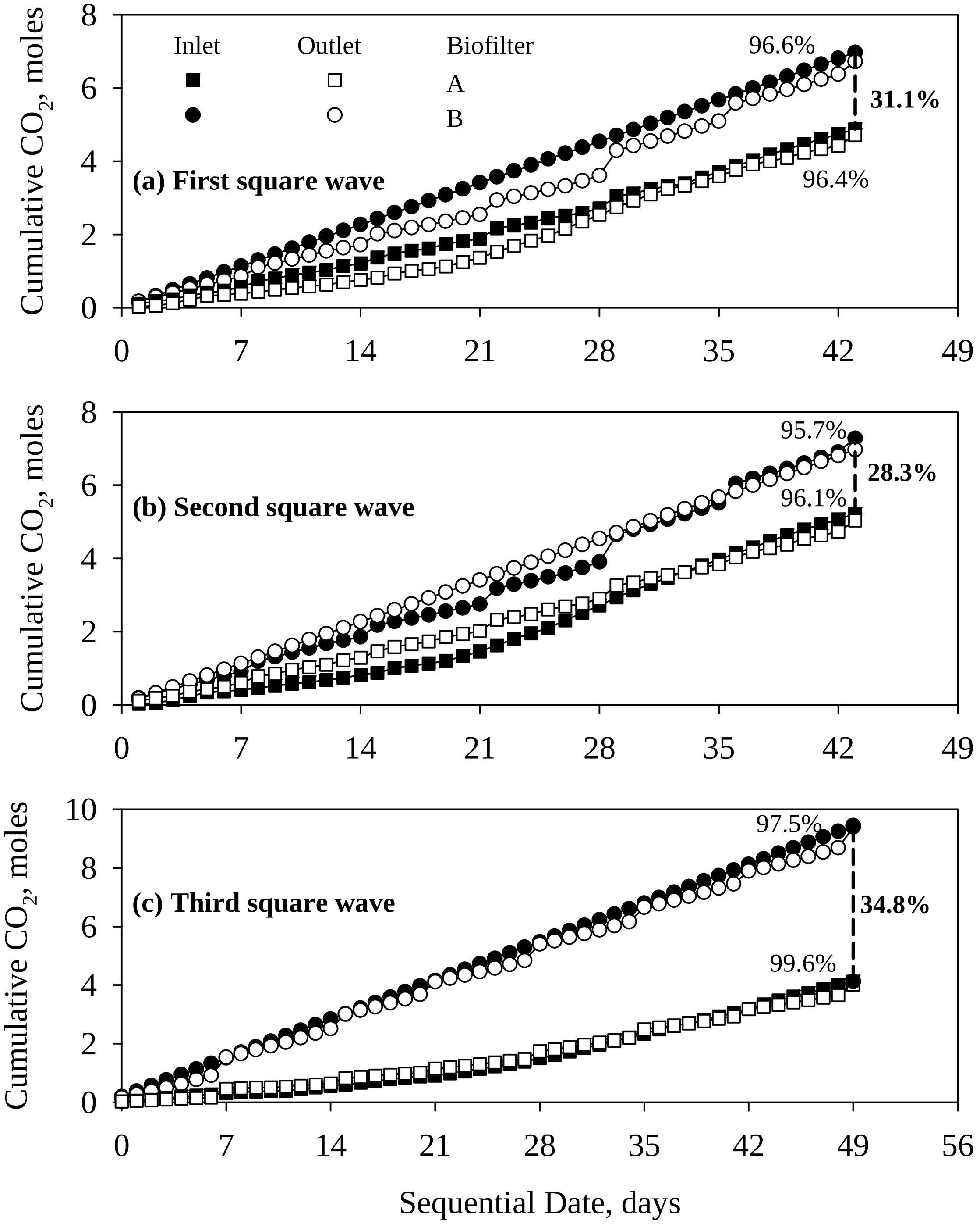


Figure 5-15 $CO_2$ closure for Biofilter “A” and Biofilter “B” with time for the three square wave feeding conditions

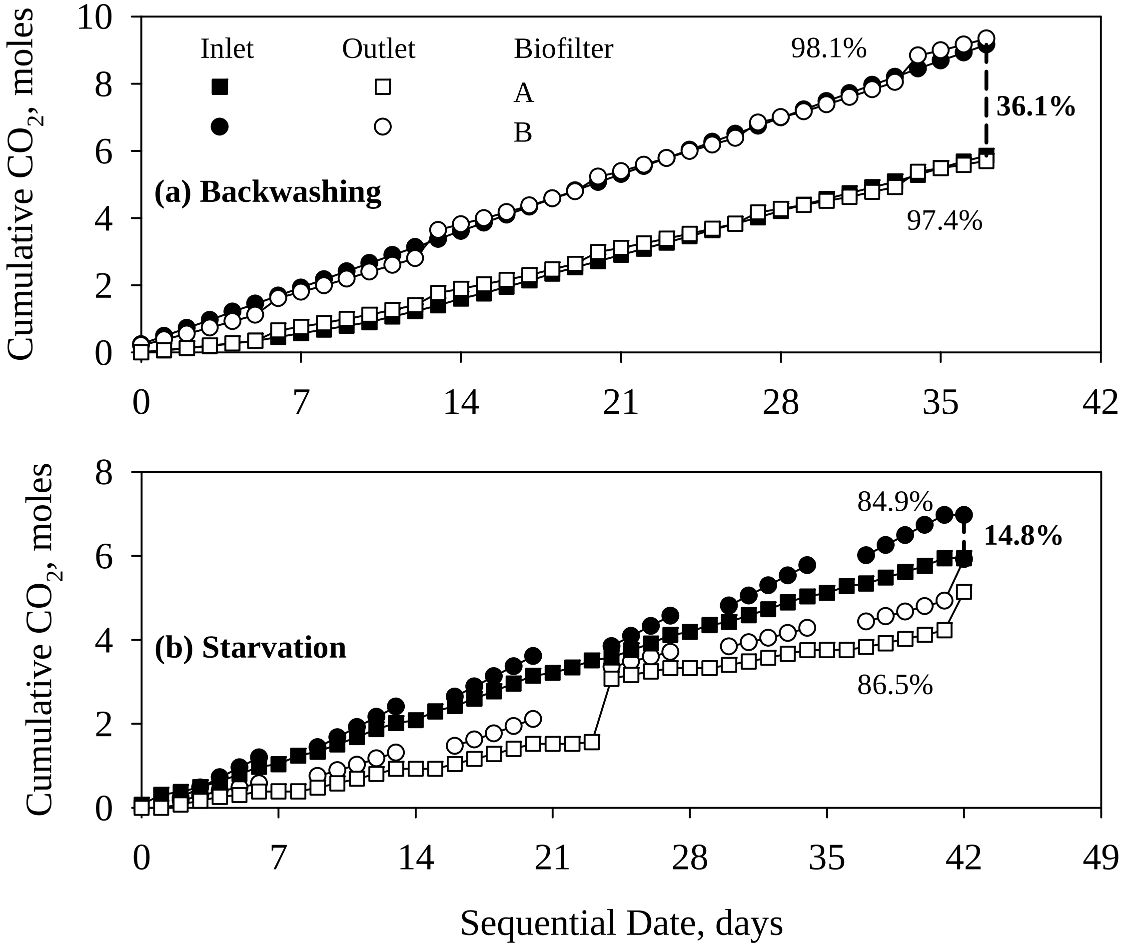


Figure 5-16 $CO_2$ closure for Biofilter “A” and Biofilter “B” with time for the fourth square wave feeding condition

### 5.4.3. Removal Kinetic Analysis

One day following backwashing, gaseous samples were taken along the media depth of the biofilter to assess removal kinetics for VOC removal during low and high peak inlet concentration periods. The kinetic analyses were based on pseudo first-order removal rate as a function of biofilter depth. By plotting the natural logarithmic scale of the ratio of residual concentration to inlet concentration as a function of depth into the biofilter (expressed as the cumulative EBRT), i.e., ($\ln(C/C_o)$ vs. time), the pseudo first order removal rate constants were obtained from the slopes of the regression lines.

Figure 5-17 represents plots of toluene and styrene first order removal rate constants under the four square wave feeding conditions. For the first three square waves, the removal rates were determined during the high and low peaks of the square waves (see Figure 5-3). In case of the fourth square wave, the removal rates were determined during the high, middle and low peaks, i.e., 700, 500, and 300 ppmv. The data shown in Figure 5-17 represent the average of three samples and the error bars represent the standard deviation. The removal rates along the biofilter media depth for MEK and MIBK could not be determined because of complete removal of MEK and MIBK within the upper 3/8 media depth. The obtained removal rates for toluene and styrene in Figure 5-17 showed that there were great difference between the low and the high peak inlet concentration in removal rates for Biofilter “B” (control unit), and the removal rates at low peak inlet concentration were apparently higher that those at high peak inlet concentration. However, the removal rates between low and high peak inlet concentration were very close for the integrated system (2-bed adsorption unit + Biofilter “A”), which could be contributed to the effective dampening of the fluctuating inlet concentration by the cyclic 2-bed adsorption unit. Furthermore, both biofilters showed higher removal rates for styrene than toluene, which was consistent to single solute results in our previous studies (Kim et al.

2005b; Kim et al. 2005c).

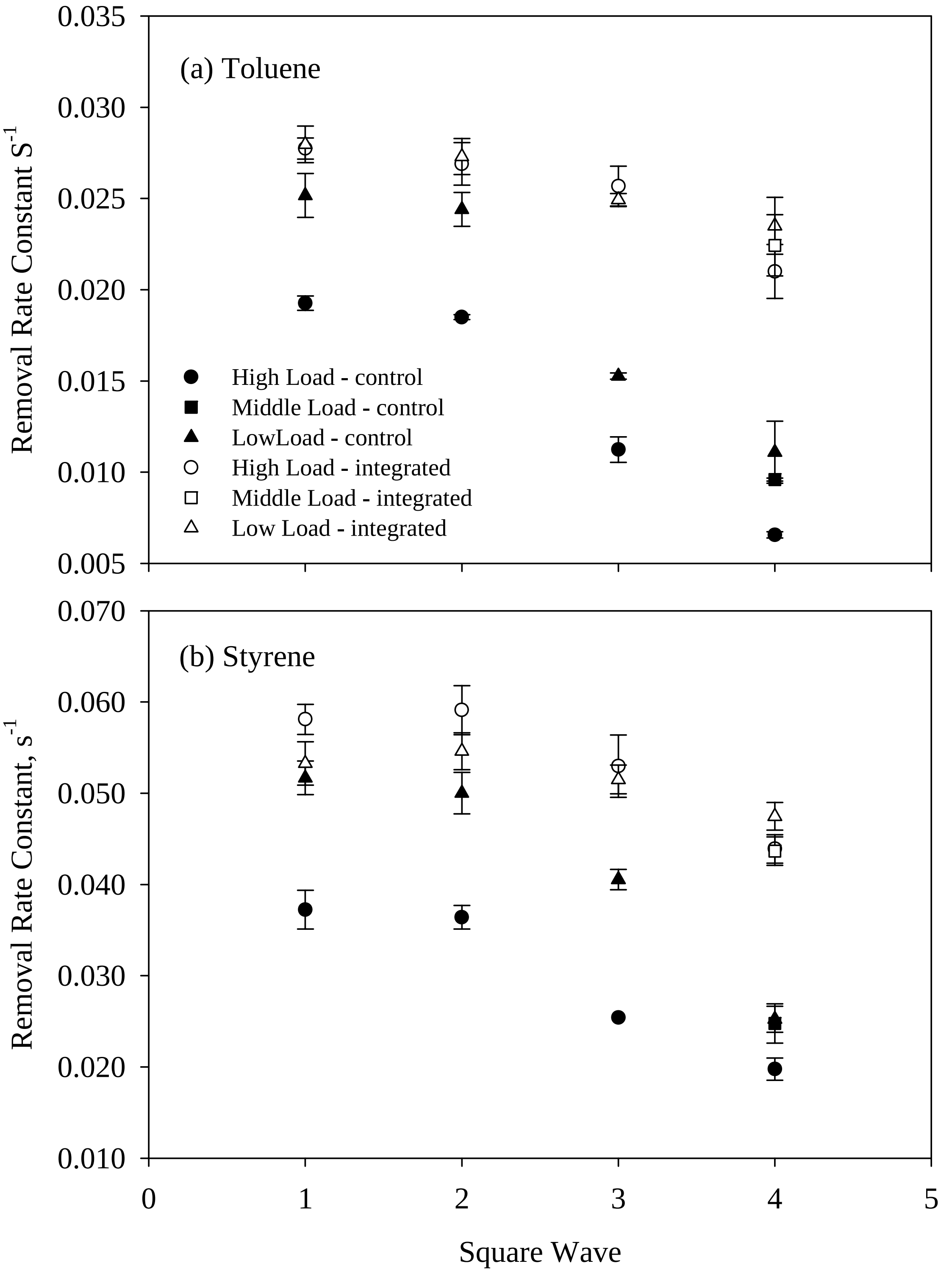


Figure 5-17 Toluene and styrene removal rates under backwashing operating conditions

## 5.5. Conclusions

This study investigated the performance of a trickling-bed air biofilter integrated with a 2-bed cyclic adsorption/desorption unit for the removal of a mixture of VOCs under four square wave feeding conditions. On comparing the performance and the removal kinetics of the control unit to the integrated system, the following conclusions could be revealed:

(1) The cyclic 2-bed adsorption/desorption unit dampened fluctuations in the inlet concentration of the VOC mixture and maintained a relative stable feeding condition to the followed biofiltration system.

