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Membrane Biotreatment of VOC-Laden Air

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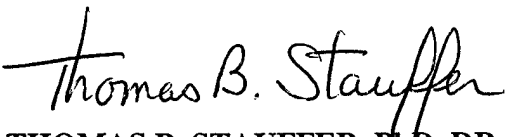
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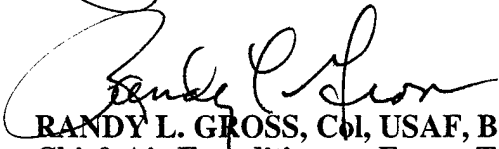
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ABSTRACT

Microporous flat-sheet and hollow-fiber membrane contactors were used to support air-liquid and liquid-liquid mass transfer interfaces. These modules were used in a two-step process designed to transfer VOCs from a contaminated air stream, through a stripping fluid, to a degradative biofilm, where the compounds are effectively mineralized. The membrane contained in the module contacting the contaminated air stream was coated on the air-contacting side with either PDD-TFE or plasma-polymerized silicone rubber. Contact times of the VOC-laden air with the membranes varied between 0.1 and 0.4 sec. VOC removal efficiencies in these modules ranged from 44% to 97%, depending primarily on the air contact time.

Octanol was used as the stripping fluid because of its low vapor pressure and water solubility, the high partitioning of VOCs into octanol from air, and it was found not to inhibit bacterial growth. The concentration of VOC in the octanol was found to affect the removal efficiency and transfer rate of VOCs into and out of the stripping fluid. Furthermore, extraction of specific compounds from the air stream into octanol was observed to be unaffected by the presence or concentration of other VOCs in the air stream.

The membrane-supported biofilm modules successfully removed VOCs from the recirculating octanol stream. Degradation of the aromatic compounds investigated (toluene, *m*-xylene) was achieved; these compounds were not observed in the aqueous phase above the biofilm. MEK biodegradation is problematic, appearing to be partially inhibited by toluene and *m*-xylene, and to be influenced by putative octanol biodegradation. Further mechanistic studies are required to ascertain the underlying mechanism.

INTRODUCTION

This project is sponsored by the Strategic Environmental Research & Development Program (SERDP) in response to the Compliance New Start Number 2 Statement of Need (CPSON2) for FY98, entitled, "VOC (Volatile Organic Compound) Control Technology for Aircraft Painting and Depainting Facilities." Driven by the Clean Air Act Amendments of 1990, quantities of VOCs and hazardous air pollutants (HAPs) in coatings are being reduced, thereby reducing emissions of ozone precursors and toxic compounds from painting operations. Additional controls are desirable or necessary to meet corrosion specifications in some instances, such as aircraft coating. The National Emissions Standard for Hazardous Air Pollutants (NESHAP) specific to aircraft painting will require the Department of Defense (DoD) to either implement volatile hazardous air pollutant (VHAP) control technology or replace existing coating formulations. Because efforts to develop replacement coatings have met with only mixed success, implementation of control technology appears to be the most promising near-term solution.

Direct treatment of VOC-laden air is problematic because of the relatively low VOC concentrations present (frequently <100 ppm) and the often high volumetric flow rates of the air stream itself (up to several hundred thousand cubic feet per minute (cfm) for aircraft painting/depainting facilities). Many researchers have investigated some manner of biofiltration system¹⁻⁴ or adsorption onto activated carbon or zeolite material with varying degrees of success⁵⁻⁶. Biofiltration units tend to be very large because of the need to contact the air with the bed for several seconds to a minute or more. Removal rates of VOCs from the air are limited by the rate of degradation attainable in the bed, which in turn is limited by the low water solubility of the VOC. The coupling of the removal and degradation processes ensures that the degradation rates attained by organisms in these beds will be significantly below their maximum. Zeolite beds have proven useful in removal of VOCs from air streams in cases where there are few VOCs present and recycling is an option. These systems, however, require significant compression of the air (high pressure

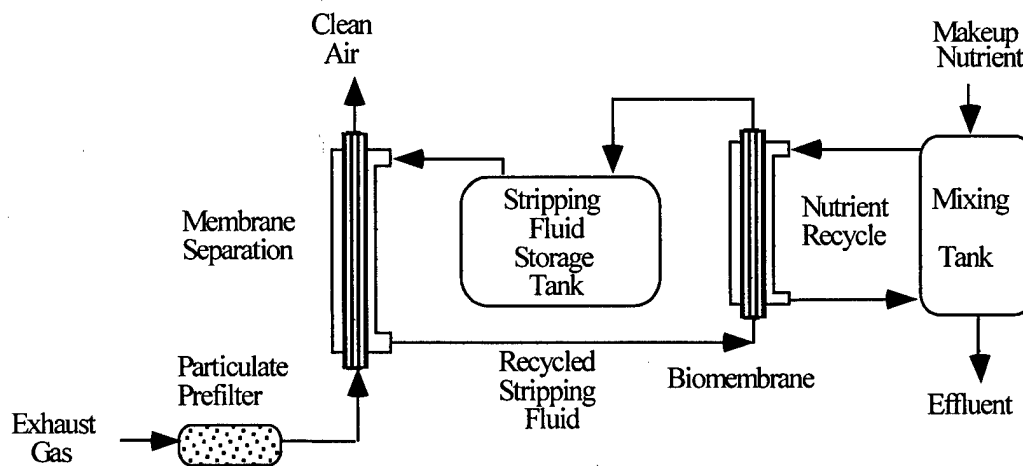
drops through the bed) and subsequent heating of the bed during regeneration. Furthermore, the VOC is simply concentrated in a smaller volume of air; further disposal is required.

