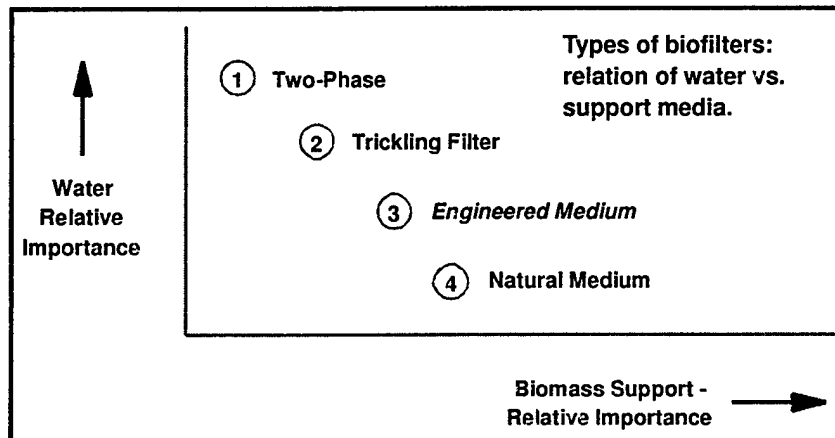




Biofiltration of Solvent Vapors from Munitions Manufacturing Operations

Byung J. Kim
Blaine F. Severin
Leslie M. Neilson



U.S. Army industrial operations sometimes involve processes that emit volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) in gaseous form. Biofilter technology can treat such gaseous emissions. When supplied with the proper balance of nutrients, buffer, temperature, and moisture conditions, the biofilter collects contaminants from the air and biologically degrades them into CO₂, water, and biomass by-products. This study provided needed bench-scale feasibility data before demonstration and validation of biofilter technology as a treatment process at the Lake City Army Ammunition Plant, Independence, MO, and for potential use in other U.S. Army Industrial Operations Commands.

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Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers (HQUSACE), under D048 Program, "Environmental Quality Technology"; Work Unit U28, "Biofilter Technology for Munitions Production VOCs." The technical monitor was Mr. Chris Vercautren, AMSIO-EQ.

The work was performed by the Environmental Processes Branch (CN-E) of the Installations Division (CN), U.S. Army Construction Engineering Research Laboratory (CERL). The CERL principal investigator was Dr. Byung J. Kim. Dr. Blaine F. Severin and Mr. Leslie M. Neilson were with MBI, Lansing, MI. All bench scale evaluation was completed at MBI. Jerome L. Benson is Chief, CECER-CN-E, and John T. Bandy is Chief, CECER-CN. The CERL technical editor was William J. Wolfe, Information Technology Laboratory.

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1 Introduction

Background

U.S. Army industrial operations sometimes involve processes that emit volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) in gaseous form. For example, one of the assembly lines at the Lake City Army Ammunition Plant (LCAAP), Independence, MO is a press manufacturing line that assembles blank munitions rounds used in training. The cap for the blank rounds is processed into a pasty material. Once this material is applied to the casing, it dries into a solid, forming a sealed cap on the round. During the manufacturing procedure, a number of solvents are added to the pasty material to make it less viscous for transfer to the shell casing. While the exact make-up of the paste is not germane to the biofiltration "off-gas" treatment process, it is important to note that minor parts of the components are carried off with the primary solvent as it evaporates. LCAAP must treat this off-gas to meet environmental regulations.

Biofilter technology provides one way to treat such gaseous emissions. A biofilter is a component used in a treatment process that cleans contaminated air by using micro-organisms growing on a biofilm fixed on solid packing/porous media such as compost, peat, soil, or an engineered material. The biofilter used in this study involved an engineered medium made of closed-cell urethane with incorporated nutrients and a pH buffer. When supplied with the proper balance of nutrients, buffer, temperature, and moisture conditions, the biofilter collects contaminants from the air and biologically degrades them into CO₂, water, and biomass by-products. This study was undertaken to demonstrate and validate biofilter technology as a treatment process for use at LCAAP, and for potential use in other U.S. Army Industrial Operations Commands.

Objectives

This report summarizes a bench-scale evaluation data of biofilter technology to provide a baseline for application of an engineered media biofilter to an Army Industrial Operations Installation. The objectives of this study were:

1. To summarize recent development of biofilter technologies and to compare engineered media biofilter with other competing technologies, based on the results of a literature review.
2. To evaluate bench-scale engineered media biofilters using an artificial gas stream representative of LCAAP's emission.
3. To develop design criteria for biofilters and to test and modify a system specifically to meet LCAAP's needs.

Approach

1. *A comprehensive literature review was conducted.* Researchers found a wealth of related research, but often found it difficult to compare observations from various studies because the support media generally differ from study to study. The bulk of the literature focuses on the feasibility of treating various contaminated gas streams containing volatile organic contaminants with biofiltration.
2. *The source of pollutants was characterized.* Table 1 lists expected concentrations of pollutants based on a preliminary analysis that assumes 22,000 lb of solvent use per year. The main solvent was identified as ethyl acetate, which was estimated to exceed 50 percent of the vapor stream contamination. The total concentration of consumable organics was initially expected to exceed 5000 µg/L. At a later date, it was found that additional ethyl acetate was being added to thin out the coating mix such that ethyl acetate was expected to exceed 85 percent of the vapor content.
3. *To outline the true magnitude of the design problem, a series of samples were collected at LCAAP.* Table 2 lists site data from three sampling dates. Note that the measure's total mass is less than 10 percent of the initial expectations at the prevalent operating conditions during sampling. The plant was, at that time, operating a 10-hr shift, 4 days/week, with an estimated vent rate of 500 scfm (standard cu ft/min). Site data were collected under the conditions existing at that time. (The building was equipped with a 500 scfm building fan.) The client wishes to install a 1000 scfm blower along with the biofilter. The biofilter will have a 1000 cu ft volume for a nominal retention time of 1 minute. Targets for the simulation, such as gas consumption, retention time, and design gas flow rate were changed numerous times during the course of this project. Laboratory tests discussed here reflect this changing assessment of the site conditions.

Table 1. Expected maximum Lake City Building 2 emissions (based on 1960 working hours per year, 22,000 lb per year solvent use, 500 scfm building fan capacity).

Compound	MW	lb/hr	ppmv at STP	µg/L
Ethyl acetate	88	5.93	807	3168
Ethanol	46	0.40	103	211
Isobutyl acetate	116	0.79	82	422
Toluene	92	1.19	154	634
2-methyl-1-propanol	74	0.08	13	42
n-butyl acetate	116	1.19	122	634
Mixed xylenes	106	0.79	89	422
n-butanol	74	0.08	13	42
Dibutyl-phthalate	278	0.00	0	0
Weighted Total	90.36	10.43	2503	5576

4. *The performance of biofilter technology was evaluated using an artificial vapor stream representative of the stream at LCAAP. Test columns were filled with an engineered medium that acted as support for micro-organisms. The columns were then inoculated with a liquid, mixed culture of micro-organisms that was found to be capable of degrading the chemicals present in the gas mixture. Two series of laboratory tests were performed. The first studied the expectations for treatment under steady-state continuous loading over a range of organic loadings. The second series of tests were necessary due to the cyclical manufacturing process at the plant. These second tests were undertaken to test the limitations of operations under a square-wave loading pattern.*

5. *Initial laboratory studies were performed at mass loading rates consistent with expectations from the site estimates (Table 1). Midway through the tests, the conditions in the laboratory were changed to match the field data in Table 2. These data were collected using the existing 500 scfm blower. The design of the biofilter is now based on 1000 scfm. Thus, the operating conditions with the 1000 scfm blower are not presently known.*

6. *Results of the study were analyzed, conclusions were drawn with respect to the application of this technology to the waste stream at LCAAP, and recommendations were made for broader practical application of this technology to other waste streams at other sites.*

Table 2. Measured concentrations at Building 2 (approximately 500 scfm building fan).

Compound	Sample 1 (avg. of 3 samples)		Sample 2 (avg. of 6 samples)		Sample 3 (avg. of 15 samples)		Average	
	ppmv	µg/L	ppmv	µg/L	ppmv	µg/L	Ppmv	µg/L
Ethyl acetate	53	189	57	206	94	341	68	246
Ethanol	ND*	ND	18	66	ND	ND	<7	<23
Isobutyl acetate	2	7	1	4	4	14	2	9
Toluene	0	2	11	38	1	3	4	14
2-methyl 1-propanol	ND	1	0	1	ND	ND	<1	<1
n-butyl acetate	1	3	1	3	ND	ND	<1	<3
Mixed xylenes	ND	ND	1	4	ND	ND	<1	<4
n-butanol	ND	ND	ND	ND	ND	ND	<1	<3
Total	56	203	89	323	99	358	<85	<303

*ND = not determined

Scope

This study focused on determining biofilter design criteria, and the empirical application of biofilter technology to the treatment of VOCs.

Mode of Technology Transfer

It is anticipated that the information generated by this study will form a baseline for biofilter design to treat other waste streams at DOD installations.

Units of Weight and Measure

U.S. standard units of measure are used throughout this report. A table of conversion factors for Standard International (SI) units is provided below.

SI conversion factors					
1 in.	=	2.54 cm	1 cu in.	=	16.39 cm ³
1 ft	=	0.305 m	1 cu ft	=	0.028 m ³
1 yd	=	0.9144 m	1 cu yd	=	0.764 m ³
1 sq in.	=	6.452 cm ²	1 gal	=	3.78 L
1 sq ft	=	0.093 m ²	1 lb	=	0.453 kg
1 sq yd	=	0.836 m ²	°F	=	(°C x 1.8) + 32

2 Literature Review

Technological Solutions for U.S. Regulatory Environment

New Regulations

Biofilters have been used for odor control since the 1960s (1). In general, this market is serviced with low-tech units treating low concentrations and high air-flow rates. The measured output, perceptible odor, is subjective. With the passing of the Clean Air Act of 1990 and the inclusion of biofilters on the list of innovative technologies within the Act, the biofilter process has received renewed attention as a means of treating volatile organic contaminants. Within the context of the Clean Air Act, it has become necessary to specify the performance of VOC control processes. As the uses for biofilters become more broadly based and the expectations of performance more stringent, these systems will necessarily become more refined (2).

The Clean Air Act Amendments of 1990 (PL 101-549) (CAAA) expand on the earlier version of the Clean Air Act of 1970 with a main thrust of tightening existing emission controls on stationary and mobile sources. The CAAA focuses on nonattainment areas, mobile sources, air toxins, acid rain, stratospheric ozone, and global climate protection. Estimates on the impact and costs of the regulations are not yet clear (3-5).

Air toxins control is defined by Title III of the CAAA, which expands the number of regulated hazardous air pollutants (HAP) from a previous total of 7 to 189 compounds. Title III of the CAAA replaces the old National Emission Standards for Hazardous Air Pollutants (NESHAP) program. NESHAP standards passed before November 1990 remain in effect until they are reviewed and revised by the USEPA. The new law requires the regulation of sources of toxic pollution.

Major sources, defined as those plants emitting at least 10 tons/year of a listed pollutant or 25 tons/year total of all listed pollutants, will be required to match targets based on average emissions from 12 percent of their competitor's best controlled plants. For new plants, the emission rates cannot exceed levels obtained by the facilities in their production class with the lowest emissions. If a facility activity is on the list of major stationary sources and is capable of emit-

ting 100 tons/year of any pollutant, then the facility is considered a major source. Any facility that produces more than 250 tons/year of any HAP is considered major, even if it is not included on the list of stationary sources (6, 7).

Area sources such as: dry cleaners using perchloroethane (PCE) and 1,1,1- trichloroethane, coke ovens, synthetic organic chemical manufacturers, commercial sterilizers, chromium electroplaters, industrial cooling towers, halogenated solvent cleaners, gasoline stations, and asbestos sources must have standards set for them that lead to 90 percent reduction of the 30 most serious source pollutants (6). Nonattainment areas are classified and scheduled for meeting compliance by the severity of pollution measured within their boundaries. Metropolitan areas with the greatest pollution have the longest time, up to 17 years, to meet the standards. Until the standards are set, the nonattainment area must meet a 3 percent per annum reduction in VOC emissions (8, 9).

The goal of the Air Toxins provisions of the CAAA is to reduce toxic emissions by 75 percent by the year 2000. Phase I of the program consists of technology-based standards. Phase II involves risk-based reductions. Phase I will be accomplished by implementation of Maximum Achievable Control Technology (MACT) established for each industry by the category standards. MACTs are focused on specific portions of a contiguous facility or the entire facility. Standards are to be developed for roughly 25 percent of the categories every 3 years. All the final standards for the categories are due on 15 November 2000 (3, 4). Any new category added to the list of categories must have standards promulgated within 2 years of addition to the list. If the USEPA fails to promulgate a set of standards, then the owner/operator of the facility must apply for an operating permit within 18 months of the original scheduled date. The permit must be signed by a registered engineer certifying that a Best Available Control Technology (BACT) is in place at the site. Sources must comply with MACT standards within 3 years of issue. One-year extensions may be available for certain sources.

Through the voluntary self-regulation plan, plants that agree to the Federal guidelines will: (1) attempt to achieve a lower compliance level, 90 percent rather than 95 percent, (2) gain a 6-year extension, which may be cost effective in postponing implementation of potentially more stringent reductions, and (3) become the industry leaders in pollution control for the purposes of becoming the 12 percent target to be matched by competitors (6). These aspects of the law create a business climate by which the BACT, for one industry with a close compliance deadline, will have a harder time being accepted than the same technology entering an industry with a longer lead schedule (9). Emissions from oil and natural gas wells are not to be considered as area sources and multiple wells are not to be aggregated as a contiguous facility (6).

The USEPA has a top-down approach for determining the BACT for emission control and reduction. First, available control options are identified. Next, technically unfeasible options are eliminated, and the remaining technologies are ranked in terms of effectiveness. After evaluating economic, environmental, and energy aspects of the most effective technologies, the BACT is chosen (10).

While the apparent minimum removal efficiency of a control technology would appear to be 95 percent, the phrasing of the law to view air pollution as area or facility emissions means that some controlled sites may opt for lower than 90 percent removal in noncritical areas. The vapor control business may also be affected by provision 182(b) of the CAAA. States must now submit plans to the USEPA for owners or operators of gasoline dispensing systems to install and operate a system for gasoline vapor recovery for emissions from the fueling of motor vehicles. Facilities selling less than 10,000 gal of gasoline per month and independent marketers selling less than 50,000 gal per month are not covered by these rules.

Local, regional, or State regulations may also limit the discharge of air toxins or hydrocarbons. For example, the South Coast Air Quality Management District Rule 1166, "Volatile Organic Compound Emissions from Decontamination of Soil" is designed to limit the emissions of VOC from soil contaminated with VOC during any type of soil remediation measure. The same district requires VOC emissions to be under 600 lb/day for stationary sources and requires commercial bakeries to control ethanol emissions, according to Rule 1153 (11, 12). Rule 1401 limits the maximum lifetime cancer risk that can be caused by emissions of 47 Carcinogenic Air Contaminants (CAC) to one chance per million unless a Best Available Control Technology for Toxics (T-BACT) is installed. Emissions of benzene and ethylene oxide are limited to just a few pounds per day in this regulatory district (8, 9).

New plant facilities must meet the stringent guidelines set out by the CAAA. After emission predictions are made for a new plant, and the building permits granted, the plant must operate correctly or the permits could be made more stringent. For example, the Lone Star Industries facility in Santa Cruz had no SO₂ emission limit specified in the building permit. After operating emissions proved to be much higher than expected, the USEPA and the local authorities implemented an SO₂ limit and forced the plant to reduce its emissions (13).

Available Technologies

There are many methods for treating waste air streams. The technologies are categorized as: dilution, masking, collection, and oxidation. Dilution technolo-

gies include: chimneys (atmospheric dispersion from emission at a high point), horizontal ducting (atmospheric dispersion from emission at a distant point), and use of a remote site (isolation with atmospheric dispersion). These methods do not treat the waste, and are becoming less acceptable under the new laws. Masking methods add masking agents or deodorants to the emitted air to disguise or counteract the malodorants. The odorants are not degraded with these methods, but the odor complaints may disappear. Collection methods, such as carbon adsorption or condensation, transfer the VOC from one physical phase to another. Usually the VOC becomes more concentrated as well. Although these methods remove VOCs from the waste air stream, they still must be treated before disposal (14). If recycling of the VOC is possible, then these methods should be considered. Oxidative technologies use temperature, catalysts, light, chemicals, or micro-organisms to oxidize the VOC into CO₂, water, and inorganic components. Each technology has advantages, disadvantages, and a range of optimal application. Factors such as airflow rate, temperature, and concentration of VOC will affect the costs of the various technologies (12, 15).

Collection Methods

Carbon

A common treatment for low concentrations of VOC is adsorption onto carbon or activated carbon (16). This method is best suited to relatively small airflow rates (less than 60,000 cfm) with concentrations less than 100 ppm (17). A highly concentrated chlorinated solvent with a very low mass flow rate would be a good candidate for adsorption (18). Often, carbon adsorption is used as a polishing step following a primary treatment technology (19). When the adsorptive capacity of the carbon is spent, the carbon must be regenerated or disposed of as a hazardous waste (17, 20, 21). With each successive regeneration, the carbon loses adsorption efficiency and capital costs for reactivation equipment can be high (18). In addition, removal effectiveness decreases as the carbon becomes saturated with water vapor. When operated under wet conditions, most VOCs do not adsorb well, but under dry conditions, the heat of absorption may create flammable conditions on the activated carbon (22).

Condensation

VOCs can be cooled or pressurized until they condense from the air. If the waste stream contains one or two components that can be recycled back into the process, condensation may be appropriate. Condensation can also be a cost effective pretreatment for another air pollution control technology (5). The cost of refrigeration will depend on the boiling point of the components, the concentration,

and the airflow rate. To be cost effective, the compound to be recovered should be a high boiling point hydrocarbon, such as a compound with 10 or more carbon atoms, and also have a recovery value (18). For mixed air streams of VOCs, the condensate may be a gummy, partially oxidized mass of VOCs that must still be disposed of (12).

Oxidative Methods

Incineration

Incineration destroys VOCs by burning them at temperatures of 600 to 1500 °C (17). The extent of degradation depends on the flammability of the compound, the incineration temperature, and the residence time in the reaction zone (5, 12, 23). An air stream with relatively constant concentrations of VOCs will perform best, but complex mixtures can easily be treated (24). Generally, streams with VOC concentrations above 2,500 ppm can be economically treated with thermal incineration (25). However, the concentration of organics must be about one fourth of the lower explosive limit (5). For example, Monsanto uses thermal oxidation to treat 60,000 cfm with 50 ppm acrylonitrile and styrene at their Port Plastics plant in Addyston, OH (17).

Three common VOC incineration designs include the thermal oxidizer, the catalytic oxidizer, and the flare incinerator. The thermal oxidizer operates by using the combustion heat available in the waste VOCs. This requires little or no external fuel (5). The catalytic oxidizer employs added fuel and a catalyst bed to burn low concentrations of VOCs. Up to 98 percent removal can be achieved with hydrocarbons such as gasoline, as well as 90 percent removal of some halogenated compounds such as TCE (12, 17). A flare is a flame atop a tower that burns combustible VOCs as the waste air is expelled from the tower. For concentrated streams that exceed the lower flammability limit, flares can be used (above 115 BTU/scf). The flame temperature is the most important factor in determining degradation since complete combustion must occur instantaneously (5). Incineration of some compounds can produce dangerous and corrosive side products such as dioxins or HCl from burning chlorinated compounds and sulfides from burning sulfonated VOCs (12, 26).

Light

Light oxidation uses UV radiation to oxidize VOCs to CO₂, water, and inorganic compounds. High energy short wave photons (180 to 280 nm) excite the VOCs. The photons also excite water vapor to form highly reactive oxygen atoms and hydroxyl radicals. The oxygen and hydroxyls react with the excited VOCs to oxidize them. The reaction rates can be enhanced by catalysts such as iron oxides

or titanium dioxide. This technology is currently an emerging technology in wastewater treatment (27).

Scrubbers

A common wet scrubber design uses a column packed with plastic or ceramic packing. Contaminated air is blown through the column while a chemical solution is recirculated over the spheres. The solution reacts with the air contaminants to produce nontoxic products. The scrubbers are usually set up so that the airflow is counter-current to the scrubber solution. Another design employs a tank full of reactive solution through which the contaminated gas is sparged (28). The columns and tanks must be built with materials resistant to corrosion. The chemical solutions are recirculated until the reaction power is used up, and then they must be replaced. Because of the reactive solutions used, safety precautions must be taken as well (18). The chemicals used include: acid, caustic, hydrogen peroxide, DeAmine (by Nutech), chlorine, ozone, hypochlorite, permanganate, lime, surfactants or other reagents to react with the contaminants. The reaction time is fast, usually seconds, but hydrocarbons and chlorinated compounds are often unaffected. For reactive VOCs like alcohols and esters, 95 percent removal can be achieved. This method is also effective for the treatment of SO_2 , and NH_3 (22, 29-31).

Gases containing SO_2 can be treated by passing them through lime to react with the sulfur. The lime can either be a wet slurry or dry and is used in a spray dryer (30). This process is often used in firing coal that contains 3 percent sulfur, and has advanced removal efficiencies of 90 to 95 percent; however, it produces gypsum (calcium sulfate), which must be disposed of. An evaporator and precipitator are two pieces of additional equipment required in this scrubbing process (28). The Statoil's refinery in Norway uses seawater to scrub sulfur compounds from the refinery flue gases using dissolved carbonate and oxygen naturally present in seawater. They claim that no environmental harm is done, and they achieve 98.8 percent removal of SO_2 and 82.8 percent removal of SO_3 (32).

An acid scrubber can be used to eliminate ammonia, but it does not affect the organic components (31). Multiple stage scrubbers use several chemicals in separate tanks to react with the various components in the waste air stream. An example of this would be a water scrubber that absorbs basic compounds, then an oxidative scrubber that reacts with the VOCs, and then a dechlorination scrubber that uses peroxide to remove excess chlorine and provide additional oxidation. When a process stream contains a few compounds, the scrubbers can be very effective; however, when multiple odorous compounds are involved, as in compost odors, the scrubbers may not meet expectations (33).

The Peninsula Composting Facility operated by Hampton Roads Sanitation District tested 16 combinations of scrubbers and still did not achieve complete removal of VOCs and odor compounds (29). The Schenectady, NY, Composting Facility installed a three-stage scrubber to treat 25,000 cfm of odorous air and achieved greater than 99.9 percent removal of ammonia, amines, mercaptans, and dimethylsulfide, but no chlorine was removed (34). For high intensity odors from continuous rendering systems of the inedible animal rendering industry, multistage scrubbers are often used. Volumes up to 10,000 cfm are treated using a venturi scrubber to remove particles and fat aerosols. One or two packed tower chemical scrubbers are then used to remove odors. Up to 99.5 percent removal is possible, depending on the inlet concentrations (35). Monsanto extensively studied chemical scrubbing to treat low level VOCs from plastic production, but achieved only 80 percent removal efficiency; another technology was chosen (17).

Biological Systems

The above treatments wash, adsorb, or oxidize VOCs, but the following biological methods do all three in one step (14, 20). A biofilter is a bioreactor system in which micro-organisms are attached to a solid support medium. Contaminated air is passed through the filter where the micro-organisms consume the organic carbon to produce CO_2 , water, and biomass (more micro-organisms) (2). Four classes of biofilters, classified on the relationship of the biofilm to the water, are: (1) two phase systems (bioscrubbers), (2) trickling filters, (3) natural medium biofilters, and (4) engineered medium biofilters. Figure 1 shows the relative reliance on water in the four systems versus the reliance on the solid support medium for the stability of the process. Because of the ability to control water better in certain systems, these systems can support optimum biological conditions because the environment (pH, nutrients, etc.) can be controlled along with the water. If designed well, biomass can also be controlled to a certain degree.

Figure 2 shows the relative control in these systems from the standpoint of the environmental conditions and biomass control. Natural bed medium does not allow for ready intervention with regard to the control aspects of pH or nutrients. The only biomass control is through replacement of the bed. Other media provide for increased control, with engineered media designed for the greatest control level. Biological systems are especially well suited to streams that have low volumes (<1000 scfm) with moderate (<1 percent) concentrations up to high volume streams (1000 to 50,000 scfm) with low concentrations (<1000 ppm). However, biofilters are not compatible with: scrubbers, multi-component recovery systems, processes with unknown vapors or vapor strengths, or heavily halogenated compounds (36).

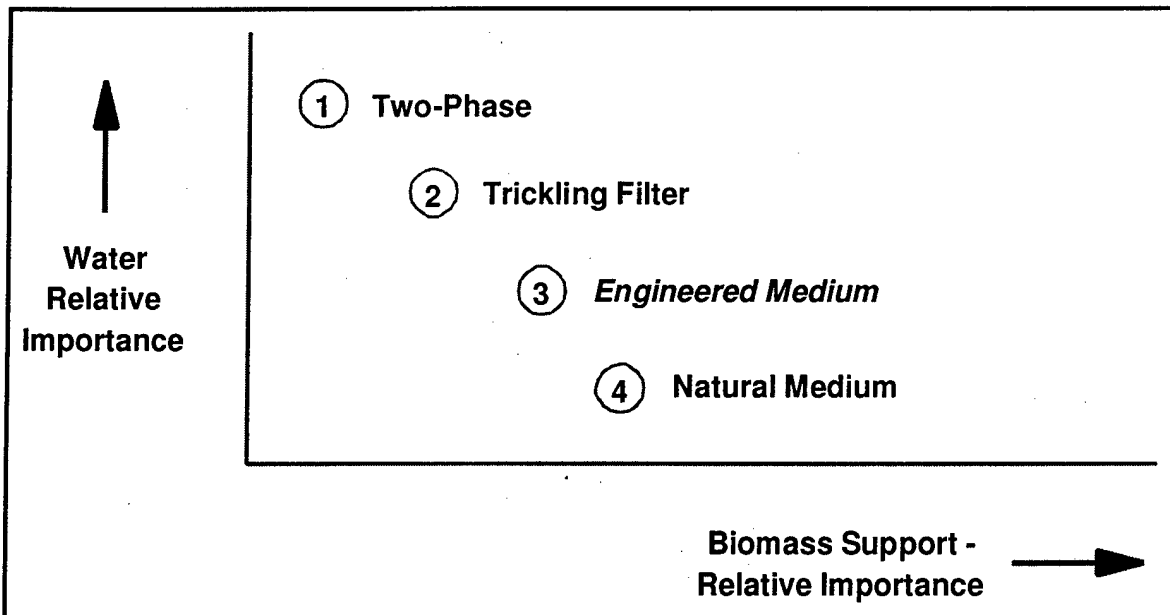


Figure 1. Types of biofilters: relation of water vs. support media.

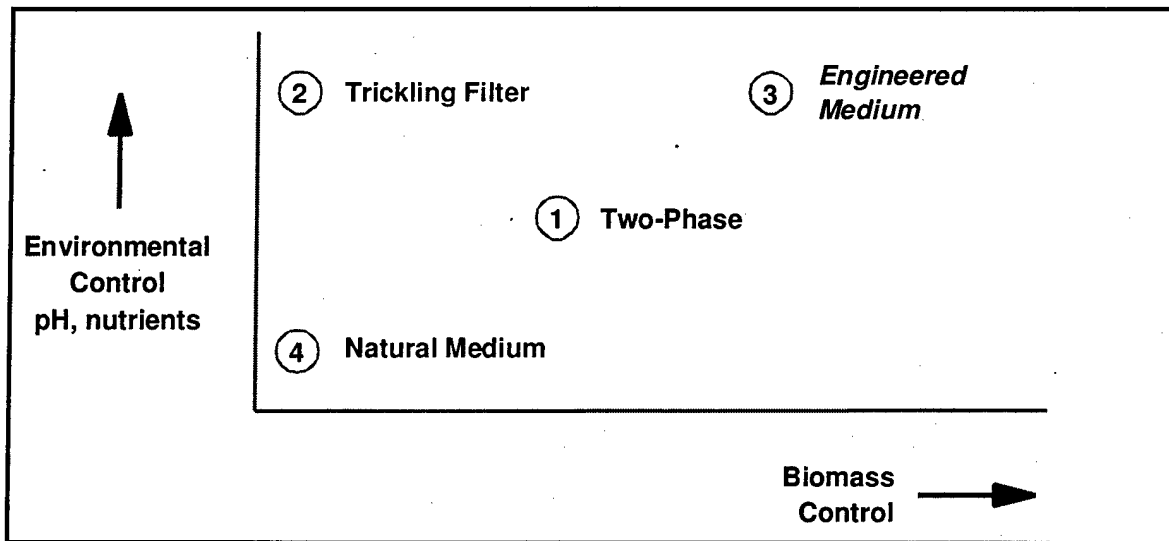


Figure 2. Types of biofilters: ease of control.

In biofilter systems, microbes are used to destroy the VOC contaminants. The systems must be maintained to sustain the microbial population. Maintenance includes moisture, temperature, nutrients, and pH buffering (37). The microbes may be present in the filter bed, or the bed may be inoculated with a specific population known to degrade certain VOCs (38).

Bioscrubbers

A bioscrubber consists of two units, a scrubber and a regeneration basin. In the scrubber compartment, water droplets flow with the waste gas, and the pollut-

ants and oxygen from the waste gas are transferred to the liquid phase (38). Biological oxidation occurs in the regeneration unit, which is typically an activated sludge basin in a wastewater treatment plant (39). Two phase systems were created to optimize liquid scrubbing of the gas in one phase and to perform the degradation in a liquid phase biological reactor. In theory, the entire reaction is dominated by absolute control of the liquid. In reality, these systems work as trickling filters because the biomass cannot be kept from inhabiting the solid support medium (40). At one water treatment plant, air was bubbled up through the activated sludge tanks, and based on smell, no odor was detected (41).