(2) The cyclic 2-bed adsorption/desorption unit functioned as feeding source during starvation periods. It offered better performance under intermittent operation due to less accumulation of the VOCs within the adsorption beds.

(3) The integrated system was validated to maintain long-term consistent high level removal of a mixture of VOCs.

(4) The pseudo first order removal rate constants varied with the fluctuation of feeding conditions for the control system, however, no apparent difference for the integrated system was seen due to the effective dampening of the cyclic 2-bed adsorption/desorption unit to the feed inlet concentration.

## 5.6. References

Kim, D. (2006). "Development of integrated treatment scheme of adsorption and biofiltration for VOCs removal," *Ph.D. dissertation in Civil and Environmental Engineering*, University of Cincinnati, Cincinnati, Ohio, USA.

Kim, D., Cai, Z., and Sorial, G. A. (2005a). "Feasibility of adsorption/desorption cycles in a two-bed adsorption unit for dampening biofilter performance fluctuation." *98th A&WMA Annual Conference and Exhibition*, Minneapolis, Minnesota.

Kim, D., Cai, Z., and Sorial, G. A. (2005b). "Behavior of trickle bed air biofilter for toluene removal: effect of non-use periods." *Environmental Progress*, 24(2), 155-161.

Kim, D., Cai, Z., and Sorial, G. A. (2005c). "Evaluation of trickle-bed air biofilter performance under periodic stressed operating conditions as a function of styrene loading." *Journal of the Air & Waste Management Association*, 55(2), 200-209.

Schnelle, K. B., and Brown, C. A. (2002). *Air pollution control technology handbook*, CRC press, Boca Raton, FL.

Sorial, G. A., Smith, F. L., Suidan, M. T., Biswas, P., and Brenner, R. C. (1995). "Evaluation of trickle-bed biofiltermedia for toluene removal." *Journal of the Air & Waste Management Association*, 45(10), 801-810.

Standard Methods for the Examination of Water and Wastewater. 20th ed., APHA, AWWA, and WEF, 1998

US EPA. *Toxic release inventory program* "Air Emissions Trends - Continued Progress

Through 2003." available on the World Wide Web at

http://www.epa.gov/tri/index.htm (accessed on April, 2004)

US EPA. *Toxic release inventory program* "Air Emissions Trends - Continued Progress

Through 2005." available on the World Wide Web at

http://www.epa.gov/tri/index.htm (accessed on June, 2006)

# CHAPTER 6

# MICROBIAL STUDY FOR TBABs TREATING INTERCHANGED VOCs AND THEIR MIXTURES

## 6.1. Abstract

Microbial communities in trickle bed air biofilters (TBABs) were evaluated under conditions of interchanging the feed volatile organic compounds (VOCs) and VOC mixtures. Three independent TBABs (Biofilter “A”, “B”, and “C”) were run under interchanging VOCs conditions with different initial VOCs. Two aromatic compounds (toluene and styrene) and two oxygenated compounds (methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK)) were interchanged as single solutes. The sequence of interchanging VOCs for Biofilter “A” was MEK, toluene, MIBK, styrene, and then back to MEK. For Biofilter “B”, the sequence of interchanging VOCs was MIBK, toluene, MEK, styrene, and then back to MIBK. For Biofilter “C”, the sequence of interchanging VOCs was styrene, MEK, toluene, MIBK, and then back to styrene. Furthermore, two other TBABs were run for two VOC mixtures. One VOC mixture was equal molar ratio of the four components and the other was based on EPA 2003 emission report.

Denaturing gradient gel electrophoresis (DGGE) analysis of 16S rRNA genes was used to assess the microbial diversity in TBABs for treating the VOC mixtures and the impact of interchanging VOCs on the bacterial community structure in the biofilters. The results from DGGE showed that the microbial community structure in the biofilter was different after each interchange of VOCs. Some bands of microbial species faded and some bands were

strengthened. For the two TBABs treating VOC mixtures, the microbial species did not show significant difference, but the richness among these species was different from each other.

## 6.2. Introduction

Biofiltration technology has recently emerged as an efficient and cost-effective technology for the control of volatile organic compounds (VOCs) emission. However, fluctuations in concentration and variation in the waste air composition is the most common situation encountered in the chemical industry, which challenges the application of biofiltration technology.

During the past decade, numerous studies were performed at the bench, pilot, or pilot-field scale reactors to evaluate the effect of inlet concentration on biofiltration performance (Sorial et al. 1993; Sorial et al. 1994; Sorial et al. 1995; Deshusses et al. 1996; Chou and Huang 1997; Pedersen and Arvin 1997; Krailas et al. 2000; Kong et al. 2001; Atoche and Moe 2004; Cai et al. 2004; Cai et al. 2005; Kim et al. 2005b; Kim et al. 2005a). Target contaminants included hydrocarbons (e.g., benzene, styrene, hexane, toluene, and naphthalene), oxygenated hydrocarbon (e.g., methanol, ethanol, diethyl ether, acetone and methyl ethyl ketone), chlorinated hydrocarbons (e.g. chlorobenzene and *o*-dichlorobenzene), and sulfur compounds (e.g., hydrogen sulfide). Factors affecting the decontamination efficiency include: nature of the contaminants, packing materials and biofilter configurations, empty bed retention time, volumetric loading rates, nutrient feed flow rates, nutrient solution pH, and flow patterns of air.

Studies on removal of VOCs mixture by biofiltration are reported by a number of researchers (Deshusses and Hamer 1993; Deshusses et al. 1995a; Deshusses et al. 1995b; Deshusses et al. 1996; Deshusses 1997; Mohseni and Allen 1999; Mohseni and Allen 2000; Aizpuru et al. 2001; Chitwood and Devinny 2001; Cox and Deshusses 2002; Yoon and Park 2002; Aizpuru et al. 2003a; Aizpuru et al. 2003b; Chang and Lu 2003; Pruden et al. 2003; Sologar et al. 2003; Atoche and Moe 2004; Moe and Qi 2004)

Few studies were reported to investigate the effect of interchanged VOC on the biofilter performance. Martin and Loehr (1996) investigated the re-acclimation following changes of contaminant in a biofilter packed with municipal compost. They found that re-acclimation from benzene to toluene was 5.5 hours, 8.1 hours from toluene to benzene, 13 days from benzene to p-xylene, and 14 days from p-xylene to benzene. It is worthwhile to note that synthetic media used in TBABs are resistant to degradation and hence offer long term operation of the biofilter as compared to natural media.

Meanwhile, with the development of biotechnologies, molecular techniques have been used to study microbial populations and microbial ecology in biofilters, which could provide information for optimizing the biofilter performance (Togashi et al. 1986; Wada et al. 1986; Ottengraf and Konings 1991; Zhang et al. 1991; Bendinger et al. 1992; Cho et al. 1992; Lipski et al. 1992; Cox et al. 1993; Sly et al. 1993; De Heyder et al. 1994; Salanitro et al. 1994; Sorokin 1994; Weckhuysen et al. 1994; Bendinger et al. 1995; Devinny and Hodge 1995; Lipski and Altendorf 1995; Weber et al. 1995; Cox et al. 1996; Klatte et al. 1996; Morgenroth et al. 1996; Schonduve et al. 1996; Ahrens et al. 1997; Arnold et al. 1997; Chung et al. 1997; Lipski and Altendorf 1997; Malhautier et al. 1997; Sukesan and Watwood 1997; Webster et al. 1997; du Plessis et al. 1998; Elsgaard 1998; Lipski et al. 1998; Malhautier et al.

1998; Reichert et al. 1998; Sakano and Kerkhof 1998; Acuna et al. 1999; Damborsky et al. 1999; Friedrich et al. 1999; Hanson et al. 1999; Juteau et al. 1999; von Keitz et al. 1999; Finkmann et al. 2000; Krailas et al. 2000; Alexandrino et al. 2001; Bruns et al. 2001; Moe and Irvine 2001; Friedrich et al. 2002; Qi et al. 2002; Friedrich et al. 2003; Knief et al. 2003; Pruden et al. 2003; Roy et al. 2003; Grove et al. 2004; Jang et al. 2004; Li and Moe 2004; Oh et al. 2004; Estevez et al. 2005; Song and Kinney 2005; Steele et al. 2005; Zilli et al. 2005; Cai et al. 2006). In the late 80's and early 90's, research on the microbial ecology in biofiltration focused on specific microbial species isolated from biofilters. Togashi et al. (1986) studied the removal of $NH_3$ by a peat biofilter. They compared the biofilter performance with and without a nitrifier. They found that the amount of bacteria was associated with the concentrations of nitrogenous compounds. Cho et al. (1992) studied the degradation of hydrogen sulfide by a specific microbe-*Xanthomonas* sp. strain DY44 isolated from dimethyl disulfide-acclimated peat. This microbial species has been proven to degrade $H_2S$ without lag time. Lipski and Altendorf (1995) identified a new species with the proposed name *Actinomadura nitritigenes* isolated from lab scale experimental biofilters treating ammonia. With the development of polymerase chain reaction and DNA sequencing technology, it is possible to amplify the target DNA sequences. More molecular techniques were introduced into environmental studies. 16S ribosomal DNA (16S rDNA) is the characteristic DNA sequences for over 95% microorganisms. Most of the microbial studies in biofiltration targeted the 16S rDNA to identify the species or to understand the microbial ecology in the systems (Ahrens et al. 1997; Lipski et al. 1998; Malhautier et al. 1998; Reichert et al. 1998; Sakano and Kerkhof 1998; Juteau et al. 1999; Finkmann et al. 2000;

Bruns et al. 2001; Friedrich et al. 2002; Roy et al. 2003; Li and Moe 2004). Juteau et al. (1999) studied the microbial diversity of a compost biofilter treating toluene vapor gas by using serum-bottle assays and mineral agar plates. They found only 15% of the isolated colonies was involved in the toluene degradation. They also found that *Pseudo-nocardia* and *Rhodococcus* were the dominant species by using 16S rRNA gene-sequence comparison. Acuna et al (1999) studied the change of the microbial populations with respect to acclimation period and operation duration. They found that the amount of toluene degrading microorganisms increased significantly with increased acclimation time. Furthermore, molecular probes and fluorescence microscopy were being used frequently to analyze microbial communities due to their quick response. Fluorescence *in situ* Hybridization (FISH) has been frequently applied to analyze samples taken from different natural and engineered environments. Friedrich et al (1999; 2003) investigated the microbial community in a biofilter treating hexane waste gas and another biofilter treating waste gas from a chicken farm (Friedrich et al. 1999) and a biofilter from an animal-rendering plant (Friedrich et al. 2003) by using FISH. They found that FISH was a powerful tool for studying biofiltration systems, when combined with digital image analysis for studying the microbial community.

Other techniques were also employed such as scanning electron microscopy (SEM), single-strand conformation polymorphism (SSCP), and community level physiological profiling (CLPP). Acuna et al. (1999) studied community response of a biofilter for the removal of toluene. The SEM observations showed that a non-uniform biofilm was developed on the surface of media and the presence of an extracellular material. Khammar et al (2005) studied the relationship between the microbial communities and VOC mixture degradation along the peat biofilter’s depth by using single-strand conformation polymorphism (SSCP). Eleven VOC mixtures which include oxygenated, aromatic, and halogenated compounds were employed as the target contaminants. They found that the microbial density distribution along the biofilter depth was related to the biodegradation efficiency.

Denaturing gradient gel electrophoresis (DGGE) is an electrophoretic separation method based on differences in melting behavior of double stranded DNA fragments. The electrophoresis takes place in a vertically placed polyacrylamide gel in a gradient of denaturants. Bruns et al. (2001) studied the microbial community in a biofilter supplied with methyl *tert*-butyl ether (MTBE) using DGGE analysis of 230 bp 16S rDNA. The DGGE profiling approaches indicated that PM-1like bands predominated in the mixtures from MTBE-grown enrichments. Li and Moe (2004) investigated microbial populations in a biofilter with methyl ethyl ketone supply. They found that microbial community structures differed as a function of height in the biofilters.

The response of microorganisms to the change of VOC employed in a biofilter was reported by Grove et al. (2004). They assessed the changes in functional diversity of the microbial community in a compost biofilter over time by employing community level physiological profiling (CLPP) with BIOLOG ECO-plates. The biofilter treated waste air stream contaminated with hexane and later with ethanol. Although no positive conclusion could be drawn due to insufficient samples taken and replication, the CLPP technique was thought to be a reliable tool to assess the variation in the community structure of a biofilter. To the best of our knowledge, no studies are reported on TBAB performance behavior on

VOC interchange.