Process Description

The feasibility of using a membrane-supported extraction and biotreatment (MBT) process to meet NESHAP standards for aircraft painting and depainting facilities was evaluated. The proposed system could both minimize the treated volume and concentrate the VOCs and HAPs within that treated volume to further reduce the size and cost of the control equipment. For simplicity, the term "VOC" used in this paper is meant to include both VOCs and HAPs.

In the MBT system, VOCs are first separated from the air stream, concentrated, then metabolized by microorganisms, forming nonhazardous cell mass and carbon dioxide (CO_2). Selective removal and concentration of VOCs from the exhaust stream enable significant reduction in the volume directed to the final control device. The system allows for independent optimization of each process: VOC removal from the air and VOC biodegradation. The system uses microporous hollow-fiber membrane contactors to mediate the extraction and concentration of VOCs from the air into an organic stripping fluid (octanol) and to provide a physical support for degradative microorganisms. Figure 1 is a schematic of the MBT system.

Figure 1: MBT System Schematic

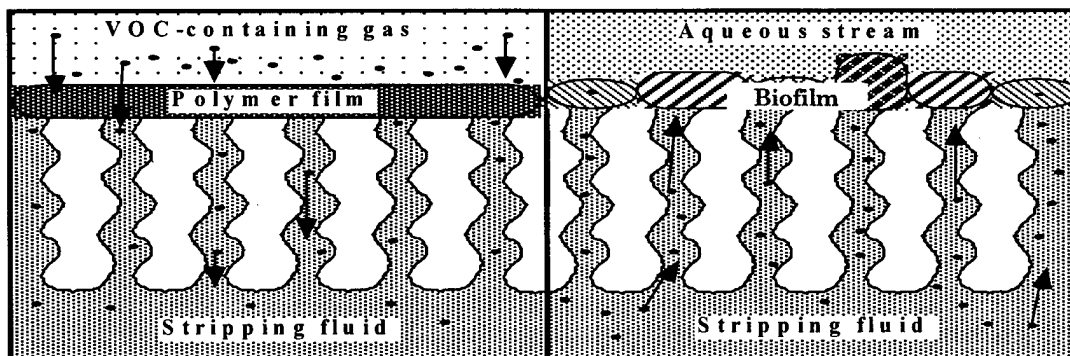


Gases enter a membrane separation/concentration (S/C) unit containing bundles of microporous hydrophobic fibers in which vapor-phase VOCs are transferred into a stripping fluid medium as shown in Figure 2 (dark particles are VOCs). The medium serves as a pollutant sink and allows accumulation of significant VOC concentrations.

Upon exiting the S/C unit, the stripping fluid is delivered to a biomembrane unit. There, the stripping fluid is circulated past one side of another microporous membrane with VOC-degrading bacteria in a film on the opposite side of the membrane. VOCs diffuse through the membrane pores (filled with organic stripping fluid) and are selectively metabolized by the bacteria, as shown in Figure 3. The solvent is then collected in a storage vessel, and recycled through the S/C unit. Outputs from the overall MBT system are clean air, CO_2 , and a mixture of water and nonhazardous cell mass.

Figure 2: VOC Extraction in the S/C Unit

Figure 3: Bioextraction of VOCs



EXPERIMENTAL RESULTS

Materials and Methods

Calibration standards for gas chromatography (GC) and high performance liquid chromatography (HPLC) analysis were prepared from pure certified standards of the compounds of interest in an aqueous medium. Three concentrations for each target compound were analyzed, in triplicate, daily throughout the analysis of test samples. At each concentration level, a single calibration was within 5 % of the average of the three calibration results. The low and medium calibration standards bracketed the expected concentration of the effluent. The medium and high standards bracketed the influent concentrations.

GC analyses

Vapor-phase samples were automatically taken from the membrane contactor apparatus by use of a multiport valve/actuator, and loaded into a sample loop for direct GC injection. Gas samples were analyzed using a Hewlett-Packard GC, Model 5890, outfitted with dual Supelco packed columns (SP-2100) run in splitless mode. The flame ionization detectors (FIDs) are connected to computing software (Chemstation 3.1). The analysis was carried out isothermally at 155 °C, with an injector temperature of 200 °C and a FID temperature of 250 °C.

Aqueous samples taken from biomembrane units were subject to pentane extraction (2:1, pentane:aqueous) for 2 minutes. The pentane phase (1-5 mL) was then injected into the HP 5890 GC, with heptane used as an internal standard. Analysis was carried out isothermally at 100 °C, with an injection temperature of 200 °C, and a FID temperature of 250 °C, using a J&W Scientific capillary column (DB-624) and FID detector connected to a Hewlett-Packard (H-P) integrator.