Trickling Filters

In a trickling filter, the scrubbing and biological oxidation processes occur simultaneously in one unit as compared to two units, as is the case with bioscrubbers (2, 39). The trickling filters consist of columns filled with packing on the surface of which a biofilm develops. Water containing nutrients is supplied at the upper side of the column. Gas is forced to rise against the cascading water flow (38). The packing can be activated carbon, stoneware rings, clay granules, porous glasses, or other materials (42). The packing material supports the microorganisms and may supply the nutrients. After several years of operation, the packing may deteriorate and need to be replenished (38). Trickling filters are modified processes similar to the classical liquid systems used for wastewater treatment. As applied to air treatment, the flow of water is altered slightly to also enhance the transport of the vaporous organics into the water layer. The organics and oxygen are then consumed from the liquid phase by the biomass on the solid support. Trickling filters are dominated by liquid-phase transport resistance and are poor performers on marginally soluble gases, or gases that have high Henry's constants. However, the high degree of liquid side control gives these units the advantage with control of pH or nutrient conditions within the reactor by altering the chemistry of the liquid side. For example, if the medium is acidified due to the pollutants, buffer can be added to the liquid to counteract the pH effect (43).

Natural Bed Biofilters

Natural bed biofilters consist of a filter bed of natural material where waste gas is forced through a layer of a biologically active packing with a thickness of 50 to 100 cm. Gas can be distributed to the bed through gravel or it can be pressurized through various duct systems (44). The packing material supports the microorganisms and supplies some if not all of the nutrients, but it must be continuously supplied sufficient water to maintain high humidity (38).

Natural bed biofilters, such as soil, peat, compost, or bark, are the best filters from the standpoint of bed cost; however, there is little control of either the environmental conditions or the biomass growth in such systems since the ability to control the water flow is lacking. The relatively small amount of water on the media allows the medium itself to be the primary adsorbent rather than the water. Thus these natural beds have an advantage in that the liquid resistance to transport is minimized. Also, these natural substances may contain the microbes required for degradation.

Various soil types have been tested, including: fertile loam, moist clay/gravel soil, dry clay/gravel soil, and sand. From the results of these tests, it is generally accepted that clay, gravel, and sand are unsuitable for use in soil beds (1). To prepare an area for a natural medium biofilter, generally a trench is excavated and a perforated pipe is laid at the bottom surrounded by gravel to distribute the air. It is covered with a loam, sandy soil, or organic material of 1 to 2 m in depth. A concrete pad can be laid below the filter to keep water from flowing into the groundwater. The upward flow of free air through the bed is 0.2 to 1.0 m/min and a 30 second retention time is recommended (41).

Engineered Medium Biofilters

Engineered medium systems are an attempt to provide the advantages of natural media with the liquid phase and biomass control available in trickling filters. The media can be foam, carbon, plastic tubes, and other materials designed according to theories of biofiltration kinetics. Although the engineered media may be more expensive than natural media, higher airflow rates and higher gas concentrations can be treated. Also, natural media have a determined finite life span, whereas engineered media, whose excess biomass may be removed from the medium by mechanical means, should prove to be considerably longer (8, 45). Thus, more air and contaminants can be treated with a smaller bed. These systems are set up in tall columns and nutrients are supplied from the media or from a nutrient solution that is occasionally passed over the column. The moisture content can be tightly controlled to maximize the absorption of more hydrophobic VOCs (2, 45).

Technology Comparisons

The best emission control technology depends on the application. Many factors need to be evaluated to make sure the technology will meet the needs of the process for the lowest cost, including: process exhaust volume (minimum, average, and maximum flows), process exhaust temperature, solvent concentrations (minimum, average, and maximum flows), solvent compositions, hours of opera-

tion per year, process volumes, natural gas and electric costs, problem VOCs (chlorinated, particulate, heavy hydrocarbons, plasticizers, etc.), equipment location (in, out, ground level, roof, etc.), number of individual emission sources involved, and plant elevation or additional static pressure drop required for process ducting. Each method of treatment has its own advantages, disadvantages, and range of optimum application (46).

If products in the waste stream can be recycled, then a collection technology should be considered. Adsorption onto carbon with regeneration to recover the product is feasible if the recovered product value is greater than the operational costs of regeneration or if it outweighs the cost of disposal. Highly concentrated chlorinated solvents are an example of this stream type (18). Condensation is best applied to pure high boiling point hydrocarbons, C10 and above. Mixed products that are condensed may cause a build up of tar in the condenser (12). One collection method, carbon adsorption, can also be cost effective without regeneration, but only for medium to high concentration streams with very low mass flow rates (18).

For contaminants that cannot be recycled, total destruction is often more cost effective than collection followed by destruction. Even a pure VOC, at very low concentrations, may be treated more cost effectively by destruction (2, 45). Destructive methods all involve oxidation of the VOCs to CO₂ and water (47). Very flammable streams, or streams that require little fuel to become flammable can be treated with thermal incineration. Some hydrocarbons at low concentrations and those that are difficult to degrade biologically, are well suited to catalytic incineration (18). In the past, odorous emissions have been treated with chemical scrubbers, but the treatment is often incomplete (17, 18).

Vapor streams of 20 to 5000 ppmv can be treated by biofiltration. The lower concentrations, up to about 1000 ppmv, especially with high airflow rates, are best treated with soil or other natural nutritive beds (48). If designed properly, biofilters are especially well suited to treat streams that vary in concentration from minute to minute (24). The higher concentrations, especially with lower airflow rates, such as less than 1000 scfm and less than 1 percent concentration can be treated cost effectively with an engineered medium biofilter (2, 36, 45). Both systems are best suited to treat vapor streams containing one or two major compounds (24). Biological processes offer a greater choice of oxidation pathways than chemical oxidation, so they treat complex odor mixtures more completely (33).

Both biofilters and carbon adsorption are well suited to combination treatment methods. The carbon can perform polishing after most of the contaminants have

been metabolized in the biofilter (19). Another technique uses carbon adsorption and desorption to even out fluctuations in stream concentrations before feeding the air into a biofilter. The contaminants are adsorbed when the concentrations are high and then desorbed when the stream concentrations decrease. Thus the biofilter receives a more constant feeding (49). Figure 3 outlines the best performance ranges for each biological technology.

Figure 4 shows the best stream concentrations and flow rates for each VOC control technology discussed above (50). Table 3 lists the advantages, disadvantages, and relative costs (reference list: 2, 5, 18, 20, 22, 35-37, 45, 47, 51-55).

Various authors have provided cost estimates and comparisons for air pollution control technologies. Because of the different assumptions used, comparisons of the various authors' data are not feasible. However, in the interest of providing some costing data, the following information was included.

Dharmavaram states that the average capital cost for a biofilter is \$20 per cfm. The annual operation cost is between \$5 to \$14 per cfm, which compares to \$18 to \$47 per cfm for scrubbing; \$105 to \$168 per cfm for incineration; and \$179 to \$210 per cfm for carbon absorption (39).

Buck and Seider state a capital cost for a 100 scfm thermal oxidizer of \$56,200 base price with a daily fuel cost of \$60 to \$95. Fuel for a 100 scfm catalytic oxidizer is \$22/day. Both systems require an additional \$6/day for vacuum or compression. To treat halogenated VOCs, the base capital cost increased to \$150,000 for 100 scfm (12).

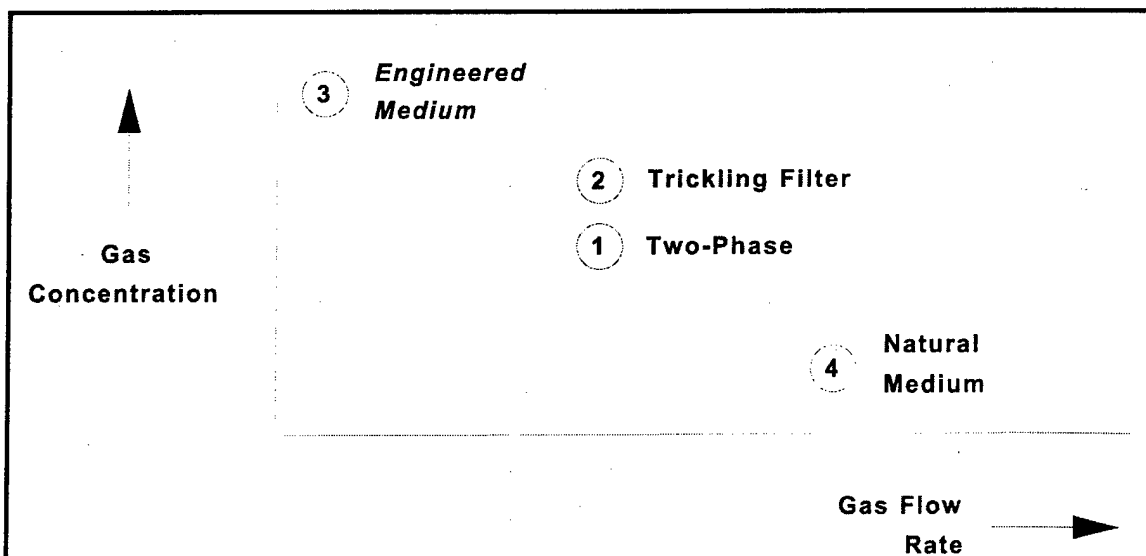


Figure 3. Types of biofilters: best performance.

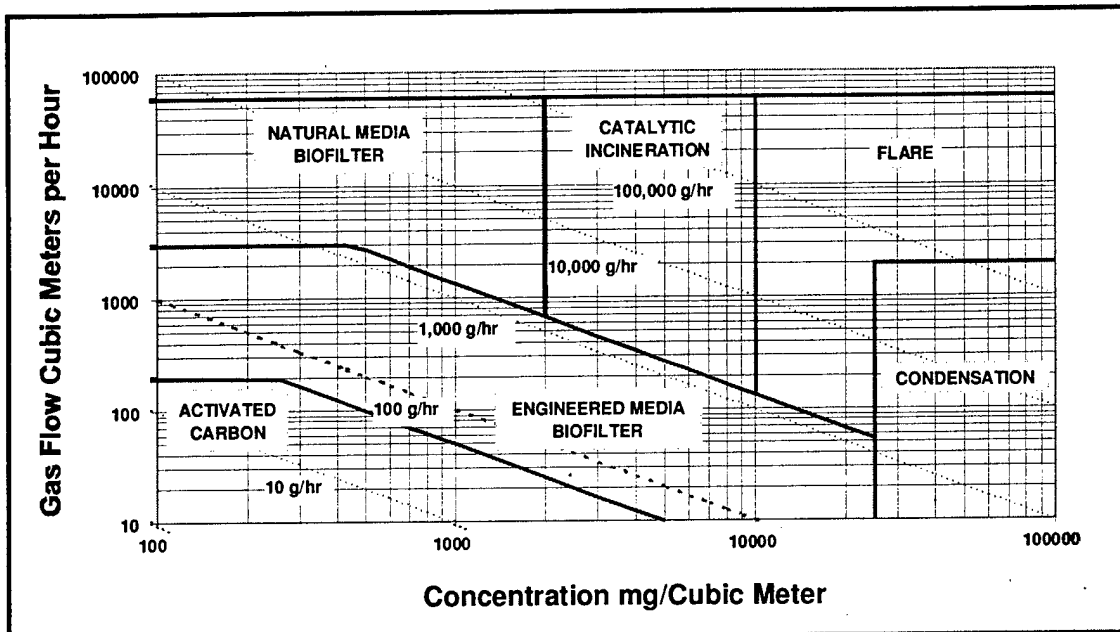


Figure 4. Utility ranges of VOCs control devices.

Table 3. Expected maximum Lake City Building 2 emissions (based on 1960 working hours per year, 22,000 lb per year solvent use, 500 scfm building fan capacity).

Compound	MW	lb/hr	ppmv at STP	µg/L
Ethyl acetate	88	5.93	807	3168
Ethanol	46	0.40	103	211
Isobutyl acetate	116	0.79	82	422
Toluene	92	1.19	154	634
2-methyl-1-propanol	74	0.08	13	42
n-butyl acetate	116	1.19	122	634
Mixed xylenes	106	0.79	89	422
n-butanol	74	0.08	13	42
Dibutyl-phthalate	278	0.00	0	0
Weighted Total	90.36	10.43	2503	5576

Nash and Seibert determined the cost of a thermal oxidizing unit to be \$1 to \$1.5 million, with \$20,000 to \$30,000 per year in operating costs. Biofilters cost about \$20,000 in capital with \$1,000/year operating costs for a 200 cfm unit (36).

Bohn and Bohn determined a soil bed biofilter capital cost to be \$8 to \$10/cfm with an operating cost due to 0.6 W/cfm for blower electricity. Carbon adsorption costs \$30 to \$50/cfm to install or \$70 to \$100/cfm if the carbon will be regenerated. Annual incineration costs are \$15/cfm while those for wet scrubbing are \$8/cfm with additional costs from using 1 W/cfm of electricity (51).

Bohn also computed costs based on the total cost per 10^6 cu ft air for incineration (\$130), chlorine (\$60), ozone (\$60), active carbon with regeneration (\$20), and biofiltration (\$8) (22).

Barshter, Paff, and King performed an economic analysis of biofilters. They determined that a 12,000 cfm biofilter would cost \$260,000 for capital and \$55,000/year for operation and maintenance costs (56).

Prokop compared scrubbing to biofiltration to treat emissions from rendering plants. While incineration, three stage wet scrubbing, and a soil bed biofilter all achieved 99 percent removals, soil beds were the most cost effective treatment method (57).

Pearson, Phillips, Green, and Scotford compared five types of emission control devices for use at a 7000 place broiler (chicken) house to reduce ammonia and odor emissions. Of the five, a biofilter and a bioscrubber were the most promising in operation and costs compared to a mop scrubber, packed column, and spray scrubber. The biofilter cost 3,945 UK pounds per m^3/s for installation of an experimental unit with 652 pounds (cost) per m^3/s for annual operation. These costs were about half that of a packed tower (58).

O'Neill, Stewart, and Phillips reviewed air pollution control technology costs from livestock buildings. Costs were calculated in terms of UK pounds per animal. They showed that biofilters were about the same costs as chimneys. Adsorption was more expensive, while catalytic and thermal incineration were the most expensive methods (15).

Industrial Scale Biofiltration

The idea of using soil to treat odors and waste is as old as burying trash. The first soil bed system biofilter was built in 1953 for treatment of odorous exit sewer gases from Long Beach, CA (47). However, it wasn't until 1957 that a soil bed biofilter was patented by Pomeroy (59). Initial industrial scale biofilters used soil beds to treat odors from wastewater treatment plants.

Mayo designed a soil bed system to treat exit sewer gases from a wastewater treatment plant on Mercer Island, WA in 1964. The system was so effective at removing odors that soil beds were installed at 13 other pump stations on the island (1). These beds required no maintenance, and residents of adjoining lots were unaware of any odors (20).

The City of Coronado, CA, installed a soil bed biofilter to control odors at the main sewage pump station in 1971. In 1987, the bed was expanded because the sludge load increased and the activated carbon filters, used for odor control, were unreliable. The land containing the soil bed was made into an outdoor shopping and restaurant area, where previously the odor was too strong for the land to be usable. Cities that have followed suit and now treat sewer gases and wastewater treatment plant odors with soil beds include: Tamarac, FL, Toenberg, Norway; A. Coors Co. in Golden, CO; and A. J. Simplot in Hermiston, OR (20).

As soil beds came into use for sewer odors in the United States, they were also being used to treat composting odors in Europe. In 1964, the first European soil bed was installed at a composting plant in Geneva-Villette Switzerland to treat 2200 cfm (3600 m³/hr) of raw odor (60). In 1967, a mature compost bed biofilter was built in Duisberg, West Germany to treat 10,000 cfm of odors with 95 to 99 percent removal from chicken manure composting. People live as close as 100 m from the plant without odor complaints (20). As confidence was gained using biofilters for odor abatement, the technology was applied to waste air from animal rendering plants. A meat waste treatment plant in Moerewa, New Zealand installed a compost biofilter based on the 9-year history of the Duisberg system. The filter was initially filled in early 1978 with compost. At first, the compost was not aged, and moisture was not controlled. After changing the bed to filtered, mature compost, the removals of H₂S were consistently 99 percent (23).

Bohn, Shimko, Ottengraf, Durfee, Ziminski, and Prokop have reviewed many other installations of biofilters (20, 61-66). European biofilters currently treat VOCs emissions from the following industries: adhesive production, coating operations, chemical manufacturing, chemical storage, film coating, investment foundries, iron foundries, print shops, waste oil recycling, coffee roasting, coca roasting, fish frying, fish rendering, pet food manufacture, slaughter houses, tobacco processing, industrial wastewater treatment plants, residential wastewater treatment plants, composting facilities, and gases extracted from landfills (8). Other industrial examples are summarized below.

Bioscrubbers

In the production of fish food, nitrogenous compounds must be treated. A bioscrubber was made aerobic in the scrubber section such that nitrification of the waste could occur. The bioreactor was operated under anaerobic conditions so that denitrification would occur in the regeneration tank. Under these conditions, 40,000 m³/hr of waste air was treated to 95 percent odor reduction (67).

The Tillman Water Reclamation Plant in Los Angeles, CA, was required to treat emissions when they requested permits for their expansion. Foul air was generated from the upstream preliminary and primary treatment processes, and the wastewater aeration tank and the activated sludge, had to be treated. The study showed that the activated sludge bioscrubber process was highly effective in reducing the net emission from the combined system, and that it used the naturally occurring micro-organisms in the waste stream. The cost analysis showed that biofiltration was a highly cost effective method of controlling VOCs emissions. The fine bubble diffusers used in the aeration tanks were the key to efficient biofiltration. These diffusers enhance VOCs removal by creating very small bubbles in the aeration tank, thus improving oxygen transfer. The system achieved 83.9 percent removal of VOCs (9).

Trickling Filters

The U.S. Department of Energy and Envirogen are testing trickling bed filters and bioscrubbers as treatments for TCE removed from contaminated aquifers. TCE is stripped with vapor extractors and then biodegraded (68). The Blue River Secondary Facilities in Kansas City, MO, use four trickling beds to treat 50,000 cfm of a variety of odorous compounds. The beds are 150 ft in diameter, 20 ft deep, and are filled with plastic media. Before installation, the city received more than 25 complaints per year. After 2 years of operation, only one odor complaint was received, for an odor not originating from the facility (69).

Natural Bed Biofilters

In sewer systems in the Netherlands, pumping sewage from small villages to larger cities caused turbulence in the sewage, and released SO_2 and H_2S into the atmosphere that caused odors and concrete corrosion. To resolve the problem, the fumes were fed through a natural bed biofilter; H_2S was reduced by 99.7 percent (70).

Biofilters were used to remove solvents from waste gases. The biofilter consisted of compost inoculated with pre-cultivated micro-organisms. Industrial plant field tests showed that formaldehyde removal was 80 percent. The filter was only 3.5 m^3 and used a water scrubber for pre-cleaning followed by a biofilter of compost/wood chips. Styrene removal efficiency was 50 percent at another plant. Two containers were piped in parallel for the first stage with another four in parallel for the second stage (71).

Envirogen used their field pilot system to treat a slip stream of spray booth discharge from a fiberglass coating process. With residence times of 15 to 30 sec-

onds, 85 to 95 percent removal of styrene was achieved, despite plant shutdowns, discontinuous daily operations, and fluctuations in the inlet concentrations on a minute-to-minute basis. The filter bed included styrene degrading micro-organisms, nutrients, and other additives (72).

Soil Beds

S.C. Johnson Co. of Racine, WI, makes consumer products packaged in aerosol cans. Propellant is released during the filling process, so a soil bed biofilter was installed to treat the propelled vapor stream. The bed is 190 m², 0.9 m deep, and has a 5-minute residence time to treat 2000 ppmv total hydrocarbons. The system worked well even in winter at temperatures of 12 to 24°C to achieve 90 percent removal. Industrial odors, propane, isobutane, and n-butane were decreased by 95 percent under warmer temperature (73).

Soil beds are used at Dow Chemical Company for waste air streams containing VOCs, such as mercaptans, as an inexpensive alternative to incineration. This enables companies such as Dow to use their incineration capacity for streams that cannot be treated biologically. The soil bed biofilter is filled with 20,000 cu ft of soil (36, 74).

Bark

A pilot scale biofilter in Gent, Belgium efficiently deodorized emissions from blanching of brussel sprouts and cauliflower by removing aldehydes, nitriles, isothiocyanates, and sulfides. A full-scale biofilter was built, 42 m², 1 m deep, and filled with tree bark. The efficiency of the 7,000 m³/hr biofilter was high for the aldehydes, but only 45 to 65 percent removal was achieved for the sulfides. After 6 months of operation, the removal efficiency decreased due to the accumulation of isothiocyanates. The build up may have inhibited the micro-organisms (75).

The Water Pollution Control Facility in Dartmouth, MA, used a bark biofilter to treat odors, sulfur compounds, and ammonia; 19,300 cfm of waste air was treated with a 45-second retention time. They found that longer retention times increased the total amount of VOCs removed (76). A hard board production plant in St. Veit used a bark compost biofilter to treat 400 to 600 m³/hr. Although the inlet gas temperature was above 40 °C, the biofilter was still effective at VOC removal (77).

Compost

GEKRO in Holland is a rendering facility. All process air is fed through perforated pipes covered in 15 in. of natural compost. It worked so well that the gas from the water treatment lagoons is also fed through the bed to treat those odors as well. Initially, chemical scrubbers had been used to remove the odors, but the biofilter worked so well that the scrubbers remain only as a back-up system (78).

In New Zealand, waste gas from an oil refining plant contains sulfur compounds. A biofilter bed of compost (garden and mushroom), with lupines to prevent compression, was filled to a depth of 0.8 m with a total bed volume of 5 to 6 m³. It was built on a concrete pad and covered with a roof. The residence time is 4 to 5 minutes, during which an inlet concentration of 350 to 5000 ppm H₂S was reduced below 1 ppm. On average, the removal was 86 to 99 percent. The only problem encountered was a build up of a strong, oily odor in the compost. Incineration was used before the biofilter was installed, but leaks in the duct work caused recurring odor problems and complaints (26).

The Monsanto Corporation had to treat 20,000 cfm of waste air with VOCs from their Saflex plastic production facility. Incineration and chemical scrubbing were their preferred methods of treatment, but they were both too expensive for this application, so a biofilter was built. The biofilter bed is compost, built over the area of a basketball court, and regularly achieves 90 percent removal rates (17).

A biofilter was installed on a muffle furnace at a metal finishing plant. Compounds that required treatment included: four types of lacquer (epoxy-phenol, alkyd-amino, alkyd-urea-formaldehyde and alkyd-amino-epoxy), alcohols, alkylcellosolves (alkyl ethers of ethylene glycol), esters, and alkylated aromatics. The total organic carbon concentration varied between 200 to 3000 mg C/Nm³. The extent of degradation depended on the compounds: 90 percent removal was obtained for alcohols, alkylcellosolves, ketones and 95 percent for esters, but only 40 percent removal for alkylated aromatics (C9-C12) was obtained. The gas load was 80 Nm³/m²-hr. The installation consisted of a water cooler, dust filter, gas humidifier, and biofilter. The biofilter had 2 columns connected in series, each with a filter bed height of 1 m and a diameter of 1 m with a total volume of 1.6 m³ of compost, which was the filter bed material. The gas stream was 50 to 150 m³-hr for 16 hrs/day. The type of lacquer was changed several times a day. Several micro-organisms were present or added to the filter bed, including *genera Nocardia* (capable of degrading aromatics) and *genera Hyphomicrobium* (capable of degrading dichloromethane). Nutrients were added, and the waste gases were cooled from 80 to 120 °C to 30 to 60 °C and humidified with an ultrasonic sprayer to almost 100 percent relative humidity (79).

A yeast production plant with a 36,000 cfm, 300 ppmv ethanol waste air stream tried biofiltration to treat the emissions. They began with a 300 cu yd compost/tree bark filter bed for 18,000 cfm of the stream. After 3 months, the bed was dry and efficiency had decreased. When the decrease in efficiency was noticed, additional water was added directly to the bed and the inlet air was humidified. Neither of the measures was able to re-establish the removal efficiency of the compost bed. Due to the compost initially being handled improperly, it dried irreversibly. The headloss or pressure drop was also observed to increase as the compost decomposed. The vapor flow rate was scaled down to 6,000 cfm to improve moisture control. The design was modified to slope the walls and corners to reduce sidewall effects, and maintenance was improved. After all these changes were implemented, 95 percent removal was achieved (56).

In 1987, Jacksonville, FL, had serious odor complaints stemming from a treatment plant. At first, a caustic scrubber tower followed by granular activated carbon was installed, but these measures were only partially successful. Then a biofilter was installed and filled with sludge and wood chips. However, the biofilter was not as effective as projected because: (1) the gas velocity was too high, giving a loading rate of 3,300 cu ft/sq ft hr which is excessive, having a residence time of only 5 seconds, (2) poor gas distribution led to channeling in the filter bed, and (3) moisture, pH, temperature, and nutrients were not monitored or maintained (80).

The VT Biofilter for waste gas purification consists of microbiologically active compost and environmentally safe added components. The filter material provides a large buffer capacity for intermittent loads and excellent moisture regulation with optimal pH stabilization. The use of the biofilter at a leather factory reduced the airborne concentrations of 3.1 mg/m³ sulfide to 0.08 mg/m³ (97.4 percent removal). The bed was 9 m³ and treated 6000 m³ air/hr (81).

The BIOBOX[®] is filled with Vamfil, a modified compost which can treat up to 20 g of carbon/m³ Vamfil/hr. Vamfil is produced by a Dutch compost company, VAM. A BIOBOX[®] was placed in service at a sewage pump in Schiedam to remove H₂S, at a polymerization plant to remove H₂S and CS₂, at a food processor in the Netherlands, and at a chemical manufacturer with solvents in the waste air stream (82).

Peat Beds

Using a filter of bark, peat, and composted sewage, Brown and Caldwell with ARCO Products Company are treating a slip stream of gasoline derived petro-

leum air emissions from a soil vapor extraction and treatment system. The biofilter removal rates were observed to be compound specific (25).

A pilot scale peat biofilter was installed at the night soil treatment plant in Atsugi, Kanagawa Prefecture, Japan. The peat was inoculated with *Thiobacillus thioparus* DW44. Hydrogen sulfide, methanethiol, dimethyl sulfide, and dimethyl disulfide in the exhaust gas were decreased by 99 percent. No remarkable decline of pH, which often causes a deterioration in bacterial activity, was observed, mainly because SO_4^- reacted with NH_3 . The inoculation of a specific sulfur degrading organism into the biofilter overcame the long acclimation periods usually required to reach steady-state, and resulted in enhanced removal efficiency of the malodorous gases (83, 84).

Engineered Medium Biofilters

The Gas Research Institute of Chicago, IL evaluated laboratory scale engineered biofilters to treat benzene, toluene, ethylbenzene, and xylenes (BTEX) from the exhaust of a glycol regeneration unit. The glycol is used to dehydrate raw field gas and is regenerated by boiling water from it. The vapor also contains BTEX. The filters were filled with MBI's proprietary pelletized media. Removal efficiency reached 95 percent with a load of $55 \text{ g/m}^3\text{-hr}$ of BTEX (2, 45).

A pilot scale engineered biofilter was installed at a soil vapor extraction site. A gas station, run by the Imperial Oil Company in Farwell, MI, had leaking underground storage tanks. The soil was cleaned by vacuum extraction, and the biofilter was used to destroy contaminants in the vapor. Throughout the study, 76 percent of the BTEX was removed with loading rates of $3.75 \text{ g/m}^3 \text{ hr}$ to $56 \text{ g/m}^3\text{hr}$, even with temperatures ranging from 23 to 90 °F (85).

Technological Innovations in Biofiltration

Theory

Mechanisms

VOCs can be removed from a vapor stream by several mechanisms in a biofilter including: absorption to water, adsorption in the filter media and biomass, non-biological transformations, and biodegradation (73). The importance of sorption phenomena will depend on the media used. For example, it is known that VOCs, ammonia, and sulfur compounds will adsorb onto granular activated carbon, soil, and peat (86, 87). It is also well known that water has a high capacity for alco-

hols, ketones, and highly soluble compounds. This process depends on the affinity between the VOCs and the media and will be affected by moisture, temperature, pH, and concentrations. Generally, once the filter media have been in contact with the waste air stream, they will reach their saturation point and will not adsorb any more VOCs. Nonbiological transformations of VOCs include hydrolysis, oxidation due to ambient oxygen, and reactions due to the pH of the media and liquid phase. The importance of these nonbiological transformations will depend on the VOCs treated, and on the operating conditions in the biofilter. The main mechanism of VOC elimination in a biofilter is biodegradation. The macro-kinetics of the elimination processes in a biofilter bed can be modeled as an absorption process in a wet biolayer, accompanied by a biological degradation reaction (38).

Specifically, the process of biodegradation involves all of the following mechanisms (86):

- mass transfer of the contaminant from the bulk gas phase to an interface
- dissolution of the contaminant from the gas phase to the liquid phase at the interface
- diffusion of the contaminant through the bulk liquid to a thin liquid film
- diffusion of the contaminant through the thin liquid film
- partitioning of the contaminant from the liquid phase to the biofilm surface
- diffusion and biodegradation of the contaminant in the biofilm
- back diffusion of the contaminant from the media to and into the biofilm.

Therefore, solubility, concentration, and biodegradability of the contaminant are important in the overall biodegradation kinetics (88). Also, medium particle composition and size, porosity, water content, airflow rate, biomass density, and the species of micro-organisms present in the filter will significantly affect the overall kinetics (89).