The objective of this research was, therefore, to investigate microbial community response under the interchange of feeding VOCs described in Chapter 2. Furthermore, the microbial community structures in biofilters with VOCs mixtures described in Chapter 3 was also compared with the microbial community structures in biofilters under single solute described by Kim (2006) and interchange of feeding VOCs.

## 6.3. Materials and Methods

Three trickle bed air biofilters namely biofilter “A”, “B”, and “C” were run in parallel under interchange of feeding VOCs. The experimental design under interchange of feeding VOCs was described in Sections 2.3.2 and 2.3.3 of Chapter 2. The experiments on VOCs mixtures were described in Chapter 3. Samples for DGGE analysis were collected once a week from the backwashing solutions of TBABs after re-acclimation to the different VOCs i.e. when 99 % of the original performance was attained. Hence, samples collected were representative for the whole media depth.

Denaturing gradient gel electrophoresis (DGGE) was applied to compare the V3 region of microorganisms in the environmental samples to determine changes of the populations during the operation of the reactors. Genomic DNA was extracted from each sample by using the Ultraclean soil DNA extraction kit (Mo Bio Laboratories, Inc.) according to the manufacturer’s instructions. The extracted DNA was used as template for the polymerase chain reaction (PCR). PCR was performed in 50 µl reaction volume containing a reaction mixture of 1X PCR buffer, 200 µM each deoxynucleoside triphosphate, 2.0 mM $MgCl_2$, 0.025U of *Taq* DNA polymerase/µl (Qiagen), and 0.5 µM of each primer on PCR thermal cycler (Applied Biosystems Model 2400 Thermal Cycler, Foster City, CA, USA). The primers were used to amplify the variable V3 region of the 16S rDNA gene. The primers were 341-358f (containing a GC clamp): '-CGCCCGCCGCGCGCGGCGGGCGGGGCGGGGGCACGGGGGGCCTACGGGAGGCAGCAG-3' and 518-534R: 5'-ATTACCGCGGCTGCTGG-3' (manufactured by the University of Cincinnati DNA Core lab). These primers were used to amplify conserved (V3) regions of the 16S rRNA genes in a wide range of bacterial species (Muyzer et al. 1993). Amplification of DNA was performed in a GeneAmp PCR system 2400 (Perkin Elmer) by using the following program: an initial denaturing step at $94^0$C for 5 min, followed by 35 cycles of denaturation at $94^0$C for 30s, annealing at $58^0$C for 30 s, extension at $72^0$C for 1 min and 30s, and final extension at $72^0$C for 10 min. PCR products were verified visually (5 µL) using 1 % agarose gel electrophoresis in 1X TBE and SYBR Green I staining (Molecular Probes).

DGGE was performed using a Bio-Rad D-Code system (Bio-Rad, Calif.) following published procedures (Muyzer et al. 1993). The PCR products were loaded onto 8% (w/V) polyacrylamide gels containing a denaturing gradient between 15 and 55% (100% denaturant defined as 7 M urea plus 40% vol/vol formamide). Electrophoresis was performed for 20 hours in 0.5 X TAE (20 mM Tris, 10 mM acetic acid, 0.5 mM EDTA, pH 8.3) at 35 volts and 60 °C. After electrophoresis, the gels were stained for 30 minutes in 1 X TAE using SYBR Green I staining (Molecular Probes). The stained gel was photographed using the Bio-Rad Gel Doc 2000 (Bio-Rad Laboratories, UK). The buffer in buffer compartment is circulated to prevent exhaustion of buffer components. In addition, the gel was kept at constant homogeneous temperature (60°C). For stability the gel (attached to the Protean II gelcore) is placed in the plastic Protean II tank. Buffer is circulated by the thermo-stat pump to the upper buffer compartment and to the tank. Via overflow it is circulated to the aquarium in which the pump is hanging. To facilitate overflow from the upper compartment we have drilled two little holes in the upper part of the core (in the 'ears'). In the DCODE system, the mixing of the buffer (and temperature homogeneity) is improved by using a magnetic stirring bean, driven by a stirrer which is placed under the DCODE system.

To compare the DGGE patterns for different samples, all PCR samples should be loaded in the same gel because the DGGE gel is a gradient gel, not a uniform gel. The gradient in one gel can not be duplicated in another gel due to difference in solution preparation and step forward in injecting the solutions. In this study, there are 16 wells in one gel, which means 16 PCR samples at most can be loaded at one time.

## 6.4. Results and Discussion

### 6.4.1. Polymerase Chain Reaction (PCR)

PCR amplification of 16S rDNA was conducted to duplicate the target characteristic DNA sequence. The PCR products were verified on an agarose gel. The agarose gel electrophoresis of PCR products for samples from Biofilter "B" is shown in Figure 6-1.

Compared with the 100 bp DNA ladder in lane 1, the PCR products in samples in Figure 6-1 were around 230 bp, which indicated that the DNA sequences-16S rDNA in all samples were amplified successfully. The PCR amplification for the samples for Biofilter "A" and

"C" from interchanging VOC described in Chapter 2 was conducted in the same way as the Biofilter "B".

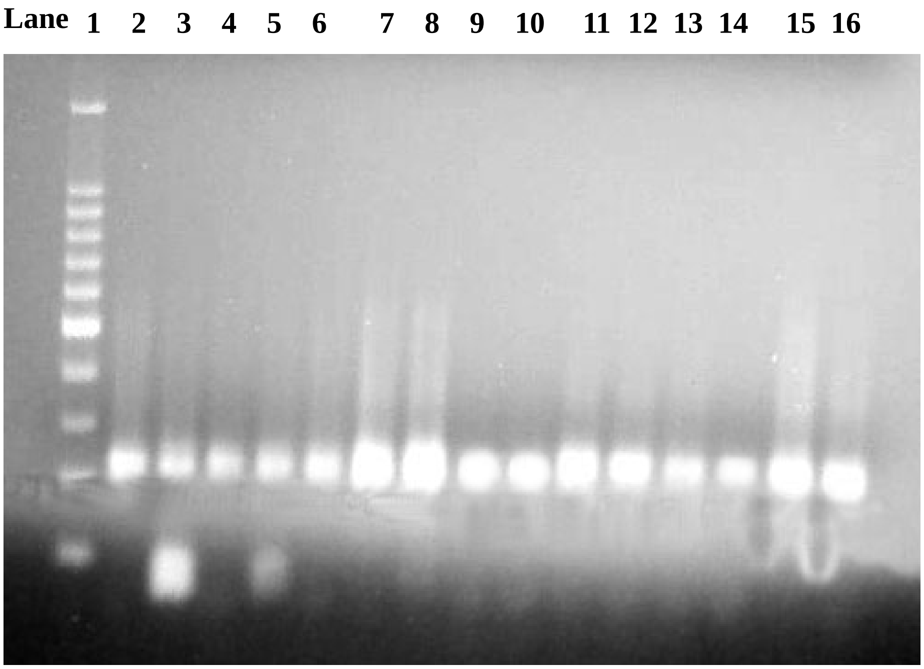


Figure 6-1 PCR amplification of 16S rDNA for samples from Biofilter "B" and mixtures biofilters (Lane 1 was the standard 100 base pair (bp) ladder (TaKaRa, Santa Ana, CA, USA) (the difference in base pairs between two bands next to each other is 100 bp). Lanes 2-14 are samples for Biofilter "B" in VOC interchanging experiments described in Chapter 2 in detail. Lanes 15-16 are samples from Biofilter "A" and "B", respectively, described in Chapter 3 in detail. Lanes 2-14 were samples of MIBK, toluene, toluene, toluene, toluene, MEK, MEK, MEK, styrene, styrene, styrene, styrene, and then back to MIBK, respectively, in sequential backwashing dates.)

### 6.4.2. Biodiversity Analysis

The majority of the bacterial community present can't be cultivated using culture-dependent approaches (Amann et al. 1995). However, with the new advancement in the 16S rRNA based molecular fingerprinting techniques, it becomes possible to measure biodiversity in activated sludge. Of the current molecular fingerprinting techniques applied to assess biodiversity in engineered and natural ecosystems: Amplified Ribosomal DNA

Restriction Analysis (ARDRA) (Smit et al. 1997), DGGE (Muyzer et al. 1993), thermal gradient gel electrophoresis (TGGE) (Eichner et al. 1999), length heterogeneity PCR (LH-PCR) (Ritchie et al. 2000), automated ribosomal intergenic spacer analysis (ARISA) (Fisher and Triplett 1999), and T-RFLP (Liu et al. 1997). T-RFLP and DGEE are the two mostly commonly used (Dunbar et al. 2000; Dunbar et al. 2001; Boon et al. 2002; LaPara et al. 2002; Stamper et al. 2003; Griffiths et al. 2004; Saikaly et al. 2005). In this study, DGGE was used as the fingerprinting technique for assessing biodiversity in the trickling bed systems.

Figure 6-2 shows the DGGE banding patterns of the 16S rDNA fragments under interchanging VOC experiments described in Chapter 2. The samples analyzed in Figure 6-2 were from the last cycle of backwashing for each interchanged VOC. Preliminary analysis of DGGE banding patterns revealed dramatic changes in the structure of the bacterial community after interchanging VOCs. Moreover, some bands that appear intense in one treatment become faint after changing the treatment and vice versa (see arrows in Figure 6-2), which indicates that the relative abundance among the different species was changed after the chang of VOCs. It is interesting to note that despite the difference in the bacterial community structure as revealed by the banding patterns in Figure 6-2, the removal efficiency after re-acclimation was 99% in the all three TBABs. Furthermore, some bands present for all interchanged VOCs, which indicated the microbial community was affected by the preceding VOC in the biofilter. For example for Biofilter “A”, it is noticed that the microbial diversity for MEK (first lane) were still available when MEK (fifth lane) was switched back. It is speculated that this microbial retention could be the possible reason for quick reacclimation to MEK as compared to MIBK (see Figure 2-6).

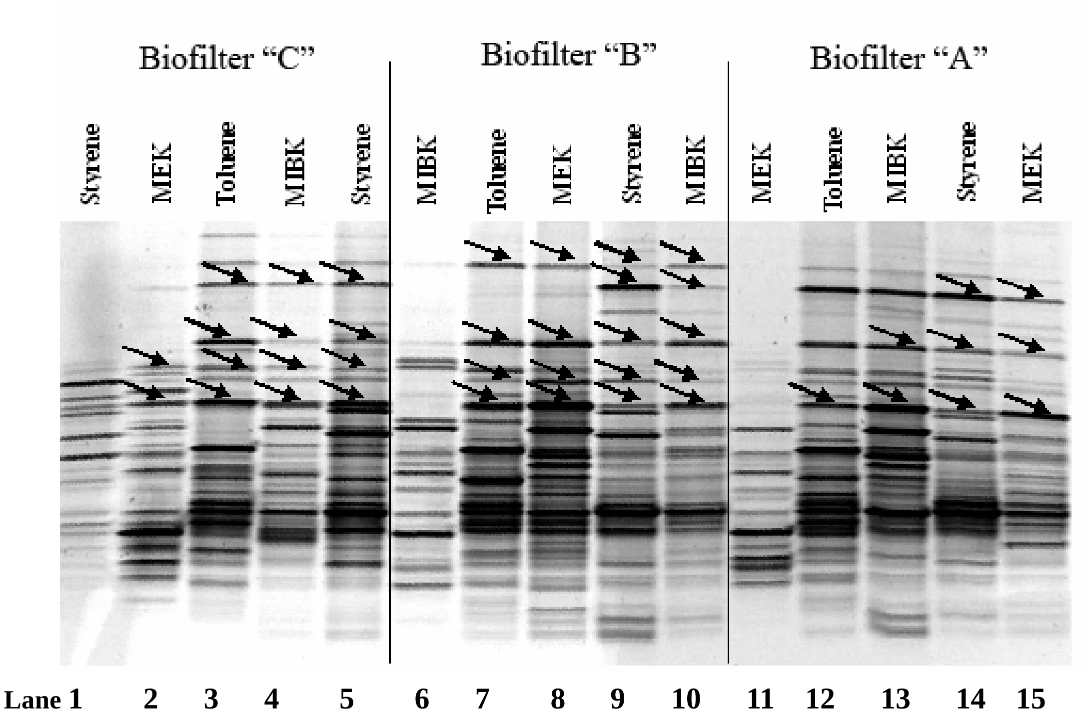


Figure 6-2 Inverted image of polyacrylamide gel stained with SYBR GREEN (Invitrogen, Carlsbad, CA, USA) showing DGGE-PCR profiles bans (230 bp) under interchanging VOC operating conditions

A dendrogram is constructed using the Euclidean distance and algorithm of Ward for DGGE profiles of samples in Figure 6-2 is shown in Figure 6-3. From the dendrogram, it can be seen that the microbial clusters for different VOCs in the three biofilters have complicated relationship between each other except for toluene. Toluene in the three biofilters was clustered next to each other which is represented by lanes 3, 7, and 12. Meanwhile, microbial communities for MEK, MIBK and styrene were clustered together in the three biofilters, as represented by lanes 2, 4, 11, by lanes 8, 10, 13, and by lanes 1, 6, 14 and 15. The independent microbial community clusters for toluene could account for the delayed re-acclimation of the biofilters when the VOC was interchanged to toluene. The microbial clusters in Biofilter "C" did not show special patterns as compared to Biofilter "A" and "B" although its EBRT was kept constant for all interchanged VOCs throughout the study at 2.02 min. This indicated that the EBRT did not have significant effect on the patterns in microbial clusters in the biofilters.