HPLC analyses

Liquid samples obtained during experimentation were stored headspace-free in labeled polypropylene microcentrifuge tubes with snap-top caps at -20°C until analysis was performed. Sample analysis was performed using a Spectra Physics HPLC equipped with a C18 column and ultraviolet-visual (UV-VIS) detector. Compound identification was based upon retention time comparisons with known standards. Refractive index detection was used to verify compound identity.

Liquid-phase samples of the stripping fluid were analyzed at 30 °C using a Spectra-Physics HPLC equipped with an Altech Ultima C18 column operated isocratically with a 50/50 acidified methanol/water

(MeOH/H₂O) flow. The detector was a UV/VIS spectrophotometer, operating in the range of 260-270 nm. Aqueous-phase samples from biomembrane experiments were analyzed, as were the liquid-phase samples. Operation was isocratic with a 20/80 acidified MeOH/H₂O flow. The detector was a UV-VIS spectrophotometer, operating in the range of 260-270 nm. Method detection limits were less than 5 ppmv for the concentrations of *m*-xylene, toluene, and methyl ethyl ketone (MEK) in air and octanol using HPLC.

Separation/Concentration Experiments

Initial evaluations of mass transfer coefficients for the membrane module were conducted by quantifying the removal of each individual VOC (*m*-xylene, toluene, MEK) from an air stream. Experiments were performed to determine the effect of airflow rate, stripping fluid flow rate, air stream VOC concentration, and stripping fluid VOC concentration on overall mass transfer coefficients. Inlet air stream concentrations were set in the range of 50 to 350 ppm on a mole per mole basis with a syringe infusion pump. Airflow rates between 1 and 5 ft³/min (28 and 140 L/min) and stripping fluid flow rates between 0.1 and 1.0 L/min were studied. Contact times for both streams were calculated based on the relevant stream flow rates and the volumes on either side of the membrane in the module. The air-side contact time was 0.1 – 0.4 sec, and the stripping fluid contact time ranged from 6 to 60 sec. Samples of inlet air, outlet air, and the stripping fluid reservoir were taken at regular intervals and analyzed to allow calculation of the overall mass transfer coefficient via an appropriate design equation for the membrane contactor.

Perfluoropolymer coated membranes

Significant effort was aimed at testing the performance and ease of application of several coatings on smaller bench-scale Celgard contactors. We acquired and tested a membrane contactor with a thin (~ 1 μm) coating of an amorphous copolymer of perfluorodimethyldioxole and tetrafluoroethylene (PDD-TFE) inside the fibers. MEK and *m*-xylene were the VOCs used in the VOC mass transfer performance (air to octanol) tests. Three conditions were examined for each compound, in duplicate, for a total of 12 experiments. Airflow rate and VOC concentration were experimental variables, while absorbent (octanol) flow was held constant. Experimental conditions were chosen to emulate our earlier work with a Celgard Liqui-Cel module with a PDD-TFE coating on the outside of the hollow fibers. Replicates were not evaluated because the VOC concentration in the solvent varied with time. Efforts were made to duplicate air and solvent flow rates, and VOC concentrations in the air stream. The results of the testing were similar to those of previously mentioned testing using a module coated with PDD-TFE on the outside of the fibers. Current results, shown in Table 1, indicate that, with PDD-TFE coated fibers, the major resistance to mass transfer may be in the coating. Table 2 shows the removal efficiencies obtained using PDD-TFE coating on the outside of the fibers. Because PDD-TFE has a relatively high resistance to mass transfer of VOCs, a better polymeric coating may be needed to improve process economics.

Table 1. Mass Transfer Coefficients

PDD-coated membranes, shell-side (outside) coating					
Compound transferred	Air Stream			Solvent Stream	
	Concentration (ppm)	Flow (L/min)	Loading ₁ (ppm/s)	Conc. (mg/L)	K_o ($\times 10^{-5}$ cm/s)
<i>m</i> -xylene	44	28	120	6.2	0.85
	50		130	6.2	0.91
	110	28	290	6.2	0.96
				6.0	1.0
	64	60	370	6.3	1.3
MEK	275		1600	5.9	1.6
	270	28	720	550	0.7
	750	28	2000	105	2.0
	1050	60	6000	1200	9.4
	2200	30	5500	980	4.3
PDD-coated membranes, tube-side (inside) coating					
<i>m</i> -xylene	40	28	110	4080	0.1
	230	60	1300	4300	2.0
	280	60	1600	850	2.7
MEK	470	28	1300	8500	-4.0
	2800	60	16000	9500	2.0
	5000	28	13000	5500	5.3

₁Indicates the relative rate of flow of VOC through the module; determined by dividing the VOC concentration by the residence time of the air in the module (shell-side volume = 175 mL).