Kinetics

The kinetics in a biofilter involve many parameters. However, a good model is very useful in determining improved reactor designs and operating regimes. Researchers have studied degradation rates and determined the kinetics of biodegradation. Because removal efficiency is independent of concentration in many biofilters, kinetics and models are discussed in terms of removal rates (90). Maximum elimination capacities are also used when discussing factors that affect kinetics. Maximum elimination capacity is the maximum mass of particular VOCs that can be degraded in a specified time by a specified volume of filter media. Also, odor measurements can be quite subjective. Whenever possible, removals are stated in terms of compounds, to provide a common basis for com-

parisons. Odor sampling is discussed in detail by van Doorn and van Harreveld (91).

At high contaminant concentrations, degradation kinetics are zero order. The biological layer has a fixed limited capability to oxidize contaminants present in excess. Above critical concentrations, removal is limited by biological activity, so the concentration of the component to be degraded becomes independent of the rate of degradation. Overall conversion decreases when higher pollutant concentrations are fed because excess contaminant passes through the filter untouched. Thus, the elimination capacity of the reactor is constant at a high inlet concentration. In the case of high inlet contaminant concentration, there is no diffusion limitation to the wet biolayer; the conversion rate is only controlled by the reaction rate (38, 41, 88, 89, 92-102).

At low inlet concentrations, or when the contaminant has low water solubility, degradation kinetics are first order. As the concentration of the component to be degraded increases, the rate of degradation increases as well. Removal of a component is controlled by the rate at which it can reach and penetrate the gas-liquid interfaces, and the rate is proportional to concentration. In other words, the biofilter is limited by diffusion of the contaminant into the biolayer, suggesting that the biolayer is not fully active. Below critical air phase concentrations, diffusion in the biolayer is the rate limiting factor. The concentrations of VOCs that the cells can digest are probably limited by diffusion in these cases. Reaction rates and the Thiele modulus may also play a role here. Diffusion limits the elimination capacity, and the capacity of the biofilter increases with the increased inlet concentration. Collectively, these are known as Michaelis-Menton enzyme kinetics (38, 41, 88, 89, 92-102).

As biofilters develop under operating conditions, distinct regions are found with regard to nutrients, pH, gas concentration, and biomass density. Thus, biofilters may have several physical regions operating under different kinetic modes. At the gas inlet, the concentration of contaminant is high and zero order kinetics prevail. Toward the gas outlet, the effluent is less concentrated, so first order kinetics may take over. Thus, in one biofilter, both types of kinetics should be considered. In the last stages of a biofilter, the design should be modified to encourage diffusion (103). In a 36-in. deep bed, concentrations were measured at various depths, 50 percent of the contaminant was degraded in the first 10 in. The mid and upper sections worked as polishers; the mid third removed 40 percent on average while the top third usually removed 10 percent (104).

Other factors will affect the kinetics including: residence time, temperature, and the presence of oxygen, nutrients, or co-metabolites. It is also well known that

increasing the residence time of the components to be degraded will increase the extent of degradation. The micro-organisms have more time to absorb, digest, and eliminate the waste (105). Biological activity doubles with each 10 °C rise in temperature within certain limits. For biofilters, the elimination capacity will also double with a 10 °C temperature rise because the microbes are more active (106).

Any factor that aids biological growth can help increase biodegradation, such as co-metabolism. A primary substrate can be fed to a biofilter that is also being fed a low concentration of a contaminant. The contaminant is then used as a secondary substrate, while a primary substrate sustains the cells (112).

Any factor that can limit biological activity will also limit biodegradation. Diffusion of oxygen into the biolayer can be limiting if the oxygen concentration in the gas stream is not high enough (107). Limited nitrogen or phosphorus can limit cell growth. Lack of these nutrients will also limit biodegradation (108-110). Performance was shown to be poor under steady-state conditions where the inlet VOCs concentrations were low because of limiting gas-phase concentrations below which the biofilms cannot be sustained (111).

Models

Using the biodegradation kinetics, models of biofilters can be designed. As the kinetics have been refined, so have the models. The models are used to size biofilters to full-scale and to indicate more efficient operating regimes (56).

The simplest models are for steady-state waste streams with one component, assuming either first or zero order kinetics (89, 98, 113, 114). Kampbell combined zero order kinetics with first order into a hyperbolic function dependent on the contaminant concentration (73). The effect of oxygen is added in Shareefdeen's biofilter model. These models assume plug flow and are more or less complex in determining diffusion rates across interfaces. Hodge added non-steady-state operation, the effect of CO₂ evolution, and the qualities of the filter media including adsorptive capacity and porosity to his model (14, 97). While the adsorptive capacity of the granular activated carbon was substantially reduced by water and microbial growth, it remained highest for the three media. The compost microbial community had a higher degradation rate constant. Biofilters packed with activated carbon provided the best maximum short-term efficiency treatment overall (14).

Smith, Biswas, Suidan, and Brenner developed a model for the trickle bed biofilter. The effects of biological growth on the hydrodynamics of flow are accounted

for. They also calculated the effects of the biological growth on the hydrodynamics of the flow. The full Monod kinetic rate expression is used in describing VOCs consumption in the biofilms. They developed the relationship between the flux into a biofilm and the corresponding biofilm thickness. This led to a prediction of the biofilm profile through the bed depth, with thicker films at the inlet of the filter where concentrations are higher and correspondingly less dense biofilms at the outlet where the concentration was lower. Eight dimensionless groups were identified that completely determined a unique solution of the model equations. For specific VOCs and biofilter packing medium, the efficiency can be expressed as a function of one of these groups. The resulting efficiency curves can then be reduced to an equation that can be used for simple empirical design correlation (111). Research by van Lith extrapolated the basic model to account for mixtures of contaminants and used it for designing filter beds up to 2000 m³ (100, 101).

Leson and Winer determined that the typical flow in a biofilter is laminar. The Reynolds number varies between 0.2 and 0.5 (115). According to Ottengraf's updated model and experimental results, co-current and countercurrent flow in a trickle bed produce equivalent degradation. The model shows that recirculation of the liquid phase reduces concentration gradients in the trickle bed (116). Ockeloen, Overcamp, and Grady also included bed height in co-current versus countercurrent operation models. They found that co-current operation was more efficient, especially with sparingly soluble contaminants (117).

Design Parameters

Theories abound in regards to biofilter kinetics and models, but pilot and full-scale units are still designed with rules of thumb and empirical scale-up (42). According to the kinetic model above, the biofilter is not diffusion limited at the concentration where the kinetics switch from first order to zero order, this is the inflection concentration (73). Thus, the equipment and nonbiological process is most efficient when operating at or above that concentration. Increasing diffusion in the biofilter will increase the inflection concentration. Diffusion kinetics are influenced by the media, the filter design, the airflow rate, and the compounds to be degraded.

Biodegradation may be the limiting factor at any inlet concentration, however, the limitations are often most obvious above the inflection concentration. Media, nutrients, moisture, pH, temperature, and the compounds to be degraded will all influence the biodegradation rate. To take advantage of the kinetics inherent in a biofilter, the first stages should be designed to maximize biological degradation, while later stages should be modified to maximize diffusion.

Reactor Design

In bioscrubbers and trickling filters, the contaminant must diffuse through a liquid phase for degradation to occur. Thus, if the contaminant is not extremely water soluble, the rate of diffusion will be slow and the inflection concentration will be low (38). Engineered and natural medium biofilters are not covered in water. Thus, contaminants may also absorb directly to the media instead of first diffusing through a liquid phase (2, 20). These systems may exhibit much higher inflection concentrations than bioscrubbers or trickling filters with insoluble contaminants.

Soil beds usually require covering a large area of land to have a large enough bed volume. This land can be covered with a greenhouse to facilitate the cultivation of shallow rooted plants which could reduce sulfate excesses and resupply soil organics. Plants would also help keep the soil loose to improve aeration and porosity (1). The plants may also take up recalcitrant compounds that are not readily degraded.

Soil beds with trenches are very inexpensive to build, but any leachate, or water flowing through the bed is not contained. Thus, if it is contaminated, it can flow into the groundwater below. Thus, new natural filter beds are made in containers. These containers can keep leachate from draining into the groundwater. In addition, they can be stacked (38, 118, 119). Therefore, the same total bed volume can have a much smaller footprint than a conventional soil bed. Also, series operation is possible so that design parameters can be modified to maximize removal at each concentration as the waste gas flows through the bed (60).

Airflows that have widely varying concentrations are not generally treated with biofilters. However, with a small carbon adsorption unit as a prefilter, biofiltration can be a viable technology. The carbon filter adsorbs contaminants when concentrations are high. When the inlet concentrations decrease, contaminants desorb from the carbon and flow into the biofilter (49, 120).

Sometimes pretreatment of the gas is required to maintain temperatures between 50 and 104 °F. Humidification of the gas, reducing aerosols present to 10 mg/m³ and removing particulates that may clog the filter pores are also required (35, 53, 121). The parameters and pH maintenance are more easily monitored and adjusted in several small beds versus one large bed (67, 119).

Carbon adsorption units can also be used as a polishing step. Biofilters are not as efficient at extremely low concentrations because the microbes starve for lack of adequate growth substrate. Therefore, to achieve extremely low exit concen-

trations, a carbon adsorption unit is sometimes a better technology to use to eliminate the last bit of contamination.

Media

Porosity of the medium will affect diffusion kinetics, as will adsorptive capacity. The hospitality of the media for micro-organisms will play a role in the biodegradation kinetics. Media should have: (1) high adsorption capacity, (2) low pressure drop, (3) high nutrient content, (4) pH buffering capacity, and (5) adequate moisture content (112). Effective biofilter solid phase media were found to be those permeable to airflow and able to support high density microbial populations. Obviously, medium choice in a biofilter is very important.

Porosity/Headloss

The porosity of particulate matter in the medium is very important. If the medium porosity is low, the pressure loss through the bed becomes high. When the medium is extremely porous, the air/medium contact time is minimal and sorption is limited. The media must also be the correct porosity to maintain moisture. One author stated a goal of 32 percent pore space (122). Natural media including tree bark, various composts and sludges, various soils, peat, wood chips, diatomaceous earth, granular activated carbon, and grass have all been tested as biofilter media, solely or in various combinations (11, 82, 102, 123, 124). After the biofilter is placed in service, the organic components of the media will break down. As the media break down, the pores are filled and the entire bed compacts (63). Soil pores are closed when trenches are dug for the gas distribution system in a full-scale natural bed biofilter. The trench digger seals the soil pores as it scrapes away the dirt. Repeated wetting and drying of filter material can also seal pores. Diffusion is severely limited from these actions (35, 101). This compression limits diffusion and overall biofilter efficiency. Headloss, or the pressure drop across the filter bed, is often used as a measure of porosity. As a bed compacts, the headloss will increase. Build up of biomass growing on the medium will also increase the headloss (102).

Soil beds are effective because VOCs are sorbed at very low loading rates under strongly aerobic conditions at the soil surface. Soil is a mix of activated carbon, silica, alumina, iron oxide, and lime. It has 40 to 50 percent porosity, 1 to 100 m²/g silica, and transition metal oxides catalyze the oxidation of inorganics. It also has a high buffer capacity, a large amount of adsorptive humic matter, and a large natural microbial population. Soil also does not irreversibly dry (20). In addition, since soil has lower porosity, slowly degraded compounds are retained longer and have a better chance of being removed. Compost is more porous than

soil, so smaller beds can be used. It is better suited to larger airflows with easily degraded VOCs. However, compost must periodically be stirred to prevent caking, and it must initially be sieved to achieve a homogeneous distribution of particles (22, 125). Fibrous peat is flexible and light and has better water permeability and lower pressure drops than soil or compost (93).

Engineered medium incorporates porous medium with supports or unique shapes to limit compression (45, 110, 116, 126, 127). In this way, headloss is consistently low. Engineered medium may use perlite, pelletized GAC, lava rock, celite, ceramic shapes, polyurethane, glass beads, and plastics as supports for the biomass (86, 110, 116, 128, 129). The engineered medium also allows bed washing, so that excess biomass can be removed (86, 114, 130). A 1- to 2-hr backwash will decrease the efficiency for several days, but overall performance stability is enhanced (130). Some medium size guidelines were set out by Wittorf, media with a random packed bed of particles 4 to 8 mm will clog quickly as will media up to 16 mm diameters. Tube form supports aligned with airflow were therefore used. They were made of polyethylene sintered with GAC ($d_i = 40$ mm, $d_a = 30$ mm) (110). Overall, porosity and headloss can easily be maintained with engineered media so that diffusion kinetics, due to porosity, are constant through the life of the filter.

Adsorption

The adsorptive capacity of the biofilter medium affects overall kinetics in several ways. During start-up, the medium adsorb contaminants until the medium capacity is reached. Adsorption is the main removal mechanism during filter start-up (14). During steady-state operation, adsorptive media can remove nonwater soluble contaminants from the air stream (21, 41). As the airflows through soil and compost pores, pollutants partition out on the surfaces. Micro-organisms oxidize the adsorbed organic gases to CO_2 and renew the soils sorption capacity (20). Difficult to degrade compounds may be retained longer in the bed, so that they are degraded more completely before emission (45, 92, 114). Additionally, the adsorptive capacity of the medium can be used to smooth contaminant concentrations for non-steady-state operation. In these cases, the filter medium adsorbs contaminants while the emission process is running. Then when the emission process is off, the contaminant back diffuses from the medium and is degraded by the biomass. The micro-organisms receive a smoothed concentration of contaminant, so biodegradation kinetics are better overall than without the smoothing process (72, 120). Soil, compost, and peat all have high natural adsorptive capacity (22, 131, 132).

Medium choice also affects biodegradation rates depending on its ability to support the microbial population. A medium that provides nutrients, retains moisture, buffers pH, and is nontoxic will support more organisms (86, 102). Organic natural medium such as compost, peat, and bark are most hospitable for microorganisms, and support the highest biodegradation rates (11). However, compost and peat can dry irreversibly if the moisture content is not maintained (22). Soil will crack and cause channeling when moisture is lost (22, 80). Engineered media may have nutrients added to overcome their inherent inert nature. Medium amendments such as calcite, limestone, and oyster shells have been added to both natural and engineered medium to increase the buffer capacity (22, 123, 128, 133). However, nutrients, moisture, and pH can also be adjusted using operational procedures. A medium that lacks nutrients should not be eliminated from consideration.

Airflow Rates

The superficial gas velocity also affects biofilter kinetics. Velocity affects diffusion, and plays a role in the moisture balance that can affect biodegradation kinetics. A high velocity gas at a certain concentration will diffuse more contaminant into the biomass and medium than a low velocity gas at the same concentration. This effect occurs when the boundary layer is disturbed by high shear from a high gas flow rate. In the first case, more total contaminant is put into the reactor, thus more diffusion occurs, and the inflection concentration is higher (106, 107, 129). However, if the total concentration of contaminant is too high, it may cause substrate inhibition or be toxic to the microorganisms (72, 118, 119, 125, 134). In many research cases, increased gas velocity decreased residence time, while the total loading of contaminant was constant and the inflection concentration decreased. Thus, the inflection concentration decreased for a given total mass of contaminant with decreased residence time because diffusion did not have enough time to occur (19, 76, 114, 135, 136).

Compounds

The compounds to be degraded affect both diffusion kinetics and biodegradation kinetics. The concentration and total mass put into the biofilter will affect diffusion kinetics. Higher concentrations will increase diffusion unless substrate inhibition occurs (119). The type of compound will also affect diffusion kinetics. If the compound is very soluble in water or the medium, diffusion will be increased with a concurrent increase in the inflection concentration (21, 41). Increased volatility of a compound will have the opposite effect, slowing diffusion (89). The type of contaminant will affect biodegradation kinetics. Bohn has made some generalizations about compounds and their degradability (Table 4) (22).

The sorption of hydrocarbons increases exponentially with carbon number, which offsets their somewhat slower biodegradability compared to analogous lighter molecular weight compounds (20). Table 5 lists compounds degraded by biofiltration.

Many VOCs are not produced at the same concentration 24 hours/day. Fortunately, the microbial flora appear to survive at least a 2-week period, during which time the filter bed is not fed VOCs (98). For example, styrene polluted air discharged from a fiberglass spray booth operation was investigated using a field pilot biofilter containing 30 cu ft of packing. The test program evaluated response to rapid changes in pollutant concentration, discontinuous daily and weekly plant operation, and extended periods of shut-down. Average removal efficiency was greater than 95 percent, as measured by on-line total hydrocarbon. On resumption of service after shutdown periods of 2 days to 2 weeks, the unit recovered to greater than 90 percent removal efficiency within 5 to 8 hours. On Monday mornings when a re-acclimation period was observed, degradation efficiency was typically 50 to 80 percent for the first few hours, depending on the vapor residence time, with a steady increase in efficiency over the next 3 to 6 hours. To minimize the re-acclimation period, a styrene feed system was installed to introduce styrene to the inlet before the spray booth operated. No re-acclimation period was observed after the feeding system was added. During normal daily operations, the spray booth was manned for two shifts, from approximately 7:00 a.m. – 12:00 midnight. The concentration of organics in the spray booth effluent stream varied from as high as 130 ppmv to as low as 13 ppmv. These extreme swings in concentration occurred some 20 to 40 times in a typical 1-hour period. The spray booth was not operated over the weekend, and the plant was shut down for 4 days over the Thanksgiving holiday and for approximately 2 weeks between Christmas and the New Year. The average concentration of organic in the inlet was 44 ppmv for the first month of operation (72).

Table 4. Biodegradability of various compounds.

Rapid VOCs	Rapid Volatile Inorganic Compounds	Slow VOCs	Very Slow VOCs
alcohols	H ₂ S	phenols hydrocarbons	halogenated hydrocarbons
aldehydes	NO _x (not N ₂ O)	methylene chloride	
ketones	SO ₂	aliphatics degrade faster than aromatics such as xylenes, toluene, benzene, and styrene	PCE
ethers	HCl		TCE (150 min retention time)
esters	NH ₃		CCl ₄
organic acids	PH ₃		PAHs
amines	SiH ₄		CS ₂
thiols	HF		pentachlorophenol
compounds w/o N or S as functional groups			

Table 5. Compounds degraded by biofiltration.

Compound	Inlet Concentration	Outlet Concentration	% Efficiency	Reference
total petroleum hydrocarbons	$6.2 \cdot 10^5$ lb/min/ft ³	$2.9 \cdot 10^5$ lb/min/ft ³	53	(25)
diesel fuel	600 mg/m ³	100 mg/m ³	83	(89)
gasoline	20,000 mg/m ³	14,000 mg/m ³	30	(89)
ethanol	5300 mg/m ³	33 mg/m ³	99	(81)
	1,000 mg/m ³	100 mg/m ³	90	(89)
isopropanol	4915 mg/m ³	<10 mg/m ³	99	(81)
acetone	5 ppbv	1 ppbv	85	(137)
benzene	$4.2 \cdot 10^{-7}$ lb/min/ft ³	$4.8 \cdot 10^{-9}$ lb/min/ft ³	99	(25)
	850 ppb	109 ppb	91	(95)
	8 ppbv	2 ppbv	80	(137)
ethyl benzene	$3.5 \cdot 10^{-7}$ lb/min/ft ³	$4.5 \cdot 10^{-8}$ lb/min/ft ³	87	(25)
toluene	$3.2 \cdot 10^{-6}$ lb/min/ft ³	$6.8 \cdot 10^{-8}$ lb/min/ft ³	98	(25)
	925 ppb	68 ppb	95	(95)
xylene	$2.3 \cdot 10^{-6}$ lb/min/ft ³	$1.4 \cdot 10^{-7}$ lb/min/ft ³	94	(25)
	224 ppb	27 ppb	91	(95)
styrene	678 mg/m ³	22 mg/m ³	96	(127)
a-pinene	75 ppmv	3 ppmv	95	(86)
trichloroethylene	4000 mg/L	200 mg/L	94	(138)
	18 ppbv	3 ppbv	85	(137)
dichloromethane	5210 mg/m ³	890 mg/m ³	83	(81)
	220 g/m ³ -hr	150 g/m ³ -hr	68	(106, 116)
	3-50 ppmv		98	(139)
hydrogen sulfide	20-2000 ppmv		>99	(140)
	17.7 ppm	0.04 ppm	99	(95)
	0.5-5 ppmv		99	(137)

Operational Parameters

Micro-Organisms

Table 6 lists species of micro-organisms suited to degrading certain compounds. Generally, the microbes should have wide tolerances to moisture, pH, and nutrients so that they are resilient to upsets in operating conditions. There are roughly 1 billion of these micro-organisms in a gram of soil or compost. Fungi are also present, with about 100,000 colony forming units in a gram of soil or compost. The fungus degrades more complicated molecules by excreting extracellular enzymes that break down polymers (22). Fungi are generally very resilient as they form spores when conditions become too harsh. Microbes that are suited to a contaminant will exhibit better kinetics than ill suited species (98). Even a well-suited microbe will perform better after it is acclimated to a specific contaminant (139, 141, 142).

Table 6. Some microorganisms used to degrade various compounds.

Compound	Microorganism	Reference
acetaldehyde, butanone, and other aldehydes and ketones	Gordona corynebacterium	(144)
degrades a-pinene to cis-verbenol and verbenone and trans sobrerol	Aspergillus niger	(86)
pinene	Pseudomonas maltophilia, Serratia maracens	(86)
phenol	Pseudomonas putida heterogeneous culture and a pure strain, Candida tropicalis, Fusarium floccuferium, and Trichosporon cutaneum	(141)
xylenes and styrene	Nocardia	(141)
1, 2 dichloroethane	Xanthobacter autotrophicus	(141)
dichloromethane	Hyphomicrobium sp. gj21, Pseudomonas putida	(106, 116, 139)
trichloroethylene	Pseudomonas cepacia 64, Pseudomonas mendocina KR-1 (with co-substrates)	(138)
sulfide	Bacillus, Mycoides and Streptomyces thiobacilli	(1, 145)
hydrogen sulfide	Xanthomonas sp. DY44	(146, 147)
hydrogen sulfide, methanethiol, dimethyl sulfide, and dimethyl disulfide	Thiobacillus thioparus Tkm, Thiobacillus thioparus DW44, Basidiomycete cephalosporium, Penicillium, Aspergillus, Trichoderma, Methy-lotrophic strain 155, Pseudomonas acid ovorans Dm ² -11	(148-153)
dimethyl sulfide	Hyphomicrobium	(154)
dimethyl disulfide	Alcaligenes, Thiobacillus thioparus	(93, 144)

Mixed populations as well as pure strains can be used with various results (141, 143). Soils, composts, and peats generally provide a consortia of microbes. Four bacteria isolated from peat biofilters, *Thiobacillus thioparus* DW44, *Thiobacillus* sp. HA43, *Xanthomonas* sp. DY44 and *Hyphomicrobium* sp. I55, were selected to enhance the removal ratios of hydrogen sulfide, methanethiol, and dimethyl sulfide in a mixed gas system. Two bacteria, DW44 and I55, which degrade hydrogen sulfide, methanethiol, dimethyl sulfide, and dimethyl disulfide, were mixed with DY44 or HA43 which degrade only hydrogen sulfide and methanethiol. Enhanced removability was observed by mixing the four species (143).

Some micro-organisms have an extremely hydrophobic cell surface, like Gordona which uses acetaldehyde, butanone, and other aldehydes and ketones. These micro-organisms can absorb contaminants directly from the gas phase, instead of from the water phase. This ability is especially useful for contaminants that are not very soluble in water. Corynebacterium and Gordona bacteria have lipase activity and these may hydrolyze the fat (144).

To avoid plugging the biofilter, micro-organism growth should be controlled. When the death rate and dead cell matter equal the growth rate then the total amount of biomass should remain constant and clogging may be avoided (66). There are several ways to control biomass including limiting nutrients, washing, and sloughing (106, 109). Washing also provides additional water to the filter bed to help maintain the moisture balance (125). Nutrient limitation is discussed below.

A few studies have been done on the emission of micro-organisms from biofilters. In general, finely structured homogeneous packing materials emit lower numbers of bacteria than more heterogeneous materials like compost or peat, and the number of molds discharged is generally low compared to the number of bacteria. The concentration of micro-organisms of a highly contaminated inlet gas is considerably reduced, but an extra contamination is observed with a low inlet contamination. It appears that the emission rate also increases at higher gas velocities (155).

Nutrients

Without nutrients, the biomass will die. Micro-organisms require oxygen, nitrogen, phosphorous, and trace minerals. In some cases, a carbon co-substrate must be fed for contaminant degradation to occur. If any of the above factors are limited, biodegradation kinetics will suffer. For example, degradation of toluene with nutrients is 80 to 100 percent, but without the nutrients removal was as low as 20 percent (118).

In the case of an engineered medium, nutrients must be fed to the biomass. In a trickle bed design, nutrients trickle down the medium and airflows up or down the packed bed. Nutrients in the leachate are recycled after nitrogen additions and pH control. Nutrients included mineral salts, yeast extract, and trace elements trickled through the filter (7). It is thought that natural medium biofilters generally provide the nutrients required (98).

Oxygen

Oxygen is required for aerobic degradation of the contaminants. If the waste gas is at a very high concentration, there may not be enough oxygen present for complete removal. A stoichiometric balance should be performed to ensure that oxygen is present in excess (63, 88). The medium shape may also affect the rate of oxygen dissolution in engineered medium. Lenskii et al. determined correlations that describe oxygen transfer in trickle bed filters. They found that increasing the liquid flow increased oxygen transfer (156).

Sareefdeen also states some oxygen correlations and incorporates oxygen into his biofilter kinetic model. Based on the typical cell composition of $CH_{1.8}O_{0.5}N_{0.2}$, he calculated that 0.25 kg of dry biomass can be produced with 1 kg of oxygen. Because oxygen is intimately involved in biodegradation, both oxygen and the VOCs must be considered to determine if oxygen flux to the biofilter may be a limiting factor. At various positions in the biolayer, either oxygen or the VOCs may be limiting, so both must be included in modeling calculations (107).

Nitrogen

Based on the typical cell, nitrogen is about 7 to 12 percent of the cell mass (157). Available nitrogen should be at 200 mg/kg or more for good microbe nutrition and cell growth (108). Ammonium chloride and ammonium sulfate have both been used to increase available nitrogen (62, 158). Both contaminant carbon uptake and mineralization could be dramatically improved following the introduction of nitrogen in the ammonium form (109). A recent CERL study indicated that nitrate was better nitrogen source than ammonia in trickling filters treating ethyl ether. A more detailed discussion will be included in a forthcoming CERL report (Work Unit U29 of this project).

To control unlimited cell growth and prevent biomass plugging, nitrogen can be limited. Because nitrogen is needed for cell growth, but is not used in the buffering system, it is an easy way to limit the cell growth without affecting pH. However, maximal removal of contaminants occurred when conditions for unlimited microbial growth were present and starvation for nitrogen significantly diminished contaminant removal. A biomass with growth arrested by nitrogen starvation is unable to carry out the net synthesis of nitrogen-containing compounds, and thus is unable to expend the same amount of energy on anabolic reactions as a biomass under unlimited growth conditions (109, 110). In addition to providing microbial nutrition, the addition of ammonium sulfate drove solvents from the leachate (110).

Phosphorous

Based on the typical cell composition, phosphorous is about 1 to 3 percent of the cell mass. Phosphorous must be provided to the biomass for growth to occur (157). Severin et al. found that 0.0048 grams of phosphorous were consumed per gram of BTEX removed (45). He also states that the engineered biofilter should be fed nutrients at a rate similar to that needed for good growth in any biological system to obtain good, sustained removals of 85 percent or more (2).

Co-Metabolites

The micro-organisms need carbon to grow and reproduce. When the carbon source is a recalcitrant contaminant, the micro-organisms may be carbon limited. Thus, feeding extra carbon may help them grow and degrade more of the contaminant. In one case, molasses was added to a nitrogen reducing biofilter. The micro-organisms acclimated faster and removed more contaminant (128).

However, if too much co-metabolite is added, the micro-organisms may not degrade all of the contaminant. A balance must be found for each system. For example, co-metabolic TCE oxidation by certain micro-organisms has been associated with enzyme inactivation and cell toxicity resulting in a rapid loss of degradative activity. Competitive inhibition of phenol oxidation has been observed with TCE concentrations as low as 10 mM, and increased co-substrate concentrations should inhibit TCE degradation. It is necessary to balance the cell density and co-substrate feed rate with the inlet concentrations of TCE to prevent loss of activity of the bioreactor (138). Another example of co-substrate addition is the addition of 2 g/L yeast extract to stimulate the growth of HA43 (93).

In an acetone degrading biofilter pilot test for DuPont, cresols, phenol, and other aromatics were also degraded. When the acetone feed was stopped, sharp decreases in biological activity was observed. This was attributed to micro-organisms being poisoned by the recalcitrant VOCs (54).

Moisture

Control of moisture levels in biofilter medium is critical to maintaining odor and/or VOCs removal performance. Lack of moisture control is perhaps the most common cause of poor biofilter performance and premature medium replacement (159). Humidity problems cause 50 to 75 percent of all biofiltration problems. Media that are too wet or too dry are prone to failure. Excess water can cause blockages that increase headloss in the filter (77, 159, 160). Too little water will cause cracks and channeling in the filter bed (23, 86). Variation in moisture content is an important factor affecting the rate of deterioration. Weather can also play an important role in moisture variation in the filter bed due to wet and dry periods. Moisture causes the medium to swell while dry weather allows the medium to shrink, due to evaporation. Evaporation is more of a problem at higher temperatures and flow rates. Shrink-swell cycles decrease filter volume and cause lumps. Thus, gas residence times are reduced and there is less water phase for micro-organisms to grow on (161).

Biofilters act like humidifiers for exhaust air, so they expend water. Even when the filter bed is not exposed to the elements, drying out will occur unless the incoming air is at least 98 percent humid. Moisture demand increases with increased temperatures, especially higher than 57 °F. The internal bed temperature also increases from oxidation occurring in the filter, which in turn increases evaporation. Moisture control can be provided by a combination of feed gas humidification and application of water to the medium surfaces (159, 160).