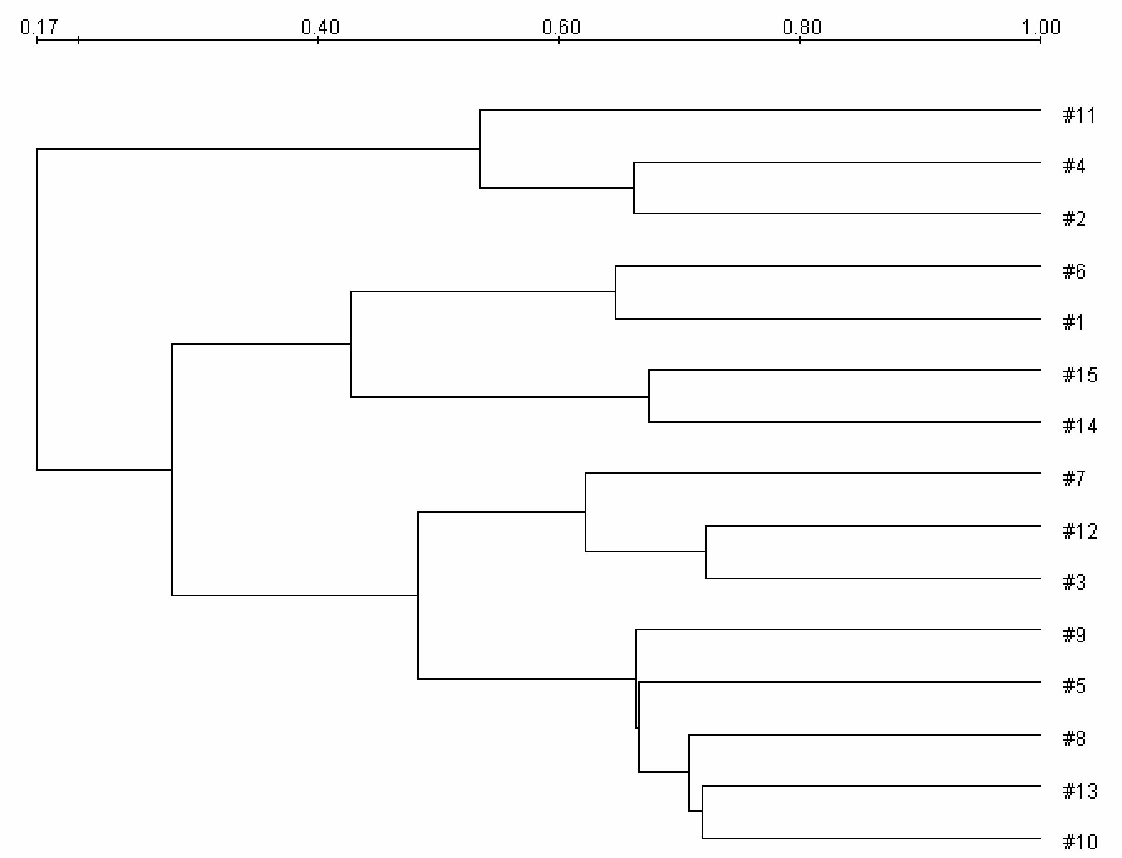


Figure 6-3 Dendrograms revealing the relatedness of PCR-DGGE fingerprints by using the algorithm of Ward and Euclidean distance for samples collected from VOC interchanging experiment

To understand how the microbial diversity responded gradually to an interchanged VOC, DGGE analysis for samples obtained from all backwashing cycles in Biofilter "B" were conducted. The DGGE profiles for Biofilter "B" are shown from lane 1 to lane 13 in Figure 6-4. The DGGE profiles for the interchanged VOC for Biofilter "B" showed clear transition from one VOC to another except for the initial interchange from MIBK which is represented by lane 1 to toluene represented by lane 2. The pattern for toluene microbial clusters represented in lane 2 showed a jump effect to the proceeded MIBK represented by lane 1. Consistent transition in the microbial clusters patterns is shown clearly in the other interchanged VOC, e.g. toluene to MEK (lane 5 to 6), MEK to styrene (lane 8 to 9), and styene to MIBK (lane 12 to 13). It can be seen clearly, from the microbial clusters patterns in Figure 6-4, that the microbial diversity for toluene is significantly different from those for MIBK, MEK, and styrene.

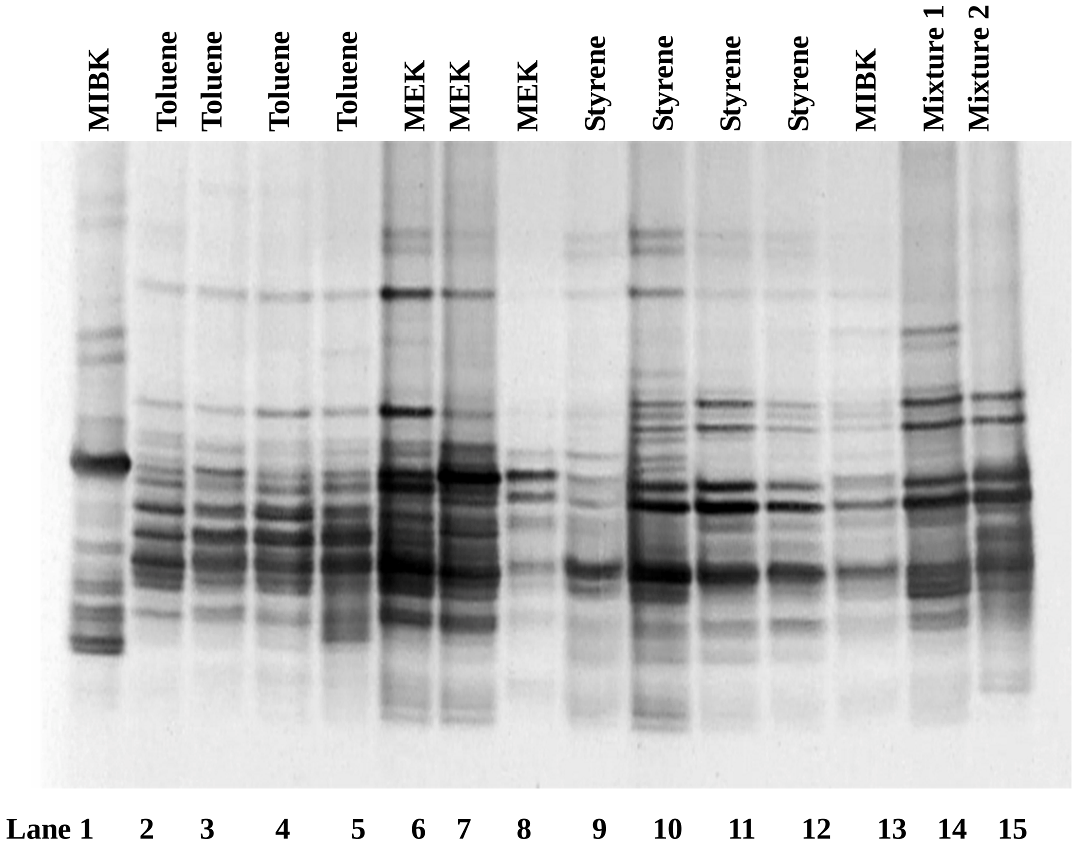


Figure 6-4 Inverted image of polyacrylamide gel stained with SYBR GREEN (Invitrogen, Carlsbad, CA, USA) showing DGGE-PCR profiles bans (230 bp) under interchanging VOC operating conditions for Biofilter "B" and VOC mixtures

To compare the microbial diversity in biofilters treating VOC mixtures with that for single

VOC solute, the DGGE profiles for the two VOC mixtures discussed in Chapter 3 are shown in lanes 14 and 15 in Figure 6-4. Due to the limit of the wells in one gel, only two samples for the two mixtures are taken from the last backwashing cycles. The microbial clusters for the two mixtures represented by lanes 14 and 15 clearly show that all bands in lanes 14 and 15 can find corresponding bands in lanes 1-13 for the single solute under interchanging conditions. The DGGE profiles for the two VOC mixtures did not show apparent difference from each other, which indicated that the relative content for each component in the VOC mixtures did not play an important role in microbial diversity.

Dendrogram constructed using the algorithm of Ward and Euclidean distance for DGGE profiles of samples in Figure 6-4 is shown in Figure 6-5. From the dendrogram, it can be concluded that microbial diversity showed relative stability for each single VOC, which indicated that microorganisms responded quickly to the new VOC after interchanging. Meanwhile, similarity in community structure between toluene represented by lanes 3 and 4 and MEK represented by lane 7, MEK represented by lane 6 and styrene represented by lanes 9, 10, and 12, toluene represented by lanes 2 and 5 and MIBK represented by lane 13 indicated the proceeded VOC had an important effect on the microbial diversity on the biofilter for the interchanged VOC. Furthermore, it’s interesting to notice that the dendrogram did not show similarity between toluene and styrene although both toluene and styrene are aromatic compounds. The similarity in community structure between lanes 14 and 15 for the two VOC mixtures supported the discussion for Figure 6-4 for the microbial diversity for the VOC mixtures.

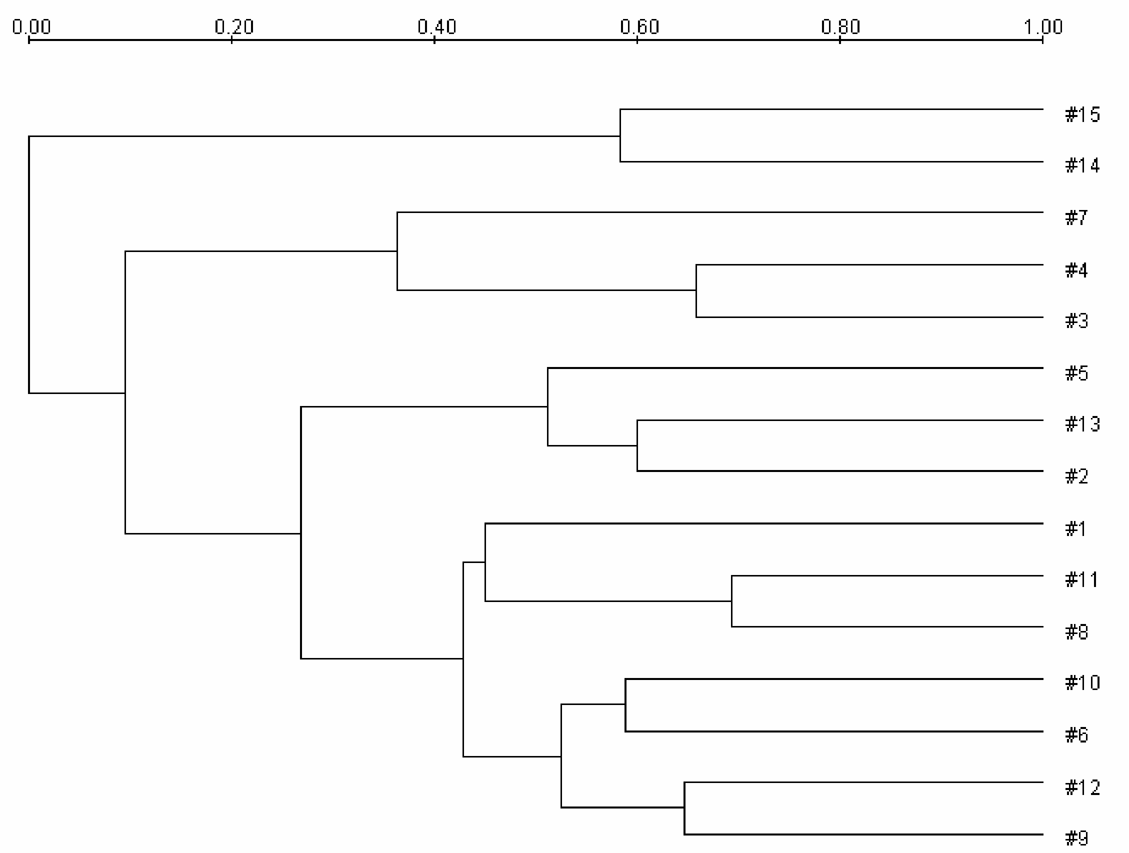


Figure 6-5 Dendrograms revealing the relatedness of PCR-DGGE fingerprints by using the algorithm of Ward and Euclidean distance for samples collected from VOC interchanging experiment for Biofilter "B" and mixtures biofilters

## 6.5. Conclusions

The results obtained in this study supported the following conclusions:

(1) The microbial diversity showed consistent transition for the interchanged VOC.