Table 2. Removal Efficiencies

PDD-coated membranes, shell-side coating				
Compound transferred	Air Concentration (ppm)	Airflow (L/min)	Loading (ppm/s)	Removal Efficiency (%)
toluene	800	105	8000	74
	900	60	5100	76
	1300	30	3700	78
MEK/toluene	500/250	60	2800/1400	80/60
	850/650	30	2400/1900	80/70

Operating equations were derived to describe the membrane separation processes. The final result for the separation/concentration unit was a design equation that relates concentration, partition coefficient, membrane surface area, and flow rate to an overall mass transfer coefficient, K_o . The K_o is based on the overall system driving force and is defined by a sum-of-resistances model. In the equation shown below for K_o in the S/C unit, the concentration (C) subscripts A and O denote the air and octanol phases, and subscripts 1 and 2 represent inlet and outlet conditions, respectively. P is the air/octanol equilibrium partition coefficient, Q is the volumetric flow of the respective phases (cm³/sec), and A_m is the membrane surface area (cm²).

$$K_o = \frac{\ln \left[\frac{C_{A2}/P - C_{O2}}{C_{A1}/P - C_{O1}} \right]}{A_m \left(\frac{1}{Q_o} - \frac{1}{Q_a P} \right)}$$

Silicone rubber coated membranes

An Applied Membrane Technologies (AMT) parallel-flow, stainless steel cylindrical membrane module, coated on the outside with plasma-polymerized silicone rubber at a nominal thickness of 1 μm , was evaluated. One of the concerns with a parallel-flow contactor design is the unknown effectiveness of the air-to-fiber contact area. Though the cylindrical parallel-flow design of the existing AMT module does not lend itself to high efficiency, it was used in preliminary testing to gather data for the design of a cross-flow module.

Five 48-minute tests were conducted with air flowing through the shell side of the module: three were conducted using *m*-xylene as the pollutant and two were conducted with MEK. Results are presented in Table 3. The air flow was typically 60 L/min and VOC removal ranged from 56 to 83 % with average overall mass transfer coefficients, K_o , of 4.4×10^{-6} to 5.0×10^{-5} cm/sec.

Table 3. Air in Shell Tests – Cylindrical Parallel-flow AMT Module

Run ID	<i>m</i> -xylene 1	<i>m</i> -xylene 2	<i>m</i> -xylene 3	MEK 1	MEK 2
Airflow (L/min)	60	60	60	28	60
Avg inlet VOC air concentration (molar ppm)	65	190	185	186	1350
Average VOC removal (%)	56	77	70	83	78
Average mass transfer coefficient, K_o (cm/s)	4.40E-06	8.30E-06	1.20E-05	2.10E-05	5.00E-05

In commercial operation, contaminated air is anticipated to flow through the shell side of a cylindrical design and the stripping fluid pumped through the tube, or lumen side. The initial set of tests on the AMT cylindrical module was run in this manner. Because of the distribution and contact shortcomings encountered, AMT suggested that a second series of tests be conducted with the air flowing through the fibers. Therefore, a second set of tests was run with the air flowing through the fibers and octanol on the shell side. Twelve runs were conducted using *m*-xylene as the pollutant. These shorter (34 min) tests were conducted with airflow rates through the lumens ranging from 5.6 to 10.3 L/min at pressure drops from 11.5 to 20 in. H₂O (292 to 508 mm/H₂O). Results are shown in Table 4. Each mass transfer rate reported in Table 4 represents an average of samples taken at four time points, and has a variance of 0.17.

Table 4. Octanol in Shell Tests – Cylindrical Parallel-flow AMT Module

Run ID	<i>mx</i> 7	<i>mx</i> 8	<i>mx</i> 9	<i>mx</i> 10	<i>mx</i> 11	<i>mx</i> 12	<i>mx</i> 13	<i>mx</i> 14	<i>mx</i> 15	<i>mx</i> 16	<i>mx</i> 17	<i>mx</i> 18
Air-side pressure drop [in. (mm) H ₂ O]	11.5 (292)	11.0 (279)	11.5 (292)	11.0 (279)	16.0 (406)	16.0 (406)	16.5 (419)	16.0 (406)	20.0 (508)	20.0 (508)	20.0 (508)	20.0 (508)
Air flow (L/min)	5.6	5.6	5.6	5.6	8.6	8.6	8.6	8.6	10.3	10.3	10.3	10.3
Avg inlet VOC air concentration (molar ppm)	68	84	261	684	92	125	457	499	76	105	274	697
Average VOC removal (%)	91	91	80	97	51	44	93	89	60	52	73	85
Average K_o (cm/s)	1.60 E-06	1.90 E-06	8.20 E-07	2.30 E-06	8.60 E-07	6.00 E-07	3.60 E-06	2.50 E-06	5.10 E-06	1.20 E-06	1.60 E-06	2.00 E-06

The K_o values (6.0×10^{-7} to 5.1×10^{-6} cm/sec) for this set of runs were consistently and significantly lower than for the air-in-shell results. As airflow decreases, or as inlet concentrations increase, average VOC removal (overall) increases, but K_o , which is affected by other physical factors, may be impacted