Without sufficient water, micro-organisms will not survive and flourish. Thus, the inflection concentration will decrease drastically if the amount of water is inappropriate for the needs of the micro-organisms (127). Aerobic microbes are generally most active when the moisture potential is in the range of 0.1 to 0.5 bars. This range corresponds to perhaps 8 to 10 percent moisture content of a sand, 20 to 25 percent of a loam soil, 40 to 50 percent of a compost bed, and 60 to 75 percent of a peat bed. This range also corresponds to a range of relative humidity in the air phase of 99.5 to 100 percent in the pores of the medium (35, 37, 93). Compared to bacteria, fungi are generally more tolerant to low water activity (158). Too little water may also encourage mite infestation, and too much moisture can encourage fungal growth (2). The reduction of the water activity may improve the mass transfer of poorly water soluble compounds (158).

Water can be applied several ways to the biofilter: humidifying the inlet air, or spraying filter material with spray nozzles, cloth hoses, and other systems. Spray must be evenly distributed throughout filter to prevent channeling (48, 98, 162). A humidification stage with a spray column and closed water recirculation circuit can also be employed (62). If water is added too quickly, ponding may result and cause headloss problems. The rate of water addition is limited to about 20 to 30 L/m²-hr. The flow of air and water through the filter will also affect moisture losses. When both the water and gas flow from top to bottom, the filter may perform better because the filter material is driest and warmest when gas enters the filter bed. Prehumidification alone will not keep the filter from drying. Biological oxidation is exothermic, so gas becomes warmer as it travels through the filter. When this occurs, it is not fully humidified so it takes water from the filter medium, which cools the reactor (101).

pH

Micro-organisms grow best at their optimal pH. However, when some compounds are degraded, acid is produced, which lowers the pH of the medium. For example, acid intermediates like acetic acid from ethyl acetate and butyl acetate may be produced when these contaminants are degraded. If the medium or leachate are not buffered, the pH will change drastically, which will affect the

micro-organisms and cause a decrease in the biodegradation kinetics (145, 163, 164).

In one case, dimethylsulfide was oxidized stoichiometrically to sulfuric acid. Due to the acidification of the inoculated biofilter, the maximum inflection concentration decreased from 30 to 12 g/m³-day after 2.5 months. This acidification was counteracted and the removal capacity was increased (up to more than 50 g/m³-day) by spraying a buffered mineral solution over the biofilter (154).

In another example, bacteria associated with hydrogen sulfide oxidation were isolated from a peat biofilter to which various concentrations of hydrogen sulfide gas were supplied. After acclimation of the peat, a facultative autotrophic bacterium, *Thiobacillus intermedius*, was primarily responsible for hydrogen sulfide oxidation. The number of cells increased at pH>3, but decreased when pH fell to <3 when breakthrough of hydrogen sulfide was finally observed. When the pH was controlled at about 3, consistent removal of hydrogen sulfide continued without a decline in the number of cells (165).

Other methods of maintaining pH include: addition of phosphate buffer solution of pH 7 every 2 days; and adding chalk, marl, or water insoluble alkalis to the medium to keep pH from dropping (62, 93). However, Allen and Yung recommend that slurries should not be used for pH control, as they add fines to the filter medium, which can decrease porosity and increase headloss (162).

Temperature

Biological activity doubles with each 10 °C rise in temperature within certain limits. For biofilters, the elimination capacity should also double with a 10 °C temperature rise because the microbes are more active (106). However, Bohn says that the optimum temperature is 100 °F (37 °C) but that the temperature response curve is rather flat from 10 to 60 °C. Careful control of biofilm temperature is not required (22). Most other authors give the same temperature range of 10 to 60 °C (93, 121, 128).

3 Methods

This chapter details the monitoring, sampling, storage, analysis, calibration and standard operating procedures that were established to ensure quality assurance/quality control (QA/QC) for the lab work that was done for this project. Where applicable, these procedures will also be observed for the VOC field scale reactor once it is in place and operating.

General Biofilter Column Information

The biofilter columns used in all of the experiments were constructed of 1 cm thick glass pieces with an ID of 10.16 cm (4 in.), and varying in length. The reactors were built using these pieces, resulting in columns approximately 92.5 cm (36.4 in.) in height with an average total volume of 18.5 L. A second set of experiments were carried out with the reactors being separated into three different stages by perforated plates made of PVC. The plates were 0.635 cm thick and had 1 cm holes punched in them such that air and liquid could easily pass through the reactor. This modification resulted in three separate stages of media 52 to 67 cm in height and 5 to 10 cm of air space between the stages (Figure 7).

The support medium used in the columns was made of a polyurethane material that had nutrients and buffer incorporated into it. Two variations of the medium were tested. The first set of experiments were set up with medium that was cut up into cubes approximately 2.5 cm in size. Due to shortcomings of the cubic medium with regard to long term compression, a second shape in the form of a cylindrical annulus was incorporated in some of the later reactors. The new shape of media had a piece of PVC tubing glued in the middle of it, with outer dimensions of roughly 3 x 4 cm and an inner radius of 1 cm.

In addition to the structure change to cut down on the compaction of the medium in the reactors, the airflow through the reactors was also reversed to an upflow direction of air for the second set of experiments. Furthermore, the biofilter columns were modified to separate the stages using plates secured into place throughout the reactors. This change was done to reduce compaction, allow improved fluidization during column washing, and more closely simulate the full-scale reactor.

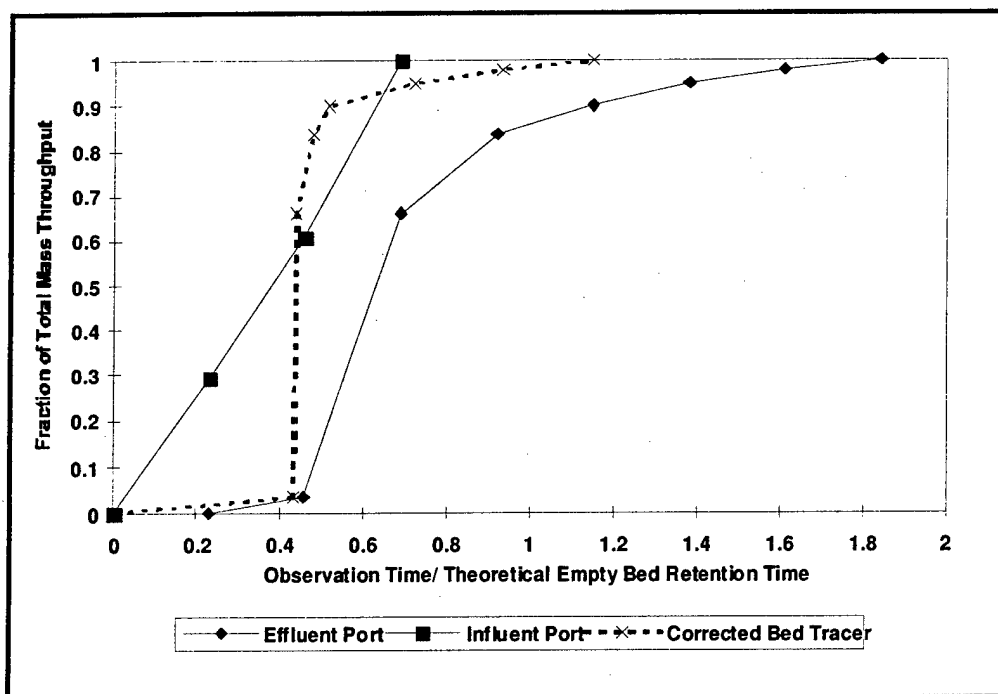


Figure 5. Column 2b tracer study (day 0).

House air, controlled using a rotometer, was used to flow air through the columns. The columns were fed using syringe pumps, Harvard Syringe (South Natick, MA) plumbed into the air lines going to the reactors. Humidification was not necessary as the leachate was monitored on a daily basis, filled to a level of 1.5 L on an "as-needed" basis, and recycled over the bed using a Masterflex pump, Cole-Parmer (Chicago, IL). The temperature of the columns was not controlled, but the temperature of the pilot plant was recorded on a daily basis and the average temperature during this time was 24 °C. The leachate was removed from the reactors daily and the pH of the leachate was measured using a pH meter. The pH was recorded and adjusted to approximately pH=7 during the first set of experiments and pH=8 during the second set using Na_2CO_3 . Removal efficiencies were monitored by performing daily injections of influent and effluent gas samples on a gas chromatograph (GC). Once per week, the leachate was replaced with a new nutrient solution. The leachate was removed and analyzed for TS/TVS, alkalinity, N and P. These analyses were done to enable a mass balance calculation.

Inoculum Isolation

A multi-step isolation procedure was used for the development of an inoculum capable of treating the target gases. The inoculum was developed through the enrichment of naturally occurring micro-organisms present in the soil. The pro-

cedure involved the successive enrichment and subsequent cultivation of micro-organisms that were capable of sustaining themselves on the substrates that they were fed as their primary carbon source. The mixed consortia of micro-organisms that were isolated were typical of those that can be found in any non-sterile soil.

There were initially three compounds targeted in this study: methyl ethyl ketone (MEK), acetone, and ethanol. Of the three compounds, MEK was determined to be the most recalcitrant and was chosen as the compound that the inoculum isolation would be focused on initially. As the project continued, the target site was changed, as was the set of target gasses. However, the culture of MEK degrading organisms thus obtained appeared completely suitable for ethyl acetate degradation, as noted below.

Isolation of Methyl Ethyl Ketone and Ethyl Acetate Degrading Microbes

The development of the inoculum was performed using a 1-L batch fermenter, New Brunswick Scientific, Inc. (Edison, NJ). The fermenter was filled with 1 L of MacLennans Minimal Salts (MMS) medium (Appendix A) and 1 percent ethanol (v/v) as a readily degradable substrate. The pH of the medium was 7 and the fermenter was run at room temperature. The fermenter was inoculated with a 5 percent soil extract, prepared by adding 5 g of soil to 95 g of distilled water. No growth was observed in the fermenter after 24 hours and the isolation attempt did not result in the successful cultivation of micro-organisms.

A second attempt was made using a soil extract prepared in a Phosphate Buffered Saline (PBS) solution, Appendix B. The fermenter was set-up the same except it contained 0.01 percent yeast extract as isolation without the addition of it was unsuccessful. Yeast extract was used as an amendment to the isolation broth to provide micro-nutrients. Bartha suggests that up to 0.05 percent yeast extract can be used without the danger of the organisms using the yeast extract as their primary source of carbon (167). This cultivation attempt yielded dense microbial growth within 24 hours. After 4 days of growth, a 15-L carboy containing the same MMS media and 30 ppm of MEK was connected to the fermenter. This solution was then passed through the fermenter at a rate of 1.0 to 1.5 ml/minute to encourage the present microbial growth to attack the MEK as a primary source of sustenance. This resulted in an enrichment chemostat that was selecting for MEK microbes. After 48 hours, dense growth was again observed and after 72 hours of continued exposure to MEK as a growth substrate, the micro-organisms were harvested in glycerol vials and frozen at -100°C .

Since ethanol was used as the carbon source for the MEK isolation, the only other compound that needed to be tested on the MEK degrading micro-organisms was acetone. The 15-L carboy was replaced with a second carboy containing MMS, 30 ppm acetone and the enrichment process was repeated. The microbes that were isolated to degrade MEK also showed the ability to degrade acetone. After 72 hours of continued exposure, the micro-organisms were harvested and stored as described above.

Once it was determined that the vapor mix would include ethyl acetate, a 1-L fermenter was set-up to determine if the previously isolated MEK organisms could degrade ethyl acetate. The same enrichment procedure was used, which resulted in a dense growth of micro-organisms after 24 hours. These microbes were also harvested and stored for future use.

Throughout the remainder of the study, as new columns were brought on-line, organisms present in the leachate of existing columns served as the inocula for the new columns.

Column Inoculation

Inoculation of the columns was accomplished by pumping nutrients, Appendix C, that contained the previously isolated microbes over the top of the packed bed and allowing it to flow down through the bed. The inoculation of the columns was from <0.1 to 11.1 percent (on a volume basis) and was varied to determine how much was actually required to ensure a quick start-up of the columns. The percent inoculation was based on the total bed volume of 15 L, so a 1 percent inoculation would consist of 150 ml of a very dense population of ethyl acetate degraders added to a volume of nutrient solution and passing it over the column bed for 48 to 96 hours, and then periodically thereafter. During start-up, the columns were fed ethyl acetate laden vapor that passed through the column and solubilized into the liquid. Subsequently, the micro-organisms began to digest the contaminant and multiply. As the micro-organism population increased, some of the microbes attached to the packing material forming a biofilm. The establishment of this biofilm is what drives the successful start-up and removal of contaminants in the biofilter column.

Monitoring and Sample Recording

Critical column operation parameters were monitored and recorded daily. This information was recorded on a Daily Monitoring Data Sheet (DMDS - Appendix

D) and filled out during each monitoring check. Any changes in experimental conditions or upsets to the columns were noted on this sheet. If changes were made to a column, they were implemented after the GC sampling was completed for the day the changes were made. Similar sheets for the VOC field reactor will be developed. The DMDS served as the official record of the conditions in a column on any given day of an experiment. The data sheets included: nutrient replacement, leachate refilling, washing procedures, bed height, changes made in column parameters, samples taken, etc. Table 7 shows a summary of the information recorded on a daily basis.

A spreadsheet was established for each column and the raw GC data was imported daily into these spreadsheets from the Turbochrom (Cuperino, CA) PC Nelson, a subsidiary of Perkin-Elmer, summary files. Leachate samples were taken from the reactors on a weekly basis and various analyses were performed. The results from these analyses were collected and recorded on data sheets or from printouts of analytical equipment that performed the analysis. These results were also entered into the spreadsheets. The other analyses of the columns included:

- Nutrient Analysis: N-NH_4^+ , P-PO_4^{3-} , N-NO_3^- , N-NO_2^- on leachate and medium
- Total Solids (TS) and Total Volatile Solids (TVS) of leachate and medium
- Alkalinity of leachate and medium
- Fungus monitoring of the biofilter exhaust
- Washing on an "as-needed" basis

Regular Sampling, Storage, Analysis and Calibration

Table 8 lists summary of the various analyses performed and the methods employed.

Table 7. Information recorded on daily monitoring data sheet.

Room temperature	°C
Gas flow rate	L/min
Leachate volume	ml
Amount of water and/or new nutrients added	ml
Leachate pH (before and after adjustment)	pH units
Amount of buffer added	ml
Headloss of column	cm
Syringe level (before and after, if refilled)	ml
Syringe rate	ml/hr

Table 8. Analytical methods for samples taken from the VOC columns.

Parameter	Method
Target Gases	Varian 3600 Gas Chromatography (GC)
Total Solids (TS)	TS dried at 105°C Standard Method 2540 B
Total Volatile Solids (TVS)	TVS Ignited at 550°C Standard Method 2540 E
N-NH ₄ ⁺	Salicylate Method*
P-PO ₄ ⁻³	QuikChem Method No.10-115-01-1-A
N-NO ₃ , N-NO ₂	QuikChem Method No.10-107-04-1-A
Alkalinity	Orion 960 Autochemistry System
Fungus Monitoring	Modified Millipore Technical Note-014
Note: Standard Methods = Examination of Water and Wastewater (17th Edition). *Salicylate Method = Communications In Soil Science Plant Analysis, 1051-1062 (1983).	

Target Gas Sampling

Sampling

Samples were taken at the influent, the effluent and at two equidistant points within the columns (representing 1/3 of the total bed volume). The 5.0 ml samples were collected with SGE 10.0 ml gas tight syringes, Alltech Associates, Inc., (Deerfield, IL) that were equipped with valves to allow samples to be transported to the GC without the risk of gas loss. Triplicate/duplicate samples at each sample port were taken in the direction of the effluent of the column to the influent to prevent disruption of any concentration gradients. The septa covering the sampling ports on the columns were checked periodically and replaced as necessary to prevent leaking. After each injection into the GC, the syringes were cleaned by flushing them several times with house air to remove any residue gas and to prevent carryover. Blank injections were made periodically and after standard injections to verify the syringe cleaning technique. On site, if any gas samples are to be taken and carried back for analysis, they will be transported in Tedlar Gas Sampling Bags, BGI Incorporated (Waltham, MA).

Analysis and Calibration

Gas phase target compounds were measured by injecting 5.0 ml of gas into a Varian 3600 GC (Walnut Creek, CA) equipped with a flame ionization detector (FID). The capillary column installed on the GC was 30 m X 0.32 mm with a 0.25 µm film thickness, manufactured by Supelco (Bellefonte, PA). The GC temperatures for the oven, injector and detector were 40, 100 and 200 °C respec-

tively. The carrier gas was helium and the flow was 4 to 5 ml/min. The gas samples that were taken from the columns were injected into the GC immediately. The data was processed using Turbochrom, a data handling software.

The standard curves for each of the target gases were made by performing triplicate injections of 10 different concentration levels of each individual component. Standards were made up in modified 2-L volumetric flasks. The volumetric flasks were modified by equipping them with gas tight valves and septa ports. These flasks were flushed with house air for 30 minutes between different standard levels. To verify the GC response for a sampling day, a triplicate injection of one concentration level of the standard curve was done. If the GC response varied greater than 10 percent, several levels of the calibration curve were checked. If these check standards also fell outside the ± 10 percent, the entire standard calibration curve was redone immediately. The slope and intercept were calculated based on the standard GC response.

Total Solids (TS) and Total Volatile Solids (TVS) Determination

The purpose of calculating the TS and TVS was to assist in determining the biofilm yield. The biofilm yield is defined as the mass of biomass formed per gram of substrate that is degraded by the biomass.

Sampling and Storage

Samples of approximately 500 ml were taken from the leachate on a weekly basis, when a column was washed and also when it was taken out of service. They were stored at 4 °C for less than 1 week in either capped plastic or Nalgene containers, a subsidiary of Subron (Rochester, NY), until they could be analyzed.

Analysis

Solids samples were done in triplicate and prepared from a well mixed leachate or wash sample. Using a wide mouth graduated pipette, 10 ml of the leachate was transferred to a weighed aluminum dish. The dishes were then transferred to a 105 °C vacuum oven and dried overnight. After drying, the samples were cooled in a desiccator for at least 15 minutes and then weighed. The increase in weight over that of the empty dish represented the total solids.

The TVS was determined by igniting the TS in a furnace at a temperature of 550 °C. All weights and volumes of the samples were recorded on a Total Solids Data Log Sheet. The TS and TVS were used to calculate the final biomass accumulation.

Phosphorus, Nitrate and Ammonia Determination

Sampling and Storage

Duplicate samples were taken from the weekly leachate or column washing samples for the nutrient analysis determination. Samples were centrifuged to remove a majority of the solids, then immediately passed through a Nalgene (subsidiary of Subron, Rochester, NY), 0.45 μm syringe filter into two 1.5 ml eppendorf tubes. The duplicate samples were placed in a $-20\text{ }^{\circ}\text{C}$ freezer until they could be transported to Michigan State University (MSU) for analysis.

Analysis

The analysis of the nutrient samples was performed by the Crop and Soil Science Laboratory at MSU using a LACHAT instrument. The principles behind the methods that were used to perform the nutrient analysis are outlined below:

- **P-PO_4^{3-}** — The orthophosphate ion reacts with ammonium molybdate and antimony potassium tartar under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex that absorbs light at 880 nm. The absorbency is proportional to the concentration of orthophosphate in the sample.
- **N-NO_3^- , N-NO_2^-** — Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color that is read at 520 nm. Nitrite can also be directly determined by reacting the sample with sulfanilamide without using the cadmium column.
- **N-NH_4^+** — KCl extracts were prepared from the frozen samples. The direct estimation of the ammonium in the extracts was done by using the salicylate method. This method relies on measuring the maximum molar absorptivity of the emerald green color that is formed when NH_3 and salicylate react in the presence of NaOCl at high pH.

Alkalinity Measurements

To maintain an acceptable pH range in the reactors, the nutrient solution was buffered to pH=8. This initial buffer was not always enough to keep the pH in the desired range once the solution circulated over the biofilter media. Therefore additional buffer solution was added to the columns leachate as needed, based on a daily pH check.

The alkalinity of the leachate or wash samples was measured, usually at the same time the TS/TVS and nutrient samples were being prepared. The alkalinity test was done on an Orion 960 Autochemistry System (Cambridge, MA). Triplicate 20 ml, well mixed samples were dispensed into 50 ml beakers using 25 ml pipettes. The samples were then titrated with 2N H_2SO_4 to an endpoint pH=4.5. The neutralization involved Na_2CO_3 , but the standard in the industry is normally expressed as $CaCO_3$, so the numbers were reported as mg/L of $CaCO_3$.

Fungus Monitoring

An area of growing concern when operating a biofiltration system is that microorganisms may be discharged in the exhaust air stream. This is justified since biofilters are engineered to provide ideal conditions for organisms that will degrade a target compound. In this study, we were requested by Lake City personnel to investigate fungal emissions based on the concern that biofilters may give off fungal or yeast spores, linked to health problems should they be given off in large numbers. Due to this, the columns were monitored once per week to check for eucaryotic micro-organisms in the off-gas exhaust of the biofilters. This was achieved by using a two-piece all glass impinger unit and as described in Technical Note-014, Millipore (Marlborough, MA). The impinger unit was fitted with tubing that could be easily connected to the exhaust of the biofilters.

The selective medium chosen for the monitoring was called Rose Bengal Medium, Appendix E. The selective agent in the media was chloramphenicol, an antibiotic that inhibits eubacterial protein synthesis. Using a sterile pipette, 30 ml of the Rose Bengal medium was transferred aseptically to the impinger unit just before sampling. The rotometer on the biofilter to be sampled was adjusted to 6 L/min, and the unit was then connected to the exhaust of a biofilter for 46 minutes. This was the amount of time it took to sample $0.283\ m^3$ (10 cu ft) of air.

After the sampling was completed, the impinger was clamped off and removed from the biofilter exhaust sample line. The impinger fluid was immediately drawn through a sterile 3-piece monitoring unit, also obtained from Millipore. The walls of the impinger were rinsed with a small amount of additional Rose Bengal Medium. This wash water was also processed through the monitoring unit. The monitoring unit contained a filter ($0.45\ \mu m$) and a pad through which the selective medium and rinse water was passed. The monitoring unit was then placed in a $28\ ^\circ C$ incubator and Colony Forming Units (CFU) numbers of eucaryotic organisms were obtained using visual observations of the units after 1 week of incubation. After each sample was completed, the impinger unit was cleaned and sterilized in an autoclave for 20 minutes.

Column Washing

It was anticipated that the column would need to be washed on a regular schedule as a form of preventative maintenance. As the laboratory study progressed this was not found to be the case, as will be discussed in more detail in the Results section of this report. Depending on the loading to each column and other factors, such as direction of airflow and medium type, each column had different washing requirements.

In general, the washing of a column consisted of removing the leachate and filling the entire column with 10 to 15 L of 1/10 nutrient solution (Appendix C) and sparging air through the column for a period of time to scrub off the attached biomass. Each time a column was washed, a portion of the washing solution that was removed from the column was saved and the same analyses were performed on the leachate samples, as described above.

Special Testing, Sampling, Storage, Analysis, and Calculations

In addition to the regular sampling and various analyses that were required to maintain the columns, there were also several other tests that were required. Some were performed before start-up, some during the course of the columns operation, while others only after a column was taken out of service.

Leak Testing

Column leak testing was done to verify the integrity of the columns once the columns were filled with the appropriate medium. The airflow was checked with a bubble meter at the influent of the column, where the contaminant was added to the air stream. The observed flow was then calculated and the bubble meter was moved to the effluent of the column where the measurement of the airflow was measured and calculated again. Differences in the two observed flow rates indicated whether there was any air leaking from the column. If there was a difference, leaks were located by squirting a soap and water solution wherever there were connections on the columns. Leaks were immediately detected because the solution bubbled on contact. Leaks were repaired and the column was retested. Columns with good integrity had an influent airflow equal to the effluent airflow.

Retention Time Distribution and Void Volume Testing

Retention time and void volume testing was performed after the results from the column leak test were completed satisfactorily. An inert tracer was injected in a

pair of the lab scale reactors at the beginning of their operation and after a period of approximately 4 weeks. The tracer studies were conducted in an effort to quantify the reduction in reactor volume as a result of biomass accumulating on the support medium. The inert tracer used in this study was helium. Helium has minimal solubility in the thin liquid layer surrounding the biomass and has no biological activity, thus it act as a conservative tracer. The presence of helium in a gas sample was measured on a Hewlett Packard 5890 GC (San Fernando, CA) equipped with a thermal conductivity detector (TCD). The GC was fitted with an Alltech Carbosphere 80/100 mesh stainless steel column (Deerfield, IL) that was 6 feet long and had a diameter of 1/8 in. The temperatures for the oven, injector and detector conditions were 200, 180, and 200 °C, respectively. The carrier gas was nitrogen and at a flow of 25 ml/min.

A 10 ml slug of high purity helium obtained from AGA (Cleveland, OH) was injected into the influent of the column. Gas samples were then taken from the effluent port or the influent port of the column using a 1 ml gas-tight syringe, Supelco (Belefon, PA), for a period of time spanning several multiples of the theoretical packed bed retention time. These gas samples were then analyzed for the presence of helium as described in the previous paragraph. This process was repeated several times each for the effluent of the column and the influent of the column. The results of these trials were averaged to come up with time course curves for the influent and effluent sections of the columns.

A cumulative summation plot was then created from the tracer data to show the average gas flow behavior. These plots showed the percent passage of tracer versus the normalized bed retention. The normalized bed retention is defined as the ration of the sample time to the expected empty bed retention time for the flow through and volume of an empty bed. This cumulative summation plot was then analyzed to develop measures of flow behavior as developed by Morrill (166). From this plot, the dimensionless time of passage of 10, 50, and 90 percent tracer passage was measured. The 90 percent time of passage was then divided by the 10 percent time of passage to calculate the Morrill index for each column.

Breakthrough Testing

The dominant removal mechanism of contaminants from the vapor stream is the biological degradation by the micro-organisms forming the biofilm. To verify that adsorption of ethyl acetate to fresh dry medium was not a major removal mechanism, breakthrough studies were performed on one biofilter column. The breakthrough study consisted of passing the target compound, in this case ethyl acetate, through fresh dry medium and sampling of the influent and effluent from the column.

Buffer Capacity Testing

Tests were conducted on the media to determine its buffering capacity. The ability of the medium to buffer against pH change is an important characteristic that can assist in preventing pH upsets in the reactor.

The buffer capacity of the media was measured by analysis of the ability of a known quantity of medium to counteract pH shifts in a small volume of water. Titrant addition and pH measurements were made using an Orion 960 Autochemistry System (Cambridge, MA). Samples of 0.5 grams of biofilter medium, that had been cut into small pieces, were mixed with 30 ml of water in a 50 ml beaker. The initial pH was measured and then increments of 0.1 N H₂SO₄ were added with the pH measured after each addition of acid. The same procedure was repeated on a fresh suspension of medium, but increments of 0.1 N NaOH were added and the pH measured after each addition. This procedure was also carried out for 30 ml of water without the biofilter media. The buffer capacity was then determined as the difference between the potential (expresses as grams of CaCO₃) of the media in water and water alone to withstand a pH shift from 8.5 to 5.5 per gram of medium.

Headloss Testing

Headloss across the reactor beds was measured in centimeters using U-tube water manometers located on each column. The headloss represents the pressure drop that occurs in forcing the air through a column filled with medium. The headloss across all lab scale columns was recorded daily.

4 Results

The results discussed first were obtained as a result of the physical and chemical tests to which the columns and medium were subjected. The second set of results that will be discussed were obtained from the operation of the laboratory columns. The majority of the laboratory data were obtained under steady-state loading conditions. Dynamic loading square-wave trials were performed later in the laboratory studies in an effort to simulate some of the problems associated with intermittent loading that the Lake City biofilter might experience. Throughout the study, six 15-L biofilters were operated under eight experimental modes. Six of the experimental modes consisted of operating the columns under steady-state loading conditions, while the other two experiments were run under square-wave loading. A general description of the column's operational conditions and individual column performances are presented in this section as well. A summary of the fungus monitoring results, which was conducted on five of the eight columns, is also included.

Physical and Chemical Testing Results

There were three series of tests performed to measure the physical properties of the biofilter medium and laboratory columns.

Tracer Study

Five helium studies were performed, as described in Chapter 3, to better define the hydraulics of the laboratory columns. In the Figures 6 through 10, cumulative sum helium recovery are plotted versus dimensionless retention time for the influent and effluent ports. A corrected "bed influence" is plotted as the difference between the time of passage between the effluent and influent. The importance of the curve on this plot is the corrected estimate of the bed retention. Standard discussion of tracer data centers on finding T_{10} , T_{50} and T_{90} , which represent the times of passing of 10, 50, and 90 percent of the tracer. Morrill indices (ratio T_{90}/T_{10}) represent the degree of mixing; where unity is perfect plug flow and any result nearing 3 is complete mixing.