(2) The community structure for VOC mixtures show high independency to the component content in the mixture.

(3) The microbial diversity for toluene did not show significant association with the other VOCs studied unlike the behavior of the other three VOCs studied.

(4) The community structure in the biofilter did not show a clear relation to the biofilter performance.

## 6.6. References

Acuna, M. E., Perez, F., Auria, R., and Revah, S. (1999). "Microbiological and kinetic aspects of a biofilter for the removal of toluene from waste gases." *Biotechnology and Bioengineering*, 63(2), 175-184.

Ahrens, A., Lipski, A., Klatte, S., Busse, H. J., Auling, G., and Altendorf, K. (1997). "Polyphasic classification of proteobacteria isolated from biofilters." *Systematic and Applied Microbiology*, 20(2), 255-267.

Aizpuru, A., Khammar, N., Malhautier, L., and Fanlo, J. L. (2003a). "Biofiltration for the treatment of complex mixtures of VOC - Influence of the packing material." *Acta Biotechnologica*, 23(2-3), 211-226.

Aizpuru, A., Malhautier, L., Roux, J. C., and Fanlo, J. L. (2001). "Biofiltration of a mixture of volatile organic emissions." *Journal of the Air & Waste Management Association*, 51(12), 1662-1670.

Aizpuru, A., Malhautier, L., Roux, J. C., and Fanlo, J. L. (2003b). "Biofiltration of a mixture of volatile organic compounds on granular activated carbon." *Biotechnology and Bioengineering*, 83(4), 479-488.

Alexandrino, M., Knief, C., and Lipski, A. (2001). "Stable isotope-labeling of styrene-degrading microorganisms in biofilters." *Applied and Environmental Microbiology*, 67(10), 4796-4804.

Amann, R. I., Ludwig, W., and Schleifer, K. H. (1995). "Phylogenetic identification and in situ detection of individual microbial cells without cultivation." *Microbiological Reviews*, 59(1), 143-169.

Arnold, M., Reittu, A., von Wright, A., Martikainen, P. J., and Suihko, M. L. (1997). "Bacterial degradation of styrene in waste gases using a peat filter." *Applied Microbiology and Biotechnology*, 48(6), 738-744.

Atoche, J. C., and Moe, W. M. (2004). "Treatment of MEK and toluene mixtures in biofilter: effect of operating strategy on performance during transient loading." *Biotechnology and Bioengineering*, 86(4), 468-481.

Bendinger, B., Kroppenstedt, R. M., Klatte, S., and Altendorf, K. (1992). "Chemotaxonomic differentiation of coryneform bacteria isolated from biofilters." *International Journal of Systematic Bacteriology*, 42(3), 474-486.

Bendinger, B., Rainey, F., Kroppenstedt, R. M., Moormann, M., and Klatte, S. (1995). "*Gordona hydrophobica* sp. nov., isolated from biofilters for waste gas treatment." *International Journal of Systematic Bacteriology*, 45(3), 544-548.

Boon, N., Windt, W. D., Verstraete, W., and Top, E. M. (2002). "Evaluation of nested PCR-DGGE (denaturing gradient gel electrophoresis) with a group-specific 16S rRNA primers for the analysis of bacterial communities from different wastewater treatment plants." *FEMS Microbiology Ecology*, 39(2), 101-112.

Bruns, M. A., Hanson, J. R., Mefford, J., and Scow, K. M. (2001). "Isolate PM1 populations are dominant and novel methyl tert-butyl ether-degrading bacteria in compost biofilter enrichments." *Environmental Microbiology*, 3(3), 220-225.

Cai, Z., Kim, D., and Sorial, G. A. (2004). "Evaluation of trickle-bed air biofilter performance for MEK removal." *Journal of Hazardous Materials*, 114(1-3), 153-158.

Cai, Z., Kim, D., and Sorial, G. A. (2005). "Removal of methyl isobutyl ketone from contaminated air by trickle-bed ai biofilter." *Journal of Environmental Engineering*, 131(9), 1322-1329.

Cai, Z., Kim, D., Sorial, G. A., Saikaly, P. E., Zein, M. M., and Oerther, D. B. (2006). "Performance and microbial diversity of trickle-bed Air biofilter under interchanging contaminants." *Engineering in Life Science*, 6(1), 37-42.

Chang, K., and Lu, C. Y. (2003). "Biofiltration of toluene and acetone mixtures by a trickle-bed air biofilter." *World Journal of Microbiology & Biotechnology*, 19(8), 791-798.

Chitwood, D. E., and Devinny, J. S. (2001). "Teatment of mixed hydrogen sulfide and organic vapors in a rock medium biofilter." *Water Environment Research*, 73(4), 426-435.

Cho, K., Hirai, M., and Shoda, M. (1992). "Degradation of hydrogen sulfide by *Xanthomonas* sp. strain DY44 isolated from peat." *Applied and Environmental Microbiology*, 58(4), 1183-1189.

Chou, M. S., and Huang, J. J. (1997). "Treatment of methylethylketone in air stream by biotrickling filters." *Journal of Environmental Engineering*, 123(6), 569-576.

Chung, Y. C., Huang, C., and Tseng, C. P. (1997). "Biotreatment of ammonia from air by an immobilized *Arthrobacter oxydans* CH8 biofilter." *Biotechnology Progess*, 13(6), 794-798.

Cox, H. H. J., and Deshusses, M. A. (2002). "Co-treatment of H2S and toluene in a biotrickling filter." *Chemical Engineering Journal*, 87(1), 101-110.

Cox, H. H. J., Houtman, J. H. M., Doddema, H. J., and Harder, W. (1993). "Enrichment of fungi and degradation of styrene in biofilters." *Biotechnology Letters*, 15(7), 737-742.

Cox, H. H. J., Magielsen, F. J., and Doddema, H. J. (1996). "Influence of the water content and water activity on styrene degradation by *Exophiala jeanselmei* in biofilters." *Applied Microbiology and Biotechnology*, 45(6), 851-856.

Damborsky, J., Damborska, M., and Pistek, V. (1999). "Sporulation as an effective strategy for the survival of bacteria in a biofilter with discontinuous operation." *Biotechnology Letters*, 21(9), 835-838.

De Heyder, B., Overmeire, A., van Langenhove, H., and Verstraete, W. (1994). "Ethene removal from a synthetic waste gas using a dry biobed." *Biotechnology and Bioengineering*, 44(5), 642-648.

Deshusses, M. A. (1997). "Transient behavior of biofilters: Start-up, carbon balances, and interactions between pollutants." *Journal of Environmental Engineering-Asce*, 123(6), 563-568.

Deshusses, M. A., and Hamer, G. (1993). "The removal of volatile ketone mixtures from air in biofilters." *Bioprocess Engineering*, 9(4), 141-146.

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

Deshusses, M. A., Hamer, G., and Dunn, I. J. (1995b). "Behavior of biofilters for waste air biotreatment.2. Experimental evaluation of a dynamic-model." *Environmental Science & Technology*, 29(4), 1059-1068.

Deshusses, M. A., Hamer, G., and Dunn, I. J. (1996). "Transient-state behavior of a biofilter removing mixtures of vapors of MEK and MIBK from air." *Biotechnology and*

*Bioengineering*, 49(5), 587-598.

Devinny, J. S., and Hodge, D. S. (1995). "Formation of acidic and toxic intermediates in overloaded ethanol biofilters." *Journal of the Air & Waste Management Association*, 45(2), 125-131.

du Plessis, C. A., Kinney, K. A., Schroeder, E. D., Chang, D. P. Y., and Scow, K. M. (1998). "Denitrification and nitric oxide reduction in an aerobic toluene-treating biofilter." *Biotechnology and Bioengineering*, 58(4), 408-415.

Dunbar, J., Ticknor, L. O., and Kuske, C. R. (2000). "Assessment of microbial diversity in four southwestern United States soils by 16S rRNA gene terminal restriction fragment analysis." *Applied and Environmental Microbiology*, 66(7), 2943-2950.

Dunbar, J., Ticknor, L. O., and Kuske, C. R. (2001). "Phylogenetic specificity and reproducibility and new method for analysis of terminal restriction fragment profiles of 16S rRNA genes from bacterial communities." *Applied and Environmental Microbiology*, 67(1), 190-197.

Eichner, C. A., Erb, R. W., Timmis, K. N., and Wagner-Dobler, I. (1999). "Thermal gradient gel electrophoresis analysis of bioprotection from pollutant shocks in the activated sludge microbial community." *Applied and Environmental Microbiology*, 65(1), 102-109.

Elsgaard, L. (1998). "Ethylene removal by a biofilter with immobilized bacteria." *Applied and Environmental Microbiology*, 64(11), 4168-4173.

Estevez, E., Veiga, M. C., and Kennes, C. (2005). "Biofiltration of waste gases with the fungi *Exophiala oligosperma* and *Paecilomyces variotii*." *Applied Microbiology and*

*Biotechnology*, 67(4), 563-568.

Finkmann, W., Altendorf, K., Stackebrandt, E., and Lipski, A. (2000). "Characterization of N2O-producing *Xanthomonas*-like isolates from biofilters as *Stenotrophomonas nitritireducens* sp. nov., *Luteimonas mephitis* gen. nov., sp. nov., and *Pseudoxanthomonas broegbernensis* gen. nov., sp. nov." *International Journal of Systematic and Evolutionary Microbiology*, 50(1), 273-282.

Fisher, M. M., and Triplett, E. W. (1999). "Automated approach for ribosomal intergenic spacer analysis of microbial diversity and its application to freshwater bacterial communities." *Applied and Environmental Microbiology*, 65(10), 4630-4636.

Friedrich, U., Langenhove, H. V., Altendorf, K., and Lipski, A. (2003). "Microbial community and physicochemical analysis of an industrial waste gas biofilter and design of 16S rRNA-targeting oligonucleotide probes." *Environmental Microbiology*, 5(3), 183-201.

Friedrich, U., Naismith, M. M., Altendorf, K., and Lipski, A. (1999). "Community analysis of biofilters using fluorescence in situ hybridization including a new probe for the Xanthomonas branch of the class Proteobacteria." *Applied and Environmental Microbiology*, 65(8), 3547-3554.

Friedrich, U., Prior, K., Altendorf, K., and Lipski, A. (2002). "High bacterial diversity of a waste gas degrading community in an industrial biofilter as shown by a 16S rDNA clone library." *Environmental Microbiology*, 4(11), 721-734.

Griffiths, B. S., Kuan, H. L., Ritz, K., Glover, L. A., McCaig, A. E., and Fenwick, C. (2004). "The relationship between microbial community structure and functional stability, tested experimentally in an upland pasture soil." *Microbial Ecology*, 47(1), 104-113.

Grove, J. A., Kautola, H., SJavadpour, S., Young, M. M., and Anderson, W. A. (2004). "Assessment of changes in the microorganism community in a biofilter." *Biochemical Engineering Journal*, 18(2), 111-114.

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

Jang, J. H., Hirai, M., and Shoda, M. (2004). "Styrene degradation by *Pseudomonas* sp. SR-5 in biofilters with organic and inorganic packing materials." *Applied Microbiology and Biotechnology*, 65(3), 349-355.

Juteau, P., Larocque, R., Rho, D., and LeDuy, A. (1999). "Analysis of the relative abundance of different types of bacteria capable of toluene degradation in a compost biofilter." *Applied Microbiology and Biotechnology*, 52(6), 863-868.

Khammar, N., Malhautier, L., Degrange, V., Lensi, R., Godon, J. J., and Fanlo, J. L. (2005). "Link between spatial structure of microbial communities and degradation of a complex mixture of volatile organic compounds in peat biofilter." *Journal of Applied Microbiology*, 98(2), 476-490.

Kim, D. (2006). "Development of integrated treatment scheme of adsorption and biofiltration for VOCs removal," *Ph.D. dissertation in Civil and Environmental Engineering*, University of Cincinnati, Cincinnati, Ohio, USA.

Kim, D., Cai, Z., and Sorial, G. A. (2005a). "Behavior of trickle bed air biofilter for toluene removal: effect of non-use periods." *Environmental Progress*, 24(2), 155-161.

Kim, D., Cai, Z., and Sorial, G. A. (2005b). "Evaluation of trickle-bed air biofilter performance under periodic stressed operating conditions as a function of styrene loading." *Journal of the Air & Waste Management Association*, 55(2), 200-209.

Klatte, S., Kroppenstedt, R. M., Schumann, P., Altendorf, K., and Rainey, F. A. (1996). "Gordona hirsuta sp. nov." *International Journal of Systematic Bacteriology*, 46(6), 876-880.

Knief, C., Altendorf, K., and Lipski, A. (2003). "Linking autotrophic activity in environmental samples with specific bacterial taxa by detection of $^{13}$C-labelled fatty acids." *Environmental Microbiology,* 5(11), 1155-1167.

Kong, Z., Farhana, L., Fulthorpe, R. R., and Allen, D. G. (2001). "Treatment of volatile organic compounds in a biotrickling filter under thermophilic conditions." *Environmental Science & Technology,* 35(21), 4347-4352.