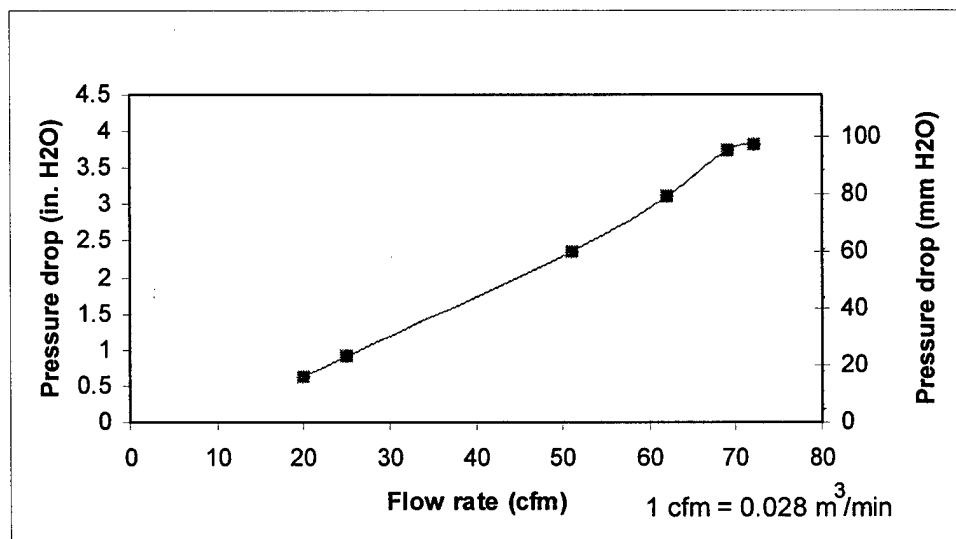
negatively. High removal efficiencies (93 and 97 %) were achieved with octanol in the shell, and high mass transfer coefficients (2.1×10^{-5} and 5.0×10^{-5}) were achieved with air in the shell.

One problem encountered in all extraction experiments was swelling of the membrane material. Occasionally, this was accompanied by "sweating" of the octanol through the membrane. It will be necessary to evaluate alternate stripping fluids as a means to ameliorate this problem.

Crossflow module testing

Flow rate and pressure drop limitations prompted evaluation of a crossflow module manufactured specifically for this project by AMT. This module contains roughly 2.3 m^2 of available membrane surface, and is packaged in a module that has air contact dimensions of roughly $3.5 \times 10 \times 1.5 \text{ in.}$ ($89 \times 254 \times 38 \text{ mm}$). As indicated in Figure 4, the air pressure drop is negligible for this module, even at high flow rates.

Figure 4: Pressure drop for AMT crossflow module



These results represent an order of magnitude improvement in pressure drop performance relative to the cylindrical module containing identically coated fibers.

Biotreatment Experiments

A series of experiments using hollow-fiber modules were performed to establish the efficacy of the proposed biotreatment module for enhanced VOC removal from the octanol. The liquid/liquid stripping efficiency of MEK (octanol to water) was determined for the biotreatment module both with and without a biofilm present. Three aqueous (absorbent) flow rates were examined, with a constant 5000-ppm MEK concentration in octanol and an octanol flow rate of 290 mL/min. Samples were taken in duplicate. Results shown in Table 5 (comparing the 301 mL/min flow, abiotic vs. biofilm) indicate that the presence of a live biofilm-enhanced MEK removal by approximately 43 %.

Table 5. Biomembrane Mass Transfer

Experiment Type	Abiotic			Biofilm
Aqueous phase	Filtered tap water			L-salts ₁
Q _{aqueous} (mL/min)	116	301	598	301
Q _{octanol} (mL/min)	290			
MEK in octanol (ppm)	5000			
Mass transfer rate (g/m ² h)	1.80	2.07	4.45	2.97

₁ pH-balanced trace nutrient source for microbiological organisms

Flat-sheet membrane reactor results

In all of these experiments, a flat-sheet membrane module was used; a basic schematic of the experimental setup is shown in Figure 5. This unit was operated with continuous flow through the module and recirculation through two equally sized reservoirs. The recirculation rate was sufficiently high (50 mL/min) to validate the approximation that the fluid in the membrane module was well mixed. The VOC was always introduced on the side opposite the film, so the two sides of the membrane will be referred to as the film side and the feed side.