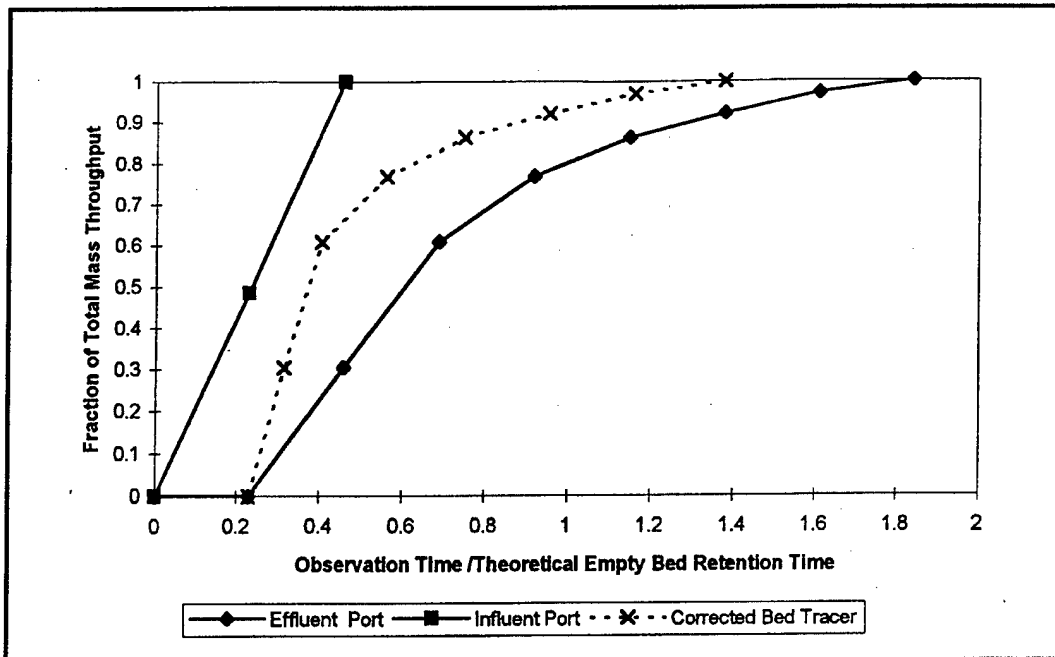


Figure 6. Column 1 tracer study (day 48).

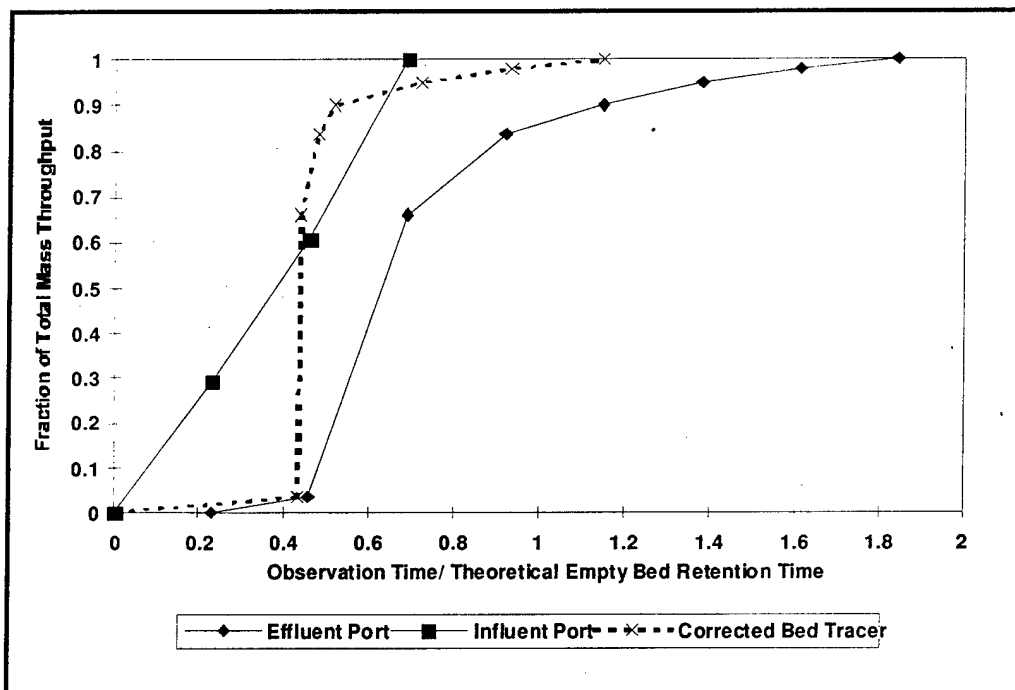


Figure 7. Column 2b tracer study (day 0).

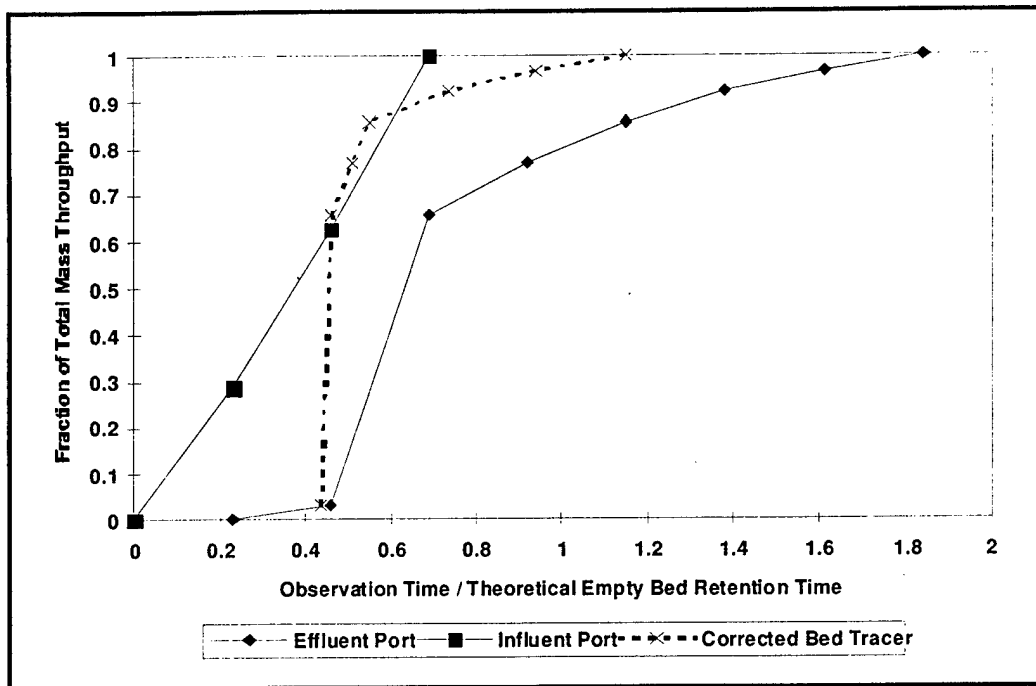


Figure 8. Column 2b tracer study (day 30).

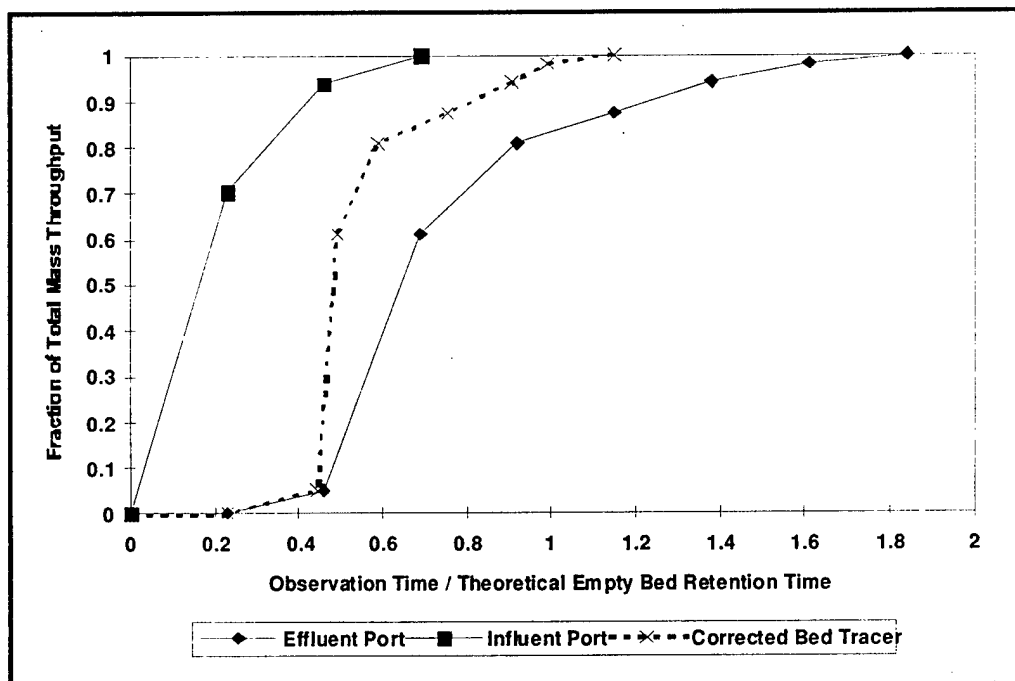


Figure 9. Column 3 tracer study (day 0).

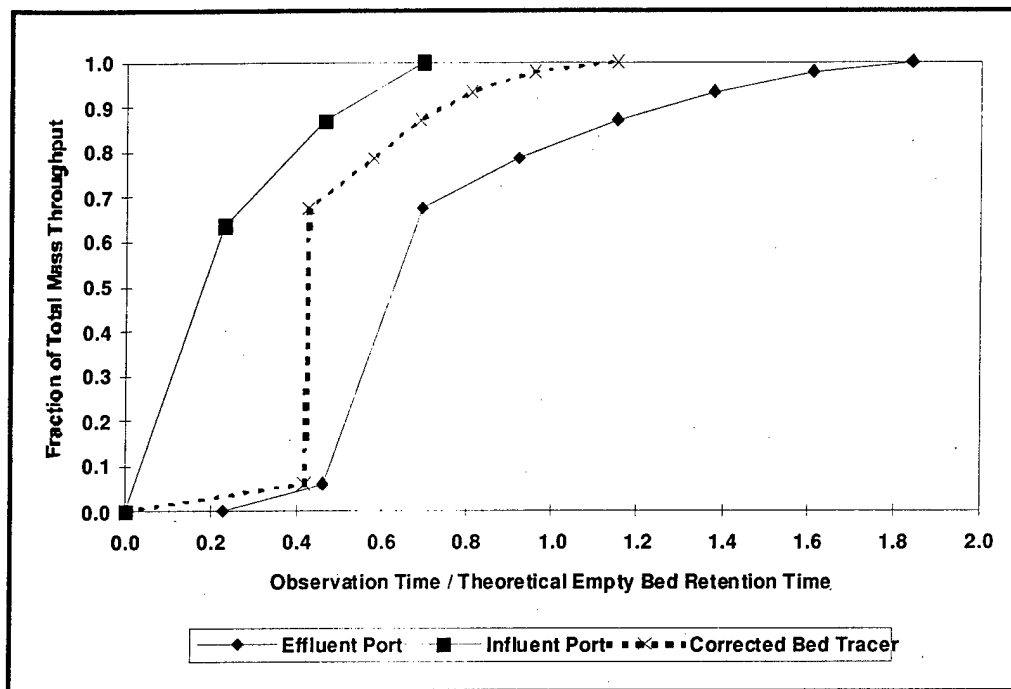


Figure 10. Column 3 tracer study (day 30).

Column 1 was constructed with the cubic foam medium. A helium tracer study was conducted on day 48 of operation. At this time, the column was being operated at 15 L/min, or a 65-second empty bed retention time. The structure of the bed had changed significantly after the bed had collapsed. High headloss (20 cm) was observed, a noted increase over starting conditions. Figure 6 is a plot of the tracer at the influent port, effluent port, and an estimate of the bed hydraulics for Column 1. Data are plotted as the cumulative sum of the fractions of the total tracer versus the ratio of the observation time. In this case, T_{10} , T_{50} and T_{90} fall at roughly 0.25, 0.6 and 1.4 bed retentions.

Four other tests were conducted, two each on Columns 2b and 3. These columns were filled with the hollow cylindrical medium. Both columns were tested on day zero and day 30 of operation. Flow rates to the columns were roughly 15 L/min for nominal empty bed retention times of 65 seconds. The data for Column 2b are presented in Figures 4.2 and 4.3. The data for Column 3 are presented in Figures 9 and 10. Times of passage, T_{10} , T_{50} , and T_{90} are summarized in Table 9. In these tests, it was observed that there was little to no increased headloss, between day zero and day 30.

It may be generalized from these results that, in a collapsed state, the cubic medium showed higher dispersion and a shorter median retention than observed with fresh and with used cylindrical medium. The cylindrical medium and internal support helped alleviate some poor flow characteristics.

Table 9. Summary of helium tracer results.

Column	Type of Medium	Day of Test	Airflow (L/m)	Nominal Empty Bed Retention (seconds)	T ₁₀	T ₅₀	T ₉₀	Morrill Dispersion Index
1	Cubic	48	15	65	0.26	0.38	0.91	3.5
2b	Cylindrical	0	15	65	0.44	0.45	0.54	1.2
2b	Cylindrical	30	15	65	0.44	0.46	0.67	1.5
3	Cylindrical	0	15	65	0.46	0.49	0.82	1.8
3	Cylindrical	30	15	65	0.42	0.43	0.76	1.8

Ethyl Acetate Breakthrough Testing on Dry Medium

An ethyl acetate gas stream was applied to a 15 L column of dry cubic medium. The influent was 100 g/m³-hr (1589.3 µg/L) ethyl acetate. A general sorption curve is presented as Figure 11. The first effluent sample at 5 minutes shows breakthrough at a concentration roughly 50 percent of the influent. Breakthrough of more than 90 percent of the influent occurred by 30 minutes. From this curve, it was calculated that a 15 L laboratory column can sorb approximately 0.72 g of ethyl acetate. With the exception of Column 6, the laboratory columns were fed a minimum of 280 g of ethyl acetate. The maximum error that could be attributed to sorption was 0.3 percent of the total contaminant removal. The effect of sorption was therefore ignored as a significant removal mechanism in the analysis of the data generated in this study.

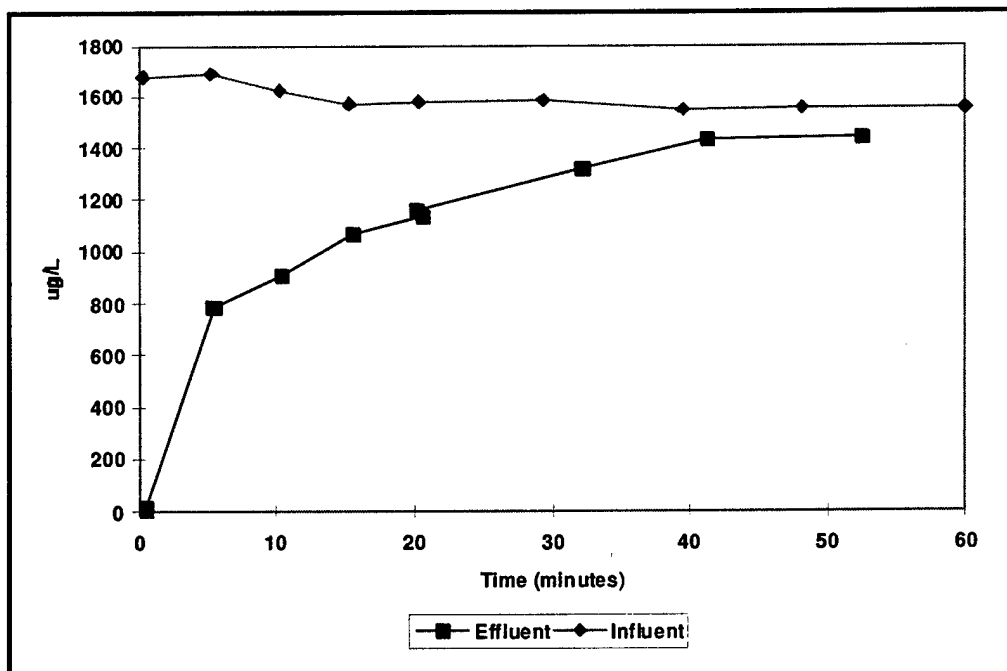


Figure 11. Ethyl acetate breakthrough study.

Buffer Capacity Determination

The buffer capacity test was carried out as described in **Headloss Testing** (p 60) and the results are reported as moles of H^+ per gram of medium. Figures 12 and 13 show the change in pH caused by the addition of base or acid. The graphs contain curves for both the medium/water mixture and the water alone. The first foam tested (Scottdel Foam 1) had a buffer capacity of 4.2×10^{-6} moles of H^+ per gram of medium. The second foam tested (Scottdel Foam 2) had a buffer capacity of 1.1×10^{-5} moles of H^+ per gram of medium. The buffering capacity caused by the water used in the testing procedure was subtracted out of the above results. Therefore, the buffer capacities reflect the amount of buffering provided by the medium.

Laboratory Columns and Biological Efficiency

There were a total of six biofilters operated under eight different conditions. The columns that will be discussed first were fed under steady-state loading conditions as summarized in **Steady-State Loading** (p 67). The second set of columns are categorized under the heading of square-wave loading and will be discussed in **Square Wave Loading** (p 82).

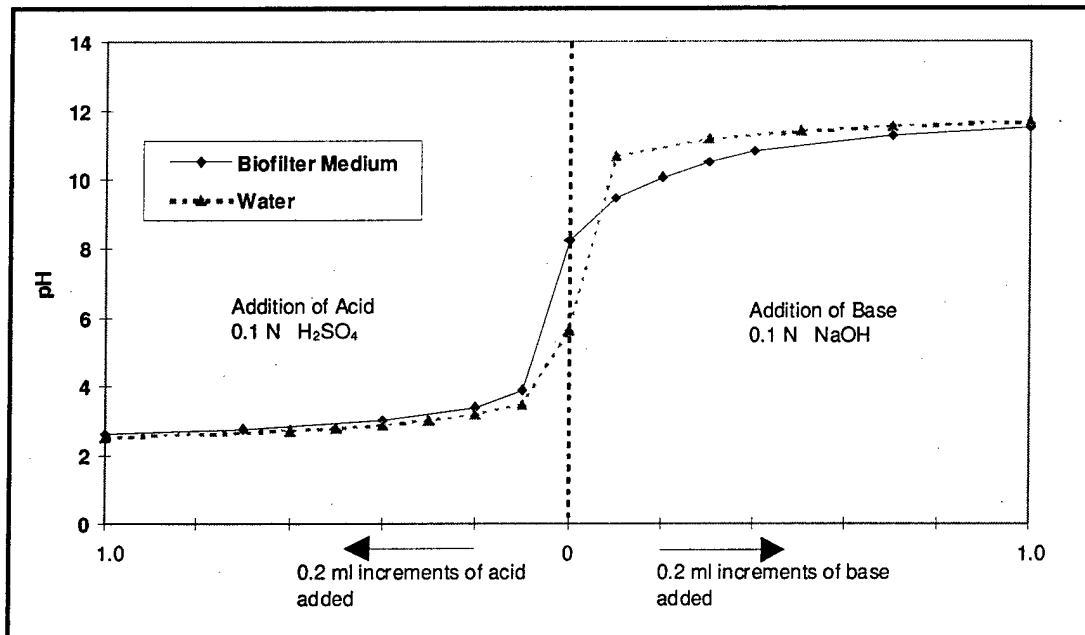


Figure 12. Buffer capacity test of biofilter medium (Scottdel Foam 1).

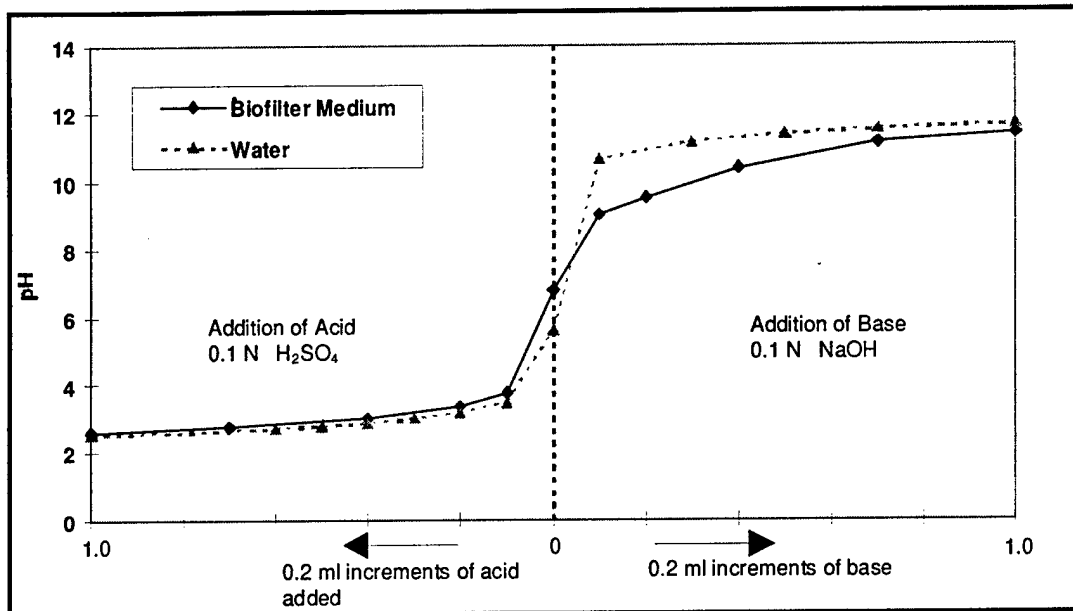


Figure 13. Buffer capacity test of biofilter medium (Scottdel Foam 2).

Steady-State Loading

An operational summary of each column fed under steady-state loading conditions is listed in Table 10. A summary of mass balance is presented in Table 11. Each column is discussed in detail.

Table 10. Steady-state column operational conditions.

Column	Days of Operation	Type of Medium	Feed	Loading (g/m ³ -hr)	Average Removal	Days to Start-Up (>90% Removal)	Inoculation Volume (% of bed)
1	>199	cubic	Ethyl Acetate	6.4-110	90%	4	0.1%
2a	54	cubic	Ethyl Acetate	55	91%	2	6.6%
2b	99	cylindrical	Low Mix	12.5-25	91%	15	0.1%
after shut-down	120-136	cylindrical	Ethyl Acetate	22.1	92%	1	—
3	99	cylindrical	Low/High Mix	75-100	91%	21	0.1%
after shut-down	120-136	cylindrical	Ethyl Acetate	22.1	93%	<1	—
4a	59	cubic	Ethyl Acetate	55	96%	10	11.1%
5	72	cubic	Ethyl Acetate	110	86%	15	0.1%

Table 11. Results of the Mass Balance Analyses for Columns 1, 2a, 2b, 3, 4a, and 5.

	Column 1	Column 2a	Column 2b	Column 3	Column 4a	Column 5
Ethyl Acetate IN/Target (g)	3110	675	646	932	987	2806
Ethyl Acetate IN/GC Data - actual (g)	2937	723	444	1789	923	3474
Ethyl Acetate OUT/GC Data - actual (g)	379	35	62	238	67	595
Ethyl Acetate TREATED/GC Data - actual (g)	2558	689	381	1550	855	1879
Total Solids OUT (g)	702.9	162.5	441.4	1121.6	228	517.4
Total Solids (g TS/ g Ethyl Acetate IN/GC Data - actual)	23.9%	22.5%	99.4%*	62.7%*	24.7%	20.5%
Total Solids (g TS/ g Ethyl Acetate TREATED/GC Data - actual)	27.5%	23.6%	115.7%*	72.3%*	26.7%	20.5%
Total Volatile OUT (g)	216.5	52.6	99.1	498.4	93.5	225
Total Volatile Solids (g TVS/g Ethyl Acetate IN/GC Data - actual)	7.4%	7.3%	22.3%*	27.9%*	10.1%	9.1%
Total Volatile Solids (g TVS/ g Ethyl Acetate TREATED/GC Data - actual)	8.5%	7.6%	25.0%*	32.1%*	10.9%	12%
Grams of Nitrogen USED	142	41.7	20.8	99.1	51.1	57
N USED (g N/g Ethyl Acetate IN/GC Data - actual)	4.8%	5.8%	4.7%*	5.5%*	5.5%	2.3%
N USED (g N/g Ethyl Acetate TREATED/GC Data - actual)	5.6%	6.1%	5.5%*	6.4%*	6%	3%
Grams of Phosphorus USED	39	12.6	0.39	25.2	16.6	34.3
P USED (g P/g Ethyl Acetate IN/GC Data - actual)	1.3%	1.7%	0.09%*	1.4%*	1.8%	1.4%
P USED (g P/g Ethyl Acetate TREATED/GC Data - actual)	1.5%	1.8%	0.1%*	1.6%*	1.9%	1.8%
Grams of Buffer as CaCO ₃ USED	178	42	95	-65	-44	-29
Buffer USED (g CaCO ₃ /g Ethyl Acetate IN/GC Data - actual)	6.1%	5.8%	21.5%*	-3.7%*	-4.8%	-1.2%
Buffer USED (g CaCO ₃ /g Ethyl Acetate OUT/GC Data - actual)	7%	6.1%	25%*	-4.2%*	-5.1%	-1.5%

*These values are not adjusted for the other minor constituents in the mix and are expressed as ethyl acetate only.

A variety of feed stocks were used throughout the study. During some of the tests, ethyl acetate was used as the sole component in the feed. In other tests, some of the columns (2b and 3) were fed with mixed component stocks. There were two stock organic mixtures; designated as "Low Mix" and "High Mix." The recipes for Low Mix and High Mix are presented in Table 12. The difference between the two recipes was the ratio of the mass ethyl acetate to the mass of minor components. In our nomenclature, "Low Mix" designates a lower fraction of minor components, whereas "High Mix" designates a greater ratio of minor components.

Table 12. Composition of feed mixes.

Compound	Low Mix% Concentration (w/w)	High Mix% Concentration (w/w)
ethyl acetate	86.6	30.5
ethyl alcohol	1.2	6.1
isobutyl acetate	2.3	12.2
toluene	3.5	18.3
2-methyl-1-propanol	0.2	1.2
n-butyl acetate	3.5	18.3
xylene	2.3	12.2
n-butanol	0.2	1.2

The different feed component mixtures were used for a variety of reasons; particularly to either enhance the concentrations of the lower components to better monitor against the lower detection limits of the GC, or to determine the capacity of the biofilters to degrade the minor components in the presence of ethyl acetate. In the following sections, descriptions of the feed mix and reasons for its use are presented. Additionally, the tables describing the operation summaries make reference to the feed mixes used during each phase of study for each column.

Column 1

Column 1 was the third column constructed and continues to be operational, over 1 year after it was inoculated. It was packed with 300 g of cubic medium to a bed height of 175-180 cm and did not have the separating PVC plates between the sections. It was inoculated with a 0.1 percent inoculation mixture consisting of 15 ml of leachate that had been removed from Column 2a and 1400 ml of nutrient solution (Appendix C). A breakdown of the operational conditions is located in Table 13. All data pertaining to ethyl acetate removal are presented in Figure 4.9.

As discussed in the following paragraphs, this column showed high initial removal efficiency, but a poor headloss trend was evidenced within the first 2 weeks. The airflow was switched from upflow to downflow and a shift in target leachate pH was made to minimize ponding and control fungal growth.

Table 13. Column 1 operational summary (reactor set up with cubic medium, airflow was upflow, target pH = 7).

Date	Time (Days)	Airflow (L/min)	Loading (g/m ³ -hr)	Leachate pH	Recycle Rate (260 ml/min)	Bed Height (cm)	Headloss (cm)
11/30	1-6	7.5	110	5.15-7.12	constant	—	0
12/6	7-13	7.5	110	4.59-7.47	15 min/day	—	0-2
12/13	14-45	7.5*	110	6.63-8.33*	15 min/day	134-113	0-20
1/14	46-51	15	12.5	7.32-8.35	15 min/day	113	1-10
1/20	52-65	15	25	6.80-8.90	15 min/day	110	2-20
2/3	66-104	15	12.5	6.97-8.80	15 min/day	110-109	2-20
3/14	105-112	35	6.4	7.15-8.60	15 min/day	109	10-30
3/21	113-119	35	21.4	6.70-8.51	15 min/day	109	6-28
3/29	120-142	35	16	6.38-8.48	15 min/day	109	6-25
4/21	143-166	35	16	5.90-8.21	twice/day*	109	7-34
5/15	167-199	35	16	6.70-8.52	15 min/day	109	8-34
6/17	Reactor is still active, but data beyond this date will not be presented in this report.						
*Airflow reversed from upflow to downflow; pH target changed from 7 to 8 on day 14							

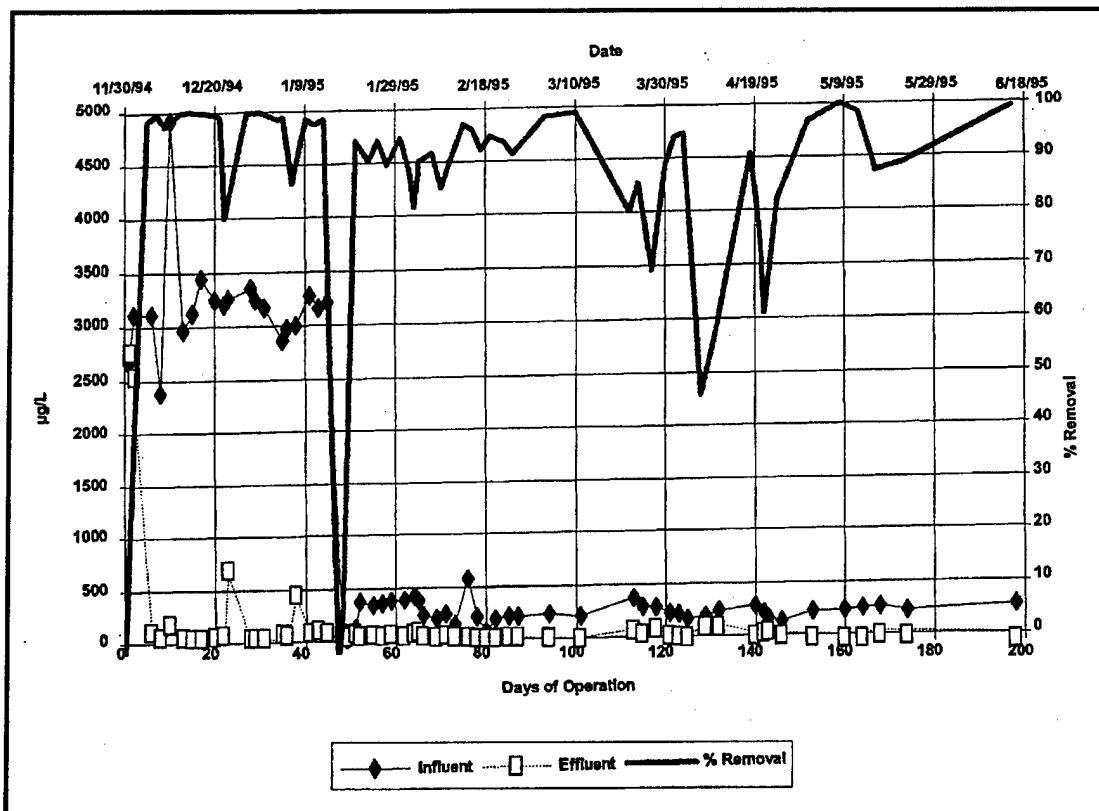


Figure 14. Ethyl acetate removal data for column 1.