Krailas, S., Pham, Q. T., Amal, R., Jiang, J. K., and Heitz, M. (2000). "Effect of inlet mass loading, water and total bacteria count on methanol elimination using upward flow and downward flow biofilters." *Journal of Chemical Technology and Biotechnology*, 75(4), 299-305.

LaPara, T. M., Nakatsu, C. H., Pantea, L. M., and Allegan, J. E. (2002). "Stability of the bacterial communities supported by a seven-stage biological process treating pharmaceutical wastewater as revealed by PCR-DGGE." *Water Research*, 36(3), 638-646.

Li, C., and Moe, W. M. (2004). "Assessment of microbial populations in methyl ethyl ketone degrading biofilters by denaturing gradient gel electrophoresis." *Applied*

*Microbiology and Biotechnology*, 64(4), 568-575.

Lipski, A., and Altendorf, K. (1995). "*Actinomadura nitritigenes* sp. nov., isolated from experimental biofilters." *International Journal of Systematic Bacteriology*, 45(4), 717-723.

Lipski, A., and Altendorf, K. (1997). "Identification of heterotrophic bacteria isolated from ammonia-supplied experimental biofilters." *Systematic and Applied Microbiology*, 20(3), 448-457.

Lipski, A., Klatte, S., Bendinger, B., and Altendorf, K. (1992). "Differentiation of Gram-negative, nonfermentative bacteria isolated from biofilters on the basis of fatty acid composition, quinone system, and physiological reaction profiles." *Applied and Environmental Microbiology*, 58(6), 2053-2065.

Lipski, A., Reichert, K., Reuter, B., Spröer, C., and Altendorf, K. (1998). "Identification of bacterial isolates from biofilters as *Paracoccus alkenifer* sp. nov. and *Paracoccus solventivorans* with emended description of *Paracoccus solventivorans*." *International Journal of Systematic Bacteriology*, 48(2), 529-536.

Liu, W. T., Marsh, T. L., Cheng, H., and Forney, L. J. (1997). "Characterization of microbial diversity by determining terminal restriction fragment length polymorphisms of genes encoding 16S rRNA." *Applied and Environmental Microbiology*, 63(11), 4516-4522.

Malhautier, L., Degorce-Dumar, J. R., Degrange, V., Bardin, R., and Le Cloirec, P. (1997). "Serological determination of *Nitrobacter* species in a deodorizing granular activated carbon filter." *Environmental Technology*, 18(3), 275-283.

Malhautier, L., Degrange, V., Guay, R., Degorce-Dumar, J. R., Bardin, R., and Le Cloirec, P.

(1998). "Estimation size and diversity of nitrifying communities in deodorizing filters using PCR and immunofluorescence." *Journal of Applied Microbiology*, 85(2), 255-262.

Martin, F. J., and Loehr, R. C. (1996). "Effect of periods of non-use on biofilter performance." *Journal of the Air & Waste Management Association*, 46(6), 539-546.

Moe, W. M., and Irvine, R. L. (2001). "Intracellular dynamics of ribonucleic acid (RNA) and protein in microorganisms from periodically operated biofilters." *Water Science and Technology*, 43(3), 241-248.

Moe, W. M., and Qi, B. (2004). "Performance of a fungal biofilter treating gas-phase solvent mixtures during intermittent loading." *Water Research*, 38(9), 2259-2268.

Mohseni, M., and Allen, D. G. (1999). "Transient performance of biofilters treating mixtures of hydrophilic and hydrophobic volatile organic compounds." *Journal of the Air & Waste Management Association*, 49(12), 1434-1441.

Mohseni, M., and Allen, D. G. (2000). "Biofiltration of mixtures of hydrophilic and hydrophobic volatile organic compounds." *Chemical Engineering Science*, 55(9), 1545-1558.

Morgenroth, E., Schroeder, E. D., Chang, D. P. Y., and Scow, K. M. (1996). "Nutrient limitation in a compost biofilter degradating hexane." *Journal of the Air & Waste Management Association*, 46(4), 300-308.

Muyzer, G., De Waal, E. C., and Uitterlinden, A. G. (1993). "Profiling of complex microbial populations by denaturing gradient gel electrophoresis analysis of polymerase chain reaction-amplified genes coding for 16S rRNA." *Applied and Environmental*

*Microbiology*, 59(3), 695-700.

Oh, Y. K., Kim, S. H., Kim, M. S., and Park, S. (2004). "Thermophilic biohydrogen production from glucose with trickling biofilter." *Biotechnology and Bioengineering*, 88(6), 690-698.

Ottengraf, S. P. P., and Konings, J. H. G. (1991). "Emission of microorganisms from biofilters." *Bioprocess Engineering*, 7(1-2), 89-96.

Pedersen, A. R., and Arvin, E. (1997). "Toluene removal in a biofilm reactor for waste gas treatment." *Water Science and Technology*, 36(1), 69-76.

Pruden, A., Sedran, M. A., Suidan, M. T., and Venosa, A. D. (2003). "Biodegradation of MTBE and BTEX in an aerobic fluidized bed reactor." *Water Science and Technology*, 47(9), 123-128.

Qi, B., Moe, W. M., and Kinney, K. A. (2002). "Biodegradation of volatile organic compounds by five fungal species." *Applied Microbiology and Biotechnology*, 58(5), 684-689.

Reichert, K., Lipski, A., Pradella, S., Stackebrandt, E., and Altendorf, K. (1998). "*Pseudonocardia asaccharolytica* sp. nov. and *Pseudonocardia sulfidoxydans* sp. nov., two new dimethyl disulfide-degrading actinomycetes and emended description of the genus *Pseudonocardia*." *International Journal of Systematic Bacteriology*, 48(2), 441-449.

Ritchie, N. J., Schutter, M. E., Dick, R. P., and Myrold, D. D. (2000). "Use of length heterogeneity PCR and fatty acid methyl ester profiles to characterize microbial communities in soil." *Applied and Environmental Microbiology*, 66(4), 1668-1675.

Roy, S., Gendron, J., Delhomenie, M. C., Bibeau, L., Heitz, M., and Brzezinski, R. (2003). "Pseudomonas putida as the dominant toluene-degrading bacterial species during air decontamination by biofiltration." *Applied Microbiology and Biotechnology*, 61(4), 366-373.

Saikaly, P. E., Stroot, P. G., and Oerther, D. B. (2005). " Use of 16S rRNA gene terminal restriction fragment analysis to assess the impact of solids retention time on the bacterial diversity of activated sludge." *Applied and Environmental Microbiology*, 71(10), 5814-5822.

Sakano, Y., and Kerkhof, L. (1998). "Assessment of changes in microbial community structure during operation of an ammonia biofilter with molecular tools." *Applied and Environmental Microbiology*, 64(12), 4877-4882.

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

Schonduve, P., Sara, M., and Friedl, A. (1996). "Influence of physiologically relevant parameters on biomass formation in a trickle-bed bioreactor used for waste gas cleaning." *Applied Microbiology and Biotechnology*, 45(1-2), 286-292.

Sly, L. I., Bryant, L. J., Cox, J. M., and Anderson, J. M. (1993). "Development of a biofilter for the removal of methane from coal mine ventilation atmospheres." *Applied Microbiology and Biotechnology*, 39(3), 400-404.

Smit, E., Leeflang, P., and Wernars, K. (1997). "Detection of shifts in microbial community structure and diversity in soil caused by copper contamination using amplified ribosomal DNA restriction analysis." *FEMS Microbiology Ecology*, 23(3), 249-261.

Sologar, V. S., Lu, Z. J., and Allen, D. G. (2003). "Biofiltration of concentrated mixtures of hydrogen sulfide and methanol." *Environmental Progress*, 22(2), 129-136.

Song, J. H., and Kinney, K. A. (2005). "Microbial response and elimination capacity in biofilters subjected to high toluene loadings." *Applied Microbiology and Biotechnology*, 68(4), 554-559.

Sorial, G. A., Smith, F. L., Suidan, M. T., Biswas, P., and Brenner, R. C. (1995). "Evaluation of trickle-bed biofiltermedia for toluene removal." *Journal of the Air & Waste Management Association*, 45(10), 801-810.

Sorial, G. A., Smith, F. L., Suidan, M. T., Smith, P. J., Biswas, P., and Brenner, R. C. "Development of aerobic biofilter design criteria for treating VOCs." *86th Annual Meeting and exhibition of the Air & Waste management Association*, Denver, CO.

Sorial, G. A., Smith, F. L., Suidan, M. T., Smith, P. J., Biswas, P., and Brenner, R. C. "Evaluation of performance of trickle bed biofilter-impact of periodic removal of accumulated biomass." *87th Annual Meeting and Exhibition of the Air & Waste Management Association*, Cincinnati, OH.

Sorokin, D. Y. (1994). "Use of microorganisms in protection of environments from pollution by sulfur compounds." *Microbiology*, 63(6), 533-547.

Stamper, D. M., Walch, M., and Jacobs, R. N. (2003). "Bacterial population changes in a membrane bioreactor for graywater treatment monitored by denaturing gradient gel electrophoretic analysis of 16S rRNA gene fragments." *Applied and Environmental Microbiology*, 69(2), 852-860.

Steele, J. A., Ozis, F., Fuhrman, J. A., and Devinny, J. S. (2005). "Structure of microbial communities in ethanol biofilters." *Chemical Engineering Journal*, 113(2-3), 135-143.

Sukesan, S., and Watwood, M. E. (1997). "Continous vapor-phase trichloroethylene biofiltration using hydrocarbon-enriched compost as filtration matrix." *Applied Microbiology and Biotechnology*, 48(5), 671-676.

Togashi, I., Suzuki, M., Hirai, M., Shoda, M., and Kubota, H. (1986). "Removal of $NH_3$ by a peat biofilter without and with nitrifier." *Journal of Fermentation Technology*, 64(5), 425-432.

von Keitz, V., Schramm, A., Altendorf, K., and Lipski, A. (1999). "Characterization of microbial communities of biofilters by phospholipid fatty acid analysis and rRNA targeted oligonucleotide probes." *Systematic and Applied Microbiology*, 22(4), 626-634.

Wada, A., Shoda, M., Kubota, H., Kobayashi, T., Fujimura, Y. K., and Kuraishi, H. (1986). "Characteristics of $H_2S$ oxidizing bacteria inhabiting a peat biofilter." *Journal of Fermentation Technology*, 64(2), 161-167.

Weber, F. J., Hage, K. C., and De Bond, J. A. M. (1995). "Growth or the fungus *Cladosporium sphaerospermum* with toluene as the sole carbon and energy source." *Applied and Environmental Microbiology*, 61(10), 3562-3566.

Webster, T. S., Devinny, J. S., Torres, E. M., and Basrai, S. S. (1997). "Microbial ecosystems in compost and granular activated carbon biofilters." *Biotechnology and Bioengineering*, 53(3), 296-303.

Weckhuysen, B., Vriens, L., and Verachtert, H. (1994). "Biotreatment of ammonia- and butanal-containing waste gases." *Applied Microbiology and Biotechnology*, 42(1), 147-152.

Yoon, I.-K., and Park, C.-H. (2002). "Effects of gas flow rate, inlet concentration and temperature on biofiltration of volatile organic compounds in a peat-packed biofilter." *Journal of Bioscience and Bioengineering*, 93(2), 165-169.

Zhang, L., Kuniyoshi, I., Hirai, M., and Shoda, M. (1991). "Oxidation of dimethyl sulfide by *Pseudomonas acidovorans* DMR-11 isolated from peat biofilter." *Biotechnology Letters*, 13(3), 223-228.

Zilli, M., Camogli, G., and Nicolella, C. (2005). "Detachment and emission of airborne bacteria in gas-phase biofilm reactors." *Biotechnology and Bioengineering*, 91(6), 707-714.

# CHAPTER 7

# CONCLUSIONS AND SUMMARY FOR THIS STUDY AND RECOMMENDATIONS FOR THE FUTURE WORK

Fluctuation in concentrations and variation in the waste air composition is most commonly encountered in industry, which challenges the application of biofiltration technology. As a potential solution to handle the limitation of the biofiltration technology, an integrated system of a cyclic 2-bed adsorption/desorption unit and trickle bed air biofilter (TBAB) is proposed and applied in this study. Five phases in this study conducted to approach the objectives proposed included: characterization of TBAB for VOC interchange under step-change loadings up to critical loadings, characterization of TBAB for VOCs mixture under two operating conditions: backwashing and starvation, evaluation of a cyclic 2-bed adsorption unit for attenuating fluctuation in the influent concentrations into the followed TBAB system, application of the integrated technology for removal of VOC mixture concerned, and microbial diversity investigation for interchanging and mixture of VOCs in TBAB. The conclusions based on the experiments can be summarized as following:

# Chapter 7 Conclusions, Summary and Recommendations

Phase I: Trickle bed air biofilters (TBABs) were evaluated under conditions of an interchange of the feed volatile organic compounds (VOCs). Conclusions that can be drawn from this study were:

(1) High removal performances could be maintained in the interchanging VOCs-fed biofilters, once the biofilters got re-acclimated to the new contaminant.