Figure 5. Flat-sheet biofilm reactor (elongated ovals represent bacterial film)

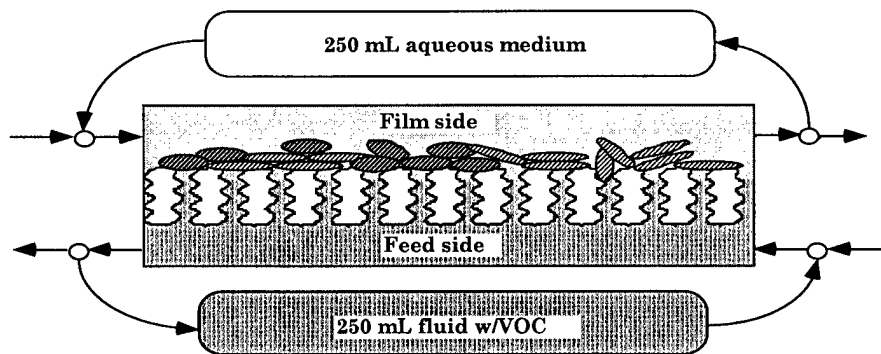
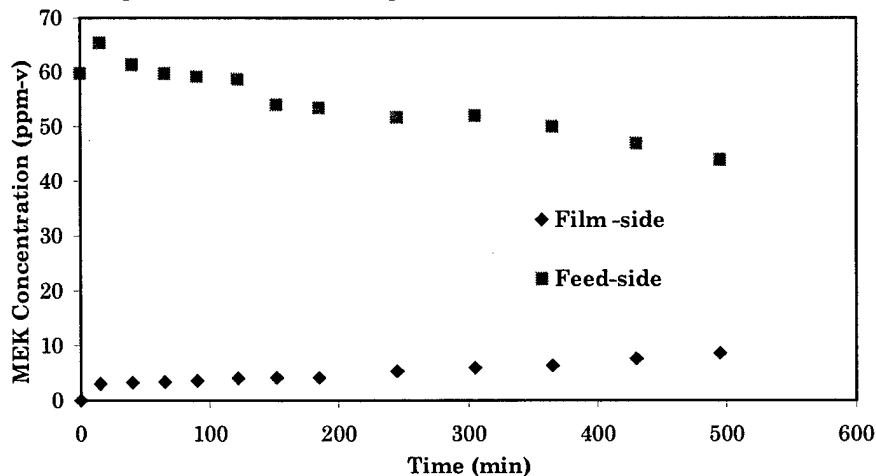


Figure 6. M-1 biofilm degradation of MEK in aqueous/octanol system



A biofilm containing an MEK-degrading bacteria (M-1) was established. Octanol containing MEK was present on the feed side of the membrane. Water and octanol were recirculated between the membrane module and equally sized reservoirs. As indicated in Figure 6, the concentrations of MEK in the octanol phase decreased more rapidly than the aqueous-phase MEK concentration increased. Consistent biodegradation of MEK occurred over the course of a 9-hour period, following transfer of MEK from the octanol across the membrane to the biofilm. This proved that transfer with biodegradation would occur under conditions where the organisms were in close contact with octanol. It also indicated that, while M-1 would grow, slowly utilizing octanol as a carbon source (data not shown), octanol metabolism would not severely inhibit MEK degradation.

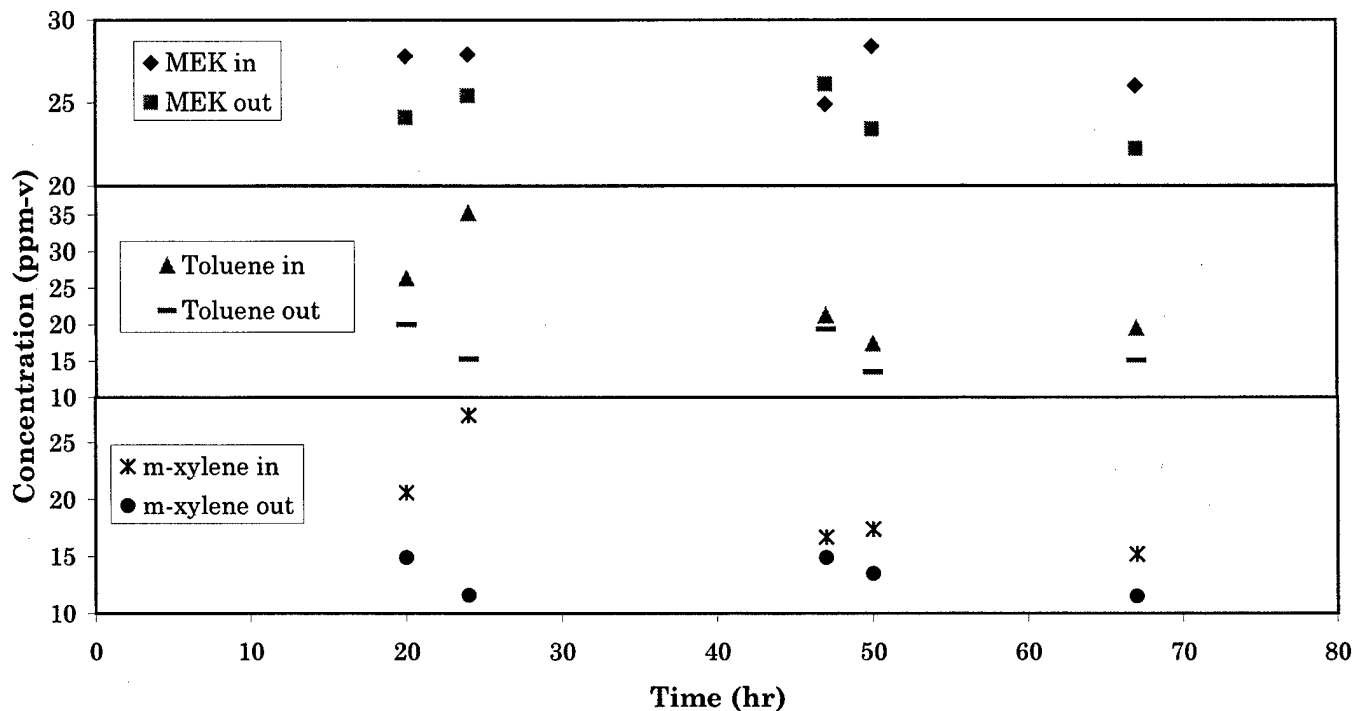
M-1 was grown in a film and exposed to a mixture of MEK and toluene in water on the feed side. The concentration of MEK in the feed stream was at 25 ppm through day 5, then increased to 50 ppm through day 25, when it was again decreased to 25 ppm. The toluene concentration in the feed was zero until day 25, when it was increased to 25 ppm. Despite prior growth on MEK, the film rapidly degraded a substantial portion of the toluene fed, decreasing the rate of MEK degradation in the process. This result was surprising, due to the fact that M-1 is an organism isolated from soil using MEK as the enrichment carbon source. However, since the soil was subjected to long-term exposure to motor fuels, toluene degradation is to be expected.