The initial empty bed retention time in the column was 2 minutes with an initial loading of ethyl acetate on the column of $110 \text{ g/m}^3\text{-hr}$ ($3207.1 \text{ } \mu\text{g/L}$). The airflow was initially upflow, but was reversed to downflow on day 15 of operation due to the high headloss. The headloss had reached 20 cm while operating in the upflow mode. After flow reversal, the headloss was reduced to 1 cm. The pH was initially targeted at 7 for the first 14 days, at which time the target pH was increased to 8 for the duration of the study. The decision was made to maintain the leachate target pH for all of the columns at this higher pH to discourage the growth of fungus. If left uncontrolled, fungal growth eventually plugged the medium in the columns restricting liquid and airflow.

Leachate was recycled continuously at 260 ml/min for 6 days. On the 7th day, leachate was recycled once per day for 15 minutes. The recycling of the leachate occurred after the pH of the leachate had been adjusted. Under these operating conditions, Column 1 reached >98 percent removal of ethyl acetate in 4 days. These conditions were maintained for 45 days during which time the removal of ethyl acetate remained consistently high, >95 percent for 18 out of 20 data points collected during steady-state.

On day 46, the loading of ethyl acetate on the reactor was lowered to $12.5 \text{ g/m}^3\text{-hr}$ ($200.4 \text{ } \mu\text{g/L}$) and the retention time was decreased to 1 minute. This resulted in a very low loading of ethyl acetate onto the column and although the detection limits of the GC should have been low enough to detect these levels, no reliable data were collected during this low loading period. Due to this, on day 52, the loading was doubled to $25 \text{ g/m}^3\text{-hr}$ ($400.9 \text{ } \mu\text{g/L}$). This resulted in improved data and >90 percent removal of ethyl acetate was observed for 7 of the 8 days that GC injections were performed. Figure 14 indicates that the removal was zero percent during this low loading period, more than likely this dip is a result of the low loading.

On day 66, a low loading target of $12.5 \text{ g/m}^3\text{-hr}$ ($200.4 \text{ } \mu\text{g/L}$), of ethyl acetate was resumed using an improved syringe pump to feed the ethyl acetate. A more reliable feed rate resulted in much better GC results. These parameters were maintained from day 66 to 104. The removal during this time period was >90 percent. The bed height also stabilized during this time period at 109 cm.

On day 105, a double operation change was made; the airflow rate was increased from 1 minute to 25 seconds and the syringe rate was halved. The rotometers that were used to control airflow to the columns were limited to a maximum reading of 35 L/min, and this is what dictated the retention time to be 25 seconds. The resulting loading to the column was $6.4 \text{ g/m}^3\text{-hr}$ ($102.6 \text{ } \mu\text{g/L}$), and in-

fluent concentration proved difficult to monitor. The GC data collected during this time were sporadic and inconsistent.

Due to the sporadic GC results that were being obtained between day 105 and 112, the loading of ethyl acetate onto the column was increased to 21.4 g/m³-hr (343.6 µg/L) on day 113. The retention time remained at 25 seconds and the removal remained sporadic. On day 120, the loading of ethyl acetate to the reactor was reduced to 16 g/m³-hr (256.9 µg/L) to more closely resemble the actual plant waste stream. Removal once again dropped off and got as low as <50 percent. Observations of the column bed indicated the biofilter was extremely dry, probably due to the high airflow through the reactor, and it was decided to recycle the leachate more often on the column, twice per day versus once per day. The headloss on the column stabilized to 8 cm during the time when the column was not recycling the leachate, but would reach 34 cm when it was recycling. The increase in leachate recycling appeared to help the removal efficiency of the reactor and the removal was >80 percent for 8 out of 9 of the last sampling days. After day 167, the routine of recycling the leachate once/day was started again and removal did not appear to be affected as it has remained >80 percent. The reactor was still active after having been in operation for more than 1 year with minimal maintenance.

Column 1 was never washed, as it was decided the columns would only be washed on an "as-needed" basis. Weekly leachate samples were taken throughout the study. This enabled a mass balance to be performed (Table 8).

Column 2a.

Similar to Column 1, Column 2a (the second column put into operation) was also packed with 300 g of cubic medium to a bed height of 175 to 180 cm and did not have the separating PVC plates between the sections. It was inoculated with 1.2 L of the isolated ethyl acetate degraders and 500 ml of nutrient solution (Appendix C). This was a large volume of inocula, approximately 6.6 percent on a volume basis. A discussion of Column 2a's operational conditions are listed in Table 14. Ethyl acetate removal data are presented in Figure 15.

The airflow to the column was upflow until day 24. Initial loading of ethyl acetate onto the column was 55 g/m³-hr (1603.6 µg/L) and the retention time of the column was 2 minutes. After inoculation, the leachate was recycled continuously over the column bed for 4 days at a rate of 420 ml/min. The removal after 48 hours was >99 percent. It remained high for the next 16 days (Figure 15). On day 5, it was decided to put a timer on the recycle pump and only recycle the leachate for 5 min/hr. The leachate pH was initially targeted at 7 until day 24.

Table 14. Column 2a operational summary (reactor set-up with cubic foam medium, airflow was upflow, target pH = 7).

Date	Time (days)	Airflow (L/min)	Loading (g/m ³ -hr)	Leachate pH	Recycle Rate (420 ml/min)	Bed Height (cm)	Headloss (cm)
11/11	1-23	7.5	55	5.98-7.76	constant	180	0-50
12/5	24-37	Reactor shut-down for cleaning, cleaned from day 28 to day 33.					
12/19	38-54	7.5*	55	6.30-9.10*	15 min/day	105-93	0- >50
1/4	Reactor shut-down and medium was washed and squeezed.						
*Airflow reversed from upflow to downflow; pH target changed from 7 to 8 on day 38							

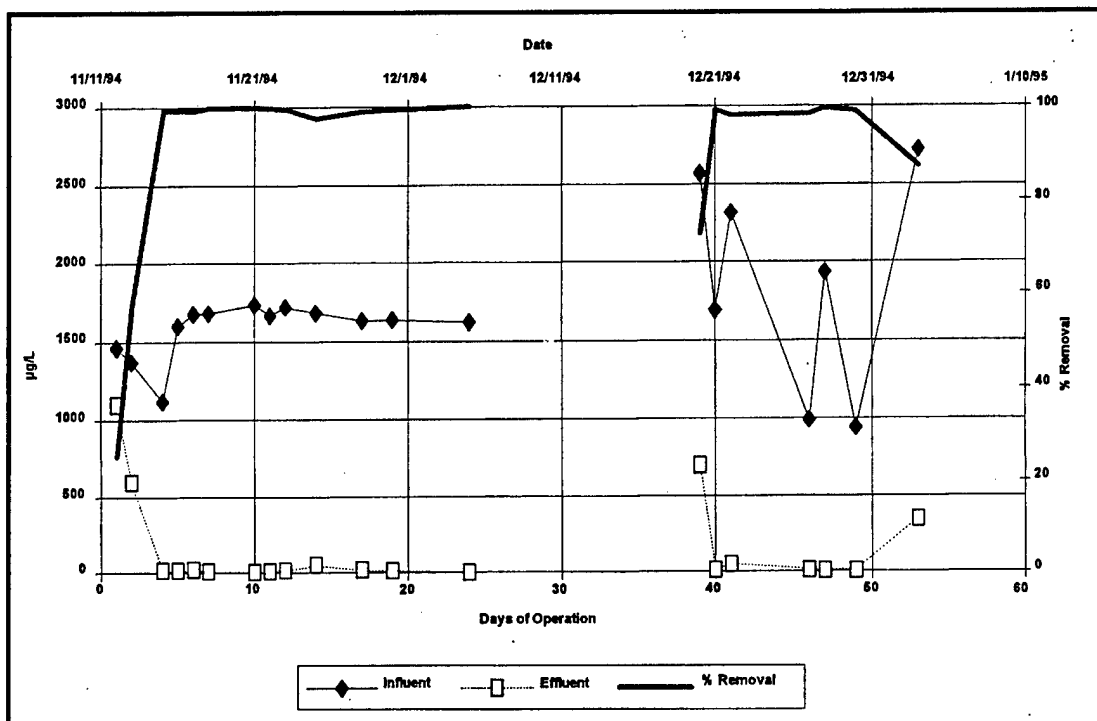


Figure 15. Ethyl acetate removal rate for column 2a.

On day 24, the column was shut-down due to high headloss (>50cm). The column had extensive biomass growth near the top of the bed. The media had collapsed and a fungal infestation had occurred. The column was taken out of service from day 24 to 37. During this period, the column was washed twice, on day 28 and days 31 to 36. The first washing procedure consisted of flooding the column with tap water and bubbling air through the bottom of the column overnight. This procedure removed a majority of the biomass, but exacerbated the compression of the media with a resultant increase in headloss.

After the first wash, it was attempted to restart the column. After restarting the column, it was noticed that fungus had started to grow near the bottom of the column bed. Due to the fungal growth, the headloss across the reactor on day 30 became so great that the fluid from the manometer was forced back into the re-

actor. A second, more aggressive wash on days 31 to 37 was necessary. In the second wash, the column was subjected to the recycling of 1600 ml of caustic (2N NaOH) without air scouring for 24 hours. After 48 hours of dormancy, the caustic was removed and the column was subjected to two washes with water to remove solids and three washes with water to remove excess caustic. Due to the aggressive and caustic nature of the wash, the column was reinoculated with 100 ml of leachate taken from Column 1 and 700 ml of nutrient solution (Appendix C), this was a 0.5 percent reinoculation.

It was felt that fungal growth and/or the direction of the airflow had caused conditions for the high headloss to occur. Therefore, after day 38, the target pH of the leachate was maintained at 8 to inhibit fungal growth, and the direction of the airflow was switched. The leachate was recycled 15 min/day after the second washing. Removal of ethyl acetate reached >90 percent within 24 hours and remained there until the headloss on the reactor again exceeded the manometer (Figure 15). This was due to a recycling error where the leachate was accidentally recycled for 2 hr rather than the target 15 min. The reactor was shut-down on day 55. Table 4.3 shows the results of the mass balance done on the column.

Column 2b

There were two physical modifications and one operational change that made this column different from Columns 1 and 2a. First it was set up with the new cylindrical, annular medium. The second modification was that PVC plates were used to separate the stages to help cut down on compaction. The first stage (top) contained 180 g of medium, the second stage (middle) had 130 g, and the third stage (bottom) 170 g. The bed height for the column was 67 cm, 57 cm, and 52 cm for the respective stages. It was operated in a downward airflow and the pH of the leachate was targeted at pH=8 on a daily basis. The operational difference for Column 2b was that it was fed a mixture of components referred to as the Low Mix, Table 4.4. This mixture contained eight of the volatile organic components in the ratio anticipated in the actual waste gas stream at the Lake City munitions plant. Table 15 summarizes the columns operational conditions.

Column 2b was the fifth experimental column constructed. It was inoculated with 15 ml of leachate from Column 1, 350 ml of nutrients (Appendix C), and 2 L of water representing a 0.1 percent inoculum. The leachate was recycled over the bed at a rate of 420 ml/hr for a period of 1 week, at which time the leachate pump was put on a timer and the leachate was recycled 15 min/hr. Initially the loading rate on the column was 25 g/m³-hr (400.9 µg/L). The removal of the ethyl acetate varied up to day 30, as indicated by Figure 16. Thereafter, the removal of ethyl acetate was high and consistent.

Table 15. Column 2b operational summary (reactor set-up with cylindrical, annular medium with PVC plates separating sections, airflow was downflow, target pH = 8).

Date	Time (Days)	Airflow (L/min)	Loading (g/m ³ -hr)	Leachate pH	Recycle Rate (260 ml/min)	Bed Height (cm)	Headloss (cm)	
1/31	1-31	15	25*	5.58-8.80	15 min/day	67/52/57	0	
3/3	32-57	15	25*	6.88-8.45	15 min/day	67/52/57	0	
3/29	58-98	15	12.5*	5.76-8.85	15 min/day	59/51/56	0	
5/9	99	Washed column.						
5/9	99-119	15	off	5.79-8.60	5 min/hr	63*/46/55	0	
5/30	120-136	15	22.1 @ 20 hr/day**	5.80-8.35	5 min/hr	63/46/55	0	
6/15	Reactor shut-down and medium was washed and squeezed.							
*low mix feed								
**ethyl acetate only								
*higher due to washing								

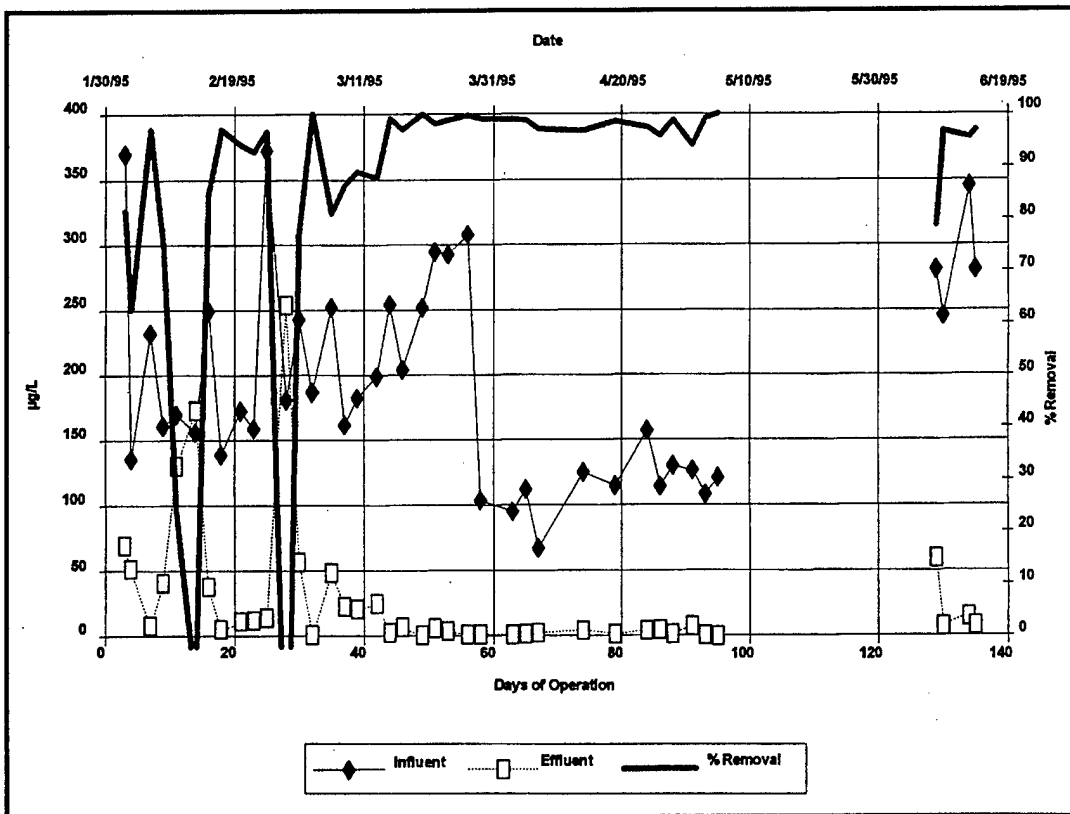


Figure 16. Ethyl acetate removal data for column 2b.

On Day 58, the loading to the column was cut in half to 12.5 g/m³-hr (200.4 µg/L) to more closely represent the actual plant. From day 1 to 62, GC results indicated that the minor components of the feed mixture were not readily degraded (Table 17). In an attempt to degrade some of the minor components such as toluene and xylenes, additional organisms obtained from a liquid treatment reactor fed on BTEX (benzene, toluene, ethyl benzene, and mixed xylenes). This was done once per week, by adding 100 ml of the BTEX organisms to the fresh

nutrients supplied during routine leachate replacement between days 63 and 98. The efficiency of minor components removal did not appear to be helped through the addition of these BTEX organisms. The results are presented (in comparison) to Column 3 results in the next subsection (Table 4.9).

A significant amount of growth, which appeared to be fungal in nature, was noticed at the top of the third stage of the reactor and the column was washed on day 99. The column was flooded with 10 L of 1/10 nutrient solution (Appendix C) and air was sparged up the column at a rate of 35 L/min for 15 minutes. This solution was then removed and replaced with another 10 L of 1/10 nutrient solution. This was bubbled through the column for 30 minutes. This was then removed and 10 L more of the diluted nutrient solution was added to the column, while 35 L/min of air was bubbled through the column for 60 minutes. After washing, the column was put into a 3-week stand-by mode (day 99 to 120). During this time, the leachate, which consisted mostly of water, was recycled over the bed 5 min/hr, and air containing no organics was fed to the reactor. The level of leachate was maintained to assure proper humidification. No additional maintenance was performed on the column during this time.

On day 120, feed was restored to the column, but consisted of ethyl acetate only. It was fed a loading of $22.1 \text{ g/m}^3\text{-hr}$ ($350.8 \text{ }\mu\text{g/L}$) for 20 hrs/day. This was the loading rate and cycle that was expected at the munitions plant during this time frame. The column responded well and >90 percent removal was observed after only 24 hours (Figure 16). The column was shut-down on day 136. No headloss was observed during this time period.

Weekly monitoring of the off gas for fungal spores was performed on Column 2b and the results will be presented in **Fungal Monitoring** (p 86). Table 11 gives the mass balance for the column.

Table 16. Removal efficiencies of minor compounds.

Compound	Column 2b (Low Mix)		Column 3 (High Mix)	
	% Removal	# of Observations	% Removal	# of Observations
ethyl alcohol	77.6	6	96.4	21
isobutyl acetate	68	10	90.6	24
toluene	60.5	27	34.8	24
2-methyl-1-propanol	—	—	96.6	23
n-butyl acetate	—	—	95.9	23
mixed xylenes	71	22	35.6	24
n-butanol	—	—	36	20

Column 3

Column 3 was set-up identically to Column 2b, except for a slightly different volume of medium in each stage; 150 g, 135 g, and 180 g in the first, second, and third stages with the height of each being 58 cm, 53 cm, and 68 cm respectively. The column was initially fed the same Low Mix as Column 2b for the first 25 days, but it proved to be too difficult to monitor the concentrations of the minor constituents. The column was thereafter fed a mixture referred to as the High Mix (Table 12). As with Column 2b, Column 3 was also operated in a downward airflow and the pH of the leachate was targeted at 8 on a daily basis. A summary of operating condition in Column 3 is presented in Table 4.8. Figure 17 shows removal results. Table 17 lists the removal efficiencies of the minor compounds for both Columns 2b and 3.

Column 3 was the sixth column constructed and put into operation. It was inoculated with 15 ml of leachate from Column 1, 1050 ml of nutrients (Appendix C) and 2 L of water, representing a 0.1 percent inoculation on a volume basis. This was recycled over the column at a rate of 420 ml/min for a period of 1 week. After this time the leachate pump was put on a timer and the leachate was recycled 15 min/hour. As with Column 2b, additional BTEX organisms were added (100 ml once per week), from days 63 to 98, when the nutrients were replaced.

Loading from day 1 to 8 of $75 \text{ g/m}^3\text{-hr}$ ($1192.0 \text{ } \mu\text{g/L}$), and was increased to $100 \text{ g/m}^3\text{-hr}$ ($1589.3 \text{ } \mu\text{g/L}$) from day 9 to 25 in an attempt to increase the loading of the minor constituents so their removal could be monitored. At this high loading rate of ethyl acetate, the removal efficiencies of the minor components were very low and sporadic. It was determined that the levels of the minor constituents were too low to be consistently tracked with the GC. Closure on the influent mass balance, between the syringe rate and the GC results, was not consistently met.

After day 26, the feed was switched to the High Mix. The column was fed this mixture at a rate of $75 \text{ g/m}^3\text{-hr}$ ($1192.0 \text{ } \mu\text{g/L}$). After the High Mix was started on the column, the influent became more constant and was able to be more reliably measured on the GC (Figure 17). Similar to Column 2b, the removal of ethyl acetate remained >90 percent until the column was put into the standby mode on day 99.

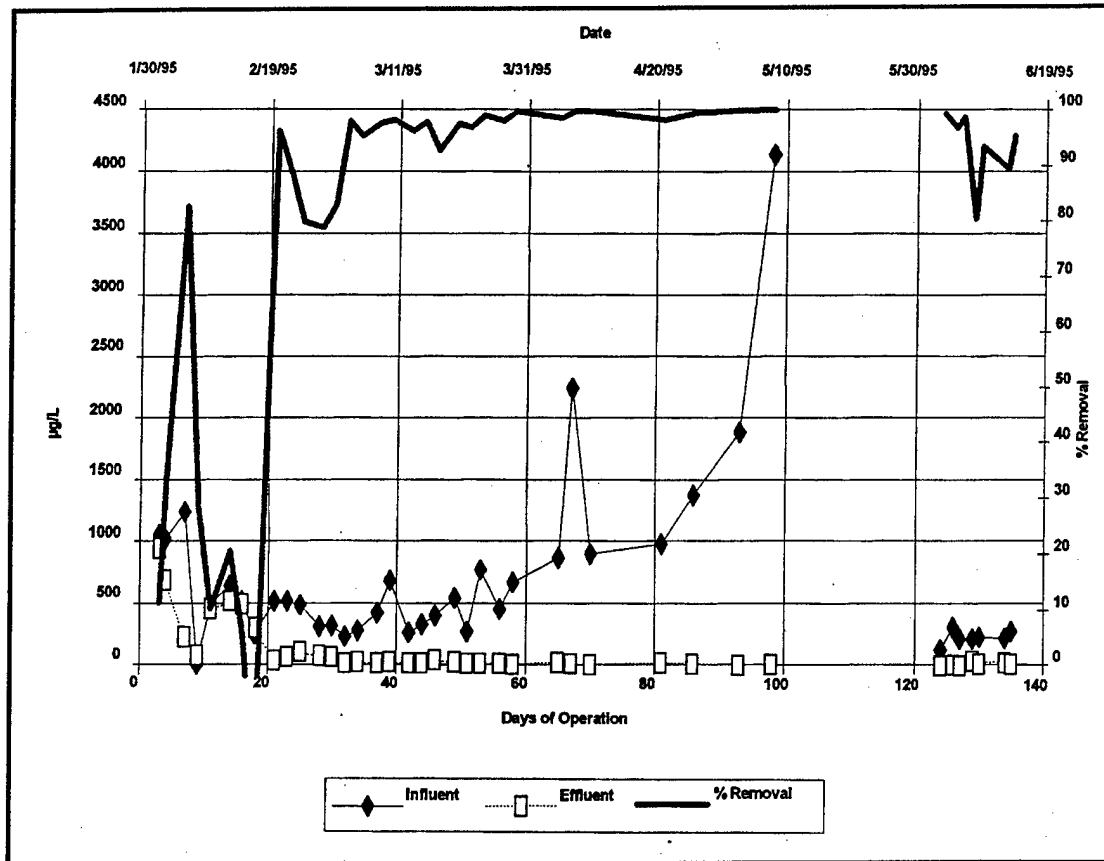


Figure 17. Ethyl acetate removal data for column 3.

The removal efficiencies of the minor compounds were better for Column 3 than for Column 2b (Table 4.9). For Column 2b, the removal data for ethyl alcohol, isobutyl acetate, toluene, and mixed xylenes ranged from 60 to 80 percent. However, the data for n-butyl acetate, 2-methyl-1-propanol and n-butanol were inconclusive and consequently were not presented. The GC analytical results for Column 3, with the concentration of ethyl acetate at a lower level, lead to better quantification of the minor constituents. For Column 3, removals of >90 percent were observed for all of the components except for toluene and xylenes, which were >30 percent.

Column 3 was washed twice during its operation, on day 63 and day 99. The first wash was not very effective, and a considerable amount of biomass remained on the medium. The wash consisted of the following: 15 L of a 1/10 nutrient solution (Appendix C) being added to the column and sparging air at a rate of 35 L/min through the column bed. After 15 minutes, the leachate was removed and the procedure was repeated. The performance of the reactor was not affected and removal remained high. On day 99, a more thorough wash as described above for Column 2b was performed. This procedure proved to be very effective, such that no biofilm could be detected visually. After washing, the re-

actor was placed in a stand-by mode and the column was treated identically as described above for Column 2b until day 120.

On day 120, after a 3-week stand-by period, a small amount of glucose (3 g) was added to the leachate before restoring the feed to the column. The recycle pump was put on a timer to recycle 5 min/hr. The sugar was added with the logic that it might activate the micro-organisms that were present. After 24 hours, the feed gas was restored to the column, but consisted of ethyl acetate only. The loading was the same as Column 2b, $22.1 \text{ g/m}^3\text{-hr}$ ($350.8 \text{ } \mu\text{g/L}$), for 20 hr/day. This column also responded well, with >90 percent removal being observed within 24 hours of start-up (Figure 17). The column was shut-down on day 136. No headloss was observed during this time period.

Column 4a

Column 4a was the first biofilter constructed, and was similar to Column 1 and 2a. It contained approximately 290 g of the cubic medium with a bed height of 175 to 180 cm. Table 18 gives the operational summary for Column 4a. Figure 18 shows the ethyl acetate treatment data.

The retention time for the column was 2 minutes throughout all days of operation. It was inoculated with 1 L of previously isolated ethyl acetate degraders and 500 ml of nutrient solution. The leachate was recycled continuously at 260 ml/min for 24 hours. On Day 2, another 1 L of ethyl acetate degraders was added and the recycle rate was increased to 420 ml/min. This resulted in an approximate inoculation of 11.1 percent on bed volume basis. The leachate was left on continuous recycle until day 12, at which time it was placed on a timer and recycled for 5 min/hr. The airflow was upward and the target leachate pH was initially 7.

Table 17. Column 4a operational summary (reactor set-up with cubic medium, airflow was upflow, target pH = 7).

Date	Time (days)	Airflow (L/min)	Loading ($\text{g/m}^3\text{-hr}$)	Leachate pH	Recycle Rate (420 ml/min)	Bed Height (cm)	Headloss (cm)
11/7	1-28	7.5	55	5.97-7.90	constant	—	0-50
12/5	29-31	7.5	55	4.99-7.41	once/day	—	15-32
12/8	32-42	7.5	55	6.52-8.50*	5 min/day	—	4-60
12/20	44	Washed column.					
12/21	45-59	7.5	55	7.02-8.20	15 min/day	115->105	0.8->man
1/4	Reactor shut-down and medium was washed and squeezed.						
*Airflow reversed from upflow to downflow on day 32; pH target changed from 7 to 8 on day 42.							

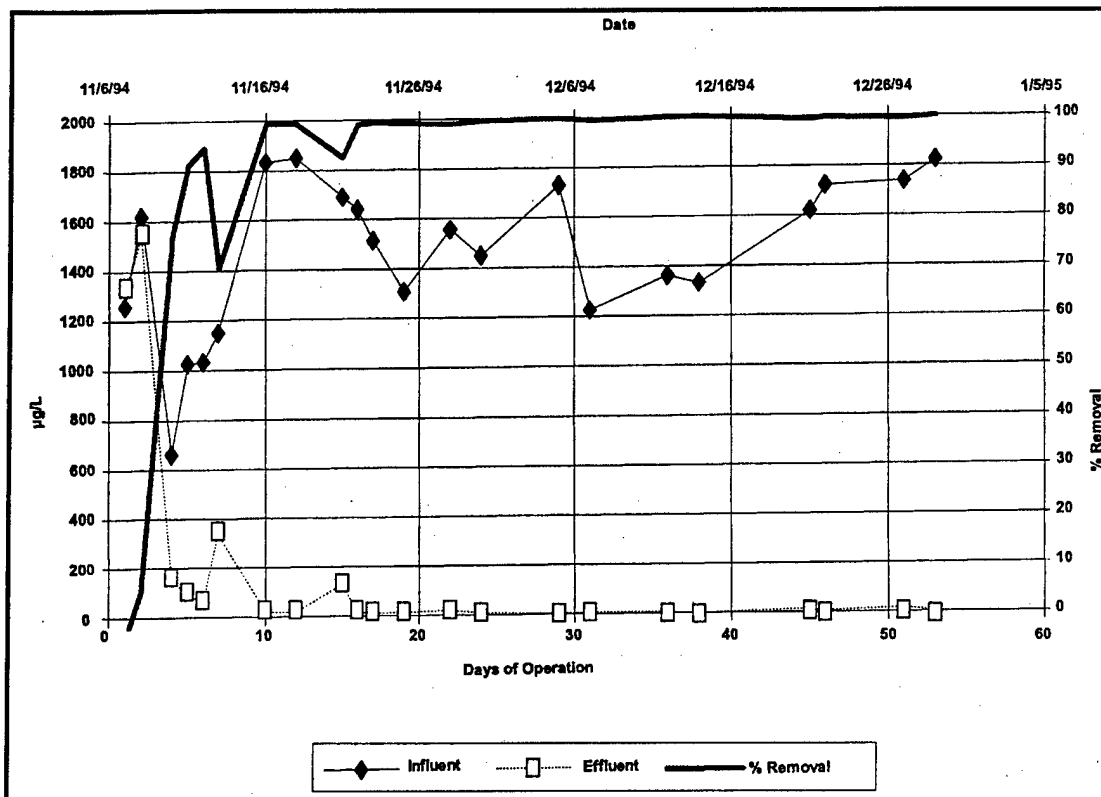


Figure 18. Ethyl acetate removal data for column 4a.