(2) Prolonged EBRT could improve the biofilter performance for aromatic compounds significantly, but no apparent effect was seen for oxygenated compounds.

(3) The biofilter easily acclimated to oxygenated compounds (MEK and MIBK), regardless of the previous compound. On the other hand, the biofilter re-acclimation was delayed for period over 2 days for the aromatic compounds (styrene and toluene).

(4) Oxygenated compounds had higher removal rate along the biofilter media than the aromatic compounds.

(5) After interchanging the feed VOCs, low ratios of COD/N were observed initially due to biomass synthesis. Nitrogen utilization difference between oxygenated compounds and aromatic compounds was reduced significantly under the interchanging conditions as compared with the difference under the single solute conditions.

(6) A good $CO_2$ closure could be attained for hydrophobic VOCs (toluene and styrene), while a lower carbon closure was attained for hydrophilic VOCs (MIBK and MEK).

Phase II: Two independent parallel trickling bed air biofilters (TBABs) (“A” and “B”) with two different VOCs mixtures were investigated. Biofilter “A” was fed equal molar ratio of the VOC mixture of toluene, styrene, MEK and MIBK. Biofilter “B” was fed a mixture based on EPA 2003 emission report with mole ratio of 0.448: 0.260: 0.234: 0.058 for toluene: styrene: MEK: MIBK, respectively. Conclusions that can be drawn from this study were:

(1) Step change in VOC concentrations revealed that over 99% removal efficiency could be maintained at an inlet mixture concentrations up to 500 ppmv (loading rate 3.94 kg COD.$m^{-3}$.$day^{-1}$) and 300 ppmv (loading rate 2.40 kg COD.$m^{-3}$.$day^{-1}$) for biofilter “A” and biofilter “B”, respectively. Toluene content in the mixtures played a major role in the biofilter overall performance. Furthermore, starvation operation helped in maintaining high level performance and could be used as another means of biomass control provided the inlet mixture concentration did not exceed 250 ppmv (2.01 kg COD.$m^{-3}$.$day^{-1}$) and 300 ppmv (2.40 kg COD.$m^{-3}$.$day^{-1}$) for biofilter “A” and biofilter “B”, respectively.

(2) Biofilter re-acclimation study showed that re-acclimation was delayed for both biofilters with increase of inlet mixture concentrations. The performance of biofilter “B” required longer time to recover than that of biofilter “A” due to the higher toluene content in biofilter “B”.

(3) Nitrogen utilization investigation indicated that biofilters required a transition period to get re-acclimated to the new operating conditions. Furthermore, there is no apparent difference in nitrogen utilization for the two biofilters.

(4) VOCs removal kinetic analysis indicated that biofilter depth utilization increased with increase of inlet mixture concentrations for both biofilters. MEK and MIBK in the mixtures were removed in the upper biofilter depth, and removal of styrene and toluene utilized more biofilter depth. Meanwhile, biofilter “B” had higher removal rates for toluene and styrene than biofilter “A”. The removal rate constant for toluene in the two mixtures studied were significantly different from the single solute.

Phase III: Buffering capacity of a 2-bed adsorption unit was evaluated. Square wave feeding conditions were employed to simulate fluctuation in the inlet concentrations. The behavior of the 2-bed adsorption unit under non-cyclic and cyclic operation indicated:

(1) A single adsorption bed failed to act as a buffering unit to the followed biofilter during the initial acclimation period and also failed to attenuate fluctuation in inlet concentrations after breakthrough.

(2) The 2-bed adsorption unit with cyclic operation succeeded in providing low effluent that will help the initial acclimation of a followed biofilter and also attenuating significantly the fluctuation in inlet concentration after stabilization.

(3) Competitive adsorption occurred in the adsorption bed for the different components in the mixture due to their differences in physicochemical properties.

Phase IV: An integrated system of a trickling-bed air biofilter and a 2-bed cyclic adsorption/desorption unit was applied for the removal of a mixture of VOCs under square wave feeding conditions. By comparing the behavior of a control experiment (stand-alone biofilter) with the integrated system in performance and removal kinetics along the biofilter depth, the following conclusions could be revealed:

(1) The cyclic 2-bed adsorption/desorption unit dampened fluctuations in the inlet concentration of the VOC mixture and maintained a relative stable feeding condition to the followed biofiltration system.

(2) The cyclic 2-bed adsorption/desorption unit functioned as feeding source during starvation periods. It offered better performance under intermittent operation due to less accumulation of the VOCs within the adsorption beds.

(3) The integrated system was validated to maintain long-term consistent high level removal of a mixture of VOCs.

(4) The pseudo first order removal rate constants varied with the fluctuation of feeding conditions for the control system, however, no apparent difference for the integrated system was seen due to the effective dampening of the cyclic 2-bed adsorption/desorption unit to the feed inlet concentration.

Phase V: Microbial communities in trickle bed air biofilters (TBABs) were evaluated under conditions of interchanging the feed volatile organic compounds (VOCs) and VOC mixtures. The results obtained supported the following conclusions:

(1) The microbial diversity showed consistent transition for the interchanged VOC.

(2) The community structure for VOC mixtures show high independency to the component content in the mixture.

(3) The microbial diversity for toluene did not show significant association with the other VOCs studied unlike the behavior of the other three VOCs studied.

(4) The community structure in the biofilter did not show a clear relation to the biofilter performance.

Based on the research conducted in this study, further studies listed below will be very interesting for further revealing the importance of the integrated system.

(1) Expanded studies applied to alkanes with much lower solubility such as methane and hexane and chlorinated benzene chemicals with much higher toxicity such as mono-chlorinated benzene and PCBs. As far as we know from this study, the VOCs biodegradation in biofilters is controlled either by VOCs mass transfer and/or oxygen transfer from gas phase to liquid phase. For the VOCs with low solubility, VOCs mass transfer will be the controlling step for the biodegradation in biofilters. Methods for improving their mass transfer will be very interesting and valuable study. A possible way to improve the mass transfer is to add surfactants into the nutrient solution.

(2) VOCs toxicity has inhibition on the microbial viability, investigation on the effect of VOCs toxicity on biofilter performance will be also valuable.

(3) Further investigation in the microbiology in the biofilters is also needed. In order to determine the dominant species for single VOC solute or VOC mixtures in a

future study, DNA sequencing and fluorescence in situ hybridization (FISH) can be employed. Microbial distribution along the media bed can also be determined by employing single strand conformation polymorphism (SSCP). Response of microbial communities and richness to the operating conditions with time will also be very valuable to understand the ecology in the biofilters. It can be determined by community level physiological profiling (CLPP).

## Appendix I: Components in the Buffered Nutrient Solution

| Component | Concentration/mg/l | chemical formula | Concentration/mg/l |
|---|---|---|---|
| $B^{3+}$ | 0.00396 | $Na_2B_4O_7{\cdot}10H_2O$ | 0.03485 |
| $Ca^{2+}$ | 0.5542 | $CaCl_2{\cdot}\ 2H_2O$ | 2.0325 |
| $Co^{2+}$ | 0.0213 | $CoCl_2{\cdot}6H_2O$ | 0.0867 |
| $Cu^{2+}$ | 0.0232 | $CuCl_2{\cdot}2H_2O$ | 0.06213 |
| $Fe^{3+}$ | 0.0323 | $FeCl_3$ | 0.0936 |
| $K^+$ | 3.5798 | $KHSO_4$ | 12.4516 |
| $Mg^{2+}$ | 0.8914 | $MgCl_2{\cdot}6H_2O$ | 7.4435 |
| $Mn^{2+}$ | 0.03986 | $MnCl_2{\cdot}4H_2O$ | 0.1436 |
| $Mo^{6+}$ | 0.0342 | $(NH_4)_6Mo_7O_{24}$ | 0.0630 |
| $NH_4^+$ | 0.0055 | | |
| $Zn^{2+}$ | 0.0476 | $ZnCl_2$ | 0.0991 |
| $Na^+$ | 36.3616 | $NaNO_3$ | 101.1111 |
| | | $NaH_2PO_4{\cdot}H_2O$ | 13.7778 |
| | | $NaHCO_3$ | 23.8933 |
| p-Aminobenzoic acid | 0.0023 | $C_7H_7NO_2$ | 0.0023 |
| Biotin | 0.000884 | $C_{10}H_{16}N_2O_3S$ | 0.000884 |
| B12 | 0.0000453 | $C_{63}H_{88}CoN_{14}O_{14}P^-$ | 0.0000453 |
| Folic acid | 0.000884 | $C_{19}H_{19}N_7O_6$ | 0.000884 |
| Nicotinic acid | 0.0023 | $C_6H_5NO_2$ | 0.0023 |
| Pantothenic acid, calcium salt | 0.0023 | $C_{18}H_{32}CaN_2O_{10}$ | 0.0023 |
| Pyridoxine hydrochloride | 0.00453 | $C_8H_{12}ClNO_3$ | 0.00453 |
| Riboflavin | 0.0023 | $C_{17}H_{20}N_4O_6$ | 0.0023 |
| Thiamin hydrochloride | 0.0023 | $C_{12}H_{18}Cl_2N_4OS$ | 0.0023 |
| Thioctic acid | 0.0023 | $C_8H_{14}O_2S_2$ | 0.0023 |

## Appendix II: Properties of Target Compounds in this Study

| | Toluene | Styrene | Methyl ethyl ketone (MEK) | Methyl isobutyl ketone (MIBK) |
|---|---|---|---|---|
| Formula | $C_7H_8$ | $C_8H_8$ | $C_4H_8O$ | $C_6H_{12}O$ |
| Molecular Weight (g/mole) | 92.14 | 104.15 | 72.1 | 100.16 |
| Water Solubility (mg/L) | 546 | 230 | 256,000 | 19,100 |
| Vapor Pressure (mmHg, 20 °C) | 22 | 5.12 | 77.5 | 15 |
| Henry's Constant | | | | |
| (atm $m^3$/mole, 25°C) | $6.74 \times 10^{-3}$ | $2.61 \times 10^{-3}$ | $4.66 \times 10^{-5}$ | $1.49 \times 10^{-5}$ |
| (dimensionless) | 0.28 | 0.109 | 0.00194 | 0.00062 |
| $K_{ow}$ ($\log K_{ow}$) [a] | 2.58 | 3.16 | 0.28 | 1.09 |
| $K_{oc}$ (ml/g) | 300 | 920 | 4.5 | 19 |
| Specific gravity | 0.867 | 0.906 | 0.805 | 0.789 |
| Air Saturated Conc. | | | | |
| (g/$m^3$, 20°C) | 110 | 31 | - | 27 |
| (g/$m^3$, 30°C) | 184 | 52 | - | 53 |
| $EC_{50}$ (mg/L) [b] | 23 | 5.5 | 3426 | 80 |
| CAS NO. | 108-88-3 | 100-42-5 | 78-93-3 | 108-10-1 |

a Octanol-water partition coefficient

b Ecotoxicity ($EC_{50}$, mg/L) of VOCs to photo-bacterium phosphoreum by the Microtox® test

## Appendix III: Analytical Methods for Gas Phase and Liquid Phase Samples

### VOCs Analyses for Gas Phase Samples

***GC Analysis:*** The concentrations of VOCs as gas phase were determined by using a GC (HP5890, Series II, Hewlett Packard, Palo Alto, CA) with a flame ionization detector (FID), and a 30-m length, 0.25-mm I.D., 0.25-μm Film thickness narrow bore column (DB 624, J&W Scientific, Folsom, CA). The GC oven temperature was programmed from 40 °C to 120 °C at a rate of 20 °C/min with a 2-min hold at 40 °C and a 2-min hold at 120 °C. The carrier gas ($N_2$) flow rate was set at 2.3 mL/min. The FID detector was used with N2 make-up gas at a flow rate of 20 mL/min, a fuel gas flow ($H_2$) of 30 mL/min, and an oxidizing gas flow (air) of 300 mL/min. The detector temperature was 250 °C. Detection limits for VOCs concentration were 0.5, 0.5, 0.25, and 0.25 ppmv for toluene, styrene, MEK, and MIBK, respectively.

***Gas Sampling:*** Gas phase samples for VOC analysis were taken with gas-tight syringes (500 μL) through low-bleed and high-puncture-tolerance silicone gas chromatograph (GC) septa installed in the sampling ports.

**VOC Standard and Calibration:** Gaseous VOCs standards were prepared in a static gas dilution bottle (SGDB). Neat multi-component VOCs of concern as liquid phase was prepared. 10 μL of the neat multi-component VOC was added to a calibrated bottle to achieve 1.0 μg/mL of vapor standard. 40 mL of the1.0 μg/mL vapor standard was added to another bottle in order to achieve 0.02 μg/mL of standard. All volumes were verified by weight by using an analytical balance. In the SGDB, the injected VOC vaporized within 2 hours. Taking out different volume of VOC as vapor from each of the two prepared bottles, the calibration points were established by GC analysis (see Table A). The density and purity of chemical products were considered in all concentration calculations listed in Table 1. Once the calibration curve was established, a check standard was injected prior to analysis in order to confirm calibration. Recalibration was done every other month. A reference standard was also prepared to ensure the accuracy of the standard prepared above. 1.0 μg/mL and 0.1 μg/mL of the reference standard were used to verify the accuracy of the standard. 1.0 μg/mL of the reference standard was prepared by using the same method for preparing the standard. 8 mL of 1.0 μg/mL of standard was added to another bottle to achieve 0.1 μg/mL of the reference standard.