A biofilm, containing both M-1 and an *m*-xylene-degrading bacteria (X-1), was established and fed toluene and MEK in an aqueous mixture, each at a concentration of 50 ppm in the feed stream. After 2 hours of continuous flow, sampling was begun. Toluene was rapidly and almost completely degraded, while MEK was degraded to a significantly lesser extent. This suggests that both M-1 and X-1 preferentially degrade toluene, to the detriment of MEK degradation.

A biofilm containing M-1 and X-1 was exposed to an octanol feed mixture containing 50 ppm each of MEK and toluene. The octanol flow rate was 2 mL/min, while the aqueous flow rate was 7 mL/min. Toluene did not appear in the aqueous stream over the course of the experiment. Essentially all of the toluene was degraded, as was one-third of the MEK (data not shown).

A mixed organism biofilm culture containing M-1 and X-1 was fed a mixture of MEK, toluene, and *m*-xylene from an aqueous stream (50 ppm of each compound). The culture's behavior and VOC removal capability were investigated, and results are shown in Figure 7. Neither toluene nor *m*-xylene appeared in the aqueous phase, and MEK appeared at low levels (<5 ppm).

Figure 7: M-1 and X-1 mixed biofilm degradation of MEK, toluene, and *m*-xylene

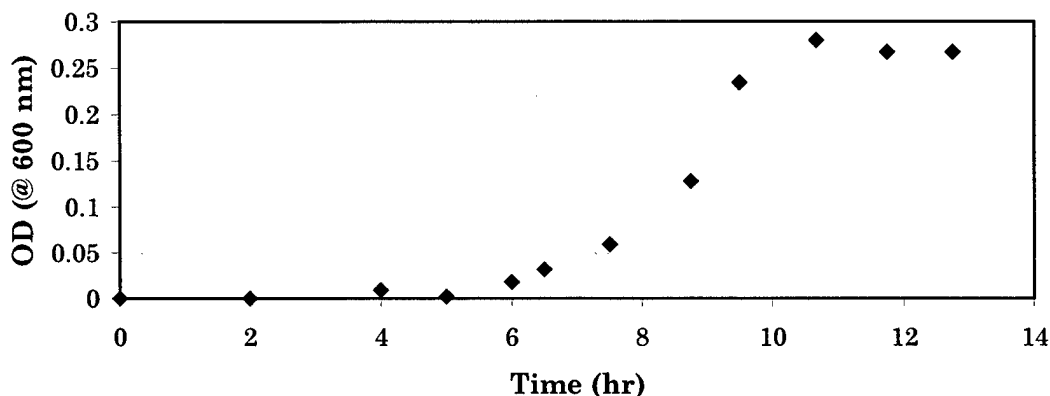


These results have significant implications for the design and operation of the biotreatment system. For example, since M-1 preferentially degrades toluene over MEK, a single biofilm module may be inadequate. Several strategies may need to be evaluated, including replacement of M-1 with an organism exhibiting higher substrate specificity for MEK, establishment of an MEK-degrading culture in the aqueous recirculation tank, or staging of biofilm modules containing different bacterial populations. The mixed culture results are more difficult to analyze. It may have been that X-1 dominated the biofilm and that the low MEK degradation rates are attributable to low population size for M-1. Such issues should be investigated more completely.

Shake flask results

The apparent inhibition of MEK degradation by toluene and *m*-xylene was investigated in a series of shake flask experiments. MEK and *m*-xylene/toluene have different solubilities in an aqueous medium. Under certain conditions in the biofilm reactor, MEK from the octanol phase will partition into the aqueous nutrient medium faster than it can be degraded by the biofilm. This will result in exposure of the biofilm to an aqueous-phase MEK concentration. The biofilm must be able to maintain degradative activity in the presence of this aqueous-phase MEK. The film must also actively degrade MEK. Suspended cell studies were undertaken to further elucidate the mechanisms of degradation of the two organisms.