The loading on the column was $55 \text{ g/m}^3\text{-hr}$ ($1603.6 \text{ } \mu\text{g/L}$). The removal efficiency of ethyl acetate reached >90 percent on day 10 and the high removal was observed. The column was washed once, on day 44, as described in the methods section. The decision to wash the column was made based on the high headloss experienced. Also on day 44, the direction of the airflow was reversed and the leachate target pH was increased to 8. After the column was washed, the efficiency immediately went back up to >90 percent removal and the leachate was only recycled 15 min/day until it was shut-down on day 59. Shut-down was due to high headloss.

Column 5

Column 5 was the fourth column constructed and was set-up similar to Columns 1, 2a and 4a. It contained approximately 290 g of the cubic medium, had a bed height of 175 to 180 cm, was operated in the upflow air mode and the leachate was initially maintained at a pH of 7. Table 19 gives a summary of Column 5's operational conditions. Figure 19 shows removal efficiency data.

The retention time on the column was 2 minutes for days 1 to 45. It was inoculated with 15 ml of leachate from Column 2a and 1400 ml of nutrient solution,

representing a 0.1 percent inoculation. There was an extraneous crimp top stuck in the bottom of the reactor for the first 4 days of operation, which resulted in the leachate/inoculum being recycled at a rate less than the target of 260 ml/min. This had an impact on the start-up such that the slow start was noticeable and unexpected. The problem was corrected on day 4 and the leachate retargeted to a flow rate of 260 ml/min. From day 8 to 38, the leachate flow target was 260 ml/min for 15 min/day. From day 39 to 45 the recycle pump was put on a timer and the leachate was recycled 1 min/hr, which caused the headloss to increase, so it was switched back to 15 min/day.

Table 18. Column 5 Operational Summary (reactor was set-up with cubic medium, airflow was upflow, target pH = 7).

Date	Time (days)	Airflow (L/min)	Loading (g/m ² -hr)	Leachate pH	Recycle Rate (260 ml/min)	Bed Height (cm)	Headloss (cm)
11/30	1-8	7.5	110	4.99-7.25	constant	—	0
12/8	9-38	7.5*	110	6.06-8.20*	15 min/day	175->147	0-5
1/7	39-45	7.5	110	6.15-8.42	1 min/hr	17->127	2-15
1/14	46-62	15	110	6.19-8.52	15 min/day	122->117	1-20
2/2	65	Washed column.					
2/3	66-72	15	150*	7.20-8.29	15 min/day	117->100	48 - >50
2/9	Reactor shut-down and medium was washed and squeezed.						

* Airflow reversed from upflow to downflow; pH target changes from 7 to 8 on day 10
 *reconnected improperly after washing, not fed properly from day 66-72

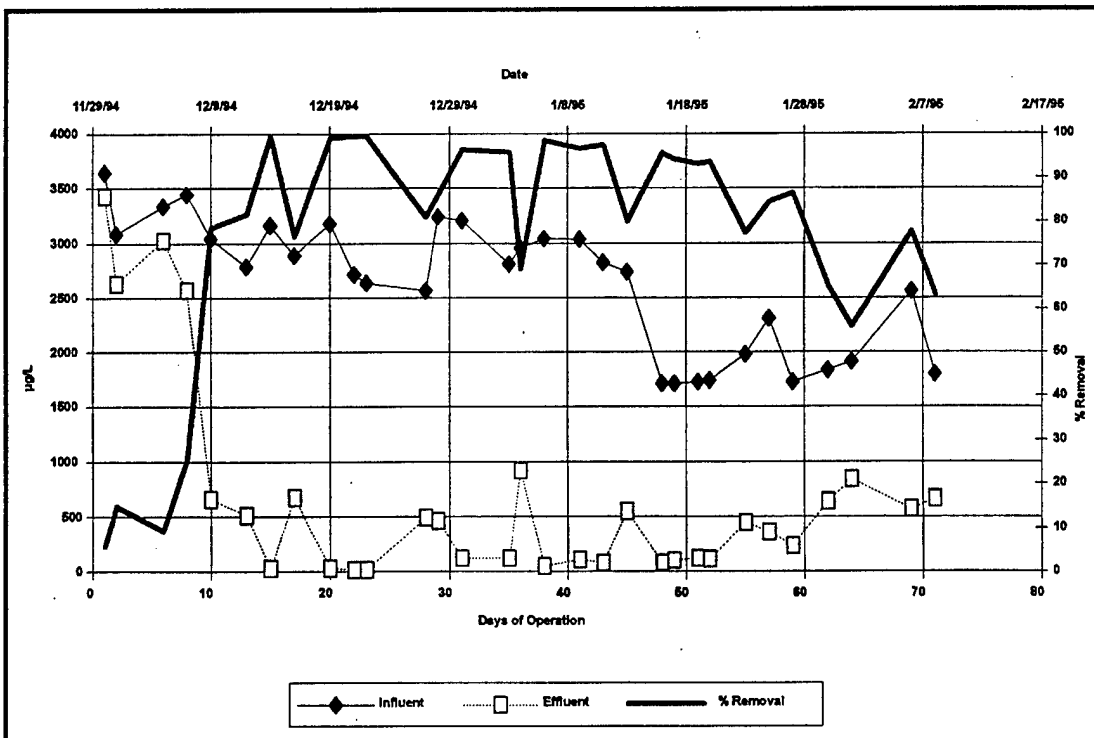


Figure 19. Ethyl acetate removal data for column 5.

The target pH for the leachate was increased to 8 on day 10 and the airflow was reversed on day 11. Loading of ethyl acetate on the column was initially $110 \text{ g/m}^3\text{-hr}$ ($3207.1 \text{ } \mu\text{g/L}$). Removal was extremely low considering the loading and slowly increased until it was >80 percent around day 10 (Figure 19). It reached >90 percent on day 15, but did not consistently remain there and fell to 80 percent. It remained like this until day 60, at which time removal efficiency began to drop off until it fell below 60 percent on day 65.

It was attempted to wash the column, as described in the Methods section on day 65, to try and restore removal efficiency. After washing, the headloss increased substantially from 20 cm to 48 cm. Although the washing procedure removed most of the biomass from the medium, visual inspection revealed that the washing procedure and set-up of the column allowed the medium to absorb a lot of liquid. After washing, the column's recycle pump was accidentally left on for 2 hours, which resulted in the liquid from the manometer being forced into the reactor. In addition to this, the feed was not restored properly resulting in a lack of feed. The column was shut down on day 72.

Square-Wave Loading

Table 20 gives an operational summary of the two columns fed under square-wave loading conditions, Columns 4b and 6. Mass balances were also done on these columns. Table 21 lists the results. Each column will then be discussed in detail, including a summary of each test condition, any changes made in the column operation, and the results of the changes.

Column 4b

Column 4b, the seventh biofilter constructed, was set-up with the new cylindrical annular medium. The reactor was built with the PVC plates separating the three stages. The first stage (top) contained 190 g of medium, the second stage (middle) had 130 g, and the third stage (bottom) 140 g. The bed height for the column was 67 cm, 51 cm, and 57 cm for the respective stages. The retention time of the column was 1 min, the airflow was downflow, and the target leachate pH was 8 (maintained throughout the experiment). Table 22 summarizes operational conditions for Column 4b. Figure 20 shows removal efficiency data.

The column was inoculated with 15 ml of leachate from Column 3, 50 ml of nutrients and 1.435 L of water, a 0.1 percent inoculation on a volume basis. This was recycled over the column at a rate of 260 to 420 ml/min for a period of 34 days. After this time the leachate pump was put on a timer and the leachate was recycled 15 min/hr for the duration of the experiment.

This reactor was set-up to obtain information on square-wave loading. The column was fed ethyl acetate for 5 hrs/day at a loading rate $50 \text{ g/m}^3\text{-hr}$ ($801.8 \text{ } \mu\text{g/L}$). During the first 30 days the reactor was in operation, the removal was <80 percent and sporadic. The influent concentration was fairly constant, but because it was so low, the biomass took a long time to establish itself on the medium.

Table 19. Results of the mass balance analyses for columns 4b and 6.

	Column 4b	Column 6
Ethyl Acetate IN/Target (g)	338	41
Ethyl Acetate IN/GC Data - actual (g)	279	31
Ethyl Acetate OUT/GC Data - actual (g)	85	10
Ethyl Acetate TREATED/GC Data - actual (g)	195	21
Total Solids OUT (g)	187.4	92.8
Total Solids (g TS/ g Ethyl Acetate IN/GC Data - actual)	67.1%	295.9%
Total Solids (g TS/ g Ethyl Acetate TREATED/GC Data - actual)	96.1%	435.8%
Total Volatile Solids OUT (g)	22.8	6.6
Total Volatile Solids (g TVS/g Ethyl Acetate IN/GC Data - actual)	8.2%	21%
Total Volatile Solids (g TVS/ g Ethyl Acetate TREATED/GC Data - actual)	11.7%	31%
Grams of Nitrogen USED	21.5	12
N USED (g N/g Ethyl Acetate IN/GC Data - actual)	7.7%	38.3%
N USED (g N/g Ethyl Acetate TREATED/GC Data - actual)	11.1%	56.5%
Grams of Phosphorus USED	4.4	4.3
P USED (g P/g Ethyl Acetate IN/GC Data - actual)	1.6%	13.8%
P USED (g P/g Ethyl Acetate TREATED/GC Data - actual)	2.3%	20.3%
Grams of Buffer as CaCO_3 USED	98	61
Buffer USED (g CaCO_3 /g Ethyl Acetate IN/GC Data - actual)	35.1%	195%
Buffer USED (g CaCO_3 /g Ethyl Acetate OUT/GC Data - actual)	50.3%	287.3%

Table 20. Column 4b operational summary (reactor set-up with cylindrical annular medium and PVC plates separating sections, airflow was downflow, target pH = 8).

Date	Time (days)	Airflow (L/min)	Loading* ($\text{g/m}^3\text{-hr}$)	Leachate pH	Recycle Rate (260-420 ml/min)	Bed Height (cm)	Headloss (cm)
2/28	1-45	15	50 @ 5 hr/day	4.15-10.10	constant	67/51/57	0
4/14	46-101	15	50 @ 5 hr/day	5.65-9.50	15 min/hr	54**/51/56	0
6/9	102-116	15	50 @ 10 hr/day	—	15 min/hr	54/51/56	0
6/23	Reactor shut-down and medium was washed and squeezed.						
*Glucose Additions: 30 g on days 25, 26, 31, 38 and 45; 15 g on day 49; 3 g on days 84, 86-88, 91, 93-104, 108-109, 112-115							
**removed some of the medium from the first stage							

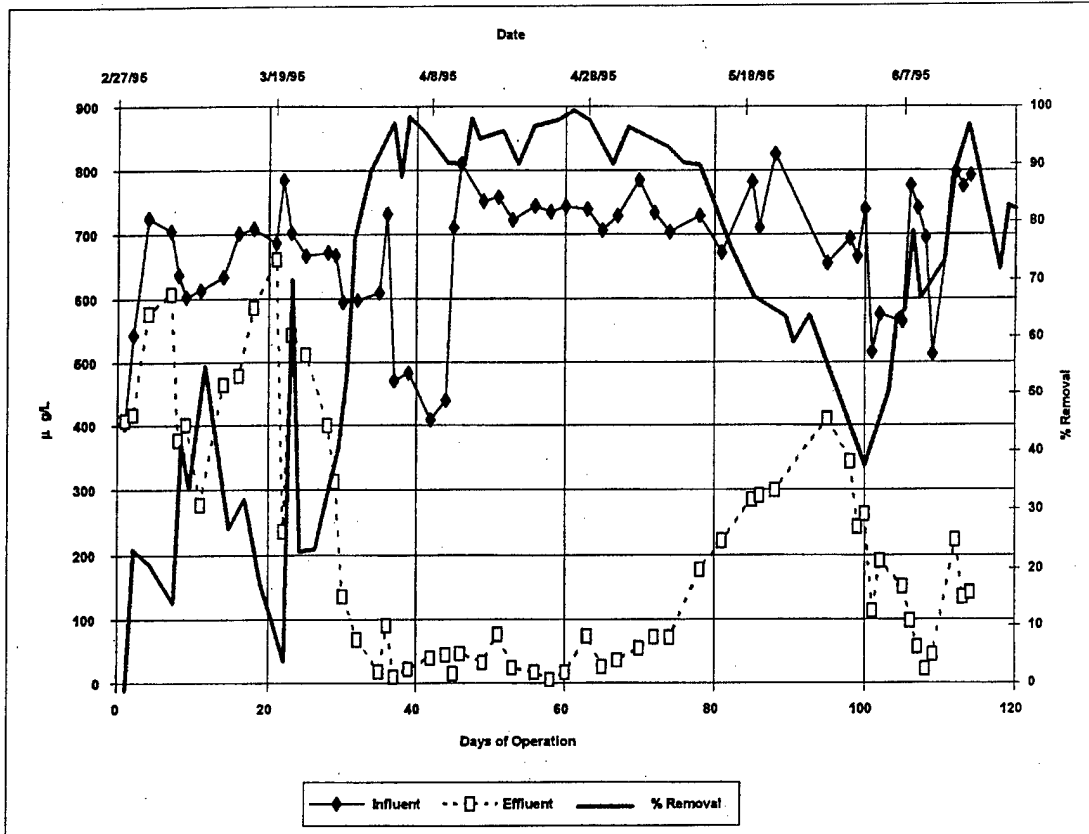


Figure 20. Ethyl acetate removal data for column 4b.

It seemed the column was "hungry" and glucose was added as a secondary substrate on day 24. Table 22 lists the amounts of glucose and the days that it was added. Once the biomass was established, the removal was >90 percent. This was evident from days 24 to 49. High removal efficiencies were retained even though no supplemental glucose was added from day 50 to 78.

From day 78 to 83, the column efficiency slowly decreased. The leachate was observed under the microscope and the density of the organisms was low. It was decided to give the microbes 3 g of glucose per day to provide a more constant food source. This was done from day 84 to 115, with only a few exceptions (see note, Table 22). By day 102, this had not been observed to increase the density of the organisms in the leachate and the removal efficiency remained low. At this time, it was decided to feed the column the same loading, except to feed it for 10 hrs/day versus 5 hrs/day. This seemed to help the removal efficiency and it slowly rose from a low of 40 percent on day 100 to >90 percent on day 115 (Figure 20). The column was shut-down on Day 115.

Column 6

Column 6 was the eighth and final biofilter constructed. It was set-up similar to Column 4b with only slight differences in the amount of the cylindrical annular

medium that was used in each stage. The first stage (top) contained 180 g of medium, the second stage (middle) had 145 g and the third stage (bottom) 180 g. The bed height for the column was 65 cm, 55 cm, and 57 cm for the respective stages. The retention time, airflow, and leachate pH were the same as stated previously for Column 4b. Table 24 and Figure 21, respectively give a summary of Column 6 operational conditions and removal efficiency data.

Before inoculating the column, it was flooded with 1/10 nutrient solution (1 L of nutrients (Appendix C) and 9 L of water). A decision was made to try this and see if it helped speed up the start-up of the column, since it had been noted that the bed of Column 4 looked dry when it was started. Column 6 was then drained and inoculated with a 0.1 percent inoculum on a volume basis. The inoculum included 15 ml of leachate from Column 1, 200 ml of nutrients, 30 g of glucose and water to 1.5 L. The glucose was added to help supplement the low loading of ethyl acetate, with the intention of helping the biomass establish itself more rapidly than was observed in Column 4b. The inoculum was recycled over the column at a rate of 260 ml/min for a period of 14 days. After this time, the leachate pump was put on a timer and the leachate was recycled 15 min/hr for the duration of the experiment.

Column 6 was also set-up to obtain information on square-wave loading dynamics, except at a much lower loading rate of $9.4 \text{ g/m}^3\text{-hr}$ ($150.3 \text{ } \mu\text{g/L}$). As with Column 4b, it was only fed for 5 hrs/day at this loading rate. During the first 30 days the reactor was in operation, the removal was <80 percent and sporadic (Figure 21). The influent concentration was fairly constant, but because it was so low, the biomass took a long time to establish itself on the medium. The start-up time to obtain 90 percent removal was 9 days. Once the biomass was established, the removal stayed around 90 percent.

Table 21. Results of off-gas monitoring of columns.

Column	Days of Operation	Days Monitored	Feed	Loading ($\text{g/m}^3\text{-hr}$)	Avg. CFU Observed per Sampling ($0.283 \text{ m}^3(10 \text{ ft}^3)$)
1	11/30/94-ongoing	70-198	Ethyl Acetate	6.4-110	5
2b	1/31/95-6/15/95	42-136	Ethyl Acetate	12.5-25	4
3	1/31/95-6/15/95	42-136	Low Mix	75-100	11*
4b	2/28/95-6/23/95	14-116	Ethyl Acetate	50 @ 5 hr/day	10
6	3/28/95-6/1/95	7-80	Low/High Mix	9.4-15 @ 5 hr/day	7

*A monitoring unit that contained 177 CFU is not included in this average.

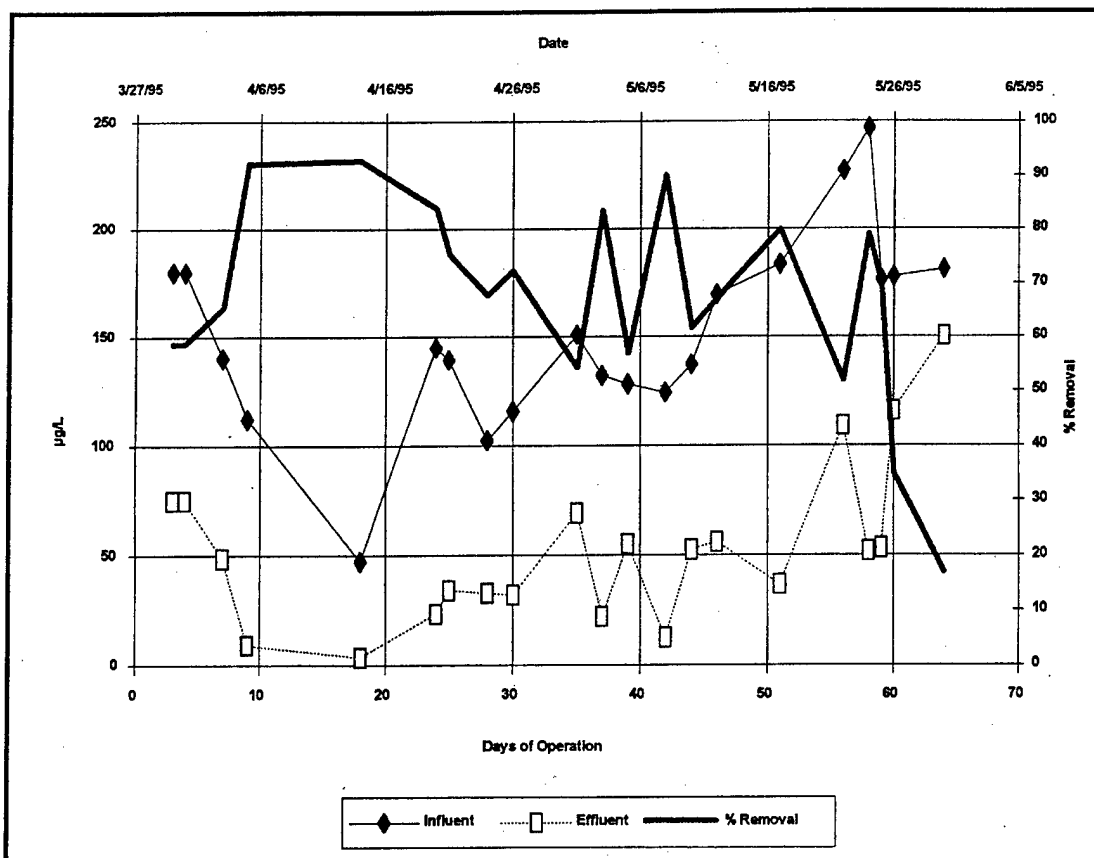


Figure 21. Ethyl acetate removal data for column 6.

In an attempt to maintain high removal efficiency, 30 g of glucose was added to the column once per week when changing out the leachate. It was thought that this might provide the microbes with something to eat when the column was not being fed ethyl acetate. The leachate was observed under the microscope on the days of glucose addition and again on the days after glucose addition. Surprisingly, the density of the organisms did not appear to increase. A slight decrease in removal efficiency was observed on day 21. It was thought that perhaps too much glucose was being fed to the column and this could interfere with ethyl acetate removal efficiency. The last glucose added was on day 21. Thereafter, glucose addition to the leachate was terminated. The removal efficiency continued to decline from day 21 to 65. The column was shut-down on day 65.

Fungal Monitoring

Five columns were monitored periodically for eucaryotic emissions during the course of the laboratory study. Each of these columns was tested under different operational parameters. Table 24 shows the days the columns were monitored and the average colony forming units (CFU) observed per sample. Each sample represents 0.283 m³ (10 ft³) of air. During the course of study, each column un-

derwent a number of operational perturbations, including the extended shut-down periods on Columns 2b and 3, as listed in Table 25.

Raw counts of the CFU observed for all the column samples and for house air are presented in Table 26.

Fungal monitoring was performed routinely for each column once per week. In some cases, several samples of the same column were taken on a given day to investigate statistical aspects of the sampling regime. Of the 87 samples that were prepared, only two had CFU counts greater than 50. Figure 22 shows the frequency distribution of total eucaryotes in the biofilter off-gas. Forty percent of the time no CFUs were found on the monitoring units and 94 percent of the sampling monitors contained less than 20 CFUs.

Table 22. Column perturbation summary.

Column	Perturbation
1	Fed ethyl acetate only. On 3/14/95 increased SGV from 110 m/hr to 226 m/hr.
2b	Fed Low Mix of components from 1/31-5/9/95. Washed on 5/9/95.
	No feed to column from 5/9-5/30/95. Fed ethyl acetate from 5/31-6/15/95.
3	Fed High Mix of components from 1/31/95-5/9/95. Washed on 4/4/95.
	Washed on 5/9/95.
	No feed to column from 5/9-5/31/95. Fed ethyl acetate from 6/1-6/15/95.
4b	Fed ethyl acetate only. Square-wave loading, 5 hr/day, 2/28-6/9/95.
	Increased Square-wave loading from 5 hr/day to 8-10 hr/day from 6/9-6/23/95.
6	Fed ethyl acetate only. Square-wave loading, 5 hr/day, during all days of operation.

Table 23. Observed CFU fungus-like (fl) and yeast-like (yl) CFU per 0.283 m³ (10 ft³) of air sampled.

Date	Column 1		Column 2b		Column 3		Column 4b		Column 6		House Air	
	FL	YL	FL	YL	FL	YL	FL	YL	FL	YL	FL	YL
2/7/95	1	0									0	0
2/10/95	0	0										
3/7/95	0	0										
3/13/95	1	0	0	0	0	0	46	0				
3/20/95	6	0	0	0	2	0	8	0				
3/27/95	9	0	0	0	0	0	2	4				
4/4/95	1	0	0	0	0	0	0	0	0	20		
4/10/95	0	0	0	1	9	1	7	0	0	1		
4/17/95	5	0	6	3	3	0	10	0	0	0	0	0
5/2/95	0	0	0	0	20	0	5	0	5	0	0	0
5/9/95	11	0	1	0	1	0	0	9	5	13	6	0
5/10/95			2	0	0	0						
5/15/95	42	0	0	0	19	0	4	16	1	19	0	0
5/22/95	0	0	4	0	3	0	0	0	0	0	4	0
5/30/95			0	0	6.25*	0.25*					0	0
5/31/95	6	0	0**	0**								
6/1/95			1	13	19.5#	0#	0	0	0	0		
6/2/95												
6/5/95	0	0	2	0	4	0	7	10	0	2	11	0
6/6/95												
6/7/95			5	0	0	20						
6/15/95	0	0	6 [⊙]	12.5 [⊙]	19 [⊙]	26 [⊙]						

* Average four times monitoring.
** Average of three times monitoring.
Average of four times monitoring. An additional monitor with 177 CFU was not averaged into this number.
[⊙] Average of two times monitoring.

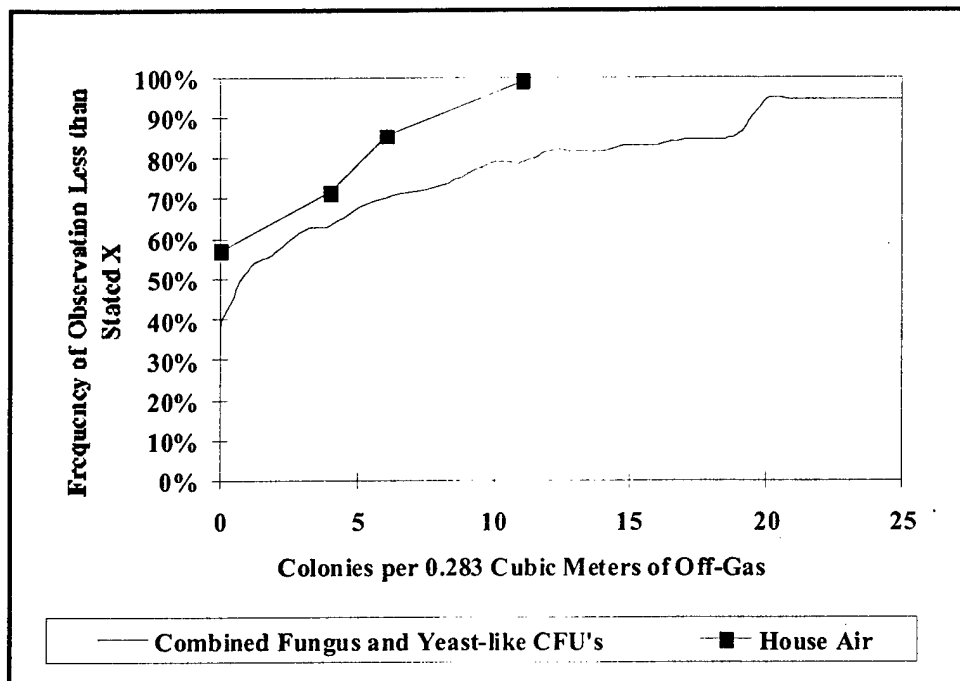


Figure 22. Frequency distribution of total eucaryotes in biofilter off-gas.

5 Discussion

This section addresses the results from the laboratory phase of the CERL work performed in preparation for the installation of the full-scale biofilter at the Lake City bullet tipping production plant.

Physical Media Testing

Three tests were performed on the medium and the columns: buffer capacity, ethyl acetate adsorption capacity, and airflow characteristics of the packed columns. The implications of these tests are presented below.

Tracer Study

The tracer results demonstrate one aspect of the feasibility of modeling the biofilter columns. The cylindrical medium used in a majority of the lab work performed has stronger plug flow characteristics than the cubic medium. The plug flow character of the cylindrical medium may have been even greater if the medium pieces had been of a smaller circumference, or if the laboratory column were of a larger diameter. A small amount of tracer was observed to pass through the columns in a short period of time, which is usually attributed to a "sidewall effect" of the column, allowing some of the gas through the column untreated. It is not anticipated that there will be "short circuiting" of gas flow in the large-scale reactor.

Medium Breakthrough Study

The breakthrough study shows that the removal of contaminants from the vapor stream by the physical process of absorption will be a minor source of removal. The gas stream expected at Lake City should be in the range of 0.03 lb/1000 cu ft (500 µg/L) at an airflow rate of 1000 scfm (28.3 m³/minute). The observed ethyl acetate sorption to the medium was 3 lb/1000 cu ft (0.72 g/15 L) so the breakthrough of the contaminants will occur in less than 2 hours. The reactor system is expected to operate for at least 1 year; the medium life is anticipated to be 3 to 5 years. At an average medium life of 4 years, with a 20 hour per day, 4 day per week, 45 week per year production operation, removal by sorption would account for less than 0.02 percent of the mass of contaminant removed.

Buffer Capacity Determination

The buffer capacity test on the medium showed that some buffering capacity resides within the medium. This additional buffering capacity is an important feature of the reactor, as it can provide a more stable environment for the microorganisms. Enhancing the medium characteristics to provide better buffering capacity will be an important step towards a more reliable and stable reactor system. A medium with the ability to provide a stable pH range during reactor operation, shut-down, cycling, or upsets will result in the microbes functioning in a more predictable and consistent manner. However, it will be seen that the total capacity of the column medium (roughly 0.15 g CaCO₃ buffer capacity) is small compared with the total buffer added to the columns during operation (42-178 g CaCO₃ buffer capacity).

Inoculation and Column Start-up

The key to a successful start-up of the columns was directly related to an active inoculum being applied to the columns, as shown by the data in Tables 7. and 17. This section will discuss the inoculum isolation procedure, as well as what determined a successful inoculation and start-up.

Inoculum Isolation

The development of an inoculum from common soil points to the versatility of natural sources of inoculum. The formation of an inoculum from a source such as this, without cultural separation and purification, results in a mixed culture. Mixed cultures are thought to be more resilient to microbial upsets that could cause a bioengineered system to shut-down. The removal of the target gases proved to be possible without a specific pure culture for each contaminant.