Appendix

## CO2 Gas Analysis

***GC Analysis:*** CO2 concentration in the gas phase were measured by chromatographic separation on a 2.4-m HayeSep Q, 80/100 column using a GC (HP 5890, Series II, Hewlett Packard, Palo Alto, CA) equipped with a thermal conductivity detector (TCD) (Hewlett Packard, Palo Alto, CA). The GC oven temperature was programmed from 50 °C to 80 °C at 10 °C/min with a 3.2 min hold at 50 °C and a 1.5 min hold at 80 °C. The carrier gas (He) flow rate was set at 30 mL/min, and the TCD detector was used with He make-up gas at A flow rate of 35 µL/min. Detection limit for CO2 concentration was 300 ppmv

***Gas Sampling:*** Gas phase samples for CO2 analysis were taken with gas-tight syringes (1000 µL) through low-bleed and high-puncture-tolerance silicone gas chromatograph (GC) septa installed in the sampling ports.

Appendix

## TOC AND IC analysis

TC and IC were analyzed by using a Shimadzu TOC 5000 analyzer (Shimadzu Corp., Tokyo,Japan). Samples were filtered through 0.45 μm nylon filters (Micron Separation, Westboro, MA) prior to the analysis.

1. ORGANIC CARBON STOCK SOLUTION PREPARATION
    - A. Dissolve 2.1254g anhydrous primary-standard-grade potassium biphthalate, $C_8H_5KO_4$ in carbon-free water and dilute to 1000ml, 1.00ml=1.00mg carbon;
    - B. Prepare 5 different concentrations (1.0, 5.0, 10.0, 20.0 and 30.0 mg/l) from A solution with super-Q water;
2. INORGANIC CARBON STOCK SOLUTION PREPARATION
    - A. Dissolve 4.4122g anhydrous sodium carbonate, $Na_2CO_3$ in water and add 3.497g anhydrous sodium bicarbonate $NaHCO_3$ , dilute to 1000ml; 1.00 ml= 1.00mg carbon
    - B. Prepare 5 different concentrations (1.0, 5.0, 10.0, 20.0 and 30.0 mg/l) from A solution with super-Q water;
3. CALIBRATION CURVE IN TOC
    - A. Blank Super-Q water
    - B. Five TC standards ( start with the lowest concentration ). Acidify the standard with 12 N HCl, sparge for 3 min and then do 5 injections with a max of 10 injections per standard. The samples that are acidified and purged will provide the non-purgeable organic carbon (NPOC)
    - C. Use the standards measured results to draw the calibration curve of TOC
4. CALIBRATION CURVE IN IC
    - A. Blank Super-Q water
    - B. Five IC standards (start with the lowest concentration ). Do 5 injections with a max of 10 injections per standard.
    - C. Use the standards measured results to draw the calibration curve of IC

## $NO_3^-$ Analysis

1. PREPARE STOCK SOLUTION
   - A. Dry potassium nitrate ($KNO_3$) in an oven at 105°C for 24 h.
   - B. Dissolve 0.7218 g in distilled or deionized water of high purity and dilute to 1000ml; 1.00ml=100µg $NO_3^-$ -N (100mg/l), preserve with 2ml $CHCl_3$.
   - C. Dilute the above solution 100ml to 1000ml with water; 1.00ml=10.0µg $NO_3^-$ -N (10mg/l), preserve with 2ml $CHCl_3$.
2. PREPARE SAMPLES
   - A. Dilute (0, 1.00, 2.00, 4.00, 5.00, 10.0, 20.0, 25.0, 30.0, 35.0ml) of 10mg/l stock solution to 50ml to get (0, 0.2, 0.4, 1.0, 2.0, 4.0, 5.0, 6.0, 7.0 mg/l) standard samples
   - B. Add 1 ml 1N HCl solution and mix thoroughly
   - C. Take 50 ml clear sample, filtered if necessary, add 1 ml 1N HCl solution and mix thoroughly
3. SPECTROPHOTOMETRIC MEASUREMENT
   - A. Read absorbance against redistilled water set at **zero** absorbance
   - B. Use a wavelength of 220 nm to obtain $NO_3^-$ reading
   - C. Use a wavelength of 275 nm to determine interference due to dissolved organic matter
4. PREPARE CALIBRATION CURVE AND SAMPLES CALCULATION
   - A. Subtract two times the absorbance reading at 275 nm from the reading from 220 nm to obtain absorbance due to $NO_3^-$
   - B. Construct a standard curve by plotting absorbance from A against $NO_3^-$-N concentration of standard.
   - C. Use corrected sample absorbances, obtain sample concentrations directly from standard curve.

NOTE: if correction value is more than 10% of the reading at 220 nm, do not use this method

## VSS Analysis for Liquid Samples

The VSS concentrations in the effluent and backwashing solution were determined according to Standard Methods 2540 G.

1. Prepare VSS filter papers
    - A. Select 4.7-cm diameter 1.5- µm glass fiber filter papers and pans for 3 samples for each analysis.
    - B. Place each filter on the filter screen, rough side up, and suck water through each, 2 times.
    - C. Place each pan with filter paper in the 550°C over for 60 minutes.
    - D. Place fresh desiccant in the scale, and in the desiccator.
    - E. Remove from the oven, place in a desiccator for 30 minutes to cool.
    - F. Weigh each pan, and leave in the desiccator for later use.
2. Filter the VSS samples
    - A. Put a mixing bar into the sample bottle and stir on stirrer.
    - B. Rinse all filtering equipment with DI water, and drain excess.
    - C. Assemble the filter apparatus, with a clean 500mL filter flask.
    - D. Put a fresh, tared filterin the filter assembly.
    - E. Fill a 100mL graduated cylinder with fresh, mixed sample.
    - F. Filter the 100mL, and “by eyeball” decide how much additional sample to filter through this paper
    - G. Record the total amount filtered for this VSS sample
    - H. Return the filter paper to the pan. Check that any torn filter material is scrapped form the filter, and added to the filter in the pan.
    - I. Place the pan aside, under a protective cover.
    - J. Repeat this procedure for each sample.
3. (Desiccation): Put all the filter pans in the 103°C oven for 2 hours.
4. Remove all pans from the oven, Place in the desiccator for 30 minutes, and weigh.
5. (Ignition): Put all filter pans in the 550°C oven for 60 minutes.
6. Remove all pan from the oven, Place in the desiccator for 30 minutes, and Weight.
7. Calculate VSS as mg/L.

## Appendix IV: Re-acclimation of Components in the Two Mixtures

**Toluene** response after backwashing and starvation in Biofilter “**A**”

Removal Efficiency, %

**Backwashing**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 54.4 | 63.7 | 73.3 | 79.0 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 63.0 | 67.3 | 62.4 | 81.0 | 87.4 | 91.3 | 98.2 | 99.9 | 99.9 |
| 250 ppmv | 65.2 | 60.0 | 24.2 | 45.4 | 72.8 | 75.4 | 73.0 | 98.5 | 99.9 |
| 500 ppmv | 27.1 | 55.1 | 91.9 | 97.4 | 94.7 | 96.8 | 99.9 | 99.9 | 99.9 |
| 1000 ppmv | 97.5 | 61.0 | 49.6 | 28.1 | 47.7 | 31.1 | 57.9 | 42.2 | 50.1 |

**Starvation**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 79.0 | 88.5 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 96.4 | 79.2 | 90.0 | 99.0 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 93.9 | 89.0 | 95.4 | 92.2 | 99.2 | 99.1 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 95.3 | 85.4 | 75.5 | 53.9 | 62.2 | 70.7 | 88.5 | 90.9 | 89.3 |
| 1000 ppmv | 85.4 | 88.2 | 88.5 | 80.1 | 25.4 | 47.6 | 55.4 | 50.3 | 55.1 |

**Styrene** response after backwashing and starvation in Biofilter “**A**”

Removal Efficiency, %

**Backwashing**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 92.6 | 97.6 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 77.2 | 91.8 | 86.8 | 79.9 | 97.6 | 99.6 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 92.3 | 98.6 | 99.0 | 92.3 | 97.6 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 96.9 | 96.8 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 1000 ppmv | 98.5 | 94.8 | 82.3 | 62.4 | 70.0 | 63.8 | 80.7 | 84.3 | 84.0 |

**Starvation**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 75.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 98.2 | 90.7 | 96.8 | 98.4 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 94.6 | 90.4 | 98.6 | 97.8 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 99.9 | 98.1 | 99.2 | 98.0 | 97.6 | 99.5 | 99.9 | 99.9 | 99.9 |
| 1000 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 75.0 | 85.7 | 85.2 | 70.4 | 70.9 |

**MEK** response after backwashing and starvation in Biofilter “**A**”

Removal Efficiency, %

**Backwashing**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 1000 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |

**Starvation**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 99.3 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 95.6 | 92.4 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 1000 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |

**MIBK** response after backwashing and starvation in Biofilter “**A**”

Removal Efficiency, %

**Backwashing**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 99.9 | 99.9 | 999 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 1000 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |

**Starvation**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 99.3 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 99.8 | 99.4 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 1000 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |

**Toluene** response after backwashing and starvation in Biofilter "**B**"

Removal Efficiency, %

**Backwashing**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 69.3 | 85.7 | 85.5 | 89.6 | 89.4 | 89.5 | 99.8 | 99.9 | 99.9 |
| 100 ppmv | 95.7 | 96.4 | 96.5 | 90.4 | 97.1 | 98.2 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 93.5 | 95.3 | 91.1 | 94.4 | 97.6 | 98.1 | 98.5 | 99.9 | 99.9 |
| 300 ppmv | 47.6 | 78.3 | 77.9 | 86.5 | 98.3 | 99.1 | 99.3 | 99.9 | 99.9 |
| 350 ppmv | 78.9 | 44.4 | 34.1 | 40.8 | 39.4 | 55.2 | 87.2 | 85.4 | 76.1 |
| 500 ppmv | 88.8 | 87.3 | 88.6 | 81.3 | 94.6 | 79.8 | 80.2 | 77.8 | 81.3 |

**Starvation**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 67.8 | 33.1 | 60.3 | 60.8 | 54.2 | 80.0 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 71.9 | 67.3 | 61.1 | 64.9 | 83.3 | 88.4 | 90.1 | 99.9 | 99.9 |
| 250 ppmv | 95.5 | 75.9 | 39.7 | 25.2 | 67.9 | 80.9 | 97.5 | 99..9 | 99.9 |
| 300 ppmv | 95.4 | 93.7 | 94.5 | 96.6 | 98.8 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 88.1 | 80.6 | 66.6 | 68.5 | 74.9 | 78.6 | 85.8 | 84.3 | 86.6 |

**Styrene** response after backwashing and starvation in Biofilter "**B**"

Removal Efficiency, %

**Backwashing**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 88.2 | 99.9 | 85.1 | 99.9 | 98.4 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 94.5 | 98.8 | 87.4 | 97.2 | 99.8 | 99.9 | 99.9 | 99.9 | 99.9 |
| 300 ppmv | 94.3 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 350 ppmv | 98.8 | 77.0 | 81.4 | 86.1 | 86.3 | 97.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 88.4 | 65.2 | 87.4 | 89.3 | 99.8 | 99.9 | 99.9 | 99.9 | 99.9 |

**Starvation**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 89.5 | 70.3 | 75.8 | 76.9 | 77.8 | 86.4 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 77.2 | 91.8 | 86.8 | 91.7 | 87.8 | 99.6 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 99.9 | 99.9 | 99.5 | 91.7 | 98.4 | 99.9 | 99.9 | 99..9 | 99.9 |
| 300 ppmv | 99.1 | 99.1 | 99.4 | 99.8 | 98.6 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 99.1 | 97.8 | 92.7 | 92.1 | 94.6 | 97.7 | 98.5 | 99.3 | 98.6 |

**MEK** response after backwashing and starvation in Biofilter "**B**"

Removal Efficiency, %

**Backwashing**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 300 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 350 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |

**Starvation**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 300 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 94.4 | 90.7 | 83.2 | 63.3 | 77.4 | 79.8 | 83.2 | 80.3 | 81.6 |

**MIBK** response after backwashing and starvation in Biofilter "**B**"

Removal Efficiency, %

**Backwashing**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 300 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 350 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |

**Starvation**

| Time/min | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
|---|---|---|---|---|---|---|---|---|---|
| 50 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 100 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 250 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 300 ppmv | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 | 99.9 |
| 500 ppmv | 94.4 | 90.7 | 83.2 | 63.3 | 77.4 | 79.8 | 83.2 | 80.3 | 81.6 |