X-1 was grown on toluene and *m*-xylene, to determine its substrate preference. As indicated in Figure 8, only one apparent growth-phase results, suggesting that toluene and *m*-xylene are equally preferred and that degradation of either does not inhibit degradation of the other.

Figure 8: X-1 growth on toluene and *m*-xylene

Growth studies of M-1 were performed with various mixtures of MEK, toluene, and *m*-xylene. The cell density, protein concentration, and concentration of the three substrates were monitored during the growth. The results of these studies are summarized in Table 6. Since multiple growth phases were observed, multiple growth rates are reported, with the primary carbon source denoted in parentheses. These results indicate that M-1 degrades toluene and *m*-xylene preferentially to MEK, and that the growth rate of M-1 on MEK is reduced as a result of toluene and *m*-xylene metabolism. It is unclear whether inhibitory byproducts are formed by M-1 during aromatic biodegradation.

Table 6. Growth of M-1 on Mixed Substrates

Substrate	Specific Growth Rate (h^{-1})	Growth patterns
MEK (200 ppm) + toluene (25 ppm)	0.35 (toluene) 0.22 (MEK)	sequential phases consuming toluene, then MEK
MEK (60 ppm) + <i>m</i> -xylene (35 ppm)	0.45 (<i>m</i> -xylene) 0.11 (MEK)	sequential phases consuming <i>m</i> -xylene, then MEK

CONCLUSIONS

Gas-liquid modules

In this study, VOC removal efficiencies in excess of 90% have been achieved using microporous hollow-fiber membrane modules. This performance compares well with results obtained by other researchers evaluating removal of selected VOCs from air streams using pervaporation.⁷⁻⁹ Poddar used uncoated hollow fibers constructed of microporous, hydrophobic polypropylene.⁷ At gas residence times between 1 and 1.5 sec, dichloromethane and toluene exit gas concentrations were lowered to 1-2 ppmv using fresh silicone oil flowing at approximately 5% of the gas flow rate. Using fibers coated with 1 μm thick plasma-polymerized nonporous polydimethylsiloxane, residence times between 5 and 7 sec were required to reduce dichloromethane to similar concentrations in the exit gas with fresh silicone oil.⁸ A mixed VOC-nitrogen (N_2) stream was also evaluated, with the results summarized in Table 7.⁹

Table 7. Absorption Data For VOC- N₂ Gas Mixture₁

VOC feed concentration ppmv	Removal % at given gas contact times		
	17 sec	5 sec	
Acetone	226	93.8	61.5
Methylene chloride	201	95.5	91.0
Toluene	204	100.0	100.0
Methanol	163	52.7	21.5
Total	794	87.4	70.6

₁Data taken from Reference 9.

The performance of our system represents a significant improvement over that studied by Sirkar and his associates.⁷⁻⁹ The gas contact time required to achieve percentage removal greater than 85% is significantly shorter in our system (0.5 versus 5 – 15 sec). The ratio of gas flow rate to stripping fluid flow rate is also higher in our system.

Biotreatment module

The membrane-supported biofilm was shown to enhance transfer of the VOCs out of the stripping fluid. Furthermore, the biofilm activity was not inhibited by long-term exposure to organic solvent (octanol). Degradation of the aromatic compounds investigated (toluene, *m*-xylene) was achieved; these compounds were not observed in the aqueous phase above the biofilm. They were consumed concurrently in some mixed substrate experiments, but sequentially metabolized in mixtures with MEK. This type of behavior is common in bioremediation studies.¹⁰⁻¹² Cometabolic degradation of compounds with similar structure is often noted and is indicative of degradative enzymes with sufficient substrate range to encompass the minor structural differences between compounds. This was certainly the case of simultaneous degradation of 2-6 dinitrotoluene (DNT) and 2-4 DNT reported by Lendeman et al.,¹¹ and is reflected in our results for toluene/*m*-xylene degradation.

Combinations of concurrent and sequential consumption are also encountered. Arcangeli and Arvin¹⁰ noted degradation of trichloroethylene (TCE) by an organism degrading toluene in two modes: concurrent degradation via cometabolism, and sequential degradation whereby toluene acted as a competitive inhibitor of TCE degradation. Other systems^{13,14} have noted sequential degradation due to inhibition of separate degradative pathways for different polymeric substrates¹⁴ and for mixtures of benzene, toluene, and *p*-xylene.¹³ Their results are similar in nature to what has been observed in this study with toluene, *m*-xylene, and MEK mixtures fed to microbial consortia.

MEK biodegradation is problematic, appearing to be partially inhibited by toluene and *m*-xylene. Further mechanistic studies are required to ascertain the underlying mechanism.

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KEY WORDS

- Membrane
- Module
- Biotreatment
- Biofiltration
- VOC
- Contactor
- Extraction
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- Separation
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- Biomembrane
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- Volatile