Inoculation

Under steady-state mass loading ranges that were greater than 25 g/m³-hr (400.9 µg/L), inoculation and start-up of the columns was accomplished by adding the inoculum and nutrient/buffer solution to the column and allowing it to recycle through the column in the presence of the contaminant stream being treated. Removal of the target compound in excess of 80 percent can be anticipated in a 9-day time frame.

The first columns that were set-up, Columns 2a and 4a, were inoculated with a large volume of starter culture. This was done to ensure a successful start-up of

the columns. It was determined that using this amount of inoculum, scaled to field reactor volumes, would prove to be an unreasonably large volume, requiring between 2200 and 3800 L for the 1000 cu ft biofilter. Faced with this potential problem, an effort was made to determine the smallest reasonable volume of inoculum that would provide a successful field start-up. The remainder of the columns were started with a culture volume of 0.1 percent on a volume basis. This amount was determined to be adequate, although start-up generally took a few days longer on most columns than had been seen on Columns 2a and 4a. In one case, however, good removals of ethyl acetate were achieved within 4 days (Column 1). Column 1 appeared to be a special case since a very large loading of ethyl acetate, $110 \text{ g/m}^3\text{-hr}$ ($2304 \text{ }\mu\text{g/L}$), may have accelerated the growth on the column.

When low loading rates were applied to the biofilter, or the biofilter was started up under square-wave loading, the low mass loading did not seem to be conducive to the rapid development of a biofilm. Biofilm formation appeared to be hindered by the relatively low quantity of the carbon source that was available to the micro-organisms. In the columns where low loading was not resulting in a healthy biofilm, a supplemental carbon source was added to the leachate to circulate over the biofilter bed. The supplemental carbon source was glucose. The glucose apparently gave the micro-organisms sufficient metabolite to establish an initial biofilm. Once the biofilm was established, the addition of the supplemental carbon source was reduced or eliminated.

Column 4b, one of the square-wave loaded columns, was initially started without glucose addition. After 24 days of poor ethyl acetate removal, a glucose addition regime was started. Within a few days, better results were observed, culminating in full start-up by day 35. The other square-wave loaded column, Column 6, also had glucose added to it and start-up appeared to occur in 9 days. The high removal of ethyl acetate on Column 6 was short lived and never thereafter achieved a consistently high removal efficiency. It would appear that the overall loading of ethyl acetate, $9.4 \text{ g/m}^3\text{-hr}$ ($150.3 \text{ }\mu\text{g/L}$) for 5 hrs/day, was too low for a healthy biomass film to become fully established, even with the additional glucose. No attempt was made to increase the amount of glucose that was added to the system. Therefore, no conclusion can be drawn as to what effect this would have had on the system at this low loading.

Column Performance

The majority of the work performed in the lab was done on ethyl acetate alone. This work was performed at three different airflow rates (superficial gas veloci-

ties) and multiple mass feed concentrations. Two columns were fed a contaminant feed that was representative of actual exhaust gas samples obtained from Lake City AAP. The first of these columns was set up to treat the mixture of compounds in approximately the proportions existing in the vapor stream at Lake City AAP. Analytical uncertainties in determining the removal of the minor constituents in this test led to the creation of a second mix, which still had the same proportions of minor constituents, but contained less ethyl acetate.

Steady-State Removal of Ethyl Acetate

The observed contaminant removal in the laboratory biofilter columns containing only ethyl acetate varied from 76 to 93 percent. When the start-up periods were excluded, the removal was 86 to 96 percent. There was no strict correlation between removal and mass loading. The columns appeared to enjoy ethyl acetate very much, with the micro-organisms metabolizing as much as could be fed. More importantly, the columns generally had very consistent removal performance during the course of their trials. The performance of Column 4a demonstrates this (Figure 18). Once the start-up phase was complete, the removal of ethyl acetate from the vapor stream was consistent, with the exception of one dip in performance, 99 percent or more. Column 4a demonstrated that a biofilter with proper moisture, nutrient, and buffer control would exhibit maximum operational removal performance.

Figure 23 further exemplifies the consistency of the performance of steady-state ethyl acetate removal. In this figure all nonstart-up data are plotted for all steady-state columns as removal versus loading ($\text{g}/\text{m}^3\text{-hr}$). The plotted line represents the best fit to all column performance of approximately 99 percent.

Removal of Contaminant Mixes

The two columns fed the mix of compounds representative of the waste gas at Lake City AAP demonstrated that ethyl acetate is degradable, even when other compounds are present. It was anticipated that the components (toluene and xylenes) would have shown better removals than the approximate range of 60 percent for Column 2b and 35 percent for Column 3, especially since additional BTEX degrading organisms were added to both columns from days 63 to 98. The minor constituents removal efficiency of Column 2b was more difficult to monitor than Column 3, which had a higher percentage of the minor constituents. Overall, based on the mass loading, removal of >90 percent of the amount of waste loaded onto the columns was consistently observed. It is encouraging that ethyl acetate degradation does not seem to be impaired by the presence of these contaminants. The inability to degrade high levels of the other components may be

due to a number of factors. One organism cannot be expected to degrade every compound effectively. Perhaps the large loading of ethyl acetate creates the condition where the organisms that consume compounds other than ethyl acetate are at some disadvantage. This is exemplified by Columns 2b and 3, which were fed the "Low and High" mixes, respectively. When fed higher concentrations of ethyl acetate, the minor components removal efficiencies increased. Therefore, it should be expected that the field-scale biofilter has the potential to perform satisfactorily if the production plant personnel should desire to change the component mix somewhat.

Dynamic Loading Removal

The key to successful application of biofilters in cyclical operation modes lies in understanding how biofilters respond to changes in the concentration of contaminant that is present in the gas flow. In this study, we operated some of the test columns under square-wave loading conditions.

Dynamic Mass Loading Removal

During the study, a total of four different dynamic flow tests were performed. Columns 4b and 6 were operated on loading cycles of 5 hours in length, 5 days per week, for the majority of their respective trial runs. Columns 2b and 3 were loaded for 20 hours per day for the last 2 weeks of their respective operational cycles. The average removal for these two columns was 92 and 93 percent respectively.

The Column 4b trial run took an exceptionally long time to start-up. In fact, start-up did not occur during the first 24 days. Start-up only began after a glucose addition regime was initiated. The initial start-up phase of the column run took 35 days to complete. From day 35 until day 80, the biofilter column removal was generally over 90 percent and relatively stable (Figure 20). Removal began to drop off at this time and attempts were made to re-establish performance by adding varying amounts of glucose. These attempts failed, and on day 102, the feed duration was changed to 10 hours per day. The column responded to this and removal increased to over 90 percent by day 115. The need for a supplemental carbon source at start-up was established by the experimental results of Column 4b. Without the supplemental carbon source, it is not certain that stable removal performance would have been initiated.

Column 6 was operated on a dynamic loading pattern of 5 hours per day and a very low mass loading, $9.4 \text{ g/m}^3\text{-hr}$ ($150.3 \text{ } \mu\text{g/L}$) for a majority of the experimental

trial. The addition of 30 g of glucose/week was not found to cause this column to perform consistently at a high removal percentage at this low dynamic feed rate. It was felt that the supplemental carbon would assist the start-up and maintenance of a healthy biofilm in the lab column, but this simultaneous feed of contaminant and glucose did not improve this low mass loaded column performance. Figure 21 shows the removal performance of Column 6.

Shut-Downs

During the course of the experimental work, it became evident that the Lake City AAP would, on occasion, shut-down for periods of time beyond the normal 3-day weekend. These shut-downs would have some undetermined effect on the biofilter and required investigation. The contaminant feed was shut off to Columns 2b and 3 during course of operation. The flow of house air was continued and the packed beds were kept moist by continuing the regularly scheduled leachate recycle. The columns were left in this operational mode for a period of 3 weeks. At the end of 3 weeks, glucose was added to Column 3 before re-establishing feed. Glucose was added to Column 3 to determine if a supplemental carbon source would speed removal start-up. Glucose was not added Column 2b. Both columns were fed ethyl acetate only at a rate of $22.1 \text{ g/m}^3\text{-hr}$ ($350.8 \text{ }\mu\text{g/L}$) 20 hr/day. There is no visual evidence that the addition of a supplemental carbon source was necessary to ensure the ethyl acetate would be efficiently removed at restart. Both columns achieved >90 percent removal within 1 day of re-addition of ethyl acetate feed.

Washing Cycles

Initially, it was thought that the columns would need to be washed on a regular basis, perhaps as often as once per month. Early in the study, it was discovered that this was not going to be the case; several of the columns did not need frequent washing. It was decided to only wash the columns as needed, which was indicated by a decrease in the removal efficiency of a column or high headloss. The first columns started (Columns 2a, 4a, and 5) contained cubic medium. On backwashing the medium, the column bed collapsed and caused column failure. Columns 2b and 3 were also washed, but they contained the new reinforced media and the columns were modified to have separating plates between the stages. These columns demonstrated that the engineered medium had the capacity to be washed, something that is of utmost importance especially with biofilters that may experience high loadings.

Headloss may not be a good indicator of the need for washing with the cylindrical annular medium, as very little headloss was ever noted with this bed packing material. Disregarding the experiences with Columns 2a, 4a, and 5 and relying only on the experiences with cylindrical medium, the following observations may be made. With these columns, we implemented a wash cycle based on a visual observation of need. Simply stated, the biomass on the medium looked thick. Column 3 was loaded at a rate of from 75-100 g/m³-hr (1192-1589 µg/L) and was washed once after 63 days of operation and again after 36 more days. Thus it required two washings for a total of 186,000 g/m³ substrate fed. Column 2b was fed 25 g/m³-hr (400.9 µg/L) for 57 days and 12.5 g/m³-hr (200.4 µg/L) for 41 days. This column could perhaps have gone longer without washing, but was washed on day 99. The total load was 46,500 g/m³ fed. Thus, at some point in between 46,500 and 93,000 g/m³, it would be prudent to consider washing a biofilter.

Washing of Column 2a was performed only after a fungus was allowed to become encrusted on the medium and plug the column. The washing intervention on this column was substantially different than the other column washes and is outlined in Appendix E. In this case, it was necessary to completely disrupt all biological growth to cleanse the column of the fungus so that the biofilter would operate correctly again. It was also necessary to reinoculate this column because all biological activity was destroyed by the washing cycle.

Biomass Yield

The yield of biomass was an important consideration in the laboratory phase of this project. Biological processes produce cells as part of the metabolism of carbon. In a biofilter, respiration increases the cell mass on the biofilter medium as a direct result of this substrate uptake. From the mass balance data obtained in the experiments, between 7.6 and 12 g of dried cell mass were produced for every 100 g of ethyl acetate treated (Tables 11 and 21). From a process point of view, the importance of biomass yield is in scheduling preventative maintenance cycles. The amount of biomass in the leachate will also be a consideration in the sewerage of the leachate from the biofilter system. It cannot be understated that growing cells require nitrogen, phosphorus, and trace minerals, which must be added to the system in proportions consistent with the cell yield.

Nutrient/Buffer Requirements

The MBI medium has a buffer and nutrient component incorporated into its matrix. This research has found that the incorporation of these components

into the structure of the medium creates a surface that the micro-organisms adhere to easily and consequently form a biofilm. The existence of these components in the medium matrix makes the calculation of a mass balance difficult. There is no discernible method to calculate the actual amounts of the buffer and nutrient constituents in the medium that were used to control the pH or that were used by the micro-organisms. We can calculate the mass balance based only of the quantity of these chemicals that were added with the buffer or nutrient solutions.

Nutrient Balance

The observed nitrogen usage by the biofilm in the columns varied between 2.3 and 7.7 g/100 g for the measured influent ethyl acetate and 3.0 to 11.1 g/100 g of the ethyl acetate measured as treated by the biofilter columns. The phosphorus use varied from 1.3 to 1.8 g/ 100 g for the measured influent ethyl acetate and 1.5 to 2.3 g/ 100 g of ethyl acetate measured as treated. These mass balance values of nutrient used are mitigated somewhat by the bio-availability of these macronutrients in the medium complex. A general microbial nutrient requirement ratio to avoid nutrient limitation is usually expressed as $C_{100}N_{10}P$. In grams, this would be 12 g nitrogen and 2.6 g phosphorus per 100 grams of carbon. Based on the amount of ethyl acetate actually fed to the columns, the supplemental nitrogen fed to the columns was between 35 and 118 percent of this idealized amount. The supplemental phosphorus fed was between 92 and 127 percent. From the mass balance numbers on the treated ethyl acetate, nitrogen used in the columns was between 46 and 170 percent and the phosphorus used was between 106 and 162 percent of the anticipated requirements of the biofilm.

The nutrient balance data suggests that the nitrogen needed for the biofilm was provided for sufficiently by the $C_{100}N_{10}P$ "rule of thumb." Only Column 4b used the nitrogen in excess of this amount. Column 4b was fed supplemental glucose, which would increase the need for nitrogen. For phosphorus, the results were somewhat different. The phosphorus used by the biofilm was usually in excess of this rule of thumb, as much as 62 percent in excess. Given the lab results, a better rule for the design of the biofilter systems for this gas stream would be $C_{100}N_{10}P_{1.5}$. This design rule would more accurately reflect how the biofilm, in these experiments, used the nutrients for this gas stream with respect to the sludge or biofilm age, as observed in the laboratory work. Given that the biofilm is capable of obtaining nitrogen and phosphorus from "old" cells that have ceased to function, it is reasonable to assume that, as the biofilm ages, less of the macronutrients will be required. Therefore, the longer the period of time between preventative maintenance cycles, the lower the mass of macronutrients that would be required to maintain the biofilter performance.

Buffer Balance

Of the calculated mass balances, the mass balance of the buffer added showed the most variance. For Columns 3, 4a, and 5 the amount of buffer removed in the leachate was greater than the amount applied. The amount of buffer used on Columns 2b, 4b, and 6 were 25 percent more than the average buffer consumption per gram of ethyl acetate treated that was observed for all columns and all tests during the study. There are three potential explanations for these widely divergent results.

First, there is an indication that the buffer incorporated in the media is available to mitigate the pH changes caused by the acid producing metabolism of the micro-organisms. The bio-availability of the buffer is an advantage of an engineered medium such that it helps the biofilm be more resistant to pH upsets. The observed results from the laboratory experiments showed that some of the buffer contained in the medium was soluble in the leachate. It is anticipated that the amount of buffering capacity will diminish over time and eventually become depleted.

A second reason for the observed buffer mass balance results pertains to the cases when significant amounts of buffer were used relative to the amount of ethyl acetate being treated. The seemingly excessive amounts of buffer used can be explained by the high control point of the pH. Carbonate was chosen as a buffering agent because of the low risk of overdosing. The natural equilibrium of the carbonate system keeps the pH from rising excessively when buffer is added to the leachate. Carbonate's natural alkalinity equilibrium is around 8.3. Therefore, significant buffering capacity is used to keep the pH=8. There is a trade-off apparent for the higher pH to keep the fungus growth in check and the higher amount of carbonate required.

Finally, there is a possibility that carbonate came out of solution as a precipitate in slurry form. Slurry was observed in Columns 4b and 6, and when the leachate was removed, a significant portion of the slurry remained in the column. Since the pH was adjusted based on the leachate sample, excess carbonate may have been added to these columns.

The quantity of buffer required for the columns showed much variability and it would appear to be highly specific to the operating conditions. Of all of the columns, only Columns 1 and 2a provide any reasonable values for the amount of buffer. The results from these columns indicate that about 6.5 g of buffer expressed as CaCO_3 will be required for every 100 g of carbon, as ethyl acetate treated.

Fungal Monitoring

Fungal spores are a concern of potential biofilter users. The uncontrolled release of fungal spores to the open atmosphere could have undetermined health effects. To gather information about the presence of fungal spores, the biofilter columns were monitored on a weekly basis for a significant part of the laboratory trials. A high degree of variability was observed between columns of approximately the same age. This could be attributed to any number of things such as: different loading rates, superficial gas velocities, forms of the medium being used, etc. Several times, multiple samples were taken from the same column, and the results obtained also had a high standard deviation. Multiple sampling and averaging of the results could present a more reliable estimate of the number of eucaryotic CFUs being discharged in the exhaust of a biofilter. However, we have no indication that completely random release can be discredited.

It was anticipated that the number of eucaryotic organisms given off when a biofilter was first started-up would be higher than after a reactor had been running for several weeks. Columns 4b and 6 were tested at start-up and demonstrated a relatively high number of CFU. It is difficult to reach a conclusion about a steady-state column from these data since Columns 4b and 6 were non steady-state columns. For columns that were operated for longer periods of time, such as Columns 1, 2b and 3, the number of CFUs observed on the monitors increased with time of operation. The leveling off of CFUs was expected, but it was not expected for the number of CFUs to fluctuate so much. It was also thought that washing the columns would show an effect on the number of CFU emitted from the biofilters. Although this was shown to be the case both times that Column 3 was washed, it showed no effect on Column 2b. This was expected since washing a column would appear to be comparable to the start-up period of a biofilter. Similar results were obtained after the extended shut-down period of Columns 2b and 3, where Column 2b showed no effect and Column 3 showed a slight increase in the number of eucaryotic emissions. Lastly, although various loading rates of ethyl acetate were fed to the columns and it was thought that this would show some effect on the columns, no correlations between loading rates and CFU could be made.

6 Translation to Field

Biofiltration is not yet an exact engineering science. No literature or scholarly models exist that allow the direct scale-up of a biofilter from known physical constants to a working field scale unit. Given this, the laboratory data we have collected for the past year is invaluable for the installation of a working system. Uncertainties exist, however, about the true make-up of the bullet tipping process contaminant gas stream. When estimates were made on a simple mass balance approach of the gas stream constituents, there seemed to be a substantial difference between the assumed and actual make-up of the gas stream. The contents of the VOC source were taken as the direct make-up of the gas stream without considering how much of the contaminants were caught up in the application. The initial estimates for Lake City AAP indicated that the VOC concentrations would be as high as $137 \text{ g/m}^3\text{-hr}$ ($4000 \text{ }\mu\text{g/L}$). Subsequent testing at the facility resulted in the discovery that the actual concentrations were much lower. Since that time, the Lake City AAP has undergone design changes to its ventilation system, and its production has increased — so the true make-up of the contaminant gas as well as the overall loading to the biofilter has more than likely changed from the data that initial and intermediate estimates were based on. The following sections detail the anticipated installation, start-up, maintenance, and sampling needs that the field unit is going to need.

Field Unit Installation

The biofilter that will be installed at the Lake City AAP, Independence, MO, will be 1000 cu ft in volume. In addition to the cement pad the unit will be placed on, the biofilter will require telephone, electrical, water, and sewer connections. The telephone connection, for the remote telemetry, will be hard wired. The biofilter will have a float switch in the leachate to actuate the water supply or the drain. It will also be equipped with a pH feedback pump actuator to control the pH of the leachate. To allow remote monitoring of the system, the biofilter will also be equipped with a Photo Ionization Detector (PID) that will make it possible to obtain qualitative measurements of removal efficiency without the need to sample manually. Although the use of a Flame Ionization Detector (FID) would have allowed for individual component monitoring, it was decided to use a PID due to the explosive nature of the waste stream.

Inoculation and Start-up of the Field Unit

Production at the Lake City AAP is expected to be 10 hours per day, 4 days per week for a single shift, and 20 hours per day, 4 days per week for a double shift duty, when the biofilter system is installed at the plant. Based on the latest sampling at the plant, it is expected that the concentration of the gas exiting the building will be closer to $12.5 \text{ g/m}^3\text{-hr}$ ($216 \text{ }\mu\text{g/L}$), much lower than the original estimate of $137 \text{ g/m}^3\text{-hr}$ ($4000 \text{ }\mu\text{g/L}$). The gas stream should be composed primarily of ethyl acetate, with the other compounds making up a minor part of the contaminant stream. The gas retention time (empty bed retention time) in the field biofilter is expected to be 1 minute.

Based on laboratory observations, the field unit will require a minimum of 28.3 L of active inoculum, a 0.1 percent inoculation. To facilitate start-up of the column, a solution made of 1/10 the concentration of the normal nutrients (Appendix C) will be applied to the column before inoculation. This startup solution will soak the media and provide a nutrient-rich environment for the micro-organisms. This solution will be circulated for a period of at least 24 hours before the inoculum is applied.

In the laboratory, it was observed that, during a cyclic loading pattern of the biofilters, a supplemental carbon source appeared to facilitate a successful start-up of the system. This was found to be the case in the laboratory columns where the loading was not only cyclic, but also extremely low, $<12.5 \text{ g/m}^3\text{-hr}$ ($<216 \text{ }\mu\text{g/L}$). Start-up will be with 22.7 kg of granulated table sugar and 1.5 kg of brewer's yeast.

After inoculation, the nutrient/yeast extract/sugar solution will be continuously recycled over the column bed while the contaminant is fed to the column. The continuous recycle of nutrients/inoculum should help establish a healthy biofilm. From past results, the biofilter system should be removing a minimum of 80 percent of the contaminant gas fed to the column within 9 days. After this start-up phase, the column system, if properly maintained, should continue to improve and should remove at least 95 percent of the ethyl acetate and a significant percentage of the other compounds that are in the vapor exhaust stream.

Buffering/Nutrient Feed

The biofilter system at the Lake City AAP will have a nutrient/pH buffering control loop. It will be possible to maintain the pH with this control loop by adding the desired buffer to the nutrient solution, which will be added based on the nu-

tritional requirements of the biofilter. With this type of nutrient/buffer system, the nutrient to buffer ratio will be an important parameter. Due to the many different parameters tested and the uncertainty of the gas stream concentration at the plant, the laboratory experimentation did not identify a precise value for the nutrient to buffer mixture. Identified as a reasonable starting point from the experimental results is the ratio of 7 g of CaCO_3 (equivalents)/100 g of ethyl acetate. The macronutrients were identified as $\text{C}_{100}\text{N}_{10}\text{P}_{1.5}$. The nutrient mix then becomes a solution of nitrogen, phosphorus, and buffer corresponding to the amounts outlined in Table 27.

In addition to the macronutrients listed above, there are also many trace vitamins and minerals that the micro-organisms will need in order to flourish. These are required in very small amounts and will be provided by adding a small amount of brewer's yeast to the nutrient mixture.

Preventative Maintenance

Preventative maintenance (PM) will be performed on the Lake City column as required, and it is anticipated that the need for PM will be quite minimal. The laboratory columns were washed when the pressure drop across the packed bed became unacceptably high or the removal efficiency dropped off. The modification of the media after the first phase of the laboratory experiments improved the media so much that in later experiments, headloss was not an issue. The reactors that were fed a higher amount of ethyl acetate, $>500 \mu\text{g/L}$, did require to be washed to remove the excess biomass to maintain high removal efficiency, but the required frequency of washing was much less than was anticipated. There appears to be operational parameters, such as contaminant loading, nutrients, and retention time that alleviate the need for washing (i.e., the biomass that is created is broken down at an equal rate).

For instance, Column 1 has never required to be washed, even though it was set-up with the cubic media. The loading onto the column was reduced significantly early in the columns operation, and in addition to that, the retention time was also lowered. Both of these changes were made to more closely mimic the field scale unit. The favorable response of Column 1 to these changes and its continued high removal of ethyl acetate after 1 year in operation are very encouraging for the field biofilter unit.

Table 24. Nutrient/buffer requirements.

Compound	per 100 grams of Ethyl Acetate (grams required)
Nitrogen	6
Phosphorus	2
CaCO ₃	7

Field Sampling/Monitoring During and After Demonstration

During the demonstration, both MBI and CERL personnel made field visits to verify biofilter performance. These visits were to verify the removal efficiency of the biofilter unit, perform a visual system check, obtain samples of the leachate for analysis, and replace the nutrient/buffer mixture.

Although the unit was equipped with a PID, the PID was not capable of accurately measuring the concentration of the individual components in the vapor exhaust stream, which varied in constituent concentration. Manual gas sampling consisted of capturing multiple air samples of the influent and effluent gas in both Tedlar bags and crimp vials. This dual method of sampling was performed in an effort to demonstrate a new sampling technique that has proven itself to be considerably more accurate in preliminary lab studies.

Samples of the leachate were obtained for an analysis of the solids content, the residual nutrient, and buffer levels. The nutrient/buffer tank was replenished during these visits, with appropriate changes to the content of the mixture based on the previous leachate analysis. As the biofilm established itself on the bed, fewer nutrients (specifically trace nutrients) needed to be added to the solution.

Lake City AAP personnel were expected to continue to analyze and monitor the system after the demonstration if it is kept at Lake City AAP.

7 Conclusions

1. This study has successfully provided bench-scale data that will support the demonstration of the use of an engineered medium as the packed bed material in a biofilter. Engineered media have several inherent advantages (more consistent characteristics) over natural media:

a. An engineered medium helps control pressure drop (headloss) of the biofilter bed.

b. An engineered medium can be washed. Significant amounts of the biomass can be scrubbed from the medium surface. By controlling biomass build-up in this manner, engineered systems can operate at higher mass loading rates, which decreases the overall size of the biofilter units. (These first two advantages were demonstrated repeatedly throughout the laboratory experiment.)

c. Engineered media are very resistant to microbial attack, in contrast to the performance of the natural bed (packing material) biofilter, which had a shorter life span as a result of microbial attack on the media.

d. Engineered media also have an advantage over natural media biofilters for biomass control. The lack of biomass control is the principle mass loading limiting factor for natural medium systems.

2. The results of the laboratory phase of the project show that biofiltration can successfully treat ethyl acetate and other minor constituents present in the LCAAP vapor stream (Tables 10 and 20). From the data collected at laboratory scale, more than 90 percent ethyl acetate removal is anticipated at full scale as well as 90 percent of the minor constituents. Note that these figures do not include the start-up phase of the experimentation, when the removal of these compounds is expected to be sporadic until consistent removal is established after approximately 7 to 10 days.

3. The study also revealed significant procedural information about inoculating the laboratory biofilter columns, and also about the result of low or cyclical mass loadings.

a. During the laboratory experimentation, biofilter start-up or "inoculation" was studied insignificant detail. To facilitate the start-up of a remote site, it is critical to understand as much about the inoculation procedure as possible.

b. For low mass loadings, $<12.5 \text{ g/m}^3\text{-hr}$ ($<200 \text{ }\mu\text{g/L}$), or cyclical loadings, the inoculum needed assistance in initiating a healthy biofilm. For biofilters treating medium to high mass loadings, $25 \text{ to } 110 \text{ g/m}^3\text{-hr}$ ($400 \text{ to } 3207 \text{ }\mu\text{g/L}$), inoculation was accomplished by applying the inoculum mixed with a nutrient solution to the packing material. The mixture was circulated around the column while the contaminated gas stream passed over the bed.

4. It was discovered that the addition of a supplemental carbon source in controlled amounts provided enough carbon for the inoculum to initiate a biofilm. The additional carbon did not make the inoculum predisposed to metabolizing only the supplemental carbon source. The researchers postulate that the mechanism involved here is solely the provision of enough carbon nutrient to start and maintain a biofilm. The use of a supplemental carbon source should not be confused with the biological term "co-metabolism." Co-metabolism is the transformation of a compound by organisms that do not obtain energy or carbon for cell growth from the transformation, and hence require an alternative source of carbon and energy. The supplemental carbon source identified in this study was glucose, which proved indispensable in establishing a healthy biofilm in columns 4b and 6.

5. Evidence also showed that the use of a supplemental carbon source can be overdone, and that continuous use of supplemental carbon may cause the biofilm to become predisposed to its digestion at the expense of the target compound.

6. This study investigated the use of pH as a fungus formation control method on the packed bed of the biofilter, and also monitored the columns' off-gas for eucaryotic discharge.

a. The control of fungus growth on a biofilter packed bed is an important concern. Fungus can plug the biofilter and increase the pressure drop of vapor flowing through the reactor. During the course of this study, it was determined that the fungus predisposed to form on the biofilter in this vapor stream was less inclined to be active when the pH control point was raised to above $\text{pH}=7$. No negative implications were found for the microbes that were being used to treat the target compounds at these higher pH ranges. Consequently, a reasonable fungus control method was found for this vapor stream.

b. The results of this study and others indicate that biofilters appear not to be a source of concern in regard to eucaryotic micro-organisms. Other types of activities that are sources of enormous amount of spore production relative to biofilters, such as those relating to agriculture (the harvesting of hay, or stored grain or fodder), are more likely to cause health hazards than biofilters. This study concludes that the advantages of reducing dangerous emissions such as benzene, toluene, ethyl benzene, mixed xylenes, formaldehyde, or styrene through treatment far outweigh the potential risk of dangerous eucaryotic organisms being discharged from a biofilter. In fact, while biofilters provide ideal conditions for the organisms that degrade these toxic compounds, these same toxic compounds may also serve to keep pathogenic eucaryotes from being able to establish a niche.

7. General information was obtained regarding the amounts of buffer and nutrient requirements to maintain biofilter removal performance. Nutrient and buffer balances proved to be the most difficult control parameters to identify. Each column trial was operated at different concentrations or mass loading with several different substrates containing vapor streams treated. A widely divergent range of mass balance percentages resulted from the different mass loading conditions. After adjusting for differences in loadings and concentrations, it was determined that about 7 g of CaCO_3 equivalents are necessary per gram of ethyl acetate treated for pH control. The addition of nitrogen and phosphorous seem reasonably governed by the relationship $C_{100}N_{10}P_{1.5}$ in this work.

8. Studies were performed to investigate the flow of the contaminant stream through the biofilter packed bed. With the use of an inert tracer, flow patterns were constructed of the columns with two different medium types. Laboratory results demonstrated a significant increase in the relative plug flow character of the biofilters when the annular cylindrical medium was tested as compared to the cubic medium. Plug flow is desirable because it creates a greater concentration gradient, increasing mass transfer. Since the rate removal or degradation of contaminants in the biofilter is generally governed by the mass transfer of the contaminant to the biofilm, biofilter packing material with higher plug flow characteristics is favored.

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